Advanced Quadrupolar NMR

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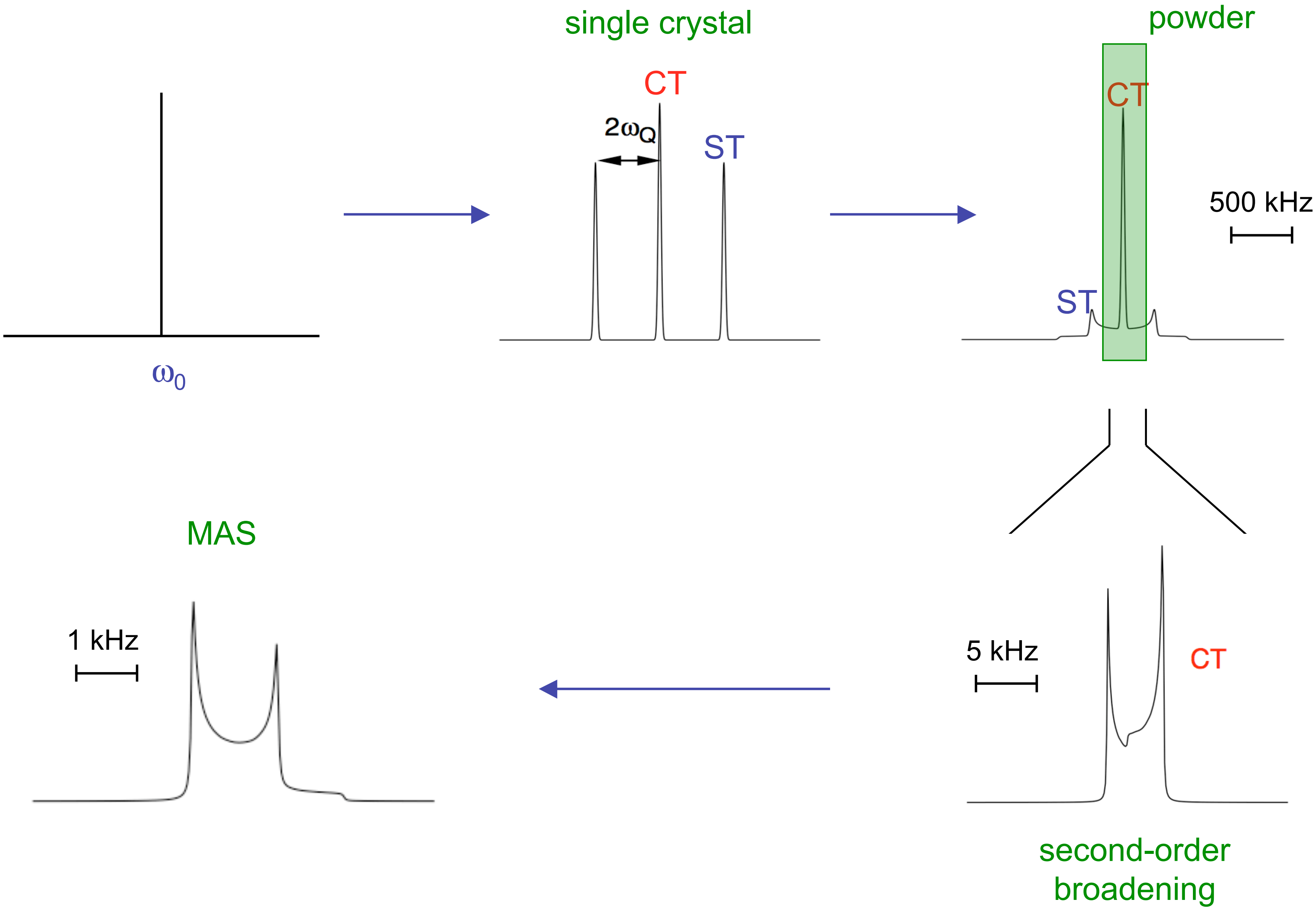
EaStCHEM

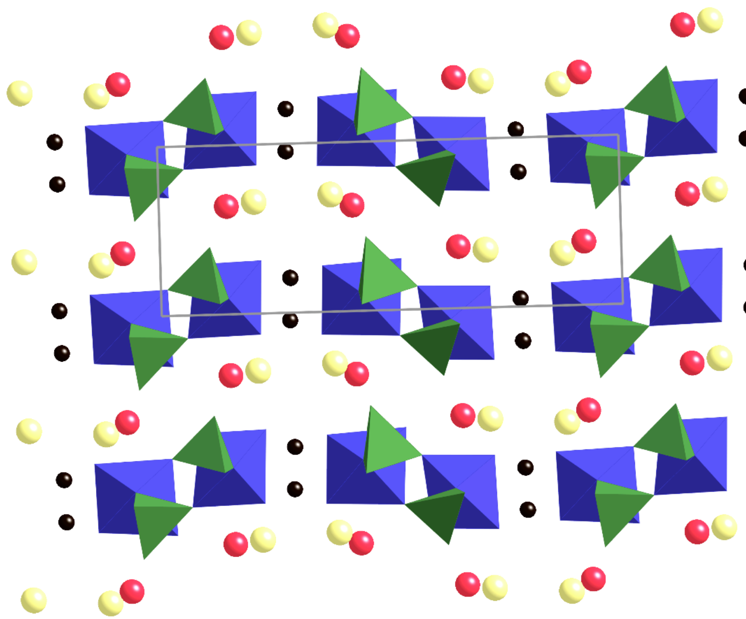
Quadrupolar nuclei: revision

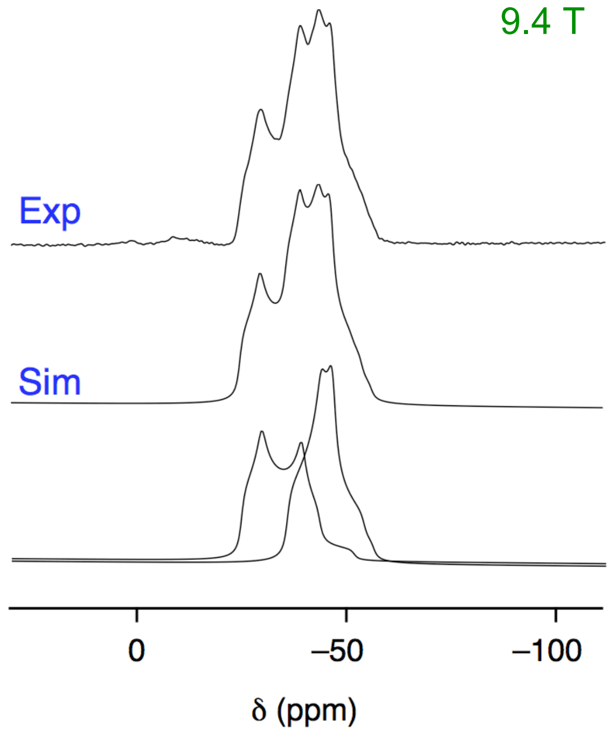


Example: ^{23}Na NMR

- Novel layered material $Na_2[(VO)_2(HPO_4)_2C_2O_4].2H_2O$
- Space group cannot be determined easily by X-ray *$P2_1/m$* or *$P2_1$*

- 2 distinct resonances by ^{23}Na MAS NMR
- Space group cannot be *$P2_1/m$*

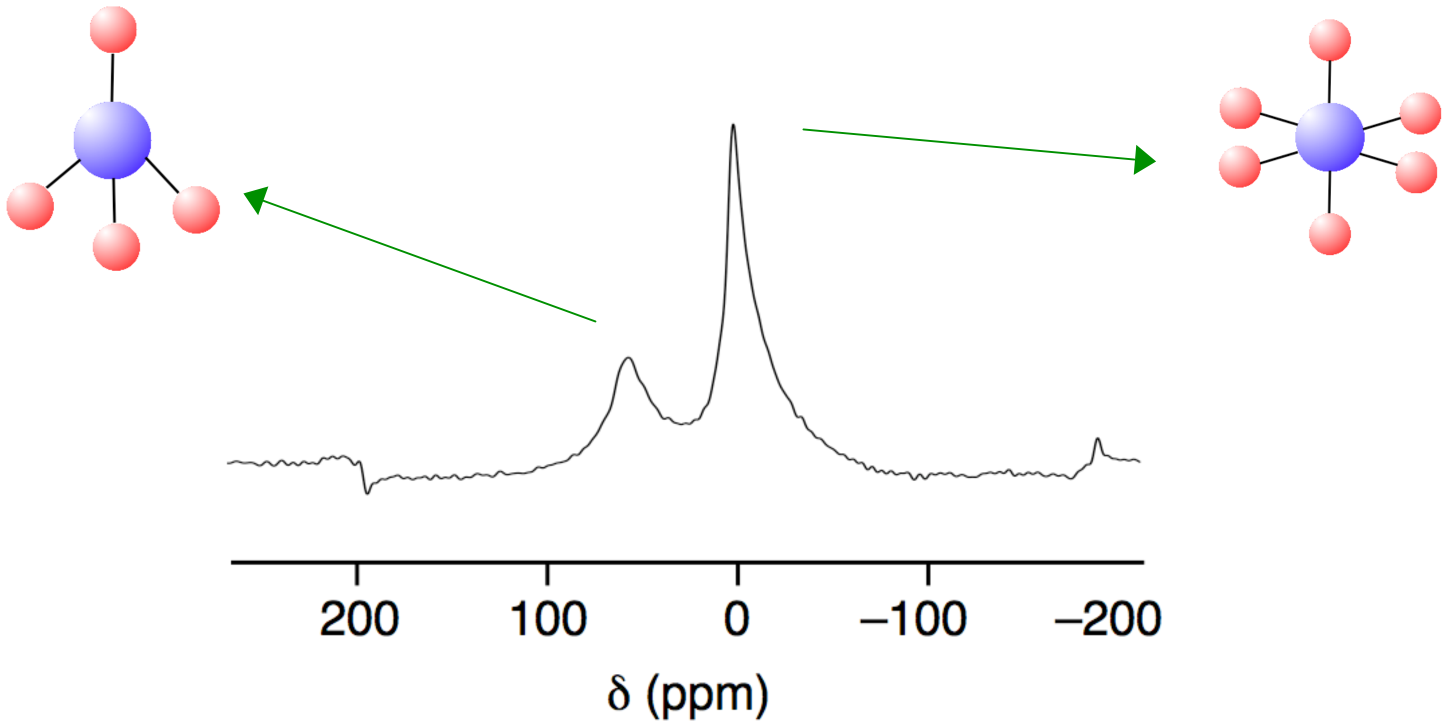




Ashbrook et al., Inorg. Chem. ***45****, 6034 (2006)*

Example: ^{27}Al NMR of minerals

- Substitution of Al into $MgSiO_3$ is important in the inner Earth
- Where does the Al substitute, the six-coordinate Mg site or the four-coordinate Si site?

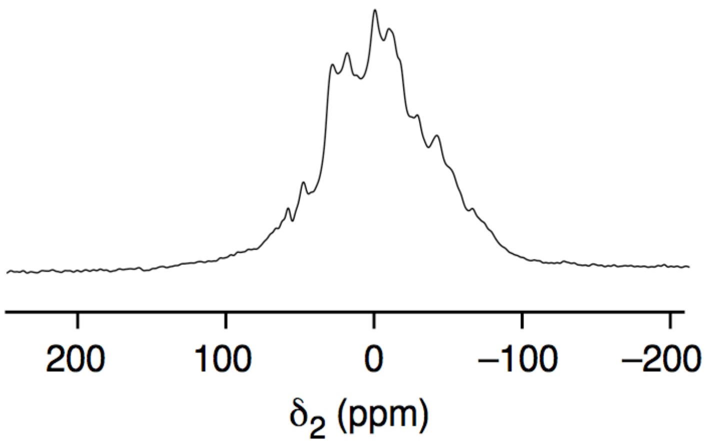


MAS lineshapes

- In many cases, the overlap of a number of broad resonances hinders spectral interpretation and assignment

^{17}O NMR of $MgSiO_3$

9.4 T MAS



How many oxygen species are present?

What are their quadrupolar and chemical shift parameters?

How can we remove the broadening and obtain a high-resolution spectrum?

High-resolution NMR?

$$\omega \propto \frac{\left(\omega_Q^{PAS}\right)^2}{\omega_0}\left[A + B\, d^2_{00}(\beta_R)\, d^2_{00}(\beta) + C\, d^4_{00}(\beta_R)\, d^4_{00}(\beta)\right]$$

Constant depending upon C_Q, I and ω_0

Isotropic shift

Second-rank anisotropic

Fourth-rank anisotropic

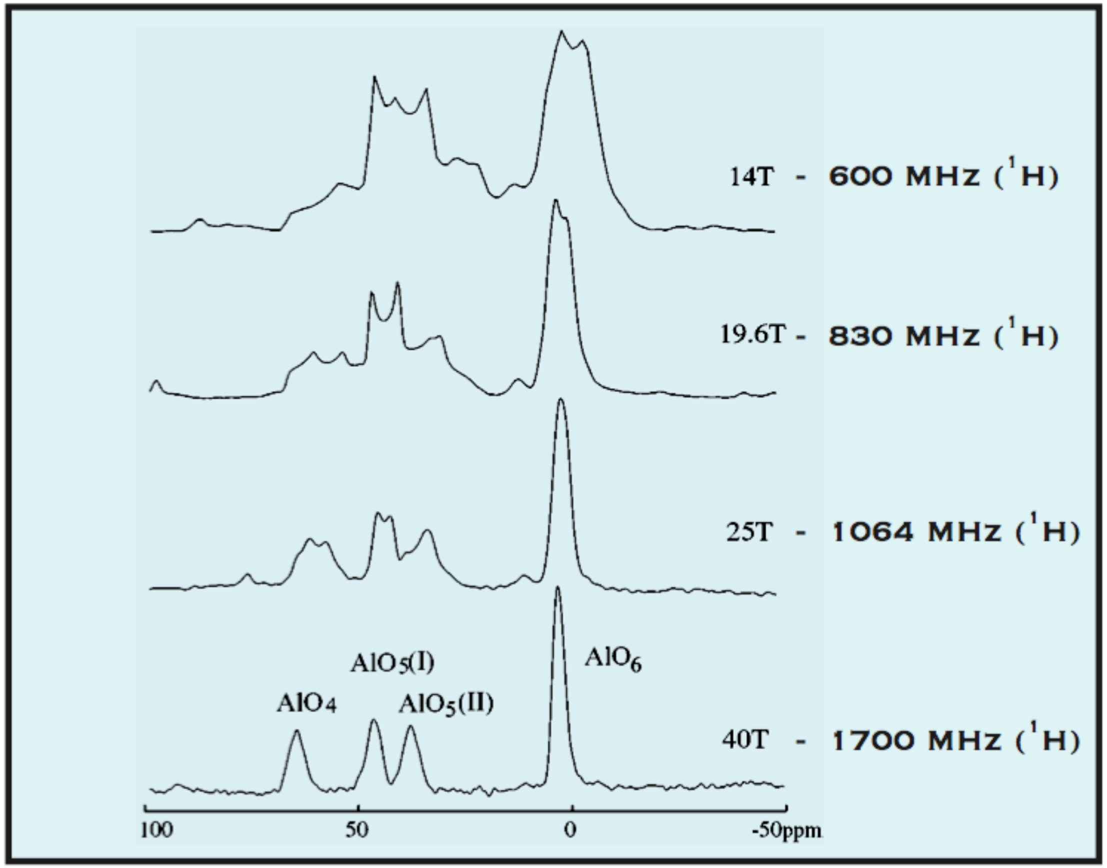
$$d^2_{00}(\beta_R) \propto (3\cos^2\beta_R - 1)$$

$$d^4_{00}(\beta_R) \propto (35\cos^4\beta_R - 30\cos^2\beta_R + 3)$$

- Need to remove anisotropic broadening whilst retaining chemical shift resolution

High-resolution NMR: High field

- The second-order quadrupolar broadening is proportional to $1/\omega_0$
- Increasing the B_0 field will decrease the broadening and improve resolution

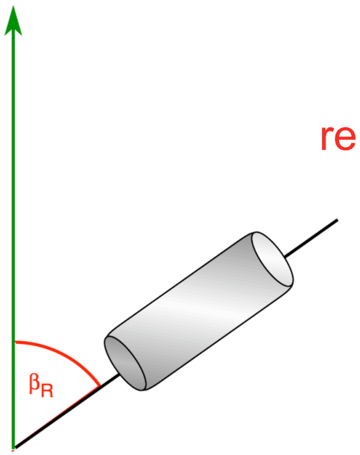


^{27}Al MAS of
$9Al_2O_3.2B_2O_3$

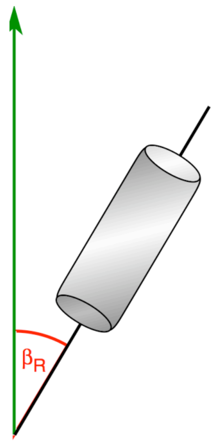
Gan et al., J. Am. Chem. Soc. ***124****, 5634 (2002)*

High-resolution NMR?

$$\omega \propto \frac{\left(\omega_Q^{PAS}\right)^2}{\omega_0}\left[A + B\, d^2_{00}\left(\beta_R\right)\, d^2_{00}\left(\beta\right) + C\, d^4_{00}\left(\beta_R\right)\, d^4_{00}\left(\beta\right)\right]$$



removed if β_R = 54.74°

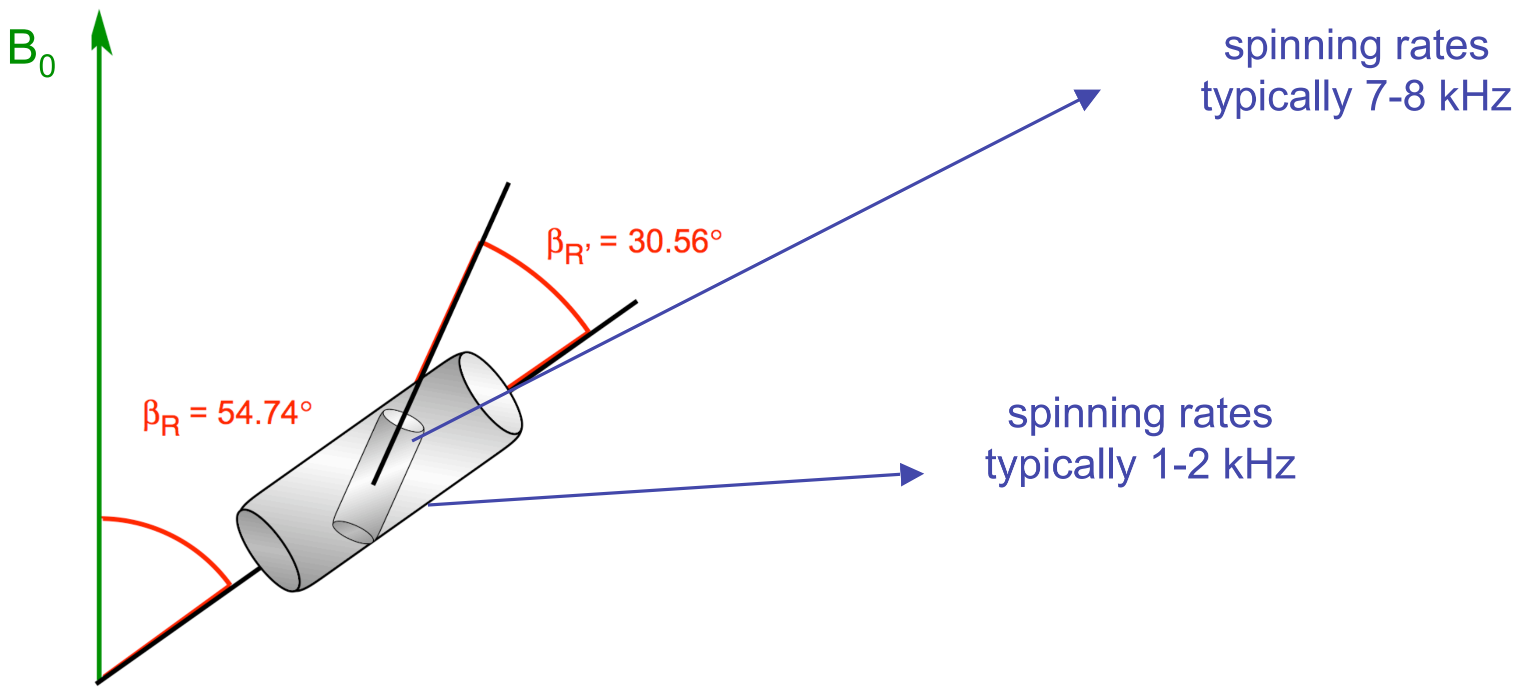


removed if β_R = 30.56° or 70.12°

- Spinning around more than one angle?

High-resolution NMR: DOR

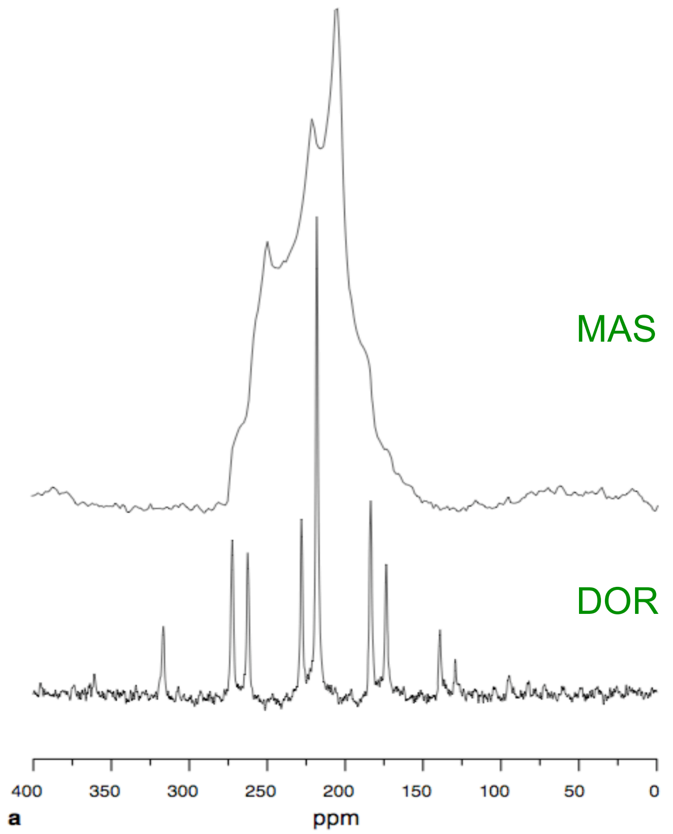
- Double rotation (DOR)
- Rotation around two angles simultaneously is able to remove second-rank and fourth-rank broadening
- Technically very complex and requires an expensive specialist probe



Samoson et al., Mol. Phys. ***65****, 1023 (1988)*

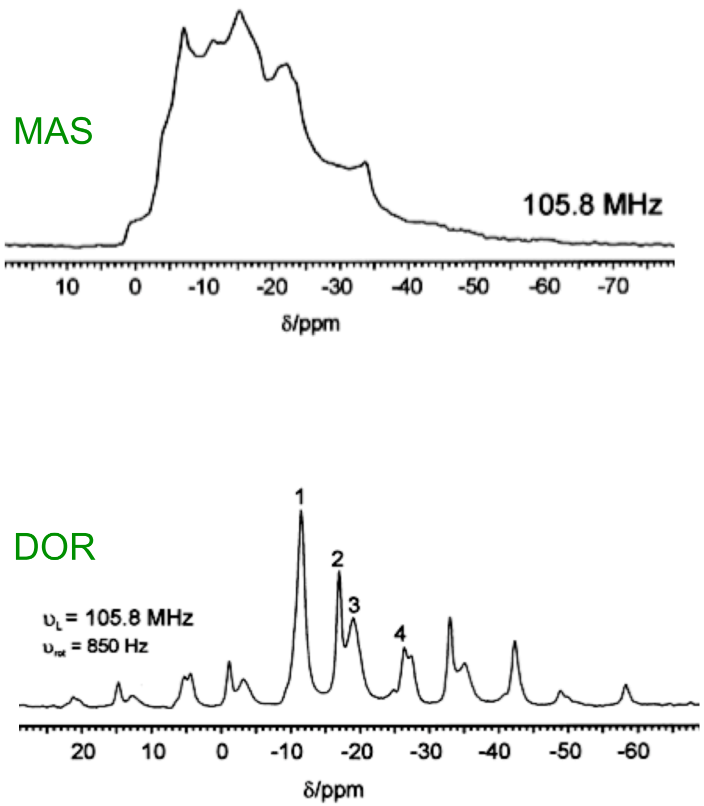
DOR examples

^{17}O NMR of alanine



Howes et al., Chem. Phys. Lett. ***421****, 42 (2006)*

^{23}Na NMR of $Na_2P_4O_7$



Engelhardt et al., Solid State NMR ***15****, 171 (1999)*

High-resolution NMR: DOR

Advantages

Quantitative

High sensitivity

Low rf required

Fast 1D experiment

Disadvantages

Special, expensive probe required

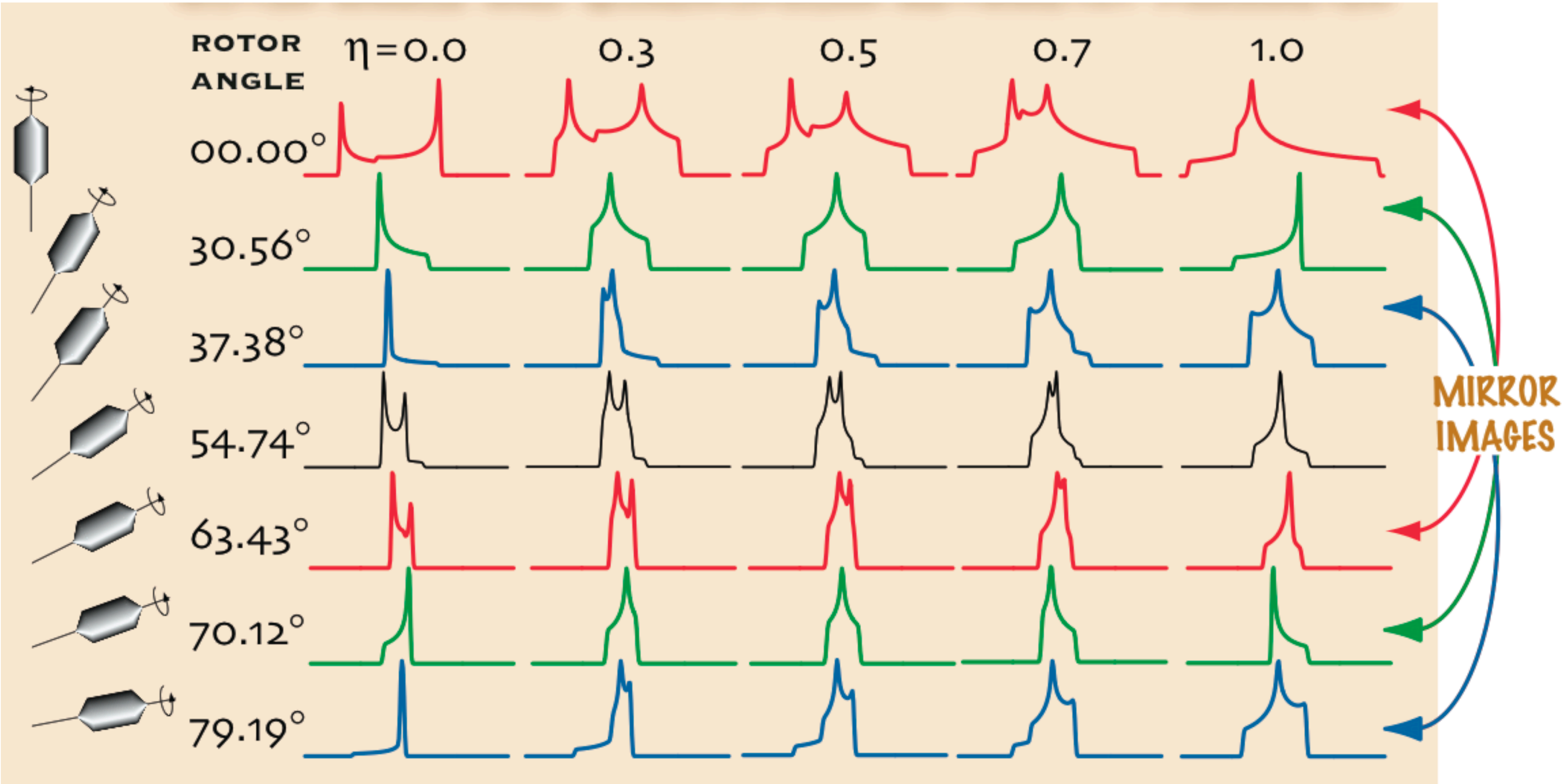
Stable spinning is difficult

Slow spinning rates available

Large coil results in poor filling factor and poor rf for decoupling

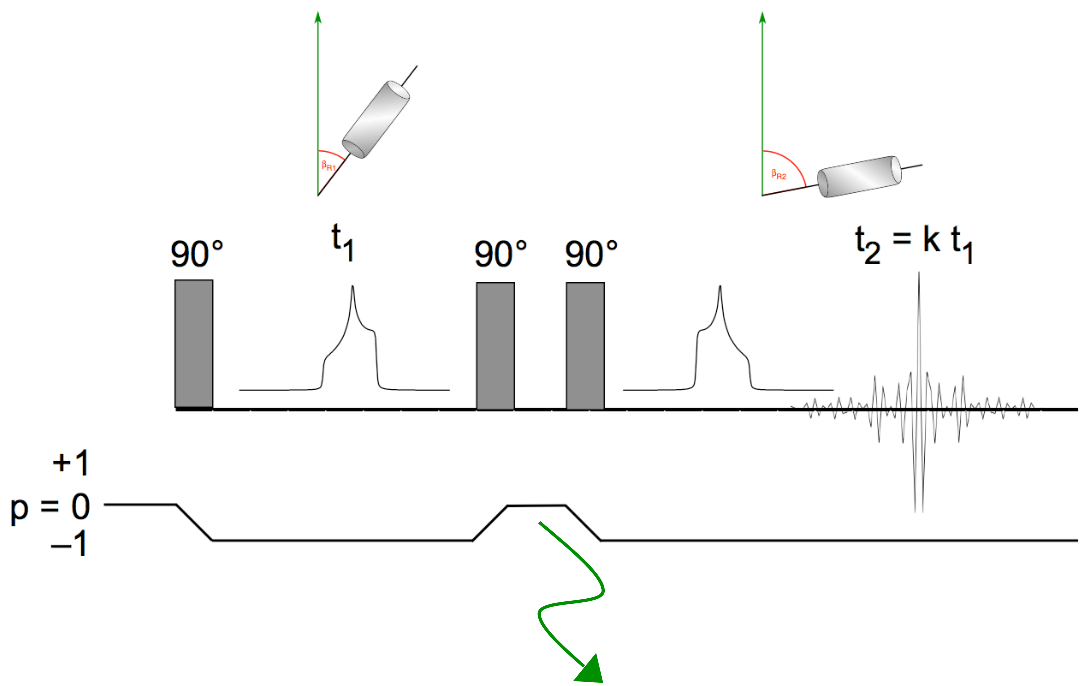
High-resolution NMR?

- Use an echo to refocus the broadening?

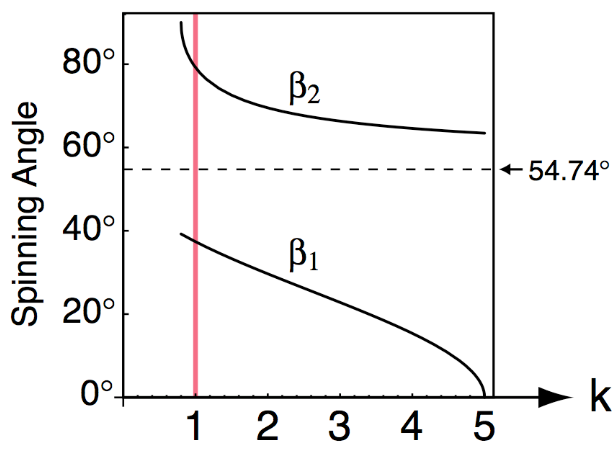


High-resolution NMR: DAS

- Dynamic angle spinning (DAS)
- Rotation around two different angles sequentially
- Angles chosen so two lineshapes are either mirror images or can be scaled to be so, refocussing anisotropic broadening in an echo
- Usually performed as two-dimensional experiment



store magnetization along
z whilst angle changes

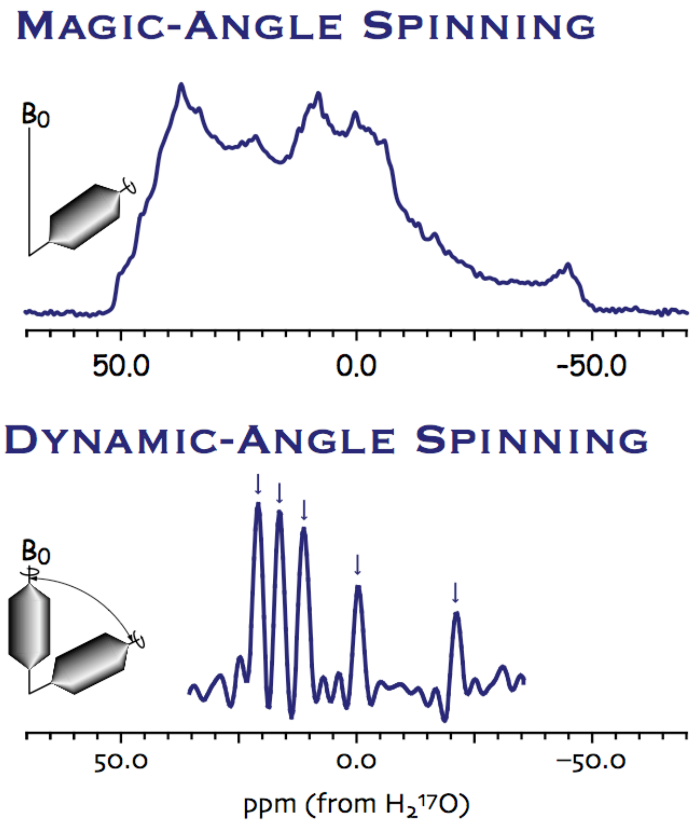


$\beta_1 = 37.38°$, $\beta_2 = 79.19°$
and k =1

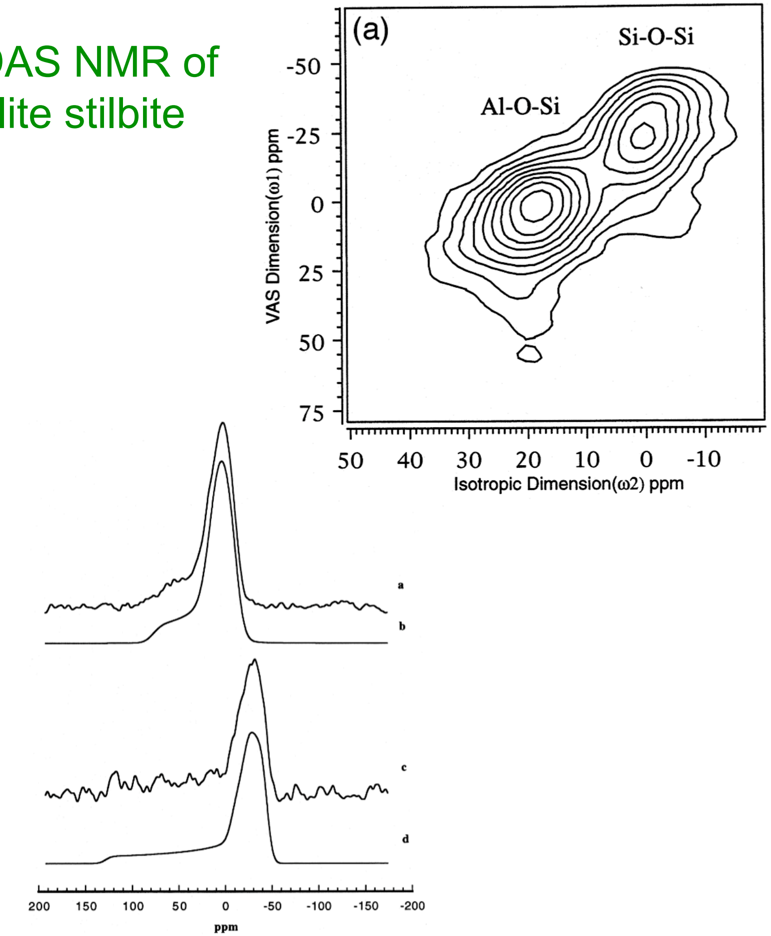
Llor and Virlet, Chem. Phys. Lett. ***152****, 248 (1988)*

DAS examples

^{17}O DAS NMR of coesite (SiO_2)



^{17}O DAS NMR of zeolite stilbite



Grandinetti et al., J. Phys. Chem. ***99****, 12341 (1995)*

Xu et al., Solid State Nucl. Magn. Reson. ***11****, 243 (1998)*

High-resolution NMR: DAS

Advantages	Disadvantages
Quantitative	Special, expensive probe required
High sensitivity	Problems with strong homonuclear dipolar couplings
Low rf required	Limited to nuclei with long T_1 relaxation
Works well for dilute nuclei	In simple experiment no MAS so dipolar broadening/CSA not removed (unless additional hop is used)

High-resolution NMR?

- Manipulation of the coefficients - a different type of echo?

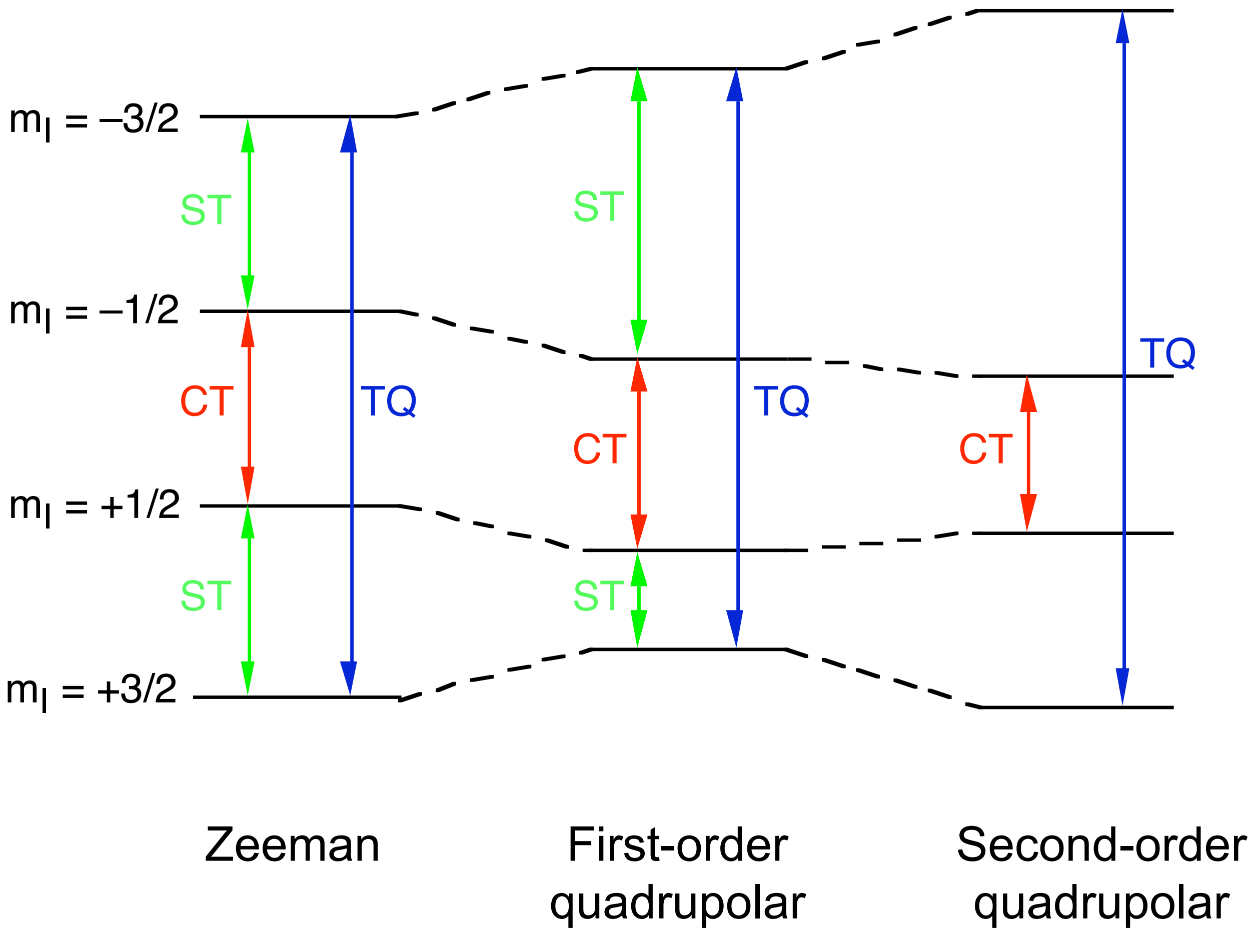
$$\omega_{CT} \propto \frac{\left(\omega_Q^{PAS}\right)^2}{\omega_0}\left[A + B\, d_{00}^2(\beta_R)\; d_{00}^2(\beta) + C\, d_{00}^4(\beta_R)\; d_{00}^4(\beta)\right]$$

$$\omega_{??} \propto \frac{\left(\omega_Q^{PAS}\right)^2}{\omega_0}\left[A' + B'\, d_{00}^2(\beta_R)\; d_{00}^2(\beta) + C'\, d_{00}^4(\beta_R)\; d_{00}^4(\beta)\right]$$

removed if $\beta_R =$ 54.74°

High-resolution NMR: MQMAS

- Which transition to choose?

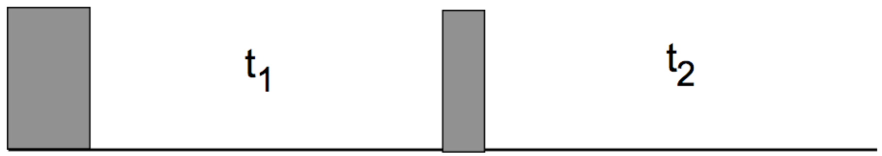


High-resolution NMR: MQMAS

Spin	Transition	A	B	C
I = 3/2	C T	–2/5	–8/7	54/35
	3 Q	6/5	0	–6/5
I = 5/2	C T	–16/15	–64/21	144/35
	3Q	–4/5	–40/7	228/35
	5 Q	20/3	40/21	–60/7

High-resolution NMR: MQMAS

Frydman et al., J. Am. Chem. Soc. ***117****, 5367 (1995)*



$$\omega_{CT} = ((\omega_Q^{PAS})^2/(\omega_0))\,[A + C\,d^4_{00}(\beta_R)\,d^4_{00}(\beta)]$$

$$\omega_{3Q} = ((\omega_Q^{PAS})^2/(\omega_0))\,[A' + C'\,d^4_{00}(\beta_R)\,d^4_{00}(\beta)]$$

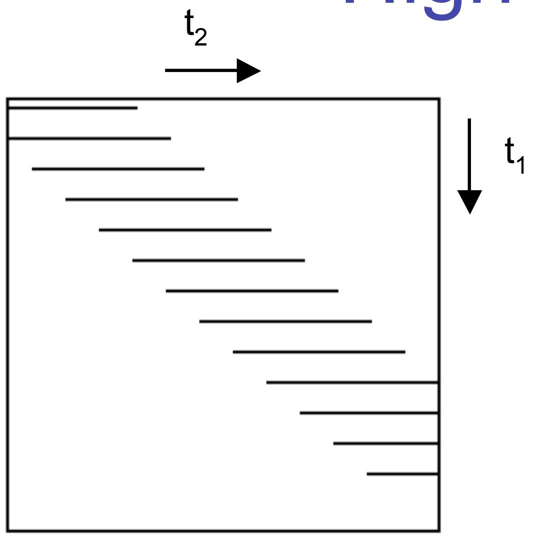
- In a multiple-quantum (MQ) MAS experiment

$$s(t_1,t_2) = \exp\{-i\,\omega_{3Q}\,t_1\} \times \exp\{-i\,\omega_{CT}\,t_2\}$$
$$s(t_1,t_2) = \exp\{-i\,(\omega_{3Q}\,t_1 + \omega_{CT}\,t_2)\}$$

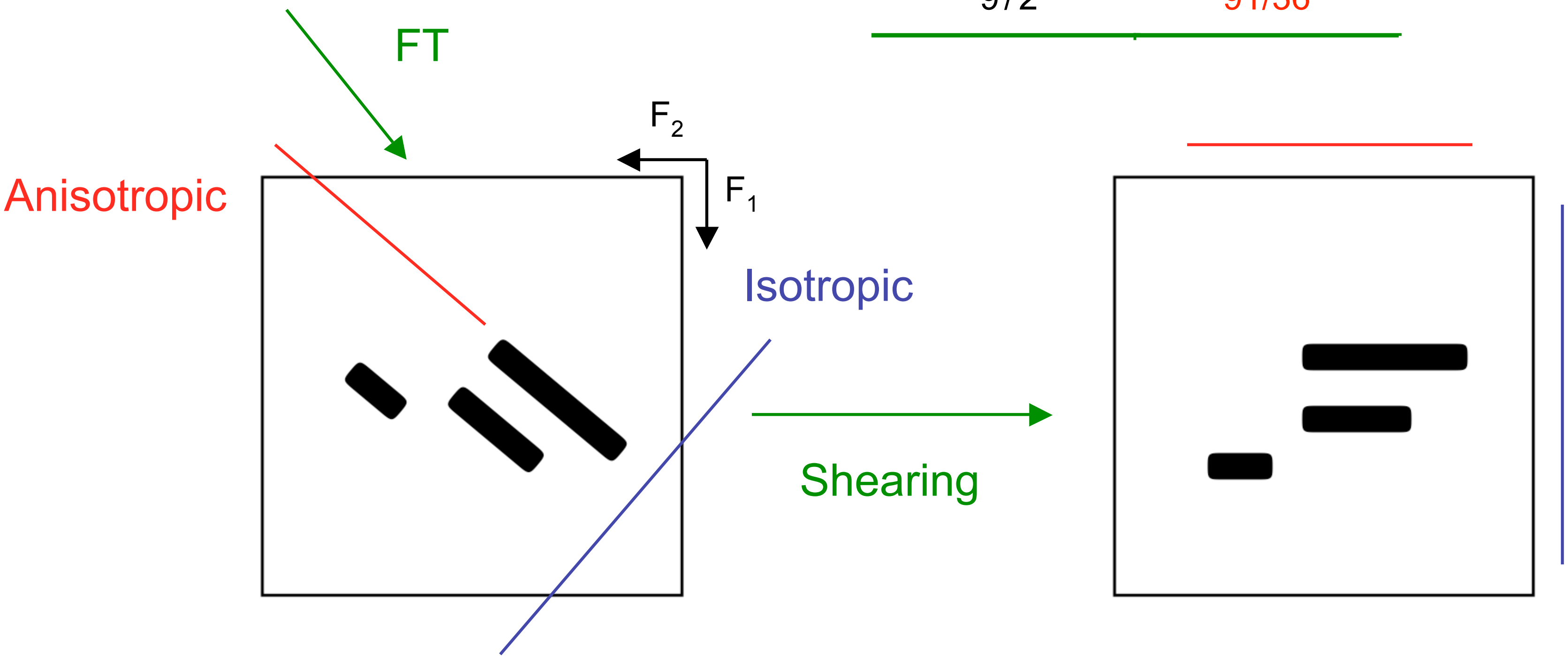
When $t_2 = -(C'/C)\,t_1$ the fourth-rank anisotropic broadening is refocussed

MQMAS ratio

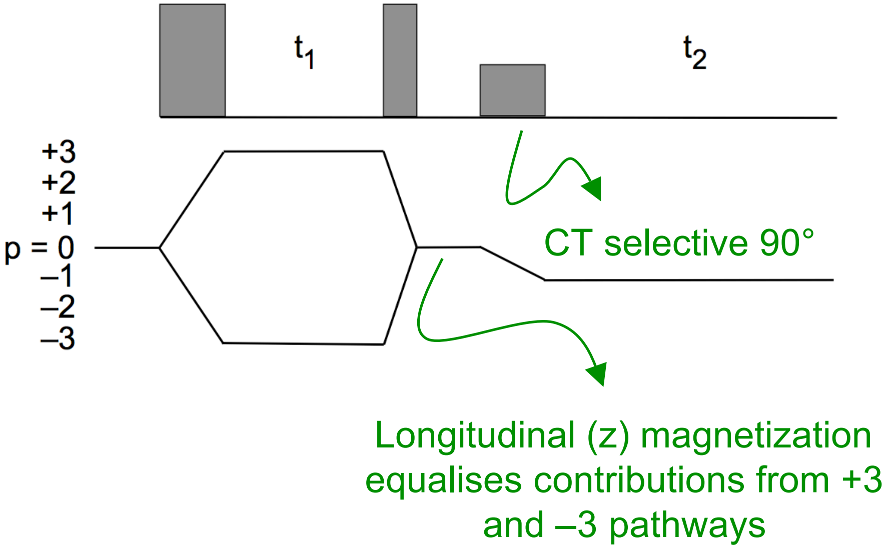
High-resolution NMR: MQMAS

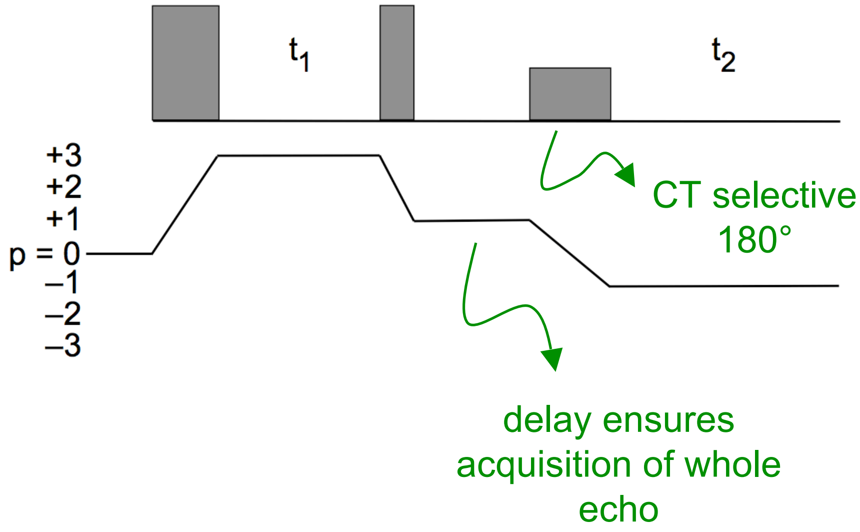


Spin	3Q ratio
3/2	−7/9
5/2	19/12
7/2	101/45
9/2	91/36



MQMAS pulse sequences





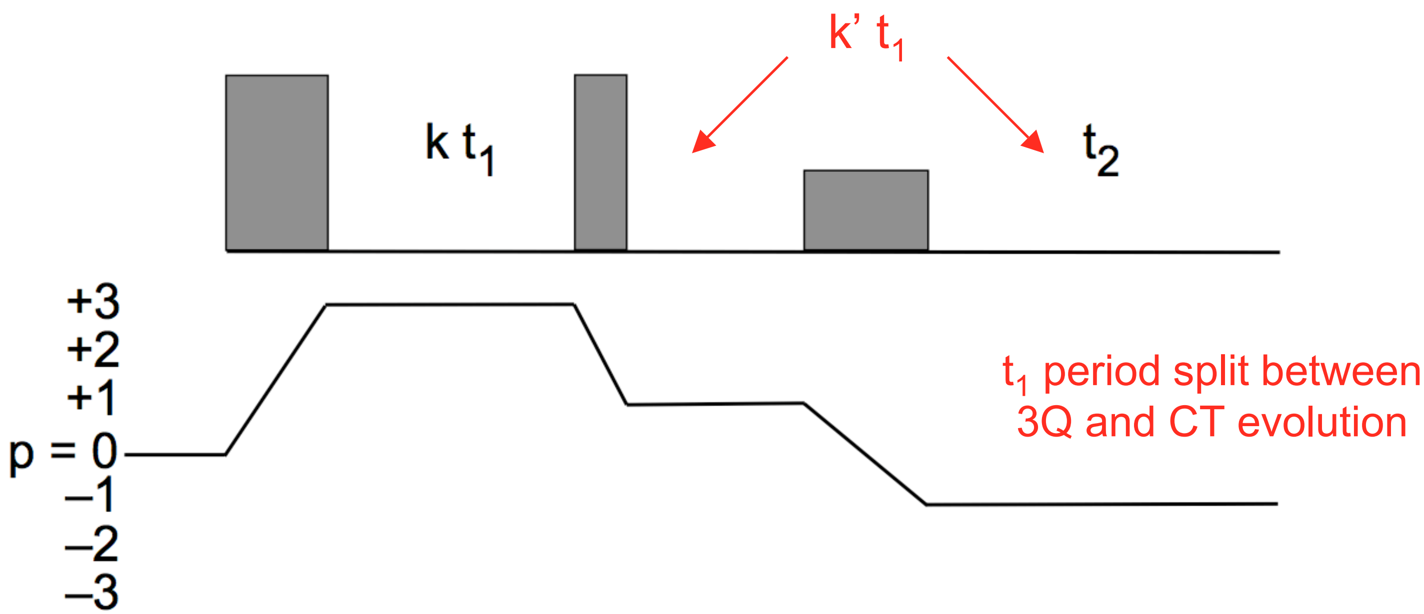
- z-filter
- Gives pure-phase lineshapes
- Requires States/TPPI
- Requires shearing
- Robust, easy to implement
- Low(est) sensitivity

Amoureux et al., J. Magn. Reson. A **123,** *16 (1996)*

- Shifted echo
- Gives pure-phase lineshapes
- No States/TPPI required
- Requires shearing
- Possible T_2 problems
- Better sensitivity

Massiot et al., Solid State NMR **6,** *73 (1996)*

MQMAS pulse sequences: split-t_1 approach

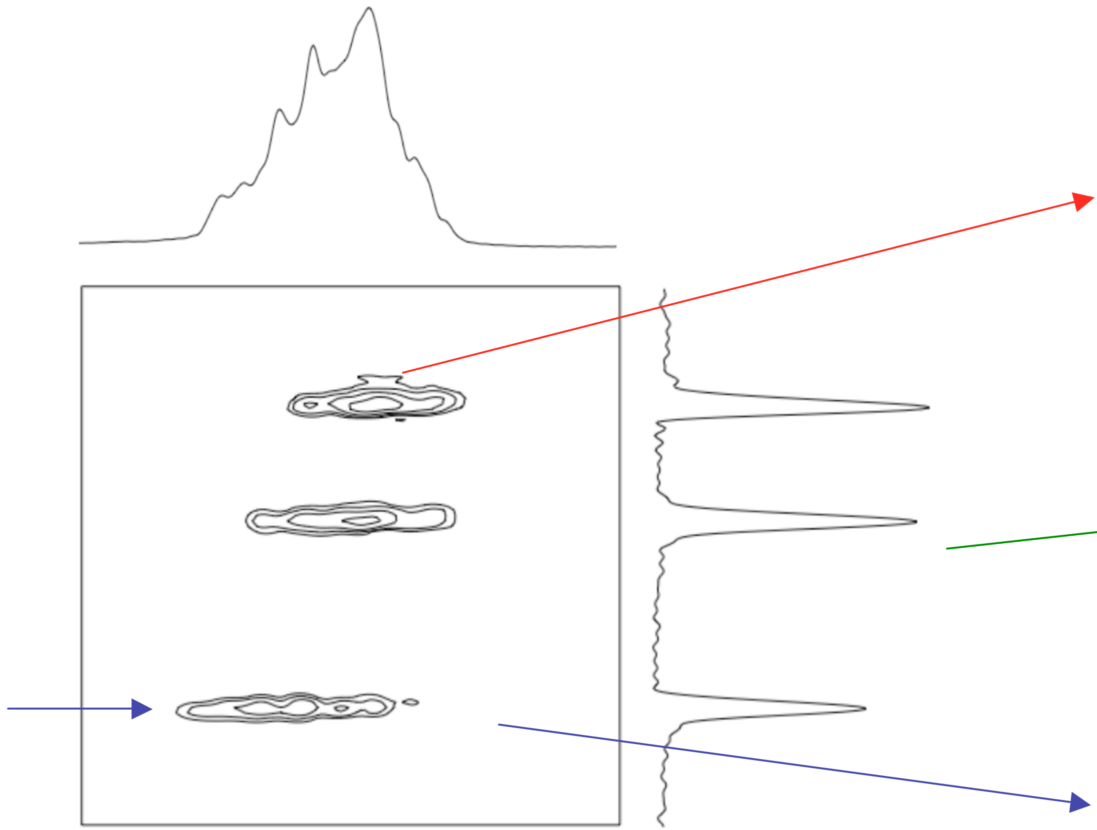


- Requires no shearing
- Can be applied to z-filter or echo experiments
- Position of k' t_1 (and values of k and k') depends upon I
- Optimum sensitivity for I = 3/2 echo experiment

Brown et al., J. Magn. Reson. **A119,** *280 (1996)*

MQMAS information content

^{23}Na NMR of sodium citrate



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

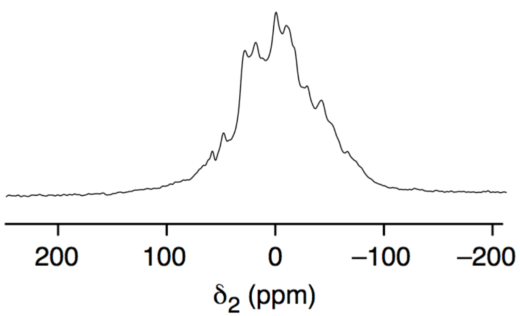
Isotropic spectrum
number of species and relative intensities

Cross-section along ridge
C_Q and η_Q

Ashbrook et al., J. Magn. Reson. ***147****, 238 (2000)*

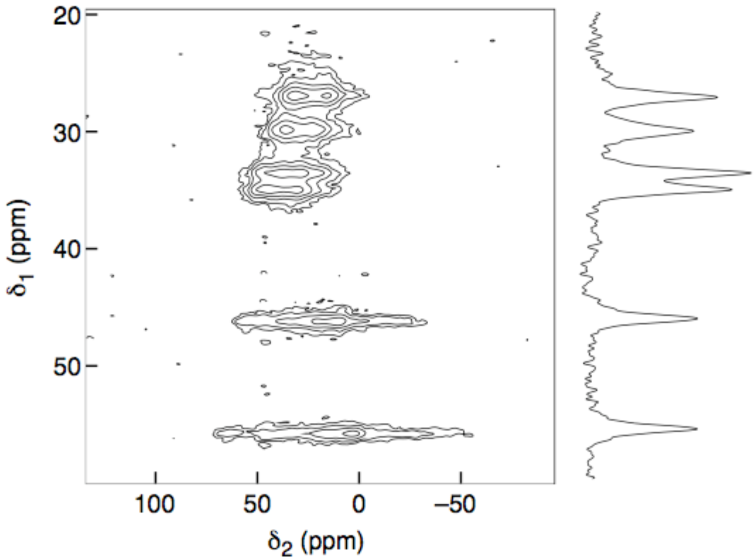
Example: ^{17}O of $MgSiO_3$

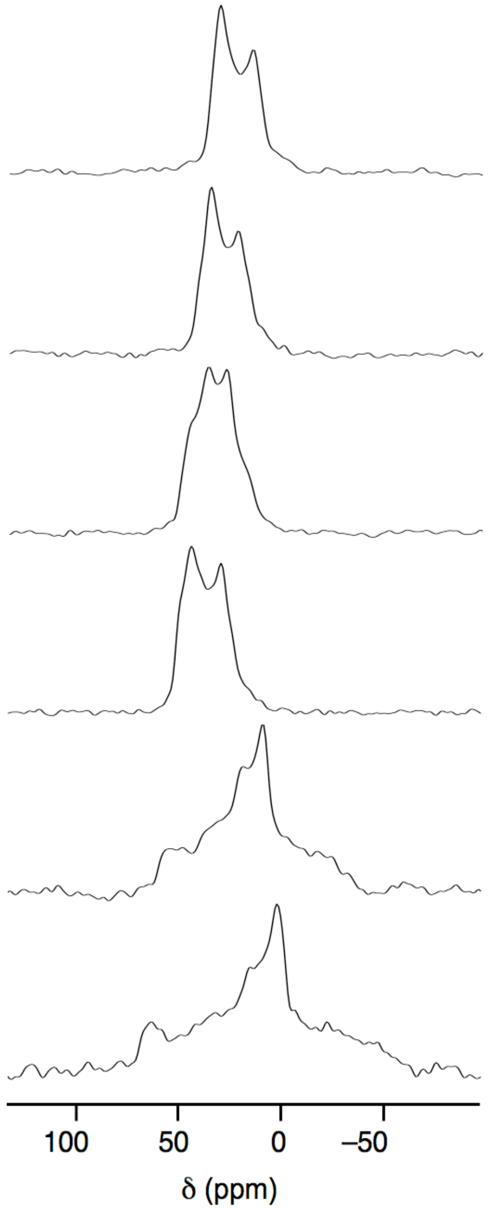
9.4 T MAS



9.4 T MQMAS

6 O



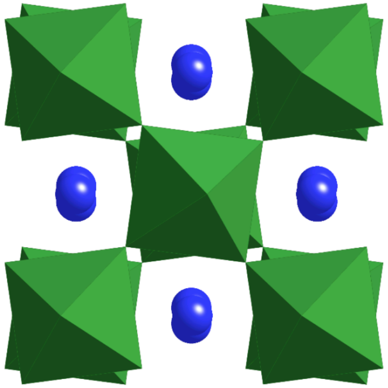


δ_{iso}	C_Q	η_Q
41 ppm	2.9 MHz	0.19
46 ppm	2.8 MHz	0.29
52 ppm	2.9 MHz	0.53
56 ppm	2.9 MHz	0.29
60 ppm	4.2 MHz	0.78
70 ppm	4.8 MHz	0.80

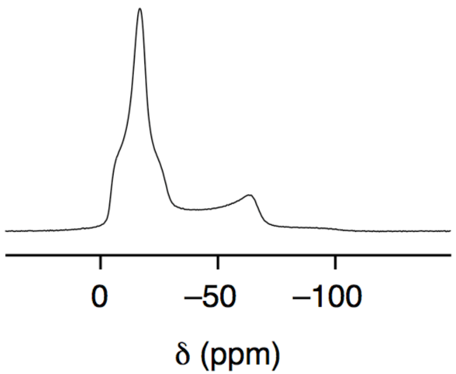
Ashbrook et al., J. Am. Chem. Soc. ***129****, 13213 (2007)*

Example: ^{23}Na of $NaNbO_3$

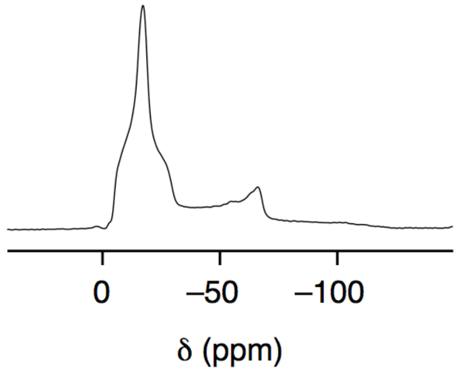
$NaNbO_3$ Pbcm



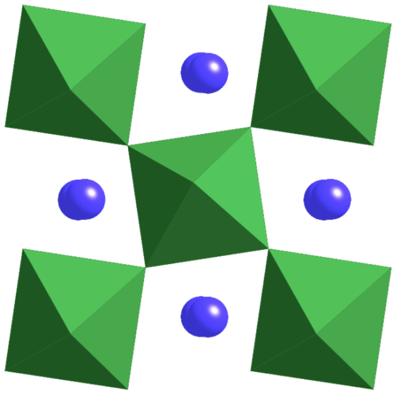
Commercial

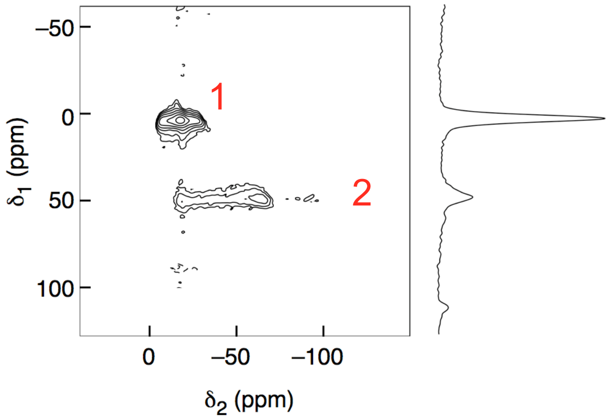


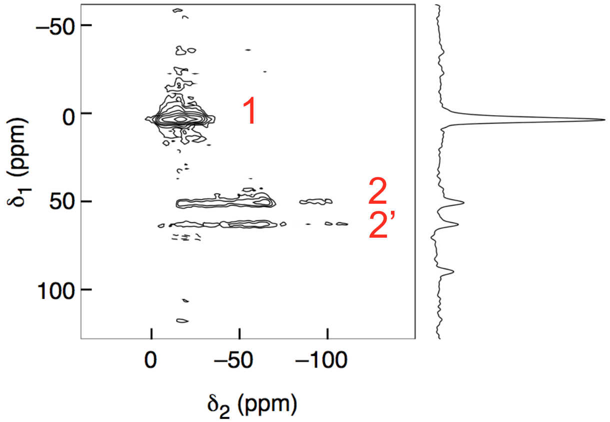
Synthetic



$NaNbO_3$ P21ma





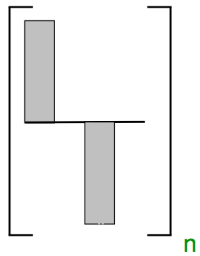


Ashbrook et al., PCCP
***8**, 3423 (2006)*

MQMAS pulse sequences: improvements

- The excitation and conversion of multiple-quantum coherences is “forbidden” by quantum mechanics leading to poor sensitivity overall

FAM

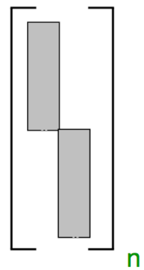


SPAM

- Approaches to improve 3Q to CT conversion

  Composite pulses, FAM, SPAM, DFS

RAPT



- Approaches to improve 3Q excitation

  Shaped pulses, RAPT-RIACT, DFS-RIACT, rotary resonance

- General improvements

  Decoupling, CPMG?

High-resolution NMR: MQMAS

Advantages

Easy to implement and no special probe required

Good for abundant nuclei

Good for nuclei with short T_1

Disadvantages

Not quantitative in most cases

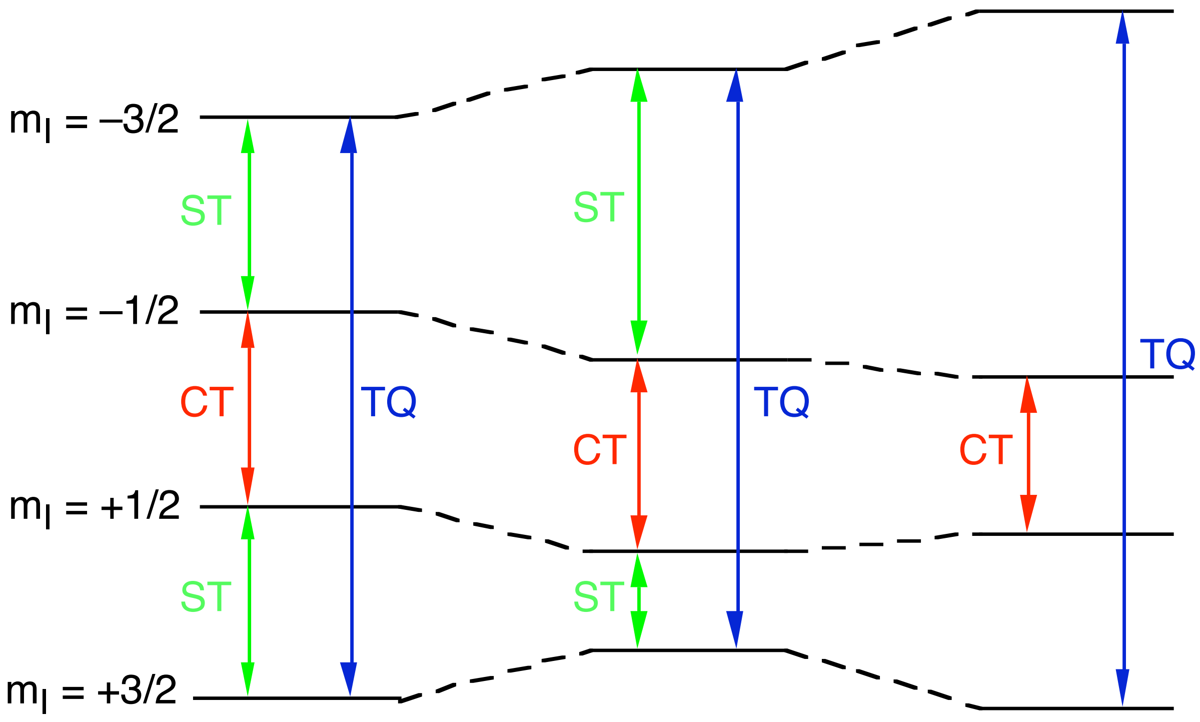
High rf required for excitation of triple-quantum coherences

Poor sensitivity for large C_Q

Complex spinning sidebands

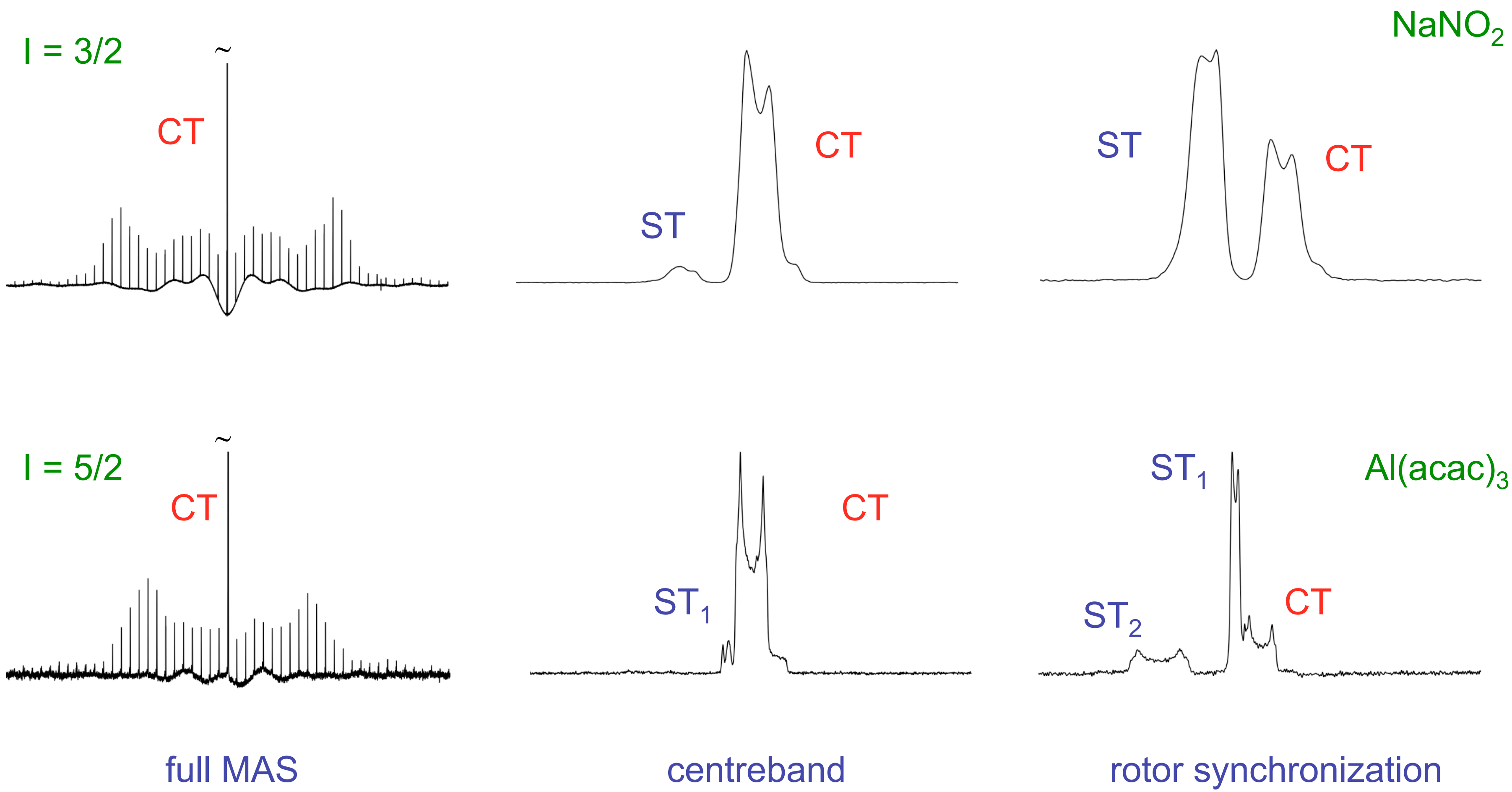
High-resolution NMR?

- Can we choose a different transition?



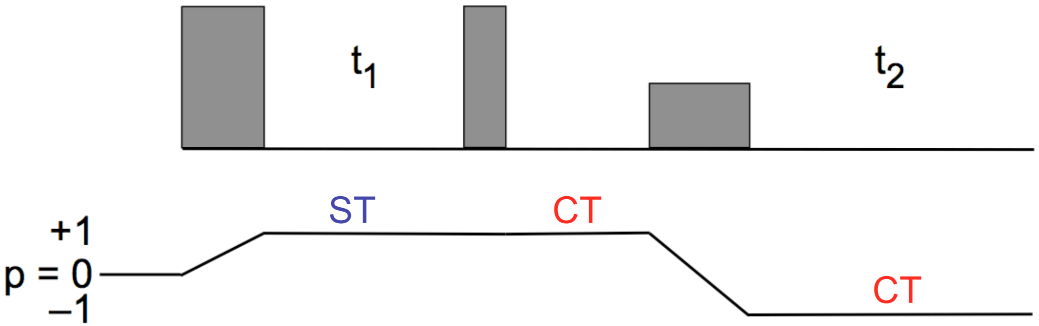
High-resolution NMR: STMAS

- Need to remove first-order quadrupolar broadening - rotor synchronization

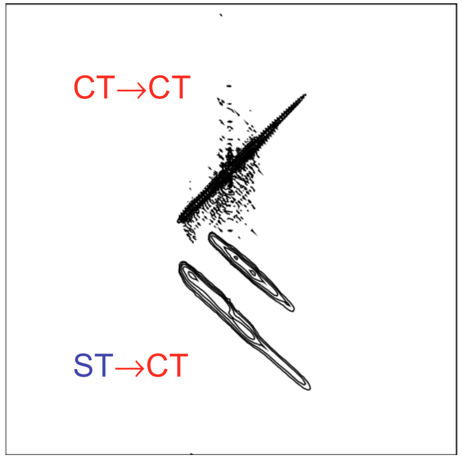


High-resolution NMR: STMAS

STMAS



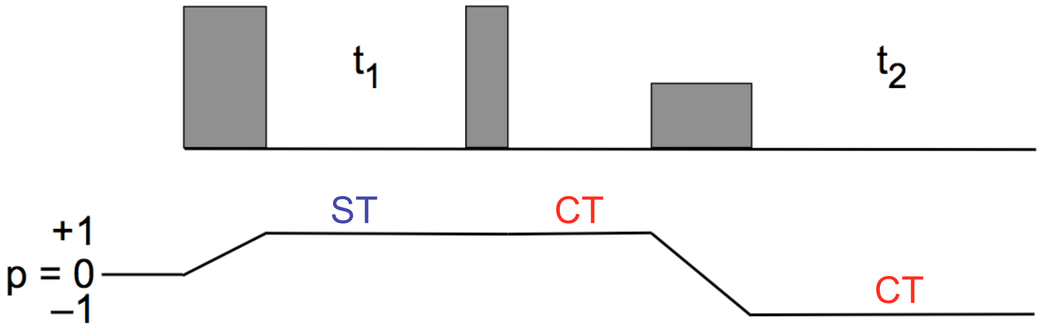
Gan, J. Am. Chem. Soc. ***122****,*
3242 (2000)

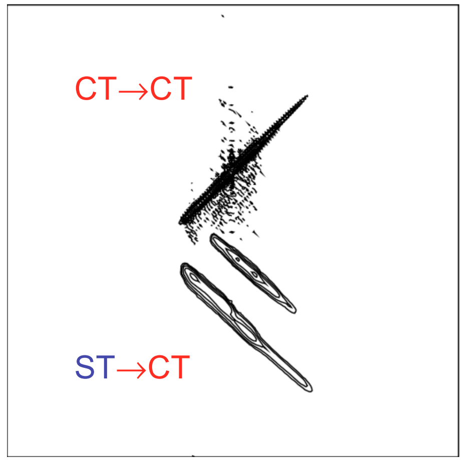


Spin	ST ratio
3/2	−8/9
5/2	7/24
7/2	28/45
9/2	55/72

High-resolution NMR: STMAS

STMAS

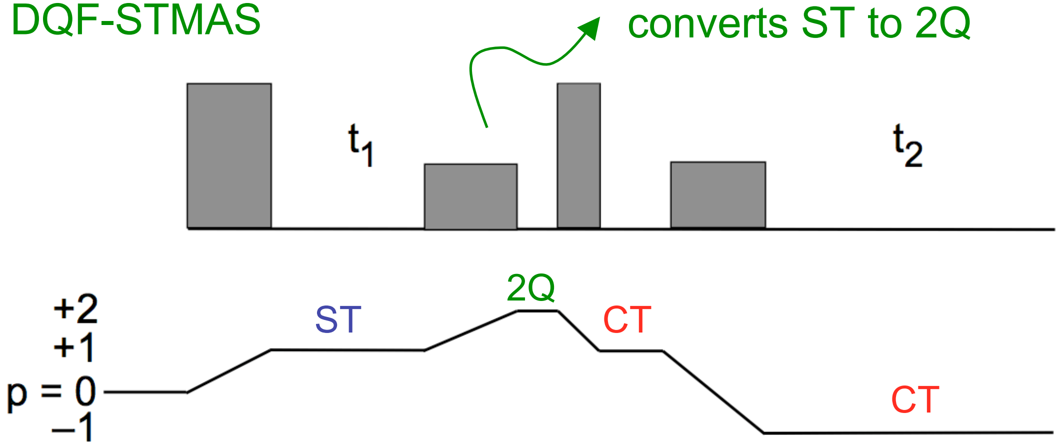


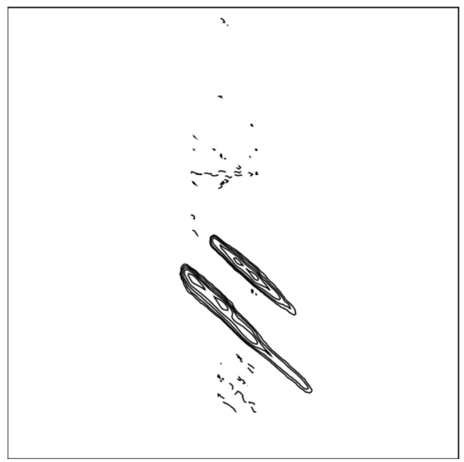


Gan, J. Am. Chem. Soc. ***122****,*
3242 (2000)

DQF-STMAS

selective 180°
converts ST to 2Q

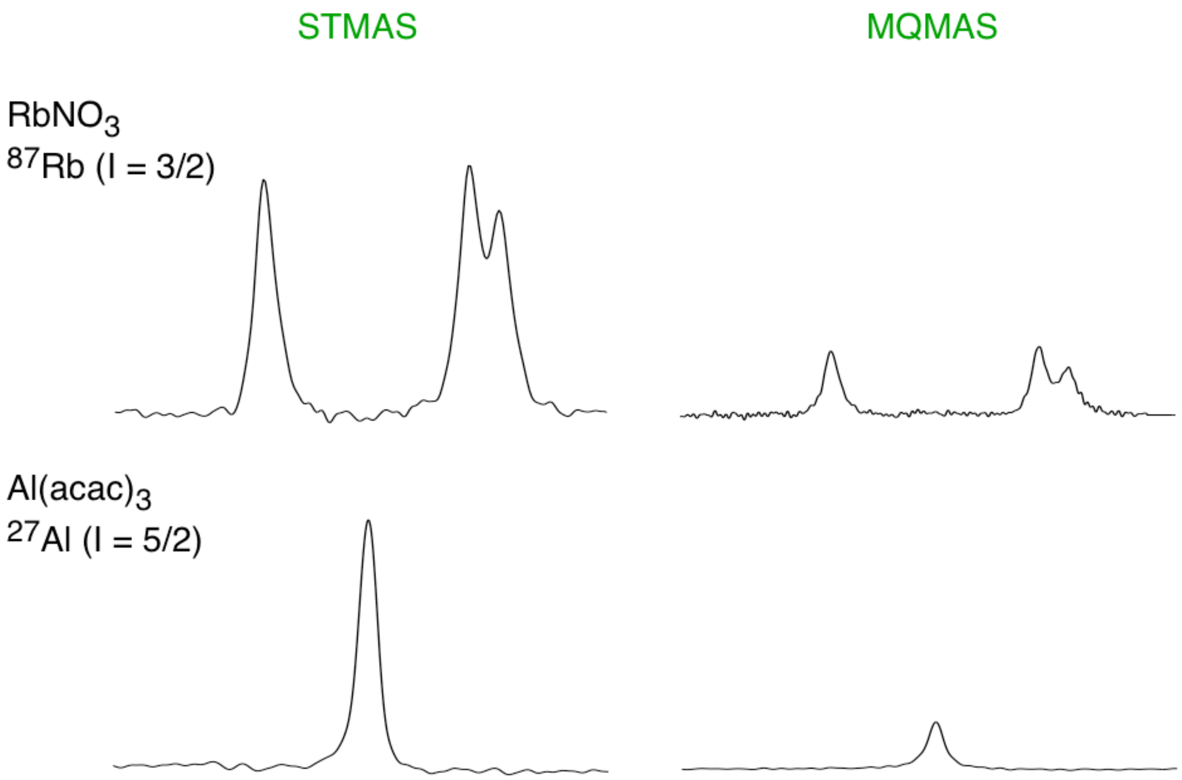




Kwak and Gan, J. Magn.
Reson. ***164****, 369 (2003)*

STMAS sensitivity

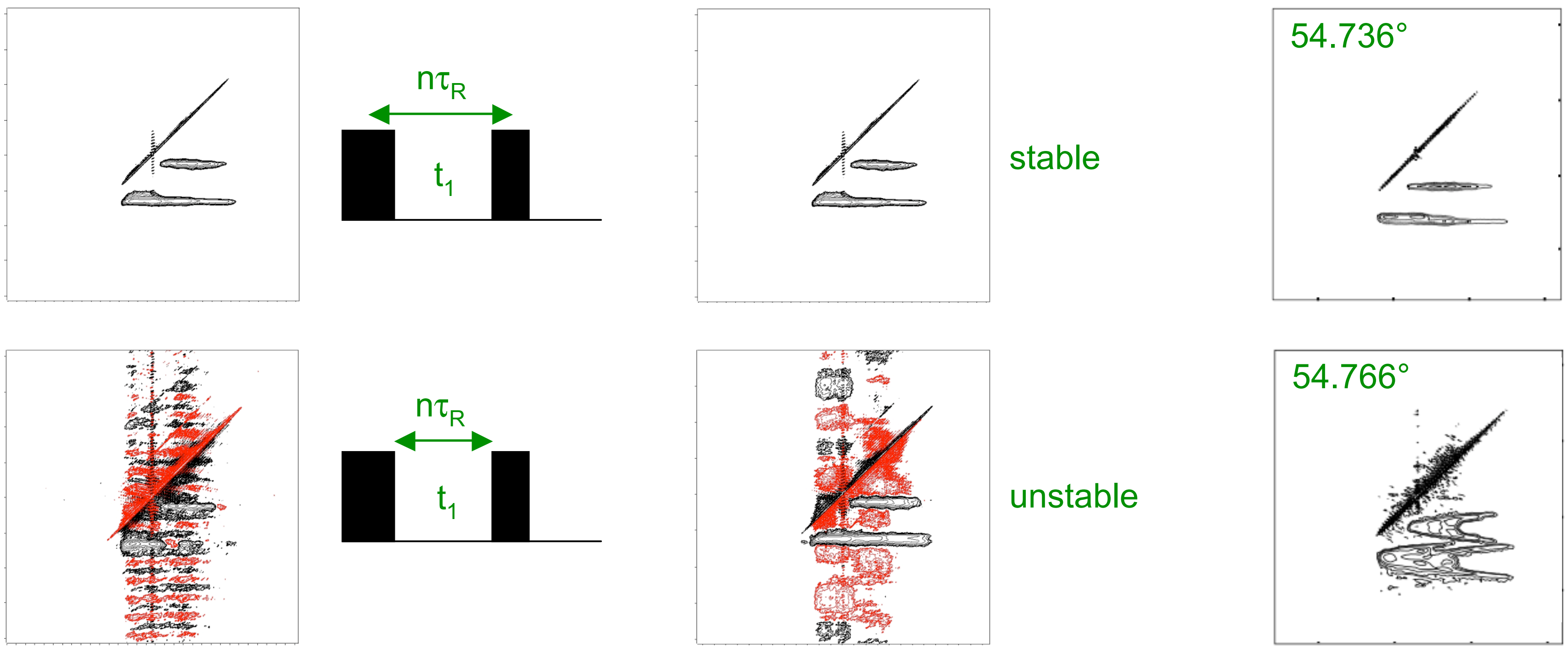
- STMAS is inherently more sensitive than MQMAS (usually factor of 2-8) owing to excitation of only single-quantum coherences



Ashbrook et al., Prog. NMR Spectros. ***45****, 53 (2004)*

STMAS experimental implementation

Precise timings | Stable spinning | Correct angle



~0.2 μs | ±1 Hz | ±0.002°

Ashbrook et al., Prog. NMR Spectros. ***45****, 53 (2004)*

High-resolution NMR: STMAS

Advantages

No special probe required

Good sensitivity

Good for abundant nuclei

Good for nuclei with short T_1

Disadvantages

Not always quantitative

High rf required for excitation of satellite transitions

Sensitive to angle misset

Requires very stable spinning speed

Problem with 3rd order effects for large C_Q

Sensitive to motional averaging

NMR of quadrupolar nuclei

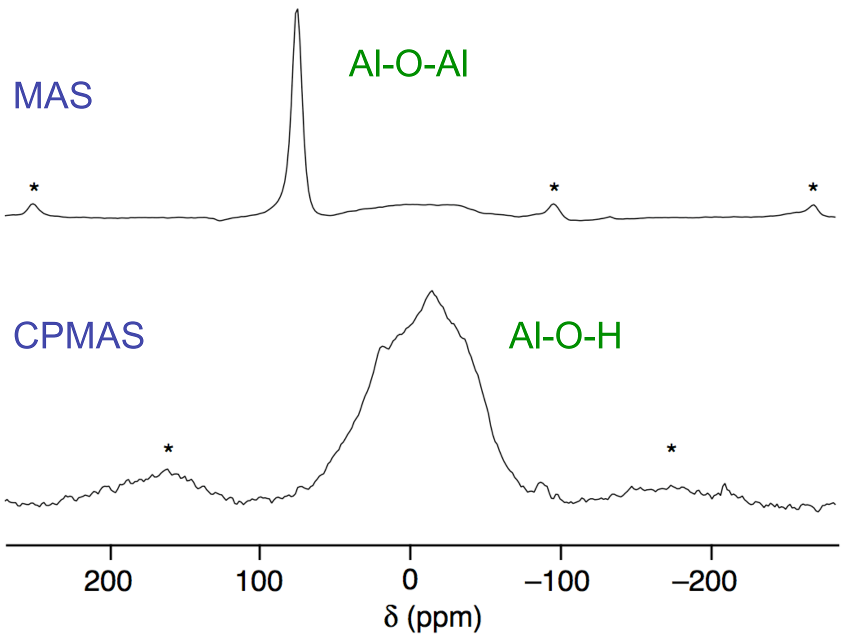
- In general, experiments performed for I = 1/2 nuclei can also be applied to quadrupolar nuclei
- Spin dynamics are usually considerably more complicated
- Results are often qualitative not quantitative
- Many sequences are adapted to incorporate pulses selective for only the central transition
- Combination with MQMAS/STMAS etc., to achieve high resolution

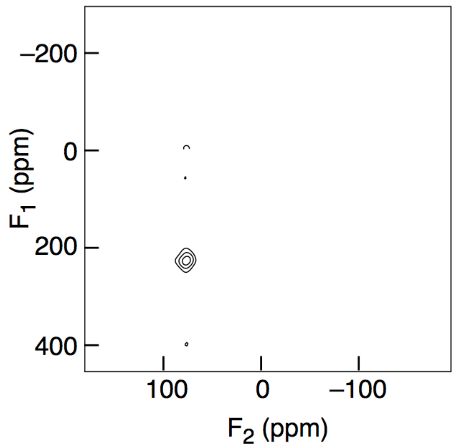
Cross polarization

REDOR, TEDOR, REAPDOR, TRAPDOR

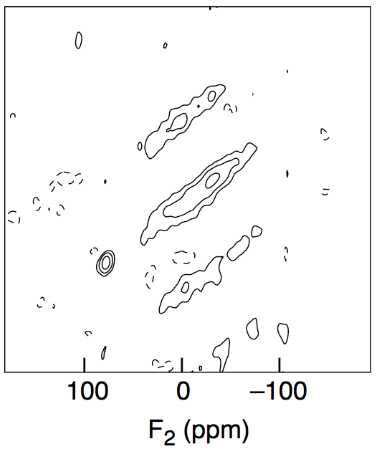
Correlation experiments: HETCOR, INEPT, TEDOR, NOESY, etc.,

Cross polarization





MQMAS

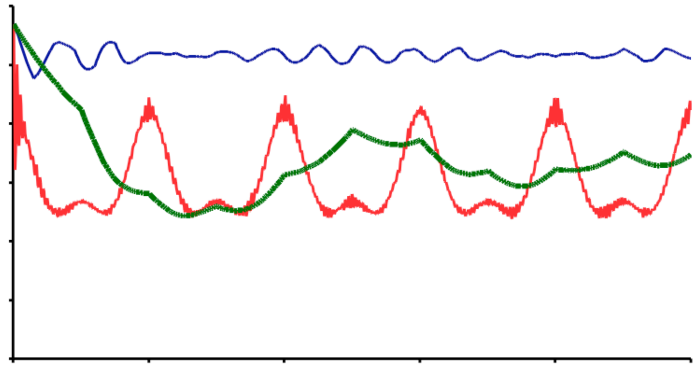


MQCPMAS

- Often more than one nutation rate in powdered sample
- Complex matching conditions
- In high field limit

$$\omega_{1S} = (I + 1/2)\,\omega_{1CT} \pm n\,\omega_R$$

- Complex spin locking behaviour
- Can be combined with high-resolution experiments

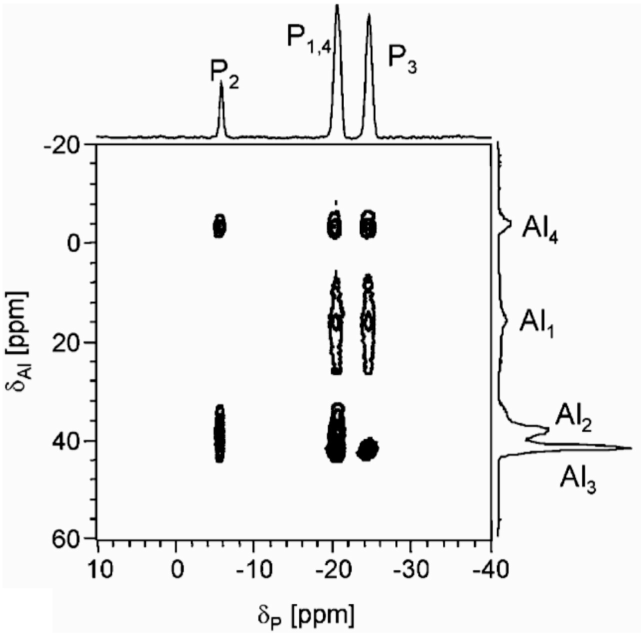


spinlocking

Ashbrook et al., J. Magn. Reson. ***147****, 238 (2000)*
Ashbrook et al., J. Chem. Phys. ***120****, 2719 (2003)*

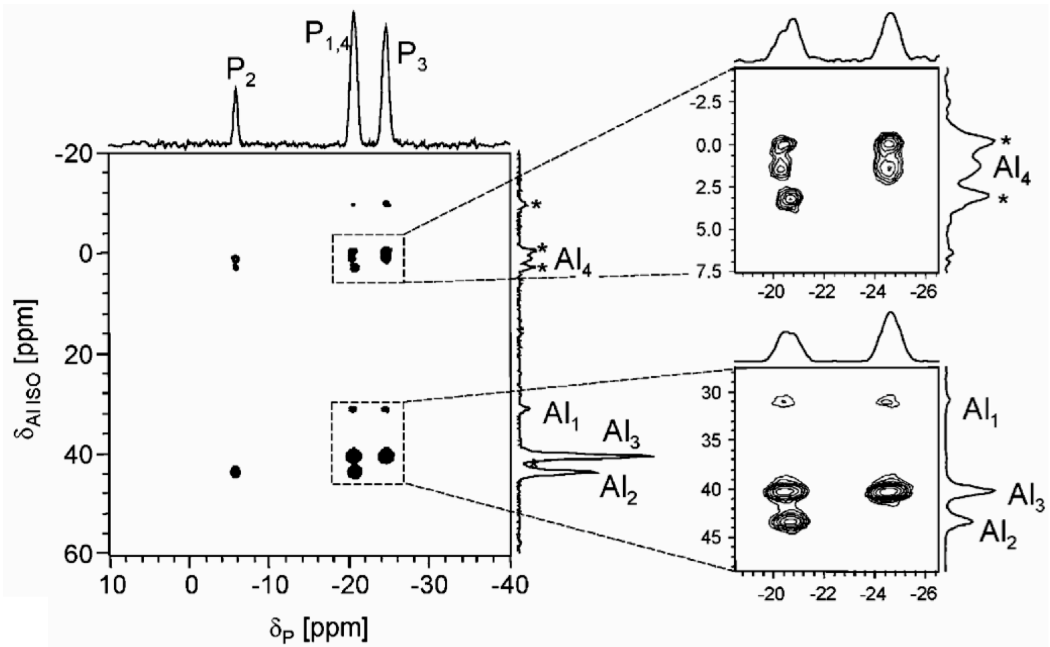
Correlation experiments

$AlPO_4$-14 as-synthesized (*ipa*)



$^{27}Al/^{31}P$ INEPT

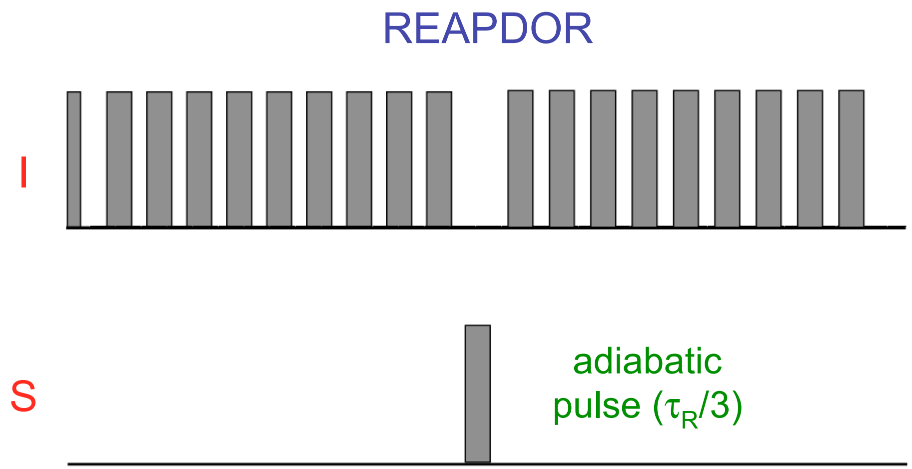
- Experiments through both the dipolar and scalar coupling have been used
- Can be combined with high-resolution experiments

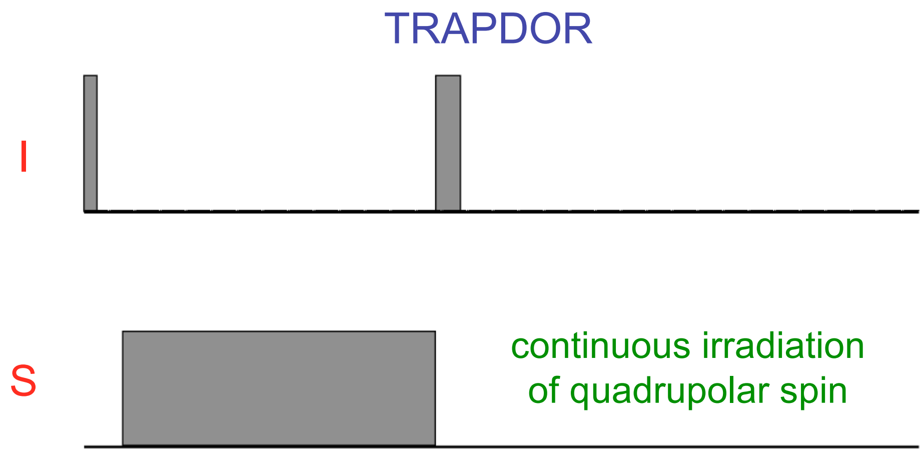


$^{27}Al/^{31}P$ MQ-INEPT

Wiench et al., Solid State Nucl. Magn. Reson. ***26****, 51 (2004)*

REAPDOR and TRAPDOR



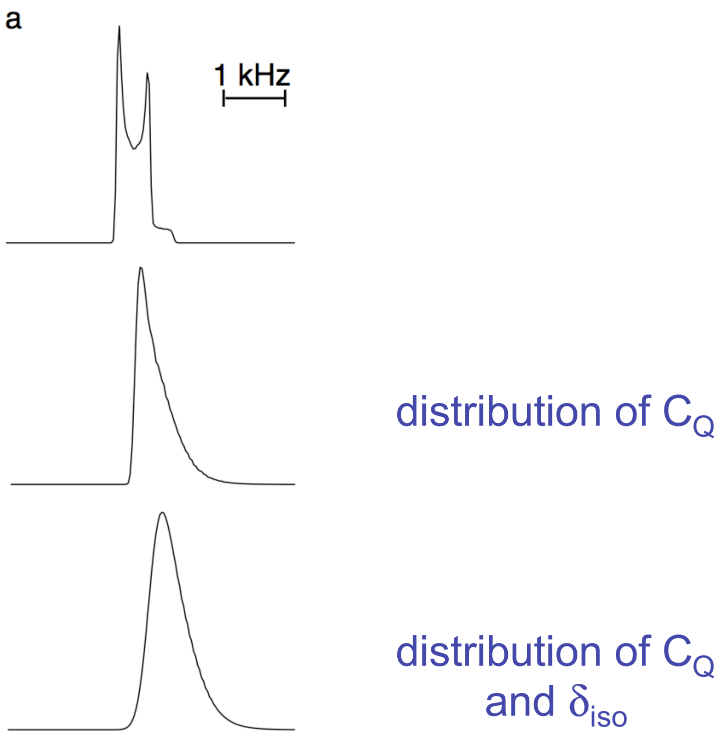


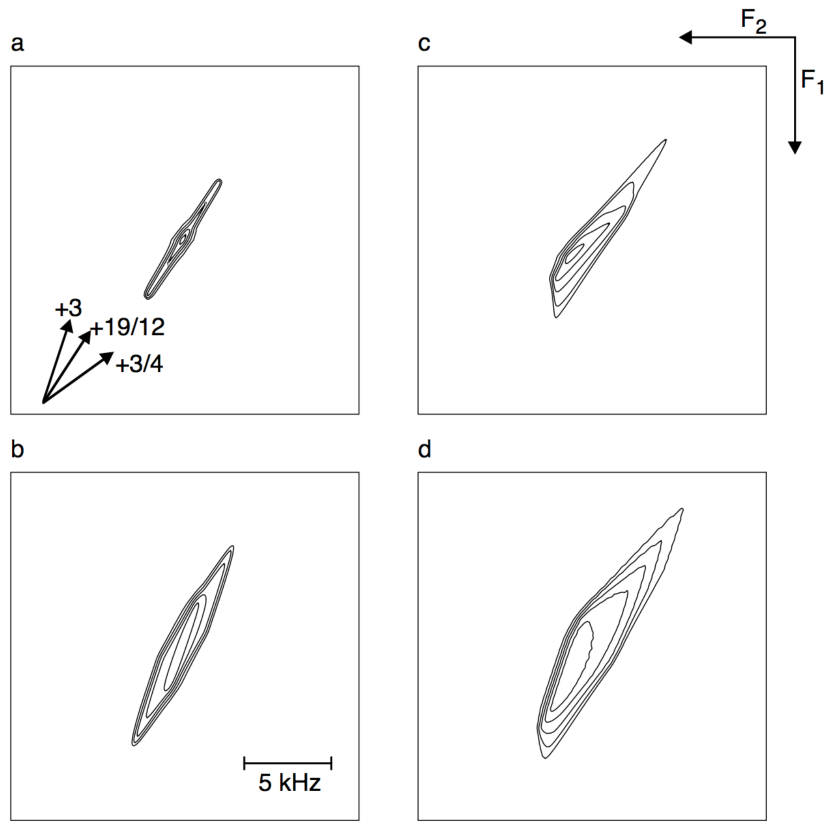
- Although REDOR can be used for quadrupolar nuclei, a train of 180° pulses is inefficient on the quadrupolar spin

- Quadrupolar specific alternatives REAPDOR and TRAPDOR
- Modulation of dipolar coupling by changing the spin states of the quadrupolar spin
- More difficult to quantify/calculate expected dephasing

Amorphous materials

- For amorphous/disordered materials there is a distribution of both chemical shift and quadrupolar parameters
- Results in a distinctive lineshape with a tail to low frequency
- In MQMAS and STMAS spectra these distributions result in broadening of the ridge lineshapes along different axes (dependent upon I and coherence type)





Amorphous materials

^{27}Al MAS NMR of γ-Al_2O_3