Problem Set #1, CHEM/BCMB 4190/6190/8189

1). Which of the following statements are *True*, *False*, or *Possibly True*, for the hypothetical element X?

      a. The ground state spin is I=0 for $^{52}_{24}X$.

      b. The ground state spin is I=0 for $^{70}_{31}X$.

      c. The ground state spin is I=1/2 for $^{45}_{21}X$.

      d. The ground state spin is I=1 for $^{48}_{22}X$.

      e. The ground state spin is I=1/2 for $^{29}_{14}X$.

2). The resonance/precession frequency of a ^1H nucleus (ν_{1H}) in a 14.09 T (Tesla) magnet is 600.0 MHz.

      a. What is the resonance frequency of a ^{13}C nucleus (ν_{13C}) in the same magnet? ($\gamma_{1H} = 26.7519 \times 10^7$ rad/Ts, $\gamma_{13C} = 6.7283 \times 10^7$ rad/Ts).

      b. What is the resonance frequency of the ^1H nucleus in a 11.74 T magnet?

3). How does the magnitude of the bulk/macroscopic magnetization compare for:

      a. ^1H and ^{13}C spins?

      b. ^1H and ^{13}C spins at natural abundance (assume the natural abundance of ^1H is 100% and ^{13}C is 1.11%)?

      c. ^1H and ^{17}O spins?

      ($\gamma_{1H} = 26.7519 \times 10^7$ rad/Ts, $\gamma_{13C} = 6.7283 \times 10^7$ rad/Ts, $\gamma_{17O} = -3.6280 \times 10^7$ rad/Ts)

4).   a. How does the sensitivity of the NMR signal compare for ^1H and ^{13}C spins?

      b. For equivalent numbers of ^1H and ^{13}C nuclei, how many more scans are necessary to produce ^{13}C spectra with signal-to-noise equivalent to ^1H spectra?

5). A diagram of the Zeeman levels/states for ^1H is shown to the right.

      a. How do you determine the number of levels/states for a given nucleus?

      b. How many levels/states are there for ^{17}O?

      c. What are the magnetic quantum numbers for the ^{17}O states?

      d. How do you determine the energy of a given state?

      e. Draw the Zeeman diagram for ^{17}O.

E

m

$-1/2$ $E = +1/2\gamma\hbar B_0$

0

$+1/2$ $E = -1/2\gamma\hbar B_0$
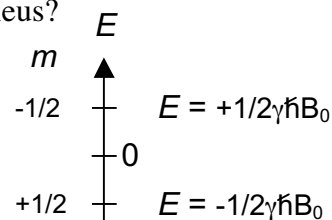
6). The frequency difference ($\Delta\nu$) between two ^1H signals in a ^1H spectrum is 3000 Hz when the spectrum is acquired with a magnetic field strength of 11.74 T (corresponding to a ^1H resonance/observe frequency of 500 MHz).

      a. What is the chemical shift difference ($\Delta\delta$) between the two signals?

      b. What would be the frequency difference between the two ^1H signals if the spectrum was acquired with a 14.09 T magnet?

      c. If the spectrum was acquired with a magnetic field strength of 14.09 T (600 MHz ^1H resonance/observe frequency), what would be the chemical shift difference?

7). The measured magnitude of $^2J_{H,H}$ for a particular AX spin system using a 500 MHz (11.74T) magnet is 4.5 Hz. What is the magnitude of this coupling using a 600 MHz (14.09T) magnet?

8). You have found that τ_ρ (pulse width/length) for a 90° ($\pi/2$) pulse for your sample is 10 μs.
   a. Sketch a bar graph of signal amplitude versus τ_ρ for your sample for τ_ρ values of 0, 5, 10, 15, 20, 25, 30, 35, and 40 μs.
   b. Explain, in general, the relationship between the transverse component of the bulk magnetization, My, τ_ρ, the pulse angle α, and the NMR signal amplitude.

9. The ^{1}H and ^{13}C NMR spectra for phenol are shown below. The chemical shifts for the ^{1}H signals are 5.4, 6.8, 6.9 and 7.25 ppm. The chemical shifts for the ^{13}C signals are 115, 121, 130, and 155 ppm. The ^{1}H and ^{13}C chemical shifts for benzene are 7.27 and 128 ppm respectively.

   a. Match the chemical shifts with the correct proton and carbon atoms:
   ^{1}H$_1$= ^{13}C$_1$=
   ^{1}H$_2$= ^{13}C$_2$=
   ^{1}H$_3$= ^{13}C$_3$=
   ^{1}H$_4$= ^{13}C$_4$=
   ^{1}H$_5$= ^{13}C$_5$=
   ^{1}H$_6$= ^{13}C$_6$=

   b. Justify your answers to 'a'. Draw resonance structures, state which nuclei are shielded or deshielded relative to one another and to benzene and why.
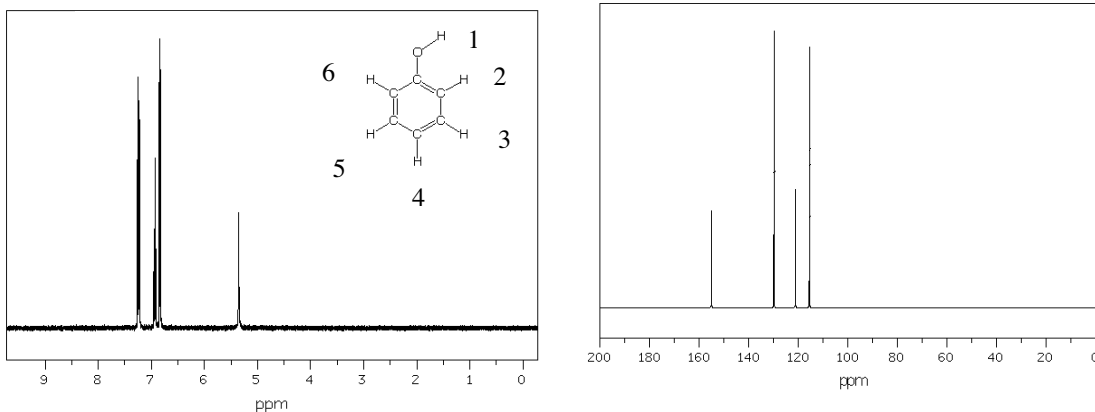
10). If the longitudinal relaxation time for a given nucleus is 10 seconds, how long after a 90° pulse will we have to wait until the magnitude of the z component of the bulk magnetization (M_z) is equal to 95% of the magnitude of the bulk magnetization before the pulse (M_0)?