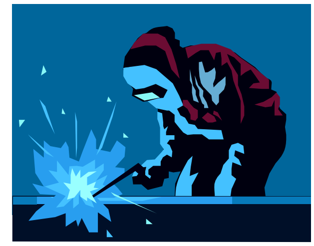
Multinuclear NMR: Easy or Difficult? (Tips for Solid-state NMR)



- How easy or difficult NMR measurements are depends on various factors. Sensitivity (S/N ratio) may be estimated in terms of receptivity given by the following formula. Large gyromagnetic ratio γ and natural abundance N_{abd} lead to large receptivity for ^{19}F and ^{27}Al, for example.

$$R_A(X) = \left| \frac{\gamma(X)}{\gamma(A)} \right|^3 \frac{I(X)\,[\,I(X)+1\,]}{I(A)\,[\,I(A)+1\,]} \frac{N_{abd}(X)}{N_{abd}(A)}$$

A : reference nucleus (^{1}H or ^{13}C) γ : gyromagnetic ratio

I : spin quantum number N_{abd} : natural abundance

- Low-γ nuclei exhibiting low NMR frequencies ($\propto \gamma$), such as ^{25}Mg and $^{47,49}Ti$, may suffer from ringing effects, making their measurements difficult.

- In solid-state NMR, it is easy to obtain high-resolution spectra for the nuclei with spin quantum number of 1/2, like ^{13}C and ^{31}P, while difficult for those having larger quantum number than 1/2, in general, because of quadrupolar broadening. Half integer spins (I=3/2, 5/2, 7/2, 9/2), such as ^{11}B and ^{23}Na, may yield high-resolution spectra via special techniques like MQMAS. These techniques are not applicable to integer spins (I=1, 3, …), such as ^{10}B and ^{14}N.

- Although ^{1}H high-power decoupling is widely utilized in solid-state NMR, the nuclei experiencing weak ^{1}H dipolar interactions like ^{29}Si require not so strong decoupling. It is difficult to decouple ^{1}H-^{1}H interactions, rendering solid-state ^{1}H measurements difficult.

- In solids, chemical shifts vary depending on the nuclear orientations (CSA: chemical shift anisotropy). For the nuclei having large CSA, such as ^{195}Pt and ^{207}Pb, magic angle sample spinning with realistic speeds cannot remove spinning sidebands.

- Another factor of long longitudinal relaxation times T_1 makes measurements difficult.

Article giving more detailed description, “T. Nakai, New Glass, 28(2),17-28 (2013)” (in Japanese) is available. The request to sales or sales promotion team is highly appreciated.

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Nucleus (Isotope)	Spin Quantum Number	Gyromagnetic Ratio ¥ (= $\gamma/2\pi$) [MHz/T]	NMR Frequency at 11.75 T ν_0 [MHz]	NMR Frequency at 24.20 T ν_0 [MHz]	Natural Abundance N_{abd} [%]	Receptivity § (Relative Sensitivity) Normalized to ^{1}H R_H (X)	Normalized to ^{13}C R_C (X)	Magnetic Dipolar Interaction with ^{1}H D (X -^{1}H) [kHz] (for Spin-1/2 Nuclei)	Chemical Shift Anisotropy Δδ (X) (for Spin-1/2 Nuclei) [ppm]	[kHz] at 11.75 T
^{1}H	1/2	42.577 48	500.28	1030.36	99.99	1	5660	—	≲ 20	≲ 10 ≲ 20
^{2}H	1	6.535 8	76.80	158.17	0.015	1.45×10^{-6}	0.00821			
^{6}Li	1	6.265 7	73.62	151.63	7.5	6.37×10^{-4}	3.61			
^{7}Li	3/2	16.547 3	194.43	400.44	92.5	0.272	1540			
^{10}B	3	4.574 5	53.75	110.70	19.7	3.91×10^{-3}	22.1			
^{11}B	3/2	13.660 5	160.51	330.58	80.1	0.132	747			
^{13}C	1/2	10.708 4	125.82	259.14	1.11	1.77×10^{-4}	1	~ 23 (for r(^{13}C -^{1}H) = 1.09 Å)	≲ 200	≲ 25 ≲ 50
^{14}N	1	3.076 6	36.15	74.45	99.63	1.00×10^{-3}	5.68	—	—	—
^{15}N	1/2	−4.314 4	50.69	104.41	0.37	3.85×10^{-6}	0.0218	~ 12 (for r(^{15}N -^{1}H) = 1.01 Å)	≲ 200	≲ 10 ≲ 20
^{17}O	5/2	−5.771 8	67.82	139.68	0.038	1.10×10^{-5}	0.0625	—	—	—
^{19}F	1/2	40.055 6	470.65	969.35	100	0.833	4710	~ 30 (for r(^{19}F -^{1}H) = 1.55 Å)	≲ 400	≲ 200 ≲ 400
^{23}Na	3/2	11.262 6	132.34	272.56	100	0.0926	524	—	—	—
^{25}Mg	5/2	−2.606 6	30.63	63.08	10.1	2.70×10^{-4}	1.53	—	—	—
^{27}Al	5/2	11.094 4	130.36	268.49	100	0.207	1170	—	—	—
^{29}Si	1/2	−8.458 9	99.39	204.70	4.69	3.68×10^{-4}	2.08	~ 4.5 (for r(^{29}Si -^{1}H) = 1.74 Å)	≲ 100	≲ 10 ≲ 20
^{31}P	1/2	17.235 7	202.52	417.10	100	0.0663	374	~ 17 (for r(^{31}P -^{1}H) = 1.43 Å)	≲ 400	≲ 80 ≲ 160
^{43}Ca	7/2	−2.865 5	33.67	69.35	0.135	8.64×10^{-6}	0.0489			
^{47}Ti	5/2	− 2.400 46	28.254	58.191	7.4	1.55×10^{-4}	0.876			
^{49}Ti	7/2	− 2.405 23	28.261	58.207	5.5	2.08×10^{-4}	1.18			
^{79}Br	3/2	10.667 2	125.34	258.15	50.69	0.0399	226			
^{87}Rb	3/2	13.931 8	163.70	337.15	27.83	0.0488	276			
^{93}Nb	9/2	10.407 1	122.28	251.85	100	0.482	2730			
^{103}Rh	1/2	− 1.340 1	15.75	32.43	100	3.12×10^{-5}	0.177	~ 0.78 (for r(^{103}Rh -^{1}H) = 1.69	≲ 2,000	≲ 30 ≲ 60
^{133}Cs	7/2	5.584 8	65.62	135.15	100	0.0475	269		—	—
^{119}Sn	1/2	− 15.869 6	186.47	384.04	8.59	4.45×10^{-3}	25.2	~ 9.1 (for r(^{119}Sn -^{1}H) = 1.70	≲ 1,000	≲ 200 ≲ 400
^{171}Yb	1/2	7.499 2	88.12	181.48	14.31	7.82×10^{-4}	4.43	~ 2.4 (for r(^{171}Yb -^{1}H) = 2.06		≲ 150 ≲ 300
^{195}Pt	1/2	9.152 6	107.54	221.49	33.8	3.36×10^{-3}	19.0	~ 7.2 (for r(^{195}Pt -^{1}H) = 1.53 Å)	≲ 5,000	≲ 500 ≲ 1,000
^{207}Pb	1/2	8.907 6	104.66	215.55	22.8	2.09×10^{-3}	11.8	~ 4.0 (for r(^{207}Pb -^{1}H) = 1.84	≲ 5,000	≲ 500 ≲ 1,000

Legend of Nucleus

Everybody's Playmate X — Good Worker X

Cinderella Nucleus X — Sleeping Beauty X

Legend of Nucleus Properties

- Spin Quantum Number X: 1/2, Half-integer, Integer
- NMR Frequency X: > 300, 100 - 300, 50 - 100, 0 - 50
- Natural Abundance X: >80 %, 10 - 80, 1 - 10, 0 - 1
- Receptivity X: High, Medium, Low
- Dipolar Int. X: No Problem, Decoupled, Challenging
- CS Aniso. X: Easy Spin-away, Can Spin-away, Untractable

† $\gamma(^1H)$ = 2.675 222 005 (± 0.000 000 063) x 10^8 [rad/s 1/T]

‡ $\gamma(^{13}C)$ = 0.672 828 410 x 10^8 [rad/s 1/T]

§ $R_A(X) = [I(X)(I(X)+1)] / [I(A)(I(A)+1)] (N_{abd}(X) / N_{abd}(A)) |\gamma(X)/\gamma(A)|^3$

$D(X\text{-}^1H) = (\mu_0/4\pi)(h^2\ ¥(X)\ ¥(^1H) / r(X\text{-}^1H)^3$ [kHz/ Å 3]

¶ $D(^1H\text{-}^1H) = (\mu_0/4\pi)(h^2\ ¥(^1H)^2 / r(^1H\text{-}^1H)^3)$ [kHz/Å^3]

= 120.120 3 [kHz/Å^3] (for r(^{1}H-^{1}H) = 1 Å)

* $h = 6.626\ 075\ 5\times10^{-34}$ [J•s] $\hbar = h/2\pi$ [(J・s) /rad] $\mu_0 = 4\pi \times 10^{-7}$ [H/m] $\mu_0/4\pi = 10^{-7}$ [H/(m・rad)]

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