

Direct dipolar interaction - utilization

Two main uses:

I: magnetization transfer

II: probing internuclear distances

Direct dipolar interaction - utilization

Probing internuclear distances

$$\hat{H}_D^{\text{hetero}} = -d \frac{1}{2} (3 \cos^2 \theta - 1) \hat{I}_z \hat{S}_z \quad \hat{H}_D^{\text{homo}} = -d \frac{1}{2} (3 \cos^2 \theta - 1) [3 \hat{I}_z \hat{S}_z - \hat{\mathbf{I}} \cdot \hat{\mathbf{S}}]$$

$$\text{with: } d = -\frac{\mu_0 \gamma_I \gamma_S \hbar}{4\pi r_{IS}^3}$$

→ Information about internuclear distances in dipolar coupling constant (r_{IS} -dependence)

→ **Dipolar coupling methods:** methods to probe the strength of dipolar interactions to study internuclear distances

→ Different spin-terms → different response to pulse sequences!!!

Direct dipolar interaction - utilization

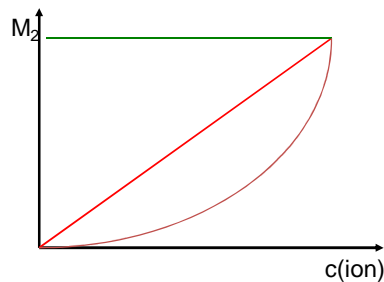
Probing internuclear distances: second moments M_2

Dipolar coupling methods:

Probe the strength of dipolar interaction

Measure for the strength of the dipolar interaction: the second moment M_2

Possibly application: study of ion distribution in disordered systems (glasses, ...)



$$M_2 \propto \sum \frac{1}{r_{ij}^6}$$

Type of ion distribution:

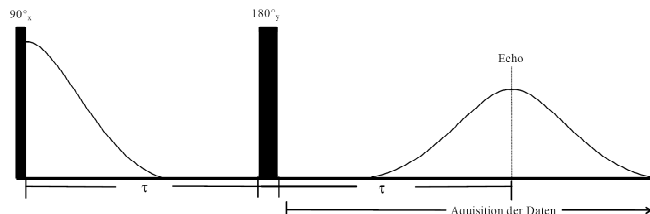
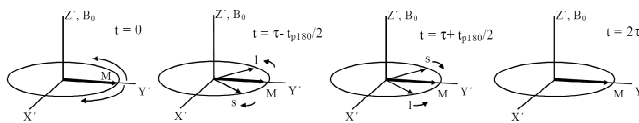
- clustered/ phase-separated
- statistical
- homogeneous

Direct dipolar interaction - utilization

Determination of homonuclear M_2 's

Spin echo decay spectroscopy

Based on a Hahn Echo:



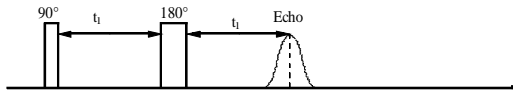
- designed for $I=1/2$ nuclei
- Refocus ($I=1/2$ nuclei):
- Field inhomogeneities
- Chemical shift anisotropy
- Heteronuclear dipolar interaction

(all interactions which are proportional to I_z)

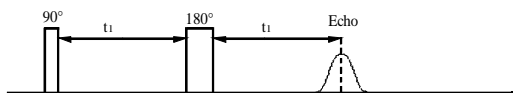
Direct dipolar interaction - utilization

Determination of homonuclear M_2 's

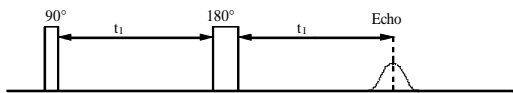
The Spin echo experiment



The Hahn Echo intensity is measured as a function of the evolution time t_1



the longer the evolution time the lower the echo intensity

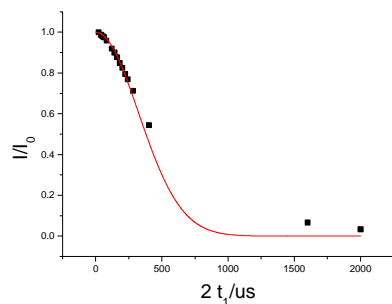


Reason for loss of signal:
Homonuclear dipolar interaction

! Note: works only for spin-1/2 or "pseudo" spin-1/2 nuclei

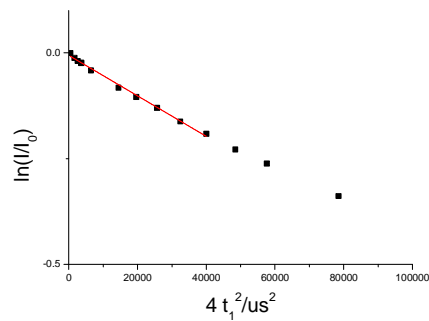
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Determination of homonuclear M_2 's



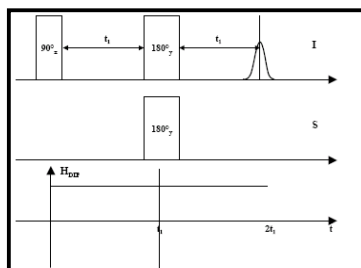
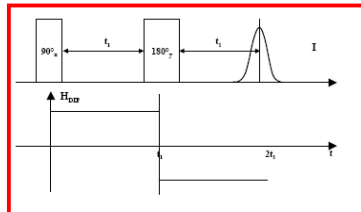
$$\frac{I(2t_1)}{I(0)} = \exp\left[-\frac{(2t_1)^2 M_2^{\text{homo}}}{2}\right]$$

determination of M_2 from a linear fit:

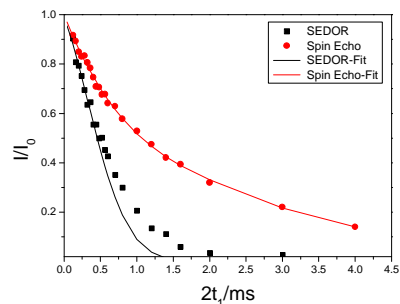


Direct dipolar interaction - utilization

Determination of heteronuclear M_2 's: SEDOR



$$\hat{H}_D^{hetero} \propto \frac{\hat{I}_Z \hat{S}_Z}{r^3} \cdot (3 \cos^2 \theta - 1)$$



$$\frac{I(2t_1)}{I(0)} = \frac{F(2t_1)}{F(0)} \cdot \exp\left(\frac{-M_2^{hetero}(2t_1)^2}{2}\right)$$

Direct dipolar interaction - utilization

Other dipolar coupling methods

Homonuclear: %

Heteronuclear:

- REDOR (rotational echo double resonance): MAS version of the SEDOR experiment

If the recoupled spin $I > 1/2$:

- Inverse REDOR

If both nuclei $I > 1/2$:

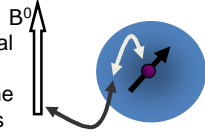
- TRAPDOR (transfer of population in double resonance)

- REAPDOR (rotational-echo adiabatic-passage double resonance)

Magnetic shielding and chemical shift theory

Magnetic shielding/Chemical shift

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



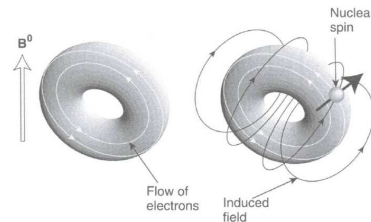
$$\hat{H}_{CS} = \hat{H}_{CS}^{iso} + \hat{H}_{CS}^{aniso}$$

- Chemical shift interaction is predominantly an intramolecular interaction

Two step process:

(1) External magnetic B_0 field induces currents in the electron clouds of the molecules

(2) Circulating electronic currents → generate an induced magnetic field $B_{MS}^{induced}$



M. Levitt, spin dynamics, 2nd edition, Wiley & sons, (2008)

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Magnetic shielding and chemical shift

Theory: magnetic shielding Hamiltonian

- Strength of induced field increases linearly with B_0 :

$$\mathbf{B}_{MS}^{induced} = \boldsymbol{\sigma} \cdot \mathbf{B}_0$$

with: $\boldsymbol{\sigma}$ "magnetic shielding" or "chemical shift" tensor

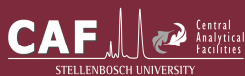
$$\boldsymbol{\sigma} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix} \text{ matrix takes into account that the induced field is usually in a different direction to } B_0$$

-Hamilton operator of the

magnetic shielding interaction: $\hat{H}_{CS} = -\gamma \mathbf{B}_{MS}^{induced} \cdot \hat{\mathbf{I}} \cong -\gamma \sigma_{zz} B_0 \hat{I}_z$

→ Energy correction term of them magnetic shielding: $E_{CS} = \hbar \sigma_{zz} B_0 m$

(energy levels for each m are shifted by the value given by this equation)

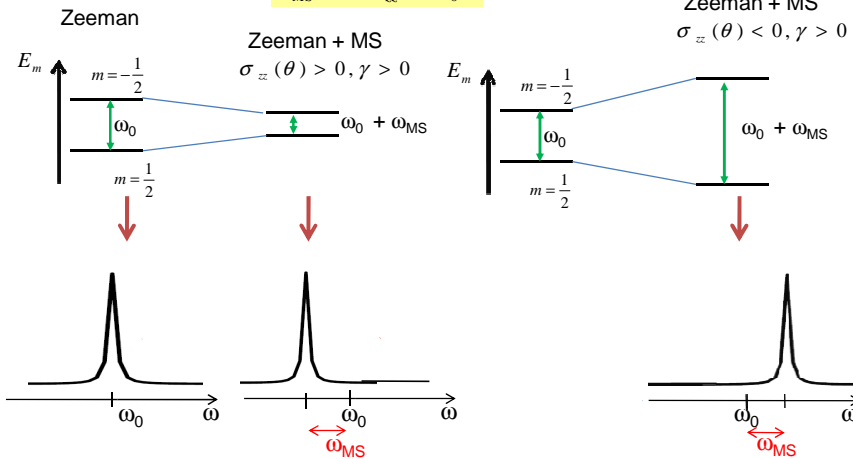


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Magnetic shielding and chemical shift

Theory: impact on the energy eigenstates

Effect on energy levels $E_{MS} = \gamma \hbar \sigma_{zz}(\theta) B_0 m$



Magnetic shielding and chemical shift

Theory: definition of the chemical shift

Definition of the chemical shift

ω_{MS} contains structural information (shielding/deshielding due to electronic environment)

BUT

- depends on B_0 field \rightarrow makes comparison between different instruments difficult
- depends on sign of γ \rightarrow confusing, since direction of the frequency shift is switched for nuclei with positive and negative γ

SOLUTION

Chemical shift:

$$\delta = \frac{\omega - \omega_{ref}}{\omega_{ref}} = \frac{(\sigma_{zz}^{lab}(ref) - \sigma_{zz}^{lab})}{1 - \sigma_{zz}^{lab}(ref)}$$

Magnetic shielding and chemical shift

Theory: the chemical shift tensor

The chemical shift tensor

magnetic shielding tensor

$$\sigma = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix}$$

elements are replaced by

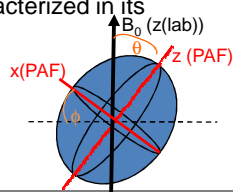
$$\delta_{\alpha\beta} = \frac{(\sigma_{\alpha\beta}(ref) - \sigma_{\alpha\beta})}{1 - \sigma_{\alpha\beta}(ref)}$$

chemical shift tensor

$$\delta = \begin{pmatrix} \delta_{xx} & \delta_{xy} & \delta_{xz} \\ \delta_{yx} & \delta_{yy} & \delta_{yz} \\ \delta_{zx} & \delta_{zy} & \delta_{zz} \end{pmatrix}$$

Very often the chemical shift tensor is represented and characterized in its principal axis frame (PAF)

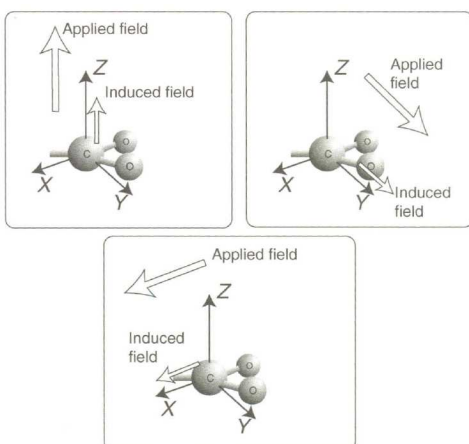
$$\delta^{PAF} = \begin{pmatrix} \delta_{xx}^{PAF} & 0 & 0 \\ 0 & \delta_{yy}^{PAF} & 0 \\ 0 & 0 & \delta_{zz}^{PAF} \end{pmatrix}$$



Magnetic shielding and chemical shift

Theory: the principal axis frame

What is the principal axis frame (PAF)?



The principal axis

example: carboxylate group

- For each nuclear site:
→ 3 special directions of the external magnetic field for which the induced field is parallel to the external field
= principal axis of the chemical shift tensor

-The PA are always perpendicular to each other

! Every nuclear site in a molecule Has, in general, cs-tensors with different PAF

Magnetic shielding and chemical shift

Theory: the cs tensor in PAF

Properties of the chemical shift tensor represented in PAF

Isotropic chemical shift: $\delta^{iso} = \frac{1}{3}(\delta_{xx} + \delta_{yy} + \delta_{zz})$ equation is valid in any frame!
sum of tensor diagonal elements is always the same

→ Determines the position of peaks in isotropic liquids

chemical shift anisotropy (CSA): $\delta^{aniso} = \delta_{zz}^{PAF} - \delta^{iso}$

→ Quantifies the deviation from isotropy of the CS tensor (solids only)

asymmetry (biaxiality): $\eta = \frac{\delta_{yy}^{PAF} - \delta_{xx}^{PAF}}{\delta^{aniso}}$ $0 \leq \eta \leq 1$

→ Quantifies the difference between the other two principal values (solids only)

convention for assigning principal values and principal axis of cs tensor:

$$|\delta_{zz}^{PAF} - \delta^{iso}| \geq |\delta_{xx}^{PAF} - \delta^{iso}| \geq |\delta_{yy}^{PAF} - \delta^{iso}|$$



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Magnetic shielding and chemical shift

Theory: properties of the isotropic chemical shift

- chemical shift (cs) range:

→ Main influence on the cs from low-lying electronic excited states.

Trend: the heavier the isotope the more low-lying electronic excited states

→ Increasing cs ranges with increasing isotope mass

(¹H: 10 ppm, ¹³C: 200 ppm, ²⁰⁵Pb several thousands ppm cs range)

- cs values: correlates with the electronegativity of neighboring groups

→ Electronegative atoms like O, Cl, F, etc. withdraw electron density of neighboring nucleus → increasing local fields → increased cs values

- Measured isotropic chemical shift is an average over rapid molecular motion (important if fast exchange reactions are present)

- Chemical shifts can be influenced by neighboring molecules

(important for solids, for example different signals for molecules in an asymmetric cell of a crystal)

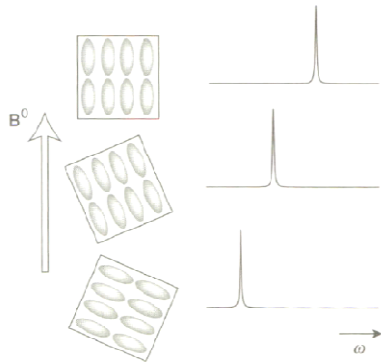


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Magnetic shielding and chemical shift

Theory: chemical shift interaction in solids

Chemical shift frequency: $\omega_{cs} = -\gamma B_0 (1 + \delta_{zz}(\theta, \phi))$



→ Example: a single crystal: the chemical shift depends on the orientation of the solid with respect to B_0

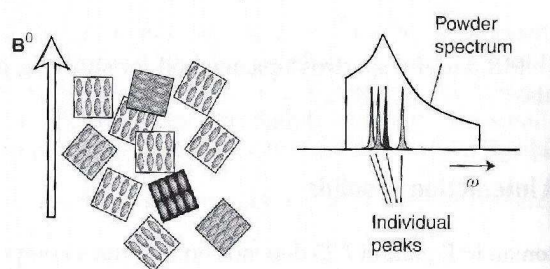
Magnetic shielding and chemical shift

Theory: chemical shift interaction in solids

A Powder spectrum

- Usually the sample is not single-crystal, but a powder

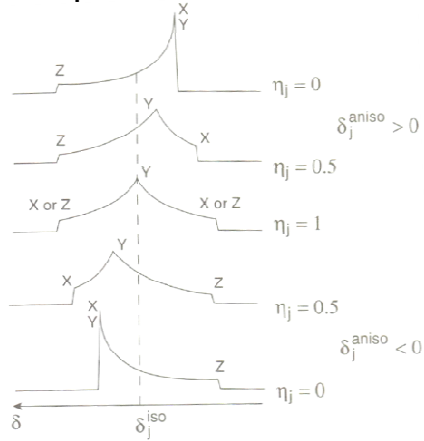
→ Molecules have all possible orientations



Magnetic shielding and chemical shift

Theory: chemical shift interaction in solids

Lineshapes of a Powder spectrum



→ Position of the center of gravity of the powder spectrum is determined by the isotropic chemical shift δ^{iso}

→ Lineshape of the powder spectrum is determined by asymmetry of chemical shift tensor η

→ Broadening of the powder pattern is determined by CSA δ^{aniso}

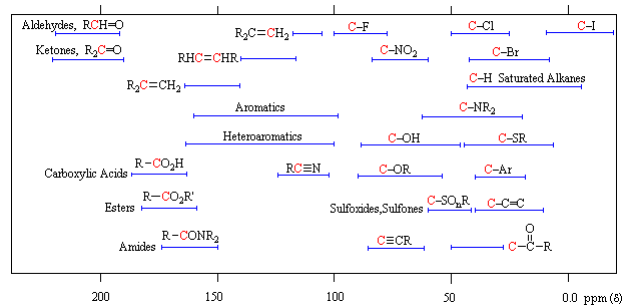
Magnetic shielding and chemical shift

Utilization: isotropic chemical shifts

Interpretation of isotropic chemical shifts: like in solution state NMR

→ Assignment of chemical environments

Example: ^{13}C chemical shift ranges:



Magnetic shielding and chemical shift

Utilization: isotropic chemical shifts

In solids:

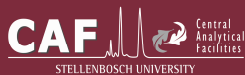
Chemical shift is influenced by neighboring molecules

→ Chemically identical molecules may have different chemical shifts depending on their structural order:

Crystalline - amorphous

Polymorphs: Crystall lattice (orthorhombic, monoclinic ...)

Experimental approach: MAS

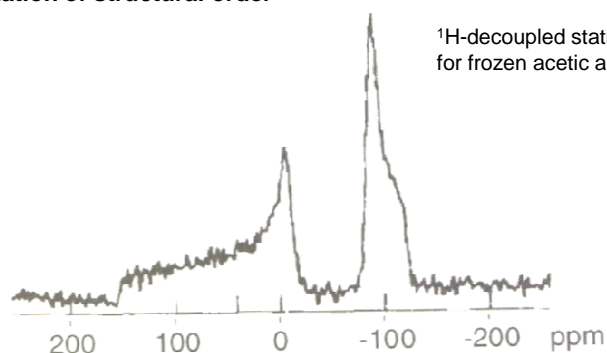


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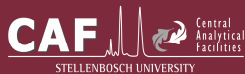
Magnetic shielding and chemical shift

Utilization: CSA and asymmetry

Characterization of structural order



Determination of CSA and η by static powder pattern
(if magnetic shielding is dominant interaction)



M. Levitt, spin dynamics, 2nd edition, Wiley & sons,(2008)

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