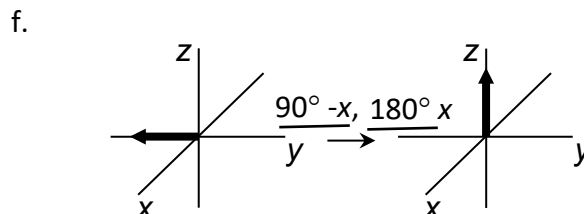
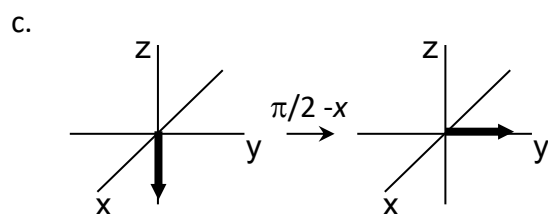
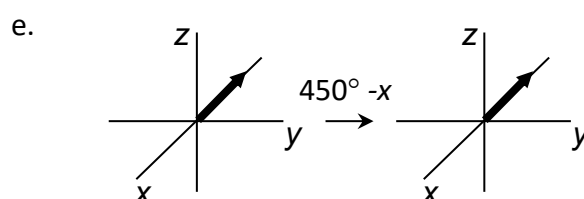
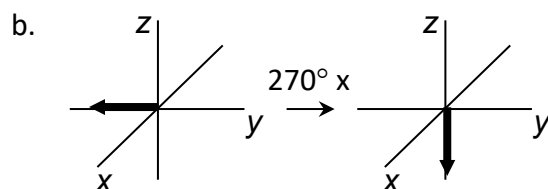
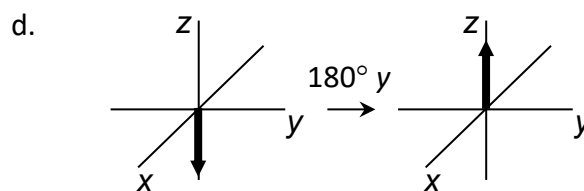
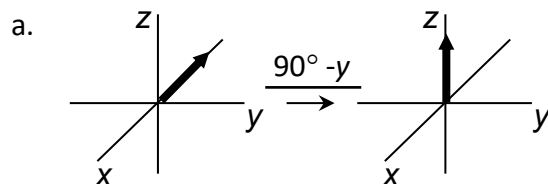
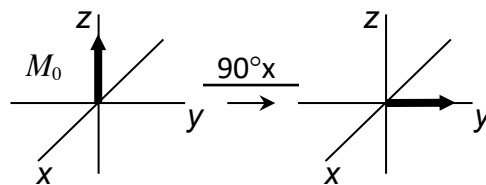


Exam 2: CHEM/BCMB 4190/6190/8189 (178 points) Thursday, 29 September, 2022

1). In the example (right), the effect of a 90° ($\pi/2$) pulse applied along the "x" axis (90° x) is shown for a bulk magnetization vector (M_0) at equilibrium (on the 'z' axis). For '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, δ , of this frequency, is assigned to be 0.0 ppm.

a. What is the actual Larmor/resonance frequency for the ^1H nuclei in H_2O using this spectrometer system, assuming the chemical shift, δ , for the ^1H in H_2O 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)**

Chemical shifts, or chemical shift changes, are frequencies (or frequency changes) normalized to the "observe frequency", i.e. the magnetic field strength expressed in MHz, as shown below. Knowing the difference in the chemical shifts for TMS and H_2O ($\Delta\delta = 4.76 - 0.0 = 4.76$ ppm), we can then calculate the frequency difference and the Larmor frequency for the ^1H nuclei in H_2O :

$$\Delta\delta = \frac{\Delta\nu}{\text{observe frequency}} \times 10^6 \quad \Delta\nu = \frac{\Delta\delta \times \text{observe frequency}}{10^6} = \frac{4.76 \times 600.0112729}{10^6}$$

$$\Delta\nu = \frac{4.76 \times 600.0112729}{10^6} = 0.0028561 \text{ MHz}$$

Remembering that higher chemical shifts correspond to higher frequencies, the Larmor frequency for H_2O is equal to $600.0112729 + 0.0028561 = 600.014129$ MHz.

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

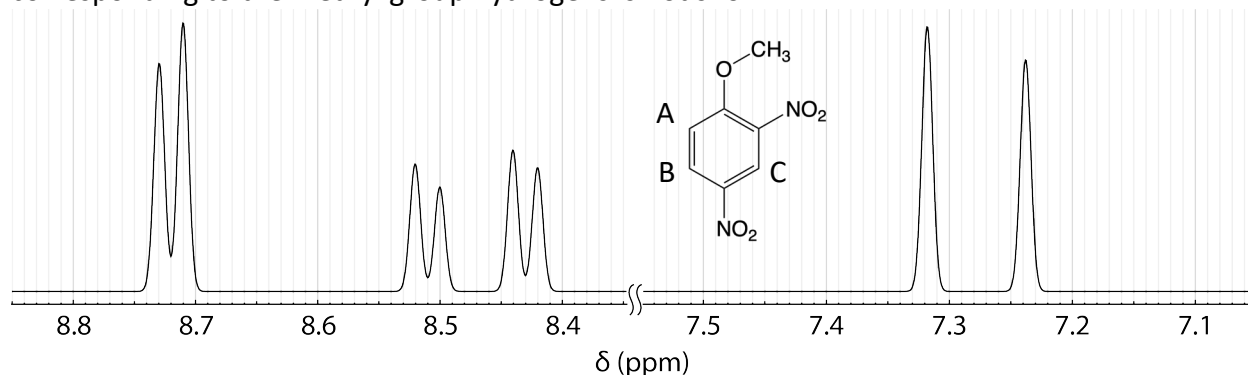
The Larmor frequency is directly proportional to magnetic field strength, as shown below, and we can calculate the frequency directly, in Hz, knowing the value for the gyromagnetic ratio of ^{13}C :

$$\nu_L = \frac{\gamma B_0}{2\pi} = \frac{\omega_0}{2\pi} = \frac{6.7283 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1} \times 7.05 \text{ T}}{2\pi} = 75.5 \text{ MHz}$$

Or, given the linear relationship of the Larmor frequency and B_0 , if the Larmor frequency at some other field strength is known, the frequency is readily calculated:

$$\nu_L = 100.6 \text{ MHz at } 9.4 \text{ T, thus, at } 7.05 \text{ T, } \nu_L = 100.6 \times \frac{7.05}{9.4} = 75.5 \text{ MHz}$$

3). The downfield region of the ^1H 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)**

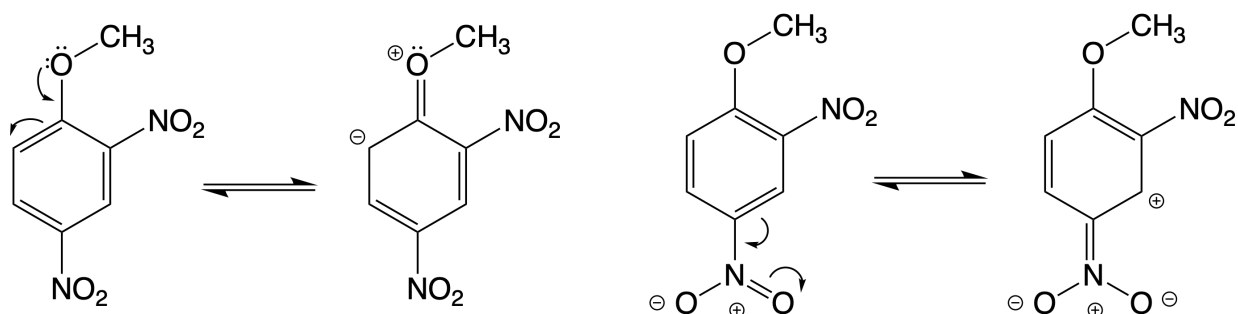
There are three signals, because there are three aromatic hydrogens (A, B, and C) all in different chemical environments.

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

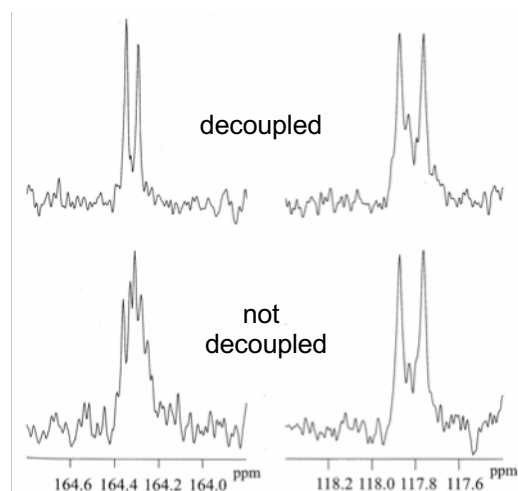
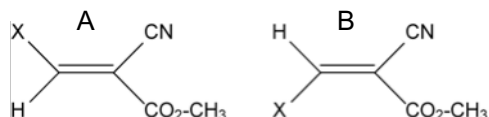
There is one larger coupling constant and one smaller coupling constant. The larger one is the three-bond coupling between nuclei A and B. From the spectrum, the large peak separation seen in the upfield signals is about 0.08 ppm, which, for 100 MHz, is 8 Hz ($^3J_{AB}=8$ Hz). The other coupling is the four-bond coupling between nuclei B and C. From the spectrum, the large peak separation seen in the downfield signals is about 0.02 ppm, which, for 100 MHz, is 2 Hz ($^4J_{BC}=2$ Hz).

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)**

From 'b', the two upfield signals, at 7.28 and 8.47 ppm, are from nuclei A and B because of the large three bond coupling constant (8 Hz). The two downfield signals, at 8.47 and 8.72 ppm, are from nuclei B and C because of the small four bond coupling constant (2 Hz). So, the signal from B must therefore be the signal at 8.47 ppm. This signal is a doublet of doublets, one large coupling constant from the three-bond coupling to A, and a smaller coupling constant from the four-bond coupling to C. The signal at 7.28 must, therefore, be from A. It is a doublet due to the three-bond coupling to B. At first glance this may seem incorrect, because the A hydrogen would be expected to be deshielded (downfield) due to the inductive (electron withdrawing) effect of the oxygen of the ether. However, the ether group is an electron releasing group, and a resonance structure can be drawn with a negative charge localized at the position of A. So, A is therefore highly shielded and far upfield. Likewise, the signal at 8.72 is from C. It is a doublet due to the four-bond coupling to B. Here, the nitro group is electron withdrawing, and a resonance structure can be drawn with a positive charge localized at the position of C. Therefore, the C hydrogen will be highly deshielded, and the furthest upfield.

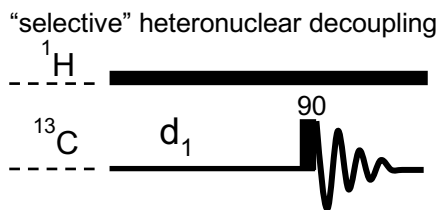


4). ^{13}C NMR spectra for one of the configurational isomers (either "A" or "B") of the alkene (below) were recorded. Two signals from the spectra (one at ~ 164.3 ppm, the other at ~ 117.8 ppm) are shown (right). The top spectrum ("decoupled") was recorded with selective decoupling of the hydrogens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



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

In the ^1H NMR spectrum, the signal from the methyl hydrogens will be a singlet. This signal/peak is from hydrogens attached to ^{12}C . The signal corresponding to the hydrogens bound to ^{13}C nuclei in the methyl group will appear as a doublet, with peaks equidistant (one upfield, one downfield) from the singlet resulting from (^1H bound to ^{12}C). The total integral of these two peaks of the doublet will be about 1% of the integral of the singlet from ^1H bound to ^{12}C , because the natural abundance of ^{13}C is about 1%. In order to perform the selective ^1H - ^{13}C decoupling, during the ^{13}C experiment, the peaks of the doublet (from ^1H bound to ^{13}C) must be selectively irradiated with very long, low power pulses in order to decouple the ^1H from the ^{13}C .



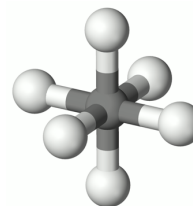
b. One of the signals shown (above) from the ^{13}C spectrum is from the $-\text{CN}$ group, and the other is from the $-\text{CO}_2-$ group. Based on the results of the selective decoupling experiment, and any other information available in the spectra, identify which nucleus gives rise to each signal. You will have to provide clear and complete justification/explanation of your answer in order to receive credit. (6 points)

It is expected that the downfield signal (~ 164.3 ppm) is from the $-\text{CO}_2-$ group because of the two electronegative oxygen atoms bonded directly to the carbon (carbon will be highly deshielded). The other signal (~ 117.8 ppm) then must be from the $-\text{CN}$ group. This is supported by the fact that nitrogen is less electronegative than oxygen, so ^{13}CN signal would be expected to be more upfield (more shielded). ^1H - ^{13}C coupling between the ^{13}C of the $-\text{CN}$ group and the ^1H nuclei of the $-\text{CH}_3$ group would be a 5-bond coupling ($\text{NC}-\text{C}-\text{C}-\text{O}-\text{C}-\text{H}_3$) and it is unlikely that it would be observed. When the methyl group hydrogens are selectively decoupled, we see no change in the signal at ~ 117.8 ppm, confirming our suspicion that this signal is from ^{13}CN . However, the ^1H - ^{13}C coupling between the ^{13}C of the $-\text{CO}_2-$ group and the ^1H nuclei of the $-\text{CH}_3$ group would be a 3-bond coupling ($\text{C}-\text{O}-\text{C}-\text{H}_3$) which most likely would be observed. When the methyl group hydrogens are selectively decoupled, we see a small splitting removed from the signal at ~ 164.3 ppm, confirming that this signal is from $^{13}\text{CO}_2$.

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).

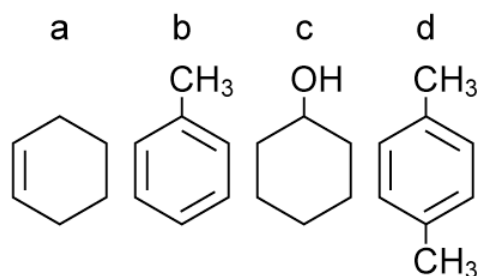
As detailed in the answer to 'b', the ^{13}C signal at ~ 164.3 ppm is from the $-\text{CO}_2-$ group, and the signal at ~ 117.8 is from the $-\text{CN}$ group. The carbon nuclei in each of these groups is three bonds away from the ethylenic hydrogen, so it would be expected that each of these signals would be split into a doublet by this coupling. This is clearly the case, as shown in the spectra. In the case of the $-\text{CO}_2-$ group, this coupling is only clearly observed in the spectrum with selective decoupling of the hydrogens from the $-\text{CH}_3$ group (top spectrum). Although coupling to the ethylenic hydrogen is seen in both signals, the coupling constants are not the same. One, to the $-\text{CN}$ group is significantly larger than the coupling to the $-\text{CO}_2-$ group. So, if the magnitudes of ethylenic couplings are dependent on conformation (cis versus trans), then one could decide if the compound is "A" or "B". As it turns out, trans ethylenic couplings are generally somewhat larger than cis ethylenic couplings, which would indicate that the spectra are from the "A" isomer.

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)

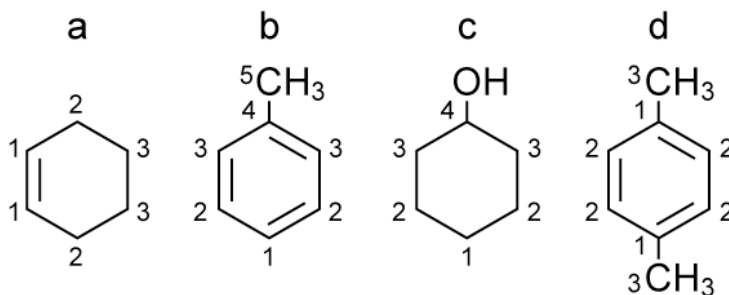


In NMR, nuclei are chemically equivalent if they are in identical chemical environments. They will then have the same chemical shift (and this does not occur coincidentally). A symmetry operation that relates the nuclei or effective symmetry imposed by rotation (for instance, the hydrogens of a methyl group) is required. In the octahedral arrangement, all fluorine nuclei are in identical chemical environments and each can be exchanged for any other by a simple symmetry operation.

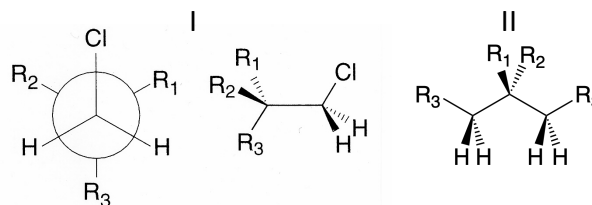
6). For each of the molecules shown (a-d, right), state the number of signals that would be observed for each in the simple ^{13}C NMR spectrum, and justify your reasoning. (8 points)



For each of the molecules, the equivalent positions are indicated in the figure below using integers, with equivalent positions indicated by equal integers. In each case, these are related by a symmetry operation, resulting in chemical equivalence. For molecule 'a', therefore, we would predict three signals in the ^{13}C NMR spectrum. Likewise, for 'b', 'c', and 'd' we would expect five, four and three signals, respectively.



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)**

They are in mirror image environments, so are enantiotopic. They have identical chemical shifts (in achiral solvents). Regardless of conformation (for instance, R_3 -C-C-Cl dihedral angle), the chemical shifts of the methylene hydrogens are the same.

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

Yes, most likely. These are equivalent due to effective symmetry due to rotation about the C-C bond between the tertiary and methylene carbon, and due to fast rotation about the individual C-C bonds between the methyl groups and the tertiary carbon. The only time this would not be the case would be if the R groups are very, very bulky, slowing rotation about the C-C bonds.

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)**

As in 'a', they are in mirror image environments, are enantiotopic, and have the same chemical shift.

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

No. If $R_1 \neq R_2$, there is no symmetry operation that exchanges the hydrogens in either of the two methylene groups. The hydrogens in each methylene group are diastereotopic, and do not have the same chemical shift. There is a symmetry operation that exchanges hydrogens in different methylene groups, but not between hydrogens in a single methylene group.

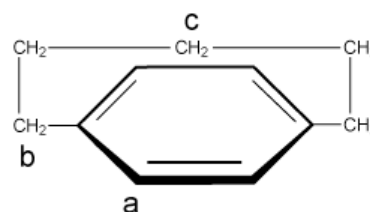
8). Here is a question I received via email from a laboratory coordinator at the New Jersey Institute of Technology (paraphrased slightly):

“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)**

The answer is ‘no’. Do the following experiment. Assume that the T_2 relaxation time is infinitely fast and T_1 is ‘normal’. Apply a 90° pulse. Because the T_2 time is infinitely short, there will be no transverse magnetization ($M_x + M_y = 0$). Also, because T_1 is ‘normal’, just after the pulse, the number of alpha and beta states will still be equal (no significant amount of T_1 relaxation has yet occurred), so $M_z = 0$. Thus, $M_x + M_y + M_z = 0$. Or do the following experiment. Apply a 180° pulse. At all times following the pulse, $M_x = 0$ and $M_y = 0$, so $M_x + M_y = 0$. Immediately following the pulse, $M_z = -M_0$. At a certain time following the pulse ($T_1 \ln(2)$), $M_z = 0$, so, at this time, $M_x + M_y + M_z = 0$. So, clearly there is no requirement that $M_x + M_y + M_z$ remains constant following a pulse.

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)**



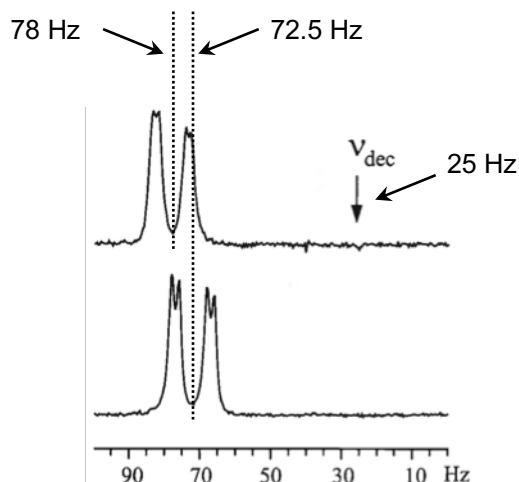
In a strong, static magnetic field (B_0), so-called ring currents are induced in the π -electron systems of aromatic rings that augment the B_0 field at the edges of the ring and oppose the B_0 field above and below the ring. Thus, hydrogens such as ‘a’ will appear highly deshielded because the effective magnetic field they experience is higher than the actual B_0 field ($\delta_a = 7.5$ ppm). Hydrogens such as ‘c’ will appear highly shielded, because the effective magnetic field they experience is smaller than the actual B_0 field ($\delta_c = -1.0$ ppm). Hydrogens such as ‘b’ will also be somewhat deshielded because they are in the plane of the ring, but not as much as those attached to the ring because they are further away from the ring ($\delta_b = 2.0$ ppm).

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)**

In selective homonuclear decoupling experiments, if the decoupling field is applied during the acquisition of the FID, signals in the spectrum can experience a frequency shift relative to their positions in the control spectrum where no decoupling field is applied. This effect is known as the Bloch-Siegert effect. The frequency shifts of the signals are known as Bloch-Siegert shifts.

b. For the ^1H 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 ν_{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)**



As long as the decoupler field strength is small, the following equation describes the Bloch-Siegert shift:

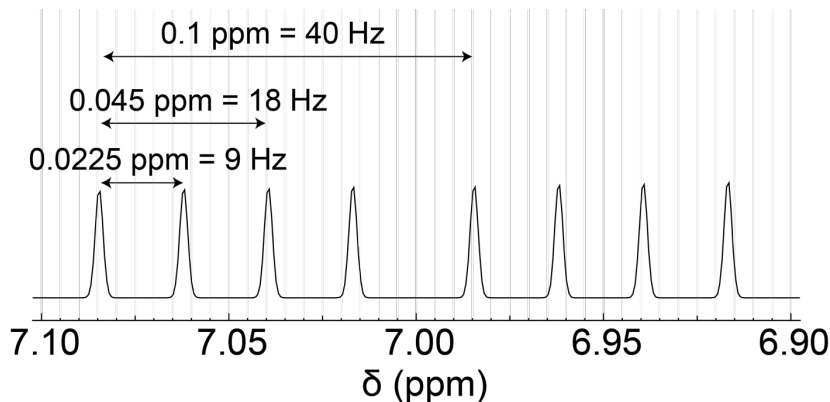
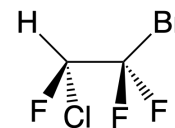
$$\Delta\nu = \nu_{\text{BS}} - \nu_o = \frac{B_2^2}{2(\Delta B)} = \frac{B_2^2}{2(\nu_o - \nu_i)}$$

where $\Delta\nu$ is the frequency shift (equal to the frequency of the signal with decoupling, ν_{BS} , minus the frequency of the signal without decoupling, ν_o), B_2 is the decoupling field strength (in Hz), and ν_i is the frequency at which the decoupling field is applied (ν_{dec}). Thus:

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

$$B_2 = \sqrt{2(\nu_{\text{BS}} - \nu_o)(\nu_o - \nu_i)} = \sqrt{2(78 - 72.5)(72.5 - 25)} = 22.37 = 23 \text{ Hz}$$

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



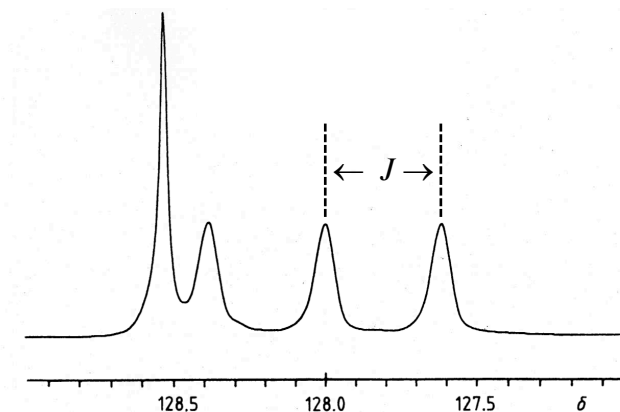
a. Describe the ^1H spectrum of the fluoroethane derivative shown above. State how many signals there are and what their multiplicities are. Justify your statements based on the nuclei present in the molecule and by determining the values of the coupling constants and demonstrating how you determined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

There is only a single ^1H nucleus in the molecule, so there can only be one signal in the spectrum. There are three ^{19}F nuclei. One is bonded to the same carbon as the ^1H nucleus, so there will be one two-bond HF coupling constant. There are two ^{19}F nuclei bonded to the other carbon, and they are diastereotopic, so there will be two three-bond HF coupling constants. So, the expected multiplicity is a doublet of doublets of doublets (8 peaks). That is what is observed. At 400 MHz, 1 ppm is 400 Hz. Given that, the coupling constants, and how they are determined, are shown above the spectrum. The two-bond coupling constant is 40 Hz ($^2J_{\text{HF}} = 40 \text{ Hz}$). The two three-bond coupling constants ($^3J_{\text{HF}}$) are 18 and 9 Hz.

b. The presence of ^1H - ^{19}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)

For coupled spins, first order spectra result when the frequency difference between the coupled nuclei is large compared to the coupling constant ($\Delta\nu \gg J$). Using a 100 MHz instrument, the Larmor frequency of ^1H is approximately 100 MHz, and the Larmor frequency of ^{19}F is 94.077 MHz. So, the frequency difference is $\sim 6,000,000 \text{ Hz}$, which is much, much larger than the largest ^1H - ^{19}F coupling constant ($^1J_{\text{HF}} = 500 \text{ Hz}$). Even if only a 1 MHz magnet were used, the frequency difference would still be 60,000 Hz, so the spectra would still be first order.

12). The ^{13}C NMR spectrum shown (right) is from a mixture of C_6H_6 (benzene) and C_6D_6 (deuterated benzene). The B_0 field was 5.87 T.



a. What are the chemical shifts of the two ^{13}C signals present? Which is from C_6H_6 and which is from C_6D_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)**

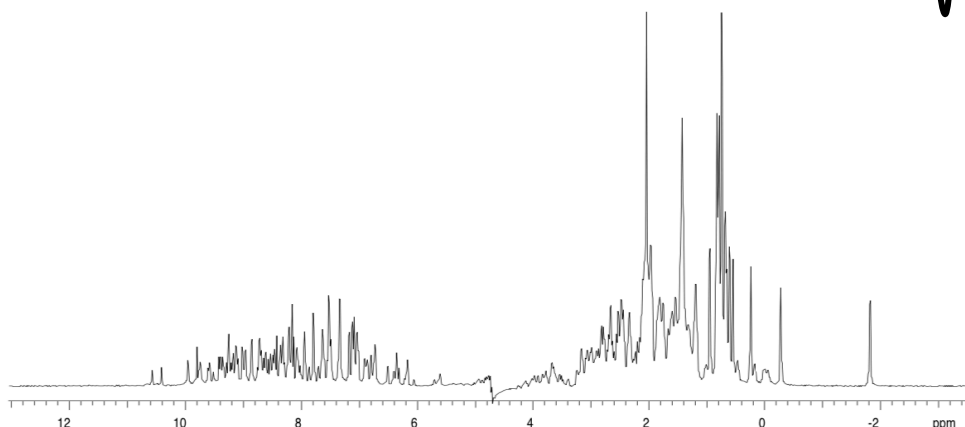
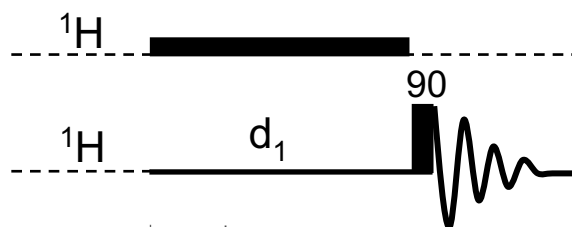
When a ^{13}C nucleus is attached to a ^1H nucleus it is split into a doublet, where the individual peaks in the doublet are of equal intensity. This is because the ^1H ($I=1/2$) nucleus can be in either the α (low energy) or β (high energy) state. Because the α and β states are nearly equally populated, the intensities of the doublet components in the ^{13}C spectrum are nearly identical. We know also that for a ^2H (D) nucleus, where $I=1$, there will be three possible energy states, $E = -1\gamma\hbar B_0$, $E = 0\gamma\hbar B_0$, and, $E = 1\gamma\hbar B_0$, and that they will be nearly equally populated. Thus, these will split the attached ^{13}C nucleus into a triplet with nearly equal intensities for the three peaks.

Therefore, the singlet at 128.53 is due to C_6H_6 . There is only one signal because the six carbons are chemically equivalent. Each ^{13}C nucleus is coupled to a directly bonded ^1H nucleus, so the ^{13}C signal should appear as a doublet. The fact that it is a singlet indicates that there was ^1H decoupling during the experiment (most likely broadband ^1H decoupling). The ^{13}C signal from the likewise chemically equivalent carbon atoms of C_6D_6 is split by coupling to the attached (quadrupolar) ^2H (D) nucleus. This coupling/splitting would not be removed by broadband ^1H decoupling (to remove this splitting would require broadband ^2H decoupling). The chemical shift is the center of the signal, at 128.0 ppm.

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

$^1J_{\text{C,D}}$ or $^1J_{^{13}\text{C,D}}$ or $^1J_{^{13}\text{C}, ^2\text{H}}$, etc.

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).



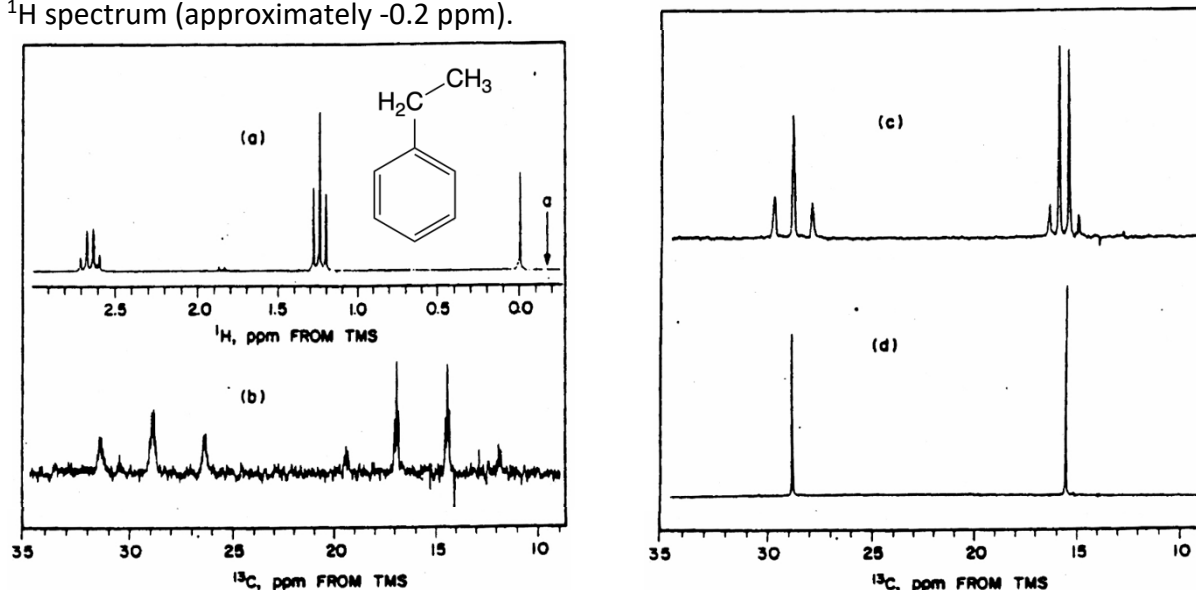
a. The signal from water is at 4.76 ppm in the spectrum. It is quite small, despite the fact that the concentration of water is 55 M (55,000 mM) and the concentration of the ubiquitin protein is only approximately 1 mM. Please explain how the pulse sequence is able to dramatically, and selectively, attenuate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

The long pulse is applied at the Larmor frequency of the ^1H nuclei of water. Because the pulse is long, the bandwidth is very narrow and it is highly selective, in this case, for water. The long pulse saturates the ^1H nuclei of the water. The subsequent 90° pulse then gives the spectrum of the protein, but, because the ^1H nuclei of the water are saturated, there is no bulk magnetization vector from the water, and, as a result, there is no signal from the water in the spectrum.

b. An unfortunate consequence of using this method to attenuate H_2O signal in aqueous protein solutions is that the signals from hydrogens in $-\text{NH}$ and $-\text{NH}_2$ groups (6 – 12 ppm) of proteins are also often slightly attenuated, but signals from $-\text{CH}$, $-\text{CH}_2$, $-\text{CH}_3$, and other carbon-bound hydrogens are not. Explain how this occurs. **(4 points)**

The hydrogens in $-\text{NH}$ and $-\text{NH}_2$ groups are labile and exchange (slowly) with hydrogens from H_2O . If the hydrogens from H_2O are saturated, and they exchange with hydrogens in $-\text{NH}$ and $-\text{NH}_2$ groups, then these signals also become attenuated because they are partially saturated.

14). The ^1H NMR spectrum for the ethyl group of ethyl benzene is shown in spectrum 'a' below, and the ^{13}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 ^1H decoupled ^{13}C spectrum is shown in spectrum 'd'. The off-resonance decoupled ^{13}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 ^1H spectrum (approximately -0.2 ppm).



a. There are three signals in the ^1H 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)

The methyl hydrogens are equivalent and give rise to one signal. It is split into a triplet due to coupling to the two equivalent neighboring methylene hydrogens. So, this is the signal at ~1.24 ppm. The methylene hydrogens are equivalent and give rise to one signal. It is split into a quartet due to coupling to the three equivalent neighboring methyl hydrogens. So, this is the signal at ~2.64 ppm. The signal at 0.0 ppm is from TMS added to the sample as a chemical shift reference. Also, the magnetic anisotropy of the benzene ring is such that the plane of the ring is the deshielding region. The methylene hydrogens are in the plane, so the signal from them should be downfield (deshielded) relative to the signal from the methyl hydrogens, which is the case.

b. There are two signals in the ^{13}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)

There are two carbon atoms in the ethyl group and two signals in the ^{13}C spectra. The methyl group is directly bonded to three hydrogen atoms, so it will be a quartet. This is the quartet centered at ~15.5 ppm. The methylene group is directly bonded to two hydrogen atoms, so it will be a triplet. This is the triplet centered at ~29 ppm.

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)**

From the ^{13}C spectrum without any decoupling ('b'), the distance between the outer components of the quartet (signal from the methyl group) is ~ 8 ppm. This is equal to $3 \times {}^1J_{\text{CH}}$, so ${}^1J_{\text{CH}} = \sim 2.67$ ppm. Coupling constants are ALWAYS reported in Hz, so, for a 300 MHz magnet (7.05 T), the resonance frequency for ^{13}C is ~ 75 MHz, so, 75 Hz/ppm. So, $2.67 \text{ ppm} \times 75 \text{ Hz/ppm} = \sim 200 \text{ Hz}$.

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)**

The equation relating the decoupler field strength (B_2 field), the initial coupling constant (J), the coupling constant in the off-resonance decoupling experiment (the 'reduced' coupling constant, J_r), and the frequency difference between the signal in the ^1H spectrum of interest and the frequency at which the decoupling field was applied ($\Delta\nu$) is:

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

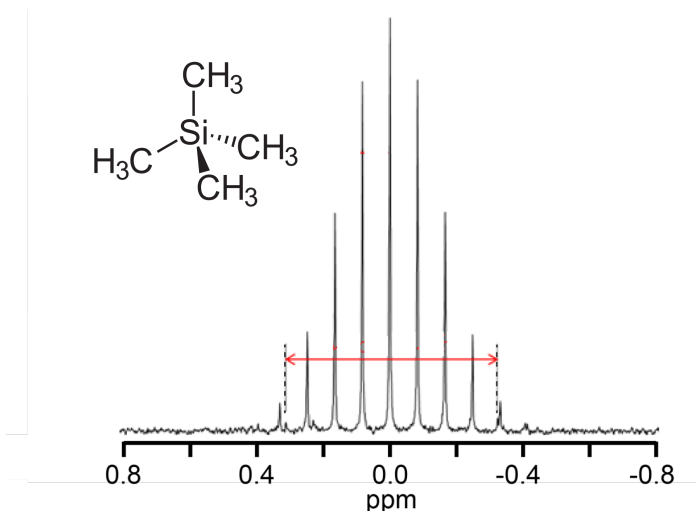
From part 'a', the signal at ~ 1.24 ppm is due to the methyl group, so this is $1.24 + 0.2 = 1.44$ ppm from the frequency of the decoupler field. For a 300 MHz magnet, 1 ppm for ^1H is 300 Hz, so 1.44 ppm is 432 Hz. So, $\Delta\nu$ is 432 Hz. We can then calculate B_2 :

$$B_2 = \frac{\Delta\nu\sqrt{J^2 - J_r^2}}{J_r} = \frac{432\sqrt{200^2 - 40^2}}{40} = \frac{432 \times 195.96}{40} = 2116 \text{ Hz}$$

If B_2 is much larger than $\Delta\nu$ ($B_2 \gg \Delta\nu$), then the approximation can be used:

$$B_2 \cong \frac{J\Delta\nu}{J_r} = \frac{200 \times 432}{40} = 2160 \text{ Hz}$$

15). The compound TMS (tetramethylsilane, right) is a symmetrical molecule where all -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 ^1H (0.00 ppm), as is the chemical shift of the ^{13}C atoms (0.00 ppm). Likewise, the chemical shift of the Si atom is often used as a chemical shift standard for ^{29}Si (0.00 ppm). The ^{29}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)**

^{29}Si is spin $\frac{1}{2}$. In TMS, the Si atom is coupled (3J) to the equivalent hydrogen atoms of the methyl groups. The 12 hydrogens will split the Si signal into 13 peaks ($n=12$, $n+1=13$). Only 9 of the peaks are observed in the spectrum shown because the signal-to-noise is not high enough to observe the smaller peaks. The relative intensities of the 13 peaks should be as shown in the last (bottom) line in the "Pascal's Triangle" shown here.

1
1 1
1 2 1
1 3 3 1
1 4 6 4 1
1 5 10 10 5 1
1 6 15 20 15 6 1
1 7 21 35 35 21 7 1
1 8 28 56 70 56 28 8 1
1 9 36 84 126 126 84 36 9 1
1 10 45 120 210 252 210 120 45 10 1
1 11 55 165 330 462 462 330 165 55 11 1
1 12 66 220 495 792 924 792 495 220 66 12 1

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)**

The ^{29}Si atom is also coupled to ^{13}C in the carbon atoms. Because only 1% of the carbon is ^{13}C , these peaks are very small, and each of them should therefore be 0.5% as large as the center component of the ^{29}Si multiplet. They are 50.8 Hz apart because that is the magnitude of the one-bond ^{29}Si - ^{13}C coupling constant.

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

The arrow shows two small peaks that are 50.8 Hz apart. If we look at the ppm scale, these peaks are located at approximately 0.32 and -0.32 ppm, or 0.64 ppm apart. So, that's 79.375 Hz/ppm. From the table at the end of this exam, we see that, for ^{29}Si , 19.865 Hz/ppm corresponds to a magnetic field strength of 2.36885 Tesla, so 79.375 corresponds to a field strength of 9.465 Tesla (or a "400 MHz" magnet approximately).

Name _____

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You may find some of the information below useful:

Table 1-1.

Properties of some nuclides of importance in NMR spectroscopy.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$P_z = m\hbar$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$\omega_0 = \gamma B_0$$

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

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

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

$$AQ = DW * TD$$

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

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

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

$$(TD \equiv NP)$$

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

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

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

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

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

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

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

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

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

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

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