Solid-state NMR : targets&methods

K. Takegoshi (Kyoto Univ.)

1) spin=1/2, rare spin, eg., ^{13}C, ^{15}N, ^{29}Si, ^{31}P, ^{113}Cd, ...

   δ_{iso} : high resolution NMR

   δ_{CSA} : Chemical-shift anisotropy

   Dipolar interactions : ^{13}C$-^{13}$C, ^{13}C$-^{15}$N

   Cross polarization (CP)

   Magic-angle spinning (MAS)

   Dipolar decoupling&recoupling

2) spin=1/2, abundant spin, i.e., ^{1}H

   δ_{iso} : high resolution NMR

   Multiple pulse decoupling

   CRAMPS

1

3) Half-integer spins, e.g. Al, Na, O....

δ_{iso} : high resolution NMR

δ_{CSA} : Chemical-shift anisotropy
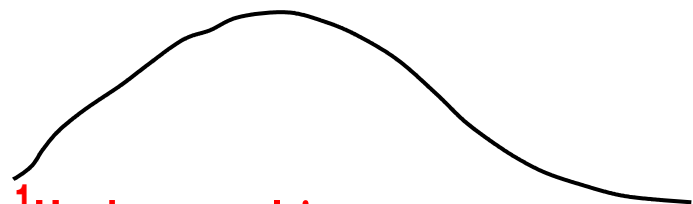
Quadrupolar coupling

MQMAS, DOR, DAS・・・

4) Integer spins, e.g. ^{2}H, ^{14}N

Quadrupolar coupling

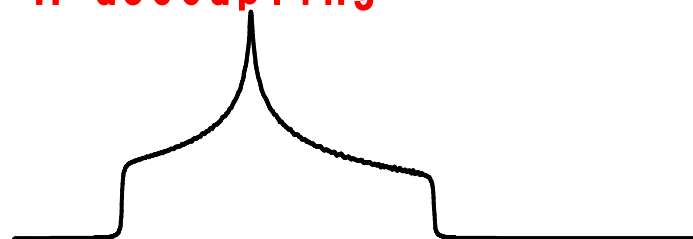So far, no practical methods
for high-resolution observation

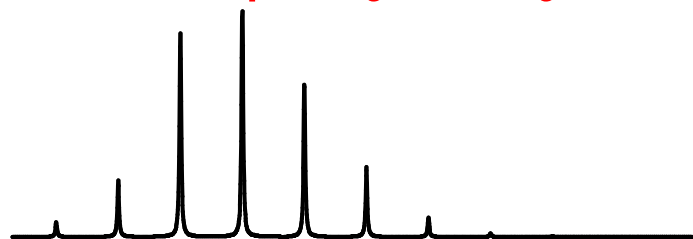# Powder NMR spectra of spin=1/2 (rare-nuclei case), eg. ^{13}C

No gadgets

^{13}C chemical-shift anisotropy

$^1H-^{13}C$ heteronuclear dipolar interactions
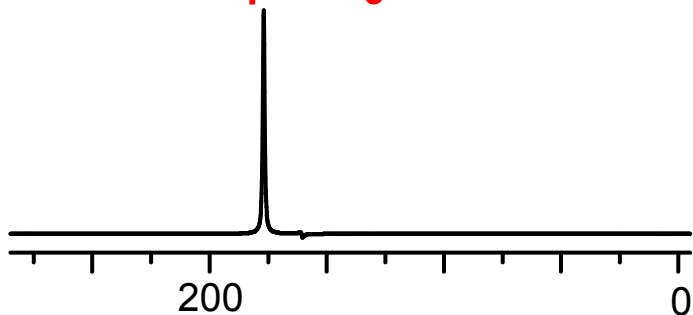
^1H decoupling

^{13}C chemical-shift anisotropy

^1H decoupling + Magic-angle spinning at 2 kHz
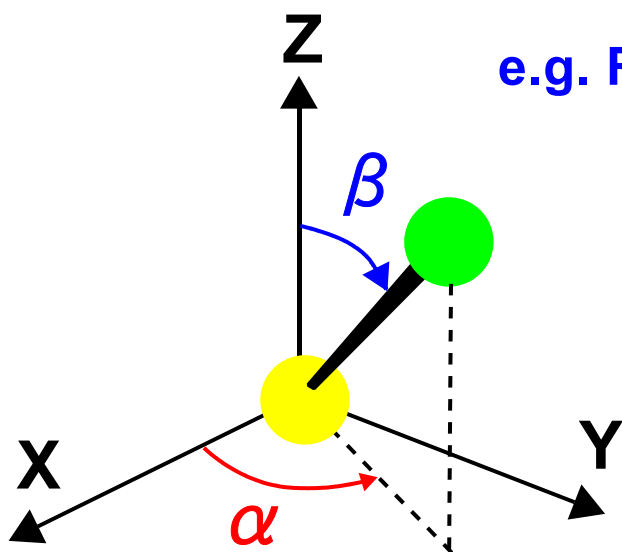
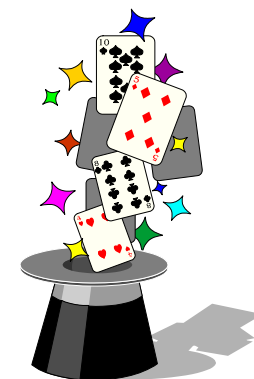^{13}C isotropic shift + spinning sidebands

^1H decoupling + MAS at 20 kHz

^{13}C isotropic shift
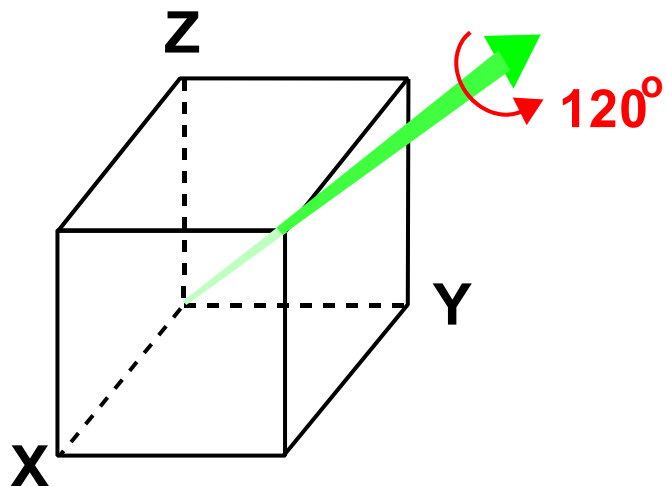
200   0

3

Magic Angle Spinning

e.g. Removal of dipolar broadening by MAS
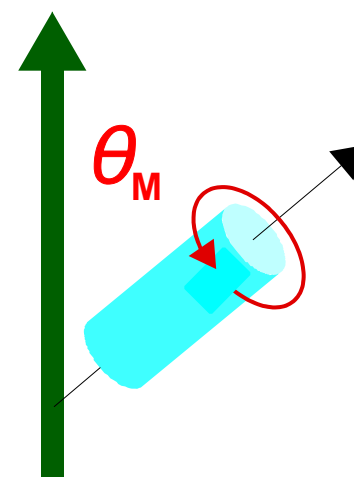
$$B // Z \quad d_Z \propto 3\cos^2\beta - 1$$

$$B // X \quad d_X \propto 3\sin^2\beta \cos^2\alpha - 1$$
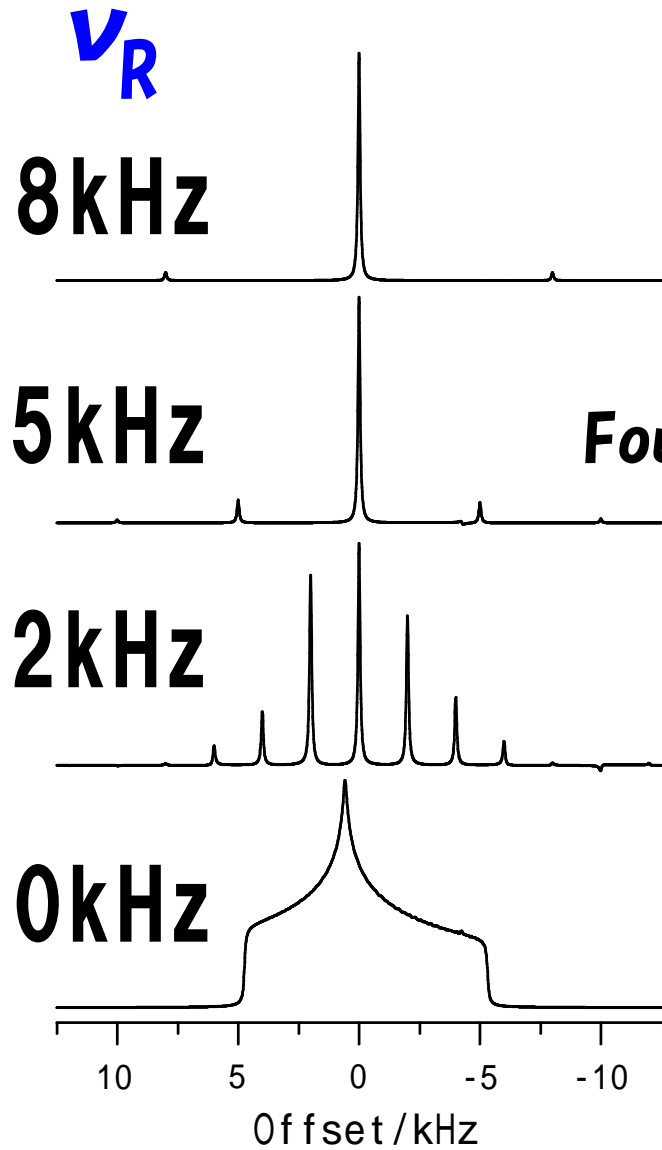
$$B // Y \quad d_Y \propto 3\sin\beta^2 \sin^2\alpha - 1$$
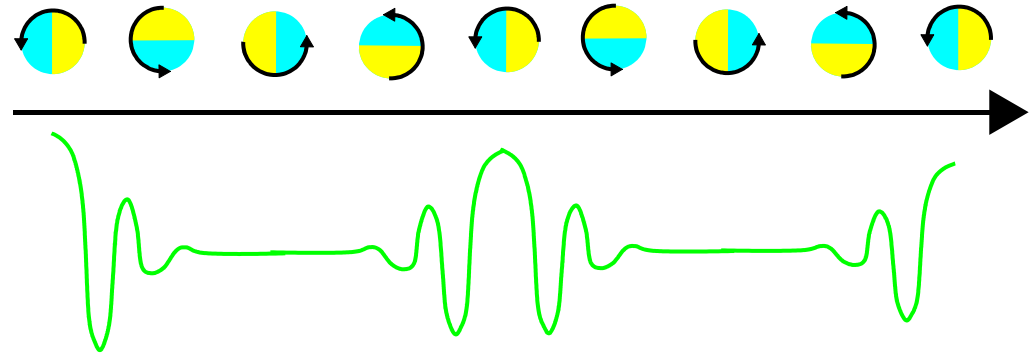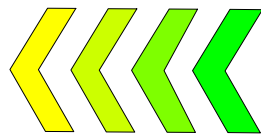
120°

$$d_X + d_Y + d_Z = 0 \text{ !!}$$

θ_M

4

Spinning sidebands

ν_R

8kHz

5kHz

2kHz

0kHz

$\nu_R \gg$ Chemical shift anisotropy

$\propto B_0$

Fourier transform

Rotational echo

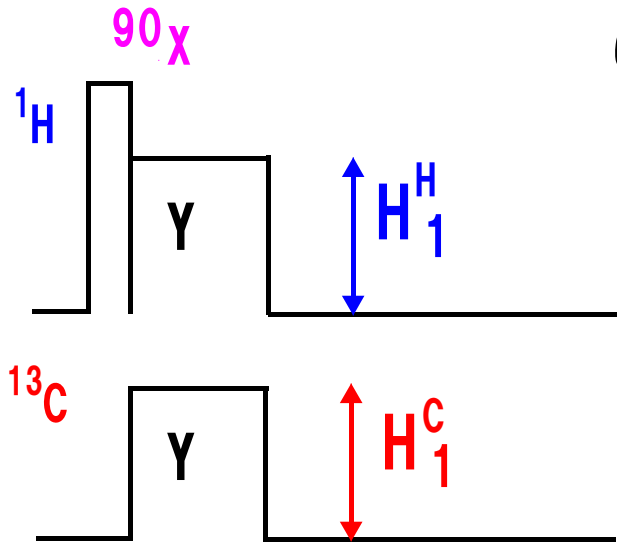10   5   0   -5   -10

Offset/kHz

4-1

Magic angle ...

$\theta = \theta_{MA} +20$

$\theta = \theta_{MA} +5$

$\theta = \theta_{MA}$

$\theta = \theta_{MA} -5$

$\theta = \theta_{MA} -20$

$\theta = 0$

280 240 200 160 120 80 40 0
Chemical Shift/ppm

H_0 θ
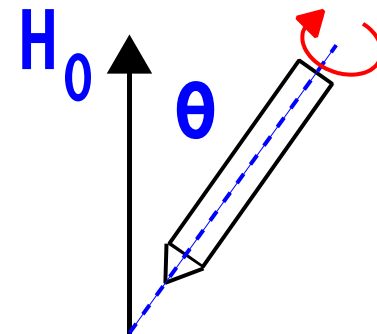
One has to adjust the angle precisely!

^{79}Br FID of KBr

$\theta = \theta_{MA}$

$\theta = \theta_{MA} -1$
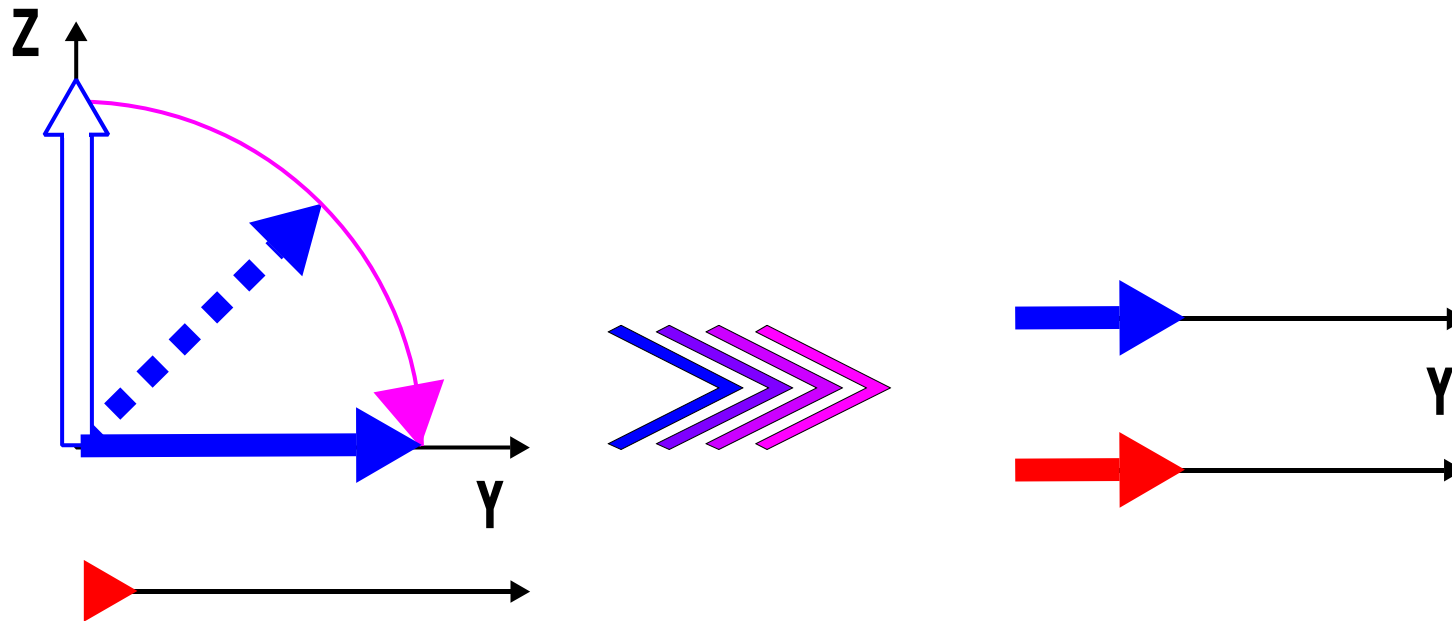
time

5
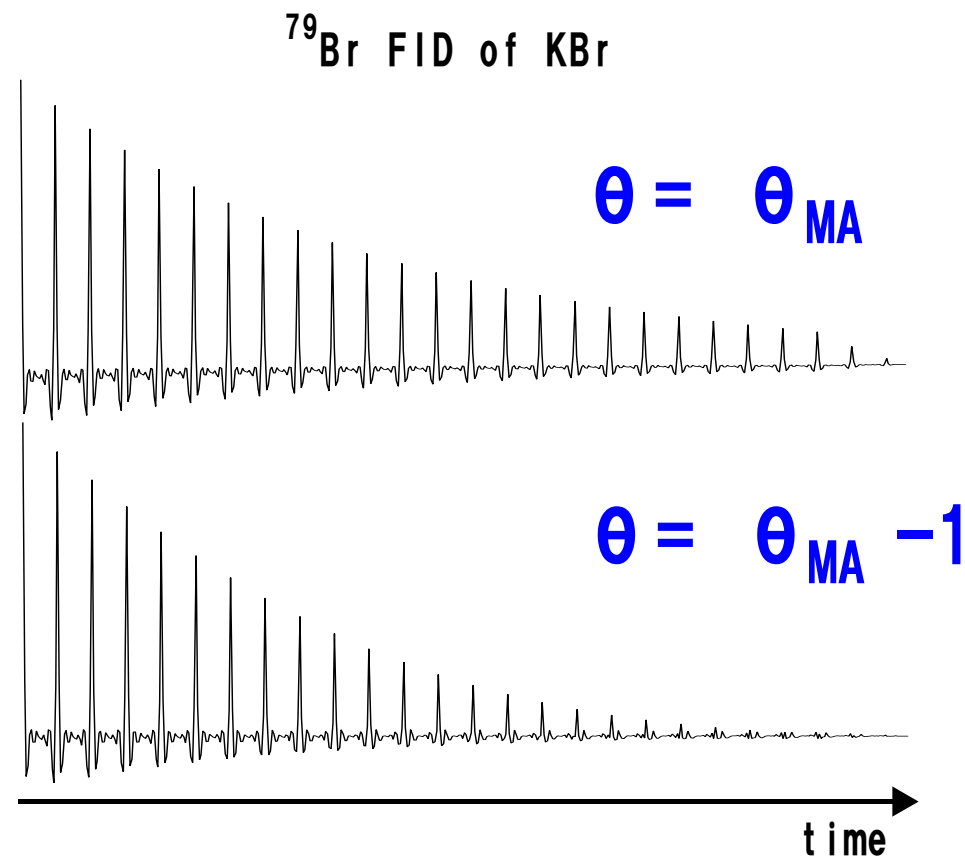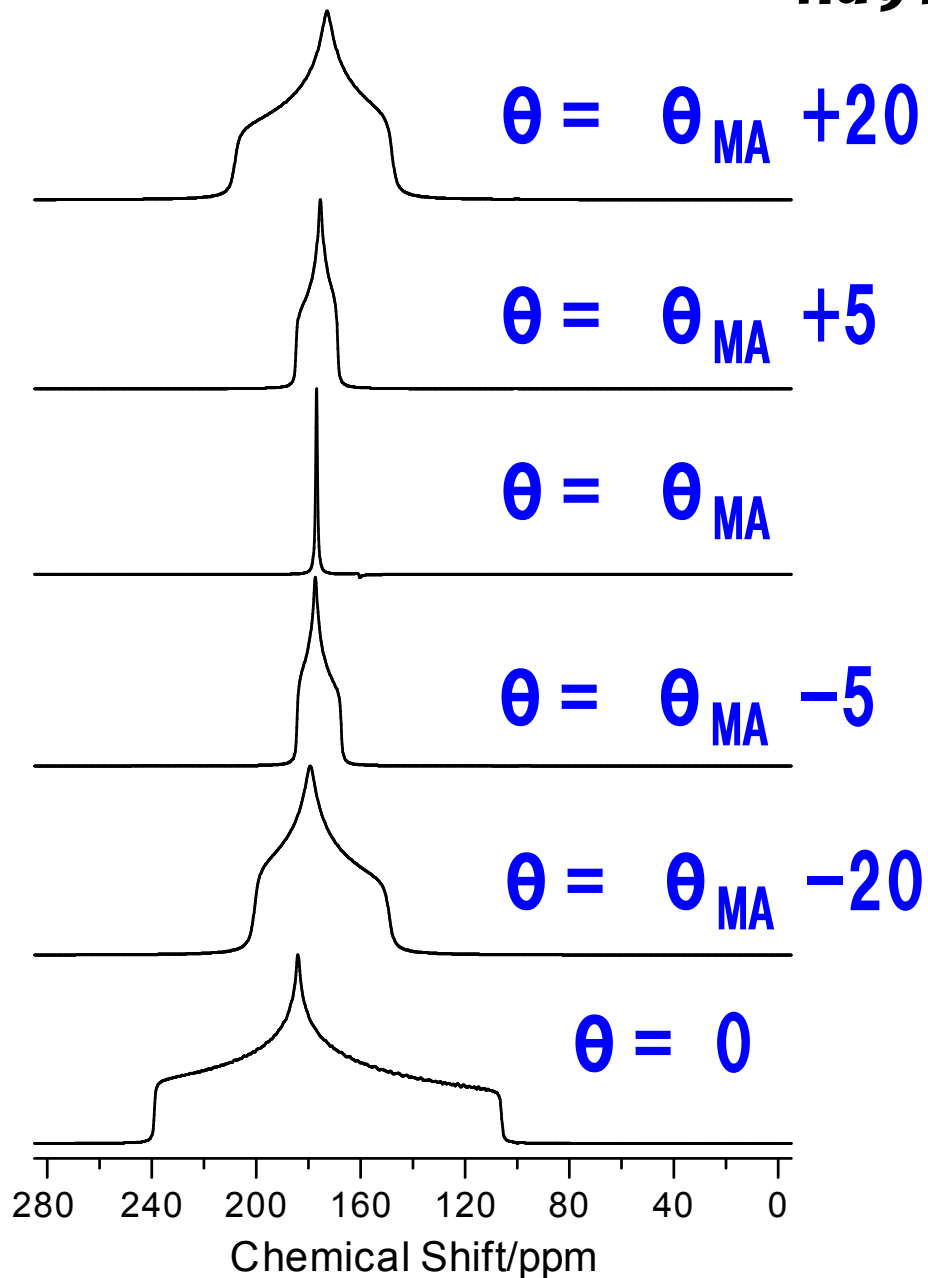
Cross polarization (CP)

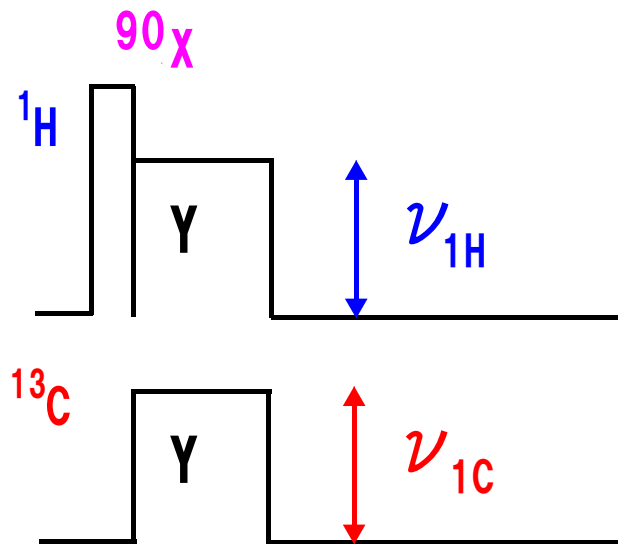$$\gamma_H H_1^H = \gamma_C H_1^C$$

Hartman-Hahn condition
$(H_1 : \text{Tesla})$
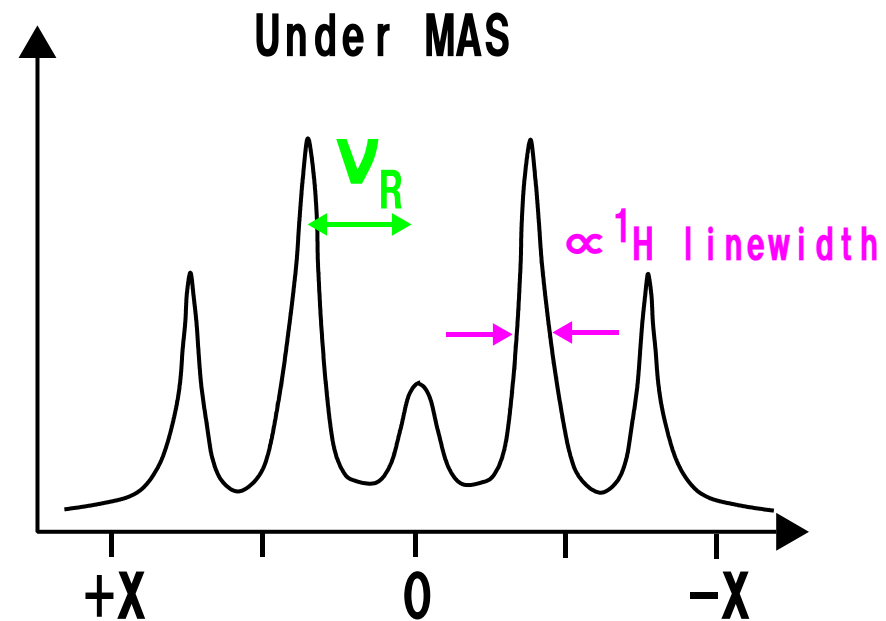
$$\nu_{1H} = \nu_{1C}$$

H-H in Frequency unit

6

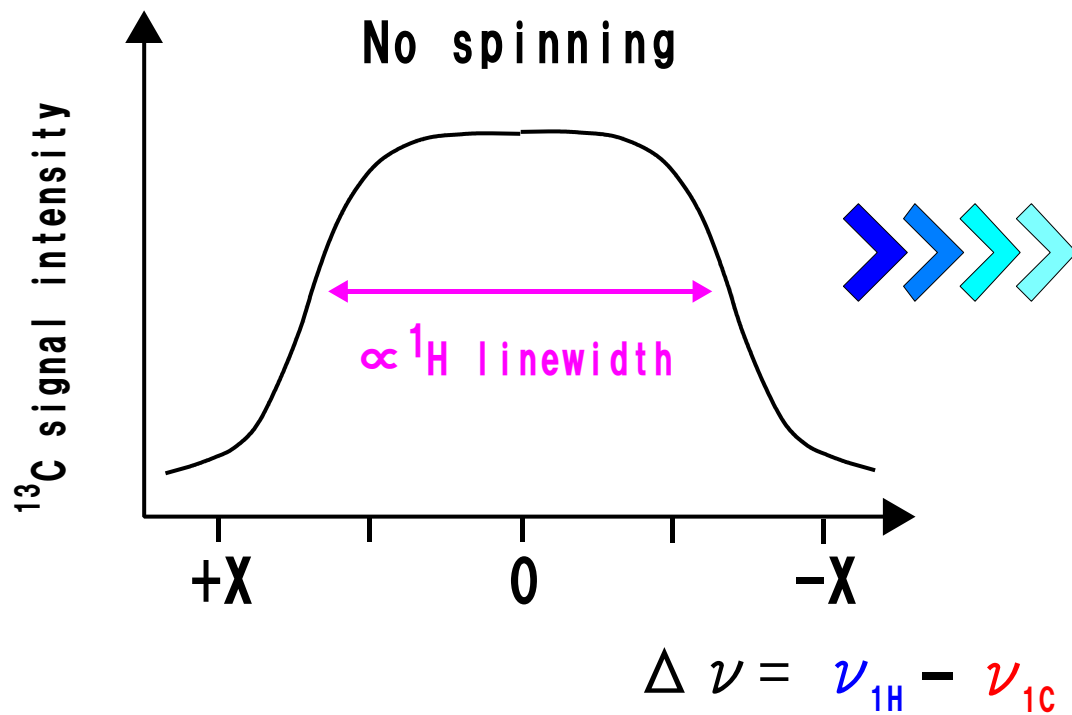# Effect of MAS on CP

H-H condition under MAS

$$\nu_{1H} = \nu_{1C} + n\, \nu_{R}$$

^1H

90_X

Y

ν_{1H}

^{13}C

Y

ν_{1C}

^{13}C signal intensity

No spinning

$\propto {}^1H$ linewidth

+X   0   −X

Under MAS

ν_R

$\propto {}^1H$ linewidth

+X   0   −X

$$\Delta \nu = \nu_{1H} - \nu_{1C}$$

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CP under MAS

For the on-resonance spin

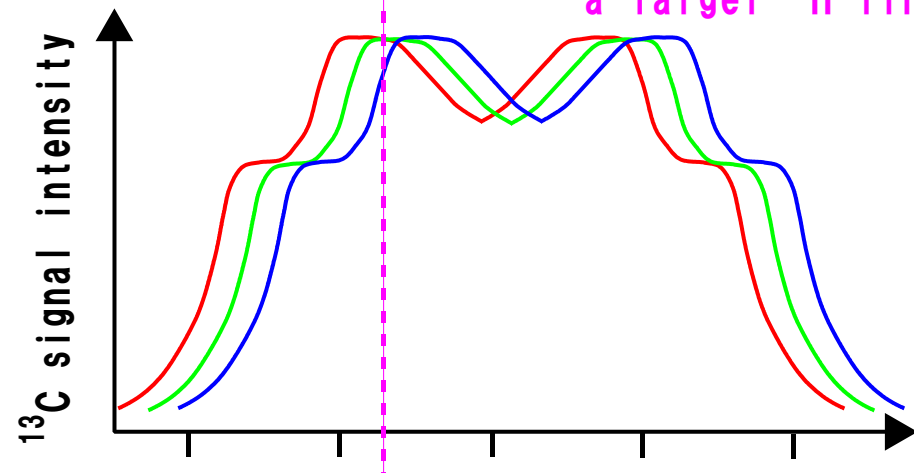$$\nu_{1H} = \nu_{1C} + n\nu_R$$
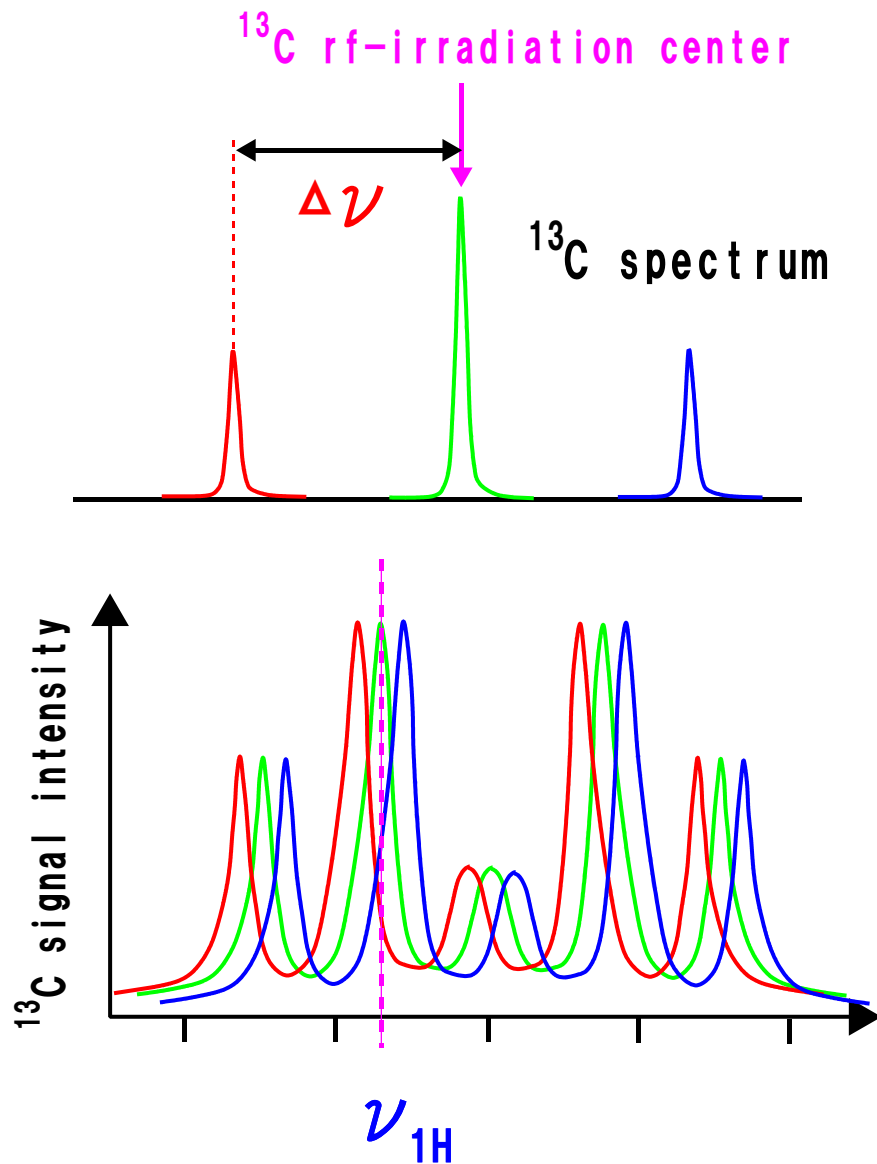
For the off-resonance spins

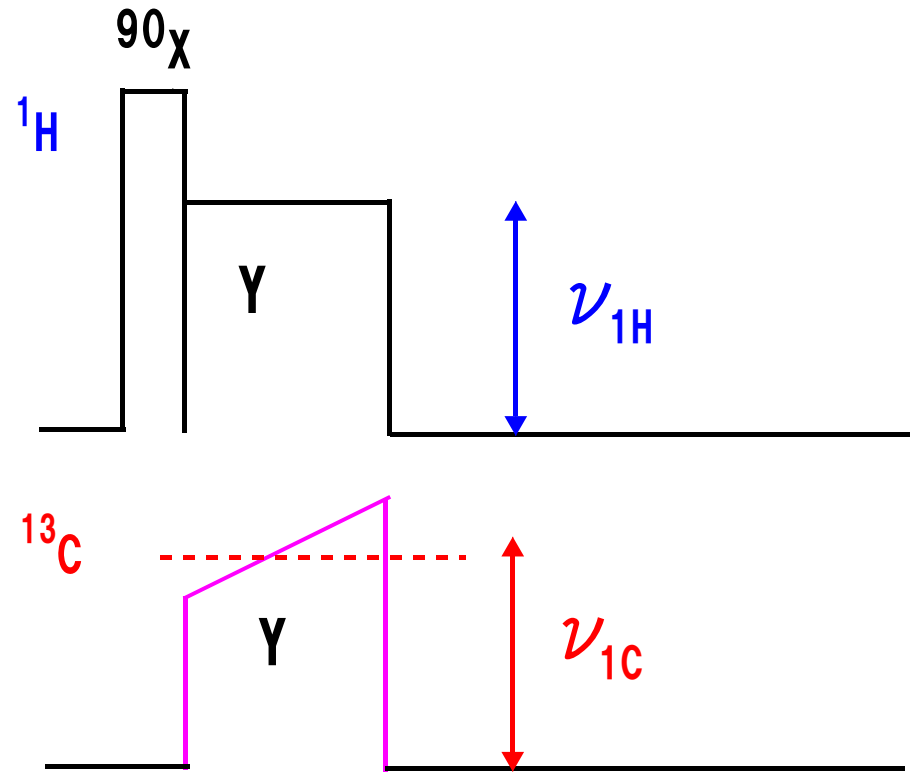$$\nu_{1H} \neq \nu_{1C}^{eff} + n\nu_R$$
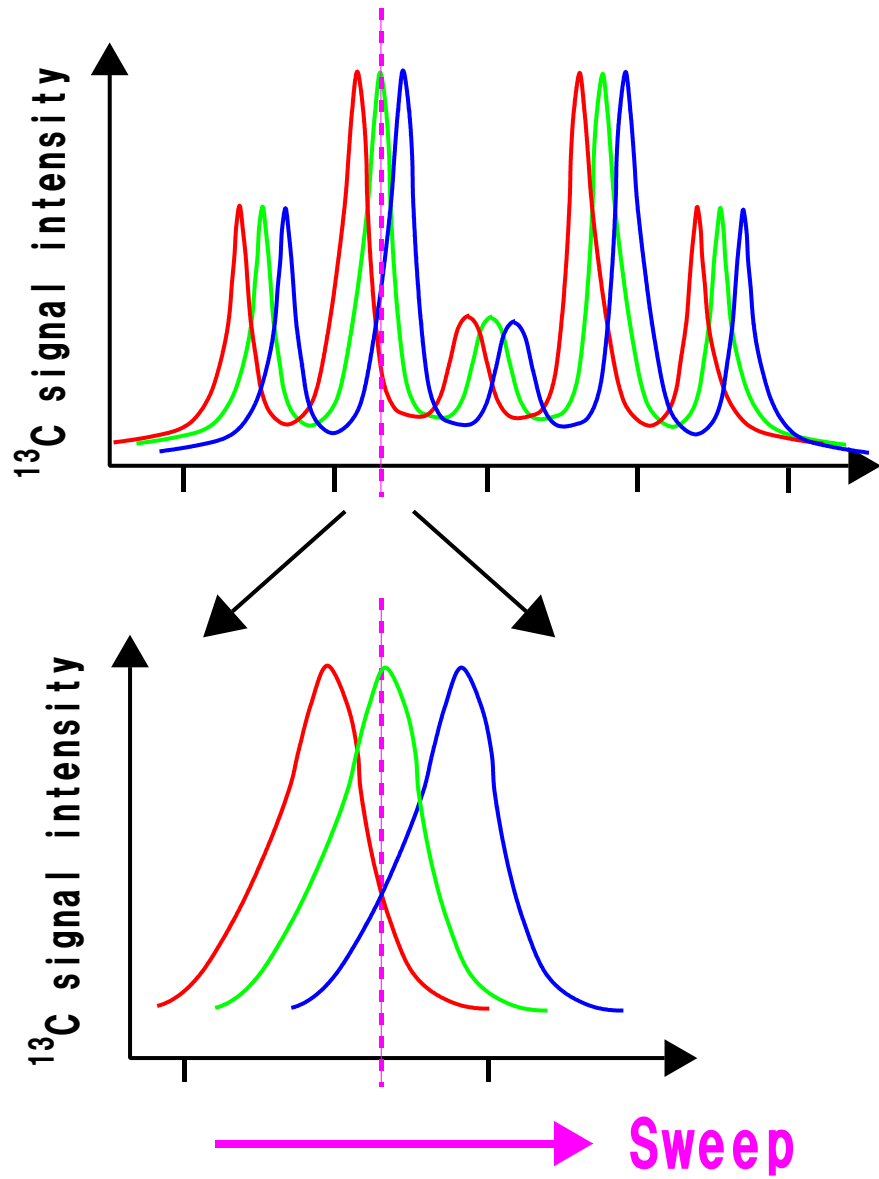
Effective field

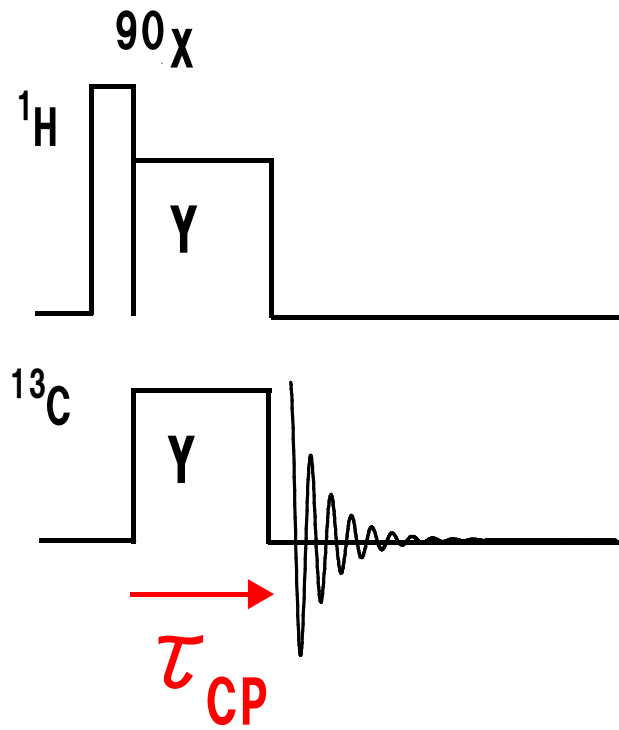$$\left|\nu_X^{eff}\right| = \sqrt{\nu_{1X}^2 + \Delta\nu_X^2}$$
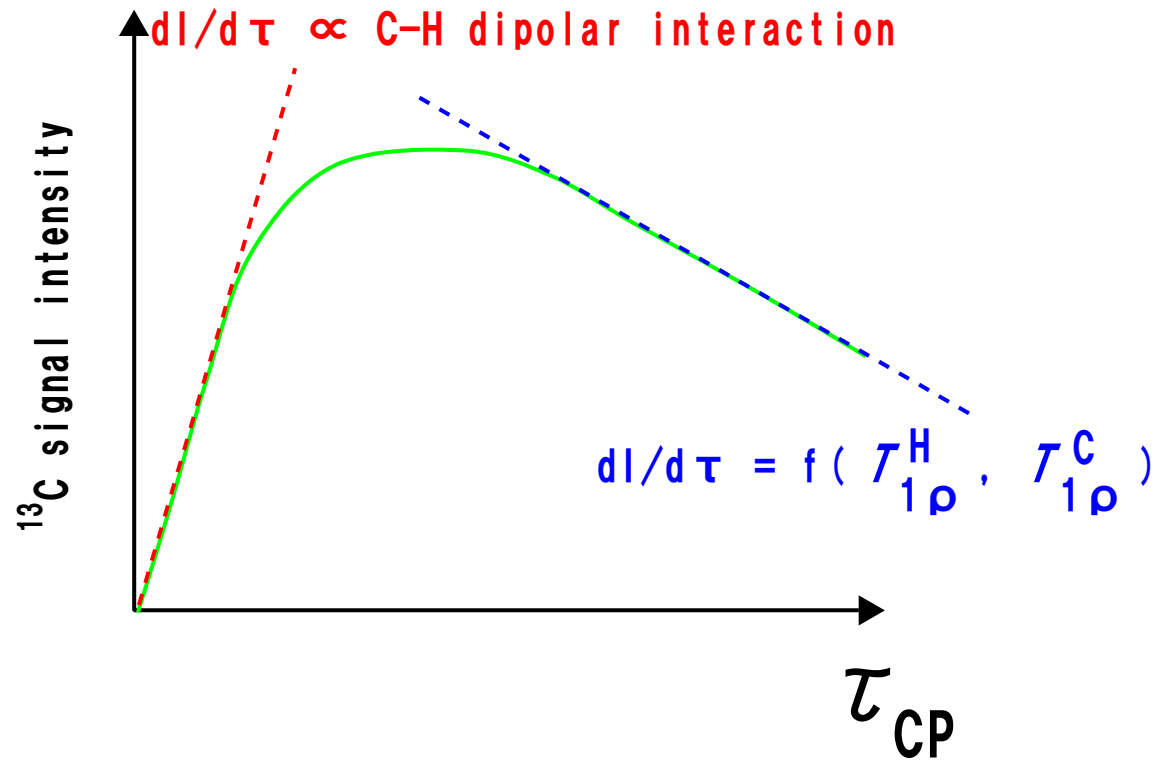
For a rigid system

a larger ^{1}H linewidt

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Ramped CP under MAS

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CP dynamics
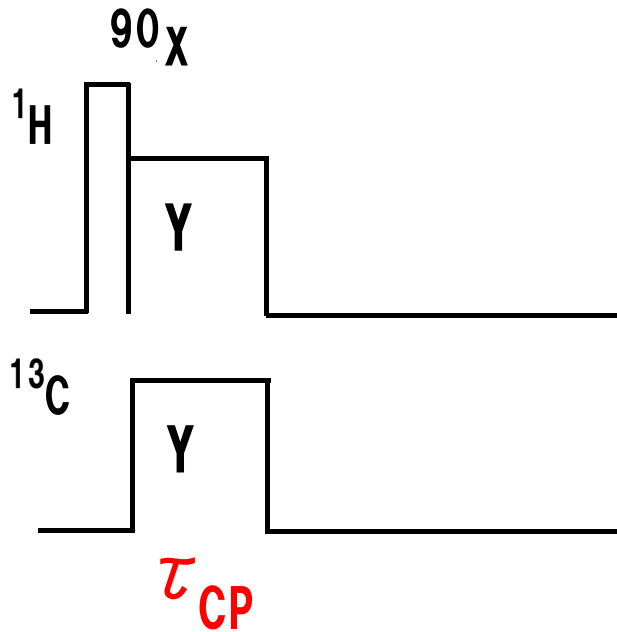

For a rigid C–H : quick buildup
Motional frequency $\sim \nu_1$: Short $T_{1\rho}$
$\longrightarrow$ quick decay

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Optimal contact time
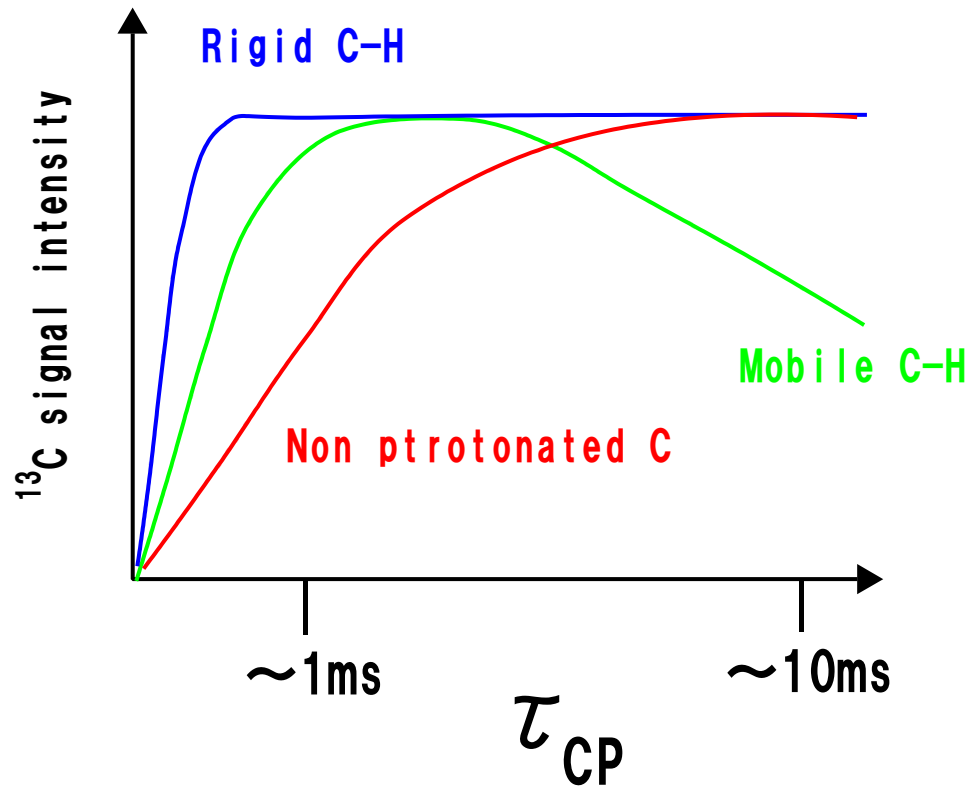
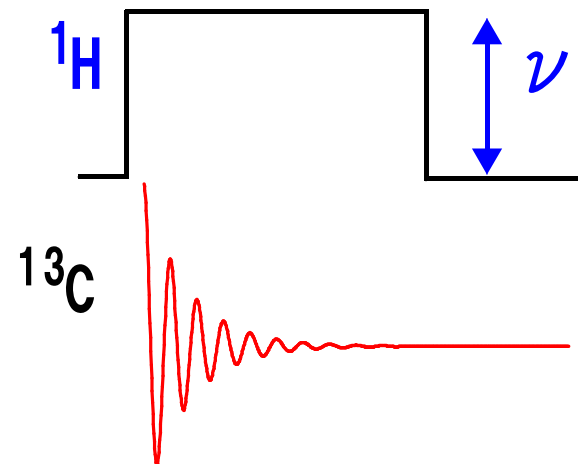
Note! Ramp CP requires a longer contact time!
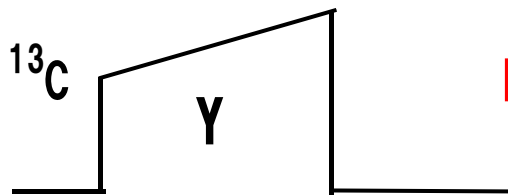
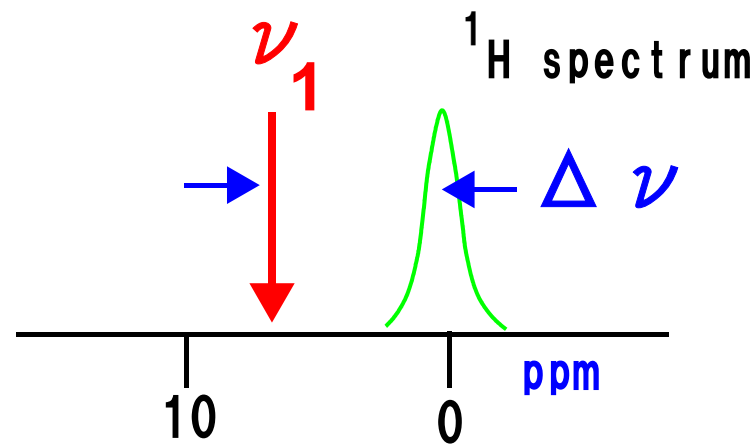Mind if your C–H system has short $T_{1\rho}$

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^{1}H decoupling

With ^{1}H decoupling

Without ^{1}H decoupling

Chemical Shift/ppm

300 200 100 0 -100

^{1}H

ν_1

^{13}C
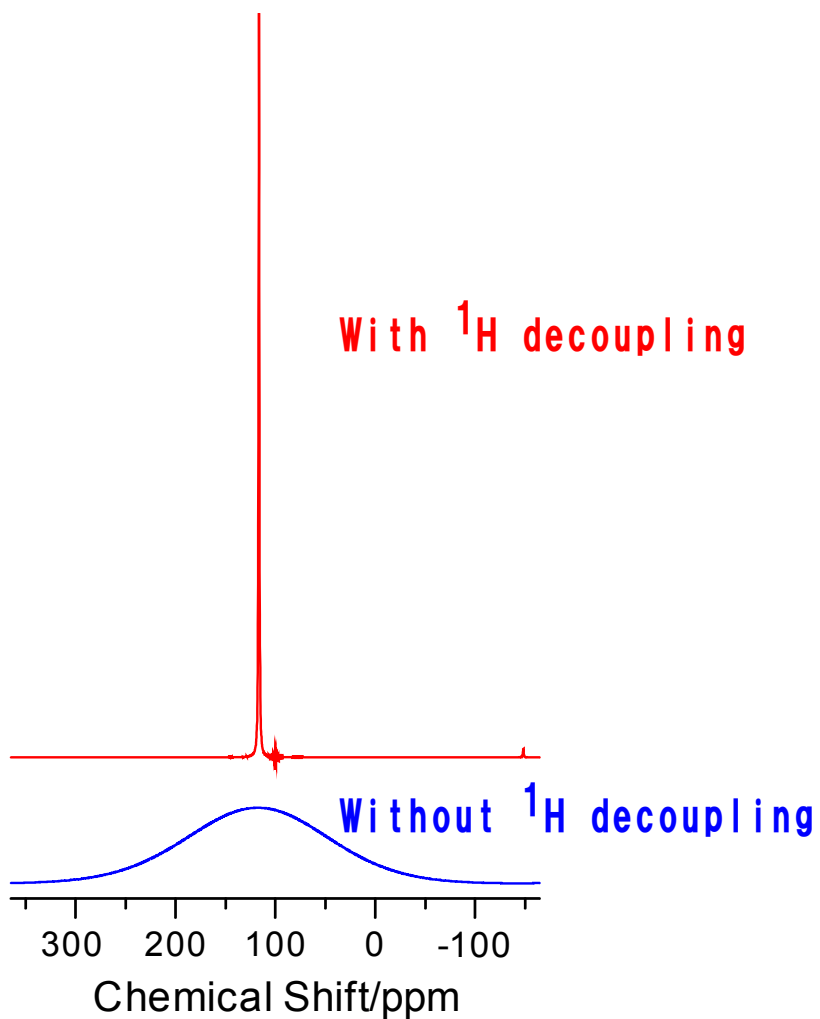
$\nu_1 \gg\ ^1H-^{13}C$ dipolar coupling
$\gg\ \sim 40$ kHz

$$d\ I_z S_z$$

irradiation on I

$$d(I_z \cos \nu_1 t\ +\ I_z \sin \nu_1 t)S_z$$

$$0$$

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Decoupling efficiency

Decoupling power

linewidth

~ C-H
interaction

ν_1

ν_1

^1H spectrum

$\Delta \nu$

10   0   ppm

Decoupling frequency

linewidth

CH$_2$
C=O
CH$_3$

10   0 ppm

$\Delta \nu$

θ

ν_1

Line width ~ cos θ

13
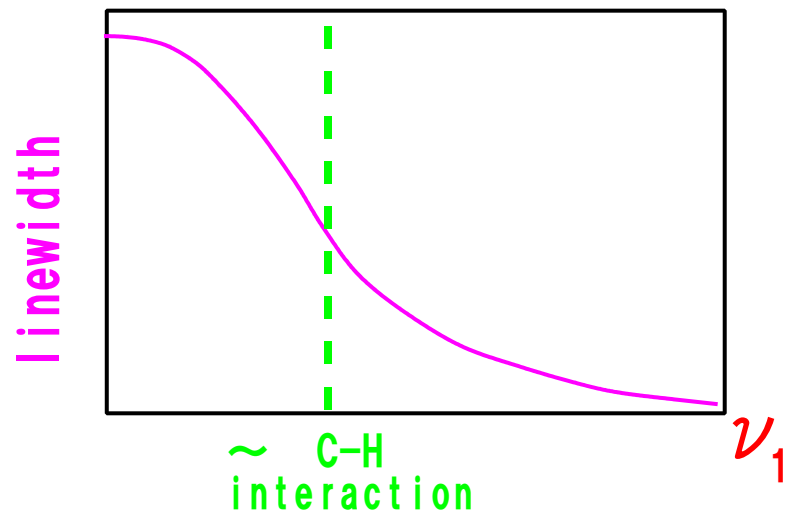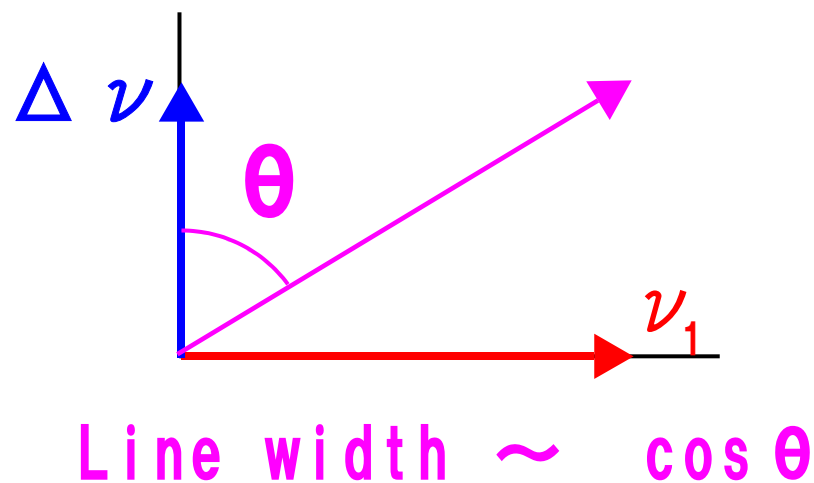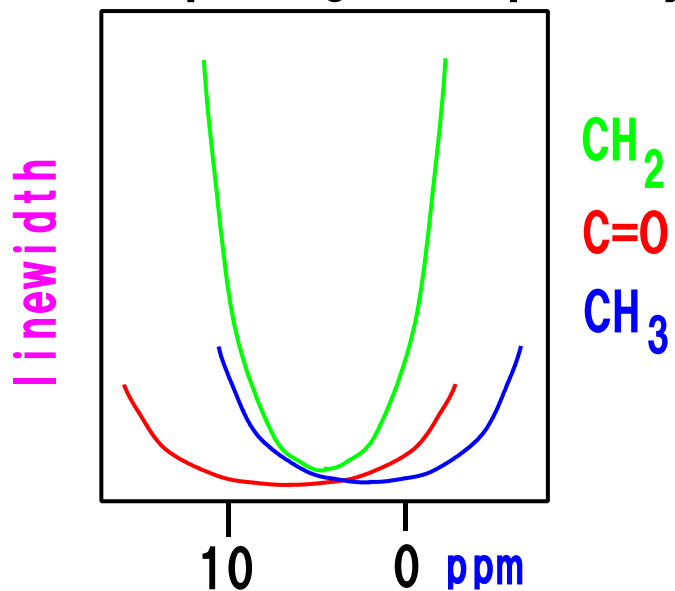
Decoupling and recoupling

X-^{13}C=O powder spectrum

δ_{iso}+ CSA + ^{13}C- X dipole

Remove
C-X dipole

Decoupling

How?

Remove CSA

Chemical Shift/ppm

δ_{iso}+ CSA

^{13}C- X dipole

Chemical Shift/ppm

Reintroduce
CSA

Chemical Shift/ppm

Recoupling

Remove CSA

MAS

δ_{iso}

Recoupling

Reintroduce
C-X dipole

Chemical Shift/ppm

14
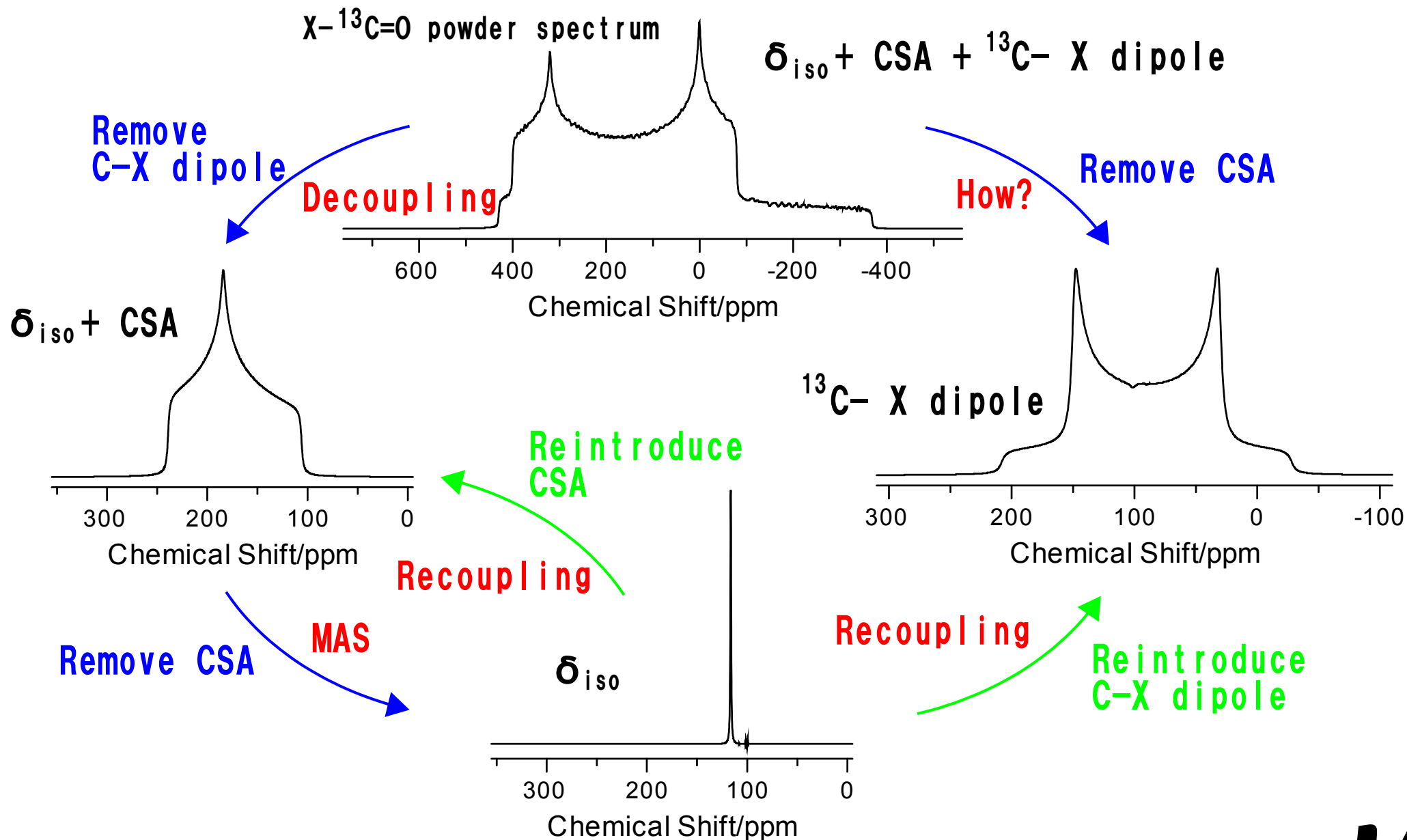
A simple case: a two I-S spin system

600 400 200 0 -200 -400
Chemical Shift/ppm

δ_{iso} + CSA + I-S dipole

300 200 100 0 -100
Chemical Shift/ppm
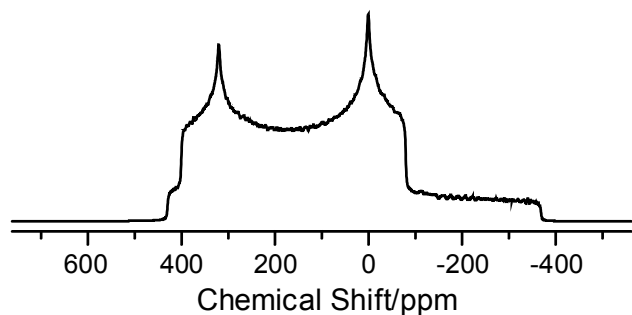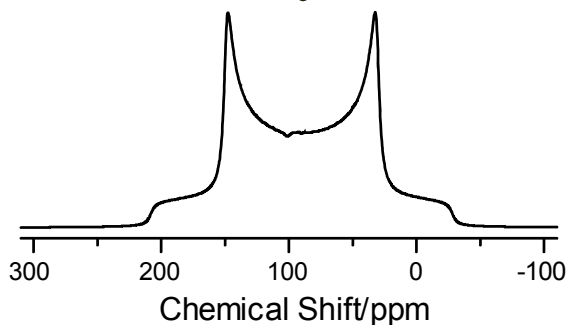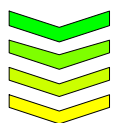
I-S dipole

I-S distance
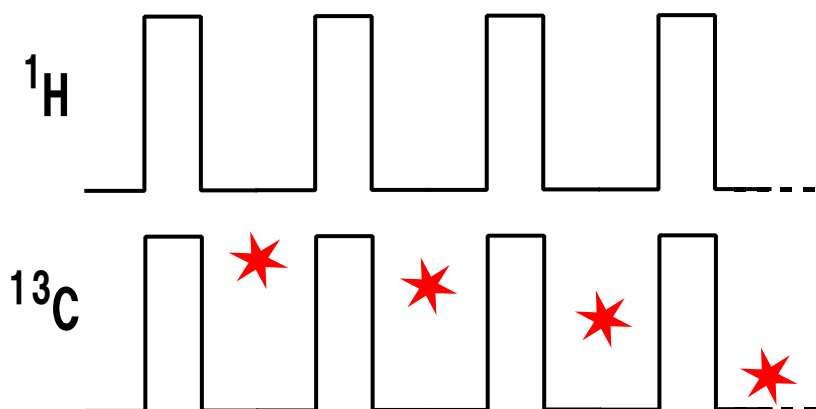
$$(\delta_{iso} + \delta_{csa})S_z + dI_z S_z \quad (1)$$

π pulse to S&I

$S_z \rightarrow -S_z$
$I_z \rightarrow -I_z$
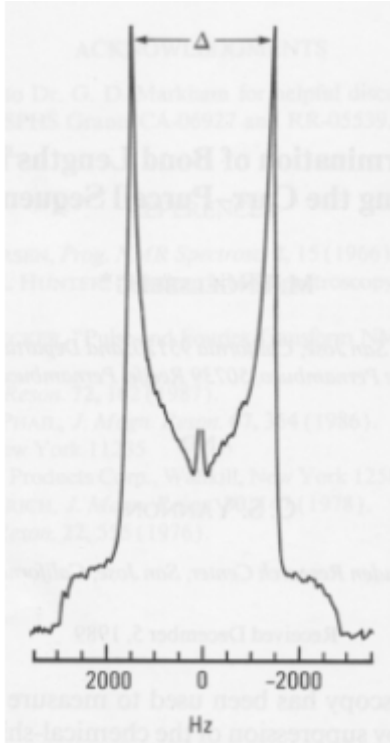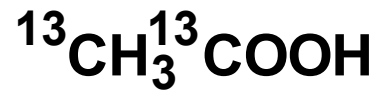
$$-(\delta_{iso} + \delta_{csa})S_z + dI_z S_z \quad (2)$$

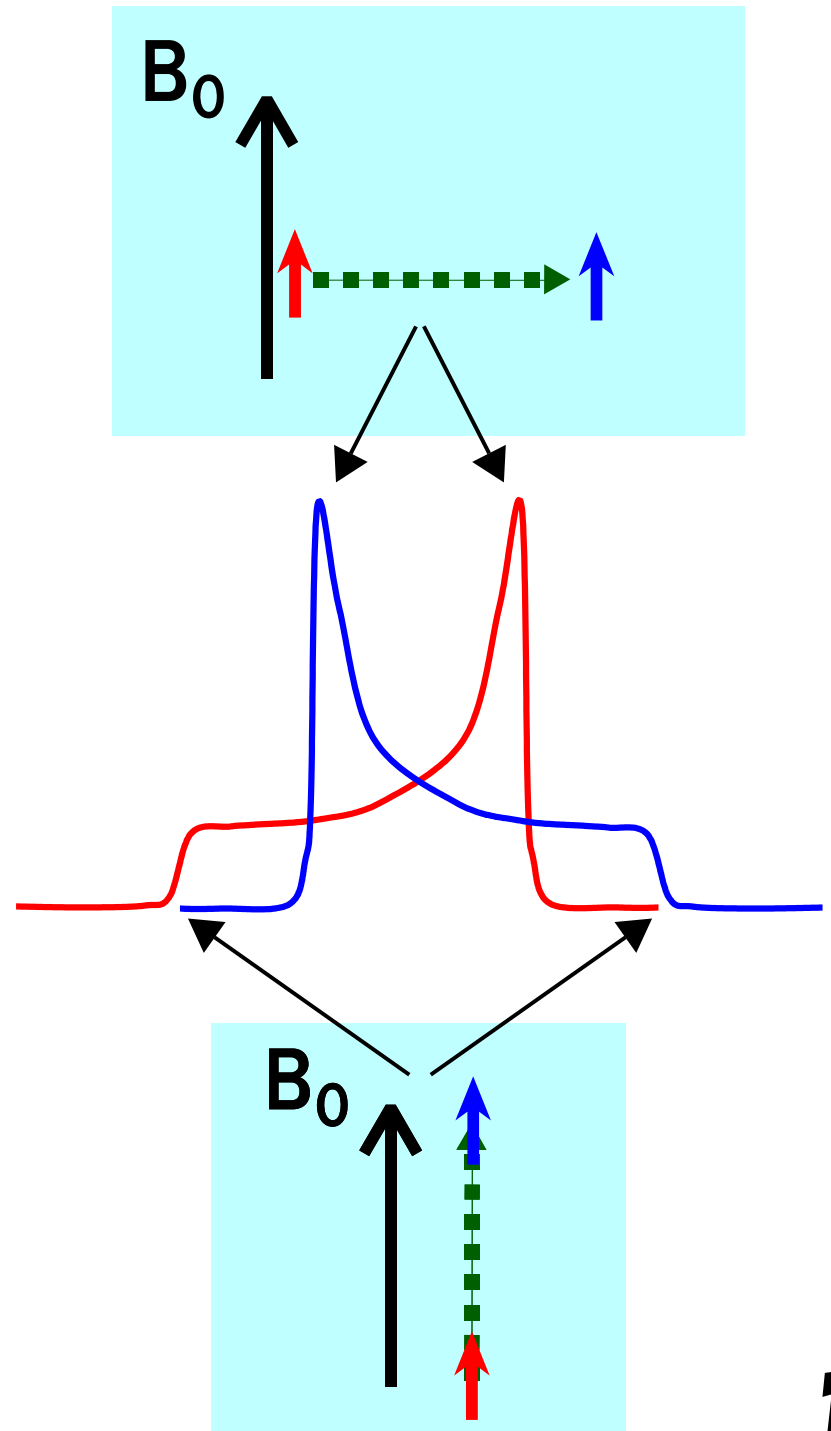$$\frac{(1)+(2)}{2} = dI_z S_z$$

π pulse trains to S&I

^{1}H

^{13}C

★ : Observe stroboscopically

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Dipolar powder pattern

$^{13}CH_3{}^{13}COOH$

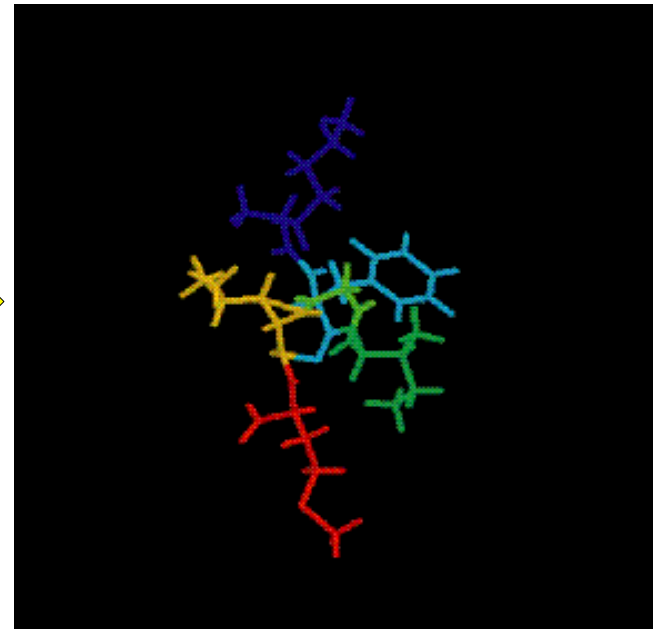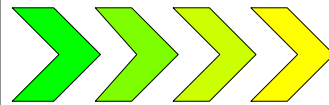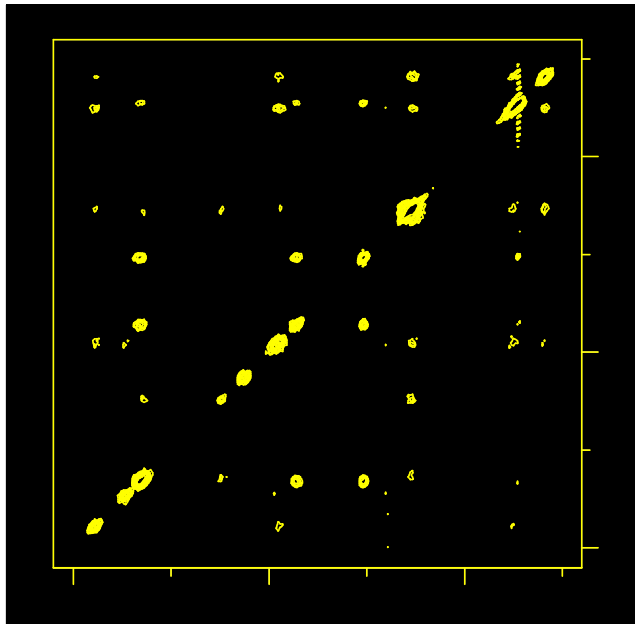$$\Delta = d_0(3\cos^2\theta - 1)/r^3$$

M. Engelsberg, C.S. Yannoni,
J. Magn. Reson., 88, 393 (1990)

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Strucutural determination by solid NMR

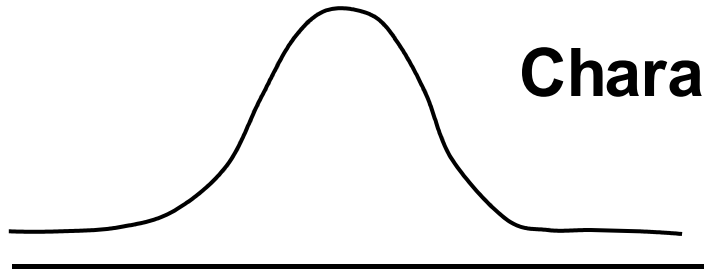Resolution of ^{1}H resonances is too bad....

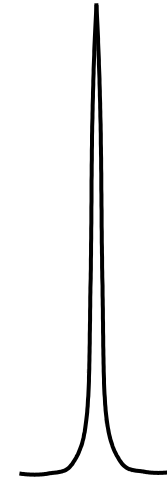We replace ^{12}C and ^{14}N by ^{13}C and ^{15}N to observed NMR...

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Uniform ^{13}C labeling

1) Spectral overlap due to anisotropic line broadening
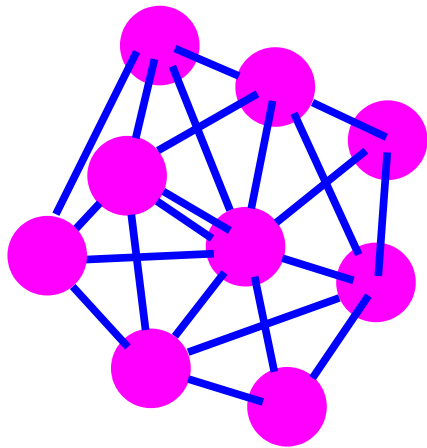
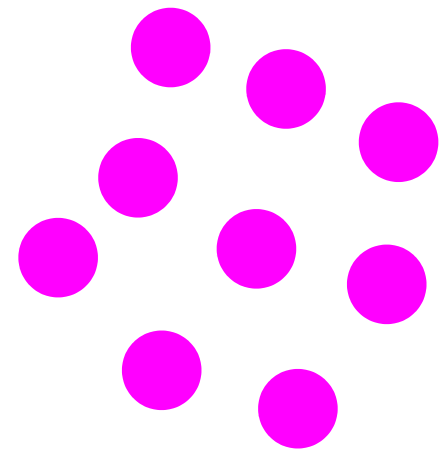**Chemical shift anisotropy & Dipole-dipole coupling**

Characterless lineshape

MAS

Remove CSA & dipolelar couplings

2) Many spin problem

$_nC_2$

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Recoupling under MAS

Spin interaction $H \sim$ [Space part] $\times$ [Spin part]

Space part $\sim$ $\cos \nu_R t$, $\cos 2 \nu_R t$ $\longrightarrow$ 0

MAS

time average

Spin part $\longrightarrow$ $S(t)$

rf

$$\int_0^\tau H(t) \, dt \qquad \longrightarrow \qquad \neq 0 \qquad \text{Recoupling}$$

Dipolar recoupling under MAS

MAS / C-X decoupling

δ_{iso}

300   200   100   0

Chemical Shift/ppm

^{13}C- X dipole

300   200   100   0   -100

Chemical Shift/ppm
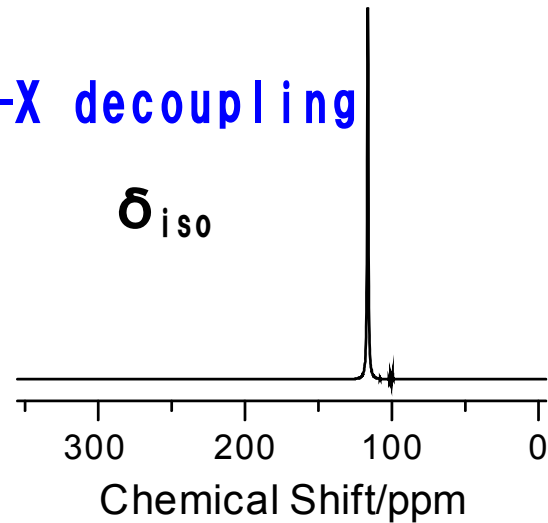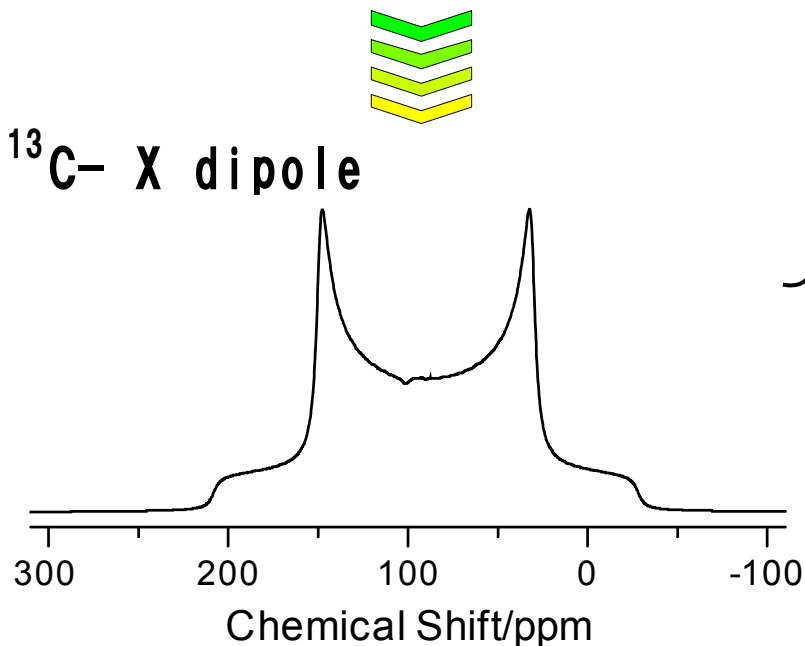
$$H_d = d(t)(I_z \cos \nu_1 t + I_x \sin \nu_1 t) S_z$$

$$d(t) = C_1 \cos(\nu_R t + \gamma) + C_2 \cos(2\nu_R t + 2\gamma)$$

$$\int_0^\tau H_d(t) dt$$
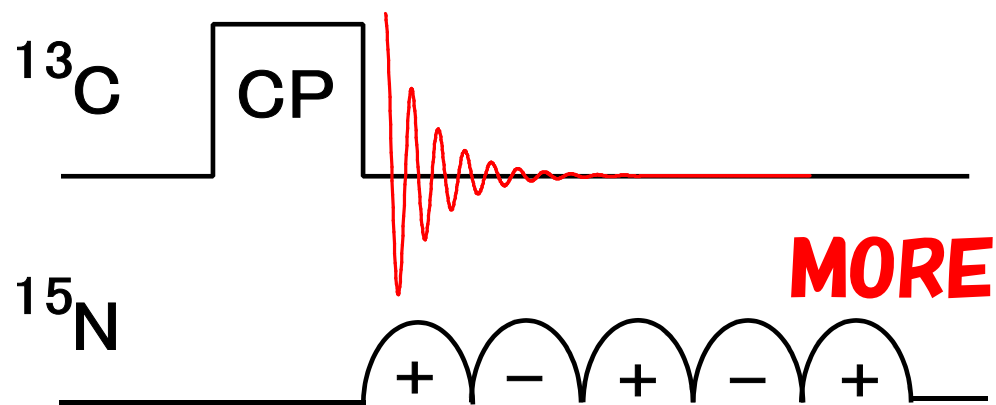
$\nu_1 \gg \nu_R$

$\longrightarrow 0$ Decoupling

$\longrightarrow \neq 0$ Recoupling

$\nu_1 = \nu_R$

(The rotary-resonance condition)

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eg. $^{13}C-^{15}N$ recoupling under MAS

^{13}C CP

MORE

^{15}N + − + − +
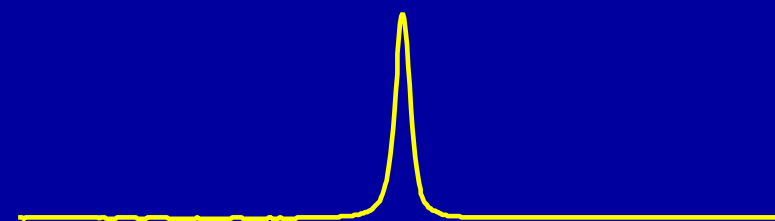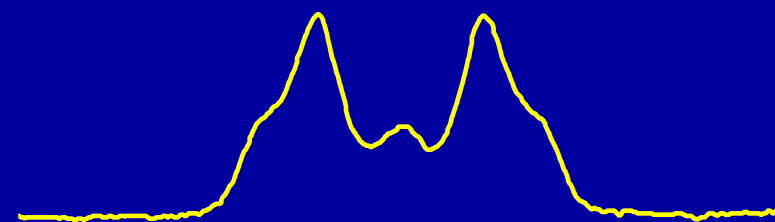
$$H_D^{CN}(t) = d(t) I_Z S_Z$$

$$H_{rf} = H_1 \cos(\omega t) S_X$$

$$\omega = \omega_{MAS} \times 1 \text{ or } 2$$
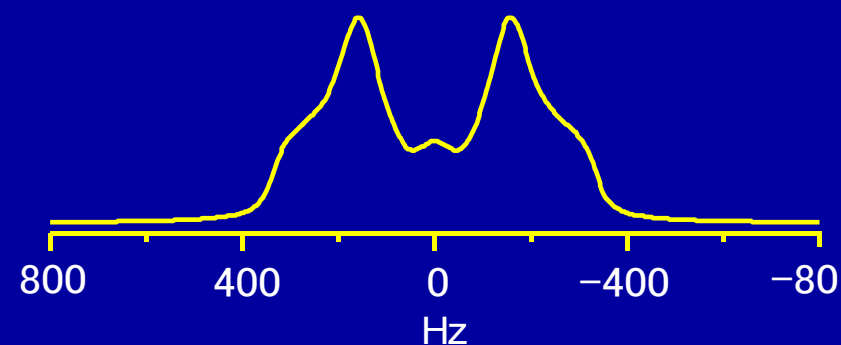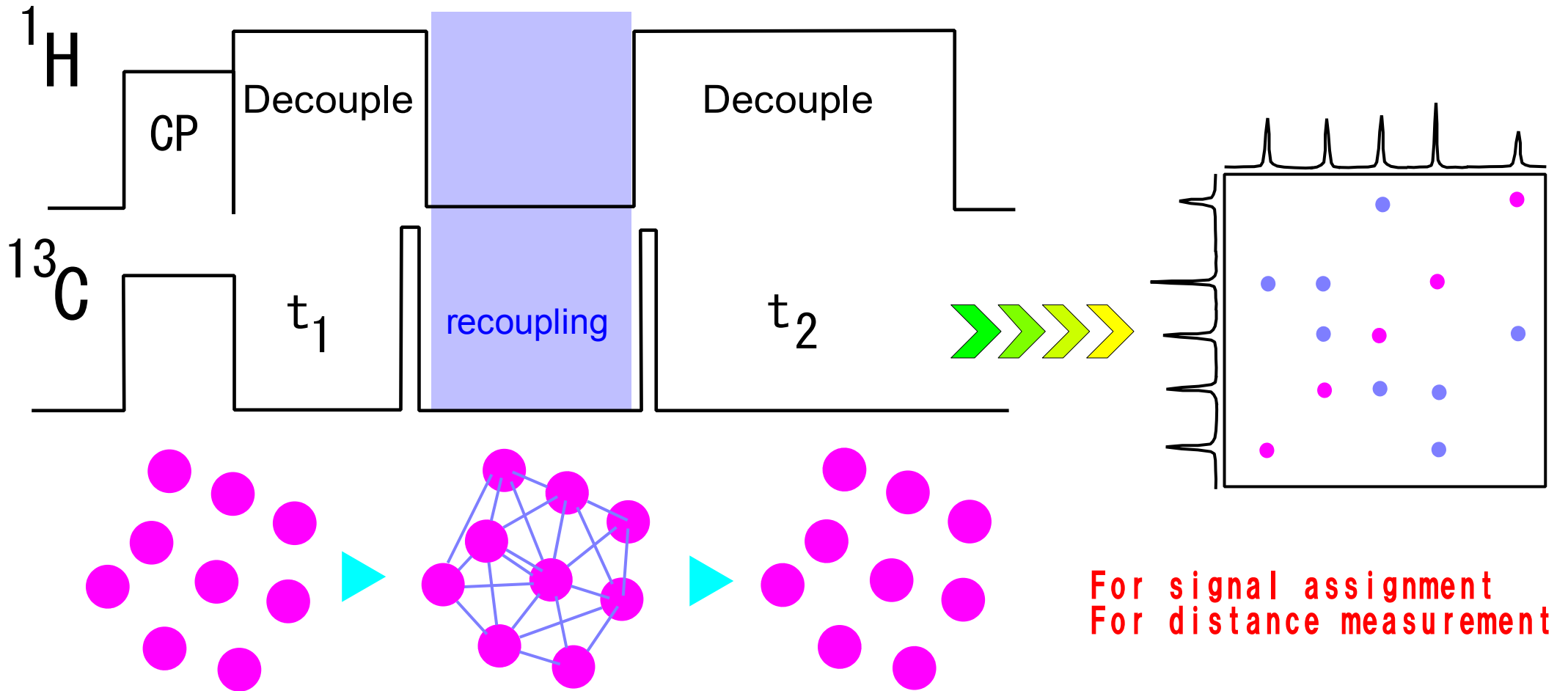
(a) conventional CPMAS

(b) MORE experimental

(c) MORE simulation

800   400   0   −400   −80

Hz

$[2-^{13}C,^{15}N]$ glycine

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Takegoshi, et al., Chem. Phys. Lett., 260 (1996) 331.

A 2D ^{13}C-^{13}C exchange experiment

^1H

CP

Decouple

recoupling

Decouple

^{13}C

t_1

t_2

For signal assignment
For distance measurement

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A 2D ^{15}N-^{13}C correlation experiment

Angles by solid NMR

B₀ → B_0

A dipolar
powder pattern

C,N-H recoupling

^1H — CP — N-H — C-H

^{15}N — CP

^{13}C — t_1 — t_2

θ_2 H

θ_1 N — C ϕ

H

C-H dipole

N-H dipole

Takegoshi, et al., Solid State NMR, 16 (2000) 271.