# Chapter 3

# Introduction

Light is the only information we have to understand processes like star formation and the origin of the chemical compositions of earth and other objects in our own solar system up to the origin of life. From the light we observe, we have to deduce everything. Thus, the first step of course is, to identify the spectral features in astronomical observations and assign them to matter (atoms, molecules, ions, grains). The second step is to derive physical properties of the emitting or absorbing particles, e.g. their temperature, their abundance, non-thermal velocities, etc.. The third step is to learn about the history of the observed region from the present information. Here, knowledge of the astrochemical processes can be very helpful. If all reaction mechanisms and rates were known, one could tell from the current composition of an observed object, what chemical evolution it probably ran through. This would allow to determine for example the age of the object.

In the laboratory astrophysics group in Cologne, spectroscopy as well as astrochemistry are pursued.

Astrochemistry is very different from chemistry on earth. The interstellar medium is usually very thin and cold compared to the typical environment on earth. The low temperatures hinder all reactions that are strongly endothermic or have high energy barriers. Thus, exothermic reactions with low barriers can be expected to have the highest rates at temperatures of some ten Kelvin. Usually, the barriers for reactions between an ion and a neutral molecule are much lower than those for the reaction between two neutrals. As ions are easily produced in space by gamma rays, free electrons, etc., ion-neutral reactions play a much stronger role in space, than they do on earth.

Another peculiarity of astrochemistry is the low number density. Many exothermic reactions have much lower rates than one would expect, because in two-body-collisions, there is no chance to get rid of the released energy. Three-body-collisions increase the rate of such reactions dramatically (the third collision partner carries away the released energy), but they can be excluded for most interstellar regions due to the low number densities.

A temperature variable ion trap apparatus (LIRTrap) is available in Cologne, two more have been built since this work started. LIRTrap allows to investigate ion-molecule reactions at temperatures between 10 and 300 K and to obtain high resolution spectra of ions.

In this work we describe several different experiments performed in the ion trap. All of them apply the very sensitive dependence of endothermic reactions on translational and internal energies of the reaction partners at low temperatures to obtain information about the reaction partners. This sensitivity allows for example to perform spectroscopy of cold trapped ions by shifting the reaction equilibrium via laser irradiation. The method is called laser induced reactions (LIR) and has been performed on several species in the past. In this work, two vibrational bands of $CH_2D^+$ have been investigated.

Additionally, efforts were made to derive a quantitative description of the LIR process itself. LIR lines often show deviations from a Gaussian line profile. Although a function is at hand to describe these profiles, it cannot be connected to the experimental parameters (with the frequency being the only exclusion). A full description of the LIR process will probably include so called state specific rate coefficients. Those constants tell with which rate two specific levels of the involved ion and neutral will react to form the products.

State specific rate coefficients have long been searched for, for several basic reactions of astrochemistry. They would allow precise predictions of chemical evolutions even of regions that are far away from thermal equilibrium, as long as the level population of the involved species is known (e.g. by spectroscopic observations). An important step in the quest for state specific rate coefficients is to reduce the number of involved states. Here, molecular hydrogen has a useful feature. It can exist in two different nuclear spin configurations. For symmetry reasons, they have to occupy different rotational levels. Therefore, a para hydrogen sample that is cooled down to ten Kelvin will occupy basically just the rotational ground state. As hydrogen comes at room temperature in a mixture of ortho and para, and spin flips are strictly forbidden, some efforts have to be made to produce para hydrogen.

The purity of the produced para hydrogen sample can be investigated in different ways. The already mentioned dependence of endothermic reactions on internal energies is one of them, Raman spectroscopy another. Both methods were used in this work. Two possible test reactions are $H_2D^+ + H_2 \leftrightharpoons H_3^+ + HD$ and $N^+ + H_2 \leftrightharpoons NH^+ + H$. Both have been applied in this work.

The latter reaction was investigated in great detail. It is the first step in the formation of interstellar ammonia and still provides challenges for laboratory astrophysics even after three decades of investigations.

# Chapter 4

# LIRTrap

Reactions between ions and neutral molecules are very important for astrochemistry. This is due to the fact, that they usually have much lower barriers than reactions between two neutral partners. Therefore, they are much more likely to happen at low temperatures. The 22-pole ion trap apparatus that will be described in the following section enables us to investigate the kinetics of such ion-molecule reactions at temperatures down to $\approx 10$ K and gas densities between $10^{10}$ and $10^{15}$ cm$^{-3}$. The chemistry under such conditions is comparable to that in e.g. cold dense molecular clouds (10 to 50 K, $10^4$ to $10^7$ cm$^{-3}$, the different types of interstellar regions are summarized e.g. in the introduction of [1]). Although the number density of the reaction gas is some orders of magnitude higher in the ion trap, it can be chosen low enough ($\approx 10^{11}$ cm$^{-3}$) to exclude three body collisions. Thus, the reactions are accelerated compared to molecular clouds, but the reaction mechanisms stay the same. The low temperatures and number densities in the trap also allow to obtain high resolution spectra of ions of astrophysical relevance, such as $H_2D^+$ and $CH_2D^+$.

## 4.1 Setup of the 22-Pole Trap

The setup of the 22-pole ion trap apparatus is sketched in Fig. 4.1. The main parts are the ion source, two quadrupole mass filters, the 22-pole trap itself and the Daly detector. Detailed descriptions of the parts can be found in [4, 5] and references therein. The current version of the 22-pole trap is described in [6].

In the ion storage source, permanently various ions are produced by electron impact on a neutral precursor gas. They are stored in the source until the next experimental cycle. At the beginning of each experimental cycle, a pulse of ions is extracted from the source into the first quadrupole mass filter. The time between two extractions of ions will be called *cycle time* in the following.

The quadrupole selects the desired mass to charge ratios for the experiment from the variety of ions produced in the source. Since in the 22-pole trap experi-

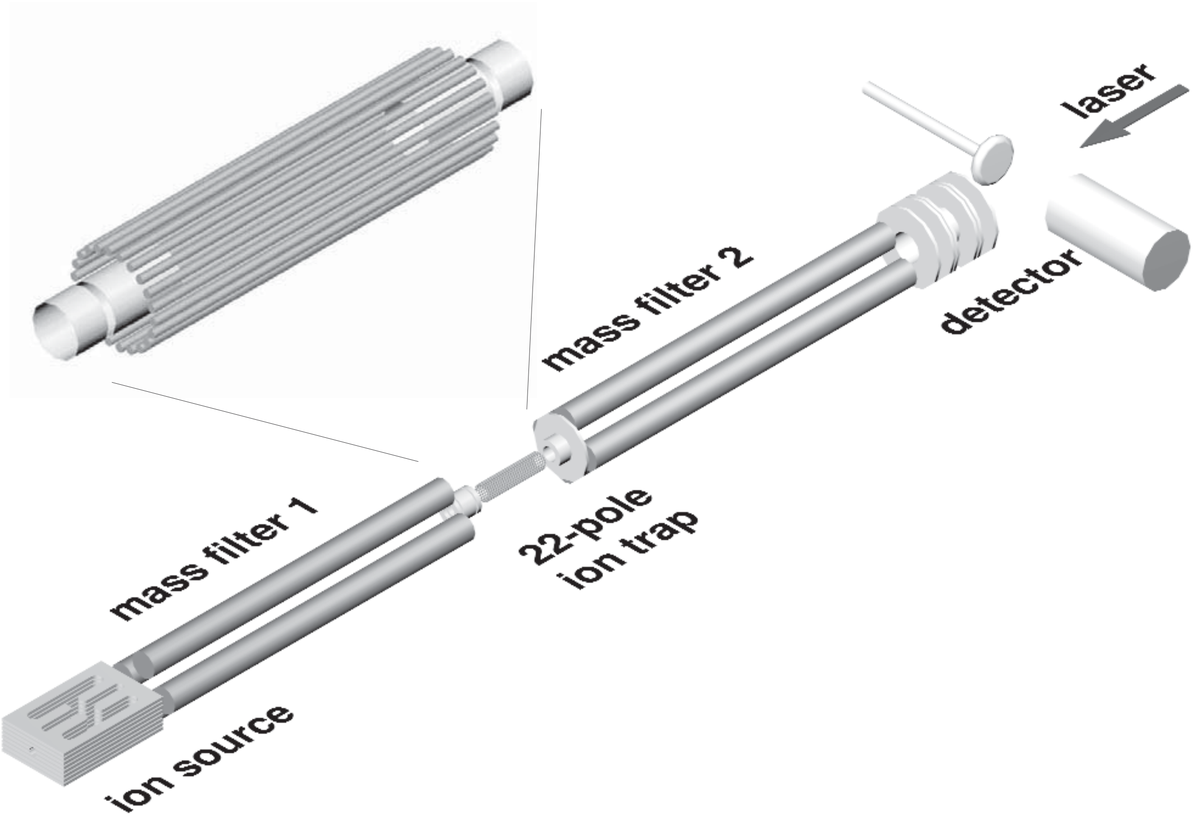

Figure 4.1: Schematic of the 22-pole ion trap (from [2]). From left to right:
*Ion Storage Source:* Production of ions by electron impact on a neutral gas.
*Quadrupole Mass Filter 1:* Selection of the mass range to be guided to the trap.
*Einzel Lens:* Focusing and directing lenses guide the ion cloud into the 22-pole.
*22-Pole Trap:* The ion cloud is stored together with a neutral reaction gas to perform experiments. Electrodes at both ends confine the axial motion of the ions (see also enlarged view). Storage times are typically several hundred ms. The trap is mounted on a cold head. At the beginning of the storage time, a dense pulse of cold He is emitted by a Piezo valve. The helium cloud cools down the ions to the cryogenic temperatures.
*Lens:* Focusing and directing lenses guide the ion cloud into the second quadrupole mass filter.
*Quadrupole Mass Filter 2:* Selects exactly one mass from the charged reaction products, to be counted in the detector.
*Acceleration Lenses:* Accelerate the ions towards the detector.
*Daly Detector [3]:* The ions are accelerated towards an aluminium knob by a voltage of −35 kV. There they produce electrons on impact, which are accelerated onto a scintillator, where they produce photons. These photons are then counted in a photomultiplier tube.
*Laser:* The whole setup is axially transparent, allowing spectroscopy with laser beams entering from the source and/or the detector side of the trap apparatus.

ments, the ions always carry exactly one elementary charge, it is sufficient to talk about mass selection in the following. There are two basic operation modes for the mass selection in quadrupoles. One is the high pass mode, in which all ions above a certain mass are guided through the quadrupole, while lighter ones are discarded. The second one is the selection of a certain mass range. The width of this range can be several or just one atomic mass unit. The ions of the selected mass(es) are guided to the ion trap. At the end of the first quadrupole, an Einzel lens focuses and directs the ion cloud into the 22-pole trap.

Inside the trap, the ion cloud is stored together with a neutral reaction gas to perform experiments. As the 22-pole confines the motion of the ions only in radial direction, two more electrodes are needed to reflect the ions at either end of the 22-pole. At the beginning and at the end of the storage time, the respective potential is decreased to let the ions enter/leave the trap. Storage times are typically several hundred ms. The trap is mounted on a closed cycle helium refrigerator to allow experiments at cryogenic temperatures (down to nominal temperatures of 10 K). For temperature control, a heating wire[1] is attached to the cold head, allowing stable nominal temperatures in the range of 10 to 30 K. Higher temperatures can be reached by switching on and off the cold head at intervals.

At the beginning of the storage time, usually a dense pulse of cold helium is present in the trap (controlled by a Piezo valve), to quickly cool down the ions to the ambient cryogenic temperatures. The neutral reaction gas is usually constantly admitted to the trap. The reaction gas is then continuously flowing through the trap chamber. Some experiments require modifications to that scheme. When the rate for thermalization processes has to be taken into account in the evaluation of measurement data, the helium buffer gas needs to be admitted to the ion trap in continuous flow instead of a pulse, so that its number density is known. When the reaction gas is freezing at the experimental temperatures, it is preferably applied via a second pulsed valve instead of continuous flow, to reduce the freezing rate. The pressures of source (precursor) and trap (reaction and buffer) gases are monitored during the measurements by ionization gauges mounted in the vacuum chambers of the first quadrupole[2] and of the ion trap[3]. As the 22-pole is surrounded by a small chamber and a cold shield, the number density of the reaction gas inside the 22-pole chamber is higher than in the surrounding vacuum chamber (see [7] for more details). The actual number density $[H_2]$ in the innermost chamber can be calculated from the pressure in the trap

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[1] Kapton heating foil

[2] Arun Microelectronics LTD, Pressure Gauge Controller NGC2 UHV

[3] Arun Microelectronics LTD, Pressure Gauge Controller PGC2 UHV

vacuum chamber $p_{\text{trap}}$ and the temperature of the neutral reaction gas (which is approximately the nominal trap temperature $T_{\text{trap}}$) as

$$[\mathrm{H}_2] = 4.18 \times 10^{17} \frac{\sqrt{\mathrm{K}}}{\mathrm{mbar} \cdot \mathrm{cm}^3} \cdot f_{\text{cal}} \cdot \frac{p_{\text{trap}}}{\sqrt{T_{\text{trap}}}} \ . \tag{4.1}$$

The factor $f_{\text{cal}}$ is derived from calibration measurements with a spinning rotor gauge[4] that is mounted to the 22-pole chamber itself.

After the exit of the 22-pole trap, the ions again pass a lens, to be guided into the second quadrupole mass filter[5]. The second quadrupole mass filter selects exactly one mass from the charged reaction products leaving the trap, to be counted in the detector. After leaving the mass filter, the ions are accelerated towards the detector by the acceleration lenses. Then they are counted in the Daly detector. More details on the operation principle of a Daly detector are given in Section 4.5 and can also be found in the original publication of Daly [3].

As is indicated by the red arrow in Figure 4.1, the setup of the 22-pole trap is axially transparent. This allows spectroscopy with laser beams entering from the front (ion source) and/or the back (detector) end of the trap.

The following sections describe the three most important types of measurements, performed in the 22-pole ion trap experiment (mass spectroscopy, reaction kinetics, and spectroscopy of ions) and the assembly of the Daly detectors for the two new ion trap experiments built in Cologne.

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[4] MKS Instruments, Spinning Rotor Gauge SRG-2CE

[5] Balzers Quadrupol-Massenspektrometer QMG 511

## 4.2 Mass Spectra

The 22-pole ion trap apparatus allows to take mass spectra of the contents of either the ion source without any storage in the trap or of the ion trap after some storage time. For this measurements, cycle time and storage time are fixed, while for each experimental cycle, the second quadrupole is set to another mass. The width of these mass steps, the mass range to be covered and the number

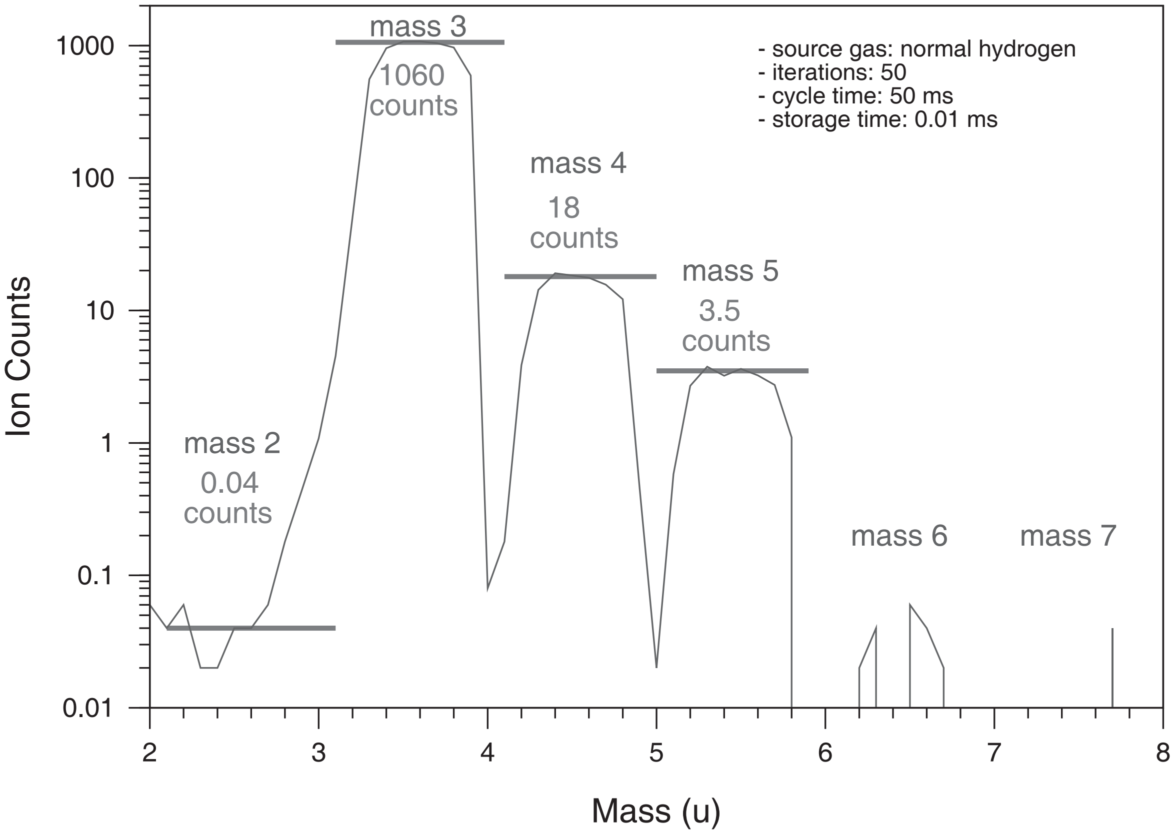

Figure 4.2: Example of a mass spectrum. Normal hydrogen was ionized in the ion source and the produced ions passed through the ion trap without storage. The first quadrupole was not in any selective mode, it served just as a guide for these measurements. The second quadrupole selected the desired masses.
The heights of the different mass peaks give information about the amount of HD the ionized gas contains. The more HD is available in the source, the higher the peaks at masses 4 u ($H_2D^+$), 5 u ($H_5^+$, $HD_2^+$), etc. will be with respect to mass 3 u ($H_3^+$). The peaks of the masses are somewhat shifted in comparison to the labels on the axis. The mass values are derived from the operation voltages of the second quadrupole. This correlation underlies slow shifts with operation time (over the range of weeks) and is not proportional over the whole mass range of interest (max. 1 - 50 u). Thus, some knowledge of the typical relative intensities of the expected mass peaks is required to assign them properly.

of iterations (how often the chosen mass range is to be scanned) are variable parameters.

Figure 4.2 shows an example of this measurement type. Here, normal hydrogen was admitted to the ion source where it was ionized. The number density in the source was around $3 \times 10^{11}$ cm$^{-3}$. The mass range of 2 to 8 u was scanned 50 times in steps of 0.1 u. For these measurements the shortest possible cycle time of 50 ms and no storage time were chosen (the exit of the ion trap opened 0.01 ms after the entrance to the trap opened, meaning that both were open simultaneously for $\approx 250$ $\mu$s and the ions could pass through the trap directly).

This method allows to investigate what types of ions are produced in the ion source. With no gas admitted to the source, it can be used to search for possible impurities in the source. These impurities might have remained there from previous experiments (like hydrocarbons) or they might leak into the source from the laboratory air (like $H_2O$ (which is always present in very small amounts), $N_2$, $O_2$, $CO_2$). When no precursor gas is available for ionization, all ionization products stem from these impurities, allowing their identification. It can also be applied to investigate the contents of the source gas, as was done in the measurements shown in Figure 4.2. These measurements were performed to compare the HD contents of normal and para hydrogen. As described in Chapter 5.1, hydrogen might loose some of its HD contents in the cold converter box, when it is converted to para hydrogen in the para hydrogen generator. Therefore, normal hydrogen and para hydrogen produced in different operation modes of the para generator were ionized, to look for changes in the ratios of the different isotopologues of $H_3^+$ ions produced in the ion source. These measurements are presented in Chapter 5.2.

Mass spectra are also very useful, when you need a quick overview of a reaction system. For this purpose, a reaction gas is admitted to the ion trap and the ions are stored in the trap for some time. Taking a broad range mass spectrum at this conditions allows to quickly identify all possible reaction products (also the ones of competing reactions with impurities in the trap). The knowledge of the products that have significant numbers after certain storage times is important to properly choose the experimental settings for the investigation of the temporal evolution of a reaction system. This measurement type will be explained in the next section.

## 4.3 Time Evolution of Chemical Reactions

The investigation of reaction kinetics for reaction systems of astrochemical relevance is one of the two most important applications of the 22-pole ion trap apparatus [8–10] and will be explained in the following. The other is spectroscopy of ions, which will be explained in Section 4.4.

The temporal evolution of a reaction system can be investigated by varying the storage time in the trap. For this purpose, usually exactly one atomic mass is selected in the first quadrupole mass filter. These ions are then stored together with the neutral reaction gas in the ion trap, which is kept at the temperature of interest. In order to measure the time dependence of the reactions happening

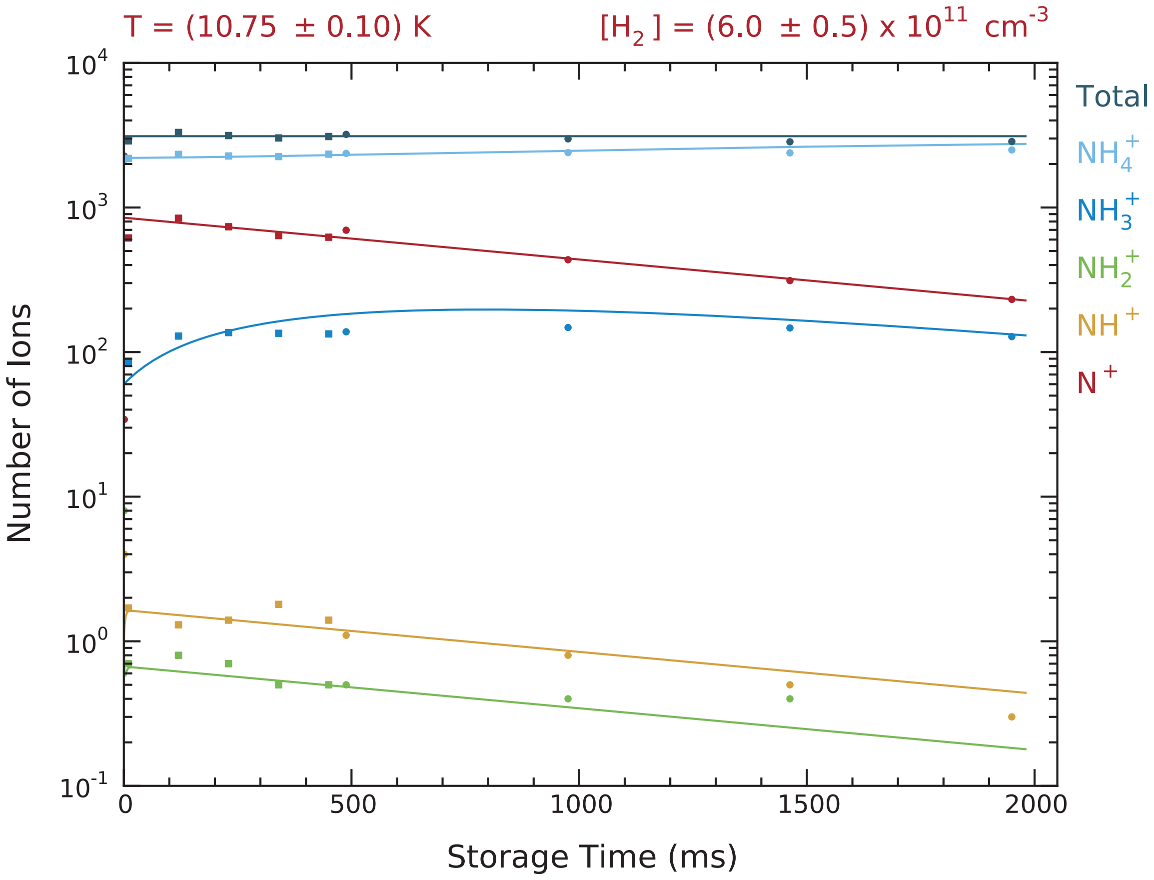

Figure 4.3: Time evolution of the reaction system $N^+ + p\text{-}H_2$ at a nominal temperature of 10.75 K. In each reaction step, an H atom is added to the ion, forming finally $NH_4^+$ (reactions (4.2) to (4.5)). The solid lines are numerical solutions of the rate equations. The following rate coefficients and ion numbers at $t = 0$ were used for the numerical simulation:
$N^+{}_0 = 850$, $k_{f1} = 1.1 \times 10^{-12}\ \frac{\mathrm{cm}^3}{\mathrm{s}}$, $NH^+{}_0 = 1$, $k_{f2} = 5.7 \times 10^{-10}\ \frac{\mathrm{cm}^3}{\mathrm{s}}$, $NH_2^+{}_0 = 1$, $k_{f3} = 1.4 \times 10^{-9}\ \frac{\mathrm{cm}^3}{\mathrm{s}}$, $NH_3^+{}_0 = 60$, $k_{f4} = 2.8 \times 10^{-12}\ \frac{\mathrm{cm}^3}{\mathrm{s}}$, $NH_4^+{}_0 = 2200$.

in the ion trap, all expected product masses have to be measured after several storage times. Therefore, the experimental cycle has to be repeated several times with different settings for the second quadrupole mass filter and different storage times. This whole series of measurements is then repeated usually 10 times to improve statistics.

Figure 4.3 shows an example of such a time scan. In this case, $N^+$ ions were stored in the ion trap together with para hydrogen at a nominal temperature of $\approx 10$ K. The following reactions are expected to occur:

$$N^+ \quad + H_2 \quad \underset{k_{b1}}{\overset{k_{f1}}{\rightleftharpoons}} \quad NH^+ + H \tag{4.2}$$

$$NH^+ + H_2 \quad \underset{k_{b2}}{\overset{k_{f2}}{\rightleftharpoons}} \quad NH_2^+ + H \tag{4.3}$$

$$NH_2^+ + H_2 \quad \underset{k_{b3}}{\overset{k_{f3}}{\rightleftharpoons}} \quad NH_3^+ + H \tag{4.4}$$

$$NH_3^+ + H_2 \quad \underset{k_{b4}}{\overset{k_{f4}}{\rightleftharpoons}} \quad NH_4^+ + H \ , \tag{4.5}$$

since no H atoms are present in the trap, we expect only the forward reactions (the reaction gas is flowing through the trap chamber continuously, meaning that all H atoms will be pumped away and be replaced by $H_2$ molecules immediately; the ions are not pumped out, since they are trapped by the electrical fields). The endothermic reaction (4.2) can be used as a test for the purity of para hydrogen (see Chapter 6). Reactions (4.2) to (4.5) are steps in the formation of interstellar ammonia $NH_3$.

The number densities of the neutral reaction gas are typically low enough to exclude three body collisions ($\approx 10^{11}$ cm$^{-3}$). This and the cryogenic temperatures allow to investigate ion-neutral reactions at conditions comparable to those in the interstellar medium (e.g. molecular clouds), but on much shorter timescales (seconds instead of years).