Academic Year 2022 – 2023
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Lab 1: Single Qubits

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Abstract

In this lab we explored the fundamentals of nuclear magnetic resonance (NMR) and performed a set of 5 experiments exploring its effects on an isolated system. In NMR, we surround an ensemble of nuclei in a relatively homogeneous magnetic field which causes each of their spins to precess along their relative +Z axes. The nuclei for these experiments were all H1 atoms inside heavy water (deuterium oxide), which all have an atomic spin of 1. Through a set of coils located along the +X and -X axes, we were able to apply a set of additional short magnetic pulses oscillating at the Lamour frequency in order to alter the spin direction and orientation of the nuclei. With these magnetic pulses we were able to perform a free induction decay, pulse length calibration, pulse amplitude calibration, longitudinal relaxation, and Hahn echo experiment.

Contents

1 Introduction

1.1 Background

1.1.1 Lamour Frequency

For this lab, we investigated the fundamentals of nuclear magnetic resonance (NMR). In NMR, we surround an ensemble of spin 1/2 nuclei in a strong and relatively homogeneous magnetic field. This magnetic field applies a magnetic moment μ to each of the nuclei in the z direction. This magnetic field causes each of the nuclei to presses around the Z axis at the Lamour frequency which is given by:

$$v_0 = -\frac{1}{2\pi}\gamma B_0$$

Where B_0 is the magnetic field strength and γ is the gyromagnetic ratio. In the case for protons $\gamma = +2.67x10^8 rads^{-1}T^{-1}$. The density matrix that models this behaviour for individual spins in the static magnetic field can be written as follows:

$$\rho_0 = \frac{1}{2}(\mathbb{I} + \epsilon\sigma_z)$$

Where σ_z is the Pauli z matrix and ϵ is the polarization factor - which is roughly around 10^{-6} for 1H spins at room temperature.

1.1.2 Chemical Shifts

The frequencies at which absorption lineshapes occur for NMR experiments scale linearly with magnetic field strength. Therefore, to make spectroscopy convenient for all NMR experiments, a reference compound known as TMS was chosen to be compound who's NMR spectrum is centered at 0. Every other compound used in NMR (including deuterium oxide which we use for this labs' experiments) are shifted by a factor of δ known as chemical shift. This is given by:

$$\delta = \frac{v - v_{\text{TMS}}}{v_{\text{TMS}}}$$

Where v is the measured field strength frequency in Hz and v_{TMS} is the measured field strength in Hz for the reference compound TMS. So, in order to pulse the most effectively on resonance for our experiments, we need to determine this chemical shift value δ. In the case of deuterium oxide for our experiments, we simply look up the Lamour frequency and subtract it against the Lamour frequency of TMS to fully determine our chemical shift δ.

1.1.3 Pulsing

A key component of doing NMR experiments is the ability to apply an additional effective field to shift the directions of the spin for the ensemble of nuclei. Typically, an additional pulse from a weak magnetic field would have little to no effect on the spins since the static field is much greater. However, an effective field in a different direction can be accomplished by applying an RF pulse oscillating between the x and -x direction at or near the Lamour frequency. This near resonant pulse has enough strength to shift the direction of the field causing the spins of the nuclei to shift accordingly.

There are two types of pulses we used to perform NMR experiments. The first is a $\pi/2$ pulse which shifts the spins 90^o from pointing in the z direction down into the transverse xy plane. The second is a π pulse which shifts the spin 180^o from pointing in the z direction down into the -z direction (see Figure

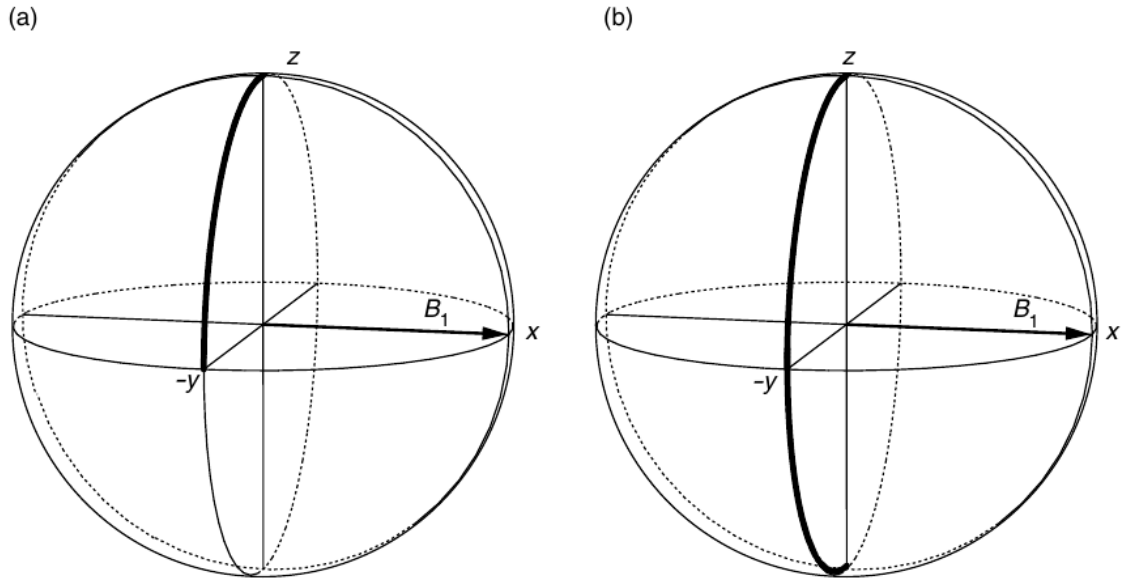

Figure 1 – Effect of on-resonant pulsing of magnetization initially aligned in +z direction for (a) $\pi/2$ pulse and (b) a π pulse. Credit to Keeler Ch 3.8 for this diagram

1 for depiction of $\pi/2$ and π pulses). These pulses are both achieved in the same manor, but done so by shifting angle of pulse through varying the pulse time. The angle of the pulse β is given by:

$$\beta = \omega_1 t_p$$

Where ω_1 is the RF field strength (or B_1 field strength) and t_p is the pulse length. In our experiments we typically fix one of these parameters and vary the other to alter the pulse angle β. Lastly, its important to note that these pulses do not vary the spin direction permanently. Due to free induction decay and spin inconsistencies of our system, the ensemble of nuclei will eventually decay back to thermal equilibrium. This is discussed in the Free Induction Decay and Relaxation sections.

1.1.4 Measurement

After pulsing, we want to be able to measure its effect on the system. This is done quite simply with coils aligned on the +x and -x axes of our device. For example, when a $\pi/2$ pulse is applied, the effective field gets pushed down into the xy plane. As the spins precess about z, the oscillating magnetic field strength can be measured a long the x and -x axis from our coils. This measurement will yield a sin wave oscillating at the apparent Lamour frequency.

2 Methods and Procedure

2.1 Setup

2.1.1 Shimming

We first calibrated the spectrometer by running the 'quick shim' program. Shimming is a process the NMR machine uses to calibrate the magnetic field and correct its homogeneity. This is done with a set of shim coils surrounding the sample. Each of these coils produces a tiny magnetic field with a particular spacial profile. When the machine is shimmed, the current through each of these coils is adjusted until the total magnetic field has regained its homogeneity.

2.2 Pulse Length Calibration

As mentioned in the Pulsing section, the angle of pulsing can simply be determined by fixing our pulse frequency ω_1 and varying our pulse length t_p. For a $\pi/2$ pulse, we expect to measure the maximum possible amplitude in the xy plane directly after the pulse. Therefore, we can experimentally determine the optimal pulse length time t_p by repeatedly pulsing at varying pulse lengths and take the pulse length with the highest peak integral on the frequency spectrum. Once this time is determined, we simply double to pulse time in order to determine the optimal pulse length for a π pulse.

2.3 Pulse Amplitude Calibration

Instead of varying our pulse length, we can instead fix our pulse length t_p and vary our RF pulse field strength ω_1 to find our optimal $\pi/2$ and π pulse. We then repeat a similar process to the pulse length experiment, where instead of varying the pulse lengths, we vary the amplitude of our pulse and record the peak integrals of each measured frequency spectrum; the highest spectrum integral will correspond to the optimal amplitude to use for a given pulse length.

2.4 Longitudinal Relaxation T_1

After a period of time, our nuclei effected by the RF pulse will begin to decay back to thermal equilibrium. This time is referred to as T_1 and its decay is given by the Boltzman equation:

$$P_\alpha = (P_\alpha(0) - P_\alpha^{eq})e^{-\tau/T_1}$$

Experimentally, we were able to get our value of T_1 by applying a π pulse and measuring the time it takes to recover back to the +Z axis (reach thermal equilibrium). However, we are only able to measure signal strength in the xy plane, so an additional $\pi/2$ pulse is done to push the spin down to measure its x component. We can then incrementally increase the delay between these two pulses and plot the results. As the pulse delay increases, the amplitude of the recovered system grows, giving us an inverted exponential increase in amplitude - modeled by the Boltzman-like equation referenced above. The plotted results can then be fitted to this equation and an estimated T_1 value can be determined.

2.5 Transverse Relaxation T_2 and T_2^*

2.5.1 T_2^* Relaxation - Inhomogeneous Broadening

Another form of relaxation comes from the inhomogeneity of the magnetic field. The spins of the ensemble of nuclei each observe a different distribution of fields in the xy plane, which causes them to accumulate phase differences over time. This T_2^* decay is very slow and will gradually increase our FID during the course of our experiments. A simple solution to counteract T_2^* decay is to reshim the sample; This will reset the magnetic field homogeneity.

T_2^* can be measured experimentally through our FID experiment when the chemical shift is 0. The full width half max of the spectrum graph is inversely related to the T_2^* relaxation time. The equation of a pure absorption spectrum lineshape is given by:

$$\Lambda(\omega) = \frac{G}{\pi((\omega - \omega_0)^2 + G^2)}$$

Where $G = 1/T_2^*$, ω_0 is the center frequency, and ω is the frequency offset from the center. Given this equation, we can solve for T_2^* relative to the FWHM of the spectrum. Doing so gives the FWHM = $2/T_2^*$

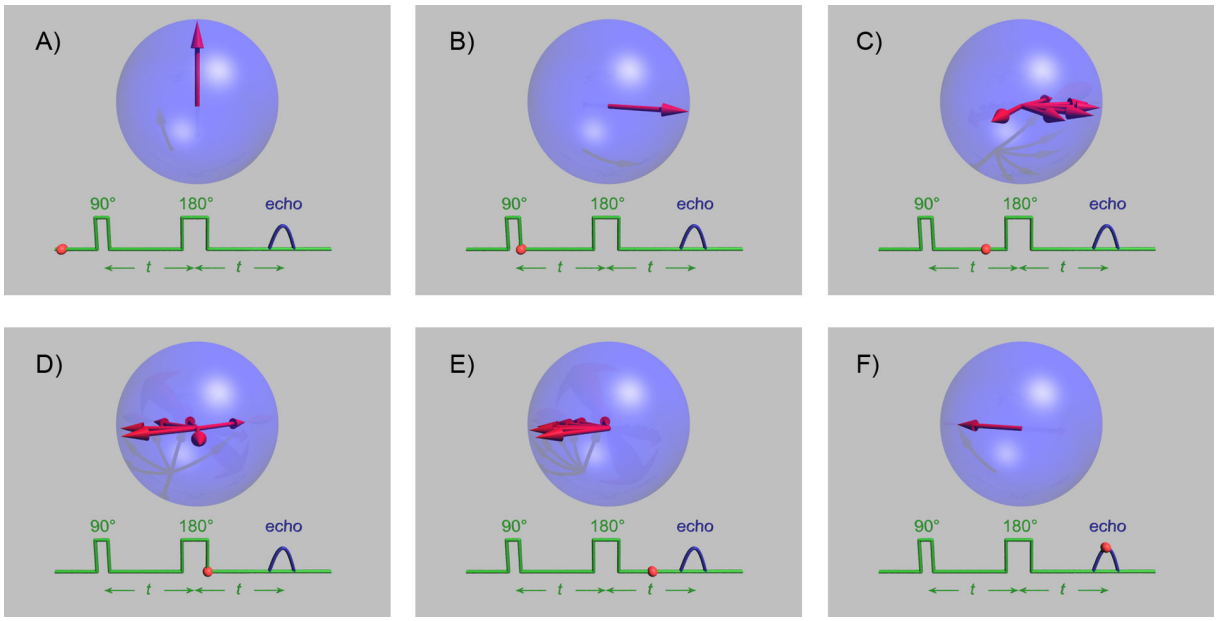

Figure 2 – Graphic of spin echo from Wikipedia. Here we see a π pulse followed by some time delay τ, a $\pi/2$ pulse, and an additional wait time of time τ before we measure an echo in the transverse direction

2.5.2 T_2 Relaxation - Homogeneous Broadening

There's an additional component of the T_2 decay that come from spin-spin coupling and phase differences between each of the nuclei in the solution. Its of course true that there's a net angular momentum of the spins in the direction of the applied field, but not all of the nuclei contribute and have differing phases. These inconsistencies contribute to the T_2 decay but don't come from the pure inhomogeneity of the magnetic field.

This decay term can be measured directly by the Hahn Echo (or spin echo) experiment. In this experiment, we completely take away the magnetic field homogeneity of our system in order to isolate this additional decay. A $\pi/2$ pulse is applied to flip the spins down into the transverse xy plane. We wait a time τ, where, some of the spins slow down and speed up due to *local* field strength inconsistencies as the net moment precesses; this causes the signal to decay. A $\pi/2$ pulse is then applied and the axis is flipped causing the slower spins to lead ahead and the faster spins to trail behind. After we wait an additional time τ, the spins will collectively rephase causing a net magnetization to be measurable in the transverse plane - creating an 'echo'. A nice diagram of this process can be seen in Figure 2.

The key component of this experiment is the echo and its measured amplitude. With longer delays of τ, the amplitude of this echo gets smaller because fewer of the phases will collectively realign over time. By repeating this experiment with longer time τ delays, we can measure the decay T_2 caused by these phase inconsistencies - without the additional decay of the field inhomogeneity.

2.5.3 Putting it all together

Both the inhomogeneous and homogeneous broadening terms together form the total relaxation. We can represent both of these terms together with the simple equation:

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \frac{1}{T^\dagger}$$

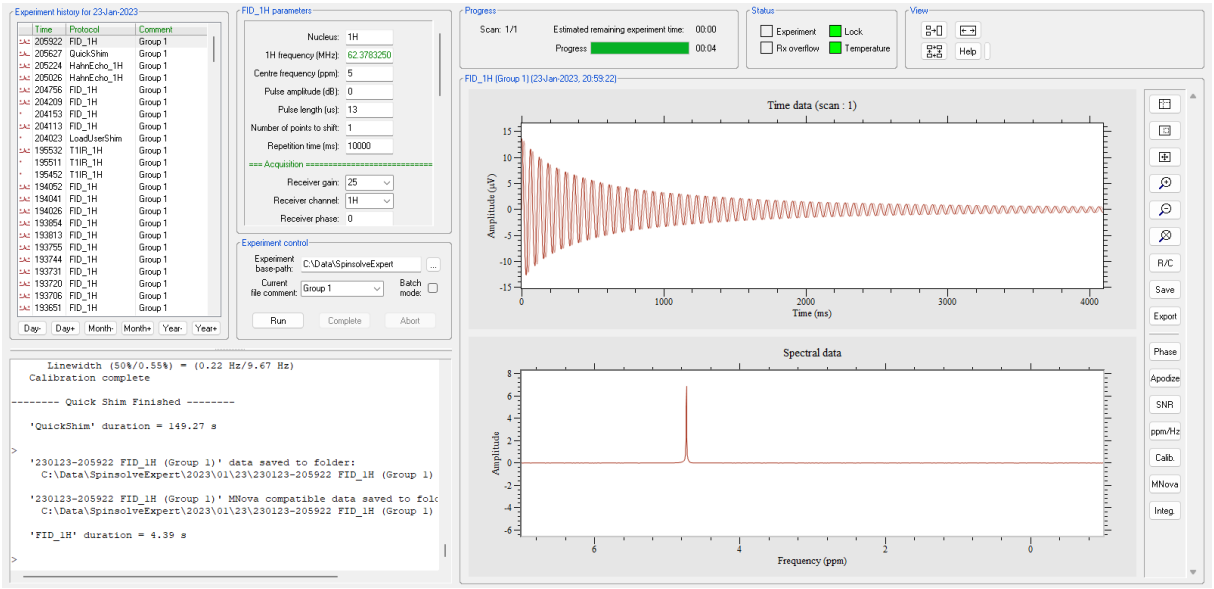

Figure 3 – Experiment 1 - $\pi/2$ pulse with off-resonant center frequency (5ppm)

Where T_2^* is the total relaxation, T_2 is the homogeneous broadening from spin/phase inconsistencies, and $T^\dagger$ is the inhomogeneous broadening from the inhomogeneity of the magnetic field. Combined, we see a gradual overall decay of our system given by a Boltzman equation (similar to the equation seen for T_1 decay).

$$\rho_{(\tau)} = \rho_{(0)} e^{i\Omega\tau} e^{-\tau/T_2^*}$$

Where the the $e^{i\Omega\tau}$ term presseses at an offset given by Ω and the $e^{-\tau/T_2^*}$ term decays to 0 in time T_2^*.

3 Results

3.1 Experiment 1 - Center Frequency and T_2^* decay

For this experiment, we verified our center frequency (or chemical shift) using a simple $\pi/2$ pulse. Our results in Figure 3 showcase what the output time data and spectrum looks like when we're slightly off of the true chemical shift value. We see a decay that is sinusoidal and a frequency spike that is very thin. When we pulse exactly on resonance with our chemical shift, we see a very clean exponential decay and well defined frequency spike. We found this chemical shift value to be 4.738ppm and our results are shown in Figure 4.

Most importantly, a spectrum graph with minimal chemical shift allows us to determine the value of T_2^* decay as mentioned in Section 2.5.1. From our analyzed results in Figure 5 we can see that we had a measured FWHM value of 0.0078. Using the pure absorption equation referenced in Section 2.5.1 we found our T_2^* decay value to be 256.4102 seconds.

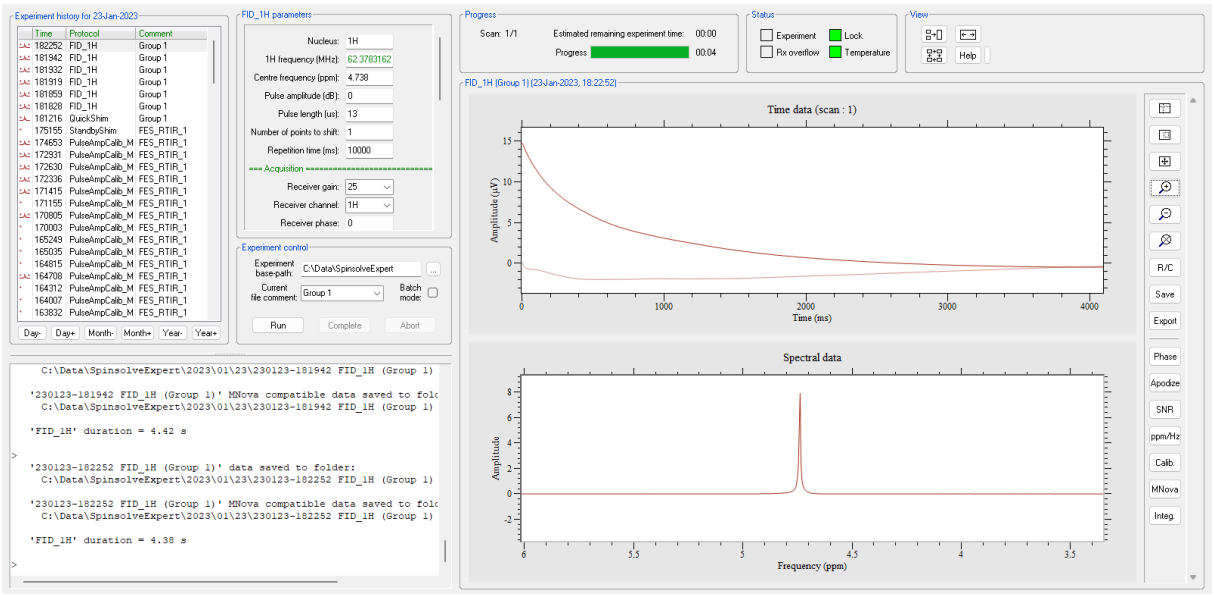

Figure 4 – Experiment 1 - $\pi/2$ pulse with on-resonant center frequency (4.738ppm)

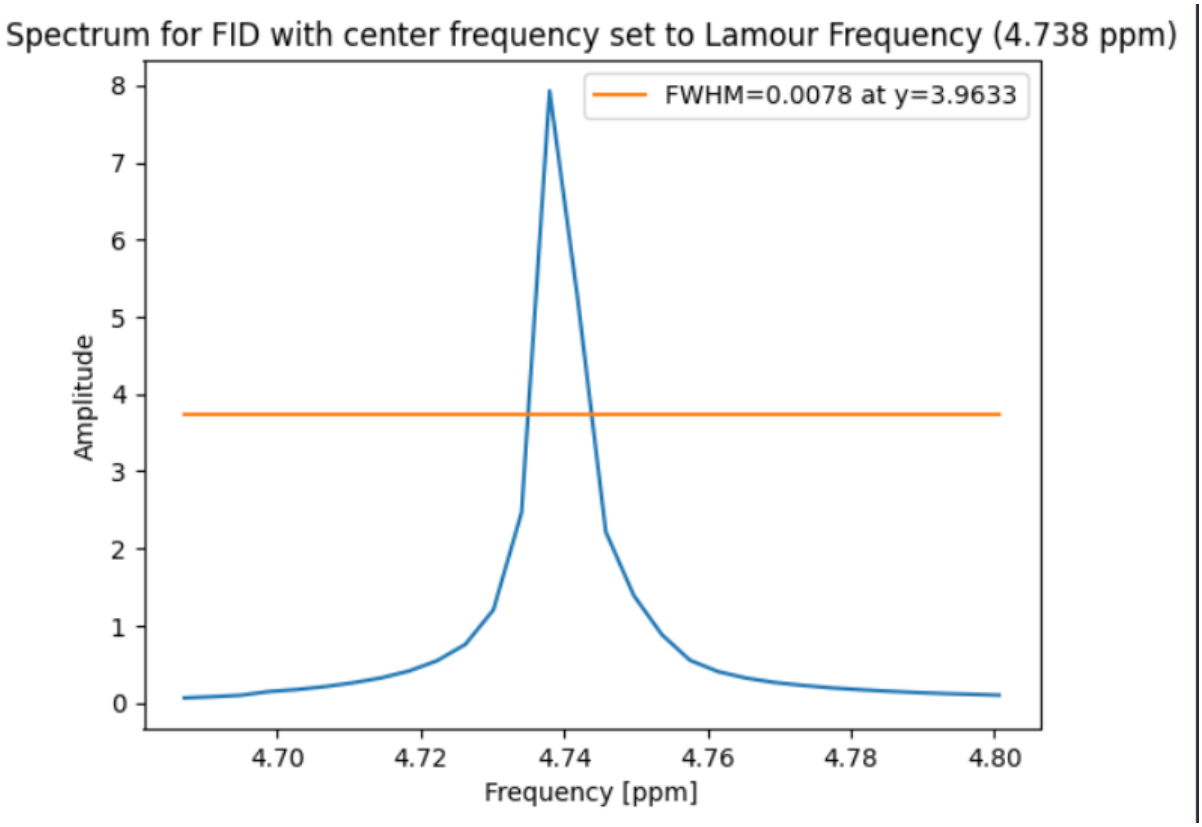

Figure 5 – Experiment 1 - T_2^* measured from full width half max at resonant frequency

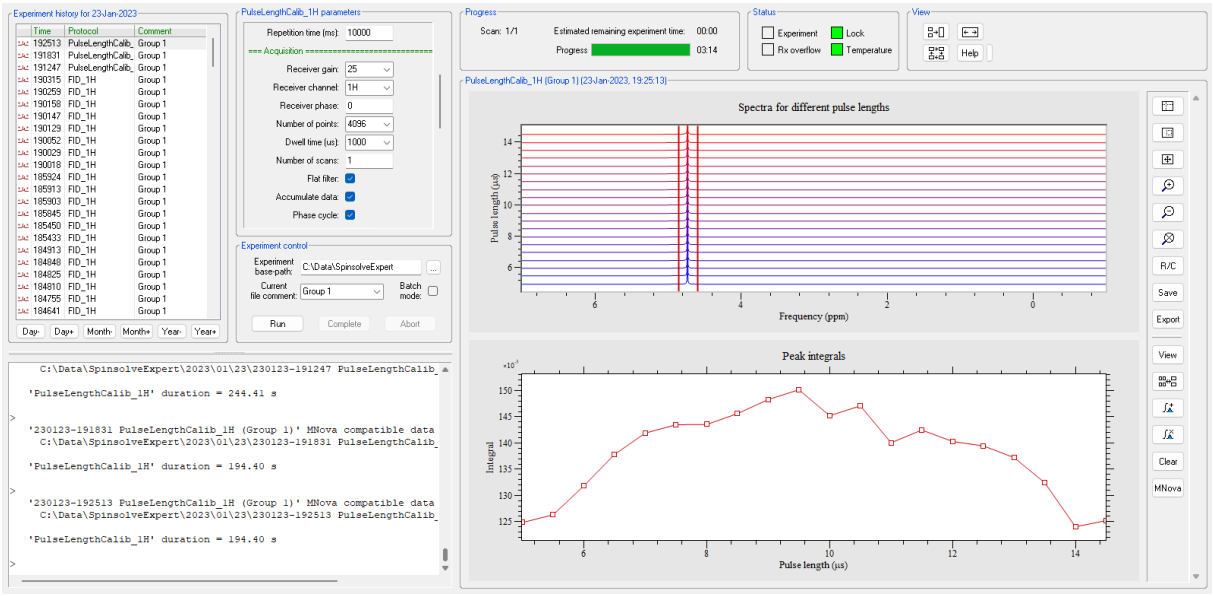

Figure 6 – Experiment 2 - Calibration of pulse lengths for a $\pi/2$ pulse of 0 dB with step sizes of 0.5 μs increments

3.2 Experiment 2 - Pulse Length Calibration

As mentioned in the Section 2.2, we can fix the pulse RF frequency and vary the pulse length to determine the optimal pulse length for a $\pi/2$ pulse. We chose to fix the RF frequency amplitude at 0 dB and varied the pulse length from 0 to 15μs at 0.5μs intervals. Our results our shown in Figure 6, where we found the optimal length to be approximately 9.5μs for a $\pi/2$ pulse.

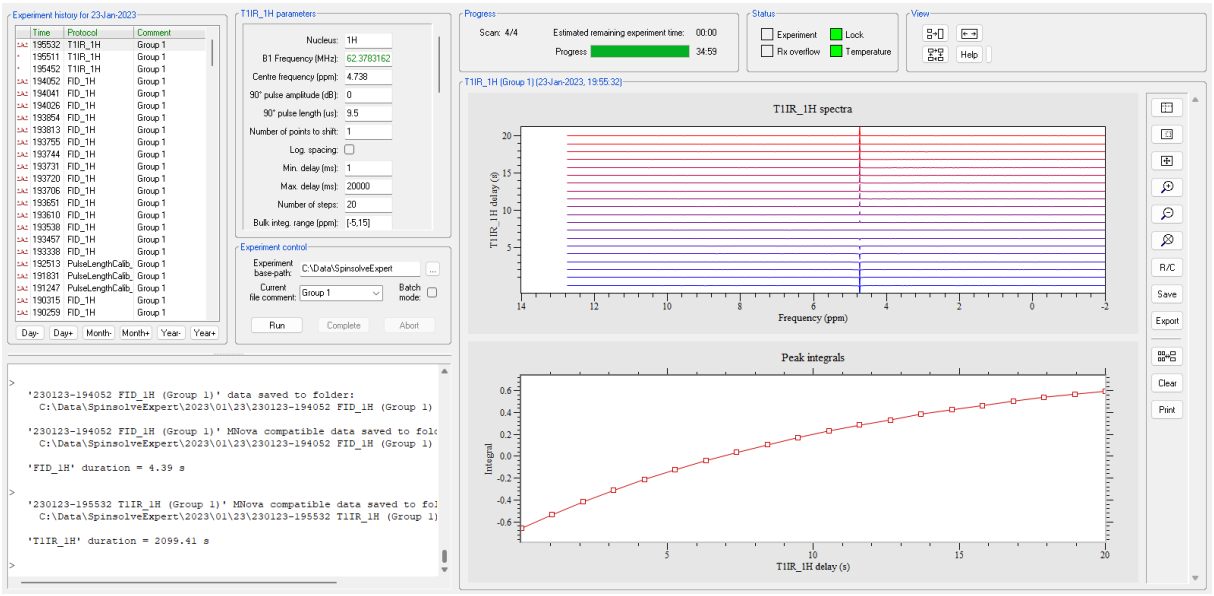

Figure 7 – Experiment 3 - Results of T1IR experiment for pulses performed at time delays from 0-20 seconds at 1 second intervals

3.3 Experiment 3 - Longitudinal Relaxation and T_1 decay

To measure the longitudinal relaxation (or T_1 decay), we performed the experiment outlined in Section 2.4 with varied time delays from 0 to 20s at 1s delay intervals. Our spectrum results and integral values are plotted in Figure 7.

In order to determine our T_1 value from our results, we took our peak integral data and fitted it to the decay equation given in Section 2.4. This resulted in a T_1 value of approximately 9.435 seconds. Our fitted curve can be seen in Figure 8.

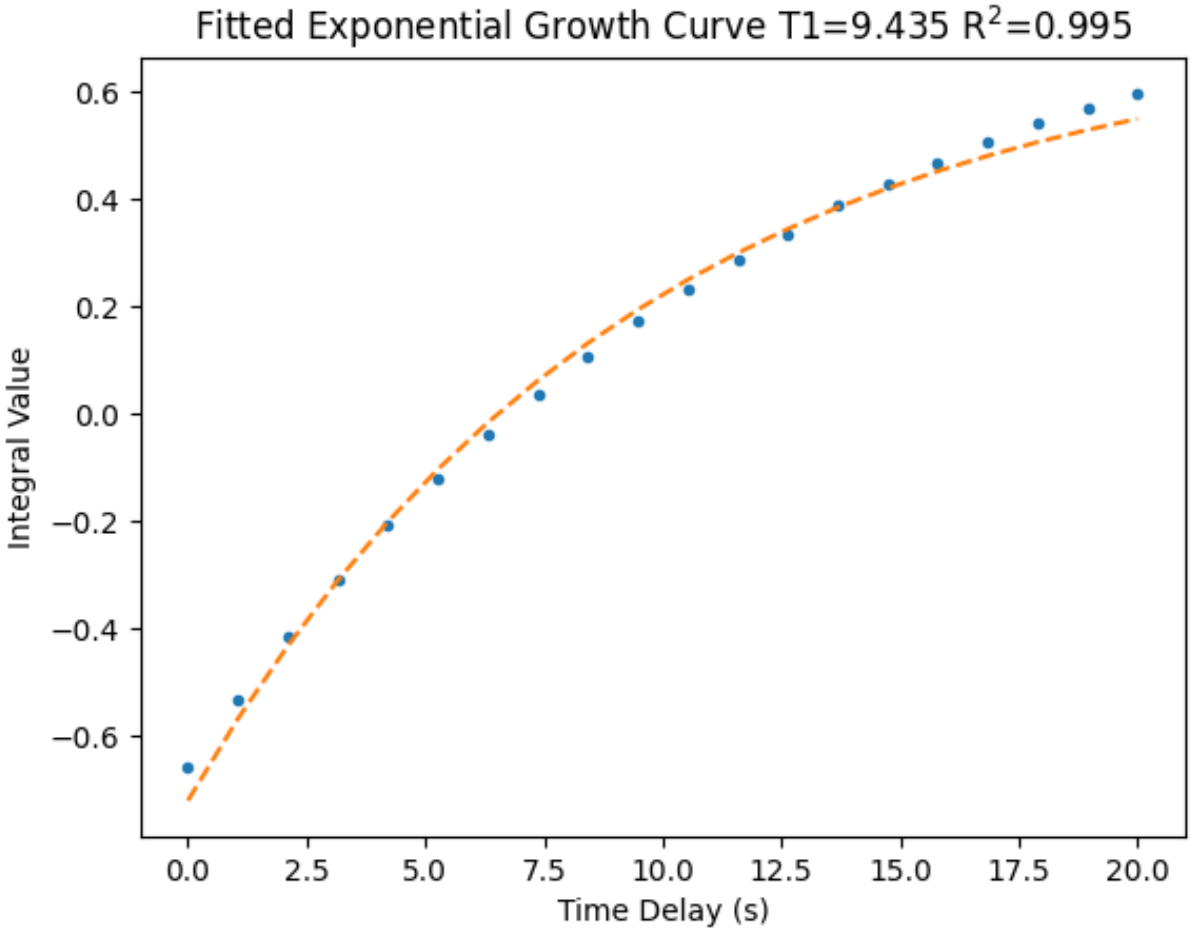

Figure 8 – Experiment 3 - Fitted T1 value to gradual decay value

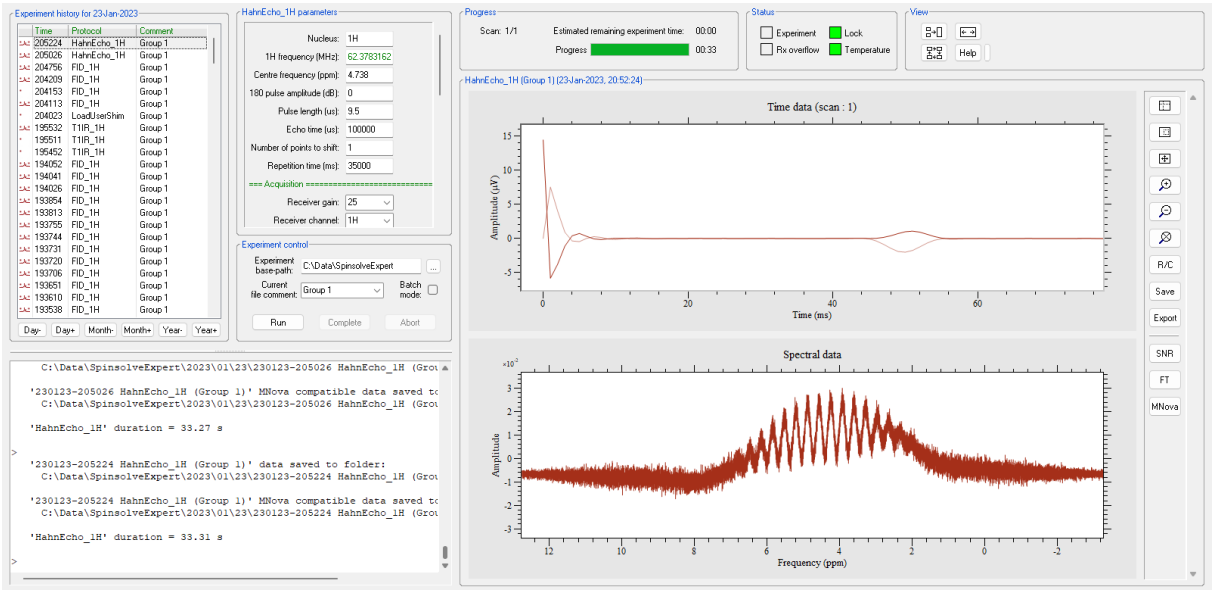

Figure 9 – Experiment 5 - Hahn echo experiment performed in a non-homogeneous field with a delay τ=50ms

3.4 Experiment 5 - Hahn Echo

For our 5th experiment, we explored the methods and effects of generating a Hahn echo in an inhomogeneous magnetic field. We began by manually altering our system's magnetic field and completely removing the homogeneity. This allowed us to visualize a Hahn echo of our spins in the transverse xy plane after a π pulse was applied, a wait time of time τ, a $\pi/2$ pulse is applied, and a final wait time of τ before measurements were recorded. Further details of this experiment our outlined in details in Section 2.5.2.

For our experiment, we chose our τ time to be 50ms (a total echo time of 100ms). This gave us a very clean spin echo measured after 50ms of our $\pi/2$ pulse. Our results are shown in Figure 9.

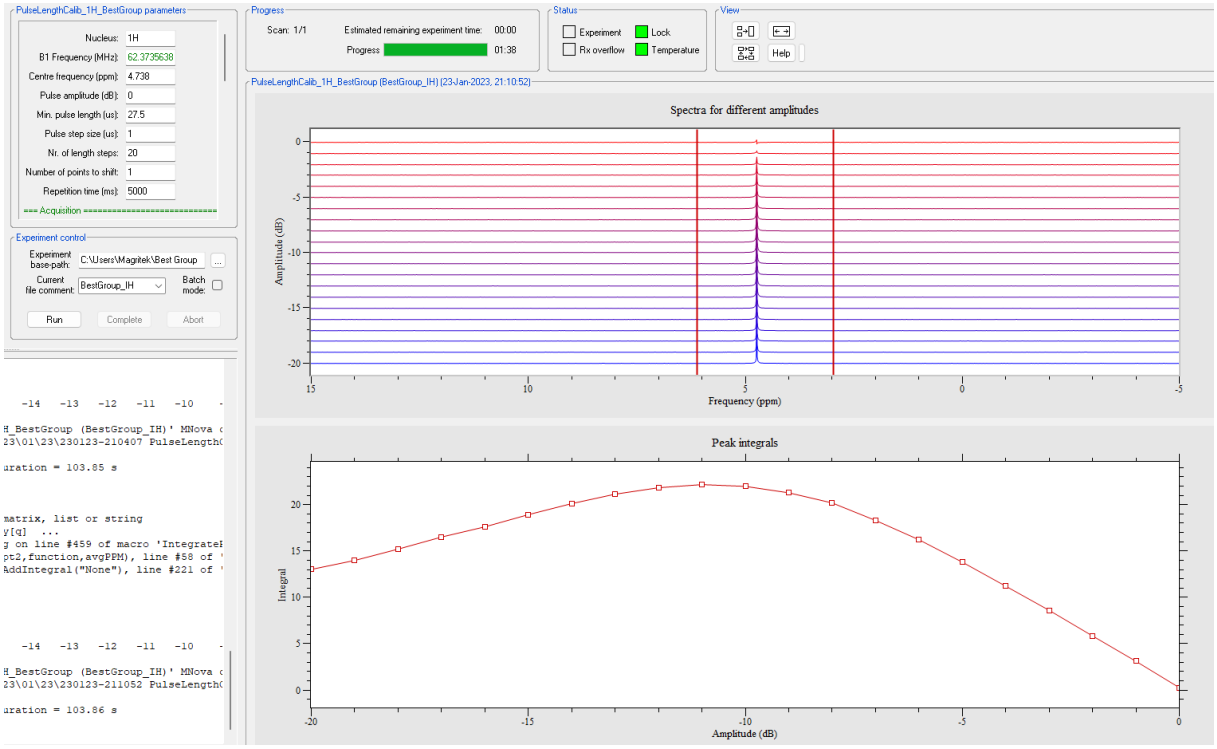

Figure 10 – Experiment 6 - Calibration of pulse amplitude for a $\pi/2$ pulse of 27.5μs with step sizes of 1 dB increments

3.5 Experiment 6 - Amplitude Calibration

For our last experiment, we performed the counterpart to experiment 2. Where, instead of fixing the pulse amplitude and varying the pulse length, we instead fixed the pulse length and varied pulse amplitude. This process is known as amplitude calibration (details of such are outlined in Section 2.3).

When calibrating for pulse amplitude, we decided to fix the pulse length at 27.5μs (the pulse length we originally found for a π pulse). We then varied the pulse amplitude from -20dB to 0dB at 1dB increments. We found a maximum measured pulse at a pulse amplitude of approximately -9dB. Our results are shown in Figure 10.

4 Discussion

4.1 T_1 Decay

From our experiment we concluded that our T_1 decay value was 9.435 seconds. After comparing this result with Mo's data and a few other groups data, we'd expect to see this value a bit closer to 10 seconds. There's a couple possibilities to why this might be slightly off. Firstly, our fit (as seen in Figure 8) is not perfect to our recorded data points. If we would have spent longer trying to more accurately to our measurements, there's a possibility we would have achieved a T_1 value closer to the expected value of 10 seconds. Secondly, this offset could have been caused by the homogeneity of our magnetic field, which would have some T_2 decay factors contribute to our measured decay. If we would have spend more time shimming our data before performing this experiment, then perhaps we would have seen slightly better results. But overall, 9.435 seems to be a fairly acceptable value since we know the T_1 decay to the return to thermal equilibrium is quick and contributes much more than T_2 decay.

4.2 T_2 Decay

Our T_2 decay was measured to be 256.4102 seconds. This agrees pretty well with the theory behind T_2 decay, since we know decays from the inhomogeneous magnetic field and spin inconsistencies will add slow and gradual decay to our system. We also concluded that this result seems to match pretty nicely with another published paper on proton NMR for human blood (which is effectively just water). This paper can be found here. In this paper, the experimentalists used a B field strength of 1.5 Tesla (which is a similar strength to our system) and found a T_2 relaxation time of 254s (+/- 26 ms) - which corresponds quite nicely with our results.

4.3 Pulse Length and Amplitude Calibration

For our pulse length calibration experiment we fixed the pulse amplitude to 0 dB and found the maximum pulse delay to be 9.5μs. This result was taken from our plotted peak integrals in Figure 6. In our amplitude calibration experiment, we fixed our pulse length to 27.5μs and found a maximum pulse at approximately -9dB. This result was taken from our plotted peak integrals in Figure 10.

Our resulting graphs were a bit noisy and we could have achieved better results in a couple of ways. Firstly, we could have shimmed our field much longer to further eliminate any T_2 decay factors. We could have also increased our dwell time to ensure our system fully decayed to thermal equilibrium before running another experiment; this would ensure that our system was started in roughly the same state for each run. Lastly, we could have reduced the intervals of each experiment, allowing us to capture more accurate results to a finer decimal point.

4.4 Hahn Echo

In experiment 5 we removed the homogeneity of our applied magnetic field, a applied a series of pulses delayed by a time τ=25ms, and successfully measured a Hahn echo at a total time of approximately 50ms. In conclusion, these results definitely match our expectation. As explained in Section 2.5.1, we know the Hahn echo experiment can be continually repeated at varying τ times to measure the T_2^* decay. Had our group had more time and understanding going into the experiment, we could have successfully reran this experiment with different times and plotted the results of our measured echo amplitudes. This calls for further experimentation and analysis into the subject. However, our group concluded that we have sufficient understanding of the topic to run this experiment again to measure the T_2^* decay if given the opportunity.

5 Conclusion

Overall, our group felt pretty confident with our measured results and processed data. We felt that this lab gave us a really good foundational understanding of NMR and how to perform experiments with an NMR system. We successfully measured the T_1 and T_2 decay of our system, which we found to be 9.435 seconds and 256.4102 seconds respectively. We were able to demonstrate the relation of pulse angle to pulse length and amplitude by running a set of calibration experiments. For our pulse length experiment, we found the optimal $\pi/2$ pulse length to be approximately 9.5μs for a 0dB amplitude pulse. For our amplitude calibration experiment, we found the optimal $\pi/2$ pulse amplitude to be approximately -9dB at a pulse length of 27.5μs. Our data and results are subject to several possible forms of error which is explained thoroughly in Section 4.

Its also worth noting that we did not measure a T_2^* decay for this lab. If we had more time, we could've ran the Hahn echo experiment several times with additional τ delay values. This would have allowed us

to measure the echo at varying amplitudes and measure the T_2^* decay without additional decay effects of the inhomogeneous field.

6 Works Cited

References

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