

Nuclear magnetic resonance in water, polystyrene, glycerine and Teflon (NMR spectroscopy)

Aims of the experiment

- To understand the basic principles of nuclear magnetic resonance spectroscopy
- To detect protons in various materials
- To learn about the signal differences of hydrogen and fluorine
- To investigate samples from everyday life for NMR signals

Principles

Some atoms behave like small magnets. They, or more precisely their nuclei, possess a magnetic moment. Such atomic nuclei can begin to resonate in an external magnetic field. This is referred to as nuclear magnetic resonance, or NMR. Nuclear magnetic resonance finds use particularly in chemistry and medicine.

In chemistry, the nuclear magnetic resonance of the atoms of a molecule is used to clarify structures (NMR spectroscopy). It provides information about the environment of atomic nuclei and therefore about the spatial configuration of atoms in a molecule. There is scarcely another method that can investigate the binding relationships in a molecule so directly. So the discovery of nuclear magnetic resonance by Block and Purcell in 1945 was a piece of good fortune for chemists.

Nuclear magnetic resonance is based in a magnetic property of atomic nuclei, their spin. Only atomic nuclei which have a spin quantum number (I) different from 0, possess a magnetic moment. Here we are dealing with nuclei with an uneven number of nucleons (protons and neutrons). Examples are hydrogen ($^1\text{H-NMR}$, 1 proton) and fluorine atoms ($^{19}\text{F-NMR}$, 9 protons, 10 neutrons). If an atomic nucleus of a (natural)

isotope is present which has an uneven number of nucleons, then it is still possible to measure signals with sensitive NMR equipment. Examples for this are $^{13}\text{C-NMR}$ and $^{15}\text{N-NMR}$.

The spin quantum number I of the nuclei quoted is $\frac{1}{2}$. Their magnetic momentum can, therefore, only take the two values $+\mu$ and $-\mu$, $+\frac{1}{2}$ and $-\frac{1}{2}$. Without an external magnetic field, the spin of the nuclei is distributed randomly. However, if a magnetic field B_0 is applied, then the nuclear moments can align themselves either parallel ($I = +\frac{1}{2}$) or antiparallel ($I = -\frac{1}{2}$) to the magnetic field.

The two orientations have a different energy. This can be made available to the nuclei with the help of an alternating electromagnetic field. In this alternating field, the atomic nuclei only change over from the low to the high energy level if the energy E (or the frequency f) of the field fulfils the following condition:

$$\Delta E = E_2 - E_1 = h \cdot f = \frac{\gamma}{2\pi} \cdot B_0$$

In this case, γ is the gyromagnetic constant, also known as the g-factor, a nuclear parameter which adopts a characteristic value for each type of atom. h is Planck's constant. The resulting NMR signal is proportional to the number N of spins



Fig. 1: Set-up of the experiment with power supply unit (DC power supply) for the electromagnets (on the left), NMR apparatus (in the middle) and NMR operating unit (on the right).

in the sample.

In this experiment, the principle of NMR spectroscopy will be explained. The NMR apparatus consists of the probe which sits on an electromagnet. This creates a homogeneous magnetic field (main magnetic field). Arranged vertically to this, an induction coil placed around the sample generates a field alternating at a high frequency. Now, either the strength of the magnetic field or the frequency of the alternating field can be varied until resonance occurs with the sample. When resonance occurs, the sample absorbs energy. Therefore, an additional amount of energy is necessary to maintain the alternating field. This signal, the NMR signal, is measurable with an oscilloscope, for example. This version of NMR spectroscopy is referred to as the *continuous wave (CW)* method.

Risk assessment

The NMR supply unit conforms with the safety regulations for electrical measuring, control and laboratory equipment according to DIN EN 61010 Section 1 and is constructed according to protection class I. It is designed for use in dry rooms which are suitable for electrical equipment or appliances.

Observe the instructions for use!

The chemicals used (water, glycerine, PTFE and polystyrene) are harmless.

Equipment

1 NMR supply unit.....	514 602
1 NMR probe.....	514 606
1 U-core with yoke	562 11
2 Coil 480 turns, 10 A	562 131
1 DC power supply 0...16 V/0...5 A.....	521 546
1 Two-channel oscilloscope	575 213
1 Safety connection lead 50 cm, red.....	500 621
1 Safety connection lead 100 cm, red.....	500 641
1 Safety connection lead 100 cm, blue	500 642

The following equipment is recommended for recording spectra:

2 Screened cable, BNC/4 mm	575 24
2 T-piece, BNC	501 091
1 Sensor-CASSY 2	524 013
1 CASSY Lab 2	524 220
PC with Windows XP/Vista/7/8	

Set-up and preparation of the experiment

Mechanical set-up of the NMR apparatus

The required equipment is shown in Figure 1 and the components of the NMR apparatus in Figure 2.

1. Mount both 10 A coils onto the U-core. These provide the electromagnets.
2. In order to construct the NMR probe, push the small modulation coils from both sides over the pole shoes up to the measuring chamber (max. gap between the coils: 35 mm, align in parallel).
3. Place the NMR probe (with the sample opening pointing upwards) evenly onto the U-core and fix it in place with fixing clamps (not too tightly).

Electrical set-up

The electrical set-up with the cable runs is shown in Figure 3.

1. Connect the 10 A coils in series to the DC power supply.
2. Connect the modulation coils in series to the MODULATION COILS output of the NMR supply unit.

3. Connect the NMR probe to the PROBE input. Do not lengthen the short BNC cable.
4. Connect the NMR SIGNAL output to the vertical deflection channel (Y) and the ΔB SIGNAL output to the horizontal deflection channel (X) of the oscilloscope.

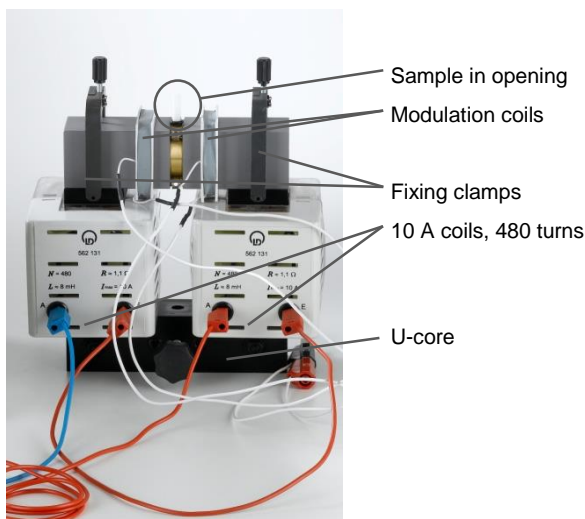


Fig. 2: Construction of the NMR apparatus and parts of the NMR probe.

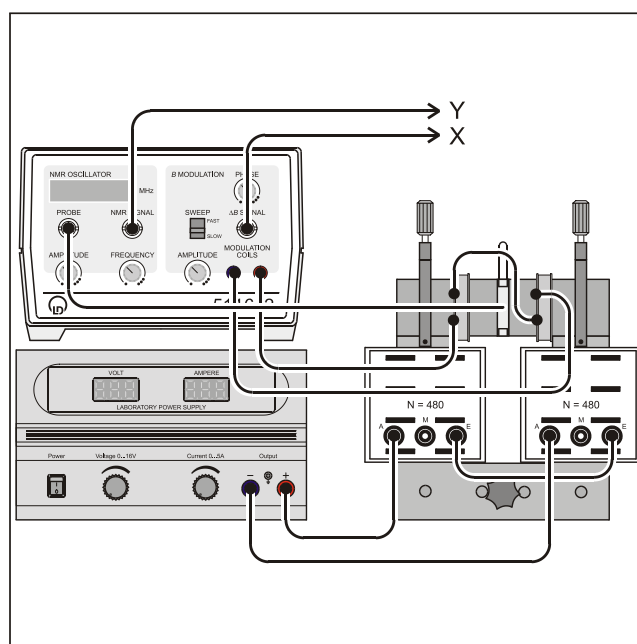


Fig. 3: Electrical set-up of the NMR apparatus (schematic diagram).

Recording of a proton NMR using the example of glycerine

Note: Glycerine ($C_3O_3H_8$) is particularly suitable for setting up the NMR equipment. It provides a strong NMR signal, as it contains 8 protons per molecule and the sample is liquid.

1. Prepare a sample tube with glycerine. Move the O-ring of the sample tube so that the sample is immersed roughly up to the centre of the measuring chamber.
2. Connect the oscilloscope according to the drawing (Fig. 3) and operate it in X-Y mode.
3. On the NMR supply unit, set the HF amplitude to minimum and the frequency and modulation amplitude to maximum. Choose FAST SWEEP and switch on the NMR supply unit.

- Increase the HF amplitude as slowly as possible until the LED lights up.
- Set a frequency of around 18.5 MHz.

Note: With some frequencies or magnetic fields, spontaneous oscillation occurs in this frequency range through the presence of many electrical appliances. This is not the NMR signal.

- Carefully place the prepared sample tube vertically into the measuring chamber.

Caution: If the sample tube is inserted at an angle, the probe coil can be damaged.

- On the DC power supply, slowly increase the magnet current through both 10 A coils until an NMR signal appears in the oscilloscope.

Note: On increasing the magnet current, the NMR signal appears as a brief deflection. Alternatively, with the defined current strength of around 3 A, the frequency on the NMR unit can be slowly reduced.

- Vary the HF amplitude slowly and optimise the NMR signal.

- Shift the NMR signal to the centre of the oscilloscope screen by varying the magnet current or the frequency and reduce the modulation amplitude at the same time. Adjust the phase of the modulation voltage so that the NMR signals for both half-waves of the modulated magnetic field coincide.

Note: The NMR signal can drift away in some cases. If this happens, regulate again if necessary.

Recording the NMRs on CASSY

- A Sensor-CASSY can be connected to record the signals.
- To do this, connect the NMR SIGNAL output to input A, and the ΔB SIGNAL output to input B of the Sensor-CASSY using screened BNC leads.
- [Load CASSY Lab settings.](#)
- For viewing in X-Y mode, choose "XY" display.
- Change to two-channel view. As well as the external magnetic field, the signal of the modulation coils is also now visible here.

Note: CASSY Lab can simulate an oscilloscope. However, the image refresh rate is very low. Once an NMR signal has been set on the oscilloscope, the evaluation in CASSY Lab can be performed by swapping the leads or using T-pieces.

Proton NMR of other samples (solid and liquid)

Other substances are available for investigation.

- Fill the empty sample tube with water, for example.
- Insert the water and polystyrene samples one after the other into the NMR unit which has previously been optimised for glycerine. Re-adjust slightly if necessary.

In addition, NMR signals can be investigated in everyday products, e.g. hand cream. Hand cream contains glycerine and water, which are detected in this way.

- Cut off around 5 cm from a straw. Fill this sample vessel with around 1 cm high of hand cream.
- Clean the straw well on the outside, so the NMR unit stays clean.
- Push an O-ring over the straw to align the sample in the middle of the measuring chamber.
- Insert the sample into the NMR unit which has previously been optimised for glycerine. Re-adjust slightly if necessary.
- Also fruit (e.g. apple) or flowers can be investigated in the same way. These always contain water which provides the NMR signal.

Fluorine NMR of PTFE

^{19}F fluorine nuclei can also be stimulated and investigated with the NMR apparatus. For this purpose, PTFE (polytetrafluoroethylene, Teflon) is used as a sample. PTFE does not contain protons, but fluorine atoms.

- Insert PTFE into the NMR apparatus that has been optimised for protons. No signal appears.
- Reduce the HF frequency or increase the magnetic field until a signal appears again. This is the signal of the fluorine nuclei.

Result of the experiment (example)

Proton NMR of glycerine

The NMR signal of glycerine in X-Y mode is shown in Figure 4. Following the deflection, there is an oscillation back to the baseline. These oscillations occur due to the changed magnetic field. They are dependent, amongst other things, on the surroundings of the protons. MRI techniques (medicine) are based on this effect.

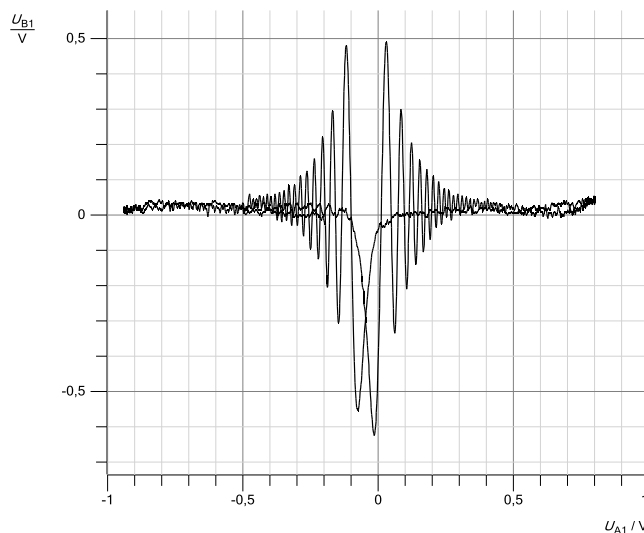


Fig. 4: NMR signal of glycerine. $f = 17.78$ MHz, $I = 3.19$ A, X-Y representation.

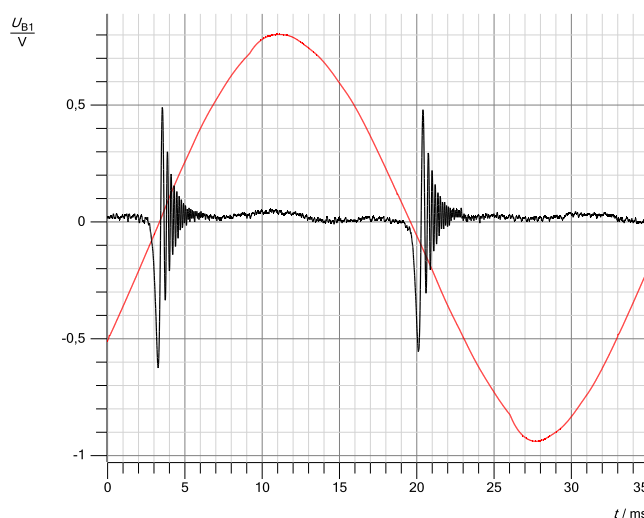


Fig. 5: NMR signal of glycerine, $f = 17.78$ MHz, $I = 3.19$ A, two-channel representation. Red: alternating magnetic field. Black: NMR signal.

It can be seen in the two-channel mode (Fig. 5) that the appearance of the signal coincides with a defined magnetic field (in the form of sinus oscillation). If the external magnetic field corresponds exactly to the resonance frequency, this stimulates the protons in the glycerine.

Proton NMR of water and polystyrene

Protons are also stimulated by the NMR signals of water and polystyrene. The NMR of water is shown in Fig. 6, the NMR of polystyrene in Fig. 7. The position and the shape of the signals correspond more or less to those of glycerine. However, the signal appears distinctly weaker owing to the smaller quantity of protons, or of the solid sample.

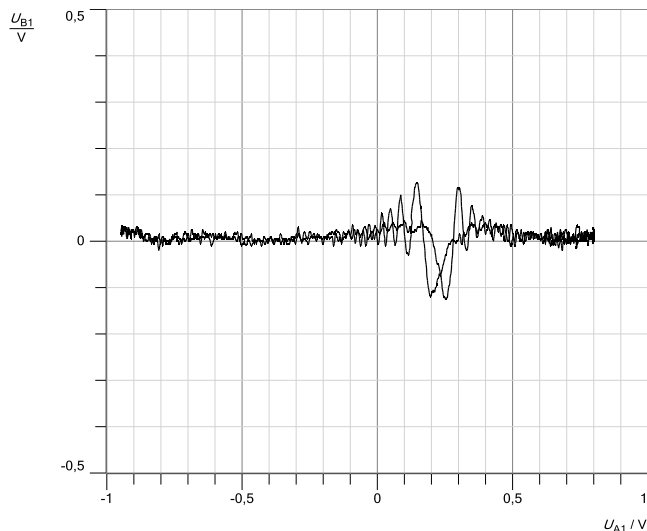


Fig. 6: NMR signal of water. $f = 17.77$ MHz, $I = 3.19$ A, X-Y representation.

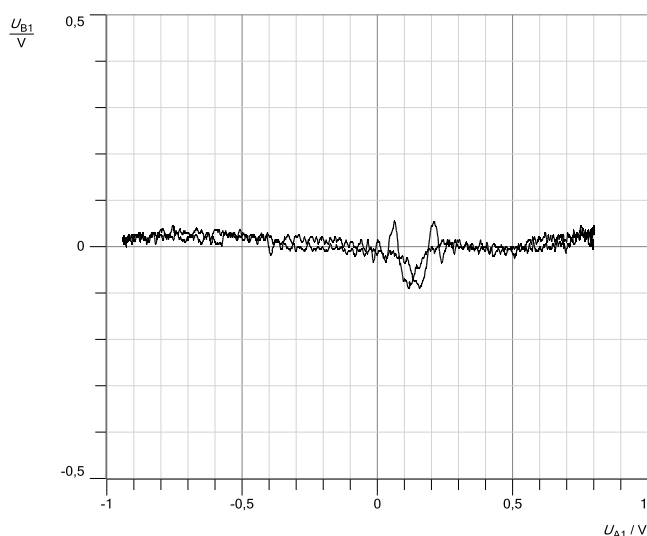


Fig. 7: NMR signal of polystyrene. $f = 17.76$ MHz, $I = 3.19$ A, X-Y representation.

Fluorine NMR of PTFE (Teflon)

The NMR signal of PTFE does not appear using the values for the proton NMR. A larger magnetic field is necessary at the same frequency (see Fig. 8). The reason for this is the changed gyromagnetic constant which depends on the type of atom.

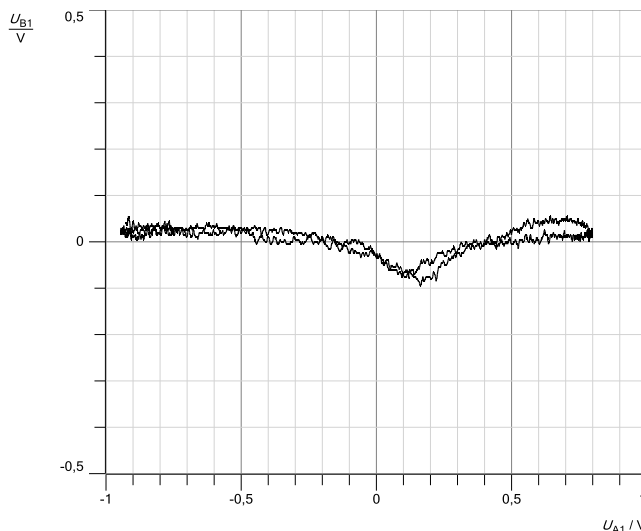


Fig. 8: NMR signal of PTFE. $f = 17.78$ MHz, $I = 3.44$ A, X-Y representation.

Remarks

The spin of a proton, for example, can adopt one of two orientations in the magnetic field. The number in a certain orientation (and therefore the energy level occupancy) depends on, amongst other things, the strength of the internal magnetic field (proportional to the gyromagnetic ratio $= 2\pi g\mu/h$) and of the external magnetic field B_0 .

In this application, a large number of nuclei are present in the sample. The difference in occupancy between the low and high energy levels with a magnetic field of $B_0 = 1$ T is, however, only around 10^{-6} ! Despite this small surplus of nuclei at the low energy level, a signal can still be detected.

In order to increase the resolution, modern NMR units use very much higher magnetic fields B_0 and, therefore, also higher frequencies (cf. the condition for resonance). This then enables the evaluation of the various resonance lines in a sample. These occur because the electron density also has an influence on the local magnetic field (shielding effect). This effect is referred to as chemical shift. In addition, each atomic nucleus creates a magnetic field itself. This is referred to as spin-spin coupling.

Further experiments

With the set-up shown here, the gyromagnetic constant or the g-factor for protons and fluorine atoms can also be determined. Measurement of the external magnetic field is necessary for this.

In such an experiment, the magnetic field is varied and the associated resonance frequency is noted. From the slope of the resulting straight line, the g-factor can be calculated. This is carried out in experiment P6.5.3.1.