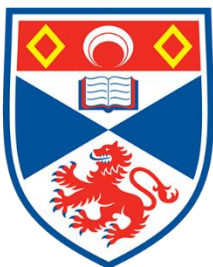


High-Field Solid-State NMR

Daniel Dawson

dmd7@st-andrews.ac.uk



University of
St Andrews



outline

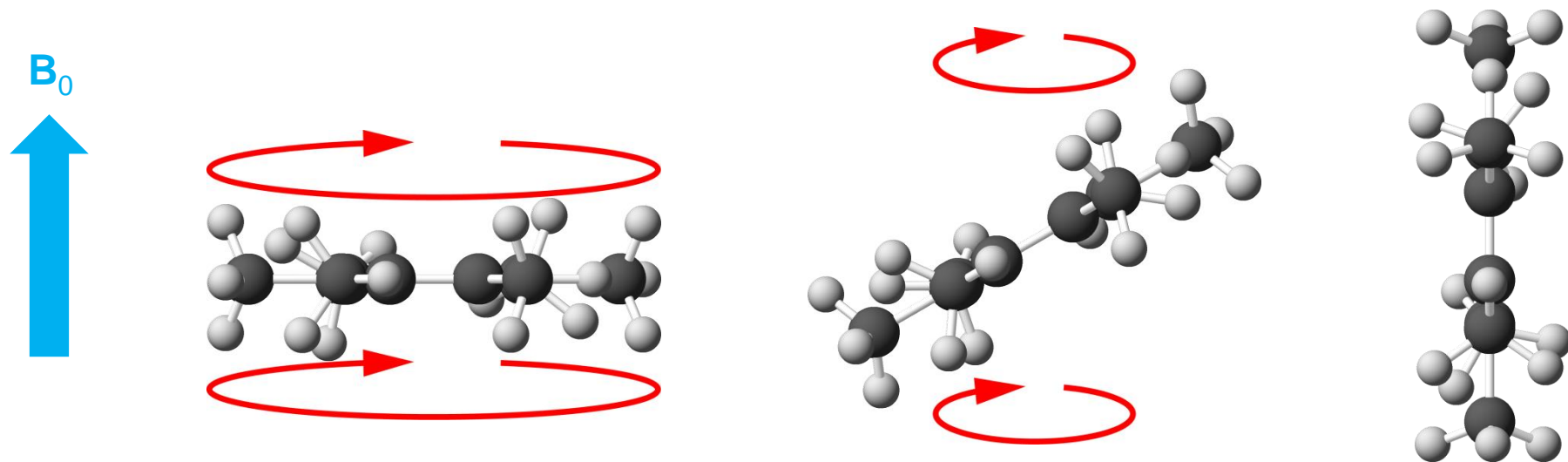
anisotropic interactions in NMR

some examples

some caveats

1. Anisotropic Interactions

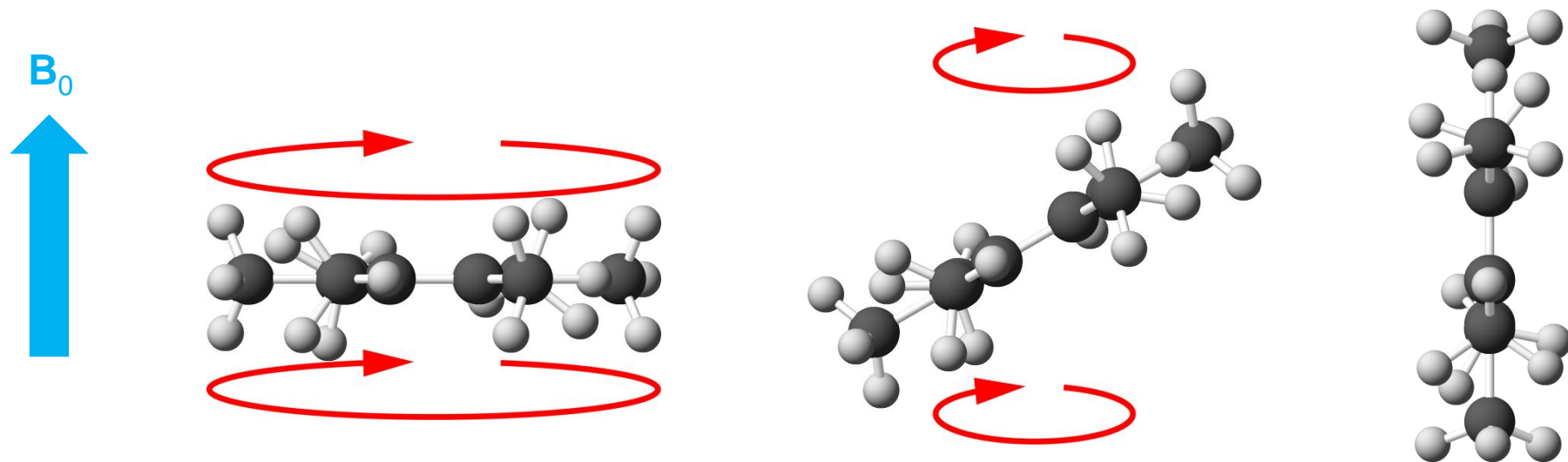
anisotropic interactions



- the induced current (shielding) depends on the orientation of the molecule relative to B_0
- we can describe this with the shielding tensor

$$\boldsymbol{\sigma} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix}$$

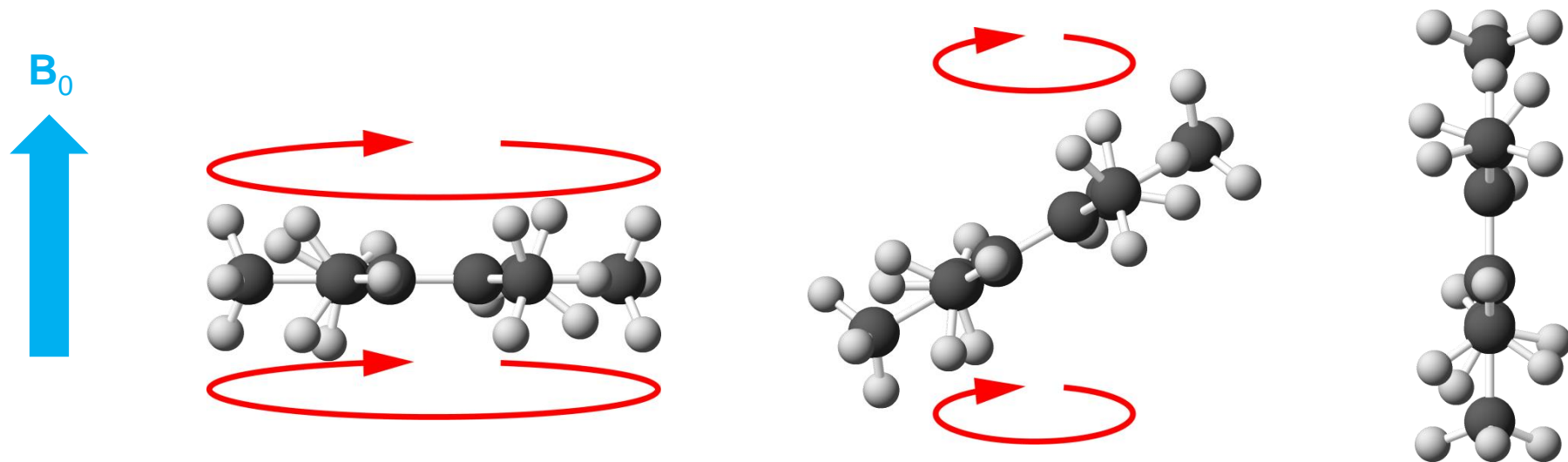
anisotropic interactions



- the induced current (shielding) depends on the orientation of the molecule relative to B_0
- the chemical shift Hamiltonian is given by

$$H_{\text{CS}} = \gamma \sigma_{xz} I_x B_0 + \gamma \sigma_{yz} I_y B_0 + \gamma \sigma_{zz} I_z B_0$$

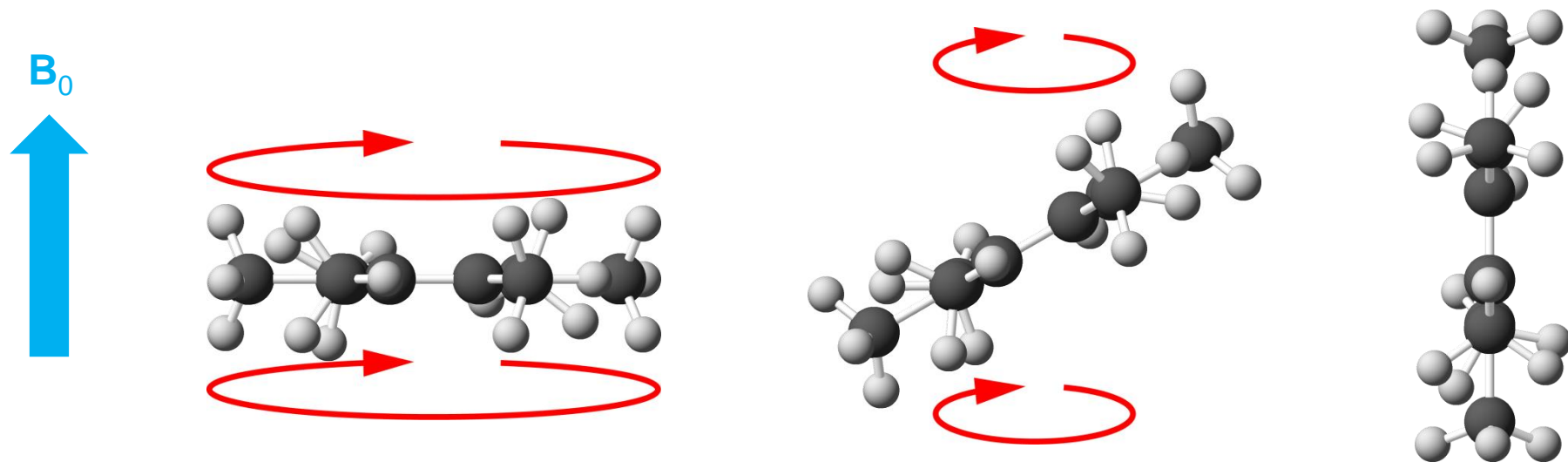
anisotropic interactions



- the induced current (shielding) depends on the orientation of the molecule relative to B_0
- in the secular approximation (B_0 lies entirely along z)

$$H_{\text{CS}} = \gamma \sigma_{zz} I_z B_0$$

anisotropic interactions



- the induced current (shielding) depends on the orientation of the molecule relative to B_0
- the orientation dependence of σ_{zz} is given by

$$\sigma_{zz} = \sigma_{\text{iso}} + \frac{\Delta\sigma_{\text{cs}}}{2} \left[(3\cos^2\theta - 1) + \eta_{\text{cs}} (\sin^2\theta \cos 2\phi) \right]$$

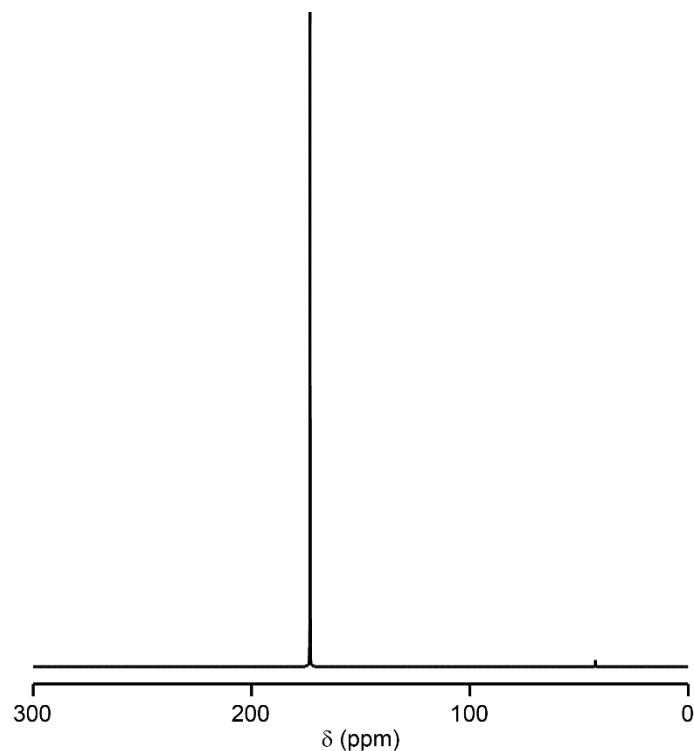
orientation independent

orientation dependent

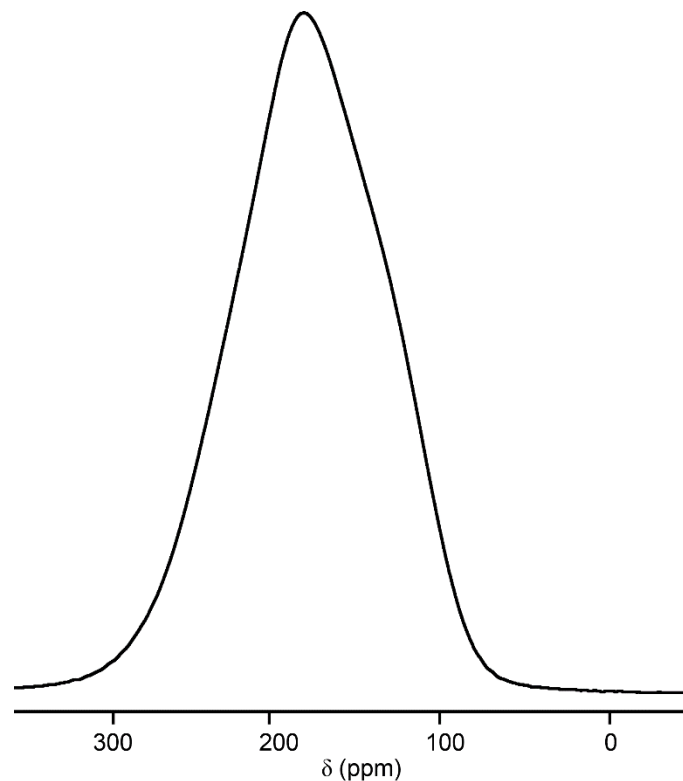
anisotropic interactions

$$\sigma_{zz} = \sigma_{\text{iso}} + \frac{\Delta\sigma_{\text{CS}}}{2} \left[(3\cos^2\theta - 1) + \eta_{\text{CS}} (\sin^2\theta \cos 2\phi) \right]$$

solution-state NMR

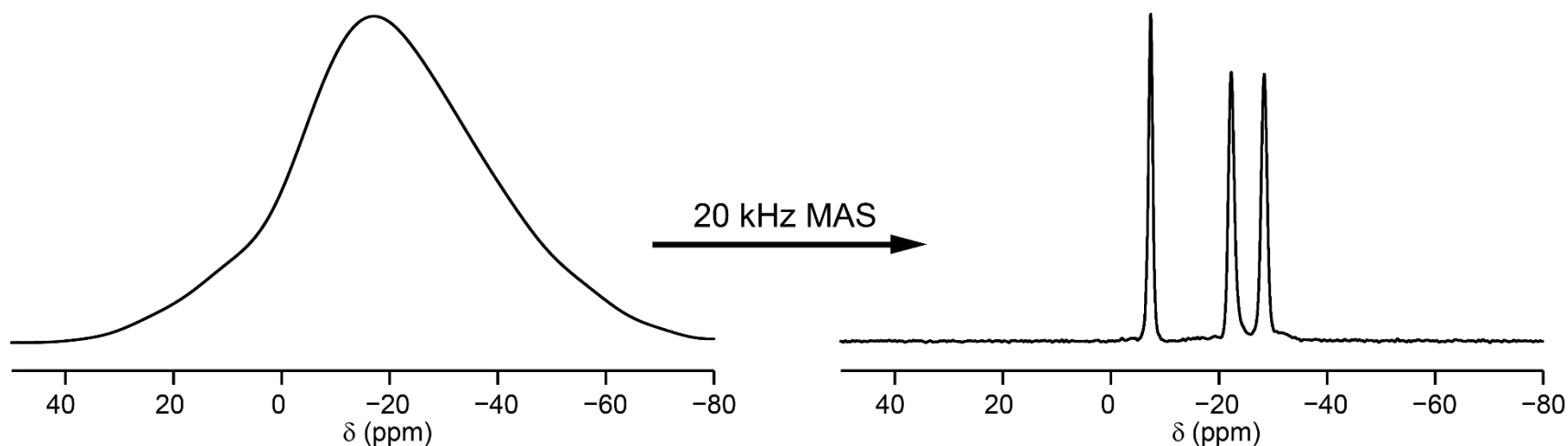


solid-state NMR



magic angle spinning

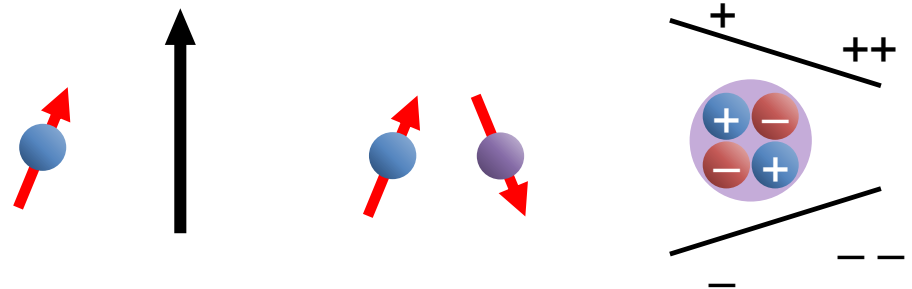
- MAS is routinely used to remove the anisotropic broadening by rapid rotation about the magic angle of 54.74°
- rotation about the body diagonal of a cube is a bit like spinning along x, y and z simultaneously, mimicking the isotropic tumbling in solution



- but which interactions did we just remove, and could they tell us anything?

NMR interactions

- interactions might be spin-field
 - chemical shift, paramagnetic shift, (Zeeman)
- ... spin-spin
 - J and dipolar coupling
- ... or spin-field gradient
 - quadrupolar coupling ($I > 1/2$ only)



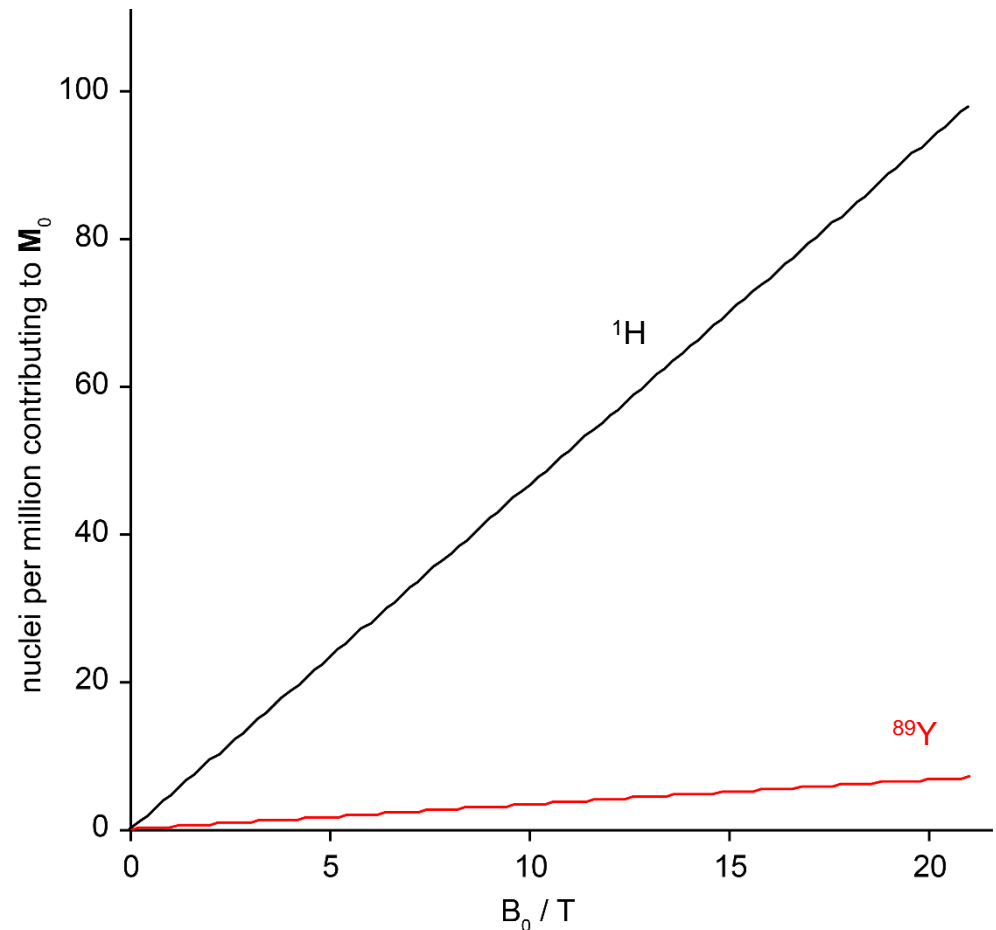
interaction	magnitude	isotropic	anisotropic
chemical shift	$\sim 10^4$ Hz	yes	first order
paramagnetic shift	$\sim 10^5$ Hz	yes	first order
J coupling	$\sim 10^1$ Hz	yes	first order
dipolar coupling	$\sim 10^5$ Hz	no	first order
quadrupolar coupling	$\sim 10^6$ Hz	yes	first and second order

variation with B_0 field

- the Zeeman interaction increases the transition energy (Larmor frequency) and alters the equilibrium population difference

$$\frac{N_{m_I+1}}{N_{m_I}} = e^{\frac{-\gamma\hbar B_0}{k_B T}}$$

- expect sensitivity to increase with B_0
- some nuclei are still very insensitive!

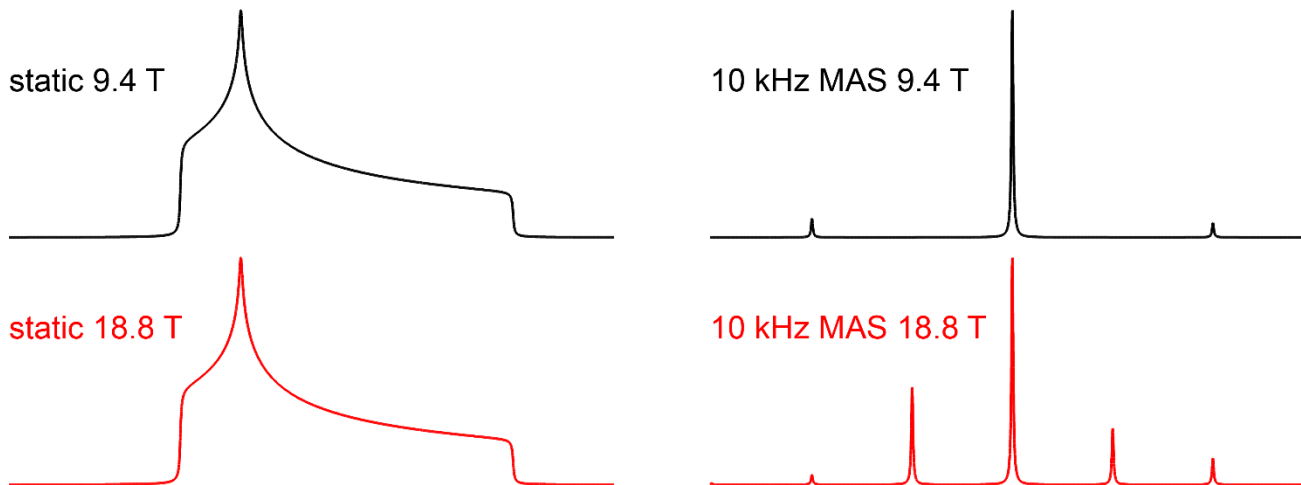


variation with B_0 field

- by design, the chemical shift doesn't change with field

$$\delta = \frac{\omega_{\text{obs}} - \omega_{\text{ref}}}{\omega_{\text{ref}}}$$

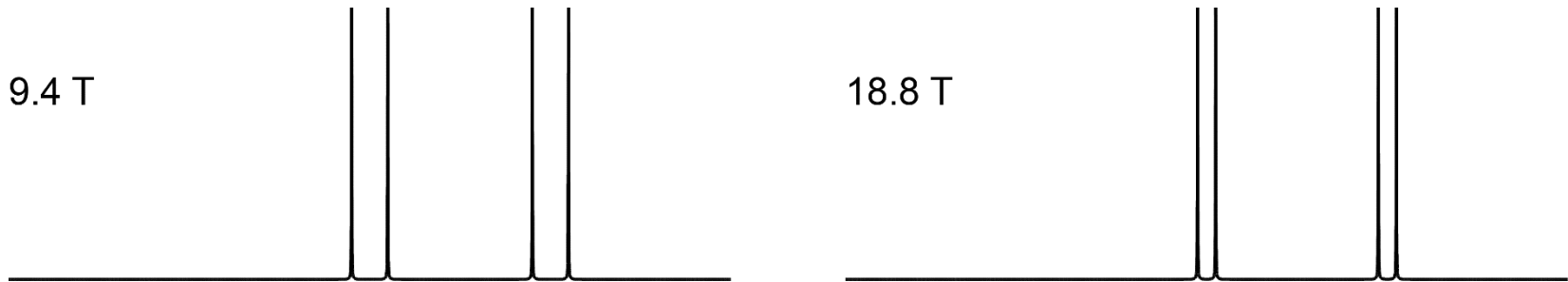
- but, because the chemical shift tensor is defined in ppm, the chemical shift anisotropy increases (in Hz) with field



- spinning sidebands are more intense at higher field
- the same is also true for the paramagnetic interaction

variation with B_0 field

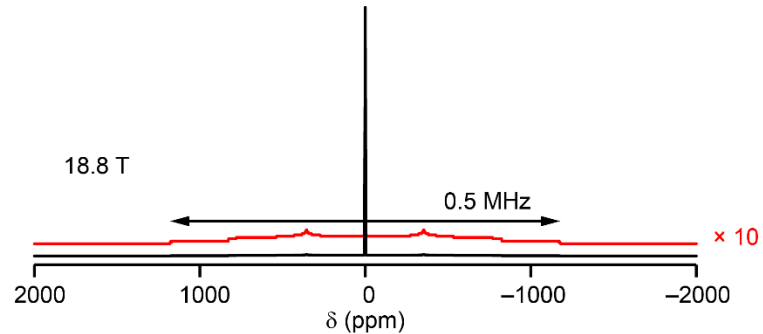
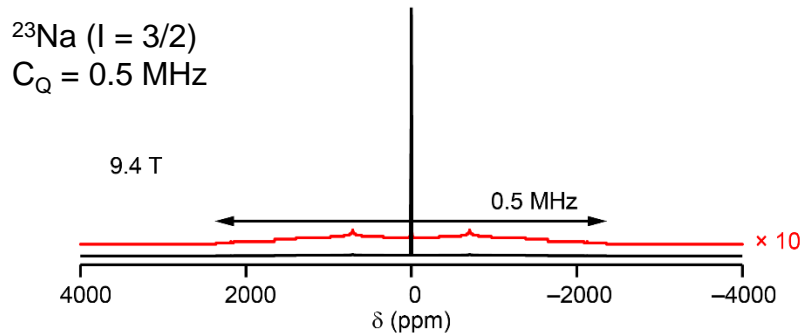
- spin-spin interactions involve internal fields, rather than the external field, so don't change with B_0



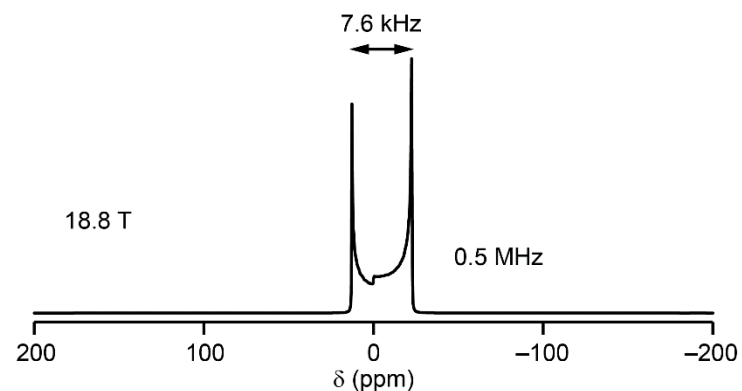
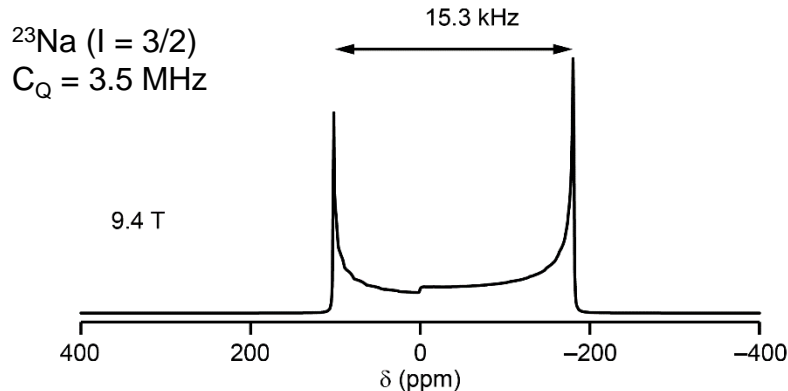
- easy way to make sense of more complicated multiplets
- can improve resolution in very crowded solution-state spectra
- the same experimental conditions (decoupling sequences, recoupling delays/pulses and MAS rate) should apply at all fields

variation with B_0 field

- the quadrupolar interaction is between the nucleus and the local electric field gradient so, to a first order, it doesn't change with field



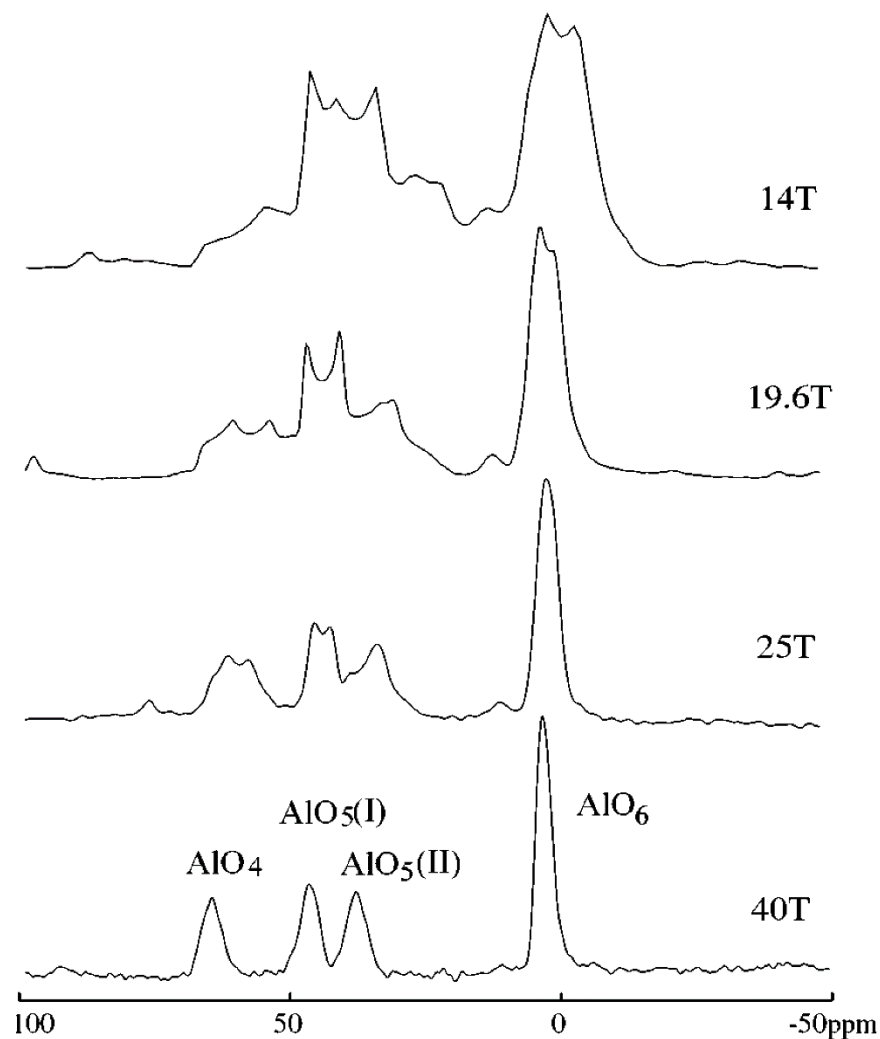
- however, the second-order term is proportional to $1/B_0$



- higher field can dramatically improve resolution for quadrupolar nuclei

variation with B_0 field

- as an extreme example, ^{27}Al MAS spectra become almost isotropic at 40 T!
- line broadening now mainly caused by extreme field drift of resistive magnet



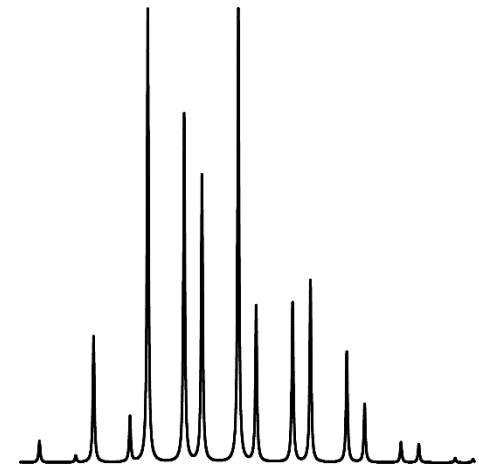
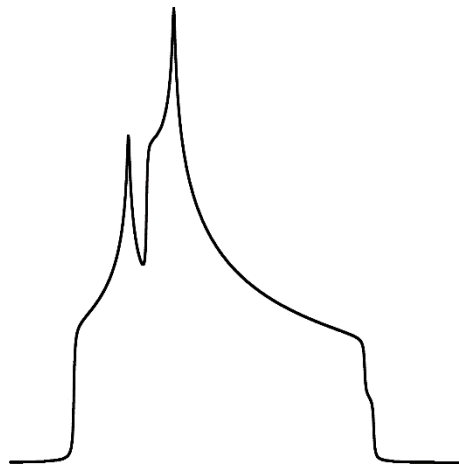
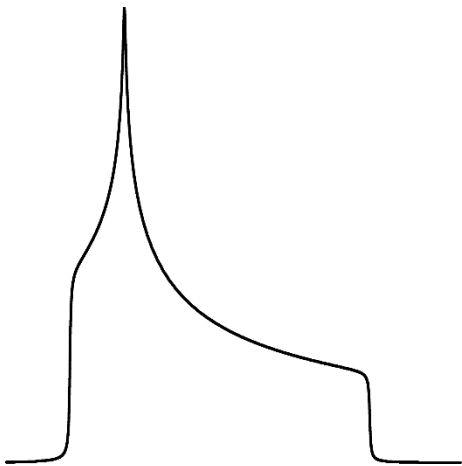
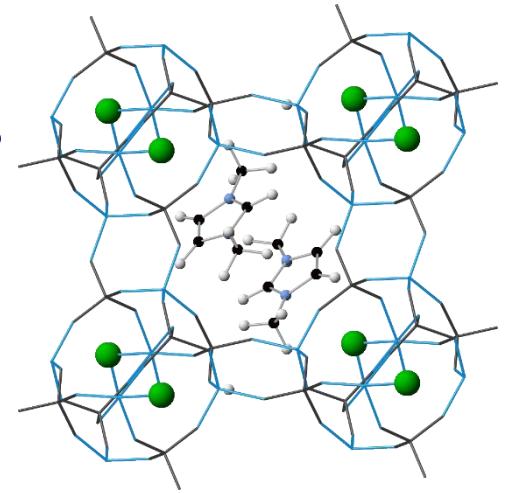
part 1 summary

interaction	variation with B_0	effect at higher field
Zeeman splitting	increases	sensitivity and resolution improvement
chemical shift	no change (in ppm)	none
chemical shift anisotropy	increases in Hz	more intense sidebands
J coupling	no change (in Hz)	resolution enhancement
dipolar coupling	no change (in Hz)	possible resolution enhancement (static samples)
quadrupolar coupling	decreases	resolution enhancement

2. Some Examples

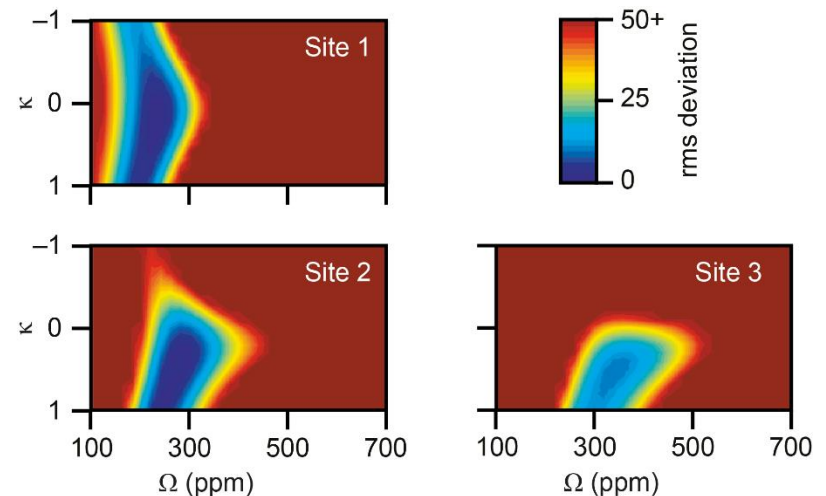
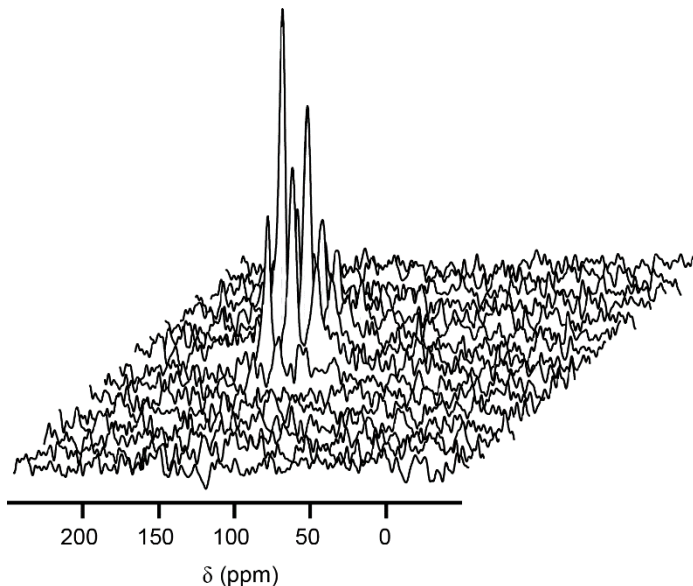
measuring small CSAs

- the Chemical Shift Anisotropy can sometimes provide additional structural information not available from δ_{iso} alone
- are ^{31}P CSAs in aluminophosphates (AlPOs) useful?
- CSA can be measured...
 - from a static spectrum
 - from slow MAS
 - using CSA-amplification methods



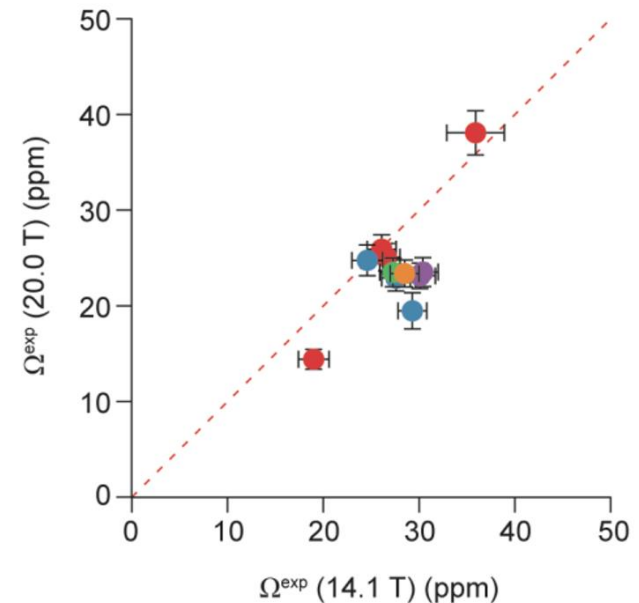
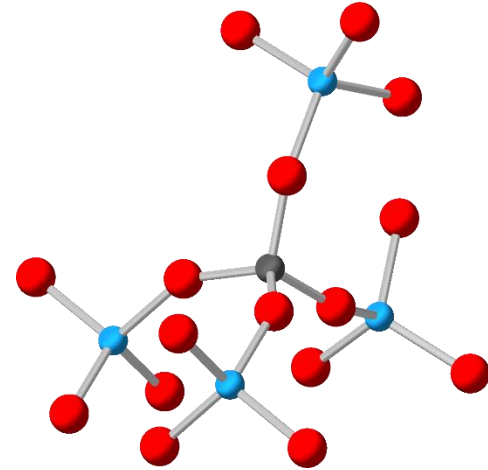
measuring small CSAs

- CSA-amplified PASS works by amplifying the CSA in the indirect dimension of a constant-time pseudo-2D experiment
- F_2 = fast MAS spectrum (no dipolar couplings, no overlapping sidebands)
- F_1 = “slow MAS” spectra for each individual site
- CSA parameters and errors can be obtained using SIMPSON



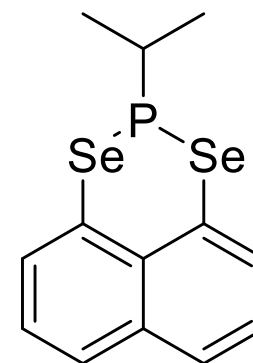
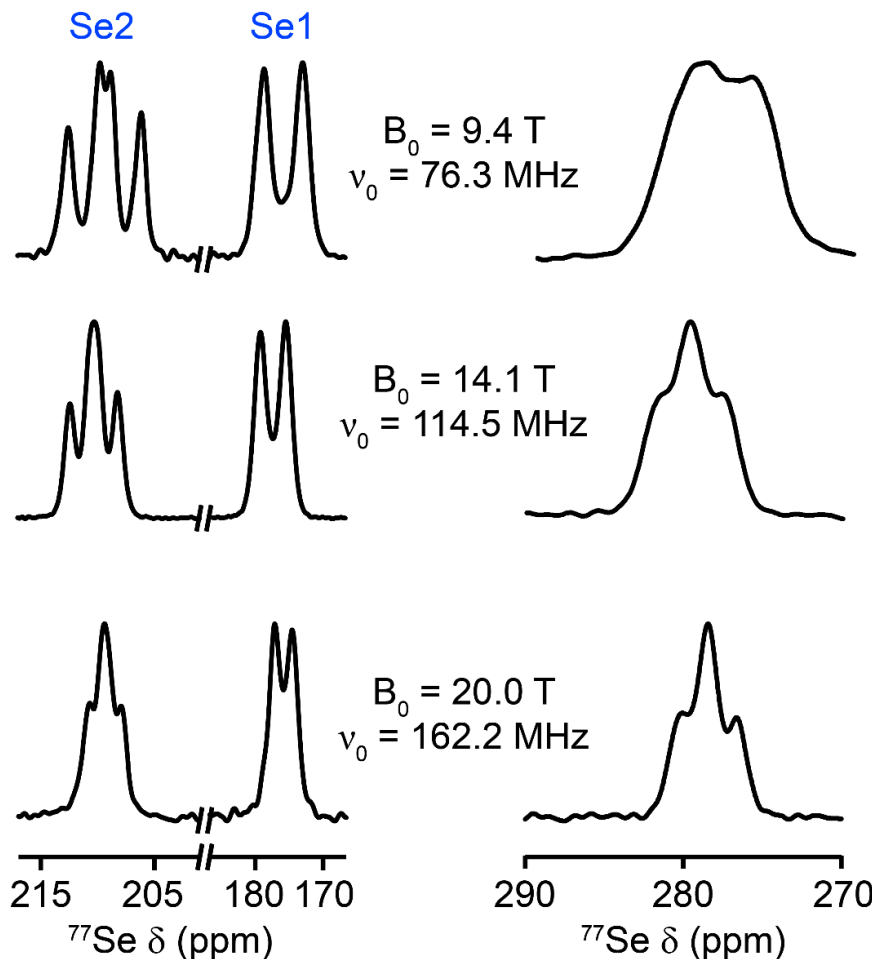
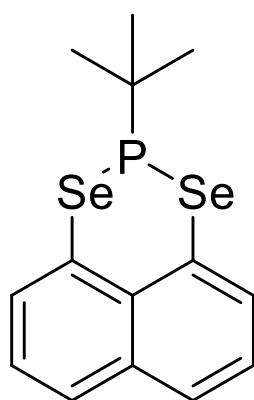
measuring small CSAs

- PO_4 tetrahedral sites in AlPOs
- for a perfect tetrahedron, the CSA is 0
- at 14.1 T, errors are large as CSAs are small
- at 20.0 T, CSAs are ~40% larger in Hz, allowing more accurate measurement
- for pure AlPO_4 frameworks, the CSA tells us that the P is tetrahedral
- probably more useful for Mg/Zn-doped AlPOs where CSAs are larger



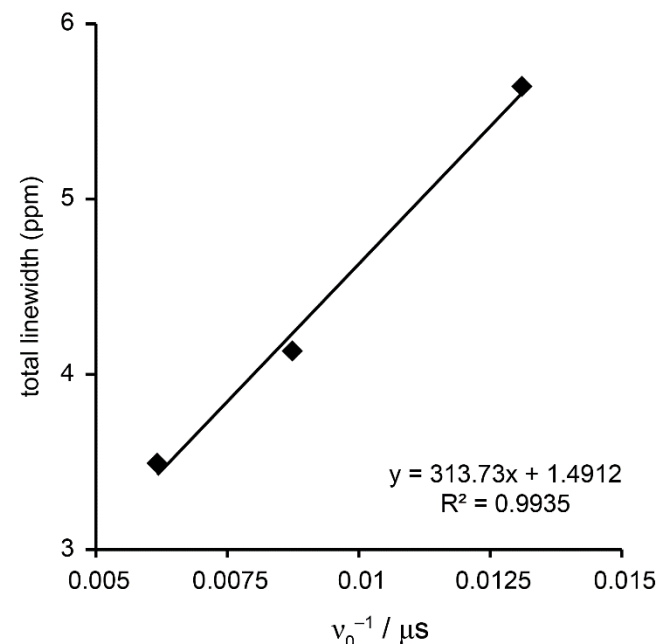
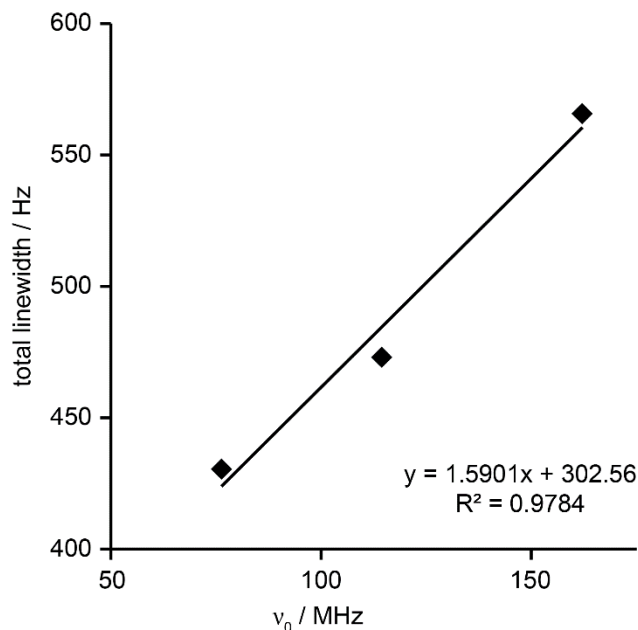
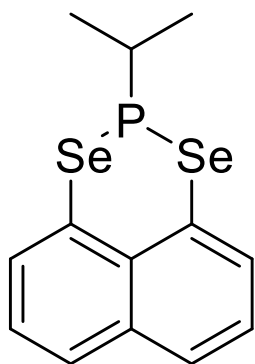
untangling J multiplets

- sometimes a “simple” molecule does something odd...



untangling J multiplets

- variable-field NMR helped identify shift/coupling contributions to lineshapes

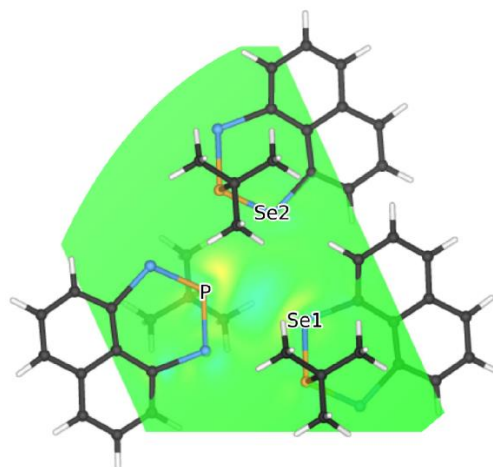
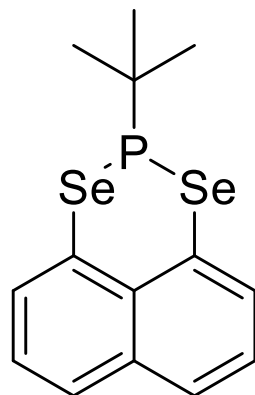


$$\text{total linewidth} = (J_1 + J_2)/2 + (\delta_1 - \delta_2)$$

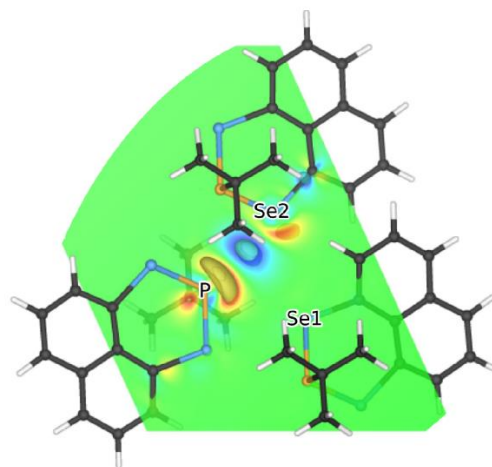
$$(J_{\text{Se1P}} + J_{\text{Se2P}})/2 \approx 310 \text{ Hz}$$
$$\delta_{\text{Se1}} - \delta_{\text{Se2}} \approx 1.5 \text{ ppm}$$

untangling J multiplets

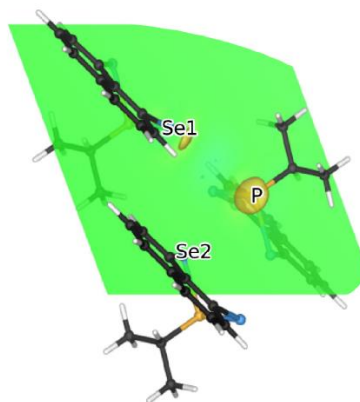
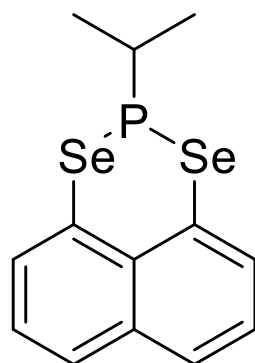
- periodic DFT calculations can help to understand the extra coupling



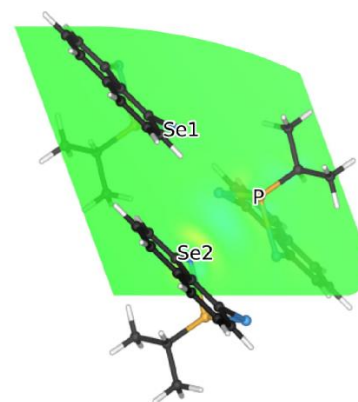
$J(\text{Se1-P}) = 66.6 \text{ Hz}$



$J(\text{Se2-P}) = 348.0 \text{ Hz}$



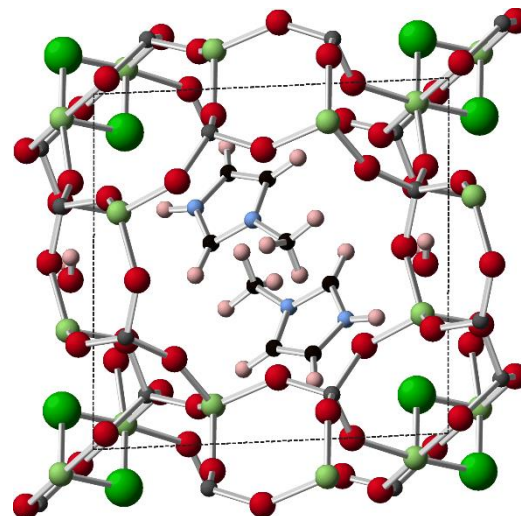
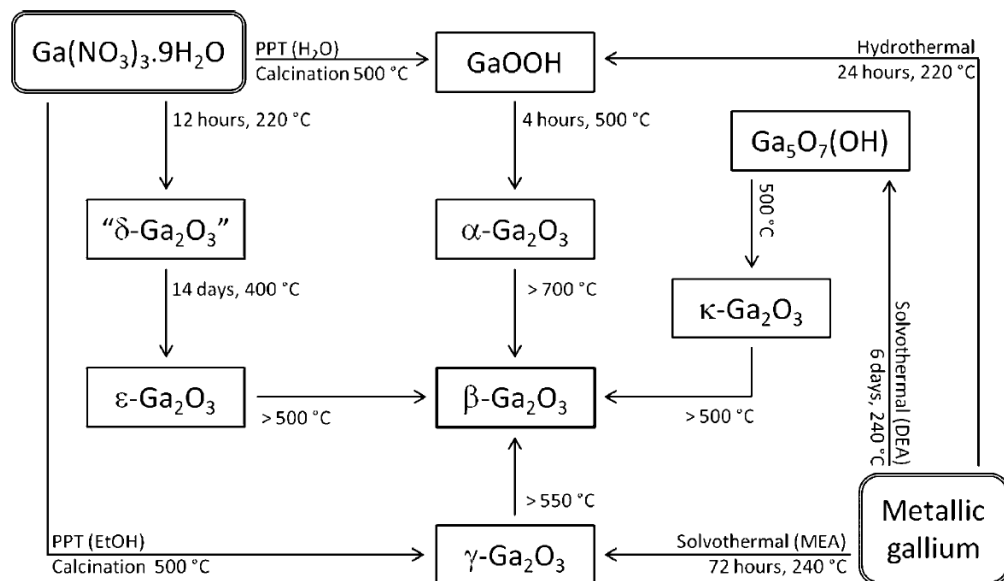
$J(\text{Se1-P}) = 64.1 \text{ Hz}$



$J(\text{Se2-P}) = 109.1 \text{ Hz}$

$^{69/71}\text{Ga}$ NMR

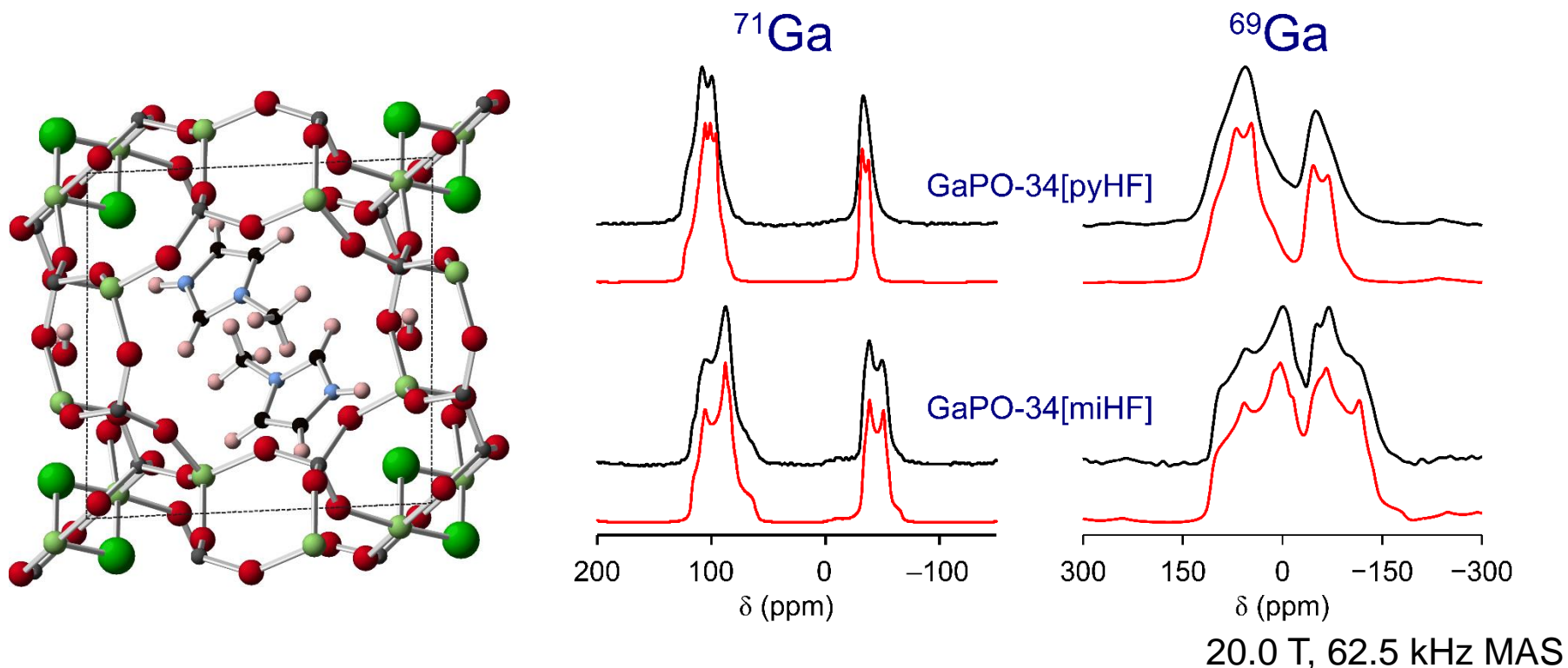
- collaboration with Richard Walton (Warwick) on Ga_2O_3 chemistry



- also interested in GaPO_4 frameworks and the comparison to AlPOs
- two NMR-active isotopes of gallium, ^{69}Ga and ^{71}Ga , both with $I = 3/2$
 - different Larmor frequencies and quadrupole moments

$^{69/71}\text{Ga}$ NMR

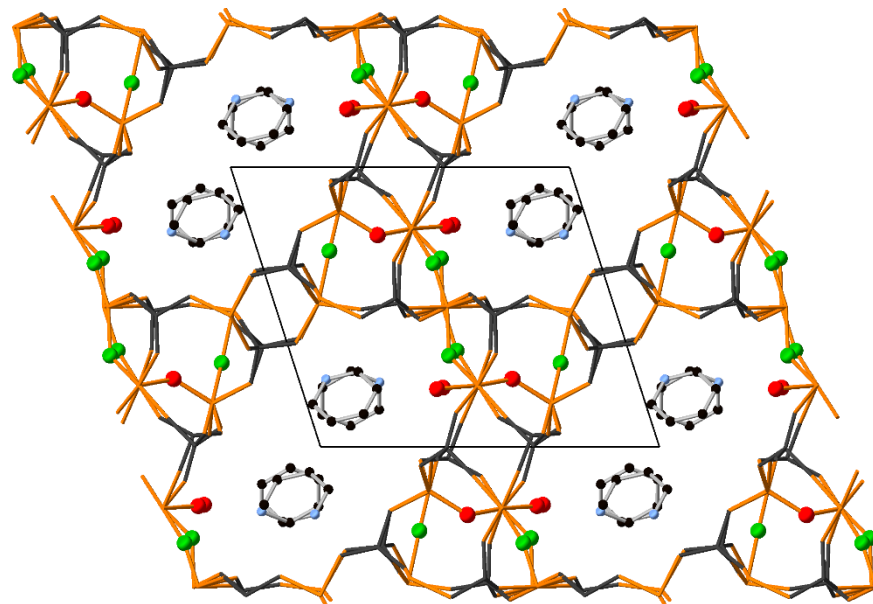
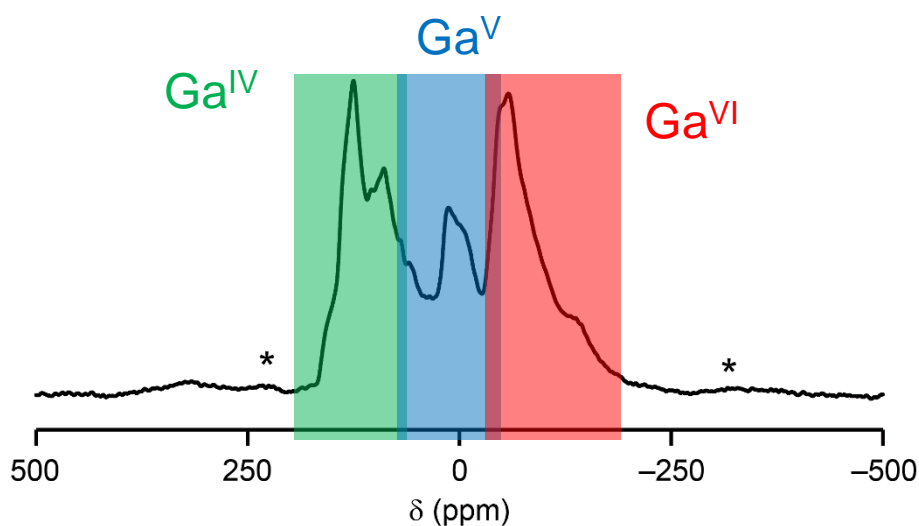
- even for the higher-resolution ^{71}Ga , high field + fast MAS is needed



- ^{69}Ga parameters should match ^{71}Ga (^{69}Ga C_Q will be scaled by ~ 1.6)
- comparing nuclei is a good check that the parameters are correct, particularly for the more disordered GaPO-34[pyHF]

$^{69/71}\text{Ga}$ NMR

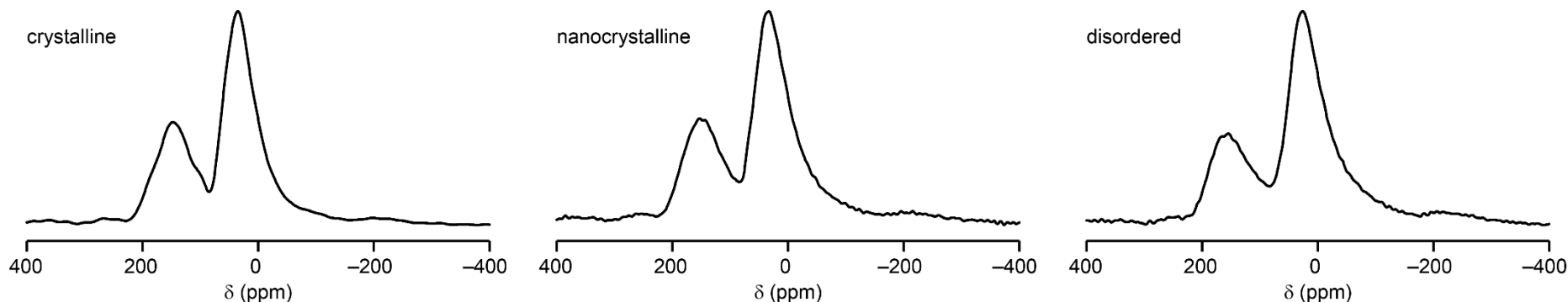
- high field is essential when trying to understand new materials



- $\text{Ga}(\text{IV}) : \text{Ga}(\text{V}) : \text{Ga}(\text{VI})$ ratio of $\sim 2 : 2 : 3$ sounds unusual
- NMR also reveals extensive disorder (OH/F, orientation of organics, *etc.*)
- high-resolution ^{71}Ga STMAS experiments gave no signal
 - indicates μs dynamics

$^{69/71}\text{Ga}$ NMR

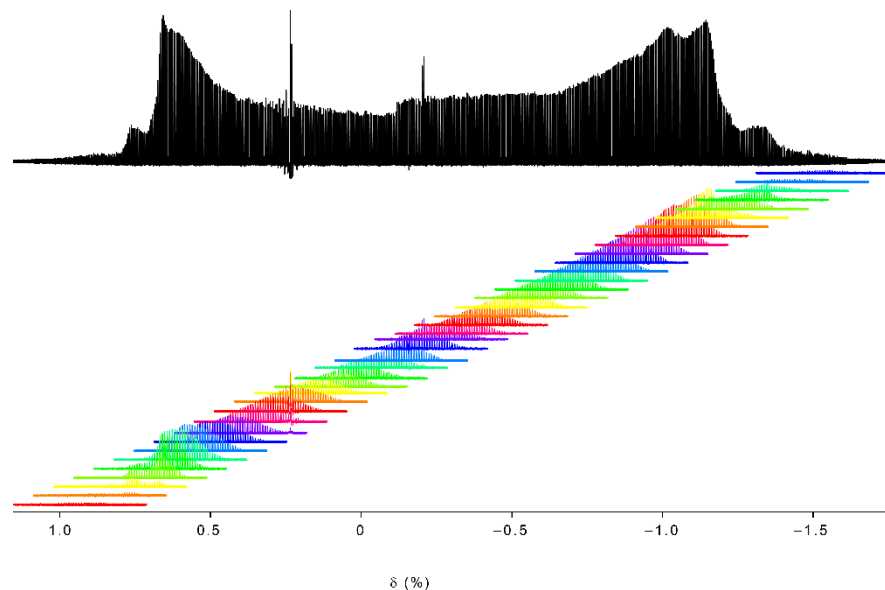
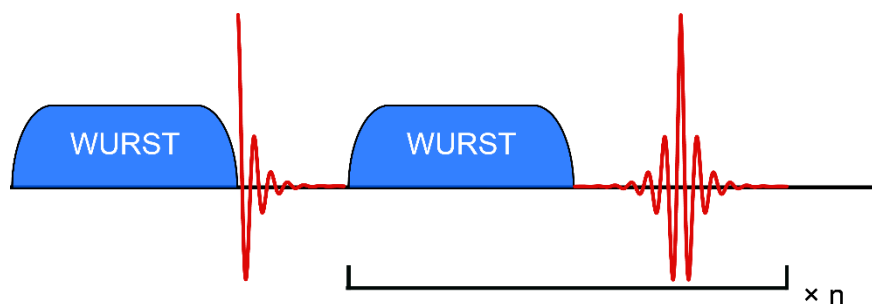
- for $\gamma\text{-Ga}_2\text{O}_3$ nanoparticles the increased resolution allowed integration of Ga(IV) : Ga(VI)



- pair distribution function analysis suggested more Ga(IV) as the particle size decreased, but NMR showed no change
- crystallographic measurements ignore the surface of the particles, whereas NMR could see both surface and bulk
- Ga(VI)-rich surface structure proposed

$^{63/65}\text{Cu}$ NMR and NQR

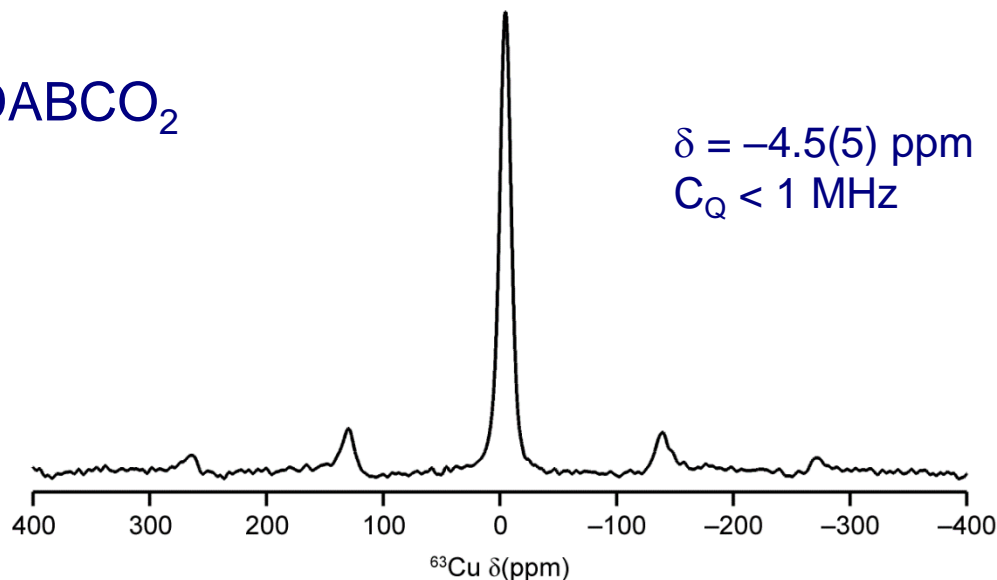
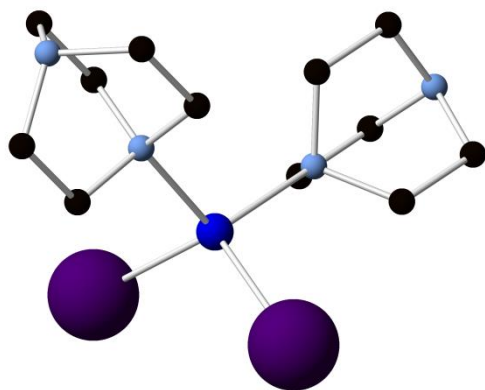
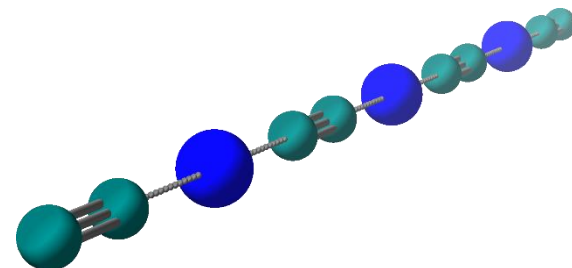
- sometimes the quadrupolar interaction is too big for MAS, even at high field
- static wideline spectra can be recorded instead, often making use of other signal enhancement methods (broadband pulses, CPMG) and frequency stepping



- important for nuclei with a large nuclear electric quadrupole moment or low γ , and elements that tend to form low-symmetry bonding geometry
 - Cl, Br, I, Cu, Ir, Mg, Zn...

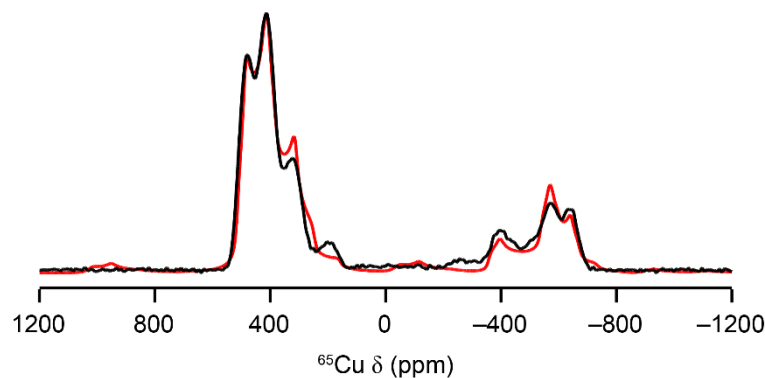
$^{63/65}\text{Cu}$ NMR and NQR

- mechanochemical synthesis of new Cu(I) frameworks
 - no chance of single crystals for structure solution
- how many distinct Cu sites are there?
- two NMR-active isotopes of Cu, ^{63}Cu and ^{65}Cu , both with $I = 3/2$, similar Q and γ
- things started off well with $\text{Cu}_2\text{I}_2\text{DABCO}_2$



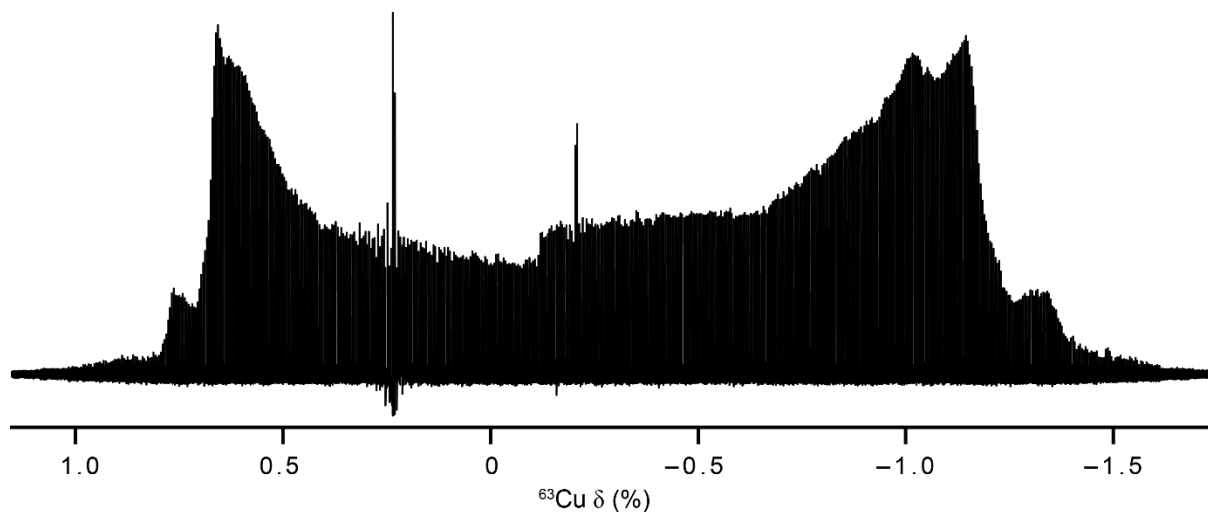
$^{63}/^{65}\text{Cu}$ NMR and NQR

- for $\text{Cu}_2(\text{SCN})_2(\text{DABCO})$, fast (~ 80 kHz) MAS at 20.0 T still worked



site	δ_{iso} (ppm)	C_Q / MHz	η_Q
Cu1	810	10.7	0.3
Cu2	800	13.8	0.4
Cu3	320	15.3	0.2
Cu4	190	10.6	0.3

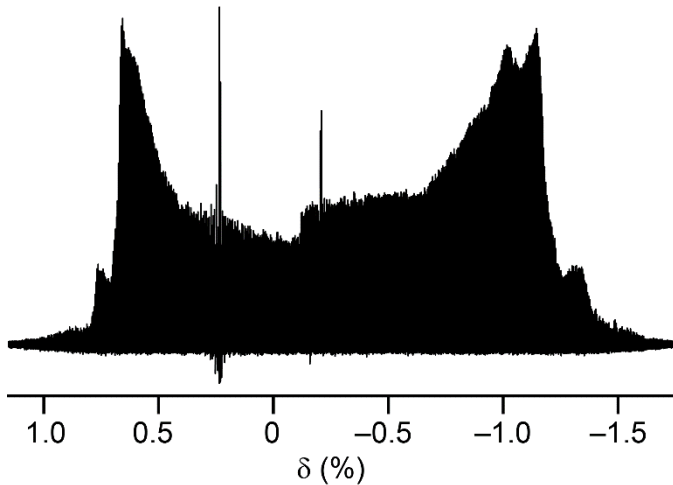
- for $\text{CuCN}(\text{mtu})$ form II (mtu = *N*-methylthiourea), C_Q is ~ 80 MHz



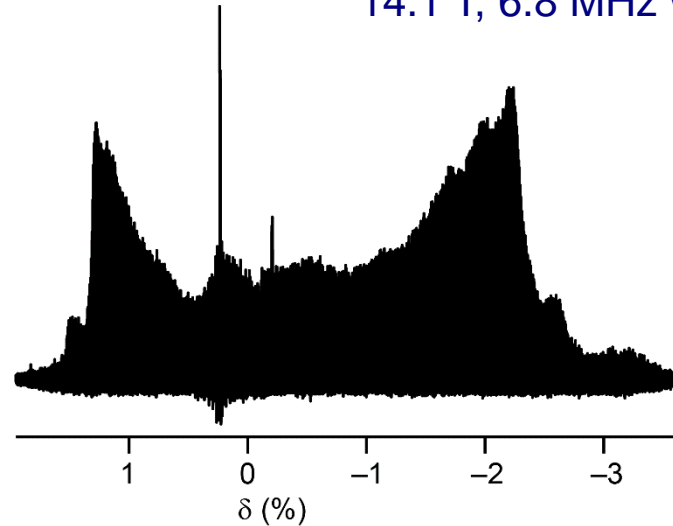
$^{63/65}\text{Cu}$ NMR and NQR

- magnitude of C_Q can be confirmed by lower field measurements...

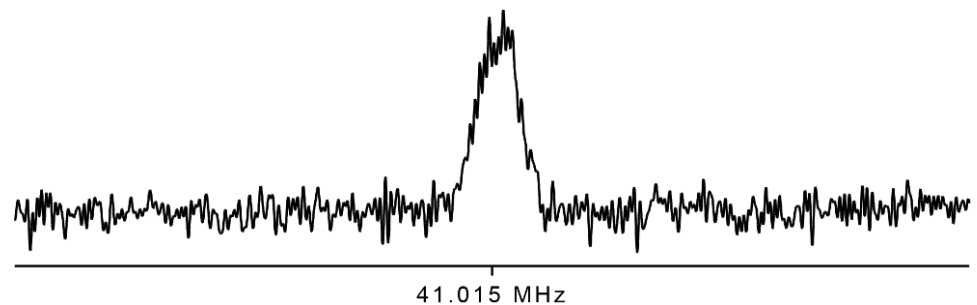
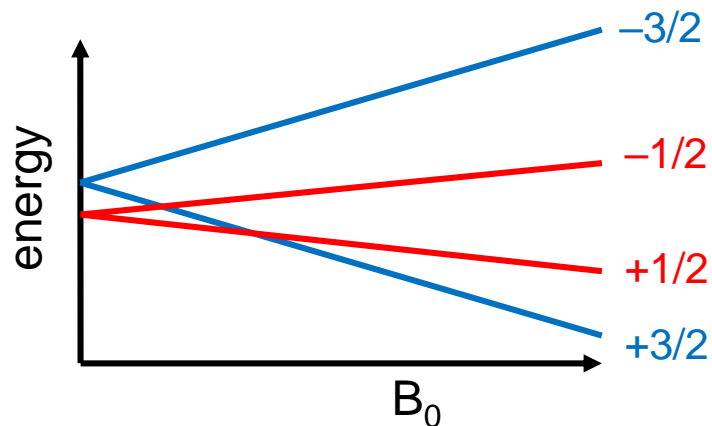
20.0 T, 4.0 MHz wide



14.1 T, 6.8 MHz wide



- ...and by no-field measurements (Nuclear Quadrupolar Resonance)



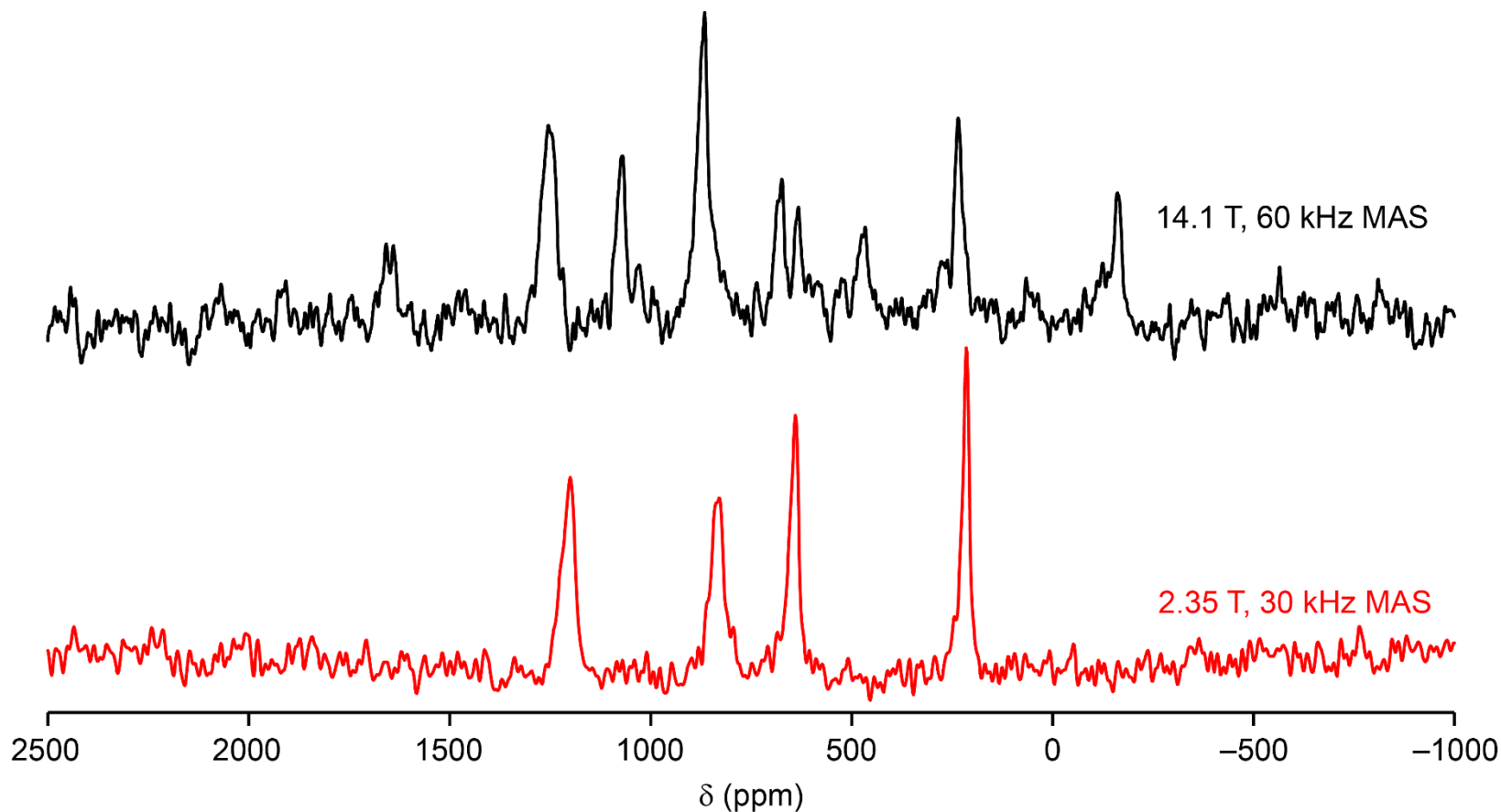
part 2 summary

- the resolution gain at high field is absolutely essential for quadrupolar nuclei (~75% of the periodic table)
- for $I = 1/2$ nuclei, the resolution gain is not so noticeable in solids, where most of the line broadening comes from inhomogeneity and particle size effects
- for understanding spectra involving anything other than the isotropic chemical shift, high field can be very useful!

3. Some Caveats

very large shift anisotropies

- high field is actually terrible for very large shift anisotropies such as the paramagnetic interaction...



other practical considerations

- many routine experiments have been found to be WORSE at high field
- ^1H - ^{13}C cross polarisation is the “workhorse” ^{13}C experiment
 - larger anisotropies (affects spin lock)
 - typically lower maximum power (affects decoupling)
- ^{89}Y MAS should be much better at 20.0 T than 14.1 T
 - sensitivity is actually comparable
 - CSA measurements are worse (very low rf)
- amplifiers aren't as well developed for high-field machines as for < 800 MHz
 - probably not an issue when you're not aiming for 100 kHz rf

final conclusions

- high field offers huge benefits to NMR in terms of sensitivity and resolution
- for solids, the biggest advantages are normally for quadrupolar nuclei
- also helpful for...
 - insensitive/dilute spins
 - complicated J multiplets
 - disordered materials
 - quadrupolar/dipolar cross terms
 - and more!
- many routine experiments or samples aren't actually worth taking to higher field at the moment...
- ...which leaves more time for the interesting experiments!

acknowledgements

- Sharon Ashbrook
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- Michele Chierotti (Turin)
- Laurent le Polles (Rennes)
- Dinu Iuga (Warwick)
- Greg Rees (Warwick)
- John Hanna (Warwick)



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