PULSE NUCLEAR MAGNETIC RESONANCE

WEEK 1 INTRO: UNDERSTANDING THE EQUIPMENT, THEORY AND MAKING MEASUREMENTS

GOALS

In this lab, you will become familiar with Pulse Nuclear Magnetic Resonance (Pulse NMR or PNMR for short), both as a concept and using the equipment to test various samples and record the results. This lab will be done in two sections, with week 1 allowing you to become familiar with the equipment and week 2 giving you the opportunity to utilize what you have learned and go further in depth with the pulse nuclear magnetic resonance.

- Proficiency with the equipment
 - Tektronix TDS 3014c Oscilloscope.
 - TeachSpin Pulsed NMR Spectrometer.
 - TeachSpin PM-1051 Magnet.
- New skills to apply from Lab
 - Understanding the theory and concept of nuclear magnetic resonance.
 - o Utilizing different settings and function of the Spectrometer.
 - Calculating different methods of relaxation time.
 - o Identifying different resultant values from various samples
- Experimental design
 - Understand how the equipment and theory work.
 - Design your own experiment!

BACKGROUND

To begin this lab, it will be beneficial for you to know and understand exactly what nuclear magnetic resonance is and how it is measured.

In 1946, the phenomenon of nuclear magnetic resonance in matter was observed by two different, independent groups: Felix Bloch of Stanford and Edward Purcell of Harvard. While both groups were working with different equipment and employing different techniques, the effect they observed was identical. When magnetic nuclei in matter were subjected to a magnetic field, the nuclei responded to a continuous radio frequency magnetic field as the field was tuned through resonance.

Several years passed until in 1950, when a postdoctoral fellow from University of Illinois named Erwin Hahn began to explore the effects of keeping a sample of condensed matter in a constant magnetic field, while subjecting it to radio frequency bursts. These rf bursts provide an oscillating magnetic field of a certain strength and frequency. By observing the matter, the effects of the transient rf signals created a spin echo signal, which is a signal from the

magnetic nuclei that occurs after a two pulse signal. This result led to a host of new technologies and applications of NMR. Using NMR allows chemistry labs to quickly identify an unknown's chemical makeup. The medical world uses MRI to "look" into the human body to identify problems and diagnose what ailment a person has. (MRI stands for magnetic resonance imaging; the word nuclear being removed to alleviate the fears of the scientifically illiterate.)

THEORY

While I'm sure you have all read the background and found it fascinating, it does little good in explaining the actual mechanism of Pulsed NMR. So, here it is. Condensed matter is made up of atoms. Every atom has a nucleus of at least one proton and (often) some neutrons. Ignoring the neutrons, the protons have a number of properties, though we are only interested in two of them for this consideration: charge and spin. Each and every proton has a positive charge associated with it, by definition. The proton also has a property known as spin (for the proton, the spin is ½, an important mechanic for quantum mechanics, but it is sufficient here to know that these two effects give rise to a magnetic moment).

This property is from the individual particle itself. If we are considering Helium, the two protons will each have spin, but in opposite orientation. This will eliminate the resultant magnetic property, and therefore, don't behave as we'd like for nuclear magnetic resonance. Fortunately for us, the only chemicals we'll be working with in this lab contain unpaired nuclear spins, or have hydrogen atoms in various places on the molecule, allowing us to observe the effects.

So, we now have a handful of atoms that are producing a faint magnetic field via their nuclear properties. The next step is to place our sample into a strong magnetic field. The interaction of the magnetic fields will strive for the lowest energy state, which will be the magnetic fields in roughly the same alignment. The stronger the external permanent field is, the more uniform the alignment is, since the particle-particle interaction will be relatively smaller.

From here, we can relate the magnetic moment of the proton μ to its angular momentum **J** with the following equation

μ=γJ

with y being a constant known as the gyromagnetic ratio. The nuclear angular moment is quantized and is given by

J=ħI

with I being the spin, discussed earlier. From this, we can calculate the magnetic energy **U** of the nucleus in the external magnetic field, which is given by the following equation

U= -μ•B (3)

(1)

(2)

A way of simplifying the system from this point is to create our own coordinate system. The most common convention for this system is to take the direction of the external magnetic field **B** and label it the positive z direction. Since we are making this assumption, we can take **(3)** and modify it further, such that

$$U=-\mu_z B_o=-\gamma \hbar I_z B_o \tag{4}$$

Now, you should know from quantum mechanics that $m_1=1,1-2,...,-1$. Using this result with the proton, which has a spin value l=1/2, l_z has only allowed values of $\pm 1/2$. Since there are only two magnetic energy states for a proton in our external magnetic field, we are left with an energy separation between the two states, which we can express as ΔU , which we can express in the following manner

$\Delta U = \gamma \hbar B_o = \hbar \omega_o$

Which gives us

 $\omega_{o=\gamma}B_{o}$ (5)

Now, the accepted value for $\gamma_{proton}=2.675 \times 10^4$, given in units of rad/sec-gauss. So, we can calculate the resonant frequency of our proton with the external magnetic field and find

$$f_o(MHz)=4.258 B_o$$
 (in kilogauss) (6)

Looking at the system that we have defined, we currently have a sample that is contained in a magnetic field which points in the +z-direction. As time goes on, there is a nuclear magnetization in the z-direction because of the unequal population of the two possible quantum states, as we have already discussed. We can call these states N₁ and N₂, which are the number of spins per unit volume in one of the two states. We can find this ratio if we so choose by assuming the system is in thermal equilibrium, and use the following Boltzmann factor

$$\frac{N_2}{N_1} = e^{-\frac{\Delta U}{kT}} \tag{7}$$

This describes the population ratio of the two populations, with k being the appropriate Boltzmann's Constant. From here, we can show that the net magnetization M_z is given by

$$M_z = (N_1 - N_2) \mu$$
 (8)

Now, what is extremely important to note is that the magnetization does NOT occur instantly. Rather, what we observe is a net magnetization occurring over some time until the sample effectively has a magnetization of \mathbf{M}_{o} , which we define as

$$M_{o}=N\frac{\mu^{2}B}{kT}$$
 (9)

The shift towards this level of magnetization can be modeled by the relatively straight-forward differential equation

$$\frac{dM_z}{dt} = \frac{M_o - M_z}{T_1} \tag{10}$$

The result can be seen below in figure 1.





Now, an extremely important concept here is the T_1 time, known as the **spin-lattice relaxation time**. This time is different depending on what sample you are testing with your PNMR setup, and is very useful in identifying various properties of a chemical that you are working with. One very useful thing we can now do with our equation **(10)** is to assign boundary conditions. If we assume that the sample is unmagnetized when placed in the magnetic field, we can allow t=0 while M_z =0. So, we are able to solve **(10)** with direct integration and we get the result

$$M_z(t) = M_o(1 - e^{-\frac{t}{T_1}})$$
(11)

The rate that magnetization approaches its thermal equilibrium is a characteristic of the material being observed. There are a variety of contributing factors to this, but typical relaxation times are on the order of microseconds to seconds (water has a spin-lattice relaxation time of 2.5 seconds, which is very difficult to measure with the setup available to you).

The arrangement of the protons is what is referred to as the lattice, even in liquids or gasses, due to the arrangement of the magnetization. One large factor that determines the T_1 time is the angular momentum of the proton. In terms of quantum mechanics, the lattice must have angular momentum states available when a spin goes from one state to the other, as previously discussed. In classical terms, this translates to the protons experiencing a torque capable of changing this angular momentum. This is a very large factor when determining the spin-lattice relaxation time.

We have been discussing the magnetization exclusively in the z-direction. Now we will consider the magnetization in the xy-plane. When in thermal equilibrium, the only magnetization is in the direction of the external field. While this is true for the net, at any time, a single proton will have some small contribution in the xy-plane. If we think of placing a collection of tiny current loops in a magnetic field (think E&M II), this becomes easier to understand why there is no net in the xy-plane. We can look at the resultant torque as

$\tau = dJ/dt$ or $\mu x B = dJ/dt$ (12)

which, for our protons, becomes

$$\mu \times \mathbf{B} = \frac{1}{\gamma \, \mathrm{dt}} \tag{13}$$

This is the classical equation for describing the time variation of the magnetic moment of the proton in a magnetic field. A visual representation has been provided in figure 2, seen below.



Figure 2: Note, the precessional frequency ω_0 has been found in (5)

Hence, if we consider the net magnetization in our sample, usually on the order of 10^{22} protons, and x and y component will be cancelled out, and all we have in the Mz component of magnetization. However, there is a way to create a transverse magnetization using radio frequency pulsed magnetic fields. The idea is to rotate the thermal equilibrium magnetization M_z into the xy-plane and create a temporary M_x and M_y component. We can describe the classical motion of the net sample via the following

$$\frac{dM}{dt} = \gamma M \times B \tag{14}$$

For this situation, B is not only our constant magnetic field, $B_0\hat{k}$, but also a rotating magnetic field of frequency ω in the xy-pane so that our total field is

$$B(t)=B_1\cos\omega t\hat{i}+B_1\sin\omega t\hat{j}+B_0\hat{k}$$
(15)

Transforming the magnetic field expression from equation (15), into a rotating coordinate system, the total magnetic field a rotating frame B* becomes

$$B_{eff}^* = B_1 \hat{i}^* + (B_0 - (\omega/\gamma) \hat{k}^*$$
 (16)

Starred variables representing our new reference frame. The classical equation of motion of the magnetization is then

$$\frac{dM}{dt} = \gamma M \times B_{eff}^{*}$$
(17)

Which shows that M will precess about B_{eff}^* in the rotating frame. From here, we can create a rotating magnetic field with a frequency $\omega_o = \gamma B_o$. If we allow our effective magnetic field, B_{eff} to be constant in a direction, say the x-direction, the magnetization M_z will precess about the magnetic field at a rate of $\Omega = \gamma B_1$ (in the rotating frame). If we turn off the field B_1 when the magnetization reaches the xy-plane, we create a transient situation where there is a net magnetization in the xy-plane. If we apply our field for twice the time it takes for the magnetization to reach the xy-plane, we will have a magnetization along the -z-direction.

So, in a physical sense, you can think of the nuclei as all aligned in the +z-direction due to the constant external field. Now, we send a radio frequency signal onto a sample, and the magnetic component of the electromagnetic

wave will begin to "tip" the nuclei in the same direction. As long as the signal remains on, it will continue to rotate the nuclei until the signal is turned off. So, if the signal is shut off once all the nuclei are aligned in the xy-plane, the external magnetic field, being the remaining field, will begin to bring the nuclei back into their original alignment. The length of the pulse, over time, is what determines the orientation of the nuclei, and subsequently the magnetization. The pulse is named for the orientation that it gives to the magnetization. If a pulse is on only long enough to go from M_z to M_x , this is called a $\pi/2$ pulse, since it changes the magnetization by 90°. Orienting the nuclei from +z to -z is a π pulse, since the orientation of the nuclei changes by 180°. You could hit the sample with a 2π pulse if you really wanted to, but the orientation would go from +z-direction to +z-direction, ultimately doing nothing other than wasting some precious time.

In the laboratory (rest) frame where the experiment, the magnetization not only precesses about your rf B_1 , but also rotates about the z-axis during the pulse. Pulse NMR signals are observed after the transmitter pulse is over, so all that is observed is the net magnetization precessing about the constant magnetic field $B_0\hat{k}$ in the xy-plane, and nothing else!

Now, suppose a sample is hit with a $\pi/2$ pulse. If our sample begins in thermal equilibrium, the resulting net magnetization will be rotated to the xy-plane where it will precess about $B_o\hat{k}$. However, this magnetization will decay back to the z-axis orientation, as seen in figure 3



Figure 3

This behavior can be modelled by the following differential equation.

$$\frac{dM_x}{dt} = -\frac{dM_x}{T_2} \text{ and } \frac{dM_y}{dt} = -\frac{dM_y}{T_2}$$
(18)

The solution being

$$M_{x,y}(t) = M_0 e^{-\frac{t}{T_2}}$$
(19)

In this case, T_2 is known as the Spin-Spin Relaxation time. A measurement of T_2 , which is the decay constant of the xy-magnetization, gives information about the distribution of local fields at the nuclear sites.

From this analysis, it appears that the spin-spin relaxation time T_2 can be determined by plotting the decay of $M_{x,y}$ after a $\pi/2$ pulse. This signal is called the free precession, better known as the free induction decay (FID). If the magnet's field were perfectly uniform over the entire sample, then the time associated with the FID would be T_2 , in most cases, however, the magnet's non-uniform nature is responsible for the observed decay constant of the FID. (Note: for this experiment, the magnet has a sweet spot that results in any T_2 <0.3ms, the FID constant is also the T_2

of the sample. If the T_2 is actually longer, the observed decay will still be about 0.3 ms. In order to deal with this, a two-pulse signal can be used, the first being a $\pi/2$ pulse, the second one used at time τ being a π pulse. This is illustrated below in figure 4.





The first line of drawings shows the sequence of pulses, and the second and third lines illustrate what the net magnetization is from start to end (the illustration showing time passing from a,b,c etc.)

The π pulse allows the xy-plane magnetization $M_{x,y}$ to rephrase to a value it would have if a perfect magnet was used. An analogue for this would be a line of racers all start from the same line. They run out at different speeds, but after a time has passed, a whistle is blown and they all turn around and race back toward the start/finish line. If everyone maintains their speed, they will all cross at the same time. The π pulse is the whistle in this metaphor. The spins in the larger field get out of phase by some varying amount in time τ , but when the π pulse is used, they continue to precess faster than M, so they return to the in-phase condition.

Hence, the real T_2 value is obtained by a series of $\pi/2-\tau-\pi$ pulse experiments, varying τ , and plotting the echo height as a function of time between the FID and the echo. This gives us the actual value for T_2 .

DEFINITIONS

Free Induction Decay-also called free precession; this is the exponential decay signal as the sample decays from $M_{x,y}$ to $M_{o.}$

Larmor Frequency-the radio frequency at which resonance can be induced on the nuclei in the sample.

Magnetization-a unit vector that indicates the orientation of the net magnetic moment of the sample.

Precession-a change in the orientation of the rotational axis of a rotating body.

RF Signal-radio wave used to pulse the sample. The magnetic component of the electromagnetic wave will spin the nuclei a set amount, depending on the length of time that it is on.

Spin-Lattice Relaxation-The mechanism in which the magnetization vector reaches thermodynamic equilibrium with its environment.

Spin-Lattice Relaxation Time-The time it takes the FID signal to reach Spin-Lattice Relaxation.

Spin-Spin Relaxation-The mechanism in which the xy-component of the Magnetization vector, described as $M_{x,y}$ decays to its equilibrium value. (In the case with a static field along the z-axis, this decays to zero).

Spin-Spin Relaxation Time- The time it takes to reach the FID signal to reach $\frac{1}{e}$ of its original value, with regards to Spin-Spin Relaxation

SETTING UP THE PNMR EXPERIMENT

Question 1	a. Begin by familiarizing yourself with your equipment. You should have an oscilloscope, a TeachSpin Pulsed NMR Spectrometer, and a TeachSpin PM-1051 Magnet.				
	Set the equipment to the following settings:				
	Initial Set-Up				
	 For the 15 MHz receiver section of the PNMR Spectrometer: GAIN should be set at about 30% of the maximum. RF OUT connects to the MIXER IN located on the 15 MHz OSC/AMP/MIXER. BLANKING should be ON. TIME CONST (ms) should be 0.01. BLANKING IN connects to BLANKING OUT on the Pulse Programmer. TUNING should be set slightly above its minimum value. DETECTOR OUT should connect to Channel 3 of the Oscilloscope. RF IN should connect to the TeachSpin Magnet. 				
	Note- These settings should not be changed throughout the experiment.				
	 For the Pulse Programmer initial set-up should have the following: A-WIDTH at its minimum. B-WIDTH at its minimum. DELAY TIME should be set to zero. MODE set at INT (does not change). REPETITION TIME set to 100 ms with VARIABLE at 10%. NUMBER OF B PULSES should be set to zero. SYNC set to A A switch set to OFF. B switch set to OFF M-G OUT connects to M-G IN in the 15 MHz OSC/AMP/MIXER. SYNC OUT connects to Channel 4 of the Oscilloscope. A+B OUT should be split with one cable connecting to Channel 1 of the scope, and the other connecting to the A+B IN in the 15 MHz OSC/AMP/MIXER. 				
	by an alarm. If this occurs, tarm the machine off.				
	Note- The repetition time is determined by multiplying the values of the two REPETITION TIME knobs. For example: 100ms at 40% VARIABLE corresponds to a repetition time of 40ms.				
	 Settings for the 15 MHz OSC/AMP/MIXER: CW-RF should always be ON. MIXER OUT connects to Channel 2 of the scope. RF OUT connects to the Magnet. M-G switch always ON. 				

LARMOR FREQUENCY

Now that the theory has been established and your station is up and running, the next step is to begin taking data and learning how to use your equipment. In order to start, the PNMR spectrometer should be set to the Larmor frequency. This is a function of the external magnetic field and the gyromagnetic ratio, and is, essentially, the frequency at which the nuclei in the sample are most responsive to the rf signal.

	Determ	Determine the Larmor Frequency				
Question 2	a.	Calcula	te what you expect the Larmor Frequency to be from the theory (you did read the			
		theory	theory, didn't you?)			
	b.	Next, f	ind the Larmor Frequency experimentally. To do this, follow these instructions:			
		i.	Insert a sample of mineral oil into the probe housing of the Magnet			
		ii.	Observe channel 1 on the scope and on the Pulse Programmer, turn switch A to ON.			
			The result should be seen in Figure 5			
		iii.	Use channel 2 of the scope to observe the MIXER OUT signal. This signal shows the difference between the two RF signals, the Larmor frequency and the driving RF signal. In order for to achieve resonance, the beat frequency should go to zero. This is achieved using the FREQUENCY ADJUST knob on the 15 MHz OSC/AMP/MIXER. It should begin looking like Figure 6 and end looking like Figure 7			
	c.	Quanti	tatively explain what is happening			



Figure 5







Figure 7

FINDING T_1 AND T_2 VALUES

The majority of the data that you can obtain from this experiment comes from the Spin-Lattice Relaxation Time, T₁ and the Spin-Spin Relaxation Time, T₂. These relaxation time values are unique to the sample that is being observed. From this data, we can extract a myriad of information about the sample itself, and we can also use this method to test an unknown to know what exactly it is we are looking at. Finding what these values are, therefore, is very important in understanding pulse nuclear magnetic resonance.

Question 3	Estimating T ₁			
Question 3	 To begin, you can estimate the value of T₁. This isn't entirely accurate, but it can give an approximation to verify against other answers. a. To begin, prepare a sample. Take a clean, empty sample tube. Make sure it has a rubber O-ring attached near the cap. Fill the tube with enough mineral oil so the sample in the tube has a height that is approximately equal to its width. (When looking at the sample, it should be roughly square). b. Place the sample in the magnet housing. c. With the magnet on, the protons should have a magnetization in the +z-direction. d. Start by only using an A pulse. Using channel 3 on the Oscilloscope, connected to DETECTOR OUT, observe the effects of an A pulse. This is displaying the total magnetization in the xy-plane. e. In order to create a π/2 pulse, adjust the A-WIDTH setting until a maximum is observed. f. Make sure there is a REPETITION TIME of 100 ms with VARIABLE at 100%, this allows 1 π/2 pulse every 100ms. (The repetition time isn't readily apparent, the variable switch is how much of the repetition time is actually used, so 40% variable of a 100 ms repetition time is actually 40ms). g. In order for the π/2 pulse to actually tip the magnetization vector into the xy-pane, the magnetization must be aligned in the z-direction, so enough time must pass for the sample to relax to this position. h. Begin decreasing the repetition time between pulses. Eventually, the signal will begin decreasing. What is the physical reason for this? i. The T₁ time is when the maximum signal is equal to 1/e of its original value. When does 			
Question 4				
Question 4				
	 In the previous question, you found an approximation for Spin-Lattice Relaxation Time. Now, you will be calculating the value, rather than simply getting an estimation. a. To begin, this method will be following what was described in the Theory section, and can be seen in Figure 4 above. b. This is a multi-pulse sequence, so to start, a π pulse is needed. In order to set your A pulse width to be able to tip the nuclei by 180°. Again, using channel 3, turn the A-WIDTH knob all the way counter-clockwise. Then, begin to increase the value. Once the signal peaks on the oscilloscope, you have found a π/2 pulse. Keep increasing the width until the signal is minimized. This is a π pulse. c. Next, for B width, turn the A pulse off, set number of pulses to 1, turn on the B pulse, sync to it, and find its first maximum point. Now we have set the A pulse to be a π pulse and the B pulse to be a π/2 pulse. d. Turn both A and B on, and leave this synced to B. As you increase the delay time, which is the time between the A and B pulses, the spin echo should be decreasing. Once it goes to zero, the experimental value for T₁ has been obtained. 			

	e. What is the physical effect happening? Refer to the theory and figure 4 above. Why is				
	this more accurate than the previous way of finding T ₁ ?				
Question 5	Calculating T ₂				
	The next step is to calculate the T_2 relaxation time. The T2 value of a sample corresponds to its				
	spin-spin relaxation time. The spin-spin relaxation is the collection of spins dispersing from a common orientation. This is caused by the non-uniform nature of the magnetic field and spin-				
	spin interactions between protons. This is seen in the lab as spin echoes which will decay over				
	time. The time in which it takes for the spin echo signal to decay to 1/e of its max value				
	corresponds to the T2 value.				
	a. To begin, set the A pulse width to generate a $\pi/2$ pulse. This sets the magnetization				
	vector into the xy-plane.				
	b. Turn the A pulse off and the B pulse on, then adjust the B-WIDTH until the first π pulse				
	has been achieved (note the π pulse must come after the first signal maximum, which is				
	the $\pi/2$ pulse).				
	c. Turn on both pulses and increase the NUBMER OF PULSES setting to 2. Set the DELAY				
	TIME such that there is a clear gap between each FID.				
	d. Begin increasing the total number of pulses. You will soon be able to clearly see the				
	exponential nature of the pulses. The Spin-Spin Relaxation Time is defined as the time in				
	which the resultant peak is at 1/e of its original (maximum) value.				
	e. See figure 8 for example of spacing between peaks.				
	f. Explain what is physically happening.				
	g. Use an outside resource to further your understanding of Spin-Spin Relaxation. Does the				
	theory make sense and agree with what you are observing? Why does the sequence of				
	pulses result in what you have seen?				



Figure 8

WEEK 2: FURTHER UNDERSTANDING OF PULSE NUCLEAR MAGNETIC RESONANCE

GOALS

Now that you are familiar with the idea of Pulse Nuclear Magnetic Resonance and the idea behind it, and have a working knowledge of how the equipment works, it is time to put this knowledge to good use! This week, you get to design your own experiment.

Ouestion 6	Designing your own experiment
	 There are several ways you can design your own experiment. Try starting with what you know the PNMR is capable of doing and expand from there. Here are some ideas to help get you started. a) So far, you have been using mineral oil, a homogenous mixture, as your sample. The reason we don't use water for this experiment is because water has a relaxation time of several seconds. However, we can change the relaxation time with the introduction of a paramagnetic ion. Why this and what is are the results? (Hint: A useful paramagnetic ion that is available in the lab is copper sulfate.) b) The relaxation times of protons in mineral oil doped with organic solvents shows effects of diffusion and correlation times. Why is this? Can you test this in the lab? Predict what will happen. c) So far you have been using a sample at a constant temperature. Will relaxation times change with varying temperatures? What is the effect? Why does this occur? While you can heat up mineral oil, a material that will show this difference more drastically is petroleum jelly. Try designing an experiment around this!

WHAT IS NUCLEAR MAGNETIC RESONANCE GOOD FOR?

Nuclear Magnetic Resonance has a wide range of applications. For chemistry, it allows chemists to determine the structure and composition of many different compounds, saving countless hours of work. By unambiguously identifying a molecule, it allows the field to move forward faster than it ever had.

In the medical field, you may already be acquainted with the use of NMR. An MRI, Magnetic Resonance Imaging, is a device that relies almost exclusively on these principles. The name was changed due to a public fear of the word "nuclear". This technology allows doctors and scientists to make great strides in research as well as diagnosing patients without having to perform invasive biopsies.

Other applications of an NMR are to determine purity in a sample, perform non-destructive testing, acquiring data (in the petroleum industry, for example), and many more. All of these have come from the idea and theory of nuclear magnetic resonance. In this lab, the student frequently goes on to experiment with NMR spectroscopy to further understand and grasp the concepts of nuclear magnetic resonance.

REFERENCES

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