NATIONAL HIGH MAGNETIC FIELD LABORATORY

High Field NMR of Quadrupolar Nuclei Using 36 T SCH Magnet

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DNP/PANACEA workshop, Tallahassee, Aug 25, 2025

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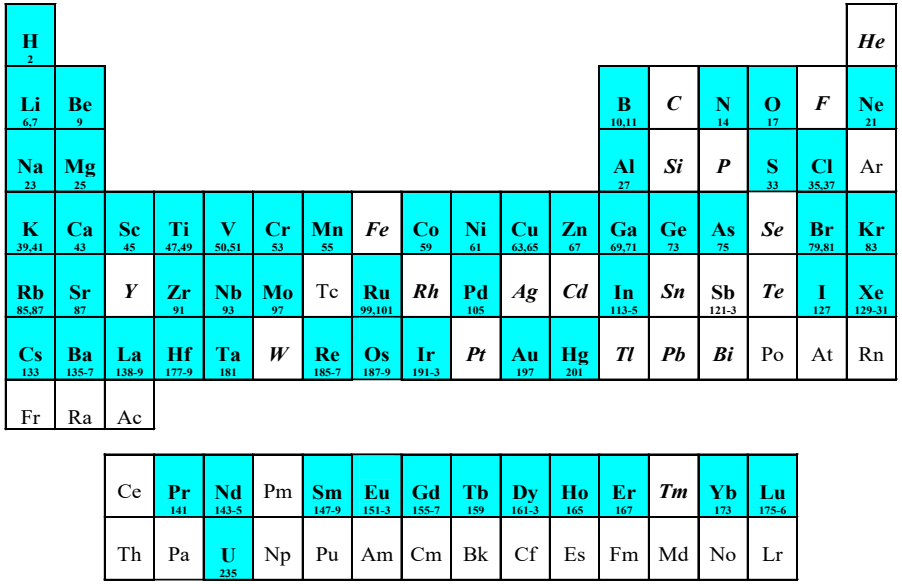
Overviews

- **Why we do solid-state NMR of quadrupolar nuclei using SCH**
- **Basics of quadrupolar NMR**
- **Commonly used experiments (MQMAS, QCPMG)**
- **Examples from crystalline to disordered, solids to solution**

NMR of Spin>1/2 Quadrupolar Nuclei



Only I=1/2 nuclear spins

Quadrupolar nuclei (I>1/2)

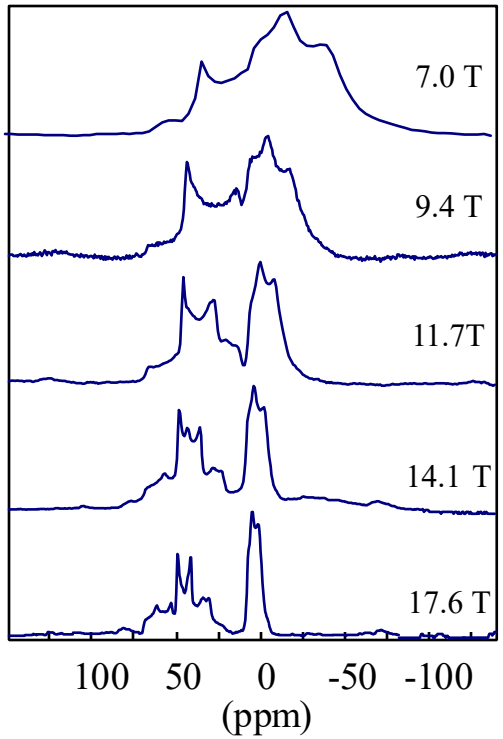
- I=1/2 ^{1}H, ^{19}F, ^{29}Si, ^{31}P…
- I=1 ^{2}H, ^{6}Li, ^{14}N.
- I=3/2 ^{7}Li, ^{11}B, ^{23}Na, $^{69,71}Ga$…
- I=5/2 ^{17}O, ^{27}Al…

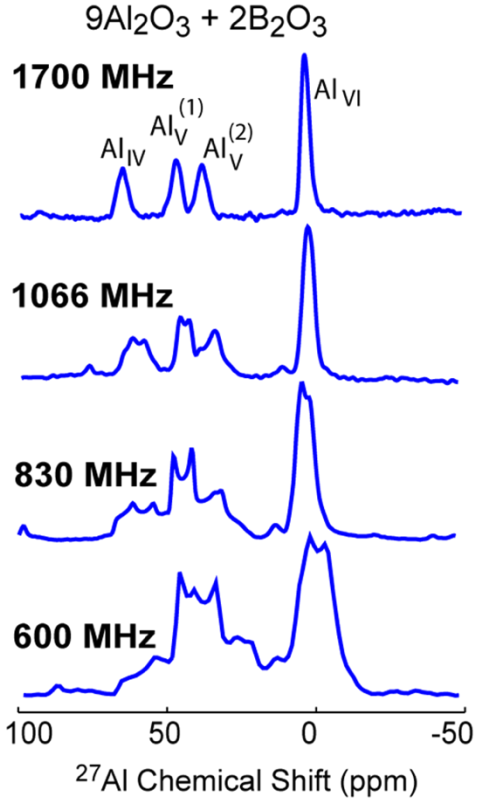
- Low-γ ^{25}Mg, ^{33}S, ^{39}K, ^{43}Ca, $^{45,47}Ti$, ^{67}Zn, ^{73}Ge, $^{95,97}Mo$, $^{99,101}Ru$

- Glasses, zeolites, catalysts
- Meso-macro-porous materials
- Nano materials
- Battery materials
- Metal-organic-framework

"Solid state NMR measurements in inorganic materials stand to benefit enormously from the availability of high field magnets". – COHMAG p.36

High Field Quadrupolar Nuclei NMR:
Resolution and Sensitivity





NMR signal

Boltzman factor B_0

Frequency B_0

Line narrowing B_0

Resolved spinning sideband

~20 gain in sensitivity

~400 in time

Gan, Z.; Gor'kov, P.; Cross, T. A.; Samoson, A.; Massiot, D. *J. Am. Chem. Soc*. **2002**, *124*, 5634–5635, https://doi.org/10.1021/ja025849p

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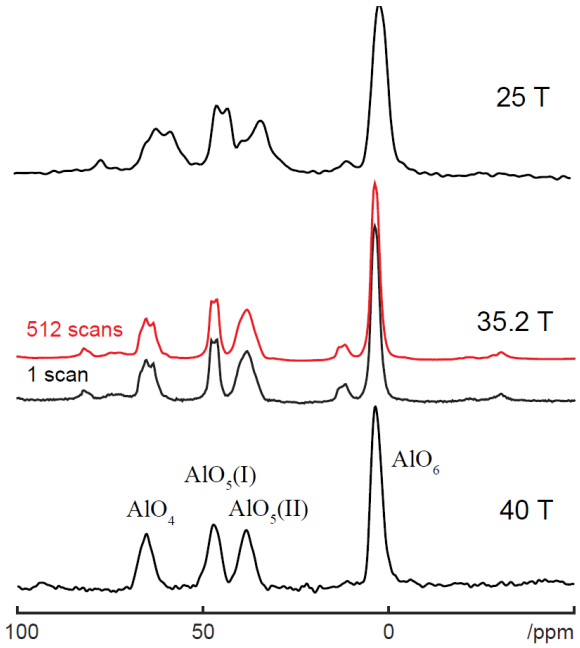
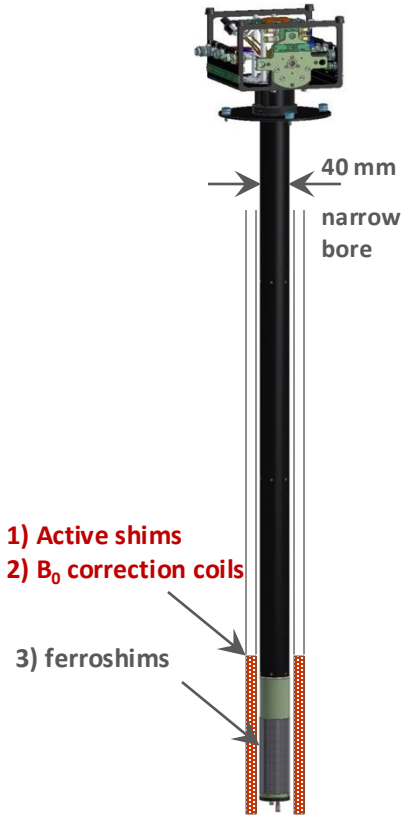
36T Series Connected Hybrid (SCH)

Made to field November 2016, commissioned December 2017





Overviews

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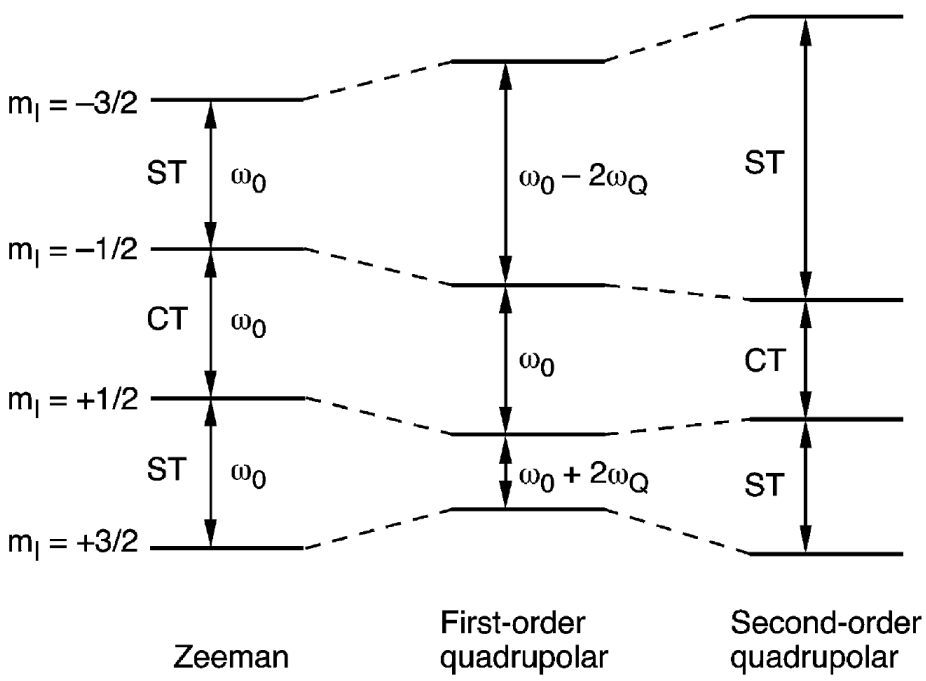
Quadrupolar Nuclei (e.g. spin = 3/2)



- For half-integer Q-nuclei, the central transition (CT) is free of 1st-order effect, broadened only by 2nd-order effect (ω_Q^2/ω_0).
- Satellite transitions (ST) are shifted by large 1st (ω_Q) plus 2nd-order effects.
- 2nd-order effect contains ranks 0, 2, 4 terms, therefore cannot be completely narrowed by magic-angle spinning (MAS).
- For integer Q-nuclei (^{14}N, spin = 1), single-quantum transition are shifted by 1st and 2nd-order effects.

Quadrupolar broadening and MAS

With sample rotation around β_R

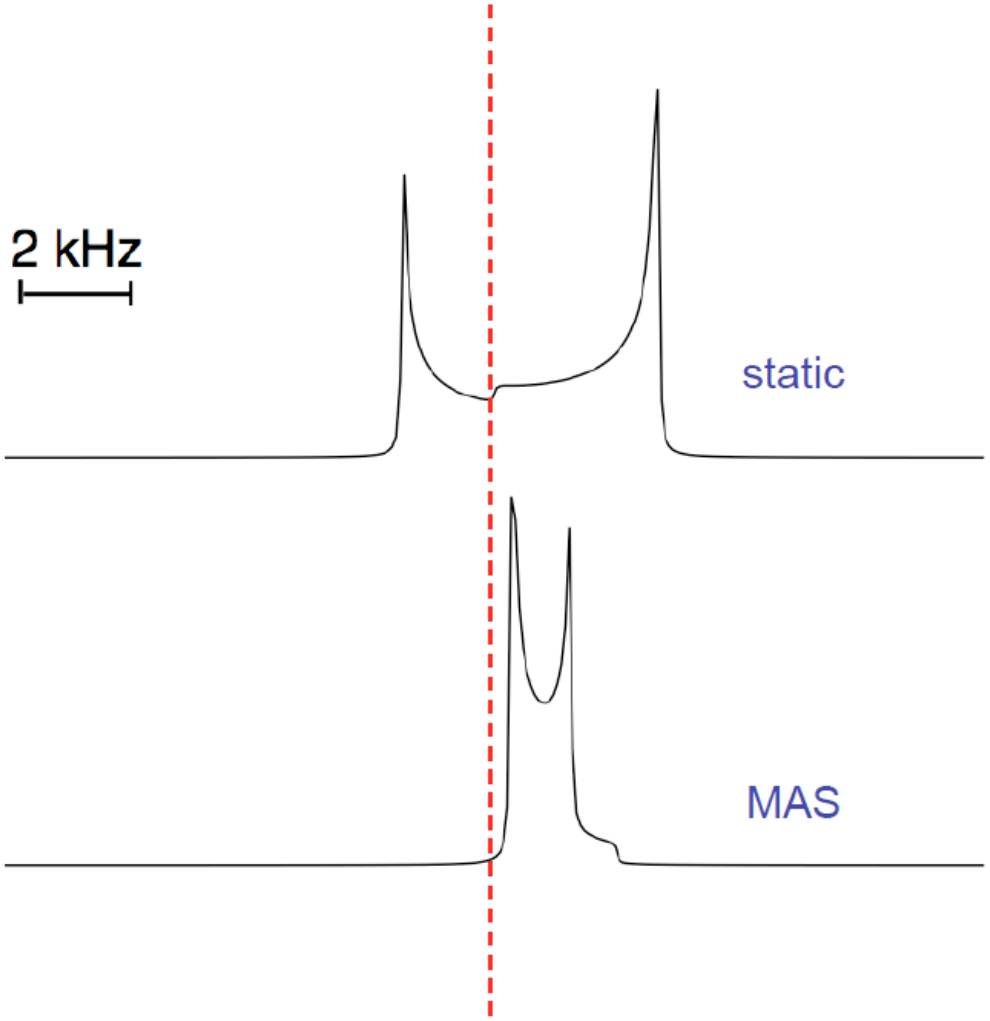
$$\omega \propto \frac{\left(\omega_Q^{PAS}\right)^2}{\omega_0}\left[A + B\, d^2_{00}\left(\beta_R\right)\, d^2_{00}\left(\beta\right) + C\, d^4_{00}\left(\beta_R\right)\, d^4_{00}\left(\beta\right)\right]$$

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

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

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

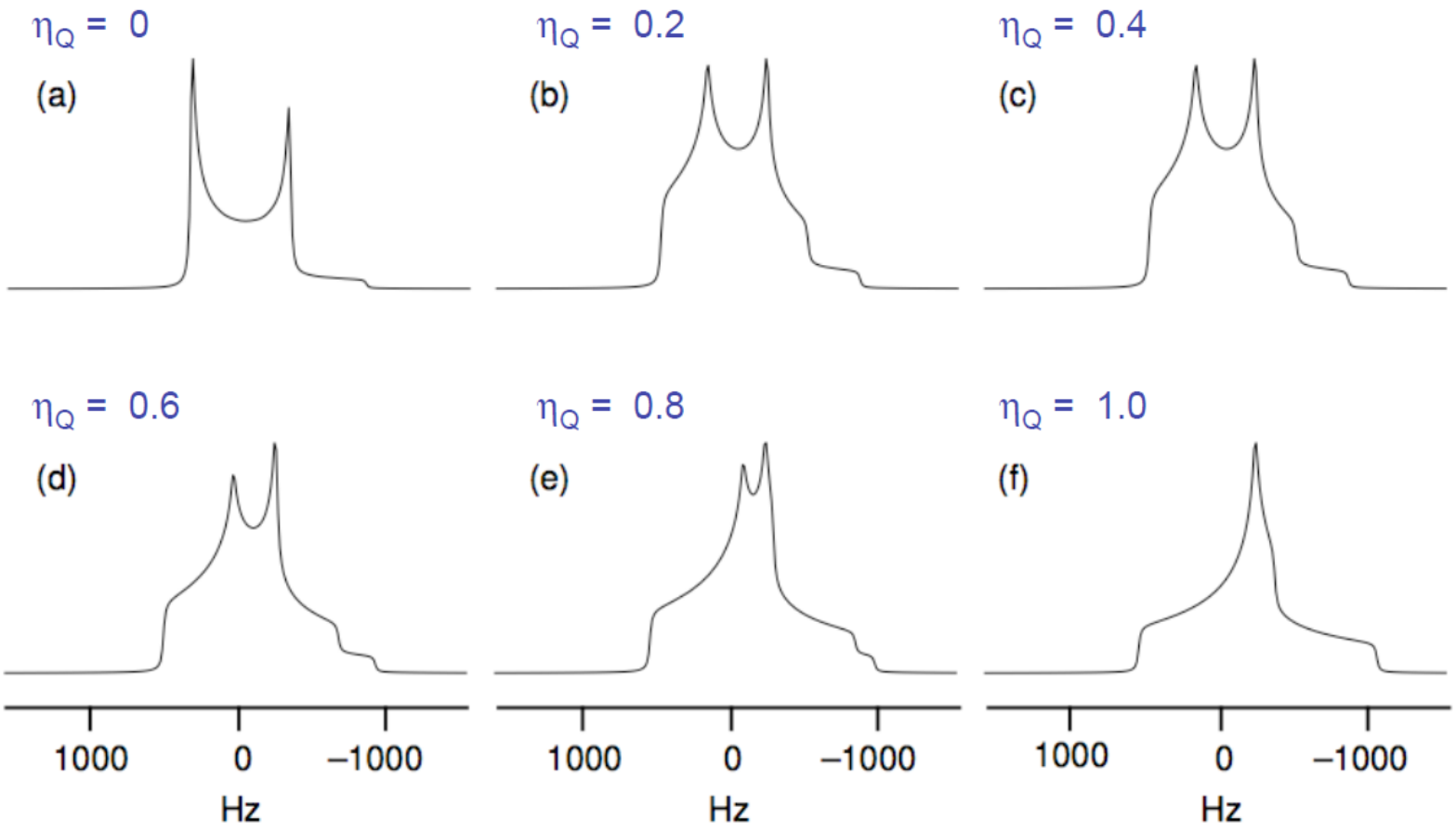
Quadrupolar broadening and MAS



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

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

Spin I = 3/2 MAS lineshapes



rf irradiation to a multi-level system

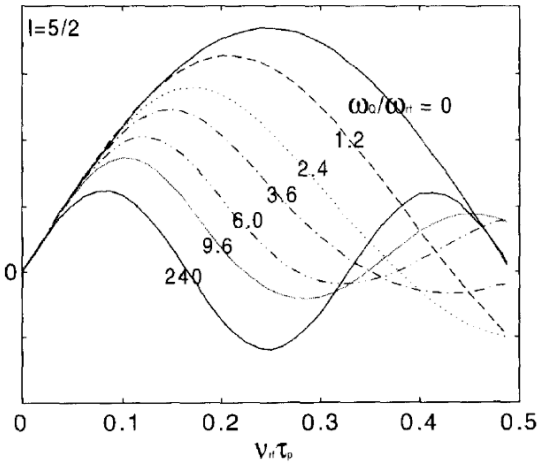
➢ **Spin dynamics under *rf* is complicated for the multiple-level systems especially in the presence of level crossing under magic-angle spinning. As the result, spin lock, cross polarization and decoupling become non-trivial and complicated as compared to spin-1/2.**

$\omega_1 >> \omega_Q^{PAS}$

"hard" pulse

"non-selective" pulse

nutation at rate of ω_1



$\omega_1 << \omega_Q^{PAS}$

"soft" pulse

"selective" pulse

CT nutation rate $(I + 1/2)\ \omega_1$

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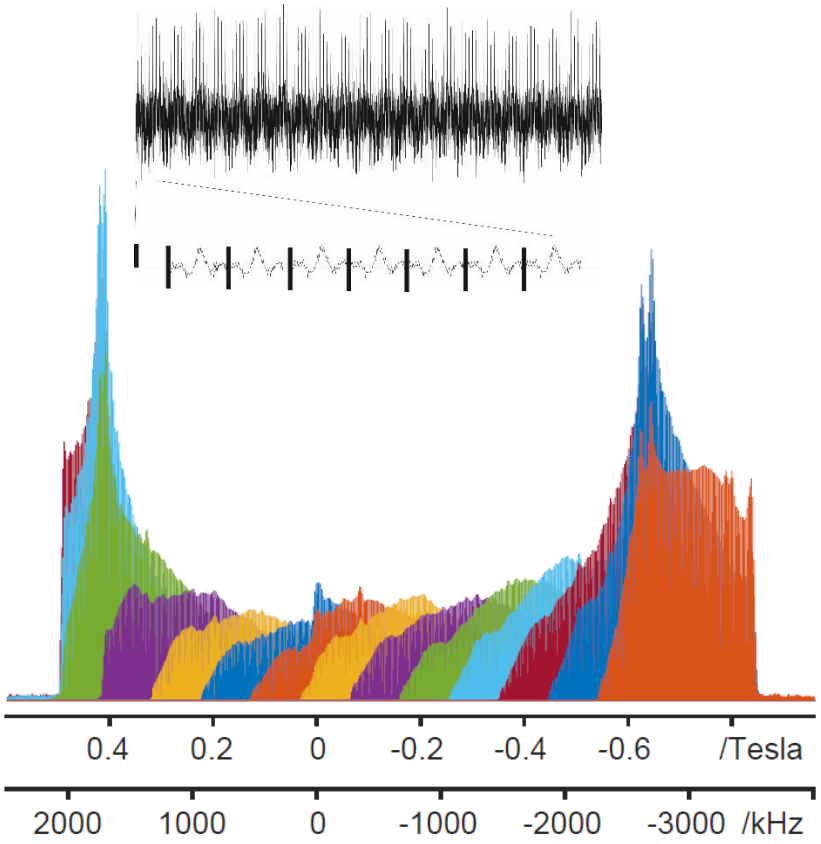
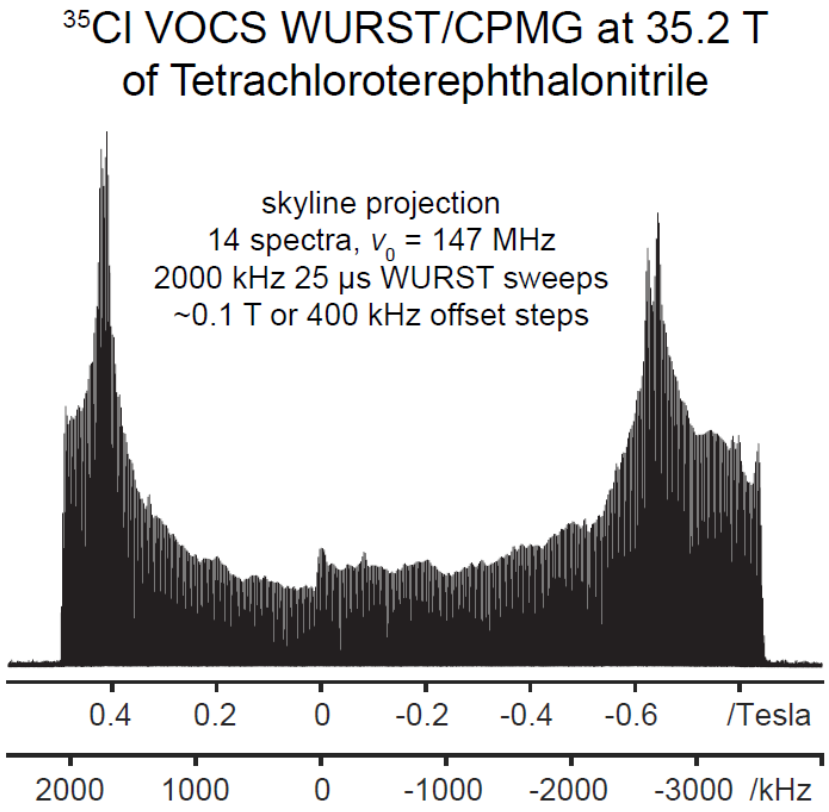
Ultrawide QCPMG by stepping field



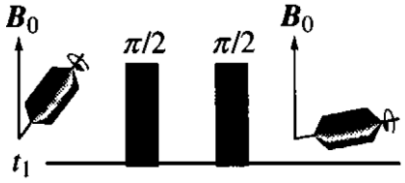


D. Bryce U. Ottawa

Methods to obtain isotropic spectra

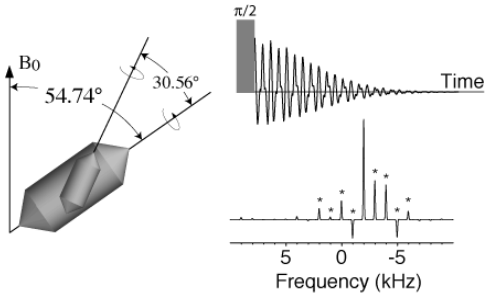
Dynamic Angle Spinning (DAS)

Llor, Virlet (1988), Pines et al (1990)



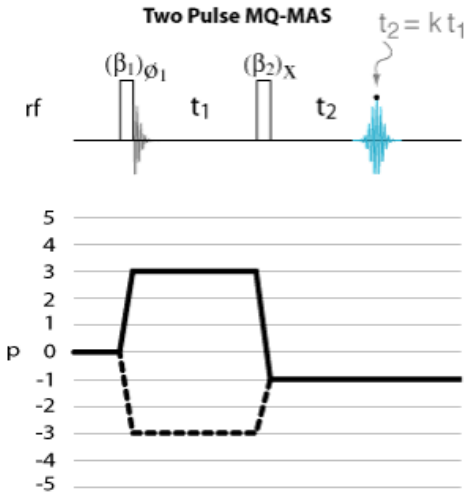
Double Rotation (DOR)

Samoson, Lippmaa, Pines (1990)



Multiple-Quantum MAS (MQMAS)

Frydman and Harwood (1995)



Satellite-Transition MAS (STMAS)

Gan (2000)

Remove Quadrupolar Broadening

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

Constant depending upon C_Q, I and ω_0

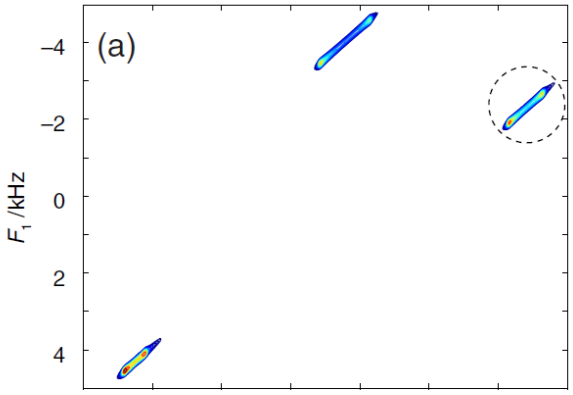
Isotropic shift

Second-rank anisotropic

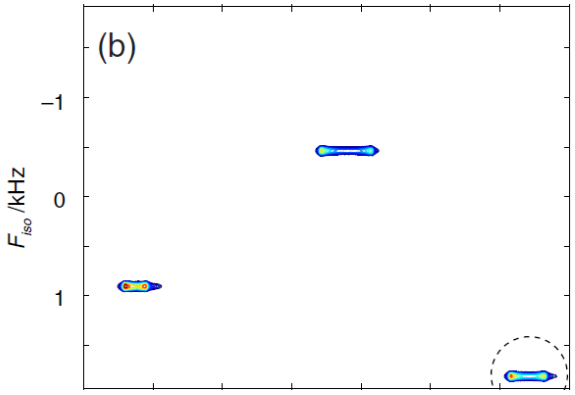
Fourth-rank anisotropic

Spin	Transition	A	B	C
I = 3/2	C T	−2/5	−8/7	54/35
	S T	4/5	4/7	−48/35
I = 5/2	C T	−16/15	−64/21	144/35
	ST_1	2/5	−4/3	6/5
	ST_2	56/15	80/21	−264/35

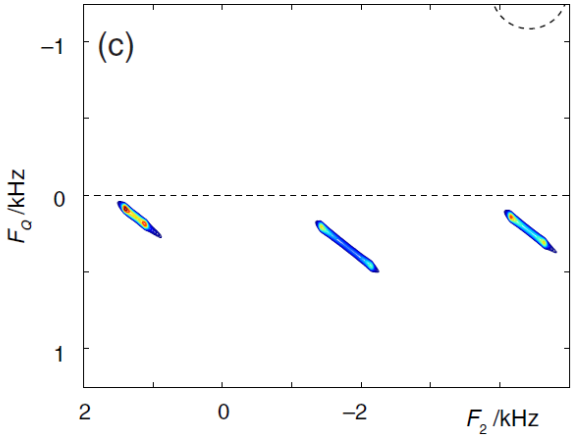
Shearing and representations



Original



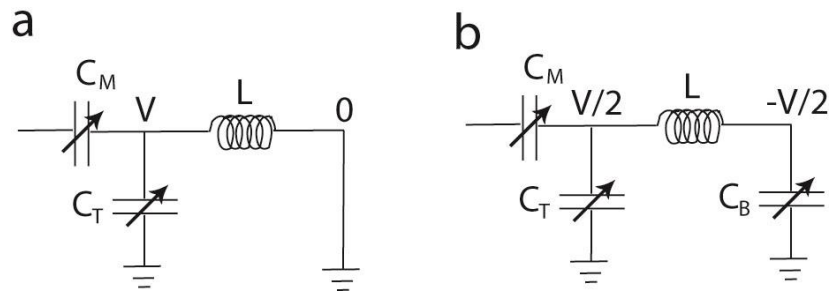
Isotropic



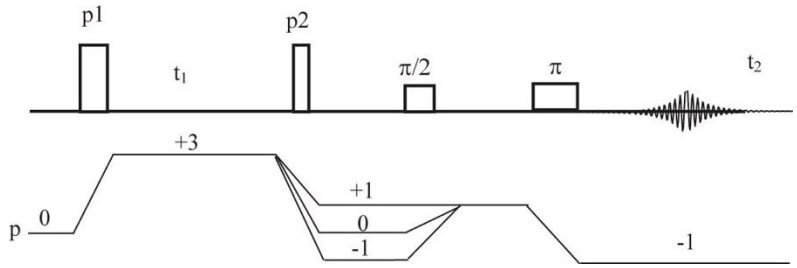
Q-representaion

Strong *rf* field

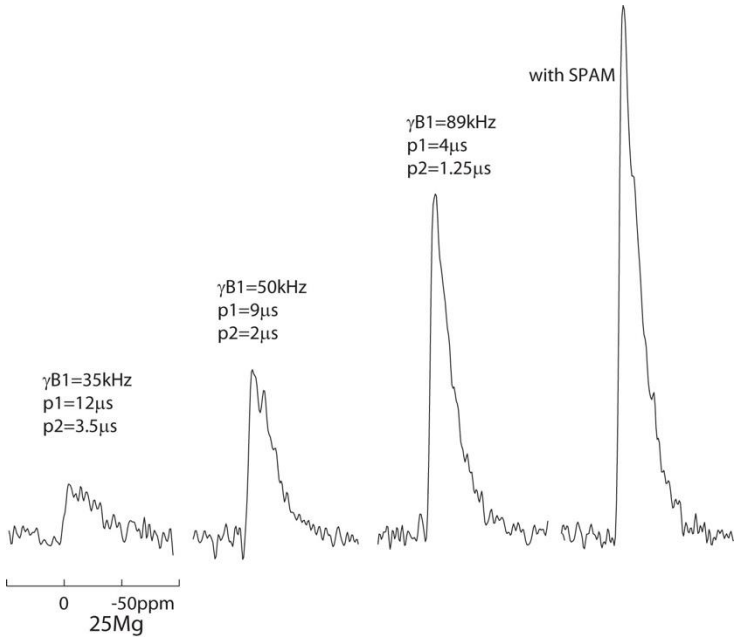
Balanced probe circuit delivers high B_1 field



Efficient SPAM-MQMAS pulse sequence

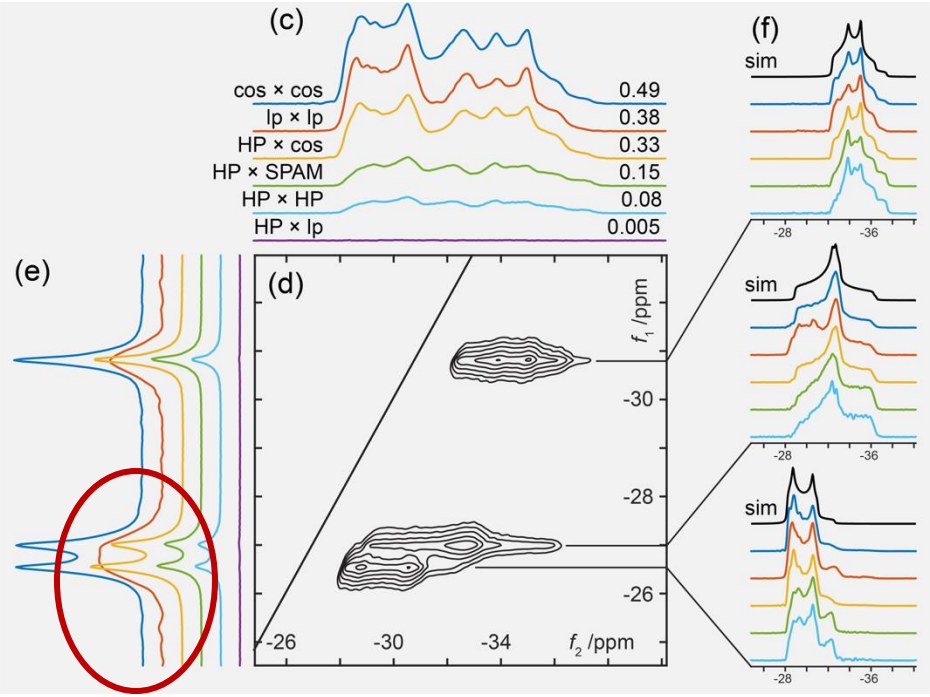


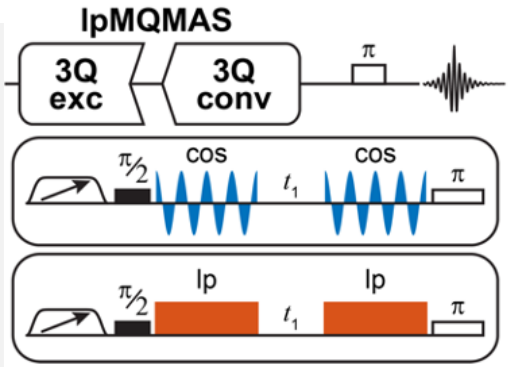
Sensitivity enhancement with high B_0, B_1 and SPAM-MQMAS for low-γ nuclei

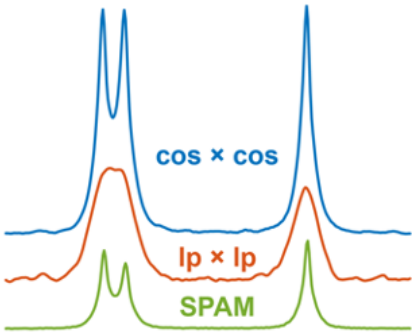


J. Magn. Reson. **200**, (2009) 2-5

Single-frequency vs Double-frequency cosine-lpMQMAS







The most efficient MQMAS sequence to date.

Hung, I.; Gan, Z. *J. Magn. Reson.*, 2021,*328*, 106994 https://doi.org/10.1016/j.jmr.2021.106994

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^{39}K MQMAS

from small to macro molecules

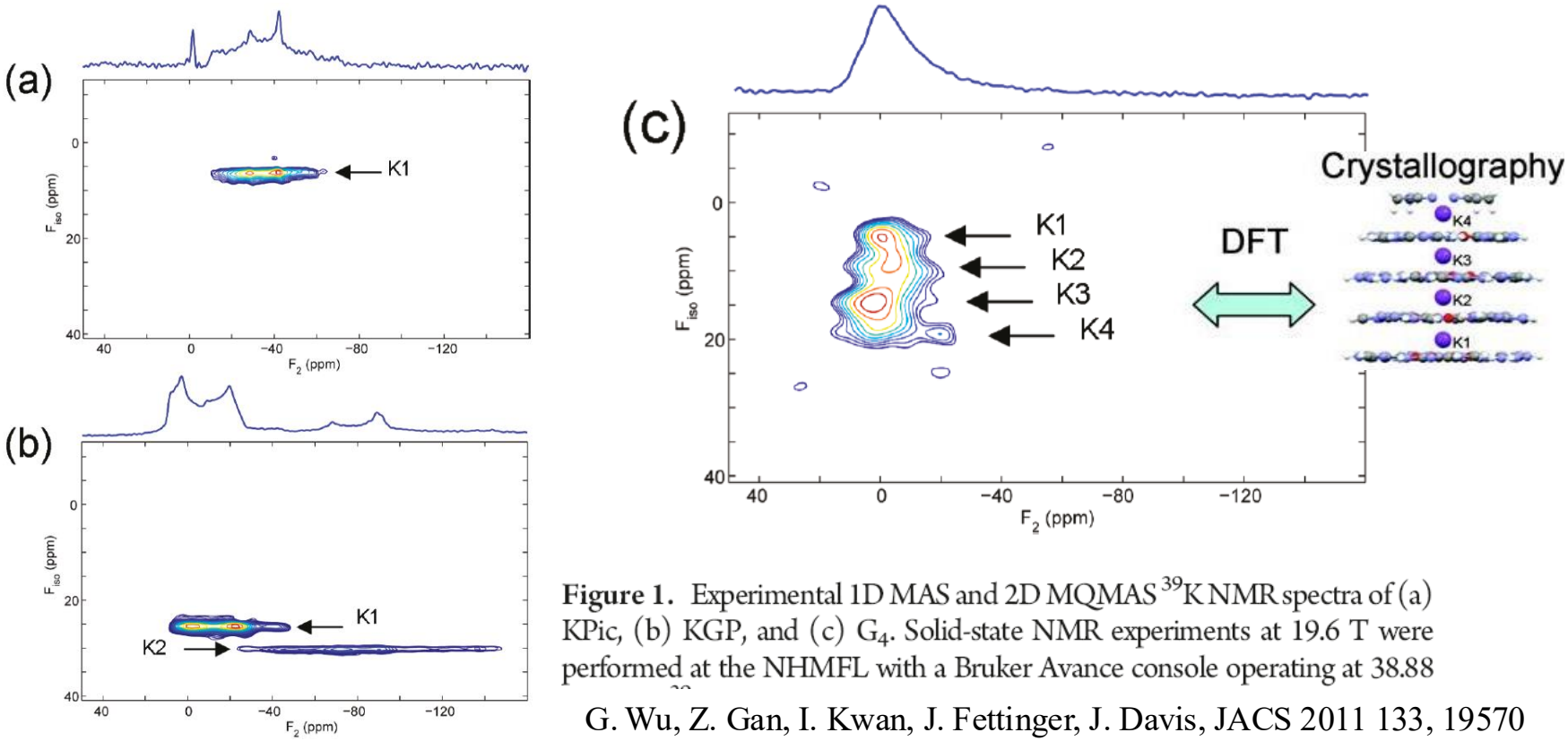


Figure 1. Experimental 1D MAS and 2D MQMAS ^{39}K NMR spectra of (a) KPic, (b) KGP, and (c) G_4. Solid-state NMR experiments at 19.6 T were performed at the NHMFL with a Bruker Avance console operating at 38.88

G. Wu, Z. Gan, I. Kwan, J. Fettinger, J. Davis, JACS 2011 133, 19570

^{25}Mg MQMAS of Layered Double Hydroxide

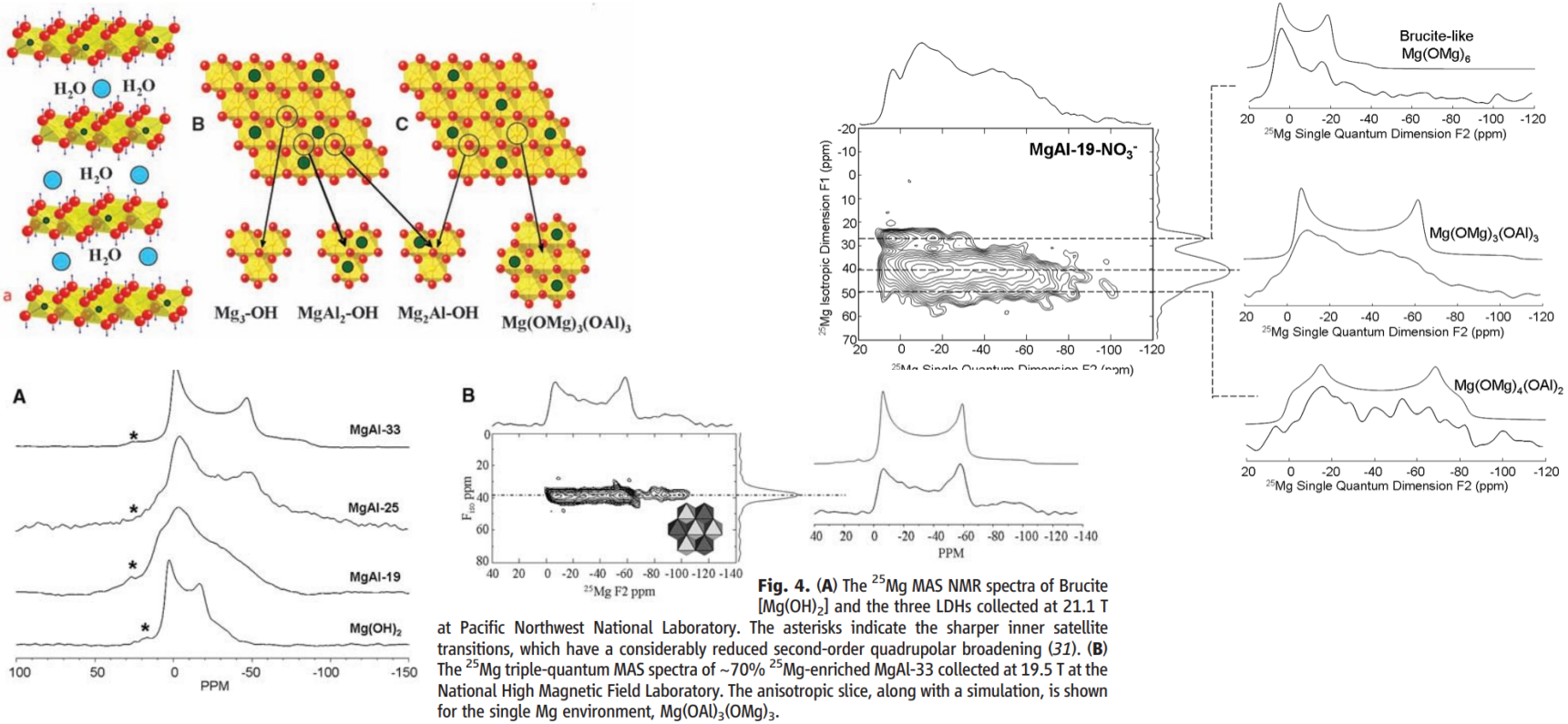
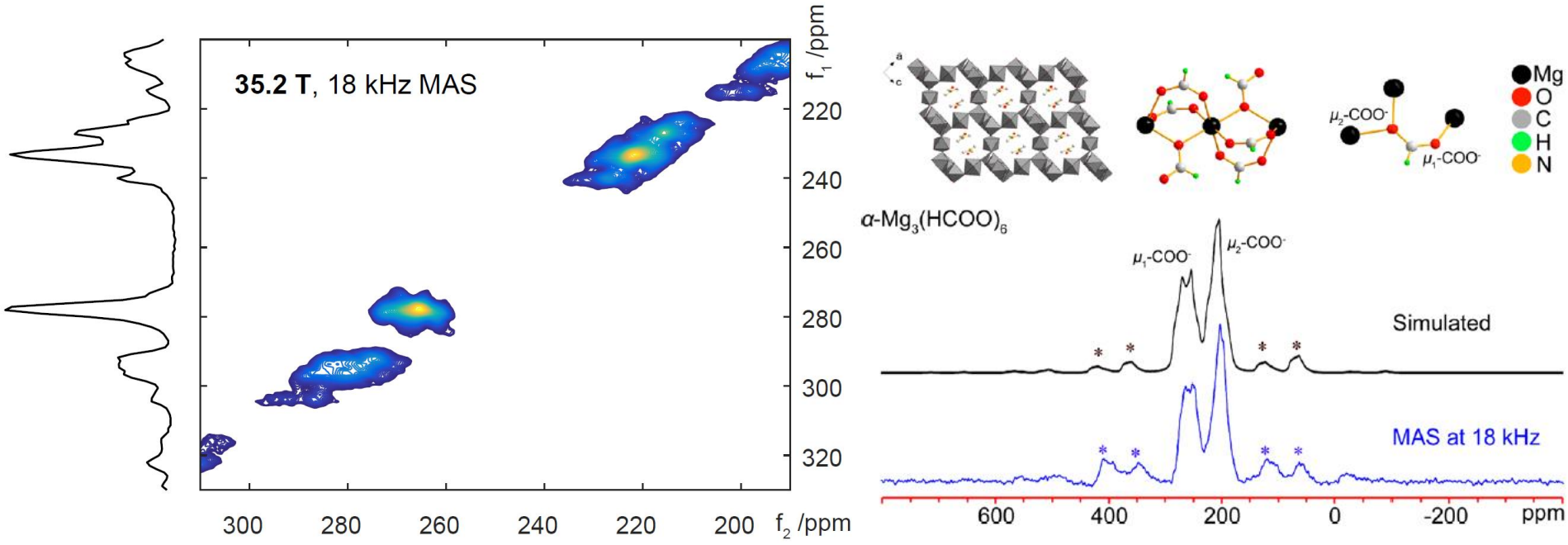


Fig. 4. (**A**) The ^{25}Mg MAS NMR spectra of Brucite [$Mg(OH)_2$] and the three LDHs collected at 21.1 T at Pacific Northwest National Laboratory. The asterisks indicate the sharper inner satellite transitions, which have a considerably reduced second-order quadrupolar broadening (*31*). (**B**) The ^{25}Mg triple-quantum MAS spectra of ~70% ^{25}Mg-enriched MgAl-33 collected at 19.5 T at the National High Magnetic Field Laboratory. The anisotropic slice, along with a simulation, is shown for the single Mg environment, $Mg(OAl)_3(OMg)_3$.

P. Sideris, U. Nielsen, Z. Gan, C. Grey *Science*, 321 (2008) 113
https://doi.org/10.1126/science.aaz0251

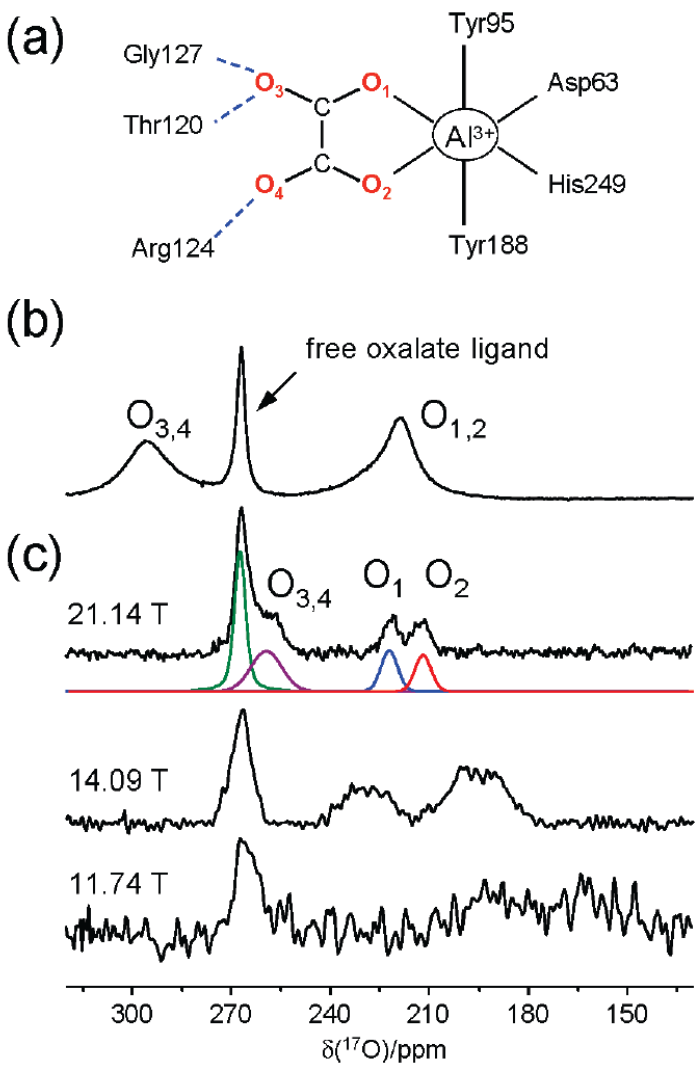
^{17}O NMR of Metal-Organic Frameworks

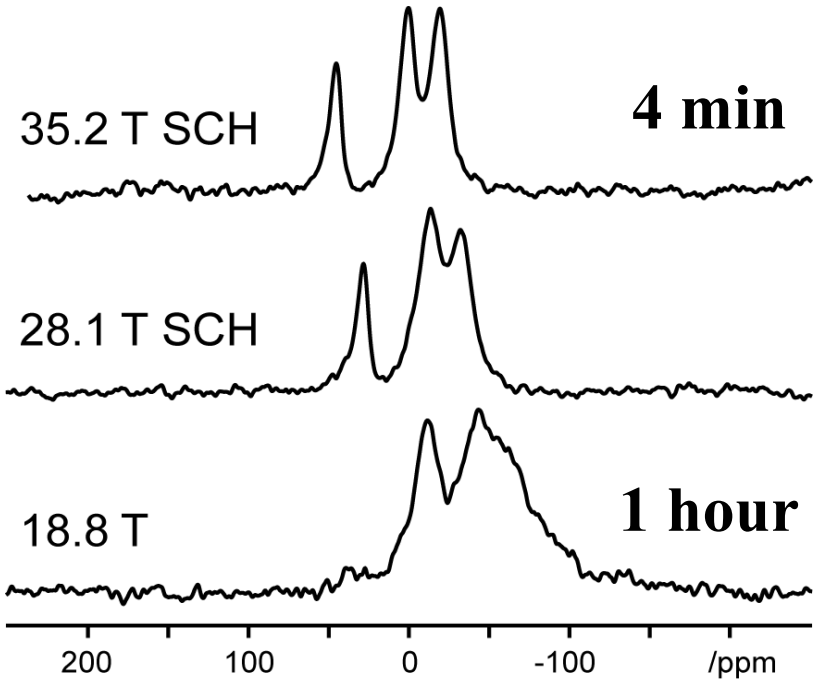


The high-field and MQMAS reveal more ^{17}O peaks in α-$Mg_3(HCOO)_6$ MOF that were not observed at 900MHz

Y. Huang U. West Ontario

^{17}O QCT Solution NMR

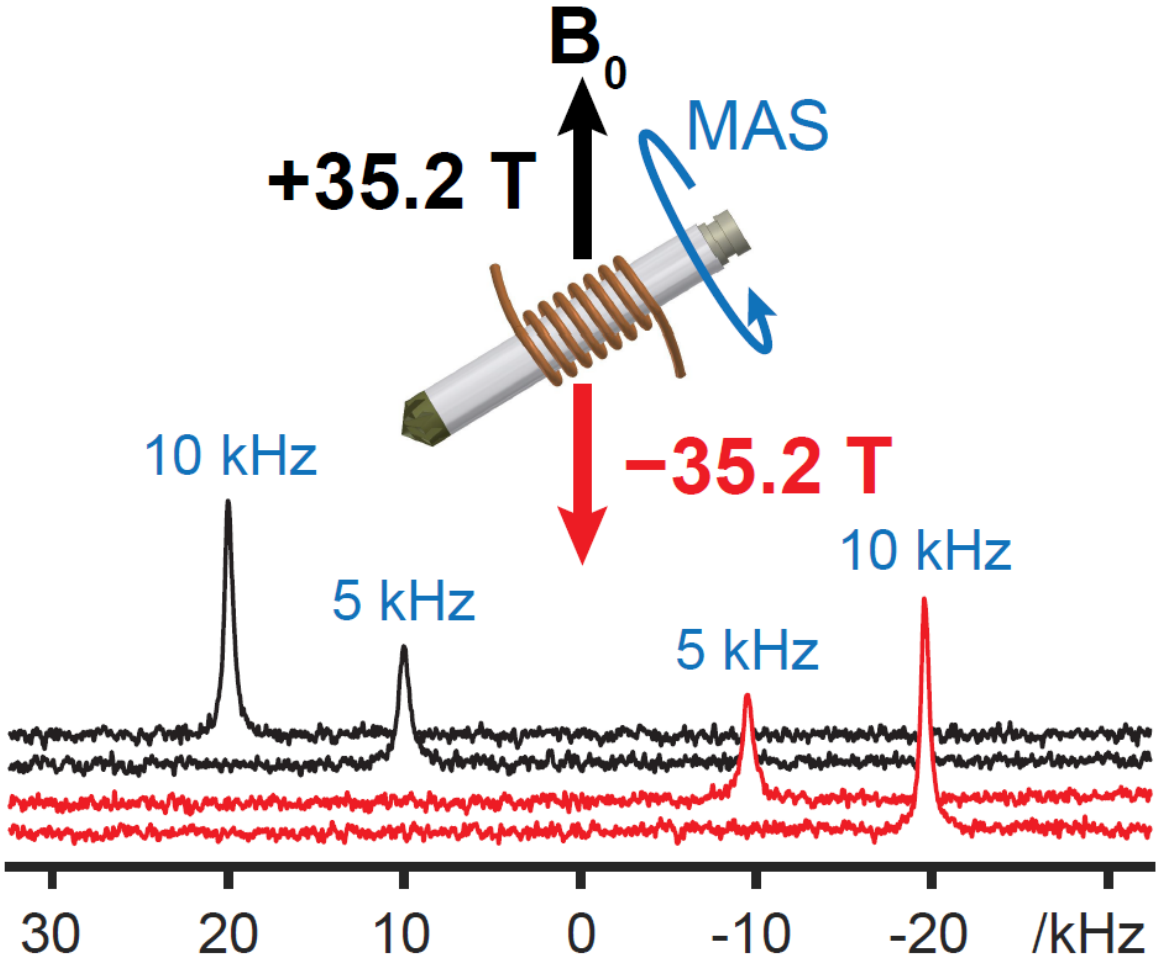




^{17}O quadrupolar central-transition (QCT) spectra of oxalate/chicken ovotransferrin and [3,5,6-^{17}O]-D-glucose in glycerol.

Gang Wu, Queen's Univ.

Field Reversal of ^{14}N Overtone MAS NMR



^{14}N overtone NMR is direct observation of DQ transition at twice of ^{14}N Larmor frequency. OT peak under MAS shifts at twice of the spinning frequency in a direction depending on the orientation between spinning axis and magnetic field direction.