F61: NMR–Spectroscopy

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May 26th, 2017

Outline

Introduction

NMR-Spectroscopy

Nuclear **M**agnetic **R**esonance

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NMR-Spectroscopy

Nuclear **M**agnetic **R**esonance

Detection of substances

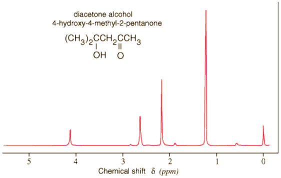

Figure: Carl Nave, Hyperphysics, hyperphysics.phy-astr.gsu.edu

Multidimensional imaging

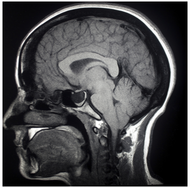

Figure: Sierra Vista Diagnostics, svdrads.com

Theoretical Concepts - Working Principle

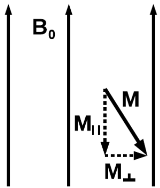

Figure: Magnetization

- Nuclei with spin I have a magnetic moment μ
- Ensemble of many nuclei: Measurable magnetization $\vec{M}$
- Minimal energy $\rightarrow$ Dipole aligned parallel to B-field
- Ground state $\rightarrow M_{\perp} = 0$

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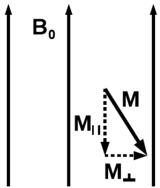

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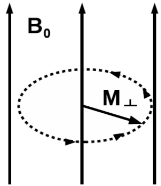

Figure: Larmor-Precession of $M_\perp$

- Nuclei with spin I have a magnetic moment μ
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- Excited states have a component $M_\perp \neq 0$
- $M_\perp$ precesses around the field lines with the Larmor frequency

$$\omega_L = \gamma B_0 \tag{1}$$

- ω_L can be measured!

Theoretical Concepts - Working Principle

How can we create an excited state ?

- An oscillating B-Field $\vec{B}_1$ rotates the magnetization $\vec{M}$ by an angle

$$\alpha = \gamma B_1 \Delta t \tag{2}$$

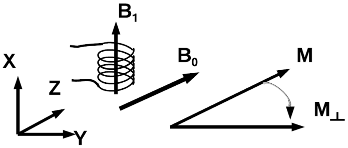

Figure: Rotation of *M* due to an HF-Pulse

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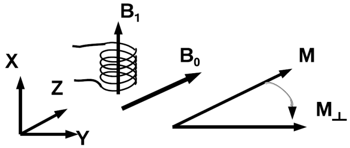


Figure: Rotation of M due to an HF-Pulse

- By choosing Δt, we can create:
  - A perpendicular magnetization (90°-Pulse)
  - An anti-parallel magnetization (180°-Pulse)

Setup and Measurement Principle

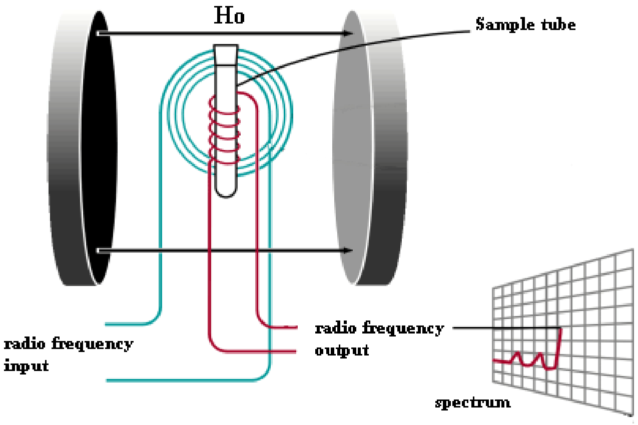


Figure: McGraw Hill Higher Education, mhhe.com

Theory of Relaxation

Excited states decay into the Ground State on a characteristic timescale.
The decay is of exponential nature and described in the *Bloch equations:*

$$\frac{dM_\perp(t)}{dt} = -\frac{M_\perp(t)}{T_2} \tag{3}$$

$$\frac{dM_\parallel(t)}{dt} = -\frac{M_\parallel(t) - M_0}{T_1} \tag{4}$$

- T_2: Spin-Lattice Relaxation
- T_1: Spin-Spin Relaxation

T_2-Measurement: Spin Echo

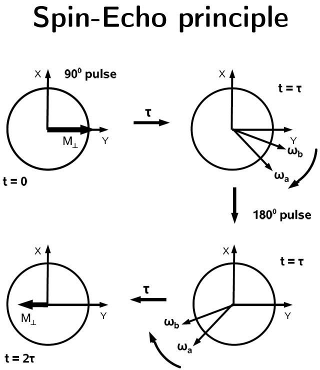


Figure: Principle of the spin-echo method

T_2-Measurement: Spin Echo

Spin-Echo principle

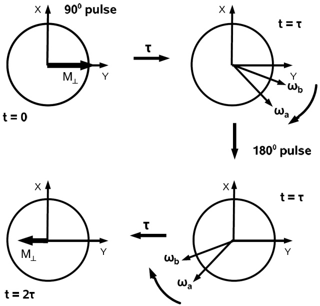


Figure: Principle of the spin-echo method

Pulse sequence

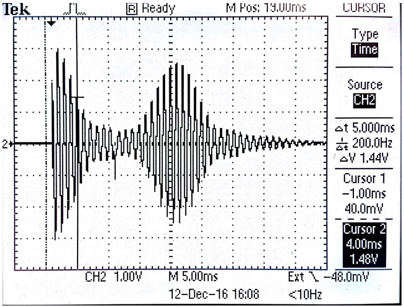
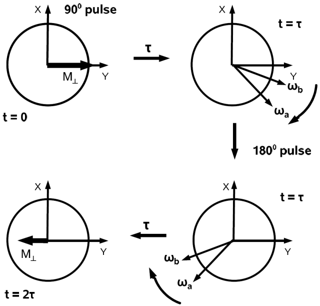


Figure: Spin-Echo measurement with $\tau = 10ms$

T_2-Measurement: Spin Echo

Spin-Echo principle



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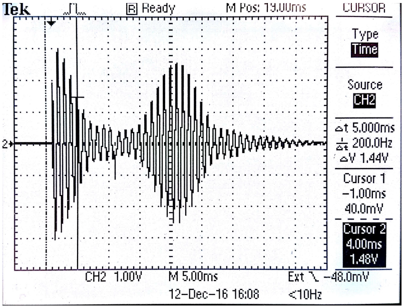

Figure: Spin-Echo measurement with $\tau = 10ms$

- **Disadvantage**: Dephasing for long measurement times!

T_2-Measurement: Spin Echo

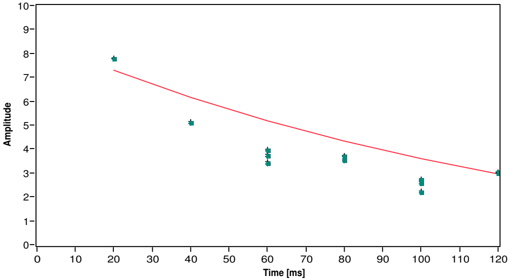

Figure: T2-Measurement Sample 1 with fit.

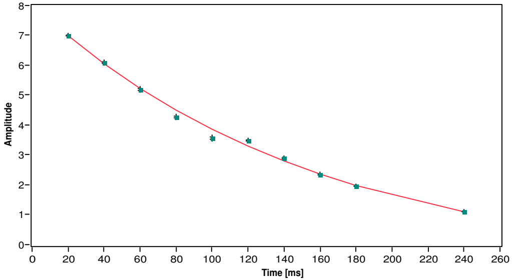

Figure: T2-Measurement Sample 3 with fit.

T_2-Measurement: Carr-Purcell Sequence

Improve dephasing problem of spin-echo method:

- Inject a 180°-Pulse on odd multiples of a time τ.
- The system is phase coherent on even multiples of a time τ.

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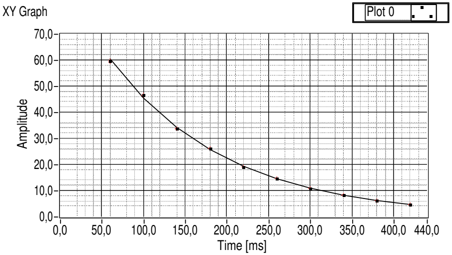

Figure: T2-Measurement using Carr-Purcell, Sample 1, with fit.

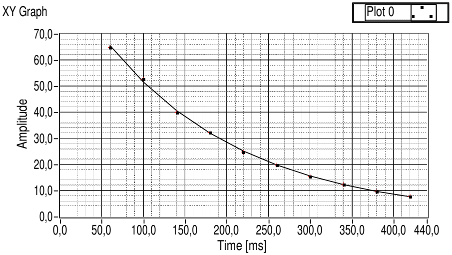

Figure: T2-Measurement using Carr-Purcell, Sample 3, with fit.

T_1-Measurement

Start with a 180°-Pulse (Anti-parallel Magnetization) and probe the magnetization after time τ with a 90°-Pulse

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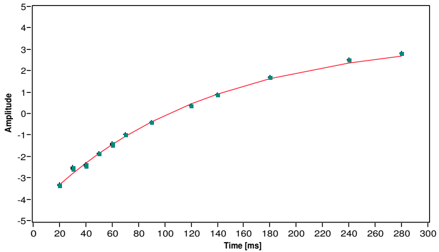

Figure: T1-Measurement Sample 1 with fit.

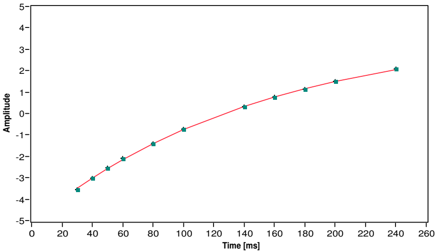

Figure: T1-Measurement Sample 3 with fit.

Relaxation Times: Evaluation

Table: Relaxation times – Measured values

Time Method	T_1 [ms] 180°-90°	T_2 [ms] Spin-Echo	T_2 [ms] Carr-Purcell
Sample 1 (Gd 1:500)	$(125,5 \pm 0,6)$	$(119,5 \pm 0,5)$	$(140,1 \pm 0,4)$
Sample 3 (Gd 1:600)	$(150,5 \pm 1,2)$	$(139,3 \pm 0,8)$	$(166,9 \pm 0,4)$

Chemical shift – theory

Aim: structure determination of chemical substances

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- electron orbitals contribute to B_0:

$$\delta\vec{B} = \sigma\vec{B}_0$$

- modification of the Larmor frequency:

$$\omega_i = \omega_L\,(1 - \sigma_i)$$

Chemical shift – theory

Aim: structure determination of chemical substances

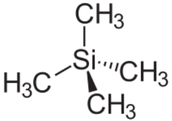
- electron orbitals contribute to B_0:

$$\delta \vec{B} = \sigma \vec{B_0}$$

- modification of the Larmor frequency:

$$\omega_i = \omega_L \left(1 - \sigma_i\right)$$

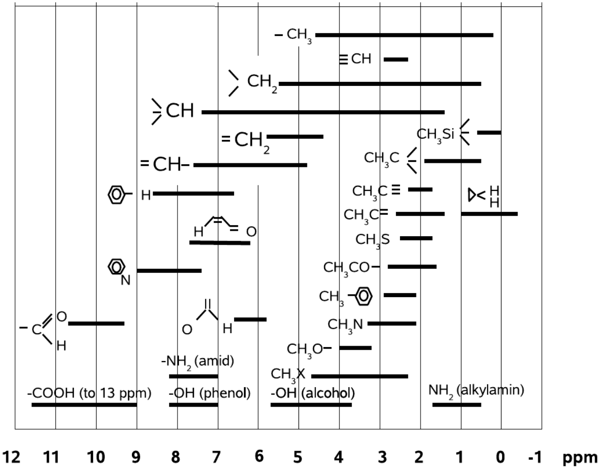
- reference substance: TMS (Tetra-Methyl-Silan)



- relative chemical shift in ppm:

$$\delta_i = \sigma_i - \sigma_{TMS} = \frac{\omega_{TMS} - \omega_i}{\omega_L}$$

Chemical shifts δ_i of compounds relative to TMS



Measurements

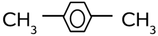
- five chemical substances, with and without TMS
- inhomogeneities and diffusion processes reduce resolution
  $\Rightarrow$ thin glass tube, put into rotation with pressure air
- result:
  - without rotation:
    FWHM = 200 Hz, I = 0,25
  - with rotation:
    FWHM = 20 Hz, I = 1,9
- energy resolution:
  $\Delta E_{NMR} = h \cdot \Delta\nu = 8,28 \cdot 10^{-14}\,\mathrm{eV}$

Idenfication of the Probes

Probe C: acetic acid $CH_3 - COOH$

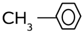
Peaks of C+ [ppm]	Peaks of C [ppm]	Chem. shift.	
$p_1 = 16,7$	$p_1 = 17,0$	$\delta_i = 11,6$	COOH-group
$p_2 = 26,2$	$p_2 = 26,6$	$\delta_i = 2,1$	Methyl group CH_3
$p_3 = 28,3$	–	–	TMS

Idenfication of the Probes

Probe B: p-Xylol 

Peaks of B+ [ppm]	Peaks of B [ppm]	Chem. shift	
$p_1 = 22,7$	$p_1 = 22,7$	$\delta_i = 7,0$	Benzene group
$p_2 = 27,5$	$p_2 = 27,5$	$\delta_i = 2,2$	Methyl group, Peak twice as high as p_1
$p_3 = 29,7$	–	–	TMS

Idenfication of the Probes

Probe E: toluol 

Peaks of E+ [ppm]	Peaks of E [ppm]	Chem. shift	
$p_1 = 19,5$	$p_1 = 23,1$	$\delta_i = 7,3$	Benzene group
$p_2 = 24,4$	$p_2 = 23,1$	$\delta_i = 2,4$	Methyl group, peaks have same hight
$p_3 = 26,8$	–	–	TMS

Idenfication of the Probes

Probe A: fluoroaceton $FCH_2 - CO - CH_3$

Peaks of A+ [ppm]	Peaks of A [ppm]	Chem. shift	
$p_1 = 22,2$	$p_1 = 23,8$	$\delta_i = 6,3$	FCH_2-group
$p_2 = 24,6$	$p_2 = 21,4$	$\delta_i = 3,9$	
$p_3 = 26,4$	$p_3 = 19,6$	$\delta_i = 2,1$	Methyl group CH_3
$p_4 = 28,5$	–	–	TMS

Idenfication of the Probes

Probe D: fluoroacetonitril $FCH_2 - CN$

Peaks of D+ [ppm]	Peaks of D [ppm]	Chem. shift	
$p_1 = 30,8$	–	–	TMS
$p_2 = 34,8$	$p_2 = 26,6$	$\delta_i = 6,4$	FCH_2 group
$p_3 = 37,2$	$p_3 = 24,2$	$delta_i = 4,0$	

one dimensional imaging – theory

- **position dependent magnet fields**
- Superposition of the static field $\vec{B_0}$ with gradient fields $\vec{B^x}$, $\vec{B^y}$, $\vec{B^z}$
- two techniques:

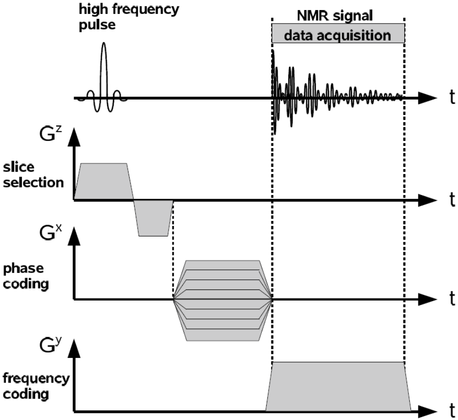
frequency coding

- Larmor frequency
  $\omega_L = \gamma(B_0 + G^z \cdot z) = \omega_L^0 + \omega_z$
- measured NMR signal $S(t)$ is Fourier transform of $M_\perp^{rot}(z)$

phase coding

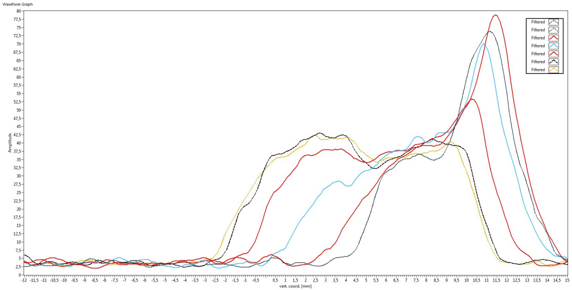
- apply gradient field, increase strength
- phase rotates: $\phi(z) = (\gamma G^z T_{Ph})z = k_z z$

two dimensional imaging – theory



One dimensional imaging measurements

- Bruker® NMR analyzer mq7.5
- Glass tube filled with 15 mm of oil
- Glass tube filled with 50 mm of water
- glass tube with teflon structure
- examination of an inflitration process:
  Fick's second law: $\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$



two dimensional imaging measurements

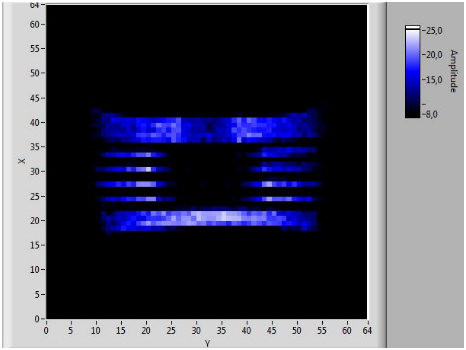


Figure: teflon structure

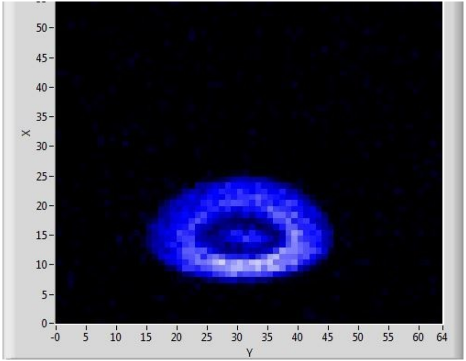


Figure: olive

two dimensional imaging measurements

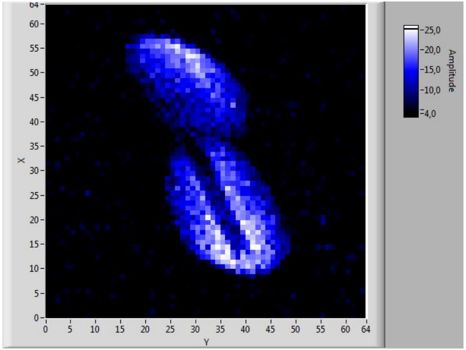


Figure: peanut shell

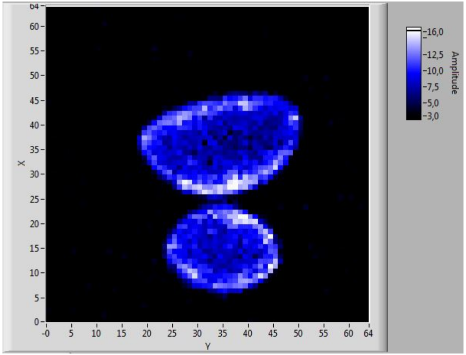


Figure: aloe vera