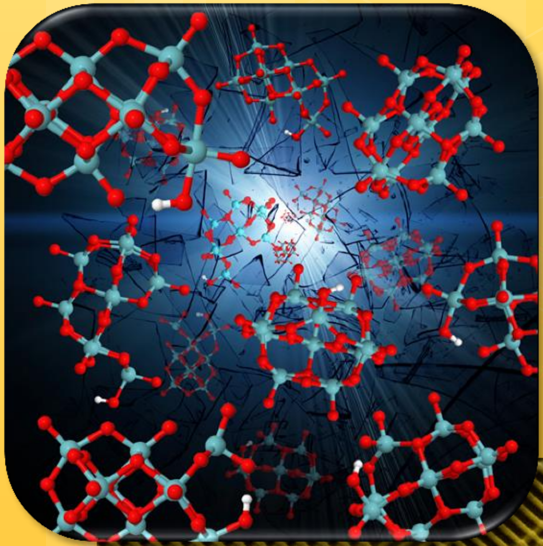
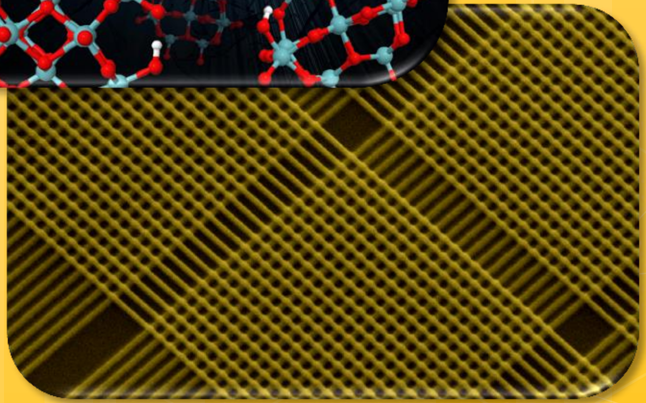
11/17/2015

CSMC



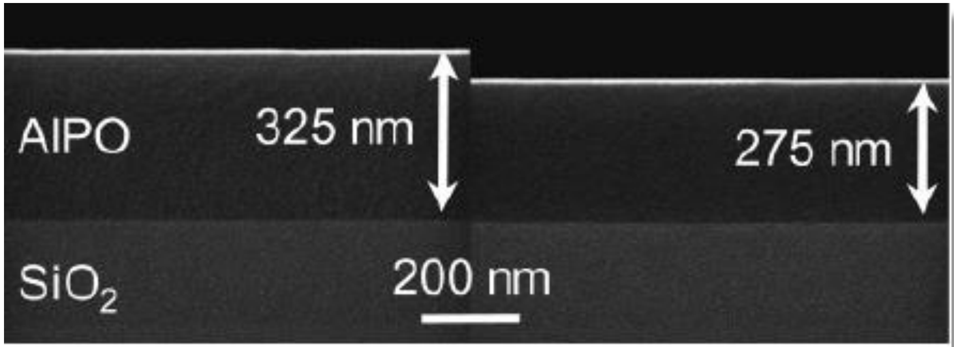


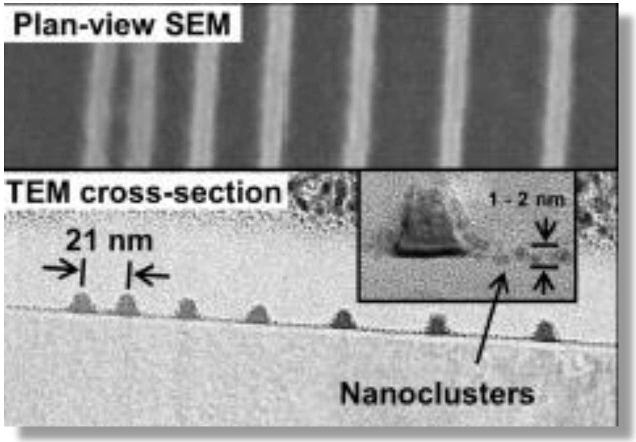
NMR of Half-Integer Quadrupolar Nuclei in Materials: Opportunities at Ultrahigh Fields

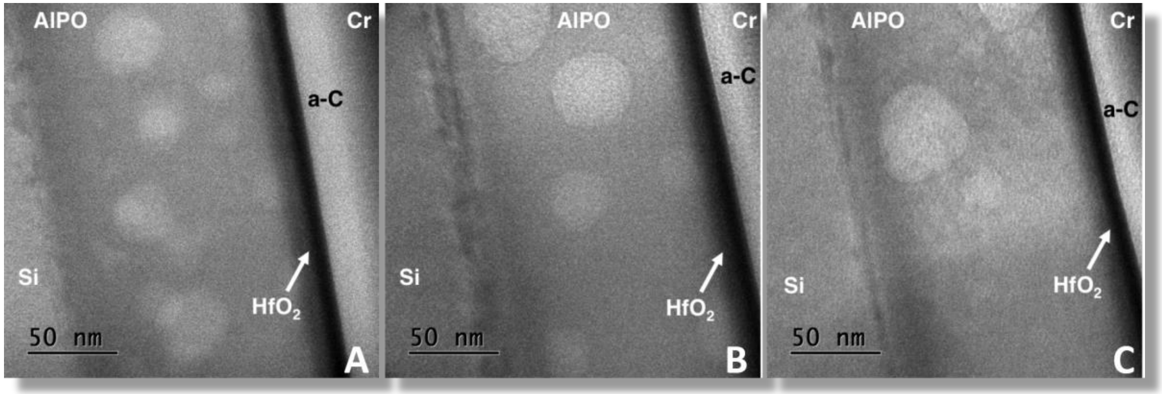
Sophia Hayes

Washington University in St. Louis

Modern Materials Science Needs New Tools for Structure Determination





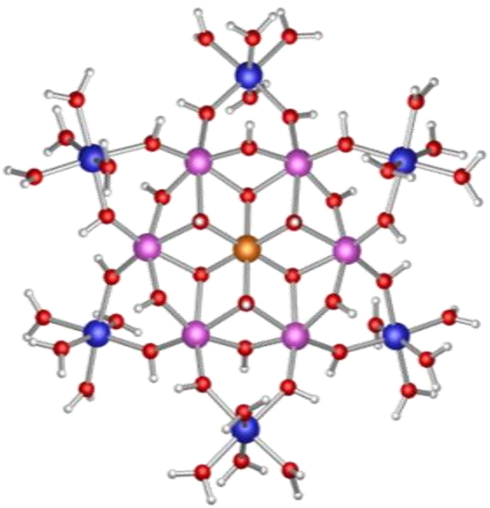


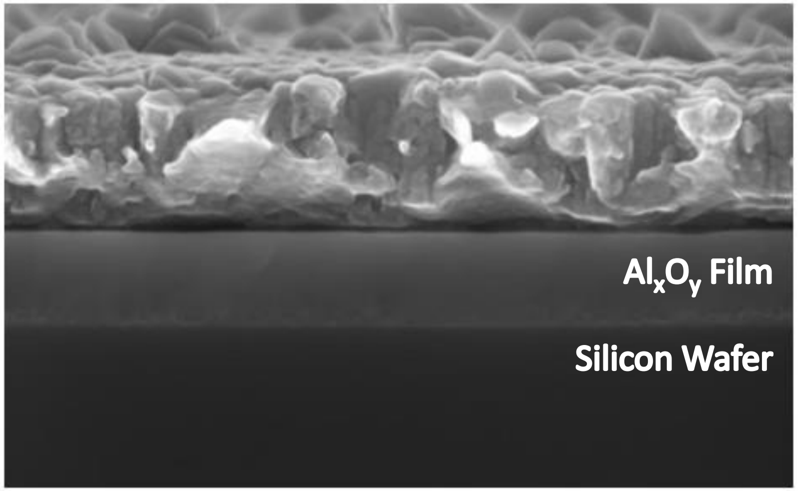
Real Materials – Apple Displays

iMac
with Retina 5K display

Oxide TFT
"..we took cues from the groundbreaking oxide thin film transistor …"

Patent
"Embodiments described herein may provide an oxide thin-film transistor (TFT) … the semiconductor layer may include or incorporate other materials, for example, zinc oxide (**ZnO**), indium oxide (**InO**), gallium oxide (**GaO**), tin oxide (**SnO_2**), indium gallium oxide (**IGO**), indium zinc oxide (**IZO**), zinc tin oxide (**ZTO**), and indium zinc tin oxide (**IZTO**) among others."



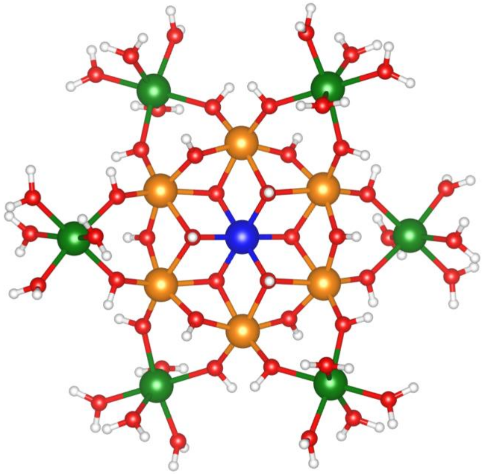


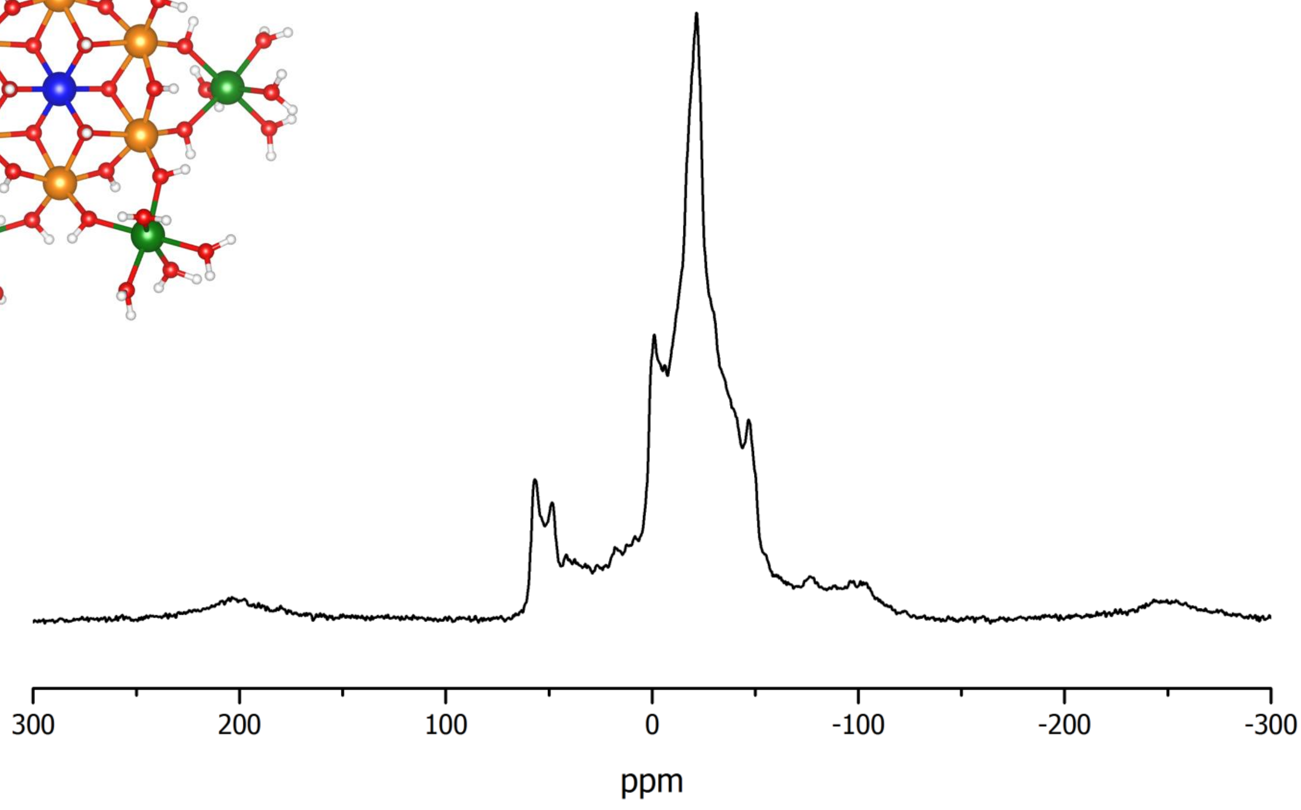
A TALE OF TWO MATERIALS: A CASE STUDY IN QUADRUPOLAR NMR

(REAL MATERIALS)

Solid-state NMR

$[Ga_{13}(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$ "Ga_{13}"

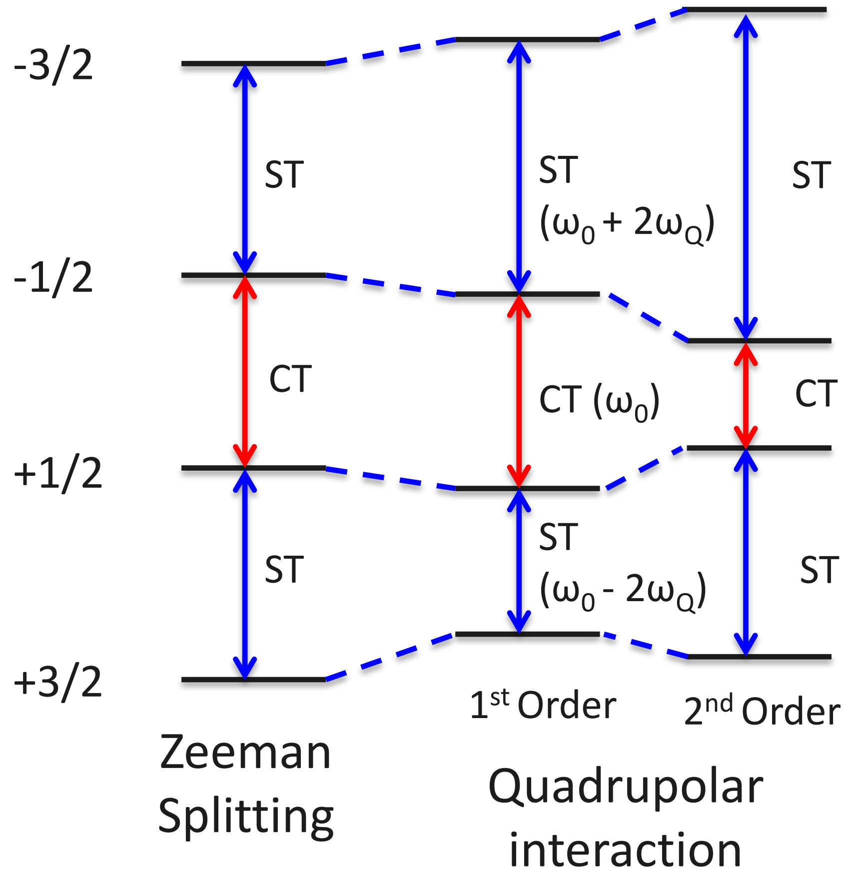




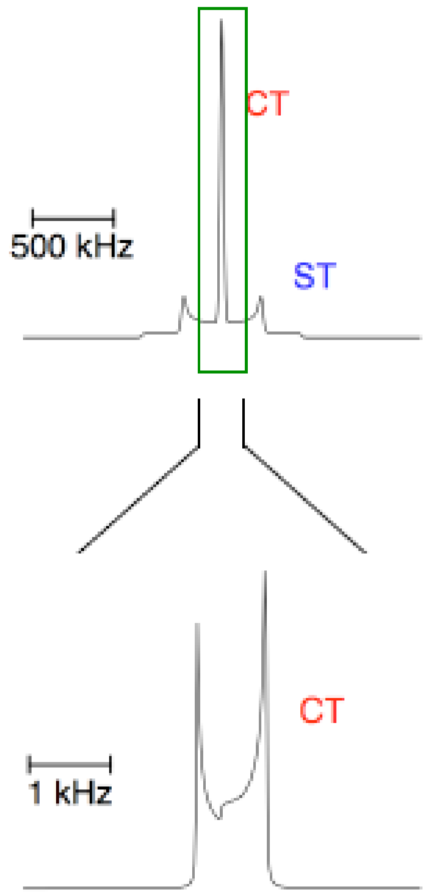
(^{71}Ga MAS, 21T Ga_{13})

Ma, Z.L. et al. "Solid State ^{69}Ga and ^{71}Ga NMR study of the nanoscale inorganic cluster $[Ga_{13}(\mu^3\text{-}OH)_6(\mu^{2}\text{-}OH)_{18}(H_2O)_{24}](NO_3)^{15}$" Chem. Mater. **2014**, *26*, 4978-4983.

Quadrupolar Nuclei



Spin 3/2



Quadrupolar Nuclei

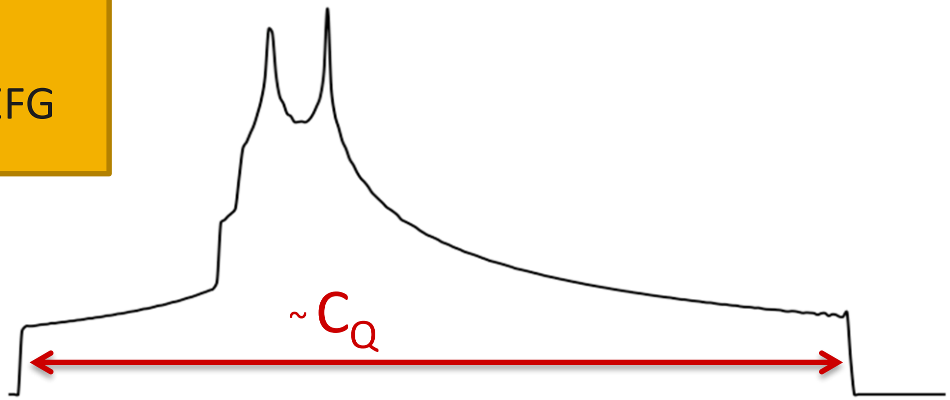
central transition lineshapes under MAS

$$C_Q = \frac{(e^2 qQ)}{h} = \frac{eQ(V_{ZZ})}{h}$$

Quadrupole Coupling Constant:

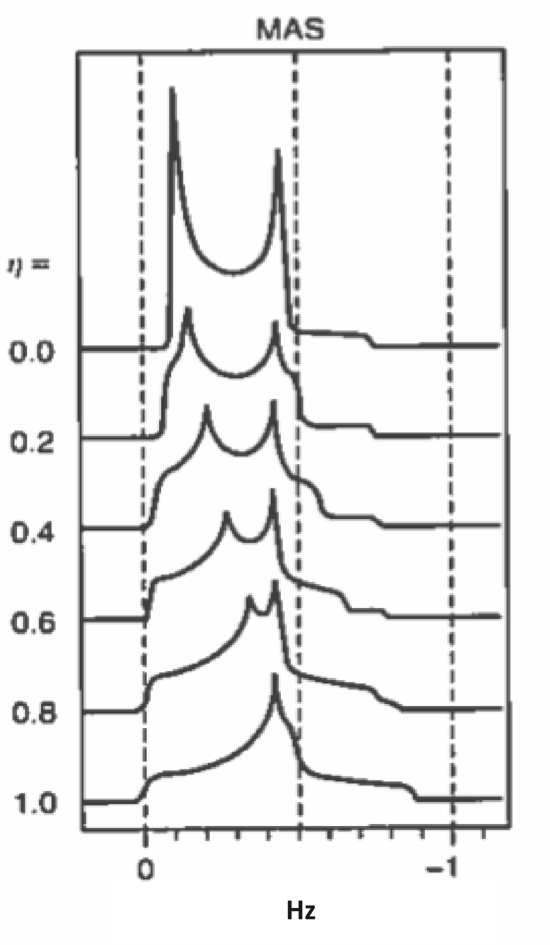
eQ = nuclear quadrupolar moment

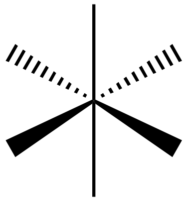
V_{zz} = largest principle component of EFG



Quadrupolar Nuclei

central transition lineshapes under MAS





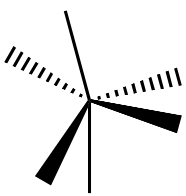
$\eta_q = 0.0$

Quadrupole Parameter:

$\eta_q = (V_{xx}-V_{yy})/V_{zz}$ $\quad 0 < \eta_q < 1$

$|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$

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



$\eta_q = 1.0$

Why is field dependence important?

Second-order quadrupolar broadening

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

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

Constant depending upon C_Q, I and ω_0

Isotropic shift

Second-rank anisotropic

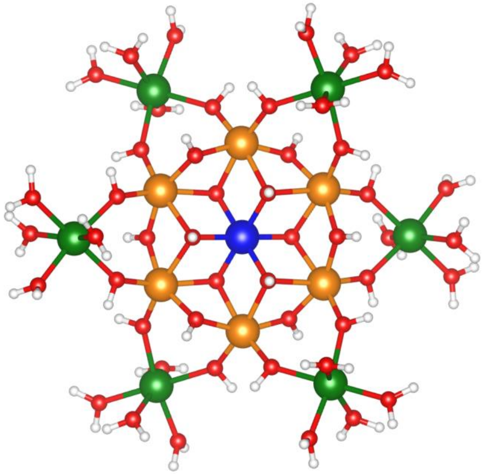
Fourth-rank anisotropic

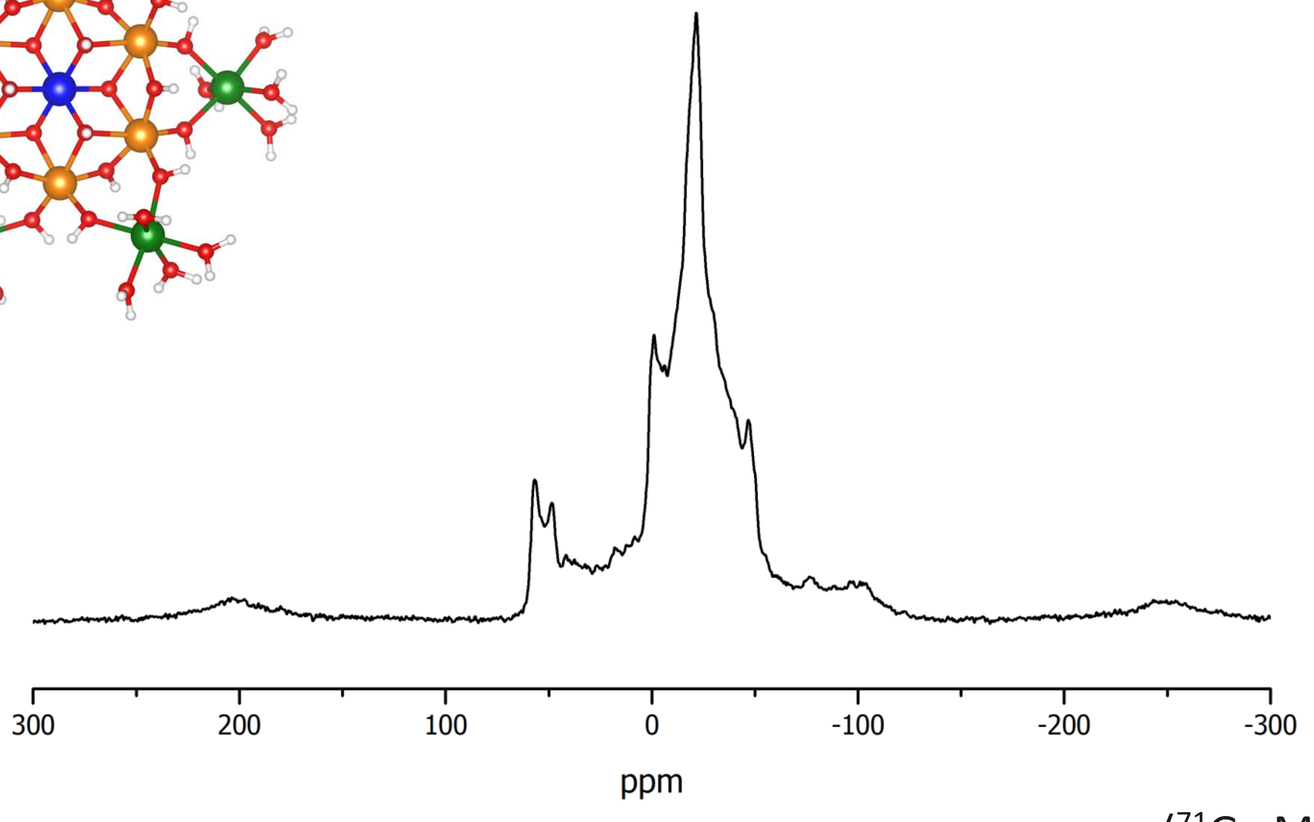
$$d^2_{00}(\theta) \propto (3\cos^2\theta - 1)$$

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

Solid-state NMR

$[Ga_{13}(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$ "Ga_{13}"





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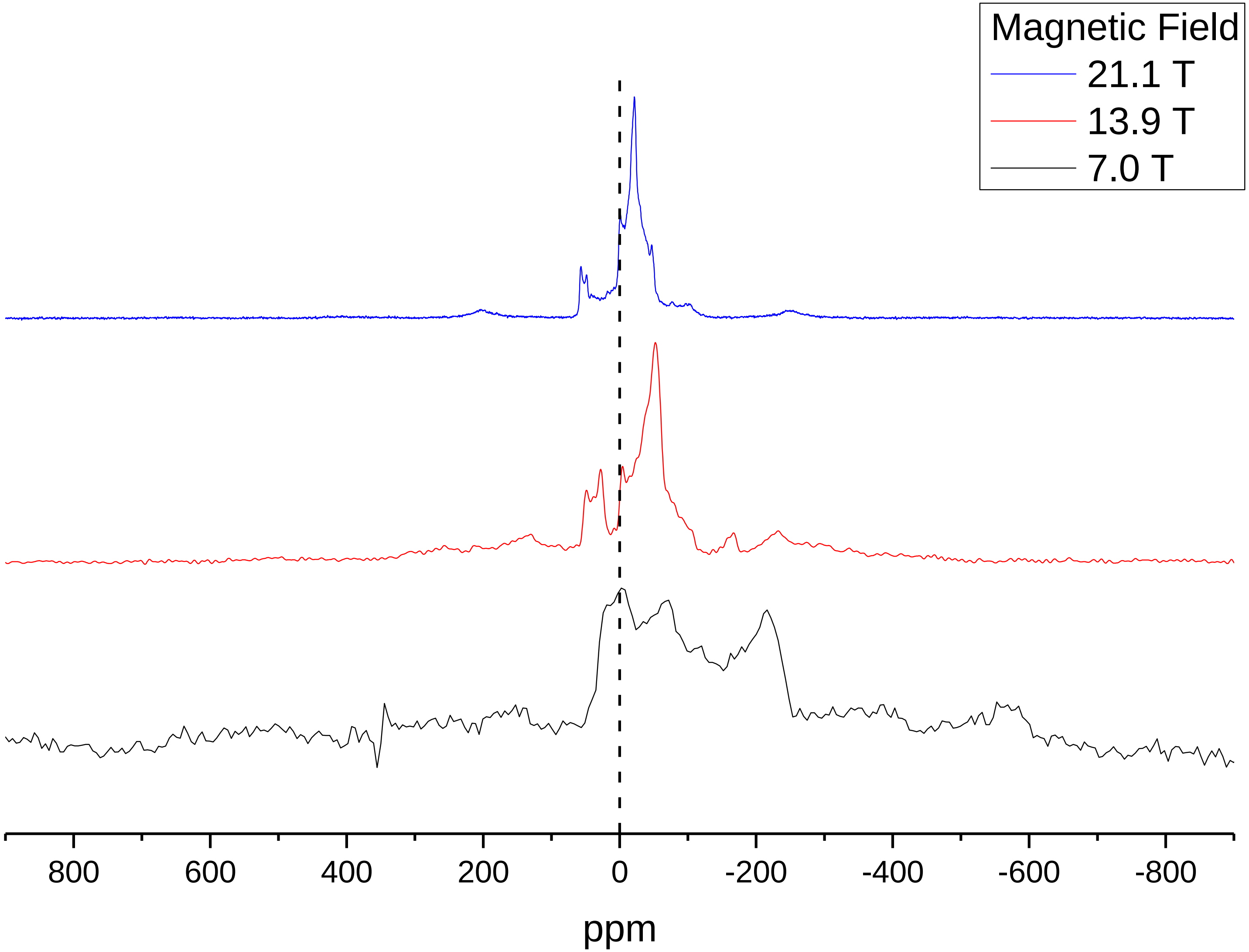
^{71}Ga NMR - Ga_{13} Field Dependence



J. Am. Chem. Soc. **1995**, *117*, 12779−12787 12779

Multiple-Quantum Magic-Angle Spinning NMR: A New Method for the Study of Quadrupolar Nuclei in Solids

Ales Medek, John S. Harwood, and Lucio Frydman*

Department of Chemistry (M/C 111), University of Illinois at Chicago, 845 W. Taylor Street, Chicago, Illinois 60607-7061

Received August 24, 1995®

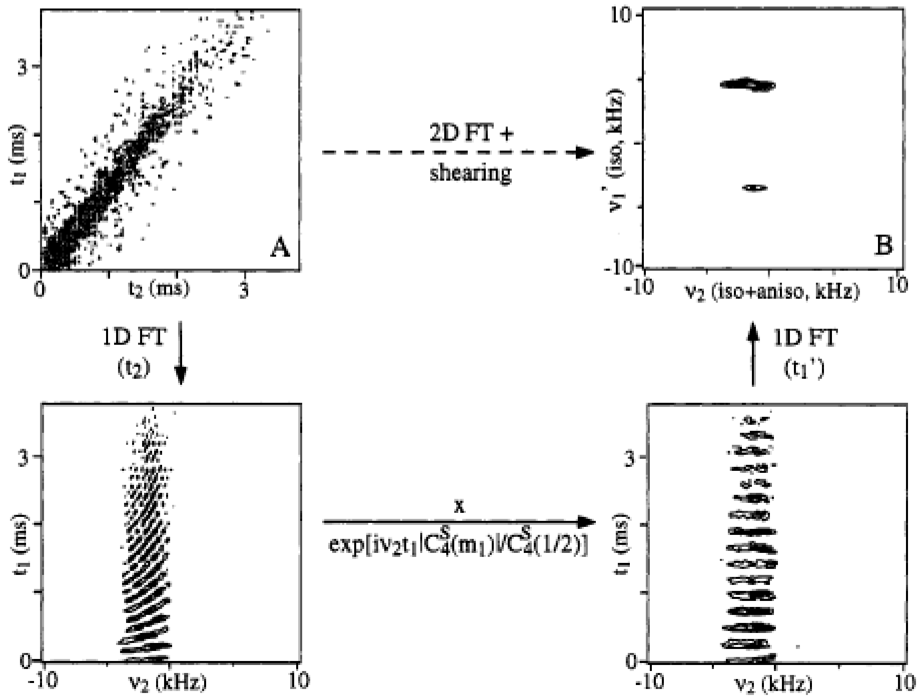


Figure 2. Two-dimensional ^{23}Na MQMAS NMR of $Na_2C_2O_4$. (A) Triple-/single-quantum correlation experiment obtained using the two-pulse sequence shown in Scheme 1. (B) Isotropic/anisotropic correlation spectrum obtained by Fourier transformation and shearing of the time-domain data; the peak at $\nu'_1 \approx 4$ kHz corresponds to the main resonance, the peak at $\nu'_1 = -3$ kHz is a spinning sideband. The shearing was implemented as illustrated in the bottom part of the figure, via a first-order t_1-dependent phase correction along ν_2.

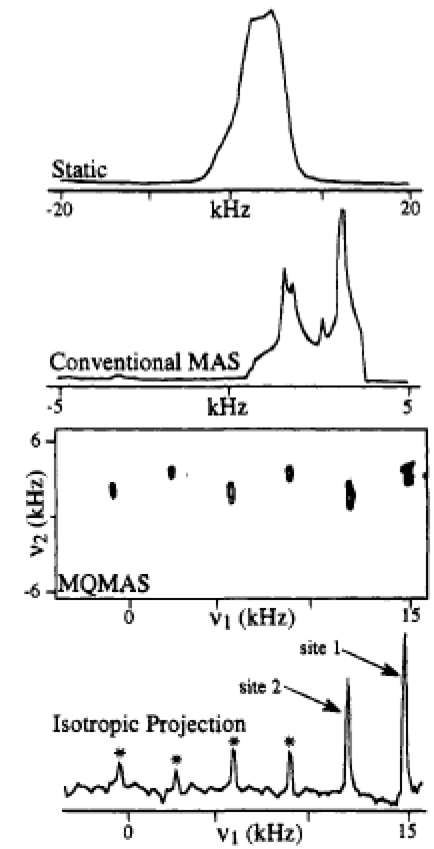


Figure 10. ^{23}Na NMR spectra of polycrystalline Na_2TeO_3 acquired under different conditions. The bottom trace corresponds to the projection of the sheared 2D MQMAS spectrum onto the isotropic (ν_1) axis; asterisks correspond to spinning sidebands.

Chemical Physics Letters 468 (2009) 330–335

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Acquisition of ultra-wideline NMR spectra from quadrupolar nuclei by frequency stepped WURST–QCPMG

Luke A. O'Dell, Aaron J. Rossini, Robert W. Schurko *

Department of Chemistry and Biochemistry, University of Windsor, 401 Sunset Avenue, Windsor, Ontario, Canada, N9B 3P4

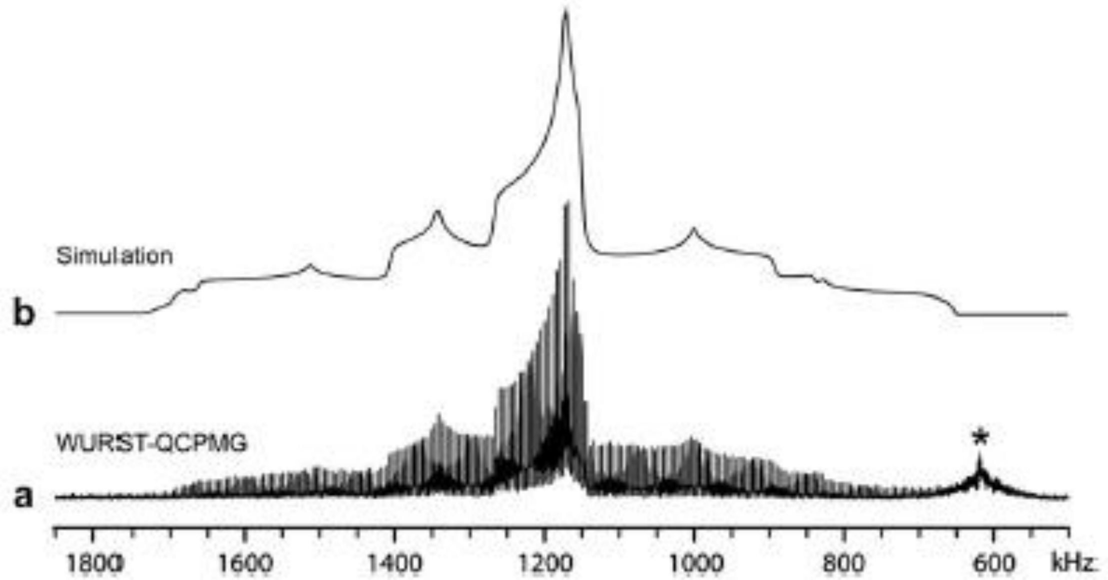

Fig. 4. (a) ^{59}Co spectrum of $Co(acac)_3$ obtained using undecoupled WURST–QCPMG. The full manifold of satellite transition is excited. The asterisk denotes FM radio interference. (b) Simulation made using parameters previously reported [28].

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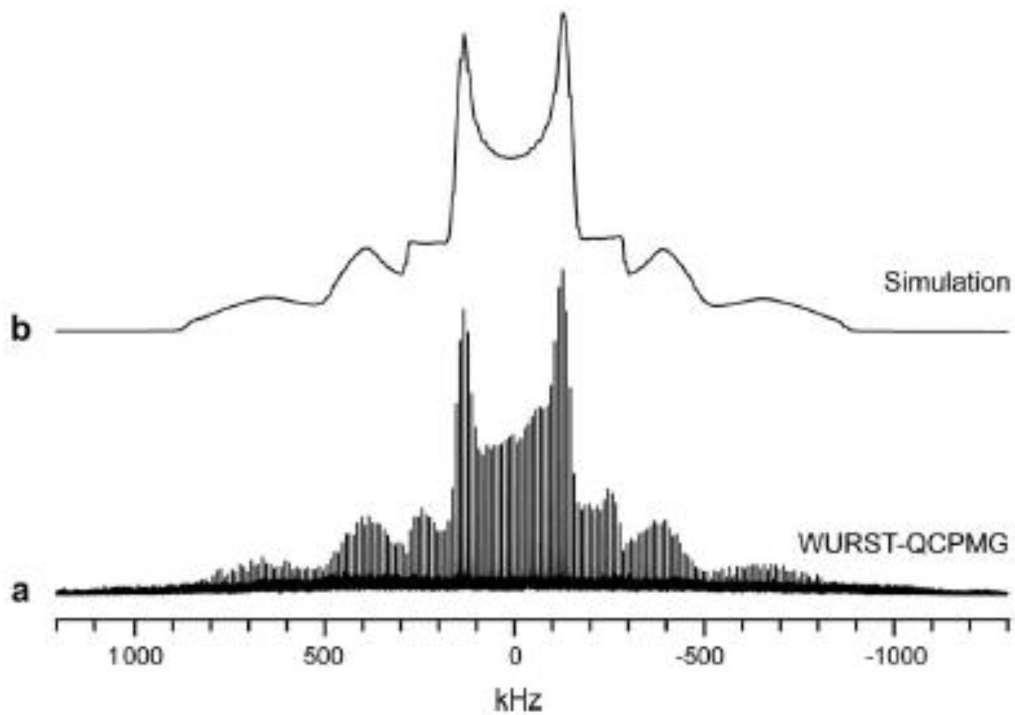
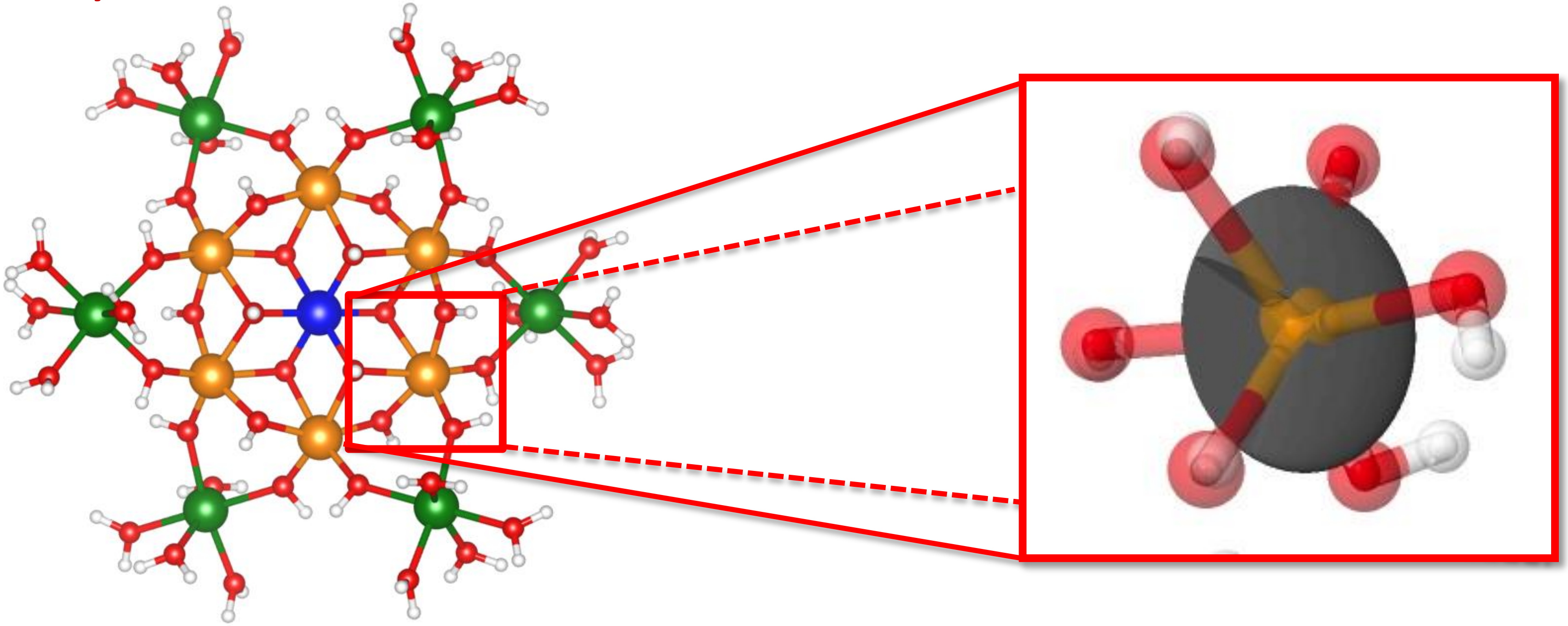


Fig. 5. (a) ^{10}B natural abundance spectrum of v-B_2O_3 obtained in a total experiment time of 0.8 h. (b) Simulation made using parameters previously reported [29].

Can First Principles Calculations Help?

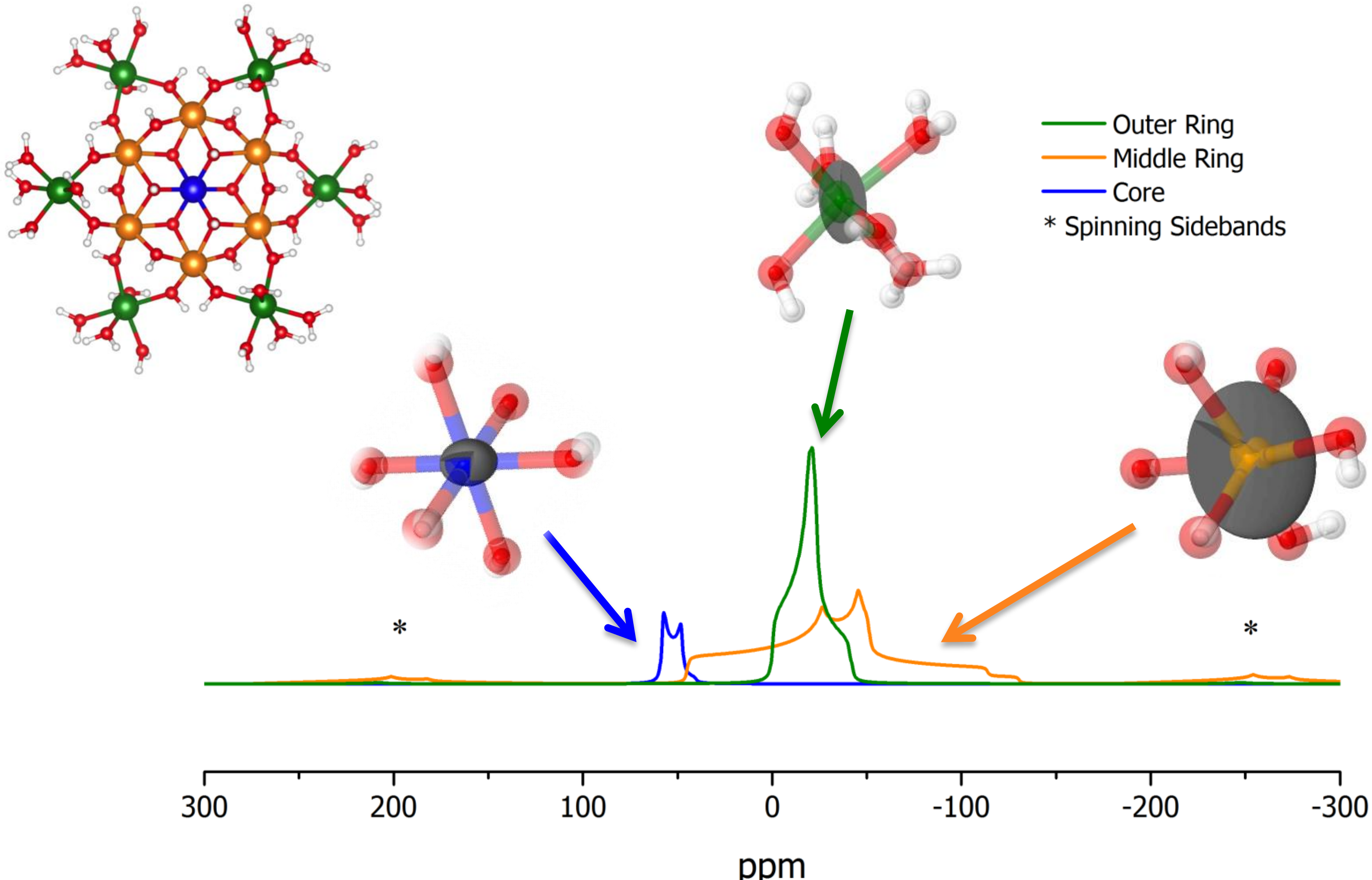
Electric Field Gradients (CASTEP, Quantum Espresso, VASP)



- EFG can be calculated based on a 3-D structure (the grey ellipsoid)

Ga_{13} NMR Model

$[Ga_{13}(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$ "Ga_{13}"



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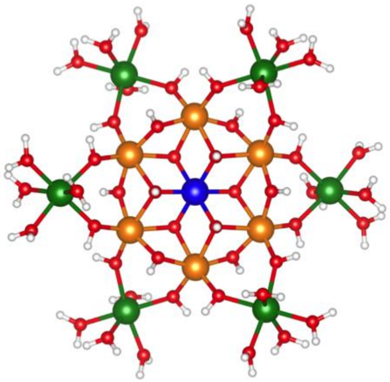

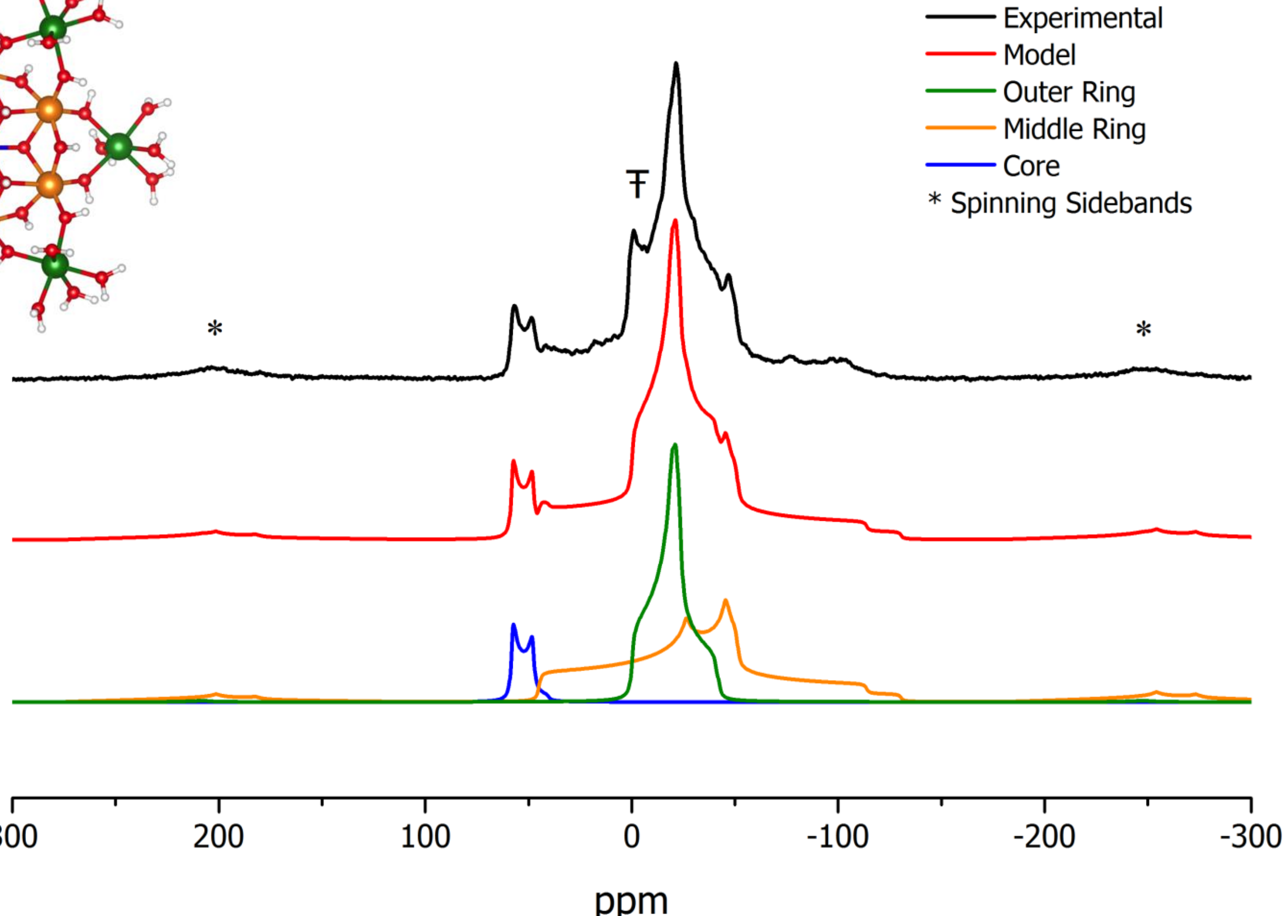

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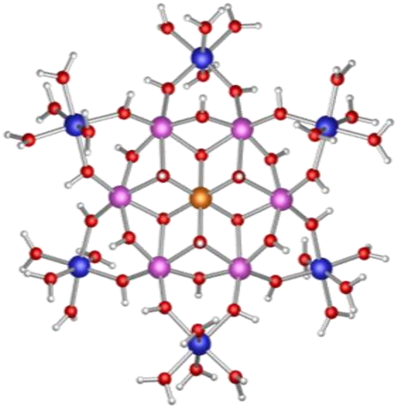
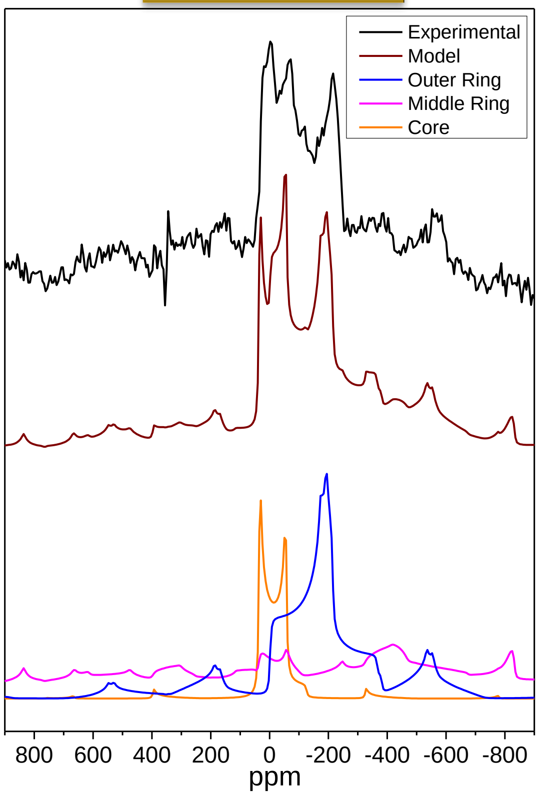
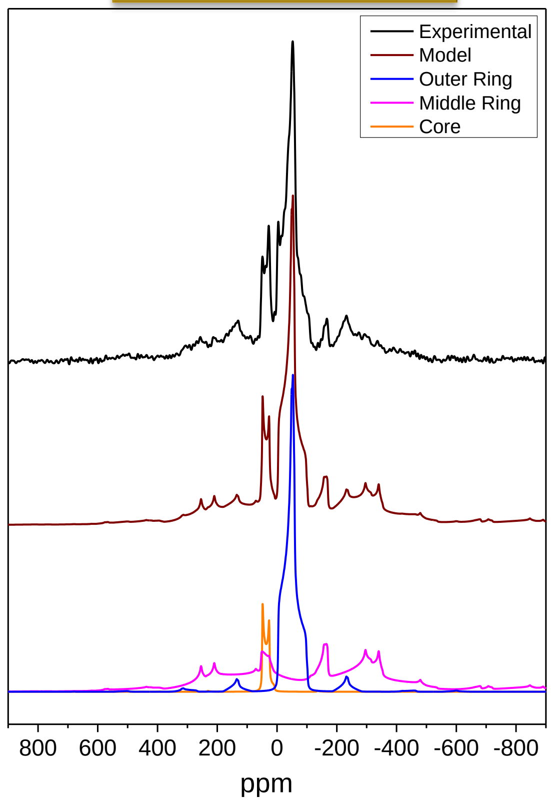
^{71}Ga NMR Ga_{13} Field Dependence



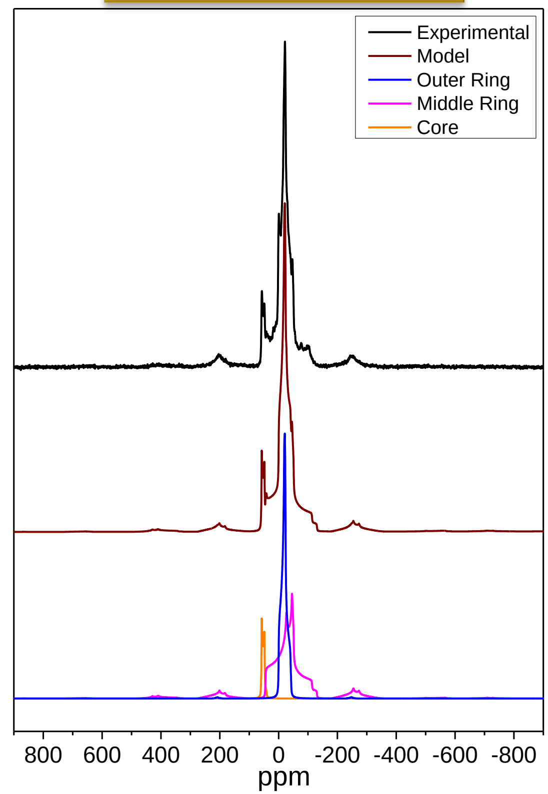
7 Tesla



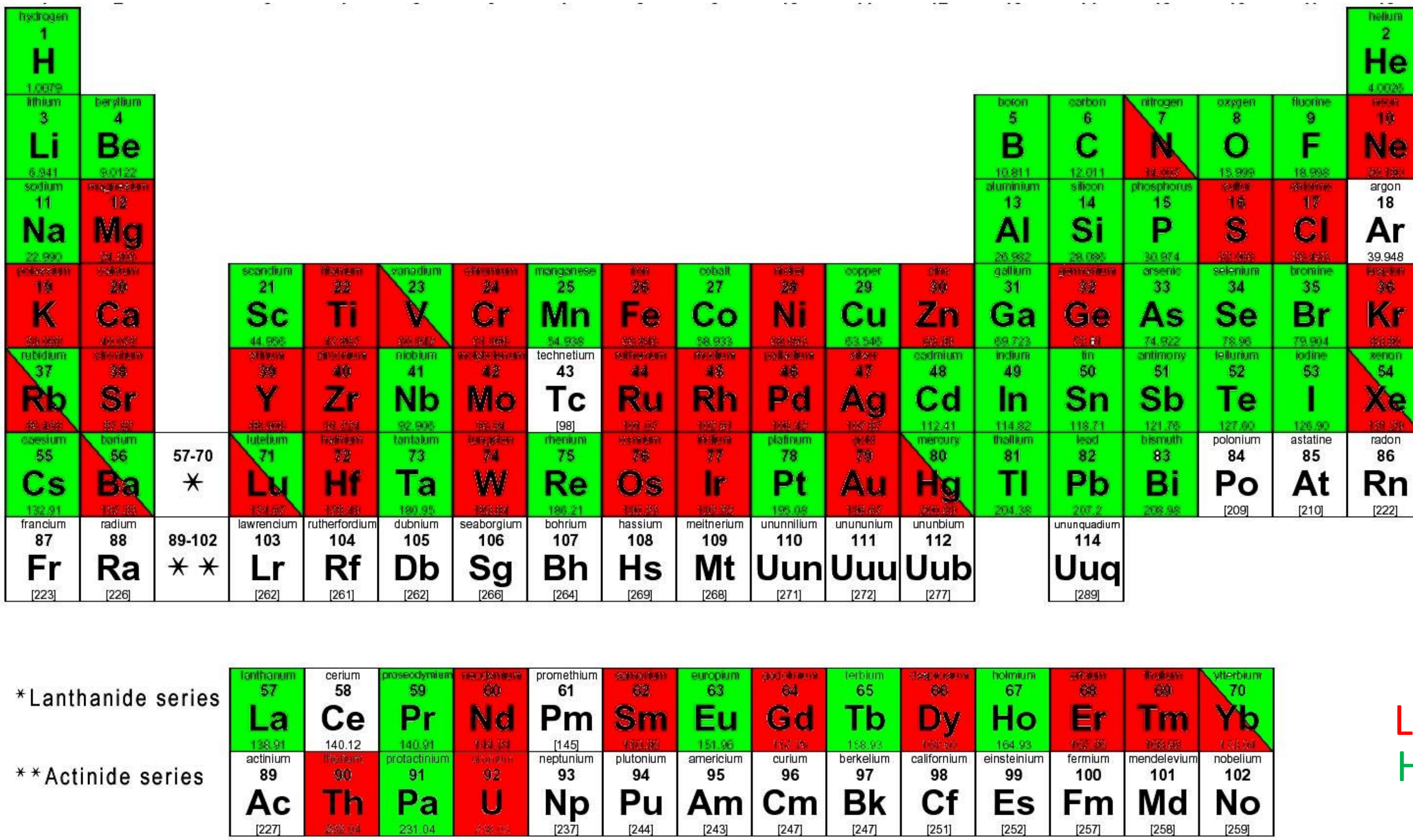
13.9 Tesla



21.1 Tesla



Periodic Table of Low γ Nuclei



Low γ

High γ

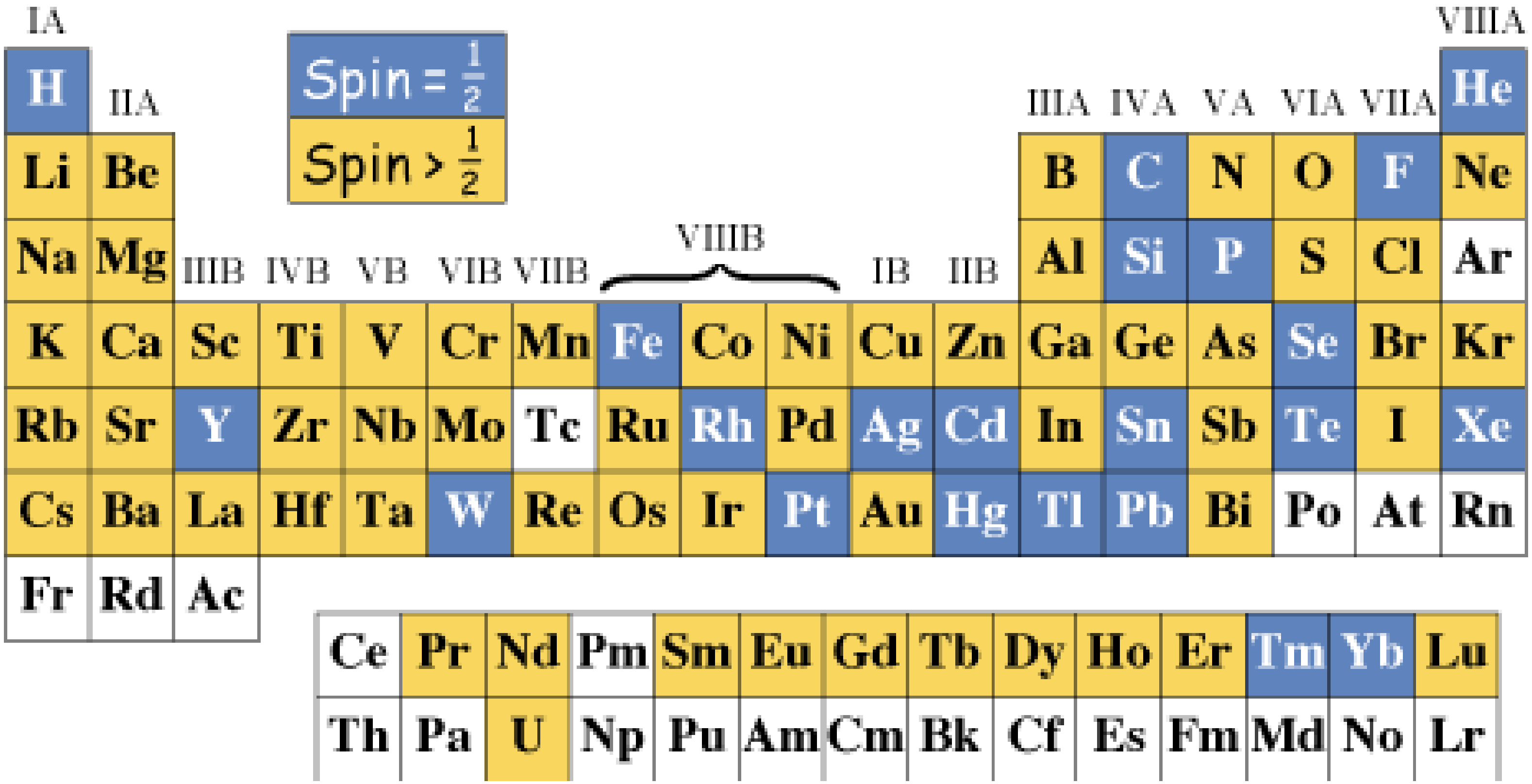
https://www2.warwick.ac.uk/fac/sci/physics/research/condensedmatt/nmr/research/methodologydevelopment/

Newly – accessible spin ½ nuclei

Table 1. Nuclei in the region of 0 to 250 MHz at a field corresponding to 1000 MHz proton frequency

Isotope	Symbol	Name	Spin	Natural Abund. %	Receptivity (rel. to 13C)	Magnetic Moment	Gamma (x 10^7 rad/Ts)	Quadrup. Moment Q/fm^2	Frequency	Reference
187	Os	Osmium	1/2	1.96000	0.00143	0.11198	0.61929	---	**22.823**	OsO4
103	Rh	Rhodium	1/2	100.00000	0.18600	-0.15310	-0.84680	---	**31.864**	Rh(acac)3 p
57	Fe	Iron	1/2	2.11900	0.00425	0.15696	0.86806	---	**32.378**	Fe(CO)5
107	Ag	Silver	1/2	51.83900	0.20500	-0.19690	-1.08892	---	**40.478**	AgNO3
183	W	Tungsten	1/2	14.31000	0.06310	0.20401	1.12824	---	**41.664**	Na2WO4
109	Ag	Silver	1/2	48.16100	0.29000	-0.22636	-1.25186	---	**46.535**	AgNO3
89	Y	Yttrium	1/2	100.00000	0.70000	-0.23801	-1.31628	---	**49.002**	Y(NO3)3
169	Tm	Thulium	1/2	100.00000	---	-0.40110	-2.21800	---	**82.900**	
15	N	Nitrogen	1/2	0.36800	0.02250	-0.49050	-2.71262	---	**101.368**	MeNO2
171	Yb	Ytterbium	1/2	14.28000	---	0.85506	4.72880	---	**174.993**	
199	Hg	Mercury	1/2	16.87000	5.89000	0.87622	4.84579	---	**179.108**	Me2Hgr
77	Se	Selenium	1/2	7.63000	3.15000	0.92678	5.12539	---	**190.715**	Me2Se
29	Si	Silicon	1/2	4.68320	2.16000	-0.96179	-5.31900	---	**198.672**	Me4Si
207	Pb	Lead	1/2	22.10000	11.80000	1.00906	5.58046	---	**209.206**	Me4Pb
111	Cd	Cadmium	1/2	12.80000	7.27000	-1.03037	-5.69831	---	**212.155**	Me2Cd
195	Pt	Platinum	1/2	33.83200	20.70000	1.05570	5.83850	---	**214.968**	Na2PtCl6
113	Cd	Cadmium	1/2	12.22000	7.94000	-1.07786	-5.96092	---	**221.932**	Me2Cd

Quadrupolar Periodic Table

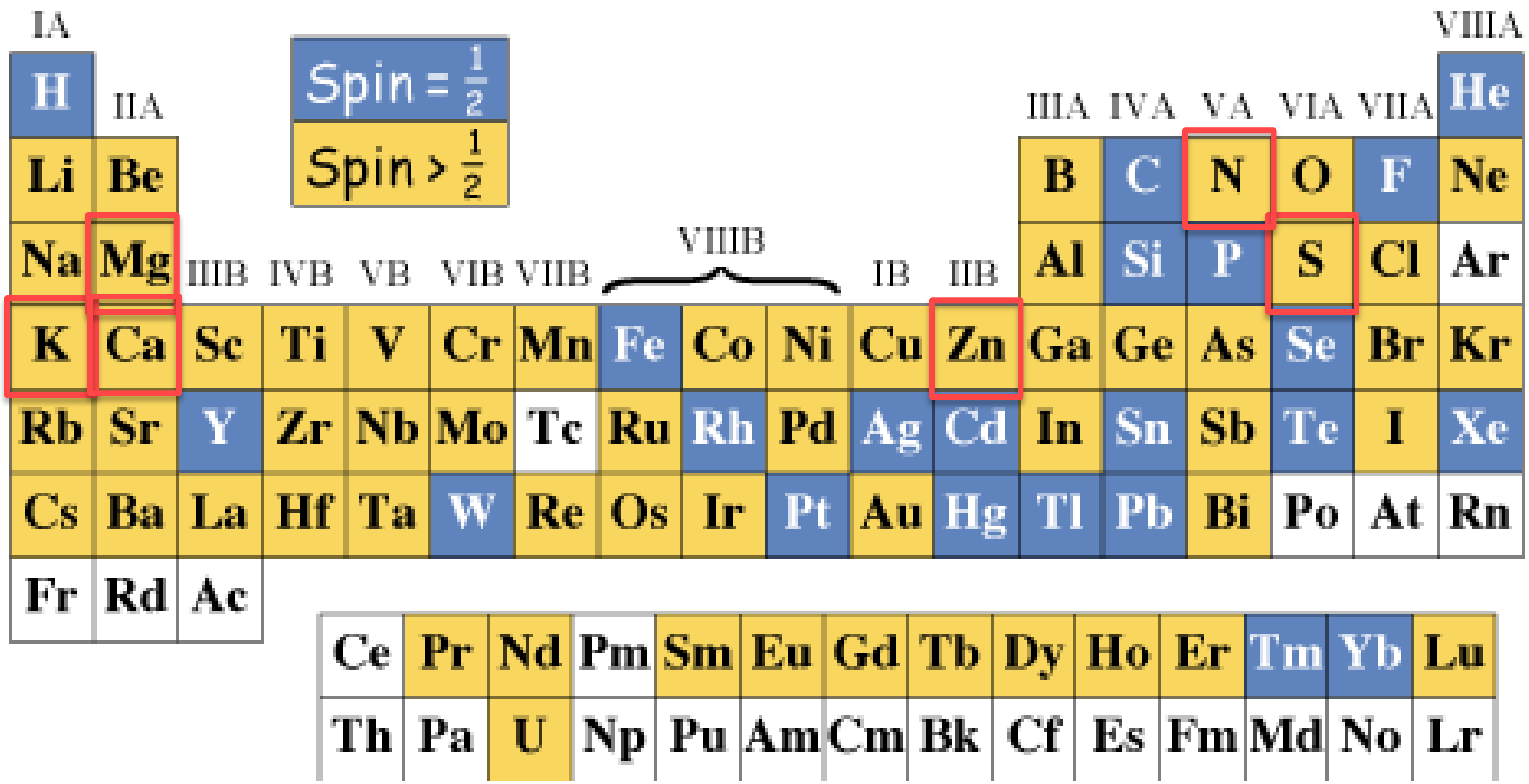


Newly-Accessible Quadrupolar Nuclei @ 1 GHz

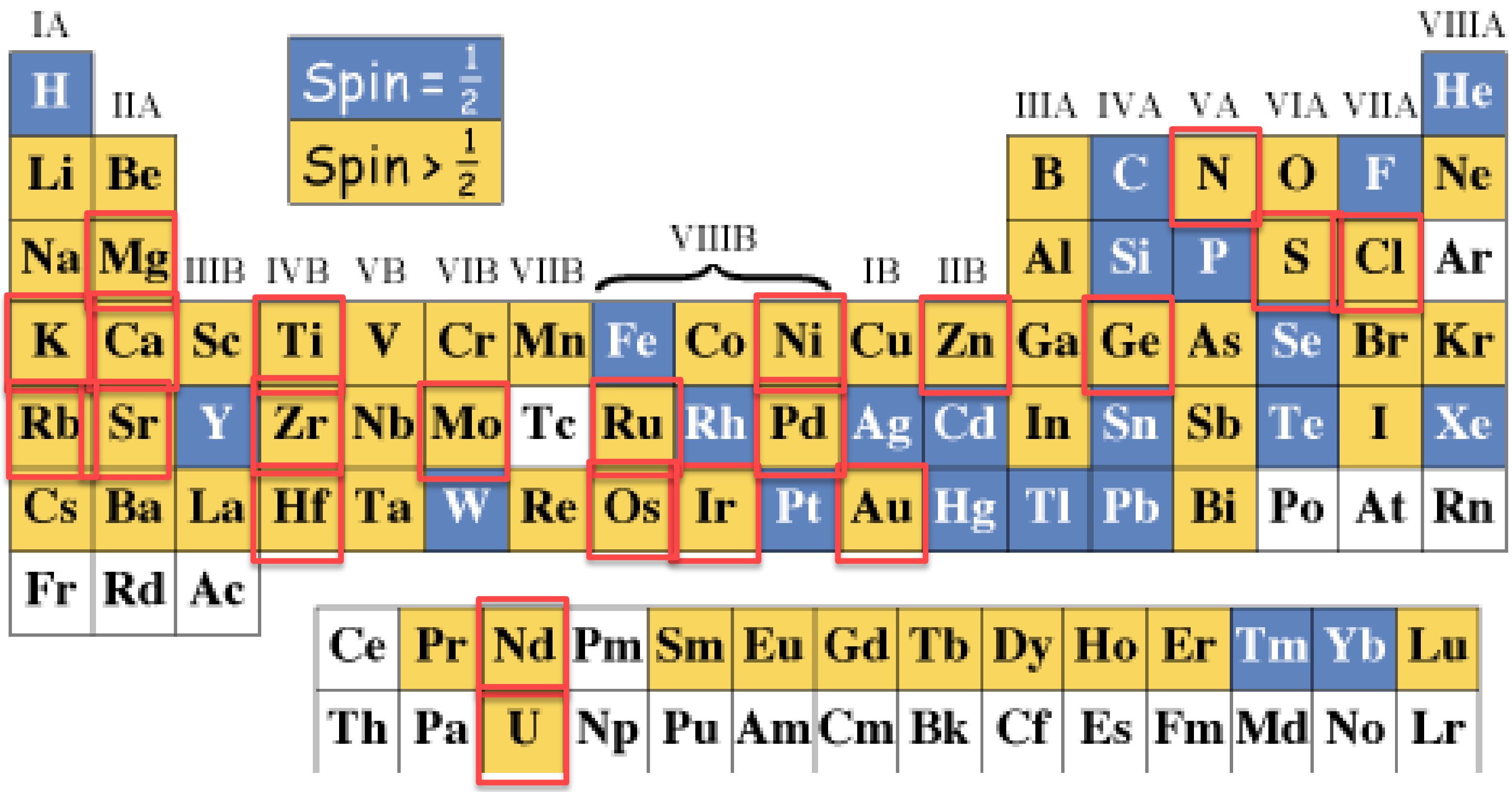
Isotope	Symbol	Name	**Spin**	Natural Abund. %	Receptivity (rel. to 13C)	Magnetic Moment	Gamma (x10^7 rad/Ts)	Quadr. Moment (Q/fm^2)	Frequency **(MHz)**
191	Ir	Iridium	**3/2**	37.3	0.06412	0.1946	0.4812	81.6	17.18
197	Au	Gold	**3/2**	100	0.16294	0.19127	0.47306	54.7	17.29
235	U	Uranium	**7/2**	0.72	---	-0.43	-0.52	493.6	18.414
193	Ir	Iridium	**3/2**	62.7	0.13765	0.2113	0.5227	75.1	18.71
179	Hf	Hafnium	**9/2**	13.62	0.43824	-0.7085	-0.6821	379.3	25.17
41	K	Potassium	**3/2**	6.7302	0.03341	0.2774	0.68607	7.11	25.613
167	Er	Erbium	**7/2**	22.93	---	-0.63935	-0.77157	356.5	28.8
155	Gd	Gadolinium	**3/2**	14.8	---	-0.33208	-0.82132	127	30.7
145	Nd	Neodymium	**7/2**	8.3	---	-0.744	-0.898	-33	33.6
161	Dy	Dysprosium	**5/2**	18.91	---	-0.5683	-0.9201	250.7	34.4
149	Sm	Samarium	**7/2**	13.82	---	-0.7616	-0.9192	7.4	34.4
73	Ge	Germanium	**9/2**	7.73	0.64118	-0.97229	-0.93603	-19.6	34.883
83	Kr	Krypton	**9/2**	11.49	1.28235	-1.07311	-1.0331	25.9	38.476
177	Hf	Hafnium	**7/2**	18.6	1.53529	0.8997	1.086	336.5	40.07
157	Gd	Gadolinium	**3/2**	15.65	---	-0.4354	-1.0769	135	40.3
147	Sm	Samarium	**7/2**	14.99	---	-0.9239	-1.115	-25.9	41.7
87	Sr	Strontium	**9/2**	7	1.11765	-1.20902	-1.16394	33.5	43.338
105	Pd	Palladium	**5/2**	22.33	1.48824	-0.76	-1.23	66	45.761
99	Ru	Ruthenium	**5/2**	12.76	0.84706	-0.7588	-1.229	7.9	46.052
39	K	Potassium	**3/2**	93.2581	2.8	0.50543	1.25006	5.85	46.664
163	Dy	Dysprosium	**5/2**	24.9	---	0.7958	1.289	264.8	48.2
173	Yb	Ytterbium	**5/2**	16.13	---	-0.80446	-1.3025	280	48.21
101	Ru	Ruthenium	**5/2**	17.06	1.59412	-0.8505	-1.377	45.7	51.614
143	Nd	Neodymium	**7/2**	12.2	---	-1.208	-1.457	-63	54.5
47	Ti	Titanium	**5/2**	7.44	0.91765	-0.93294	-1.5105	30.2	56.375
49	Ti	Titanium	**7/2**	5.41	1.20588	-1.25201	-1.51095	24.7	56.39
53	Cr	Chromium	**3/2**	9.501	0.50765	-0.61263	-1.5152	-15	56.525
40	K	Potassium	**4**	0.0117	0.0036	-1.45132	-1.55429	-7.3	58.02
25	Mg	Magnesium	**5/2**	10	1.57647	-1.0122	-1.63887	19.94	61.216
67	Zn	Zinc	**5/2**	4.1	0.69412	1.03556	1.67669	15	62.568
95	Mo	Molybdenum	**5/2**	15.92	3.06471	-1.082	-1.751	-2.2	65.169
201	Hg	Mercury	**3/2**	13.18	1.15882	-0.72325	-1.78877	38.6	66.116
97	Mo	Molybdenum	**5/2**	9.55	1.95882	-1.105	-1.788	25.5	66.537
43	Ca	Calcium	**7/2**	0.135	0.05106	-1.49407	-1.80307	-4.08	67.3
14	N	Nitrogen	**1**	99.632	5.88235	0.571	1.93378	2.044	72.263
33	S	Sulfur	**3/2**	0.76	0.10118	0.83117	2.05568	-6.78	76.76
189	Os	Osmium	**3/2**	16.15	2.32353	0.85197	2.10713	85.6	77.654
21	Ne	Neon	**3/2**	0.27	0.03912	-0.85438	-2.11308	10.155	78.943
176	Lu	Lutetium	**7**	2.59	---	3.388	2.1684	497	81.31
37	Cl	Chlorine	**3/2**	24.22	3.87647	0.8832	2.18437	-6.435	81.557
131	Xe	Xenon	**3/2**	21.18	3.50588	0.89319	2.20908	-11.4	82.439
61	Ni	Nickel	**3/2**	1.1399	0.24059	-0.96827	-2.3948	16.2	89.361
91	Zr	Zirconium	**5/2**	11.22	6.29412	-1.54246	-2.49743	-17.6	92.963
85	Rb	Rubidium	**5/2**	72.17	45.11765	1.60131	2.59271	27.6	96.549

www.nyu.edu/cgi-bin/cgiwrap/aj39/NMRmap.cgi

Low-γ Quadrupolar Periodic Table (Living Systems)



Low-γ Quadrupolar Periodic Table (Materials)



Low-γ Quadrupolar Periodic Table

Let’s imagine … what could be next?

What can we study tomorrow that we can’t do today?