NMR Training Course

9th September 2021
Adolfo Botana, PhD
JEOL UK Demo Lab

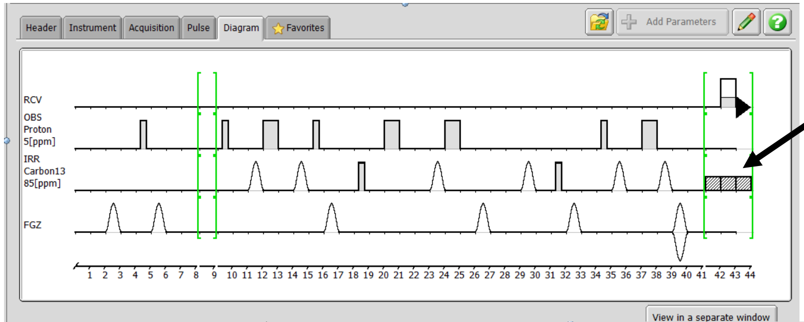
Power handling liquids probes

Power handling

- Probes can get damaged if they receive more RF than they can handle, this damage may extend to other elements in the spectrometer
- Clearly exceeding safe RF power levels will trigger an alarm in the RF amplifiers, but RF amplifiers can typically handle more power than the probes, so RF power levels below this limit may still damage the probe
- There is an absolute limit of maximum power that probes can tolerate at each frequency. RF irradiation beyond this level will likely damage the probe
- At lower power levels it is possible to irradiate longer. See following tables to evaluate how long can RF irradiation be at different power levels
- **Do not exceed the maximum irradiation time at each attenuation level**
- **In Delta a larger attenuation number [dB] results in lower RF power**
- **Maximum irradiation at Square pulse power is 1[ms] for HF and 0.2[ms] for LF**
- **Maximum decoupling power is 1.5W for 1H and 19F, and 5W for other nuclei. It is not guaranteed probe will survive if decoupling at this power level continuously.**
- The **maximum duty cycle** for decoupling at maximum power and with CPMG experiment types is: **5%**
- % is used for reference in solids.
- Power is used for reference, it varies with probes and nuclei. Typically maximum power for 1H is 30W and maximum continuous power is 1.5W. If different, the table should be modified accordingly
- Pulsewidth is used for reference on how it theoretically scales with attenuation

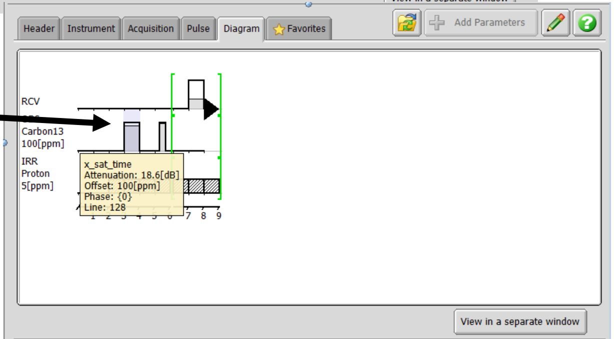
Power handling

- **Power limits are safe limits, not an objective. Always use the lowest power level that allows you to obtain good results (if you want your probe to last longer).**
- **Always check power levels when using a pulse sequence for the first time**
- **Exceeding the power levels in these tables will void the warranty**
- **In case of doubt, ask!**
- Check Diagram to quickly find any long RF irradiation



Carbon 13 decoupling: Check irr_atn_dec, if less attenuation (more power) than CW, evaluate duty cycle: is acquisition time less than maximum irradiation time at this attenuation?

Long pulse (double line at the top): click on it to find out pulse length parameter, x_sat_time, and check its power level and duty cycle



x_sat_time
Attenuation: 18.6[dB]
Offset: 100[ppm]
Phase: {0}
Line: 128

Power handling HF channel

Attenuation	power	**irradiation**	% (Voltage)	pulsewidth
x_atn+0[dB]	30W	**1ms**	100%	10us
x_atn+3[dB]	15W	**5ms**	70%	
x_atn+6[dB]	7.5W	**25ms**	50%	20us
x_atn+9[dB]	3.75W	**125ms**	35%	
x_atn+12[dB]	1.88W	**625ms**	25%	40us
x_atn+15[dB]	1W	**CW**	17.7%	

These are the maximum irradiation times with a duty cycle of 2%, at the specified attenuations (x_atn= attenuation level for the 90 pulse in probe specifications)

In general, do not use attenuation levels below **x_atn+18[dB]** for **decoupling**

[This table assumes attenuation changes linearly and irradiation is then calculated from Square pulse attenuation; but amplifiers are not so linear at the highest power, so a safety margin is recommended]

Power handling LF channel

Attenuation	power	irradiation	% (Voltage)	pulsewidth
x_atn+0[dB]	160W	0.2ms	100%	10us
x_atn+3[dB]	80W	1 ms	70%	
x_atn+6[dB]	40W	5 ms	50%	20us
x_atn+9[dB]	20W	25ms	35%	
x_atn+12[dB]	10W	125ms	25%	40us
x_atn+15[dB]	5W	625ms	17.7%	
x_atn+18[dB]	2W	CW	12.5%	80us

These are the maximum irradiation times with a duty cycle of 2%, at the specified attenuations (x_atn= attenuation level for the 90 pulse in probe specifications)

In general, do not use attenuation levels below **x_atn+21[dB]** for **decoupling**

[This table assumes attenuation changes linearly and irradiation is then calculated from Square pulse attenuation; but amplifiers are not so linear at the highest power, so a safety margin is recommended]

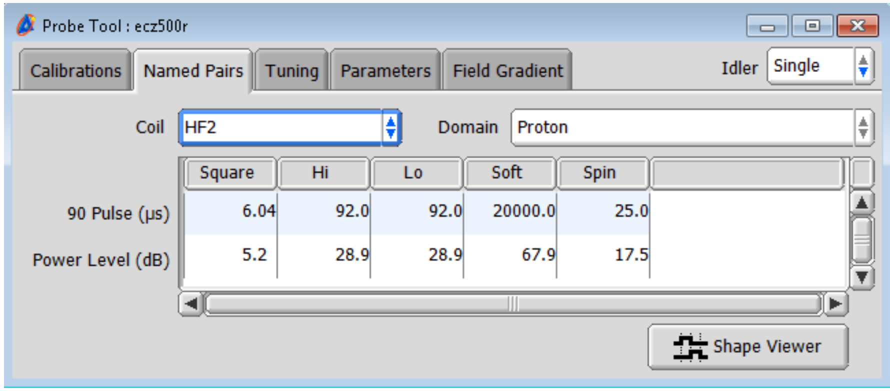
400 ROYAL specifications

LCT		**Maximum power**		**Maximum continuous power**		**Other nuclei**
		W	**dB**	W	**dB**	
	1H	30		1.5		
	19F	30		1.5		
X	31P	50		5		Lithium7, Tin117, Tin119
X	11B	50		5		Bromine81, Copper63, Copper65, Gallium71, Praseodymium141, Rubidium87, Sodium23, Tellurium125, Vanadium51, Xenon129
A	13C	80		5		Aluminum27, Bromine79, Europium151, Gallium69, Manganese55, Niobium93, Scandium45, Tellurium123, Terbium159
A	29Si	80		5		Antimony121, Cadmium111, Cadmium113, Cobalt59, Holmium165, Indium113, Indium115, Iodine127, Lead207, Platinum195, Rhenium185, Rhenium187, Technetium99
A	2H	80		5		Arsenic75, Bismuth209, Lithium6, Mercury199, Selenium77, Ytterbium171
B	17O	150		5		Antimony123, Beryllium9, Cesium133, Lanthanum138, Lanthanum139, Lutetium175, Tantalum181
C	15N	150		5		Boron10, Barium137, Europium153
D	39K	80		5		Silver109

Lock	15		-

🟩 Measured

Probe tool



Idler: Single

Coil: HF2

Domain: Proton

	Square	Hi	Lo	Soft	Spin
90 Pulse (μs)	6.04	92.0	92.0	20000.0	25.0
Power Level (dB)	5.2	28.9	28.9	67.9	17.5

- Named pairs tab contains the calibrations for each nucleus
- Square is used for hard pulses
- Hi is used for decoupling during acquisition
- Lo is used for decoupling during relaxation delay
    - Normally Hi/Lo pulses are set lower than CW decoupling for safety
    - *Note Wurst(xx) and BUSS decouplings do not use Hi/Lo decoupling
- Soft is used for shaped pulses
    - **There may be some exceptions
- Spin is used for spin-lock pulses (TOCSY, saturation-recovery, etc.)
- Nuclei not calibrated appear with 1[us] 90 pulse at 79[dB]
- Note different calibrations for Proton and Fluorine in the HFX probe. Idler can be Single or Dual

Power handling solids

Power handling AutoMAS 3.2 400 MHz

1H (HF) channel

Attenuation	**power**	**irradiation**	**% (Voltage)**	**pulsewidth**
x_atn+0[db]	80W	**50 ms**	**100%**	2.7 us
x_atn+3[db]	40W	**100 ms**	**70%**	
x_atn+6[db]	20W	**200 ms**	**50%**	5.4 us

13C (LF) channel

Attenuation	**power**	**irradiation**	**% (Voltage)**	**pulsewidth**
x_atn+0[db]	220W	**5 ms**	**100%**	2.5 us
x_atn+3[db]	110W	**10 ms**	**70%**	
x_atn+6[db]	55W	**20 ms**	**50%**	5.0 us

Maximum 1.25 % duty cycle

	^{1}H/^{19}F	**^{31}P/^{7}Li/^{11}B**	**^{23}Na/^{27}Al/^{13}C**	**^{207}Pb**	**^{29}Si**	**^{6}Li**	**^{15}N**
Maximum decoupling power(W):	80	176	220	248	248	256	272

Maximum input power: Maximum decoupling power * 1.25

Power handling HXMAS 4mm 400 MHz

1H (HF) channel

Attenuation	**power**	**irradiation**	**% (Voltage)**	**pulsewidth**
x_atn+0[db]	48W	**80 ms**	**100%**	3.9 us
x_atn+3[db]	24W	**160 ms**	**70%**	
x_atn+6[db]	12W	**320 ms**	**50%**	7.8 us

13C (LF) channel

Attenuation	**power**	**irradiation**	**% (Voltage)**	**pulsewidth**
x_atn+0[db]	144W	**5 ms**	**100%**	3.7 us
x_atn+3[db]	72W	**10 ms**	**70%**	
x_atn+6[db]	36W	**20 ms**	**50%**	7.4 us

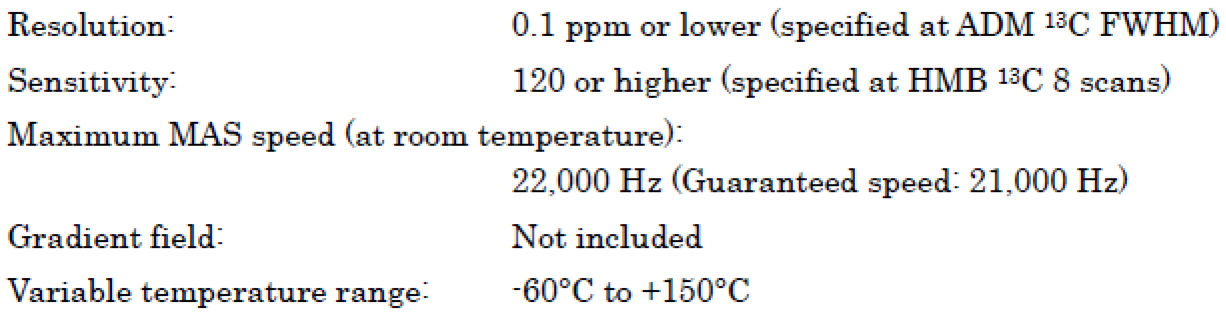
Maximum 1.6 % duty cycle

	^{1}H/^{19}F	**^{31}P/^{7}Li/^{11}B**	**^{23}Na/^{27}Al/^{13}C**	**^{207}Pb**	**^{29}Si**	**^{6}Li**	**^{15}N**
Maximum decoupling power(W):	48	112	144	160	160	184	224

Maximum input power: Maximum decoupling power * 1.25

AutoMAS 3.2mm vs HXMAS 4mm

- AutoMAS



Resolution: 0.1 ppm or lower (specified at ADM ^{13}C FWHM)

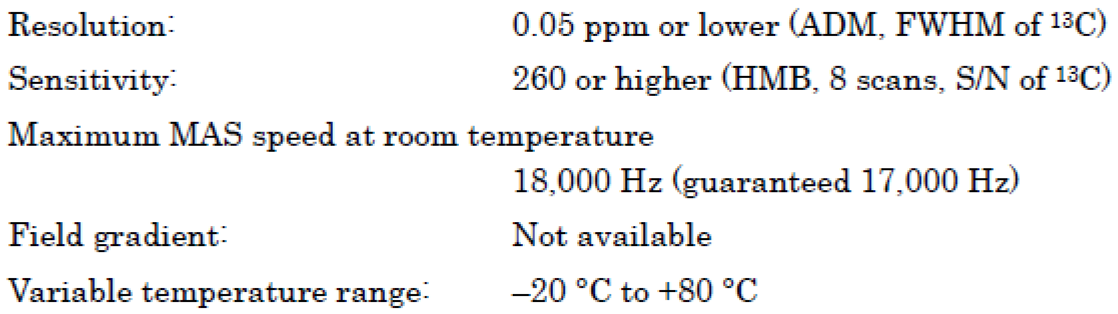
Sensitivity: 120 or higher (specified at HMB ^{13}C 8 scans)

Maximum MAS speed (at room temperature):
22,000 Hz (Guaranteed speed: 21,000 Hz)

Gradient field: Not included

Variable temperature range: -60°C to +150°C

- HXMAS



Resolution: 0.05 ppm or lower (ADM, FWHM of ^{13}C)

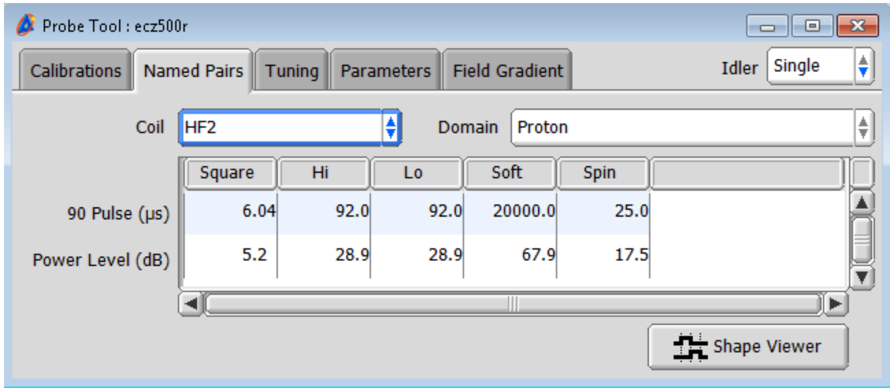
Sensitivity: 260 or higher (HMB, 8 scans, S/N of ^{13}C)

Maximum MAS speed at room temperature
18,000 Hz (guaranteed 17,000 Hz)

Field gradient: Not available

Variable temperature range: –20 °C to +80 °C

Probe tool



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Coil: HF2

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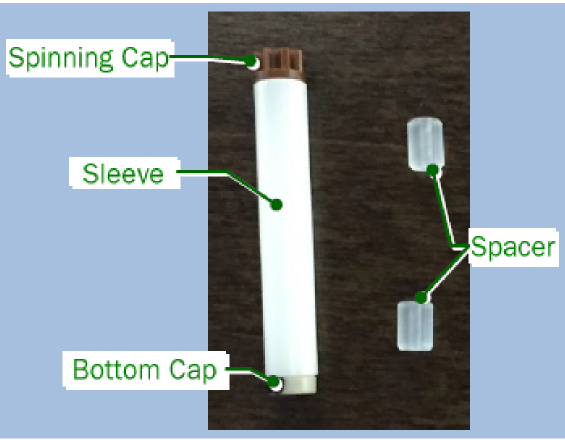
- Named pairs tab contains the calibrations for each nucleus
- Square is used for hard pulses
- ~~Hi is used for decoupling during acquisition~~
- ~~Lo is used for decoupling during relaxation delay~~
  - ~~Normally Hi/Lo pulses are set lower than CW decoupling for safety~~
  - ~~*Note Wurst(xx) and BUSS decouplings do not use Hi/Lo decoupling~~
- ~~Soft is used for shaped pulses~~
  - ~~**There may be some exceptions~~
- ~~Spin is used for spin-lock pulses (TOCSY, saturation-recovery, etc.)~~
- Nuclei not calibrated appear with 1[us] 90 pulse at 79[dB]
- ~~Note different calibrations for Proton and Fluorine in the HFX probe. Idler can be Single or Dual~~

In standard solids experiments only the Square calibration is used.

CP, decoupling or other calibrations are not saved in probe tool

Standard Tube

NM-05420ST4 (4mm) / NM-05410ST32 (3.2mm)

Items	Materials	
Spinning Cap	Vespel ®*1	
Bottom Cap	PEEK *2	
Sleeve (Color : White)	Zirconia (ZrO_2)	
Spacer	PCTFE*3	

*1 : Vespel ®: A trademark or registered trademark of E.I. du Pont de Nemours and Company or its affiliates.

*2:PEEK: PolyEther Ether Ketone

*3:PCTFE: Poly Chloro Tri Fluoro Ethylene

Spinning Detection Maker : Black permanent ink pen

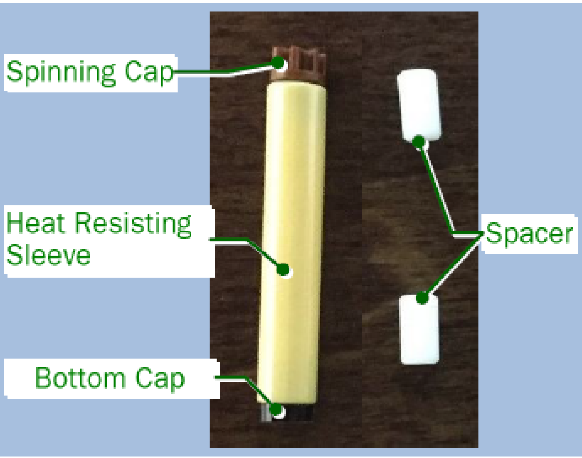
		NM-05420ST4 (4mm)	NM-05410ST32 (3.2mm)
Maximum MAS speed (Guaranteed MAS speed)	At room temperature	18,000 Hz (17,000 Hz)	22,000 Hz (21,000Hz)
	At high temperature VT	16,000 Hz (15,000 Hz)	19,000 Hz (18,000 Hz)
	At low temperature VT	14,000 Hz (13,000 Hz)	17,000 Hz (16,000 Hz)
Variable Temperature Range	with spacer	-100 to +80 ℃	
	without spacer	-100 to +150 ℃	

The MAS speed of the sample tube is limited by changing the temperature.

The usable temperature range varies depending on the presence or absence of spacers.

Heat Resisting Tube

NM-05470HST4 (4mm) / NM-05460HST32 (3.2mm)

Items	Materials	
Spinning Cap	Vespel ®*1	
Bottom Cap	PEEK *2	
Sleeve (Color : Yellow)	Heat Resisting Zirconia (ZrO_2)	
Spacer	PTFE*3	

*1 : Vespel ®: A trademark or registered trademark of E.I. du Pont de Nemours and Company or its affiliates.

*2:PEEK: PolyEther Ether Ketone

*3:PTFE: Poly Tetra Fluoro Ethylene

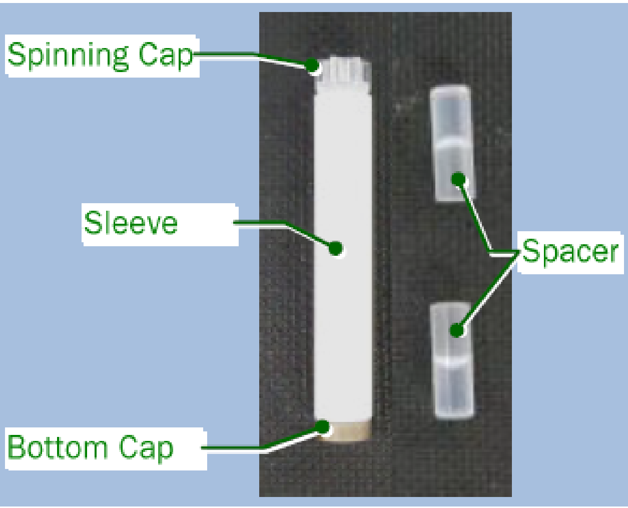
Spinning Detection Maker : Black permanent ink pen

		NM-05470HST4 (4mm)	NM-05460HST32 (3.2mm)
Maximum MAS speed (Guaranteed MAS speed)	At room temperature	18,000 Hz (17,000 Hz)	22,000 Hz (21,000Hz)
	At high temperature VT	16,000 Hz (15,000 Hz)	19,000 Hz (18,000 Hz)
	At low temperature VT	14,000 Hz (13,000 Hz)	17,000 Hz (16,000 Hz)
Variable Temperature Range		-100 to +200 ℃	

✍ The MAS speed of the sample tube is limited by changing the temperature.

■ Sealing Tube

NM-05450SST4 (4mm) / NM-05440SST32 (3.2mm)

Items	Materials	
Spinning Cap	PCTFE*1	
Bottom Cap	PCTFE*1	
Sleeve (Color : White)	Zirconia (ZrO_2)	
Spacer	PCTFE*1	
*1:PTFE: Poly Tetra Fluoro Ethylene		

Spinning Detection Maker : Gold permanent ink pen

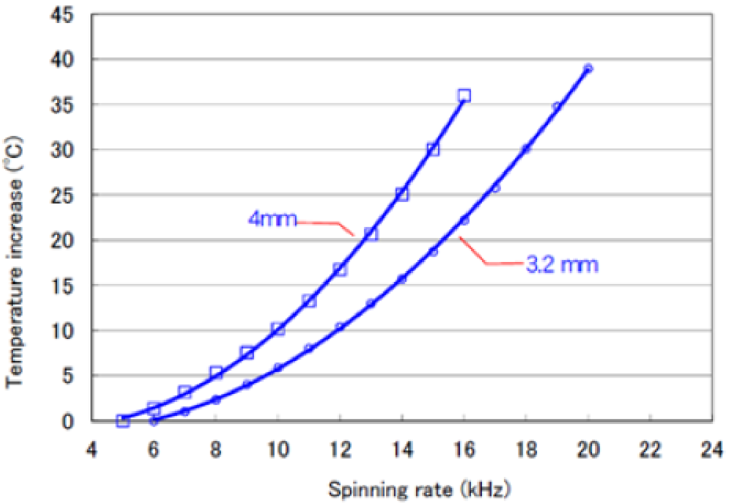
		NM-05450SST4 (4mm)	NM-05440SST32 (3.2mm)
Maximum MAS speed (Guaranteed MAS speed)	At room temperature	9,000 Hz (8,000 Hz)	10,000 Hz (9,000Hz)
	At high temperature VT	6,500 Hz	8,000 Hz
Variable Temperature Range		-20 to +50 ℃	

✍ The MAS speed of the sample tube is limited by changing the temperature.

Too much a sample

If it too much sample in the solid sample tube, the cap cannot close completely.
If the sample tube is spinning while the cap is not completely closed, the cap may remove out during spinning, the probe causes to damage.

Especially, solid-state NMR increases the temperature of the sample itself by spinning the sample tube at high speed.



KBr can be used as a thermometer.
ΔT= 0.025 ppm/K
https://dx.doi.org/10.1016%2Fj.jmr.2008.09.019

Generally, the sample volume increases due to thermal expansion as the sample temperature rises.
Although the coefficient of thermal expansion varies depending on the sample, if there are too many samples, the expanded sample pushes up the cap, which may cause the cap to come off the sleeve.

Therefore, it is better to fill a little less sample in the solid sample tube.

Thermal expansion
Glass << Metal << Resin
Metal is 4 times larger than glass, and resin is 20-30 times larger than glass.

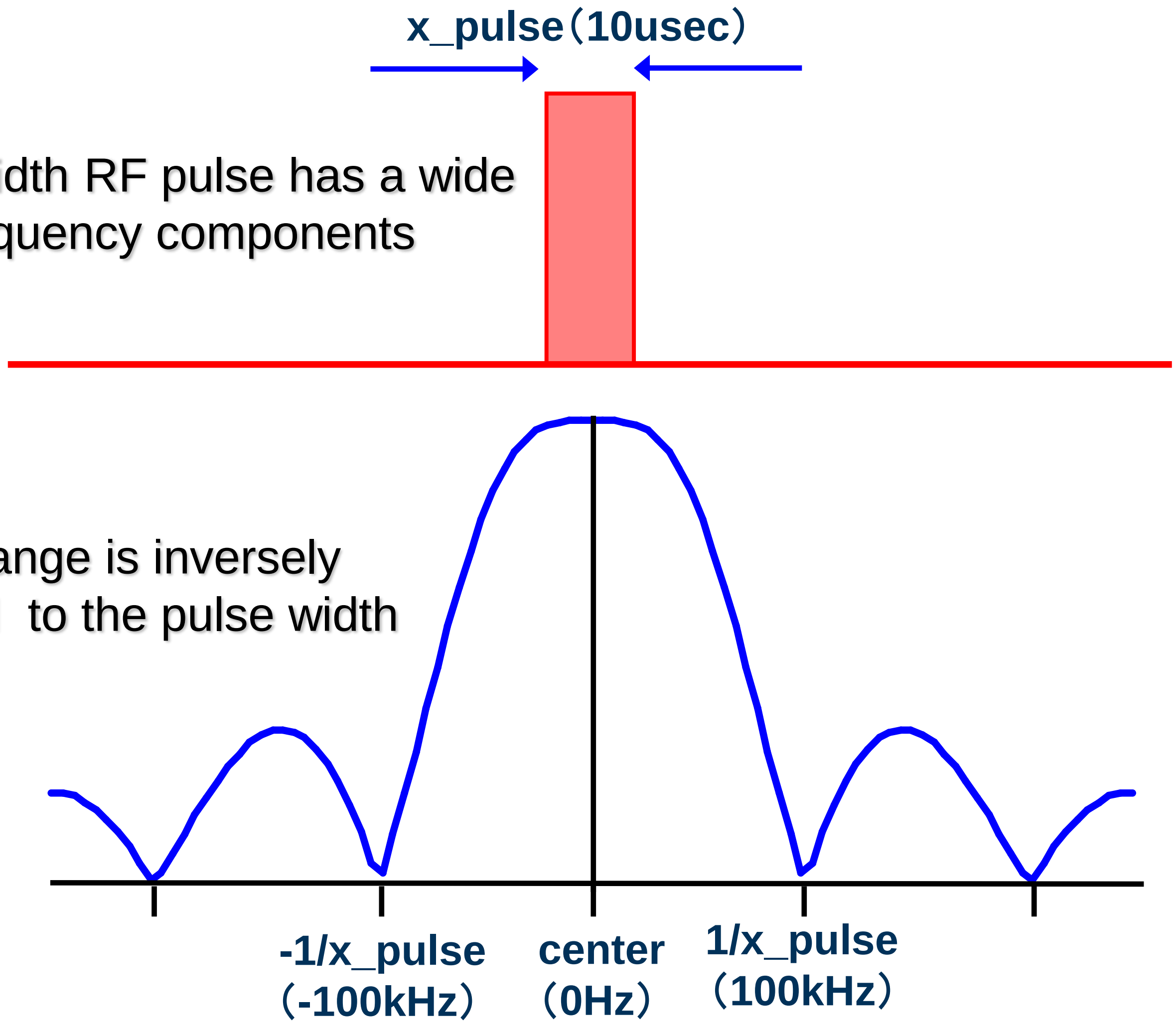
Webinars

- An Introduction to Solid-State NMR https://attendee.gotowebinar.com/register/1588889267810221067
- Solid-State NMR Tutorial: Sample Packing, Standard Samples & Sample Spinning https://attendee.gotowebinar.com/register/8621407423140093454
- More webinars:

  https://www.jeol.co.jp/en/news/seminar/webseminar/movie_index.html

Pulse hard vs soft

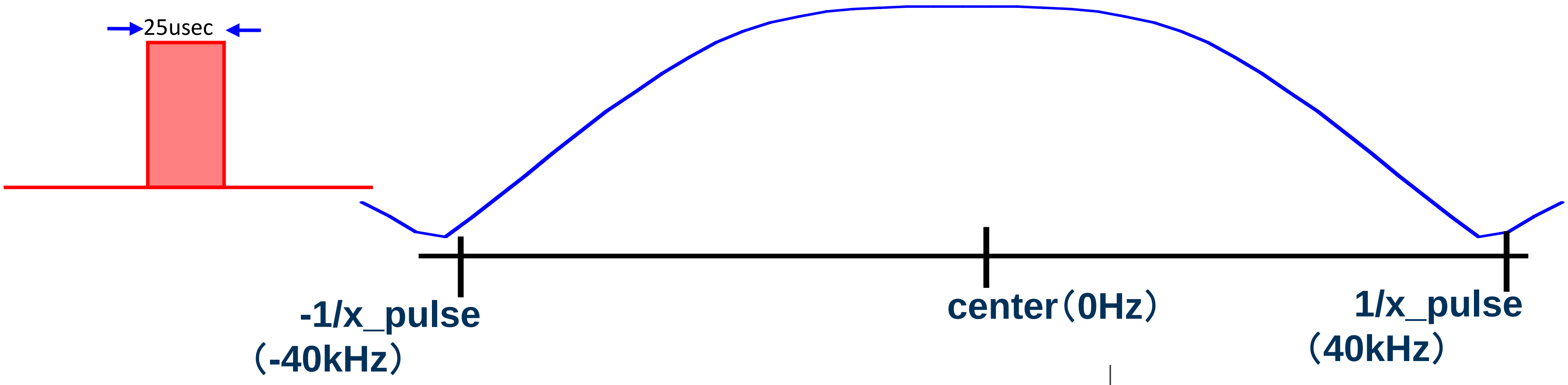
Excitation profile of a 90 degree pulse

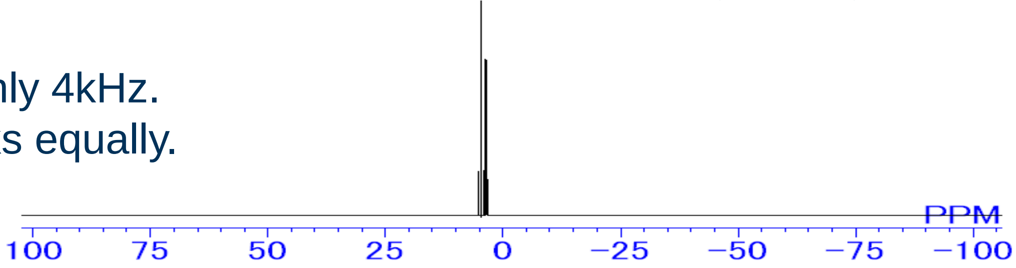


The short width RF pulse has a wide range of frequency components

Excitation range is inversely proportional to the pulse width

Excitation profile of a 90 degree pulse

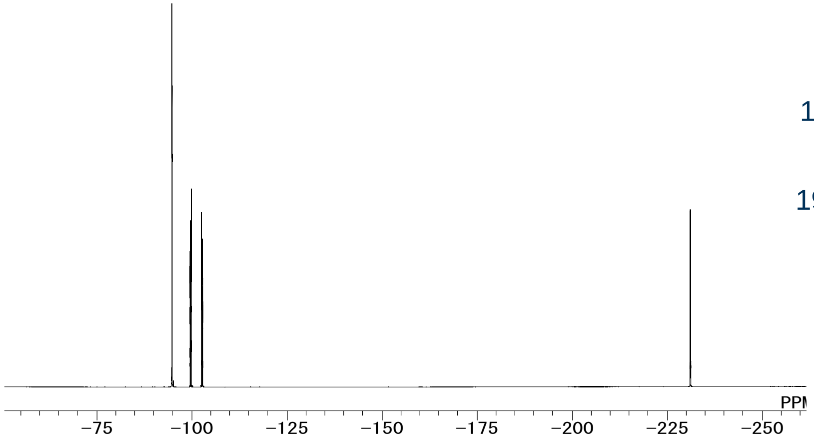




^{1}H 10ppm at a 400MHz machine is only 4kHz.
A 25usec pulse can excite all ^{1}H peaks equally.

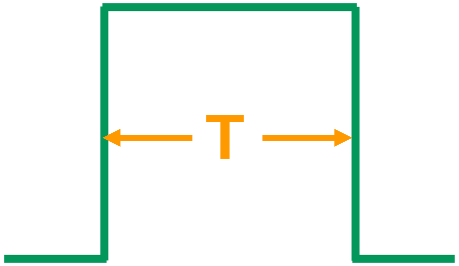
^{19}F peak at -230ppm will be excited very weakly

^{19}F on a 400MHz instrument

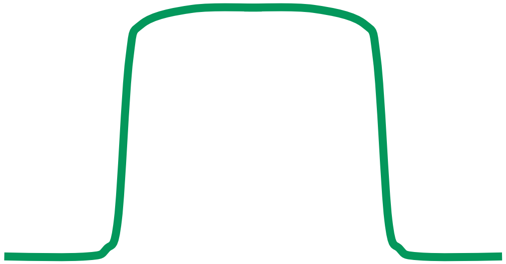


Rectangular pulses

- Referred to as “hard” pulses
- Effective at exciting broad bandwidths, with relatively flat excitation over the frequency range 0 to ~1/T Hz
- Shorter pulses lead to broader excitation (1/T is larger)
- Poor choice for selective (narrow frequency range) excitation (need <u>very</u> long t!)



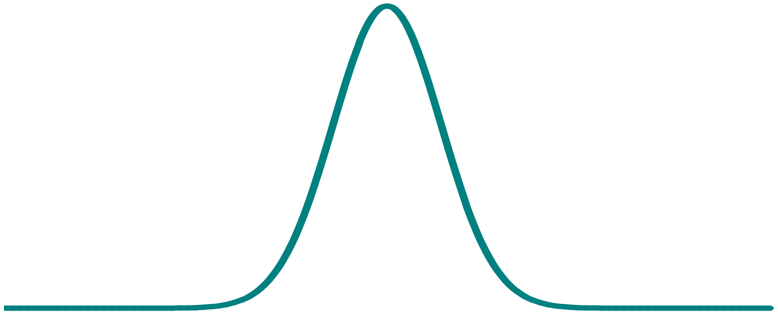
Ideal rectangular



Actual rectangular

Gaussian pulses

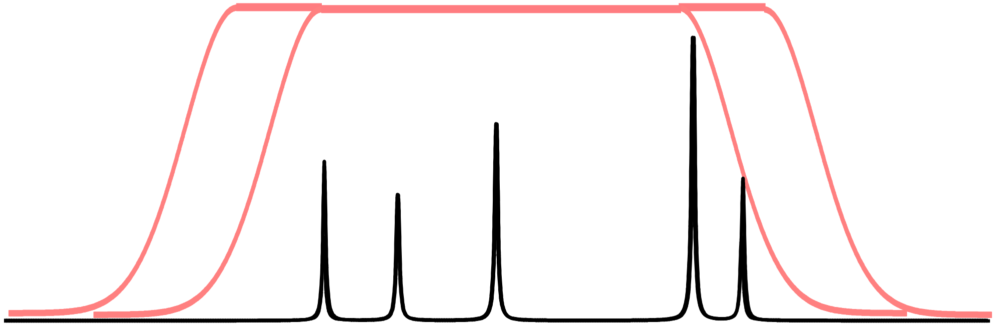
- Referred to as “soft” pulses
- Excitation profile is also Gaussian (narrow with relatively rapid falloff)
- Shorter pulses correspond to narrow excitation profiles
- Useful for selective pulses

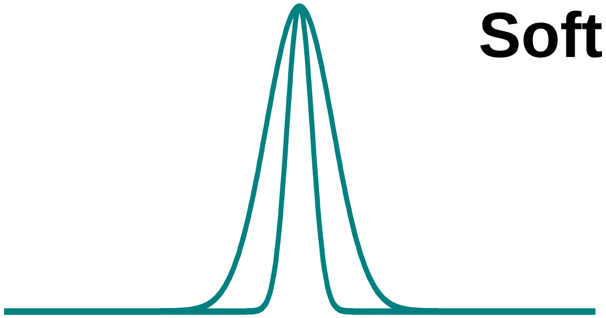


Gaussian

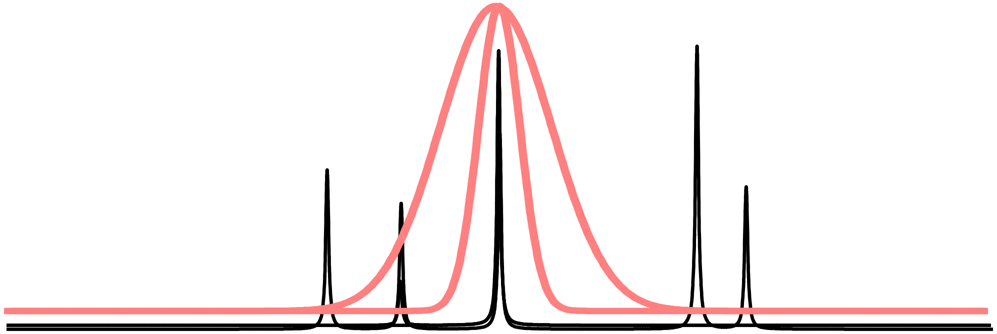
Hard *vs.* soft pulses

Hard





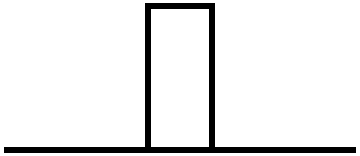
Soft



Adiabatic pulses

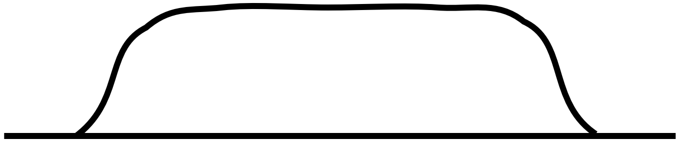
Rectangular pulses

- + Very short pulse width (µs)
- – Small excitation profile
- – High power

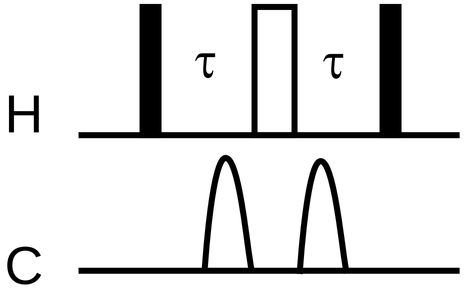


Adiabatic pulses

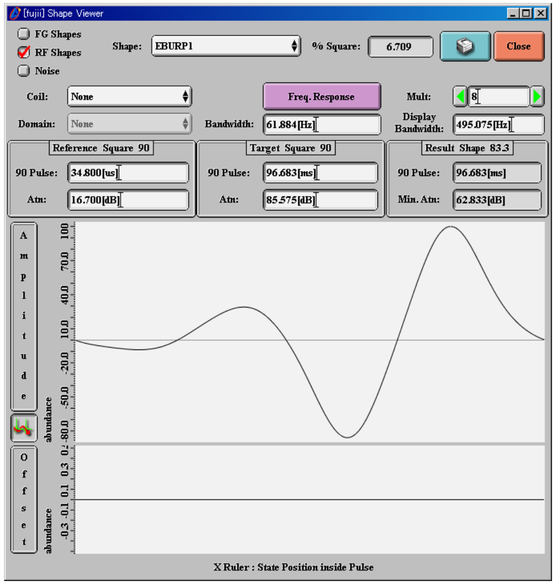
- → Adiabatic pulses do frequency sweep of kHz to MHz, spin magnetization follows the slow (adiabatic) inversion profile
- → Replace bandwidth-critical 180° pulses by adiabatic pulses
- + Extremely wide excitation bandwidth (essential for fields ≥ 600 MHz!)
- + Low power
- – Long pulses (typ. 1-50 ms) have to be compensated in pulse sequences



adiabatic INEPT



Example of shaped pulse



[fujii] Shape Viewer

☐ FG Shapes
☑ RF Shapes
☐ Noise

Shape: EBURP1
% Square: 6.709

Coil: None
Domain: None
Bandwidth: 61.884[Hz]
Mult: 8
Display Bandwidth: 495.075[Hz]

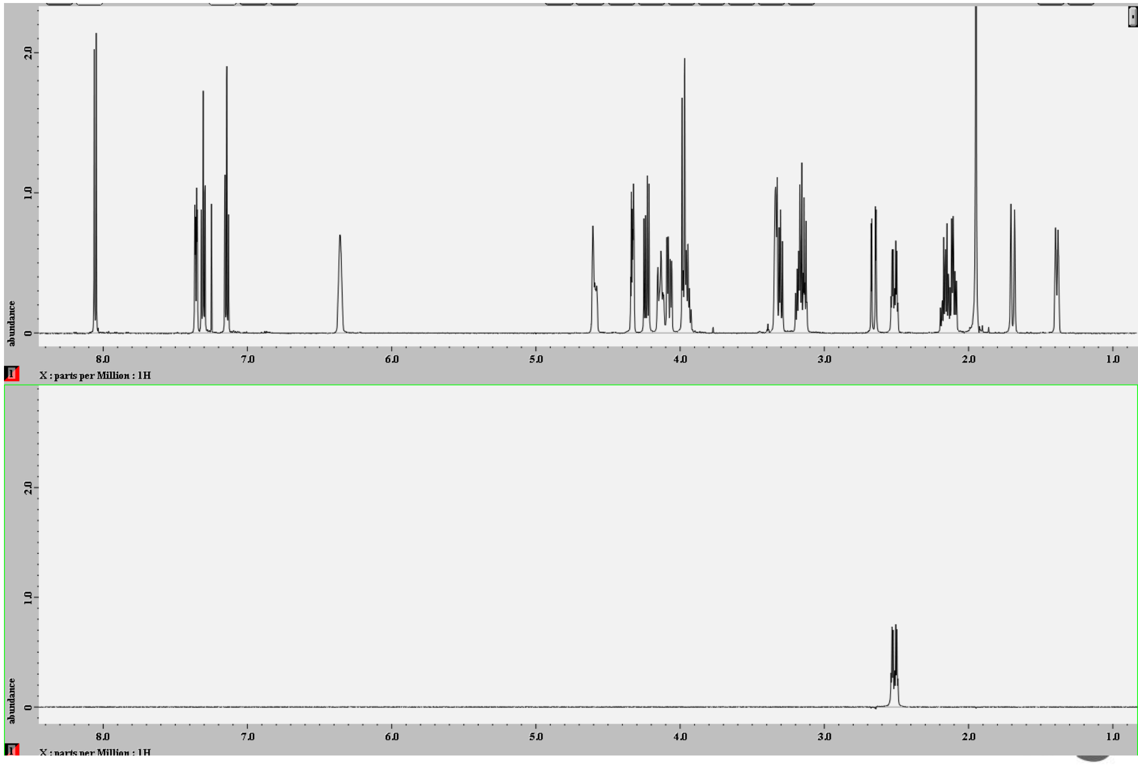
Reference Square 90
90 Pulse: 34.800[us]
Atn: 16.700[dB]

Target Square 90
90 Pulse: 96.683[ms]
Atn: 85.575[dB]

Result Shape 83.3
90 Pulse: 96.683[ms]
Min. Atn: 62.833[dB]

X Ruler : State Position inside Pulse

96msec EBURP pulse time domain shape (upper) and a result (right lower)

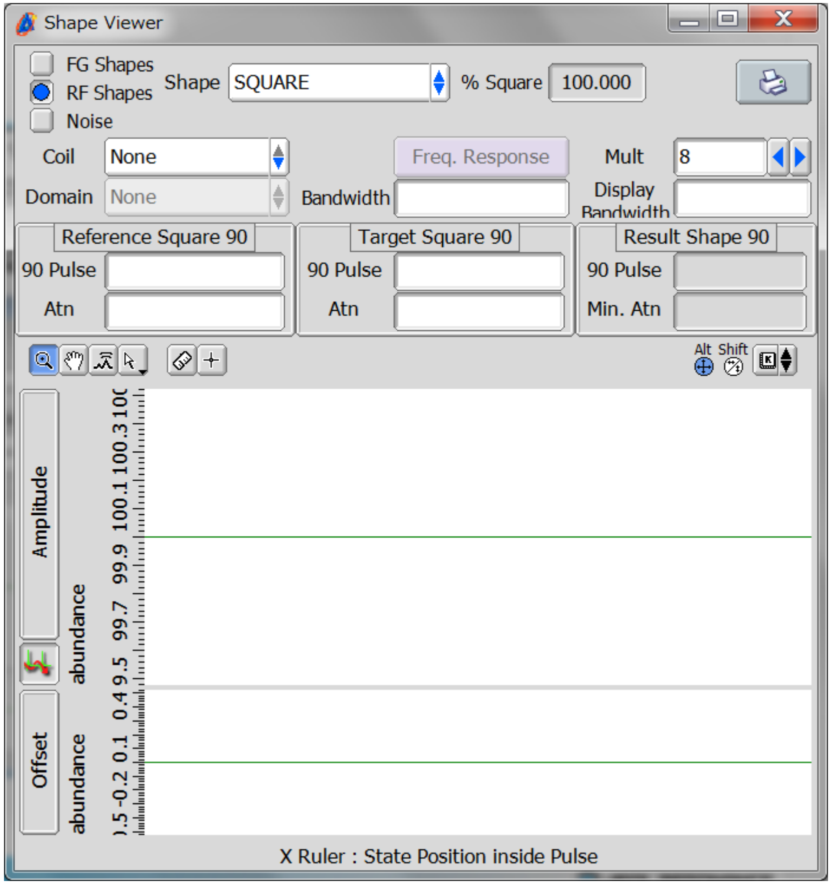


Fluorine excitation (hard pulse in a ECZ-S 400)

Shape Viewer

Shape Viewer

The tool which calculates the attenuator value for each shaped pulses automatically from the value of square pulse

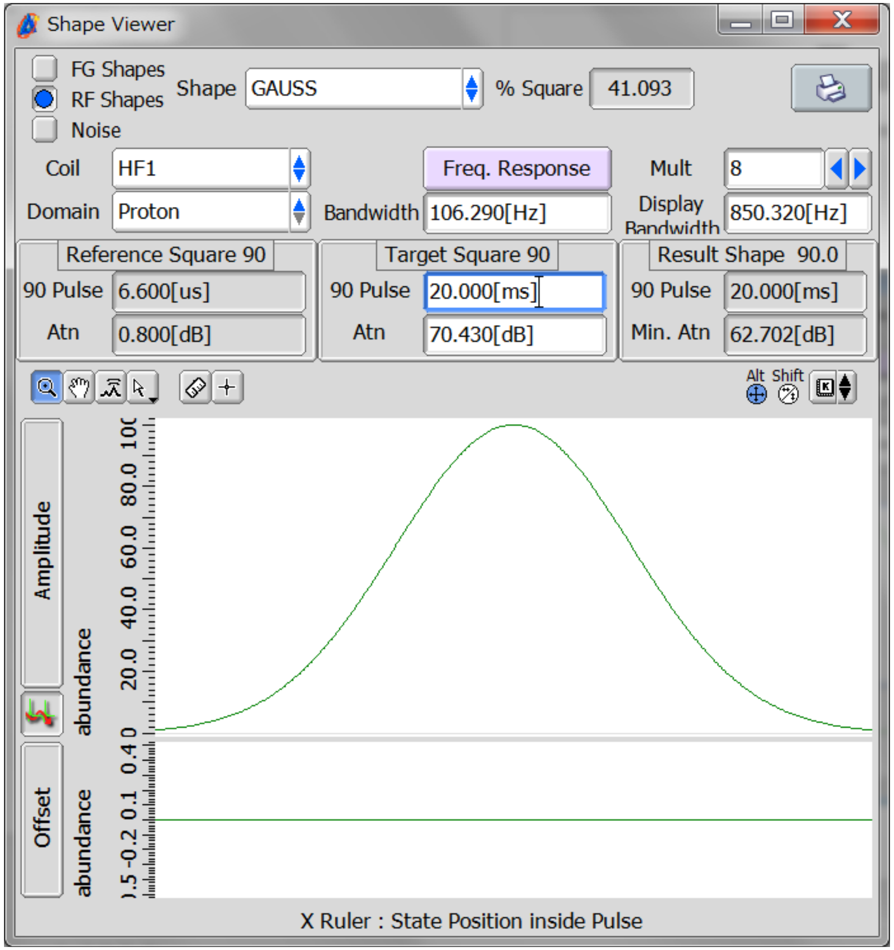


Shape Viewer

☐ FG Shapes
● RF Shapes
☐ Noise

Shape: SQUARE
% Square: 100.000
Coil: None
Domain: None
Mult: 8

Functions of Shape Viewer



Shape Viewer

○ FG Shapes
● RF Shapes
○ Noise

Shape GAUSS
% Square 41.093

Coil HF1
Domain Proton
Mult 8
Bandwidth 106.290[Hz]
Display Bandwidth 850.320[Hz]

Reference Square 90
90 Pulse 6.600[us]
Atn 0.800[dB]

Target Square 90
90 Pulse 20.000[ms]
Atn 70.430[dB]

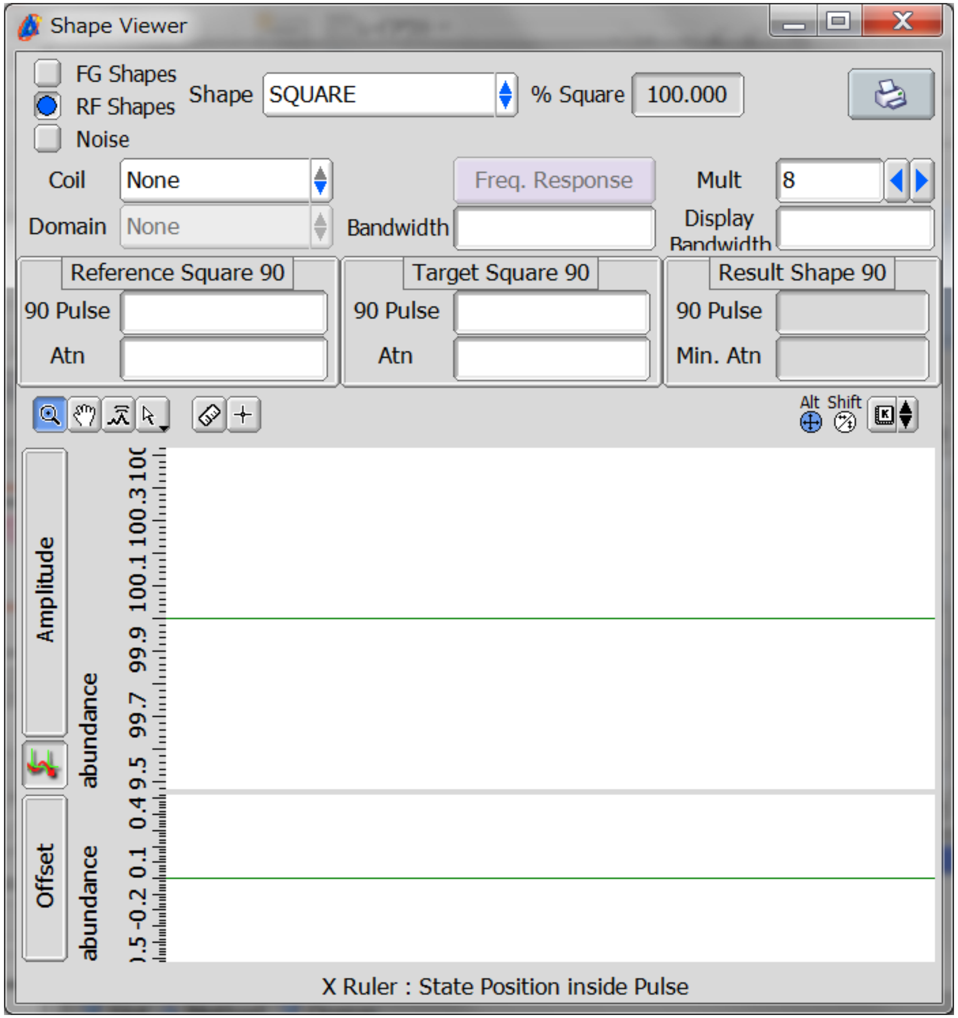
Result Shape 90.0
90 Pulse 20.000[ms]
Min. Atn 62.702[dB]

X Ruler : State Position inside Pulse

Main functions of Shape Viewer

- Calculation of pulse width
- Graphical shape review
- Profile of excitation
- Simulation of exciting region

How to calculate the pulse width



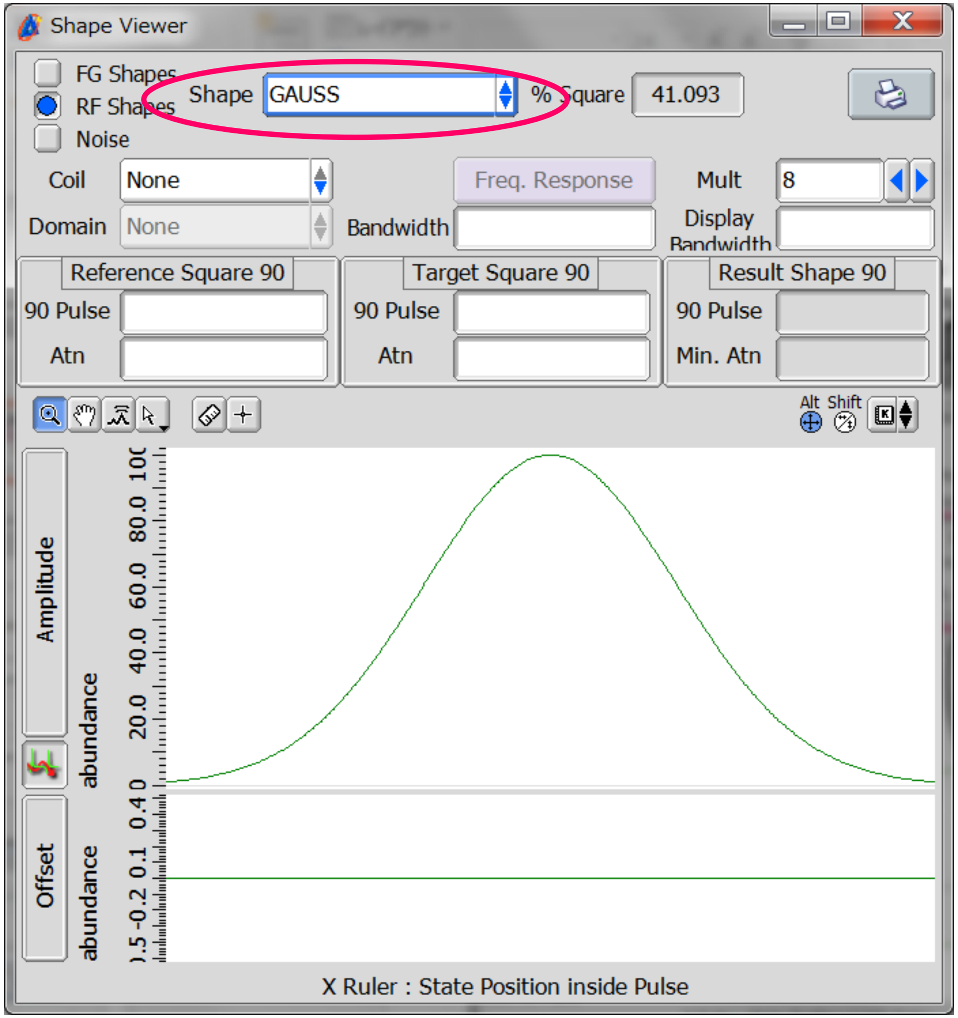
Shape Viewer

○ FG Shapes
● RF Shapes
○ Noise

Shape: SQUARE
% Square: 100.000
Coil: None
Domain: None
Mult: 8

1. **Select the target shape**
2. **Select a nucleus to “Domain”**
3. **Input the target pulse width**

How to calculate the pulse width



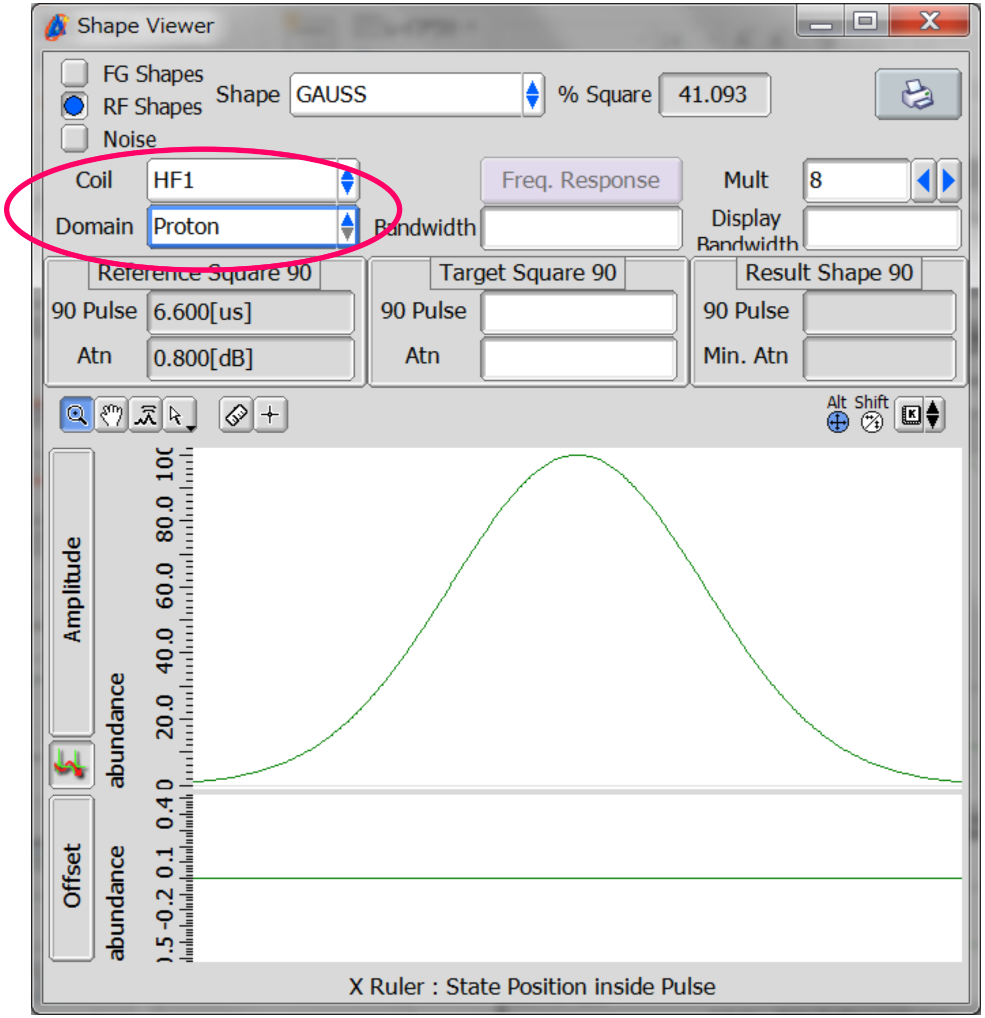
Shape Viewer

☐ FG Shapes
● RF Shapes
☐ Noise

Shape: GAUSS
% Square: 41.093
Coil: None
Domain: None
Mult: 8

1. **Select the target shape**
2. **Select a nucleus to “Domain”**
3. **Input the target pulse width**

How to calculate the pulse width



Shape Viewer

○ FG Shapes
● RF Shapes
○ Noise

Shape: GAUSS

% Square: 41.093

Coil: HF1

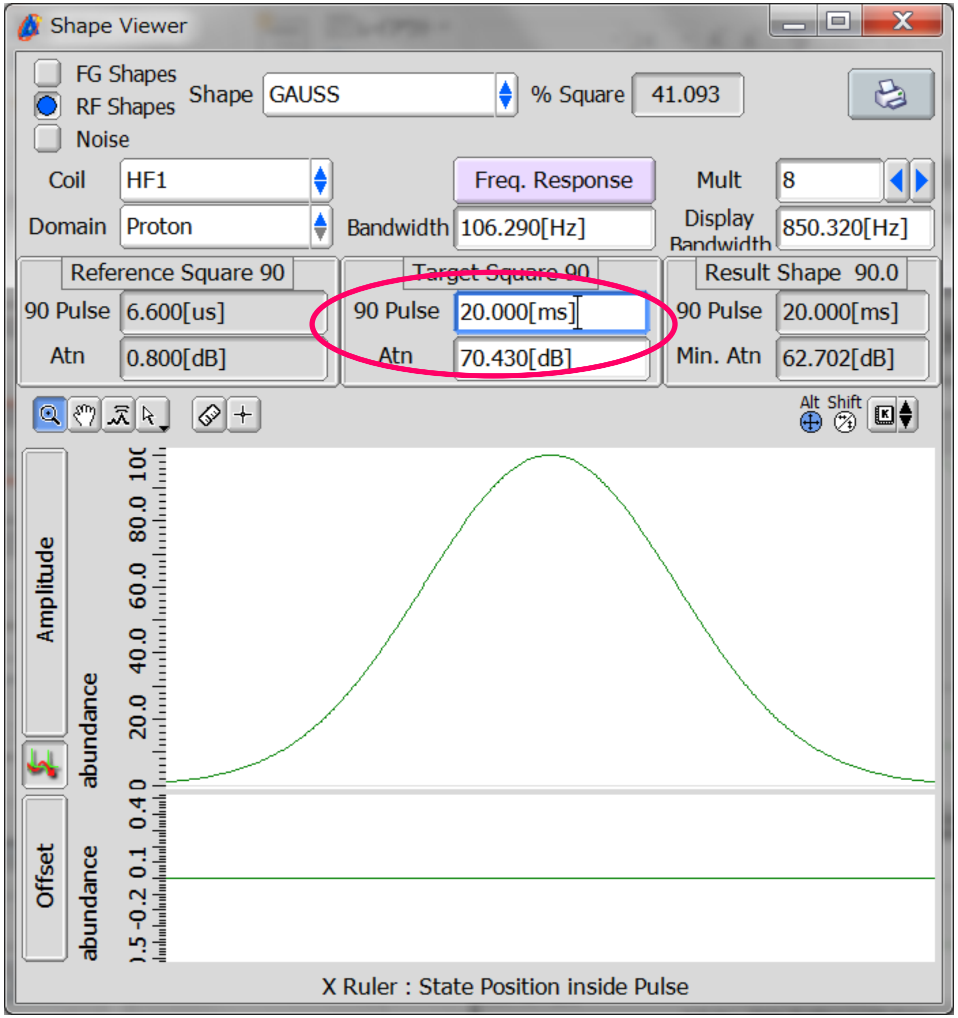
Domain: Proton

Mult: 8

Reference Square 90
90 Pulse: 6.600[us]
Atn: 0.800[dB]

1. **Select the target shape**
2. **Select a nucleus to "Domain"**
3. **Input the target pulse width**

How to calculate the pulse width



Shape Viewer

☐ FG Shapes
● RF Shapes
☐ Noise

Shape: GAUSS
% Square: 41.093
Coil: HF1
Mult: 8
Domain: Proton
Bandwidth: 106.290[Hz]
Display Bandwidth: 850.320[Hz]

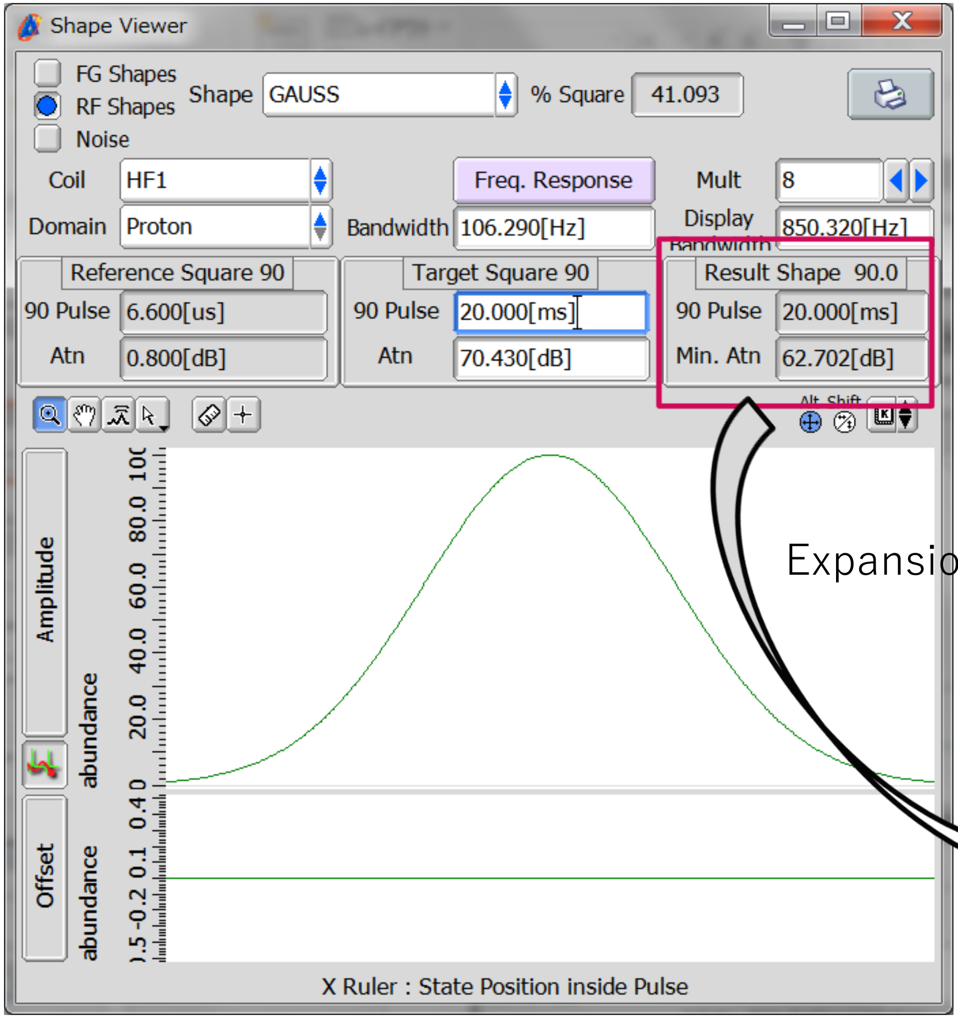
Reference Square 90
90 Pulse: 6.600[us]
Atn: 0.800[dB]

Target Square 90
90 Pulse: 20.000[ms]
Atn: 70.430[dB]

Result Shape 90.0
90 Pulse: 20.000[ms]
Min. Atn: 62.702[dB]

1. Select the target shape
2. Select a nucleus to “Domain”
3. **Input the target pulse width**

How to calculate the pulse width



Shape Viewer

☐ FG Shapes
● RF Shapes
☐ Noise

Shape: GAUSS
% Square: 41.093

Coil: HF1
Mult: 8

Domain: Proton
Bandwidth: 106.290[Hz]
Display Bandwidth: 850.320[Hz]

Reference Square 90
90 Pulse: 6.600[us]
Atn: 0.800[dB]

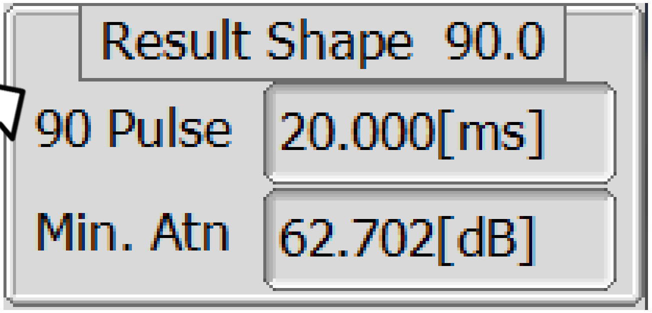
Target Square 90
90 Pulse: 20.000[ms]
Atn: 70.430[dB]

Result Shape 90.0
90 Pulse: 20.000[ms]
Min. Atn: 62.702[dB]

1. **Select the target shape**
2. **Select a nucleus to “Domain”**
3. **Input the target pulse width**

Expansion

The result for GAUSS pulse



Result Shape 90.0
90 Pulse: 20.000[ms]
Min. Atn: 62.702[dB]

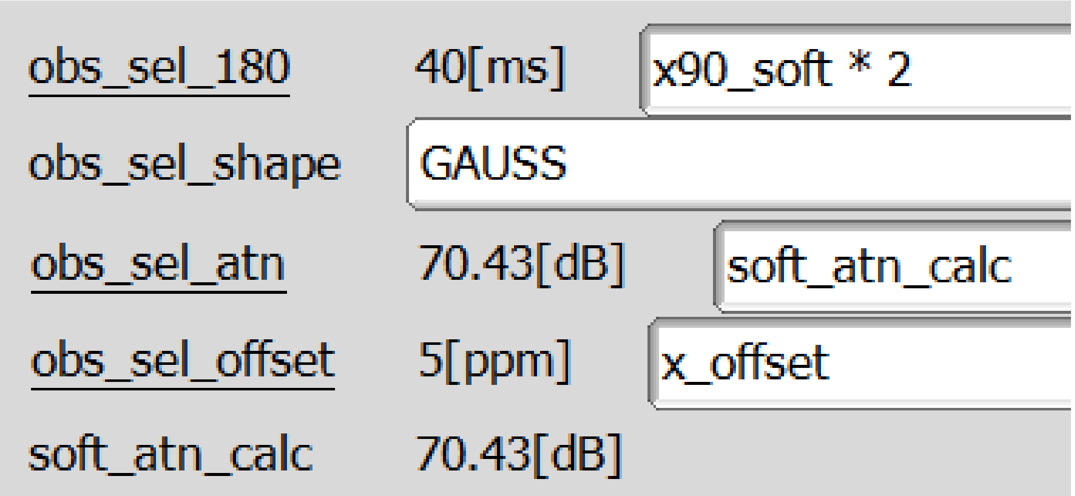
How to put the result into experiment

Pulse width of selective reverse (180 degree) pulse

Attenuator of selective pulse

Offset of selective pulse

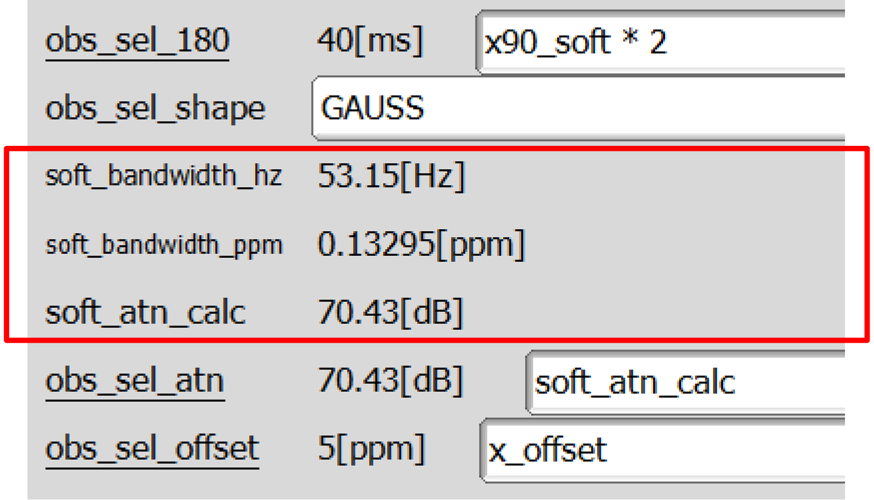
Shape of selective pulse



obs_sel_180	40[ms]	x90_soft * 2
obs_sel_shape	GAUSS	
obs_sel_atn	70.43[dB]	soft_atn_calc
obs_sel_offset	5[ppm]	x_offset
soft_atn_calc	70.43[dB]	

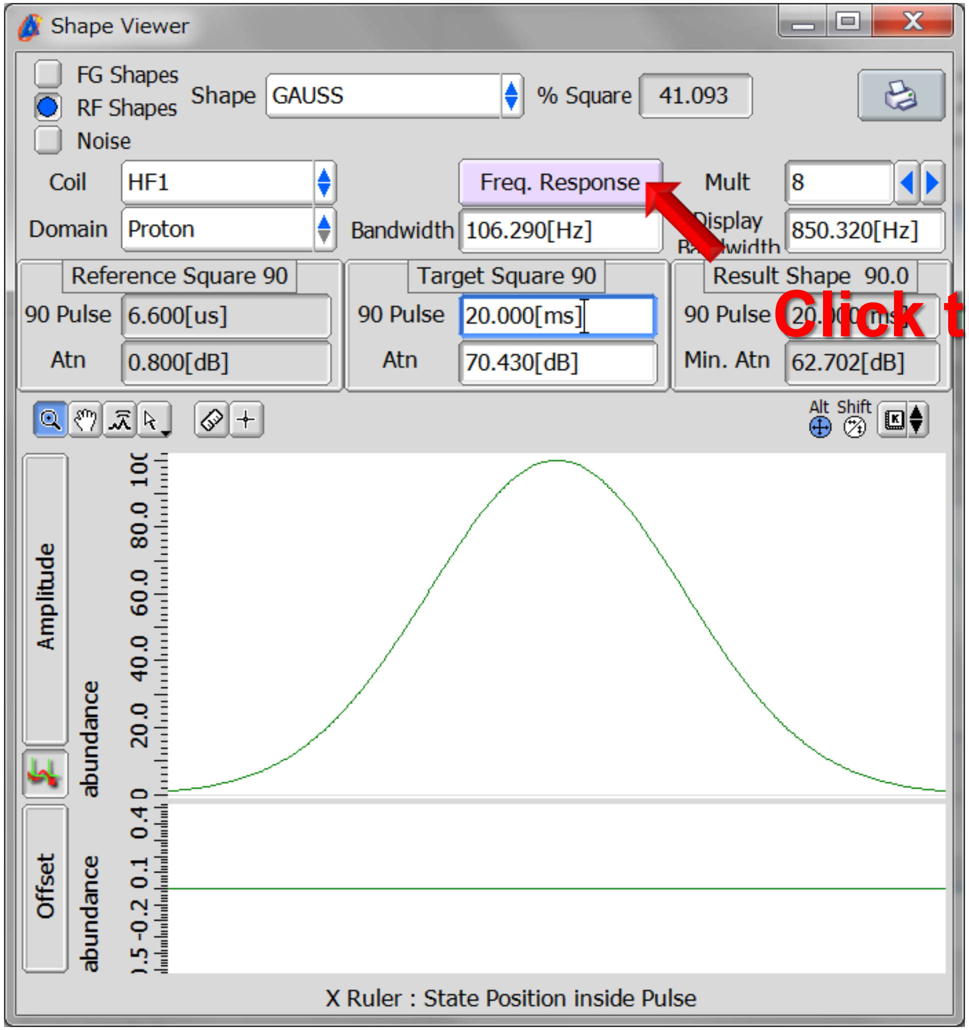
··· from V5.1.0

Automatically calculated



obs_sel_180	40[ms]	x90_soft * 2
obs_sel_shape	GAUSS	
soft_bandwidth_hz	53.15[Hz]	
soft_bandwidth_ppm	0.13295[ppm]	
soft_atn_calc	70.43[dB]	
obs_sel_atn	70.43[dB]	soft_atn_calc
obs_sel_offset	5[ppm]	x_offset

Display the profile of Frequency Response



Shape Viewer

☐ FG Shapes
● RF Shapes
☐ Noise

Shape: GAUSS
% Square: 41.093

Coil: HF1
Domain: Proton

Freq. Response
Bandwidth: 106.290[Hz]
Mult: 8
Display Bandwidth: 850.320[Hz]

Reference Square 90
90 Pulse: 6.600[us]
Atn: 0.800[dB]

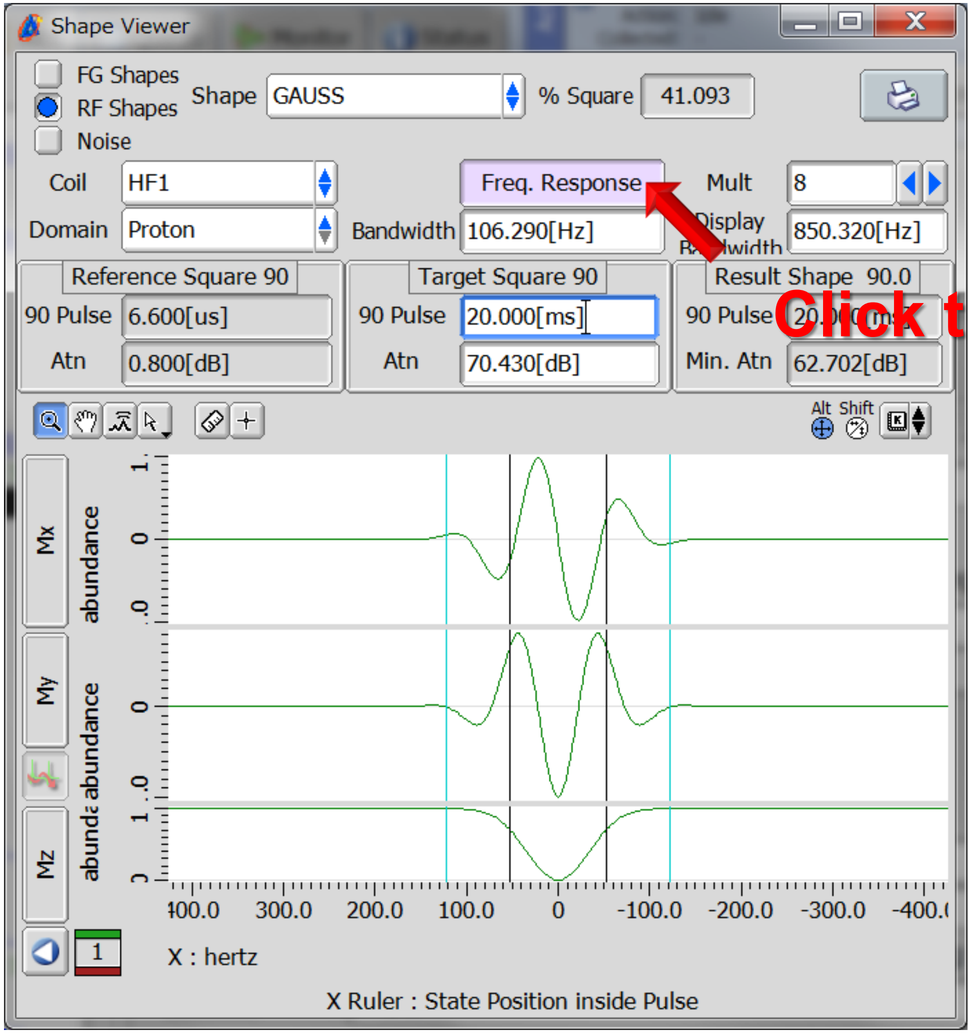
Target Square 90
90 Pulse: 20.000[ms]
Atn: 70.430[dB]

Result Shape 90.0
90 Pulse: 20.000[ms]
Min. Atn: 62.702[dB]

X Ruler : State Position inside Pulse

Click the "Freq. Response" button

Display the profile of Frequency Response



☐ FG Shapes
● RF Shapes
☐ Noise

Shape GAUSS
% Square 41.093
Coil HF1
Domain Proton
Mult 8
Bandwidth 106.290[Hz]
Display Bandwidth 850.320[Hz]

Reference Square 90
90 Pulse 6.600[us]
Atn 0.800[dB]

Target Square 90
90 Pulse 20.000[ms]
Atn 70.430[dB]

Result Shape 90.0
90 Pulse 20.000[ms]
Min. Atn 62.702[dB]

X : hertz

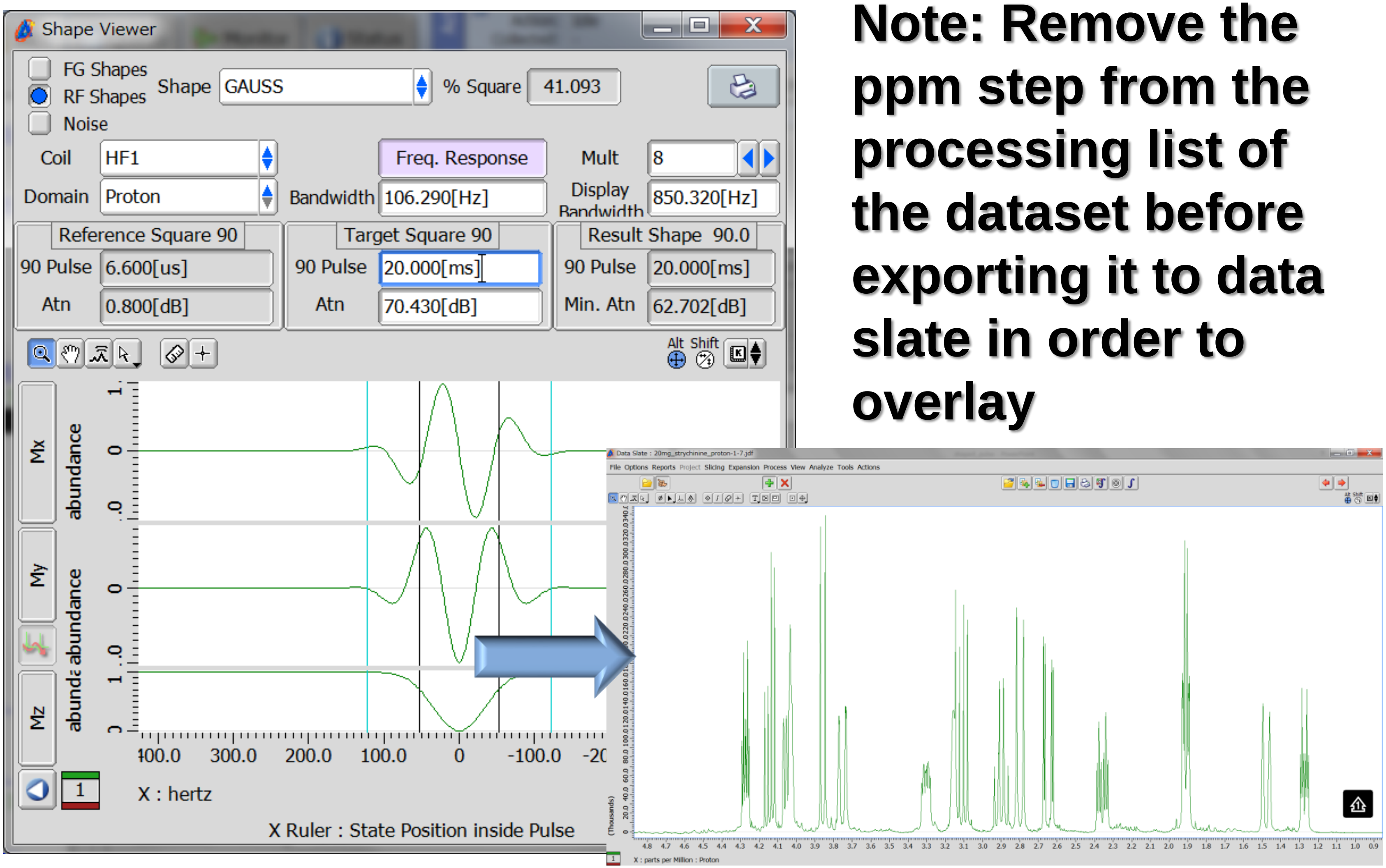
X Ruler : State Position inside Pulse

Click the “Freq. Response” button

The excitation profile for X axis and Y axis

The excitation profile for Z axis

Compare the profile with the actual spectrum



Shape Viewer

☐ FG Shapes
● RF Shapes
☐ Noise

Shape: GAUSS
% Square: 41.093
Coil: HF1
Domain: Proton
Freq. Response
Bandwidth: 106.290[Hz]
Mult: 8
Display Bandwidth: 850.320[Hz]

Reference Square 90
90 Pulse: 6.600[us]
Atn: 0.800[dB]

Target Square 90
90 Pulse: 20.000[ms]
Atn: 70.430[dB]

Result Shape 90.0
90 Pulse: 20.000[ms]
Min. Atn: 62.702[dB]

X : hertz

X Ruler : State Position inside Pulse

Data Slate : 20mg_strychinine_proton-1-7.jdf

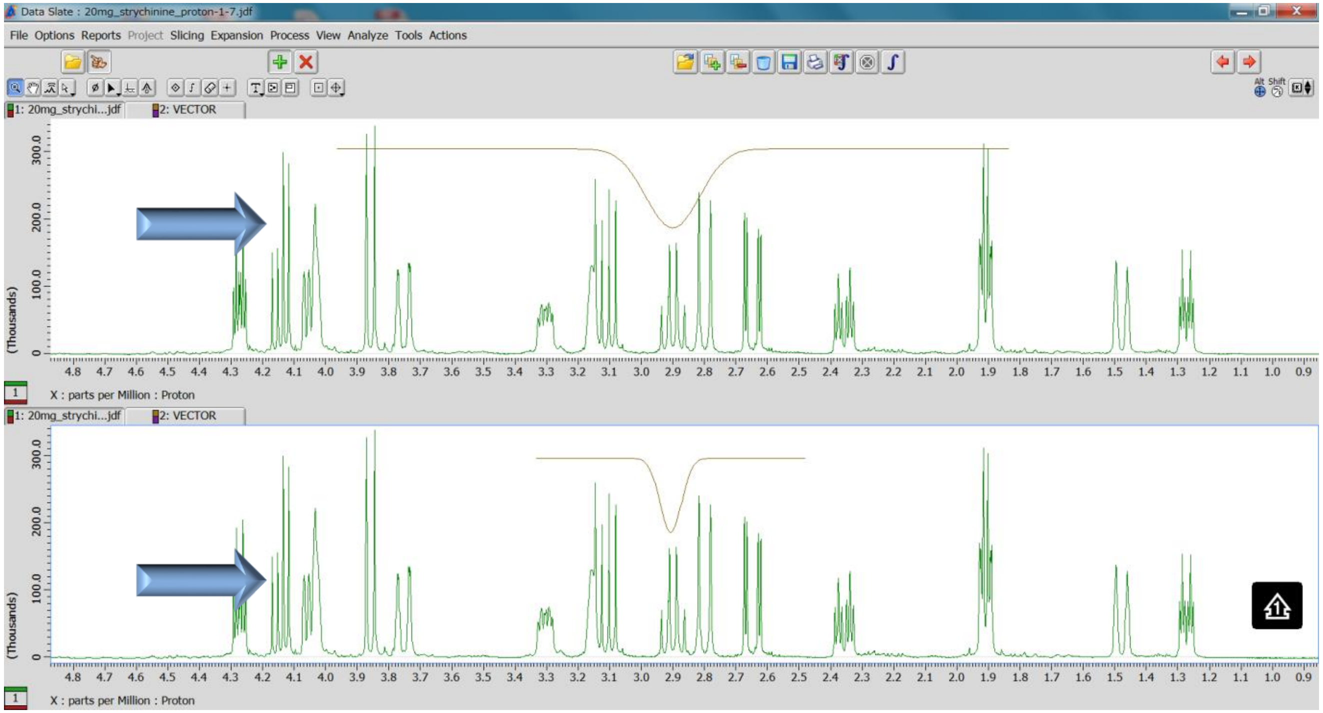
Note: Remove the ppm step from the processing list of the dataset before exporting it to data slate in order to overlay

Overlay the profile to spectrum

Compare the profile with the actual spectrum

20[ms] Gaussian pulse

50[ms] Gaussian pulse

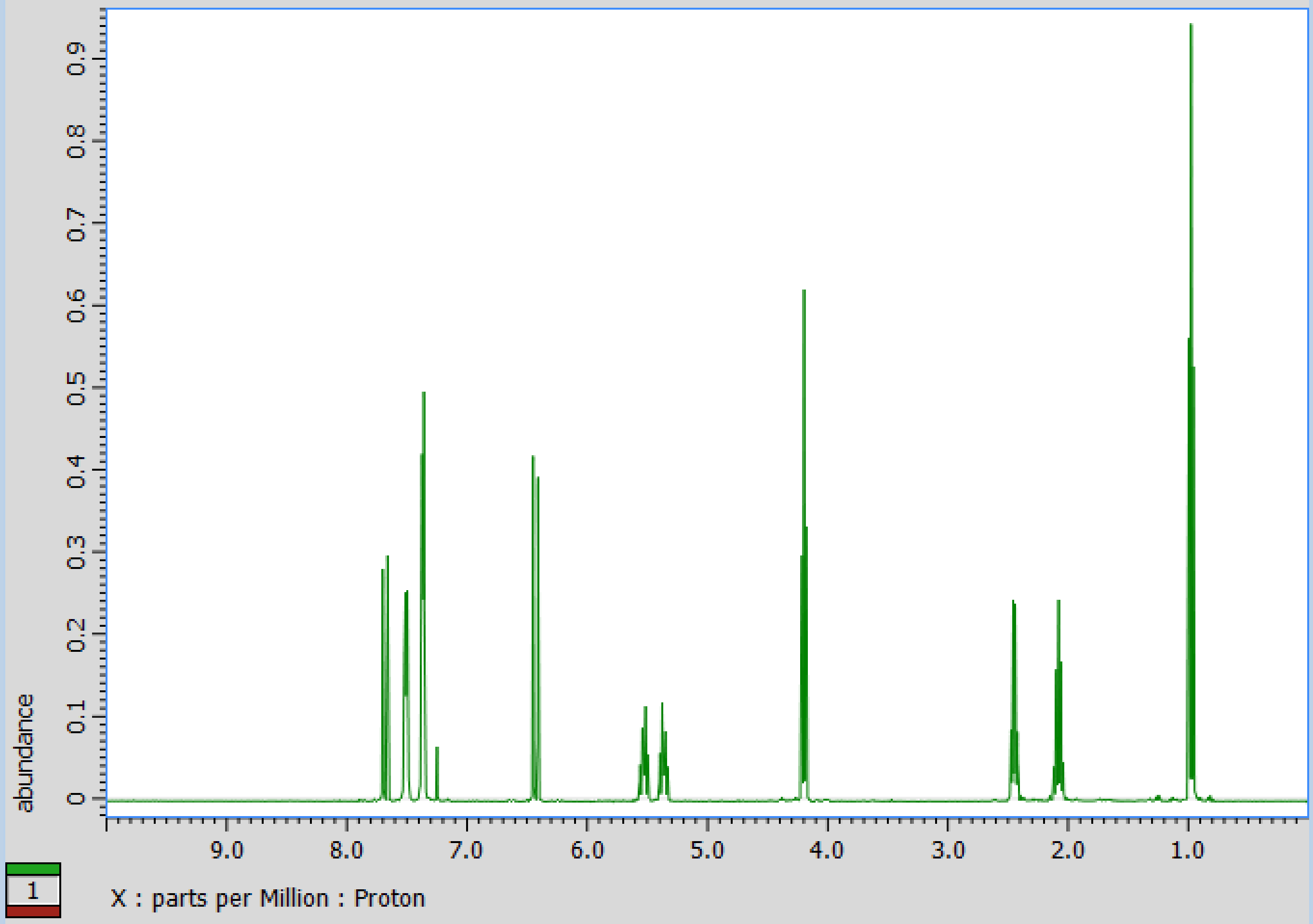


50[ms] is better for selecting the peak at 2.9[ppm]

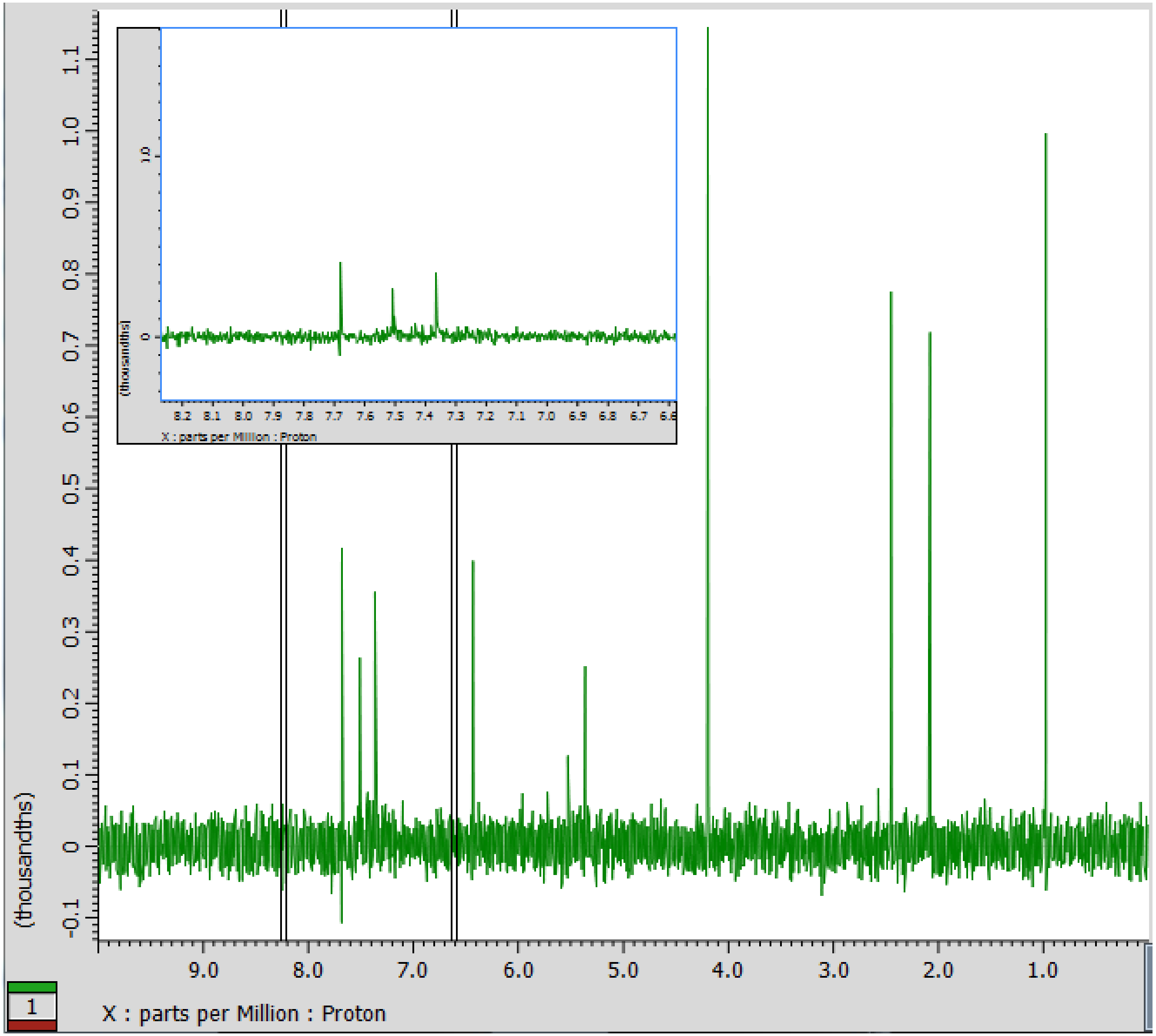
Pure shift

https://www.nmr.chemistry.manchester.ac.uk/?q=node/421

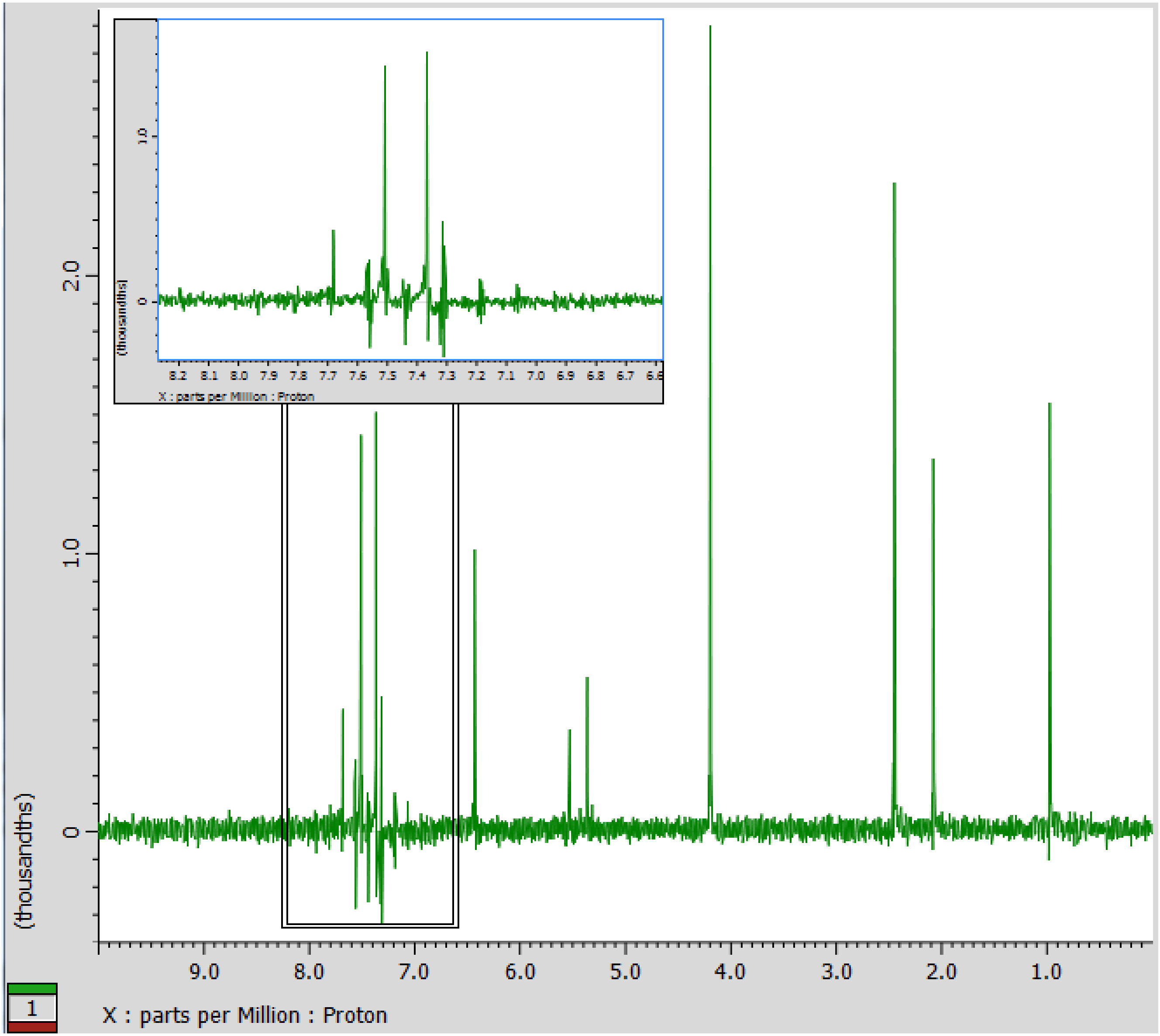
Proton


abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
1
X : parts per Million : Proton

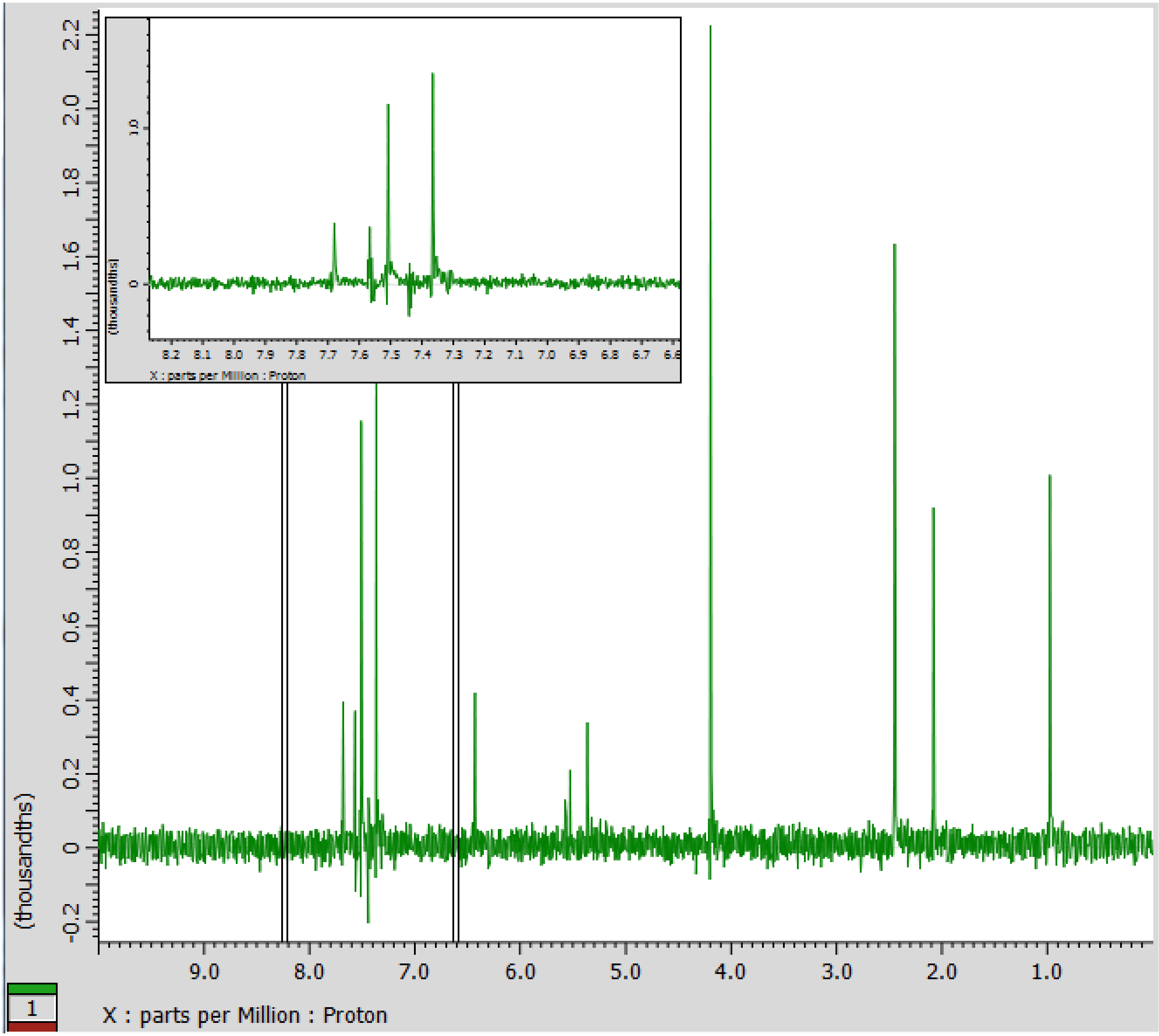
Zangger-Sterk



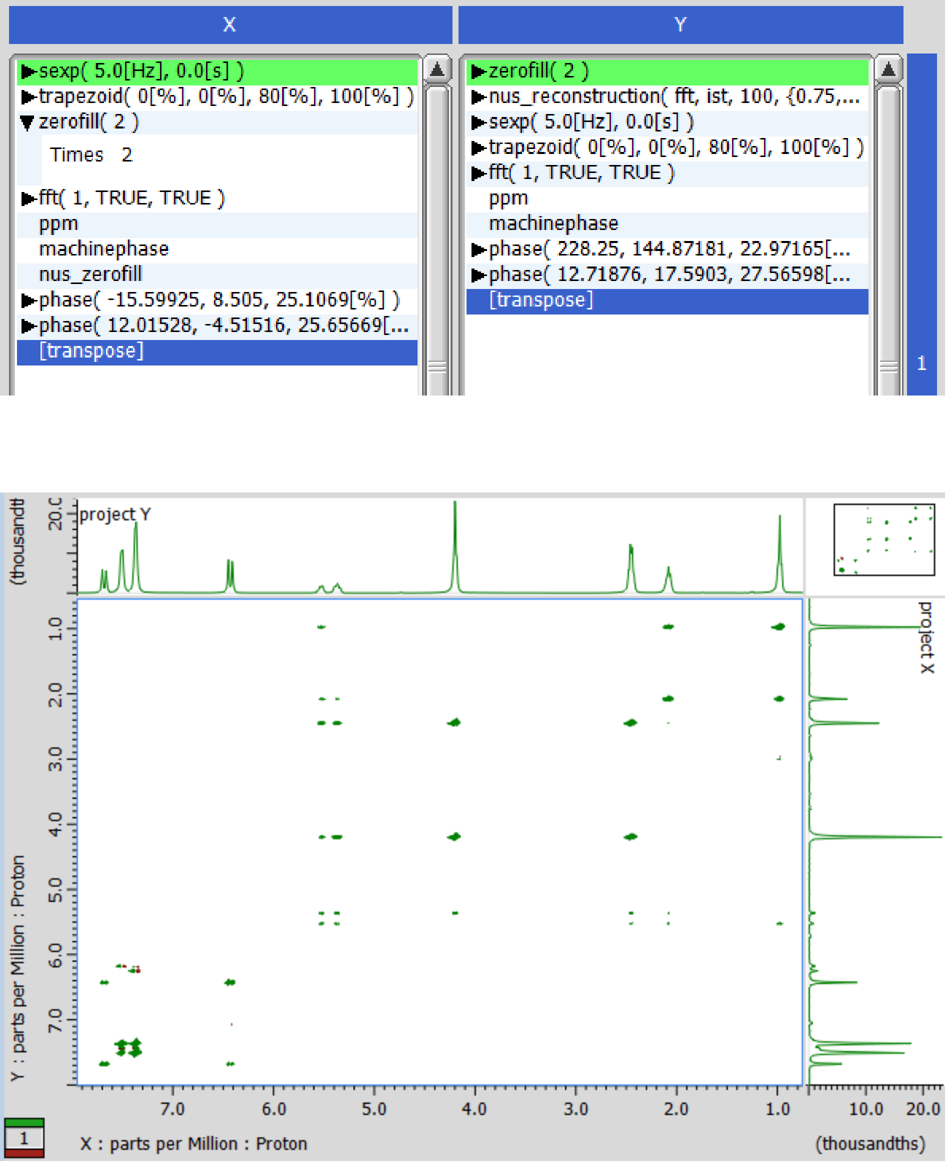
PSYCHE


(thousandths)
0
1.0
2.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
X : parts per Million : Proton
1
(thousandths)
0
1.0
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
X : parts per Million : Proton

TSE-PSYCHE


(thousandths)
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
-0.2
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
X : parts per Million : Proton
1
(thousandths)
1.0
0
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
X : parts per Million : Proton

PSYCHE-TOCSY (F1) + NUS + Covariance

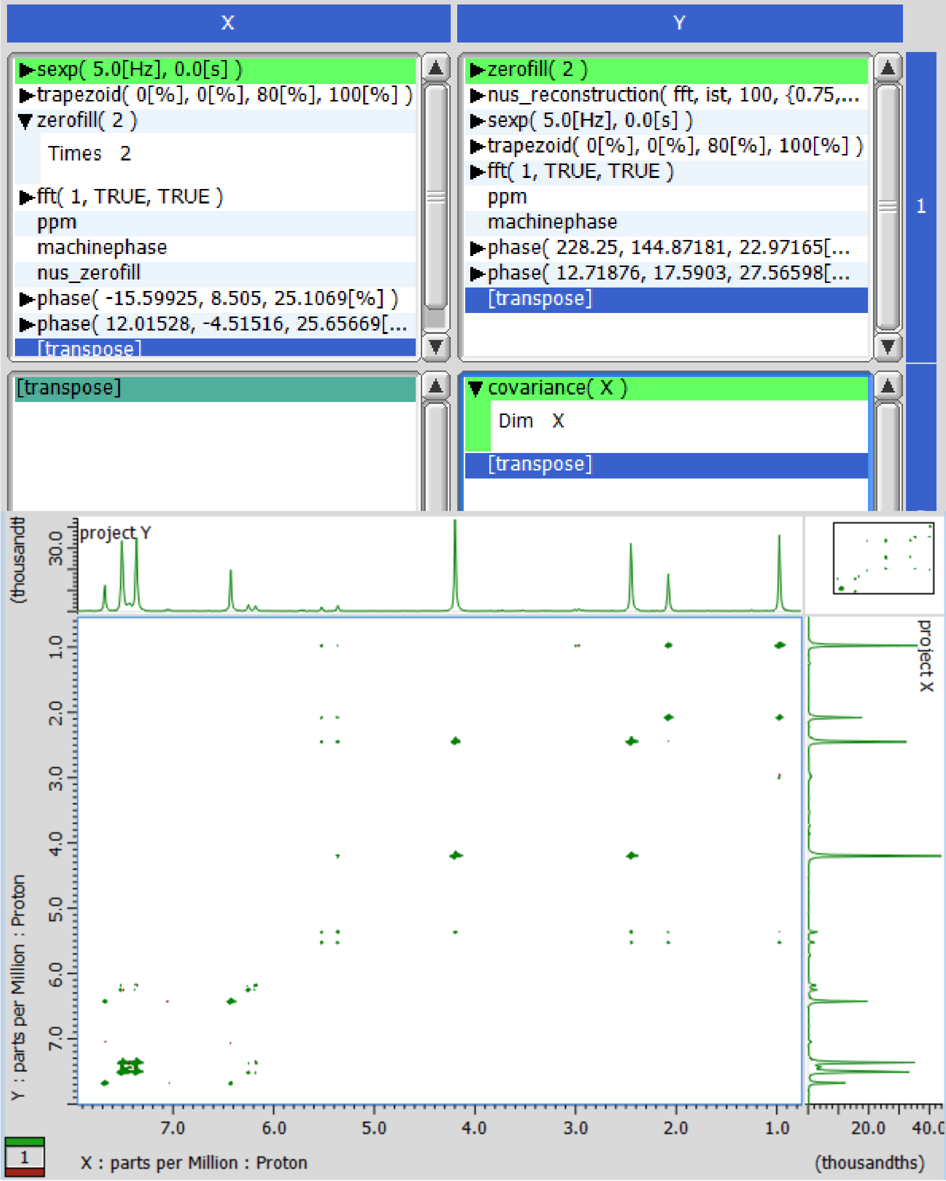


X

```
▶sexp( 5.0[Hz], 0.0[s] )
▶trapezoid( 0[%], 0[%], 80[%], 100[%] )
▼zerofill( 2 )
   Times   2
▶fft( 1, TRUE, TRUE )
 ppm
 machinephase
 nus_zerofill
▶phase( -15.59925, 8.505, 25.1069[%] )
▶phase( 12.01528, -4.51516, 25.65669[...
 [transpose]
```

Y

```
▶zerofill( 2 )
▶nus_reconstruction( fft, ist, 100, {0.75,...
▶sexp( 5.0[Hz], 0.0[s] )
▶trapezoid( 0[%], 0[%], 80[%], 100[%] )
▶fft( 1, TRUE, TRUE )
 ppm
 machinephase
▶phase( 228.25, 144.87181, 22.97165[...
▶phase( 12.71876, 17.5903, 27.56598[...
 [transpose]
```



X

```
▶sexp( 5.0[Hz], 0.0[s] )
▶trapezoid( 0[%], 0[%], 80[%], 100[%] )
▼zerofill( 2 )
   Times   2
▶fft( 1, TRUE, TRUE )
 ppm
 machinephase
 nus_zerofill
▶phase( -15.59925, 8.505, 25.1069[%] )
▶phase( 12.01528, -4.51516, 25.65669[...
 [transpose]
```

```
[transpose]
```

Y

```
▶zerofill( 2 )
▶nus_reconstruction( fft, ist, 100, {0.75,...
▶sexp( 5.0[Hz], 0.0[s] )
▶trapezoid( 0[%], 0[%], 80[%], 100[%] )
▶fft( 1, TRUE, TRUE )
 ppm
 machinephase
▶phase( 228.25, 144.87181, 22.97165[...
▶phase( 12.71876, 17.5903, 27.56598[...
 [transpose]
```

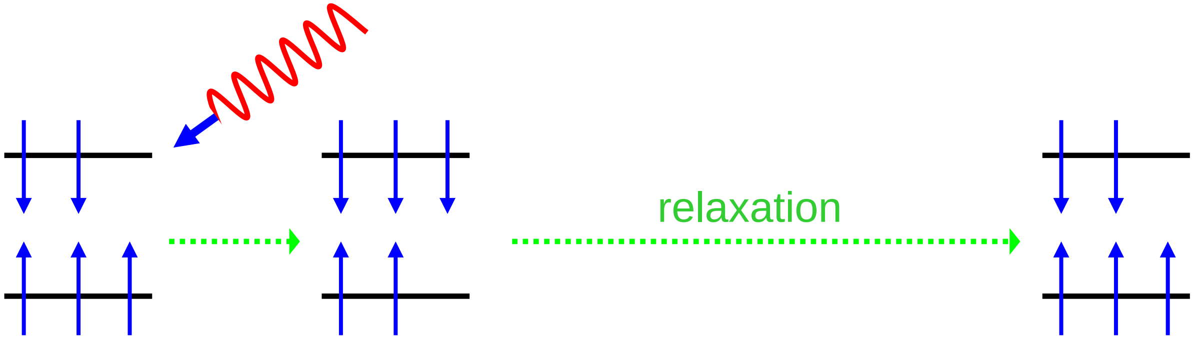
```
▼covariance( X )
   Dim   X
 [transpose]
```

Relaxation

Relaxation

- Exponential processes
- Longitudinal, or spin-lattice, relaxation (T_1)
- T_1 relaxation mechanisms
- Transverse, or spin-spin, relaxation (T_2)

Relaxation

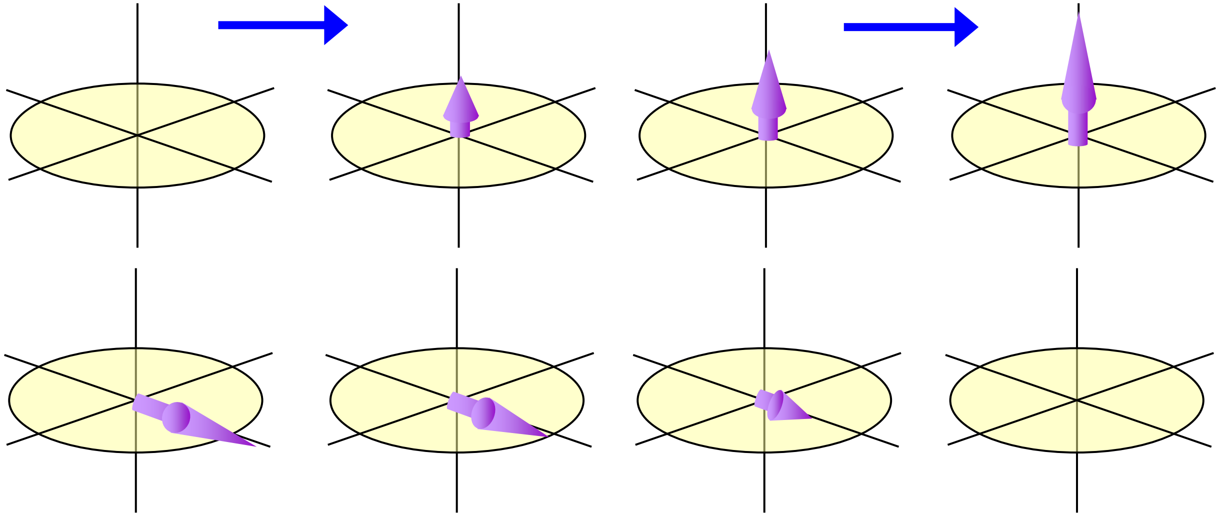


equilibrium state excited state equilibrium state

Z component recoveries to the initial equilibrium state

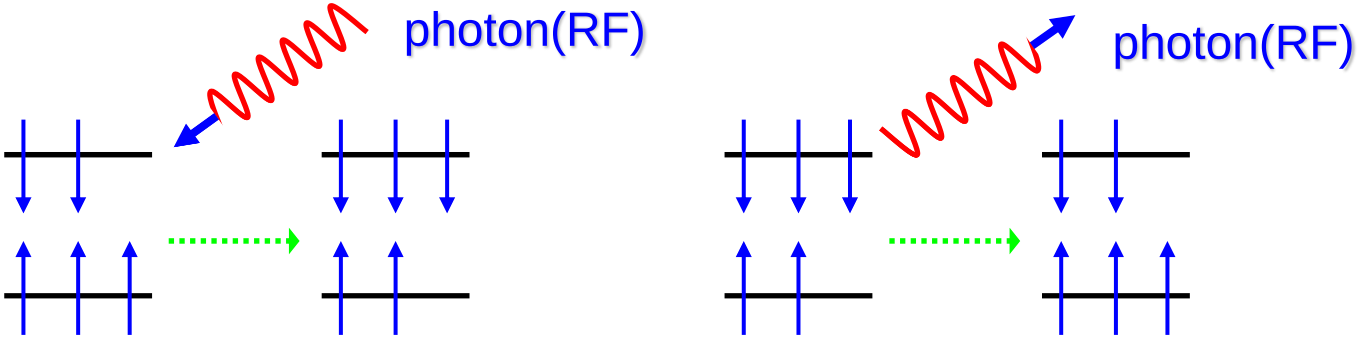
T_1 relaxation

T_2 relaxation



XY component decays to zero (also the initial equilibrium state)

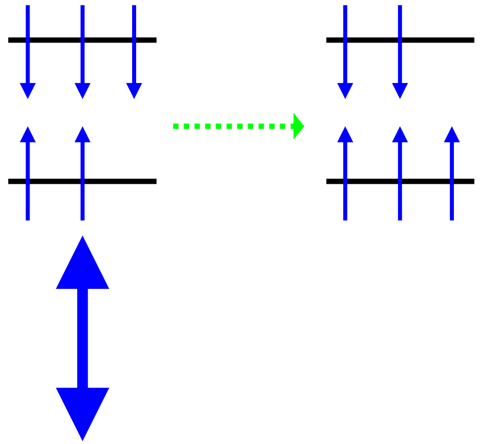
What causes relaxation in NMR?



In case UV or VIS, the energy gap ΔE is large and
the relaxation is dominated by spontaneous emission of photon.
However, the energy gap in NMR is extremely small
If spontaneous emission of photon dominates the relaxation in NMR,
T_1 is estimated to 10^9-10^{10}sec (30years-300years!) even at a high field machine

What causes relaxation in NMR?

excited state equilibrium state

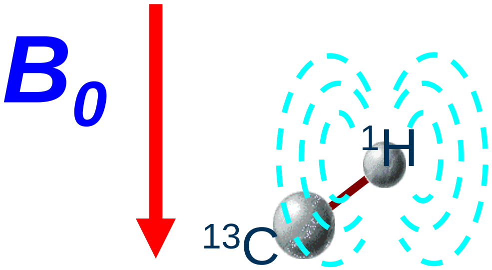


NMR relaxation is the random NMR transition caused by interaction with thermal reservoir (or lattice)

Thermal reservoir

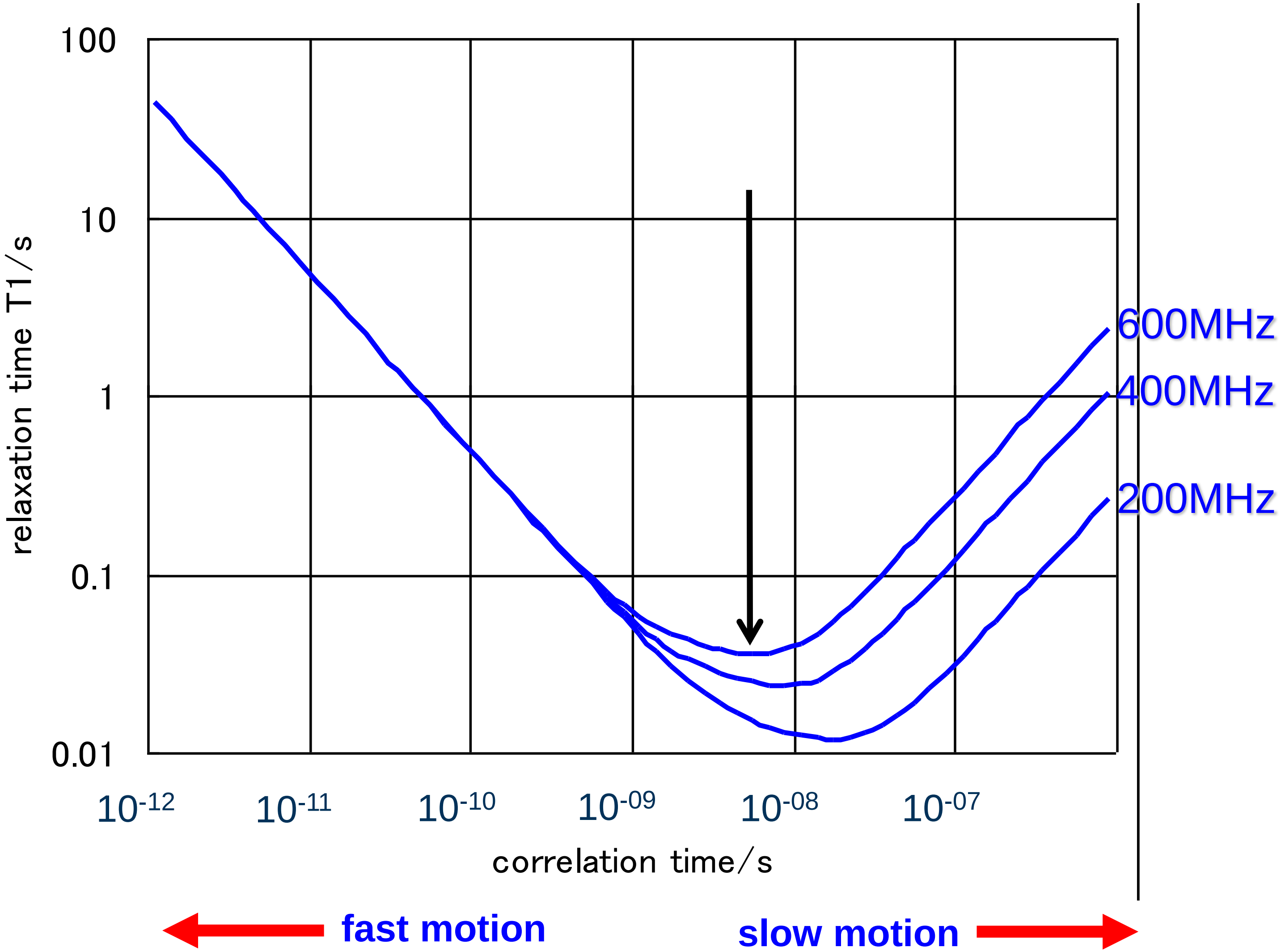
Any time dependent interaction can be "thermal reservoir", which are molecular rotation, vibration, collations ,,,,

The primary interaction to cause NMR relaxation in liquid state is dipole-dipole interaction between two nuclear spins.
^{13}C at the right picture experiences dipole field from ^{1}H. The dipole field changes an angle to B_0 with molecular tumbling in liquid.



Molecular motion vs T_1

Molecular motion = resonance frequency at a 600MHz machine



T_1 mechanisms

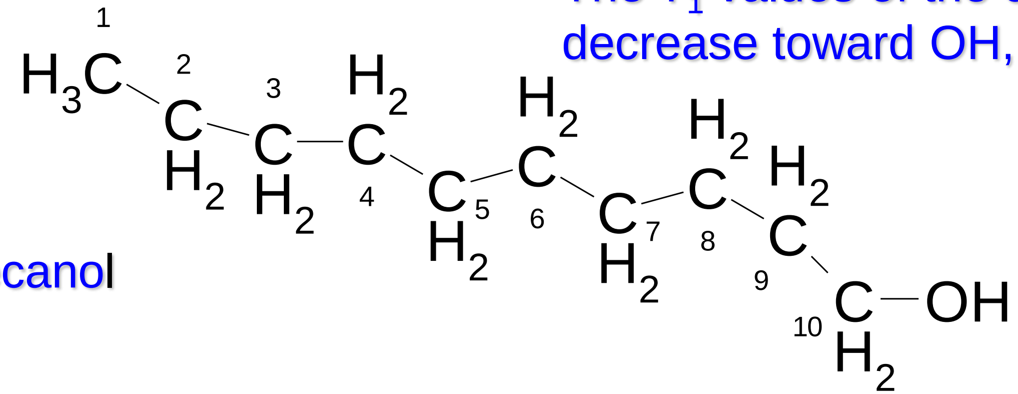
- Relaxation occurs when nearby local fields fluctuate at the Larmor frequency of a nucleus
  - Chemical shift anisotropy (CSA)
  - Quadrupolar interactions (Q)
  - Scalar coupling (SC)
  - Electron-spin interactions (ES)
  - Spin rotation (SR)
  - Dipole-dipole interactions (DD)

Relaxation related Information and NMR parameter

- Molecular structure
- Molecular mobility
- Inter-molecule interaction
- Chemical exchange
- NMR spectrum and experimental condition
  - sensitivity
  - accuracy of integration
  - pulse program parameter optimization

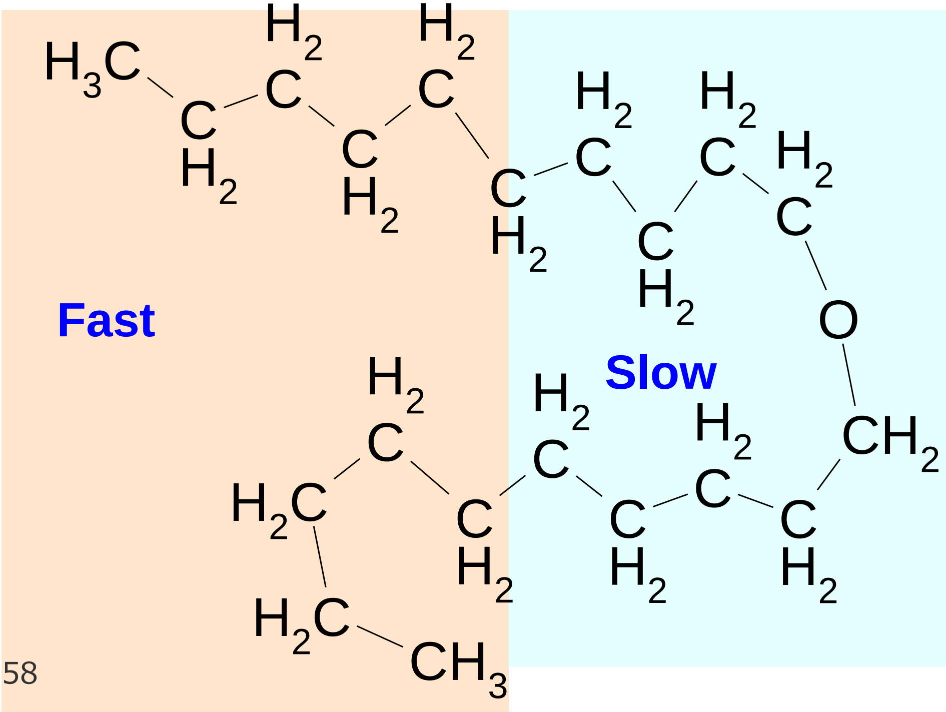
Molecular interaction elucidated by NMR relaxation

The T_1 values of the carbons decrease toward OH, why?



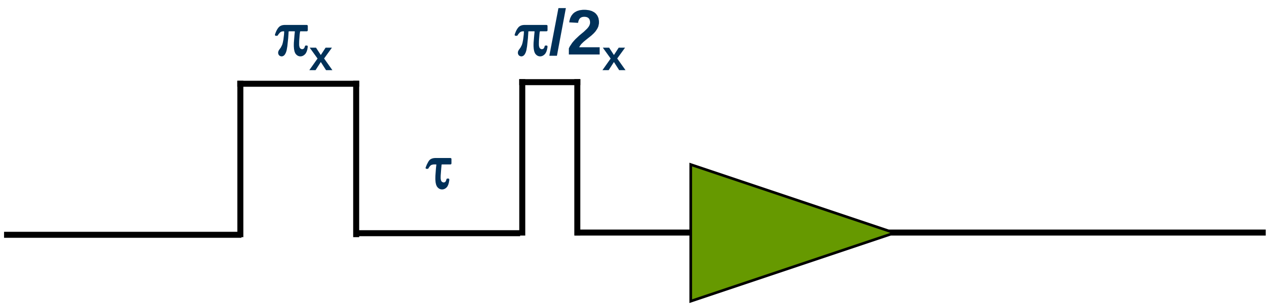
n-decanol

Carbon	T_1/sec
1	3.1
2	2.2
3	1.6
4	1.1
5	0.84
6	0.84
7	0.84
8	0.77
9	0.77
10	0.65



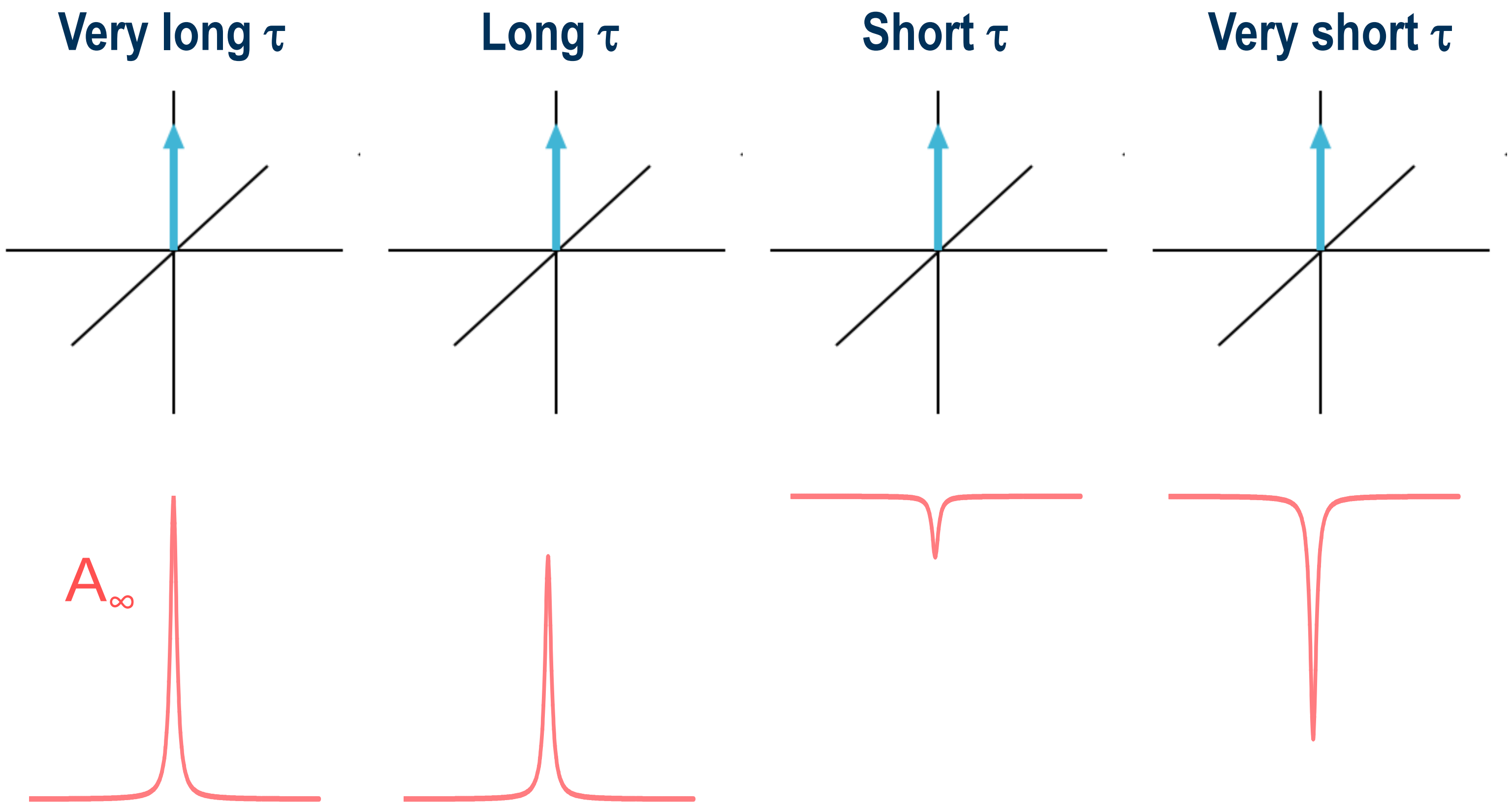
Those T_1 values prove the two molecular complex by hydrogen bound

T_1 by inversion recovery



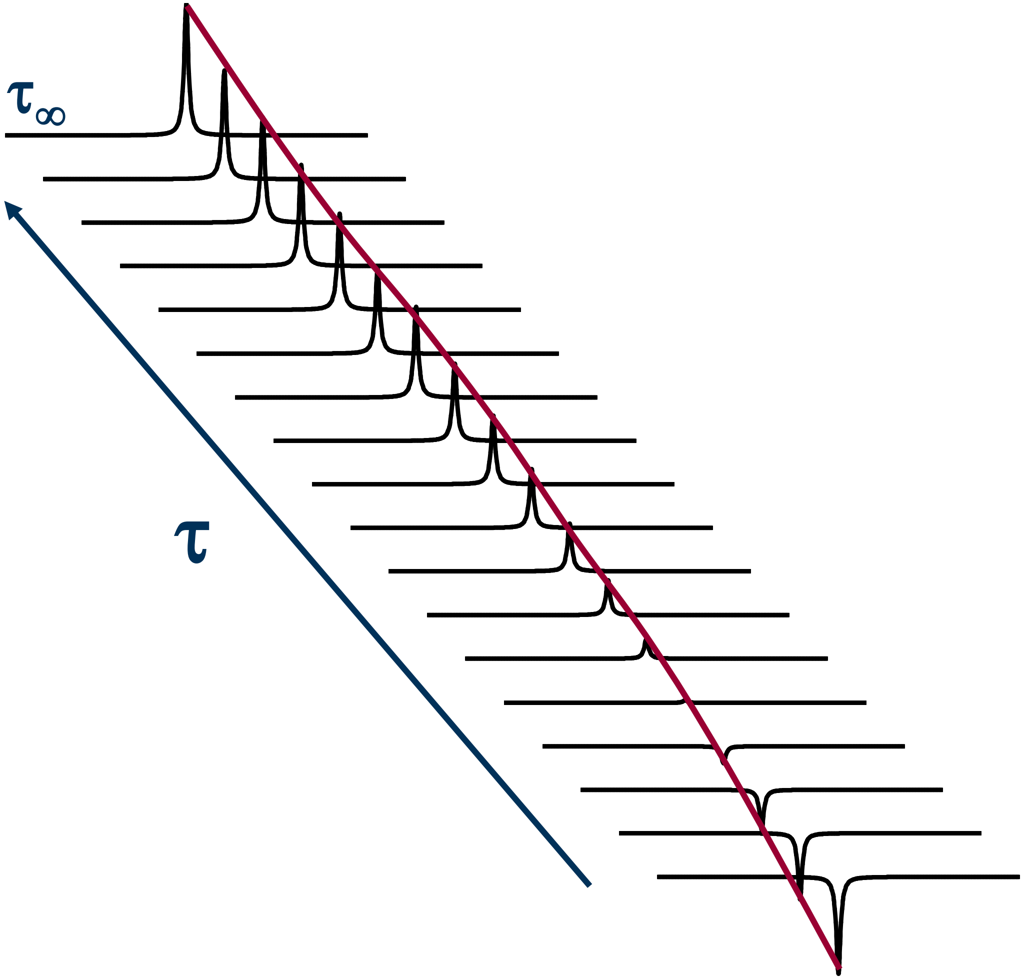
- Measure intensity as τ is varied
- Plot ln $(A_\infty - A)$ *vs.* τ or fit data

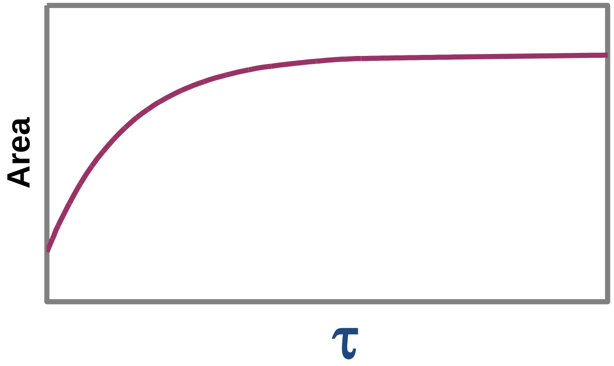
T_1 by inversion recovery

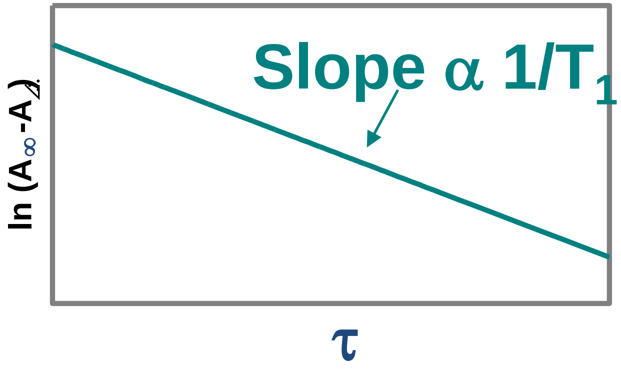


$$A = A_\infty(1 - 2e^{-\tau/T_1})$$

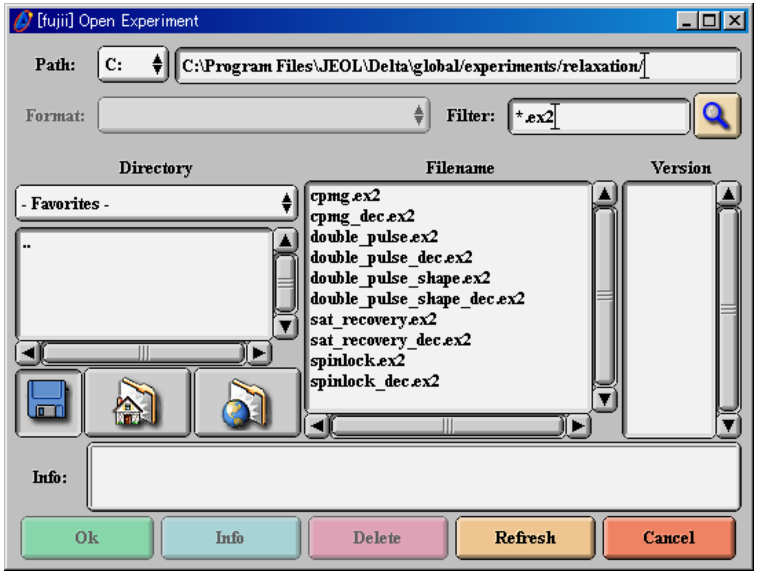
Area *versus* τ







"Quick" T_1 test


[fujii] Open Experiment

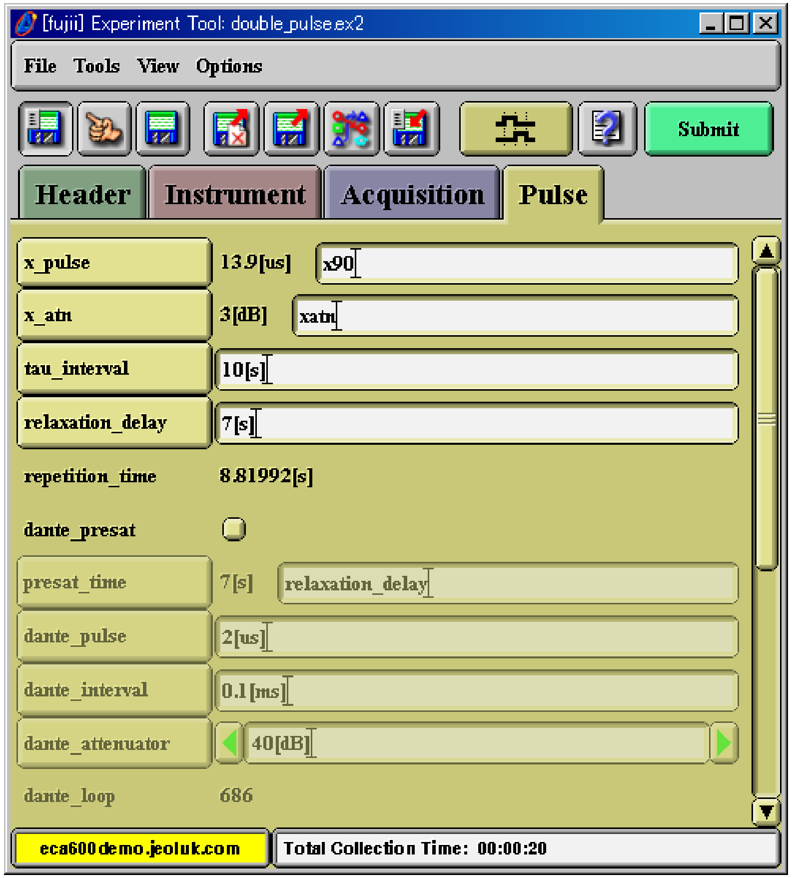
Path: C: C:\Program Files\JEOL\Delta\global/experiments/relaxation/

Format:

Filter: *.ex2

cpmg.ex2
cpmg_dec.ex2
double_pulse.ex2
double_pulse_dec.ex2
double_pulse_shape.ex2
double_pulse_shape_dec.ex2
sat_recovery.ex2
sat_recovery_dec.ex2
spinlock.ex2
spinlock_dec.ex2

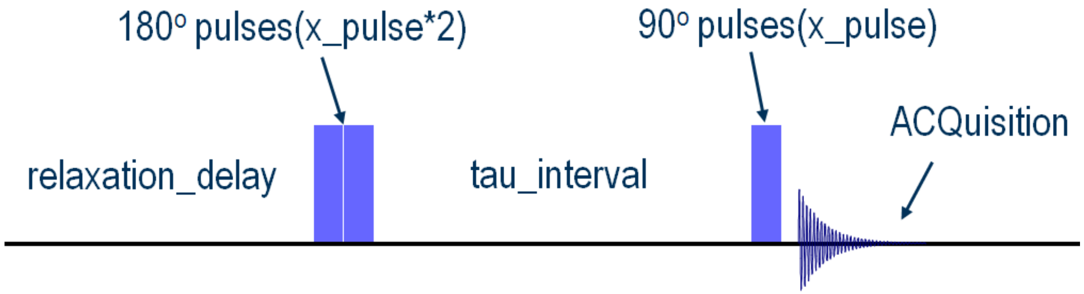
Info:


[fujii] Experiment Tool: double_pulse.ex2

x_pulse 13.9[us] x90
x_atn 3[dB] xatn
tau_interval 10[s]
relaxation_delay 7[s]
repetition_time 8.81992[s]
dante_presat ○
presat_time 7[s] relaxation_delay
dante_pulse 2[us]
dante_interval 0.1[ms]
dante_attenuator 40[dB]
dante_loop 686

eca600demo.jeoluk.com

Total Collection Time: 00:00:20


180° pulses(x_pulse*2)

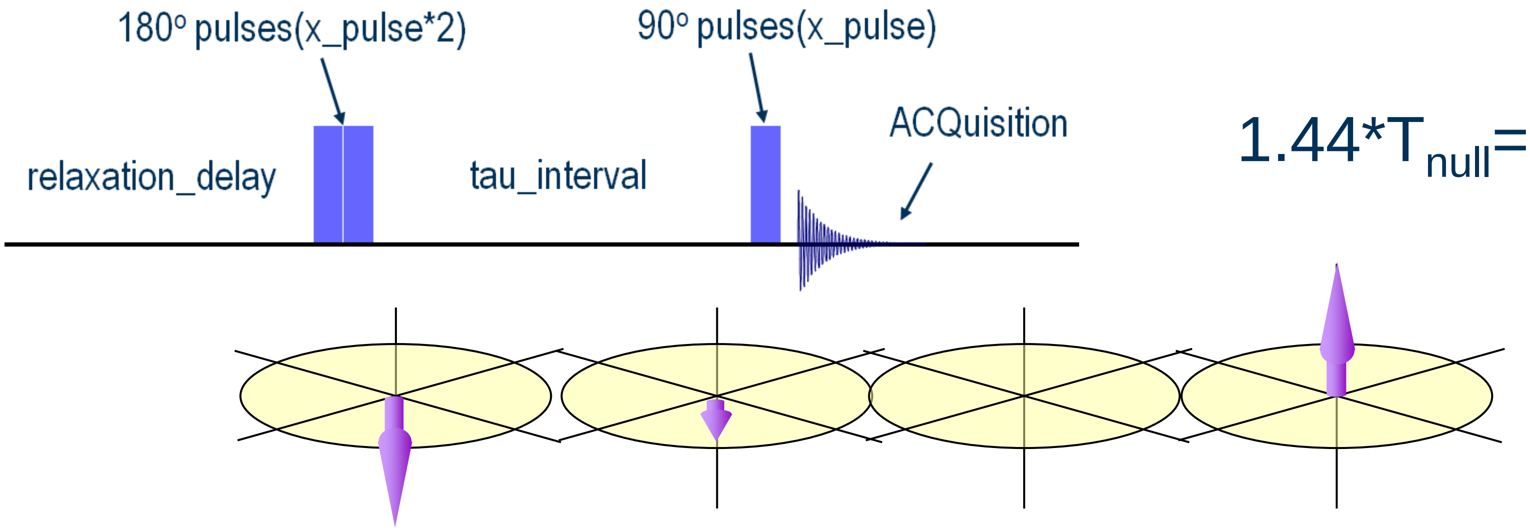
90° pulses(x_pulse)

relaxation_delay

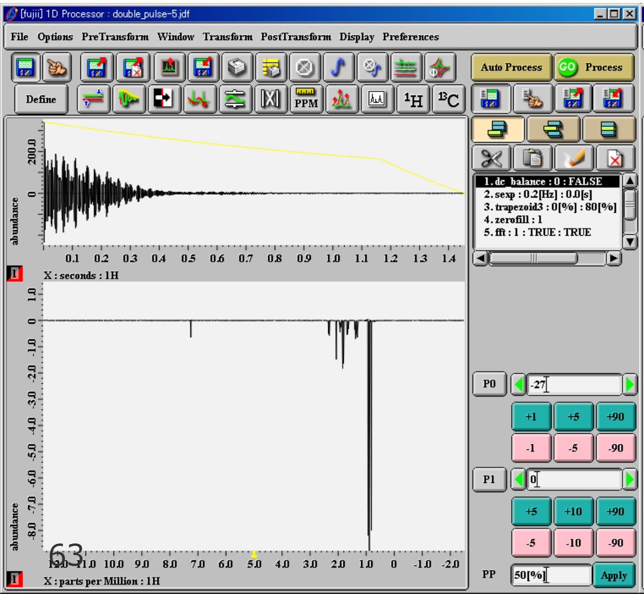
tau_interval

ACQuisition

"Quick" T_1 test

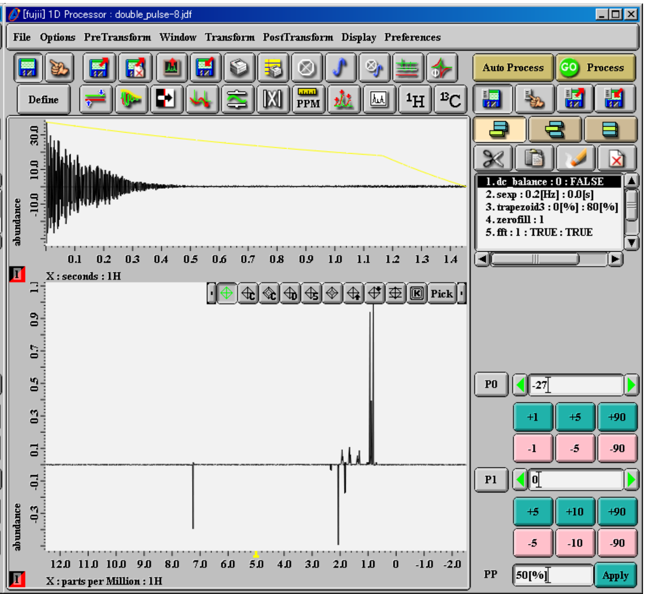


$$1.44*T_{null}=T_1$$


[fujii] 1D Processor : double_pulse-5.jdf

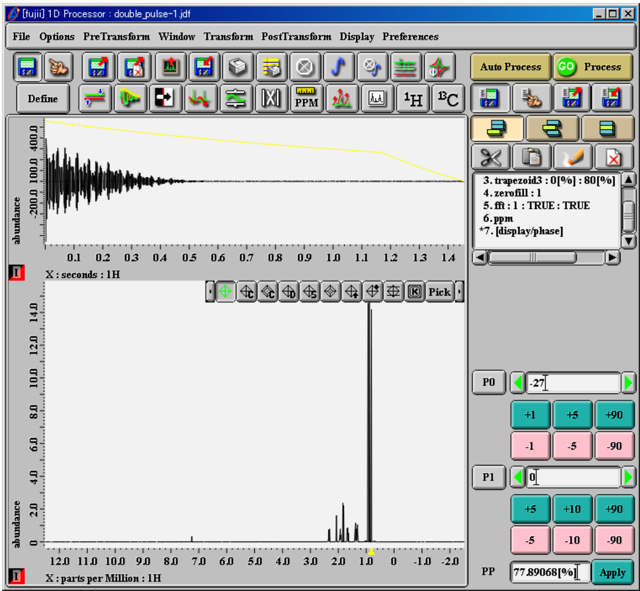
1. dc_balance : 0 : FALSE
2. sexp : 0.2[Hz] : 0.0[s]
3. trapezoid3 : 0[%] : 80[%]
4. zerofill : 1
5. fft : 1 : TRUE : TRUE

P0: -27
P1: 0
PP: 50[%]


[fujii] 1D Processor : double_pulse-8.jdf

1. dc_balance : 0 : FALSE
2. sexp : 0.2[Hz] : 0.0[s]
3. trapezoid3 : 0[%] : 80[%]
4. zerofill : 1
5. fft : 1 : TRUE : TRUE

P0: -27
P1: 0
PP: 50[%]


[fujii] 1D Processor : double_pulse-1.jdf

3. trapezoid3 : 0[%] : 80[%]
4. zerofill : 1
5. fft : 1 : TRUE : TRUE
6. ppm
*7. [display/phase]

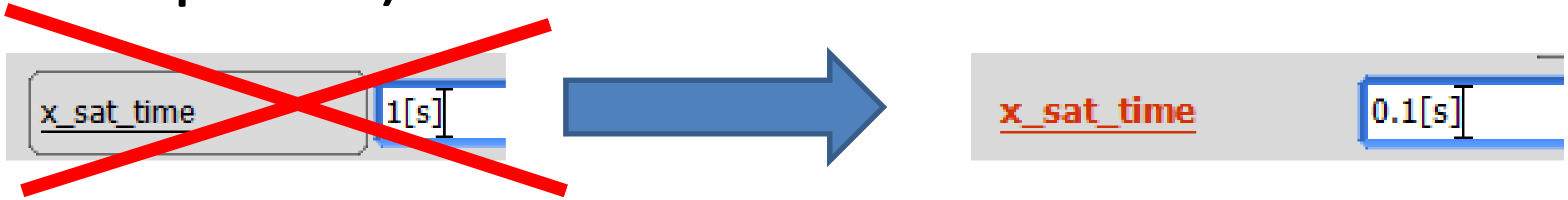
P0: -27
P1: 0
PP: 77.89068[%]

Quick T_1 measurement: Saturation recovery

- Avoid long recovery delays

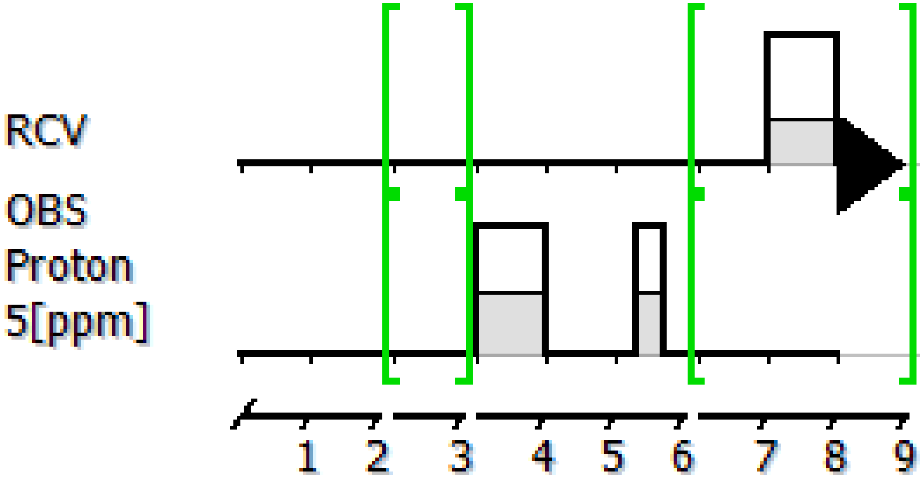
relaxation_delay 1[s]

- Correct the saturation time (1[s] may damage the probe)



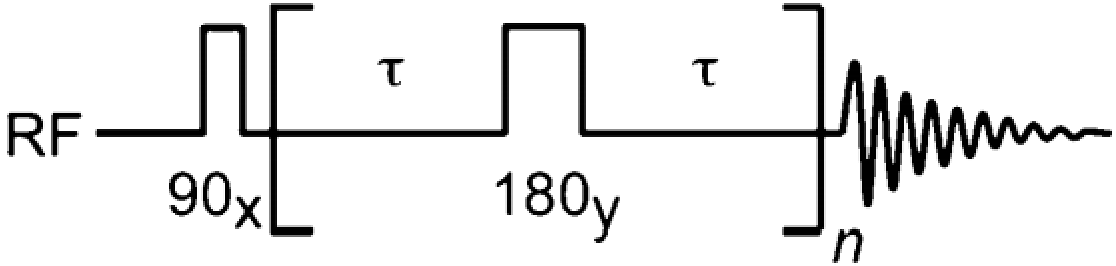
~~x_sat_time 1[s]~~

x_sat_time 0.1[s]



T_2 measurement

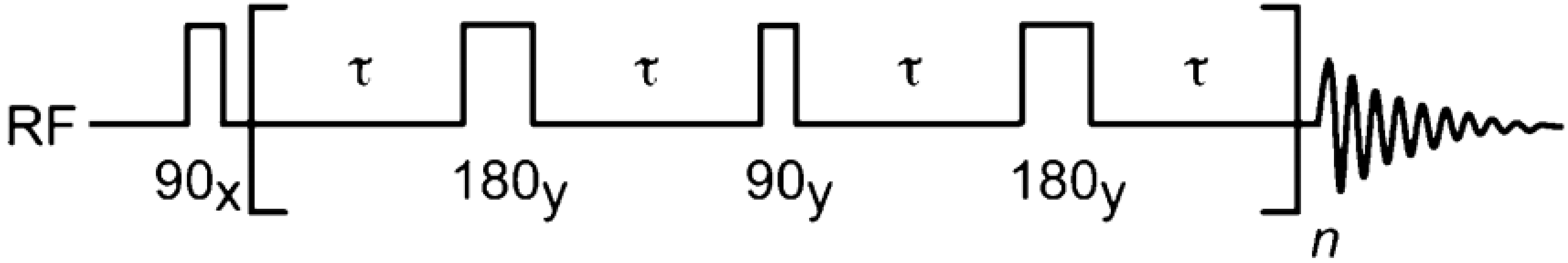
- CPMG



- Increase n to increase the time magnetization is in transverse plane
- J-modulation problems
  - – τ needs to be very short <2ms
  - – Heating problems
  - – Result is a mixture of T_2 and $T_{1\rho}$
- Isotropic mixing

T_2 measurement

- Project



- Train of perfect spin echos
  - J-modulation is quenched for τJ << 1
- τ can be as long as 5ms
- Planar mixing (about half as fast as isotropic mixing)

https://doi.org/10.1039/c1cc16699a

How to array tau_interval / delay_list?

- Saturation recovery: Exponential from $T_1/10$ to $10*T_1$
- Inversion recovery: Logarithmic base 0.3 from $T_1/20$ to $5*T_1$

(if last tau_interval is not long enough, use non-linear fitting)

- CPMG / Project: Logarithmic base 0.3 from $T_1/50$ to $2.5*T_1$

Solvent suppression

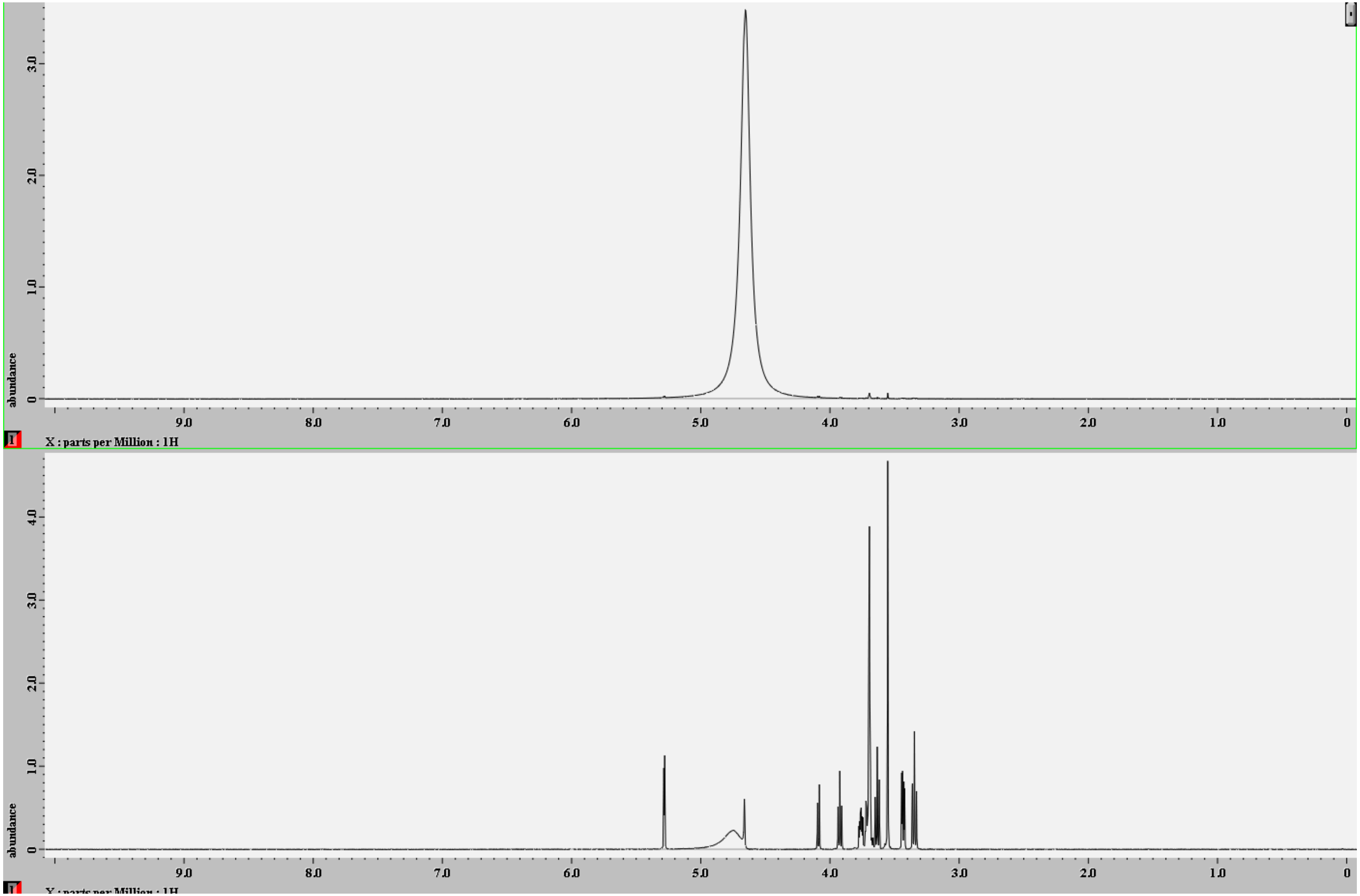
Solvent Suppression

- Ideally NMR samples are dissolved in fully deuterated solvent, this provides the lock signal and also will not appear in the spectrum
- Large protonated signals will prevent the observation of small signals due to the dynamic range limitation of the spectrometer
- They may also obscure signals, contributing to T_1-noise and baseline distortions
- The solution to these problems is to remove the solvent signal

Suppression methods

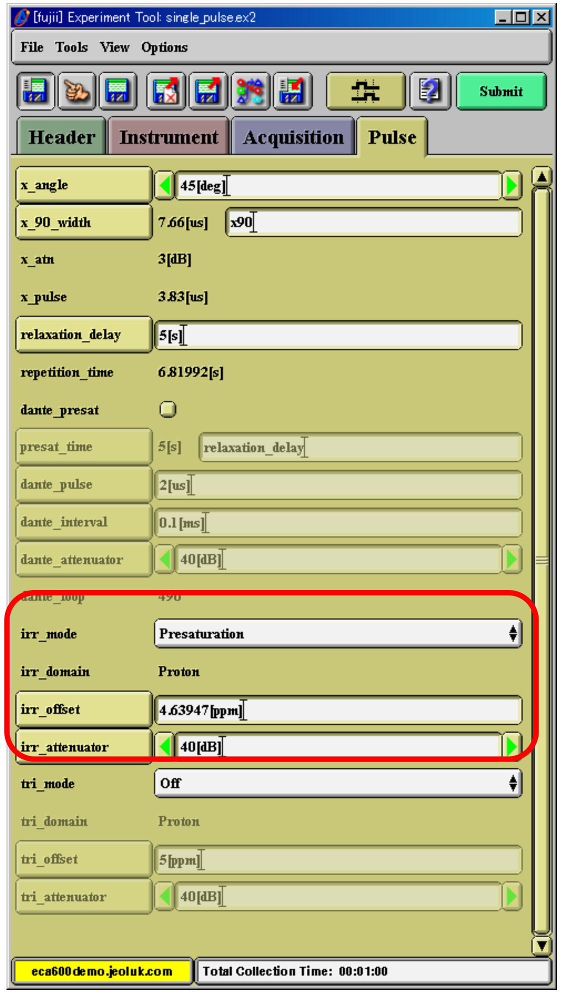
- There are many different ways available to suppress solvents, but fundamentally these fall into three categories:
  - One can presaturate the solvent resonance with weak, continuous rf at its frequency
  - Manipulate the solvent magnetization to produce zero magnitude (“jump and return”)
  - Use pulsed field gradients (WATERGATE, WET) to eliminate solvent resonances
- All methods work best when the sample is well shimmed!

Pre-saturation to suppress a solvent signal



Pre-saturation to suppress a solvent signal

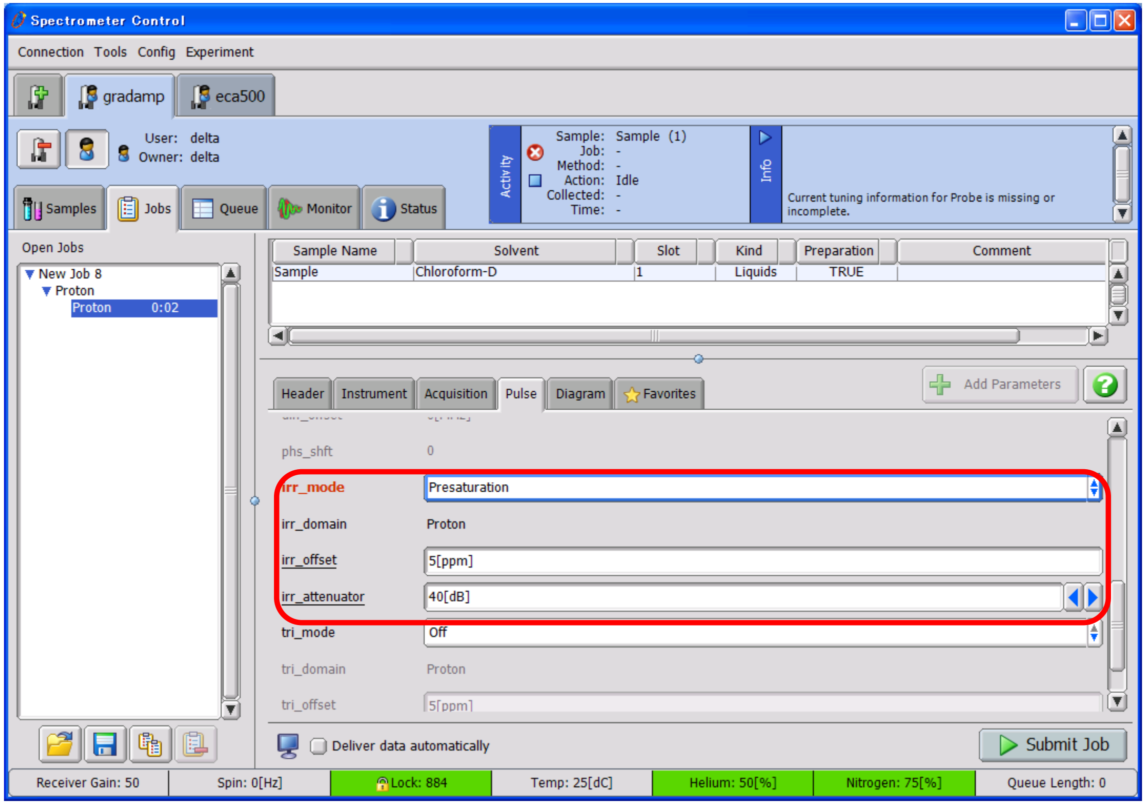
Delta version 4 series



x_angle 45[deg]
x_90_width 7.66[us] x90
x_atn 3[dB]
x_pulse 3.83[us]
relaxation_delay 5[s]
repetition_time 6.81992[s]
dante_presat ○
presat_time 5[s] relaxation_delay
dante_pulse 2[us]
dante_interval 0.1[ms]
dante_attenuator 40[dB]
dante_loop 490
irr_mode Presaturation
irr_domain Proton
irr_offset 4.63947[ppm]
irr_attenuator 40[dB]
tri_mode Off
tri_domain Proton
tri_offset 5[ppm]
tri_attenuator 40[dB]

eca600demo.jeoluk.com
Total Collection Time: 00:01:00

Delta version 5 series



User: delta
Owner: delta

Sample: Sample (1)
Job: -
Method: -
Action: Idle
Collected: -
Time: -

Current tuning information for Probe is missing or incomplete.

Open Jobs
New Job 8
Proton
Proton 0:02

Sample Name	Solvent	Slot	Kind	Preparation	Comment
Sample	Chloroform-D	1	Liquids	TRUE	

phs_shft 0
irr_mode Presaturation
irr_domain Proton
irr_offset 5[ppm]
irr_attenuator 40[dB]
tri_mode Off
tri_domain Proton
tri_offset 5[ppm]

☐ Deliver data automatically

Receiver Gain: 50
Spin: 0[Hz]
Lock: 884
Temp: 25[dC]
Helium: 50[%]
Nitrogen: 75[%]
Queue Length: 0

Presaturation Methods

- The basic presaturation is a long, low power, irradiation at the solvent position
- Better results can be obtained with methods that only excite the regions with good r.f. homogeneity, which excludes peripheral regions contributing to the water ‘hump’
- Presaturation methods are
  - simple and reliable
  - suppress exchangeable protons

Gradient solvent suppression methods

- These work by using pulsed field gradients acting to dephase the solvent signal.

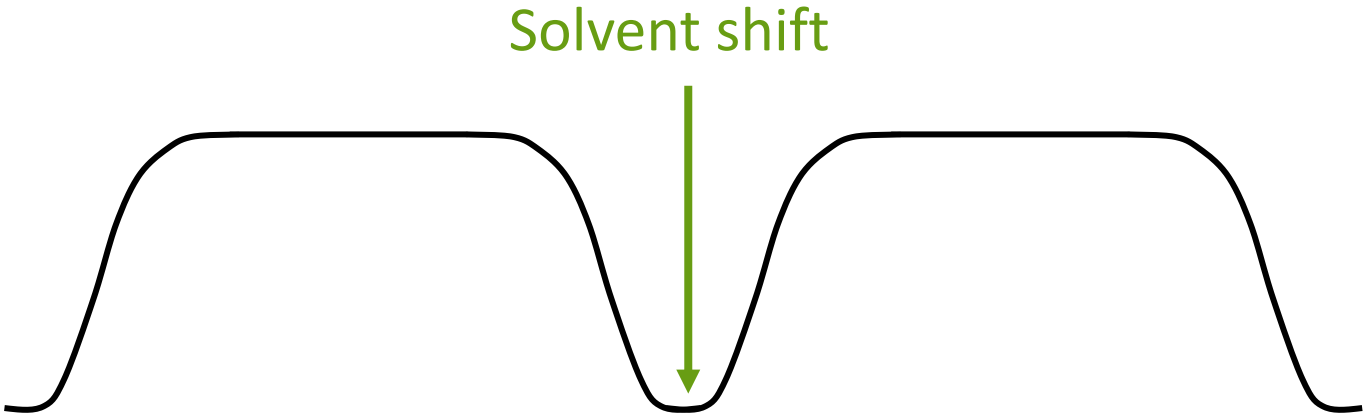
WATERGATE (Water suppression by Gradient Tailored Excitation)
Good for protein and bio-molecule sample with water.
Exchangeable protons are observable.

WET (Water suppression enhanced through T_1 effect)
Because we can remove ^{13}C satellite signals, this is good for organic solvent suppression (No-D NMR and LC-NMR).

Watergate method

Water Suppression by Gradient Tailored Excitation

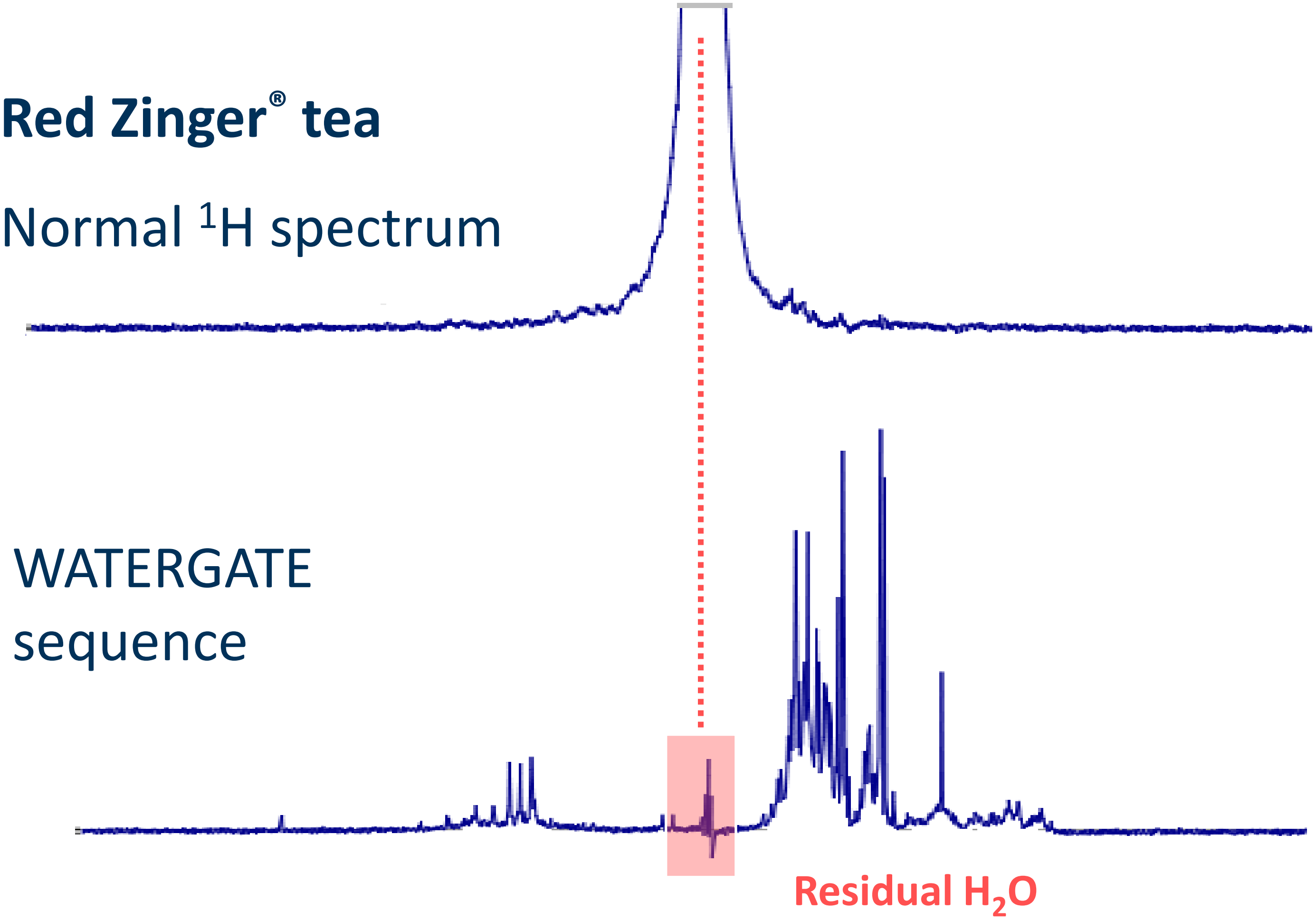
Excitation profile



(Nonsolvent resonances near the solvent are also attenuated)

Experiment name in Delta: wgh.jxp (Delta V5), wgh.ex2 (Delta V4)

Watergate of herbal tea



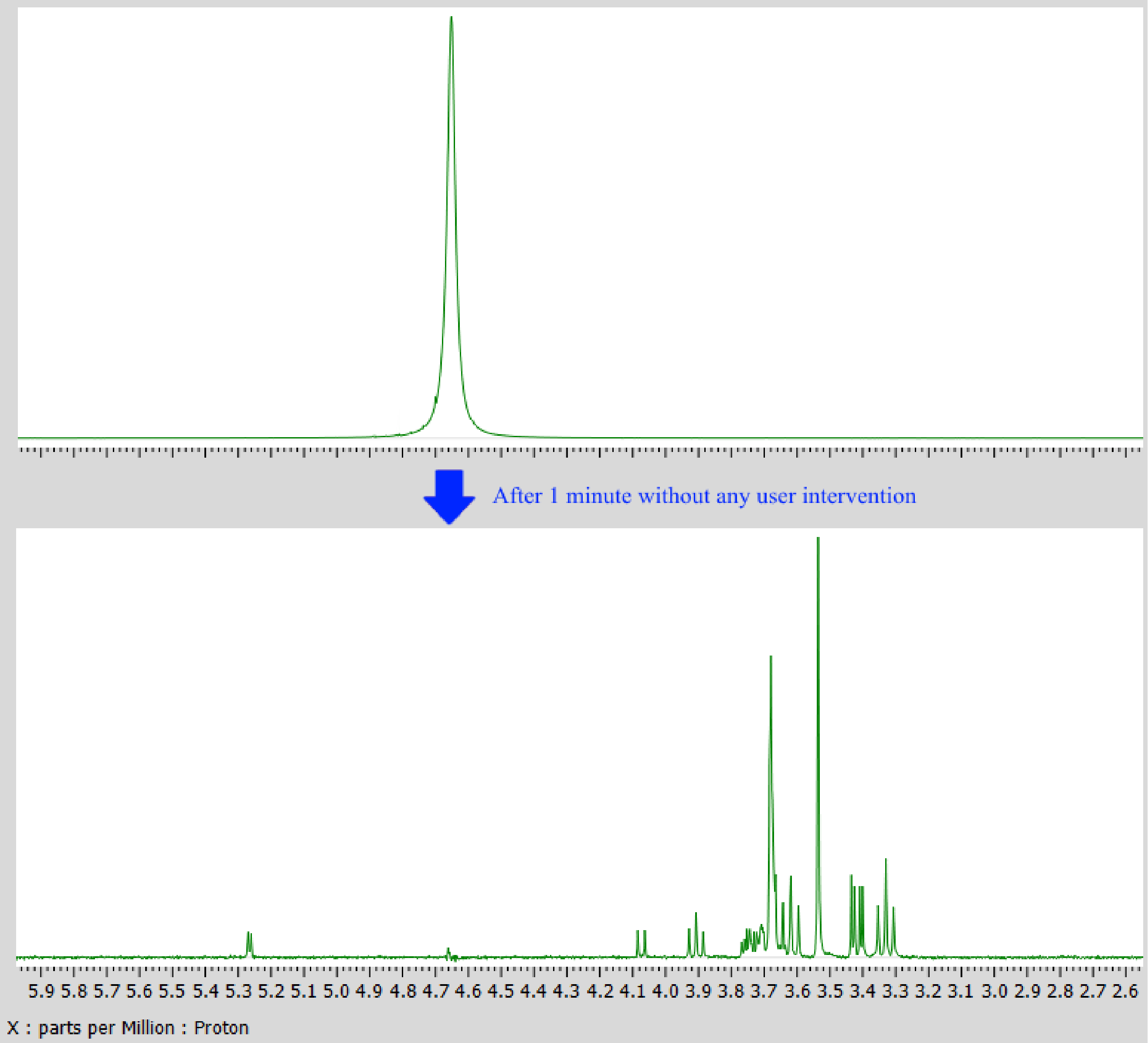
Red Zinger® tea

Normal ^1H spectrum

WATERGATE sequence

Residual H_2O

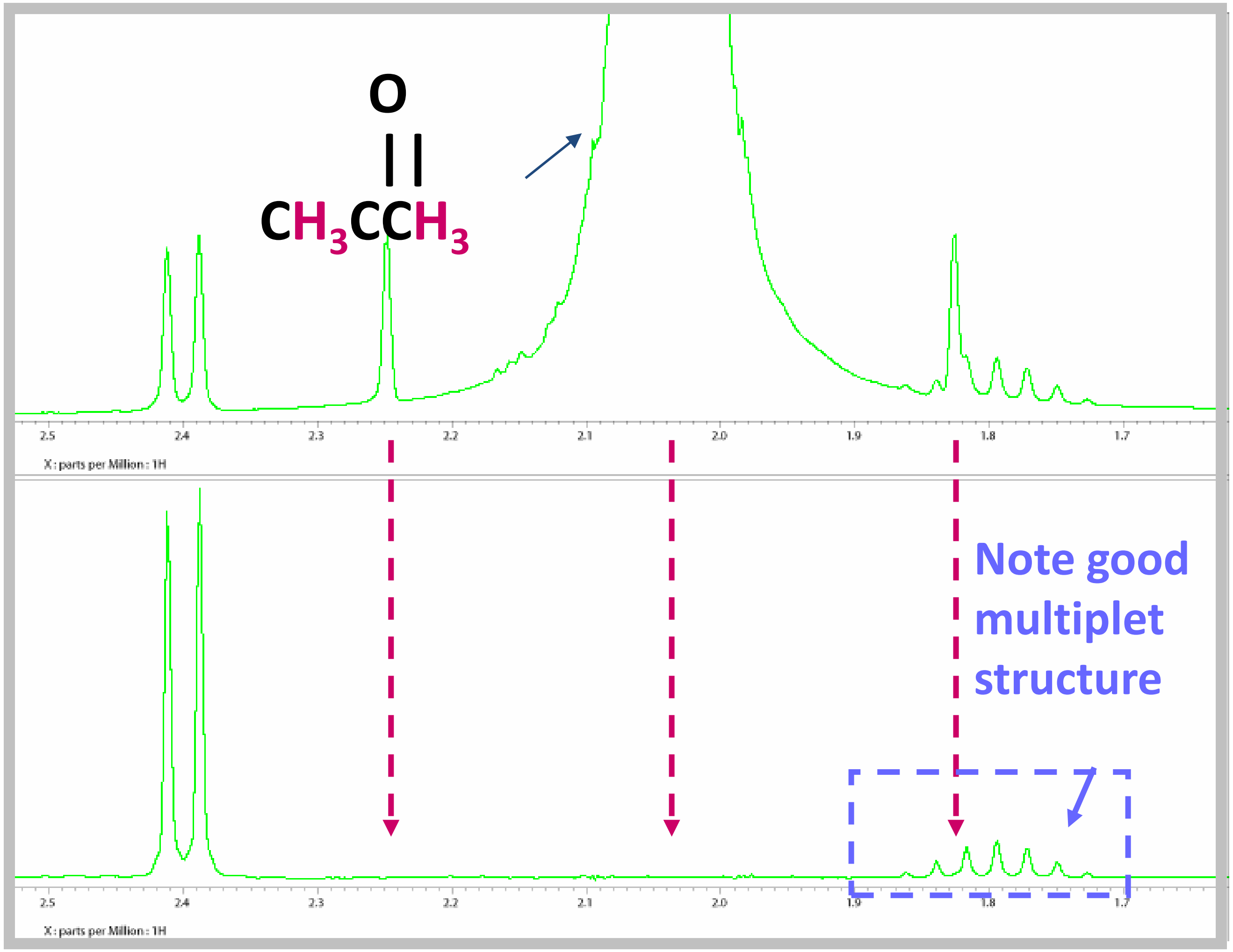
Robust5 method for solvent suppression



2mM sucrose sample
90% H_2O /
10% D_2O

Experiment based on perfect spin echo with 180 pulses replaced by Watergate blocks

Wet result (use noD script)



Note good multiplet structure

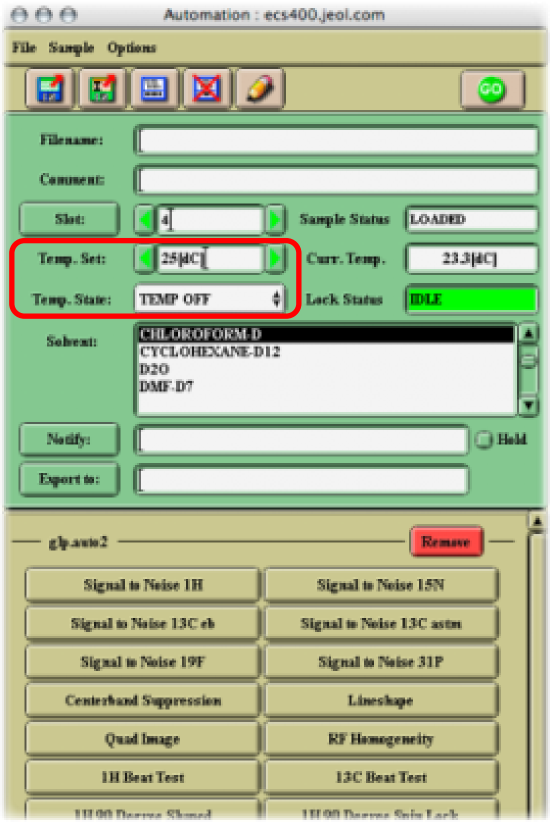
Experiment name in Delta: single_pulse_wet_slp.jxp (Delta V5), single_pulse_wet_slp.ex2 (Delta V4)

VT

VT in automation

- Delta can be configured to set a temperature for each sample:

Delta version 4 series



Automation : ecs400.jeol.com

Slot: 4

Sample Status: LOADED

Temp. Set: 25[dC]

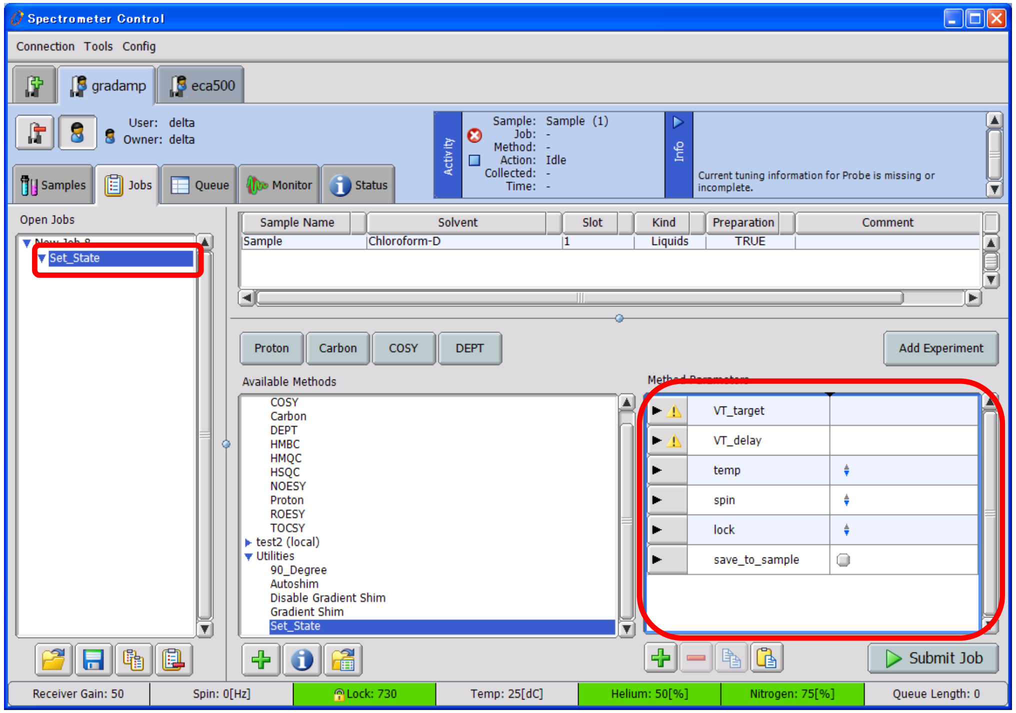
Curr. Temp.: 23.3[dC]

Temp. State: TEMP OFF

Lock Status: IDLE

Solvent: CHLOROFORM-D

Delta version 5 series



Spectrometer Control

User: delta
Owner: delta

Sample: Sample (1)
Job: -
Method: -
Action: Idle
Collected: -
Time: -

Current tuning information for Probe is missing or incomplete.

Sample Name	Solvent	Slot	Kind	Preparation	Comment
Sample	Chloroform-D	1	Liquids	TRUE	

Open Jobs: New Job 8 › Set_State

Method Parameters:

VT_target
VT_delay
temp
spin
lock
save_to_sample ○

Receiver Gain: 50 | Spin: 0[Hz] | Lock: 730 | Temp: 25[dC] | Helium: 50[%] | Nitrogen: 75[%] | Queue Length: 0

Low Temperature

- Delta can maintain a low temperature with FTS system at zero degrees C.
- Remember to change the switch in VT controller panel

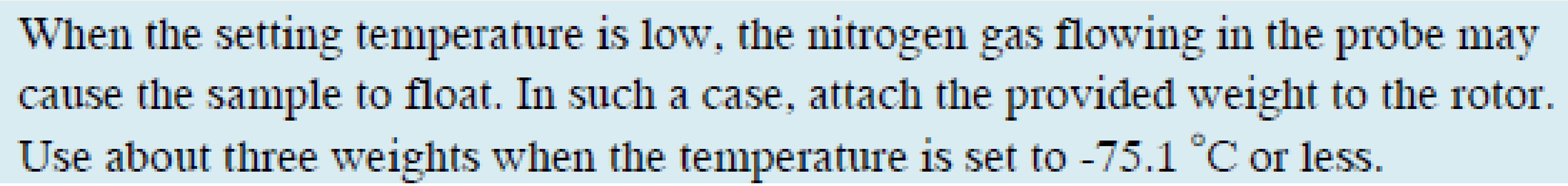
VT Nitrogen Dewar

- The VT dewar ‘trunk’ attaches to the probe heater. The probe heater acts in conjunction with the dewar to provide precise and stable low-temperature control by N_2 boil-off .

VT Dewar Setup

VT Nitrogen dewar usage

- Check Handling of hardware manual



When the setting temperature is low, the nitrogen gas flowing in the probe may cause the sample to float. In such a case, attach the provided weight to the rotor. Use about three weights when the temperature is set to -75.1 °C or less.

If there is trouble ejecting sample
there are two eject air adjustments
at the back of the console.
Eject valve is for when VT is used.
Eject-S is for when no VT is used.

VT runs

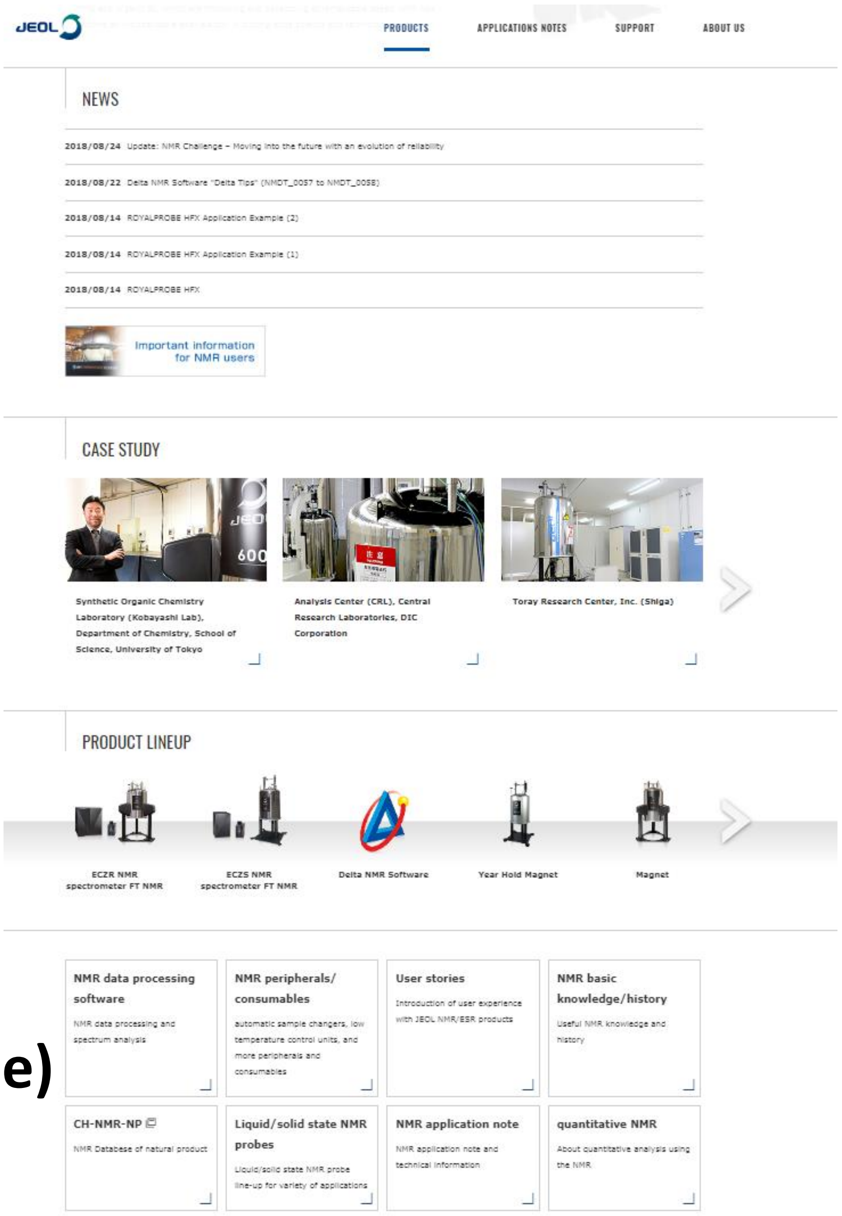
- To run the same sample at a number of different temperatures
  - Note solvent freezing / boiling point
    - eg. CDCl3 (m.p. -63.5C, b.p. +61.2C)
  - Only take VT to within 10-15C of these limits
    - eg. CDCl3 min ca. -50C / max ca. +50C
  - Re-tune sample at ca. 30 degrees C intervals
  - Gradually change temperature to prevent thermal shock of the glass tube or the insert in the probe. I recommend no more than 20C change every 5 min. Array of VT_proton methods allow this

Thank you

You can discover more at

- http://www.jeol.co.jp/en/ **(Products -> NMR)**
  - Description of our products
  - Free processing software
  - Free natural products database
  - Application notes
  - Events
  - And more

- http://nmrsupport.jeol.com/ **(license)**



NEWS

2018/08/24 Update: NMR Challenge – Moving into the future with an evolution of reliability

2018/08/22 Delta NMR Software "Delta Tips" (NMDT_0057 to NMDT_0058)

2018/08/14 ROYALPROBE HFX Application Example (2)

2018/08/14 ROYALPROBE HFX Application Example (1)

2018/08/14 ROYALPROBE HFX

Important information for NMR users

CASE STUDY

Synthetic Organic Chemistry Laboratory (Kobayashi Lab), Department of Chemistry, School of Science, University of Tokyo

Analysis Center (CRL), Central Research Laboratories, DIC Corporation

Toray Research Center, Inc. (Shiga)

PRODUCT LINEUP

ECZR NMR spectrometer FT NMR

ECZS NMR spectrometer FT NMR

Delta NMR Software

Year Hold Magnet

Magnet

NMR data processing software
NMR data processing and spectrum analysis

NMR peripherals/consumables
automatic sample changers, low temperature control units, and more peripherals and consumables

User stories
Introduction of user experience with JEOL NMR/ESR products

NMR basic knowledge/history
Useful NMR knowledge and history

CH-NMR-NP
NMR Database of natural product

Liquid/solid state NMR probes
Liquid/solid state NMR probe line-up for variety of applications

NMR application note
NMR application note and technical information

quantitative NMR
About quantitative analysis using the NMR