

PHYS 360A/B
Experiment 20: Nuclear Magnetic Resonance

Mikhail Roslikov Kamalesh Paluru

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Contents

1	Introduction	4
2	Theoretical Background	5
2.1	Spin in a Magnetic Field	5
2.2	Measuring the Spin	6
3	Experimental Design and Procedure	8
4	Analysis	10
4.1	Finding Resonance	10
4.1.1	Voltage at $t = 0\text{s}$	10
4.1.2	Free Induction Decay	12
4.2	The Free Induction Decay and T_2	12
4.2.1	Finding T_2	12
4.3	Measurement of T_1	14
5	Conclusion	15

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.

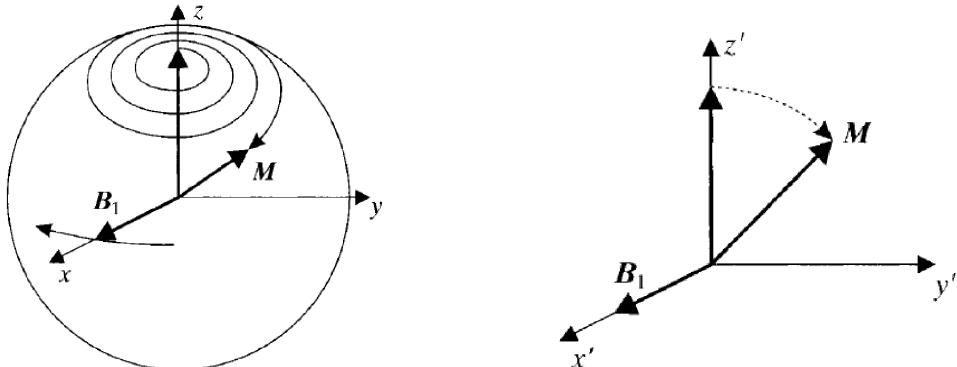


Figure 1: Diagram of proton spin precessing. Source: Experiment 20 Manual (originally from Medical Imaging: Signals and Systems, Pearson Prentice Hall)

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.

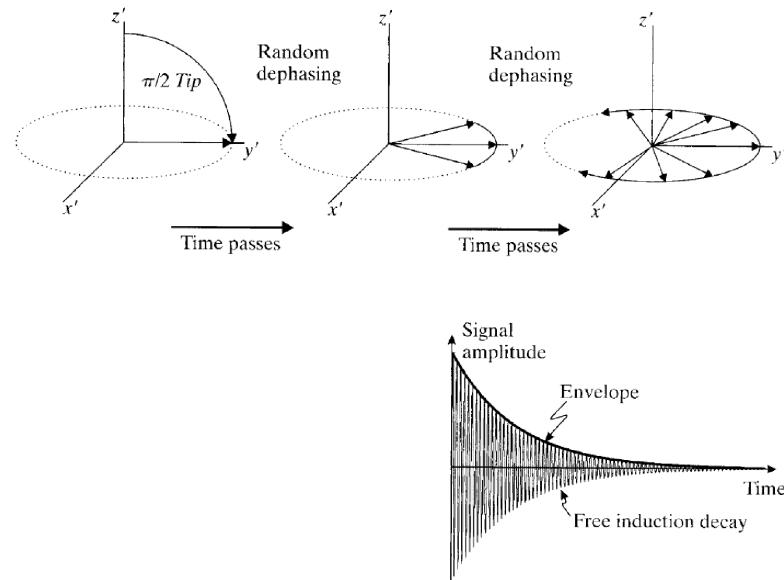


Figure 2: Diagram after an RF pulse is applied. Source: Experiment 20 Manual (originally from Medical Imaging: Signals and Systems, Pearson Prentice Hall)

- 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} .

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 (T_2), inversion recovery, spin-echo.



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

Procedure Overview

- **B.1: Finding Resonance**
 - Place water sample in magnet, set spectrometer settings, and adjust for a 90° pulse to achieve resonance.
- **B.2: The FID and T_2^***
 - Using water, alcohol, and rubber samples, adjust spectrometer settings, acquire an exponential FID, and determine T_2^* for each sample.
- **B.3: Measurement of T_1**

- 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

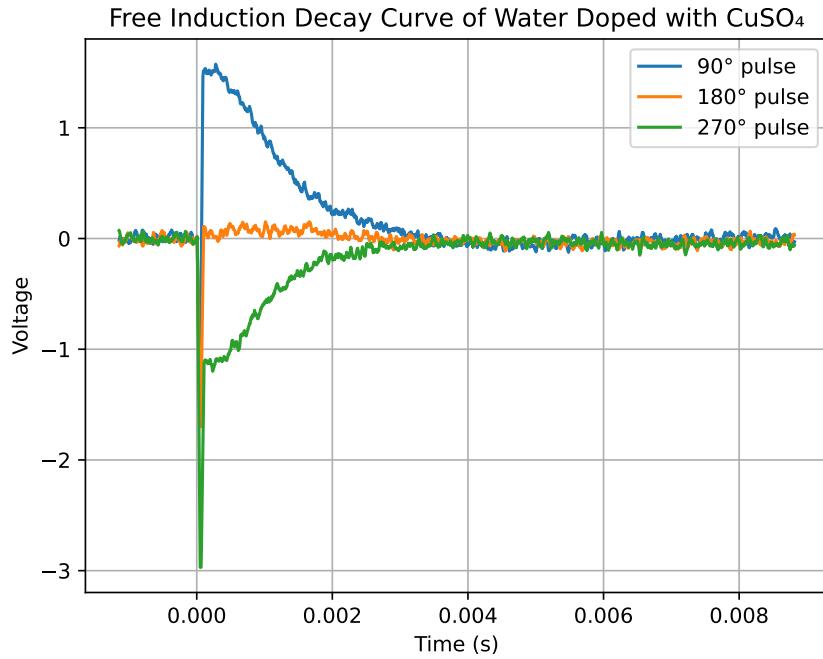
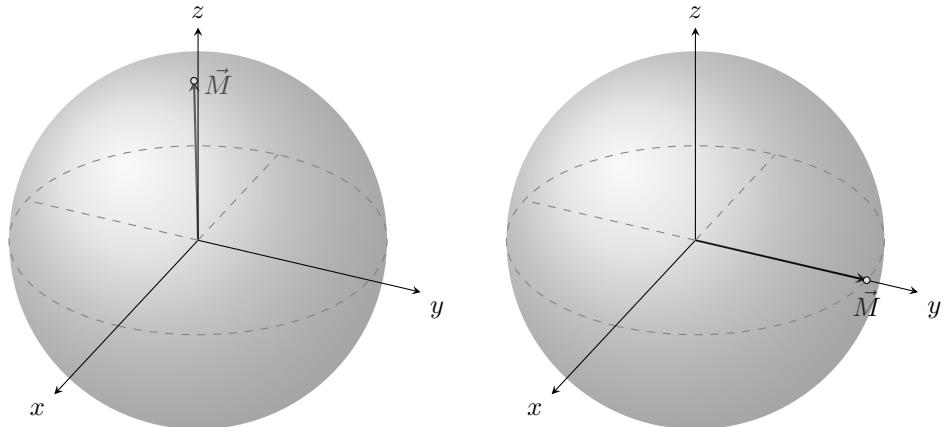


Figure 4: Free Induction Decay NMR signals for 90°, 180°, and 270° pulses

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:



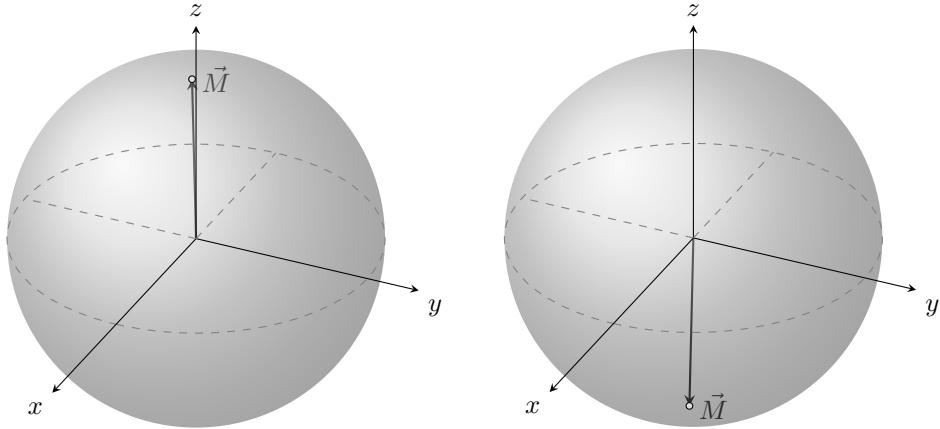
- Now, nearly half the spins are in the “up” state and the other half are in the “down” state.
- Since \vec{M} is in the $x-y$ plane, the z component of the magnetization vector vanishes:

$$M_z = 0$$

- 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

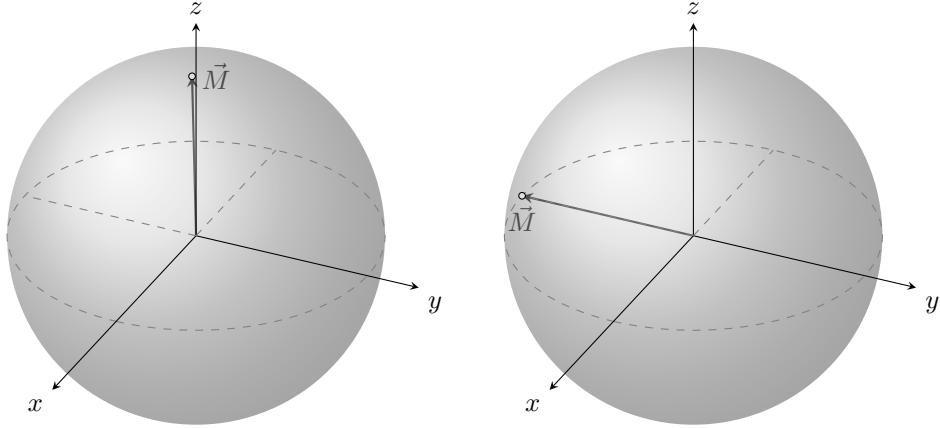
- If we apply the pulse for twice as long (increase the pulse width to twice that of the 90° pulse), we rotate the magnetization vector by 180° :



- 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:

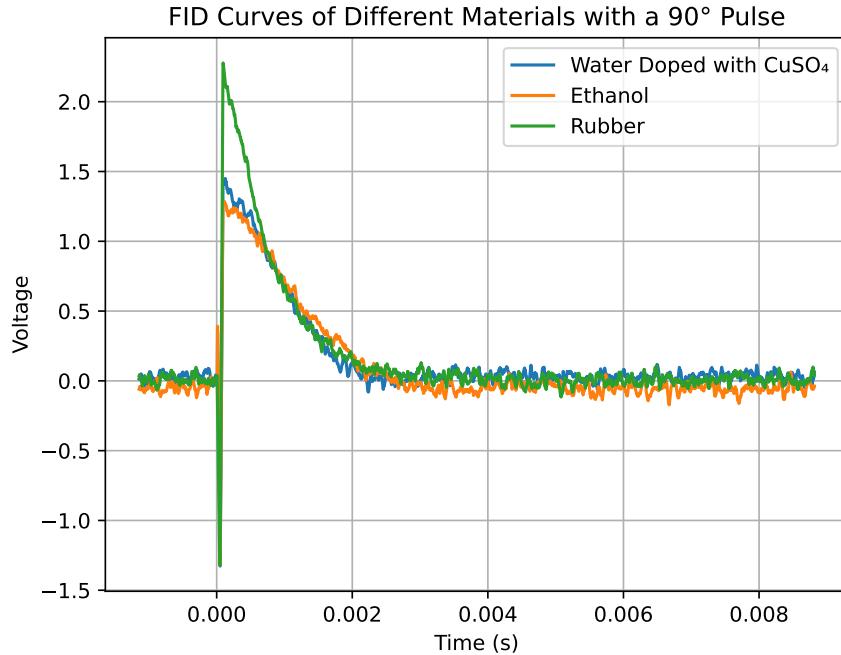


Figure 5: FID for the 90° pulse in water doped with CuSO_4 , ethanol, and rubber

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:

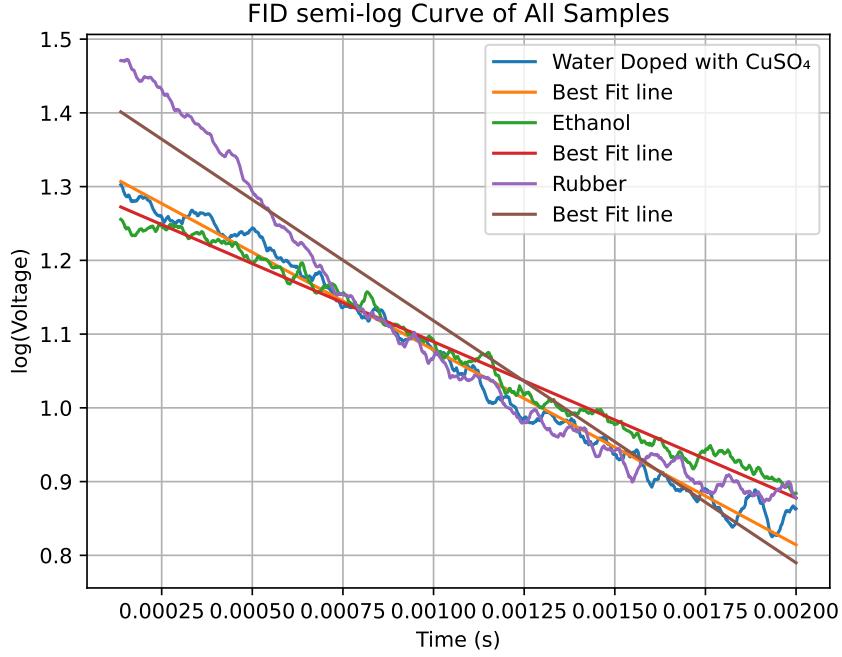


Figure 6: $\ln(M_{xy}) = -\frac{t}{T_2^*} + \ln(M_0)$ plotted for the three traces in Figure 5

- 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:

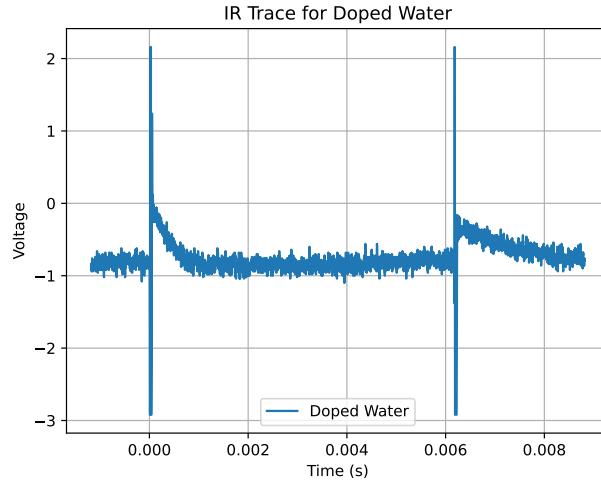


Figure 7: IR trace for water doped in CuSO₄

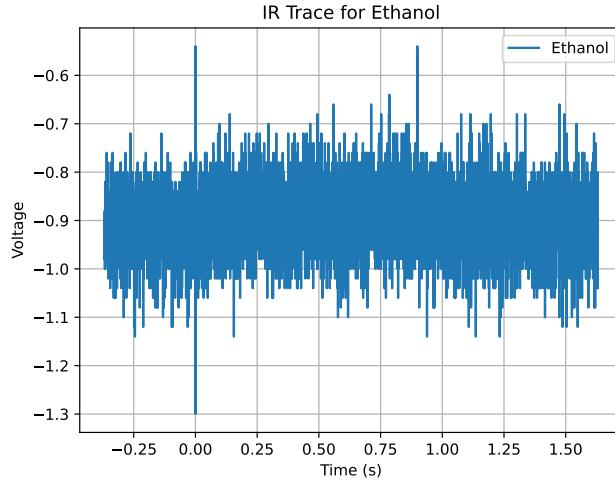


Figure 8: IR trace for Ethanol

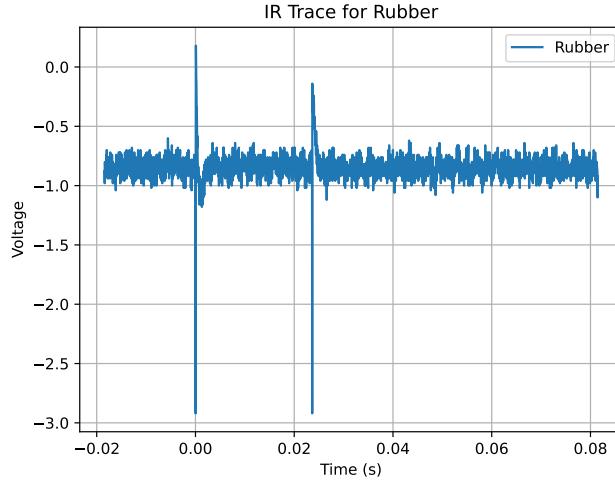


Figure 9: IR trace for Rubber

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

5 Conclusion