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Chemistry and photophysics of polycyclic aromatic hydrocarbons in the interstellar medium

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Chapter 2

The Experimental Setup

THE experiments described in chapters 3 through 5 were performed with the 'Paultje' setup, which is shown in Figure 2.1. This setup is a tandem mass spectrometer developed and built to study ultrafast dynamics in isolated large molecules in the gas phase (Bari et al., 2011). The setup consists of an electrospray ionization source that produces the molecular ions. These ions are fed into an ion funnel which phase space compresses the initial ion cloud into a narrow beam. Subsequently, the ions are guided along by a quadrupole ion guide, which at a later stage has been replaced by an octopole ion guide. The ion guide provides radial confinement of the ions, and diaphragm electrodes at the beginning and end of the ion guide can be used for axial confinement. Combining these, the ion guide can be used for short term storage of the molecular ions. Lowering the potential on the last diaphragm pulses the ions into a quadrupole mass filter which removes any contaminants from the ion beam. This filtered ion beam is then injected into the Paul ion trap, where it can be trapped for several seconds up to a minute. Simultaneous injection of helium into the trap allows for collisional cooling of the molecular ions to room temperature. Once trapped, the ions can be exposed to a beam of hydrogen atoms or photons, depending on the goal of the experiment. Hereafter, the ions are extracted into a linear time-of-flight mass spectrometer to study the masses of the trap contents.

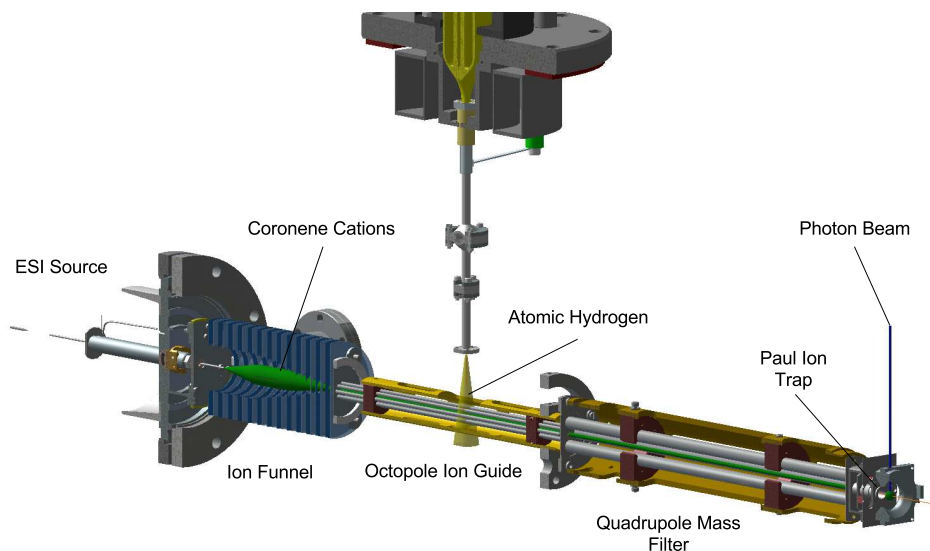


Figure 2.1 – A schematic depiction of the experimental setup. This image does not show the field free region of the TOF mass spectrometer on the right side of the Paul trap.

2.1 Electrospray Ionization

Electrospray ionization (ESI) is a powerful technique to produce gas-phase molecular ions in a gentle manner. This leaves the molecules intact in the gas phase, as opposed to less subtle techniques such as thermal evaporation. The combination of leaving the molecule intact and being able to handle all sorts of molecules regardless of their size makes it a technique that is very well suited to study biomolecules (Gaskell, 1997). Nowadays, electrospray ionization is a standard technique applied in mass spectrometers that are used in biochemical and clinical environments, and in 2002 John Fenn received the Nobel Prize in Chemistry for his pioneering work in this technique.

Most large molecules with molecular masses of hundreds or thousands of atomic mass units (amu) do not evaporate easily. Moreover, these molecules fragment easily when heated to the point of evaporation. With electrospray ionization these molecules can be brought into the gas phase without fragmenting.

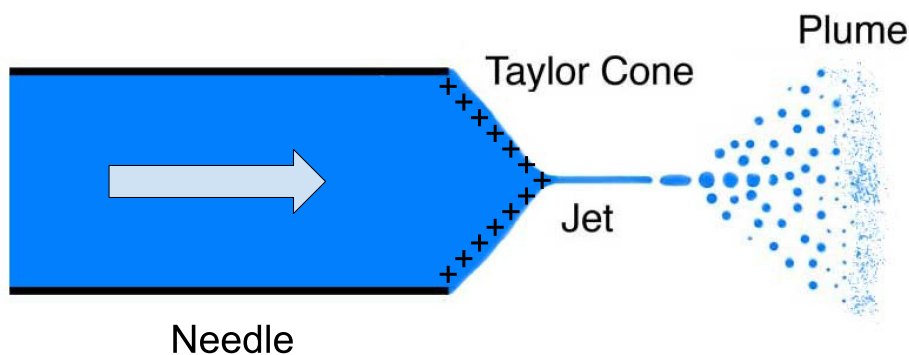


Figure 2.2 – A schematic depiction of the Taylor cone that is formed at the tip of the needle during electrospray ionization. Note the fission into smaller droplets once the electrostatic repulsion exceeds the surface tension of the droplet. This eventually leads to the single molecular ions drifting into the setup.

For electrospray, charged molecules are dissolved in a polar solvent, typically water or an alcohol. This solution is pumped through a needle which is set at a high potential, typically a few kV. The needle is a few mm away from a capillary that provides an opening from the ambient pressure to the vacuum conditions of the setup. As the capillary is kept at a potential no higher than 200 V, there is a steep potential gradient between the needle and the capillary. In combination with the presence of the charged molecules in the solution, a so-called Taylor cone is formed at the tip of the needle, with the charged molecules spread out evenly on the surface because of mutual electrostatic repulsion. Due to the solution being pumped constantly, a small jet emanates from the Taylor cone, as is shown in Figure 2.2. This jet divides into small droplets, which are all moving towards the capillary due to the present electric field. The charged molecules within these droplets all move to the droplet surface as a result of their mutual electrostatic repulsion. Moreover, the small droplets continue to evaporate solvent molecules, until the electrostatic repulsion exceeds the surface tension. Once this happens, the droplet fissions into smaller droplets, which in turn evaporate their solvent molecules, etc. This process ends when only individual gas-phase molecular ions remain.

The electrospray method works particularly well for biomolecules, as they are very easy to charge through protonation. Putting proteins or oligonucleotides in a slightly acidic buffer solution is all it takes to charge them. The lack of hydroxyl- and aminogroups makes PAH molecules such as coronene, our PAH of choice, more difficult to charge through acid-base reactions. We therefore employ a solution of 10 mM AgNO₃ in HPLC-grade methanol to charge coronene molecules by means of ionization.

A sample is prepared by adding 50 μL of the AgNO₃ solution to 650 μL of a saturated solution of coronene in methanol. The Ag⁺ ions perform a charge exchange reaction with the coronene molecules, leading to the formation of coronene cations. This sample solution is then ready for electrospray.

2.2 Ion Funnel

Once inside the main setup, the molecular ions enter the ion funnel, a series of stacked, concentric ring electrodes with a decreasing inner radius, as shown in Figure 2.3. The initial cloud of ions is forced towards the central axis of the funnel by a radio-frequency (RF) field applied to the ring electrodes. This RF field varies in phase with each ring, such that each electrode is in antiphase with its two neighbours.

In addition to the RF field, a static potential is superimposed on each ring electrode such that the ion funnel acts as a voltage ladder, drawing the ions through the funnel. As the ions pass through the increasingly narrower ring electrodes, the original ion cloud is confined into a narrow beam. Simultaneous cooling by collisions with neutral air molecules allows for a compression of the phase-space these ions inhabit (Guan & Marshall, 1996; Shaffer et al., 1997; Kelly et al., 2010; Silveira et al., 2010).

This phase-space compression is necessary for the production of a narrow beam of molecular ions. Monitoring and regulating the pressure is therefore paramount to the production of a proper ion beam. If the pressure is too low, there is no collisional cooling, resulting in an ion beam with an energy that is too high. These energetic molecular ions cannot be trapped in the Paul ion trap and they will just fly through the trap. A too high pressure in the ion funnel will result in many collisions at such a rate that the molecular ion fragments before leaving the funnel.

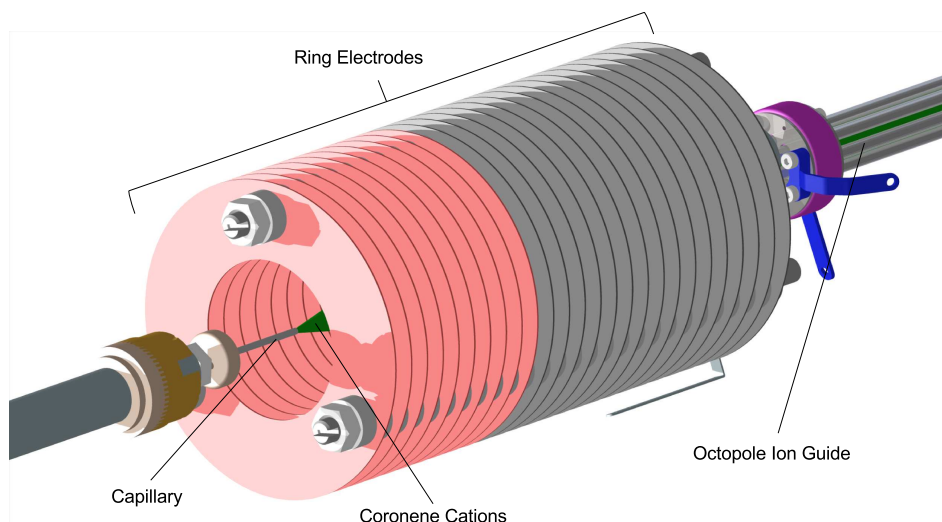


Figure 2.3 – A schematic depiction of the ion funnel. The end of the capillary is visible on the left, and the emerging cloud of molecular ions is shown in green. After phase space compression in the ion funnel, the ions continue into the ion guide, shown on the right.

2.3 Ion Guide

After the ion funnel has confined the beam, the ions are led into an RF ion guide, as is shown in Figure 2.4. This ion guide consists of a linear quadrupole, later replaced by an octopole, and diaphragms at both ends. Although initially mainly used for further compressing the ion beam, the two diaphragms make it possible to use the RF ion guide as a linear trap.

Elevating the voltage on the last diaphragm creates a blockage, causing the ions to bounce back and forth between the diaphragms, while the RF multipole provides radial confinement. Simultaneously, new ions are injected into the ion guide from the ion funnel, increasing the number of ions in the ion guide. Eventually the voltage on the last diaphragm is lowered and the ions are pulsed into the next stage. This temporary storage enables the injection of more ions into the Paul trap, which makes for a higher target density and a clearer signal in the experiments. Moreover, this trapping ability is used in chapter 5 for the production of

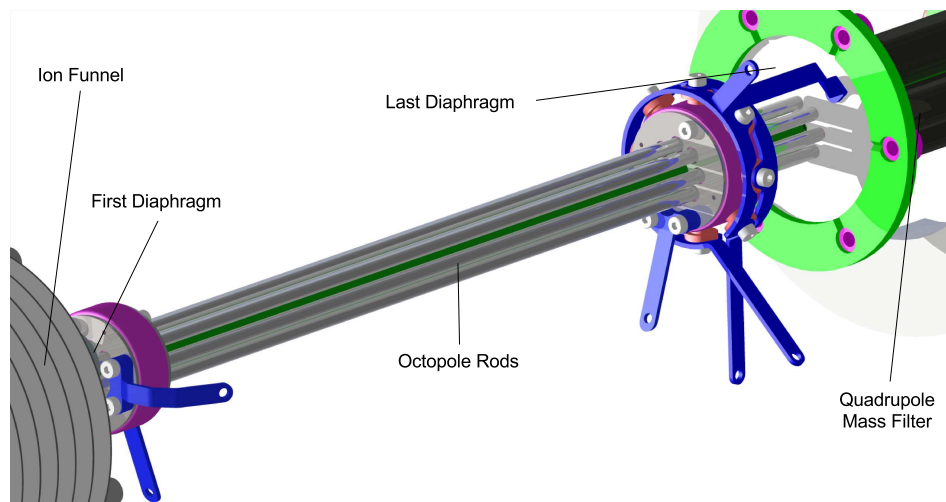


Figure 2.4 – A schematic depiction of the octopole ion guide. Molecular ions enter from the ion funnel (shown on the left) and continue into the quadrupole mass filter (shown on the right).

superhydrogenated coronene ions, and a more detailed description of this procedure is given in section 2.7

2.4 Mass Filter

The mass filter is in place to remove contaminants from the ion beam. Molecules may fragment in the earlier stages of the setup, or a solution contains multiple charge states of the same molecule. This produces background signals that are difficult to correct for, but these can be eliminated using a quadrupole mass filter, which is shown in Figure 2.5. The working principle behind a mass filter is that an RF signal is applied to the four rods of the mass filter in such a way that neighbouring rods are in opposite phase and opposite rods are in identical phase. In addition, a DC voltage is superimposed on the rods. This turns the equations of motion for an ion inside the filter into the Mathieu equations, where the DC voltage U_{DC} , RF voltage U_{RF} , RF frequency ω , ion mass m , and the ion charge z determine the solution for the equation of motion (Paul, 1990). The properties of the Mathieu equations make it possible to choose U_{DC} , U_{RF} , and ω in such a way that only a particle with mass m will follow a stable trajectory, and any other ions will be driven away from the ion beam.

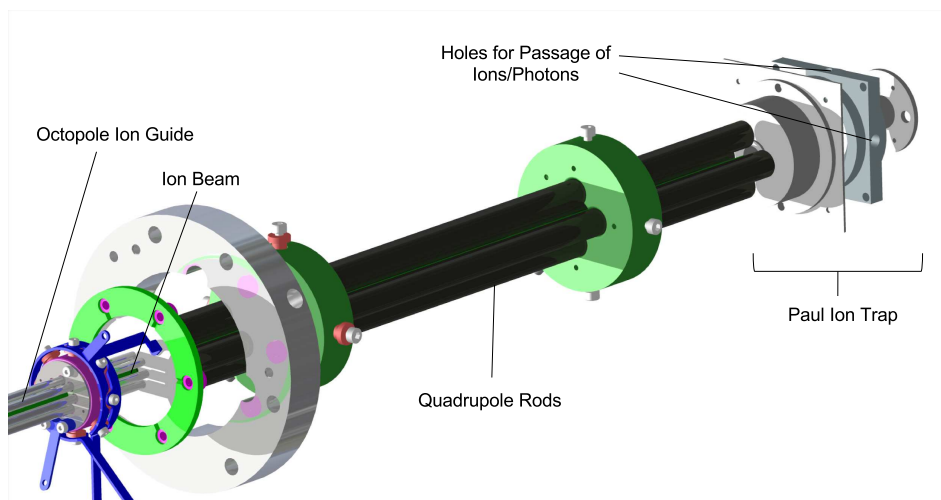


Figure 2.5 – A schematic depiction of the quadrupole mass filter. The unfiltered ion beam enters the mass filter from the ion guide on the left and the filtered beam of molecular ions is injected into the Paul trap, which is shown in the top right corner.

2.5 Paul Ion Trap

After passage through the mass filter, the mass-selected ion beam is injected into the Paul ion trap. During injection room temperature helium is pulsed into the trap to allow for collisional cooling, reducing the ion energy and increasing the number of trapped ions.

The ion trap in this setup is a commercially available quadrupole ion trap (C-1251, Jordan TOF Products, Inc.) where the trapping region is approximately 1 mm in diameter. Consisting of a ring electrode wedged between two endcaps, an RF field on these electrodes keeps the ions in place. The trapping surface of these electrodes resembles that of a hyperboloid (Paul, 1990). A hole is bored on each side of the ring electrode, which allow for the passage of photon beams, ion beams, and atomic hydrogen through the cloud of trapped ions.

2.6 Mass Spectrometer

Linear time-of-flight (TOF) mass spectrometry is used for the characterization of the trap contents. Application of an extraction voltage on the two end-caps of the Paul trap ejects the trap contents into the TOF tube,

where the ions undergo field-free motion. In this field-free region, the ions are separated by their respective mass-over-charge ratio. Particles with the same charge z have the same kinetic energy, since they have been accelerated by the same electric field ΔV : $E_{\text{kin}} = z\Delta V$. However $E_{\text{kin}} = \frac{1}{2}mv^2$, with m the mass of the particle and v its velocity. This means that particles with a higher m/z will travel slower and will thus arrive on the detector at a later time than particles with a lower m/z .

If the molecular ions are separated sufficiently in terms of arrival time and detected with a high enough time resolution, the time of arrival of each ion can be converted to a mass-over-charge ratio. At the end of the TOF tube, the ions are detected with a set of chevron-stacked micro-channel plates connected to a 1 GHz digitizer. With this equipment, we have achieved a mass resolution of $\frac{m}{\Delta m} = 300$.

2.7 Hydrogen Source

The key element in our setup that allows us to do unprecedented work on the hydrogenation of PAH molecules is the interfacing with an atomic hydrogen source. This source can be placed either on top of the Paul trap, or on top of the linear ion guide. The effects of this placement are discussed in section 2.7.1.

The hydrogen source itself is a Slevin type RF discharge source using microwaves to create a hydrogen plasma (Slevin & Stirling, 1981). It consists of a water-cooled pyrex tube placed inside a metal RF resonance cage surrounded by a helical RF antenna. The resonance cavity is a $\lambda/4$ resonator and fed with a 23.6 MHz microwave signal at a total RF power of approximately 20 W. This resonating RF field causes the hydrogen gas to dissociate into a hydrogen plasma (Toennies et al., 1979). The pressure of the hydrogen gas in the source can be varied, but generally an operational pressure of 1 mbar is used.

The beam emanating from the hydrogen source is characterized using a beam of 30 keV $^4\text{He}^{2+}$ ions. For this characterization, both beams are interfaced with the Paul ion trap: the hydrogen beam coming from the top and the helium beam coming from the side. The helium beam is pulsed using a deflection electrode, and as the beam passes through the Paul trap the helium ions ionize both hydrogen atoms and molecules. Simultaneous extraction into the TOF mass spectrometry allows for the determination of the degree of dissociation of the hydrogen beam. Two such mass spectra

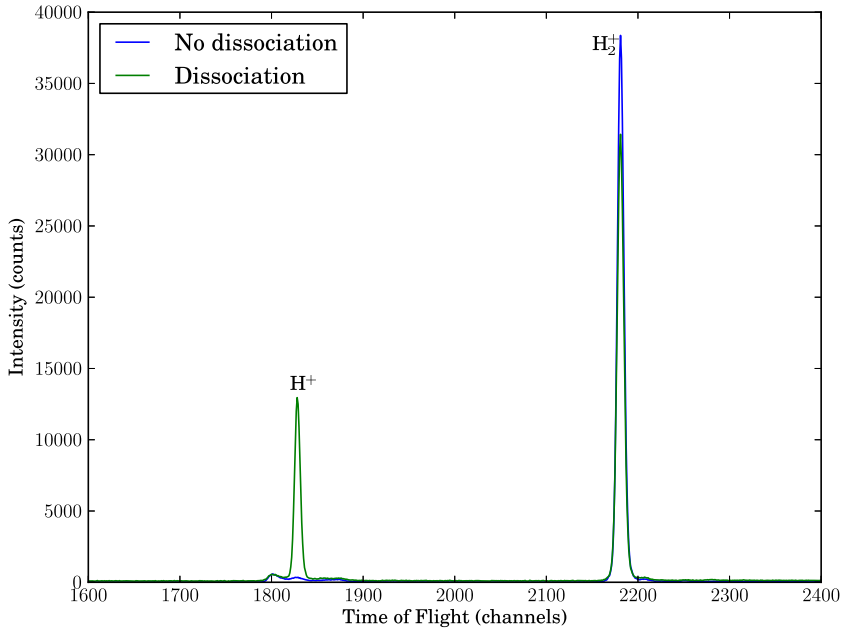


Figure 2.6 – The TOF mass spectra for the hydrogen source. The blue line depicts the mass spectrum for a beam of molecular hydrogen, whereas the green line shows the mass spectrum when the RF field is applied to create the hydrogen plasma. The peak at channel 1830 is indicative of protons, and the peak at 2180 shows the H_2^+ ions.

are shown in Figure 2.6, one for a beam of molecular hydrogen, and one for the partially dissociated beam.

From the recorded TOF spectra we establish the relative number of H^+ and H_2^+ ions produced by passage of the helium beam. We use the known cross sections for the ionization of H and H_2 by 30 keV $^4\text{He}^{2+}$ to convert this to a dissociation degree (Shah & Gilbody, 1978; Hoekstra, 1990; Hoekstra et al., 1991). With these cross sections it is also possible to correct for the effect of dissociative ionization by the $^4\text{He}^{2+}$ beam, where the interaction between a helium ion and an H_2 molecule results in the production of one or two protons.

The hydrogen beam characterization is done for a series of pressures in the source, as well for different RF powers. We find that in the range of operational pressures employed for the hydrogen source there is a critical

power of approximately 8 W. It is not possible to establish a plasma with an applied RF power lower than this value. Above an RF power of 8 W, the degree of dissociation of the hydrogen present in the trap center is approximately 30% for the full operational range of pressures and RF powers.

2.7.1 Placement of the Hydrogen Source

Depending on the type of experiment performed, the H source can be placed at two different stages of the setup, as is shown in Figure 2.7. When the hydrogen source is placed on top of the Paul trap, it enables the exposure of the trap contents to H atoms. This configuration is used to study the superhydrogenation of coronene cations, since all the products of superhydrogenation remain in the trap and can thus be detected in the mass spectrometer. This method is used for the studies in chapters 3 and 4.

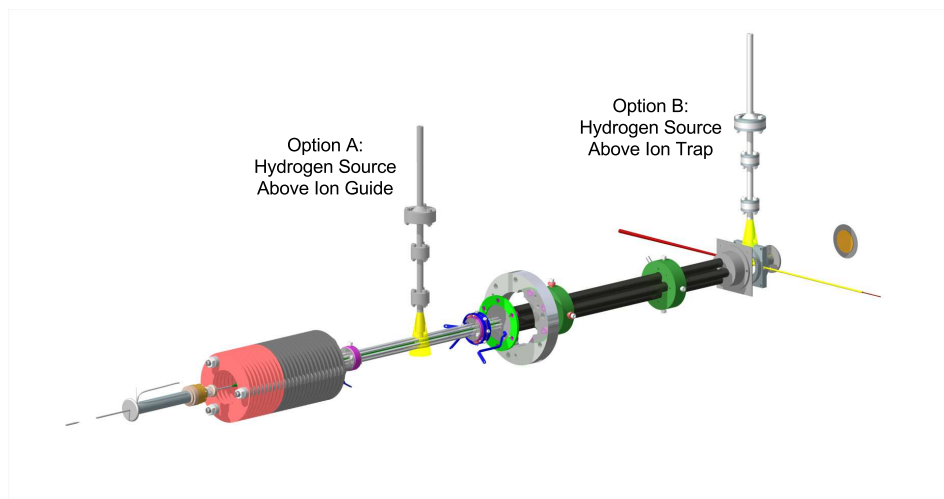


Figure 2.7 – A schematic depiction of the two locations where the hydrogen source can be placed. For the VUV absorption experiments the hydrogen source is mounted above the octopole ion guide (Option A), and to study the hydrogen attachment itself the source is mounted above the Paul ion trap (Option B).

This placement of the hydrogen source will yield a population of hydrogenation states inside the Paul trap. While this provides useful data to study the kinetics of the hydrogenation process, it is an undesirable

target for experiments involving exposure to photons, such as those in chapter 5. For these photo-experiments it is imperative to have a well-defined target, to ensure that the origin of every photoproduct is known.

A single hydrogenation state target can be attained by placing the hydrogen source on top of the octopole ion guide, before the mass filter. An elevated potential on the end diaphragm of the octopole turns it into a linear trap in which the coronene cations can be superhydrogenated. Afterwards, a temporary lowering of the diaphragm potential pushes the ions into the quadrupole mass filter, where the undesired hydrogenation states are filtered out. The subsequent injection into the Paul trap produces a target of a single hydrogenation state.

