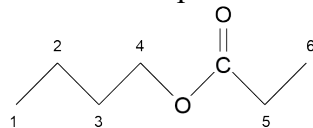
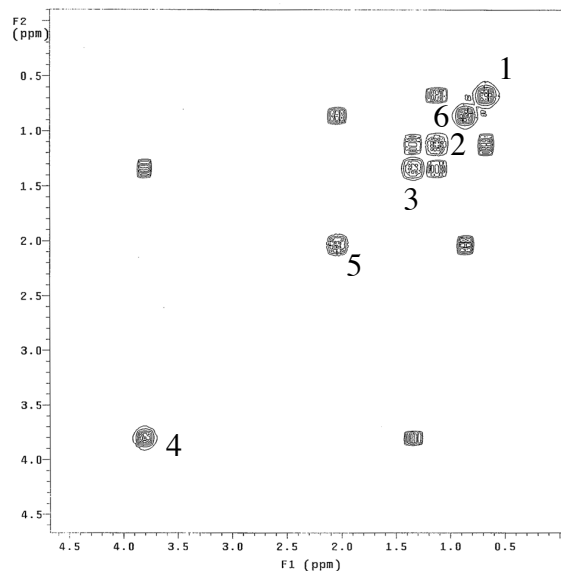


Exam 4: CHEM/BCMB 4190/6190/8189 (152 points) Tuesday, 23 November, 2021

1). The ^1H - ^1H COSY spectrum for butyl propionate is shown. The spectrum shows six diagonal signals (3.8, 2.1, 1.3, 1.1, 0.9 and 0.7 ppm) and a number of crosspeaks.



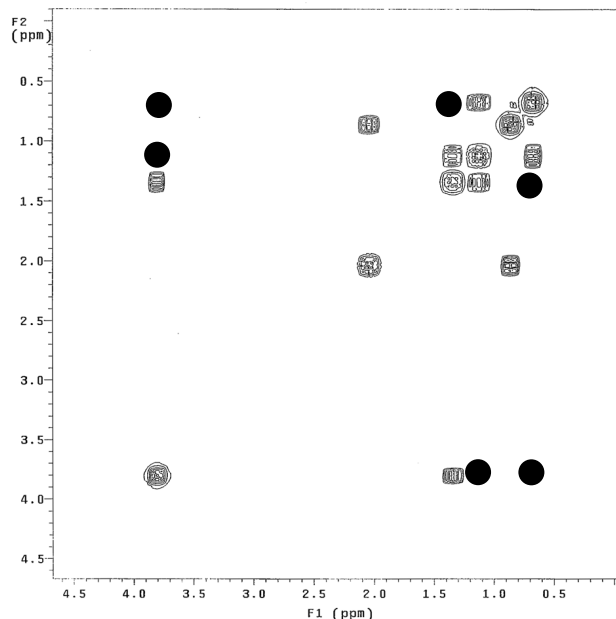
a. Please provide chemical shift assignments for the hydrogens in butyl propionate. You will have to provide a detailed justification for credit. You should begin by defining how many different ^1H signals you would expect to see in the spectrum, with an explanation of your rationale. You must detail your justification for your assignments for credit. (8 points)



First, for each methyl group, the hydrogens in that group would be equivalent based on rapid rotation of the methyl group about the C-C bond. The hydrogens in each methylene would be equivalent to one another because they are each in identical environments due to symmetry and molecular averaging about the C-C and C-O bonds. Thus, one would expect six signals, which correspond to the six distinct observed chemical shifts.

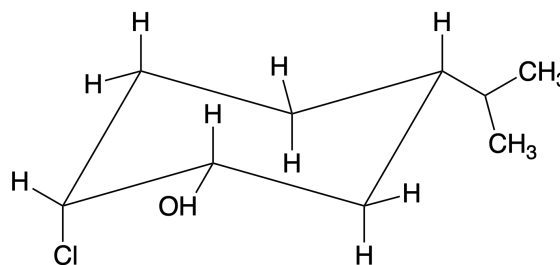
The methylene hydrogens at position 4 would be expected to give rise to the signal at 3.8 ppm because of deshielding by direct attachment of the carbon at position 4 to the oxygen. The hydrogens at position 4 will be coupled (3-bond) to those at position 3, so there should be a single crosspeak for the signal at 3.8 ppm. There is one crosspeak, at 1.3 ppm, thus the methylene hydrogens at position 3 would be expected to give rise to this signal at 1.3 ppm. Besides the coupling to the hydrogens at position 4, the hydrogens at position 3 will also be coupled to the hydrogens at position 2, so there should be two crosspeaks for the signal at 1.3 ppm. One is at 3.8 ppm, for coupling to the hydrogens at position 4, and the second is at 1.1 ppm for coupling to the hydrogens at position 2. So, the methylene hydrogens at position 2 give rise to the signal at 1.1 ppm. Besides the coupling to the hydrogens at position 3, the hydrogens at position 2 will also be coupled to the hydrogens at position 1, so there should be two crosspeaks for the signal at 1.1 ppm. One is at 1.3 ppm, for coupling to the hydrogens at position 3, and the second is at 0.7 ppm, for coupling to the methyl hydrogens at position 1. So, the methyl hydrogens at position 1 give rise to the signal at 0.7 ppm. There are only two signals remaining, one at 0.9 ppm and the other at 2.1 ppm. There is a crosspeak indicating coupling between the hydrogens that give rise to the signal at 0.9 and those giving rise to the signal at 2.1. Thus, the signal at 0.9 most likely arises from the methyl hydrogens at position 6, and the signal at 2.1 arises from the hydrogens at position 5. It would be expected that the signal from the methylene hydrogens is upfield from the methyl signal due to deshielding from the directly bonded C=O group.

b. On the COSY spectrum of butyl propionate shown (below, right), draw additional signals/crosspeaks that you would expect to observe in a TOCSY spectrum of butyl propionate. You will have to explain your reasoning to receive credit. **(6 points)**

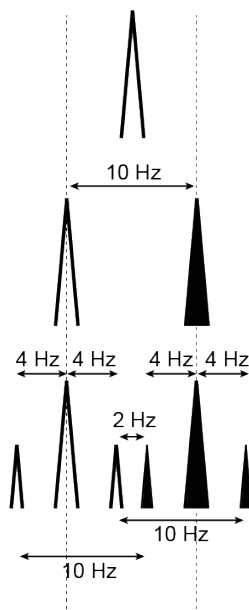


For a very short mixing time, we would not expect to see any additional signals/crosspeaks, as the TOCSY with a short mixing time typically only shows crosspeaks for 2- and 3-bond couplings, like the COSY. However, for an appropriately long mixing time, we would expect to see all possible crosspeaks corresponding to the chemical shifts of hydrogens from positions 1, 2, 3 and 4. This would mean crosspeaks, in addition to those observed in the COSY spectrum, for coupling between hydrogens at positions 1 and 3, 1 and 4, and 2 and 4. Because of the intervening ester oxygen and carbonyl carbon, there would not be correlations from hydrogens at 5 and 6 with the other hydrogens.

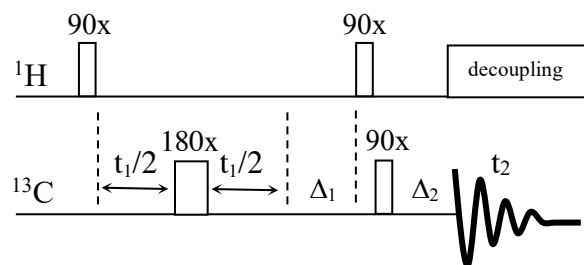
2). Draw the ^1H NMR signal you would observe in a simple one-dimensional ^1H NMR spectrum for the hydrogen on the carbon bearing the hydroxyl group in the molecule shown. For credit you will have to explain the multiplet structure, justify why it appears as it does, and you will have to indicate and justify distances between peaks in the signal, estimated coupling constants, and relative peak intensities. Assume that no 4-bond, 5-bond, or more-bond couplings contribute to the splitting of the signal. **(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, which is in the axial position, and two of the three adjacent hydrogens, which are in the equatorial positions, are the same, approximately 60 degrees, so the coupling constants to each would be approximately equal, and would be small (approximately 4 Hz), as indicated by the Karplus relationship. These couplings then would result in an apparent triplet with approximately 4 Hz spacing between the peaks. The coupling to the third hydrogen is an axial-axial coupling, so the dihedral angle between these hydrogens is 180 degrees. According to the Karplus relationship, this will be a large coupling, for instance 10 Hz. This will split the triplet into two triplets. The center peaks of the triplets will be 10 Hz apart. So, the multiplet is a doublet of triplets with normal triplet intensities of 1:2:1.



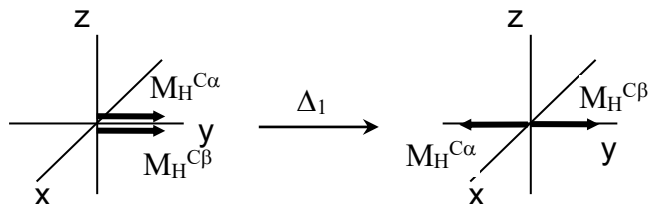
3). The pulse sequence for a modified HETCOR pulse sequence is shown (right). Delays Δ_1 and Δ_2 have been added, as has a 180° pulse.



a). Explain the purpose of the 180° pulse and how it accomplishes this purpose. (4 points)

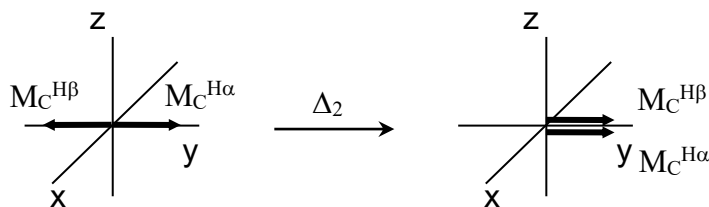
The 180° pulse is present to remove splitting of the signal in the indirectly detected dimension (^1H dimension) due to ^{13}C coupling to ^1H . The pulse is centered in the t_1 evolution period. Following the first pulse, the $M_{\text{H}}^{\text{C}\alpha}$ and $M_{\text{H}}^{\text{C}\beta}$ vectors are both pointed along the same (y) axis. During the first $t_1/2$ period they move apart by a specified amount. The 180° ^{13}C pulse reverses their directions, so they are refocused along the same axis at the end of the second $t_1/2$ time period. So, no net evolution of the coupling has occurred, and because of that, there is no splitting of signal in the F_1 (^1H , indirectly detected) dimension.

b). Explain the purpose of the Δ_1 delay and how it accomplishes this purpose. Your explanation must include what the proper value of Δ_1 should be. You may want to include vector diagrams to assist in your explanation. (4 points)



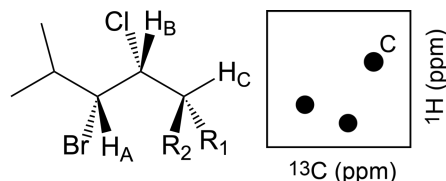
The Δ_1 delay should be set to $1/(2 \ ^1J_{\text{CH}})$. At the end of the t_1 evolution period, because of the spin lock ($t_1/2 - 180 - t_1/2$), the $M_{\text{H}}^{\text{C}\alpha}$ and $M_{\text{H}}^{\text{C}\beta}$ vectors are refocused along the same axis in the transverse plane. With The Δ_1 delay set to $1/(2 \ ^1J_{\text{CH}})$, the -CH vectors move apart from one another by 180° so that they are opposite in phase just before the (second) ^1H 90° pulse. In this way, the ^1H 90° pulse converts the -y and y components of these vectors equally to z or -z magnetization, respectively, giving maximum polarization transfer and maximum sensitivity.

c). Explain the purpose of the Δ_2 delay and how it accomplishes this purpose. Your explanation must include what the proper value of Δ_2 should be. You may want to include vector diagrams to assist in your explanation. (4 points)



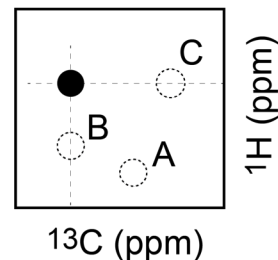
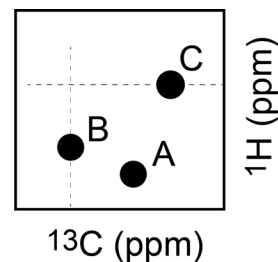
For a -CH group (one-bond coupling), the phase angle change between the vectors $M_C^{H\alpha}$ and $M_C^{H\beta}$ during the delay Δ_2 will be equal to $2\pi^1J_{CH}\Delta_2$. When Δ_2 is equal to $1/(2^1J_{CH})$, then the angle is π radians or 180° . Because the angle between the vectors is 180° before Δ_2 , then after Δ_2 the angle between them will be zero degrees: in other words the vectors will be refocused. Thus, when Δ_2 is equal to $1/(2J_{CH})$, the vectors will be refocused just before the acquisition period and broadband 1H decoupling can be applied during acquisition to eliminate peak splitting in the directly detected (^{13}C) dimension.

d). The HETCOR experiment shown above was used to acquire the HETCOR spectrum of the molecule shown (right). The region of the spectrum showing the correlations from H_A , H_B , and H_C is shown. It is known which signal belongs to H_C , but it is not known which of



the remaining two signals belongs to H_A and which belongs to H_B . If the delays Δ_1 and Δ_2 in the HETCOR experiment are set to 50 ms instead of the usual value, it is possible to show which signal is from H_A , and which is from H_B . Please explain in detail how this is accomplished. (10 points)

If the values of Δ_1 and Δ_2 are set to $1/(2J)$, as they should be, then 50 ms corresponds to a value of J equal to 10 Hz. This is approximately equal to common values of $^2J_{CH}$ in organic molecules. So, the magnetization that is refocused is the two-bond ^{13}C - 1H coupling. In the molecule shown, the two-bond coupling between H_C and the carbon bound to H_B would then be refocused, but the three-bond coupling between H_C and H_A would not be refocused as well. Therefore, in the modified HETCOR spectrum, with Δ_1 and Δ_2 set to 50 ms, a signal would be observed at the 1H chemical shift of H_C and the ^{13}C chemical shift of the carbon bound to H_B (lower spectrum, right). So, this would identify the signal with the most downfield ^{13}C shift as arising from B.



4). The COSY spectrum for menthol is shown (next page), along with the 1D ^1H spectrum of menthol, the structure of menthol and the correct ^1H assignments. Circled in the COSY spectrum is a crosspeak (and the symmetry related crosspeak) that remains unassigned. Scheme IV (next page) shows coupling constants for the indicated ^1H pairs in compounds 15-18.

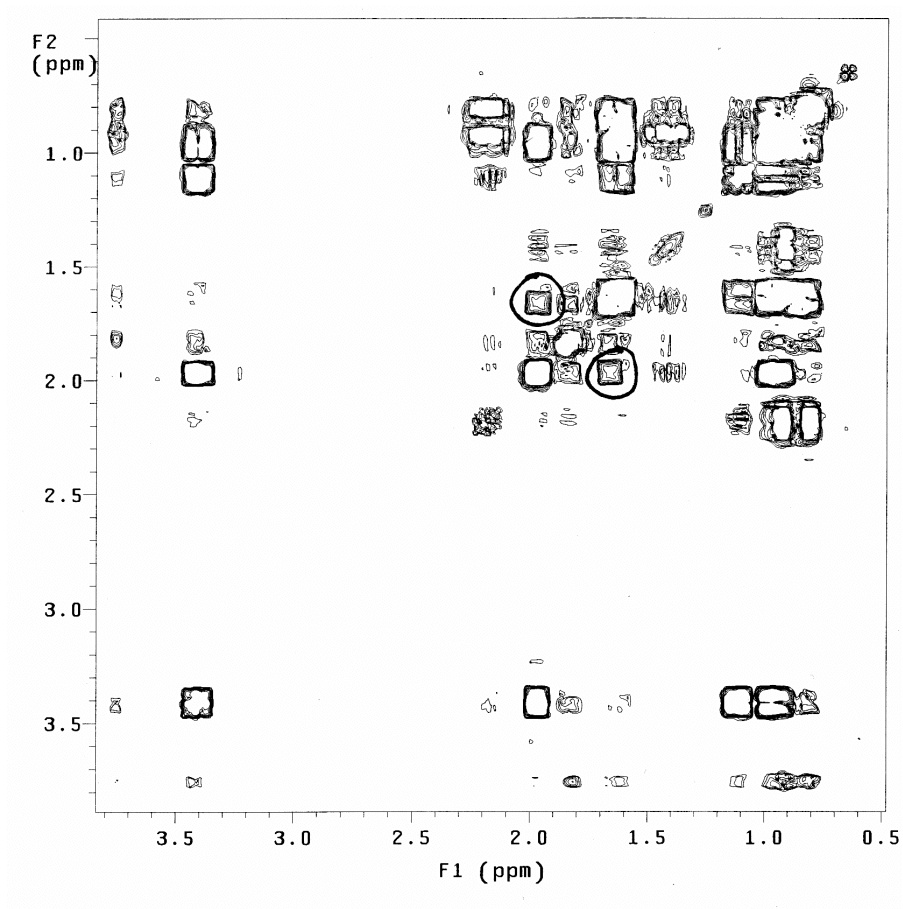
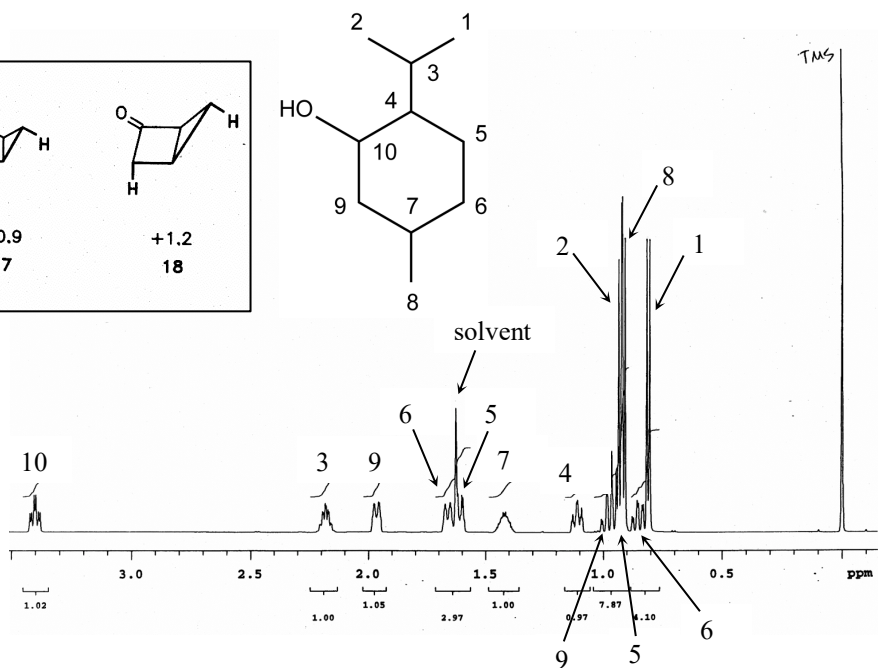
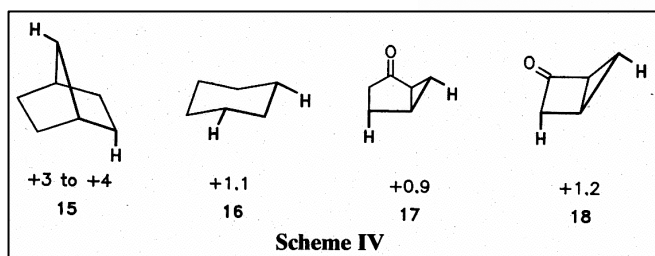
- a. Please give a concise explanation of Scheme IV. You must explain what point this figure/scheme is trying to make, AND, you must explain what this has to do with COSY. (6 points)

^1H - ^1H couplings through more than 3 bonds (H-C-C-H) are normally very small. This is the reason that crosspeaks for protons more than 3 bonds away from one another normally do not appear in COSY spectra. However, as shown in Scheme IV, in some cases, couplings through 4 bonds are substantial (1 Hz or more). For instance, when the four bonds linking the nuclei form a fixed “W” conformation, the couplings can be reasonably large (up to 4 Hz). In these cases, crosspeaks for coupled protons can be observed in COSY spectra.

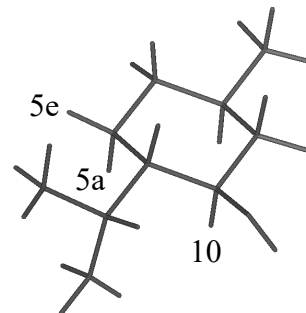
- b. Assign the circled crosspeak(s). For credit you must clearly and completely justify your assignment(s). (6 points)

The chemical shifts of the crosspeaks indicate that one of the ‘9’ and one of the ‘6’ protons are involved. Given Scheme IV (structure 16), which suggests that a substantial four-bond coupling should be observed between the equatorial positions across the ring (“W” conformation), the best assignment for the crosspeak would be that it arises from the equatorial protons at ‘9’ and ‘6’.

Name _____

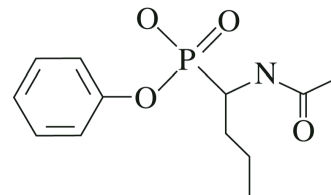


5). In menthol, the distance between proton 10 and proton 5a (axial) is 2.48 Å, whereas the distance between proton 10 and proton 5e (equatorial) is 3.65 Å. In a NOESY experiment, if the intensity of the crosspeak between 10 and 5a is 100 (arbitrary units), what would be the expected intensity for the crosspeak between 10 and 5e? You will have to show your work for credit. (6 points)



We know that the intensity of a crosspeak in a NOESY spectrum (assuming that our mixing time was reasonable) is proportional to $1/r^6$, where r is the internuclear (interproton) distance. In this case, the longer distance is $3.65/2.48 = 1.47$ times longer than the shorter distance, and thus the ratio of NOE intensities would be expected to be $(1.47)^6 = 10$. Because the intensity of the NOE crosspeak for the shorter distance is 100, the expected intensity for the longer distance would be $100/10 = 10$.

6). You synthesized the phosphonate compound (right) in your laboratory using routine methods. You are collecting ^{13}C NMR spectra on this compound and would like to remove the ^{13}C - ^{31}P coupling (splitting) by performing broadband ^{31}P decoupling. You also realize that there will be an enhancement in S/N (signal-to-noise) due to the ^{13}C - ^{31}P NOE.



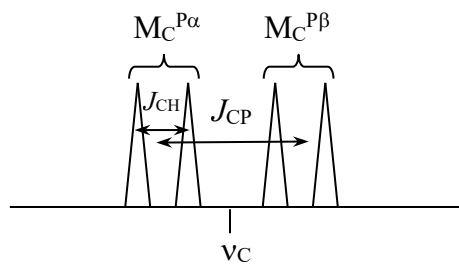
a. Calculate the percentage increase in S/N due to the ^{13}C - ^{31}P NOE (for the ^{13}C nucleus bound to the phosphorous atom) when applying broadband ^{31}P decoupling versus no decoupling. You will have to show your work for credit (4 points)

For small molecules, for an AX spin system, the maximum fractional NOE enhancement, η , is equal to $\gamma_a/(2\gamma_x)$ where γ_a is the gyromagnetic ratio for the nucleus that is saturated (decoupled) and γ_x is the gyromagnetic ratio for the nucleus that is observed. Thus,

$$\eta = \frac{\gamma_a}{2\gamma_x} = \frac{10.8394 \times 10^7}{2 \times 6.7283 \times 10^7} = 0.8055, \text{ or an } 80.55\% \text{ maximal enhancement.}$$

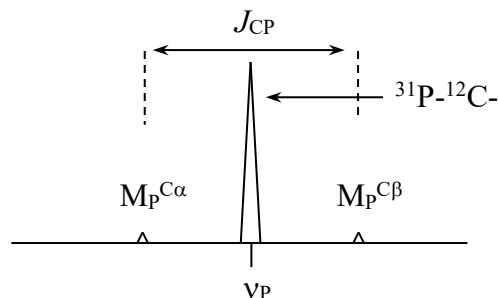
- b. Without any decoupling, what will the signal from the carbon bonded to the phosphorous atom look like in a normal 1D, ^{13}C spectrum? Draw the signal and explain the multiplet structure. (4 points)

The carbon nucleus in question will be coupled to its directly bonded proton, resulting in a doublet. The doublet will be split into a doublet of doublets by coupling to the ^{31}P (spin 1/2) nucleus. Thus, the signal will be a doublet of doublets, assuming a natural abundance sample (phosphorous is 100% ^{31}P , whereas carbon is only ~1% ^{13}C – so there is no splitting of the ^{13}C signal by the neighboring carbon because it is ^{12}C).



- c. In a normal, 1D, ^{31}P spectrum (no decoupling), what will the signal from the ^{31}P nucleus look like? Draw the signal and explain the multiplet structure. (6 points)

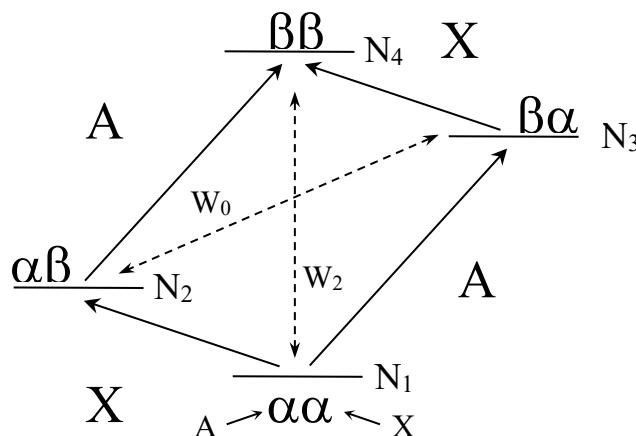
The ^{31}P signal is a singlet at natural abundance. One might see ^{13}C “satellite” signals flanking the singlet, corresponding to the doublet resulting from the natural abundance (1%) ^{13}C and the ^{13}C - ^{31}P coupling.



- d. Is ^{31}P a ‘good’ NMR nucleus? Explain in detail. (4 points)

^{31}P is a spin 1/2 nucleus. Its natural abundance is 100%! Its gyromagnetic ratio is $10.8394 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}$, which is a bit less than 1/2 that of a proton but still substantially larger than ^{13}C . Its relative sensitivity (for equal numbers of nuclei) is about 5 times better than ^{13}C . Thus, it is a quite good nucleus: pretty high sensitivity, spin 1/2, and very high natural abundance.

7). Consider the populations N_1 , N_2 , N_3 and N_4 of the $\alpha\alpha$, $\alpha\beta$, $\beta\alpha$ and $\beta\beta$ states, respectively, for a ^1H - ^1H spin system (spins 'A' and 'X') without J coupling (no coupling between A and X). The energy diagram for this system is depicted (right), where the A's represent the transitions of one of the ^1H nuclei, and the X's represent the transitions of the other ^1H nucleus. We will define ΔH as the difference in the number of spins in α and β states for A, and ΔH will also represent the difference in the number of spins in α and β states for X.



a. Write down the equilibrium values for N_1 - N_4 and the equilibrium population differences for the A and X transitions (please show how you calculate the A and X transition population differences). Assume that $N_4 = N$. **(6 points)**

$$N_4 = N$$

$$N_3 = N + \Delta H$$

$$N_2 = N + \Delta H$$

$$N_1 = N + 2\Delta H$$

$$A = N_2 - N_4 = N_1 - N_3 = \Delta H$$

$$X = N_3 - N_4 = N_1 - N_2 = \Delta H$$

b. On the energy diagram above, draw dashed lines showing the W_0 (zero quantum) and W_2 (double quantum) relaxation pathways. Make sure to clearly, correctly and unambiguously label each pathway. **(4 points)**

The W_2 pathway connects the $\beta\beta$ and $\alpha\alpha$ states, whereas the W_0 pathway connects the $\alpha\beta$ and $\beta\alpha$ states.

c. (fill in the blanks) The W_0 and W_2 pathways do not operate with equal efficiencies for all molecules. For large molecules, the W_0 pathway is more efficient, whereas for small molecules the W_2 pathway is more efficient. **(2 points)**

The W_0 and W_2 pathways do not operate with equal efficiencies with all sizes of molecules. For large molecules, the W_0 pathway is more efficient, whereas for small molecules the W_2 pathway is more efficient.

d. For a particular medium-sized molecule, the efficiencies of the W_0 and W_2 pathways for relaxation are identical. If we perform a simple NOE experiment by selective saturation of both of the A transitions, what are the new values for N_1 - N_4 and the population differences for the A and X transitions after saturation but without considering any relaxation? Then, what are the resulting values for N_1 - N_4 and the population differences for the X transitions including relaxation via W_0 and W_2 pathways (assume that the number of spins (δ) relaxing via the W_0 pathway is equal to the number relaxing through the W_2 pathway)? **(12 points)**

Before any relaxation takes place, the values for N_1 - N_4 and the population differences for the A and X transitions are:

$$N_4 = N + \Delta H/2$$

$$N_3 = N + 3\Delta H/2$$

$$N_2 = N + \Delta H/2$$

$$N_1 = N + 3\Delta H/2$$

$$A = N_2 - N_4 = N_1 - N_3 = 0$$

$$X = N_3 - N_4 = N_1 - N_2 = \Delta H$$

If we assume that δ spins relax via W_2 (add δ to N_1 , subtract δ from N_4) and W_0 (add δ to N_2 , subtract δ from N_3) then the new values for N_1 - N_4 and new population differences for X become:

$$N_4 = N + \Delta H/2 - \delta$$

$$N_3 = N + 3\Delta H/2 - \delta$$

$$N_2 = N + \Delta H/2 + \delta$$

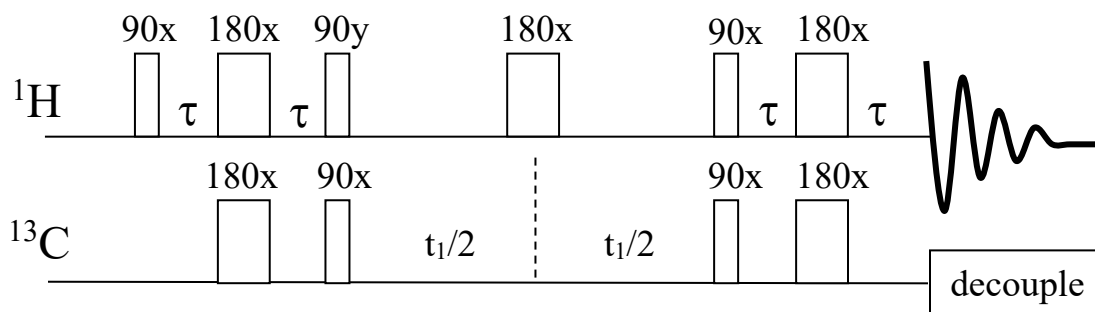
$$N_1 = N + 3\Delta H/2 + \delta$$

$$X = N_3 - N_4 = N_1 - N_2 = \Delta H$$

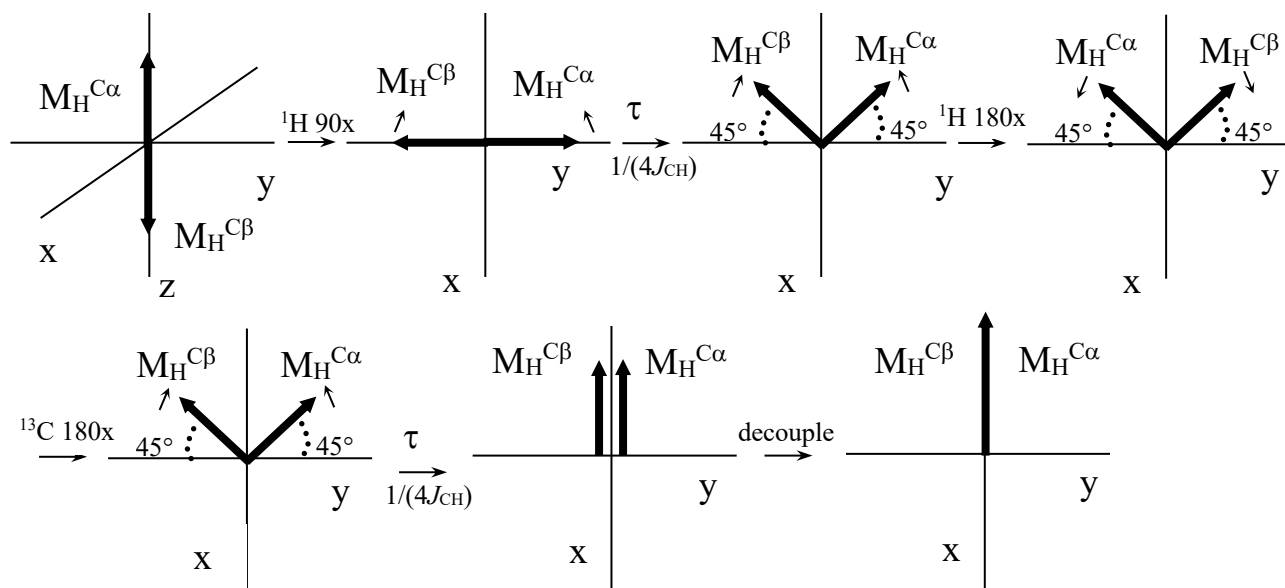
e. Explain your result to question 'd' in terms of medium-sized molecules in general. **(6 points)**

The result in 'd' suggests that when both W_0 and W_2 are operating with equal efficiencies, the population differences for the X transitions following saturation do not differ from those at equilibrium, i.e. there is no NOE enhancement. Thus, in general, for medium-sized molecules, neither the W_0 nor the W_2 pathway predominates, but both are operative, and the balance of W_0 and W_2 prevents observation of measurable NOE effects.

8). The HSQC pulse sequence is shown below.



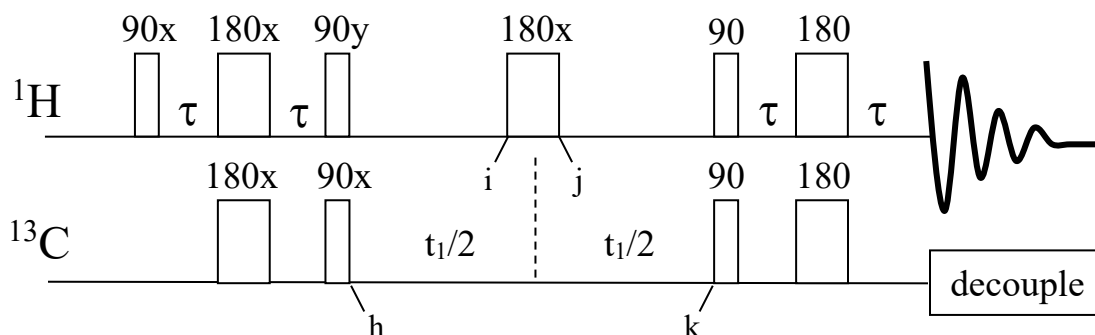
a. The magnetization vectors just after the second 90° ^{13}C pulse are shown below. Complete the vector diagrams for the remaining steps in the HSQC sequence (assume a simple ^1H - $^{13}\text{CCl}_3$ system and a τ of $1/(4J_{\text{CH}})$). Make sure to label properly the vectors, indicate the directions that the vectors are moving, and indicate important angles between the vectors or the vectors and the axes. (6 points)



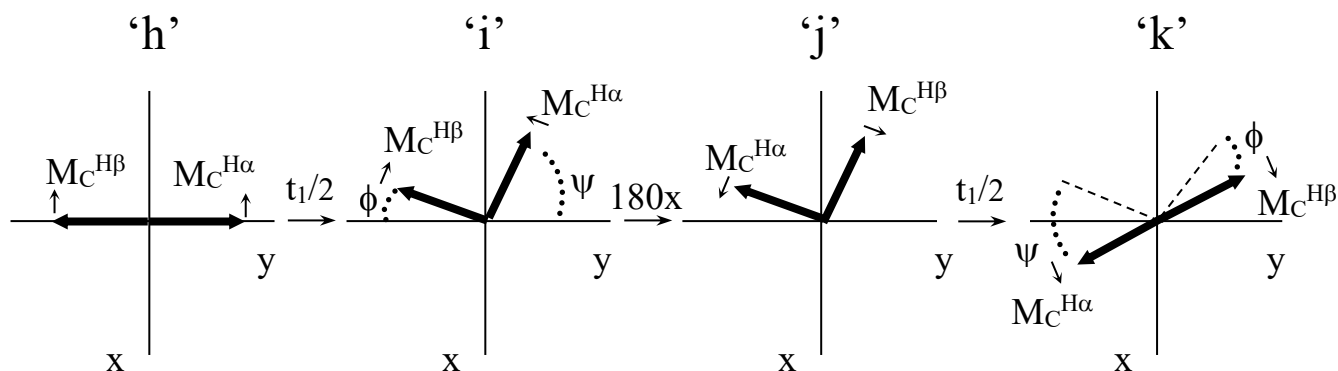
b. For the previous example, a simple ^1H - $^{13}\text{CCl}_3$ system, a value of $1/(4J_{\text{CH}})$ is appropriate for τ in the HSQC experiment. If, instead, you were considering a methylene group ($^{13}\text{CH}_2\text{-Cl}_2$), what would be the appropriate value of τ ? Please provide a detailed explanation. (6 points)

The appropriate value for τ is still $1/(4J_{\text{CH}})$. The signal from each ^1H nucleus is always split into a doublet by $^1J_{\text{CH}}$, thus $1/(4J_{\text{CH}})$ always assures that the angle between the vectors is appropriate (for instance, 180° after the third τ period, as demonstrated above). Also, the values of $^1J_{\text{CH}}$ for methine, methylene, and methyl groups are pretty similar (120-160 Hz), and so an average value for τ can be used with good results.

9). The HSQC pulse sequence is shown below.



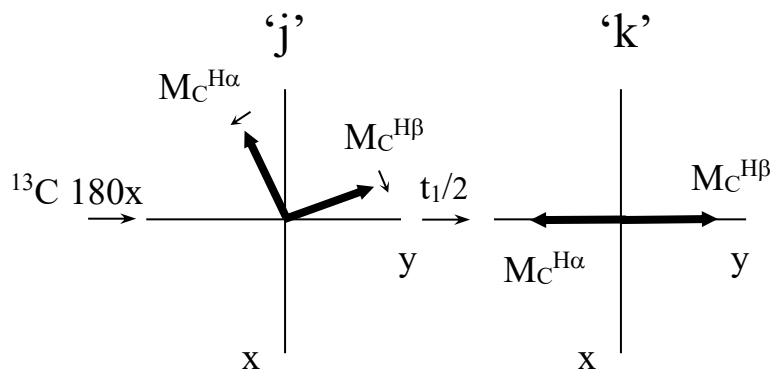
The magnetization vectors present at point 'h' in the pulse sequence are shown, as are the vectors at points 'i', 'j', and 'k' for a simple spin system. The vector $M_{\text{C}^{\text{H}\alpha}}$ precesses slower than the reference frequency, and $M_{\text{C}^{\text{H}\beta}}$ precesses faster than the reference frequency, such that after $t_1/2$, the vectors have moved ψ and ϕ degrees, respectively, away from the y axis.



a. What is the role of the ^1H 180° pulse in the middle of the t_1 evolution period? You should state exactly why the pulse is there, and how it accomplishes its intended task. **(4 points)**

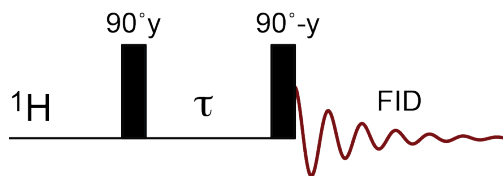
The 180° pulse in the middle of the t_1 evolution period decouples ^1H from ^{13}C , so the splitting of ^{13}C by ^1H is not observed in the indirect (t_1) dimension. As shown in the vector diagrams, there is no net evolution of the C-H coupling constant between points 'h' and 'k' in the sequence, effectively decoupling H from C during t_1 .

b. As shown above, at point 'k' in the sequence, the two vectors ($M_C^{H\alpha}$ and $M_C^{H\beta}$) are antiphase with respect to one another (180° out of phase with one another), and this is an essential condition for the pulse sequence to function properly. If we replace the ^1H 180° pulse in the center of the t_1 evolution period with a ^{13}C 180° pulse, we get the same result, as shown in the vector diagrams for points 'j' and 'k' below: the ^{13}C magnetization components are 180° out of phase with one another at point 'k'. So, the question is, why can't we replace the ^1H 180° pulse with a ^{13}C 180° pulse in the pulse sequence? **(8 points)**



If a ^{13}C 180° pulse is added in place of the ^1H 180° pulse, then the ^{13}C chemical shift evolution period (t_1) becomes a spin echo period instead, which refocuses the chemical shifts so that there is no chemical shift evolution. As shown in the vector diagrams for this case, regardless of the chemical shift, the magnetization will refocus. Thus, there will be no chemical shift evolution, which is the point of the t_1 delay period, so the signals in t_1 will not be separated according to their ^{13}C chemical shifts.

10). The “jump-return” NMR experiment (right) is designed to permit suppression of large signals in 1D spectra, such as those from solvent. It can be used, for instance, to suppress the large signal from H₂O in ¹H NMR spectra of samples prepared in aqueous solutions. This experiment does not provide equal excitation of all regions of the spectrum, so the region of interest is chosen, and then the parameters of the experiment are adjusted to both suppress the solvent signal and excite the signals in the region of interest. First, the carrier or reference frequency is set at the Larmor frequency of the signal (solvent) that is to be suppressed. Then, the delay τ is adjusted to $1/(4\Delta\nu)$, where $\Delta\nu$ is the frequency difference between the center of the region of interest (ν_H) and the solvent signal (ν_{H_2O}). So, $\tau = 1/(4\Delta\nu) = 1/(4(\nu_H - \nu_{H_2O}))$.

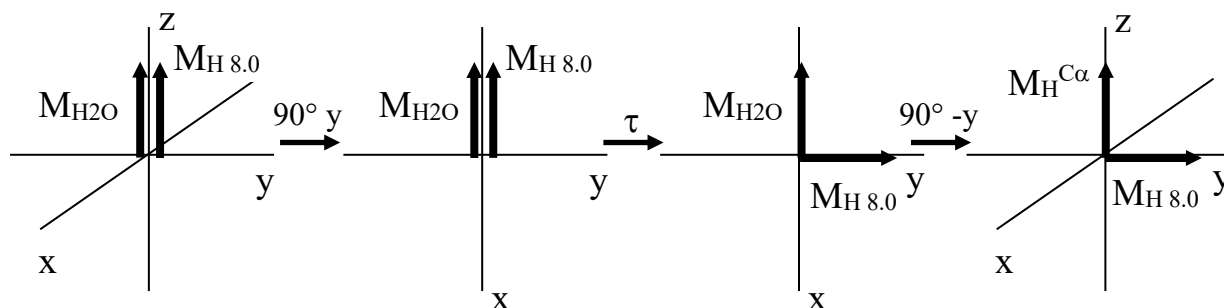


Consider the use of the jump-return experiment for a sample in H₂O using a 600 MHz instrument. The goal is to suppress the H₂O signal at 4.75 ppm with maximal excitation of a ¹H signal at 8.0 ppm.

a). How long, in seconds, should the delay τ be? You must do the appropriate calculations, report an answer, and show your work for credit. **(4 points)**

The chemical shift difference between the H₂O signal (4.75 ppm) and the signal at 8.0 ppm (8.0 ppm) is 3.25 ppm (8.0-4.75=3.25). For a 600 MHz instrument, there are 600 Hz/ppm, so $3.25 \text{ ppm} \times 600 \text{ Hz/ppm} = 1950 \text{ Hz} = \Delta\nu$. The delay τ is adjusted to be $1/(4\Delta\nu)$, so $\tau = 1/(4 \times 1950 \text{ Hz}) = 0.0001282 \text{ s}$, or $128.2 \mu\text{s}$.

b). Using vector diagrams, describe what happens during the pulse sequence. Then, provide a detailed explanation of how the pulse sequence suppresses the solvent signal while maximizing the signal of interest. **(8 points)**



At thermal equilibrium, the M_0 vectors of the H_2O (M_{H_2O}) and the signal of interest at 8.0 ppm ($M_{H\ 8.0}$) are both aligned along the $+z$ axis, as usual. The 90° 'y' pulse moves both vectors to the $-x$ axis. During the τ (delay) period, the M_{H_2O} stays on the $-x$ axis because the reference/carrier frequency is equal to the Larmor frequency of the H_2O . The $M_{H\ 8.0}$ vector, which is moving faster (more downfield) than the M_{H_2O} vector, moves clockwise in the x - y plane by 90 degrees, because the τ delay is set to $1/4(\Delta\nu)$. So, after the τ delay, the $M_{H\ 8.0}$ vector is aligned along the $+y$ axis. The final 90° '-y' pulse moves M_{H_2O} back to the $+z$ axis, and the $M_{H\ 8.0}$ vector stays on $+y$. So, because the bulk M_0 vector for H_2O is back along the $+z$ axis, it cannot be observed. Therefore, the signal from H_2O is suppressed. The M_0 vector for the signal at 8.0 is aligned along $+y$, so it will give a positive signal of maximum amplitude.

c). Assume there is also another 1H nucleus in the sample with a chemical shift of 1.5 ppm. What will the signal of this 1H nucleus look like if the experiment above is performed as described above (with the τ period optimized for the signal at 8.0 ppm and the carrier/reference set at the Larmor frequency of the H_2O signal)? You will have to provide a detailed explanation/justification for credit. **(6 points)**

This signal is also 3.25 ppm (1950 Hz) away from the H_2O signal, however it is precessing slower than the reference frequency (and H_2O frequency). During the τ delay the M_0 vector corresponding to this 1H nucleus will move more slowly than the M_0 vector for H_2O , and it will be 90 degrees away from the H_2O vector at the end of the τ delay. Thus, it will be aligned along the $-y$ axis. The final 90° '-y' pulse does not affect the position of this vector. So, the signal will be negative (opposite in phase to the signal at 8.0 ppm), and of maximum amplitude.

Name _____

THIS PAGE IS BLANK. FEEL FREE TO USE IT AS “SCRATCH” IF YOU LIKE

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:

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

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

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

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

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

$$P_z = m\hbar$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$\omega_0 = \gamma B_0$$

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

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

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

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

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

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

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

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

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

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

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

$$AQ = DW * TD$$

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

$$(TD \equiv NP)$$

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

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

$$\Delta \nu \gg J$$

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

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

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