MASS SPECTROSCOPY

> **CAUTION!** By opening a gas valve or turning something on or off at the wrong time, you could cause major damage (tens of thousands of dollars) to this experiment. If you are not sure what you are doing, please talk to your instructor.

You are expected to conduct an independent experiment of your own design on the second day. Rather than be a comprehensive lab manual, this document is meant to help you guide yourself through this experiment as preparation for conducting independent work. This document consists of four parts: (1) a brief description a Quadrupole Mass Spectrometer (QMS) Residual Gas Analyzer (RGA), (2) a brief introduction to vacuum science, (3) a series of measurements to get you acquainted with the instrument, and (4) some ideas for your independent experiment.

The mass spectrometer that you'll be using was purchased in 2005 with your College Based Fee money. You can find the operation manual in the laboratory or online at
http://www.thinksrs.com/downloads/PDFs/Manuals/RGAm.pdf

(1) What is a Quadrupole Mass Spectrometer (QMS)?

In Physics 133, you likely learned how a constant magnetic field mass spectrometer works whereby gas molecules are first ionized and then accelerated by a constant DC voltage into a region of magnetic field oriented perpendicular to the path of the ions. The Lorentz force causes the ions to move in a circular path of a radius proportional to the square root of the mass of the ion…. Or more correctly said, "to the square root of the *mass to charge ratio* of the ion". The difference in this statement becomes important because a doubly ionized ion acts the same as an ion with half the mass.

I once heard "if you give me a force, I can make a mass spectrometer with it." I'm sure you can imagine that you could make a gravitational mass spectrometer for instance… but it wouldn't be practical. Please find out how the QMS works to separate molecules based on their charge to mass ratios using both DC and oscillating electric fields. Please look at the manual, paying special attention to how the electrons are produced and accelerated to ionize the gas sample; how the ions are then accelerated into the quadrupole field; how the quadrupole filter is able to deconfine all but a single mass to charge ratio (pgs. 3-9); and how they are detected in a Faraday Cup. Please look at the diagrams in chapter 3 illustrating how the device works.

On pgs. 2-4 of the QMS manual you see there are 4 modes of operation that are described more fully on pgs. 5-7 and thereafter. You can use the QMS to watch the population of a single charge-to-mass species change over time, or gather a full spectrum of masses (in analog or digital), or get a total pressure measurement. In spectrum mode, the results are displayed as pressure versus mass to charge ratio. To do this experiment successfully, it is crucially important that you be aware that the QMS does not *measure* the pressure of a mass to charge ratio, it calculates pressure from the number of events measured by the detector at the end of the quadrupole filter. By measuring the number of detected ions, it infers the population density (N/V) and then calculates pressure from our gas law equation assuming room temperature. However, the proportionality between population density and number of detected ions will be

different for different gasses and conditions. Why? Because when the ionizing electrons hit molecules, many thing can happen with different probabilities: an ionization, multiple ionizations (more than one electron ejected), fragmenting (breaking the molecule apart - see pgs. 2-9 and 5-19). Additionally, passage through the quadrupole filter is affected by the presence of neutral molecules (background pressure) and the mass of the ion being selected. Lastly, the detector is a Faraday Cup, which simply measures charge, meaning that all doubly ionized molecules will count as two. Pages 2-11 describe a rigorous calibration process that can be used to determine absolute pressures, but this is not what we want to do with this experiment. Pages 5-19 describe how you can use the software to analyze a given mass spectrum. In any case, it is not safe to compare the absolute pressures of different substances with precision, but if a signal increases, it is likely that this is because of a pressure increase of the associated compound.

(2) What is vacuum science?

Why do we need very low pressures to use the QMS? At higher pressures, ions will not be produced with the same efficiency, nor travel unimpeded down the length of the quadrupole filter to the detector (see pgs. 2-12). At the low pressures necessary, air does not act like a fluid. The rarefied gas molecules move "ballistically," independently at about the speed of sound until they hit something, bounce off, stick, or pass through the pump and are removed. It is useful to remember that at 10^{-6} Torr (a reasonable pressure for our vacuum chamber) the mean free path of an air molecule is about 50 meters, and surfaces are exposed to a monolayer in one second. This means on average, every atom of the surface is struck by an air molecule each second. Ultra High Vacuum (UHV) experiments require that the surfaces don't get contaminated and so if the experiment lasts 1000 seconds, then the pressure should be around 10^{-10} Torr, so that during the course of the experiment, only a tenth of the surface atoms interact with a background molecule. (See appendix A if you want to go through some "back of the envelope" calculations).

You'll often find a significant water peak at 18 amu, and an OH^+ fragment at 17 amu because the polar water molecule sticks to the metal surfaces and desorbs over time. Water is the nemesis of vacuum scientists for this reason and most UHV experiments require that the chamber first be baked at about 200°C while pumping.

Laboratory Report

Your report should include a schematic of your experiment indicating all the chambers, pumps, valves, QMS RGA, and gas sources associated with your experiment. A look at the diagram on p. 265 in *A User's Guide to Vacuum Technology* by O'Hanlon *may* help. The book should be provided. Your report should make clear how gas molecules are flowing through your machine. Do you know how a turbo pump and/or a rotary pump work? Do you know what pressure ranges they are good for? For these pressure ranges, please know the mean free path of a molecule. When we get to very low pressures, we don't usually say "air", we say "molecules"… why is that? See Appendix A for details. You should also be prepared to describe how a thermocouple gauge works, and how a Bayard-Alpert ionization gauge works. The thermocouple gauge can only measure pressures greater than $6x10^{-4}$ Torr, which is likely the highest pressure that the QMS RGA can handle. So if you see the pressure go up to $7x10^{-4}$ Torr, please turn off the RGA

until the pressure drops back below 7×10^{-4} Torr again. Also, please provide a brief description and drawing of the mass spectrometer (manual chapter 3 may be helpful).

3) Basic Activities (Try to do on Day 1)

You will take the following samples: Background from the vacuum chamber under high vacuum, atmospheric air, Neon, Krypton, and Nitrogen. You can do Helium and Argon if you like. It is a good idea to save each scan and also save a background scan between each measurement. Start with a background vacuum measurement.

Do *not* turn on the mass spectrometer until you've proved to the satisfaction of your lab instructor that (a) you can identify the pieces of the vacuum system (i.e., the pg. 265 figure) and explain how the vacuum system functions; (b) you can point out the vacuum gauges and the readout for each, say what kind they are, explain how they work, and explain the units in which vacuum pressure is measured; (c) you can explain what a mass spectrometer is and what is does.

Do *not* use the gas-dosing system until you've explained to your instructor how you are going to do it, while making sure that the pressure in the feed lines never gets much over atmospheric pressure – that is, please know how the regulators on the gas canisters work. There is a T-shaped brass union combining gas lines from two places, the pump (to pump things out and away), and a long piece of rubber tubing that you can attach to a gas source (like one of the gas canisters). You will need to clean out the dosing line in order to does a pure sample. Does this procedure make sense?

1) Connect the long hose to the new system you wish to introduce. Make sure that the pressure in this line is only a few PSI greater than atmospheric pressure. Keep in mind that the round gauge on the "dosing line" measures "gauge pressure" or pressure relative to atmospheric pressure (about 14.7 PSI). That is, a measurement of 1 PSI means a pressure of 15.7 PSI.
2) Close the valve to the new gas source and open the valve to the pump and pump down the dosing manifold.
3) Close the valve to the vacuum pump.
4) Open the valve to the gas sample.
5) Repeat 2-4 two or three times to purge the line of all impurities. Every time you open the valve to the pump, you'll notice it makes a little noise and kicks out a little "smoke" which is just some of the vacuum pump oil being kicked out with the pumped gas. This will happen **a lot** if you pump on the line while the other end is open to your gas source, wasting precious gas and filling the air with backing pump oil – so please don't do this.
6) Leave the line under pressure slightly greater than atmosphere and then you can open the needle valve with the mechanical readout to let gas into the vacuum chamber.

The needle valve is "closed" at 0005, so please don't close it any further. Also, please open the valve slowly paying attention that the pressure in the vacuum chamber does not exceed 10^{-5} Torr.

Conduct an analysis of the introduced gas samples making sure you do the following:
1) Provide a scan in your write up identifying each peak.

2) Do a background subtraction for the interesting peaks.   You can do this yourself, or you can do it automatically as described on pgs. 5-17 of the manual.
3) For atmosphere, are the ratios of gasses what you expect? Are there "interesting" peaks that are not what you expect.
4) Calculate (from tables or otherwise) what energy an electron would need to singly, doubly, triply ionize each of your introduced samples. Do you know what the energy of the bombarding electron is? What ionization states do you predict are possible?
5) For the introduced samples, look for peaks at half the expected value, a third the expected value and one 4th of the expected value. What are the ratios of these peaks to those of the peak at the expected mass value?
6) How is the spectrum of nitrogen different from those of the noble gasses? Why is this?
7) Compare the relative populations of krypton isotopes with that of naturally occurring krypton. Why should (or shouldn't) the QMS measurements of relative populations of isotopes be correct?

4) Creative Activity (Day 2)
- If you introduce a solution, like a milkshake or Pepsi, you'll find that the signal will be indistinguishable from water… why? So this may not be a good exercise.
- If you introduce some vapors that require heating, such as heating a heavy oil or wax, you'll find that the substance will begin condensing further down the dosing line where the temperature is lower. In winter of 2014, we had condensate in the needle valve that shut the needle valve down until we heated the valve and pumped on it from both sides while we opened it much higher than usual. Let's not do this again.
- Make your analysis as quantitative as possible. What are the ratios of different peaks (after you've subtracted background)? What is the ratio you would expect from the sample you've introduced into the chamber?

You are encouraged to be creative and design your own experiment. This will require some time *before* you enter the lab on the second day. **Please plan this beforehand.**

Here are some possibilities to think about:
1. Measure the "cracking patterns" of larger volatile molecules. Identify all the peaks and try to explain where they come from.
2. Look for "trace" elements or isotopes of low abundance. The mass spectrometer has a large dynamics range, and putting it on a log scale allows you to see many very weak peaks that aren't visible on a linear scale.
3. Take a look at the manual and identify the Focus Voltage and the electron ionization potential. Find out how to change these voltages manually. As you change them, what happens? Why? Is the signal to noise optimized with the present configuration? For which samples is it optimized best? Please leave the system in the same configuration as it was when you arrived!
4. Investigate a process like combustion. All you need is a lighter (what's in the lighter?) or alcohol. What is created when it is burned? What are the ratios? What "should" the ratios of combustion products be? Please do this without burning down the lab.
5. Respiration is also a combustion process – see 4 above.
     These are just some examples of what you could do. It's great if you come up with your own experiment, but again please plan ahead.

Appendix A

I remember from graduate school that, at 10^{-6} Torr the mean free path of a molecule is about a meter (which is wrong) and surfaces are exposed to a monolayer in one second (which is correct). This means on average, every atom of the surface is struck by an air molecule each second. Let's see if these two approximations are reasonable. What do we know?

$$m_{nitrogen} = 28 \text{ g/mole}$$

$$\rho_{liquid\_nitrogen} = 807 \text{ kg/m}^3 = 1.74 \times 10^{28}/\text{m}^3$$

$$\rho_{air\_at\_STP} = 1.3 \text{ kg/m}^3 = 2.80 \times 10^{25}/\text{m}^3$$

$$\rho_{air\_at\_microTorr} = 3.7 \times 10^{16}/\text{m}^3$$

$$P_{atmosphere} = 760 \text{ Torr}$$

$$\rho = (\lambda \sigma)^{-1}$$

Where ρ is density, λ is the mean free path, and σ is the collision cross section. We can estimate the intermolecular distance of liquid nitrogen to be about 3.9 angstroms and therefore the collision cross section should be about $\pi r^2 = 4.7 \times 10^{-19}$ m^2. Using the last of the above equations, we can estimate the mean free path for an atmospheric air molecule to be about 7.6 nm. As mean free path is inversely proportional to pressure, we extrapolate the mean free path at 10^{-6} Torr to be about 58 m, so the life of a molecule in high vacuum is even more ballistic than I had imagined. It is important to know that for this calculation, we used the "hard wall Fermi repulsion" caused by the overlapping of the electron orbitals. However, the Van der Waals attractive forces extend much further, and while they are not strong enough to reflect a molecule at high angles, this weaker attraction may be sufficient to change the trajectory of the ion in the quadrupole filter enough for the ion to not be detected. So it may be necessary to have pressures well below 10^{-4} T in order for the majority of the molecules to pass through the quadrupole filter without a de-confining "collision."

We can find the surface density of liquid nitrogen molecules on the liquid surface to be the bulk density to the (2/3) power. Dividing this by the density of nitrogen at 10^{-6} Torr, we find that the average molecule must travel about 180 meters before hitting the surface. The atoms are traveling at the speed of sound, 340 m/s, but we only use the z component by dividing by $\sqrt{3}$. We find that it should take about a second for the average molecule at 10^{-6} Torr to strike the surface.