

Nuclear magnetic resonance in polystyrene, glycerine and teflon

Objects

- Nuclear Magnetic Resonance on protons and fluorine in liquids and solid samples
- Determination of the line width of the fluorine resonance
- Determination the g-factor of protons and fluorine

Principles

Nuclear magnetic resonance (NMR) was discovered by Bloch and Purcell in 1945. NMR spectroscopy is nowadays an important standard method in chemistry and biology. In medical applications NMR has established under the name Magnetic Resonance Imaging (MRI) as an imaging method for clinical diagnosis supplementary to scanning techniques involving x-ray and ultra sound. This experiment demonstrates the basic phenomenon of NMR on liquid and solid samples and gives first insight into spectroscopic applications in chemistry and biology.

NMR is based on the magnetic properties of the nucleus. Atoms with a nucleus which possesses a nuclear spin I have a magnetic moment μ_n according the relation:

$$\mu = -g \cdot \mu_n \cdot I \quad (I)$$

μ_n : nuclear magneton

g : g-factor

The nuclear magnets μ can orientate only in distinct directions in respect to a static magnetic field B_0 . Each spin orientation corresponds to a particular energy level which is given by:

$$E_k = -g \cdot \mu_n \cdot B_0 \cdot k \quad \text{with } k = -I, -I+1, \dots, +I \quad (II)$$

When a sample is placed in a static magnetic field B_0 the nuclear spins are distributed over the energy levels according the Boltzmann-equation:

$$\frac{N_k}{N_{k+1}} = \exp\left(-\frac{E_{k+1} - E_k}{k_B T}\right) \quad (III)$$

k_B : Boltzmann constant

N_k : Number of spins in level k

The spins may be excited to jump between adjacent energy levels E_k when the sample is exposed to a magnetic field B_1 of high frequency ν which is perpendicular to the static field B_0 . Therefore the frequency ν have to match exactly the energy spacing. This is called resonance ($\Delta k = 1$):

$$h \cdot \nu = E_{k+1} - E_k = -g \cdot \mu_n \cdot B_0 \quad (IV)$$

h : Planck's constant

In this experiment the NMR signals of Hydrogen nuclei (protons) and fluorine nuclei are observed. Both nuclei have a spin of $I = \frac{1}{2}$. and thus according to equation (II) they have only two possible orientations in respect to the magnetic field B_0 (Fig. 1). In order to detect the spin transitions between these two energy levels the sample is placed in an rf coil which is located between the gap of a homogeneous field B_0 . Additionally, the static magnetic field B_0 is modulated at constant frequency ν by the use two modulation coils. Thus in this setup the resonance signal is observed in dependence of the magnetic field. Each time when the resonance condition (i. e. equation IV) is fulfilled energy is absorbed from the rf coil due to the spin transitions. The NMR signal is proportional to the number of spins N in the sample.

For example, an hydrogen nucleus the resonance frequency in a magnetic field is about 42.5 MHz. The precise value depends on the chemical environment of the hydrogen atom as in addition to the external magnetic field B_0 the local internal field of electrons and nuclei in the near vicinity also acts on the hydrogen nucleus. This is called chemical shift and makes NMR to an important spectroscopic method for chemistry and biology.

The line width of the NMR resonance line is influenced by the nature of the surrounding elements and on the temperature. The analysis of line width as function of these factors yields comprehensive information about chemical and physical characteristics of the various sample components. The full width of half maximum (Fig. 1) is under some circumstances a measure for the relaxation time T_2 :

$$\Delta B \sim \Delta \nu \sim \frac{1}{T_2} \quad (V)$$

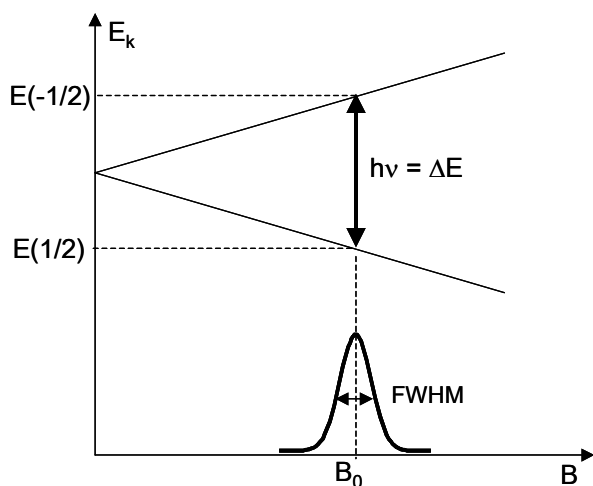


Fig. 1: Energy splitting of a nucleus of $I = \frac{1}{2}$ in the magnetic field B_0 . One line is observed in the NMR spectrum from which the full width at half maximum (FWHM) can be determined.

Setup

- Mount the two coils on the U-core.
- Slide the modulation coils onto the pole shoes and mount the NMR-probe evenly on the U-core.
- Connect the two coils in series with the DC power supply according Fig. 2.
- Connect the modulation coils in series with the "MODULATION" output of the NMR supply unit.
- Connect the NMR-probe to the input "PROBE" of the NMR supply unit.
- Connect the output "NMR SIGNAL" to the channel of vertical deflection and the output "ΔB SIGNAL" to the channel of horizontal deflection of the oscilloscope.

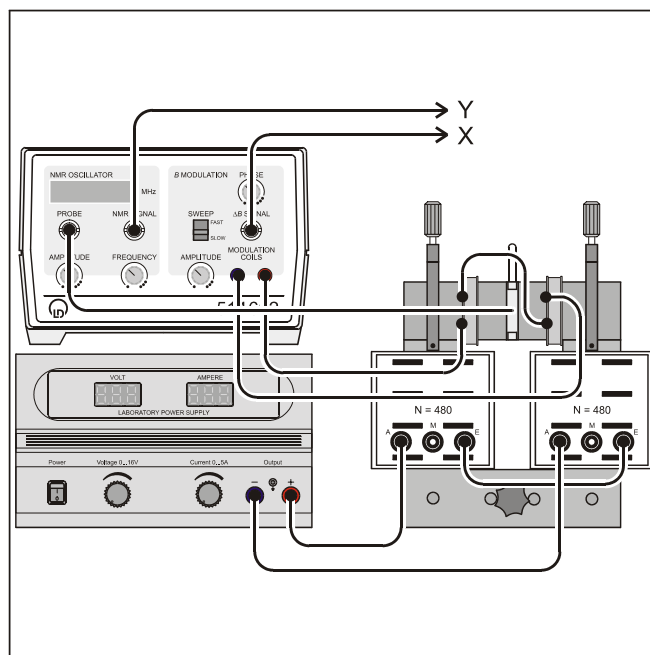


Fig. 2: Electrical setup of the NMR experiment, schematically.

Apparatus

1 NMR-probe unit.....	514 606
1 NMR-supply unit.....	514 602
1 U-core with yoke	562 11
2 Coils, 10 A, 480 turns.....	562 131
1 DC-power supply 0...16 V, 0...5 A.....	521 545
1 Analog Oscilloscope HM 303	575211
2 BNC cables, 1m	501 02
or	
1 Sensor CASSY USB	524010USB
1 CASSY Lab	524 200
2 Screen cables BNC/4mm.....	575 24
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

additionally recommended:

1 Universal Measuring Instrument Physics	531 835
1 Combi B-Sensor S	5240381
1 Extension Cable, 15-pole	501 11

Carrying out the experiment

a) NMR on liquid and solid samples with protons

- Set the oscilloscope to xy-mode
- Select fast sweep and set the modulation amplitude to a large value
- Set the value of the frequency to a maximum value.
- Slowly enhance the HF amplitude until the red LED lights up and a frequency of about 19 MHz is displayed.
- Reduce the frequency to a value of about 18.5 MHz.
- Shift the O-ring of the glycerine sample tube (8 protons) so that the sample will be located approximately in the center of the measuring chamber.
- Carefully insert the sample tube into the measuring chamber.
Remark: if the sample tube is inserted at an angle with too much force the rf coil can be damaged.
- Slowly increase the current through the 10 A coils until an NMR signal appears on the oscilloscope of the screen.

- Optimize the NMR signal by slowly varying the HF amplitude.
- Shift the NMR signal to the center of oscilloscope screen by varying the magnet current or the frequency and adjust the modulation amplitude.
- Adjust the phase of the signal until the signal of up and down sweep coincide.

Remark: If you want to record the signals connect the apparatus to the Sensor CASSY.

- Repeat the experiment for a water sample, the polystyrene sample and the polytetrafluorethylene sample.

b) NMR of solid a sample with fluorine nuclei

- Repeat the experiment of part a) for the polytetrafluorethylene sample (PTFE).
- Determine first how much a unit (e. g. from a major tick of the x-axis to the other) on the oscilloscope screen of the horizontal deflection is in frequency units. This can be achieved by shifting the peak of NMR signal with the frequency button to a scale mark (e. g. tick of the x-axis) and note the frequency. Then shift the signal to the next scale mark and note again the frequency.
- Measure the line width at half maximum (FWHM) of the resonance line in units of the oscilloscope screen.

c) Application in Chemistry (NMR Spectroscopy)

As an introduction to the application of NMR in chemistry the NMR signal of e. g. hand cream can be investigated. Hand cream naturally contains a lot of glycerine and depending on the type of hand cream also water.

The spins of the hydrogen nuclei of the glycerine molecule can be detected by first optimizing the NMR apparatus with the glycerine sample according experiment part a) and then be compared with the signal of the hand cream.

- Prepare a piece of a straw of about 50 mm of length an fill it with hand cream (filling height approximately 10 mm to 15 mm).
- Clean the straw thoroughly, in particular, make sure that no hand cream is at the lower end of the straw to avoid pollution of the measuring chamber.
- Shift an O-ring over the straw so that the sample will be located approximately in the center of the measuring chamber.
- now optimize the NMR apparatus for the glycerine sample according experiment part a).
- Carefully remove the glycerine sample from the measuring chamber and insert the straw with the hand cream sample carefully.
- If necessary tune the frequency and observe the signal. Depending on the amount of sample it may be necessary to tune the frequency, too.

d) Application in Biology (Spectroscopy)

As an introduction to the application of NMR in biology the NMR signal of e. g. an apple or plant can be investigated. Fruits like apples, green pepper etc. naturally contain water. The same holds for plants as for example flowers.

The spins of the hydrogen nuclei of the water molecule can be detected by first optimizing the NMR apparatus with the water sample according experiment part a) and then be compared with the signal of an apple or a plant.

- Prepare a piece of a straw of about 50 mm of length an fill it with the fruit flesh of an apple (filling height approximately 10 mm to 15 mm).
- Clean the straw thoroughly, in particular, make sure that no apple pieces are at the lower end of the straw to avoid pollution of the measuring chamber.
- Shift an O-ring over the straw so that the sample will be located approximately in the center of the measuring chamber.
- now optimize the NMR apparatus for the water sample according experiment part a).
- Carefully remove the water sample from the measuring chamber and insert the straw with the apple sample carefully.
- If necessary tune the frequency and observe the signal. Depending on the amount of sample it may be necessary to tune the frequency, too.
- Similarly, the NMR signal of protons in the stem of plants can be observed. Note, the stem should have a medium diameter.

e) Determination of the g-factor (Teslameter required)

- Tune the NMR apparatus according to experiment part a) for the glycerine sample at about 18 MHz and measure the frequency.
- Carefully remove the sample from the measuring chamber and measure the magnetic field with the Tangential B-Probe in the measuring chamber.
- Place the Tangential B-Probe according Fig. 3 at the pole shoes and measure the magnetic field.

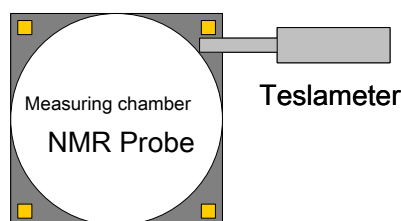


Fig. 3. Schematic depiction for placing the Tangential B-Probe between the pole shoes of the magnet.

- Tune the NMR apparatus for the water sample at lower and higher frequencies by varying the current through the 10 A coils and measure the frequency and the magnetic flux density.
- Repeat the experiment for the polytetrafluorethylene (PTFE) sample.

Measuring example

a) NMR on liquid and solid samples with protons

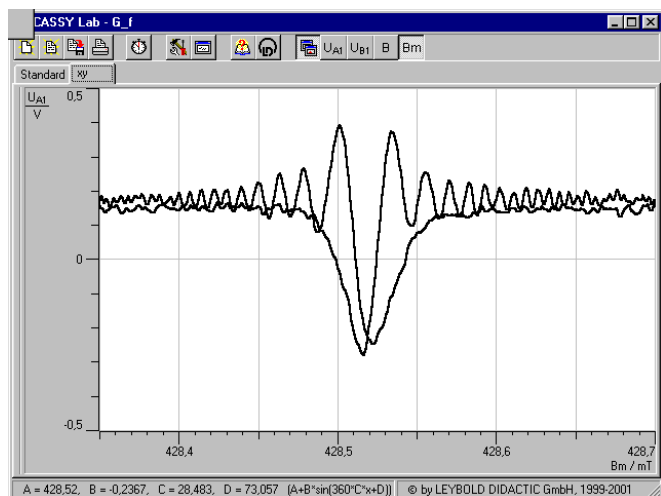


Fig 4 Glycerine, $\nu = 18.25$ MHz, $I = 3.6$ A, XY-display.

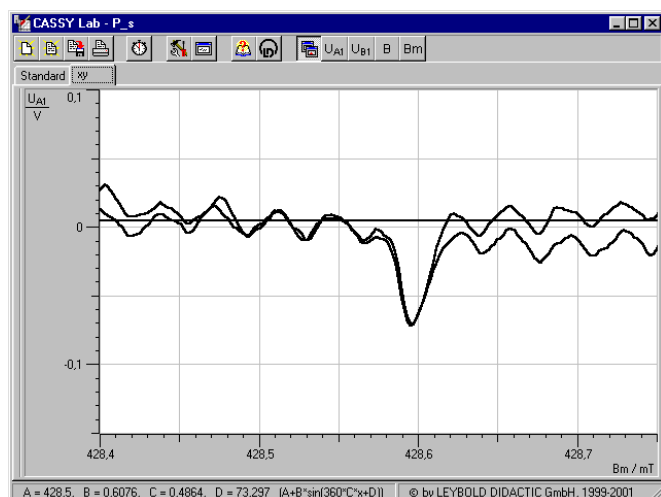


Fig 5: Polystyrene, $\nu = 18.25$ MHz, $I = 3.6$ A, XY-display.

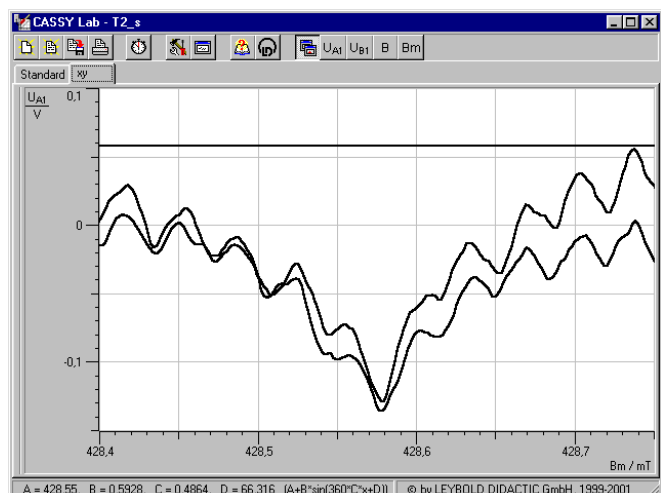


Fig 6: Polytetrafluorethylene, $\nu = 17.17$ MHz, $I = 3.6$ A, XY-display.

b) NMR of solid a sample with fluorine nuclei

oscilloscope unit Δ in frequency units:

$$\Delta = \nu_1 - \nu_2 = 18.2921 \text{ MHz} - 18.2763 \text{ MHz} = 7.9 \text{ kHz}$$

which gives a FWHM in frequency units: $\Delta\nu = 6 \text{ kHz}$

c) Application in Chemistry (NMR Spectroscopy)

The shape and the position of the signal is approximately the same as for the glycerine sample shown in Fig. 4. The intensity depends on the amount of the hydrogen nuclei in the investigated sample.

d) Application in Biology (Spectroscopy)

The shape and the position of the signal is approximately the same as for the water sample. The intensity depends on the amount of the hydrogen nuclei in the investigated sample.

e) Determination of the g-factor (Teslameter required)

Table 1: Resonance frequency ν and magnetic flux B_0 for the glycerine sample. The values of the flux density have been corrected by according the value in the measuring chamber.

$\frac{B_0}{\text{mT}}$	$\frac{\nu}{\text{MHz}}$
358	16.01
369	16.50
384	17.02
396	17.51
409	18.01
420	18.50
433	19,01
442	19.47

Table 2: Resonance frequency ν and magnetic flux B_0 for the polytetrafluorethylene sample. The values of the flux density have been corrected by according the value in the measuring chamber.

$\frac{B_0}{\text{mT}}$	$\frac{\nu}{\text{MHz}}$
372	16.00
386	16.50
396	17.01
409	17.50
422	18.01
434	19.01
445	19.00
459	19.48

Evaluation and results

a) NMR on liquid and solid samples with protons

If a sample contains hydrogen nuclei an NMR signal can be observed. The sample can be a liquid or a solid (powder) sample. However, due to the structure of the sample a significant difference in line width is observed for the NMR on Hydrogen nuclei, e. g. the glycerine sample (liquid) has a smaller line width compared to the polystyrene sample (solid).

b) NMR of solid a sample with fluorine nuclei

The line width at half maximum of the fluorine resonance line can be determined to

$$\Delta\nu \approx 6 \text{ KHz.}$$

The line width is mostly determined by the homogeneity of the magnetic field B_0 which is of the order of 3 kHz ($\approx 80 \mu\text{T}$).

c) Application in Chemistry (NMR Spectroscopy)

From the fact that the NMR signal for glycerine and hand cream appears at about the same resonance frequency and magnetic field proves that the NMR can be used to probe chemical elements. Advanced NMR spectroscopy uses this to determine number and type of chemical groups of molecules.

d) Application in Biology (Spectroscopy)

Depending on the freshness of the apple sample (many hydrogen nuclei) an intense signal can be observed. This shows that NMR can be applied also to in vitro samples. This fact allows modern NMR-techniques to obtain images from the body and has thus become an important diagnostic method supplementary to x-ray and ultra-sonics.

e) Determination of the g-factor (Teslameter required)

According the resonance condition (equation (IV)) the g-factor of glycerine and polytetrafluorethylene (PTFE)

$$g = \frac{h}{\mu_n} \cdot \frac{\nu}{B_0} \quad (\text{V})$$

$$\text{with } h = 6.626 \cdot 10^{-34} \text{ Js}$$

$$\mu_n = 5.051 \cdot 10^{-27} \frac{\text{J}}{\text{T}}$$

can be estimated by determining the slope ν/B_0 from the plot of the resonance frequency as function of the magnetic field (Fig. 7).

value for Hydrogen: $g_H = 5.8$

Literature: 5.5857

value for fluorine: $g_F = 5.6$

Literature: 5.2567

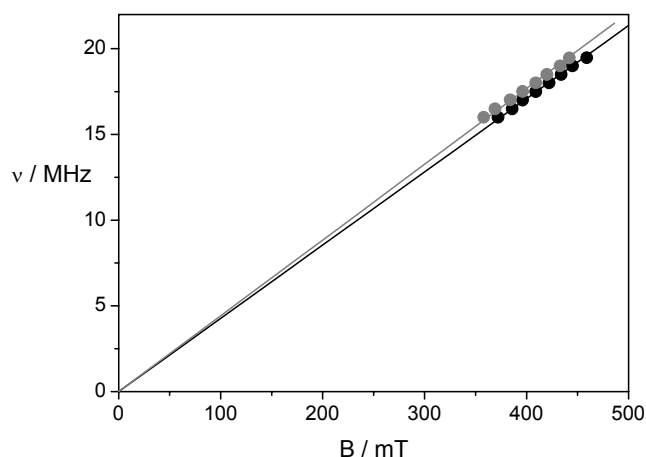


Fig. 7: Resonance frequency of glycerine (grey) and PTFE (black) as function of the magnetic field B_0 to determine the g-factor.

Supplementary information

The nuclear spin e. g. of a proton can be oriented in one of two ways in respect to the magnetic field. The extent to which one orientation (energy state) is favored over the other depends on the strength of the small nuclear magnet (proportional to gyromagnetic ratio = $2\pi \cdot g \cdot \mu_n / h$) and the strength of the magnetic field B_0 .

In practice, a rather huge number (approaching Avogadro's number) of nuclei are in the sample that is placed in a magnetic field. The distribution of nuclei in the different energy states (i.e. the orientation of nuclear spins) under conditions in which the nuclear spin system is unperturbed by application of any rf energy can be estimated by the use of Boltzmann equation (III). At room temperatures the difference between the lower and the upper level for protons (the population of the spin states) at $B_0 = 1 \text{ T}$ is only about 10^{-6} ! Without this small excess number of nuclei in the lower energy state, an NMR signal could not be detected.

For that reason modern applications of NMR spectroscopy use higher fields B_0 and according to the resonance condition (equation (IV)) higher frequencies. This allows to resolve the various resonance lines in the NMR spectrum which are due to various nuclei of a sample. Further the signal is measured in the time domain by sophisticated pulsed NMR techniques. The NMR-spectrum is obtained by (Fast-Fourier-Transformation (FFT)). Thus NMR spectroscopy has become an important tool in many areas (e. g. petroleum, cosmetics and pharmaceutical industries) for the determination of molecular structures and the analysis of the content of a sample (e. g. in quality control). For 3D-NMR imaging techniques as used in medical applications in addition to the pulsed NMR techniques a field gradient is necessary to distinguish the NMR signal of spins from different locations within the sample.

