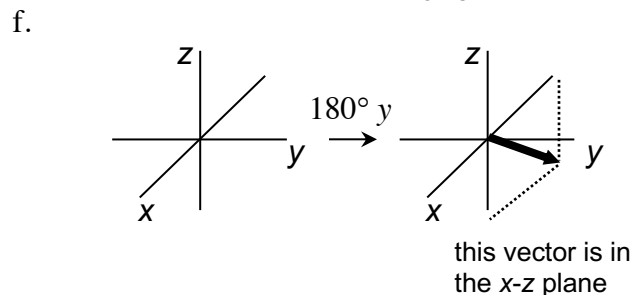
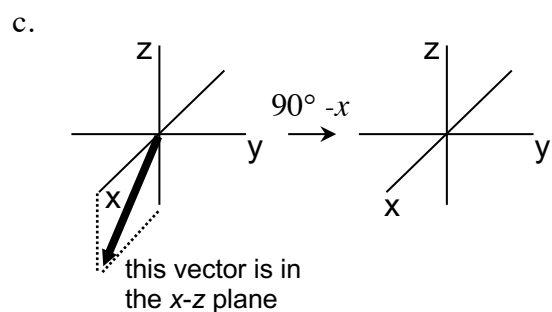
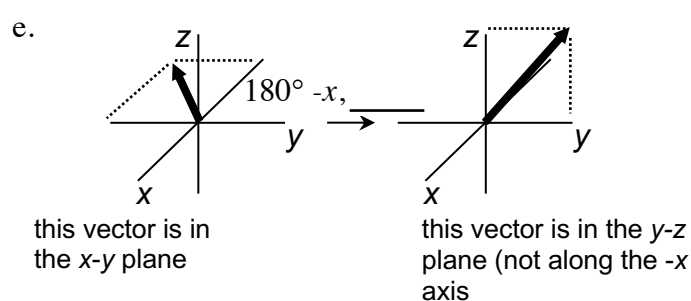
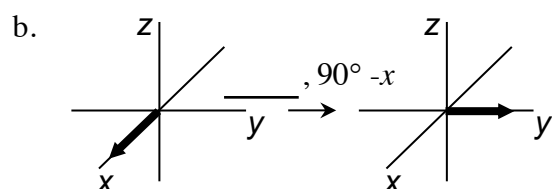
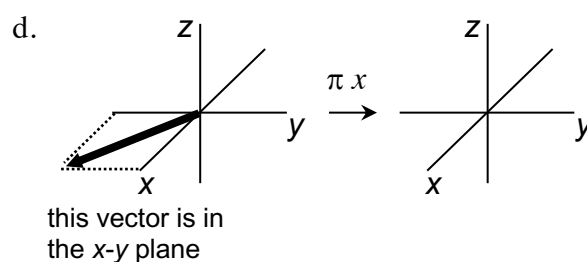
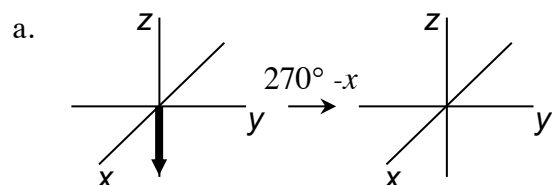
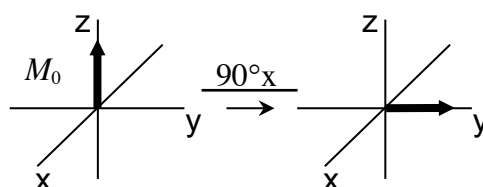


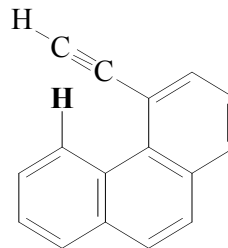
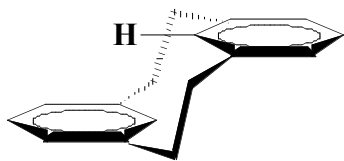
Exam 3: CHEM/BCMB 4190/6190/8189 (142 points) Thursday, 27 October, 2020

1). In the example (right), the effect of a 90° ($\pi/2$) pulse applied along the “x” axis (90°_x) is shown for a bulk magnetization vector (M_0) at equilibrium (on the ‘z’ axis). For ‘a’, ‘c’, ‘d’ and ‘f’ below, show the effects of the indicated pulses by drawing the missing (originating or resulting) vectors on the coordinate axes. For ‘b’ and ‘e’, fill in the blank with the correct pulse that will promote the indicated movement of the bulk magnetization vector (there may be more than one correct answer for some of these). Also, pulses along $+z$ or $-z$ are not permitted (**12 points**)

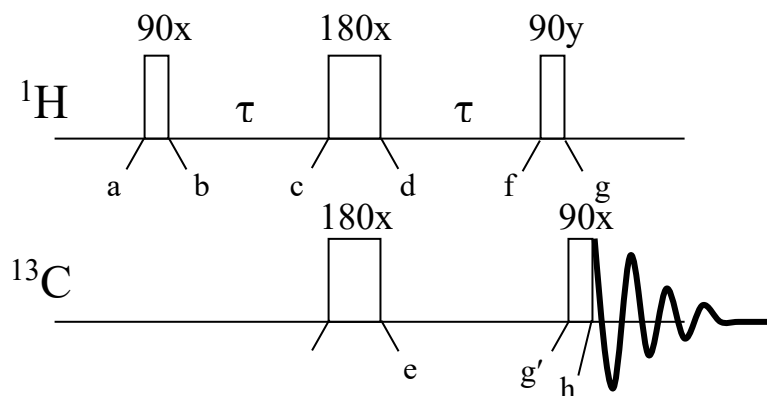


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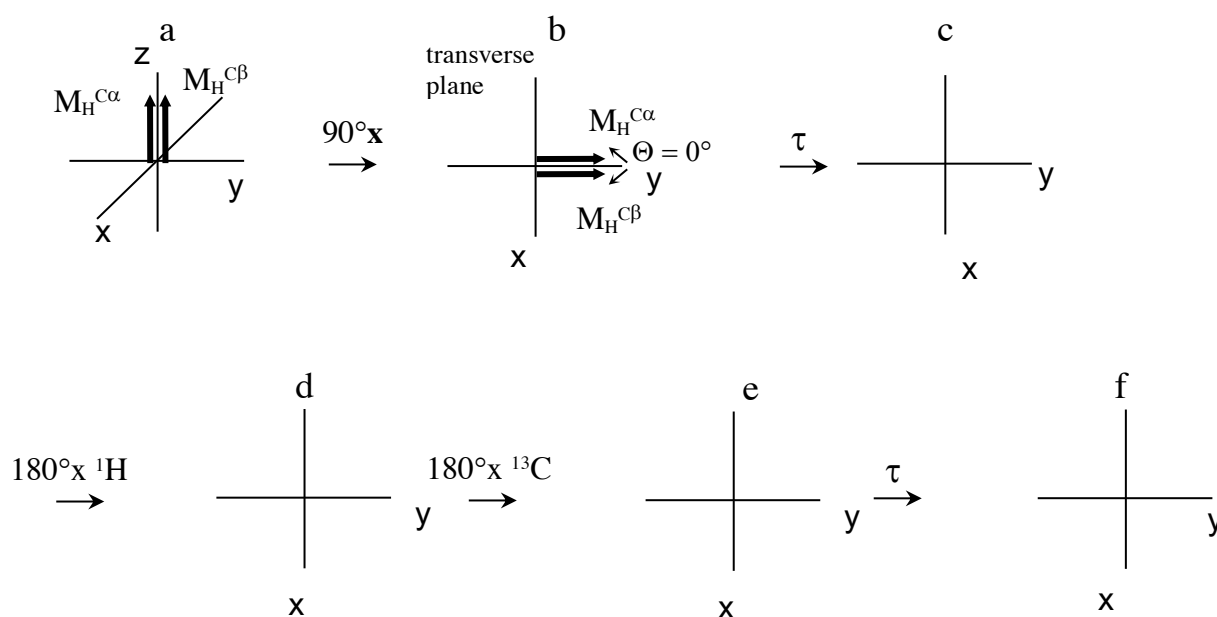
2). For benzene, the ^1H chemical shift of the hydrogens is 7.27 ppm. For ethane, ethylene, and acetylene, the ^1H chemical shifts of the hydrogens are 1.96, 5.84, and 2.88 ppm, respectively. Estimate the chemical shift of the shown (bolded) hydrogen atom in each of the two molecules shown below. You will need to thoroughly explain and justify your answers. (6 points)



3). The diagram (right) shows the INEPT pulse sequence. Consider the effect of this pulse sequence on heteronuclear (^{13}C - ^1H) J coupling, ignoring the effects of magnetic field inhomogeneity. We will consider a simple ^1H - ^{13}C - spin system (i.e. $^{13}\text{CHCl}_3$) with a Larmor frequency equal to our reference frequency, $\nu_{\text{H}} = \nu_{\text{rf}}$. We will assume that the delay τ is equal to $1/(4J_{\text{CH}})$.

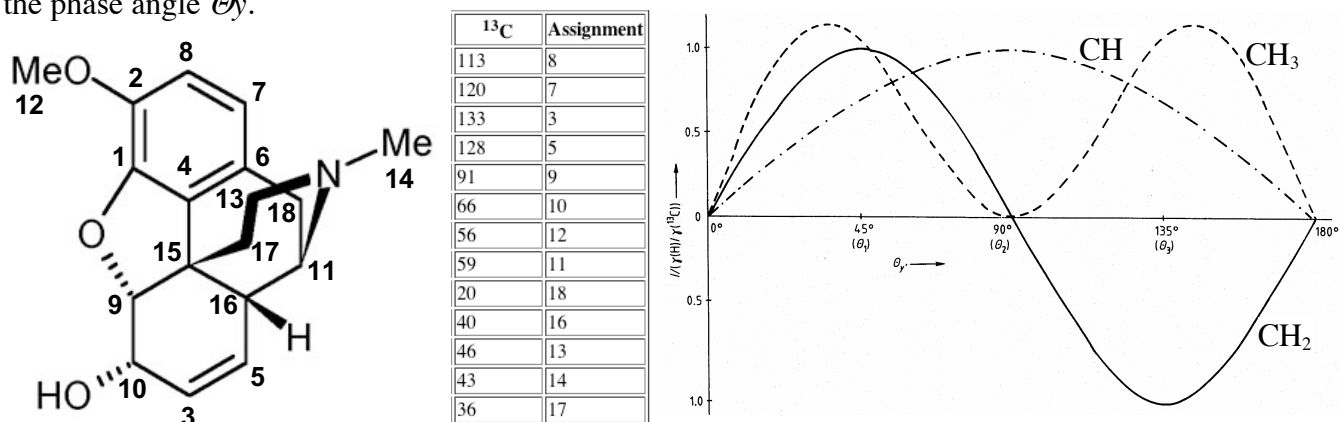


a. Complete the vector diagrams below for points 'c', 'd', 'e', and 'f' in the pulse sequence. Be sure to label the vectors ($M_{\text{H}}^{\text{C}\alpha}$, $M_{\text{H}}^{\text{C}\beta}$), to include arrows indicating the direction of precession for the vectors in the rotating frame, and to indicate the angle (Θ) between the vectors at each point. (4 points)



b. On the same vector diagrams (a-f), include the vectors for an additional ^{13}C - ^1H spin system where the ^1H nucleus has a Larmor frequency that is faster than the reference frequency (in rad/s) by an amount $5\pi J_{\text{CH}}$ ($\nu_{\text{H}_2} = 5\pi J_{\text{CH}} + \nu_{\text{rf}}$). Label the vectors ($M_{\text{H}_2}^{\text{C}\alpha}$, $M_{\text{H}_2}^{\text{C}\beta}$) to distinguish them from the others. (6 points)

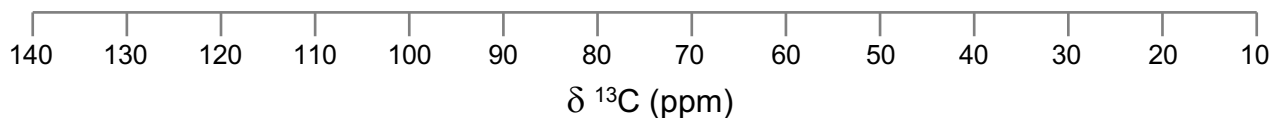
4). In the DEPT experiment, the pulse angle (θ_y , pulse width) of the third ^1H pulse (applied along the 'y' axis) can be set to any value in order to achieve the desired result. Shown in the diagram below (right) are the intensities of signals from $-\text{CH}$, $-\text{CH}_2$, $-\text{CH}_3$ groups as a function of the phase angle θ_y .



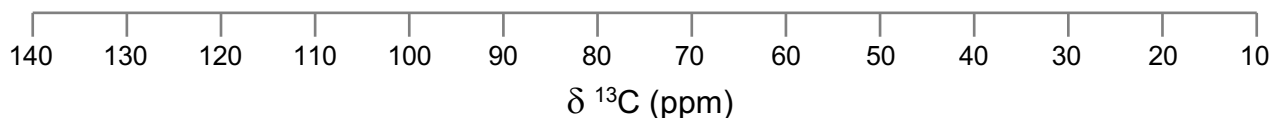
For the molecule codeine (above, left), the ^{13}C chemical shifts for thirteen of the eighteen carbon atoms are shown (above, center).

a. For the thirteen ^{13}C atoms assigned above, sketch the signals that will be observed in DEPT(90), DEPT(135), and DEPT(45)-DEPT(135) spectra below: **(12 points)**

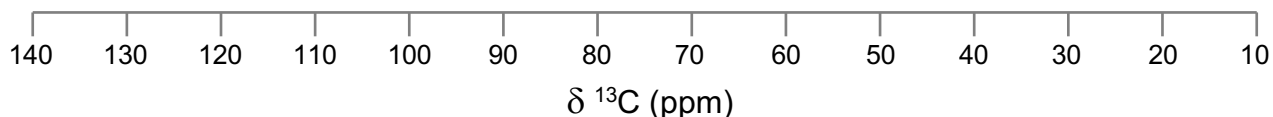
DEPT(90)



DEPT(135)



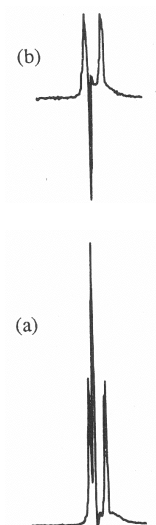
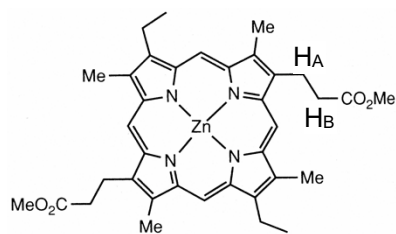
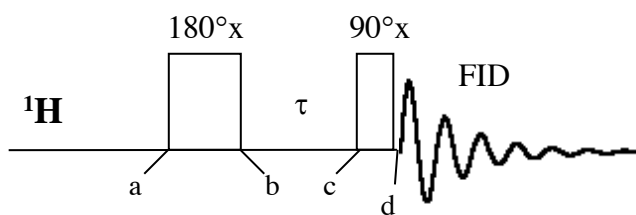
DEPT(45)-DEPT(135)



Name _____

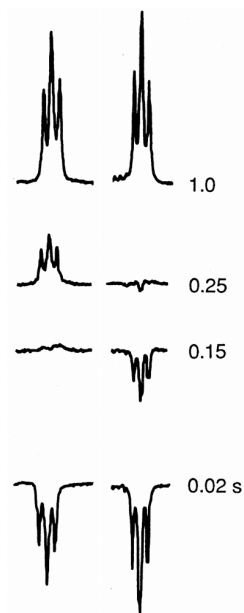
- b. Explain your reasoning, in detail, for your answers to part 'a'. **(8 points)**

5). Inversion-recovery experiments were performed on the porphyrin molecule (below) in order to measure the ^1H longitudinal relaxation time constants (T_1).



a. The methyl proton region of the ^1H spectrum of this porphyrin molecule is shown in 'a' (right, below). The same region is shown for the inversion recovery experiment with the time delay $\tau = 0.55$ s ('b', right, above). Explain thoroughly the spectra shown, including the number of signals, multiplet structures, assignment of hydrogens that give rise to the signals, and a complete rationale for your answers. (6 points)

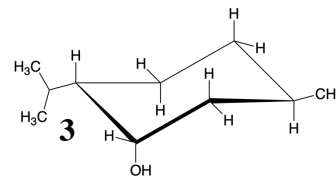
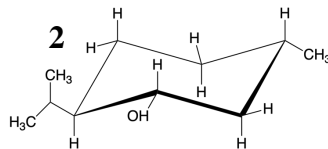
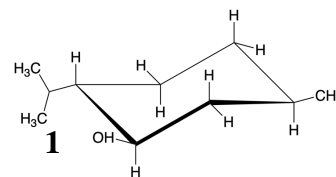
b. Methylene hydrogen regions of the spectrum from the inversion recovery experiment are shown (right) at τ delay times of 0.02, 0.15, 0.25 and 1.0 s. The two signals shown are from the methylene hydrogens H_A and H_B as indicated in the porphyrin structure shown above. The chemical shifts for the signals are unknown. Which signal is from hydrogens H_A and which is from hydrogens H_B . Please provide a detailed explanation for your assignments. **(4 points)**



c. Estimate the value of T_1 for the hydrogen that gives the signal shown on the left in part 'b'. You must do a calculation and show a result for credit. **(4 points)**

6). Shown (right) are three isomers of menthol ('1' is (-)-menthol, '2' is (+)-menthol, '3' is (+)-neomenthol). For separate samples of each isomer, simple one-dimensional ^1H NMR spectra are collected under identical conditions.

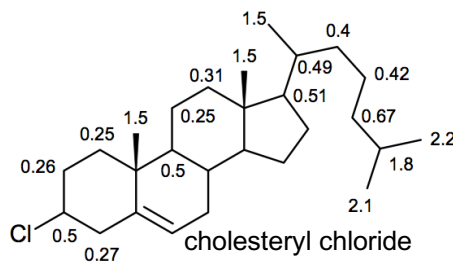
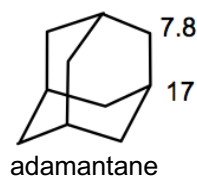
a. Using only the simple one-dimensional ^1H NMR spectra, describe how you would unambiguously distinguish between the sample containing (-)-menthol ('1') and the sample containing (+)-menthol ('2'). (6 points)



b. If you compare the simple one-dimensional ^1H NMR spectrum of the sample containing (-)-menthol and the spectrum of the sample containing (+)-neomenthol, which signals would you expect would show the most significant changes. You will have to explain for credit, and your explanation must include the origins of the changes. **(8 points)**

c. Sketch the ^1H NMR signal you would observe in a simple one-dimensional ^1H NMR spectrum for the hydrogen on the carbon bearing the hydroxyl group in (+)-neomenthol. For credit you will have to explain the multiplet structure, justify why it appears as it does, and you will have to indicate distances between peaks in the signal and coupling constants. **(8 points)**

7). The values of the ^{13}C T_1 relaxation times (seconds) are shown for nuclei in the compounds shown below.

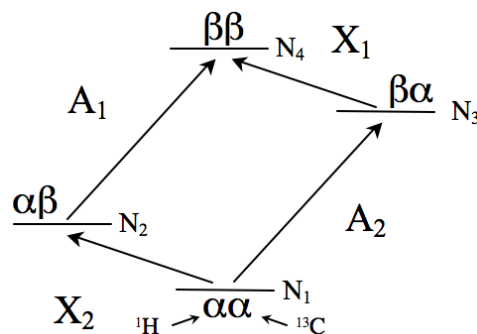


- a. In adamantane, please explain why the ^{13}C relaxation times for the adjacent nuclei are so different. Your explanation will have to address the principles underlying the differences to receive credit. **(4 points)**
- b. Please explain why, in cholesteryl chloride, the T_1 values for the methyl groups are larger than for any of the other nuclei shown. If necessary, you must reconcile this with your answer to part 'a'. Your explanation will have to address the principles underlying the differences to receive credit. **(4 points)**

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c. On the side chain of cholesteryl chloride there are two methyl groups with ^{13}C T_1 relaxation time constants (2.2 and 2.1) significantly larger than those for the other methyl groups in the molecule (1.5). Please explain why this is. Your explanation will have to address the principles underlying the differences to receive credit. **(6 points)**

8). Consider the populations N_1 , N_2 , N_3 and N_4 of the $\alpha\alpha$, $\alpha\beta$, $\beta\alpha$ and $\beta\beta$ states respectively for a ^1H - ^{13}C spin system. The energy diagram for this system is depicted (right), where A_1 and A_2 are the ^1H transitions, and X_1 and X_2 are the ^{13}C transitions. We will define ΔH as the difference in the number of spins in α and β states for ^1H , and ΔX as the difference in the number of spins in α and β states for ^{13}C .



a. Write down expressions for the equilibrium values of N_1 , N_2 , N_3 and N_4 . Assume $N_4=N$. (4 points)

b. Write down expressions for the population differences for the transitions A_1 , A_2 , X_1 and X_2 . (4 points)

c. In the SPI experiment, to enhance the signals for the ^{13}C transitions, normally either the A_1 or A_2 ^1H transition is excited. Instead, you are going to excite the X_2 ^{13}C transition and see what the effect is on the ^{13}C signals and the ^1H signals. Write down expressions for the populations N_1 , N_2 , N_3 and N_4 after exciting (180° pulse on) the X_2 transition. (4 points)

d. Now, write down expressions for the population differences for the transitions A_1 , A_2 , X_1 and X_2 (after exciting the X_2 transition). For the X transitions, the final expressions should be written in terms of ΔX , and for the A transitions the final expressions should be written in terms of ΔH . (4 points)

e. Draw vector diagrams depicting the bulk magnetization vectors corresponding to the A and X transitions before and after selective excitation of the X_2 transition. Make sure to label properly the individual vectors and indicate their magnitudes. **(4 points)**

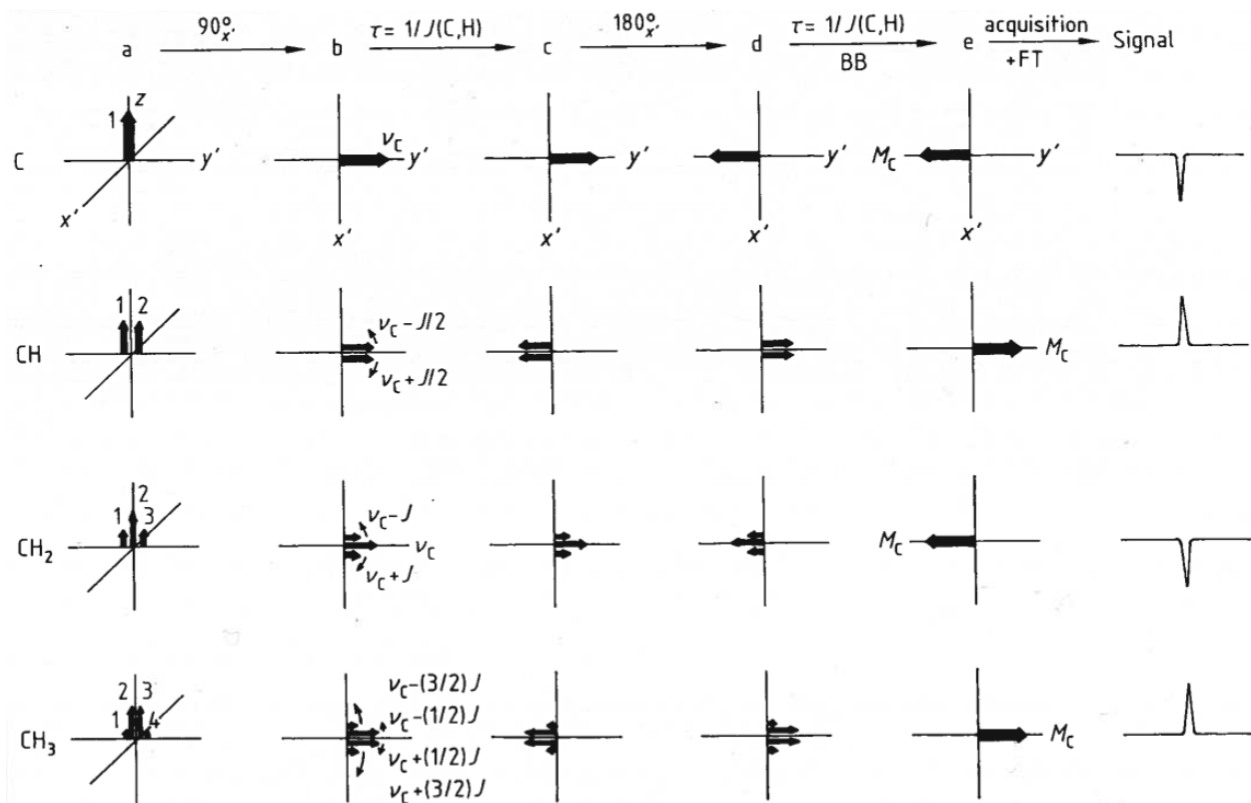
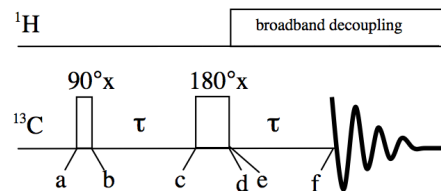
f. For the simple two spin system (^1H - ^{13}C), draw the ^1H and ^{13}C signals that you would expect in 1D ^1H and ^{13}C NMR spectra for a compound at natural isotopic abundance (for instance, CHCl_3) before and after selective excitation of the X_2 transition. Make sure to label properly the individual peaks in the spectra/signals and indicate their magnitudes. Also indicate Larmor frequencies and coupling constants. **(4 points)**

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g. Explain why you would want to excite one of the X (^{13}C) transitions in an SPI experiment? (4 points)

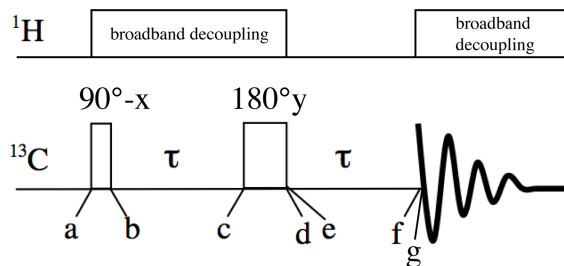
9). The spin-echo Attached Proton Test experiment (right, top) can be used to determine the number of protons attached to a given carbon atom with τ set to $1/(J_{CH})$.

Shown below are vector diagrams for each point in the spin echo pulse sequence for -C-, -CH-, -CH₂-, and -CH₃ groups using the spin-echo pulse sequence with $\tau = 1/(J_{CH})$ (in each case, the reference frequency is chosen to be equal to the Larmor frequency). Also shown is the Fourier transformation of the signal collected at point 'f' in each case.



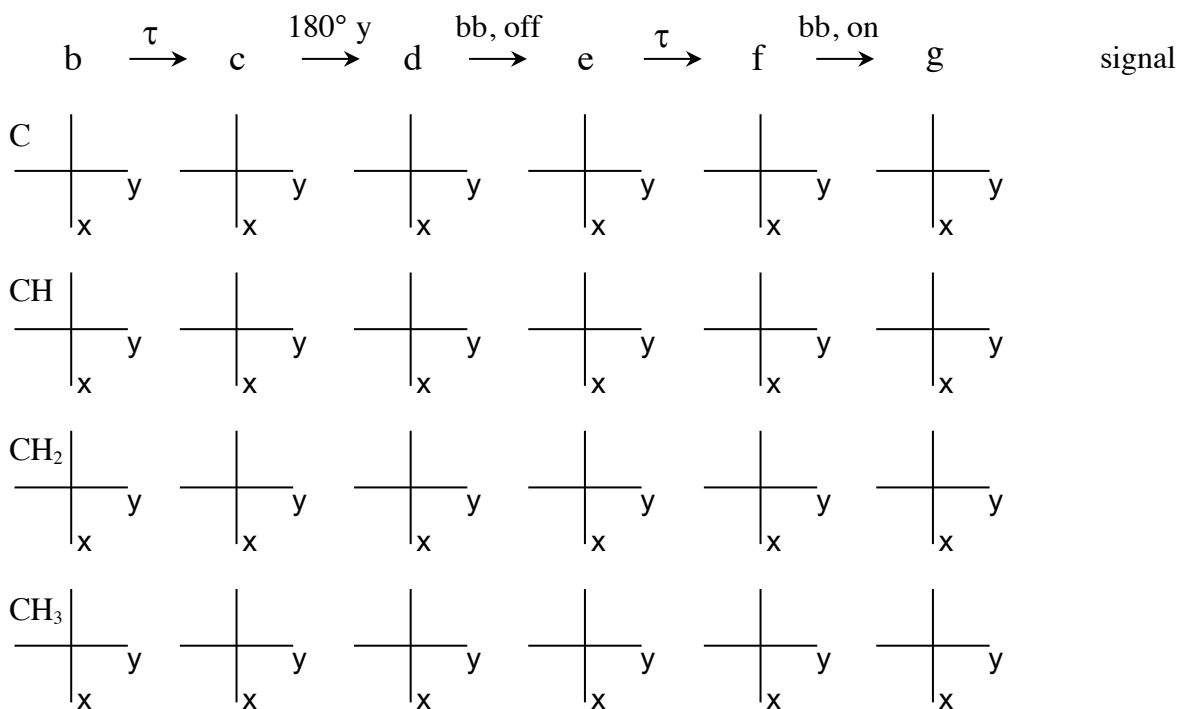
An alternate pulse sequence for the APT has been proposed (right). With τ set to $1/(J_{CH})$, it is your job to evaluate if this is a viable alternate to the pulse sequence shown above. Here, assume:

- broadband decoupling is ON at point 'a' and remains on until point 'e' (turned OFF between points 'd' and 'e')
- broadband decoupling is OFF at point 'e' through point 'f'
- broadband decoupling is ON at point 'g' (just before acquisition begins)



(Question continues on next page)

Use vector diagrams such as those shown above. Draw vector diagrams for -C, -CH, -CH₂, and -CH₃ vectors with $\tau = 1/(J_{\text{CH}})$ for each point in the alternate spin-echo/APT pulse sequence. Indicate on your diagrams the angle(s) between vector components and the direction of rotation of vector components. Also sketch the Fourier transform of the signal that you will obtain from the FID that is collected beginning at point 'g'. Then, discuss any useful differences between the two experiments. For each case, assume the Larmor frequency is equal to the reference frequency. (16 points)



Name _____

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You may find some of the information below useful:

Table 1-1.

Properties of some nuclides of importance in NMR spectroscopy.

Nuclide	Spin I	Electric quadrupole moment ^{a)} [eQ] [10^{-28} m^2]	Natural abundance) [%]	Relative sensitivity ^{b)}	Gyromagnetic ratio $\gamma^a)$ [$10^7 \text{ rad T}^{-1} \text{ s}^{-1}$]	NMR frequency [MHz] ^{b)} ($B_0 = 2.3488 \text{ T}$)
^1H	1/2	–	99.985	1.00	26.7519	100.0
^2H	1	2.87×10^{-3}	0.015	9.65×10^3	4.1066	15.351
$^3\text{H}^c)$	1/2	–	–	1.21	28.5350	106.664
^6Li	1	-6.4×10^{-4}	7.42	8.5×10^{-3}	3.9371	14.716
^{10}B	3	8.5×10^{-2}	19.58	1.99×10^{-2}	2.8747	10.746
^{11}B	3/2	4.1×10^{-2}	80.42	0.17	8.5847	32.084
^{12}C	0	–	98.9	–	–	–
^{13}C	1/2	–	1.108	1.59×10^{-2}	6.7283	25.144
^{14}N	1	1.67×10^{-2}	99.63	1.01×10^{-3}	1.9338	7.224
^{15}N	1/2	–	0.37	1.04×10^{-3}	-2.7126	10.133
^{16}O	0	–	99.96	–	–	–
^{17}O	5/2	-2.6×10^{-2}	0.037	2.91×10^{-2}	-3.6280	13.557
^{19}F	1/2	–	100	0.83	25.1815	94.077
^{23}Na	3/2	0.1	100	9.25×10^{-2}	7.0704	26.451
^{25}Mg	5/2	0.22	10.13	2.67×10^{-3}	-1.6389	6.1195
^{29}Si	1/2	–	4.70	7.84×10^{-3}	-5.3190	19.865
^{31}P	1/2	–	100	6.63×10^{-2}	10.8394	40.481
^{39}K	3/2	5.5×10^{-2}	93.1	5.08×10^{-4}	1.2499	4.667
^{43}Ca	7/2	-5.0×10^{-2}	0.145	6.40×10^{-3}	-1.8028	6.728
^{57}Fe	1/2	–	2.19	3.37×10^{-5}	0.8687	3.231
^{59}Co	7/2	0.42	100	0.28	6.3015	23.614
^{119}Sn	1/2	–	8.58	5.18×10^{-2}	-10.0318	37.272
^{133}Cs	7/2	-3.0×10^{-3}	100	4.74×10^{-2}	3.5339	13.117
^{195}Pt	1/2	–	33.8	9.94×10^{-3}	5.8383	21.499

B_0 (Tesla, T)	Resonance frequencies (MHz)	
	^1H	^{13}C
9.4	400	100.6
11.74	500	125.7
14.09	600	150.9
18.79	800	201.2

$$\gamma_{^1\text{H}} = 26.7519 \times 10^7 \text{ rad/T/s}, I = 1/2$$

$$\gamma_{^{10}\text{B}} = 2.8747 \times 10^7 \text{ rad/T/s}, I = 3$$

$$\gamma_{^{11}\text{B}} = 8.5847 \times 10^7 \text{ rad/T/s}, I = 3/2$$

$$\gamma_{^{13}\text{C}} = 6.7283 \times 10^7 \text{ rad/T/s}, I = 1/2$$

$$\gamma_{^{15}\text{N}} = -2.7126 \times 10^7 \text{ rad/T/s}, I = 1/2$$

$$\gamma_{^{17}\text{O}} = -3.6280 \times 10^7 \text{ rad/T/s}, I = 5/2$$

You may find some of the following information or equations useful:

$$k_B = 1.381 \times 10^{-23} \text{ J/K}$$

$$\text{Avagadro's number} = 6.02214179 \times 10^{23} \text{ mol}^{-1}$$

$$h = 6.626 \times 10^{-34} \text{ Js}$$

$$\hbar = h/(2\pi)$$

$$P = \hbar \sqrt{I(I+1)}$$

$$P_z = m\hbar$$

$$\mu = \gamma P = \hbar \gamma \sqrt{I(I+1)}$$

$$\text{for } m = \frac{1}{2}, \cos(\theta) = \frac{m\hbar}{\hbar \sqrt{I(I+1)}} = \frac{m}{\sqrt{I(I+1)}}$$

$$\pi/2 \text{ radians} = 90^\circ$$

$$M_0 = \frac{N\gamma^2 \hbar^2 B_0 I(I+1)}{3k_B T}$$

$$B_2 = \frac{\Delta \nu \sqrt{J^2 - J_r^2}}{J_r} = \frac{J \Delta \nu}{J_r}$$

$$\varepsilon \propto dM/dt = \gamma M_0 B = \frac{N\gamma^3 \hbar^2 B_0^2 I(I+1)}{3k_B T}$$

$$\Delta \nu = \nu_{BS} - \nu_0 = \frac{B_2^2}{2(\Delta B)} = \frac{B_2^2}{2(\nu_0 - \nu_i)}$$

$$S/N \propto NS^{1/2} \text{ (signal-to-noise improves with (number of scans)}^{1/2})$$

$$m = (-I, -I+1, \dots, I-1, I)$$

$$\Theta = \gamma B_1 \tau_p$$

$$E = -\mu_z B_0 = -m\gamma \hbar B_0$$

$$\frac{N_\beta}{N_\alpha} \approx 1 - \left(\frac{\gamma \hbar B_0}{k_B T} \right)$$

$$\Delta E = \mu_z B_0 = \gamma \hbar B_0 = h\nu_L = h\nu_1$$

$$B_{eff} = B_0(1 - \sigma)$$

$$\nu_L = |\gamma/(2\pi)| B_0 = \omega_0/(2\pi)$$

$$\nu_L = \frac{\gamma}{2\pi} (1 - \sigma) B_0$$

$$\omega_0 = \gamma B_0$$

$$\Delta \delta = \frac{\Delta \nu}{\text{observe frequency}} \times 10^6$$

$$SW = 1/(2DW) = \text{Nyquist frequency } (\nu_{NQ})/2$$

$$M_y = M_0 e^{-t/T_2^*}$$

$$AQ = DW * TD$$

$$M_z = M_0 (1 - e^{-t/T_1})$$

$$DR = 2SW/TD = 1/AQ$$

$$M_z = M_0 (1 - 2e^{-t/T_1})$$

$$(TD \equiv NP)$$

$$\Delta \nu_{1/2} = \frac{1}{\pi T_2^*}$$

$$\cos \alpha_{\text{Ernst}} = e^{-((d_1 + AQ)/T_1)}$$

$$\pi/2 \text{ radians} = 90^\circ$$

$$\frac{1}{T_2^*} = \frac{\gamma \Delta B_0}{2} + \frac{1}{T_2} \quad \frac{1}{T_2^*} = \frac{1}{T_2} + \frac{1}{T_2(B_0)}$$

$$t_{\text{zero}} = T_1 \ln(2)$$

$$1 + \gamma_A/\gamma_X \quad 1 - \gamma_A/\gamma_X$$

$$\eta = \gamma_a / (2\gamma_x)$$

$$\text{multiplicity} = 2nI + 1$$

$$I = (1 + \eta) I_0$$

$$\Theta = 2\pi J \tau$$

$$I \propto 1/r^6$$