

A9: Pulsed Nuclear Magnetic Resonance

1. Overview and summary of the goals

Nuclear magnetic resonance is used to a large extent for material investigations in physics and chemistry. The spectrum of applications ranges from chemical analysis of compounds in solution to the investigation of diamagnetic and magnetic solids and to the structural investigation of molecules, such as proteins. Magnetic resonance tomography as used for medical diagnosis is based on pulsed NMR spectroscopy.

The experiment should teach the substantial methods coherent experiments in pulsed nuclear magnetic resonance (pulse sequences, spin echoes). An understanding of the spin dynamics should be achieved. In particular the dependence of longitudinal and transverse relaxation times of the **hydrogen cores** in liquid water on the concentration of paramagnetic salts is examined.

2. Theory

Most atomic nuclei possess **nuclear spin** $I \neq 0$ in their ground states (exception: gg-nuclei). With this nuclear spin a magnetic moment m_I is connected [1]

$$\vec{m}_I = g_K \mu_K \vec{I} = \gamma_I \hbar \vec{I} \quad (1)$$

with g_K the nuclear g-factor, $\mu_K = 5.05079 \cdot 10^{-27}$ J/T the nuclear magneton and γ_I the **gyromagnetic relationship** of the regarded core ($\gamma_I = 2.67522 \cdot 10^8$ rad/(s*T) for protons). In an external magnetic field B_0 the **orientation quantization** of the nuclear spin leads to discrete energy levels [1]:

$$E = E_0 - g_K \mu_K B_0 M_I \quad (2)$$

The magnetic nuclear spin quantum number M_I has values from $-I, -I+1 \dots$ to $\dots +I$. In a macroscopic sample the occupation of the energy levels follows the Boltzmann distribution*. In thermal equilibrium a macroscopic magnetization M_0 arises as a result of the following relationship [1]:

$$\vec{M}_0 = \frac{N g_K^2 \mu_K^2 I(I+1)}{3kT} \vec{B}_0 \quad (3)$$

N is here the number of nuclear spins per unit volume, k the Boltzmann constant and T the absolute temperature.

Similarly to the electron spin resonance experiment (A8) transitions between the energy levels (2) can be induced by applying a perpendicular oscillating electric field $B_1(t)$. For these transitions the selection rule is $\Delta M_I = \pm 1$.

The topics in **bold** font must be mastered at the begin of the experiment.

The **resonance condition**:

$$h\nu = g_K \mu_K B_0 = \gamma_I \hbar B_0 \quad (4)$$

has to be fulfilled. It can be shown that the expectation value of the magnetic moment μ_I in the static field B_0 behaves according to the classical motion equation [1]. The **motion equation of the macroscopic magnetization \mathbf{M}** is given through [2]:

$$\frac{d}{dt} \vec{M} = \gamma_I \vec{M} \times \vec{B}_0 \quad (5)$$

If \mathbf{M} and B_0 are not collinear, the magnetization precesses around B_0 with the **Larmor frequency** [2]:

$$\vec{\omega}_0 = -\gamma_I \vec{B}_0 \quad (6)$$

When an additional oscillating magnetic field $B_1(t)$ is applied, then B_0 in equation (5) is replaced by the vector sum of B_0 and $B_1(t)$ [2]. For an oscillating field $B_1(t)$, polarized perpendicularly to B_0 , and with an angular velocity ω equal to the Larmor frequency ω_0 a simplified mathematical description can be found in a **rotating coordinate system**. In the case of resonance $\omega = \gamma_I B_0$ the motion equation is [2]:

$$\left(\frac{\partial}{\partial t} \vec{M} \right)_{\text{rot}} = \gamma_I \vec{M} \times \vec{B}_1 \quad (7)$$

The magnetization \mathbf{M} precesses around B_1 , whose direction is stationary in the rotating coordinate system, with the angular speed [2]:

$$\vec{\omega}_1 = \frac{d\alpha}{dt} = -\gamma_I \vec{B}_1 \quad (8)$$

α describes the angle around which the magnetization \mathbf{M} rotates from its original orientation. The angle is determined by the product of the pulse duration with the field strength B_1 . The pulses are named after this angle α (e.g. 90° or 180° - pulses) [2]. After switching the alternating field off, \mathbf{M} precesses according to equation (5) around B_0 and thereby produces the nuclear spin resonance signal in a sample coil. A 90° -pulse produces the maximum signal amplitude, which reduces in time due to different relaxation processes (**Free induction decay**, FID) [2]. The behavior of the magnetization \mathbf{M} under the influence of B_1 and of relaxation processes can be described by the **Bloch equations** [1, 2]. One differentiates between **spin-spin relaxation** and **spin-lattice relaxation** processes. The first causes a dephasing of the transversal magnetization components (perpendicular to B_0). In the rotating coordinate system:

$$\frac{dM_{x,y}}{dt} = -\frac{M_{x,y}}{T_2} \quad (9)$$

whereby **T₂ is the transversal relaxation time**. The observed macroscopic transverse magnetization thus reduces exponentially.

An **inhomogeneity ΔB of the static magnetic field B₀** additionally leads to a dephasing of the transversal components. A magnetic moment in a local field B₀+ΔB rotates with Δω= γ_l ΔB. The FID signal of the total sample is described by an integration over all magnetic moments:

$$S(t) \propto \int_{-\infty}^{+\infty} h(\Delta\omega)\cos(\Delta\omega t)d\Delta\omega \quad (10)$$

H (Δω) is the distribution function of the Larmor frequencies, which is caused e.g. by the inhomogeneity of the static magnetic field. The time-dependent FID signal, thereby is the fourier-transform of the magnetic field distribution. For a Gauss-shaped distribution function

$$h(\Delta\omega) \propto \exp\left\{\frac{-\ln(2)\Delta\omega^2}{\Delta\omega_{1/2}^2}\right\} \quad (11)$$

this leads to time constants for the FID signal decrease to the 1/e - value of:

$$T_2^* = \frac{\ln(2)}{\gamma_l \Delta B_{1/2}} \quad (12)$$

T₂* is substantially shorter in this experiment than the actual spin-spin relaxation time T₂. The inhomogeneity-conditioned process is however reversible and can be eliminated by a **spin-echo experiment** (90°, τ, 180°, τ, echo) [2]. From the dependence of the echo amplitude on τ then the spin-spin relaxation time T₂ can be deduced. The **Carr-Purcell-** and the improved **Meiboom-Gill methods** produce a whole sequence of echoes in one measurement, thereby saving measurement time[2].

The **spin-lattice relaxation** causes the reconstruction of the equilibrium magnetization parallel to B₀ (z-direction) with the **longitudinal relaxation time T₁** under energy exchange between the spin system and the surrounding medium:

$$\frac{dM_z}{dt} = -\frac{(M_z - M_0)}{T_1} \quad (13)$$

This can be measured with a 180°, τ, 90°-pulse sequence called '**inversion recovery**'. Since the reconstruction of the longitudinal magnetization M₀ inevitably also causes decreasing transversal magnetization components [2] the following relationship holds:

$$T_2 \leq T_1 \quad (14)$$

Both **relaxation processes**, longitudinal and transversal, are induced through time-dependent magnetic perturbation fields, and are thus no spontaneous processes [1, 2]. Paramagnetic ions in the sample solution (in the attempt Cu^{2+}) leads, because of the large magnetic moment of the unpaired electron, to particularly large local perturbation fields, which shortens the nuclear spin relaxation times T_1 and T_2 drastically [1, chapter 13.4].

3. Function mode of the used devices

A pulse spectrometer of the company TeachSpin, named PS2-A, will be used. The manual is in the practical course folder [3]. Please make yourself familiar with the substantial components of such a pulse spectrometer [2/3]. The nuclear spin resonance signals are represented on an oscilloscope as a function of the time. Signal amplitudes can be measured with an integrated digital voltmeter.

4. References to the investigational procedure

A light mineral oil sample will be used for the adjustment of the setup. Here the T_1 and T_2 relaxation times are given in the TeachSpin manual.

As samples three CuSO_4 -solutions in H_2O in the following concentrations should be used:

1: 0.05 molar CuSO_4 ; 2: 0.1 molar CuSO_4 ; 3: 0.2 molar CuSO_4 . The relaxation times T_1 and T_2 should be determined for the samples 1 to 3 by semi logarithmic representation of the signal amplitudes over the time. The zero crossing at the y-axis (and/or the asymptotic final value) therefore should be determined exactly.

5. Questions promoting the understanding of the experiment

Which influence do false adjusted pulses have on the determination of the relaxation times T_1 and T_2 ?

Which influence does diffusion within the solution of nuclear spins has on the relaxation times T_1 and T_2 ?

Which relation between relaxation times and the concentration on Copper sulfate ions one expects qualitatively?

6. Tasks

a) Adjust the eigen-frequency of the circuit, containing the sample coil, by changing the capacities of the inbuilt capacitors, such that it matches the applied radio frequency needed for excitation of the proton resonance in this set-up. (see TeachSpin-manual).

b) Adjust the 90° and 180° -pulses and consider the influence of the repetition rate [4, in particular chapter 3 and 5].

c) Determine the inhomogeneity of the static magnetic field using the FID signals of two different samples and the assumption that here: $T_2^* \ll T_2$.

d) Determine T_2 for the samples 1 – 3 with the following methods 1: $90^\circ, \tau, 180^\circ, \tau$ –method (spin echo) , 2: Carr Purcell method, 3: Meiboom – Gill method.

e) Determine T_1 for the samples 1 – 3 using the $180^\circ, \tau, 90^\circ$ - method (inversion recovery)..

f) Plot the relaxation times T_1 and T_2 dependend on the concentration of CuSO_4 in a suitable diagram and determine the associated proportional factors.

7. Literature

[1] A. Carrington und A. D. McLachlan " Introduction to Magnetic Resonance", Harper & Row, New York (1969), insbesondere Kapitel 1 und 11.

[2] T. C. Farrar and E. D. Becker "Pulse and Fourier Transform NMR", Academic Press, New York (1971), insbesondere Kapitel 1 und 3.

[3] Manual of the PS2-A spectrometer (TeachSpin).

Further literature:

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- A. Abragam " The Principles of Nuclear Magnetism", Oxford Press (1961)

- D. Shaw "Fourier Transform N.M.R. Spectroscopy", Elsevier (1976)

NMR in modern applications (protein structure determination and medical diagnostics):

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