Solid State NMR workshop 2011:
An introduction to Solid State NMR spectroscopy

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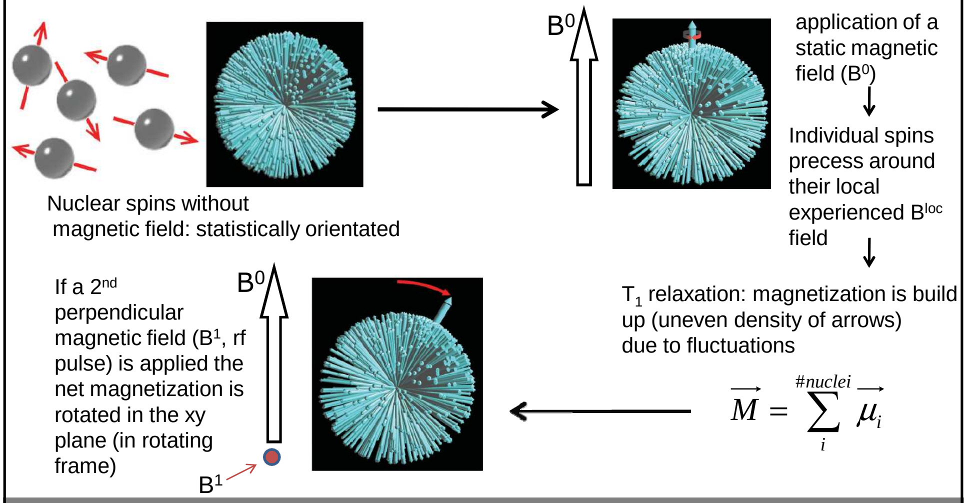
(Solid State NMR specialist/ researcher)

General NMR basics

Interaction between nuclear spins and applied magnetic fields



Nuclear spins without magnetic field: statistically orientated

application of a static magnetic field (B^0)
↓
Individual spins precess around their local experienced B^{loc} field
↓
T_1 relaxation: magnetization is build up (uneven density of arrows) due to fluctuations

$$\overrightarrow{M} = \sum_{i}^{\#nuclei} \overrightarrow{\mu_i}$$

If a 2nd perpendicular magnetic field (B^1, rf pulse) is applied the net magnetization is rotated in the xy plane (in rotating frame)

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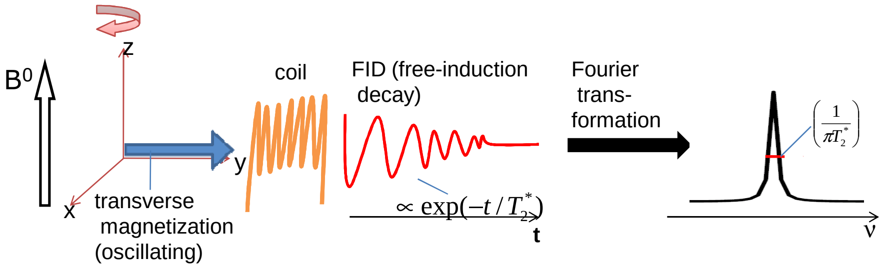
L.G. Hanson, Conc. Magn. Reson. A,32A(5), 329-340, (2008)

General NMR basics

Detection of transverse magnetization



Rotating magnetic moment → rotating magnetic field → Electric field (Maxwell's equation)

→ Sets electrons in a wire coil (close to the sample) in motion → Oscillating current in coil = FID

General NMR basics

… to summarize

"The NMR spectrometer is basically a device capable of

- (i) magnetizing the nuclear spins with a large applied magnetic field
- (ii) rotating the spin polarizations by radiofrequency pulses to produce transverse nuclear magnetization
- (iii) detecting the small oscillating electric currents induced by the precessing transverse spin magnetization.

To some extent, everything else is details. "

M. Levitt, spin dynamics, Wiley & sons, 2002

General NMR basics

The classical approach

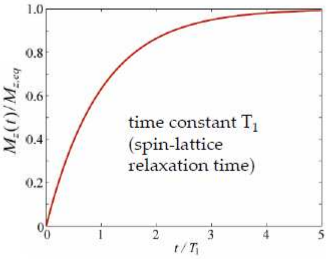
We deal with the macroscopic sizes i.e. the magnetization represented by the vector model

Bloch's equation (describing magnetization in the rotating frame):

$$M_x = M_{x_0} \cdot \exp\left(-\frac{t}{T_2^*}\right)$$

$$M_y = M_{y_0} \cdot \exp\left(-\frac{t}{T_2^*}\right)$$

$$M_z = \left(M_{z_0} - M_0\right) \cdot \exp\left(-\frac{t}{T_1}\right) + M_0$$



General NMR basics

The quantum mechanical approach

- for the description of properties of individual spins

- Multispin systems are represented by a spin density matrix

General NMR basics

The Zeeman interaction

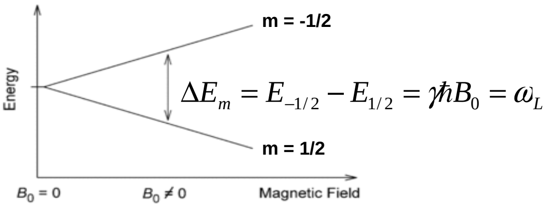
= interaction of a nuclear magnetic moment with the B_0-field

- represented by the Zeeman-Hamilton operator: $\hat{H}_Z = \hat{\mu}\vec{B}_0 = -\gamma\hbar B_0 \hat{I}_z$

- Not all possible spin orientations relative to the B_0-field have a well-defined energy. Only the nuclear spin eigenstates (“Zeeman states”) are associated with real, well-defined energy values E_m (“energy eigenvalues”)

$$E_m = -\gamma m \hbar B_0$$

γ gyromagnetic ratio
$\hbar$ Planck constant
m magnetic quantum number
$m = I, I-1, \ldots, -I$



$$\Delta E_m = E_{-1/2} - E_{1/2} = \gamma\hbar B_0 = \omega_L$$

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General NMR basics

The Zeeman interaction: Energy level diagrams in NMR

General rules to construct them:

→ the magnetic quantum number ***m*** has values from +**I** (nuclear spin) to **–I** quantizied by steps of **1**

$m = I, I-1, \ldots, -I$

→ the total number of energy eigenstates is $2I+1$

→ $m = I$ is associated with the lowest energy level due to the negative sign of $E_m = -\gamma m \hbar B_0$

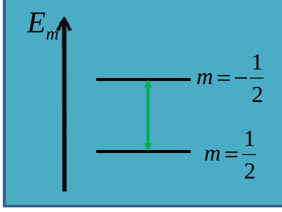
→ $\Delta E_m = \omega_L$ for neighbored energy levels
⇒ equidistant distance between the energy levels

→“allowed transitions” between neighbored levels only ($\Delta m = \pm 1$)

for I=1/2 spin:

$m = \frac{1}{2}, -\frac{1}{2}$

$2\left(\frac{1}{2}\right) + 1 =$ 2# energy levels



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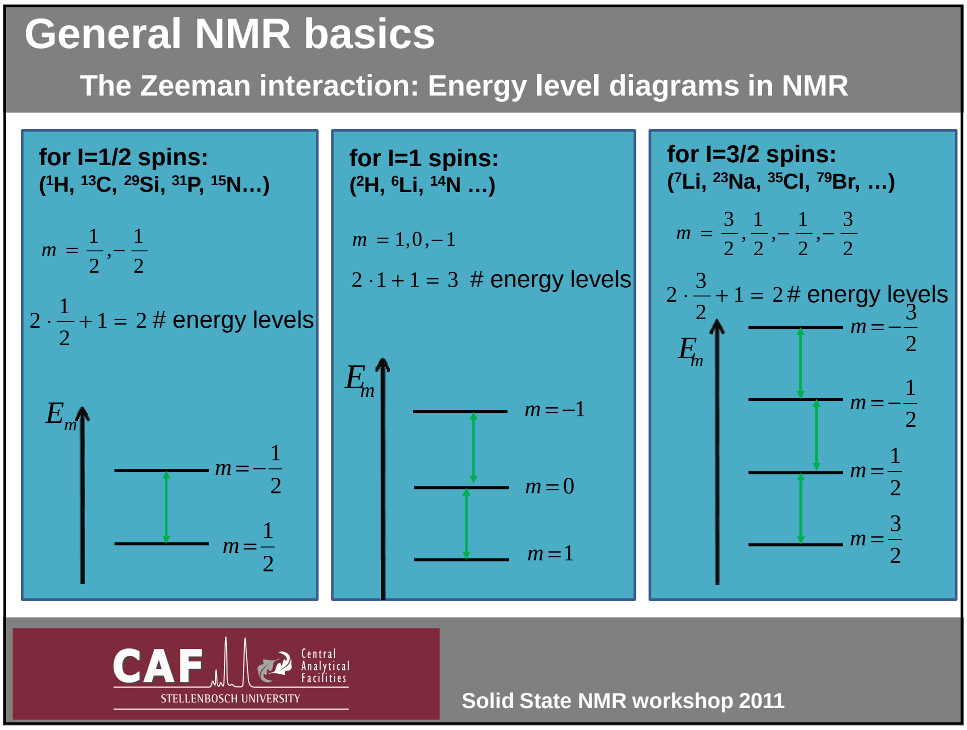


General NMR basics

The Zeeman interaction: Energy level diagrams in NMR

for I=1/2 spins:
(^{1}H, ^{13}C, ^{29}Si, ^{31}P, ^{15}N…)

$m = \frac{1}{2}, -\frac{1}{2}$

$2\cdot\frac{1}{2}+1 = 2$ # energy levels

for I=1 spins:
(^{2}H, ^{6}Li, ^{14}N …)

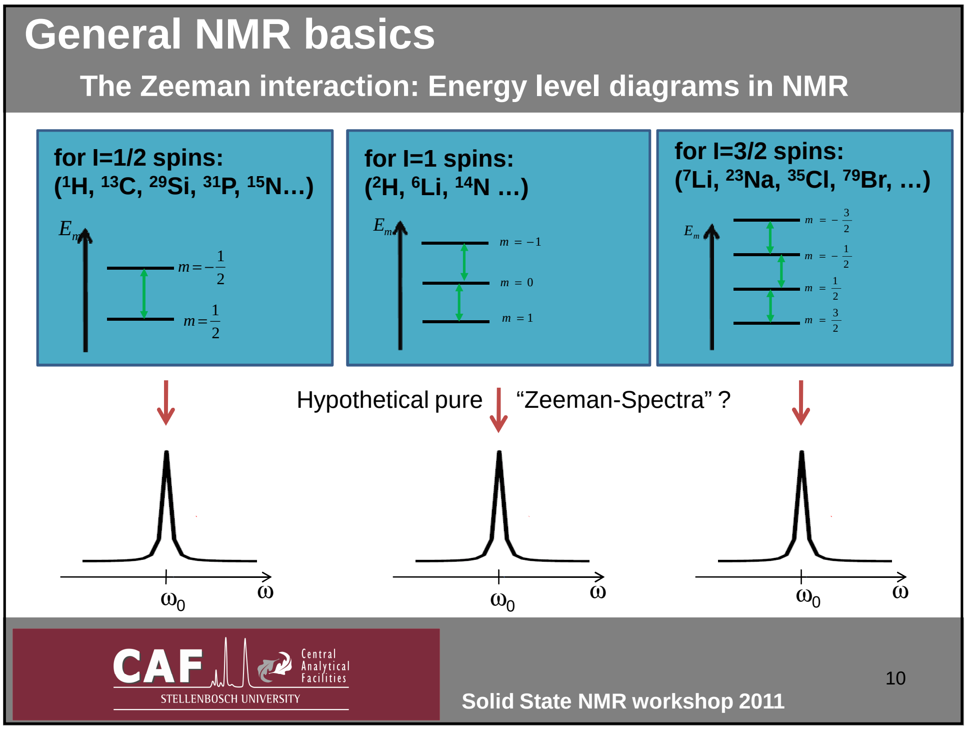
$m = 1, 0, -1$

$2\cdot 1+1 = 3$ # energy levels

for I=3/2 spins:
(^{7}Li, ^{23}Na, ^{35}Cl, ^{79}Br, …)

$m = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$

$2\cdot\frac{3}{2}+1 = 2$# energy levels



General NMR basics

The Zeeman interaction: Energy level diagrams in NMR

for I=1/2 spins:
(^{1}H, ^{13}C, ^{29}Si, ^{31}P, ^{15}N…)

for I=1 spins:
(^{2}H, ^{6}Li, ^{14}N …)

for I=3/2 spins:
(^{7}Li, ^{23}Na, ^{35}Cl, ^{79}Br, …)

Hypothetical pure “Zeeman-Spectra” ?

General NMR basics

Internal interaction – an overview

Not much information!

“the carrier of information”

Internal interactions = interaction between the nuclear spin with internal magnetic and electronic fields

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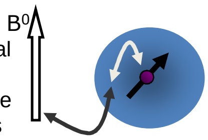
General NMR basics

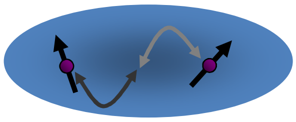
Internal interaction – an overview

Magnetic shielding/Chemical shift

= indirect magnetic interaction of the external magnetic field and the nuclear spins through the involvement of electrons

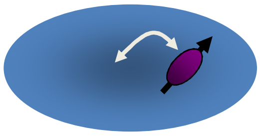


J-coupling



= indirect magnetic interactions of nuclear spins with each other through the involvement of electrons

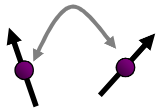
Quadrupolar couplings



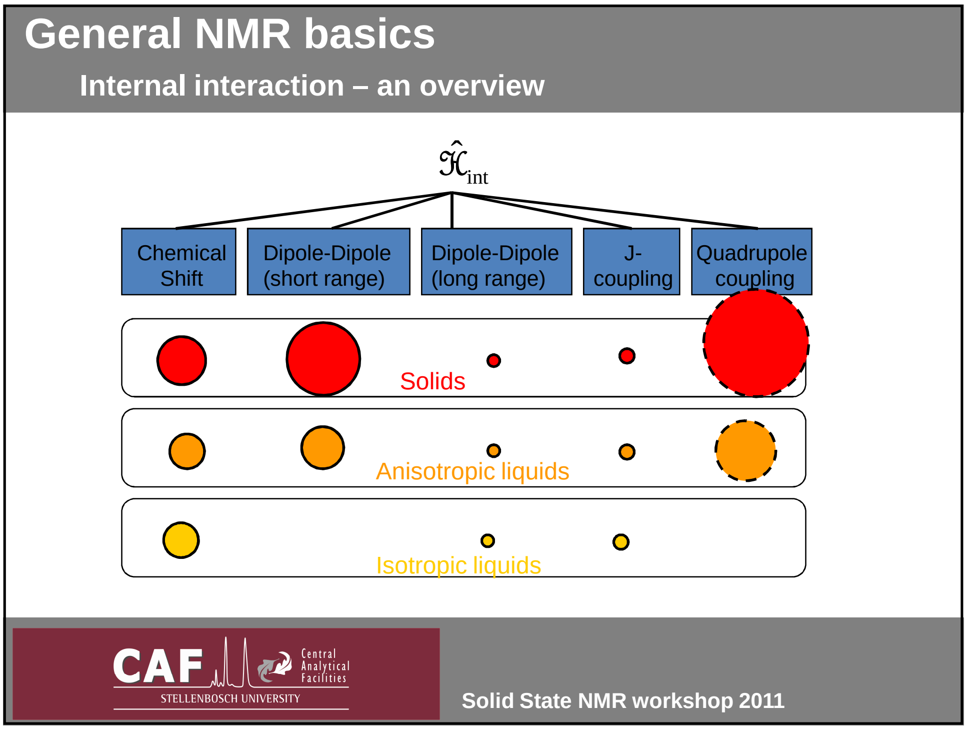
= electric interaction of spin >1/2 nuclei with the surrounding electric fields

(interaction between a quadrupolar moment with an electric field gradient)

Direct dipole-dipole couplings



Direct magnetic interactions of nuclear spins with each other



General NMR basics

Internal interaction – an overview

$\hat{\mathcal{H}}_{\text{int}}$

Chemical Shift | Dipole-Dipole (short range) | Dipole-Dipole (long range) | J-coupling | Quadrupole coupling

Solids

Anisotropic liquids

Isotropic liquids

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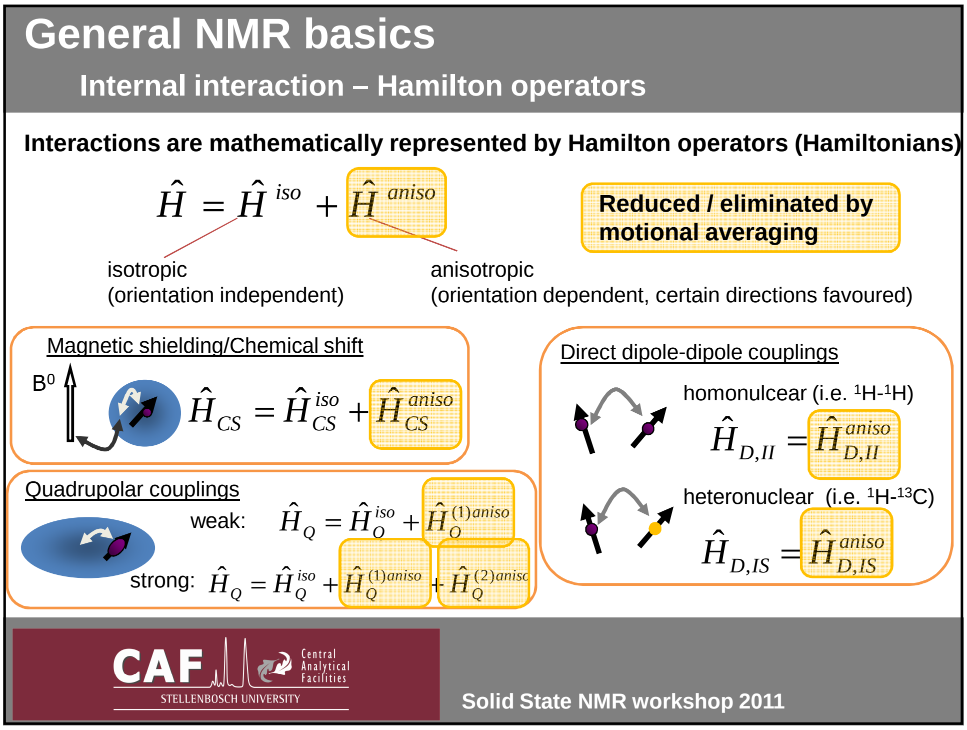

General NMR basics

Internal interaction – Hamilton operators

Interactions are mathematically represented by Hamilton operators (Hamiltonians)

$$\hat{H} = \hat{H}^{iso} + \hat{H}^{aniso}$$

Reduced / eliminated by motional averaging

isotropic
(orientation independent)

anisotropic
(orientation dependent, certain directions favoured)

Magnetic shielding/Chemical shift

B^0

$$\hat{H}_{CS} = \hat{H}_{CS}^{iso} + \hat{H}_{CS}^{aniso}$$

Direct dipole-dipole couplings

homonulcear (i.e. ^{1}H-^{1}H)

$$\hat{H}_{D,II} = \hat{H}_{D,II}^{aniso}$$

heteronuclear (i.e. ^{1}H-^{13}C)

$$\hat{H}_{D,IS} = \hat{H}_{D,IS}^{aniso}$$

Quadrupolar couplings

weak: $\hat{H}_Q = \hat{H}_Q^{iso} + \hat{H}_Q^{(1)aniso}$

strong: $\hat{H}_Q = \hat{H}_Q^{iso} + \hat{H}_Q^{(1)aniso} + \hat{H}_Q^{(2)anisc}$

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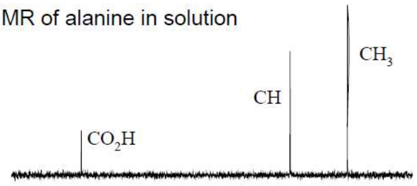
General NMR basics

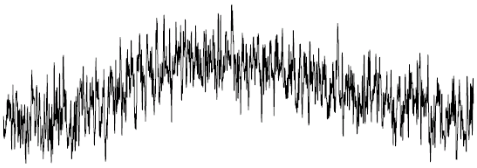
Impact of motional averaging on a NMR spectrum

^{13}C NMR of alanine in solution



all anisotropic internal interactions are averaged out due to Brown's molecular motion (complete motional averaging)

^{13}C NMR of solid alanine



in (rigid) solids:
anisotropic interactions are (fully) present resulting in broad, feature-less spectra

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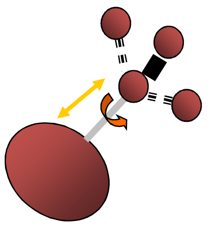
General NMR basics

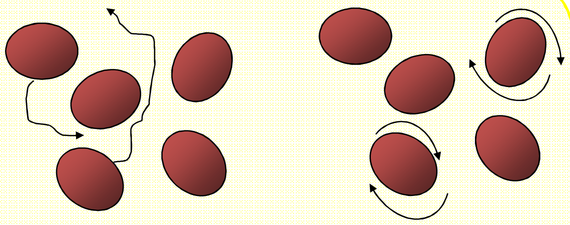
motional averaging

Strength of internal magnetic interactions of solids and liquids are very different from each other due to motional averaging

Modes of molecular motion



internal molecular motion:
-vibration
-rotation around bonds

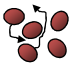
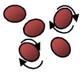


translation:
- diffusion
- flow

rotation

General NMR basics

motional averaging in liquids and solids

States of matter	Intramolecular motion	translation	rotation	
isotropic Liquid (water)	fast	fast and isotropic	fast and isotropic	anisotropic internal interactions are averaged out resulting in narrow NMR peaks
anisotropic liquid /liquid crystal (soap film)	fast	fast and anisotropic	fast and anisotropic	anisotropic interactions are only partially averaged out resulting in more complicated NMR spectra
solids	can be fast, but usually restricted	usually neglible	restricted	anisotropic interactions usually present leading to broad and complicated lines

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General NMR basics

motional averaging in liquids and solids

→ Distinction solids – liquids depends on mobility in the sample

Distinction mobile – immobile depends on timescale!

Examples:
- timescale: microseconds

→ water resists deformations and appears as hard as a solid

(you can test this by diving into a swimming pool stomach-first)

- timescale: several centuries

→ glass behaves like a liquid

(windows of old chruches are thicker at the bottom than on the top. Glass has flowed under gravity like a liquid)

→ **Timescales are important!**

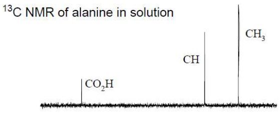
Structural characterization

Solution vs. solid state NMR

Energy of spin system: $\hat{H}_{total} = \hat{H}_Z + \hat{H}_{RF} + \hat{H}_{int}$

All NMR spectra are results of the energy differences of the nuclear spin eigen states, which are shifted by internal spin interactions.

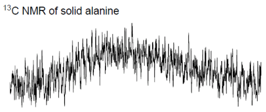
Solutions:



$$\hat{H}_{int} = \hat{H}^{iso}_{CS} + \hat{H}_J$$

→ Structural parameters:
- Isotropic chemical shift
- J coupling

Solids



$$\hat{H}_{int} = \hat{H}^{iso}_{CS} + \hat{H}^{aniso}_{CS} + \hat{H}^{aniso}_{D,hetero}$$

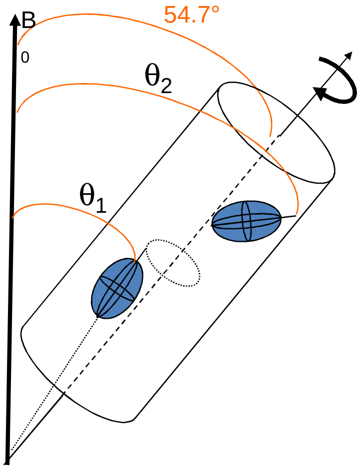
$$^{iso}_{homo} + \hat{H}^{iso}_{Q} + \hat{H}^{(1)aniso}_{Q} + \hat{H}^{(2)aniso}_{Q}$$

→ Information overload!

We need special solid state NMR techniques to obtain useful spectra!

Methods for structural characterization

magic angle spinning (MAS)- setup

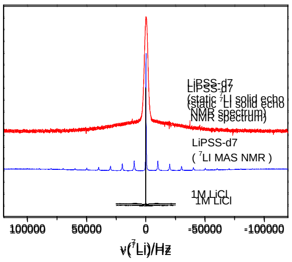


If the spinning is fast enough:

$$\langle \theta_1 \rangle = \langle \theta_2 \rangle = 54.7°$$

How fast?

Spinning frequency >> width of the static spectrum

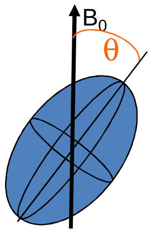


Methods for structural characterization

magic angle spinning (MAS)

$$\hat{H}_{int} = \hat{H}^{iso}_{CS} + \cancel{\hat{H}^{aniso}_{CS}} + \cancel{\hat{H}^{aniso}_{D,hetero}} + \cancel{\hat{H}^{aniso}_{D,homo}} + \hat{H}^{iso}_{Q} + \cancel{\hat{H}^{(1)aniso}_{Q}} + \hat{H}^{(2)aniso}_{Q}$$

(CSA)

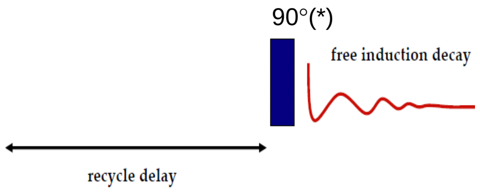


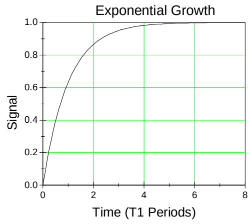
proportional to: $\left(3\cos^2\theta - 1\right)$

if θ=54.7°("magic angle") then $\left(3\cos^2\theta - 1\right) = 0$

Methods for structural characterization

A simple experiment - one pulse MAS





- (*) 90° pulse for spin-1/2 nuclei, special rules for quadrupolar nuclei

!Note: very different measurement parameters compared to solution state NMR

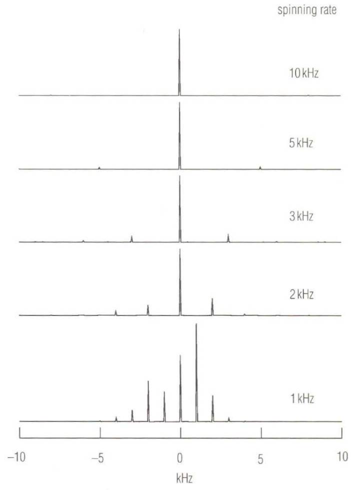
- often much shorter pulses (pulse length very important)
- more power (1000W amplifier)
- acquisition time in order of few ms
- very short dead time (3-8 µs)
- very short dwell times (0.5 to 10 µs)

-Recyle delay:

- 5 ×T_1 quantitative
- 1.2 × T_1 best S/N for a certain time period, but not quantitative

Methods for structural characterization

MAS- the isotropic line(s) and spinning sidebands



If the spinning speed ≤ width of the static spectrum

→ Spinning sidebands arise apart from the isotropic line in distance of the spinning speed

How to distinguish the isotropic line from spinning sidebands?

- position independent of spinning speed

! Note: not necessarily the most intense line!

! Note: for quantitative analysis spinning sidebands must be considered!

M. Duer, Introduction to Solid-State NMR spectroscopy, Blackwell Science (2004)

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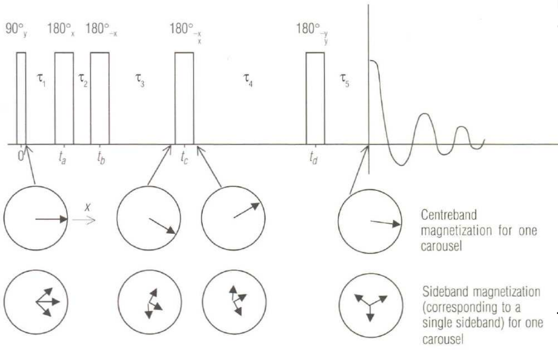
Methods for structural characterization

TOSS MAS

TOSS= to<u></u>tal suppression of spinning sidebands



If more than one positions:
→Difficult to distinguish between spinning sidebands and isotropic line

→solution: TOSS method

-principle: the magnetization associated with the isotropic lines is (almost fully) refocused, while the magnetization contributions of the spinning sidebands (ss) is destroyed

-doesn't work well if there are many ss (small residual ss, phase distortions)

- TOSS experiments are NOT quantitative!

M. Duer, Introduction to Solid-State NMR spectroscopy, Blackwell Science (2004)

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Study of dynamics in solids

timescales and methods

Timescale of dynamic process	**SS NMR method**
“fast” 10^{-9} to 10^{-6} s (local mobility like molecular vibrations and rotations)	T_1 relaxation studies
“medium” “NMR time window” 10^{-5} to 10^{-2} s (ion jumps, chain mobility in polymers)	Static lineshape analysis $T_{1\rho}$ relaxation studies
“slow” 10^{-3} to 10 s (chemical exchange)	2D exchange experiments

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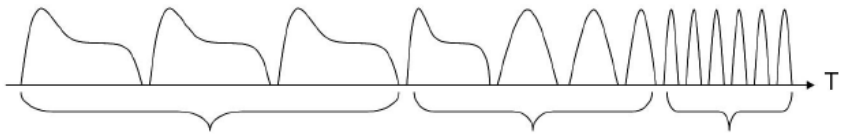
Study of dynamics in solids

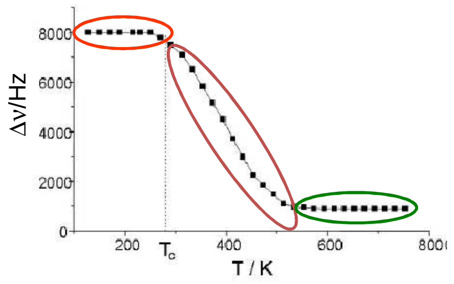
static lineshape analysis



slow motion limit: $\tau_c >> (\Delta\nu)^{-1}$

motional narrowing: $\tau_c \sim (\Delta\nu)^{-1}$

fast motion limit: $\tau_c << (\Delta\nu)^{-1}$



study of dynamic processes
→ µs - ms

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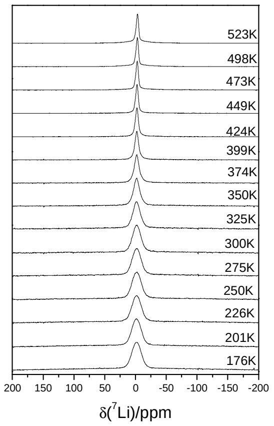
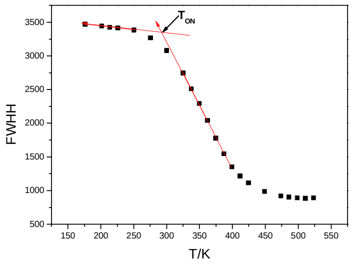
Study of dynamics in solids

static lineshape analysis – application example

Estimation of activation energies for ion jumps in ion conducting materials





Waugh-Fedin equation[1]:

$$E_a[\text{eV}] \approx 1.6177\ 10^{-3} \cdot T_{ON}[\text{K}]$$

[1] J.S. Waugh, I. Fedin, *Sov. Phys. –Solid State*, **4**, 1633, (1963)

Study of dynamics in solids

static lineshape analysis – application example

Estimation of activation energies for ion jumps in ion conducting materials

Advantage

- Good method complementary to conductivity studies, because mobility of an ion can be studied selectively
- ion translation only is in the NMR time window, forward and back jumps are too fast

Disadvantage

- only mobile ions lead to motional narrowing, the degree of mobile relative to immobile ions is not known