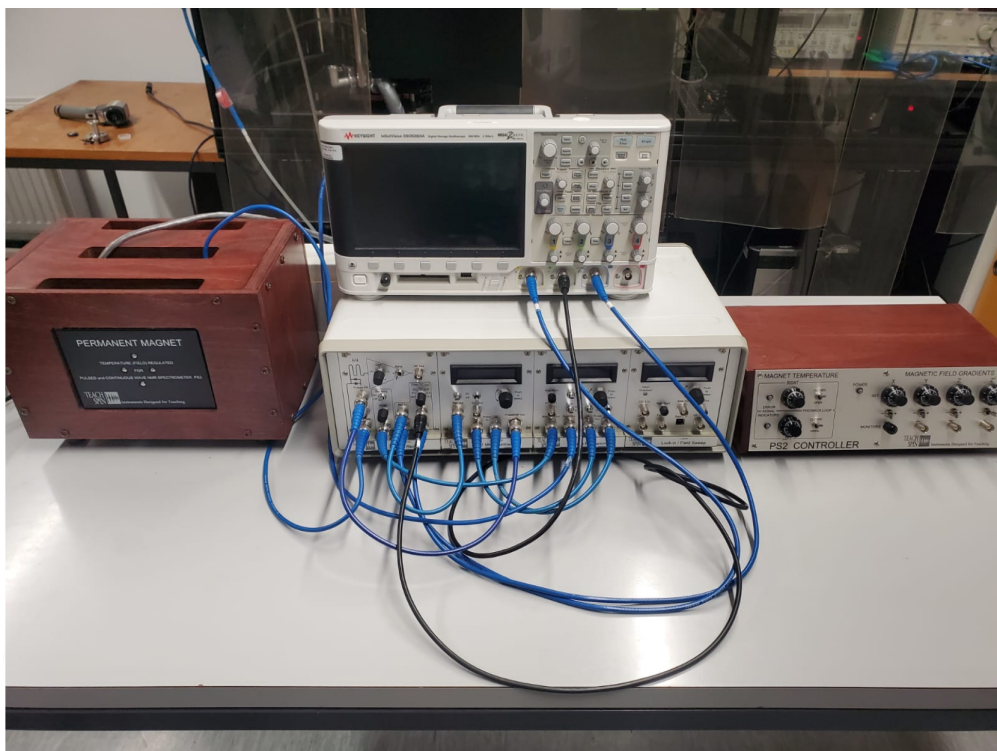

SOLID-STATE NUCLEAR MAGNETIC RESONANCE

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1 Introduction

This experiment is about pulsed nuclear magnetic resonance, relaxation times and the practical work with a spectrometer.

Nuclear magnetic resonance (NMR) in condensed matter was discovered in 1946 by Edward Purcell and Felix Bloch. They used different instruments, however both placed a sample containing magnetic nuclei in a uniform magnetic field and observed the response of those nuclei to a continuous radio frequency magnetic field as the field was tuned through resonance. Those discoveries became the basis for a new type of spectroscopy, which is now one of the most important tools available to physicists, chemists, geologists and biologists.

A few years later, in 1950, Erwin Hahn explored the response of the magnetic nuclei to pulse bursts of radio frequency magnetic fields. During these experiments he discovered a „spin echo“ signal. Later in the instructions you will learn how this echo is created and how it can be used for spectroscopy. However, this discovery gave birth to a new technique for studying magnetic resonance. Originally pulsed NMR only had a few practitioners, but over time pulsed NMR has become the dominant commercial instrumentation for most research applications. By using Fourier transformations of the transient response, it is possible to achieve NMR spectroscopy with very high resolution. Cheap and fast computers made these calculations practical, making pulsed NMR the method of choice for most laboratories.

NMR spectroscopy has a wide field of uses. The technology has found its way into medicine, where magnetic resonance imaging (MRI) is used to create three dimensional images that give detailed information about the inner working of living systems. In physics and chemistry however, NMR spectroscopy is used to characterize minerals. NMR is a microscopic method that probes the nuclei and their immediate surroundings, capable of measuring the local field at atomic nuclei. Therefore if an molecule is containing several atoms of the same element in various different configurations, the NMR signal for all of them will be different. This microscopic nature makes NMR spectroscopy an extremely useful and often unique tool to characterize a sample. In this experiment two kinds of nuclei will be investigated. To get a detectable signal, we need many molecules of the same configuration to occur within the sample. Hydrogen (protons) and fluorine are very abundant and give particularly strong signals. Therefore these nuclei will be used as samples in this experiment.

Through reading the instructions and executing the different tasks of the experiment you will learn the basics of the theory behind pulsed NMR and how you can practically use pulsed NMR to analyse different samples. The next pages will give you an overview over the most important things you need to know, to understand the physics behind the measurements you are going to take during this experiment. After this theoretical introduction into pulsed NMR, you will have the opportunity to work practically with a NMR spectrometer to analyse the different samples that are present in the laboratory.

2 Outline of the Physics

2.1 Theory

In this experiment we want to study magnetic resonance. To observe magnetic resonance it is necessary to have a system with both a **magnetic moment** μ and an **angular momentum** \mathbf{J} . You can think of the investigated nuclei as small spinning bar magnets. These magnets are spinning with an angular momentum and an magnetic moment, which are related by the following vector equation:

$$\mu = \gamma \mathbf{J}. \quad (1)$$

The proportionality factor γ is called the **“gyromagnetic ratio”**. This value is unique to each kind of nucleus used in the experiment.

The angular momentum is quantized by units of the Dirac constant \hbar as:

$$\hbar = \frac{h}{2\pi}$$

$$\mathbf{J} = \hbar \mathbf{I}. \quad (2)$$

I is the spin of the nucleus. The projection of this spin m_I is given by:

$$m_I = I, I-1, I-2, I-3, \dots, -I.$$

In this experiment, only nuclei with a spin of one half are investigated, resulting in m_I values of:

$$m_I = \pm 1/2.$$

The application of an external magnetic field, introduces the magnetic energy U :

$$U = -\boldsymbol{\mu} \cdot \mathbf{B}. \quad (3)$$

For a magnetic field in z-direction the magnetic energy becomes:

$$U = -\mu_z B_0 = -\gamma \hbar I_z B_0. \quad (4)$$

As discussed before I_z can only take two values, therefore the energy separates into two magnetic energy states, when a constant magnetic field is applied.

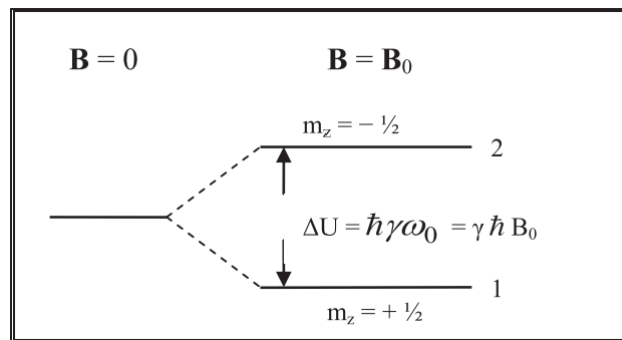


Figure 1: Separation of energy states in a magnetic field.

The separation of the two energy states can be described in terms of an angular frequency, resulting in the following important relation:

$$\Delta U = \hbar \omega_0 = \gamma \hbar B_0, \quad (5)$$

or

$$\omega_0 = \gamma B_0. \quad (6)$$

This equation describes the **fundamental resonance equation** and can be used to calculate the angular frequency for a given magnetic field or to calculate the magnetic field by a given angular frequency. All you need to know is the gyromagnetic ratio of the used nuclei.

In this experiment we use two different kinds of nuclei, the hydrogen nuclei which consists only of protons, and the fluorine nuclei, which consists of protons and neutrons. The gyromagnetic ratios of hydrogen and fluorine are:

For the proton: $\gamma_{\text{proton}} = 2.675 \times 10^8 \text{ rad/sec} - \text{tesla}$.
 For Fluorine: $\gamma_{\text{fluorine}} = 2.517 \times 10^8 \text{ rad/sec} - \text{tesla}$

2.1.1 Magnetization in z-direction

By placing a sample in a magnetic field in z-direction a magnetisation of the nucleons is established parallel to the applied magnetic field. This magnetisation is called the thermal equilibrium magnetisation. It occurs because of the two different quantum states that are available, which are shown in Figure 1. If N_1 and N_2 are the number of spins in the respective states, the ratio of these two populations is given by the Boltzmann factor:

$$\frac{N_2}{N_1} = e^{\frac{\Delta U}{kT}} = e^{\frac{\hbar\omega_0}{kT}}. \quad (7)$$

The unequal population of both energy states induces a magnetisation of:

$$M_Z = (N_1 - N_2) \mu. \quad (8)$$

In thermal equilibrium the magnetization per unit volume for N ($N = N_1 + N_2$) magnetic moments is:

$$M_0 = N\mu \tanh\left(\frac{\mu B}{kT}\right) \approx N\frac{\mu^2 B}{kT}. \quad (9)$$

This magnetization however **does not appear instantaneously**. As described in Figure 2, it takes time for the magnetization to build up. For most systems the z-component of the magnetization will grow exponentially.

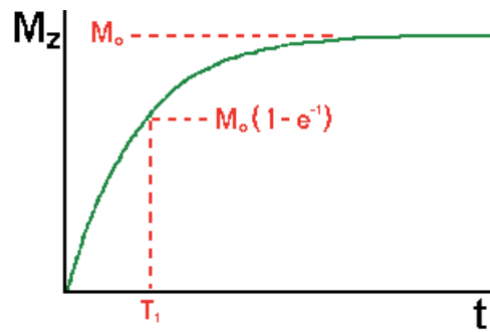


Figure 2: Exponential growth of magnetisation over time

The characteristic time for the build-up of the magnetisation is called the **spin-lattice relaxation time** T_1 . With this spin relaxation time we can write the following equation for the temporal evolution of the magnetization in z-direction:

$$M_z(t) = M_0 \left(1 - e^{-\frac{t}{T_1}}\right). \quad (10)$$

The spin-lattice relaxation time T_1 is characteristic for each sample and therefore investigated by spectrometry. It ranges from microseconds to seconds. This rather extended range of times is based on various material-dependent relaxation processes of the protons. The study of these processes is a fundamental topic in magnetic resonance. We want to look at two approaches that explain the differences in the relaxation times:

First we can look at the energy states of the nuclei in thermal equilibrium. Without a magnetic field the two energy states are occupied equally ($N_1 = N_2$). In thermal equilibrium however, more protons are in the lower energy state than the upper, because of the magnetisation of the magnetic field. Therefore energy has to be transferred from the nuclei to the surroundings of the nuclei (from here on referred to as the lattice). This interaction between nuclei and lattice is the reason this relaxation time is called spin-lattice relaxation time and is dependent on the investigated material.

But the energy transfer is not the only explanation for the differences in the relaxation times. Each proton has angular momentum, which has to be transferred to the lattice during magnetization. In classical physics terms we need a sufficient torque which allows to change the angular momentum. In quantum mechanics terms the lattice must have angular momentum states available, when a spin goes from $m_I = -1/2$ to $m_I = +1/2$.

The existence of such states usually is the critical determining factor in explaining the differences between the different spin-lattice relaxation times T_1 .

2.1.2 Magnetization in the x-y plane

Now, after we discussed the magnetization in z-direction, we want to look at the magnetization in the x-y plane. In thermal equilibrium the net magnetization of the sample is represented by M_z : In the constant magnetic field, the magnetic moment executes a precessional motion around the magnetic field. A torque τ is causing the angular momentum to change, given by:

$$\tau = \frac{d\mathbf{J}}{dt} \quad \text{or} \quad \boldsymbol{\mu} \times \mathbf{B} = \frac{d\mathbf{J}}{dt}. \quad (11)$$

For our nuclei, this equation becomes:

$$\boldsymbol{\mu} \times \mathbf{B} = \frac{1}{\gamma} \frac{d\boldsymbol{\mu}}{dt}. \quad (12)$$

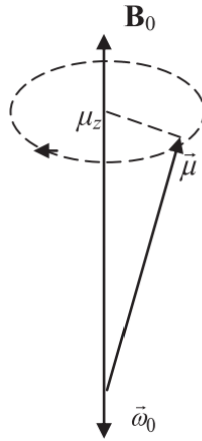


Figure 3: Precessional motion about B_0

Figure 3 shows this precessional motion. The frequency at which the protons precess around B_0 , the so-called **Larmor frequency**, matches the same frequency as the resonance frequency in the fundamental resonance condition.

If we now add up all the individual components of μ we see that all the μ_z components add up to M_z , but the components of the x- and y-components add up to zero. If we want to generate a magnetization in x-direction we will need a definite phase of the x-components. In thermal equilibrium, the orientation of the x- and y-components is random. But we can **create** such a transverse magnetization, using **radio frequency pulsed magnetic fields**.

We can rotate the thermal equilibrium magnetization M_z into the x-y plane, by adding a rotating magnetic field. The classical motion of the net magnetization of the entire sample can be described by:

$$\frac{d\mathbf{M}}{dt} = \gamma \mathbf{M} \times \mathbf{B}. \quad (13)$$

In this general case \mathbf{B} can be composed of any magnetic field, including time dependent rotating fields. We can now create a magnetic field that rotates in the x-y plane, written as:

$$\mathbf{B}(\mathbf{t}) = B_1 \cos \omega t \hat{i} + B_1 \sin \omega t \hat{j} + B_0 \hat{k}. \quad (14)$$

To work with this rotating magnetic field, we analyse our magnetization from a rotating coordinate system, which rotates with the same frequency ω as the rotating magnetic field. The axis of this new rotating coordinate system are named x^* , y^* and z^* . Based on the matching rotation frequencies, the rotating field appears to be stationary along the x^* axis, simplifying the discussion of the magnetic field. However, from the point of view of the rotating coordinate system, B_0 and B_1 are not the only magnetic fields. We have to add an **effective field** along the z^* axis. An additional $-\frac{\omega}{\gamma}\hat{k}^*$ must be included, justified by the following argument:

We earlier discussed that the magnetisation precesses around a static magnetic field with the precessional frequency ω_0 . Now, our coordinate system also rotates with this frequency. If both, the coordinate system and the magnetization, rotate with the same frequency, the magnetization appears to be stationary in our new rotating coordinate system.

This means there can be no torque on the magnetic moment, which could change the magnetization. This can be achieved when the magnetic field in the rotating system is zero, in which case the torque on \mathbf{M} would also always be zero. To get the magnetic field to zero we add our effective field, which is equal to $B_0\hat{k}^* = -\frac{\omega}{\gamma}\hat{k}^*$. The rotating coordinate system and the resulting magnetic fields are shown in figure 4.

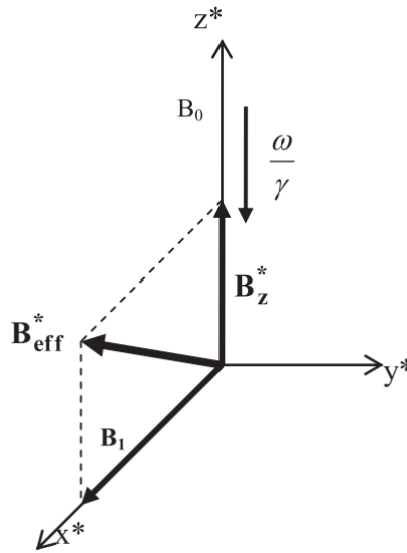


Figure 4: Effective magnetic field

We get a total magnet field in the rotating frame \mathbf{B}^* :

$$\mathbf{B}_{\text{eff}}^* = B_1\hat{i}^* + \left(B_0 - \frac{\omega}{\gamma}\right)\hat{k}^*. \quad (15)$$

The classical equation of motion of the magnetization as observed in the rotating frame is then

$$\left.\frac{d\mathbf{M}}{dt}\right|_{\text{rot}} = \gamma\mathbf{M} \times \mathbf{B}_{\text{eff}}^*, \quad (16)$$

which shows that \mathbf{M} will precess around $\mathbf{B}_{\text{eff}}^*$ in the rotating frame.

Now we have all the information we need to rotate our magnetization into the x-y plane and thereby create a magnetization M_x .

We first create a rotating magnetic field with frequency

$$\omega_0 = \gamma B_0.$$

This magnetic field $\mathbf{B}_{\text{eff}}^*$ is stationary in the x^* -direction. M_z begins to precess around this magnetic field at a rate $\Omega = \gamma B_1$. If we now turn off the magnetic field at the right moment, we can rotate the magnetization fully into the x - y plane. This rotation process is shown in figure 5.

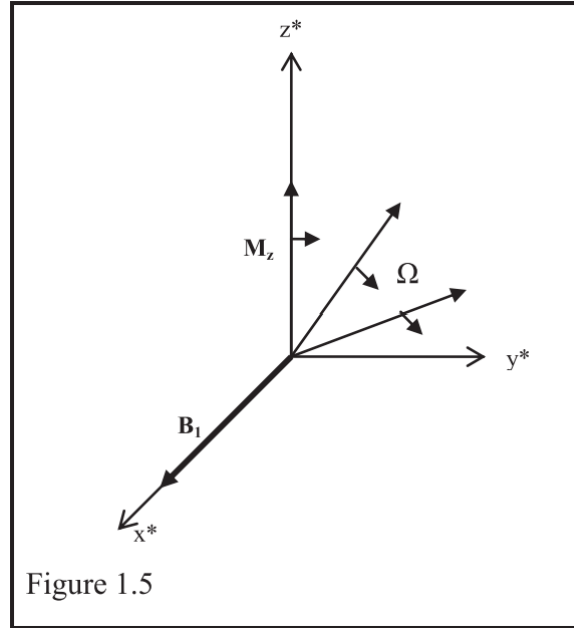


Figure 5: Rotation of the magnetisation into the x - y plane

We call those rotating magnetic fields „pulses“.

Different magnetisation's can be achieved by applying the following pulses:

$$\begin{aligned} 90^\circ \text{ or } \pi/2 \text{ pulse} &\rightarrow M_z \rightarrow M_y. \\ 180^\circ \text{ or } \pi \text{ pulse} &\rightarrow M_z \rightarrow -M_z. \\ 360^\circ \text{ or } 2\pi \text{ pulse} &\rightarrow M_z \rightarrow M_z. \end{aligned}$$

In reality this magnetization is not stable due to local fields. The magnetisation not only precesses around B_1 , but also around \hat{k} .

After a 90° pulse the net equilibrium magnetisation will rotate into the x - y plane. But there is not only the rotating magnetic field. There is also the constant magnetic field $B_0 \hat{k}$. The magnetisation will precess about this magnetic field $B_0 \hat{k}$. This means the magnetisation we created will not last forever. For most systems the magnetization will decay exponentially with a new relaxation time T_2 . The equations that describe the decay in the rotating coordinate system, which is depicted in figure 6, are:

$$\frac{dM_{x^*}}{dt} = -\frac{M_{x^*}}{T_2} \quad \text{and} \quad \frac{dM_{y^*}}{dt} = -\frac{M_{y^*}}{T_2}. \quad (17)$$

The solutions of these differential equations are:

$$M_{x^*} = M_0 e^{-\frac{t}{T_2}} \quad \text{and} \quad M_{y^*} = M_0 e^{-\frac{t}{T_2}}. \quad (18)$$

This relaxation time T_2 is called the **Spin-Spin Relaxation Time**.

2.1.3 Measuring the Spin-Spin Relaxation Time

A measurement of T_2 gives information about the distribution of local fields at the nuclear sites. Each nucleus is itself a magnet and is projecting a magnetic field at its neighbours. Therefore there must be a distribution of

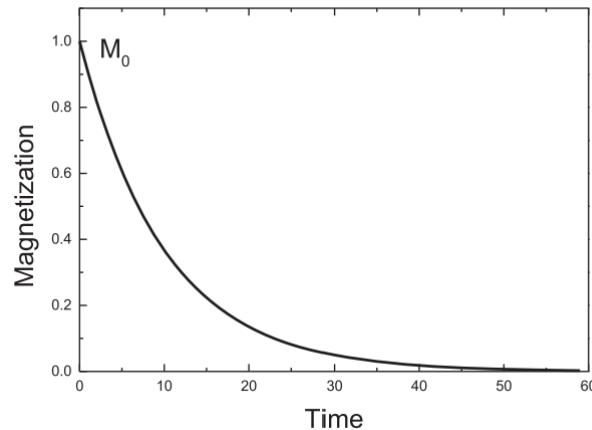


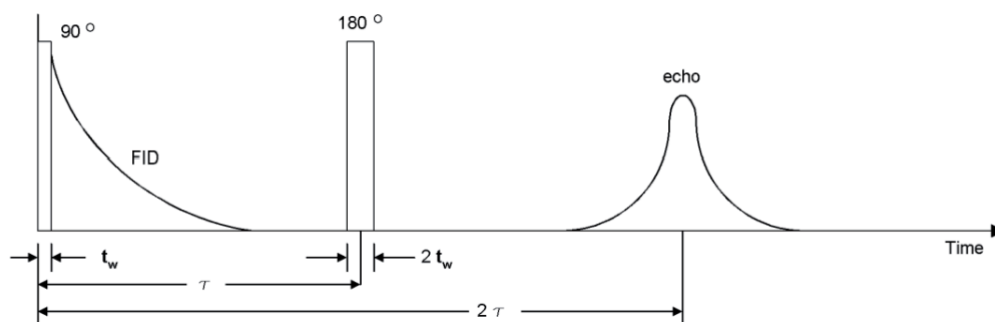
Figure 6: Exponential decay of the magnetisation

local fields, resulting in a distribution of different frequencies.

Due to these differences in the local fields we can not directly measure the decay of M_x to get the relaxation time T_2 after a 90° pulse. The signal that we get for this kind of measurement is called the **free induction decay** (FID) and has a decay time of T_2^* . T_2^* and T_2 would be equal for a perfect magnetic field. The field used in this experiment has sufficient uniformity at the centre to produce a 5 ms decay time. For a measurement where T_2 is 5 ms or smaller the FID and the T_2 measurements are the same. But for decay times longer than this we can't assume a perfect magnetic field. Because of the inhomogeneities the nuclei will precess with different decay times, based on the strength of the local magnetic field. This is a problem for determining T_2 and with conventional NMR we would have to try to improve the homogeneity of our magnetic field to solve this problem. A more convenient way to measure T_2 is the application of an sophisticated pulsed NMR measurement scheme.

By using a sequence of pulses we can use the **Spin Echo Method** to determine T_2 . This method uses two pulses instead of just a single 90° pulse. The first pulse is still a 90° pulse, but this pulse is followed up by a second 180° pulse after a time τ . To understand how this can help us compensate the different precession times, we have to understand what happens to the magnetization during the pulse sequence.

The first pulse is a 90° pulse. This pulse rotates the magnetisation into the x-y plane. After the first pulse the magnetization will begin to dephase. All of the nuclei will dephase at a different speed, depending on the strength of the local magnetic field. After a time τ we give a 180° pulse to flip the magnetization to the opposite direction. The nuclei now precesses back at the same speed they dephased before, the ones that dephased with higher speed before now rotate back with higher speed and the ones that dephased slower after the 90° pulse now also rotate back slower. This means that at 2τ the magnetisation rephases and forms an echo. These processes are depicted in figure 7 and figure 8.

Figure 7: 90° - 180° pulse sequence

This process can be visualised by a race on a racetrack, where every runner runs with its own constant speed. After a bit of time the field will separate, with the faster runners getting ahead of the slower ones. Then there is

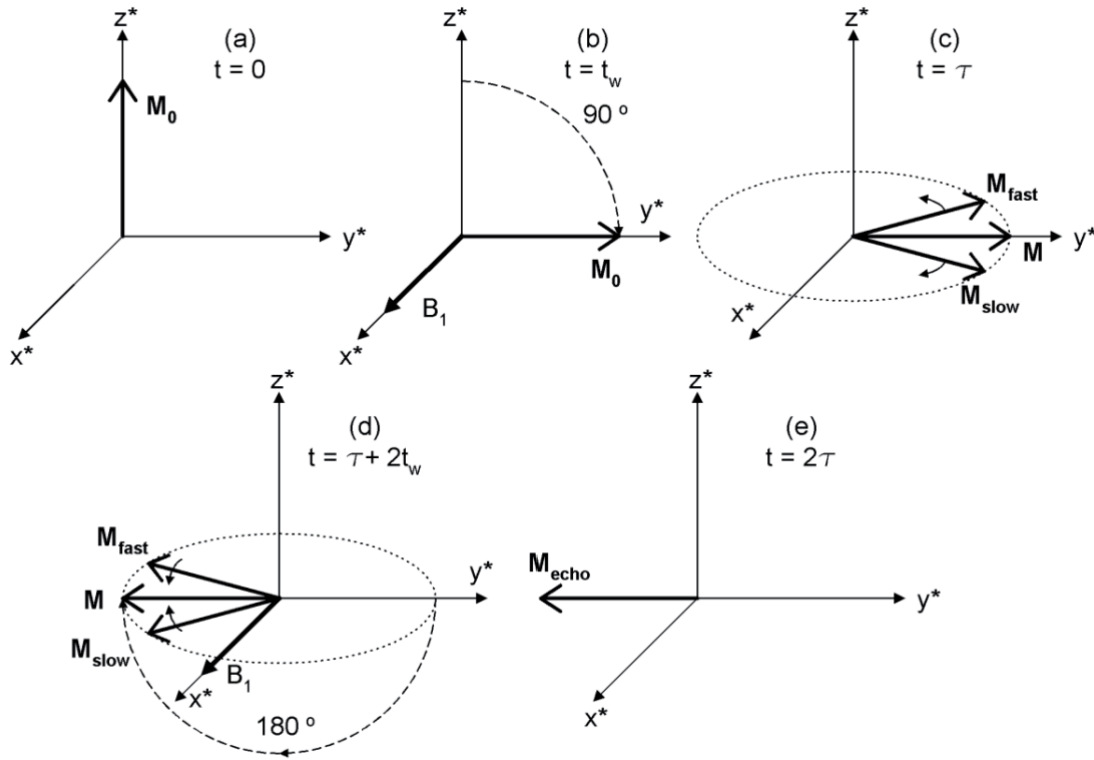


Figure 8: Progression of the magnetisation in the rotating frame

- a) Magnetisation in thermal equilibrium
- b) Rotation of the magnetisation into the x-y plane after a 90° pulse
- c) Dephasing of the magnetisation
- d) Flipped magnetisation after a 180° pulse
- e) Rephasing of the magnetisation and formation of an echo

a signal, where every runner has to turn around and run in the other direction. Now the slowest runners are at the front and the fastest runners are the ones furthest back. But because of their faster speed they will get closer until all runners will meet again at the starting line.

In pulsed NMR the speed of the runners is equal to the speed at which the magnetisation dephases. And the signal for the runners to turn around is represented by the 180° pulse.

However the maximum height of the Echo after the 180° -pulse is not the same as the maximum height of the FID. Some loss of $M_{x,y}$ magnetization has occurred, due to stochastic fluctuation in the local fields. This decay of magnetisation can be used to determine T_2 . To measure the actual T_2 we can use a series of $90^\circ > \tau > 180^\circ$ pulse experiments, varying τ , and then plotting the echo height as a function of time between the FID and the echo.

The x-y-magnetization as measured by the maximum echo height is written as:

$$M_{xy}(2\tau) = M_0 e^{-\frac{2\tau}{T_2}} \quad (19)$$

2.2 Questions for checkup

After reading the chapter „Outline of the physics“ you can check if you understood the theory behind pulsed NMR in general and the measurements you are supposed to do in this experiment. If you can't answer the following questions you should read the explanations in the text above again. If you can answer all the questions you can continue reading the instructions for the experiment.

1. Why is the spin-lattice relaxation time a relevant measurement for spectrometry?
2. How can you create magnetisation in x-direction?
3. How does the magnetisation in the x-y plane change for a 180° -, 90° - and 45° - pulse?
4. Why is the created magnetisation in the x-y plane not stable?
5. Why can you usually not just measure the decay time of M_x to determine T_2 ?
6. What is a spin echo? How can you use it to measure T_2 ?

3 Introduction to the Spectrometer

3.1 Experimental setup

The experimental setup consists of three major parts, that are depicted in figures 9, 10 and 11. The first part is a **magnet** (figure 9), with an integrated RF (radio frequency) sample probe mounted inside. The magnetic field of this magnet is about 0.5 T. The samples can be placed into the sample coil, which sits perpendicular to the constant magnetic field inside the magnet. The sample coil serves two purposes. Its first role is as a transmitter coil, supplying an oscillating RF field which can change the orientation of the net magnetisation. Its second role is as a pickup coil, sensing the precession of any component of the magnetisation which is in the x-y plane.

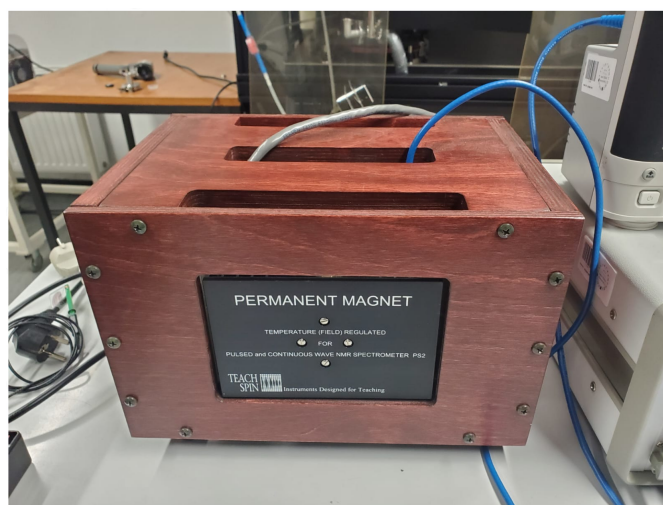


Figure 9: Magnet

The magnet is linked to the **PS2 controller** (figure 10), the second component of the setup. This controller adjusts the magnet temperature and the gradient of the field to create a stable and homogeneous magnetic field.



Figure 10: PS2 Controller

The third part is the **Mainframe** (figure 11). The mainframe consists of a receiver, a synthesizer, a pulse programmer, a lock-in and a build-in DC power supply, which powers all three components of the setup. With this mainframe we can set up the parameters of our measurements. The synthesizer generates a frequency, where we want to set the Larmor frequency of our sample. The pulse programmer is there to create the pulse that we need to rotate the magnetisation. We can control the following parameters:

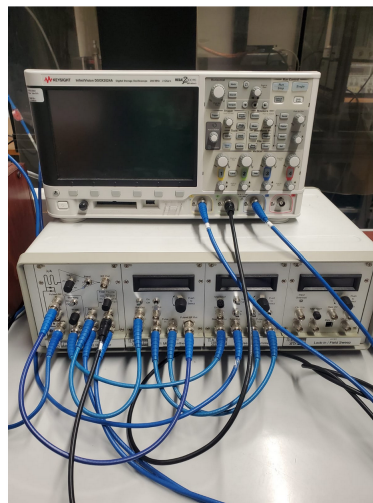


Figure 11: Mainframe

Synthesizer settings

- F:** Frequency of the internal synthesizer
- P:** the relative phase of the reference signal being routed to the receiver module
- A:** Amplitude of the continuous wave RF output signal
- S:** the sweep of the NMR RF frequency

Pulse Programmer settings

A: Length of the first pulse (pulse A)

B: Length of the second pulse (pulse B)

τ : Time between pulse A and pulse B

N: Number of repetitions of pulse B

P: Period

To set up most of our experiments you have to change the settings of the pulse programmer to create different combinations of pulses. You can create two different pulses, named pulse A and pulse B. The length of both of these pulses can be set individually and pulse B can be repeated N-times with a Period of P. After the first pulse is completed, the second pulse starts after a time τ .

To select and change these parameters you have to use the push-to-select knob below the screen of the part of the mainframe you want to change. By rotating the knob you can switch between the different possible parameters. You can then select a parameter by pushing the knob into the panel, until there is an audible signal, that indicates that the parameter has been selected. When the parameter is selected rotating the knob will allow you to select the decimal place you want to change and then change the value of the selected parameter. Once the parameter is changed to the correct value, pushing the knob into the panel until you hear the audible signal will bring you back to the selection of the different parameters.

The signal of the spectrometer will be depicted by a digital oscilloscope.

3.2 Default Settings

When you start the spectrometer you don't have to set every parameter by hand. There already are settings that have been programmed into the PS2-A mainframe electronics. Before you start your experiments you should check if all the settings are correct to avoid any systematic mistakes.

Syntesizer	Pulse Programmer
F: 18.00000 mHz	A: 0.02 μs
P: -180 °	B: 0.02 μs
A: - 10 dBm	τ : 0.0001s
S: 0 kHz/V	N: 0
	P: 0.2 ms

Write down every parameter you are changing before you start to take measurements!

4 Experiments

4.1 Set Up

To start the experiments, we first need to set up the spectrometer. Before we can work with the samples, we have to tune the RF probe to the Larmor precession frequency of the protons in the ambient magnetic field. To achieve this we can use a pickup probe, that can be placed inside the sample chamber, and a single A pulse that is repeated with a period P. With this pickup probe we can measure the RF field **during the pulse**. The signal on your screen now is not a magnetic resonance signal, but the RF field itself inside the solenoid during the pulse. To get a good view of this signal you need to set the following settings on the mainframe and the oscilloscope:

Mainframe settings

A_{len} : 2.5 μs

P : 100ms

Oscilloscope settings

Trigger: Ext, Normal, Rising, > 0.1 Volt, positive slope

Sweep: 2 μ s/division

Channel 1: 5 V/div, DC, full bandwidth

If the magnetic field inside the solenoid is at maximum height, the RF solenoid is tuned to resonance at the spectrometer's synthesized frequency. Therefore we have to maximize the signal of the RF field. This is possible by adjusting the capacitors on the **tuning side**. Changing the adjustment of these capacitors should change the amplitude of the pickup signal. The capacitor is shown in figure 12.

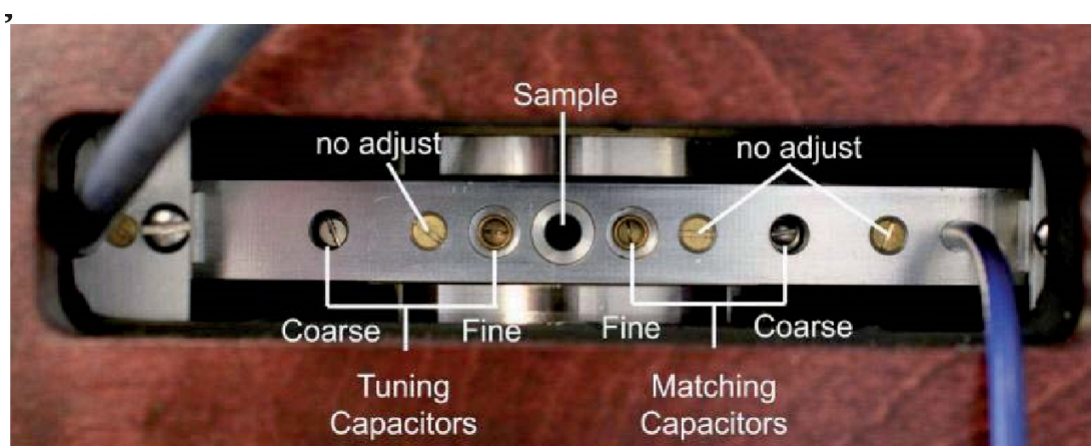


Figure 12: Illustration of the capacitors. **Important:** Adjust only the tuning capacitors, not the matching capacitors.

Try to adjust for maximum amplitude.

4.2 First Measurements

After setting up the spectrometer we can now start our first measurements. These first experiments should get you a good understanding of the measurements in the later experiments. We use mineral oil for all of the following measurements. Mineral oil is a good choice for these basic experiments, due to its high density of protons. We now want to observe the precessing magnetisation after the pulse have been turned off. Therefore we have to change the time scale on the oscilloscope to microseconds.

To get familiar with the spectrometer and the adjustments take the following measurements and interpret your results:

- (1) Use the settings of the pulse programmer to create a 90° -pulse. Explain the signal on your screen. Compare the signal to a 180° -pulse and interpret the difference.
- (2) Examine the settings of the magnetic field with the PS2 controller. Try to find the maximum decay time you can achieve by changing the settings of the magnetic field.
- (3) Discuss how you can determine, that the spectrometer is on resonance (the free precession frequency is the same as that of the spectrometer's synthesizer).
- (4) Calculate the approximate magnetic field during the pulse using the fundamental resonance equation.
- (5) Observe the signal of the resonance frequency on the screen for two minutes. Describe what you see and interpret your observations.

- (6) Change the gain of the spectrometer. Explain what happens when you set a gain that is too high.
- (7) Describe qualitative how the NMR-signal changes for different filter-TC values.
- (8) Discuss what happens when the signal of the spectrometer is off resonance. Explain what happens when you tune the spectrometer „way “ off resonance.
- (9) Use the settings of the pulse programmer to create a second pulse B. Estimate reasonable settings to create an echo. To activate the multi-pulse sequence the „B “switch on the oscilloscopes has to be turned on.

4.3 Study of the mineral oil probe

After you familiarised yourself with the spectrometer and the different possible settings, we now want to study three different samples, using pulsed NMR spectrometry. The first sample you are going to analyse is the mineral oil sample, you already used for the first measurements.

In your first measurements, you should already have determined the lengths of the 90° - and the 180° - pulses. With these pulses known, we can set up the signal to maximum resonance. To get the best possible signal you need to set the frequency of the spectrometer to the resonance frequency of the sample. This can be achieved by tuning of the frequency until the mixer signal at channel 2 resembles the FID curve. Then you need to set the pulse length of the A pulse to the length of a 90° -pulse. Adjust the gradient of the magnetic field to get a maximum width of the FID. Repeat this process until you get the maximum possible amplitude. When you have adjusted the resonance, we can now look at the different free induction decay signals that are created by the different pulses. The created signal should look like the signal shown in figure 13.

Create a 90° -pulse to get the FID signal of the probe. Plot the FID signal and use a Fit-function to determine T_2^* .

Hint: You can use equation (18) as a foundation for your fit. You can replace T_2 with T_2^ and use this exponential Fit to determine T_2^* .*

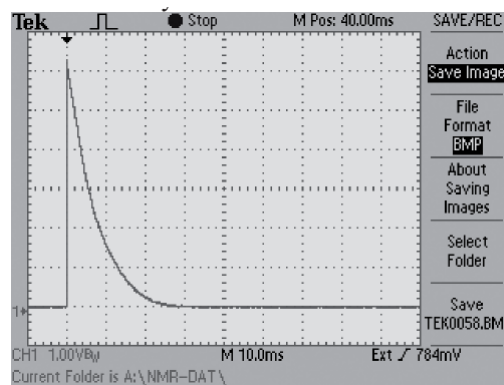


Figure 13: FID Mineral Oil

The decay times we are interested in are T_1 and T_2 . We are going to use multiple methods to determine these decay times. The first method we want to use is the determination of T_1 using different periods P . It is possible to determine T_1 by varying the length of the Period P : For smaller periods the magnetisation can not fully recover to the equilibrium state of the magnetic field, resulting in a smaller magnetisation after the next pulse. By measuring the amplitude of the magnetisation against the period time P we can determine the spin-lattice relaxation time.

Measure the amplitude of the spectrometers signal for different period times P . Start with a period time of 10 ms. Take multiple measurements for different periods until you have a period time of 300 ms. Plot your results and determine T_1 by fitting your experimental data.

Hint: It is helpful to start with smaller steps between the different P values to get a better fit, because the difference between the different FID-Peaks should be higher for small periods.

A second method to determine the spin-lattice relaxation time is the multi pulse method. To determine T_1 we use a 180° -pulse followed by a 90° -pulse. Try to understand what happens to the magnetisation after these two pulses. In this measurement we want to vary the time between the two pulses τ to determine T_1 .

Measure the amplitude of the magnetisation for different τ values. Start with $\tau=0.0001$ s. Plot your results and determine T_1 by fitting your data. Think about the function you have to use to fit your results.

Hint: The amplitude of the magnetisation will become smaller for your first measurements until it reaches a minimum. After this minimum the magnetisation will grow again. You have to take enough measurements to measure over this minimum. To fit your data you have to mirror the values that are located before this minimum along the x-axis.

After you have determined the spin-lattice relaxation time we now want to measure the spin-spin relaxation time of the mineral oil probe. We will again use multiple methods to determine T_2 . The first method we are going to use is the Hahn Echo method. This is the echo method you should be familiar with. We are using two pulses to create an echo. The first pulse we create is a 90° -pulse and the second pulse is a 180° -pulse. To determine T_2 you need to measure the amplitude of the magnetisation for different times τ .

Measure the amplitude of the magnetisation for different τ using a 90° -pulse followed by a 180° -pulse. Start with $\tau=0.002$ s. Plot your results and determine T_2 by using an exponential fit.

The Hahn-echo method only uses two pulses, but we can also determine the spin-spin relaxation time by using a sequence of pulses. The two possible ways we want to discuss, are the „Carr-Purcell“ and the „Meiboom-Gill“ method.

The Carr-Purcell method uses a multiple pulse sequence, which reduces the effect of diffusion on the measurement of T_2 . After the first 90° -pulse is applied, the pulse is followed by multiple 180° -pulses:

$$90^\circ - \tau - 180^\circ - - 2\tau - - 180^\circ - - 2\tau - - 180^\circ - - 2\tau - - 180^\circ - - \text{etc.}$$

This way we do not create a single echo, but a series of echoes equally spaced between the 180° -pulses. The maximum height of these echos will exponentially decay, which makes it possible to determine the spin-spin relaxation time by analysing this exponential decay. The time interval 2τ has to be short compared to the time of self diffusion of the spins through the field gradients. If this is the case, the influence of diffusion on the measurement of T_2 can be reduced significantly.

The Meiboom-Gill method is the second method using a sequence of pulses and has a practical advantage over the Carr-Purcell method: In a real experiment it is not possible to produce perfect 180° -pulses. This is a problem with the high number of pulses we are using. If the apparatus for example produces a 182° -pulse, we would have an error of 60° after 20 pulses. The value you are measuring for T_2 is too small. The Meiboom-Gill method reduces this accumulated rotation error. The pulse sequence of this method provides a phase shift of 90° between the pulses. This prevents the accumulated error to the first order, resulting in a more accurate measurement of T_2 . The difference in the created signal for using the Meiboom-Gill or the Carr-Purcell method is depicted in figure 14:

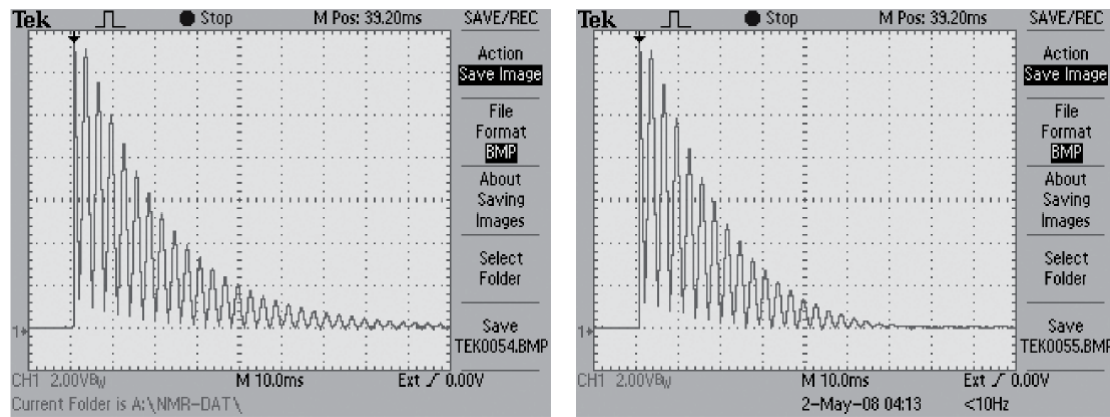


Figure 14: Exemplary Meiboom-Gill (left) and Carr-Purcell (right) measurement.

Turn the Maiboom-Gill switch off. Take a measurement using Carr-Purcell and save the data. Determine T_2 by plotting the saved data and fitting the maximum amplitudes with an exponential fit.

Turn the Meiboom-Gill switch on. Take a measurement using Meiboom-Gill and save your data. Determine T_2 by also making an exponential fit.

Compare the different values of T_2 you have determined by using the Echo Method and the different pulse sequence methods.

You can set the number of pulses N to about 30 to get a good picture of the decay.

4.4 Study of the distilled water (DIW)

The mineral oil sample used until now, had a very high density of protons. Now, we want to study a probe with a lower density than mineral oil. For the following measurements we take distilled water as the sample. Because of the new sample, you first have to find the duration's of the 90° - and the 180° -pulse again.

Determine the 90° - and the 180° - pulses, by changing the setting of the pulse duration of pulse A.

With these pulses known, you can create the FID signal of the DIW sample. A typical FID signal of DIW can be observed in figure 15. You can compare the FID of the probe to the FID of the mineral oil sample.

Create a 90° -pulse to get the FID signal of the sample. Plot the FID signal and use a model to determine T_2^* .

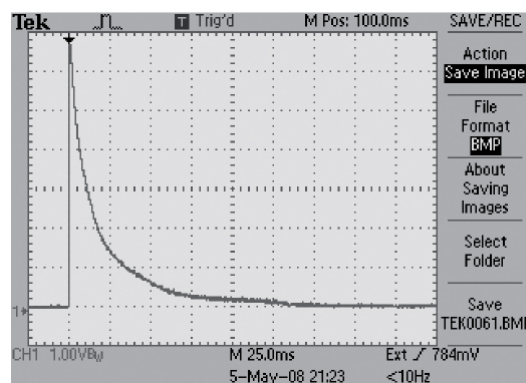


Figure 15: FID of distilled water

To determine the real T_2 of the DIW sample, we want to use the Meiboom-Gill method. The number of pulses should be high to get a good result. You can use $N=70$ and $\tau=2$ -10 ms for your measurements.

Take multiple measurements using a multiple pulse sequence with the Meiboom-Gill switch turned on. Determine T_2 by fitting all your measurements and taking the mean of your different Fit-parameters.

4.5 Study of fluorine

The last sample we want to study in this experiment is fluorine. The difference between the fluorine probe and the two samples that we used in the measurements before is, that we now analyse fluorine nuclei instead of protons. Because of this, we need to adjust the resonance frequency before we start to take any measurements with the fluorine sample. To adjust the resonance frequency, you have to turn the „Band “switch on the receiver part of the mainframe from p to f. You can then again use the pickup coil to adjust the RF field to the maximum amplitude. Remember that you have to change the time scale of the oscilloscope when you switch between the sample and the pickup coil to see the different signals.

After you adjusted the resonance frequency, you can now start with the measurements for the fluorine sample. You first need to determine the durations of the 90° - and the 180° - pulses for the fluorine sample.

Adjust the resonance frequency of the spectrometer for the fluorine sample. Determine the durations of the 90° - and the 180° - pulses.

Similar to the other two samples, we also start with the FID signal for the fluorine sample. However, because we are now using fluorine nuclei instead of protons, the FID signal of the sample should look different compared to the first two measurements.

The different signals can be explained by considering, that there are different „kinds“ of fluorine nuclei in the sample. This does not mean, that there are different fluorine isotopes in the sample. There are only F^{19} nuclei in the sample. But the fluorine nuclei in this complex liquid may be located at different parts of the molecule with different local surroundings. These different local surroundings create different local magnetic fields. Because it is the total field at the nucleus that determines the precession frequency, different nuclear sites create different precession frequencies. This is called „Chemical Shift“. By using fast Fourier transformation (FFT) chemical shifts can be used to analyse how many different fluorine sites are in the sample.

Create a 90° -pulse to get the FID signal of the sample. Plot the FID signal and use a Fit-function to determine T_2^* .

To analyse the fluorine nuclei, we want to measure the spin-lattice relaxation time. Use different period times P to determine T_1 of the fluorine sample, similar to the measurement of T_1 of the mineral oil sample.

Measure the amplitude of the spectrometer's signal for different period times P. Determine T_1 by plotting your data and using an exponential fit.

Compare the spin-lattice relaxation times of the protons and the fluorine sample you have determined.

To determine how many fluorine sites are in the sample, we will look at the FFT of the FID signal. The spectrometer's frequency has to be off resonance when you create the FFT of the FID signal. Like shown in figure 16, the FFT of the signal should give you distinct peaks. Each peak is indicating a different fluorine site. To create the FFT of the signal, you have to tune the spectrometer's frequency off resonance. You then have to push the „Acquire “button (this is found in the „Waveform “section on the oscilloscope) and select „averaging“. Go to the „Math “section of the oscilloscope and select „FFT“. This should give you the FFT of the FID signal.

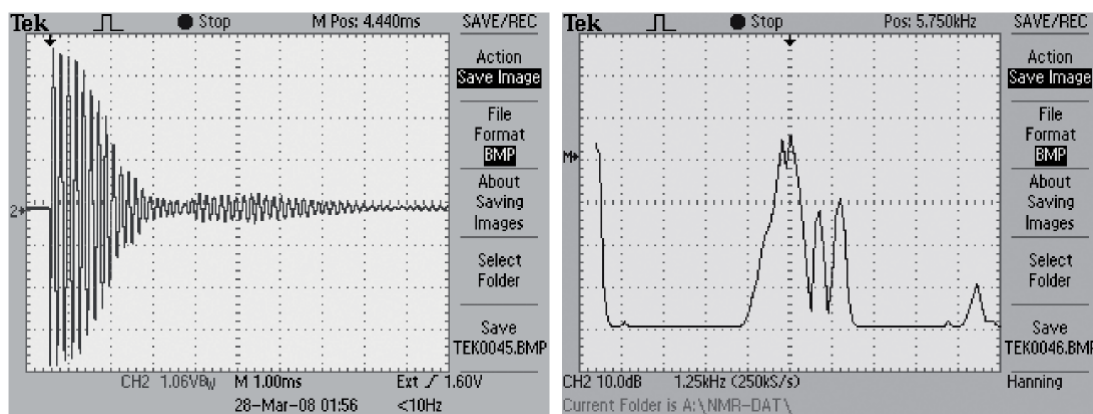


Figure 16: FID of the fluorine sample with the spectrometer's frequency off resonance (left) und FFT of the TID signal (right)

Tune the spectrometer's frequency off resonance. Create the FID signal with the spectrometer's frequency tuned off resonance. Create the FFT of the FID signal and analyse how many fluorine sites are inside your sample.

4.6 Problem solving

It might happen, that you do not get an optimal signal right away even if you set the right settings because something else, that is harder to notice has gone wrong. Because of that, here are some helpful ideas what you can check to find any mistakes you might have not seen in the first place:

The first potential problem is that the correct volume of sample is used for all experiments. Too much sample leads to a big error. This can be explained, when we look at the uniformity of the magnetic field of the RF coil. The coil itself is about 12mm long, but only about half of its length produces a magnetic field that has sufficient uniformity. Therefore the height of the volume of sample should only be about 5 mm, which then should be placed in the middle of the RF coil. To ensure that the sample sits in the middle of the magnetic field, the stop-ring that holds the sample, has to be located 39 mm above the centre of the sample volume. This ring might have changed its position, so if you do not get the right signal, try to check if the ring that locates the sample in the middle of the RF coil still is at the right position. Figure 17 shows the correct volume and placement of the sample.

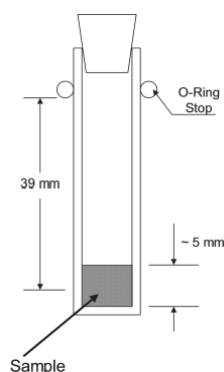


Figure 17: Sample volume and placement

An other common mistake is, to set all the settings for the mainframe, but to forget to check if the settings of the oscilloscope are also correct. The time scale you have to use changes a few times during the experiments. Some things have to be observed with a time scale of micro-seconds, others with a time scale of milli-seconds. If the signal on your oscilloscopes screen does not look like you expected, maybe the settings of the oscilloscope have to be changed.

It is also possible, that you created the correct signal, but you can not see it because it is outside of the oscilloscopes screen. If you do not get a visible signal, you can try to zoom out or change the offset of the x-axis,

to see if the signal you created is outside of the oscilloscopes screen.

But even if you think you got all the settings right, there are some settings that are easily overlooked. The most common settings that are overlooked when experimenting with the spectrometer are the „**Band**“ switch and the number of repetitions **N**. The Band-switch has two positions. It can be set to one for the proton samples and one for the fluorine samples. Because the experiments start with the proton samples, the switch has to be set to p for the first measurements. The last measurements with fluorine require you to set the switch to f (previous groups might have left the switch on f). Checking if the band switch is set correctly might solve problems you have with your signal, if the switch was in the wrong position previously. An other easily overlooked mistake is to leave the number of pulse repetitions **N** on zero. When the experiment requires you to set multiple pulses, it is possible that you only set the length of the A and the B pulse and then think that you are finished. But without also setting **N** correctly the multi pulse sequence will not work.

The last classic mistake, that may sound simple, but can save you a lot of time when you check for this early when your signal does not appear, is to look if all the cables are plugged in correctly. There are a lot of cables to connect the mainframe, the magnet, the controller and the oscilloscope and some of them need to be switched during the experiments. If for example you did not connected your spectrometer with the output of the oscilloscope after you connected it with the pickup coil, there can not be a signal on your oscilloscopes screen. So especially if you get no signal, check is every cable is plugged in to the correct location.

5 Laboratory check-list

For a better overview of your tasks during the experiment, you should print out, or otherwise bring, the following table to the experiment:

Task		Done ?
Set up		
1.	Tune the spectrometers frequency on resonance	
First Measurements		
2.	Create a 90° - and a 180° -pulse	
3.	Examine the setting of the magnetic field	
4.	Determine if the spectrometer is on resonance	
5.	Calculate the magnetic field	
6.	Observe the signal of the resonance frequency	
7.	Change the gain of the spectrometer	
8.	Use different filter TC-values	
9.	Tune the spectrometers frequency off resonance	
10.	Create an echo using two pulses	
Mineral Oil sample		
11.	Determine the durations of the 90° - and 180° -pulses	
12.	Create the FID signal and determine T_2^*	
13.	Determine T_1 by varying P	
14.	Determine T_1 by varying τ	
15.	Determine T_2 using the Hahn echo method	
16.	Determine T_2 using the Carr-Purcell method	
17.	Determine T_2 using the Meiboom-Gill method	
DIW sample		
18.	Determine the durations of the 90° - and 180° -pulses	
19.	Create the FID signal and determine T_2^*	
20.	Determine T_2 using using multiple Meiboom-Gill measurements	
Fluorine sample		
21.	Adjust the resonance frequency for fluorine	
22.	Create the FID signal and determine T_2^*	
23.	Determine T_1 by varying P	
24.	Create the FFT signal of the fluorine sample	

When you have completed all these tasks you have finished the laboratory and you can start to write your report. Here are a few important things to remember when writing the report:

Everything you have done, should be presented in your report.

If your data does not result in the expected results, try to analyse what may have gone wrong, or why your data could not proof the expected results.

Name every plot and every table you create. Your plots and tables should be integrated into your text.

Do not forget to name your axis for every plot you create.

When you do not know how to analyse your data, look at the hints in the instruction and look at the different equations in the theory part in the beginning of this instruction.

Include your names, student ID's and email-addresses in your report.