NMR Discovery Series:
Solid State NMR

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Outline

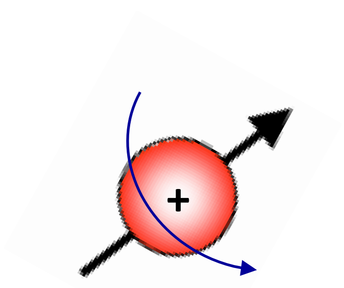
- **Solution NMR Basics**
- **Spin Interactions**
- **SSNMR Techniques**
- **SSNMR Hardware**
- **SSNMR Applications**

Solution NMR Basics

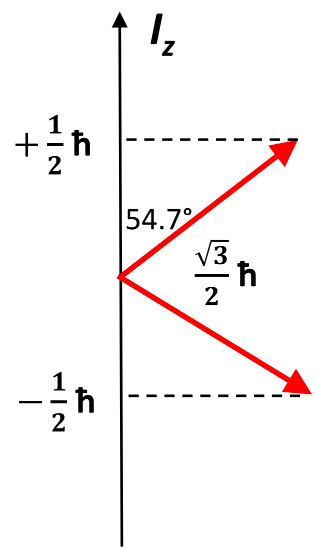
Nuclear Spin Angular Momentum

- **Nucleus** has a property called **spin**, an intrinsic property like *mass* and *charge*.
- **Spin** is a form of **Angular Momentum**, but not the classical angular momentum.
- ***Spin Angular Momentum*** is a vector, with a magnitude of $L = [I(I+1)]^{1/2}\,\hbar$.

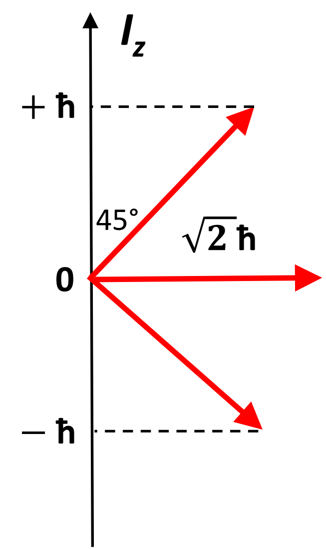
  where I is the *spin quantum number*.
- The projection (measurable) of the angular momentum along the **z-axis** is $I_z = m\,\hbar$.
- m is the *spin projection quantum number*, which takes values $[-I, -I+1, \ldots, +I]$.
- Pictorially, spin ½ and 1 can be represented as:



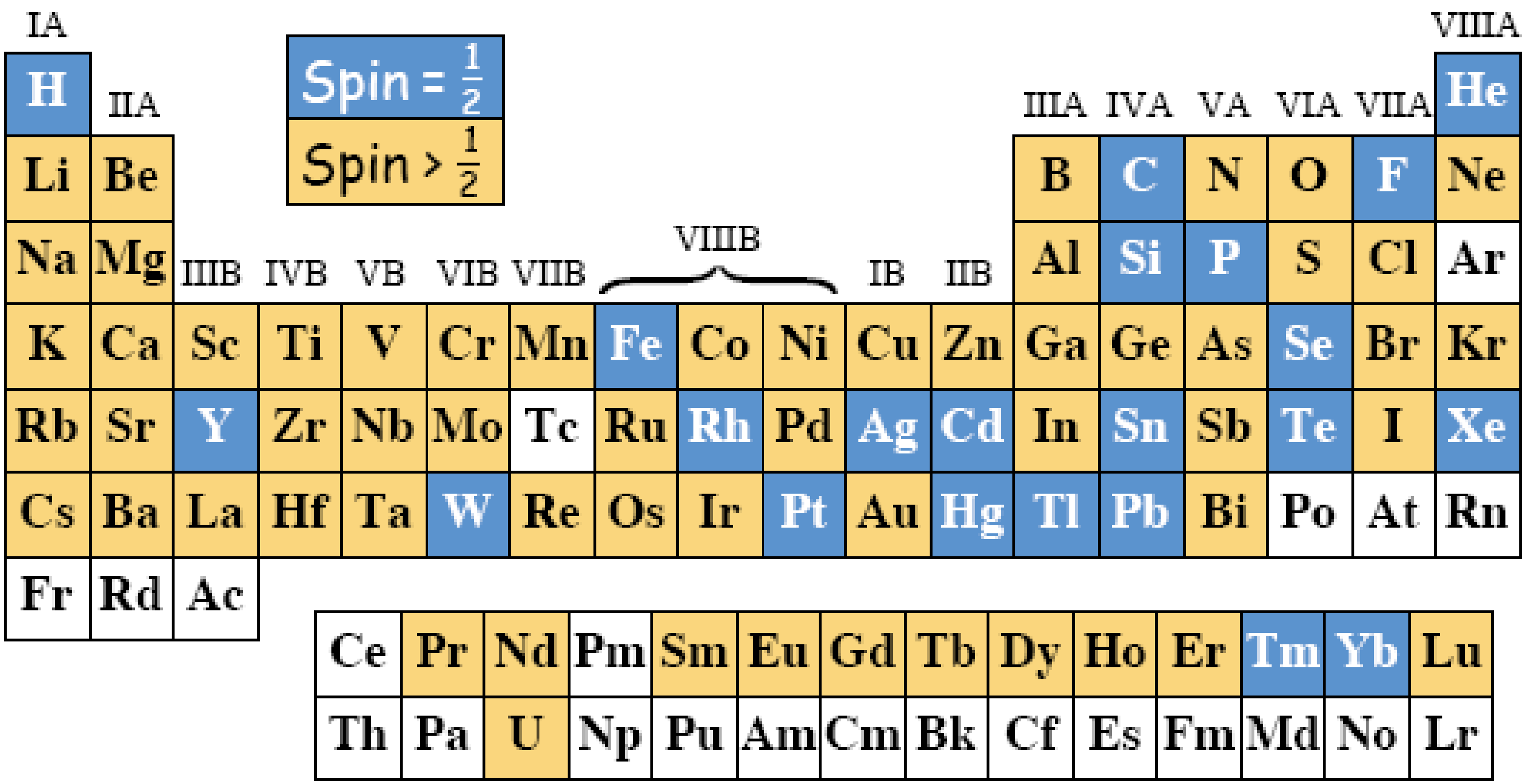
nuclear spin



Spin I = 1/2



Spin I = 1


Spin = 1/2
Spin > 1/2
IA
IIA
IIIB IVB VB VIB VIIB VIIIB IB IIB
IIIA IVA VA VIA VIIA
VIIIA
H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl Ar
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
Fr Rd Ac
Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr

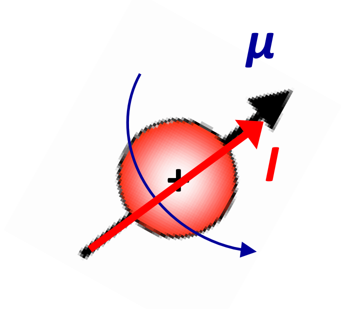
Nuclear Spin (Quantum Number)

- **Nuclear spin *I*** can take integer or half-integer values.
- For larger nuclei, it is not obvious what the spin should be (Shell Model).
- There are some rules the nuclei do follow with respect to nuclear spin.

Mass Number	Number of Protons	Number of Neutrons	Spin (I)	Examples
Even	Even	Even	0	^{12}C, ^{16}O
	Odd	Odd	1, 2, 3, …	^{2}H, ^{6}Li
Odd	Even	Odd	$\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$	^{13}C, ^{17}O
	Odd	Even	$\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$	^{15}N, ^{19}F

Magnetic Moment and Gyromagnetic Ratio

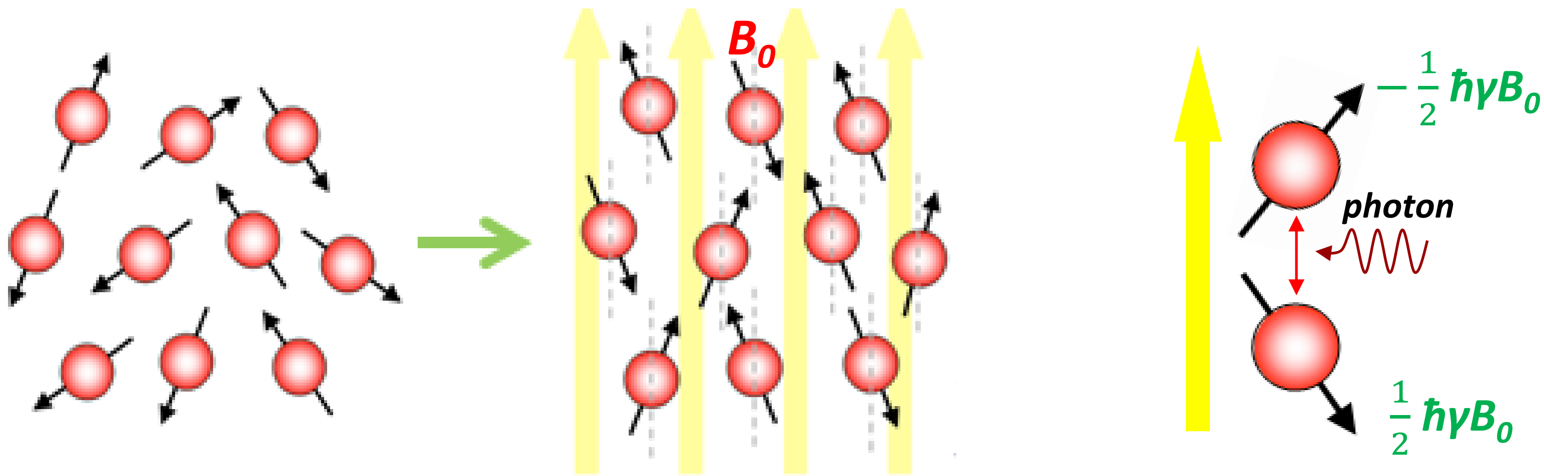
- The spin of a charged particle is associated with a magnetic dipole moment.
- **Nuclear Spin *I*** is associated with a **Magnetic Moment *μ***.
- *Magnetic Moment* is related to the *Nuclear Spin* by $\mu = \gamma I$.
- ***γ*** is the **gyromagnetic ratio**. Each nucleus has its specific ***γ***.



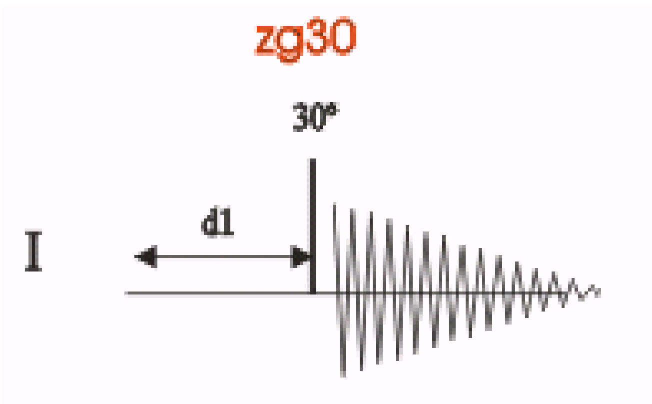
Nuclei	Spin	γ (10^7 rad/T*s)	ν (MHz)	Natural Abundance
^{1}H	½	26.7519	500.00	99.985
^{2}H	1	4.1066	76.75	0.015
^{13}C	½	6.7283	125.72	1.108
^{15}N	½	-2.7120	50.66	0.365
^{19}F	½	25.1810	470.38	100.0
^{31}P	½	10.8410	202.40	100.0

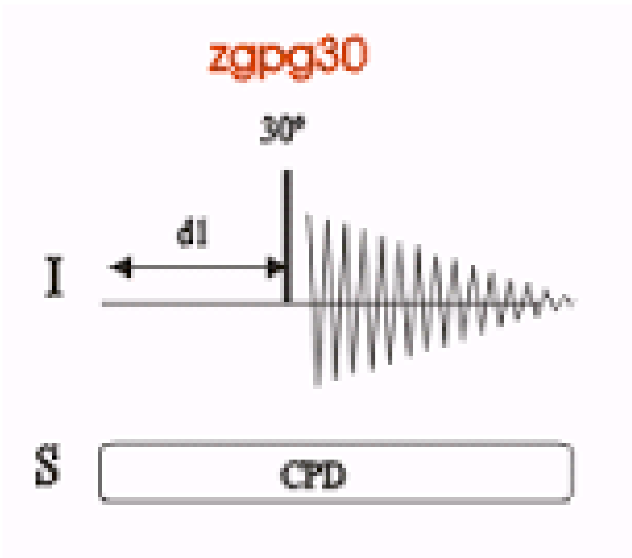
$B_0 = 11.74$ T

Nuclear Spin in a Magnetic Field



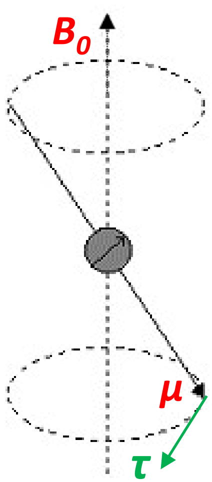
- Nuclear Spins are randomly oriented when no magnetic field is present.
- In a static magnetic field, nuclear spins (like 'tiny bar magnets') align up/against according to the applied magnetic field (**Zeeman** Interaction).
- The energy of a particular oriented nuclear spin is $E = -\mu\cdot B_0$.
- Along z-axis (measurable), the energy can be expressed as $E = -\mu_z B_0 = -m\hbar\gamma B_0$.
- For spin ½ nuclei, there are **two energy levels**. Photons with proper energy $\Delta E = \hbar\gamma B_0$ (frequency: $\nu = \Delta E/h = \gamma B_0/2\pi$) can excite the spins between the two energy levels. Signal will then be observed when the system returns to equilibrium.

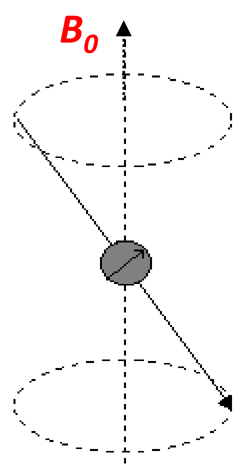

zg30
30°
d1
I

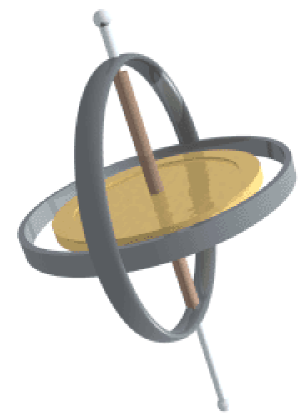

zgpg30
30°
d1
I
S
CPD

Larmor Precession

- Magnetic Moment in an external magnetic field will experience a **torque**, $\boldsymbol{\tau} = \boldsymbol{\mu} \times \boldsymbol{B_0}$.
- The torque then causes the magnetic moment to precess around the direction of the magnetic field. This is called **Larmor precession**.
- The frequency of precession works out to be $\boldsymbol{\nu} = \boldsymbol{\gamma B_0/2\pi}$, the **Larmor frequency**.

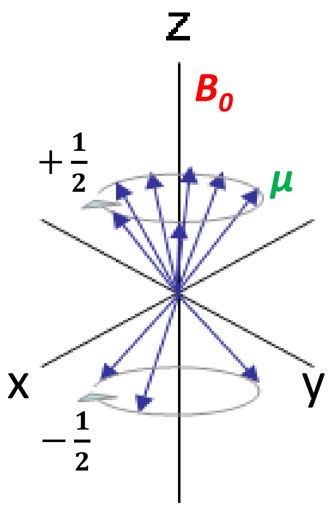


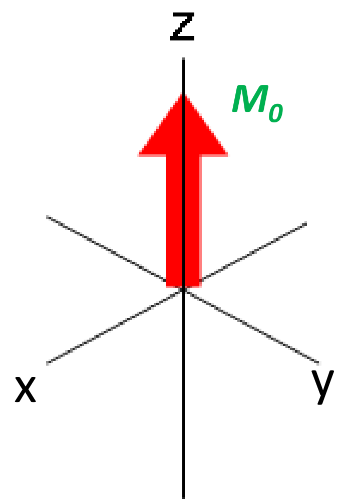



gyroscope

Bulk Magnetization

- In a real sample, there is a large number of nuclear spins, precessing at the Larmor frequency when in an external magnetic field.
- Based on *Boltzmann distribution*, there will be slightly more spins spin up (at lower energy state) than those spin down.
- This leads to a net contribution of magnetic moment along the field $\boldsymbol{B_0}$, called **Magnetization**.

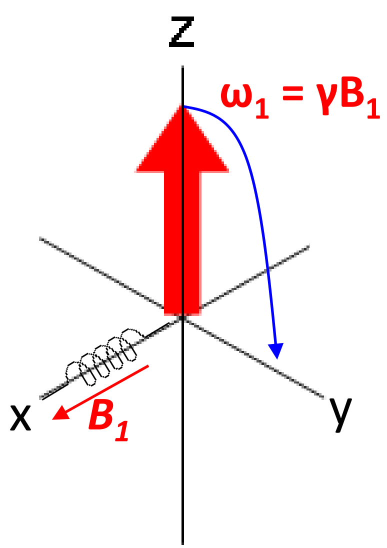


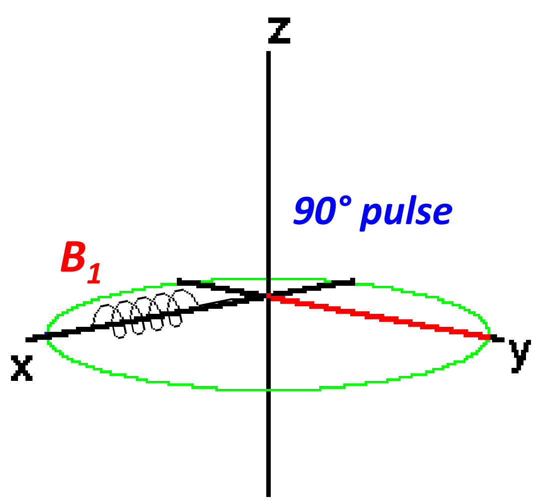


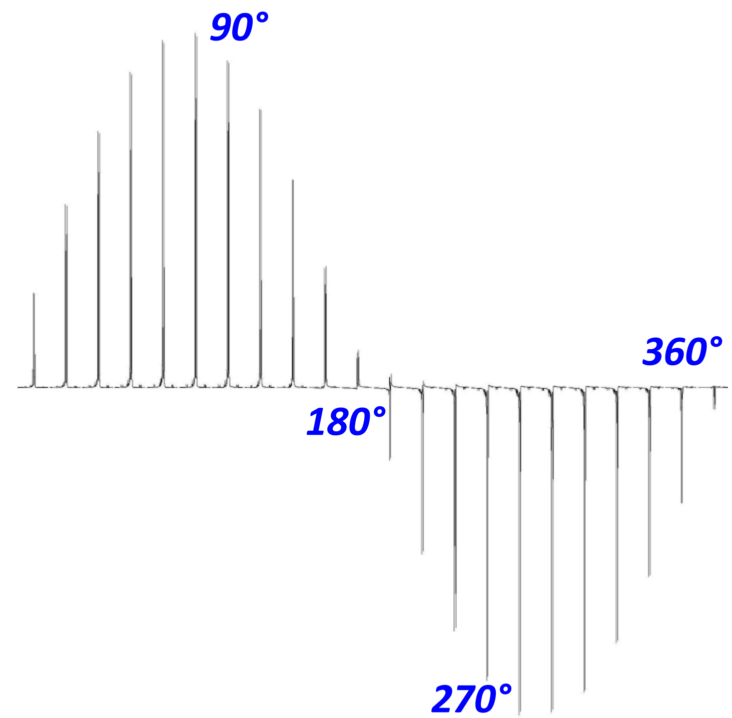
$$M_0 = \mu_0 \frac{N\gamma^2\hbar^2 I(I+1)B_0}{3kT}$$

RF Pulse and Flip Angle

- Another magnetic field $\boldsymbol{B_1}$ is needed and can be produced using an **RF pulse**.
- A $\boldsymbol{B_1}$ field along x-axis will cause the Magnetization to precess in the yz-plane.
- By controlling the length of the RF pulse, the magnetization can be put in specific places in the yz-plane, eg. along y-axis.
- The angle the magnetization rotated is called Flip Angle, eg. 90° pluse.

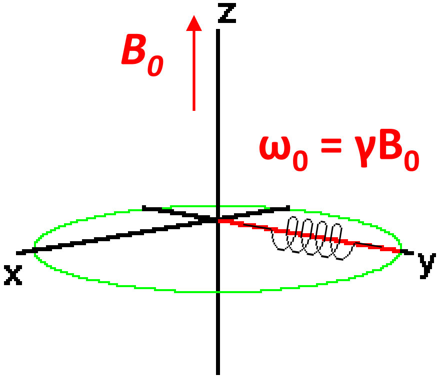


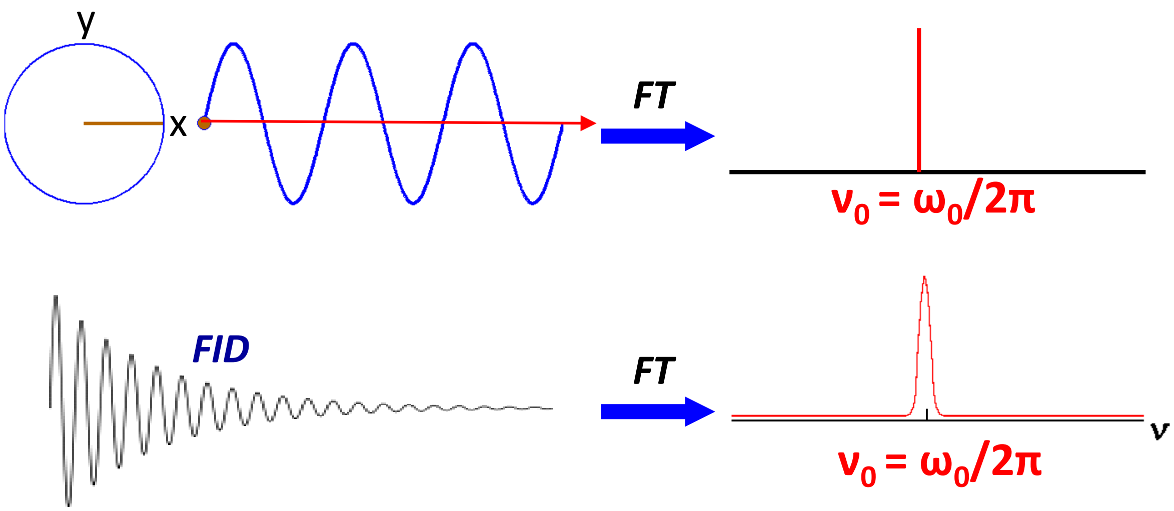




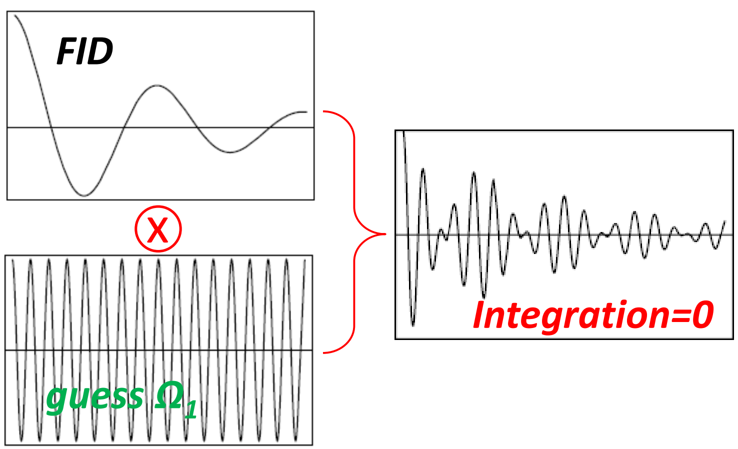
NMR Signal

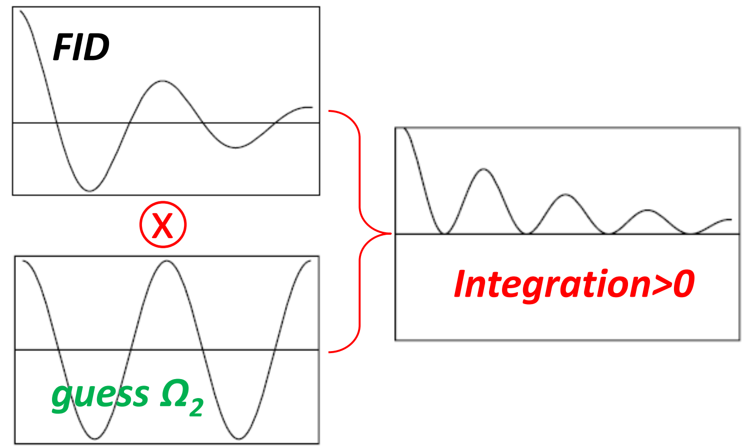
- After a 90° pulse, the magnetization ends up along y-axis.
- When the RF pulse stops, the $\boldsymbol{B_0}$ field makes the magnetization to precess on the **xy-plane**. This will induce a current in the coil.
- If detecting along y-axis, a **cosine** wave will be observed. This signal can then be **Fourier Transferred** to give a signal at the precession frequency, Larmor frequency.
- In a real system, the signal becomes weaker (decaying) with time, due to **relaxation**.
- ***FID:*** Free Induction Decay (Free precession Induced Decaying signal).

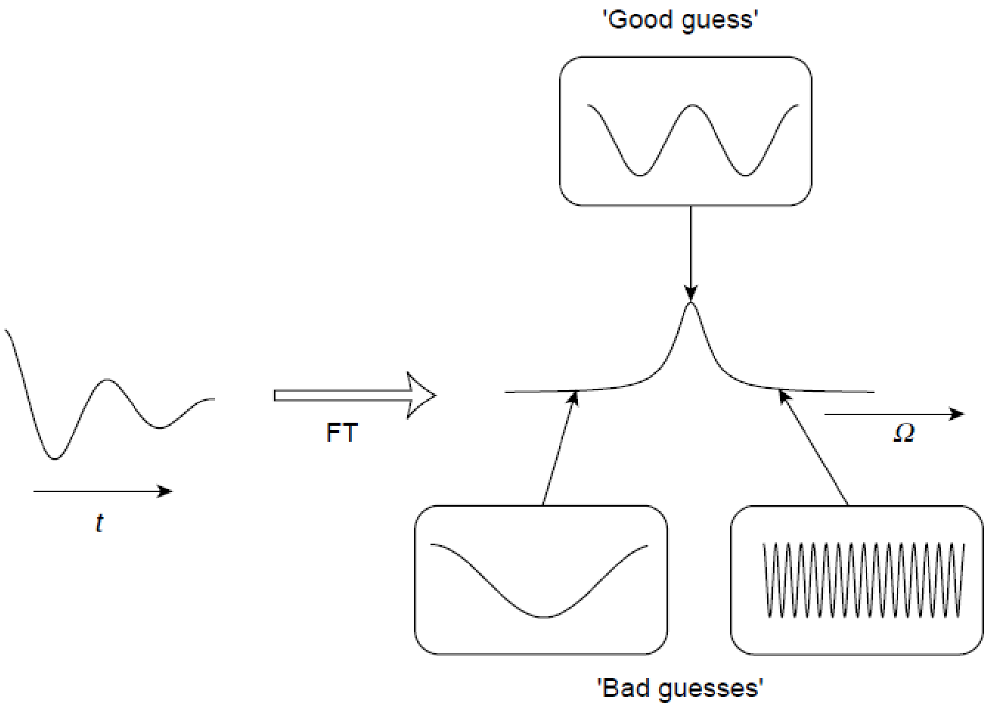




Fourier Transform







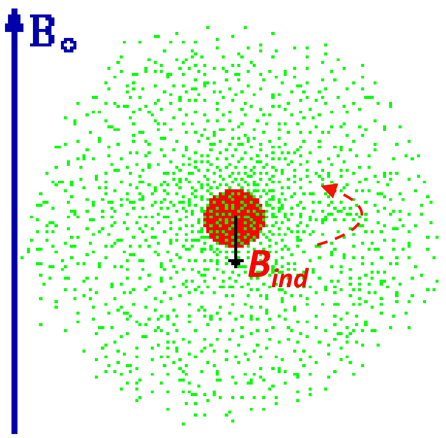
Fourier transform is basically a mathematic method to extract the frequencies and intensities of the sine/cosine waves that 'buried' in the complex FID.

$$S_\ell(\Omega) = \int_0^\infty s_\ell(t) \exp\{-i\Omega t\}\, dt$$

Chemical Shielding

H nuclei are basically all the same in different molecules →

^{1}H NMR signals should be all at same frequencies ???



- $\omega = \gamma(B_0 - B_{ind}) = \gamma(B_0 - \sigma B_0) = \gamma B_0(1-\sigma) = \omega_0(1-\sigma)$
- **σ is characteristic for H in different groups.**

	HO	CH$_2$	CH$_3$
ν (11.74 T):	500.0024	500.0018	500.0006 MHz
ν (5.87 T):	250.0012	250.0009	250.0003 MHz
σ:	0.0000262	0.0000274	0.0000298

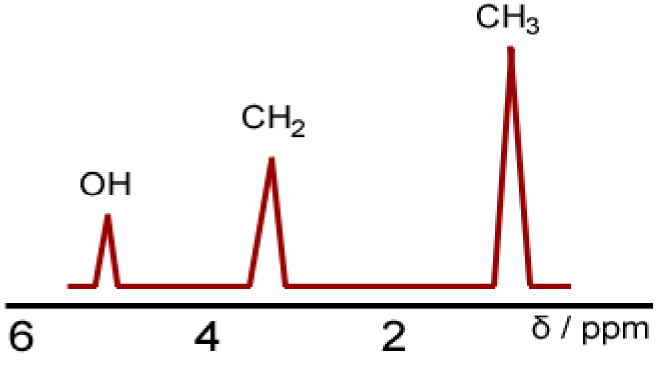
Chemical Shift

	$HO—CH_2—CH_3$		
ν (11.74 T):	500.0024	500.0018	500.0006 MHz
ν (5.87 T):	250.0012	250.0009	250.0003 MHz
σ:	0.0000262	0.0000274	0.0000298
δ (ppm):	4.8	3.6	1.2

Chemical shift

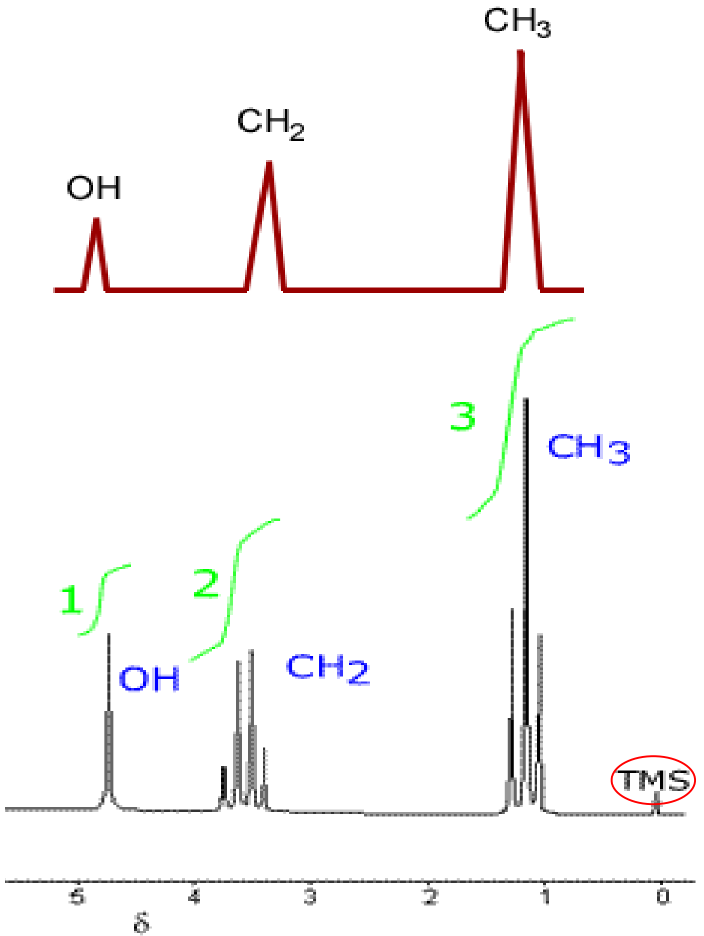
$$\delta = (\nu - \nu_{ref}) / \nu_0$$

where $\nu = \omega/2\pi$

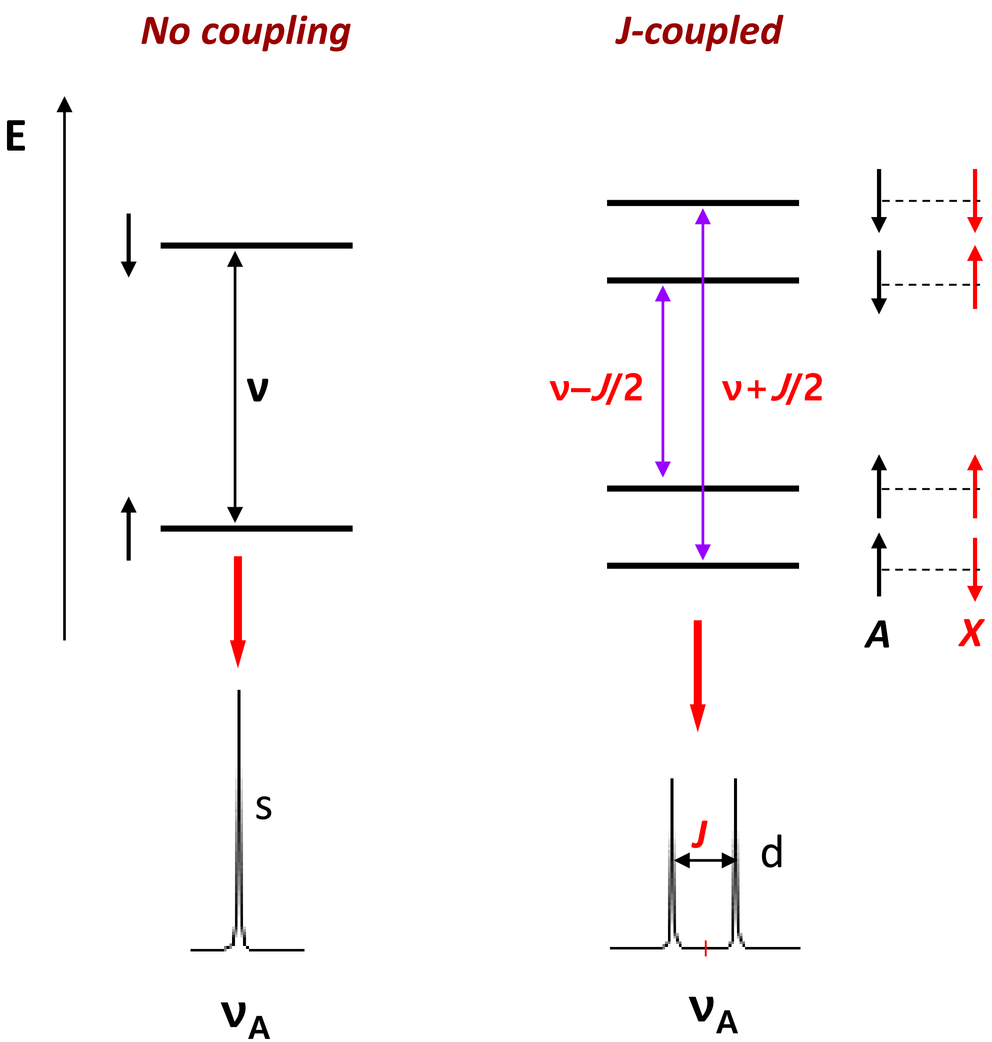


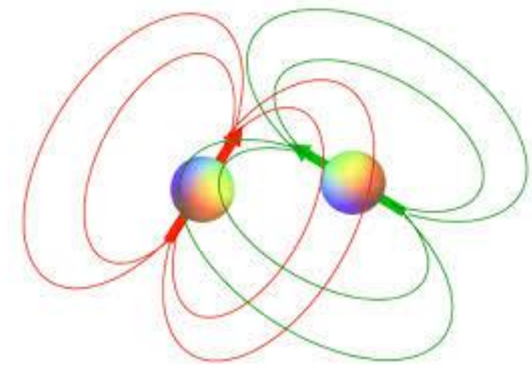
Intensities

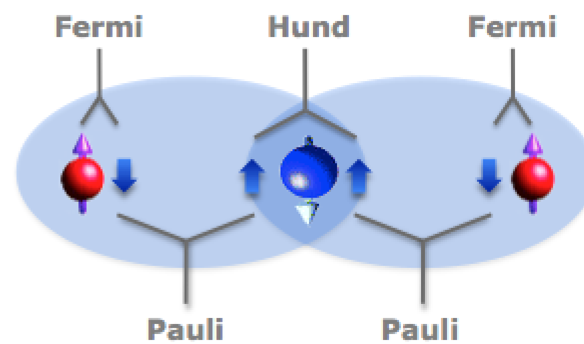
1:2:3


OH
CH2
CH3
1
2
3
OH
CH2
CH3
TMS
5
4
3
2
1
0
δ

Spin-Spin (J) Coupling (1)

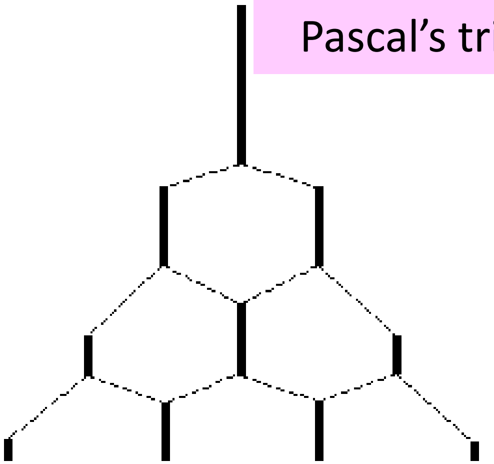






Indirect spin-spin coupling

Spin-Spin (J) Coupling (2)



Pascal's triangle

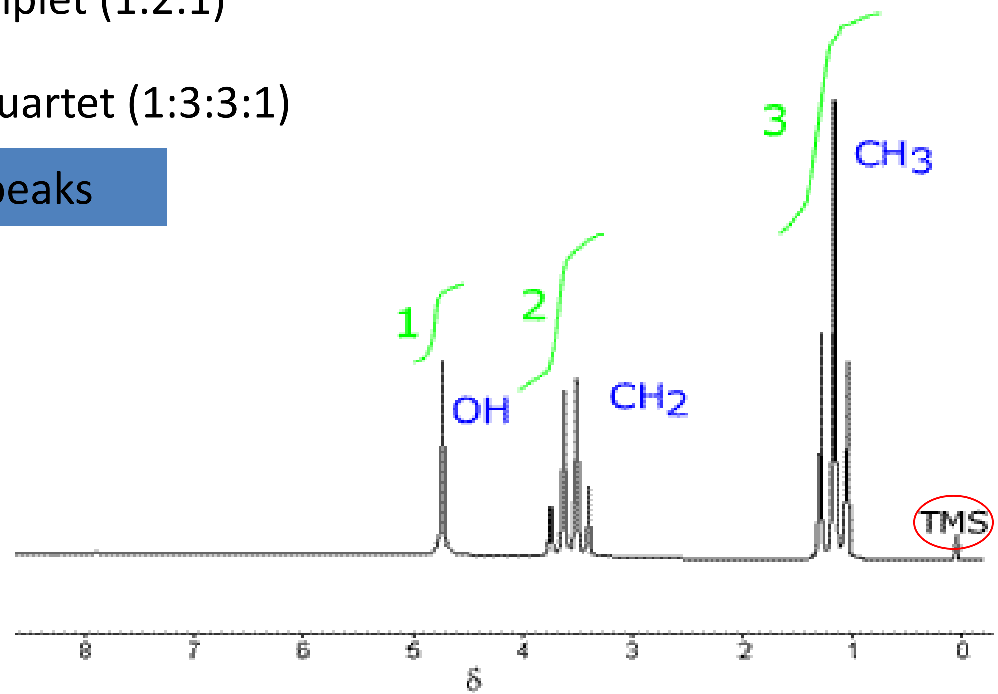
singlet

1H: doublet (1:1)

2H: triplet (1:2:1)

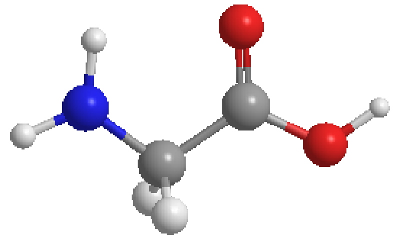
3H: quartet (1:3:3:1)

n adjacent H → (n+1) peaks

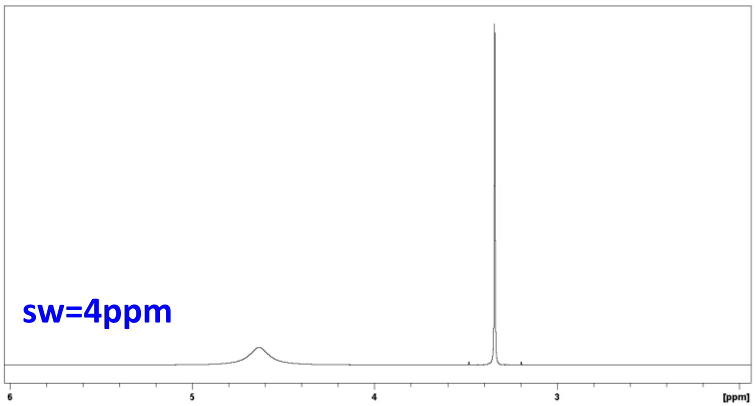


Glycine – ^{1}H & ^{13}C NMR

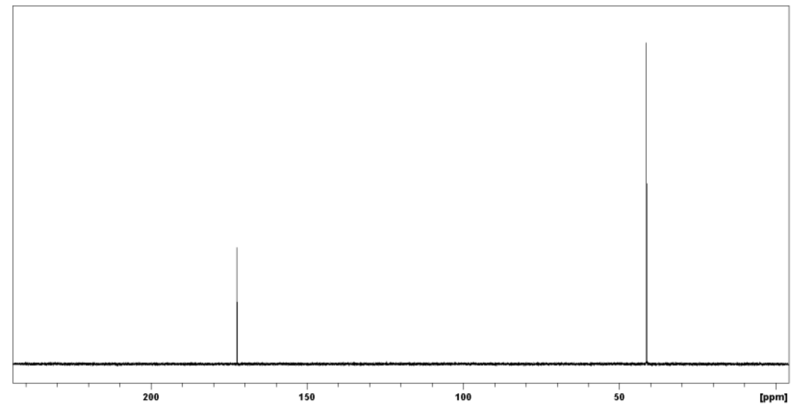
glycine

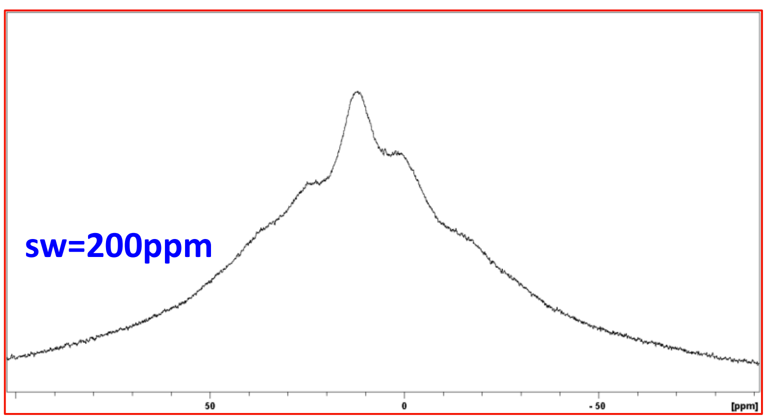


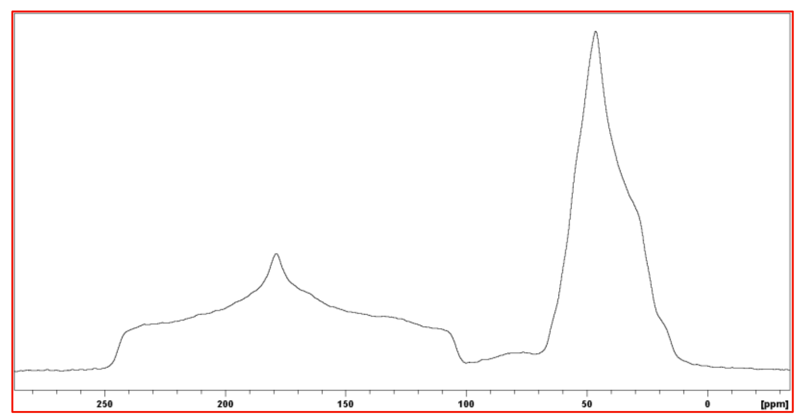
^{1}H



^{13}C

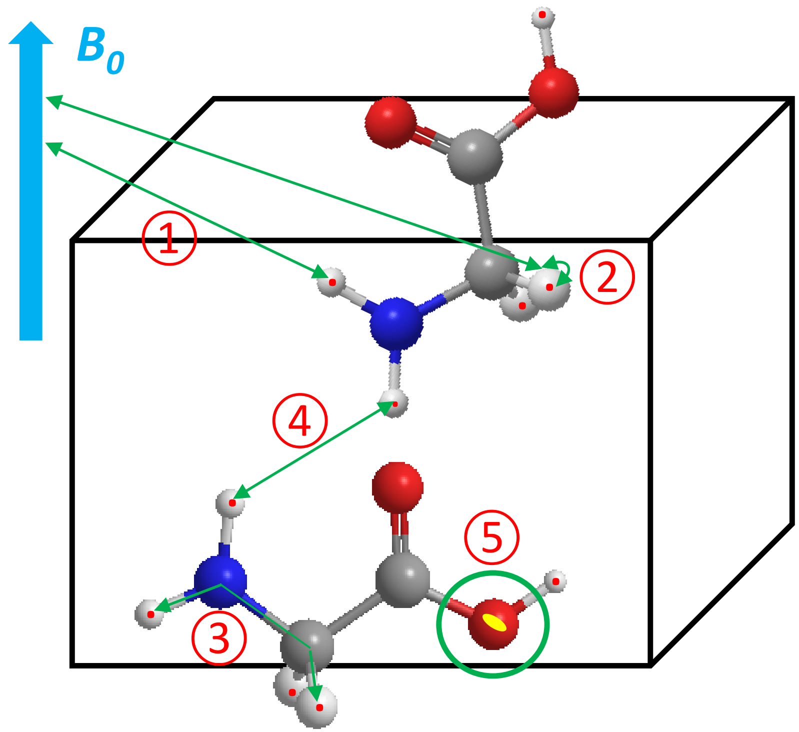






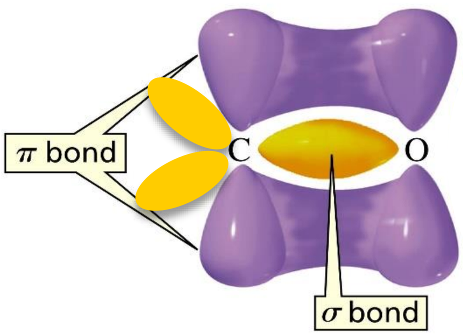
Spin Interactions

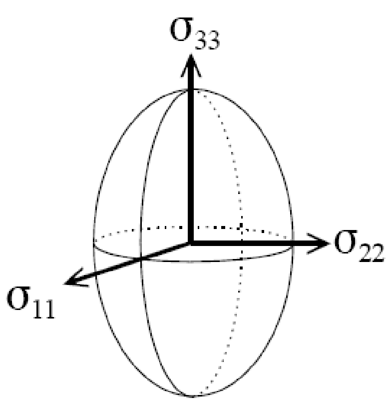
Spin Interaction Overview

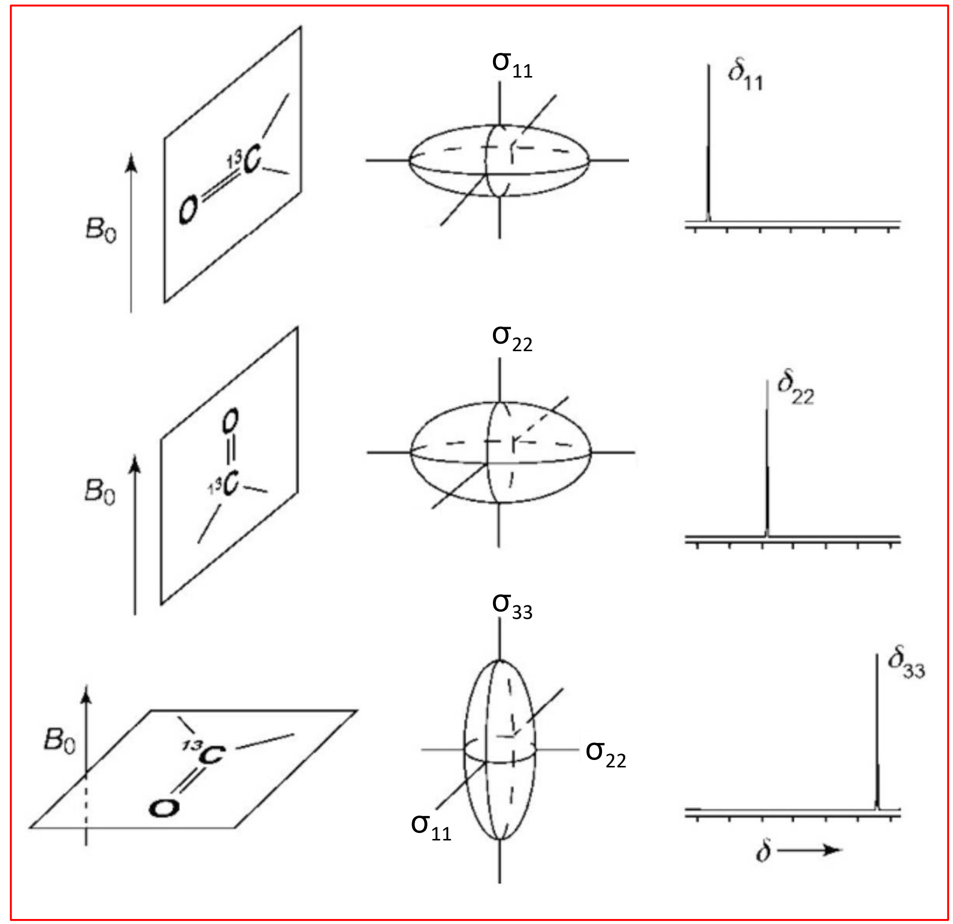


	Interaction	Origin
①	Zeeman	Spin – Field B_0
②	Shielding	Spin – Field B_e
③	J-coupling	Spin – Spin
④	Dipolar	Spin – Spin
⑤	Quadrupolar	Spin – e-Field

Chemical Shielding Anisotropy (1)



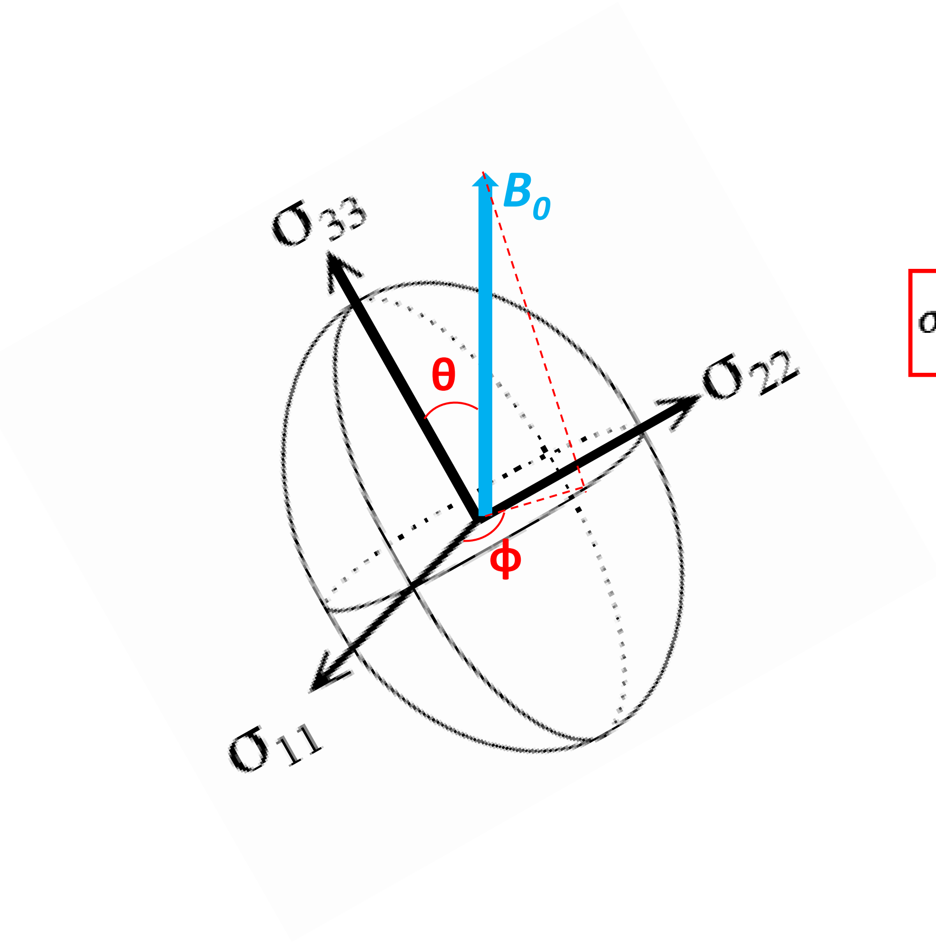




$$\sigma^{PAS} = \begin{pmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{pmatrix}$$

CSA Tensor

Chemical Shielding Anisotropy (2)



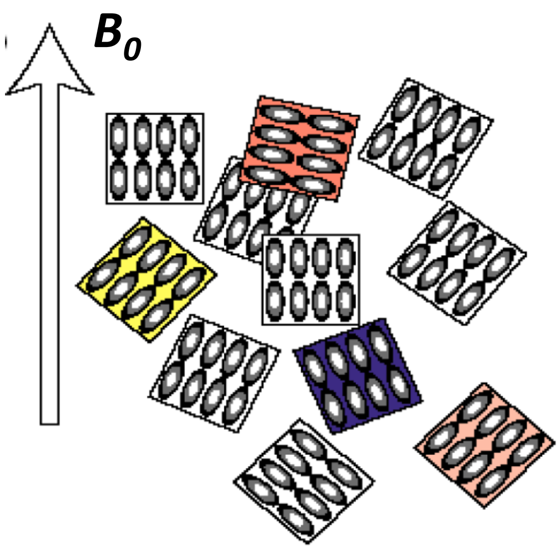
$$\sigma_{zz} = \sigma_{iso} + \frac{\Delta\sigma}{2}\left[(3\cos^2\theta - 1) + \eta(\sin^2\theta\cos 2\phi)\right]$$

$\sigma_{iso} = (\sigma_{11} + \sigma_{22} + \sigma_{33}) / 3$

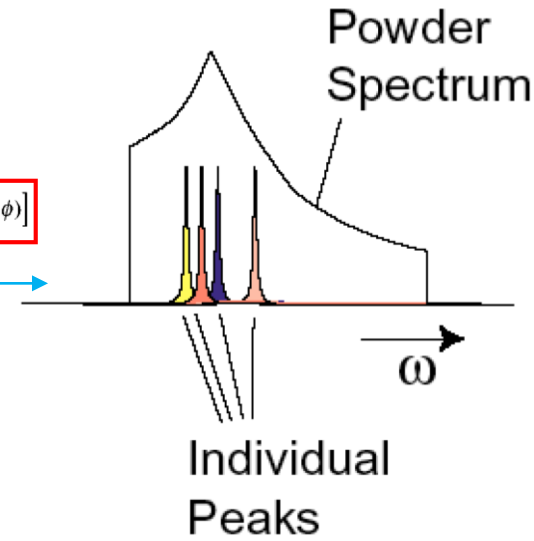
$\Delta\sigma = \sigma_{33} - \sigma_{iso}$

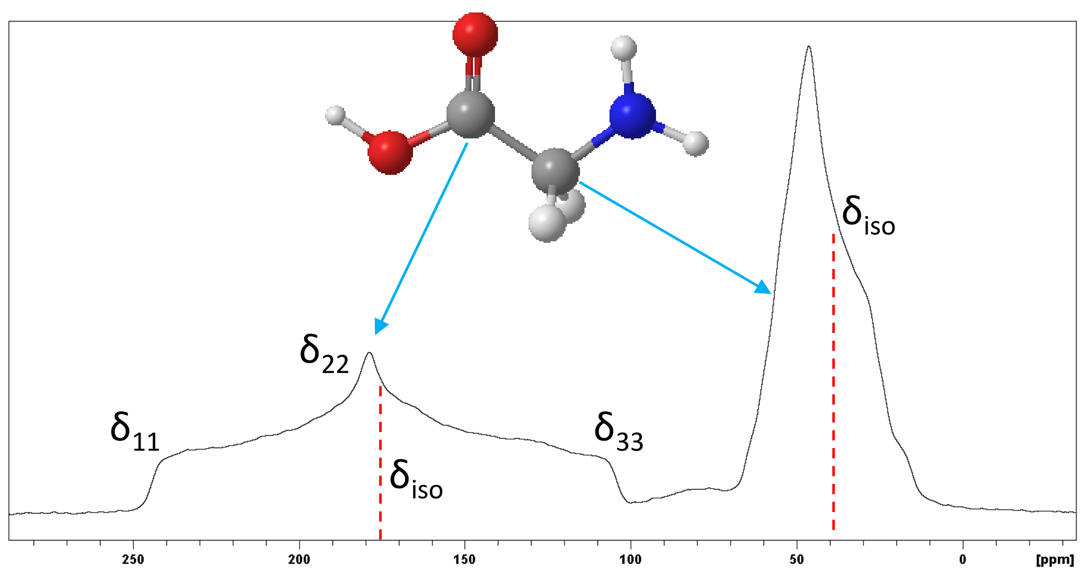
$\eta = (\sigma_{11} - \sigma_{22}) / \Delta\sigma$

Chemical Shielding Anisotropy (3)

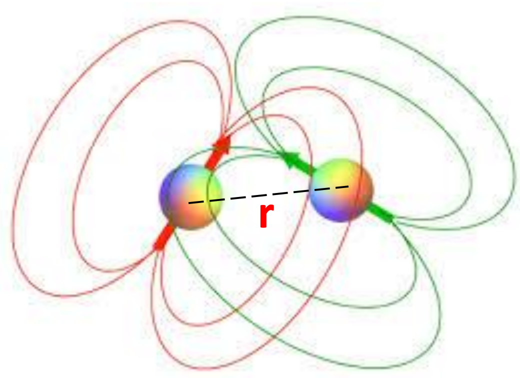


$$\sigma_{zz} = \sigma_{iso} + \frac{\Delta\sigma}{2}\left[(3\cos^2\theta - 1) + \eta(\sin^2\theta\cos 2\phi)\right]$$





Dipolar Interaction (1)



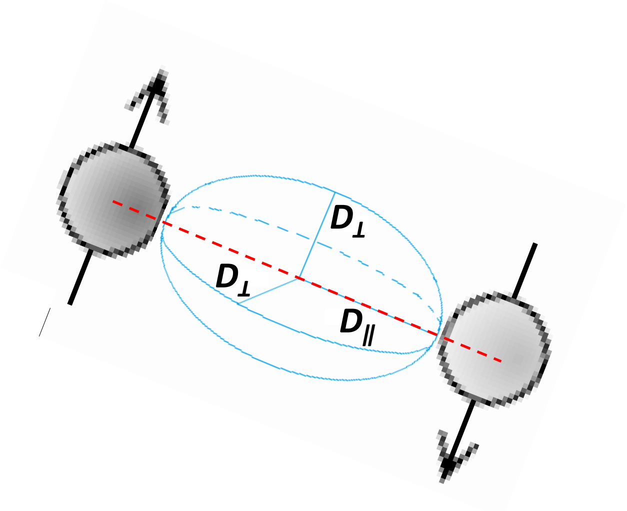
Dipolar-dipolar coupling constant

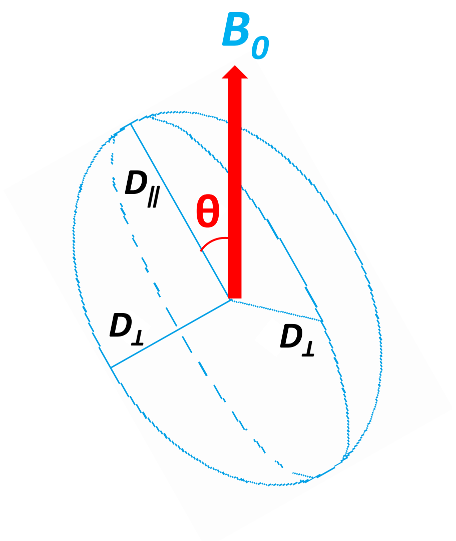
$$R^{DD} = \frac{\mu_0 \hbar}{4\pi} \frac{\gamma_I \gamma_S}{r^3}$$

Dipolar-dipolar coupling examples

Nuclei	Function group	Distance (Å)	Dipolar (kHz)
H—H	CH_2 and CH_3	1.6	29
	H-C-C-H	2.3	10
C—H	C-H	1.0	30
	C-C-H	2.0	4

Dipolar Interaction (2)





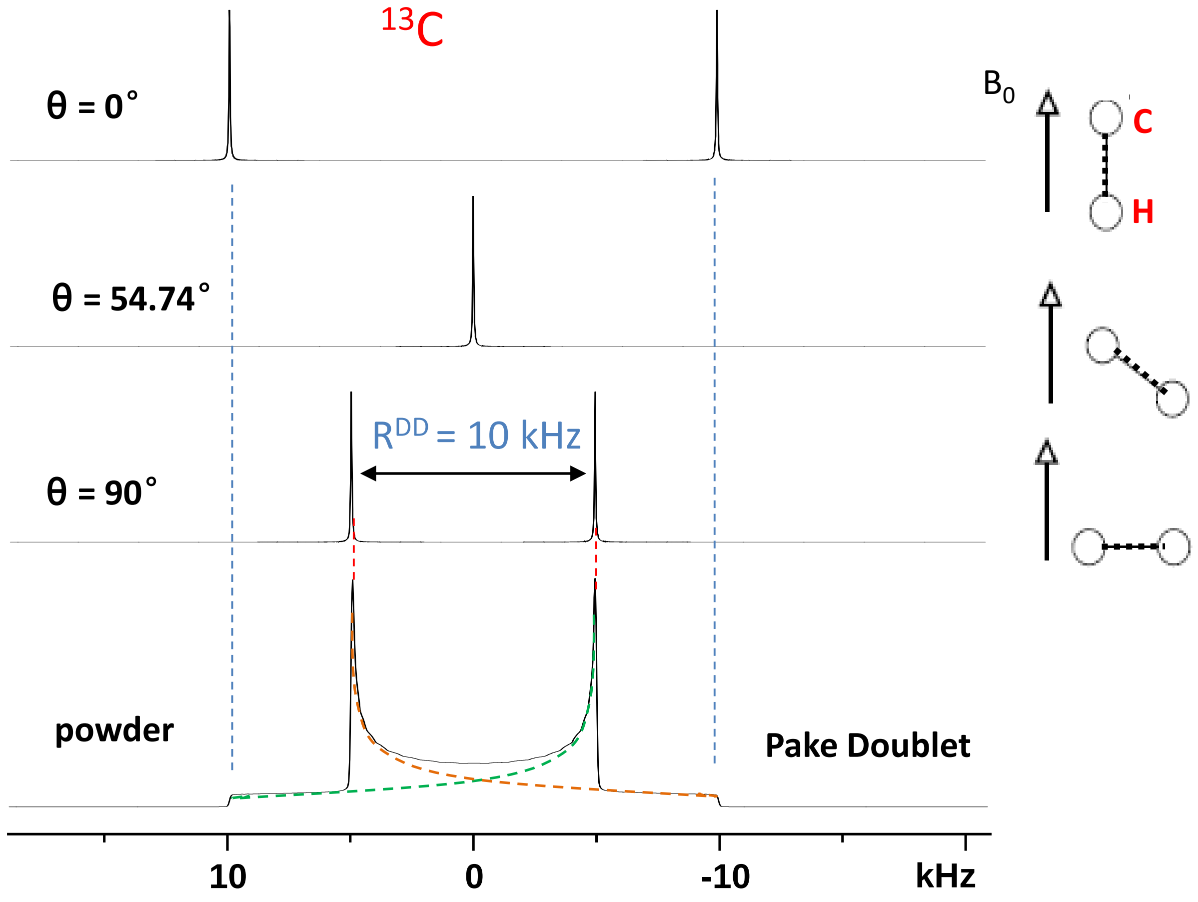
$$\boldsymbol{D}^{\mathrm{PAS}} = \begin{pmatrix} \boldsymbol{D}_{\perp} & 0 & 0 \\ 0 & \boldsymbol{D}_{\perp} & 0 \\ 0 & 0 & -\boldsymbol{D}_{\parallel} \end{pmatrix}$$

$$\boldsymbol{D}_{\parallel} = \mathrm{R}^{\mathrm{DD}}$$

$$\boldsymbol{D}_{\perp} = \frac{1}{2}\mathrm{R}^{\mathrm{DD}}$$

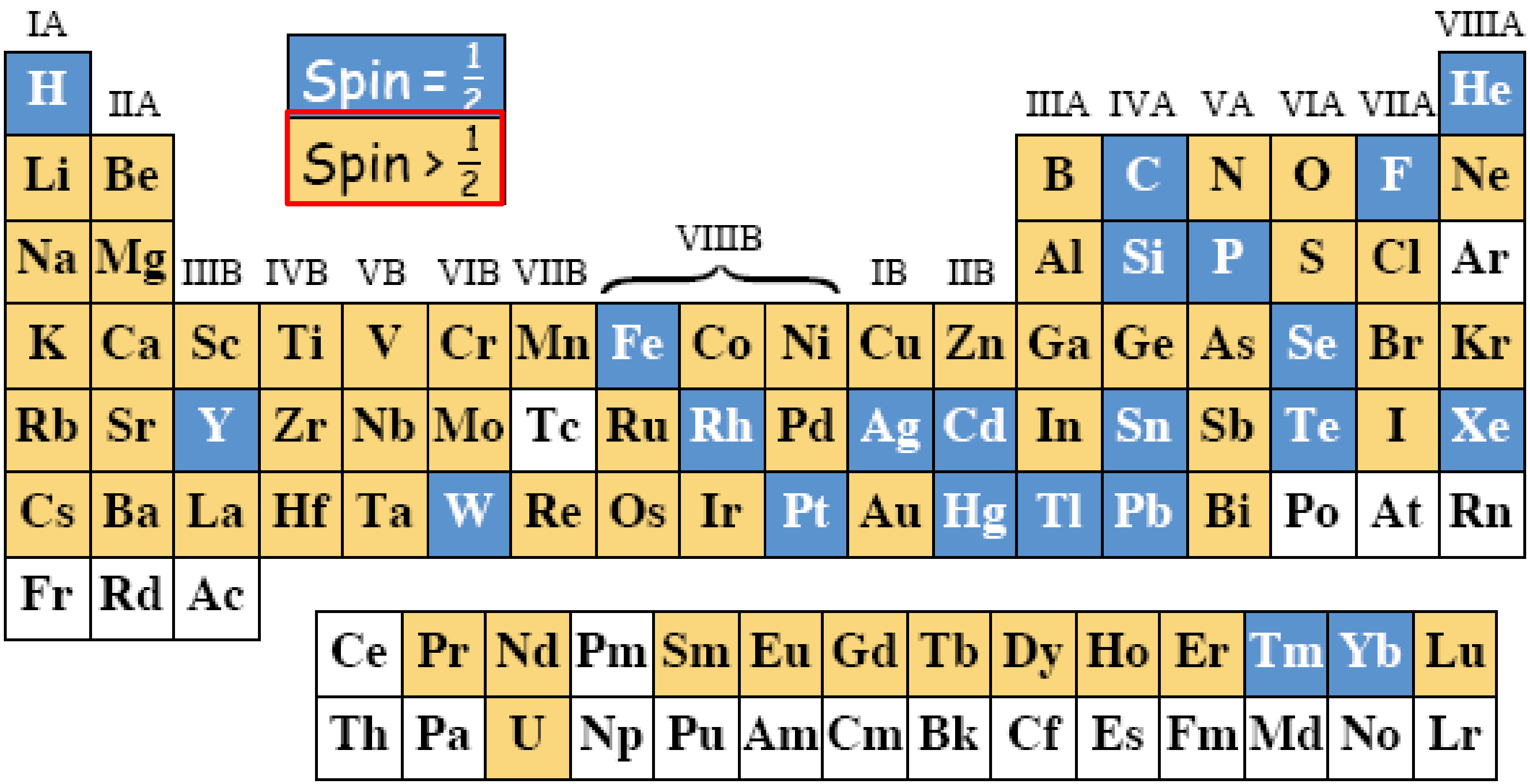
$\mathrm{R}^{\mathrm{DD}}\,(3\cos^2\theta - 1)/2$

Dipolar Interaction (3)

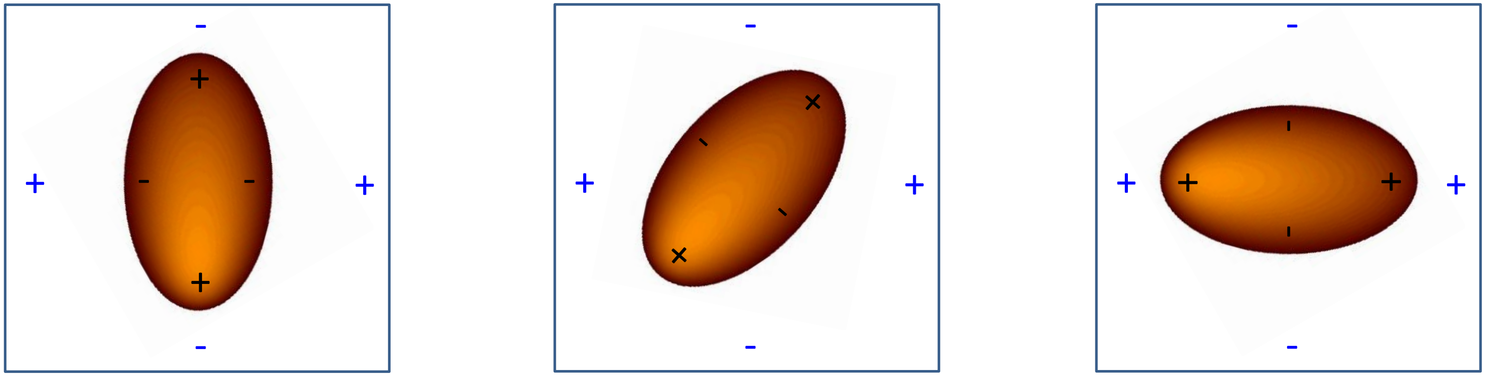


$$R^{DD}\,\frac{1}{2}(3\cos^2\theta - 1)$$

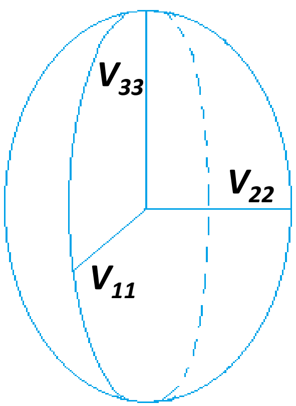
Quadrupolar Interaction (1)



Quadrupolar Interaction (2)



low energy | mid energy | high energy



EFG tensor

$$C_Q = \frac{eQ \cdot V_{33}}{h}$$

$$\eta_Q = \frac{V_{11} - V_{22}}{V_{33}}$$

Q: nuclear quadrupole moment,

unit: per m^2.

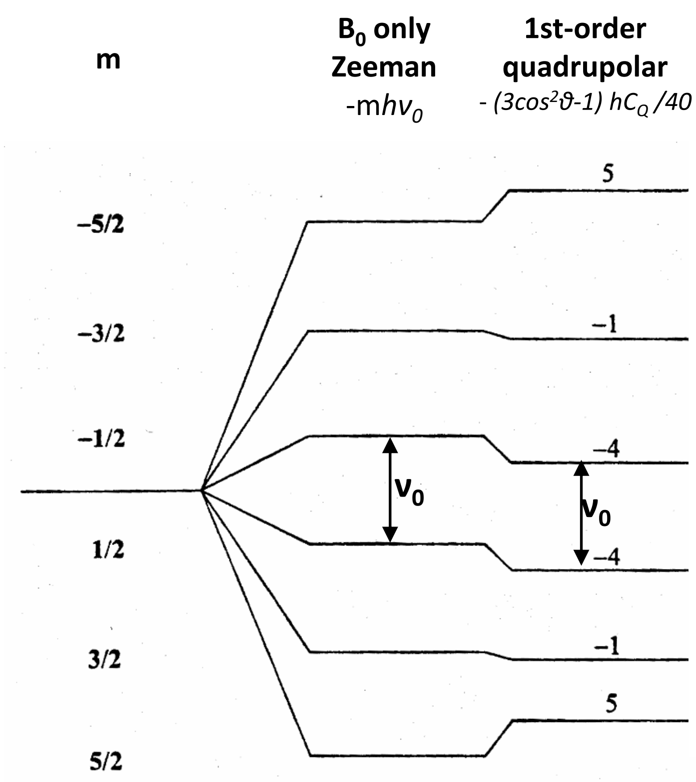
V_{33}: electric field gradient,

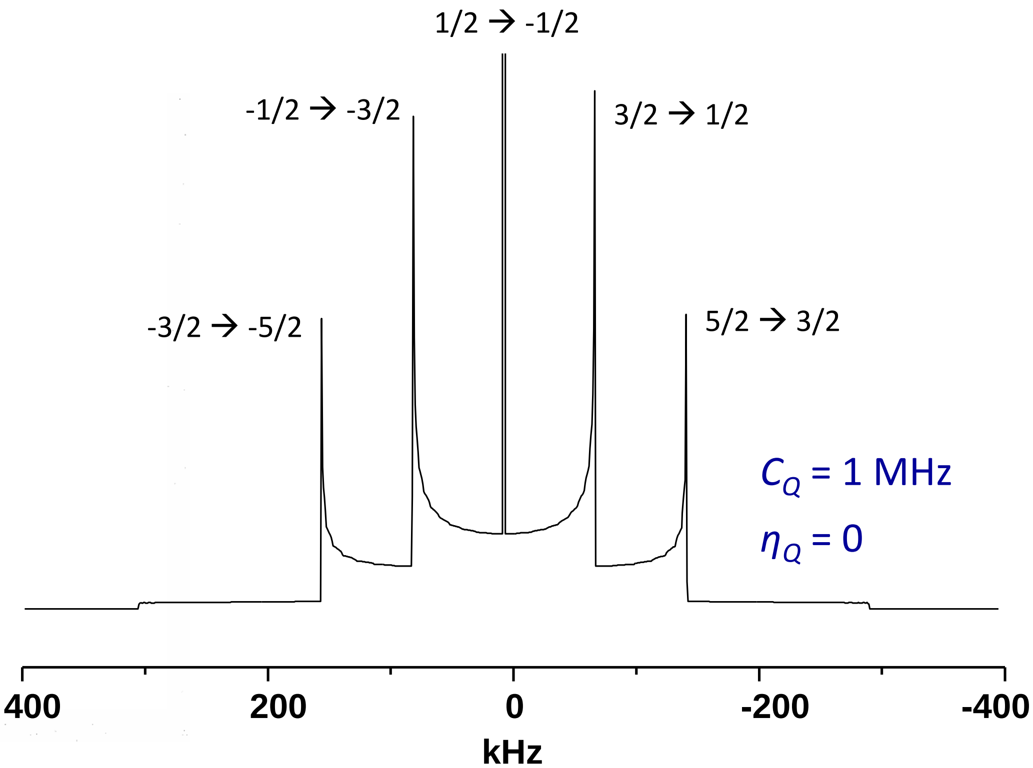
unit: volts/m^2.

Quadrupolar Interaction (3)

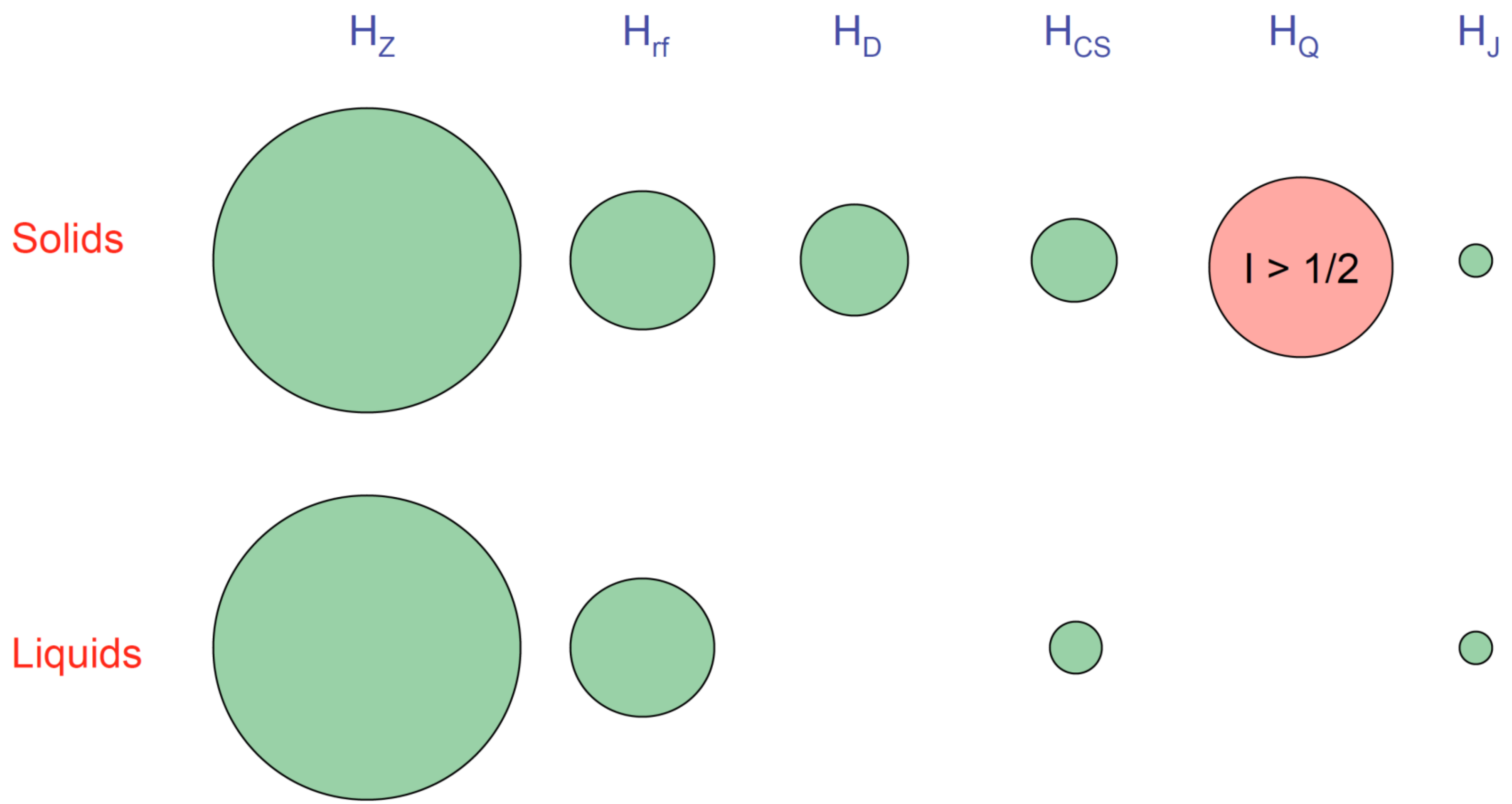
1st-order quadrupolar interaction

$H_Q^{(1)} = (\nu_Q/4)\,[I_z^2 - I(I+1)/3]\,[3\cos^2\theta - 1 + \frac{1}{2}\,\eta_Q \sin^2\theta \cos 2\varphi]$ $\nu_Q = 6\pi C_Q/[2I(2I-1)]$



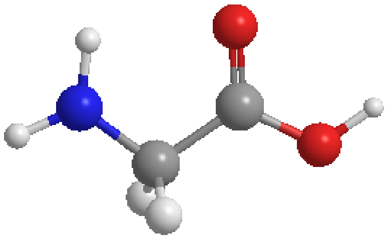


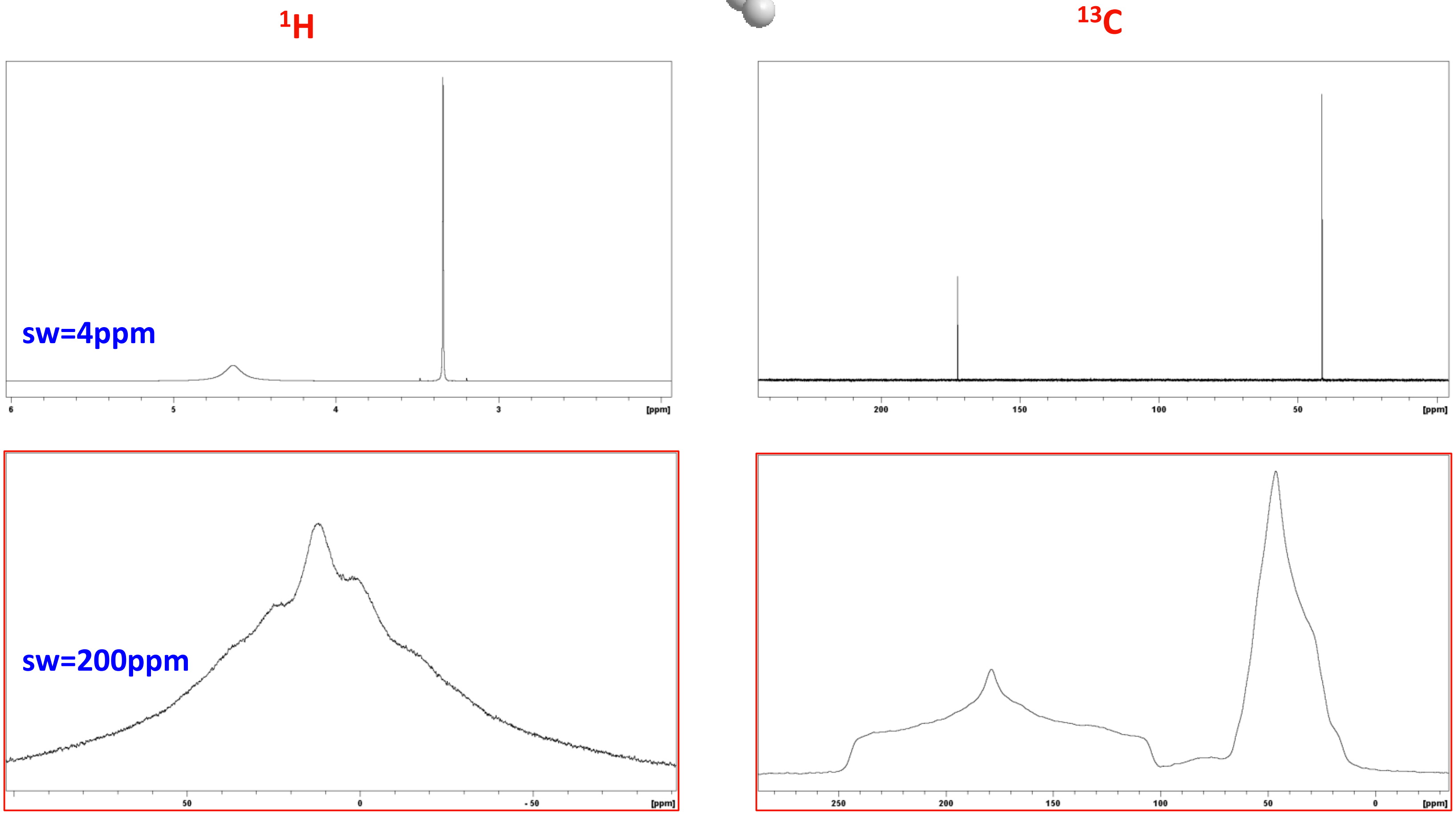
Solid vs. Solution NMR



Glycine – ^{1}H & ^{13}C NMR

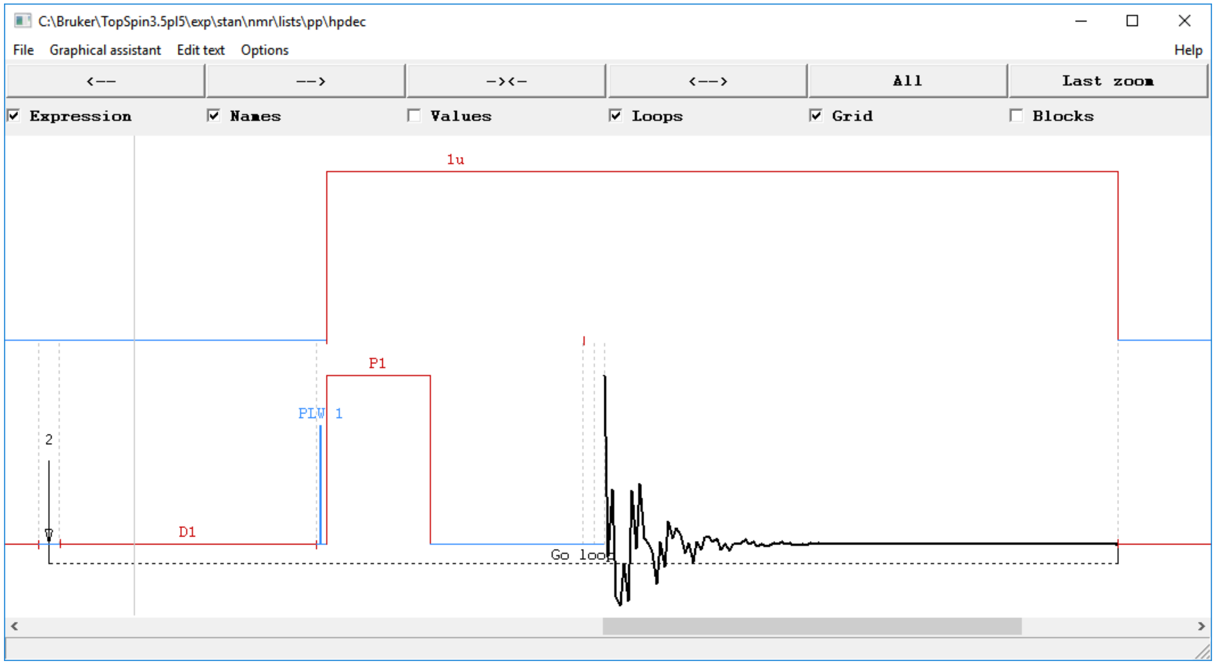
glycine

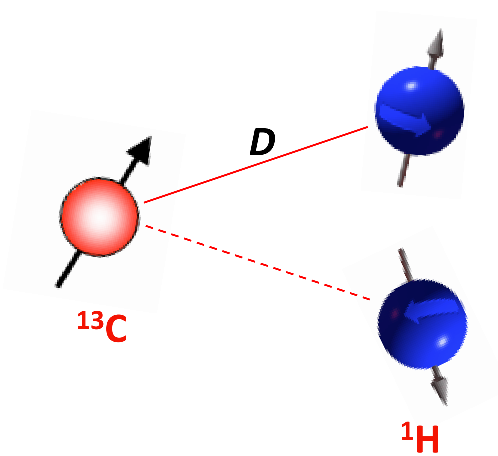


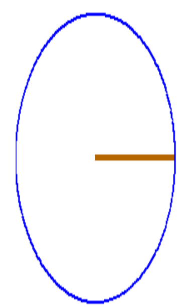


SSNMR Techniques

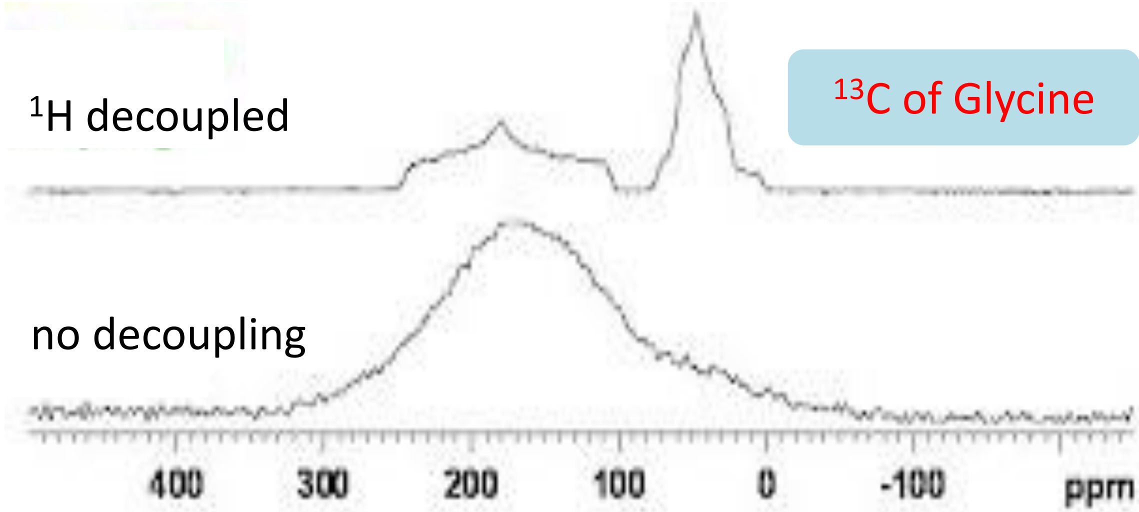
High Power Decoupling (1)

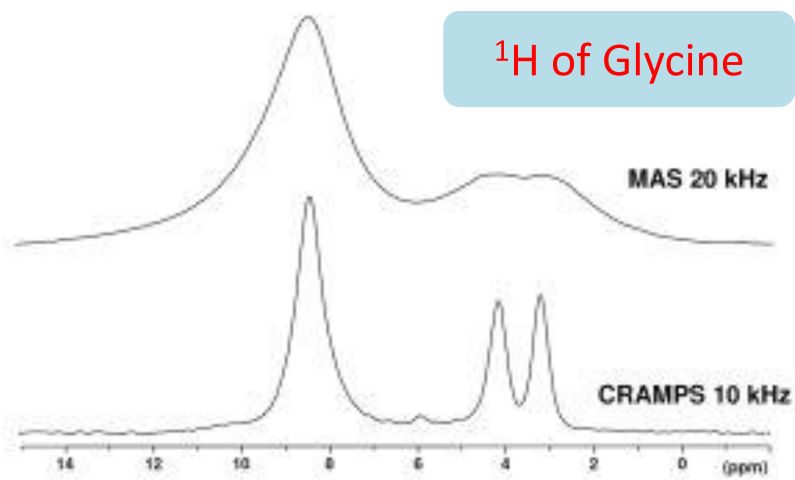






High Power Decoupling (2)





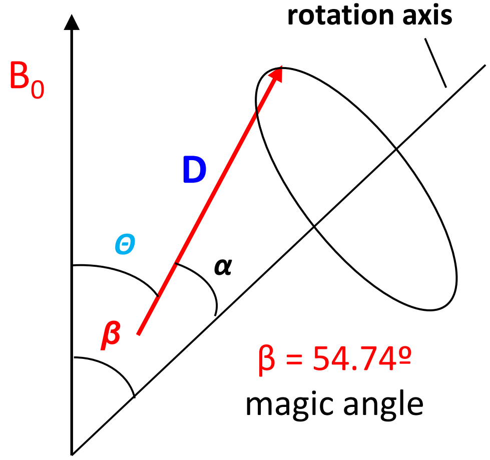
Magic Angle Spinning (MAS) (1)

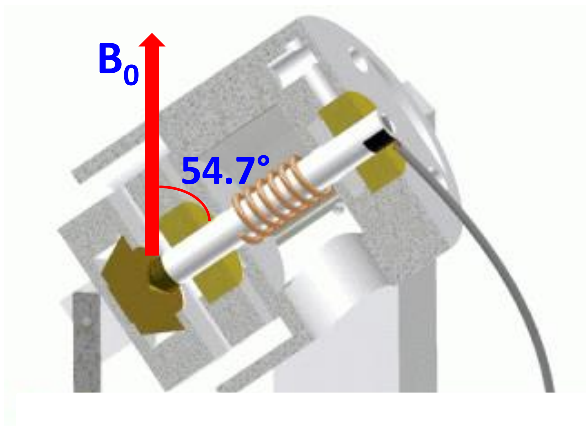
$$\sigma_{zz} = \sigma_{iso} + \frac{\Delta\sigma}{2}\left[(3\cos^2\theta - 1) + \eta(\sin^2\theta\cos 2\phi)\right]$$

$$R^{DD}\,(3\cos^2\theta - 1)/2$$

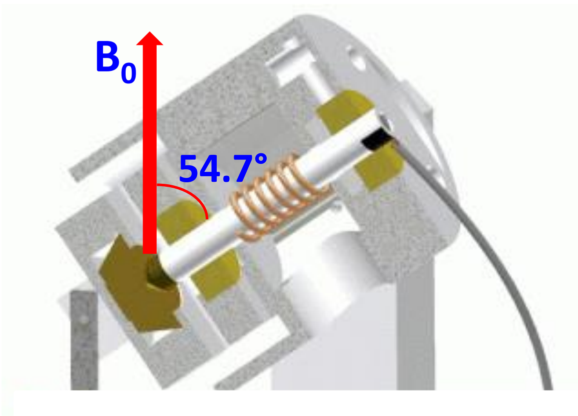
$$H_Q^{(1)} = (\nu_Q/4)\,[I_z^2 - I(I+1)/3]\,[3\cos^2\theta - 1 + \tfrac{1}{2}\,\eta_Q\sin^2\theta\cos 2\varphi]$$

$$\langle 3\cos^2\theta - 1\rangle = \tfrac{1}{2}(3\cos^2\alpha - 1)(3\cos^2\beta - 1) + 3/2\,[\sin 2\alpha\sin 2\beta\cos\omega_r t + \sin^2\alpha\sin^2\beta\cos 2\omega_r t]$$





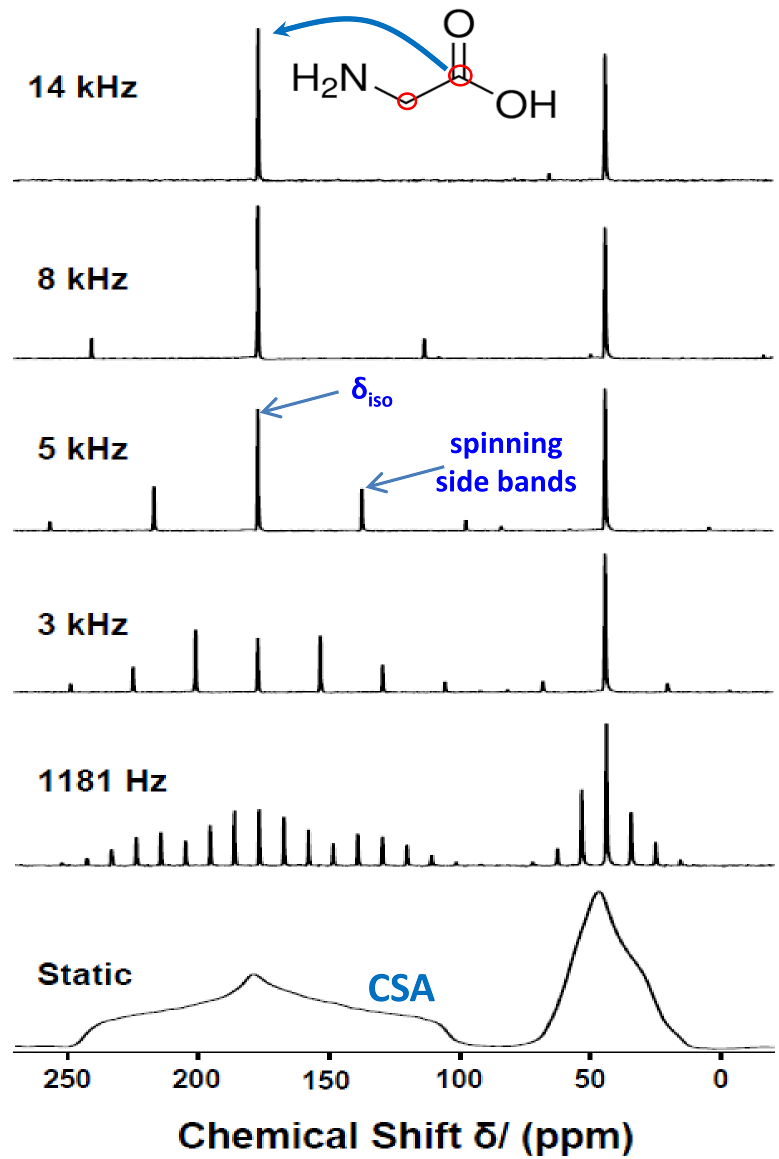
Magic Angle Spinning (MAS) (2)



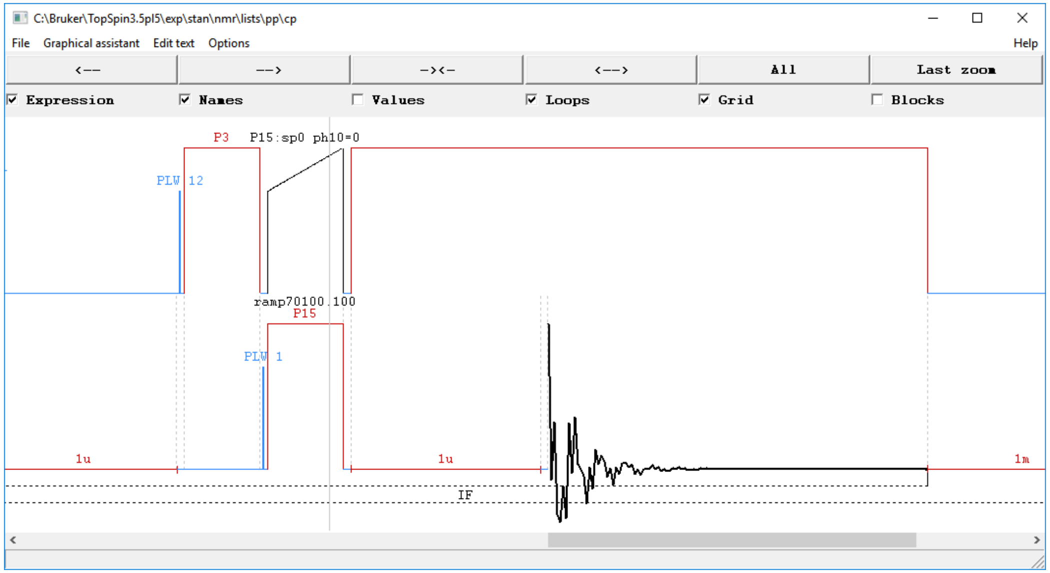
$$\langle 3\cos^2\theta - 1\rangle =$$

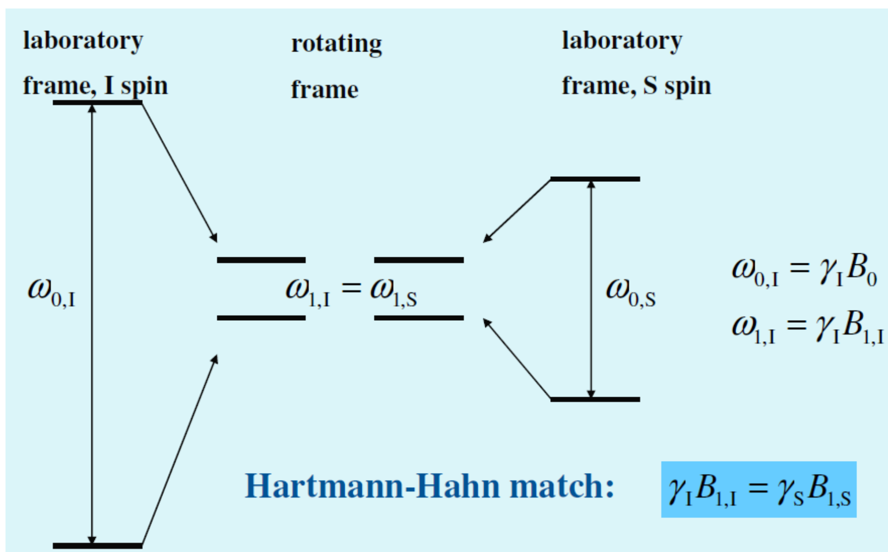
$$\tfrac{1}{2}\,(3\cos^2\alpha - 1)\,(3\cos^2\beta - 1)$$

$$+\ \tfrac{3}{2}\,[\sin 2\alpha \sin 2\beta \cos \omega_r t + \sin^2\alpha \sin^2\beta \cos 2\omega_r t]$$

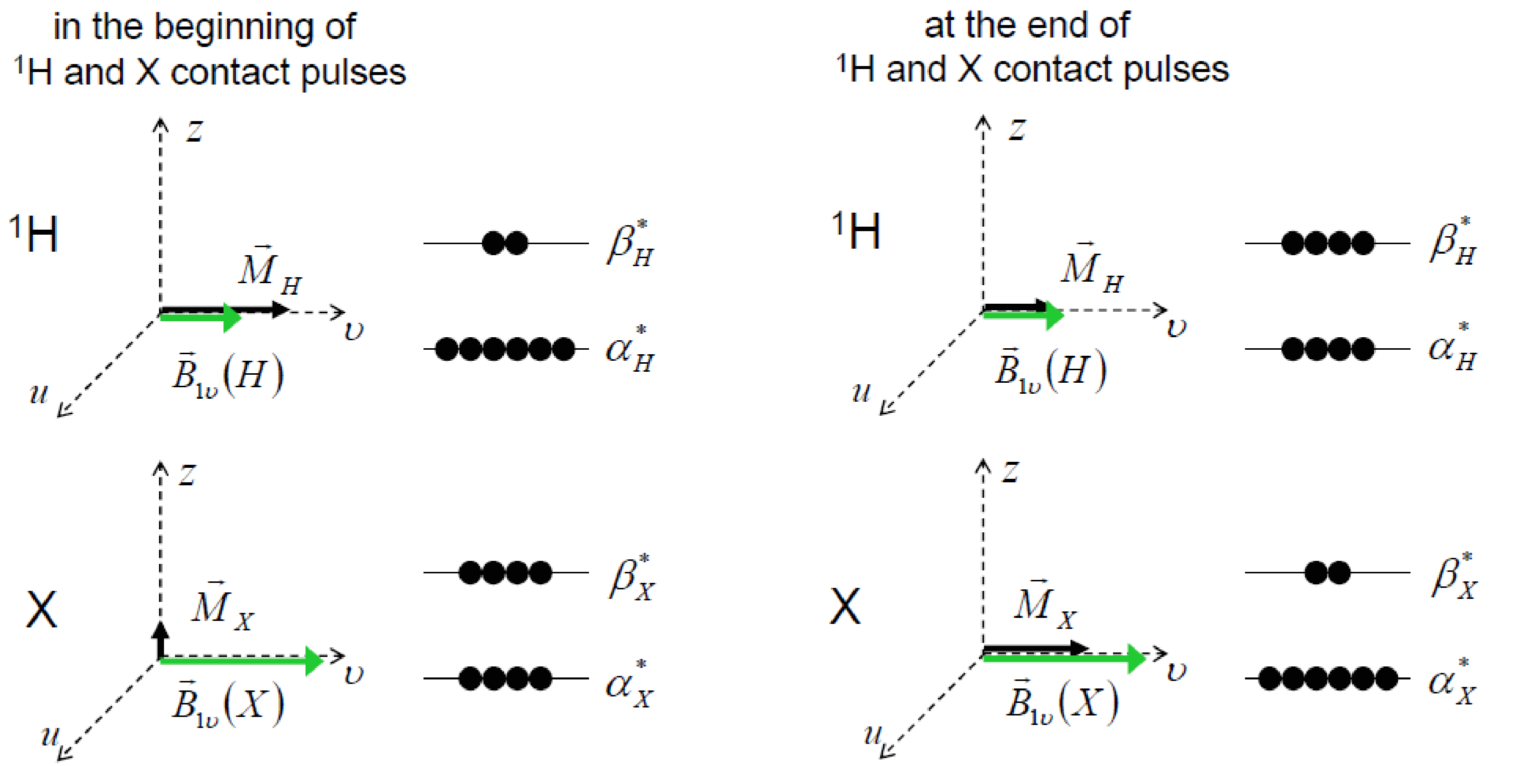


Cross Polarization (CP) (1)





Cross Polarization (CP) (2)



Cross Polarization (CP) (3)

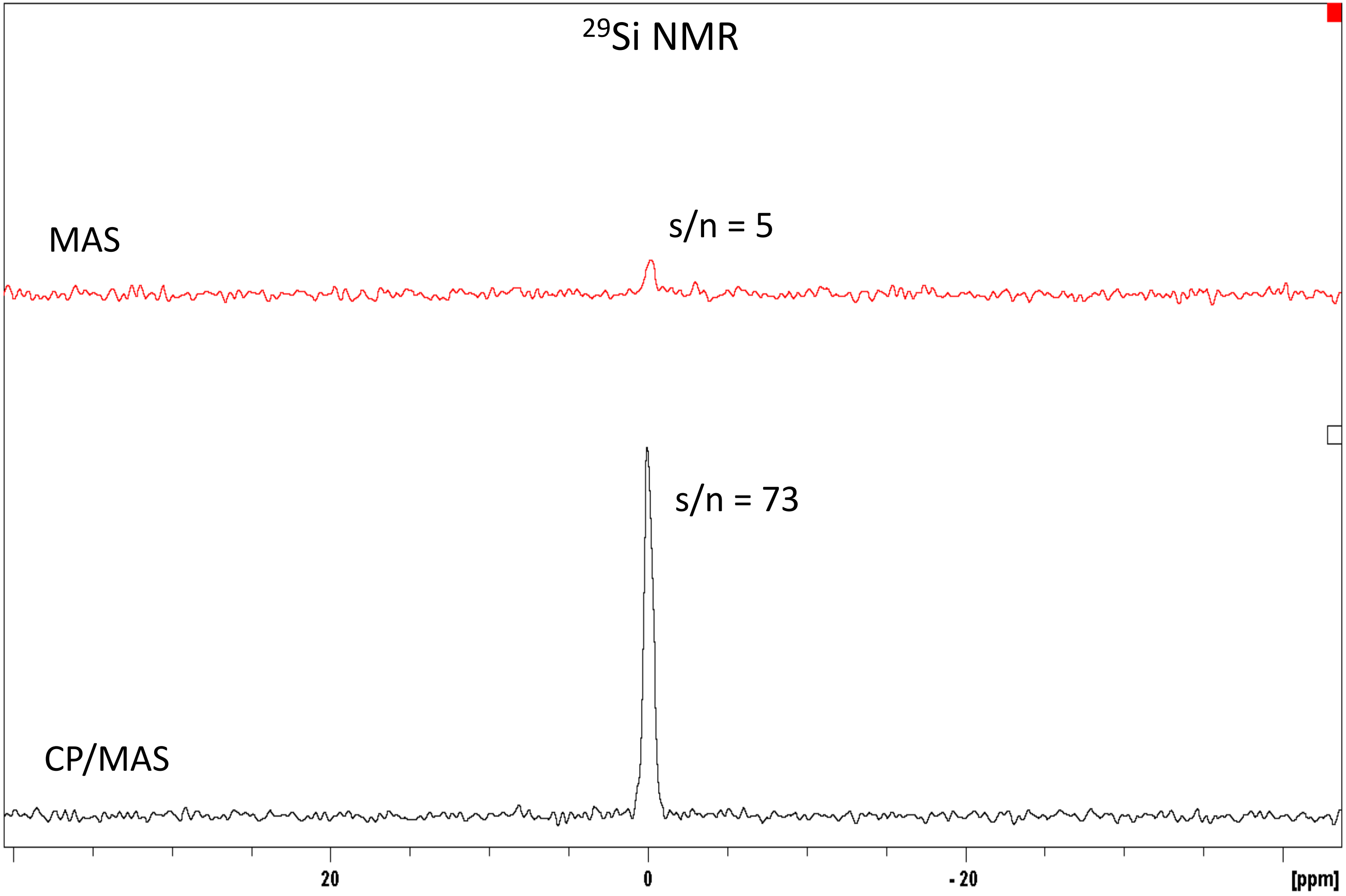
- Signal enhancement by polarization transfer:

$$\frac{\gamma_I}{\gamma_S} \cdot \frac{1}{1+\varepsilon} \qquad \varepsilon = \frac{N_S}{N_I}$$

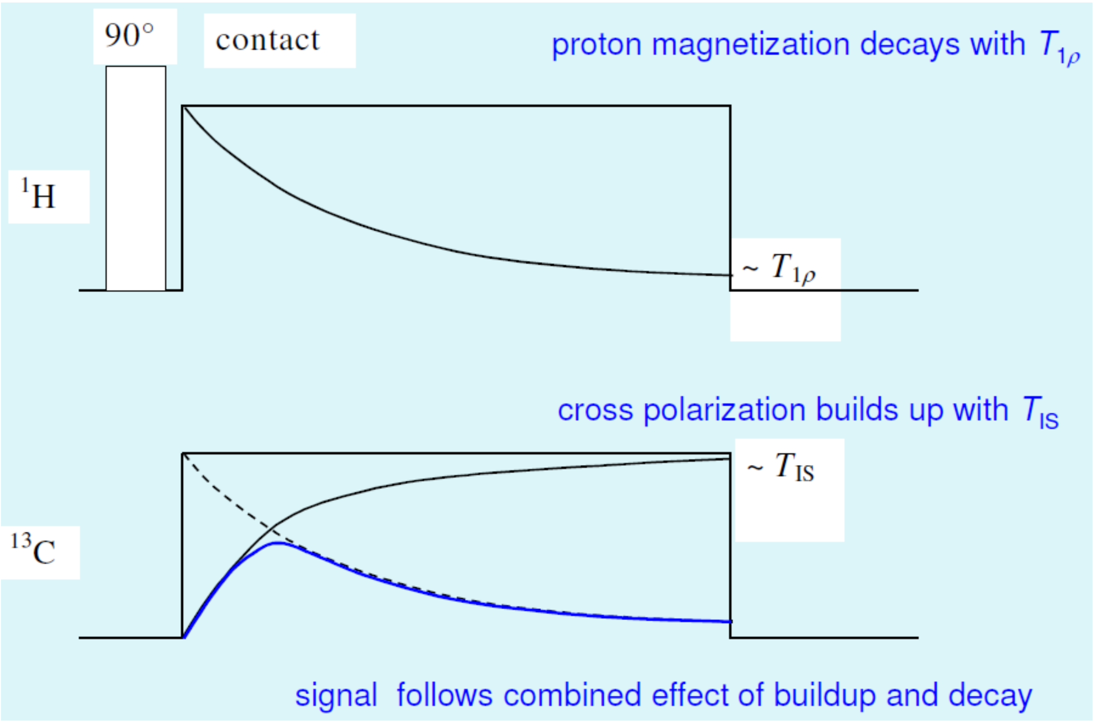
Nucleus	N.A.	Max enhancement factor
^{13}C	1.11%	4
^{15}N	0.37%	10
^{29}Si	4.70%	5
^{31}P	100%	2.5

- Faster repetition: recycle delay ~1.25 $T_1(^1H)$

Cross Polarization (CP) (4)



Cross Polarization (CP) (5)



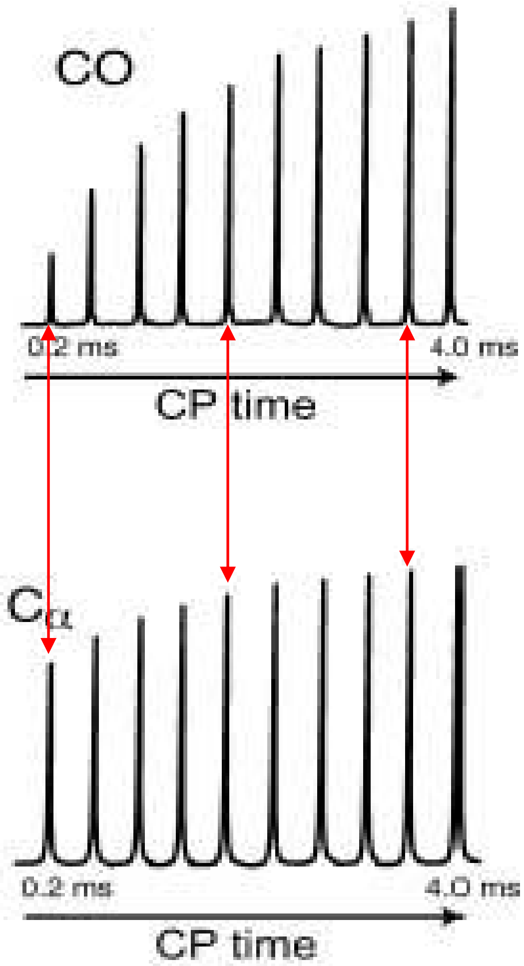
$$I(t) = I_0(1 - T_{IS}/T^{I}_{1\rho})^{-1}[\exp(-t/T^{I}_{1\rho}) - \exp(-t/T_{IS})]$$

$$\frac{1}{T_{IS}} = \frac{3}{2}\sqrt{\frac{2\pi}{5}\frac{M_{2,IS}}{\sqrt{M_{2,II}}}}$$

Second Moments, reflect the strength of dipolar interactions.

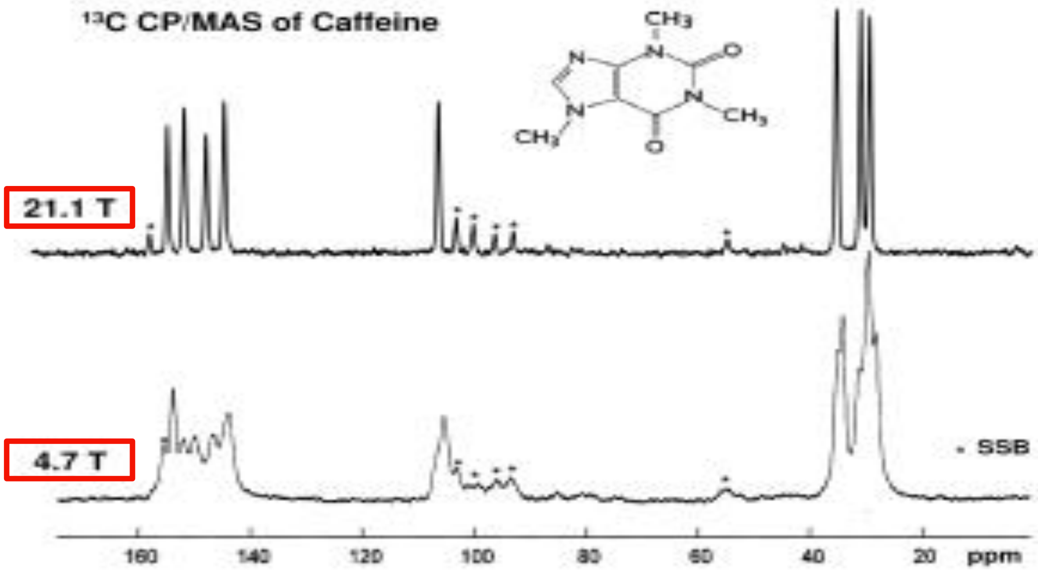
Cross Polarization (CP) (6)

- Note: signal intensities can not be used for quantitation.

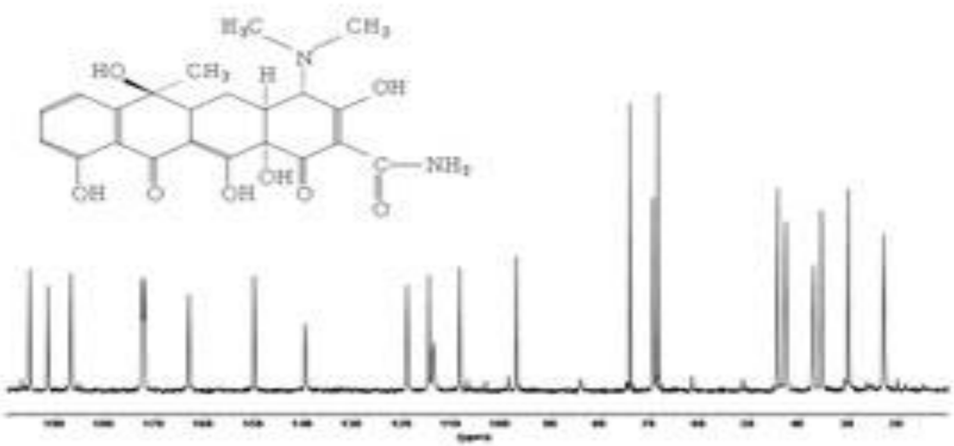


CP + MAS + Decoupling

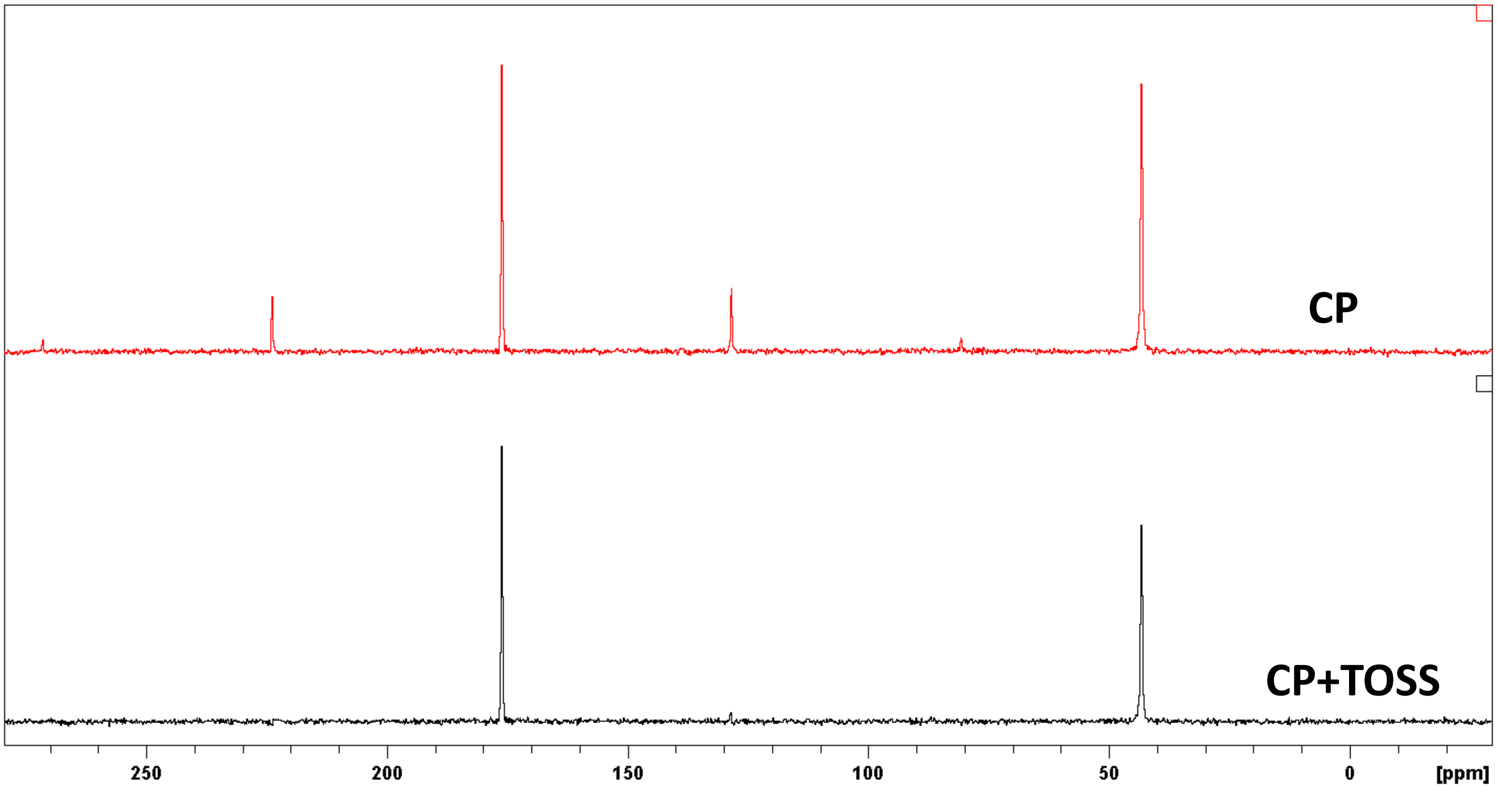
^{13}C NMR

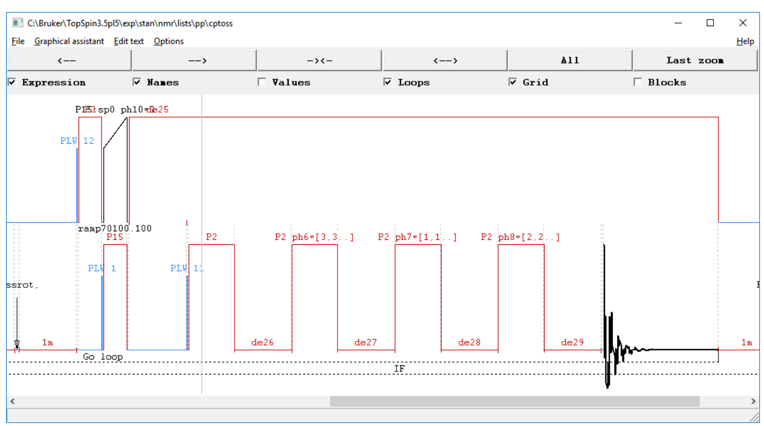


13C CP/MAS of Tetracycline hydrochloride (21.1 T, MAS 20 kHz)

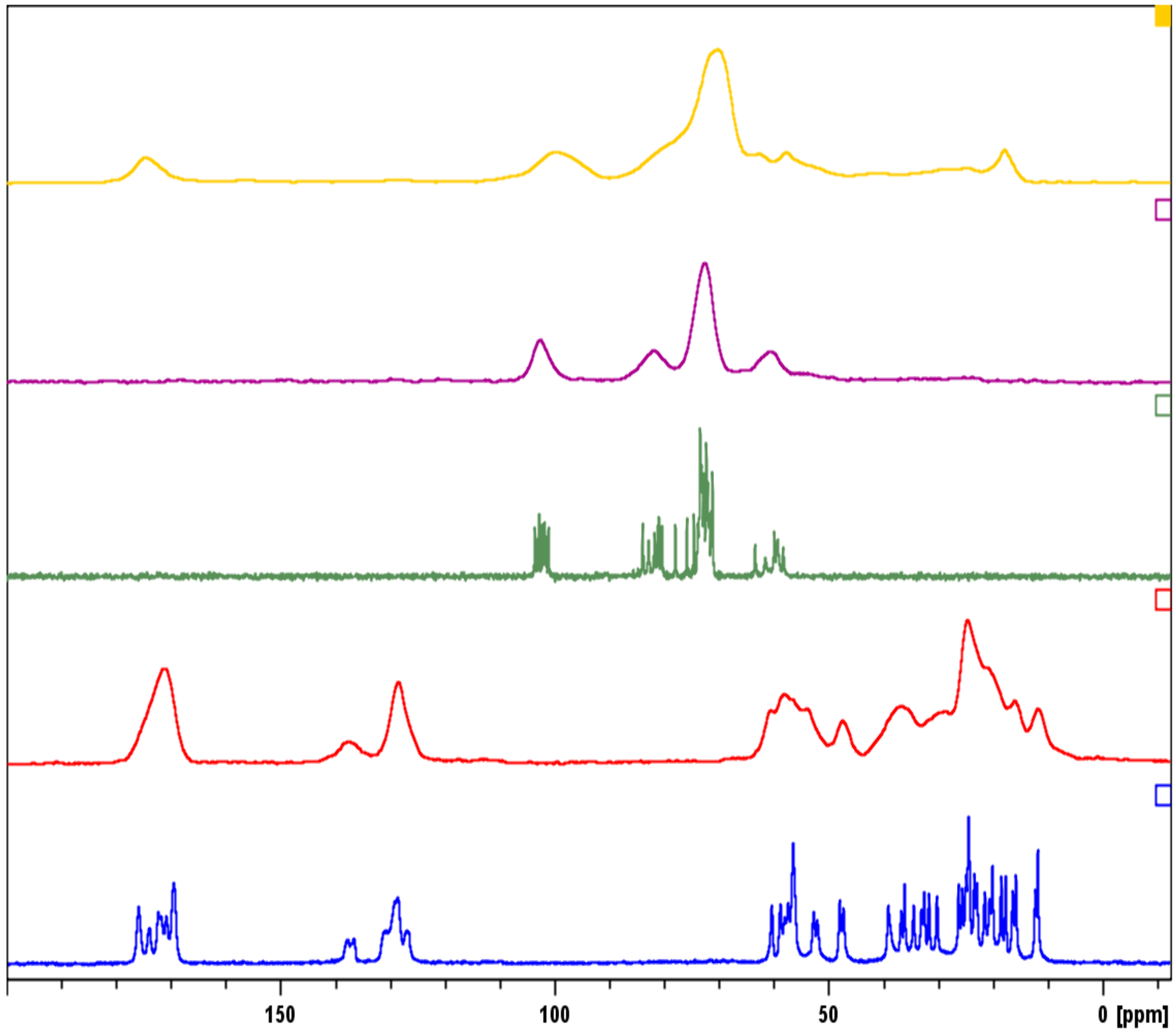


CP + TOSS


CP
CP+TOSS
250
200
150
100
50
0
[ppm]

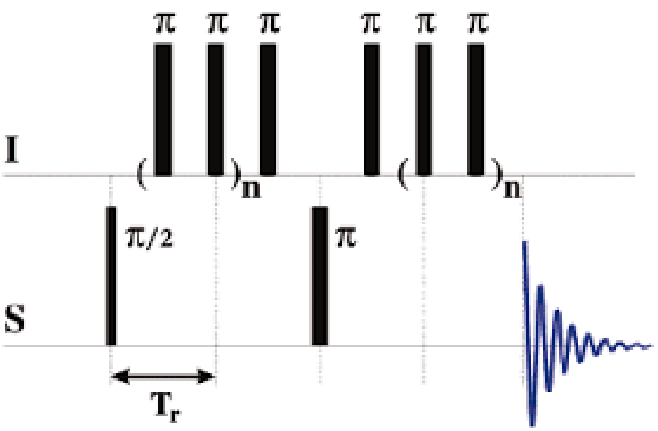

C:\Bruker\TopSpin3.5pl5\exp\stan\nmr\lists\pp\cptoss
File
Graphical assistant
Edit text
Options
Help
<--
-->
-><-
<-->
All
Last zoom
Expression
Names
Values
Loops
Grid
Blocks
sp0
PLW 12
ramp70100.100
P15
P2
P2 ph6=[3,3..]
P2 ph7=[1,1..]
P2 ph8=[2,2..]
PLW 1
PLW 11
ssrot,
1m
de26
de27
de28
de29
Go loop
IF

CP + MAS + TOSS + Decoupling

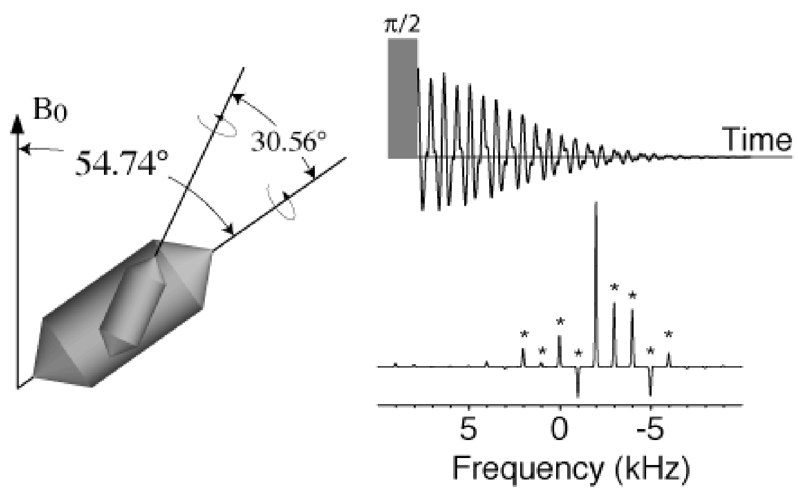


Other SSNMR Techniques

- Dipolar recoupling: REDOR, TRAPDOR.
- 2D: ^{1}H-^{13}C HETCOR, ^{13}C-^{13}C RFDR/PDSD, ^{1}H-^{1}H CRAMPS.
- ^{2}H: static wideline.
- Quadrupolar nuclei: MQ-MAS, VAS, DOR.



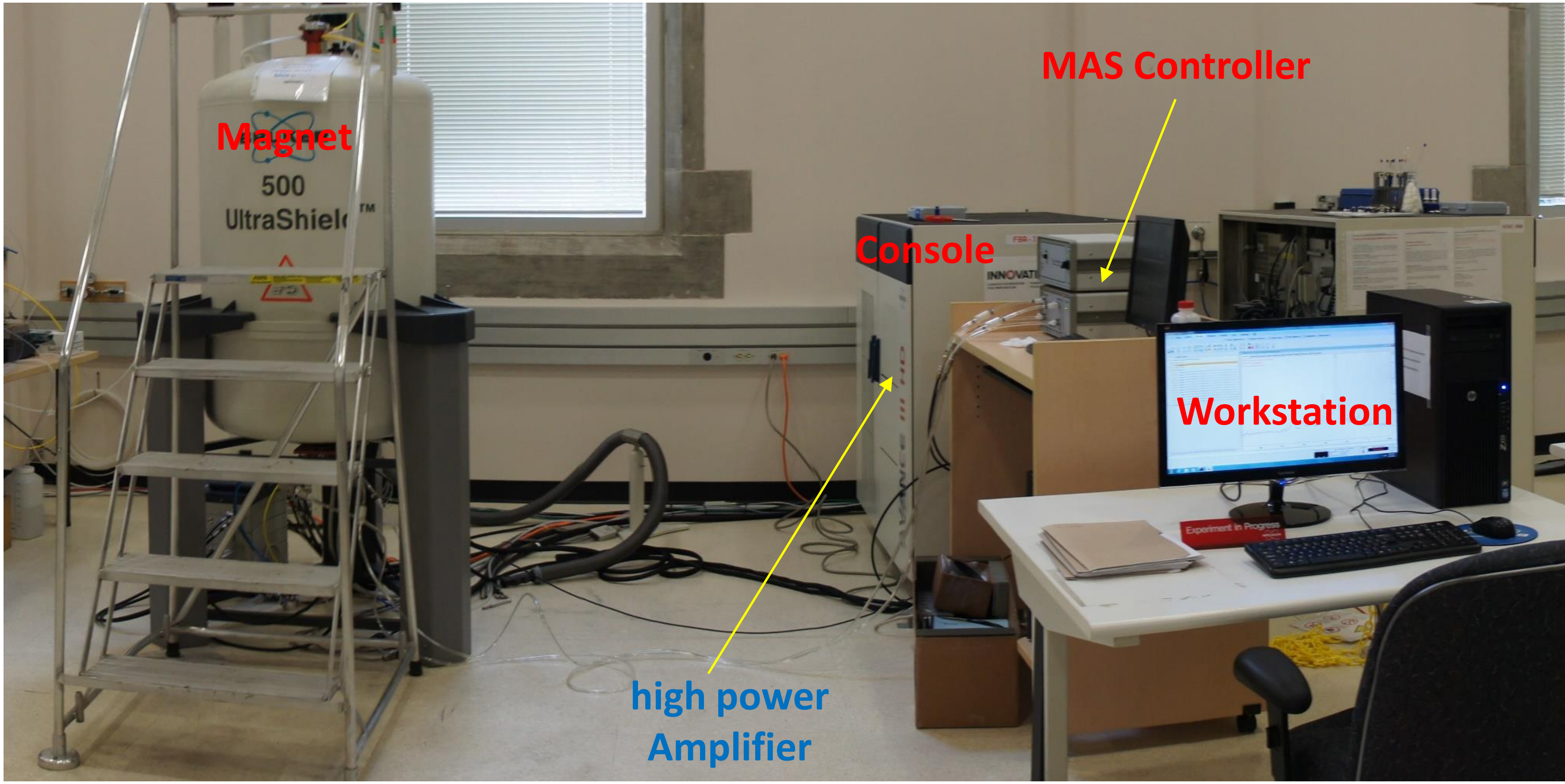
REDOR



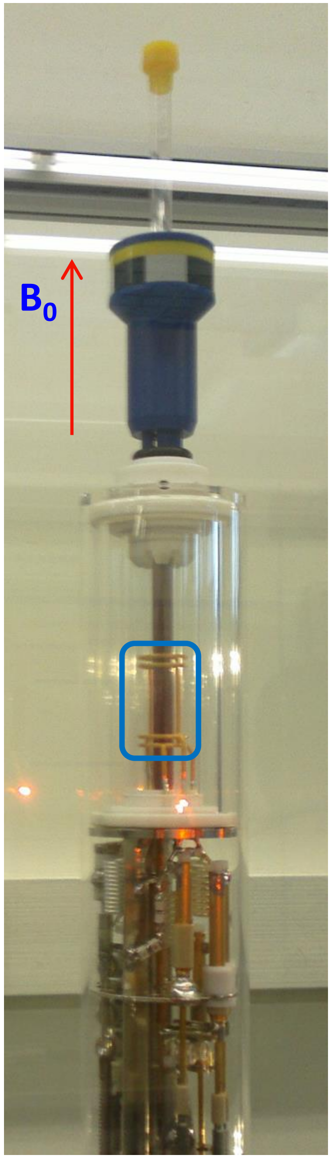
DOR

SSNMR Hardware

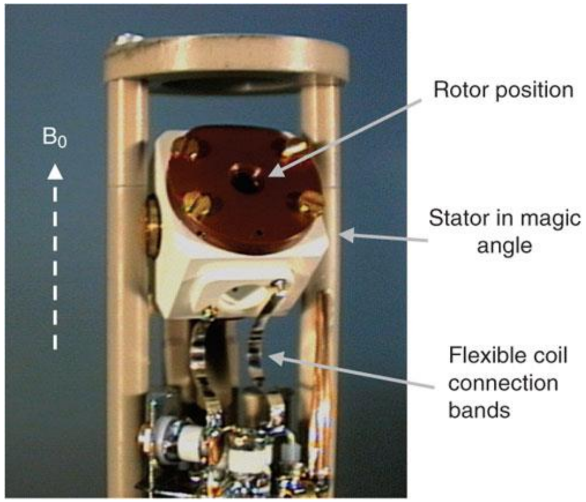
NMR Spectrometer

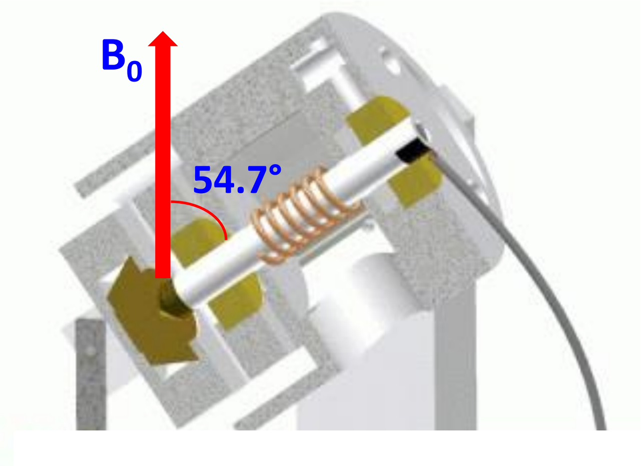


CPMAS Probe

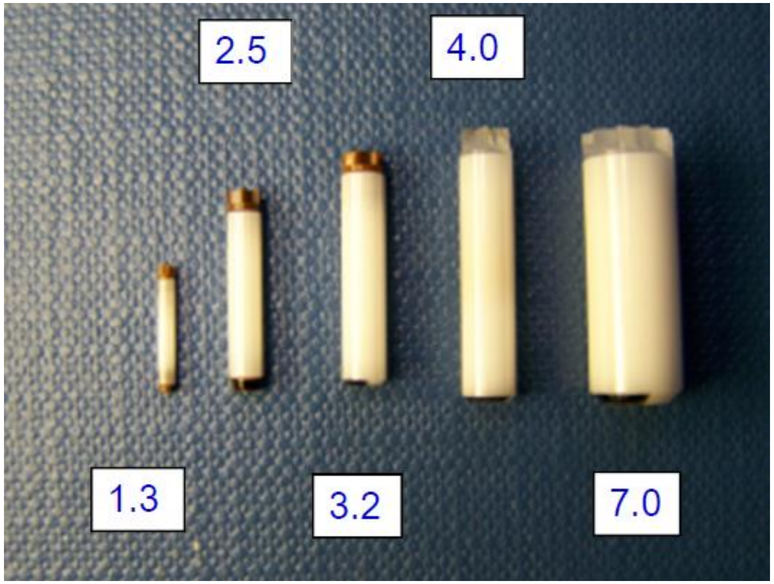

B_0


Doty Scientific Inc.


B_0
Rotor position
Stator in magic angle
Flexible coil connection bands


B_0
54.7°

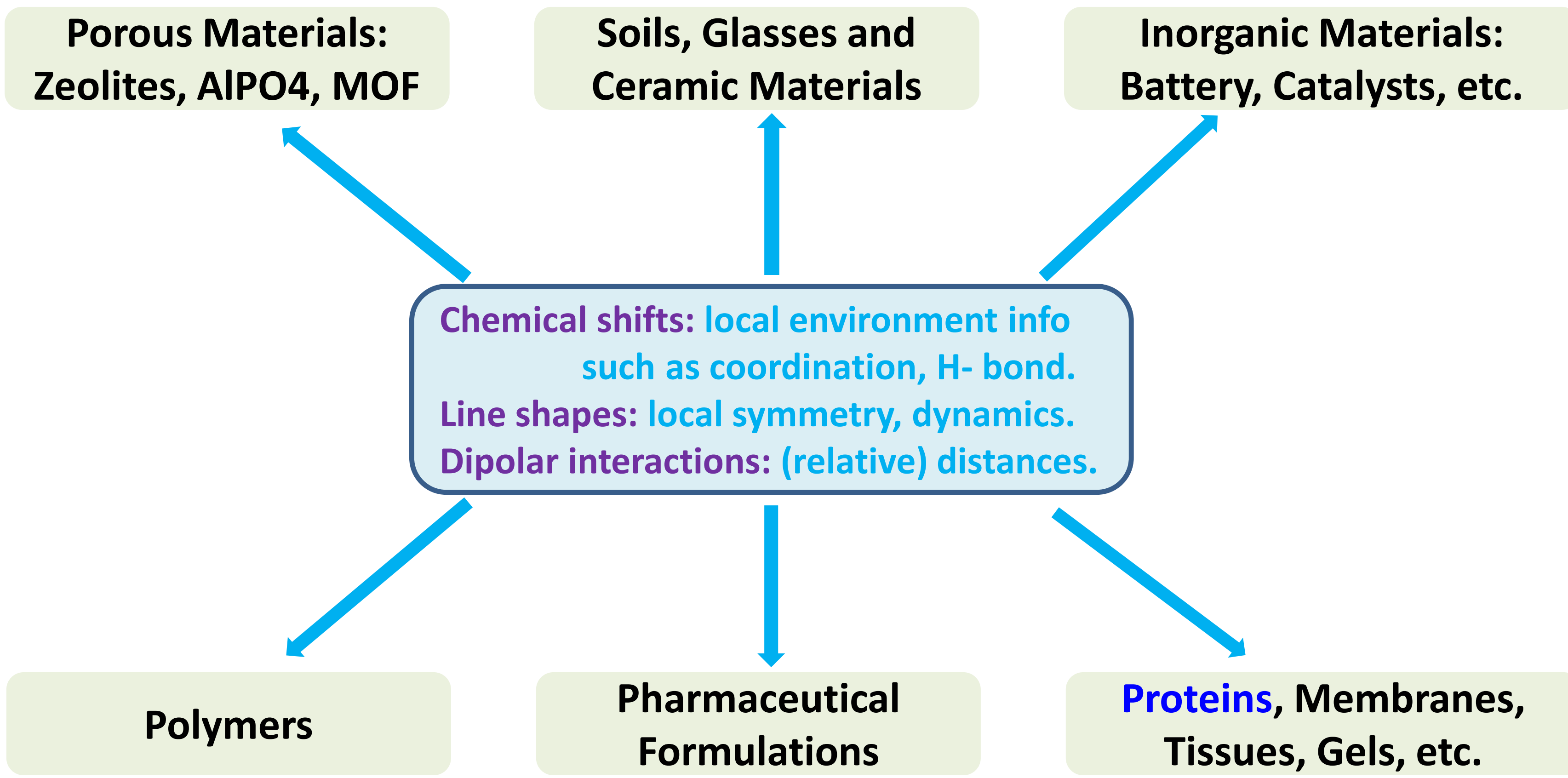
MAS Stator and Rotors



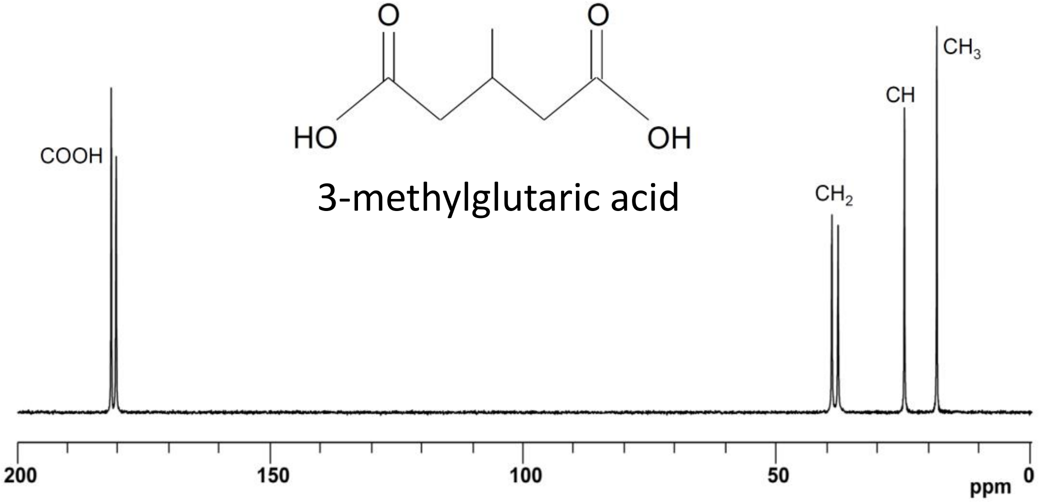
Rotor size (mm)	1.3	2.5	3.2	4.0	7.0
Max Spinning (kHz)	67	35	24	15	7
Sample Volume (µL)	--	11	30	71	240

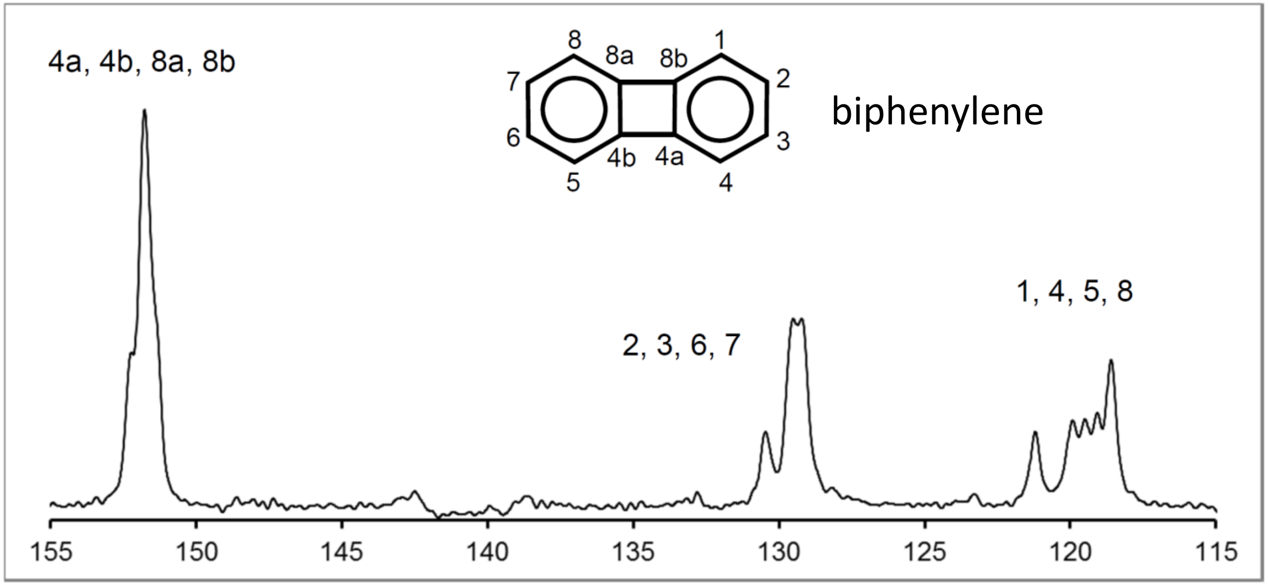
SSNMR Applications

Solid State NMR Applications



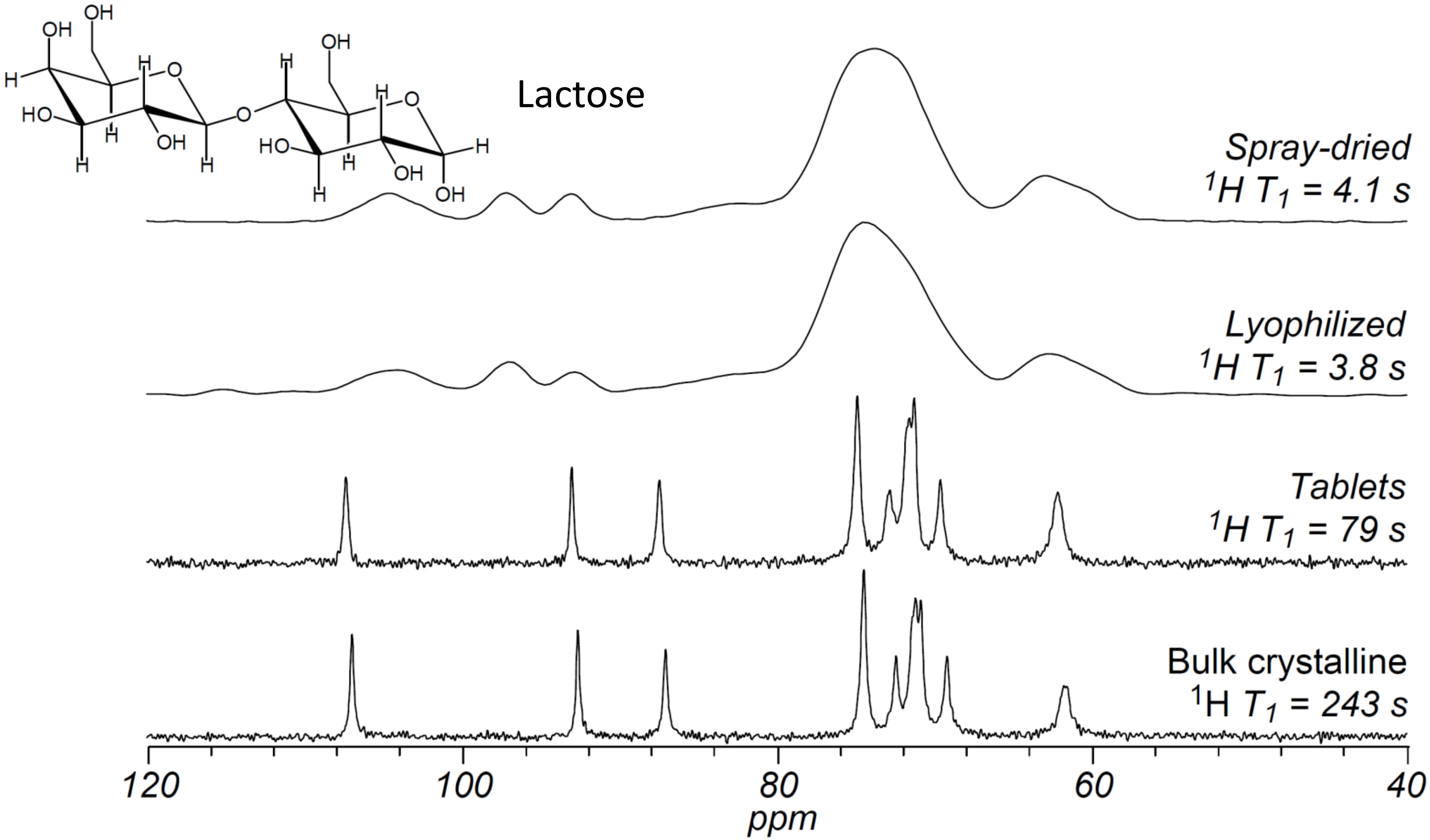
SS-NMR Applications – Site Identification (^{13}C)





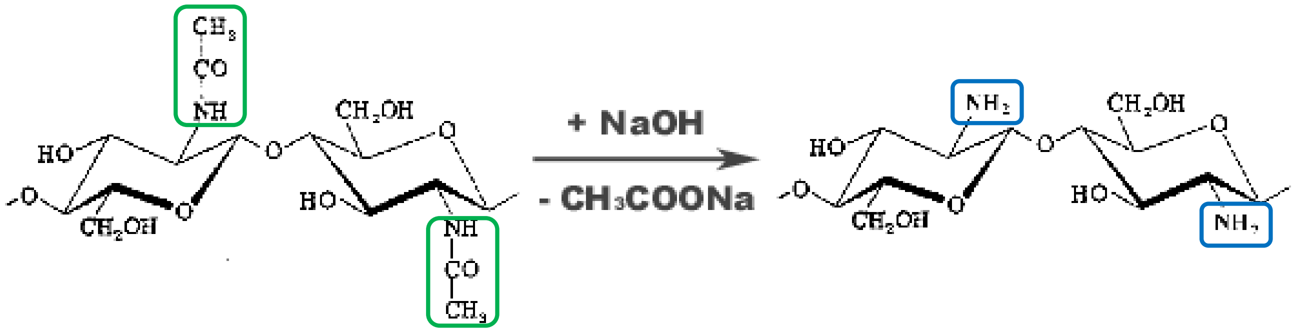
D. Barich et al. J. Phys. Chem. A 104 (2000) 8290.

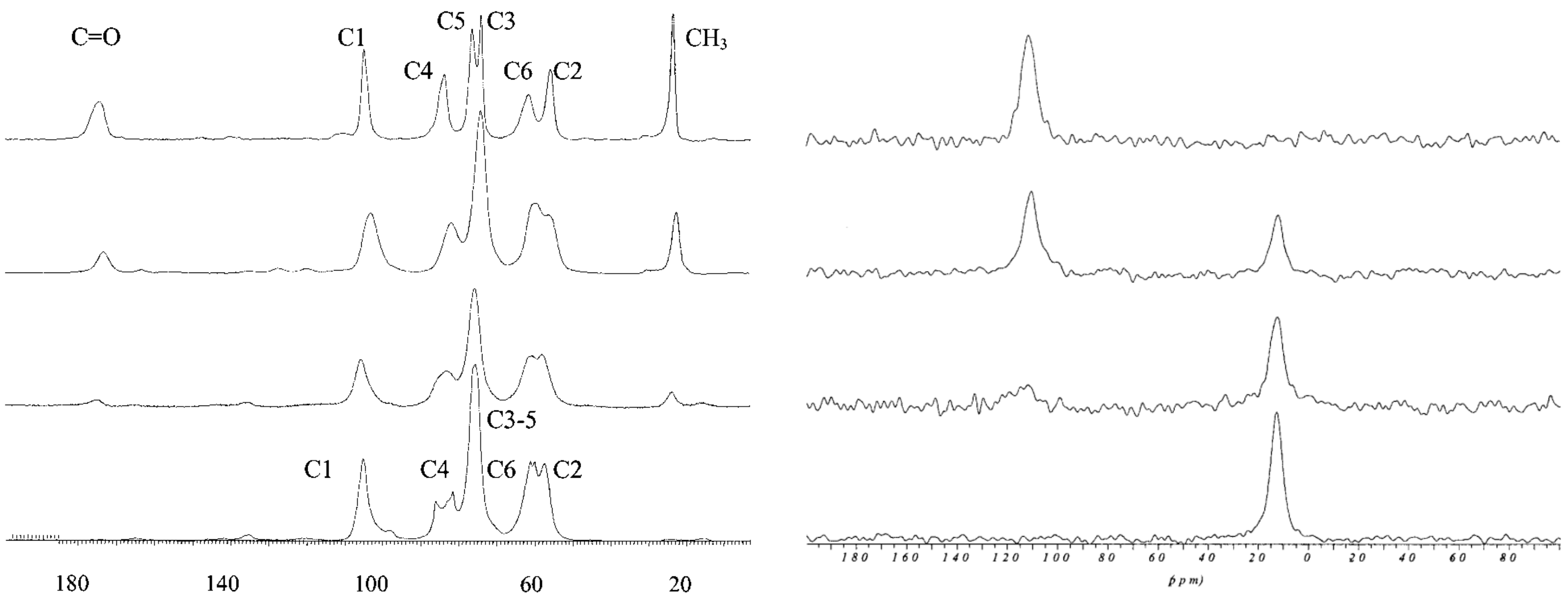
SS-NMR Applications – Crystalline vs Amorphous



SS-NMR Applications – Biopolymers

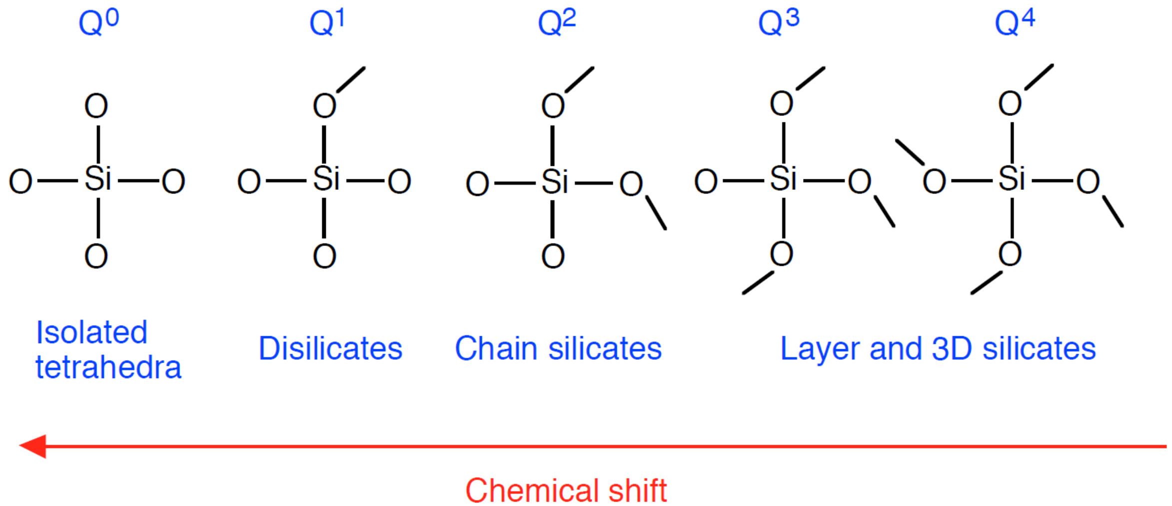
Chitin deacetylase to Chitosan

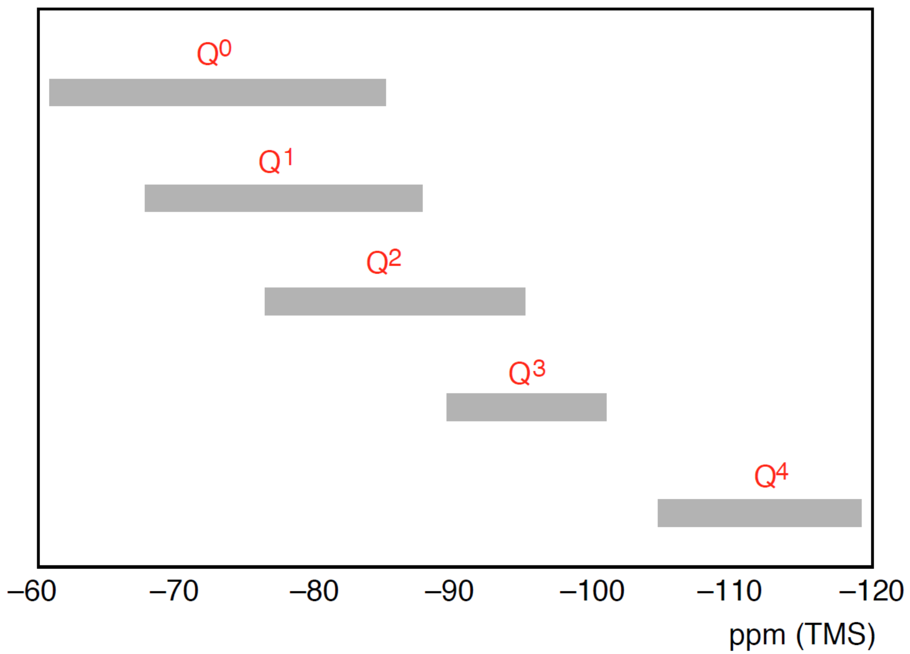




Heux, et al. Biomacromolecules 1 (2000) 746.

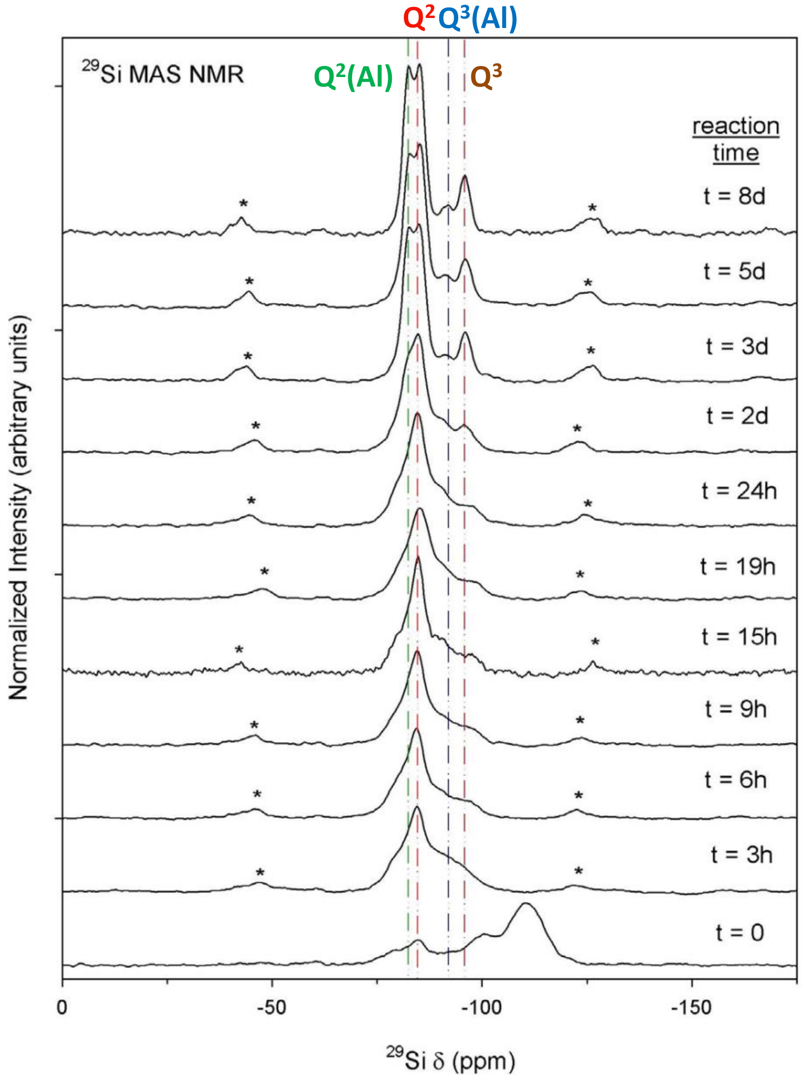
SS-NMR Applications – Porous Materials (^{29}Si)

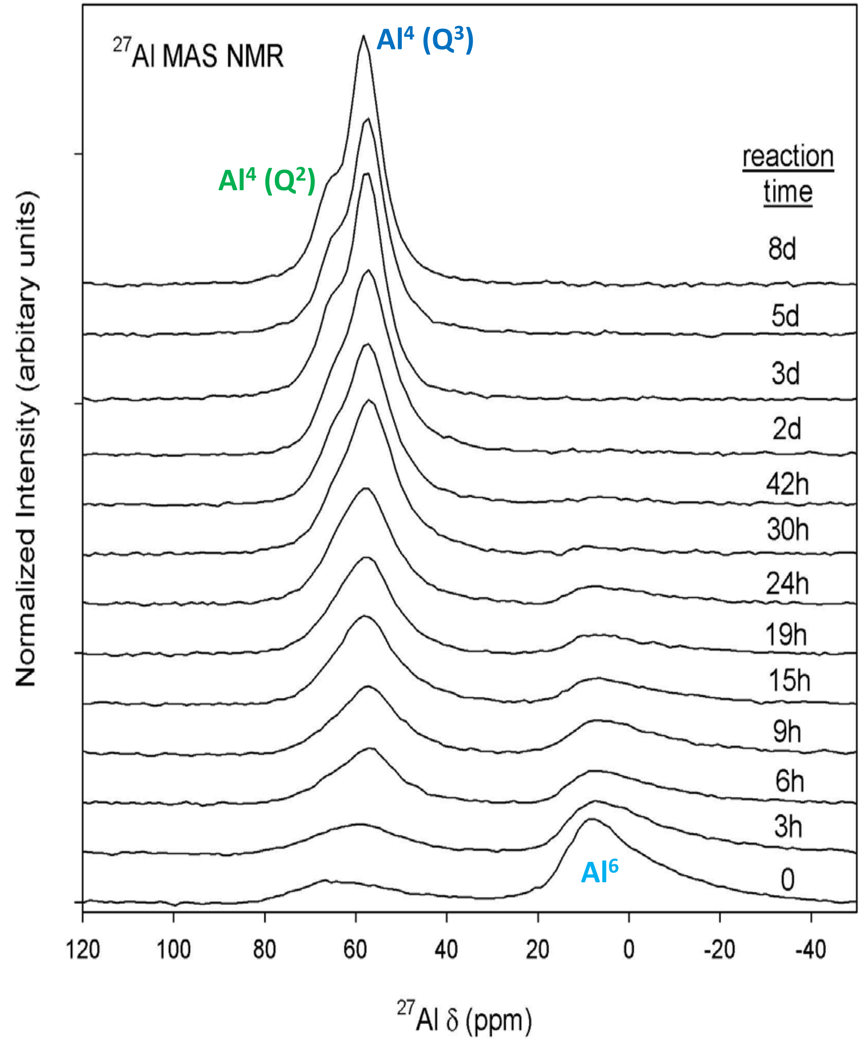




SS-NMR Applications – Monitoring Reactions

Amorphous SiO_2 & Al_2O_3 + … → mineral 'Tobermorite'

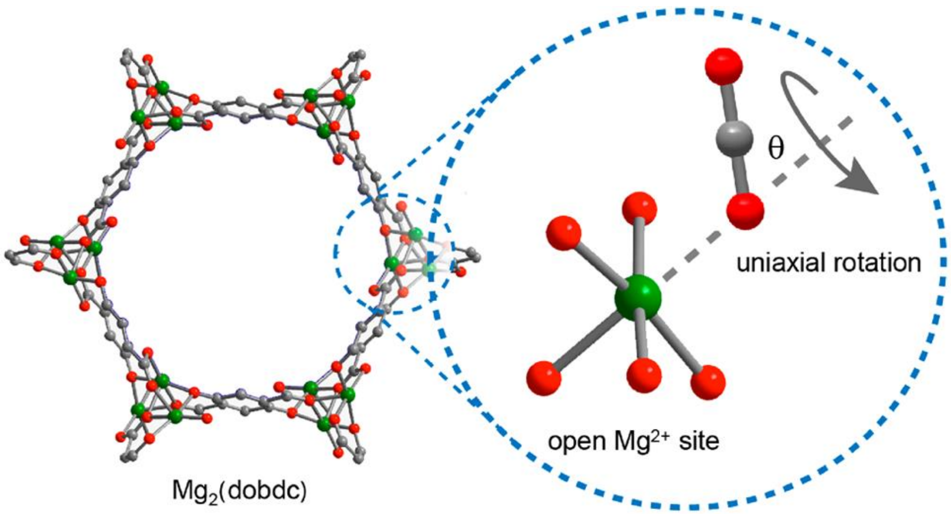


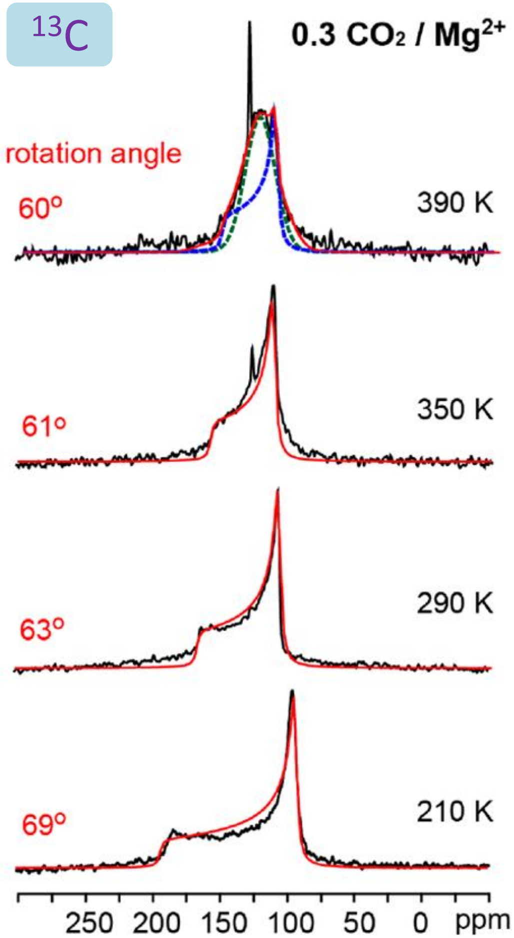


J. Houston et al. Geochem. Trans. 10 (2009) 1.

SS-NMR Applications – Host-Guest Interaction

$^{13}CO_2$ captures in Mg_2(dobdc), a MOF with 1.1 nm channels.

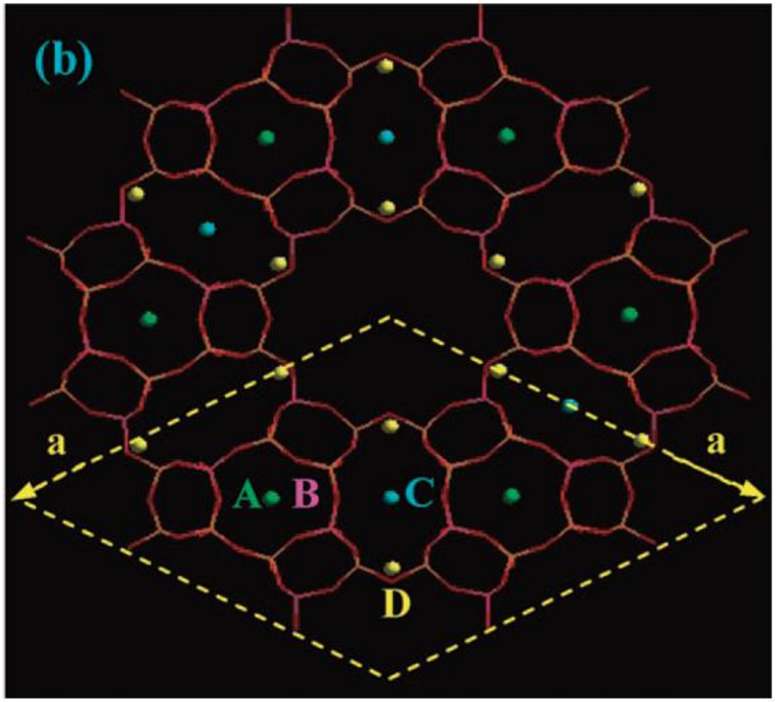




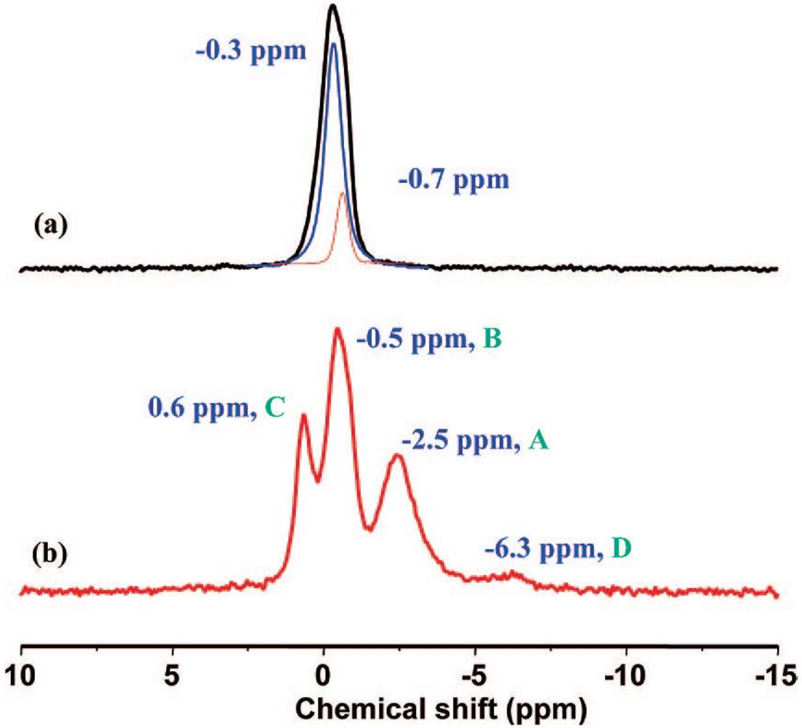
Kong, et al. J. Am. Chem. Soc. 134 (2012) 14341

SS-NMR Applications – Host-Guest Interaction

Zeolite LiK-L

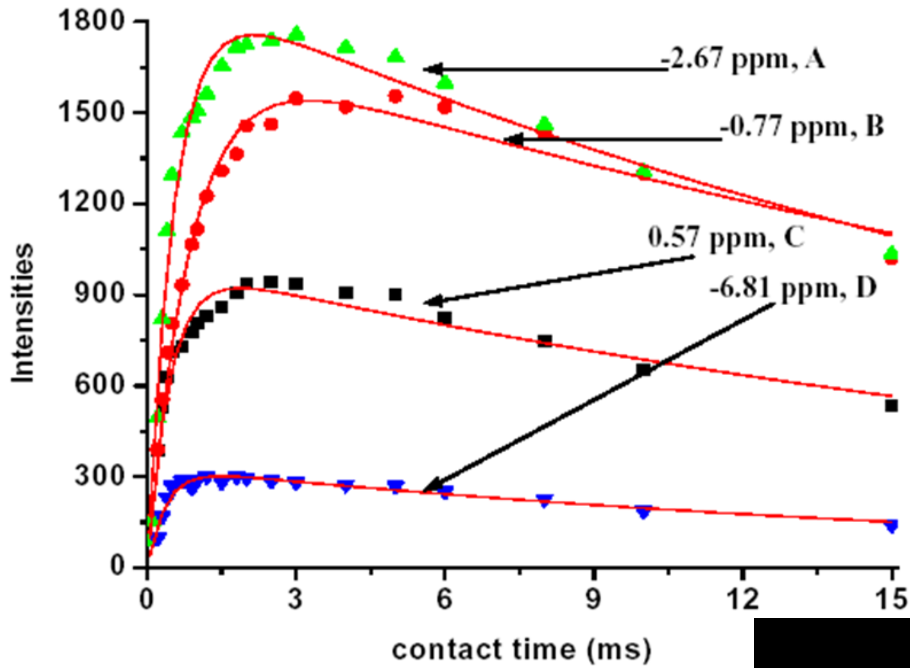


Toluene Adsorption: ^{7}Li MAS



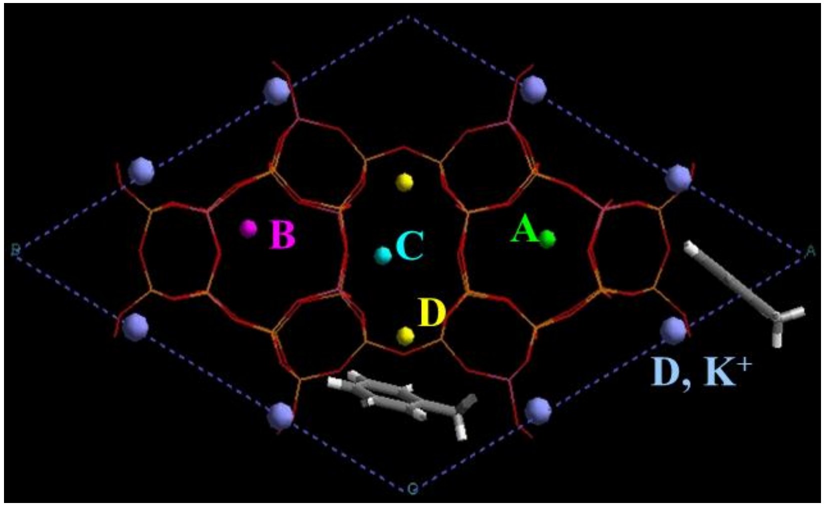
Zhu, et al. J. Phys. Chem. C 112 (2008) 14241

SS-NMR Applications – Relative Distances



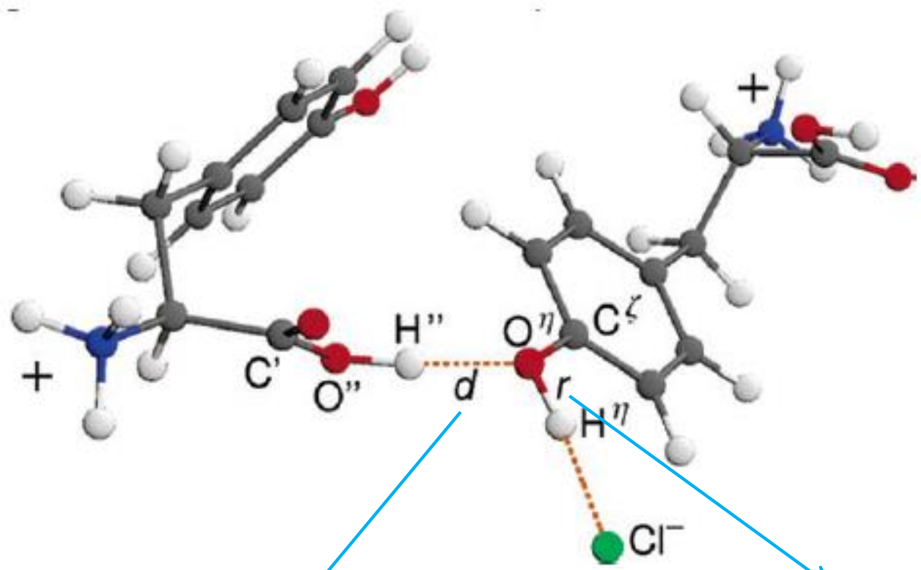
Li^+ sites	T_{CP} (ms)
A	0.60
B	0.97
C	0.50
D	0.41

- **Didpolar coupling strength:**
  D > C > A > B
- **Approximate distances (units: Å) between cation and ring proton:**
  D (2.7) < C (6.6) < A (7.0) < B (10.3)



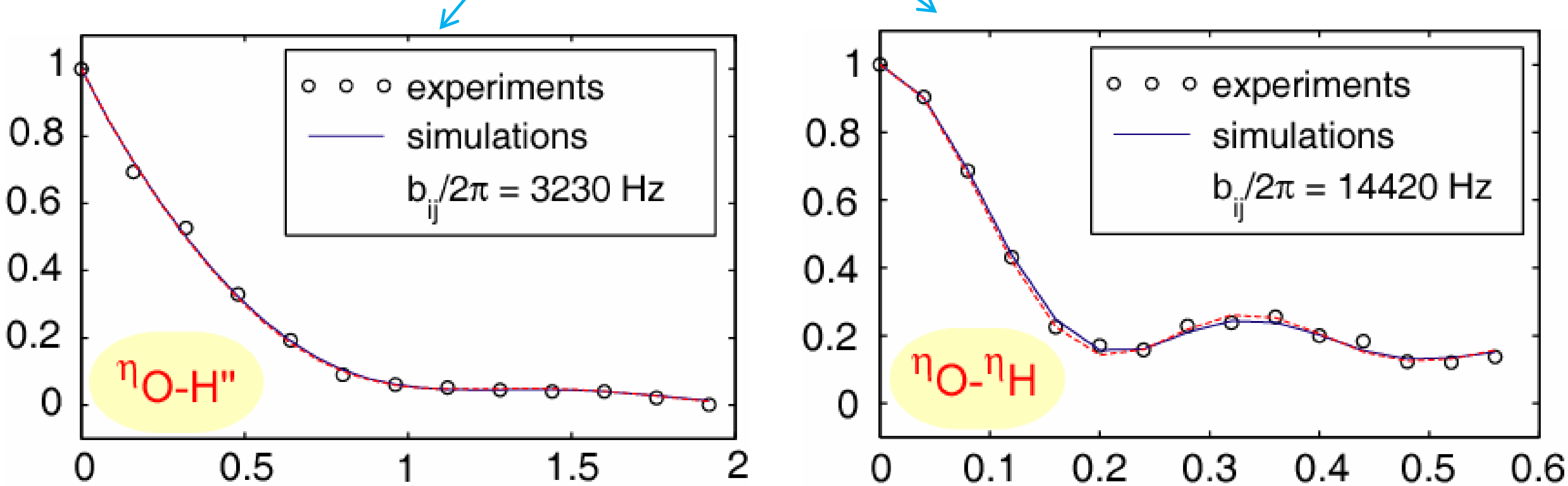
Zhu, et al. J. Phys. Chem. C 112 (2008) 14241

SS-NMR Applications – Measure Distances



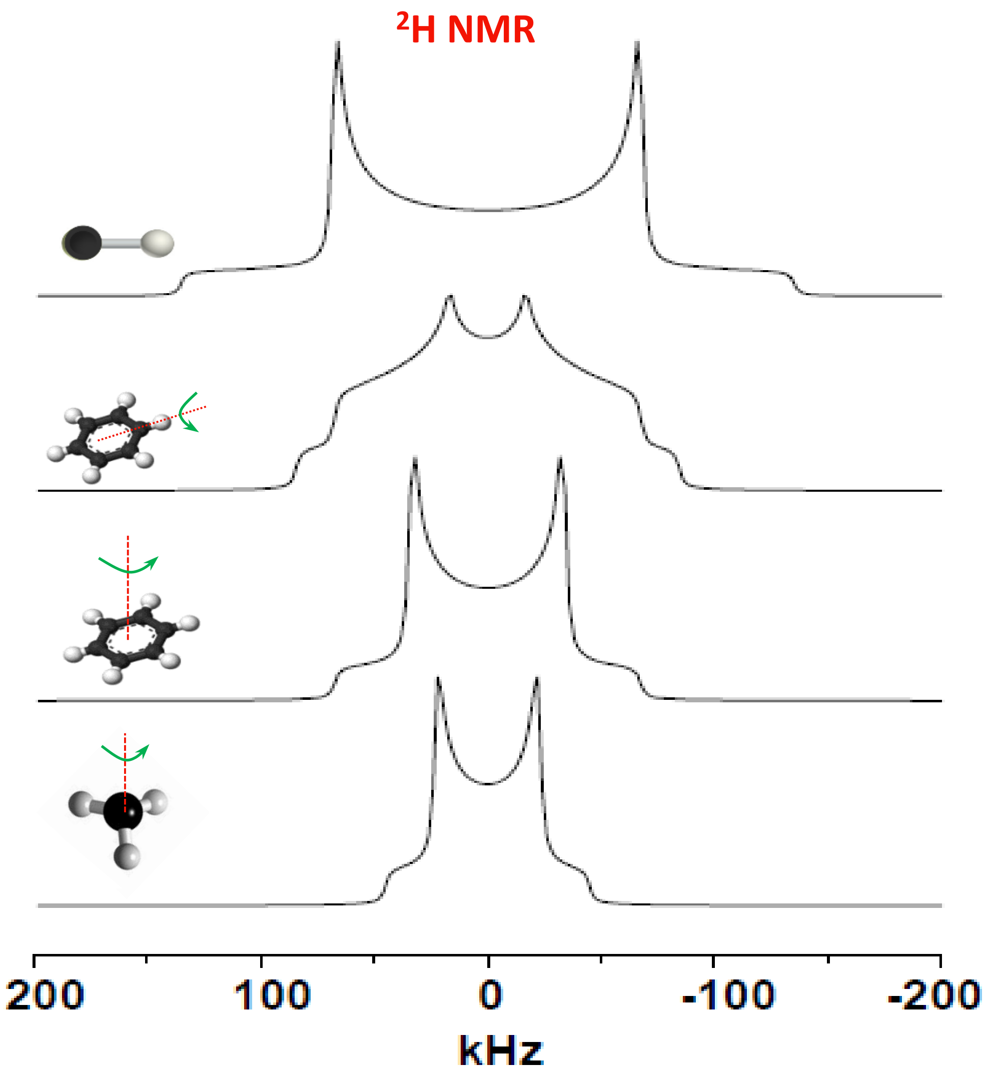
[η-^{17}O]L-Tyrosine·HCl
@ 800 MHz, 50 kHz

	r (Å)	d (Å)
NMR	1.03	1.71
neutron	0.99	1.61



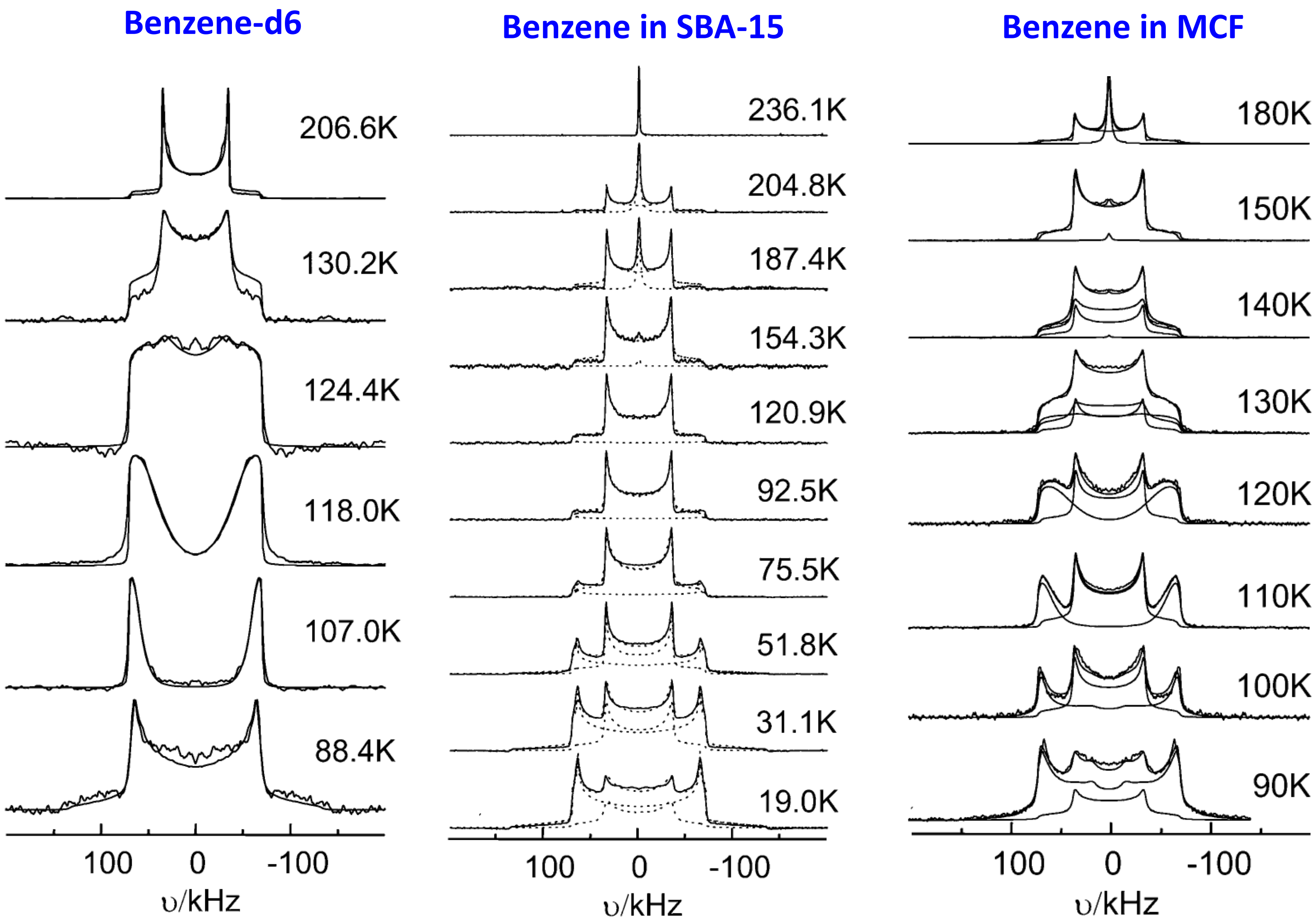
A. Brinkmann et al. J. Am. Chem. Soc. 128 (2006) 14758

Solid NMR Applications – Dynamics (1)



Solid NMR Applications – Dynamics (2)

^2H NMR



G. Buntkowsky et al., PCCP 9 (2007) 4843

Our SS-NMR Capability

- ***Probe:*** 4-mm CP/MAS Probe
- ***MAS rate:*** max 18 kHz
- ***Nuclei:*** ^{15}N, ^{2}H, ^{29}Si, ^{13}C, ^{27}Al, ^{31}P / ^{19}F, ^{1}H

  ^{65}Cu, ^{91}Zr, ^{61}Ni, ^{95}Mo, ^{183}W.
- ***Experiments:*** Static, MAS, CPMAS
- ***Sample Size:*** 60 – 160 µL
- ***Sample Form:*** powder, gel, etc.

Summary

- *Solution NMR Basics*
- *Spin Interactions:* *σ, J, D, Q*.
- *SSNMR Techniques:* Decoupling, MAS, CP.
- *SSNMR Hardware:* CP/MAS probe.
- *SSNMR Applications*

NMR Reading Materials

Books:

1. Understanding NMR Spectroscopy, Second Edition, by James Keeler.
2. Spin Dynamics: Basics of Nuclear Magnetic Resonance, by Malcolm H. Levitt.
3. Solid-State NMR Spectroscopy Principles and Applications, by Melinda J. Duer.
4. NMR Crystallography, by Robin K. Harris, Roderick E. Wasylishen, Melinda J. Duer.
5. Multinuclear Solid-State NMR of Inorganic Materials, by K. MacKenzie, M. Smith.
6. Essential Mathematics for NMR and MRI Spectroscopists, by Keith Brown.
7. https://www.cis.rit.edu/htbooks/nmr/, by Dr. Joseph Hornak.

Videos:

1. https://www.youtube.com/watch?v=vRHfYWg9GXM, by Prof. James Nowich (UC Irvine).
2. https://www.youtube.com/watch?v=A502rWNKZyI, by Dr. James Keeler (Queensland).
3. https://www.youtube.com/watch?v=OJbBcCdqvIA&t=16s, by Prof. Malcolm Levitt (Southampton, solid state NMR).