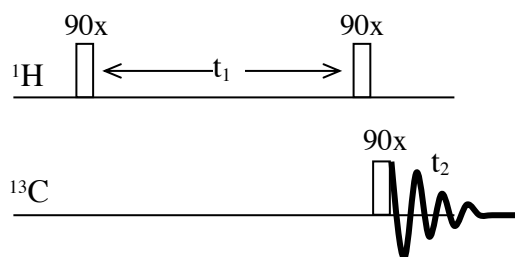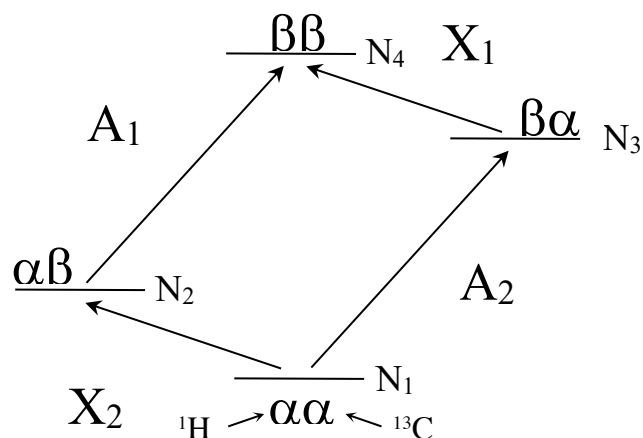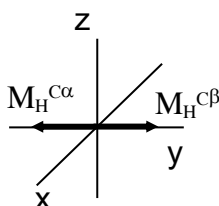**Exam 4: CHEM/BCMB 4190/6190/8189 (154 points) Tuesday, 24 November, 2020**

1). Consider the HETCOR pulse sequence, and the energy diagram for the simple ^{1}H-^{13}C spin system (i.e. CHCl$_3$).

Just *before* the second ^{1}H 90° pulse, for a particular t_1 value, the $M_H^{C\alpha}$ and $M_H^{C\beta}$ vectors happen to be positioned along the –y and y axes, respectively.

a. Define the populations for the individual states N_1-N_4 and the population differences for the A_1, A_2, X_1 and X_2 transitions *both <u>before</u>* the beginning of the pulse sequence and *<u>after</u>* the second ^{1}H 90° pulse (assuming the particular value of t_1 mentioned above, and no relaxation losses during t_1). Assume that $N_4=N$ at equilibrium, and ΔH is the difference in the number of spins in α and β states for ^{1}H, and ΔX is the difference in the number of spins in α and β states for ^{13}C. Also, define the relationship between ΔH and ΔX. (**8 points**)

After the second ^{1}H pulse, the $M_H^{C\beta}$ vector will be inverted from its equilibrium position (-z), whereas the $M_H^{C\alpha}$ vector will be in the same position as it was at equilibrium (z). Thus, the N_2 and N_4 populations are inverted after the second ^{1}H pulse. Also, the ratio of ΔH and ΔX is the ratio of their gyromagnetic ratios, which is ~4:

equilibrium (beginning of pulse sequence)

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

after second ^{1}H pulse

$N_4 = N + \Delta H$
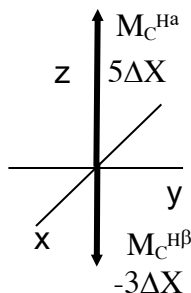$N_3 = N + \Delta X$
$N_2 = N$
$N_1 = N + \Delta H + \Delta X$
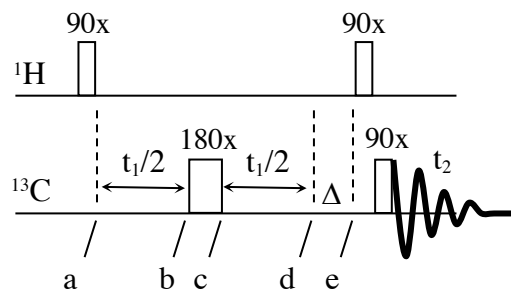$A_1 = N_2 - N_4 = -\Delta H$
$A_2 = N_1 - N_3 = \Delta H$
$X_1 = N_3 - N_4 = \Delta X - \Delta H = -3\Delta X$
$X_2 = N_1 - N_2 = \Delta X + \Delta H = 5\Delta X$

b. Draw the vectors $M_C^{H\alpha}$ and $M_C^{H\beta}$ that are present just before the ^{13}C pulse. Make sure to label each with the correct name ($M_C^{H\alpha}$ or $M_C^{H\beta}$) and with the proper magnitude (expressed in terms of ΔX). (**4 points**)

c. In the modified HETCOR experiment (right) an additional pulse (^{13}C 180° x) and an additional delay (Δ) have been added in order to remove the $^1J_{CH}$ splitting in the t_1 dimension (decouple). For the simple ^1H-^{13}C spin system (i.e. CHCl$_3$), at point "a" in the sequence, the $M_H^{C\alpha}$ and $M_H^{C\beta}$ vectors are positioned as shown below (in the transverse plane). For an arbitrary value of $t_1/2$, the vectors have moved into the positions shown in "b".
Show the results at points "c" and "d". Then explain why decoupling is achieved. (**8 points**)
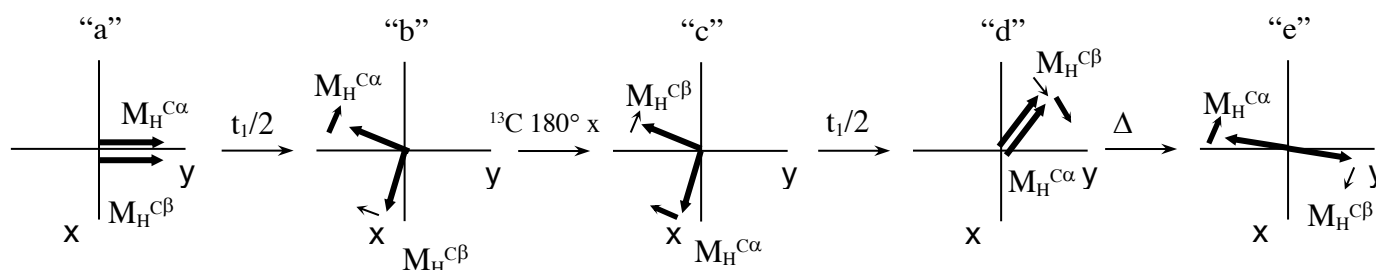

Decoupling is achieved because the $^1J_{CH}$ coupling is refocused during the $t_1/2$- ^{13}C 180x-$t_1/2$ period. At "d", the $M_H^{C\alpha}$ and $M_H^{C\beta}$ vectors are refocused, and the net precession to this point for each vector is the same.

d. The delay Δ has to be set appropriately in order for the pulse sequence to operate properly. What value should Δ be set to? Please explain your answer both by showing the results at "e" and by explaining why the value of Δ that you selected is appropriate. (**6 points**)

The Δ delay should be set to $1/(2\ ^1J_{CH})$. This allows the refocused $M_H^{C\alpha}$ and $M_H^{C\beta}$ vectors at "d" to move apart from one another by 180° so that they are opposite in phase at "e". In this way, the ^1H 90°x pulse at "e" then converts the -y and y components of these vectors equally to z or -z magnetization, respectively, giving maximum polarization transfer and maximum sensitivity.

2). Shown (below, right) are the chemical structure and 1D, ¹H NMR spectrum of ethylmethacrylate. The five individual signals in the spectrum are labeled **A-E**.
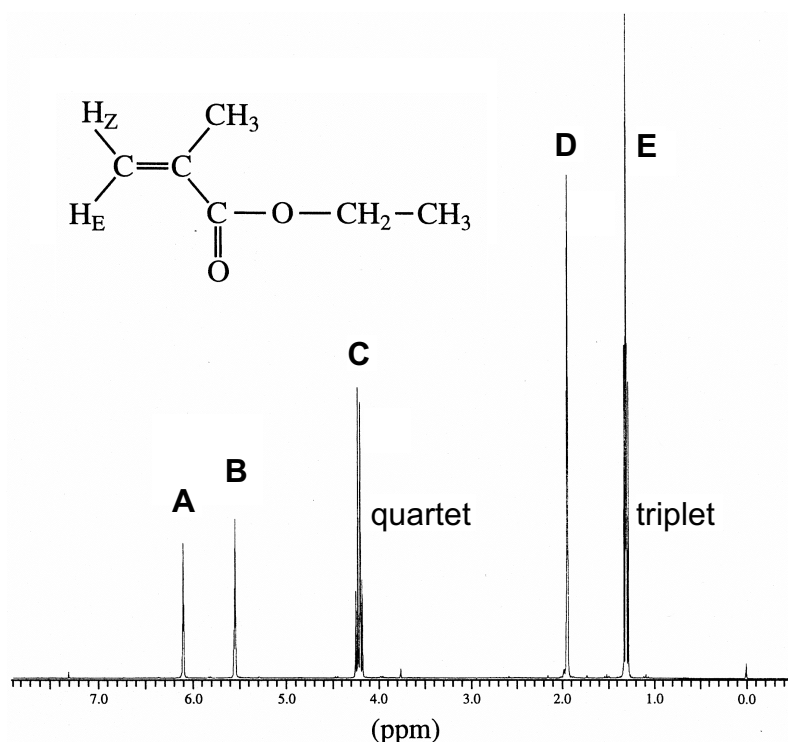
a. Assign each of the five signals (A, B, C, D, and E) in the 1D, ¹H NMR spectrum of ethylmethacrylate to a hydrogen or hydrogens in the molecule. Justify (explain) each of your assignments. In your justifications make sure to include signal multiplicity. (**6 points**)

*For the –CH₂-CH₃ group, the coupling of the two methylene hydrogens splits the signal from the (equivalent) methyl hydrogens into a triplet, and the three methyl group hydrogens split the signal from the (equivalent) methylene hydrogens into a quartet. Therefore, signal **E** must result from the methyl hydrogens of the ethyl group, and signal **C** must result from the methylene hydrogens of the ethyl group. Also, due to the attachment of the methylene group to the oxygen, these hydrogens would be shifted downfield (deshielded) relative to the methyl group. Signal **D** must result from the remaining methyl group, as it is a singlet (hydrogens equivalent), and its intensity is much larger than the downfield shifted singlets, which correspond to the ethylenic hydrogens H_E and H_Z. One would expect that signal **A** would result from H_E because H_E is closer to the electron-withdrawing influence of the carbonyl group, leaving signal **B** to correspond to H_Z. However, H_Z and H_E cannot be unambiguously assigned based on this information alone.*

b. Shown (right) is the result of a 1D selective difference NOE experiment on ethylmethacrylate. There are five observable signals in this spectrum (6.1, 5.55, 4.2, 1.95, and 1.3 ppm).
-Explain how a 1D selective difference NOE experiment works.
-Explain in detail the relative magnitudes and signs of these signals in the spectrum shown.
-Explain in detail why the results of this experiment are consistent with the assignments that you made (part 'a'), or why they are not. (**10 points**)

irradiate

(ppm)
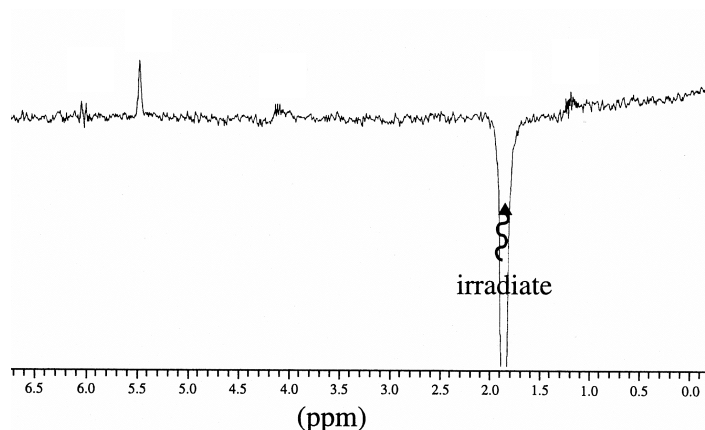
In a difference NOE experiment, a normal 1D spectrum is subtracted from a spectrum where a given signal (in this case, the signal from the methyl group at ~ 1.9 ppm) is saturated (irradiated). Signals that are then observed in the difference spectrum result from NOE enhancement from the hydrogen(s) that give rise to the irradiated signal. The exception is the signal in the difference spectrum that results from the irradiated hydrogen(s), which appears as a very large signal opposite in phase to the others. Selective irradiation of a signal removes it from the irradiated spectrum, which, when subtracted from the spectrum without irradiation, results in a large negative peak. In the spectrum above, very small positive peaks for three of the signals indicate very small NOE enhancements when the signal at D is saturated, which is consistent with the assignments above and the distances between the respective hydrogens. The larger signal at 5.5 ppm is consistent with the assignments in 'a', as the distance between the methyl group (D) and H_Z shorter than the distance between the methyl group D and the other hydrogens in the molecule, resulting in a larger NOE enhancement of the signal corresponding to H_Z (B).

c. Shown (right) is the result of a second selective difference NOE experiment on ethylmethacrylate. Are the results consistent with the results of the experiment presented in 'b' above? Are they consistent with your assignments from 'a'? Please explain. (**8 points**)

irradiate

(ppm)
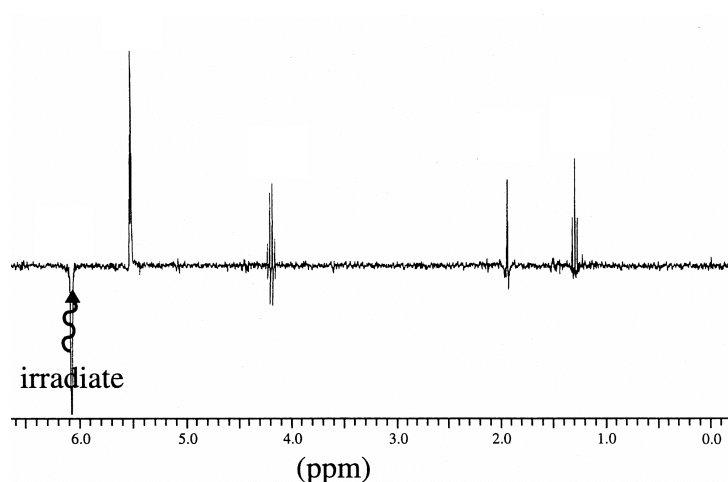
In this second difference NOE spectrum, the signal from H_E is irradiated. The closest hydrogen to H_E is H_Z, which shows a large NOE enhancement, as expected. Furthermore, we would expect that this would be the only large NOE enhancement, because the distance between H_E and H_Z is much shorter than the distance from H_E to any of the other hydrogens in the molecule. If our assignments of H_Z and H_E were incorrect, we would expect not only a large NOE enhancement to the other ehylenic hydrogen, but also to the ethylenic methyl group. Thus, the results here are consistent both with our original assignments and with the results in 'b'.

3). In a particular molecule, the distance between H_a and H_b is known to be 3.92 angstroms. In a NOESY spectrum, the intensity of the crosspeak between these hydrogens is 2827 (arbitrary units). In the same NOESY spectrum, the intensity of the crosspeak between H_c and H_d in the same molecule is 13627. What is the distance between H_c and H_d? (**6 points**)

> *The intensities of crosspeaks in NOESY spectra are proportional to $1/r^6$ where r is the internuclear distance. In this instance, the intensity increased by a factor of $13627/2827=4.820$, and thus r decreased by a factor X where $X^6=4.820$, or $X=1.300$. So $3.92/1.300=3.015$, so the H_c-H_d distance is 3.015 angstroms.*

4). In a simple 1D, ^1H experiment, the intensity of the signal from H_E is 7.53 (arbitrary units). If we now saturate the signal from H_Z, what would be the signal intensity of H_E if we assume the maximum possible (distance independent) NOE enhancement is produced? (**6 points**)

> *The maximum enhancement for small molecules, η, is equal to half of the ratio of the gyromagnetic ratio of the saturated nucleus (γ_a) to the observed nucleus (γ_x):*
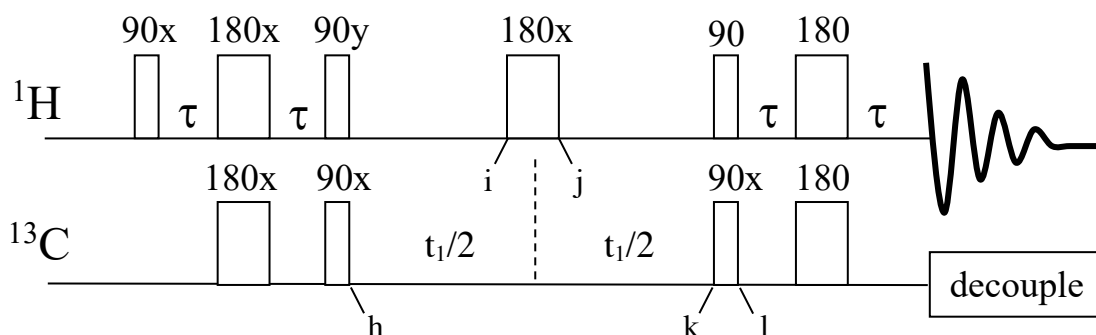
$$\eta = \gamma_a/(2 \times \gamma_x)$$

> *The intensity of the enhanced signal, I is then related to the original intensity by:*

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

> *For the case in question, $\eta = \frac{1}{2}$ because $\gamma_a = \gamma_x$, so $I = (1 + \frac{1}{2})\, I_0 = 1.5 \times 7.53 = 11.3$.*

5). The pulse sequence for the HSQC experiment is shown below.

a. At the end of the final τ period (just before acquisition and decoupling begin), sketch what the vectors $M_H^{C\alpha}$ and $M_H^{C\beta}$ look like for a simple -CH group. Use an appropriate system of axes, and label the vectors. Also sketch the vectors for a different -CH group that has a Larmor frequency that is different than the Larmor frequency of the first.
Provide any necessary explanation/justification. (**4 points**)

All the vectors will be in the transverse plane, all refocused and in phase. Their relative magnitudes will depend on chemical shift.
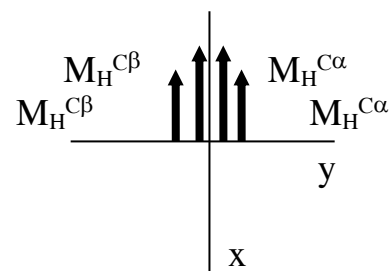

b. Explain why it is necessary for the vectors that you have drawn in 'a' to be positioned the way that you have drawn them. (**4 points**)

At the end of the experiment (just before acquisition), all vectors must be refocused with respect to coupling and chemical shift to allow for broadband decoupling during acquisition and phase coherence of the signals.

6). Below is a region of the 2D ^{1}H, ^{1}H-COSY spectrum for the azo-sugar whose structure is also shown below. This region shows diagonal and cross peaks for hydrogens on carbons 2-6. Above the COSY spectrum is shown the 1D ^{1}H spectrum.

a. Label correctly the diagonal peaks (for instance "3,3" to indicate the diagonal peak for the proton on carbon 3), *and* label correctly the crosspeaks on one side of the diagonal (for instance, "5,2" for a crosspeak resulting from protons on carbons 5 and 2). Note that the methylene hydrogens at 6 are NOT equivalent. The 1D spectrum is shown above the COSY spectrum. Use the numbering as shown on the molecular structure below. (**10 points**).
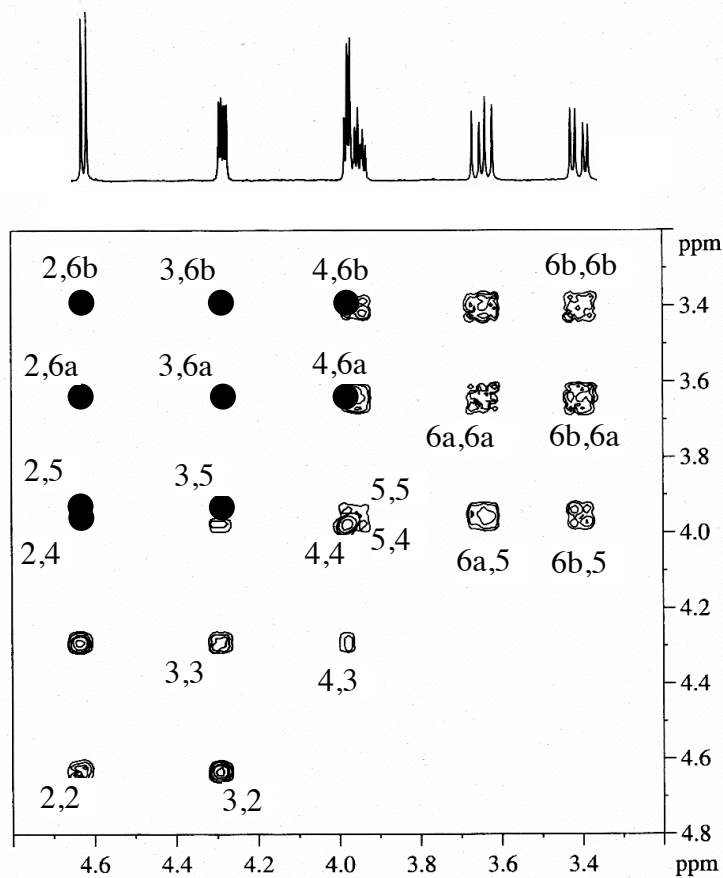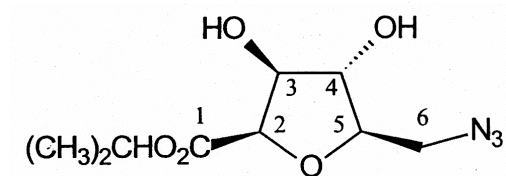
b. On the other side of the diagonal, draw additional crosspeaks that you might expect to be observed in a TOCSY spectrum. Label these additional peaks appropriately. Also, what does TOCSY stand for? (**8 points**)

Total Correlation Spectroscopy

7). Shown (right) is the pulse sequence for the heteronuclear two-dimensional *J*-resolved experiment.


a). What parameter is measured in the directly detected dimension? (**2 points**)

　　^{13}C chemical shift

b). What parameter is measured in the indirectly detected dimension? (**2 points**)

　　J_{CH}

c). What is the role of the ^{13}C 180°y pulse? Why is it necessary (or is it?) to include this pulse? For full credit you will have to use vector diagrams to illustrate you point(s) and provide a complete but concise explanation. (**10 points**)
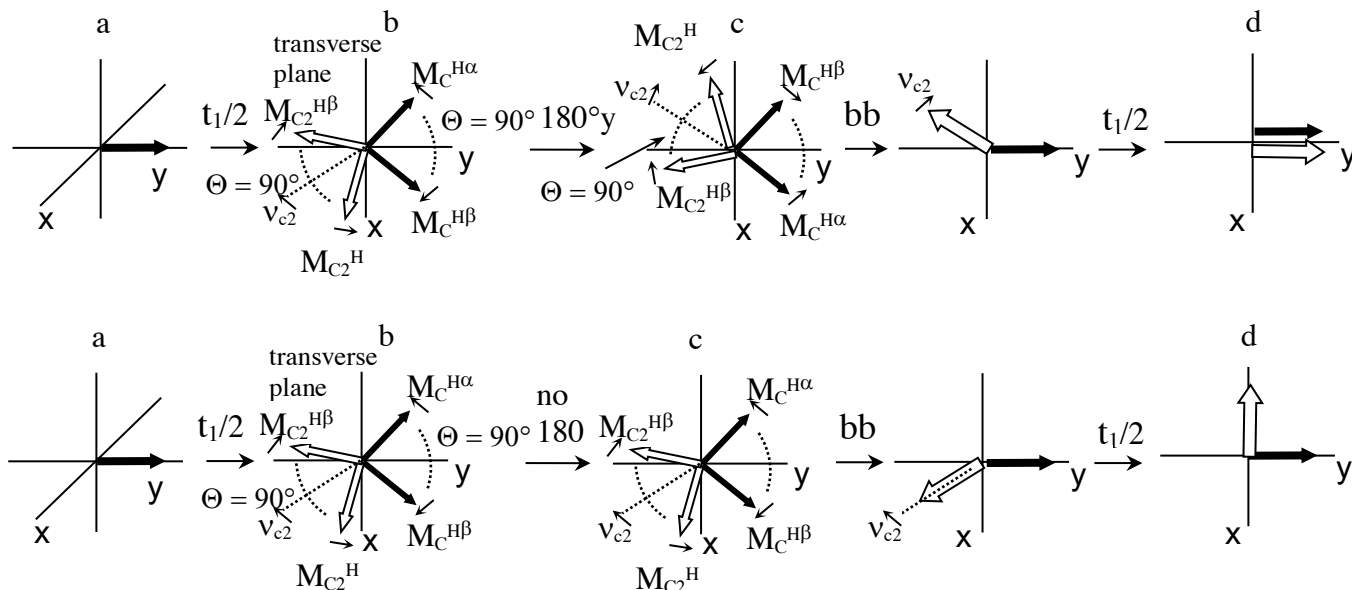

The ^{13}C 180° pulse is necessary for chemical shift refocusing. As shown above (top), when included, this pulse reflects the individual vectors through the 'y' axis so that during the second $t_1/2$ period the chemical shifts refocus, in this case along the 'y' axis. If not included, as shown above (bottom), the chemical shifts do not refocus at 'd', and so the individual peaks in the spectrum are out of phase.

The ^{13}C 180° pulse also removes the effects of magnetic field inhomogeneity. During the first $t_1/2$ period, because of magnetic field inhomogeneity, the spins that comprise both $M_C^{H\alpha}$ and $M_C^{H\beta}$ start to fan out from the bulk because they experience slightly different magnetic fields. At 'b', the ^{13}C 180°y pulse is applied. This pulse reflects all vectors through the 'y' axis. The fanning out of the spins due to magnetic field inhomogeneity is, then, refocused during the second $t_1/2$ period, as this is unaffected by the decoupler. Thus, at d, the effects of magnetic field inhomogeneity have also been refocused.

8). The ^{13}C and ^{1}H chemical shifts and $^1J_{CH}$ coupling constants for isopentyl acetate are shown below:

carbon	δ ^{13}C (ppm)	δ ^{1}H (ppm)	$^1J_{CH}$ (Hz)
-C^{1}H$_3$	21	2.1	120
-C^2	171	-	-
-C^{3}H$_2$	63	4.1	130
-C^{4}H$_2$	37	1.5	130
-C^{5}H	25	1.7	140
-C^{6}H$_3$	23	0.9	120
-C^{7}H$_3$	23	0.9	120

$$O$$
$$\|$$
$$C^1H_3-C^2-O-C^3H_2-C^4H_2-C^5H-C^6H_3$$
$$|$$
$$C^7H_3$$
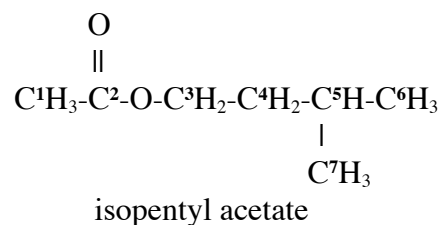
isopentyl acetate

Draw the heteronuclear two-dimensional *J*-resolved spectrum of isopentyl acetate. Label the axes properly, and indicate which is F$_1$ (indirectly detected dimension) and which is F$_2$ (directly detected dimension). (**10 points**)
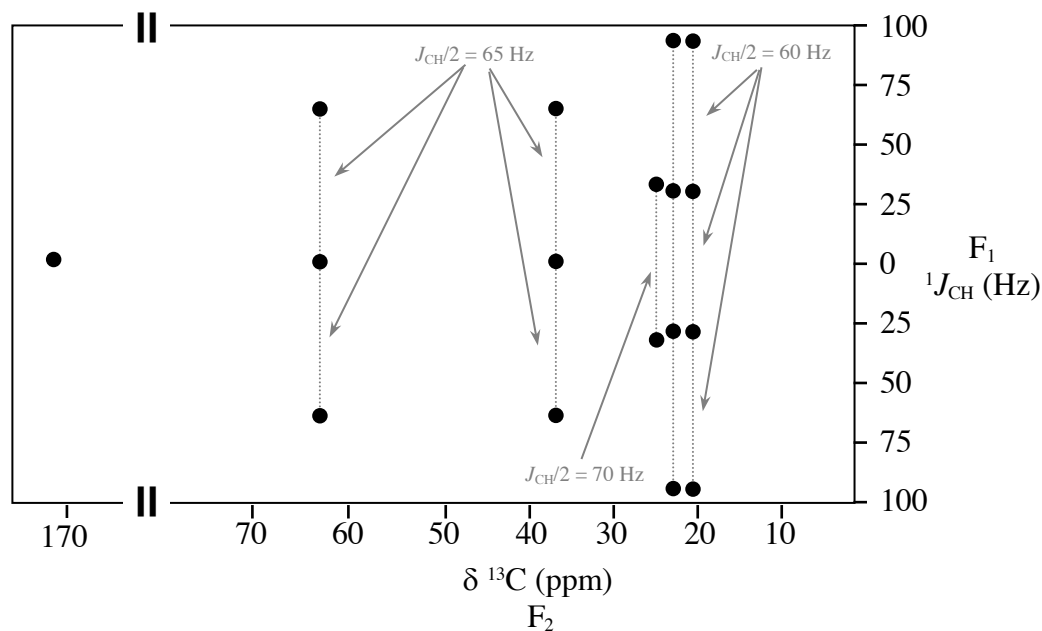
The two methyl groups labeled '6' and '7' are equivalent, and so give rise to a single signal in F$_2$ at 23 ppm. The quaternary carbon, whose ^{13}C chemical shift is 171 ppm (F$_2$), shows up as a singlet in F$_1$ (no large coupling with any protons).

9). Draw the heteronuclear two-dimensional ^1H, ^{13}C-HSQC spectrum of isopentyl acetate (see question 8). Label the axes properly, and indicate which is F_1 (indirectly detected dimension) and which is F_2 (directly detected dimension). (**10 points**)
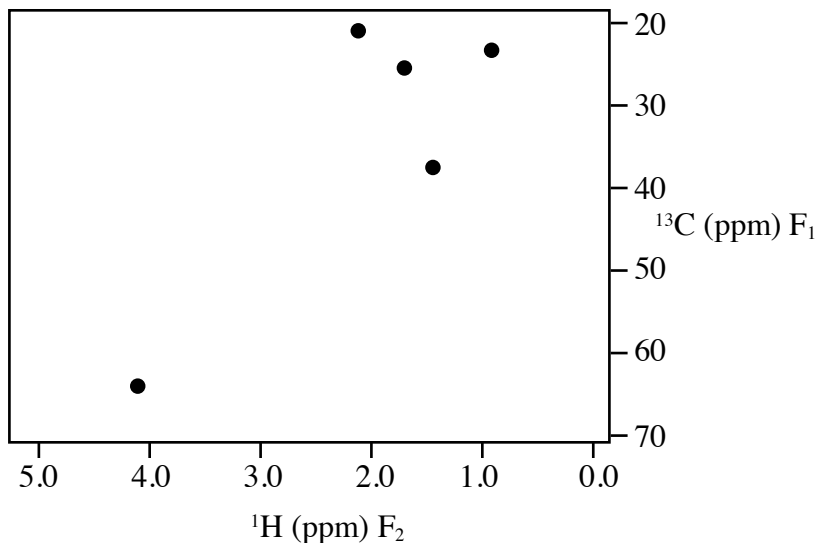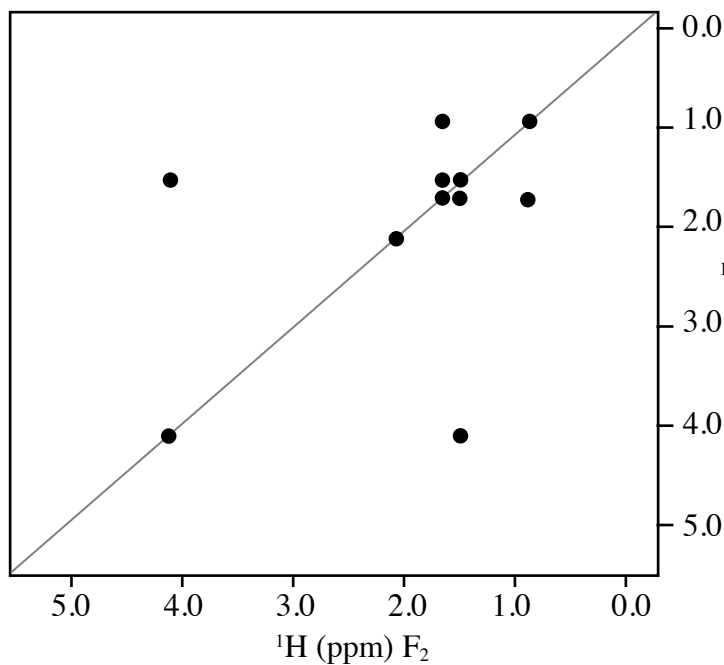

**10).** Draw the two-dimensional ^1H, ^1H-COSY spectrum of isopentyl acetate (see question 8). Label the axes properly, and indicate which is F_1 (indirectly detected dimension) and which is F_2 (directly detected dimension). State clearly any assumptions you make regarding which cross peaks appear. (**10 points**)

Only cross peaks resulting from two or three bond couplings are shown

10). 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**)
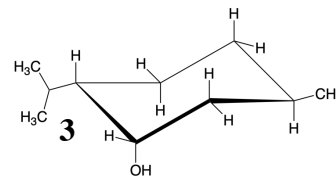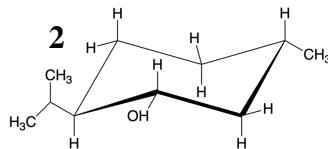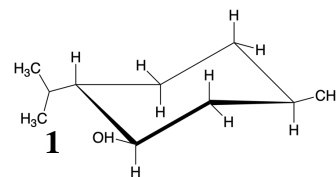
These two molecules are identical in every way except that the hydroxyl has moved to the other side of the ring. You can see this if you flip (+)-menthol 180 degrees about a horizontal axis in the plane of the page. There is no way to distinguish them based on simple one-dimensional ^{1}H NMR spectra. They are mirror image isomers.
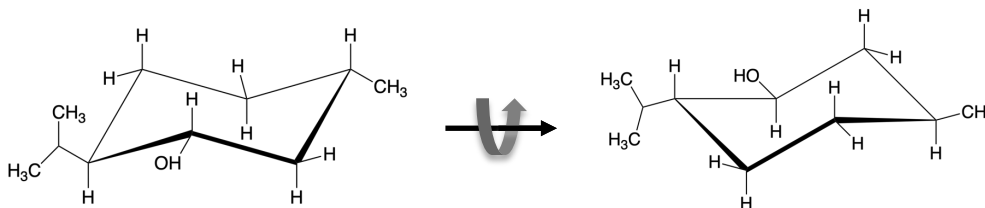
b. If you compare the simple one-dimensional ^1H NMR spectrum of the sample containing (-)-menthol and the spectrum of the sample containing (+)-neomenthol, which signals would you expect would show the most significant changes. You will have to explain for credit, and your explanation must include the origins of the changes. (**8 points**)

*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 ^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**)

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.
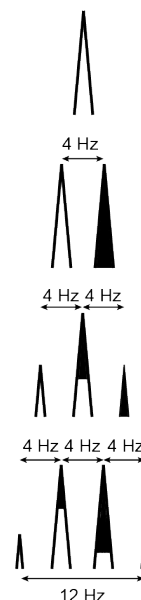
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You may find some of the information below useful:

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 γ[a] $[10^7\ rad\ T^{-1}\ s^{-1}]$	NMR frequency [MHz][b] (B_0 = 2.3488 T)
^1H	1/2	–	99.985	1.00	26.7519	100.0
^2H	1	2.87 x 10^{-3}	0.015	9.65 x 10^3	4.1066	15.351
^3H[c]	1/2	–	–	1.21	28.5350	106.664
^6Li	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)	
	^1H	^{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_{13C} = 6.7283 x 10^7 rad/T/s, I = 1/2

γ_{10B} = 2.8747 x 10^7 rad/T/s, I = 3 γ_{15N} = -2.7126 x 10^7 rad/T/s, I = 1/2

γ_{11B} = 8.5847 x 10^7 rad/T/s, I = 3/2 γ_{17O} = -3.6280 x 10^7 rad/T/s, I = 5/2

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

$k_B = 1.381 \times 10^{-23}$ J/K $\qquad$ Avagadro's number $= 6.02214179 \times 10^{23}$ mol^{-1}

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

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

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

$\pi/2$ radians $= 90°$

$M_0 = \dfrac{N\gamma^2\hbar^2 B_0 I(I+1)}{3k_B T}$ $\qquad\qquad$ $B_2 = \dfrac{\Delta v\sqrt{J^2 - J_r^2}}{J_r} = \dfrac{J\Delta v}{J_r}$

$\varepsilon \propto dM/dt = \gamma M_0 B = \dfrac{N\gamma^3\hbar^2 B_0{}^2 I(I+1)}{3k_B T}$ $\qquad$ $\Delta v = v_{BS} - v_0 = \dfrac{B_2^2}{2(\Delta B)} = \dfrac{B_2^2}{2(v_0 - v_i)}$

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

$m = (-I, -I+1, \ldots, I-1, I)$ $\qquad\qquad$ $\Theta = \gamma B_1 \tau_p$

$E = -\mu_Z B_0 = -m\gamma\hbar B_0$ $\qquad\qquad$ $\dfrac{N_\beta}{N_\alpha} \approx 1 - \left(\dfrac{\gamma\hbar B_0}{k_B T}\right)$

$\Delta E = \mu_Z B_0 = \gamma\hbar B_0 = h v_L = h v_1$ $\qquad$ $B_{eff} = B_0(1-\sigma)$

$v_L = |\gamma/(2\pi)| B_0 = \omega_0/(2\pi)$ $\qquad\qquad$ $\upsilon_L = \dfrac{\gamma}{2\pi}(1-\sigma)B_0$

$\omega_0 = \gamma B_0$

$\Delta\delta = \dfrac{\Delta v}{\text{observe frequency}} \times 10^6$

$\qquad\qquad\qquad\qquad\qquad\qquad$ SW$=1/(2$DW$)=$Nyquist frequency $(v_{NQ})/2$

$M_y = M_0 e^{-t/T_2^*}$ $\qquad\qquad\qquad\qquad$ AQ$=$DW$*$TD

$M_z = M_0(1 - e^{-t/T_1})$ $\qquad\qquad\qquad$ DR$=2$SW$/$TD$=1/$AQ

$M_z = M_0(1 - 2e^{-t/T_1})$ $\qquad\qquad\qquad$ (TD$\equiv$NP)

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

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

$\dfrac{1}{T_2^*} = \dfrac{\gamma\Delta B_0}{2} + \dfrac{1}{T_2}$ $\quad$ $\dfrac{1}{T_2^*} = \dfrac{1}{T_2} + \dfrac{1}{T_2(B_0)}$ $\qquad$ $\pi/2$ radians $= 90°$

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

$\eta = \gamma_a / (2\gamma_x)$ $\qquad\qquad\qquad\qquad\qquad$ $1 + \gamma_A/\gamma_X$ $\quad$ $1 - \gamma_A/\gamma_X$

$I = (1 + \eta) I_0$

$I \propto 1/r^6$ $\qquad\qquad\qquad\qquad\qquad\qquad$ multiplicity$=2nI + 1$

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