Avance I Solid State NMR

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Applications
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Outline

DAY 1

- Introduction
- Basic setup procedures
- Productivity tools

DAY 2

- Setup Cross Polarization Experiments
- CP Pulse programs, include and protection files

DAY 3

- Various basic CP experiments
- Relaxation experiments with CP
- Other spin 1/2 X - nuclei than ^{13}C

DAY 4

- Quadrupolar nuclei, solidsecho and mqmas
- Advanced NMR experiments

Introduction

NMR: Tool for structural analysis

NMR in liquids:

- Tools for structure determination:
  - Chemical Shift (CS) for distinction of electronic environment.
  - J coupling for identification of spin system - creation of coherence
  - NOE for distance constraints (dipole dipole interaction)
  - Weakly aligned systems (direct dipole - interaction)

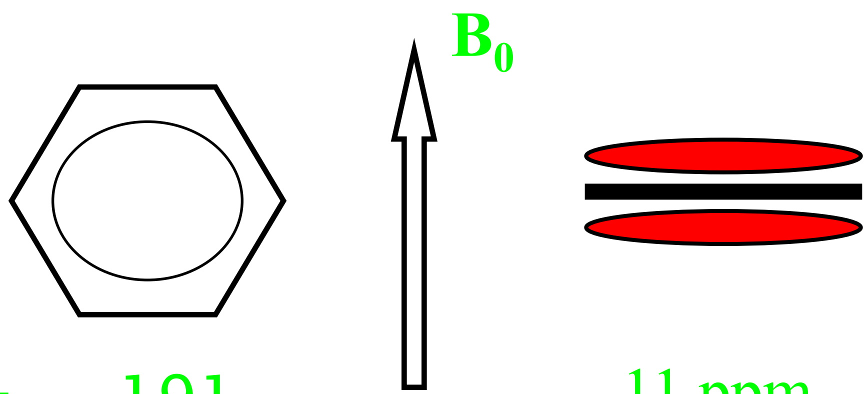
NMR in Solids

- All interactions are present full structural information available
  - Dipole Dipole interaction (DD)
  - Chemical Shift Anisotropy (CSA) and isotropic Chemical Shift (CS)
  - Quadrupole interaction (Q) for spin >1/2
  - J-interaction (very weak)

- Problem: Entanglement of the information

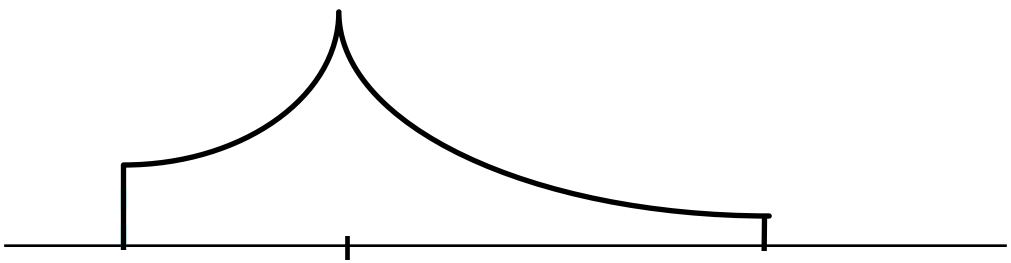
- Solution: Average as many interactions as possible by tayloring the interaction Hamiltonian through:
  - Sample rotation at the magic angle: Magic Angle Spinning (MAS)
  - Heteronuclear decoupling schemes: continuous wave (cw) or time proportional phase modulation (TPPM) technique, etc
  - Combination of heteronuclear decoupling and sample rotation
  - ...etc...

Chemical Shift Anisotropy CSA

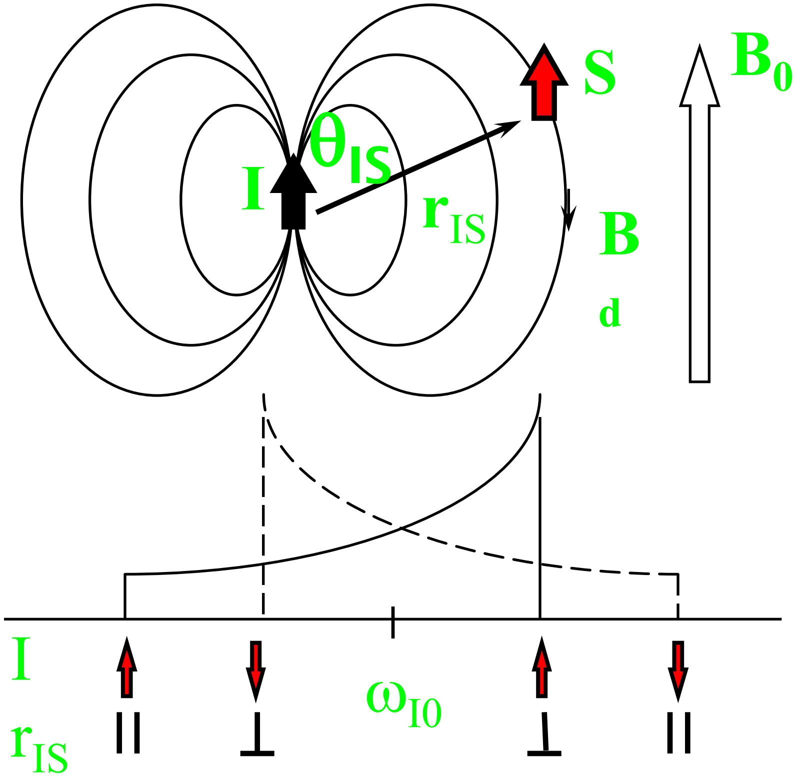


^{13}C chemical shift: σ_{xx} =191 ppm 11 ppm

Powder pattern: three principal components σ_{xx}, σ_{yy}, σ_{zz}.



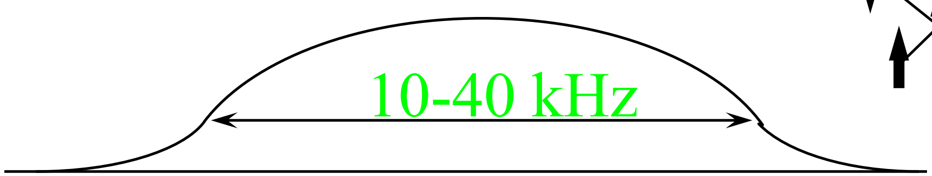
Dipole Dipole Interaction DD

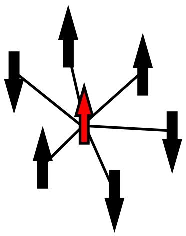


Local field B_{loc} at spin S: Vector sum of Zeeman field B_0 and dipolar field B_d generated by spin I.

$$D_{IS} \approx \frac{\gamma_I \gamma_S}{r_{IS}^3}\left(3\cos^2(\theta_{IS}) - 1\right)$$

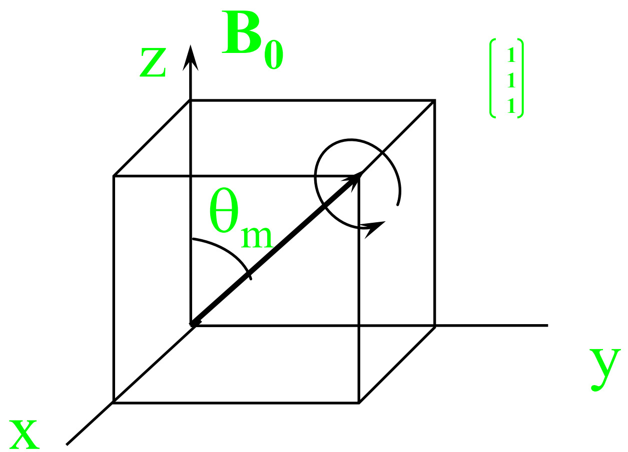
Single Spin pair: Pake doublet

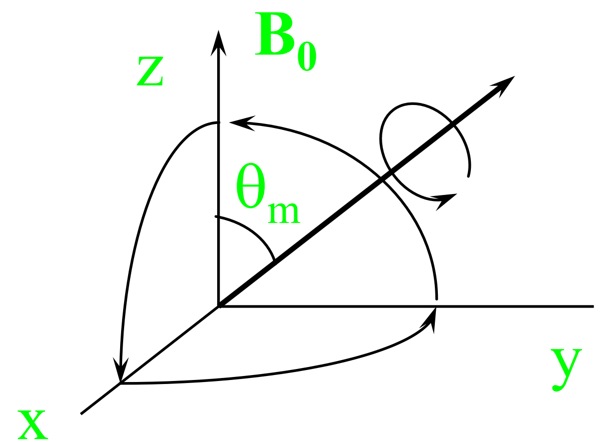


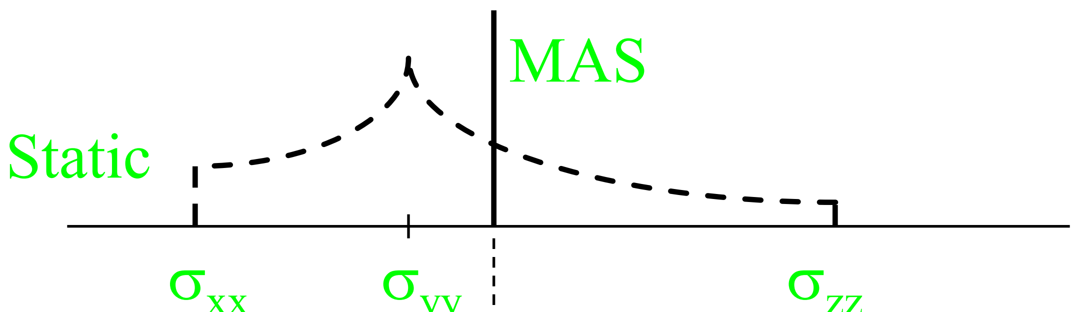


Multiple spin couplings: broad featureless hump.

Magic Angle Spinning

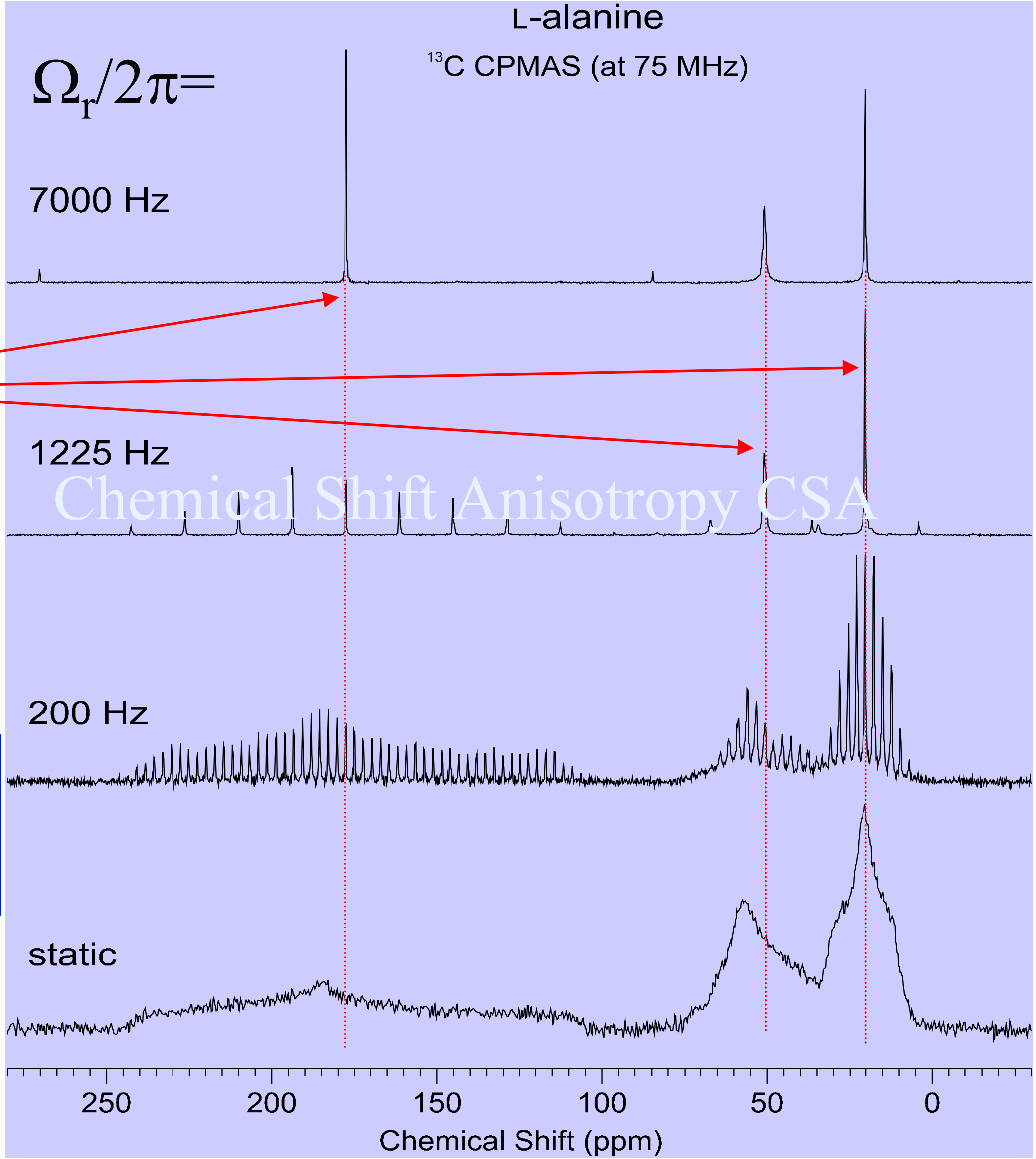






$$\sigma_{iso} = 1/3(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$$

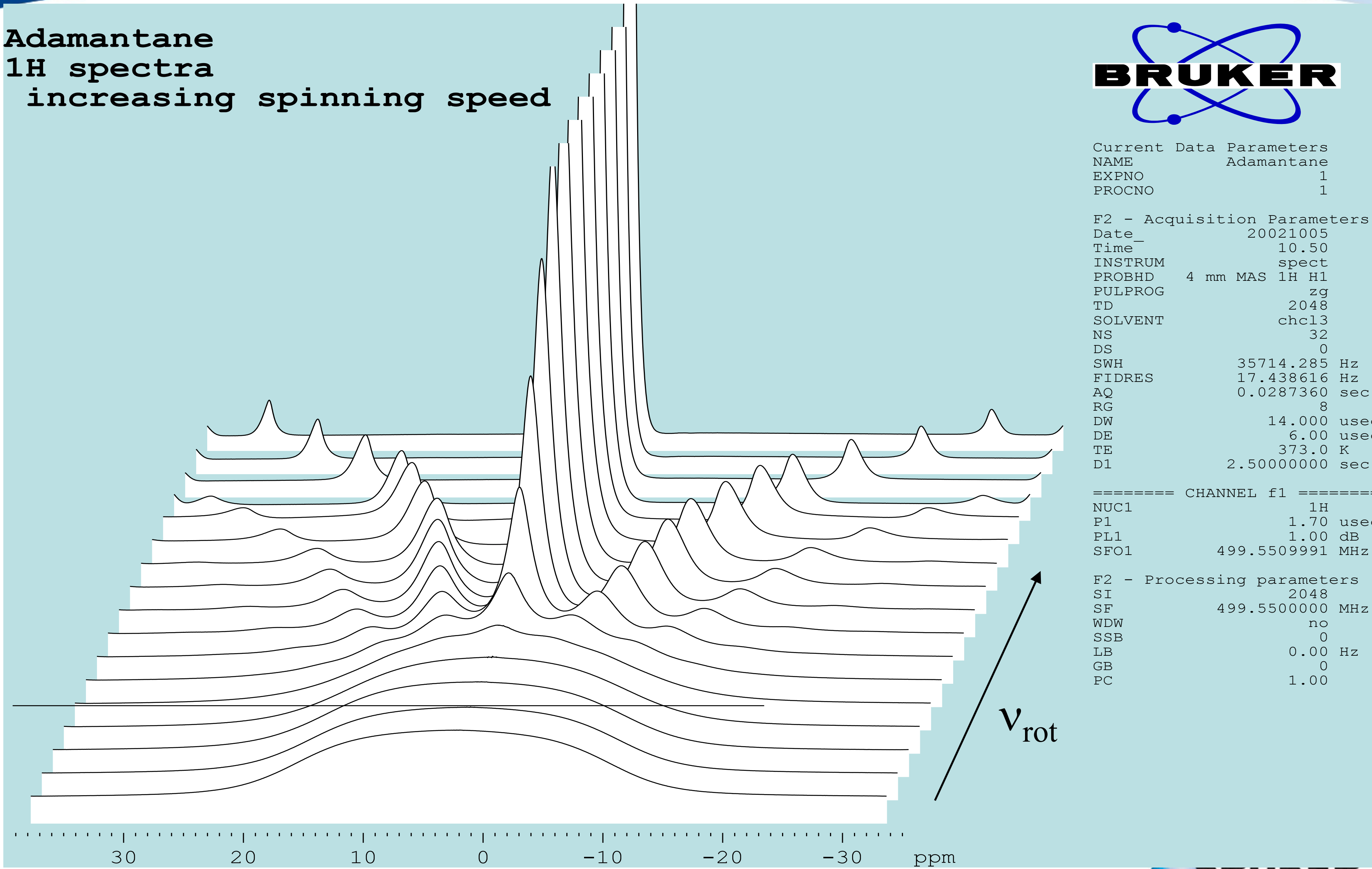
Averaging CSA powder pattern



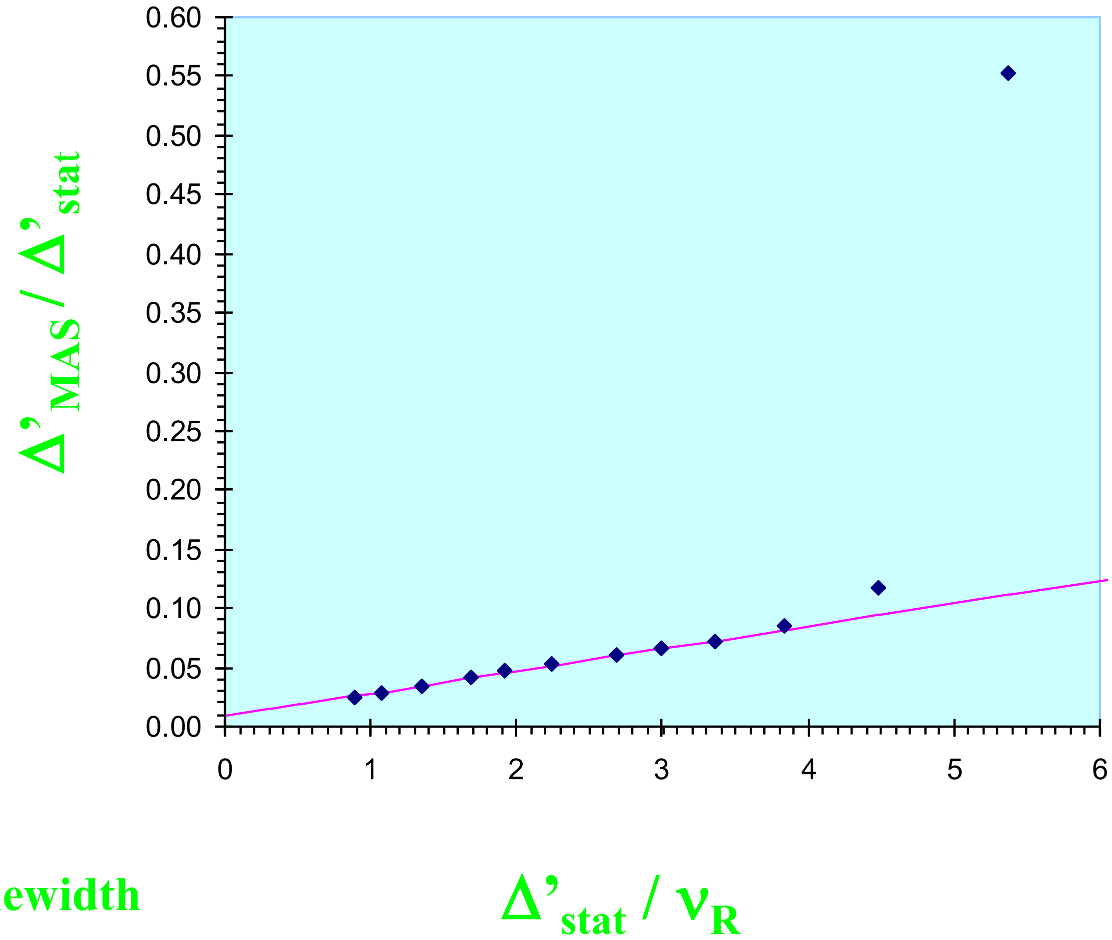
Note! CS position Not necessarily at extremum of CSA powder pattern

$\sigma_{iso} = (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})/3$

Averaging DD powder pattern



Averaging DD interactions



Δ'_{stat} static linewidth

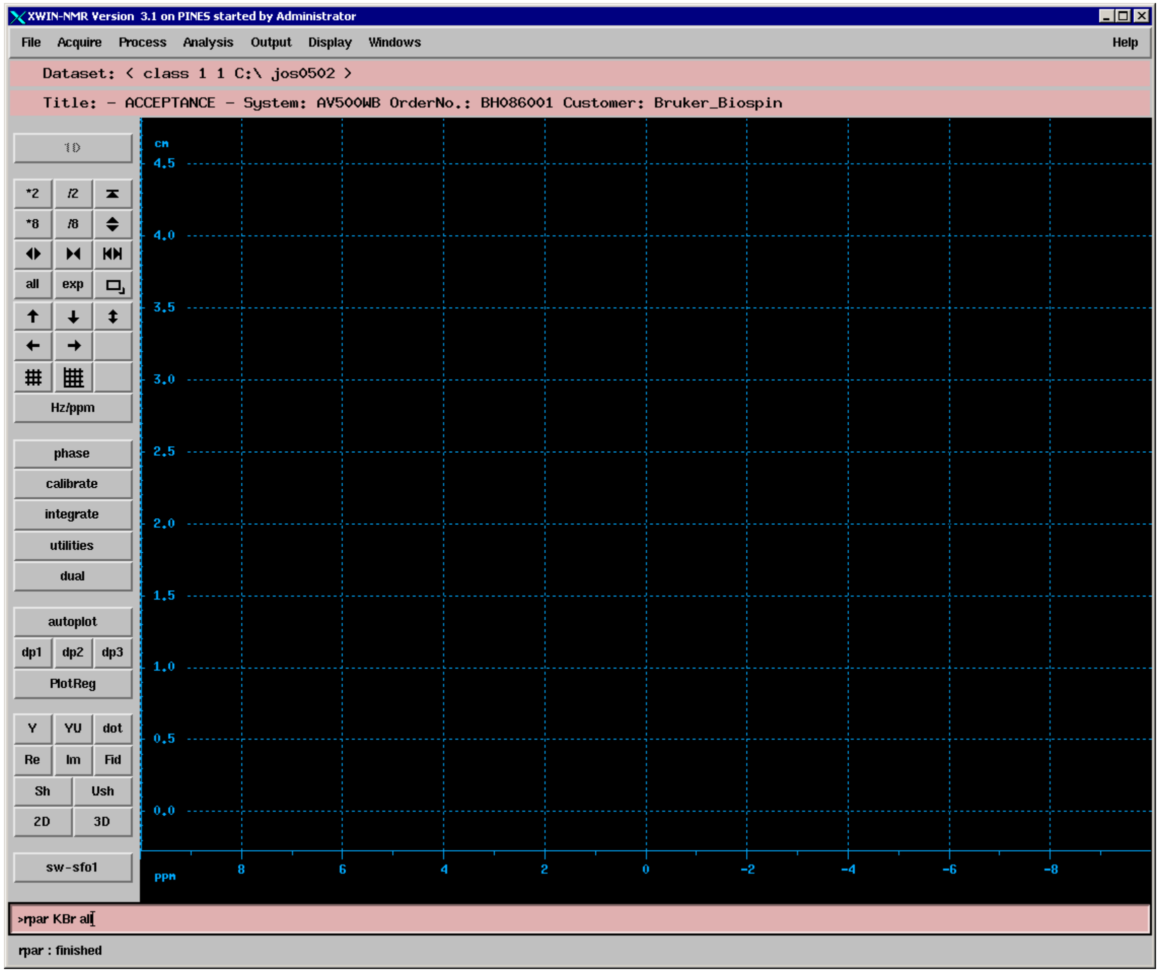
Δ'_{MAS} linewidth at ν_R

ν_R Spinning speed

← Increasing spinning speed

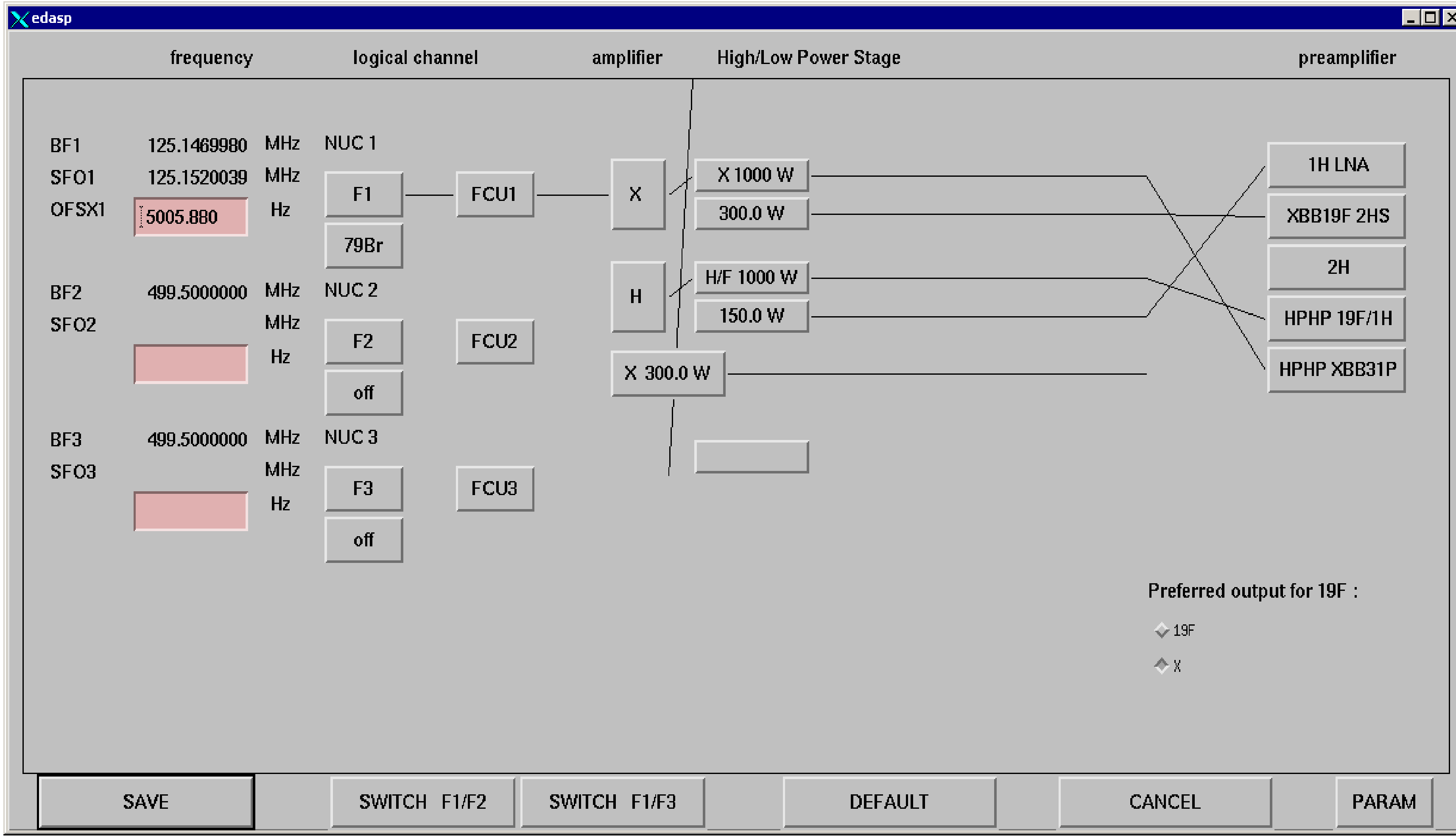
Magic Angle Setup

- Use KBr sample,
- Call parameter set KBr by typing rpar KBr



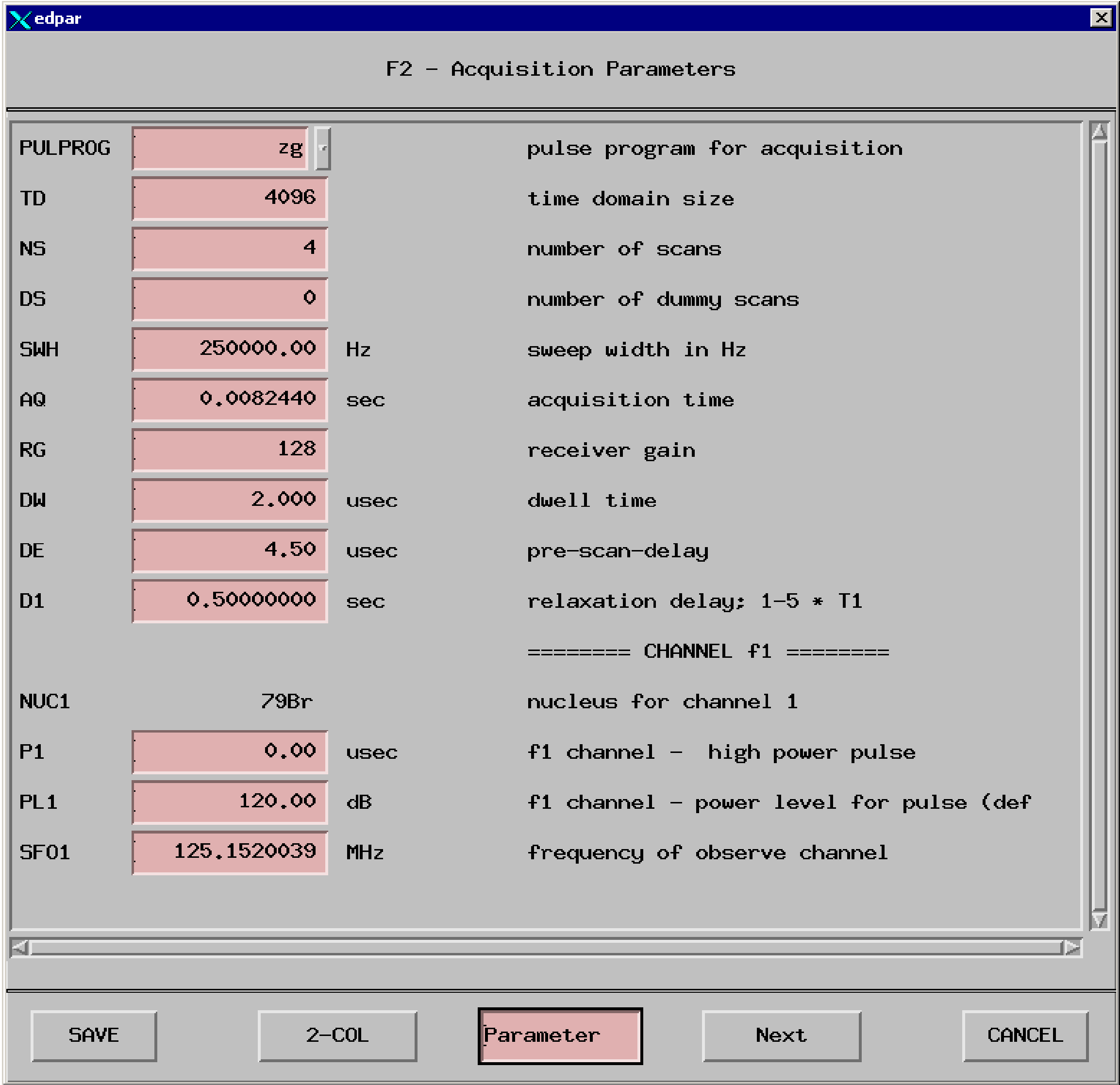
Magic Angle Setup

Check or set routing using edasp:



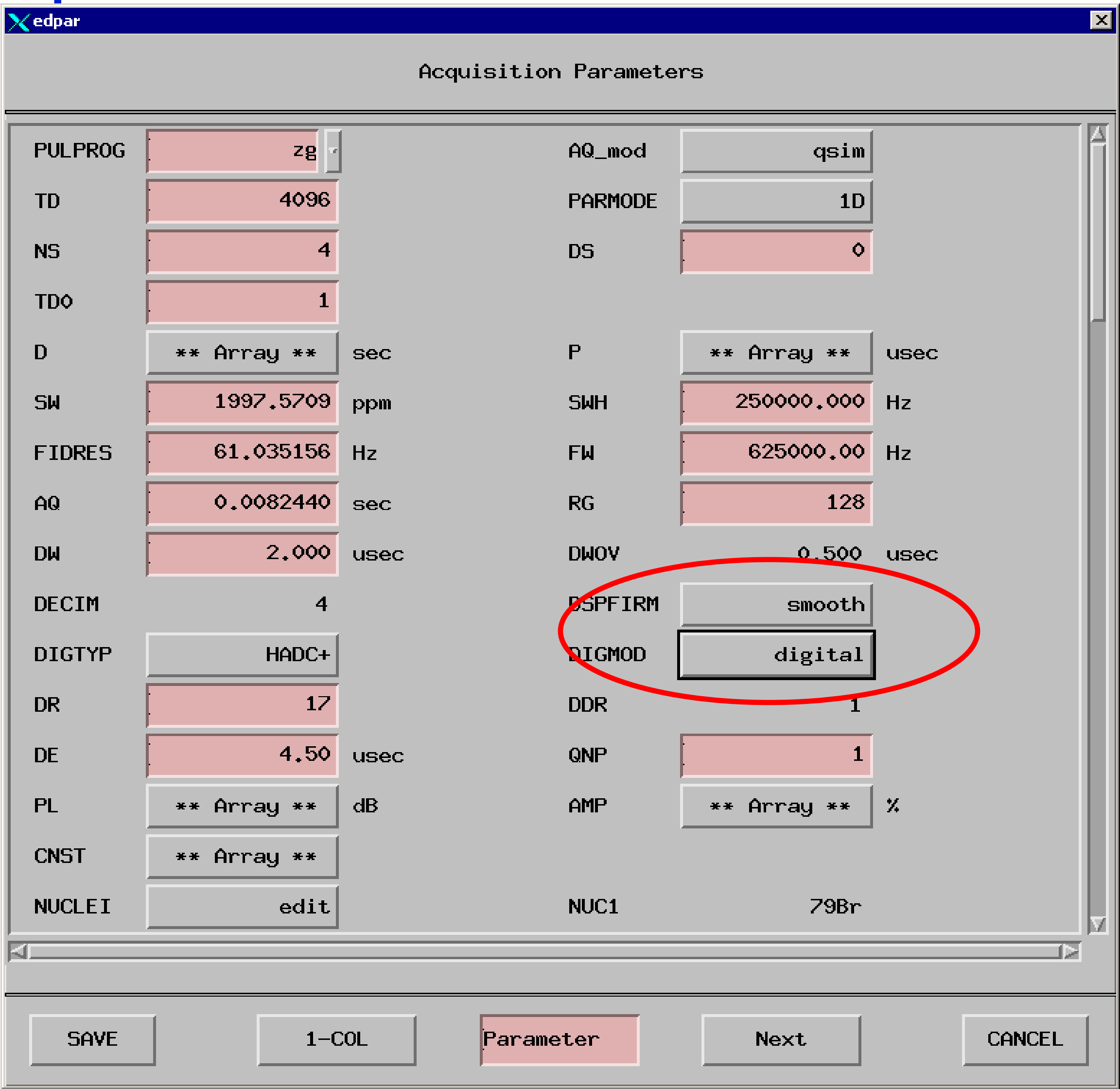
Magic Angle Setup

- Check parameters in the ased:



Magic Angle Setup

- Check parameters in the eda:

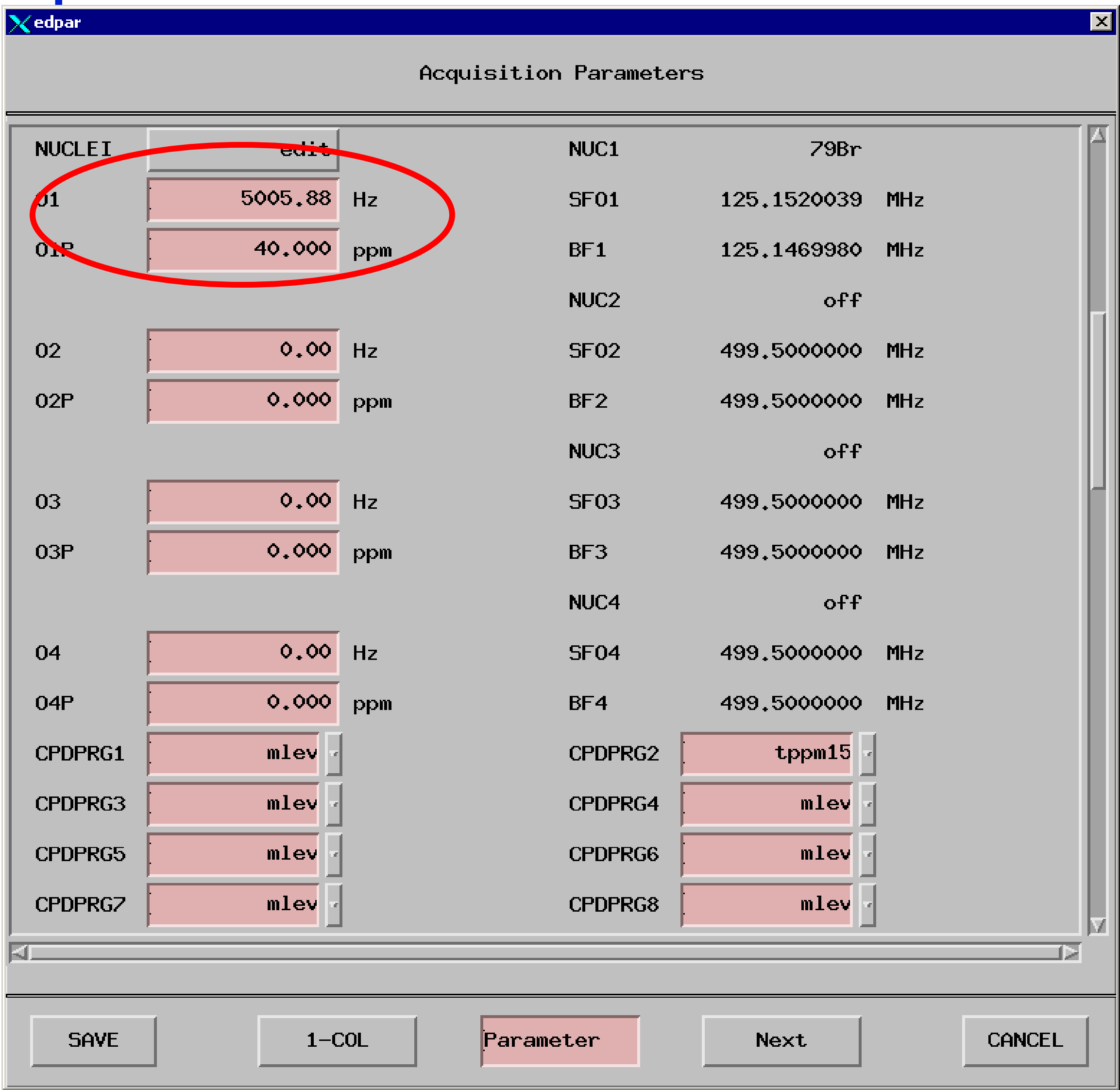


Magic Angle Setup

- Alternative choice of parameters:
- Check parameters in the eda:
  - Use: DIGMOD = analog and
    SW = 100000 Hz

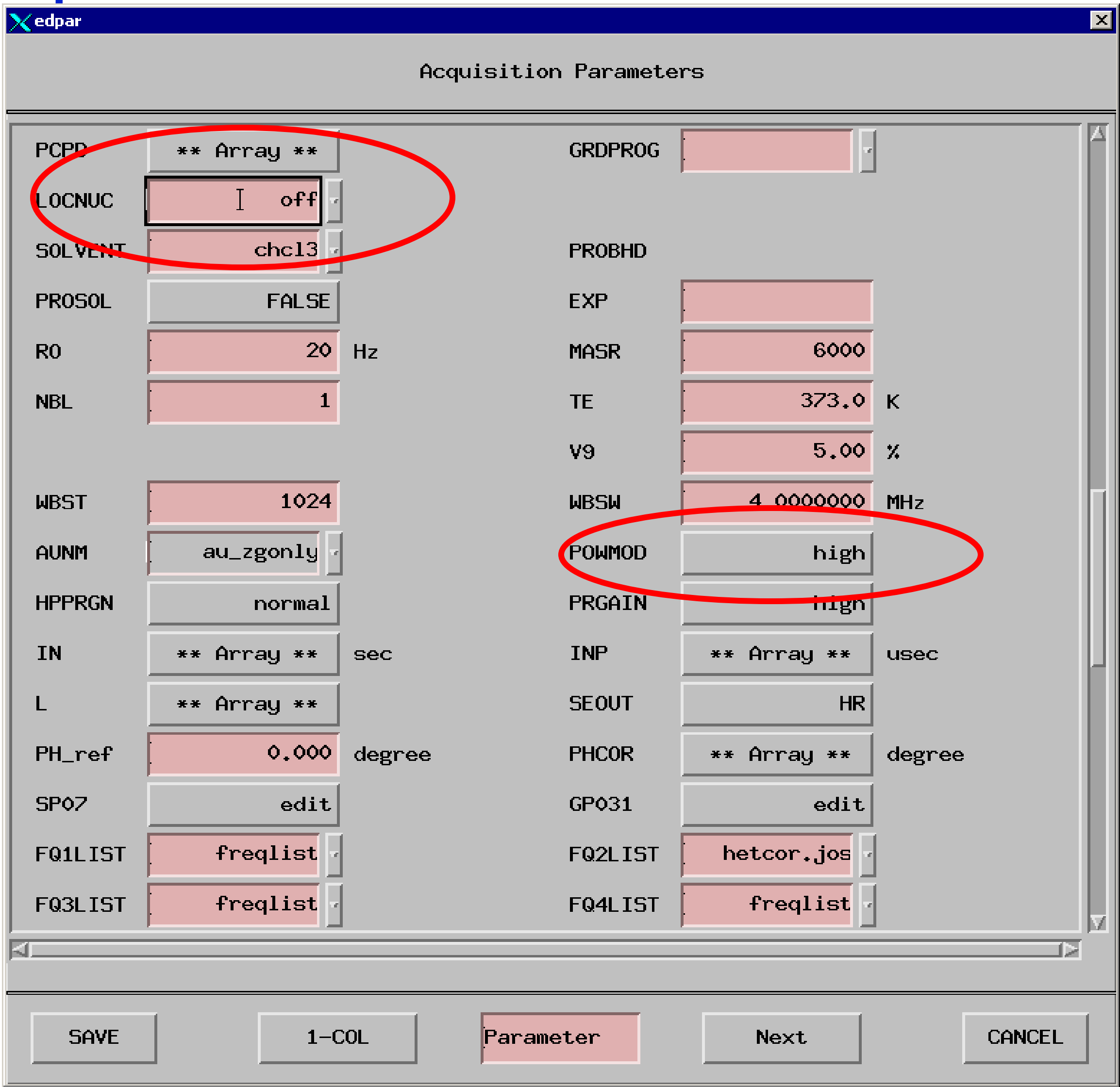
Magic Angle Setup

- Check parameters in the eda:



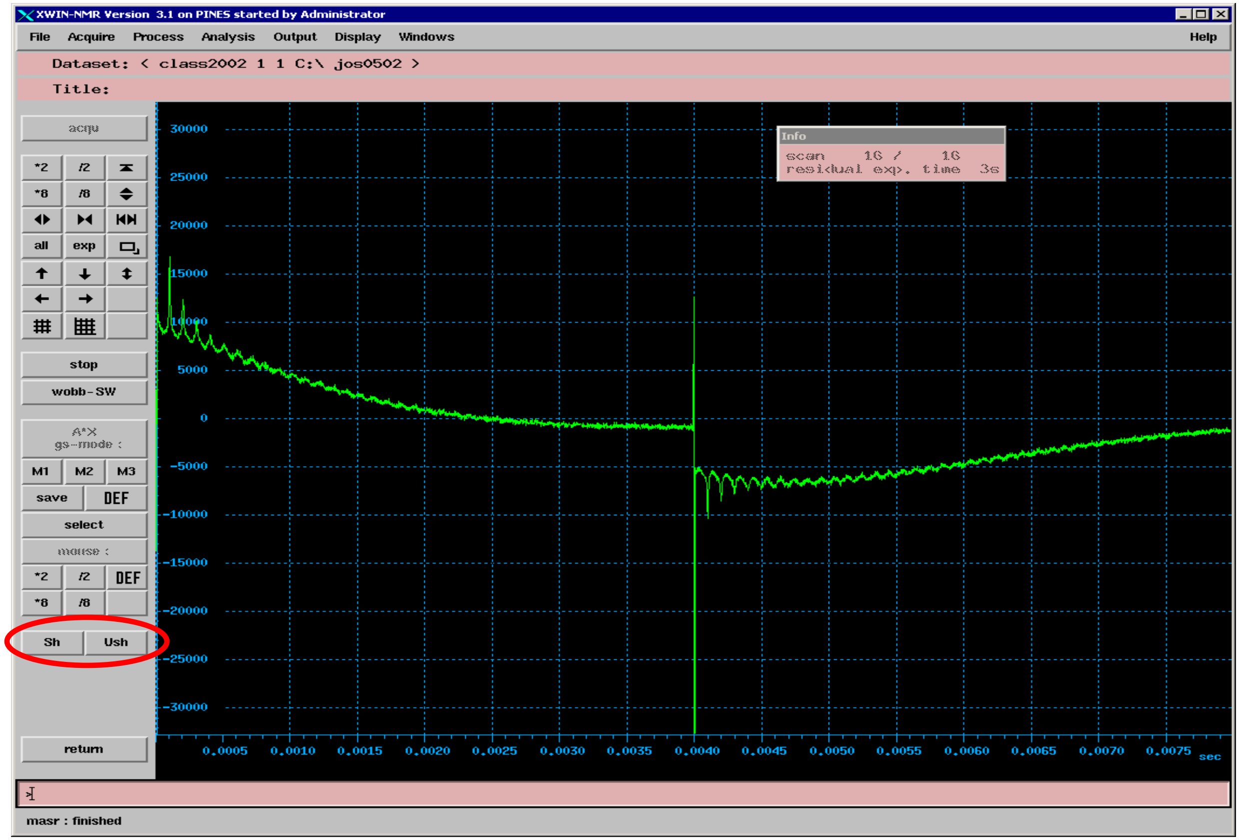
Magic Angle Setup

- Check parameters in the eda:



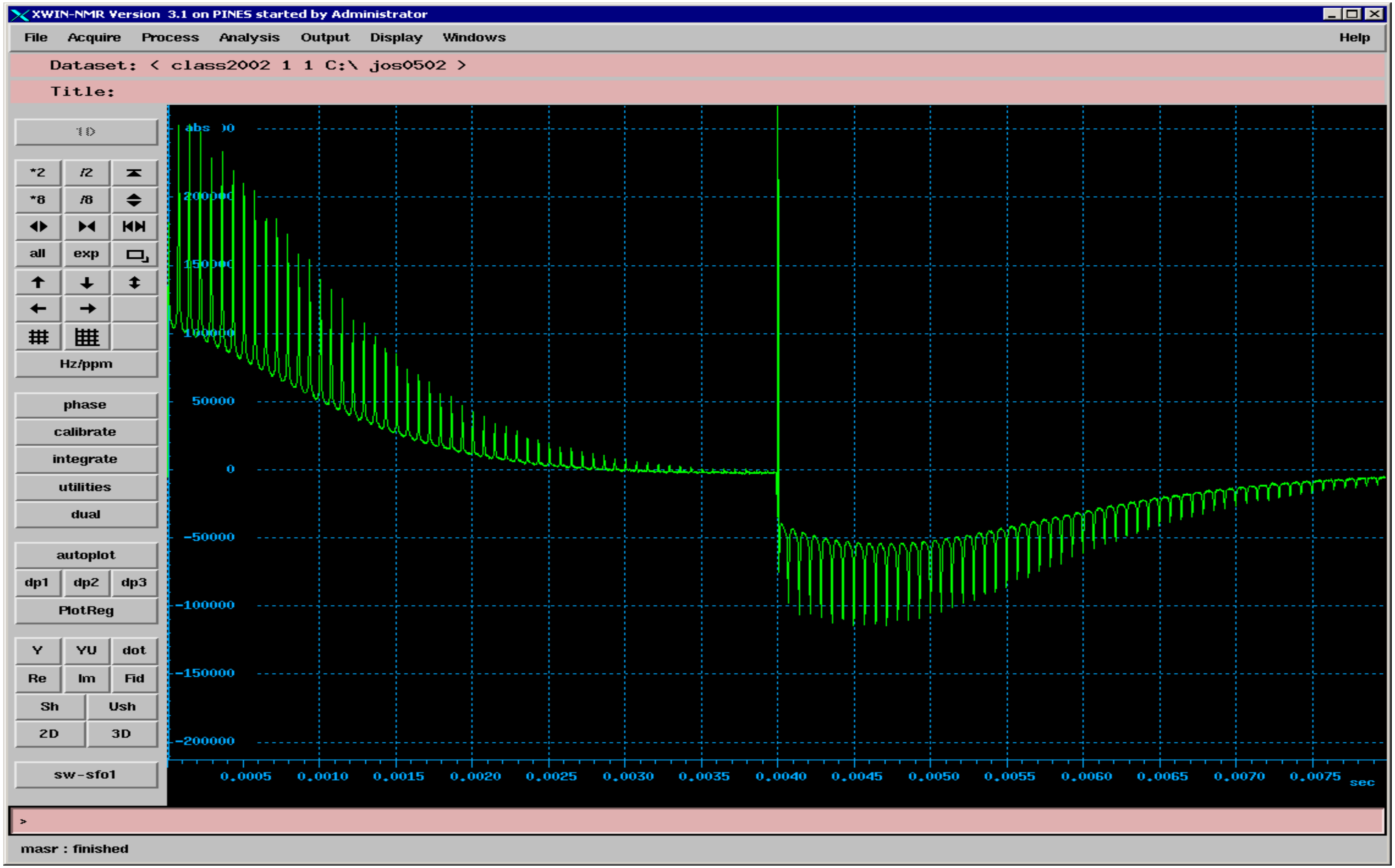
Magic Angle Setup

- Match and tune probe
- Enter value for power level pl1 and pulse width p1 into ased
- Open the acquisition window and type gs:



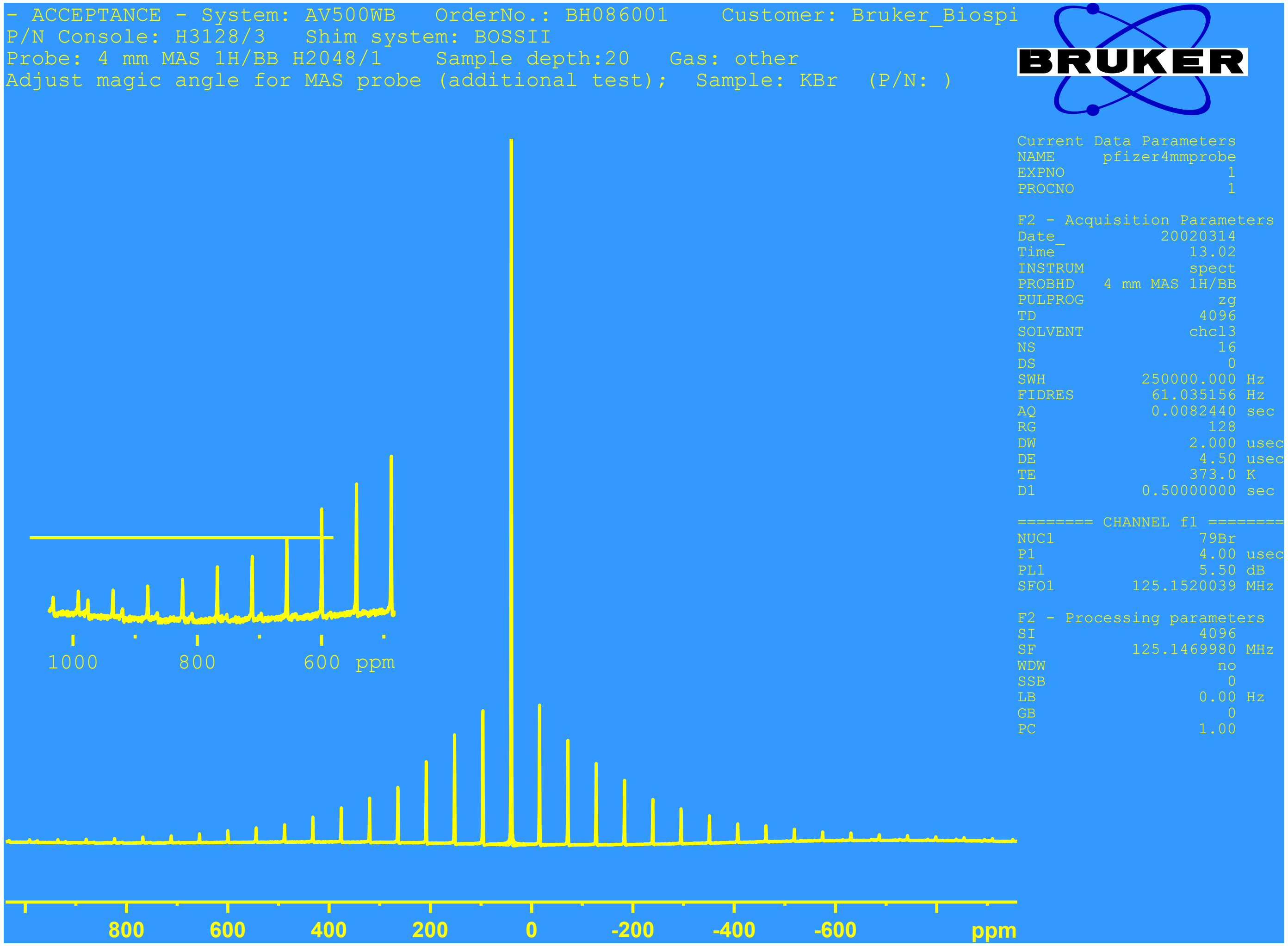
Magic Angle Setup

- Optimize rotation echos by changing the magic angle adjustment: goal:



Magic Angle Setup

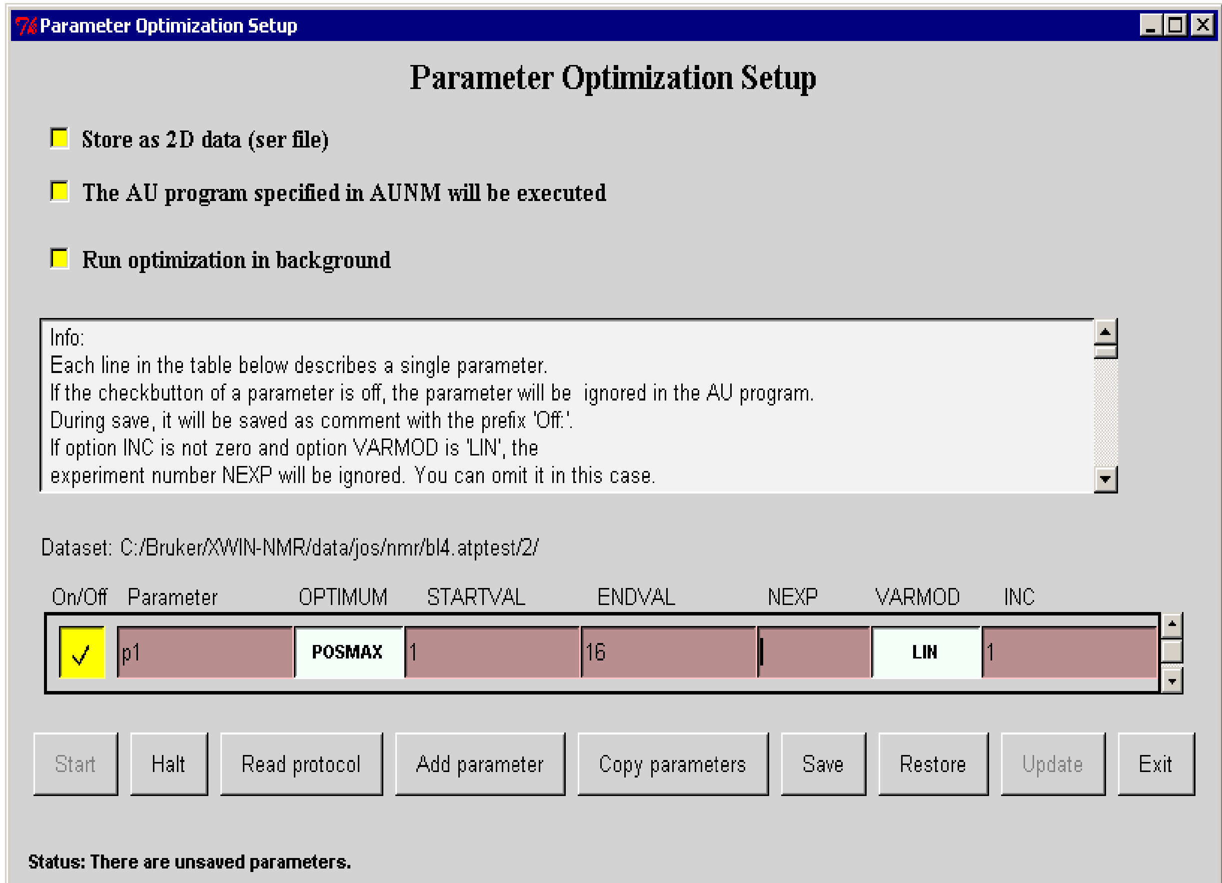
- Acquired KBr spectrum:



BRUKER BIOSPIN

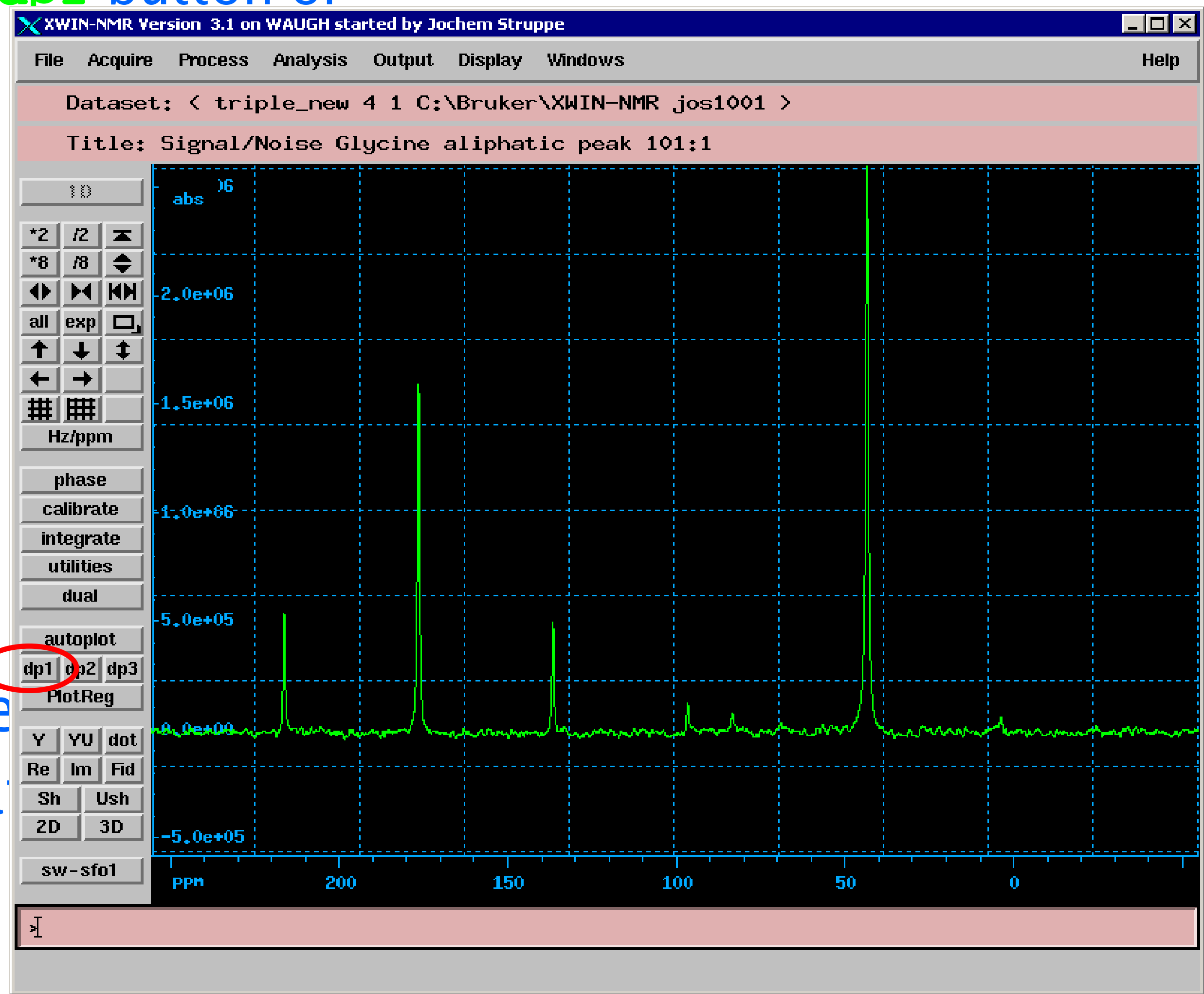
Parameter optimization

- Optimize pulse width:
  - Set power level and optimize pulse width
  - Set pulse width and optimize power level
- Use **POPT**



Parameter optimization

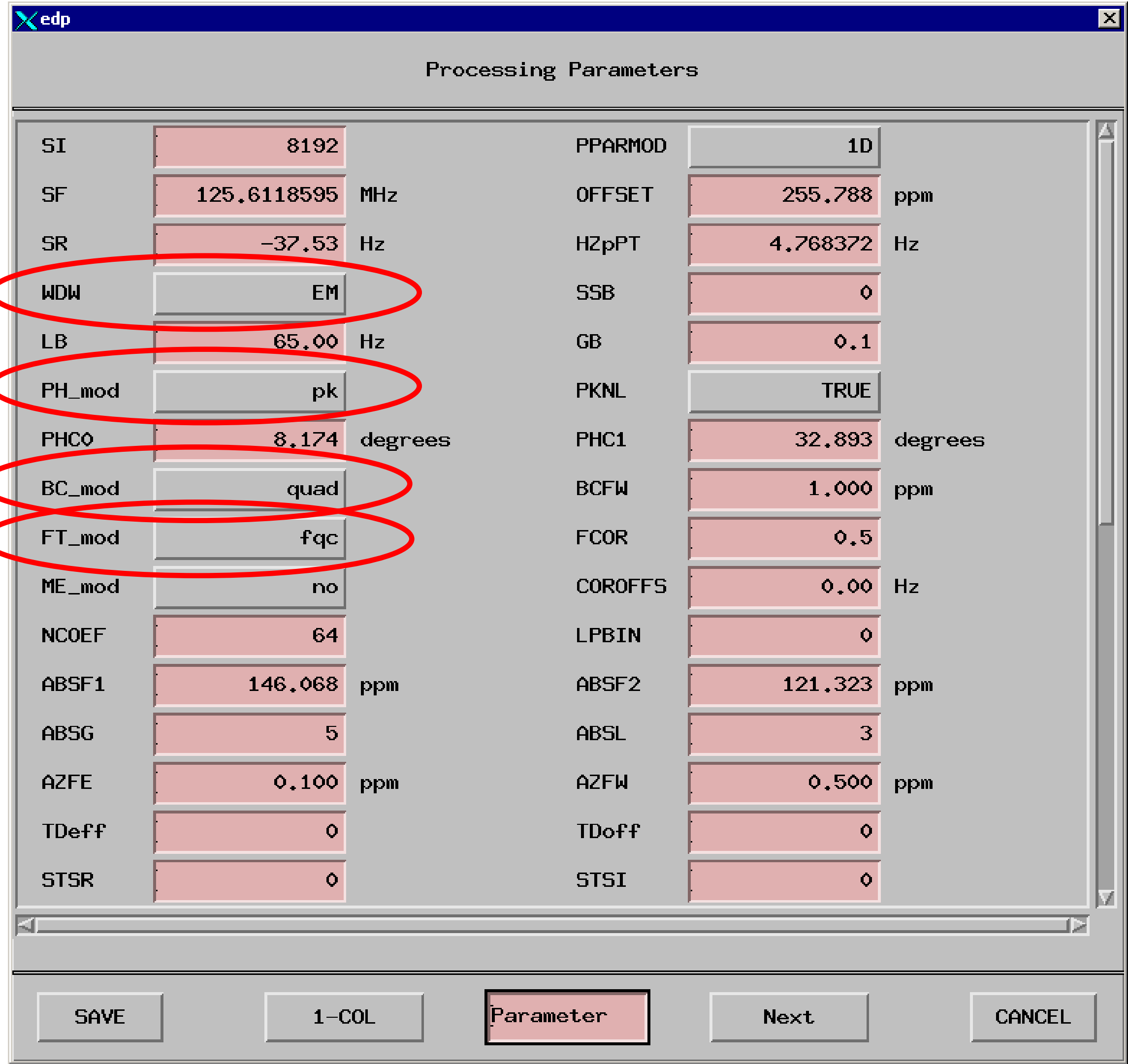
- Before starting **POPT**:
- set spectral region parameters
  - Either by clicking **dp1** button or
  - Enter parameter F1P, F2P
- make sure processing parameters are se for processing da using **trf**



Parameter optimization

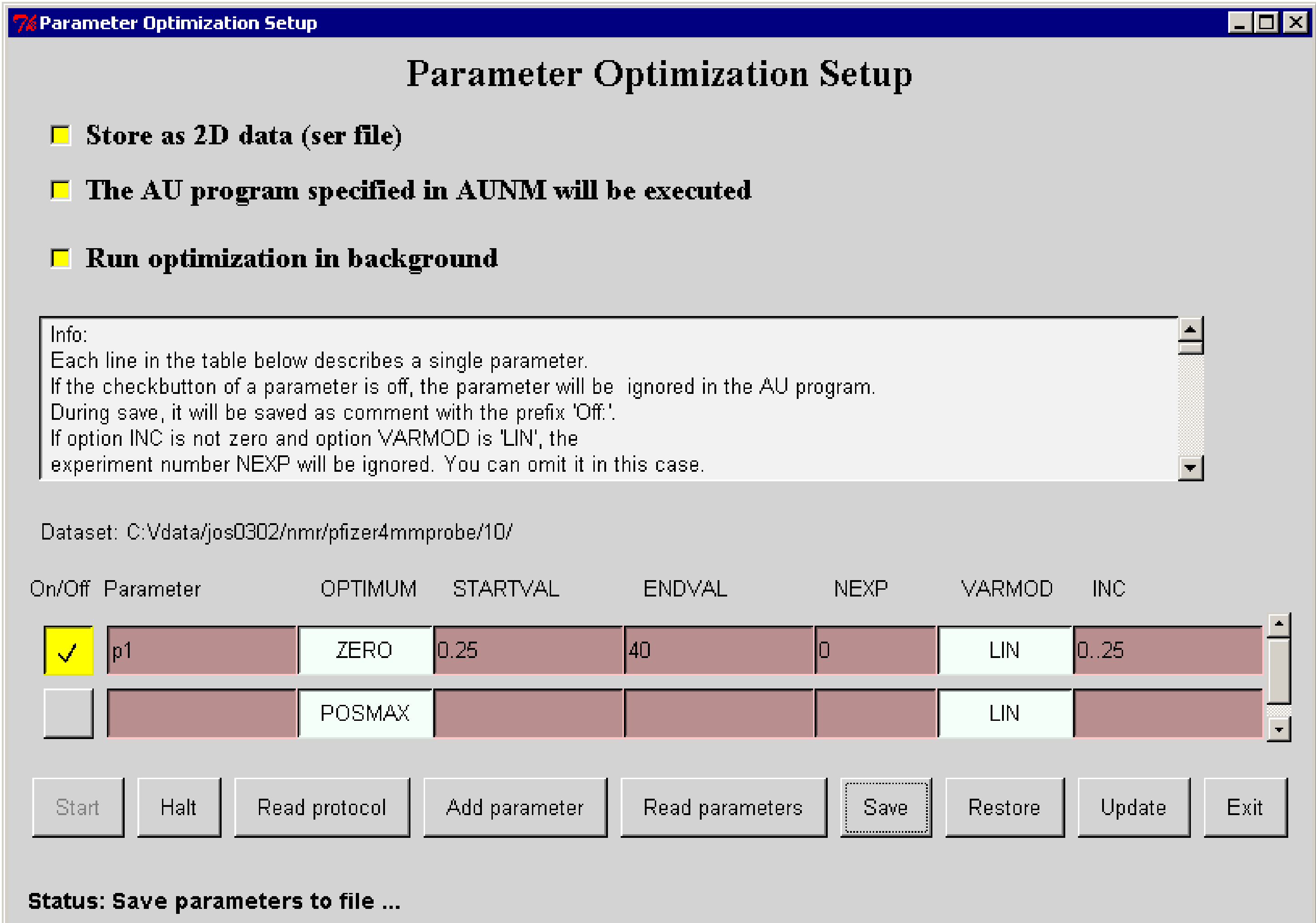
trf - uses processing instruction parameters

- WDW
- Ph_mod
- BC_mod
- FT_mod

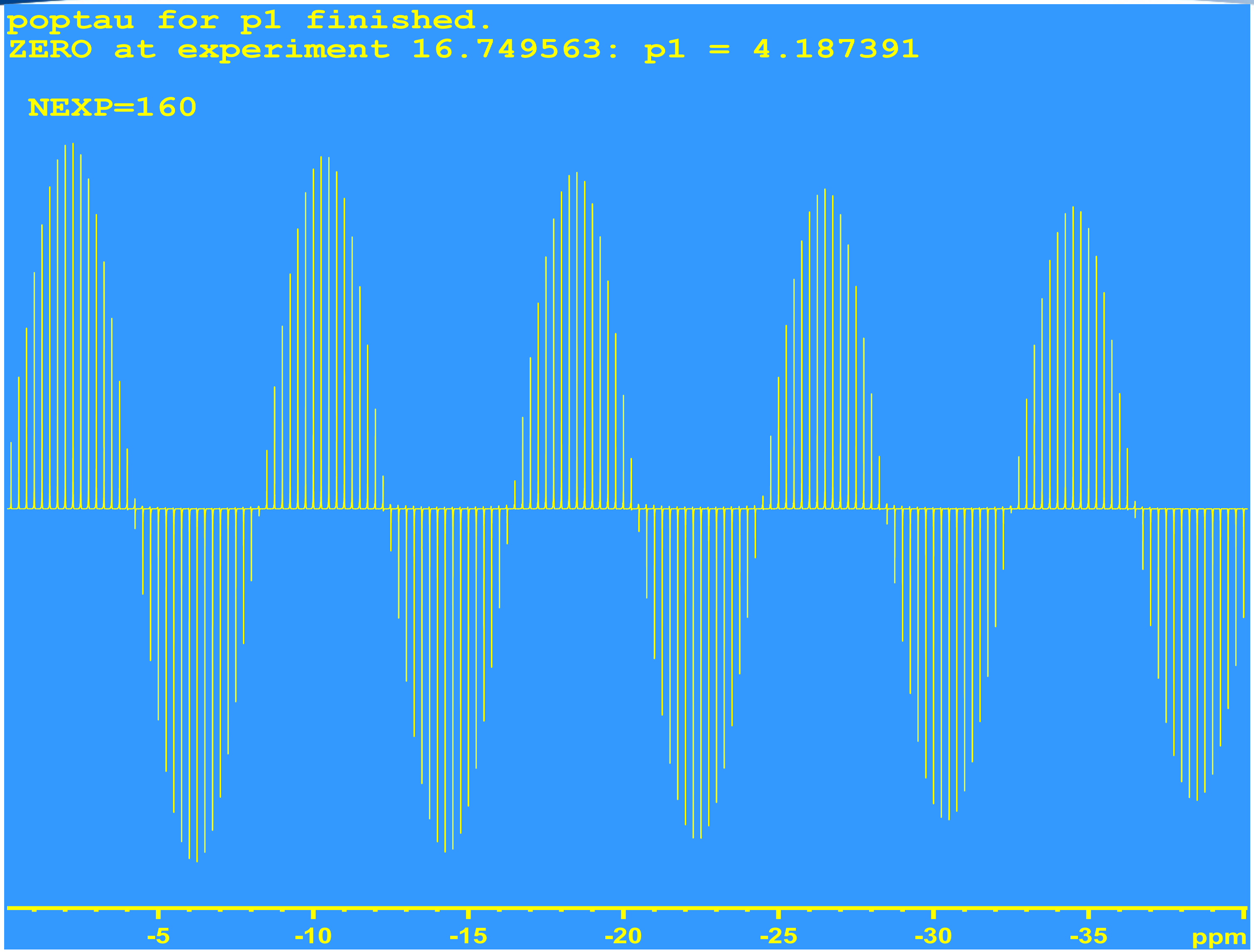


Parameter optimization

- Everything set up - start `popt`:

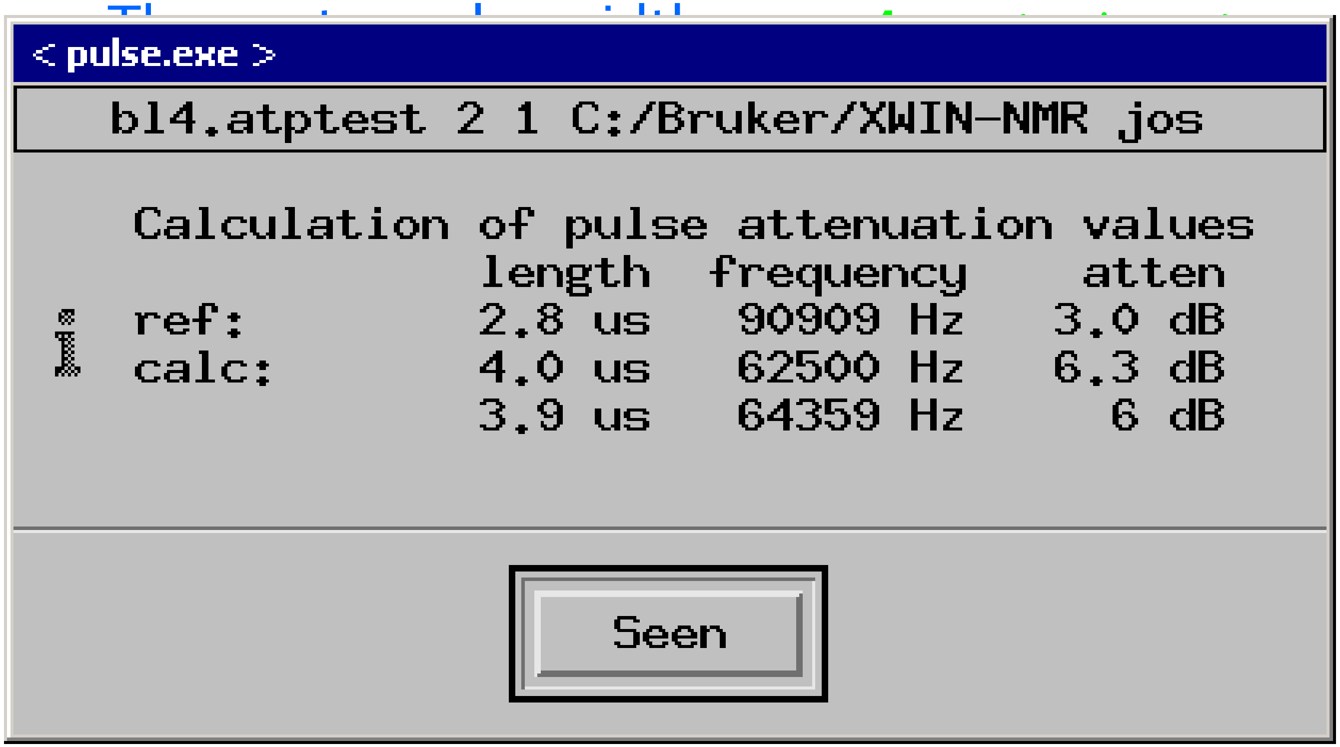


Parameter optimization



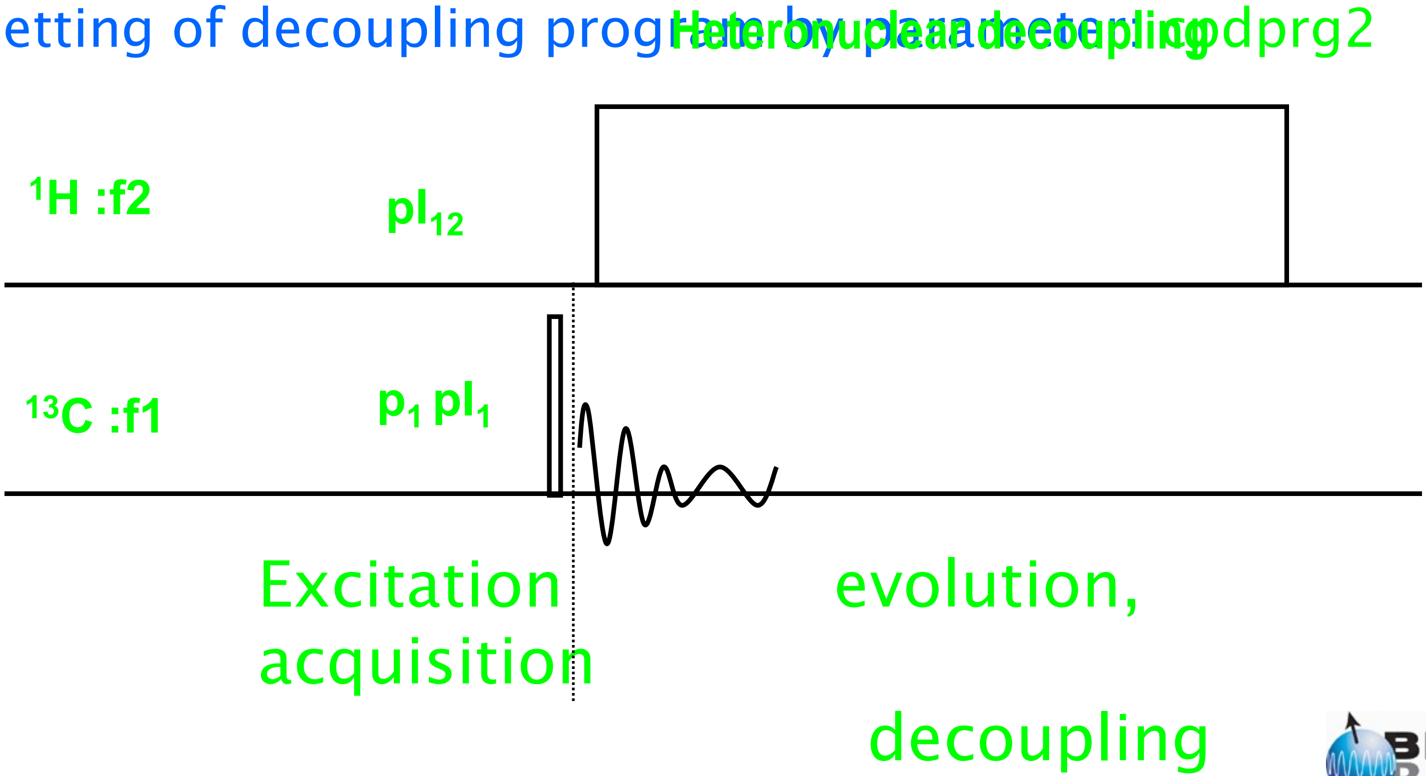
Parameter optimization

- If result not satisfying - pulse width too large or too small:
  - Use au program **PULSE** to calculate correct pulse
  - Verify calculation with **POPT**
- **Use of** **Pulse: xau pulse**



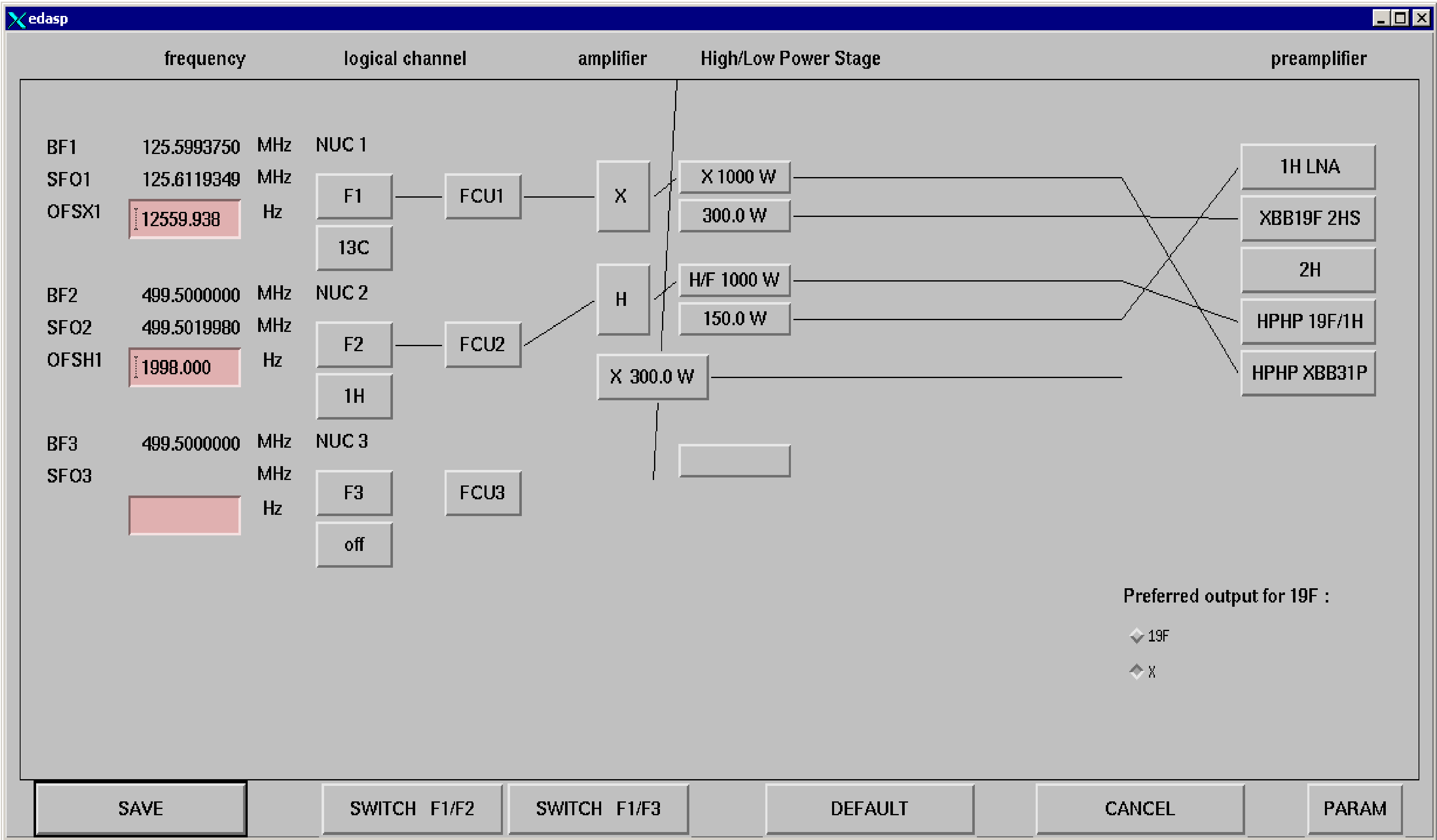
Setup Direct Polarization Experiments

- Direct Polarization ^{13}C for pulse power measurement:
  - Parameter file: C13SOL
  - Pulse program: hpdec.av
  - See header in pulse program.
  - Edit pulse program with: edcpul <pp-name>
  - Setting of decoupling program by parameter: cpdprg2



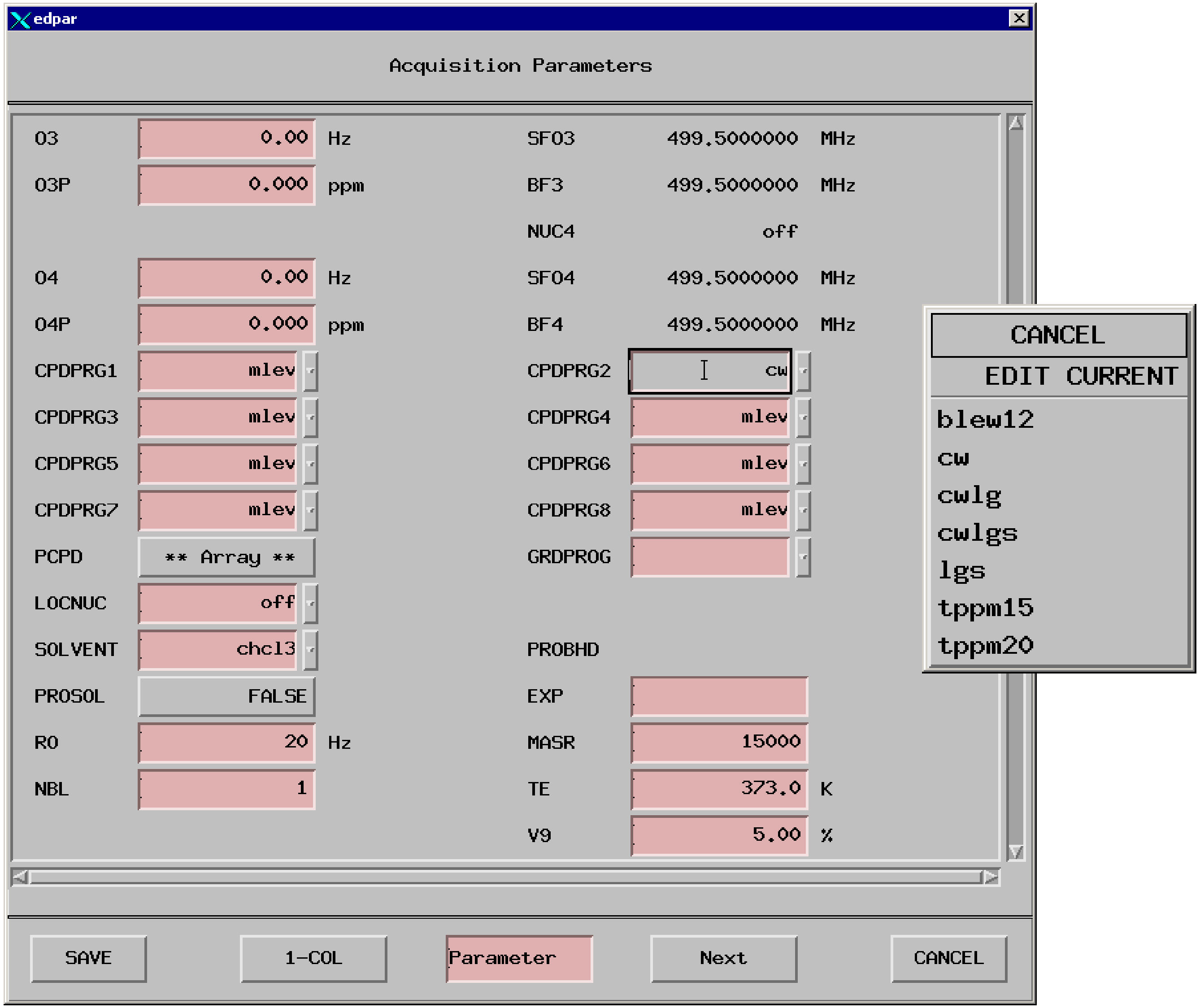
Setup Direct Polarization Experiments

- EDASP display:



Setup Direct Polarization Experiments

- EDA cpdprg2:



Setup Direct Polarization Experiments

- Pulse program:

```
;hpdec.av

1 ze                           ;set RCU to replace mode
2 d1 do:f2                     ;recycle delay
  (p1 ph1):f1                  ;pulse on F1; power level pl1
  1u cpds2:f2                  ;use cpdprg2 cw or tppm at pl12
  go=2 ph31                    ;adc is finished,
  1m do:f2                     ;turn decoupling off
  wr #0                        ;save data in current data set
exit
ph0= 0                         ;constant phase for acquisition
ph1= 0 1 2 3                   ;simple pulse phase list
ph31=0 1 2 3                   ;signal routing corresponds to
                               ;pulse phase list
```

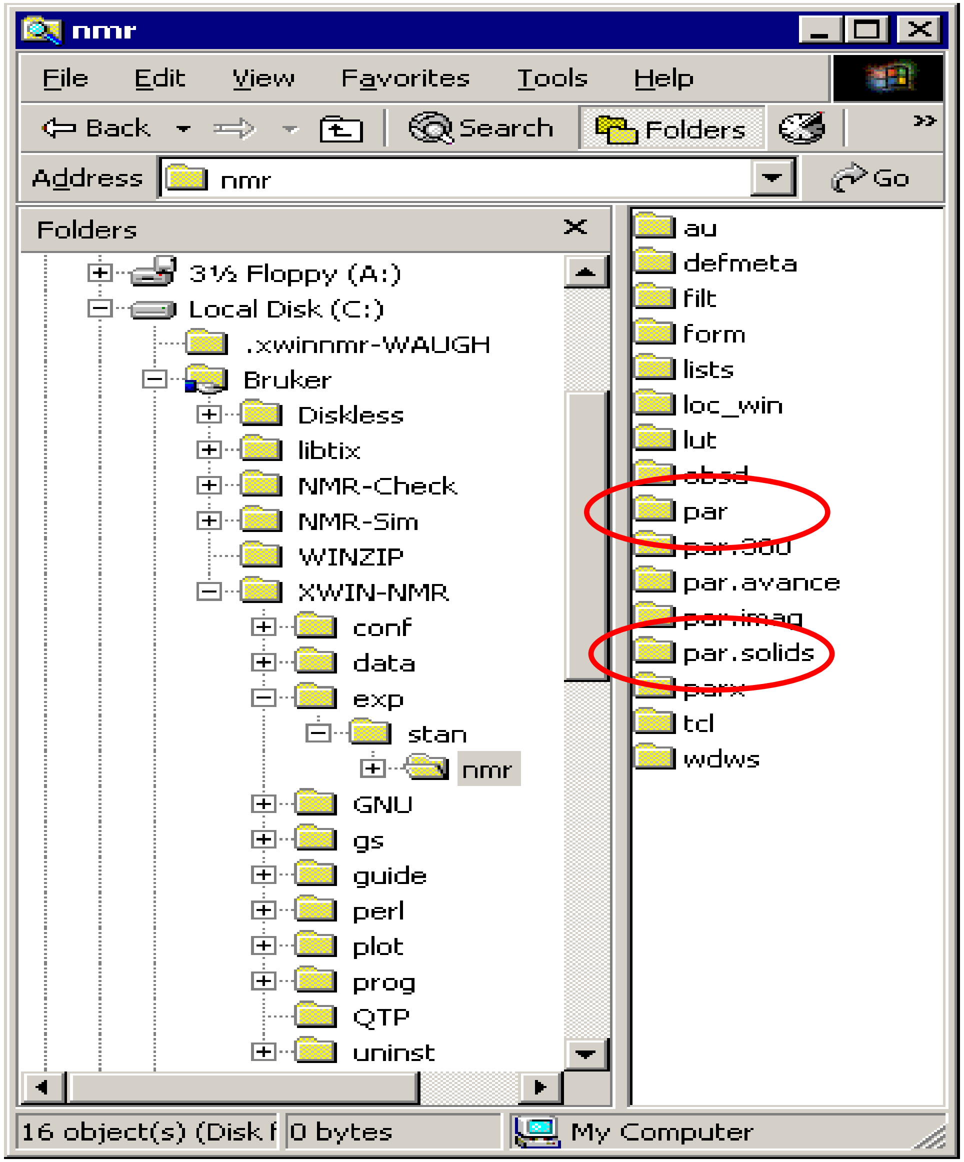
Setup Direct Polarization Experiments

- Decoupling program:

```
   0.5u pl=pl12
1  100up:0 fq=cnst21
   jump to 1
```

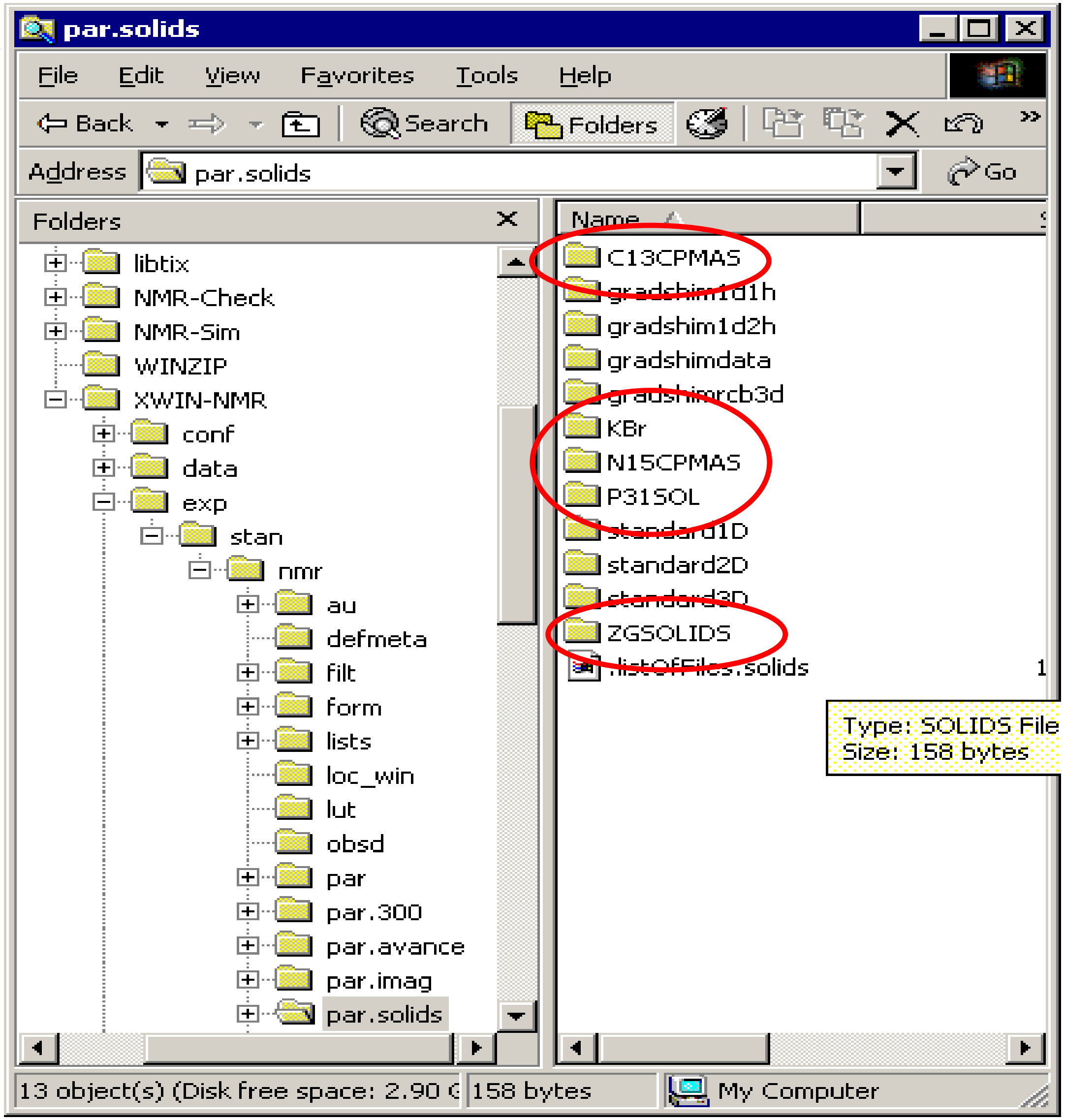
Productivity Tools

- Location of parmeter sets



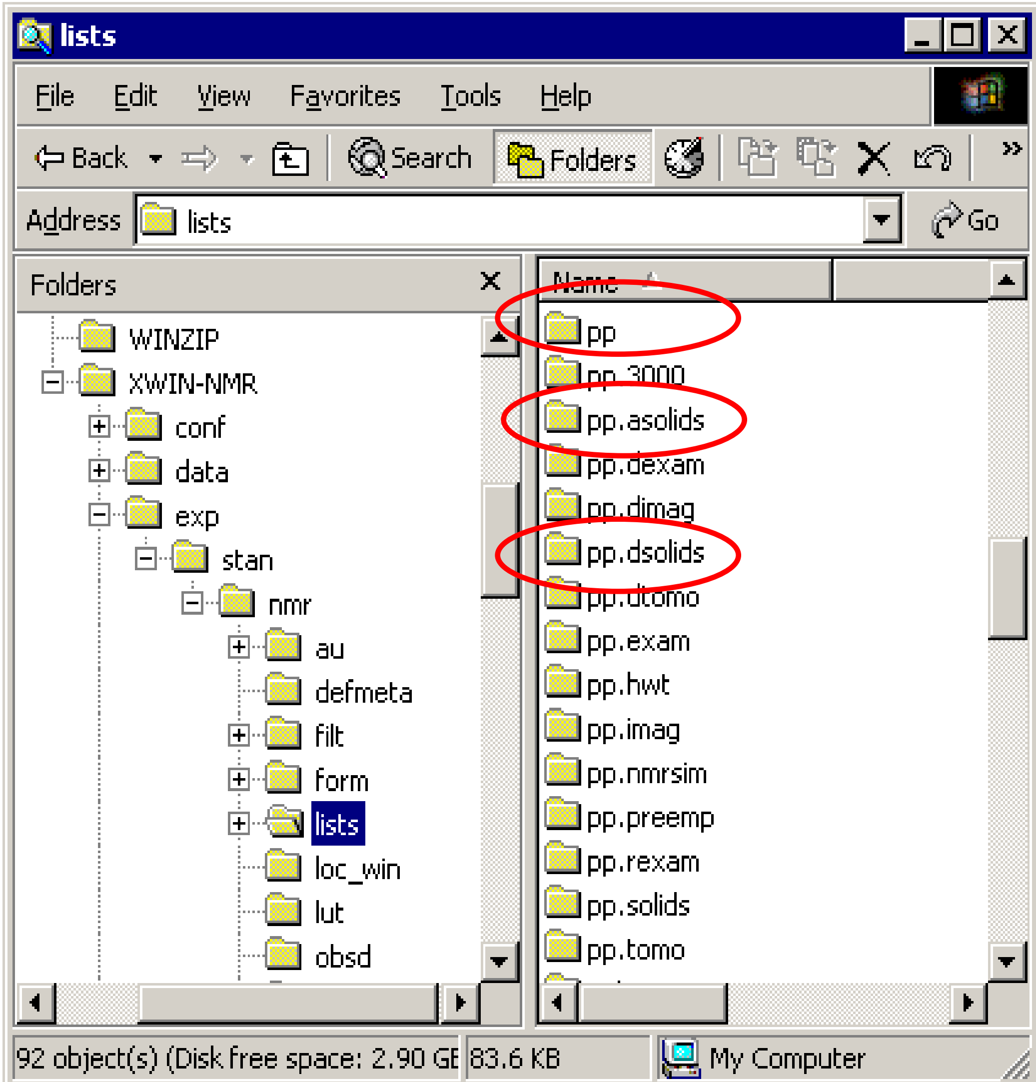
Productivity Tools

- Parmeter sets



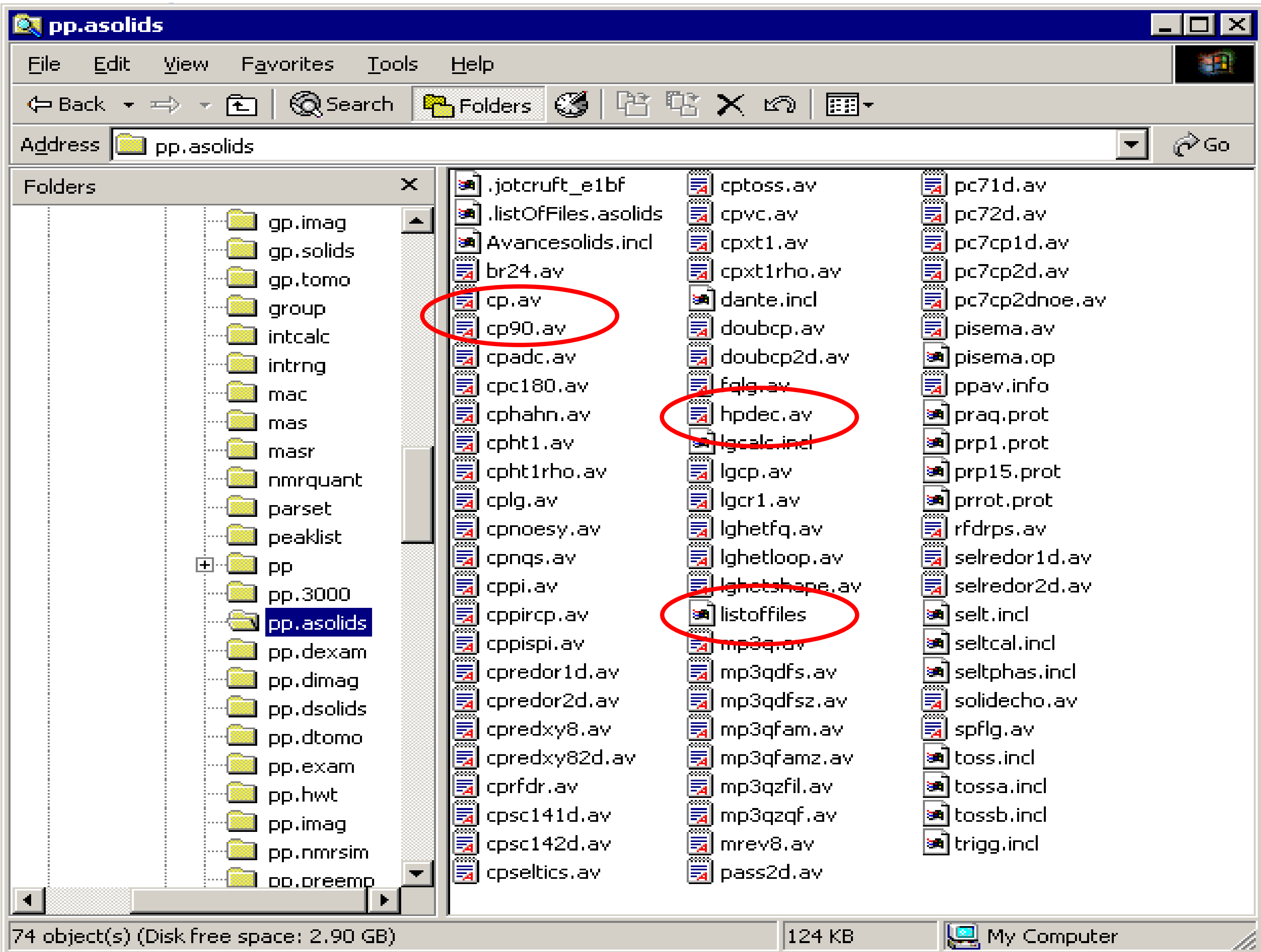
Productivity Tools

- Pulse Programs, etc



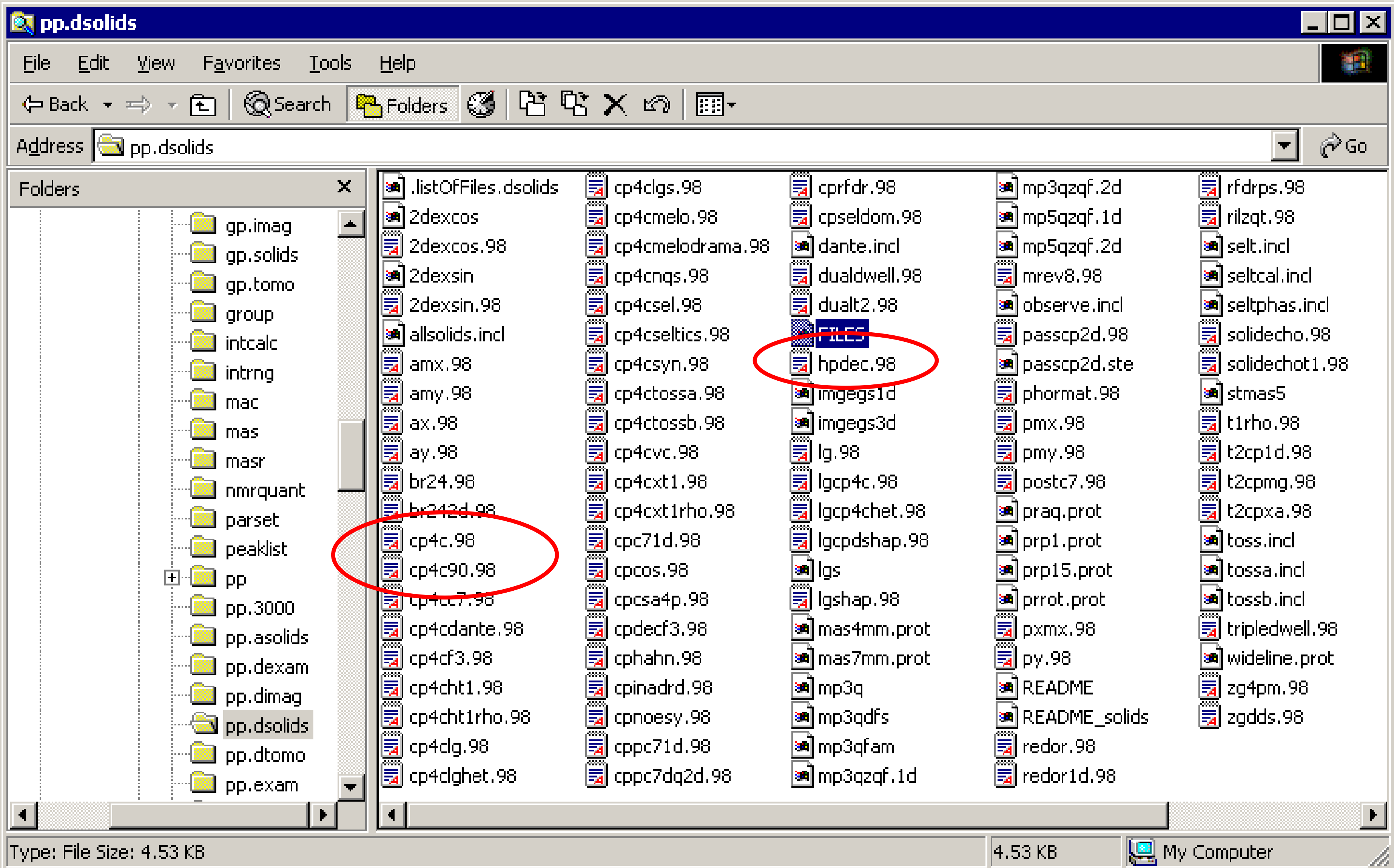
Productivity Tools

- Pulse Programs for consoles with AQS (SGU) el



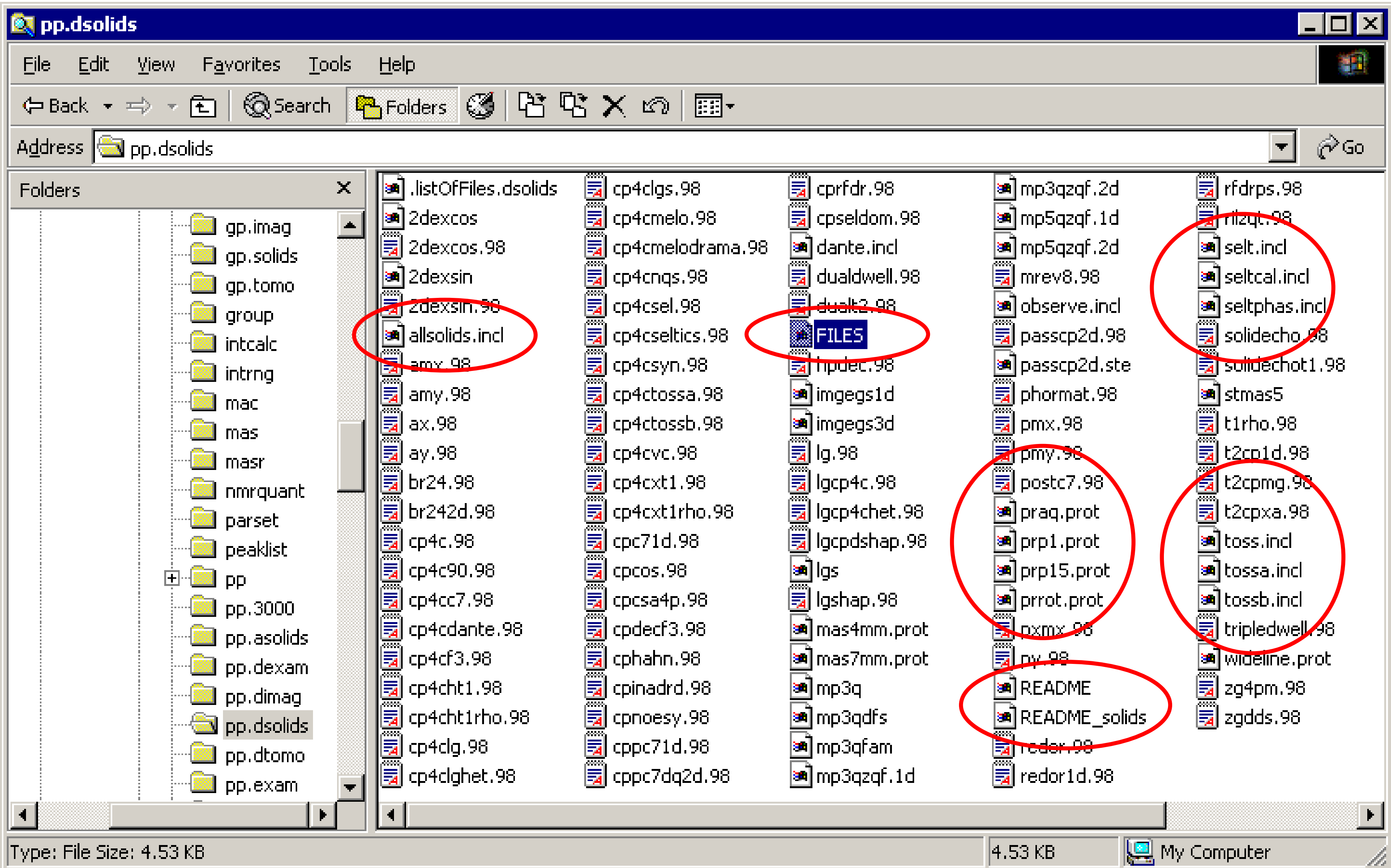
Productivity Tools

- Pulse Programs for consoles with AQX electronic



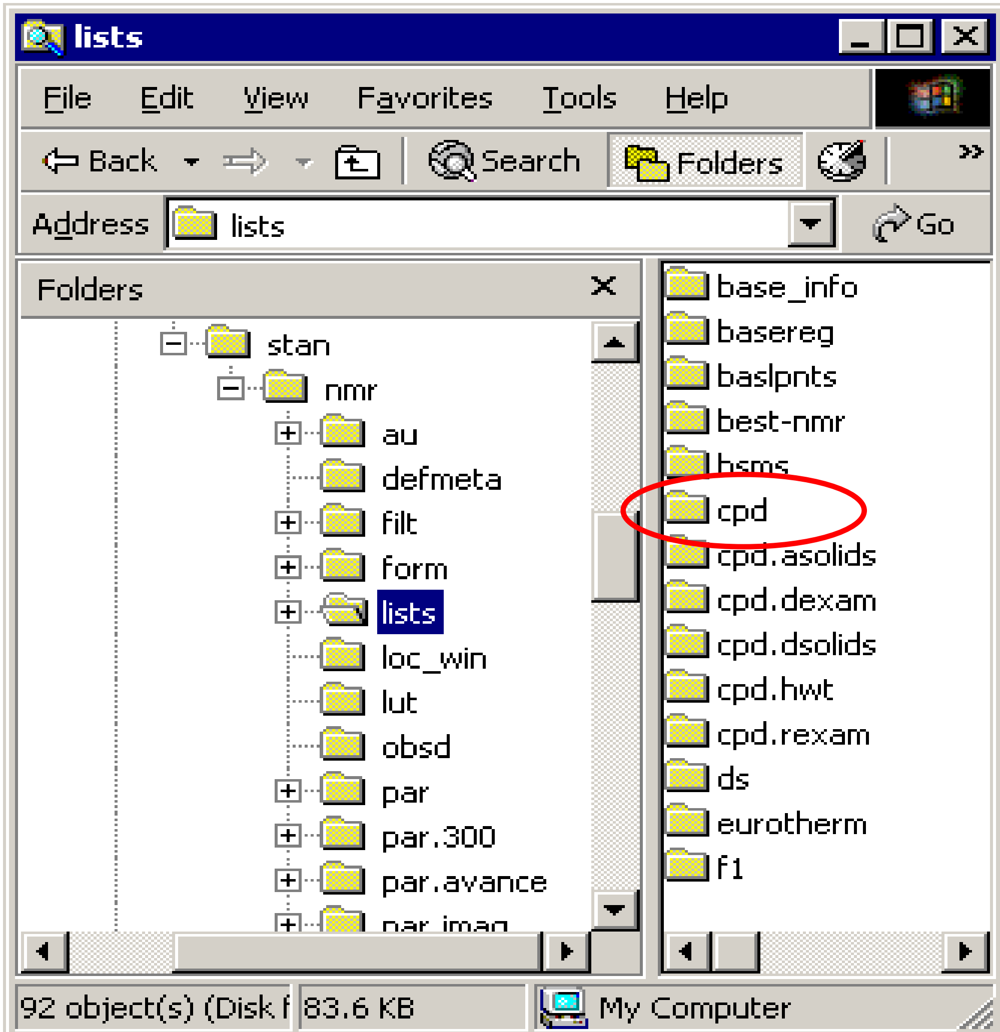
Productivity Tools

- Pulse Programs for consoles with AQX electronic



Productivity Tools

- Composit Pulse Decoupling (CPD) Programs



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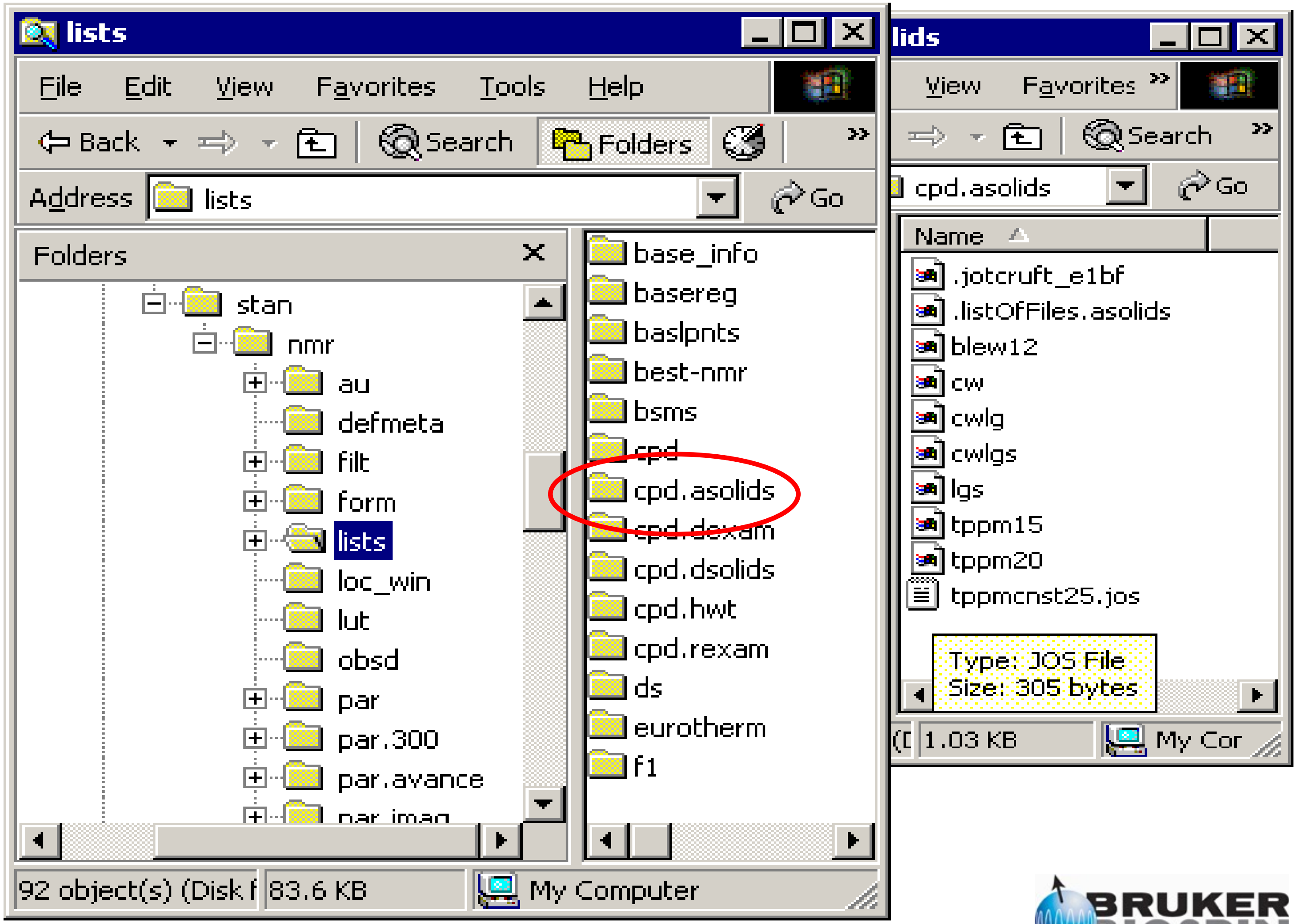

Productivity Tools

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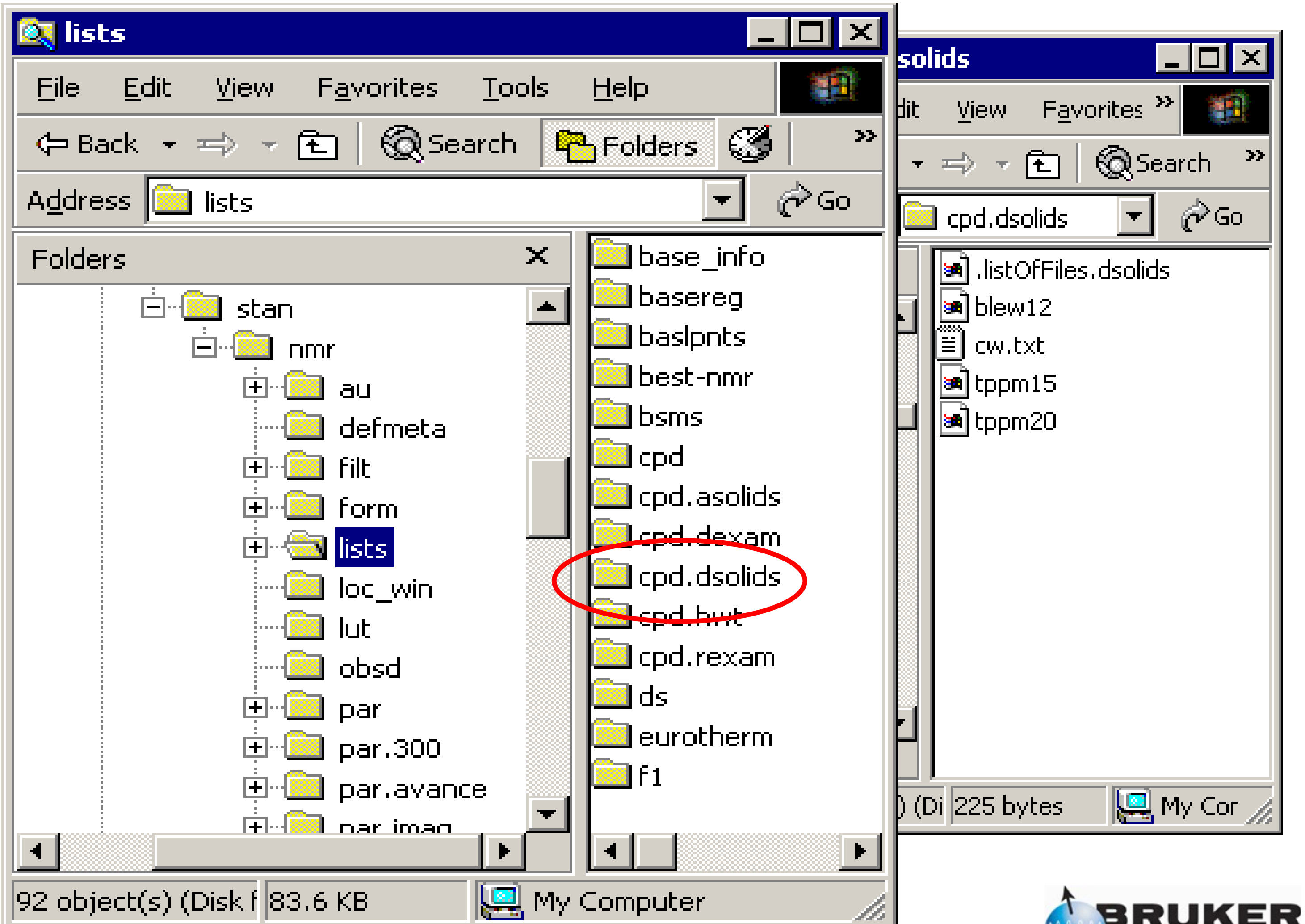
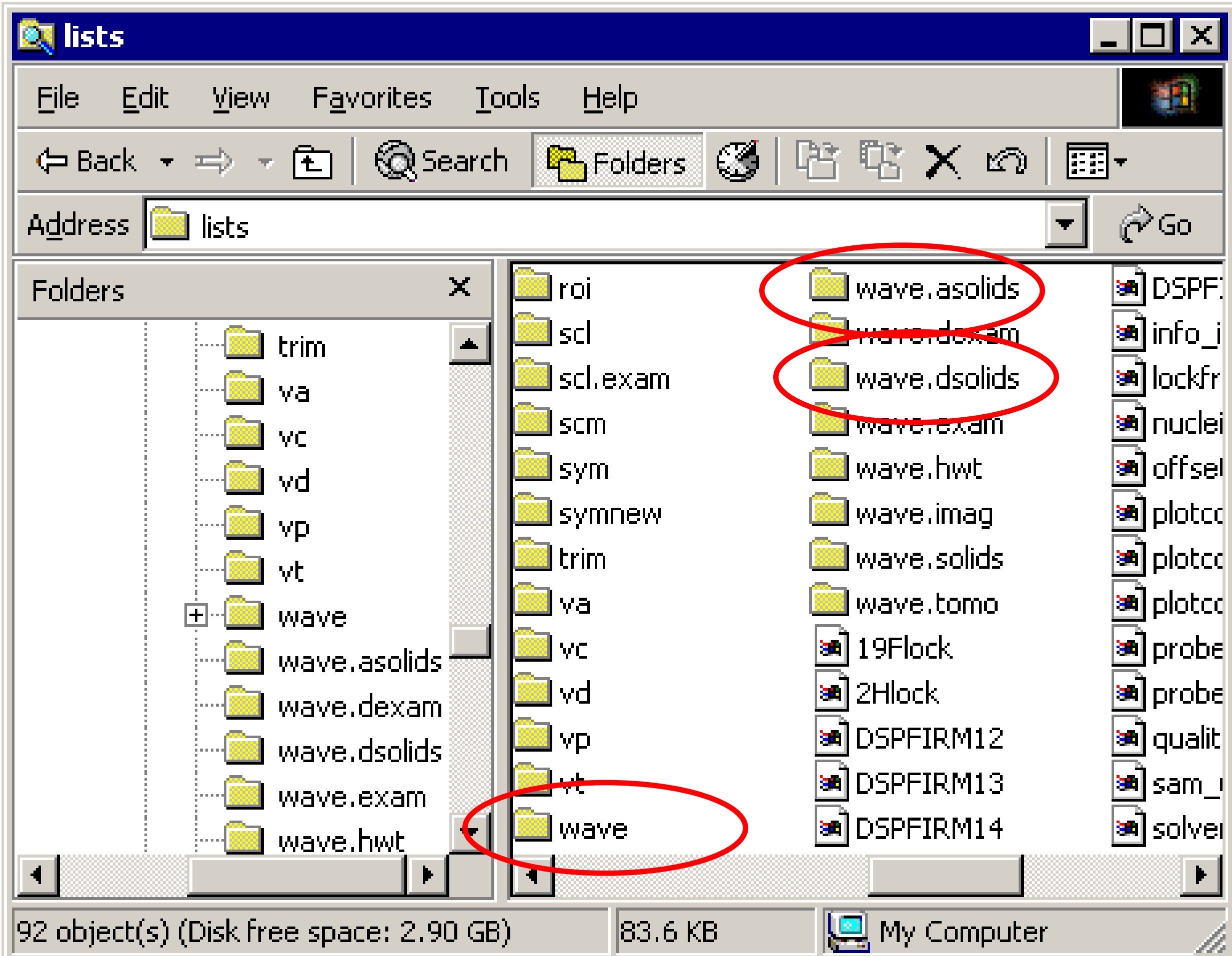


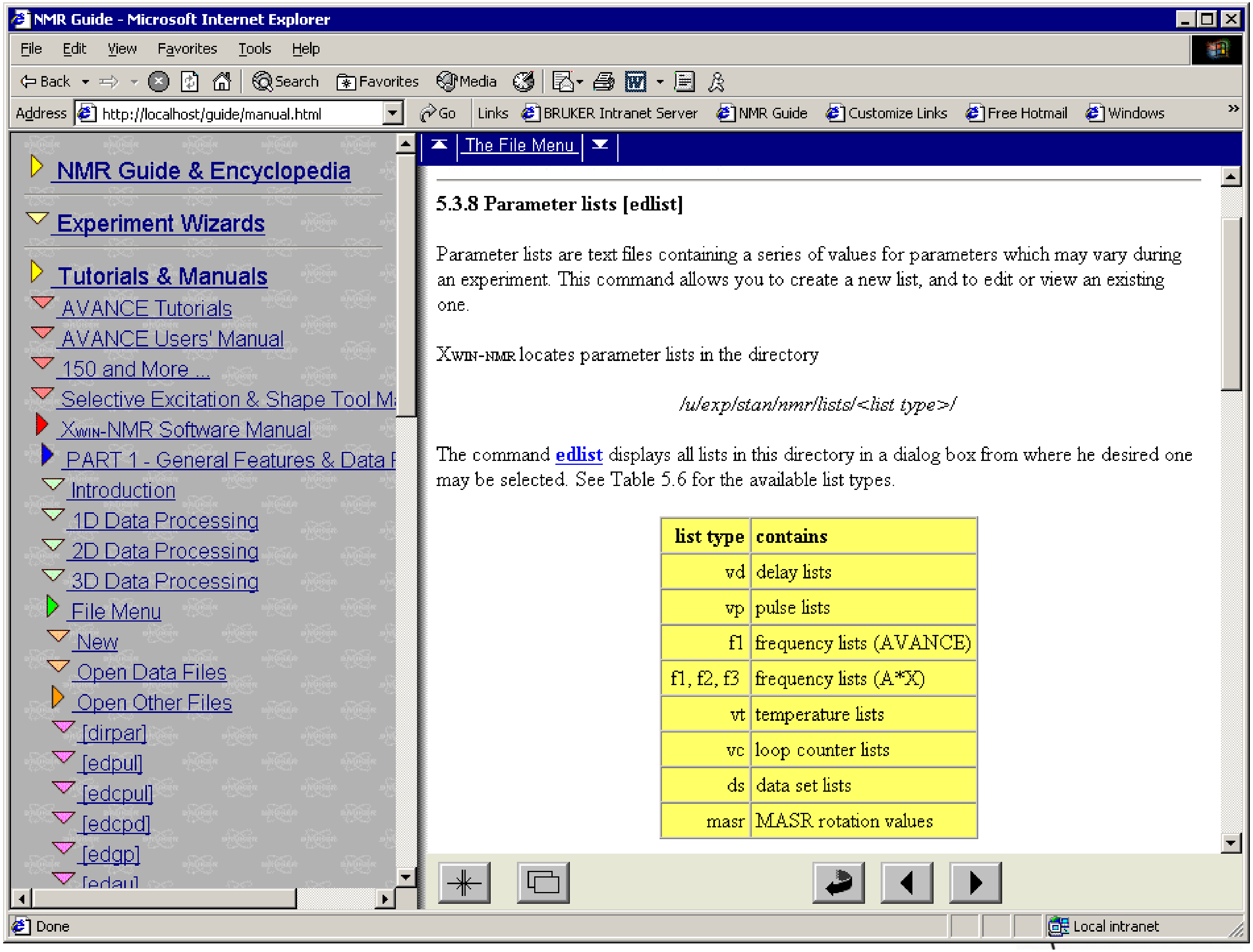
Productivity Tools

- Shape Files (CPD)

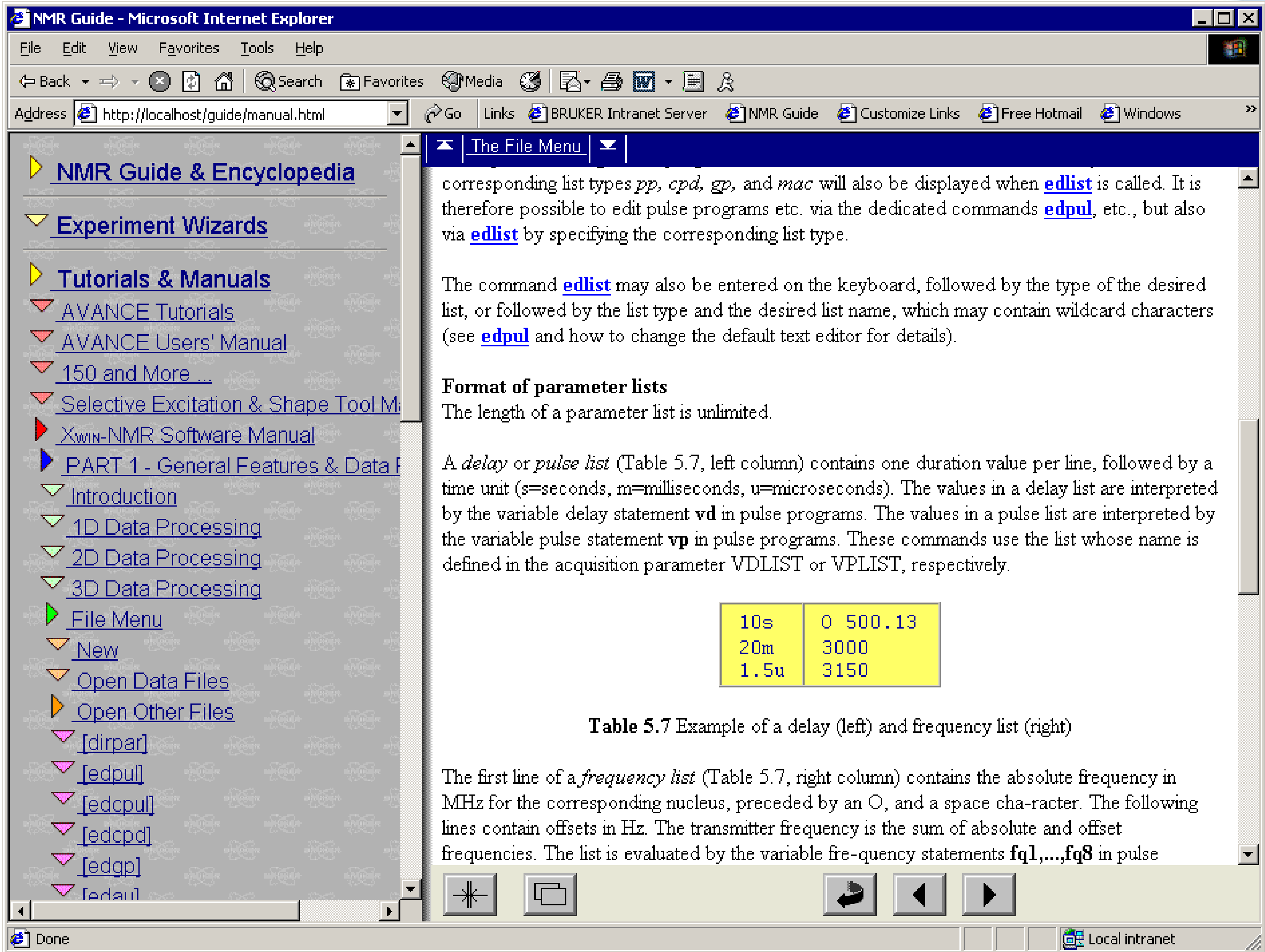


Productivity Tools

- Lists

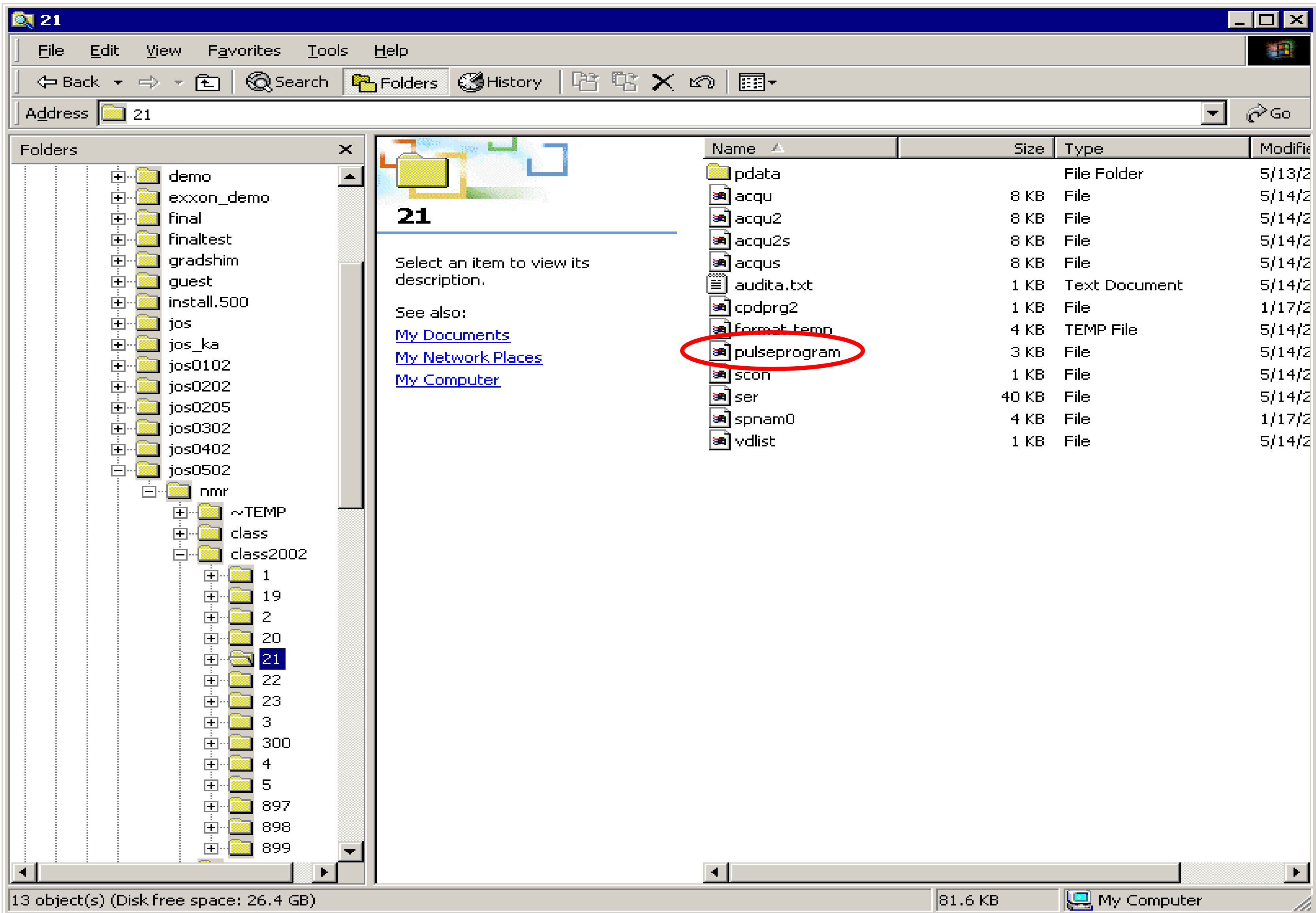


Productivity Tools



Productivity Tools

- Information in stored data sets



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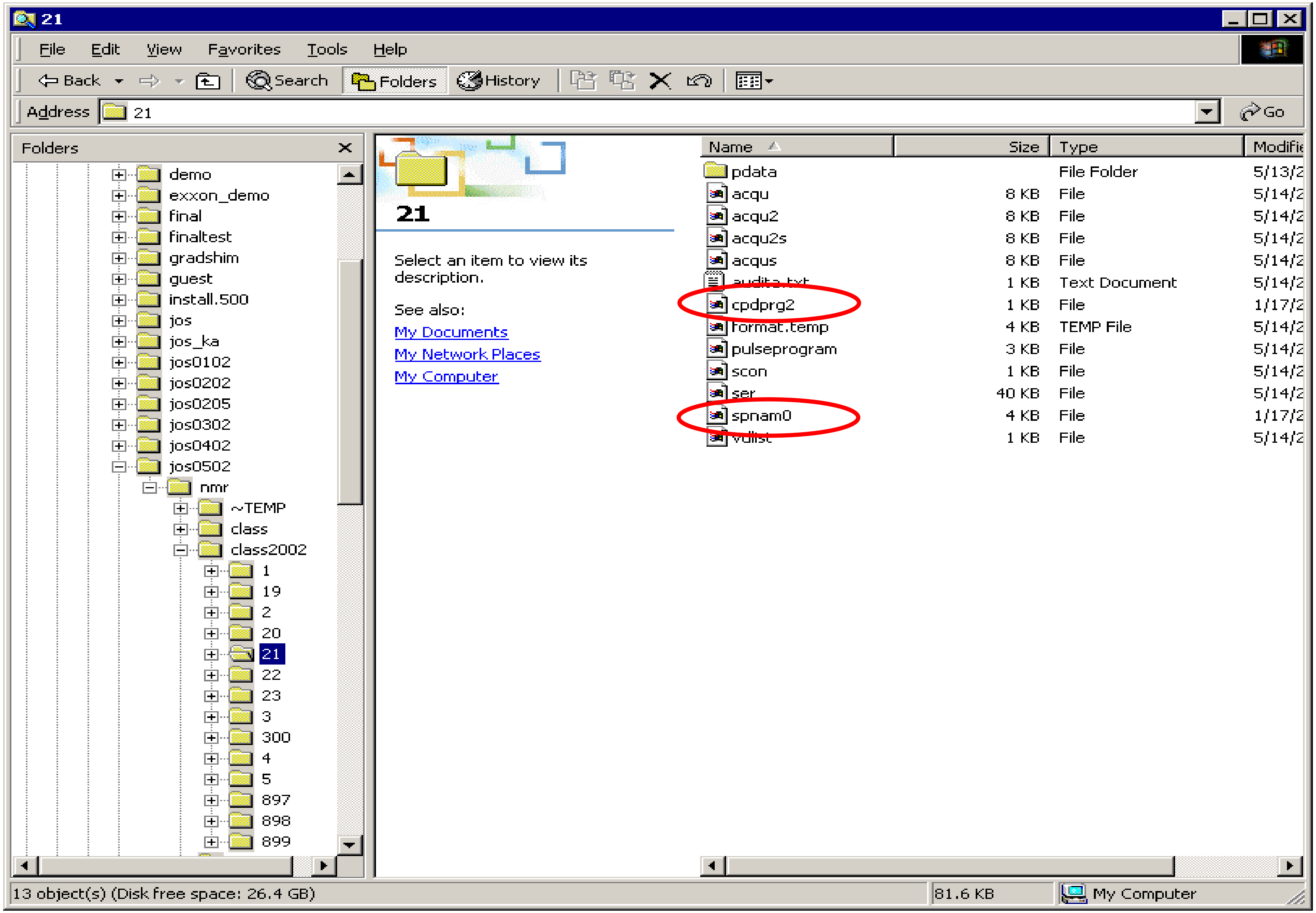

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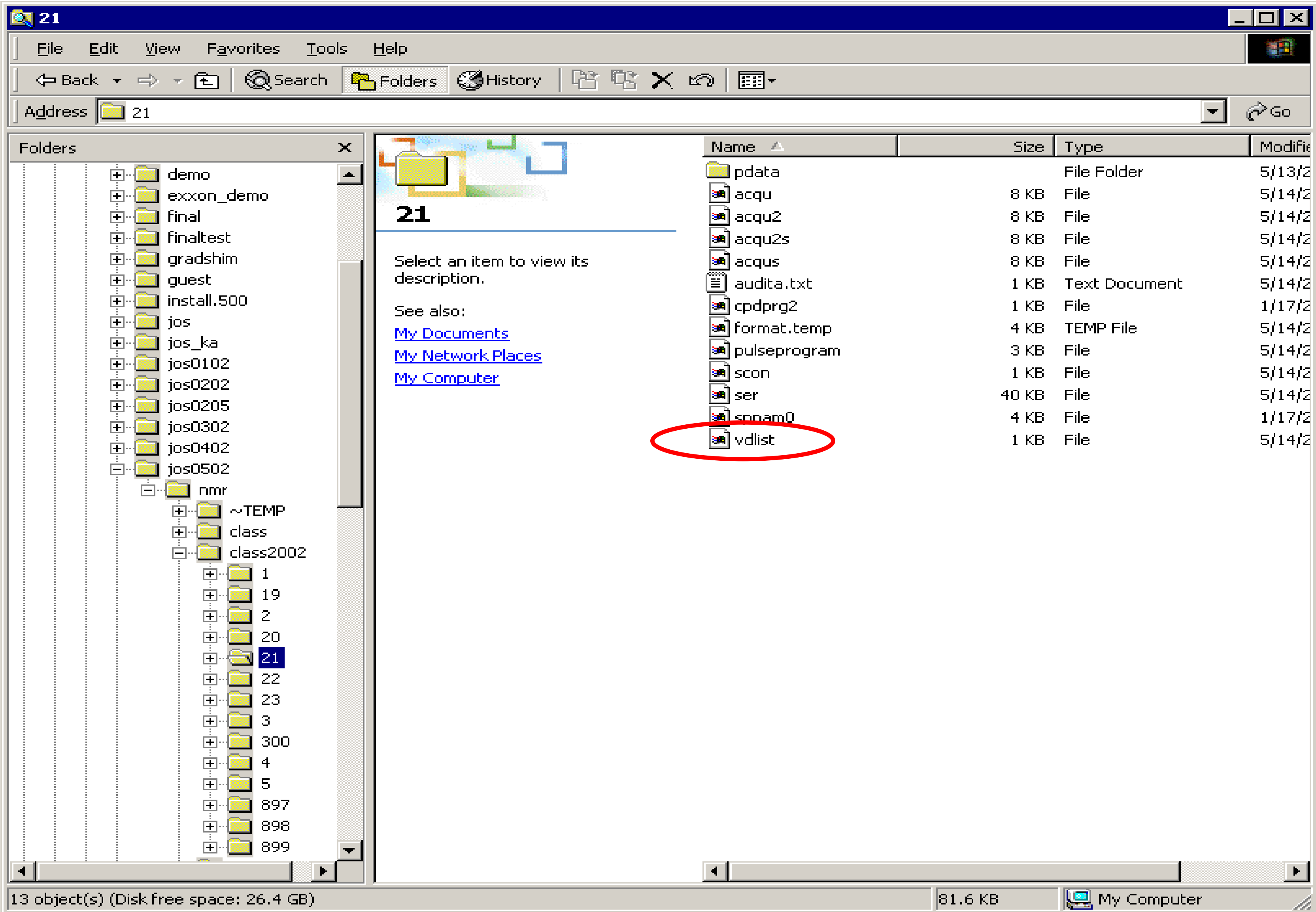

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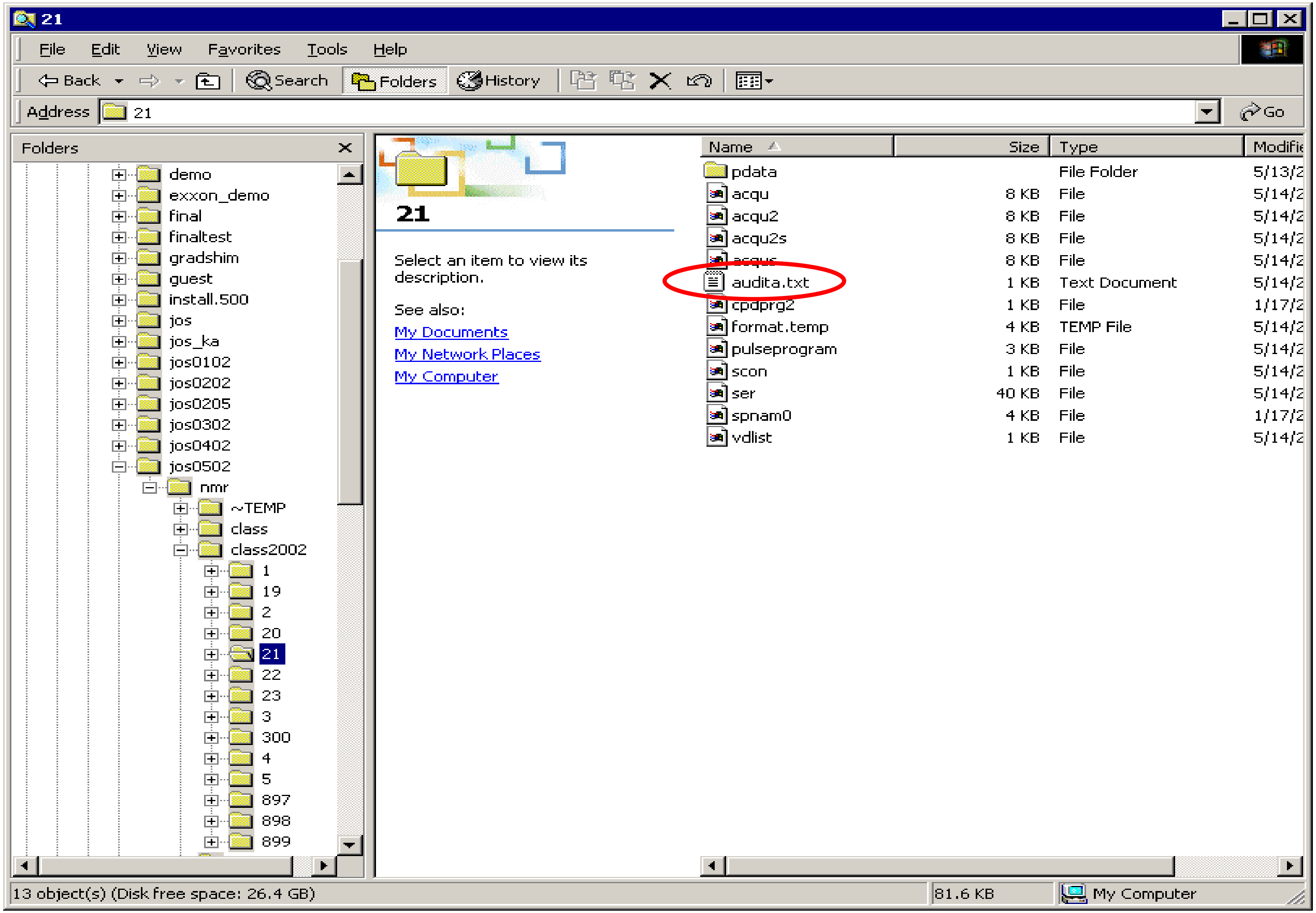


Productivity Tools

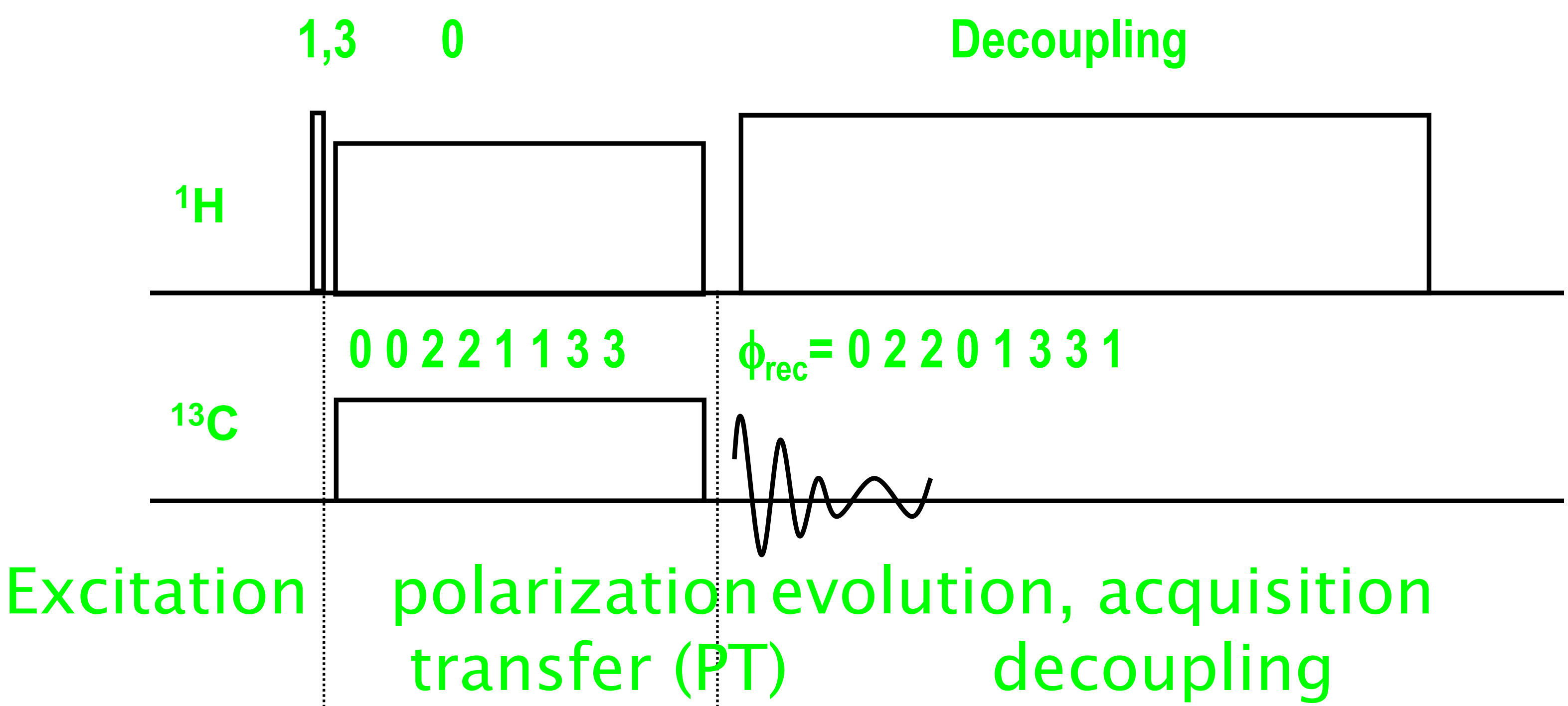
- Audit trail:

```
##TITLE= Audit trail, XWIN-NMR       Version 3.1
##JCAMPDX= 5.01
##ORIGIN= Bruker Analytik GmbH
##OWNER= Administrator
$$ C:\/data/jos0502/nmr/class2002/21/audita.txt
##AUDIT TRAIL=  $$ (NUMBER, WHEN, WHO, WHERE, WHAT)
(   1,<2002-05-14 14:05:23.73 -400>,<Administrator>,<PINES>,
      <created by zg
       data hash MD5: 1K * 10
       CC B6 7F 0A F5 94 FA F5 9F C6 50 C4 BD 68 5B 33>)
##END=

$$ hash MD5
$$ BF 3A 92 C9 76 50 C1 F1 D3 0F 62 F4 28 A3 46 19
```

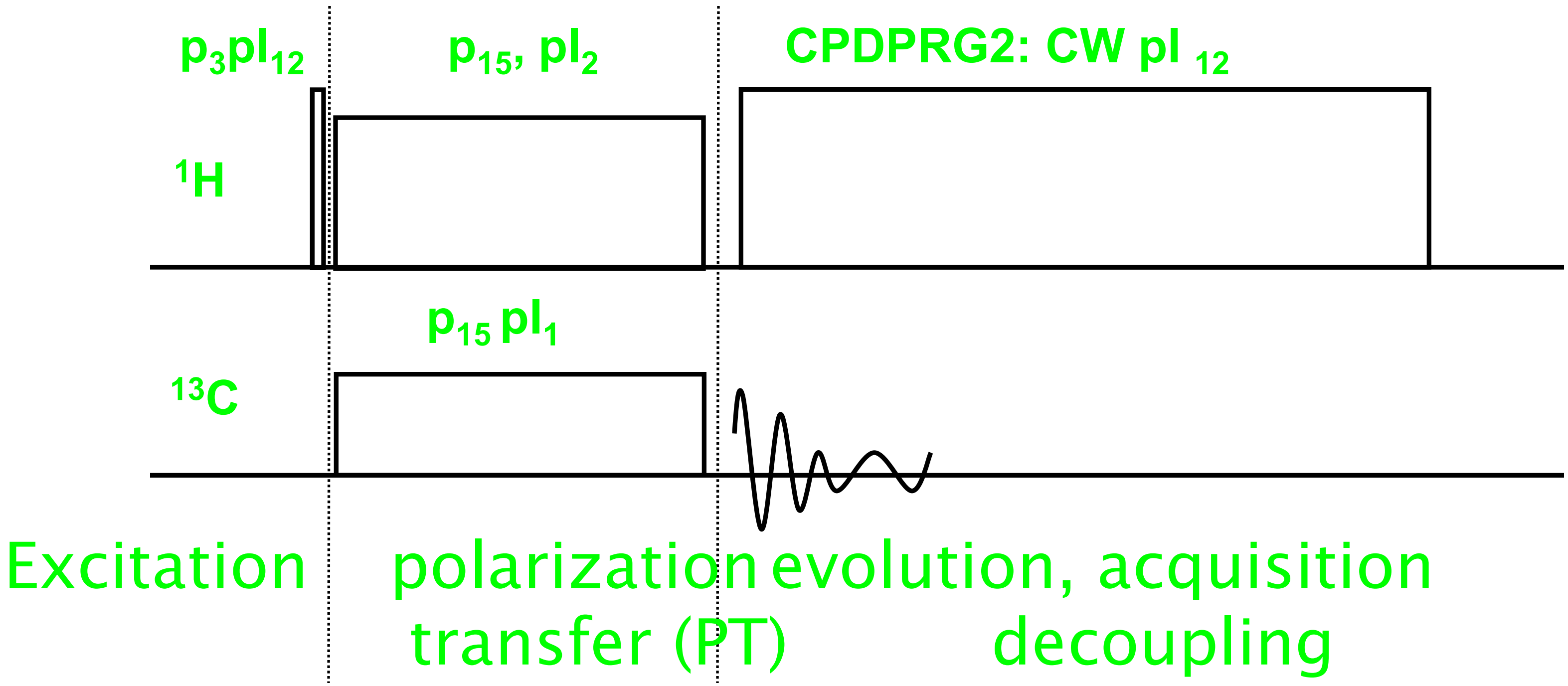
Setup Cross Polarization Experiments

- General setup for cross polarization cp experiment
  - Parameter set: C13CPMAS
  - Pulse program: cp.av or cp90.av
  - See header in pulse program.
  - Edit pulse program with: edcpul <pp-name>



Setup Cross Polarization Experiments

- General setup for cross polarization cp experiment
  - Conventions in solids CPMAS release pulse programs:



Setup Cross Polarization Experiments

- Conventions in release pulse programs:
  - f2 - ^{1}H channel, f1 - ^{13}C channel (observe)
  - f1 channel: pl1 for contact, pl11 for pulses etc after CP
  - f2 channel: pl2 for contact, spnam0 for shape, p3 at pl12 for excitation and heteronuclear decoupling, pl13 for homonuclear FSLG/PMLG decoupling, p15 for contact pulse width.
  - Other parameters: see header in pulse program.
  - Edit pulse program with: edcpul <pp-name>

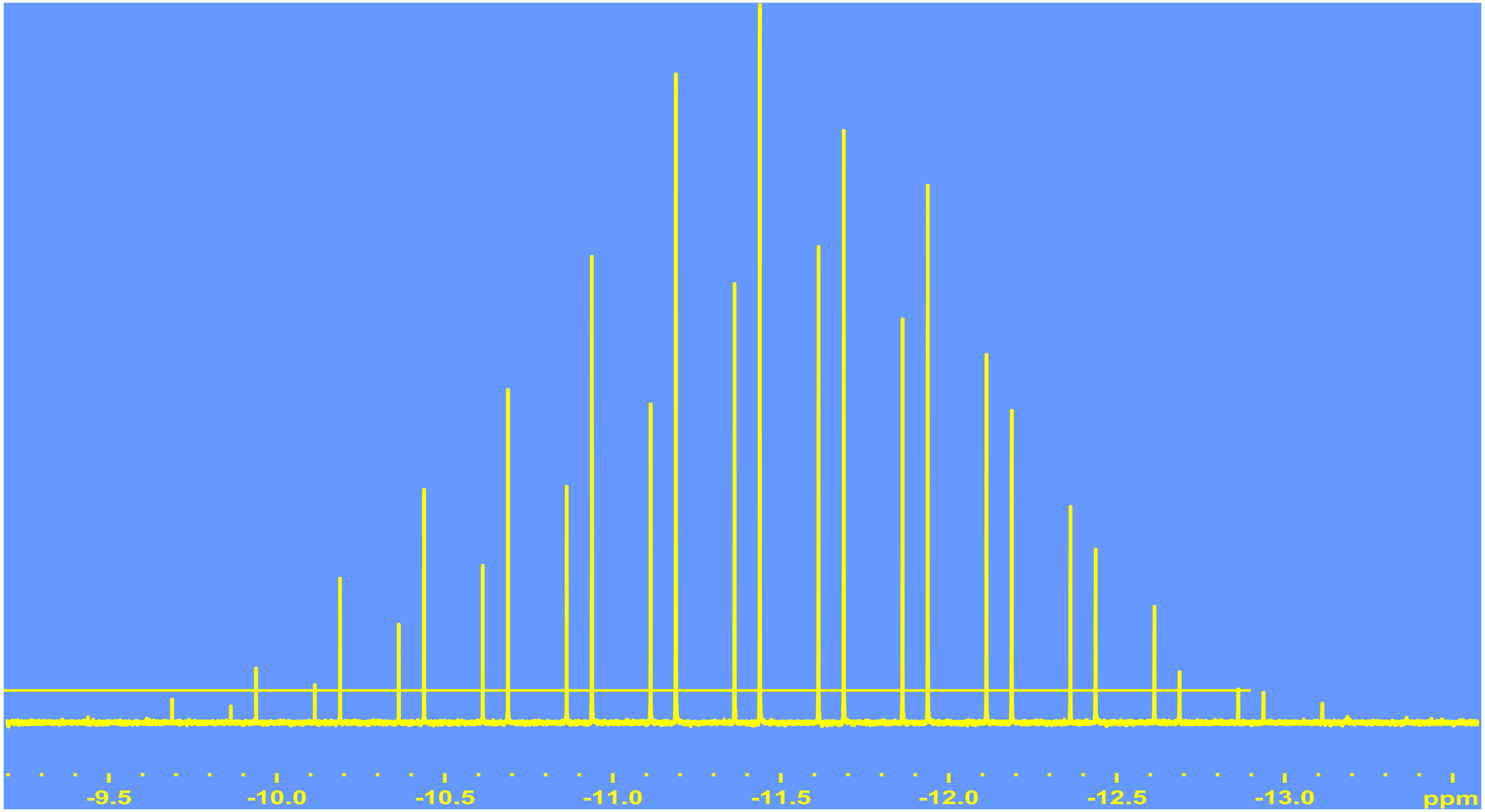
Setup Cross Polarization Experiments

- Setup from scratch:
  - Set the magic angle with KBr
  - Measure ^{1}H 4us pulse width on adamantane - spin as fast as probe permits.
  - Measure ^{13}C 4us pulses on adamantane with direct polarization using high power decoupling experiment with patameter set C13SOL, pulse program hpdec.av (spin 2 -3 kHz)

    ^{1}H decoupling pl12=pl(4us)+3dB permits 50ms<aq <0.5s.
  - Use obtained power levels and pulses for CP experiment load pulse program cp.av or cp90.av. Set p15=3-4ms
  - Optimize HH match with POPT on pl1 or pl2

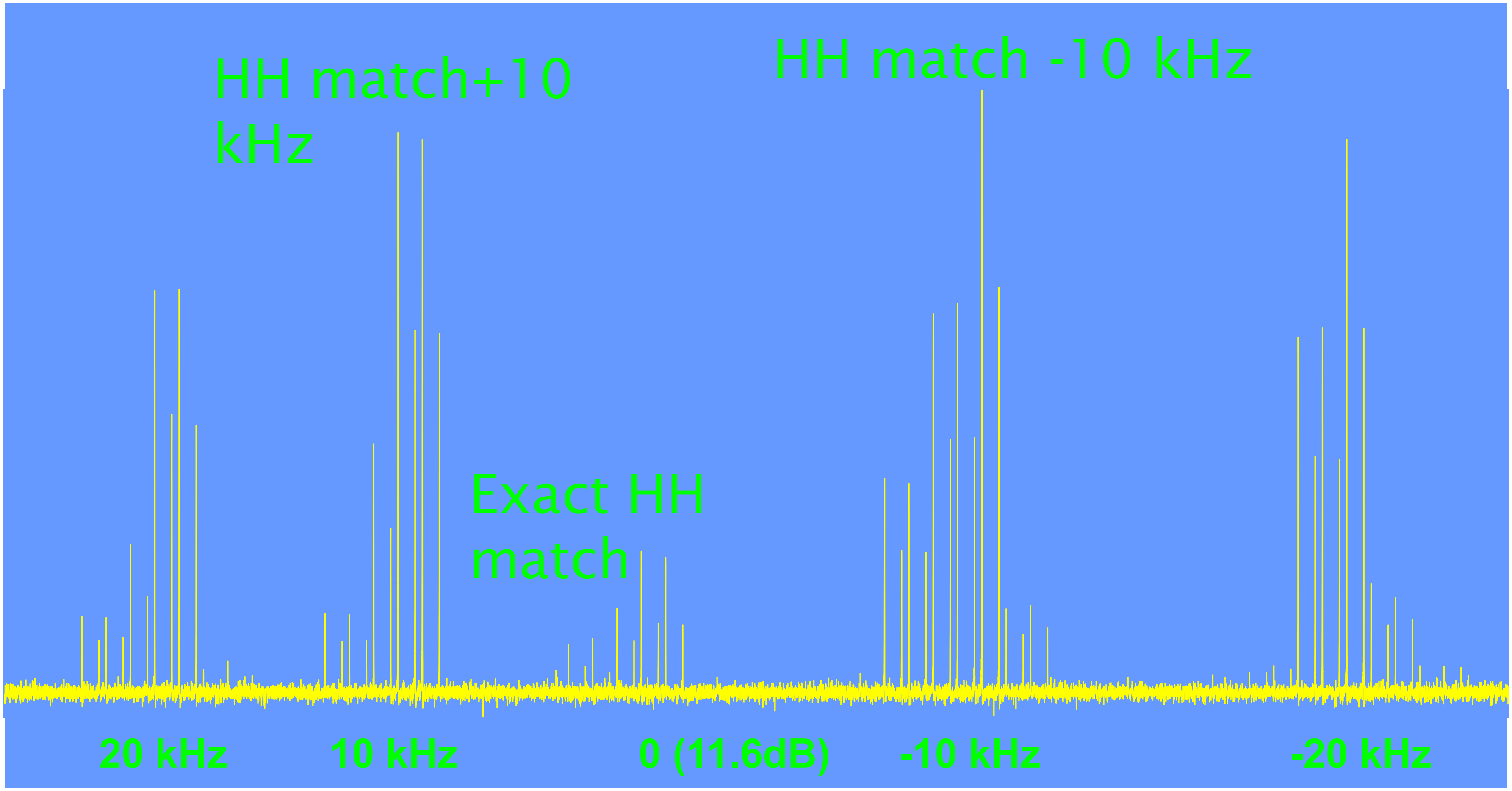
Setup Cross Polarization Experiments

- HH matching profile using POPT
  - Adamantane, 2 kHz spinning.



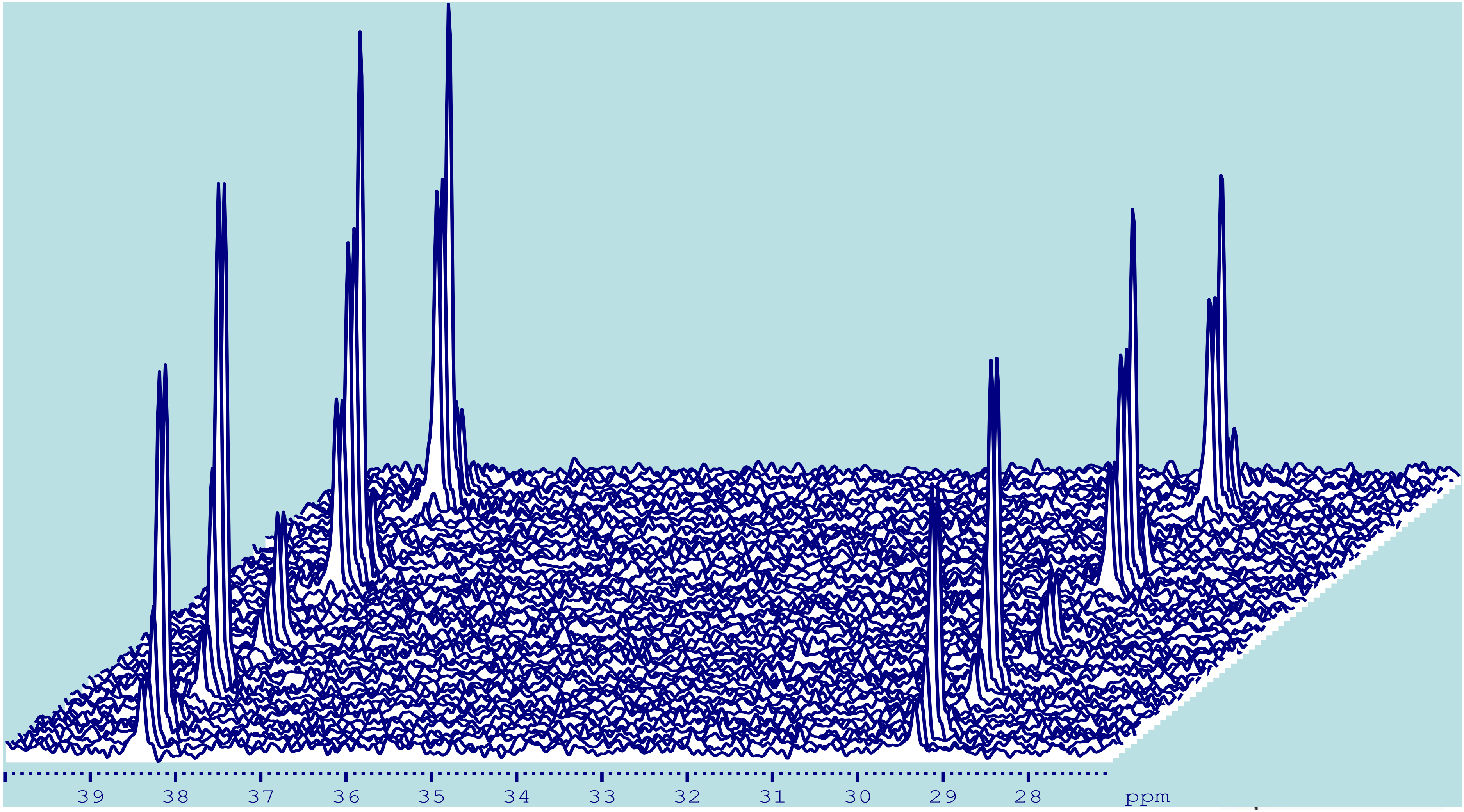
Setup Cross Polarization Experiments

- HH matching profile using POPT
  - Adamantane, 10 kHz spinning.



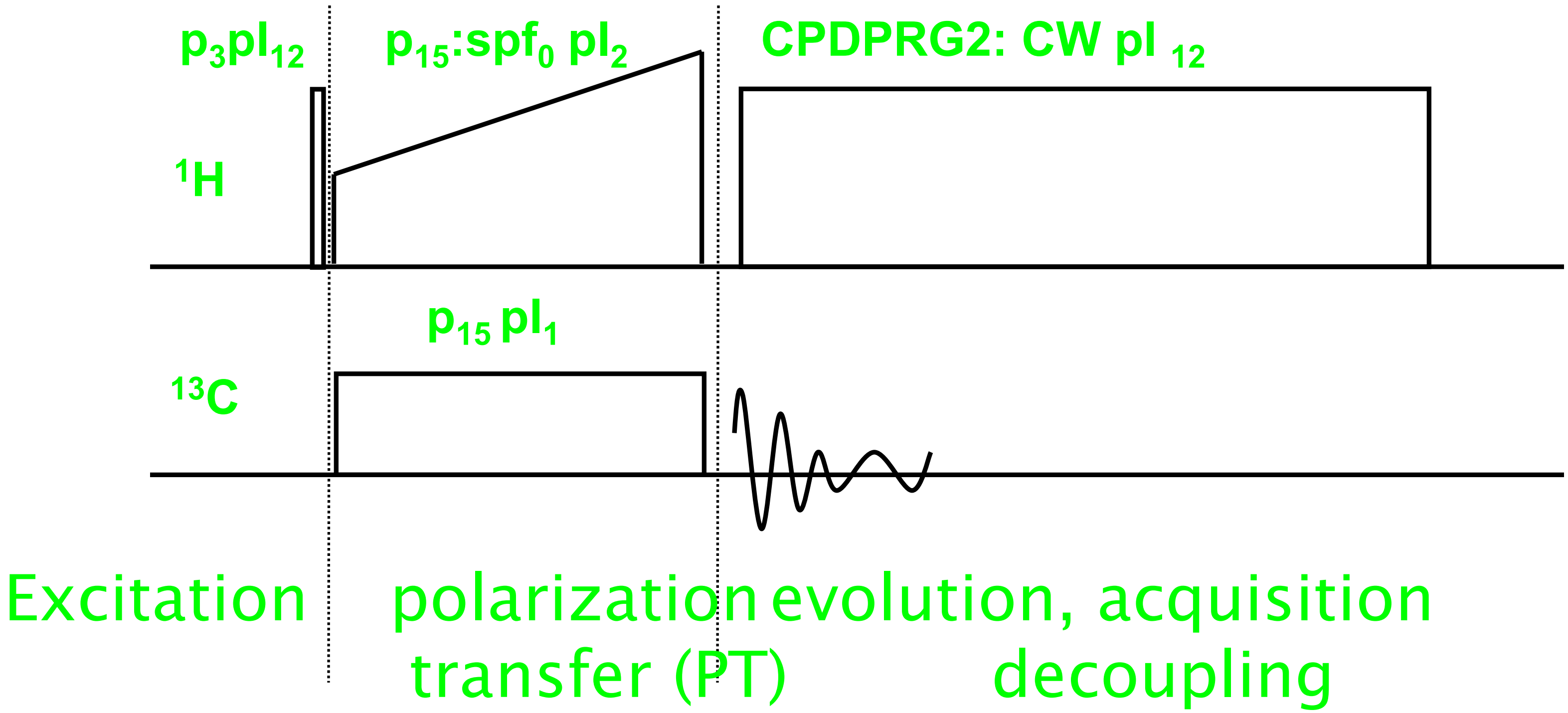
Setup Cross Polarization Experiments

- HH matching profile from pseudo 2D data (POPT)



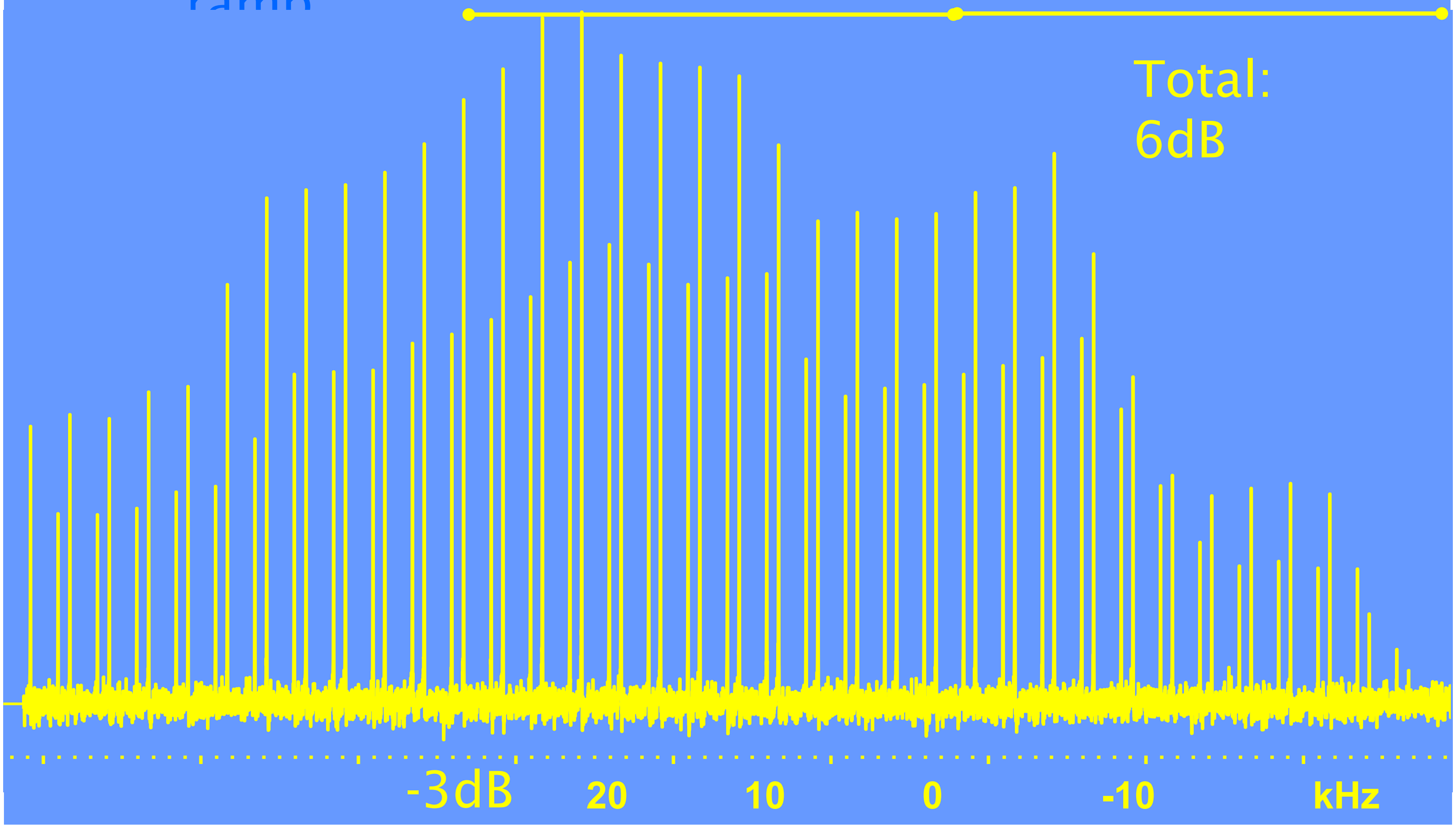
Setup Cross Polarization Experiments

- CP experiment using ramped rf-field during contact



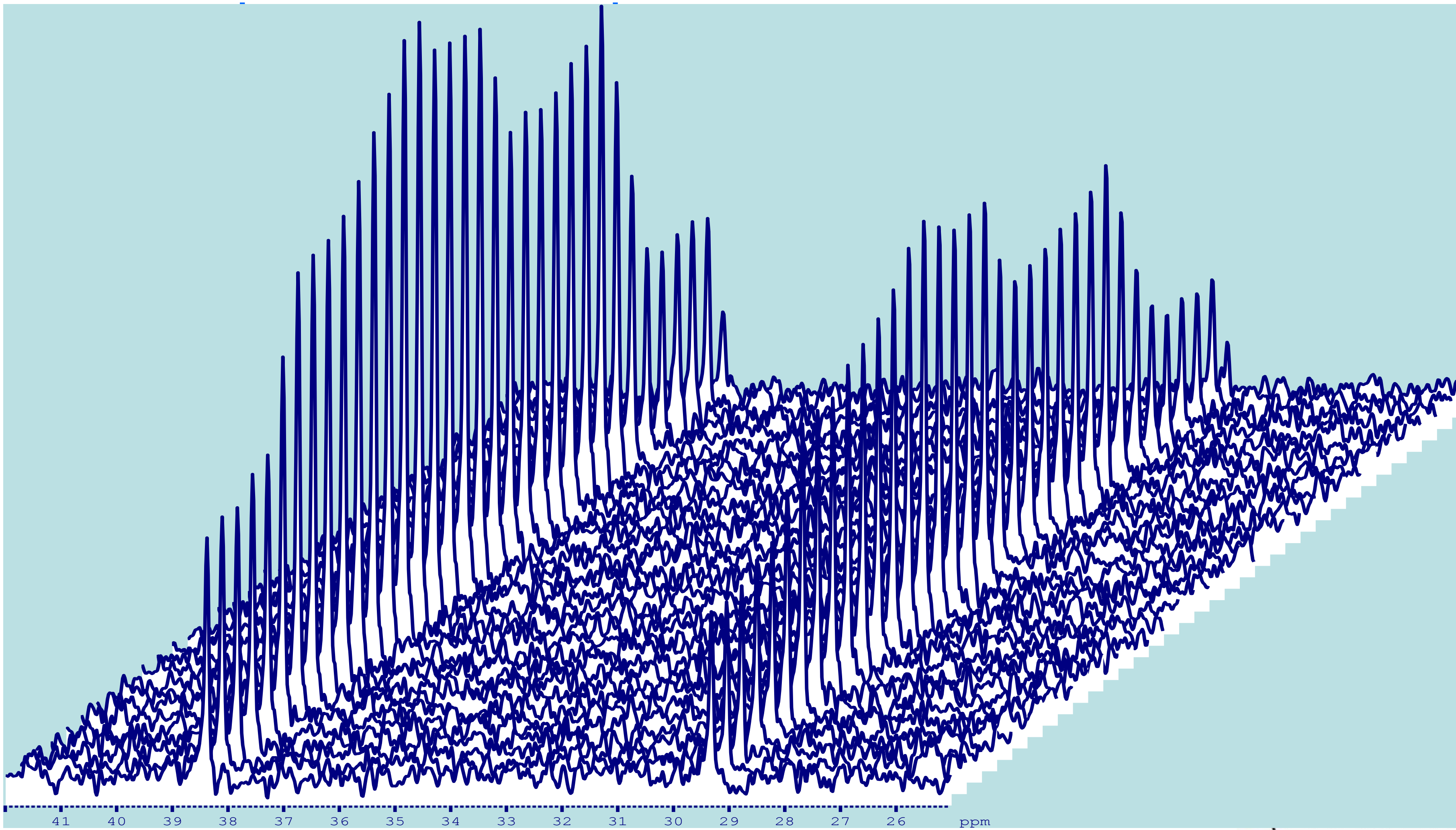
Setup Cross Polarization Experiments

- HH matching profile from POPT
  - Adamantane, 10 kHz spinning, with 50% ramp



Setup Cross Polarization Experiments

- HH matching profile from pseudo 2D data (POPT)



Setup Cross Polarization Experiments

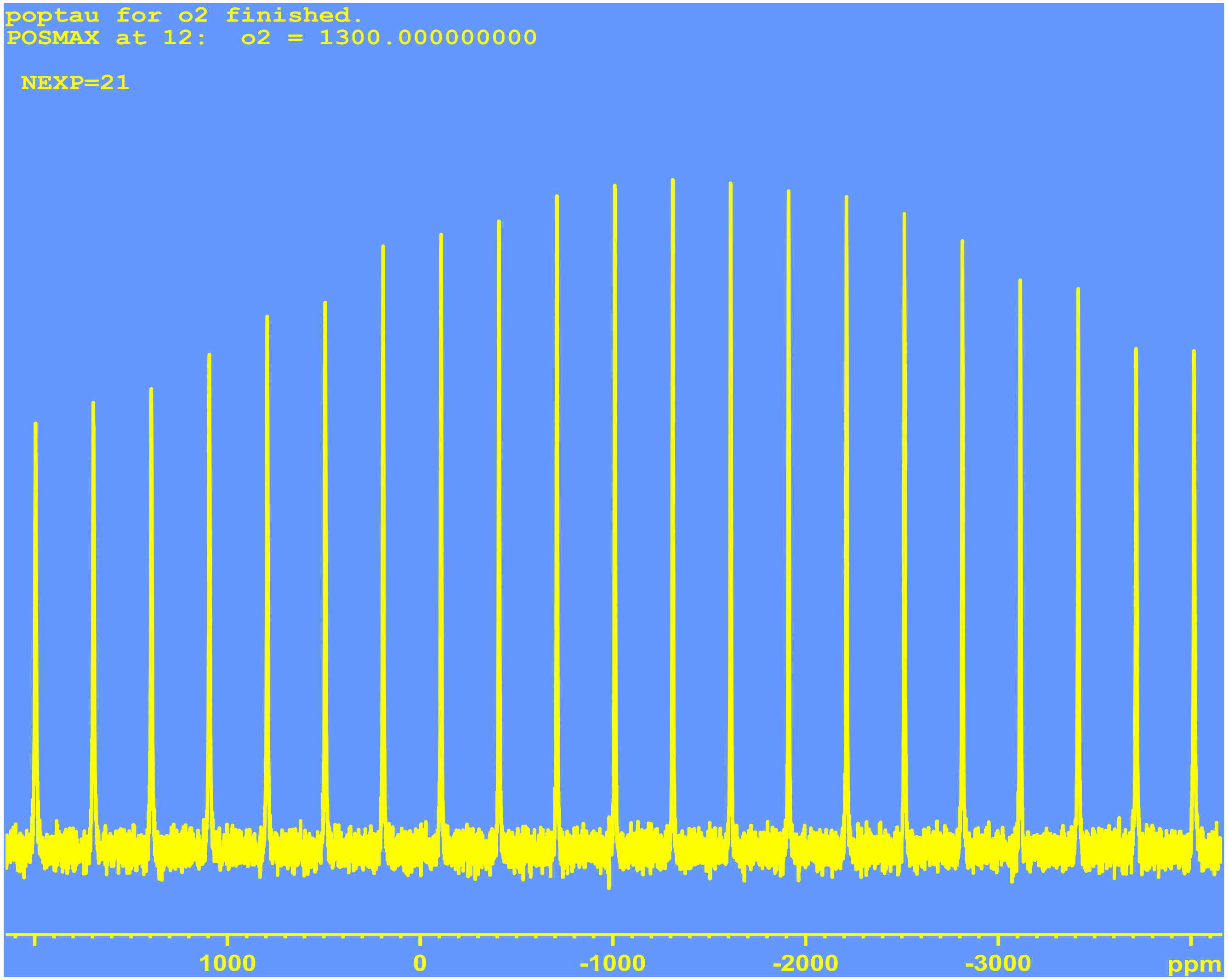
- General parameter optimization after initial setup with adamantane:
  - Determine HH match on glycine: load parameter set C13CPMAS
  - Measure p3 at pl12 (choose pl12 = pl2, if pl2 is the power level for a 4us pulse)
  - For followng steps with high decoupling power, use protection scheme to avoid acquisition time, aq>50ms.
  - Calculate required pulse width for maximum decoupling field in kHz
  - Calculate pl12 for p3=2.5us using au-program **`pulse`** on dummy experiment.
  - Verify that calculated pl12 gives p3 = 2.5us with POPT.
  - Optimize decoupling on Glycine - use POPT for proton carrier frequency o2, use steps <= 500 Hz

Decoupling, general remarks

- High power decoupling in solids is done by strong continuous on resonance rf irradiation.
- Decoupling becomes better with higher rf field strength.
  - Power limitations of high power decoupling
    - Sample heating
    - Probe arcing, probe destruction
- Decoupling is optimized if rf carrier is set on resonance

Setup Cross Polarization Experiments

Glycine, decoupling O2 dependence, aliphatic peak displayed in the POPT window:



Setup Cross Polarization Experiments

- Calculate maximum decoupling power
  - Get specification sheet, e.g. for widebore probes: 2.5mm 150kHz; 4mm 100 kHz; 7mm 70 kHz
  - e.g. max decoupling field is given 100kHz $p3 = \frac{1}{4 \bullet 100kHz} = 2.5\mu s$
  - Set power level 3 dB below that maximum and approach maximum slowly (1dB steps watching for arcing) (important if probe has not been used for a while).
- Use maximum decoupling power for Glycine setup

Setup Cross Polarization Experiments

- Problems of high power cw decoupling
  - cw irradiation has poor bandwidth
    - Particularly problematic at higher fields - CS dispersion
  - Power limitations
- Alternative decoupling schemes needed for more bandwidth and less power

Setup Cross Polarization Experiments

- For spectrometers of 400MHz and higher, improved heteronuclear decoupling is achieved by:
  - Time proportional phase modulation (TPPM)
    - Phase toggling for constant length with certain phase steps

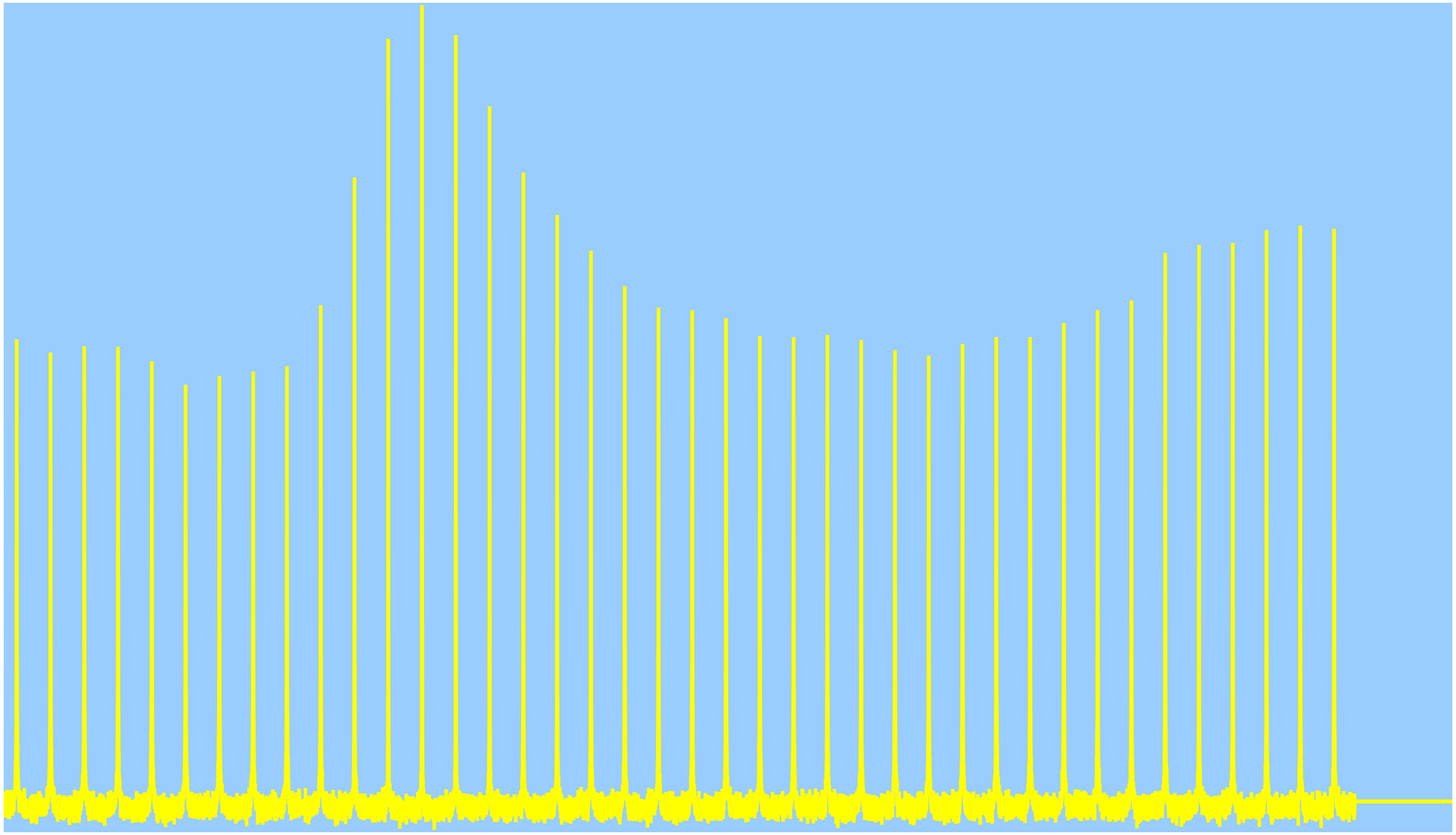
- e.g. CPD program TPPM15:

```
0.3u fq=cnst21
  0.5u pl=pl12
1 p31:0
  p31:15
  p31:0
  ..
  p31:0
  p30:15
jump to 1
```

    - Tip: p31 is approximately 180° pulse, e.g. for 100 kHz decoupling, p3 = 2.5 µs, p31 ~ 4.8 µs

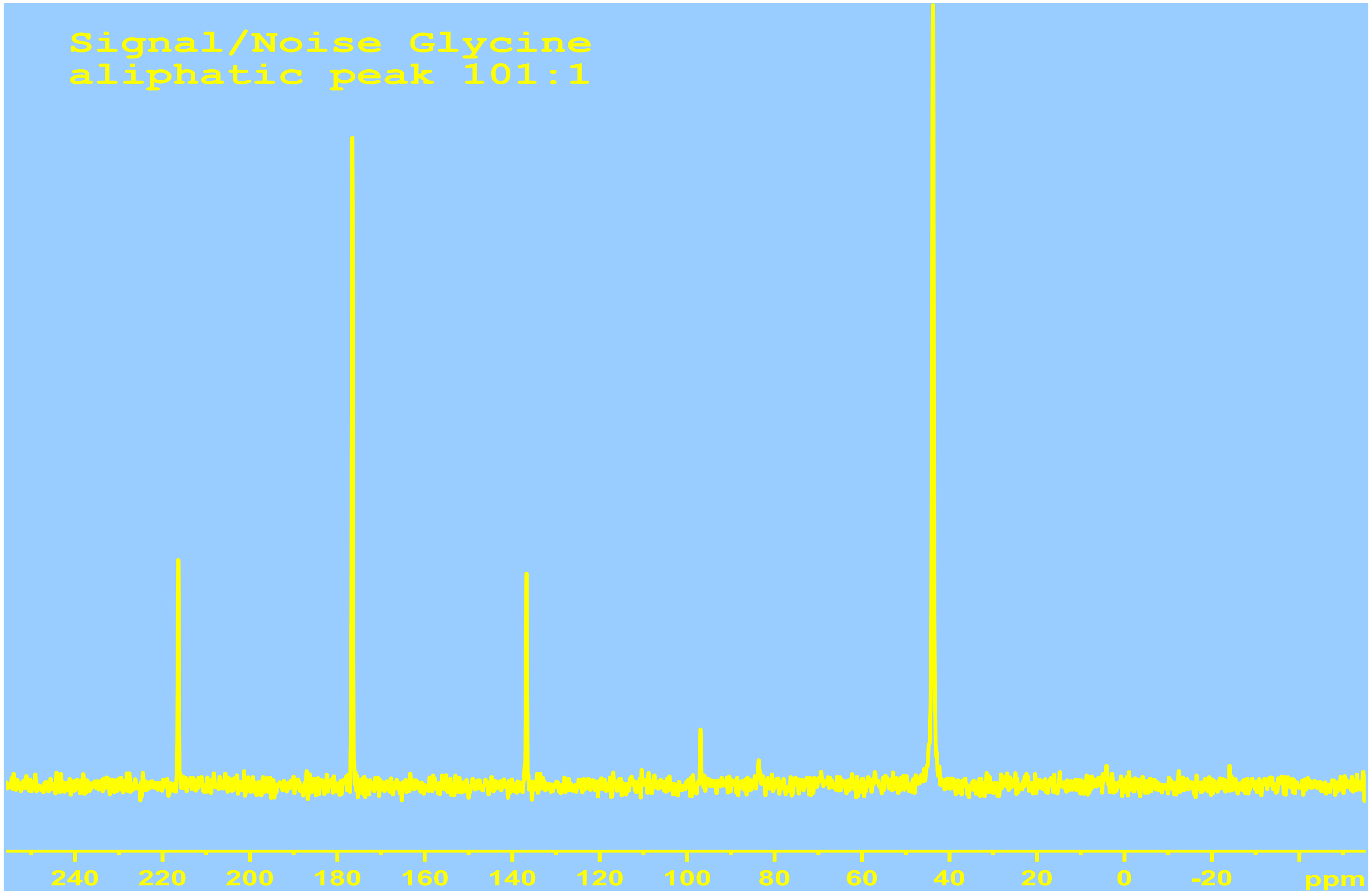
Setup Cross Polarization Experiments

- Optimize heteronuclear decoupling (TPPM)



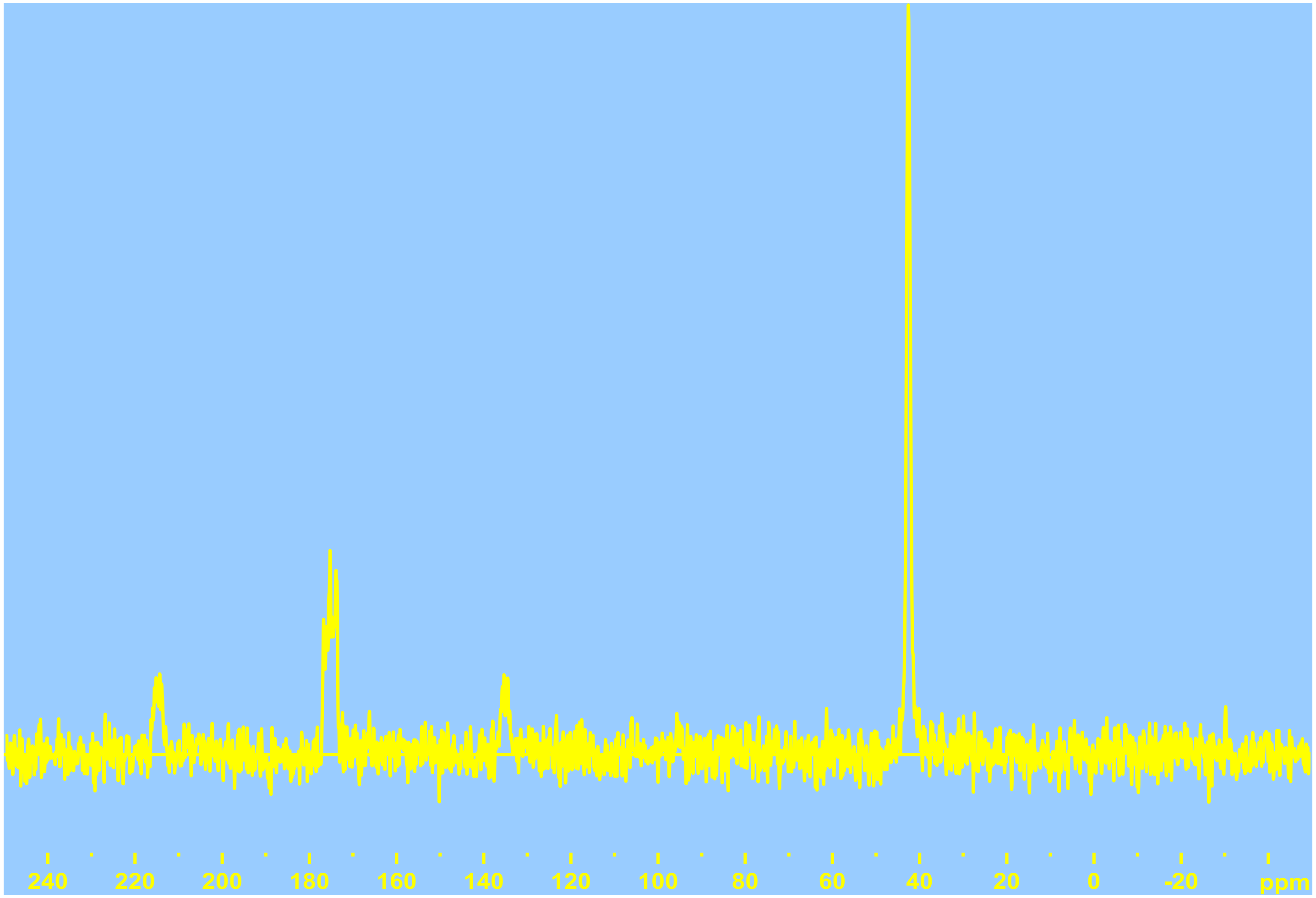
Setup Cross Polarization Experiments

Sensitivity measurement on glycine



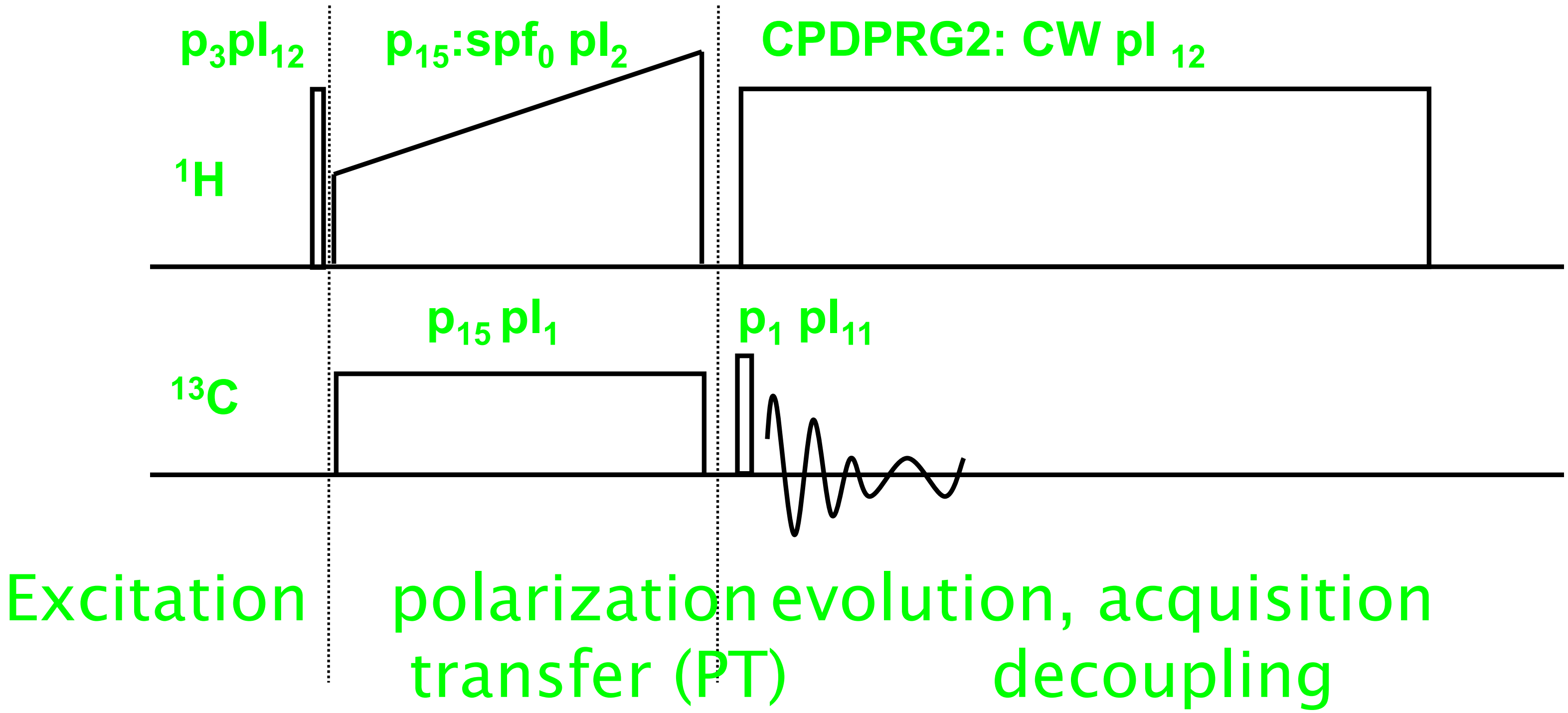
Setup Cross Polarization Experiments

Glycine Magic Angle > 1º off.



Setup Cross Polarization Experiments

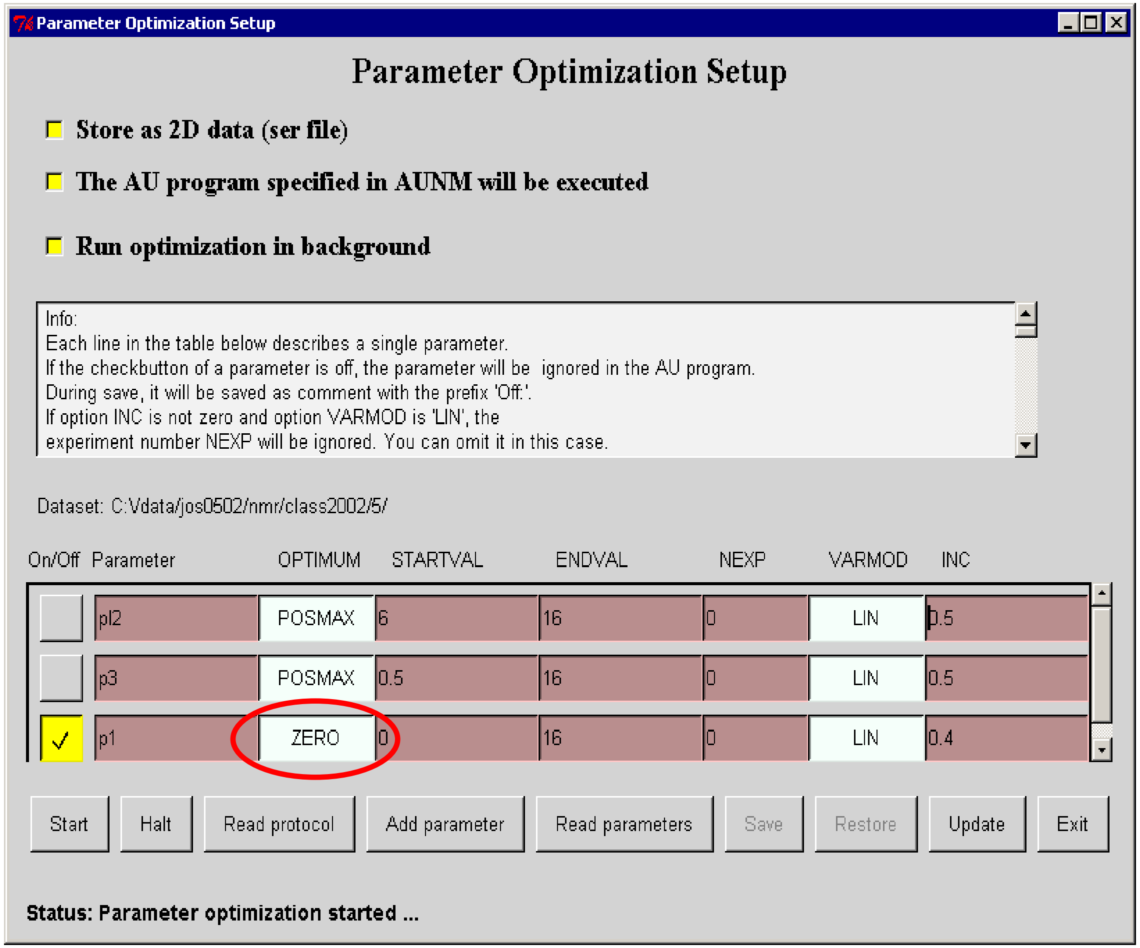
- Measuring pulse widths after polarization transfer
  - Pulse program cp90.av



Setup Cross Polarization Experiments

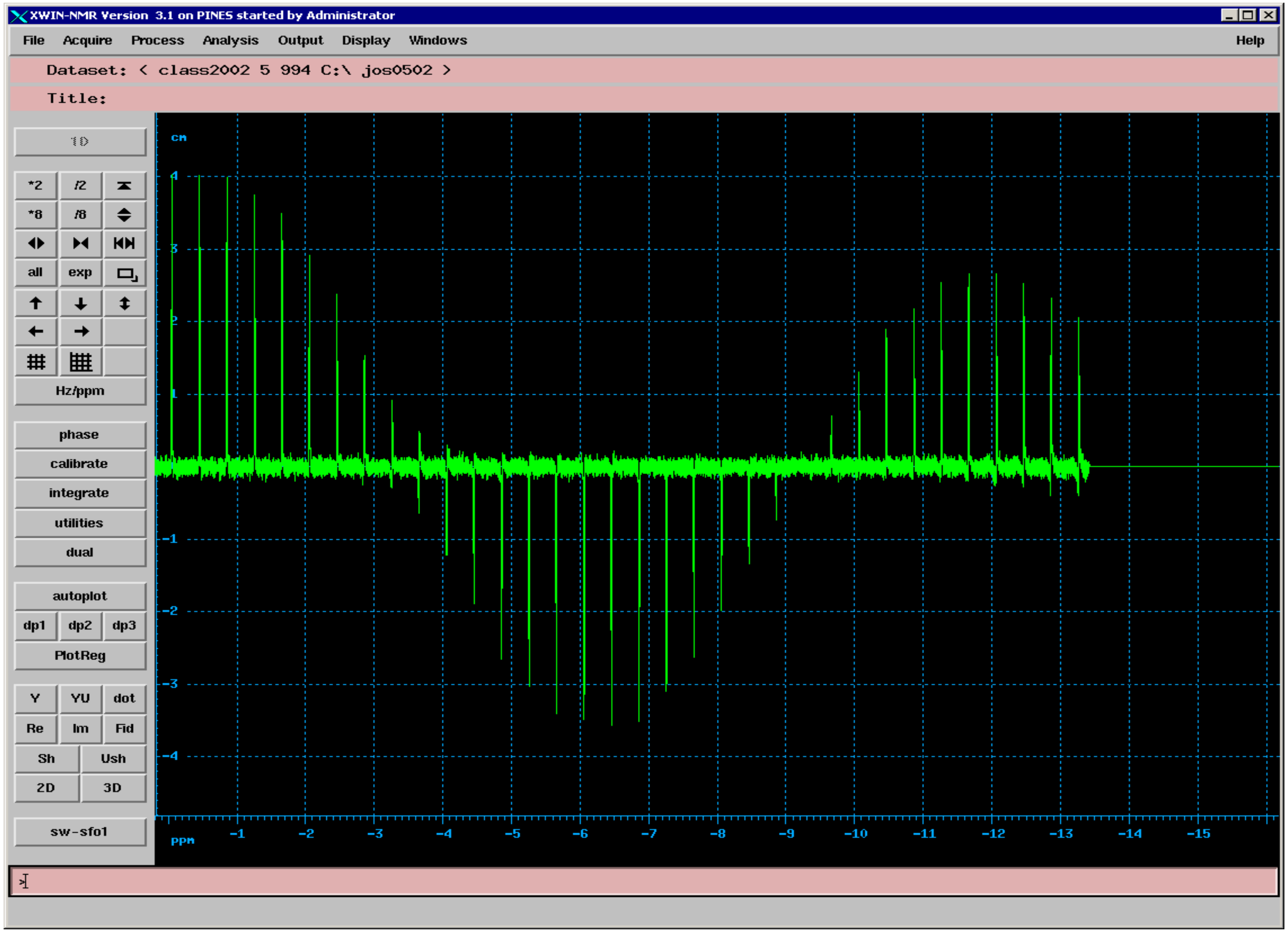
- Measure ^{13}C pulse p_1 with POPT: note a 90 degree pulse after CP with a phase orthogonal to the phase of the contact pulse results in ±z-magnetization!

- Therefore: Optimize for Zero signal.



Setup Cross Polarization Experiments

- POPT result,



Cross Polarization Experiments

- Pulse programming:

```
;cp.av basic cp experiment
;written by HF 1.3.2001
;set: p3 proton 90 at power level pl12
;cpdprg2 cw, tppm (at pl12), or lgs, cwlg. Cwlgs
  ;(LG-decouplinghere pl13 is used instead of pl12)

;d1 :recycle delay
;p3 :f2 90 deg pulse at pl12
;p15 :contact time at pl1 (f1) and pl2 (f2)
;p31 :pulse interval for CPD
;pl1 :f1 power level for CP
;pl2 :f2 power level for CP
;pl12 :f2 power level for 90 deg + decoupling
;pl13 :f2 power level in case of LG decoupling
;cnst20 :decoupling RF field in Hz
;cnst24 :additional LG-offset
```

Cross Polarization Experiments

- Pulse programming:

```
#include <lgcalc.incl>
"p30=p31-0.4u"
#include <trigg.incl>
;10 usec trigger pulse at TCU connector I cable 6

#include <Avancesolids.incl>

1 ze                 ;accumulate into an empty memory
2 d1 do:f2           ;recycle delay, decoupler off
  #include <prp15.prot>
           ;make sure p15 does not exceed 10 msec
  #include <praq.prot>
  ;allows max. 50 msec acquisition time, nmrsu
;may change  to max. 1s at less than 5 % duty cycle
;and reduced decoupling field
```

Cross Polarization Experiments

- Pulse programming:

```
 1u fq=cnst21:f2
  10u pl12:f2 pl1:f1      ;pl12 for F2, pl1 for F1
  trigg                   ;trigger for scope, 10 usec
  p3:f2 ph1         ;proton 90 pulse
  0.3u
  (p15 ph2):f1 (p15:spf0 pl2 ph10):f2
              ;contact pulse with square or ramp
              ;shape on F2, at pl2 proton power level

  1u cpds2:f2
    ;pl12 is used here with tppm, pl13 with cwlg, cwlgs
  go=2 ph31
  1m do:f2          ;decoupler off
  wr #0             ;save data to disk
HaltAcqu, 1m        ;jump address for protection files
exit                ;quit
```

Cross Polarization Experiments

- Protection schemes:

```
#include <prp15.prot>
                    ;make sure p15 does not exceed 10 msec
    #include <praq.prot>
    ;allows max. 50 msec acquisition time, nmrsu
;may change  to max. 1s at less than 5 % duty cycle
;and reduced decoupling field


   wr #0                         ;save data to disk
HaltAcqu, 1m             ;jump address for protection files
exit                     ;quit
```

Cross Polarization Experiments

- Protection schemes:

```
#include <prp15.prot>
            ;make sure p15 does not exceed 10 msec
#include <praq.prot>
;allows max. 50 msec acquisition time, nmrsu
;may change  to max. 1s at less than 5 % duty cycle
;and reduced decoupling field


  wr #0                    ;save data to disk
HaltAcqu, 1m         ;jump address for protection files
exit                 ;quit
```

Cross Polarization Experiments

- Protection schemes:

```
#include <prp15.prot>
            ;make sure p15 does not exceed 10 msec
#include <praq.prot>
  ;allows max. 50 msec acquisition time, nmrsu
;may change  to max. 1s at less than 5 % duty cycle
;and reduced decoupling field


  wr #0                        ;save data to disk
HaltAcqu, 1m            ;jump address for protection files
exit                    ;quit
```

END first day

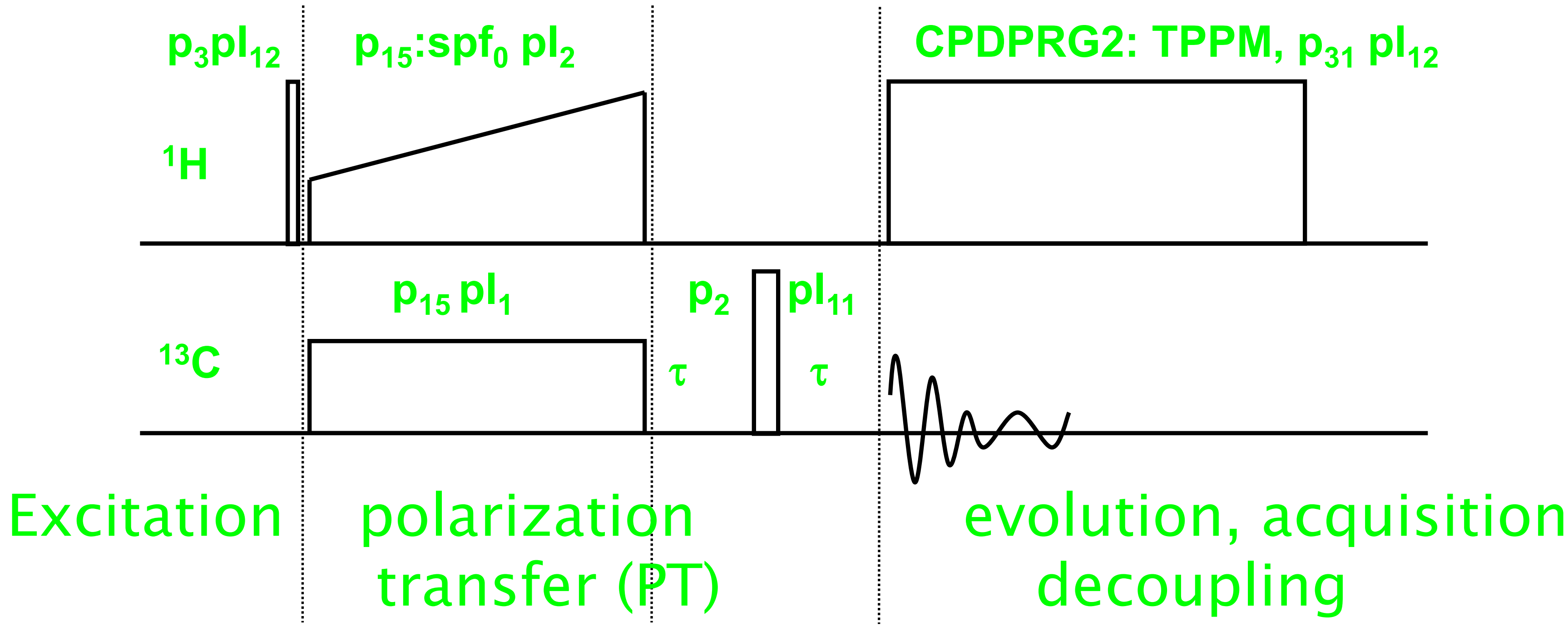
Advanced CP Experiments

- Various experiments:
  - Variable spinning speed experiments
    - Use au program: multimas
  - Variable Contact time experiments
    - Pulse sequence: cpvc.av or cp4cvc.98
  - Spinning sideband suppression:
    - Pulse sequences: cptoss.av or cp4ctossa.98, cptossb.98

      cpseltics.av or cp4cseltics.98
  - Non Quarternary suppression:
    - Pulse sequence: cpnqs.av or cp4cnqs.98

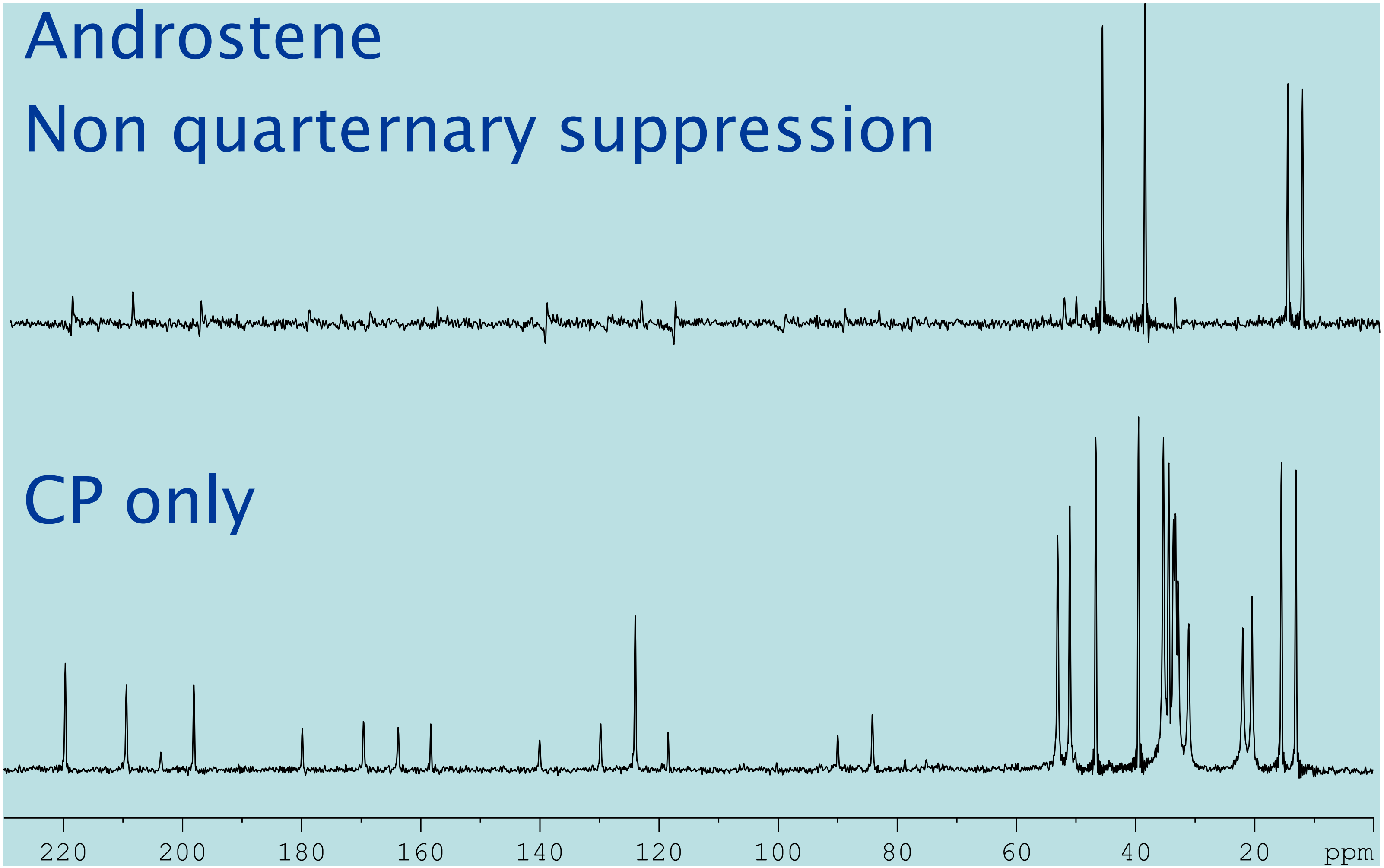
Advanced CP Experiments

- Non quarternary suppression or dipolar dephasing experiment



Advanced CP Experiments

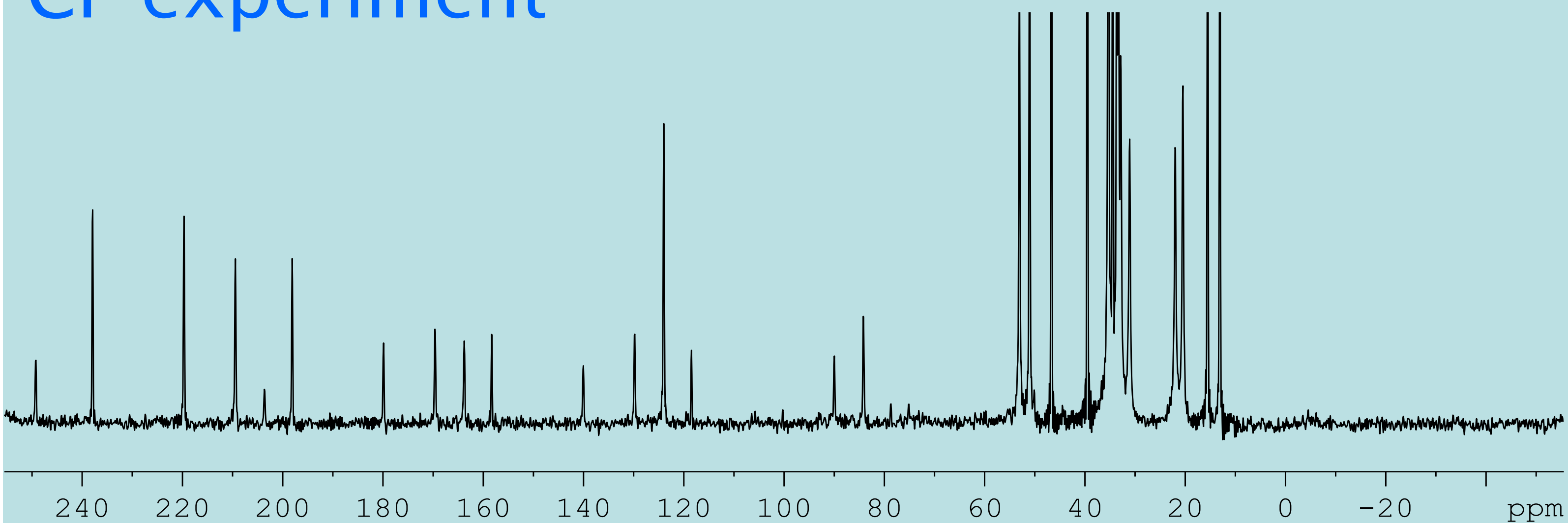
- Androstene



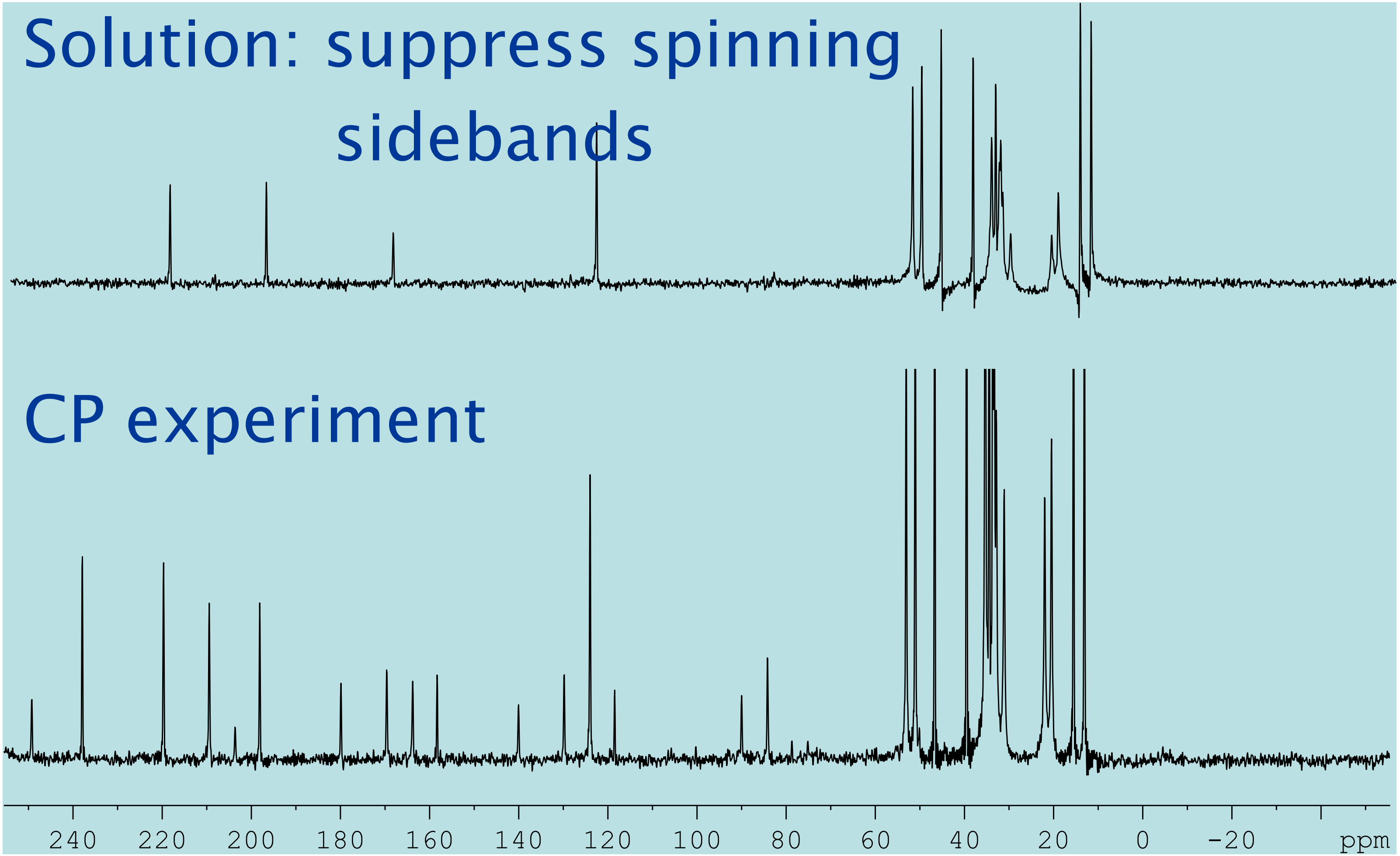
Advanced CP Experiments

- Problem: through spinning sidebands too crowded spectra:

CP experiment

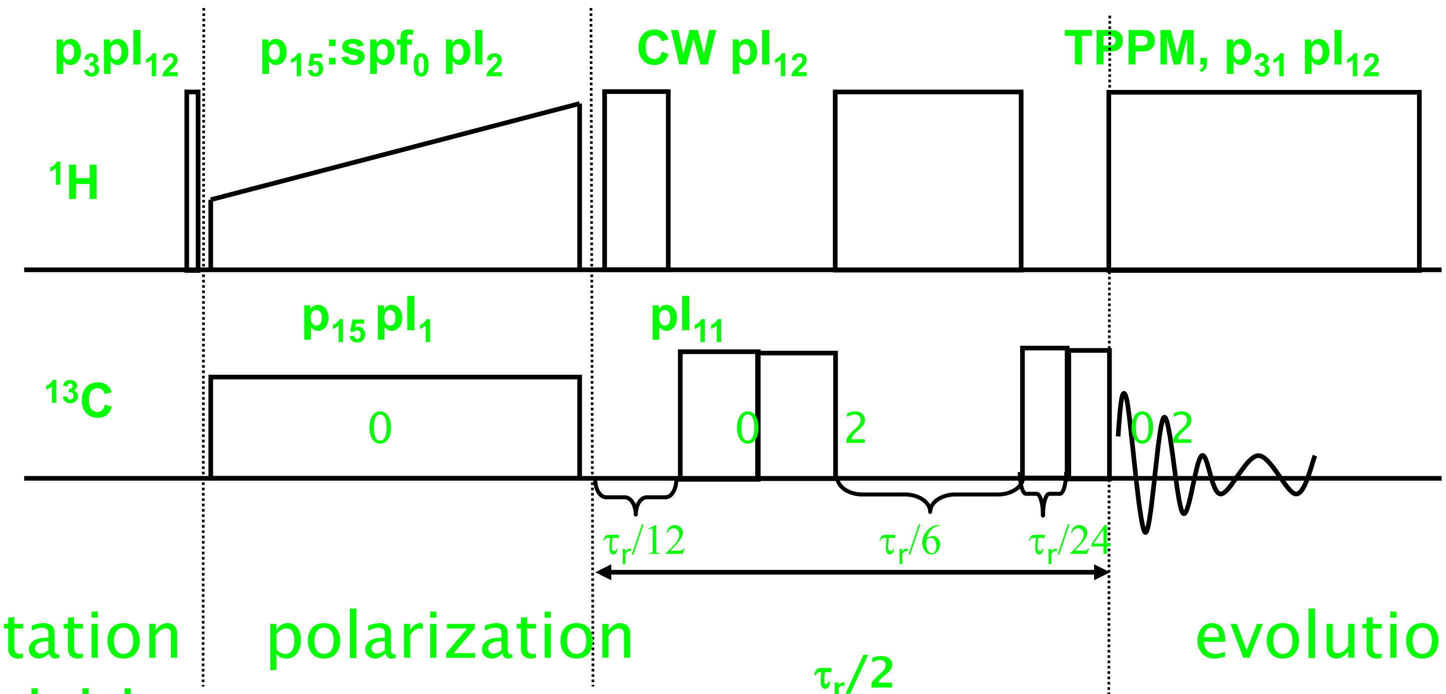


Advanced CP Experiments



Advanced CP Experiments

- Seltics



Excitation

acquisition

polarization

transfer (PT)

evolution,

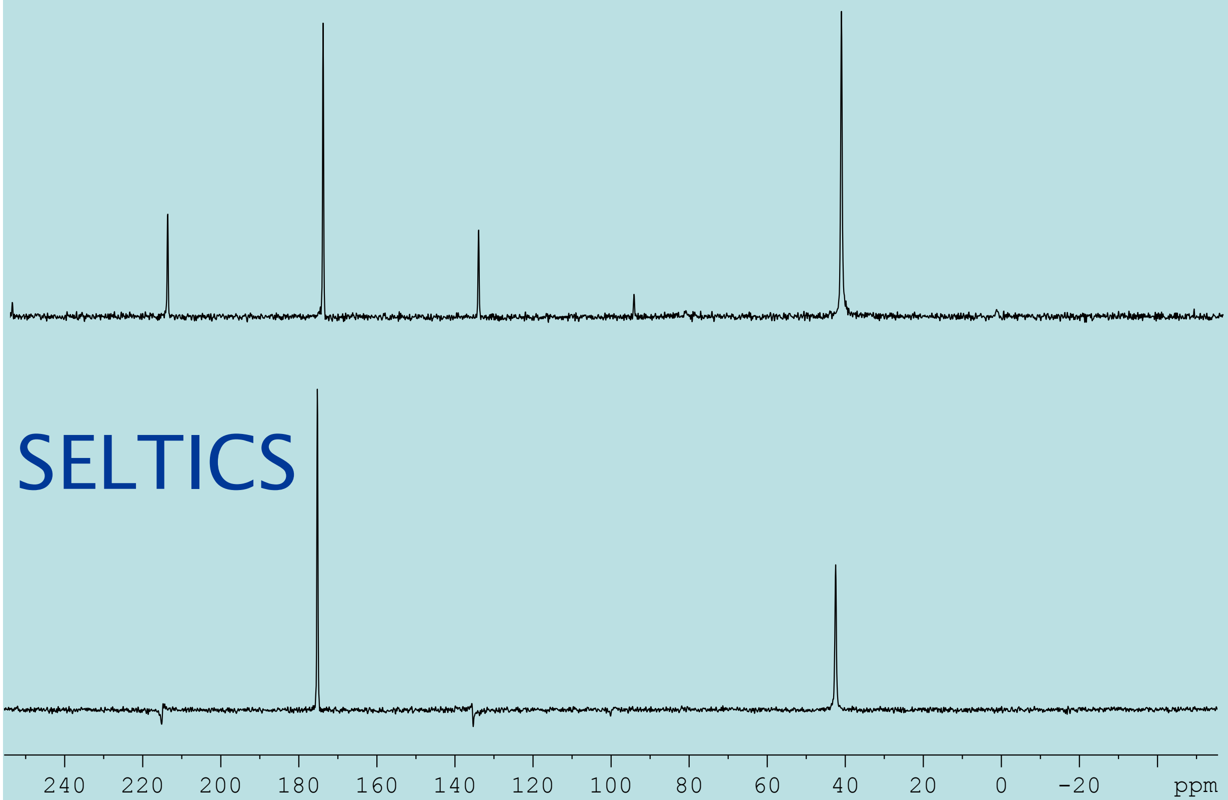
decoupling

Advanced CP Experiments

- Glycine CP

Class June 2001

Sample: Glycine
Rotation rate: 5kHz
SELTICS



SELTICS

Current Data Parameters
NAME class
EXPNO 300
PROCNO 1

F2 - Acquisition Parameters
Date_ 20010604
Time 11.49
INSTRUM spect
PROBHD 4 mm MAS 1H/BB
PULPROG cp
TD 2176
SOLVENT chcl3
NS 5
DS 0
SWH 39062.500 Hz
FIDRES 17.951517 Hz
AQ 0.0279156 sec
RG 512
DW 12.800 usec
DE 6.00 usec
TE 373.0 K
D1 10.00000000 sec

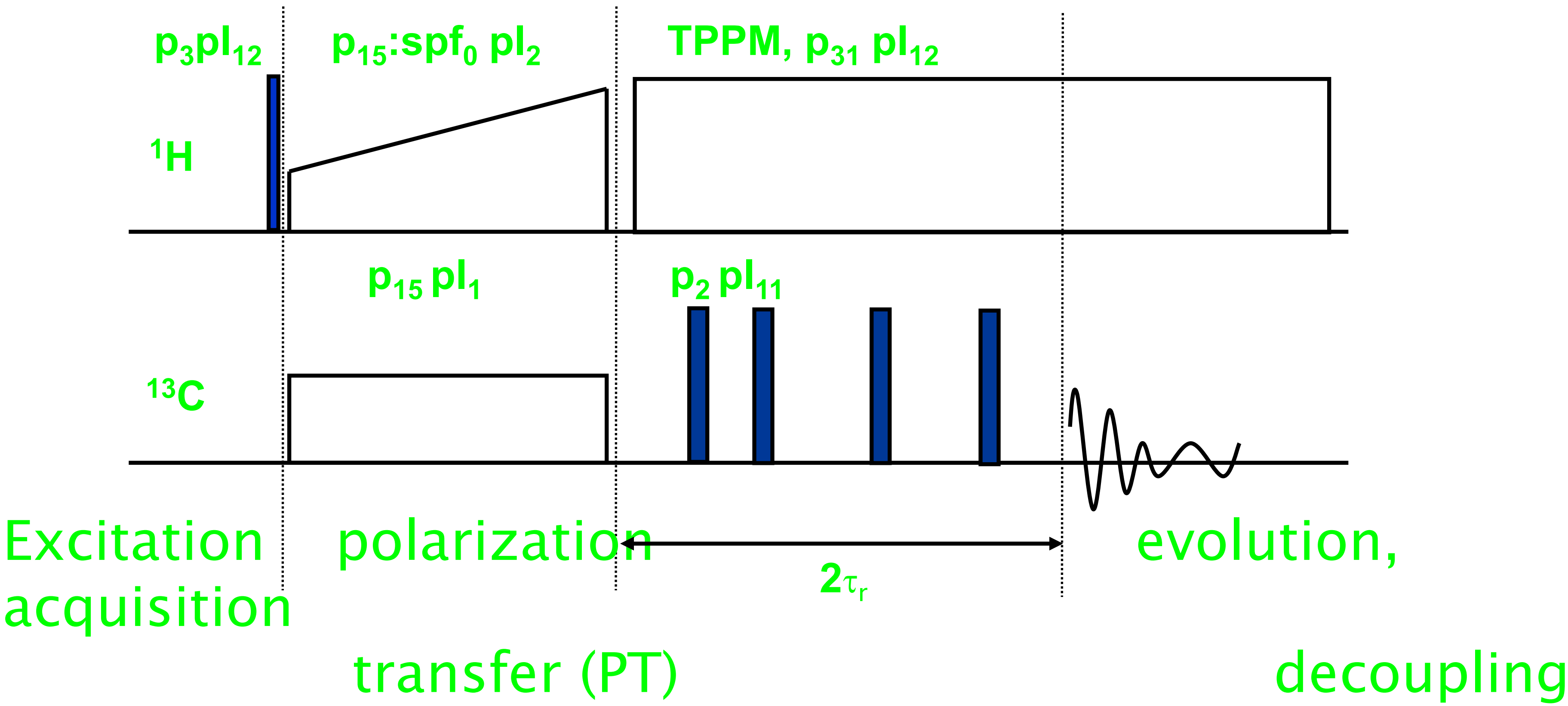
======== CHANNEL f1 ========
NUC1 13C
P15 1000.00 usec
PL1 12.10 dB
SFO1 125.6118849 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
FQ1LIST freqlist
NUC2 1H
P3 3.00 usec
P31 6.00 usec
PL2 120.00 dB
PL12 4.00 dB
SFO2 499.5012500 MHz
SP0 -1.00 dB
SPNAM0 ramp.64
SPOFF0 0.00 Hz

F2 - Processing parameters
SI 4096
SF 125.5993250 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

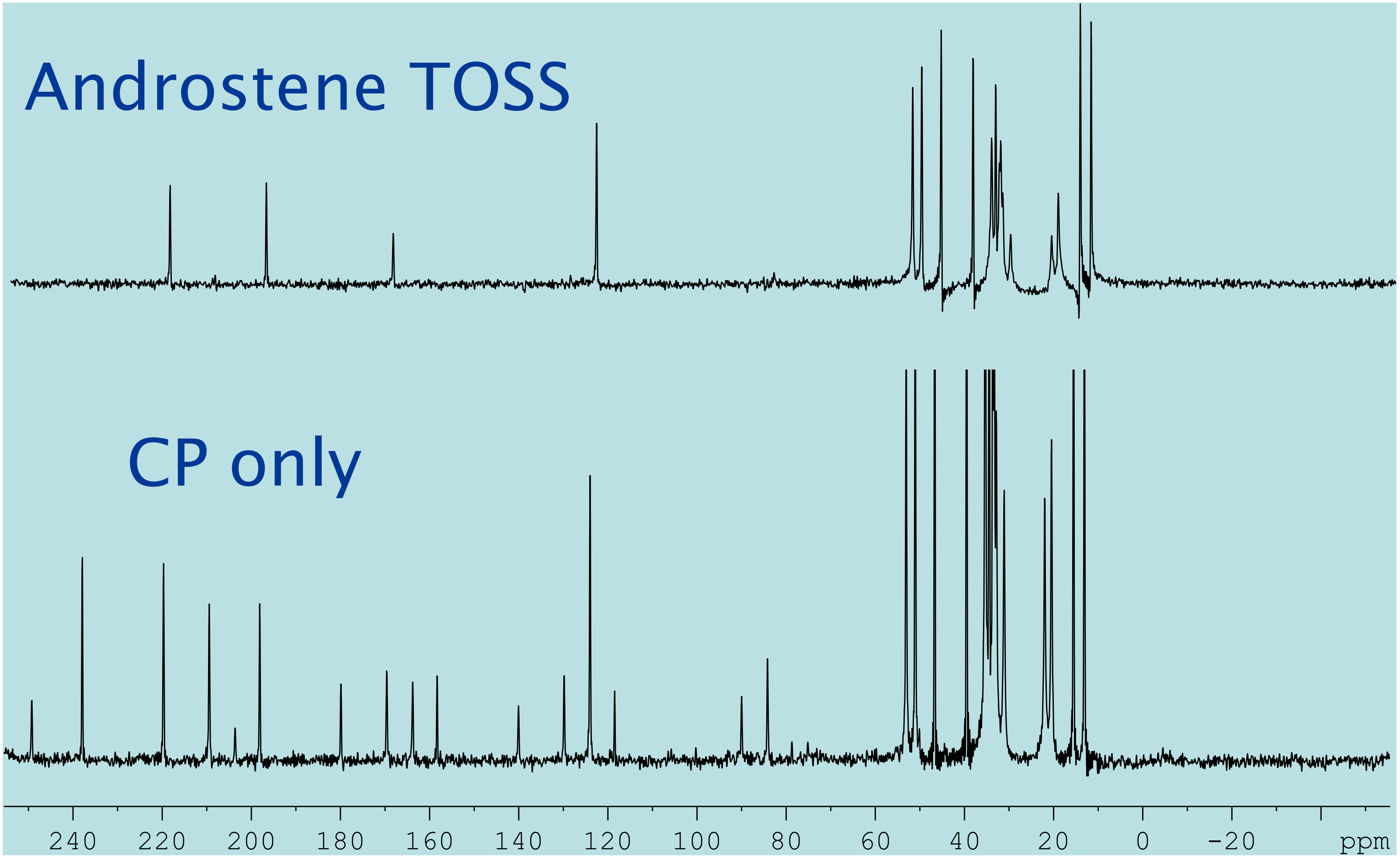
Advanced CP Experiments

- TOSS



Advanced CP Experiments

- Androstene TOSS



Advanced CP Experiments

- Relaxation- and other pseudo 2D experiments
  - Using POPT
  - Using 2D pulse program 2D parameter set and
    - Variable delay or variable pulse list

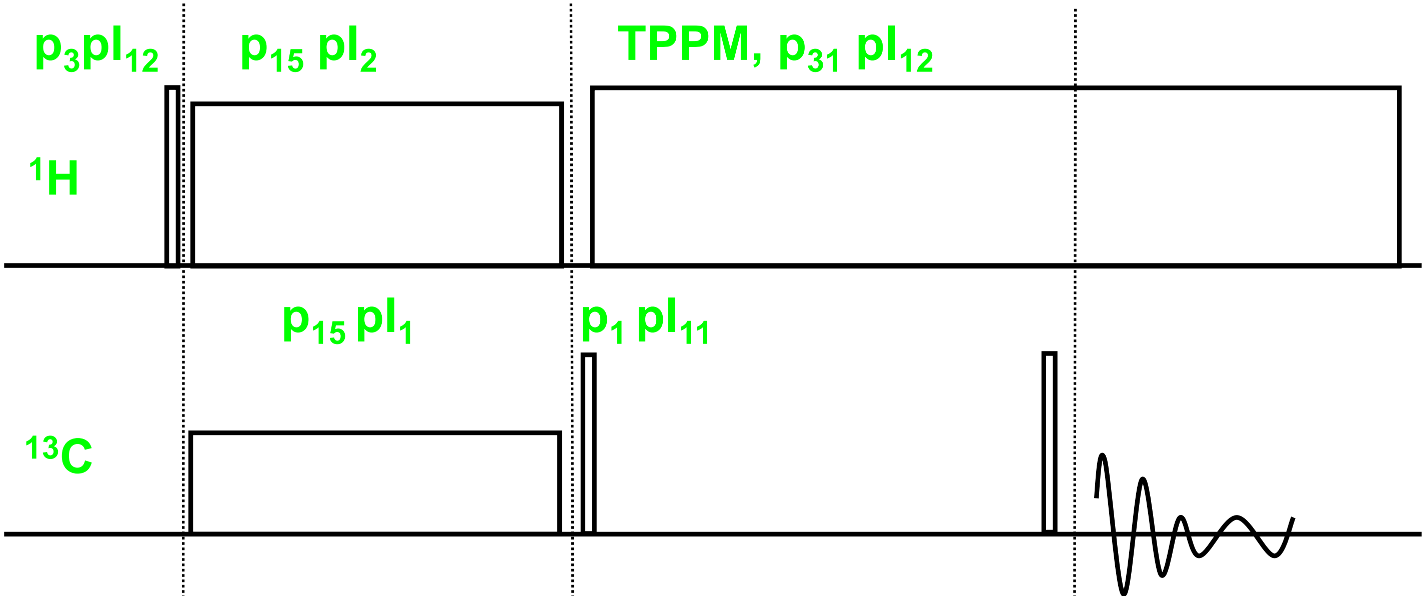
Advanced CP Experiments

- Lists are in the 'lists' directory, where also pp etc resides
  - Lists are textfiles,
    - delay lists (vdlist) units is seconds
    - Variable pulse lists (vplist) unit is us

Variable delay list	Variable pulse list
4m	400u
16m	1600u
10m	1m
6m	3m
4m	5m
10m	10m
17m	15m
11m	18m
18m	30m
12m	

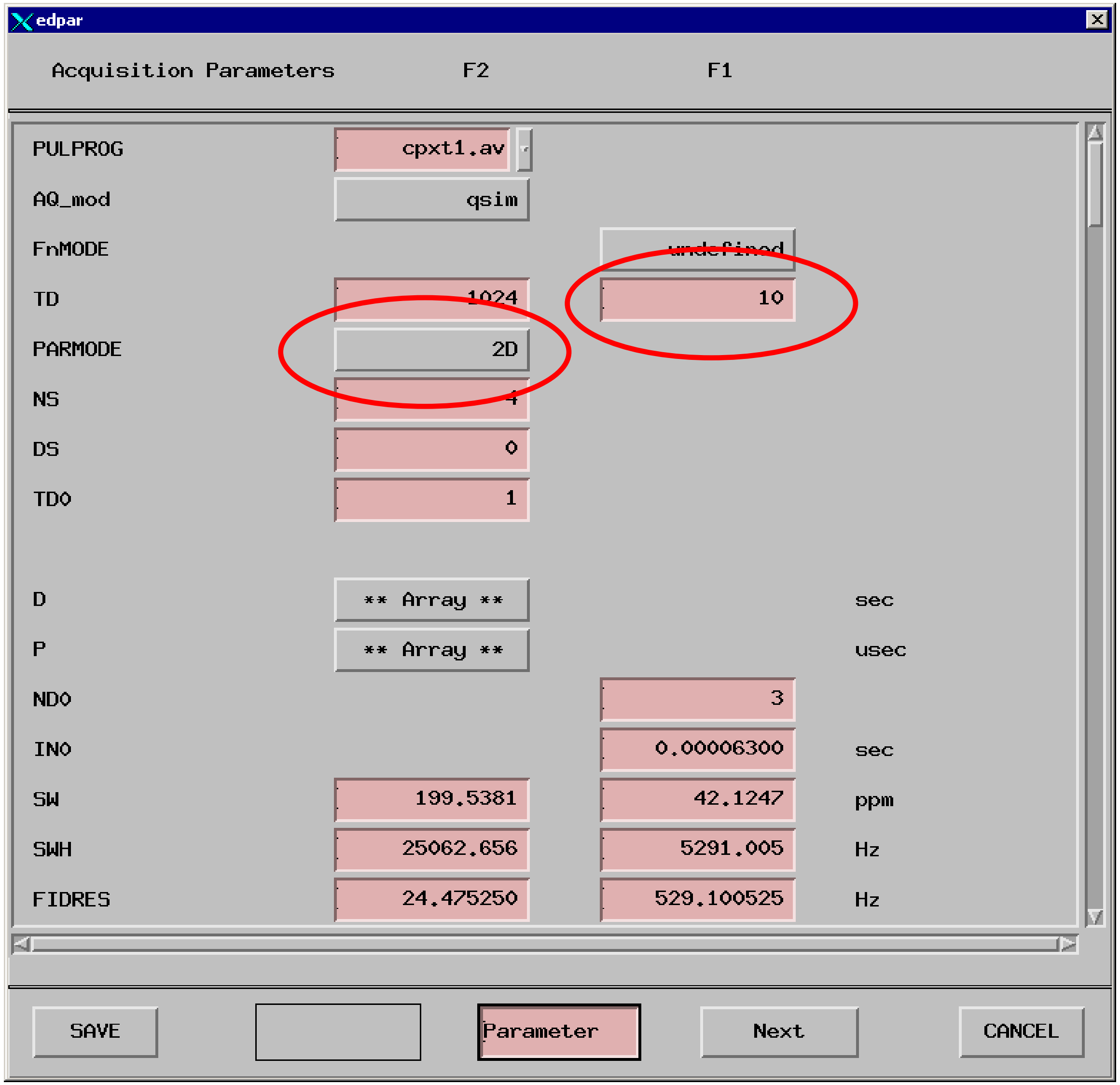
Relaxation Experiments

- T_1 relaxation experiment ^{13}C:

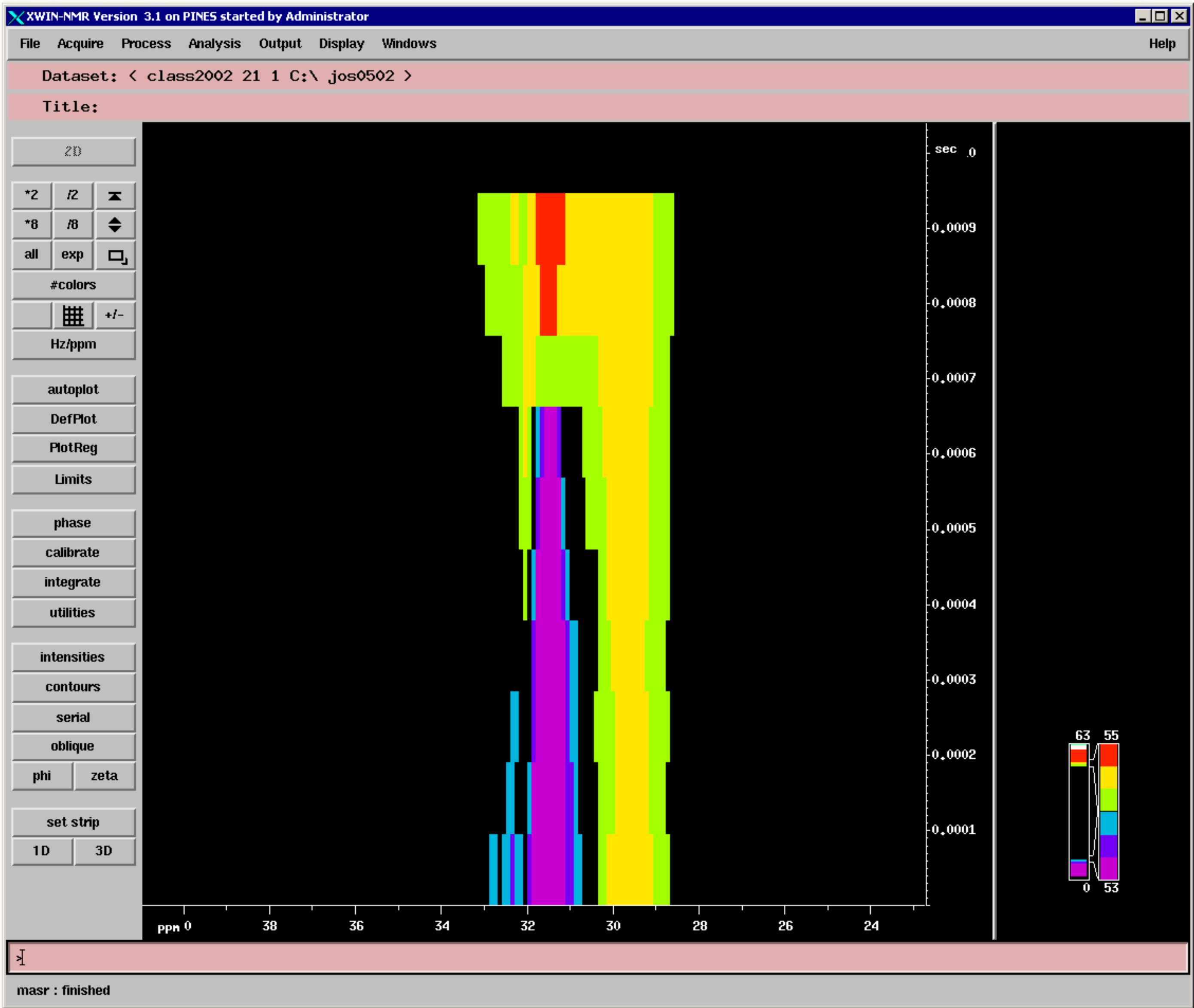


Excitation | polarization transfer (PT) | relaxation delay | evolution, acquisition decoupling

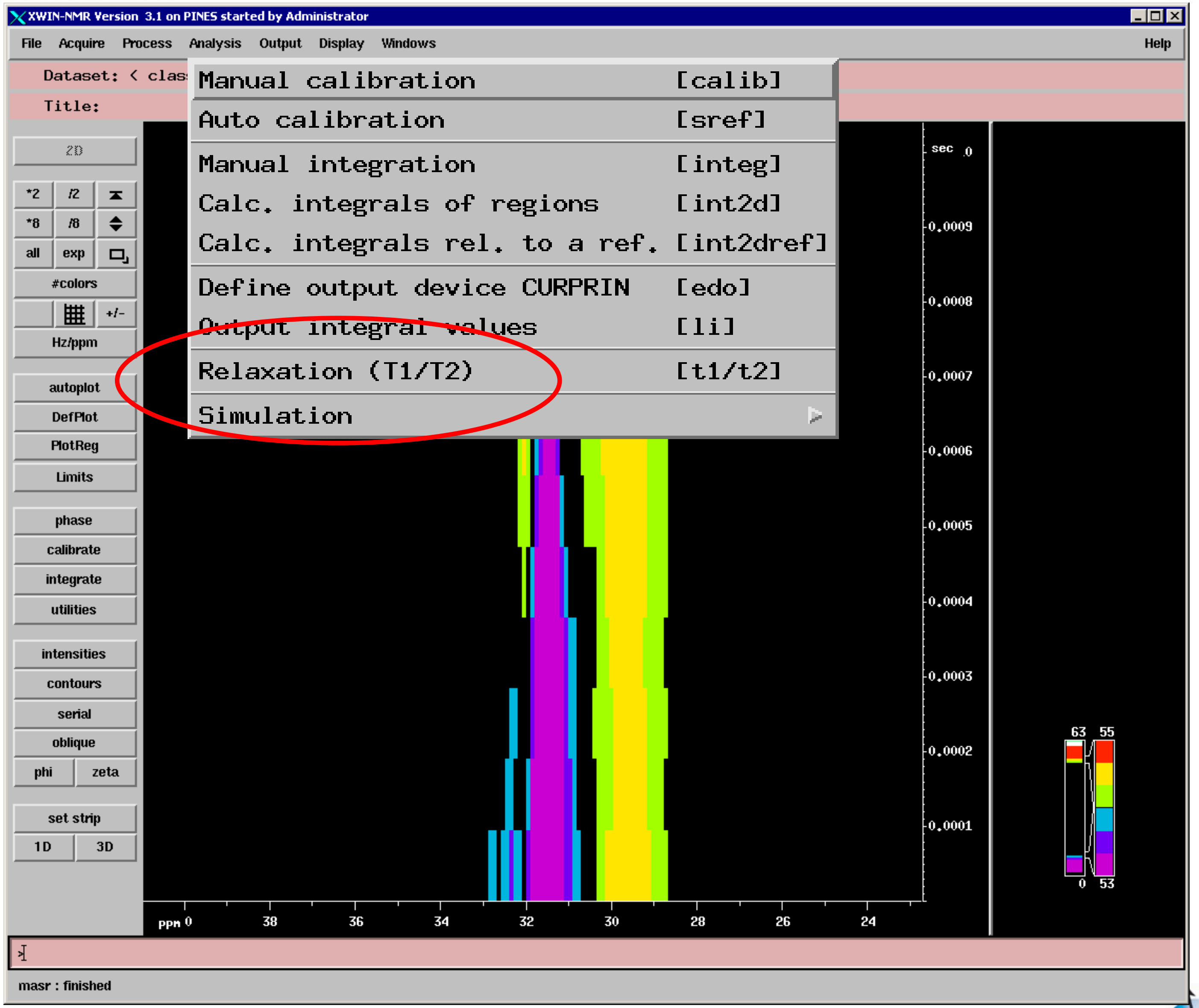
Relaxation Experiments



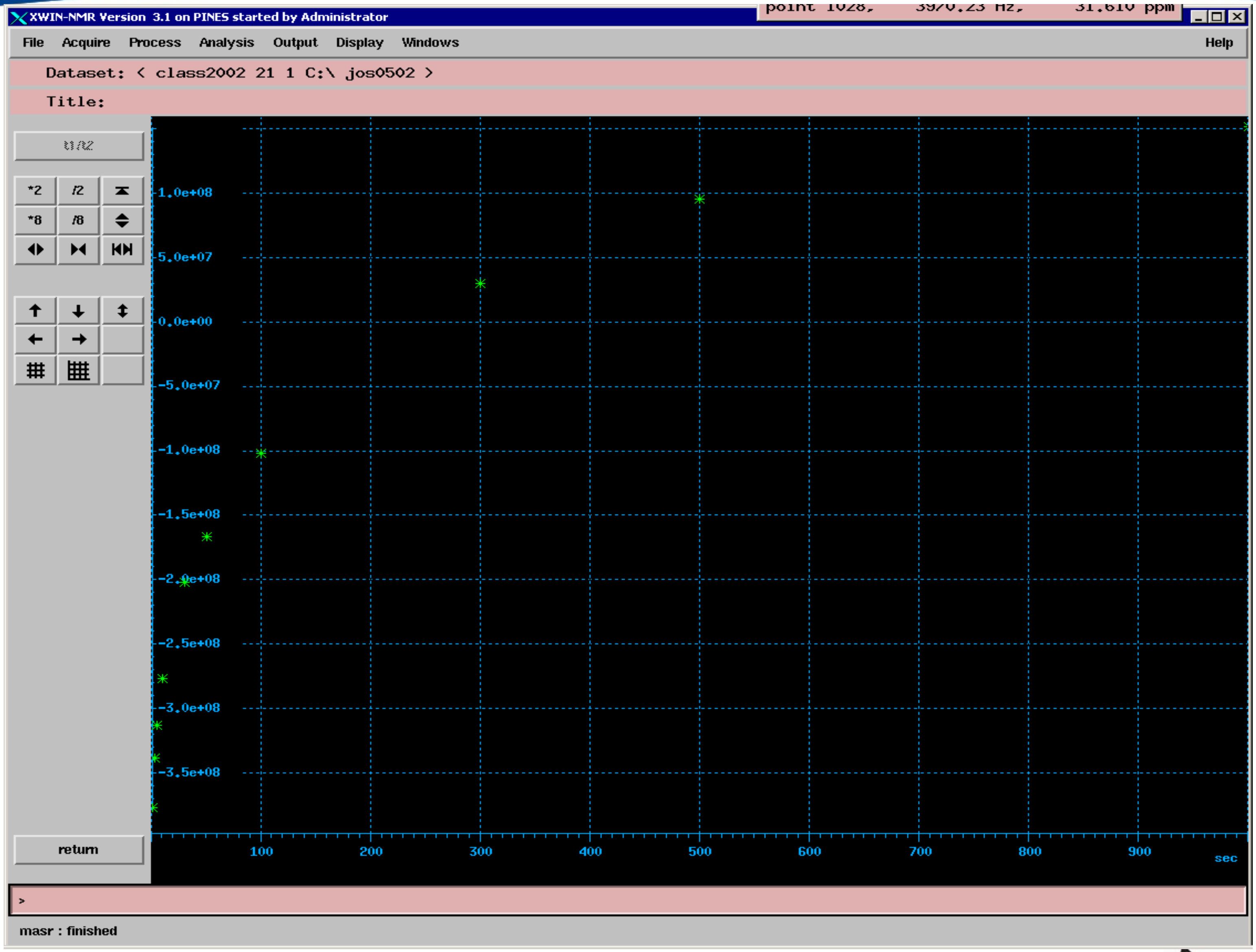
T_1 Relaxation Experiment on PE



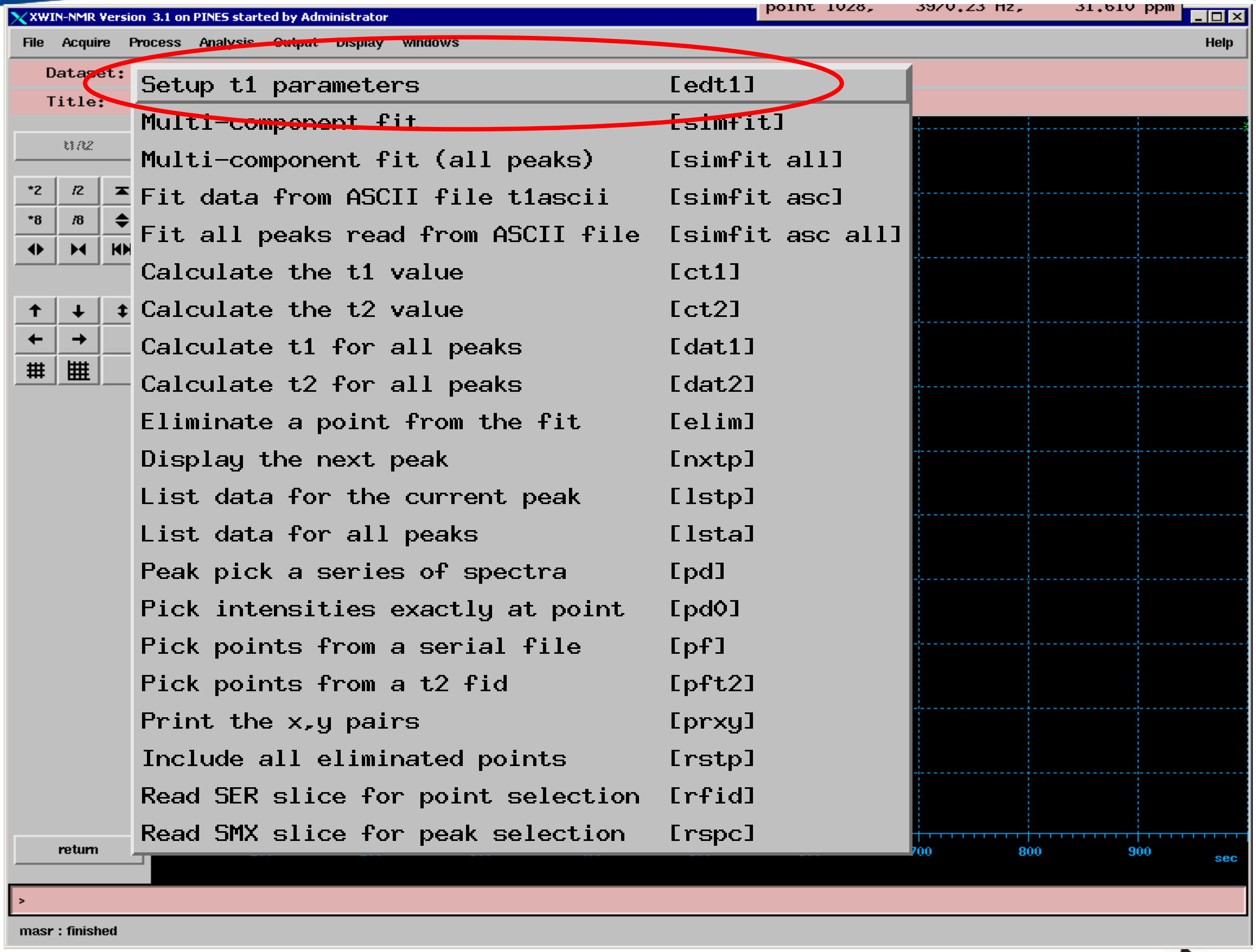
T_1 Relaxation Experiment on PE



T_1 Relaxation Experiment on PE



T_1 Relaxation Experiment on PE



T_1 Relaxation Experiment on PE

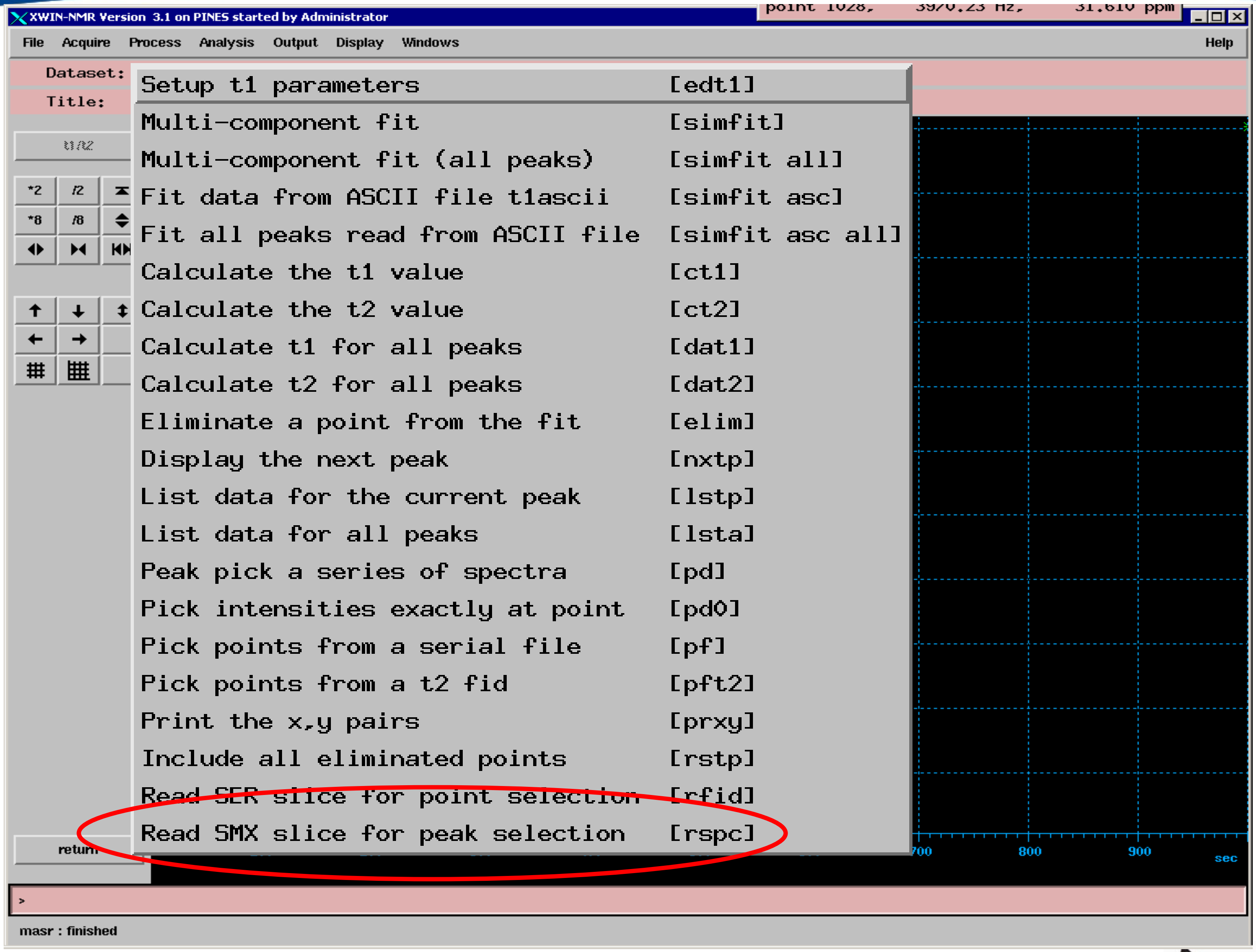
edt1

T1 Parameters

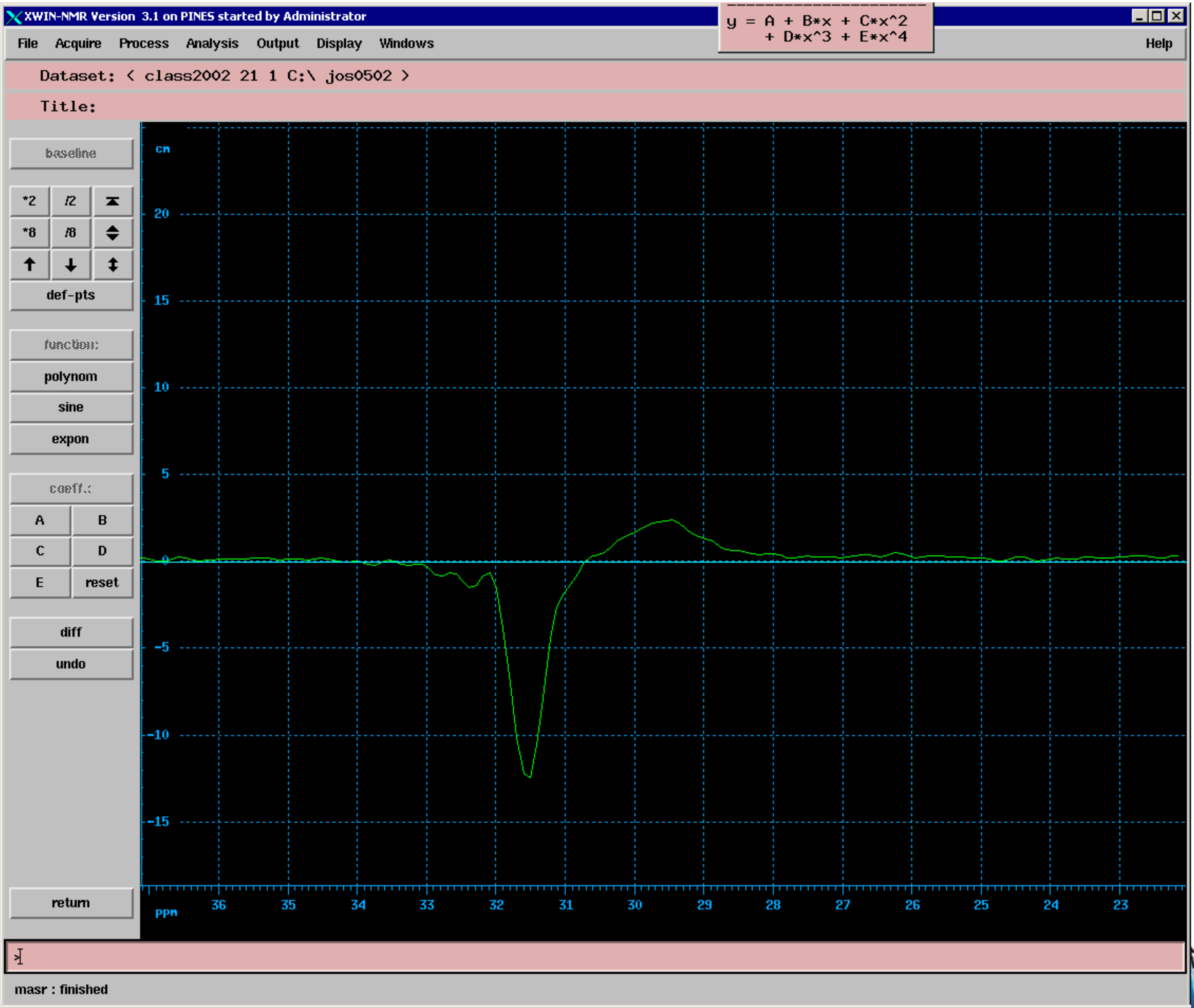
NUMPNTS	10	Number of data points used for fit
FITTYPE	intensity	Use peak areas or intensities for fit
LISTTYP	vdlist	Name of list file with x-coordinates
LISTINC	0.001	Increment used if LISTTYP=auto
CURSOR	1	Position of current peak in spectra
DRIFT	5	Allowed peak drift for peak picking
START	1	First slice to peak pick from
INC	1	Increment for the next slice
X_START	1	Start of x axis
X_END	1000	End of x axis
Y_START	-3.76998e+08	Start of y axis
Y_END	1.50822e+08	End of y axis
FCTTYPE	t1/t2	Type of fitting function
NUMTERM	3	Number of terms to vary in fit function
COMPNO	1	Number of components
EDGUESS	ed	Setup guesses for fit parameters

SAVE | 2-COL | Parameter | Next | CANCEL

T_1 Relaxation Experiment on PE

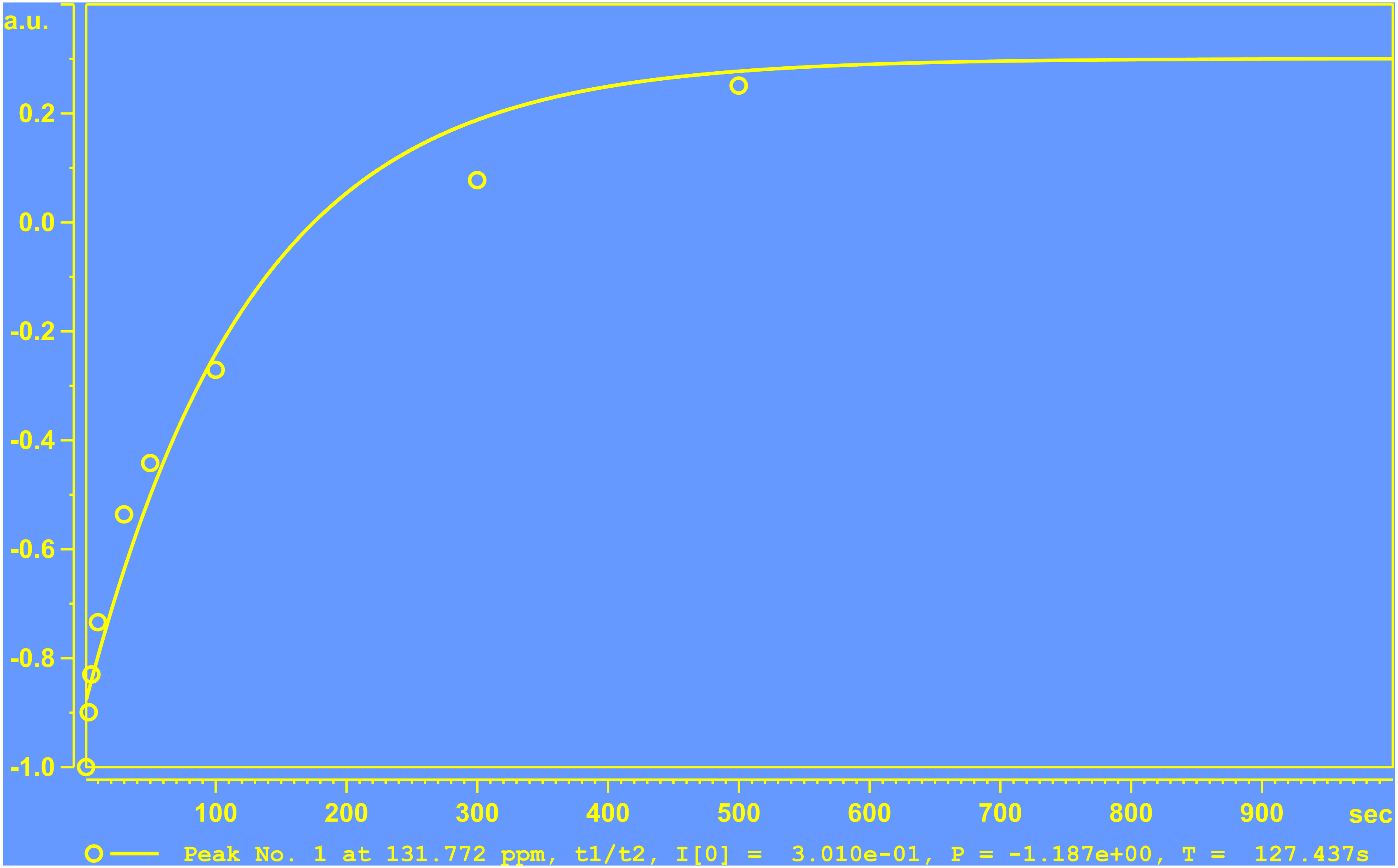


T_1 Relaxation Experiment on PE

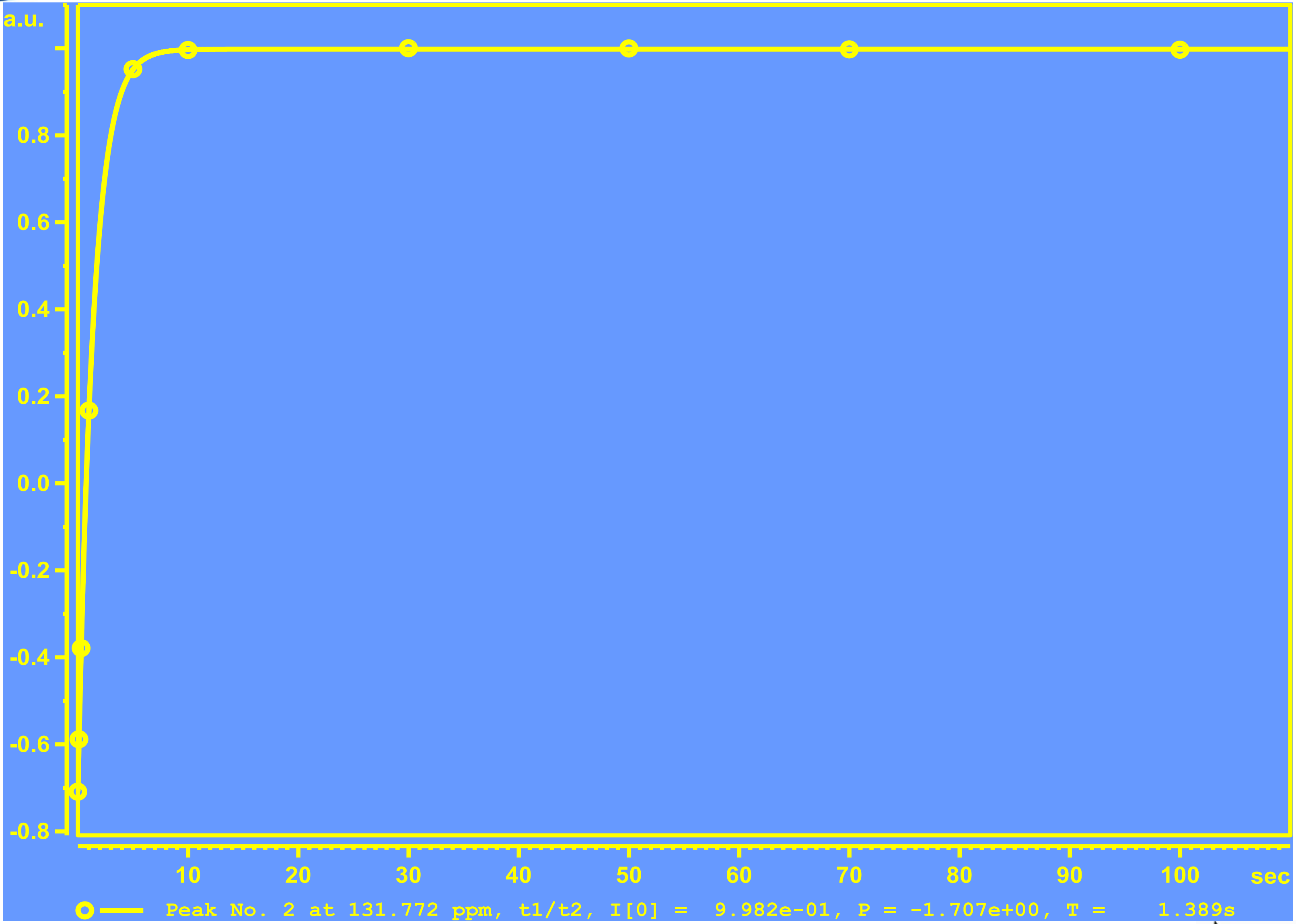


T_1 Relaxation Experiment on PE

- PE ^{13}C T_1 experiment T1/T2 module

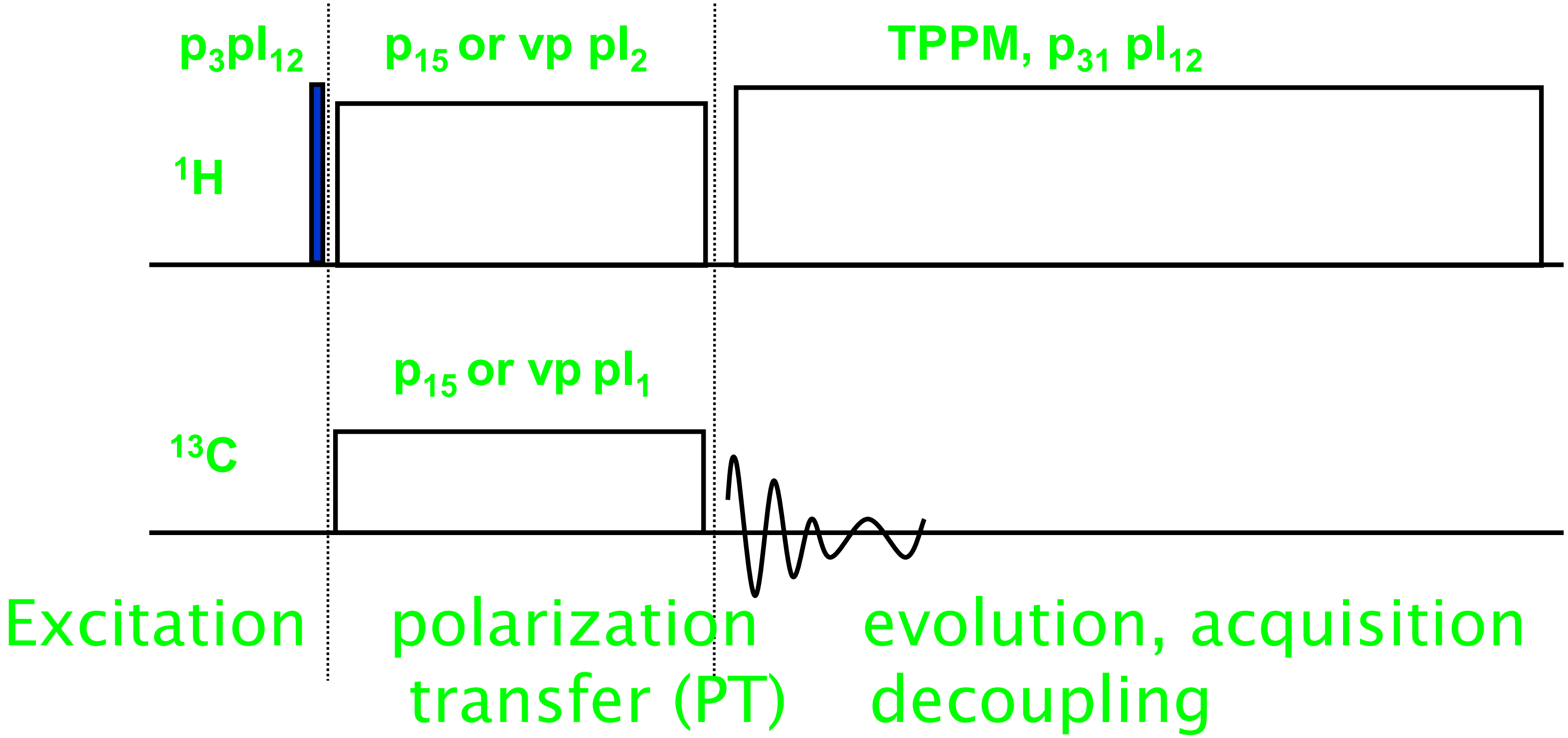


T_1 Relaxation Experiment on Adamantane



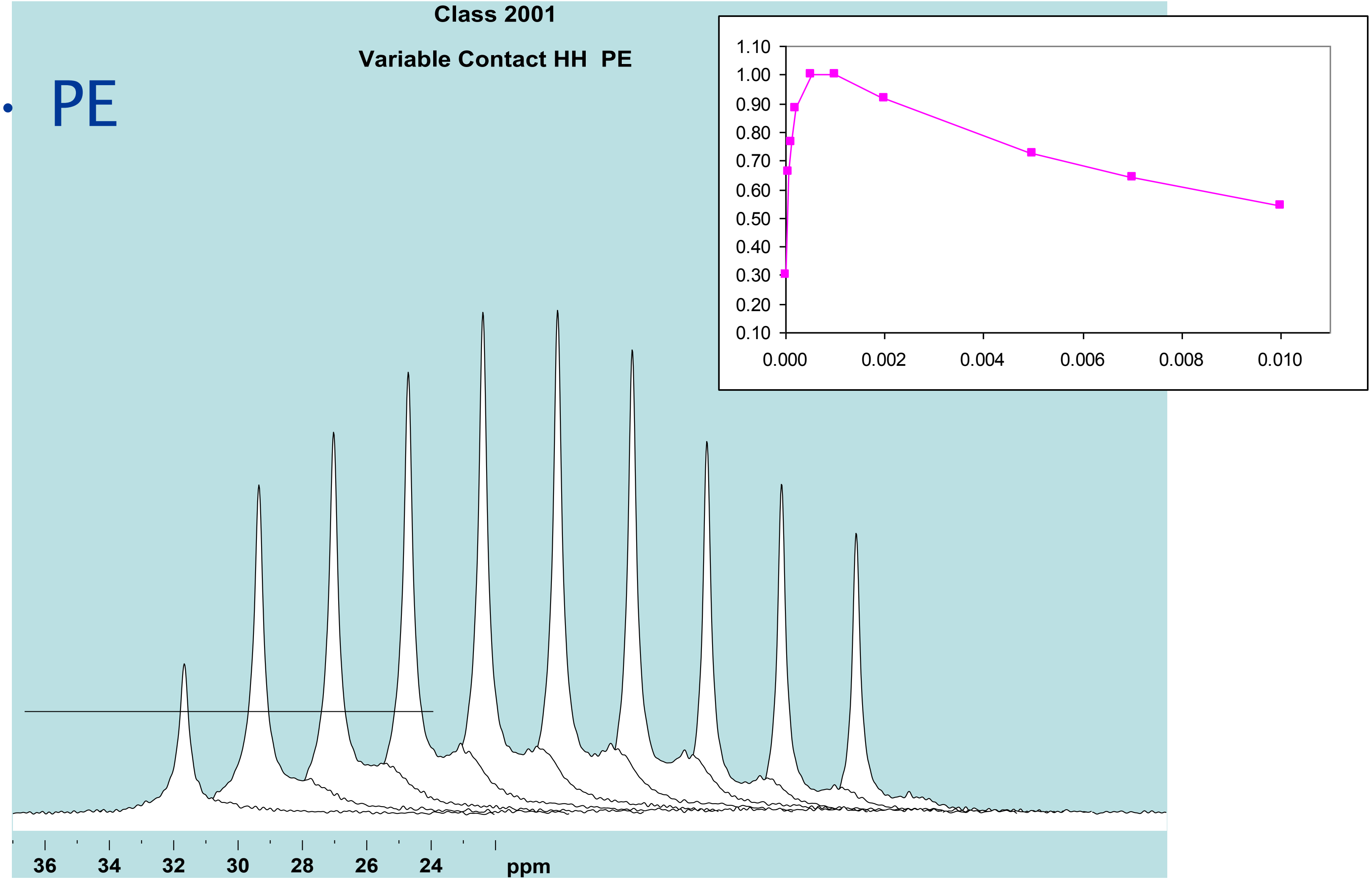
Variable Contact Experiment

- Variable contact, increment p15 or use vp-list



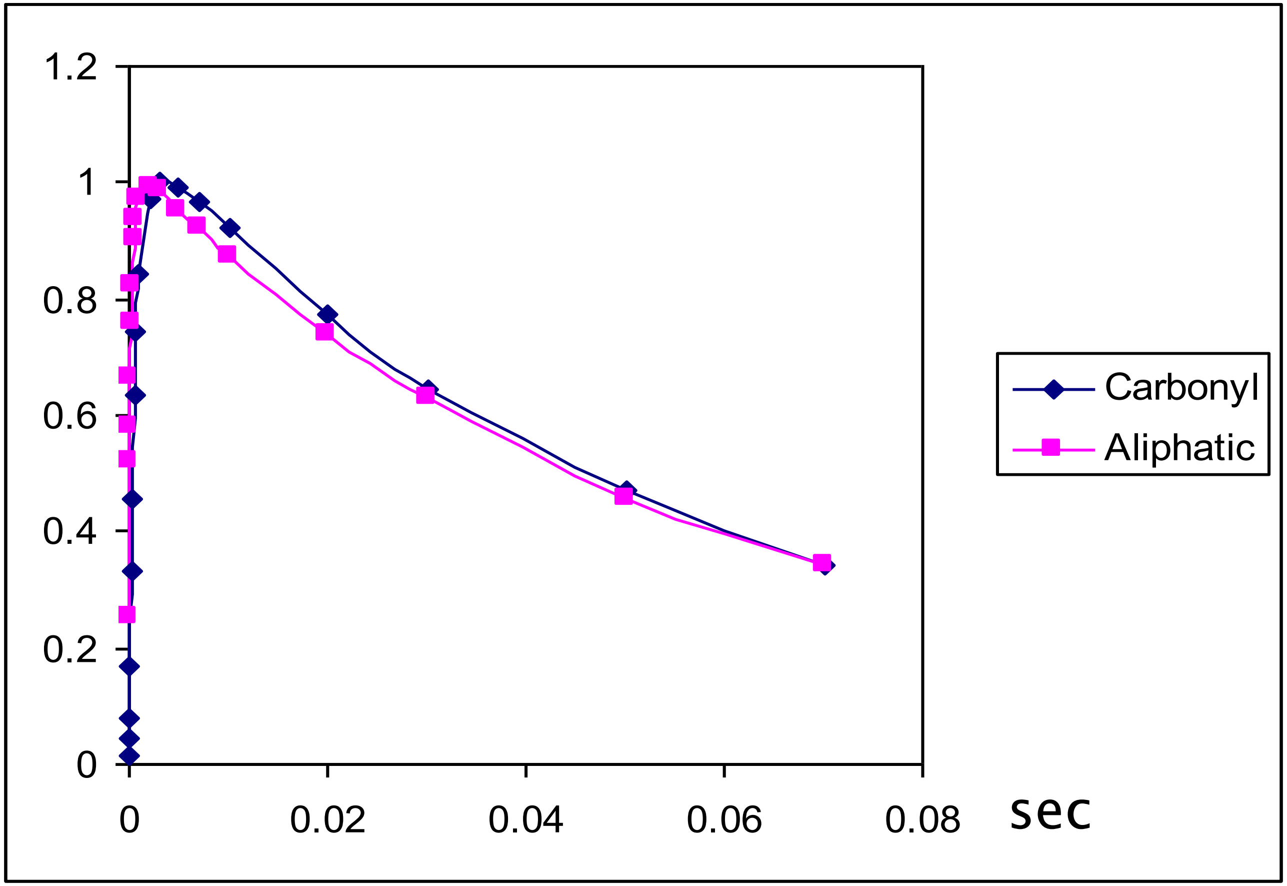
Variable Contact Experiment

- PE



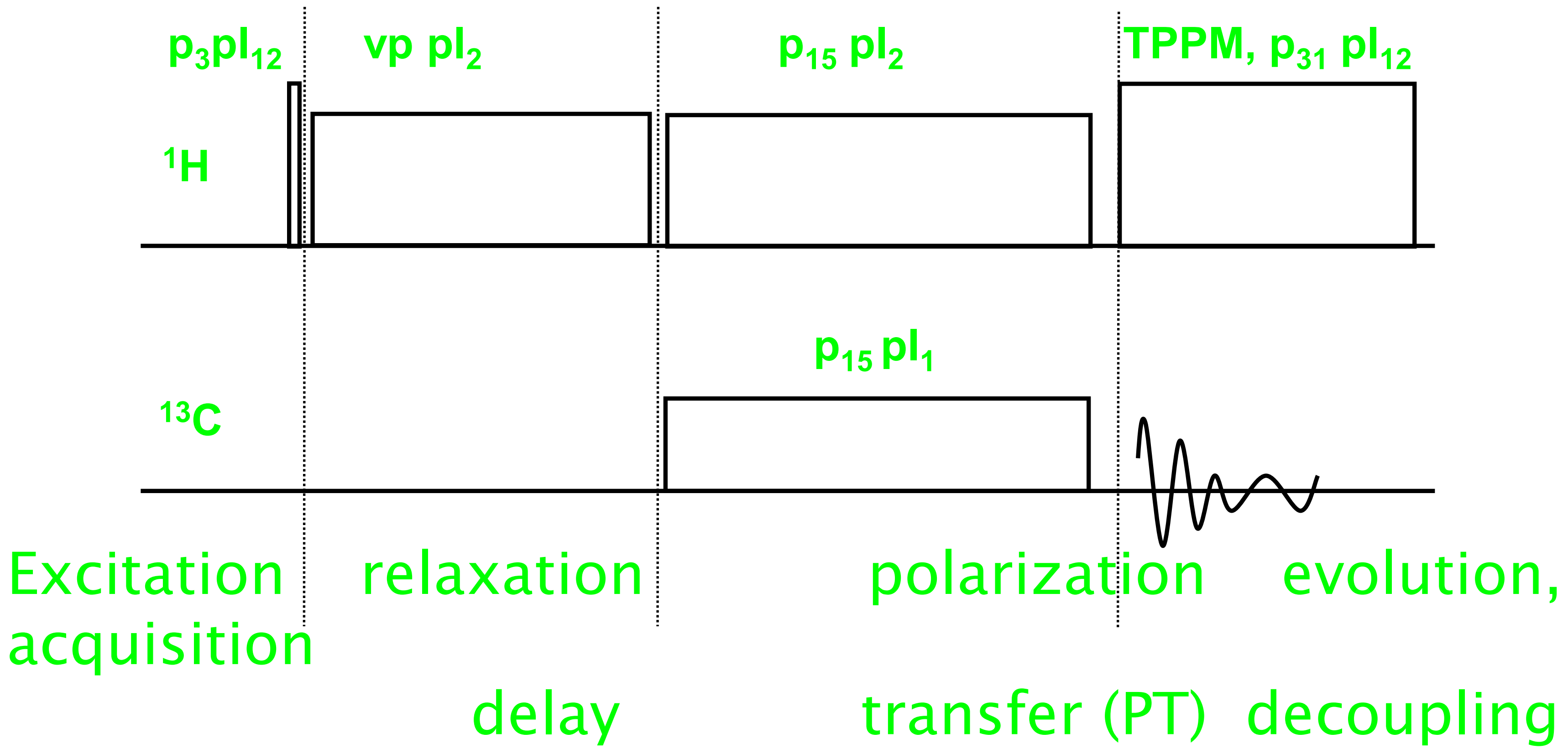
Advanced CP Experiments

- Glycine variable contact



Cross Polarization Experiments

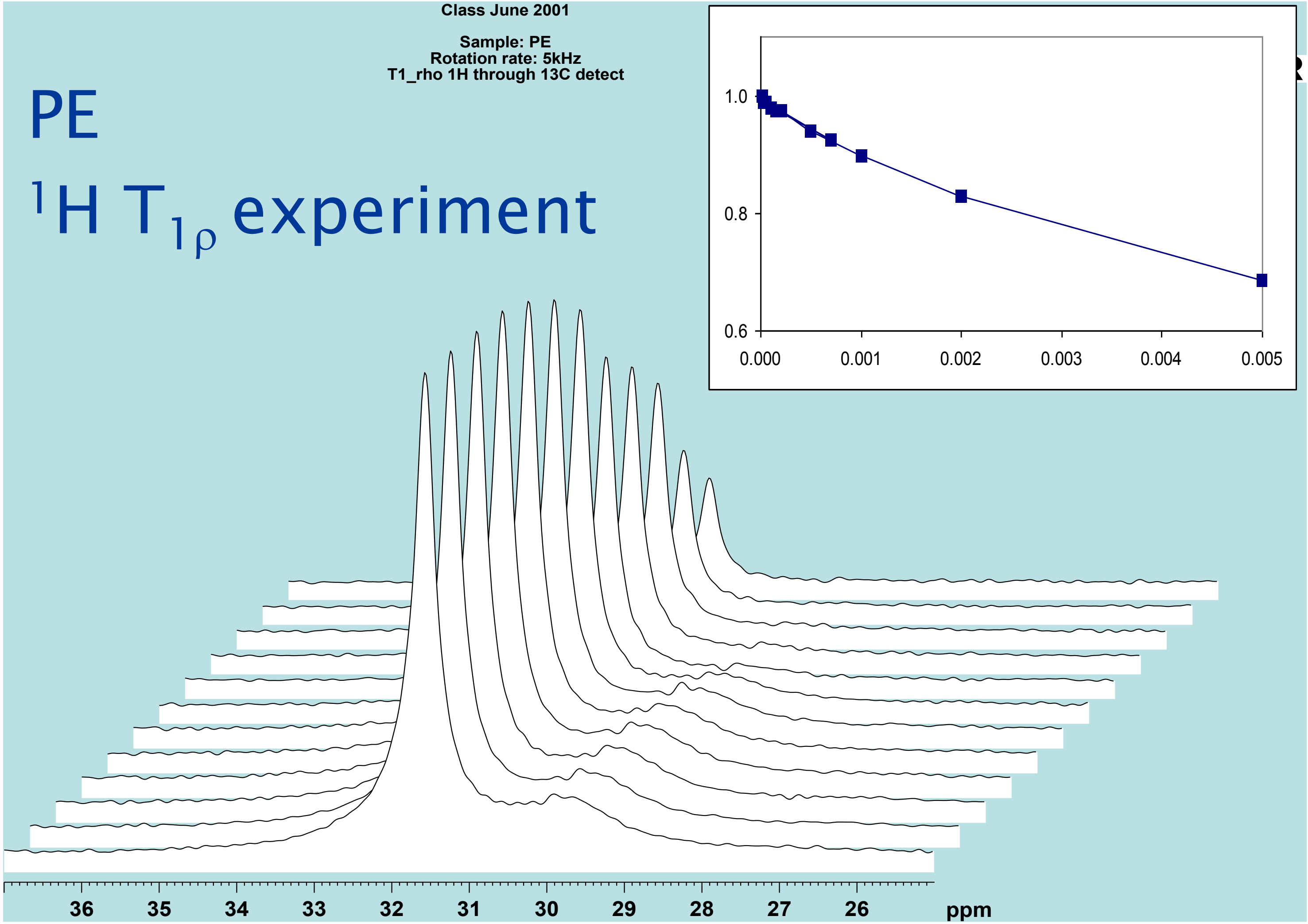
- T_{1rho} relaxation experiment ^{1}H



Cross Polarization Experiments

- PE

  $^1H\ T_{1\rho}$ experiment

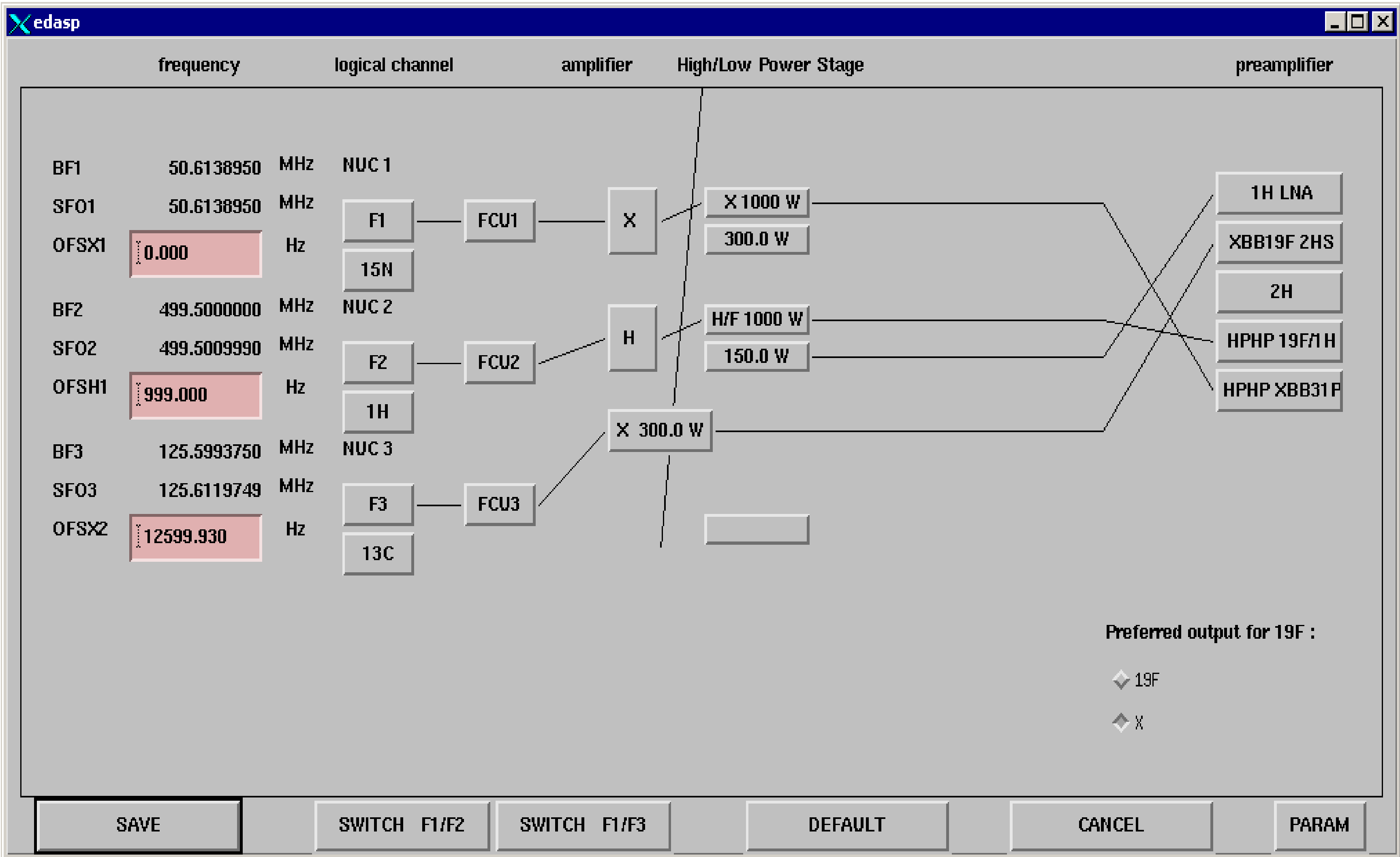


Triple Resonance Experiments

- Setup:
  - Adjust ^{15}N parameters
  - Get ^{13}C parameters
  - Load triple resonance experiment
  - some fine adjustments

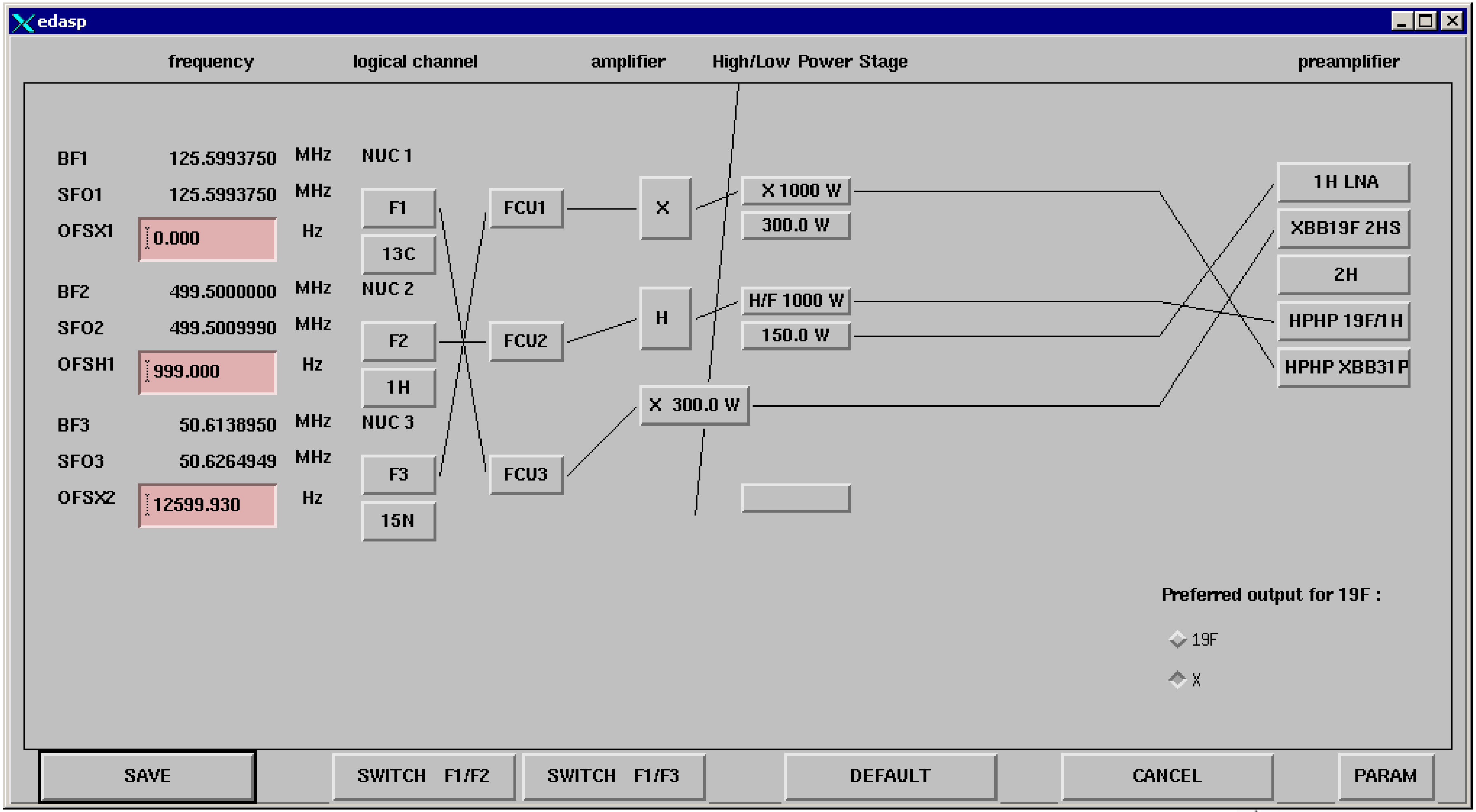
Triple Resonance Experiments

- ^{15}N setup



Triple Resonance Experiments

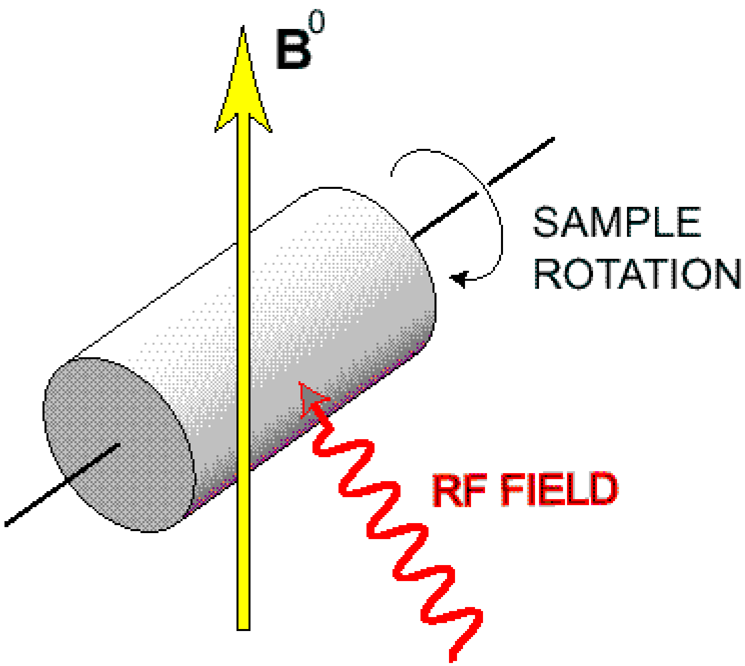
- ^{13}C setup



Introduction REDOR

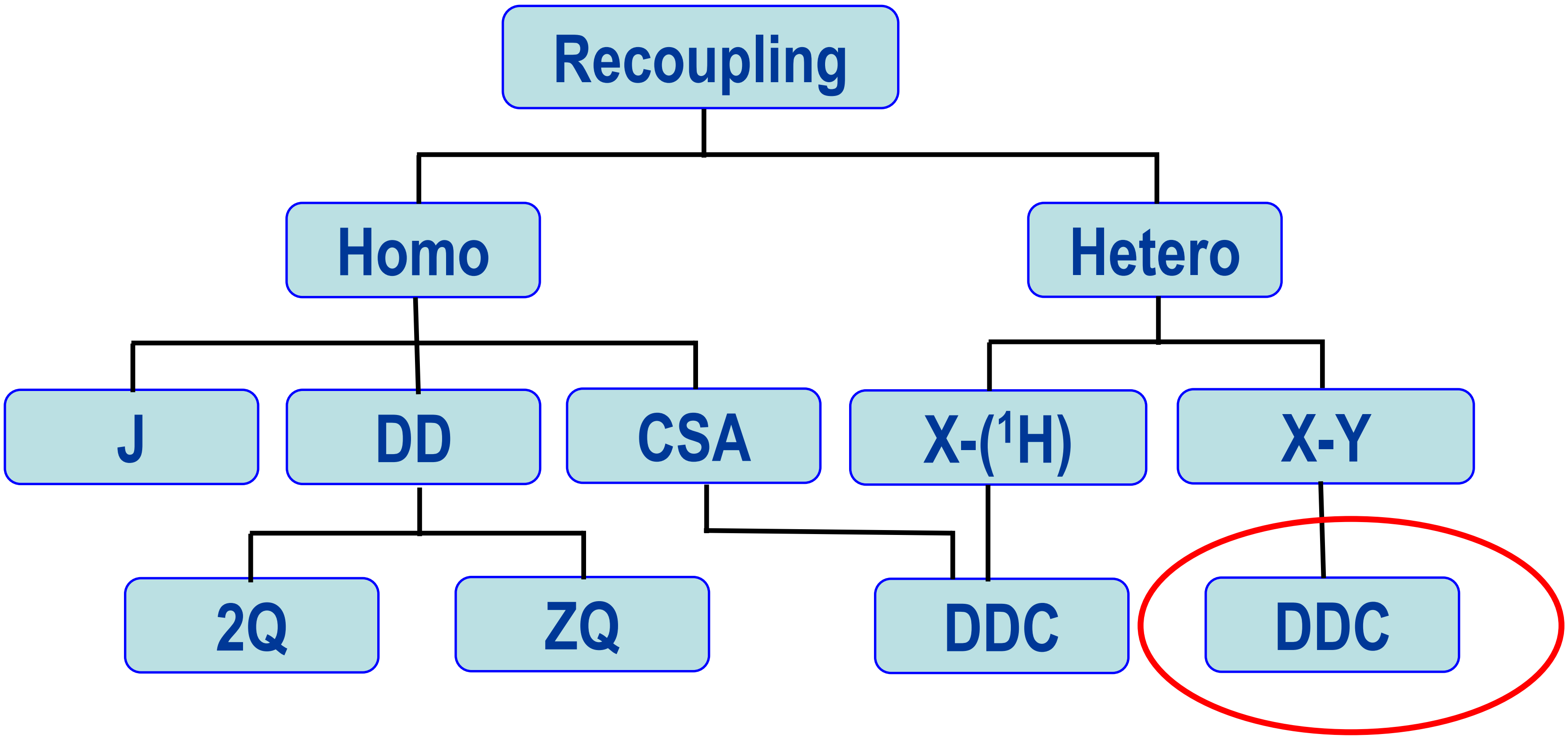
NMR in solid systems:

- Average by MAS
- Problem now: Lost information through averaging
- Solution: MAS + Radio Frequency (RF) field ⟶ Recoupling
- Create heteronuclear Dipole Dipole Correlation (DDC)



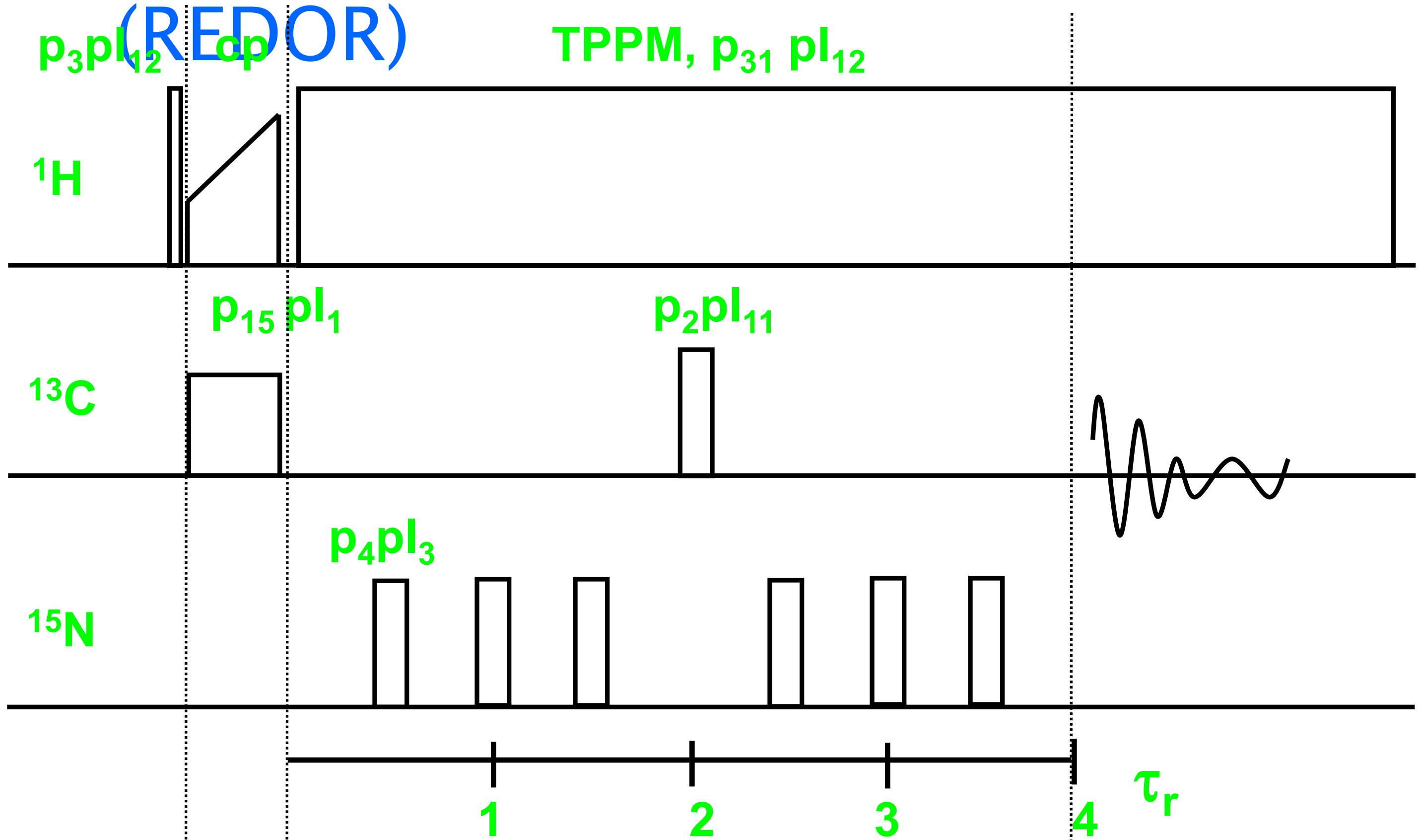
Introduction REDOR

- Types of Recoupling



Triple Resonance Experiments

- Rotational Echo Double Resonance (REDOR)



Excitation PT rotor synchronized evolution,

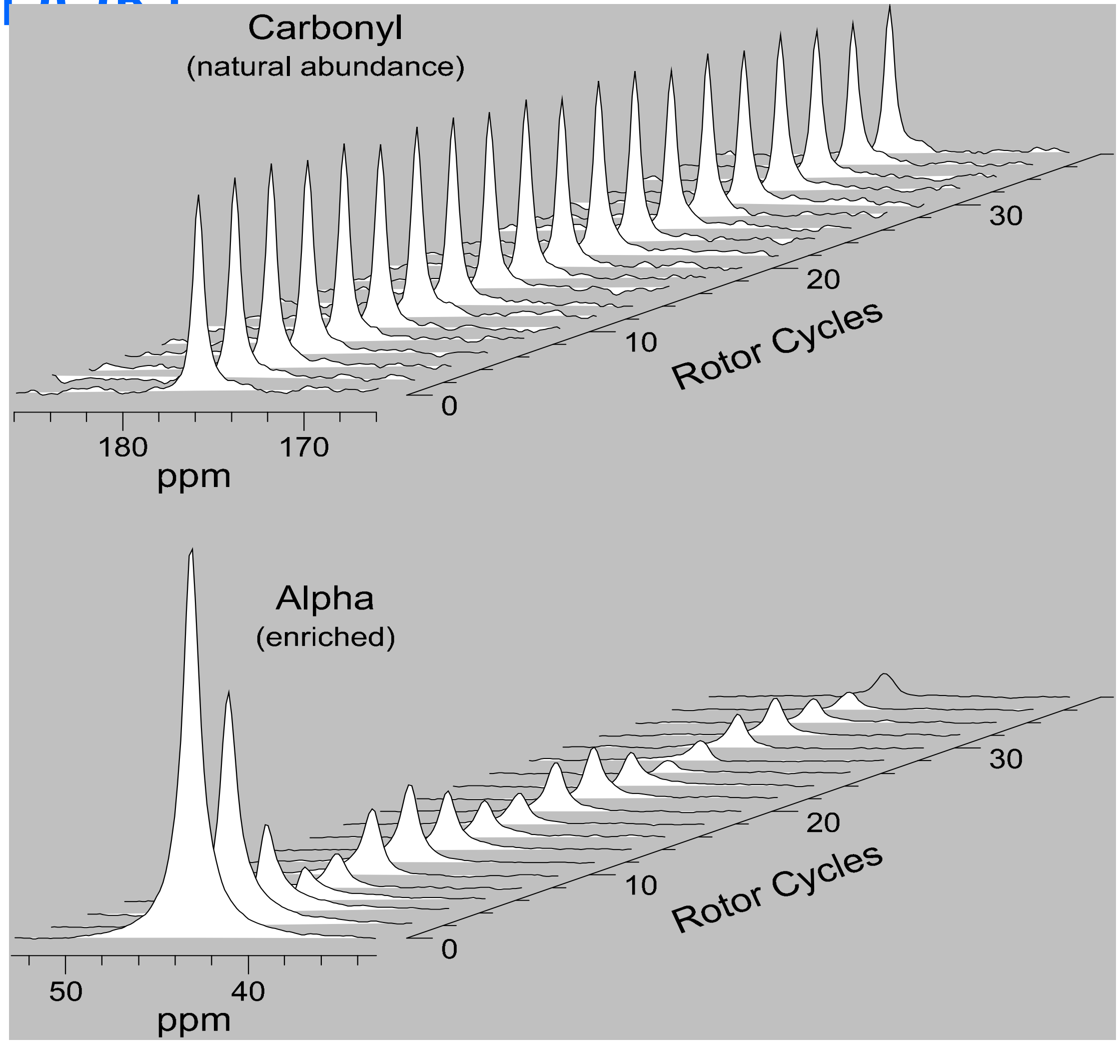
acquisition

heteronuclear decoupling

dipolar recoupling

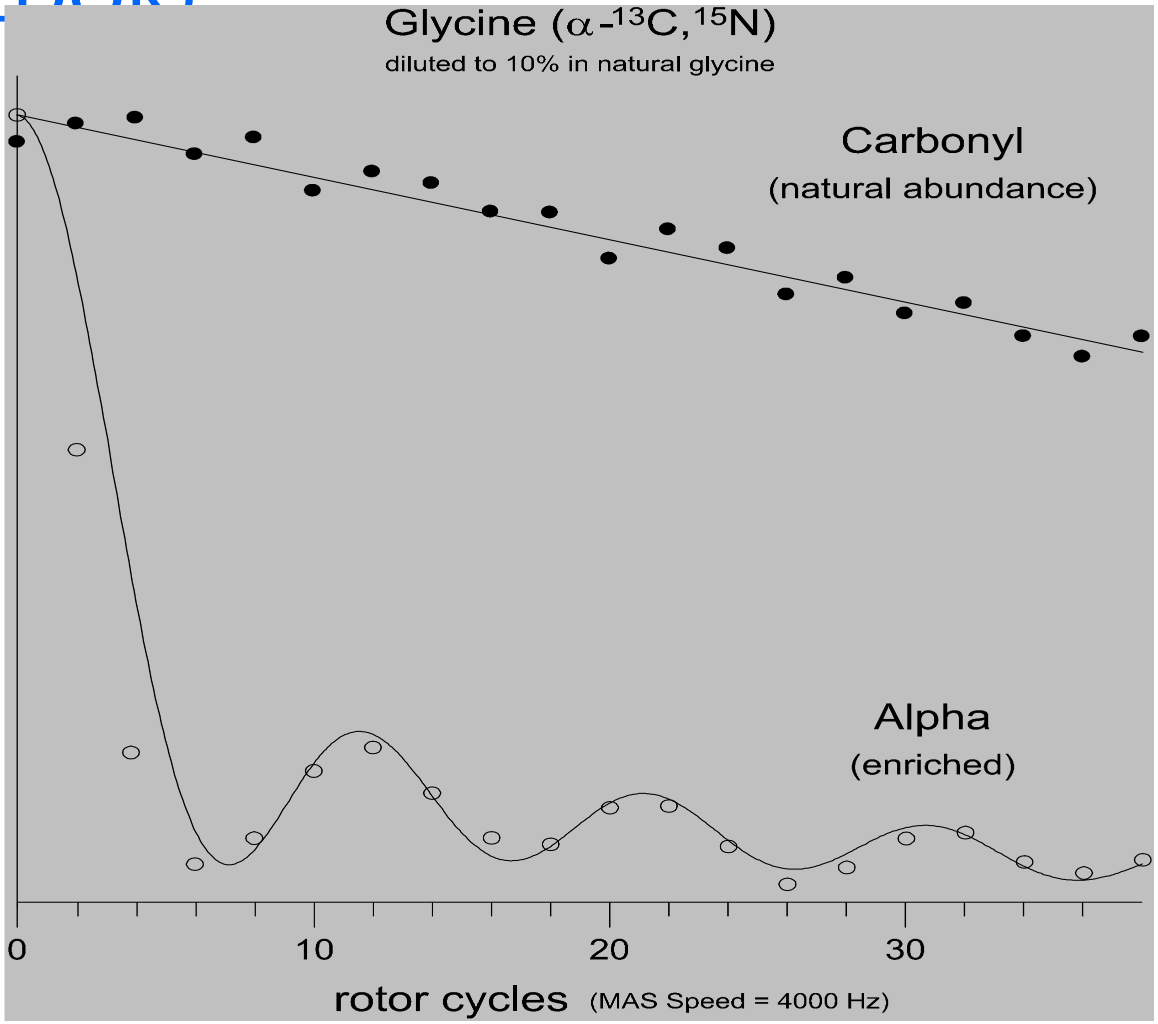
Triple Resonance Experiments

- Rotational Echo Double Resonance (REDOR)



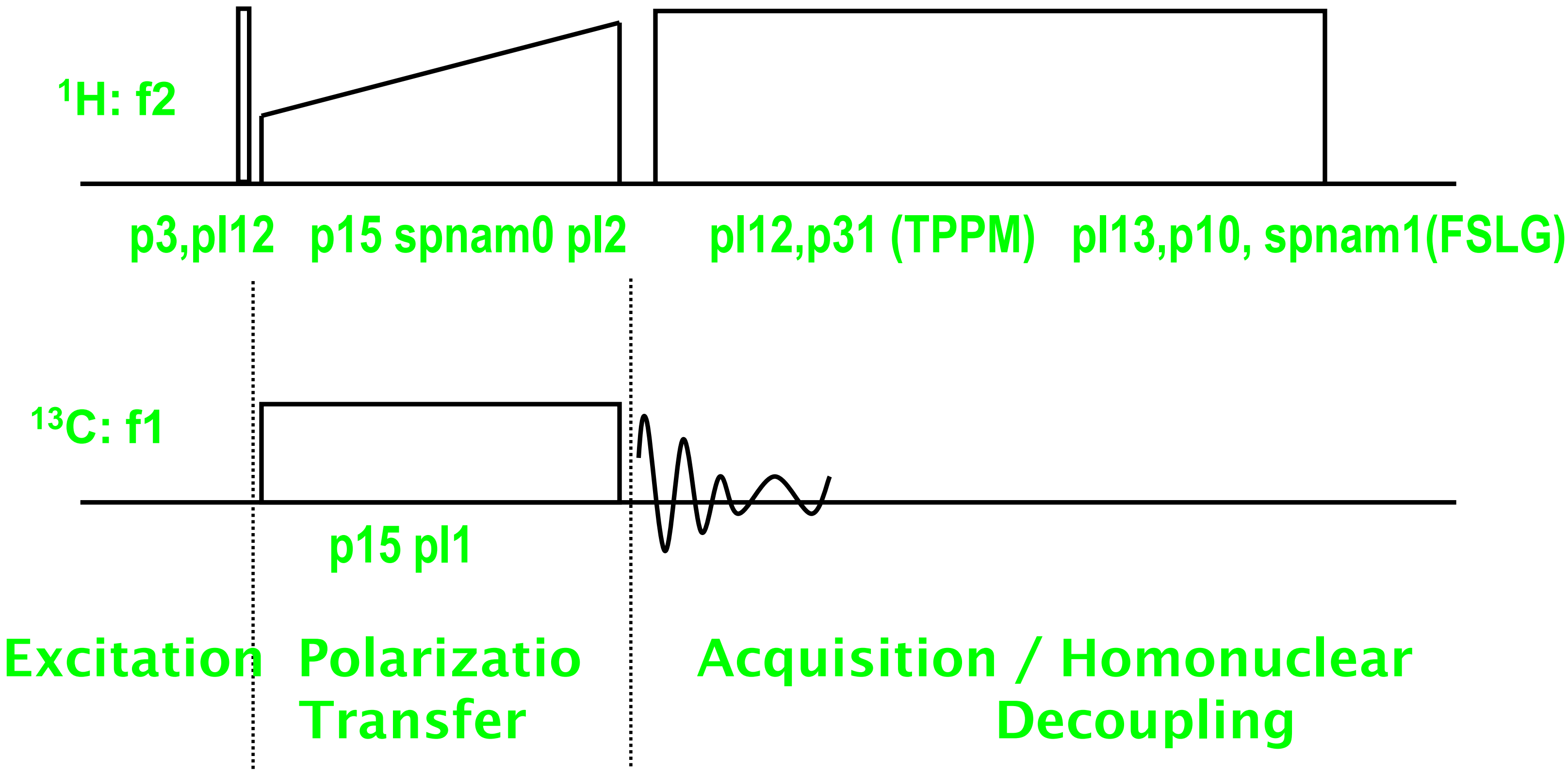
Triple Resonance Experiments

- Rotational Echo Double Resonance (REDOR)

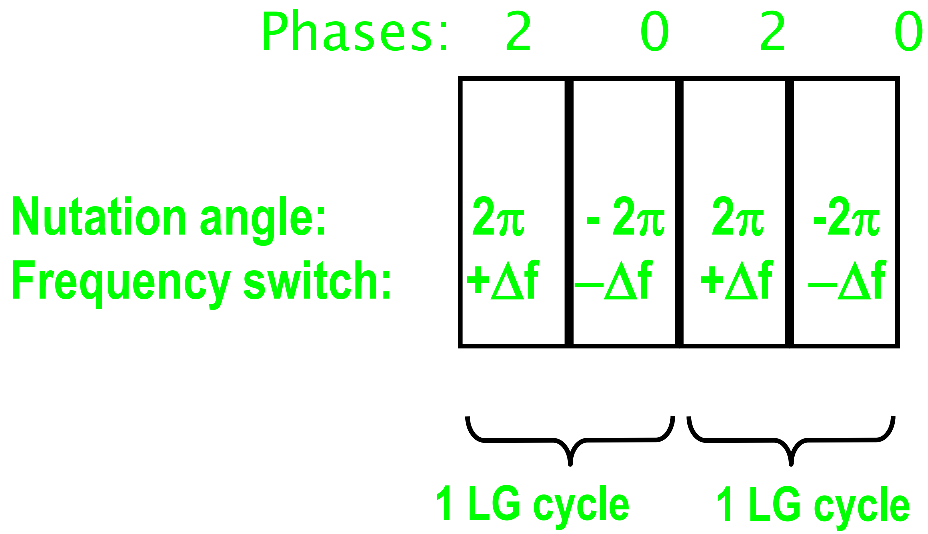


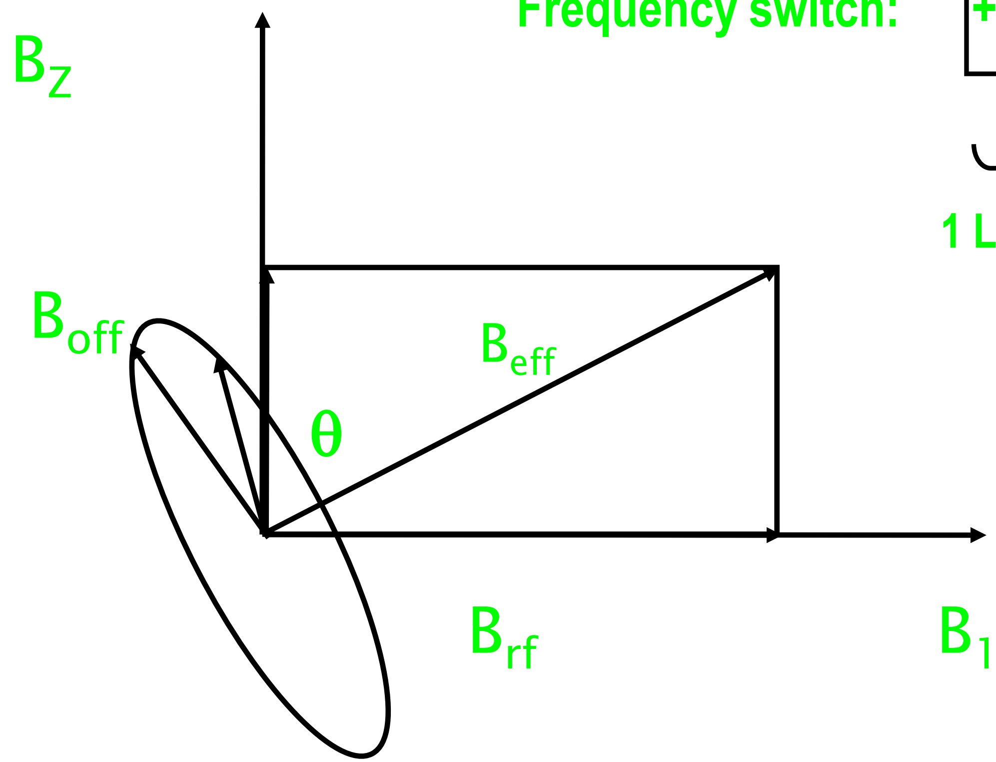
FSLG Experiments Setup

Basic experimental scheme: Measures J coupling



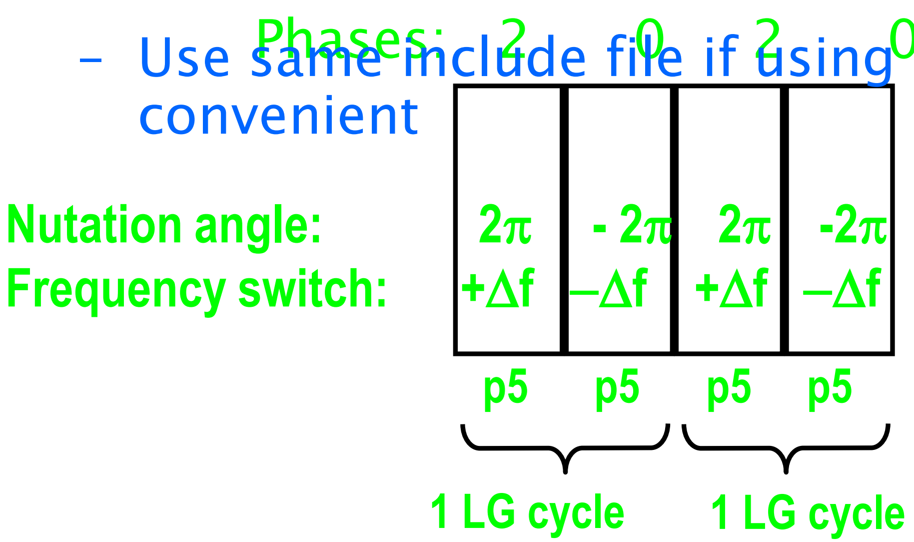
FSLG Experiments





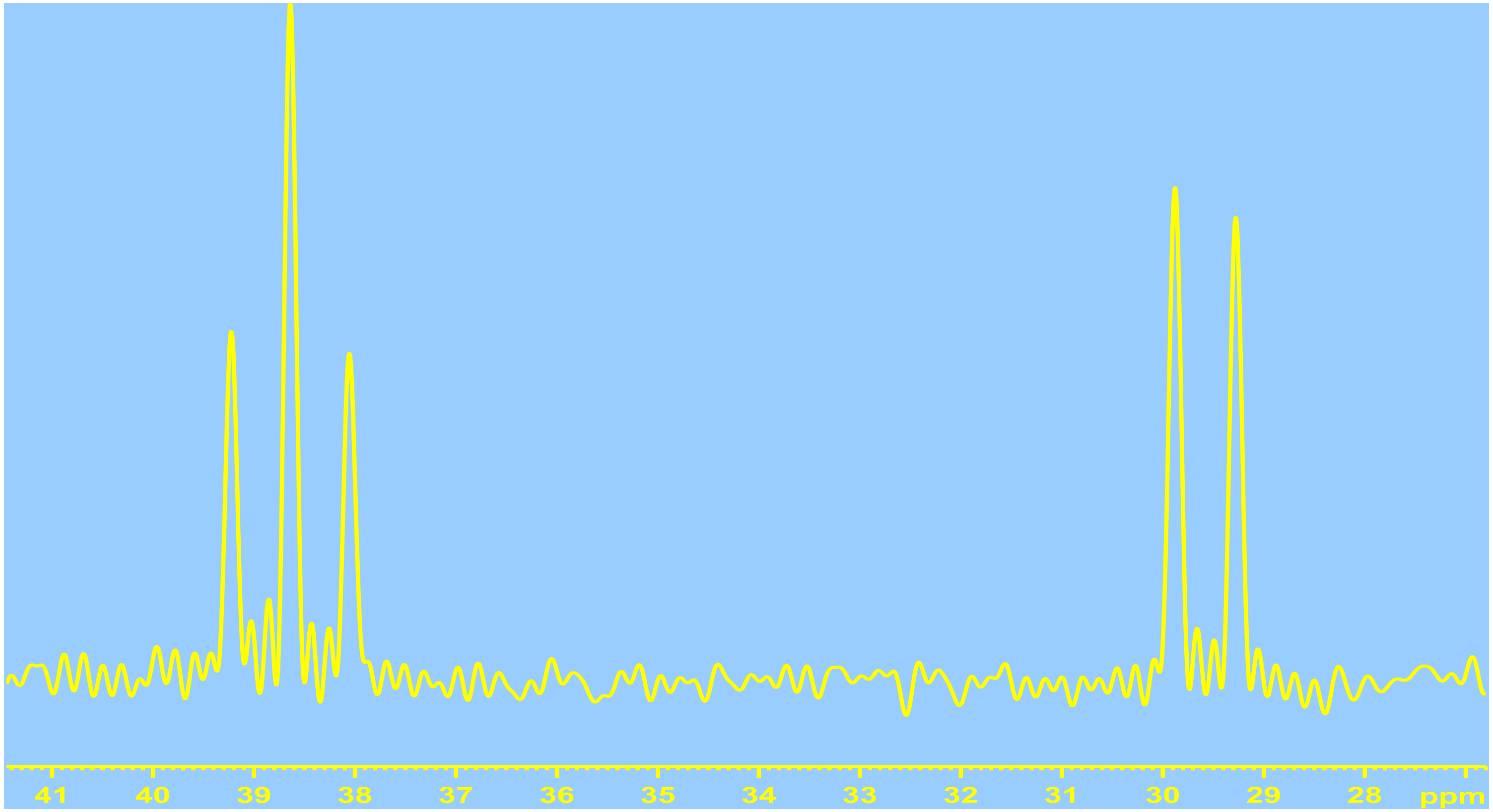
FSLG Experiments

- Conventions:
  - Use include file: lgcalc.incl
    - Uses cnst20 for B1 field in Hz and calculates
      - p5 294 degree pulse
      - cnst21=0 for on resonance
      - cnst22 and cnst23 for ± LGfrequency offset, **+Δf –Δf**
      - cnst24 for offset of center of ± LGfrequency offsets
  - Use same include file if using PMLG shape as well - convenient



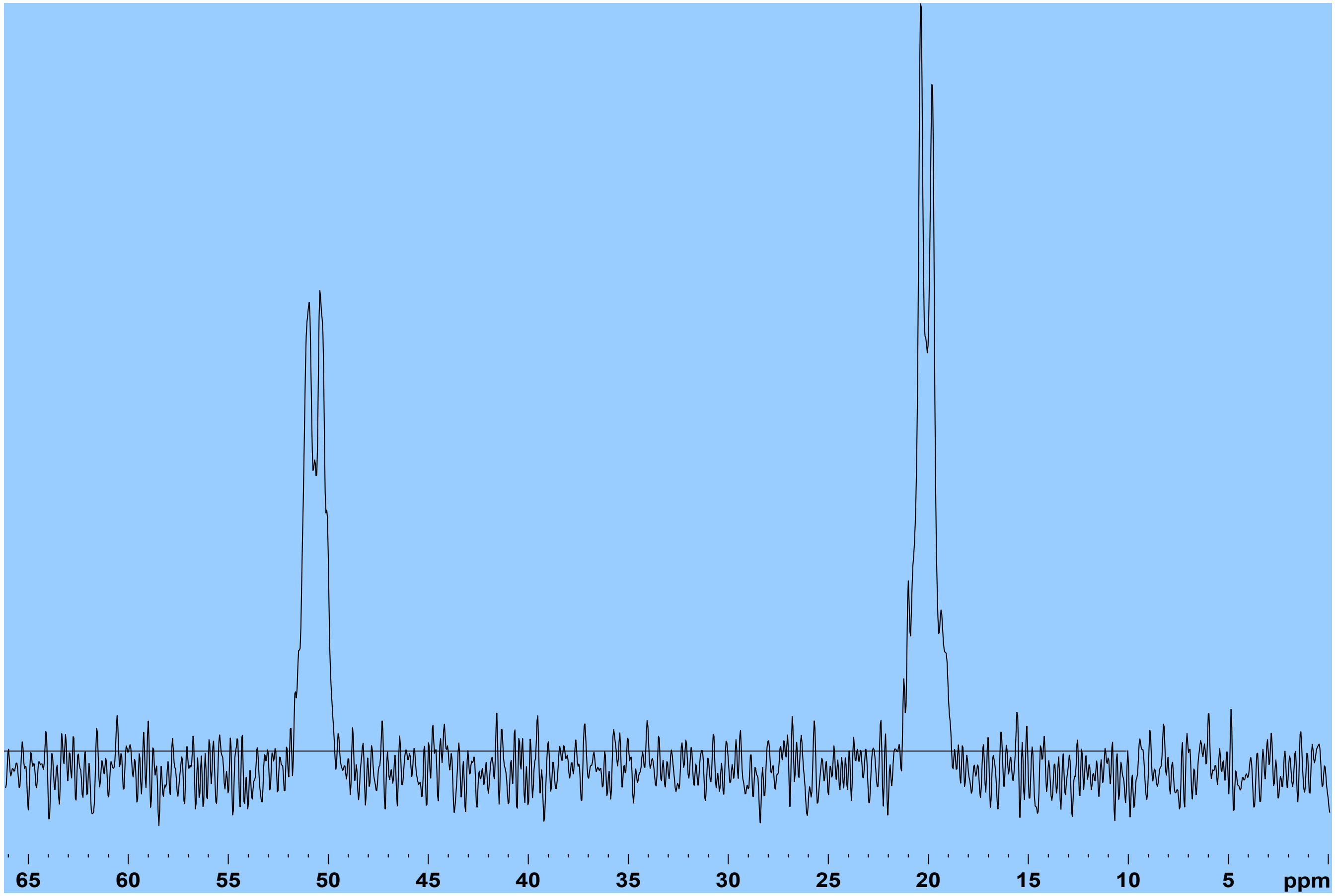
FSLG Experiments

- Homonuclear decoupling during acquisition:
  - J-coupling resolved on adamantane
  - Optimized for best splitting, width and depth
  - Spinning speed 7 kHz



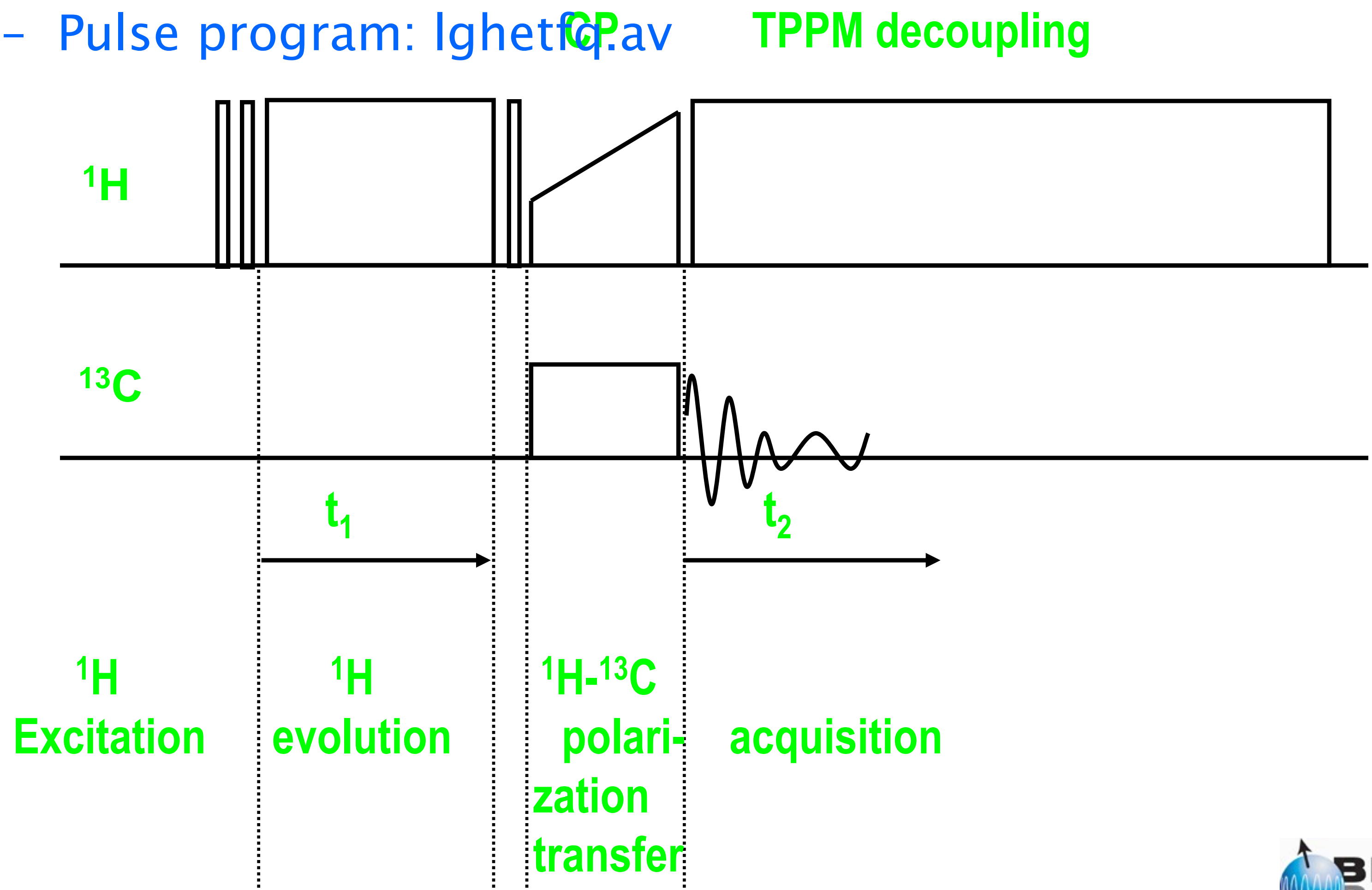
FSLG Experiments

- Homonuclear decoupling during acquisition:
  - J-coupling resolved on alanine
  - Optimized for best splitting, width and depth
  - Spinning speed 12.5 kHz



FSLG Experiments

- **Application: Heteronuclear correlation spectroscopy**
  - B.-J. van Rossum et al. JMR124 (1997)
  - Pulse program: lghetfq.av



FSLG Experiments

- Tips for pulse programming
    - set parameters simultaneously

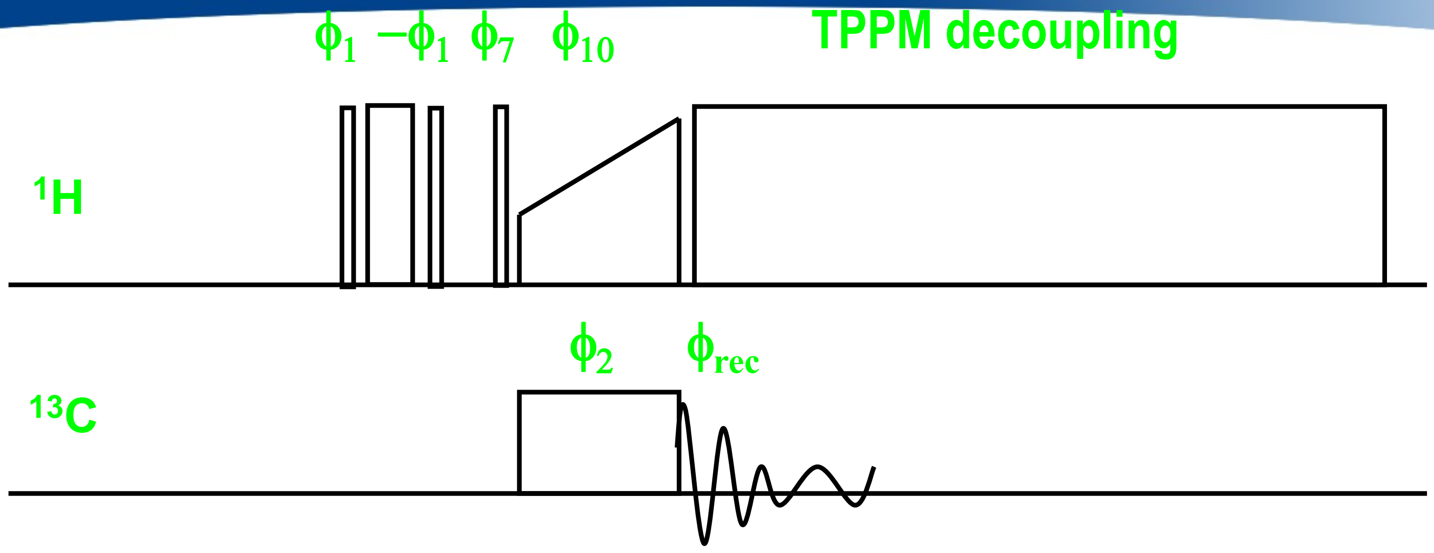
e.g. instead of

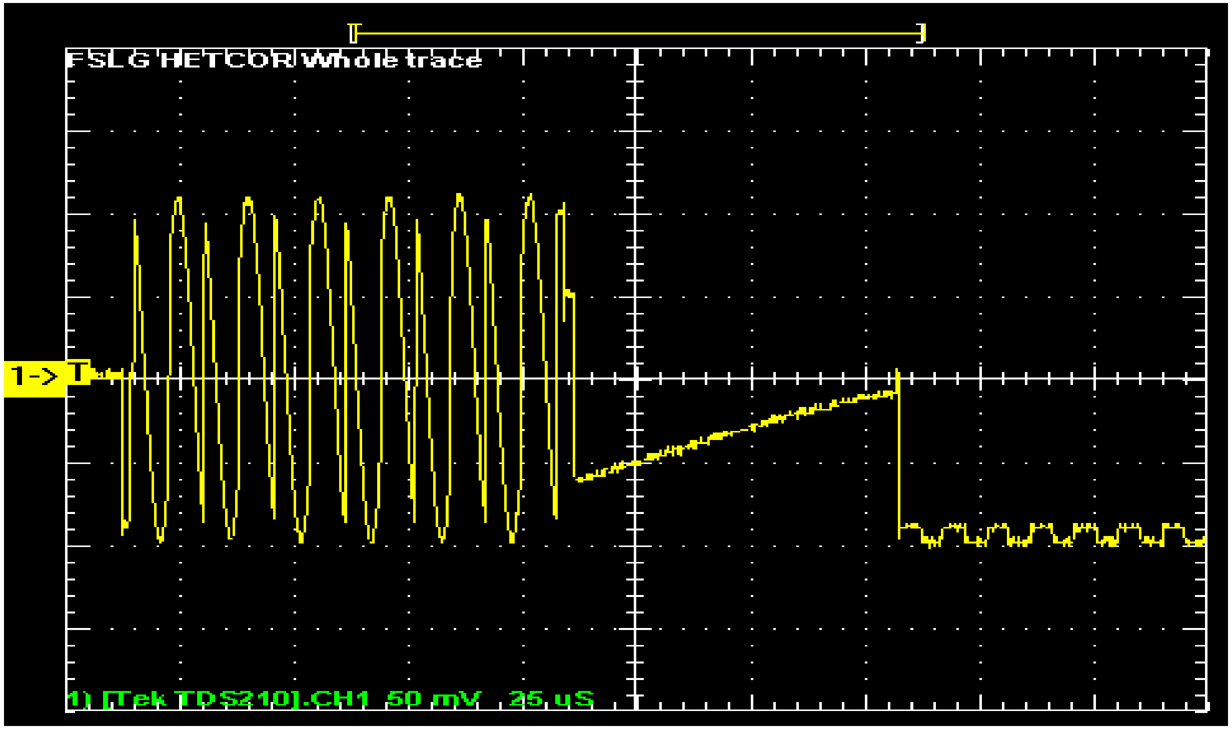
```
1u fq=cnst21:f2
1u pl13:f2
(p23 ph7):f2
```

FSLG Sequence in AV Pulse Program:

```
3  (p5 ph3 fq=cnst22 pl13):f2        ;+LG frequency
    p5:f2 ph4 fq=cnst23:f2           ;-LG frequency
    p5:f2 ph3 fq=cnst22:f2                  ;+LG frequency
    p5:f2 ph4 fq=cnst23:f2           ;-LG frequency
    lo to 3 times l1 ;l1 increment of t1 in F1 dimension
```

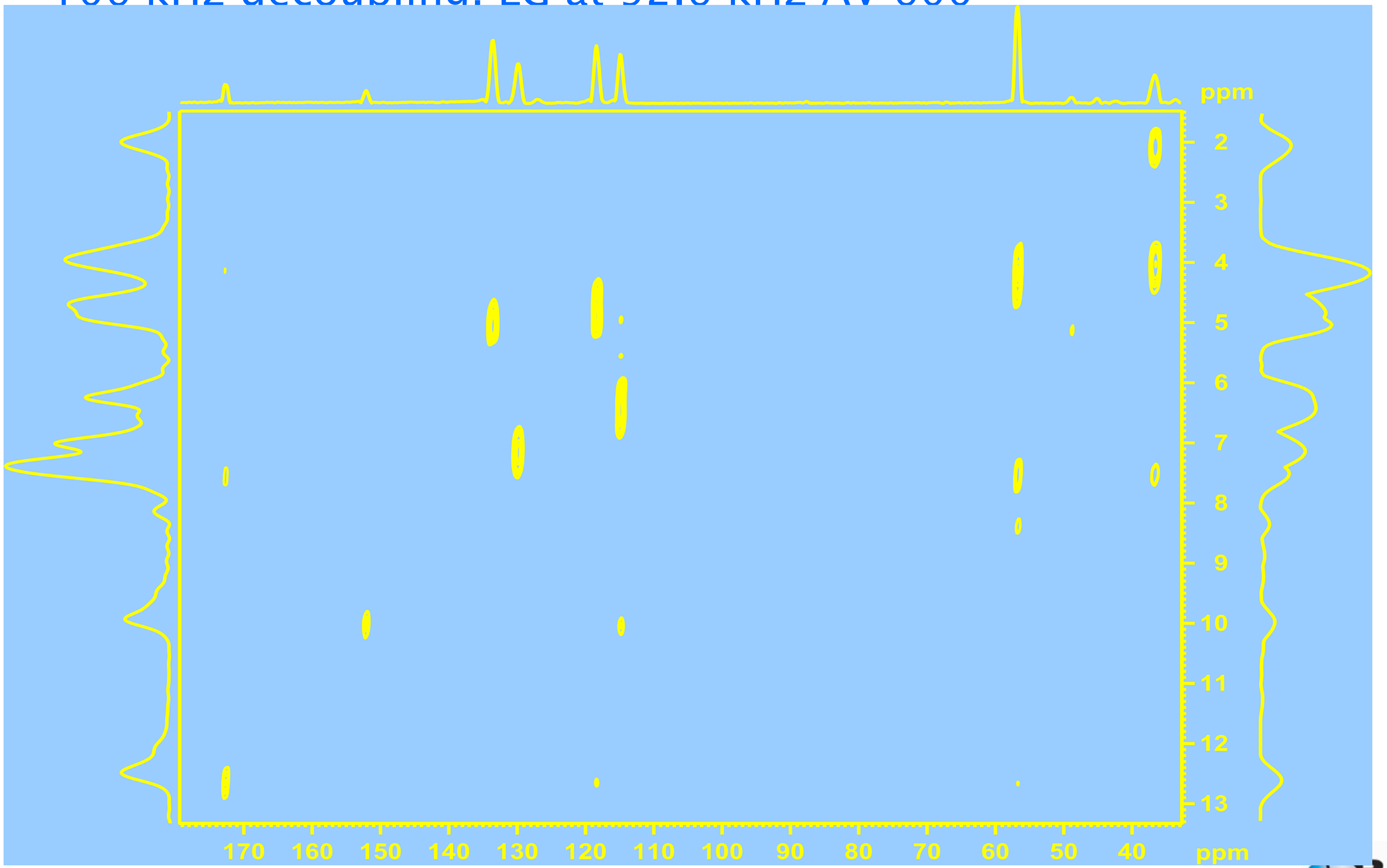
FSLG Experiments





FSLG Experiments

FSLG/HETCOR tyrosine HCl
right trace: projection
left trace: BR-24 CRAMPS on the same 4mm CP/MAS probe
106 kHz decoupling, LG at 92.6 kHz AV 600



PMLG Experiments

- Frequency switch through phase ramps:

$$2\pi f = \partial\theta / \partial\tau$$

- Create phase ramp use: AU program pmlg_vega
- Au program uses Vinogradows results to calculate shape
  - Choices in au program:
    - number of slices per 294 degree pulse
    - number of fslg-cycles per block (x,x_bar)
    - Time reversed blocks (x_bar,x)

$$(x\bar{x})_n(\bar{x}x)_n$$

E. Vinogradow, P.K. Madhu, and S. Vega, Chem. Phys. Lett. 314, 443-450 (1999)

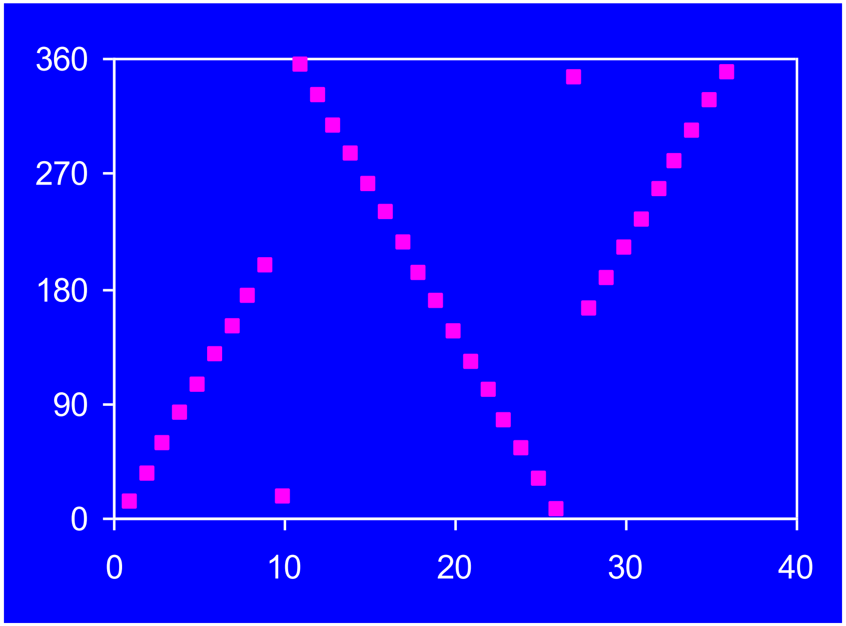
BRUKER BIOSPIN

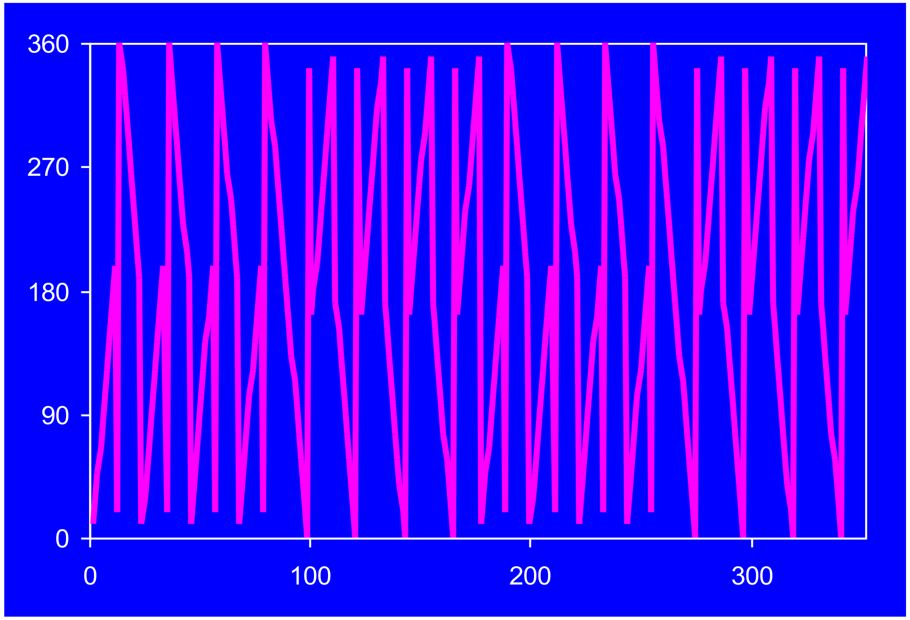
PMLG Experiments

- Typical PMLG shapes

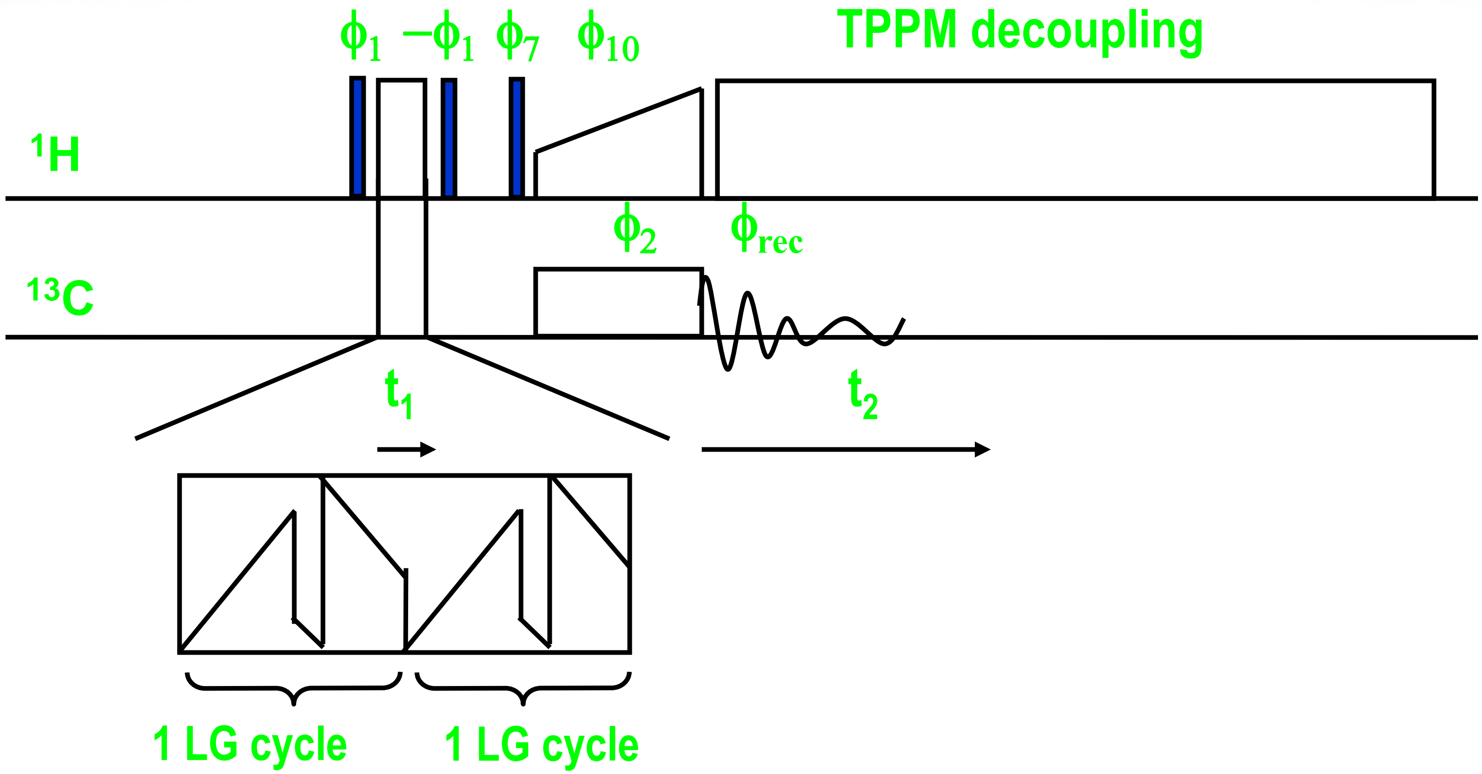
$$(x\bar{x})(\bar{x}x)$$

$$(x\bar{x})_4(\bar{x}x)_4(x\bar{x})_4(\bar{x}x)_4$$





PMLG Experiments



Pulse Program using normal shape: lghetshape.av

Pulse Program using fast shape: lghetloop.av

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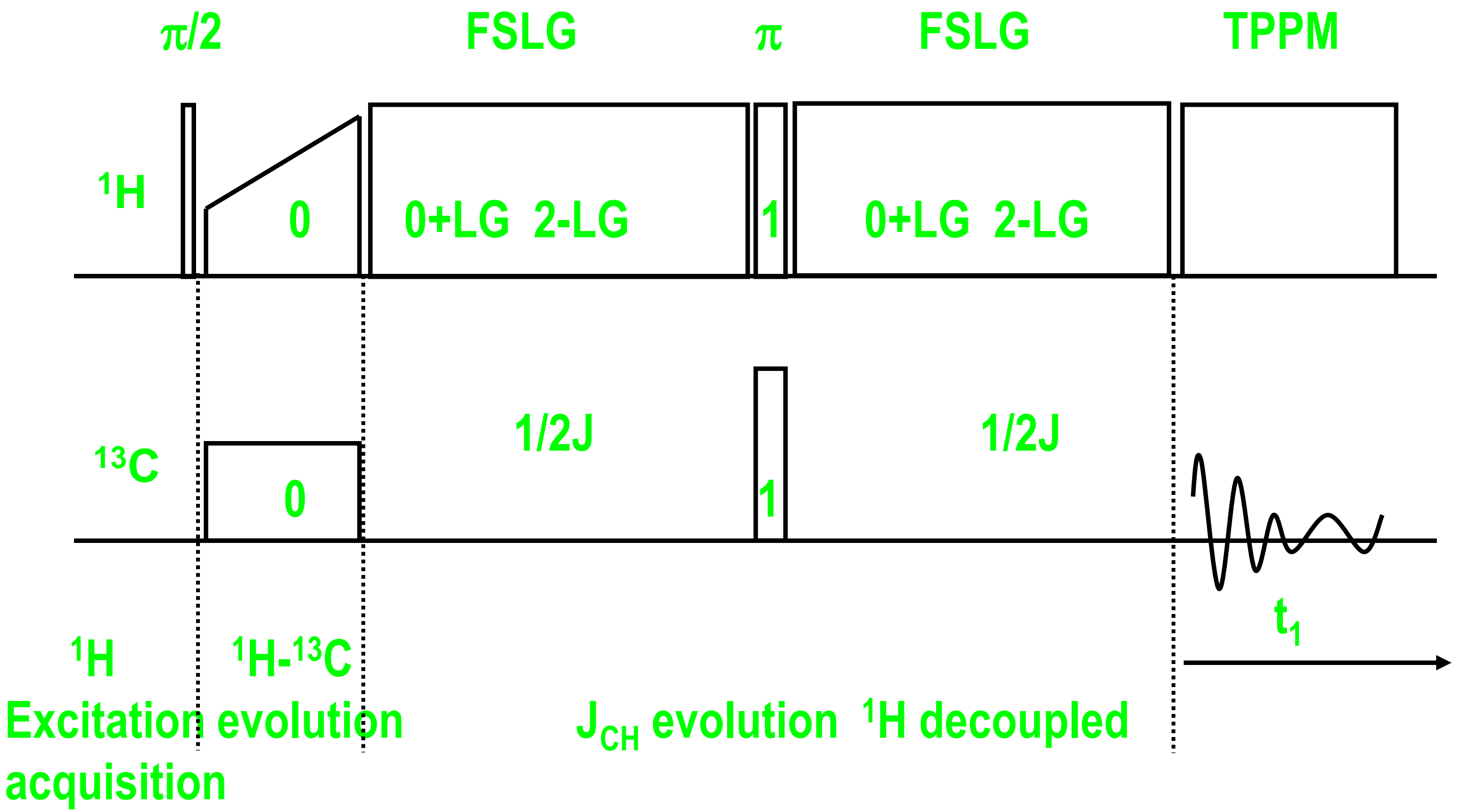
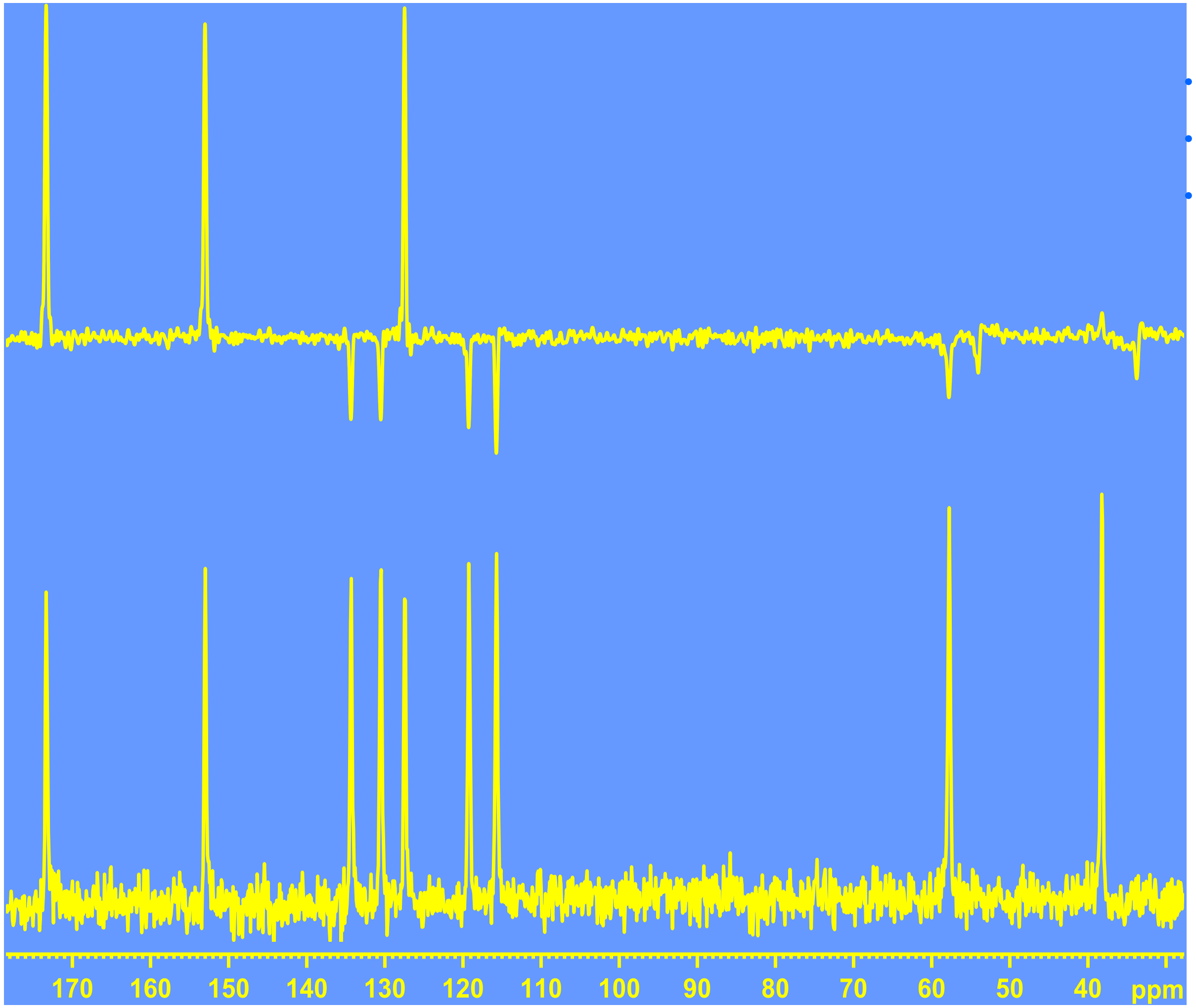
Experiments using FSLG or PMLG

- Attached Proton Test in Solid State NMR



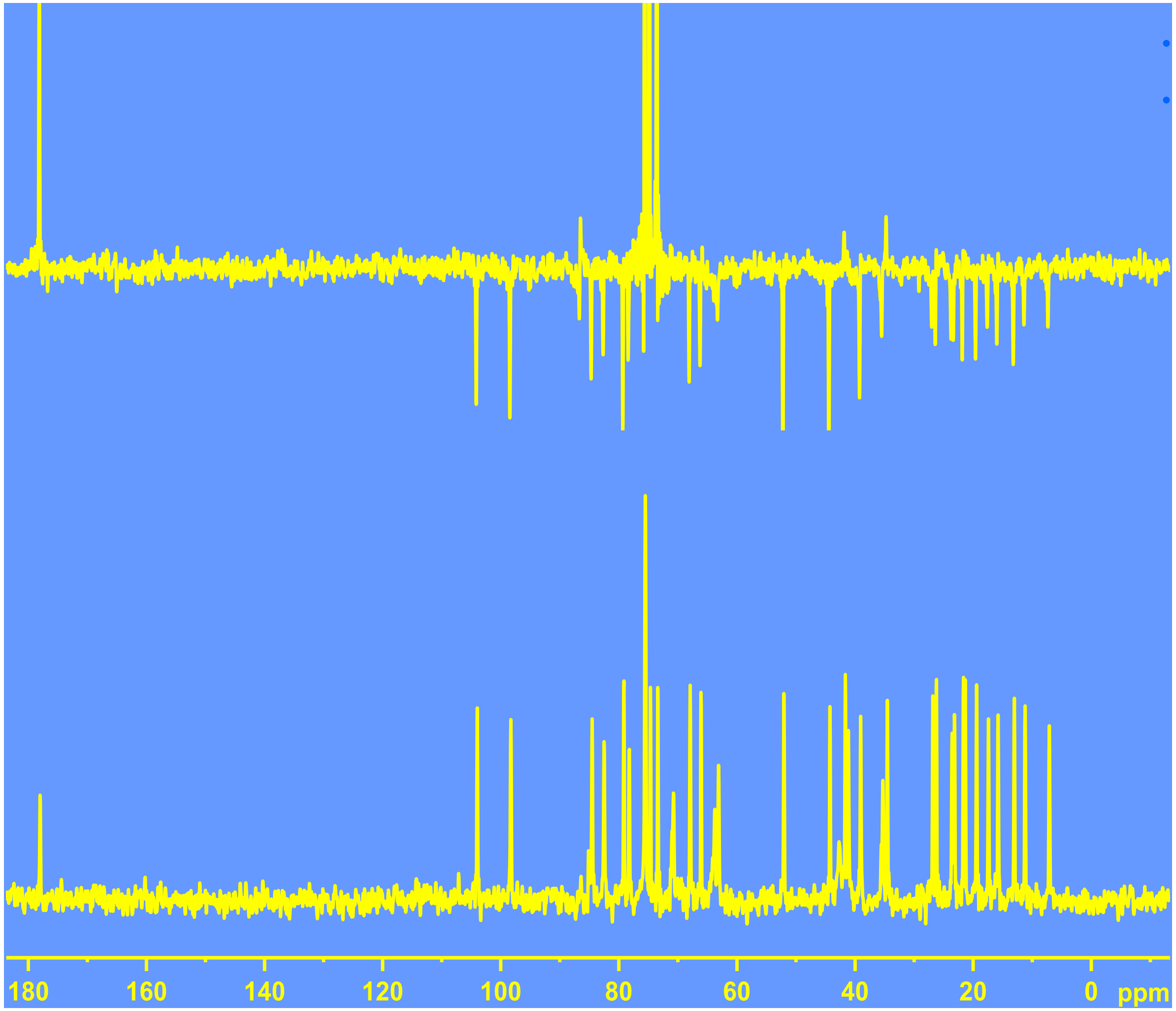
A. Lesage, S. Steuernagel, L. Emsley, J. Am. Chem. Soc. 1998, 120, 7095-7100

Attached Proton Test



- Avance 500 WB
- Tyrosine HCl
- 4 mm DVT probe
  - $^{1}H/^{13}C$, 1 ms contact
  - ±80.6 kHz frequency switch
  - ^{13}C rf field: 67 kHz
  - ^{1}H rf field:
    - 67 kHz contact
    - 114 kHz TPPM and FSLG
  - τ = 5.5 ms
  - 256 scans
  - 2.5 s recycle delay

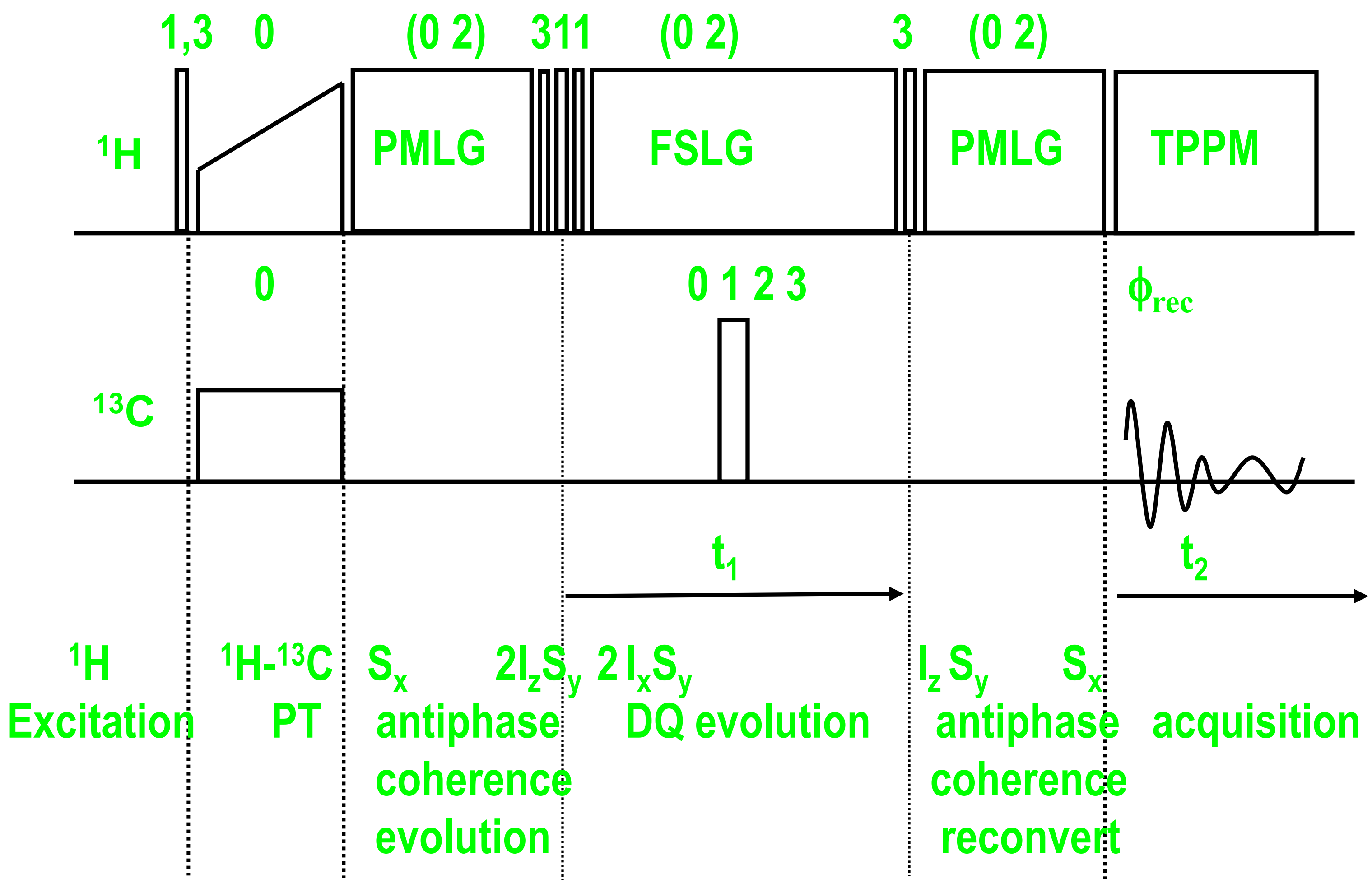
Attached Proton Test



- Avance 500 WB
- 4 mm DVT probe
  - – $^{1}H/^{13}C$, 1 ms contact
  - – ±80.6 kHz frequency switch
  - – ^{13}C rf field: 67 kHz
  - – ^{1}H rf field:
    - –67 kHz contact
    - –114 kHz TPPM and FSLG
  - – τ = 5.5 ms
  - – 256 scans
  - – 2.5 s recycle delay

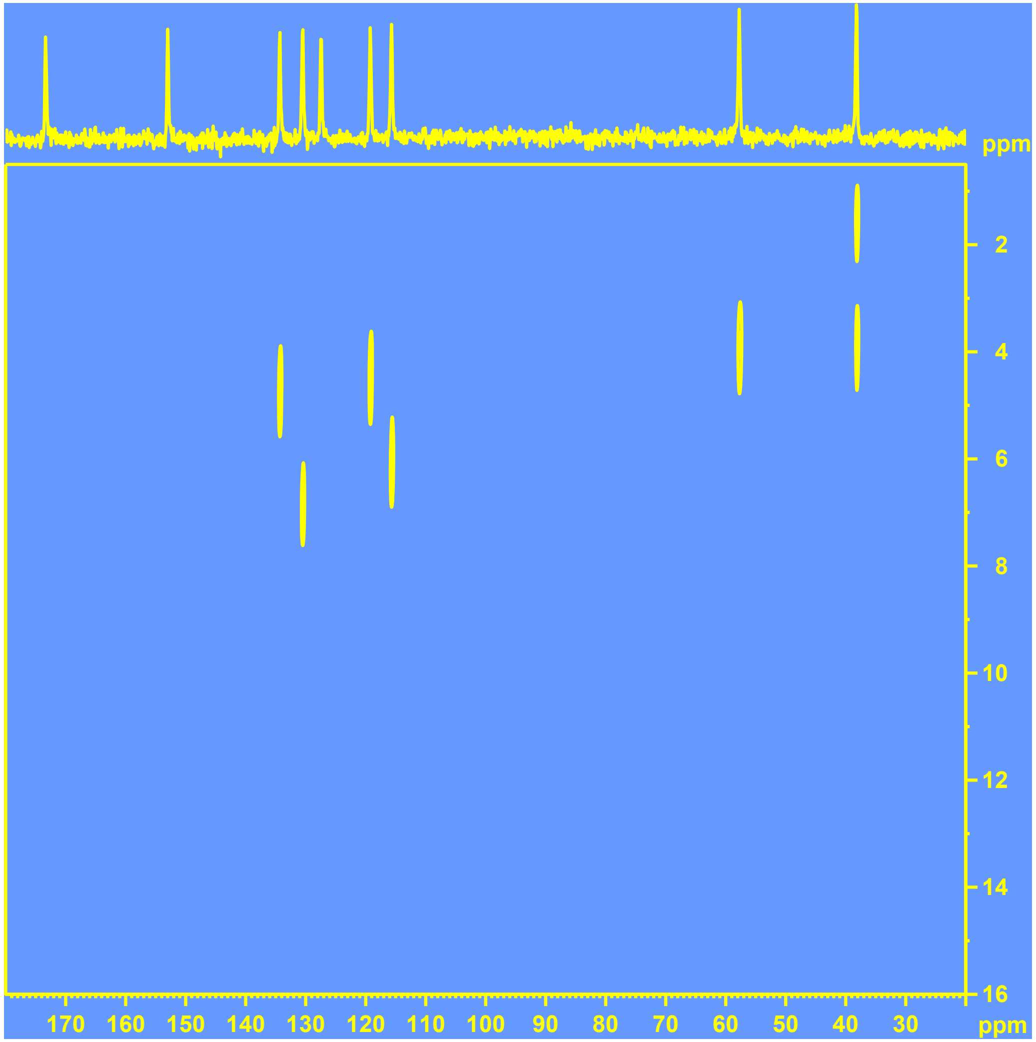
Experiments using FSLG or PMLG

- MAS-J- HMQC



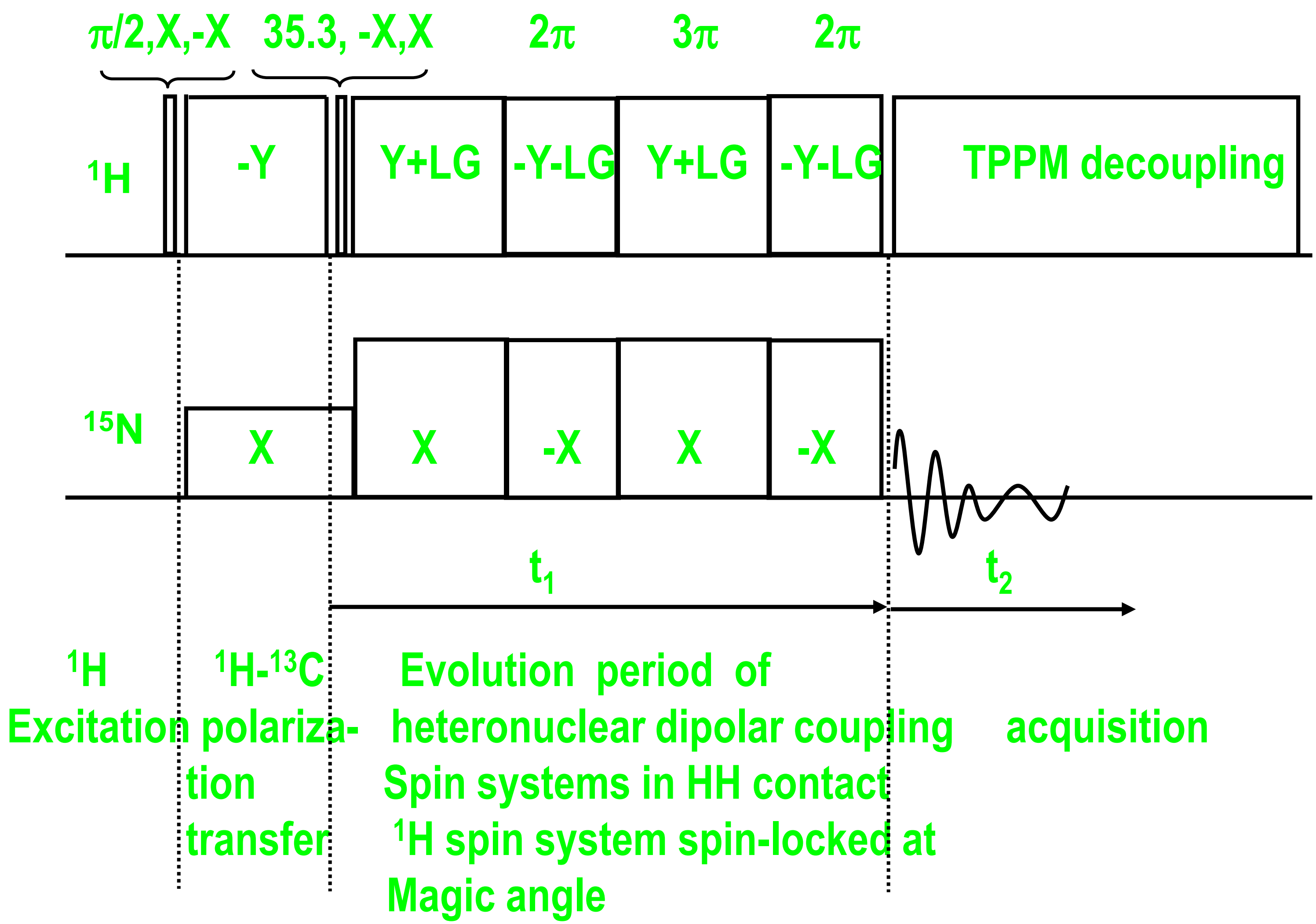
MAS-J-HMQC

- Avance 500 WB
- 4 mm DVT probe
  - $^{1}H/^{13}C$, 1 ms contact
  - ±80.6 kHz frequency switch
  - ^{13}C rf field: 67 kHz
  - ^{1}H rf field:
    - 67 kHz contact
    - 114 kHz TPPM and FSLG
  - 96 scans
  - 2.5 s recycle delay



Experiments using FSLG or PMLG

- PISEMA



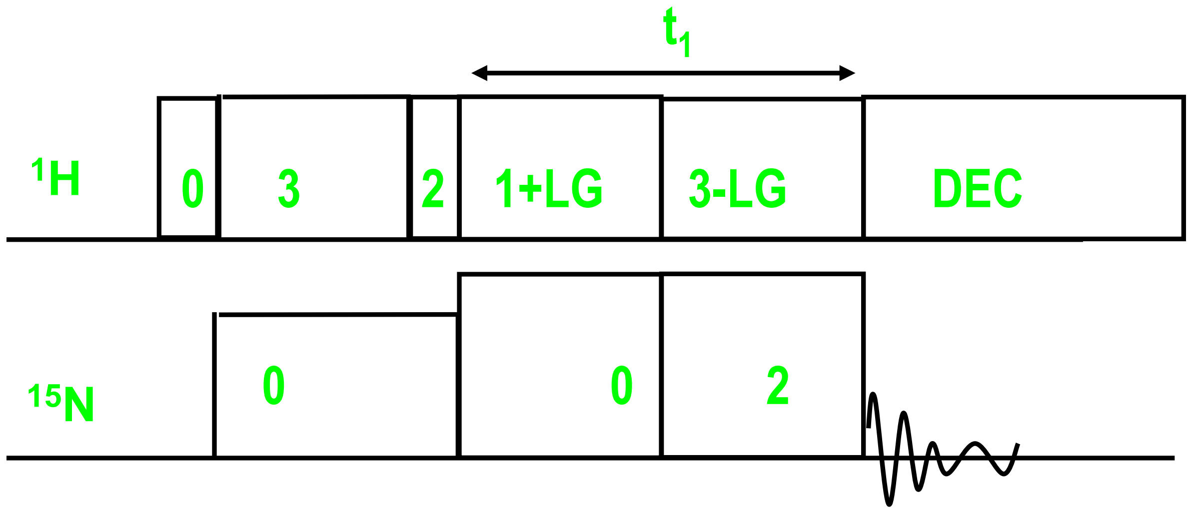
Experiments using FSLG or PMLG

- PISEMA setup
  - Determine all pulses and power levels using ^{15}N labeled Glycine with 1D CP experiments:
    - ^{1}H pulses and power levels
    - Calculate LG frequency
    - ^{15}N pulses and power levels
    - Set LG frequency and calculate required power level for ^{15}N
    - optimize HH contact by variation of power level for ^{15}N

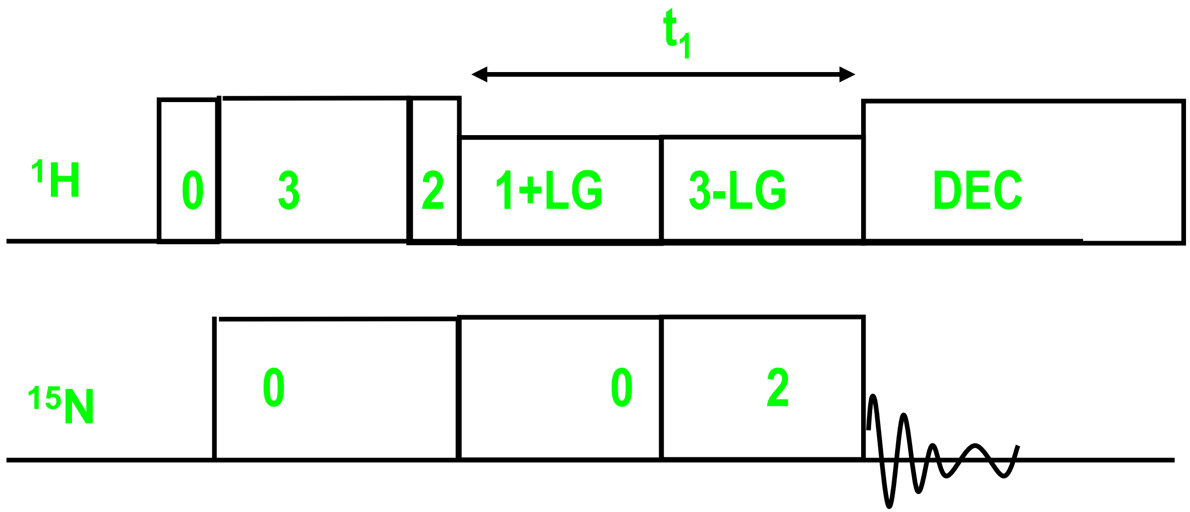
  Alternatively:
    - Measure ^{1}H pulses and power levels
    - Calculate LG frequency assuming ^{1}H B_1 field is effective field. Calculate required power level cange for ^{1}H
    - Set LG frequency and calculated power level for ^{1}H
    - optimize HH contact by variation of power level for ^{1}H

Experiments using FSLG or PMLG

- Version 1

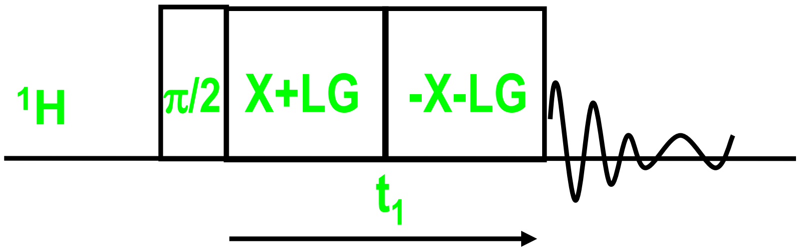


- Version 2

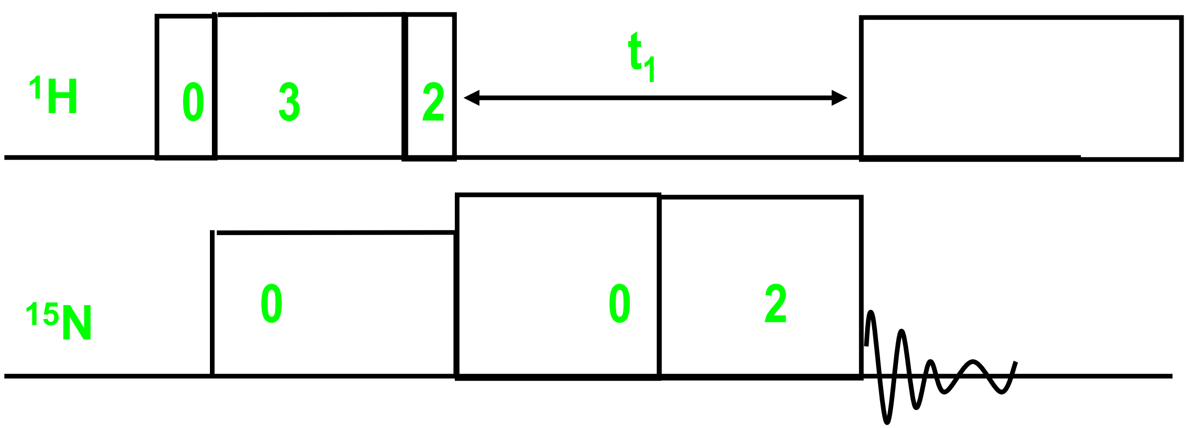


Experiments using FSLG or PMLG

- PISEMA setup additional experiments
  - Optimize LG decoupling using water sample
    - Check resonance
    - measure scaling factor
    - (Measure reflected power using directional coupler)

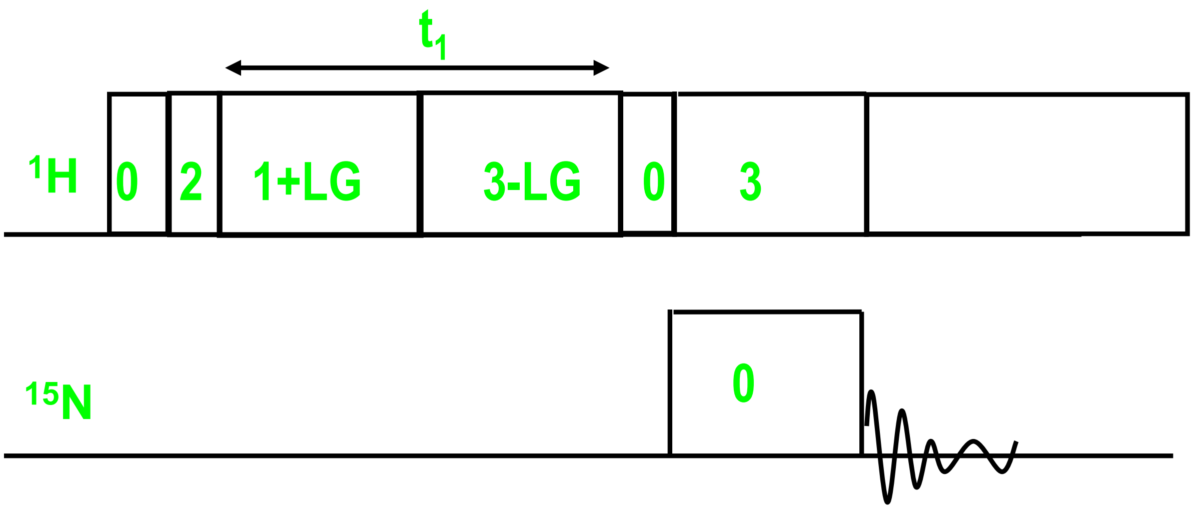


  - Test spin lock ^{15}N -
    - no oscillation of ^{15}N magnetization during spin lock



Experiments using FSLG or PMLG

- PISEMA setup
  - Test spin lock ^{1}H

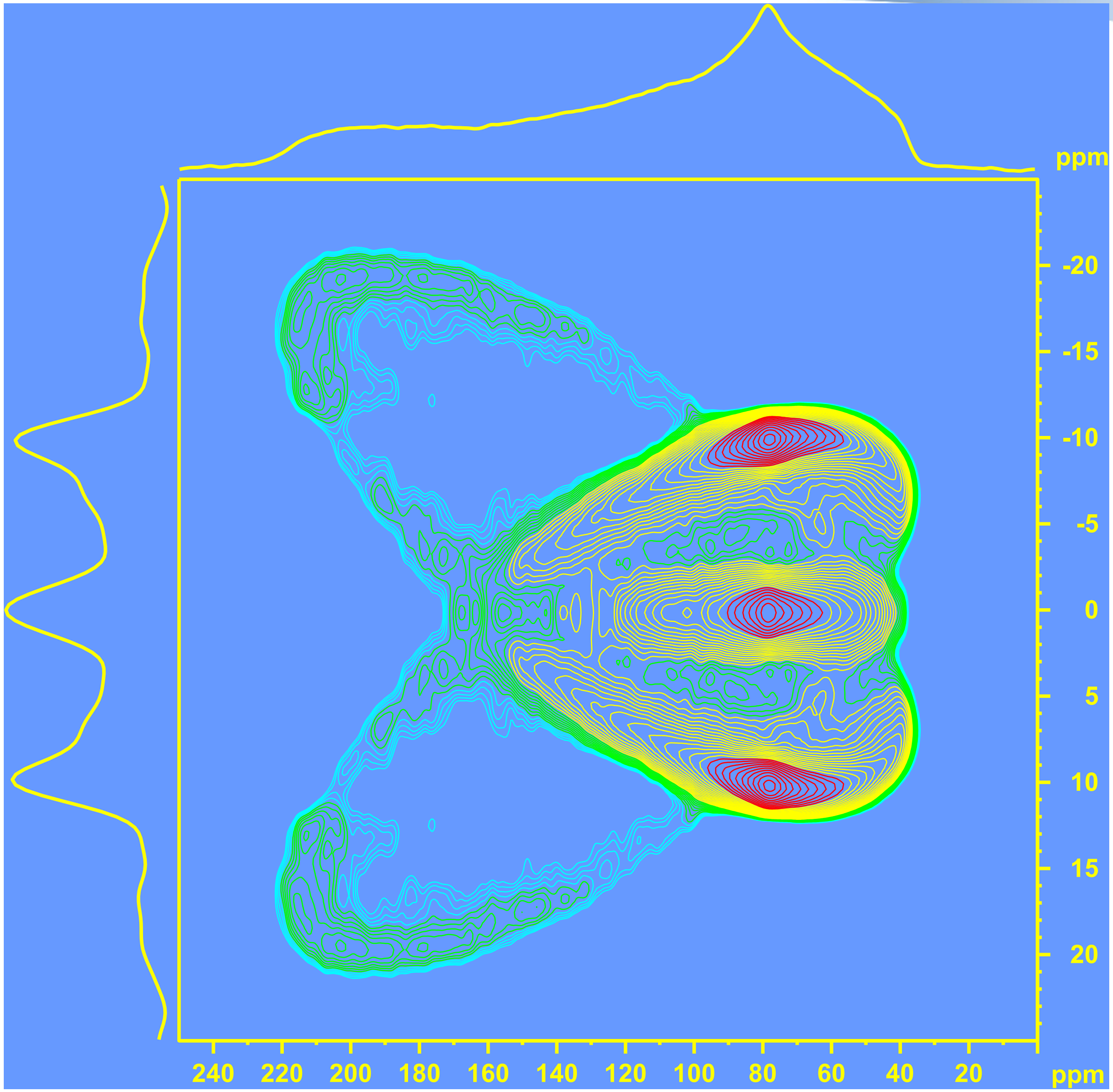


A. Ramamoorthy, C.H. Wu, and S.J. Opella, *Experimental aspects of mulridimensional Solid State NMR Correlation Spectroscopy,*

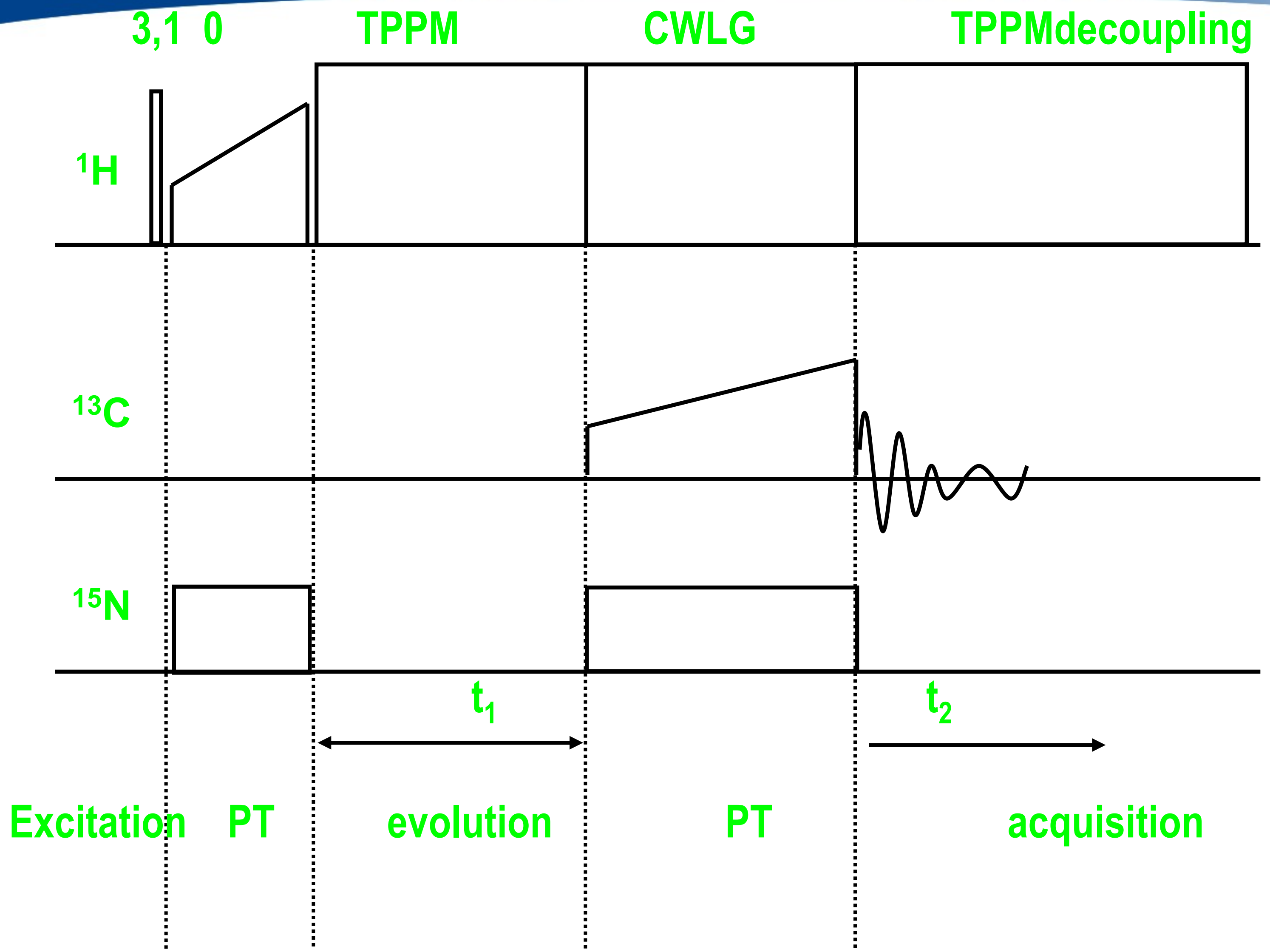
J. Magn. Reson. 140, 131-140 (1999)

PISEMA

- Avance 500 WB
- 4 mm DVT probe
  - $^1H/^{15}N$, 5 ms contact
  - ±46600 Hz frequency switch
  - ^{15}N rf field: 80.5 kHz
  - ^1H rf field:
    - 65.8 kHz (FSLG)
    - 80.5 kHz TPPM and HH contact
  - 32 scans
  - 30 s recycle delay
  - 8 h experiment time



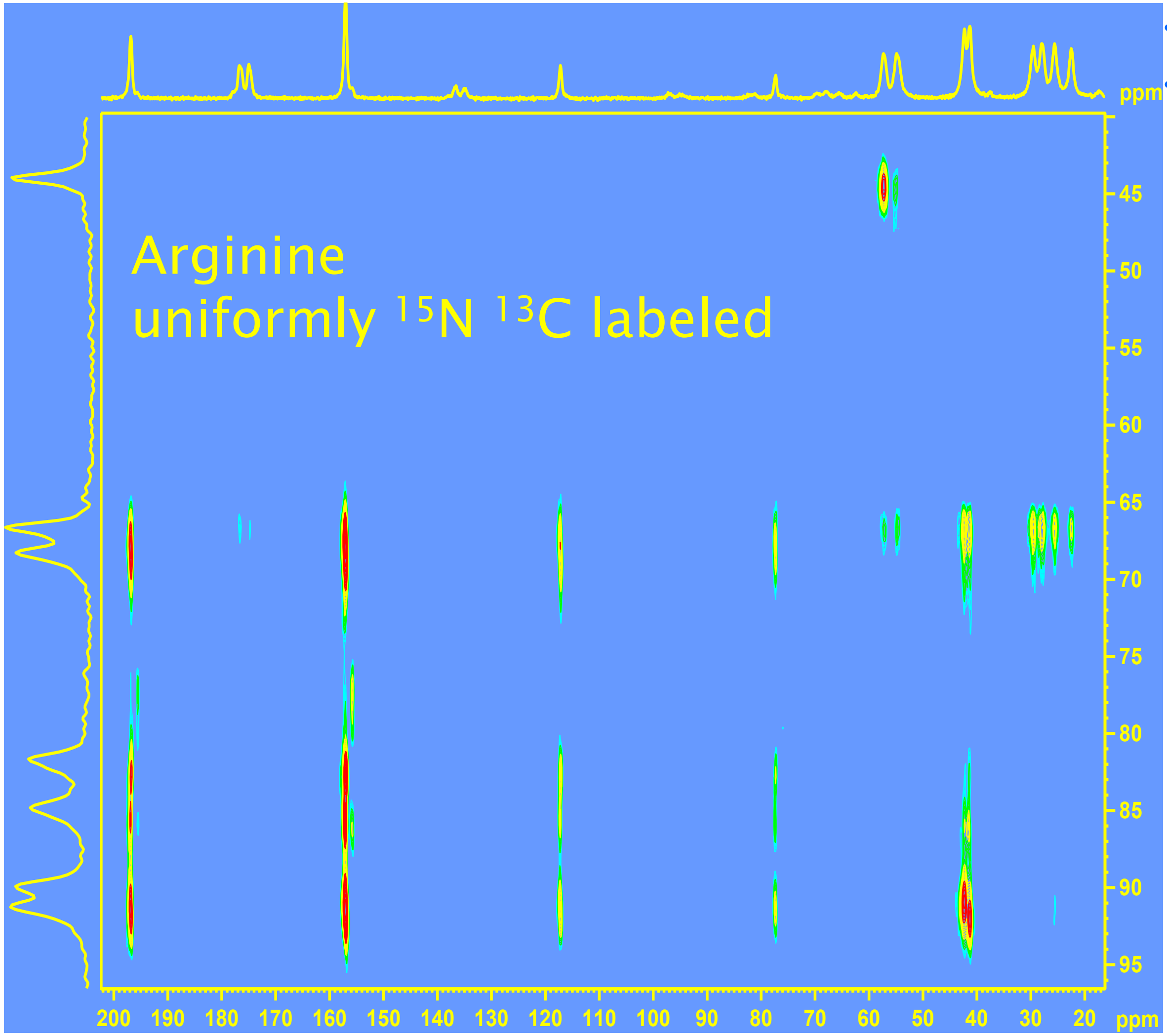
Double Cross Polarization



Double Cross Polarization

- DCP setup
  - Setup routing as in the DCP experiments
  - Use normal CP experiments to optimize HH for ^{15}N
  - Use normal CP experiment to optmize HH for ^{13}C without changing parameters on ^{1}H channel
  - Load DCP pulse program and all parameters as determined except the power level for HH contact between ^{15}N and ^{13}C. Subtract 3dB in power level for ^{13}C if ramp is used.
  - Calculate LG frequency offset for cw-LG decoupling during the second polarization transfer step
  - Run experiment as 1D and optimize ^{13}C contact
  - Load real sample setup 2D experiment .

Double Cross Polarization

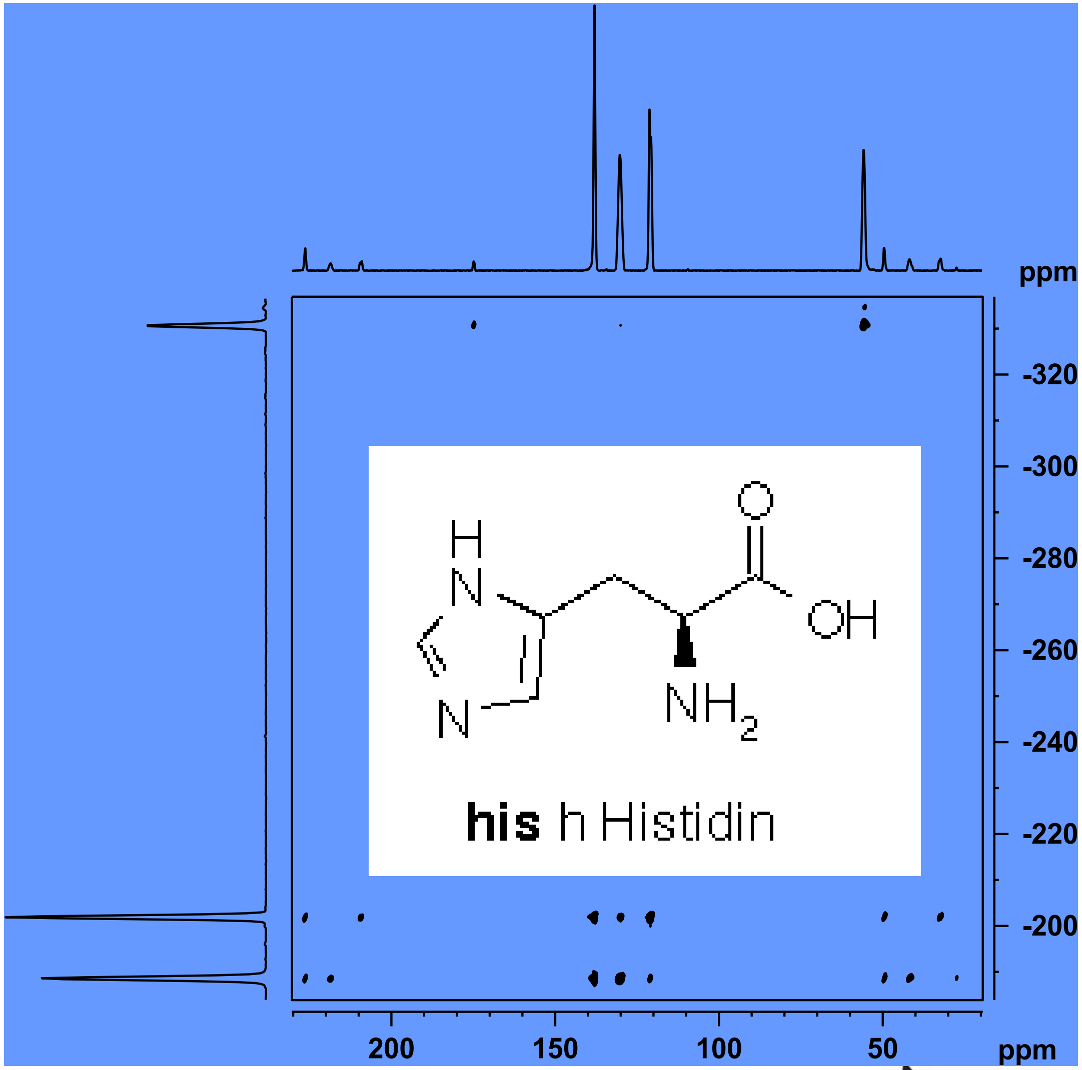


- Avance 500 WB
- 4 mm probe
  - $^1H/^{15}N$, 1 ms contact
  - $^{15}N/^{13}C$, 5 ms contact
  - variable amplitude (50% ramp)
  - ^{15}N rf field: 35 kHz
  - ^{13}C rf field 35 kHz
  - ^1H rf field: 72 kHz

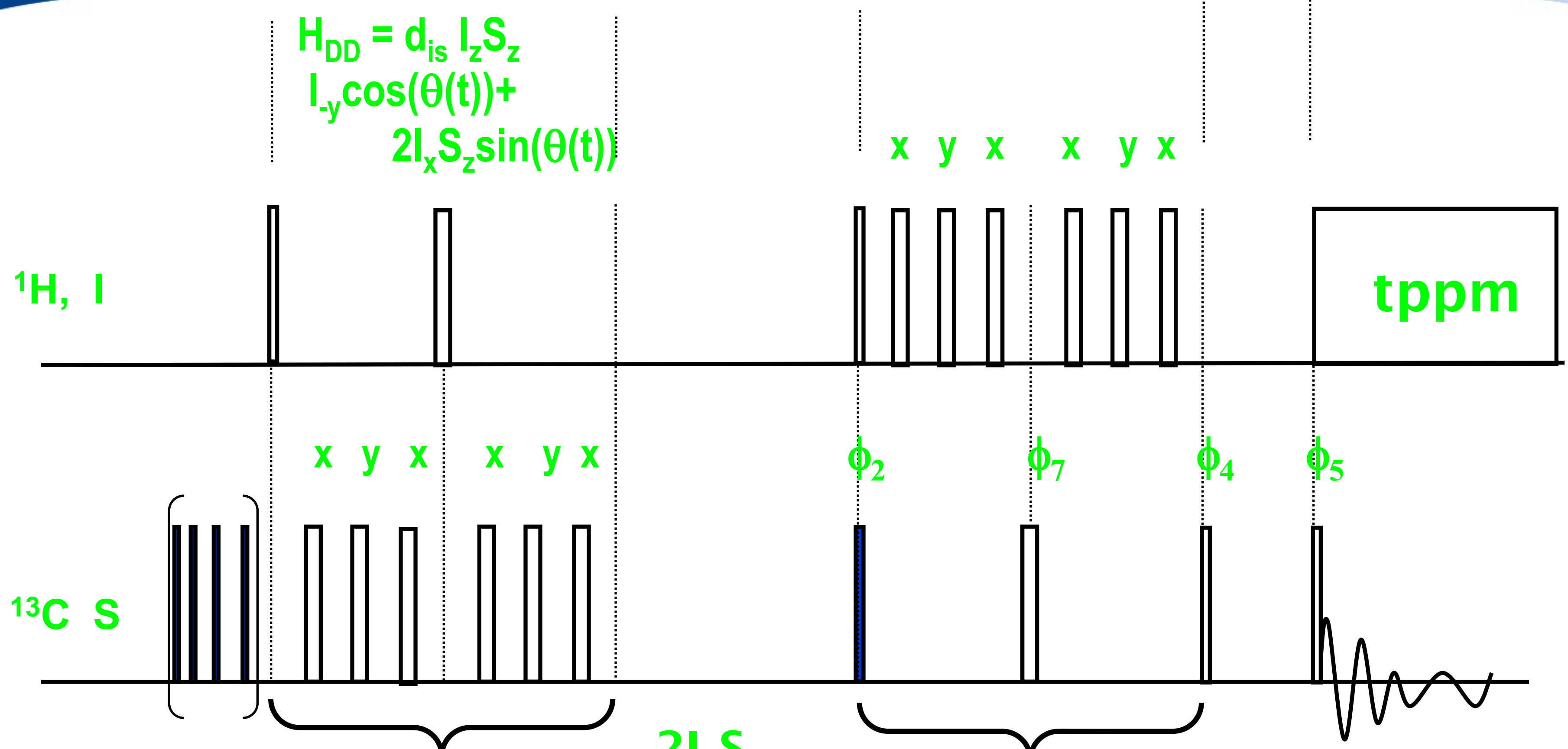
Double Cross Polarization

Avance 600 WB
2.5 mm probe

- $^{1}H/^{15}N$, 2 ms contact
- $^{15}N/^{13}C$, 1 ms contact variable amplitude (50 % ramp)
- ^{15}N RF field: 60 kHz
- ^{13}C RF field: 60 kHz
- ^{1}H RF field: 100 kHz



Recoupled Polarization Transfer HSQC

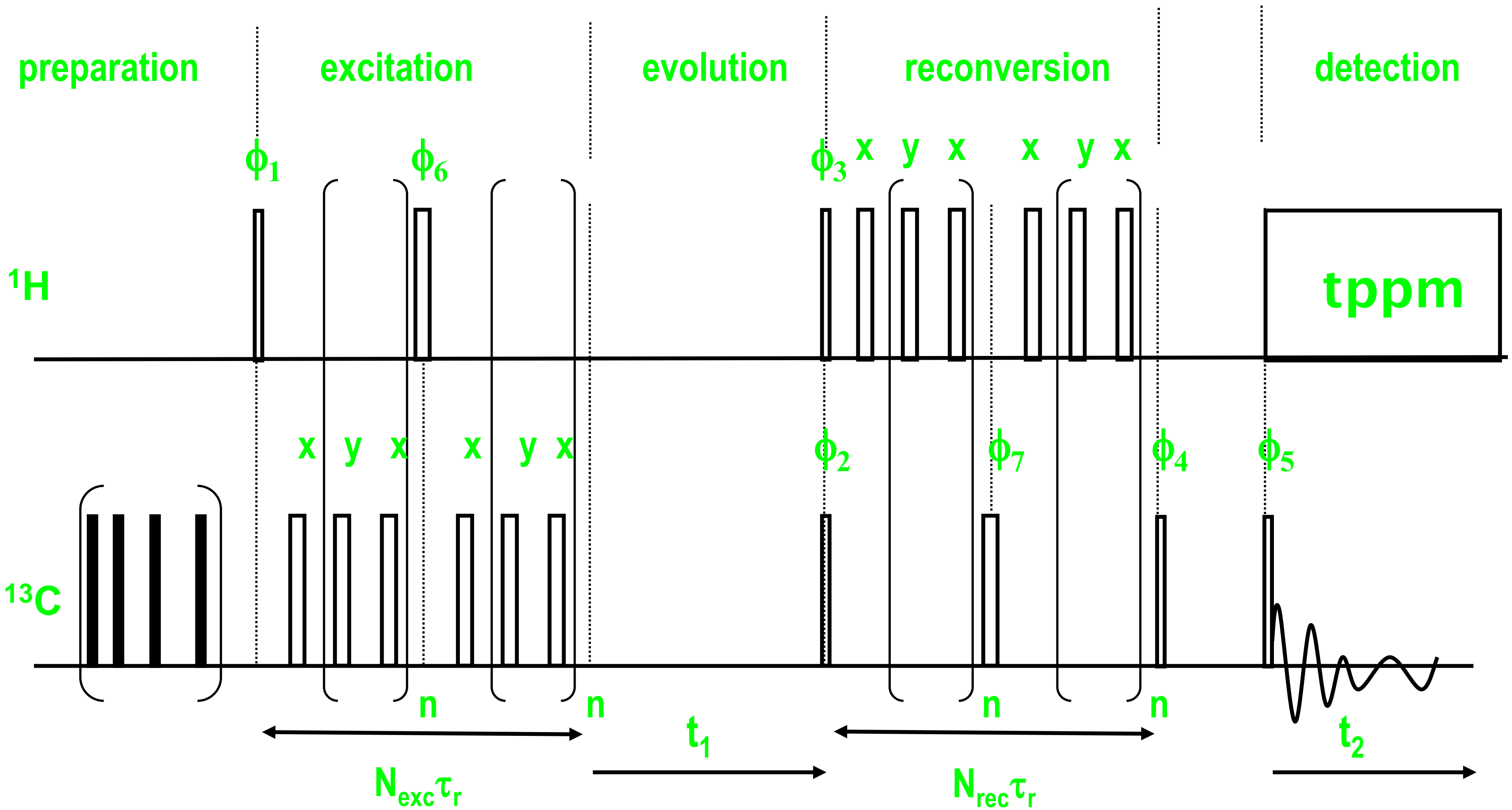


Redor Block
I_xS_z excitation
through spin pair
Dipole dipole
interaction

$2I_xS_z$
evolutio
n

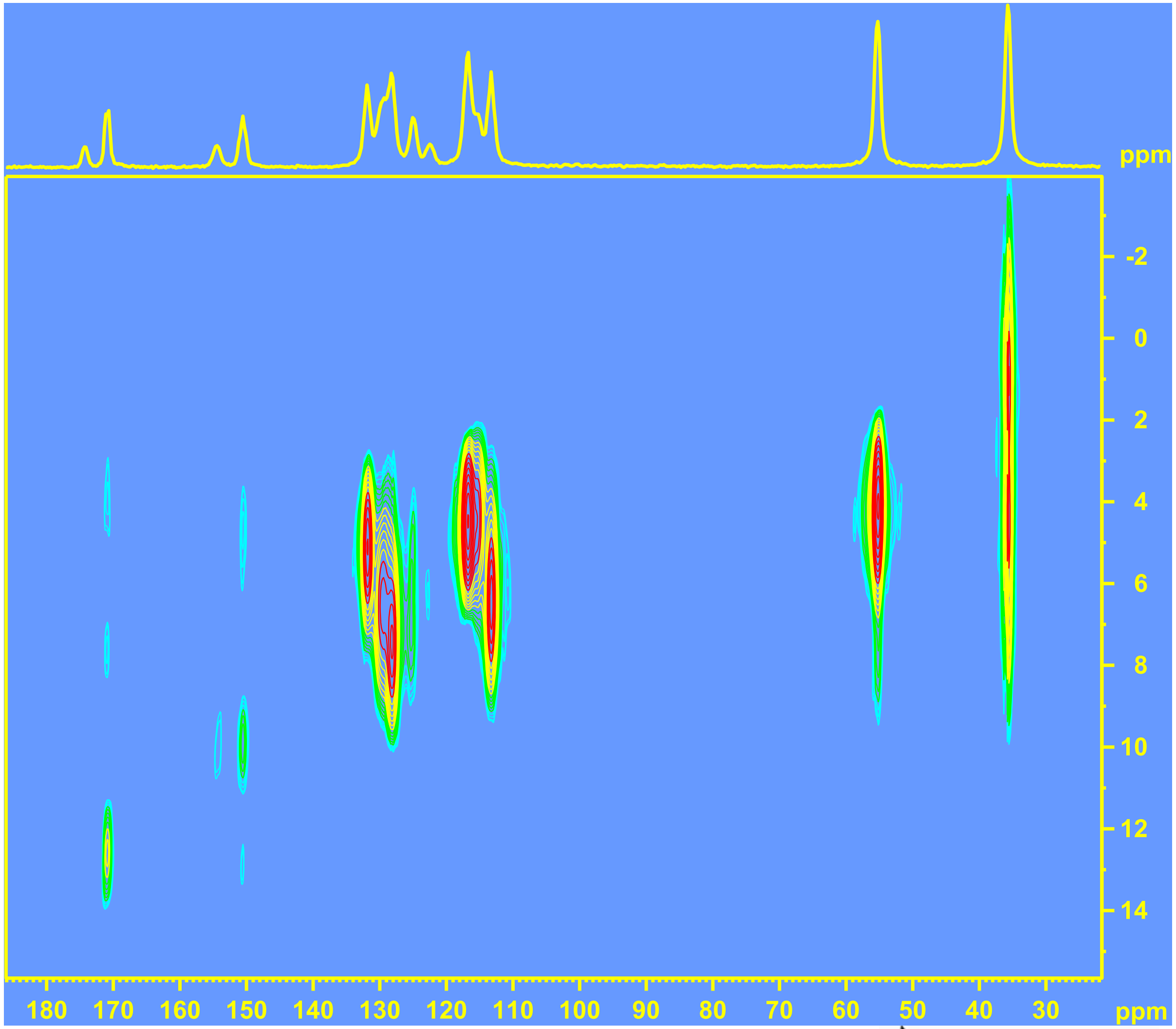
Inverted Redor
Block
S_{-y} reconversion
From I_zS_x
antiphase
coherence

Recoupled Polarization Transfer HSQC



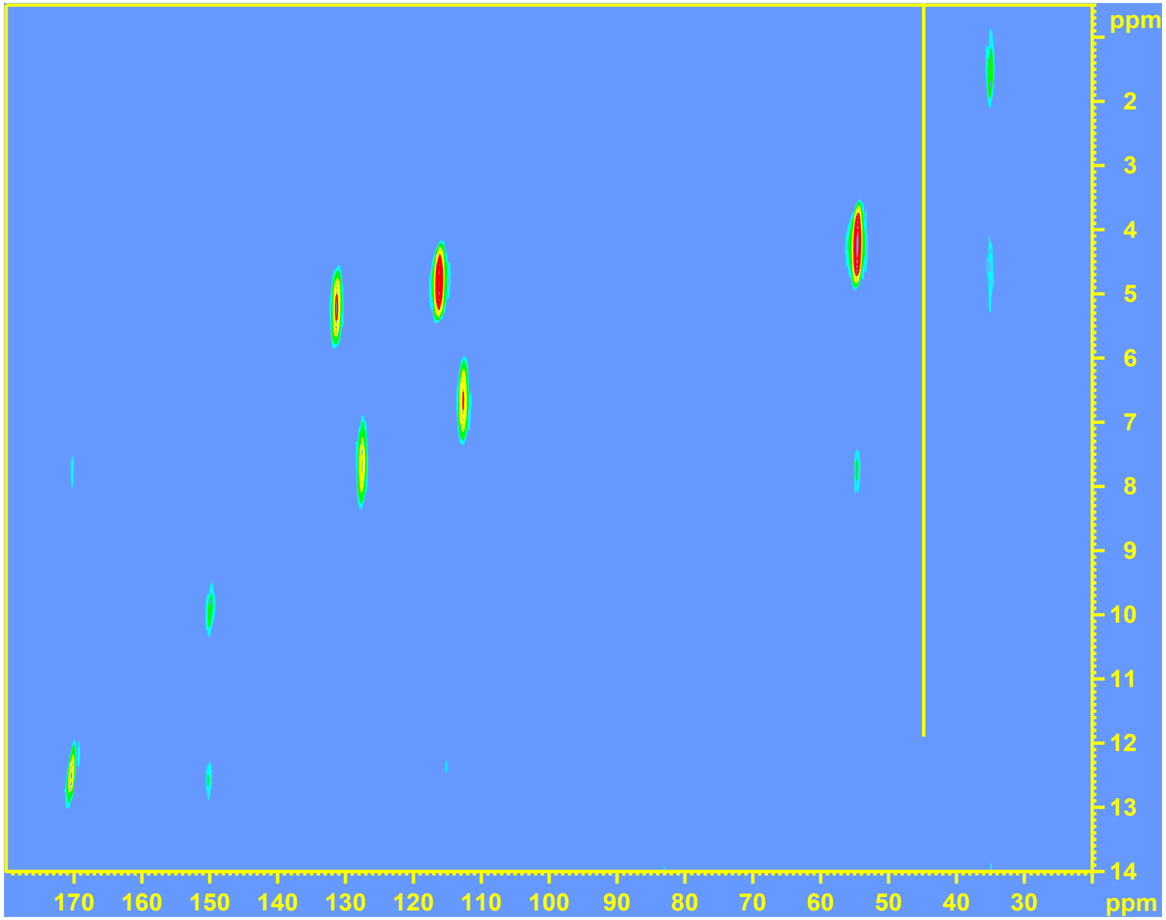
Recoupled Polarization Transfer HSQC

- Avance 500 WB
- Tyrosine HCl uniformly labeled
- 2.5 mm probe
  - 33 kHz sample rotation
  - 16 scans
  - $^{13}C\ \pi/2 = 2.3$ us
  - $^{1}H\ \pi/2 = 1.3$ us
  - 38 min experiment



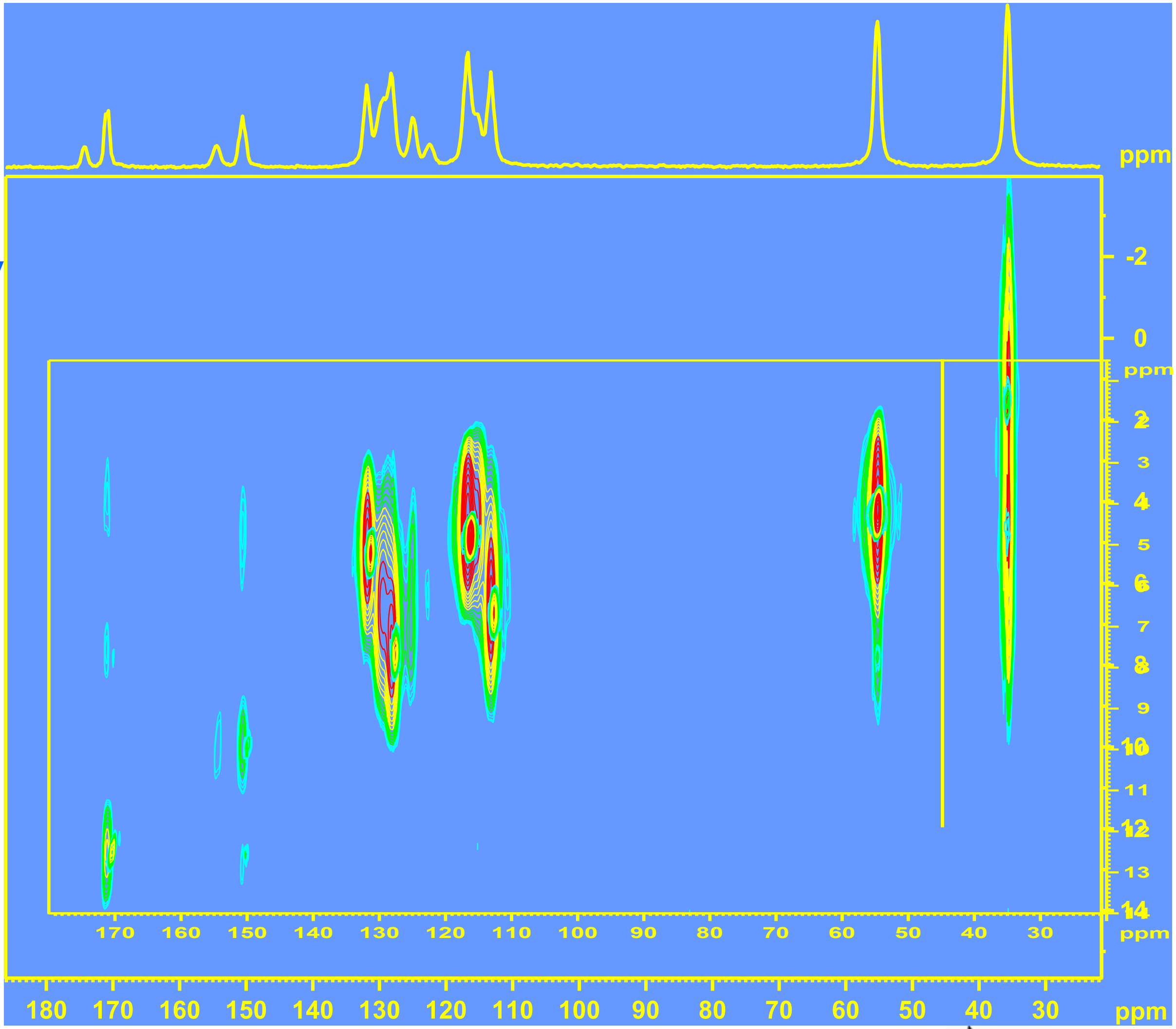
Recoupled Polarization Transfer HSQC

- Avance 700 SB
  - Courtesy of Graf et al.
- Tyrosine HCl uniformly labeled
- 2.5 mm probe
  - 33 kHz sample rotation
  - 37 min experiment



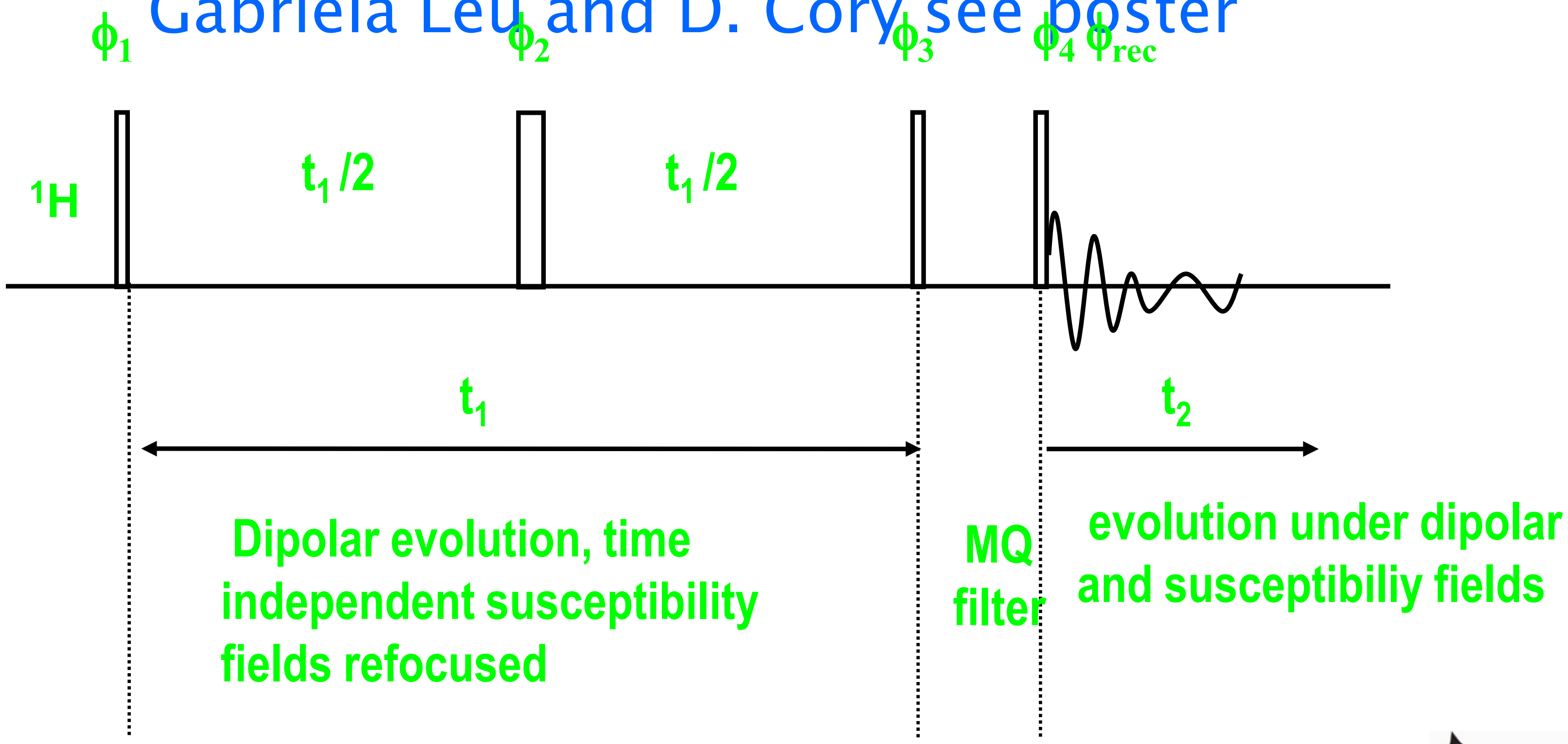
Recoupled Polarization Transfer HSQC

- Avance 700 SB
    - Courtesy of Graf et al.
- Tyrosine HCl uniformly labeled
- 2.5 mm probe
    - 33 kHz sample rotation
    -

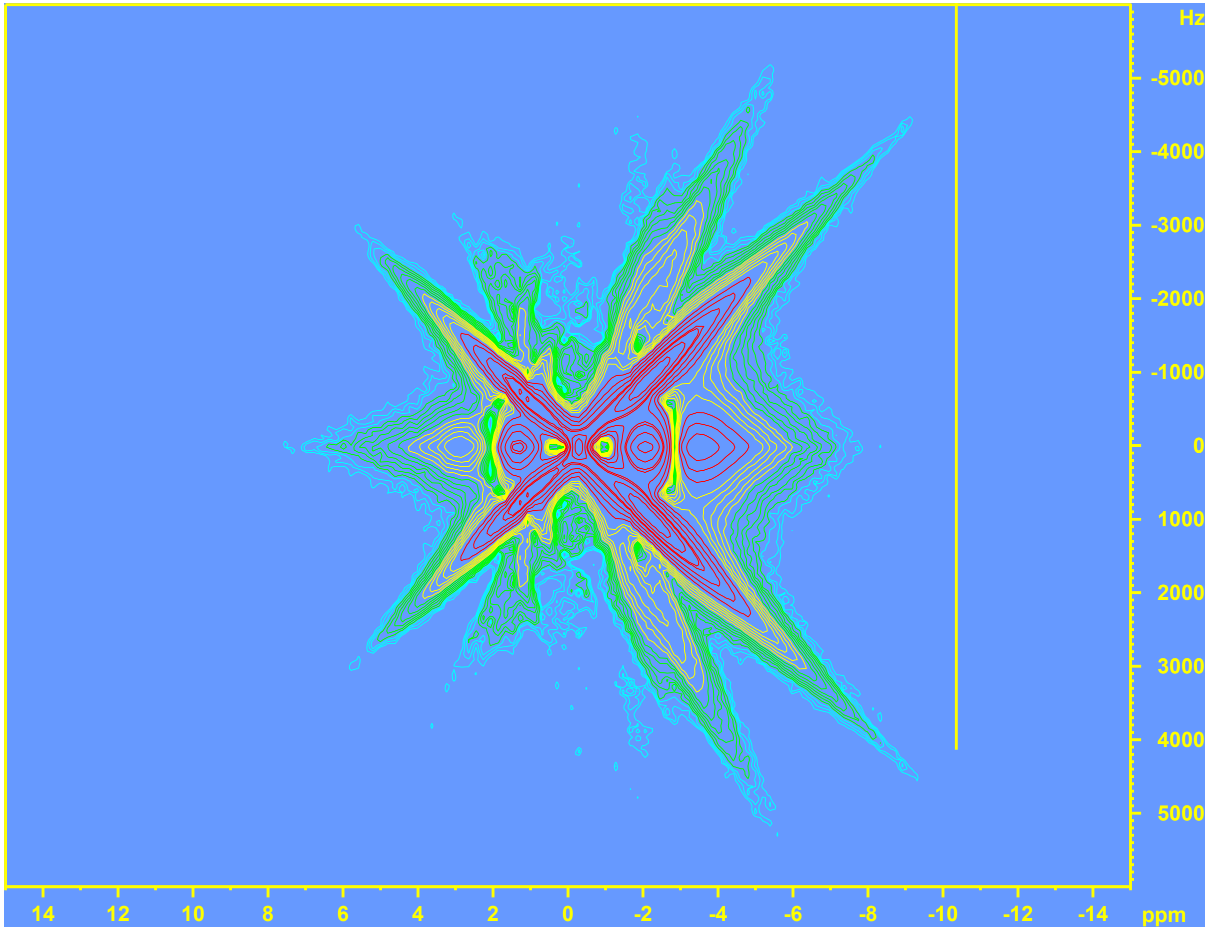


Separated local field spectroscopy

- Separated Local Field Spectroscopy
  - Experiment correlates susceptibility+dipol dipole interaction with dipole dipole interaction in f1.
  - Gabriela Leu and D. Cory, see poster



Separated local field spectroscopy



Separated local field spectroscopy