

A52 Basics of NMR (The nuclear Zeeman effect)

Objective of the experiment

NMR spectroscopy is an important characterization method in chemistry. By means of a simple experimental setup the basic principles behind this measurement are to be understood.

The aim of this experiment is to measure the dependence of the nuclear resonance frequency on the applied magnetic field of a proton-containing sample and to determine the gyromagnetic ratio. Furthermore, the magnetic moment of the proton, the g-factor, the Zeemann splitting in the field as well as the occupation of the energy levels are to be calculated.

Basics

For the successful performance of the experiment knowledge of the theoretical principles of the Zeemann effect and of magnetic resonance is required. The following basics can only provide an overview and cannot replace a textbook.

Many elementary particles, including protons, electrons and neutrons, have their own angular momentum (spin). The spin of a nucleus is vectorially composed of the spins of the nuclear building blocks, the nucleons (proton and neutron), whereby in many cases a non-vanishing total nuclear spin results. The angular momentum is subject to the rules of quantum mechanics. For the absolute value of the angular momentum $|\vec{P}|$ the quantum condition predicts:

$$|\vec{P}| = \hbar \cdot \sqrt{I(I+1)} \quad (1)$$

At which $\hbar \cdot 2\pi = h = 6,626 \cdot 10^{-34}$ Js is the Planck constant and I is the nuclear spin quantum number. I can take integer or half-numbered values, for protons, i.e. the nuclei of hydrogen ^1H , I is $1/2$. The angular momentum $|\vec{P}|$ can be described as a vector which direction is parallel to the axis of rotation. Since atomic nuclei are electrically charged, the angular momentum generates a magnetic dipole moment $|\vec{\mu}|$ which is proportional to $|\vec{P}|$:

$$|\vec{\mu}| = \gamma \cdot |\vec{P}| \quad (2)$$

And therefore:

$$|\vec{\mu}| = \gamma \cdot \hbar \cdot \sqrt{I(I+1)} \quad (3)$$

γ is a constant characteristic for each core type and is called gyromagnetic ratio. The combination of equations 1 und 2 zu 3 shows that as a result of angular momentum quantization, the absolute value of the magnetic moment is also quantized. In analogy to the treatment of electron spin, the gyromagnetic ratio is often expressed by the nuclear magneton and the nuclear g factor:

$$\gamma \cdot \hbar = \mu_N \cdot g_I \quad (4)$$

With the nuclear magneton $\mu_N = \frac{e \cdot \hbar}{2m_P} = 5,051 \cdot 10^{-27} \frac{\text{J}}{\text{T}}$; e is the elementary charge and m_P the mass

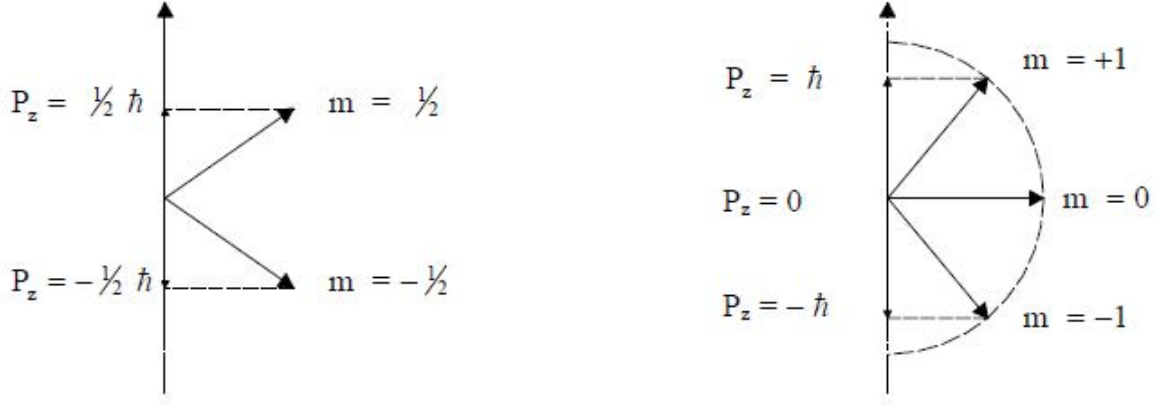


Fig. 1: Direction quantization of the z -component of the angular momentum for the two nuclear spin quantum numbers $I = 1/2$ und $I = 1$

of the proton. (T (Tesla) is the measure of the magnetic flux density in SI units, see also below).

If the core is brought into a static magnetic field with angular momentum $|\vec{P}|$ the direction of the magnetic field is a "preferred direction" and the angular momentum is oriented in such a way that its component in the direction of the field P_z is an integer or half-digit multiple of $\hbar$:

$$P_z = m \cdot \hbar \quad (5)$$

At which the magnetic quantum number m can take integer values from $-I$ up to $+I$, i.e. $2I + 1$ values ($m = -I, -I+1, \dots, I-1, I$). This behavior is called direction quantization. Fig.1 shows two examples of quantization of direction for $I = 1/2$ und $I = 1$. Thus, for the component of the magnetic dipole moment in the field direction, one obtains:

$$\mu_z = m \cdot \hbar \cdot \gamma \quad (6)$$

If the magnetic field is described by the magnetic flux density $|\vec{B}|$ with components $B_x = B_y$ and $B_z = B_0$ (unit $1 \text{ T} = 1 \text{ Tesla} = 1 \frac{\text{Vs}}{\text{m}^2}$), the magnetic dipole moment $|\vec{\mu}|$ is linked up with $|\vec{B}|$ via the cross product

$$|\vec{L}| = |\vec{\mu}| \times |\vec{B}| \quad (7)$$

causing, according to classical description, a torque $|\vec{L}|$ that tries to align the magnetic dipole moment in the field direction. In doing so, $|\vec{\mu}|$ tries to escape the perpendicular force acting on it according to the law of precession. This causes $|\vec{\mu}|$ to preceed around $|\vec{B}|$ with the so called Larmor frequency ω_0 (ω_0 in $\frac{\text{rad}}{\text{s}}$ ν , in $\frac{1}{\text{s}}$) (Fig. 2).

$$\omega_0 = 2\pi\nu_0 = \gamma \cdot B_0 \quad (8)$$

In contrast to the classical law of precession only certain angles between $|\vec{\mu}|$ and $|\vec{B}|$ are allowed (Fig.1). Furthermore, the energy of the magnetic dipole in the magnetic field is given by:

$$E = -\mu_z B_0 = -m\gamma\hbar B_0 \quad (9)$$

This results in $2I + 1$ energy states (Zeeman levels) for the nucleus in a magnetic field. The energy

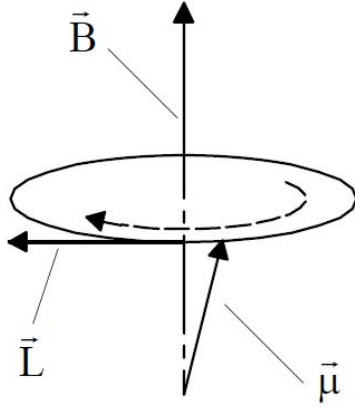


Fig. 2: Precession of the magneticmoment

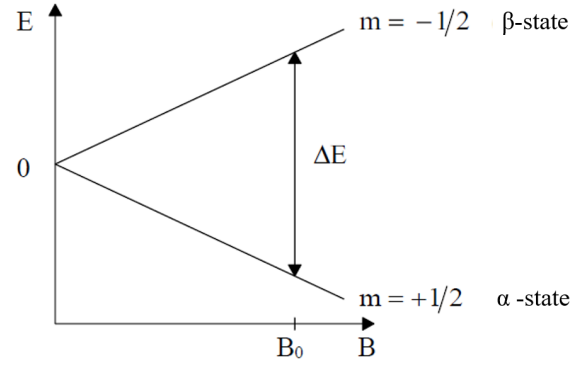


Fig. 3: Zeemann-splitting ΔE within the magnetic field B_0

difference between the levels is proportional to B_0 (Fig. 3). For the proton, two energy values E_α and E_β are obtained corresponding to $m = +1/2$ and $m = -1/2$:

$$\begin{aligned} E_\alpha &= E_{+\frac{1}{2}} = -\frac{1}{2}\gamma\hbar B_0 \\ E_\beta &= E_{-\frac{1}{2}} = \frac{1}{2}\gamma\hbar B_0 \end{aligned} \quad (10)$$

Wherein the α -state μ_z is parallel to the field direction (energetically most favorable arrangement) and for the state β its antiparallel (Fig. 3).

The splitting of the energy states and the associated resonance effects at transitions between the energy levels form the physical basis of NMR spectroscopy.

For N nuclei in the magnetic field the occupation of the states α and β is according to the Boltzmann-distribution:

$$\frac{N_\alpha}{N_\beta} = \exp\left(\frac{-\Delta E}{kT}\right) \approx 1 - \frac{\Delta E}{kT} = 1 - \frac{\gamma\hbar\Delta B_0}{kT} \quad (11)$$

$k = 1,3805 \cdot 10^{-23} \frac{\text{J}}{\text{K}}$ is the Boltzmann constant and T the temperatur in Kelvin. Because $\Delta E \ll kT$ the linear approximation in equation 11 is allowed. In the nuclear resonance experiment, transitions between the levels are excited by using a transmitting coil with the frequency:

$$\Delta E = \hbar\omega_0 = \gamma\hbar B_0 \quad (12)$$

According to the selection rules only transitions with $\Delta m = 1$ are allowed. The corresponding frequency is in the high-frequency range, i.e. compared to other spectroscopy types (e.g. UV, VIS or IR) at very low frequencies. NMR is a type of spectroscopy at very low energies with $\Delta E \ll kT$ and therefore often called radiofrequency spectroscopy.

After excitation the difference in occupation is eliminated. Without relaxation processes the system would be saturated and no more absorption would take place. Through different relaxation processes the system tries to get back into the initial state.

The principle of NMR spectroscopy is based on the fact that the effective magnetic field depends strongly on the chemical environment of the active nuclei. In NMR spectra, this difference is called

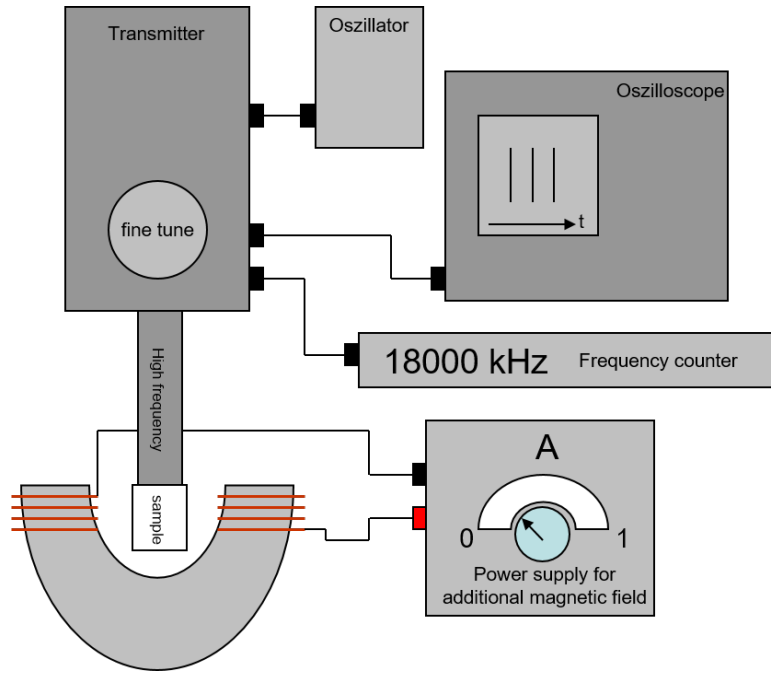


Fig. 4: Scheme of the experimental setup.

chemical shift δ :

$$\delta = \frac{\nu_{\text{pr}} - \nu_{\text{ref}}}{\nu_{\text{ref}}} \quad (13)$$

ν_{ref} und ν_{pr} are the Lamor frequencies of a reference substance and the sample. δ is usually give in ppm. In a molecule the given chemical environment causes for every NMR active nuclei a unique chemical shift and intensity. Hence, a molecule can be identified.

Experimental section

Measuring principles

In the special form of the nuclear resonance experiment used here (Fig. 4), electromagnetic waves in the radio frequency range are generated in an oscillator. The proton-containing sample (here glycerine) is located in the magnetic field inside a coil which is connected to the transmitter via a high-frequency bridge. The bridge is adjusted in such a way that no current flows. In case of resonance, energy is transferred from the coil to the sample. This changes the alternating-current resistance and the resonance can be detected.

For this purpose, the frequency of the high-frequency generator is brought close to the resonant frequency and is then modulated periodically $B(t) = B_m + \Delta B \sin(\omega_m t)$ around the mean value B_m . If, at a certain time T , $B(t)$ corresponds to $B_0 = \frac{2\pi\nu_0}{\gamma}$ (Equ. 8) a signal appears on the oscilloscope. Because of the periodical modulation a series of lines appears (Fig. 5). If the mean of B_m is the same as B_0 the lines are equidistant. Conversely, the frequency counter shows the exact resonance frequency.

Procedure

Turn every device on (5 switches). Before make sure, that the voltage and current of the power supply of the additional magnetic field are 0.

Set the frequency with the rotary switch “FINE TUNE” on the upper side of the oscillator to ca. 18000

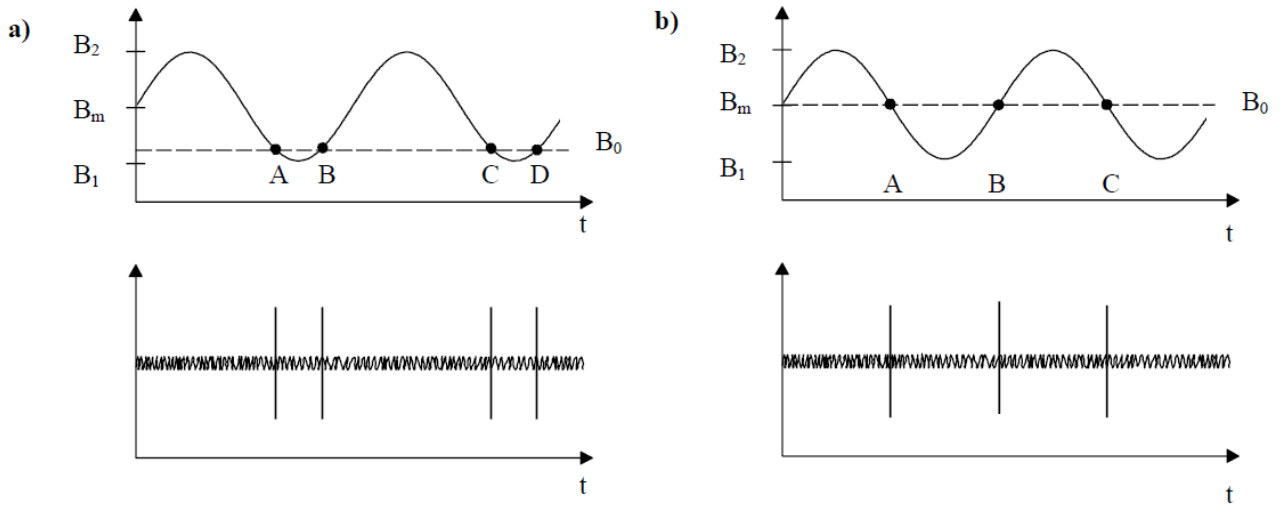


Fig. 5: A sinusoidal modulation varies the field around a mean value B_m between an upper limit B_1 and a lower limit B_2 . If the instantaneous value $B(t)$ just corresponds to the resonance field strength $B_0 = \frac{2\pi\nu_0}{\gamma}$, energy absorption occurs. This is the case for points A, B, C, D. so that the sketched figure in a) is seen on the oscilloscope. If B_0 coincides with B_m points A, B, C, D are equidistant, see b).

kHz (corresponds to 18 MHz). The absorption signal that appears first corresponds to that in Fig. 5a. Then carefully rotate the frequency until the distance between the peaks becomes equidistant (see Fig. 5b), and read the frequency.

Then change the magnetic field with the additional power supply. The current is to be changed in 150 mA steps up to a maximum current of 1.5 A. The potentiometer must then be set to 0, the power source switched off and the polarity of the supply lines at the power source reversed (red plug in black device socket and black plug in red device socket). Repeat the entire measurement six times. You should have 6 data sets containing values from -1.5-1.5 A.

Evaluation

NOTE:

A maximum error estimation should be made for all calculated values. For tasks 1-3, a comparison with literature values should also be made.

1. Determination of the gyromagnetic ratio: From the determined angular frequencies ν , ω is calculated (Equ. 8). For $I = 0\text{A}$ the magnetic field is $B_0 = 0.432398\text{ T}$ and changes in positive and negative direction with 2.8112 mT/A . The mean value and the statistical error of the mean value is calculated from the six frequencies for a given current. Further evaluation is then carried out with the Origin program. In a new workbook, the magnetic field strength (calculated from the currents) is entered as x and the mean value of the associated frequency as y . The errors of the frequency are entered in a further column. This column is then set as y -error (Fig. 6). Now all cells are selected and plotted in a scatter diagram. The slope of the linear fit then corresponds to the gyromagnetic ratio according to equation 8. The error calculations are carried out with the given standard error (Fig. 7).
2. The g-factor is calculated from the gyromagnetic ratio.

3. Calculation of the magnetic dipole moment of the proton (Equ. 6).
4. Calculation of the Zeeman-splitting in the magnetic field B_0 (J, cm^{-1} , eV and nm).
5. Derive the approximation of the exponential function (Equ. 11) and then calculate and discuss the population difference between α and β at room temperature.
6. Which other nuclei are also NMR-active (at least 3)?

What you should know!

Quantization of angular momentum, quantization of direction, Zeeman effect, nuclear magnetic resonance condition, structure of a nuclear resonance spectrometer, chemical shift, most important applications of nuclear magnetic resonance, NMR spectra

Books

- P. W. Atkins, J. De Paula, J. Keeler, *Atkins' Physical chemistry, Eleventh edition. ed.*, Oxford University Press, Oxford, United Kingdom ; New York, NY, **2018**.
- H. Friebolin, *Basic one- and two-dimensional NMR spectroscopy*, 5th completely rev. and enlarged ed., WILEY-VCH, Weinheim, **2011**.
- H. Günther, *NMR spectroscopy : basic principles, concepts, and applications in chemistry*, 2nd ed., Wiley, Chichester ; New York, **1995**.

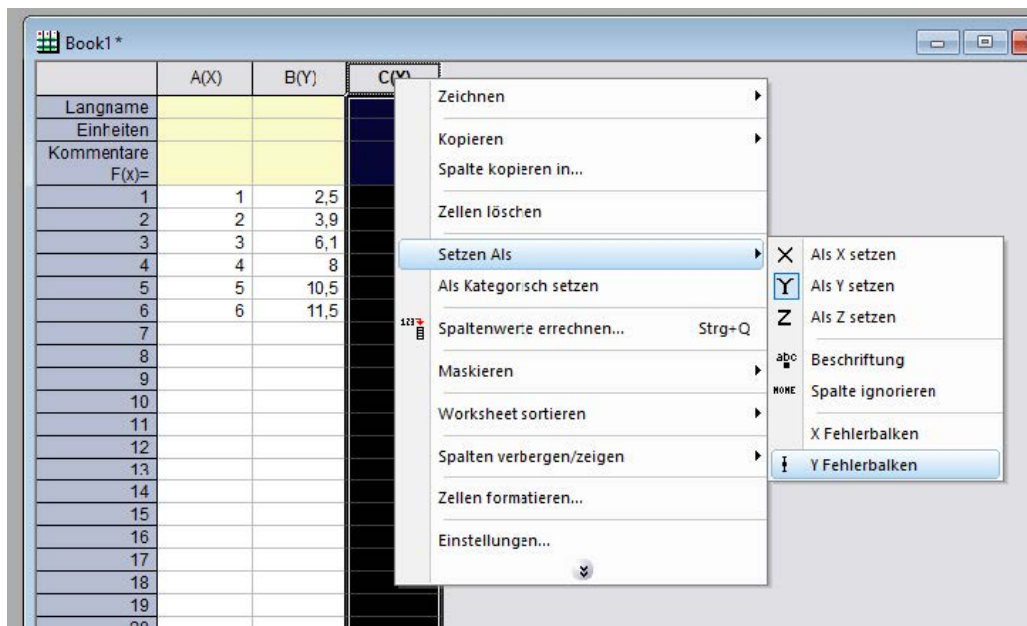


Fig. 6: Setting of the y -error in Origin

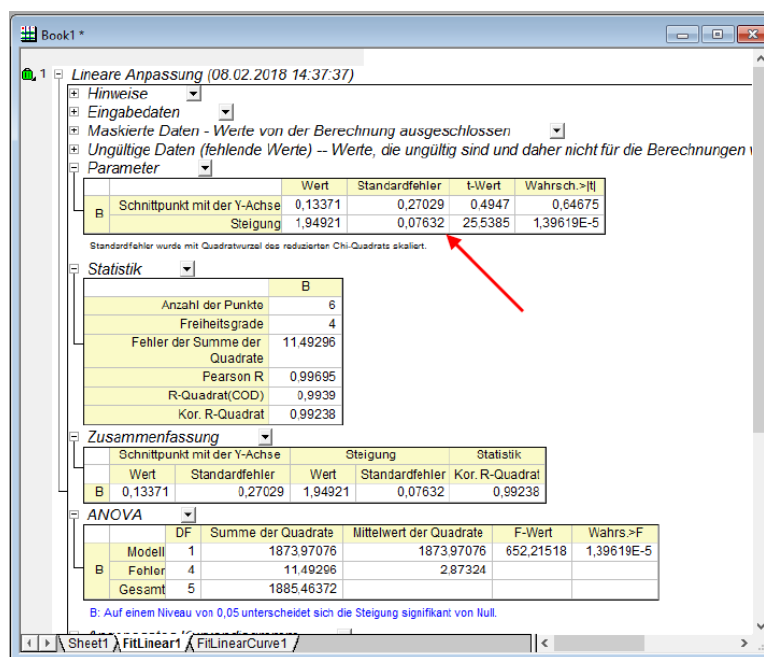


Fig. 7: Error of the linear fit