

Chem 998 Problem Set #6: Due Friday, April 30 in class

1. Harris, Problem 2-6: Show your work.
2. Harris, Problem 2-9: Show your work.
3. Harris, Problem 2-13: Show your work.
4. The homonuclear dipole coupling between two nuclei A and B in a strong magnetic field is:

$$(\mu_0/4\pi)(\gamma_A\gamma_B\hbar/2r^3)(1-3\cos^2\theta)(3I_{Az}I_{Bz} - \mathbf{I}_A \cdot \mathbf{I}_B)$$

where  $\mu_0$  is the permeability constant,  $r$  is the internuclear distance, and  $\theta$  is the angle between the internuclear vector and the external magnetic field direction.

Rewrite this expression in terms of the  $I_{Az}$ ,  $I_{Bz}$ ,  $I_{A+}$ ,  $I_{B+}$ ,  $I_{A-}$ , and  $I_{B-}$  operators.

5. (A) Consider the NMR spectrum for the two protons of the molecule 2-chloroacrylonitrile.

$$\delta_A = 6.1 \text{ ppm}$$

$$\delta_B = 6.0 \text{ ppm}$$

$$J = 2.0 \text{ Hz}$$

Explicitly calculate the energy/h (i.e. frequency) levels and the single quantum transition frequencies for (1)  $\nu_0 = 40 \text{ MHz}$  and (2)  $\nu_0 = 400 \text{ MHz}$ . Do the calculations to 0.1 Hz precision. Qualitatively draw the NMR spectrum in each case. Assuming that NMR linewidths are independent of magnetic field strength, does one obtain better resolved (and easier to understand) spectra at lower or at higher magnetic field strength?

(B) Let us now consider sensitivity. Using  $h = 6.626 \times 10^{-34} \text{ Joule-s}$ ,  $k_B = 1.381 \times 10^{-23} \text{ Joule/K}$ , and  $T = 300 \text{ K}$ , calculate the relative Boltzmann populations of the energy levels in for:

(1)  $\nu_0 = 40 \text{ MHz}$

(2)  $\nu_0 = 400 \text{ MHz}$ .

Assign a population of 1.0 to the lowest energy level and do the calculations to the sixth decimal precision, i.e. x.xxxxxx .

(C) Just considering these relative populations, which Larmor frequency will give stronger signals? Give the relative sensitivity of 400 MHz NMR spectra to 40 MHz NMR spectra.

(D) Give the relative sensitivity of 30 K and 300 K NMR spectra.