1. In one of the NMR instruments I have worked with, protons with a magnetogyric ratio $2.6752 \times 10^8 \text{T}^{-1} \text{sec}^{-1}$ had a Larmor precession frequency of 400 MHz. What was the magnetic field strength of this NMR’s magnet (in Tesla)?

$$\omega = \frac{\gamma B_0}{2\pi}$$

$$400,000,000 = \frac{2.6752 \times 10^8 B_0}{2\pi}$$

$$B_0 = \frac{2\pi(400,000,000)}{2.6752 \times 10^8}$$

$$= 9.3947 \text{Tesla}$$

2. In an NMR spectrum, what is meant by Chemical Shift? What is meant by coupling? What are the physical processes that cause these two effects? When you examine NMR spectra from instruments with different magnetic fields, why is the coupling measured in Hertz, and the chemical shift measured in ppm?

   Chemical shift is the overall frequency of a resonance peak, and it is physically based on how the given nucleus is shielded or deshielded from the overall magnetic field by the electrons around the nucleus. The coupling, or spin-spin coupling is a splitting that occurs at a given resonance peak due to the magnetic field of nearby nuclei. The magnetic field of these nearby nuclei is relayed to the to increase or decrease to the local magnetic field by interactions of electrons around the nuclei.

   The frequency that a given peak resonates at is directly proportional to the external magnetic field. The chemical shift scale, in ppm, is proportional to the external field so that peaks with the same chemical shift always appear at the same ppm value on different magnets with different field strengths. Coupling is measured in Hz because is an interaction energy, and energy is directly proportional to frequency, and the coupling will have the same energy or frequency no matter what the size of the external magnetic field.
3. Predict the appearance of the proton spectrum of the compound \( \text{CH}_3\text{-O-CH}_2\text{-CH}_3 \). Give a rough idea of what the chemical shift for each group should be, the spin-spin coupling patterns that should be seen, and what the integral of the spectrum should look like.

Let's do this with a color code

\[ \text{CH}_3\text{-O-CH}_2\text{-CH}_3 \]

The Blue \( \text{CH}_3 \) is the furthest from the O so it will be the most shielded and the furthest upfield, I would guess about 1 ppm.

The Green and Red protons are close to the oxygen so they will be deshielded and shifted downfield, probably about 4 ppm. I would put the \( \text{CH}_3 \) slightly upfield from the \( \text{CH}_2 \) because the extra proton would give it slightly better shielding.

The Red \( \text{CH}_3 \) should be a single peak because it will not be coupled to the other protons. The Green \( \text{CH}_2 \) should be split into a 4-plet due to the blue \( \text{CH}_3 \), and the blue \( \text{CH}_3 \) should be split into a triplet due to the green \( \text{CH}_2 \).

If the integral of the red \( \text{CH}_3 \) is set to 3, the integral over the green \( \text{CH}_2 \) 4plet will be 2, and the integral of the blue \( \text{CH}_3 \) triplet will be 3.

Sorry Dr. Gabel is not around this week, so there are no electron microscopy questions.

4. Diagram and explain how electrospray ionization works.

A diagram similar to figure 20-9

A solution is pumped through the needle, and the needle is at a potential of several KV with respect to the electrode around it. This creates a spray of charged droplets. The droplets then pass through a capillary where the solvent is evaporated and the charge density on the droplet increases until the charge-charge interactions make the droplet explode into even smaller droplets. This continues until all the solvent is gone, and the charge has been transferred to the molecule of interest. The charged molecule is then accelerated into the mass spectrometer.

5. Diagram and explain how matrix assisted laser desorption works.

A diagram like Figure 20-7

A solution of the analyte and cations is adsorbed onto the surface of a matrix. Once the solvent is evaporated, the matrix/analyte/cation mix is placed in a vacuum chamber and struck with a pulse of laser light. The laser light is tuned to an absorption band of the matrix, so the laser light energy is converted into heat energy which makes the region where the light hit explode. As it explodes the molecule of interest and associated cations are released into the vacuum, where and accelerating voltage moves the charged ion into the mass spectrometer.

6. Diagram and explain how an electron impact source works.

A diagram like figure 20-3

A gas containing the molecule of interest enters a chamber. A filament above the chamber is heated and held at a potential of 70V relative to the bottom of the chamber. This makes the electrons emitted from the filament move through the chamber containing the gas sample. As these electrons move through the vapor, they have a high enough energy to remove an electron from the molecule of interest, and this results in a charged molecular ion with an extremely high energy. This high energy, and the inherent reactivity of the charged molecular ion results in the molecule fragmenting into many smaller ions. A small accelerating voltage then moves these ions into the mass spectrometer.
Take home

7. Make a ballpark estimate of how much more sensitive our new 300MHz NMR will be when compared to our current 90 MHz machine. Do this by first determining the magnetic field of these two instruments, then use this field strength to find the number of protons in the higher and lower magnetic states in each magnet so you can determine how much larger the population difference is with the higher magnetic field.

Using the equation:

\[
\frac{N_j}{N_0} = \exp\left(\frac{-\gamma \hbar B_0}{2\pi kT}\right)
\]

I used 298 for T and excel so I could put in all the constants to 5 sig figs and I got the following results:

\[
\frac{N_j}{N_0} \text{ for the 90 MHz machine } = 0.999985506 \\
\text{ for the 300 MHz machine } = 0.999952
\]

If I set \(N_0\) at 1 million then the number of molecules in the excited state \(N_j\) is:

999985.5058 (Call it 999986) for the 90 MHz

999951.7 (call it 999952) for the 300 MHz

Calculating difference in atoms in the two states as \(N_0 - N_j\) you have a population difference of:

14 for the 90

48 for the 300

48/14 = 3.4 so you should have 3.4 x better signal in the 300 because there is a 3.4 times large difference in the population between the two states.

The actual signal to noise is larger than this because there are other factors that are not properly taken into account in this simple model.

8A. The ion-accelerating voltage in a particular quadrupole mass spectrometer is 5.00V. How long will it takes a singly charged benzene ion to travel the 15.0 cm length of the rod assembly? Assume that the initial velocity of the ion in the z direction is zero.

Kinetic Energy = zeV = \(1/2 \cdot mv^2\)

z e V = 1/2 m v^2

\(v = \sqrt{2 \cdot zeV/m}\)

z = 1

e = charge on electron = 1.6x10\(^{-19}\)

V = 5

m = mass of ion in kg = \((6(12.01) + 6(1.008))/1000)6.022\times10^{23} = 1.3\times10^{-25}\)

\(v = 3515 \text{ m/sec}\)

Drift time = \(L/v = 0.15/3515\text{ m/s}\)

= 4.27\times10^{-5} \text{ sec}

= 42.7 \mu\text{sec}\)
8B. Contrast this to a Time of Flight mass analyzer. Assume the length of a drift tube is 1 meter, the accelerating voltage is 5000V and you are analyzing a singly charged protein molecule with a molar mass of 10,000. Explain why there is such a large difference in accelerating voltages in TOF and Quad mass spectrometers.

\[
\text{Kinetic Energy} = zeV = \frac{1}{2} mv^2 \\
z eV = \frac{1}{2} m v^2 \\
v = \sqrt{2 zeV/m} \\
z = 1 \\
e = \text{charge on electron} = 1.6 \times 10^{-19} \\
V = 5000 \\
m = \text{mass of ion in kg} = \frac{10,000}{1000} \times 6.022 \times 10^{23} \\
\quad = 1.66 \times 10^{-23} \\
\]

\[
v = 9823 \text{ m/sec} \\
\text{Drift time} = \frac{L}{v} = \frac{1.0}{9823} \text{m/sec} \\
\quad = 1.02 \times 10^{-4} \text{ sec} \\
\quad = 101 \mu\text{sec}
\]