Pure shift NMR spectroscopy
Tips and tricks

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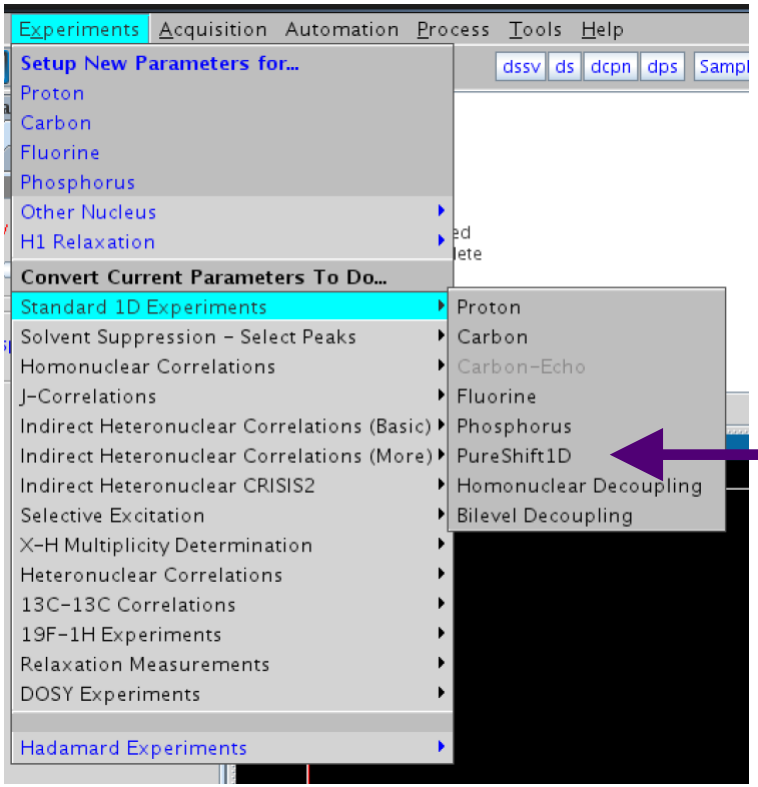
IVAN NMR Users Group Workshop

Online, 14th Jun 2021

Collect a pure shift spectrum with the absolute minimum effort

VnmrJ 4.2 has a basic pure shift experiment included



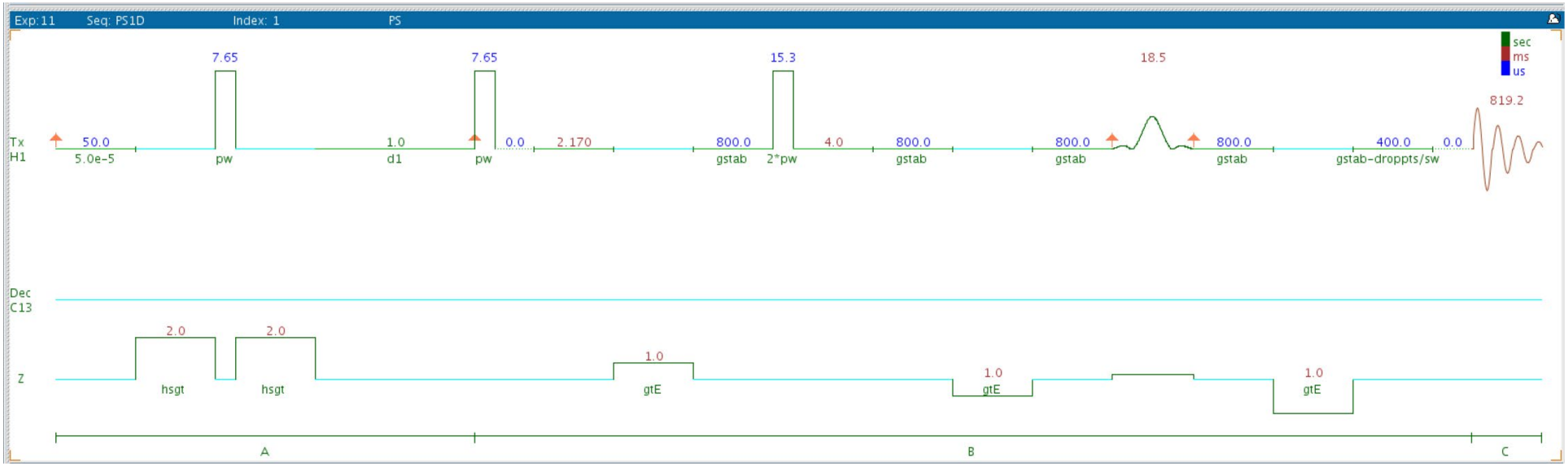
Collect a standard ^{1}H NMR spectrum then select *PureShift1D* from the *Experiments* list

Collect a pure shift spectrum with the absolute minimum effort

VNMRJ 4.2 default experiment uses Zangger Sterk element for active spin refocusing

100 Hz (18.5 ms) Rsnob

Experiment Time: 7 m 45 s



Collect a pure shift spectrum with the absolute minimum effort

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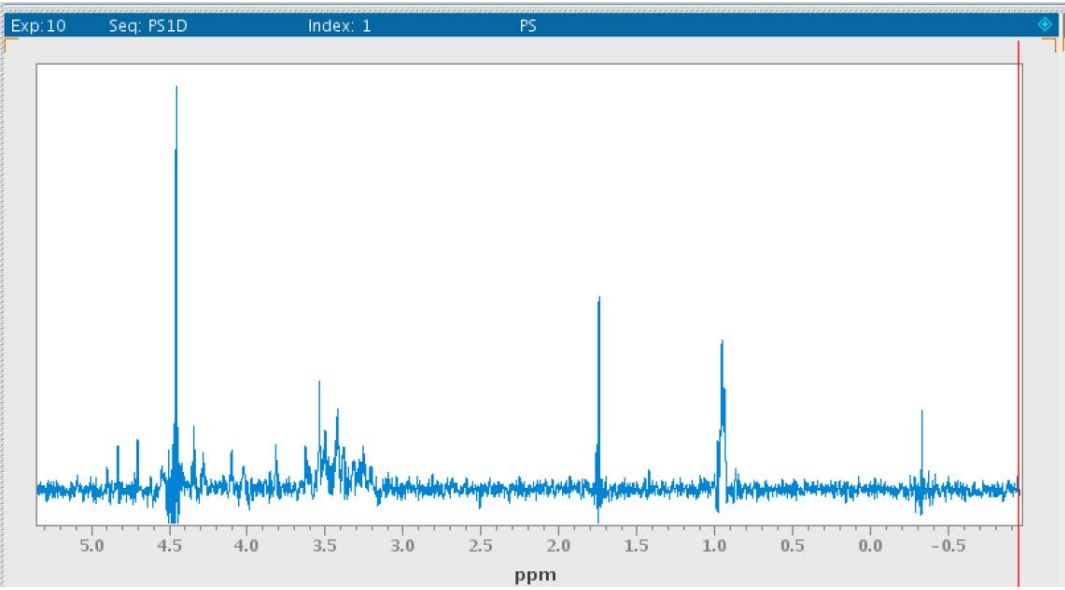
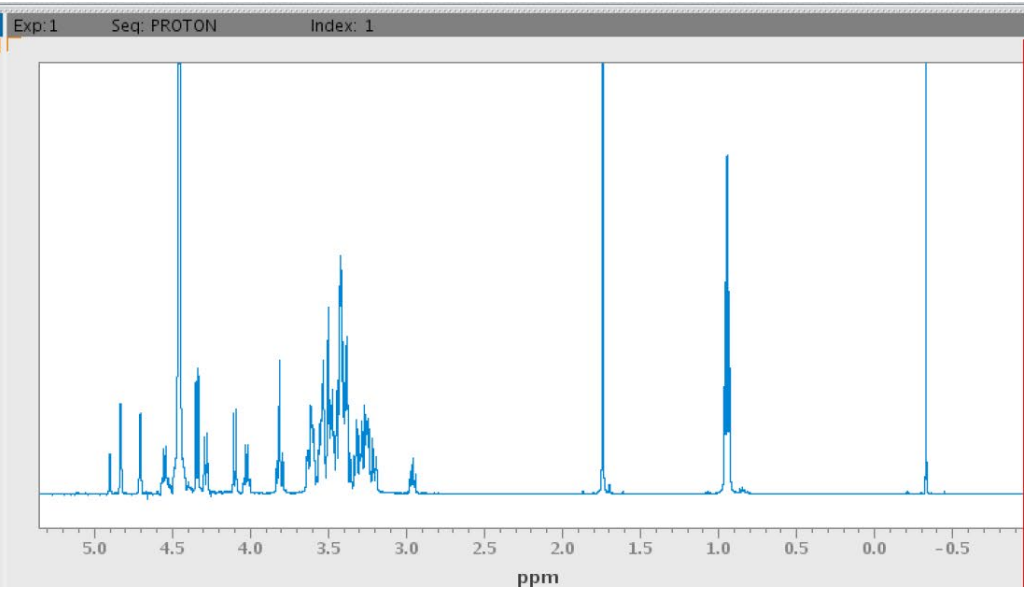
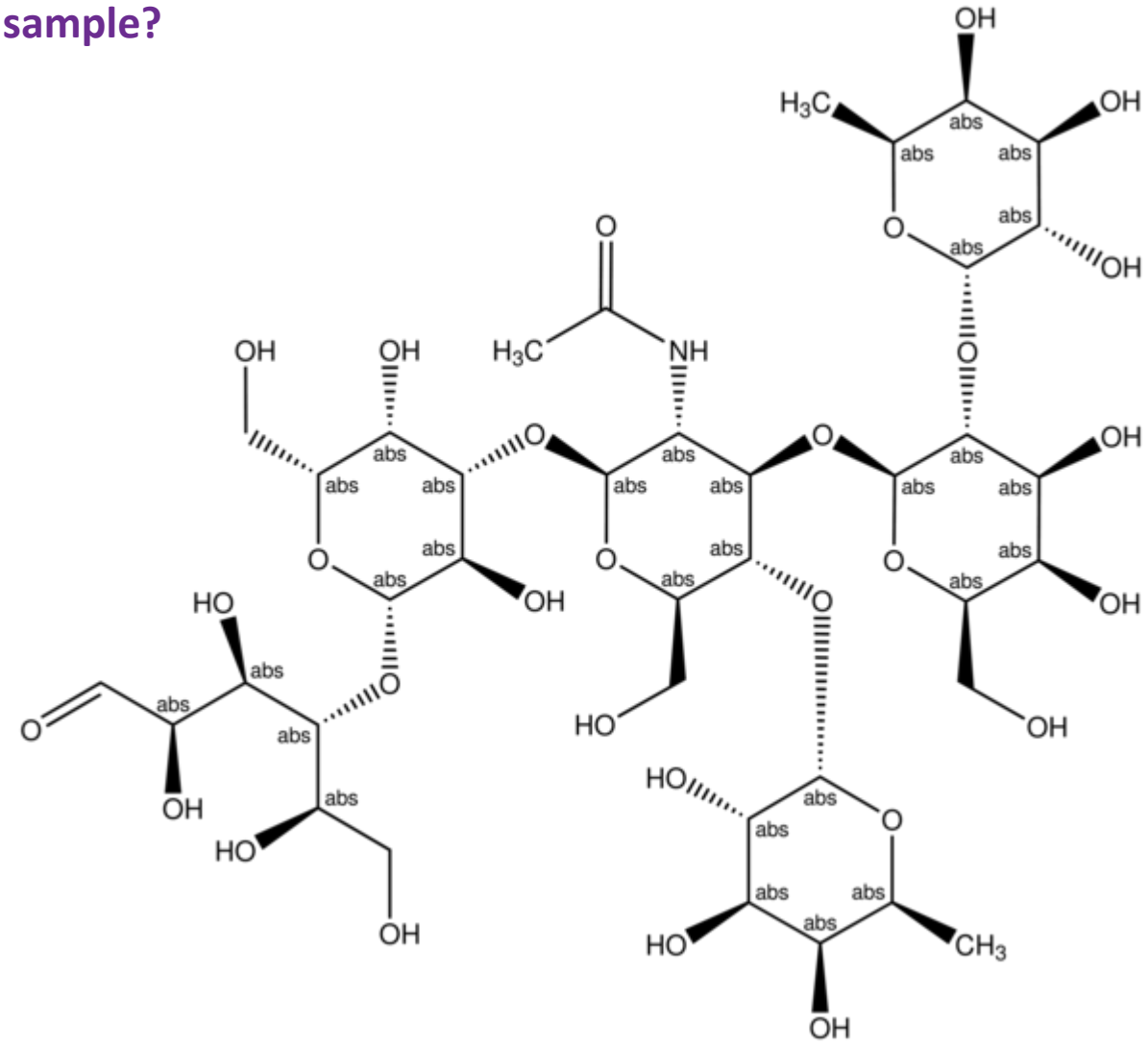




A simple sample?



Lacto-N-difucohexanose I
25 mM
D_2O

Use: Highest concentration possible
Highest sensitivity instrument available
Most appropriate pure shift method for the sample

University of Manchester Pure Shift Experiments

https://nmr.chemistry.manchester.ac.uk/pureshift

Workshop on pure shift NMR

Copies of slides for the talks given at the *Workshop on pure shift NMR*, Manchester, 12th Sept 2017 can be accessed via this link.

A data archive containing pure shift pulse sequences, processing software and sample experimental data is available for download via this link.

Workshop on pure shift NMR - downloads

Data Archives, including instructions, sequences, parameter files and example data.

Bruker
Software only (< 1 Mb): Pure_shift_archive_Bruker_software_only.zip (updated: Jan 2018).
Full (262 Mb): Pure_shift_archive_Bruker.zip (updated: Jan 2018).
Bruker PSYCHE manual: Bruker_PSYCHE_PS_manual.pdf.

N.B. Topspin is not yet fully compatible with the floating point data acquisition used in Neo consoles, so in some versions of Topspin is may be necessary to convert interferogram pure shift data to integer form (e.g. with the Bruker AU programme sertoint.ptg) before processing with UoM_proc_1d_2d_if or pshift.

Varian
Software only(< 1 Mb): Pure_shift_archive_Varian_software_only.zip.
Full (26 Mb): Pure_shift_archive_Varian.zip.
Manual: UoM_PureShiftNMR_Varian_Manual_rev1.pdf.

Varian only for Inova
Software only(< 1 Mb): Pure_shift_archive_Varian_Inova_software_only.zip.
Full (6 Mb): Pure_shift_archive_Varian_Inova.zip.
Manual: UoM_PureShiftNMR_Varian_Manual_rev1_Inova.pdf.

2 Installation instructions

Download the Varian package from the Manchester NMR Methodology Group's website (http://nmr.chemistry.manchester.ac.uk/pureshift).

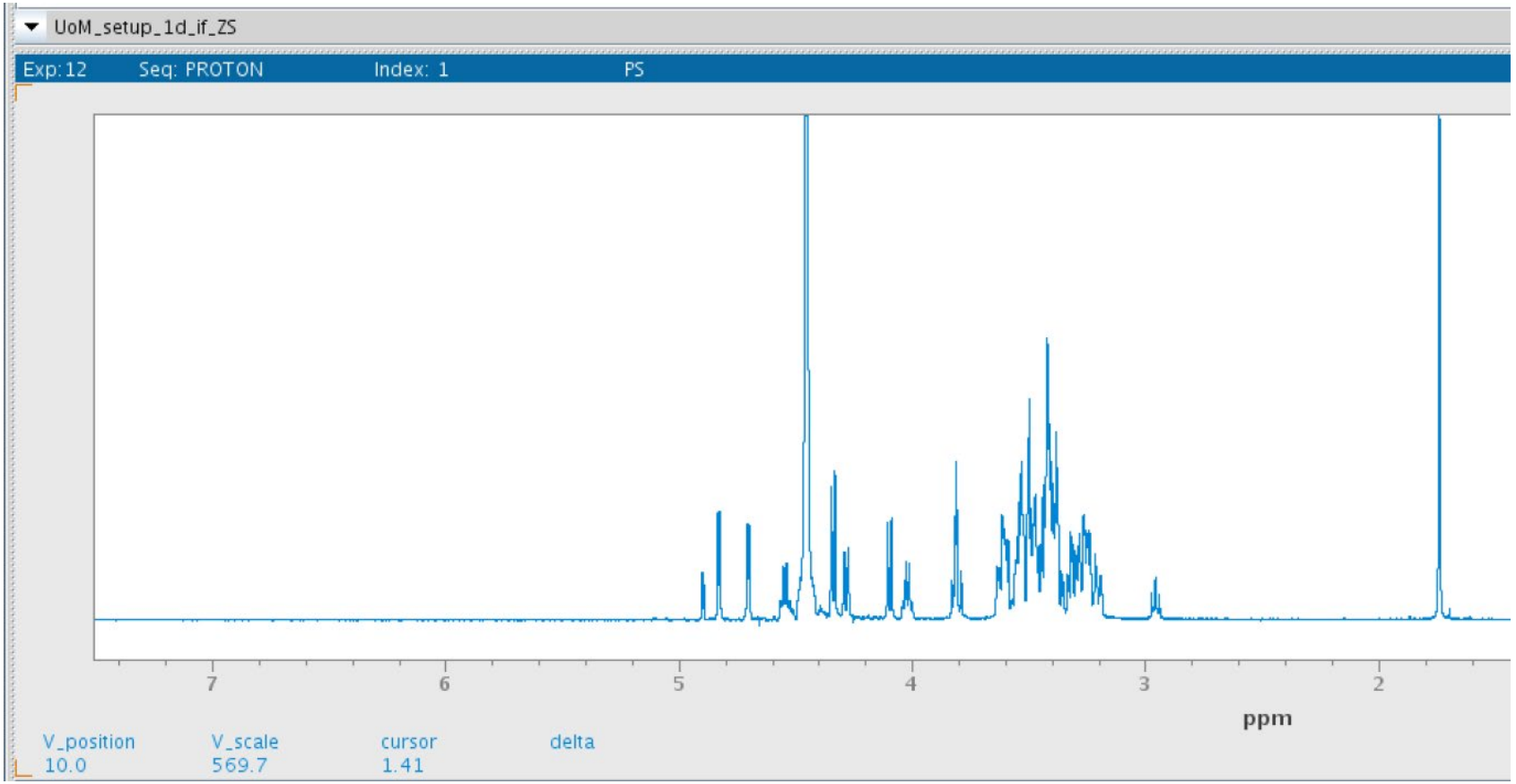
- Un-compress the archive
- Copy the contents of /psglib and /maclib to your pulse sequence (e.g. local user installation: /home/vnmr1/vnmrsys/psglib [vnmr1=linux user name]) and macro (e.g. /home/vnmr1/vnmrsys/maclib) directories.
  e.g. cp –p –r [path of downloaded package]/psglib /home/vnmr1/vnmrsys/psglib/.
- Copy the /wavelib/kp_WURST40 to /home/vnmr1/vnmrsys/wavelib/decoupling/
- Copy the /wavelib/kp2_wurst180 to /home/vnmr1/vnmrsys/wavelib/inversion/
- Copy the /wavelib/psyche to /home/vnmr1/vnmrsys/wavelib/inversion/
- Compile the new pulse sequences using seqgen

Setup and Processing Macros

1D interferogram experiments	**Pulse sequence filename**	**Setup macro (from ^{1}H)**	**Processing macro**
BS (band-selective)	UoM_1d_if_PS.c	UoM_setup_1d_if_BS	UoM_proc_1d_if
Zangger-Sterk		UoM_setup_1d_if_ZS	
PSYCHE (**P**ure **S**hift **Y**ielded by **CH**irp **E**xcitation)		UoM_setup_1d_if_PSYCHE	
TSE-PSYCHE (**T**riple **S**pin **E**cho **P**ure **S**hift **Y**ielded by **CH**irp **E**xcitation)	UoM_1d_if_TSEPSYCHE.c	UoM_setup_1d_if_TSEPSYCHE	
BIRD (**BI**linear **R**otation **D**ecoupling)	UoM_1d_if_BIRD.c	UoM_setup_1d_if_BIRD	
real-time experiments			
1D BS	UoM_1d_rt_PS.c	UoM_setup_1d_rt_BS	UoM_proc_1d_rt
1D Zangger-Sterk		UoM_setup_1d_rt_ZS	
1D BIRD	UoM_2d_rt_PS_HSQC.c	UoM_setup_1d_rt_BIRD	UoM_proc_2d_rt
2D HSQC		UoM_setup_2d_rt_BIRD_HSQC	

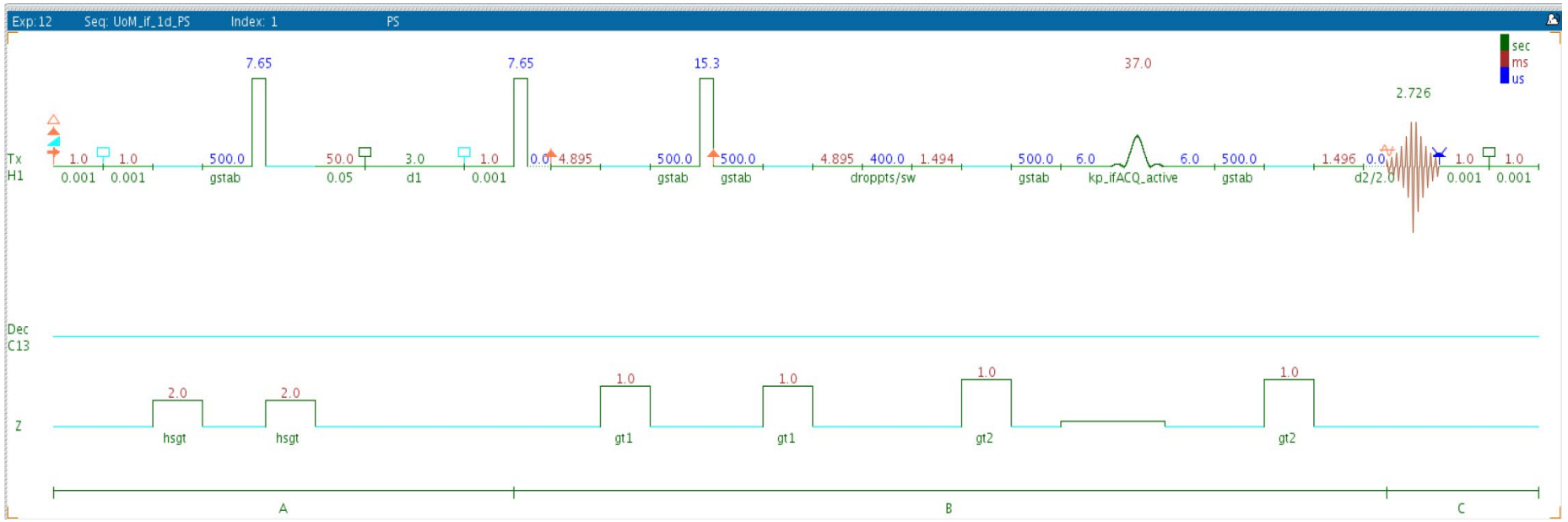
Setting up a Pure Shift Experiment

1. Acquire conventional ^{1}H spectrum
2. Run Setup macro: UoM_setup_1d_if_ZS



Setting up a Pure Shift Experiment

1. Acquire 1H spectrum
2. Run Setup macro: UoM_setup_1d_if_ZS



Zangger Sterk
37 ms
50 Hz Rsnob

Time: 4 m 40 s

Processing a Pure Shift Experiment

Setup and Processing Macros

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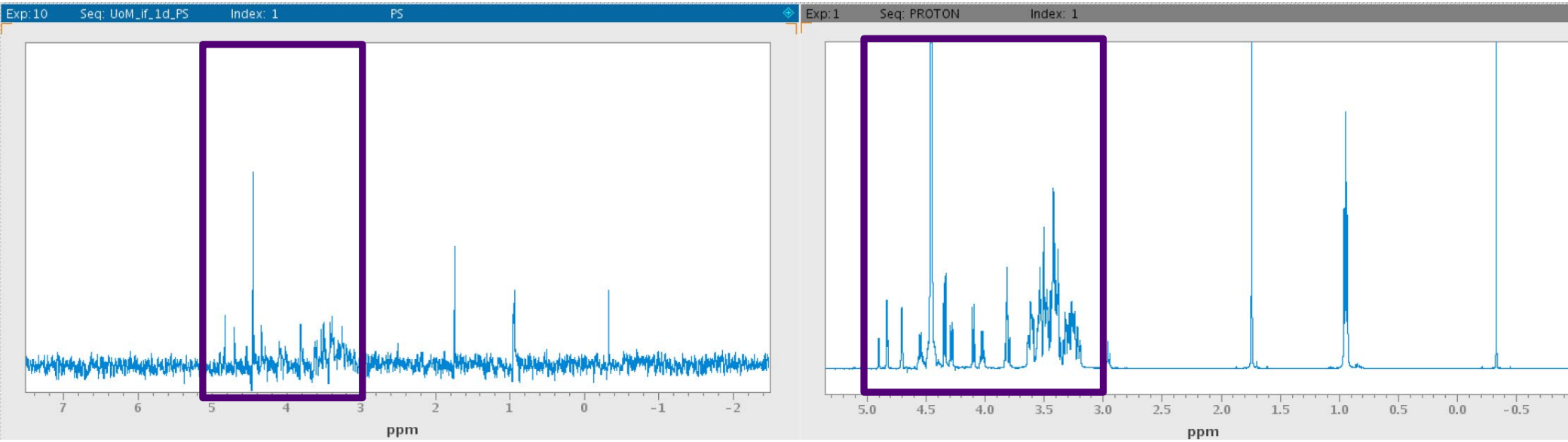
Zangger-Sterk		UoM_setup_1d_if_ZS	
PSYCHE (**P**ure **S**hift **Y**ielded by **CH**irp **E**xcitation)		UoM_setup_1d_if_PSYCHE	
TSE-PSYCHE (**T**riple **S**pin **E**cho **P**ure **S**hift **Y**ielded by **CH**irp **E**xcitation)	UoM_1d_if_TSEPSYCHE.c	UoM_setup_1d_if_TSEPSYCHE	
BIRD (**BI**linear **R**otation **D**ecoupling)	UoM_1d_if_BIRD.c	UoM_setup_1d_if_BIRD	
real-time experiments			
1D BS	UoM_1d_rt_PS.c	UoM_setup_1d_rt_BS	UoM_proc_1d_rt
1D Zangger-Sterk		UoM_setup_1d_rt_ZS	
1D BIRD	UoM_2d_rt_PS_HSQC.c	UoM_setup_1d_rt_BIRD	UoM_proc_2d_rt
2D HSQC		UoM_setup_2d_rt_BIRD_HSQC	

Optimising ZS Pure Shift Experiments



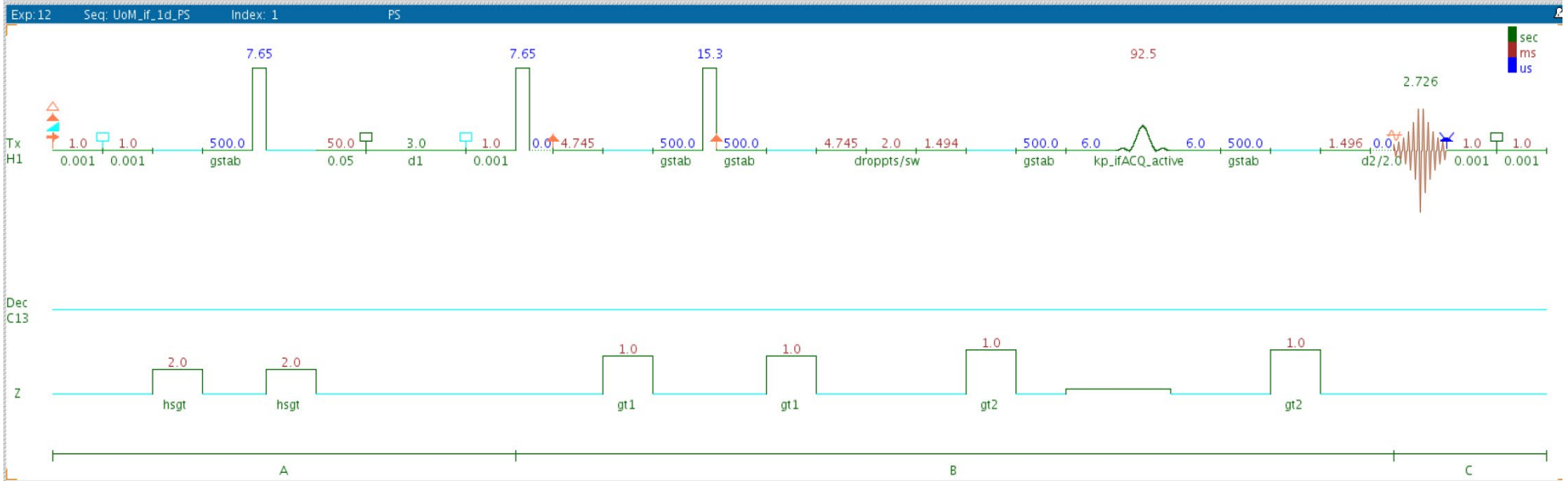
Sensitivity of Zangger-Sterk pure shift experiments depends on the spectral width. Select the region where overlap occurs.

Optimising ZS Pure Shift Experiments

dps error
sw1 must be an integer submultiple of sw

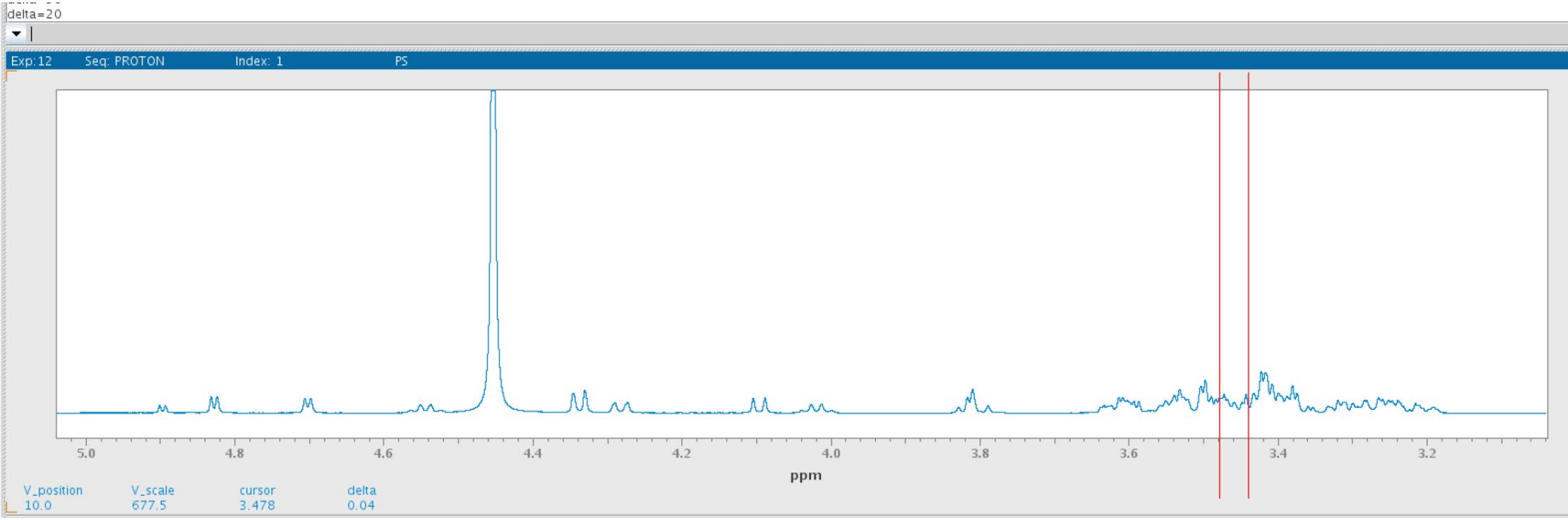
```
UoM_setup_1d_if_ZS
 Calibration based on ref_pw90 =  7.65, ref_pwr = 58
 dps error: run '/home/vnmr1/vnmrsys/seqlib/UoM_if_1d_PS' pulse sequence failed.
 sw1 must be an integer submultiple of sw..
sw1? sw?
  sw1 = 39.0625
  sw = 1000
sw1=40
dps
r1=1/sw1 r1?
  r1 = 0.025
bw_a=20 go('check') dps
 Calibration based on ref_pw90 =  7.65, ref_pwr = 58
 go check complete
```

Set *sw1* between 40 and 50 Hz
Check that *sw/sw1* is an integer



Optimising ZS Pure Shift Experiments

Set *sw* to ^{1}H spectrum of region of interest (1 kHz?)
Set *bw_a* to frequency difference of closest coupled signals (20 Hz?)

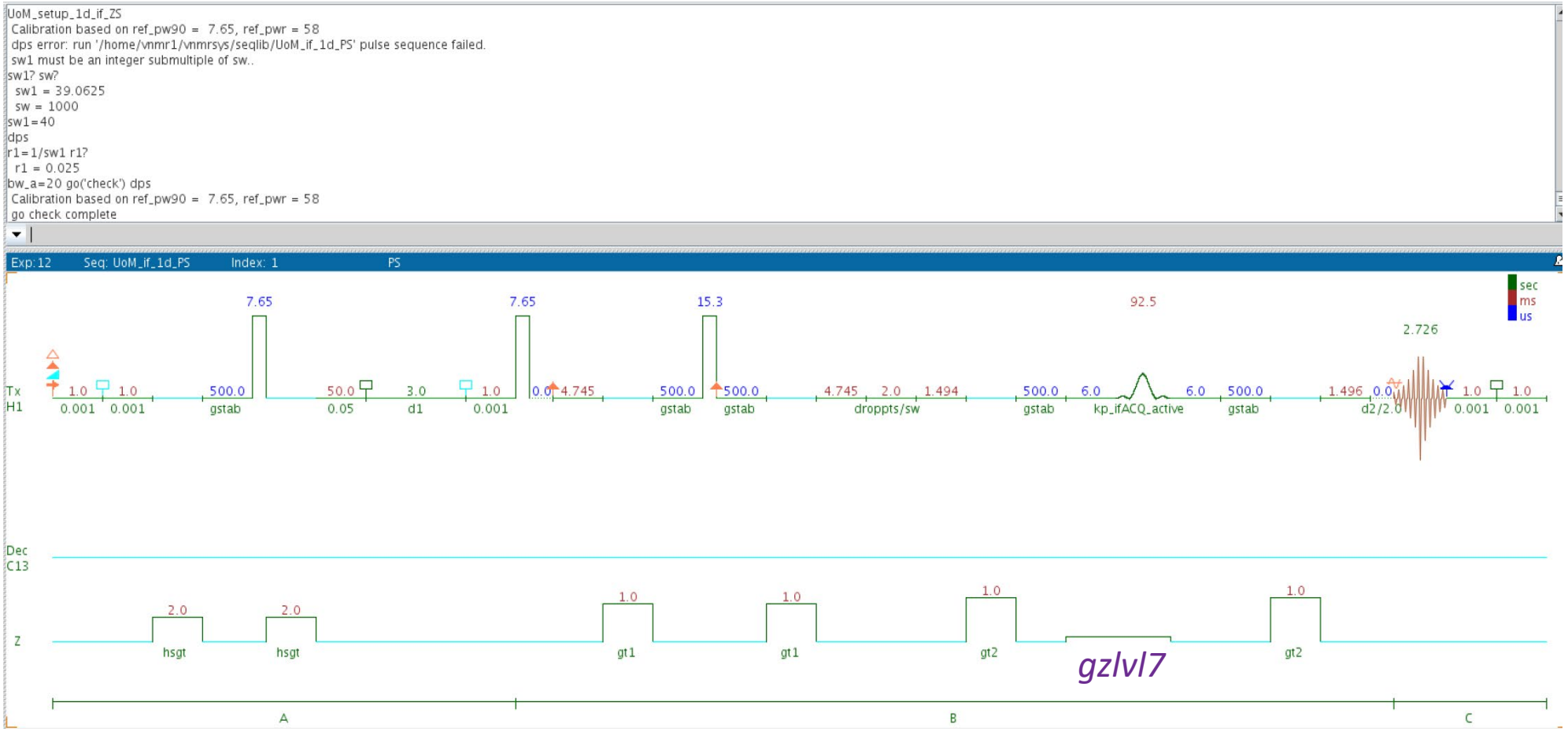


Pulse selectivity is determined by the spectrum

Optimising ZS Pure Shift Experiments

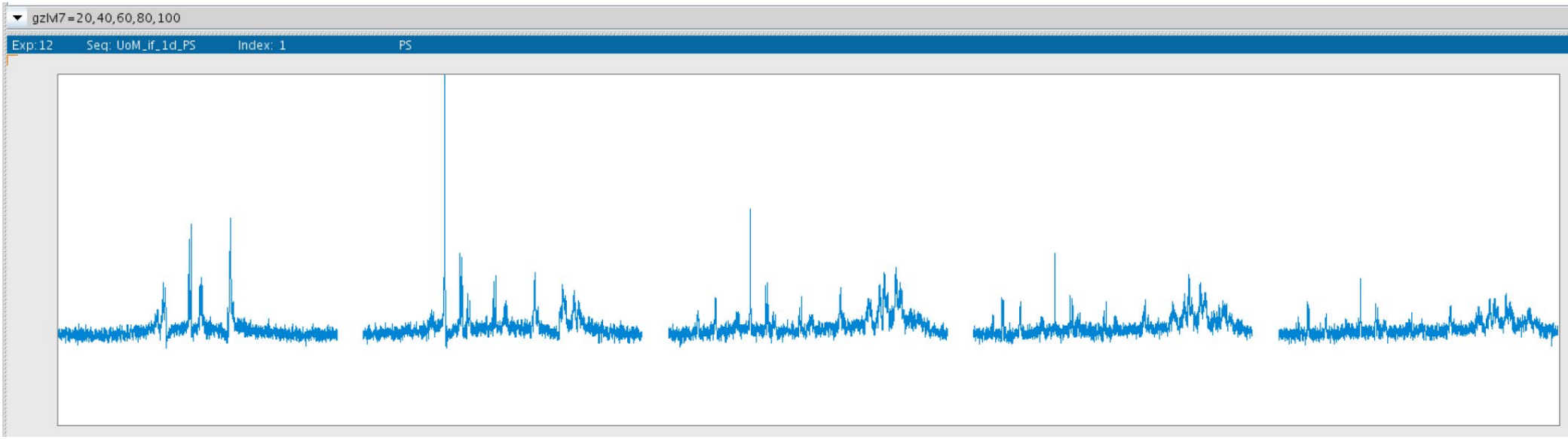
Pulse selectivity is determined by the spectrum

Sensitivity depends on the field gradient during the selective pulse



Optimising ZS Pure Shift Experiments

Array *gzlvl7*
could calculate, but better to calibrate

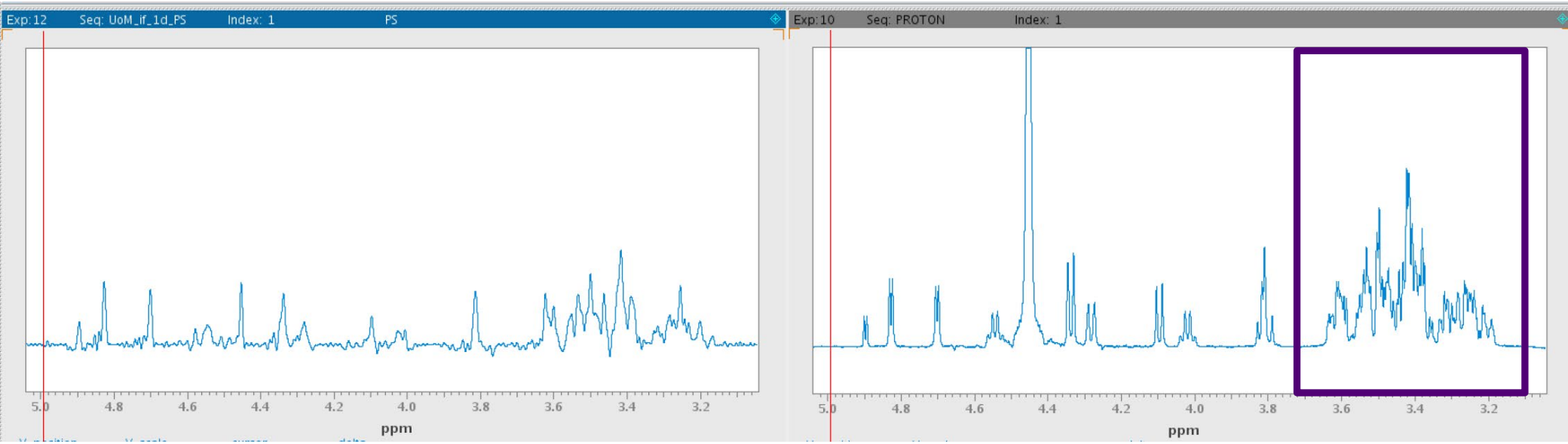


gzlvl7 too low
Not all signals refocused

gzlvl7 too high
Signal intensity drops

Optimum? ZS Pure Shift Experiment

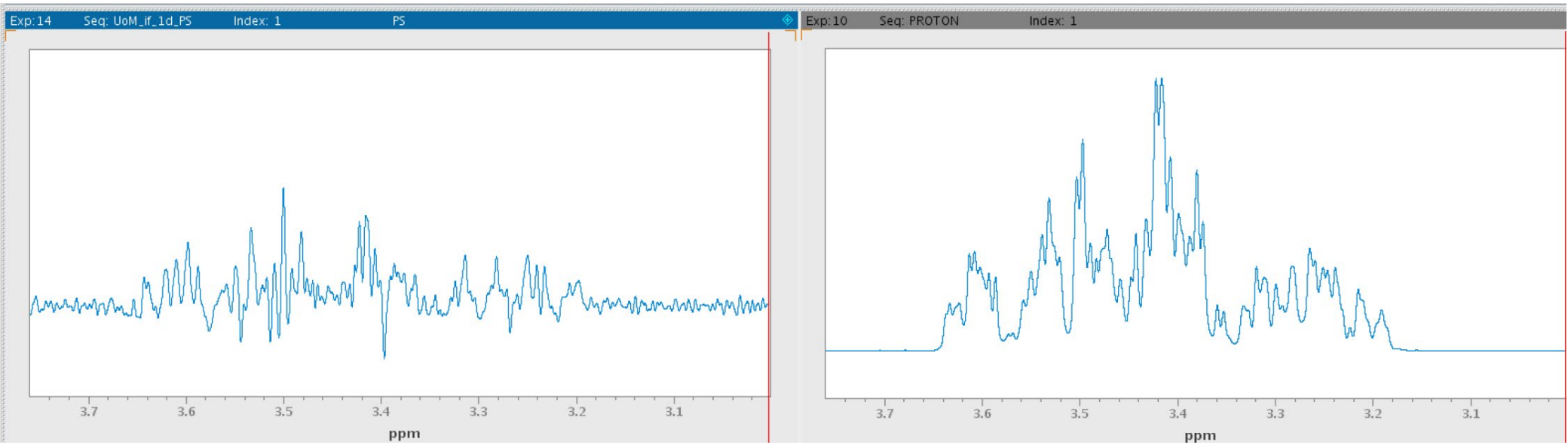
Set ni to 16
Increase nt to improve SNR
Acquire
Process



Try narrower region
Try lower bandwidth pulse (10 Hz)
200 ms duration so T_2 becomes a significant factor

What next

Pulse bandwidth *bw_a*: 10 Hz
Field Gradient *gzlvl7*: 25
Increase nt to improve SNR



Most signals resolved
Some distortion due to strong coupling or <10 Hz separation of coupled signals
Switch to 2D PSYCHE TOCSY or 2D BIRD HSQC

Macros

https://nmr.chemistry.manchester.ac.uk/pureshift

1D interferogram experiments	Pulse sequence filename	Setup macro (from ^{1}H)	Processing macro	Ref.
BS (band-selective)	UoM_1d_if_PS.c	UoM_setup_1d_if_BS	UoM_proc_1d_if	1
Zangger-Sterk		UoM_setup_1d_if_ZS		2
PSYCHE (**P**ure **S**hift **Y**ielded by **CH**irp **E**xcitation)		UoM_setup_1d_if_PSYCHE		3
TSE-PSYCHE (**T**riple **S**pin **E**cho **P**ure **S**hift **Y**ielded by **CH**irp **E**xcitation)	UoM_1d_if_TSEPSYCHE.c	UoM_setup_1d_if_TSEPSYCHE		4
BIRD (**BI**linear **R**otation **D**ecoupling)	UoM_1d_if_BIRD.c	UoM_setup_1d_if_BIRD		5
real-time experiments				
1D BS	UoM_1d_rt_PS.c	UoM_setup_1d_rt_BS	UoM_proc_1d_rt	2c,6
1D Zangger-Sterk		UoM_setup_1d_rt_ZS		7
1D BIRD	UoM_2d_rt_PS_HSQC.c	UoM_setup_1d_rt_BIRD	UoM_proc_2d_rt	8
2D HSQC		UoM_setup_2d_rt_BIRD_HSQC		9

Questions?

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