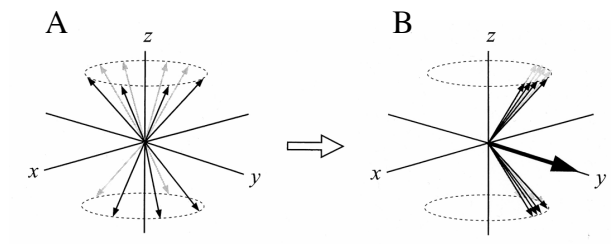**Exam 1: CHEM/BCMB 4190/6190/8189   (107 points)   Thursday, 10 September, 2020**

1). At thermal equilibrium, the microscopic view of an ensemble of spins in a magnetic field can be illustrated by individual magnetic dipoles precessing about the axis corresponding to the magnetic field (B_0) direction (z axis), as shown in the figure (panel A).

a. The result in panel B of the figure is achieved by applying an electromagnetic pulse to the nuclear ensemble in panel A at the Larmor frequency of the nuclei. What was the pulse angle used to obtain this result. You will have to fully explain your answer for credit. (**6 points**)

b. What is relationship between N_α and N_β in panel B? For credit, you will have to explain how you know this based on the macroscopic result shown in panel B? (**4 points**)

2). For an electromagnetic pulse applied for 5 μs (at the Larmor frequency for a particular nucleus), the pulse angle is 45 degrees ($\pi/4$ radians). The magnitude of the B_1 field used to apply the pulse is 0.00062379 T.

a. Calculate the value of the gyromagnetic ratio for this nucleus? You will need to show your work for credit. (**6 points**)

b. What is the identity of the nucleus from 'a'. You will have to explain how you arrived at your answer for credit. (**4 points**)

c. Define "precession frequency" as it applies to NMR. Use complete sentences and no symbols, equations or drawings. (**4 points**)

3). The NMR signal (the observed FID) in the plot below results from a sample of a compound that has a single ^1H nucleus ($CHCl_3$, for instance). The length of the period (Δt) of the cosine-modulated signal is equal to $1/\Delta v$, as is shown on the plot.
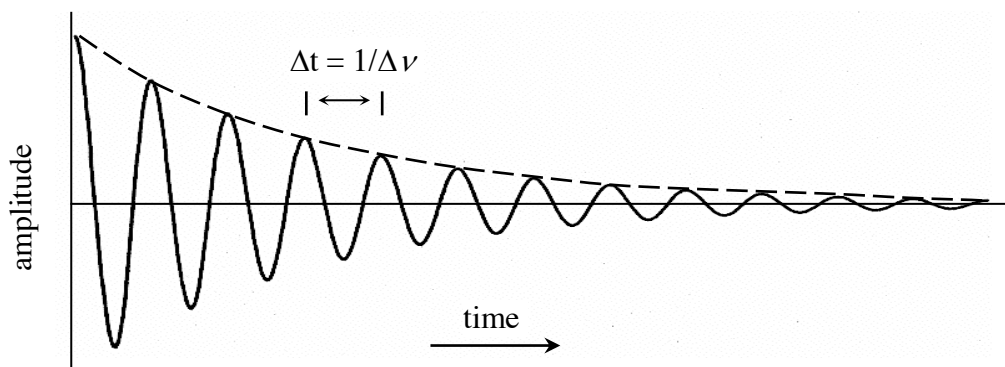
a. What is the frequency observed in the FID for this nucleus if Δt is 0.0011 s? (**2 points**)

b. What is the difference, in Hz, between the Larmor precession frequency for this nucleus and the frequency of the B_1 field (pulse) used to get the signal. You will have to explain your reasoning for credit. (**4 points**)

c. The dashed line follows the decay of the amplitude of the signal with time. If, after 1 second, the amplitude of the signal is 1/2 what it was initially, what is the effective T_2 (i.e. T_2^*)? (**4 points**)

d. After Fourier transformation of the signal, calculate the width of the frequency-domain signal (in Hz) at half of its maximum amplitude? You will have to show your work and arrive at an answer for credit. (**4 points**)

e. If the ^1H signal was acquired using a 7 T magnet (B_0 field 7 Tesla) what will be the approximate resonance frequency (in MHz) of the ^{13}C nuclei in $CHCl_3$ if the ^{13}C spectrum were acquired using the same magnet. You must do a calculation and show your work for credit. (**4 points**)

f. For a sample of $CHCl_3$, explain how you would determine experimentally what the 270° pulse width/length is for the single ^1H resonance in your sample? (**4 points**)

4). You record an ^{15}N NMR spectrum of your compound using 100 scans. You realize that you need to improve the sensitivity (signal-to-noise) by 5-fold. How many scans will be required to record a spectrum with 5 times the signal-to-noise? **(4 points)**

5). A diagram of the Zeeman levels/states for ^{13}C is shown to the right. Draw the Zeeman diagram for ^{10}B. **(4 points)**

$$E$$

m

-1/2 —— $E = +1/2\ \gamma\ \hbar\ B_0$

—— $E = 0$

+1/2 —— $E = -1/2\ \gamma\ \hbar\ B_0$
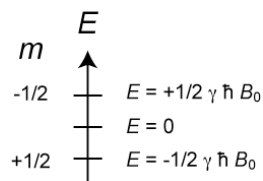
6). If we directly compare ^{10}B spins and ^{13}C spins;

a. What is the ratio of the bulk/macroscopic magnetization ($M_{0\ ^{10}B}/M_{0\ ^{13}C}$) produced for equal numbers of nuclei? **(6 points)**

b. How does the sensitivity of the NMR signal compare for ^{10}B and ^{13}C spins? **(6 points)**

7). Fill in the blanks to make the following statements true:

a). In NMR, the applied (B_1) field is applied _____ to the static (B_0) field. (**2 points**)

b). At equilibrium, for an ensemble of spin ½ nuclei in a magnetic field the number of alpha (α) spins (N_α) = X, and the number of beta (β) spins (N_β) = Y. Immediately following a 90° pulse along the y axis, the number of α spins = _____ and the number of β spins = _____. (**2 points**)

c). The number of Zeeman energy levels/states for ^{17}O is _____. (**2 points**)

d). For a spin ½ nucleus at equilibrium in a magnetic field, the alpha (α) state has a magnetic quantum number of _____, its energy is _____ than that of the beta (β) state, and the z component of its associated magnetic moment, μ_z, is aligned _____ to the magnetic field. (**3 points**)

8). For a sample of $CHCl_3$, you apply a very long (seconds), low power pulse at the ^1H frequency of the single ^1H nucleus in the molecule. Immediately after this pulse, you apply a normal, high power 90 degree pulse at the same frequency and then record the FID. Sketch what you would expect the FID to look like. Also, sketch the spectrum you would expect to observe following Fourier transformation of the FID. You must thoroughly explain your answers for credit. (**6 points**).

9). When you record the ^{1}H NMR spectrum of a particular compound, you observe the spectrum shown above (right). However, you know from published data that the spectrum should look like that shown below (right). Both spectra were recorded at the same magnetic field strength (400 MHz).
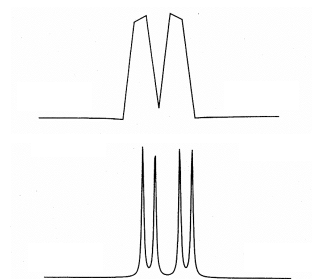
Using the same magnetic field strength (400 MHz), suggest two changes that you might make in how you acquire the ^{1}H NMR spectrum of this compound so that the spectrum looks more like the bottom spectrum shown (right). You must justify/explain your answers for credit. (**4 points**)

10). You decide to record a ^{1}H spectrum using only 90 degree pulses. You decide that you will collect 4 scans. After each pulse, you decide to wait long enough for 99.9% of the magnetization to return to thermal equilibrium before applying the next pulse. If T_1 for your sample is 5 seconds, how long will the time between pulses be? (**6 points**)

11). Paramagnetic compounds have an unpaired electron that can promote very efficient and fast NMR relaxation. In cases where such compounds interact with other molecules in solution, they can increase substantially the relaxation rates of nuclei in those molecules.

a. Why might it be important to make sure that NMR samples, in general, are clean and do not contain significant amounts of impurities that are paramagnetic? Please explain for credit. (**4 points**)

b. It is a reasonably common practice to sometimes deliberately add certain paramagnetic compounds to NMR samples for the purpose of decreasing T_1 relaxation times. Why might this be useful? Please explain for credit. (**4 points**)

12). There are two contributors to the NMR relaxation parameter T_2*. Please identify these contributors and their origins and how they contribute, microscopically, to relaxation in the transverse plane. (**8 points**)

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You may find some of the information below useful:

Table 1-1.
Properties of some nuclides of importance in NMR spectroscopy.

Nuclide	Spin I	Electric quadrupole moment[a] $[eQ]$ $[10^{-28}\ m^2]$	Natural abundance) [%]	Relative sensitivity[b]	Gyromagnetic ratio γ[a] $[10^7\ rad\ T^{-1}\ s^{-1}]$	NMR frequency [MHz][b] $(B_0 = 2.3488\ T)$
^1H	1/2	–	99.985	1.00	26.7519	100.0
^2H	1	2.87×10^{-3}	0.015	9.65×10^3	4.1066	15.351
^3H[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

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

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

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

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

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

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

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

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

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

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

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

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

$P_Z = m\hbar$

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

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

$\pi/2$ radians $= 90°$

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

$B_2 = \dfrac{\Delta v\sqrt{J^2 - J_r^2}}{J_r} = \dfrac{J\Delta v}{J_r}$

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

$\Delta v = v_{BS} - v_0 = \dfrac{B_2^2}{2(\Delta B)} = \dfrac{B_2^2}{2(v_0 - v_i)}$

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

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

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

$\Delta E = \mu_Z B_0 = \gamma\hbar B_0 = h v_L = h v_1$

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

$\omega_0 = \gamma B_0$

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

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

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

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

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

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

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

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

$I = (1 + \eta) I_0$

$I \propto 1/r^6$

$\Theta = \gamma B_1 \tau_p$

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

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

$v_L = \dfrac{\gamma}{2\pi}(1 - \sigma)B_0$

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

AQ$=$DW$*$TD

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

(TD$\equiv$NP)

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

$\pi/2$ radians $= 90°$

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

multiplicity$=2nI + 1$

$\Theta = 2\pi J\tau$