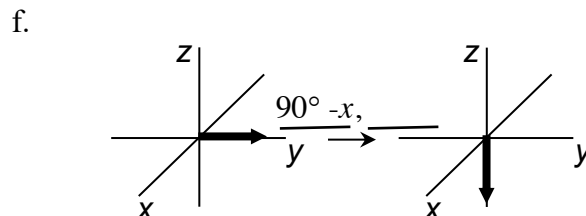
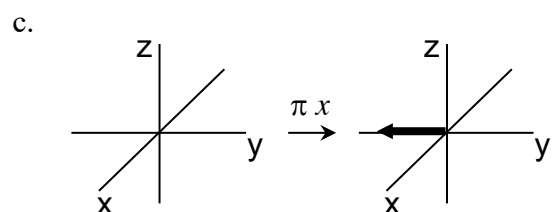
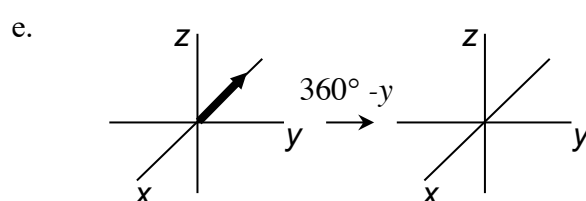
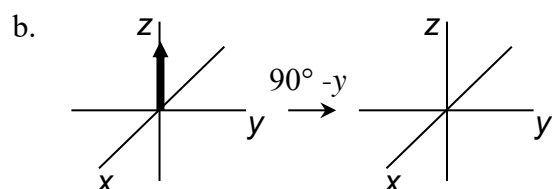
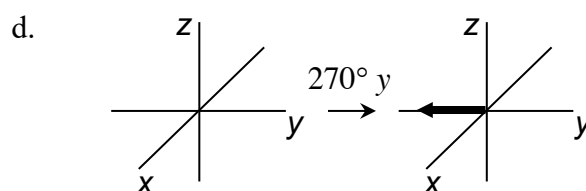
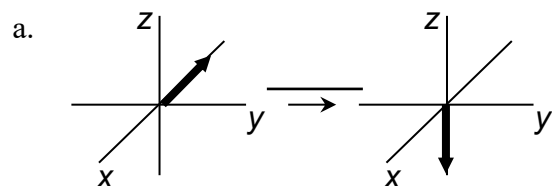
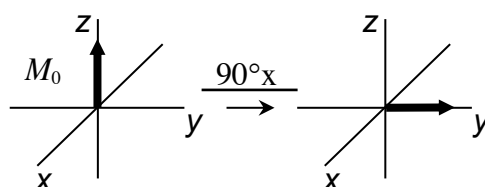
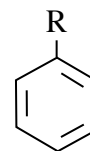


**Exam 2: CHEM/BCMB 4190/6190/8189 (146 points) Thursday, 30 September, 2021**

1). In the example (right), the effect of a  $90^\circ$  ( $\pi/2$ ) pulse applied along the “x” axis ( $90^\circ x$ ) is shown for a bulk magnetization vector ( $M_0$ ) at equilibrium (on the ‘z’ axis). For ‘b’, ‘c’, ‘d’ and ‘e’ below, show the effects of the indicated pulses by drawing the missing (originating or resulting) vectors on the coordinate axes. For ‘a’ and ‘f’, fill in the blank with the correct pulse (angle and axis along which it is applied) that will promote the indicated movement of the bulk magnetization vector. For ‘f’, first consider the effect of the first pulse, then fill in the blank with the correct second pulse that gives the correct final result. There may be more than one correct answer for some. (12 points)

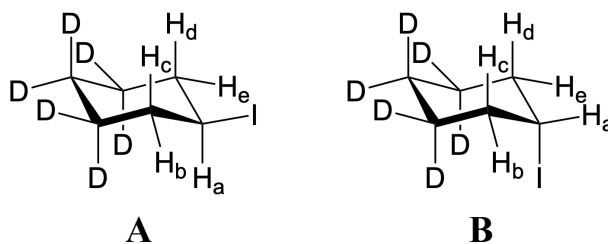


2). For monosubstituted benzene molecules of the type shown at the right, the chemical shifts at the ortho, meta, and para positions can be calculated by the following simple empirical relationship:  $\delta^1\text{H} = 7.27 + \delta_{\text{corr}}$ , where  $\delta_{\text{corr}}$  is an empirical correction factor from a table, and is specific for the ortho ( $\delta_{\text{ortho}}$ ), meta ( $\delta_{\text{meta}}$ ), or para ( $\delta_{\text{para}}$ ) position. For instance, when  $\text{R} = -\text{OCOCH}_3$ ,  $\delta^1\text{H}_{\text{para}} = 7.27 + (\delta_{\text{para}}) = 7.27 + (-0.13) = 7.14$  ppm. For  $\text{R} = -\text{COR}$  and  $\text{R} = -\text{NH}_2$ , the entries for  $\delta_{\text{ortho}}$ ,  $\delta_{\text{meta}}$ , and  $\delta_{\text{para}}$  are missing from the table below. The numerical values for these entries are, from smallest to largest, -0.75, -0.65, -0.25, 0.14, 0.21, and 0.62. Your job is to put these numbers in their correct places in the table. In order to receive credit, you will have to a). draw appropriate chemical structures to justify your table entries, and b). discuss why certain positions are more/less shielded relative to others. (16 pts)



R	$\delta_{\text{corr}}$		
	$\delta_{\text{ortho}}$	$\delta_{\text{meta}}$	$\delta_{\text{para}}$
-COR			
-NH <sub>2</sub>			
-OCOCH <sub>3</sub>	-0.25	0.03	-0.13

3). The two chair conformers of hexa-deuteroiodocyclohexane are shown (right). In these structures, the deuterium ( $^2\text{H}$ ) atoms are represented by 'D'. The  $^1\text{H}$  NMR spectrum of this compound was acquired, with broadband decoupling of deuterium, at very low temperature.



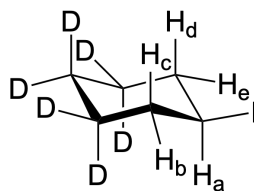
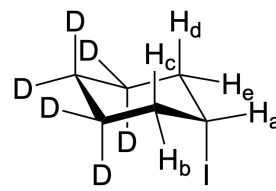
a). *In general*, why might it be advantageous, in some cases, to acquire NMR spectra at low temperature. (2 points)

b). For compounds such as cyclohexane derivatives, why might it be advantageous, under some circumstances, to acquire the spectra at very low temperature. (4 points)

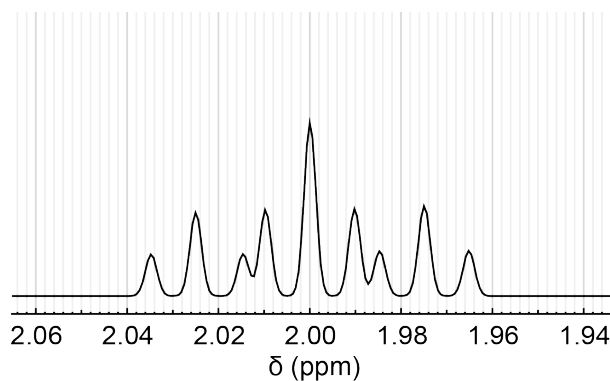
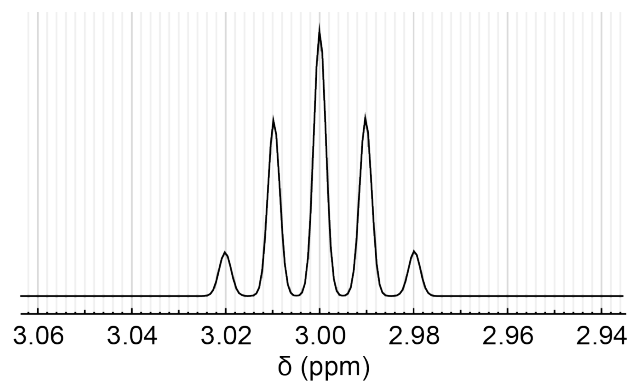
c). In a  $^1\text{H}$  NMR spectrum of only conformer 'A' of hexa-deuteroiodocyclohexane, how many signals would you expect to see? Likewise, in a  $^1\text{H}$  NMR spectrum of only conformer 'B' of hexa-deuteroiodocyclohexane, how many signals would you expect to see? You will have to justify your answers for credit. **(6 points)**

d). In a  $^{13}\text{C}$  NMR spectrum of only conformer 'A' of hexa-deuteroiodocyclohexane, how many signals would you expect to see? Likewise, in a  $^{13}\text{C}$  NMR spectrum of only conformer 'B' of hexa-deuteroiodocyclohexane, how many signals would you expect to see? You will have to justify your answers for credit. **(6 points)**

e). In the  $^1\text{H}$  NMR spectrum of hexa-deuteroiodocyclohexane, acquired with broadband decoupling of deuterium, at very low temperature using a 400 MHz magnet, the signals below are from hydrogen 'Ha'.

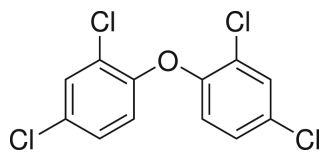
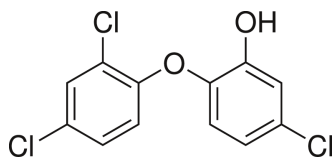
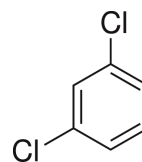
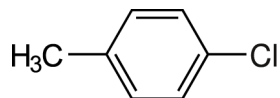
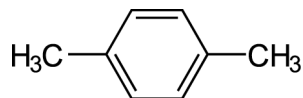
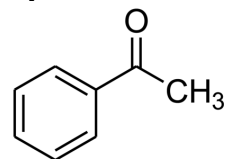
**A****B**

Which conformer, 'A' or 'B', gives the signal below on the left for 'Ha', and which gives the signal below on the right for 'Ha'? You will have to provide a strong justification for credit. As part of this justification, you will have to determine the values of the coupling constants in each signal and assign them to the correct coupled  $^1\text{H}$  nuclei. You also will have to describe the multiplicity of each signal and why that particular multiplicity is observed, based on the structure and the coupling constants. **(8 points)**



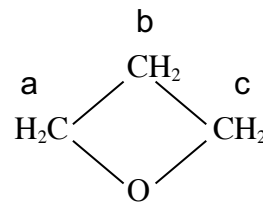
4). In a magnetic field (600 MHz), the energy difference between the lowest and highest energy states for a particular nucleus ( $\gamma = 2.00 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}$ ) is  $2.080 \times 10^{-25} \text{ J}$ . What is the spin angular momentum quantum number,  $I$ , for this nucleus? You will have to show your work and explain your answer for credit. **(6 points)**

5). How many signals will there be in  $^{13}\text{C}$  NMR spectra of each of the following compounds? You will have to justify your reasoning in each case for credit. (12 points)

**A****B****C****D****E****F**

6). The following questions regarding the molecule oxetane (right).

a. Are the hydrogens labeled 'a' homotopic, enantiotopic, or diastereotopic? **(2 points)**



b. Are the hydrogens labeled 'b' homotopic, enantiotopic, or diastereotopic? **(2 points)**

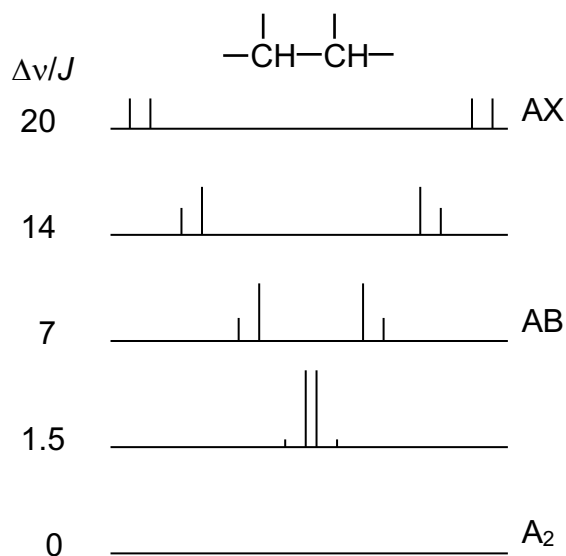
c. Will the hydrogens labeled 'c' always have the same chemical shift? You will have to explain for credit. **(4 points)**

d. Sketch the signals that would appear in the  $^1\text{H}$  NMR spectrum of oxetane in  $\text{CDCl}_3$ . Clearly indicate which hydrogens give rise to each signal. For each multiplet, indicate the expected relative intensities of the individual peaks in that multiplet. For credit you will have to explain in detail your signals/answers. **(6 points)**



Name \_\_\_\_\_

7). The  $^1\text{H}$  NMR spectra (right) show the signals from two hydrogens on adjacent carbon atoms that are coupled ( $^3J$ ) to one another. From top to bottom, the spectra clearly demonstrate the spectral changes that occur when the difference between the Larmor frequencies of the two hydrogens decreases. The spin system designations (AX, AB,  $A_2$ ) are shown. A space is provided for the  $A_2$  spectrum but the spectrum is not shown.

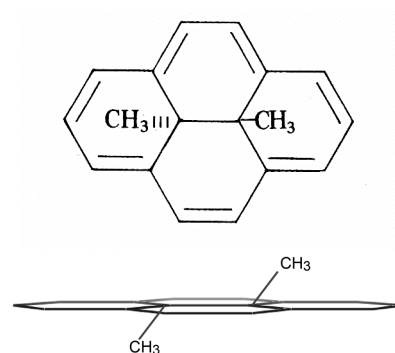


a. What are 'AX' and 'AB' spin systems? (4 points)

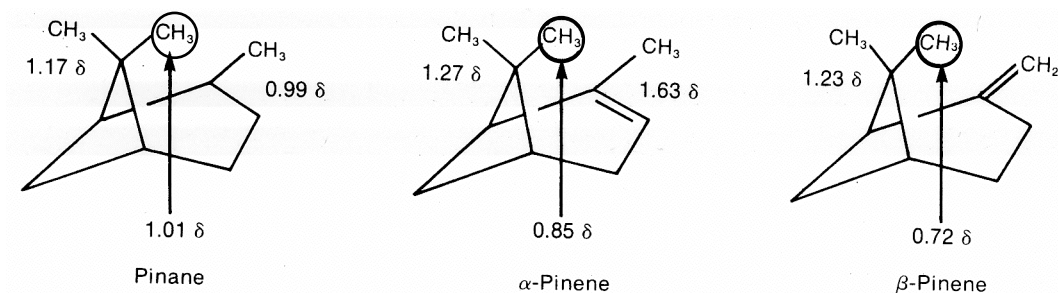
b. Draw the expected  $A_2$  spectrum in the space provided above. Provide an explanation/justification for your answer. Your explanation (and drawing) should include the expected intensity of the signals/peaks in the  $A_2$  system relative to the intensities of the peaks in the AX system. (6 points).

c. What word or term in NMR spectroscopy is also used to describe nuclei that comprise  $A_2$  systems? Please explain. (4 points)

8). The chemical shifts of the hydrogen nuclei in benzene are 7.28 ppm. *Estimate* the chemical shifts for the equivalent hydrogens of the methyl groups in the dimethylpyrene compound shown (right). *To receive credit you will have to provide a good justification for your estimate.* (4 points)



9). The  $^1\text{H}$  NMR chemical shifts (ppm) for the hydrogen nuclei in the indicated (circled) methyl groups in pinane and  $\alpha$ - and  $\beta$ -pinene are shown below. Provide an explanation for the variation of these methyl (circled)  $^1\text{H}$  chemical shifts between pinane,  $\alpha$ -pinene, and  $\beta$ -pinene. (6 points)

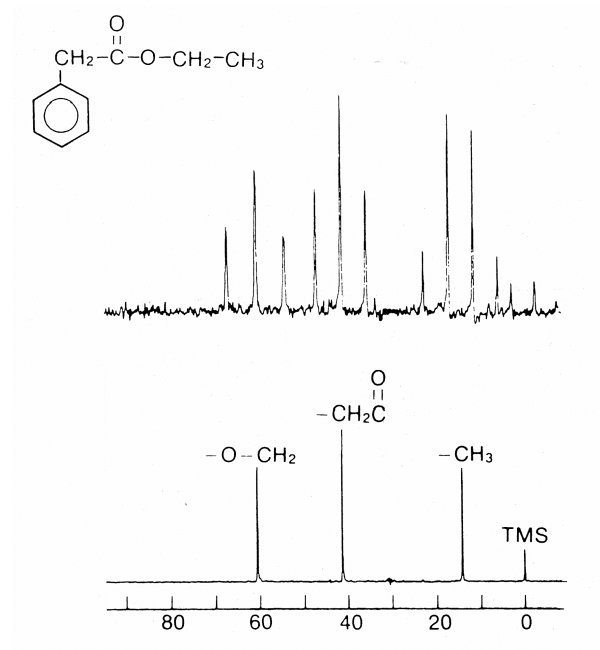
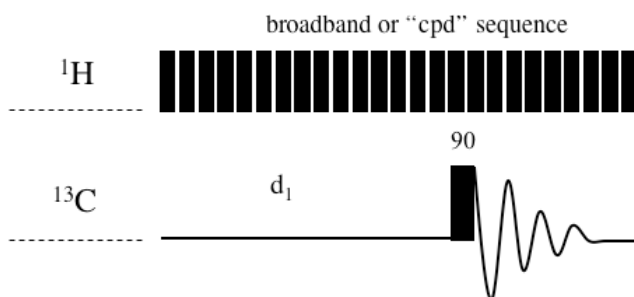


**10).** Please explain what “shielding” means with respect to NMR. Please use complete sentences and avoid using symbols, equations and drawings. Your explanation should address the relationship between shielding and resonance frequency. **(6 points)**

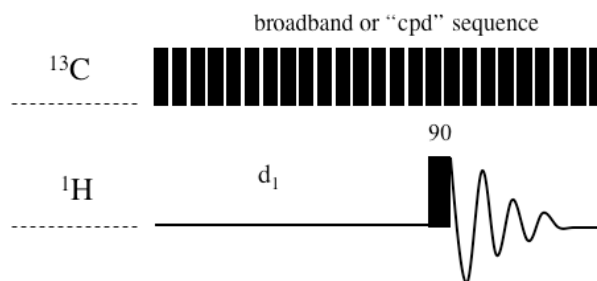
**11).** For a sample of  $\text{CHCl}_3$ , you apply a very long (seconds), low power pulse at the  $^1\text{H}$  frequency of the single  $^1\text{H}$  nucleus in the molecule. Immediately after this pulse, you apply a normal, high power 90 degree pulse at the same frequency and then record the FID. Sketch what you would expect the FID to look like. Also, sketch the spectrum you would expect to observe following Fourier transformation of the FID. You must thoroughly explain your answers for credit. **(6 points)**.

**12).** Circle the word in each pair of parentheses that makes the following statement true: As the value for the shielding constant,  $\sigma$ , decreases, this indicates (decreased / increased) shielding of a nucleus, a/an (decrease / increase) in the effective magnetic field experienced by the nucleus, a/an (downfield / upfield) shift in the chemical shift, and a (lower / higher) resonance frequency for the nucleus. **(4 points)**

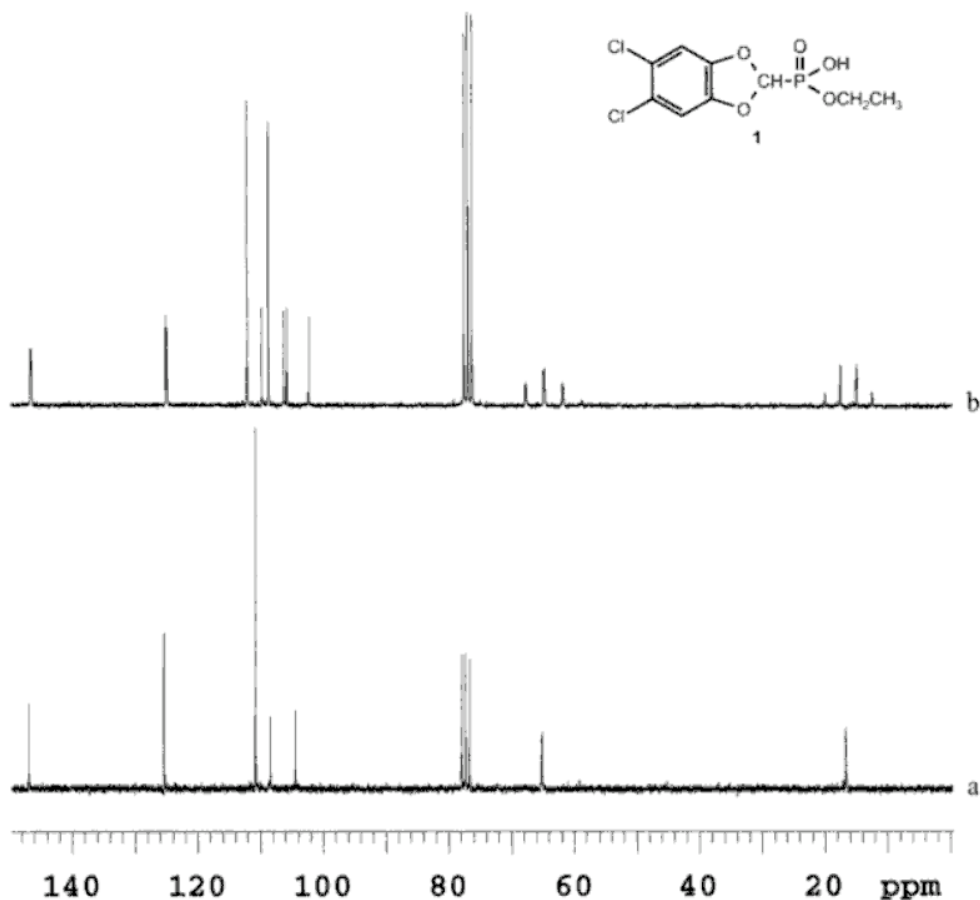
13). For ethyl phenylacetate, the regions from ~ 0-90 ppm of the  $^1\text{H}$ -coupled (top) and  $^1\text{H}$ -decoupled (bottom)  $^{13}\text{C}$  NMR spectrum are shown (right). The pulse sequence used to record the decoupled spectrum on natural isotopic abundance phenylacetate is shown below.



Sketch the simple  $^1\text{H}$  NMR spectrum of the  $-\text{O}-\text{CH}_2-\text{CH}_3$  group of ethyl phenylacetate. Then sketch the  $^1\text{H}$  NMR spectrum that you would observe if you recorded the  $^1\text{H}$  spectrum of natural isotopic abundance phenylacetate with  $^{13}\text{C}$  broadband decoupling (pulse sequence shown at right). You will have to explain the appearance of each signal in the spectra, and the differences observed when using the decoupling sequence. (4 points)



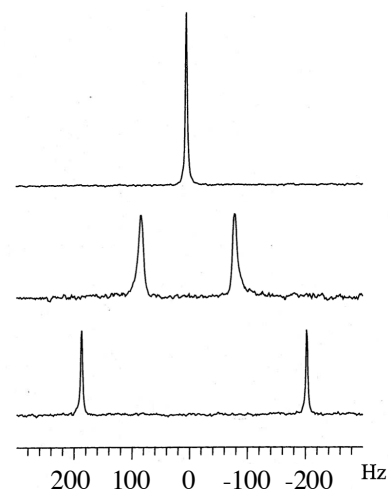
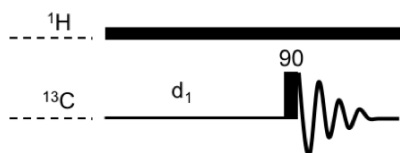
14). Shown (right) are two  $^{13}\text{C}$  spectra of the compound shown. One was acquired with broadband  $^1\text{H}$ -decoupling, and the other with gated  $^1\text{H}$ -decoupling. The signal at 78 ppm is due to solvent.



a. Which spectrum was acquired with broadband  $^1\text{H}$ -decoupling and which was acquired with gated broadband  $^1\text{H}$ -decoupling. You must explain your reasoning for credit. (4 points)

b. Given the signal-to-noise of each spectrum, what can you conclude about the differences between acquisition parameters for these two spectra? You must explain your reasoning for credit. (4 points)

15). The  $^{13}\text{C}$  NMR spectrum (right, bottom) shows the  $^{13}\text{C}$ - $^1\text{H}$  doublet from a methine group in the molecule  $\text{CHX}_3$ , where 'X' are halides (i.e., chloroform). The spectrum at the top shows the results of selective, on-resonance, decoupling of  $^1\text{H}$  from  $^{13}\text{C}$  in this molecule. This is done with the pulse sequence below with the decoupler frequency matching the Larmor frequency of the  $^1\text{H}$  in the molecule. As a result, the  $^{13}\text{C}$  signal is decoupled from the  $^1\text{H}$  and appears as a singlet. The spectrum in the center (right) is the result of off-resonance decoupling of  $^1\text{H}$ , where the decoupler frequency is not at the Larmor frequency of the  $^1\text{H}$ . The multiplet has partially collapsed (the apparent coupling constant is smaller than the actual value).



a. What determines the difference between the actual and observed coupling constants (in Hz) in an off-resonance decoupling experiment such as the one described for the spectrum above? (4 points)

b. Calculate the difference between the Larmor frequency of the  $^1\text{H}$  in the molecule and the frequency at which the decoupling field is applied for the off-resonance experiment shown above if the decoupler field strength ( $B_2$ ) used is 10 kHz. (4 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 <sup>a)</sup> [ $eQ$ ] [ $10^{-28} \text{ m}^2$ ]	Natural abundance) [%]	Relative sensitivity <sup>b)</sup>	Gyromagnetic ratio $\gamma^a)$ [ $10^7 \text{ rad T}^{-1} \text{ s}^{-1}$ ]	NMR frequency [MHz] <sup>b)</sup> ( $B_0 = 2.3488 \text{ T}$ )
$^1\text{H}$	1/2	–	99.985	1.00	26.7519	100.0
$^2\text{H}$	1	$2.87 \times 10^{-3}$	0.015	$9.65 \times 10^3$	4.1066	15.351
$^3\text{H}^c)$	1/2	–	–	1.21	28.5350	106.664
$^6\text{Li}$	1	$-6.4 \times 10^{-4}$	7.42	$8.5 \times 10^{-3}$	3.9371	14.716
$^{10}\text{B}$	3	$8.5 \times 10^{-2}$	19.58	$1.99 \times 10^{-2}$	2.8747	10.746
$^{11}\text{B}$	3/2	$4.1 \times 10^{-2}$	80.42	0.17	8.5847	32.084
$^{12}\text{C}$	0	–	98.9	–	–	–
$^{13}\text{C}$	1/2	–	1.108	$1.59 \times 10^{-2}$	6.7283	25.144
$^{14}\text{N}$	1	$1.67 \times 10^{-2}$	99.63	$1.01 \times 10^{-3}$	1.9338	7.224
$^{15}\text{N}$	1/2	–	0.37	$1.04 \times 10^{-3}$	-2.7126	10.133
$^{16}\text{O}$	0	–	99.96	–	–	–
$^{17}\text{O}$	5/2	$-2.6 \times 10^{-2}$	0.037	$2.91 \times 10^{-2}$	-3.6280	13.557
$^{19}\text{F}$	1/2	–	100	0.83	25.1815	94.077
$^{23}\text{Na}$	3/2	0.1	100	$9.25 \times 10^{-2}$	7.0704	26.451
$^{25}\text{Mg}$	5/2	0.22	10.13	$2.67 \times 10^{-3}$	-1.6389	6.1195
$^{29}\text{Si}$	1/2	–	4.70	$7.84 \times 10^{-3}$	-5.3190	19.865
$^{31}\text{P}$	1/2	–	100	$6.63 \times 10^{-2}$	10.8394	40.481
$^{39}\text{K}$	3/2	$5.5 \times 10^{-2}$	93.1	$5.08 \times 10^{-4}$	1.2499	4.667
$^{43}\text{Ca}$	7/2	$-5.0 \times 10^{-2}$	0.145	$6.40 \times 10^{-3}$	-1.8028	6.728
$^{57}\text{Fe}$	1/2	–	2.19	$3.37 \times 10^{-5}$	0.8687	3.231
$^{59}\text{Co}$	7/2	0.42	100	0.28	6.3015	23.614
$^{119}\text{Sn}$	1/2	–	8.58	$5.18 \times 10^{-2}$	-10.0318	37.272
$^{133}\text{Cs}$	7/2	$-3.0 \times 10^{-3}$	100	$4.74 \times 10^{-2}$	3.5339	13.117
$^{195}\text{Pt}$	1/2	–	33.8	$9.94 \times 10^{-3}$	5.8383	21.499

$B_0$ (Tesla, T)	Resonance frequencies (MHz)	
	$^1\text{H}$	$^{13}\text{C}$
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:**

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

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

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

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

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

$$P_z = m\hbar$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$\omega_0 = \gamma B_0$$

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

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

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

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

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

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

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

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

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

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

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

$$AQ = DW * TD$$

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

$$(TD \equiv NP)$$

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

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

$$\Delta \nu \gg J$$

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

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

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