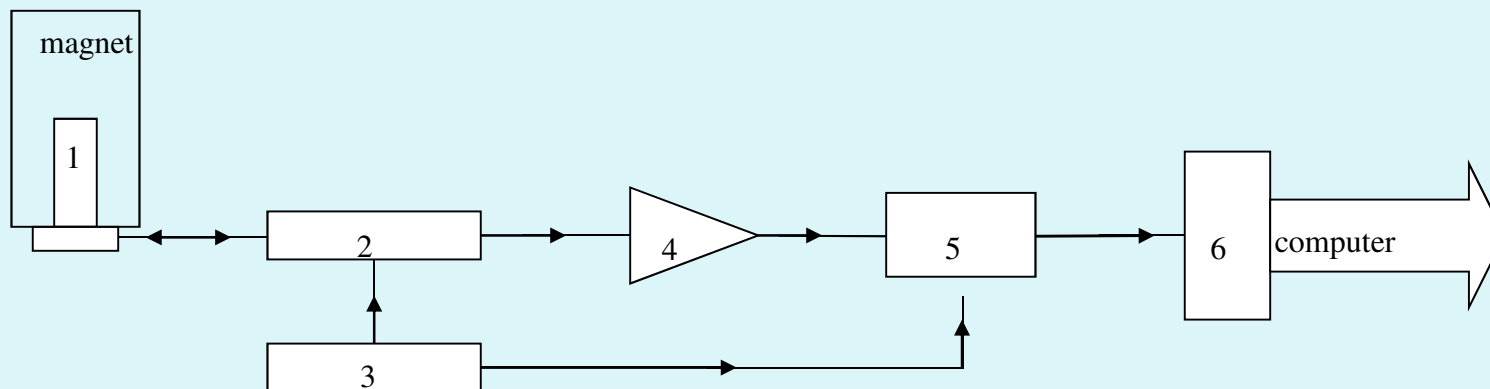Principios Básicos de RMN en sólidos destinado a usuarios

Gustavo Monti

Fa.M.A.F. – Universidad Nacional de Córdoba – Argentina

Block diagrama of a traditional NMR spectrometer.

1 probe,

2 signal preamplifier,

3 transmitter and power amplifier,

4 receptor,

5 detector (here the RF signal from the nuclei is converted into audio frequency signal),

6 analog to digital converter.

NMR spectrometers for solids are also characterized by the following specifications:

superconductors magnets have of 89 mm inner hole diameter (large diameter) to accommodate the probe which houses the sample.

Probes are equipped with MAS to obtain high resolution spectra.

RF amplifiers have high power to irradiate wide lines for decoupling.

Pneumatic drives are used to rotate the samples.

CPMAS probe, 7 mm rotor, coil and its stator.

4.7 T superconducting magnet, equivalent to a frequency of 300 MHz for protons.

1000 MHz (1 GHz) magnet

Nuclear Magnetic Resonance Spectrometer, Bruker Avance II
1) Computer
2) frequency generator, transmission and reception
3) High Power Amplifier
4) pneumatic unit sample rotation
5) Temperature control
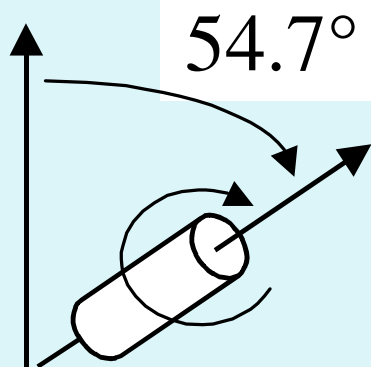6) Control of magnetic field external homogenization coils

Overview

Setup procedures for

- magic angle adjustment

- probe shimming

- cross polarization: Hartmann-Hahn match

- decoupling considerations

Why Do CP/MAS?

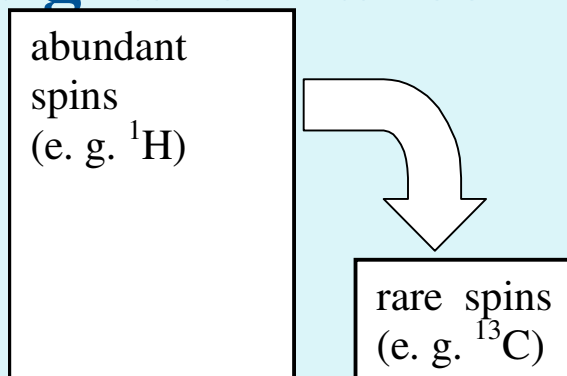**MAS = Magic Angle Spinning $\Rightarrow$ line narrowing**

54.7°

$$\left(3\cos^2\theta - 1\right)\overset{!}{=}0 \Leftrightarrow \theta = 54.7°$$

CP = Cross Polarization $\Rightarrow$ signal enhancement: γ_I/γ_S
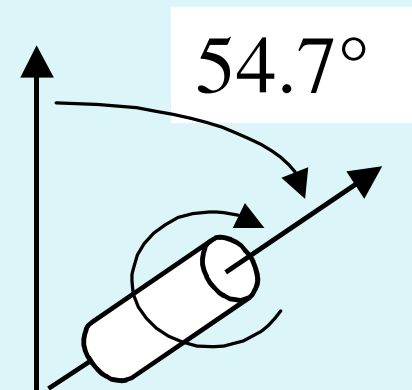
$^1H \Rightarrow {}^{13}C$: x 4

$^1H \Rightarrow {}^{15}N$: x 10

abundant
spins
(e. g. ^1H)

rare spins
(e. g. ^{13}C)

Magic Angle Adjustment

Requirements for setup sample:
- sensitive to angle setting:
  - large interaction to be averaged by MAS
  - narrow lines achievable
  - more sensitive than samples of interest
- easy to observe:
  - large signal
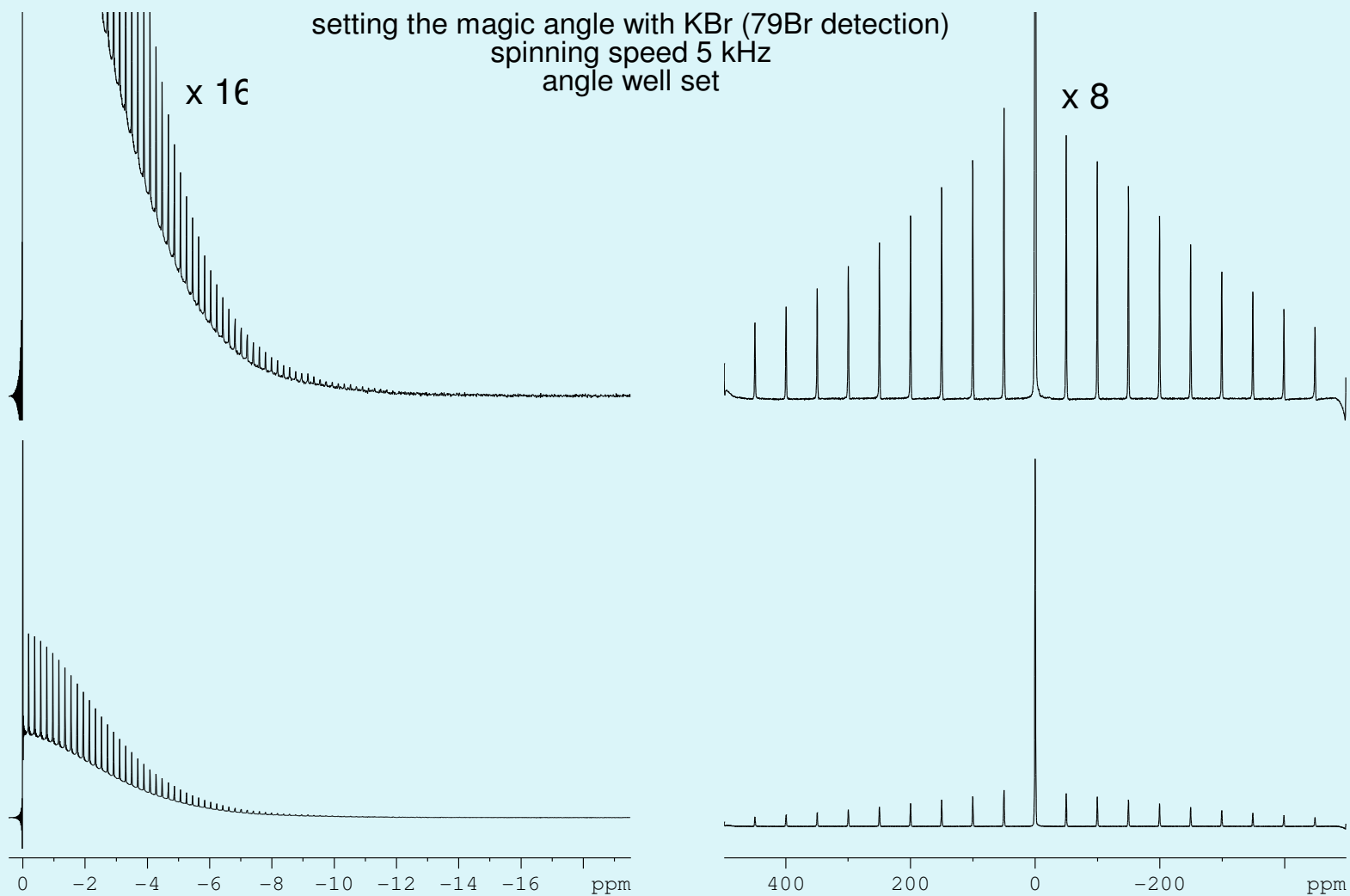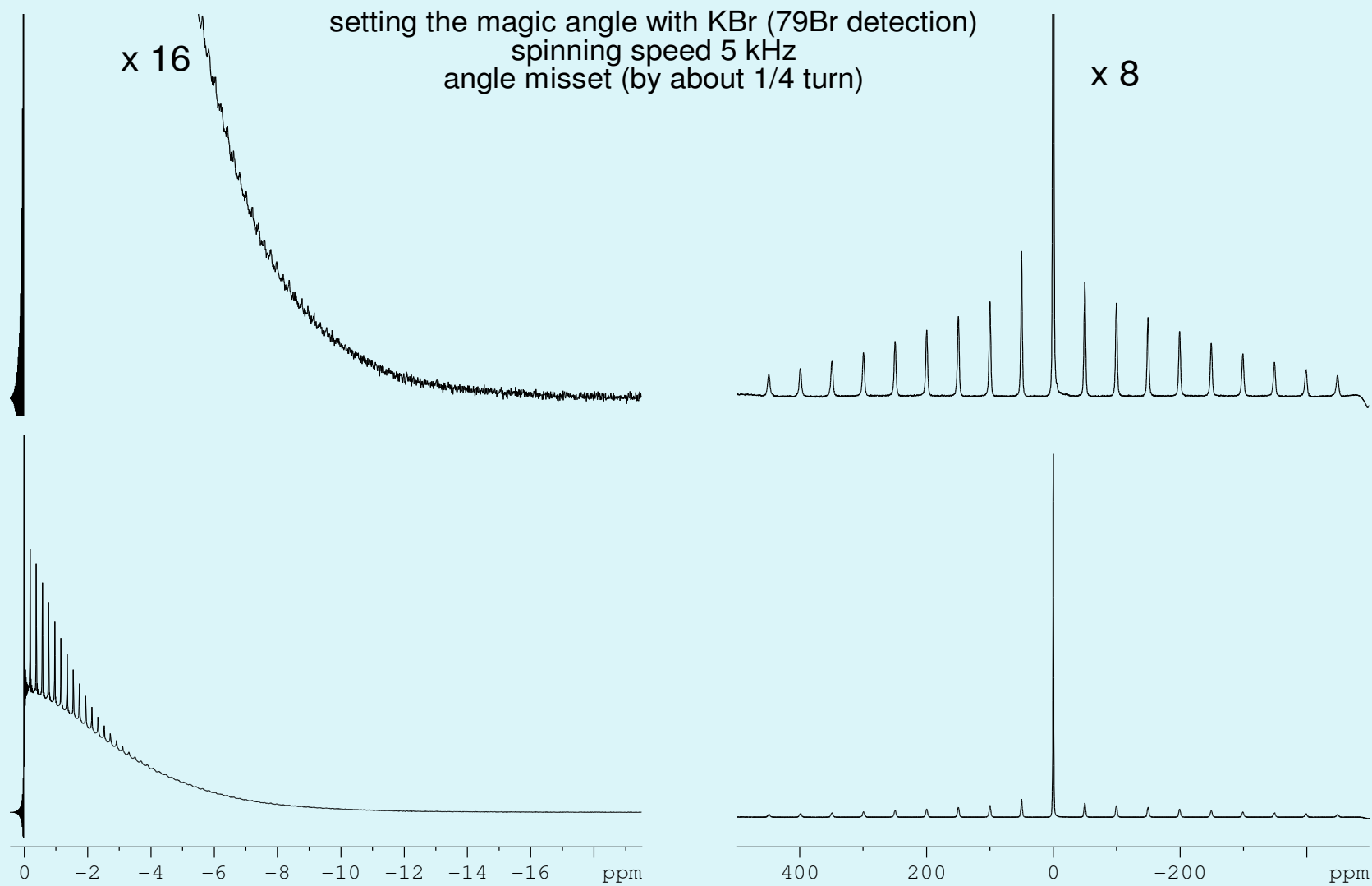 - at desired observe frequency

54.7°

Magic Angle Adjustment

Standard setup sample (^{13}C work):
KBr with ^{79}Br detection

- criterion: spinning sidebands

- sensitive to magic angle due to broad (MHz) quadrupolar interaction

- narrow lines

- close to ^{13}C frequency (300 MHz spectrometer: 75.16 MHz vs. 75.43 MHz), no change in routing, filters, preamplifier, probe range etc. required
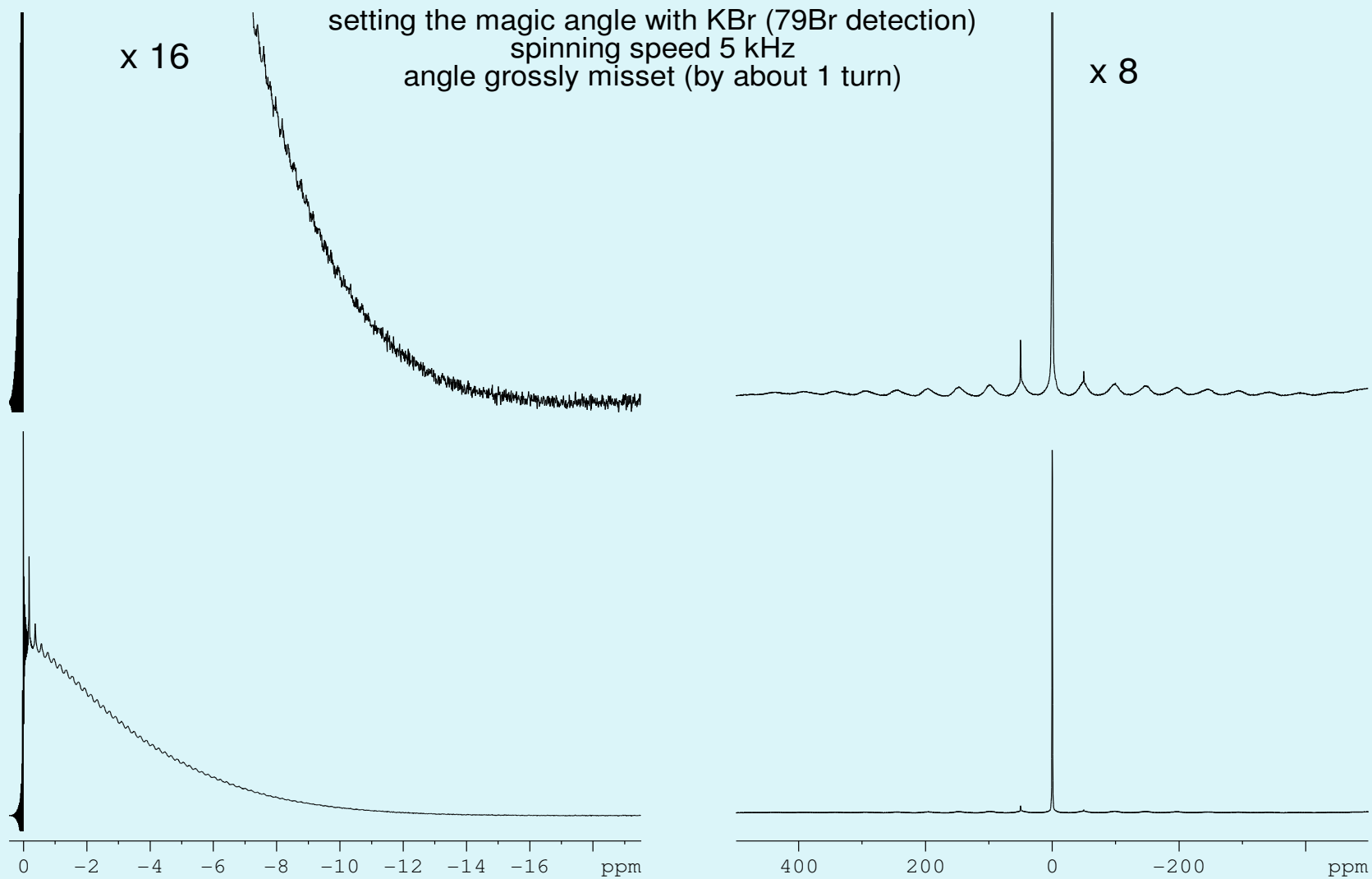
- good S/N (single scan)

Magic Angle Adjustment

setting the magic angle with KBr (79Br detection)
spinning speed 5 kHz
angle well set

x 16

x 8

0   −2   −4   −6   −8   −10   −12   −14   −16   ppm

400   200   0   −200   ppm

Magic Angle Adjustment

x 16

setting the magic angle with KBr (79Br detection)
spinning speed 5 kHz
angle misset (by about 1/4 turn)

x 8

0   −2   −4   −6   −8   −10   −12   −14   −16   ppm

400   200   0   −200   ppm

Magic Angle Adjustment

x 16

setting the magic angle with KBr (79Br detection)
spinning speed 5 kHz
angle grossly misset (by about 1 turn)

x 8

| 0 | −2 | −4 | −6 | −8 | −10 | −12 | −14 | −16 | ppm |

| 400 | 200 | 0 | −200 | ppm |

Probe Shimming

Some hints:

- shimming is done on FID or spectrum (no lock used)

- usually requirements are less demanding as compared to liquids
(e. g. ^{13}C: < 10 Hz)

- MAS on axis and off axis shims are a combination of standard on axis (z, z^2, ...) and off axis (x, y, ...) shims

- at high spinning speeds: MAS off axis shims less important

Probe Shimming

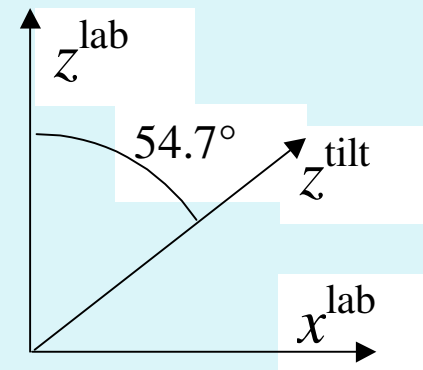relation of MAS (tilted) and laboratory frame shims

$$B_z^{\text{tilt}} = \frac{1}{\sqrt{3}} B_z^{\text{lab}} - \frac{\sqrt{2}}{\sqrt{3}} B_x^{\text{lab}}$$

first order

$$B_x^{\text{tilt}} = \frac{1}{\sqrt{3}} B_x^{\text{lab}} - \frac{\sqrt{2}}{\sqrt{3}} B_z^{\text{lab}}$$

$$B_y^{\text{tilt}} = B_y^{\text{lab}}$$

z^{lab}, $54.7°$, z^{tilt}, x^{lab}

$$B_{z^2}^{\text{tilt}} = B_{(x^2-y^2)}^{\text{lab}} - 2\sqrt{2} B_{zx}^{\text{lab}}$$

second order

$$B_{zx}^{\text{tilt}} = -\frac{1}{3} B_{zx}^{\text{lab}} + \frac{\sqrt{2}}{6} B_{z^2}^{\text{lab}} - \frac{\sqrt{2}}{6} B_{(x^2-y^2)}^{\text{lab}}$$

A. Sodickson and D. G. Cory,
J. Magn. Reso. 128, 87 (1997)

$$B_{zy}^{\text{tilt}} = \frac{1}{\sqrt{3}} B_{zy}^{\text{lab}} - \frac{\sqrt{2}}{\sqrt{3}} B_{xy}^{\text{lab}}$$

$\vdots$
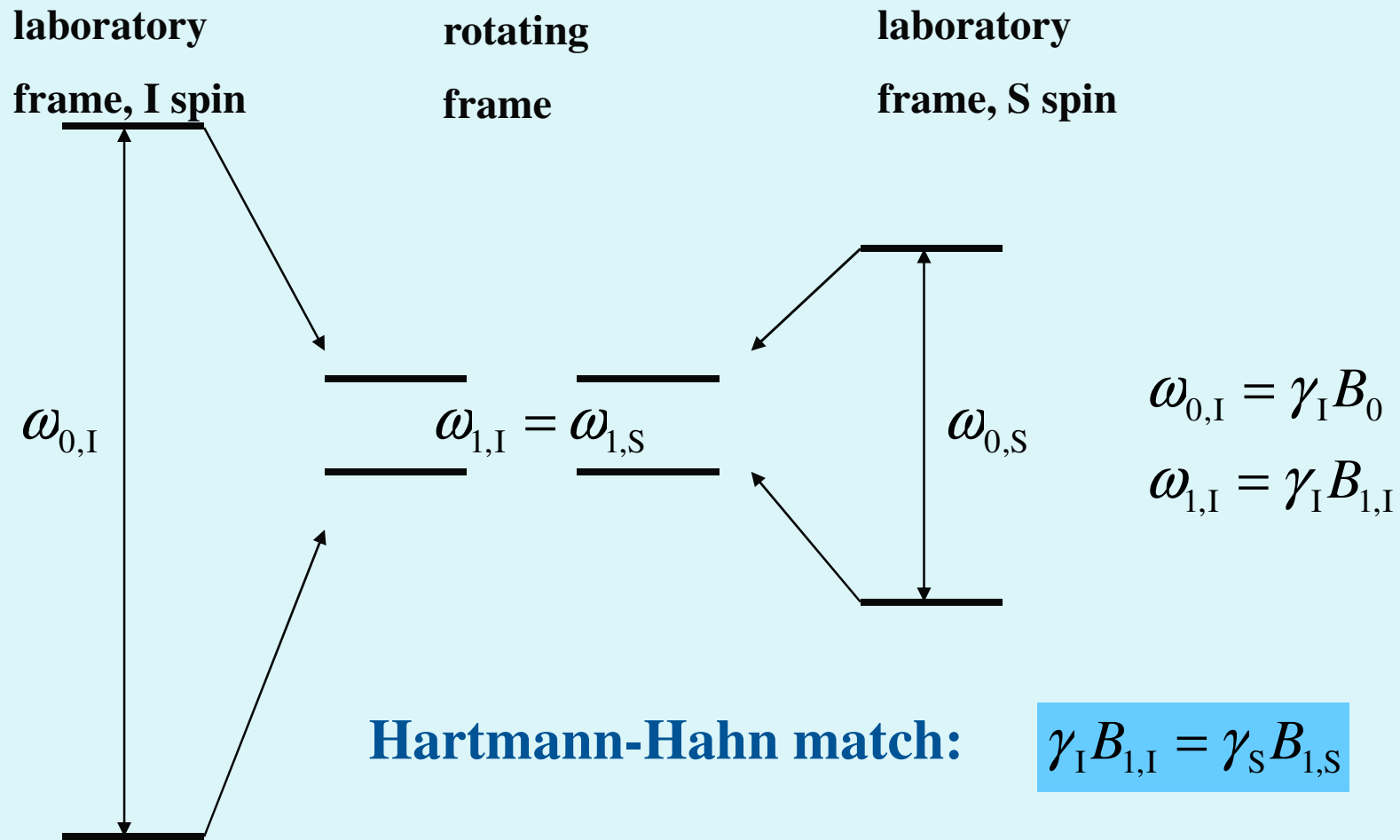
Probe Shimming

^{13}C resolution with adamantane
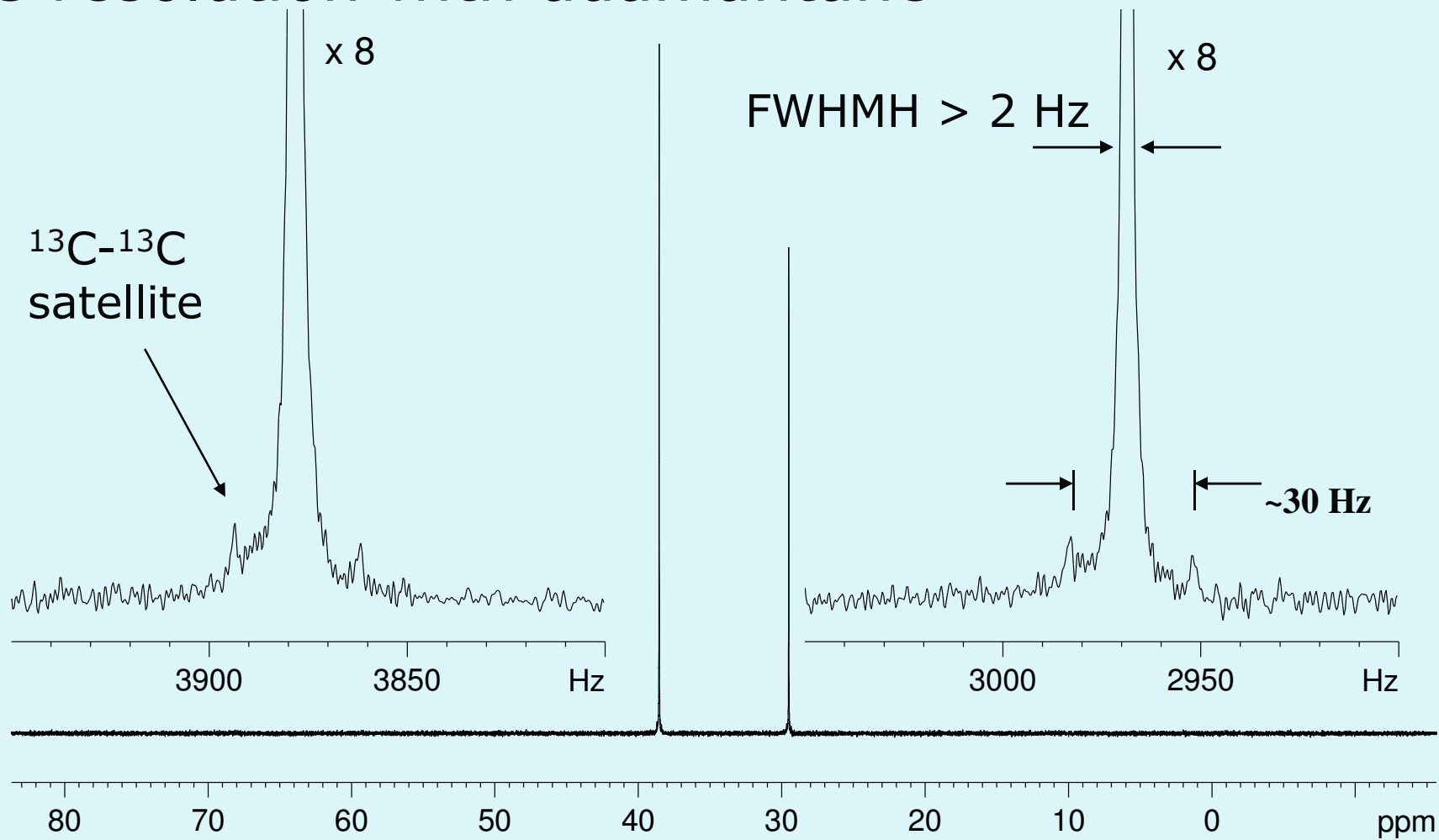
Cross Polarization - Basic Principles

energy level matching: Hartmann-Hahn matching

laboratory frame, I spin

rotating frame

laboratory frame, S spin

$\omega_{0,I}$

$\omega_{1,I} = \omega_{1,S}$

$\omega_{0,S}$

$$\omega_{0,I} = \gamma_I B_0$$

$$\omega_{1,I} = \gamma_I B_{1,I}$$

Hartmann-Hahn match: $\quad \gamma_I B_{1,I} = \gamma_S B_{1,S}$

Basic CP(MAS) Pulse Sequence

90_x

^1H

contact

decoupling

^{13}C

contact

aquire
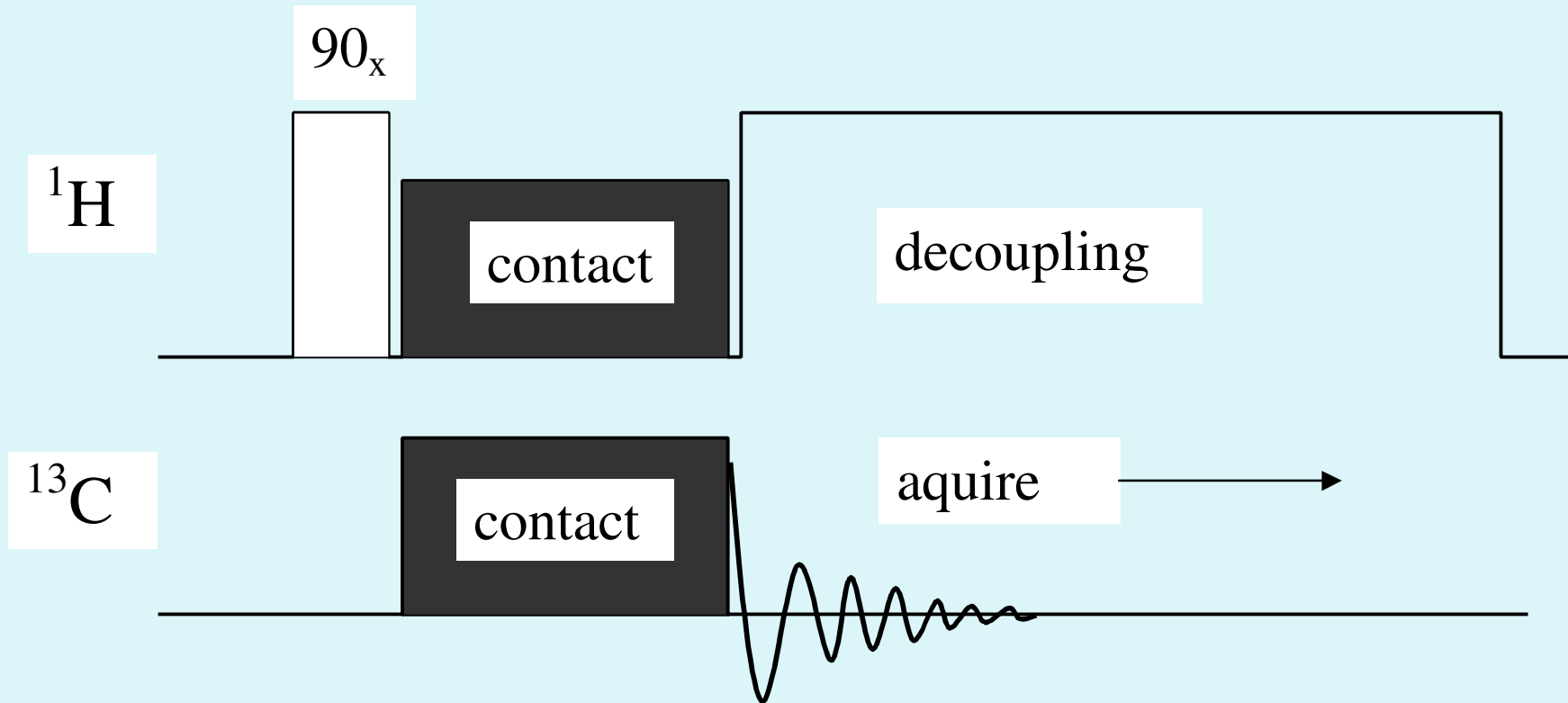
Cross Polarization

What can be achieved:

signal enhancement by polarization transfer: $\dfrac{\gamma_I}{\gamma_S} \cdot \dfrac{1}{1+\varepsilon}$

$$\varepsilon = \frac{N_S}{N_I}$$

nucleus	natural abundance	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 ~ 5 $T_{1,^1H}$

usually $T_{1,^1H} \ll T_{1,^{13}C}$ ($T_{1,^{15}N}$ ...)

Cross polarisation: criteria

robustness:

      width of Hartmann-Hahn-condition

      dependence on rotation frequency

$$\gamma_1 B_1 = \gamma_2 B_1 + n \cdot 2\pi v_{rot}$$

efficiency

$$f_{max} = \frac{\gamma_{^1H}}{\gamma_X}$$

recycle delay is now determined by ^1H T_1

BUT: consider probe duty cycle!!

CPMAS spectrum of glycine (5 kHz spinning speed)

Carbxyl ^{13}C:
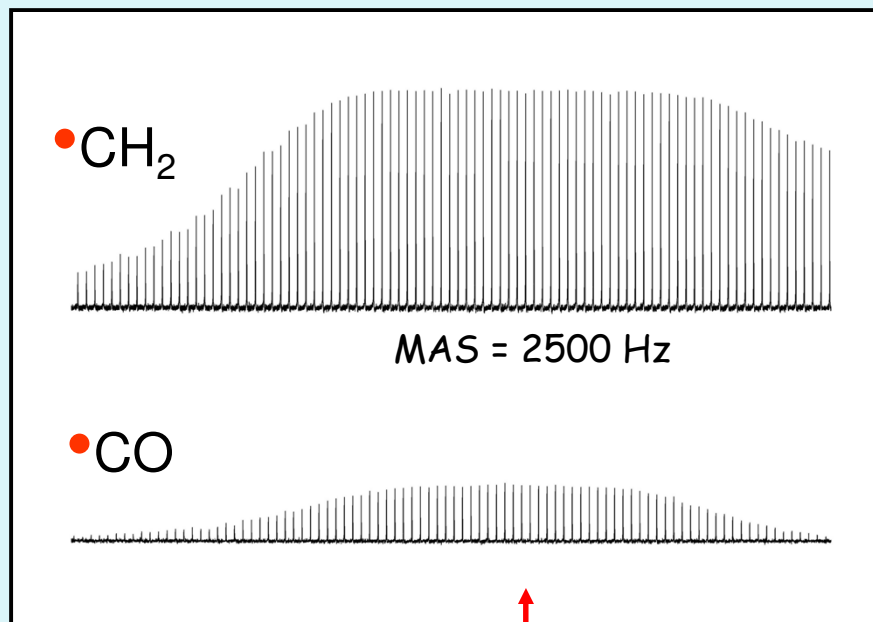- sensitive HH match
- easy to decouple
- sensitive to angle

$$HOOC-CH_2-NH_2$$
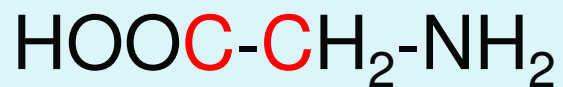
$^{13}C_a$:
- broad HH match
- high power decoupling
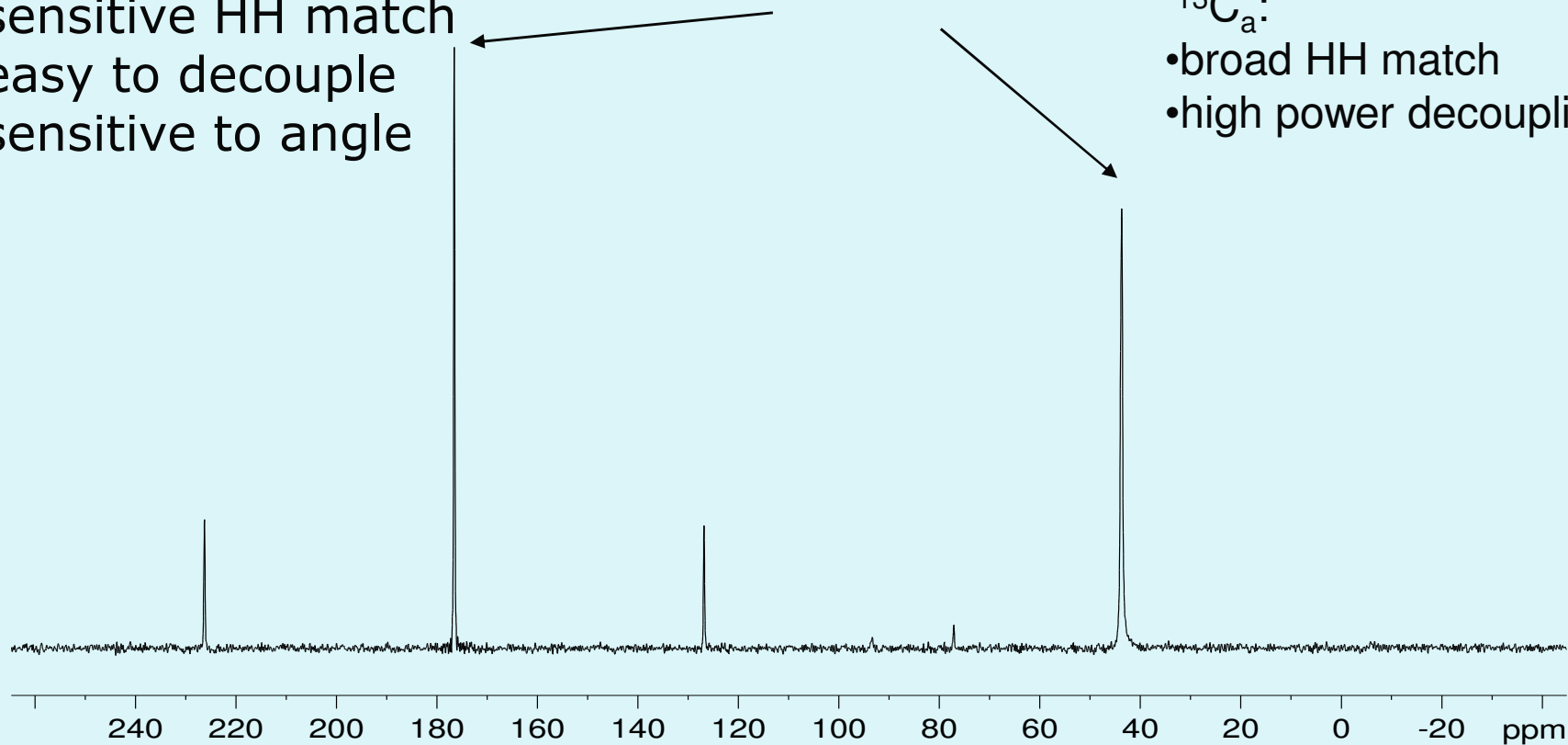
Hartmann-Hahn matching profiles

Glycine ^{13}C signal amplitudes as function of ^{1}H RF field
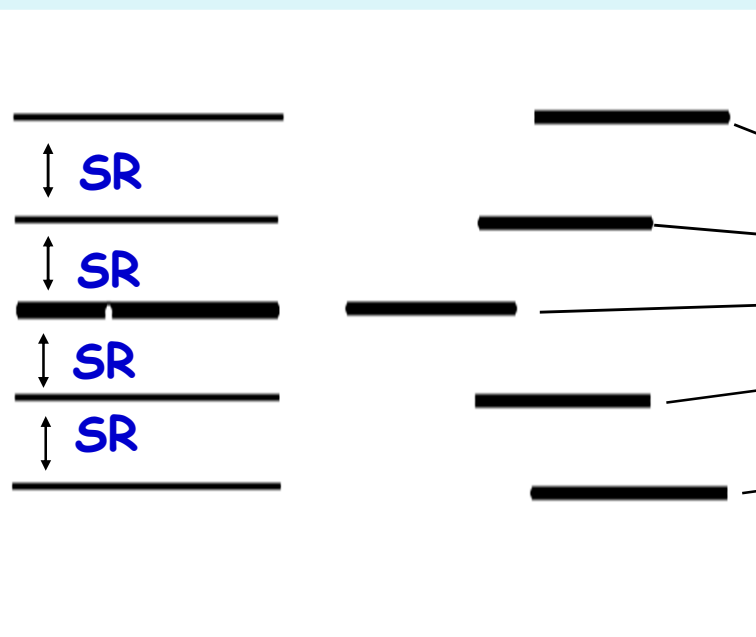^{13}C RF field constant at 45 kHz
using square pulses for CP

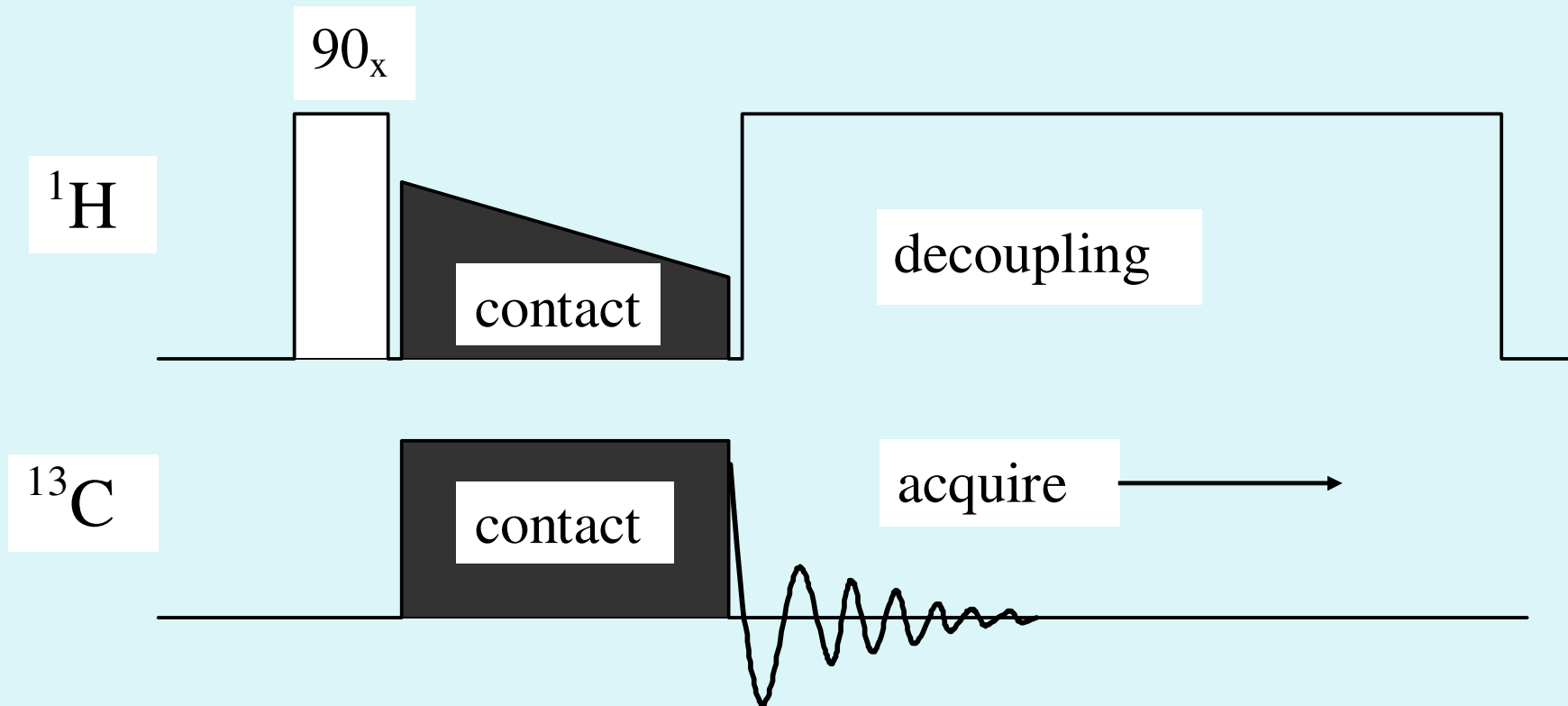# Hartmann-Hahn matching profiles

What is the reason for these intensity modulations?
The homonuclear proton-proton dipole coupling is modulated by the spin rate!

Proton   matching carbon
energy level   energy level

CH_2

MAS = 12500 Hz

CO

SR
SR
SR
SR

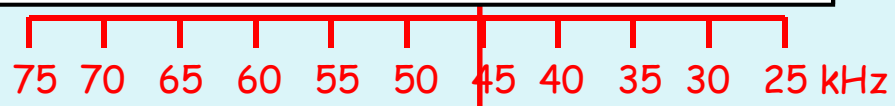75 70 65 60 55 50 45 40 35 30 25 kHz
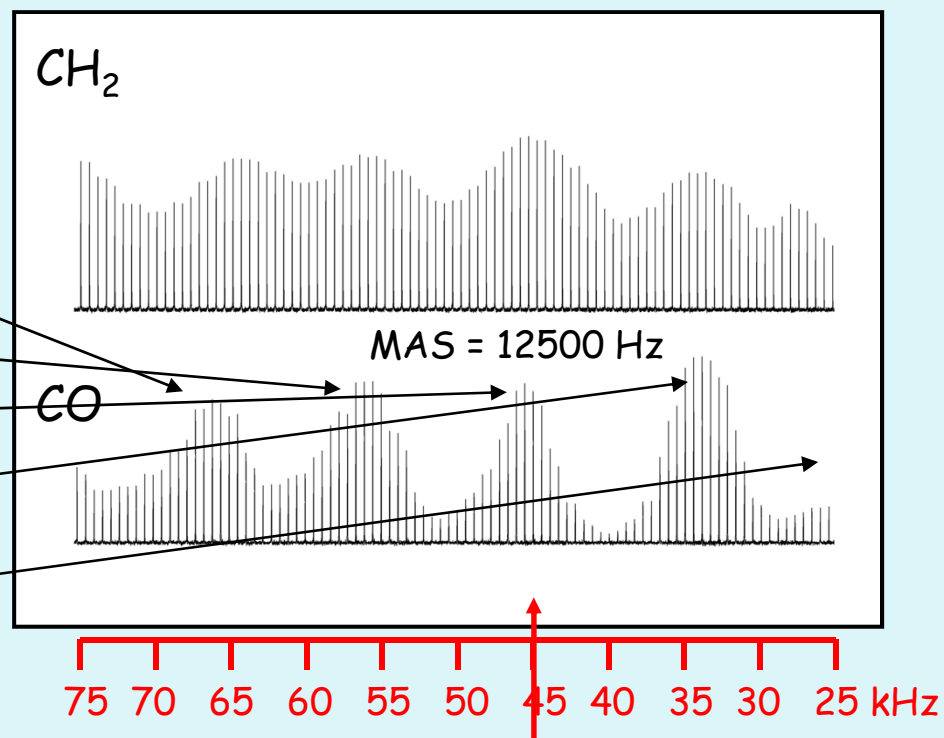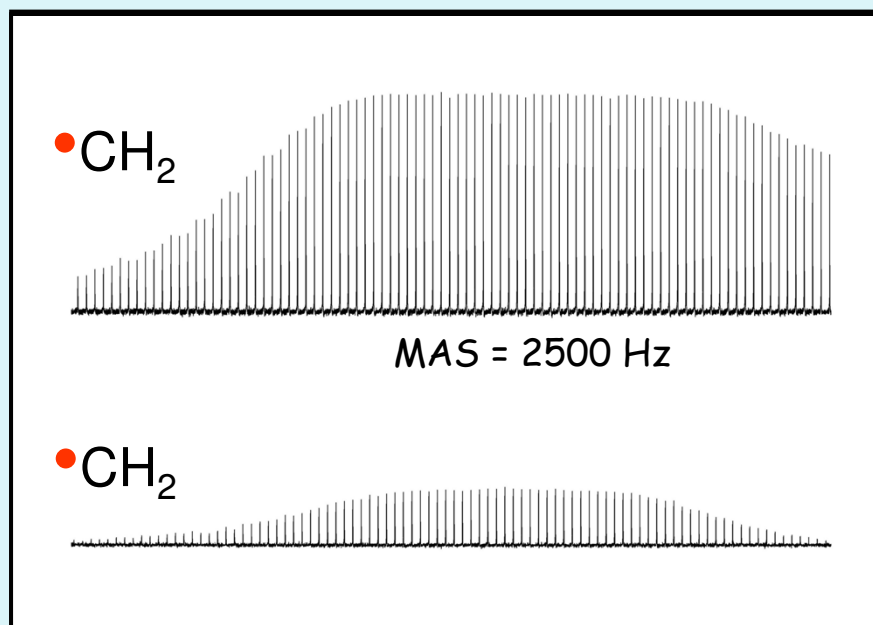
Ha-Ha-match

Ramped (Variable Amplitude) Cross Polarization
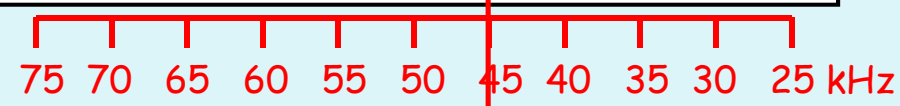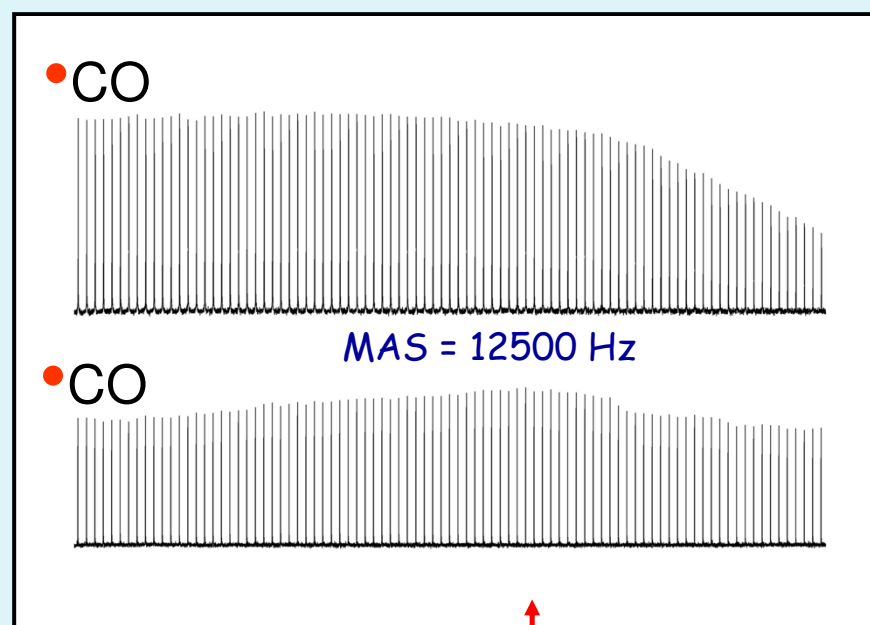
Hartmann-Hahn matching profiles

Glycine ^{13}C signal amplitudes as function of ^1H RF field
^{13}C RF field constant at 45 kHz
using ramp pulse for CP from 100% to 50% amplitude

VACP: possible problems
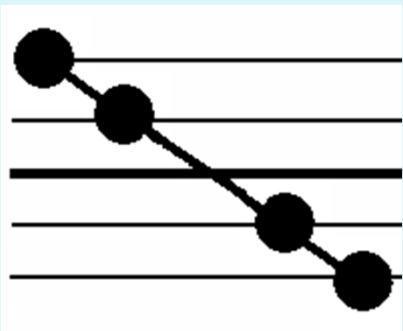

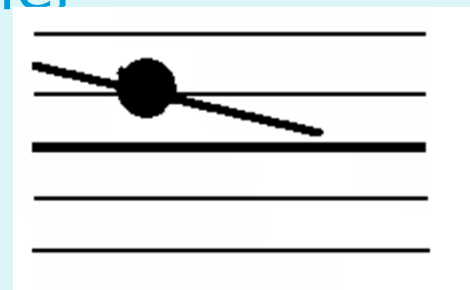Actual transfer occurs during precise match to
spinning sideband!

-transfer does not occur during the whole pulse

-proton spin lock field not at constant high
 level, proton $T_{1\rho}$ may be shortened

Optimum setup:
Flat (10)% ramp over first sideband to higher power, just to compensate for misset and drift.

However:
Must be optimised for spin rate!

Cross Polarization Dynamics
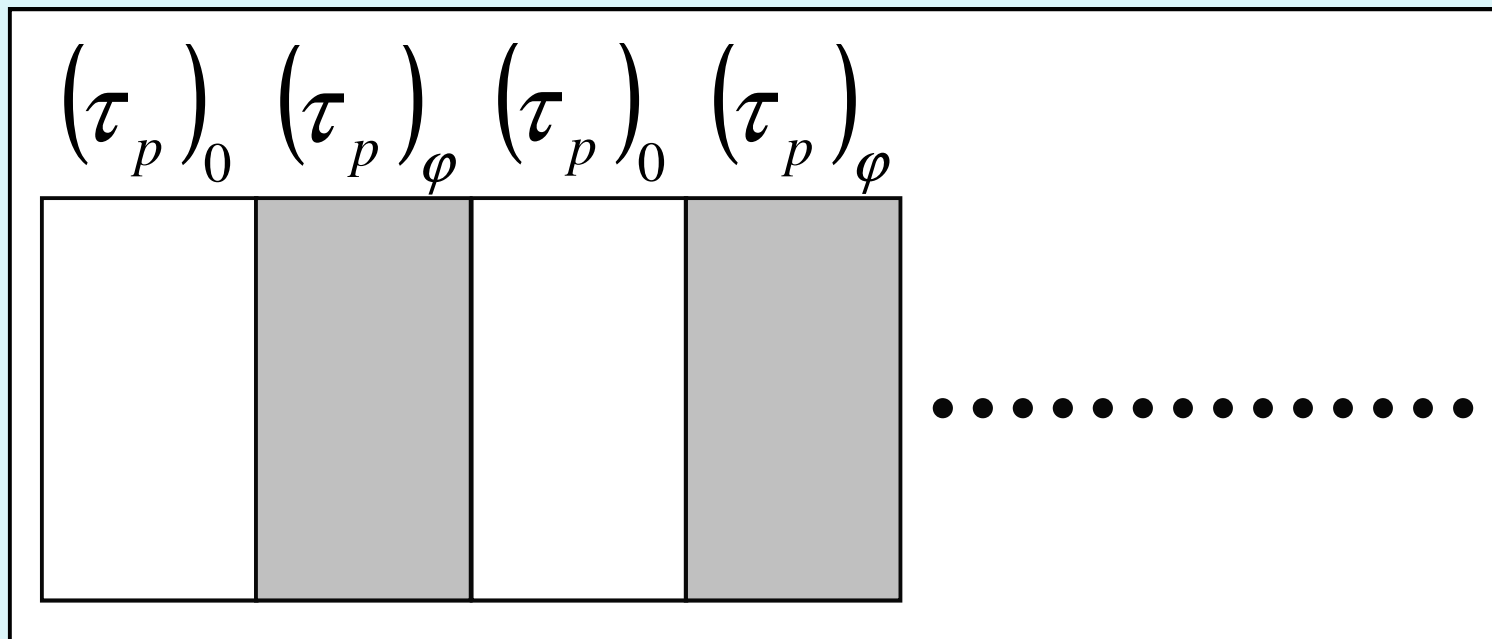
contact time, practical considerations for ^{13}C

- short T_{IS} ($\sim$500 ms): directly attached protons (-CH_3, -CH_2-, >CH-)

- long T_{IS} (>1 - 2 ms): quaternary carbons (>C<, -COO-, substituted aromatic systems, ...), high mobility

- short $T_{1\rho}$: paramagnetic systems/impurities (e.g. in coal), high mobility

TPPM decoupling

TPPM = *T*wo *P*ulse *P*hase *M*odulation
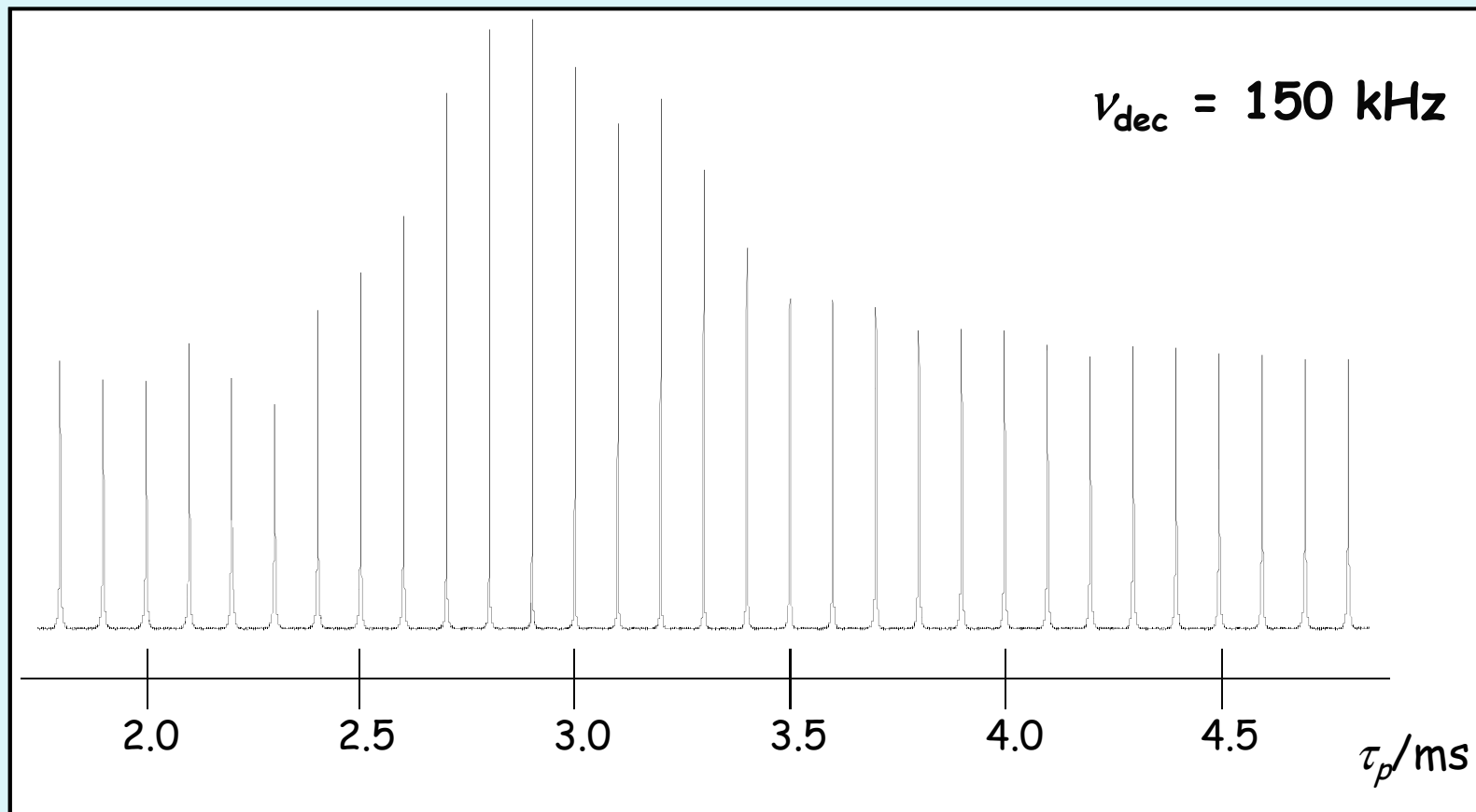
$$(\tau_p)_0 \; (\tau_p)_\varphi \; (\tau_p)_0 \; (\tau_p)_\varphi$$

pulse duration: $\tau_p \approx \tau_p - \varepsilon$: $\varepsilon \approx$ 0 – 0.6 µs, to be optimised!
phase step: $\varphi \approx 15°$, optimise, if needed!

TPPM: optimisation of τ_p

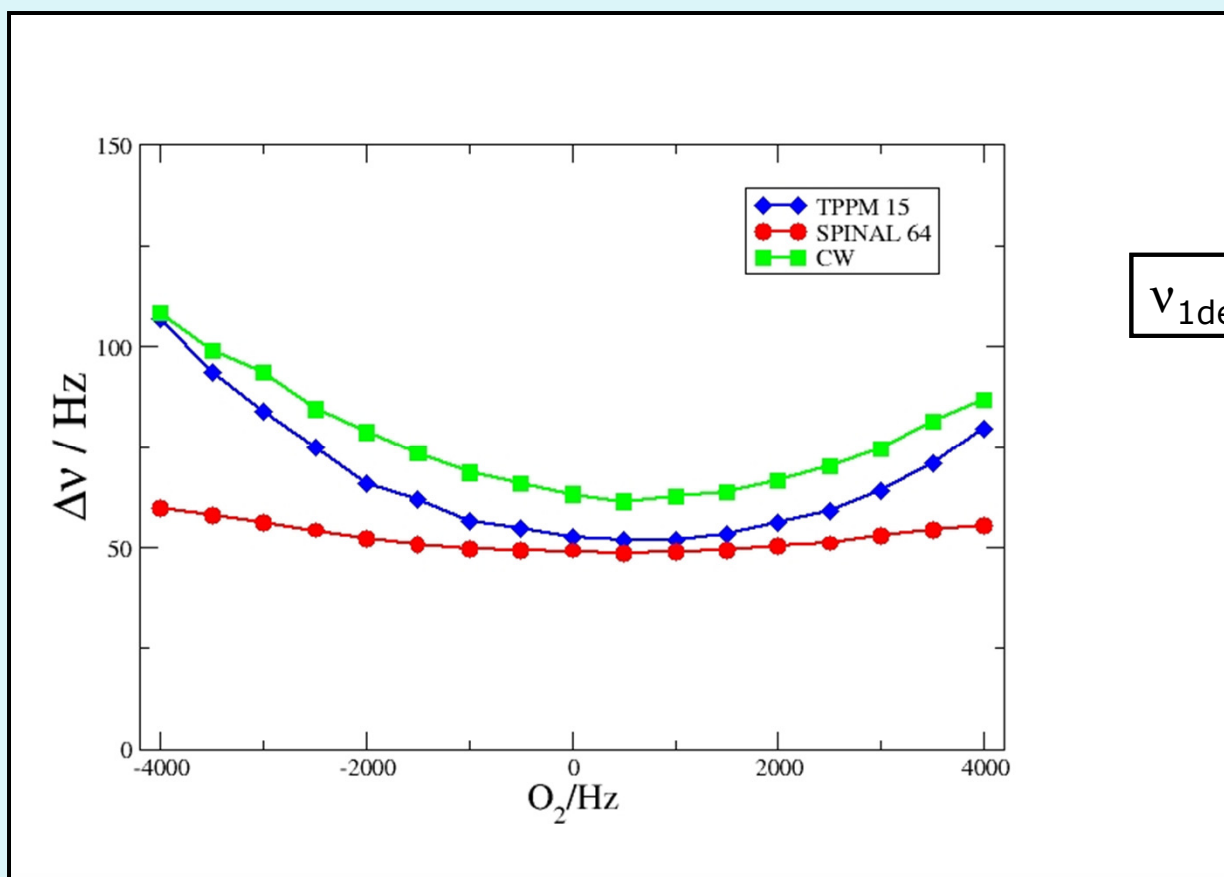C_α signal in glycine-1,2-^{13}C-^{15}N, ν_{rot}= 30 kHz, φ = 15°

optimum pulse length: τ_p = 2.9 μs, ($\tau_\square$ = 3.2 μs)

SPINAL decoupling

SPINAL = **S**mall **P**hase **I**ncremental **A**lternation

$$\tau_\varphi \quad \tau_{\varphi'} \quad \tau_{\varphi''} \quad \tau_{\varphi'''}$$

basic cycle:
Q= φ φ' φ'' φ'''...   = 10° -10° 15° -15° 20° -20° 15° -15°
Q= -φ -φ' -φ'' -φ'''... = -10° 10° -15° 15° -20° 20° -15° 15°

super cycles:
SPINAL16 = Q Q̲   SPINAL32 = Q Q̲ Q̲ Q
SPINAL64 = Q Q̲ Q̲ Q Q̲ Q Q Q̲
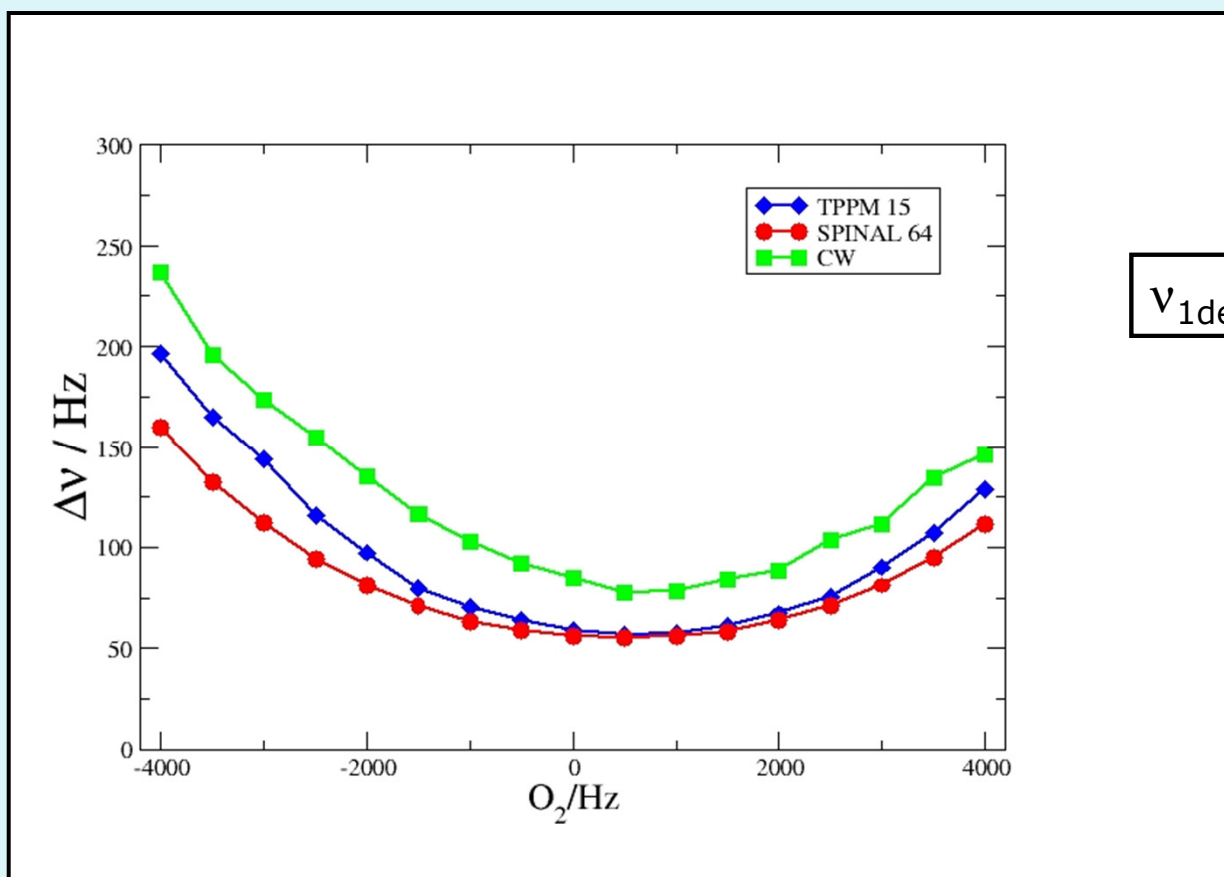SPINAL128 = Q Q̲ Q̲ Q Q̲ Q Q Q̲ Q̲ Q Q Q̲ Q Q̲ Q̲ Q

Decoupling bandwidth - comparison

Line width of C_α in Glycine at ν_{rot} = 5 kHz, 400 MHz

ν_{1dec} = 100 kHz

Decoupling bandwidth - comparison
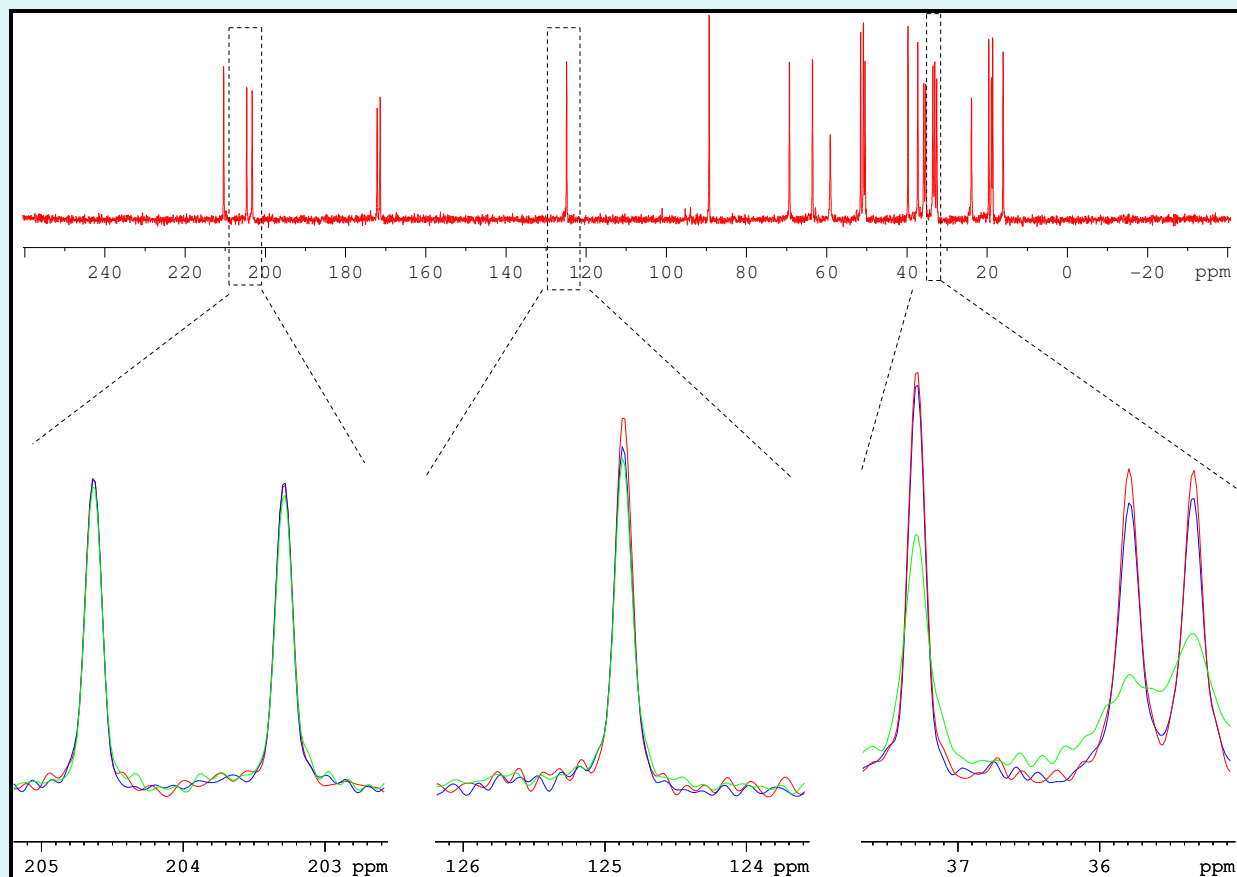
Line width of C_α in Glycine at ν_{rot} = 5 kHz, 400 MHz

ν_{1dec} = 70 kHz

Residual line width

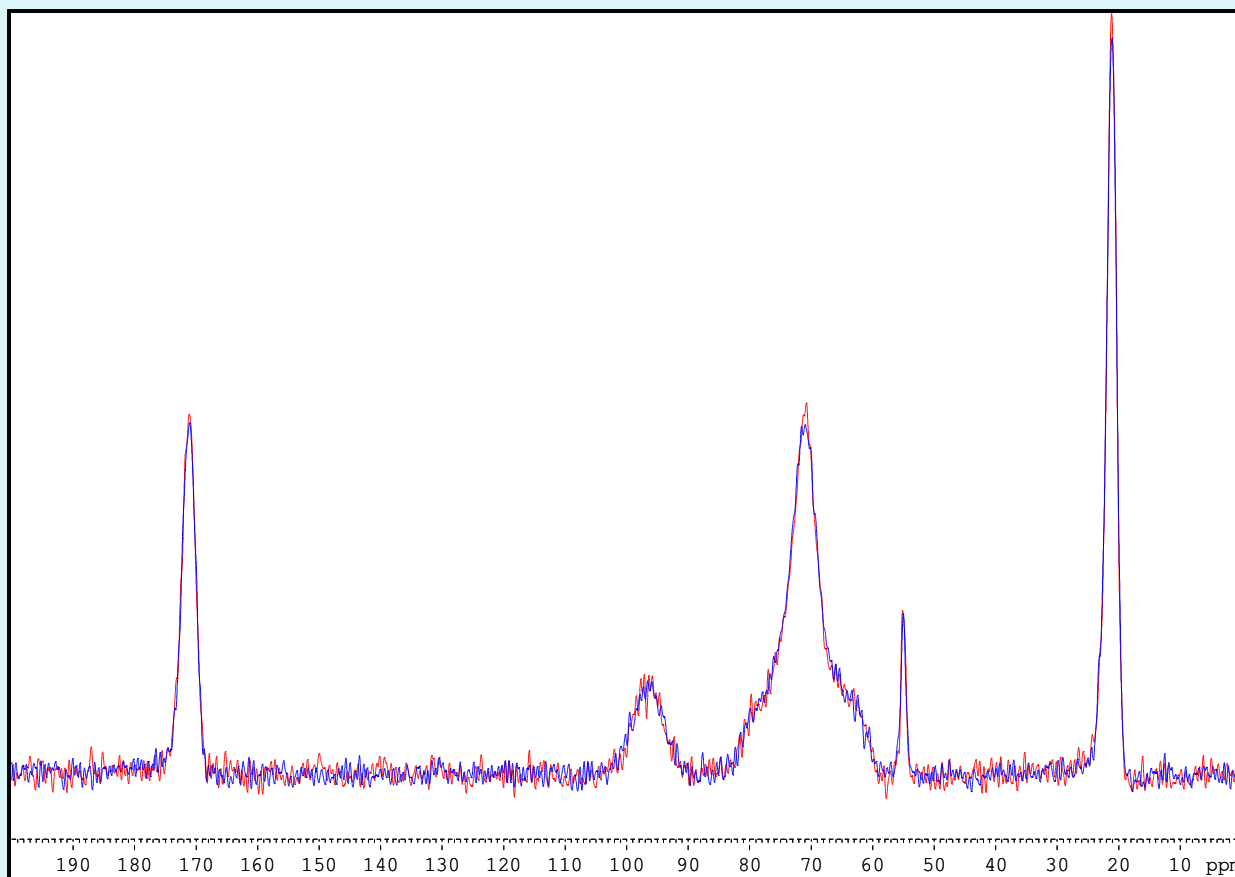^{13}C CP spectra of cortisone acetate at $\nu_{dec} = 104$ kHz and $\nu_{rot} = 11$ kHz, 400 MHz
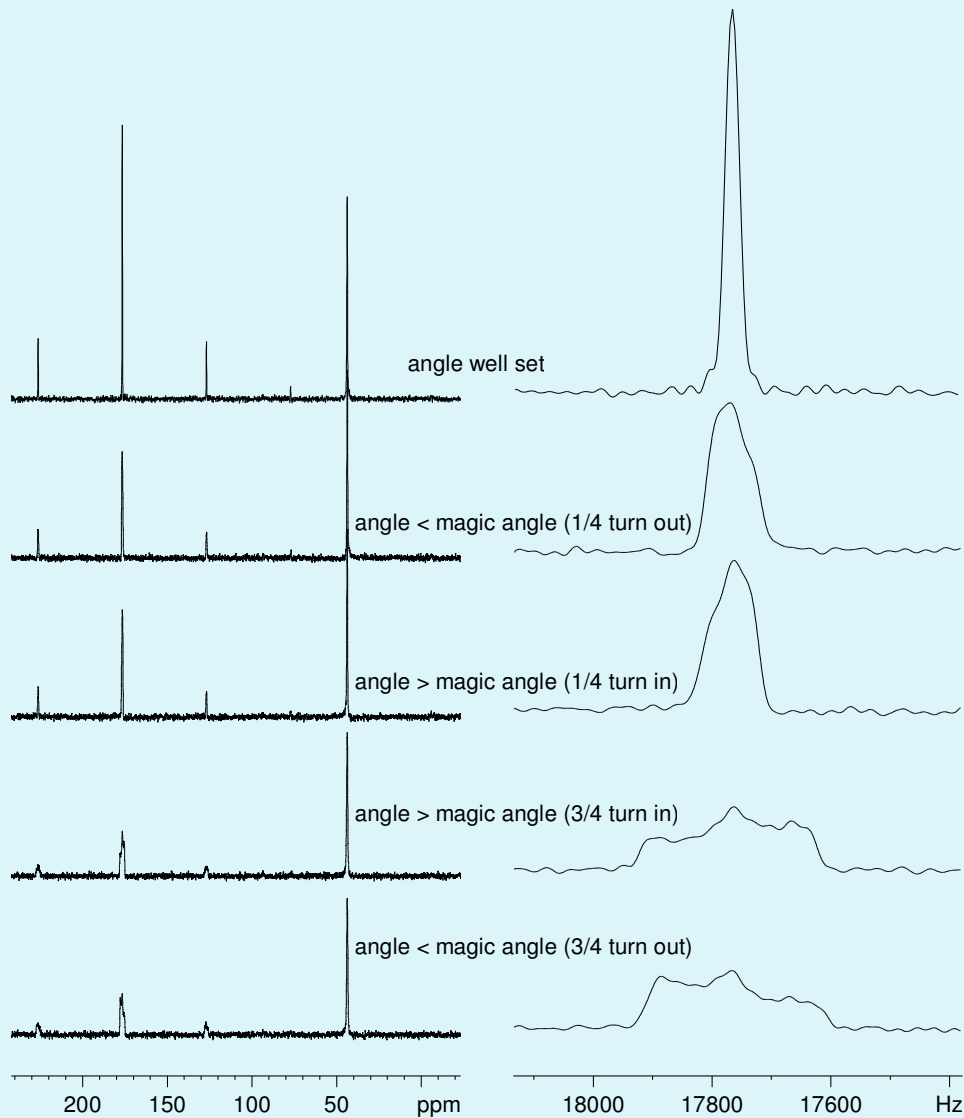
SPINAL 64
TPPM 15
CW

Residual line width

^{13}C CP spectra of starch at ν_{dec} = 104 kHz and ν_{rot} = 11 kHz, 400 MHz

SPINAL 64
TPPM 15

CPMAS Setup with Glycine

angle well set

angle < magic angle (1/4 turn out)

angle > magic angle (1/4 turn in)

angle > magic angle (3/4 turn in)

angle < magic angle (3/4 turn out)

200   150   100   50   ppm

18000   17800   17600   Hz

^{13}C-carbonyl
- HH-match
- magic angle setting
- (probe shimming)

$^{13}C_a$
- decoupling
  - power
  - offset
  - method
- S/N

Cross Polarization for Various Nuclei

• standard: $I=1/2 \Rightarrow S=1/2$:

• most frequent:

$$I = {}^{1}H \Rightarrow S = {}^{13}C, \, {}^{15}N, \, {}^{29}Si, \, {}^{31}P$$

• less common, but worthwile:

$$I = {}^{1}H \Rightarrow S = {}^{77}Se, \, {}^{89}Y, \, {}^{113}Cd, \, {}^{119}Sn, \, {}^{129}Xe, \, {}^{195}Pt, \, {}^{199}Hg, \, {}^{207}Pb$$

• fluorinated materials:

$$I = {}^{19}F \Rightarrow S = {}^{13}C, \, {}^{15}N, \, {}^{29}Si, \, {}^{31}P, \, \dots$$

• low g nuclei (e. g. ${}^{15}N$): more X and/or less ${}^{1}H$ power

• quadrupolar nuclei: different story …

HOOC-CH$_2$-NH$_2$
7mm probe
ramped CP
5 kHz spinning speed
4 scans

- Standard: $I = \frac{1}{2} \rightarrow S = \frac{1}{2}$
  - Most frequent:
    - $I = {}^{1}H \rightarrow S = {}^{13}C, {}^{15}N, {}^{29}Si, {}^{31}P$
  - Less common, but worthwhile:
    - $I = {}^{1}H \rightarrow S = {}^{77}Se, {}^{89}Y, {}^{113}Cd, {}^{119}Sn, {}^{129}Xe, {}^{195}Pt, {}^{199}Hg, {}^{207}Pb$
  - Fluorinated materials:
    - $I = {}^{19}F \rightarrow S = {}^{13}C, {}^{15}N, {}^{29}Si, {}^{31}P$
  - Low γ nuclei (e.g. ${}^{15}N$): more X and/or less ${}^{1}H$ power
  - Quadrupolar nuclei: different story

- Experiment will be simple, if
  - Natural abundance is high
  - Larmor frequency is high
  - CP can be used in case of spin $\frac{1}{2}$ nuclei
    - difficult, if $T_{IS} \gg T_{1\rho}$, e.g. for low γ nuclei

- Spin I must be considered
  - For spin $> \frac{1}{2}$ selectivity and connectivity information is more important than gain in sensitivity
  - Consider elements with several isotopes

- Elements with several NMR aktive isotopes
  - ^{6}Li ^{7}Li
  - ^{10}B ^{11}B
  - ^{14}N ^{15}N
  - ^{35}Cl ^{37}Cl
  - ^{39}K ^{41}K
  - ^{47}Ti ^{49}Ti
  - ^{50}V ^{51}V
  - ^{63}Cu ^{65}Cu
  - ^{69}Ga ^{71}Ga
  - ^{77}Se ^{79}Se
  - ^{79}Br ^{81}Br
  - ^{85}Rb ^{87}Rb
  - ^{95}Mo ^{97}Mo
  - ^{99}Ru ^{101}Ru
  - ^{101}Rh ^{103}Rh
  - ^{107}Ag ^{109}Ag
  - ^{111}Cd ^{113}Cd
  - ^{113}In ^{115}In
  - ^{115}Sn ^{117}Sn ^{119}Sn

  - ^{121}Sb ^{123}Sb
  - ^{123}Te ^{125}Te
  - ^{129}Xe ^{131}Xe
  - ^{135}Ba ^{137}Ba
  - ^{138}La ^{139}La
  - ^{147}Sm ^{149}Sm
  - ^{151}Eu ^{153}Eu
  - ^{155}Gd ^{157}Gd
  - ^{161}Dy ^{163}Dy
  - ^{171}Yb ^{175}Yb
  - ^{175}Lu ^{176}Lu
  - ^{177}Hf ^{179}Hf
  - ^{185}Re ^{187}Re
  - ^{187}Os ^{189}Os
  - ^{191}Ir ^{193}Ir
  - ^{199}Hg ^{201}Hg
  - ^{203}Tl ^{205}Tl

  - Spin ½
  - Spin n
  - Spin n/2

- > 99 % natl. abundance
  - ^{9}Be, ^{14}N, ^{19}F, ^{23}Na
  - ^{27}Al, ^{31}P, ^{45}Sc, ^{55}Mn
  - ^{59}Co, ^{75}As, ^{89}Y, ^{93}Nb
  - ^{103}Rh, ^{127}I, ^{133}Cs, ^{139}La
  - ^{141}Pr, ^{159}Tb, ^{165}Ho, ^{169}Tm
  - ^{181}Ta, ^{197}Au, ^{209}Bi

nucl. natl. abundance	$\gamma_X > \gamma_{C-13}$	$\gamma_{C-13} \geq \gamma_X \geq \gamma_{N-15}$	$\gamma_{N-15} > \gamma_X$
100-70%	^{19}F ^{31}P		^{89}Y ^{103}Rh ^{169}Tm
70-50%	^{203}Tl $^{205}\mathbf{Tl}$		^{107}Ag $^{109}\mathbf{Ag}$
50-10%	^{129}Xe	^{111}Cd $^{113}\mathbf{Cd}$ ^{171}Yb ^{195}Pt ^{199}Hg ^{207}Pb	^{183}W
< 10%	^{3}He ^{115}Sn ^{117}Sn $^{119}\mathbf{Sn}$ ^{123}Te $^{125}\mathbf{Te}$	^{13}C ^{15}N ^{29}Si ^{77}Se	^{57}Fe ^{187}Os
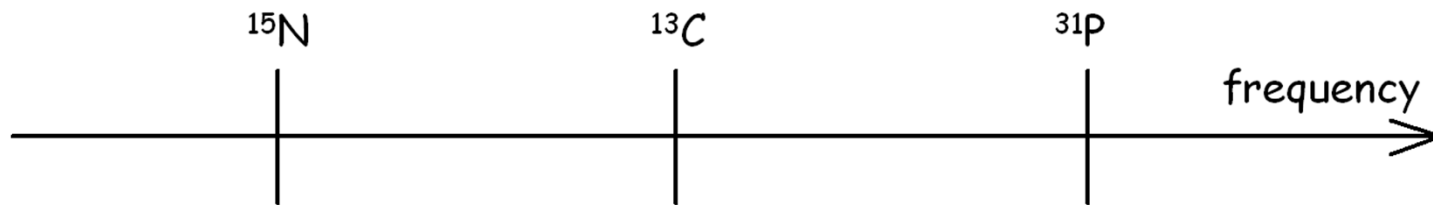
nucleus	^{15}N	^{13}C	^{31}P
Larmor frequency [MHz]	40	100	162
X power at CP match [≈W]	500	200	150
relative attenuation X [dB]	-2	0	3
RF field [kHz]	55	63	65
relative attenuation ^1H [dB]	2	0	0

CP of "exotic" nuclei
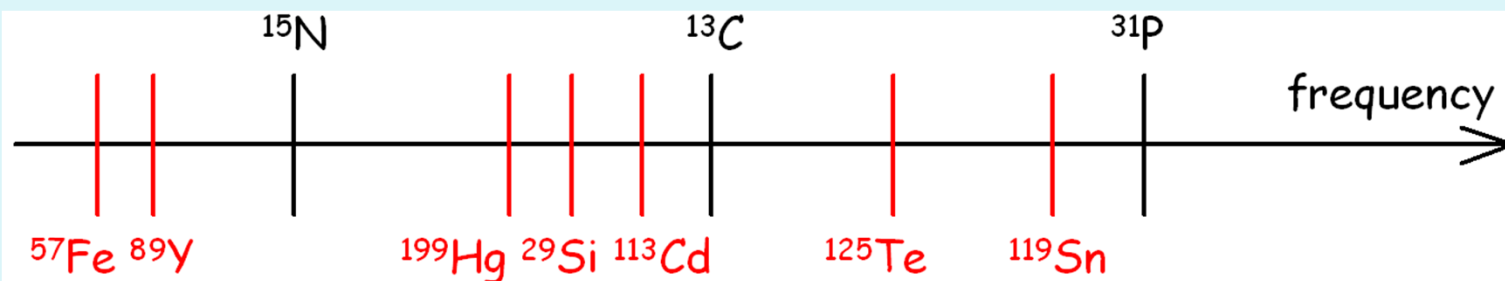
nucleus	^{15}N	^{13}C	^{31}P
Larmor frequency [MHz]	40	100	162
X power at CP match [≈W]	500	200	150
relative attenuation X [dB]	-2	0	3
RF field [kHz]	55	63	65
relative attenuation ^1H [dB]	2	0	0

Some reference compounds for CP set-up

nucleus	sample	shift (ppm)	relative to	contact (ms)	recycle (s)	frequency (MHz) rel. to 200	remarks
^{15}N	glycine, enriched	-345	CH_3NO_2	5	10	20.280213	natl. abundance: visible in 1 scan
^{29}Si	Q_8M_8	12.4 (t) -110 (o)	TMS	5	10	39.758361	easy but expensive
^{31}P	$(NH_4)H_2PO_4$	0	H_3PO_4	1	4	81.013812	anything will do
^{77}Se	H_2SeO_3		$Se(Me)_2$	3	4	38.217585	1 scan, but poisonous easy, narrow
	$(NH_4)_2SeO_4$	-1040.2				38.128907	
^{89}Y	$Y(NO_3)_3*H_2O$	-53.2	sol. in H_2O	10	10	9.807451	visible after 1 scan FT
^{113}Cd	$Cd(NO_3)*4H_2O$	-100	1m $Cd(ClO_4)_2$	15	8	44.381609	
^{119}Sn	$Sn(cyclohexyl)_4$	-97.35	$Sn(Me)_4$	1	20	74.639360	easy, 1 scan
^{129}Xe	Xe at 40b in hydroquinone clathrate, 3 hours	222	Xe in air	30	5	55.333703	Xe in air is visible overnight (single pulse)
^{199}Hg	$Hg(OAc)_2$	-2487 -2493	$Hg(Me)_2$	5	10	35.765352	16 scans, 125 kHz, 4K points (lots of sidebands)
^{207}Pb	$Pb(phe)_4$					41.861650	1 scan, poisonous, no good set-up
	$Pb(p-tol)_4$	-148.8	$Pb(Me)_4$	5	12	41.863710	better, but also poisonous, 1 scan