Chemistry and photophysics of polycyclic aromatic hydrocarbons in the interstellar medium

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In this thesis I focus on several closely related questions regarding the chemical activity of PAHs in the interstellar medium. One of the primary questions we address is “Can PAHs be important catalysts for the formation of H\textsubscript{2} in space?” To understand this catalysis better, it is necessary to know how PAHs react with hydrogen atoms. Since the catalysis takes place in the harsh radiation conditions of the interstellar medium, it is important to ask “Can PAHs and their reaction products survive exposure to UV radiation?” Once the effects of UV radiation are known, there is the final question “How do PAHs contribute to the formation of H\textsubscript{2} in space?”

In chapters 3 and 4 of this thesis, we have experimentally studied the reactivity of PAHs with hydrogen atoms, and shown that PAHs can be easily hydrogenated. To address how PAHs and superhydrogenated PAHs can survive in environments subject to strong UV fields, we have interfaced our setup with the BESSY II synchrotron in Berlin and used its VUV radiation to mimic some of the reactions taking place in the ISM, as shown in chapter 5. In chapter 6 we use a numerical model to show how PAHs catalyze the formation of H\textsubscript{2} in space. The main results of each chapter of this thesis are summarized below.

Chapter 3: I have experimentally studied the reaction between PAHs and hydrogen atoms. A Paul ion trap is used to trap cations of coronene, a PAH that we use as a probe for all PAHs. The trapped coronene is then exposed to a beam of atomic hydrogen, and subsequent mass spectrometry allows for determination of the trap contents. The mass
spectra reveal that the hydrogen atoms react with the coronene cations to form superhydrogenated coronene cations, where the extra H atoms are chemically bound to the molecule. The experiments also show that the incoming gas phase H atoms have to overcome thermal barriers of alternating heights.

Chapter 4: I study what happens to the coronene cations after extended exposure to H atoms, with exposures up to a minute. Such a long exposure time leads to the full hydrogenation of the coronene cation, where every carbon atom is bearing an additional H atom. The alternating barriers found in chapter 3 are observed for every second hydrogenation up to full hydrogenation of the coronene cation. The mass spectra also reveal that coronene with 5, 11, or 17 extra H atoms are the most abundant, and we refer to these as magic numbers of hydrogen atoms. Comparison with DFT calculations shows that for these magic numbers the binding energy is higher than for other hydrogenation states and that for the next hydrogenation reaction the H atom has to overcome a high barrier (0.11 - 0.32 eV).

Chapter 5: I experimentally investigate how regular and superhydrogenated PAHs react to UV radiation. For these experiments we have used the BESSY II synchrotron in Berlin. The entire experimental setup was temporarily moved to the experimental hall in Berlin such that the superhydrogenated coronene cations could be exposed to VUV photons. The superhydrogenated coronene cations are trapped in the Paul ion trap and exposed to VUV radiation with a photon energy between 12 and 30 eV. Mass spectrometry immediately after VUV exposure reveals the ionization and fragmentation patterns for each photon energy. Comparison with the results for regular coronene shows that upon absorption of a photon, superhydrogenated coronene is far more likely to lose the extra H atom than regular coronene. Above the ionization threshold, regular coronene is almost exclusively subject to ionization without loss of H atoms, whereas for superhydrogenated coronene dissociative ionization is the norm.

We also compare the experimental results with an RRK model that allows for the extrapolation of the experimental results to the full range of photon energies that are most relevant to the ISM. These extrapolations show that superhydrogenated coronene will easily lose its extra H atoms in interstellar space, whereas regular coronene will be mostly ionized.
without any dissociation taking place. This implies that in radiation rich environments, such as PDRs, superhydrogenated coronene will be very rare.

The model can be used to extrapolate to different PAH sizes as well. When PAHs contain more than approximately 100 C atoms, they are large enough to dissipate the excitation energy without losing an excess H atom. Superhydrogenated PAHs may thus exist in space, provided that they are large enough, although currently it is estimated that most PAHs in the ISM contain between 20 and 100 carbon atoms.

Chapter 6: I have studied the capability of PAHs to form H$_2$ in radiation-rich interstellar environments. A numerical code is used to evaluate the formation of H$_2$ throughout an entire series of PDRs of varying number densities and radiation fields. We cover the number densities between $10^3$ and $10^6.5$ cm$^{-3}$ and the radiation intensities between $10^2$ and $10^5$ $G_0$. This model includes a chemical network with coronene as a probe for interstellar PAHs, and we consider the different chemical and photoprocesses that these molecules are subject to. The rates of H$_2$ formation are calculated for both PAHs and dust grains, and we observe how these rates affect the transition from atomic to molecular hydrogen inside a PDR. The results of these simulations show that PAHs can have a large effect on the overall structure of the PDR, and significantly change the column density of the H/H$_2$ transition. Moreover, we compare the outcome of our models with observations, and it is clear that H$_2$ formation on PAHs can explain the observed rates of H$_2$ formation in PDRs, which cannot be explained by catalysis on dust grains.

To summarize, this thesis shows that the addition of H atoms to coronene cations is subject to thermal barriers for every second addition up to full hydrogenation, and that superhydrogenated coronene cations with a magic number of extra H atoms are more stable than others. Moreover, these extra H atoms are easily removed by UV radiation, and only larger PAHs can be superhydrogenated in the ISM. That notwithstanding, PAHs can have a large influence on the total rate of H$_2$ formation in PDRs, where the rate of H$_2$ formation by PAHs can be as high as $10^{-16}$ cm$^3$s$^{-1}$. Therefore, the H$_2$ forming capabilities of PAHs should be included in models for PDRs.
7.1 Outlook & Future Experiments

Currently, there are still many open questions regarding the presence of PAHs in the ISM. With the exception of fullerenes, there has not been a unique identification of a single PAH molecule yet. Although such an identification would be the most definite proof for PAHs in interstellar space, it is very unlikely to happen due to the band nature of the IR emission of these molecules.

In this thesis we have compared the photostability of superhydrogenated PAHs to that of regularly hydrogenated PAHs. However, in the interstellar medium a large fraction of PAHs is expected to be in a dehydrogenated state. The full dehydrogenation of PAHs has been observed experimentally by exposure to broadband UV radiation, but the exposure time is sufficiently short (0.5 s) that there is no vibrational relaxation between the different loss events. To understand the step-by-step dehydrogenation process more accurately, it is important to study the photoprocessing of partially dehydrogenated PAHs. One way to conduct such an experiment is by modifying the experimental procedure used in chapter 5. After a single VUV exposure, the trap contents are exposed to a stored waveform inverse Fourier transform (SWIFT) pulse, removing all trap contents with the exception of a single hydrogenation state. This single hydrogenation state is then exposed to another pulse of UV radiation, allowing for the study of the photoabsorption behaviour of the partially dehydrogenated PAH.

While the identification of a single PAH molecule in space has not yet been achieved, it is possible to derive PAH properties from their emission spectra. An IR emission spectrum of the Orion Bar (see Figure 7.1) shows emission features between 3.4 and 3.6 μm next to the 3.3 μm C-H aromatic stretch feature. The origin of these features is still unknown, but the explanations that have been offered include anharmonicity of the vibrational transitions and emission by superhydrogenated PAHs. DFT calculations predict that coronene cations with 5, 11, or 17 additional H atoms would produce these emission features, which can be investigated experimentally by IR action spectroscopy on superhydrogenated PAHs. The necessary intensity in IR light can be obtained from an infrared free electron laser, such as the FELIX facility in Nijmegen. Performing these experiments is an important step where laboratory astrochemistry can
Given the complementary roles of PAHs and dust grains in the formation of H$_2$ it is important to investigate whether PAHs can be important catalysts for the formation of other species as well. This can be studied by letting PAHs react with the more abundant atoms and molecules such as oxygen, the fourth most abundant atom in interstellar space. In a pathfinding experiment performed at the LERMA laboratory in Cergy, monolayers of both regular coronene and superhydrogenated coronene on a substrate of highly ordered pyrolytic graphite have been exposed to a beam of oxygen atoms. The sample is subsequently analyzed by thermally programmed desorption (TPD), where the surface temperature increases linearly and the masses of the desorbing species are studied with a quadrupole mass spectrometer.

The intensities of different masses are compared to a reference measurement that consists of only coronene (M300). These differential intensities
Figure 7.2 – Differential mass spectra of the coronene + H, coronene + H + O, and the coronene + O measurements. The masses associated with coronene and its isotopologues are in black, smaller fragments are in green, superhydrogenated masses are colored blue and masses that involve coronene with at least one oxygen atom are colored red. The three panels show the results for coronene exposed to hydrogen atoms (top), both hydrogen and oxygen atoms (middle), and only oxygen atoms (bottom).

are shown in Figure [7.2] where the different masses are color coded according to their originating process: loss of carbon atoms (green, M274 - M277), regular coronene (black, M299 - M302), superhydrogenation (blue, M303 - M312), and oxygenation (red, M316 - M338). The first tentative results show that superhydrogenation of the coronene molecule makes it easier for an oxygen atom to attach to the molecule as well. Moreover, adding any atom to the coronene molecule appears to weaken the carbon skeleton indicated by an increase of the fragmentation masses. However, a more thorough investigation is necessary for definitive conclusions.

Summarizing, the future study of PAHs in space should be directed at better understanding their IR emission bands. Furthermore, it is important
to understand the complete dynamics of both the addition and the removal of hydrogen atoms from PAH molecules. Last, the possibility of reactions between PAHs and atoms other than hydrogen should be explored to get a full understanding and appreciation of the astrochemical influences of PAHs.