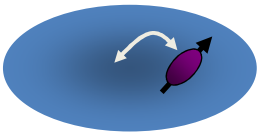
Quadrupolar coupling

theory

Quadrupolar couplings



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

Very often as strong as Zeeman interaction!

interaction between a quadrupole moment (Q) with an electric field gradient (EFG)

→ Electric field gradient (EFG): ???

→ Electric quadrudpole moment: ???

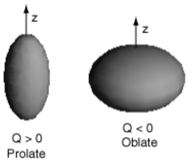
Quadrupolar coupling

Theory: the electric quadrupole moment Q

- Feature of all nuclei with spin>1/2:

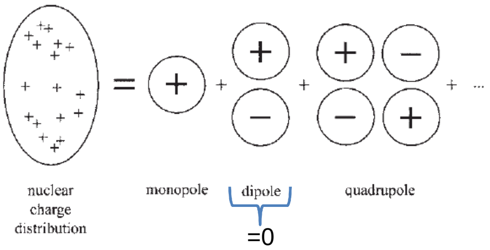
non-spherical distribution of the nuclear charge

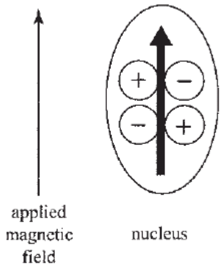
(75% of all NMR active nulcei)



The quadrupole moment is fixed within the nucleus:
→alignment along B0 field through the spin

- The non-spherical charge distribution can be described mathematically by a multipole expansion:





Quadrupolar coupling

Theory: the electric quadrupole moment Q

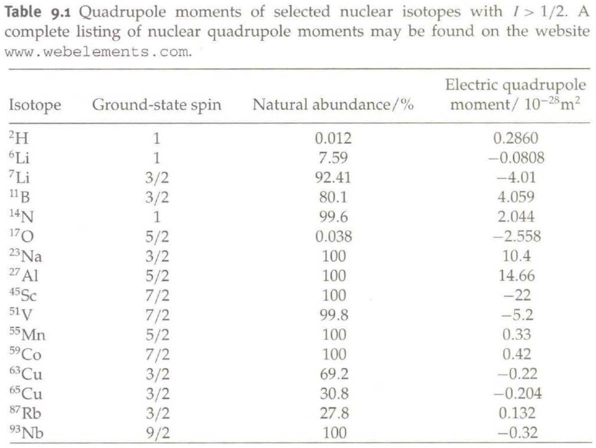


Table 9.1 Quadrupole moments of selected nuclear isotopes with $I > 1/2$. A complete listing of nuclear quadrupole moments may be found on the website `www.webelements.com`.

Isotope	Ground-state spin	Natural abundance/%	Electric quadrupole moment/ $10^{-28}\mathrm{m}^2$
^{2}H	1	0.012	0.2860
^{6}Li	1	7.59	−0.0808
^{7}Li	3/2	92.41	−4.01
^{11}B	3/2	80.1	4.059
^{14}N	1	99.6	2.044
^{17}O	5/2	0.038	−2.558
^{23}Na	3/2	100	10.4
^{27}Al	5/2	100	14.66
^{45}Sc	7/2	100	−22
^{51}V	7/2	99.8	−5.2
^{55}Mn	5/2	100	0.33
^{59}Co	7/2	100	0.42
^{63}Cu	3/2	69.2	−0.22
^{65}Cu	3/2	30.8	−0.204
^{87}Rb	3/2	27.8	0.132
^{93}Nb	9/2	100	−0.32

!!! The strength of quadrupolar coupling depends on Q AND the EFG!

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

Quadrupolar coupling

Theory: the electric field gradient (EFG)

- arises if **electron density is non-spherical distributed**
= feature of the electronic environment (depends on compound, morphology…)

- Mathematically described by an tensor (like the chemical shift tensor):

$$\mathbf{V} = \begin{pmatrix} V_{xx} & V_{xy} & V_{xz} \\ V_{yx} & V_{yy} & V_{yz} \\ V_{zx} & V_{zy} & V_{zz} \end{pmatrix}$$

$$\mathbf{V}^{PAF} = \begin{pmatrix} V_{XX}^{PAF} & 0 & 0 \\ 0 & V_{YY}^{PAF} & 0 \\ 0 & 0 & V_{ZZ}^{PAF} \end{pmatrix}$$

The trace of the EFG tensor is zero:

$$V_{XX} + V_{YY} + V_{ZZ} \\ = V_{XX}^{PAF} + V_{YY}^{PAF} + V_{ZZ}^{PAF} = 0$$

Quadrupolar coupling

Theory: parameters of the EFG tensor

Analog calculation like for the chemical shift tensor:

- isotropic component: $V^{iso} = \frac{1}{3}\left(V_{XX} + V_{YY} + V_{ZZ}\right) = 0$ (because the trace of the EFG tensor is zero)

→ no isotropic component of the EFG tensor

- anisotropy: $V^{aniso} = V_{zz}^{PAF} - V^{iso} = V_{zz}^{PAF} - 0 = V_{zz}^{PAF}$ with: $V_{zz}^{PAF} = eq$

→ anisotropy of the EFG tensor is the largest component of the vector

- asymmetry: $\eta_Q = \frac{V_{yy}^{PAF} - V_{xx}^{PAF}}{V^{aniso}}$ $0 \le \eta_Q \le 1$

Quadrupolar coupling

Theory: the quadrupolar Hamiltonian

In the PAF: $\hat{H}_Q = \underbrace{\frac{eq \cdot eQ}{\hbar}}_{} \cdot \frac{1}{4I(2I-1)}\left[3\hat{I}_{z^{PAF}} - \hat{\mathbf{I}}^2 + \frac{1}{2}\left(\hat{I}_{x^{PAF}}^2 - \hat{I}_{y^{PAF}}^2\right)\right]$

Quadrupolar
coupling constant [rad/s]:

Quadrupolar coupling constant [Hz]: $C_Q = \frac{eq \cdot eQ}{h}$

→ Measure of the strength for the quadrupolar interaction

Quadrupolar coupling

Theory: impact on the NMR energy level

So far:
- all interactions were considered as perturbations of the Zeeman interaction:

$$\hat{H} = \hat{H}_Z + \hat{H}_X$$

this perturbation theory approach is valid , if the interaction X is small compared to the Zeeman interaction

→ for quadrupolar coupling very often not the case!

Perturbation theory must be expanded:

$$\hat{H} = \hat{H}_Z + \hat{H}_Q^{(1)} + \hat{H}_Q^{(2)} + \ldots$$

$$\hat{H}_Q^{(1)} \downarrow E_Q^{(1)} \qquad \hat{H}_Q^{(2)} \downarrow E_Q^{(2)}$$

"first order/ second order energy correction term of the quadrupolar coupling interaction"

Quadrupolar coupling

Theory: impact on the NMR energy level

Energy correction terms of

- First order:

Can be averaged out by MAS !

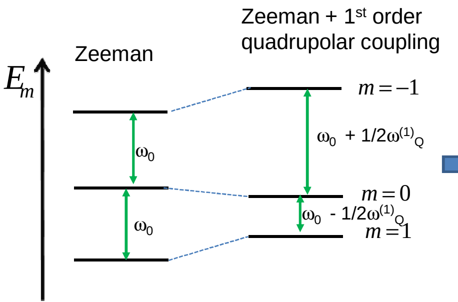
$$E^{(1)}_{Q_m} = \frac{eq \cdot eQ}{4I(2I-1)}\left(3m^2 - I(I+1)\right)\frac{1}{2}\left[\left(3\cos^2\theta - 1\right) + \eta_Q \cos 2\phi \sin^2\theta\right]$$

$= C_Q h$

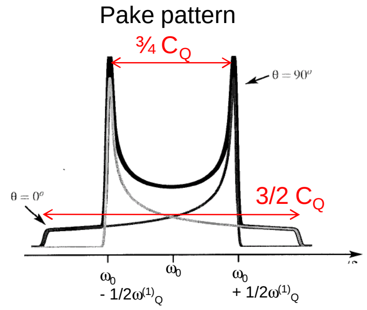
Same energy shifts for +m and –m!
→Central transition (m=1/2↔m=-1/2) is not affected!

Quadrupolar coupling

Spin-1 nuclei: energy diagramms and lineshapes



η_Q=0



- Only natural I=1 spins: ^{2}H, ^{6}Li and ^{14}N

-^{6}Li: - nuclei with smallest Q
  - usually Pake pattern can't be observed due to distribution of C_Q
  → Gaussian lineshapes

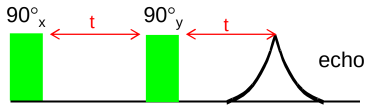
-^{14}N: - small Q, but often strong EFGs → quadrupolar coupling in order of several MHz
  → hard to impossible to measure

Quadrupolar coupling

Spin-1 nuclei: ^{2}H NMR

→Low Q, C_Qs typically about 130 kHz
→ correspond to an FID decay within 5 µs (dead time about 4 µs)
→ ^{2}H NMR spectra can be measured using the Solid Echo pulse sequence

The Solid Echo (quadrupole echo) pulse sequence:

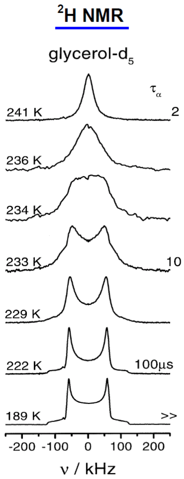


-designed for spin-1 nuclei
-can refocus 1st order quadrupolar coupling and homonuclear dipolar coupling

-Variation for spin-3/2 nulei:
90°$_x$-t-64°$_y$-t-aq

Quadrupolar coupling

^{2}H NMR: study of dynamics in solids



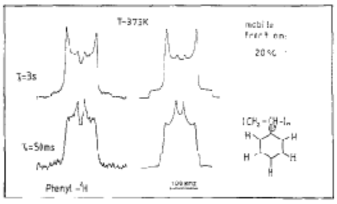
fast motion limit

Slow motion limit

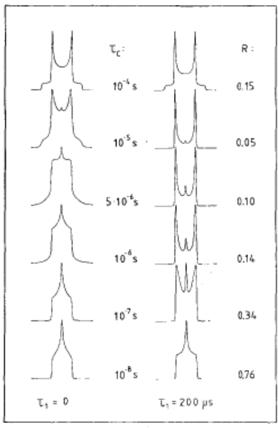
motional narrowing:

→ advantage of ^{2}H NMR:

Differentiation of motion types !



^{2}H spectra of PS-d5 showing the influence of 180° phenyl flips

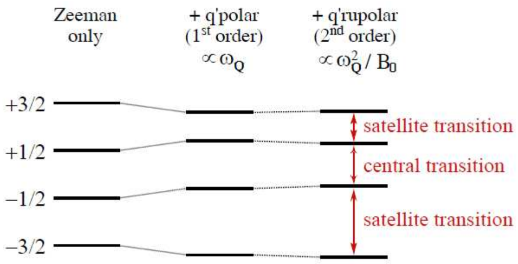


calculated ^{2}H spectra for two site jumps

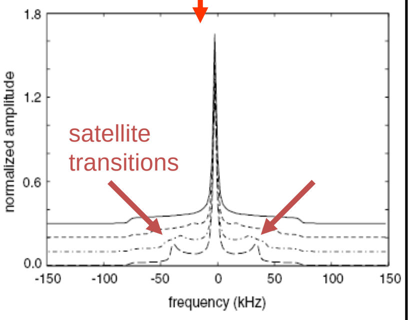
Spiess, H.W.; Colloid & Polymer Sci., **256,** 193-209, (1983)

Quadrupolar coupling

Spin-3/2 nuclei: energy diagramms and lineshapes



central transition



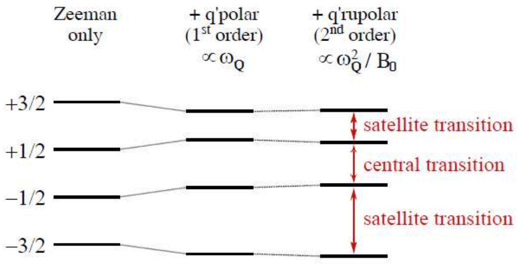
satellite transitions

Fig. 6. Simulations of powder pattern spectra for spin $I = 3/2$ for a coupling constant $e^2qQ/h = 100$ kHz and various asymmetry parameters. To simulate the dipolar broadening of the pattern the spectra were convoluted with a 100 Hz wide Lorentzian line-shape. The spectra were shifted vertically for clarity. From top to bottom η was 1, 0.5, 0.2, and 0

R. Böhmer, K.R. Jeffrey, M.Vogel;
J. Prog. Nucl. Magn. Reson. Spectrosc., **50,** 87-174, (2007)

Quadrupolar coupling

Spin-3/2 nuclei: hard and soft pulses



Homogenous excitation:
→Central as well satellite transitions are excited
→Requires short pulses with high amplitudes ("hard pulse")
→ 90°(solid)= 90°(solution)

Selective excitation:
→Only central transition is excited
→ requires long pulses with a small amplitude ("soft pulse")
→ 90°(solid)=1/2 × 90°(solution)

**In both cases:
sinus-nutation curve!**

Quadrupolar coupling

Spin-3/2 nuclei: hard and soft pulses

Should I use hard or soft pulses?

→ Depends on the purpose of the measurement!

Example:
^{23}Na Spin Echo Decay spectroscopy requires selective excitation!
(to study average ^{23}Na-^{23}Na distances)

Quantitative one pulse MAS experiments require a homogenous excitation!

Quadrupolar coupling

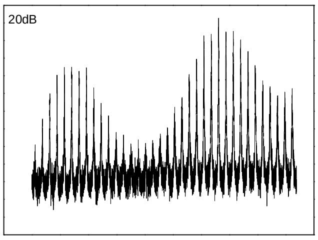
Spin-3/2 nuclei: hard and soft pulses

Non-symmetrical nutation curve without negative intensities!

???

→Not homogenous,
not selective excitation either!

nutation curve:



-Central transition and satellite transitions are partially excited.

Try to avoid this scenario!
-Increase pulse power level → homogenous exc.
- decrease pulse power level → selective exc.

In real world: sometimes not achieveable!

→ Use pulses with the length: 90°/(I+1/2)

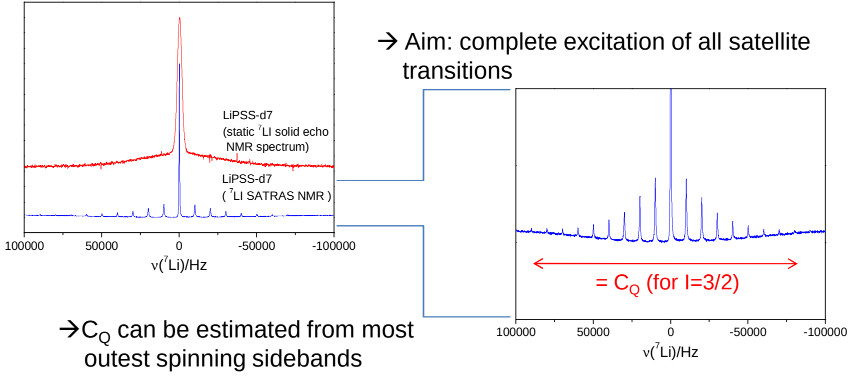
Quadrupolar coupling

MAS experiments: weak quadrupolar coupling

Satellite Transition spectroscopy (SATRAS)

= MAS experiment using hard pulses and big spectral width (and many scans)

→ Aim: complete excitation of all satellite transitions



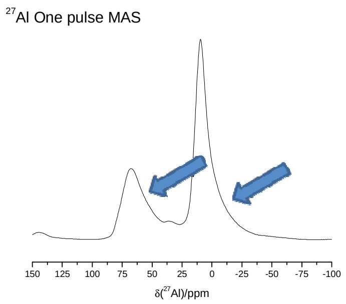
→C_Q can be estimated from most outest spinning sidebands

Quadrupolar coupling

MAS experiments: strong quadrupolar coupling

- First and second order quadrupolar coupling perturbations

→ Interpretation of one pulse MAS NMR spectra complicated



Reason: affected by 2nd order quadrupolar interaction

→Isotropic chemical shift can't be determined from peak position

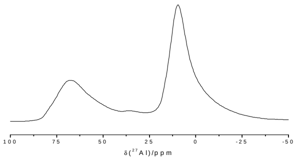
Typical: asymmetric lineshape (due to distribution of quadrupolar coupling constants)
→ could cover different positions!

Quadrupolar coupling

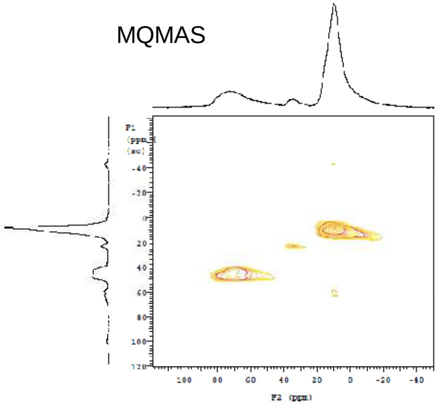
MAS experiments: strong quadrupolar coupling

The multiple-quantum MAS (MQMAS) experiment

one pulse MAS



MQMAS



MQMAS :
2D experiment to obtain
high-resolution spectra of half-integer quadrupolar nuclei

Some wise, closing words… ☺

Before you start any Solid State NMR experiments, please … :

-Be aware that solution state and solid state NMR are very different techniques (different strengths and weaknesses)

-Think about:
What is your research question?
→ What experiments could be useful to answer this question?

Accept that you won't find a recipe to interpret Solid State NMR results!
→Interpretation requires understanding of
- solid state NMR (interactions, their impact on the spectra, methods)
- your material (what nuclei, nuclei environment, morphology,…)

→ Practice makes perfect! ☺

I hope this workshop was a first step in understanding Solid State NMR!

Thank you for your attention!

Quadrupolar coupling

Theory: impact on the NMR energy level

Energy correction terms of

- Second order:

- no orientation dependence
  → isotropic component

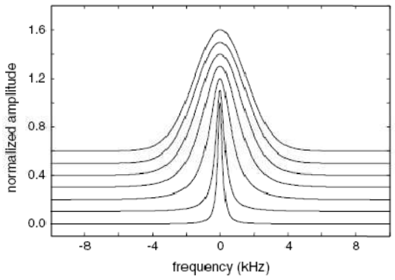
$$
\begin{aligned}
E_{Q_m}^{(2)} = -\left(\frac{eq\cdot eQ}{4I(2I-1)}\right)^2 \frac{m}{\omega_0} \times \Bigg\{ & -\frac{1}{5}\left(I(I+1)-3m^2\right)\left(3+\eta_Q^2\right) \\
& +\frac{1}{28}\left(8I(I+1)-12m^2-3\right)\left[\left(\eta_Q^2-3\right)\left(3\cos^2\theta-1\right)+6\eta_Q\sin^2\theta\cos 2\phi\right] \\
& +\frac{1}{8}\left(18I(I+1)-34m^2-5\right)\Bigg[\frac{1}{140}\left(18+\eta_Q^2\right)\left(35\cos^4\theta-30\cos^2\theta+3\right) \\
& +\frac{3}{7}\eta_Q\sin^2\theta\left(7\cos^2\theta-1\right)\cos 2\phi+\frac{1}{4}\eta_Q^2\sin^4\theta\cos 4\phi\Bigg]\Bigg\}
\end{aligned}
$$

-Increases with $(C_Q/h)^2$

- Energy shifts in opposite directions for +m and –m!

-Proportional to $1/B_0$
→ 2nd order quadrupolar coupling is reduced at strong magnetic fields!!

-Complicated orientation dependence
→ can't be averaged out by MAS!



slow motion limit:
Gaussian line

motional narrowing:
superposition of a Gaussian and a Lorentzian line

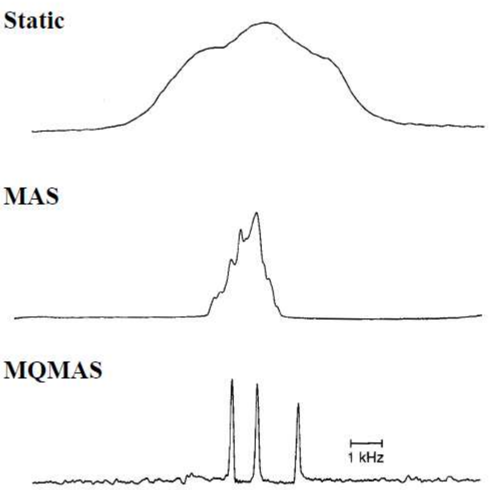
fast motion limit:
Lorentzian line

R. Böhmer, K.R. Jeffrey, M.Vogel; J. Prog. Nucl. Magn. Reson. Spectrosc., **50,** 87-174, (2007)

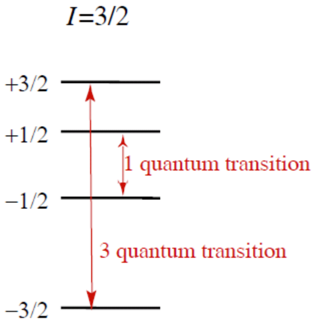
MQMAS in action

^{23}Na spectra (105.8 MHz)
of sodium citrate

S. C. Wimperis



N.B. Horizontal scale varies

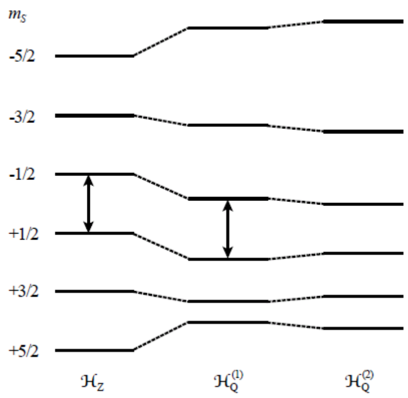


- 1Q and 3Q transition frequencies are unaffected by 1st order quadrupole interaction
- Contributions of isotropic and 2nd order components are non-zero but *different*
- Multiple Quantum Magic-Angle Spinning (MQMAS) correlates 1Q and 3Q frequencies to separate isotropic and 2nd order effects
- 2D experiment that suppresses quadrupole broadening with standard MAS hardware!

Solid state NMR has been applied to:

organic complexes
zeolites
microporous solids
minerals
glasses
food products
ceramics
semiconductors
archaelogical specimens
resins

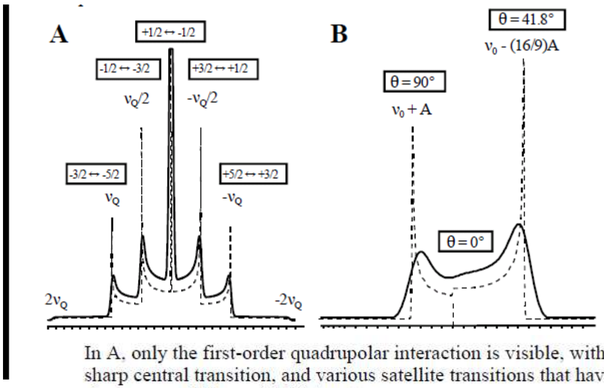
inorganic complexes
mesoporous solids
aluminosilicates/phosphates
biological molecules
cements
wood
bones
metals and alloys
polymers
surfaces



Solid state NMR has been applied to:

organic complexes
zeolites
microporous solids
minerals
glasses
food products
ceramics
semiconductors
archaelogical specimens
resins

inorganic complex
mesoporous solid
aluminosilicates/p
biological molecu
cements
wood
bones
metals and alloys
polymers
surfaces



In A, only the first-order quadrupolar interaction is visible, with a sharp central transition, and various satellite transitions that have shapes resembling axial CSA patterns.

In B, the value of C_Q is much larger. The satellite transitions broaden anddisappear and only the central transition spectrum is left (which is unaffected by first-order interactions). It still has a strange shape due to the orientation dependence of the second-order quadrupolar frequency.

---

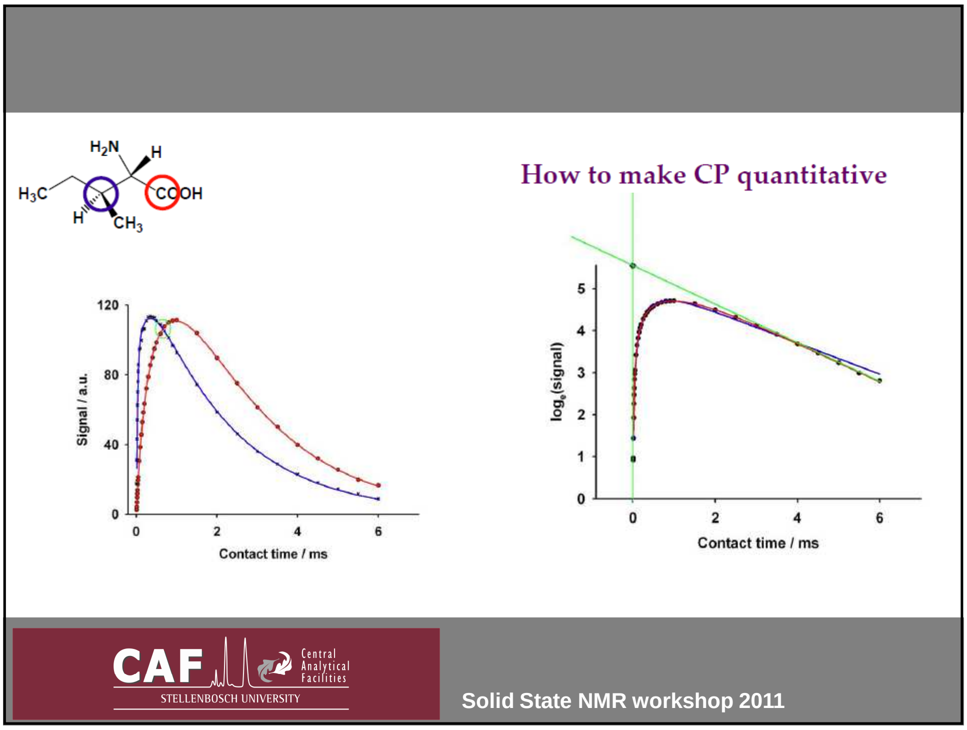
repetitions (constant experiment time)	recycle / T_1	relative S/N
8	5	1.00
12	3.33	1.19
32	1.2	1.41
80	0.5	1.25
400	0.1	0.68

tip-angle = $\cos^{-1}(e^{-t/T_1})$

"Ernst" angle

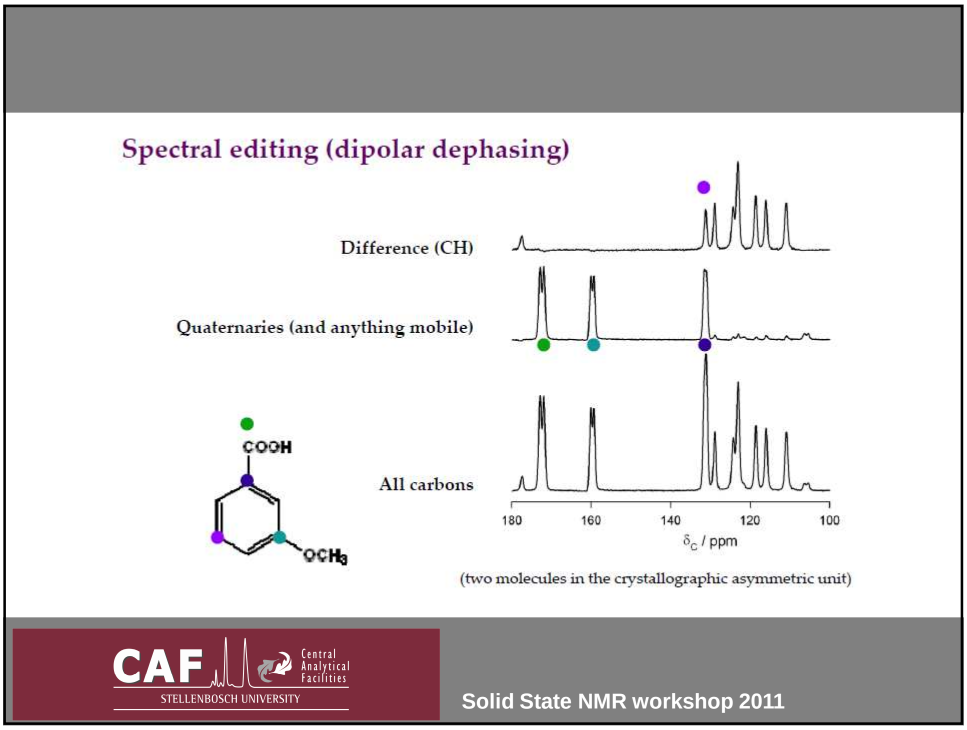
tip-angle < 90/(I+½)

quadrupoles



How to make CP quantitative

Solid State NMR workshop 2011



Spectral editing (dipolar dephasing)

Difference (CH)

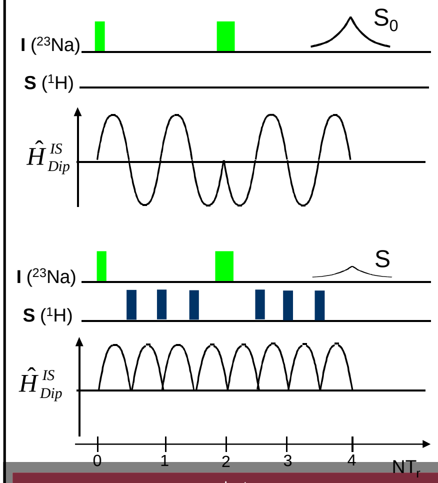
Quaternaries (and anything mobile)

All carbons

(two molecules in the crystallographic asymmetric unit)

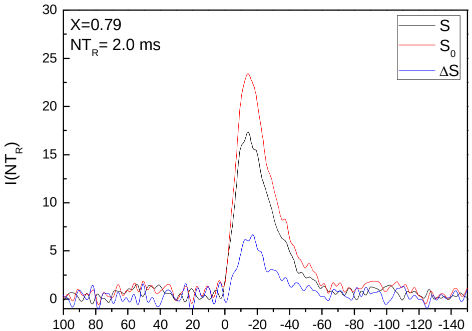
Solid State NMR workshop 2011

The REDOR pulse sequence:



REDOR= Rotational Echo Double Resonance

$$\hat{H}^{IS}_{Dip} \propto \frac{\hat{I}_Z \hat{S}_Z}{r^3}\left(3\cos^2\theta - 1\right)$$



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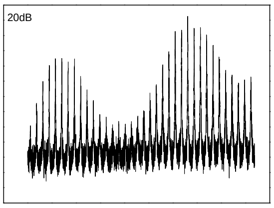
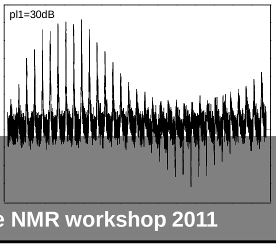
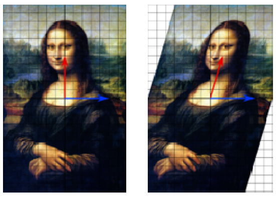
nutation curves:



no selective excitation of the central transition !



In this shear mapping the red arrow changes direction but the blue arrow does not. Therefore the blue arrow is an eigenvector, with eigenvalue 1 as its length is unchanged.



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