Training Material Number : UMAL-1507-01 Author : Sun-Phil Han Date : 2024-02-20

UNIST
ULSAN NATIONAL INSTITUTE OF SCIENCE AND TECHNOLOGY

Nuclear Magnetic Resonance spectroscopy

Normal Operation Training Course

1. Syllabus

NMR Training, 2024

- Training Schedule

Contents

Qualification for NMR operation

1. NMR self-user training

1) Theory class (Sun-Phil Han, 4174)

2) Operation class (Sun-Phil Han, 4174)

2. Practice NMR yourself

- Exercise operation with self-user over 3 times
  or request to manager by e-mail

3. Attend the NMR test

- Request for self-user test by e-mail
- The manager reserves a test time on UNIST portal.
- Test time : 30min
- Explain about NMR principle (2 ~ 3 questions)
- Acquire NMR data by using Bruker automation system(Icon-NMR)
- You have to get a self-user in one month

2. Basic principles

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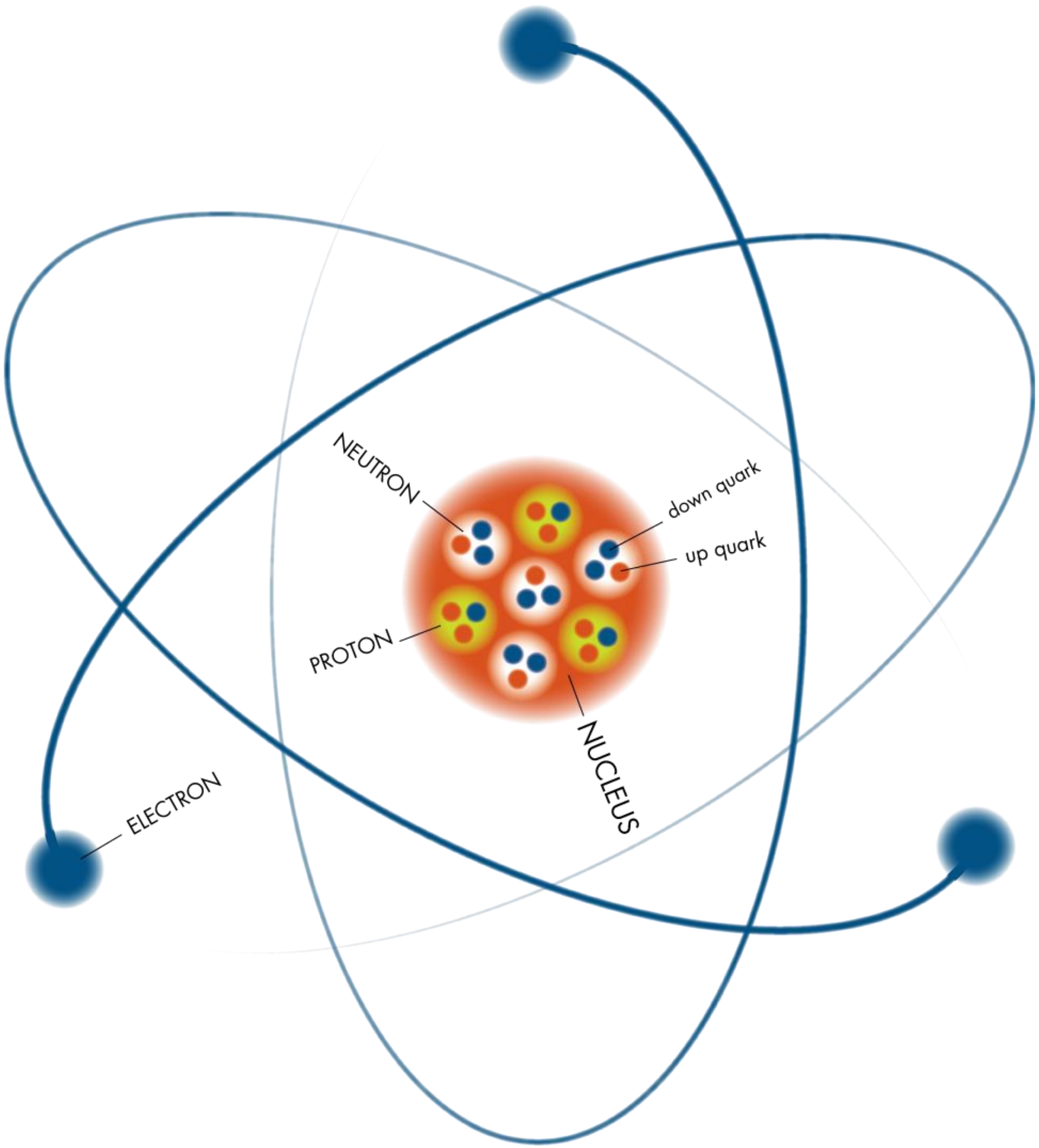
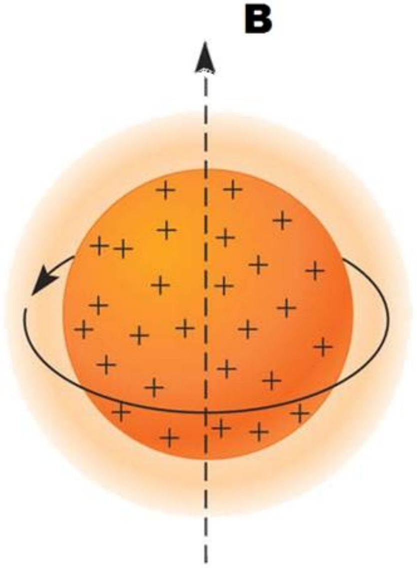
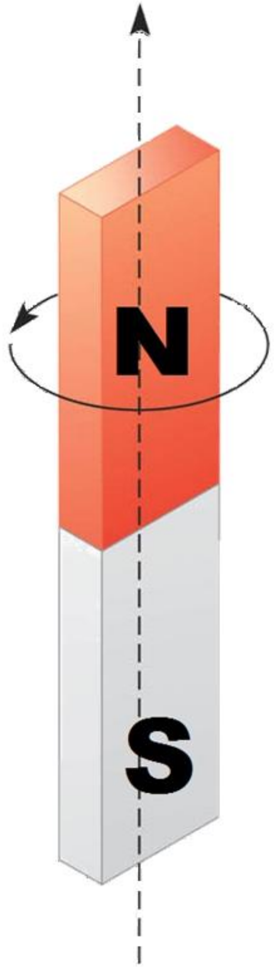
Atom

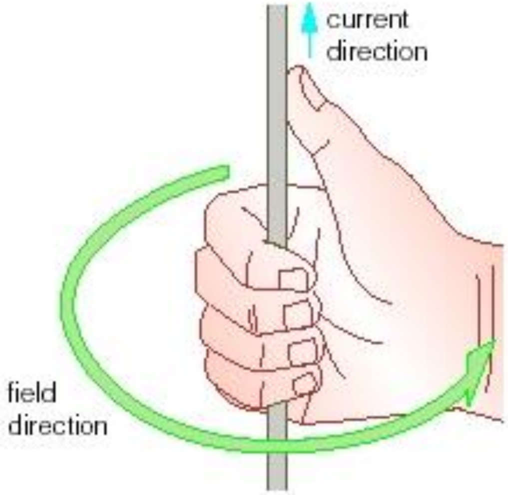


Ampere`s law



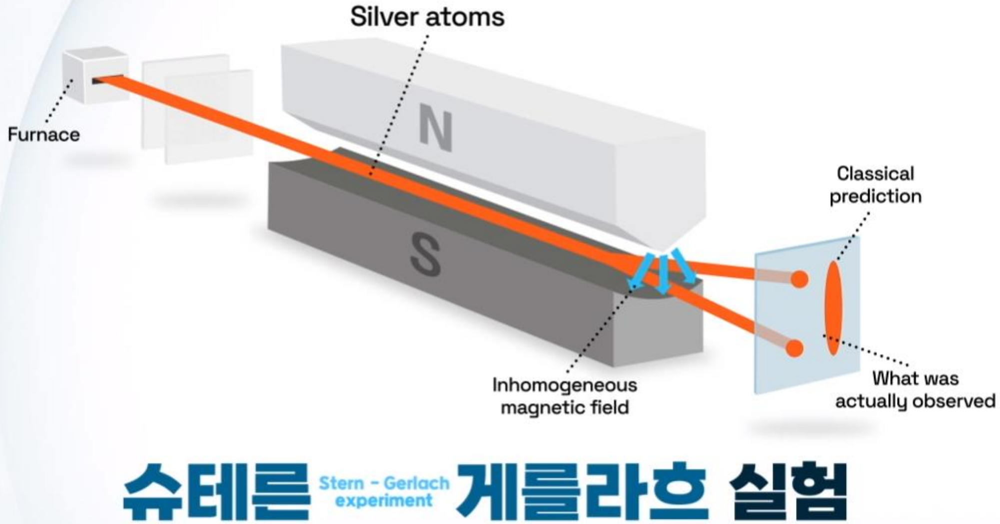
Magnetic moment





Ampere`s law

지만 효과 (Zeeman effect)



정상 지만 효과

자기장 내에서 spectrum이 홀수개로 갈라짐

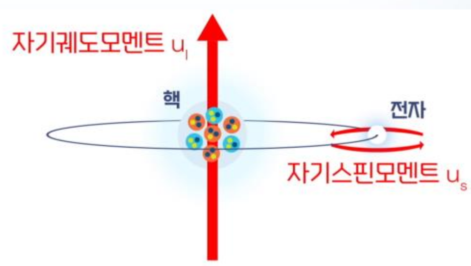
=2l+1

비정상 지만 효과

스핀양자수(ms)에 따라 specturm이 짝수 개로 나뉨

= 2ms+1

이름	기호	값	물리량
주양자수 (Principal Quantum Number)	n	1, 2, 3, 4 ···	전자 에너지 (오비탈 크기)
각운동량 양자수 (Angular Momentum Quantum Number)	l	0, 1, 2, 3, 4 ···	궤도 각운동량의 크기 (오비탈 모양)
자기양자수 (Magnetic Quantum Number)	m_l	-l, ··· , -1, 0, 1, ···, l	궤도 각운동량의 방향 (오비탈 배향)
스핀양자수 (Spin Quantum Number)	m_s	+1/2 (up) -1/2 (down)	전자 스핀 방향

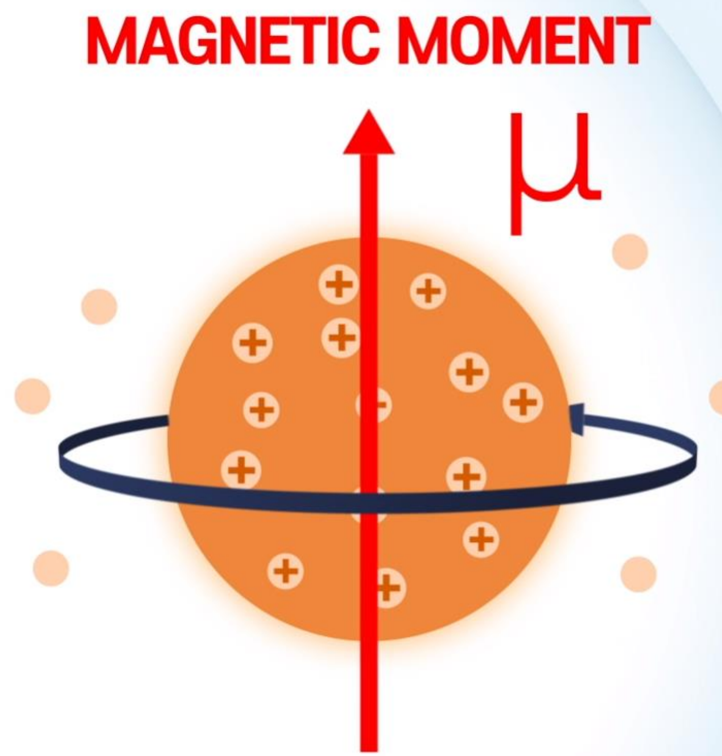


이름	기호	값	물리량
핵스핀양자수 (Nuclear Spin Quantum Number)		+1/2 (up) -1/2 (down)	핵 스핀 방향

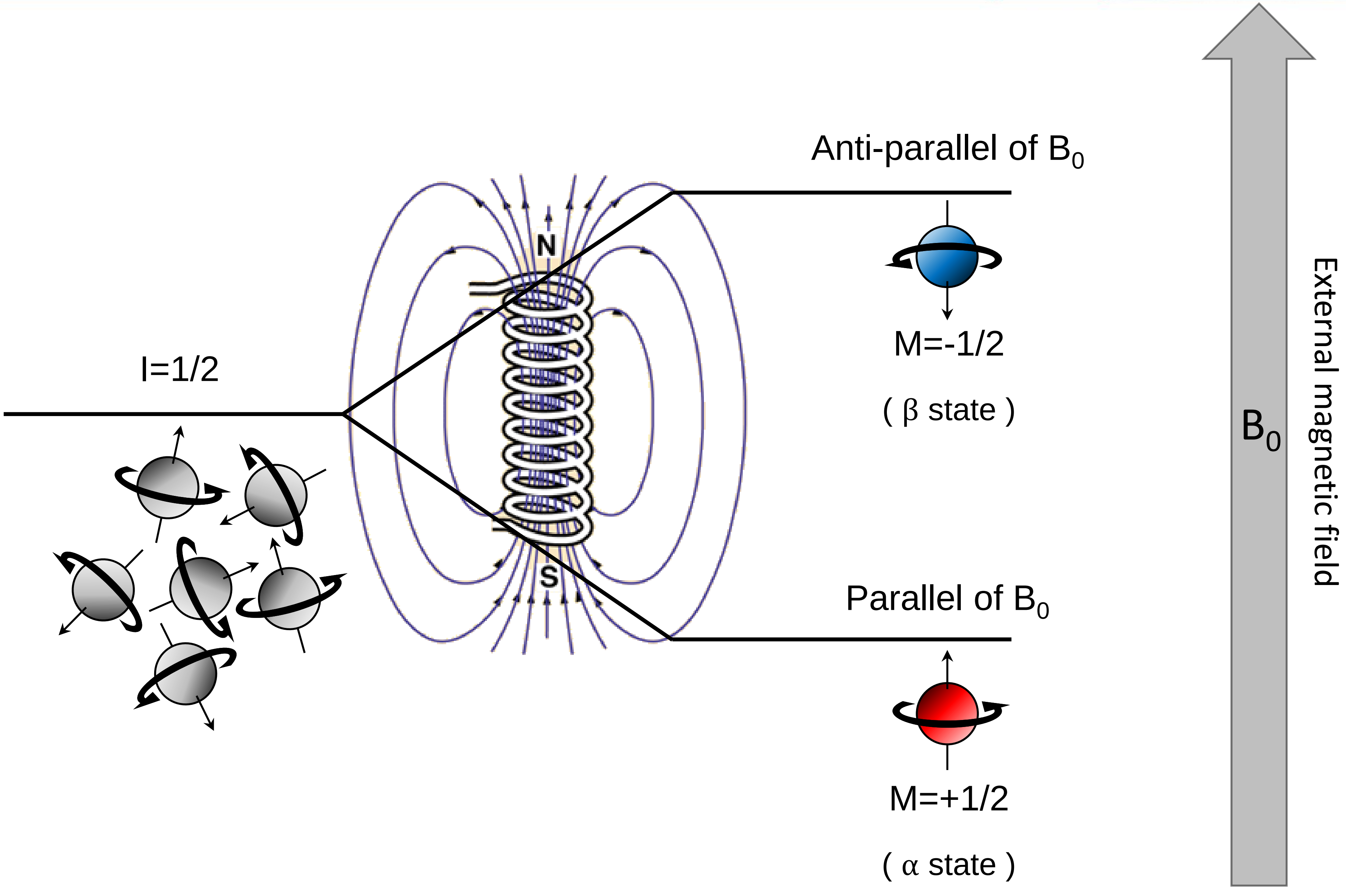
자기 모멘트 (Magnetic moment)

$$\mu = \gamma I$$

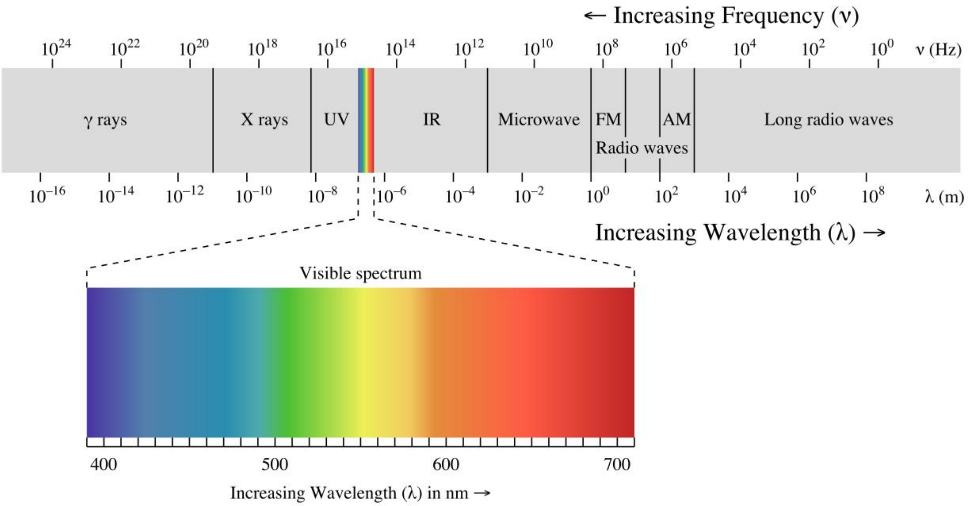
- **μ : 핵자기모멘트** (Nuclear magnetic moment)
- **γ : 자기회전비율** (Gyromagnetic moment)
- **I : 핵스핀양자수** (Nuclear spin quantum number)

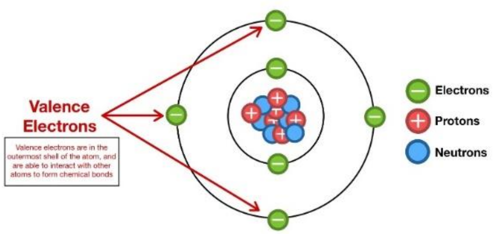


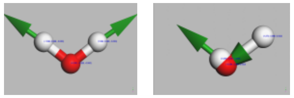
Energy states splitting (B_0)

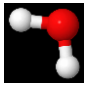


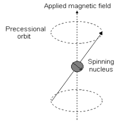
Electromagnetic spectrum





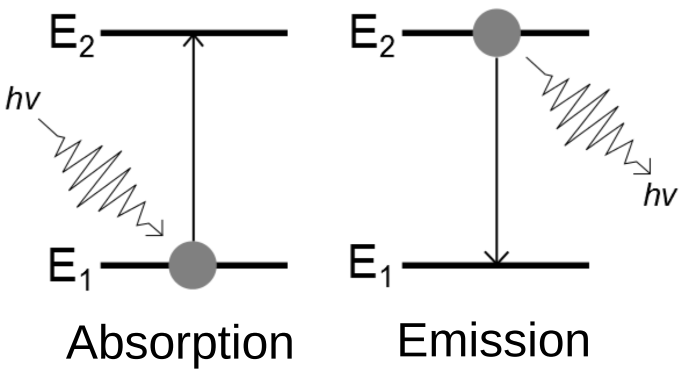




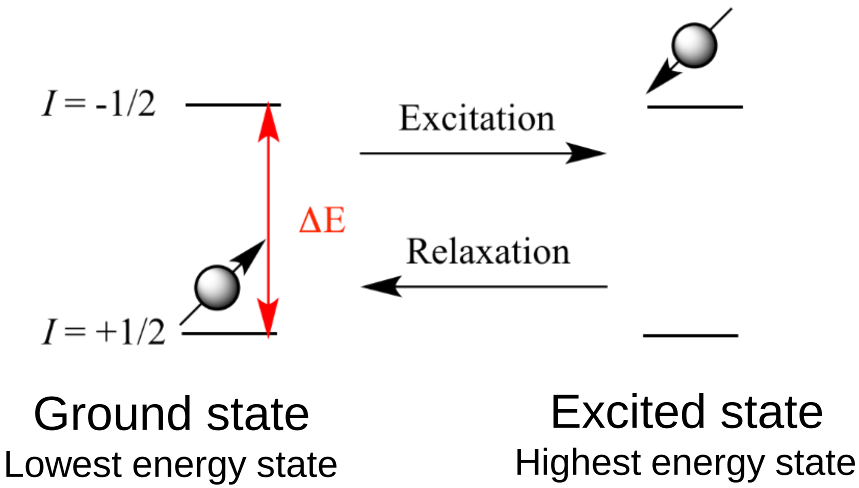


Region of electromagnetic spectrum	Interaction	Spectroscopic technique
Y− ray	Nuclear	Mossbauer spectroscopy
X-ray	Core-level electron	X-ray absorption spectroscopy
Ultraviolet (UV)	Valence electron	UV/Vis spectroscopy
Visible (Vis)	Valence electron	UV/Vis spectroscopy
Infrared (IR)	Molecular vibration	IR spectroscopy Raman spectroscopy
Microwave	Molecular rotation	Microwave spectroscopy
Radio-wave	Nuclear spin	Nuclear magnetic resonance spectroscopy

Spectroscopy



Spectroscopy



NMR

I (Nuclear spin quantum number)

Table 1. General rules for determination of nuclear spin quantum numbers

Mass Number	Number of Protons	Number of Neutrons	Spin (I)	Example
Even	Even	Even	0	^{16}O
0, 2, 4, 6 …	Odd	Odd	Integer (1,2,...)	^{2}H
Odd	Even	Odd	Half-Integer (1/2, 3/2,...)	^{13}C
1, 3, 5, 7 …	Odd	Even	Half-Integer (1/2, 3/2,...)	^{15}N

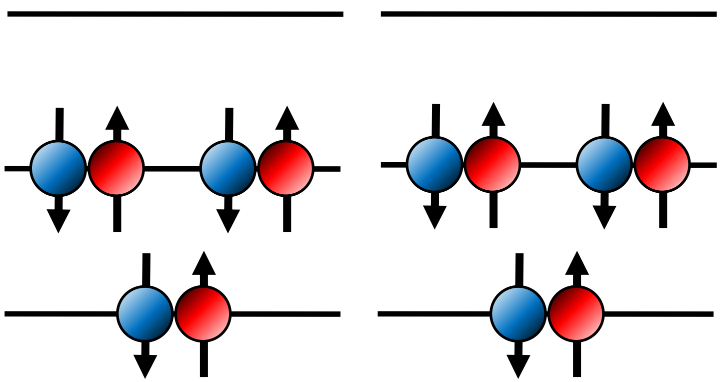
Nucleus	Spin	Resonance frequency (MHz) in field of 2.3487 T	g value
^{1}H	$\frac{1}{2}$	100.00	5.585
^{10}B	3	10.75	0.6002
^{11}B	$\frac{3}{2}$	32.08	1.792
^{13}C	$\frac{1}{2}$	25.14	1.404
^{14}N	1	7.22	0.4036
^{15}N	$\frac{1}{2}$	10.13	−0.5660
^{17}O	$\frac{5}{2}$	13.56	−0.7572
^{19}F	$\frac{1}{2}$	94.07	5.255
^{29}Si	$\frac{1}{2}$	19.87	−1.110
^{31}P	$\frac{1}{2}$	40.48	2.261
^{35}Cl	$\frac{3}{2}$	9.80	0.5472
^{37}Cl	$\frac{3}{2}$	8.16	0.4555
^{107}Ag	$\frac{1}{2}$	4.05	−0.2260
^{119}Sn	$\frac{1}{2}$	37.27	−2.082
^{127}I	$\frac{5}{2}$	20.00	1.118
^{199}Hg	$\frac{1}{2}$	17.83	0.996

Table 5-2 Quadrupole moments, linewidth factors and receptivities of some spin $>\frac{1}{2}$ nuclides[(a)]

Nuclide	*Spin*	*Quadrupole moment*	*Linewidth factor*	*Relative receptivity*	
	I	$Q/10^{-28}$ m^2	10^{56} ℓ/m^4	D^P	D^C
^{2}H	1	$2{\cdot}8\times10^{-3}$	$3{\cdot}9\times10^{-5}$	$1{\cdot}45\times10^{-6}$	$8{\cdot}21\times10^{-3}$
^{6}Li	1	-8×10^{-4}	$3{\cdot}2\times10^{-6}$	$6{\cdot}31\times10^{-4}$	3·58
^{7}Li	$\frac{3}{2}$	-4×10^{-2}	$2{\cdot}1\times10^{-3}$	0·272	$1{\cdot}54\times10^{3}$
^{10}B	3	$8{\cdot}5\times10^{-2}$	$1{\cdot}4\times10^{-3}$	$3{\cdot}93\times10^{-3}$	22·3
^{11}B	$\frac{3}{2}$	$4{\cdot}1\times10^{-2}$	$2{\cdot}2\times10^{-3}$	0·133	$7{\cdot}52\times10^{2}$
^{14}N	1	1×10^{-2}	5×10^{-4}	$1{\cdot}00\times10^{-3}$	5·69
^{17}O	$\frac{5}{2}$	$-2{\cdot}6\times10^{-2}$	$2{\cdot}2\times10^{-4}$	$1{\cdot}08\times10^{-5}$	$6{\cdot}11\times10^{-2}$
^{35}Cl	$\frac{3}{2}$	−0·10	$1{\cdot}3\times10^{-2}$	$3{\cdot}56\times10^{-3}$	20·2
^{37}Cl	$\frac{3}{2}$	$-7{\cdot}9\times10^{-2}$	$8{\cdot}3\times10^{-3}$	$6{\cdot}66\times10^{-4}$	3·78
^{59}Co	$\frac{7}{2}$	0·38	$2{\cdot}0\times10^{-2}$	0·277	$1{\cdot}57\times10^{3}$
^{75}As	$\frac{3}{2}$	0·29	0·11	$2{\cdot}53\times10^{-2}$	$1{\cdot}44\times10^{2}$
^{127}I	$\frac{5}{2}$	−0·79	0·20	$9{\cdot}50\times10^{-2}$	$5{\cdot}39\times10^{2}$
^{133}Cs	$\frac{7}{2}$	-3×10^{-3}	$1{\cdot}2\times10^{-6}$	$4{\cdot}82\times10^{-2}$	$2{\cdot}73\times10^{2}$
^{181}Ta	$\frac{7}{2}$	3	1·2	$3{\cdot}65\times10^{-2}$	$2{\cdot}07\times10^{2}$

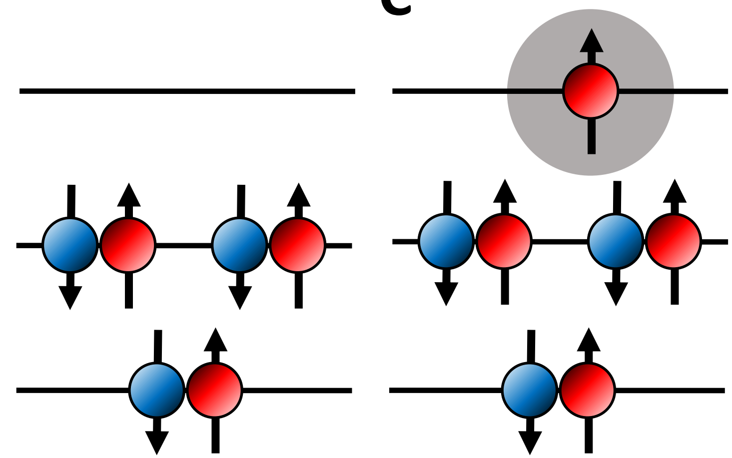
I (Nuclear spin quantum number)

I = 0
^{12}C

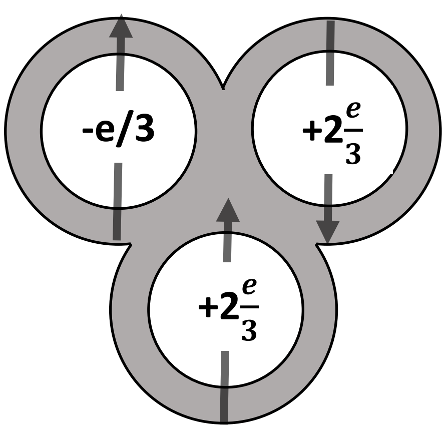


Proton Neutron

I = 1/2
^{13}C

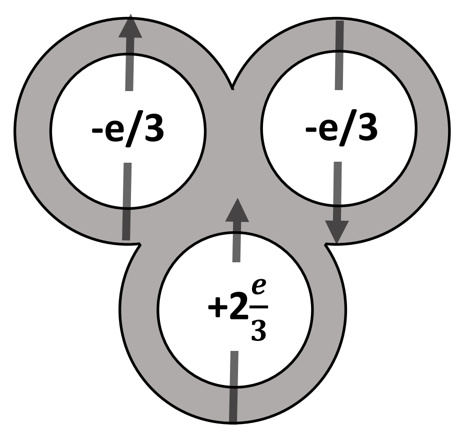


Proton Neutron



Proton

Charge = +e
Spin = 1/2

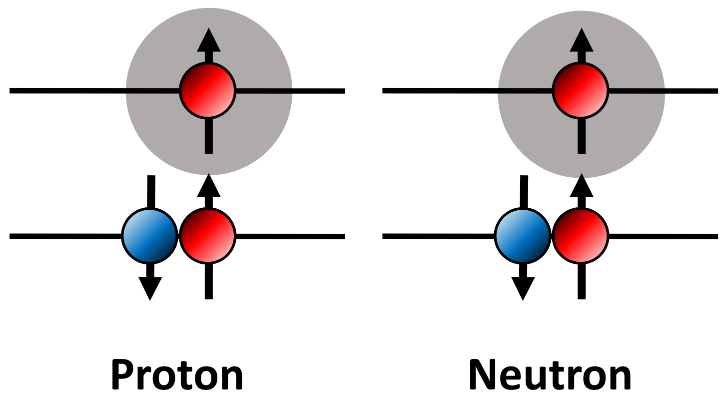


Neutron

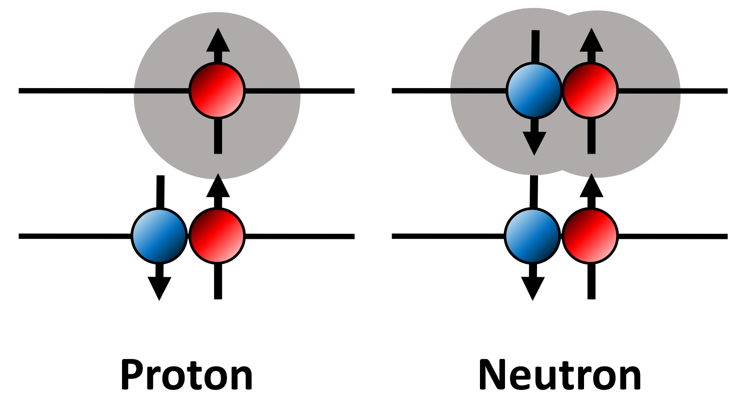
Charge = 0
Spin = 1/2

I (Nuclear spin quantum number)

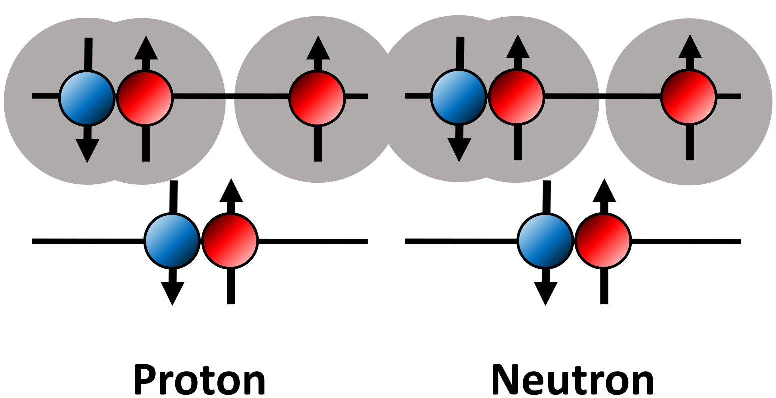
I = 1
^{6}Li



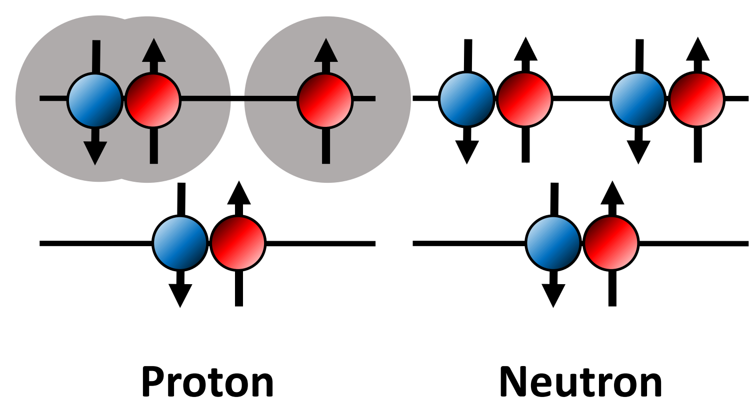
I = 3/2
^{7}Li



I = 3
^{10}B



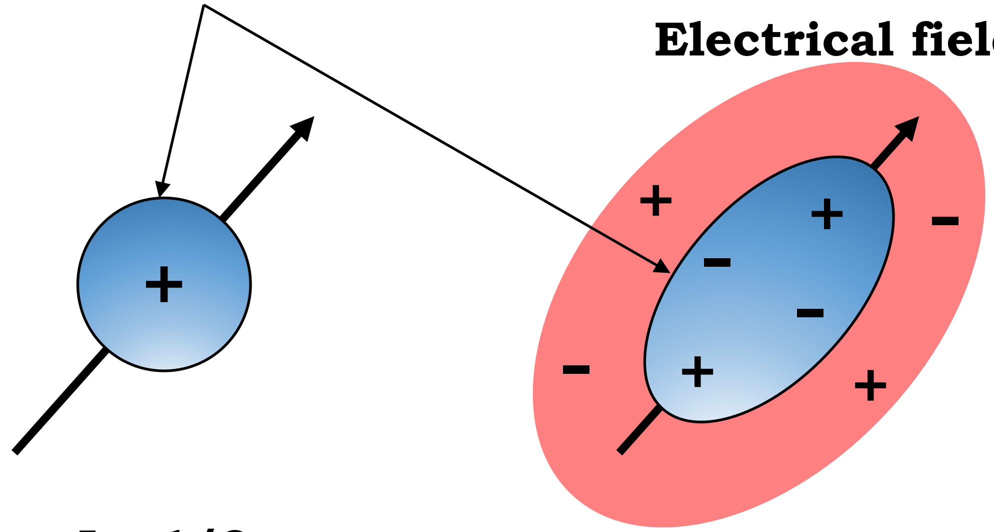
I = 3/2
^{11}B



I (Nuclear spin quantum number)

Nuclear charge distribution

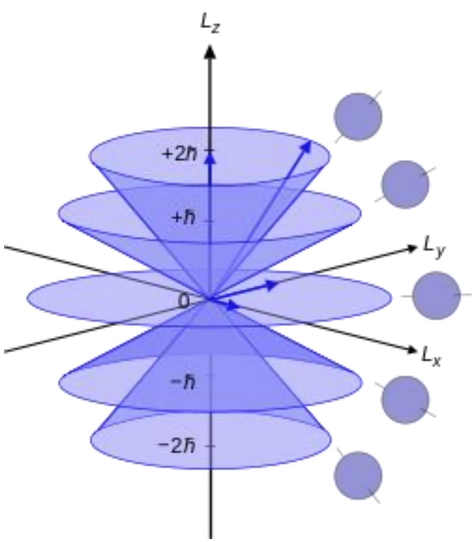
Electrical field gradient



I = 1/2

I > 1/2

<2nl+1 rule>



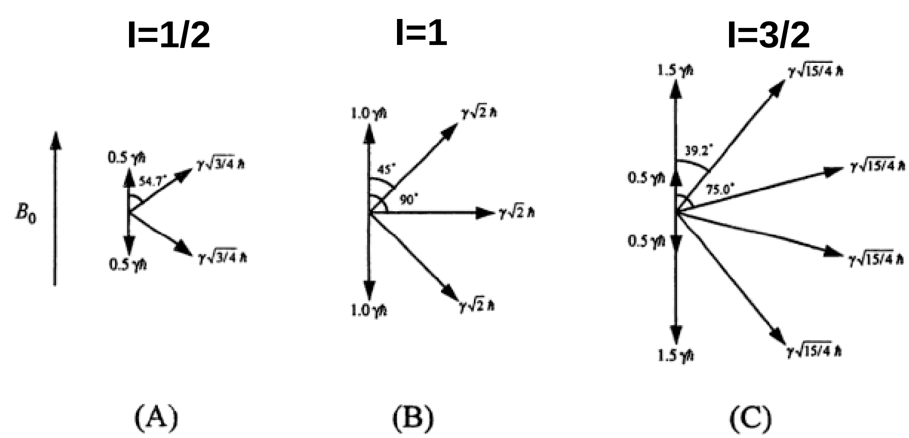
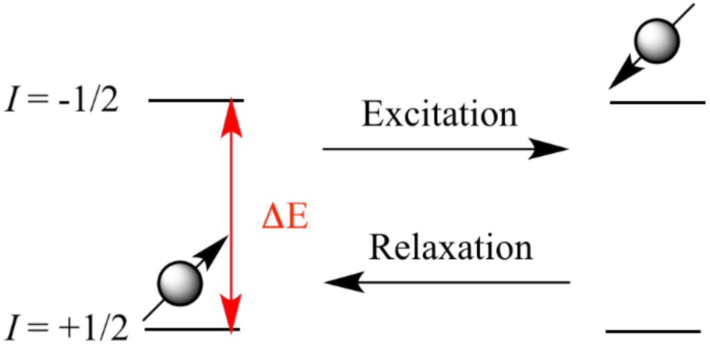


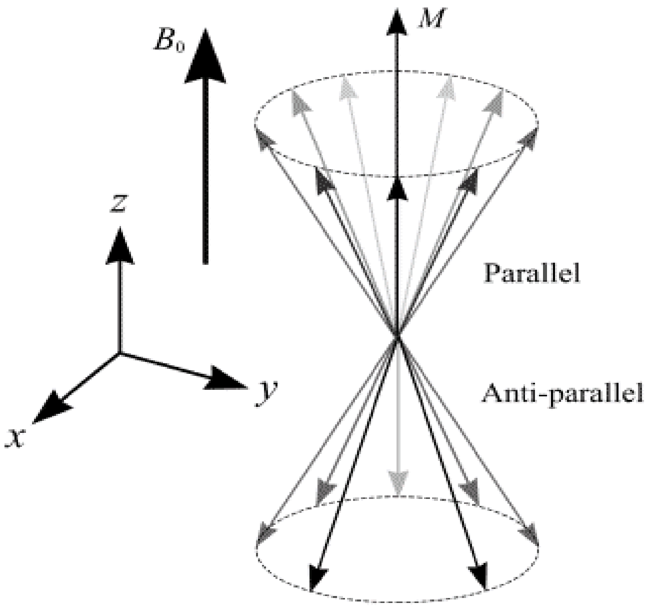
Figure 1.5 The actual magnitudes of nuclear magnetic moment vectors and their components along the z axis for nuclei with (A) spin-$\frac{1}{2}$, (B) spin-1, and (C) spin-3/2.

M_Z (Net magnetization)



Ground state
Lowest energy state

Excited state
Highest energy state



NMR

M_Z (Net magnetization)

Energy term

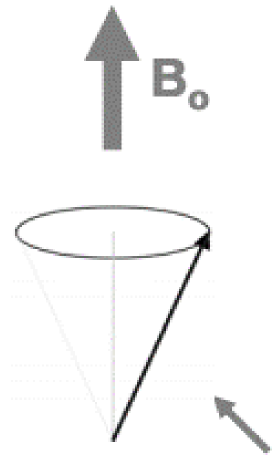
$\frac{N^-}{N^+} = \exp(\frac{-\Delta U}{kT}) = \exp(\frac{-h\omega_0}{kT})$

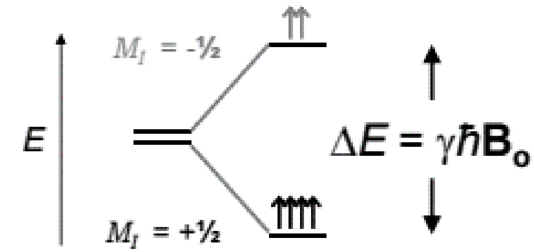
$\omega^0 = -\gamma \mathbf{B}_0$

$\frac{N_{antipar}}{N_{par}} = e^{-\frac{\Delta E}{kT}}$

$\frac{N_a}{N_b} = e^{\frac{\gamma h B_0}{kT}}$

$$E_m = \frac{\gamma n h}{2\pi} B_0$$





$\Delta E = h\nu$

E_m = Energy of quantum state m (J)
γ = Gyromagnetic ratio ($T^{-1}s^{-1}$)
h = Planck`s constant ($6.628 \times 10^{-34}\ J\ s$)
B_0 = Applied magnetic field (2.35 T = 100MHz)

Nuclei precess at the Larmor frequency. → $\nu_0 = \frac{\gamma B_0}{2\pi}$

- Different for different nuclei
- Depends on field strength

$$\Delta E_m = [\tfrac{1}{2} - \left(-\tfrac{1}{2}\right)] \frac{\gamma h}{2\pi} B_0 = \frac{\gamma h}{2\pi} B_0$$

$$\Delta E = \frac{(2.68 \times 10^8\ T^{-1}s^{-1})(6.628 \times 10^{-34}\ Js)(9.38\ T)}{2\pi} = 2.650 \times 10^{-25}\ J$$

$$V = \frac{\Delta E}{h} = \frac{2.650 \times 10^{-25}\ J}{6.626 \times 10^{-34}\ Js} = 400 \times 10^6\ s^{-1} = 400\ MHz$$

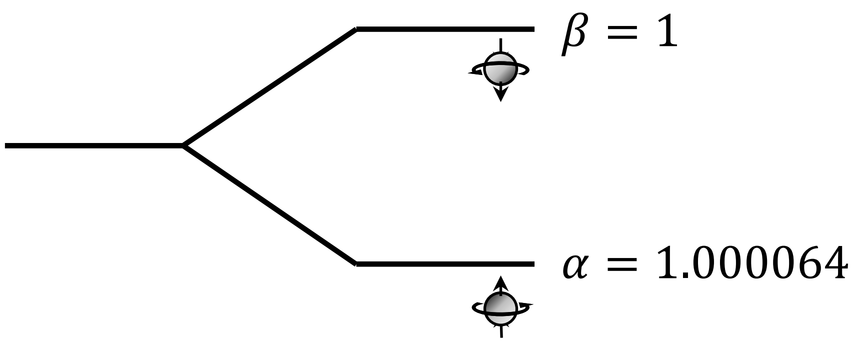
Boltzmann distribution

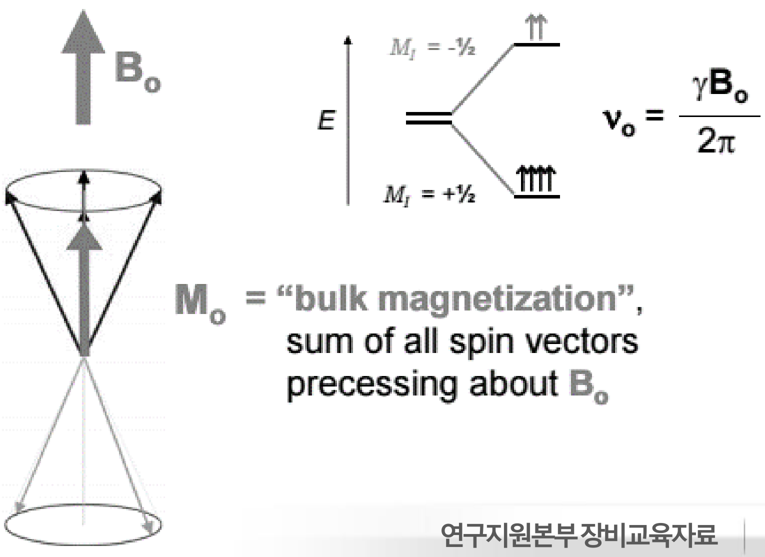
$$V = \frac{N_\beta}{N_\alpha} = e^{\frac{\Delta E}{kT}}$$

For $^{1}H\ \ in\ 9.38\ T\ magnet\ field$

$$\frac{N_\beta}{N_\alpha} = e^{\frac{2.650 \times 10^{-25}\ J}{(1.38 \times 10^{-23}\ J/K)(298\ K)}} = e^{0.0000403} = 1.000064$$

$\alpha : \beta = 1.000064 : 1 \quad \rightarrow \quad 10^{-5}\ (Thermal\ Equilibration)$





Factors of sensitivity

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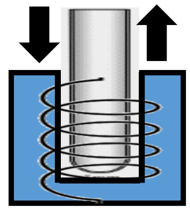
L-N2 (77K) -> S/N ratio = 2~3 times
L-He (4K) -> S/N ratio = 4 time

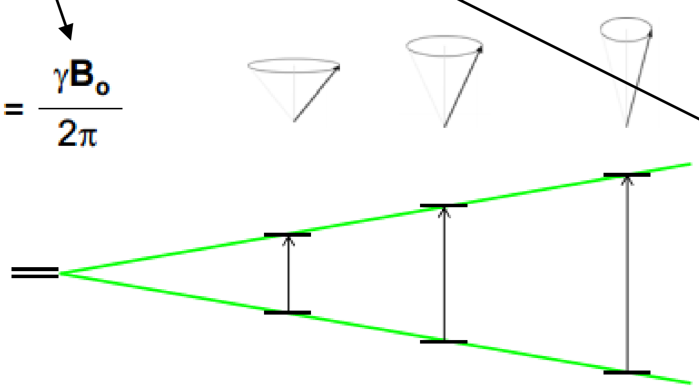
$$\frac{N_\beta}{N_\alpha} = e^{-\left(\frac{\gamma h B_0}{2\pi k T}\right)}$$

To enhance sensitivity

$B_0 \uparrow \quad \gamma \uparrow \quad T \downarrow$



$$\nu_o = \frac{\gamma B_o}{2\pi}$$



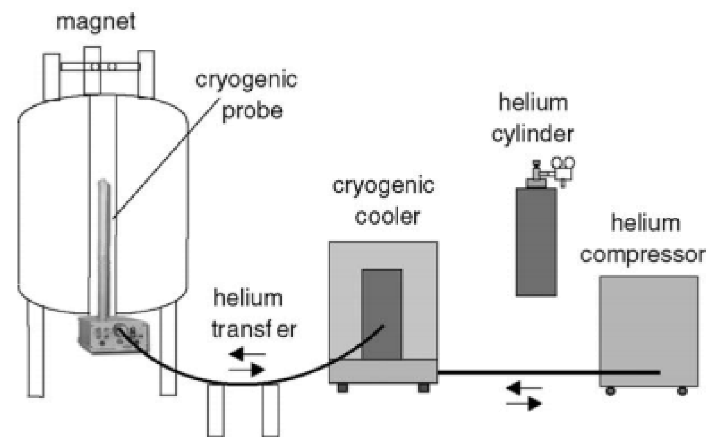
B_o	4.73 T	9.46 T	11.75 T
ν_o (^1H)	200 MHz	400 MHz	500 MHz
ν_o (^{13}C)	50 MHz	100 MHz	125 MHz

100 MHz = 2.35 T

Nuclei of Major Interest to NMR Spectroscopists

	Isotope	Abundance (%)	Z	Spin	μ^a	$\gamma \times 10^{-8b}$	Relative[c] sensitivity	ν_0 at 1T (MHz)
great nucleus.	^1H	99.9844	1	1/2	2.7927	2.6752	1	42.577
	^2H	0.0156	1	1	0.8574	0.4107		6.536
	^{10}B	18.83	5	3	1.8006	0.2875		4.575
	^{11}B	81.17	5	3/2	2.6880	0.8583		13.660
not so great.	^{13}C	1.108	6	1/2	0.7022	0.6726	X 32	10.705
	^{14}N	99.635	7	1	0.4036	0.1933		3.076
poor.	^{15}N	0.365	7	1/2	−0.2830	−0.2711	X 300	.315
also great.	^{19}F	100	9	1/2	2.6273	2.5167	0.83	40.055
	^{29}Si	4.70	14	1/2	−0.5548	−0.5316		8.460
also great.	^{31}P	100	15	1/2	1.1305	1.0829	6.65×10^{-2}	17.235

[a] Magnetic moment in units of the nuclear magneton, $eh/(4\pi M_p c)$.
[b] Magnetogyric ratio in SI units.
[c] For equal numbers of nuclei at constant field.



S/N (Signal to Noise) ratio

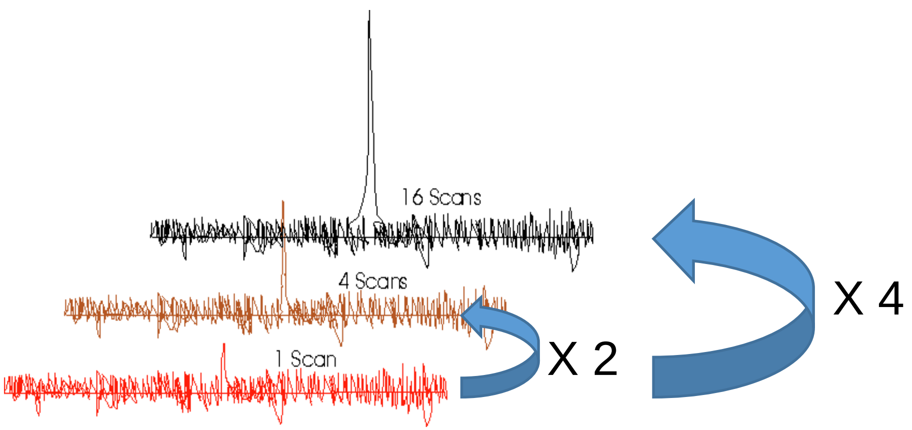
$$S/N \sim n\,\gamma^{5/2}\,B_0^{\;3/2}\,(NS)^{1/2}$$

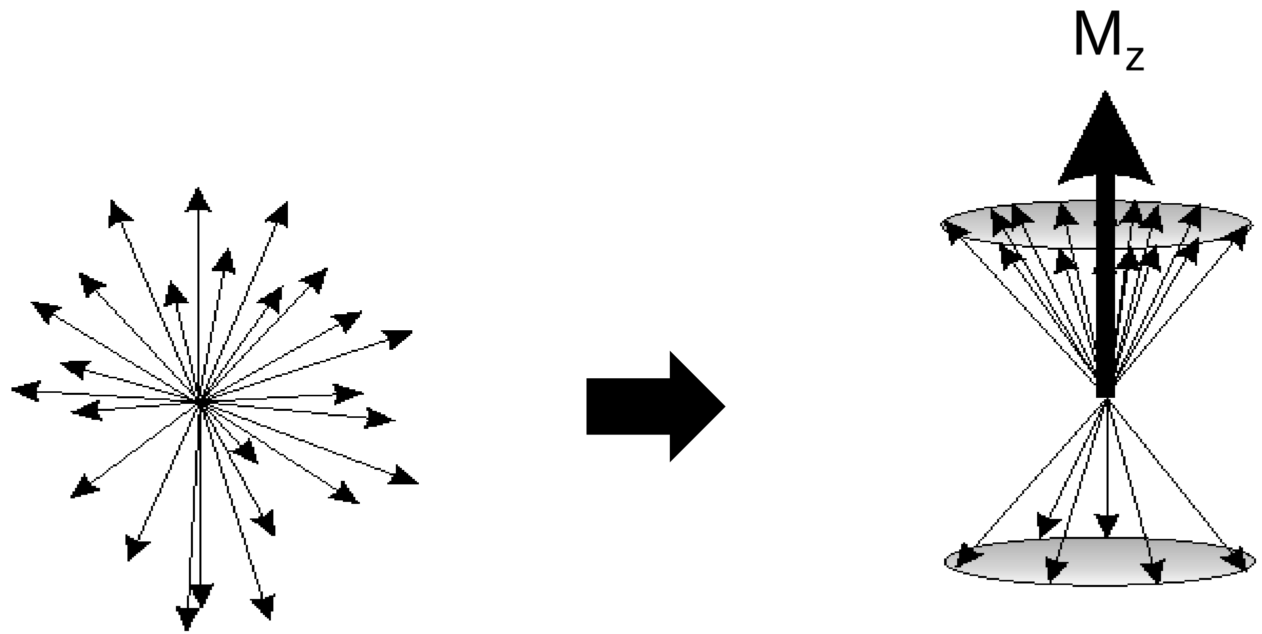
Number of spins　　Number of scans

1. 핵의 개수에 비례(몰수, 몰농도에 비례)
2. 비교자기장/기존자기장의 3/2 제곱만큼 감도 상승
3. 스캔수의 ½ 제곱

600 MHz + Cryo(N2) = 950 MHz

	S/N ratio	Time
$\left(\frac{600}{400}\right)^{3/2}$	$= 1.84$	3.38
$\left(\frac{950}{600}\right)^{3/2}$	$= 1.99$	3.96
$\left(\frac{950}{400}\right)^{3/2}$	$= 3.66$	13.40





No magnetic field (B_0)

Spins in magnetic field (B_0)

3. Pulse sequence

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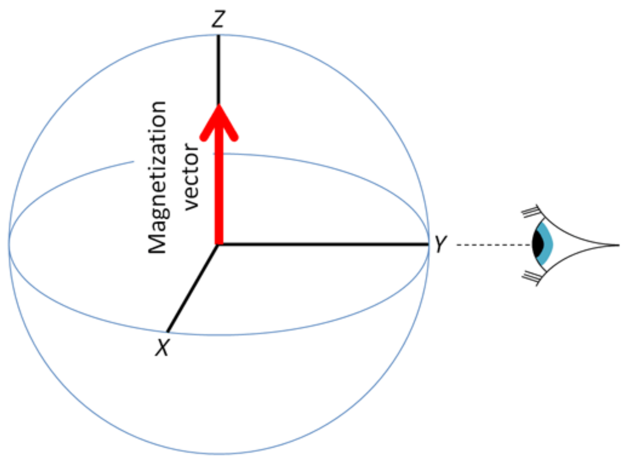
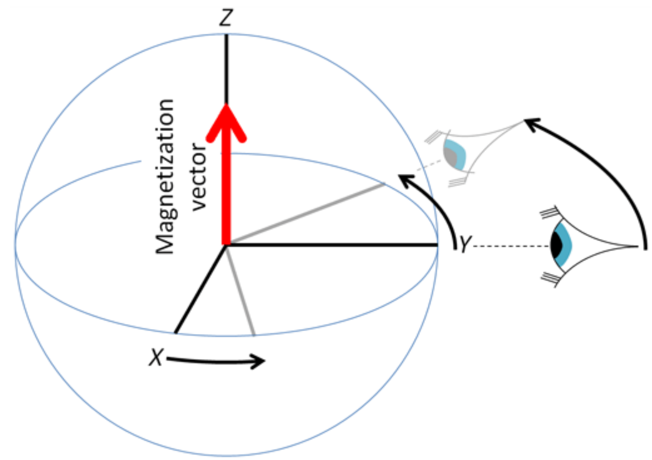
Laboratory & Rotating frame

<Laboratory frame>



<Rotating frame>

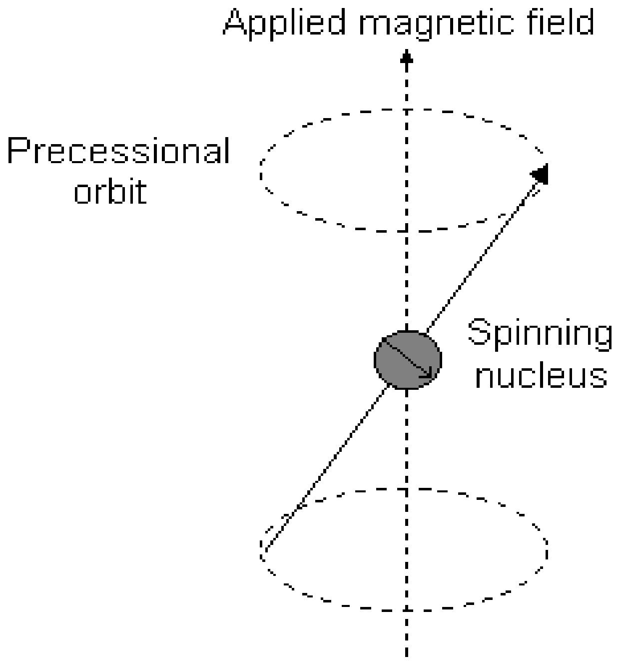


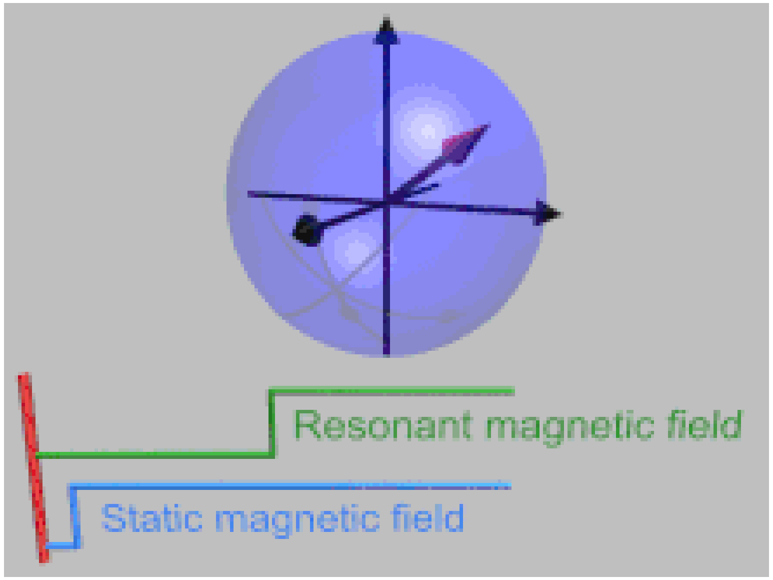
Merry-go-round viewed from the laboratory frame

Merry-go-round viewed from the rotating frame

http://chem.ch.huji.ac.il/nmr/techniques/1d/pulseq.htm

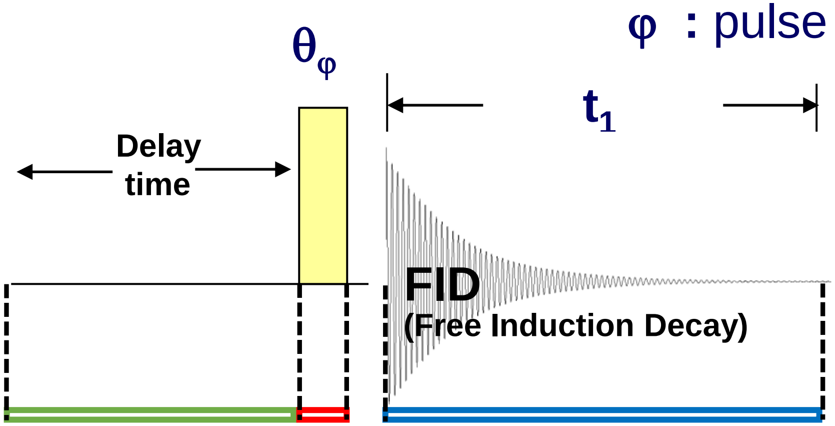
Laboratory & Rotating frame

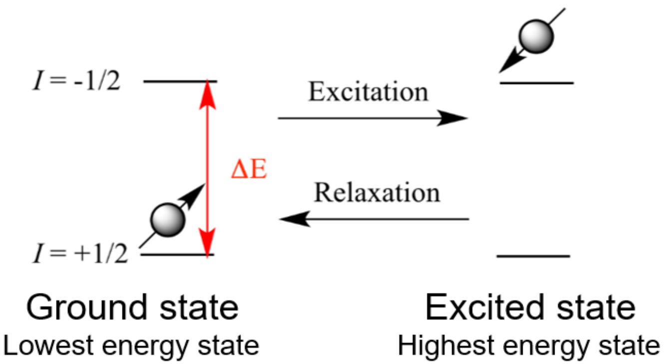




Basic 1D NMR

θ : pulse width(μs)
φ : pulse phase

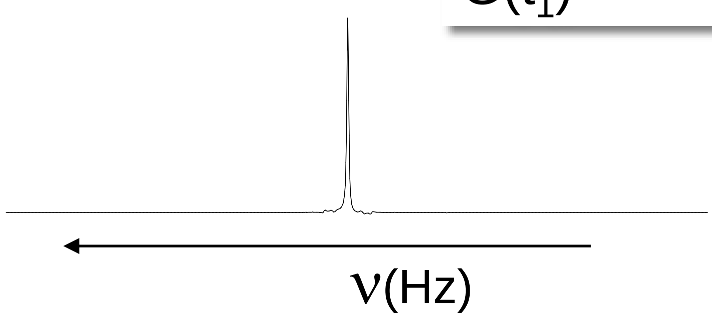




NMR

Fourier Transformation

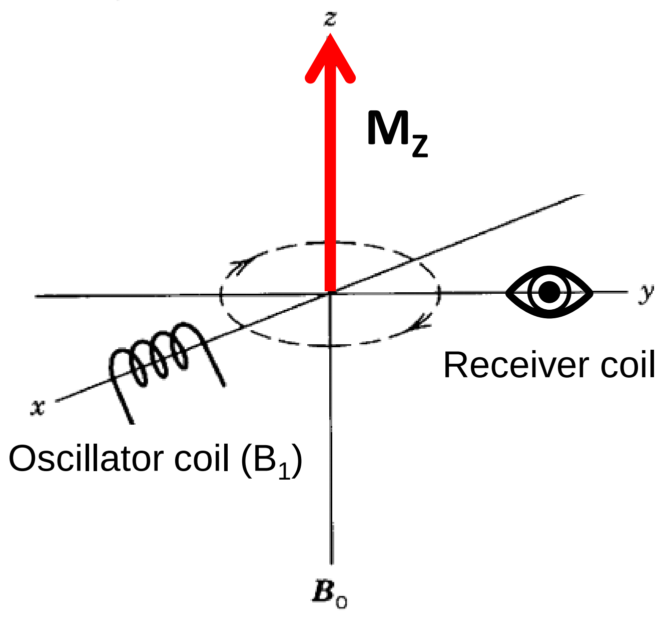
$$G(t_1) \xrightarrow{FT} g(f_1)$$

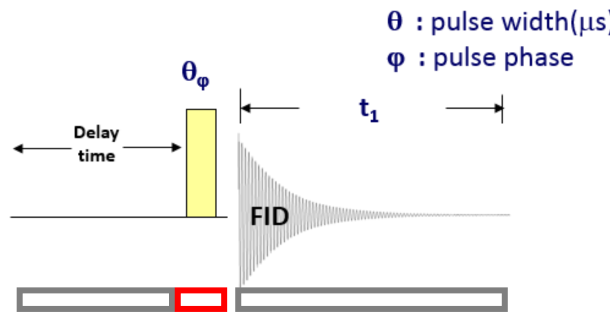


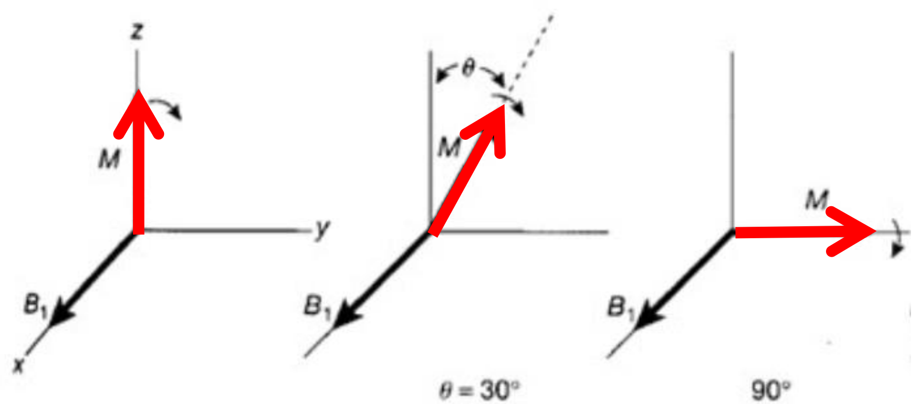
Parameter

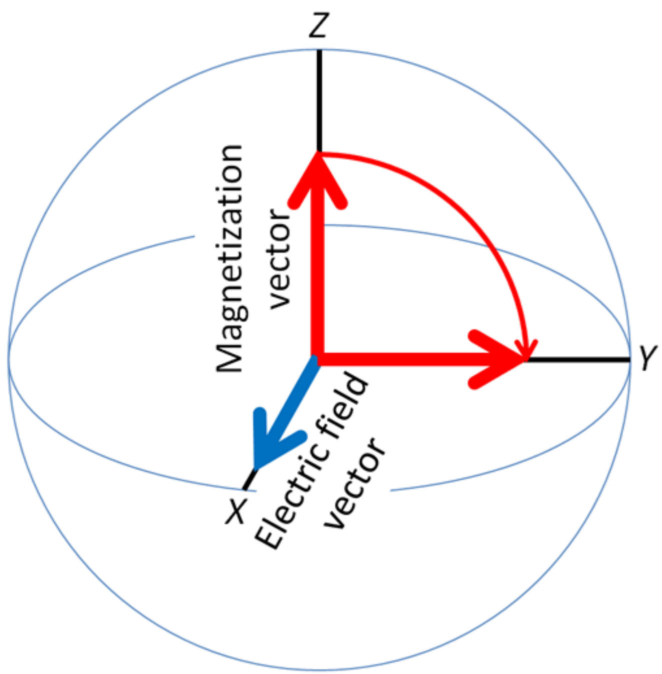
- D1 (Relaxation delay time)
- P1 (Pulse width)
  PLW1 (Power level)
- AQ (Acquisition time)

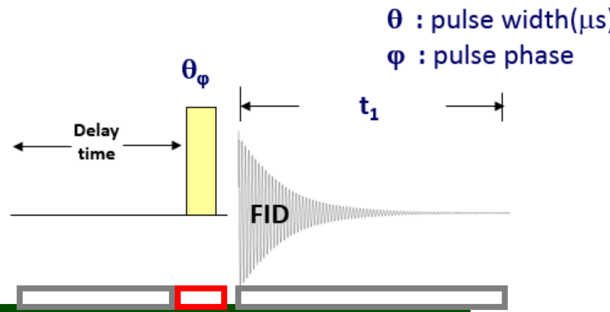
Excitation


z
M_Z
y
Receiver coil
x
Oscillator coil (B_1)
B_0

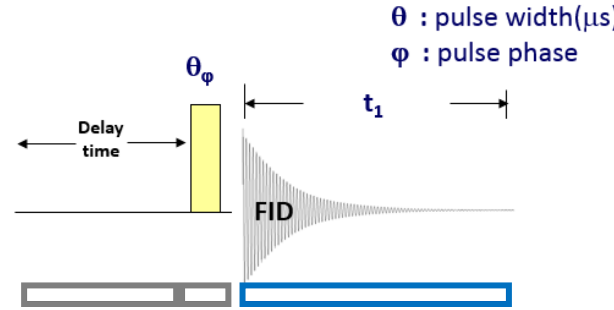

θ : pulse width(μs)
φ : pulse phase
θ_φ
Delay time
t_1
FID


z
M
y
B_1
x
θ
M
B_1
θ = 30°
M
B_1
90°


Z
Magnetization vector
Y
X
Electric field vector

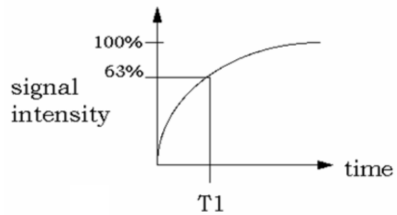

θ : pulse width(μs)
φ : pulse phase
θ_φ
t_1
Delay time
FID

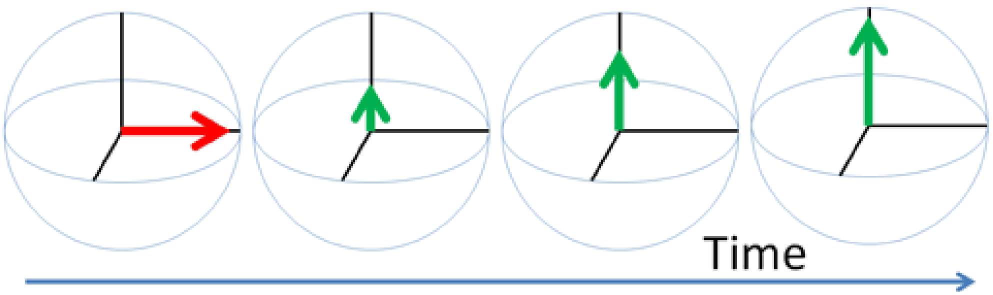
Relaxation



T1 relaxation (recovery)

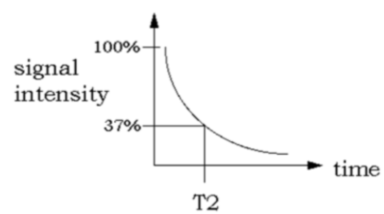
- longitudinal relaxation
- spin-lattice relaxation

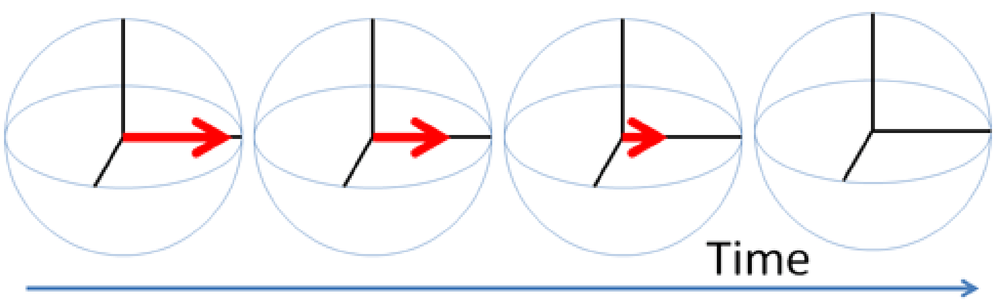


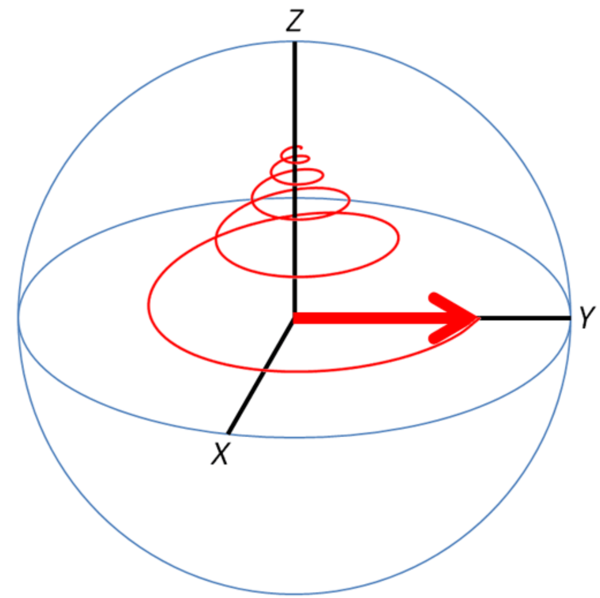


T2 relaxation (decay)

- transverse relaxation
- spin-spin relaxation

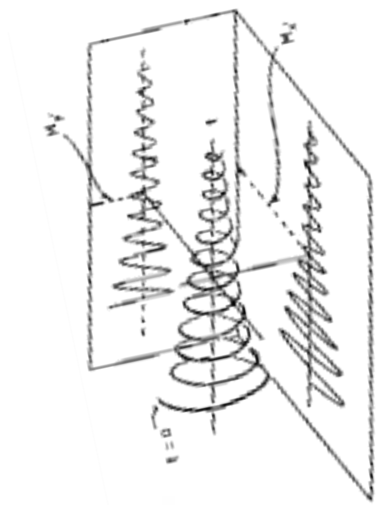


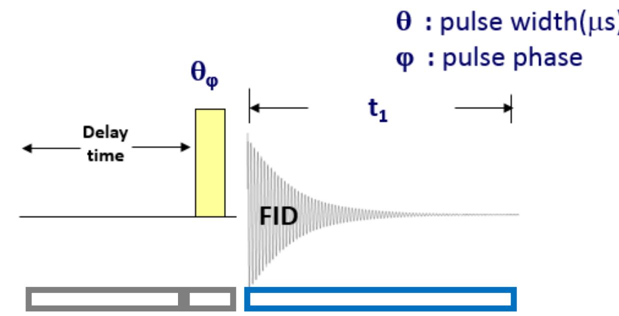


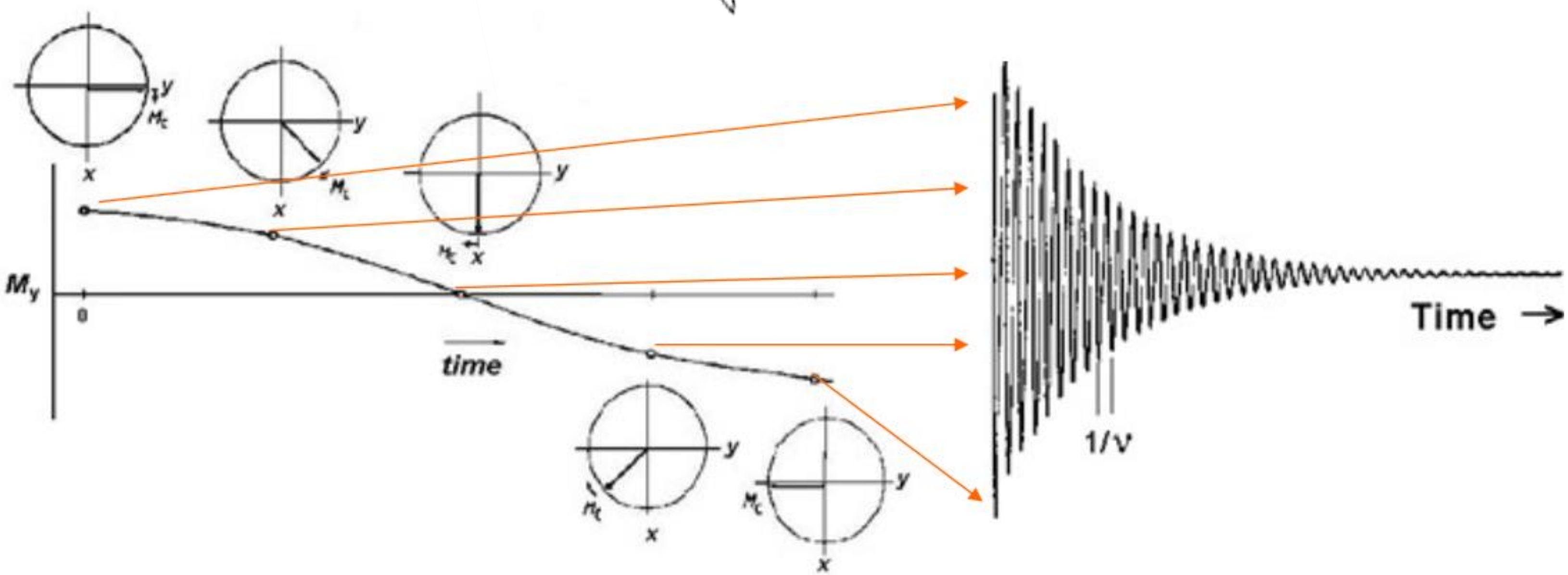


http://www.youtube.com/watch?v=ZHtfnNAz-UM&list=PL40F1EE0DF59D777A
http://www.youtube.com/watch?v=LvyADhrgc_s&list=PL40F1EE0DF59D777A

FID (Free Induction Decay)

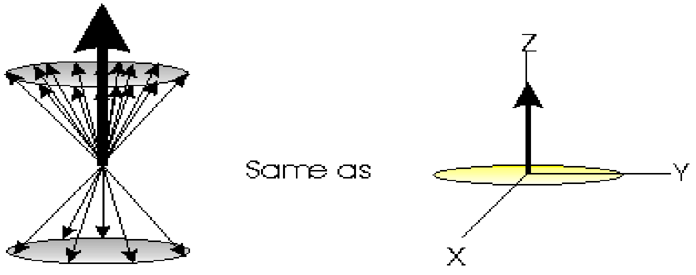


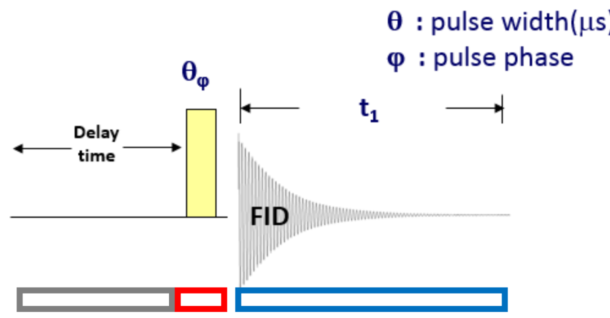


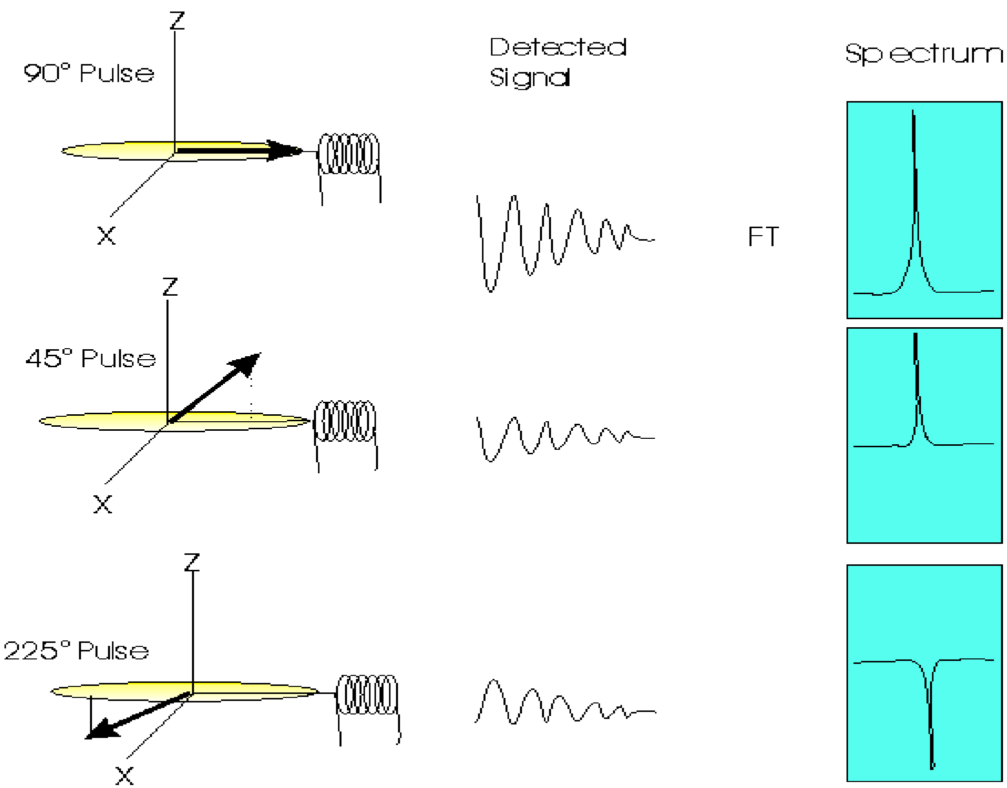


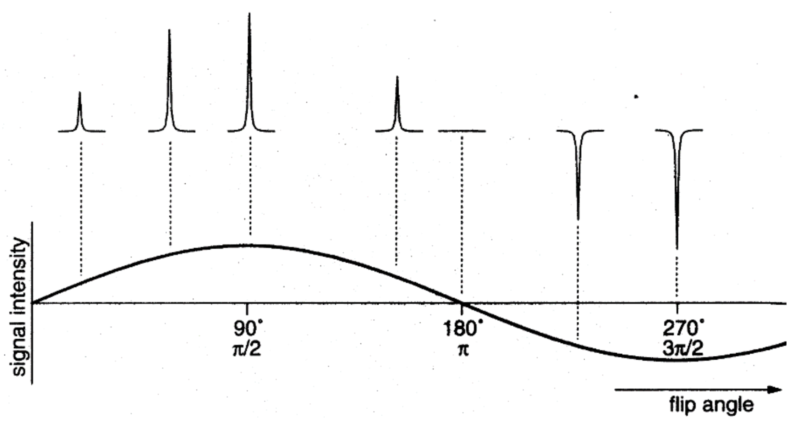
https://www.youtube.com/watch?v=lKp67IqQjH4&index=1&list=PL40F1EE0DF59D777A

Pulse width (pw) 90°



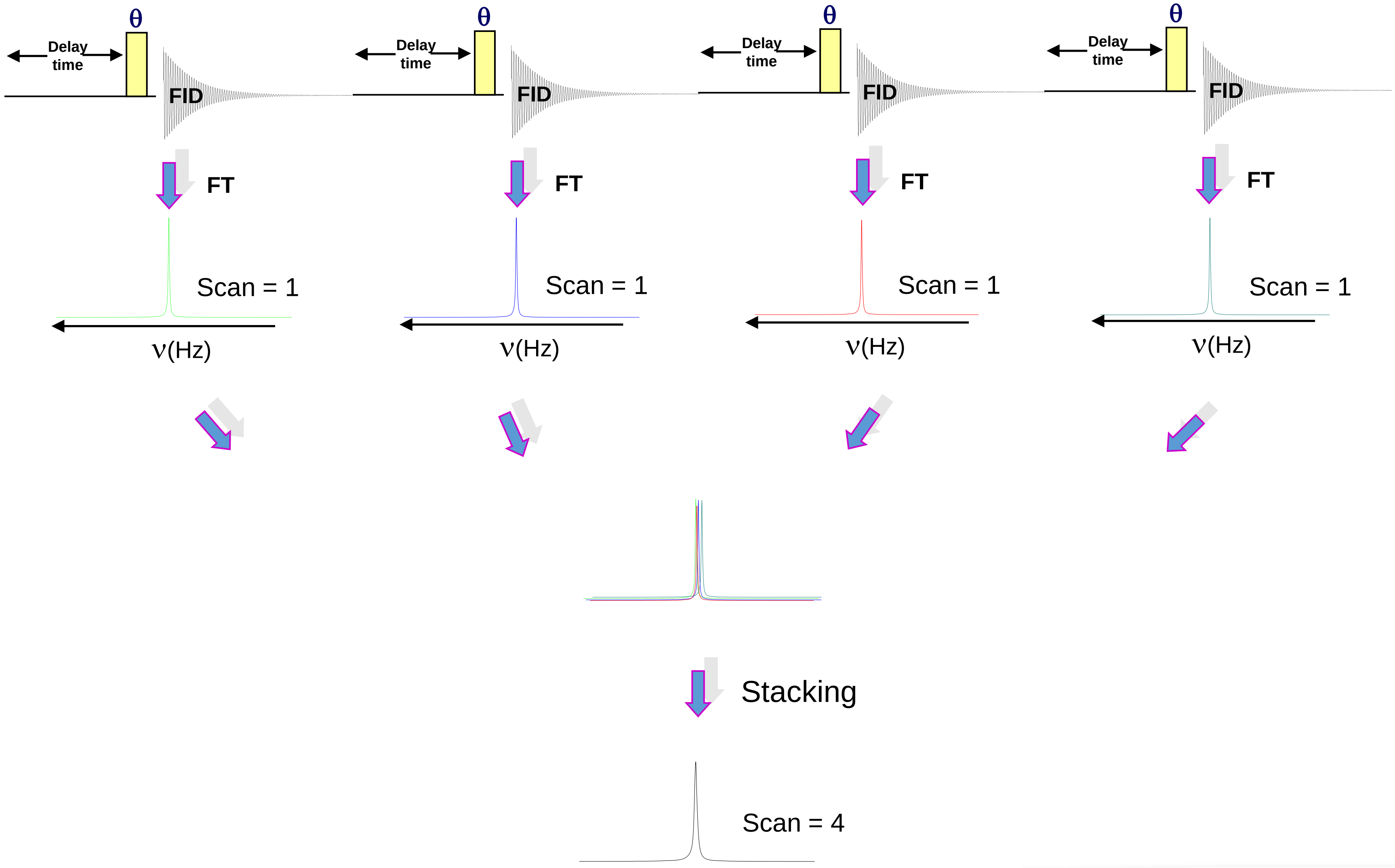




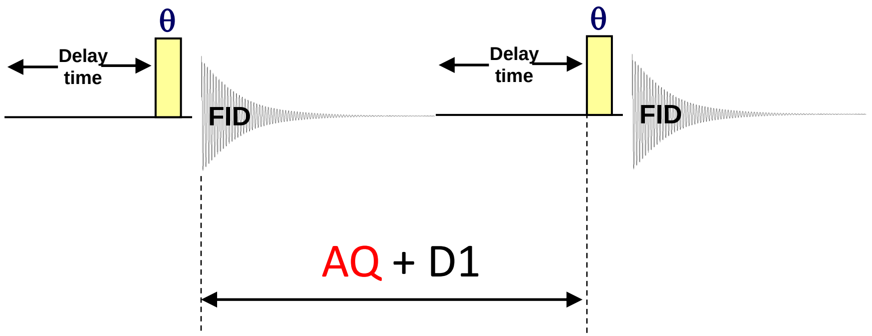


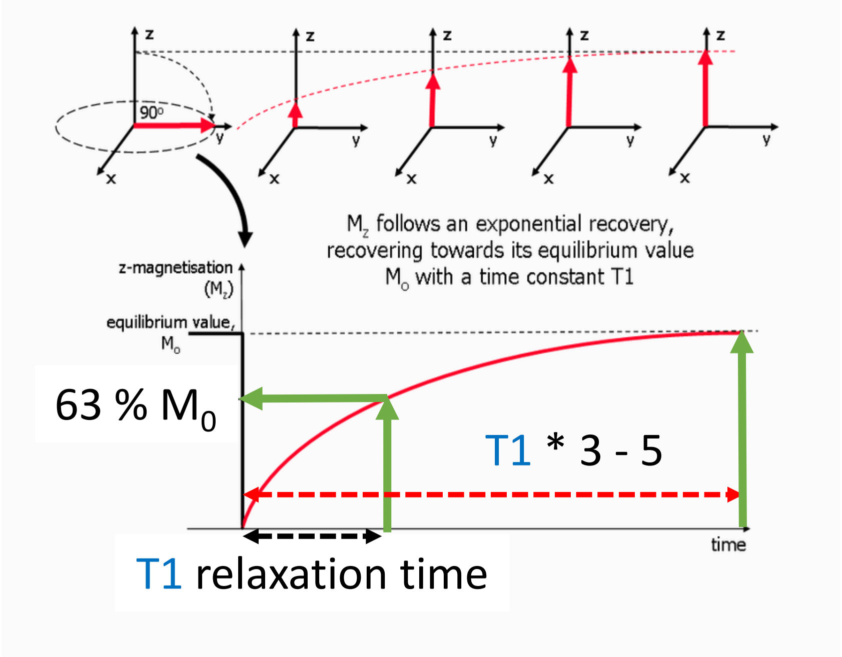
Data acquisition process

For example, number of scan = 4



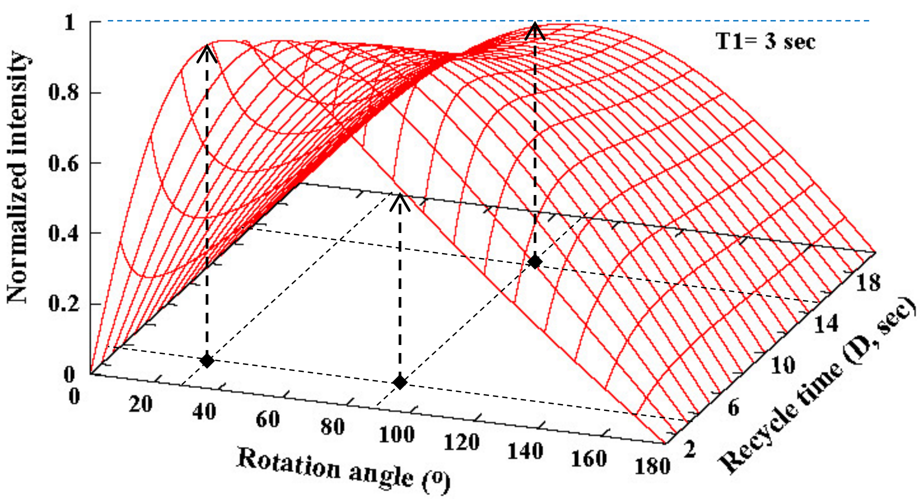
D1 (Recycle delay time for Quantitative NMR)





AQ + D1 = T1 * 1.3 **(Maximum S/N ratio)**
= T1 * 3 (Integration accuracy = 90 %)
= T1 * 5 **(Integration accuracy = 99 %)**
= T1 * 7 (Integration accuracy = 99.9 %)

Figure 2: Sensitivity Dependence on Rotation Angle and Recycle Time

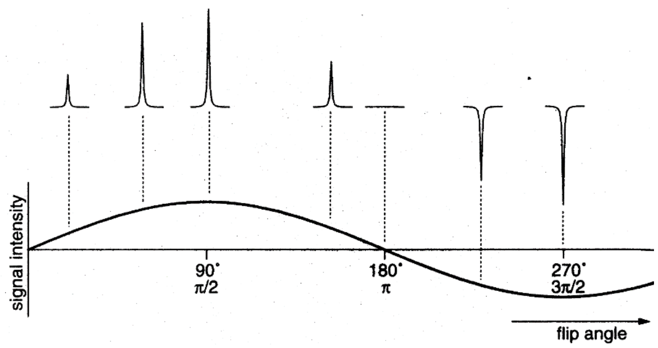


T1 = 3 s
AQ + D1 = T1 * 5
AQ + D1 = 15 s for 90°
AQ + D1 = 5 s for 30° [1/3]
(Low angle = short experiment time)

Parameter calibration

1. Find **P1** (for 90 °, maximum intensity)

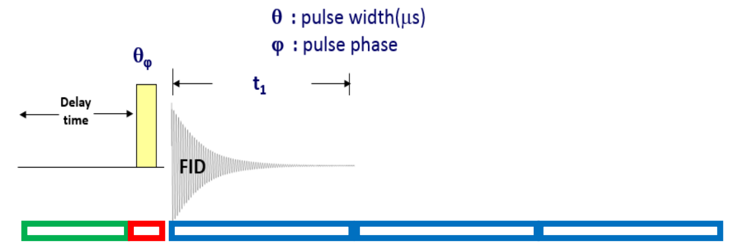
1) Find P1 for 180 ° (zero intensity)
2) ½ (P1 for 180 °) = P1 for 90 °

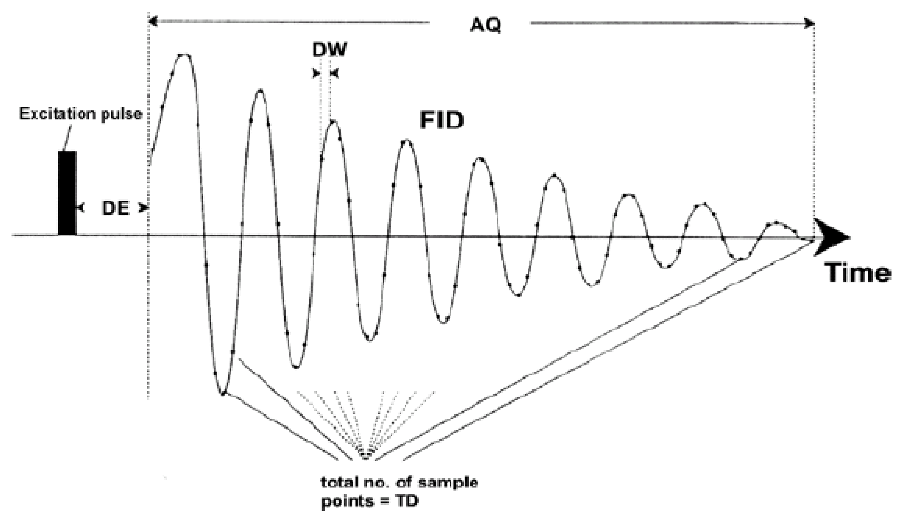


2. Find **D1**
1) AQ + D1 = T1 * 3 ~ 5
2) Measure T1 relaxation time
   a. t1ir1d (Find D7null, short exp.)
   b. t1ir (Find T1, long exp.)

T1 * ln(2) = D7null
T1 = D7null * 1.443

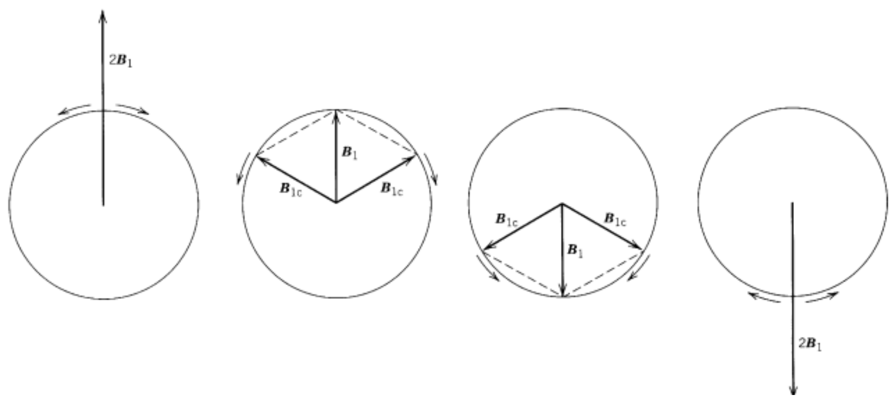
3. Find **AQ**
1) **AQ** = FID * 2 – 3
= dwell time * complex point

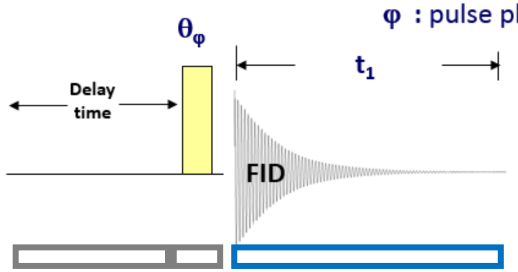


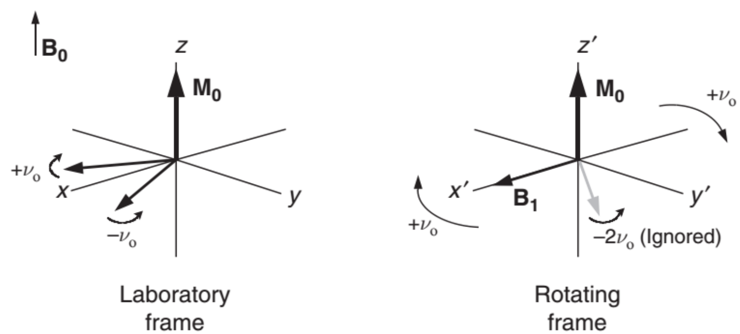


T2 relaxation

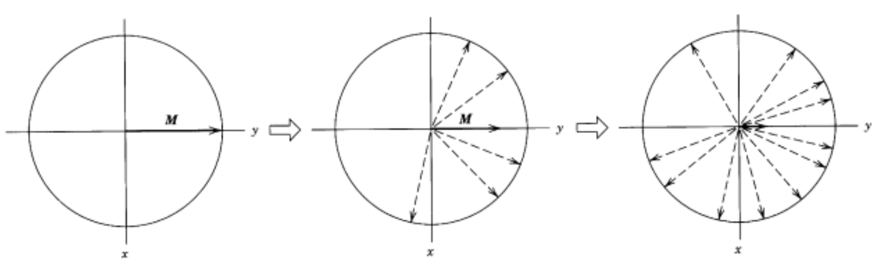
T2





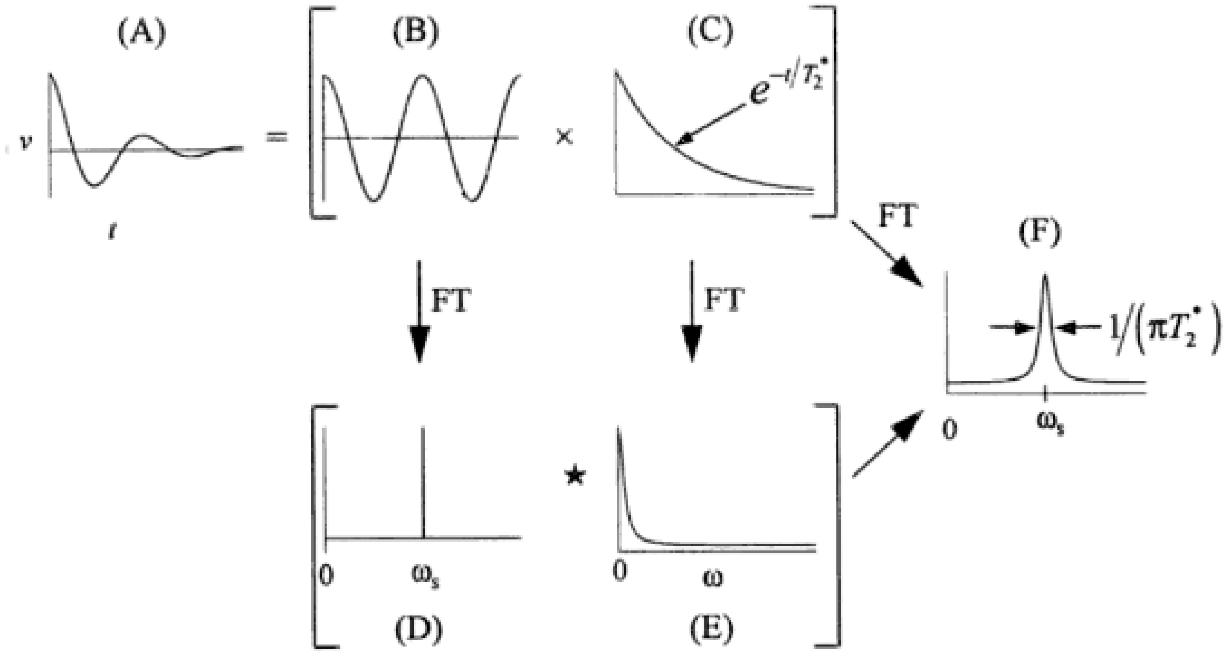


T2*



http://chem.ch.huji.ac.il/nmr/techniques/1d/pulseq.htm

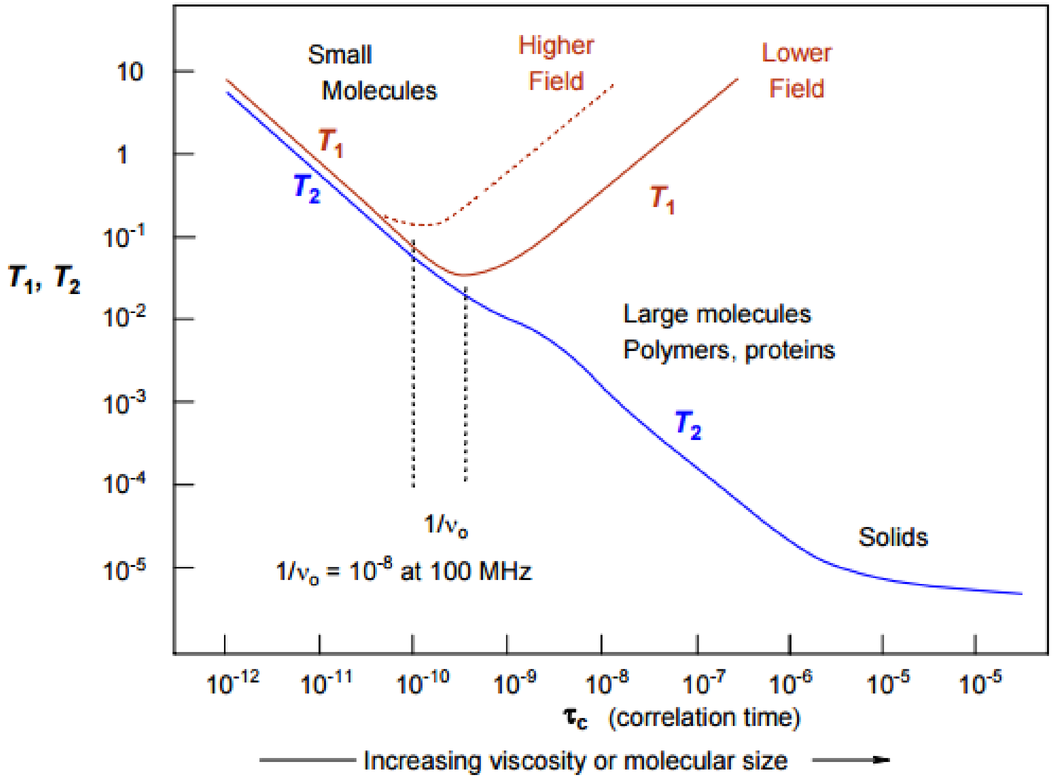
T_2* relaxation time (T_2 in rotating frame)



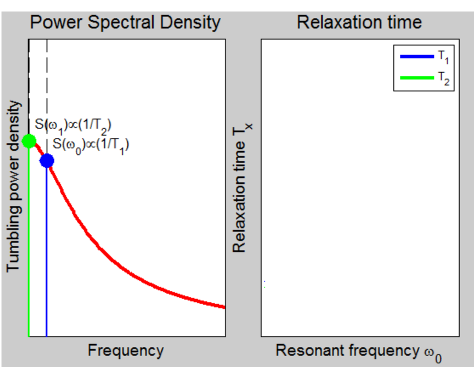
$$\Delta\nu \cdot \Delta t \geq 1$$

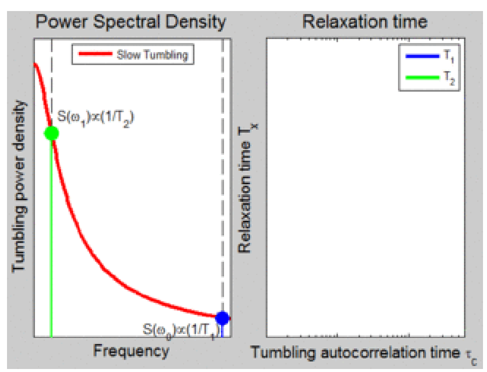
If Δt (i.e., T_2*) is small, then $\Delta\nu$ is large, and the peak is therefore broad. T_2*, whose major component is field inhomogeneity is the principal determining factor for peak width since T_2* is always less than T_1 or T_2.

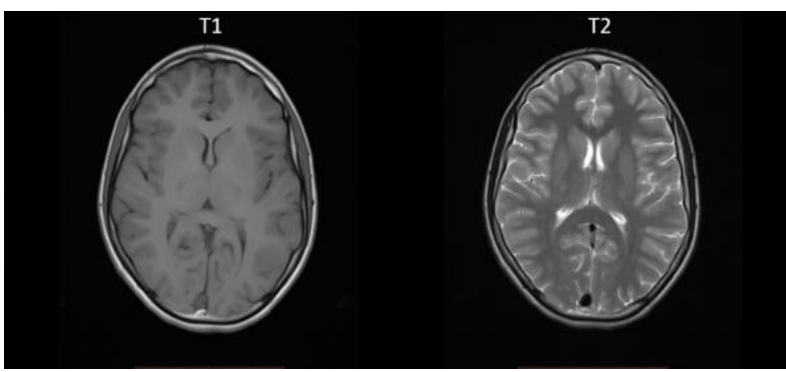
Tumbling rate vs Magnetic field



Tissue	T1 (msec)	T2 (msec)
Water/CSF	4000	2000
Gray matter	900	90
Muscle	900	50
Liver	500 **Dark**	40 **Dark**
Fat	250 **Bright**	70 **Bright**
Tendon	400	5
Proteins	250	0.1- 1.0
Ice	5000	0.001

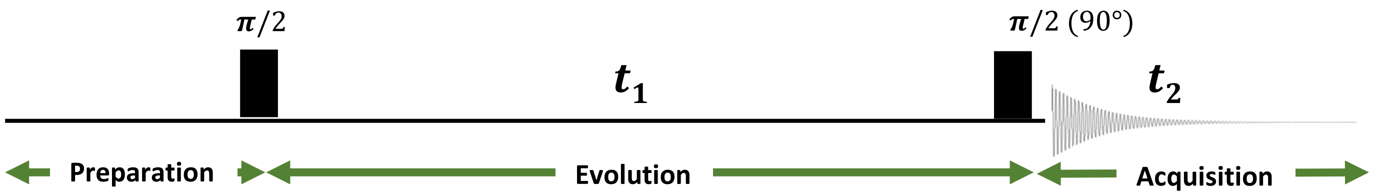




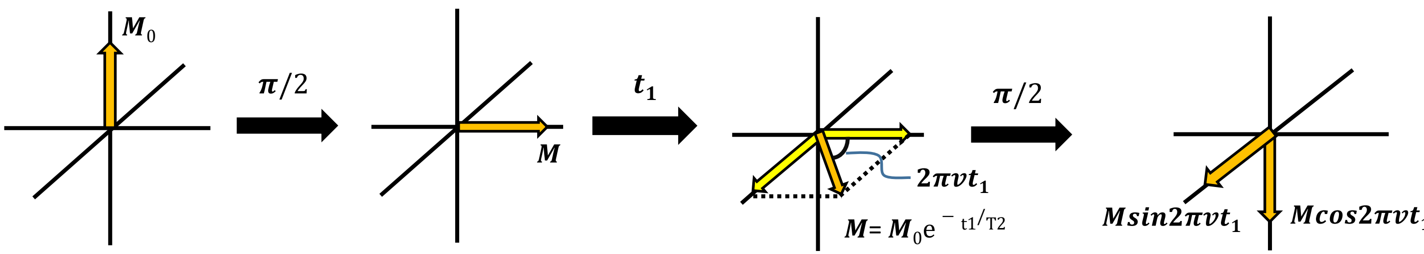


COSY (Correlation SpectroscopY)

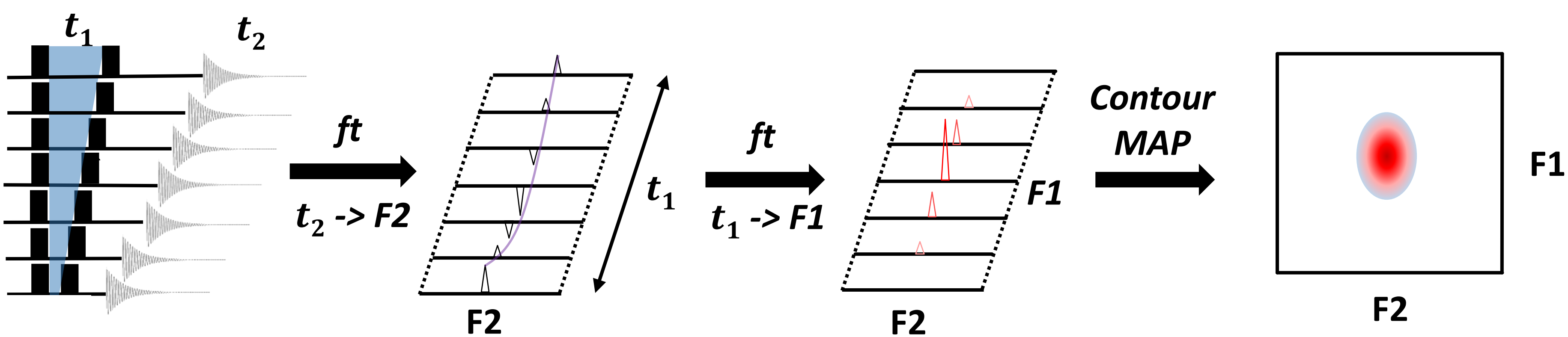
<Pulse sequence of COSY>



<Vector of 2D NMR>



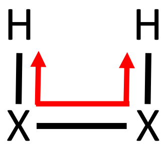
<Example of 2D NMR >



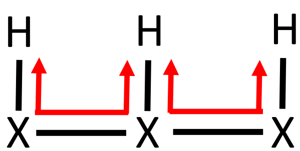
Correlation in 2D NMR

Bonding

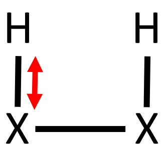
Scalar coupling (J Coupling)



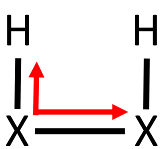
J_{2HH} ~ J_{3HH} — **1H-1H COSY**



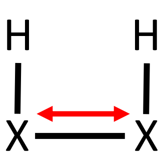
J_{2HH} ~ J_{5HH} — **1H-1H TOCSY**



J_{1HX} — **1H-X HSQC**
1H-X HMQC
X->1H HETCOR



J_{2HX} ~ J_{3HX} — **1H-X HMBC**



J_{1XX} — **X-X COSY**
X-X INADEQUATE
H-X-X-H
AQDEQUATE

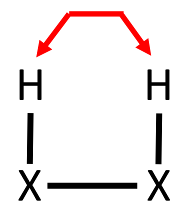
Space

Dipolar coupling

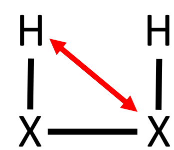
NOESY = Small, Large molecules (along T1)
ROESY = Middle molecules (along T2)

Small < 700 Da < Middle < 1.2 kDa < Large

Distance = 3 ~ 5 Å



1H-1H NOESY
1H-1H ROESY



2D HOESY

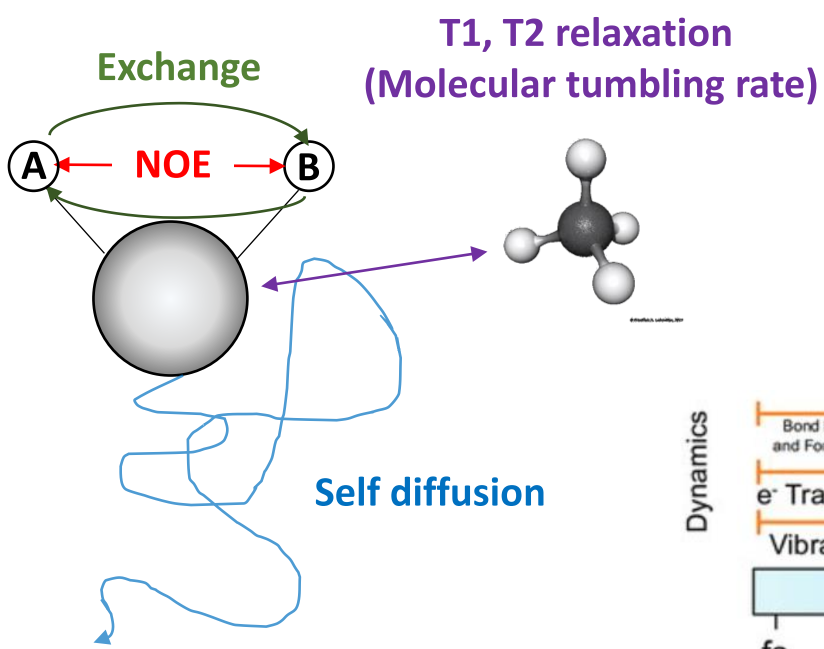
Motion

Self-Diffusion — **DOSY (Diffusion)**

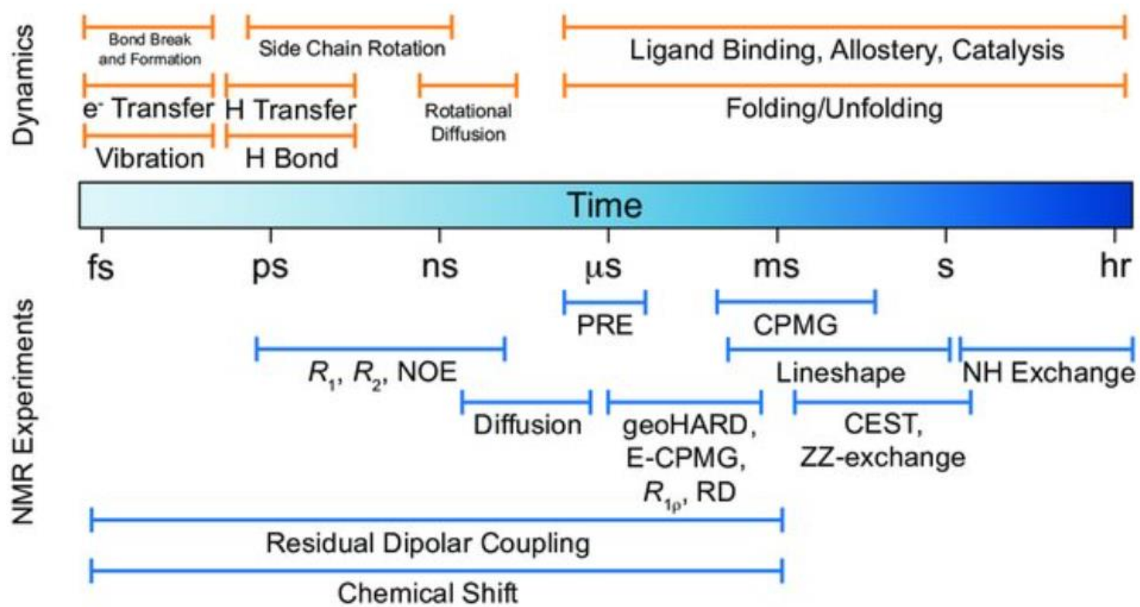
Tumbling — **T1 (Inversion recovery)**
T2 (CPMG)

Protein dynamics elucidated by NMR technique, 2013

Correlation in 2D NMR



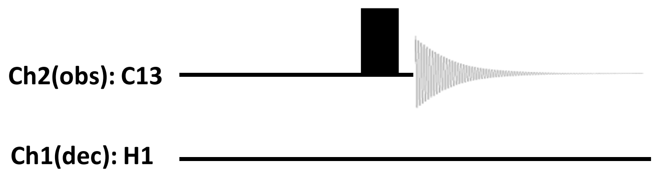
Exchange (EXSY)
NOE (NOESY/ROESY)
Diffusion (DOSY)
T1, T2 (Inversion recovery, CPMG)



Protein dynamics elucidated by NMR technique, 2013

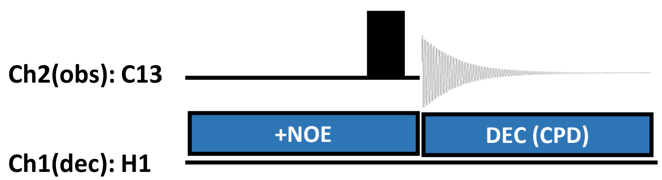
C13 with or without 1H Decoupling

zg (-NOE, -DEC)

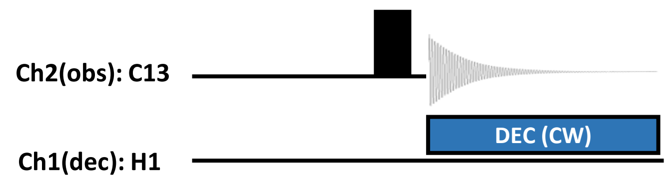


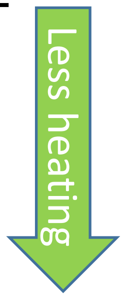
zggd (+NOE, -DEC)

zgdc (+NOE, +DEC)



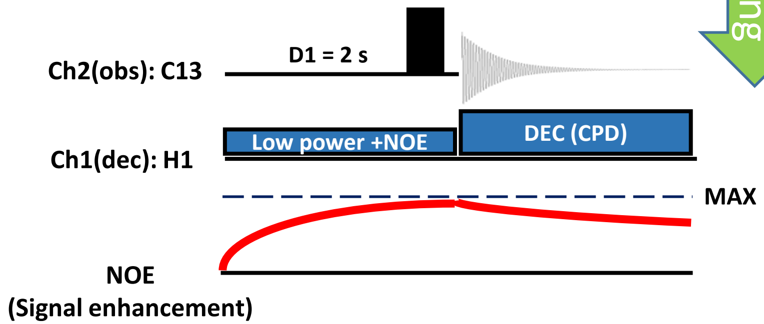
zgcw (-NOE, +DEC_CW)





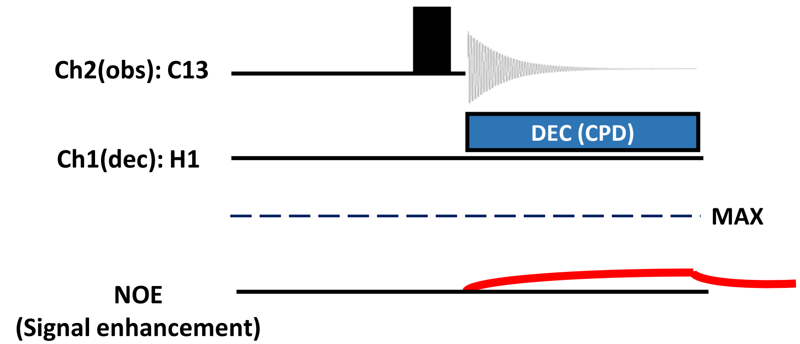
C13CPD

zgpg (+NOE, +DEC_Intensity)



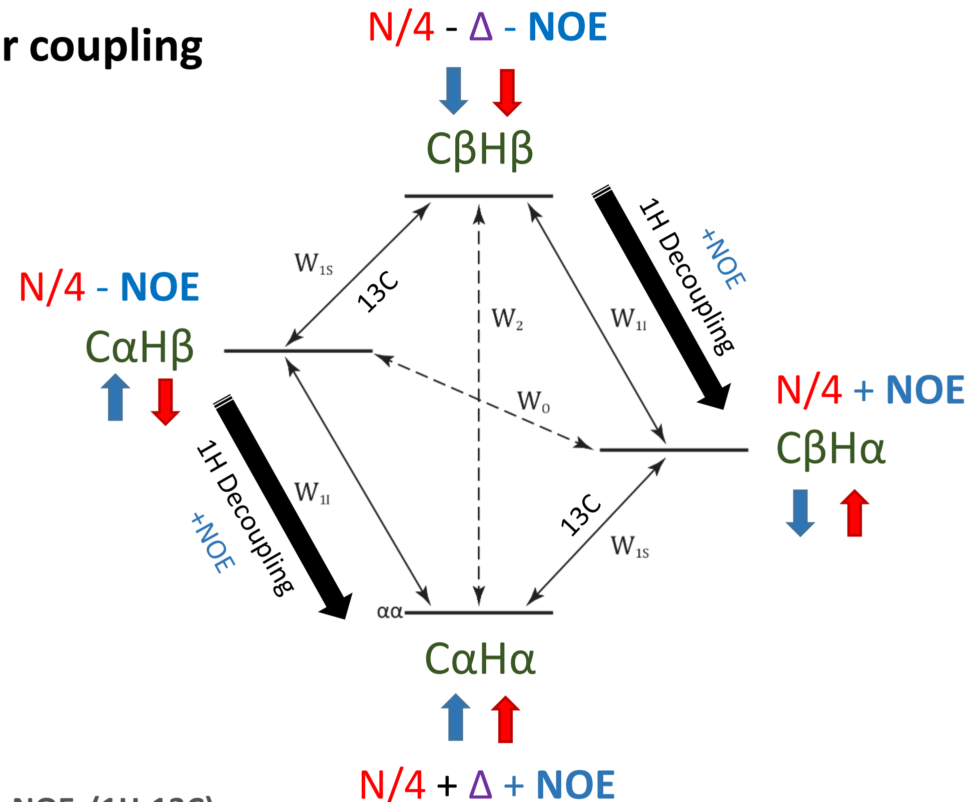
C13IG

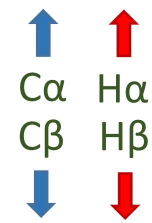
zgig (-NOE, +DEC, Integration)



NOE (Nuclear Overhauser Effect)

Dipolar coupling





W (Transition Probability)

W_0 = Zero quantum

W_1 = Single quantum

W_2 = Double quantum

W_{1L} = 1H transition

W_{1S} = 13C transition

N = Total Nucleus

Δ = Population

Hetero NOE (1H-13C)

$$NOE = 1 + \frac{1}{2} * (\frac{r_H}{r_C})$$

$$NOE = 1 + 1.998$$

$NOE = 3$ (Maximum enhancement)

Cross-relaxation rate

$$NOE = 1 + \frac{1}{2} * \frac{W_2 - W_0}{2w_1 + w_2 + w_0} * (\frac{r_H}{r_C})$$

Total longitudinal dipolar relaxation rate

4. Chemical shift

Electron density

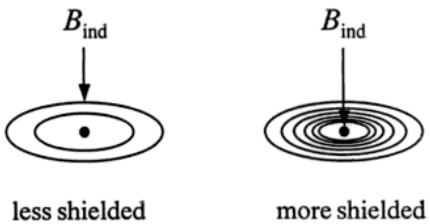
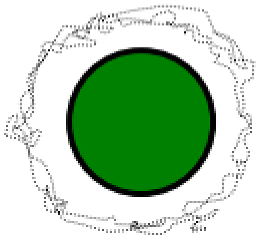
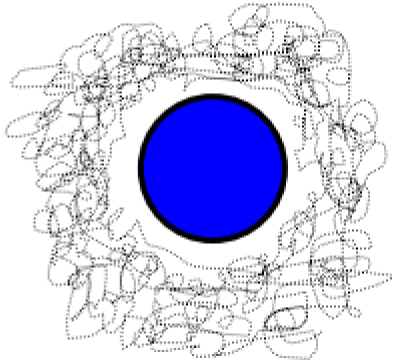


Figure 1.11 Nuclear shielding.



Carbonyl

- Less e- density
- Nucleus 'deshielded' from B_0
- Feels the field (B_{eff}) more

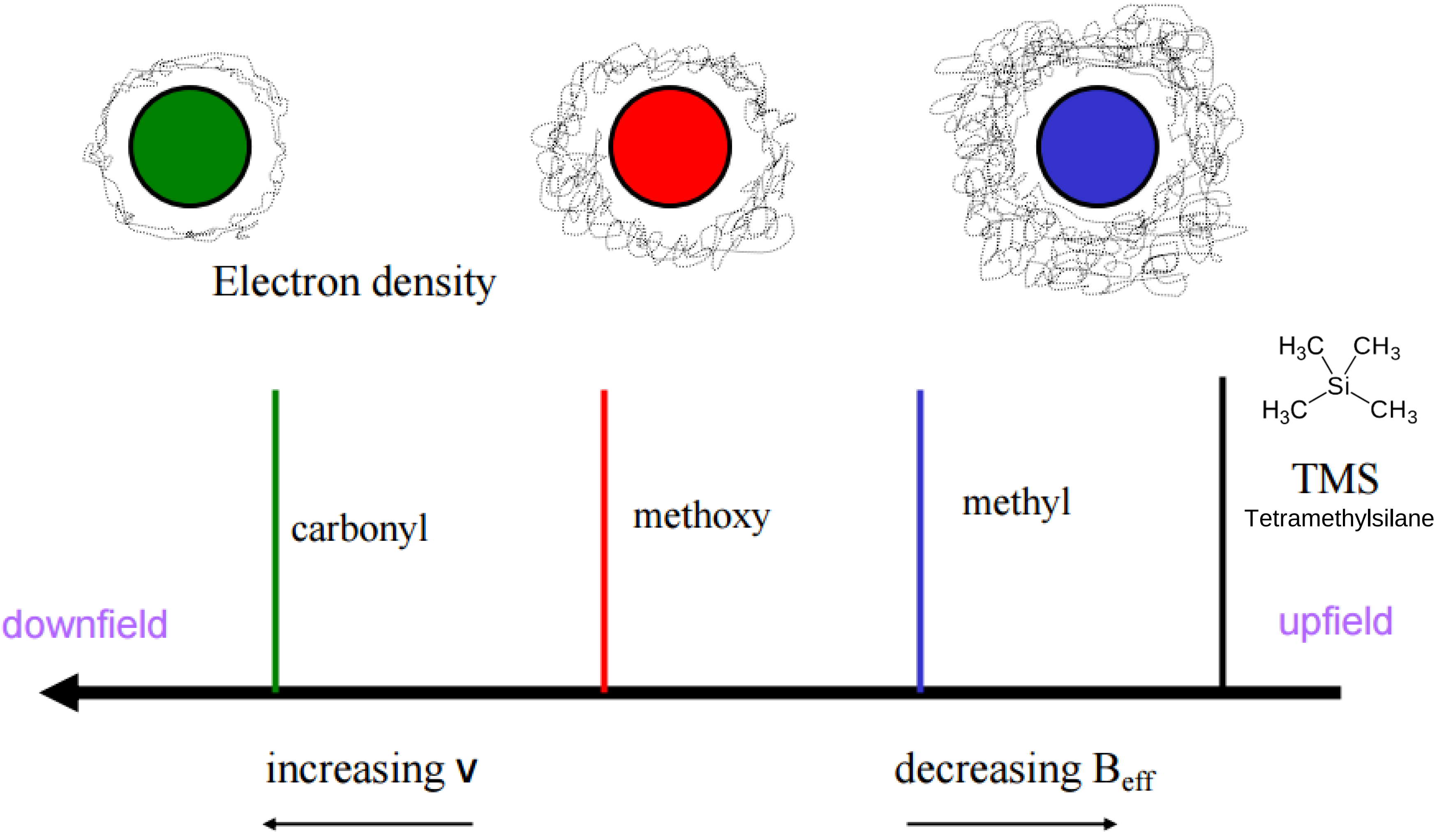


Methyl

- More e- density
- Nucleus 'shielded' from B_0 by e^-
- Feels the field (B_{eff}) less

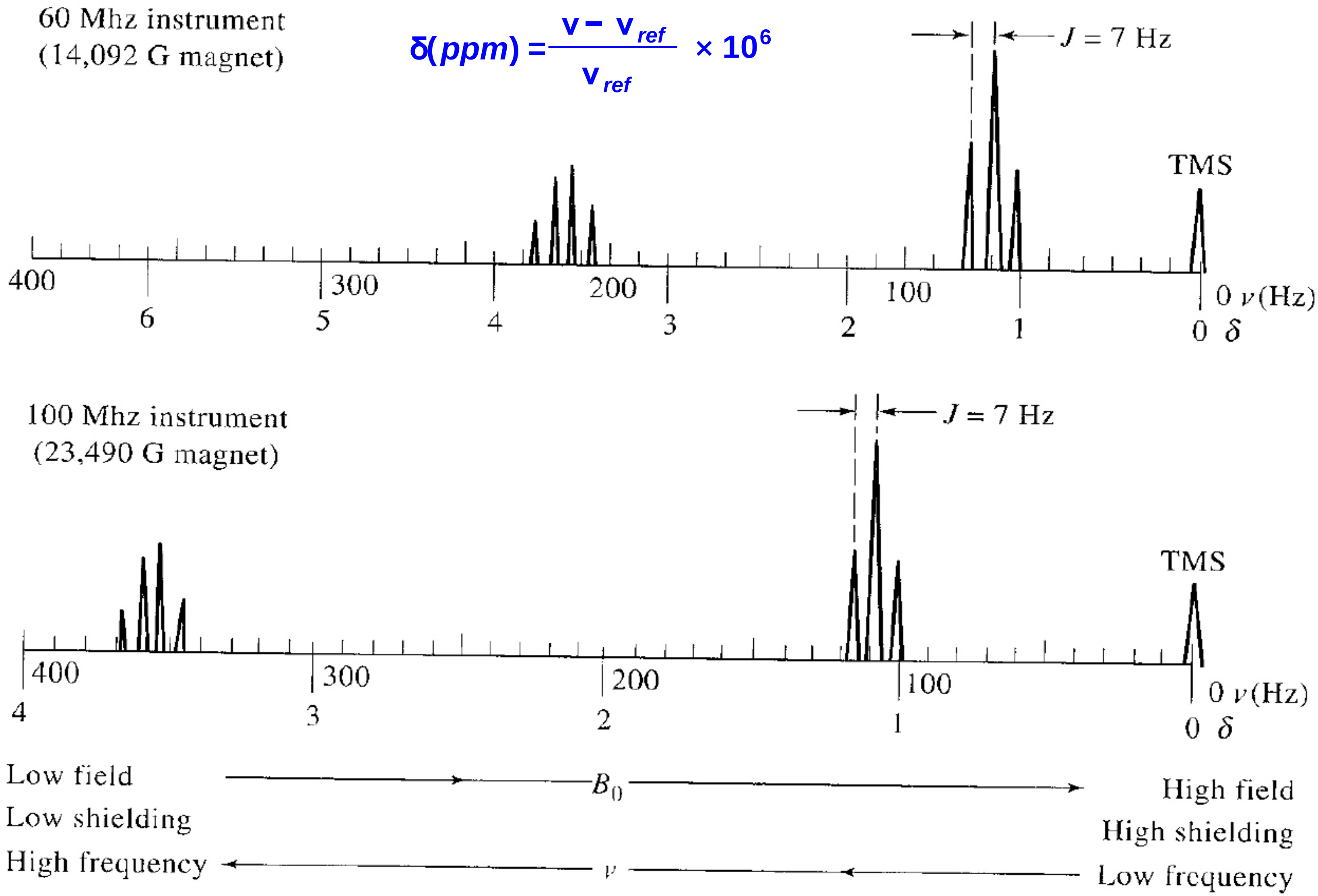
http://web.mit.edu/speclab/www/PDF/DCIF-IntroNMRpart1-theory-o07.pdf

Electron density

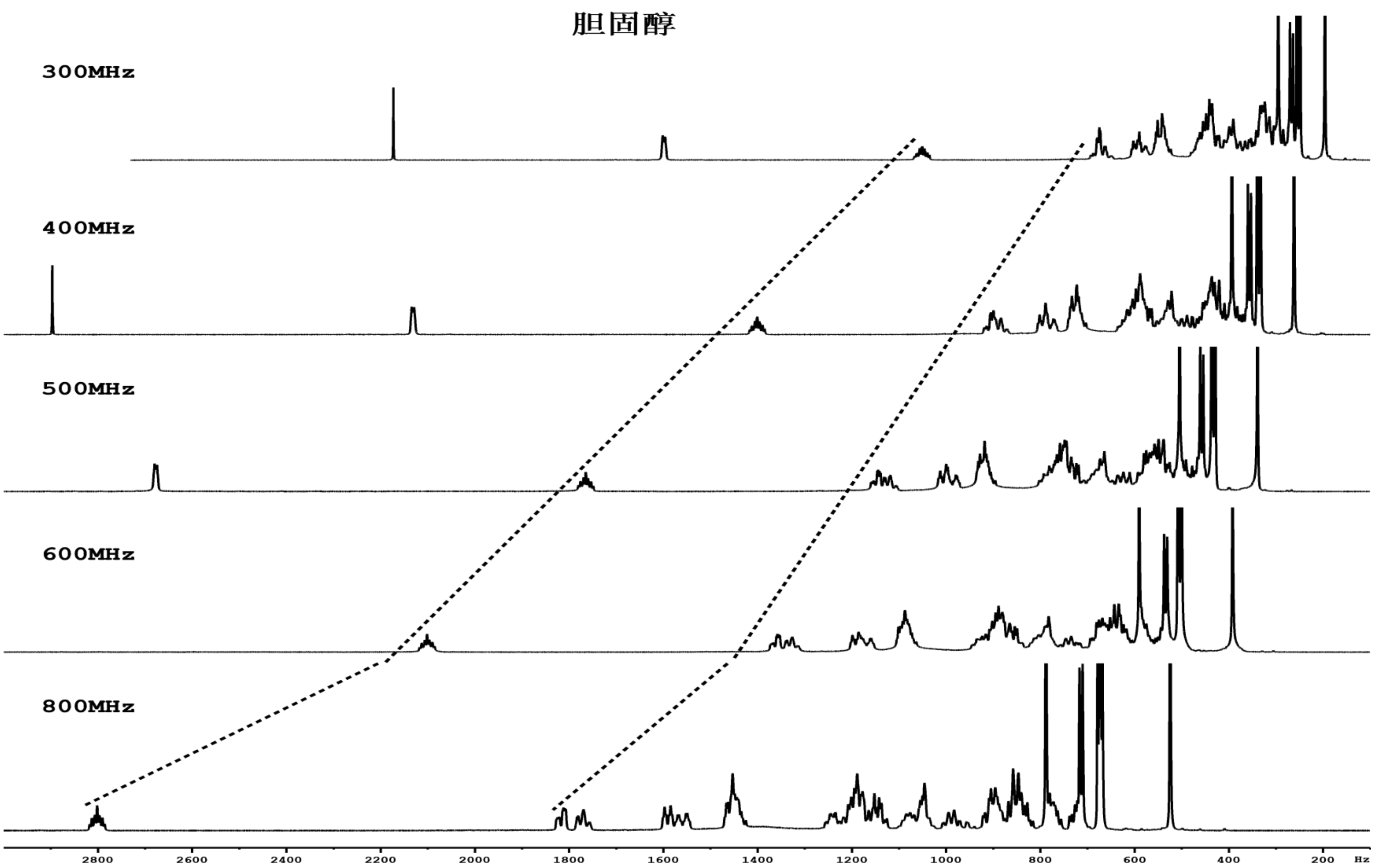


Chemical shift

$$\delta(ppm) = \frac{\nu - \nu_{ref}}{\nu_{ref}} \times 10^6$$

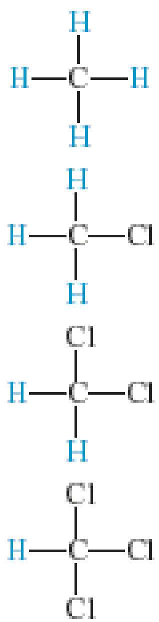


Chemical shift



^{1}H chemical shift

TABLE 13-2 Chemical Shifts of the Chloromethanes



Compound	*Chemical Shift*	*Difference*
H—C(H)(H)—H	δ0.2	
		2.8 ppm
H—C(H)(H)—Cl	δ3.0	
		2.3 ppm
H—C(Cl)(H)—Cl	δ5.3	
		1.9 ppm
H—C(Cl)(Cl)—Cl	δ7.2	

Note: Each chlorine atom added changes the chemical shift of the remaining methyl protons by about 2 to 3 ppm. These changes are nearly additive.

- More electronegative atoms deshield more and give larger shift values.
- Effect decreases with distance.
- Additional electronegative atoms cause increase in chemical shift.

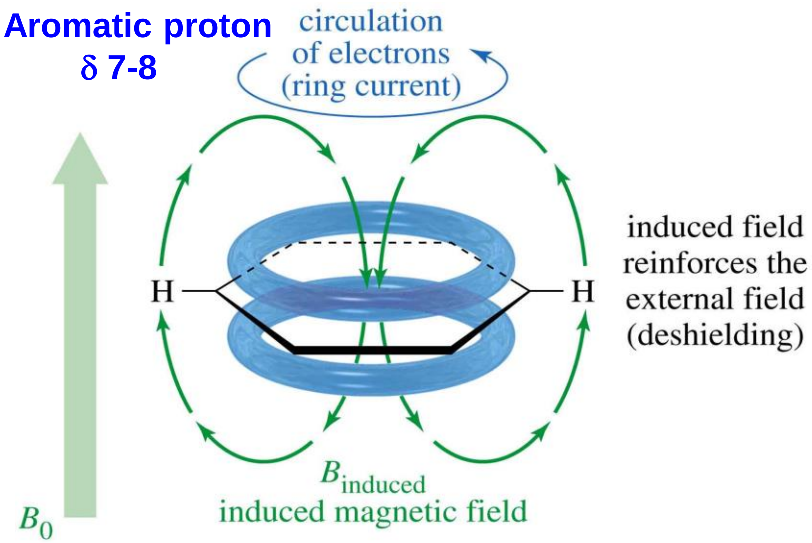
[1]H chemical shift

Type of Proton	Approximate δ	Type of Proton	Approximate δ
alkane ($-CH_3$)	0.9	$>C=C<$ ($-CH_3$ on C)	1.7
alkane ($-CH_2-$)	1.3	$Ph-H$	7.2
alkane ($-\overset{\vert}{C}H-$)	1.4	$Ph-CH_3$	2.3
$-C(=O)-CH_3$	2.1	$R-CHO$	9–10
$-C\equiv C-H$	2.5	$R-COOH$	10–12
$R-CH_2-X$ (X = halogen, O)	3–4	$R-OH$	variable, about 2–5
$>C=C<$ ($-H$ on C)	5–6	$Ar-OH$	variable, about 4–7
		$R-NH_2$	variable, about 1.5–4

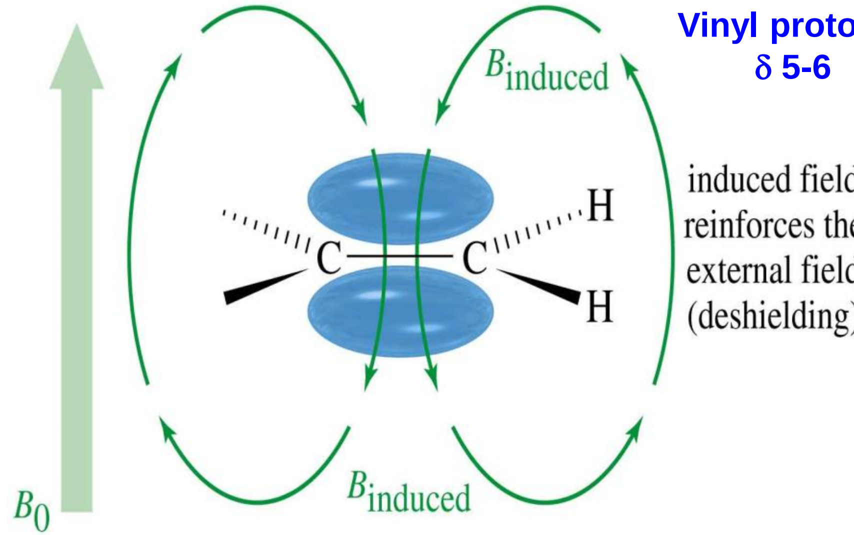
Note: These values are approximate, as all chemical shifts are affected by neighboring substituents. The numbers given here assume that alkyl groups are the only other substituents present. A more complete table of chemical shifts appears in Appendix 1.

^{1}H chemical shift

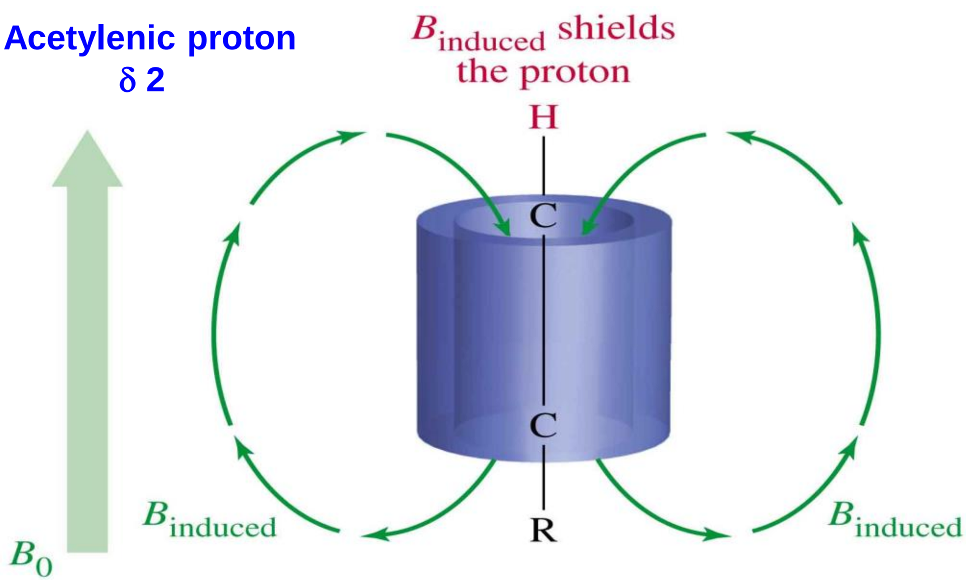
Aromatic proton
δ 7-8



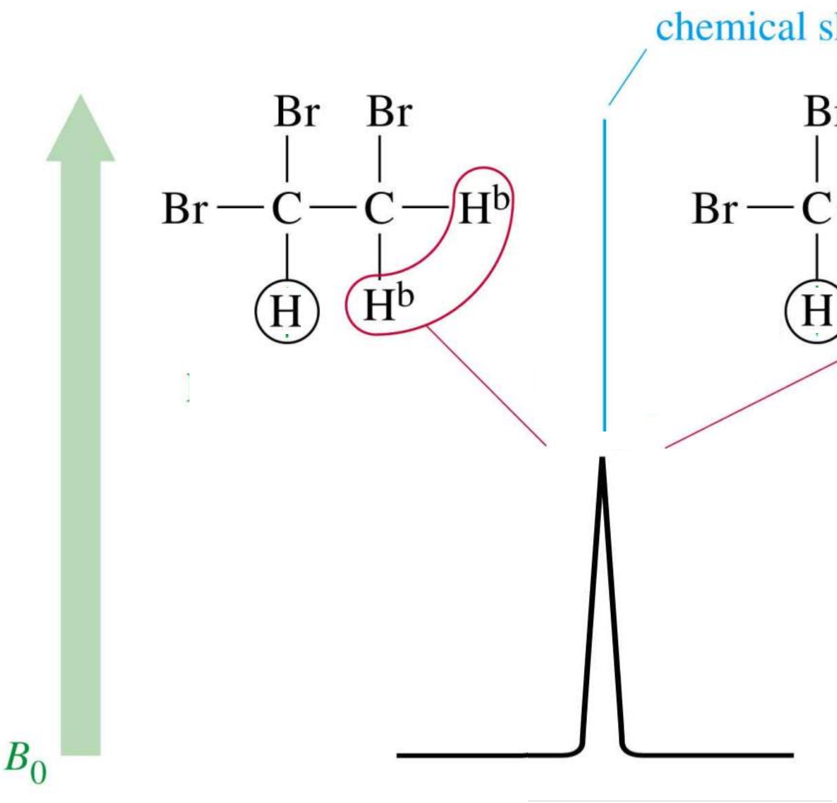
Vinyl proton
δ 5-6

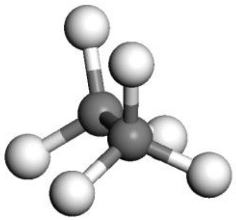


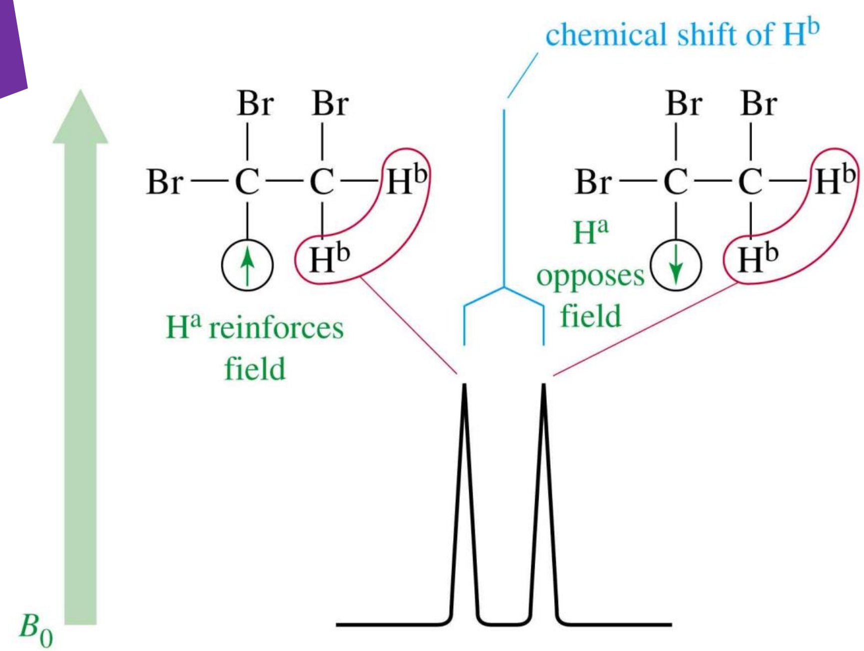
Acetylenic proton
δ 2



Spin-Spin (J) coupling







Spin-Spin (J) coupling – N+1 rule

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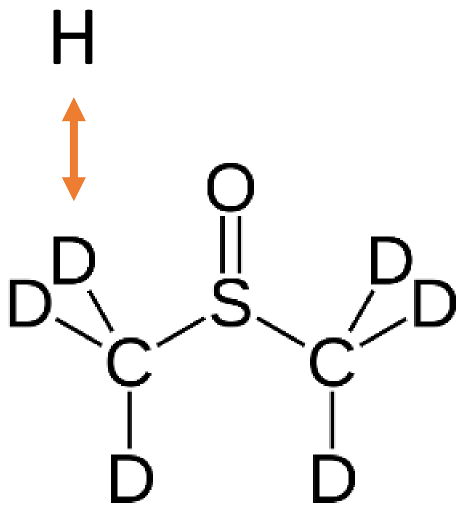
Peak splits by J-coupling → Pascal's triangle

n	n+1	Intensity ratio	Multiplicity
0	1	1	Singlet
1	2	1 1	Doublet
2	3	1 2 1	Triplet
3	4	1 3 3 1	Quartet
4	5	1 4 6 4 1	Quintet
5	6	1 5 10 10 5 1	Sextet

n: number of equivalent neighboring nuclear

2nI+1 rule

H(Proton): I=1/2
D(Deuterium): I=1



2nI+1 rule

N = Number of neighbor nuclear
I = Nuclear spin quantum number

$2J_{HD}$: 2 * 2 * 1 + 1 = 5 (Quintet)
$2J_{HH}$: 2 * 2 * 1/2 + 1 = 3 (Triplet)

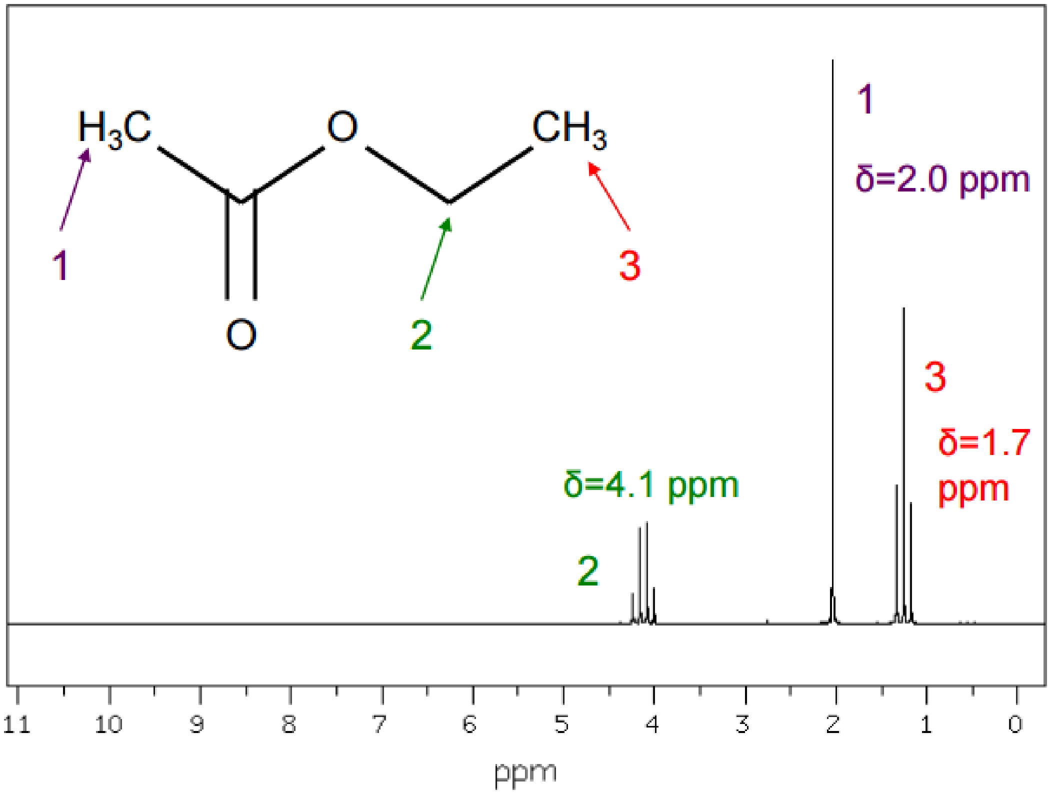
Coupling constant
$2J_{HD}$ = Hz

ex) DMSO-D6 <-> DMSO-D5+H1 <-> DMSO-H6

None	Quintet	Triplet

Spin-Spin (J) coupling – Ethyl acetate

Ethyl acetate



Spin-Spin Splitting patterns

1. Singlet. 3 equivalent protons. Not coupled to any neighboring protons.

2. Quartet. 2 equivalent protons. Split (1:3:3:1) because coupled to the 3 [1]Hs at the 2 position.

3. Triplet. 3 equivalent protons. Split (1:2:1) because coupled to the 2 [1]Hs at the 3 position.

Multiplicity = N (# of neighbors) + 1

NMR Information

<Data>

1. Chemical shift (shielding/deshielding)
2. Spin-Spin coupling
3. Peak integral
4. Relaxation
5. Diffusion coefficient

<Application>

1. Qualitative/Quantitative
2. Structure assign
3. Dynamics/Kinetics
4. Purification

<Industry>

1. Organic chemistry
2. Metabolomics
3. Drug development
4. QC/QA
5. Polymer

5. Tuning & Matching

Lock & Shim

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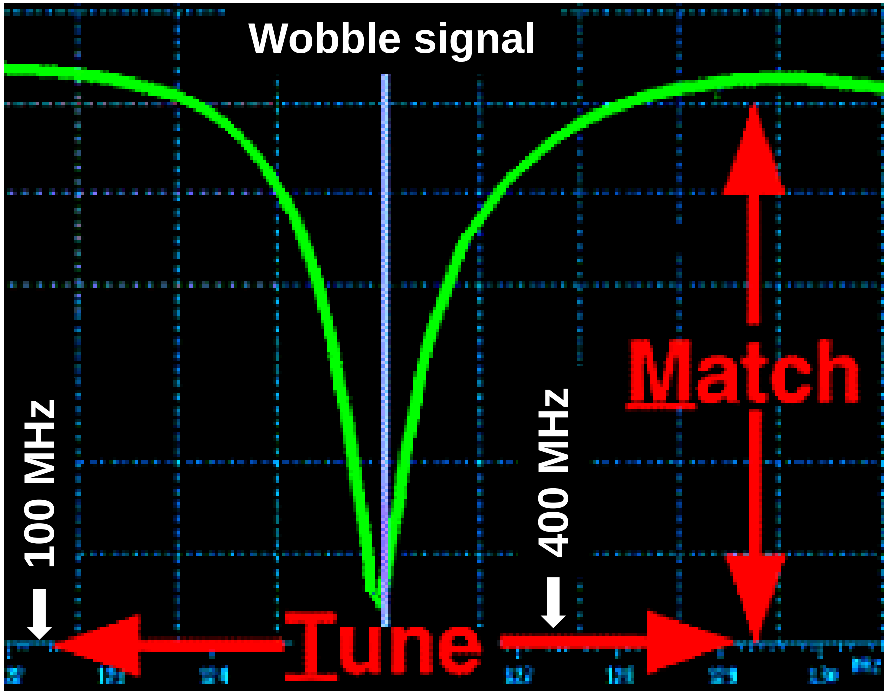
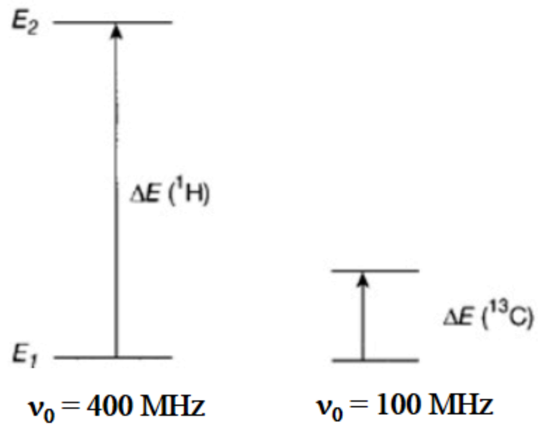
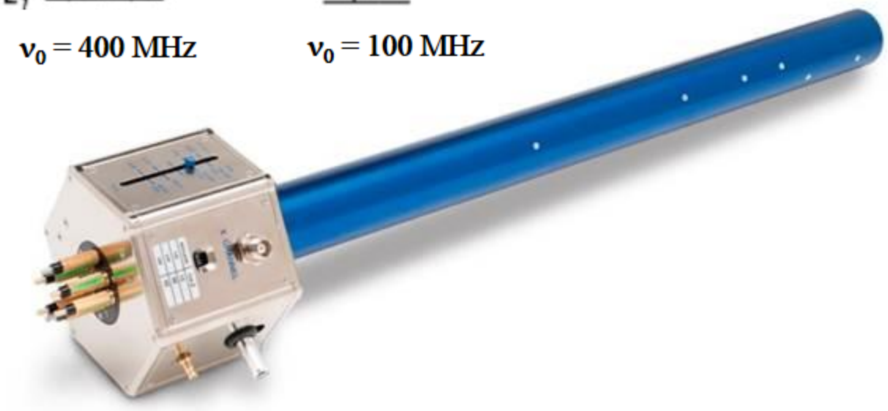
Tuning & Matching



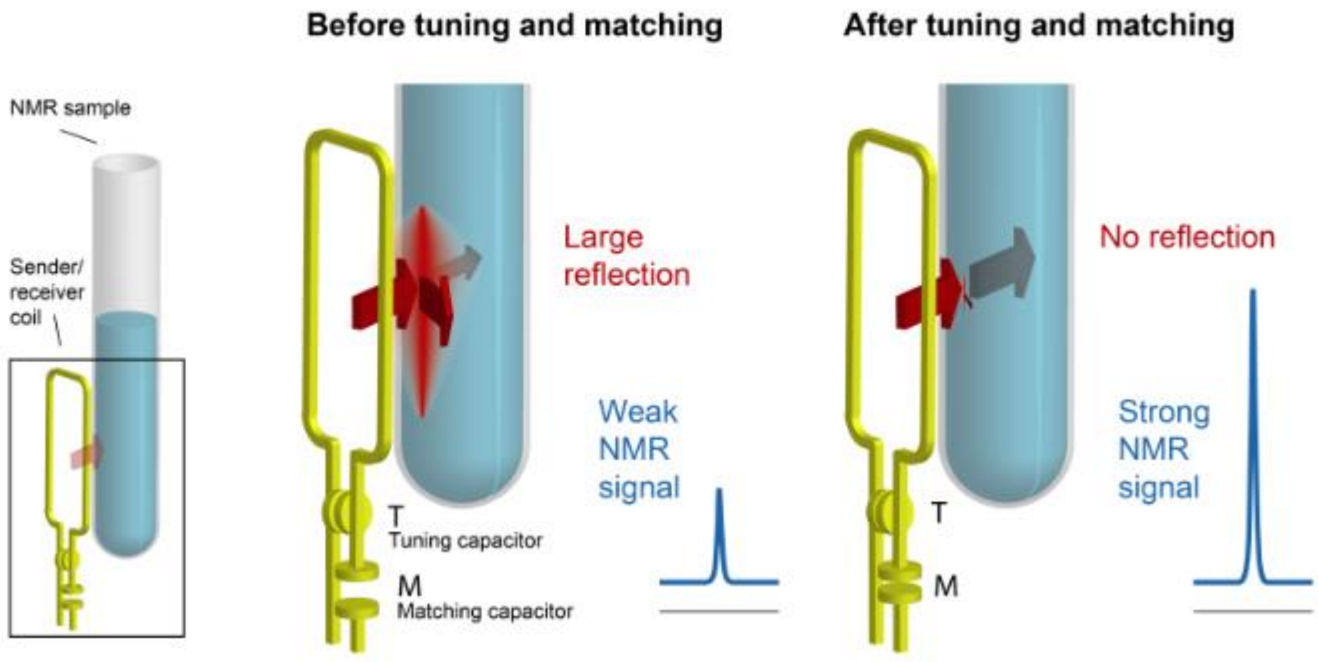


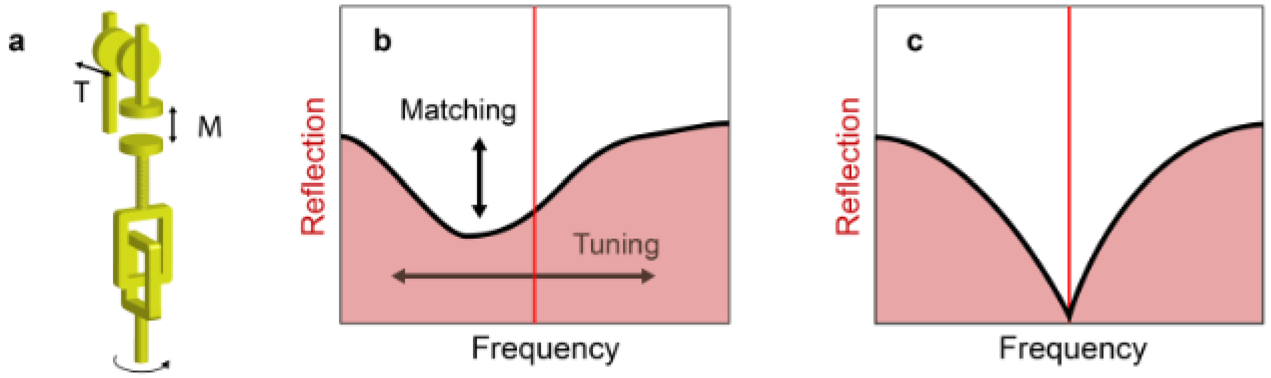


Tuning is the process of adjusting this frequency until it coincides with the frequency of the pulses transmitted to the circuit. For example, the frequency at which the ^{1}H resonant circuit is most sensitive must be set to **the carrier frequency of the ^{1}H pulses**.

Matching is the process of adjusting the impedance of the resonant circuit until it corresponds with the impedance of the transmission line connected to it. **This impedance is 50Ω**;. Correct matching minimizes the power that is transmitted to the coil

Tuning & Matching

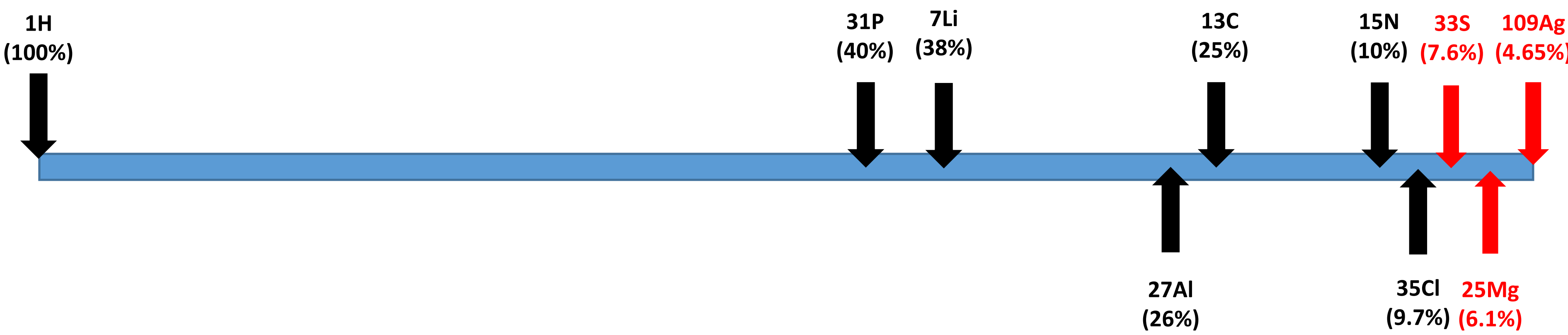




Tuning & Matching

5mm DB auto-X probe (Varian 600) [Tune & Match range = 31P (40%) ~ 15N (10%)]
5mm BBO Probe (Bruker 400) [Tune & Match range = 31P (40%) ~ 15N (10%)]
-> 31P(40%), 13C (25%), 15N(10%), 35Cl(9.7%)

Smart probe or I-probe [Tune & Match range = 31P (40%) ~ 109Ag (4.65%)]
-> 31P(40%), 13C (25%), 15N(10%), 35Cl(9.7%), 33S (7.6%), 14N(7.2%), 25Mg(6.1%), 109Ag (4.65%)



https://kodu.ut.ee/~laurit/AK2/NMR_tables_Bruker2012.pdf

NMR Frequency table

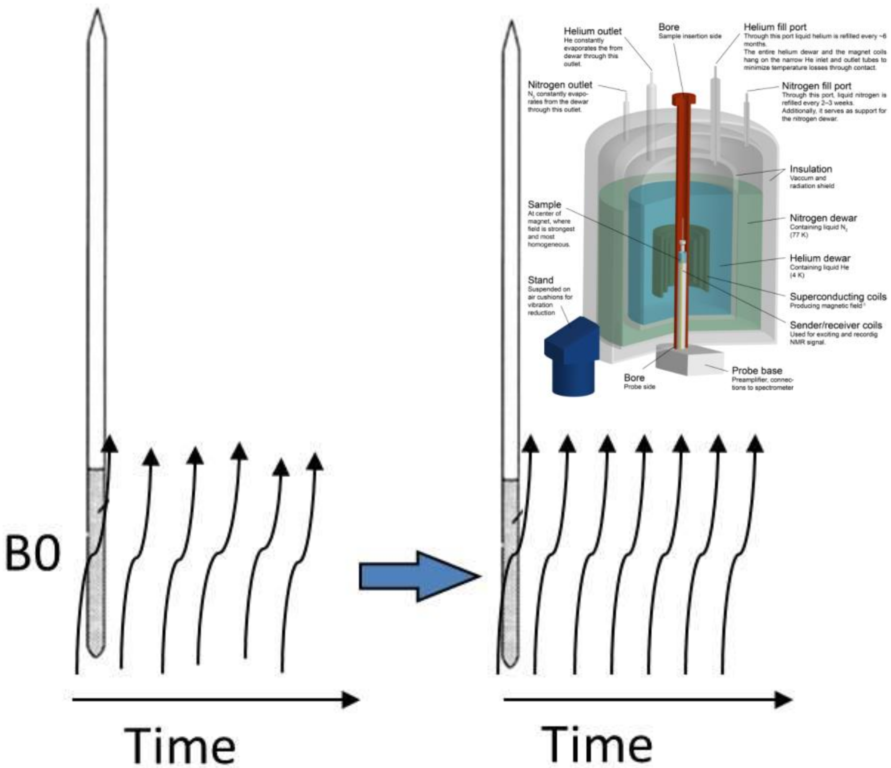
		Theoretical NMR Freq. (free atom)	Molar Receptivity (rel. ^1H)	Receptivity at Nat. Abund. (rel. ^{13}C)	Reference Sample	Measured. NMR Freq. (rel. ^1H ref.)
A	Sym	ν_0 [MHz]	$R_M(H)$	$R_{NA}(C)$	Reference	Ξ [MHz]
1	n	68.4979	3.21E−01			
1	H	100.0000	**1.00E+00**	5.87E+03	1% Me_4Si in $CDCl_3$	100.000000
2	D	15.3506	9.65E−03	6.52E−03	$(CD_3)_4Si$ neat	15.350609
3	T	106.6640	1.21E+00		TMS-T_1	106.663974
3	He	76.1767	4.42E−01	3.48E−03	He gas	76.178976
6	Li	14.7170	8.50E−03	3.79E+00	9.7 m LiCl in D_2O	14.716086
7	Li	38.8667	2.94E−01	1.59E+03	9.7 m LiCl in D_2O	38.863797
9	Be	14.0536	1.39E−02	8.15E+01	0.43 m $BeSO_4$ in D_2O	14.051813
10	B	10.7456	1.99E−02	2.32E+01	15% $BF_3.Et_2O$ in $CDCl_3$	10.743658
11	B	32.0897	1.65E−01	7.77E+02	15% $BF_3.Et_2O$ in $CDCl_3$	32.083974
13	C	25.1504	1.59E−02	**1.00E+00**	1% Me_4Si in $CDCl_3$	25.145020
					DSS in D_2O	25.144953
14	N	7.2285	1.01E−03	5.90E+00	$MeNO_2$ + 10% $CDCl_3$	7.226317
15	N	10.1398	1.04E−03	2.23E−02	$MeNO_2$ + 10% $CDCl_3$	10.136767
					liquid NH_3	10.132767
17	O	13.5617	2.91E−02	6.50E−02	D_2O	13.556457
19	F	94.0570	8.32E−01	4.89E+03	CCl_3F	94.094011
21	Ne	7.8987	2.46E−03	3.91E−02	Neon gas, 1.1 MPa	7.894296
23	Na	26.4683	9.27E−02	5.45E+02	0.1 M NaCl in D_2O	26.451900
25	Mg	6.1260	2.68E−03	1.58E+00	11 M $MgCl_2$ in D_2O	6.121635
26	Al	10.0399	4.05E−02			
27	Al	26.0774	2.07E−01	1.22E+03	1.1 m $Al(NO_3)_3$ in D_2O	26.056859
29	Si	19.8826	7.86E−03	2.16E+00	1% Me_4Si in $CDCl_3$	19.867187
31	P	40.5178	6.65E−02	3.91E+02	H_3PO_4 external	40.480742
					$(MeO)_3PO$ internal	40.480864
33	S	7.6842	2.27E−03	1.00E−01	$(NH_4)_2SO_4$ in D_2O (sat.)	7.676000
35	Cl	9.8093	4.72E−03	2.10E+01	0.1 M NaCl in D_2O	9.797909
37	Cl	8.1652	2.72E−03	3.88E+00	0.1 M NaCl in D_2O	8.155725
39	Ar	8.1228	1.13E−02			
39	K	4.6727	5.10E−04	2.79E+00	0.1 M KCl in D_2O	4.666373
40	K	5.8099	5.23E−03	3.59E−03	0.1 M KCl in D_2O	5.802018
41	K	2.5648	8.44E−05	3.34E−02	0.1 M KCl in D_2O	2.561305
41	Ca	8.1575	1.14E−02			
43	Ca	6.7399	6.43E−03	5.10E−02	0.1 M $CaCl_2$ in D_2O	6.730029
45	Sc	24.3299	3.02E−01	1.78E+03	0.06 M $Sc(NO_3)_3$ in D_2O	24.291747
47	Ti	5.6464	2.10E−03	9.18E−01	$TiCl_4$ neat + 10% C_6D_{12}	5.637534
49	Ti	5.6479	3.78E−03	1.20E+00	$TiCl_4$ neat + 10% C_6D_{12}	5.639037
50	V	9.9829	5.57E−02	8.18E−01	$VOCl_3$ + 5% C_6D_6	9.970309
51	V	26.3362	3.84E−01	2.25E+03	$VOCl_3$ + 5% C_6D_6	26.302948
53	Cr	5.6638	9.08E−04	5.07E−01	K_2CrO_4 in D_2O (sat.)	5.652496
53	Mn	25.6983	3.56E−01			
55	Mn	24.8400	1.79E−01	1.05E+03	0.82 m $KMnO_4$ in D_2O	24.789218
57	Fe	3.2448	3.42E−05	4.25E−03	$Fe(CO)_5$ + 20% C_6D_6	3.237778
59	Fe	4.0079	3.22E−04			
59	Co	23.6676	2.78E−01	1.64E+03	0.56 m $K_3[Co(CN)_6]$ in D_2O	23.727074
60	Co	13.6026	1.01E−01			
61	Ni	8.9517	3.59E−03	2.40E−01	$Ni(CO)_4$ + 5% C_6D_6	8.936051
63	Cu	26.5839	9.39E−02	3.82E+02	$[Cu(CH_3CN)_4][ClO_4]$ in CH_3CN (sat.) + 5% C_6D_6	26.515473
65	Cu	28.4250	1.15E−01	2.08E+02	$[Cu(CH_3CN)_4][ClO_4]$ in CH_3CN (sat.) + 5% C_6D_6	28.403693
67	Zn	6.2675	2.87E−03	6.92E−01	$Zn(NO_3)_2$ in D_2O (sat.)	6.256803
69	Ga	24.0685	6.97E−02	2.46E+02	1.1 m $Ga(NO_3)_3$ in D_2O	24.001354
71	Ga	30.5813	1.43E−01	3.35E+02	1.1 m $Ga(NO_3)_3$ in D_2O	30.496704
73	Ge	3.4989	1.41E−03	6.44E−01	Me_4Ge + 5% C_6D_6	3.488315
75	As	17.1804	2.54E−02	1.49E+02	0.5 M $NaAsF_6$ in CD_3CN	17.122614
77	Se	19.1587	7.03E−03	3.15E+00	Me_2Se + 5% C_6D_6	19.071513
79	Se	5.2072	2.97E−03			
79	Br	25.1404	7.94E−02	2.37E+02	0.01 M NaBr in D_2O	25.053980
81	Br	27.0997	9.95E−02	2.88E+02	0.01 M NaBr in D_2O	27.006518
83	Kr	3.8617	1.90E−03	1.28E+00	Kr gas	3.847600
85	Rb	9.6916	1.06E−02	4.50E+01	0.01 M RbCl in D_2O	9.654943
87	Rb	32.8436	1.77E−01	2.90E+02	0.01 M RbCl in D_2O	32.720454
87	Sr	4.3508	2.72E−03	1.12E+00	0.5 M $SrCl_2$ in D_2O	4.333822
89	Y	4.9203	1.19E−04	7.00E−01	$Y(NO_3)_3$ in H_2O/D_2O	4.900198
91	Zr	9.3354	9.49E−03	6.26E+00	$Zr(C_5H_5)_2Cl_2$ in CH_2Cl_2 (sat.) + 5% C_6D_6	9.296298
93	Nb	24.5488	4.88E−01	2.87E+03	$K[NbCl_6]$ in CH_3CN / CD_3CN (sat.)	24.476170
95	Mo	6.5467	3.27E−03	3.06E+00	2 M Na_2MoO_4 in D_2O	6.516926
97	Mo	6.6849	3.49E−03	1.96E+00	2 M Na_2MoO_4 in D_2O	6.653695
99	Mo	13.4272	2.42E−03			
99	Tc	22.6161	3.82E−01		NH_4TcO_4 in H_2O / D_2O	22.508326
99	Ru	4.5903	1.13E−03	8.46E−01	0.3 M $K_4[Ru(CN)_6]$ in D_2O	4.605151
101	Ru	5.1274	1.57E−03	1.58E+00	0.3 M $K_4[Ru(CN)_6]$ in D_2O	5.161369
103	Rh	3.1652	3.17E−05	1.86E−01	$Rh(acac)_3$ in $CDCl_3$ (sat.)	3.186447
105	Pd	4.5975	1.13E−03	1.49E+00	K_2PdCl_6 in D_2O (sat.)	4.576100
107	Ag	4.0704	6.74E−05	2.05E−01	$AgNO_3$ in D_2O (sat.)	4.047819
109	Ag	4.6795	1.02E−04	2.90E−01	$AgNO_3$ in D_2O (sat.)	4.653533
111	Cd	21.3003	9.66E−03	7.27E+00	Me_2Cd neat liq.	21.215480
113	Cd	22.2820	1.11E−02	7.94E+00	Me_2Cd neat liq.	22.193175
113	In	21.9963	3.51E−01	8.85E+01	0.1 M $In(NO_3)_3$ in D_2O + 0.5 M DNO_3	21.865755
115	In	22.0436	3.53E−01	1.99E+03	0.1 M $In(NO_3)_3$ in D_2O + 0.5 M DNO_3	21.912629
115	Sn	32.8994	3.56E−02	7.11E−01	Me_4Sn + 5% C_6D_6	32.718749
117	Sn	35.8430	4.60E−02	2.08E+01	Me_4Sn + 5% C_6D_6	35.632259
119	Sn	37.4986	5.27E−02	2.66E+01	Me_4Sn + 5% C_6D_6	37.290632
121	Sb	24.0858	1.63E−01	5.48E+02	$KSbCl_6$ in CH_3CN / CD_3CN (sat.)	23.930577
123	Sb	13.0425	4.66E−02	1.17E+02	$KSbCl_6$ in CH_3CN / CD_3CN (sat.)	12.959217
125	Sb	13.4527	5.11E−02			
123	Te	26.3870	1.84E−02	9.61E−01	Me_2Te + 5% C_6D_6	26.169742
125	Te	31.8136	3.22E−02	1.34E+01	Me_2Te + 5% C_6D_6	31.549769
127	I	20.1462	9.54E−02	5.60E+02	0.01 M KI in D_2O	20.007486
129	I	13.4067	5.06E−02			
129	Xe	27.8560	2.16E−02	3.35E+01	$XeOF_4$ neat liq.	27.810186
131	Xe	8.2575	2.82E−03	3.51E+00	$XeOF_4$ neat liq.	8.243921
133	Cs	13.2073	4.84E−02	2.84E+02	0.1 M $CsNO_3$ in D_2O	13.116142
135	Ba	10.0092	5.01E−03	1.94E+00	0.5 M $BaCl_2$ in D_2O	9.934457
137	Ba	11.1874	7.00E−03	4.62E+00	0.5 M $BaCl_2$ in D_2O	11.112928
137	La	13.7852	5.50E−02			
138	La	13.2970	9.40E−02	4.97E−01	$LaCl_3$ in D_2O / H_2O	13.194300
139	La	14.2356	6.06E−02	3.56E+02	0.01 M $LaCl_3$ in D_2O	14.125641
139	Ce	12.6514	1.01E−02			
141	Ce	5.5755	3.64E−03			
141	Pr	30.6168	3.35E−01	1.97E+03		
143	Nd	5.4476	3.39E−03	2.43E+00		
145	Nd	3.3555	7.93E−04	3.87E−01		
145	Pm	27.2124	2.35E−01			
147	Sm	4.1678	1.52E−03	1.34E+00		
149	Sm	3.4358	8.52E−04	6.92E−01		
151	Eu	24.8614	1.79E−01	5.04E+02		
153	Eu	10.9737	1.54E−02	4.73E+01		
155	Gd	3.0697	1.45E−04	1.26E−01		
157	Gd	4.0258	3.26E−04	3.00E−01		
159	Tb	24.0376	6.94E−02	4.08E+02		
161	Dy	3.4374	4.74E−04	5.26E−01		
163	Dy	4.8195	1.31E−03	1.91E+00		
163	Ho	21.6369	2.13E−01			
165	Ho	21.1356	1.98E−01	1.16E+03		
166	Ho	9.2072	5.83E−02		(+6 keV excited state)	
167	Er	2.8842	5.04E−04	6.77E−01		
169	Er	17.3658	5.24E−03			
169	Tm	8.2711	5.66E−04	3.32E+00		
171	Tm	8.1637	5.44E−04			
171	Yb	17.6762	5.52E−03	4.63E+00	0.171 M $Yb(\eta\text{-}C_5Me_5)_2(THF)_2$ in THF	17.499306
173	Yb	4.8688	1.35E−03	1.28E+00		
175	Lu	11.4185	3.13E−02	1.79E+02		

A	Sym	ν_o [MHz]	R_M(H)	R_{NA}(C)	Reference	Ξ [MHz]
176	Lu	8.1049	3.98E-02	6.05E+00		
177	Hf	4.0588	1.40E-03	1.53E+00		
179	Hf	2.5502	5.47E-04	4.38E-01		
179	Ta	11.7085	3.37E-02			
180	Ta	9.5979	1.06E-01	7.48E-02	(+77 keV excited state)	
181	Ta	12.1254	3.74E-02	2.20E+02	$KTaCl_6$ in CH_3CN (sat.)	11.989600
183	W	4.2174	7.50E-05	6.31E-02	1 M Na_2WO_4 in D_2O	4.166387
185	Re	22.8233	1.39E-01	3.05E+02	0.1 M $KReO_4$ in D_2O	22.524600
187	Re	23.0568	1.43E-01	5.26E+02	0.1 M $KReO_4$ in D_2O	22.751600
187	Os	2.3149	1.24E-05	1.43E-03	0.98 M OsO_4 in CCl_4	2.282331
189	Os	7.8765	2.44E-03	2.32E+00	0.98 M OsO_4 in CCl_4	7.765400
191	Ir	1.7986	2.91E-05	6.38E-02		
193	Ir	1.9538	3.73E-05	1.37E-01		
195	Pt	21.8243	1.04E-02	2.07E+01	1.2 M Na_2PtCl_6 in D_2O	21.496784
197	Au	1.7683	2.76E-05	1.62E-01		
199	Hg	18.1136	5.94E-03	5.89E+00	Me_2Hg neat liq. (toxic!)	17.910822
201	Hg	6.6864	1.49E-03	1.16E+00	Me_2Hg neat liq. (toxic!)	6.611583
203	Tl	58.0862	1.96E-01	3.40E+02	$Tl(NO_3)_3$	57.123200
205	Tl	58.6575	2.02E-01	8.36E+02	$Tl(NO_3)_3$	57.683838
205	Pb	5.0966	1.54E-03			
207	Pb	20.8458	9.06E-03	1.18E+01	Me_4Pb + 5% C_6D_6	20.920599
209	Bi	16.3525	1.44E-01	8.48E+02	$Bi(NO_3)_3$ sat. in conc. HNO_3 + 50% D_2O	16.069288
209	Po	24.3479	1.44E-02			
211	Rn	21.5193	9.97E-03			
212	Fr	16.5423	1.81E-01			
225	Ra	26.2814	1.82E-02			
227	Ac	13.1288	1.13E-02			
229	Th	3.2941	4.17E-04			
231	Pa	23.9899	6.90E-02	4.06E+02		
233	U	4.2251	8.80E-04			
235	U	1.9437	1.54E-04	6.53E-03	UF_6 + 10% C_6D_6	1.841400
238	U					
237	Np	22.4860	1.33E-01			
239	Pu	7.2686	3.84E-04			
241	Pu	4.8696	1.35E-03			
241	Am	11.3146	1.69E-02			
243	Am	10.7417	1.45E-02			
243	Cm	2.9361	2.95E-04			
245	Cm	2.5576	3.51E-04			
247	Cm	1.4720	1.05E-04			
249	Bk	10.2302	2.25E-02			
253	Es	20.9719	1.94E-01			

Locking & Shimming

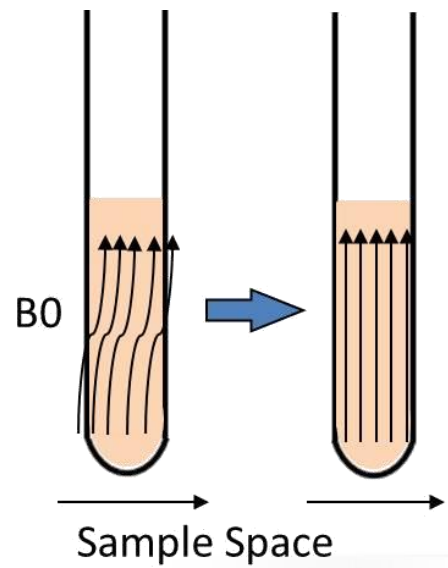
Locking B_0

Locking is to stabilize B_0 time to time. When locking is activated, the feedback-control of B_0 is achieved by reading the ^2H signal and adjusting the Z_0 shim.

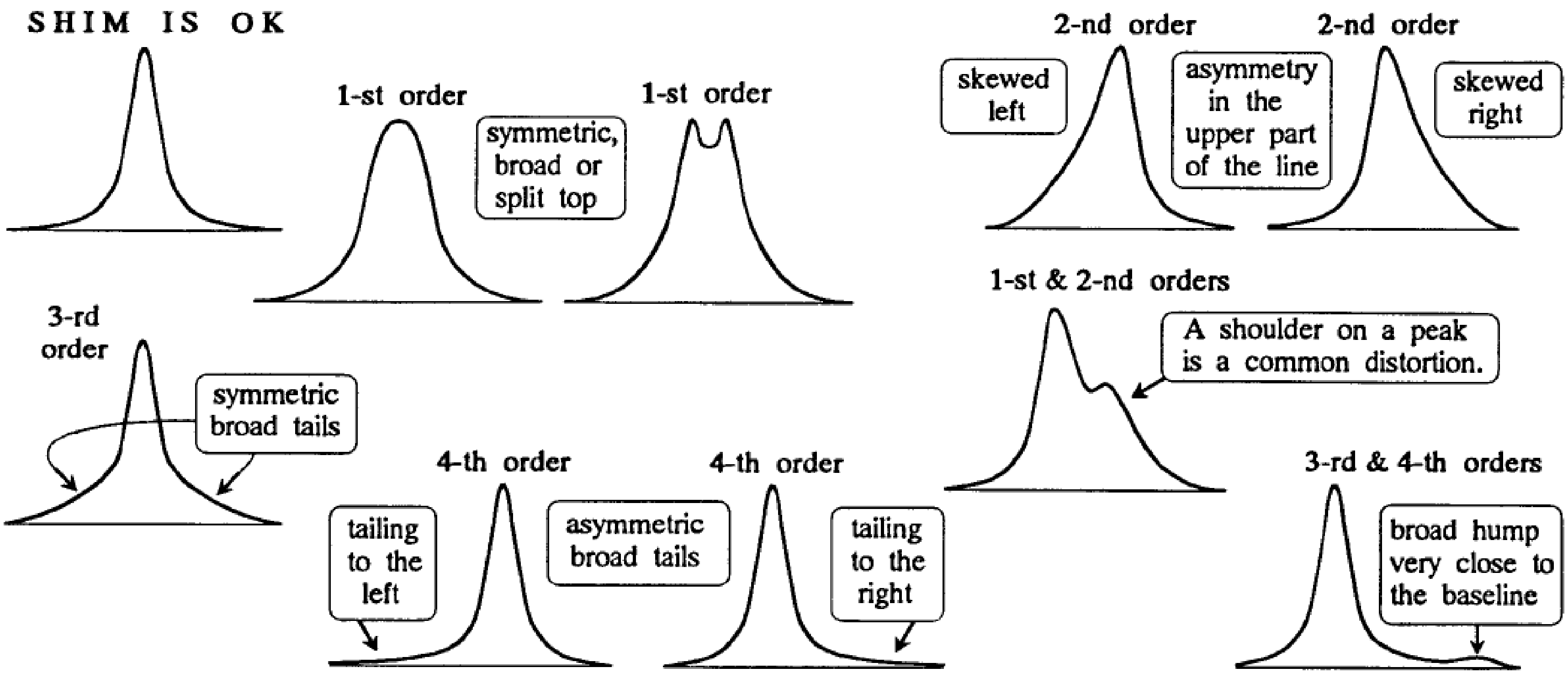


Shimming B_0

Shimming is to homogenize B_0 in the sample space. Bio-NMR uses about 40 different shims to achieve this goal. The main shim sets that users must check are Z1, Z2, Z3, Z4, X1, Y1, XZ, and YZ.



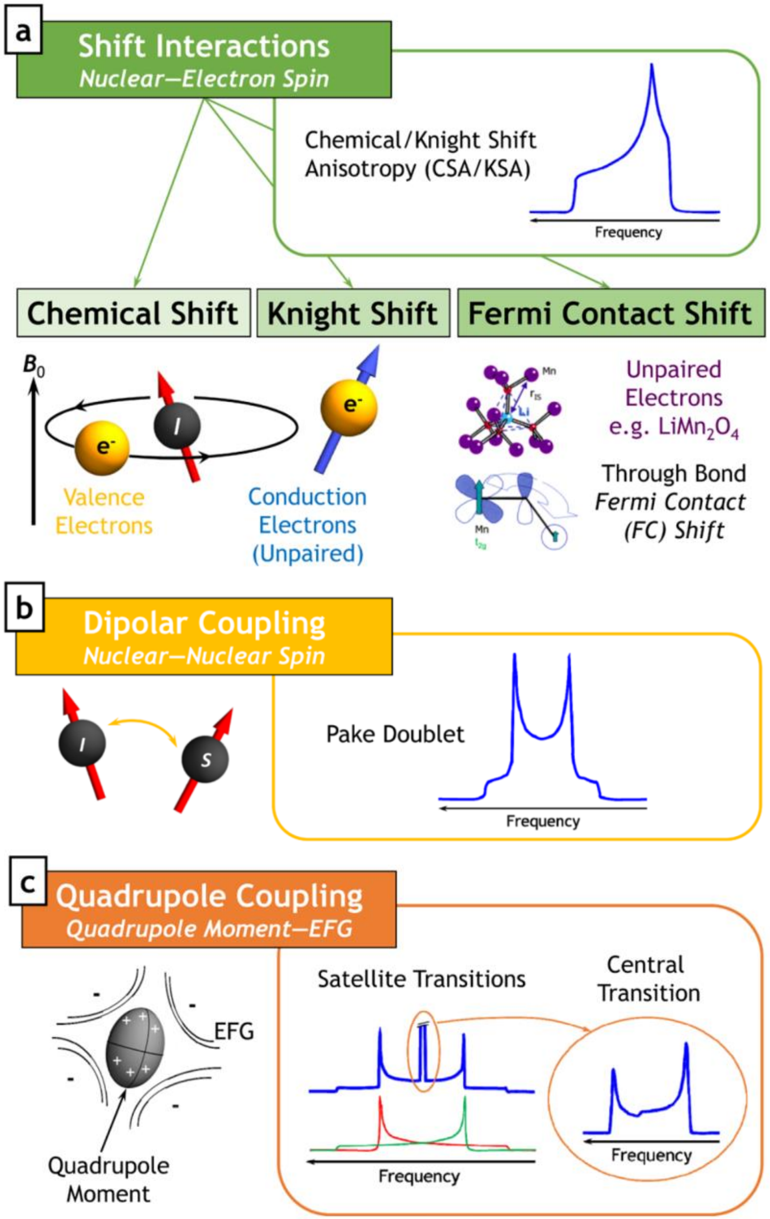
Shimming

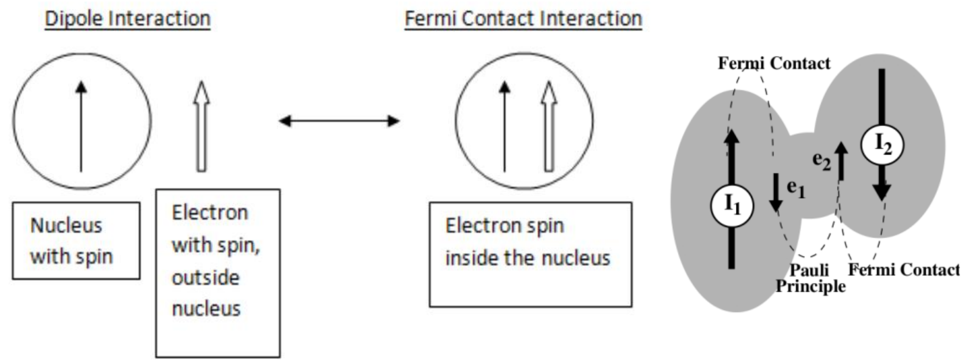


SKETCHES OF LINE DISTORTIONS CAUSED BY VARIOUS GRADIENTS

6. Solid-state NMR

Interaction in Solid-state NMR





Chemical shift: Interaction for valence electron

Knight shift: Interaction for unpaired electron

Energy state

2nI+1 = 4

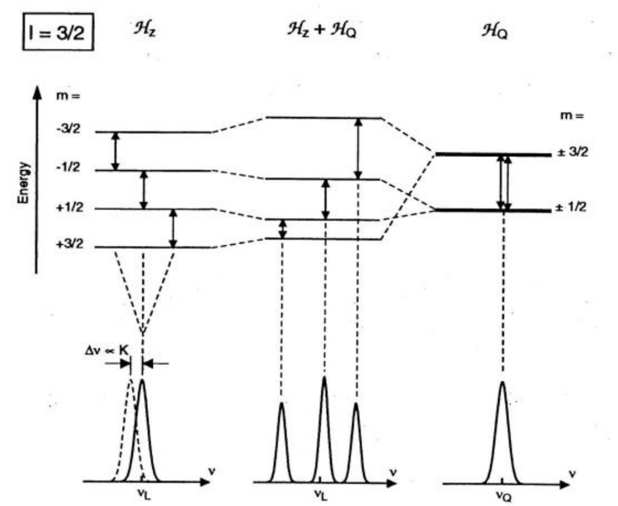


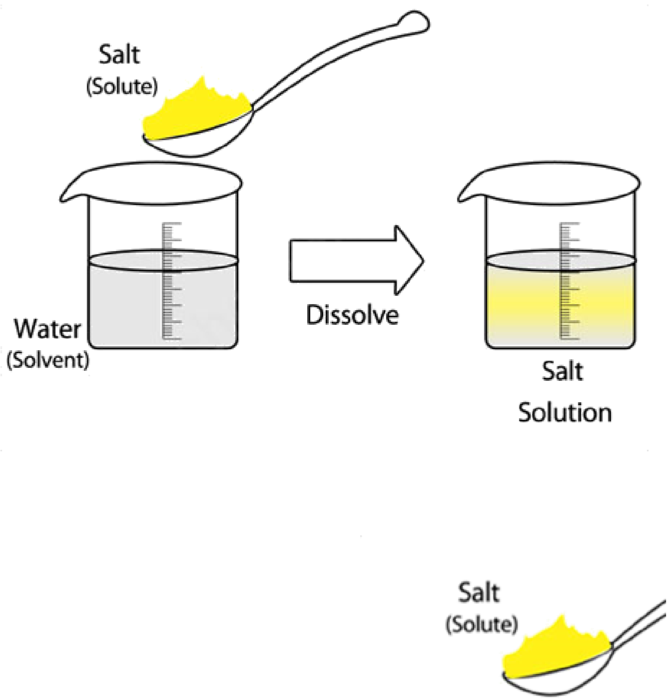
Figure 2.2: Result of the combination of the Zeeman and the quadrupole interaction for a Spin $I = 3/2$ nuclei in an external magnetic field.

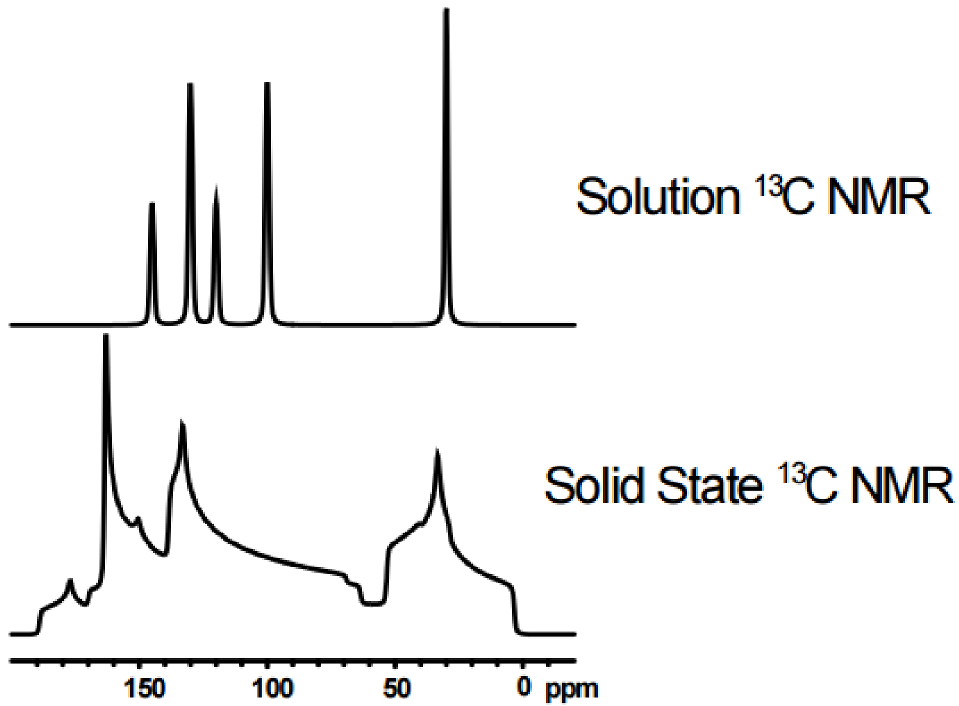
Hamiltonian in NMR

$$H_{TOTAL} = H_Z + H_D + H_{SC} + H_{CS} + H_Q + \cdots$$

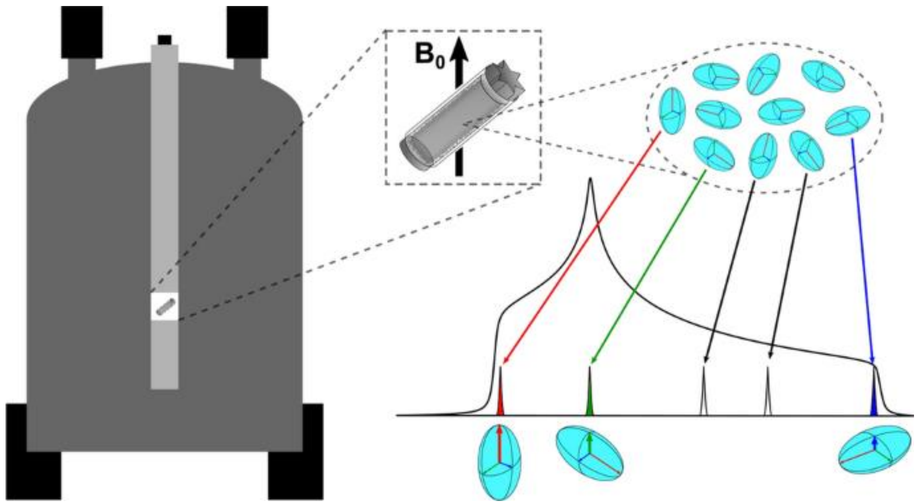
13C NMR At 9.4 T	Zeeman	Dipolar	Scalar (J-coupling)	Chemical shift	Quadrupolar
	H_Z	H_D (Through space between spin)	H_{SC} (Through bond of electrons)	H_{CS}	H_Q
In solution	100 MHz	0 kHz	~ 400 Hz	Isotropic value	0
In solid	100 MHz	Up to 100 kHz	Up to 10 kHz	Up to 100 kHz CSA (Chemical Shift Anisotropy)	Up to MHz
How to remove		Dipolar decoupling	Scalar decoupling	MAS (Magic Angle Spinning)	MAS (Magic Angle Spinning) High field NMR

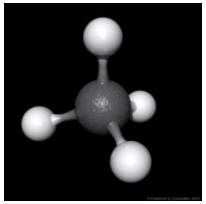
Solid-state NMR



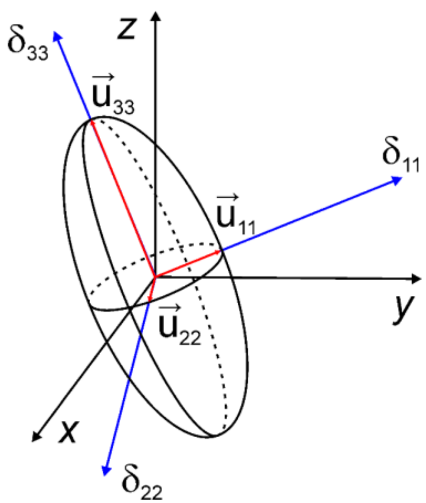


CSA (Chemical Shift Anisotropy)





Isotropic value (Solution)



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

$$\delta = u^{-1} \cdot \delta_{PAS} \cdot u$$

$$\text{where } \delta_{PAS} = \begin{pmatrix} \delta_{11} & 0 & 0 \\ 0 & \delta_{22} & 0 \\ 0 & 0 & \delta_{33} \end{pmatrix}$$

$$\text{and } u = (\overrightarrow{u_{11}}, \overrightarrow{u_{22}}, \overrightarrow{u_{33}})$$

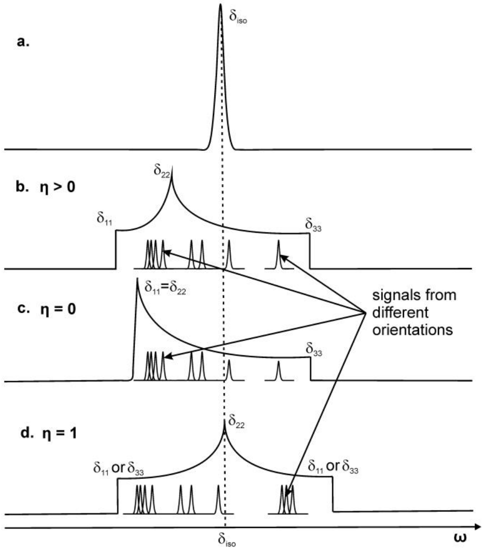


Figure 2.12. The effect of CSA on NMR spectra: a) Isotropic signal in solution-state NMR as a result of rapid motional averaging. b, c and d) Powder patterns observed at different values of the asymmetry parameter η.

asymmetry parameter = η (eta)

Magic Angle Spinning (MAS)

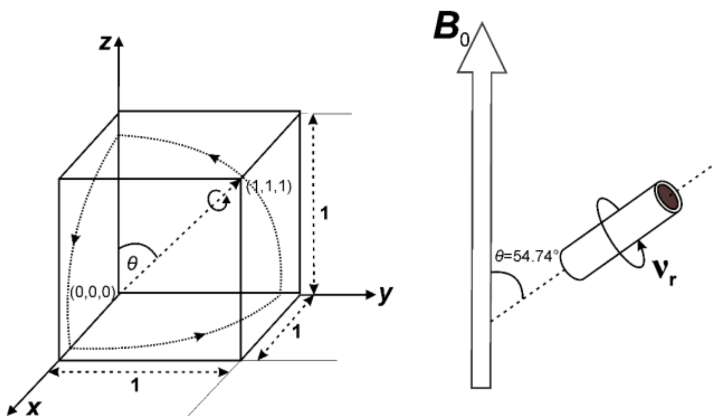


Figure 2.17. The unit cube representation of the magic angle (*left*) and sample rotation at the magic angle with a frequency $\mathbf{v}_r$ (*right*).

Isotropic value

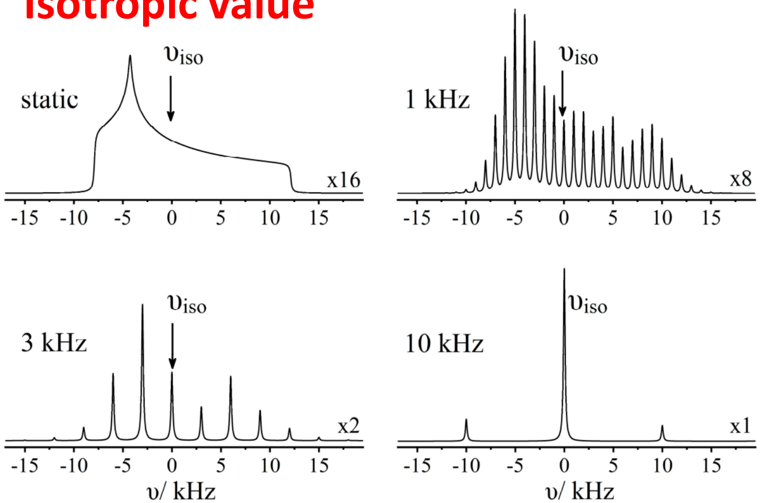


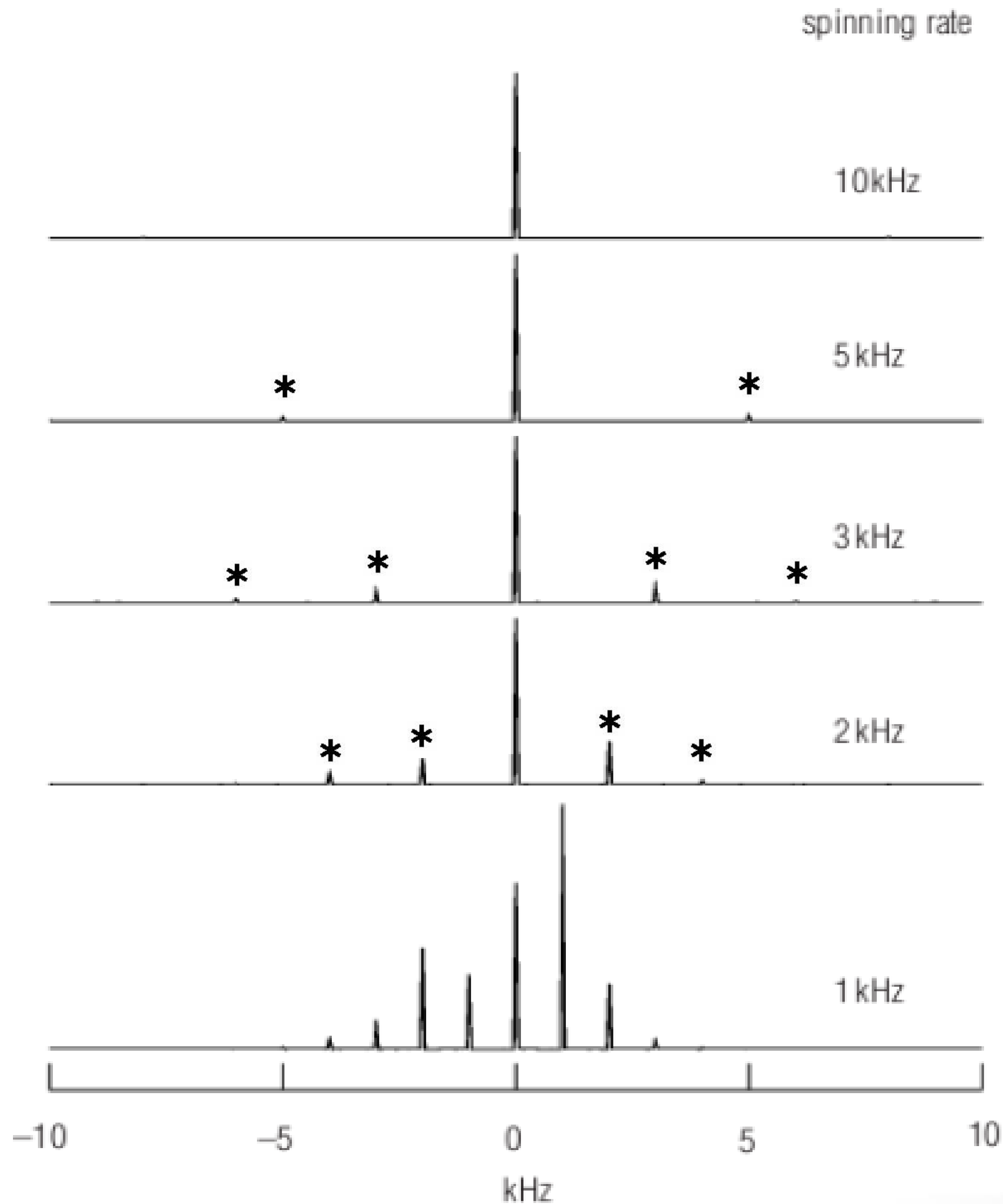
Figure 3. Numerical simulations demonstrating the effect of magic-angle spinning (MAS) upon the solid-state NMR line shape of a spin-1/2 nucleus with dominant line broadening due to the magnetic shielding anisotropy. Spinning sidebands are located at integer multiples of the rotor frequency.

$$\omega_P(\theta) = 2\pi\nu_P(\theta) = \gamma B_0\left(1 - \sigma_{iso} - \frac{1}{3}\Delta\sigma\left(3cos^2\theta - 1\right)\right)$$

θ = 54.7∘

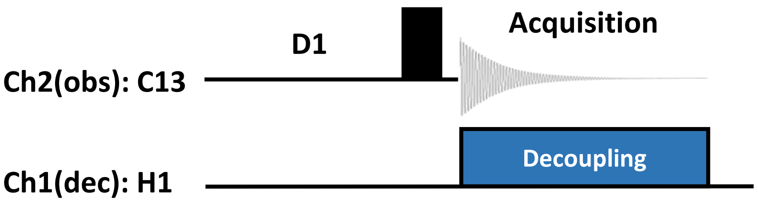
3cos^2θ – 1 = 0

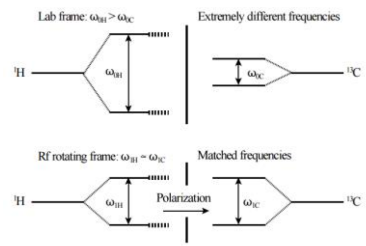
Spinning side-band



Pulse sequence in Solid-state NMR

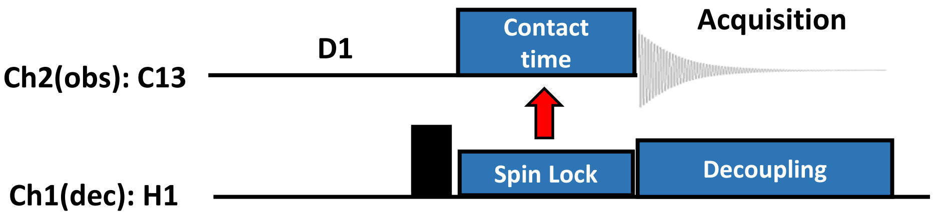
DP (Direct-Polarization, One-pulse)



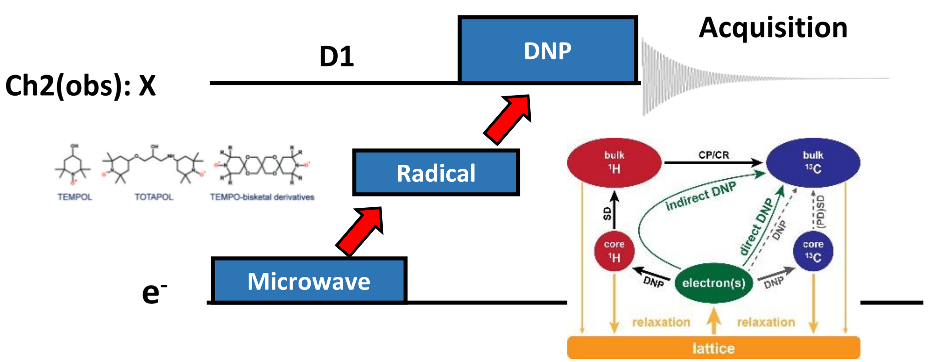


Hartmann Hahn match

CP (Cross-Polarization)

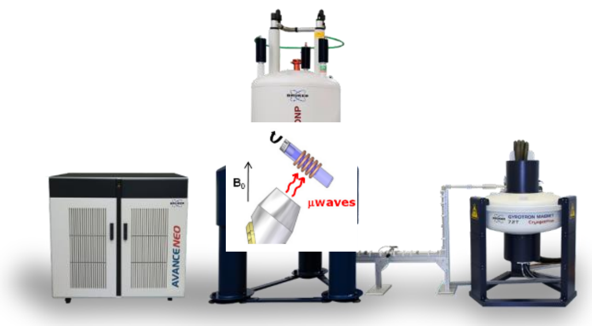


DNP (Dynamic-Nuclear-Polarization)



Gyrotron (L-He)

Klystron (L-N2, efficiency = 80%)



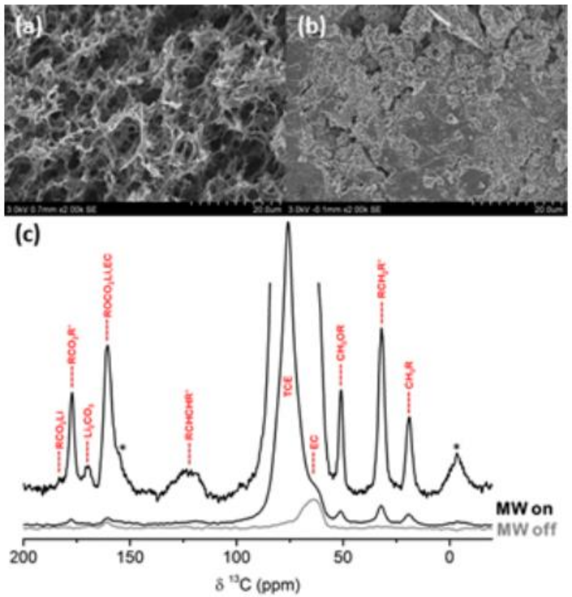


Figure 1 Scanning electron microscope (SEM) images of the rGO anode (a) before and (b) after one electrochemical cycle. (c) 1H-

Application of solid state NMR

Organic complexes
Inorganic complexes
Zeolites
Mesoporous solids
Microporous solids
Aluminosilicates/phosphates
Minerals
Biological molecules
Glasses
Cements

Food products
Wood
Ceramics
Bones
Semiconductors
Metals and alloys
Archaelogical specimens
Polymers
Resins
Surfaces

But, Fine particle + at least 20mg

http://www.theresonance.com/nmr-tutorial-mas-rotor-filling/

7. Hardware

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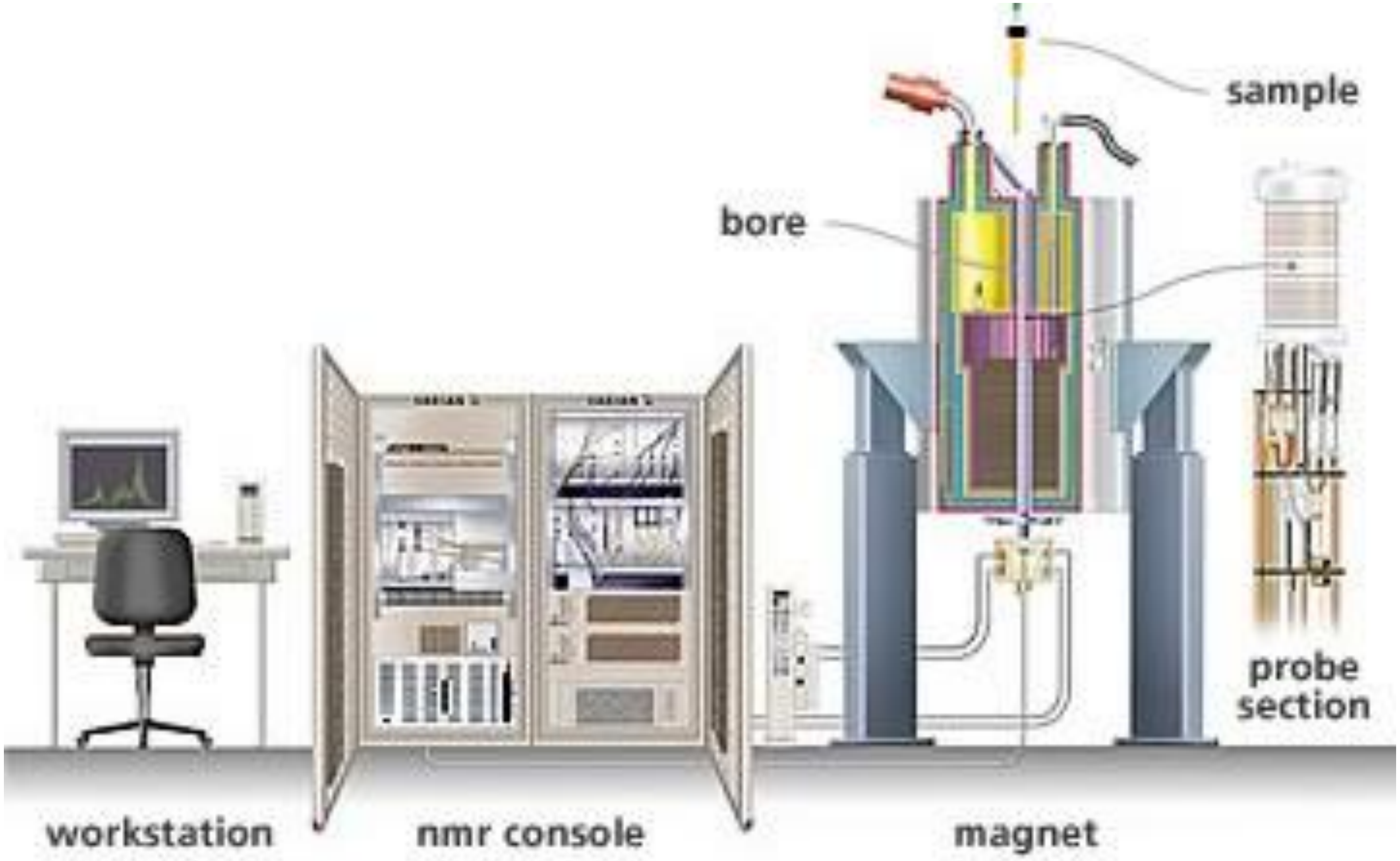
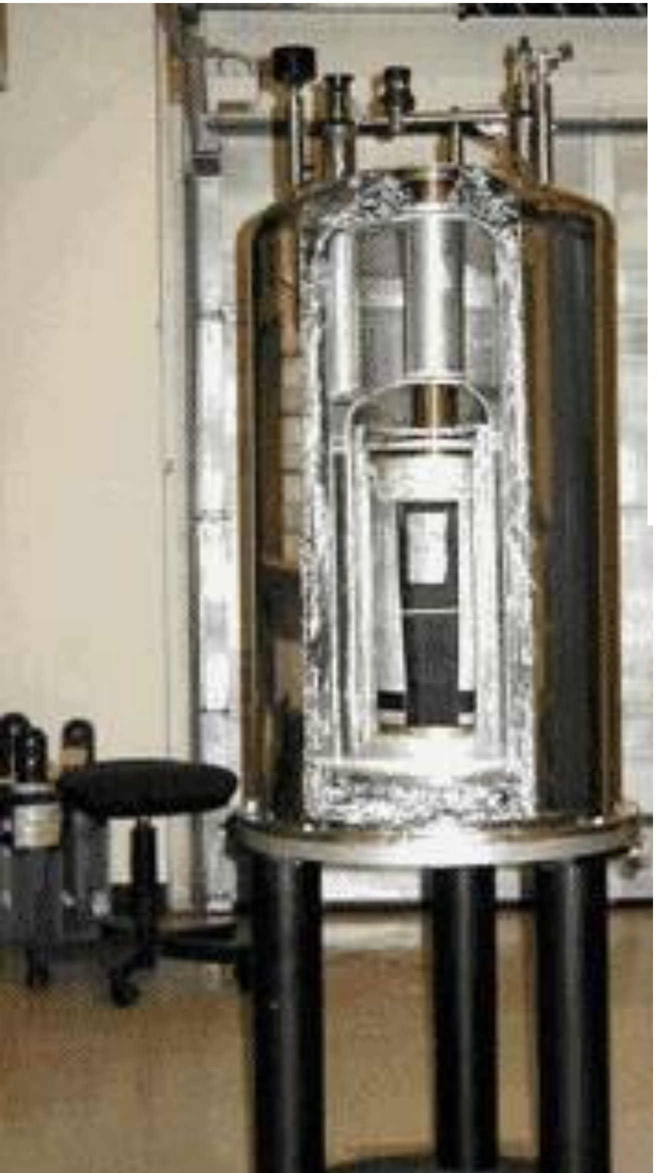
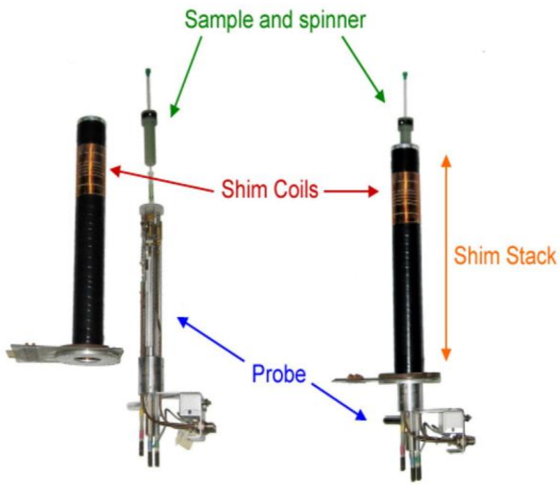
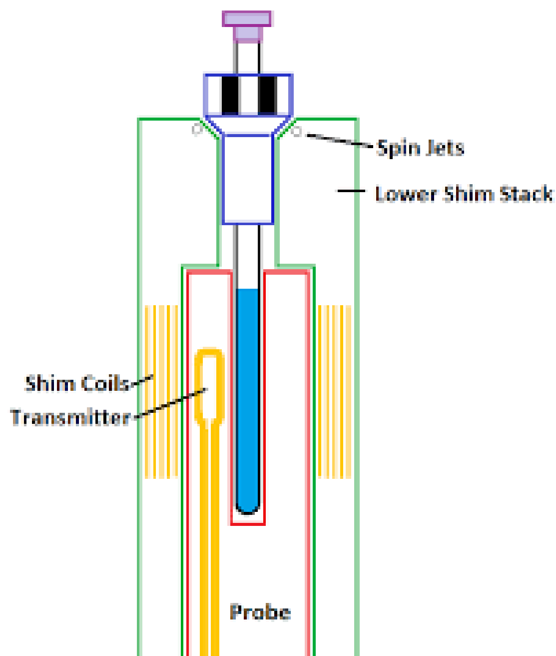
NMR diagram

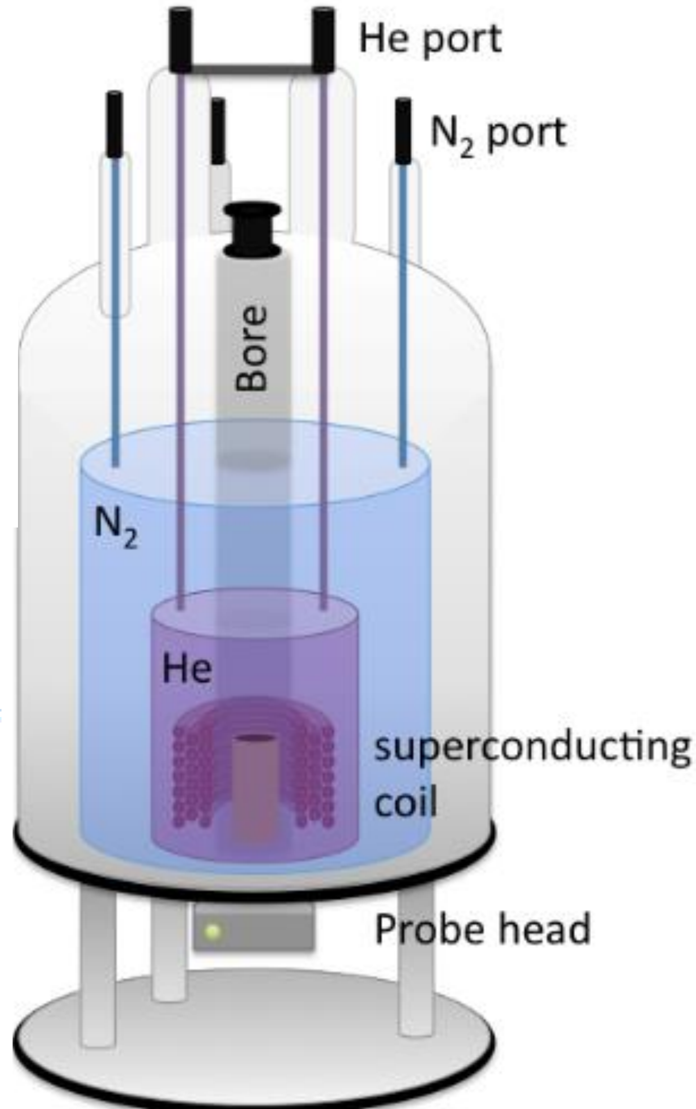


Magnet diagram









Varian 600 MHz NMR

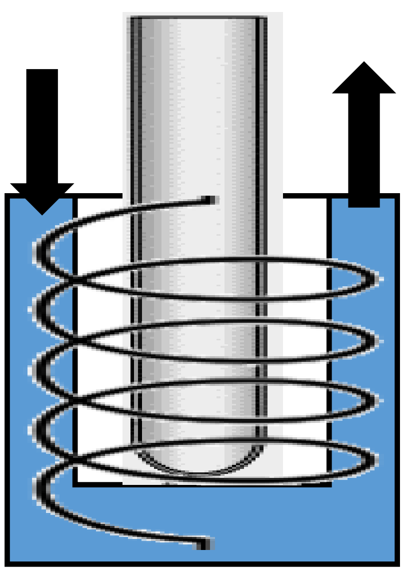
	600 MHz NMR
Location	102-B119
Measurement Type	Self / Request
Model	VNMRS 600 (Varian)
Magnet	14.1 T
Channel	3 channel
Probe	5 mm PFG Auto X DB probe 5 mm Automated triple resonance probe 4 mm Nano TM probe 1.6 mm triple resonance HXY MAS solid probe 5 mm double resonance MAS solid probe
Auto-sampler	X
Auto-tuning & matching	-
Power	100 W / 300 W / 300 W
Channel	Ch1 : ^{1}H, ^{19}F Ch2 : 170MHz(^{31}P) ~ 150 MHz (^{13}C) Ch3 : 150MHz(^{13}C) ~ 60 MHz (^{15}N)
Temperature	-60 ~ 100 ˚C

Bruker 400 MHz NMR

	400 MHz NMR
Location	102-B119
Measurement Type	Self / Request
Model	AVANCE III HD (Bruker)
Magnet	9.4 T
Channel	2 channel
Probe	BBO probe
Auto-sampler	O
Auto-tuning & matching	O
Power	100 W / 500 W
Channel	Ch1 : ^{1}H, ^{19}F Ch2 : 160MHz(^{13}C) ~ 49 MHz (^{15}N)
Temperature	-150 (20) ~ 150 ˚C

Cryogenic Bruker 600 MHz NMR (Jan, 2023)

	600 MHz NMR
Location	102-B119
Measurement Type	Self / Request
Model	AVANCE NEO
Magnet	14.1 T
Channel	2 channel
Probe	5 mm **Prodigy probe** 5 mm I-probe
Auto-sampler	O
Auto-tuning & matching	O
Power	300 W / 500 W
Channel	Ch1 : ^{1}H Ch2 : 240MHz(^{31}P) ~ 27.6 MHz (^{109}Ag), ^{19}F
Temperature	-150 ~ 150 ˚C



<S/N ratio>
L-N2 (77K) -> 2~3배
L-He (4K) -> 4배

8. Pre-treatment

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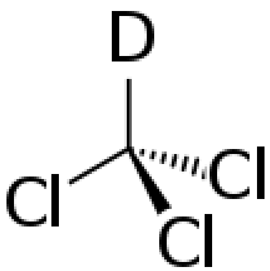
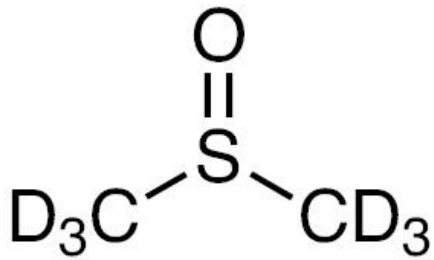
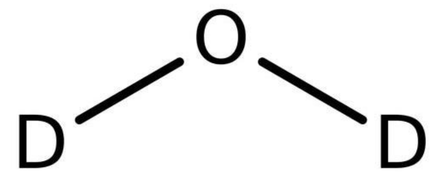
NMR solvent

Dielectric constant : Polar > 20 > Non-polar

NMR Solvent Storage
Avoid light & moisture: All NMR solvent
Store refrigerator (4°C): CDCl3, THF-D8







CDCl3
- Dielectric constant: 4.8

- Advantage:
  - Cheap,
  - Easily Removed

- Disadvantage:
  - Light sensitive(Contain HCl)
  - Toxic, carcinogenic
  - Weak lock signal
  - Easily evaporated

DMSO-D6
- Dielectric constant: 46.7

- Advantage:
  - Strong lock signal

- Disadvantage:
  - High price
  - Highly viscosity
  - Easily contain water
  - M.P.: 20 ~ 22 °C (Freeze RT)
  - Hard removed

D2O
- Dielectric constant: 78.5
- Advantage:
  - Cheap

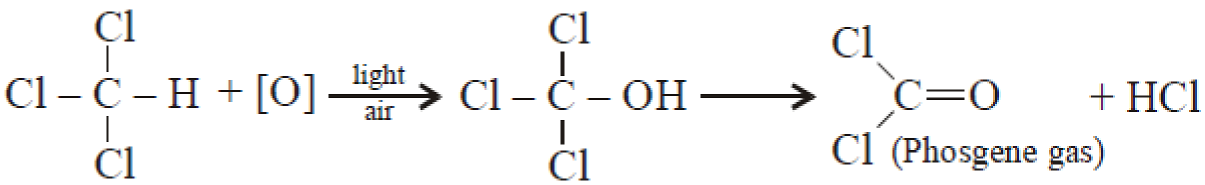
- Disadvantage:
  - Exchange OH and NH
  - Easily contain water
  - Chemical shift (Temp. dependent)
  - Hard removed

https://m.blog.naver.com/PostView.naver?isHttpsRedirect=true&blogId=release&logNo=50091986445

Caution

CDCl3 + Light -> HCl

- Use silver foil
  (Stabilizer, radical scavenger)
- Use molecular sieve
  (Eliminate H_2O)



Change of chemical shift

- Temperature
- pH
- Concentration

HOD peaks

- Related residual H_2O
- Slow exchange H_2O and HOD
  → two peaks
  (singlet H_2O, 1:1:1 triplet HOD)
- Hydrogen bond
  → Broad peak of HOD

How to remove residual water

→ Use Molecular Sieve 3~5 g in 100g ($CDCl_3$)

- 3 Å: Adsorption of polar liquid (NH_3, H_2O)
- 4 Å: Adsorption of Non-polar liquid
  (H_2O, CO_2, SO_2, H_2S, C_2H_4, C_2H_6, C_3H_6, EtOH)
- 5 Å: Adsorption of Linear C_xH_x to n-C_4H_{10}
  Alcohols to C_4H_9OH
  C_4H_9SH

https://m.blog.naver.com/PostView.naver?isHttpsRedirect=true&blogId=release&logNo=50091986445

Quality of sample tube

Thin wall (Precision-Glass)
- **Temp 120 °C**
- Critical shimming quality (low Fe_2O_3)
- **Good volume reproducibility**
- High sample volume in RF coil

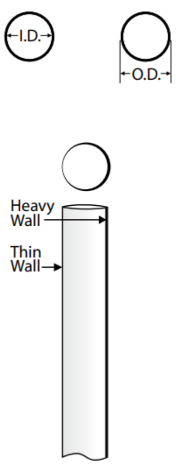
• 535-PP-7 (600 MHz grade, $40)
• 527-PP-7 (400 MHz grade, $25)

Economy (Middle MW)
- **MW<1500**, RT

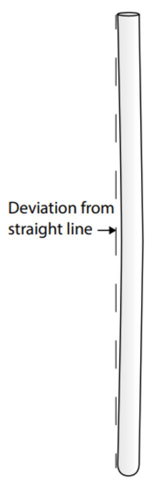
• WG-1241-7 (600 MHz grade, $10)
• WG-1228-7 (400 MHz grade, $9)

High-Throughput (low MW)

• up to 600 MHz, **MW<250**, RT
• WG-1000 ($2)



Example of a NMR tube with poor concentricity



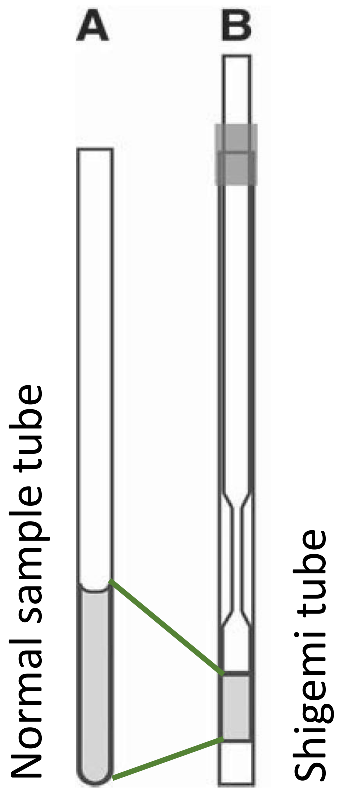
Example of poor camber

5mm Thin-Wall NMR Tube Comparison Table

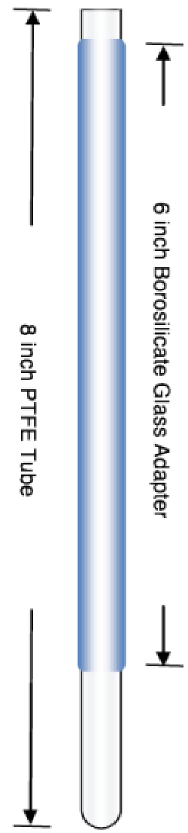
	High-Throughput	Economy	Precision (Glass)	Precision (Quartz)	Precision (Suprasil)
Material	Type 1 Class B Borosilicate Glass	Type 1 Class B Borosilicate Glass	Type 1 Class A Borosilicate Glass	Clear Fused Quartz	Synthetic Quartz
Impact On Shimming Quality By Paramagnetic Impurities	Medium (1200ppm Fe_2O_3)	Medium (1200ppm Fe_2O_3)	Small (400ppm Fe_2O_3)	None (0.5ppm Fe_2O_3)	None (<0.005ppm Fe_2O_3)
Maximum Working Temperature	Ambient	Ambient	230° C	1300° C	1300° C
Sample Volume Reproducibility	10%	10%	0.5%	0.5%	0.5%
Recommended Applications	Small molecule experiments up to 600 MHz (MW<250)	1D NMR experiments with small organic molecules (MW<1500)	Experiments requiring critical shimming quality (high-field, multi-dimension, multi-nuclei)	^{11}B NMR, rapid cooling/heating experiments, photochemistry studies	Photochemistry studies with deep UV light source

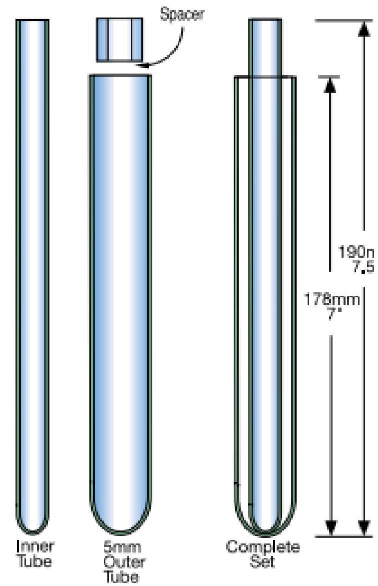
https://www.rototec-spintec.com/flyer/wilmad/NMR_Catalog_2020.pdf

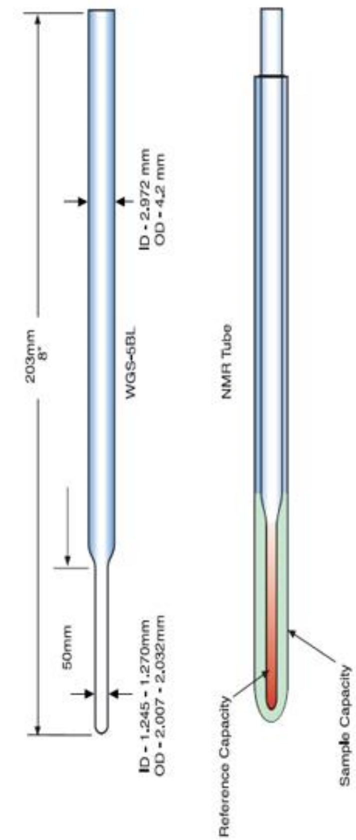
Special purpose sample tube



Reduce sample volume (1/3)







Shigemi tube
$ 300 - 400
- Increase 16% SNR
- Low con. or low volume

PTFE tube
$ 60
- HF or 29Si NMR

Coaxial tube
$ 40 – 50 (+ $ 50)
- Non-deuterated sample
- Quantitative NMR
- Referencing

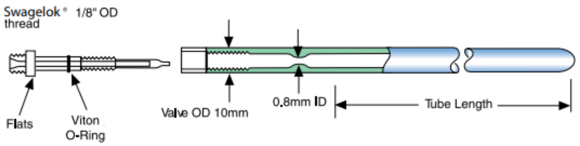
Stem Coaxial tube
$ 40 – 50 (+ $ 50)
- Non-deuterated sample
- Quantitative NMR
- Referencing

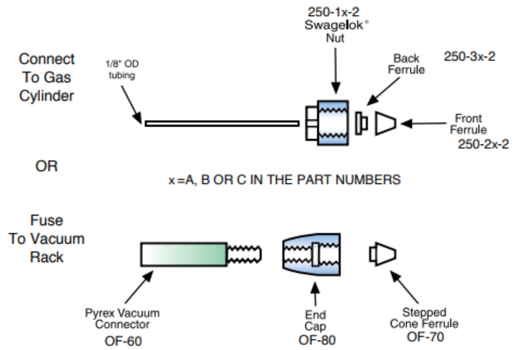
https://www.rototec-spintec.com/flyer/wilmad/NMR_Catalog_2020.pdf

Special purpose tube & cap

Pressure/Vacuum Sample Tube

Wilmad's Pressure/Vacuum Tube is the most reliable NMR tube for medium range pressure (<300 psi) experiments in the market. It is designed to connect to a 1/8" metal (stainless steel or brass) vacuum line using SwageLok® fittings or a rubber vacuum hose and a glass connector (OF-60). The PV-ANV valve is made of PTFE and all other parts are Pyrex® or equivalent glass. Valve is opened simply by turning counterclockwise.





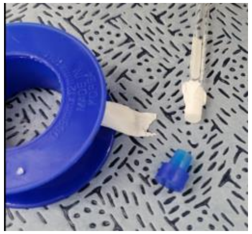
Each Pressure/Vacuum tube is supplied with a PV-ANV valve, but not with a Swagelok® nut or ferrules. Order these separately (see connectors table).

Low Pressure/Vacuum Tubes

Wilmad's Low Pressure/Vacuum (LPV) tube is ideal for anaerobic and gas-tight NMR experiments, and offers a convenient flame-free sealing solution for air sensitive or volatile liquid samples.

- Robust sealing system allows pressure build-up inside the sample
- Greaseless PTFE piston provides a 100% contamination-free seal
- Redesigned with a 4X larger sealing surface; eliminates leaks and greatly increases lifetime when compared to traditional J. Young tubes
- Axial symmetric design guarantees application in spinning experiments
- Due to the nature of glass, Extreme Caution should be exercised when using at elevated or reduced pressures since a tiny scratch on the glass surface would significantly lower the tensile strength. Adequate safety shielding should always be used when working in these conditions.

Ethyl Vinyl Acetate Cap
- Cheap
- Avoid $CDCl_3$, Acetone-D6



Ethyl Vinyl Acetate Cap
+ Teflon tape
- Cheap
- Use $CDCl_3$, Acetone-D6

PTFE Cap
$ 16 (or $ 5 economy ver.)
- Use $CDCl_3$, Acetone-D6, HF

https://www.rototec-spintec.com/flyer/wilmad/NMR_Catalog_2020.pdf

Volume and concentration

- Sample volume = 500 ul (400 ~ 700 ul)

- Sample concentration

1. 1H: 0.05 mM ~ 10 mM (Too high concentration cause Line-broadening effect)

2. 13C, 2D NMR(COSY, NOESY, TOCSY, etc.): 10 mM ~ 100 mM

3. 15N, 17O, Hetero 2D NMR (HSQC, HMBC, HMQC, etc.): 100 mM < Highest concentration

   ex) Sample A (MW=200), 0.05 mg / 500 ul = 0.5 mM = 100 ppm

   Sample A (MW=200), 1 mg / 500 ul = 10 mM = 2000 ppm

   Sample B (MW=500), 25 mg / 500 ul = 100 mM

Referencing

<Internal reference>

1. Sample + NMR solvent (CDCl3, D2O, DMSO-D6, etc.) + reference compound (TMS, DSS)

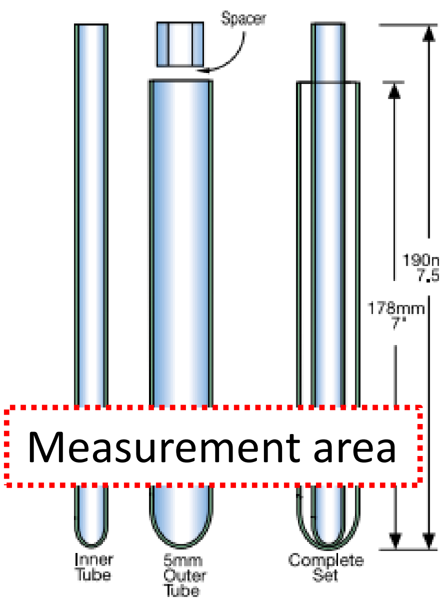
<External reference>

2-1. Sample + NMR solvent (CDCl3, D2O, DMSO-D6, etc.)

2-2. Reference sample (P31: TPP = -17.57 ppm, F19: TFT: -63.72 ppm)

3. Coaxial sample tube (Evans method)

- Inner tube: NMR solvent or Reference
- Outer tube: Sample



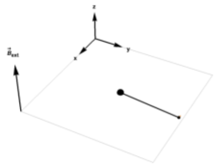
- None deuterated solvent condition -> No Lock / No auto shim -> Poor or not easy measurement
- NMR solvent and Referencing (+Quantitative NMR)

Paramagnetic effect

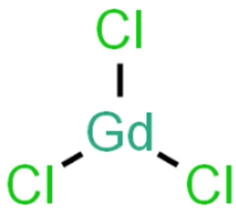
- Degassing

Oxygen (Paramagnetic) -> Short T1&T2 relaxation-> **Quench** for NMR signal -> Purge N2 or Ar gas

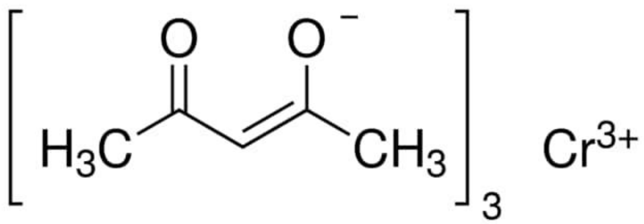
- Doping agent (Use Paramagnetic agent)



- Reduce T1 & T2 -> Short experiment time
- Line broadening effect (poor shimming)
- Add paramagnetic material concentration: 1 mM (1H), 25 mM – 50 mM (13C)



GdCl3
Gadolinium(III) chloride



Cr(acac)3
Chromium(III) acetylacetonate

CuSO4, MnCl2, NiCl2

Dielectric constant : Polar > 20 > Non-polar

https://onlinelibrary.wiley.com/doi/full/10.1002/masy.201300034

- Wash sample tube to acetone or ethanol.

  Cheap sample tube dry-situation tilted state in oven make possible bending

  (Sample tube bending test → rolls the ground If bending

  sample tube spins, quartz glass in probe has some damage.)

Probe Bottom

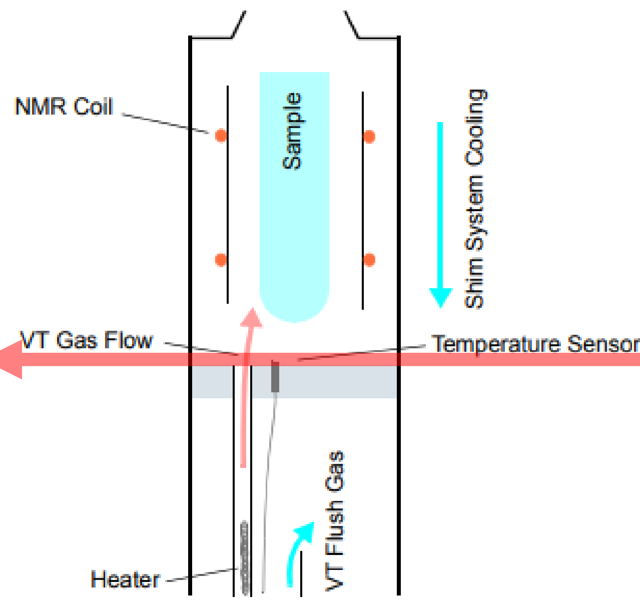
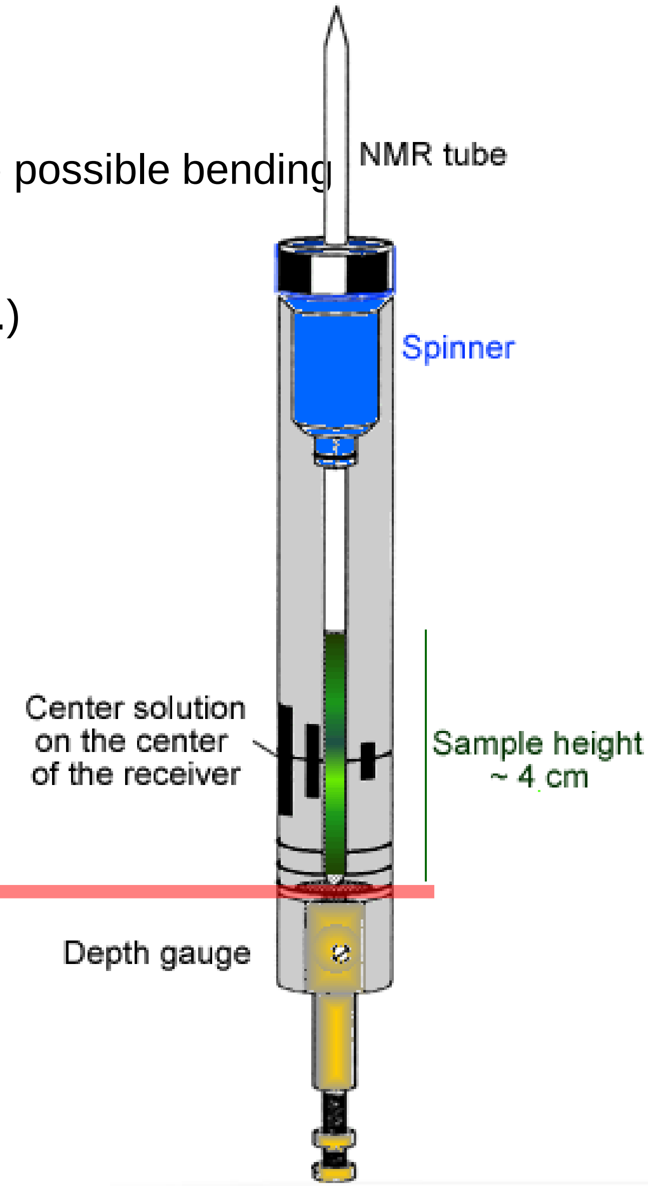


Figure 3.1 Sketch of sample temperature control in a NMR probe

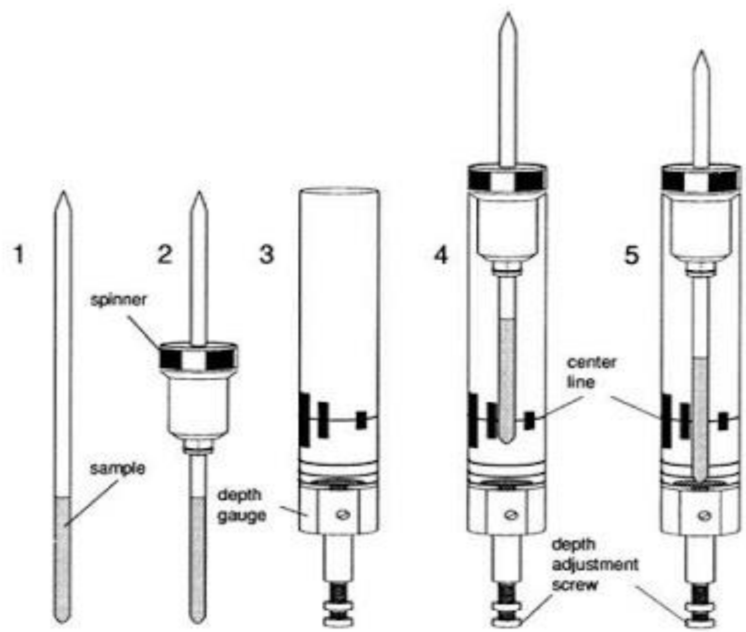


Sample preparation

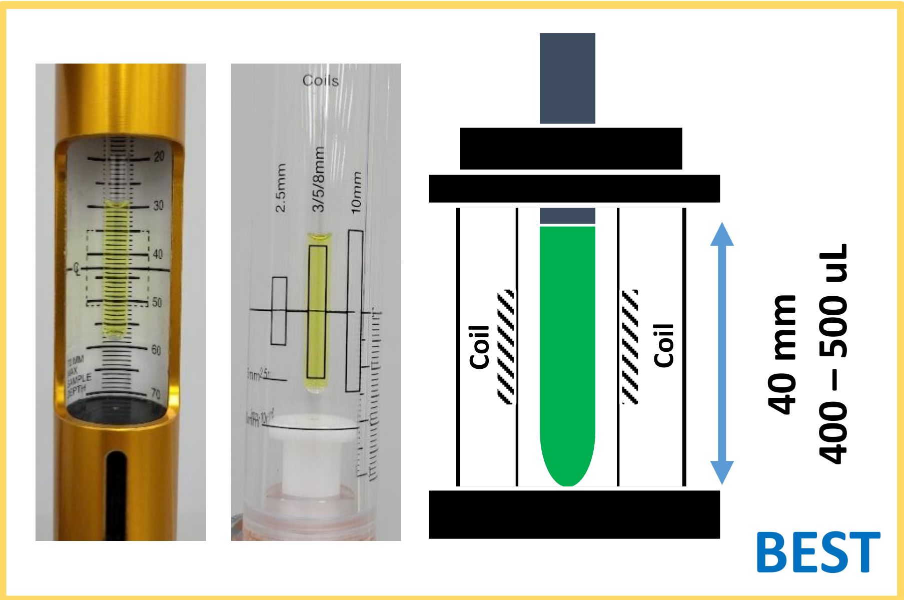
1. Perfect solution sample filters syringe filter.

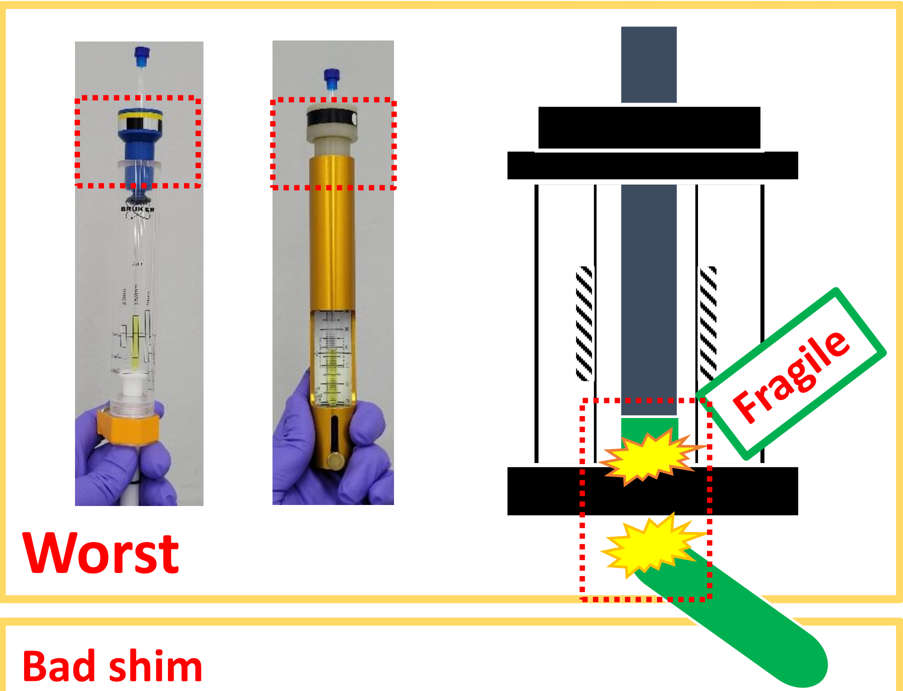
   (If your sample has insolubility, It makes low resolution and sensitivity about peak)
2. 5 mm sample tube inserts sample 0.5 ml (500 μl, 4cm)
3. Spinner placed on depth gauge insert sample tube

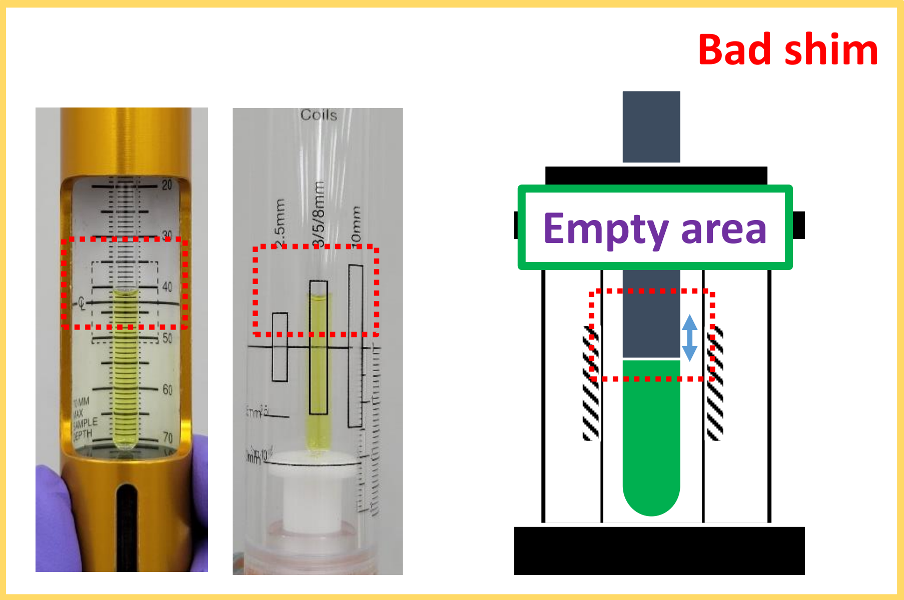
   (※ Don`t touch O-ring)
4. Check location depth gauge center (dash line square) with sample tube
5. Remove depth gauge.

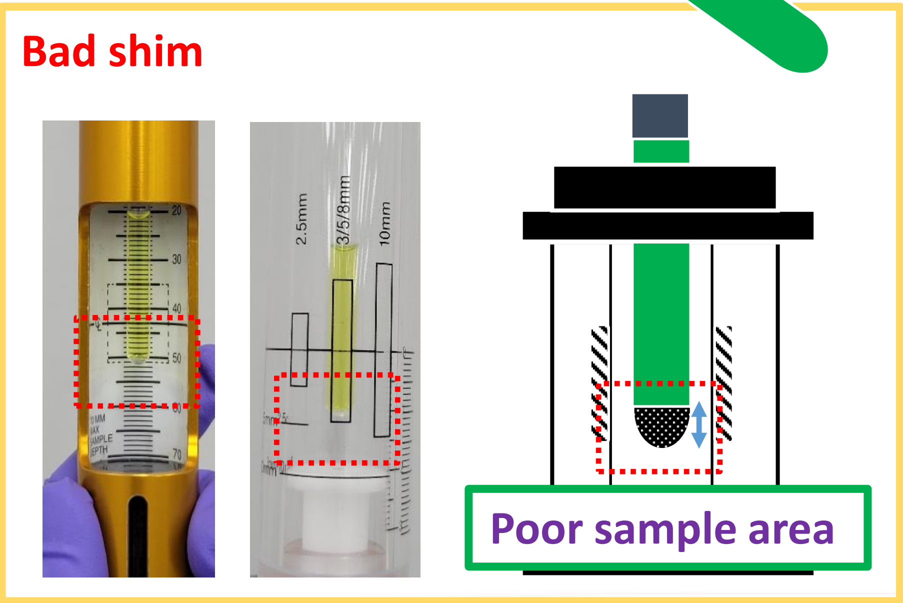


Sample volume and height





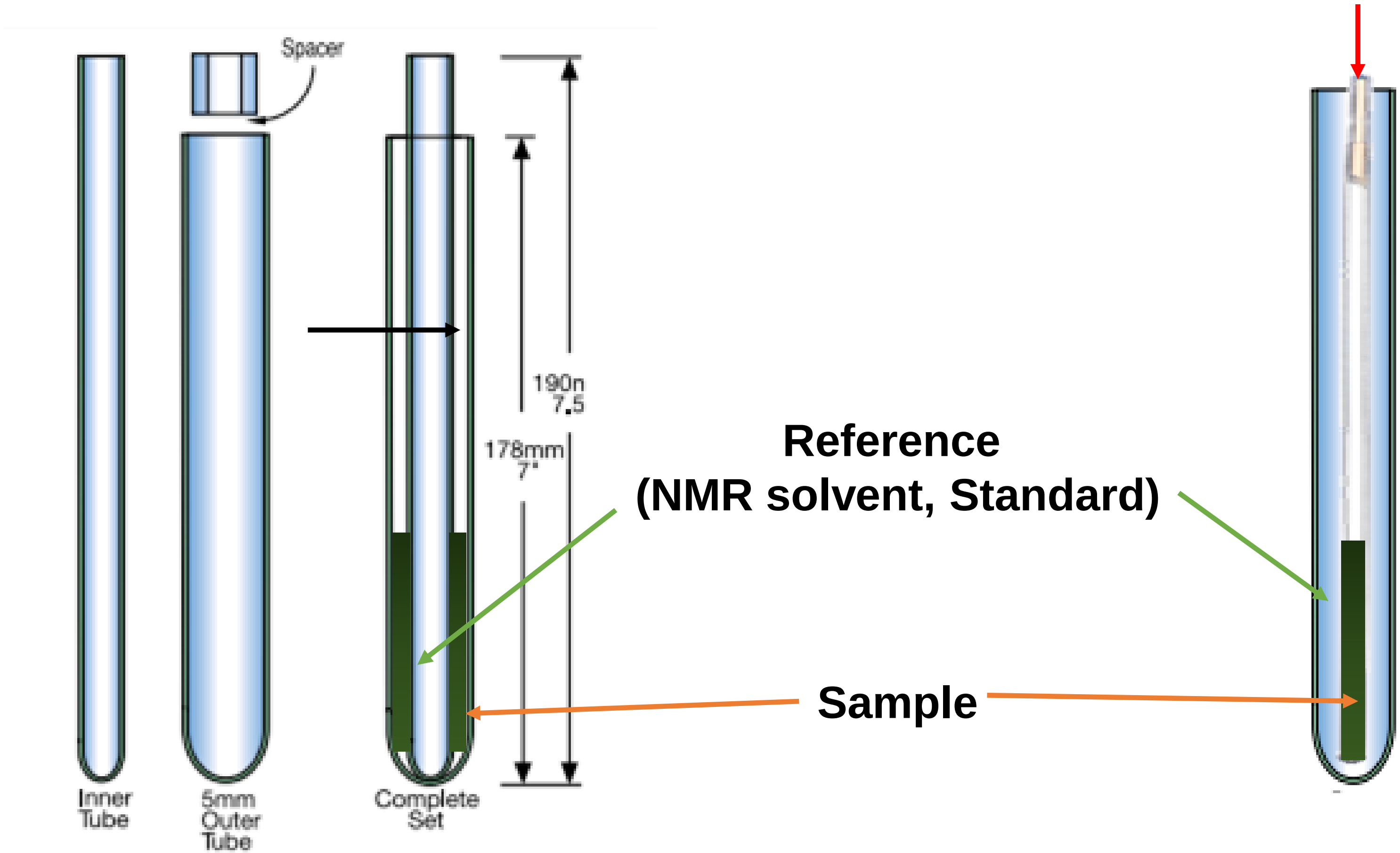




Sampling for PF6 or Toxic sample

Standard Evans method

PTFE tube



Coaxial tube

9. Operation Manual

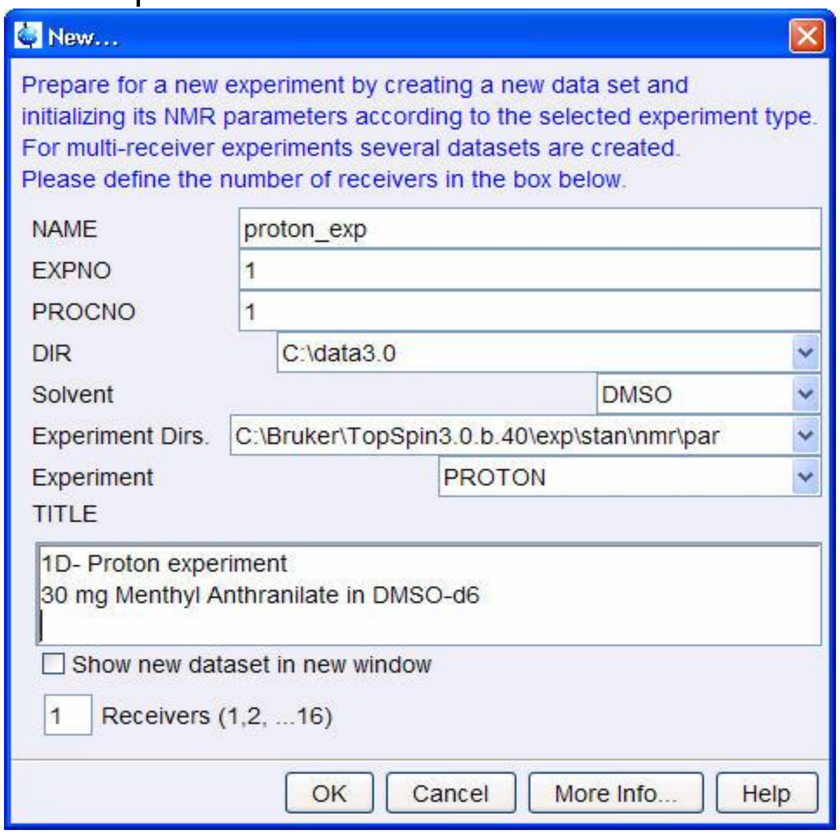
9-1. Manually Operation

ULSAN NATIONAL INSTITUTE OF SCIENCE AND TECHNOLOGY

1. Create Dataset

Click **Create Dataset** (edc) - Start tab.

Insert parameter value.



Experiment name : ex) 20160908_Test_1

Experiment number : ex) 1(1H), 2(13C), 10(2D) (1~999)

Processing number: ex) 1

Data save route ex) \ data

NMR solvent

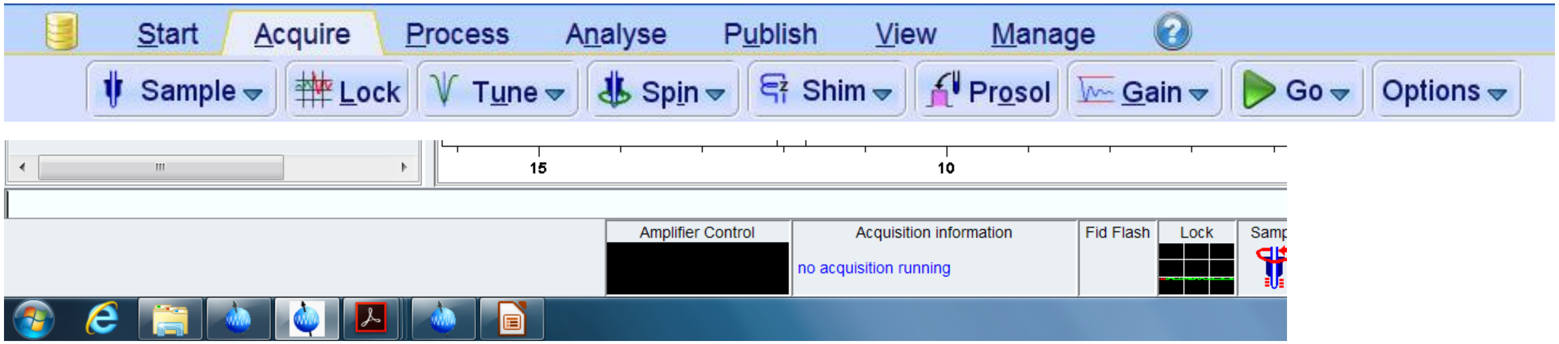
Parameter set

ex) proton - PROTON, carbon - C13CPD

Direct type or select

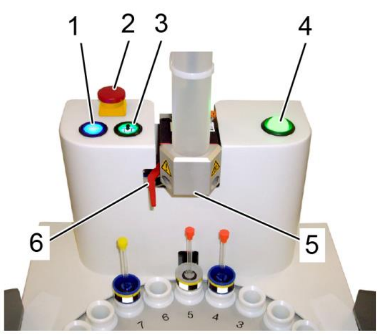
Sample information.

2. Sample insertion into the magnet



Insert : Prompt types **sx #** (sample holder number)

Eject : Prompt types **sx ej**



1. Rotate carousel clockwise blue push button (enabled)
2. Emergency stop button
3. Inject/Eject green push button (enabled)
4. State LED (green showing *idle* state)
5. Sample gate (open)
6. Sample over length latch

- Press the blue button to rotate the carousel so that the sample carrier to measure next is below the Transport tube gate.

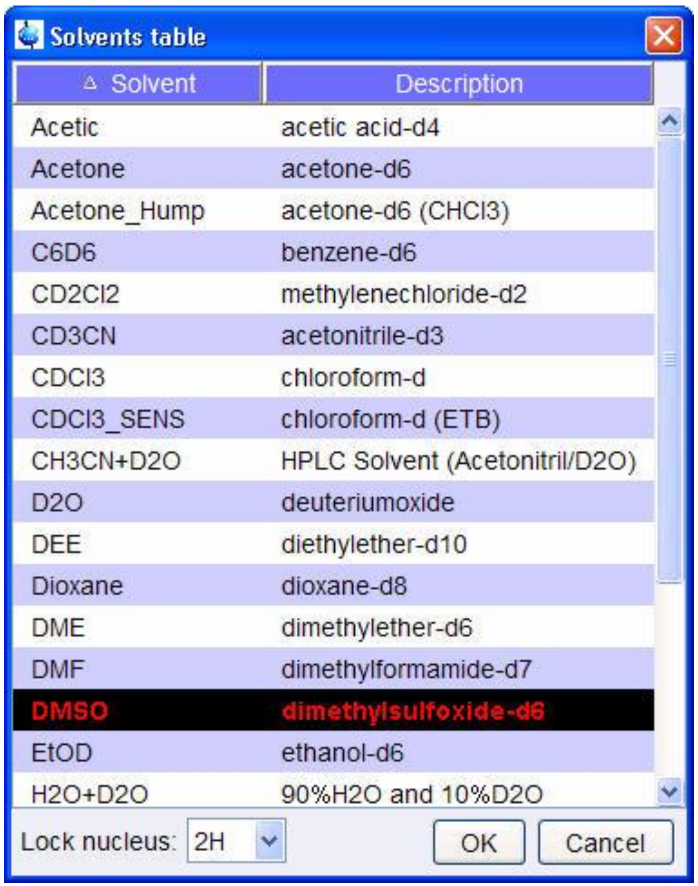
- When pressing the Inject/Eject button the sample carrier below the Transport tube gate will be lifted towards the Transport tube and transported to the magnet bore.

- When pressing the Inject/Eject button a second time the sample carrier will be removed from the magnet bore and transported to the SampleCase and placed in the holder below the Transport tube gate.

※ (XXX) or bold character are command. Could use command line.

3. Lock

Click Lock (lock) - Acquire tab

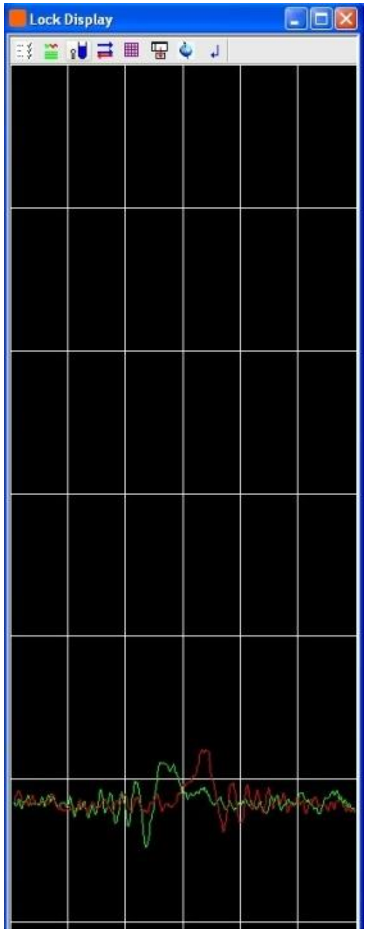


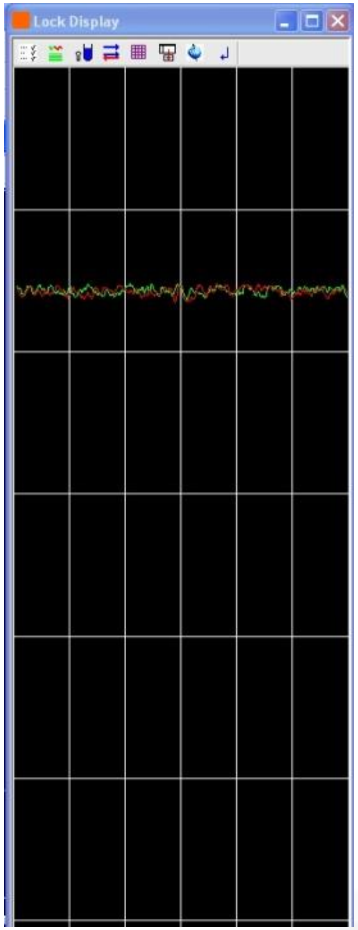
Solvent	Description
Acetic	acetic acid-d4
Acetone	acetone-d6
Acetone_Hump	acetone-d6 (CHCl3)
C6D6	benzene-d6
CD2Cl2	methylenechloride-d2
CD3CN	acetonitrile-d3
CDCl3	chloroform-d
CDCl3_SENS	chloroform-d (ETB)
CH3CN+D2O	HPLC Solvent (Acetonitril/D2O)
D2O	deuteriumoxide
DEE	diethylether-d10
Dioxane	dioxane-d8
DME	dimethylether-d6
DMF	dimethylformamide-d7
DMSO	dimethylsulfoxide-d6
EtOD	ethanol-d6
H2O+D2O	90%H2O and 10%D2O

Choice lock solvent
(or, "**lock used-NMR-solvent**" ex) **lock DMSO**).

3. Lock

Lock-complete condition display lock level on state line.
If lock level is so high, control lock power or lock gain. (proper lock level = 50 ~ 60)





4. Tune

Click 

(atma)

5. Spinning

Click 

(ro on)

6. Shimming

Click 

(tg)

7. Prosol

Click 

(getprosol)

8. Receiver gain

Click 

(rga)

9. Parameter

Number of scan : Prompt types **ns** (edit #)

Relaxation delay : Prompt types **de** (edit #)

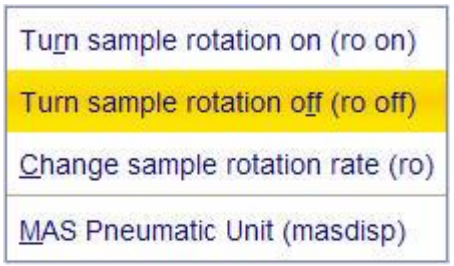
10. Acquisition

Click 

(zg)

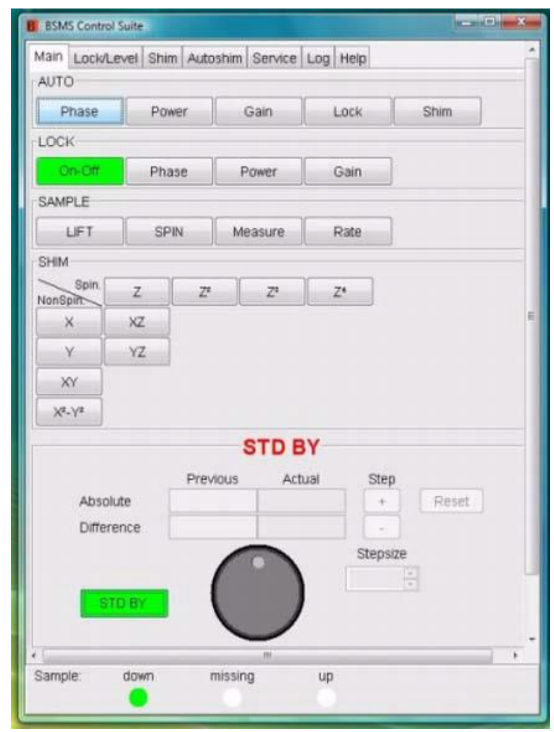
Experiment end

Click 



Stop sample rotation (ro off) spinning

Type **bsmsdisp** on command line
Click lock On-Off (Stop lock)



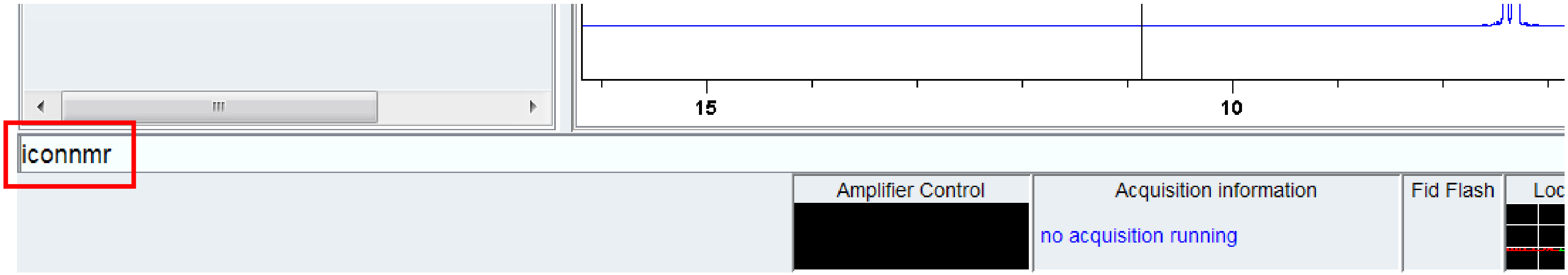
To use manually operation

1) **sx #** - Insert sample into magnet
2) **edc** - Create new experiments room
3) **rsh** - Refresh optimized shim-map
4) **ro on** – spinning on
5) **lock** - Locking
6) **atma** - Auto tuning & matching
7) **getprosol** - Update standard parameter [ex, p1, plw1]
8) **ased** - Change parameter [ex, ns(number of scan), d1(delay time)]
9) **topshim** - shimming
10) **rga** - Auto-adjust receiver gain
11) **zg** - start experiment
12) **efp** - Fourier transformation
13) **apk** - auto-phase correction
14) **absn** - auto-baseline correction
15) **ro off** – spinning off
16) **sx ej** – sample eject

If automation system is connecting, sx command is not working.

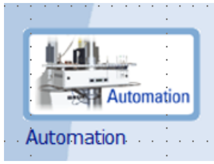
9-2. Automation (Icon-NMR)

1. Open Icon-NMR



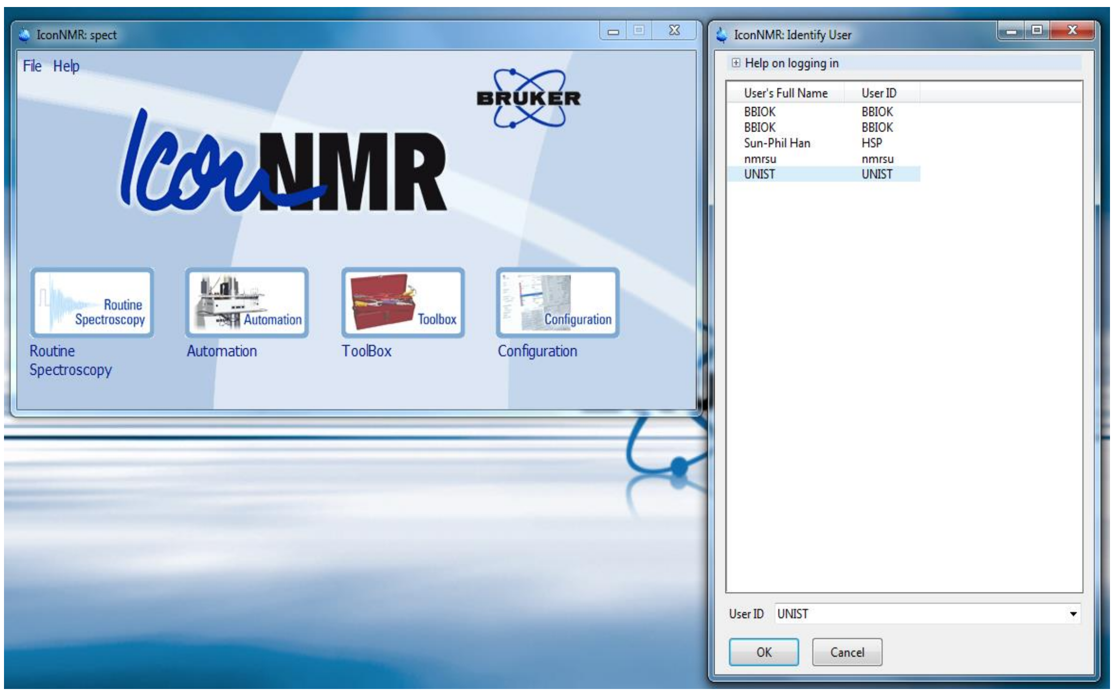
To open Icon-NMR : Prompt types **iconnmr**

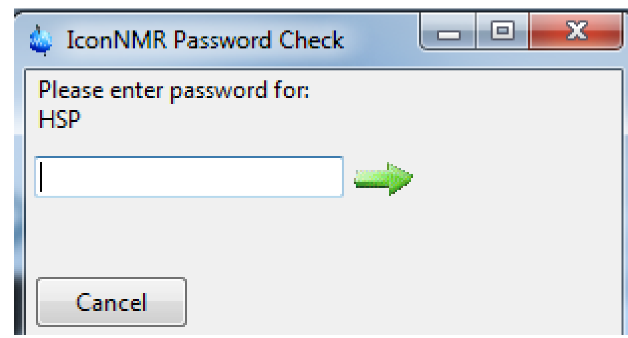
2. Automation

Click  Automation

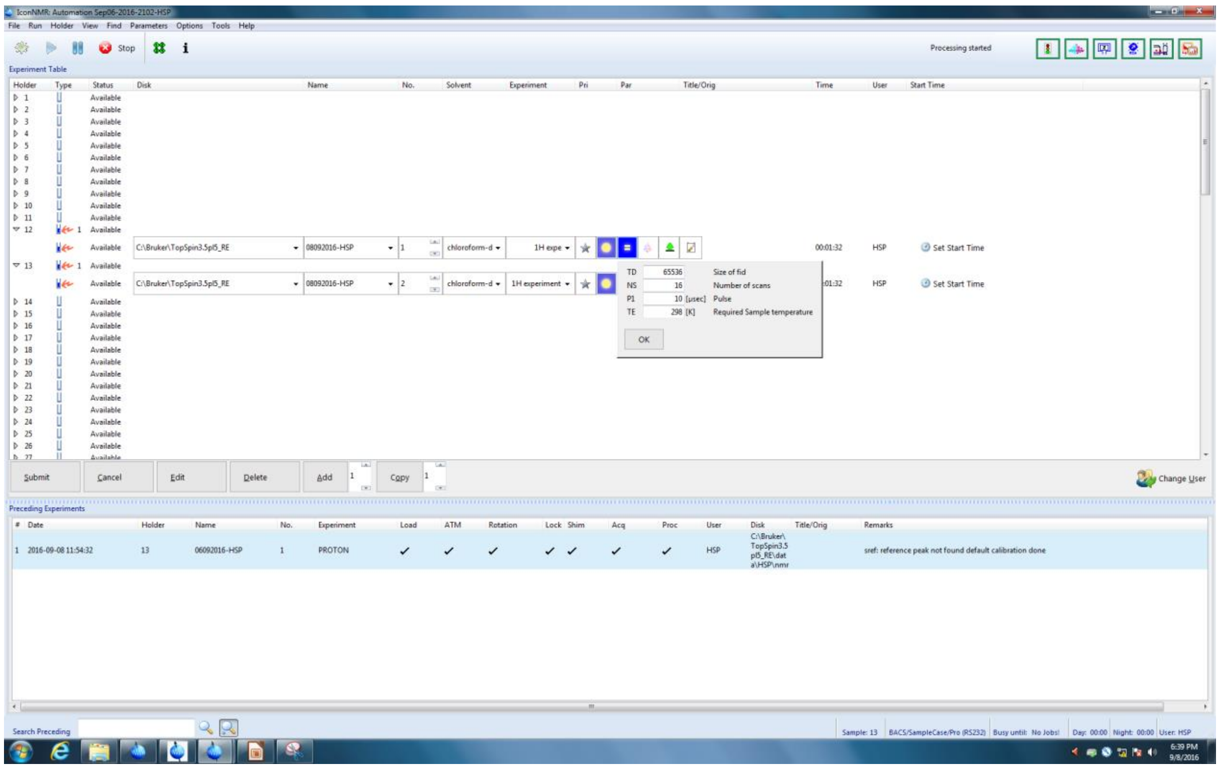
3. Login

Select user ID
Insert password





4. Experiment Table



1) Check holder status

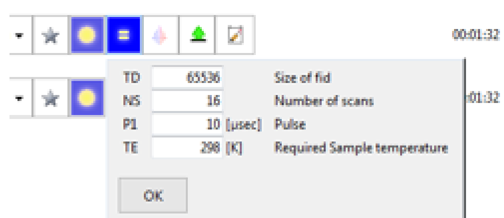
2) Double click
empty holder (1~24)

3) Type sample name

4) Change No.
(experiments number)

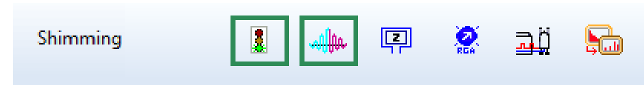
5) Select NMR solvent

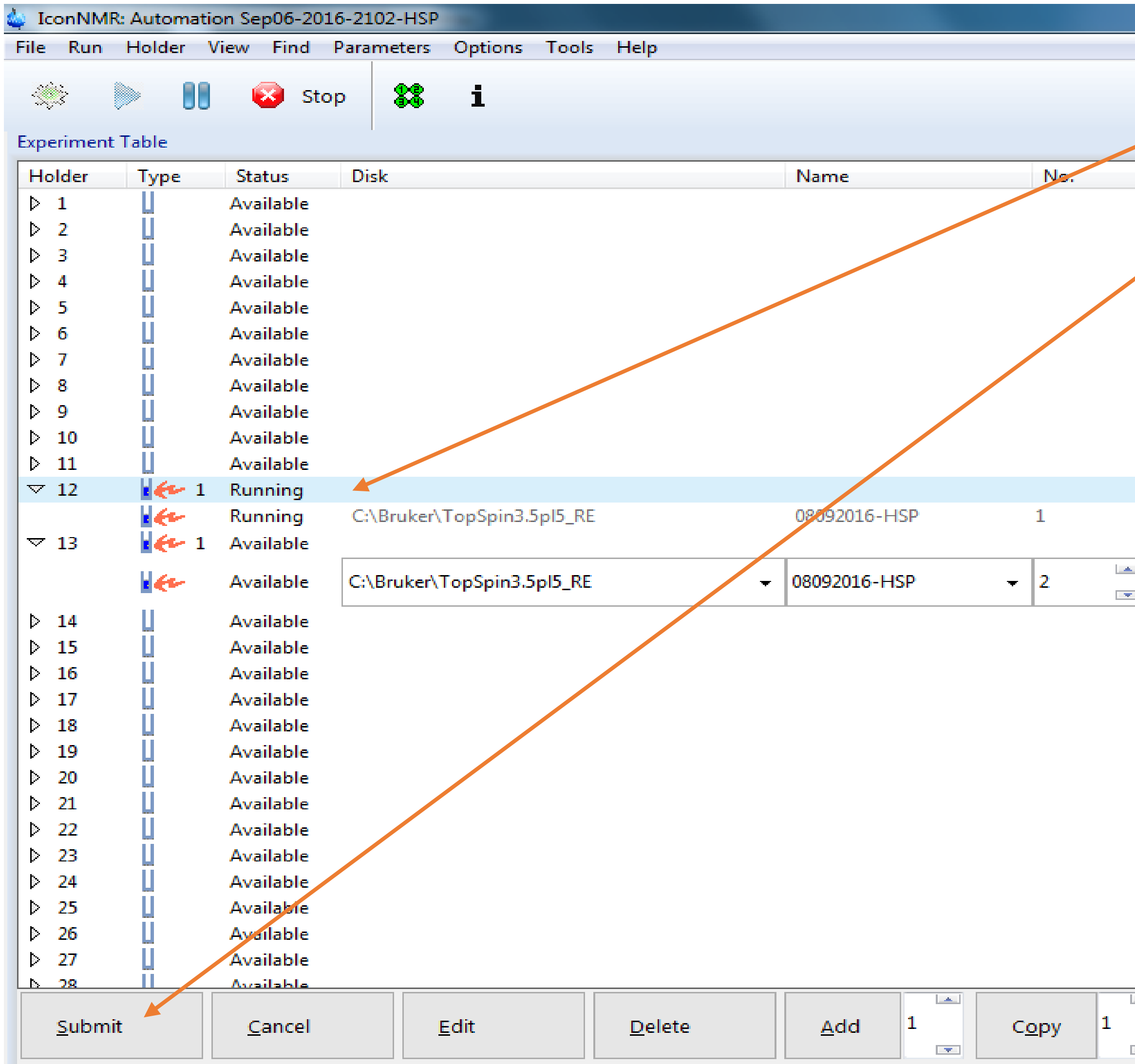
6) Choice Experiment
(Proton, 13CCPD, 13CIG, etc.)



7) Change parameter value
(ns, p1, d1 .. etc) 

5. Acquisition

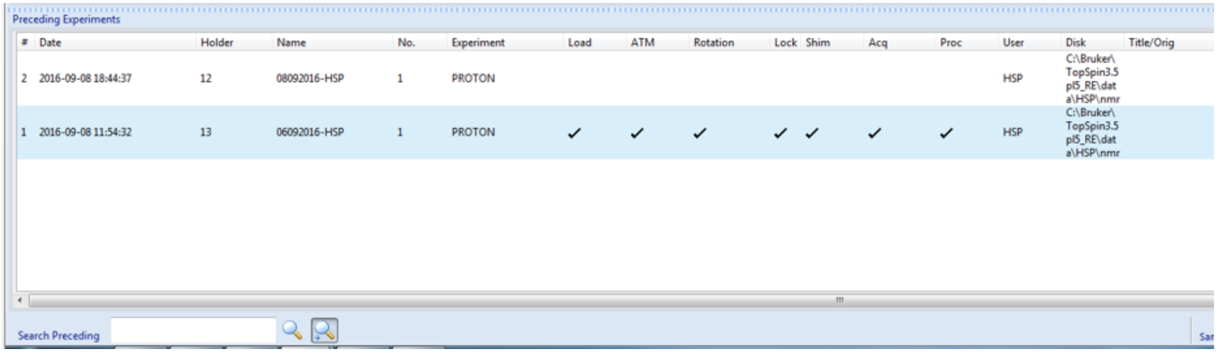




5) Choice experiment holder

6) Click submit

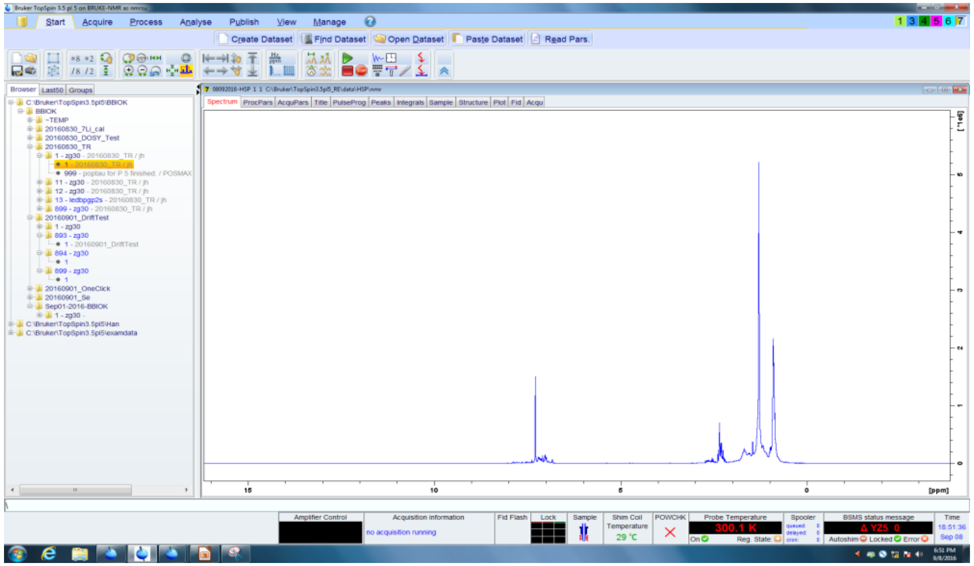
6. Check NMR data



#	Date	Holder	Name	No.	Experiment	Load	ATM	Rotation	Lock	Shim	Acq	Proc	User	Disk	Title/Orig
2	2016-09-08 18:44:37	12	08092016-HSP	1	PROTON								HSP	C:\Bruker\TopSpin3.5pl5_RE\data\HSP\nmr	
1	2016-09-08 11:54:32	13	06092016-HSP	1	PROTON	✓	✓	✓	✓	✓	✓	✓	HSP	C:\Bruker\TopSpin3.5pl5_RE\data\HSP\nmr	

7) Double-Click
Preceding Experiments tap

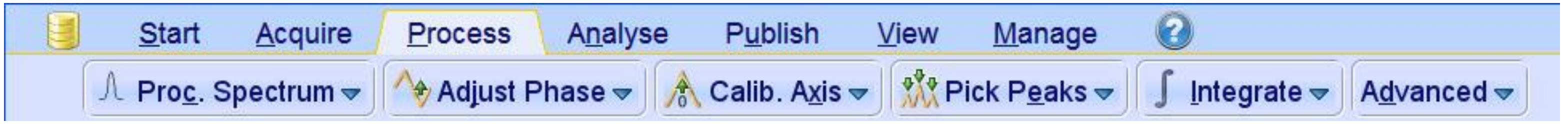
8) Show NMR-spectrum



7. Data Route (FID)

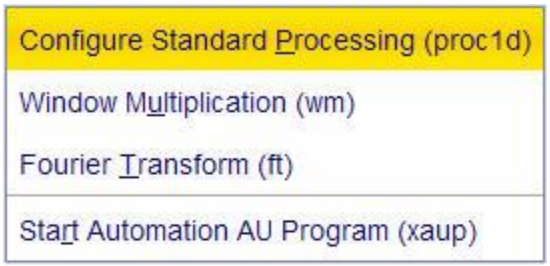
10. Processing

Processing

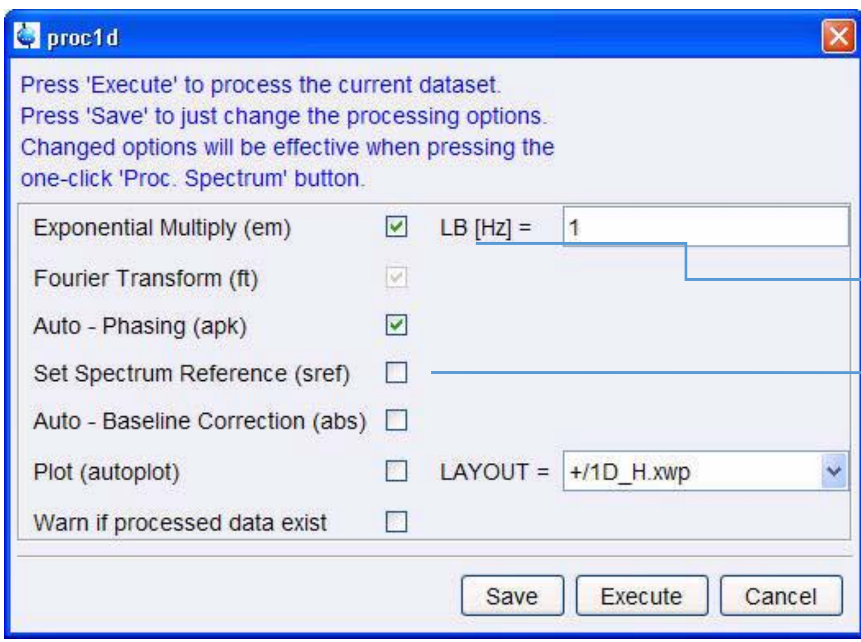


Click 

down arrow



Click Configure Standard Processing (proc1d)



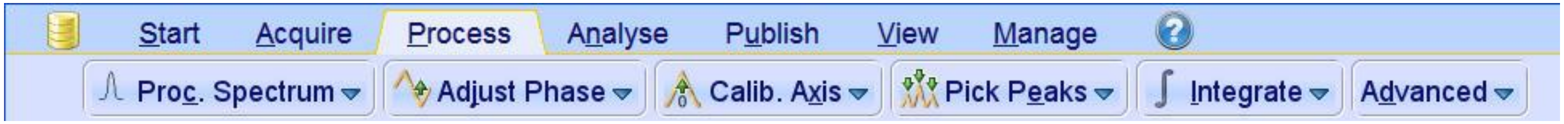
LB↑ -> sensitivity ↑, resolution ↓
Default 0.3 (^1H)
Sensitivity 1 ~ 3 (^{13}C)

If reference useTMS , check TMS.
TMS - chemical shift = 0 (Automation)

*** To save**

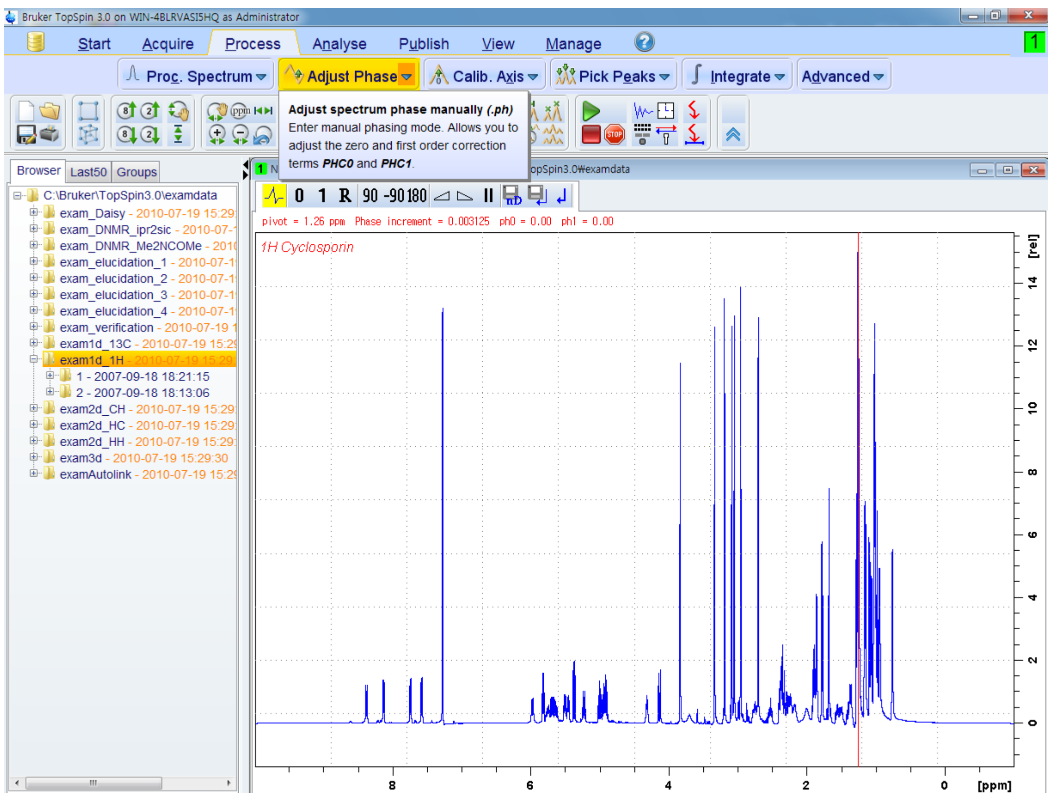
Click 

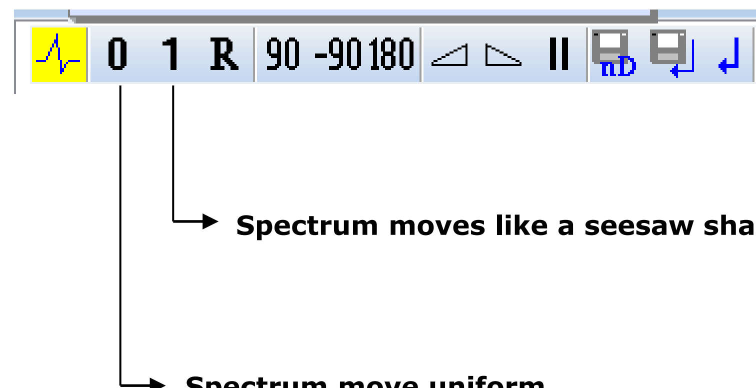
Processing



Process tab 

After **apk**(Auto – Phasing), phase-correction through manual phasing

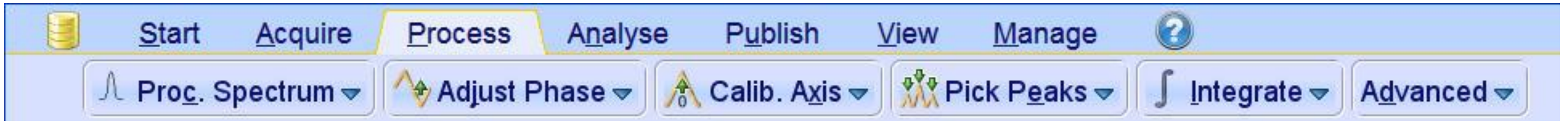




Spectrum moves like a seesaw shape

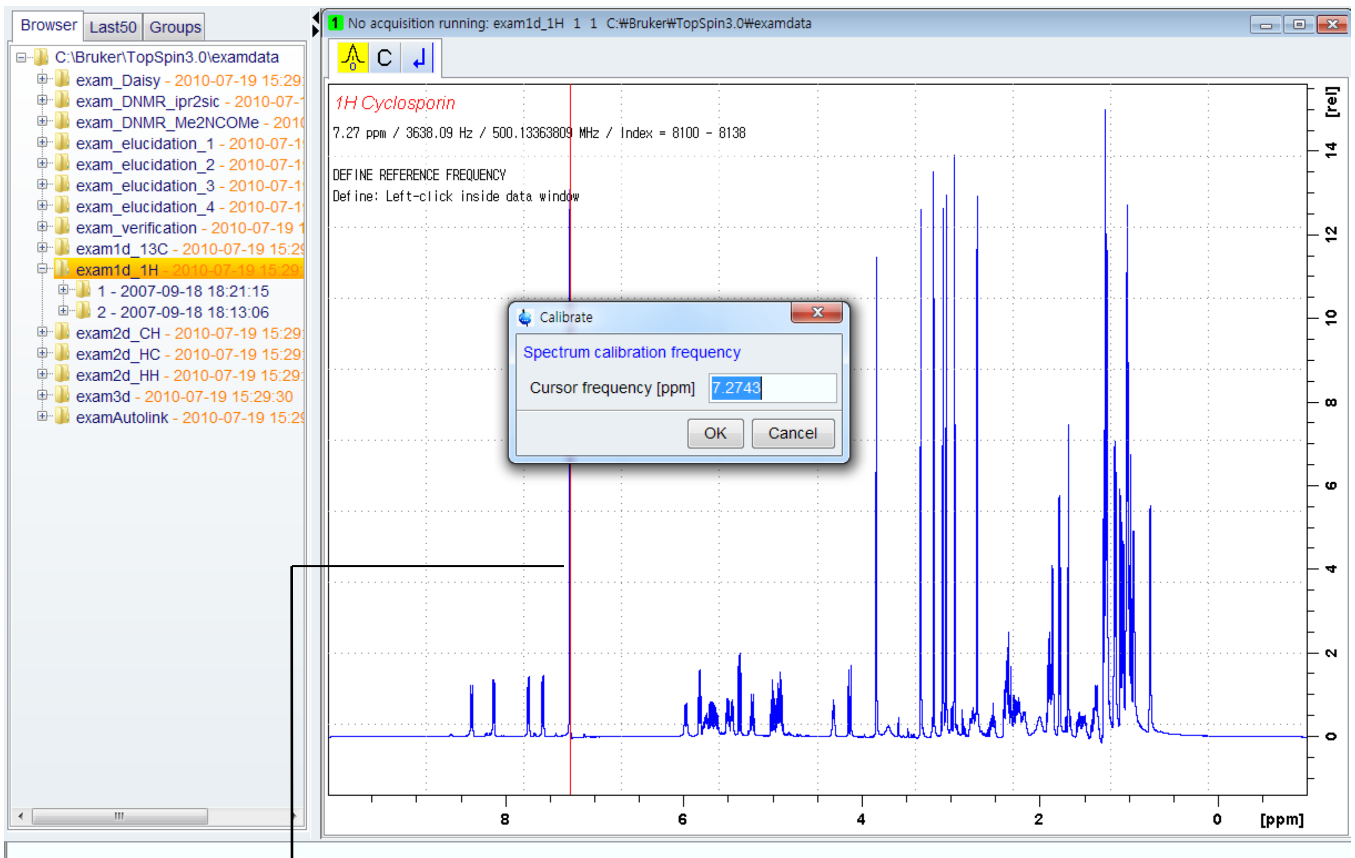
Spectrum move uniform

Processing



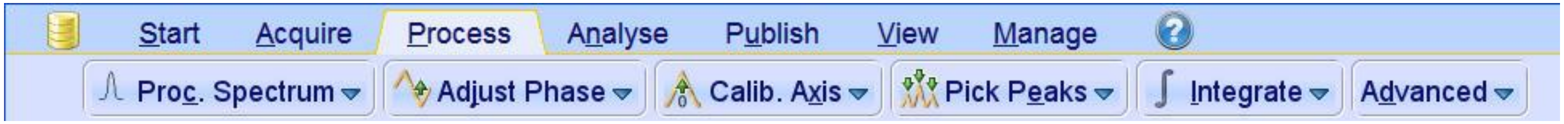
Click 

. Change chemical shift.

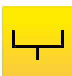


마우스 왼쪽 버튼을 이용하여 알고 있는 **peak**를 클릭 하고 정확한 값을 넣어 준다.

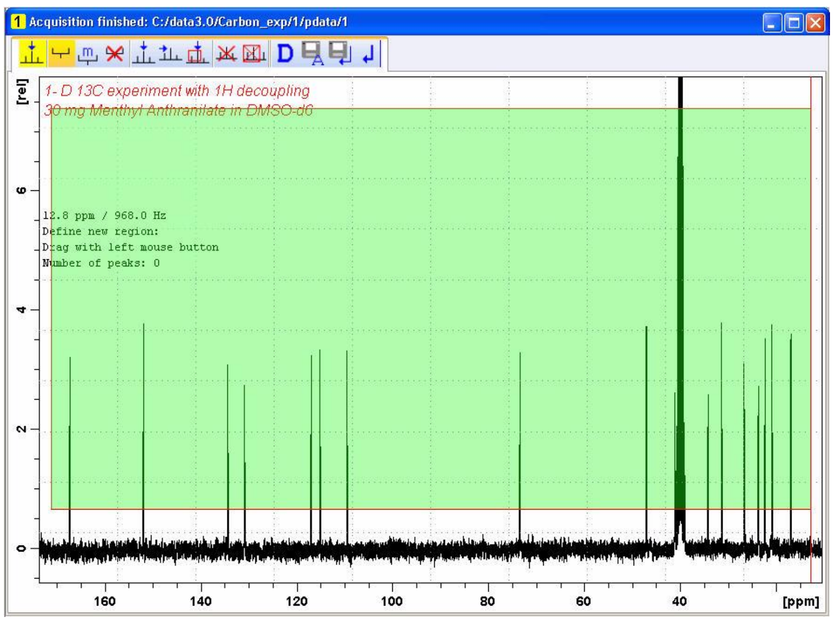
Processing

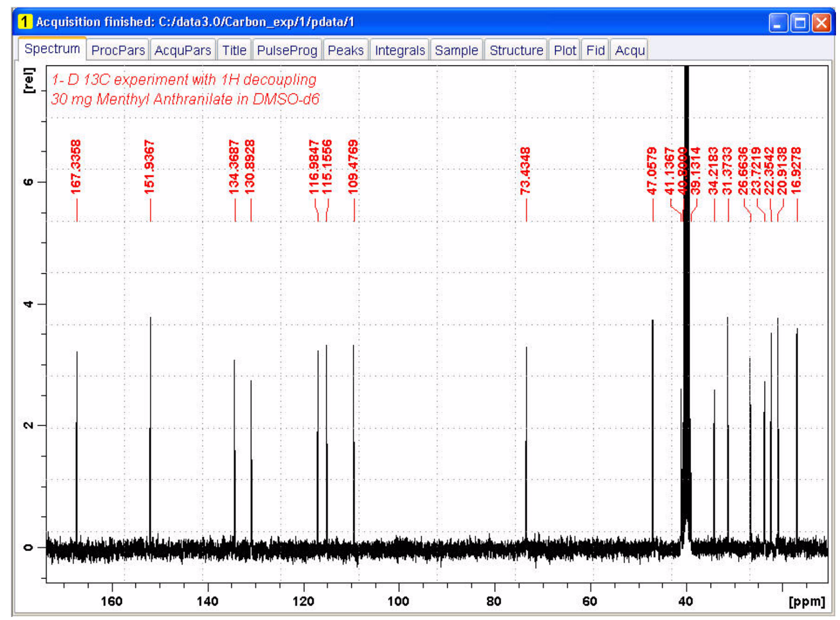


Click 

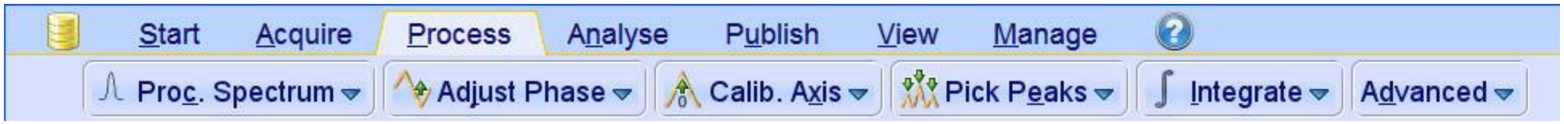
Click 

Drag left-mouse. (Peak located on square box)





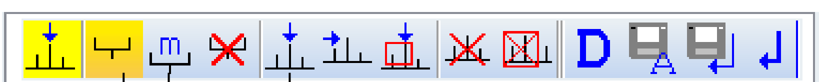
Processing



Click 

Control threshold and choice peak

ex) 0.5 higher than peak picking
> mi 0.5
> pps

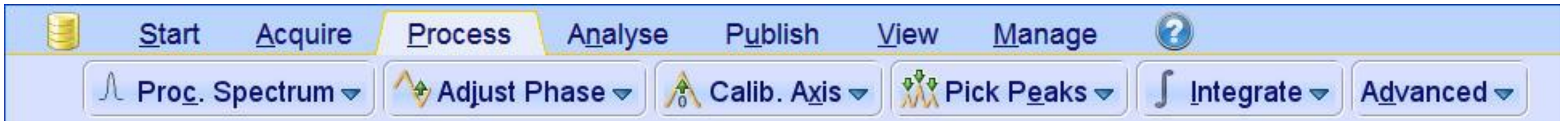


Plus one peak.

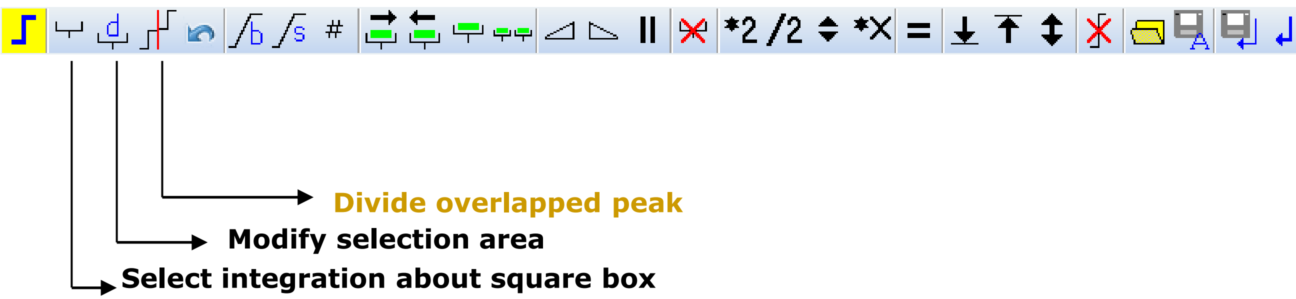
Modify selection area.

Select peak about square box

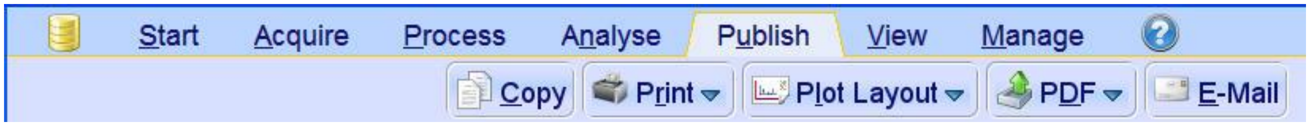
Processing



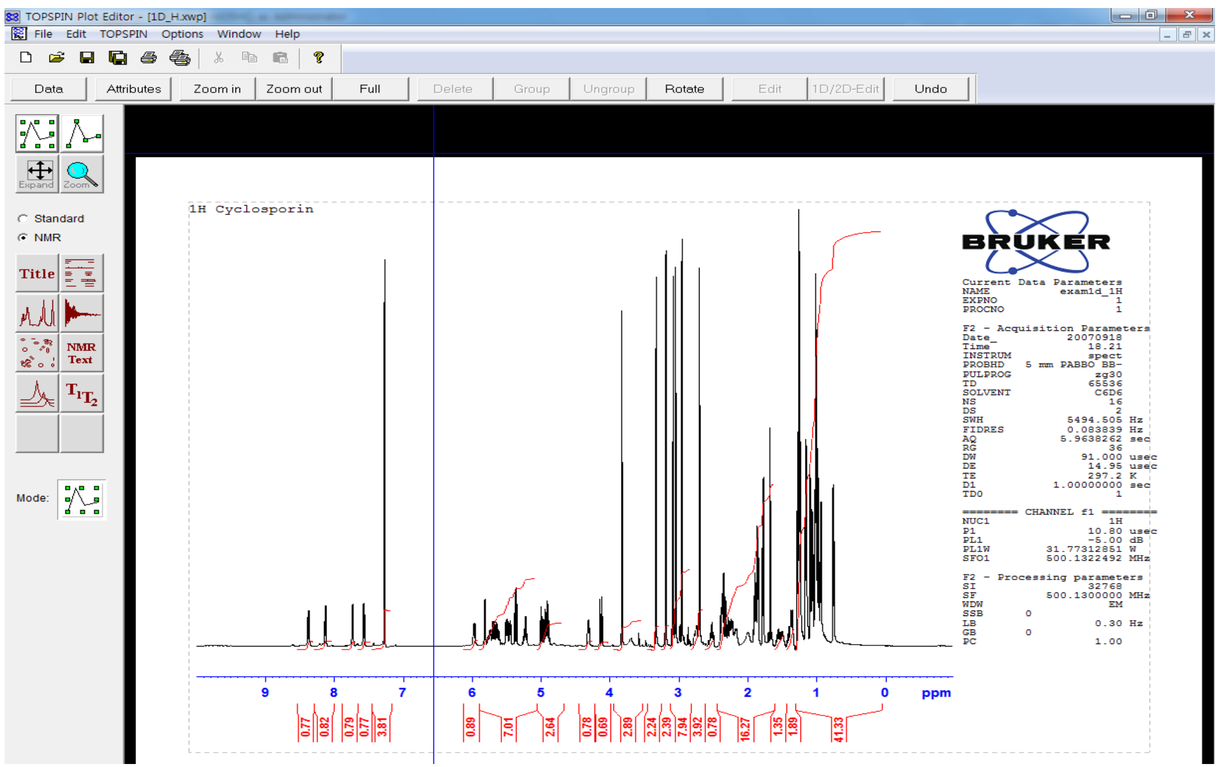
Click 



Plotting



Click 



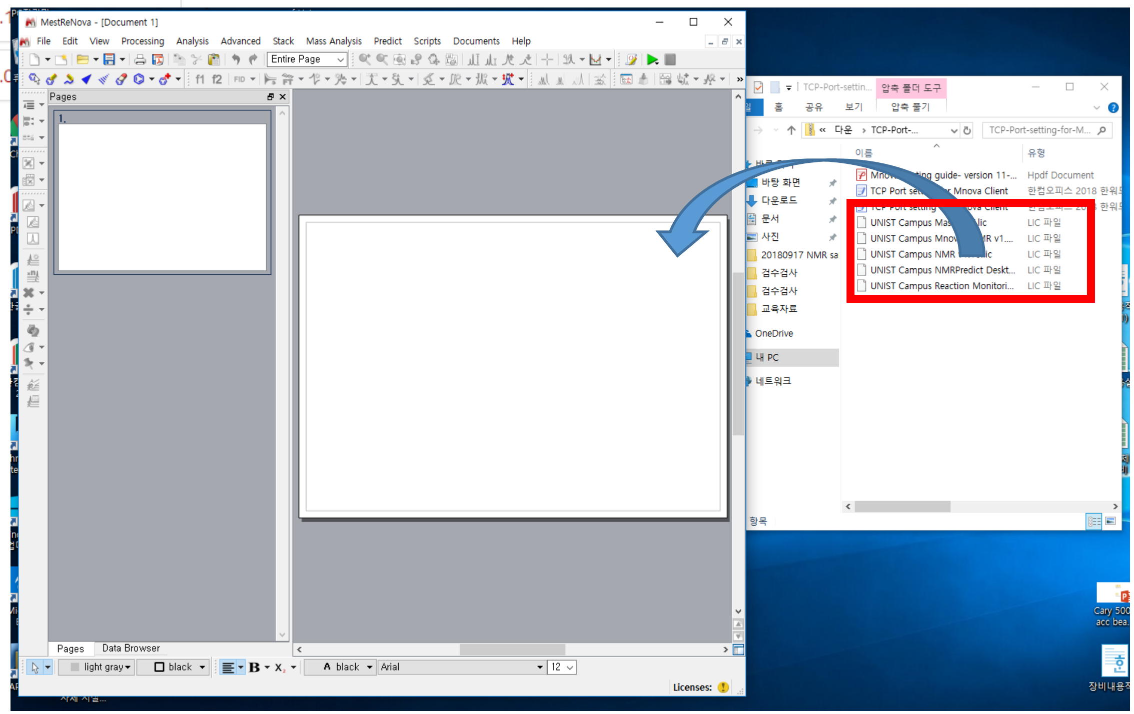
Mnova

https://ucrf.unist.ac.kr/en/mnova-installation/

Download previous versions.

If you hold an old Mnova license we really encourage you to update it. However if you need an older installer, here is a full list of releases:

12.0.2	11.0.4	10.0.2	9.1.0
12.0.1	11.0.3	10.0.1	9.0.1
12.0.0	11.0.2	10.0.0	9.0.0
	11.0.1		
	11.0.		

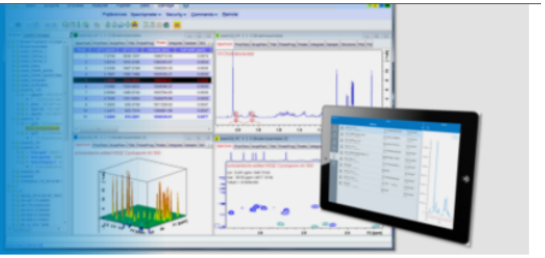


Topspin - free

https://www.bruker.com/nc/service/support-upgrades/software-downloads/nmr/free-topspin-processing/download-page.html

Free TopSpin Processing for Academia

Contact



Home - Service - Support & Upgrades - Software Downloads - NMR - Free TopSpin processing - Download Page

Free TopSpin processing software for academia

TopSpin processing software is free for academia and governmental institutions only

In order to provide students, researchers and teachers with unlimited access to the best tools for off-line NMR processing, Bruker is making their market leading NMR processing software TopSpin available free of charge for all academic users. In addition to Bruker NMR data, the software is able to process data acquired on Agilent, Varian and Jeol systems, as well as read any data provided in JCAMP format.

Access to the download section

Please note: Access to this download section is restricted to academic customers. Please register for a customer account here.

In case you already have an account on bruker.com please log in to download the TopSpin processing package.
By downloading the free TopSpin processing software, you confirm that you are employed by- or studying at an academic- or governmental institution and that you use the software exclusively in this context.

As a registered academic or governmental customer, you will have access to software updates and patches for:

- Free TopSpin processing software for Windows, Linux and MAC OS X
- Free Dynamics Center for Windows, Linux and MAC

Disclaimer

The download and use of the free software for commercial organizations or companies is prohibited. To download software for a commercial organization, please follow this link.

UBTS

https://ubts.co.kr/

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온라인강좌

미래기술혁신융합형인재양성사업단

온라인강좌 | UNIST

UNIST

2023 | **2022**

슈퍼컴퓨터 | XRD | **NMR** | 방사광 빔라인

UNIST | NMR 이론

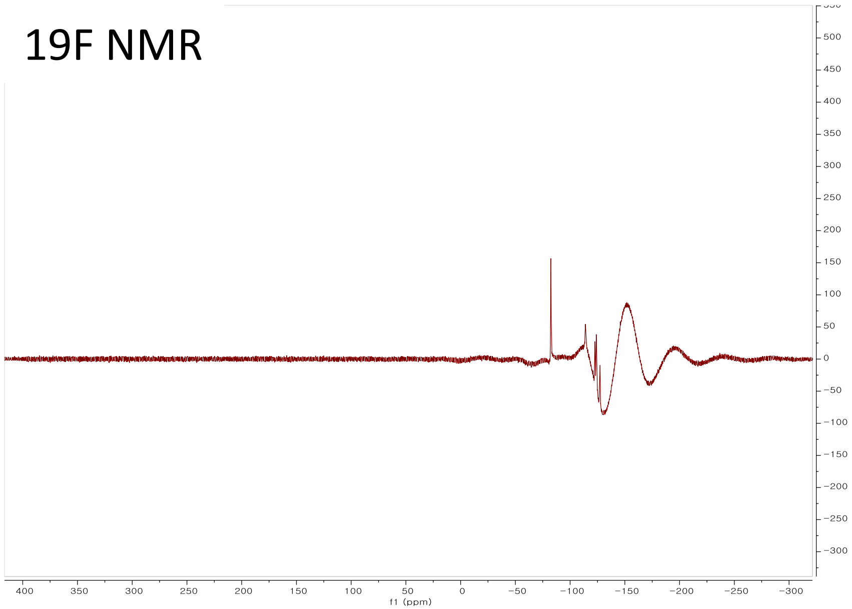
UNIST 연구지원본부

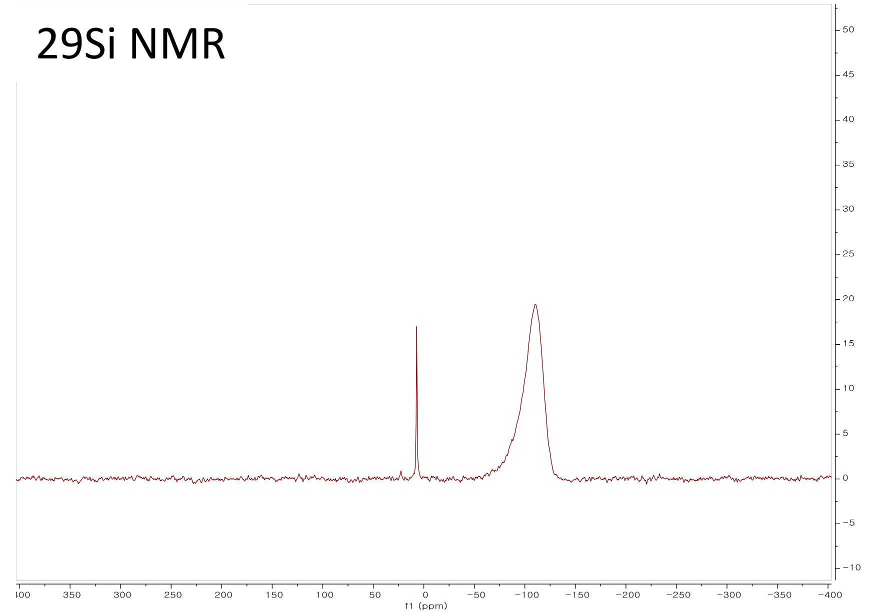
NMR 장비의 작동 원리와 사용 목적, 이용 분야에 대해 학습할 수 있습니다.

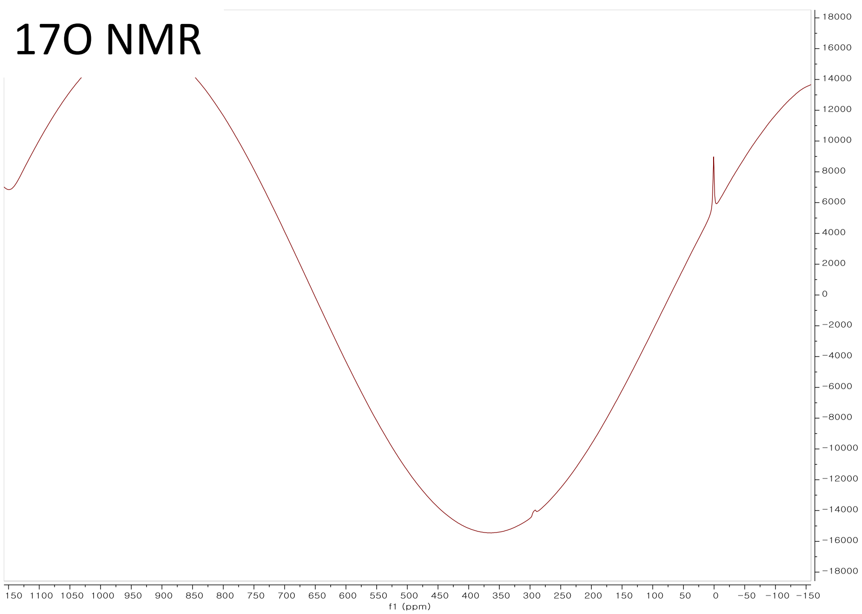
11. Technical Knowhow

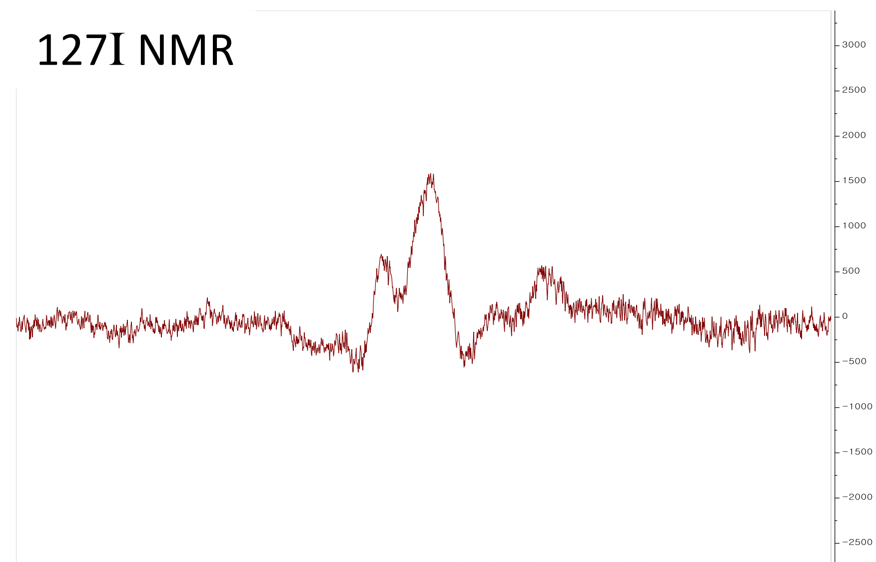
ULSAN NATIONAL INSTITUTE OF SCIENCE AND TECHNOLOGY

Poor background

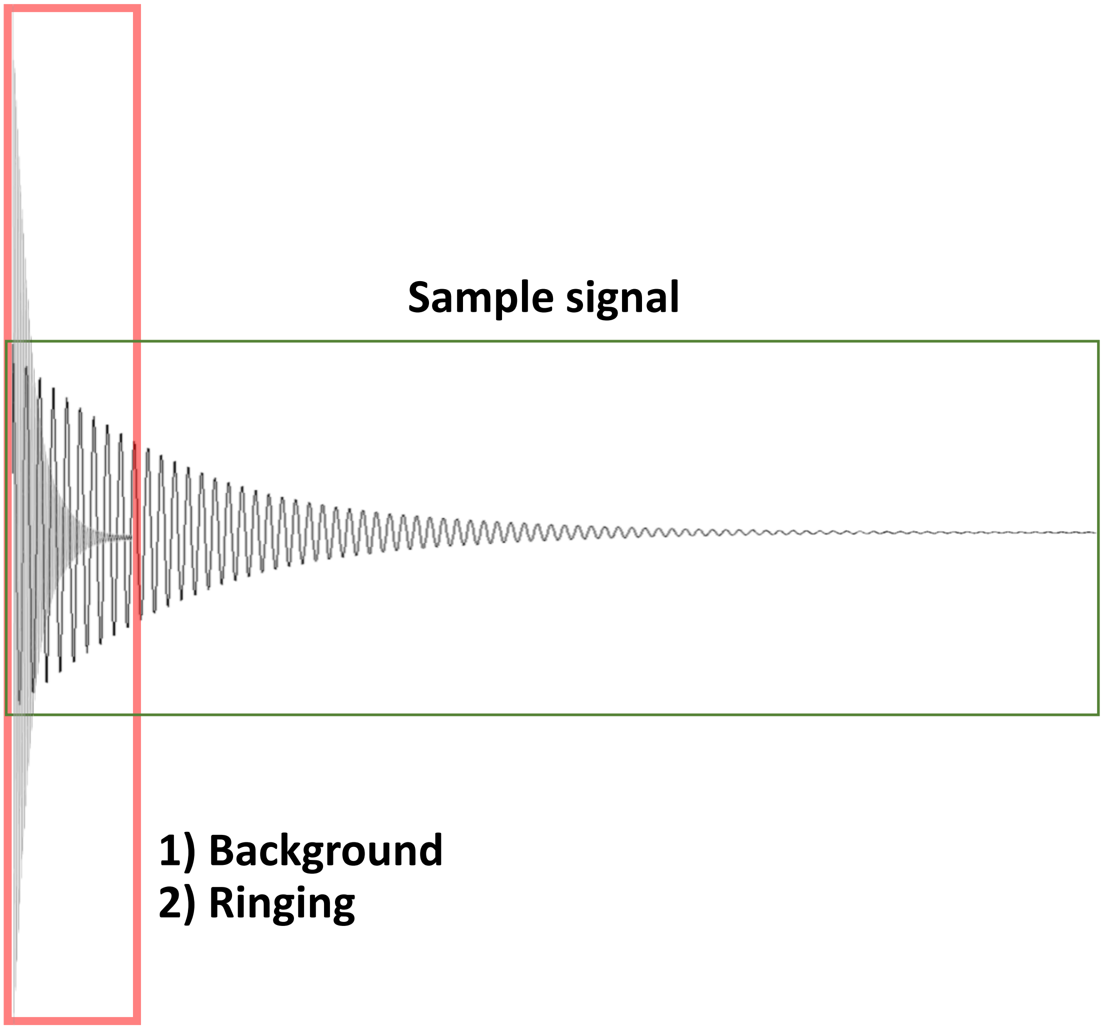








Poor background signal in NMR



1) Material

Borosilicate
Background: 11B, 17O, 29Si

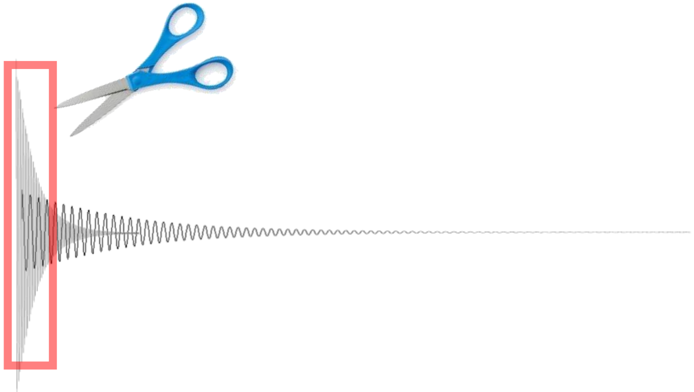
PTFE (Teflon)
Background:1H, 13C, 19F

2) Ringing

How to remove background signal

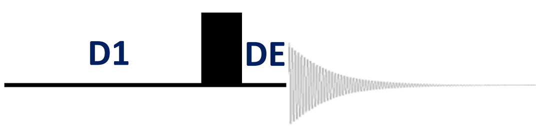
<Solution NMR>

1) Cut off signal (Processing)



2) Prescan Delay (DE)

Ch(obs): X



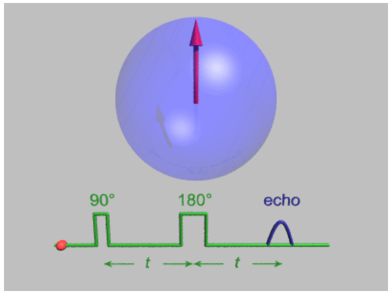
DE = 30 - 40 μs (Normally 4 - 25 μs)

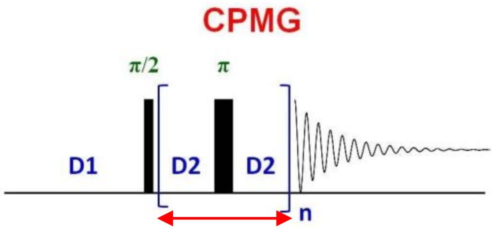
For suppress "bad background signal"

1) **Probe materials (Solid signal)**
2) **Ringing**
   -> Short D1 ex. 17O -> D1 = 0.1 – 0.2 s

3) CPMG (Spin echo)

- Suppress magnetic field inhomogeneous (T2)





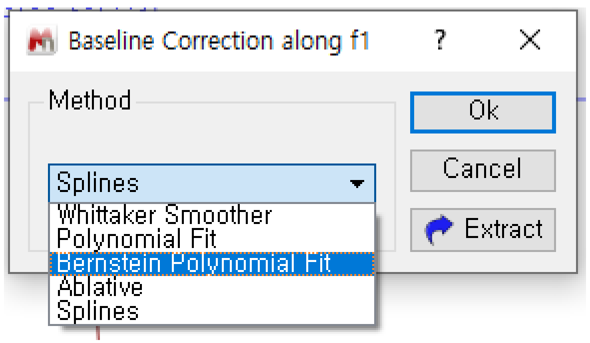
2 - 3 ms

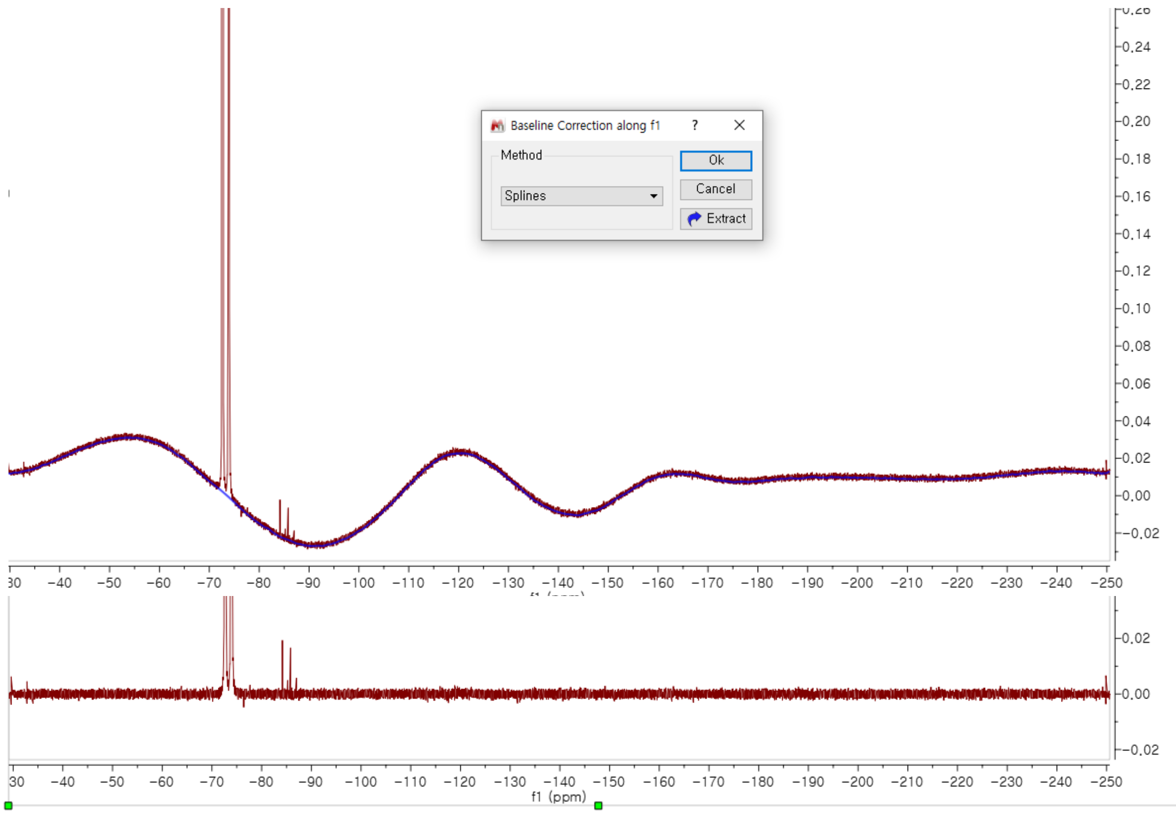
D2 = 1 ms (0.001 s)

Teflon decay time < 1 ms

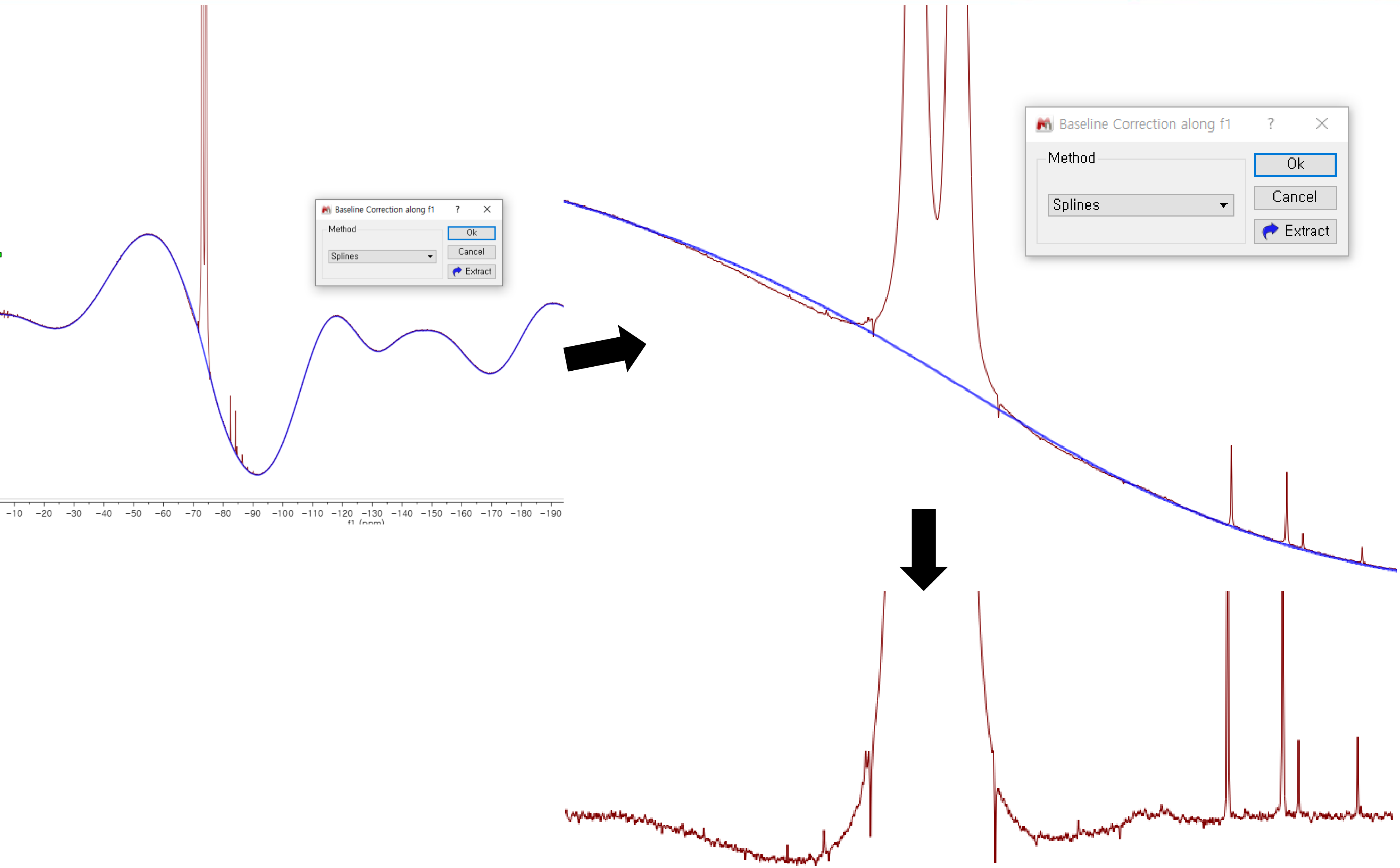
Baseline correction (Processing)

Polynomial Fit = 2 - 3
(or Bernstein Polynomial Fit)

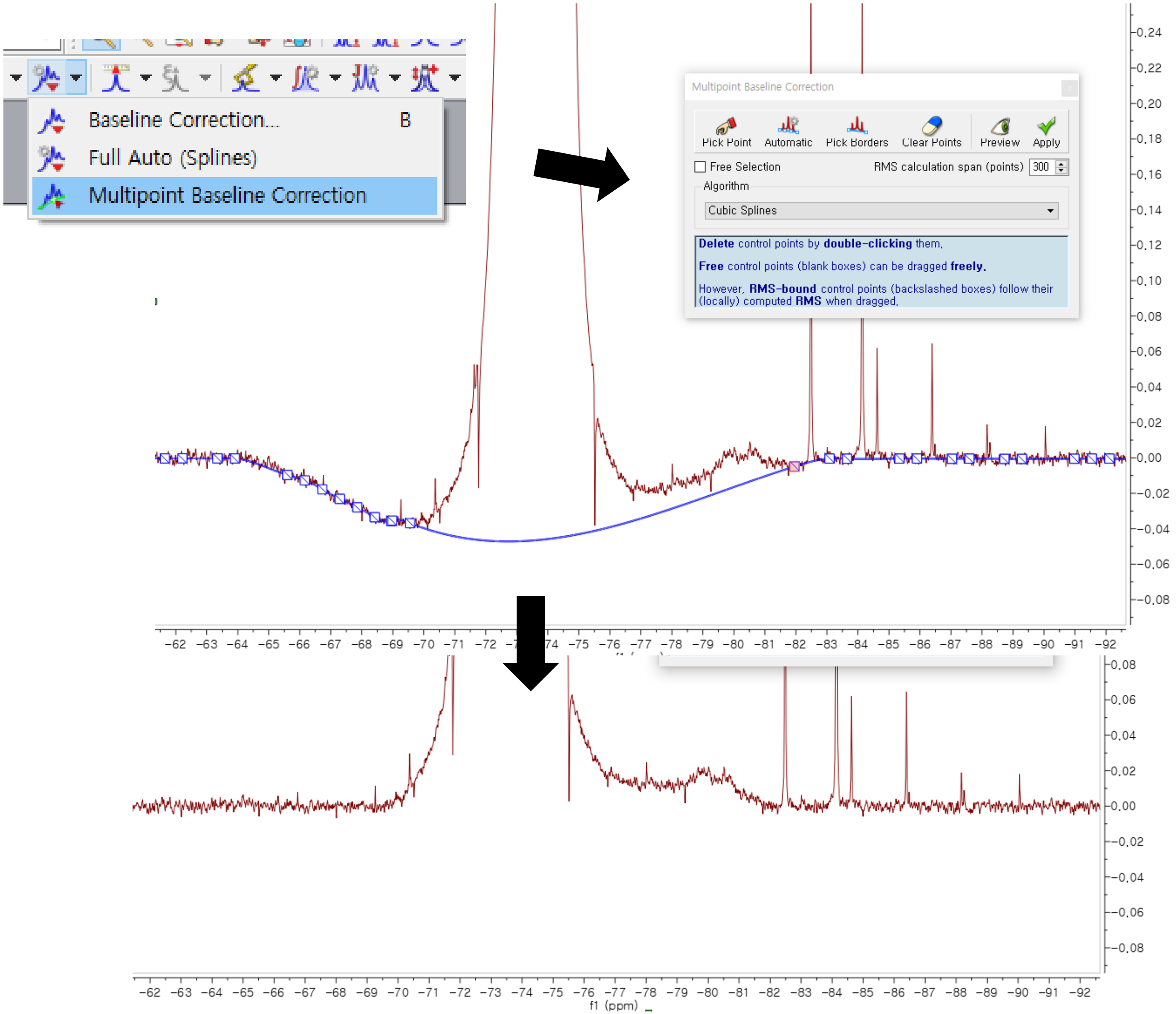




Baseline correction (Processing)

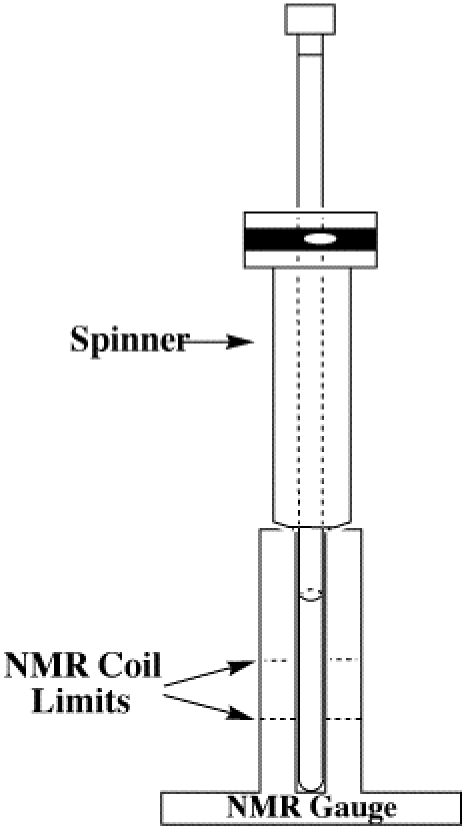


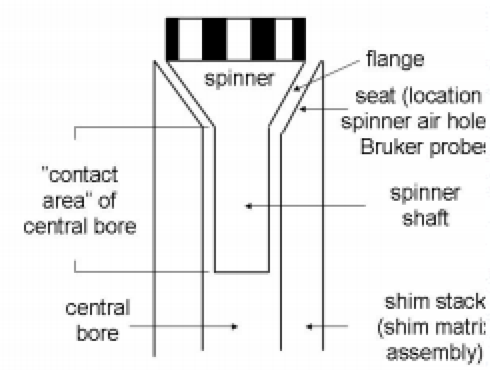
Multipoint baseline correction (Processing)

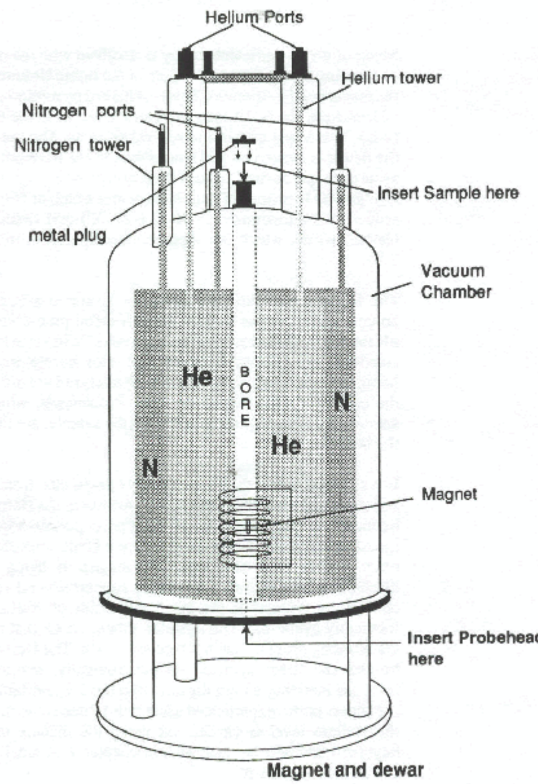


12. Caution

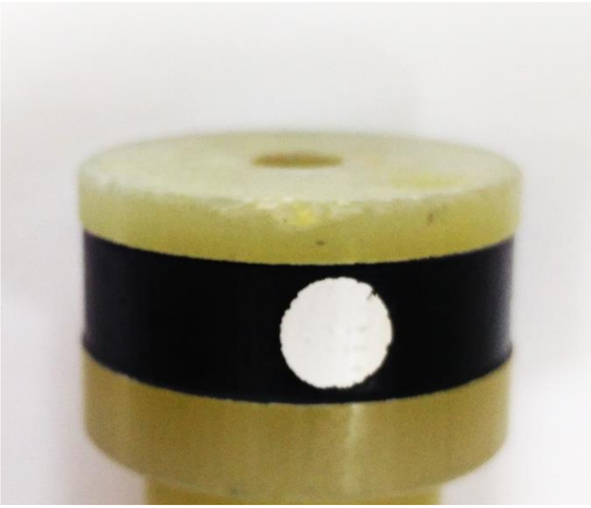
Consist of magnet

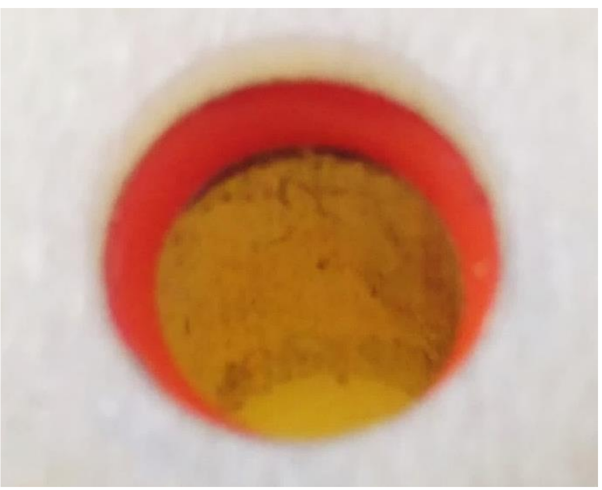


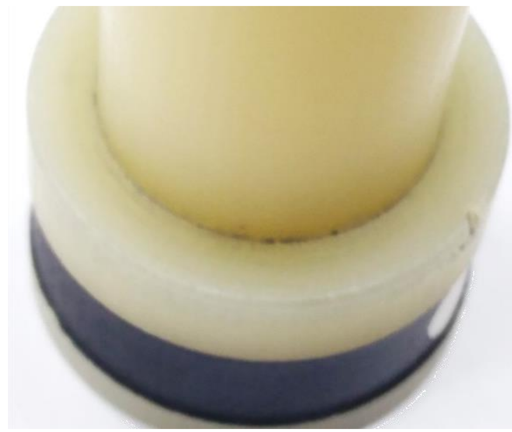


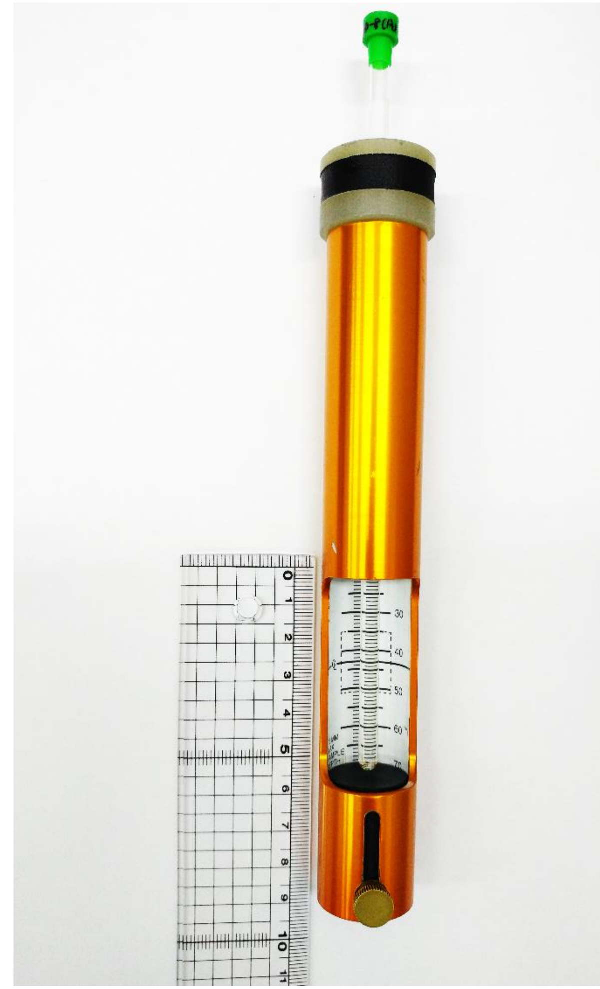


Spinner damage

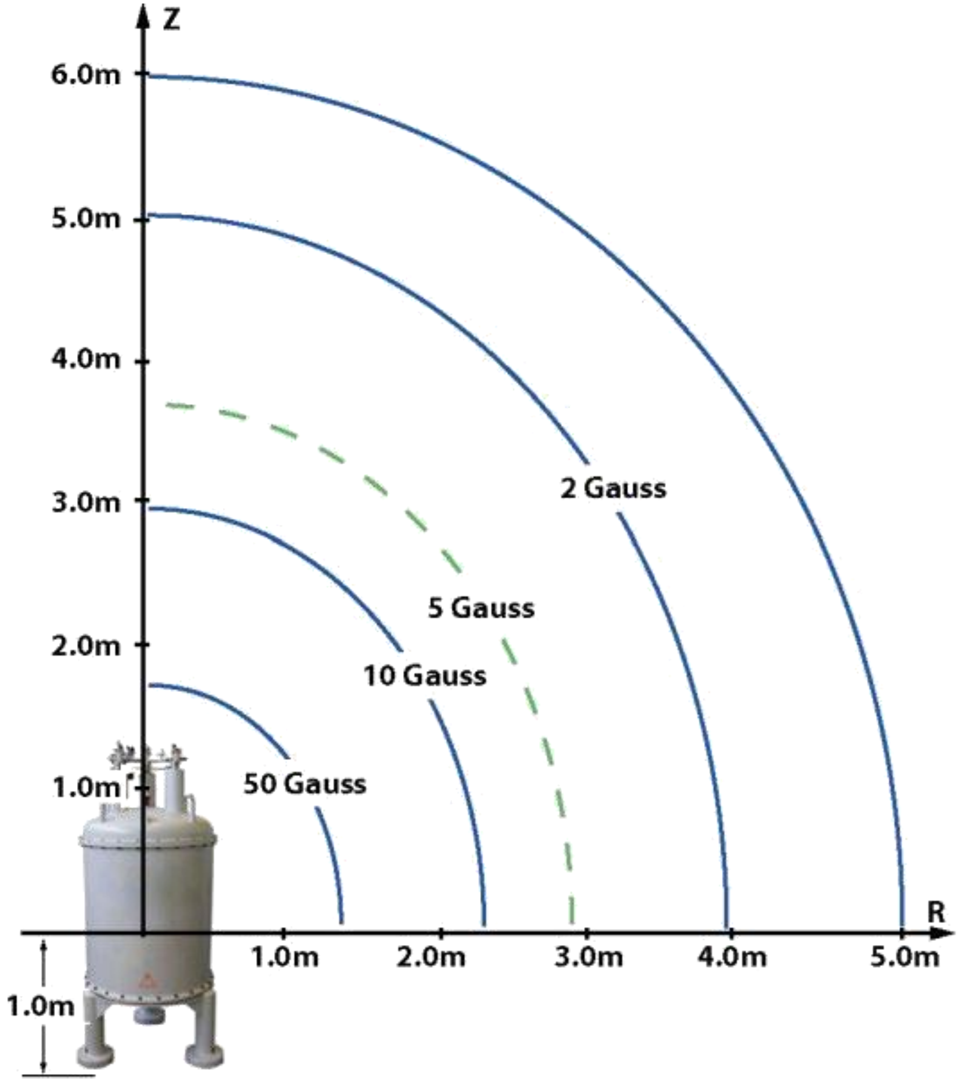








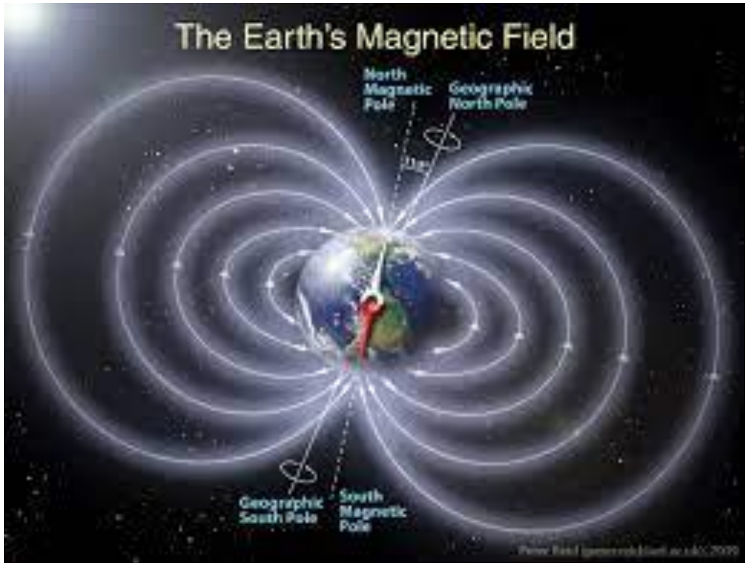
5 Gauss line



5 Gauss line

‘Safe’ levels of static magnetic field exposure for general purpose

Earth`s Magnetic field = 0.5 gauss



Warning Signs

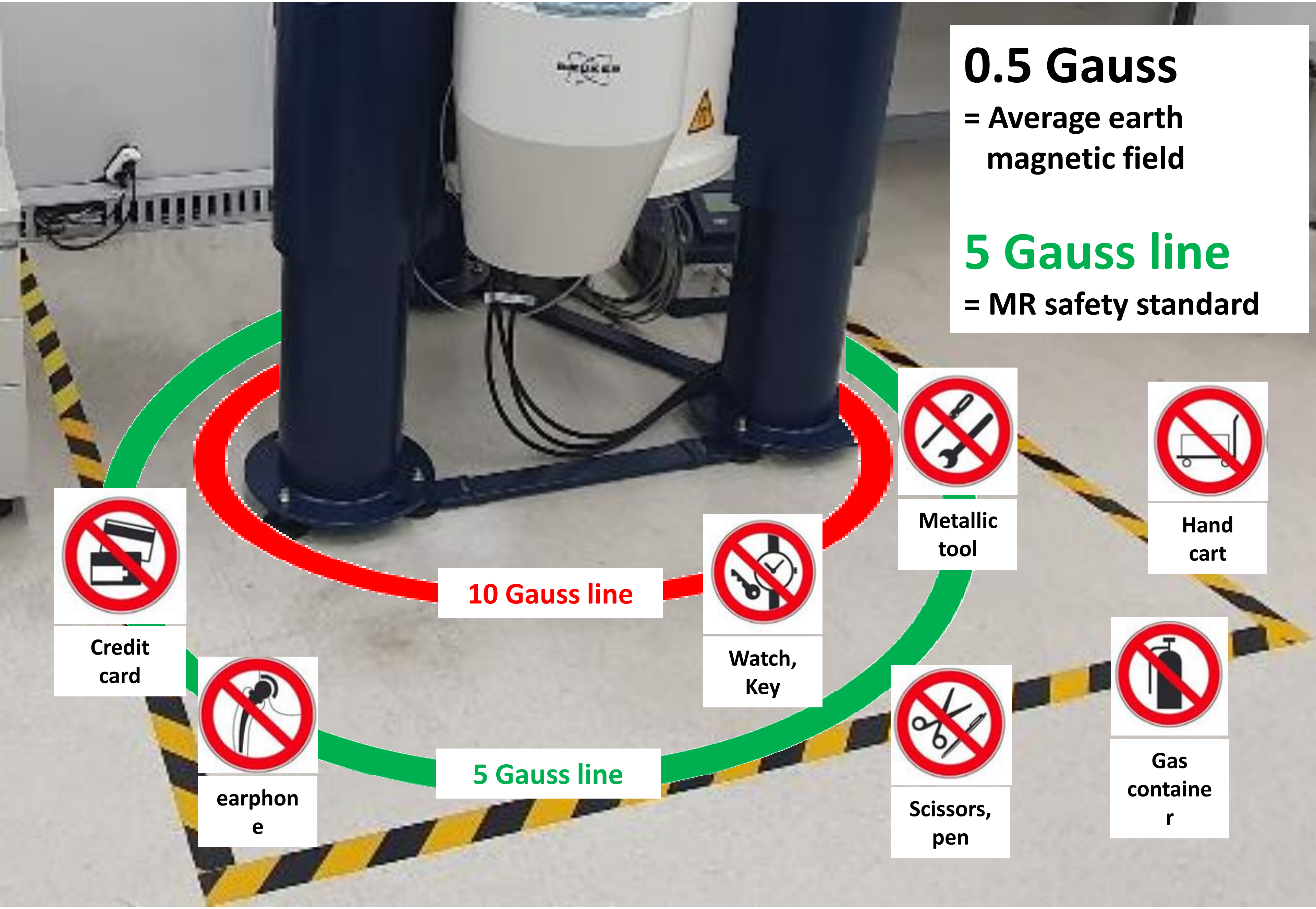
Caution: Extremely high magnetic stray fields.

Caution: Watches and electronic or electro-mechanical devices may be damaged.

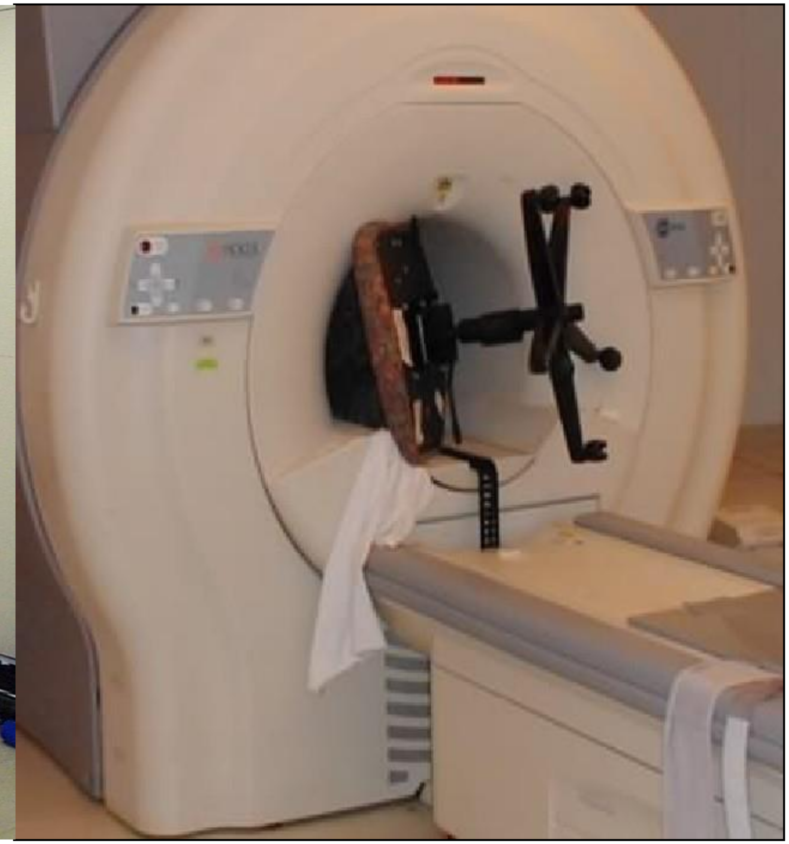
Danger: No entrance for people carrying pace-makers.

Caution: Credit cards, magnetic storage media as tapes, floppy disks or hard disks, may be damaged.

Danger: No entrance for people carrying medical implants.


0.5 Gauss
= Average earth magnetic field
5 Gauss line
= MR safety standard
Metallic tool
Hand cart
10 Gauss line
Watch, Key
Credit card
earphone
5 Gauss line
Scissors, pen
Gas container

Magnet safety



Magnet safety

Human Body react to Oxygen-Deficiency

O2 Concentration 21%

Symptoms

Natural air

O2 Concentration 18%

Symptoms

Limit level for not causing serious health problems. Continuous ventilation is required

O2 Concentration 16%-12%

Symptoms

Rapid breathing, Increase in pulse rate, Loss of concentration, Headache, Nausea, Ear ringing

O2 Concentration 14%-9%

Symptoms

Stupor, Headache, Nausea, Cyanosis, Faintness on the entire body

O2 Concentration 10%-6%

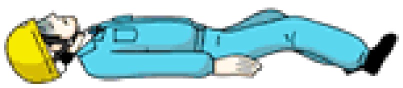
Symptoms

Comatose, Loss of consciousness, Muscle spasm on the entire body

O2 Concentration 6% or less

Symptoms

Unconsciousness, Comatose, Cessation of breathing, Cardiac arrest, Die in 6 minutes



Magnet quench

https://www.youtube.com/watch?v=4dbQxyrhZ2A&t=63s

https://youtu.be/d-G3Kg-7n_M?t=5

13. FAQ

-자주 하는 질문

-장비 이용료

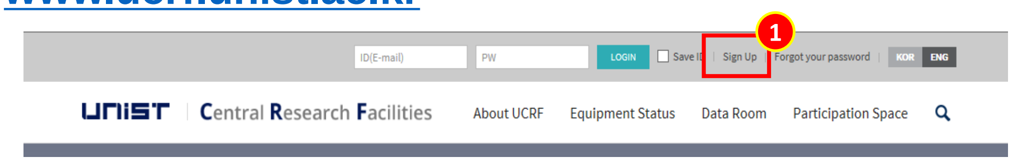
Equipment fee

Model	Reservation time unit	Daily maximum reservation time	Cancelable timing	Fee	
Bruker 600 MHz NMR	10 min.	unlimited	1.0 hr	Client	10,000/10min
				Self-user	5,000/10min
				Acc. used	3,000/10min
Bruker 400 MHz NMR	10 min.	1 hr (2 PM to 8 PM, weekdays)	1.0 hr	Client	5,000/10min
				Self-user	2,500/10min
				Acc. used	3,300/10min

Reservation control information

Create Account

www.ucrf.unist.ac.kr



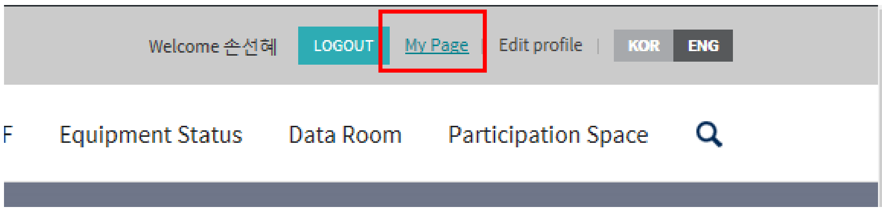
1. Click [Sign up].
2. Click [UNIST Member].
3. Input [Portal id/pw]_Click [Confirm].

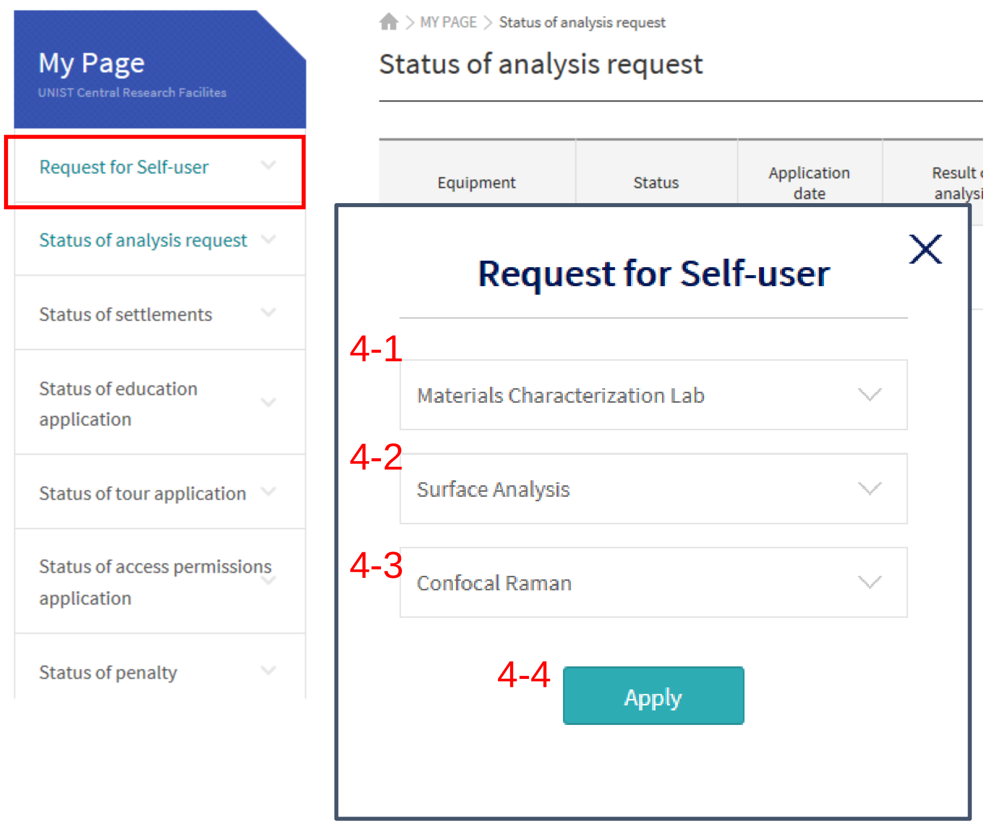
   Please check your information.
4. Input professor name in [Principal investigation]

   _Click [Professor search]_Click professor name.
5. Click [Create Account].

Request for Self-user

www.ucrf.unist.ac.kr



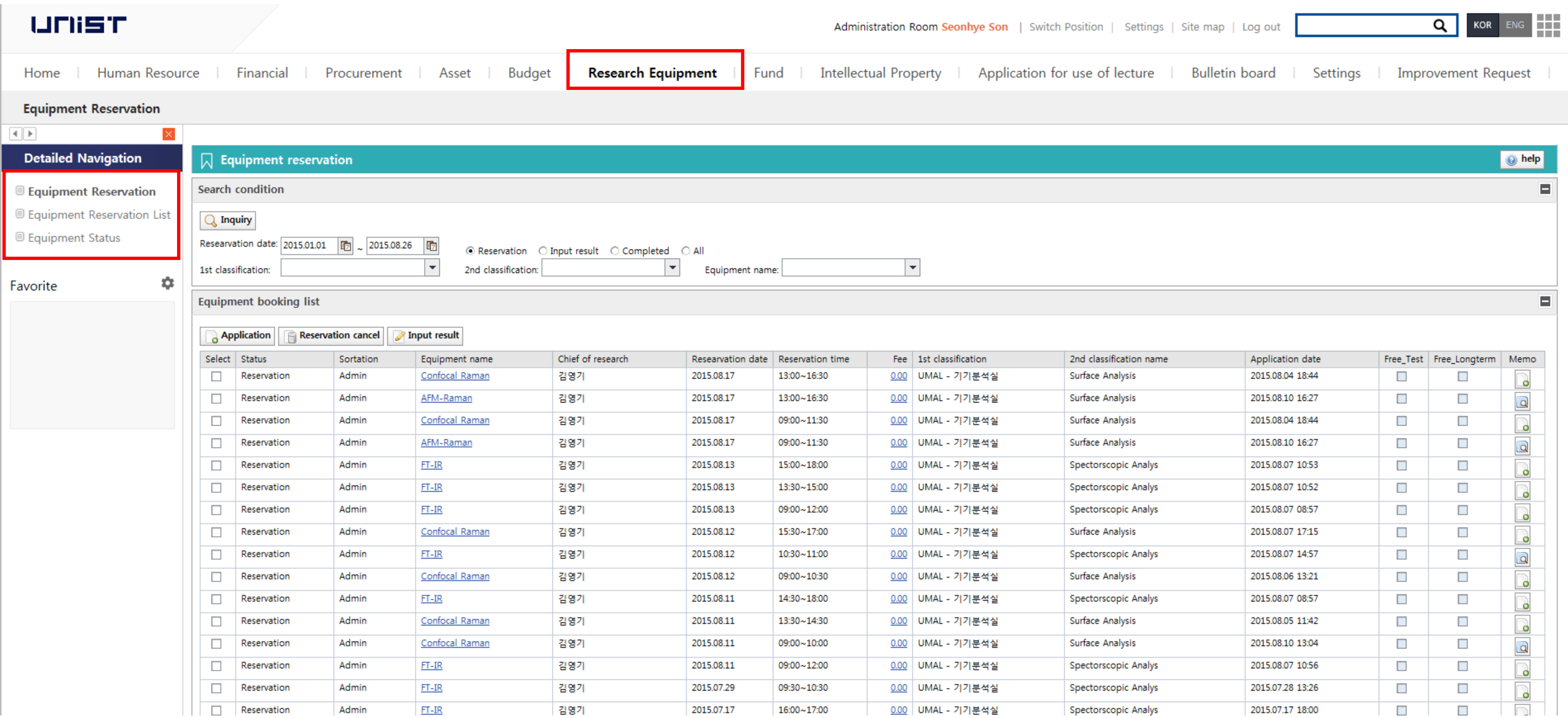


After pass the test,

1. Login UCRF website.
2. Click [My Page].
3. Click [Request for Self user].
4. Select the equipment.
    1) Select [Materials Characterization Lab].
    2) Select [Surface Analysis].
    3) Select [Confocal Raman].
    4) Click [Apply].

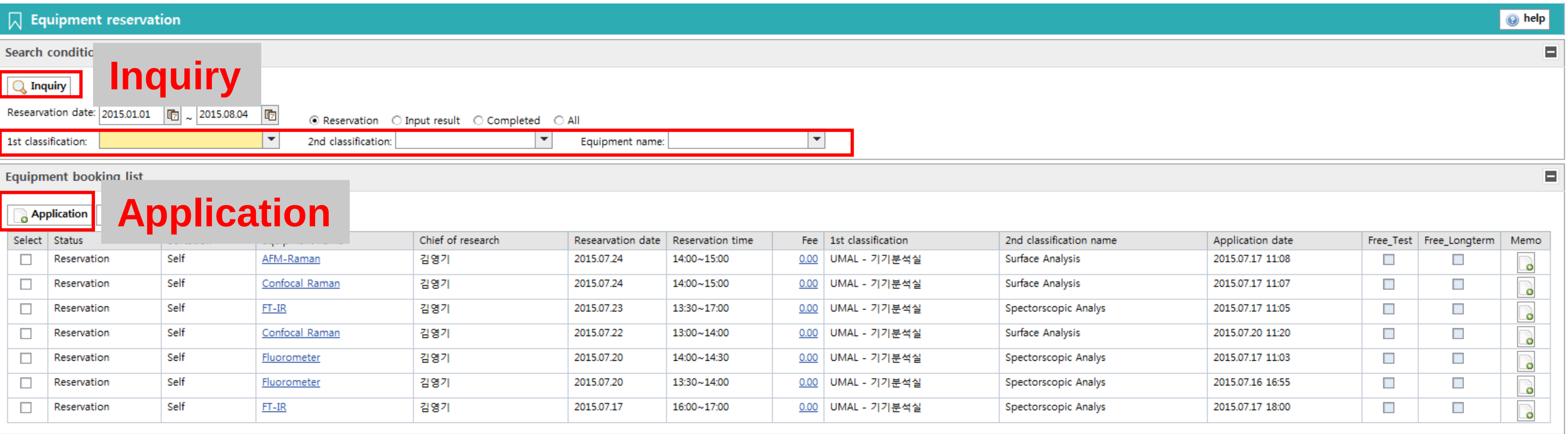
Reservation

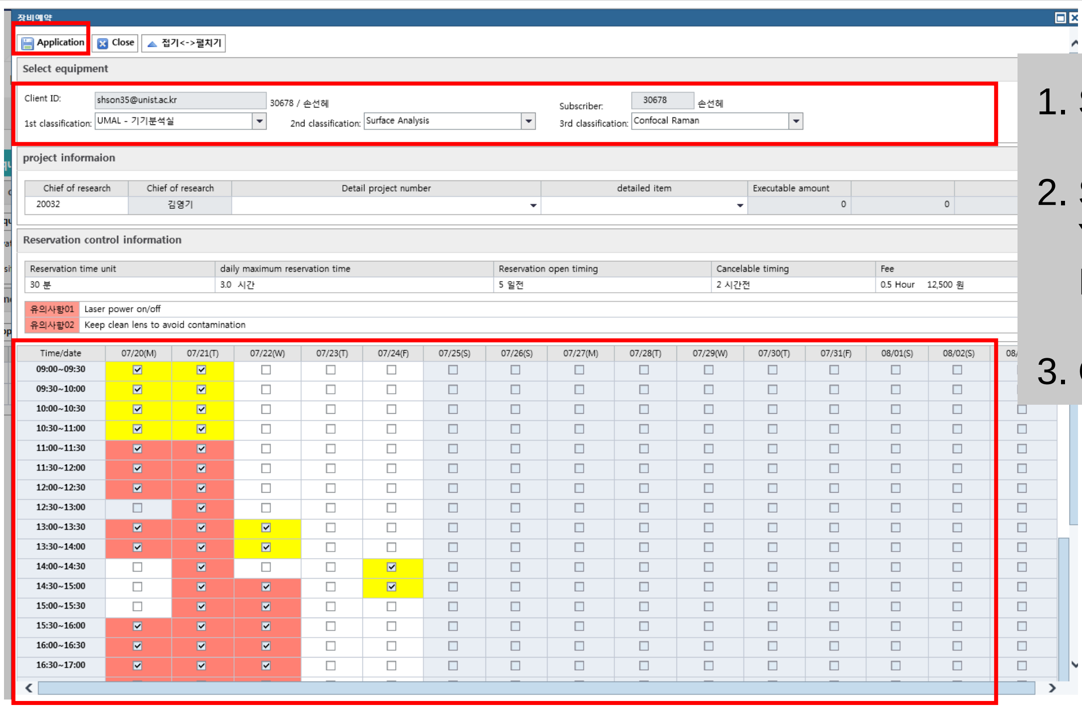
portal.unist.ac.kr – Research Equipment– Equipment reservation/input result



Select	Status	Sortation	Equipment name	Chief of research	Researvation date	Reservation time	Fee	1st classification	2nd classification name	Application date	Free_Test	Free_Longterm	Memo
	Reservation	Admin	Confocal Raman	김영기	2015.08.17	13:00~16:30	0.00	UMAL - 기기분석실	Surface Analysis	2015.08.04 18:44			
	Reservation	Admin	AFM-Raman	김영기	2015.08.17	13:00~16:30	0.00	UMAL - 기기분석실	Surface Analysis	2015.08.10 16:27			
	Reservation	Admin	Confocal Raman	김영기	2015.08.17	09:00~11:30	0.00	UMAL - 기기분석실	Surface Analysis	2015.08.04 18:44			
	Reservation	Admin	AFM-Raman	김영기	2015.08.17	09:00~11:30	0.00	UMAL - 기기분석실	Surface Analysis	2015.08.10 16:27			
	Reservation	Admin	FT-IR	김영기	2015.08.13	15:00~18:00	0.00	UMAL - 기기분석실	Spectorscopic Analys	2015.08.07 10:53			
	Reservation	Admin	FT-IR	김영기	2015.08.13	13:30~15:00	0.00	UMAL - 기기분석실	Spectorscopic Analys	2015.08.07 10:52			
	Reservation	Admin	FT-IR	김영기	2015.08.13	09:00~12:00	0.00	UMAL - 기기분석실	Spectorscopic Analys	2015.08.07 08:57			
	Reservation	Admin	Confocal Raman	김영기	2015.08.12	15:30~17:00	0.00	UMAL - 기기분석실	Surface Analysis	2015.08.07 17:15			
	Reservation	Admin	FT-IR	김영기	2015.08.12	10:30~11:00	0.00	UMAL - 기기분석실	Spectorscopic Analys	2015.08.07 14:57			
	Reservation	Admin	Confocal Raman	김영기	2015.08.12	09:00~10:30	0.00	UMAL - 기기분석실	Surface Analysis	2015.08.06 13:21			
	Reservation	Admin	FT-IR	김영기	2015.08.11	14:30~18:00	0.00	UMAL - 기기분석실	Spectorscopic Analys	2015.08.07 08:57			
	Reservation	Admin	Confocal Raman	김영기	2015.08.11	13:30~14:30	0.00	UMAL - 기기분석실	Surface Analysis	2015.08.05 11:42			
	Reservation	Admin	Confocal Raman	김영기	2015.08.11	09:00~10:00	0.00	UMAL - 기기분석실	Surface Analysis	2015.08.10 13:04			
	Reservation	Admin	FT-IR	김영기	2015.08.11	09:00~12:00	0.00	UMAL - 기기분석실	Spectorscopic Analys	2015.08.07 10:56			
	Reservation	Admin	FT-IR	김영기	2015.07.29	09:30~10:30	0.00	UMAL - 기기분석실	Spectorscopic Analys	2015.07.28 13:26			
	Reservation	Admin	FT-IR	김영기	2015.07.17	16:00~17:00	0.00	UMAL - 기기분석실	Spectorscopic Analys	2015.07.17 18:00			

Reservation



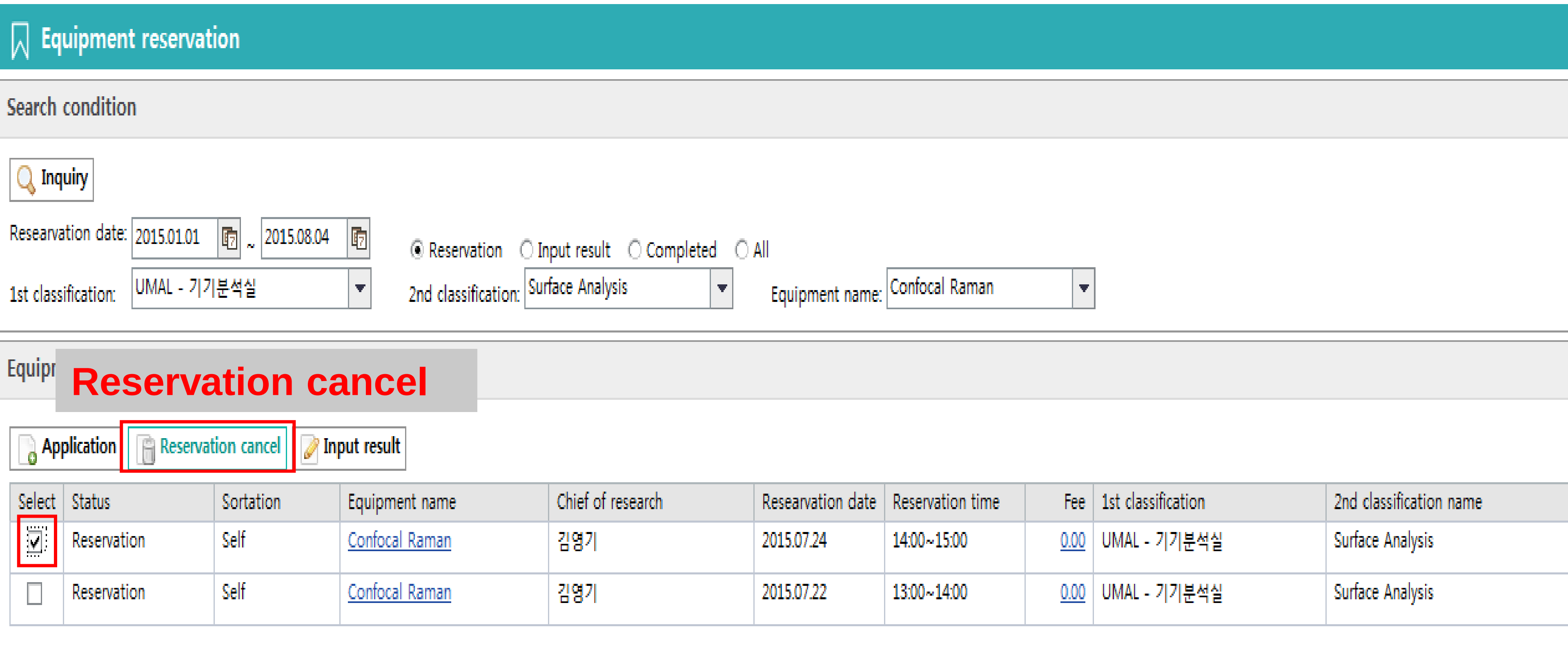


1. Select the classification and equipment

2. Select the time you want on white box.
   Yellow box : my reservation
   Red box : others reservation

3. Click [Application].

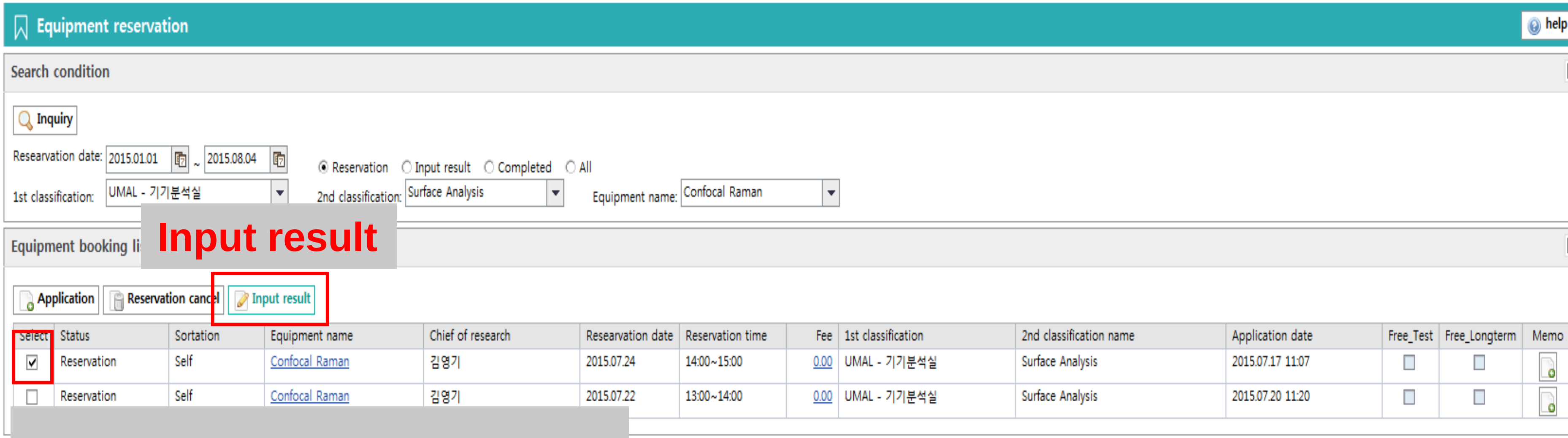
Reservation cancel



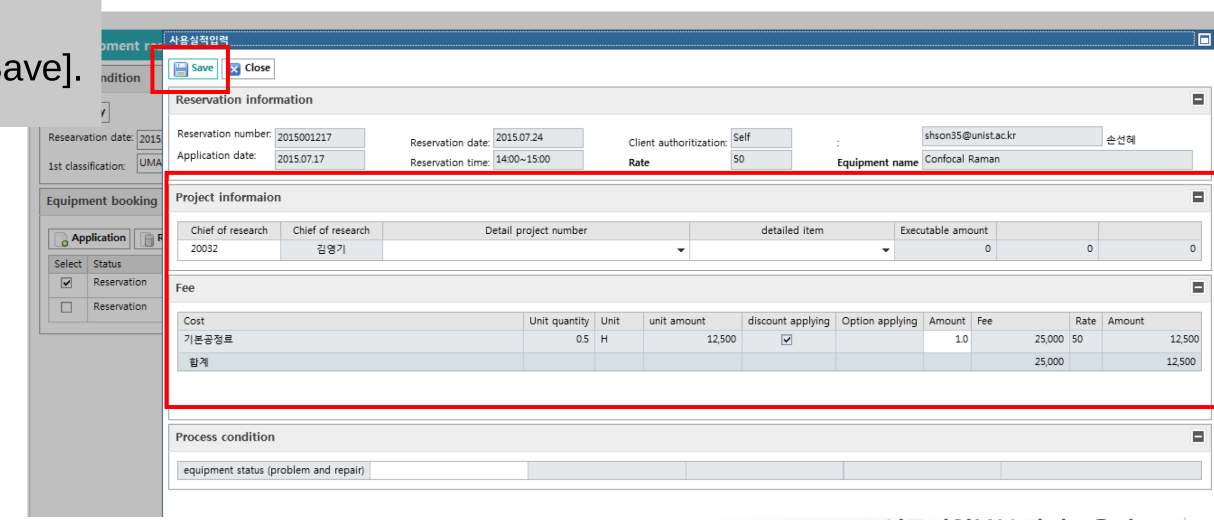
1. Select the reservation.
2. Click the [Reservation cancel].

Input result

After measurement, you have to input result instead of filling in log sheet



1. Select the reservation.
2. Click the [Input result].
3. Check the information and click [Save].



Penalty points for users of equipment

- 벌점 부과 기준

No.	벌점 부과 내용	벌점
	[장비 사용 자격]	
1	해당 장비에 대하여 직접 사용이 허가 되지 않은 사용자가 기기를 사용	5
2	장비 예약하지 않고 장비 사용	3
3	장비 예약자 본인이 아닌 자가 장비를 사용	3
	[장비 사용 예약]	
4	허용시간 이외의 시간에 장비 예약 및 사용	1
5	장비 예약시간을 초과하여, 예약시간 종료 전에 초과시간에 대한 예약없이 장비 사용	1
6	장비 예약 취소 사실 통보 없이 해당 시간에 장비 사용하지 않은 경우	3
7	「연구지원본부 운영지침」제7조의 내용을 기준으로, 장비 예약 취소 기한이 지나서 예약을 취소한 경우	1
8	예약 후 장비담당자에게 통보하지 않고 기기 사용	1
	[부주의한 행동]	
9	장비 사용 중 허용되지 않은 기능 조작	3
10	장비 사용 중 장비의 이상이나 고장 발견 후 담당자에게 즉시 고지하지 않은 경우	3
11	사용자 부주의로 기기 손상 및 고장	5
12	사용자 부주의로 장비 부속품 분실 또는 파손	5
13	장비 사용 후 장비사용일지를 작성하지 않거나 허위 작성 또는 일부만 작성	1
14	담당자가 장비 또는 시설의 정상적인 작동과 안전을 유지하는 데에 반드시 파악해야할 시료의 정보를 제공하지 않아 장비 손상 및 고장을 초래	3
15	야간 또는 장비 담당자의 정규 근무시간이 아닌 때에 장비 사용 후 소등. 출입문단속. 주변 정리 등을 확인하지 않고 퇴실	3
16	유독 물질 및 가스의 누출 또는 화재 발생의 위험을 초래	5
17	타인의 개인물품(분석 및 공정 소모품 및 기자재)을 사전 동의 없이 사용하거나 훔치는 행위	5

Penalty points for users of equipment

- Penalty points criteria

No.	Behaviors subject to penalty points	Penalty pts.
	[Eligibility to use equipment]	
1	Unauthorized use of equipment without permission	5
2	Use of equipment without a reservation	3
3	Someone other than the equipment lessee used the equipment	3
	[Reservations for using equipment]	
4	Reserved and used equipment outside of permitted hours	1
5	Use of equipment beyond the time reserved without making another reservation beforehand for extra time	1
6	Failed to use the equipment durng the reserved time and did not cancel reservation in advance	3
7	Cancelling reservations for equipment after the cancellation deadline, under Article 7, Guideline for the Operation of the UNIST Central Research Facilities (UCRF)	1
8	Use of any equipment without giving a prior notice to the equipment manager, after making a reservation	1
	[Careless behaviors]	
9	Using functions on the equipment that are not permitted	3
10	Failure to promptly notify the manager of any errors or failures detected during use	3
11	Negligence that resulted in damages or failure to the equipment	5
12	Negligence that resulted in loss or damage to an equipment component or part	5
13	Failure to record in the equipment usage log after using any equipment, or misrepresentation or partial representation of the facts	1
14	Failure to provide specimen information required by the equipment manager to ensure normal operations and safety of equipment or facilities, thus resulting in damage or failure to the equipment	3
15	Leaving the laboratory without putting the laboratory back in order, without turning off the lights, or without properly locking the entrance door, after using equipment at nighttime or during the equipment manager's off-hours	3
16	Causing leakage of toxic substances, gases, or causing risk of fire	5
17	Using or stealing someone's personal items (e.g. supplies, equipment or materials for analysis and process) without prior consent	5

Penalty points for users of equipment

- Follow-up Actions after Imposing Penalty Points

구분	벌점	조치내용
[장비사용자 개인]		
개인에게 부과된 벌점 합산	≥ 5 points	장비 담당자가 사용자 및 지도교수에게 이메일로 통보(벌점 8점 이상일 시 장비 사용이 3개월간 금지됨을 공지)하고 해당 사용자의 벌점 내역을 기기실에 게시
	≥ 8 points	장비 담당자가 사용자 및 지도교수에게 사용자의 해당 장비 사용이 3개월간 금지되고 재교육 후 사용이 가능함을 이메일로 통보하고 지도교수에게 공문 발송, 해당 사용자의 벌점 내역을 기기실에 게시
(사용자 소속 연구실)		
동일 연구실에서 동일 장비에 대하여 연구실 소속 학생들에게 부과된 벌점 합산	≥ 12 points	장비 담당자가 지도교수와 해당 사용자에게 벌점 15점 이상일 시 해당 연구실의 해당 장비 사용이 3개월간 금지됨을 이메일로 통보
	≥ 15 points	장비 담당자가 지도교수에게 해당 연구실의 해당 장비 사용이 3개월간 금지됨을 이메일로 통보, 지도교수에게 공문 발송, 해당 사용자의 벌점 내역을 기기실에 게시
동일 연구실에서 연구지원본부 전체 장비에 대하여 연구실 소속 학생들에게 부과된 벌점 합산	≥ 20 points	연구지원본부에서 지도교수와 소속 학생에게 벌점 25점 이상일 시 해당 연구실의 연구지원본부 전체 장비 사용이 1개월간 금지됨을 이메일로 통보
	≥ 25 points	연구지원본부에서 지도교수와 소속 학생에게 해당 연구실의 연구지원본부 전체 장비 사용이 1개월간 금지됨을 이메일로 통보, 지도교수에게 공문 발송, 해당 벌점 내역을 연구지원본부 게시판에 게시

Penalty points for users of equipment

- Follow-up Actions after Imposing Penalty Points

Classification	Penalty pts.	Follow-up actions
(Individual users of equipment)		
Sum up penalty poin ts imposed to indivi duals	≥ 5 points	Equipment manager will notify user(s) and their supervising professor by email of their penalty points total, and shall post the details of their penalty points on the bulletin board of the equip ment room. Users with penalty points 8 points or higher may not use the relevant equipment f or 3 months.
	≥ 8 points	Equipment manager will notify user(s) and their supervising professor by email that the user(s) may not use the relevant equipment for 3 months until they complete the re-orientation cours e; will also forward an official notice to their supervising professor; and will post details of their penalty points on the bulletin board of the equipment room.
(User's laboratory)		
Sum up penalty poin ts imposed on the st udents in the labora tory for the same eq uipment in the same laboratory	≥ 12 points	Equipment manager will notify the user(s) and their supervising professor by email that user(s) with penalty points 15 points or higher may not use the relevant equipment in the laboratory f or 3 months.
	≥ 15 points	Equipment manager will email the supervising professor to inform that the user(s) may not use the relevant equipment in the laboratory for 3 months; will also forward an official notice to th eir supervising professor; and will post the details of their penalty points on the bulletin board of the equipment room.
Sum up penalty poin ts imposed on the st udents in the labora tory for all UCRF equ ipment in the same l aboratory	≥ 20 points	UCRF will notify students and their supervising professor by email that the user(s) with 25 pena lty points or higher may not use any UCRF equipment in the laboratory for 1 month.
	≥ 25 points	UCRF will notify students and their supervising professor by email that user(s) may not use any UCRF equipment in the laboratory for 1 month; will also forward official notice to their supervis ing professor; and will post details of their penalty points on the bulletin board of UCRF.

14. Basic information

ULSAN NATIONAL INSTITUTE OF
SCIENCE AND TECHNOLOGY

NMR Specifications

	Varian 600 MHz NMR	Bruker 600 MHz NMR	Bruker 400 MHz NMR
Location	102-B119	102-B119	102-B119
Measurement Type	Self / Request	Self / Request	Self / Request
Model	VNMRS 600 (Varian)	AVANCE NEO (Bruker)	AVANCE III HD (Bruker)
Magnet	14.1 T	9.4 T	9.4 T
Channel	3 channel	2 channel	2 channel
Probe	▪ 5 mm PFG Auto X DB probe ▪ 5 mm Automated triple resonance probe ▪ 4 mm Nano TM probe ▪ 1.6 mm triple resonance HXY MAS **solid** probe ▪ 5 mm double resonance MAS **solid** probe	▪ Prodigy probe ▪ 5 mm i-probe	▪ BBO probe
Auto-sampler	X	O	O
Auto-tuning & matching	O	O	O
Power	100 W / 300 W / 300 W	100 W / 500 W	100 W / 500 W
Channel	▪ Ch1 : ^{1}H, ^{19}F ▪ Ch2 : 170MHz(^{31}P) ~ 150 MHz (^{13}C) ▪ Ch3 : 150MHz(^{13}C) ~ 60 MHz (^{15}N)	▪ Ch1: ^{1}H, ^{19}F ▪ Ch2: 170MHz(^{31}P) ~ 150 MHz (^{13}C)	▪ Ch1: ^{1}H, ^{19}F ▪ Ch2: 160MHz(^{13}C) ~ 49 MHz (^{15}N)
Temperature	- 80 ~ 90 ˚C	- 40 ~ 150 ˚C - 150 ~ 150 ˚C	- 150(20) ~ 150 ˚C

NMR probe

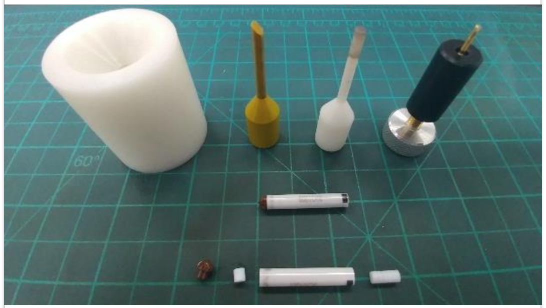
5mm PFG Auto X DB	5mm PFG Auto Triple	5 mm Double MAS [Solid]	1.6 mm Triple MAS [Solid]
			
102-B119	102-B119	102-B119	102-B119
의뢰 / 자율사용 가능	의뢰 / 자율사용 가능	의뢰가능	의뢰가능
Solution NMR	Solution NMR	Solid-state NMR	Solid-state NMR
^{1}H-^{19}F / ^{15}N-^{31}P (56 ~ 155 MHz)	^{1}H / ^{13}C / ^{15}N	^{1}H-^{19}F / ^{15}N-^{31}P	^{1}H-^{19}F / ^{15}N-^{31}P / ^{15}N-^{31}P
-80 ~ 130 ˚C	-20 ~ 80 ˚C	RT.	-50 ~ 50 ˚C
X Broad-Band experiment	Triple resonance experiment	One-pulse, CP-MAS	One-pulse, CP-MAS
20 Hz	20 Hz	5-12 kHz	8-40 kHz
5 mm sample tube	5 mm sample tube	5 mm rotor	1.6 mm rotor
500 μl 이상	500 μl 이상	Fine powder 1 g 이상	Fine powder 20 mg 이상

NMR probe

4mm Nano-probe	XR-401	5 mm One probe [Solution]	5 mm BBO probe [Solution]
			
102-B119	102-B119	102-B119	102-B119
의뢰가능	의뢰가능	의뢰 / 자율사용가능	의뢰 / 자율사용가능
HR-MAS NMR	Temperature control unit	Solution NMR (Agilent 400)	Solution NMR (Bruker 400)
^{1}H-^{19}F / ^{15}N-^{31}P	^{1}H / ^{13}C / ^{15}N	^{1}H-^{19}F / ^{15}N-^{31}P	^{1}H-^{19}F / ^{15}N-^{31}P
0 ~ 50 ˚C	-40(-60) ~ 100 ˚C	-80 ~ 130 ˚C	0 ~ 50 ˚C
HR-MAS experiment	Temperature control	X Broad-Band experiment	X Broad-Band experiment
2.5 kHz	-	20 Hz	20 Hz
4 mm sampling tube	-	5 mm sample tube	5 mm sample tube
100 µl 이상	-	500 µl 이상	500 µl 이상

NMR sample preparation

5 mm rotor

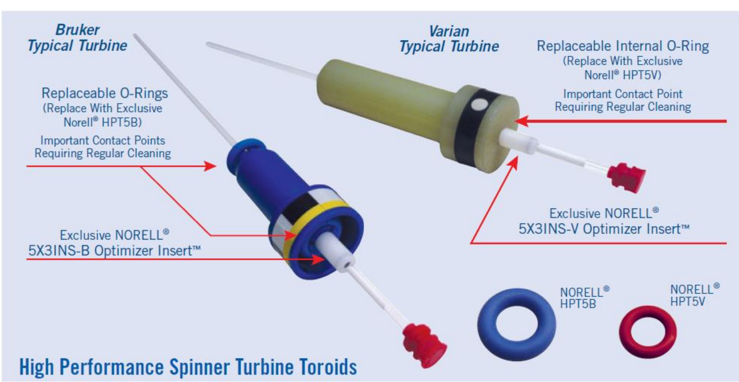


1.6 mm rotor

4 mm sampling tube

NMR spinner

Standard Sample Holder



Temperature limit

Ceramic
Variable

STV-5
-40 ~ 60 ˚C

POM
0 ~ 80 ˚C

Ceramic
-150 ~ 180 ˚C

15. Emergency

-장비 작동

-연락 체계

Emergency

UNIST
ULSAN NATIONAL INSTITUTE OF SCIENCE AND TECHNOLOGY

연구실 번호 (Laboratory No.)	자연과학관 B119호
연구실명 (Laboratory Name)	핵자기공명분광기실 NMR Laboratory
연구실 안전담당자 (Safety Manager)	Sun-Phil Han 내선(Extension) (4174)

★ Please do not hesitate to contact <u>"Safety Manager"</u>, if you have any queries or urgent business.
(문의 사항 또는 급한 용무가 있을 시, <u>"연구실 안전담당자"</u>에게 연락 요망)

원외 주요 연락처
External Main Telephone

소방서 Fire Station	119
경찰서 Police Station	112
좋은삼정병원 Hospital	052)220-7500

화재,폭발,가스·화학약품누출등응급상황발생시

Fire, Explosion, Gas and Chemical Leak etc.

응급상황 발생시 Emergency Call

052) 217-0119

16. Case Study

Li salt & Electrolyte

리튬이온전지 리튬염 종류 및 특징

종류	분자량 (MW)	녹는점 (℃)	분해온도 (℃)	이온전도도(mS/cm) In PC	이온전도도(mS/cm) In EC/DMC
$LiPF_6$	151.9	200	80	5.8	10.7
$LiBF_4$	93.9	293	100	3.4	4.9
$LiASF_6$	195.9	340	100	5.7	11.1
$LiClO_4$	106.4	236	100	5.6	8.4
$LiCF_3SO_3$	155.9	300	100	1.7	-

자료: 전자부품연구원

전해질 종류 및 특성

	액체 전해질		겔 폴리머 전해질	고체 전해질	
	유기 전해질	이온성 액체		폴리머 전해질	무기 전해질
구성	유기용매 + 리튬염	이온성 액체 + 리튬염	폴리머 + 유기용매 + 리튬염	폴리머(가교제 + 가소제) + 리튬염	산화계 황화계
이온전도도	~10^{-2}(S/cm)	~10^{-3}(S/cm)	~10^{-3}(S/cm)	~10^{-5}(S/cm)	~10^{-3}(S/cm)
저온 특성	좋음	좋음	좋음	나쁨	좋음
고온 안정성	나쁨	아주 좋음	좋음	아주 좋음	아주 좋음
예	$LiPF_6$ in EC/DEC	LiTFSI in EMITFSI	$LiPF_6$ + PVdF-HFP + EC/DEC	LiTFSI + PEGDME + BPA	$Li_{1+x}Al_xGe_{2-x}(PO_4)_3$ Li_2S-P_2S_5

자료: 한국화학연구원

Solution NMR

1D NMR: 1H, 13C, 17O, 19F, 31P, 33S
T1/T2 analysis
DOSY NMR

HR-MAS NMR

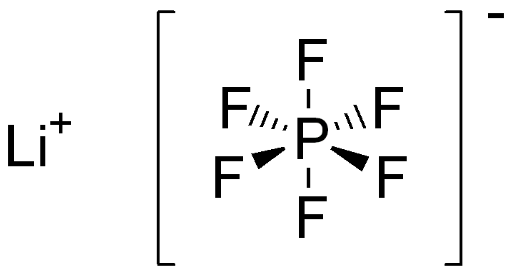
Solid-state NMR

1D NMR: 1H, 13C, 17O, 19F, 31P, 33S
T1/T2 analysis
Solid DOSY NMR
2D NMR: MQ-MAS

[키움증권 리서치센터 산업분석 보고서] 차세대 배터리

2nI+1 rule

P(Phosphorus): I=1/2
F(Fluorine): I=1/2

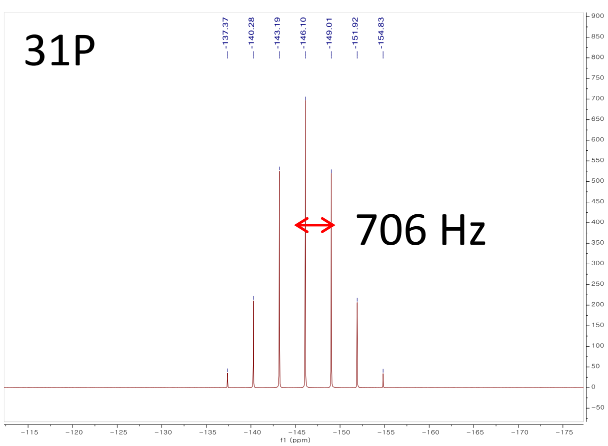


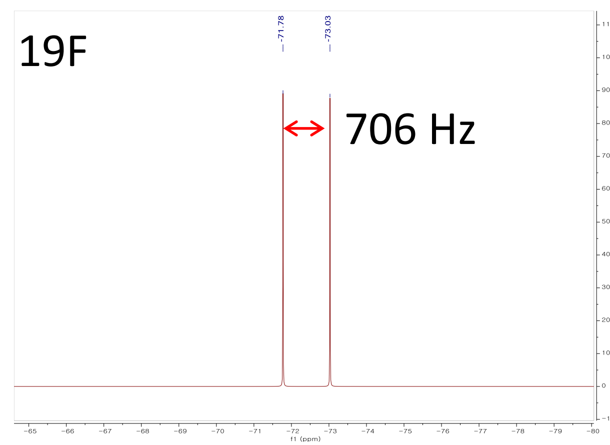
2nI+1 rule

N = Number of neighbor nuclear
I = Nuclear spin quantum number

$1J_{PF}$: 2 * 6 * 1/2 + 1 = 7 (Septet)
$1J_{FP}$: 2 * 1 * 1/2 + 1 = 2 (Doublet)

Coupling constant
$1J_{PF} = 1J_{FP}$ = 706 Hz





Application

29Si

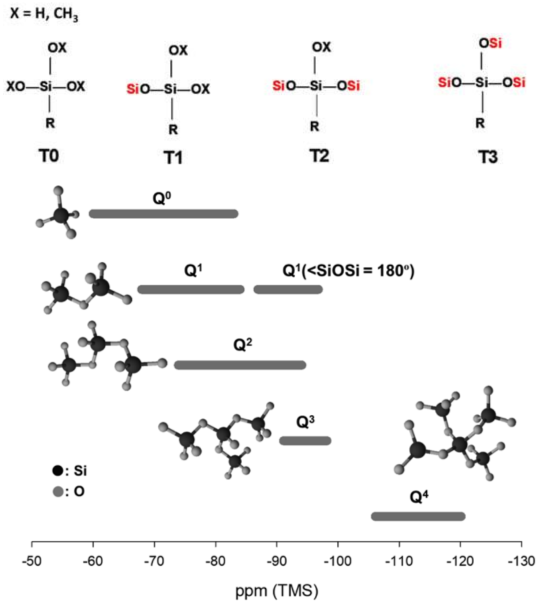
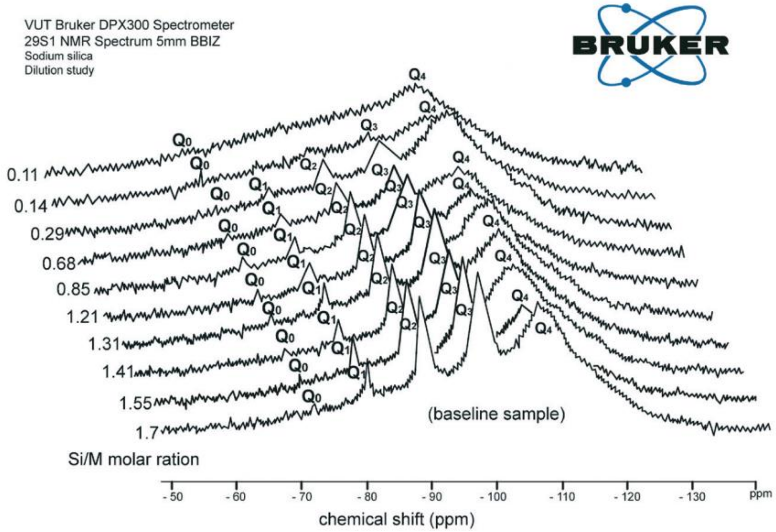
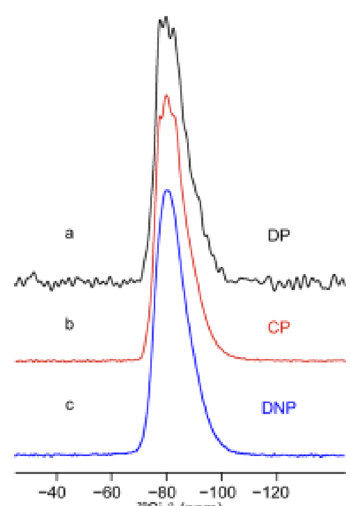
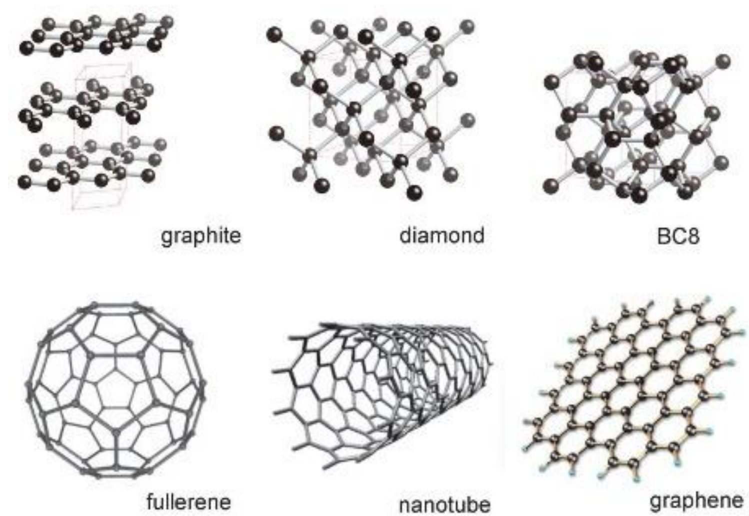


Fig. 2. Classification of silicate minerals according to the degree of polymerization of SiO_4 and their chemical shifts in ^{29}Si NMR (adapted from Magi et al. [31]).





13C



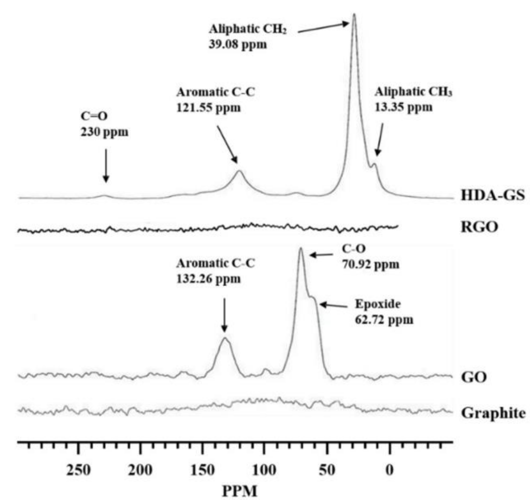
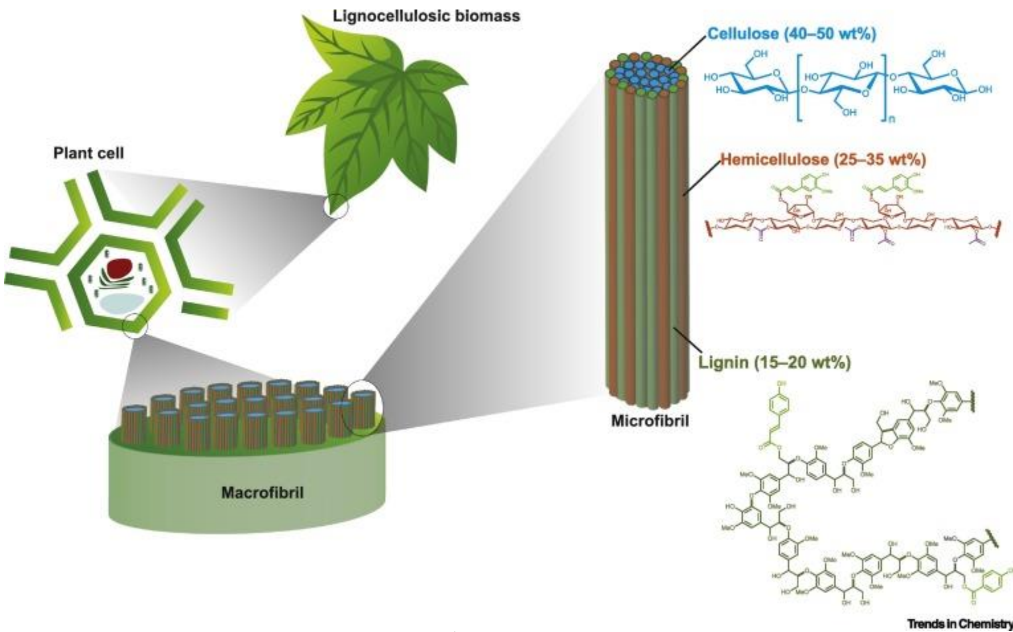
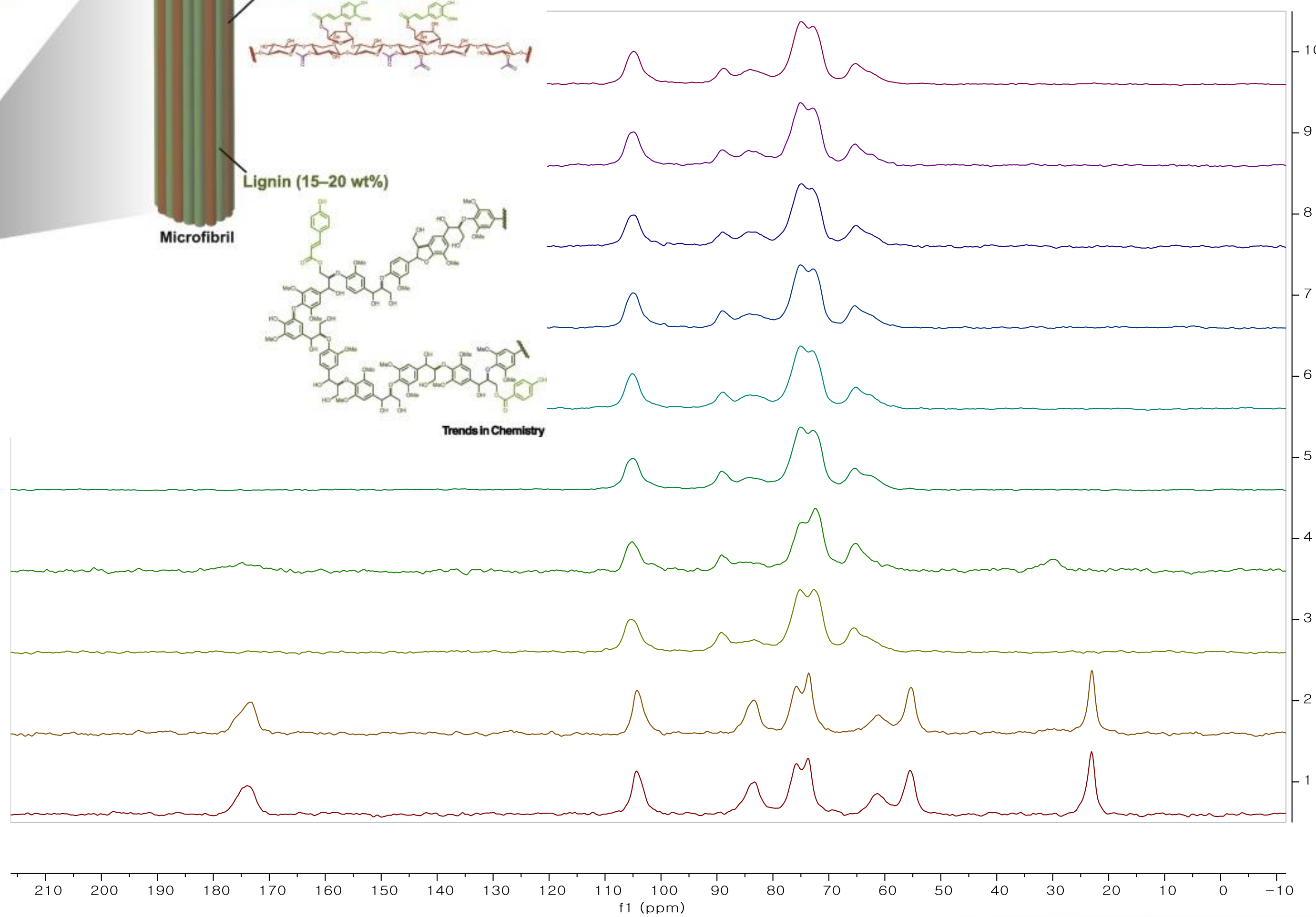


Figure 3. ^{13}C-NMR spectra of the fillers based on graphite.

Application (Lignin)

Solid-state NMR (1H, 13C / DP, CP-MAS)





G-quadruplex 가 Li ion의 이동속도를 향상시킴

G-quadruplex의 이온채널 형성 분석

ScienceAdvances AAAS **Manuscript Template**

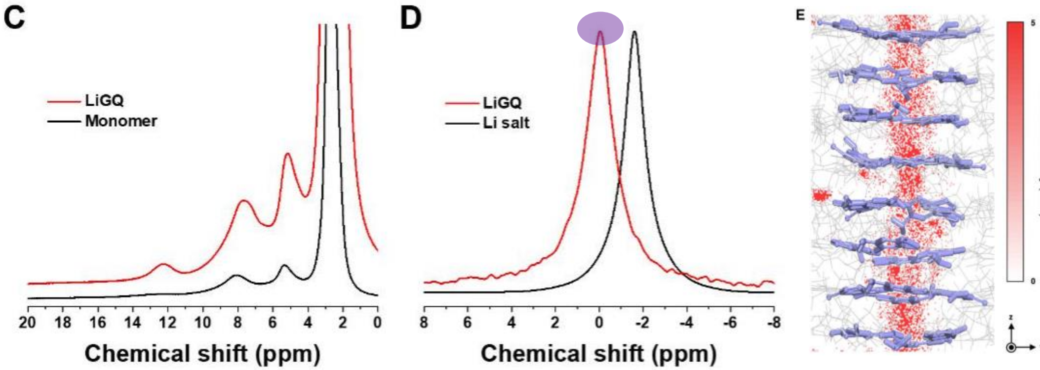
FRONT MATTER

Title

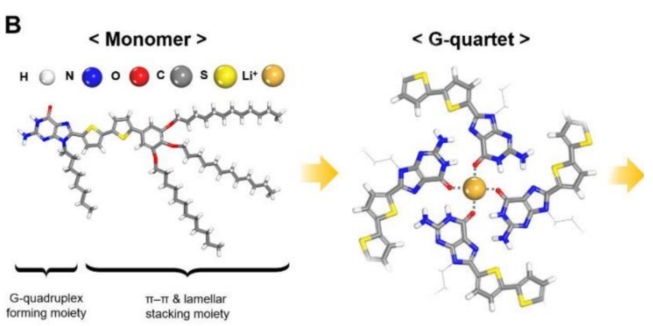
Ion slippage through Li^{+}-centered G-quadruplex

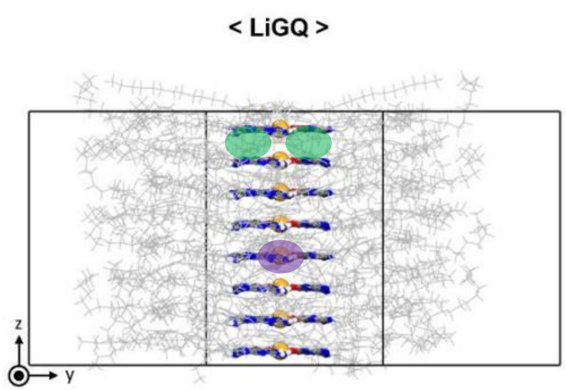
Authors

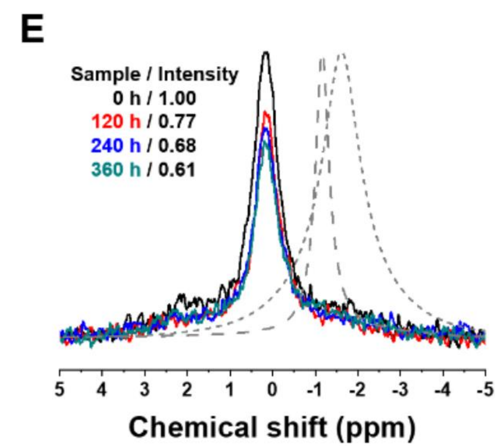
Seok-Kyu Cho,[1]† Kyung Min Lee,[2]† So-Huei Kang,[2,3]† Kihun Jeong,[4] Sun-Phil Han,[5] Ji Eun Lee,[2] Seungho Lee,[6] Tae Joo Shin,[5] Ja-Hyoung Ryu,[6] Changduk Yang,[2]* Sang Kyu Kwak,[2]* Sang-Young Lee[4]*



shows a π–π stacking distance of ~3.4 Å. MAS (**C**) 1H and (**D**) ^{7}Li NMR spectra of the LiGQ. A characteristic ^{1}H NMR peak at 12 ppm exhibits the Hoogsteen hydrogen bond of G-quartet assembly. The deshielded singlet ^{7}Li NMR peak at −0.044 ppm reveals the isolation of Li^{+} from its counter anion. (**E**) Contour plot of Li^{+} number density of the LiGQ under an electric field. Red bar indicates the 2D number density of Li^{+} projected to the *yz*-plane.

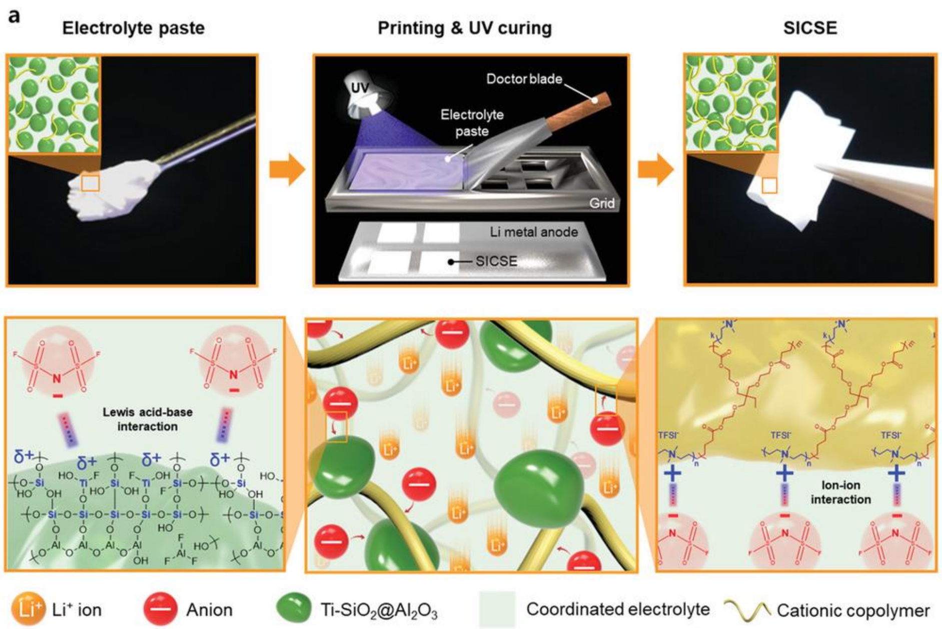






이온전도 메커니즘 확인

고체전해질 첨가제 분석



ADVANCED ENERGY MATERIALS

Research Article | Full Access

Single-Ion Conducting Soft Electrolytes for Semi-Solid Lithium Metal Batteries Enabling Cell Fabrication and Operation under Ambient Conditions

Kyeong-Seok Oh, Jung-Hui Kim, Se-Hee Kim, Dongrak Oh, Sun-Phil Han, Kwangeun Jung, Zhuyi Wang, Liyi Shi, Yongxiang Su, Taeeun Yim, Shuai Yuan, Sang-Young Lee

First published: 08 August 2021 | https://doi.org/10.1002/aenm.202101813 | Citations: 3

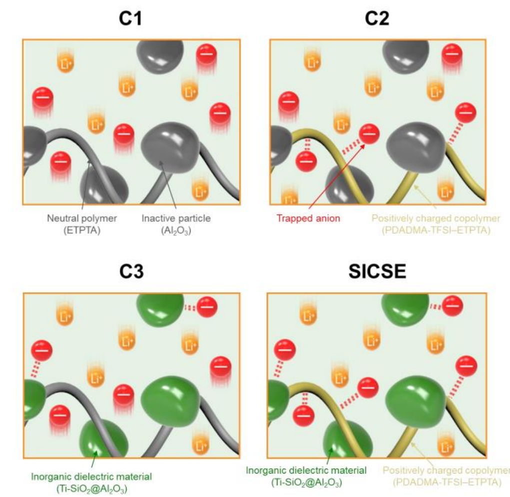
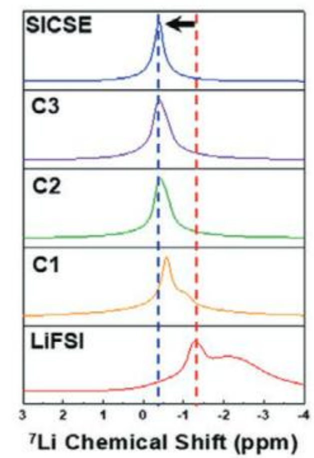
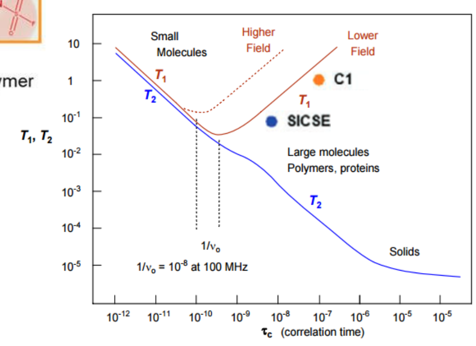
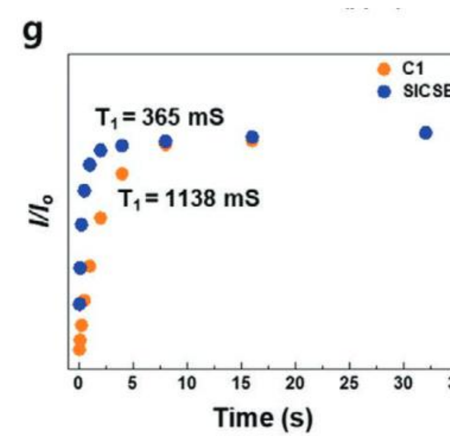


Figure S9. Conceptual illustration depicting the ion transport phenomena of the control samples (C1, C2, and C3) and SICSE, along with their chemical structure and anion trapping sites.



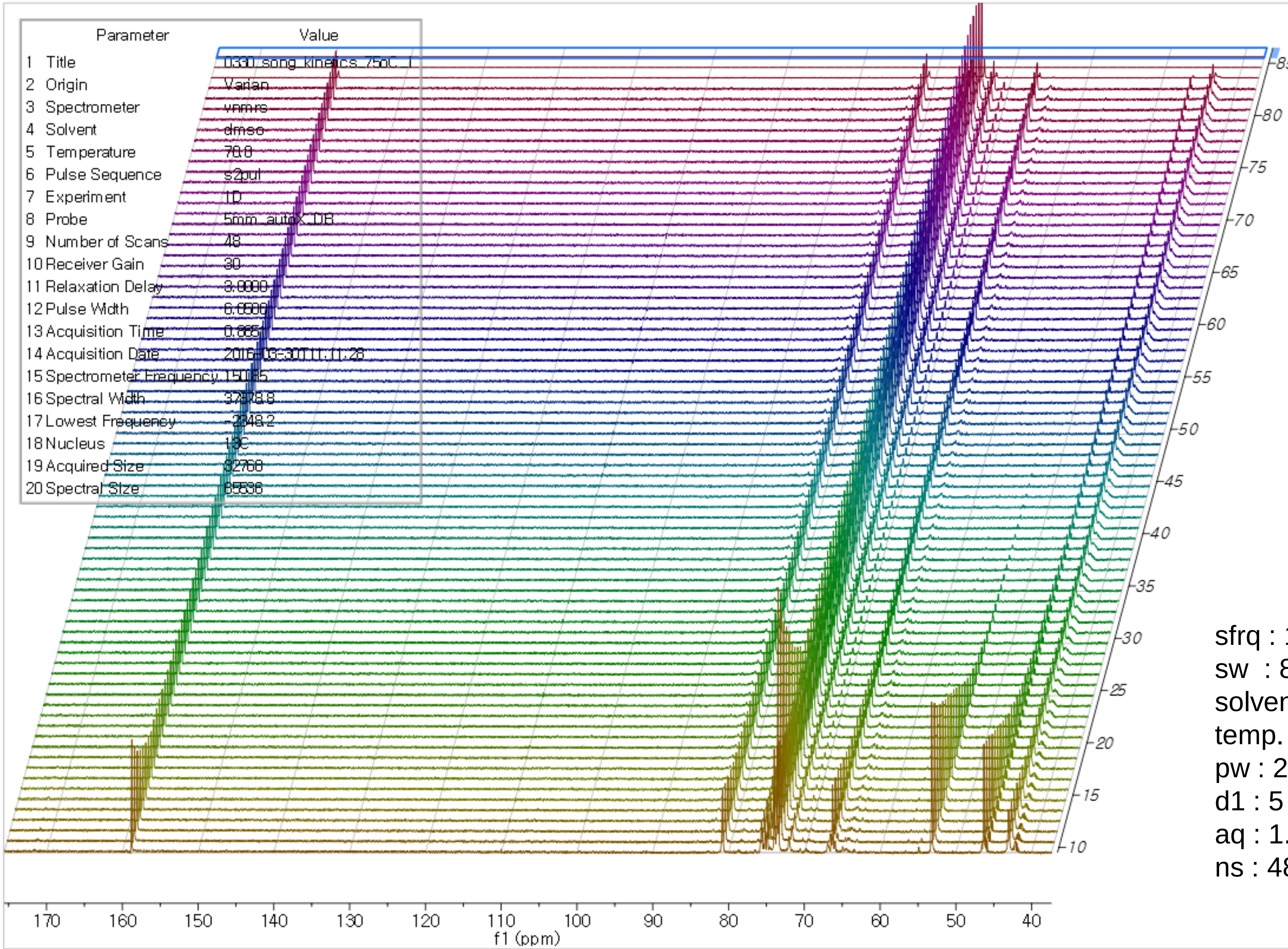
d) ^{7}Li NMR spectra of the SICSE, control samples (C1, C2, and C3), and LiFSI





g) Inversion–recovery plots obtained from ^{7}Li MAS NMR spectra.

Real-time analysis

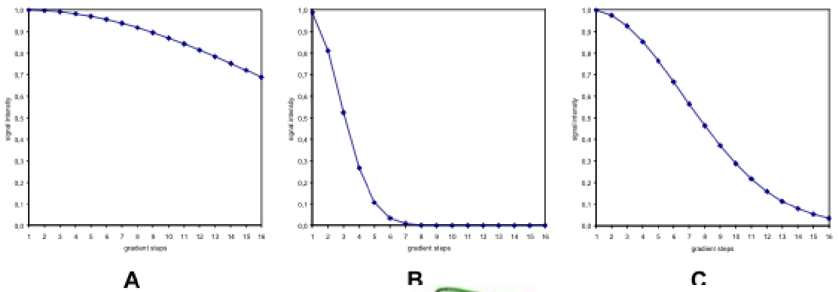


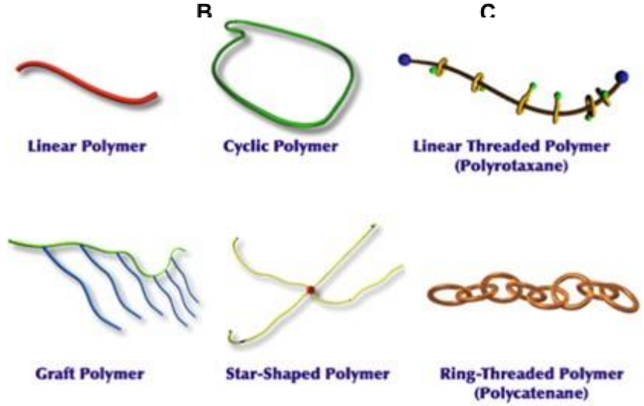
sfrq : 150.85
sw : 8389.3
solvent : DMSO
temp. : 343 K
pw : 20 (45 °)
d1 : 5
aq : 1.953
ns : 48 (24h array exp.)

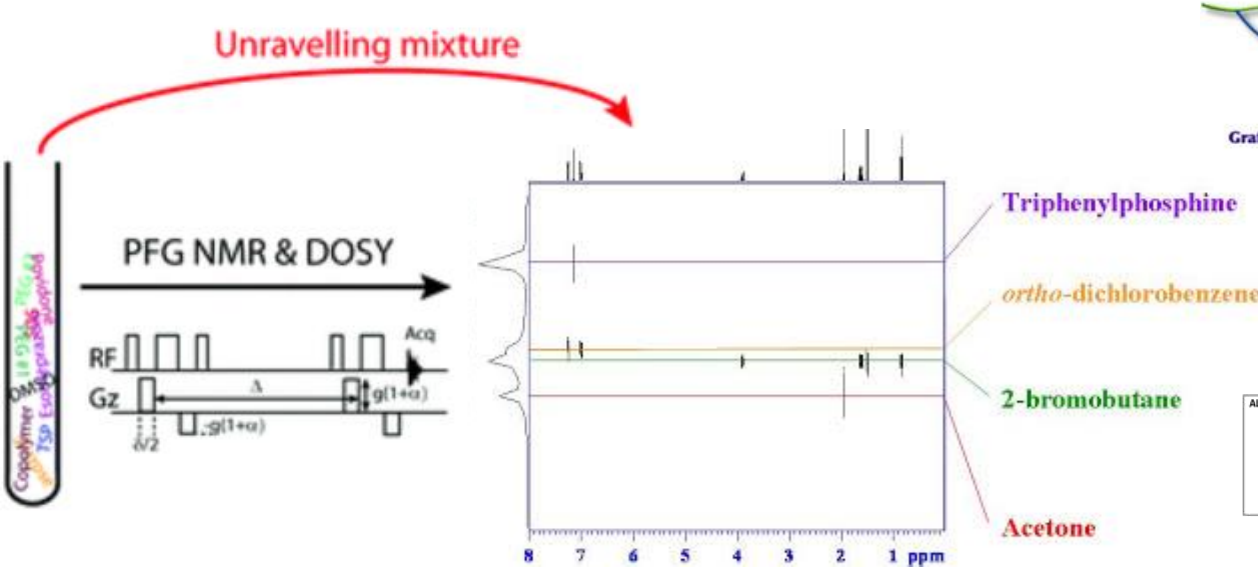
Diffusion Ordered SpectroscopY

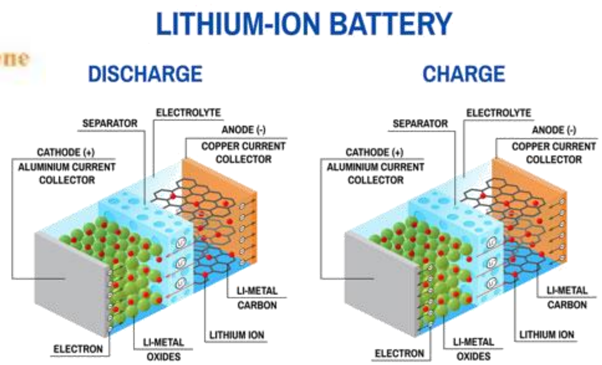
$$D = \frac{kT}{6\pi\eta r_s}$$

$$I/I_0 = e^{\left(-Dg^2\delta^2\sigma^2g^2\Delta'\right)}$$

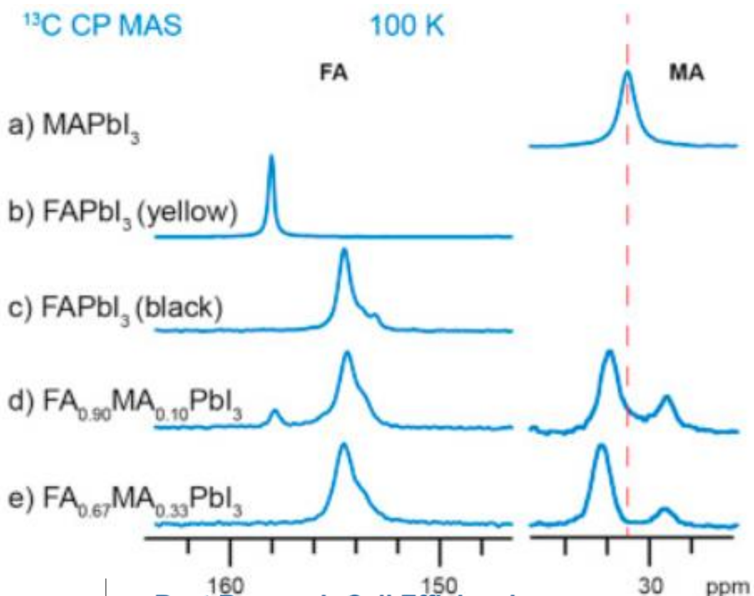


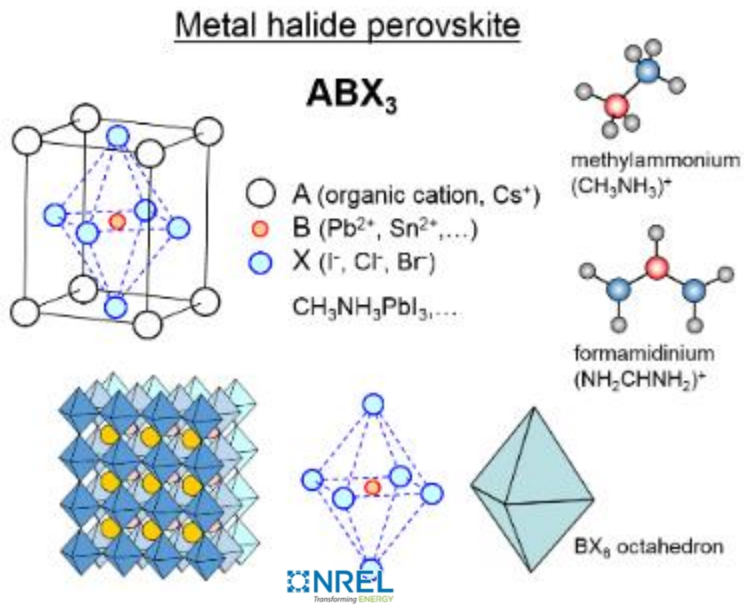


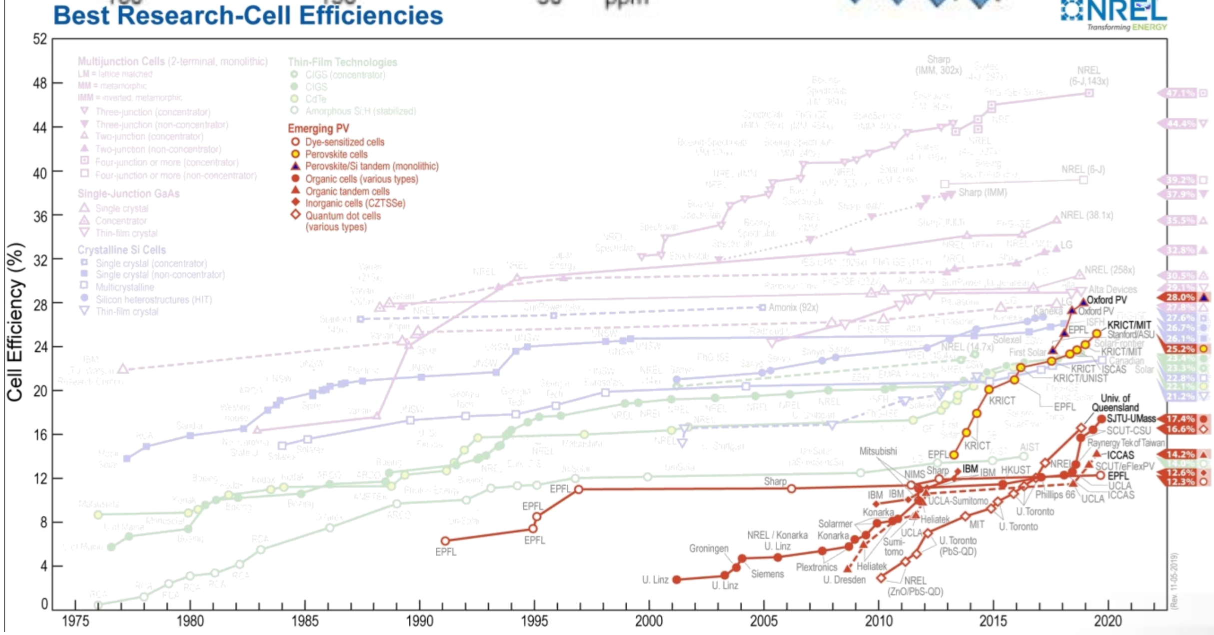




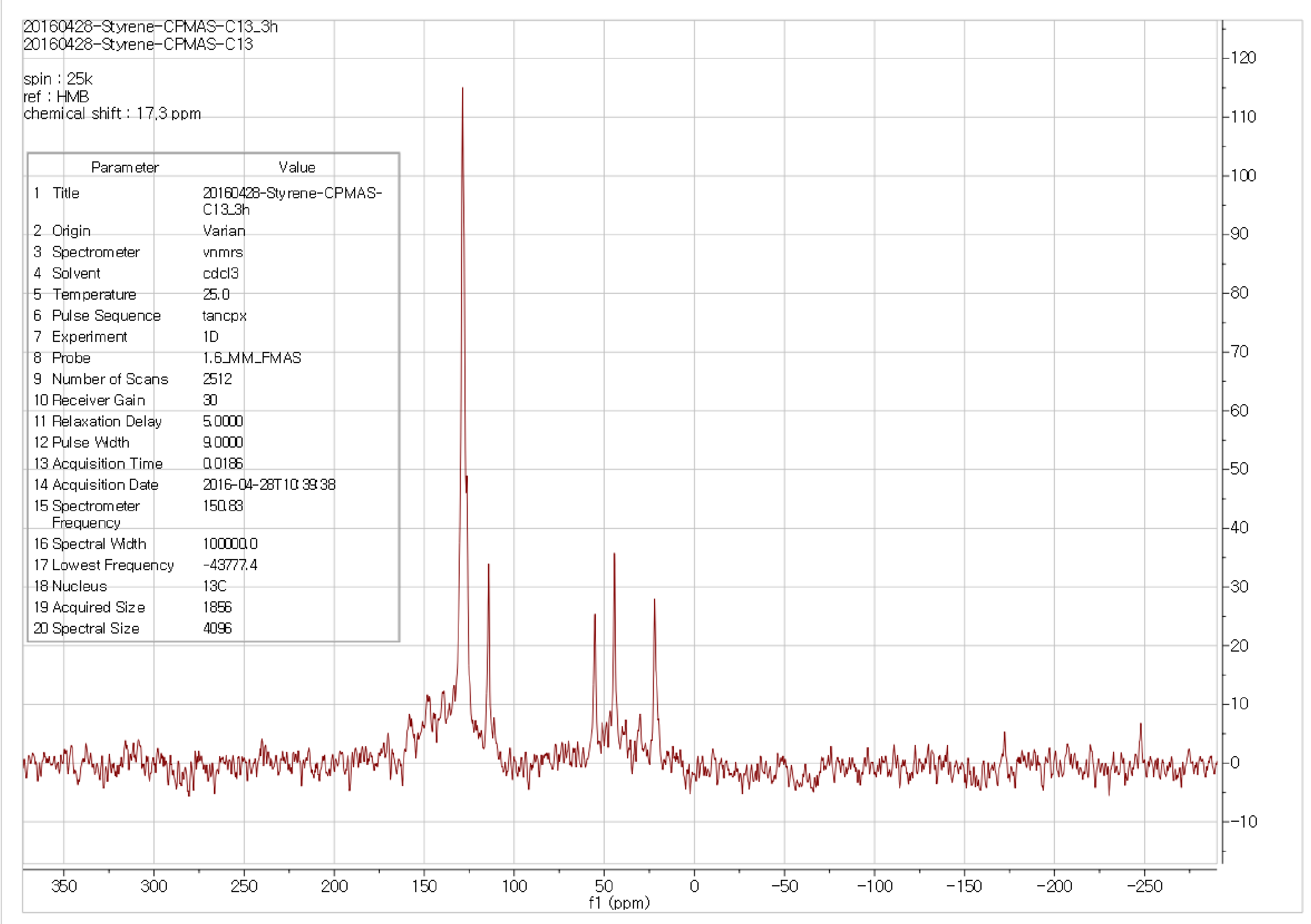
Solid-state NMR (Perovskite)



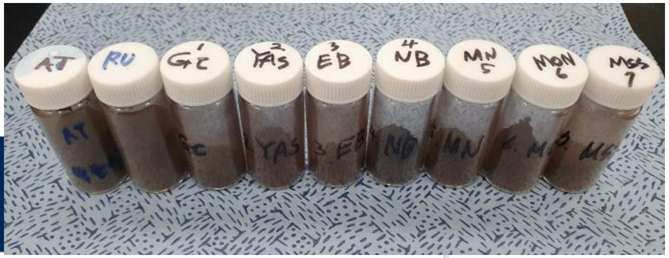




^{13}C Solid-state NMR (CP-MAS)



^{13}C Solid-state NMR (Coal)



NMR을 이용한 Pulverized Coal 조성분석

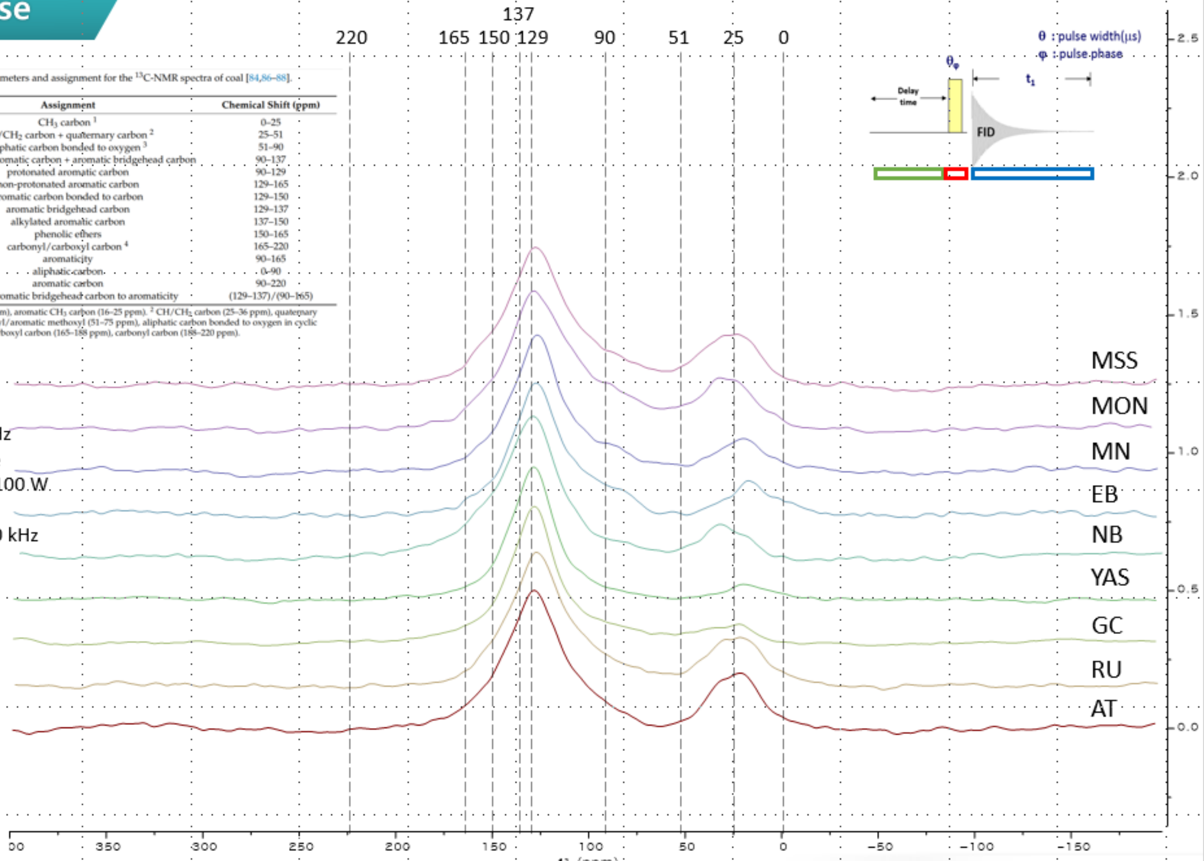
One-Pulse

Table 2. Structure parameters and assignment for the ^{13}C-NMR spectra of coal [84,86–88].

Parameter	Assignment	Chemical Shift (ppm)
f_{al}^{*}	CH_3 carbon [1]	0–25
f_{al}^{H}	CH/CH_2 carbon + quaternary carbon [2]	25–51
f_{al}^{O}	aliphatic carbon bonded to oxygen [3]	51–90
f_{a}^{H+B}	protonated aromatic carbon + aromatic bridgehead carbon	90–137
f_{a}^{H}	protonated aromatic carbon	90–129
f_{a}^{N}	non-protonated aromatic carbon	129–165
f_{a}^{B+S}	aromatic carbon bonded to carbon	129–150
f_{a}^{B}	aromatic bridgehead carbon	129–137
f_{a}^{S}	alkylated aromatic carbon	137–150
f_{a}^{P}	phenolic ethers	150–165
f_{a}^{C}	carbonyl/carboxyl carbon [4]	165–220
f_{a}^{CP}	aromaticity	90–165
f_{al}^{C}	aliphatic carbon	0–90
f_{ar}^{C}	aromatic carbon	90–220
X_{BP}	ratio of aromatic bridgehead carbon to aromaticity	(129–137)/(90–165)

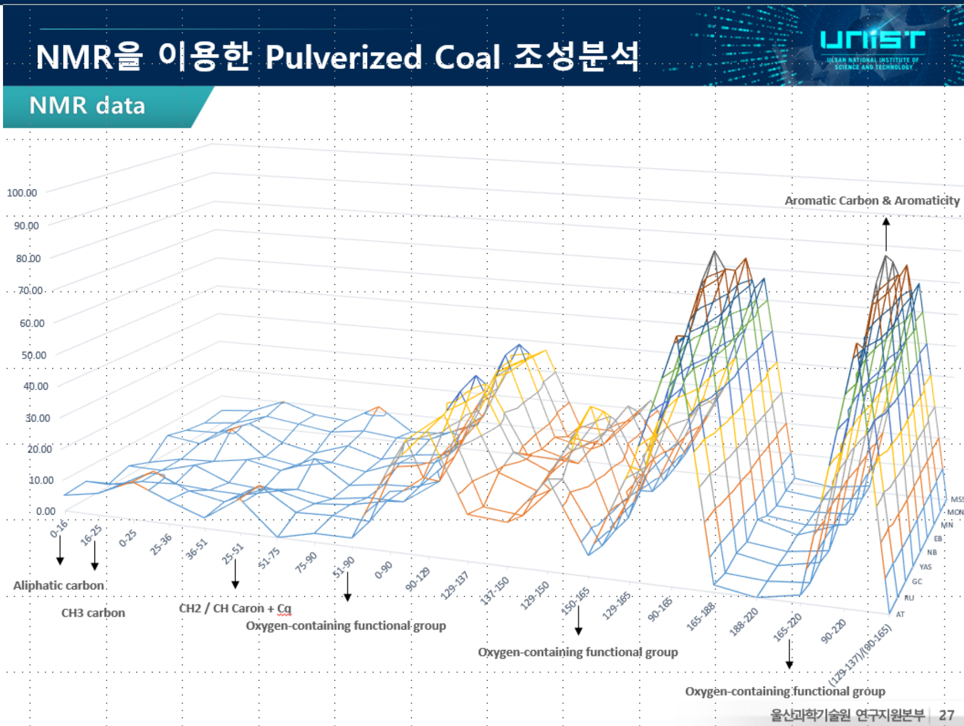
[1] Aliphatic CH_3 carbon (0–16 ppm), aromatic CH_3 carbon (16–25 ppm). [2] CH/CH_2 carbon (25–36 ppm), quaternary carbon (36–51 ppm). [3] Methoxyl/aromatic methoxyl (51–75 ppm), aliphatic carbon bonded to oxygen in cyclic hydrocarbon (75–90 ppm). [4] Carboxyl carbon (165–188 ppm), carbonyl carbon (188–220 ppm).

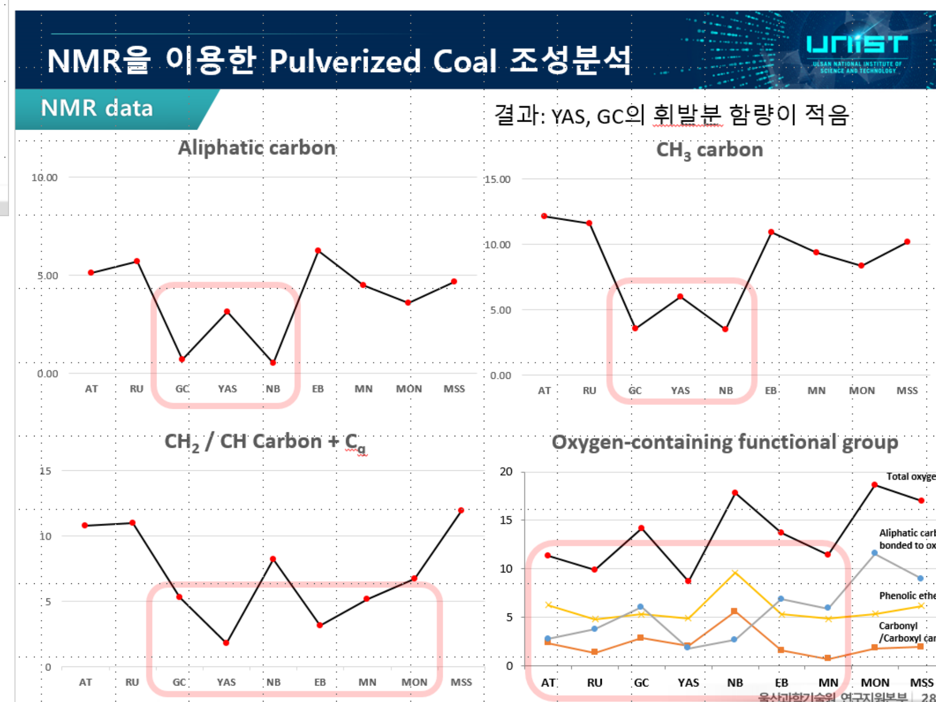
UNIST
Model: Varian
Magnet: 600 MHz
Pulse: One-Pulse
1H Decoupling: 100 W
Rotor: 1.6 mm
Spinning rate: 40 kHz
NS: 1024
D1: 60



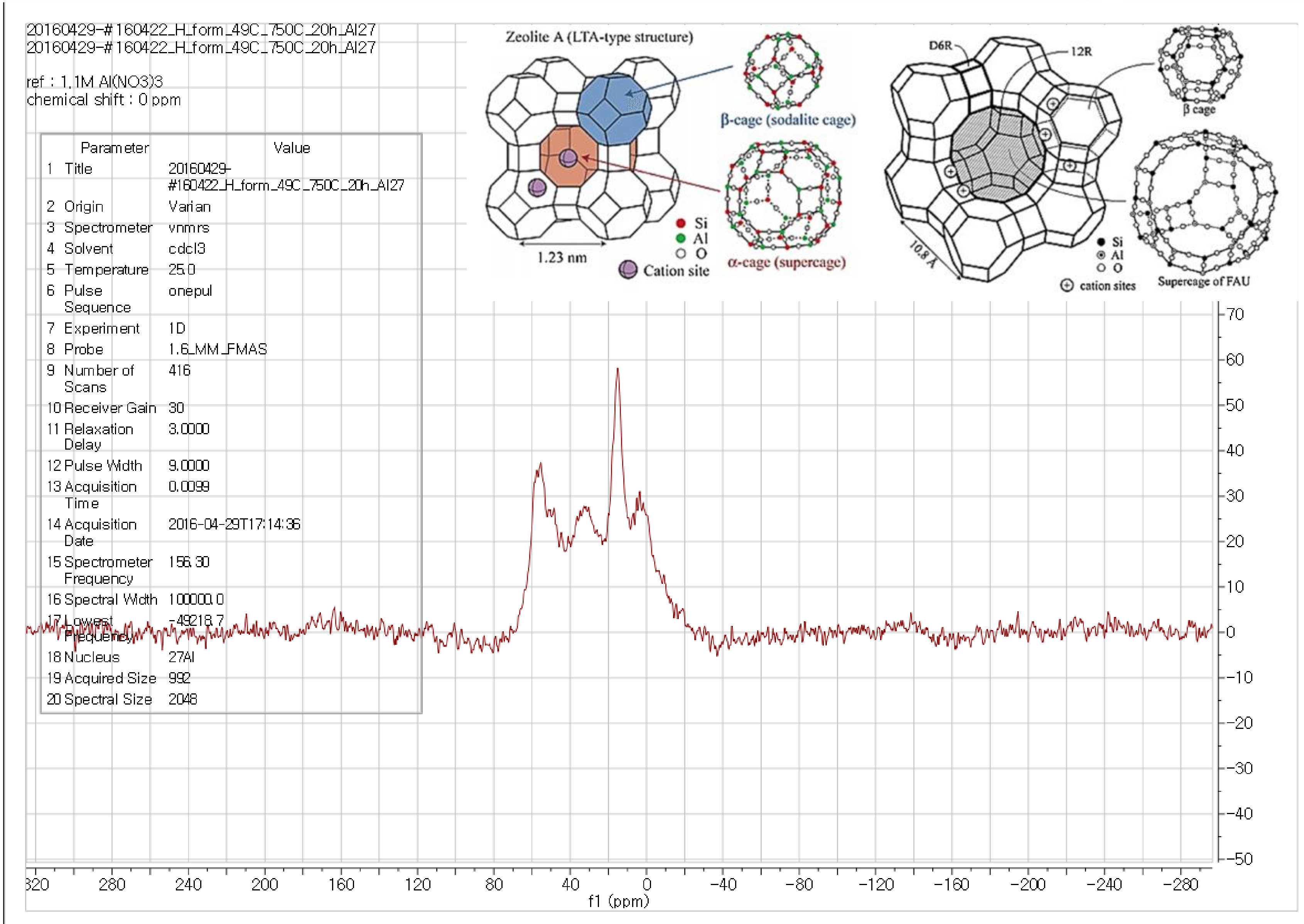
울산과학기술원 연구지원본부 18

^{13}C Solid-state NMR (Coal)





^{27}Al Solid-state NMR (Zeolite)



	Parameter	Value
1	Title	20160429-#160422_H_form_49C_750C_20h_Al27
2	Origin	Varian
3	Spectrometer	vnmrs
4	Solvent	cdcl3
5	Temperature	25.0
6	Pulse Sequence	onepul
7	Experiment	1D
8	Probe	1.6_MM_FMAS
9	Number of Scans	416
10	Receiver Gain	30
11	Relaxation Delay	3.0000
12	Pulse Width	9.0000
13	Acquisition Time	0.0099
14	Acquisition Date	2016-04-29T17:14:36
15	Spectrometer Frequency	156.30
16	Spectral Width	100000.0
17	Lowest Frequency	-49218.7
18	Nucleus	27Al
19	Acquired Size	992
20	Spectral Size	2048

Application of solid state NMR

- Organic complexes
- Inorganic complexes
- Zeolites
- Mesoporous solids
- Microporous solids
- Aluminosilicates/phosphates
- Minerals
- Biological molecules
- Glasses
- Cements
- Food products
- Wood
- Ceramics
- Bones
- Semiconductors
- Metals and alloys
- Archaelogical specimens
- Polymers
- Resins
- Surfaces

But, Fine particle + at least 20mg

http://www.theresonance.com/nmr-tutorial-mas-rotor-filling/

17. References

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-참고논문

-웹사이트

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  Varian (Korea)
  http://www.varianinc.com (http://www.varian.co.kr)

  JEOL (Korea)
  http://www.jeol.com (http://www.jeol.co.kr)

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  http://www.spectroscopynow.com

  The basics of NMR
  http://www.cis.rit.edu/htbooks/nmr/bnmr.htm

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Journal

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  J. Biomolecular NMR
  http://www.wkap.nl/journals/jbnmr

  Solid State Nuclear Magnetic Resonance
  http://www.elsevier.com/locate/ssnmr

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  Nature
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  Science
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<Solution NMR>

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<Solid-state NMR>

1) Basic theory

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- b. NMR spectroscopy of Biological Solids by A. Ramamoorthy, 2006, CRC Press

18. Attachments

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