PRAKTISCHE PROBLEME DER KERNRESONANZSPEKTROSKOPIE 2023

RF-Pulse für verschiedenste Anwendungen

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Bruker BioSpin

Topics

01 What are shaped and adiabatic pulses?

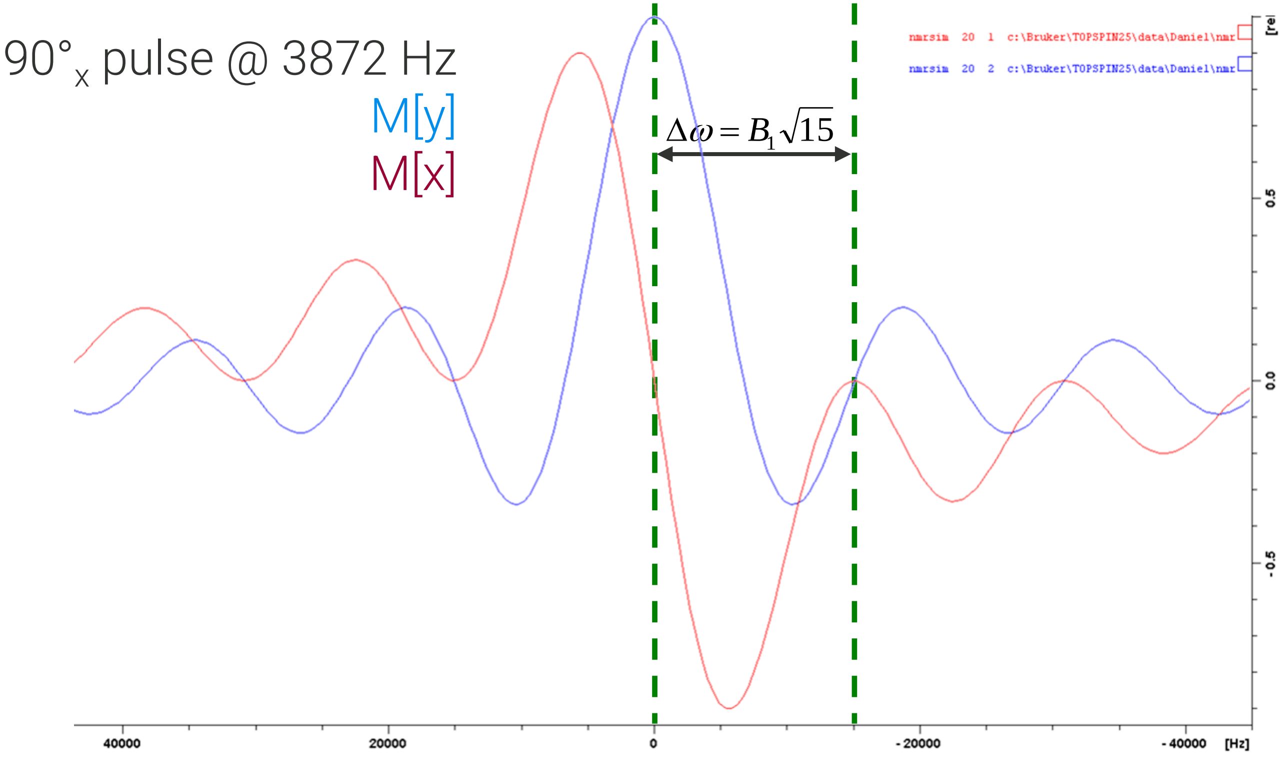
02 Using shaped pulses

03 What are the applications of shaped pulses?

04 How can automation be used in creating shaped pulses?

The short way – matched length rectangular pulses

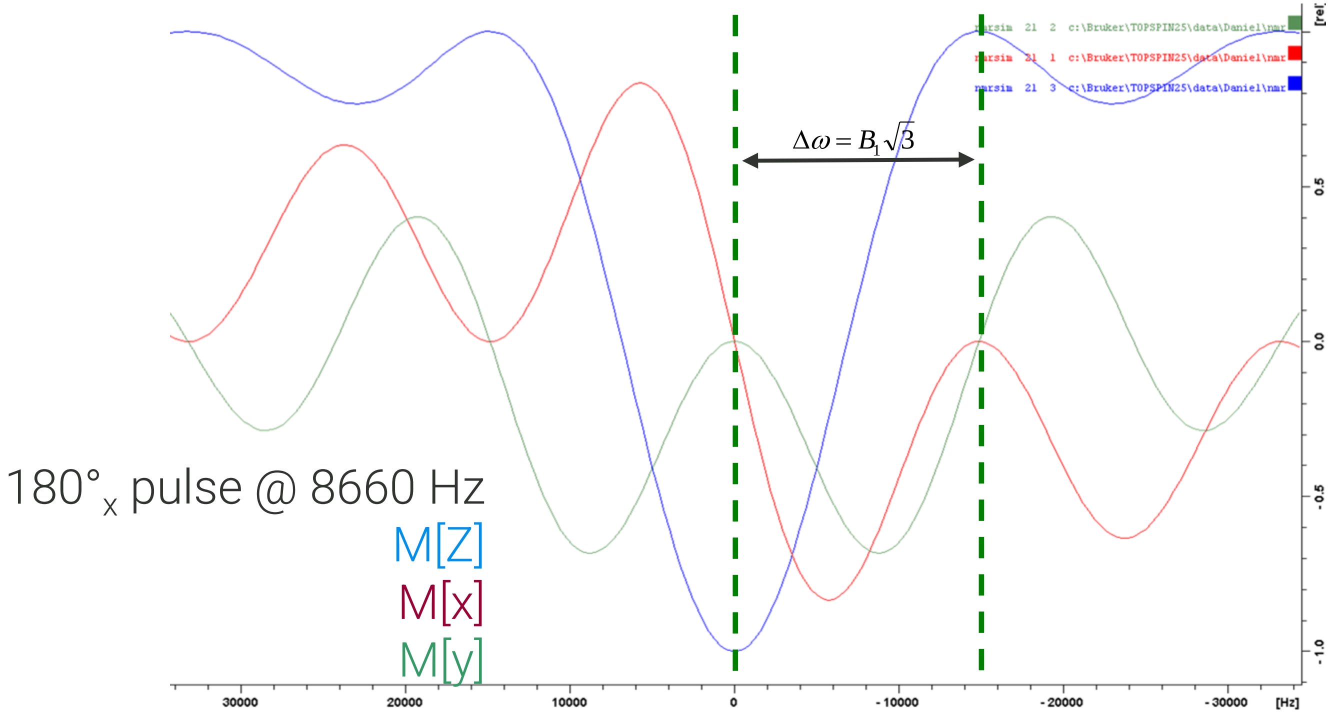
- Using rectangular pulses as bandselective pulses:



- E.g. 15 kHz separation: $B_1 = \frac{\Delta\omega}{\sqrt{15}} = 3872 \quad B_1 = \frac{1}{4\tau_p} \Leftrightarrow \tau_p = \frac{1}{4B_1} = 64\mu s$

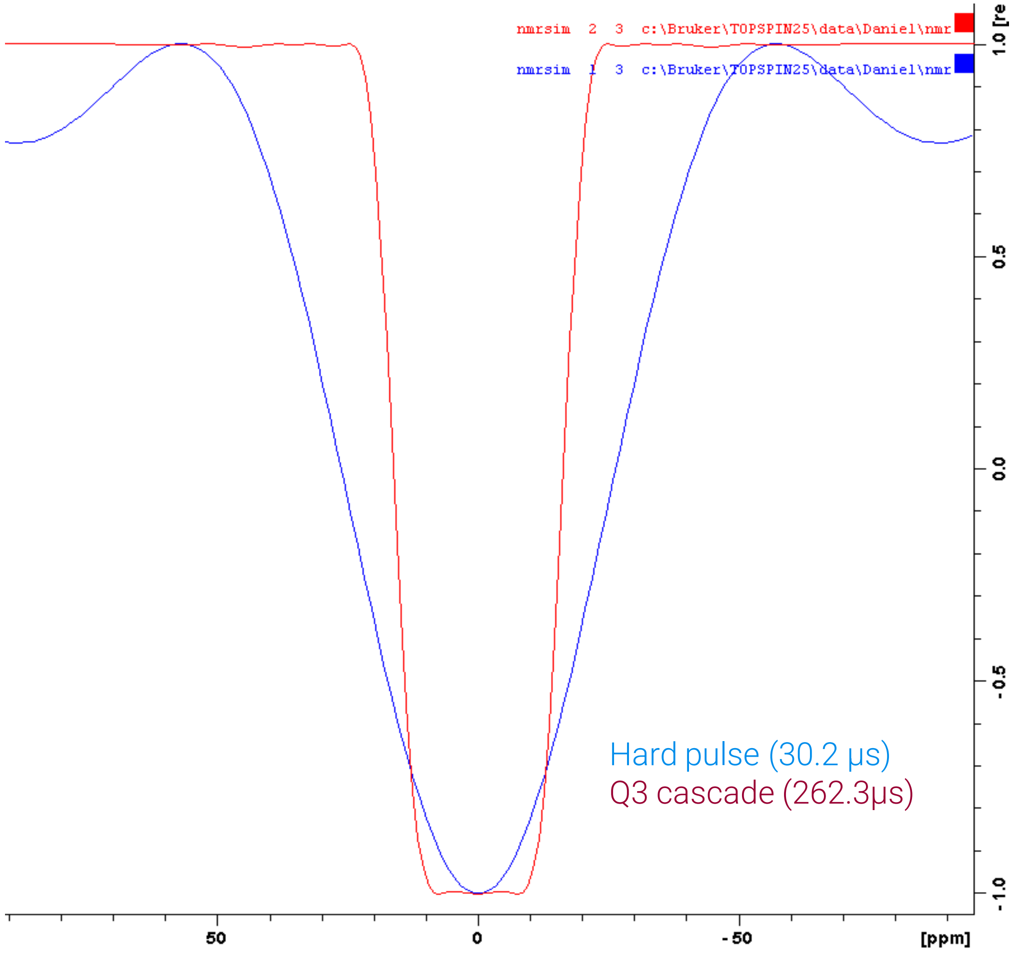
The short way – matched length rectangular pulses

- Using rectangular pulses as bandselective pulses:



- E.g. 15 kHz separation: $B_1 = \dfrac{\Delta\omega}{\sqrt{3}} = 8660$ $\quad B_1 = \dfrac{1}{4\tau_p} \Leftrightarrow \tau_p = \dfrac{1}{4B_1} = 58\mu s$

Why not just hard pulses?



- Clear discrimenation of exactly 2 frequencies
  - Varying behaviour in between
  - Wide transition regions
  - No “plateau” for uniform excitation/inversion…

Shaped pulses

Definitions

NMR was developed simultaneously by Edward Purcell and Felix Bloch in 1946. The experimental method and theoretical interpretation they developed is continuous-wave NMR.
Pulsed NMR technique was introduced in 1950 by Erwin Hahn.

Historically

- ‘Shaped pulses' or 'selective pulses' were used for the excitation of a limited bandwidth (e.g. a single multiplet)

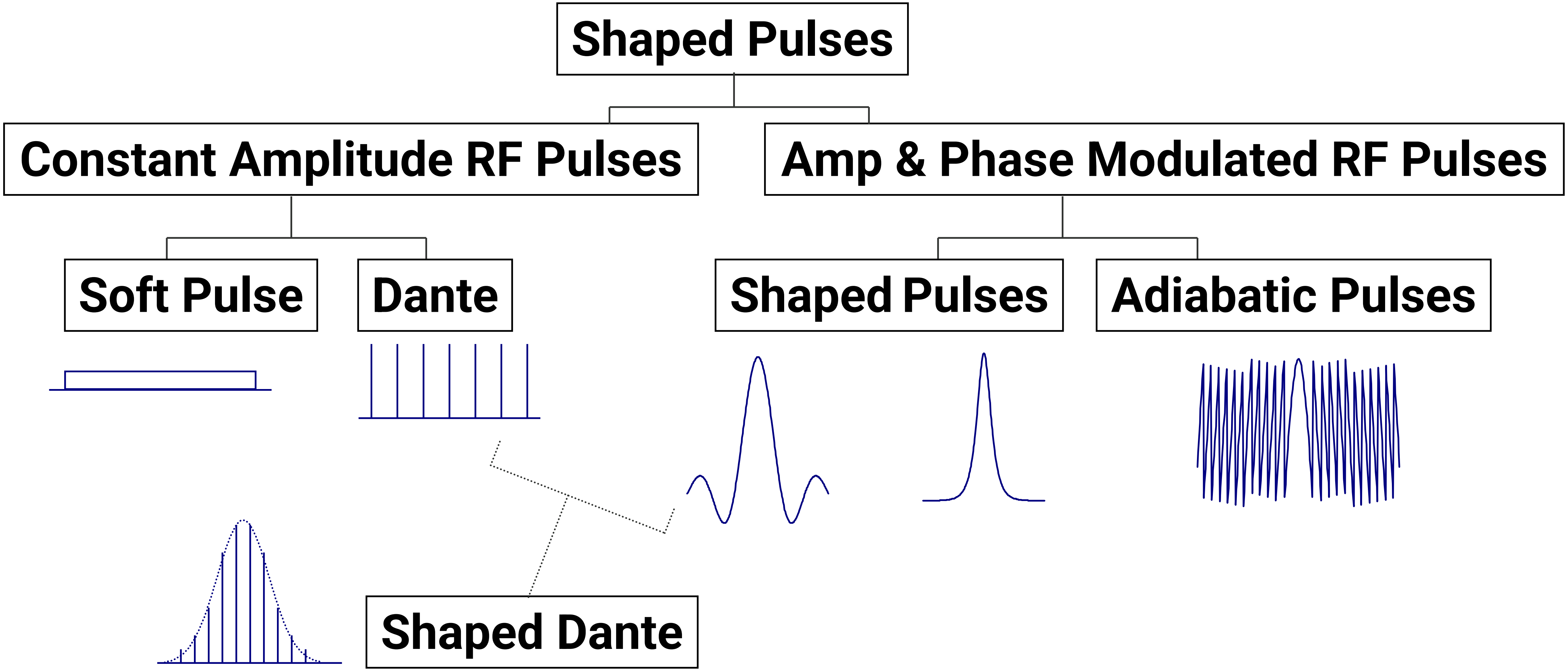
Today

- 'Shaped pulses' are not necessarily selective pulses
- 'Shaped pulses' are pulses with a customized bandwidth and behavior by utilizing amplitude, phase and/or frequency modulation

Bandwidth considerations:

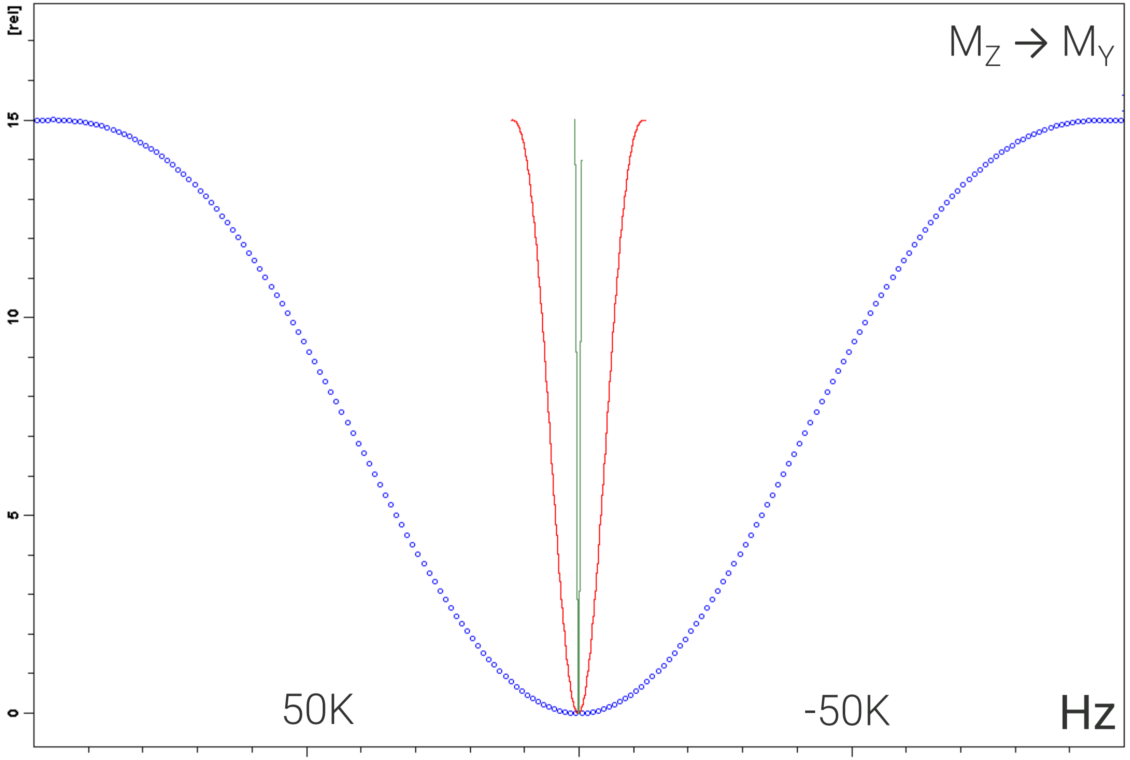
- selective excitation / inversion / refocusing of a 'small' bandwidth:
  e.g. refocusing Gaussian pulse in selcogp, selmlgp, selnogp, etc.
- selective excitation / inversion / refocusing of a 'larger' bandwidth:
  e.g. SNOB, BURP pulses for band selective excitation in HSQC, selective decoupling in bio-NMR experiments
- wideband inversion at lowest power level possible (e.g. CHIRP and WURST decoupling pulses).
  The adiabatic condition met over a large frequency range by making efficient use of available power.

Definitions



Soft Pulse: Soft pulse vs. hard pulse

- The typical hard pulse is designed to yield some flip angle over a large bandwidth.
- A soft pulse can be tailored to provide the same flip angle, but over a much smaller bandwidth, therefore selective and using less power.



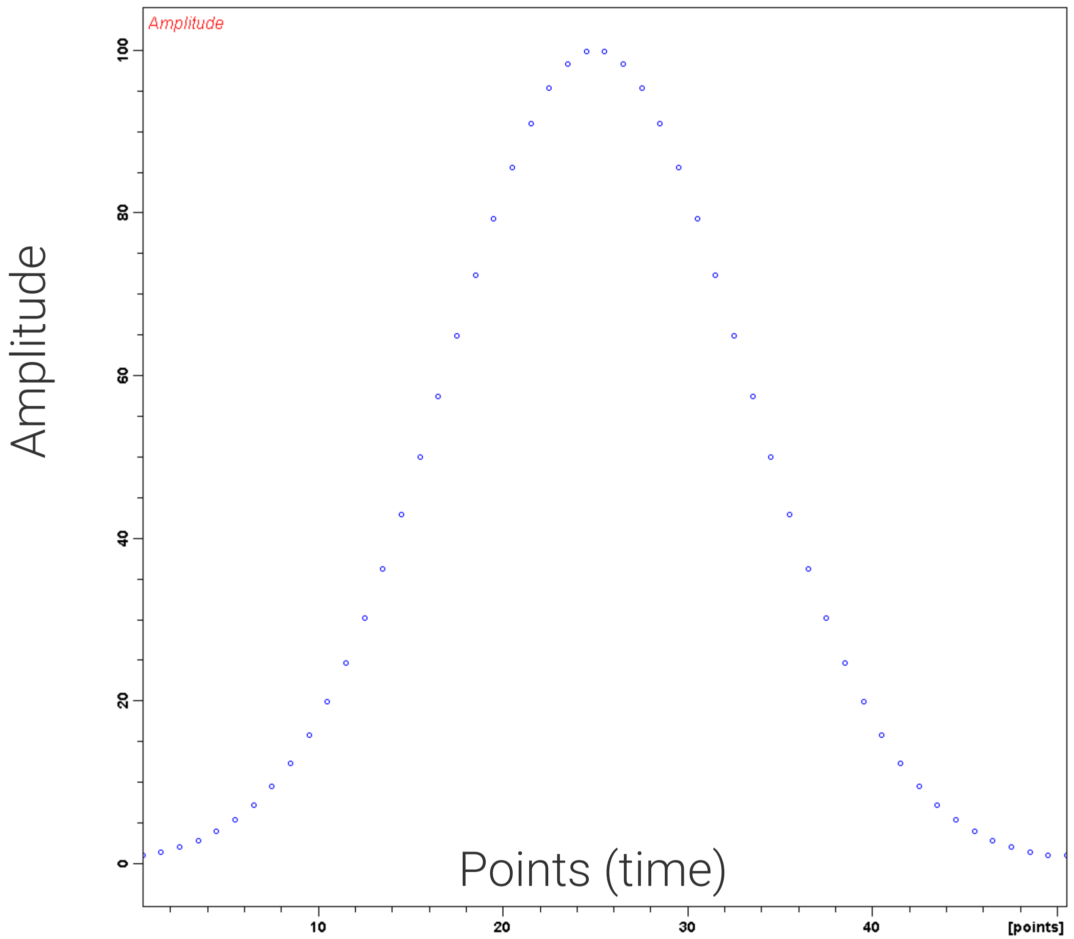
Blue – 10us "hard pulse" ("square" or "rectangular")

Red – 80us "softer pulse"
18dB less power

Green – 1280us "soft pulse"
42dB less power

Shaped Pulse: RF pulse modulation

- The RF pulse is modulated over the duration of the pulse
  - Amplitude
  - Phase



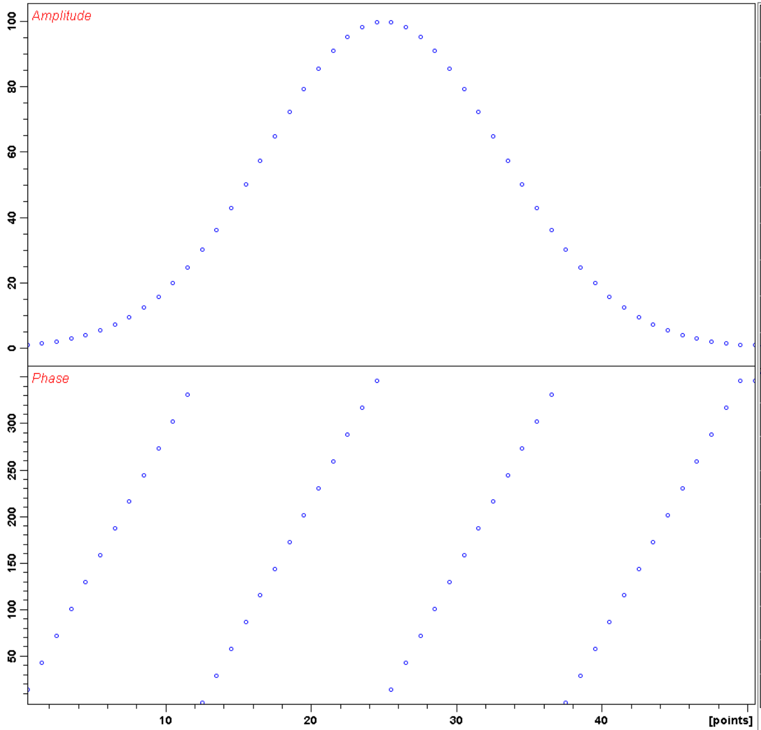
Gaussian shape, 50 points

Shape is defined by amplitude value vs. point. The shape is then implemented by defining the duration of the pulse.

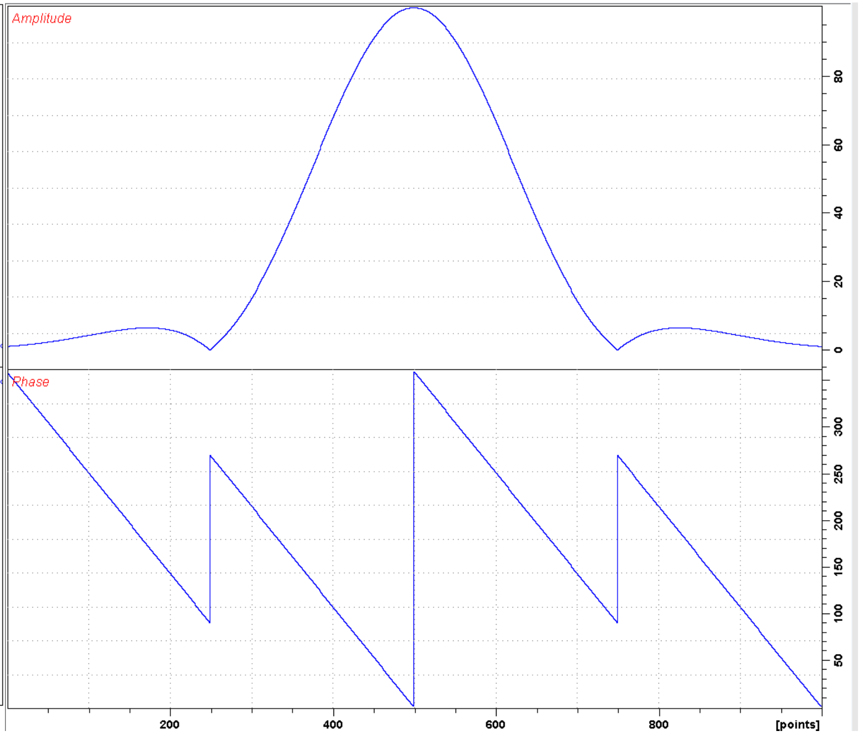
Different shapes can be utilized to attain specific excitation profiles.

Shaped Pulse: Phase Modulation

- In addition to amplitude, the phase of a pulse can also be varied during its duration.
- Phase modulation is used to attain frequency specific goals such as frequency offset or multiple frequency irradiation.



Frequency offset = 1000Hz



2 frequencies 100Hz and 200Hz from o1

Properties of shaped pulses: bandwidth factor

Pulse bandwidth is the range at which the excitation (inversion, refocusing) drops to 70.8% of the max (a reduction of 3 dB)

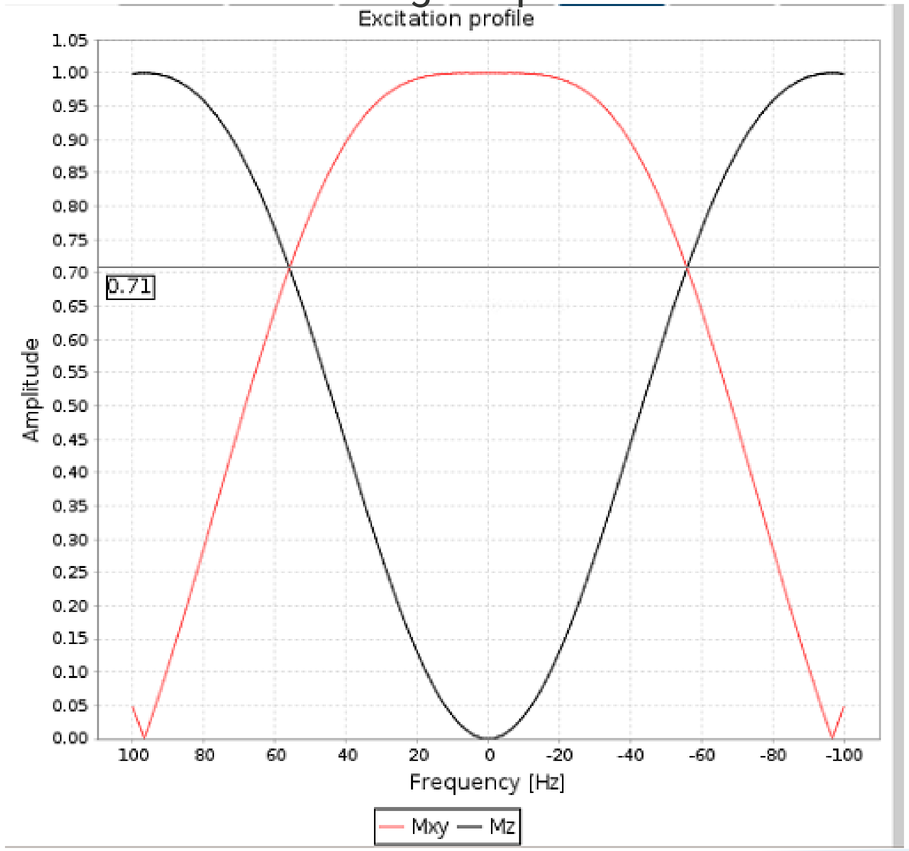
For a rectangular 90-degree pulse of 10000 us, the magnitude of the transverse magnetization drops to 70.8% at +/- 55.8 Hz, so the bandwidth is 111.6 Hz

P = BWFAC / Δω:
P – pulse duration and bandwidth – Δω are inversely proportional.
Coefficient is called bandwidth factor.

A pulse of a given duration with a larger BWFAC excites larger bandwidth than a pulse with a smaller BWFAC.

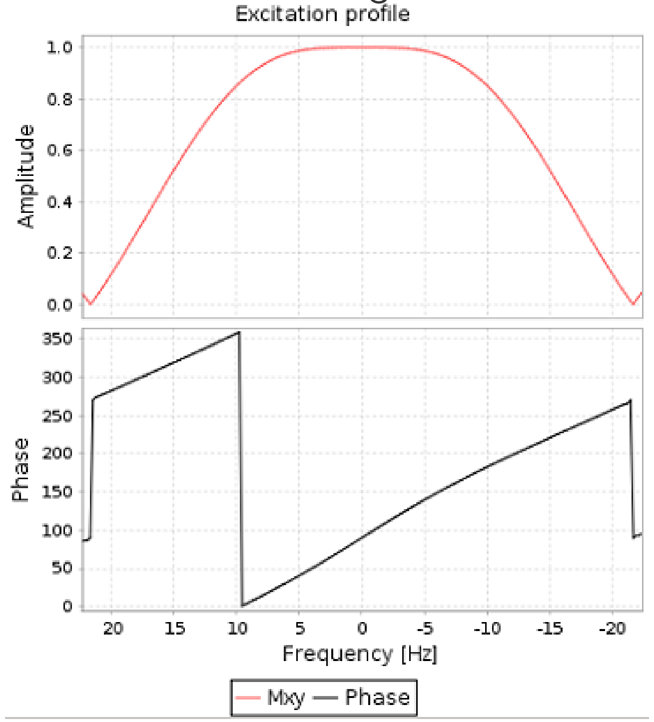
Shape	BWFAC	SW, Hz	P, us	P, us	SW, Hz
Square 90	1.116	1000	1116	1000	1116
Square 180	0.39	1000	390	1000	390
Gaus1.1000	2.122	1000	2122	1000	2122
Sinc1.1000	1.606	1000	1606	1000	1606

Rectangular pulse

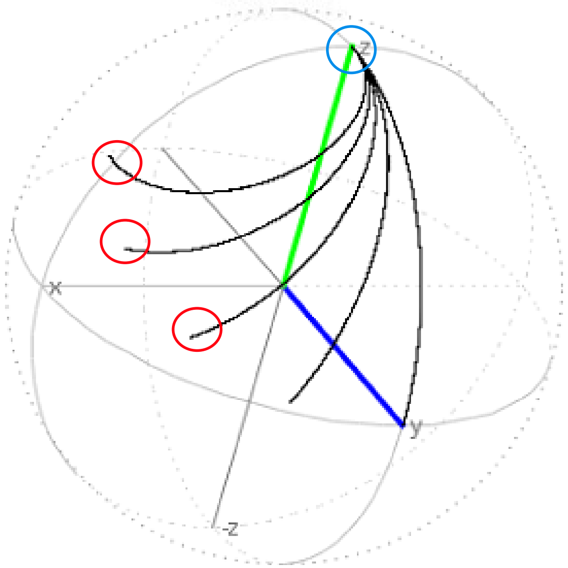


Offset effects: phase

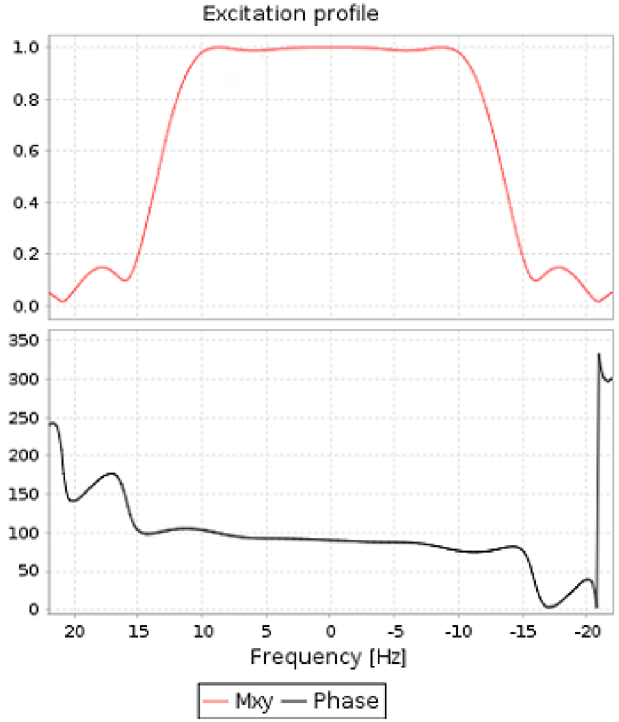
Rectangular



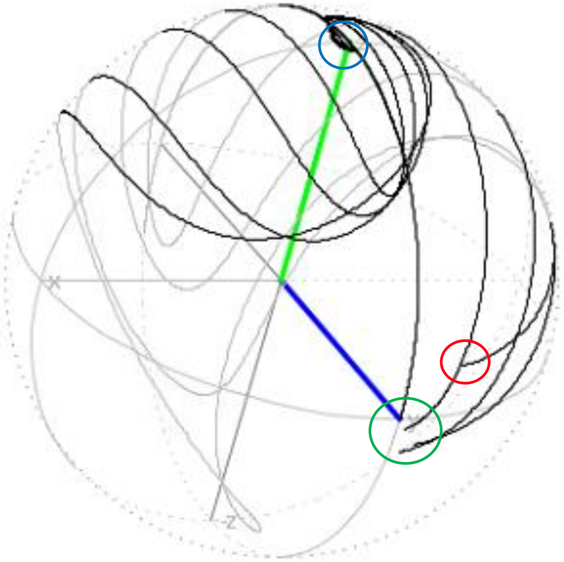
Spin evolution:
5 offsets
from 0 to 12.5 Hz



Eburp.2

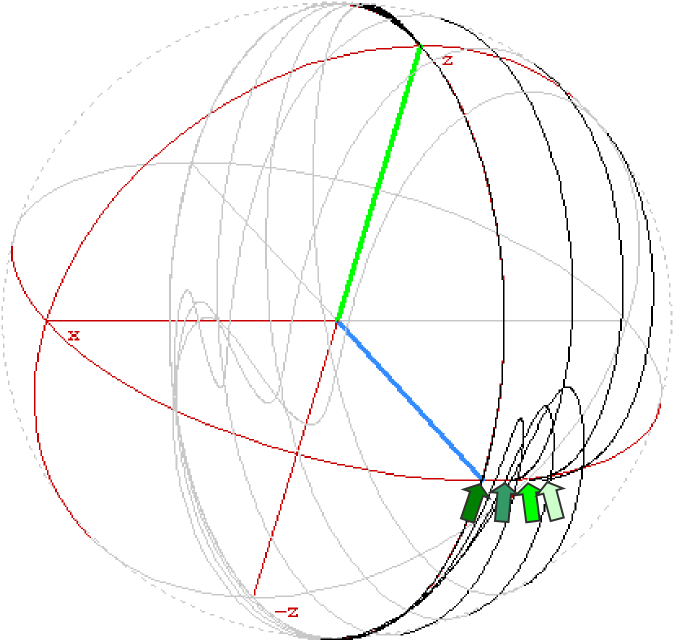


Spin evolution:
5 offsets
from 0 to 12.5 Hz

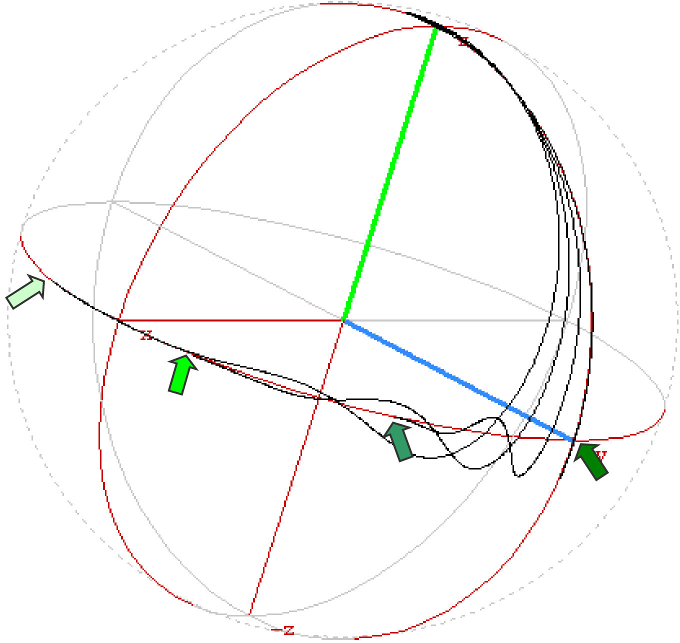


Desired offset effects – chemical shift (and J-coupling) evolution

2 ms Q5 gauss cascade



2 ms polychromatic pulse (PC9)



- Some pulses allow for evolution of J coupling and/or chemical shift during a large portion of the pulse length
  - Magnetization transfer is achieved already during the pulse, allowing for shortened transfer delays

Composite pulses: 90x180y90x (90x240y90x, …)

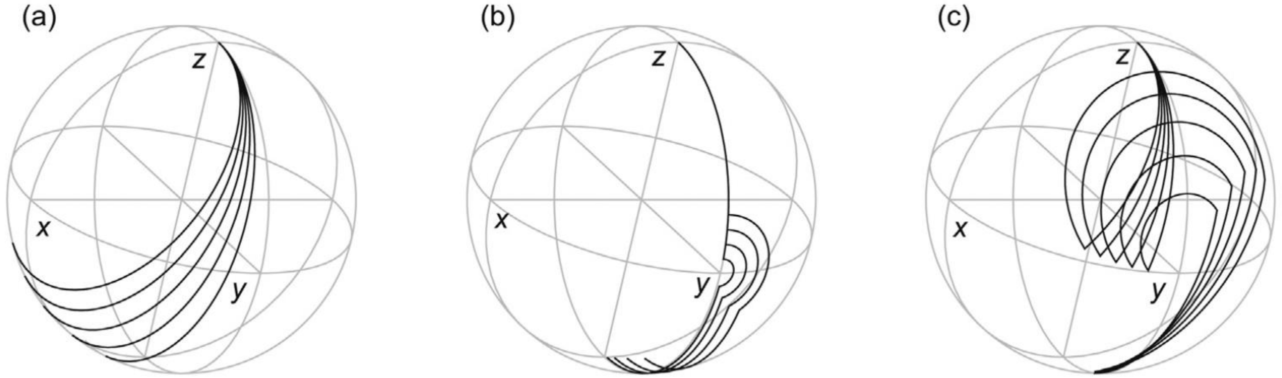
Three main problems that lead to degraded sensitivity and potentially introduces artefacts:

a) limited excitation, inversion/refocusing profile;

b) phase errors

c) B_1 inhomogeneity / pulse miscalibration

Composite pulses – series of hard pulses with different phases concatenated one after another.



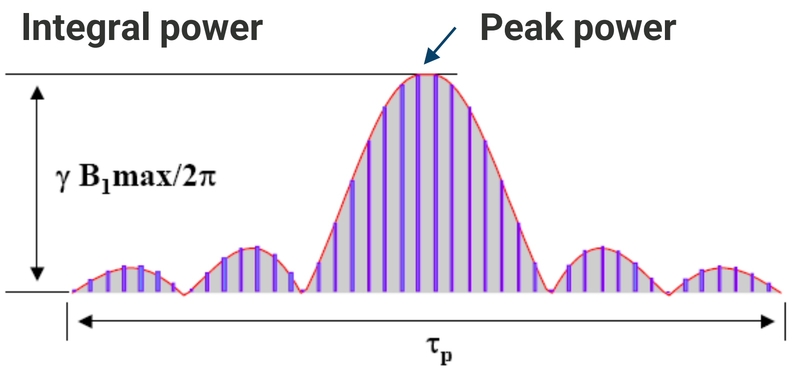
180_x pulse
Resonance offset
0.2-0.6 γB_1

$90_x 180_y 90_x$ pulse
B_1 inhomogeneity

$90_x 180_y 90_x$ pulse
Resonance offset
0.2-0.6 γB_1

Compensation against B1 inhomogeneity, resonance offset

Properties of shaped pulses: integral power and integral factor



Shaped pulse*	$I = \sum (A_i) * \gamma B_1max/2\pi * \tau_p$
Square pulse	$I = \gamma B_1max/2\pi * \tau_p$

Integral factor is the integral ratio of a shaped pulse and a 100% square pulse of the same length

Integral factor, together with the pulse duration, defines pulse power level compared to a 100% square pulse.

$$\Delta dB = 20 * \log_{10}\left(\frac{P_2^{sq}}{P_1^{sq}}\right) = 20 * \log_{10}\left(\frac{P_2^{sh} * INTEGFAC}{P_1^{sq}}\right);$$

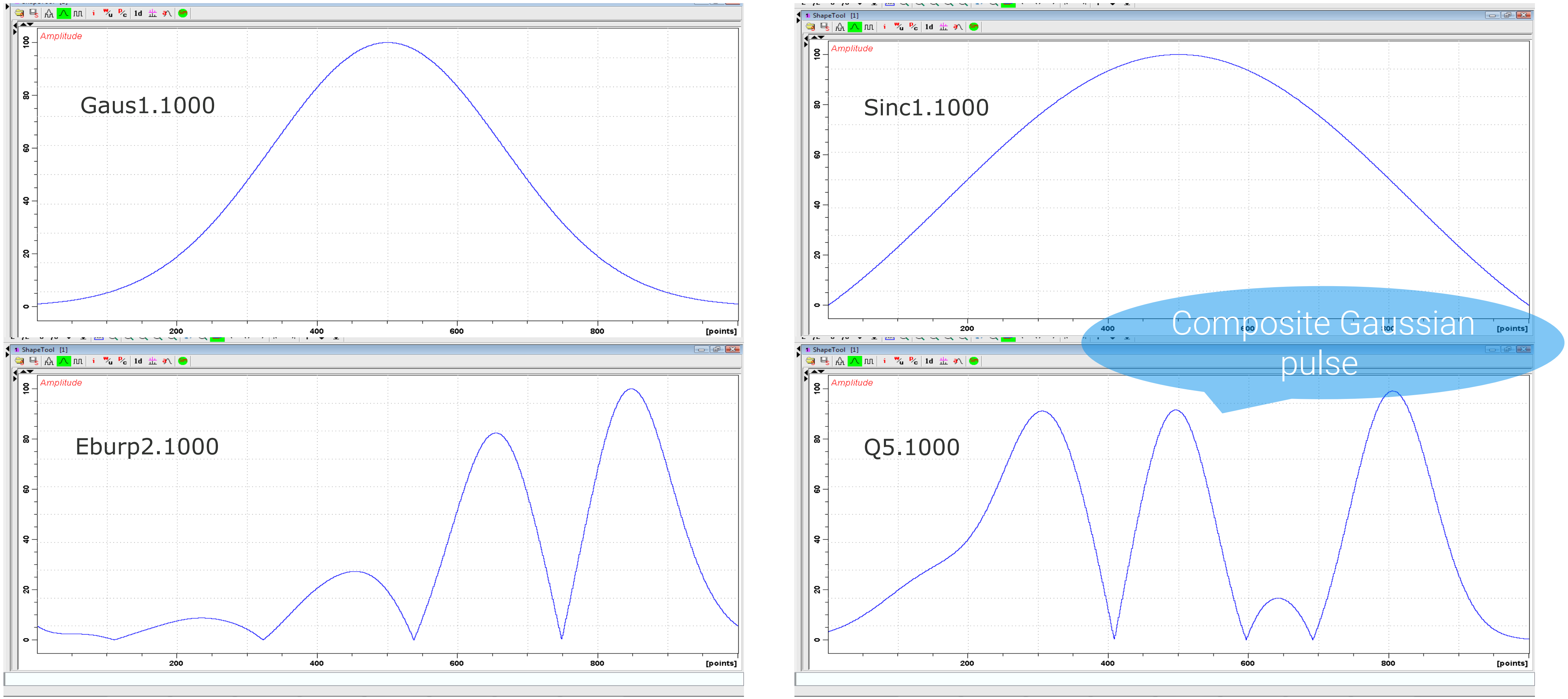
$$PLW_2 = PLW_1 * \left(\frac{P_1^{sq}}{P_2^{sq}}\right)^2 = PLW_1 * \left(\frac{P_1^{sq}}{P_2^{sh} * INTEGFAC}\right)^2;$$

$$\gamma B_{1max} = \frac{1}{4 * P_{90}^{sq}} = \frac{1}{4 * P_{90}^{sh} * INTEGFAC}$$

Twice as long pulse requires 4 times lower power or +6.02 dB (for a given INTEGFAC)

Bandwidth factor, Integral and Excitation bandwidth comparision

$M_Z \rightarrow M_Y$

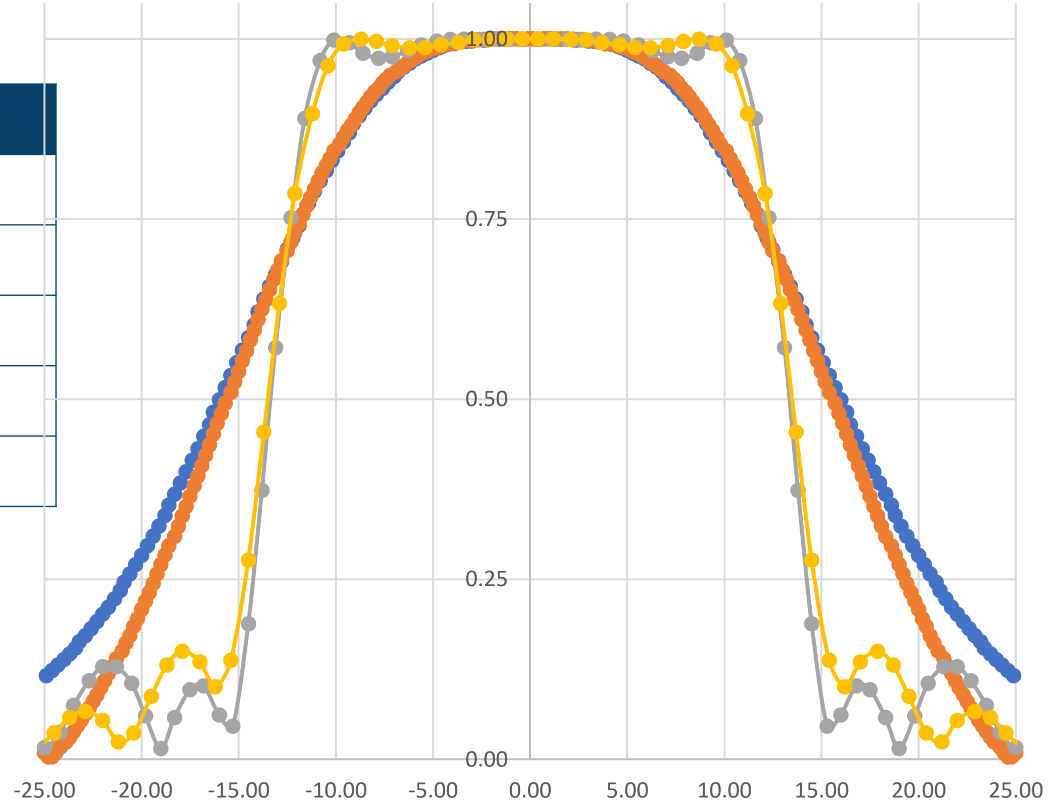


Some examples and formulas

If you want to selectively excite a 25Hz bandwidth …

Shape	BWFAC	P, us	INTEGFAC	γB_{1max} (Hz)	ΔdB *
Square	1.116	44640	1	5.6	74.9
Gaus1.1000	2.122	84880	0.412	7.2	72.8
Sinc1.1000	1.606	64240	0.589	6.6	73.5
Eburp2.1000	4.95	198080	0.061	20.7	63.6
Q5.1000	6.18	247200	0.055	18.6	64.5

* to 8 us 90-degree pulse



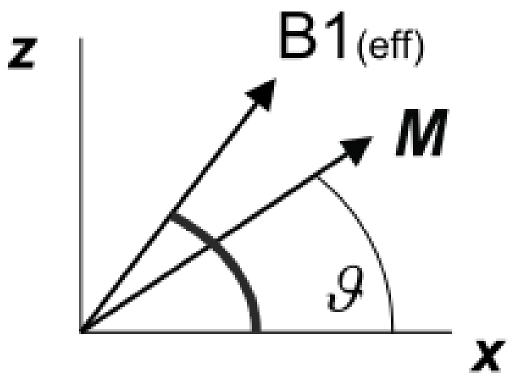
Gaussian pulse cascade pulses (Q3/5, G3/4), BURP, SNOB and some other pulses are so-called top-hat excitation pulses.

They are used for selective uniform excitation/inversion of a defined spectral region with minimal distortions outside of the region.

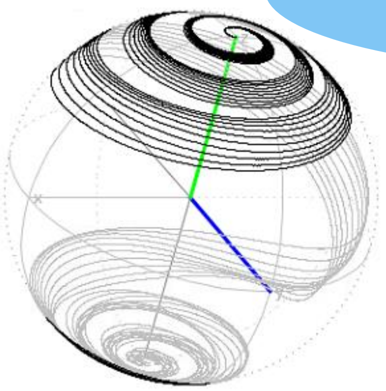
Adiabatic pulses for inversion and refocusing

Adiabatic Pulses

- Radiofrequency (RF) pulse which utilizes a swept frequency in combination with varying amplitude, specifically utilizing slow passage of B_1 through resonance
- Adiabatic pulses are frequency swept broadband inversion or refocusing pulses. The adiabatic condition is satisfied if the rate of the frequency sweep keeps the magnetization over the bandwidth locked by the applied RF field.



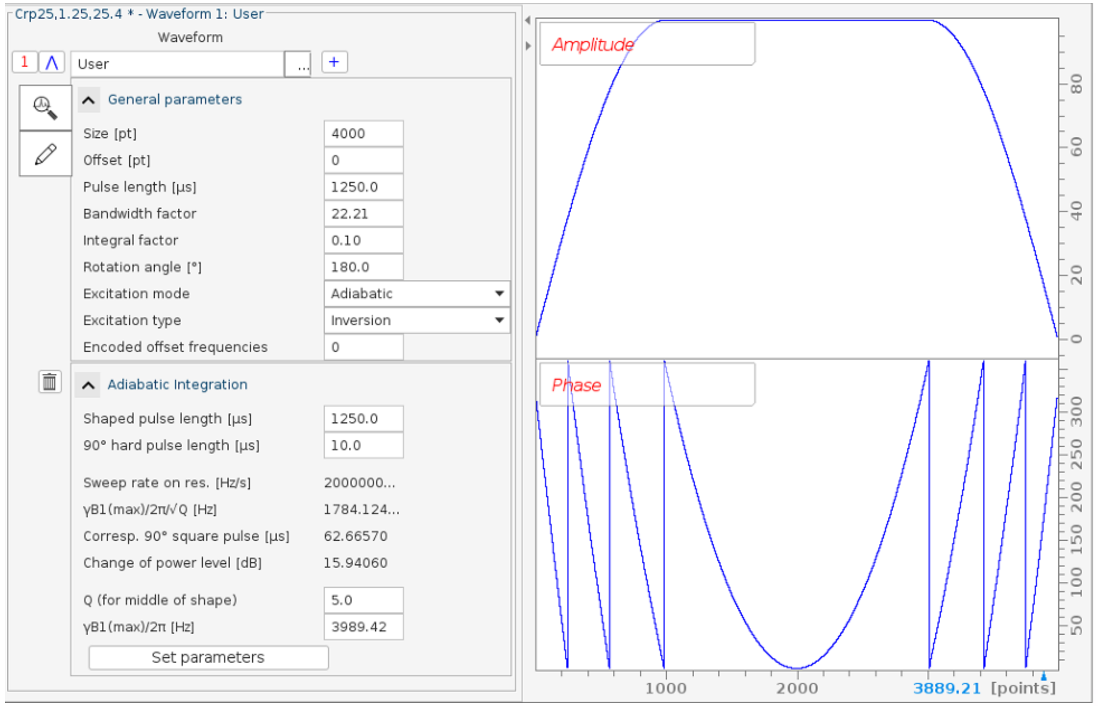
Resemble CW-NMR

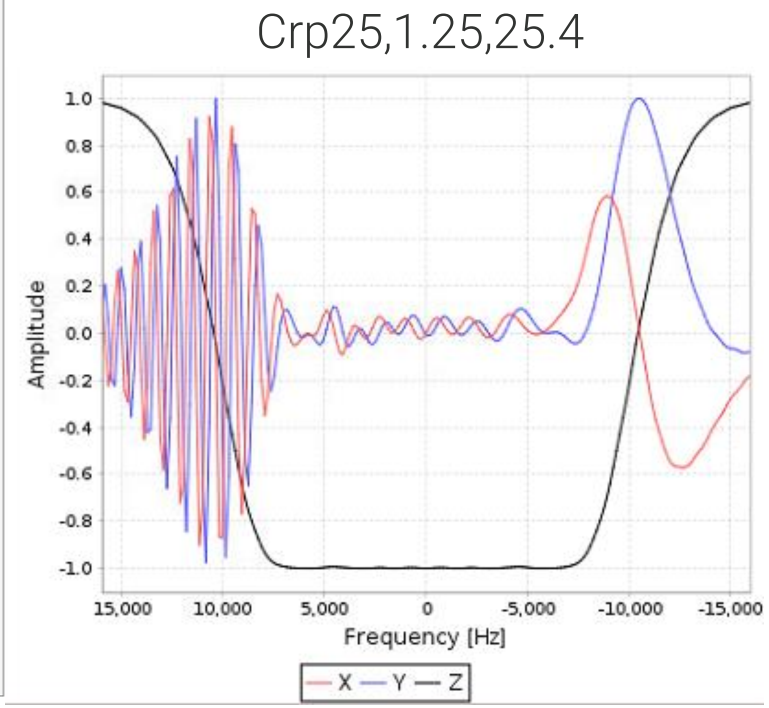


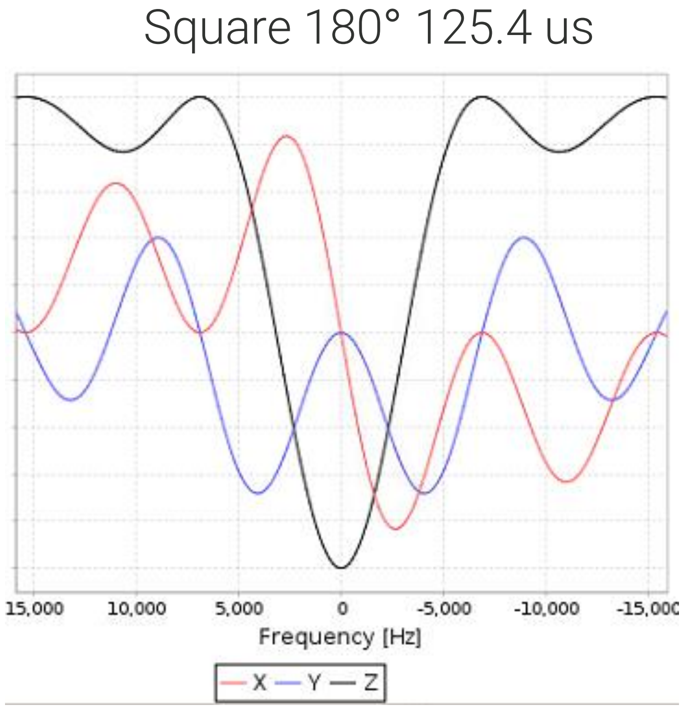
Crp25.1.25 - trajectories of 10 magnetization vectors spaced 250 Hz apart

The definition of adiabatic condition requires that the magnetization vector M follows the trajectory of the effective radio frequency field vector $B1_{eff}$. With adiabatic pulses spins having different resonance frequencies are inverted at different times, unlike hard pulses where all spins are affected simultaneously.

Inversion profile and power levels for adiabatic pulses

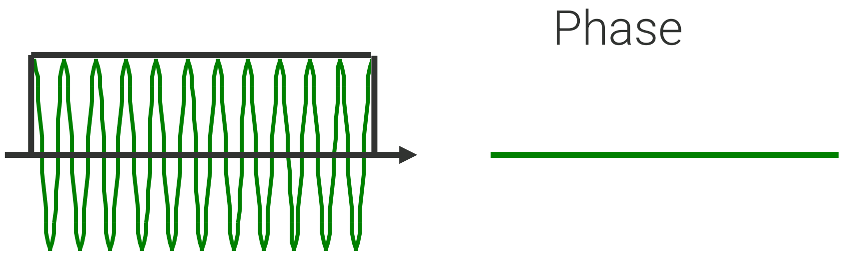




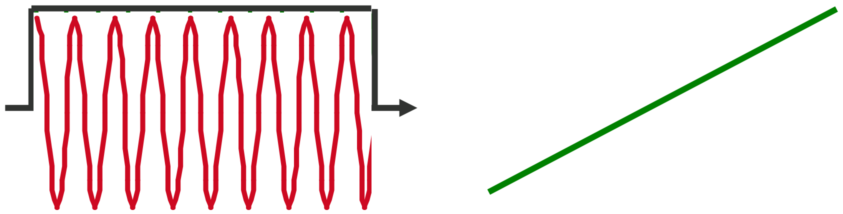


- Crp25,1.25,25.4 – Chirp pulse with 25 kHz sweep width, 1.25 ms duration, 25% sine smoothed, 4k points.
- Real inversion is ca. 70% of declared – 18 kHz
- Power corresponds to 90° pulse of 62.7 us

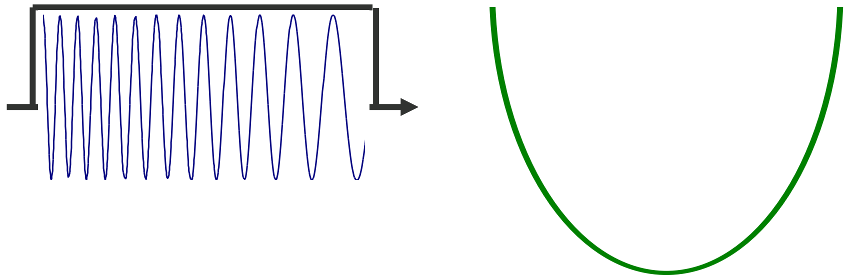
RF pulse: phase and frequency relation



Rectangular pulse with constant phase during the pulse: “on resonance” with transmitter offset



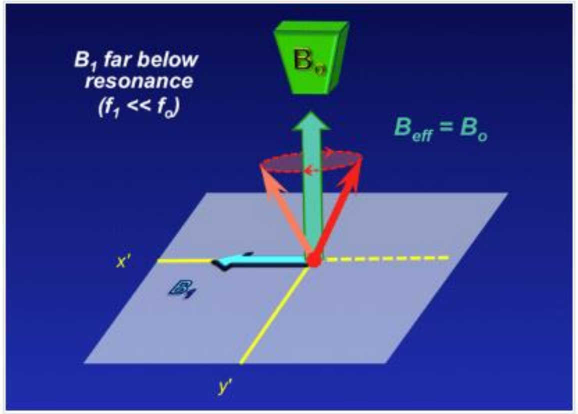
Rectangular pulse with linear phase change: “off resonance” with respect to transmitter offset



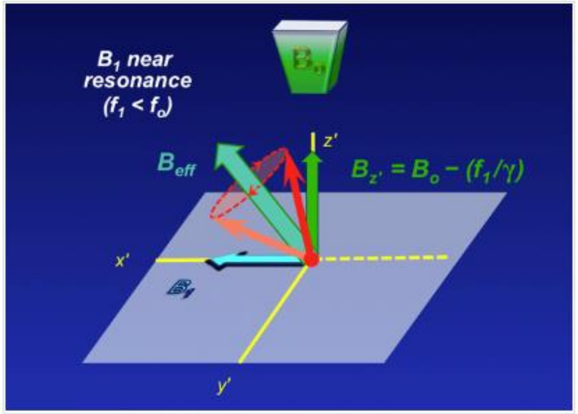
Rectangular Pulse with quadratic phase change: “frequency sweep” from far off-resonance through resonance

$f \ll f < f_o > f \gg f$

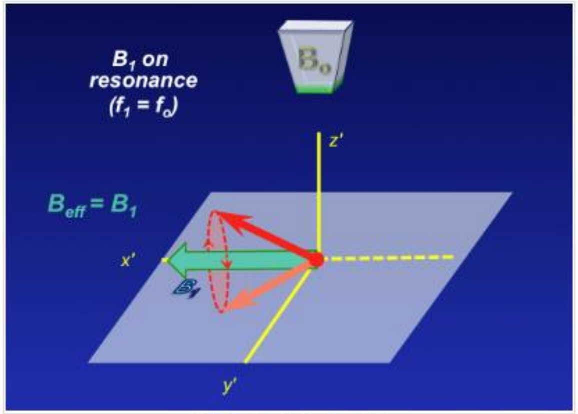
Adiabatic pulse



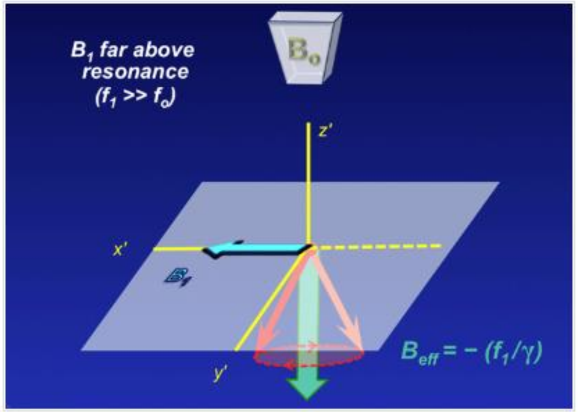
Adiabatic following #1.



Adiabatic following #2.



Adiabatic following #3.



Adiabatic following #4. (Adiabatic inversion)

- B_1 is applied as a long continuous wave rather than a short pulse
- The frequency of B_1 is slowly ramped from below to above resonance
- M will follow B_1 to inversion
- The adiabatic condition is formally expressed by $|d\theta/dt| << \gamma|B_{eff}|$ where θ = the angle made by B_{eff} with the y'-z' plane
- Provided that the B_1 field is strong enough and applied slowly enough, the adiabatic condition, M will follow B_{eff} during the B_1 frequency sweep

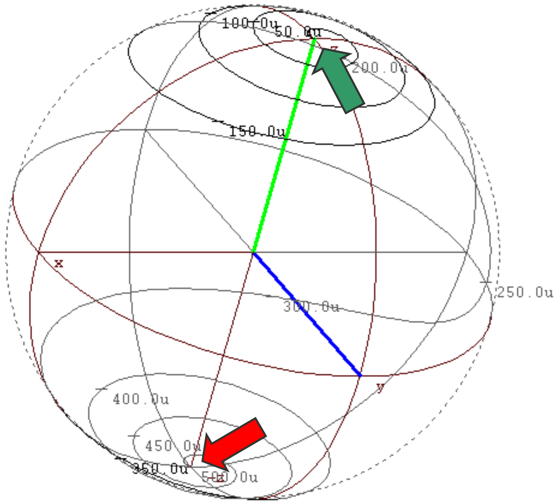
Adiabatic pulses - advantages

- Wide inversion bandwidth
  - Typical examples are 13C HSQC, 19F CPMG
  - Adiabatic decoupling requires less power and gives wider decoupling range
  - Broad and flat inversion profiles which produces increased S/N at the edges of a spectrum
- Insensitive to B1 inhomogeneity
  - Increased signal-to-noise
  - Clean spectra – right coherences are generated
- Insensitive to power missetings
  - Salty samples - increased signal-to-noise

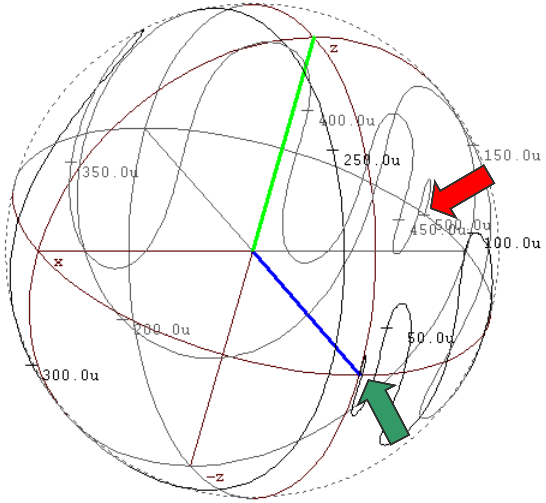
Adiabatic pulses - some useful rules of thumb

- The power for an adiabatic inversion or refocusing ^{13}C pulse is approximately the same as that for a 25 us ^{13}C high power 90^{o} pulse.
- The nominal sweep width of the adiabatic pulse for inversion or refocusing (not decoupling) should be ~1.5 x SW
- The nominal sweep width of the adiabatic pulse for adiabatic decoupling should be ~1.25 x SW (decoupling field).
- The length of the adiabatic decoupling pulse should be < 1/(5*J).
- To minimize power requirements, the recommended Q (quality factor , $Q = \frac{\omega_{eff}}{|d\theta/dt|}$) for decoupling is 2 to 3 (instead of 5).

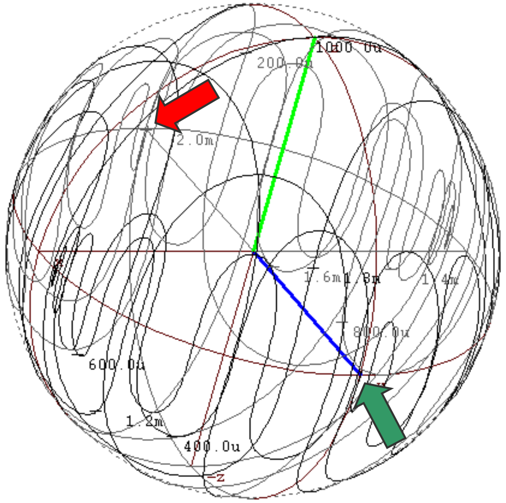
Adiabatic pulses - Limitations



Chirp Z -> -Z



Chirp Y -> -Y

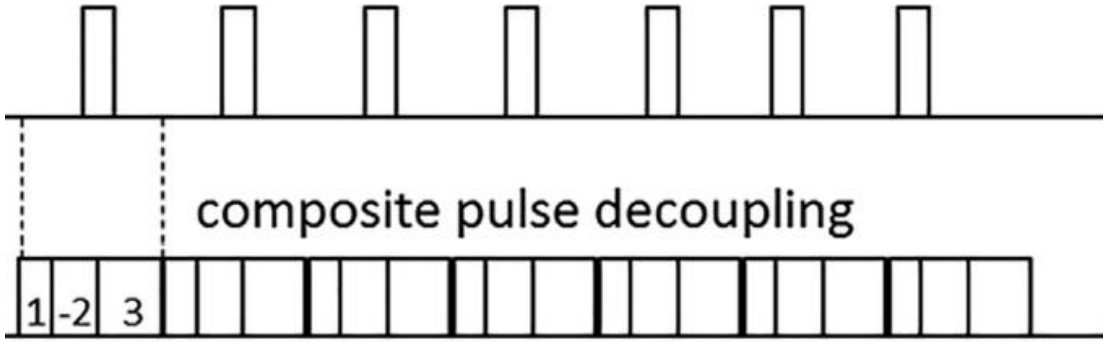


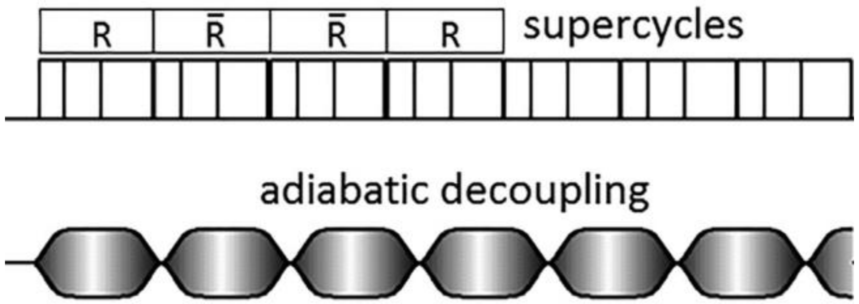
Composite (1:2:1) Chirp Y -> -Y

- Regular adiabatic pulses produce a non linear phase shift.
- This can be overcome by either using pairwise adiabatic pulses or a single composite adiabatic pulse
- Composite Adiabatic pulses can run into the power limitations of a probe (e.g. on ^{15}N)

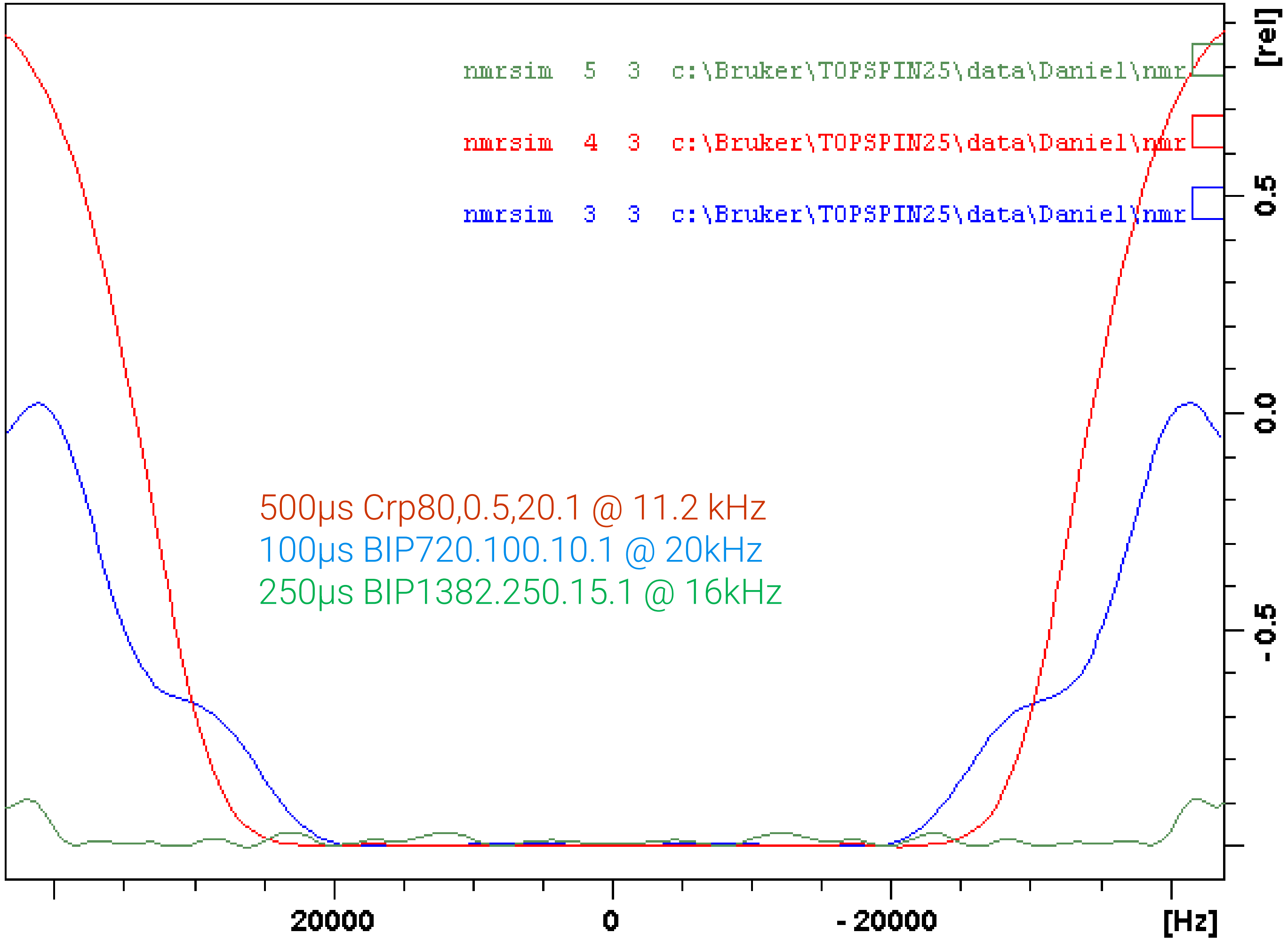
Typical Adiabatic pulses

- Adiabatic inversion : Crp32, Crp48…
- Adiabatic refocusing : in XY plane with composite pulse Crp60comp.4 – a composite 1:2:1 pulse
  Transverse magnetization during the pulse accumulates offset-dependent phase error. With 1:2:1 pulse, which is reminiscent of 90-180-90 composite pulse, the central component enables refocusing of the phase error originating from the first pulse by the last, third pulse.
- J-compensated Adiabatic Pulses – Crp60_xfilt.2: sweep rate matches change J coupling at different chemical shifts for proteins and nucleic acids
- Adiabatic decoupling





Not exactly adiabatic – broadband inversion pulses (BIP)



- Generally shorter than adiabatic pulses
- Slightly outperform adiabatic pulses at the same power level.
- Similar miscalibration tolerance
- Longer BIP variations allow for much higher bandwidth (at the cost of „flatness“)

Use of shaped pulses in a pulse sequence

Shaped pulses in pulse sequences

^ Channel f1

SFO1 [MHz]	799.8097581		Frequency of ch. 1
O1 [Hz, ppm]	3758.10	4.699	Frequency of ch. 1
NUC1	1H	Edit...	Nucleus for channel 1
P1 [µsec]	10.840		F1 channel - 90 degree high power pulse
p2 [µsec]	21.68		F1 channel - 180 degree high power pulse
P12 [µsec]	2000.000		F1 channel - 180 degree shaped pulse (Squa100.1000) [2 msec]
PLW0 [W, dB]	0	1000.00	0W
PLW1 [W, dB]	9.7724	-9.90	F1 channel - power level for pulse (default)
SPNAM 1	Sinc1.1000	... E	File name for SP1
SPOAL1	0.500		Phase alignment of freq. offset in SP1
SPOFFS1 [Hz]	0		Offset frequency for SP1
SPW1 [W, -dBW]	0.0033111	24.80	F1 channel - shaped pulse 180 degre

```
d16 pl0:f1
(p12:sp1 ph2:r):f1
4u
d12 pl1:f1
```

SPOAL1: Phase Alignment
- 0 Beginning of pulse (flip-back)
- 0.5 Center of pulse (refocusing)
- 1.0 End of pulse (excitation)

SPOFFS: Frequency Offset
Offset for shaped pulse in relation to o1

Prosol table

Saved Observe and Saved Decouple Prosol Parameter Set for:

Probe: Z81999_0001 PA QXI 600S3 H-C/N/F-D-05 Z Select_...

Solvent: generic

Pulse Assign File: /opt/topspin4.2.0.b.7/exp/stan/nmr/lists/prosol/pulseassign/triple Select

	Observe		Decouple
Nucleus	13C		13C

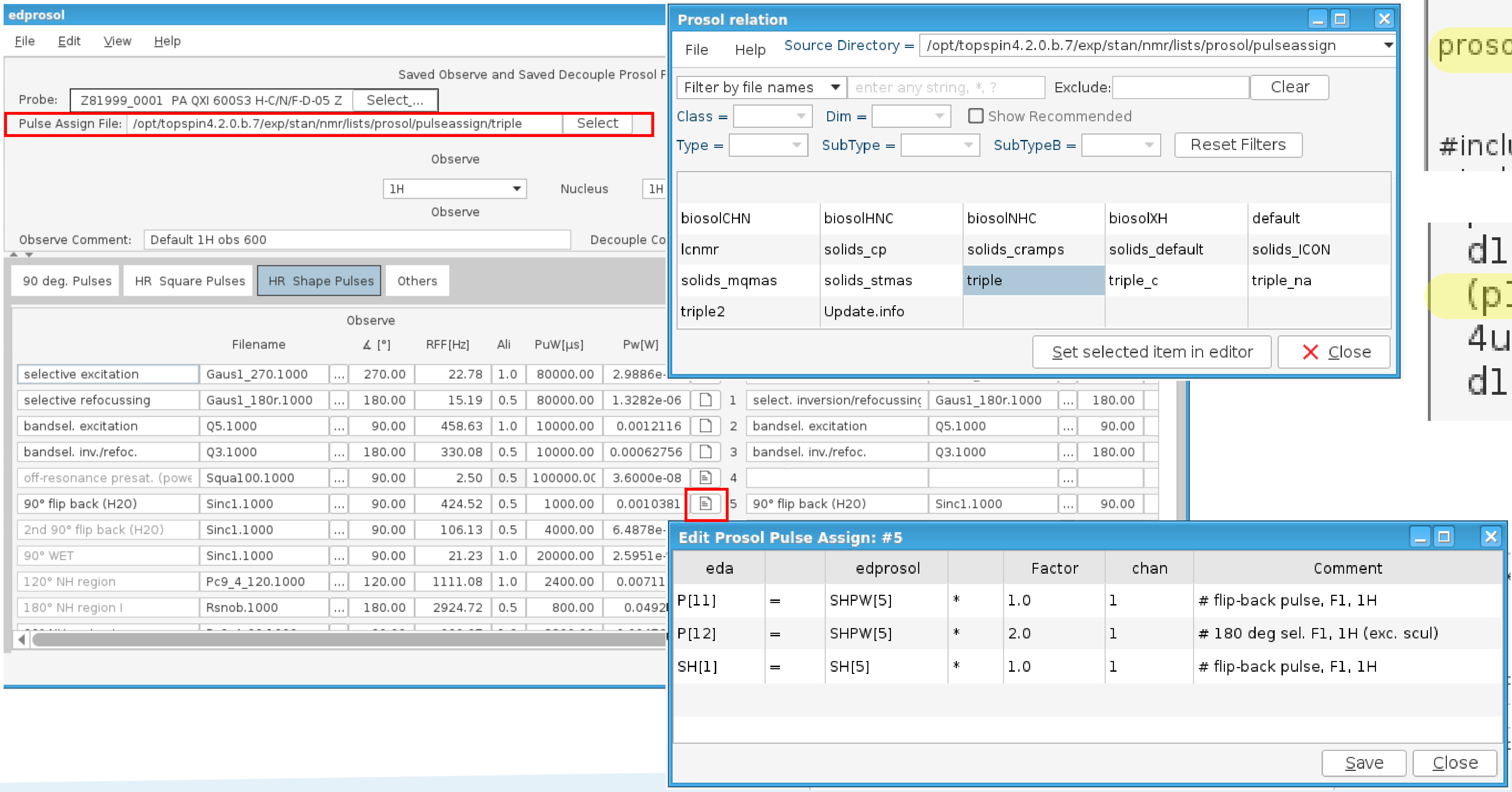
Observe Comment: Default 13C obs 600

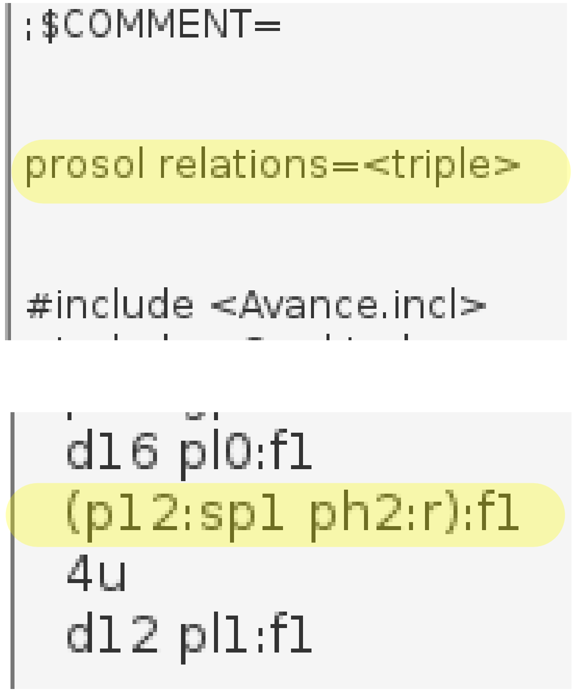
Decouple Comment: Default 13C dec 600

90 deg. Pulses | HR Square Pulses | **HR Shape Pulses** | Others

Observe	Filename	∡ [°]	RFF[Hz]	Ali	PuW[µs]	Pw[W]	rel	#	Decouple	Filename	∡ [°]	RFF[Hz]	Ali	PuW[µs]	Pw[W]	rel
selective excitation	Q5.1000	90.00	114.66	1.0	40000.00	0.00075724		0	selective excitation	Q5.1000	90.00	114.66	1.0	40000.00	0.00075724	
select. inversion/refocussing	Q3_surbop.1	180.00	103.75	0.5	40000.00	0.00061998		1	select. inversion/refocussing	Q3_surbop.1	180.00	103.75	0.5	40000.00	0.00061998	
bandsel. excitation	Q5.1000	90.00	1528.77	1.0	3000.00	0.13462		2	bandsel. excitation	Q5.1000	90.00	1528.77	1.0	3000.00	0.13462	
bandsel. inv./refoc.	Q3_surbop.1	180.00	1313.26	0.5	3160.00	0.099340		3	bandsel. inv./refoc.	Q3_surbop.1	180.00	1313.26	0.5	3160.00	0.099340	
adiabatic inversion	Crp60,0.5,20.1	180.00	9772.05	0.5	500.00	5.5004		4	adiabatic inversion	Crp60,0.5,20.1	180.00	9772.05	0.5	500.00	5.5004	
adiabatic refocussing	Crp60comp.4	180.00	9772.05	0.5	2000.00	5.5004		5	adiabatic refocussing	Crp60comp.4	180.00	9772.05	0.5	2000.00	5.5004	
Cali/CO 90°	Q5_sebop.1	90.00	15092.00	1.0	350.00	13.119		6	Cali/CO 90°	Q5_sebop.1	90.00	15092.00	1.0	350.00	13.119	
Cali/CO 90° timerev.	Q5tr_sebop.1	90.00	15092.00	0.0	350.00	13.119		7	Cali/CO 90° timerev.	Q5tr_sebop.1	90.00	15092.00	0.0	350.00	13.119	
Cali/CO 180°	Q3_surbop.1	180.00	15370.00	0.5	270.00	13.607		8	Cali/CO 180°	Q3_surbop.1	180.00	15370.00	0.5	270.00	13.607	
Calpha sel. 90°	Q5.1000	90.00	3057.55	1.0	1500.00	0.53848		9	Calpha sel. 90°	Q5.1000	90.00	3057.55	1.0	1500.00	0.53848	
Calpha sel. 90° timerev.	Q5tr.1000	90.00	3057.55	0.0	1500.00	0.53848		10	Calpha sel. 90° timerev.	Q5tr.1000	90.00	3057.55	0.0	1500.00	0.53848	
								12	adiabatic decoupling	Crp42,1.5,20.2	180.00	3656.37	0.5	1500.00	0.77006	
								13	adiab. decoupling (bilev par	Crp42,0.75,20.2	180.00	5170.88	0.5	750.00	1.5401	
x-filter (adiabatic 180)	Crp60_xfilt.2	180.00	5253.49	0.5	1730.00	1.5897		19	x-filter (adiabatic 180)	Crp60_xfilt.2	180.00	5253.49	0.5	1730.00	1.5897	
								34	low power adiabatic decoup	Crp38,2.5,25.4	180.00	2199.62	0.5	2500.00	0.27869	
								35	low power adiab. decoupling	Crp38,1.25,25.4	180.00	3110.73	0.5	1250.00	0.55737	

Shaped pulses in pulse sequences and prosol table





Shaped pulses in pulse sequences and explicit programming

Pulses and power levels are coming from prosol

SFO1 [MHz]	600.1328206	
O1 [Hz, ppm]	2820.61	4.700
NUC1	1H	Edit...
P1 [µsec]	10.840	
p2 [µsec]	21.68	
P12 [µsec]	2000.000	
PLW0 [W, dB]	0	1000.00
PLW1 [W, dB]	9.7724	-9.90
SPNAM 1	Sinc1.1000	... E
SPOAL1	0.500	
SPOFFS1 [Hz]	0	
SPW1 [W, -dBW]	0.0033111	24.80
Gradient channel		
GPNAM 1	SMSQ10.100	... E
GPZ1 [%]	31.00	
GPNAM 2	SMSQ10.100	... E
GPZ2 [%]	11.00	
P16 [µsec]	1000.000	

Pulses, gradients, power level calculations are explicitly programmed

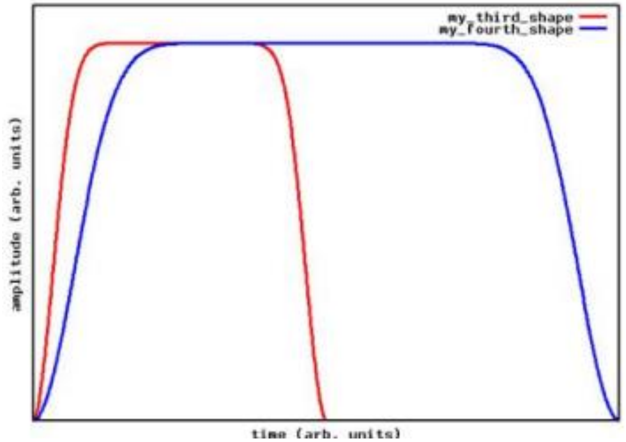
SFO1 [MHz]	600.1328206	
O1 [Hz, ppm]	2820.61	
NUC1	1H	Edit...
P1 [µsec]	10.840	
p2 [µsec]	21.68	
p12 [µsec]	2000.00	
PLW1 [W, dB]	9.7724	
spnam1	Sinc1.1000	
spoal1	0.5000000	
spoffs1 [Hz]	0	
spw1 [W, -dBW]	0.0033111	
INTEGFAC1	0.5889000	
Gradient channel		
gpnam1	SMSQ10.100	
gpz1 [%]	31.00	
gpnam2	SMSQ10.100	
gpz2 [%]	11.00	
p16 [µsec]	1000.00	

```
#include <Avance.incl>
#include <Grad.incl>
#include <Delay.incl>


"p2=p1*2"
"p12=2m"


"spnam1='Sinc1.1000'"
"spoal1=0.5"
"spoffs1=0"
"spw1=plw1*pow(p1*180/(p12*90*integfac1),2)"

"p16=1m"
"gpnam1='SMSQ10.100'"
"gpnam2='SMSQ10.100'"
"gpz1=31"
"gpz2=11"

"d12=20u"
"TAU=de+p1*2/3.1416+50u"
```

Shaped pulses in pulse sequences and wavemaker

- WaveMaker is a software for pulse shaping that is based on waveform definitions within the pulse programs.
- This avoids any need to modify the PROSOL tables when new or non-standard shaped pulses and decoupling or mixing waveforms are required.
- It also adds flexibility and improves portability of many standard and user developed experiments and pulse programs.
- Porting the WaveMaker based pulse programs to NMR systems of different field strength is straightforward and typically requires no further adjustments and PROSOL updates.

```
#include <Avance.incl>
create_shape(sp1, gaus90, name=mygauss, length=1000us, numPoints=1000)

1 ze
2 30m
d1
4u pl0:f1
p11:sp1:f1 ph1:r
go=2 ph31
30m mc #0 to 2 F0(zd)
exit
```



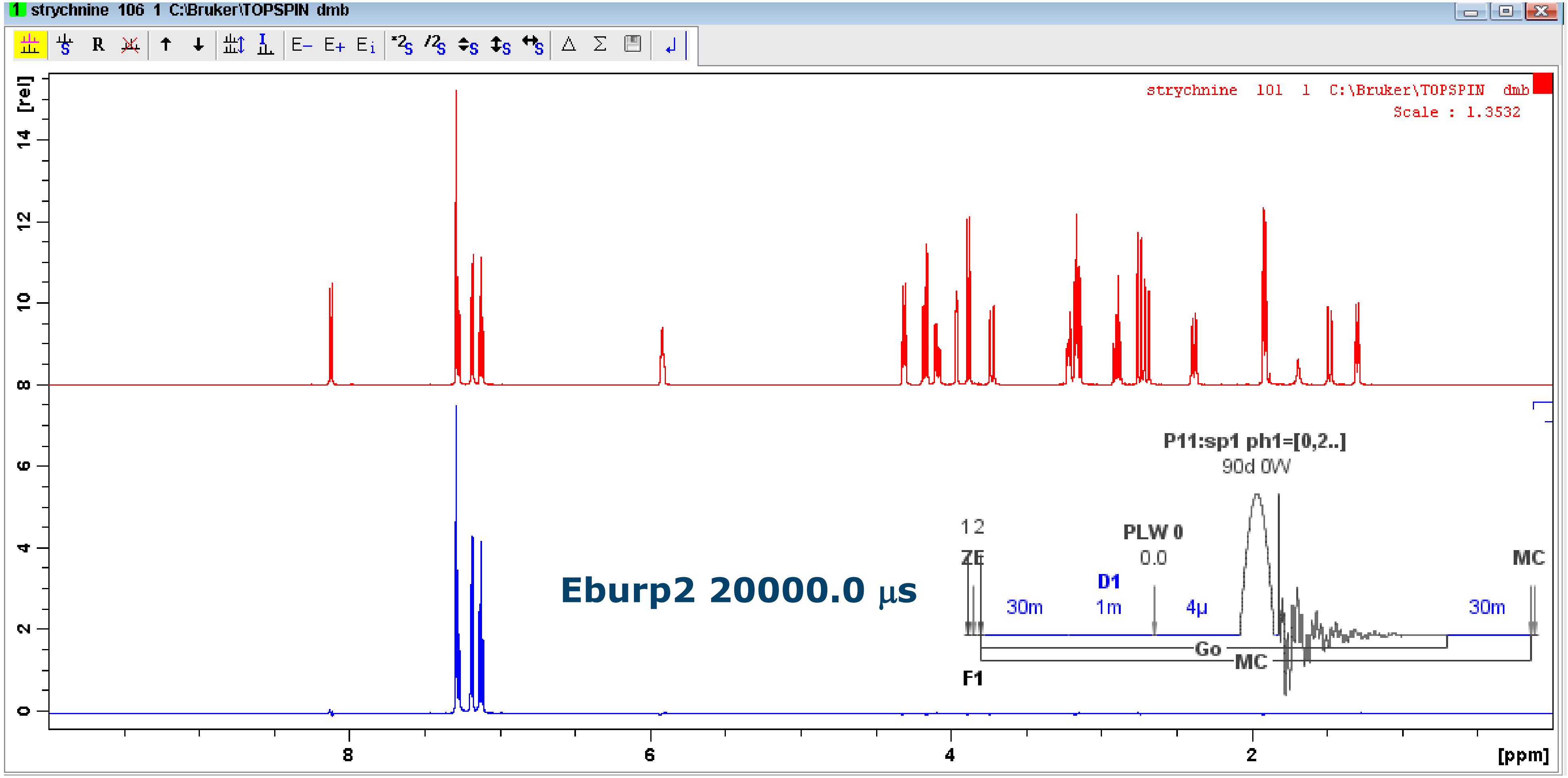

```
define delay dur
"dur=10ms"
create_shape(sp1, cawurst, length=$dur ms, name=my_third_shape)
"dur=dur*2"
create_shape(sp2, cawurst, length=$dur ms, name=my_fourth_shape)
```

Applications

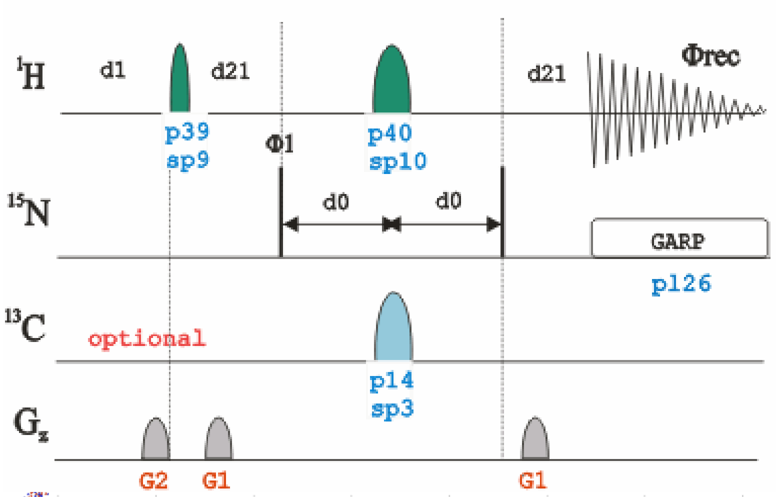
Criteria for the selection of a shaped pulse

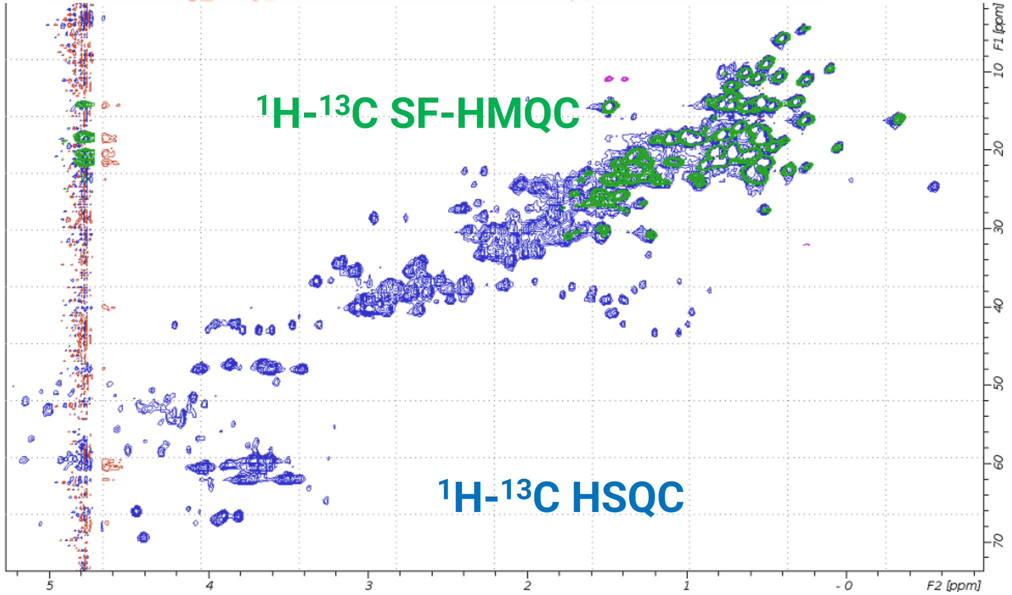
1. Selectivity
   a. the region of interest should be irradiated as selectively as possible / as broad as possible
   b. the excitation profile should be rectangular and flat on top (uniform excitation)
   c. negligible excitation outside or in certain regions outside: HNCA, refocus CO; zero excitation of water
2. Length & Power
   a. the pulse should be as short as possible as relaxation and J-evolution take place during shaped pulses
   b. lowest possible integral power or peak power
3. Phase
   a. the pulse should give pure phase within the region of interest
   b. phase response should be uniform (self-refocussing)
4. Versatility
   a. ideally one pulse would be suitable for all kind of rotations
   b. 90-exitation (M_z -> M_{xy}), 180-inversion (M_z -> M_{-z}), 180-refocussing (M_{xy} -> M_{-x-y}) or other rotations

Applications: selective excitation



Applications: semi-selective SOFAST-HMQC





NH-selective shaped pulses for BEST/Sofast NMR Experiments:

p39 sp23 — p39: f1 channel - 120 degree shaped pulse for excitation
sp23= Pc9_4_120.1000 (120o) (3.0ms at 600.13 Mhz)
(or Q5.1000 (90o) (2.0ms at 600.13 MHz))

p40 sp24 — p40: f1 channel - 180 degree shaped pulse for refocussing
sp24= Rsnob.1000 (1.0ms at 600.13 Mhz)

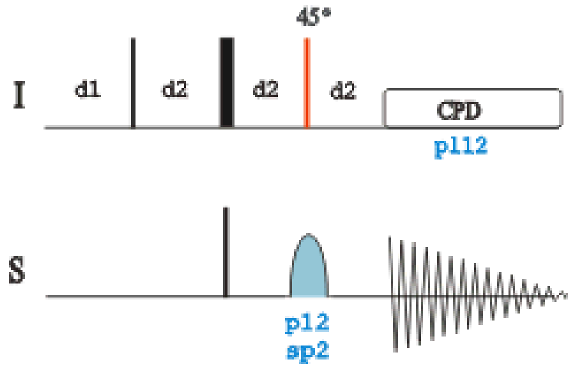
p41 sp25 — p41: f1 channel - 90 degree shaped pulse for excitation
sp25=sp27= Pc9_4_90.1000 (3.0ms at 600.13 Mhz)

p42 sp26 — p42: f1 channel - 180 degree shaped pulse for refocussing
sp26= Reburp.1000 (2.0ms at 600.13 Mhz)

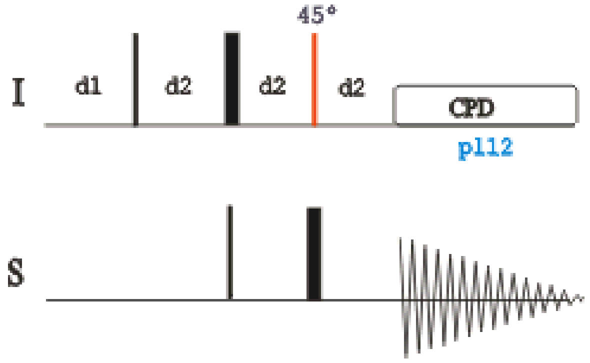
p43 sp28 — p43: f1 channel - 90 degree shaped pulse for excitation
sp28= Eburp2.1000 (1.92ms at 600.13 Mhz)
sp29= Eburp2tr.1000 (1.92ms at 600.13 Mhz)

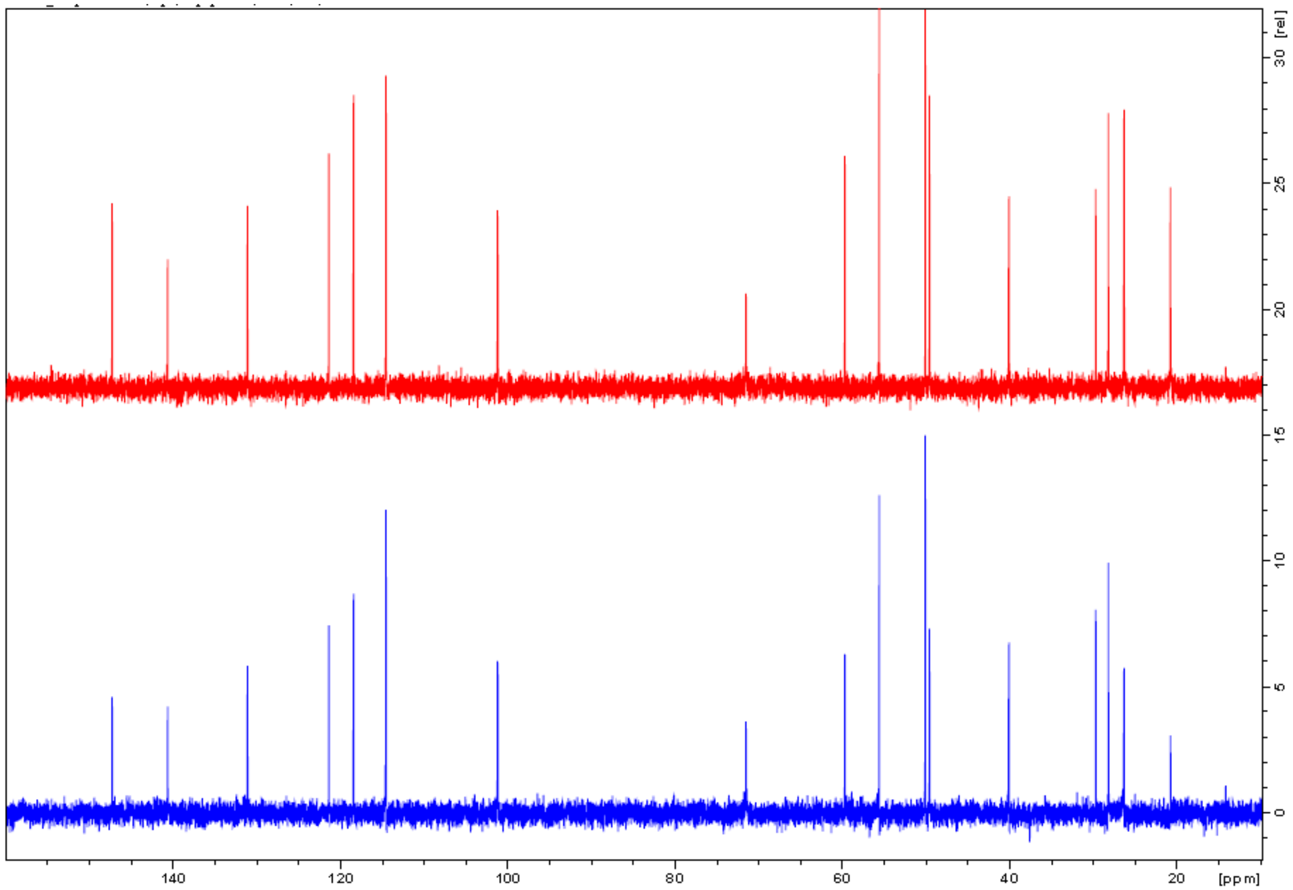
p44 sp30 — p44: f1 channel - 180 degree shaped pulse for refocussing
sp30= Bip720,50,20.1 (200us at 600.13 MHz)

Adiabatic pulses



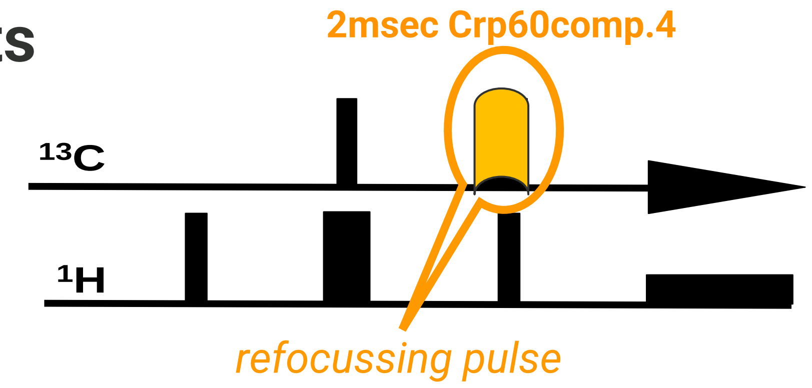
2msec Crp60comp.4

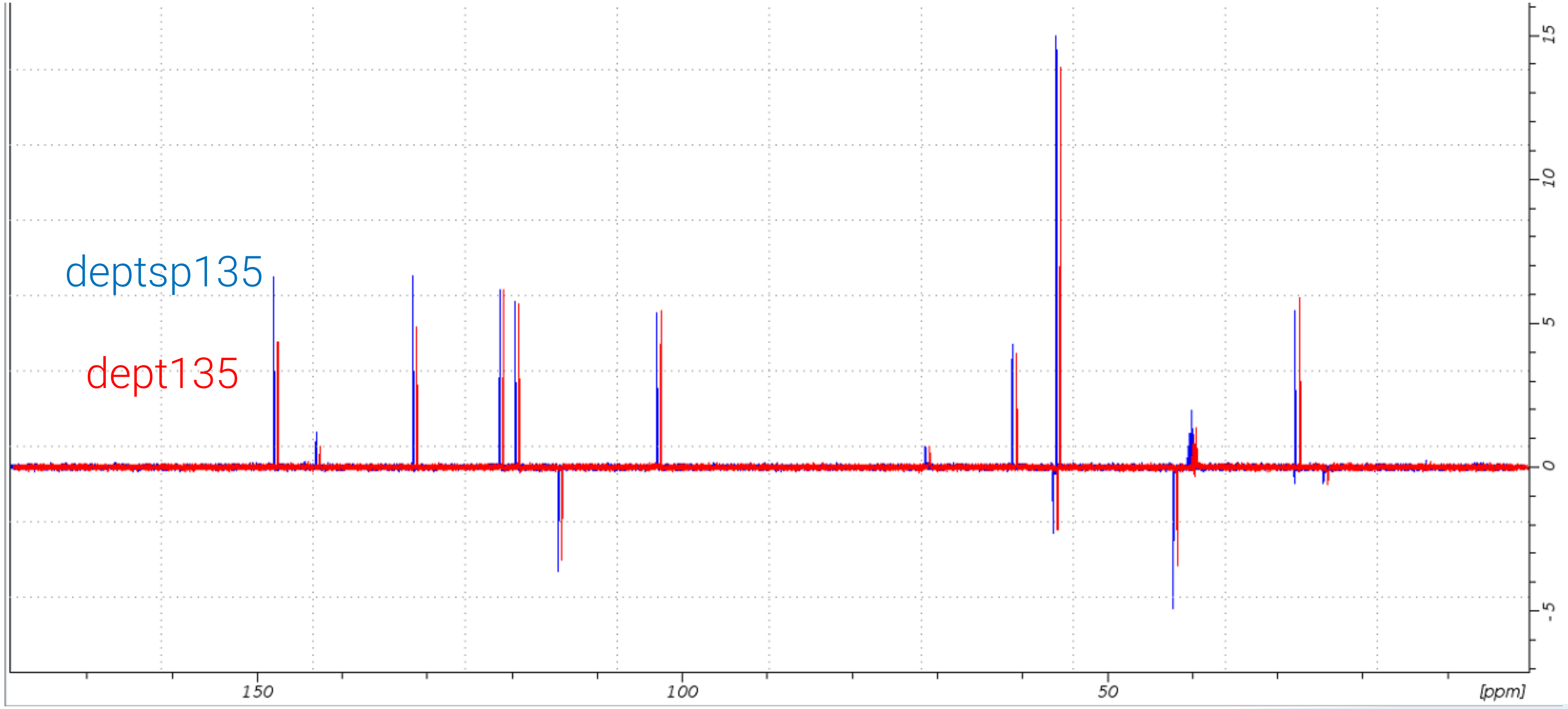




Adiabatic pulses in ^{13}C DEPT experiments

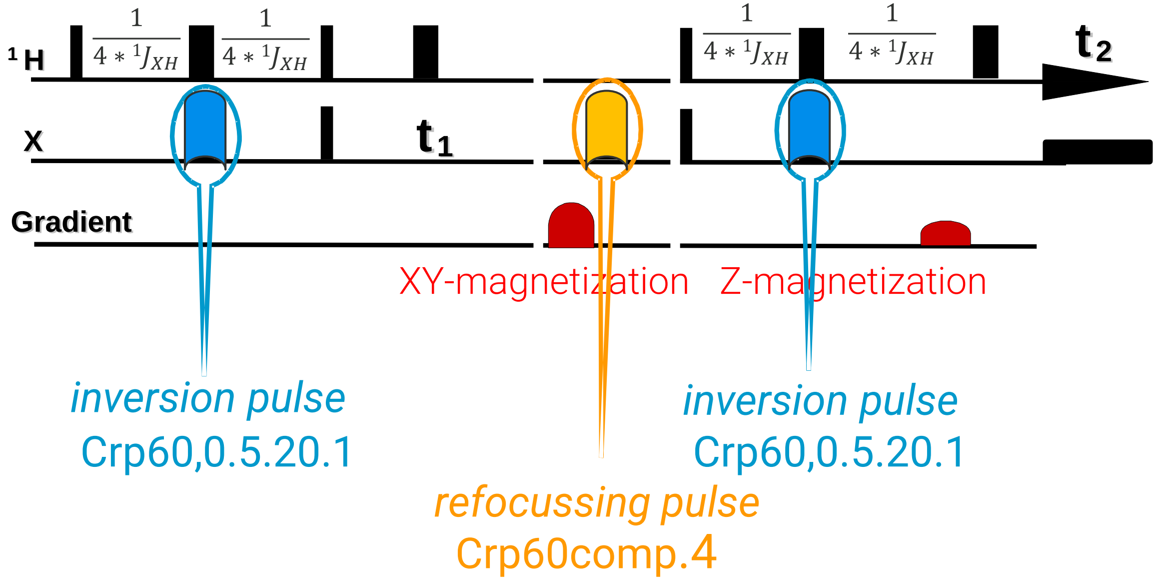
- dept45/90/135
- deptsp45/90/135/q – with adiabatic refocusing





Adiabatic pulses in ^{13}C HSQC experiments

- hsqcetgpsp – with adiabatic inversion only – faster relaxing molecules
- hsqcetgpsp.2 – with adiabatic inversion and refocusing - mind the relaxation

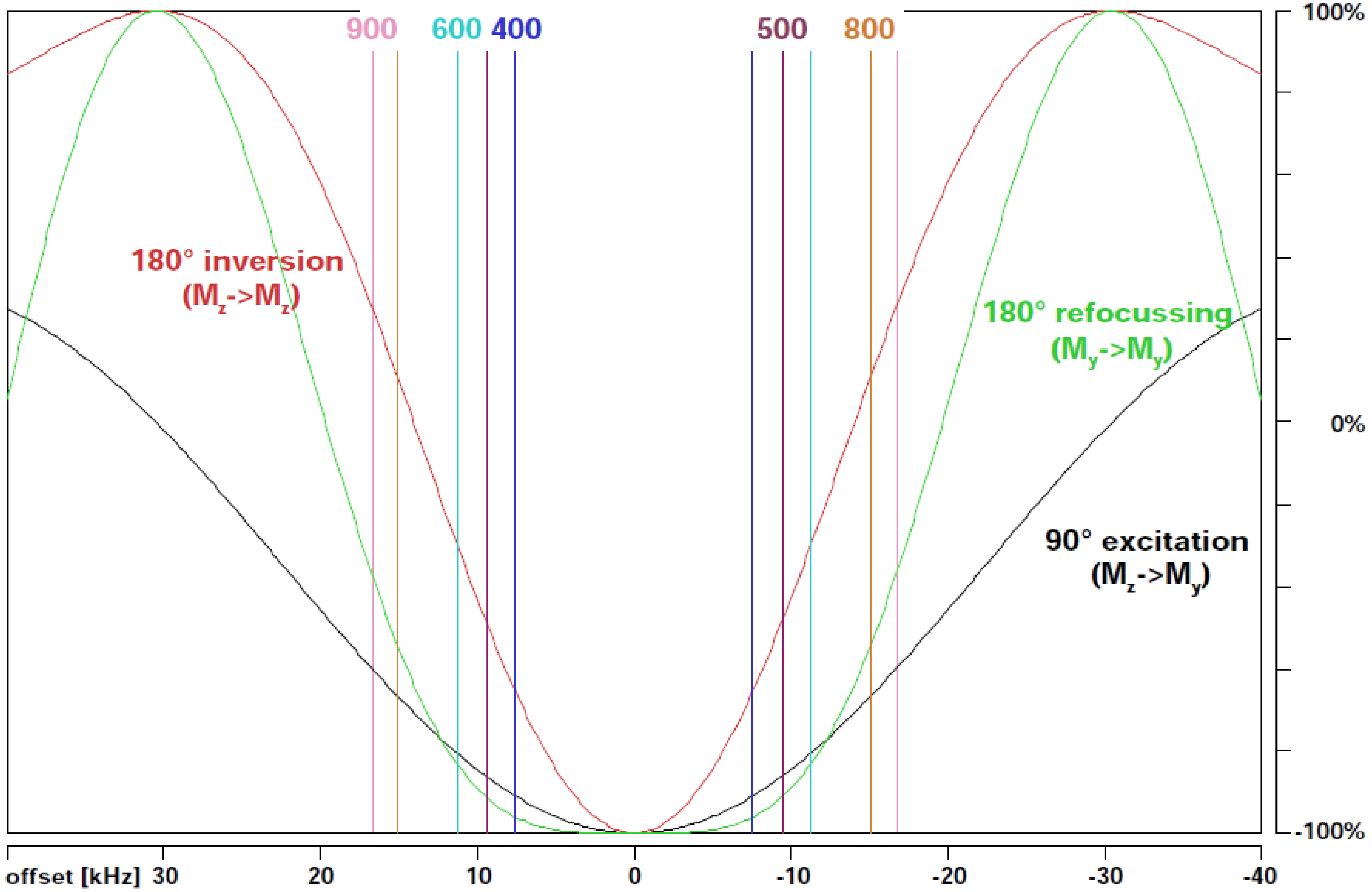


^{13}C pulse bandwidth

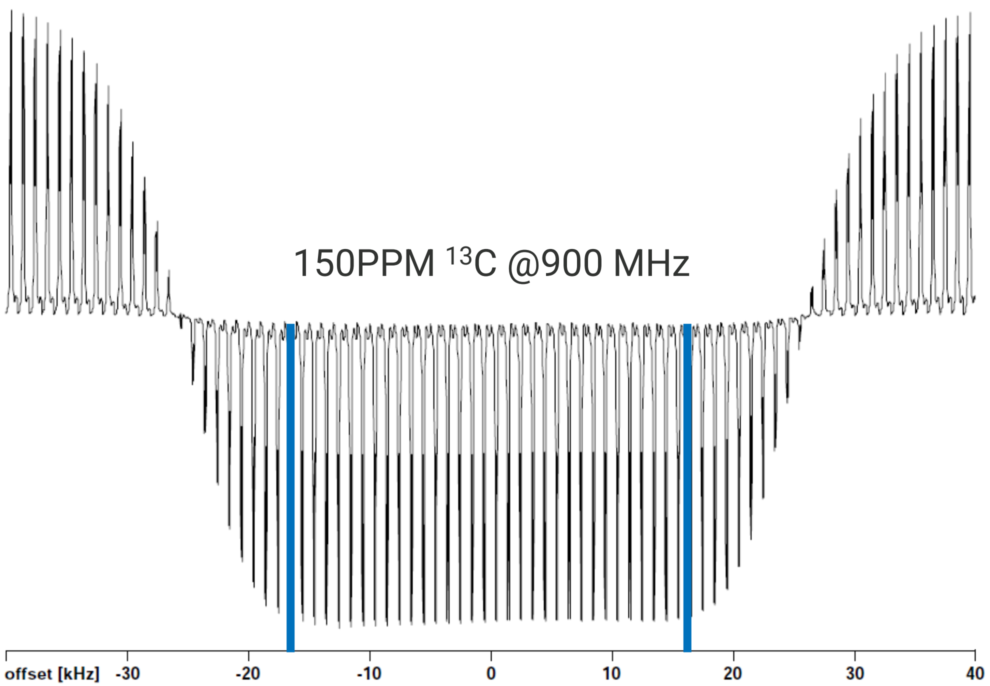
shaped pulse: rectangular

simulation
14.2 µsec
17605.6 Hz

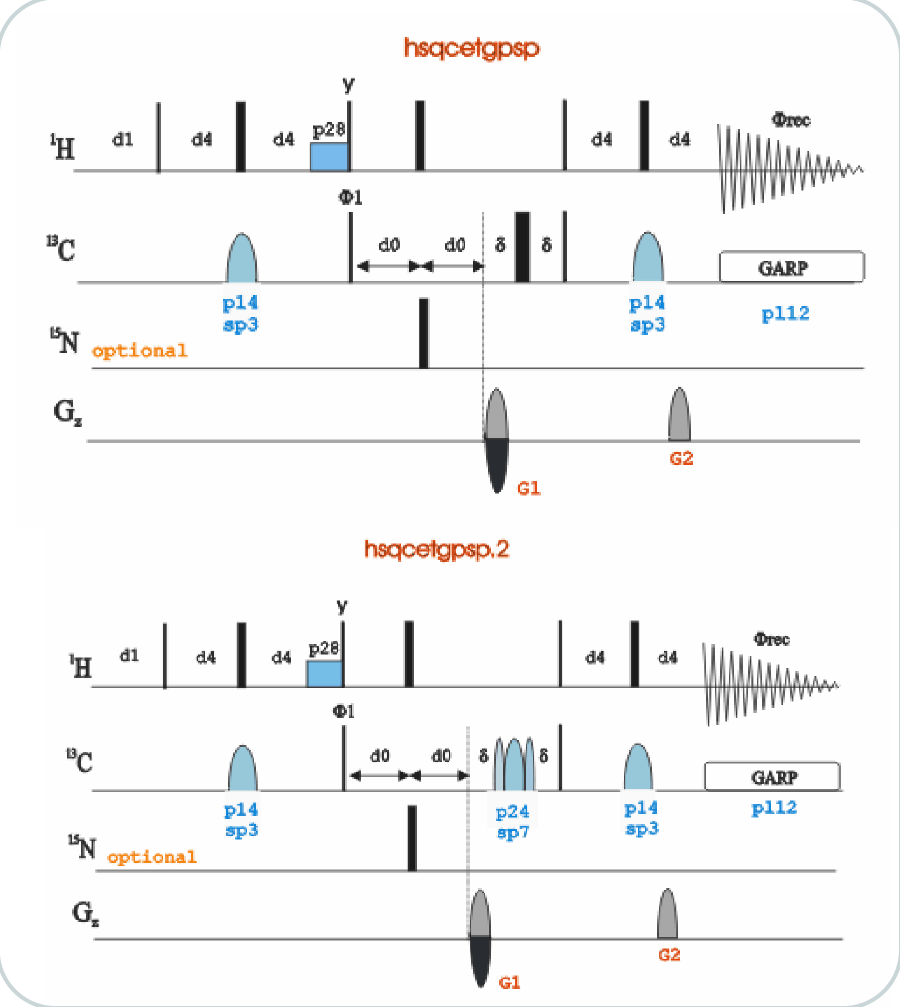
region of ±75 ppm for different field strength (MHz ^{1}H)



Crp60,0.5,20.1

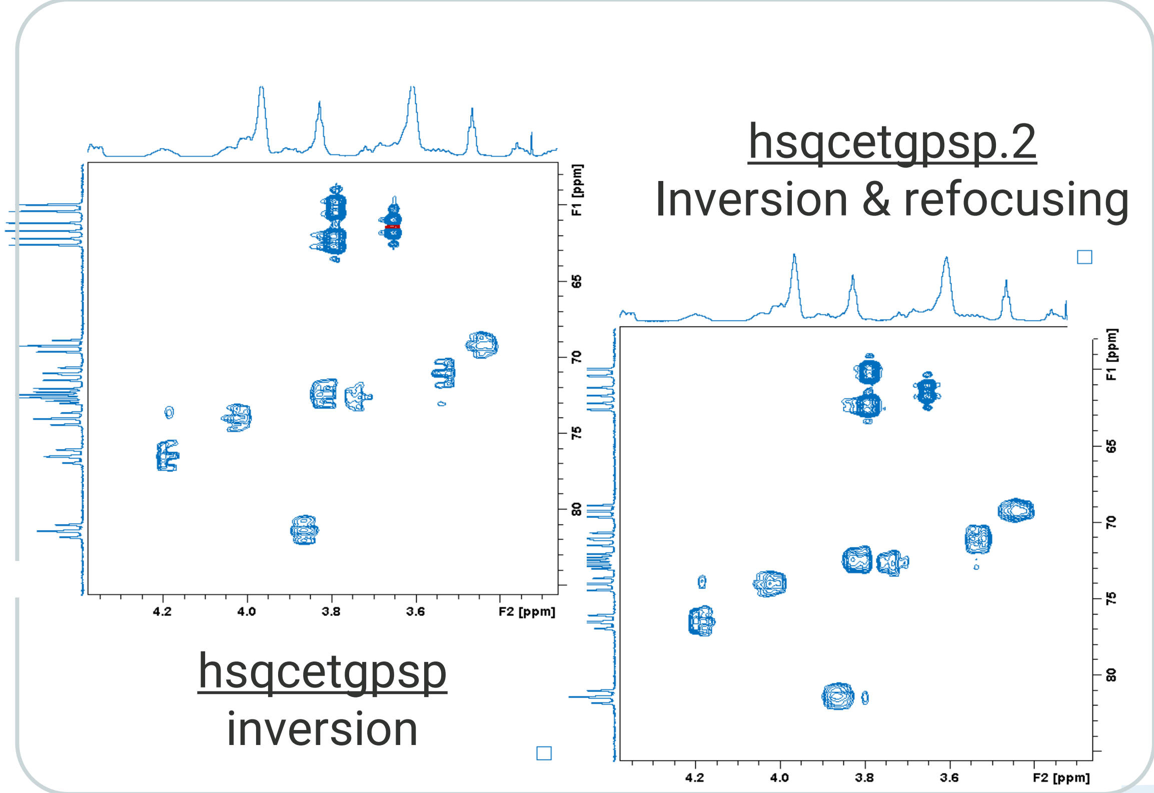


Adiabatic pulses: ^{1}H-^{13}C HSQC

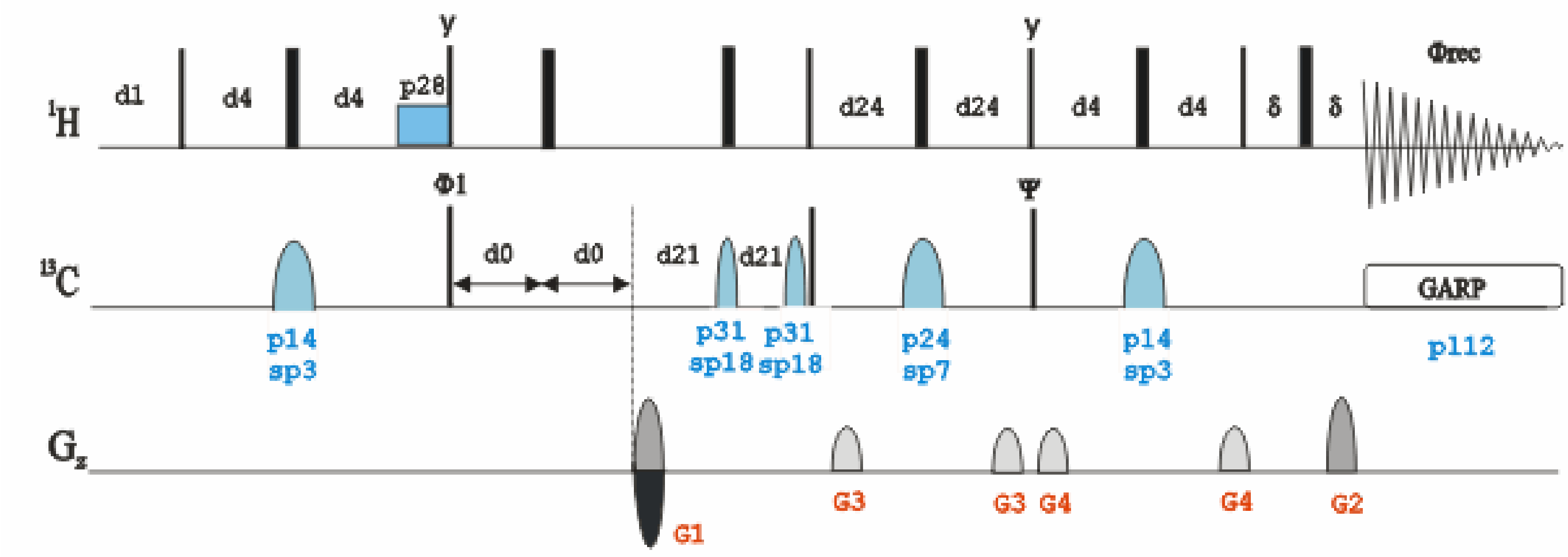


Adiabatic pulses:
Inversion (p14) = 0.5 ms
Refocusing (p24) = 2.0 ms

Hard 180 Pulse: 16 us



Adiabatic pulses: multiplicity edited ^{1}H-^{13}C HSQC

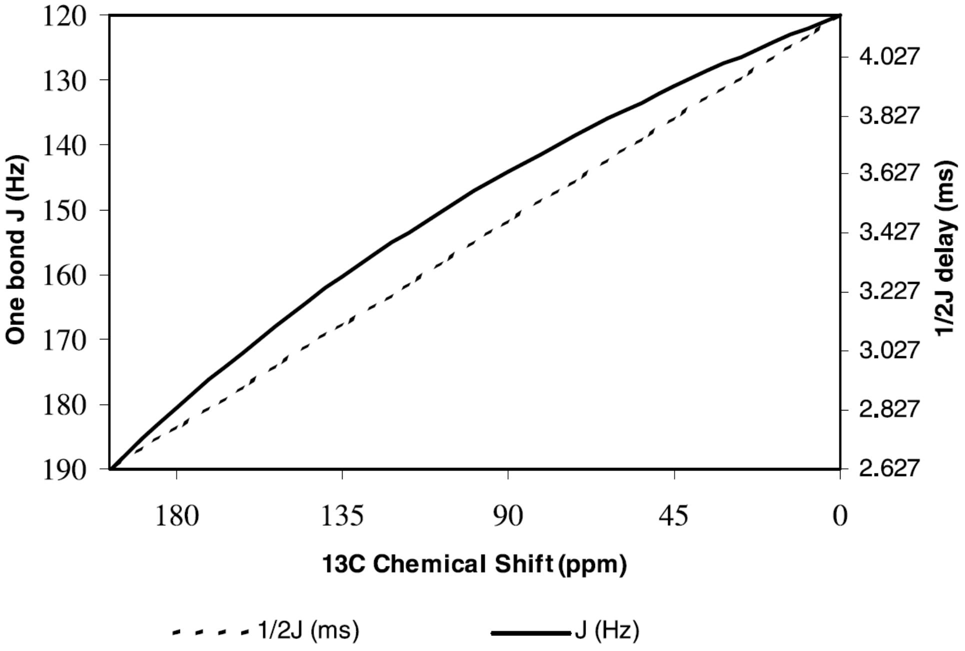


- Usage of J compensated matched sweep adiabatic pulses

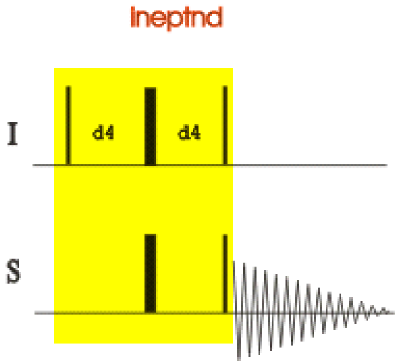
Matched sweep adiabatic pulses

Typical small molecule: $^{1}J_{CH}$: 120-250Hz

protonated ^{13}C chemical shift: 10-195ppm

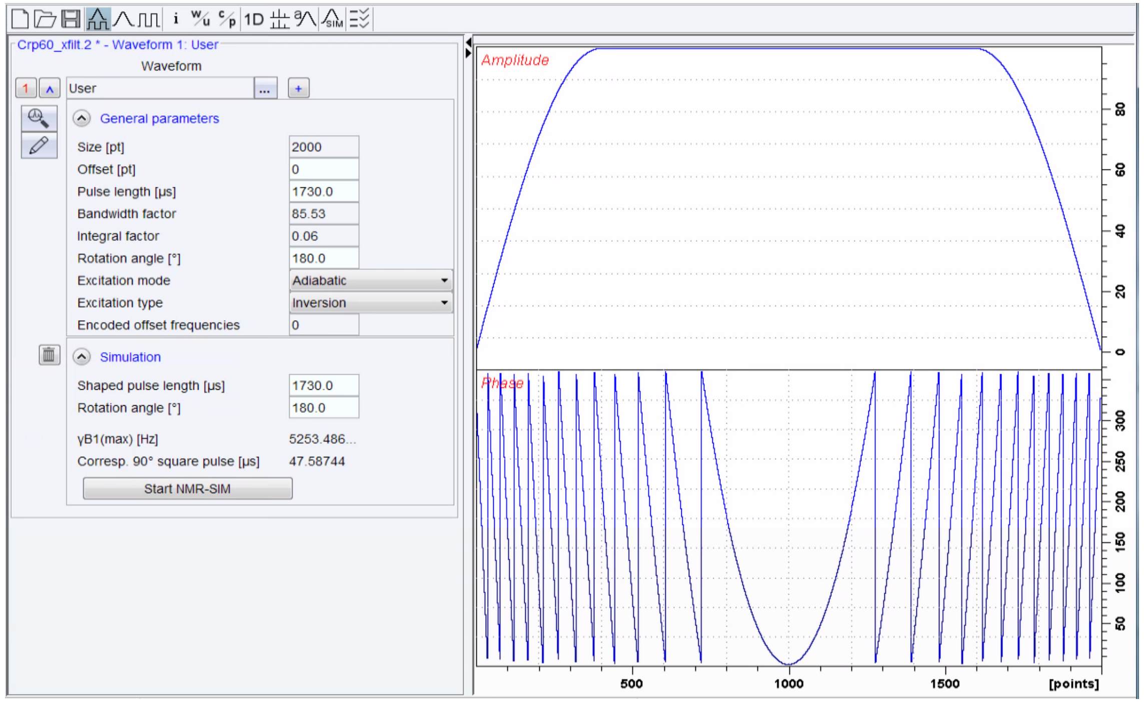


From: Boyer, R.D. et al, J. Mag. Reson.165 (2003) 253-259

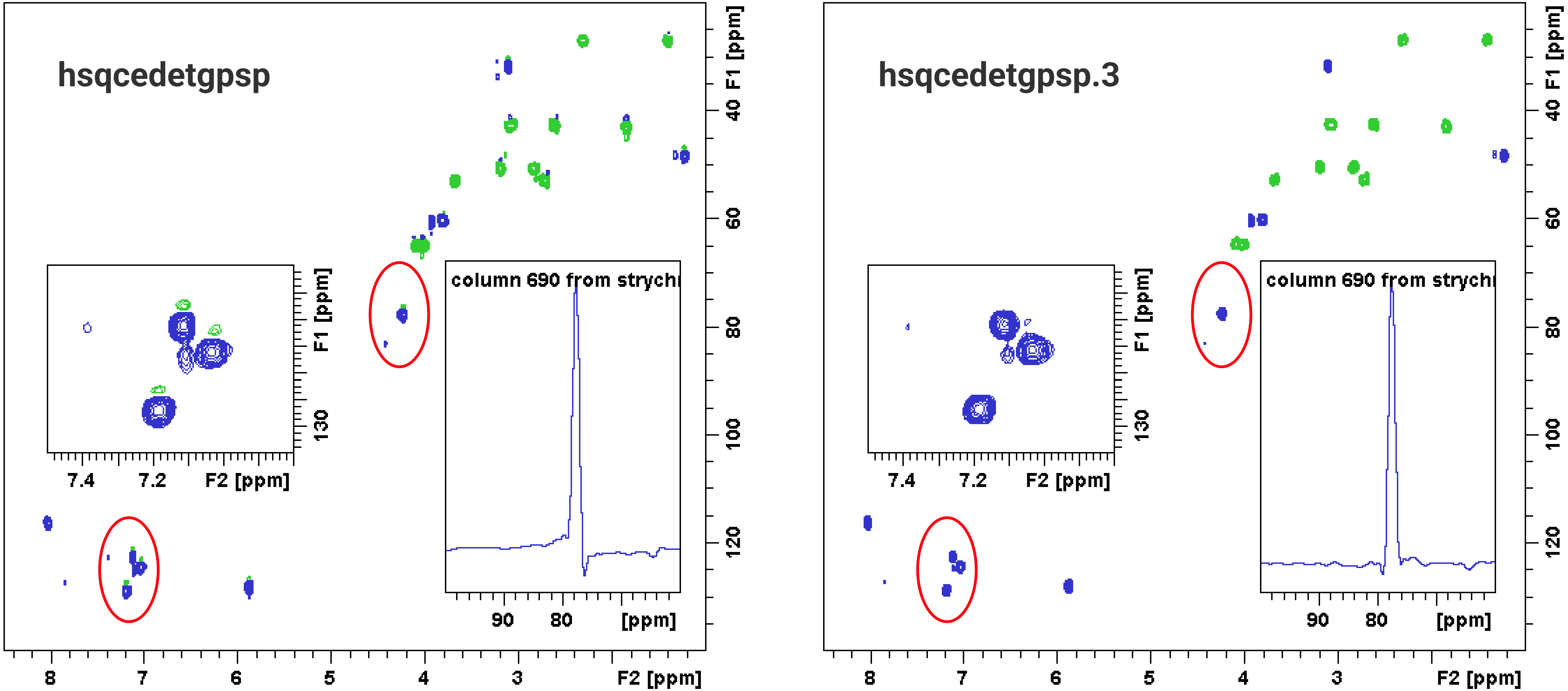


$$P_{opt} = \frac{J_{max} - J_{min}}{4 * J_{max} * J_{min}}$$

optimum sweep duration for a pulse to match a range of coupling constants between J_{max} and J_{min}.

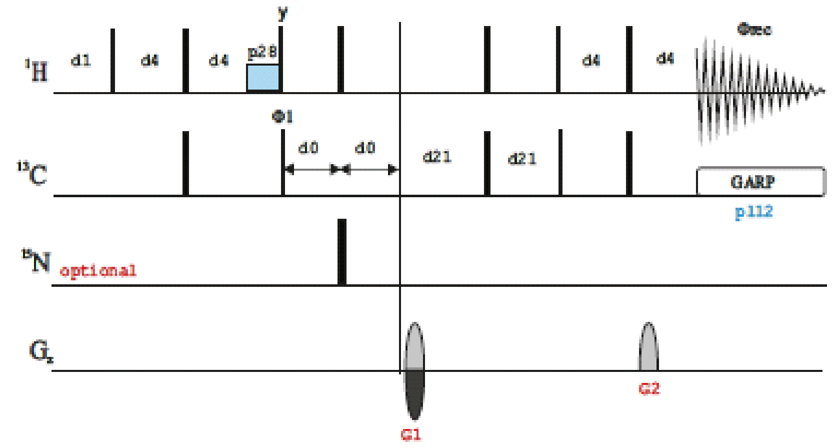


Matched sweep adiabatic pulses



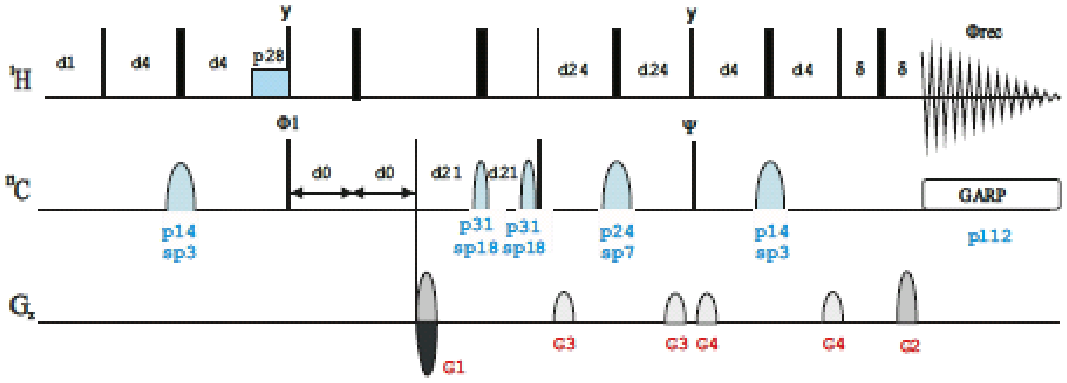
Adiabatic pulses: multiplicity edited ^{1}H-^{13}C HSQC

hsqcedetgp



No adiabatic 13C pulses

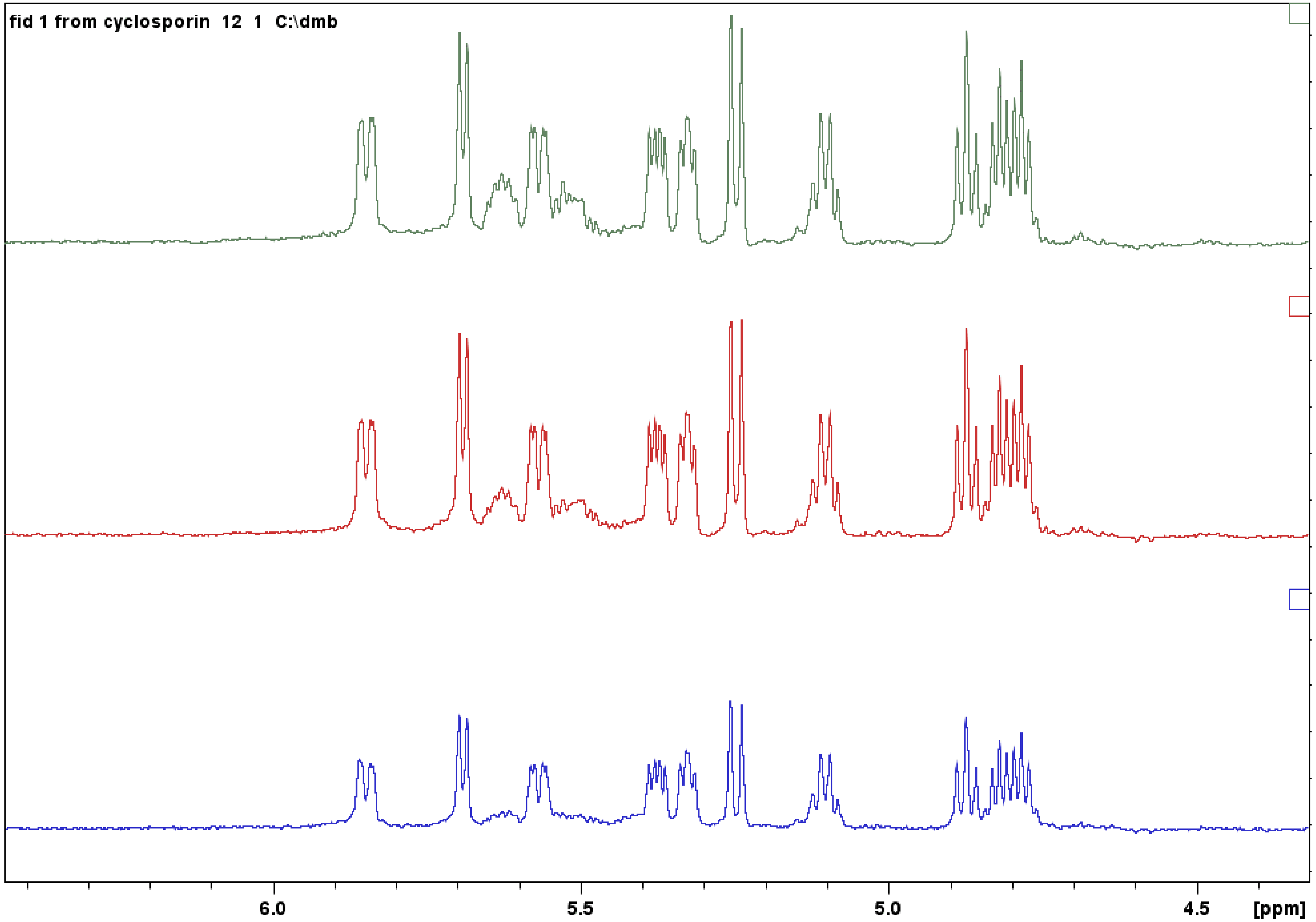
hsqcedetgpsisp2.3



(p14:sp3 ph6):f2	adiabatic inversion - Crp60,0.5,20.1
(p24:sp7 ph1):f2	adiabatic refocusing - Crp60comp.4
(p31:sp18 ph1):f2	matched sweep adiabatic - Crp60_xfilt.2
bi_p5m4sp_4sp.2	bilevel adiabatic decoupling - Crp42,1.5,20.2

Typical pulses for 600MHz

Adiabatic pulses: multiplicity edited ^{1}H-^{13}C HSQC



hsqcedetgpsisp2.3 – 13C adiabatic pulses for inversion and refocusing

hsqcedetgpsisp2 - 13C adiabatic pulses for inversion

hsqcedetgp - no 13C adiabatic pulses

HSQC pulse sequences

HSQC pulse seq	Feature	Comments
ed	edited	
si	sensitivity improvement	Line shapes might be distorted Longer pulse sequence, for proteins may give opposite result
lr	long range	
jc	j-coupling measurement	
f3	15N	
ct	constant time	no $^{1}J_{CC}$ coupling present, sharper lines, for labeled samples
pr|wt	Water suppression	
di, ml, no, ro	TOCSY, NOESY	
_bbhd	Broad-band homodec	
_bshd	Band-selective homodec	

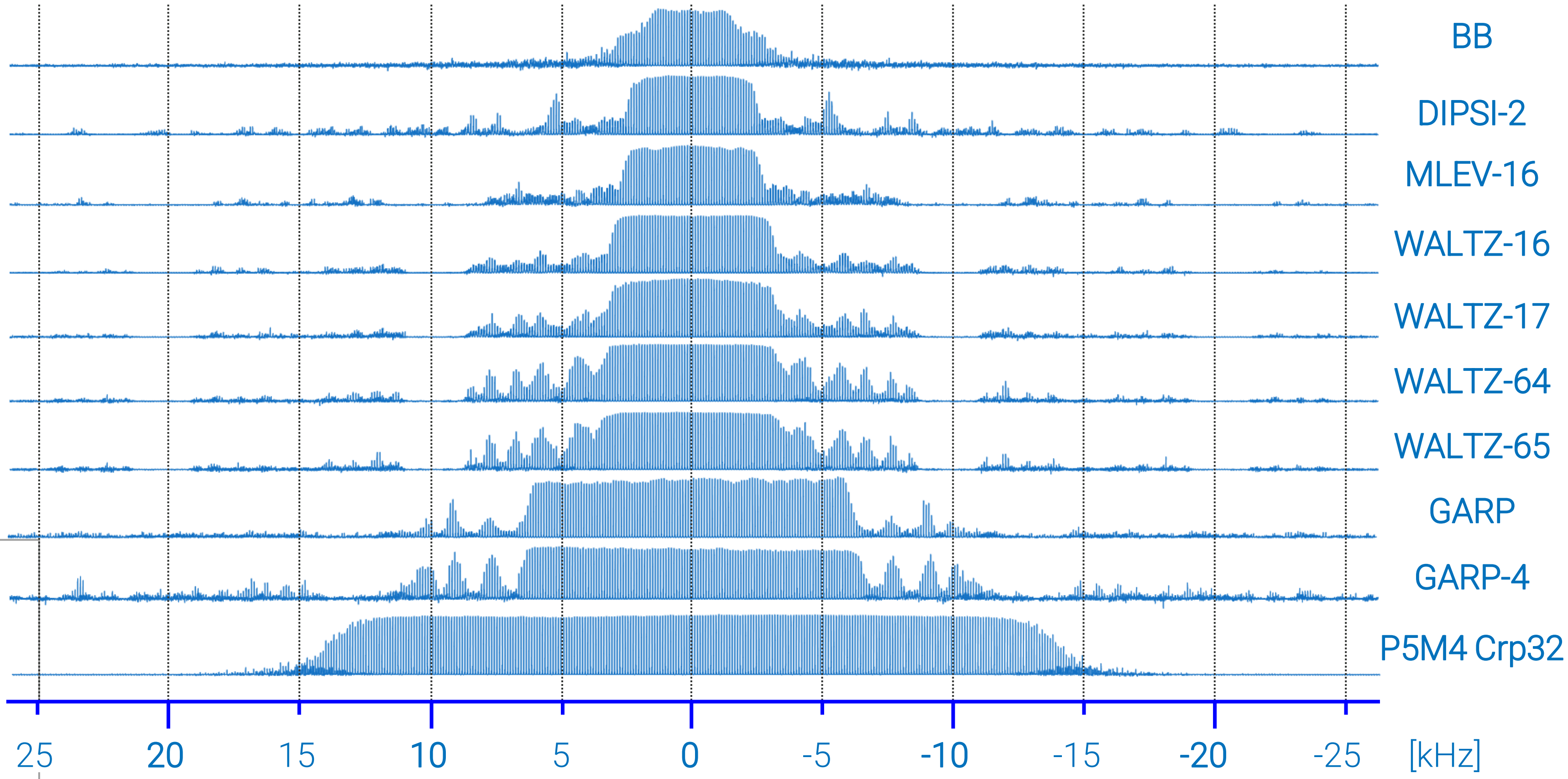
HSQC pulse sequences

hsqcetgpsisp hsqcetgpsisp.2		Adiabatic 180-degree inversion pulses All 180-degree pulses are adiabatic
hsqcetgpsisp2 hsqcetgpsisp2.2 hsqcetgpsisp2.3	With gradients in back INEPT	Adiabatic 180-degree inversion pulses All 180-degree pulses are adiabatic + COSY artefacts suppression
hsqcedetgpsisp2 hsqcedetgpsisp2.2 hsqcedetgpsisp2.3 hsqcedetgpsisp2.4*	With gradients in back INEPT Edited	Adiabatic 180-degree inversion pulses All 180-degree pulses are adiabatic Matched sweep adiabatic pulses + COSY artefacts suppression
hsqcetgpsp hsqcetgpsp.2 hsqcetgpsp.3	No SI, with optional F3 decoupling Proteins	Adiabatic 180-degree inversion pulses All 180-degree pulses are adiabatic, refocusing using composite Crp Refocusing using pair of Crp pulses

* Small molecules – cleanest spectrum but longer pulse sequence duration – mind the relaxations

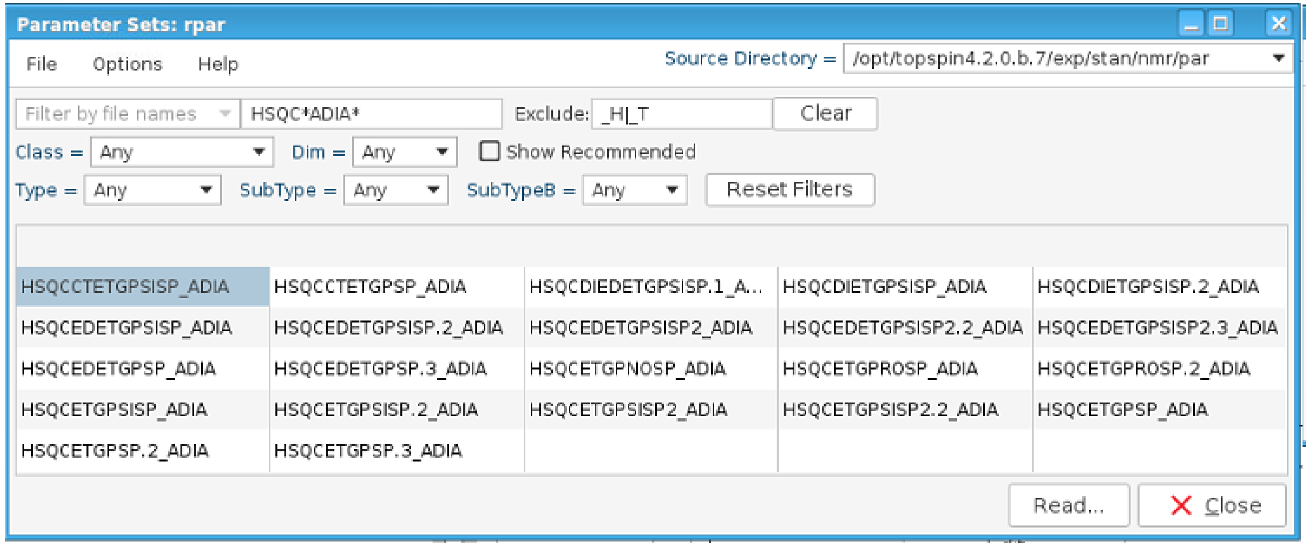
Decoupling

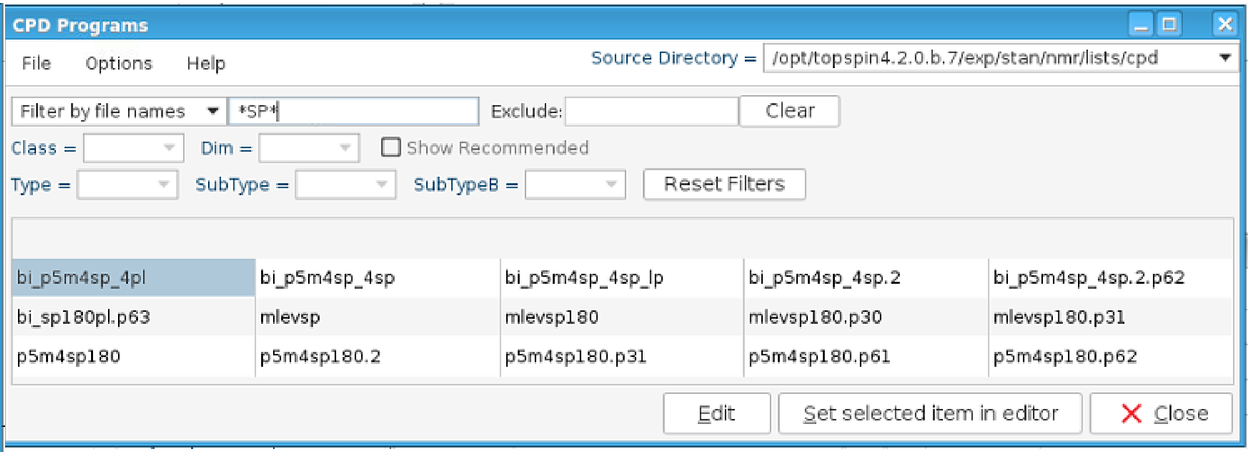
γB1 2.5 kHz decoupling field,
PCPD 100 us



Higher RF peak power
2.9 kHz, coresponds to 85.8 us
But lower integral power due to
smoothed Crp shape

HSQC Parameter Sets and decoupling programs





Several standard parameter sets which employ adiabatic decoupling are available.

Recommended for spectrometers ≥ 500MHz

For adiabatic decoupling pulse quality factor Q can be reduced from 5 to 2-3, which gives 2.2-4 dB lower power. Hence lower sample heating

Thank you!

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