Solid-state NMR Spectroscopy - An Introduction

Rene Verel
verelr@ethz.ch
HCI D117

❖ Outline

General Principles of NMR Spectroscopy

Interactions relevant to NMR Spectroscopy (and their information content)

Differences between solution and solid state NMR

Selected/Special experimental techniques

❖ 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

M.H. Levitt: "Spin Dynamics: Basics of Nuclear Magnetic Resonance", John Wiley & Sons, 2001
J. Keeler: "Understanding NMR Spectroscopy", John Wiley & Sons, 2005.

M. Duer: "Introduction to solid-state NMR", Blackwell Science Ltd (Oxford), 2004.
K. Schmidt-Rohr, H.W. Spiess: "Multidimensional Solid-State NMR and Polymers", Academic Press, 1994.

NMR Spectroscopy - A short Introduction

- Many Nuclei have an Inherent Angular Moment (or Spin) which is quantized and characterised by a spin quantum number

$$I = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots, 6$$

- Associated with the Spin is a Magnetic Moment

$$\vec{\mu} = \gamma \vec{I}$$

- The z-component of the spin angular momentum can only assume $2I + 1$ different values.

$$\mu_z = \gamma I_z = \frac{\gamma m h}{2\pi} \text{ with } m = -I, -I+1, \ldots, I-1, I$$

- In an external magnetic field along z, this gives an energy

$$E = -\mu_z B_0 = -\frac{\gamma m h}{2\pi} B_0$$

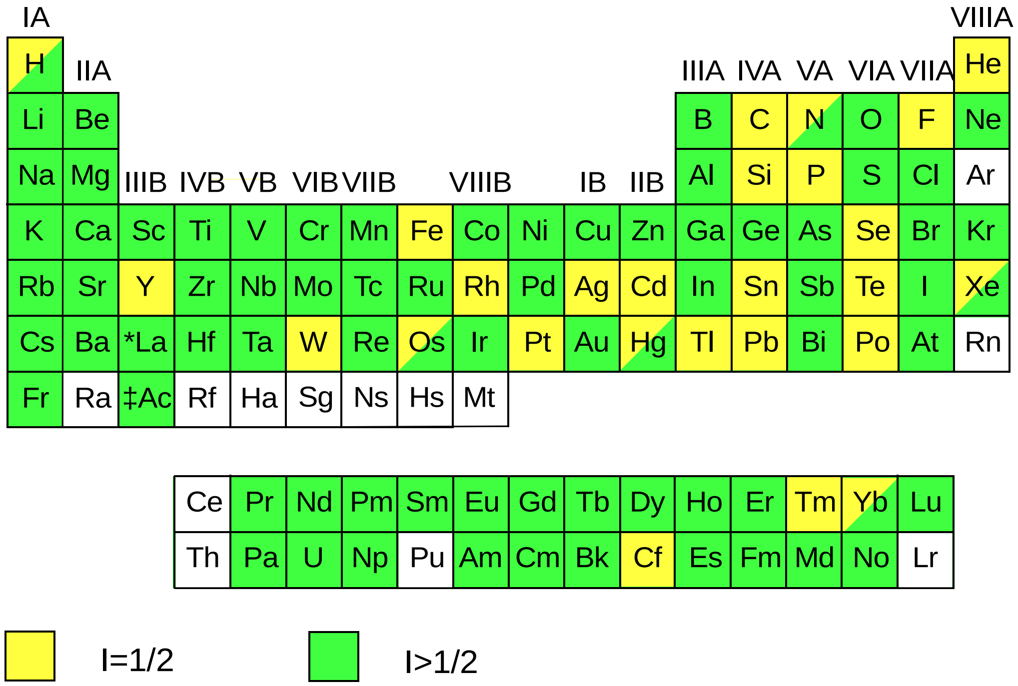
- The energy difference or resonance frequency is then

$$\Delta E = -\frac{\gamma h}{2\pi} B_0 \text{ or } \omega = -\gamma B_0$$

- The populations of the states is given by a Boltzmann Distribution

$$\frac{N_{1/2}}{N_{-1/2}} = e^{\Delta E/(kT)} \approx 1.0002$$

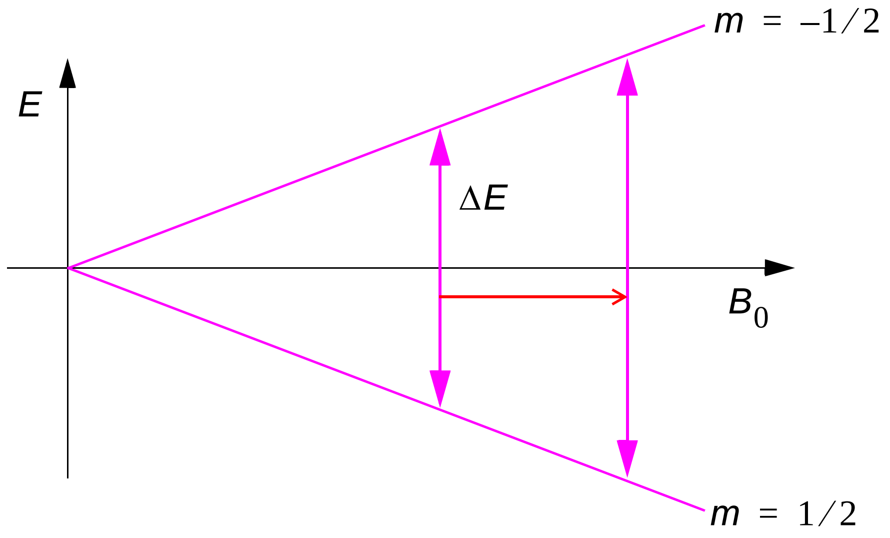
NMR Spectroscopy - A short Introduction



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

NMR Spectroscopy - A short Introduction

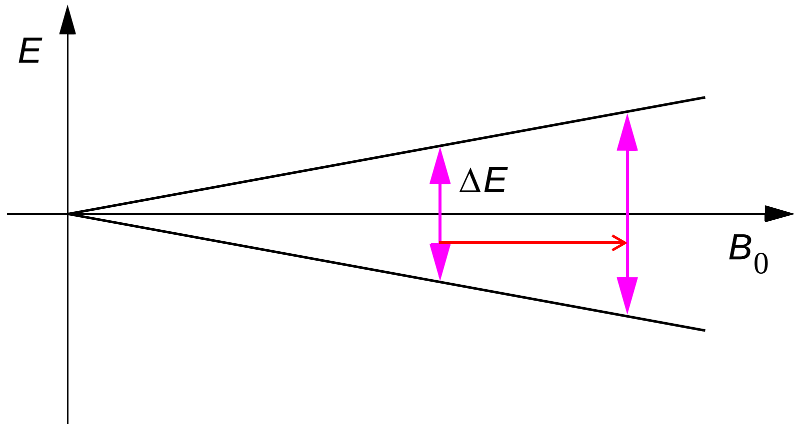
$$\Delta E = -\frac{\gamma h}{2\pi} B_0$$



Properties of some nucleotides of importance to NMR

Nucleotide	gyromagnetic ratio γ [10^7 rad T^{-1} s^{-1}]	Natural Abundance [%]	ν_0 [MHz] (B_0 = 9.4 T)	ν_0 [MHz] (B_0 = 14.1 T)
^{1}H	26.7519	99.985	400.0	600.0
^{13}C	6.7283	1.108	100.2	150.9
^{15}N	- 2.7126	0.370	40.3	60.8
^{19}F	25.1815	100.000	376.3	564.5
^{31}P	10.8394	100.000	161.9	242.9

NMR Spectroscopy - A short Introduction



$$\Delta E = -\frac{\gamma h}{2\pi} B_0$$

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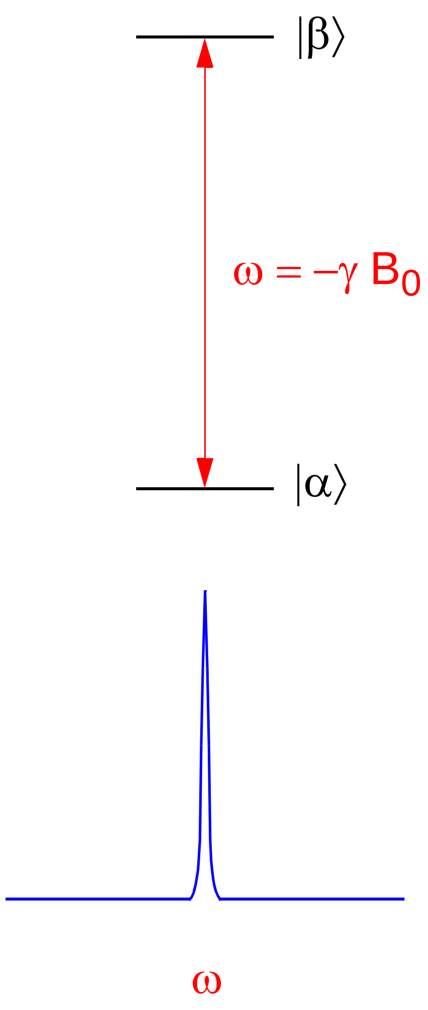
NMR Interactions

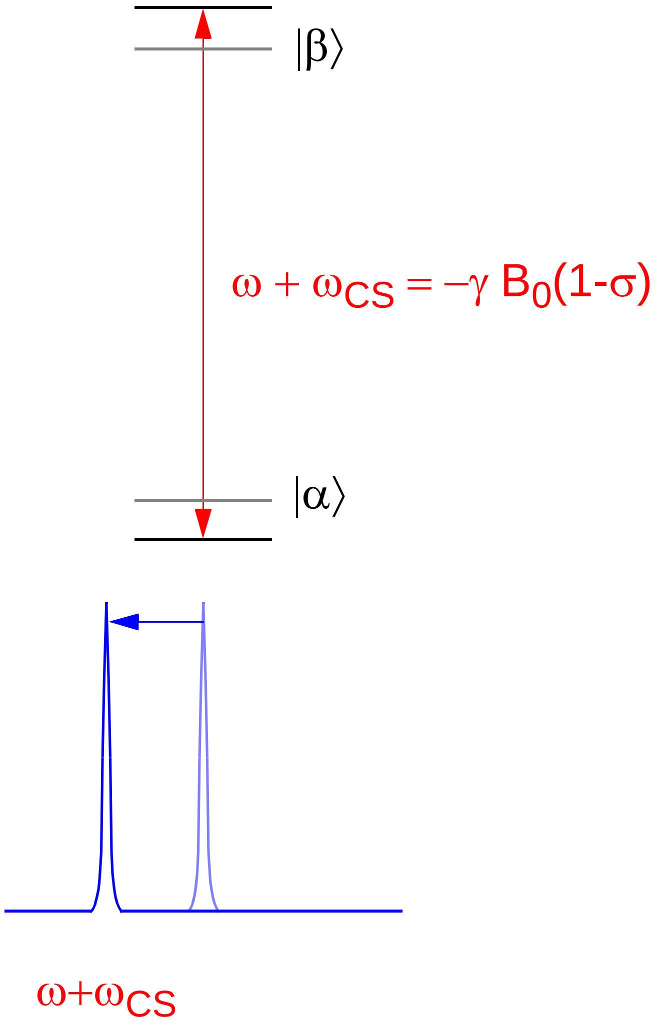
❖ Zeeman Interaction	10^6-10^9 Hz
❖ Rf Field Under experimental control for Spin rotations	10^0-10^5 Hz
❖ Chemical Shift Interaction Reports on local electronic environment	10^2-10^4 Hz
❖ Magnetic Dipole-Dipole Interaction Reports on the distance between two coupled spins.	10^2-10^5 Hz
❖ Scalar J-Coupling 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 $I > 1/2$

- Zeeman Interaction

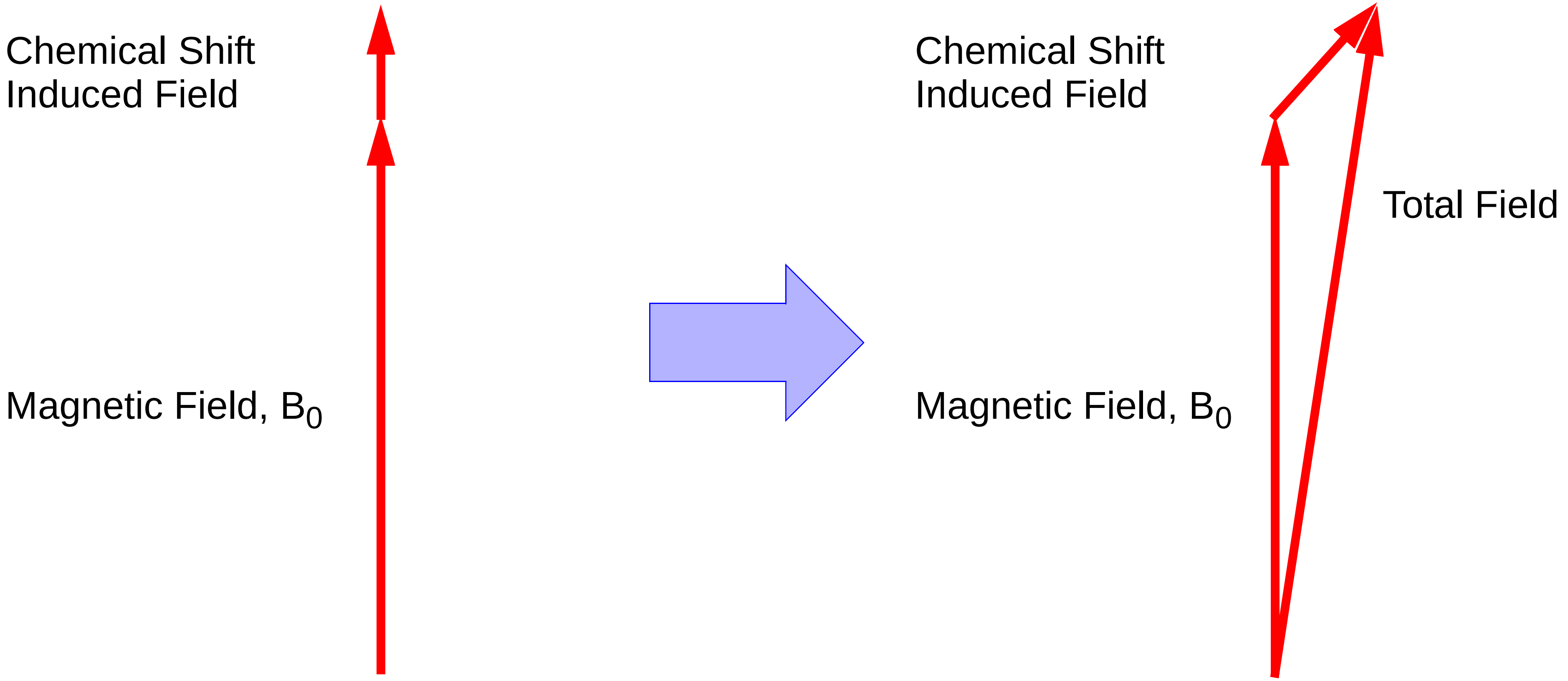


- Zeeman + Chemical Shift



NMR Interactions - Tensors

- In contrast to what we assumed up to now, the Chemical Shift interaction (like all tensorial interactions in NMR) does not only change the magnitude but *also changes the direction* of the Field.
- How big this change is (often) depends on the orientation of the molecular frame with respect to the static magnetic field.



NMR Interactions - Tensors

- The chemical shift, dipolar and quadrupole can be described by second rank tensors.

$$\underset{\sim}{A}_{PAS}^{(k,n)} = \begin{bmatrix} A_{11} & 0 & 0 \\ 0 & A_{22} & 0 \\ 0 & 0 & A_{33} \end{bmatrix}$$

- The general form of the Hamiltonian is given by

$$\hat{H}^{(k,n)} = \vec{\hat{I}}_k \cdot A^{(k,n)} \cdot \vec{\hat{I}}_n$$

- High Field Approximation (example Chemical Shift)

$$\begin{aligned} \hat{H}_{CS}^{(k)} &= \vec{\hat{I}}_k \cdot (-\gamma_k)\underset{\sim}{\sigma}^{(k)} \cdot \vec{B}_0 \\ &= (-\gamma_k)(\hat{I}_{kx}, \hat{I}_{ky}, \hat{I}_{kz}) \cdot \begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{bmatrix} \cdot \begin{bmatrix} 0 \\ 0 \\ B_0 \end{bmatrix} \\ &= \sigma_{xz}\omega_0^{(k)}\hat{I}_{kx} + \sigma_{yz}\omega_0^{(k)}\hat{I}_{ky} + \sigma_{zz}\omega_0^{(k)}\hat{I}_{kz} \end{aligned}$$

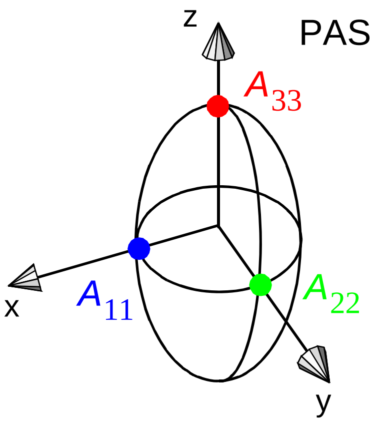
Orientation dependent

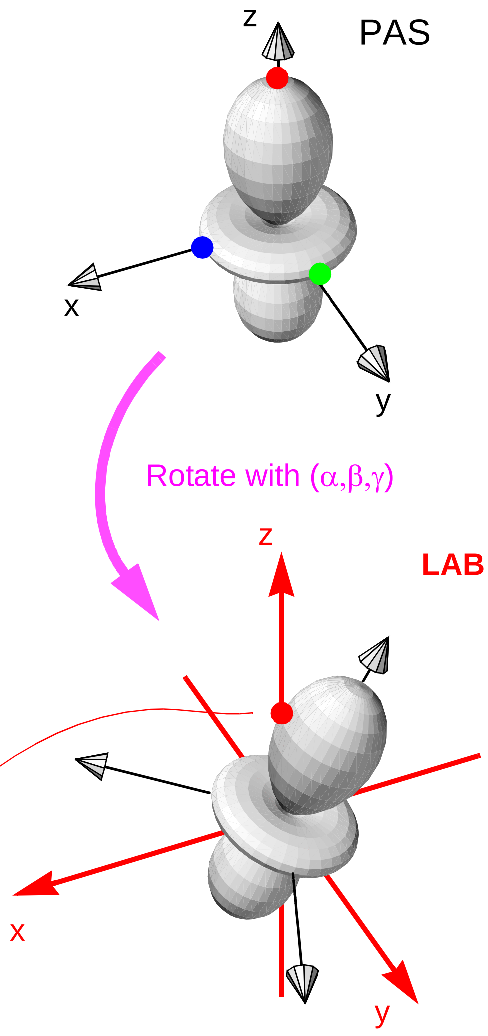
NMR Interactions - Tensors

$$\underset{\sim}{A}^{(k,n)}_{PAS} = \begin{bmatrix} A_{11} & 0 & 0 \\ 0 & A_{22} & 0 \\ 0 & 0 & A_{33} \end{bmatrix}$$

Rotate with (α,β,γ)

$$\underset{\sim}{A}^{(k,n)}_{LAB} = \begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{bmatrix}$$





$$\hat{H}^{(k)}_{CS} = \sigma_{xz}\omega_0^{(k)}\hat{I}_{kx} + \sigma_{yz}\omega_0^{(k)}\hat{I}_{ky} + \sigma_{zz}\omega_0^{(k)}\hat{I}_{kz}$$

$$= \xcancel{\sigma_{xz}\omega_0^{(k)}\hat{I}_{kx} + \sigma_{yz}\omega_0^{(k)}\hat{I}_{ky}} + \sigma_{zz}\omega_0^{(k)}\hat{I}_{kz}$$

High Field Approximation

NMR Interactions - Tensors

- The Zeeman interaction is given by (See slide 2)

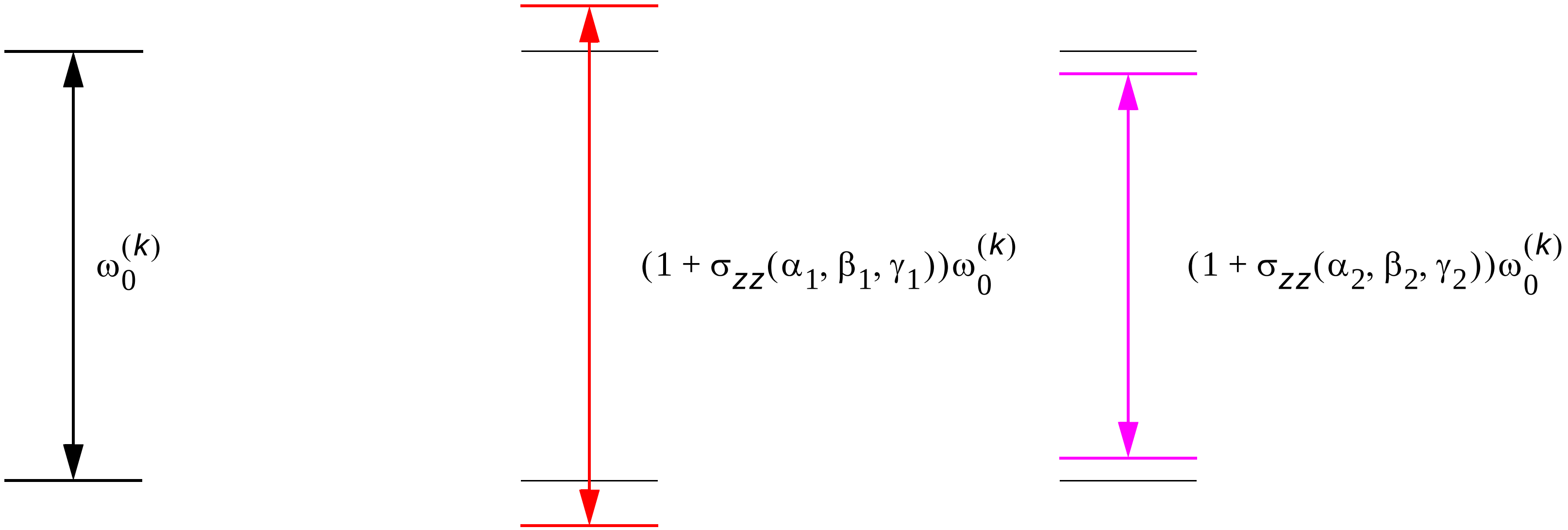
$$\hat{H}_Z^{(k)} = -\gamma \hat{I}_{kz} B_0 = \omega_0^{(k)} \hat{I}_{kz}$$

- The Chemical Shift (with high field approximation)

$$\hat{H}_{CS}^{(k)} = \sigma_{zz}\omega_0^{(k)}\hat{I}_{kz}$$

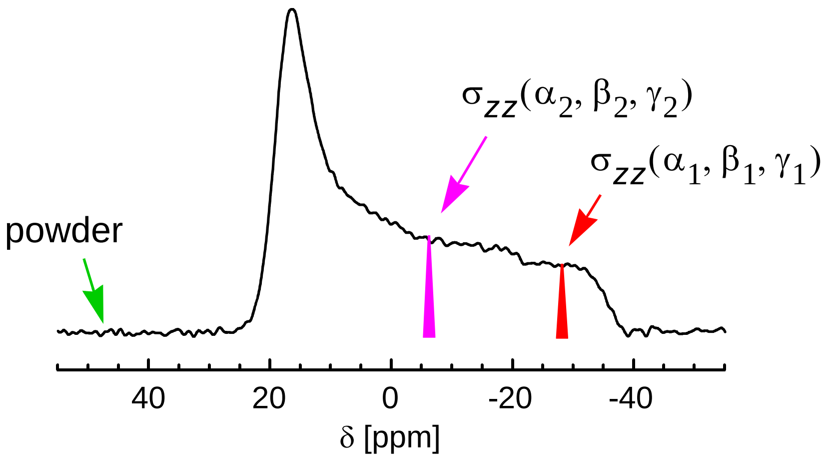
- The total Hamiltonian is: $\hat{H}^{(k)} = \hat{H}_Z^{(k)} + \hat{H}_{CS}^{(k)} = (1+\sigma_{zz})\omega_0^{(k)}\hat{I}_{kz}$

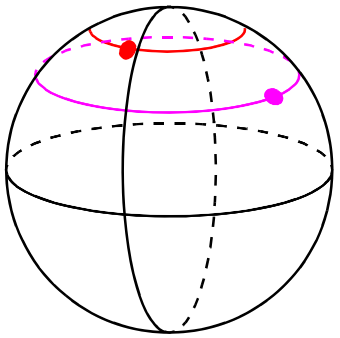
Parts per Million (ppm) !



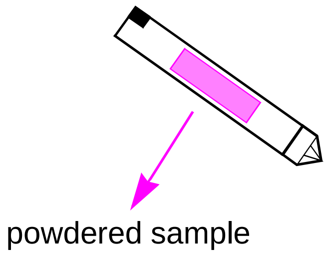
NMR Interactions - Tensors

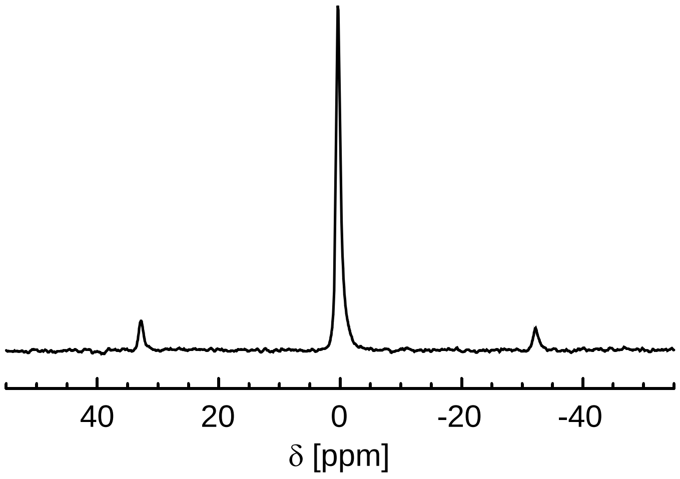
- Orientation dependency of the signal

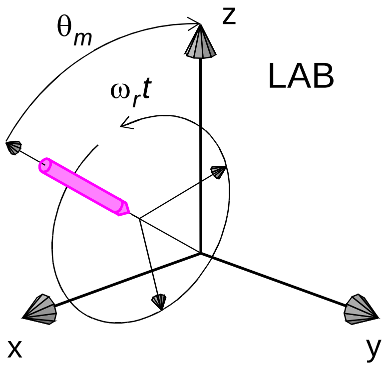




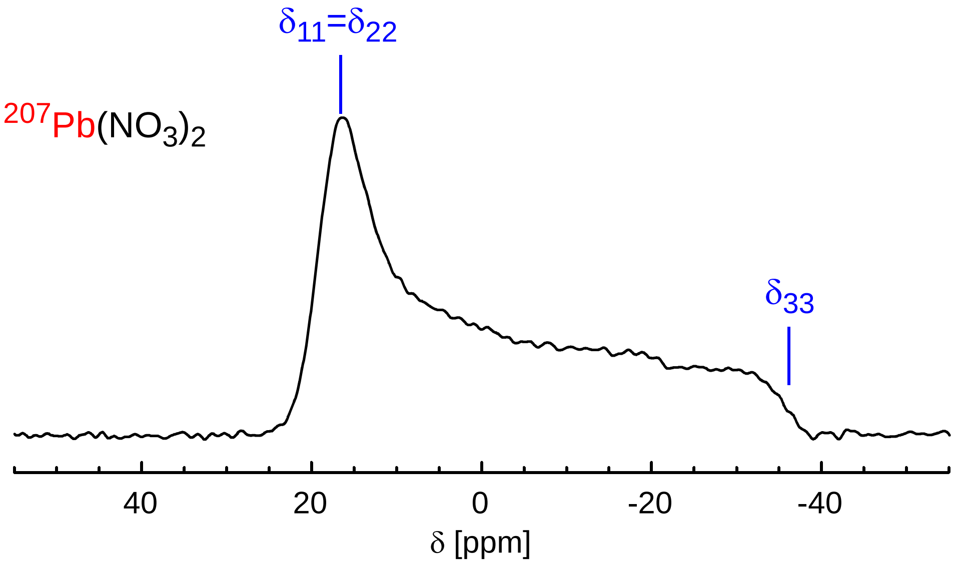
- Magic Angle Spinning (MAS)







NMR Interactions - Tensors



Tensor Characterization

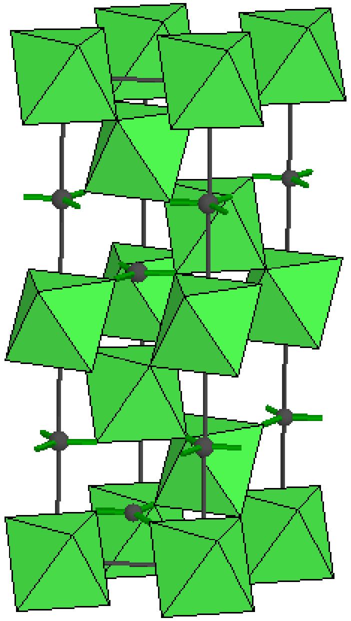
$\delta_{11}, \delta_{22}, \delta_{33}$

$$\begin{aligned} \delta_{\text{iso}} &= \frac{1}{3}(\delta_{11}+\delta_{22}+\delta_{33}) \\ \text{span} &= \Omega = \delta_{11}-\delta_{33} > 0 \\ \text{skew} &= \kappa = 3(\delta_{22}-\delta_{\text{iso}})/\Omega \end{aligned}$$

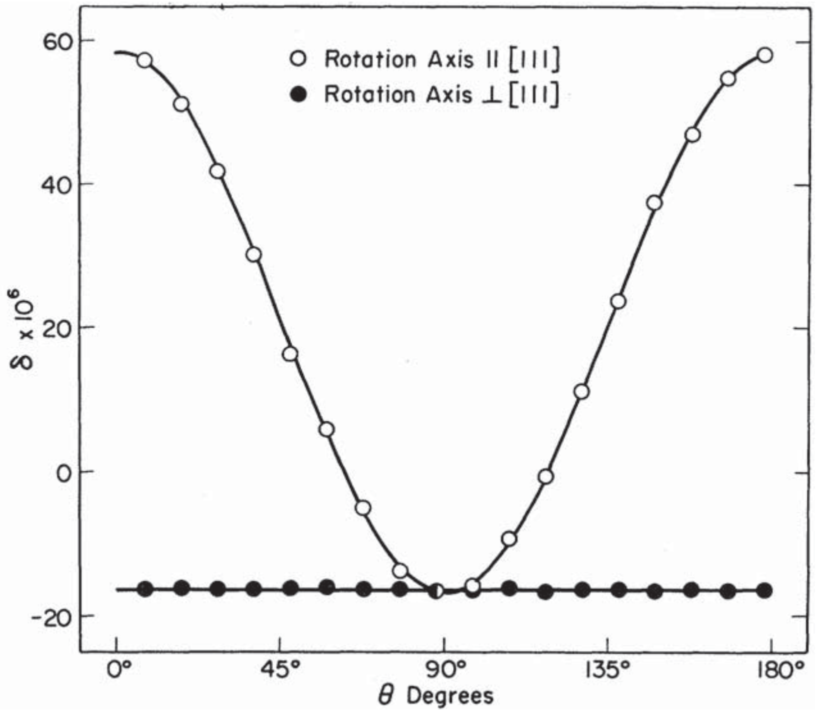
$$\begin{aligned} \delta_{\text{iso}} &= \frac{1}{3}(\delta_{11}+\delta_{22}+\delta_{33}) \\ |\delta_{zz}-\delta_{\text{iso}}| &\geq |\delta_{xx}-\delta_{\text{iso}}| \geq |\delta_{yy}-\delta_{\text{iso}}| \\ \text{anisotropy} &= \delta = \delta_{zz}-\delta_{\text{iso}} \\ \text{asymmetry} &= \eta = 3(\delta_{yy}-\delta_{xx})/\delta \end{aligned}$$

Single Crystal Rotation Plots

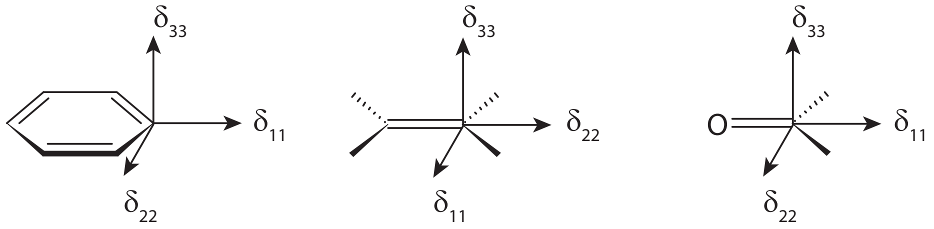
x-ray crystal structure of calcite ($CaCO_3$)



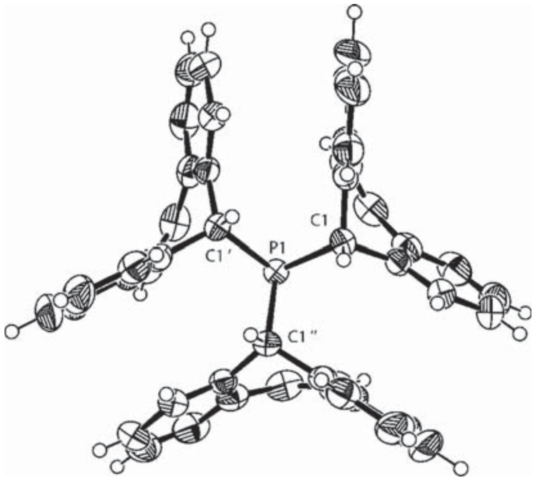
^{13}C single crystal NMR rotation plot of calcite



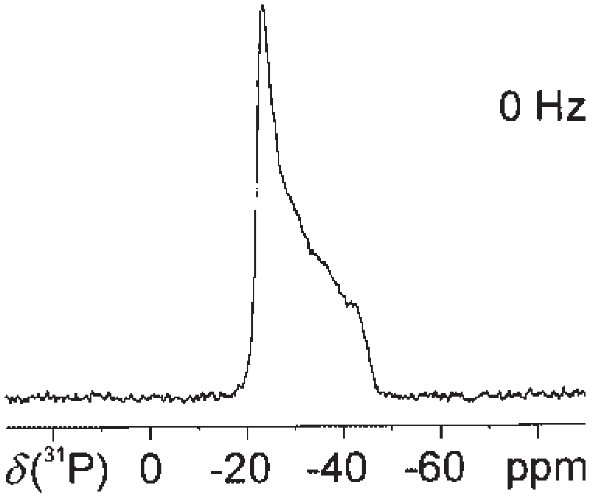
Chemical Shift Tensors : Effect of Symmetry



View of trop$_3$P along the threefold symmetry axis

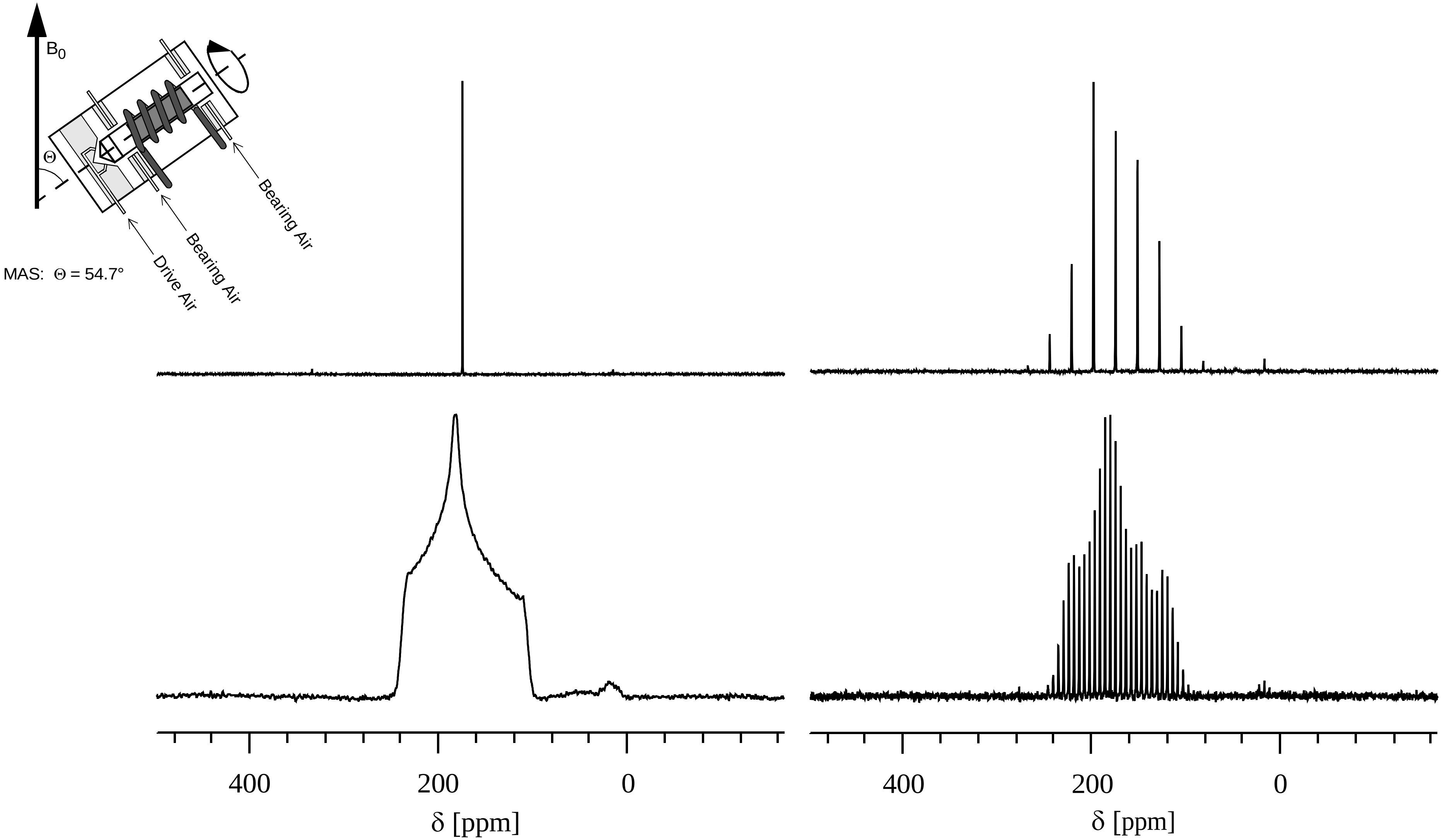


202 MHz ^{31}P NMR spectrum on a static sample showing the axial tensor,σ_{11}=σ_{22}=-24.0 and σ_{33}=-43.0 ppm



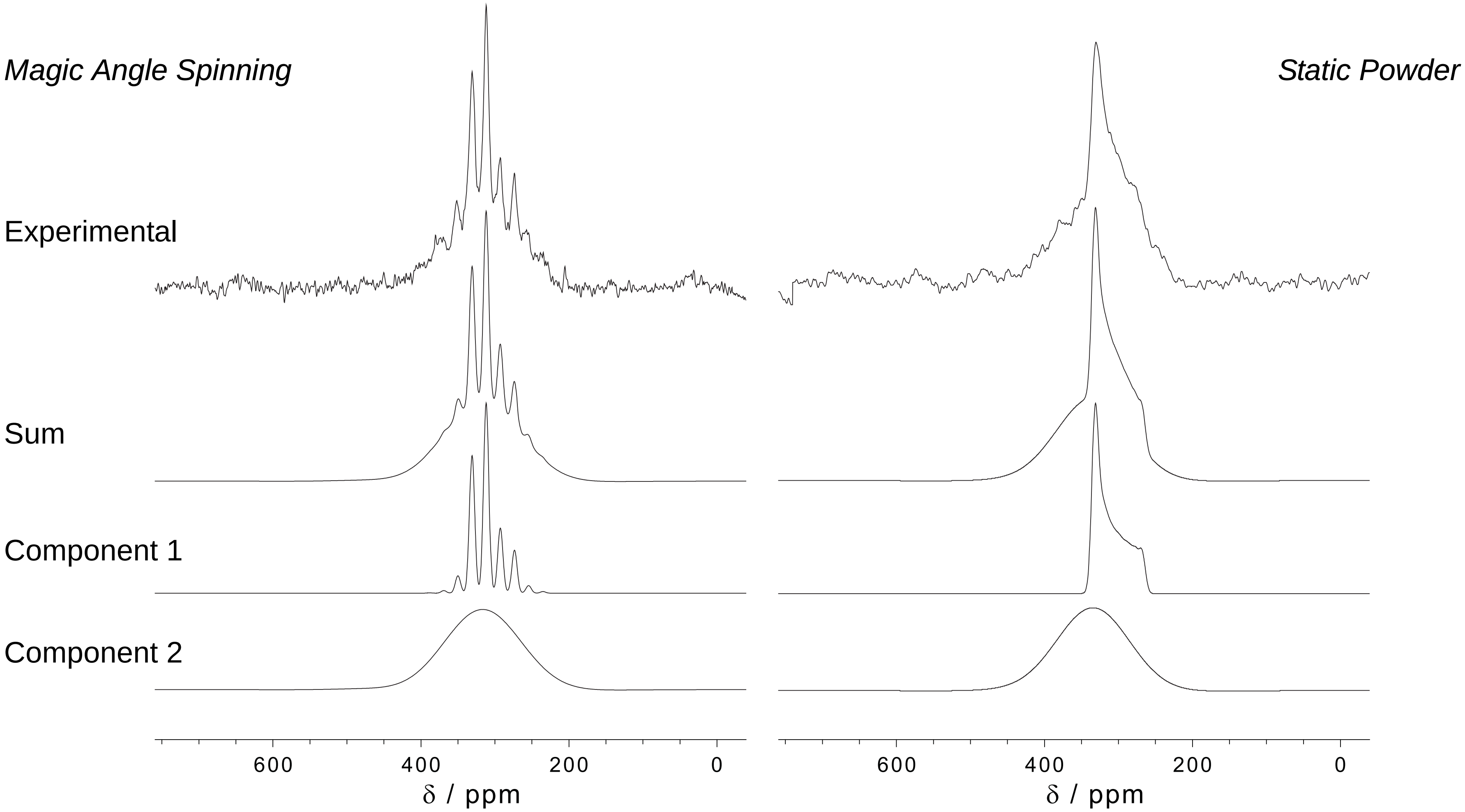
NMR Interactions - Tensors

- 1-^{13}C-Alanine



NMR Interactions - Tensors

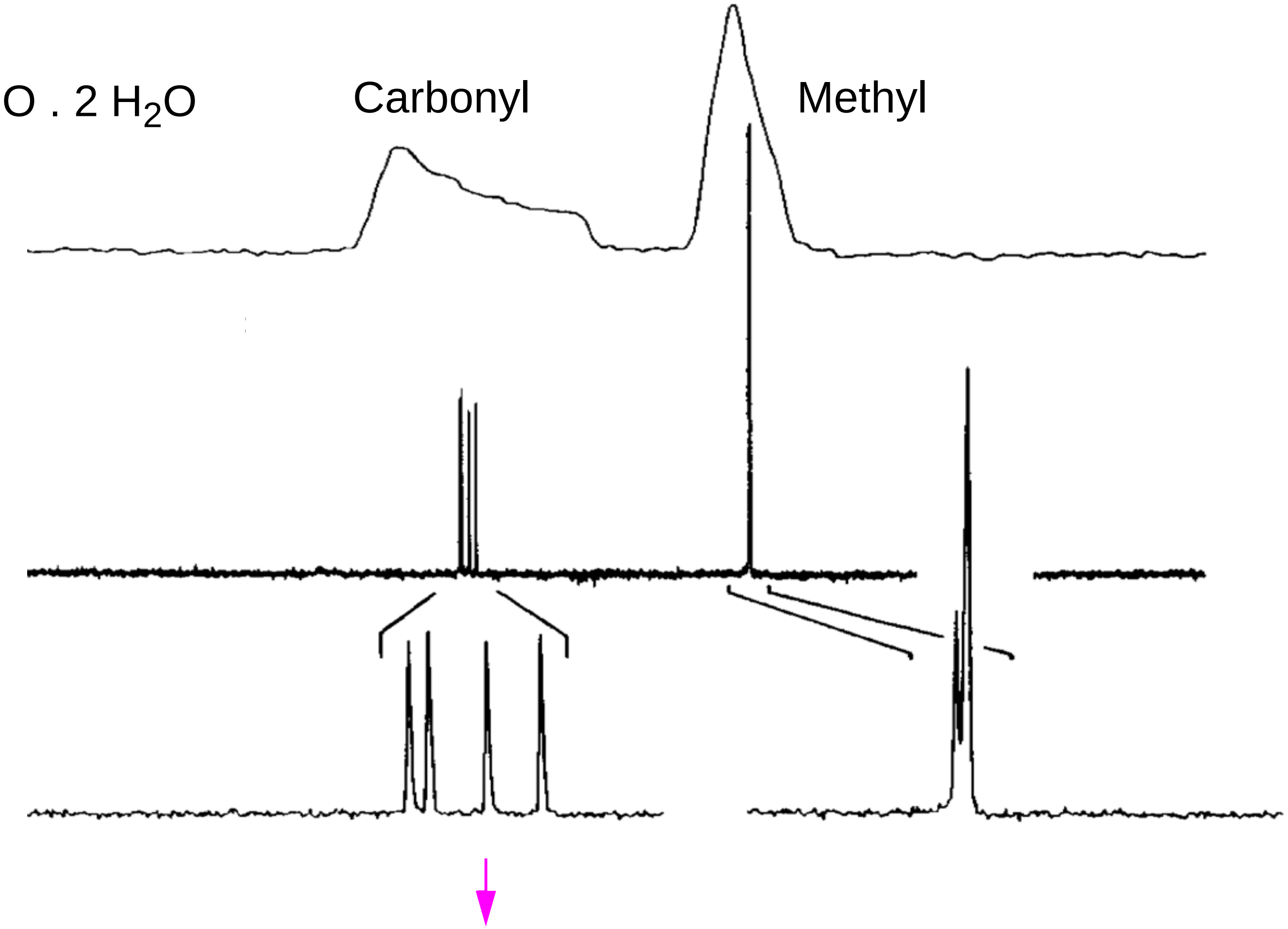
- ^{29}Si solid-state NMR on $Li_{12}Ag_{1-x}Si_4$ (x=0.15)
- Component 1: σ_{iso}= 311 ppm, δ=-47.5 ppm, η=0.2
- Component 2: σ_{iso}= 316 ppm, linewidth = 130 ppm



NMR Interactions - Chemical Shift

- Information vs. Resolution

Ca $CH_3COO \cdot 2\ H_2O$

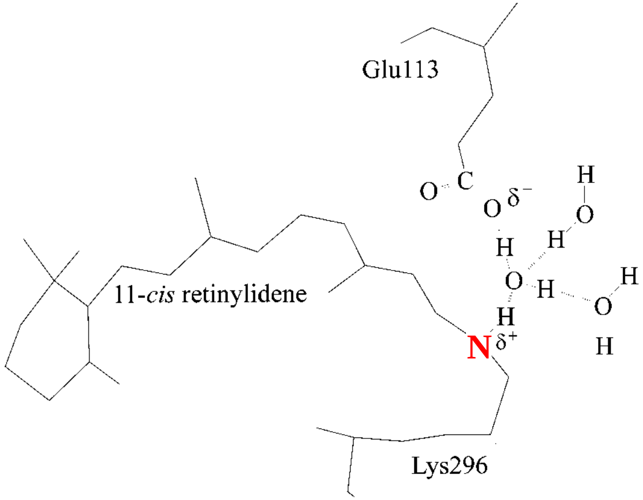


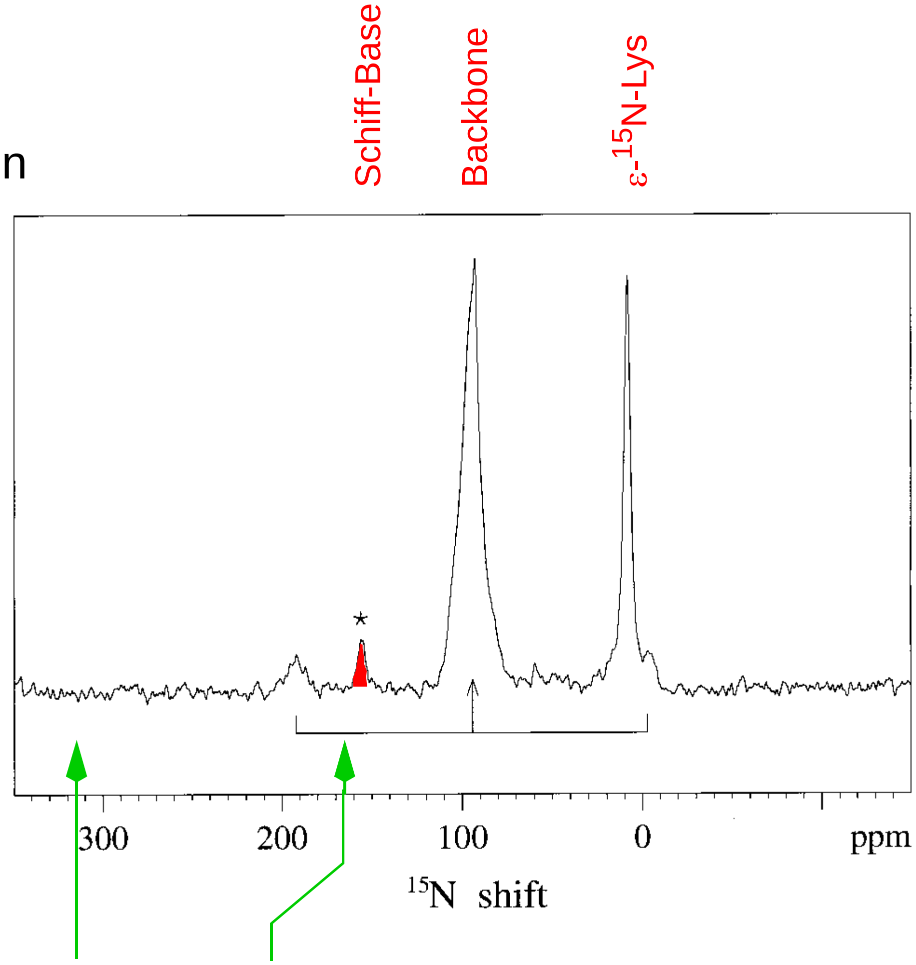
4 Inequivalent molecules

NMR Interactions - Chemical Shift

❖Structural Information: Protonation State from the isotropic chemical shift of ^{15}N

- ● $[\alpha,\varepsilon\text{-}^{15}N_2]$-Leucine-Labelled Rhodopsin
- ● 11 Leucine residues in total

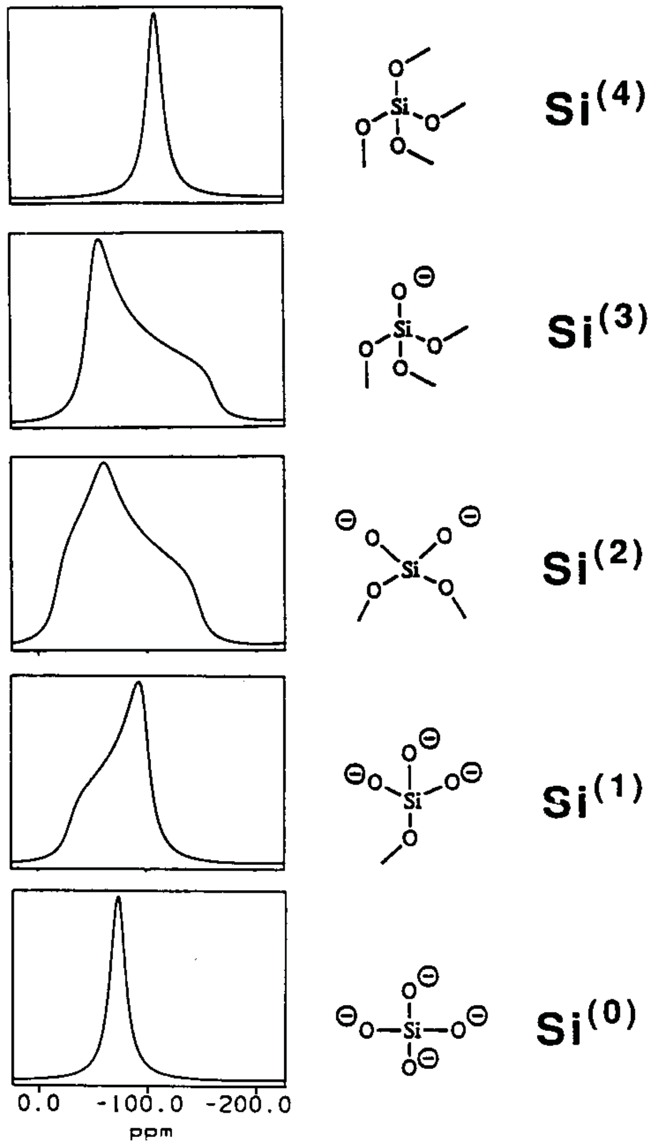




Model Compound unprotonated / protonated

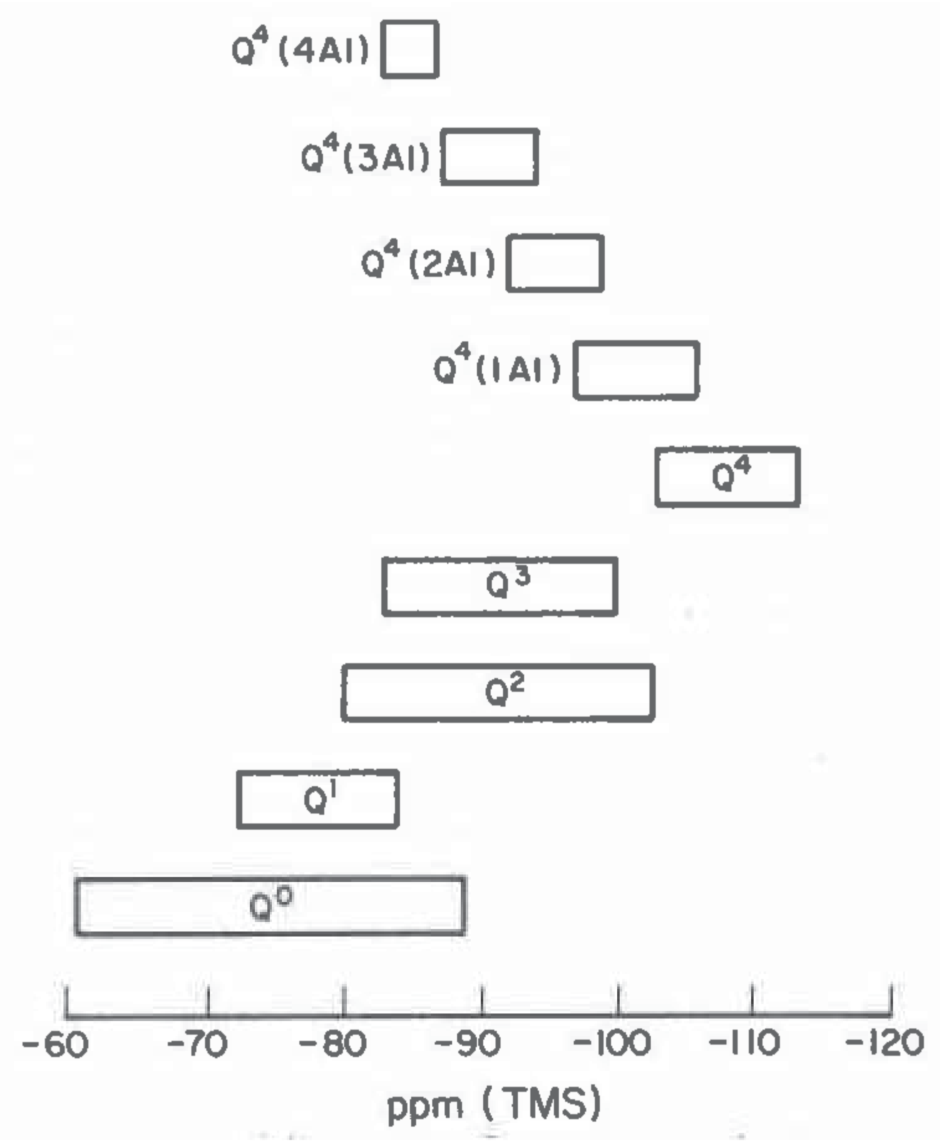
NMR Interactions - Chemical Shift

- Structural Information from ^{29}Si Chemical Shifts



NMR Interactions - Chemical Shift

- Structural Information from ^{29}Si Chemical Shifts

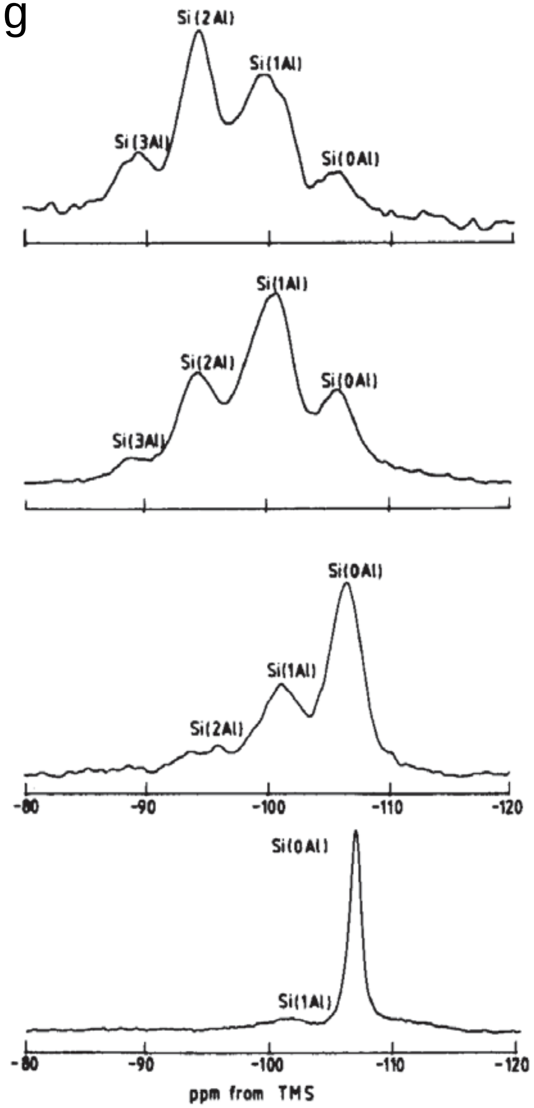


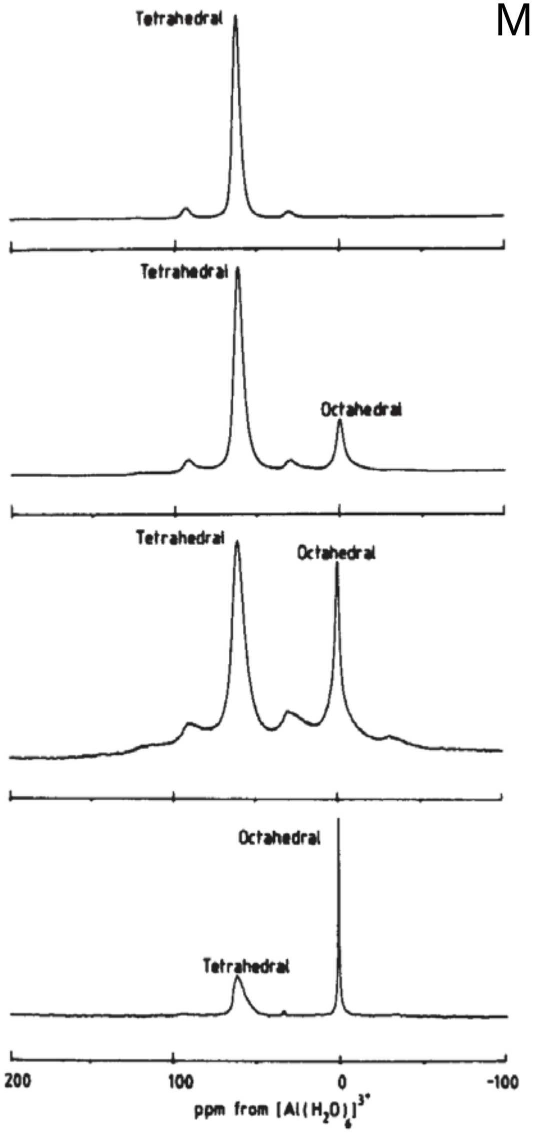
NMR Interactions - Chemical Shift

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

Magic Angle Spinning
^{29}Si NMR

Decreasing amount of Al

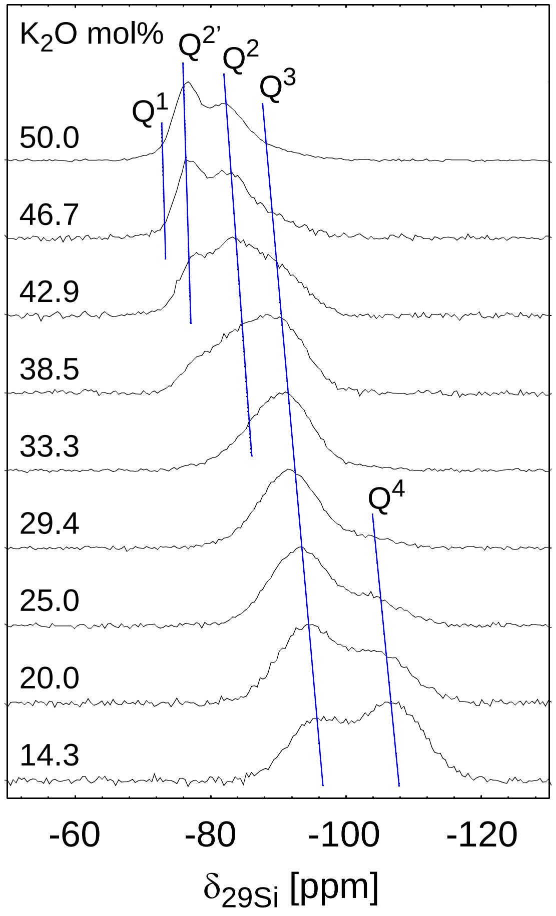




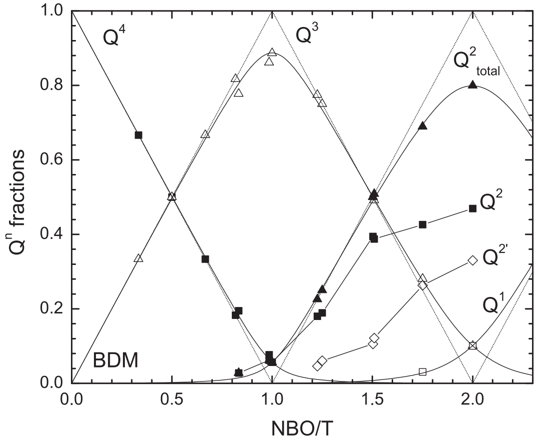
Magic Angle Spinning
^{27}Al NMR

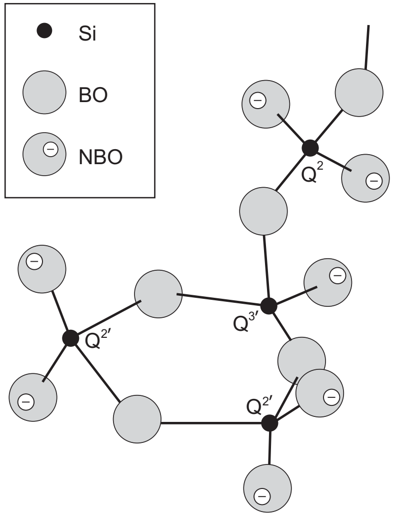
^{29}Si MAS NMR of Potassium Silicate Glasses

- Detection and Quantification of Q^2 sites in three membered rings

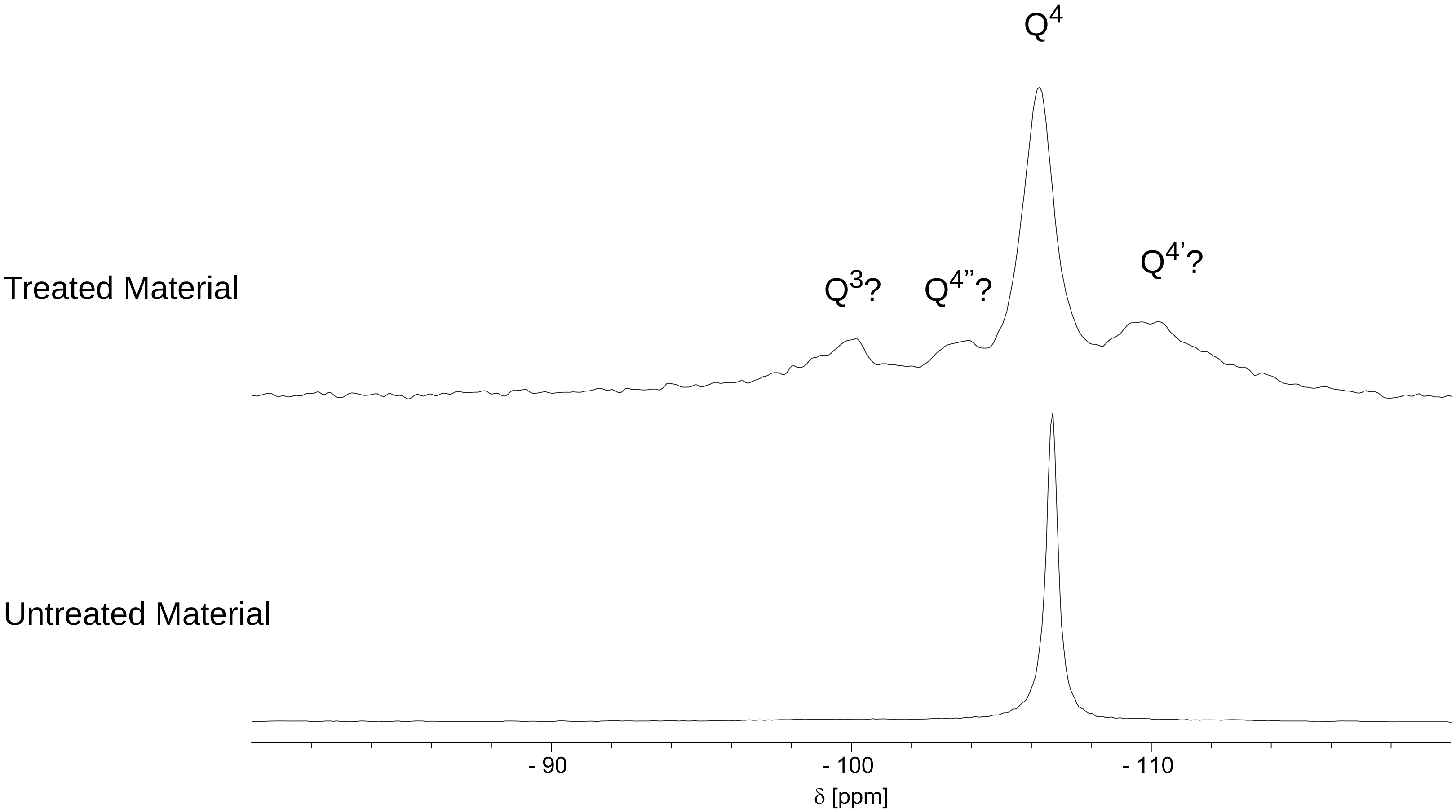


Deconvolution

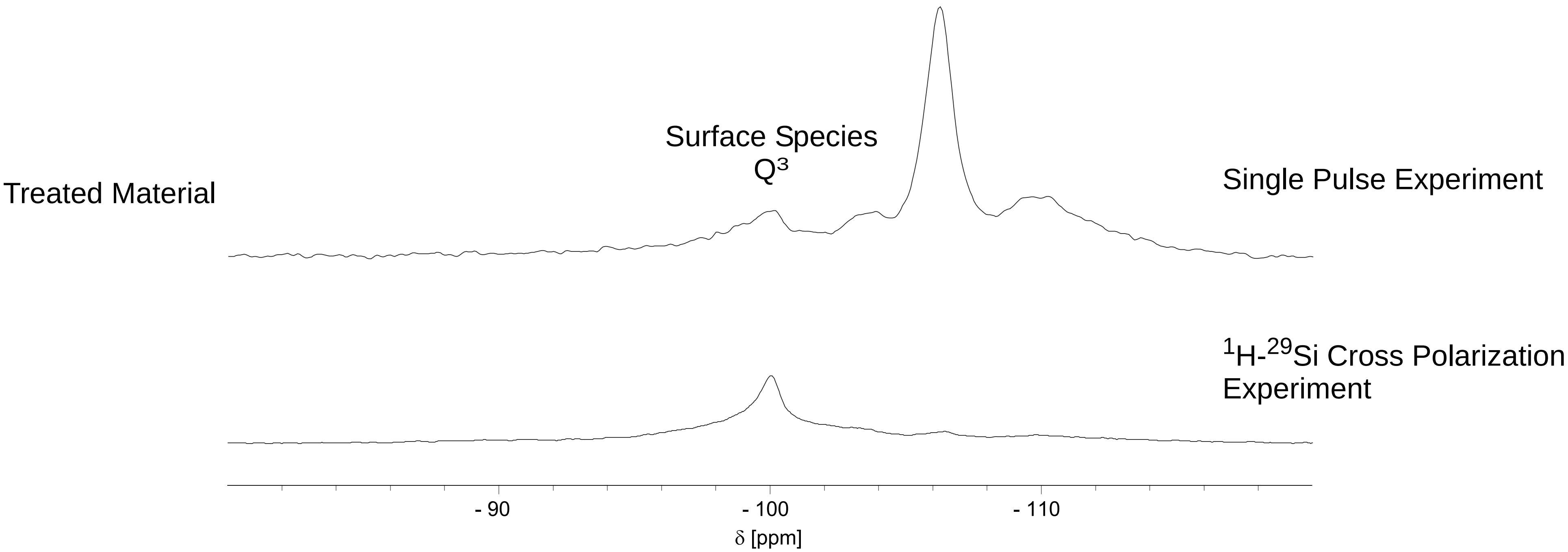




^{29}Si MAS NMR of Treated Zeolites



^{29}Si MAS NMR of Treated Zeolites



NMR Interactions - Dipole

- The representation of the dipolar tensor is given by:

$$\underset{\sim}{D}_{PAS}^{(k,n)} = -2\frac{\mu_0}{4\pi}\frac{\gamma_k\gamma_n}{r_{kn}^3}\frac{h}{2\pi}\begin{bmatrix}-\frac{1}{2} & 0 & 0\\ 0 & -\frac{1}{2} & 0\\ 0 & 0 & 1\end{bmatrix}$$

- The dipolar Hamiltonian is given by

$$\begin{aligned}\hat{H}^{(k,n)} &= \vec{\hat{I}}_k \cdot \underset{\sim}{D}^{(k,n)} \cdot \vec{\hat{I}}_n\\ &= -\frac{\mu_0}{4\pi}\frac{\gamma_k\gamma_n}{r_{kn}^3}\frac{h}{2\pi}(\hat{A}+\hat{B}+\hat{C}+\hat{D}+\hat{E}+\hat{F})\end{aligned}$$

$$\hat{A} = 2\hat{I}_{kz}\hat{I}_{nz}\frac{(3\cos^2\theta-1)}{2}$$

$$\hat{B} = -\frac{1}{2}\left(\hat{I}_k^+\hat{I}_n^- + \hat{I}_k^-\hat{I}_n^+\right)\frac{(3\cos^2\theta-1)}{2}$$

$$\hat{C} = \left(\hat{I}_k^+\hat{I}_{nz} + \hat{I}_{kz}\hat{I}_n^+\right)\frac{(3\sin\theta\cos\theta e^{-i\varphi})}{2}$$

$$\hat{D} = \left(\hat{I}_k^-\hat{I}_{nz} + \hat{I}_{kz}\hat{I}_n^-\right)\frac{(3\sin\theta\cos\theta e^{i\varphi})}{2}$$

$$\hat{E} = \frac{1}{2}\left(\hat{I}_k^+\hat{I}_n^+\right)\frac{(3\sin^2\theta e^{-2i\varphi})}{2}$$

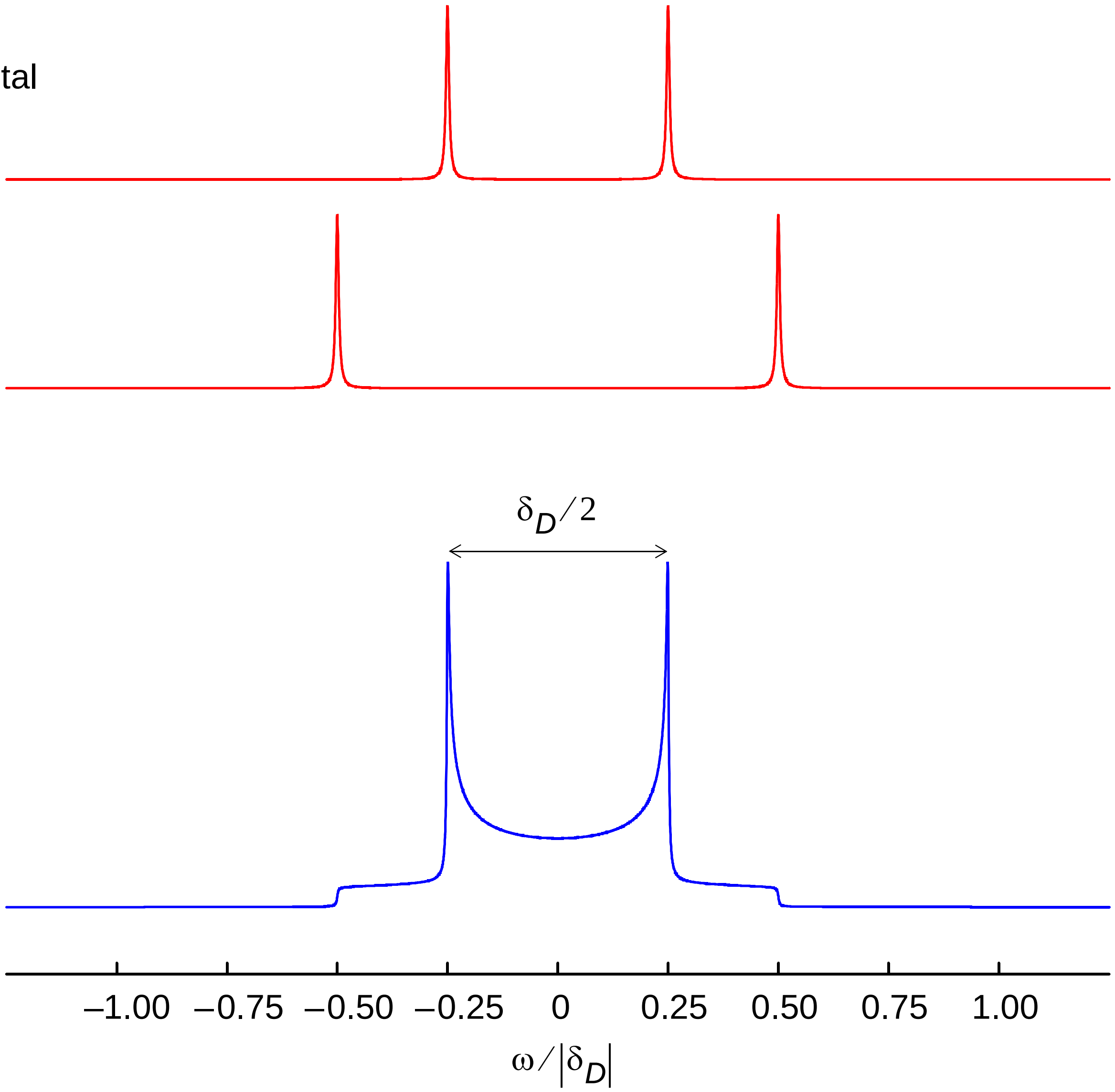
$$\hat{F} = \frac{1}{2}\left(\hat{I}_k^-\hat{I}_n^-\right)\frac{(3\sin^2\theta e^{2i\varphi})}{2}$$

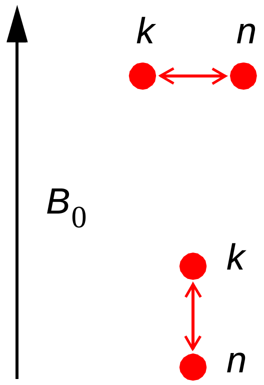
NMR Interactions - Dipole

- Orientation Dependency of the Dipole Interaction

Single Crystal

Powder



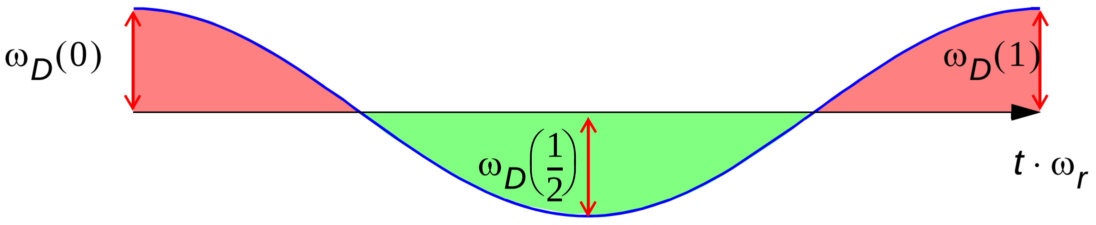


$$\delta_D = -2\frac{\mu_0}{4\pi}\frac{\gamma_k\gamma_n}{r_{kn}^3}\frac{h}{2\pi}$$

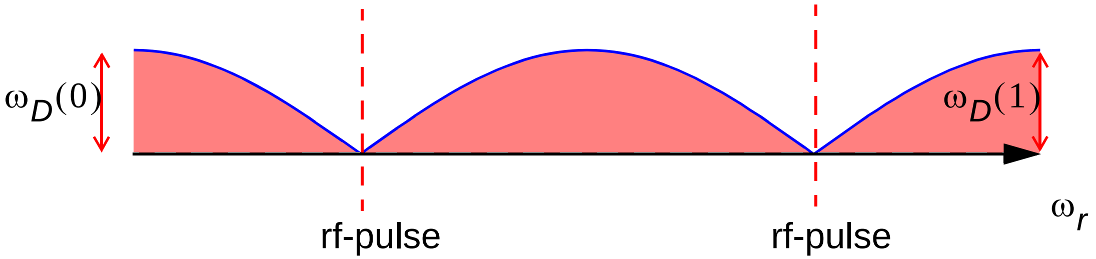
Dipolar Recoupling

- MAS makes the dipolar coupling time dependent with an average value of zero

$$\omega_D(t) = \delta_D \cdot \frac{(3\cos^2\theta - 1)}{2} \cdot \cos(\omega_r t)$$

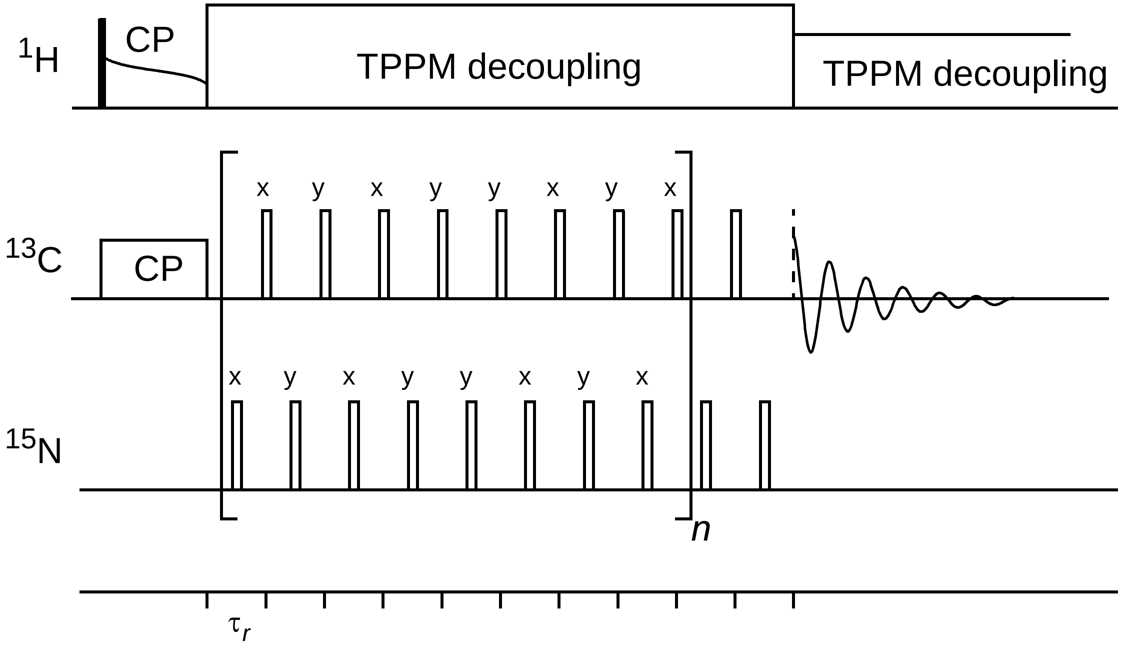


- Rf(-pulses) can interfere and cause a non-zero average of the dipolar coupling.



Rotational Echo DOuble Resonance (REDOR).

- Recoupling of the heteronuclear dipolar coupling under MAS.

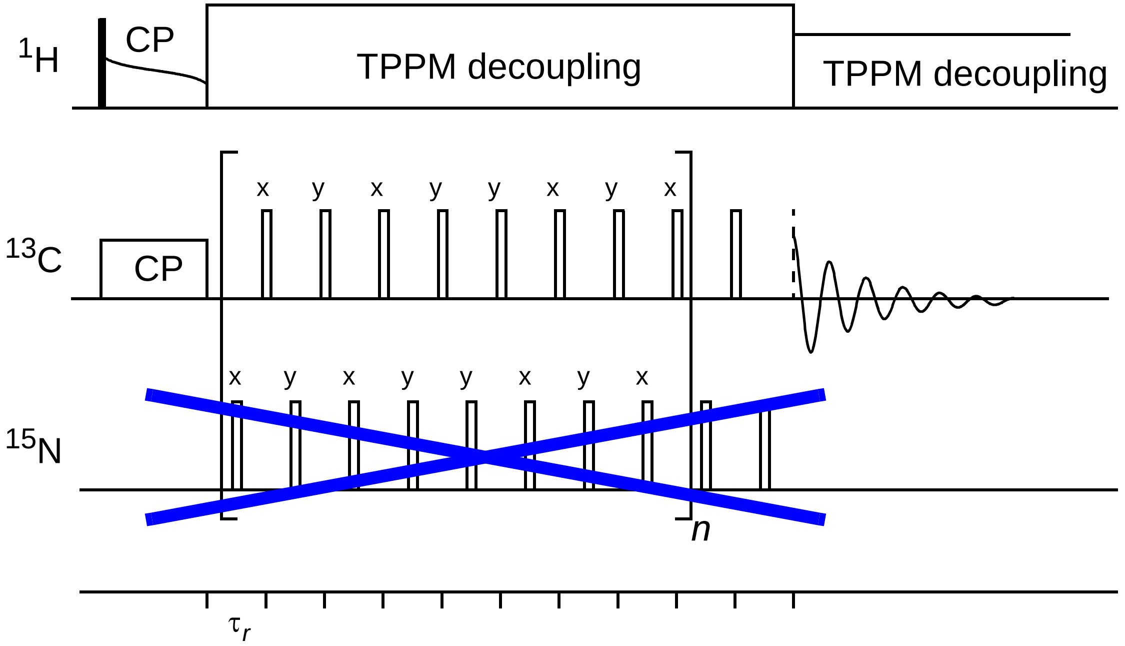


- Alternating experiments ***with*** pulses on ^{15}N channel (recoupling of dipolar interaction)
  and ***without*** pulses on ^{15}N channel (reference experiment)

See: T. Gullion, J. Schaefer, *J. Magn. Reson.*, **81** (1989) 196.

Rotational Echo DOuble Resonance (REDOR).

- Recoupling of the heteronuclear dipolar coupling under MAS.

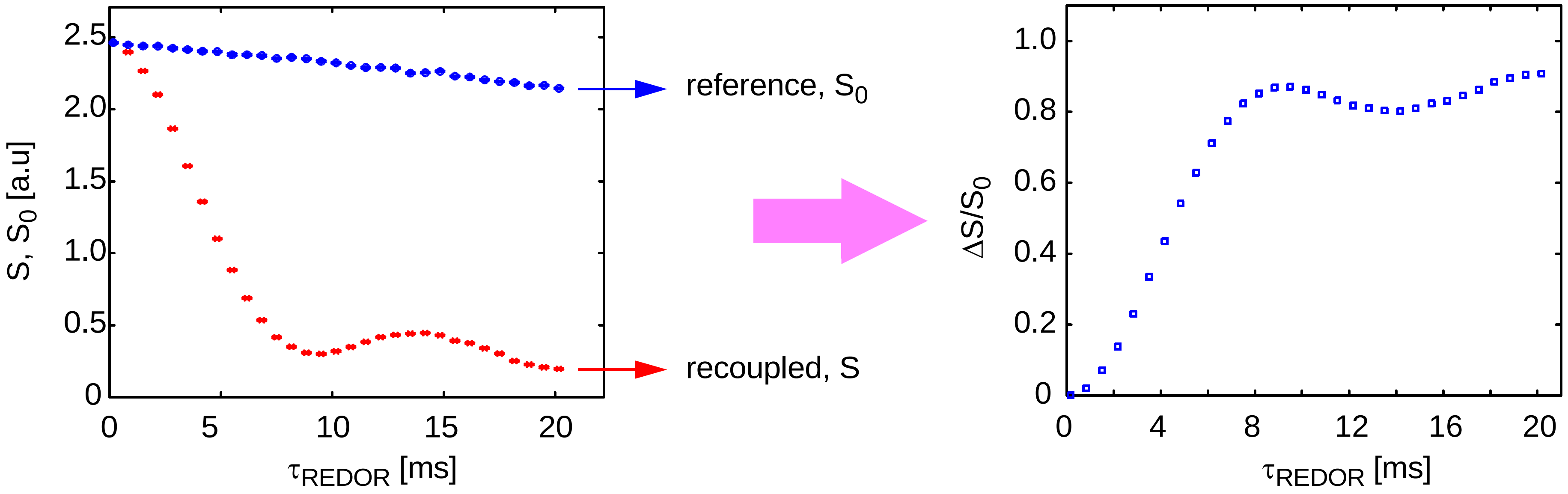


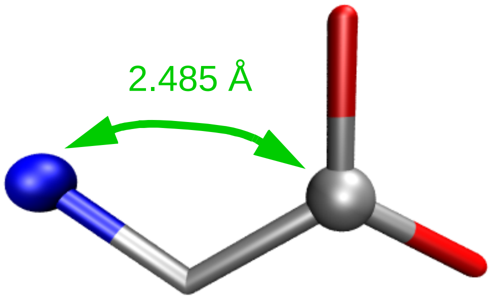
- Alternating experiments ***with*** pulses on ^{15}N channel (recoupling of dipolar interaction)
  and ***without*** pulses on ^{15}N channel (reference experiment)

See: T. Gullion, J. Schaefer, *J. Magn. Reson.*, **81** (1989) 196.

REDOR Example: Glycine.

- 10% ^{13}CO-^{15}N-Glycine in 90% nat. ab. Glycine.





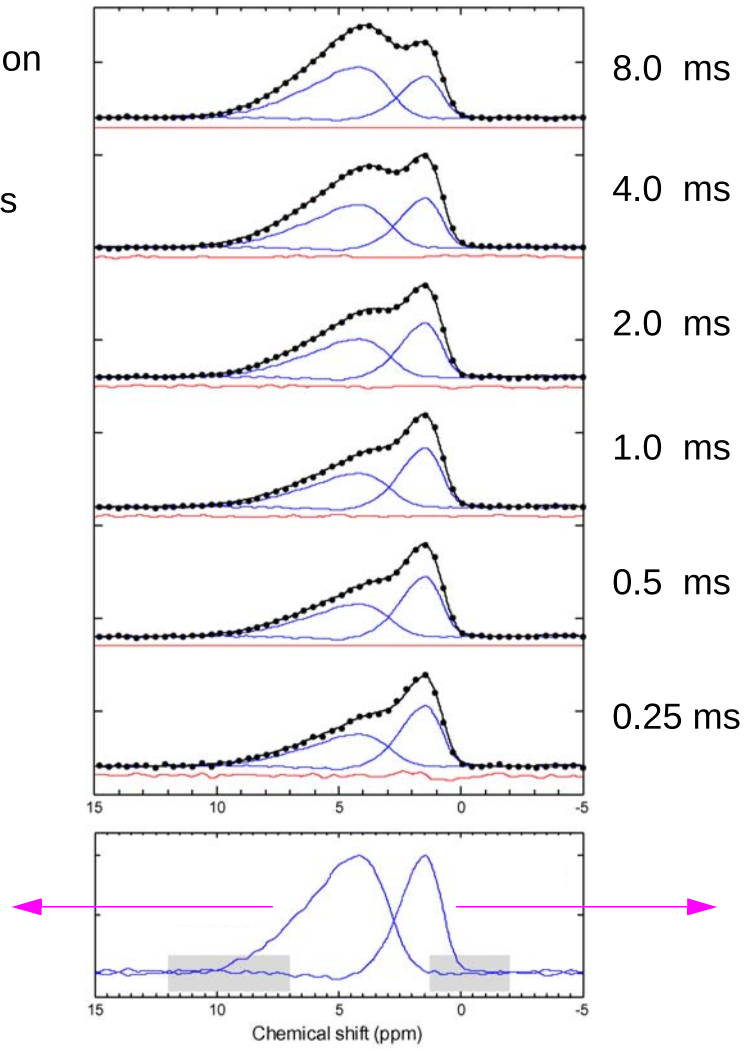
Heteronuclear Dipolar Recoupling

- Distance based proximity filter using Cross Polarization

^{1}H Spectra acquired after polarization transfer from ^{27}Al to ^{1}H

Shorter recoupling durations selects stronger ^{27}Al-^{1}H couplings (and shorter distances)

Jadeite glass, 0.62% H_2O



8.0 ms

4.0 ms

2.0 ms

1.0 ms

0.5 ms

0.25 ms

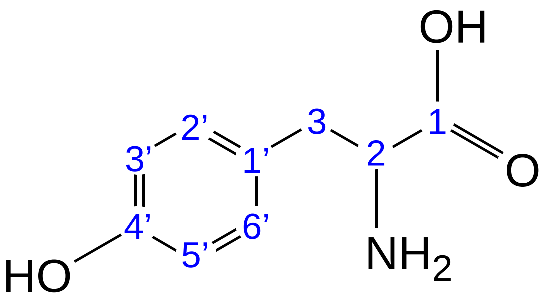
“Far from Al” (8.0 - 0.5 ms)

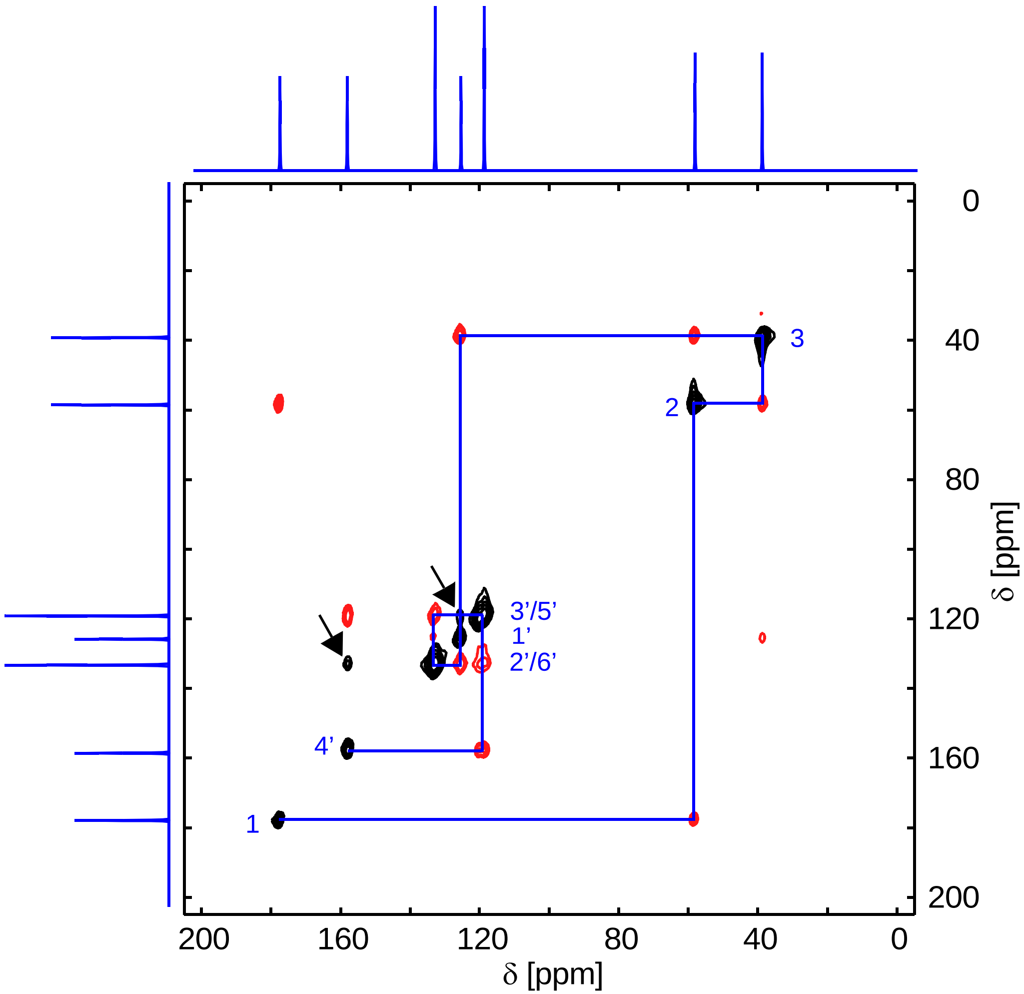
“Close to Al” (0.5 - 8-0 ms)

Homonuclear Dipolar Recoupling

- Structure determination through 2D correlations

U-^{13}C-Tyrosine



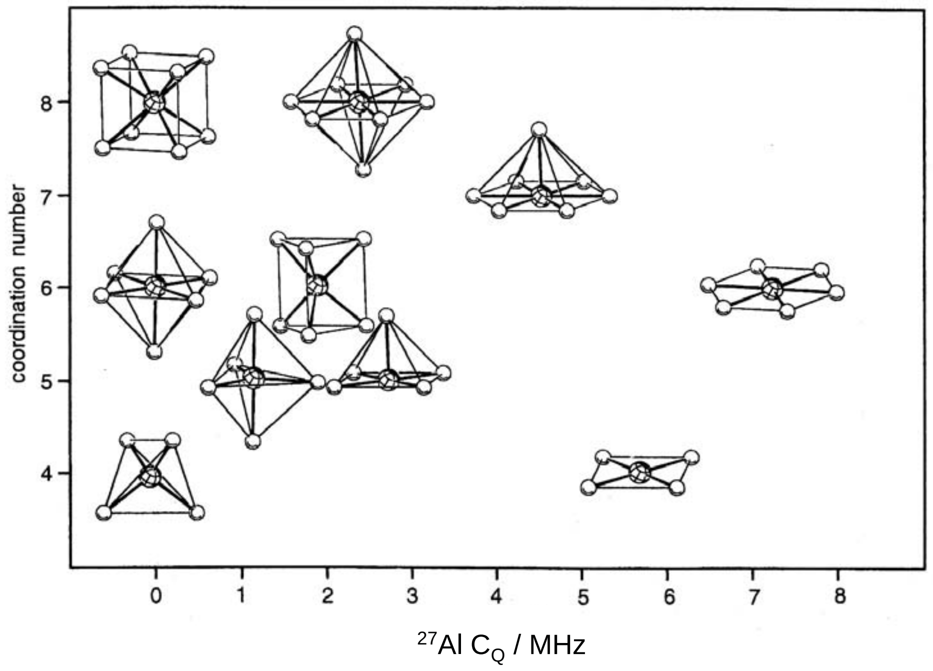


NMR Interactions - Quadrupole

- 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
- Quadrupolar Hamiltonian is given by:

$$\hat{H}^{(k)} = \frac{eQ2\pi}{2I(2I-1)h}\vec{\hat{I}}_k \cdot \underset{\sim}{V} \cdot \vec{\hat{I}}_k$$

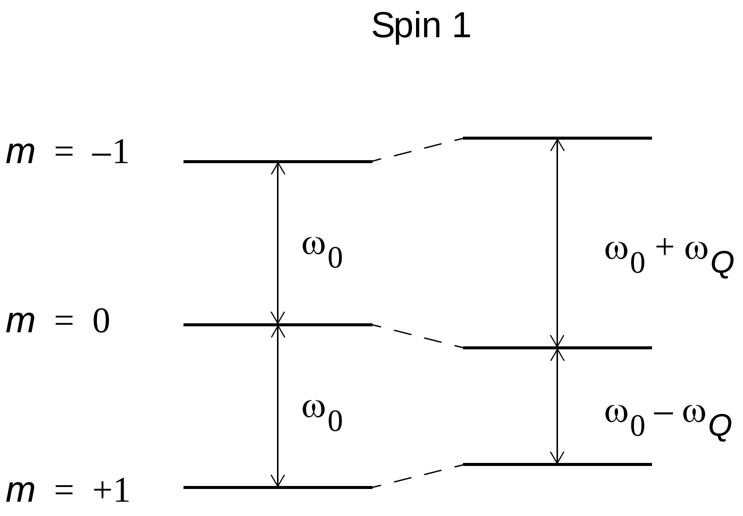
- The Quadrupole Coupling Constant, $C_Q = \frac{eQV_{zz}}{2I(2I-1)h}$ depends on the system

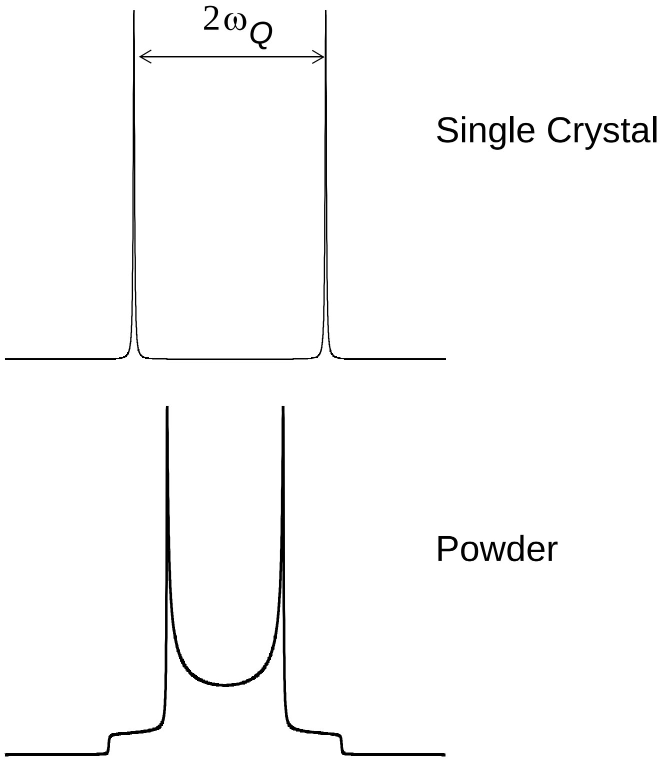


NMR Interactions - Quadrupole

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

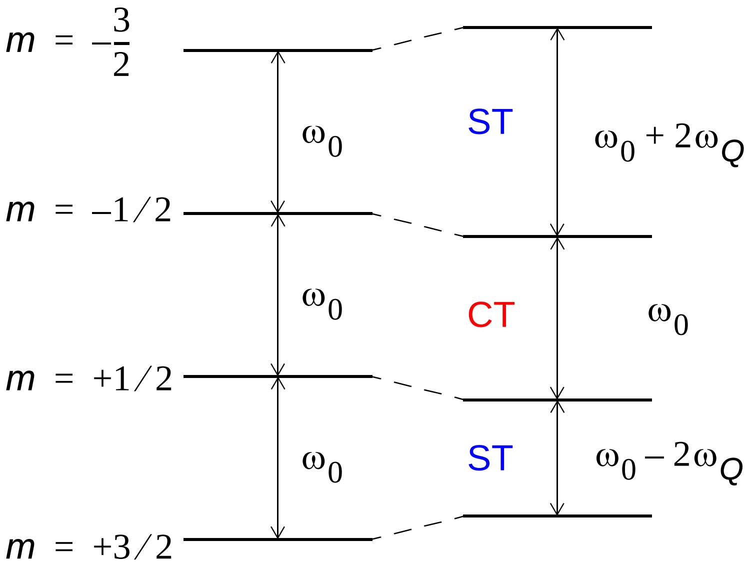
$$\omega_Q = \frac{3eQV_{zz}}{4I(2I-1)h}\frac{1}{2}(3\cos^2\theta - 1 + \eta_Q \sin^2\theta \cos 2\gamma)$$

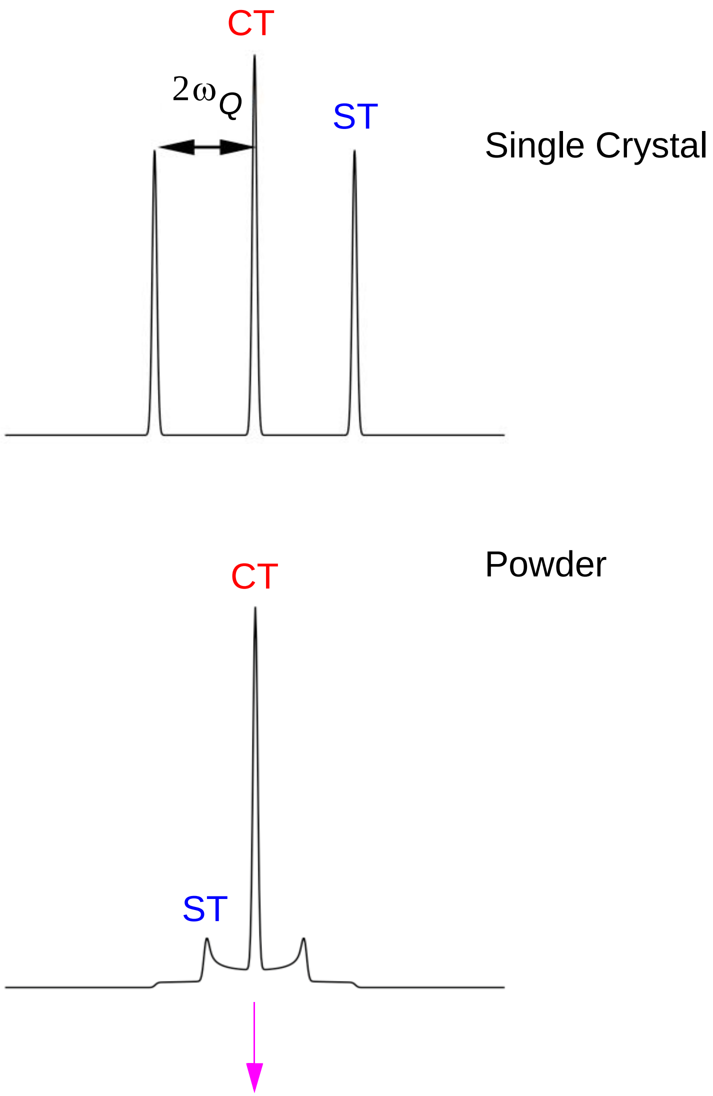




NMR Interactions - Quadrupole

Spin 3/2





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

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

- Second Order Term

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

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

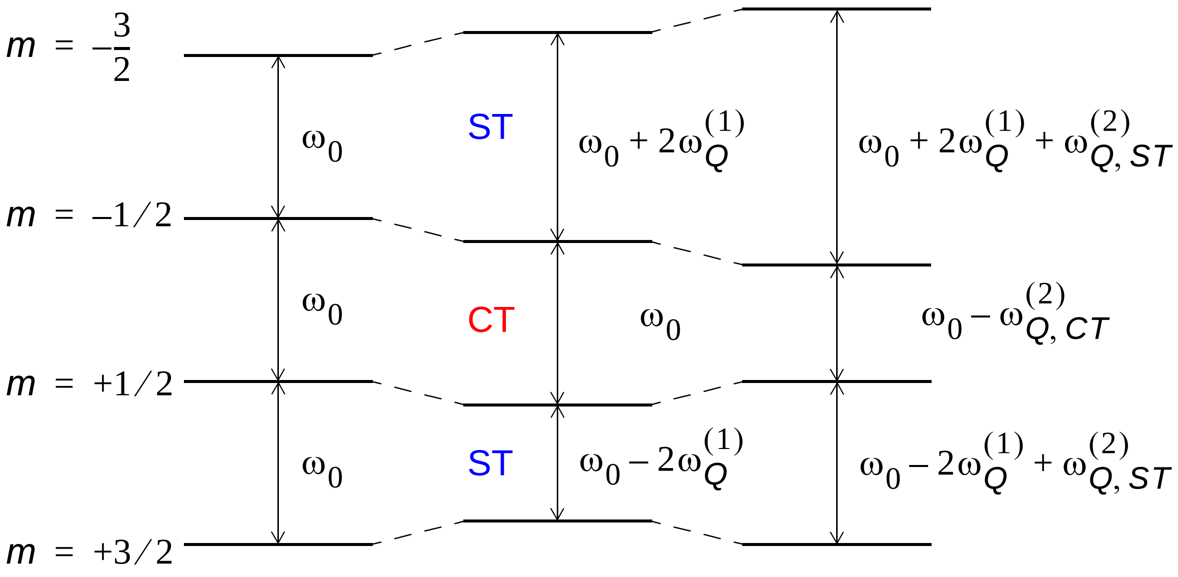
$$d_{00}^{(4)}(\theta) \propto 35\cos^4\theta - 30\cos^2\theta + 3$$

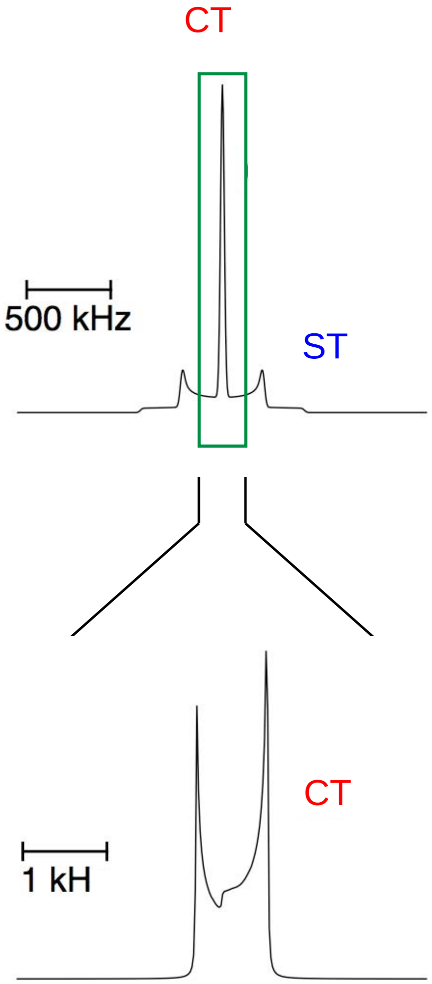
- The Second Order Term:

Scales with the inverse of the Larmor Frequency (and therefore with B_0)
Contains an orientation indenpendent term (A)
Contains a second rank term (B)
Contains a fourth rank term (C)

NMR Interactions - Quadrupole

Spin 3/2



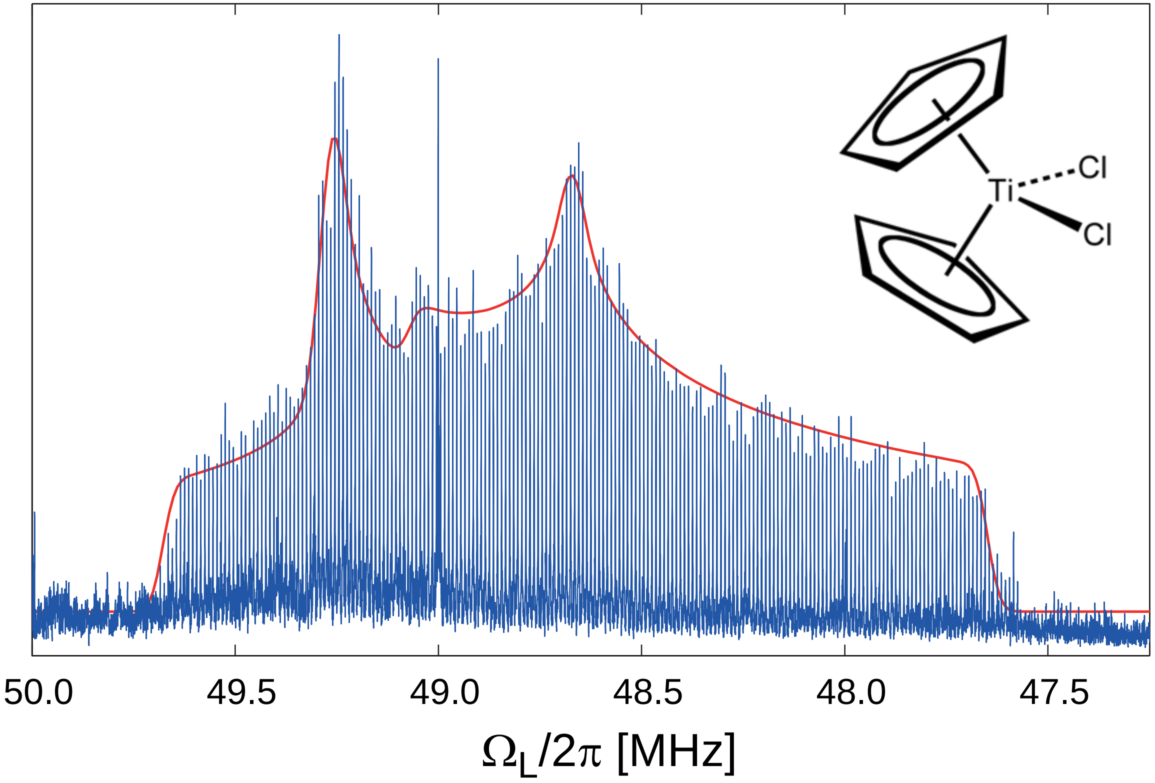


NMR Interactions - Quadrupole

Titanocene dichloride

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

C_Q = 22.18 (+/- 0.03) MHz
η_Q = 0.612 (+/- 0.003)



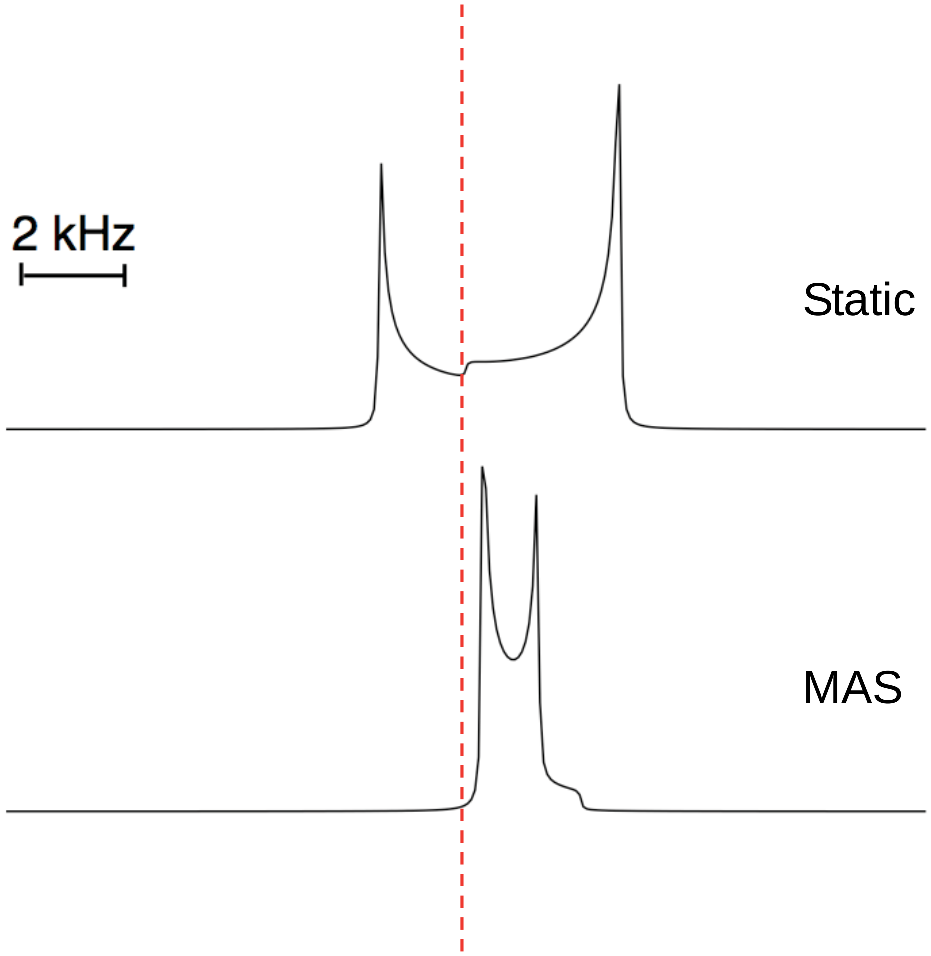
NMR Interactions - Quadrupole

- Magic Angle Spinning of Quadrupoles with second order effects

Central Transition line is narrowed

Fourth rank term (C) remains

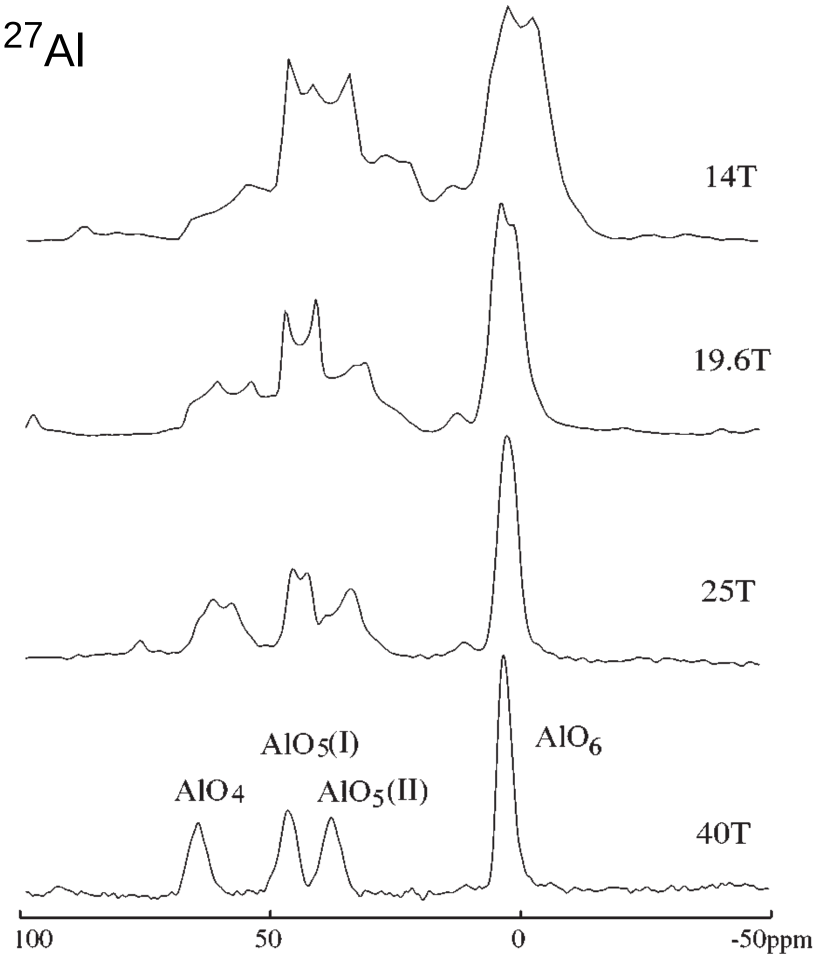
Isotropic term (A) remains



NMR Interactions - Quadrupole

- Second order Quadrupole and Magnetic Field Strength

Isotropic and fourth rank term scale with $1/\omega_0$



$9Al_2O_3.2B_2O_3$

Quadrupole Interaction: High Resolution

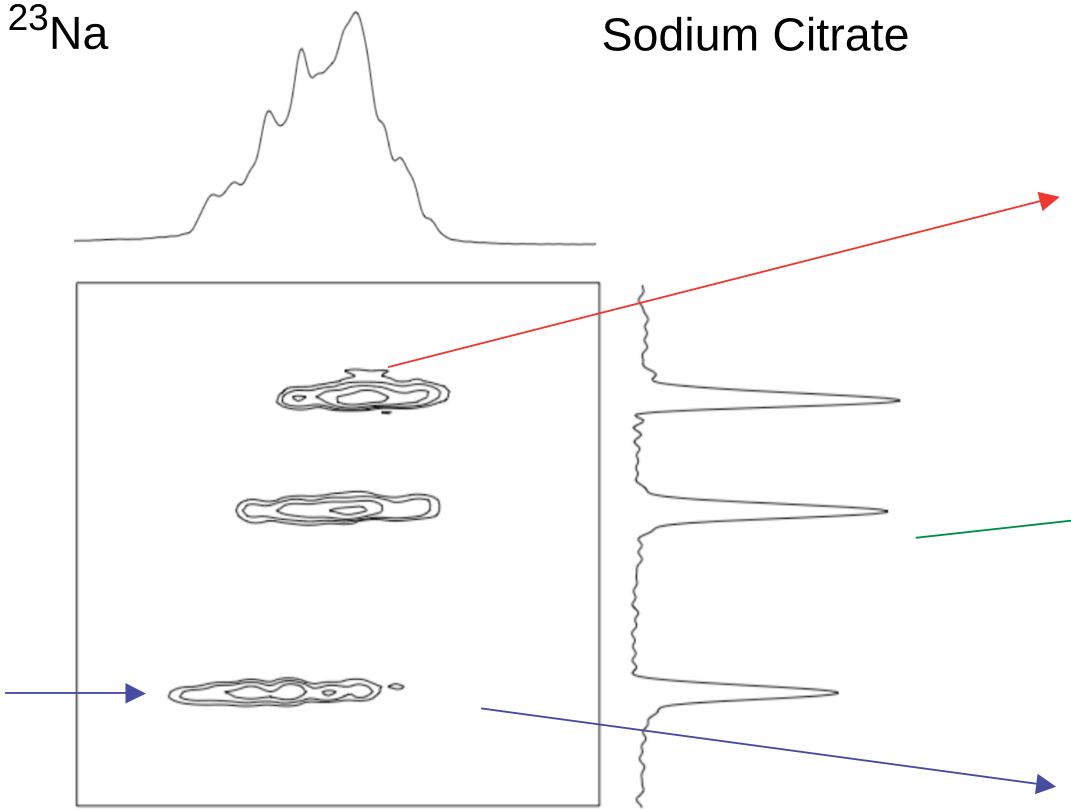
- Is it possible to get high resolution Spectra of Quadrupoles?

Well, yes:

1. Go to very high field
2. Rotate around two axes simultanously (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



Position of centre of gravity of ridge
δ_{iso} and P_Q

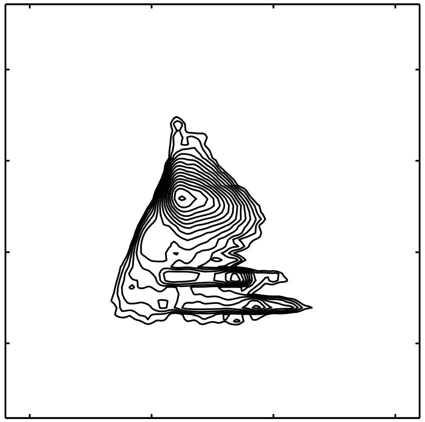
Isotropic spectrum
number of species and relative intensities

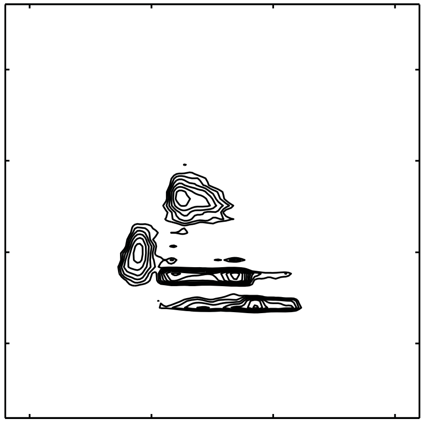
Cross-section along ridge
C_Q and η_Q

Quadrupole Interaction: MQMAS

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

No Calcination





Calcination at 1000 °C

From Sr-hydroxide precursor