Mass Spectrometry: Quadrupole Mass Filter

The mass spectrometer is essentially an instrument which can be used to measure the mass, or more correctly the mass/charge ratio, of ionized atoms or other electrically charged particles. Mass spectrometers are now used in physics, geology, chemistry, biology and medicine to determine compositions, to measure isotopic ratios, for detecting leaks in vacuum systems, and in homeland security.

Mass Spectrometer Designs

The first mass spectrographs were invented almost 100 years ago, by A.J. Dempster, F.W. Aston and others, and have therefore been in continuous development over a very long period. However the principle of using electric and magnetic fields to accelerate and establish the trajectories of ions inside the spectrometer according to their mass/charge ratio is common to all the different designs. The following description of Dempster's original mass spectrograph is a simple illustration of these physical principles:

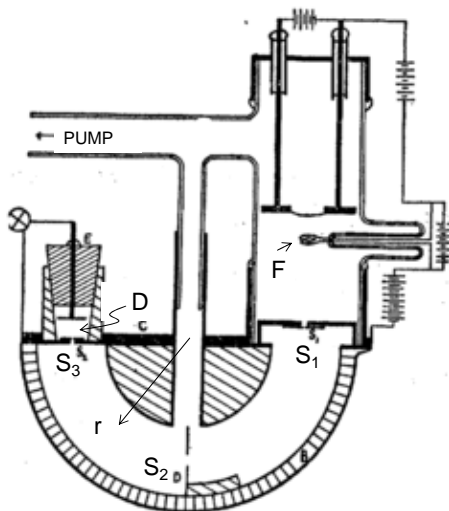The magnetic sector spectrograph

Fig. 1: **Dempster's Mass Spectrograph (1918)**. Atoms/molecules are first ionized by electrons emitted from the hot filament (F) and then accelerated towards the entrance slit (S_1). The ions then follow a semicircular trajectory established by the Lorentz force in a uniform magnetic field. The radius of the trajectory, r, is defined by three slits (S_1, S_2, and S_3). Ions with this selected trajectory are then detected by the detector D.

How the magnetic sector mass spectrograph works:

Equating the Lorentz force with the centripetal force gives:

$$qvB = mv^2/r \tag{1}$$

where q is the charge on the ion (usually +e), B the magnetic field, m is the mass of the ion and r the radius of the ion trajectory.

Classically, the speed of the ion, v, is related to its accelerating voltage V, by

$$\tfrac{1}{2}mv^2 = qV \tag{2}$$

Eliminating v from (1) and (2) gives:

$$\frac{m}{q} = \frac{B^2 r^2}{2V} \tag{3}$$

Therefore, for fixed radius of curvature, an ion with a particular mass/charge ratio m/q can be isolated and measured by an appropriate combination of magnetic field B and accelerating voltage V. In these early designs, it was convenient to fix B (using a permanent magnet) and scan V in order to measure the mass spectrum of the different species present in the vacuum chamber of the spectrometer.

The Quadrupole Mass Spectrometer

In practice, it is difficult to achieve very stable and spatially uniform magnetic fields, especially with permanent magnets. These difficulties can lead to degradation of the mass resolution and drifts in the calibration of the instrument. In addition, the presence of stray magnetic fields can affect other instruments that may be used in conjunction with a mass spectrometer, for example, electron energy analyzers. In the early 1950's it was realized, by W. Paul (shared Nobel Prize in Physics, 1989) that use of magnetic fields could be eliminated altogether by a clever design which uses alternating quadrupolar electric fields rather than magnetic fields, hence the name Quadrupole Mass Spectrometer. This is the design that is currently in widespread use for residual gas analysis. It is highly stable and has excellent mass resolution. With high sensitivity electron multipliers, it can measure partial pressures down to 10^{-14} Torr!

The operation of the Quadrupole Mass Spectrometer (QMS) is not quite so simple to understand as the magnetic sector design, but it is extremely elegant and involves some beautiful mathematics, and therefore the details are worth appreciating. First, the overall layout:
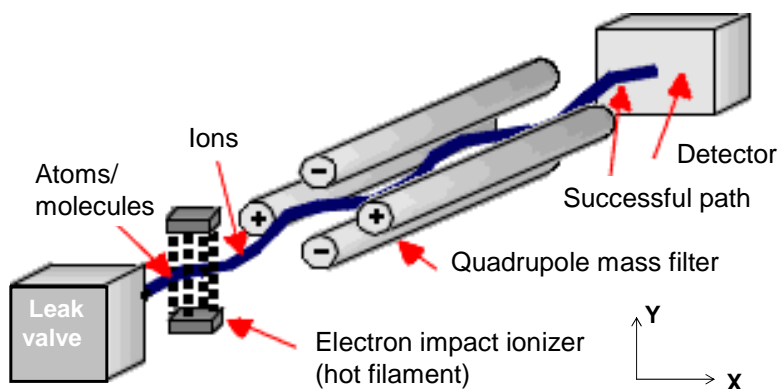
Fig. 2: *Schematic of a quadrupole mass filter.*

A quadrupole mass spectrometer consists of an ionizer (bombardment by electrons from a hot filament), an ion accelerator, and a mass filter consisting of four parallel metal rods arranged as in the figure above. Two opposite rods have an applied potential of $(U+V\cos(\omega t))$ and the other two rods have a potential of $-(U+V\cos(\omega t))$, where U is a dc voltage and $V\cos(\omega t)$ is an ac voltage. The applied voltages affect the trajectory of ions traveling down the flight path centered between the four rods. For given dc and ac voltages, only ions of a certain mass-to-charge ratio pass through the quadrupole filter and all other ions are thrown out of their original path. A mass spectrum is obtained by monitoring the ions passing through the quadrupole filter as the voltages on the rods are varied. There are two methods: varying ω and holding U and V constant, or varying U and V with (U/V) fixed for a constant angular frequency, ω.

The general principle of operation of the mass filter can be visualized *qualitatively* as follows: light ions (low mass to charge ratio) are able to follow the alternating component of the field. For the X-direction, those ions will stay in phase with the RF drive, gain energy from the field and oscillate with increasingly large amplitude until they encounter one of the rods and are discharged. Therefore the X-direction is a **high-pass mass filter**: only high masses will be transmitted to the other end of the quadrupole without striking the X-electrodes. On the other hand, in the Y-direction, heavy ions will be unstable because of the defocusing effect of the DC component, but some lighter ions will be stabilized by the AC component if its magnitude is such as to correct the trajectory whenever its amplitude tends to increase. Thus the Y-direction is a **low-pass mass** filter: only low masses will be transmitted to the other end of the quadrupole without striking the Y electrodes. By a suitable choice of RF/DC ratio, the two directions together give a mass filter which is capable of resolving individual atomic masses.

The attractive features of the quadrupole as a mass analyzer are evident from the above discussion: the quadrupole provides a convenient filter which can be tuned to the desired mass by varying the amplitude of the RF voltage, V; the mass selectivity (i.e. resolution

can also be varied electronically by simply adjusting the DC/RF ratio. Simultaneously varying the amplitude of the DC and RF voltages (at fixed ω) allows the entire mass spectrum to be scanned. More details of the construction and specifications of the Stanford Research Systems QMS can be found in the instrument manual.

Mathematical Analysis of the Quadrupole Mass Filter

The *X*- and *Y*-motions of an ion with mass *m* and charge *q* are described by the following equations of motion for the three separate coordinate axes:

$$\frac{d^2x}{dt^2} = -\left(\frac{e}{m}\right)\frac{[U + V\cos(\omega t)]}{r_0^2}\, x, \qquad \text{4(a)}$$

$$\frac{d^2y}{dt^2} = \left(\frac{e}{m}\right)\frac{[U + V\cos(\omega t)]}{r_0^2}\, y, \qquad \text{4(b)}$$

$$\frac{d^2z}{dt^2} = 0. \qquad \text{4(c)}$$

where $2r_0$ is the closest distance between the four electrodes of the QMS and e is the magnitude of the electron charge (assume singly charged ions).

These equations are simply Newton's equations of motion with:

Force = (ion charge)*(electric field).

Note that the motion along the z-axis is unaffected by the potential on the quadrupole electrodes.

Equations 4(a) and 4(b) are examples of **Mathieu's equation**, first solved in 1868 for a completely different problem (mechanical vibrations of a drum head). [Note that the same equations are extremely important in other areas of physics also, for example in general relativity and in solid state physics. They are related to the wave equation for electrons in periodic solids, the solutions of which are known as Bloch functions, and lead to electronic band structure.

The Mathieu equations can only be solved numerically.   The important characteristic of the solutions is that they are only stable (real) for a certain range of values of U and V. The regions of stable solutions are shown below as a function of U and V. The region (in pink) where the stable solutions of both 4(a) [x-motion] and 4(b) [y-motion] intersect is where the quadrupole mass filter operates.   More details on the application of the Mathieu equations to the QMS can be found in an excellent review by R.E. March, An Introduction to Quadrupole Ion Trap Mass Spectrometry, Journal of Mass Spectrometry **32**, 351-369 (1997).
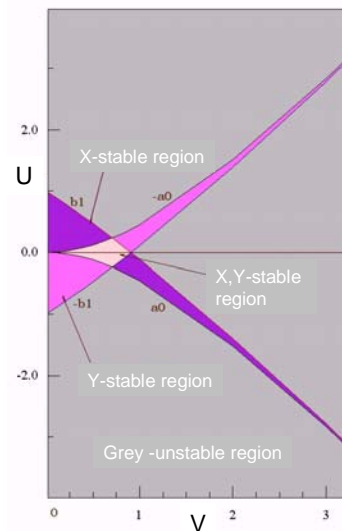

Fig. 3: Range of stability for QMS trajectories obeying Mathieu's Equation. X-motion is stable in the purple band and Y-motion in the magenta band. The stable operating condition for a given mass/charge is where these two bands overlap (pink).

Procedure

1. Turn on the vacuum gauge. This is a composite electronic gauge consisting of a Pirani Gauge (for measuring pressure in the region between atmospheric pressure (~760 Torr) and approximately 10^{-4} Torr. At this lower pressure the Penning Gauge will be activated automatically. The Penning Gauge uses the small electrical current generated by the motion of residual ionized gas molecules between high voltage electrodes in the gauge housing. For further details on vacuum gauges consult the excellent articles on Wikipedia.

2. Turn on the vacuum pump by pressing the fourth button down (lowest one) on the panel. The roughing pump and the turbo pump will start together. You will hear the stator of the turbo pump slowly accelerating. After a few minutes the pressure should stabilize at around 10^{-6} Torr as the turbo comes up to its full operating speed. If the pressure does not come down to this value, check that the leak valve is fully closed (use a wrench to turn the hex nut **clockwise**). DO NOT overtighten the leak valve –when you feel a modest resistance, stop turning. **Clockwise to close** the leak valve – **counter-clockwise to open it.   Do not proceed to step 3 unless the pressure is below 10^{-5} Torr.**

3. Turn on the power to the RGA. There is a switch on the back of the unit. "On" is marked with a circle with a vertical line thought it. Now open the RGA 3.0 software that controls the Quadrupole Mass Spectrometer. When you see the window for the operation of the QMS, go to the "Head" menu on the toolbar and select "**Connector List**

Settings". When the dialog box comes up showing the connector settings, press "Update RGA List" (lower left of the panel). Look for COM 2, click on it so it is highlighted, and press the "Connect" button (upper left of panel). COM 2 should now show as active on the list. A green LED (5th one from the left, labeled RS 232) will light on the back of the unit when the computer is communicating with the QMS.

4. At this point you can activate a scan, but the sensitivity will not be so good because you didn't yet turn on the filament of the electron impact ionizer. Try it with the filament off first, to see that you can actually get a mass spectrum just from whatever ions are present in the residual gas. Next turn on the filament either from the "Head" menu, or by pressing the icon for the filament on the toolbar. Before you turn on the filament, check that the pressure is less than 10^{-4} Torr. **DO NOT OPERATE the QMS at pressures greater than 10^{-4} Torr**. When the filament is activated, a green LED will light on the back of the QMS (the second LED from the left)

5. Now you are ready to operate the QMS and take spectra.

Suggested Experiments

1. ***Residual Gas Analysis.*** Take a scan of the residual gas inside the vacuum chamber at a pressure of 10^{-6} Torr or lower. The log scale is best, because it lets you see the very weak peaks from low concentrations of the various constituents of the residual gas. The largest peaks seen are likely to be due to nitrogen, oxygen, and H_2O. Note that molecules can be dissociated and each may cause more than one peak. For example, nitrogen can appear as N^{+2}, N^{-1}; and H_2O as H_2O^+, OH^+,0^+, etc. Compare the concentrations of the different species with what is expected from tables of atmospheric constituents. Questions: is the concentration of these constituents the same as in the atmosphere outside the vacuum chamber? Why not? Are there any strong peaks in the spectrum you cannot account for? Why are they there? A number of other features of the mass spectrum may strike you as surprising. You can explore them with this highly sensitive apparatus.

2***. Isotopic ratio of Neon***. There is a cylinder of neon gas near the mass spectrometer. Open the main valve on the cylinder. Set the pressure regulator on the cylinder to give a few PSI pressure on the low pressure gauge. Open the small valve slightly for a few seconds to flush out air, and then hook up the tube to the threads on the leak valve connector. . Adjust the leak valve to give a pressure 5×10^{-5} Torr on the vacuum gauge. Record a mass spectrum. Neon has two naturally occurring isotopes. The lower mass one has a mass of 19.999 amu. Find the mass of the other isotope of neon and use the ratio of the two peak heights to estimate the ratio of the two isotopes.

3. ***Pumping rate***. You may have noticed by now that the concentration ratios you measure in these experiments are not exactly what you expected, particularly for the lighter atoms and molecules like oxygen, nitrogen and hydrogen (where did that come from and why is there so much of it?). You may also have noticed that there is a slight excess of the lighter species relative to the heavier atoms. This is because the type of

pump we are using for these experiments, the turbomolecular pump (TMP) is not equally efficient at pumping species with different masses. It is great for the heavier elements, but not so good for the very light elements. In this experiment you will find out why, quantitatively.

First a few words about the TMP. It is constructed (See Fig. 4) of a series of angled blades rotating at very high speed, rather like a jet engine. The rotation rate for the model pump we use (TCP 50?) is xxx Hz.

Fig 4. shows a cut-away of the construction of a turbopump.

The operation of this type of pump can be modeled very simply by recalling the basic physics of **elastic collisions**. When a molecule encounters one of the fast moving blades momentum will be transferred to the molecule in such a way that the molecule will leave the blade with its velocity vector reversed plus an additional component equal to the velocity of the blade. If the velocity of the blade is v_b and that of the molecule, v_m, then the final velocity after the collision will be $v_m + 2v_b$, assuming the molecule's velocity is normal to the blade and initially towards it. The pumping rate for a particular gas should be directly related to the fractional increase in its momentum as a result of colliding with the blade. Accordingly, the pumping rate should be proportional to $2v_b/v_m$. When $v_m \gtrsim v_b$ then the pumping efficiency should fall off rapidly. Bearing in mind that v_m, the RMS speed of the molecule, is determined thermally:

$$\tfrac{1}{2} m v_m^2 \cong kT \qquad\qquad\qquad (5)$$

where k = Boltzmann's constant and T is the absolute temperature, the lighter atoms and molecules will have higher RMS speeds. In other words,

$$v_m \sim m^{-\frac{1}{2}}$$

So, the pumping efficiency should increase approximately as $m^{\frac{1}{2}}$ for the turbomolecular pump.

Make measurements to test this relationship. Suggested gases are H_2, He, O_2, N_2. Some of these are already present in the system (e.g. H_2), whereas others (e.g. He) are not, in any significant concentration. Helium would therefore have to be added. This is easily done by blowing a little He from a cylinder close to the inlet of the leak valve. Calculate the RMS speeds of the molecules you will use and compare them with the blade tip velocity of the turbopump (You are given the rotation rate, -estimate the radius of the blade and calculate).

In performing this experiment you can make use of the gate valve between the pump and the RGA. By partially closing the gate valve you will be able to slow down the overall pumping rate equally for all gases. Adjust the gate valve (large round knob) to give easily measurable pumping rates. **Do not overextend the gate valve**. As soon as you feel force increasing, stop turning.

Procedure for measuring pumping rate: From the Scan menu, set up a **multiple species time scan** on the RGA software so that the concentration of each of the selected gases is measured as a function of time. The software will make a simultaneous plot of the concentration of each species as a function of time. Open the leak valve until the pressure reaches about 5×10^{-5} Torr. Partially close the gate valve until the pressure reaches 2×10^{-5} Torr. When you have this set up, start the scan and quickly close the leak valve using the wrench (remember **clockwise to close** it). The aim here is to fit each of the curves with an exponential and find the time constant for each species. Finally, plot the time constant vs. $m^{-\frac{1}{2}}$ for each of the species you measured.

Other experiments: 1. Mass spectrometry is sensitive enough to detect small concentrations of molecular species in the atmosphere as you have seen. It is often used as a sensitive detection technique for toxic chemicals and explosives. You can use the system to "sniff" for certain chemicals. Try this on some selected solvents like toluene, acetone or chemicals such as hydrogen peroxide (or coffee if you like, but don't bring it into the lab in a coffee cup!). It turns out that a well trained dog is cheaper and more sensitive than the best mass spectrometer, hence their use at airports.
2. You may not have realized it, but the apparatus you have been working with is the basis of the gas centrifuge for isotope enrichment. You are not permitted to enrich uranium hexafluoride without special permission from Ramon!

Pre-Lab Questions
1. How does a turbopump work?
2. How are low pressures measured?
3. How could one use the mass spectrometer to detect leaks in a vacuum system?

Reading
H. Duckworth, Mass Spectrometry (copy available in lab).
A. Nier, The Mass Spectrometer (Scientific American)
Vacuum Technology: Wikipedia has good articles on gauges and pumps.