
Lab 2: Two Qubits Using NMR

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Abstract

In this lab we explored a set of 6 NMR experiments on a simple two qubit system of H1 and C13 within molecules of chloroform. The H1 and C13 spins are heteronuclear and experience coupling. We explore the effects this spin coupling has on our system and how to properly measure each spin energy transition. We also analyze the effects of noise in our system and examine methods to improve our signal to noise ratio (SNR) - especially for C13, which precesses at a relatively low Larmour frequency and is therefore more susceptible to system noise.

The experiments include a free induction decay and inverse relaxation experiment of H1 to measure the H1 T_2^* and T_1 decay values. We conducted a free induction decay and inverse relaxation experiment on C13. We used the results and methods from our C13 experiments to explore various ways to increase our SNR. This includes using the WALTZ-16 method to decouple our H1 atoms from the C13 and taking advantage of the Nuclear Overhauser Effect to relax some noise within our system.

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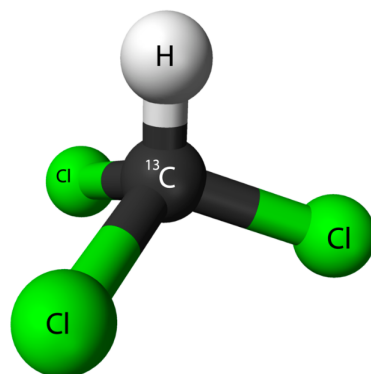


Figure 1 – Molecule of Chloroform. The C13 and H1 atoms of the molecule have a spin of 1/2 and experience spin coupling, allowing us to do NMR experiments with two qubits

1 Introduction

1.1 Background

1.2 Chloroform

The molecule used in this NMR lab was Chloroform (CHCl_3) surrounded in a solution of deuterated acetone. The concentration of acetone is very low compared to that of the chloroform. The interactions between the two molecules is negligible. Therefore we can pretty much ignore it. A majority of the chloroform in the solution are composed of isotopes of H1 and C13 which each have a spin of 1/2. Both natural possible isotopes of chlorine have a spin of 3/2, which all experience quadrupolar coupling to applied electric fields. This causes the chlorine to experience very fast T_1 relaxation rates, which cause them to self-decouple and can be effectively ignored. When we do pulse experiments, we'll actually see transitions for each of the chlorine molecules. But their resonant frequencies are very far off from the frequencies of C13 and H1, so they don't interfere with our spectral results.

1.3 Larmour Frequency

As we explored in Lab 1, we know that each nuclei will precess at its given Larmour frequency in the direction of the applied magnetic field. This rate of precession is given by the gyromagnetic ratio of our nuclei. The gyromagnetic ratio is $\approx 26.75 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}$ and $\approx 6.72 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}$ respectfully. This implies that H1 processes at roughly 4 times the speed of C13, and thus, has 4 times as much energy on our measured spectral graphs. This is important because it allows us selectively drive transitions of each of these spins with ease. However, this also comes at a consequence. C13 has such a low Larmour frequency, that its measured energy spectrum is extremely sensitive to noise within our system. As I will explain later, this is the primary reason why we need to find methods to increase the SNR within our system.

1.4 Spin Coupling

A set of two coupled spins will consists of two doublets, which are each split by the same energy amount. Each of these peaks correspond to the energy of transition for the H1 and C13 in our chloroform molecules. The spin energy interaction between these two atoms is known as J coupling; it can be measured by taking the energy difference between the two doublet spectrum peaks. The J coupling comes from the magnetic fields from each nuclei acting on each other. Since the H1 and C13 are neighboring nuclei in a molecule of chloroform, they are close enough to experience this J coupling interaction. Lastly, its worth noting

that the energy of J coupling is very weak compared to that of the applied magnetic field. However, this coupling still has impact on the dynamics of our system and its effects are worth exploring.

1.5 Signal to Noise Ratio (SNR)

Signal to noise ratio (SNR) is an important concept in NMR - especially when working with atoms that have slow Larmour frequencies such as C13. The higher the SNR value, the better our signal is relative to the noise within our system. SNR can be improved through a variety of methods:

- Reduce the amount of noise accumulated from our measured pulse by limiting our dwell time.
- Only measure a reasonable amount of data points. Measuring too many points over a given timestep will pick up more noise throughout and decrease our overall SNR.
- Use advantageous effects of the Nuclear Overhauser Effect to cross-relax the spins within our system and reduce our noise.
- Decouple the H1 spins from the C13 spins. This will produce a single spectra for the spin transition instead of two. This can be done with the WALTZ-16 method, where we pulse the H1 channel with a sequence of 16 π pulses so that the hydrogen stays in the spin down state instead of in thermal equilibrium. This allows us to measure only C13 coupled to H1 in the spin down state

1.6 Relaxation Revisited

As we saw in lab 1, relaxation is the process by which our system returns to thermal equilibrium. In thermal equilibrium the populations even out to the levels given by the Boltzman distribution. This leads to no transverse magnetization in our system, or in other words, no coherences are longer present.

1.6.1 Dynamics of Population Change

The equilibrium net magnetization comes from the uneven populations of the α and β spins. The net magnetization in the z direction is proportional to the spin population difference given by:

$$M_z \propto (n_\alpha - n_\beta)$$

Where n_α and n_β are the populations of the two corresponding spin energy levels. When one of these population values increase (due to a π or $\pi/2$ pulse for example), relaxation will immediately begin to drive the system back into thermal equilibrium. The rate at which is given by the following equations for spin states α and β :

$$\begin{aligned}\frac{dn_\alpha}{dt} &= -Wn_\alpha + Wn_\beta \\ \frac{dn_\beta}{dt} &= -Wn_\beta + Wn_\alpha\end{aligned}$$

Where Wn_i is the rate of loss for spin states α and β respectively. These equations can be rewritten in terms of the deviation from thermal equilibrium of the α and β spin populations. This is important because the populations of the two spin states won't be completely equal at thermal equilibrium; their respective thermal equilibrium populations will be relative the the Boltzman distribution. Therefore, we can write:

$$\begin{aligned}\frac{dn_\alpha}{dt} &= W(n_\beta - n_\beta^0) - W(n_\alpha - n_\alpha^0) \\ \frac{dn_\beta}{dt} &= W(n_\alpha - n_\alpha^0) - W(n_\beta - n_\beta^0)\end{aligned}$$

In these equations, n_α^0 and n_β^0 are the population of the spin states at equilibrium. Therefore we can see that as the populations increase, the rate of relaxation of the corresponding spin will rise. This creates the relaxation effect of our system, formally given by the T_1 time.

1.6.2 Nuclear Overhauser Effect (NOE)

In brief summary, the Nuclear Overhauser effect is the possible double quantum transition of our two spin system during relaxation. Normally, this is not allowed in quantum mechanics. However, NOE is somewhat of an exception. For example, let's say we have a source spin S and an additional spin of interest I . If we apply a pulse on S to take our system out of thermal equilibrium, we'll have a greater population of S in the spin down (higher energy state). As mentioned in the previous section, this population difference will drive a rate of change back into thermal equilibrium due to relaxation. For the case of small molecules (like chloroform) there's a possible transition pathway given by W_2 . In this pathway, there's a possibility that I and S in the spin-down/spin-down state will relax together into the spin-up/spin-up state. This occurs because of the spin coupling. Where, the S spin effectively 'relaxes the I spin with it'. Due to this effect, we see a larger excess of spins in the ground state after this W_2 transition. This results in a higher peak frequency of our S spectrum when measuring. NOE can be taken advantage of to increase the amplitude of our output spectrum, thereby increasing our SNR for our measured results.

2 Methods and Procedure

2.1 Free Induction Decay of H1

2.1.1 T_2^* of H1

As discussed and observed in lab 1, we can apply a $\pi/2$ pulse on resonance with the Larmour frequency of the H1 and observe the relaxation back into thermal equilibrium. This experiment is how we measure the T_2^* decay of the H1 atoms in our chloroform solution. This T_2^* measurement is done by observing the full width half max of both spectrum peaks at the resonant pulse frequency of H1 and taking an average of the two. We can then find the T_2^* decay from relation that $\text{FWHM} = 2/T_2^*$.

2.1.2 Observed Spectral Peaks

Unlike the lab 1 experiment where observed a single peak in the spectral data, we will observe two peaks. Each of these correspond to the H1 spin energy transitions - specifically for the H1 atoms coupled to C13 atoms in their corresponding chloroform molecules. It's worth noting that not all of the carbon atoms are C13 isotopes; some are instead C12. This is due to manufacturing impurities and the instability of C13 (which causes it to decay very gradually into C12 over time). The relative concentration of C12 is very small, but can be observed very slightly; it will produce a very small peak on our spectral graph for H1 transitions coupled to C12 atoms. We can use this C12 spectral peak and compare it to the others to measure the concentration of C13 to C12 in our chloroform solution.

2.1.3 J Coupling

Lastly, we can use this experiment to measure the J coupling term of our two spin system. We do so by taking a difference between the doublet's max amplitude peaks, converting it Hz, and multiplying it by our reference frequency.

2.2 T_1 Relaxation of H1 and C13

In lab 1 we observed the effects of longitudinal relaxation (T_1) for D2O. For this lab we can do the same experiment we did in lab 1 for each nuclei - both the H1 and C13. We simply apply an inversion-recovery

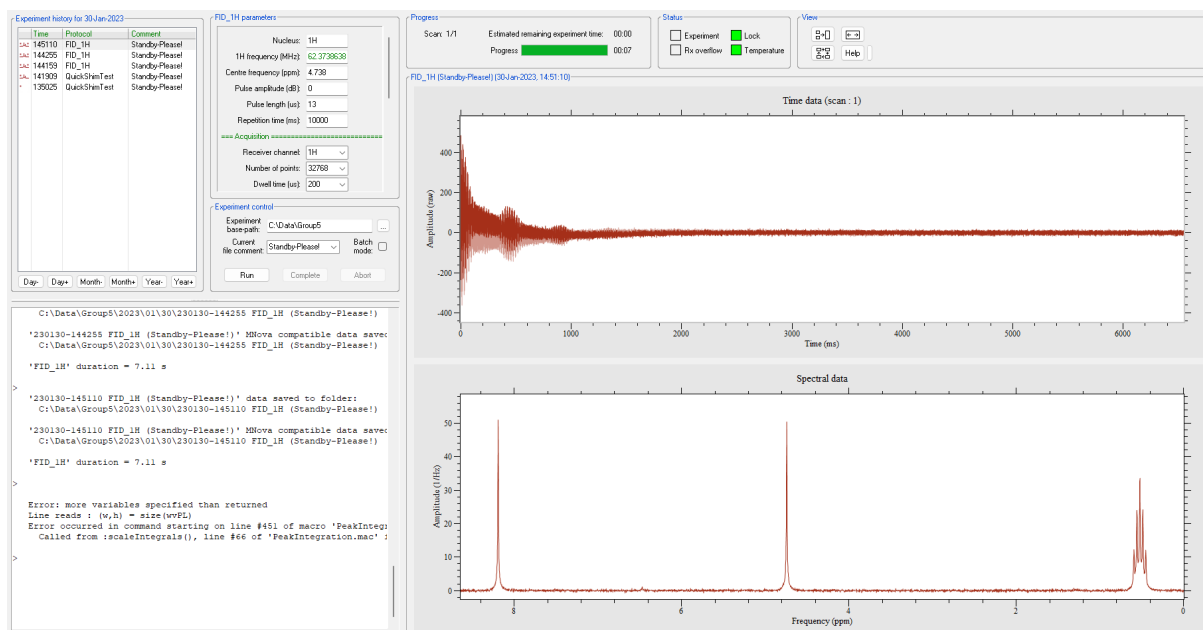


Figure 2 – Experiment 1 - FID of H1

pulse and observe the decay of the system back to thermal equilibrium. We cannot measure the relaxation in the z direction, so an additional $\pi/2$ pulse is applied to bring the signal down into the transverse xy plane for measurement. By systematically increasing the delays between the π pulse and $\pi/2$ measurement pulse, we can plot our results and fit the curve to the Boltzman equation given by T_1 decay to get its value. Further details of the experimental methods and procedure are covered in lab 1.

2.3 C13 Pulse Length Calibration

Its important to know the optimal $\pi/2$ pulse lengths for our H1 and C13 nuclei. This is so that we can achieve the maximum spin population transfer down into xy plane when performing various NMR experiments; doing so maximizes our experimental accuracy.

We successfully calibrated our pulse length and amplitude for H1 in Lab 1. For this lab, we simply do the same for C13.

3 Results and Discussion

3.1 Experiment 1 - Free Induction Decay of H1

The results of our H1 free induction decay are shown in Figure 2. In the resulting spectral graph, we see two peaks. Each of these peaks represent the spin energy transitions of the H1 atoms coupled to C13 atoms in our chloroform molecules. As mentioned earlier, we know that spin down is the higher energy state. Therefore we can identify the left peak to be H1 transitions coupled to C13 in the spin down state and the right peak to be H1 transitions coupled to C13 in the spin up state. Additionally, using our procedure outlined in Section 2.1.3, we were able to calculate our J coupling to be 206.9604 Hz.

We observed a slight peak in our spectrum around the 6.25ppm frequency range. This corresponds to the H1 transition coupled to the small amount of C12 in our sample. By comparing this peak integral to the peak integrals of our H1 coupled to C13, we were able to determine the relative weight of C13 to C12 in

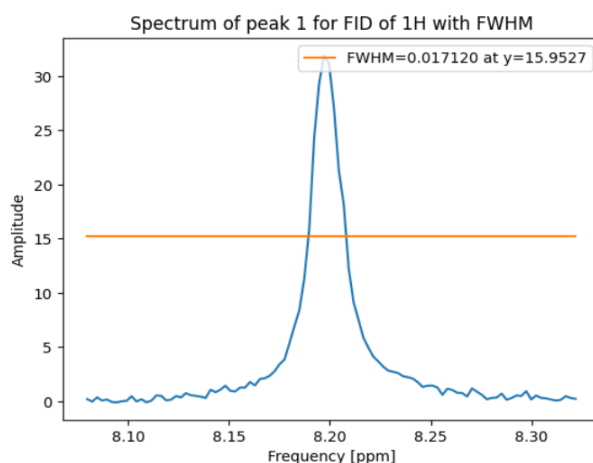


Figure 3 – Experiment 1 - FWHM of peak 1 centered around 8.20ppm

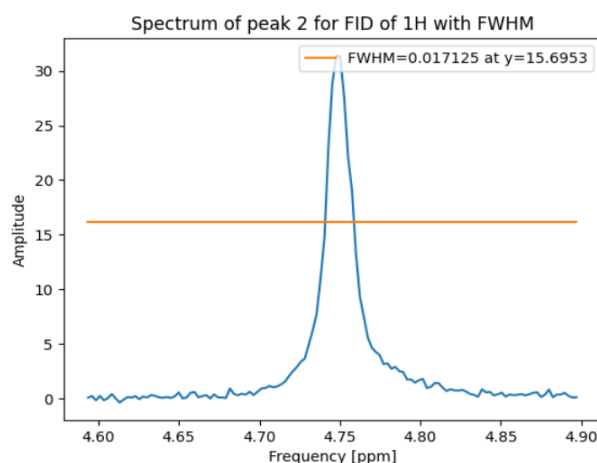


Figure 4 – Experiment 1 - FWHM of peak 2 centered around 4.75ppm

our solution.

Lastly, we can use the FWHM of our peaks to calculate the T_2^* decay of our H1. Doing so gave us an average T_2^* value of 116.82 seconds between our two peaks.

3.2 Experiment 2 - T_1 Relaxation of H1

As shown in Figure 5, we performed an inverse relaxation experiment on our H1. We then took our peak integrals of our spectrum and fit them to the T_1 Boltzman equation to get a T_1 time of 4.011 seconds. Our plotted fit curve is shown in Figure 6

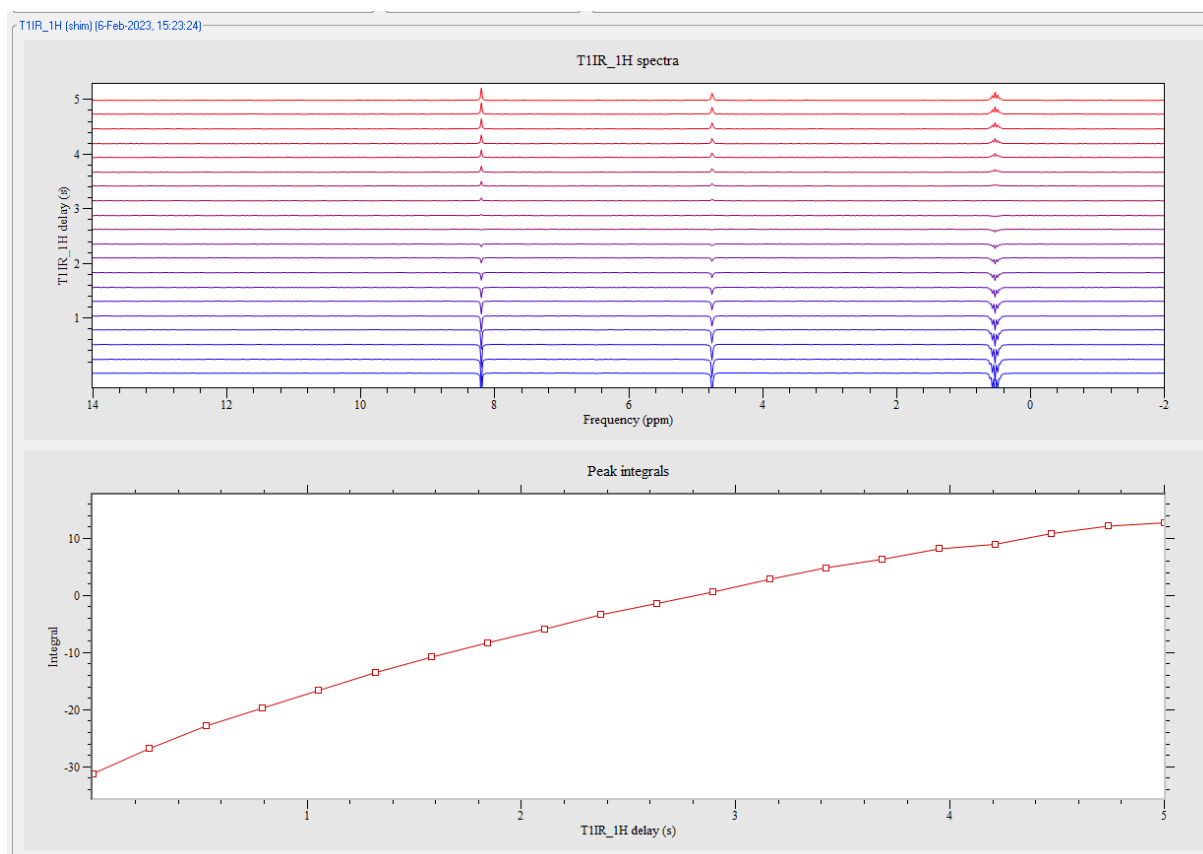


Figure 5 – Experiment 2 - Graph of peak integrals from H1 T_1 relaxation experiment

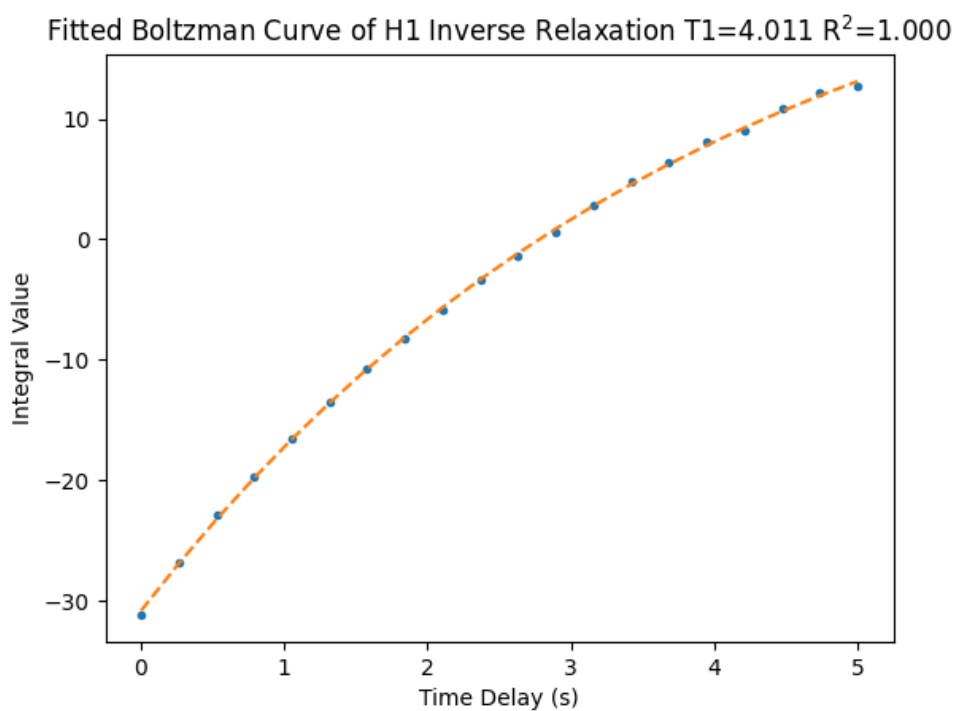


Figure 6 – Experiment 2 - Fitted relaxation integrals to Boltzman Equation to get T_1 of 4.011 seconds with R^2 fit value ≈ 1.0

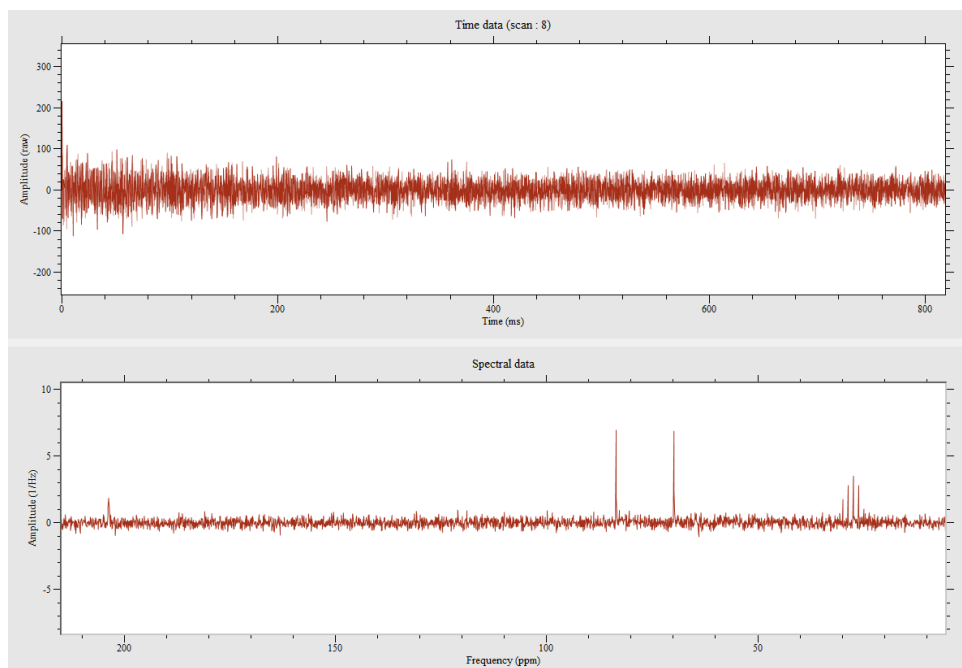


Figure 7 – Experiment 3 - Free induction decay for C13

3.3 Experiment 3 - Free Induction Decay of C13

We performed an experiment similar to Experiment 1, but this time for the C13 spins instead of H1. Our plotted experimental results are shown in Figure 7. We observed two peaks that correspond to the C11 spin energy transitions. The leftmost peak is C13 atoms coupled to H1 in the spin down state (higher energy) and the rightmost peak is the C13 atoms coupled to H1 in the spin up state (lower energy). Using our procedure outlined in Section 2.1.3, we were able to calculate our J coupling to be 205.4520 Hz.

3.4 Experiment 4 - Pulse Length Calibration of C13

For experiment 4, we performed a calibration for the $\pi/2$ pulse of C13. This procedure was very similar to the pulse length calibration experiment performed in lab 1. However, to successfully pulse C13, we need to pulse at a much lower amplitude and a significantly longer period of time due to its significantly lower gyromagnetic ratio than H1. We pulsed at an amplitude of -5.9 dB and started with a pulse length of 70 μs . We performed 20 pulse steps each at 0.5 μs increments to eventually stop at a pulse length of 80 μs .

Our plotted results are shown in Figure 8. Our results were quite noisy and bad. This was due primarily to the fact that C13 has a much lower gyromagnetic ratio than H1 (roughly 4 times as small), which causes it precess much slower. This in turn decreases our SNR because we're attempting to measure a much lower frequency - which is much more sensitive to background noise of our system. We also see dispersion curves, which implies that we were measuring along the wrong axis. To improve this, we could've repeated our experiment with an adjusted offset axis so that we would measure proper absorption curves. We could have also limited our time window and amount of pulses considerably, this would've honed in closer to the actual pulse length and reduce some noise in the system. Lastly, we could have decoupled our C13 spins to greatly increase our SNR.

To improve our dispersion curves seen in resulting peaks, we multiplied the spectral data by a factor of

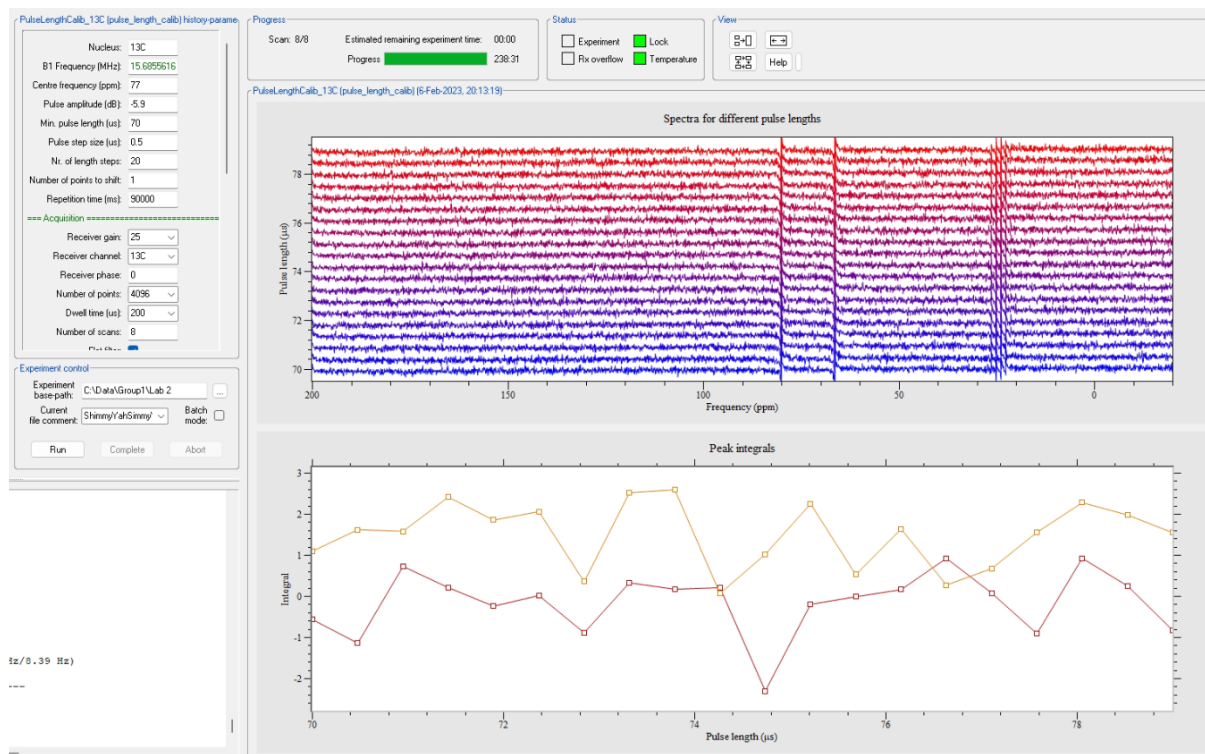


Figure 8 – Experiment 4 - C13 pulse length calibration

$e^{-i\pi/2}$ to shift them into absorption line-shapes. Our plotted peak integrals for the shifted peak 1 C13 data is shown in Figure 9. From these results, we arrived at a optimal $\pi/2$ pulse length of 77.5 μs for our C13.

3.5 Experiment 5 - NOE and Polarization Transfer to Increase SNR

In experiment 5, we performed another free induction decay experiment for C13. This time, we took advantage of the NOE which is outlined in Section 1.6.2. This resulted in a less noisy spectrum with a single frequency spike for C13. This increased our SNR slightly and demonstrates the benefits of using NOE to reduce noise in low frequency environments. Our experimental results are shown in Figure 10.

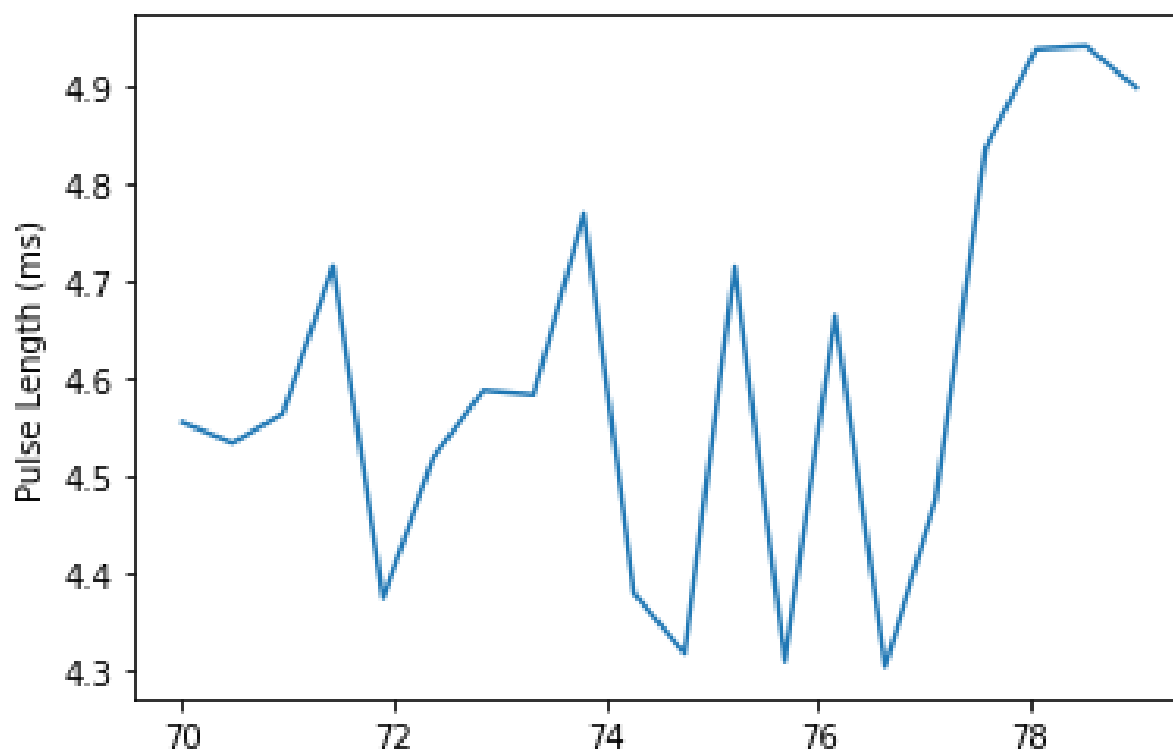


Figure 9 – Experiment 4 - Plot of peak 1 integrals after spectral data was shifted by $e^{-i\pi/2}$.

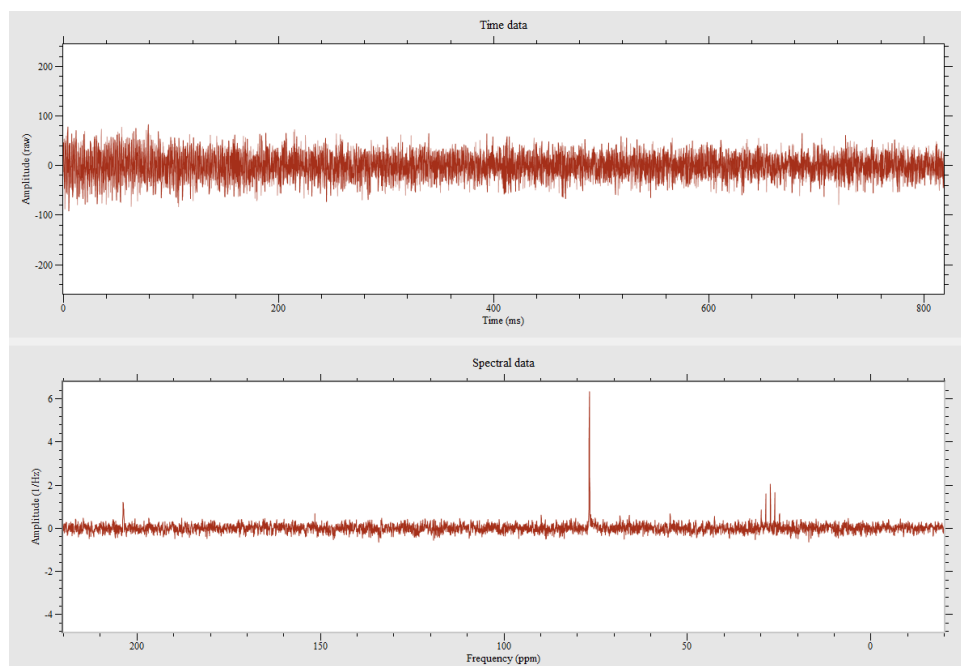


Figure 10 – Experiment 5 - C13 free induction decay with advantage of the Nuclear Overhauser Effect to increase our SNR. A single frequency spike was recorded, at a much higher amplitude

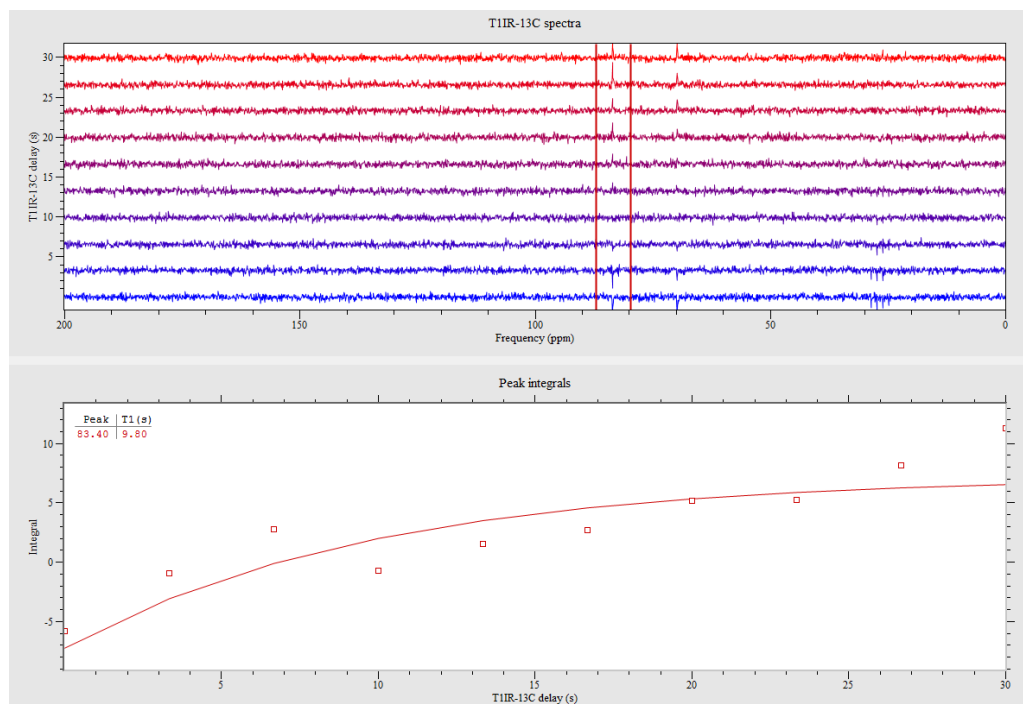


Figure 11 – Experiment 6 - T_1 relaxation experiment with no decoupling. A low SNR was observed and a T_1 time of 9.80 seconds was measured

3.6 Experiment 6 - T_1 Relaxation of C13 With and Without Decoupling

Lastly, we performed two T_1 relaxation experiments for C13: one with coupling to the H1, and another with 'decoupling' of the two spins. We measured and plotted both experiments to take a look at the T_1 times associated with them. We know from our previous C13 experiments that C13 pulse experiments have very high SNR. Decoupling the C13 to the H1 spins will significantly increase our SNR and yield a more accurate T_1 decay value. This experimental decoupling is achieved through the WALTZ-16 method, which is briefly outlined in Section 1.5.

Our first experiment with no decoupling is shown in Figure 11. As we can see, we had a fairly low SNR value and a measured T_1 time of 9.8 seconds. Our second experiment had the WALTZ-16 method applied to decouple the H1 spins to the C13. Our results of this experiment are shown in Figure 12. Due to the decoupling, we observed a single absorption lineshape instead of our usual two. This corresponds to all the H1s forced into the spin down state due to the successive π pulses in the H1 channel. This second experiment yielded us a much better SNR and a T_1 value of 15.40 seconds.

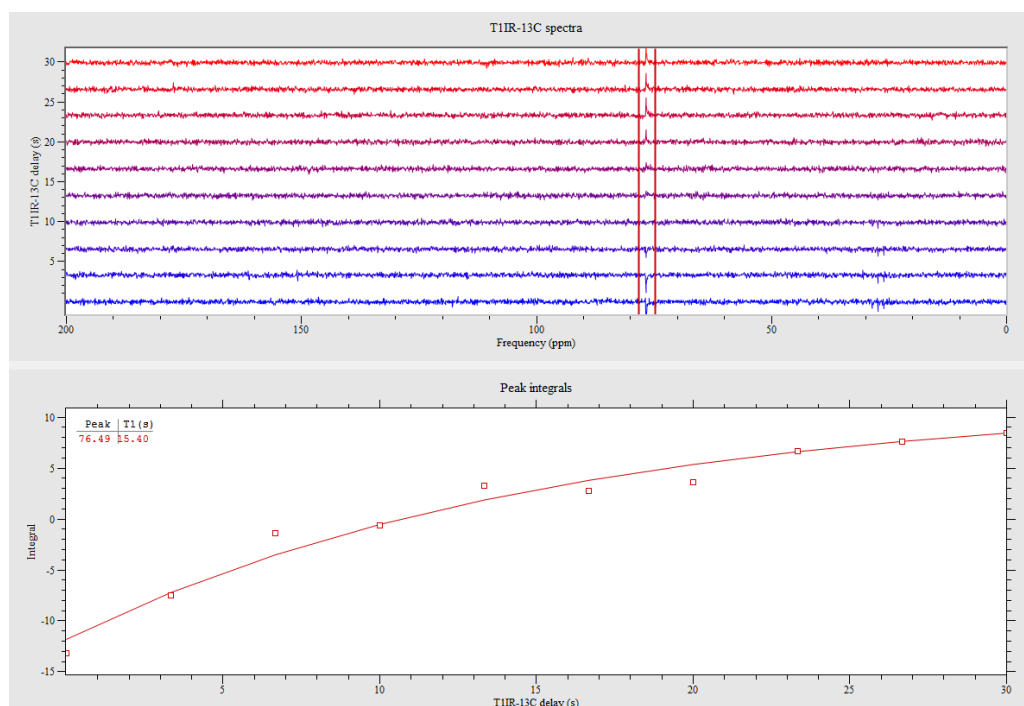


Figure 12 – Experiment 6 - T_1 relaxation experiment with decoupling. A higher SNR was observed and a T_1 time of 15.40 seconds was measured

4 Conclusion

In this lab, we measured a J coupling value of 206.9604 Hz from our H1 spectra and a J coupling value of 205.4520 Hz from our C13 spectra. These are quite good results considering that the Kill, Chaung, and Laflamme paper measured around 215 Hz for their C13 and H1 coupling. We an inverse relaxation experiment on H1 and achieved a T_1 time of 4.011 seconds. This is significantly lower than the T_1 we measured for D2O in lab 1, which is most likely attributed to the spin coupling and differing structure of our chloroform molecule. We performed a pulse length calibration experiment for C13. Unfortunately, we ended up getting noisy results measured along the wrong axis. We attempted to correct for this by exporting the dispersion spectrum and shifting it by $e^{-i\pi/2}$. This error corrected method yielded decent results and our group concluded on a $\pi/2$ C13 pulse length of $77.5\mu\text{s}$ (at -5.9dB). These experimental results could have been improved if we introduced a method to increase our SNR - such as H1 spin decoupling. Lastly, we analyzed the impacts of noise in a series of C13 pulse experiments. This included a FID experiment where we took advantage of the Nuclear Overhauser Effect to reduce our overall noise and a FID experiment with the WALTZ-16 method applied to decouple the H1 spins from our measured C13 spin transitions. We concluded that this decoupling method greatly increased our SNR and we were able to measure a T_1 time of 15.40 seconds.

5 Works Cited

References

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