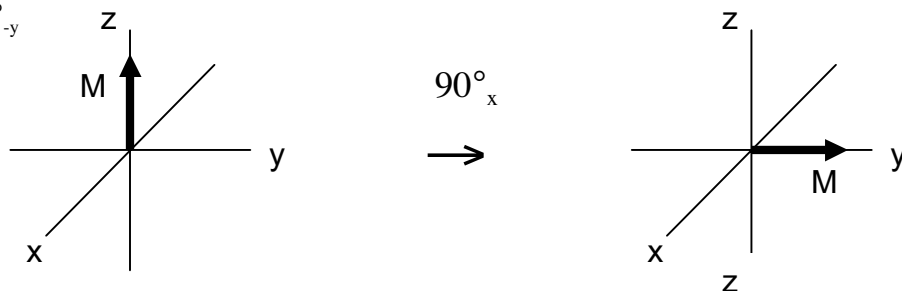
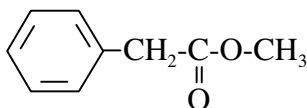


Problem Set #2, CHEM/BCMB 4190/6190/8189

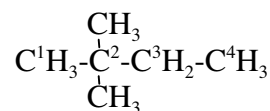
1). The effect on the bulk magnetization vector, M , of a 90° ($\pi/2$) pulse applied along the “x” axis (90°_x) is shown below. Show what effect the following pulses would have: 90°_{-x} , 90°_{-y} , 180°_y , 270°_x , 270°_{-y}



2). Using Shooley’s rule for methylene groups, predict the ^1H chemical shift for the (equivalent) methylene protons of the following compound:



3). Using the Grant and Paul incremental system for alkanes, predict the ^{13}C chemical shifts for all of the non-equivalent ^{13}C nuclei in 2,2-dimethylbutane (the actual shifts are; $\delta^{13}\text{C}^1=29.1$, $\delta^{13}\text{C}^2=30.6$, $\delta^{13}\text{C}^3=36.9$, and $\delta^{13}\text{C}^4=8.9$ ppm):

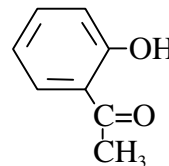
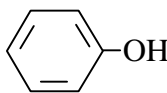


4). In a 1% solution, the chemical shift of the hydroxyl ^1H of phenol is approximately 4.37 ppm. The chemical shift increases with concentration up to 7.45 ppm at 100%. Conversely, the chemical shift of the hydroxyl ^1H of *o*-hydroxyacetophenone is very high (12.05 ppm), and is invariant with concentration.

a. Why does the chemical shift of the ^1H of the hydroxyl of phenol change with concentration, and why does the chemical shift increase when the concentration increases?

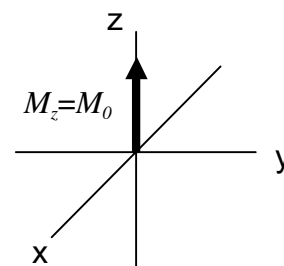
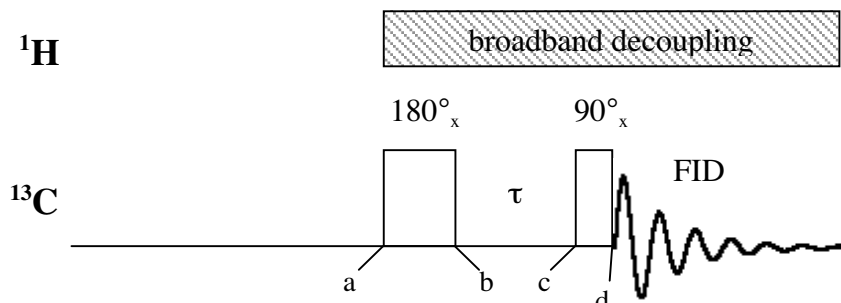
b. Why is the chemical shift of the ^1H of the hydroxyl of *o*-hydroxyacetophenone so high?

c. Why does the chemical shift of the ^1H of the hydroxyl of *o*-hydroxyacetophenone not change with concentration?



5). If the longitudinal relaxation time for a given nucleus is 10 seconds, how long after a 180° 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)?

6). The following diagram represents the pulse sequence (experiment) used to measure T_1 for ^{13}C nuclei:



- At point 'a', just before the first (180°_x) pulse, the magnitude of the longitudinal component of the bulk ^{13}C magnetization (M_z) is equal to the magnitude of the equilibrium magnetization (M_0), as shown in the vector diagram at the right. Draw similar diagrams for points 'b', 'c', and 'd' showing the effects of the pulses and delays, assuming $\tau=0.0$ seconds.
- After point 'd', if we record the FID (for $\tau=0.0$ s) and perform a Fourier transform on it, what will the resulting signal look like (sketch the signal)?
- Draw sketches of the vector diagrams at points 'c' and 'd' and the Fourier transforms of the FIDs collected after point 'd' for increasing values of τ .
- At some value of τ (see question 'c'), the magnitude of the longitudinal component of the bulk magnetization is zero ($M_z=0$) at point 'c', and the Fourier transform of the FID reveals no signal. If T_1 is 10 seconds, at what value of τ does this occur?
- You find that when τ is 10s, there is no signal at point 'd'. What is T_1 ?
- In order to measure T_1 properly, we measure the amplitude of the signal (Fourier transform of the FID) as a function of τ and fit the data to the appropriate first order equation. We should wait for a time equal to at least $5T_1$ between successive experiments in order to allow for re-equilibration of the bulk magnetization. If T_1 is 10 s, and if we wait for $5T_1$ between experiments, how complete is the re-equilibration (assume $\tau=0$, the acquisition time=0 and the 90° pulse width is also=0)?