

Chem 434 Hour Exam III

All questions worth 14 points, you may skip 1 question

1. Compare an EI source with a CI source for molecular mass spectrometry. In this comparison include a rough sketch of the ionization chamber, a brief description of the ionization process, and a comparison of the resulting ions obtained.

EI

Diagram similar to Figure 20-3 of text.

Electrons emitted from source accelerated through 70V potential. Compartment has molecular gas at $\sim 10^{-5}$ torr. As electrons stream past gas molecules, electrons are knocked free from molecule. This weakens bonds in the molecule and the molecule fragments in many different ways, so you end up with many fragments and few molecular ions

CI

Diagram looks the same. Electron potential the same. Main difference is that chamber has CH_4 gas @ 1 torr. Under these conditions it is the CH_4 that gets ionized to CH_4^+ , and CH_3^+ . These then collided with other methanes to produce CH_5^+ , C_2H_5^+ . These, in turn, will collide with the molecule you want to analyze to make primarily MH_2^+ and M^+ ions so you observe $(\text{M}+1)^+$ and $(\text{M}-1)^+$ ions.

2. Give a brief description of Electrospray ionization and MALDI ionization sources for mass spectrometry.

Electrospray would have a diagram like Figure 20-8 of text. Used in HPLC/MS.

Solution is sprayed out of a needle that is held at several 1000's of volts potential. This potential makes positively charged molecules cluster in the droplets shooting out of the needle. As the droplets pass through a drying gas and then into a vacuum chamber, the solvent evaporates and the positive charges are transferred to the molecules to make $\text{M}+1$, $\text{M}+2$, ... $\text{M}+n$ ions. No fragmentation.

MALDI (Matrix Assisted Laser Desorption/Ionization) The molecule-of-interest is dissolved in a aqueous solution with a large excess of a second compound, called the matrix, that will be used to absorb laser light. Drops of this solution are then allowed to evaporate on a target material. The target is then placed in a Time of Flight Mass Spectrometer, and a beam of laser light is shot at the target for a brief pulse. During this light pulse, the matrix absorbs the light and is instantly vaporized. In this process the molecule-of-interest is also blasted into the gas phase and is given a positive charge. A potential is used to move these ions into the Spectrometer with a set kinetic energy.

3. Explain how a quadrupolar mass spectrometer works. How does it compare to a time of flight mass spectrometer

Diagram for a Quadrupolar mass spec looks similar to Figure 11-4 of your text. One set of rods on opposite sides is +, other set of rods is negative. During a scan the DC potential of rods is ramped up as well as an additional AC variation. One set of poles acts as a high pass filter allowing only ions above a certain mass pass through the quadrupole chamber. The other set of poles acts as a low mass filter only allowing ions below a certain mass through the chamber. The net effect is that at a certain DC and AC setting only 1 mass can pass through the chamber. During a scan the DC and AC settings are changed so only certain masses can reach the mass detector at the end of a chamber, and a computer keeps track of how many ions of each mass are detected during the scan. Each scan takes a fraction of a second, so the Quadrupolar mass spectrometer can operate continuously.

In a time-of-flight spectrometer, ions are released into the gas phase in a single burst (usually when a laser light beam blasts molecules off of a matrix) and are accelerated into a vacuum chamber at a constant voltage, so they all have the same kinetic energy. Since they have the same kinetic energy it takes the large molecules longer to travel through the vacuum chamber than the smaller molecules. So by simply measuring the 'time-of-flight' one has a direct measure of the ionic mass. Since all ions must be released at a given time, this machine cannot operate continuously

4A. What are the names, values, and physical meaning of the quantum numbers associated with electron orbitals.

Principle Quantum number (n) Integers >0 , Energy or size of orbital

Angular Momentum Number (l) Integers between 0 and $n-1$ shape

Magnetic Quantum Number (m_l) integers between $-l$ and $+l$, orientation

Electron Spin Quantum Number (m_s) $+1/2$ or $-1/2$

4B. What are the names, values, and physical meaning of the quantum numbers associated with the nucleus.

Nuclear Spin Quantum Number (I) Integers or $1/2$ integers

Magnetic Quantum Number (m) integers between $-I$ to $+I$

4C. What do nuclear quantum numbers have to do our ability to obtain an NMR spectrum for a given atom.

If $I=0$, no net spin in nucleus, so no NMR signal

If $I=1/2$, only 2 m states, so simple NMR

If $I \neq 0$ or $1/2$, multiple m states, so complex NMR

5. A hypothetical intermediate in the chemical ionization of C_2H_6 might be $C_2H_7^+$. Now intermediates like this only exist transiently within the CI ionization chamber, but suppose there was some way you could pull out the $C_2H_7^+$ ion and put it into an NMR. What would the NMR spectrum look like? What is what chemical shift would you expect for the CH_3 group and the CH_4^+ group, and why? What coupling pattern would you see on the CH_4^+ peak due to coupling with the CH_3 protons (give both number of peaks and relative intensities)? What coupling pattern would you expect to see on the CH_3 peak due to the CH_4^+ protons (give both number of peaks and relative intensities)?

I would expect the CH_4^+ signal to be even higher upfield than the CH_3 signal because of the extra electron. Like any signal adjacent to a CH_3 , the CH_4^+ signal should be split into a 4-plet with ratio 1:3:3:1. The CH_3 signal will be split into 5 peaks (4+1) and the ratio of the peaks will be 1:4:6:4:1 $(X+1)^4$

6. Make a rough diagram and label the key components of a superconducting NMR magnet.

Inner chamber a coil of Niobium/tin or niobium/titanium wire

(Class notes had this mistakenly as Ni, so I accepted this)

Cooled to 4K with liquid Helium

Outer chamber Liquid N_2 (takes to $\sim -75^\circ C$)

Take home questions

7. If you were doing a mass spectrum of CBr_2H_2 , the molecular ion would be CBr_2H_2^+ . Predict the masses of all the possible isotope peaks associated with this molecular ion, and calculate the relative intensity of each peak..

Calculations done on spreadsheet, isotopes with populations of <1% were ignored

172	173	174	175	176	177
0.252225	0.002774475	0.494361062		0.242237	0.002665
51		100		49	

8. In class I showed that at room temperature with our 2.11 Tesla NMR magnet there are about 999,986 protons in the excited state for every 1,000,000 protons in the ground state for a difference of 14 in 1,000,000. How many protons are in the excited state at the same temperature in a 7.05 Tesla magnet. What is the difference in population now? Since the NMR signal is proportional to this population difference, How much better is the signal in this higher field NMR?

$$\Delta E = \gamma h B_0 / 2\pi$$

$$\text{for 2.11 Tesla mag} = 2.11 \times 6.626 \times 10^{-34} \times 2.67 \times 10^8 / 2(3.1415) = 5.94 \times 10^{-26} \text{ J}$$

$$\text{for 7.05 Tesla mag} = 7.05 \times 6.626 \times 10^{-34} \times 2.67 \times 10^8 / 2(3.1415) = 1.98 \times 10^{-25} \text{ J}$$

$$N_e / N_o = e^{-\Delta E / RT}$$

$$2.11 \text{ Tesla} = e^{-5.94 \times 10^{-26} / (1.38 \times 10^{-23}) 298} ; e^{-1.44 \times 10^{-5}} = .9999856$$

$$7.05 \text{ Tesla} = e^{-1.98 \times 10^{-25} / (1.38 \times 10^{-23}) 298} ; e^{-4.815 \times 10^{-5}} = .999952$$

Assuming 1,000,000 atoms in ground state in the 2.11 Tesla magnet there are 999,986 in excited, for a difference of 14 in 1 million

Assuming 1,000,000 atoms in ground state in the 7.05 Tesla magnet there are 999,952 in excited, for a difference of 48 in 1 million

$48/14 = 3.4 \times$ as many molecules that can be excited or $3.4 \times$ the signal

Note: The real boost in S/N comes from the peak width. On the 2.11 Tesla machine a 1 Hz wide line has a width of about .01 ppm. On the 7.05 Tesla magnet the line width is about .001 ppm, or 10 times narrower. Since the overall integral or area of the peak is the same, if the base of the peak is 10 times narrower, the height of the peak must be 10 times higher!. Thus you S/N is $3.4 \times$ better based on population and $10 \times$ better based on increased resolution, so you overall S/N is $34 \times$ better! (Plus, on a machine costing 800-900K they will use even better electronics, so the noise is even lower making the S/N even higher!)