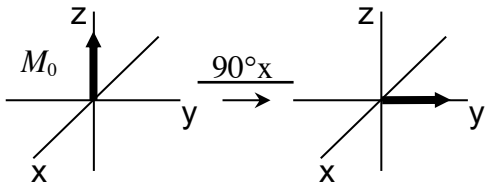
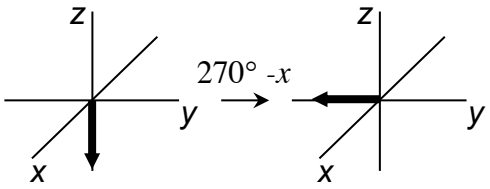
Name _____

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

1). In the example (right), the effect of a 90° (π/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)**



a.



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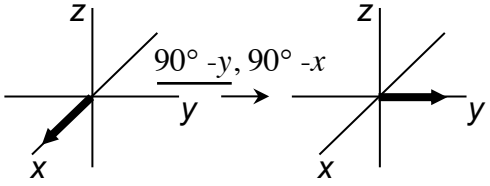

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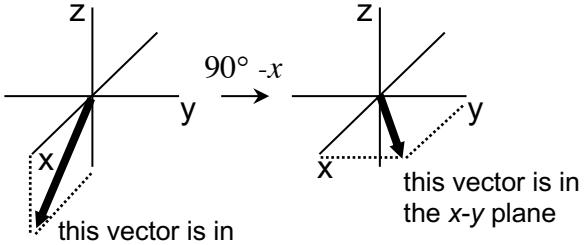
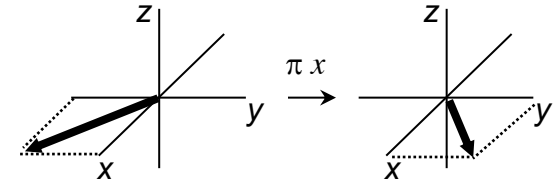


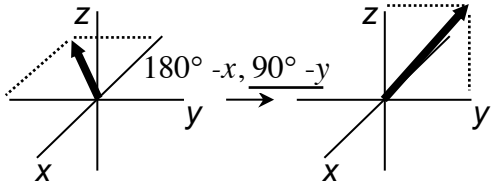
d.



this vector is in the *x-y* plane

this vector is in the *x-y* plane

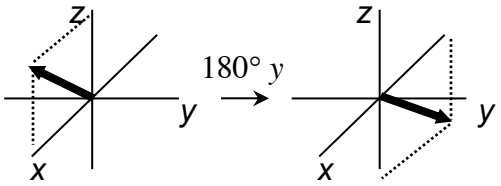
e.



this vector is in the *x-y* plane

this vector is in the *y-z* plane (not along the -*x* axis

f.



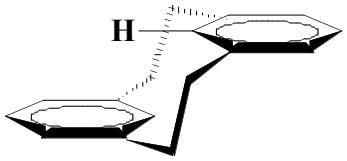
this vector is in the *x-z* plane

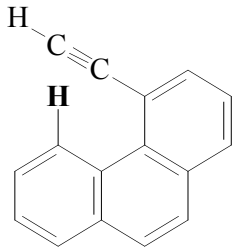
this vector is in the *x-z* plane

Note: as stated in the question, for some of these there may be more than one answer. For instance, for 'b', 270°y would be a correct answer.

Name _____

2). For benzene, the ^{1}H chemical shift of the hydrogens is 7.27 ppm. For ethane, ethylene, and acetylene, the ^{1}H 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**)

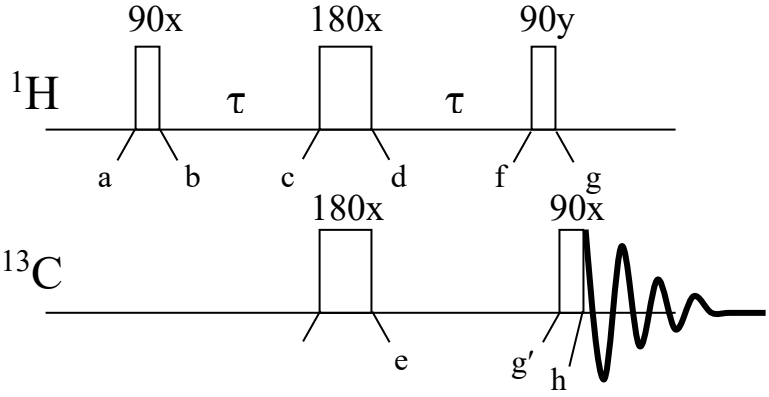




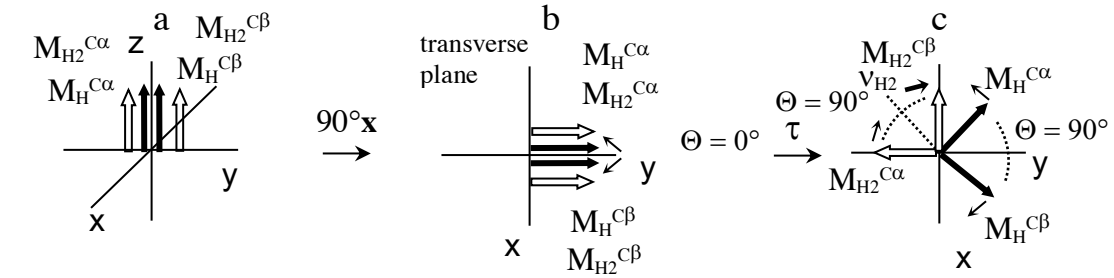
The chemical shift of the hydrogen in the molecule on the left is approximately -3 ppm. The chemical shift for a hydrogen in a benzene ring is normally about 7.27. However, this hydrogen is placed directly above the plane of a second benzene ring. The magnetic anisotropy of the benzene ring is such that above the plane is the shielding region. Thus, this hydrogen will have a substantially reduced chemical shift. The chemical shift of the hydrogen in the molecule on the right is approximately 10. In the absence of the acetylene group, its chemical shift would be about 7.27. However, this hydrogen is placed in the deshielding region of the acetylene group. Thus, the chemical shift is dramatically increased.

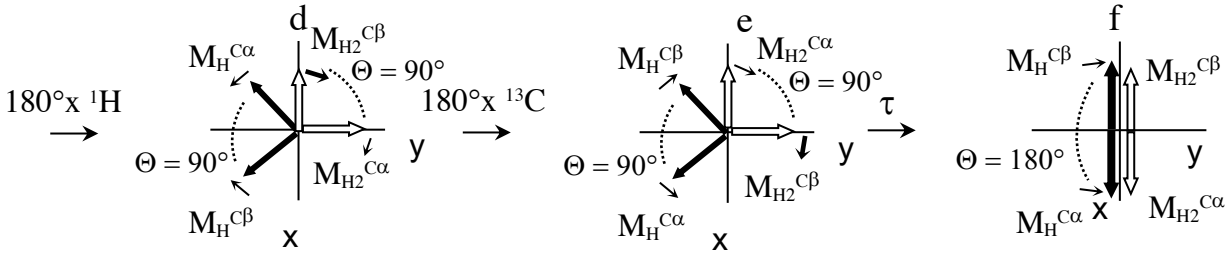
Name _____

3). The diagram (right) shows the INEPT pulse sequence. Consider the effect of this pulse sequence on heteronuclear (-^{13}C-^{1}H) *J* coupling, ignoring the effects of magnetic field inhomogeneity. We will consider a simple ^{1}H-^{13}C- spin system (i.e. $^{13}CHCl_3$) with a Larmor frequency equal to our reference frequency, $\nu_H=\nu_{rf}$. We will assume that the delay τ is equal to $1/(4J_{CH})$.



a. Complete the vector diagrams below for points 'c', 'd', 'e', and 'f' in the pulse sequence. Be sure to label the vectors ($M_H^{C\alpha}$, $M_H^{C\beta}$), 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-^{1}H spin system where the ^{1}H nucleus has a Larmor frequency that is faster than the reference frequency (in rad/s) by an amount $5\pi J_{CH}$ ($\nu_{H2} = 5\pi J_{CH} + \nu_{rf}$). Label the vectors ($M_{H2}^{C\alpha}$, $M_{H2}^{C\beta}$) to distinguish them from the others. (**6 points**)

$5\pi J_{CH}$ rad/s in $1/(4J_{CH})$ seconds is $5\pi/4$ radians. If $\pi/2$ radians is 90 degrees, then $5\pi/4$ radians is 225 degrees, which is the angle that the dashed line in 'c' (Larmor frequency for second set of vectors) traveled (clockwise) from the y-axis during $1/(4J_{CH})$.

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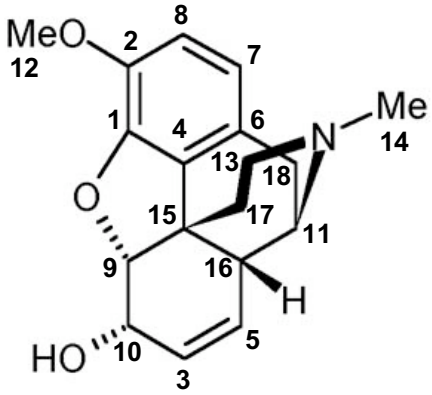
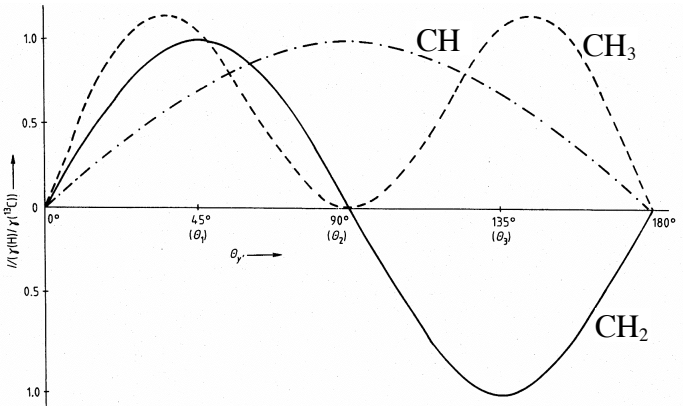
4). In the DEPT experiment, the pulse angle (*Θy*, pulse width) of the third ^{1}H pulse (applied along the '*y*' axis) can be set to any value in order to achieve the desired result. Shown in the diagram below (right) are the intensities of signals from –CH, -CH_2, -CH_3 groups as a function of the phase angle *Θy*.

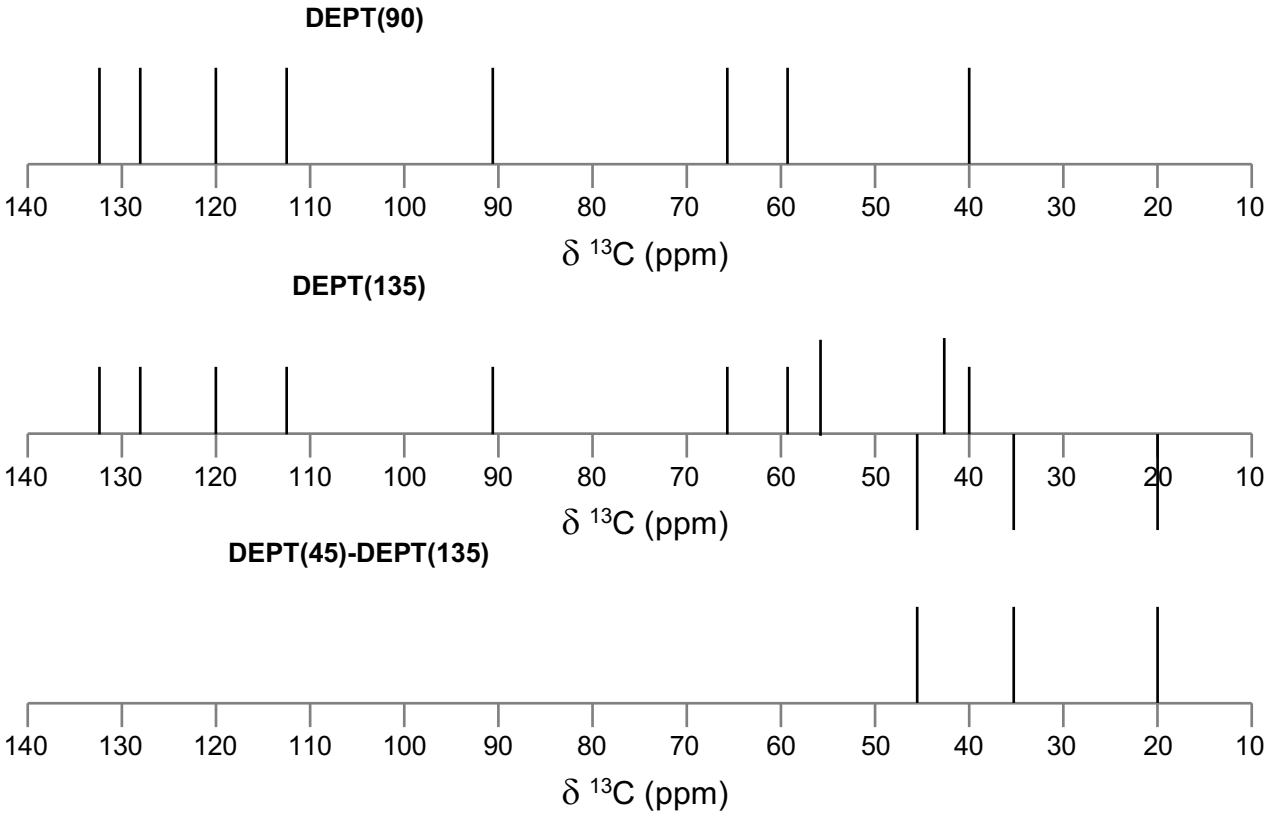


^{13}C	Assignment
113	8
120	7
133	3
128	5
91	9
66	10
56	12
59	11
20	18
40	16
46	13
43	14
36	17



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**)

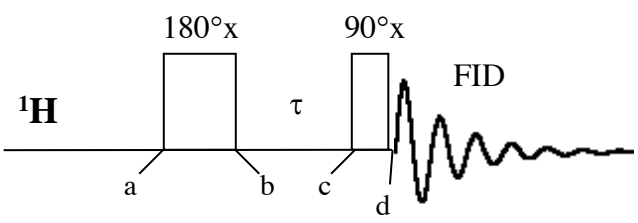


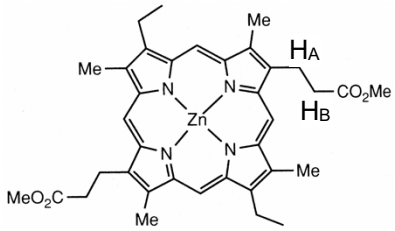
b. Explain your reasoning, in detail, for your answers to part 'a'. (**8 points**)

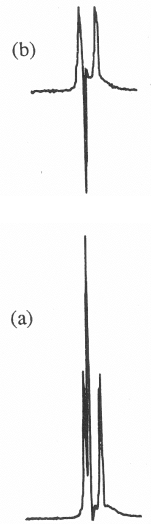
For the codeine molecule, of the assigned ^{13}C chemical shifts shown in the table, eight of these are for methine (-CH) groups, three for methylene ($-CH_2$) groups, and two for methyl ($-CH_3$) groups. For the "DEPT(90)" experiment, as shown in the plot above, when the pulse angle (Θy) is 90 degrees, no signals are observed from $-CH_2$ and $-CH_3$ groups, and positive signals are observed from -CH groups. Thus, eight signals are observed in this experiment, corresponding to the eight -CH groups, at the chemical shifts listed in the table. For the "DEPT(45)-DEPT(135)" experiment, the signal intensities from -CH and $-CH_3$ groups when Θy is 45 degrees are the same as when Θy is 135 degrees. Subtracting the signals observed when Θy is 135 degrees from the signals observed when Θy is 45 degrees leaves no signals for these groups. However, for $-CH_2$ groups, when Θy is 45 degrees the intensities are maximal with positive phase, and they are also maximal, but with negative phase, when Θy is 135 degrees. Thus, subtracting these gives very large signals for $-CH_2$ groups. Therefore, for codeine, three large signals will be observed in the "DEPT(45)-DEPT(135)" experiment from the three $-CH_2$ groups. For the "DEPT(135)" experiment, from the plot above, when Θy is 135 degrees, signals of near maximal intensity with positive phase will be observed for $-CH_3$ groups (two signals for codeine) and signals of near maximal intensity with negative phase will be observed for $-CH_2$ groups (three signals for codeine). Signals from -CH groups will also be observed (8 signals for codeine), but their intensities are attenuated (positive phase).

Name _____

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







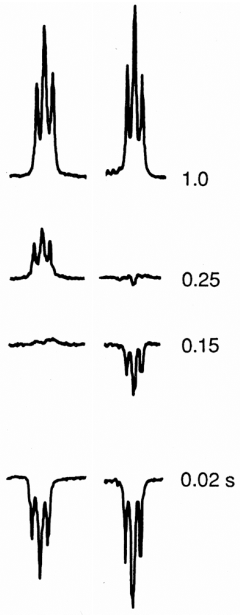
a. The methyl proton region of the ^{1}H spectrum of this porphyrin molecule is shown in 'a' (right, below). The same region is shown for the inversion recovery experiment with the time delay τ = 0.55 s ('b', right, above). Explain thoroughly the spectra shown, including the number of signals, multiplet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

There are three types of methyl groups in the molecule, each of which gives a singlet (no ^{1}H atoms 4 bonds or less away) in the ^{1}H NMR spectrum. There is one pair of equivalent ester methyl groups, and two chemically distinct (nonequivalent) pairs of methyl groups attached directly to the macrocycle. Thus, there are three methyl signals in the ^{1}H NMR spectrum, all singlets.

In the inversion-recovery spectrum, after a τ delay of 0.55 s, the signal from one pair of hydrogens is phased down relative to the other two, indicating little signal decay following the initial 180° pulse. This indicates that the T_1 relaxation time for the hydrogens on the methyl groups of this pair is substantially longer than for the other two pairs. From the porphyrin structure, it is logical to assume that the relaxation times for the two pairs of methyl groups attached directly to the macrocycle would be similar to one another. In addition, methyl hydrogens at the end of the long methyl ester side chains would be expected to be more mobile (shorter correlation time, τ_c, longer T_1) than the hydrogens of the methyl groups attached directly to the macrocycle (longer correlation time, τ_c, shorter T_1). Thus, the most upfield and the most downfield signals in the spectra are due to the methyl groups attached directly to the macrocycle, and the center signal is due to the hydrogens on the ester methyl groups.

Name _____

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**)



The hydrogens from the methylene group closest to the macrocycle (H_A) would exhibit reduced mobility (longer τ_c) relative to the hydrogens from the methylene group nearer the methyl ester end of the methyl ester side chain (H_B, shorter τ_c). Thus, the relaxation rate for H_A would be expected to be faster (smaller T_1) than the rate for H_B (larger T_1). The signal on the left shows the faster relaxation time, thus it is the signal from H_A, and the signal on the right corresponds to H_B.

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**)

In the inversion-recovery sequence, a 180° pulse on magnetization initially at equilibrium (+z) inverts the spin populations to give -z magnetization, with $M_Z = -M_0$. The 180° pulse is followed by a variable delay (τ), which is then followed by a 90° pulse to create the observable transverse magnetization. We know that, following a 180° pulse, the return of bulk magnetization along z to equilibrium ($M_Z = M_0$) is described by the following first order equation:

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

For the relaxation data shown, the magnitude of the signal on the left is near zero when the value of the delay τ is 0.15 s. So, we'll call this value of τ, when the magnitude of the signal is near zero, τ_{zero}. We then rearrange the equation to easily calculate T_1:

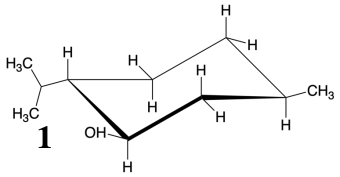
$$M_z = M_0(\,1 - 2e^{(-t/T_1)}\,) \qquad 0 = M_0(\,1 - 2e^{(-\tau_{zero}/T_1)}\,) \qquad -M_0 = -M_0 2e^{(-\tau_{zero}/T_1)}$$

$$1/2 = e^{(-\tau_{zero}/T_1)} \qquad \ln(1/2) = -\tau_{zero}/T_1 \qquad T_1 = \tau_{zero}/\ln(2)$$

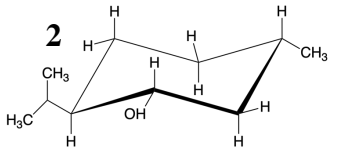
$$Thus, \quad T_1 \approx 0.15/\ln(2) = 0.216\ s$$

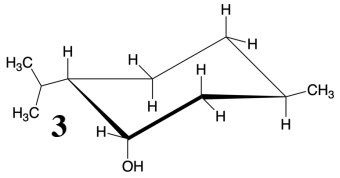
Name _____

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 ^{1}H NMR spectra are collected under identical conditions.

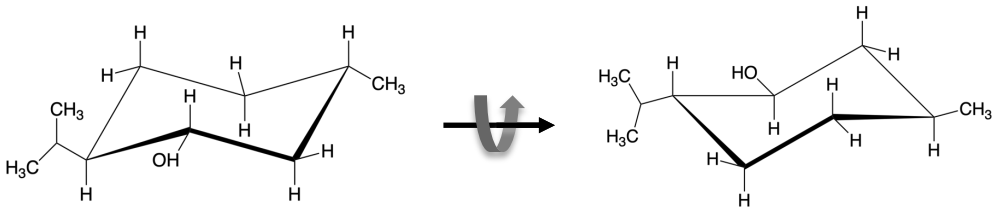


a. Using only the simple one-dimensional ^{1}H NMR spectra, describe how you would unambiguously distinguish between the sample containing (-)-menthol ('**1**') and the sample containing (+)-menthol ('**2**'). (**6 points**)





These two molecules are identical in every way except that the hydroxyl has moved to the other side of the ring. You can see this if you flip (+)-menthol 180 degrees about a horizontal axis in the plane of the page. There is no way to distinguish them based on simple one-dimensional ^{1}H NMR spectra. They are mirror image isomers.

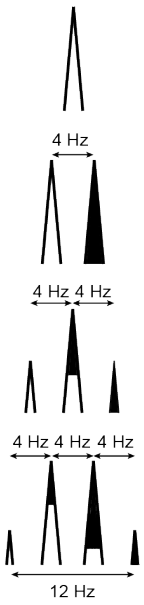


b. If you compare the simple one-dimensional ^{1}H NMR spectrum of the sample containing (-)-menthol and the spectrum of the sample containing (+)-neomenthol, which signals would you expect would show the most significant changes. You will have to explain for credit, and your explanation must include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

The signals that would show the most significant changes would be those from the hydrogen on the hydroxyl carbon, the hydrogen on the carbon bearing the isopropyl group, and the methylene hydrogens adjacent to the hydroxyl carbon. These two molecules are identical except that in (-)-menthol the hydroxyl group is equatorial and the hydrogen on the same carbon is axial, whereas in (+)-neomenthol the hydroxyl is axial and the hydrogen on the same carbon is equatorial. In (-)-menthol the hydrogen on the same carbon as the hydroxyl group is axial, and there are two adjacent axial hydrogens and one adjacent equatorial hydrogen. Thus, according to the Karplus relationship, the two axial-axial couplings will result in large coupling constants due to the large (180 degree) dihedral angles between the hydrogens, whereas the dihedral angle to the adjacent axial hydrogen is approximately 60 degrees resulting in a small dihedral angle. However, in (+)-neomenthol the hydrogen on the same carbon as the hydroxyl is equatorial, so all dihedral angles with adjacent hydrogens are approximately 60 degrees, so all coupling constants will be small. So, the multiplet structure for this hydrogen will be significantly different in the spectra of these two isomers. The signal from the hydrogen on the carbon bearing the isopropyl group also will change significantly, because a large coupling (axial-axial, to the hydrogen on the hydroxyl carbon in (-)-menthol) will be replace by a smaller one (now axial-equatorial, to the hydrogen on the hydroxyl carbon in (+)-neomenthol). Likewise, for the axial hydrogen on the methylene carbon adjacent to the hydroxyl carbon, a large axial-axial coupling to the axial hydrogen on the hydroxyl carbon (in (-)-menthol) is replaced with a small axial-equatorial coupling (in (+)-neomenthol).

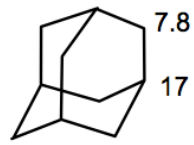
c. Sketch the ^{1}H NMR signal you would observe in a simple one-dimensional ^{1}H NMR spectrum for the hydrogen on the carbon bearing the hydroxyl group in (+)-neomenthol. For credit you will have to explain the multiplet structure, justify why it appears as it does, and you will have to indicate distances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

Formally, this hydrogen is coupled to three adjacent, non-equivalent hydrogens, so the multiplet would be a doublet of doublet of doublets. However, the dihedral angles between this hydrogen and each of the three adjacent hydrogens are the same, approximately 60 degrees, so the coupling constants to each would be approximately equal, and would be small, as indicated by the Karplus relationship. We'll assume all coupling constants are 4 Hz. Due to peak overlap, the multiplet will resemble a quartet with 4 Hz between all pairs of adjacent peaks in the multiplet.

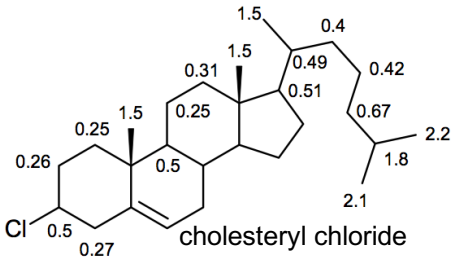


Name _____

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



adamantane



cholesteryl chloride

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**)

The principle contributors to T_1 relaxation are dipole-dipole interactions. For ^{13}C nuclei, dipole-dipole interactions with hydrogen nuclei, in particular directly bonded hydrogens, have large influences on T_1 relaxation. The effect scales with the number of directly attached hydrogens, so ^{13}C nuclei in methene groups ($-CH_2$), with two attached hydrogens, typically relax faster than ^{13}C nuclei in methine groups (-CH), with only a single attached hydrogen. This is shown for the indicated ^{13}C nuclei in adamantane, where the T_1 relaxation time constant for the methine group (17 s) is much longer than for the methene group (7.8 s).

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**)

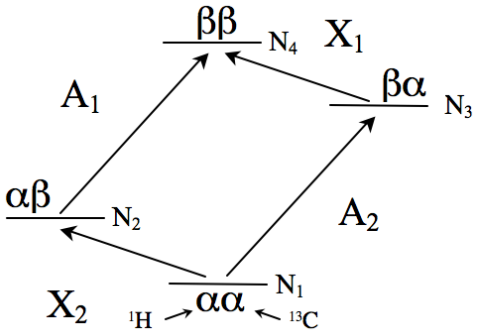
As described in 'a', the dipole-dipole interactions with hydrogen nuclei, in particular directly bonded hydrogens, have large influences on T_1 relaxation, with the expectation that relaxation times are shortest for ^{13}C nuclei in methyl groups ($-CH_3$) with three hydrogens attached, longer for ^{13}C nuclei in methene groups ($-CH_2$), with two attached hydrogens, and longest for ^{13}C nuclei in methine groups (-CH), with only a single hydrogen attached. However, in cholesteryl chloride the relaxation times for ^{13}C nuclei in methyl groups are the longest. Given that this is not significantly the result of motional anisotropy, which is suggested by the shape of the molecule, it must indicate much shorter effective correlation times, τ_c, for the methyl groups, leading to longer T_1 times. This must be the result of very fast rotation about the C-C bond of the methyl group, and, in fact, this is the case.

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**)

The effective correlation times for nuclei are a measure of mobility (rate of positional change or mobility), and they are roughly proportional to $1/T_1$. The sidechain of cholesteryl chloride would be expected to experience less conformational and motional restriction and would overall be more mobile than the ring structure part of the molecule. Thus, we would expect that the ^{13}C T_1 values for the methyl groups at the end of the side chain would be significantly larger than the other methyl groups.

Name _____

8). Consider the populations N_1, N_2, N_3 and N_4 of the αα, αβ, βα and ββ 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**)

$N_4 = N$
$N_3 = N + \Delta X$
$N_2 = N + \Delta H$
$N_1 = N + \Delta H + \Delta X$

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

$A_1 = N_2 - N_4 = \Delta H$
$A_2 = N_1 - N_3 = \Delta H$
$X_1 = N_3 - N_4 = \Delta X$
$X_2 = N_1 - N_2 = \Delta X$

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**)

$N_4 = N$
$N_3 = N + \Delta X$
$N_2 = N + \Delta H + \Delta X$
$N_1 = N + \Delta H$

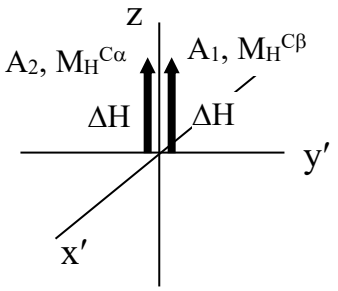
d. Now, write down expressions for the population differences for the transitions A_1, A_2, X_1 and X_2 (after exciting the X_2 transition). For the X transitions, the final expressions should be written in terms of ΔX, and for the A transitions the final expressions should be written in terms of ΔH.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

$A_1 = N_2 - N_4 = \Delta H + \Delta X = 1.25\ \Delta H$
$A_2 = N_1 - N_3 = \Delta H - \Delta X = 0.75\ \Delta H$
$X_1 = N_3 - N_4 = \Delta X$
$X_2 = N_1 - N_2 = -\Delta X$

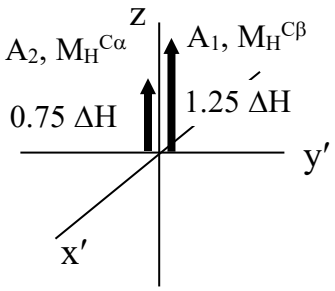
Name _____

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**)

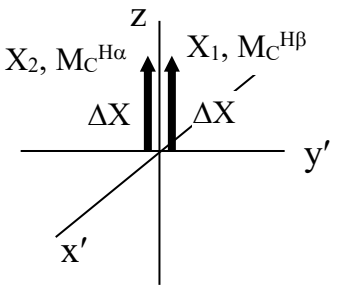
A transitions before



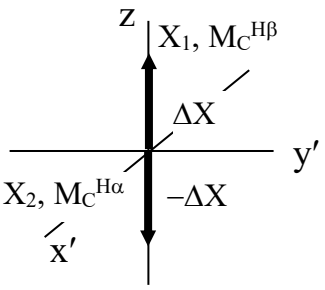
A transitions after



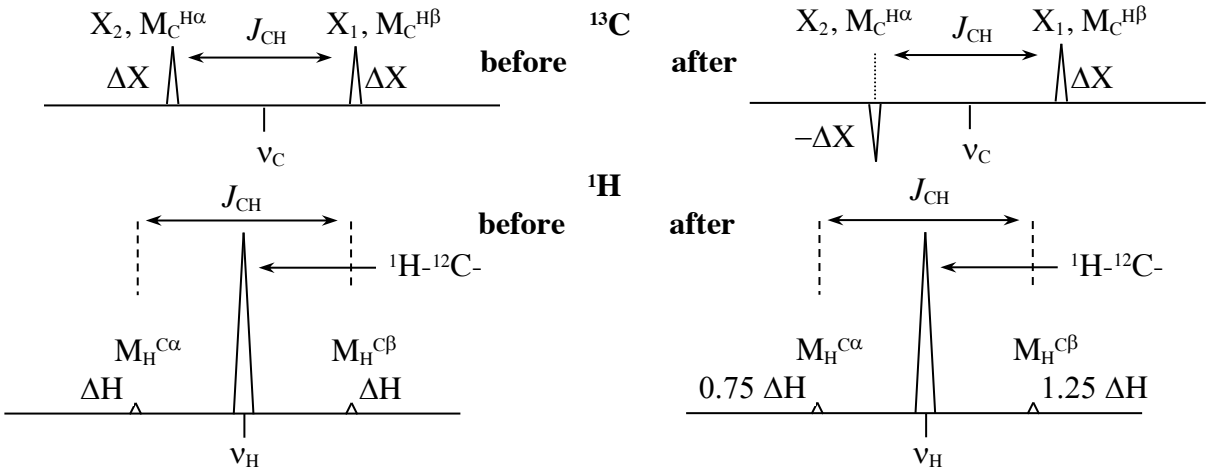
X transitions before



X transitions after



f. For the simple two spin system (^{1}H-^{13}C), draw the ^{1}H and ^{13}C signals that you would expect in 1D ^{1}H 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**)

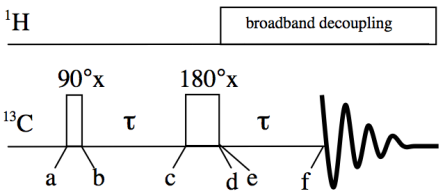


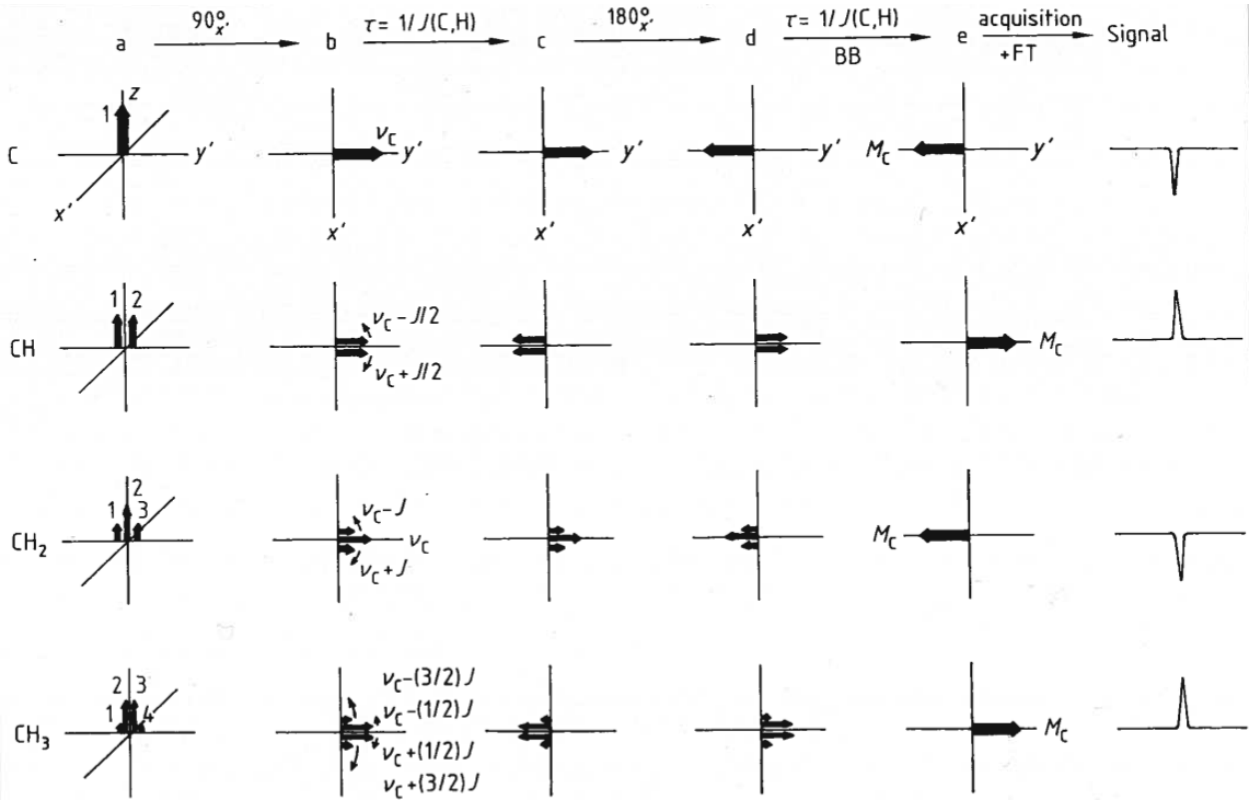
g. Explain why you would want to excite one of the X (^{13}C) transitions in an SPI experiment? (**4 points**)

There is really no good reason. SPI, and other polarization transfer methods, are used to transfer polarization from the sensitive nucleus (^{1}H) to the insensitive nucleus (^{13}C or ^{15}N). In the above example, we did the opposite, and clearly there was no advantage to doing so. The magnitude of the ^{1}H-^{12}C transition in the ^{1}H spectrum of course does not change, and on average there is no improvement in the magnitudes of the ^{1}H-^{13}C transitions.

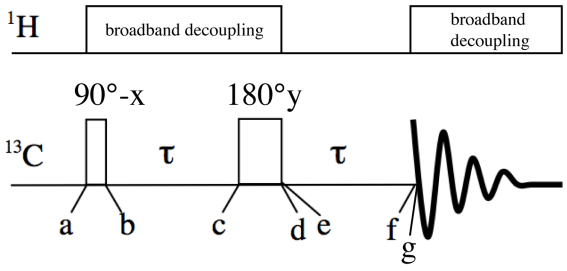
Name _____

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, -CH_2, and -CH_3 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:

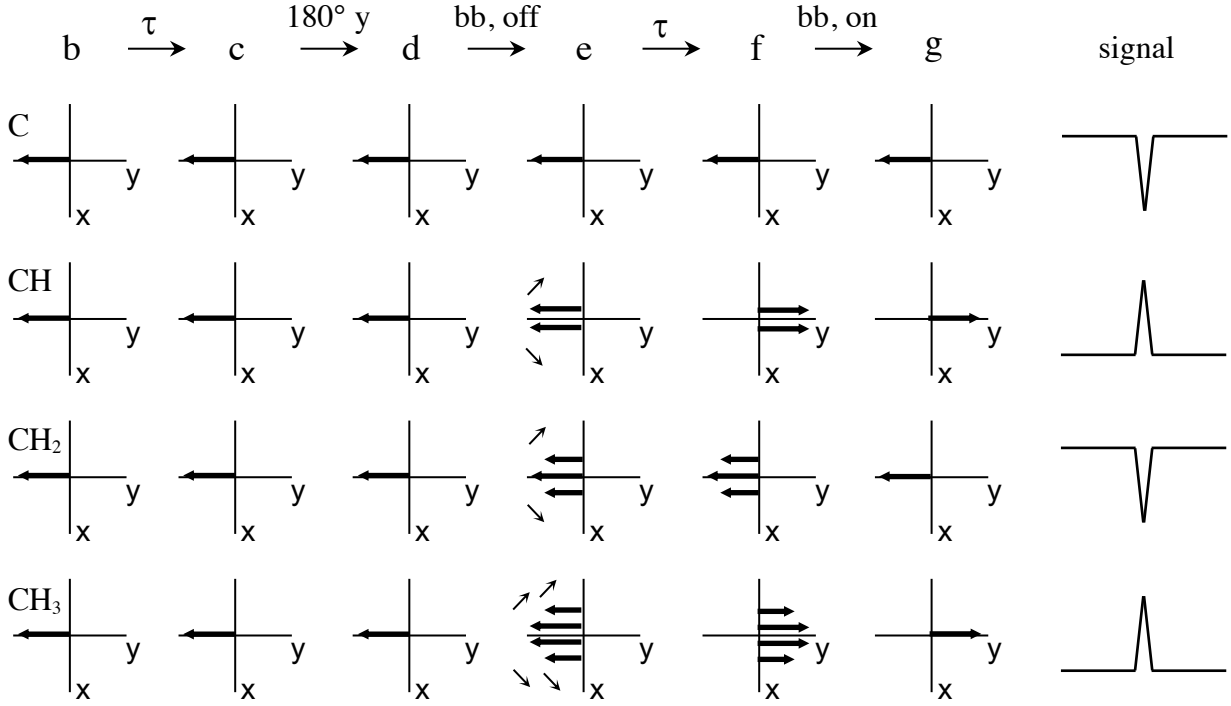


-broadband decoupling is ON at point 'a' and remains on until point 'e' (turned OFF between points 'd' and 'e')
-broadband decoupling is OFF at point 'e' through point 'f'
-broadband decoupling is ON at point 'g' (just before acquisition begins)

(*Question continues on next page*)

Name _____

Use vector diagrams such as those shown above. Draw vector diagrams for -C, -CH, -CH_2, and -CH_3 vectors with $\tau = 1/(J_{CH})$ 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**)



For -CH, the two vectors move apart 360 degrees (2π radians) during $\tau = 1/J$ ($\Theta = 2\pi J\tau$). For -CH_2, the two outer component vectors move apart 720 degrees (4π radians) during $\tau = 1/J$ ($\Theta = 2\pi 2J\tau$). For –CH_3, the two outer component vectors move apart 1080 degrees (6π radians) during $\tau = 1/J$ ($\Theta = 2\pi 3J\tau$), whereas the two inner components move apart by 360 degrees, just as the vectors in -CH groups.

This alternate pulse sequence gives the same results as the other.

Name _____

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Name _____

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 γ[a] [10^7 rad T^{-1} s^{-1}]	NMR frequency [MHz][b] (B_0 = 2.3488 T)
^{1}H	1/2	–	99.985	1.00	26.7519	100.0
^{2}H	1	2.87 x 10^{-3}	0.015	9.65 x 10^{3}	4.1066	15.351
^{3}H[c]	1/2	–	–	1.21	28.5350	106.664
^{6}Li	1	–6.4 x 10^{-4}	7.42	8.5 x 10^{-3}	3.9371	14.716
^{10}B	3	8.5 x 10^{-2}	19.58	1.99 x 10^{-2}	2.8747	10.746
^{11}B	3/2	4.1 x 10^{-2}	80.42	0.17	8.5847	32.084
^{12}C	0	–	98.9	–	–	–
^{13}C	1/2	–	1.108	1.59 x 10^{-2}	6.7283	25.144
^{14}N	1	1.67 x 10^{-2}	99.63	1.01 x 10^{-3}	1.9338	7.224
^{15}N	1/2	–	0.37	1.04 x 10^{-3}	–2.7126	10.133
^{16}O	0	–	99.96	–	–	–
^{17}O	5/2	–2.6 x 10^{-2}	0.037	2.91 x 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 x 10^{-2}	7.0704	26.451
^{25}Mg	5/2	0.22	10.13	2.67 x 10^{-3}	–1.6389	6.1195
^{29}Si	1/2	–	4.70	7.84 x 10^{-3}	–5.3190	19.865
^{31}P	1/2	–	100	6.63 x 10^{-2}	10.8394	40.481
^{39}K	3/2	5.5 x 10^{-2}	93.1	5.08 x 10^{-4}	1.2499	4.667
^{43}Ca	7/2	–5.0 x 10^{-2}	0.145	6.40 x 10^{-3}	–1.8028	6.728
^{57}Fe	1/2	–	2.19	3.37 x 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 x 10^{-2}	–10.0318	37.272
^{133}Cs	7/2	–3.0 x 10^{-3}	100	4.74 x 10^{-2}	3.5339	13.117
^{195}Pt	1/2	–	33.8	9.94 x 10^{-3}	5.8383	21.499

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

γ_{1H} = 26.7519 x 10^7 rad/T/s, I = 1/2
γ_{10B} = 2.8747 x 10^7 rad/T/s, I = 3
γ_{11B} = 8.5847 x 10^7 rad/T/s, I = 3/2
γ_{13C} = 6.7283 x 10^7 rad/T/s, I = 1/2
γ_{15N} = -2.7126 x 10^7 rad/T/s, I = 1/2
γ_{17O} = -3.6280 x 10^7 rad/T/s, I = 5/2

Name _____

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

k_B = 1.381 x 10^{-23} J/K Avagadro's number = 6.02214179 x 10^{23} mol^{-1}

h = 6.626 x 10^{-34} Js $\hbar = h/(2\pi)$

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

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

π/2 radians = 90°

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

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

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

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

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

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

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

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

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

$$\omega_0 = \gamma B_0$$

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

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

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

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

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

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

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

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

$I = (1 + \eta) I_0$

$I \propto 1/r^6$

$\Theta = \gamma B_1 \tau_p$

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

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

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

SW=1/(2DW)=Nyquist frequency (ν_{NQ})/2

AQ=DW*TD

DR=2SW/TD=1/AQ

(TD≡NP)

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

π/2 radians = 90°

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

multiplicity=$2nI + 1$

$\Theta = 2\pi J\tau$