Fysik I
KTH
Aug 01

AM 69 – Mass Spectroscopy

The aim of this laboratory exercise is to get acquainted with modern computer controlled mass spectroscopic techniques including vacuum technology and some of its applications in atomic, molecular and nuclear physics, astronomy, geology and archeology as well as in analytical chemistry and industrial use

I. Introduction

Determinations of masses of atoms and molecules have played a fundamental role in the development of modern atomic and molecular as well as nuclear physics. Thus, increasing accuracy in measurements of the masses M of the elements in the 1920- ies showed that they were not exacly proportional to integer mass numbers A as earlier thought, but the difference M-A was found to vary throughout the periodic system. This indirectly led to the discovery of the neutron and the modern concept of the atomic nucleus with fundamental applications to astrophysics, geology , archeology , energy production etc.

If molecules are bombarded with photons or electrons they break up in their atomic and molecular constituents which may be analyzed in a mass spectrometer yielding a unique "fingerprint" of the studied molecule. Accordingly molecular mass spectroscopy is a very important tool in analytical chemistry , in medicine as well as in numerous industrial applications.

2. Atomic masses, isotopic abundances

According to the modern concept of an atom and its nucleus, a neutral element in the periodic system with atomic number **Z** has got **Z** orbital electrons and a nucleus containing **Z** protons and **N** neutrons (see Fig. 1). The sum **Z+N** is the mass number **A** and an element **X** is written

$$ {}^{A}_{Z}\mathbf{X} $$

A given element **X** (i.e. a fixed proton number **Z**) may occur with different number of neutrons. These various species are called different isotopes of the given element and they have identical chemical properties (in a first approximation) since **Z** and hence the number of orbital electrons are constant. The modern unit of atomic masses (1 u) is defined as 1/12 of the mass of the carbon isotope ${}^{12}{}_{6}C$ which replaces the older mass unit (1 amu) defined as 1/16 of the mass of ${}^{16}{}_{8}O$. .

Defined in this way, one might think that atomic masses M in general are integer numbers indicating the sum $Z*m_p$ and $N*m_n$ of the masses of the protons m_p, and neutrons m_n (with $m_p= m_n = 1$). However, this is not the case for two main reasons:

1. In reality $m_p \neq m_n \neq 1$. (Actually $m_p = 1.0073$ u; $m_n = 1.0087$ u).
2. Energy is needed for keeping the nucleons (i.e. protons and neutrons) together. This binding energy B(Z,A) is taken from the energy content (mc^2) of the atomic constituents ie. Z protons, Z electrons and N neutrons. Thus, the real atomic mass M (Z, A) will be reduced to

$$M(Z, A) = Z(m_p + m_e) + N^*m_n - B(Z, A)/c^2 \qquad (1)$$

Relation (1) is called the semiempirical mass formula and the difference **Δ**= M(Z, A) - A is called **mass defect** or **mass excess**. **Δ** has been experimentally measured for most of the known isotopes throughout the periodic system and is found in tables of isotopes.

One given element usually has got one or more **stable** isotopes and several **unstable** i.e. radioactive isotopes. The most common radioactive decay is the β decay in which either a neutron is converted to a proton:

$$n \rightarrow p + e- \qquad (\beta^- \text{ decay}) \qquad (2)$$

or a proton to a neutron:

$$p \rightarrow n + e^+ \qquad (\beta^+ \text{ decay}) \qquad (3)$$

An alternative way of converting a proton to a neutron is the capture of an orbital electron:

$$p + e^- \rightarrow n \qquad (\text{e capture}) \qquad (4)$$

These decays take place within a certain half-life $T_{1/2}$ (defined as the time necessary for half of the nuclei of a given sample to decay) and all the three processes (2) - (4) change both Z and N while A remains constant. Thus the nuclear properties and the possible decay modes determine which isotopes of a given element are stable. Fig. 2 shows some examples of this. Thus Fig.2 a) shows the masses of known isotopes with A = 12. The stable isotope (i.e. $^{12}{}_6C$ is that with the smallest mass. $^{12}{}_5B$ and $^{12}{}_7N$ are heavier and decay to $^{12}{}_6C$ with β^- and β^+ emission, respectively, with short half-lives. For A = 13 (Fig. 2 b)) $^{13}{}_6C$ has the smallest mass and is a stable isotope to which $^{13}{}_5B$ and $^{13}{}_7N$ decay by β^- and β^+ emission, respectively. For A=84 (Fig. 2c)) the mass has two minimum points a.t Z = 36 (Kr) .and Z = 38 (Sr). and both $^{84}{}_{36}Kr$ and $^{84}{}_{38}Sr$ are therefore stable isotopes to which neighbouring elements with the same A decay via β^- or e capture processes

Thus we learn from Figs 2 a) and 2 b) that carbon has got two stable isotopes ^{12}C and ^{13}C. The abundances of these isotopes measured on terrestial samples are 98.9% and 1.1 %, respectively, yielding an average mass of natural carbon = 12.011 u. As another example Fig. 3 shows a mass spectrum of natural krypton. As seen from this figure krypton has six stable isotopes with A = 78, 80, 82, 83, 84, 86 with a weighted average mass = 83.80 u. The isotopic abundances of a given element may vary from place to place in the universe dependent on the "prehistory" of the formation of the given element in the actual environment. Inversely, measurements of relative isotopic abundances is an extremely important way of determining the age of astronomical objects. Thus the age of the earth has been determined with some 1 % accuracy in this way using, in particular, the abundance ratio of ^{86}Sr and ^{87}Sr in normal and in rubidium containing minerals. In the latter case the ^{87}Sr content is increased because of the decay of $^{87}Rb(T_{1/2} = 4.7 * 10^{10}$ years) → ^{87}Sr which yields an age of the minerals = $(4.53 \pm 0.04)*10^9$ years. Similar ages have been found from mass spectroscopic studies of minerals from the Moon, Mars and meteorites, which proves that all these members of the solar system were formed simultaneously.

Another famous "clock" is the ^{14}C method for dating archeological species up to about 100 000 years old. In short the method is based upon the fact that ^{14}C is continuously formed in the upper atmosphere by cosmic ray bombardment of nitrogen. $^{14}CO_2$ molecules are subsequently formed and absorbed by living organic matter such as trees. When the tree is cut and the wood is used for producing various objects, it stops acquiring new ^{14}C and its original ^{14}C content decays with $T_{1/2} = 5730$ years. Thus the decrease of the ^{14}C /^{12}C isotopic ratio compared to that of a living tree is a direct indicator of the age of the object.

A fundamental difficulty in mass spectroscopy of species with very low abundances (such as in ^{14}C dating) is that ordinary spectrometers only select the mass number A and they can not differ between ions having the same mass numbers . Also the measurements are very time consuming in view of low count rates. Therefore, in recent years particle accelerators are frequently used in high-sensitivity mass spectroscopy. The main advantages with particle accelerators are that selections may be made of masses as well as charges and that impurities may be eliminated using stripping and negative ion beam techniques. As an example, modern accelerator technology has pushed the sensitivity limit to about 10^{-15} in the ^{14}C /^{12}C ratio and only 1 milligram sample is needed to determine ages up to 100 000 years

3. Molecular masses, quantitative chemical analysis

Molecular mass spectroscopy is one of the most important tools in analytical chemistry , biochemistry and in industrial research. The development of molecular mass spectroscopy in recent years includes couplings to gas chromatographs and advanced computer systems which enables analysis of nanogram quantities of mixtures of very complex molecules with high speed and accuracy .

A particular simple example of molecular mass spectroscopy is the analysis of hydrocarbons. Fig. 4 shows a mass spectrum of methane and ethane where the original molecules have been ionized and cracked-up in their possible atomic and molecular constituents by electron impact. Thus cracking and ionization of methane (CH_4) could give H^+, H_2^+, C^+, CH^+, CH_2^+, CH_3^+ and CH_4^+ with mass numbers A = 1,2,12,13,14, 15 and 16, respectively. Hereby, as seen from Fig. 4 a, the production of CH_4^+ (only ionization of the parent molecule without cracking) is the most abundant process following electron bombardment of CH_4 closely followed by the production of CH_3^+ . Less abundant are the fragments CH_2^+ and CH^+ , while the peaks from H^+, H_2^+ and C^+ are weak. It is obvious that the mass spectrom in Fig. 4a is unique for methane and forms an accurate "fingerprint" of this molecule. In the same way the mass spectrum displayed in Fig. 4b is unique for ethane with the ionized parent molecule ($C_2H_6^+$) being the heaviest product (A = 30) and a strong production of $C_2H_2^+$, $C_2H_3^+$, $C_2H_4^+$ (maximum) and $C_2H_5^+$ at A = 26 - 29 and only a small production of CH_2^+ , CH_3^+ and CH_4^+ .

4. The quadrupole mass analyzer

There are a great variety of constructions of mass spectrometers. most of which are based upon various combinations of electric and magnetic fields. One fairly modern version is the quadrupole mass spectrometer (**QMS**) and this construction has got a widespread use because of its small size and fast scanning possibilities. A sketch of such a system is shown in Fig. 5. The gas to be examined is let into an ion source which in principle is a small vacuum chamber with a built in electron gun which ionizes the gas and accelerates the ions towards the four electrodes forming the quadrupole analyzer with subsequent detector . The latter may in its simpliest form be a sensitive current meter. A closer view of the quadrupole analyzer is displayed in Fig. 6. The four electrodes have hyperbolic, platinum coated surfaces with opposite surfaces electrically connected, thus having the same voltages. A dc voltage +U and -U are supplied to the two pairs with a superimposed high frequency (2.3 MHz) ac voltage ±V* cos(ωt). If the equations of motion are solved for this field configuration it is found that the ion orbits are stable within the electrodes only for one given ratio U/V (≈0,165 with the presently used analyzer) corresponding to the transmission of only one certain mass m for a given value of U (and V). All other masses are not transmitted because these ions go into unstable orbits and hit the electrodes and become neutralized after a few oscillations. Thus, a recording of a mass spectrum is accomplished by varying U and V at the same rate keeping the ratio U/V constant.

This functioning of a quadrupole analyzer follows from the solutions to the equations of motion which may be set up by considering the potential **Φ** between the electrodes.

$$\Phi = (U + V \cos \omega t)\frac{x^2 - y^2}{r_0^2} \tag{5}$$

which yield the components of the E-field:

$$\begin{aligned} E_x &= -\frac{\partial \Phi}{\partial x} = -\frac{2x}{r_0^2}(U + V \cos \omega t) \\ E_y &= -\frac{\partial \Phi}{\partial y} = +\frac{2y}{r_0^2}(U + V \cos \omega t) \\ E_z &= -\frac{\partial \Phi}{\partial z} = 0 \end{aligned} \tag{6}$$

and hence the equations of motion:

$$\begin{aligned} m\frac{d^2x}{dt^2} &= eE = -\frac{2ex}{r_0^2}(U + V \cos \omega t) \\ m\frac{d^2y}{dt^2} &= eE = +\frac{2ey}{r_0^2}(U + V \cos \omega t) \\ m\frac{d^2z}{dt^2} &= eE = 0 \end{aligned} \tag{7}$$

Note that the QMS selects ions with a given e/m ratio. Thus, for instance, $^{40}Ar^{+}$ ions can not be distinguished from $^{80}Kr^{2+}$ etc.

To this laboratory exercise numerical solutions to these equations are calculated using a computer program (see section 5.4 below). Figure 7 shows an example of such a simulation of an orbit with the oscillations in the x- as well as the y-direction using the parameters m= 40 u, V =555 volts and U/V =0,163.

5. Practical performance of the equipment

5.1 The vacuum system

At ordinary atmospheric pressure at the earth (= 760 mm mercury = 101.3 kPa = 1013 millibar) free particles may just move a very short distance (10^{-6} cm) before they collide with the air molecules. Since the mean free path λ between two collisions is inversely proportional to the gas pressure, this means that the pressure has to be reduced to about 10^{-8} of the atmospheric pressure (i.e. to 10^{-5} millibar) to get λ of the order of meters. Accordingly all equipments in atomic and subatomic physics involving the propagation of particles must operate under high vacuum (10^{-5} millibar or better) corresponding to a density of some 10^{11} molecules per cm^3. This is still a very poor vacuum as compared to the conditions in the universe where the average density is about 10^{-5} protons per cm^3, while "dense" interstellar clouds where new stars are born may have densities up to 10^5 molecules per cm^3. For this reason vacuum technology is an essential part in modern experimental physics involving production, acceleration and detections of free particles. Fig. 8 shows a general picture of the mass spectroscopy equipment including the vacuum system with its rotary pumps and turbomolecular pump. The rotary pump is the one most generally adopted in the vacuum industry today for the production of pressures down to 10^{-2} to 10^{-3} mbar. Fig. 9a illustrates, in schematic form, the cross-section of a typical rotary-vane pump. The mechanism, which is lubricated by oil, consists of a housing (stator) with a cylindrical bore into which is fitted a rotor. The rotor is offset in relation to the stator bore and fits closely against the stator in one position. The stator bore in this area has a curvature equal to that of the rotor accurately machined across the whole width of the stator bore. The rotor contains two blades (generally spring loaded) which slide in diametrically opposed slots. Thus, as the rotor turns, the tips of the blades are in contact with the stator wall at all times. Fig. 9b shows four stages in one revolution of the rotor. The cycle is divided into induction, isolation, compression and exhaust phases. During operation gas molecules entering the inlet of the pump pass into the volume created by the eccentric mounting of the rotor in the stator. The crescent-shaped gas volume is then compressed, forcing the exhaust value open and permitting gas discharge. Note that there are two pumping "cycles" per revolution. In order to produce a seal which will combat the very high pressure difference between the intet and discharge sections, the gap between the rotor and stator is required to be of a very small order (typically 0.025 mm). To complete the seal, a thin oil film is continuously maintained between the components by oil drawn from the oil reservoir into the pump interior. The seals necessary between the blade edges and tips and the stator are made in the same way. The circulating oil is ejected back into the reservoir through the exhause valve together with the pumped gas. The ultimate pressure is limited by back-leakage between the suction and discharge compartments and by outgassing of the lubricating oil .

To reach a better vacuum as needed in mass spectroscopy, a rotary pump has to be combined with a high vacuum pump such as a turbomolecular pump. A turbomolecular pump is a gas transfer pump which operates like an axial flow compressor used on a jet engine. Sets of moving blades, separated by stationary blades, rotate at high (up to 60000 rev min^{-1}), receiving and compressing gas from a high vacuum chamber and delivering it to the rotary pump on the outlet side. Turbomolecular pumps are designed to operate under molecular flow conditions. The physical basis for the pumping action is the interaction effect between a molecule and a moving surface. The short but finite residence time occurring when a molecule strikes a surface results in the molecule acquiring an additional velocity component in the direction of the moving surface (see Fig. 10 a). The orientation of the moving (rotor) blades and stationary (stator) blades to the axial direction in a turbomolecular pump is as shown in Fig. 10 b. The molecule shown incident on a rotor blade will reside on the surface for a short time and then will probably leave in the direction shown due to the lateral movement of the blade and its pitch. The stator blades are also pitched. Their pitch direction is such that they preferentially transmit molecules that have left the rotors and are moving axially down the pump. Molecules moving in the reverse direction (back-diffusion) are likely to be reflected back (as shown). The other major effect of the stators is to stop the sidewards movement of molecules that have been struck by the rotors, directing the molecule vecocities forther into the axial direction down the pump. It is rather difficult to explain the pumping mechanism of a turbomolecular pump diagrammatically because of the high rotational speed involved. However, as a result it is more probable that the molecules will be driven towards the direction of the exhaust of the pump rather than towards the inlet. For the blades to be effective with rapidly moving molecules, the blade speeds must approach the molecule speeds, otherwise the molecules will pass through the rotor regions without being struck. For a rotor travelling at 60 000 rev min^{-1} and with a mean blade diameter of 7.5 cm, its blade tip speed is around 236 m s^{-1}. By comparison, the average speed for nitrogen molecules at 20^0 C is 470 m s^{-1}. Heavier molecules will be slower, lighter molecules faster, such as hydrogen at 1900 m s^{-1}. Thus lighter molecules are more difficult for turbomolecular pumps to pump, because they are more likely to pass through the rotors without being hit by a blade, increasing the likelihood of back-diffusion of the gas. However, even for hydrogen, a final vacuum is obtained which is 10^3 times better than the inlet pressure maintained by the rotary pump. The final vacuum normally achieved with the present rotary + turbomolecular pump system usually is around $10^{-5} – 10^{-6}$ mbar .

5.2 The experimental chamber

To assure the proper conditions for the mass analyser to work, the head of the QMS is mounted permanently in the vacuum chamber (see Fig.8). When the QMS is in operation a good vacuum in the range of 10^{-5}- 10^{-6} mbar is necessary to be maintained in the chamber which is directly connected to the turbo pump. A high pressure may cause a damage of delicate parts of the QMS, **so never start the instrument before checking the vacuum.** If a lower background pressure (e.g. the pressure in the chamber in the absence of experimental gas) is required it may be necessary to heat ('bake') the chamber to speed up the pumping process. Heating up causes outgassing and 'cleans up' the chamber. For this purpose an oven is mounted on the chamber which allows to bake up the system up to a few hundreds degrees. However, because same vacuum connections includes uobber O-rings, the baking temperature must not exceed 70° C . The experimental gas is let in from the gas bottles via a capillary pipe to the gas inlet system which consists of a pressure converting gas inlet valve with a flow regulator which is backed by the gas handling rotory pump when roughing valve is open.

5.3 Operation

The QMS is fully computer controlled by the unit “TWare Lite”. Operational hints are given in the “User guide” to this unit

5.4 Computer simulation

A Matlab program simulates the functioning of the mass filter by solving numerically and the equations of motion (7). Program ***kv1*** shows the motion along the quadrupole and ***kv2*** the motion perpendicular to this. Call the Matlab program . Write ***kv1*** or ***kv2*** to activate the programs. Answer the questions and give the phase angle (in radians), V and m (u). Check if the calculated orbitals are stable and print the result (compare Fig. 7). It is practical to perform this computer simulation of the orbits during the pumping down time of the mass spectrometer .

6. Tasks

There are a great variety of measuring tasks which can be performed using the present mass spectroscopy equipment. For instance:

- Mass spectra of hydrocarbons and mixtures of hydrocarbons (cf Fig. 4).
- Mass spectra of unknown gases supplied by the assistant.
- Analysis of air samples collected for instance from the city streets.
- Abundances of rare gas isotopes (cf Fig. 3).

Closer instructions will be given by the assistant in each separate case.

7. To be given to the assistant

1. Plots of measured known atomic and molecular mass spectra with mass assignments.
2. Plots of the mass spectra of the 'unknown' species including analyses

A table of atomic masses is found in Serway, Moses, Moyer 'Modern Physics' (Appendix B)

Fig. 1 Modern concept of an atom and its nucleus. The atomic number Z of an element in the periodic system denotes the orbital electrons which determines the chemical properties of the actual element. The nucleus contains Z protons and N neutrons. A given element Z may have different number of neutrons which are called different isotopes of the element. Most isotopes are radioactive and disintegrate into other isotopes of other elements via various decay processes. Although the size of the atomic nucleus (which is very exaggerated in the figure) is typically 10^5 times smaller than that of the atom as a whole, practically the whole atomic mass is made up by the nucleus.

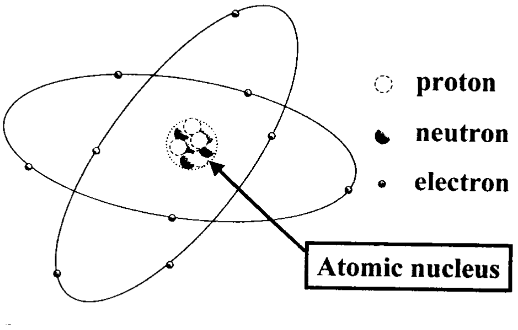


Fig. 2 Atomic masses M of various elements Z with mass numbers A= 12,13 and 84. For a given mass number, the stable isotopes in nature are those having the smallest mass. Other combinations of protons and neutrons form radioactive isotopes which disintegrate with certain half-lives (given in the figure) to stable isotopes via β-decay. Thus, as seen from the figure, the only stable isotopes for A=12 and 13 are $^{12}_{6}C$ and $^{13}_{6}C$, respectively.

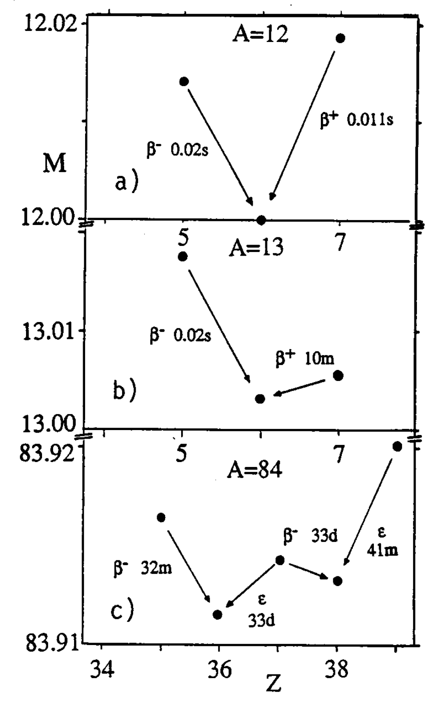
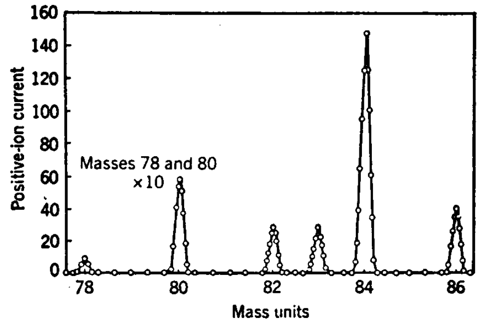


Fig. 3 Mass spectrum of natural Krypton (Kr) which has got six stable isotopes. The odd masses A= 79, 81 and 85 are missing since they are radioactive and do not exist in nature.



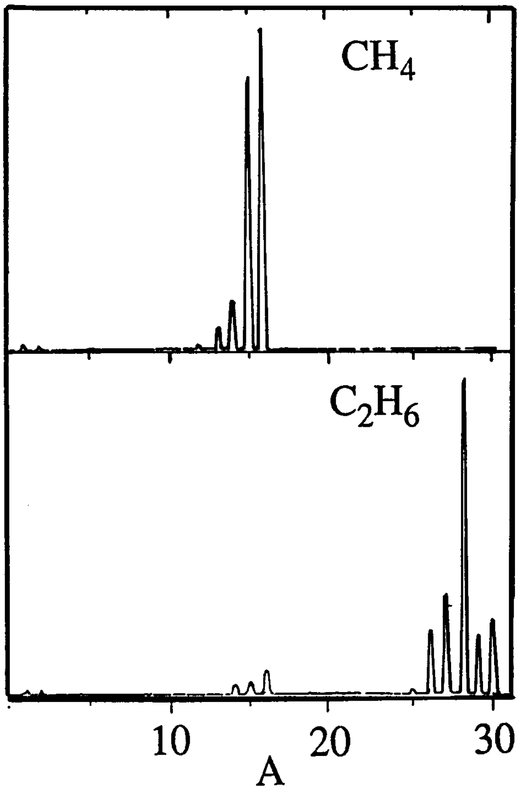


Fig. 4 Mass spectrum of CH_4 (methane) and C_2H_6 (ethane) obtained by ionization and cracking using an electron beam. For instance cracking of CH_4 yields ionized fragments H, H_2, C, CH, CH_2 and CH_3 in the order of increasing probability.

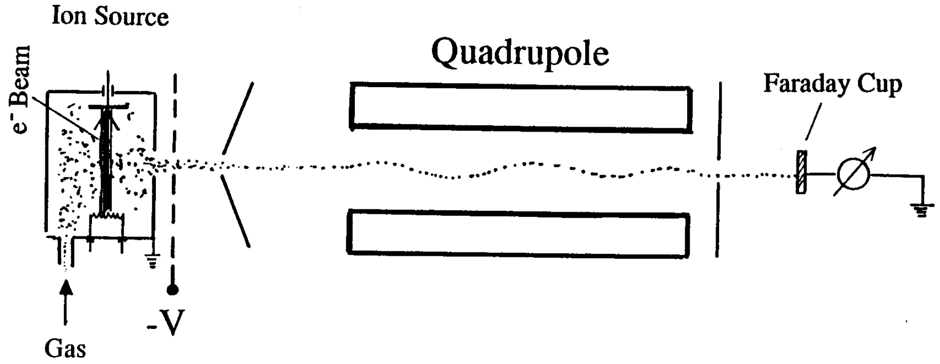


Fig. 5 Principles of a quadrupole mass spectrometer (QMS) system. The gaseous species to be examined are introduced into the ion source where ionization and cracking is accomplished for instance using an electron beam. The ions are extracted from the ion source using a negative voltage and the ion beam passes through the centre of four quadrupole rods (see Fig. 6) where a mass selection takes place before the ions are detected for instance using a Faraday cup.

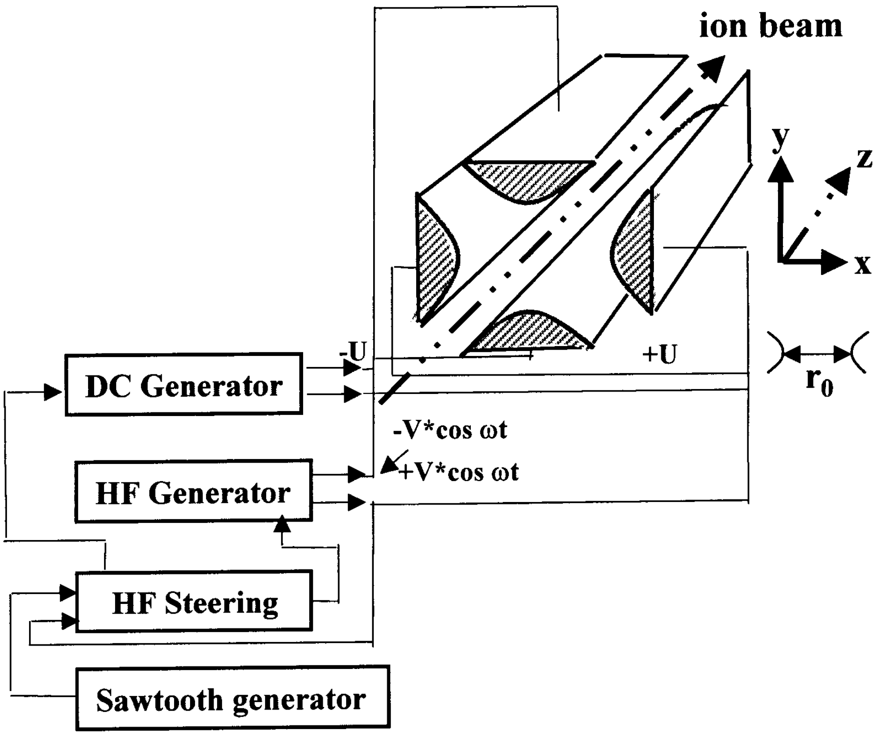


Fig. 6 The four mass selecting quadrupole rods used in the present QMS system with electric connections. The hyperbolic rods are connected to DC voltages ±U as well as superimposed high frequency (2,3 MHz) AC voltages ±V*cos ωt. As follows from equations (5)- (7) this combination yields a mass selection and mass spectra may be obtained by varying U and V at the same rate keeping the ratio U/V constant.

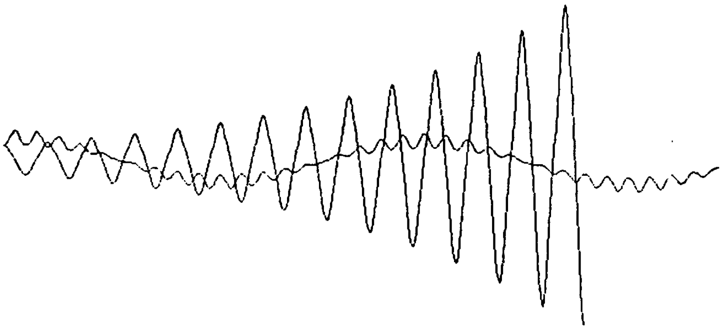


Fig. 7 Display of a calculated ion-orbit (in the x- as well as the y-direction) using input parameters m= 40 u, V=555 volts and U/V= 0,163.

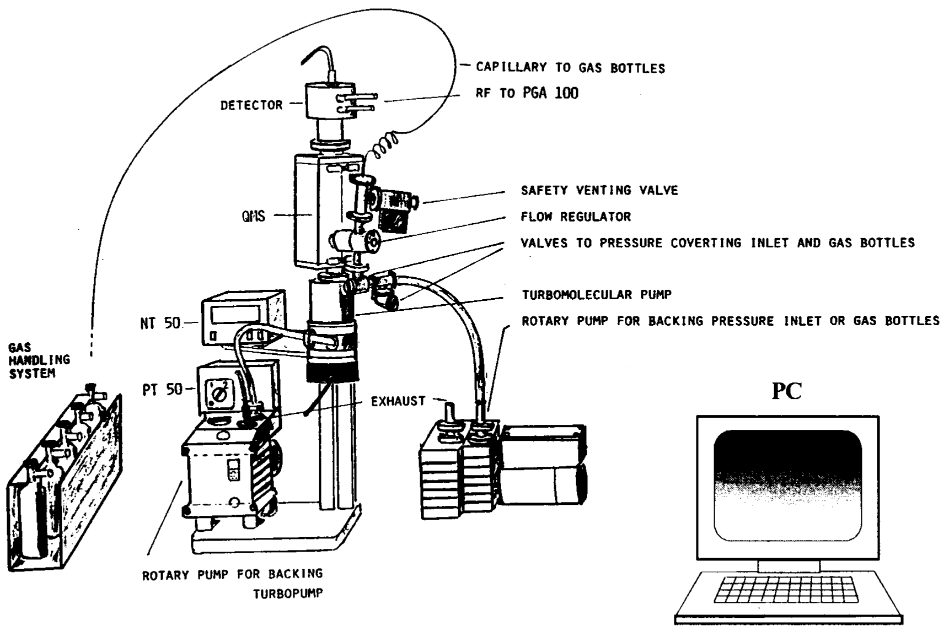


Fig. 8 General view of the mass spectrometer system used in the present laboratory exercise.

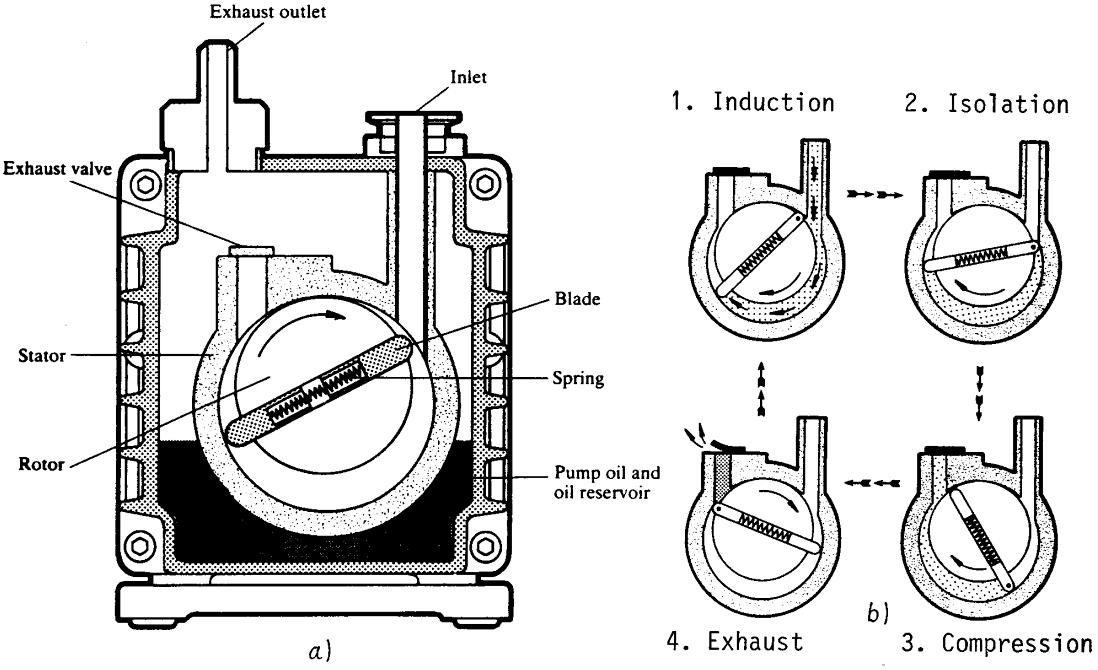


Fig. 9 a) Schematic of a rotary-vane pump. b) Four steps in the cycle of a rotary-vane pump.

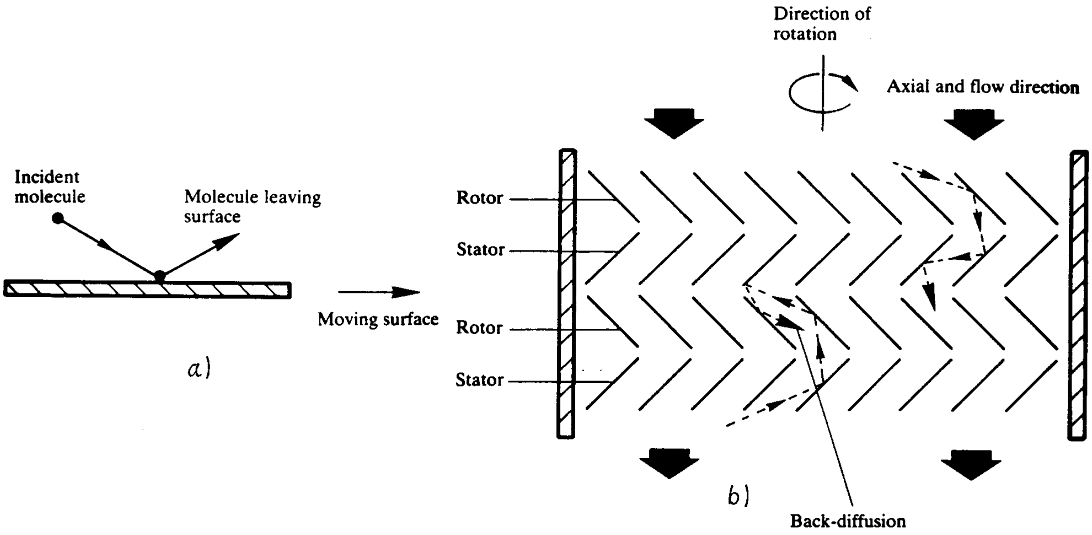


Fig. 10 The working principles of a turbomolecular pump. a) Interactions between a moving surface and an incident molecule. b) The orientations of rotors and stators in a turbomolecular pump.