

Understanding Precessional Frequency, Spin-Lattice and Spin-Spin Interactions in Pulsed Nuclear Magnetic Resonance Spectroscopy

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Introduction

Nuclear Magnetic Resonance (NMR) spectroscopy is a very powerful technique that is an essential component to current research in chemistry and biochemistry. This technique also has important clinical applications in medicine. This spectroscopy involves transitions between different spin states of the nucleus (most commonly ^1H and ^{13}C) and is greatly simplified since we only need to consider a finite number of spin orientations that exist for the ground state of the nucleus. NMR is essential to the identification and structural determination of new compounds. This spectroscopy may also be used to explore dynamical features of chemical systems; e.g., rotational and translational motion, conformational transformations and other isomerizations.

In order to obtain good NMR spectroscopy results, it is important to understand how the instrument works and how to determine important variables such as spin-lattice and spin-spin relaxation values, which are important variables when setting up an NMR spectroscopy experiment. In this lab experiment, you will be using a TeachSpin PS2-A pulsed NMR instrument with a permanent magnet. The instrument was designed purely as a device to teach and educate people on how pulsed NMR works. We will not be concerned with chemical shifts and identification of an unknown or functional groups in this experiment. Instead, we will focus on the physical nature of what happens to a sample when it is put into a magnetic field and then pulsed with RF signals to introduce “behavioral” changes in the sample allowing us to “see” and measure the sample. The goals of this experiment are the following: 1) Understand Larmor frequency and how it is affected by the size of the magnetic field and the gyromagnetic ratio. 2) Understand and observe what happens when an NMR instrument is tuned to the Larmor frequency and the magnetic field is shimmed. 3) Measure spin-lattice relaxation (T1) and spin-spin relaxation (T2) times for heavy mineral oil, light mineral oil, pure water and water with FeCl_3 . 4) Explain how T1 and T2 are affected by the nature of the molecule being studied and how these values are influenced by the addition of ions. 5) Understand and explain the importance of T1 and T2 values when conducting NMR experiments.

Theory

NMR is a resonance spectroscopy that is used to probe excitations between different spin states of nuclei. It may be distinguished from the more familiar “optical” spectroscopies in two ways. First, it employs two external fields to probe the system – a constant (DC) magnetic field and an oscillating (AC) magnetic field. By varying the strength of the DC field, the energy difference between the ground and excited spin states is changed, so that the resonance or Larmor precession occurs at the same frequency as the AC field. This method of changing the gap between energy levels is different than the optical spectroscopies in which they are usually fixed. Second, the excitations involve the spin systems of nuclei. The spin of these particles is weakly coupled to other molecular movements (rotational and vibrational) known as spin-lattice interactions, as well as spin interactions with other nuclei in the molecule, known as spin-spin interactions. These weak couplings allow for interesting and useful spectroscopic methods to be

employed; *e.g.*, saturation of the transitions. Here we provide a short fundamental discussion on the aspects related to nuclear energy splittings, precessional (Larmor) frequency, spin-lattice and spin-spin relaxation. You should also review reference literature with more complete discussions on these topics [1,2].

Magnetic resonance is based on the observation that a particle with spin (s) carry an associated magnetic moment (u)

$$\vec{u} = \gamma \vec{s}, \quad (1)$$

where γ is called the gyromagnetic ratio [1-4] and is specific to each nucleus. The Zeeman effect describes the energy (E) of such a particle when it interacts with an externally applied magnetic field (**Figure 1**).

$$E = -\vec{u} \cdot \vec{B}_0. \quad (2)$$

In order to evaluate the scalar product in Eq. 2, we need to multiply u_z , the projection of u on the magnetic field vector (z), with B_0 . Using the fundamental quantum relationship between the magnetic quantum number (m) and the spin value (s)

$$s_z = \hbar m_z \quad (3)$$

we obtain

$$u_z = \gamma \hbar m_z \quad (4)$$

and

$$E = (\gamma m_z \hbar B_0) = u_z B_0 \quad (5)$$

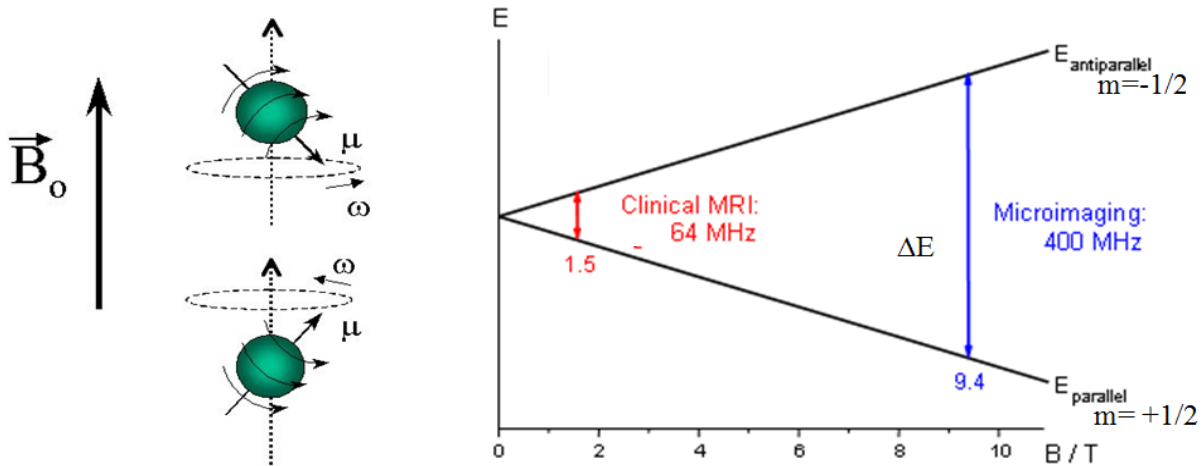


Figure 1: (left) Representation of the spin precession about an applied magnetic field at the Larmor frequency. (right) Energy level splitting of a proton that is either aligned with the magnetic field or antiparallel to the field.

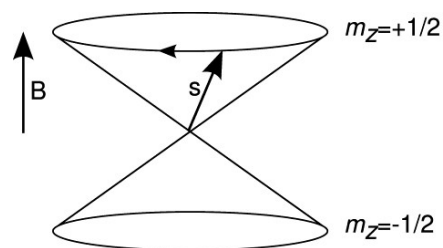
For a particle with $s = 1/2$, such as a proton, m_z can only take the two distinct values $+1/2$ or $-1/2$, describing the two spin-states that are often called the “spin-up” and the “spin down” state. s and m_z describe the state of the particle completely. Due to the uncertainty relation we cannot know the projection of s onto a different axis (*e.g.* m_x) at the same time. In order to change between the two spin states, m_z needs to change by one unit. Therefore the energy difference associated for this transition for a proton is given by

$$\Delta E = (\gamma m_{1/2} \hbar B_0) - (\gamma m_{-1/2} \hbar B_0) = \gamma \hbar B_0 \quad (6)$$

Or in terms of the resonance frequency (f) and the corresponding angular velocity ω of such a transition, the relation is

$$\Delta E = \hbar\omega = \hbar 2\pi f = hf \quad (7)$$

The resonance frequency is determined by the proton's precessional rate or frequency. In a semi-classical picture, the spin is said to precess on the surface of a cone around the magnetic field vector (**Figure 2**). By combining eq. 6 with eq. 7, we can see that the precession frequency, known as the Larmor Frequency, is ultimately given by the magnitude of the magnetic field and by the gyromagnetic ratio.



$$f = (\gamma B_0)/2\pi \quad (8)$$

Figure 2: Precession of a proton in a magnetic field

For a proton, $\gamma = 267.5$ (C/kg). This value is often reported as 42.58 MHz/T, which is the same as the value given here multiplied by 2π [3]. Therefore, when the magnetic field is 7.05 Tesla ($\text{kg}/(\text{A}\cdot\text{s}^2)$) or 70,500 Gauss, the resonance (Larmor) frequency for a proton is about 300 MHz (in the radio frequency range). You will explore this fundamental relationship for a classical spin system using the Magnetic Torque ($M\tau$) instrument.

Spin-lattice and spin-spin relaxation

Different physical processes are responsible for the relaxation of the components of the nuclear spin magnetization vector \mathbf{M} parallel and perpendicular to the external magnetic field, \mathbf{B}_0 (which is conventionally oriented along the z axis). These two principal relaxation processes are termed spin-lattice and spin-spin relaxation or T_1 and T_2 respectively.

The process called spin-lattice relaxation, also called "longitudinal magnetic" relaxation, refers to the mean time (T_1) for a nucleus to return back to its thermal equilibrium state in its surroundings (the lattice) after it has been exposed to an rf signal (pulse). Once the nuclear spin population is relaxed to equilibrium conditions in the magnetic field, it can be probed again. Precessing nuclei can also fall out of alignment with each other (returning the net magnetization vector to a non-precessing field) and stop producing a signal. This is called spin-spin or transverse relaxation and the time required for this process to occur is referred to as T_2 . Because of the difference in the actual relaxation mechanisms involved (for example, inter-molecular vs. intra-molecular magnetic dipole-dipole interactions), T_1 is usually longer than T_2 . This means that spin-lattice relaxation is slower because of smaller dipole-dipole interaction effects. A nucleus with a long T_2 relaxation time gives rise to a very sharp NMR peak in the FT-NMR spectrum for a very homogeneous ("well-shimmed") static magnetic field, whereas nuclei with shorter T_2 values give rise to broad FT-NMR peaks even when the magnet is shimmed well. Both T_1 and T_2 depend on the rate of molecular motions as well as the gyromagnetic ratios of both the resonating and their strongly interacting, next-neighbor nuclei that are not at resonance.

Determination of T_1 (Inversion-Recovery Method)

A two pulse inversion-recovery sequence can be used to determine T_1 . The pulse sequence is:

$$180^0 \text{---} \tau \text{---} 90^0 \text{ FID}$$

The first pulse (180^0) inverts the z -component of the magnetization from M_z to $-M_z$, but the spectrometer cannot detect magnetization along the z -axis. It only measures net magnetization in the x - y plane. So a second pulse (90^0) is used to rotate the net z -component of the magnetization into the x - y plane where the magnetization can produce a measurable signal $M_y(\tau)$ or $M_x(\tau)$. A series of $M(\tau)$ values can be obtained by varying the delay time (τ) in between the pulses. The recovery is an exponential process and is observed when we plot $M(\tau)$ versus τ . From the curve, we can measure M_{eq} , (the thermal equilibrium magnetization). The quantitative expression of this process is:

$$M(\tau) = M_{eq}(1 - 2e^{-\tau/T_1}) \quad (9)$$

Equation (9) can be transformed to the following form:

$$\ln \left[\frac{M_{eq} - M(\tau)}{2M_{eq}} \right] = \frac{-\tau}{T_1} \quad (10)$$

A plot of the $\ln((M_{eq}-M(\tau))/2M_{eq})$ versus τ reveals a linear graph. The slope of this graph is equal to $-1/T_1$.

Determination of T_2 in the pulsed NMR spectrometer

Before the invention of pulsed NMR spectroscopy, the only way to measure the real T_2 of a sample was to improve the magnet homogeneity and make the sample smaller, but time-resolved NMR spectroscopy changed this. A two-pulse spin echo sequence can be used to determine T_2 . The pulse sequence is:

$$90^0 \text{---} \tau \text{---} 180^0 \text{---} \tau \text{---} \text{echo } (2\tau)$$

The spin echo process is described in detail in the supplemental handout. The first pulse (90^0) is used to rotate the thermal equilibrium magnetization (M_{eq}) from the z -axis to the y -axis followed by the short interpulse time delay τ . The second pulse (180^0) flips the magnetization across the x - y plane. After the 180^0 pulse, the spins in the higher field (ω_f) get out of phase and precess faster than ω_o , but at 2τ they return to the in-phase condition. The slower precessing spins (ω_s) at the lower field get out of phase and rephase again after a time 2τ . The net magnetization in the x - y plane is decreasing and will finally decay to zero. This rephasing of the spins generates a spin-echo signal that can be used to measure T_2 . The net x - y magnetization as measured by the maximum echo is written as:

$$M_{x,y}(2\tau) = M_{eq}e^{-2\tau/T_2} \quad (11)$$

Equation (11) can be transformed to:

$$\ln(M_{x,y}(2\tau)) = \frac{-2\tau}{T_2} + \ln(M_{eq}) \quad (12)$$

A linear curve with a slope of $(-1/T_2)$ is obtained as we plot $\ln(M_{x,y}(2\tau))$ versus 2τ . So T_2 can be calculated from the slope.

Laboratory Procedure

This experiment involves two primary components. One, you will measure the precessional frequency of a spinning magnetic dipole (a cue ball fitted with a magnet) as you vary the magnetic field using the $M\tau$ instrument (**Figure 3**). In doing so, you will be able to determine the gyromagnetic ratio for the cue ball as well as gain an appreciation for the behavior of a proton in a magnetic field. In addition, you will use the TeachSpin PSA-2 instrument to investigate spin-lattice and spin-spin relaxation for four different chemical samples. In doing so, you will learn about how to set pulse sequences for an NMR experiment, the importance of T1 and T2 values when setting an NMR pulse sequence and how the chemical nature of the samples affects these relaxation times. Because time may be short depending on the level of difficulty you encounter with the NMR set up, proceed with part 2 first and complete part 1 if there is enough time in the lab period.

Part 1: Gyromagnetic measurements with the $M\tau$ instrument.

This part of the laboratory exercise has two components. First you will determine the magnitude of a classical magnetic dipole moment by a measurement of its precession frequency in an external magnetic field. Second, you will induce ‘spin flips’ in this system by the application of a transverse rotating magnetic field.

A photograph of the apparatus is shown in **Figure 3**. It consists of a pair of coils that generate a static magnetic field at its center.



Figure 3: The $M\tau$ instrument used to simulate the Larmor frequency.

The cue ball between the coils has a magnetic disc mounted in its center and has a handle that you can use to spin it. The equivalent radius of the magnetic coils is 0.109 m and their equivalent separation is 0.138 m. This geometry generates a field at the center of the coils that is 1.36×10^{-3} Tesla/Amp. The instrument has a strobe light that you will use to determine the spin frequency of the cue ball.

1. Place the ball in the air bearing and turn on the instrument and the air flow, but set the current through the coils to zero so that no magnetic field is applied.
2. Spin the cue ball in the air bearing with the handle pointing straight up. If the spinning cue ball is wobbling, softly place your fingertip on the handle and it will stabilize.

3. Turn on the magnetic field by applying current through the coils. Does the direction of the cue ball's spin axis change? In other words, does it precess?
4. Turn off the magnetic field and now adjust the cue ball's spin angle so that the handle is point at an angle away from straight up. An angle in the "10 o'clock position (about 45-60 degrees) usually works well.
5. Turn on the magnetic field again. Does the direction of the cue ball's spin axis change? How does going through this little demonstration correlate to the rf pulse in an actual NMR?

Now it is time to collect quantitative data to determine the gyromagnetic ratio of the cue ball. With the magnetic field turned on, a torque is generated and the cue ball will begin to precess (rotate about the direction of the magnetic field axis) and as you increase the size of the magnetic field, the precession frequency should change (eq. 8). By knowing the magnetic field strength and measuring the precessional frequency of the cue ball, you can determine its gyromagnetic ratio. When conducting the experiment it is important to keep the spin of the cue ball constant. You will find a small white dot on top of the cue ball handle. The goal is to use this marker along with the strobe light to monitor the spin frequency and adjust as necessary. Usually a spin frequency of about 5 Hz works well. With this value held constant, the relationship between the magnetic field strength and the precessional frequency should be linear. The slope of the linear relationship between $2\pi/f$ on the y-axis (remember that you are actually collecting the time for one precession, so f is the inverse of your value) versus the magnetic field strength will be equal to the gyromagnetic ratio of the cue ball. Note that the magnetic field strength is dependent on the amp setting you select. Specifically,

$$B \text{ (magnetic field of coil) (Tesla)} = 1.36 \times 10^{-3} \text{ (Tesla/amp)} \times \text{amps} \quad (1 \text{ Tesla} = \text{kg}/(\text{A s}^2))$$

6. The spin angular momentum of the ball may be determined by using the strobe light. Fix the frequency of the strobe light to a value around 5 to 5.5 Hz. Record the frequency that you choose and use this frequency for all of your measurements. In order to clearly see how the strobe light illuminates the white dot on the cue ball's handle, the room should be darkened. When the spin velocity of the cue ball matches the frequency of the strobe light, the white dot on the ball's handle will appear stationary.
7. Turn on the apparatus so that the air bearing is working. Leave the field gradient off and set the field direction to 'up' and set the current to 1 amp. Have a stopwatch ready but do not yet turn on the coil current.
8. Before you begin making measurements, practice spinning the ball and setting it at a 10 o'clock angle. A good technique is to spin the ball and then use the tip of your fingernail to direct it to spin about the handle's axis with the handle oriented toward the strobe light. Notice that the frequency of the ball's spin changes with time (approximately exponentially). It is because of this decay that a strobe frequency of about 5 Hz is used. At this frequency the rotational frequency does not change significantly during the time it takes the ball to precess through one period. When you master the technique of spinning the ball and orienting its axis, you can begin measurements.
9. Leave the current off, spin the ball up, adjust it so that it is illuminated by the strobe light and watch the white dot. At first you will see the white dot move around, but as the ball slows down, the white dot will begin to have a regular rotation of its own. This rotation will slow down until the white dot stops.

10. As soon as the dot stops, turn on the field (current) and measure the time it takes the ball to precess through one full orbit (i.e., the period of the orbit). Record this time and the current.
11. Perform the same procedure as above, but this time use a current of 1.5 amps.
12. Continue in this manner (steps of 0.5 amps) until the current reaches 4 amps.
13. Record your data in a table that gives the current, the magnetic field strength, the precession period and the spin frequency of the cue ball.
14. Verify that your measurements change in a linear manner using an Excel plot and determine γ for the cue ball. Repeat measurements as needed to obtain good results.

Part 2: Determination of T1 and T2 for four chemical samples.

In this part of the experiment we will now use the TeachSpin PSA-2 instrument. The samples we will use are heavy and light mineral oil, pure water and water with FeCl₃ in it. This array of samples should give good examples of how molecular size and the presence of paramagnetic species affect T1 and T2 values.

1. The instrument should always be left on (**Figure 4**). If it is off, turn on instrument (toggle switch on the back) and the oscilloscope (on top).
2. Flip the toggle switch for both magnetic temperature controllers to open. The instrumentation and magnet need to warm up and equilibrate for about 15 minutes before continuing.
3. After 15 minutes, adjust the magnet temperature dials so that the indicator lights are off (this is right between a green and red indicator light). Once this is achieved, flip both toggle switches to “closed”.
4. Turn all 4 magnetic field gradient pod dials to zero and all toggle switched below the dials to negative (-). These are the controls used to shim the magnet (which we will do very soon).

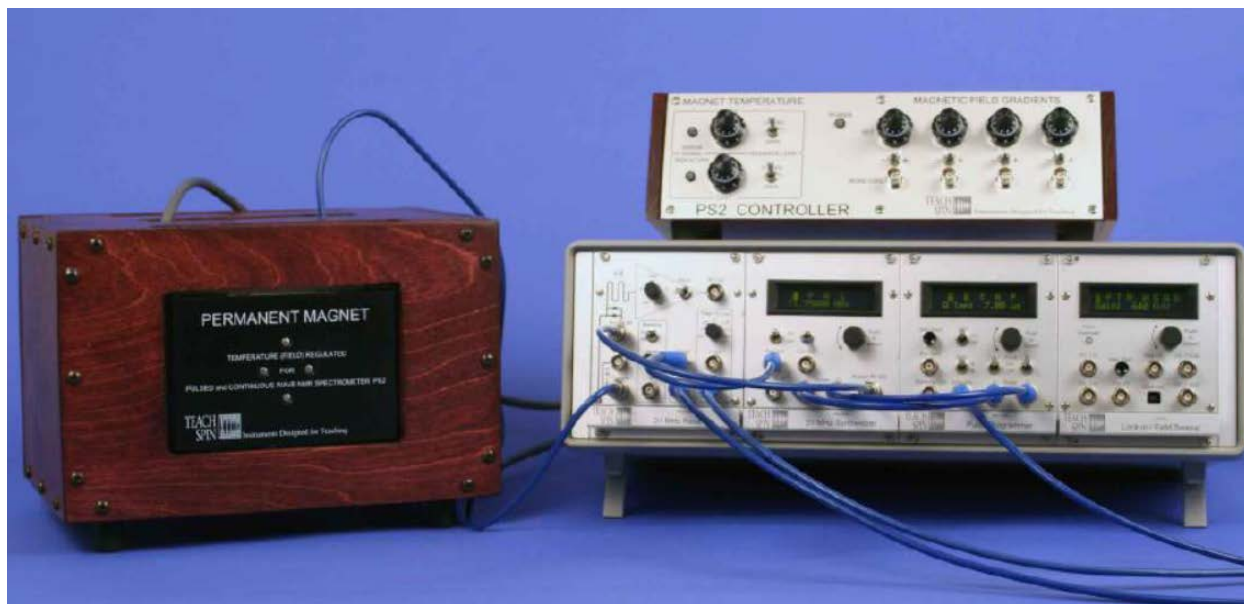


Figure 4: The PS2-A Spectrometer: Magnet, Mainframe and PS2 Controller

Below the PS2 Controller is the signal processor. You will only be using a few of these adjustments. You will not need anything on the unit to the far right called the “Lock-in/Field

Sweep” or on the far left called the “21 MHz Receiver”. In the 21 MHz synthesizer unit, you will only adjust the Frequency (Larmor frequency for protons). Most of the work will be done with the “Pulse Programmer” unit. On these two units, you use the black dial knob to adjust parameters. This “push-to-select” knob is used in three stages:

- A. Rotate the knob to display the desired parameter.
- B. Push the knob into the panel and hold for a second or two until a beep indicates that the parameter has been selected.
- C. Now you can change the value of the selected parameter by rotating the knob until your chosen value is displayed.

Play with these controls a bit to become familiar with operation and refer to the appendix for more information.

Setting the Frequency for the Precession of a Proton

For this unit, the approximate Larmor frequency is 21.6 MHz.

5. On the “Synthesizer” unit, scroll until the “F” (Frequency) option is underlined.
6. Push the button and now adjust the Frequency to 21.65000 MHz.
7. Check both the Synthesizer and Pulse Programmer units to make sure the following default values are set.

Table 1: Default PSA-2 settings

SYNTHESIZER	PULSE PROGRAMMER
F (Frequency): 21.65000 MHz	A (A (first) pulse length): 0.02 μ s
P (Refer Phase): -180°	B (B (second) pulse length): 0.02 μ s
A (CW Pwr): -10 dBm	t (time between pulses): 0.0001 s
S (Sweep): 0 kHz/V	N (number of B pulses): 0
	P (repeat pulse sequence period) 0.2 ms

Tuning (shim) the Magnet

Before you place a sample into the NMR and search for your first NMR signal, you must tune and shim the instrument to the Larmor precession frequency of the proton in the ambient magnetic field. Since the spectrometer has no “pickoff points” in which you can examine the RF currents through the solenoid, a “pickup probe” (**Figure 5**) is provided which can be inserted into the sample chamber to measure the RF fields during the pulse.



Figure 5: RF probe

8. Place the RF pickup in the magnet sample holder. Attach the BNC connector to Channel 1 of the **oscilloscope**.
9. Set the A pulse to 2.5 μ s.
10. Set the Period to 1.00ms
11. Make sure the following toggle switch positions are correct on the Pulse Programmer:
Sync: A A Pulse: On B Pulse: Off

12. Adjust the Oscilloscope settings:

- Push the “TRIG MENU” button. On the right part of the screen you’ll see options. Set these to the following; Type- edge; Source-ext; Slope - Rising; Mode – Normal; Coupling – DC. With the Trigger level dial, adjust it to 0.1 V (see display)
- Push the “MEASURE” button. Makes sure it is set to Channel 1 and the measurement method (second option from top on the display) is set to Pk-Pk. This will give you the size in volts of your signal.
- On the Horizontal menu use the SEC/DIV and adjust to 1.00 $\mu\text{s}/\text{DIV}$. You can adjust the positioning of the signal on the screen by using the Horizontal and Vertical knobs. A DIV is simply the divisions (grid) on the display.
- Set Channel 1 to 5.00 V/DIV.

With this time scale on your ‘scope, you are observing the RF field inside the solenoid DURING THE PULSE. This is *not* a magnetic resonance signal. If the RF Sample Probe is properly tuned, you should observe an RF burst of about 60 volts peak-to-peak lasting about 3 μs (Figure 6), but these numbers are rough- focus more on the shape the signal. If you do not find this to be the case, notify your TA.

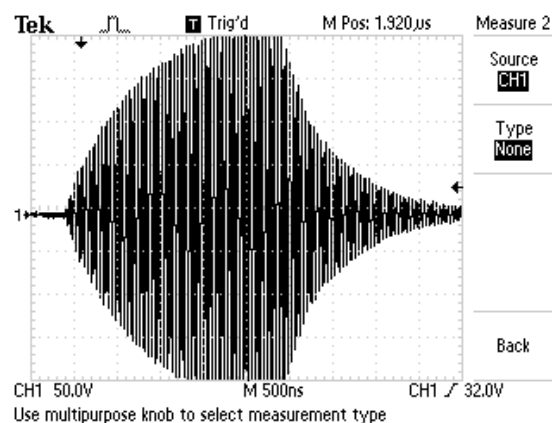


Figure 6: RF field inside the sample cavity during the pulse.

Once you have confirmed the RF pulse, disconnect the RF pickup from Channel 1 of the oscilloscope and reconnect Channel 1 back to the *Env Out* from the receiver.

First Experiment

You are now ready to do your first magnetic resonance experiment with the instrument. Start with mineral oil sample provided. Since you now wish to observe the precessing magnetization (collection of spins) AFTER THE RF PULSE HAS BEEN TURNED OFF, you need to change the time scale on the oscilloscope (step 13 below). The RF burst that tips the magnetization from its thermal equilibrium orientation along the z-axis (the direction of the DC magnetic field) to create some transient component along the x-y plane, does so on a time scale of microseconds. But this x-y magnetization precesses in the x-y plane for times of the order of milliseconds. Thus, the sweep times on the oscilloscope need to be adjusted accordingly.

- Set the Period to the value shown in **Table 2** for your sample being investigated.
- Make sure the O-ring on the mineral oil sample tube (used to keep the sample from falling into the magnet cavity) is exactly 39 mm from the center of the sample solution to the bottom of the O-ring before placing it into the magnet.
- The oscilloscope sweep time should be adjusted to 1.0 -2.5ms/div.

16. Channel 1 of the oscilloscope should be connected *Env Out* from the receiver. You also need to make sure the following toggle switch positions are correct on the Pulse Programmer:
Sync: A A Pulse: On B Pulse: Off
17. Turn on Channel 2 by pushing the CH 2 MENU button. Adjust the scaling as needed. You will use this signal to fine tune the Larmor frequency. You want this signal to not oscillate, but rather look like a decay curve similar to your actual signal on channel (Figure 7). Adjust the frequency until you get it to look like a simple decay curve with no oscillations. Your peak may look more rounded than those shown below, which is fine; it can vary with different usage of the instrument.

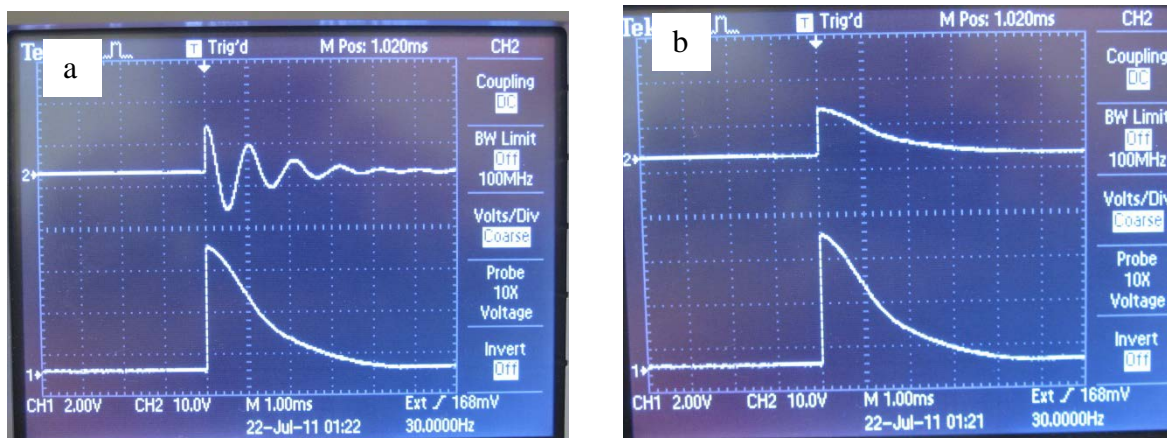


Figure 7: Signal from the sample (channel 1) and the resonance frequency (channel 2). In (a) the resonance frequency of the instrument is not properly tuned as evidence by the sinusoidal wave pattern. In (b) the resonance frequency is well tuned.

18. Now we need to shim the magnet field to make it homogeneous over the entire sample volume. To do this, use the 4 gradient pods on the PS2 Controller. Spin the dials and also try both “-“ and “+” with the toggle switches. The goal is to get the signal decay length as long as possible (Figure 8). As you do this, the Larmor frequency will probably de-tune slightly. So once you get the signal as long as possible, **go back and re-tune the frequency** and go back and forth between them to get the best looking signal. Make sure to keep record of this frequency.

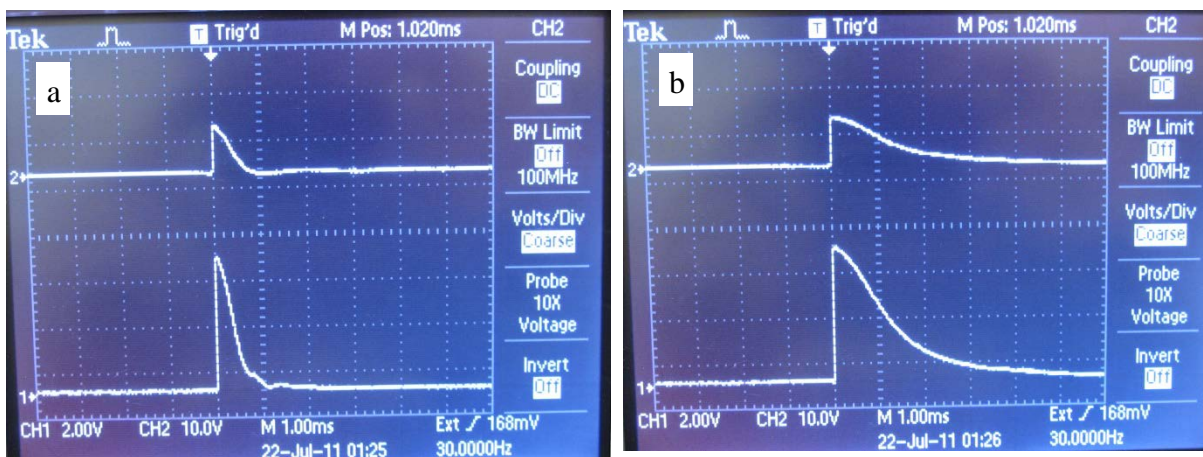


Figure 8: Signal from the sample (channel 1) and the resonance frequency (channel 2). In (a) the magnet is not homogeneous (shimmed) properly tuned as evidence by the shortened decay time. In (b) the field gradients have been adjusted appropriately to maximize the signal decay time.

19. Be sure to also do a screen capture at this point. To do this insert the USB drive provided. Make sure the “save” light on the ‘scope is green. If not, push the “Save/Recall” button. On the second option down from the top, make sure “Saves All To Files” is selected. Now go back to then “Measure” menu and then click the print button on the oscilloscope.

Determine the 90 and 180 degree pulse length for light mineral oil

Now we must determine the length of time needed for a 90° pulse and a 180° pulse so that you can find the samples’ relaxation times with the correct sequence. The experimental criterion for obtaining a 180° pulse, that is an RF burst that rotates the thermal equilibrium magnetization from the + z to - z axis, is a pulse approximately twice as long as a 90° pulse, yet one that leaves no FID signal after it. Remember that an appropriate 90° pulse will tip spins into the x-y plane and will be detected and viewed as your signal. Therefore, the pulse length that achieves the biggest signal is the 90° .

20. Adjust the A pulse length until you reach a signal maximum. In theory this is the 90 degree pulse length.
21. Again, according to theory, the 180 pulse should be double in length. So now continue to increase the pulse length until the signal goes back down and reaches a minimum. It really should be nearly un-observable at this point. If not, then contact your TA about further adjustments need for the instrument.
22. Record both these values. They will be used to setup the two pulse experiment used to determine T1 for your sample.

Determine T1 for light mineral oil

Now that you have found the 90 and 180 pulse lengths for the sample, T1 can be determined by using the pulse sequence discussed in the intro of 180 pulse \rightarrow tau \rightarrow 90 pulse and measuring the signal intensity change with respect to changes in tau (t). To get the instrument to do two pulses, we now need to turn on the “B” pulse and increase the time period so that the spins have enough time between successive pulsings to relax back to equilibrium.

23. Leave the A pulse set to the 180 pulse time, where there is no signal present.
24. Set tau to 0.0500 sec.
25. Set the B pulse to the 90 degree pulse length.
26. Set the number of B pulses in a sequence (N) to 1.
27. Set the period (P) to 5 seconds.
28. Set the Sync toggle switch to B (there is no signal on A, so we want to get the scope to trigger when there is a signal after the B pulse)
29. Finally, turn on the B Pulse toggle switch. Now you should see the signal. Adjust scaling as needed to keep it on scale for a good screen capture
30. Now you need to collect the signal peak height as it changes with tau for the range given in **Table 2**. The signal height is given as the “Ch 1 M(t)” value measured in units of volts. Make sure to take measurements at an interval that will provide you with at 10-15 values of

Mt. To get $M(\text{eq})$ increase τ to a value higher enough to provide a maximum peak value. This is typically 2 to 3 times the values of τ you are using for measurement. The best way to estimate if you are getting close to $M(\text{eq})$ is to plot τ vs M_t and look at the logarithmic nature of the curve.

31. Use this information and the graphing technique described above in the theory section to get T_1 of light mineral oil.

Determine T_2 for light mineral oil

The spin-spin relaxation time (T_2) describes the decay rate of the magnetization within the x-y plane back to equilibrium after a 90 degree pulse. T_2 can be determined by utilizing a spin echo experiment which involves the following pulse sequence, $90^\circ \rightarrow \tau \rightarrow 180^\circ \rightarrow \tau \rightarrow \text{echo}$ signal.

32. Follow the steps given above for T_1 measurement, but be sure to **change the pulse sequence** so that you are now obtaining data to measure T_2 .
33. Special note: the peak you're looking for during this measurement is actually the second peak that you see after the arrow on the top of the screen. You're looking for a nicely Gaussian-shaped peak that you may need to track as it moves while τ is being changed for your measurements. If you are unsure of what peak to use, consult your TA.

Now that you have collect all the data necessary for determining the T_1 and T_2 for light mineral oil, you can go back through these procedures, **starting at step 13**, and do the same thing for the three other samples. Make sure to collect data over the τ range listed in **Table 2**. You should collect at least 10-15 data point through this range.

Table 2: Data collection τ range and period. A-len and B-len should stay the same. Note than T_1 for water is in the sec range (not ms). *The τ ranges given below are more guidelines than anything: go to the edges of the range and see if it is a good fit for the sample. If not, adjust the range to get the greatest number of data points for the peaks that you're seeing.*

Sample	τ range for T_1	τ range for T_2	Period
light mineral oil	30-200 ms	10-40 ms	200 ms
heavy mineral oil	50-150 ms	6-60 ms	200 ms
pure water	1.7-3.0 sec	8-140 ms	5 sec
water w/ FeCl_3	240-600 ms	10-100 ms	800 ms

Clean-Up

Return all settings back to the default starting conditions shown in **Table 1**. Set the shim gradients back to zero and leave the toggle switches all on "+". Set the magnet temperature toggle switches to "open". Turn off the oscilloscope. **DO NOT** turn off the PSA-2 instrument. Make sure to return all samples back to their proper location in the holder. If you saved screen capture images on the thumb drive, take the thumb drive and insert it into the computer and pull all images off. Make sure to delete the mages off of the thumb drive so that it is empty as ready to go for the next group.

Data Analysis

Mt instrument

Construct a table of your data and show sample calculations. Graph your data and analyze it for the slope. Use the slope to determine the gyromagnetic ratio of the cue ball.

PS2-A instrument

Provide the logarithmic and linearized graphs used to obtain T1 and T2 for each sample. Be sure to include the curve fitting equation and well as the R² value. Provide information for the A and B pulse lengths used in the experiments as well as tables for the tau and Mt data collected.

Items to include in your discussion

1. Why (and in what direction) does the Larmor precessional frequency change with magnetic field? Think in terms of basic physics and angular momentum. Another way to ask this question is, Why is there no precession when the cue ball is spinning with the handle pointed straight up?
2. Thinking in terms of basic physics and angular momentum, why is there no precession when the cue ball is spinning with the handle pointed straight up?
3. You physically tip the cue ball to observe the precessional period. In an actual NMR what cause this tip?
4. How does the gyromagnetic ratio of the cue ball compare to that of a proton?
5. Explain in your own words what are T1 and T2. Why are they important values to know when conducting NMR experiments?
6. What affects the T1 and T2 time lengths?
7. Why is T1 always longer than T2?
8. Compare your four samples to each other and explain any trends observed as well as why some have longer (or shorter) relaxation times.
9. Is the percent difference between T1 and T2 the same for each sample? Explain any variations observed.
10. How and why does the addition of FeCl₃ to the water sample affect relaxation times?
11. Using what you observed in question 6 above, can you create a method to quantitatively determine the FeCl₃ in water using the TeachSpin PS-2 instrument?

References

1. Atkins, P. W. *Physical Chemistry*, 6th Edition (freeman, 1998, NY). Although any good Physical Chemistry textbook (like Engle) will have fundamental information about NMR.
2. Carrington, A. and McLachlan, A. D. *Introduction to Magnetic Resonance*. (Chapman and Hill, 1979, London).
3. Hornack, J. *The Basics of NMR*, <http://www.cis.rit.edu/htbooks/nmr/>. accessed August 2011.
4. Bradley, W.G. *Fundamentals of MRI: Parts I and II*, <http://www.e-radiography.net/mri/mri%20oct.htm>. accessed August 2011.
5. Lorigan, G.A.; Minto, R.E.; Zhang, W. (2001) *Teaching the Fundamentals of Pulsed NMR Spectroscopy in an Undergraduate Physical Chemistry Laboratory*. J.Chem. Ed. 78(7) pp 956-958.
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