CHEM*2070  Problem Set #6

1. What is the resonance frequency of a proton in a magnetic field of 14.1 T?

2. Draw an energy level diagram for a $^{43}$Ca nucleus in a magnetic field. Label the energy levels according to their m values. Also show the allowed transitions.

3. What will the resonance frequency of $^{43}$Ca be on a “600 MHz” NMR spectrometer?

4. a) Calculate the resonance frequency of an unshielded $^{199}$Hg nucleus in a magnetic field of 9.4T.
b) Now what will the frequency of a $^{199}$Hg nucleus in a molecule be if the shielding value is 1738 ppm?

5. The chemical shift of the CH$_3$ protons in acetaldehyde (ethanal) is $\delta = 2.20$ ppm and that of the CHO proton is 9.70 ppm (w.r.t. TMS). What are the frequency differences (in Hz) when the applied magnetic field is a) 1.5T and b) 18.8T?

6. I recently used a “200 MHz” spectrometer to observe $^{129}$Xe and $^{131}$Xe. At what frequencies would one find these nuclei.

7. Sketch the form of the $^1$H NMR spectrum of a natural sample of the reducing agent BH$_4^-$, allowing for the relative abundances of $^{10}$B and $^{11}$B in the sample. Also note that $^{10}$B and $^{11}$B have different I and $\gamma$ values).

8. Sketch the spectrum for an A$_3$M$_2$X$_4$ spectrum, where A, M and X are protons with distinctly different chemical shifts and $J_{AM} = 8J_{AX} = 20J_{MX}$.

9. Sketch the $^{13}$C, $^1$H and $^2$H spectra of the deuterium enriched molecule methane-d$_2$. Draw the coupling patterns to scale!

10. Use the additivity rules to predict the $^{13}$C chemical shifts for 3,5-dichloroanisole. Why would there be a problem using the additivity of chemical shifts in predicting the spectrum of 2,6-dichloroanisole?
11. The one-bond coupling $^{1}J(^{13}C, ^{1}H)$ in cyclopropane is 161 Hz. What is the hybridization of the carbons in cyclopropane? What is the predicted value of $^{1}J(^{13}C, ^{13}C)$? Account for the hybridization based on the structure of cyclopropane.

12. Consider the $^{1}H$ NMR spectrum of methanol in a solution of cyclohexane (C$_{6}$H$_{12}$). It is observed that the CH$_{3}$ chemical shift, $\delta$(CH$_{3}$), does not change much as the concentration increases, but $\delta$(OH) increases. a) explain this observation. b) how might one determine the true $\delta$(OH) value?

13. Relating hybridization to s-character:
A simple model for one-bond coupling constants, $^{1}J$, is that the magnitude of $^{1}J$ depends on the amount of electron density at the nucleus. This is called the “Fermi contact” mechanism for spin-spin coupling. Consider $^{1}J(^{13}C, ^{1}H)$, which depends on hybridization of the C atomic orbitals. Carbon 1s is not involved in hybridization, so look up the equations for the 2s and 2p orbitals (see your CHEM*2060 text book to find the radial wavefunctions). Then work out the probabilities of 2s and 2p electrons being at the nucleus. Using this information explain the relationship between $^{1}J(^{13}C, ^{1}H)$ and hybridization.

14. (optional)
Consider a fragment of a macromolecule that can be in one of two conformations shown below. Use the Karplus equation to draw the spectra of each proton (or equivalent set of protons) for each conformation. You will need the additional information that $^{2}J(H,H) = 12$ Hz.