

Mass Spectrometry



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0 Motivation

Today, a quadrupole mass spectrometer is the most important tool for analysing gas compositions. It is a very compact and reliable device.

In ultra-high vacuum technology (UHV) the mass spectrometer is a very useful tool to analyse vacuum properties. So nearly every UHV system has a quadrupole mass spectrometer included. When the desired pressure is not reached, a mass spectrometer provides valuable evidence of an existing problem, e.g. the amount of water is too high or compounds of oil from the pumps can be found. Also very small leakages can be detected in the chamber by using helium as a test gas.

In addition, a mass spectrometer is used for chemical analysis of sample compositions. Thermo-sorption spectroscopy measures the gas components desorbing from a sample surface are measured with respect to the applied sample temperature.

This lab course experiment teaches the physics and handling of a quadrupole mass spectrometer and the interpretation of mass spectra. In addition the participant should get first-hand experience with ultra-high vacuum technology, which is very important in surface science research.

1 The Quadrupole Mass Spectrometer

A quadrupole mass spectrometer (QMS) is a device used for mass spectroscopy of ions or charged molecules by their specific charge. The QMS was first theoretically suggested by W. Paul and H. Steinwedel 1953 and experimentally realised in 1954 by W. Paul and M. Raether. A quadrupole mass spectrometer consists of three main parts. First, an ionization unit in order to charge up the atoms/molecules. Second, the quadrupole mass filter, which can only be passed by the charged molecules with a specific mass. This mass can be controlled by the applied voltages to the quadrupole. And third, a detector to measure the ion current which passed the mass filter.

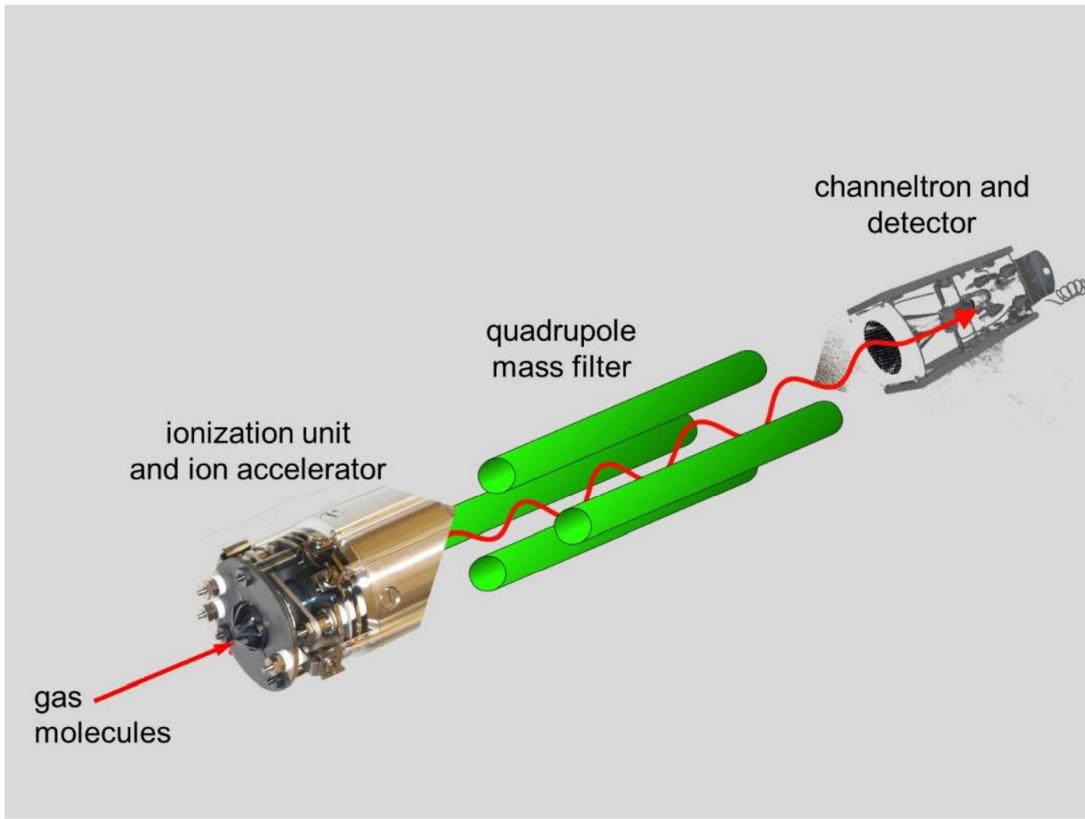


Fig. 1: The quadrupole mass spectrometer consists of three main parts: The ionization unit, the quadrupole mass filter and the ion detector unit.

1.1 The Ionization Unit

Fig. 1.1.1 shows a photo and a schematic drawing of the ionization unit. It consists of a heated filament, which emits electrons. These electrons are accelerated to a cylindrical grid electrode (ion formation chamber). On their way to the grid electrode the electrons can hit other atoms, which emit more electrons. The developed electron avalanche increases the current (depending on the pressure). Some of these electrons hit the grid and are absorbed. Others pass the grid and hit a gas atom in the formation chamber. This atom is also ionized and emits a second electron. Later the remaining two electrons will again be absorbed by the grid electrode. The created positive ion is extracted from the formation chamber by the extraction slit, which is on ground potential. Two additional slits will further accelerate and focus the ion beam into the quadrupole. The needed energy for the ionization process depends on the type of gas. Typically used values are between 50eV and 150eV (see Fig. 1.2.2).

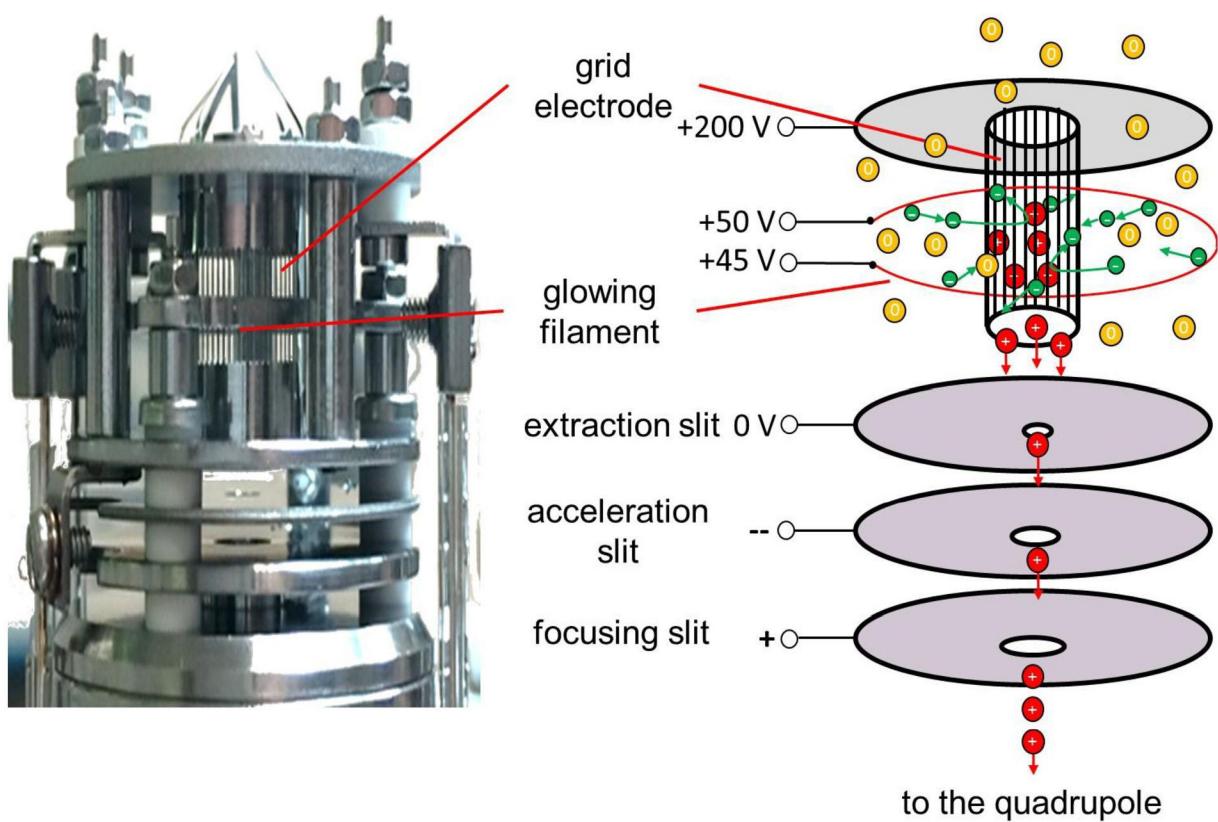


Fig. 1.1.1: Photo and schematic drawing of the ionization and acceleration unit.

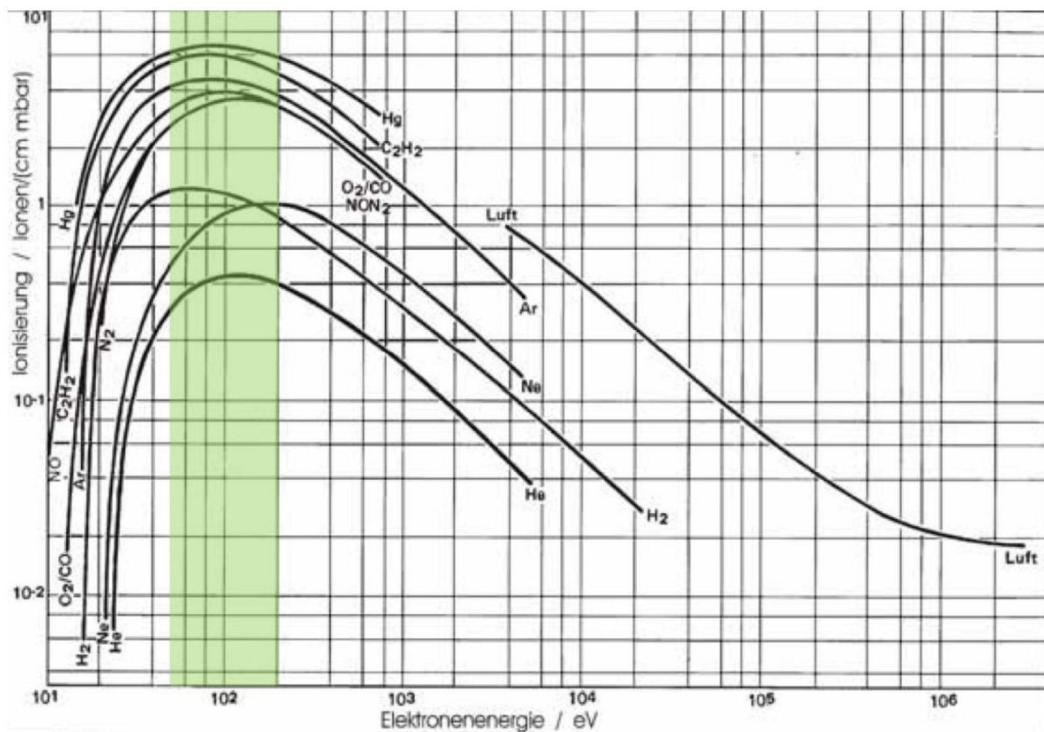


Fig. 1.1.2: Ionization energies of some selected gases [1]. In the green shaded area the highest ionization rates are expected

1.2 The Quadrupole Mass Filter

A quadrupole mass filter is an arrangement of four metallic rods with a hyperbolic shape. An applied voltage to these electrodes generate an electromagnetic field (see Fig. 1.2.1). If amplitude and frequency of the field are chosen correctly, ions or molecules with a specific mass to charge ratio are confined in the x/y-plane, while the movement in the z-direction is not restricted. Therefore these ions with an additional momentum along the z-axis can pass the quadrupole and will be detected. Let us have a closer look to the field properties which are needed to run a QMS.

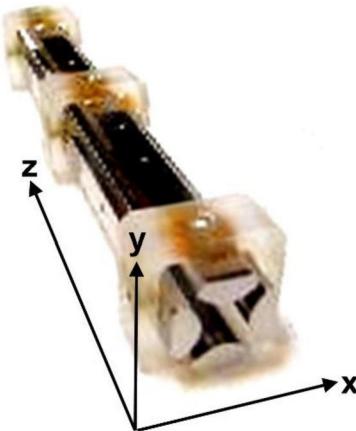


Fig. 1.2.1: The quadrupole mass filter is an arrangement of four metallic rods, used as electrodes, which generate an alternating electromagnetic field.

We start with the underlying force, the Lorentz force:

$$\underline{F} = q(\underline{E} + \underline{v} \times \underline{B}).$$

In order to confine the ions in the x/y-plane we have to apply a repulsive force, i.e., a force which increases with the radial position of the ion:

$$\underline{F} \propto r^n \frac{\underline{r}}{|\underline{r}|}$$

For $n = 1$ the potential can be written as

$$\Phi(\underline{r}, t) = \Phi_0(\underline{r}, t) \cdot (\alpha x^2 + \beta y^2 + \gamma z^2),$$

which has to fulfill the Laplace equation

$$\nabla^2 \Phi(\underline{r}, t) = 0,$$

neglecting any volume charge between the electrodes. This requires

$$\alpha + \beta + \gamma = 0,$$

which can be realized, i.e., by $\alpha = \beta$ and $\gamma = -2\alpha$. This is the potential of a three dimensional “Paul Trap” (3D ion trap) and will not be discussed in detail. The potential of a linear ion trap or a quadrupole can be realized by $\alpha = -\beta$ and $\gamma = 0$. The ideal quadrupole field is generated by hyperbolic electrodes as shown in Fig. 1.2.2 (left). Assuming that the electrodes are aligned along z-direction and that the distance between the $(0,0,z)$ -axis and the vertices of the hyperbolic electrodes is r_0 , the potential can be written as:

$$\Phi(x, y, z, t) = \Phi_0(t) \cdot \frac{x^2 - y^2}{r_0^2},$$

with a potential $\pm \Phi_0(t)/2$ applied to adjacent electrodes.

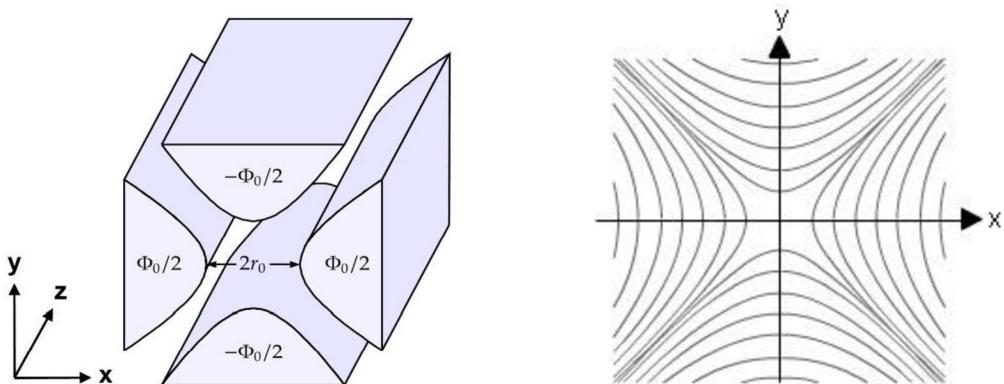


Fig. 1.2.2: Left: Hyperbolic electrodes of an ideal quadrupole mass spectrometer. The distance between opposite vertices of the hyperbolas is $2r_0$. Right: Equipotential lines for a fixed voltage applied to the electrodes (right) [2].

Thus, the potential has infinitesimal translation symmetry along the z-axis and no force is affecting ion movement along the z-direction. Fig. 1.2.2 (right) shows the equipotential lines for a fixed voltage applied to the electrodes. As can be seen in the 3D plot of this potential in Fig. 1.2.3, the field focuses charged particles in one direction, e.g., the x-direction, while it defocuses in the y-direction, causing the ions hit the y-electrodes and disappear.

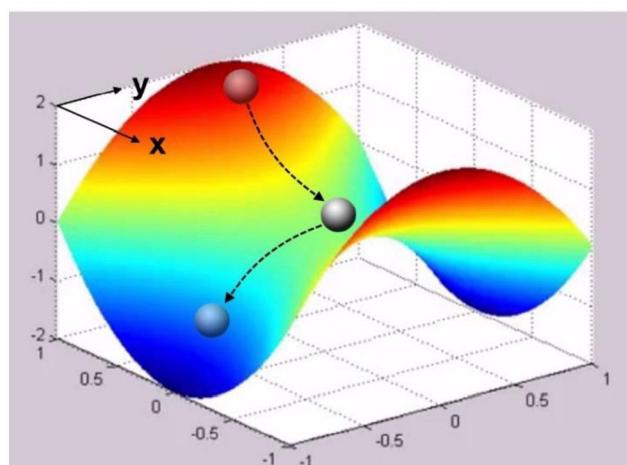


Fig. 1.2.3: 3D plot of the fixed potential. A negatively charged ion (grey ball) is focused in x-direction and defocused in y-direction. This ion will hit the y-electrode [3].

By only using electro static fields it is not possible to create a stable positron for a charge in the x/y-plane. Therefore an alternating voltage U_{AC} is applied to the electrodes with a phase shift of 180° between the x- and y-direction. Additional a constant voltage offset U_{DC} is applied. Adopting an appropriate angular frequency ω of the alternating voltage (typically around $f = \omega/2\pi = 1 - 2$ MHz), an alternating focussing and defocussing of the ions in x- and y-direction can be realised.

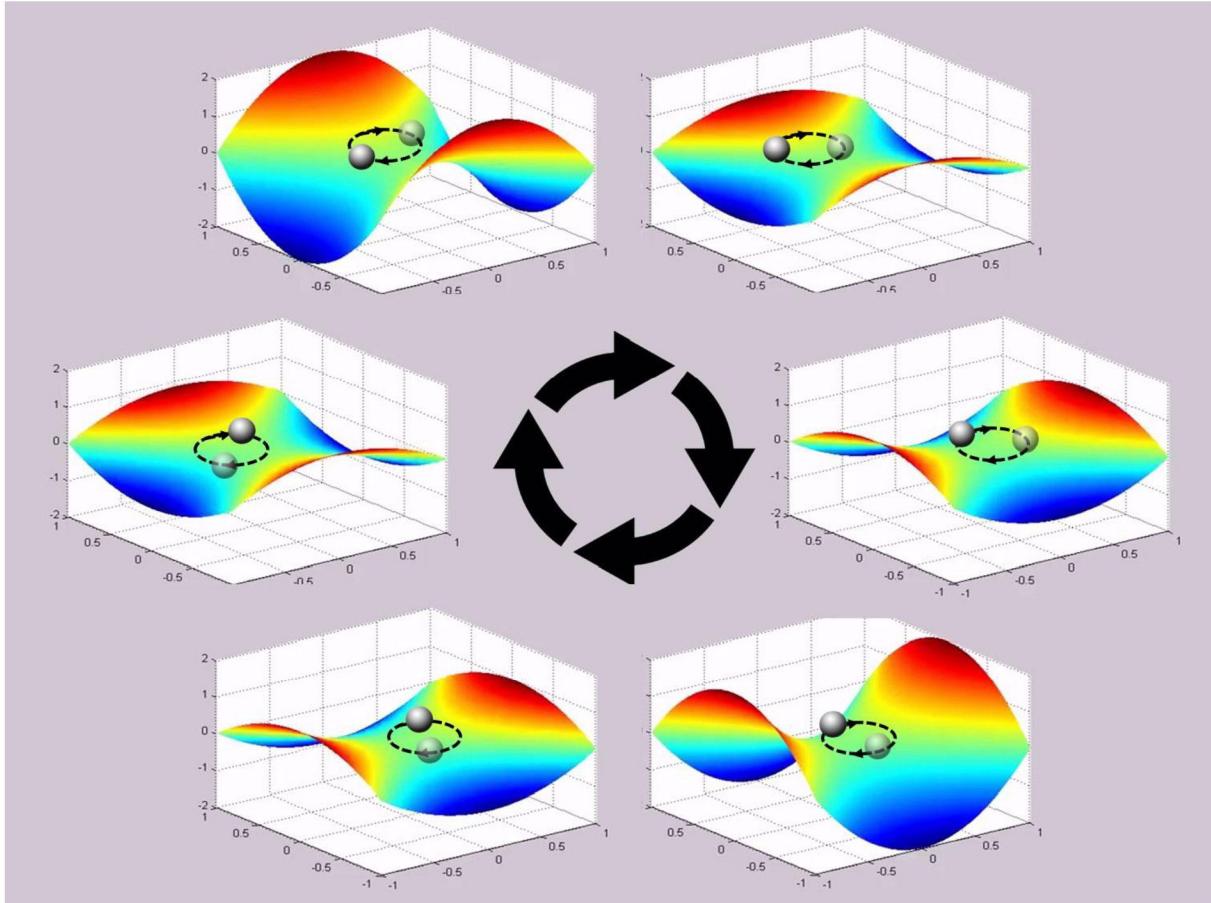


Fig. 1.2.4: 3D plot of an alternating potential in x- and y-direction with a phase shift of 180° . Depending on the frequency, amplitude and dimensions of the quadrupole an ion (grey ball) with a specific mass and charge circulates around the center and is therefore confined in the x/y-plane [3].

The resulting potential is given by

$$\Phi(x, y, z, t) = (U_{DC} + U_{AC} \cos(\omega t)) \cdot \frac{x^2 - y^2}{r_0^2}.$$

The equation of motion of an ion with charge q and mass m can be derived easily

$$m\ddot{r} = qE = -q\nabla\Phi(x, y, t)$$

$$\Leftrightarrow m \cdot \begin{pmatrix} \ddot{x} \\ \ddot{y} \\ \ddot{z} \end{pmatrix} = -q \cdot \begin{pmatrix} (U_{DC} + U_{AC} \cos(\omega t)) \cdot \frac{2x}{r_0^2} \\ (U_{DC} + U_{AC} \cos(\omega t)) \cdot \frac{-2y}{r_0^2} \\ 0 \end{pmatrix}$$

$$\Leftrightarrow \begin{pmatrix} m\ddot{x} + (U_{DC} + U_{AC} \cos(\omega t)) \cdot \frac{2qx}{r_0^2} \\ m\ddot{y} + (U_{DC} + U_{AC} \cos(\omega t)) \cdot \frac{-2qy}{r_0^2} \\ m\ddot{z} \end{pmatrix} = 0$$

The z component describes a linear movement of the ion along the z-axis because there is no force in that direction. The x and y components are homogeneous differential equations of second order, which cannot be solved analytically in this form. The movement in x- and y-direction can be written as Mathieu's differential equations:

$$\frac{dx^2}{d\tau^2} + (a_x - 2b_x \cos(2\tau)) \cdot x = 0$$

$$\frac{dy^2}{d\tau^2} + (a_y - 2b_y \cos(2\tau)) \cdot y = 0$$

This differential equations differ only in definition of their transformation parameters:

$$a_x = -a_y = \frac{8qU_{DC}}{mr_0^2\omega^2}$$

$$b_x = -b_y = \frac{4qU_{AC}}{mr_0^2\omega^2}$$

$$\tau = \frac{\omega t}{2}$$

Herein $a_{xy}/4$ gives the ratio of potential energy in the dc voltage field to the kinetic energy of the oscillation, whereas $b_{xy}/2$ denotes the ratio of potential energy in the ac field to the kinetic energy of the oscillation:

$$\frac{a_x}{4} = -\frac{a_y}{4} = \frac{2qU_{DC}}{mr_0^2\omega^2} = \frac{qU_{DC}}{\frac{1}{2}mv^2} = \frac{E_{pot}^{DC}}{E_{kin}^{AC}}$$

$$\frac{b_x}{2} = -\frac{b_y}{2} = -\frac{2qU_{AC}}{mr_0^2\omega^2} = \frac{qU_{AC}}{\frac{1}{2}mv^2} = \frac{E_{pot}^{AC}}{E_{kin}^{AC}}$$

The solution of Mathieu's differential equations is known already and can be written as a superposition of two linear independent parts, which consists of a sum of exponential functions:

$$x(\tau) = Ae^{i\beta\tau} \sum_{n=-\infty}^{\infty} C_n e^{2int} + Be^{-i\beta\tau} \sum_{n=-\infty}^{\infty} C_n e^{-2int},$$

while A and B can be determined by the initial conditions $x(\tau = 0), \dot{x}(\tau = 0)$, the characteristic exponent $i\beta$ defines the properties of the solution and therefore the movement of the ions in the quadrupole. If $i\beta$ consists of a real part, the $e^{\pm i\beta\tau}$ tends to infinity and therefore also $x(t)$ (and $y(t)$). The consequence is that the ion moves far away from the center, hits the electrodes and cannot pass the quadrupole. To get a periodic and stable solution $i\beta$ must be purely imaginary. A more detailed mathematical analysis exhibits, that solutions with integer β are periodic, but unstable solutions, as the amplitude of the oscillation increases continuously.

If we rewrite the formula by using the Euler equation ($e^{\pm ix} = \cos(x) \pm i \sin(x)$), addition theorems and $\tau = \omega/2 \cdot t$, we can learn something about the frequency of the ion movement in the quadrupole:

$$x(\tau) = D \sum_{n=-\infty}^{\infty} C_n \cos\left((2n+\beta)\frac{\omega}{2}t\right) + E \sum_{n=-\infty}^{\infty} C_n \sin\left((2n+\beta)\frac{\omega}{2}t\right),$$

Where D and E are linear combinations of A and B . From this equation the oscillation amplitudes C_n and angular frequencies ω_n ($f_0 = \beta \frac{f}{2}$) of the ions in the quadrupole with respect to the frequency of the ac voltage ω can be determined by:

$$\omega_n = (2n+\beta)\frac{\omega}{2}, f_n = (2n+\beta)\frac{f}{2}$$

The lowest possible frequency is given by $n=0$: $f_0 = \beta \frac{f}{2}$

The parameter $i\beta$ can be calculated from the transformation parameters a_{xy} and b_{xy} . For a detailed analysis of the stable solution for the x movement, we plot the parameter a_x with respect to b_x . Notice that for the y movement the stable solutions have exactly the same shape, only with flipped axis due to $a_y = -a_x$ and $b_y = -b_x$. Fig.1.2.5 shows the areas of stable solutions bounded by Mathieu's functions. A stable movement of the ions through the quadrupole is only possible for values given by the grey shaded triangular area, i.e., the area of stable movement in x - and y -direction. This means that the red working line, given by $a_x/b_x = 2U_{DC}/U_{AC}$, must cut the grey shaded area. Δb can be adjusted by the slope of the working line.

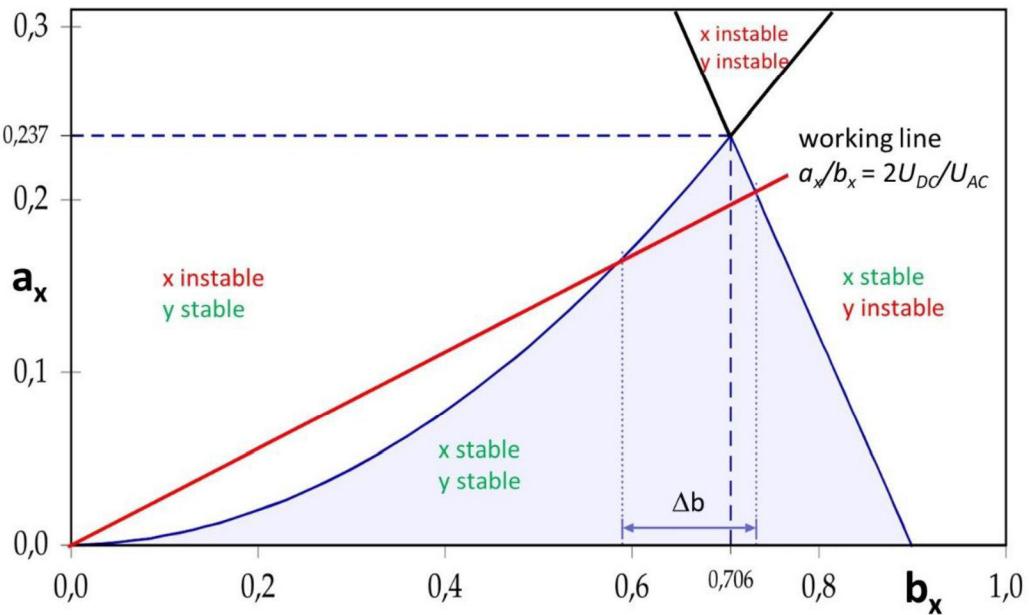


Fig. 1.2.5: Parameter a plotted versus b of Mathieu's differential equation. Values of the grey shaded area give stable solutions for the ion movement in x - and y -direction. The working line (red) is set to a fixed ratio of a/b [7].

The diagram in Fig 1.2.5 can also be transformed in a plot of U_{DC} with respect to U_{AC} , which gives a more practical information about the necessary adjustment of the applied voltages (see Fig. 1.2.6). The red working line $U_{DC}/U_{AC} = a_x/2b_x$ and the stable areas for different masses of ions are plotted (for constant ω and r_0). If the voltages are scanned with the constant ratio given by the working line, only ions with a mass m (and charge q) inside the grey stability area can pass the quadrupole. Ions with a mass outside this area will hit the electrodes. The working line defines an interval ΔU_{AC} , which can be directly assigned to a mass interval Δm . The mass resolution can be adjusted by changing the slope of the working line and can be calculated by:

$$\frac{m}{\Delta m} = \frac{0.126}{0.1678 - \frac{U_{DC}}{U_{AC}}}.$$

To increase the mass resolution (decrease Δm) the working line must be set a bit below the maximum of the stable area. Reasonable values for the slope of the working line are found within the red area shown in Fig. 1.2.6. The minimum of the slope is given by the overlapping of the stability areas for the masses, which shall be resolved. The maximum slope is given by the maximum of the stability areas.

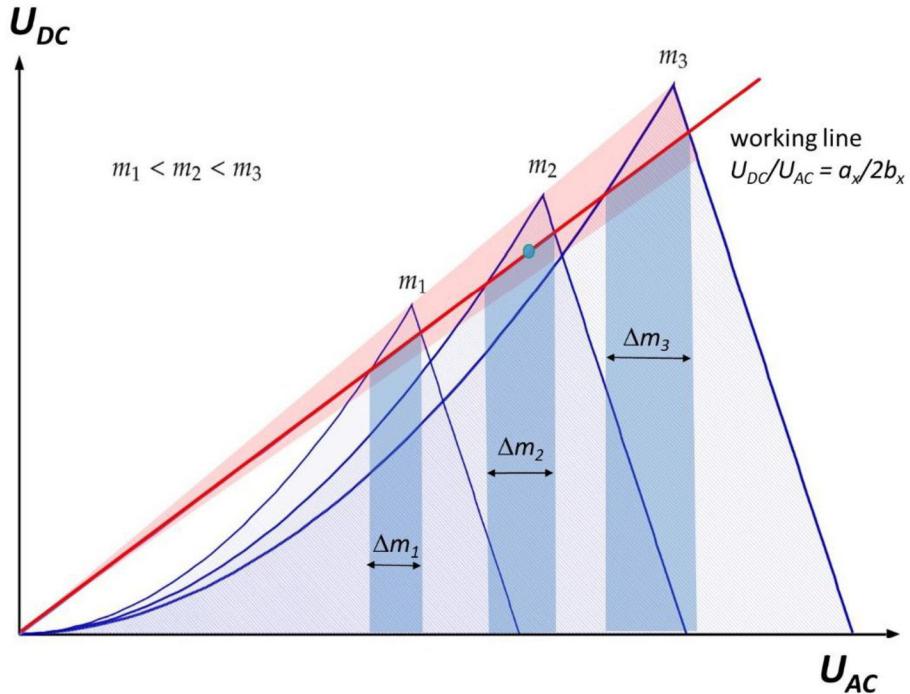


Fig. 1.2.6: Solutions for different ion masses with respect to the applied ac and dc voltage. By scanning U_{AC} along the working line different masses m_1 , m_2 , m_3 , which pass the quadrupole, can be selected. The mass resolution Δm depends on the slope of the working line (reasonable values for the slope are shown in the red shaded area) [7].

Assuming a working point as indicated by the green dot in Fig. 1.2.6, typical trajectories of the ions in x- and y-direction are shown in Fig 1.2.7. For ions with mass m_1 the defocusing force in the x-direction is too strong and therefore the oscillation amplitude increases until the ions hit the electrodes. Ions with m_2 show a stable movement in x- and y-direction and can pass the quadrupole. Ions with m_3 are too heavy and not stable in y-direction. If $U_{DC}=0V$ is chosen and only U_{AC} is varied the quadrupole works as a high pass filter. In this case all masses have stable solutions but with increasing U_{AC} small masses are cut off. The area under the observed spectrum is proportional to the total pressure in the system. If the total pressure is known, this information can be used to determine the partial pressure of certain gases.

Notice that the solutions for a real quadrupole differs a bit from the ideal one. Because of the finite length and distance of the electrodes the expected mass peaks are not rectangular any more. As a result of the finite distance of the electrodes some ions with the correct mass and certain initial conditions will also hit the electrodes. This effect is more distinct on the high mass side, causing an asymmetric rounded peak (see Fig. 1.2.8). Due to the finite length of the electrodes some ions with the wrong mass can pass the quadrupole anyhow, which leads to a broadening of the peaks (Fig. 1.2.8.). This happens if the increasing amplitude (for an unstable solution) is not high enough at the end of the quadrupole to hit the electrode.

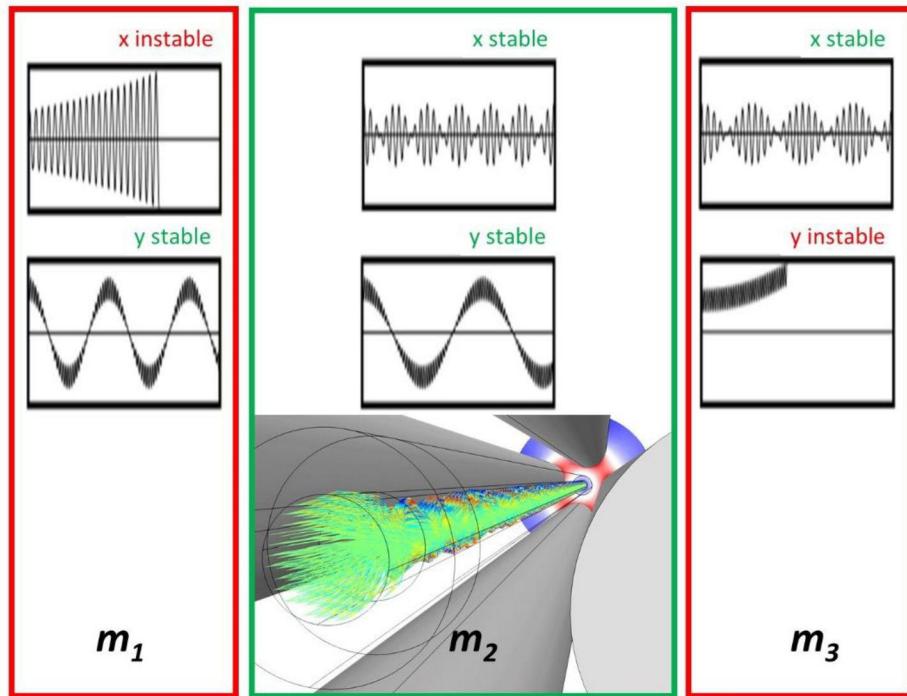


Fig. 1.2.7: Examples for ion movements in x- and y-direction depending on the area in the U_{DC}/U_{AC} -plane (Fig. 1.2.6). Only in the stable area (grey shaded in Fig. 1.2.6) the ions show periodic movements without an increasing amplitude, thus let them pass the quadrupole (see also 3D simulation in the middle of ion trajectories through the quadrupole of different initial values) [4].

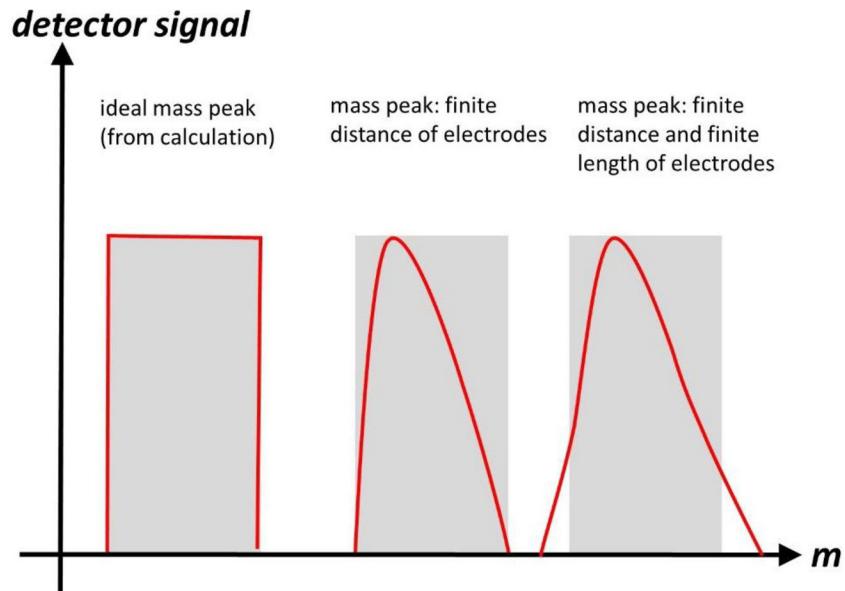


Fig. 1.2.8: Ideal and real shape of the measured mass peaks [5]. For comparison the grey box indicates the ideal rectangular shape of the mass peak derived from the calculation.

1.3 The Detector Unit

The ion detection unit consist of a secondary electron amplifier (SEM) followed by a Faraday cup, i.e., an anode which collects the electrons. The measured current is proportional to the amount of incoming ions. The SEM is a channeltron which amplifies the ion current. It consists of a curved insulated tube, which is covered by a high ohmic layer (range of $G\Omega$). A voltage of about 1000 V is applied between the two ends of the tube. Thus the potential increases constantly along the tube. In addition the inner surface of the tube is covered by a thin cesium layer. The Cs reduces the working function of the metal. If an incoming ion hits the wall of the tube, a few electrons leave the metallic surface. These electrons will again hit the inner wall of the tube and more electrons are released. The electron avalanche reaches the end of the tube and is detected at the anode (Faraday cup). The amplification factor strongly depends on the applied voltage.

Warning: The surface of the channeltron can be damaged if the channeltron is getting to hot $T > 150^\circ\text{C}$ (Cs will evaporate) or the vacuum pressure is too high, i.e. $p > 10^{-5}$ mbar (the Cs will be sputtered away by the high current).

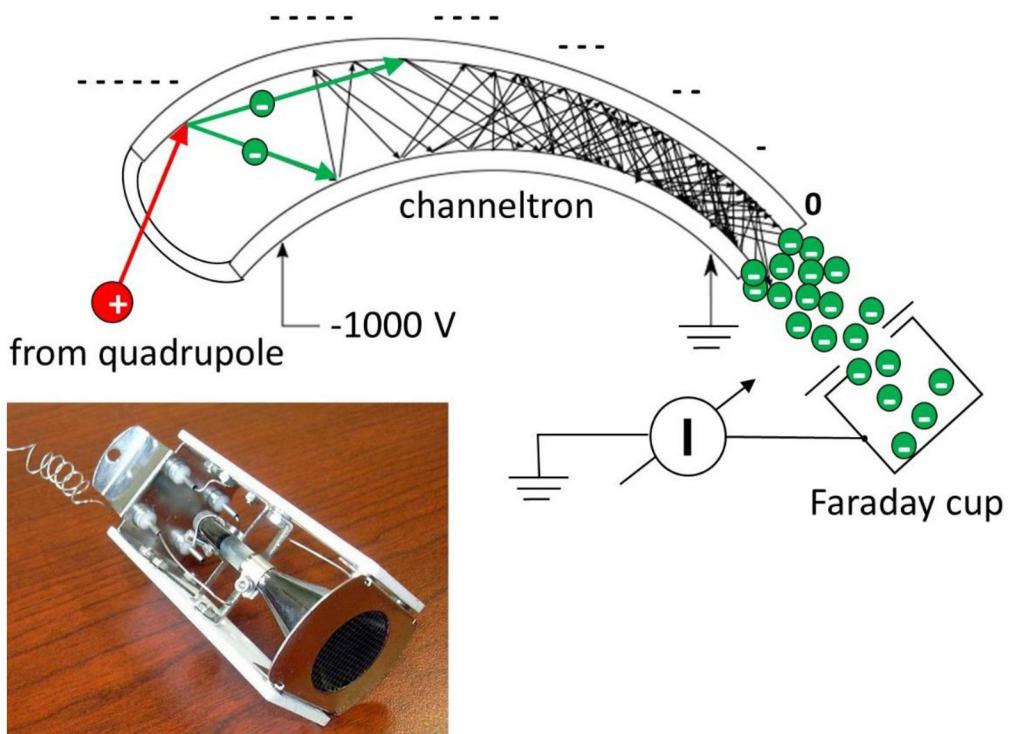


Fig. 1.3.1: Basic design of the ion detection unit. The channeltron (SEM) amplifies the ion current by using an electron avalanche effect. The Faraday cup selects the electrons and the current can be measured by a sensitive ampère meter (built in the QMS electronics) [6].

The calibration factors C_1 and C_2 of the channeltron depend exponentially on the applied voltage and can be described as:

$$I = I_0 \cdot 10^{C_1 U_{SEV} + C_2 U_{SEV}},$$

where I is the measured ion current at the Faraday cup, I_0 is a pre-factor depending on the peak amplitude and U_{SEM} represents the applied voltage to the channeltron.

1.4 Measuring Residual Gas Components

In this lab course experiment the residual gas components are measure in an ultra-high vacuum chamber made from stainless steel.

The remaining residual gas components of a good stainless steel UHV chamber usually are hydrogen and carbon monoxide. Notice, that the hot filaments in the ionization unit of the mass spectrometer and the Bayard-Alpert gauge can crack the gas molecules and new compounds can be formed. Therefore the remaining mass peaks in an UHV chamber are:

- mass 1 (H)
- mass 2 (H₂)
- mass 12 (C)
- mass 16 (O)
- mass 28 (CO)
- mass 44 (CO₂)

Hydrogen is stored within the steel and can only be reduced by baking the chamber for a long time at 400°C. The CO desorption gives the pressure limit of a stainless steel chamber, which is in the range of 10⁻¹¹ mbar to 10⁻¹⁰ mbar. To reach such a good pressure the adsorbed water (mass 18/17) must be removed from the chamber surface by baking it at about 150°C. Sometimes compounds of oil from the mechanical pumps can be found in the mass spectrum (groups of mass peaks, which repeat with a distance of 14 mass units = always one CH₂ group more). This can only be removed by cleaning the whole chamber with soap and other solvents. A good indication for a leakage are the following mass peaks in the spectrum:

- N₂ (mass 28/14)
- O₂ (mass 32/16)
- Ar (mass 40/20)

2 Ultra-high Vacuum

The classification of vacuum depending on the achievable pressure is shown in the table:

Classification	pressure
rough vacuum	1000 mbar - 1 mbar
medium vacuum	1 mbar - 10^{-3} mbar
high vacuum, HV	10^{-3} mbar - 10^{-7} mbar
ultra-high vacuum, UHV	10^{-7} mbar - 10^{-10} mbar
extreme high vacuum, XHV	< 10^{-10} mbar

Tab. 2.0: Classification of vacuum pressure ranges.

Fig. 2.0 gives an overview over vacuum classification, generation, measurement and technical relevance.

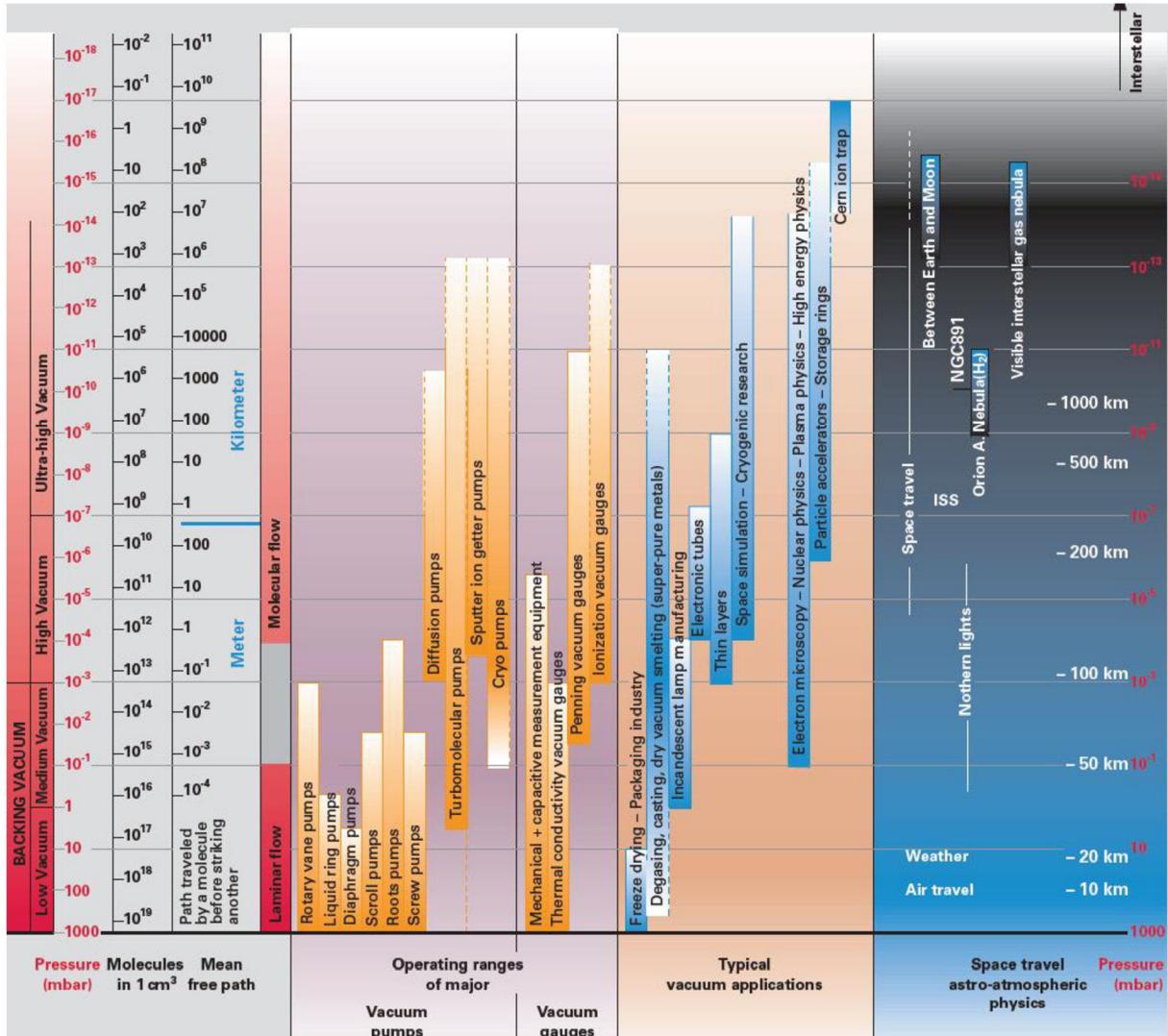


Fig. 2.0: Vacuum at a glance (image taken from the Vacuum Technology Book of Pfeiffer Vacuum GmbH [9]).

In this experiment we use an ultrahigh vacuum chamber made from stainless steel. All flanges are sealed with copper gaskets (CF standard). The used UHV valves have also a metal sealing. The pressure is in the range of $10^{-10} - 10^{-9}$ mbar. Notice that the mean free path of the gas molecules is about 100km.

2.1 Generation of Ultra High Vacuum

To reach ultrahigh vacuum pressures in a chamber special types of vacuum pumps are needed. Typical UHV pumps are:

- ion getter pumps,
- turbomolecular pumps,
- sublimation pumps,
- oil diffusion pumps
- cryogenic pumps.

All of these pumps cannot be used directly at ambient pressure to pump the recipient. Therefore additional rough vacuum pumps are needed to create a medium or high vacuum first, before switching on the ultrahigh vacuum pumps. A rough vacuum can be created by rotary pumps, membrane or scroll pumps. In this experiment the external pumping station is equipped with a rotary pump which can reach a pressure of about 10^{-3} mbar.

The Rotary Pump

Fig. 2.1.1 shows the operating principle of the pump. The pumping system consists of a housing (1), an eccentrically installed rotor (2), vanes (3) that move radially under centrifugal and resilient forces and the inlet and outlet (4). The inlet valve is designed as a vacuum safety valve that is always open during operation. The working chamber (5) is located inside the housing and is restricted by the stator, rotor and the vanes. The eccentrically installed rotor and vanes divide the working chamber into two separate compartments with variable volumes. As the rotor turns, gas flows into the enlarging suction chamber until it is sealed off by the second vane. The enclosed gas is then compressed until the outlet valve opens against the atmospheric pressure. The sealing is provided by oil [9].

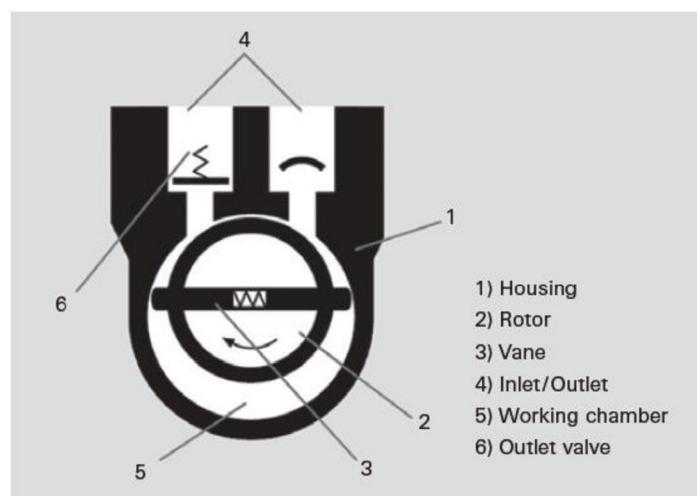


Fig. 2.1.1: Sketch of a rotary pump [9].

The Turbomolecular Pump

Usually a turbomolecular pump is used as the second pumping stage. The turbomolecular pump was developed and patented at Pfeiffer Vacuum in 1958 by Dr. W. Becker. Turbomolecular pumps belong to the category of kinetic vacuum pumps. Their design is similar to that of a turbine. A multi-stage, turbine-like rotor with bladed disks rotates in a housing. Interposed mirror-invertedly between the rotor disks are bladed stator disks having similar geometries [9]. Typical rotation speeds are 1000-1500Hz depending on the size of the pump. Pumping speeds of 60-300l/s are quite usual. To reach a pressure of $<10^{-9}$ mbar the chamber has to be heated up to 100-200°C in order to get rid of the adsorbed water at the stainless steel surfaces, thus reducing the outgassing rate.



Fig. 2.1.2: View inside a turbomolecular pump [10].