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Interstellar catalysts and the PAH universe

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SUMMARY

Our universe seems a dark and empty space. However, the universe is the habitat of a variety of molecules that contribute to forming galaxies, solar systems, and planets. Molecules ubiquitous in the universe are called "Polycyclic Aromatic Hydrocarbons" (namely PAHs). They are molecules formed by a carbon skeleton that looks like a honeycomb (hexagonal rings) with hydrogens attached to their edges (examples of PAHs are shown in Fig. 5.22). PAHs lock up an important fraction of the elemental carbon (about 20%) in the universe and they help to maintain the physical and chemical balance in certain regions of the universe. PAHs are, amongst others, formed in the surrounding of a carbon-rich star. However, future observational, experimental, and theoretical investigations are necessary to fully understand their formation.

Studying how molecules react in the universe is indispensable to understand important physical and chemical processes as well as how life emerged. The hypothesized pathways to the formation of organic molecules in space are divided into bottom-up and top-down approaches. The bottom-up chemistry consists of building complex molecules starting from a small molecule or an atom forming a bigger one. The top-down approach consists of forming complex molecules breaking down big structures into smaller ones. The breaking down process might occur through energetic processes such as radiation.

Our universe is a hostile environment in which extreme physical conditions might impede chemical processes.

Molecules, as well as solid materials such as minerals, are capable to reduces the energy required to form molecular species, and such type of process is called catalysis, and catalysts are the atomic, molecular, or solid entities responsible for this process. PAHs are known to offer molecular surfaces (process 1 in Fig. 5.22) on which small atoms, such as the most abundant atomic hydrogen, can meet and react forming molecular

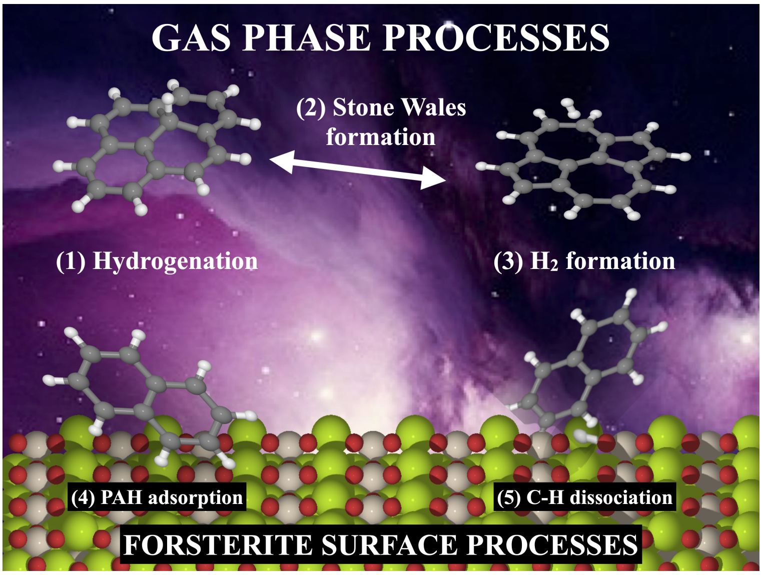

Figure 5.22: Scheme of the chemical processes studied in this thesis: chemical reactions occurring in the gas-phase, from 1 to 3, and on forsterite surface from 4 to 5.

hydrogen (process 3 in Fig. 5.22). This process is in general impeded without the presence of PAHs or dust grains. In some regions of the interstellar medium (the medium between the stars) such as the so-called photo-dissociation regions, the presence of strong radiation fields does not allow the formation of molecular entities. However, PAHs can catalyze the molecular hydrogen formation (process 3 in Fig. 5.22) more efficiently with respect to other surfaces such as dust grains.

It is still not clear how molecules are adsorbed on mineral grains in the interstellar medium and how they are delivered into the solar system and, thus, this is still under investigation. We find PAHs along with other molecular species such as amino acids (the building blocks of life) in the solar system and specifically in meteorites. Hence, meteorites lock up different organic species that might have been formed in the early stage of our solar system. The key questions of astrochemistry and cosmochemistry are related to shedding light on the role of molecules in the universe and the formation of the so-called organic inventory of the solar system. Specifically, how the elemental carbon locked in PAHs might be linked to the diverse organic species found in meteorites.

This thesis aims to understand the catalytic process that leads to the formation of molecular hydrogen in the interstellar medium (process 3 in Fig. 5.22) and the breakdown of PAHs in asteroidal settings (process 5 in Fig. 5.22). This has been achieved using density functional theory (DFT) which is a quantum chemical method allowing to model large organic molecules and predict their reactivity. **Chapter 2** and **3** of this thesis aim to understand the catalytic process that leads to molecular hydrogen formation. **Chapter 4** and **5** focus on the accuracy of quantum chemistry methods to model the interaction of PAHs and forsterite as well as the chemical processes occurring on forsterite surfaces.

PAHs and Molecular Hydrogen

I studied, using quantum chemical methods, the hydrogenation sequence that leads to the formation of fully hydrogenated pentacene, a linear PAH. This is to explain the presence of several hydrogenated pentacenes (pentacenes with different numbers of extra hydrogens attached to their surfaces) found in the experiments (**Chapter 2**). In **Chapter 3**, I studied the mechanism that leads to the formation of Stone-Wales pyrene (processes 1-3 in Fig. 5.22), a PAH with two heptagons and pentagons. Specifically, an atomic hydrogen can reduce the energy necessary to the formation of the Stone Wales which in turn can catalyze the formation of molecular hydrogen.

PAHs and the Forsterite Mineral

In **Chapter 4**, I tested the DFT methods in order to study the interaction of organic molecules on forsterite. I found that the new DFT-D4 approach which takes into consideration the long range interactions between the molecule and the surface can be used to accurately model PAHs on a silicate mineral surface such as forsterite (a magnesium silicate) using a low computational power. In the last chapter (**chapter 5**), using the DFT methods tested in **chapter 4**, I investigated the adsorption of a set of PAHs on the forsterite surface (process 5 in Fig. 5.22) and forsterite defective surfaces. Specifically, I modeled a defective forsterite surface with the presence of an iron and another one with nickel replacing a magnesium atom. Furthermore, I investigated the so-called Schottky defect which is formed by the lack of adjacent magnesium and an oxygen atom (a vacancy surface). The Schottky vacancy shows to have high catalytic activity for a barrierless breaking of the carbon-hydrogen bond of PAHs (process 5 in Fig. 5.22).

Future Investigations

Future development of quantum chemical methods as well as experimental studies and observation with the launch of the James Webb Space Telescope will clarify the link between PAHs and the so-called complex organic molecules found in the solar system.