Characterization of Catalysts and Surfaces with Nuclear Magnetic Resonance

René Verel

Laboratorium für Anorganische Chemie,
ETH Zürich, HCI D117
verelr@ethz.ch
NMR Spectroscopy - An Introduction

Rene Verel
verelr@ethz.ch
HCI D117

❖ Outline

General Principles of NMR Spectroscopy
Interactions in NMR Spectroscopy
Information content of NMR Interactions
Characterization of (Molecular) Structure by NMR

❖ Courses

PCIV: Magnetic Resonance B.H. Meier, M.C. Ernst, G. Jeschke yearly
Structure Determination by NMR M. Ebert yearly
Advanced Magnetic Resonance M.C. Ernst approx. every third year

❖ Books


Principles of Spectroscopy

- The purpose is to obtain information about the molecular and/or atomic structure of matter.

- The method is to use the interaction between EM radiation and matter.
  1. Absorption/Emission of Energy by the system
     \[ \Delta E = E_2 - E_1 = h\nu \]
  2. Interaction with Electric or Magnetic part of the radiation
  3. Characteristic frequency of radiation for each type of spectroscopy.

![Diagram showing energy levels and transitions](image-url)
The Nuclear Spin

- Nuclear Property
- The inherent Angular Momentum of a Nucleus
- Purely Quantum Mechanic
- The magnitude of the Nuclear Spin is given by:

\[ p = |p| = \frac{h}{2\pi} \sqrt{l(l+1)} \]

- The Spin Quantum number, \( l \), is a property of the nuclear species.
The Nuclear Magnetic Moment

- The Nuclear Spin implies a Nuclear Magnetic Moment
- Vector parallel with the Nuclear Spin
- Proportional to the Spin with the gyromagnetic ratio, $\gamma$
  
  $\mu = \gamma \cdot p$

- The gyromagnetic ratio is a property of the nuclear species
Orientational Quantization States

In a (strong) external magnetic field the component of the nuclear spin along that field is quantized

\[ p_z = \frac{\hbar}{2\pi} l \quad \mu_z = \gamma \frac{\hbar}{2\pi} l \]
\[ = \frac{\hbar}{2\pi} (l - 1) \quad = \gamma \frac{\hbar}{2\pi} (l - 1) \]
\[ = \frac{\hbar}{2\pi} (l - 2) \quad = \gamma \frac{\hbar}{2\pi} (l - 2) \]
\[ \ldots \quad \ldots \]
\[ = \frac{\hbar}{2\pi} (-l) \quad = \gamma \frac{\hbar}{2\pi} (-l) \]

OR

\[ p_z = \frac{\hbar}{2\pi} m \quad \mu_z = \gamma \frac{\hbar}{2\pi} m \]

where \[ m \in [-l, -l+1, -l+2, \ldots, l] \]
### Spin Quantum Numbers

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Spin Quantum Number</th>
<th>Magnetic Quantum Number</th>
</tr>
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<tbody>
<tr>
<td>$^{12}$C, $^{18}$O</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>$^{1}H$, $^{13}$C, $^{15}$N, $^{19}$F, $^{31}$P</td>
<td>1/2</td>
<td>-1/2, +1/2</td>
</tr>
<tr>
<td>$^{2}$H, $^{14}$N</td>
<td>1</td>
<td>-1, 0, +1</td>
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<tr>
<td>$^{7}$Li, $^{23}$Na, $^{37}$Cl, $^{87}$Ru</td>
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<td>-3/2, -1/2, 1/2, 3/2</td>
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<tr>
<td>$^{17}$O, $^{25}$Mg, $^{27}$Al</td>
<td>5/2</td>
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<tr>
<td>$^{45}$Sc, $^{51}$V, $^{59}$Co</td>
<td>7/2</td>
<td>-7/2, -5/2, -3/2, -1/2, 1/2, 3/2, 5/2, 7/2</td>
</tr>
</tbody>
</table>

**Table Note:**
- Yellow box indicates $I=1/2$.
- Green box indicates $I>1/2$.

### Periodic Table

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<tr>
<th>IA</th>
<th>IIA</th>
<th>IIIB</th>
<th>IVB</th>
<th>VB</th>
<th>VIB</th>
<th>VIIB</th>
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<th>VA</th>
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<td>K</td>
<td>Rb</td>
<td>Cs</td>
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<td>*La</td>
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<td>Hf</td>
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<td>Br</td>
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<td>Co</td>
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<td>Cu</td>
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<td>Re</td>
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<td>Bi</td>
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<td>Rn</td>
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<td></td>
</tr>
</tbody>
</table>

**Notes:**
- $^I$ indicates the spin quantum number.
- $^m$ indicates the magnetic quantum number.

**Isotope Spin Quantum Numbers:**
- $^{12}$C, $^{18}$O: $I=0$; $m=-1/2, +1/2$.
- $^{1}$H, $^{13}$C, $^{15}$N, $^{19}$F, $^{31}$P: $I=1/2$, $m=-1/2, +1/2$.
- $^{2}$H, $^{14}$N: $I=1$, $m=-1, 0, +1$.
- $^{7}$Li, $^{23}$Na, $^{37}$Cl, $^{87}$Ru: $I=3/2$, $m=-3/2, -1/2, 1/2, 3/2$.
- $^{17}$O, $^{25}$Mg, $^{27}$Al: $I=5/2$, $m=-5/2, -3/2, -1/2, 1/2, 3/2, 5/2$.
- $^{45}$Sc, $^{51}$V, $^{59}$Co: $I=7/2$, $m=-7/2, -5/2, -3/2, -1/2, 1/2, 3/2, 5/2, 7/2$.
Zeeman Interaction Energies

- A (nuclear) magnetic Moment interacts with a magnetic field with an energy

\[ E_m = -m \cdot \gamma \cdot \frac{h}{2\pi} \cdot B_0 \]

\[ \Delta E = \frac{\gamma \hbar B_0}{2\pi} \]

\[ \Delta E = \Delta E_{m+1} - E_m = -\gamma \cdot \frac{h}{2\pi} \cdot B_0 \]
Boltzmann Population

- The populations of the states is given by a Boltzmann Distribution
  \[ \frac{N_\alpha}{N_\beta} = e^{\frac{\Delta E}{kT}} \approx 1 + \frac{\Delta E}{kT} \approx 1.000064 \]

- Signal Strength is proportional to the difference between Boltzmann Populations
  \[ \Delta E = \frac{-\gamma h}{2\pi} \cdot B_0 \]
# NMR Signal Strength

- The energy difference is usually given in frequency units

\[ \nu_0 = \frac{-\gamma}{2\pi} \cdot B_0 \]

## Properties of some nucleotides of importance to NMR

<table>
<thead>
<tr>
<th>Nucleotide</th>
<th>gyromagnetic ratio $\gamma$ [10$^7$ rad T$^{-1}$ s$^{-1}$]</th>
<th>Natural Abundance [%]</th>
<th>$\nu_0$ [MHz] ($B_0 = 4.7$ T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$H</td>
<td>26.7519</td>
<td>99.985</td>
<td>200.0</td>
</tr>
<tr>
<td>$^{13}$C</td>
<td>6.7283</td>
<td>1.108</td>
<td>50.1</td>
</tr>
<tr>
<td>$^{15}$N</td>
<td>-2.7126</td>
<td>0.370</td>
<td>20.2</td>
</tr>
<tr>
<td>$^{19}$F</td>
<td>25.1815</td>
<td>100.000</td>
<td>188.2</td>
</tr>
<tr>
<td>$^{31}$P</td>
<td>10.8394</td>
<td>100.000</td>
<td>81.0</td>
</tr>
</tbody>
</table>

**More Signal**

- Higher Magnetic Field ($B_0$)
- Higher gyromagnetic Ratio ($\gamma$)
- More Spins (e.g. higher nat. ab.)
- Lower Temperature
NMR Interactions

- **Zeeman Interaction**  
  10^6-10^9 Hz
- **Rf Field**
  Under experimental control for Spin rotations  
  10^0-10^5 Hz
- **Chemical Shift Interaction**
  Reports on local electronic environment  
  10^2-10^4 Hz
- **Magnetic Dipole-Dipole Interaction**
  Reports on the distance between two coupled spins.  
  10^2-10^5 Hz
- **Scalar J-Coupling**
  Reports on chemical bonds between two spins.  
  10^0-10^2 Hz
- **Quadrupole Coupling**
  Reports on the electric field gradient around the nucleus.  
  10^0-10^7 Hz

Only for I > 1/2
Chemical Shift

- The exact frequency of a nucleus depends on the local electronic structure
  \[ B_{\text{eff}} = B_0 - \sigma \cdot B_0 \]
  or
  \[ v_{\text{eff}} = \frac{\gamma}{2\pi} \cdot B_0 \cdot (1 - \sigma) \]

- The shielding constant \( \sigma \) is the sum of many effects (diamagnetic-, paramagnetic, ringcurrent-, intermolecular-effects) and is rather difficult to calculate accurately.

- The chemical shift modifies the magnetic field on a part per million scale (ppm).
  (e.g. when \( v_0 = 400 \) MHz, then 1 ppm = 400 MHz x 10^{-6} = 400 Hz)
Chemical Shift

- The Integral of a signal is proportional to the number of nuclei.
- Some effects distort value of an integral more or less severely.
- The chemical shift of a given nucleus depends on the (chemical) environment of that nucleus.
- Lots of empirical knowledge about the value of the chemical shift in a given environment.
Chemical Shift

- The chemical shift of a given nucleus depends on the (chemical) environment of that nucleus.
- Lots of empirical knowledge about the value of the chemical shift in a given environment.
- The chemical shift (in ppm) is a relative scale to a reference compound (usually TMS for $^1\text{H}$ and $^{13}\text{C}$).
Structure Determination

- Brucine (C\textsubscript{23}H\textsubscript{26}N\textsubscript{2}O\textsubscript{4})

![Chemical structure of Brucine]

- \textsuperscript{1}H NMR spectrum
- \textsuperscript{13}C NMR spectrum
Structure Determination

- Brucine ($C_{23}H_{26}N_2O_4$)
Structure Determination

- Brucine ($\text{C}_{23}\text{H}_{26}\text{N}_{2}\text{O}_{4}$)
The reactivity of acyl chlorides towards Na(OCP)


\[
2 \text{Na(OCP)} + 2 \text{MesCl} \rightarrow \text{MesC} = \text{O} = \text{P} - \text{O} = \text{Mes} \\
\]

\[\text{Mes = } \]

\[31^P \text{ } -35\degree\text{C / 17 h}\]
Reaction Kinetics

❖ The reactivity of acyl chlorides towards Na(OCP)

Reaction Kinetics

The reactivity of acyl chlorides towards Na(OCP)  

Table 1:

<table>
<thead>
<tr>
<th></th>
<th>Forward reaction</th>
<th>Reverse reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$</td>
<td>$2.36 \times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>$k_2$</td>
<td>4.98</td>
<td>$k_{2r}$ 1.47</td>
</tr>
<tr>
<td>$k_3$</td>
<td>$2.08 \times 10^{-2}$</td>
<td>$k_{3r}$ 5.02 $\times 10^{-3}$</td>
</tr>
<tr>
<td>$k_4$</td>
<td>$8.40 \times 10^{-1}$</td>
<td>$k_{4r}$ 3.64 $\times 10^{-4}$</td>
</tr>
<tr>
<td>$k_5$</td>
<td>$8.19 \times 10^{-2}$</td>
<td></td>
</tr>
</tbody>
</table>
Molecular Weight Determination

Diffusion (DOSY) $^1$H NMR as an Alternative Method for Molecular Weight Determination of Poly(ethylene furanoate) (PEF) Polyesters


$$\frac{I(g)}{I(0)} = \exp\left(-\gamma g\delta^2 D\left(\Delta - \frac{\delta}{3}\right)\right)$$

$D$: Diffusion Coefficient
$g,\delta,\Delta$: Experimental Parameters
Molecular Weight Determination

- Diffusion (DOSY) 1H NMR as an Alternative Method for Molecular Weight Determination of Poly(ethylene furanoate) (PEF) Polyesters

- Calibration Curves using PET reference samples

- Usually: Stokes-Einstein

\[ r = \frac{kT}{6\pi\eta D} \]
Molecular Weight Determination

- Diffusion (DOSY) 1H NMR as an Alternative Method for Molecular Weight Determination of Poly(ethylene furanoate) (PEF) Polyesters

Catalyst Stability

- Selective Production of Carbon Monoxide via Methane Oxychlorination over Vanadyl Pyrophosphate

Catalyst Stability

- Selective Production of Carbon Monoxide via Methane Oxychlorination over Vanadyl Pyrophosphate

- $V^{4+}$ and $V^{3+}$ are paramagnetic. *Strong* shift of the (spatially close by) $^{31}$P resonances through the Hyperfine interaction.
Catalyst adsorbed Species

- CO$_2$-to-Methanol Hydrogenation on Zirconia-Supported Copper Nanoparticles: Reaction Intermediates and the Role of the Metal–Support Interface
  DOI: 10.1002/anie.201610166

\[
\begin{align*}
\text{CO}_2 + \frac{1}{2} \text{H}_2 & \rightarrow \text{H}^+ \quad \text{13C} \quad \text{D}^+ \\
\text{Zr} \cdots \text{Zr} & \quad \text{Zr} \cdots \text{Zr} \\
\text{H/D exchange} & \\
\text{13C} \quad \text{D} & \quad \text{13C} \quad \text{D} \\
\text{Zr} \cdots \text{Zr} & \quad \text{Zr} \cdots \text{Zr}
\end{align*}
\]
Catalyst adsorbed Species

- CO$_2$-to-Methanol Hydrogenation on Zirconia-Supported Copper Nanoparticles: Reaction Intermediates and the Role of the Metal–Support Interface

DOI: 10.1002/anie.201610166

**Figure S18.** Liquid-state $^1$H NMR after washing Cu/ZrO$_2$ with D$_2$O after the two steps hydrogenation of $^{13}$CO$_2$. A doublet of pentet centered at 3.24 ppm can be observed, related to the $^1$H-13C and $^1$H-2D J-couplings. This is consistent with a $^{13}$CHD$_2$ group. This signal merges into a single peak at 3.24 ppm when a $^{13}$C decoupling pulse is applied. The other peaks are impurities introduced during the process. They do not change upon $^{13}$C decoupling.

**Figure S19.** Liquid-state $^{2}$D NMR after washing Cu/ZrO$_2$ with H$_2$O after the two steps hydrogenation of $^{13}$CO$_2$. A doublet centered at 3.19 ppm can be observed, related to the $^2$D-$^{13}$C J-coupling. No fine structure can be distinguished (no $^1$H decoupling was applied).
Chemical Shift in solids

- No Brownian Motion but “static” molecules
- The Chemical Shift is dependent on the orientation wrt the Magnetic Field (Rank 2 Tensor)

\[
\begin{align*}
\text{induzierte Elektronenbewegung} & \quad \text{1s-Orbital} \\
\text{induziertes magnetisches Moment } \mu \text{ am Kern} & \quad B_0
\end{align*}
\]

\[
\begin{align*}
\text{13C} & \quad \text{H} & 13 \text{ ppm} \\
\text{13C} & \quad \text{H} & 148 \text{ ppm} \\
\text{13C} & \quad & 223 \text{ ppm}
\end{align*}
\]
Chemical Shift in solids

- Orientation dependency of the signal
- Three Euler Angles ($\alpha, \beta, \gamma$) needed to orient a “molecule”.
- Not all orientations are equally prevalent in a uniform and random powder. (only one polar but many equatorial)
Chemical Shift in solids

- A tensor is characterized by its three principal components \( (\delta_{11}, \delta_{22}, \delta_{33}) \)
- In general all three are different and easy to determine from a powder spectrum
- The principal components are connected to the molecular frame
Chemical Shift in solids

- Alternative parameterizations for the tensor characterization are common

![Graph showing chemical shift measurements](image)

**Tensor Characterization:**

\[
\begin{align*}
\delta_{11}, \delta_{22}, \delta_{33} & \\
\delta_{\text{iso}} &= \frac{1}{3}(\delta_{11} + \delta_{22} + \delta_{33}) & \delta_{\text{iso}} &= \frac{1}{3}(\delta_{11} + \delta_{22} + \delta_{33}) \\
\text{span} &= \Omega = \delta_{11} - \delta_{33} > 0 & \quad |\delta_{zz} - \delta_{\text{iso}}| & \geq |\delta_{xx} - \delta_{\text{iso}}| \geq |\delta_{yy} - \delta_{\text{iso}}| \\
\text{skew} &= \kappa = 3(\delta_{22} - \delta_{\text{iso}})/\Omega & \quad \text{anisotropy} &= \delta = \delta_{zz} - \delta_{\text{iso}} \\
\end{align*}
\]

asymmetry = \eta = 3(\delta_{yy} - \delta_{xx})/\delta
When two (or more) principal values are equal, it tells us about the local symmetry around the nucleus.

202 MHz $^{31}\text{P}$ NMR spectrum on a static sample showing the axial tensor, $\sigma_{11} = \sigma_{22} = -24.0$ and $\sigma_{33} = -43.0$ ppm.

View of trop$_3\text{P}$ along the threefold symmetry axis.
Chemical Shift in solids

- Symmetry *might* be an effect of dynamic averaging.
  E.g. Rotor Phases lead to averaging of tensor elements

1. Hexamethylbenzene
2. Benzene
3. Permethylferrocene

<table>
<thead>
<tr>
<th></th>
<th>$\delta_{11}$</th>
<th>$\delta_{22}$</th>
<th>$\delta_{33}$</th>
<th>$\delta_{\text{iso}}$</th>
<th>$\Omega$</th>
<th>$\kappa$</th>
</tr>
</thead>
<tbody>
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<td><strong>Hexamethylbenzene</strong></td>
<td>87</td>
<td>232</td>
<td>154</td>
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<td>137</td>
<td>208</td>
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<td>187</td>
<td>13</td>
<td>129</td>
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<tr>
<td><strong>Permethylferrocene</strong></td>
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<td>127</td>
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<td>23</td>
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<td>104</td>
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<td></td>
<td>289</td>
<td>101</td>
<td>101</td>
<td>34</td>
<td>79</td>
<td>67</td>
</tr>
</tbody>
</table>
## Chemical Shift in solids

### Tris-Ethene Complex of Silver Cations

#### $^{13}$C NMR of Ethene and Complexes

<table>
<thead>
<tr>
<th>#</th>
<th>$\delta_{11}$</th>
<th>$\delta_{22}$</th>
<th>$\delta_{33}$</th>
<th>$\delta_{iso}$</th>
<th>$\Omega$</th>
<th>$\kappa$</th>
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<td>1</td>
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<td>112</td>
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<tr>
<td>3</td>
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<tr>
<td>4</td>
<td>134</td>
<td>65</td>
<td>-11</td>
<td>63</td>
<td>145</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Chemical shifts of principle tensor components in ppm relative to TMS. (1) Free Ethene, (2) $[\text{Ag}(\eta^2-C_2H_4)_3][\text{Al(OR)}_4]$, (3) $[\text{Ag}(\eta^2-C_2H_4)][\text{Al(OC(CH}_3)(CF}_3)_2]_4$, (4) Zeise's Salt.
Chemical Shift in solids

- Structural Information from $^{29}\text{Si}$ Chemical Shifts

- $\text{Si}^{(4)}$
- $\text{Si}^{(3)}$
- $\text{Si}^{(2)}$
- $\text{Si}^{(1)}$
- $\text{Si}^{(0)}$
Powder Lineshapes

- Information vs. Resolution

Ca CH₃COO · 2 H₂O

Carbonyl

Methyl

4 Inequivalent molecules
Magic Angle Spinning (MAS)

- $1^{13}$C-Alanine

MAS: $\theta = 54.7^\circ$

Bearing Air

Drive Air

Very Fast

Static

Slow

$\delta$ [ppm]
Chemical Shift in solids - MAS

- Structural Information from $^{29}$Si Chemical Shifts
$^{29}$Si MAS NMR of Potassium Silicate Glasses

- Detection and Quantification of $Q^2$ sites in three membered rings
NMR Interactions - Chemical Shift

- Effect of $^{27}$Al neighbours on $^{29}$Si Chemical Shifts

Magic Angle Spinning

$^{29}$Si NMR

Decreasing amount of Al

- Magic Angle Spinning

$^{27}$Al NMR
$^{29}$Si MAS NMR of Treated Zeolites

Untreated Material

Treated Material

Q$^3$?  Q$^4$?  Q$^4''$?  Q$^4'$?
$^{29}\text{Si MAS NMR of Treated Zeolites}$

- Surface Species $Q^3$
- Single Pulse Experiment
- $^1\text{H} - ^{29}\text{Si Cross Polarization Experiment}$
NMR Interactions - Quadrupole

- For $I > 1/2$, nuclei have a non-spherical charge distribution in the nucleus and this gives rise to a quadrupole moment.

- The Quadrupole moment interacts with the electric field gradient.

- The Quadrupole Coupling Constant, $C_Q = \frac{eQV_{zz}}{2I(2I-1)\hbar}$, depends on the system.

Diagram showing the relationship between coordination number and $^{27}$Al $C_Q$ in MHz.
NMR Interactions - Quadrupole

Going through the mathematics and applying the secular approximation we get a frequency caused by the quarupole interaction

\[
\omega_Q = \frac{3eQV_{zz}}{4l(2l-1)\hbar^2} \left( 3\cos^2 \theta - 1 + \eta_Q \sin^2 \theta \cos 2\gamma \right)
\]

**Spin 1**

- \( m = -1 \)
  - \( \omega_0 - \omega_Q \)
  - \( \omega_0 \)
  - \( \omega_0 + \omega_Q \)

- \( m = 0 \)
  - \( \omega_0 \)

- \( m = +1 \)
  - \( \omega_0 - \omega_Q \)
  - \( \omega_0 \)
  - \( \omega_0 + \omega_Q \)

**Single Crystal**

- \( 2\omega_Q \)

**Powder**
NMR Interactions - Quadrupole

Spin 3/2

\[ m = \frac{3}{2} \]

\[ m = -\frac{1}{2} \]

\[ m = +\frac{1}{2} \]

\[ m = +\frac{3}{2} \]

\[ \omega_0 \]

ST

CT

\[ \omega_0 + 2\omega_Q \]

\[ \omega_0 \]

CT

ST

\[ \omega_0 - 2\omega_Q \]

The Central Transition has NO Angular Dependency
NMR Interactions - Quadrupole

- Often the Quadrupolar Interaction is big and the first order approximation is not good enough.

- First Order Term

\[ \omega_Q^{(1)} = \frac{3eQV_{zz}}{4I(2I-1)\hbar^2} \frac{1}{1 + \eta_Q \sin^2 \theta \cos \gamma} (3 \cos^2 \theta - 1) \]

- Second Order Term

\[ \omega_Q^{(2)} \propto \left( \frac{3eQV_{zz}}{4I(2I-1)\hbar} \right)^2 \frac{1}{\omega_0} (A + Bd_{00}^{(2)}(\theta) + Cd_{00}^{(4)}(\theta)) \]

\[ d_{00}^{(2)}(\theta) \propto 3 \cos^2 \theta - 1 \]

\[ d_{00}^{(4)}(\theta) \propto 35 \cos^4 \theta - 30 \cos^2 \theta + 3 \]

- The Second Order Term:

  Scales with the inverse of the Larmor Frequency (and therefore with B₀)
  Contains an orientation independent term (A)
  Contains a second rank term (B)
  Contains a fourth rank term (C)
NMR Interactions - Quadrupole

**Spin 3/2**

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

\[
\begin{align*}
\omega_0 & \quad \omega_0 + 2\omega_Q^{(1)} & & \omega_0 + 2\omega_Q^{(1)} + \omega_{Q,ST} \\
\omega_0 & \quad \omega_0 & & \omega_0 - \omega_{Q,CT}^{(2)} \\
\omega_0 & \quad \omega_0 - 2\omega_Q^{(1)} & & \omega_0 - 2\omega_Q^{(1)} + \omega_{Q,ST}^{(2)}
\end{align*}
\]
Titanocene dichloride

Static powder QCPMG experiment at $B_0=11.7$ T ($^1$H 500 MHz)

$C_Q = 22.18$ (+/- 0.03) MHz

$\eta_Q = 0.612$ (+/- 0.003)
NMR Interactions - Quadrupole

- Magic Angle Spinning of Quadrupoles with second order effects

Central Transition line is narrowed

Fourth rank term (C) remains

Isotropic term (A) remains

Static

MAS
NMR Interactions - Quadrupole

- Second order Quadrupole and Magnetic Field Strength

Isotropic and fourth rank term scale with $1/\omega_0$
Quadrupole Interaction: High Resolution

Is it possible to get high resolution Spectra of Quadrupoles?

Well, yes:
1. Go to very high field
2. Rotate around two axes simultaneously (DOR)
3. Rotate around two axes consecutively (DAS)
4. Use the different but related 2nd order shifts of the ST and CT (MQMAS and STMAS)
Quadrupole Interaction: MQMAS

- Correlation between Triple Quantum and Single Quantum Coherence in a 2D experiment

\[ ^{23}\text{Na} \]

Sodium Citrate

Position of centre of gravity of ridge
\[ \delta_{\text{iso}} \text{ and } P_Q \]

Isotropic spectrum
number of species and relative intensities

Cross-section along ridge
\[ C_Q \text{ and } \eta_Q \]
Quadrupole Interaction: MQMAS

- Direct evidence of the effect of synthesis conditions on aluminum siting in zeolite ferrierite: A 27Al MQ MAS NMR study
Quadrupole Interaction: MQMAS

$^{27}\text{Al}$ MQMAS on differently prepared Sr/Al mixed oxides with Sr/Al = 1.25.

No Calcination

Calcination at 1000 °C

From Sr-hydroxide precursor