

Introduction to Quadrupolar NMR

Sharon Ashbrook

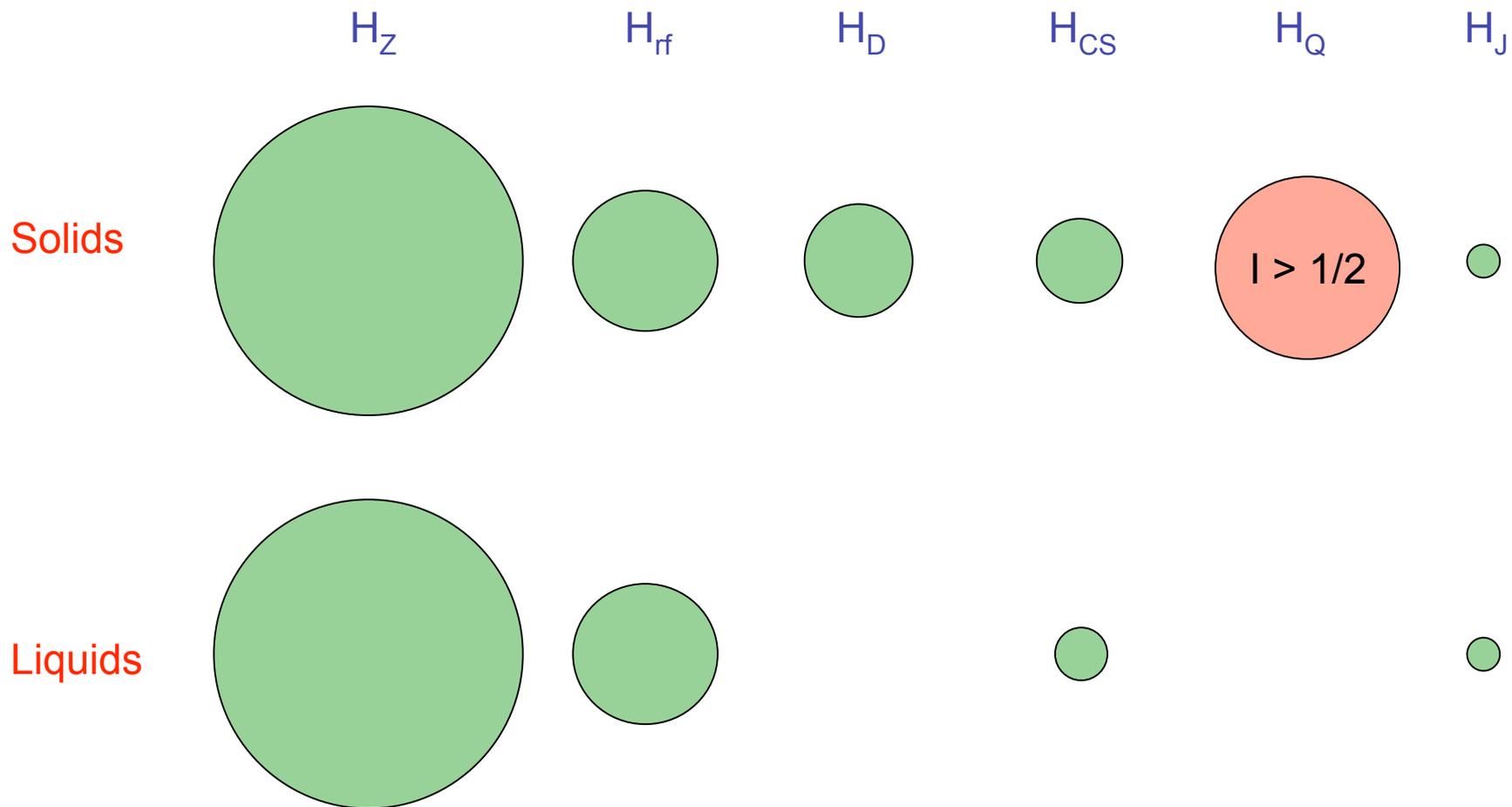
School of Chemistry, University of St Andrews



University
of
St Andrews



Interactions in NMR



Quadrupolar nuclei

The Periodic Table of the Elements

1 H Hydrogen 1.00794																	2 He Helium 4.003
3 Li Lithium 6.941	4 Be Beryllium 9.012182											5 B Boron 10.811	6 C Carbon 12.0107	7 N Nitrogen 14.00674	8 O Oxygen 15.9994	9 F Fluorine 18.9984032	10 Ne Neon 20.1797
11 Na Sodium 22.989770	12 Mg Magnesium 24.3050											13 Al Aluminum 26.981538	14 Si Silicon 28.0855	15 P Phosphorus 30.973761	16 S Sulfur 32.066	17 Cl Chlorine 35.4527	18 Ar Argon 39.948
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955910	22 Ti Titanium 47.867	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938049	26 Fe Iron 55.845	27 Co Cobalt 58.933200	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.723	32 Ge Germanium 72.61	33 As Arsenic 74.92160	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.90447	54 Xe Xenon 131.29
55 Cs Cesium 132.90545	56 Ba Barium 137.327	57 La Lanthanum 138.9055	72 Hf Hafnium 178.49	73 Ta Tantalum 180.9479	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.078	79 Au Gold 196.96655	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98038	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)
87 Fr Francium (223)	88 Ra Radium (226)	89 Ac Actinium (227)	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (263)	107 Bh Bohrium (262)	108 Hs Hassium (265)	109 Mt Meitnerium (266)	110 (269)	111 (272)	112 (277)	113	114				

$I = 1/2$

Quadrupolar

58 Ce Cerium 140.116	59 Pr Praseodymium 140.90765	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92534	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93032	68 Er Erbium 167.26	69 Tm Thulium 168.93421	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967
90 Th Thorium 232.0381	91 Pa Protactinium 231.03588	92 U Uranium 238.0289	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)

Quadrupolar nuclei

$$I = 1$$

Deuterium
Lithium-6
Nitrogen-14

$$I = 5/2$$

Oxygen-17
Magnesium-25
Aluminium-27

$$I = 3/2$$

Lithium-7
Boron-11
Sodium-23
Chlorine-35
Potassium-39
Gallium-71
Rubidium-87

$$I = 7/2$$

Scandium-45
Vanadium-51
Cobalt-59

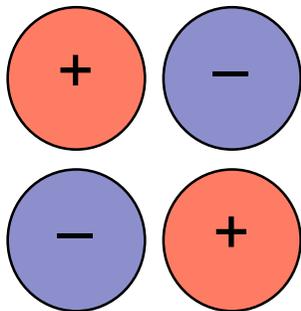
$$I = 9/2$$

Niobium-93

Origin of the quadrupolar interaction

- Nuclear structure can be described by expansion as a series of multipoles

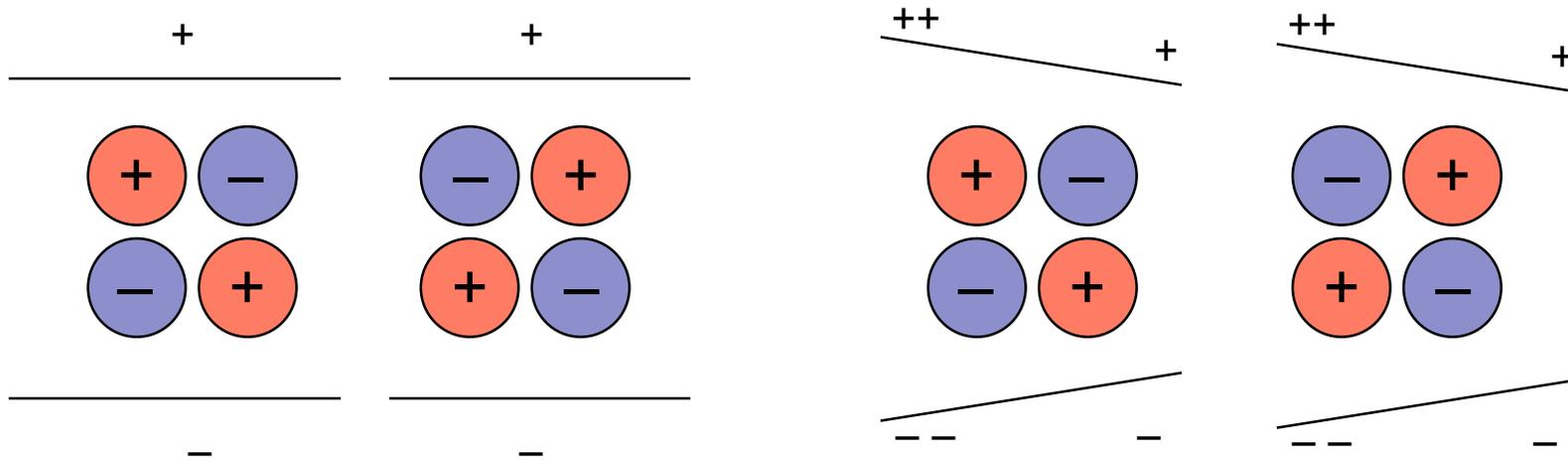
Spin	monopole	dipole	quadrupole	octapole
$I = 0$	electric	0	0	0
$I = 1/2$	electric	magnetic	0	0
$I = 1$	electric	magnetic	electric	0
$I = 3/2$	electric	magnetic	electric	magnetic



- Nuclei with spin quantum number $I > 1/2$ have a non spherical distribution of charge in the nucleus
- This gives rise to a quadrupole moment (eQ)

Origin of the quadrupolar interaction

- The quadrupole moment interacts with the electric field gradient (EFG) present at the nucleus (eq)



- The interaction is anisotropic, i.e., depends upon orientation

Quadrupolar Hamiltonian

- The frame where V is diagonal is called the principal axis system (PAS)

$$\begin{pmatrix} V_{xx} & V_{xy} & V_{xz} \\ V_{yx} & V_{yy} & V_{yz} \\ V_{zx} & V_{zy} & V_{zz} \end{pmatrix} \xleftrightarrow{\text{Rotation}} \begin{pmatrix} V_{xx} & 0 & 0 \\ 0 & V_{yy} & 0 \\ 0 & 0 & V_{zz} \end{pmatrix}$$

principal components

$$|V_{zz}| > |V_{xx}| > |V_{yy}|$$

$$V_{zz} + V_{xx} + V_{yy} = 0$$

- This gives the Hamiltonian in the PAS

$$H_Q^{\text{PAS}} = \frac{3eQV_{zz}}{4I(2I-1)\hbar} \left[I_z^2 - \frac{1}{3}I(I+1) + \frac{\eta_Q}{3}(I_x^2 - I_y^2) \right]$$

Definitions

- Magnitude (also QCC, NQCC, C_q , χ_Q , χ)

$$C_Q = (eQV_{ZZ}) / h = (eQeq) / h$$

- Quadrupolar splitting parameter

$$\omega_Q^{\text{PAS}} = 3C_Q / 4I(2I - 1) \quad (\text{or } \omega_Q^{\text{PAS}} = 3C_Q / 2I(2I - 1))$$

- Asymmetry (cross-sectional shape)

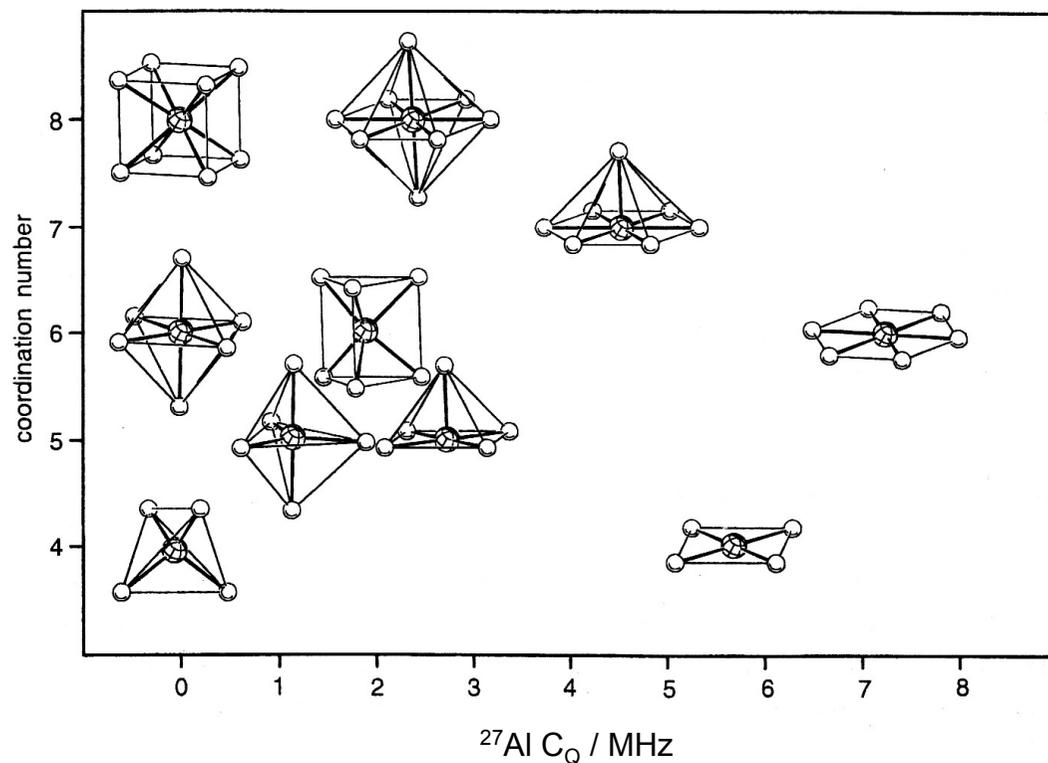
$$\eta_Q = (V_{XX} - V_{YY}) / V_{ZZ} \quad \text{with } 0 < \eta_Q < 1$$

- Quadrupolar product

$$P_Q = C_Q (1 + \eta_Q^2/3)^{1/2}$$

Origin of the EFG

- The EFG is caused by the distribution of charges in the system
- We can estimate to a first approximation that it arises from the coordinating atoms
- In reality longer range interactions need to be included



For high symmetry $C_Q = 0$

C_Q increases as symmetry drops

Exact C_Q depends also on eQ

After Kentgens et al.,
Geoderma **80**, 271 (1997)

Perturbation theory

- Neglecting dipolar and CSA contributions, we can write the total Hamiltonian as the sum of the Zeeman and and quadrupolar Hamiltonians

$$H = H_Z + H_Q$$

- Although often large, the quadrupolar interaction is usually much smaller than the dominant Zeeman interaction

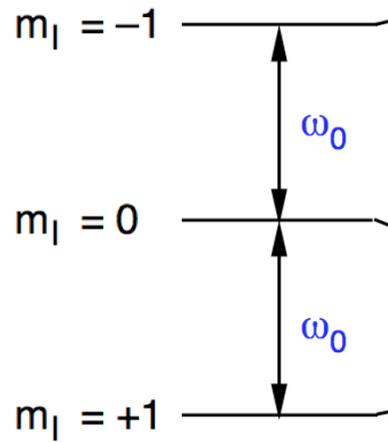
$$C_Q \sim 0 \text{ to } 30 \text{ MHz}$$

- Its effect on the nuclear energy levels may therefore be described as a perturbation (or a correction) to the Zeeman levels

First-order approximation

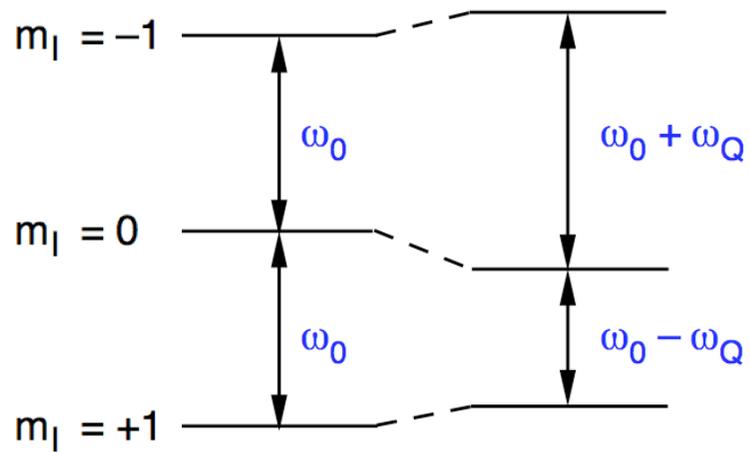
$$E = E_Z + E_Q$$

Spin $I = 1$



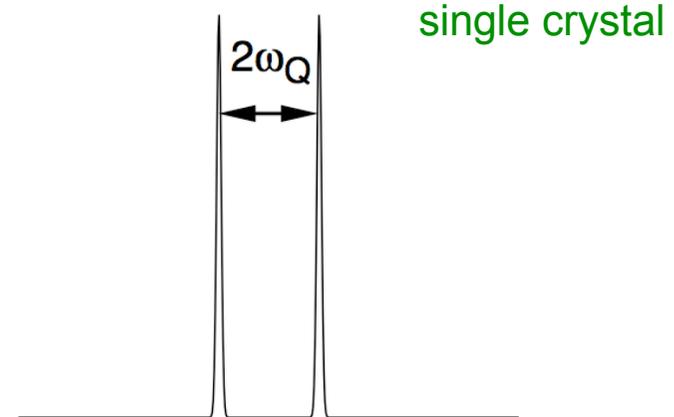
Zeeman

Spin I = 1



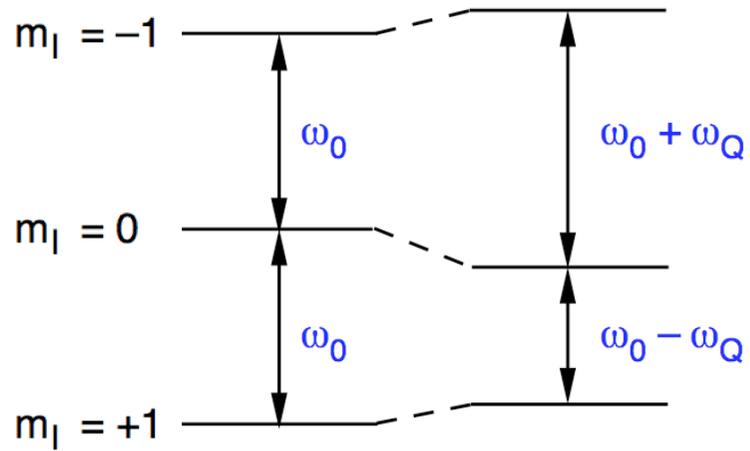
Zeeman

Quadrupolar



$$\omega_Q = \omega_Q^{\text{PAS}} \frac{1}{2} (3 \cos^2 \theta - 1 + \eta_Q \sin^2 \theta \cos 2\gamma)$$

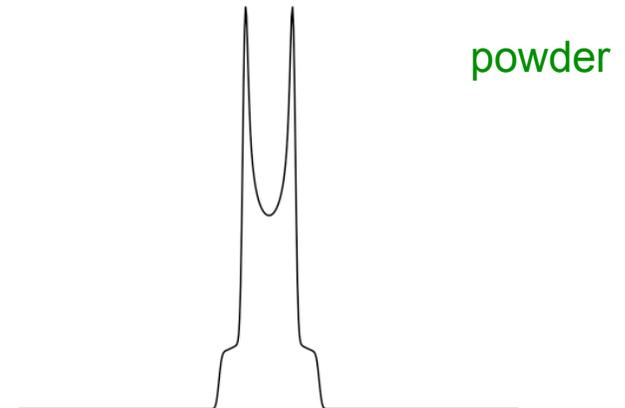
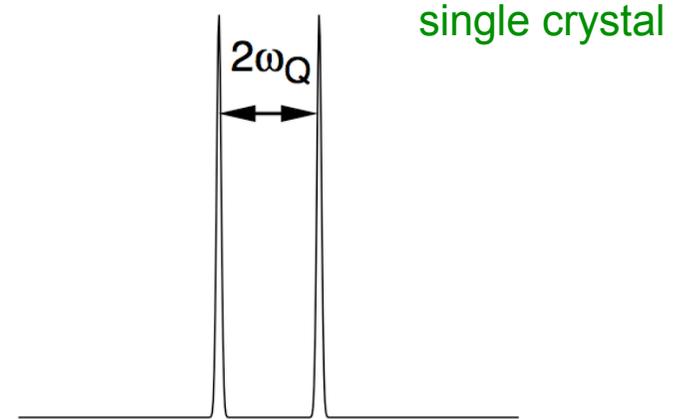
Spin I = 1



Zeeman

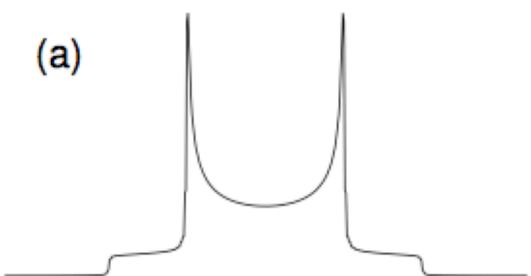
Quadrupolar

$$\omega_Q = \omega_Q^{\text{PAS}} \frac{1}{2} (3 \cos^2 \theta - 1 + \eta_Q \sin^2 \theta \cos 2\gamma)$$

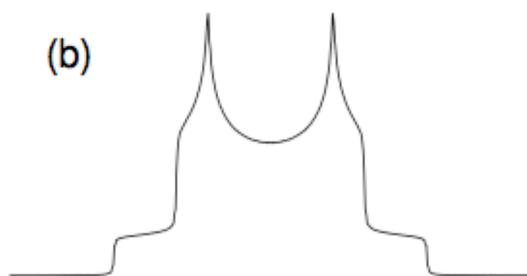


Spin $I = 1$ lineshapes

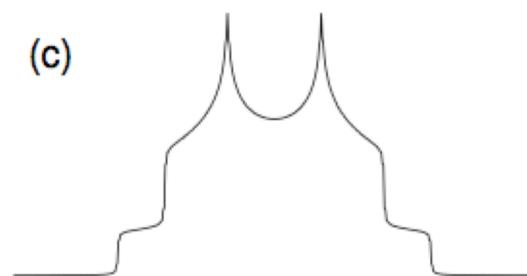
$\eta_Q = 0$



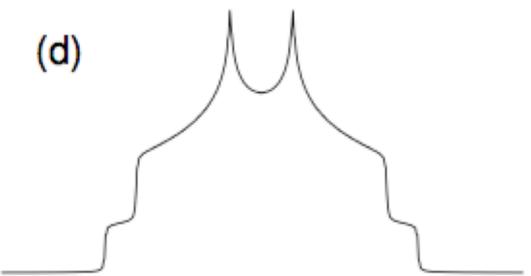
$\eta_Q = 0.2$



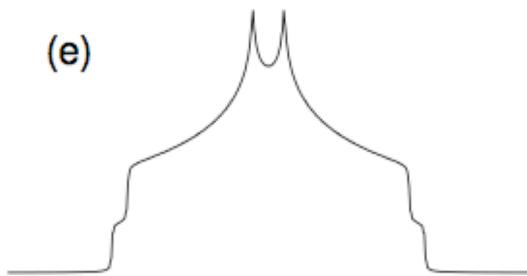
$\eta_Q = 0.4$



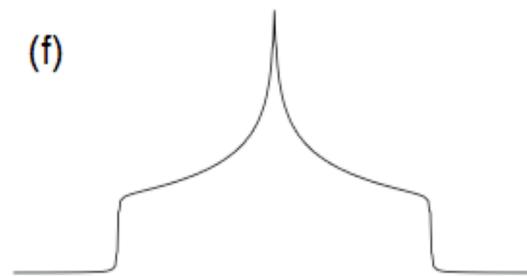
$\eta_Q = 0.6$



$\eta_Q = 0.8$



$\eta_Q = 1.0$



150 0 -150

kHz

150 0 -150

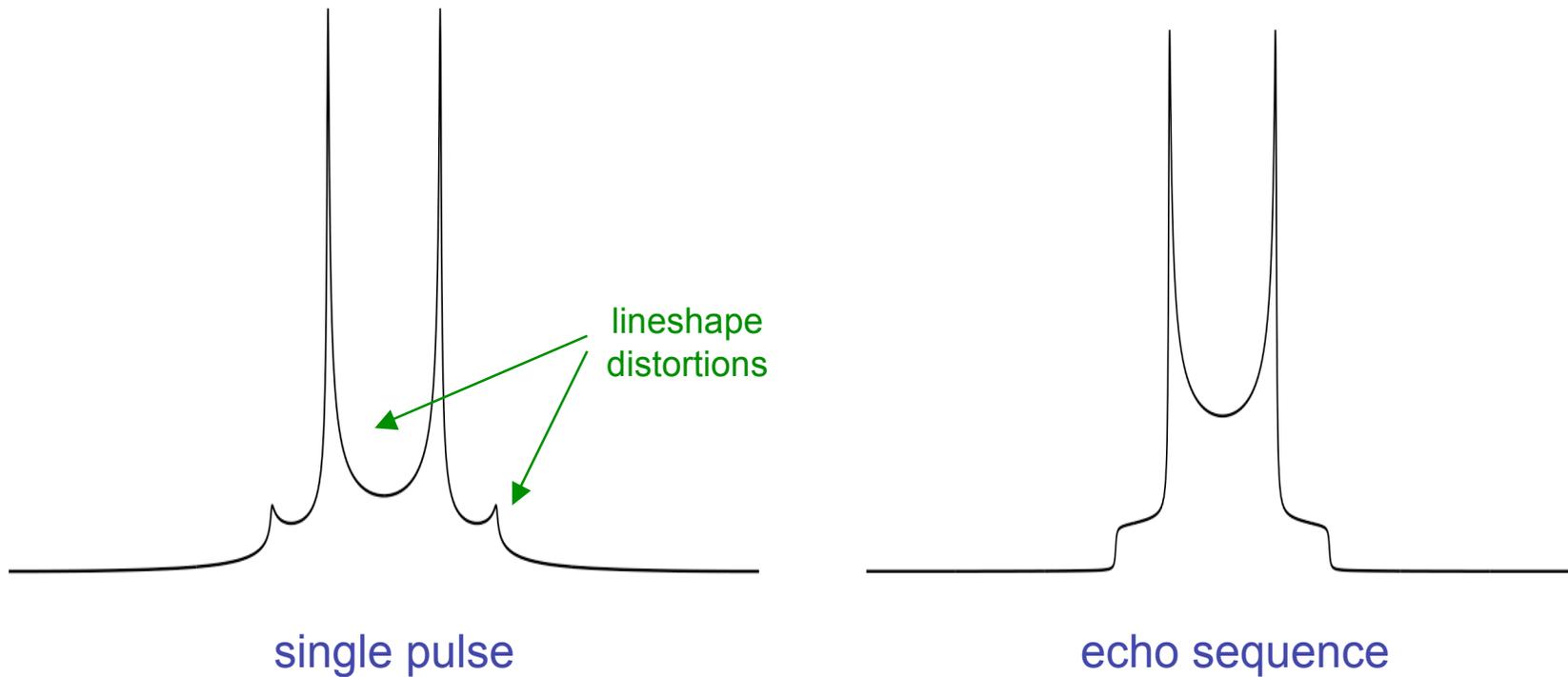
kHz

150 0 -150

kHz

Experimental acquisition

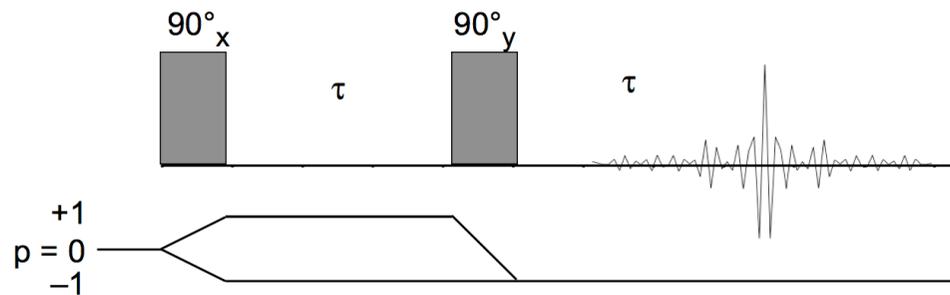
- The broad quadrupolar lineshapes can be difficult to acquire accurately
- Solution is to use an echo pulse sequence



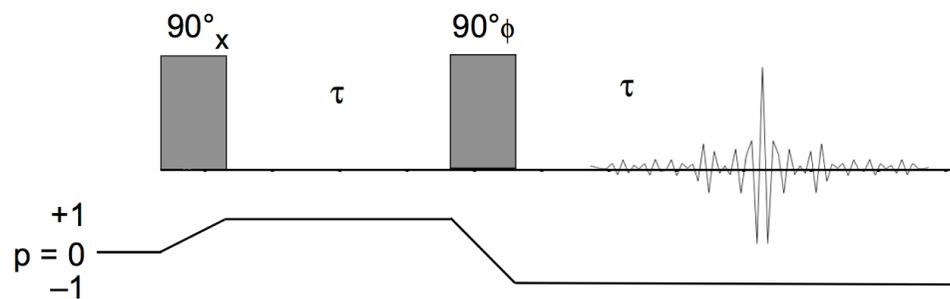
Experimental acquisition

- To refocus the quadrupolar broadening we need a **quadrupolar echo**

$$90^\circ_x - \tau - 90^\circ_y$$



Selection of $p = \pm 1$
coherences pathways
refocuses quadrupolar
broadening and gives
good S/N



Selection of $p = +1$
coherence (“Exorcycle”)
refocuses quadrupolar
broadening and CSA but
lower S/N

See Antonijevic et al., *J. Magn. Reson.* **164**, 343 (2003)

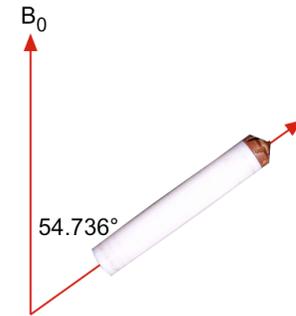
Effect of MAS

static

$$\omega = \omega_Q^{\text{PAS}} d_{00}^2(\beta)$$

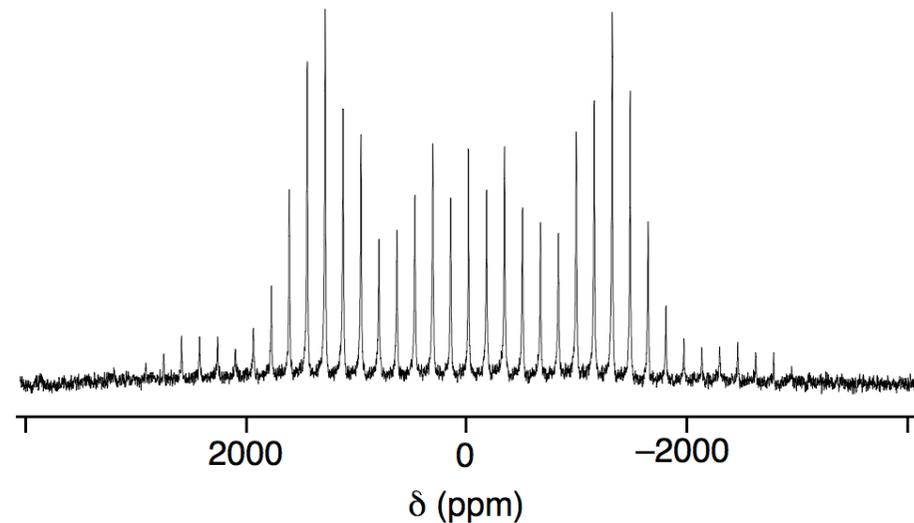
MAS

$$\omega = \omega_Q^{\text{PAS}} d_{00}^2(\beta) d_{00}^2(\beta_R)$$

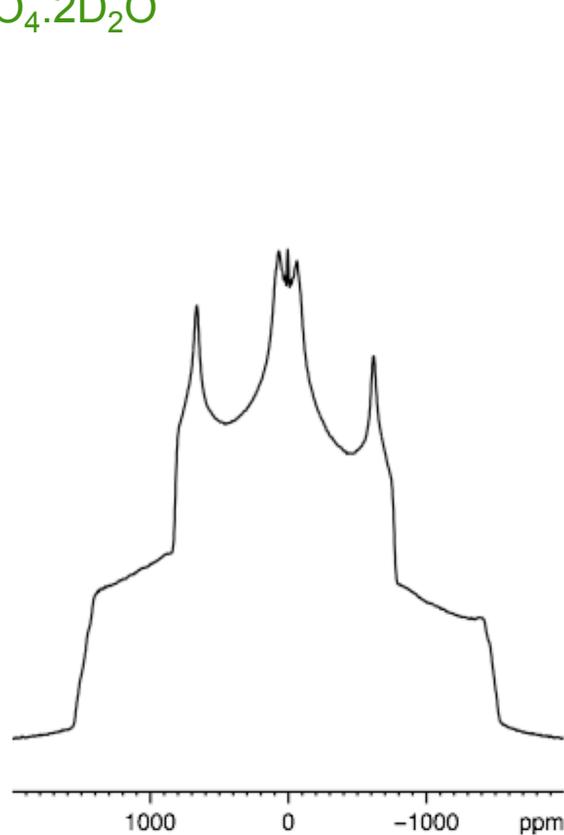


^2H MAS NMR of $\text{Mg}(\text{OD})_2$

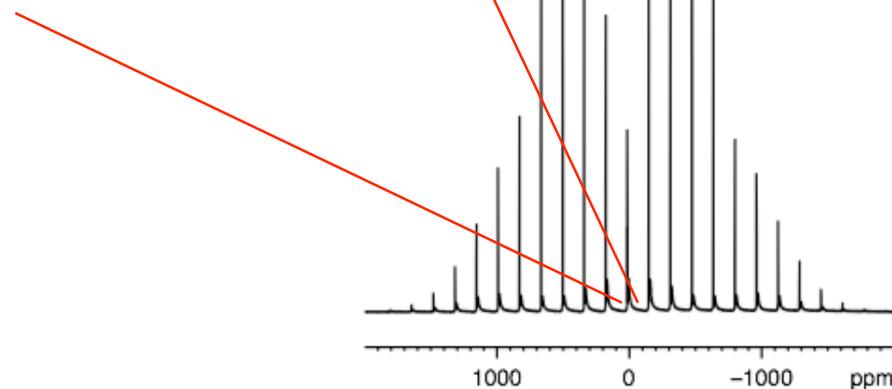
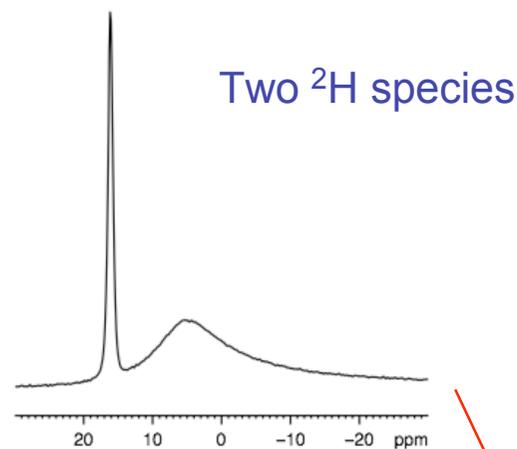
- The quadrupolar broadening has a similar orientational dependence to dipolar and CSA interactions and so can be removed by magic angle spinning
- The magnitude of the interaction is often such that many spinning sidebands are observed even at fast MAS rates



Example: ^2H NMR of oxalic acid



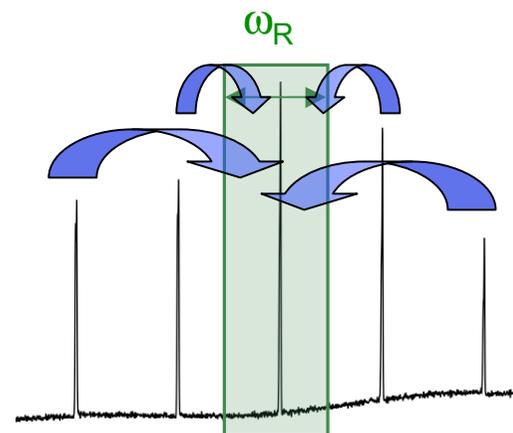
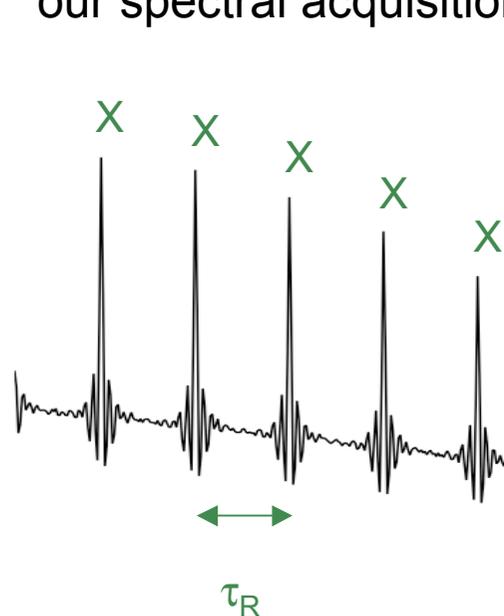
static



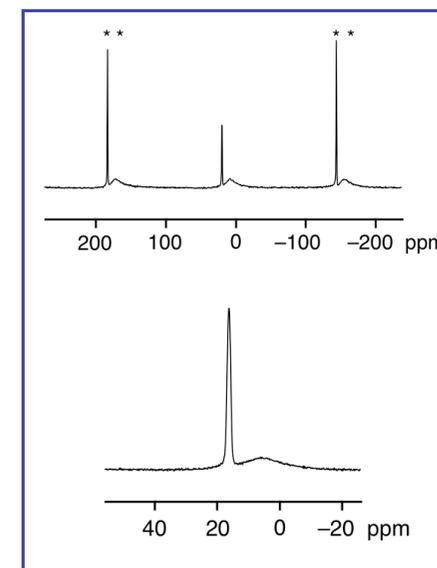
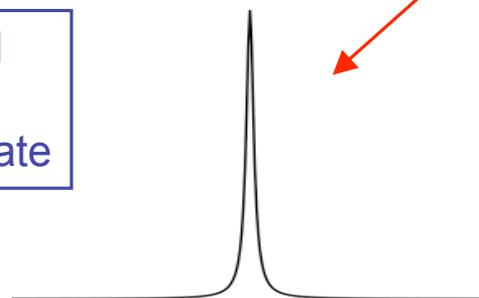
MAS

Rotor synchronization

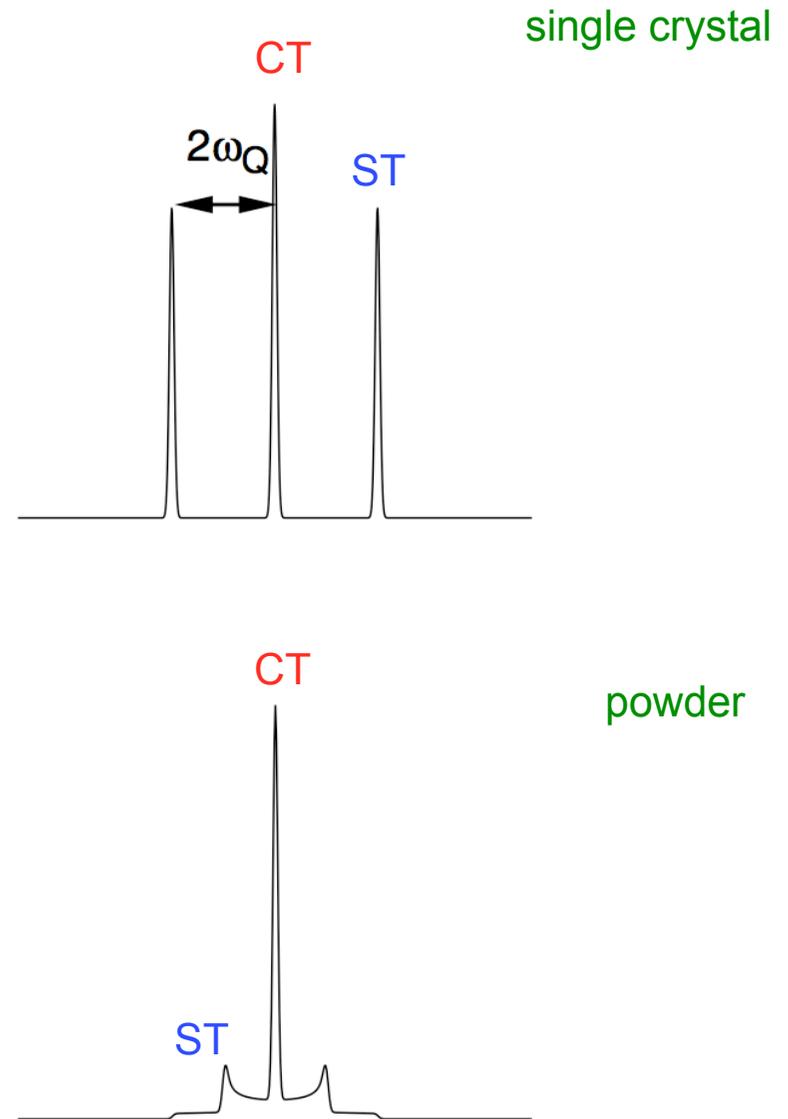
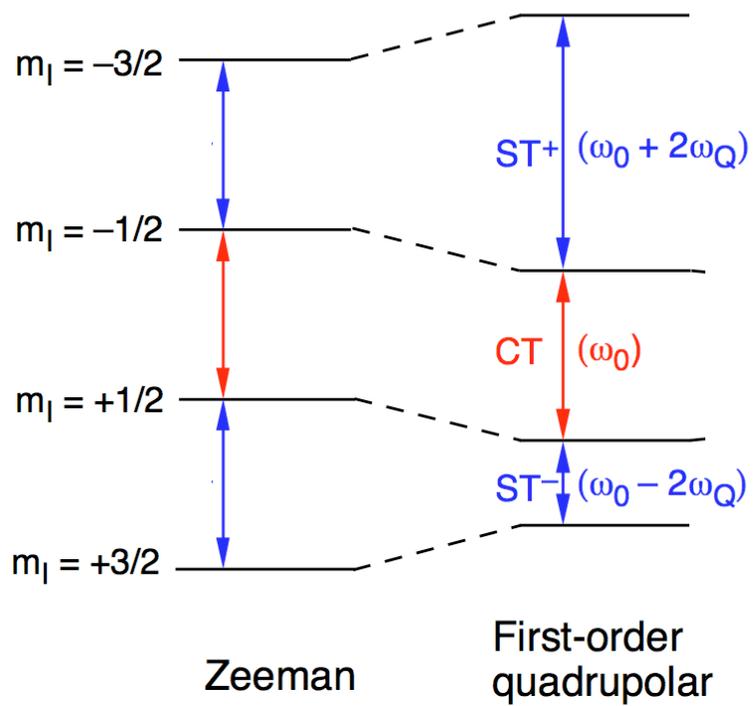
- To improve sensitivity and ensure accurate lineshapes we can rotor synchronize our spectral acquisition



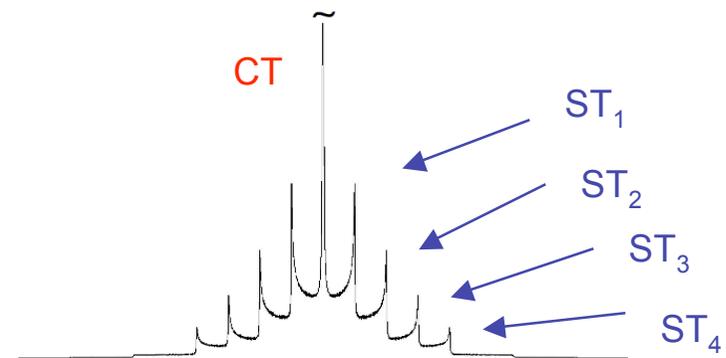
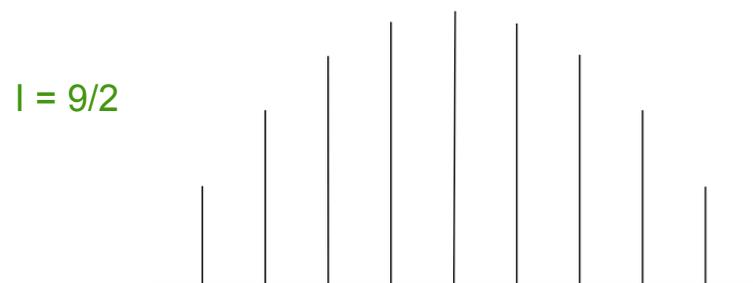
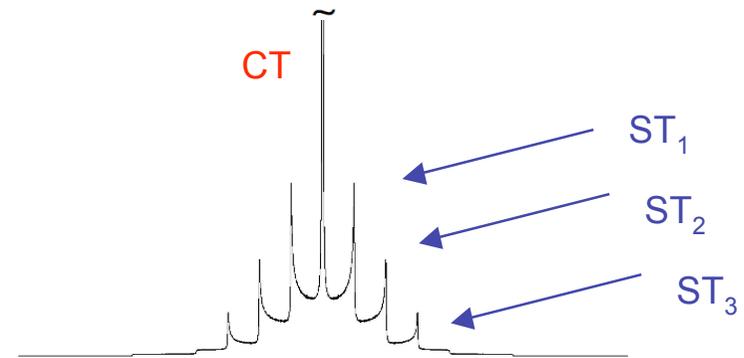
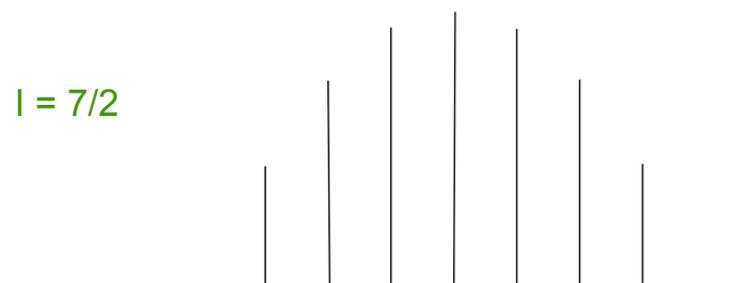
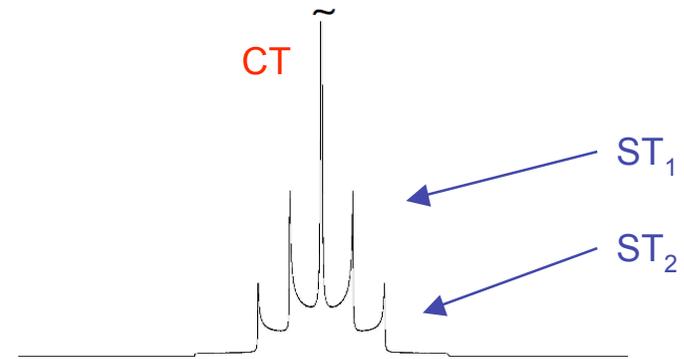
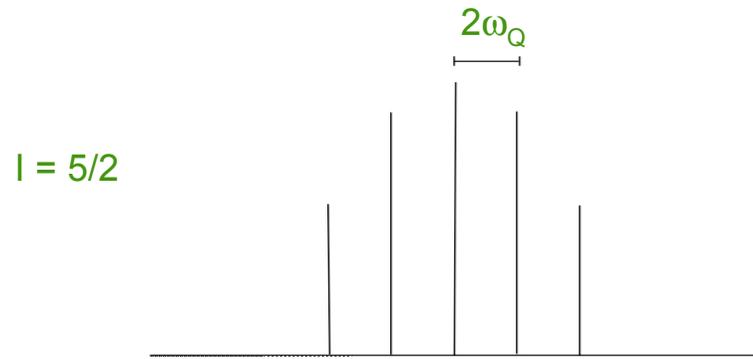
Dwell time equal to rotor period
Spectral width equal to spinning rate



Spin $I = 3/2$

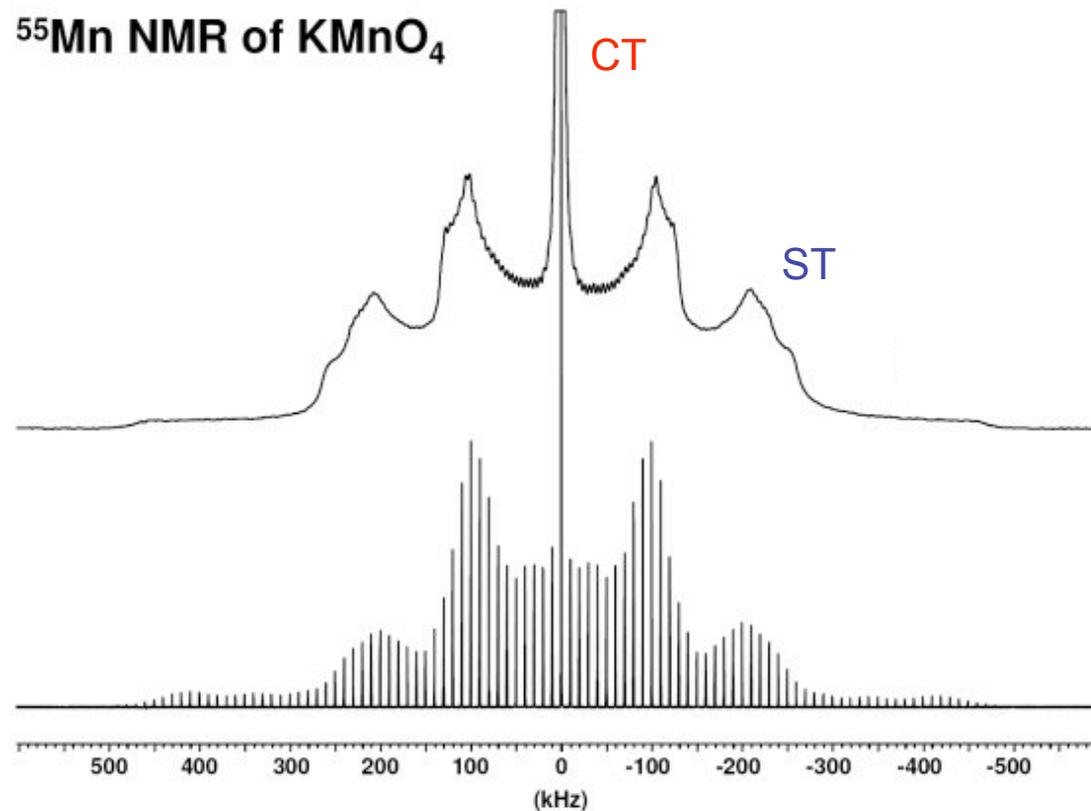


High spin systems



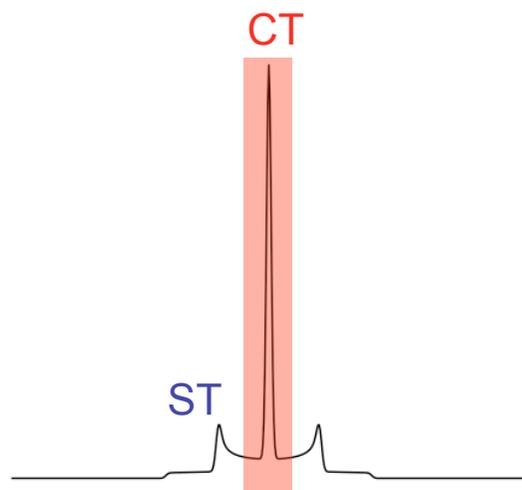
Effect of MAS

- As for spin $I = 1$, the quadrupolar broadening in the ST (proportional to $3\cos^2\theta - 1$) can be removed by magic-angle spinning
- The magnitude of the interaction is often such that many spinning sidebands are observed even at fast MAS rates

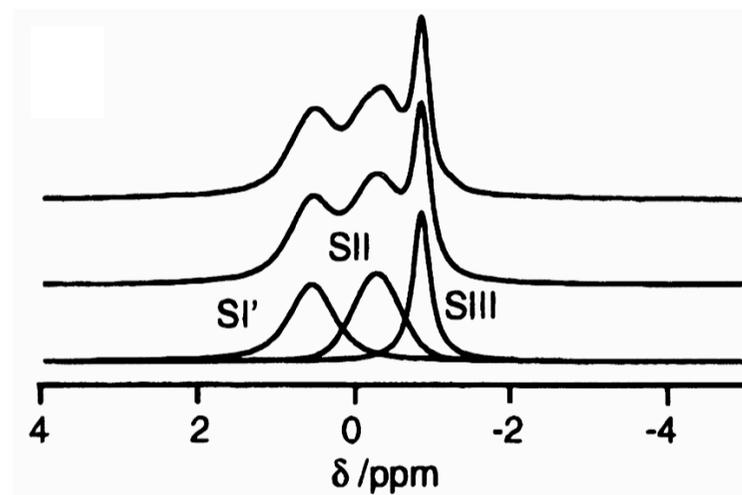


CT observation

- In many cases the ST are so broad they are rarely observed (or excited) and so we focus attention only on the CT



^7Li MAS NMR of zeolite LiSX,
showing three Li species



*Feuerstein et al., Micro.
Meso. Mater.* **26**, 27 (1998)

Second-order quadrupolar broadening

- When the perturbing interaction is large the first-order correction described previously may not be sufficient to fully describe the system and we need to use higher-order correction terms

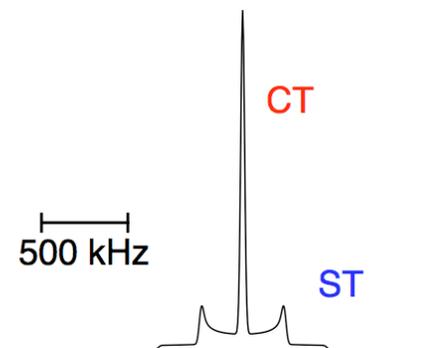
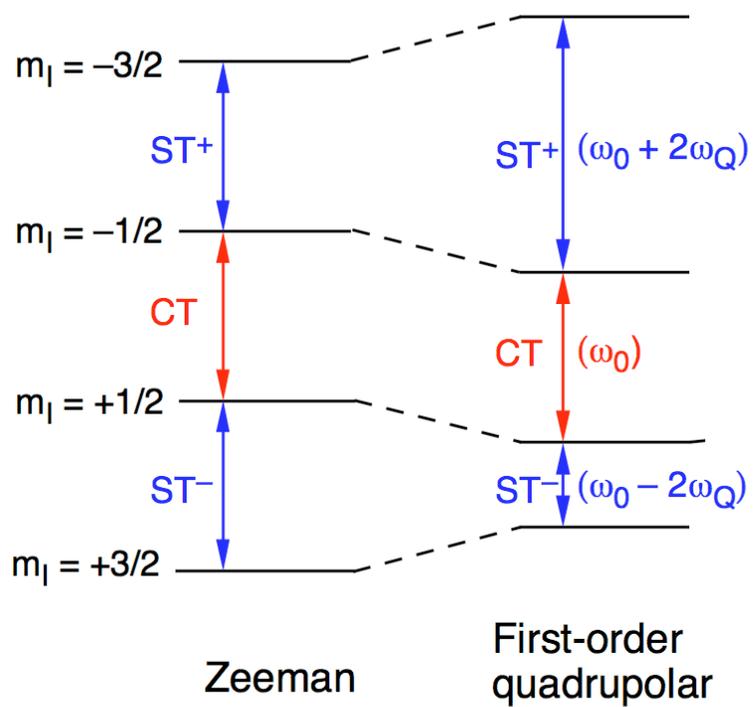
$$E = E_Z + E_Q^{(1)} + E_Q^{(2)} + E_Q^{(3)} + \dots$$

- For the quadrupolar interaction, the perturbation to a second-order approximation often needs to be considered

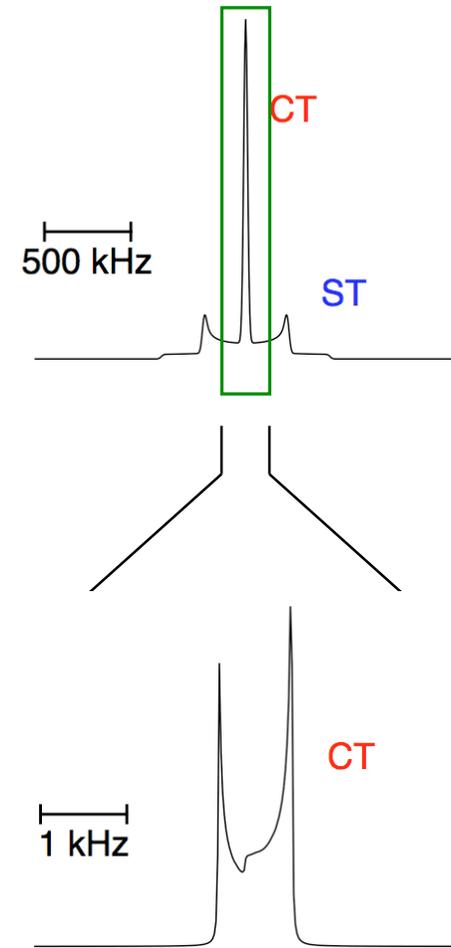
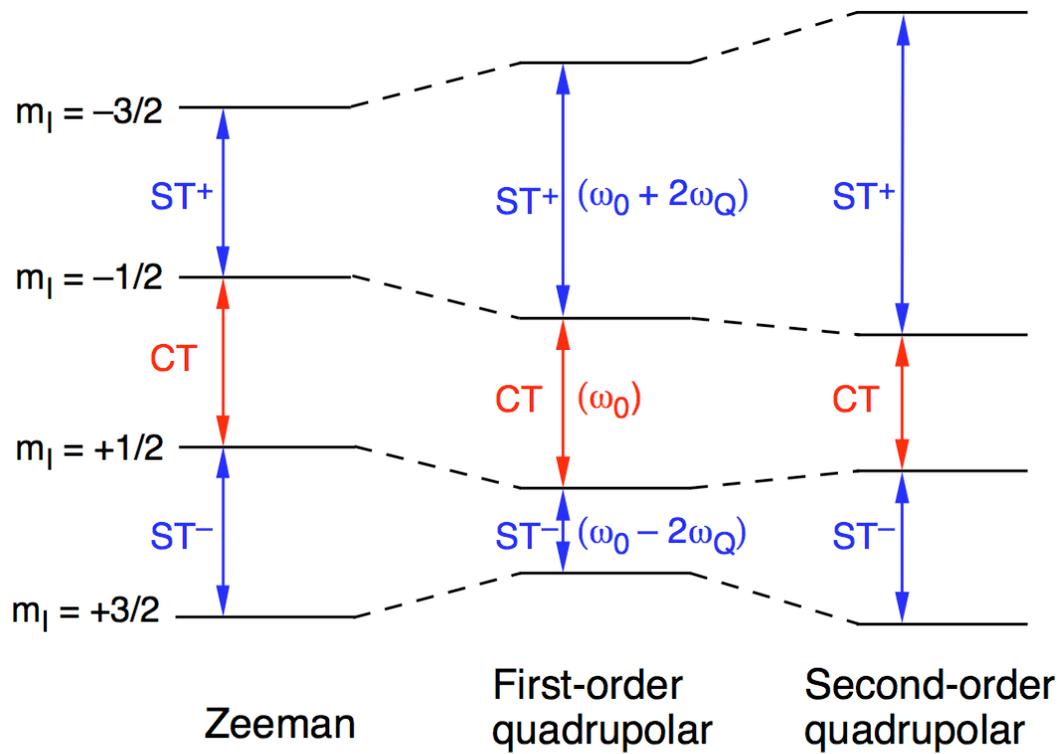
$$E = E_Z + E_Q^{(1)} + E_Q^{(2)}$$

- The second-order correction is much smaller than the first-order correction

Spin $I = 3/2$



Spin I = 3/2



Second-order quadrupolar broadening

- Second-order quadrupolar frequency for an energy level/transition can be described (for $\eta_Q = 0$) by

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

Constant depending upon C_Q , I and ω_0

Isotropic shift

Second-rank anisotropic

Fourth-rank anisotropic

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

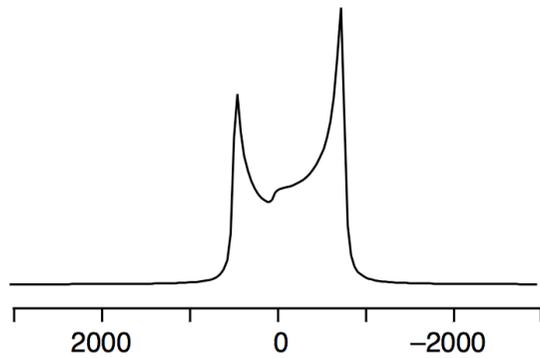
$$d_{00}^4(\theta) \propto (35 \cos^4 \theta - 30 \cos^2 \theta + 3)$$

Second-order quadrupolar broadening

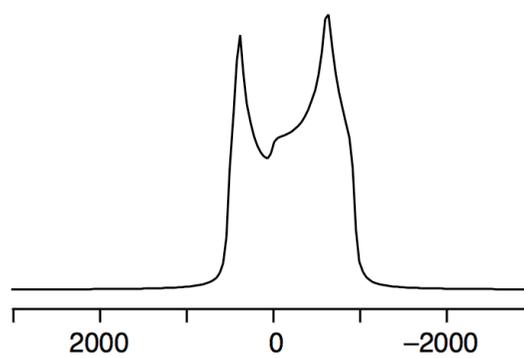
Spin	Transition	A	B	C
$I = 3/2$	CT	$-2/5$	$-8/7$	$54/35$
	ST	$4/5$	$4/7$	$-48/35$
$I = 5/2$	CT	$-16/15$	$-64/21$	$144/35$
	ST ₁	$2/5$	$-4/3$	$6/5$
	ST ₂	$56/15$	$80/21$	$-264/35$

Spin I = 3/2 CT lineshapes

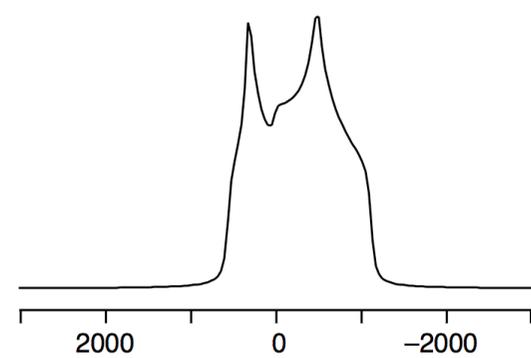
$\eta_Q = 0$



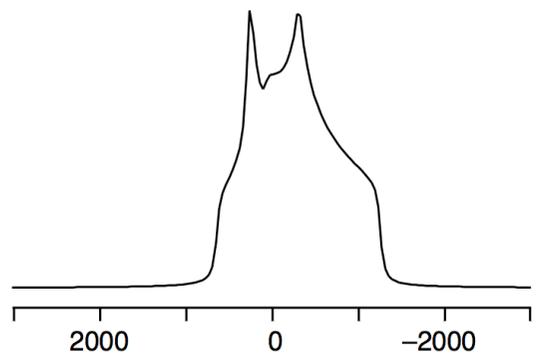
$\eta_Q = 0.2$



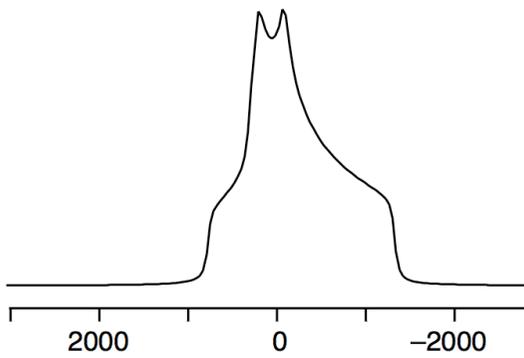
$\eta_Q = 0.4$



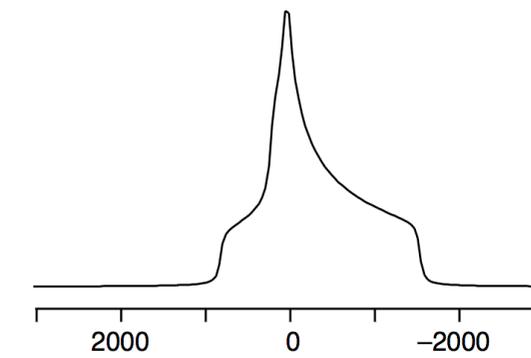
$\eta_Q = 0.6$



$\eta_Q = 0.8$



$\eta_Q = 1.0$



Quadrupolar broadening and MAS

With sample rotation around β_R

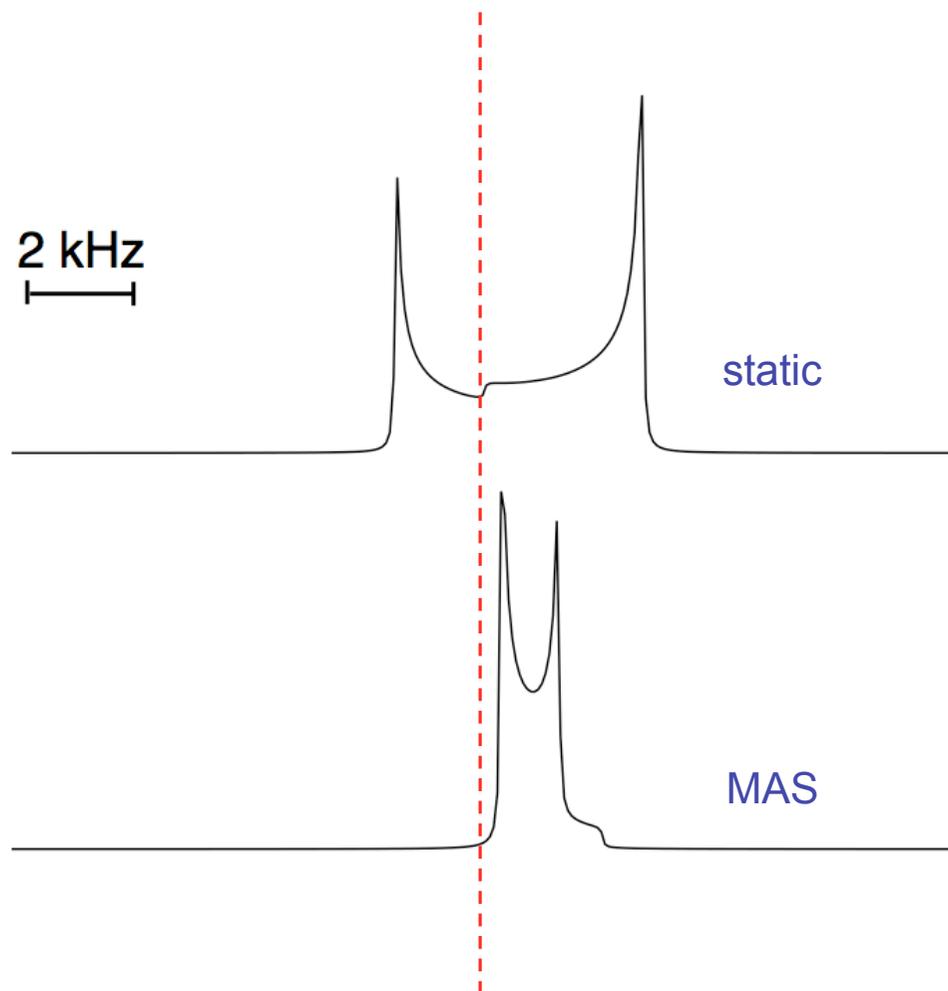
$$\omega \propto \frac{(\omega_Q^{\text{PAS}})^2}{\omega_0} \left[A + B d_{00}^2(\beta_R) d_{00}^2(\beta) + C d_{00}^4(\beta_R) d_{00}^4(\beta) \right]$$

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

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

- Second-rank term $d_{00}^2(\beta_R) = 0$ when $\beta_R = 54.736^\circ$
- But $d_{00}^4(54.736^\circ) \neq 0$, so although the lineshape is narrowed under MAS the quadrupolar broadening is not completely removed
- To ensure $d_{00}^4(\beta_R) = 0$, β_R must be 30.56° or 70.12°

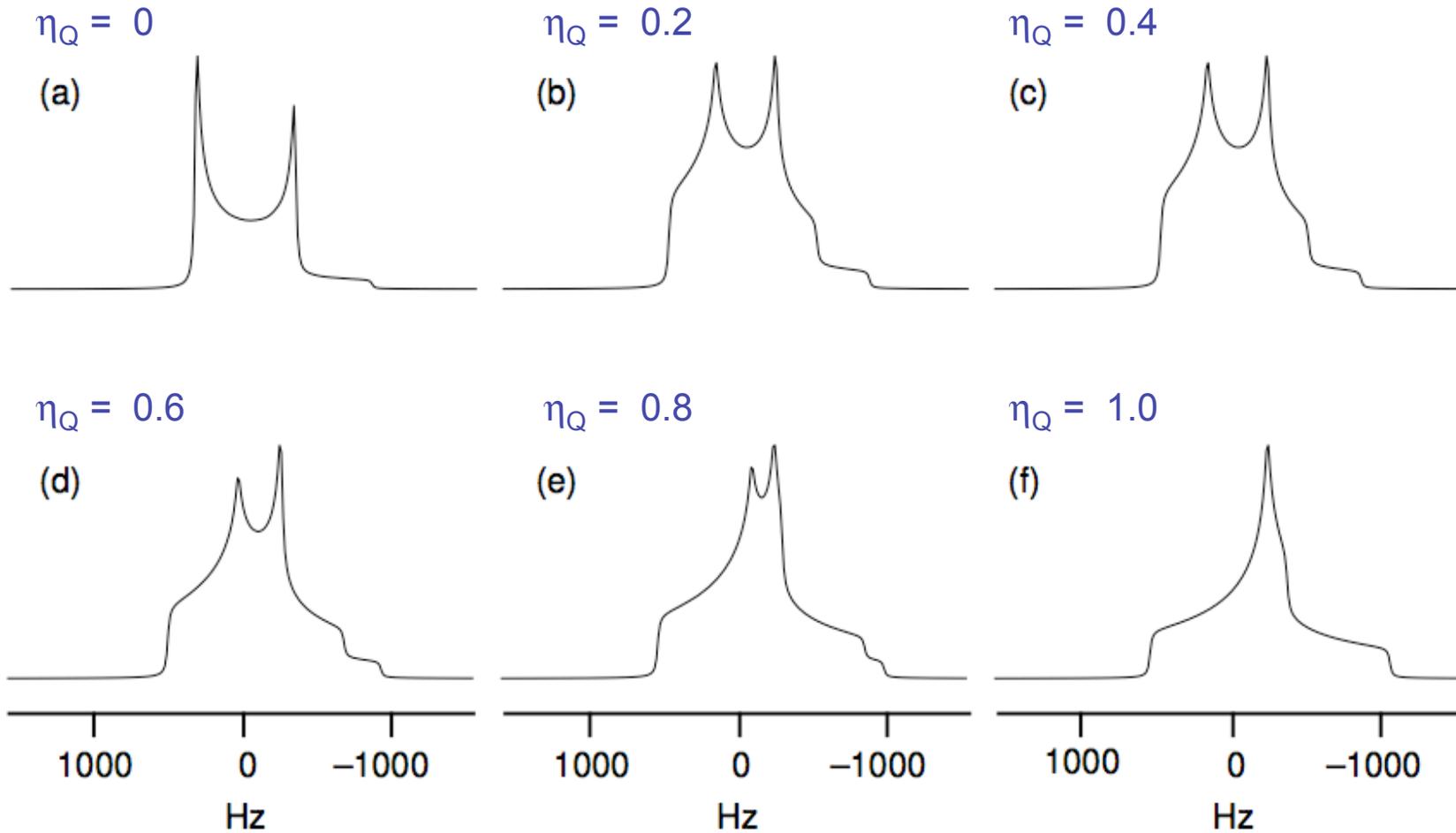
Quadrupolar broadening and MAS



- Lineshape is significantly narrowed by MAS
- Fourth-rank anisotropic quadrupolar broadening remains
- Isotropic quadrupolar shift

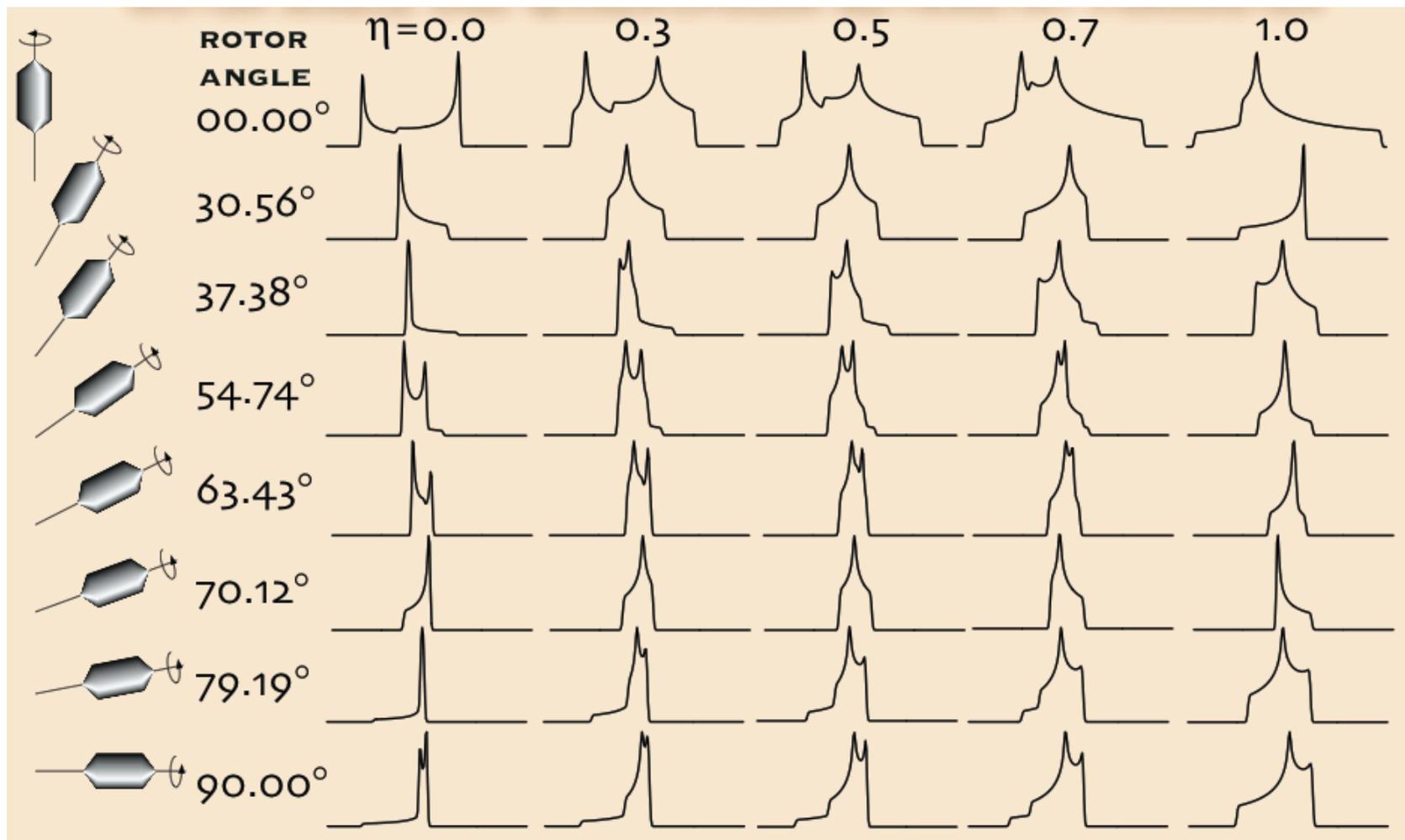
$$\propto ((\omega_Q^{\text{PAS}})^2/\omega_0) A (1 + \eta_Q^2/3)$$

Spin $I = 3/2$ MAS lineshapes



Spin $I = 3/2$ VAS lineshapes

- No single angle is able to remove both the second-rank and fourth-rank second-order quadrupolar broadening



Experimental acquisition

- We use MAS in order to ensure dipolar interactions and CSA is removed along with the second-rank quadrupolar broadening
- A pulse rarely executes the perfect rotation, unless ω_1 is greater than any offsets present in the system

$$\omega_1 \gg \omega_Q^{\text{PAS}}$$

“hard” pulse

“non-selective” pulse

nutration at rate of ω_1

$$\omega_1 \ll \omega_Q^{\text{PAS}}$$

“soft” pulse

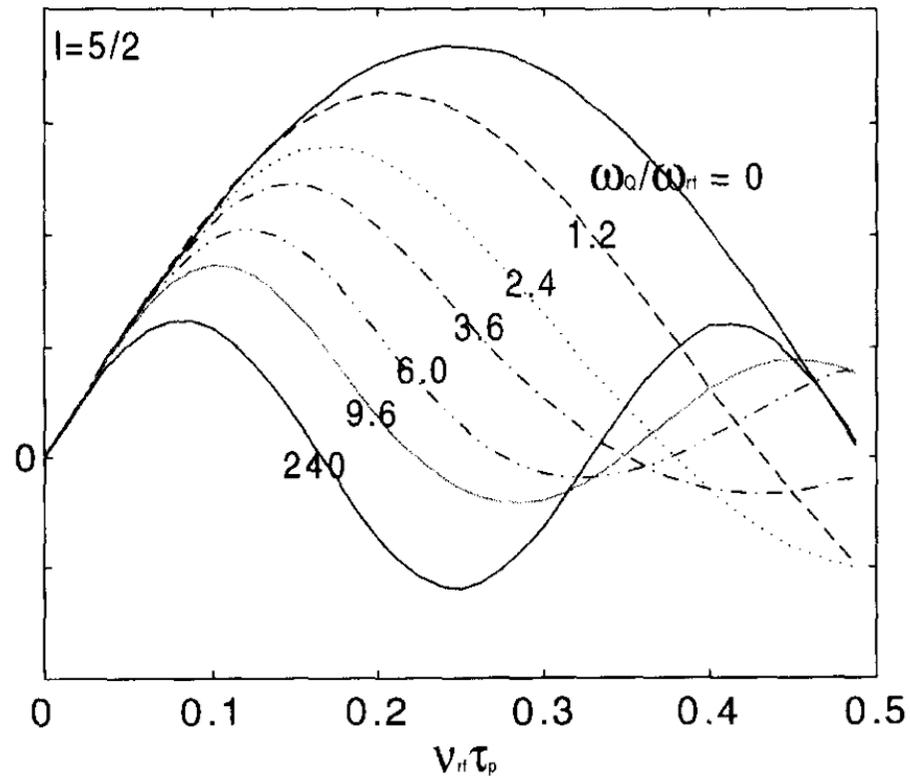
“selective” pulse

CT nutration rate $(1 + 1/2) \omega_1$

different nutration rates
depending on ω_1 and ω_Q^{PAS}

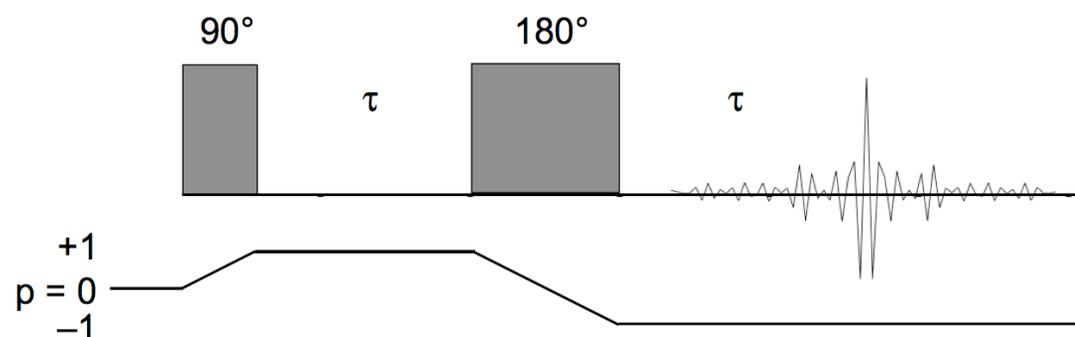
Experimental acquisition

- For CT gradual progression from ω_1 to $(l + 1/2) \omega_1$ as ω_Q^{PAS} increases
- Use low power pulses to ensure CT selectivity and minimal lineshape distortion



Experimental acquisition

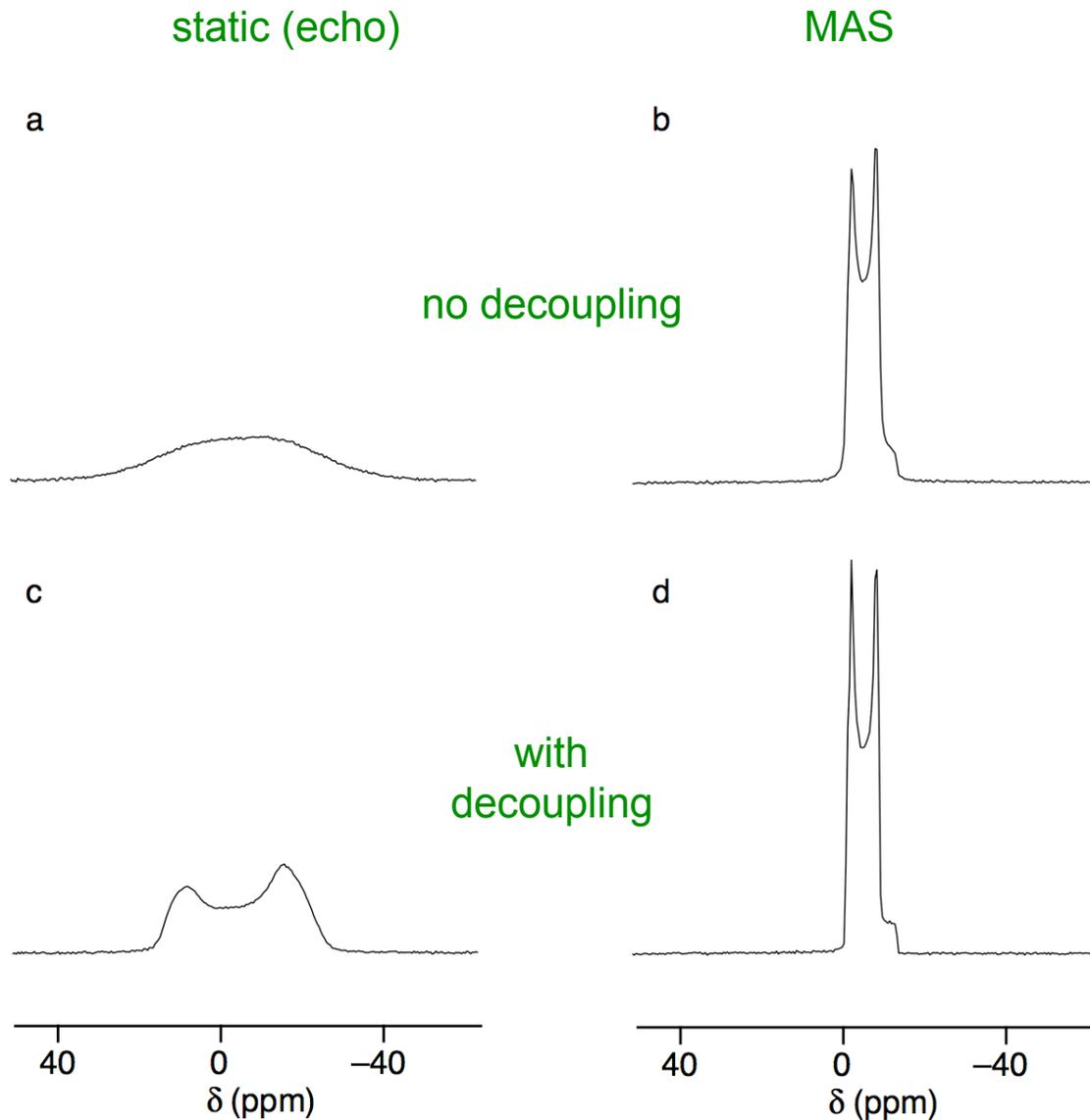
- If the second-order quadrupolar broadening interaction is large we may require an echo to acquire the broad CT lineshapes
- To refocus second-order quadrupolar broadening we need a **spin** or **Hahn echo** **not** a **quadrupolar echo**



For CT observation
low-power selective
pulses are used (~ 15 -
 $30 \mu\text{s}$ for 90°)

- The τ duration should be chosen to minimise any T_2 differences either between sites or across a powder lineshape
- For best results, τ should also be synchronized with the rotor (i.e., $\tau = n \tau_R$)

Experimental acquisition

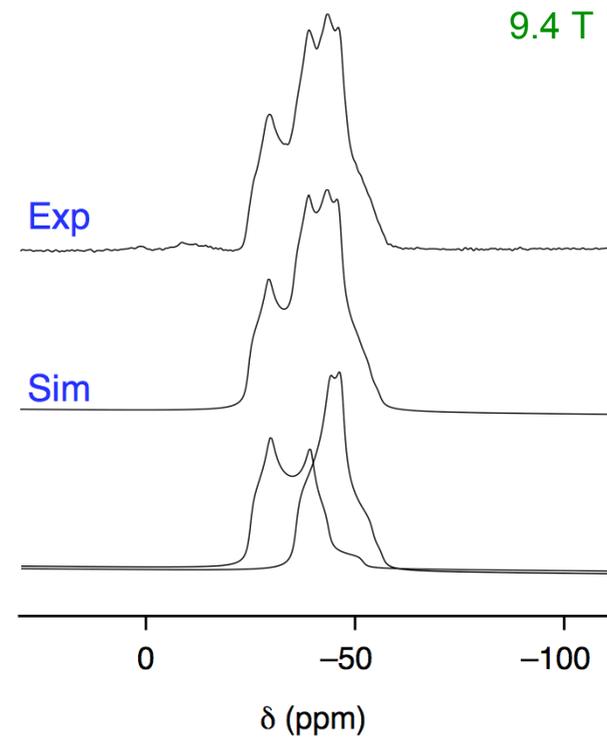
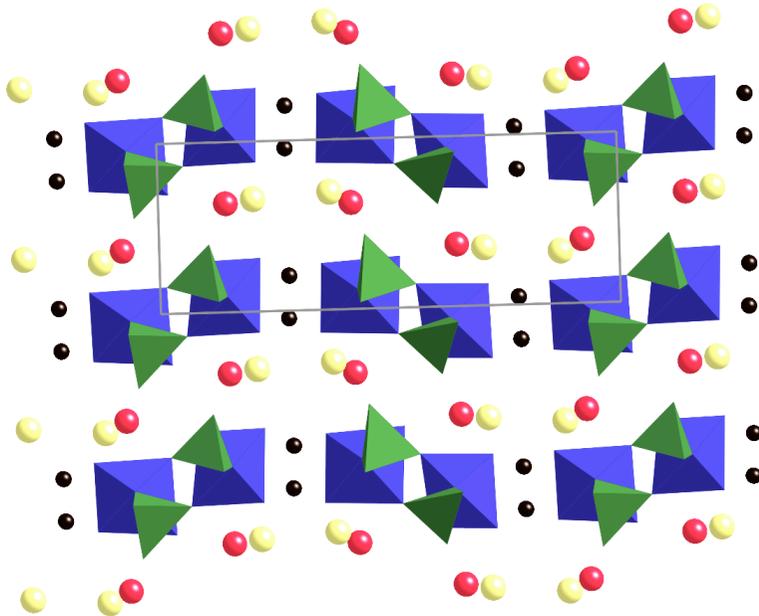


^{27}Al NMR of
aluminium
acetylacetonate

$C_Q = 3.0$ MHz
 $\eta_Q = 0.15$
 $\delta_{\text{iso}} = 0$ ppm

Example: ^{23}Na NMR

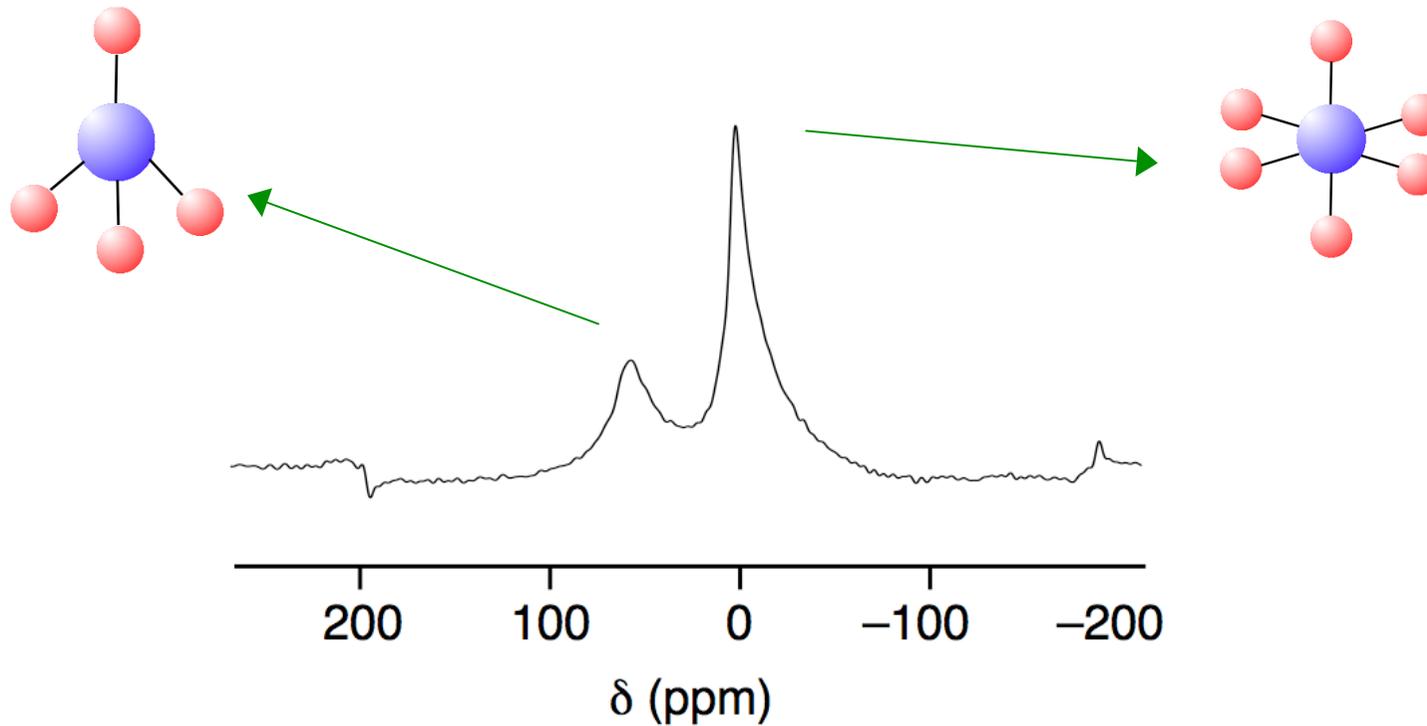
- Novel layered material $\text{Na}_2[(\text{VO})_2(\text{HPO}_4)_2\text{C}_2\text{O}_4]\cdot 2\text{H}_2\text{O}$
- Space group cannot be determined easily by X-ray $P2_1/m$ or $P2_1$
- 2 distinct resonances by ^{23}Na MAS NMR
- Space group cannot be $P2_1/m$



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?

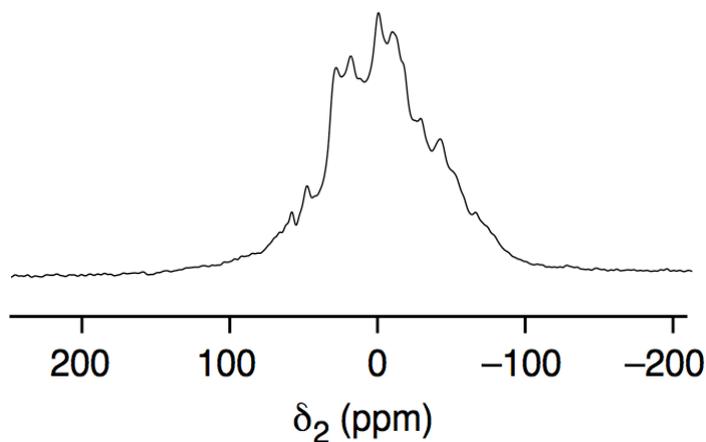


MAS lineshapes

- 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?