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Interstellar catalysts and the PAH universe

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CHAPTER 1

INTRODUCTION

Chemistry is a scientific discipline that has the aim to study how elements combine to form “complex systems”. Citing the Britannica encyclopedia, “chemistry is the science that deals with the properties, composition, and structure of substances”.¹ Astrochemistry is the discipline that studies the interaction of atoms and molecules as well as their chemical and physical properties in space. Astrochemistry is a field that bridges astronomy and chemistry, and is also called molecular astrophysics. Although astrochemistry studies the chemistry of the medium between the stars (interstellar medium, called ISM), cosmochemistry is the study of molecular formation in solar system objects such as asteroids, comets, and planets.²

The key questions of astrochemistry are: What is the role of molecules in the evolution of the universe? How can molecules be used to probe the universe? What is the organic inventory of regions of star and planet formation? Are interstellar molecules related to the molecular inventory of the Earth and the terrestrial planets in the solar system? Hence the aim of astrochemistry is to study how molecules regulate the chemical and physical conditions that lead to galaxy and planet formations. This entails the formation and processing of molecules in the ISM and their delivery to solar system objects. Finally, one of the current hot topics revolves around the formation of the building blocks of life, such as glycine.²

Almost 14 billion years ago, after the Big Bang explosion, subatomic particles such as quarks and electrons started to build up the first hydrogen and helium nucleus in the range of 3 minutes. Only after about 300.000 years, they formed the first atomic hydrogen and helium. Once the first atomic and molecular species are formed the timescale required to form complex molecular entities such as us increases manifold. However,

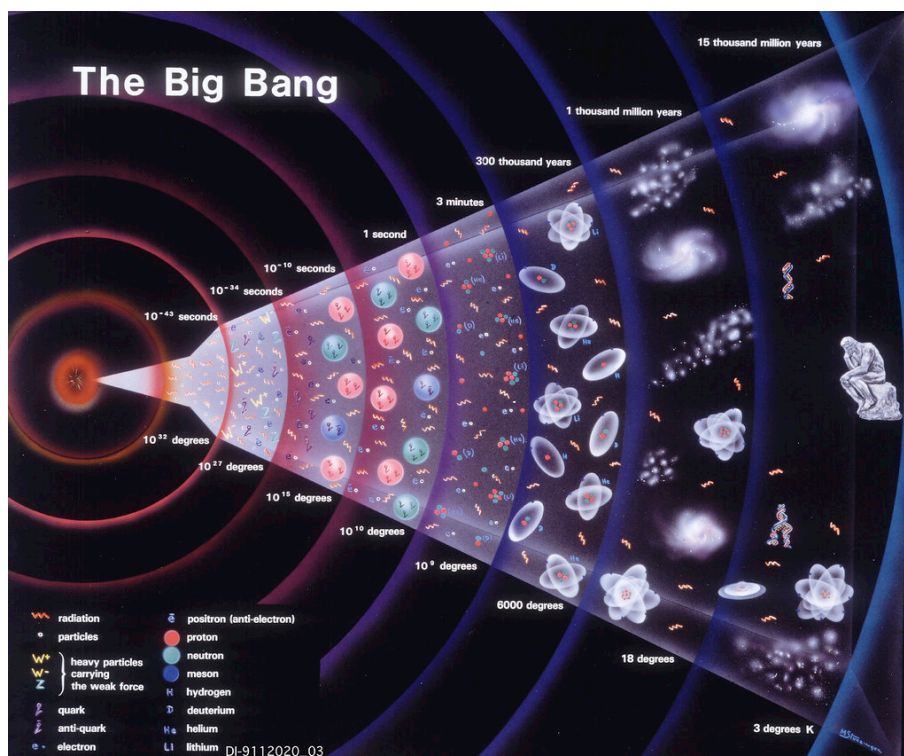


Figure 1.1: The timescale of subatomic, atomic, molecular and supramolecular formation from the big bang until today.⁴

molecules have all the time of the universe to meet, collide and react.³

Every substance on Earth and in space undergoes a transformation that releases or absorbs energy. This energy is converted into many forms and one of the most important is thermal energy.⁵ The latter is a consequence of molecular and/or atomic collisions that cause the formation and the breaking of bonds. Hence, atomic and molecular collisions are responsible to build the so-called complex organic molecules.

Besides the chemical reactivity in space, the identification of molecular composition in objects far from Earth is an important consequence of the light interaction from a nearby star.^{6,7} The light interaction with a molecular entity promotes electronic excitation which is partially converted into vibrational modes. After a relaxation process, the molecule emits to a precise and detectable wavelength in space. Hence, astronomical observations play an important role in the identification and characterization of molecular composition in space as a consequence of their rotational, vibrational, and electronic excitations.⁶

Over 200 species have been detected in space by astronomical obser-

vations. The diversity of molecular species in space varies from the most simple one such as H_2 to more complex ones such as fullerenes, C_{60} , C_{70} and, no less important, polycyclic aromatic hydrocarbons (PAHs).⁸ The latter locks up about 20% of the carbon in the universe and, hence, makes up a considerable fraction of the organic inventory of the universe.⁸ Could this PAH reservoir be related to the molecular inventory of the Earth and the terrestrial planets in our solar system? For example, could the PAHs be altered and the carbon used in the formation of complex molecular species?

The aim of this thesis is, using quantum chemistry methods, to shed light on the chemical reactivity and catalysis involving the most abundant and observed molecular species in the universe such as PAHs. Specifically, the studied PAH samples of this thesis are, pentacene, pyrene, naphthalene, anthracene, fluoranthene, pyrene, coronene, and benzocoronene.

1.1. Modeling Interstellar Catalysts

Before discussing in detail the role of PAHs in the universe, a short explanation of chemical modeling and interstellar catalysts must be introduced. These are the keys to understanding the molecular complexity of our universe and, hence, the study of bond formation and destruction routes at the atomistic level. This will be followed by a detailed section (*Chemical Processes in the Universe*) on the role of molecules in the ISM and solar system and the theoretical methods to study the complexity of our universe (*The Basis of Quantum Chemistry Methods*).

1.1.1. Chemical Modeling

The prediction of molecular abundances that evolve in time is investigated through astronomical models that make use of kinetic rate equations with parameters derived from astronomical observations (*i.e.*, column density, density, temperature) and quantum chemistry calculations (*i.e.*, binding and activation energy).⁹ Astronomical modeling aims to study the kinetics and reactivity of molecular species in the interstellar environment⁹ with input parameters obtained from concomitant chemical modeling (this includes classical and quantum approaches).¹⁰ The latter, more generically, aims to study the kinetics and reactivity of molecular species in every environment. These two approaches to modeling are complementary and both are needed for a proper characterization of the chemical routes driving molecular complexity in space.

Within the chemical modeling, the energy of atomic species as a function of their position, named "Potential Energy Surface" (PES), explains how atomic and molecular species are interconnected. When two species come close to the equilibrium of the electronic repulsion and the electronic

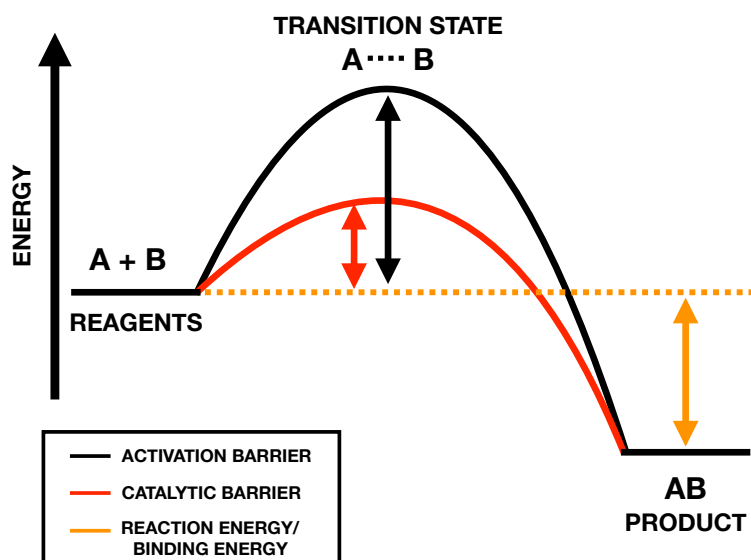


Figure 1.2: Schematic representation of a transition state and a catalytic process of connecting two generic atoms, A and B, forming a molecule, AB.

attraction, they form an imaginary species located in the maximum of a PES called transition state (TS), shown in Fig. 1.2. The TS is a molecular configuration that corresponds to the bottle-neck in potential energy along the reaction coordinate. A TS cannot be detected in lab or in space since it is purely a transitory state. However, the TS allows estimating the energy barrier or activation energy (the difference in energy between the TS and the reagent). Hence, the energy that the system needs to overcome to form the products. On the contrary, the reaction energy (the difference in energy between the product and the reagent) tells us how favorable is the reaction based on the quantity of energy released (exoergic process) and/or required (endoergic process).¹¹ The binding energy is a measure of how much energy we need to provide to dissociate the molecule or to desorb a molecule from a surface or another molecule.¹² Hence, the binding energy is the inverse of reaction energy (energy difference between the reagent and the product shown in Fig. 1.2). Transition state theory (TST)¹³ provides a good explanation of chemical processes at thermodynamic equilibrium and allows to derive the kinetic rate of a process. The harsh environment of space does not allow molecules to reach thermodynamic equilibrium, and generally, kinetics is the dominant factor.¹⁴

1.1.2. Catalysis

Catalysis is a way to increase the rate of a chemical process. A catalyst can be anything, including a radical, a molecule, or a surface that reduces the large energy barrier associated with the formation of the product. Usually, the efficiency of a catalyst is expressed in terms of the turn over number or frequency, the number of cycles in which the catalyst takes part in the reaction (undergoing chemical transformation) and regenerates in a loop. However, not all catalysts are regenerated during the process and some of them might lose their catalytic activity due to the degradation of the active site of the catalyst (the site that binds the reagent).¹⁰

The investigation of the transition state and the reaction pathways requires sophisticated quantum chemical methods such as density functional theory (DFT), see subsection 1.3.1, the most common quantum chemistry method to model organic molecules and solid surfaces.^{11,12} In space, grains,¹⁵ radical hydrogens¹⁶ and PAHs¹⁶⁻¹⁸ are mainly responsible for catalytic processes.

1.2. Chemical Processes in the Universe

The known pathways to the hypothesized formation of molecular complexity go through the bottom-up, from small to big (from Fig. 1.3 (a) to (d)), and top-down, from big to small (from Fig. 1.3 (e) to (d)) approach.⁸ Although the focus of this thesis is related only to the processes reported in Fig. 1.3 (f) and (d), (a) summary of all hypothesized chemical processes that occur in space will clarify the general aim of this study and, therefore, the big picture (building the organic inventory of solar system). Hence, subsections from 2.1 to 2.6 will provide detailed explanations of the chemical processes occurring in space.

1.2.1. Bottom-Up Approach

The bottom-up approach starts in so-called dark molecular clouds (Fig. 1.3 (a)), cold and dense regions of the ISM.⁸ Here, atomic carbon is locked up in the CO molecule, a stable and less-reactive molecule. Catalysts such as silicate grains and water ice can gather these CO molecules on their surfaces and activate them.^{19,20} During the hydrogenation of CO molecule, formaldehyde (H₂CO) and methanol (CH₃OH) can be produced (Fig. 1.3 (b)).²¹ In regions of ISM surrounding a new protostar (hot core regions), cosmic rays and UV photons can promote further radical attachment and loss to form more complex molecular species, whereas thermal processes might favor the formation of large size molecules (Fig. 1.3 (c)).⁸ Shocks and the heating of the ice sputter the molecules in the gas phase where they can collide and react via ion-neutral and neutral-neutral reactions.⁸

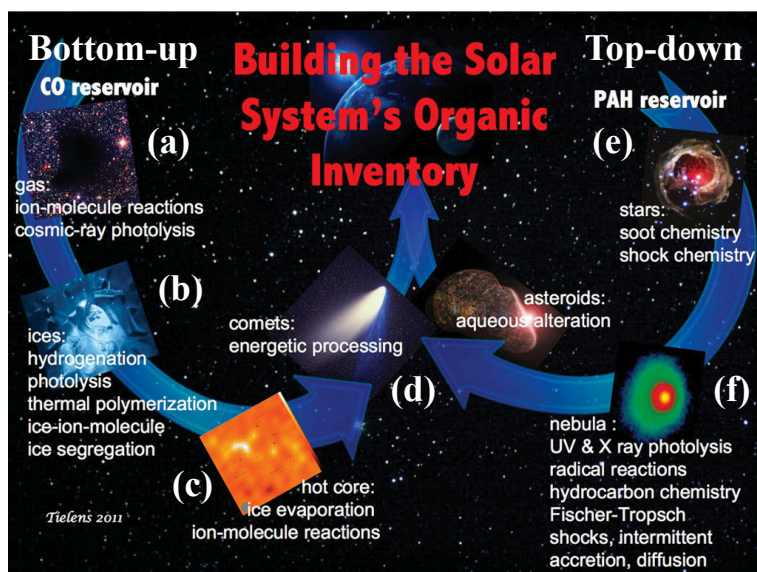


Figure 1.3: Modified scheme of molecular formation from CO and PAHs (bottom-up and top-down approaches, respectively) reported by Tielens.⁸

1.2.2. Top-Down Approach

The top-down approach builds molecular complexity by dismantling big molecules into small ones that can react with other species with heteroatoms, such as nitrogen (N) and oxygen (O) atoms, forming more complex molecules, *e.g.*, amino acids.^{8,22} This approach starts with the formation of large PAHs²³ (from 50 to 200 atoms) in the envelope of AGB stars (Fig. 1.3 (e)).²⁴ PAHs are formed in the gas phase soot chemistry, and further processed by energetic photons such as X-ray and UV. In hot core regions, PAHs can be attacked by H and OH radicals formed during the warming phase of a new protostar (Fig. 1.3 (f)).²⁵

Finally, all the products from the top-down and bottom-up chemistry will be collected and further processed by comets and planetesimals (Fig. 1.3 (d)).⁸ Specifically, PAHs can be gathered by grains in the solar nebula. These grains coagulate to bigger and bigger particles that form the building blocks from which asteroids are formed. Part of the parent body (asteroids) may be broken up into meteorites that fall on Earth. In the parent body, further chemical processes may occur such as the aqueous alteration (alteration of the mineral composition promoted by water). Water present in the asteroid will start to react with the dominant mineral phase made by olivine structure ($(\text{Mg,Fe})_2\text{SiO}_4$), in a temperature range between 20 and 140°, to form a mineral called serpentine ($\text{Mg}_2\text{Si}_2\text{O}_5(\text{OH})_4$). During the conversion from olivine to clay, it has been hypothesized that the proton

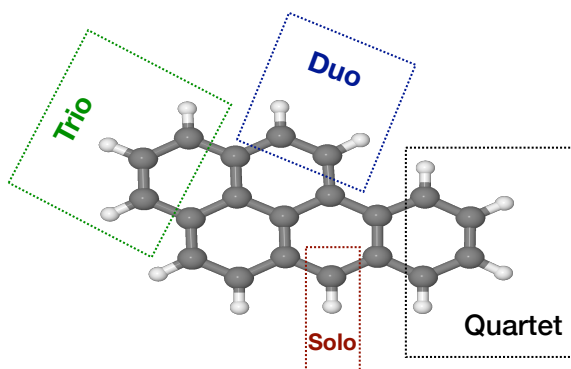


Figure 1.4: Astronomical classification of the hydrogens of a PAH.

exchange between PAHs and olivine might break them down into small aliphatic units. The formed fragments might react with CO_2 and NH_3 , via the so-called Strecker reaction, forming amino acids such as glycine.²²

1.2.3. Polycyclic Aromatic Hydrocarbons

Polycyclic Aromatic Hydrocarbons (PAHs) are organic molecules present everywhere on our planet and in the universe. They are the main focus of this thesis. Here, I give a short introduction on PAHs in the universe, building up from their formation and detection to the rationale for their importance for the research described in this thesis.

PAHs are conjugated compounds with perfect planar sp^2 carbons that provide them with distinct stability and resistance to the reactivity of other species and high temperatures.^{2,26} PAHs are observed everywhere in the interstellar medium.² Depending on the temperature and radiation, they are present in their neutral, cationic and anionic forms.²⁶ Their carbon skeleton structures (Fig. 1.4) have been classified by the astronomers based on the IR signature of specific vibrational modes of the C-H and C-C bond (Fig. 1.5).²⁷ However, none of the single whole structures of PAHs has been yet identified in space. Brett McGuire recently characterized the first spectroscopic signature of benzonitrile ($\text{C}_6\text{H}_5\text{CN}$) that has been thought to be a possible precursor of PAHs, as the first step to identify the chemical pathway that leads to PAH formation in the ISM.²⁸

When PAHs absorb a UV photon, they are electronically excited, this process is very infrequently (depending on the physical condition of the region, this occurs from 1 day to 1 year). Due to their limited heating capacity, they become very hot (about 1000 K) but they rapidly relax, cooling down, in the order of seconds, and emitting in the IR. In contrast, for grains with sizes larger than 10 nm, the heating and cooling timescales are

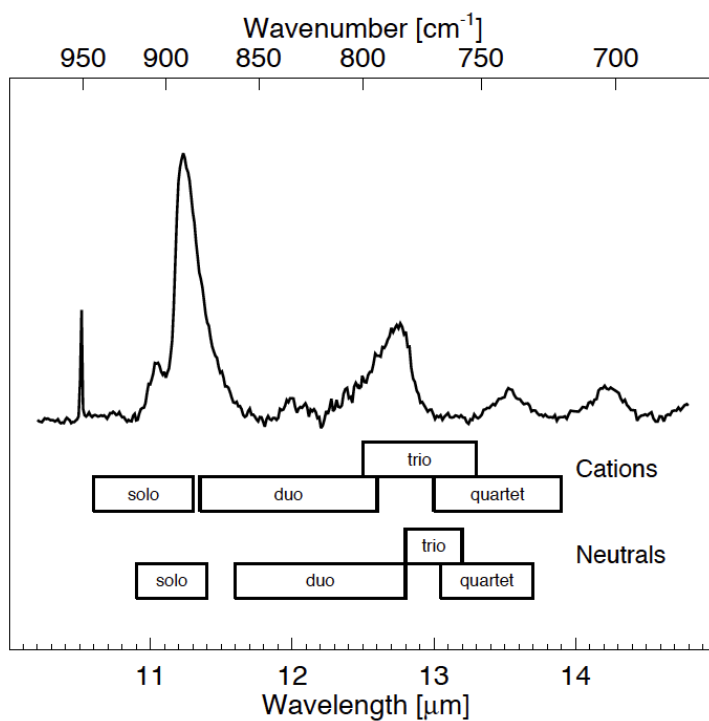


Figure 1.5: The average IR spectrum of out of plane C-H bending modes of PAHs and the associate range of solo, duo, trio, and quartet hydrogens (see Fig. 1.4) reported by Hony *et al.*²⁹

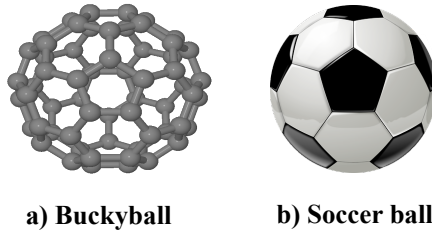


Figure 1.6: Fullerene structure (a) compared to the soccer ball structure (b).

comparable and these species are in radiative equilibrium, resulting in low temperatures.² However for PAHs, the IR emission is in competition with the H-loss. With a typical binding energy of 4.5 eV, this is energetically feasible. For high UV photon fluxes, more than one H might be lost forming a graphene-like structure that can isomerize resulting in the so-called buckyball fullerene (C60), shown in Fig. 1.6 (a).³⁰

Observationally, astronomers identified a direct correlation between PAH destruction and fullerene formation as a function of the distance from the star.³¹

PAHs in the ISM might be found as isolated molecules in the gas phase or they can be part of the dust composition. Due to the electronic delocalization of the π ring, they can form van der Waals complexes with each other.³² However, the stability of these complexes decreases with the increasing radiation field leading to a single PAH cation in the gas phase.^{2,32} Due to their photo-electric heating properties, they regulate the phase structure of galaxies and star formations.²⁶ PAHs, due to their chemical properties, might be great catalysts. For instance, they are thought to be responsible for molecular hydrogen formation in photo-dissociation regions (see subsection 2.4).¹⁷

1.2.4. Molecular Hydrogen Formation

The most abundant molecule in the universe is molecular hydrogen (H_2). The latter has been observed abundantly in dense molecular clouds, but also in high UV radiation field environments such as the so called photo-dissociation regions (PDR).³³ The UV radiation field is so strong that H_2 is rapidly photo dissociated. As H_2 is observed to be very abundant, this requires a rapid reformation process.³⁴

In diffuse clouds, small (0.01-0.1 μm) solid dust grains made by carbonaceous materials or minerals, are thought to provide surfaces on which radical hydrogen can diffuse, gather and react. Hence, grains offer surfaces in which atoms have all the time of the universe to form molecular species, *e.g.*, molecular hydrogen, and more complex ones.³⁵⁻³⁷ However,

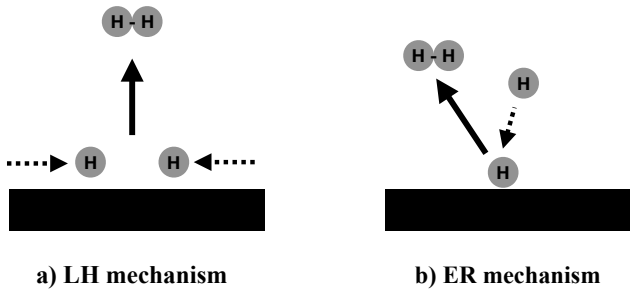


Figure 1.7: Schematic representation of molecular hydrogen formation through Langmuir–Hinshelwood (LH) and Eley–Rideal (ER) mechanism on a solid surface.

in a PDR, due to the high temperature of the dust, hydrogen cannot bind with the surface, and H₂ formation on grain surfaces would be very inefficient.³⁸ If PAHs are present, hot hydrogen radicals bind strongly with the PAH surface, unable to be released.^{16,39,40}

For the case of silicate grains, the most favorable mechanism for molecular hydrogen formation is the diffusion of one or two hydrogen radicals followed by a desorption process (Langmuir–Hinshelwood, LH, mechanism shown in Fig. 1.7 (a)).³³ On PAHs, the desorption process of two atomic hydrogens, forming the molecular one, is not favorable and requires overcoming a barrier of about 4.8 eV.¹⁶ However, the addition of more than two hydrogens on the PAHs might promote the H₂ formation. Ideally, PAHs might fully host as many hydrogen radicals as many carbon sites are available, becoming superhydrogenated PAHs.^{39,41} However, this is not always the case. In fact for the case of coronene, in the PDRs, the hydrogenation will not exceed three extra hydrogen atoms chemisorbed on the carbon sites due to the competition between H-loss and H-gain.⁴¹

The most favorable mechanism is the Eley–Rideal (ER, shown in Fig. 1.7 (b)) in which upon the chemisorption of hydrogen, on a carbon site, it can be extracted, through barrierless reaction, from radical hydrogen that chemisorbs on top of it.¹⁷ Hence, PAHs act as efficient catalysts for molecular hydrogen formation.

1.2.5. From ISM to Solar System: The Organic Inventory

Silicate dust grains are formed in the envelope of the red giant branch (RGB) and the asymptotic giant branch (AGB).⁴² About 15% of the dust has the composition of crystalline olivine and pyroxene such as forsterite (Mg₂SiO₄) and enstatite (MgSiO₃). Forsterite condenses in the dust at high temperatures (about 1400K) and partially transforms to enstatite at somewhat lower temperatures.⁴² At high temperatures, silicates can adjust to

their most stable form, the crystalline structure. But at temperatures below the glass temperature, amorphous materials, without long range order, result.^{43,44} Dust propagates in the ISM processed by shocks and only submicron-size, or smaller, silicate grains survive sputtering, thermal erosion, and grain-grain collisions.⁴⁵ Grains can have also carbonaceous nature including silicon carbide (SiC), which was recognized by astronomers through the strong Si-C stretching mode at 11.3 μm .^{42,43} Furthermore, about 10% of the dust composition is composed of hydrocarbons, both aliphatic and aromatic, observed at 3-15 μm .⁴²

During the collapse of a molecular cloud core resulting in the formation of a spinning disk, materials start to accrete and, therefore, organics and silicate dust will be incorporated forming planetesimals and cometesimals, and ultimately planets.⁴⁶ During the accretion period, carbonaceous chondrite materials are formed, called chondrites due to the presence of chondrules, mm-sized inorganic mineral grains, and carbonaceous due to their organic composition. Carbonaceous chondrites are considered primitive because they did not suffer from major transformation and, therefore, they contain a record of the organic and inorganic composition of the early solar system. About five tons of meteorites that fall on earth every year are of the family of carbonaceous chondrites.⁴⁷

The organic composition of carbonaceous chondrites can be divided into soluble (SOM) and insoluble (IOM) organic matter. However, almost 95% of the carbon in carbonaceous chondrites are composed by IOM. The analysis of these materials requires usually high mass spectroscopy resolution. Almost 140000 molecules have been identified in carbonaceous chondrites meteorites.⁴⁷

Table 1.1 show the families of extraterrestrial organic molecules found in Murchinson meteorites and their abundance. It is still unclear how those molecules were formed, however, it has been suggested that the presence of molecules formed in the circumstellar environment (*i.e.*, formaldehyde and PAHs) might have played an important role during the aqueous alteration of the parent body.⁴⁸

The IOM composition of Murchinson (*i.e.*, macromolecular materials) is very difficult to characterize with spectroscopy, whereas the SOM characterization (the rest of compounds in Table 1.1) helped to identify important building block's of life such as amino acids. Here, the large abundance of L-amino acids (with respect to the usual D-amino acids abundant in terrestrial environments) helped to identify the extraterrestrial nature of these compounds.⁴⁹ However, possible formation routes of complex organic molecules are still to be clarified. It is quite possible that multiple pathways and catalytic processes are involved. In particular, it is unclear whether these species have already been formed in the solar nebula and incorporated in the asteroid body or that they have been formed after the incorporation, inside the parent body, due to the catalytic activity of the minerals.

Composition	Concentration ($\mu\text{g}^*\text{g}^{-1}$)
Alyphatic hydrocarbons	12–35
Aromatic hydrocarbons	15–28
Alcohols	11
Aldehydes	11
Amino acids	60
Ketones	16
Carbon dioxide	106
Carbon monoxide	0.06
Methane	0.14
Monocarboxylic Acids	332
Dicarboxylic Acids	25.7
α -hydroxycarboxylic Acids	14.6
Sugars	60
Ammonia	19
Amines	8
Urea	25
Basic N-heterocycles (pyridines, quinolines)	0.05–0.5
Pyridinecarboxylic acids	>7
Dicarboximides	>50
Pyrimidines (uracil and thymine)	0.06
Purines	1.2
Benzothiophenes	0.3
Sulfonic acids	67
Phosphonic acids	1.5
Macromolecular material	1.45 (%)

Table 1.1: Composition and concentration of organic species found in Murchison meteorites reported and studied by Sephton.⁴⁷

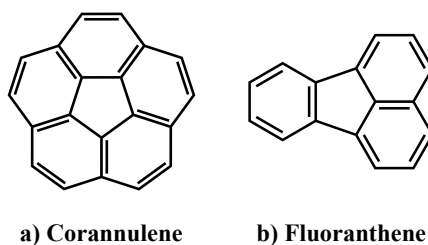


Figure 1.8: Skeletal structure of corannulene (a) and fluoranthene (b).

During the aqueous alteration, PAHs might breakdown and form fragments that can react with other molecular species helping to build up complex organic molecules listed in Table 1.1. The migration of water from the interior of the parent body to the surface helps to transport and concentrate PAHs in the parent body.⁵⁰ For instance, the large abundance of alkylated PAHs, detected in Murchison and Mukundpura meteorites, might be the result of aqueous alteration of the parent body.^{51,52} However, it is not yet clear why large PAHs (more than five aromatic ring units) have not been detected in these meteorites and, thus, this is still under investigation.⁵³

1.2.6. Defects

Defects in solid materials might have great importance in astrochemistry and cosmochemistry since their reactivity might contribute to promote the chemical complexity of our universe.^{12,16} In this section, I provide an overview of several types of defects that might be formed in PAHs and minerals.

PAHs are commonly known as perfect planar structures with six-membered rings. However, sometimes they might have different ring arrangements, similar to fullerene (*e.g.*, pentagons), in which other types of ring shapes are present. For instance, corannulene and fluoranthene are two examples of PAHs with a five-membered ring, shown in Fig. 1.8 (a) and (b), respectively. Different ring arrangements, doping with a metal or hetero-atom, and the lack of one or more atoms in the PAH lattice are called defects. Since PAHs might be considered small graphene-like structures, they can have graphene-like defects.⁵⁴ Defects might be promoted by radiation or chemical reactions, which might occur in the harsh space environment even though only a few studies addressed the defect formations and stabilities in PAHs.^{16,55,56} Fig. 1.9 (a), (b), and (c) show three examples of defects such as Stone-Wales (two seven- and five-membered ring modification), mono and divacancy (removal of one or more atoms) in a graphene-like structure.⁵⁴ The Stone-Wales defect⁵⁷ is particularly

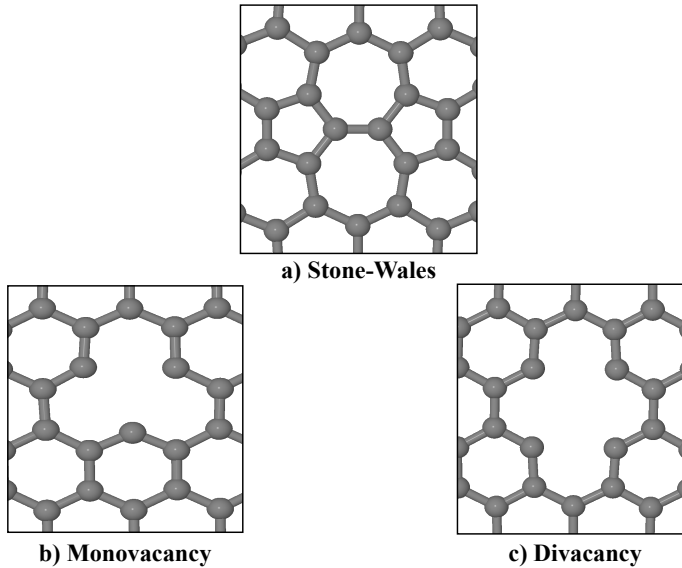


Figure 1.9: Stone-Wales (a), mono (b) and di (c) vacancy defects on a graphene-like structure.

interesting in astrophysics since it has characteristic infrared absorption features that can explain the undefined infrared bands observed at 6.9 and 6.14 μm in the ISM.⁵⁸

Besides PAHs, defects are ubiquitous also in crystalline materials such as minerals. These defects break the periodicity of the crystal lattice. In particular, defects can be located around a single atom, therefore a point, namely point defects.⁵⁹ For instance vacancies (Fig. 1.10 (c) and (d)) as well as the substitution of an atom with another one (doping, such as in Fig. 1.10 (b)) are two examples of point defects. Other types of defects can be present in the bulk of the crystal (bulk defects) and/or along a specific direction of the lattice structure (line and planar defects).⁵⁹

In this thesis, we focus on the point defects since those are able to locally modify the chemical reactivity of the system making them catalytic.^{16,60} When a solid system is ionic and formed by the same number of cation (A^+) and an anion (B^-) maintaining the neutrality of the system, several types of point defects might occur (Fig. 1.10).⁶¹ Besides the doping and the single vacancy, another type of vacancy, named Schottky vacancy, takes place when two opposite charged ions leave the crystal lattice.⁶¹ In this way, the system maintains its neutral charge. There are two types of Schottky defects, one might occur when a cation and anion leave from two distant sites (Fig. 1.10 (e)) and the other one from adjacent sites (Fig. 1.10 (f)). The latter constitutes a neutral divacancy.⁶¹

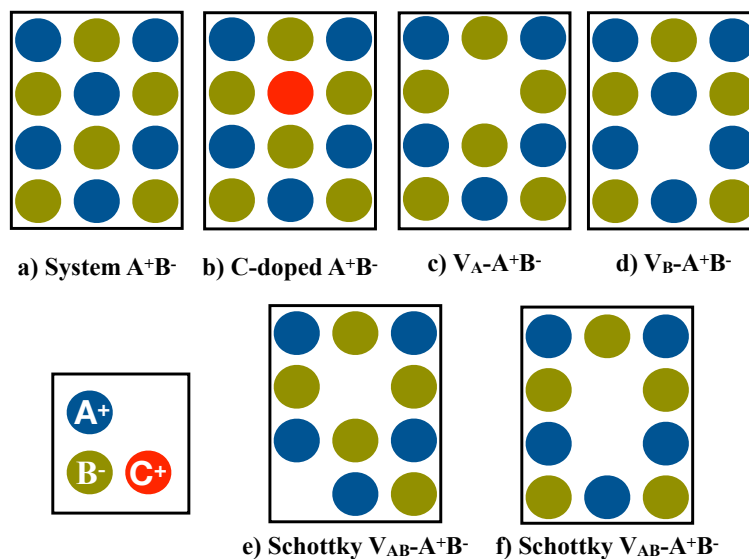


Figure 1.10: Example of point defects in a ionic lattice A^+B^- : (a) Non-defective lattice (pristine), (b) doped lattice, (c),(d),(e) and (f) vacancy (V) lattice.

On forsterite, Schottky defects might be formed due to the reaction of the mineral with water, even in a small amount.⁶² This defect, thus, might have great relevance in asteroidal settings.⁶³

1.3. The Basis of Quantum Chemistry Methods

In order to study the reactivity of molecular species, in space, quantum chemistry² can provide meaningful insights describing the so-called potential energy surface (PES) landscape. Fig. 1.2 shown an example of a two-dimensional potential energy curve. As discussed in subsection 1.1, a PES provides meaningful information such as minima (reagents, intermediates, and products) and so-called saddle points, which are associated to transition states. The difference in energy between minima or minimum and saddle point provides the binding energies, reaction energies, and energy barriers, as shown in Fig. 1.2.¹¹

The so-called Born-Oppenheimer approximation states that the nuclear and electronic wave functions can be treated separately, because of the large difference between the electron mass and the masses of atomic nuclei, and, therefore, the time scales on which they move. Thus, we can approximately solve the non-relativistic time-independent electronic Schrödinger equation:

$$\hat{H}\Psi = E\Psi \quad (1.1)$$

\hat{H} is the Hamiltonian operator that includes the kinetic energy of the electrons, the potential energy of the electrons and nuclei, the potential energy of each nucleus-electron interaction, electron-electron interaction, and nucleus-nucleus interaction as well as dispersion energy (electronic long-range interactions). E is the electronic energy and Ψ is the electronic wave function that is often approximated by a linear combination of basis functions.¹¹ Obtaining a good estimation of the electronic interactions (correlation) is the main problem of solving the Schrödinger equation due to the many electronic contributions (many-body problem).¹¹

Several methods, in quantum chemistry, have been developed to solve the Schrödinger equation. For instance, the Hartree-Fock (HF) method can approximate the Ψ as a single Slater determinant of N one-electron spin orbitals (product of a spatial orbital and its spin functions):

$$\Psi_{HF} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \Psi_1(\vec{r}_1) & \dots & \Psi_N(\vec{r}_1) \\ \vdots & \ddots & \vdots \\ \Psi_1(\vec{r}_N) & \dots & \Psi_N(\vec{r}_N) \end{vmatrix} \quad (1.2)$$

N is the number of electrons, \vec{r} is the coordinate, Ψ_N is the N one-electron spin-orbital. The Slater determinant in equation (1.2) makes sure that the wave function is antisymmetric, on exchanging two-electrons with respect to their position, and using the spin-orbitals as an orthonormal basis.¹¹ The baseline of this method is that the electrons move independently with respect to each other considering their average position. The electrons feel the Coulomb repulsion and a exchanging interaction (they exchange their positions) due to the antisymmetrization. For all these reasons, the HF method is known as mean-field theory and, also, self-consistent field (SCF) since the Schrödinger equation is solved iteratively starting from a guessed spin-orbital.¹¹ The consequence of using an approximated wave function to solve the Schrödinger equation is that the electronic energy will be always higher than the true energy (variational problem).¹¹

In order to improve on the major shortcoming of HF theory, namely electronic correlation, so-called post-Hartree Fock methods have been developed. One of these methods, coupled-cluster characterized by iterative inclusion of single and double excitations with perturbative inclusion of triple excitations, CCSD(T), is nowadays often seen as the gold standard of computational chemistry.¹¹

1.3.1. Density Functional Theory

One way to calculate the ground state energy of a molecule or collection of molecules is to make use of Density Functional Theory (DFT) developed by Walter Kohn and co-workers⁶⁴ who received the nobel prize for this in

1998. DFT is a cheap and accurate way based on a single Slater Determinant that replaces the N -dimensional wave function by a 3-dimensional electron distribution function. Hence, this method is a convenient alternative to wave function-based methods to model large systems with a computational cost similar to Hartree Fock and accuracy similar or lower to Post-Hartree-Fock methods.^{11,64}

DFT is based on the two Hohenberg-Kohn (HK) theorems.⁶⁵ *The ground state energy ($E[\rho]$) can be expressed as integral (\int) of the sum of an external potential $v(r)$ of an interacting electron gas in the ground state and a universal functional $F[\rho(r)]$ of the density (i.e., a function of another function) of a multi-electron system:*

$$E[\rho] = \int v(r)\rho(r)dr + F[\rho(r)] \quad (1.3)$$

This is the first Hohenberg-Kohn theorem⁶⁵ that announces the existence of a functional. The latter cannot be identified exactly which is one of the main problems of DFT. The $F[\rho(r)]$ can be expressed as sum of functional contributions:

$$F[\rho(r)] = T[\rho(r)] + Q[\rho(r)] + E_{ee}[\rho(r)] \quad (1.4)$$

$T[\rho(r)]$ is the kinetic energy, $Q[\rho(r)]$ is the known classical Coulomb interaction, and $E_{ee}[\rho(r)]$ is the energy of a quantum contribution of the electron-electron repulsion.

$T[\rho(r)]$ has two contributions, one is the known contribution of electron interactions ($T_{known}[\rho(r)]$) and a second contribution, describing the Pauli exclusion principle, that is unknown ($T_{unknown}[\rho(r)]$). The unknown contribution and $E_{ee}[\rho(r)]$ can be written as:

$$E_{xc}[\rho(r)] = E_{ee}[\rho(r)] + T_{unknown}[\rho(r)] \quad (1.5)$$

$E_{xc}[\rho(r)]$ is a new functional that is named exchange-correlation functional that includes the unknown contribution of the ground state energy.

Therefore, the energy of a ground state system ($E[\rho(r)]$) can be written as:

$$E[\rho(r)] = E_{known}[\rho(r)] + E_{xc}[\rho(r)] \quad (1.6)$$

the $E_{known}[\rho(r)]$ includes the electron kinetic energy and the Coulomb interactions between the nuclei and the electrons, electron pairs, and nuclei pairs.

The second Hohenberg-Kohn theorem, following in the footsteps of the variational problem,¹¹ defines that *the ground state energy will be higher or equal than the true ground-state energy when a trial electron density $[\rho']$ function is used to solve the Schrödinger equation:*

$$E[\rho'(r)] \geq E[\rho(r)] \quad (1.7)$$

$E[\rho(\mathbf{r})]$ is also defined as electronic energy and its accuracy is related to the used exchange-correlation functionals (Eq. 1.5).¹¹

Kohn and Sham overcame the difficulties of modeling a many-body system of interactive electrons, using an alternative method to solve the Schrödinger equation. The so-called Kohn Sham (KS) equation is based on one single Slater determinant of spin-orbitals with a local effective potential:

$$\left[\frac{-\hbar^2}{2m} \Delta^2 + V(\rho(\mathbf{r})) + V_H(\rho(\mathbf{r})) + V_{xc}(\rho(\mathbf{r})) \right] \rho_i(\mathbf{r}) = E[\rho_i(\mathbf{r})] \rho_i(\mathbf{r}) \quad (1.8)$$

\hbar is the reduced Planck constant ($h/2\pi$), m is the mass of the electron, $V(\rho(\mathbf{r}))$ is the potential of the electron and the nuclei, $V_H(\rho(\mathbf{r}))$ is the Hartree potential (the electrostatic potential of the electron charge density), whereas $V_{xc}(\rho(\mathbf{r}))$ is the functional derivative of the exchange-correlation energy:

$$V_{xc}(\rho(\mathbf{r})) = \frac{\delta E_{xc}(\rho(\mathbf{r}))}{\delta \rho(\mathbf{r})} \quad (1.9)$$

This approximation overcomes the issue to define the $T_{unknown}[\rho(\mathbf{r})]$ of the functional and introduces a one-electron interactive system.¹¹ In this way the energy of a system, with non-interactive electrons, can be described as the single contribution of multiple terms (electronic kinetic energy, Coulomb interactions, and exchange-correlation energy). In this way, the approximated system has the same density as a real system of interacting electrons with a low computational cost.¹¹

In order to solve the Kohn-Sham equation, we need to know $\rho(\mathbf{r})$, but in order to know $\rho(\mathbf{r})$, we need to solve the Kohn-Sham equation. A way to overcome this difficulty is to use the self-consistent field⁶⁶ (SCF) method. SCF method consists of using a trial electron density ($\rho'(\mathbf{r})$) to solve the Kohn-Sham equation and then compare the calculated electron density distribution to the initial one. The electron density distribution function is updated and used for the following iteration cycle and this process is continued until a specified accuracy is achieved.¹¹

1.3.2. Exchange-Correlation Functionals

Over the years, several classes of exchange-correlation functionals have been developed: Local-density approximation (LDA), local spin-density approximation (LSDA), generalized gradient approximation (GGA), meta GGA, hybrid GGA and hybrid meta GGA.¹¹ These classes are schematized in Fig. 1.11.

LDA and LSDA uses a uniform electron gas to define the E_{xc} , however, this ignores that the electron density is not uniform. To overcome the

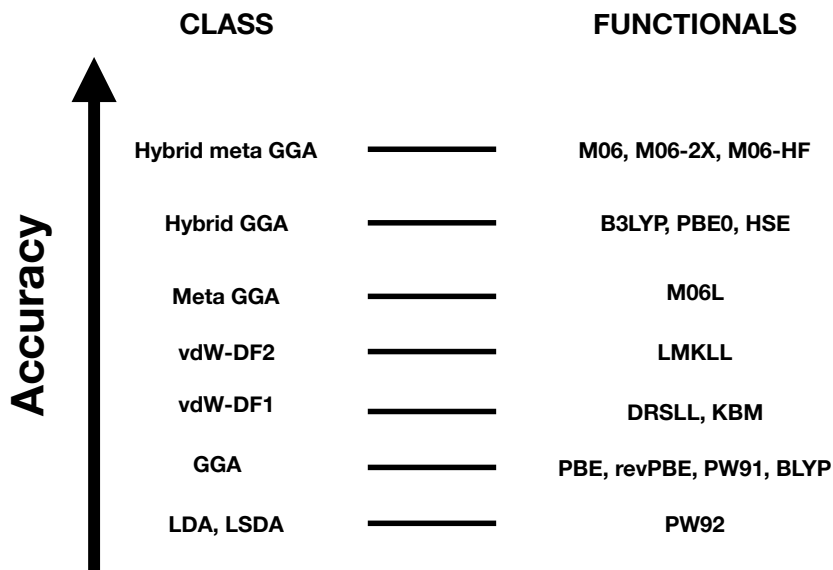


Figure 1.11: Jacob's ladder scheme of seven classes of exchange-correlation functionals, including Van der Waals functionals, according to Perdew *et al.*⁶⁷ For each class, some of the commonly used functionals are reported.⁶⁸⁻⁷⁷

non-homogeneity of the electron density, one can use GGA functionals, such as PBE and PW91,⁶⁹ that make use of the first derivative of the electron density. However, both functionals are far from being perfect and accurate especially for highly correlated systems and van der Waals complexes.⁷⁸ More accurate than GGA is the meta-GGA that makes use of the Laplacian, *i.e.*, the second derivative of the electron density.¹¹ Meta-GGAs widely used are the so-called "Minnesota Functionals" such as M06-L.⁷⁷ In order to increase the accuracy of DFT functionals, the integration of the exact exchange part using a wave function-based method, such as Hartree Fock, can be included in the exchange-correlation functional. Such type of functionals are called hybrid functionals.¹¹ In astrochemistry, the Becke three parameters Lee-Yang-Parr functional (B3LYP)⁷⁴ is one of the most used and employed hybrid GGA to compute both spectra and studying reaction pathways.⁷⁹ However, hybrid functionals such as B3LYP poorly describe all systems in which the dispersion energy (non-covalent interactions) plays an important role.⁸⁰ To overcome this issue, Donald Truhlar developed also the hybrid version of the meta-GGA functionals, such as M06 and M06-2X, that include a certain percent of the exact Hartree Fock exchange.⁷⁷

However, it is not always possible to employ hybrid functionals and

meta-GGA functionals. This is particularly the case for computational demanding periodic systems (solid-state).¹²

Commonly, DFT functionals do not take into account the dispersion forces that are long-distance interactions between two molecules or an atom and a molecule.⁸¹ Therefore, in order to accurately describe non-covalent interactions such as Van der Waals and London dispersion forces, the use of van der Waals functionals (vdW-DF) based on the electron density is needed.⁸² VdW-DFs describe the exchange-correlation energy (E_{xc}^{vdW-DF}) as:

$$E_{xc}^{vdW-DF} = E_{xc} + E_c^{nl} \quad (1.10)$$

E_{xc} is the exchange energy of the functional that lies at the basis of the particular vdW-DF used, for instance revPBE.⁷⁰ E_c^{nl} is the non-local dispersion energy and also contributes to the correlation of interacting electrons at a short distance. The original vdW-DF is DRSL that takes its name from the developers Dion, Rydberg, Schröder, Langreth, Lundqvist.⁷² The advantage of this vdW-DF⁸² and its upgraded version vdW-DF2^{83,84} is that the dispersion energy is self-consistently included via the charge density. Another way to estimate the dispersion energy is to employ empirical corrections called DFT-D ("DFT-Dispersion") developed by Prof. Grimme's groups.⁸¹ Sometimes DFT-D method uses damping functions, such as that one developed by Becke-Johnson⁸⁵ (BJ damping), to avoid overcounting the correlation at intermediate distances.⁸¹

1.3.3. Basis Sets, Periodic Approach and Electronic Structure

In order to overcome the mathematical complexity of solving the Schrodinger equation, we need to use a finite set of basis functions, named basis sets.¹¹ In this way, the orbitals can be expressed as a linear combination of basis functions. The most commonly used basis sets employed for gas-phase calculations are localized atomic orbitals (LCAO) that are centered on the atomic positions. When there are multiple basis functions (single, double, triple, etc.) for a single valence orbital, we define single zeta basis set (SZ), double zeta basis set (DZ), and so on.¹¹ Sometimes basis sets might include one or more polarization functions and diffusive functions. These extra functions include the polarization of the electron density and the flexibility of the atomic orbitals to enlarge and change shape to account for dipole moments or anions, respectively.¹¹ It is commonly mandatory to use polarization functions to obtain publishable results. LCAO basis sets are commonly implemented in DFT codes for gas phase calculations such as Gaussian,⁸⁶ NWChem⁸⁷ and PSI4.⁸⁸ For solid systems, periodic boundary conditions (PBC) must be applied to the model that is placed in a box called unit cell. The unit cell is defined by three lattice vectors and by

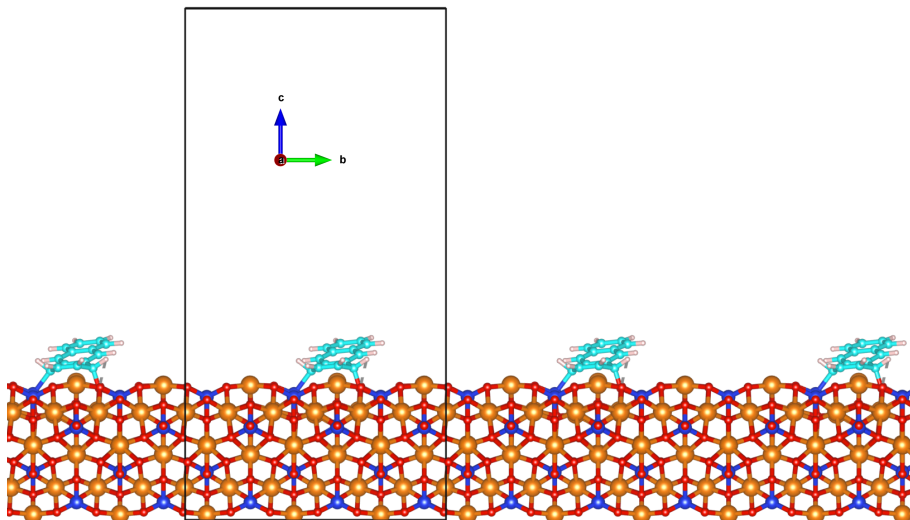


Figure 1.12: Translation symmetry along the axis (a) of a naphthalene unit chemisorbed on a forsterite (Mg_2SiO_4) surface. The box is the unit cell defined by the vector (a), (b) and (c).

repeating in the three corresponding spatial directions, the translational symmetry of a crystalline structure is obtained, as shown in Fig. 1.12.⁸⁹ In order to solve the Schrödinger equation for a periodic system, it is more convenient for the wave function (Ψ) to take the form of a plane-wave in a periodic potential, mathematically, described by Bloch's theorem:⁸⁹

$$\Psi(r) = e^{ik \cdot r} p(r) \quad (1.11)$$

r is the atomic position, e is the Euler's number, i is the imaginary unit, k is the set of reciprocal lattice vectors (Brillouin's zone) and p is a periodic expansion in r space directions. Plane waves basis sets (PW) are the most commonly used basis sets for periodic structures. PWs are not centered in the nuclei and they fill uniformly the region of space occupied by the system inside the unit cell. The number of plane waves are defined by a cutoff energy.⁸⁹ To obtain accurate results, a higher cutoff energy must be carefully selected which carries high computational cost. A way to avoid the use of large basis sets is to fix the core electrons of each atoms using pseudopotentials.⁸⁹ Core electrons are not that important to describe the chemical bond which is the reason why several pseudopotentials have been implemented for PW codes such as the ultrasoft pseudopotentials and projector augmented-wave (PAW).^{90,91} Therefore, PWs are the most common basis sets used for solid systems implemented in codes such as VASP,⁹² Quantum Espresso,⁹³ Abinit⁹⁴ and GPAW.⁹⁵

LCAO can also be employed in periodic systems multiplying them for the phase $e^{ik\cdot r}$ using the Bloch's theorem.^{96,97} Widely used periodic DFT codes with LCAO are SIESTA⁹⁸ and Crystal.⁹⁹ LCAO is less commonly used, with respect to PWs, due to the basis set superposition error¹⁰⁰ (BSSE). BSSE is an error of the basis sets that overestimates the energy of a system composed of any two closely interacting entities, *e.g.*, a dimer or an adsorbed molecule. This is caused by the electron density described by functions centered on other nuclei.¹² A widely used procedure to overcome the BSSE, for an adsorbed atomic or molecular species (A) onto another one (B), adduct AB, is to use the counterpoise method¹⁰¹ (CP):

$$\Delta E_{CP} = (E_{A[ghost]B} + E_{AB[ghost]}) - (E_{A^*} + E_{B^*}) \quad (1.12)$$

ΔE_{CP} is the counterpoise energy correction that will be added to the binding energy to obtain the CP corrected energy. E_{A^*} is the energy of a single point calculation of the adduct AB deprived by B. E_{B^*} is energy of a single point calculation of the adduct AB deprived by A. $E_{A[ghost]B}$ is the energy of a single point calculation of the adduct AB in which the basis sets of A has been deprived of the A nuclei (ghost atoms) and $E_{AB[ghost]}$ is vice-versa. PW basis sets do not suffer from the BSSE since they uniformly fill the space occupied by the system and, therefore, they are considered the standard for periodic calculations. However, they can be orders of magnitude more computationally expensive than LCAO basis sets when surfaces are modeled.¹² This is caused by the filling nature of PWs that uniformly occupies the vacuum region in the unit cell, the empty space facing the surface as shown in Fig. 1.12. On the contrary, LCAOs are only centered in the atomic positions. This is the reason why we need to account for a large number of PWs to obtain accurate results, which in turn are computationally demanding. Therefore, LCAOs even though less accurate than PWs are widely used for large systems. On top of this, the CP correction reduces the binding energy obtaining results comparable with PWs methods.¹²

The bands, namely the periodic orbitals, defined by Bloch's electrons can be estimated for each k-points.⁸⁹ The k-points can be easily sampled for a calculation using the Monkhorst Pack¹⁰² scheme and they are inversely proportional to the unit cell.⁸⁹ The interpolation of the eigenvalue for each k-point defines the band structure in which, for a specific energy range, the projection of the single atomic orbital on the total crystal orbital defines the Projected Density of State (PDOS, the contribution of an atomic orbital to the total electronic structure).⁸⁹

1.4. This Thesis

This thesis is a quantum chemical study of important catalytic processes that occur in the ISM and solar system involving PAHs. The content of this thesis is as follows:

Chapter 2, Superhydrogenation of Pentacene: the Reactivity of Zigzag-Edges. This chapter is a combined theoretical and experimental effort between Leiden Observatory, Milan University, and Aarhus University. The aim of this study is to understand the hydrogen sequence that leads to superhydrogenated pentacene molecule (a pentacene completely hydrogenated) and explains the so-called magic numbers shown in the mass spectra peaking at a pentacene molecule with 2, 4, 6, 10, 16, and 22 extra hydrogens attached. Study the hydrogenation sequence of PAHs and therefore their hydrogenated intermediates that range from a single hydrogenation to a full hydrogenation is important to understand their potential catalytic role for molecular hydrogen formation.

In this study we clarified the role of binding energy with respect to barrier energy in the hydrogenation sequence of pentacene. Specifically, the binding energy tells us about the stability of hydrogenated species, whereas the barrier energy allows us to identify species with longer lifetimes, that control the magic numbers. Moreover, the hydrogen sequence revealed a possible route for nanotubular formation. Based on the DFT calculations, linear PAHs such as pentacene are more reactive with respect to pericondensed PAHs such coronene and, therefore, they might play important roles in catalyzing H_2 in the PDRs.

Chapter 3, Do Defects in PAHs Promote Catalytic Activity in Space? Stone-Wales Pyrene as a Test Case. In line with chapter 2, the hydrogenation of PAHs might open up new chemical reactivity. The aim of this work is to identify possible catalytic routes for the formation of the Stone-Wales defect and molecular hydrogen formation catalyzed by this defect. Using DFT methods, we found that the hydrogen radical is able to catalyze Stone-Wales formation in a prototype PAH such as pyrene reducing the barrier by about 2 eV. Once the SW defect is formed, it is stable due to the large barrier in the backward reaction. The defect also increases the reactivity of the PAH toward hydrogen chemisorption and reduces the barrier for molecular hydrogen extraction. Hence, catalysts such as H and PAHs may play an important role for isomerization and catalytic conversion of H to H_2 in the ISM.

Chapter 4, Interaction of Aromatic Molecules with Forsterite: Accuracy of the Periodic DFT-D4 Method. Prior to studying the interaction of PAHs on silicates, specifically the forsterite mineral (chapter 5), an accurate DFT method to compute surface phenomena at the inorganic

interface of the mineral needed to be identified. We tested DFT methods, using both LCAO and PW, for the adsorption of benzene, naphthalene and benzocoronene on the [010] forsterite surface and transition metal-doped surfaces (Fe and Ni). We tested the empirical dispersion corrected PBE (PBE-D4) functional and a van der Waals functional (DRSLL), comparing their results with PW methods. Furthermore, we clarified the role of BSSE which is indispensable to accurately predict binding energies, comparable to those obtained by PW methods. In order to evaluate the accuracy of PBE-D4 and DRSLL, when transition metals are employed, we modeled a small system, benzene-transition metal cation complexes, as a reference for big-scale systems, and we compared the results with post-HF methods. PBE-D4 with LCAO provided a good description of the binding energy of PAHs on forsterite surfaces, agreeing well with PW and post-HF methods.

Chapter 5, Adsorption of PAHs and C₆₀ onto Forsterite: C-H Bond Activation by the Schottky Vacancy. Using the PBE-D4 approach benchmarked in chapter 4, we study the adsorption of a sample of PAHs (naphthalene, anthracene, fluoranthene, pyrene, coronene, and benzocoronene), along with fullerene, on [010]-forsterite and its defective surfaces (Fe, Ni-doping and MgO Schottky vacancy). The aim is to study the interaction of PAHs and C₆₀ onto (010) forsterite surfaces and the C-H activation (bond breaking) of PAHs catalyzed by the Schottky defect. This has important implications for studying the chemical evolution of these molecules in the ISM and the solar system.

PAHs and C₆₀ adsorbs with high stability on the Fe and pristine (010) forsterite surfaces with respect to Ni one. The adsorption of these species is driven by the number of atomic interactions with the surface and the surface area of the molecule. The Schottky vacancy surface showed different reactivity with respect to pristine and transition metal surfaces. This is due to the orientation of the PAHs adsorbing onto the surface. The parallel adsorption with respect to the surface leads to strong adsorption and chemisorption of naphthalene, anthracene, fluoranthene, benzocoronene, and fullerene with the formation of stable C-O and C-Si covalent bonds. Pyrene and coronene prefer to be only physisorbed forcing the vacancy to reconstruct (local bond formation between the atoms) their Si and O atoms, whereas the fullerene cage is stabilized by the formation of covalent bonds.

The perpendicular adsorption of PAHs onto the Schottky vacancy surface leads to the breaking of the C-H bond of PAHs through an exoergic and barrierless process. This effect is promoted by the formation of Frustrated Lewis Pairs (FLP) in the vacancy. These FLPs are localized Lewis acids and bases that cannot bind due to geometrical hindrance and, hence, this causes the strong catalytic activity of the vacancy surface.

The Schottky vacancy has shown great catalytic potential that might trigger the breakdown reaction of PAHs in asteroidal settings. This, thus, has great implications for understanding the organic inventory formation

of the solar system.

1.5. Future Perspectives

This study carried out during the four years of this PhD contributes to identifying the role of linear and defective PAHs in molecular hydrogen production and partially answers the question: What is the role of interstellar molecules in the evolution of the Universe?

The employing of accurate computational methods to study the organic evolution of PAHs on minerals is the starting point that can be used as guidance for future studies. This will contribute to answering the question: How are PAHs related to the molecular inventory of the Earth and the terrestrial planets in the solar system? Future experimental studies using sophisticated techniques such as scanning electron, tunneling microscopy, and atomic force microscopy (SEM, STM, and AFM respectively), will help to obtain images of the local density of state of those PAHs on the mineral surface, whereas temperature-programmed desorption (TPD) will estimate their binding energy to the surface.² This will help to further verify and confirm the accuracy of the periodic DFT-D4 method employed in this thesis.

Future quantum chemistry development, which I will personally carry out during my post-doc at Chicago University, of multi-reference methods on periodic systems will open a new future frontier for astrochemistry. Specifically, further development of density matrix embedding theory¹⁰³ for periodic systems will allow the inclusion of multi-reference methods to accurately model strongly correlated systems such as the adsorption and reaction of PAHs on minerals containing transition metals. On top of this, future studies on surrogated machine learning methods¹⁰⁴ will contribute to correctly predict the structure of defects in solid materials, such as forsterite, that are not in thermodynamic equilibrium (*e.g.*, in the ISM environment). This cannot be predicted using only chemical intuition such as the case of amorphous materials and the formation of reconstructions of the atoms in the defect.¹⁰⁴

On the astronomical side, the launch of the James Webb Space Telescope (JWST) with its high spatial and spectral resolution and its high sensitivity will allow us to characterize PAHs in protoplanetary disks. As the PAH emission is sensitive to the local physical conditions (*e.g.*, temperature and pressure), this will contribute to answering the key question: how can molecules be used to probe the Universe?^{23,105,106} Moreover, combining computational, experimental, and observational studies will shed light on the formation, diffusion, and chemical activation of PAHs from the ISM to the solar system. Thus, this will clarify the link between interstellar PAHs and the organic inventory of meteorites. Future studies will need to address the IR characterization of PAHs with defects (*e.g.*, Stone-Wales) in

support of future JWST observations.

Studies on the hydrogenation sequence of mineral-supported PAHs might further explain the formation of complex organic molecules in interstellar environment. Moreover, data from NASA's missions (OSIRIS-REx¹⁰⁷ and Lucy¹⁰⁸) will further support future theoretical studies on shedding light on the catalysis of PAHs during the aqueous alteration of asteroids, specifically their role in catalyzing the proton exchange with the mineral as well as their role as precursors of complex organic molecules. In particular, the OSIRIS-REx mission – launched by NASA in 2016 – will return about 60 grams of asteroid material (asteroid 101955 Bennu) to Earth in September of 2023. Detailed analysis of its mineral and carbonaceous content may shed further light on the organic composition of primitive objects in the solar system.