

PHYS 360A/B
Experiment 20: Nuclear Magnetic Resonance

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October 17, 2023

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Abstract

1 Introduction

Hello World!

2 Theoretical Background

2.1 Spin in a Magnetic Field

- Nuclei with spin inherently exhibit a magnetic dipole moment, denoted as $\vec{\mu}$. In classical terms, one can liken this to a minuscule bar magnet.
- Upon positioning such a magnet within an external magnetic field, characterized as $\vec{B}_0 = B_0 \hat{z}$, and presuming the spin axis (aligned with $\vec{\mu}$) is misaligned with \vec{B}_0 , it undergoes a torque, mathematically expressed as $\vec{\tau} = \vec{\mu} \times \vec{B}_0$, and commences a precession around the magnetic field.
- The Larmor relation governs the frequency of this precession: $f_0 = \frac{\omega_0}{2\pi} = \frac{\gamma B_0}{2\pi}$, where γ stands for the gyromagnetic ratio—a metric that ties the magnetic moment to the angular momentum. Significantly, this ratio is nucleus-specific. For instance, in the context of protons (or 1H nuclei predominantly utilized in MRI), a 1 Tesla magnetic field corresponds to $f_0 = 42.57 \text{ MHz}$.
- Quantum mechanics introduces another layer of nuance. It posits that nuclear spin is quantized. Each specific nucleus possesses an intrinsic, fixed spin. Such quantization results in the dipole moment $\vec{\mu}$ precessing, in the face of a uniform external magnetic field \vec{B}_0 , only at sharply defined angles relative to \vec{B}_0 .
- With respect to protons, $\vec{\mu}$ adopts merely two orientations concerning \vec{B}_0 : either parallel (denoted as spin "up") or antiparallel (or spin "down") to \vec{B}_0 . These orientations carry distinct energy levels in the \vec{B}_0 field. Such energy differentiation results in an imbalance, with "up" spins slightly outweighing the "down" spins, leading to a discernible macroscopic magnetization \vec{M} along \vec{B}_0 .
- An auxiliary magnetic field \vec{B}_1 , when tuned to the Larmor frequency f_0 , can modulate the spin energy level populations, which tilts \vec{M} away from the z-direction, inducing a precession around \vec{B}_0 at frequency f_0 . For convenience, this behavior of \vec{M} is often assessed classically. The torque experienced by the magnetization due to the rotation of \vec{B}_1 is given by $\vec{\tau} = \vec{M} \times \vec{B}_1$.
- It's pivotal to understand motion in the "rotating frame", a reference frame oscillating at the Larmor frequency around \vec{B}_0 (or the z-axis). In this context, \vec{B}_0 remains stationary in both the laboratory and rotating frames, implying the z' -axis in the rotating frame mirrors the z-axis in the lab frame. Consequently, the stationary \vec{B}_1 in the rotating frame instigates \vec{M} to revolve about \vec{B}_1 , remaining within the $z'y'$ -plane.

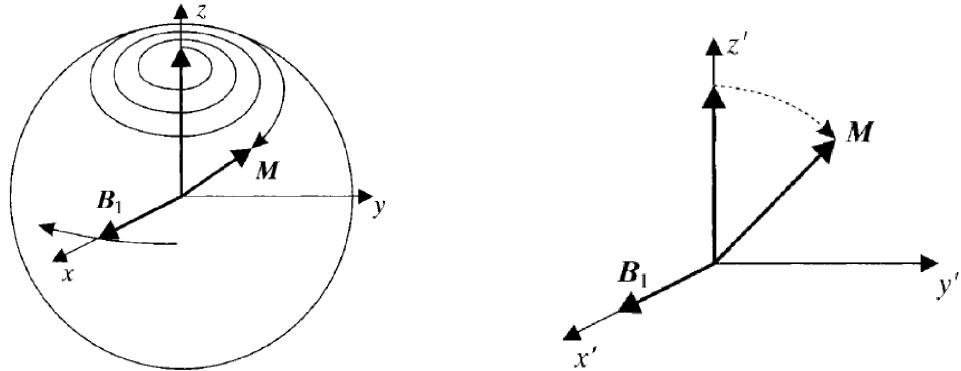


Figure 1: Diagram of proton spin precessing. Source: Experiment 20 Manual (originally from Medical Imaging: Signals and Systems, Pearson Prentice Hall)

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2.2 Measuring the Spin

- The magnetization vector \vec{M} can be manipulated using various radio-frequency (rf) pulse schemes.
 - Applying a rf pulse of amplitude B_1 and duration τ_P such that \vec{M} is rotated into the xy-plane results in a $\pi/2$ pulse.
 - Doubling τ_P produces a π pulse, rotating \vec{M} into the negative z-direction.
- The characteristic time for the magnetization in the xy-plane, M_{xy} , to decay is denoted T_2 , known as the spin-spin relaxation time.
 - Over time, spins release the energy they obtained through the application of the $\pi/2$ pulse and return to equilibrium.
 - When the magnetization regrows along the z-axis to equilibrium value B_0 , it's characterized by time T_1 , called the spin-lattice relaxation time.
- As \vec{M} precesses around \vec{B}_0 , any xy-plane component induces an emf in a surrounding sample coil.
 - This is described by Faraday's Law: $\text{emf} = -N \frac{d\phi_B}{dt}$ due to \vec{M} .
 - The recorded signal from this precessing magnetization is termed the free induction decay (FID).
- In a standard sample, individual magnetic moments contributing to \vec{M} are in varied magnetic environments.
 - This is due to local, internal magnetic fields from neighboring spins and inhomogeneities in the B_0 field.
 - After magnetization is directed into the xy-plane, spins begin to dephase, reducing the net M vector in the xy-plane and consequently the induced signal.
- Once \vec{M} has a component in the xy-plane, individual spins constituting this component start precessing at different rates. This causes spins to dephase, leading to a reduction in the overall magnitude of the xy-component of the magnetization vector \vec{M} .

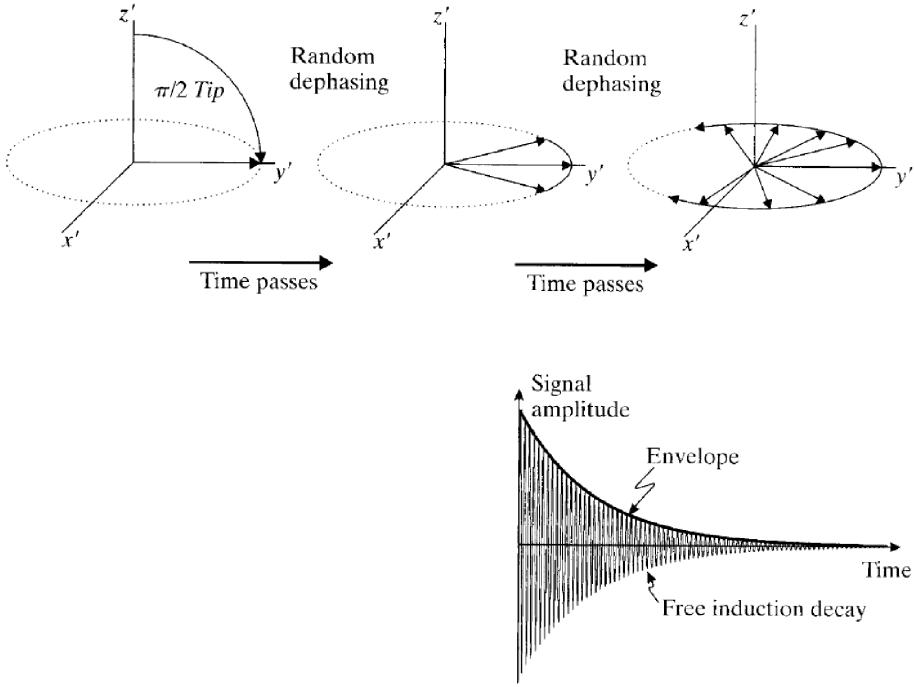


Figure 2: Diagram after an RF pulse is applied. Source: Experiment 20 Manual (originally from Medical Imaging: Signals and Systems, Pearson Prentice Hall)

3 Experimental Design and Procedure

Apparatus Overview

- Using a Self-sustained pulse Nuclear Magnetic Resonance (NMR) spectrometer.
- Analyzing samples of water enriched with copper sulfate, a vinyl eraser, and ethanol.
- Components of the Spectrometer:
 - Pulse programming unit
 - Source of frequency
 - RF pulse modulation system
 - Transmission unit
 - NMR probing mechanism
 - NMR signal detection and reception system
 - Permanent magnet
- Functionality: Subject samples (in sealed glass tubes) to RF magnetic pulses; integration with an oscilloscope for real-time observation and recording.
- Integrated Experimental Procedures: Free induction decay (T2), inversion recovery, spin-echo.

Procedure Overview

- **B.1: Finding Resonance**



Figure 3: Photo of the NMR machine used. Source: Experiment 20 Manual

- Place water sample in magnet, set spectrometer settings, and adjust for a 90° pulse to achieve resonance.

- **B.2: The FID and $T2^*$**

- Using water, alcohol, and rubber samples, adjust spectrometer settings, acquire an exponential FID, and determine $T2^*$ for each sample.

- **B.3: Measurement of $T1$**

- Using water, alcohol, and rubber samples, adjust spectrometer for two 90° pulses, determine τ for $M_z(\tau) = M_0/2$, and compare $T1$ values for each sample.

- **B.4: Measurement of $T1$ with Inversion-Recovery Sequence**

- Using water, alcohol, and rubber samples, adjust spectrometer for 180° and 90° pulses, record FID for varying τ , and determine $T1$ using linear slope and zero-crossing methods.

- **B.5: Hahn Echo**

- Using water, alcohol, and rubber samples, adjust spectrometer for 90° and 180° pulses, observe the echo signal, and determine $T2$ for each sample.

- **B.6: Freezing**

- Place water sample in magnet, adjust spectrometer settings, achieve an exponential FID, then freeze the sample in liquid nitrogen and observe changes in the signal.

4 Analysis

4.1 Finding Resonance

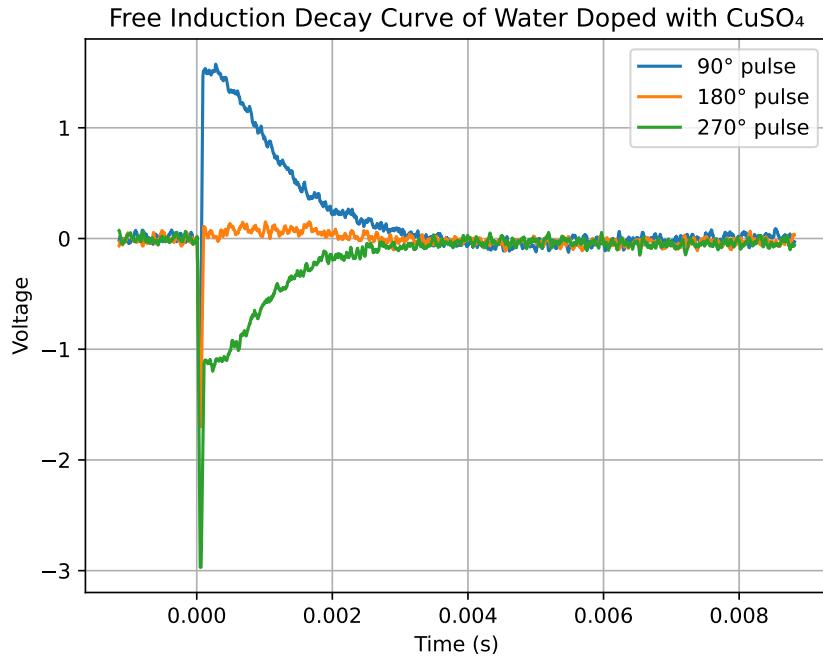
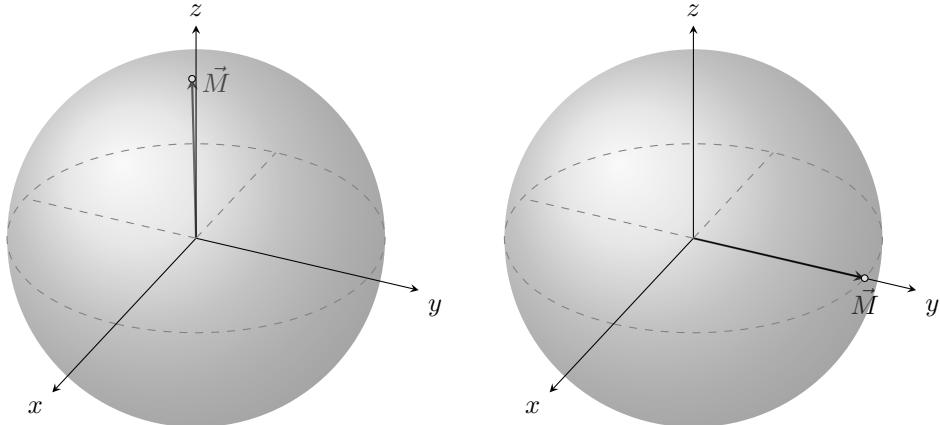


Figure 4: Free Induction Decay NMR signals for 90°, 180°, and 270° pulses

4.1.1 Voltage at t = 0s

90° Pulse

- A 90° pulse is a pulse that is applied long enough to tip the magnetization vector by 90° from its initial direction (at a small angle with the positive z-axis) in the rotating frame:



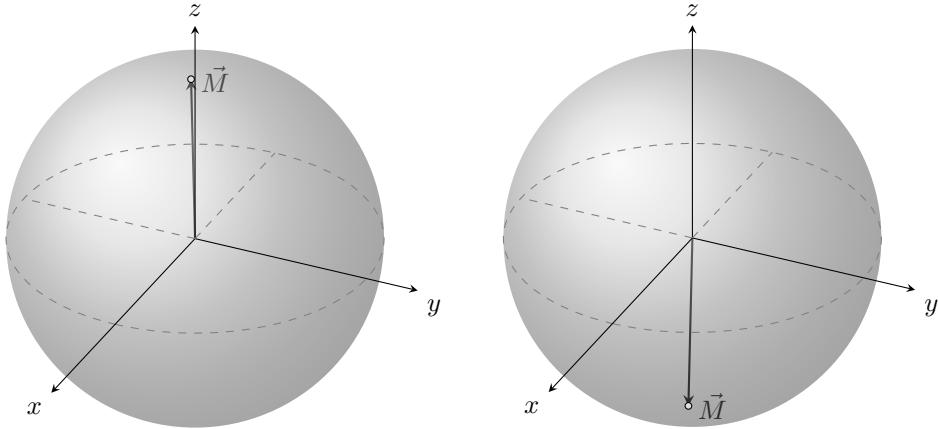
- Now, nearly half the spins are in the “up” state and the other half are in the “down” state.
- Since \vec{M} is in the $x-y$ plane, the z component of the magnetization vector vanishes:

$$M_z = 0$$

- This is a higher energy state than the equilibrium state with the magnetization vector, \vec{M} , pointing along the positive z-axis.
- The receiver gain was adjusted so that the precessing \vec{M} induced¹ a current in the coil as shown in the 90° trace of Figure 4.

180° Pulse

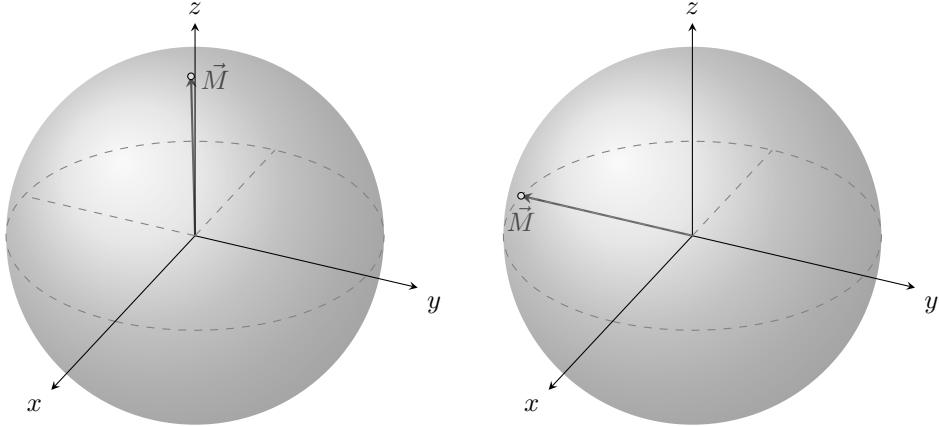
- If we apply the pulse for twice as long (increase the pulse width to twice that of the 90° pulse), we rotate the magnetization vector by 180° :



- Most of the spin are now in the “down” state.
- However, this magnetization vector doesn’t induce current in the coils since the component in the x-y plane is nearly 0.

270° Pulse

- This time, the pulse is applied long enough to rotate \vec{M} by an additional 180° from the 90° case:



- That is, \vec{M} returns to the x-y plane but is anti-parallel to \vec{M} in the 90° pulse case:

$$\vec{M}_{270^\circ} = -\vec{M}_{90^\circ}$$

- It hence precesses in the opposite sense of rotation as the 90° case².

¹According to Faraday’s law.

²And vice versa.

- According to Faraday's law, the direction of the current \vec{M}_{180° induces in the coil is opposite to that of \vec{M}_{90° .
- This is why we see a current that is $-I_{90^\circ}$ induced in the 270° case in Figure 4.

4.1.2 Free Induction Decay

- For all three pulses, we see that the signal vanishes over time.
- Recall that for the 90° and 270° pulses, the magnetization vector is in the x-y plane.
- Because of small variations in the magnetic field that the magnetic moments, $\vec{\mu}$, for each particle experience, the magnetic moments being to randomly dephase.
- They spread out in the x-y plane causing the magnetization vector and hence the induced current to vanish as a whole.

4.2 The Free Induction Decay and T_2

- In this section, we take a closer look at the FID observed in the 90° and 270° traces of Figure 4 (for different samples).
- For the same 90° pulse, we have the following FID traces:

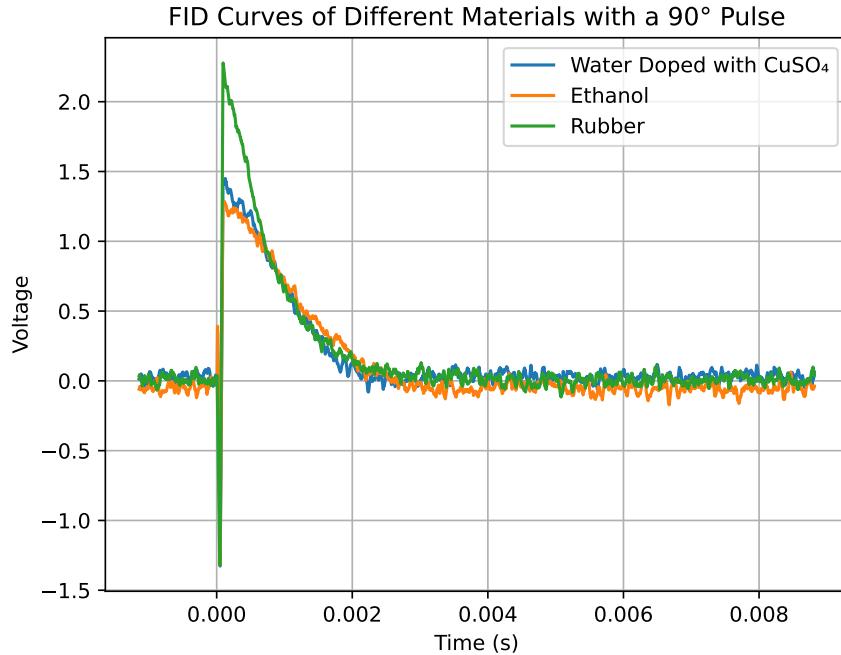


Figure 5: FID for the 90° pulse in water doped with CuSO_4 , ethanol, and rubber

4.2.1 Finding T_2

Analytically

- On plotting the traces in Figure 5 on a semi-log graph (along with the best fit lines), we get:

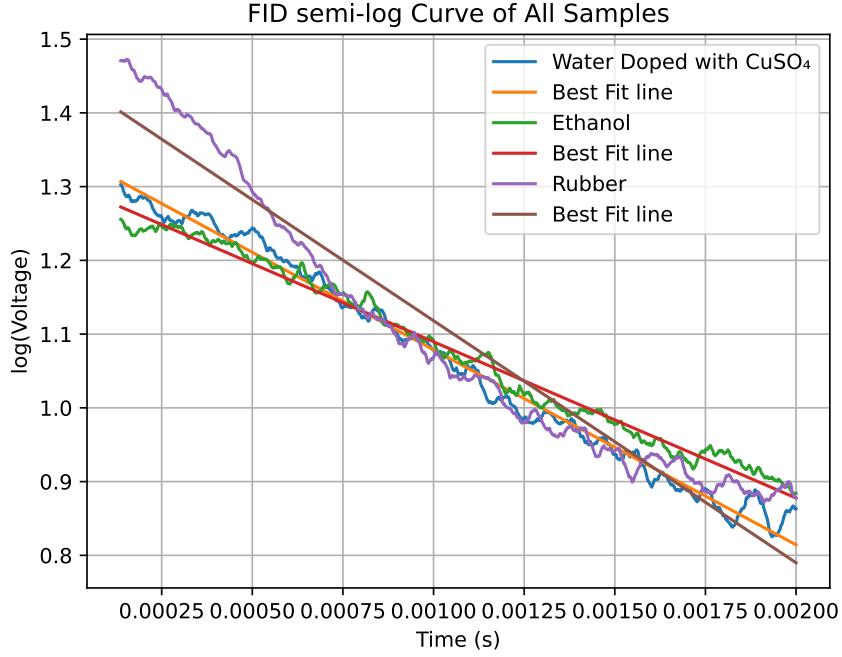


Figure 6: $\ln(M_{xy}) = -\frac{t}{T_2^*} + \ln(M_0)$ plotted for the three traces in Figure 5

- We can find T_2^* using the following equation:

$$M_{xy}(t) = M_0 e^{-\frac{t}{T_2^*}}$$

Here, $M_{xy}(t)$ is the trace seen in Figure 5,
 M_0 is the magnetization at $t = 0$,
 t is the time.

- We can take the \ln of both sides to get:

$$\ln(M_{xy}) = \ln(M_0) + \ln\left(e^{-\frac{t}{T_2^*}}\right)$$

$$\ln(M_{xy}) = -\frac{t}{T_2^*} + \ln(M_0)$$

- Comparing this to $y = mx + c$, we see that the slope, m , is given by:

$$m = -\frac{1}{T_2^*}$$

$$\implies T_2^* = -\frac{1}{m}$$

Sample Calculation

- Consider $m = -328.236\text{s}^{-1}$ for Doped Water in Table 1:

$$T_2^* = -\frac{1}{-328.236\text{s}^{-1}}$$

$$T_2^* = -\frac{1}{-328.236}$$

$$T_2^* = 0.003047\text{s}$$

	Slope	T_2 (s)
Doped Water	-328.236	0.003047
Ethanol	-264.426	0.003782
Rubber	-211.89	0.004719

Table 1: Slopes of best fit lines and calculated T_2^*

- We can hence find T_2^* from the slopes of the best fit lines in Figure 6 for the other samples:

Estimation

- We can find an estimation for T_2^* directly from the FID traces.
- For $t = T_2^*$, we have:

$$M_{xy}(T_2^*) = M_0 e^{-1}$$

$$\frac{M_{xy}(T_2^*)}{M_0} \approx 0.37$$

$$M_{xy}(T_2^*) \approx 0.37 M_0$$

- We can estimate the time at which $M_{xy}(T_2^*)$ is approximately $0.37 \cdot M_0$:

	M_0	$0.37 M_0$	T_2 (s)
Doped Water	1.46	0.540	0.00112
Ethanol	1.40	0.518	0.00122
Rubber	2.40	0.888	0.00089

Table 2: Estimate of T_2^* using the initial magnetization

4.3 Measurement of T_1

- In this section, we perform an Inversion Recovery (IR) experiment to find the spin-lattice relaxation time, T_1 .
- We use two 90° pulses $t = \tau$ apart:

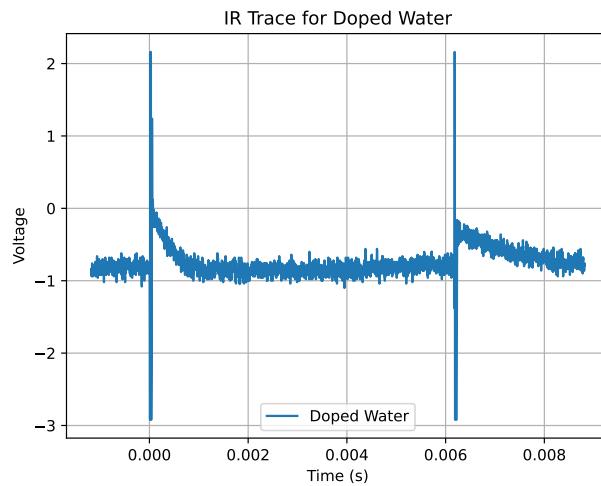


Figure 7: IR trace for water doped in CuSO₄

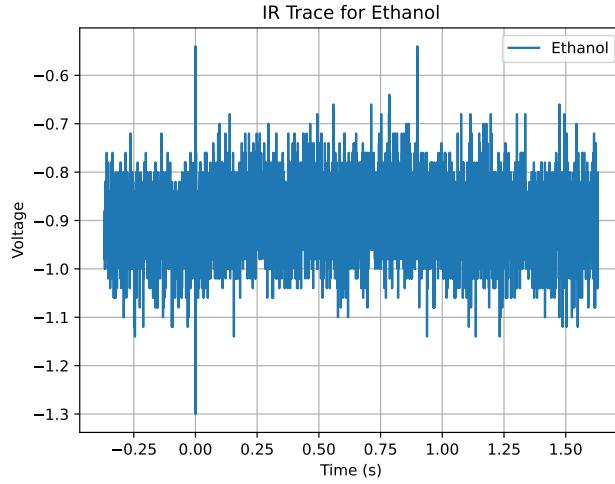


Figure 8: IR trace for Ethanol

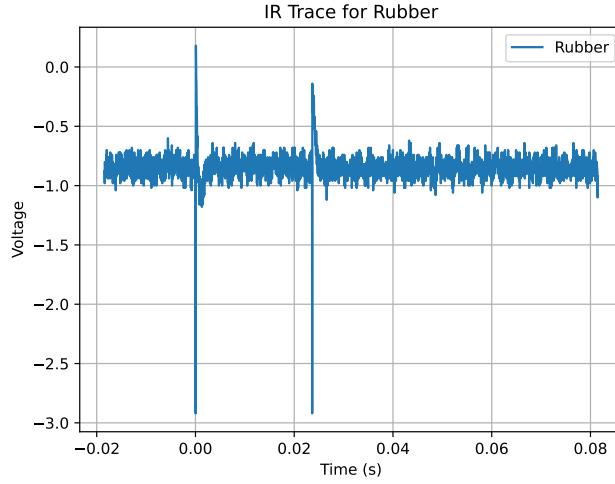


Figure 9: IR trace for Rubber

4.3.1 Calculating T_1

- To find T_1 , we use the following equation:

$$M_z(\tau) = M_0 \left(1 - e^{-\frac{\tau}{T_1}} \right)$$

- Since we already chose to record the data such that $M_z(\tau) = \frac{M_0}{2}$:

$$\frac{M_0}{2} = M_0 \left(1 - e^{-\frac{\tau}{T_1}} \right)$$

$$\frac{1}{2} = 1 - e^{-\frac{\tau}{T_1}}$$

$$\ln \left(e^{-\frac{\tau}{T_1}} \right) = \ln \left(\frac{1}{2} \right)$$

$$-\frac{\tau}{T_1} = -0.693$$

$$\frac{\tau}{T_1} = 0.693$$

$$T_1 = \frac{\tau}{0.693}$$

- Where τ is the distance between peaks³:

- $\tau_{\text{doped H}_2\text{O}} = 0.006205\text{s} - 0.000030\text{s} = 0.006175\text{s}$
- $\tau_{\text{ethanol}} = 0.898870\text{s} - 0.000248\text{s} = 0.898622\text{s}$
- $\tau_{\text{rubber}} = 0.023670\text{s} - 0.000088\text{s} = 0.023582\text{s}$

- And so $T_1 = \frac{\tau}{0.693}$ becomes:

	τ (s)	T_1 (s)
Doped Water	0.006175	0.008911
Ethanol	0.898622	1.296713
Rubber	0.023582	0.034029

Table 3: T_1 calculated from τ

4.4 Measurement of T_1 with Inversion-Recovery Sequence

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4.5 Freezing Water

In the concluding segment of this experiment, the pulse scheme is set to the Free-Induction Decay (FID) configuration, employing a singular 90-degree pulse on the water specimen. The distinguishing aspect this time is that the water sample is subjected to freezing via liquid nitrogen prior to its placement in the spectrometer for the pulse application.

The NMR settings were adjusted to maximize the signal for the liquid water doped with copper sulphate. Upon achieving optimal settings, the sample was then frozen with liquid nitrogen and the NMR signal was examined once more.

The unfrozen water sample displayed a pronounced decay curve, signifying a strong NMR signal. However, a stark contrast was observed post-freezing, where the signal vanished entirely. Delving into the potential reasons behind the zero signal in the frozen water scenario, it's imperative to mention that the magnetization vector \vec{M} is composed of individual nuclear spins within the samples. A plausible hypothesis could be that upon transitioning into a solid crystalline state, the nuclei become stationary, hindering any alteration in their spin orientations. This conjecture is challenged by the observed signals from the solid rubber sample, although it isn't as solid as the ice.

³This was done by finding where the peaks happen in the data.

5 Conclusion