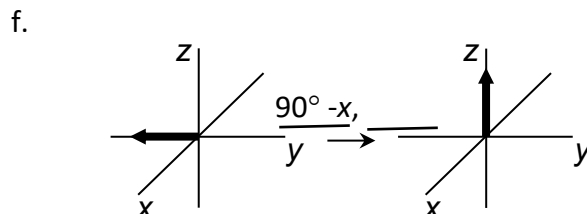
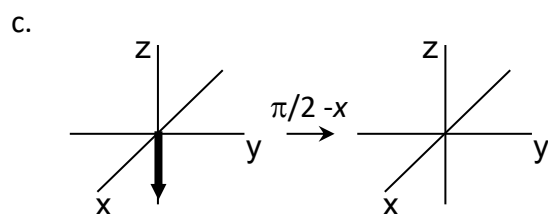
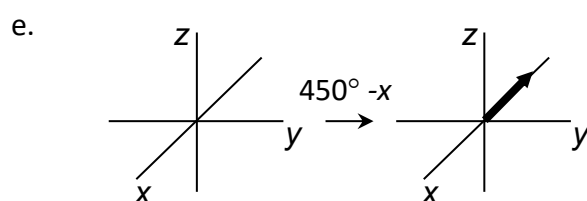
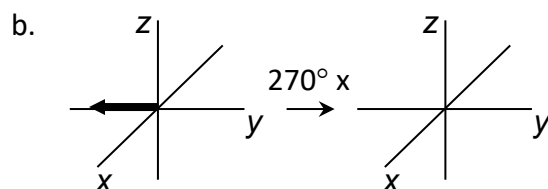
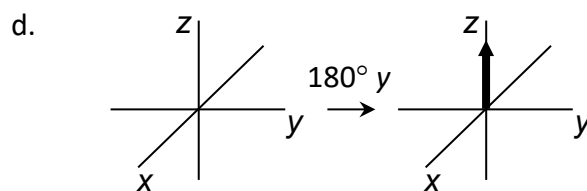
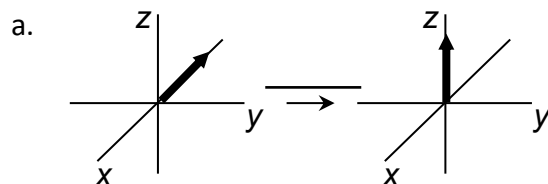
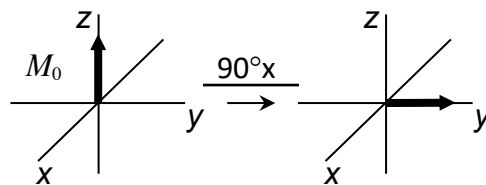


**Exam 2: CHEM/BCMB 4190/6190/8189 (178 points) Thursday, 29 September, 2022**

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)**

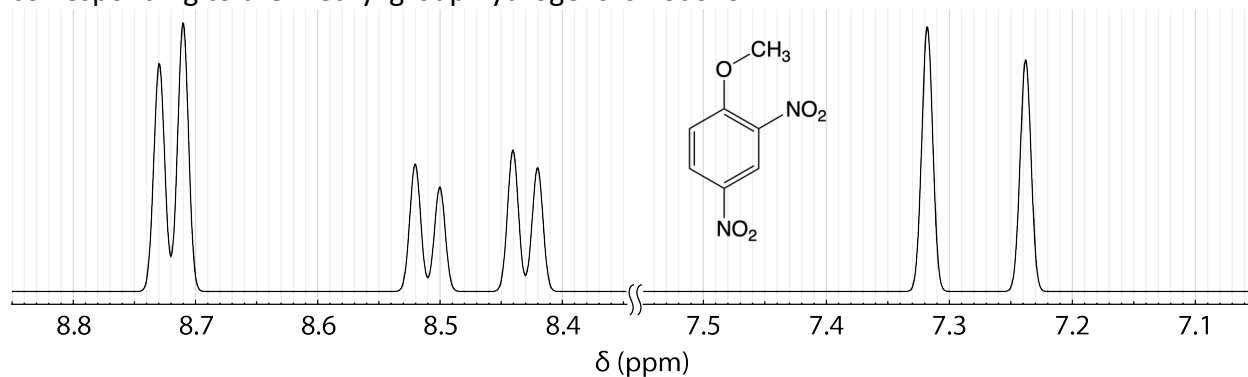


2). For a particular 600 MHz spectrometer system, the actual Larmor/resonance frequency for the hydrogens of TMS is 600.0112729 MHz. The chemical shift,  $\delta$ , of this frequency, is assigned to be 0.0 ppm.

a. What is the actual Larmor/resonance frequency for the  $^1\text{H}$  nuclei in  $\text{H}_2\text{O}$  using this spectrometer system, assuming the chemical shift,  $\delta$ , for the  $^1\text{H}$  in  $\text{H}_2\text{O}$  is 4.76 ppm relative to TMS? You will have to do a calculation or calculations, show your work, and get an answer for credit. **(6 points)**

b. What is the Larmor/resonance frequency for  $^{13}\text{C}$  at a magnetic field strength of 7.05 Tesla ( $B_0=7.05\text{ T}$ )? You will have to do a calculation and show your work for credit. **(4 points)**

3). The downfield region of the  $^1\text{H}$  NMR spectrum (100 MHz) of a benzene derivative (inset) is shown below. The signals from all of the aromatic hydrogens appear in this region. The signal corresponding to the methyl group hydrogens is not shown.



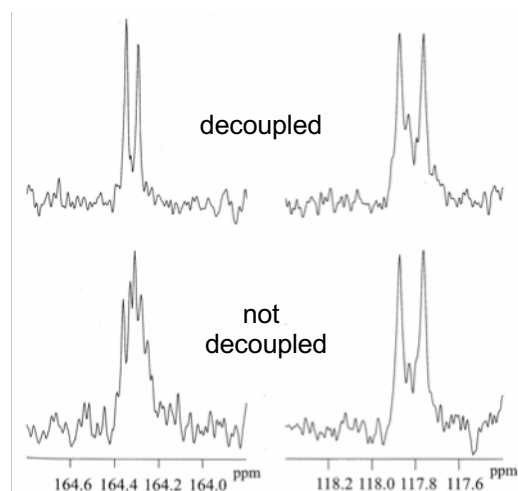
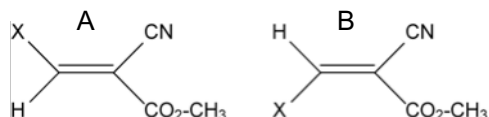
a. How many signals are there in this region of the spectrum? You will have to explain, basing your explanation on the number and type of hydrogens giving rise to the signals. **(4 points)**

b. From the spectrum, estimate the magnitudes of the coupling constants. Your answer must be in Hz. You also must state clearly what  $^1\text{H}$  nuclei give rise to the coupling/splitting. **(6 points)**

Name \_\_\_\_\_

c. Clearly state which hydrogen results in each signal. You must clearly justify the chemical shift of each hydrogen. You must justify the multiplicity (splitting pattern) of each signal. **(8 points)**

4).  $^{13}\text{C}$  NMR spectra for one of the configurational isomers (either "A" or "B") of the alkene (below) were recorded. Two signals from the spectra (one at  $\sim 164.3$  ppm, the other at  $\sim 117.8$  ppm) are shown (right). The top spectrum ("decoupled") was recorded with selective decoupling of the hydrogens on the  $-\text{CH}_3$  group. The bottom spectrum ("no decoupling") was recorded without decoupling.

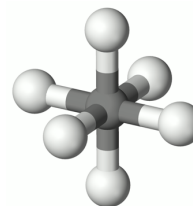


a. Explain in detail how selective  $^1\text{H}$ - $^{13}\text{C}$  decoupling of the hydrogens of the  $-\text{CH}_3$  in this molecule is performed. (4 points)

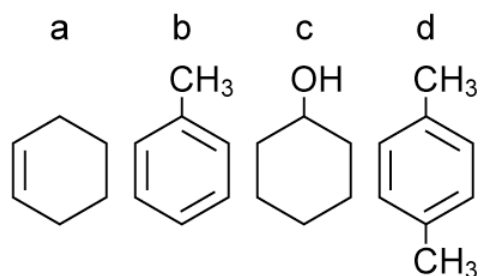
b. One of the signals shown (above) from the  $^{13}\text{C}$  spectrum is from the -CN group, and the other is from the -CO<sub>2</sub>- group. Based on the results of the selective decoupling experiment, and any other information available in the spectra, identify which nucleus gives rise to each signal. You will have to provide clear and complete justification/explanation of your answer in order to receive credit. **(6 points)**

c. Which of the two configurational isomers of the alkene compound shown, "A", or "B", gives rise to the spectra shown above? You must clearly and thoroughly justify your answer for credit. **(6 points)**.

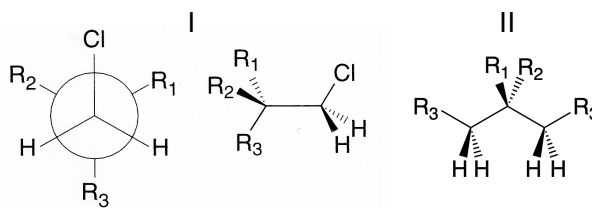
5). In the  $[\text{PF}_6]^-$  ion (right), the fluorides are octahedrally arranged and they are chemically equivalent. Please explain completely what is meant by chemical equivalence, and why the fluorine nuclei in this ion are chemically equivalent. (4 points)



6). For each of the molecules shown (a-d, right), state the number of signals that would be observed for each in the simple  $^{13}\text{C}$  NMR spectrum, and justify your reasoning. (8 points)



7). Consider the molecules shown (I and II, right). For each of the questions, you will have to provide an adequate explanation for credit.



a. For I, if  $R_1=R_2=R_3=H$ , do the methylene hydrogens have the same chemical shift? Are they homotopic, enantiotopic, diastereotopic, or something else. Please explain. **(4 points)**

b. For I, if  $R_1=R_2=R_3=CH_3$ , are the nine methyl hydrogens equivalent? Please explain. **(4 points)**

c. For I, if  $R_1=R_2=CH_3$  and  $R_3=Cl$ , do the methylene hydrogens have the same chemical shift? Are they homotopic, enantiotopic, diastereotopic, or something else. Please explain. **(4 points)**

d. For II, if  $R_1 \neq R_2$ , do either pair of methylene hydrogens have the same chemical shift? Please explain. **(4 points)**

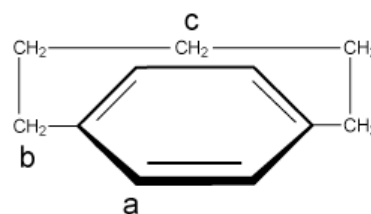


8). Here is a question I received via email from a laboratory coordinator at the New Jersey Institute of Technology (paraphrased slightly):

*“Following a pulse, the magnetization vectors  $M_x$  and  $M_y$  begin to decrease as a function of time due to  $T_2$  relaxation, and  $M_z$  increases as a function of time due to  $T_1$  relaxation. Will the magnitude of the sum of the vectors  $M_x$ ,  $M_y$  and  $M_z$  remain the same?”*

Please provide a correct answer. You must clearly explain your answer and give an example that clearly illustrates your answer. **(6 points)**

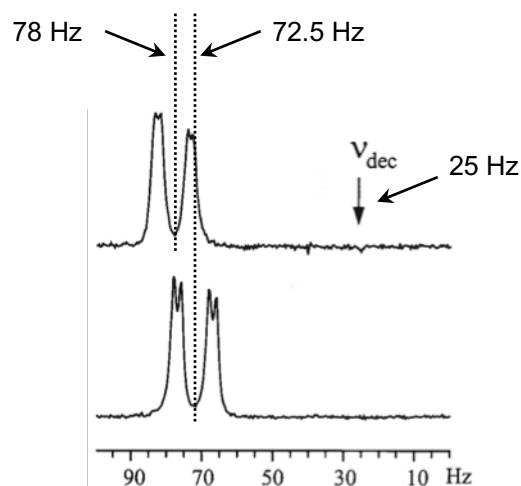
9). In the compound shown (right), three groups of hydrogen nuclei are labeled a, b, and c. The chemical shifts of these are -1.0 ppm, 2.0 ppm and 7.5 ppm, from high to low field. Match the correct shift with the correct nucleus. You must justify all of your answers (no “by default”). (NOTE: although it may not be clear from the drawing, the methylene group ‘c’ is positioned above the plane of the ring). **(6 points)**



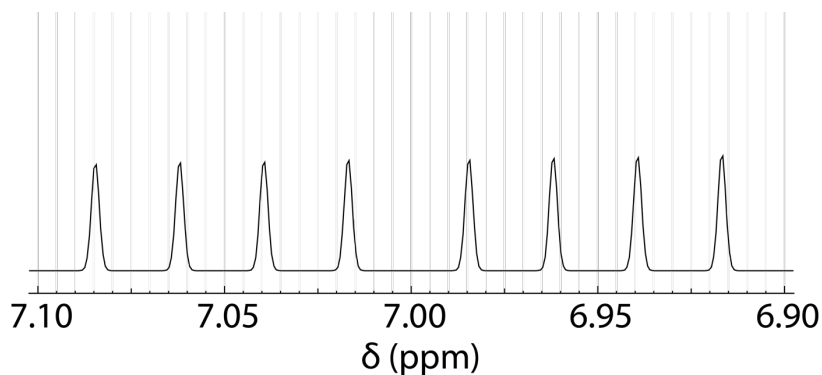
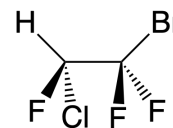
10). The Bloch-Siegert effect/shift can be used to measure the field strength of a long, low power selective pulse, such as that used for homonuclear decoupling. Likewise, the off resonance homonuclear decoupling method can also be used to measure decoupling field strength.

a. Explain or define what the Bloch-Siegert shift is? (4 points)

b. For the  $^1\text{H}$  spectra shown (right), the spectrum on bottom was recorded without decoupling, whereas the spectrum on top was recorded with a low power decoupling field applied at  $\nu_{\text{dec}}$  during the entire experiment. Calculate the strength of the decoupler field (in Hz) that was applied. You must do a calculation and show your work for credit. (6 points)



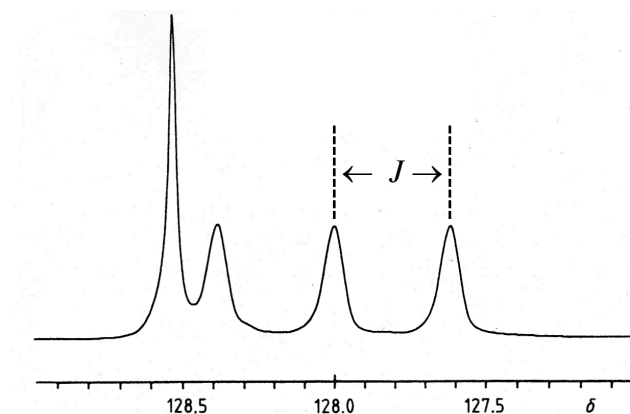
11). In NMR spectra of organic molecules containing fluorine, the coupling between  $^1\text{H}$  and  $^{19}\text{F}$  can result in peak splitting. The one-bond  $^1\text{H}$ - $^{19}\text{F}$  coupling constant ( $^1J_{\text{HF}}$ ) is about 500 Hz. Two-bond HF ( $^1\text{H}$ - $^{19}\text{F}$ ) coupling constants ( $^2J_{\text{HF}}$ ) are typically 30-60 Hz. The three-bond HF coupling constants ( $^3J_{\text{HF}}$ ) are typically 5-20 Hz. The  $^1\text{H}$  NMR spectrum (400 MHz) of a fluoroethane derivative (right) is shown below.



a. Describe the  $^1\text{H}$  spectrum of the fluoroethane derivative shown above. State how many signals there are and what their multiplicities are. Justify your statements based on the nuclei present in the molecule and by determining the values of the coupling constants and demonstrating how you determined them. (6 points)

b. The presence of  $^1\text{H}$ - $^{19}\text{F}$  coupling never results in second order spectra. Please explain why. You should do some sort of quantitative demonstration to back up your claims. (8 points)

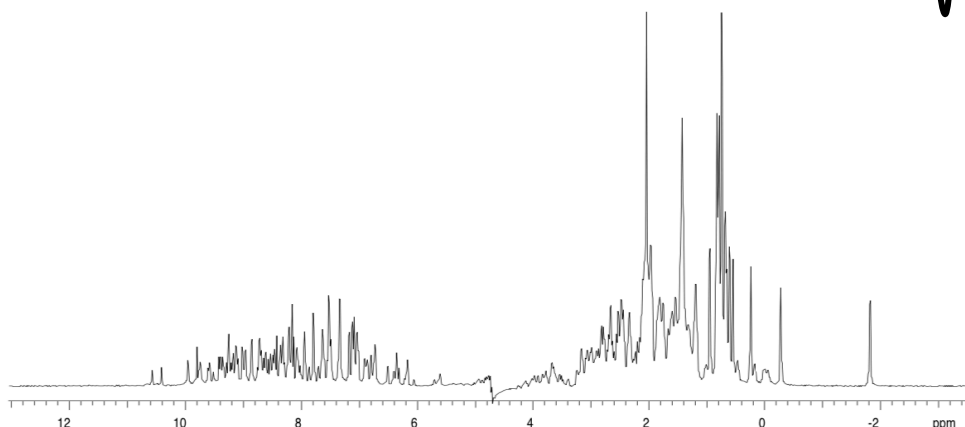
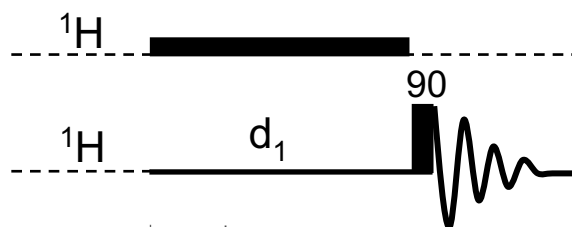
12). The  $^{13}\text{C}$  NMR spectrum shown (right) is from a mixture of  $\text{C}_6\text{H}_6$  (benzene) and  $\text{C}_6\text{D}_6$  (deuterated benzene). The  $B_0$  field was 5.87 T.



a. What are the chemical shifts of the two  $^{13}\text{C}$  signals present? Which is from  $\text{C}_6\text{H}_6$  and which is from  $\text{C}_6\text{D}_6$ ? You will have to explain your answer for credit. This will include a detailed analysis of multiplet structures, including intensities of peaks in multiplets. **(6 points)**

b. What is the correct nomenclature for the indicated coupling constant? **(4 points)**

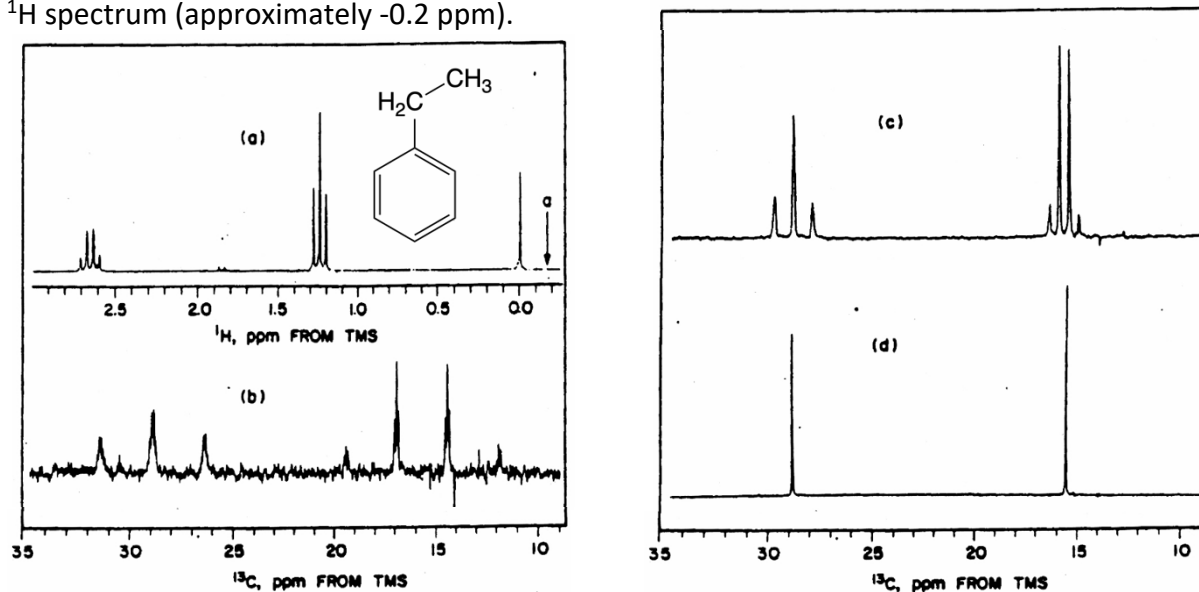
**13).** The spectrum (below) is of a protein molecule called ubiquitin. The concentration of the ubiquitin in the sample is 1 mM. The protein is dissolved in water at neutral pH. The pulse sequence used to acquire the spectrum is shown (right).



**a.** The signal from water is at 4.76 ppm in the spectrum. It is quite small, despite the fact that the concentration of water is 55 M (55,000 mM) and the concentration of the ubiquitin protein is only approximately 1 mM. Please explain how the pulse sequence is able to dramatically, and selectively, attenuate the signal from water. **(6 points)**

**b.** An unfortunate consequence of using this method to attenuate H<sub>2</sub>O signal in aqueous protein solutions is that the signals from hydrogens in -NH and -NH<sub>2</sub> groups (6 – 12 ppm) of proteins are also often slightly attenuated, but signals from -CH, -CH<sub>2</sub>, -CH<sub>3</sub>, and other carbon-bound hydrogens are not. Explain how this occurs. **(4 points)**

14). The  $^1\text{H}$  NMR spectrum for the ethyl group of ethyl benzene is shown in spectrum 'a' below, and the  $^{13}\text{C}$  spectrum, without any decoupling, is shown in spectrum 'b'. These spectra were acquired with a 300 MHz magnet (7.05 T). The fully broadband  $^1\text{H}$  decoupled  $^{13}\text{C}$  spectrum is shown in spectrum 'd'. The off-resonance decoupled  $^{13}\text{C}$  spectrum is shown in spectrum 'c'. The frequency at which the off-resonance decoupling field was applied is indicated by the arrow in the  $^1\text{H}$  spectrum (approximately -0.2 ppm).



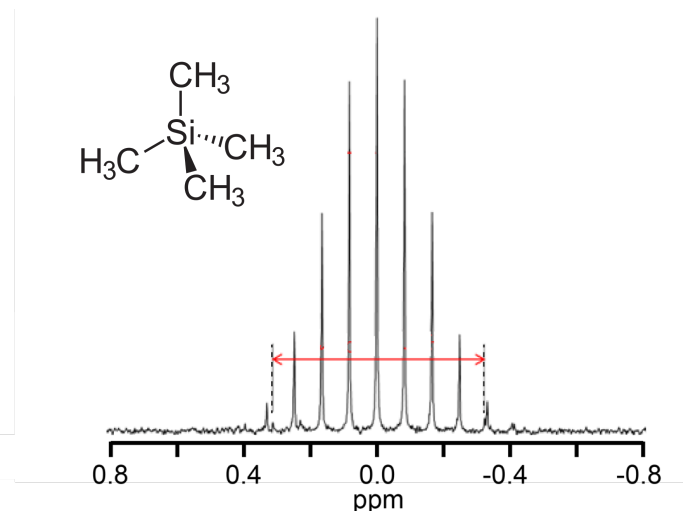
a. There are three signals in the  $^1\text{H}$  spectrum of the ethyl group of ethyl benzene. Assign each signal to the correct hydrogen or hydrogen nuclei that give rise to it. You will have to explain and justify your reasoning. (4 points)

b. There are two signals in the  $^{13}\text{C}$  spectrum of the ethyl group of ethyl benzene. Assign each signal to the correct carbon nucleus or nuclei that give rise to it. You will have to explain and justify your reasoning. (4 points)

c. For the methyl group, estimate the -C-H coupling constant. You will have to explain, do a calculation, and give an answer. **(6 points)**

d. If the -C-H coupling constant for the methyl group is 200 Hz, and it is reduced to 40 Hz by the off-resonance decoupling, what is the decoupler field strength that was used for the off-resonance decoupling? Assume that the frequency at which the off-resonance decoupling field was applied -0.2 ppm, as indicated in spectrum 'a'. You will have to do a calculation and get a result. **(6 points)**

**15).** The compound TMS (tetramethylsilane, right) is a symmetrical molecule where all  $\text{-CH}_3$  groups are in identical chemical environments. The chemical shift of the hydrogen atoms is used as a universal chemical shift standard in organic chemistry for  $^1\text{H}$  (0.00 ppm), as is the chemical shift of the  $^{13}\text{C}$  atoms (0.00 ppm). Likewise, the chemical shift of the Si atom is often used as a chemical shift standard for  $^{29}\text{Si}$  (0.00 ppm). The  $^{29}\text{Si}$  NMR spectrum of TMS is shown (right).



**a.** Please explain why the spectrum looks as it does. Your explanation should include an explanation of how many signals/peaks should be observed, are observed, and why, and the relative intensities of the peaks. **(8 points)**



**b.** In the spectrum is an arrow pointing to two dashed vertical lines. These dashed lines point to two very small peaks that clearly are not part of the larger multiplet. The lines are 50.8 Hz apart (length of the arrow in Hz). Please explain what gives rise to these two small peaks, why they are small, what their approximate intensities should be, and why they are 50.8 Hz apart. **(4 points)**

**c.** What field strength, in Tesla, was the magnet that was used to acquire this  $^{29}\text{Si}$  spectrum? You will have to perform a calculation and show your work for credit. **(6 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:**

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

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

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

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

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

$$P_z = m\hbar$$

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

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

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

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

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

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

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

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

$$m = (-I, -I+1, -I+2, \dots, I) \quad (2I+1)$$

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

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

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

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

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

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

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

$$\omega_0 = \gamma B_0$$

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

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

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

$$AQ = DW * TD$$

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

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

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

$$(TD \equiv NP)$$

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

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

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

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

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

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

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

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

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

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

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