ENGLISH SUMMARY

Astrochemistry studies the formation and fragmentation processes of molecules in the interstellar medium, where the conditions for chemistry are very different from those on Earth since densities and temperatures are far lower and the ultraviolet radiation is stronger and can easily break down most complexes. These molecules are not only interesting from the perspective of the chemical reactions they can undergo under the exotic conditions of space, but also because they can be used to trace the physical conditions of the regions where they reside. Since ultraviolet light is efficient when it comes to destroying molecules, a large part of the research in astrochemistry has been focused on more "shielded" regions, where the density is high for the general interstellar medium (but still low when compared to those typically found on Earth) and thus the more destructive photons cannot enter deep inside the region. However, it has been known for some time that large carbon molecules can survive far longer than others in highly irradiated environments due to their high stability.

Among those relevant for space, the best studied chemical reactions are those that occur on the surface of dust grains, which are intermixed with the gas in the interstellar medium. In regions of space where ultraviolet radiation cannot penetrate efficiently and the temperatures drops to only a few dozen degrees above absolute zero, atoms and molecules can freeze on top of dust grains. This increases the chance for them to interact with each other and react to form more complex molecules. This type of reactions in the gas phase can be efficient for a few molecules, but are generally much less likely to occur. This mechanism, where small units are joined together (either in the gas phase or as part of ices), is referred to as "bottom-up" interstellar chemistry.

As mentioned before, large carbon molecules are observed to survive for longer under physical conditions that can quickly destroy most other molecules. Of these, the most abundant are polycyclic aromatic hydrocarbons (PAHs), a whole family of molecules which can be observed by their vibrational emission lines in the mid-infrared. PAHs correspond to molecules consisting of multiple rings joined together (thus polycyclic), and characterized by "aromatic" bonds (a specific type of chemical bonding where some of the electrons are delocalized over the surface of the molecule). The joined rings resemble honeycomb cells, with the vertexes made out of carbon atoms, and the outer edge is terminated by hydrogen atoms. These molecules are typically large, with their carbon content estimated to be between fifty and a hundred atoms. Even though these hydrocarbons are highly stable, they will eventually fragment as well and their destruction can form product molecules very different from those cre-

ated on icy dust grain surfaces. This process can have also different molecules as a starting point, but the abundance and stability of PAHs makes them ideal candidates to dominate this type of chemical reactions. This approach to interstellar chemistry is known as "top-down", and its characterization and impact in astronomy is the main focus of this thesis.

PAHs are not the only large, stable molecule known to exist in the interstellar medium. Less than a decade ago, the fullerene family of molecules were also detected through their mid-infrared emission in multiple galactic and extragalactic objects. Unlike PAHs, fullerenes have a closed cage rather than planar structure and contain exclusively carbon atoms, with a mixture of pentagons and hexagons. The most stable and representative fullerene is buckminsterfullerene, which contains sixty carbon atoms and resembles an old fashioned, black and white football. It has been hypothesized that fullerenes can be formed through the fragmentation of PAHs in areas of the interstellar medium known as photodissociation regions (PDR). These correspond to zones where the strong radiation fields dominate the chemical and physical processes of the interstellar medium. Their name stems from the fact that it is within these regions that the transition between atomic and molecular gas takes place. The side of the PDR which faces the radiation field is dominated by neutral, atomic gas and, as the distance from the source of photons increases, the density increments as well and the particles coalesce into molecules, gradually passing into what is called the molecular cloud.

The exact zone of transition between atomic and molecular gas inside PDRs depends on which molecule is being considered. The first molecule to form (if we look at the PDR from the radiation source and into the molecular cloud) is molecular hydrogen (H_2), which is also the most abundant molecule in the universe. H_2 cannot be formed in the gas phase under the conditions of the interstellar medium, instead requiring catalytic reactions to account for its formation rate. The most common such reaction consists on the deposition of hydrogen atoms onto the surface of interstellar dust grains, where they can react and be released as molecular hydrogen. However, observations of the H_2 formation rate in dense PDRs show that it is about a hundred times larger than the formation rate expected from reactions on dust grains. Reactions involving PAHs have been considered in attempts to reconcile H_2 formation models, but thus far the results have been unsatisfactory.

Much of this thesis work is based on experimental data, collected using the instrument for photodynamics of PAHs (i-PoP). This consists of a quadrupole ion trap attached to a time-of-flight reflectron mass spectrometer. The molecules studied are evaporated using an oven under high vacuum (with pressure about 10^{-10} times lower than atmospheric) and ionized through collisions with electrons. The ions thus formed are then stored in the quadrupole ion trap, where they are irradiated using a laser. The mixture of the original molecule and its fragmentation products are then observed through the time-of-flight mass spectrometer, where species with different masses arrive at the detector at different times. This allows for an understanding of the composition of the photoproducts, but lacks direct evidence on the specific structures formed at each mass.

This thesis deals with the photofragmentation of PAHs in the interstellar medium, with special emphasis on the formation of fullerenes and molecular hydrogen. While these are certainly not the only possible products of PAH fragmentation, they are of

particular relevance for astronomy and their high stability makes them ideal probes of top-down chemical processing. Fullerenes appear to be an abundant species in the interstellar medium and there is strong evidence suggesting that they are the source of some of the diffuse interstellar bands (DIBs). The DIBs are one of the longest standing open questions in astronomy, having been discovered almost a hundred years ago, they appear as absorption lines in the spectra of stars, but its origin is clearly interstellar. The carrier of the DIBs are thought to be molecular but no undisputed identification has been provided. Molecular hydrogen is the most abundant molecule in the universe, but its formation rate in dense PDRs cannot be accounted for using only reactions on dust grains or direct PAH photodissociation. PAHs are known to be abundant in dense PDRs and to fragment at the PDR front (the transition zone between molecular and atomic hydrogen). Isomerization reactions, where the molecular structure changes without the loss of atoms, can enhance H_2 formation from PAH. The approach followed here to investigate both these processes is based on a combination of observations, experiments, theoretical calculations and computational models.

The question of fullerene formation has been addressed in chapter II by using mid- and far-infrared data from *Spitzer* and *Herschel* on a sample of seven PDRs. The abundance of PAHs and fullerenes show evidence of formation trends within resolved sources, but universal trends among all PDRs were not found when taking into account either the radiation field or the ratio of the radiation field over the atomic hydrogen density (related to hydrogen recombination). The sources where fullerenes were conclusively detected have physical conditions consistent with full dehydrogenation of large PAHs, the first step in fullerene formation in a top-down model. However, the abundance of fullerenes, as well as the lack of an overall trend suggest that other parameters, such as PDR age, play a key factor in fullerene formation.

Chapter III provides experimental evidence for the formation of fullerenes from large PAHs. By comparing the photodissociation pattern in mass spectra of PAHs and fullerenes, both clearly display the same "magic numbers". These correspond to fullerene structures with higher stability than others with similar mass. Additionally, both species were also irradiated using light with a 532 nm wavelength, at which the C_{60}^+ fullerene does not absorb light. Experiments using fullerenes showed that all fragmentation stops when the fragments reach the mass of C_{60}^+. PAHs can dissociate further, but the "magic number" pattern disappears after C_{60}^+ and a high fraction of the C_{60}^+ peak remains even at high laser power. This experimental work shows solid evidence for top-down formation of fullerenes in the interstellar medium.

PAH dehydrogenation is a critical process in tackling both questions posed on this thesis. It is the first step in the formation of fullerenes, and it is the instance in which molecular hydrogen can proceed. As such, an extensive study of this process is presented in chapter IV. The first four hydrogen losses from a sample of nine PAHs were studied experimentally, specifically focusing on the ratio between odd and even hydrogen losses as they hold key information on the competition between sequential atomic hydrogen loss and molecular hydrogen loss. For three of the PAHs, a model of the fragmentation process including the possibility of hydrogen mobility along the edge of the molecule, was made on the base of quantum chemical calculations. The experimental results were compared to those of the model and the hydrogen mobility reactions

were found to be critical in explaining the fragmentation process. Molecular hydrogen formation was found to grow in importance as PAH size increases.

To assess the importance of molecular hydrogen formation from PAHs in the context of dense PDRs, the previous results were used to modify an existing model of PAH photodissociation in PDRs. A selection of three PAHs, spanning the possible dehydrogenation scenarios (i.e.: H-loss dominated, H_2-loss dominated and competitive), are presented in chapter V. In PAHs for which H-loss dominates or the two loss processes are in high competition, the molecular hydrogen formation efficiency is not significantly different from those derived in other studies. If the PAH dehydrogenation is dominated by H_2-loss, the efficiency increases by a factor $\sim$20. While this increase is not enough to match the observed formation rate, it reduces the disparity by a great margin. Further work on the size dependence of the dissociation rates has the potential of clearing up this issue.