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 tailoring 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:

$\sigma_{xx} = 191$ ppm

11 ppm

Powder pattern:

three principal components $\sigma_{xx}, \sigma_{yy}, \sigma_{zz}$. 

$\sigma_{xx} \quad \sigma_{yy} \quad \sigma_{zz}$
Local field $B_{\text{loc}}$ 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

\[ \sigma_{\text{iso}} = \frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) \]
Averaging CSA powder pattern

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

$$\sigma_{\text{iso}} = \frac{(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})}{3}$$
Adamantane
1H spectra
increasing spinning speed

Averaging DD powder pattern

Current Data Parameters
NAME         Adamantane
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20021005
Time              10.50
INSTRUM           spect
PROBHD   4 mm MAS 1H H1
PULPROG              zg
TD                 2048
SOLVENT           chcl3
NS                   32
DS                    0
SWH           35714.285 Hz
FIDRES        17.438616 Hz
AQ                    0.0287360 sec
RG                    8
DW               14.000 usec
DE                6.00 usec
TE                373.0 K
D1           2.50000000 sec

-------- CHANNEL f1 --------
NUC1                 1H
P1                 1.70 usec
PL1                1.00 dB
SFO1        499.5509991 MHz

F2 - Processing parameters
SI                 2048
SF          499.5500000 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
PC                 1.00
Averaging DD interactions

$\Delta'_\text{stat}$ static linewidth
$\Delta'_{\text{MAS}}$ linewidth at $\nu_R$
$\nu_R$ Spinning speed

$\Delta'_\text{stat} / \nu_R$ Increasing spinning speed
Magic Angle Setup

• Use KBr sample,
• Call parameter set KBr by typing rpar KBr
Check or set routing using edasp:
Magic Angle Setup

- Check parameters in the ased:

```
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PULPROG</td>
<td>zg</td>
<td>Pulse program for acquisition</td>
</tr>
<tr>
<td>TD</td>
<td>4096</td>
<td>Time domain size</td>
</tr>
<tr>
<td>NS</td>
<td>4</td>
<td>Number of scans</td>
</tr>
<tr>
<td>DS</td>
<td>0</td>
<td>Number of dummy scans</td>
</tr>
<tr>
<td>SWH</td>
<td>250000.00 Hz</td>
<td>Sweep width in Hz</td>
</tr>
<tr>
<td>AQ</td>
<td>0.0082440 sec</td>
<td>Acquisition time</td>
</tr>
<tr>
<td>RG</td>
<td>128</td>
<td>Receiver gain</td>
</tr>
<tr>
<td>DW</td>
<td>2.000 usec</td>
<td>Dwell time</td>
</tr>
<tr>
<td>DE</td>
<td>4.50 usec</td>
<td>Pre-scan-delay</td>
</tr>
<tr>
<td>D1</td>
<td>0.50000000 sec</td>
<td>Relaxation delay; 1-5 * T1</td>
</tr>
<tr>
<td>NUC1</td>
<td>79Br</td>
<td>Nucleus for channel 1</td>
</tr>
<tr>
<td>P1</td>
<td>0.00 usec</td>
<td>F1 channel – high power pulse</td>
</tr>
<tr>
<td>PL1</td>
<td>120.00 dB</td>
<td>F1 channel – power level for pulse (def</td>
</tr>
<tr>
<td>SF01</td>
<td>125.1520039 MHz</td>
<td>Frequency of observe channel</td>
</tr>
</tbody>
</table>
```

----- CHANNEL f1 -----

SAVE  2-COL  Parameter  Next  CANCEL
• 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:**

![Acquisition Parameters Screen](image)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Frequency</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>5005.88 Hz</td>
<td>125,1520039 MHz</td>
<td></td>
</tr>
<tr>
<td>01P</td>
<td>40,000 ppm</td>
<td>125,1469980 MHz</td>
<td></td>
</tr>
<tr>
<td>02</td>
<td>0.00 Hz</td>
<td>499,5000000 MHz</td>
<td></td>
</tr>
<tr>
<td>02P</td>
<td>0.00 ppm</td>
<td>499,5000000 MHz</td>
<td></td>
</tr>
<tr>
<td>03</td>
<td>0.00 Hz</td>
<td>499,5000000 MHz</td>
<td></td>
</tr>
<tr>
<td>03P</td>
<td>0.00 ppm</td>
<td>499,5000000 MHz</td>
<td></td>
</tr>
<tr>
<td>04</td>
<td>0.00 Hz</td>
<td>499,5000000 MHz</td>
<td></td>
</tr>
<tr>
<td>04P</td>
<td>0.00 ppm</td>
<td>499,5000000 MHz</td>
<td></td>
</tr>
<tr>
<td>CPDPREG1</td>
<td>mlev</td>
<td>tppm15</td>
<td></td>
</tr>
<tr>
<td>CPDPREG2</td>
<td>mlev</td>
<td>mlev</td>
<td></td>
</tr>
<tr>
<td>CPDPREG3</td>
<td>mlev</td>
<td>mlev</td>
<td></td>
</tr>
<tr>
<td>CPDPREG4</td>
<td>mlev</td>
<td>mlev</td>
<td></td>
</tr>
<tr>
<td>CPDPREG5</td>
<td>mlev</td>
<td>mlev</td>
<td></td>
</tr>
<tr>
<td>CPDPREG6</td>
<td>mlev</td>
<td>mlev</td>
<td></td>
</tr>
<tr>
<td>CPDPREG7</td>
<td>mlev</td>
<td>mlev</td>
<td></td>
</tr>
</tbody>
</table>
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:
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 set for processing data 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 Setup

- Store as 2D data (ser file)
- The AU program specified in AUNM will be executed
- Run optimization in background

Info:
Each line in the table below describes a single parameter.
If the checkbox of a parameter is off, the parameter will be ignored in the AU program.
During save, it will be saved as comment with the prefix 'Off'.
If option INC is not zero and option VARMOD is LIN, the experiment number NEXP will be ignored. You can omit it in this case.

Dataset: C:\data/jcs0302/nmr/pfizer4mmprobe/10/

<table>
<thead>
<tr>
<th>On/Off</th>
<th>Parameter</th>
<th>OPTIMUM</th>
<th>STARTVAL</th>
<th>ENDVAL</th>
<th>NEXP</th>
<th>VARMOD</th>
<th>INC</th>
</tr>
</thead>
<tbody>
<tr>
<td>✔️</td>
<td>pl</td>
<td>ZERO</td>
<td>0.25</td>
<td>40</td>
<td>0</td>
<td>LIN</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>POSMAX</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Start | Halt | Read protocol | Add parameter | Read parameters | Save | Restore | Update | Exit

Status: Save parameters to file ...
Parameter optimization

poptau for p1 finished.
ZERO at experiment 16.749563: p1 = 4.187391

NEXP=160
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**
  - Enter pulse width: e.g. 4us <return>
Setup Direct Polarization Experiments

- Direct Polarization $^{13}\text{C}$ 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: `dpreg2`

Diagram:
- $^{1}\text{H} : f_2$
- $p_{l_{12}}$
- $^{13}\text{C} : f_1$
- $p_1 p_{l_1}$

Excitation, acquisition, evolution, decoupling
Setup Direct Polarization Experiments

- EDASP display:

Prefered output for 19F:
- 19F
- X
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 parameter sets
Productivity Tools

- Parameter sets
Productivity Tools

- Pulse Programs, etc
Productivity Tools

- Pulse Programs for consoles with AQS (SGU) electron
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
Productivity Tools

- Composit Pulse Decoupling (CPD) Programs
Productivity Tools

• Composit Pulse Decoupling (CPD) Programs
Productivity Tools

- Shape Files (CPD)
Productivity Tools

- Lists

5.3.8 Parameter lists [edlist]

Parameter lists are text files containing a series of values for parameters which may vary during an experiment. This command allows you to create a new list, and to edit or view an existing one.

Xwn-nmr locates parameter lists in the directory

```
/w/exp/stan/nmr/lists/<list type>/
```

The command `edlist` displays all lists in this directory in a dialog box from where one may be selected. See Table 5.6 for the available list types.

<table>
<thead>
<tr>
<th>list type</th>
<th>contains</th>
</tr>
</thead>
<tbody>
<tr>
<td>vd</td>
<td>delay lists</td>
</tr>
<tr>
<td>vp</td>
<td>pulse lists</td>
</tr>
<tr>
<td>f1</td>
<td>frequency lists (AVANCE)</td>
</tr>
<tr>
<td>f1, f2, f3</td>
<td>frequency lists (A,X)</td>
</tr>
<tr>
<td>vt</td>
<td>temperature lists</td>
</tr>
<tr>
<td>wc</td>
<td>loop counter lists</td>
</tr>
<tr>
<td>ds</td>
<td>data set lists</td>
</tr>
<tr>
<td>masr</td>
<td>MUSR rotation values</td>
</tr>
</tbody>
</table>
corresponding list types *pp*, *cpd*, *gp*, and *mac* will also be displayed when *edlist* is called. It is therefore possible to edit pulse programs etc. via the dedicated commands *edpul*, etc., but also via *edlist* by specifying the corresponding list type.

The command *edlist* may also be entered on the keyboard, followed by the type of the desired list, or followed by the list type and the desired list name, which may contain wildcard characters (see *edpul* and how to change the default text editor for details).

**Format of parameter lists**

The length of a parameter list is unlimited.

A *delay* or *pulse list* (Table 5.7, left column) contains one duration value per line, followed by a time unit (s=seconds, m=milliseconds, u= microseconds). The values in a delay list are interpreted by the variable delay statement *vd* in pulse programs. The values in a pulse list are interpreted by the variable pulse statement *vp* in pulse programs. These commands use the list whose name is defined in the acquisition parameter *VDLIST or VPLIST*, respectively.

<table>
<thead>
<tr>
<th>Delay Value</th>
<th>Frequency Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>10s</td>
<td>0.500.13</td>
</tr>
<tr>
<td>20m</td>
<td>3000</td>
</tr>
<tr>
<td>1.5u</td>
<td>3150</td>
</tr>
</tbody>
</table>

**Table 5.7 Example of a delay (left) and frequency list (right)**

The first line of a *frequency list* (Table 5.7, right column) contains the absolute frequency in MHz for the corresponding nucleus, preceded by an O, and a space character. The following lines contain offsets in Hz. The transmitter frequency is the sum of absolute and offset frequencies. The list is evaluated by the variable frequency statements *f01,...,f08* in pulse
Productivity Tools

- Information in stored data sets

<table>
<thead>
<tr>
<th>Name</th>
<th>Size</th>
<th>Type</th>
<th>Modified</th>
</tr>
</thead>
<tbody>
<tr>
<td>pdta</td>
<td>8 KB</td>
<td>File Folder</td>
<td>5/13/2</td>
</tr>
<tr>
<td>acqu</td>
<td>8 KB</td>
<td>File</td>
<td>5/14/2</td>
</tr>
<tr>
<td>acqu2</td>
<td>8 KB</td>
<td>File</td>
<td>5/14/2</td>
</tr>
<tr>
<td>acqu2s</td>
<td>8 KB</td>
<td>File</td>
<td>5/14/2</td>
</tr>
<tr>
<td>acquus</td>
<td>8 KB</td>
<td>File</td>
<td>5/14/2</td>
</tr>
<tr>
<td>audita.txt</td>
<td>1 KB</td>
<td>Text Document</td>
<td>5/14/2</td>
</tr>
<tr>
<td>ccppng2</td>
<td>1 KB</td>
<td>File</td>
<td>1/17/2</td>
</tr>
<tr>
<td>format.err</td>
<td>4 KB</td>
<td>TEMP File</td>
<td>5/14/2</td>
</tr>
<tr>
<td>pulseprogram</td>
<td></td>
<td>TEMP File</td>
<td>5/14/2</td>
</tr>
<tr>
<td>scanf</td>
<td>1 KB</td>
<td>File</td>
<td>5/14/2</td>
</tr>
<tr>
<td>xer</td>
<td>40 KB</td>
<td>File</td>
<td>5/14/2</td>
</tr>
<tr>
<td>spnam0</td>
<td>4 KB</td>
<td>File</td>
<td>1/17/2</td>
</tr>
<tr>
<td>vclist</td>
<td>1 KB</td>
<td>File</td>
<td>5/14/2</td>
</tr>
</tbody>
</table>
Productivity Tools

- Information in stored data sets
Productivity Tools

- Information in stored data sets
Productivity Tools

- Information in stored data sets
Audit trail:

```plaintext
#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>,<PINN>,<created by zg
 data hash MD5: 1K * 10
   CC B6 7F 0A F5 94 FA F5 9F C6 50 C4 BD 68 5B 33>)

$$ hash MD5
$$ 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:

  - **Excitation**
  - **polarization evolution, acquisition**
  - **transfer (PT)**
  - **decoupling**

  ![Diagram showing pulse sequences for CPDPRG2: CW pulse](image-url)
- 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 parameter 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.

![Diagram showing HH matching profile at different kHz frequencies](image-url)
Setup Cross Polarization Experiments

- HH matching profile from pseudo 2D data (POPT)
Setup Cross Polarization Experiments

- CP experiment using ramped rf-field during contact

Excitation | polarization evolution, acquisition transfer (PT) | decoupling
Setup Cross Polarization Experiments

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

\[
p_3 = \frac{1}{4 \times 100kHz} = 2.5 \mu s
\]

• **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=p112
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

Signal/Noise Glycine
aliphatic peak 101:1
Setup Cross Polarization Experiments

Glycine Magic Angle > 1º off.
Setup Cross Polarization Experiments

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

\[ \begin{align*}
\text{Excitation} & \quad \text{polarization evolution, acquisition transfer (PT)} \quad \text{decoupling} \\
^1\text{H} & \quad \text{p}_3 \text{pl}_{12} \quad \text{p}_{15}:\text{spf}_0 \text{pl}_2 \quad \text{CPDPRG2: CW pl}_{12} \\
^1\text{C} & \quad \text{p}_{15} \text{pl}_1 \quad \text{p}_1 \text{pl}_{11}
\end{align*} \]
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 $\pm z$-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-decoupling here 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:**

```c
#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:

\texttt{1u \text{fq} = \text{cnst21}:f2}

\texttt{10u \text{pl12}:f2 \text{pl1}:f1 \quad ;\text{pl12 for F2, pl1 for F1}}

\texttt{\text{trigg} \quad \quad \quad ;\text{trigger for scope, 10 usec}}

\texttt{\text{p3}:f2 \text{ph1} \quad \quad ;\text{proton 90 pulse}}

\texttt{0.3u}

\texttt{(\text{p15 \text{ph2}}):f1 (\text{p15}:\text{spf0} \text{pl2 \text{ph10}}):f2}

\texttt{;\text{contact pulse with square or ramp}}

\texttt{;\text{shape on F2, at pl2 proton power level}}

\texttt{1u \text{cpds2}:f2}

\texttt{;\text{pl12 is used here with tppm, pl13 with cwlg, cwlg}}

\texttt{\text{go} = \text{2 ph31}}

\texttt{1m \text{do}:f2 \quad ;\text{decoupler off}}

\texttt{\text{wr} \#0 \quad \quad \quad ;\text{save data to disk}}

\texttt{\text{HaltAcqu, 1m} \quad ;\text{jump address for protection files}}

\texttt{\text{exit}}

\texttt{;\text{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
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    ; 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:

```c
#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
Non quarternary suppression or dipolar dephasing experiment

Excitation    polarization evolution, acquisition decoupling

\begin{align*}
\text{\textsuperscript{1}H} & : p_3 p_{l_{12}} \\
\text{\textsuperscript{13}C} & : p_{15} : s p_{f_0} p_{l_2} \\
\text{CPDPRG2: TPPM, } & p_{31} p_{l_{12}} \\
\end{align*}
Advanced CP Experiments

- Androstene
  Non quarternary suppression

CP only
Advanced CP Experiments

- Problem: through spinning sidebands too crowded spectra:

CP experiment
Advanced CP Experiments

Solution: suppress spinning sidebands

CP experiment
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

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
TO                  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               10.00000000 sec
GB                 0
PC                 1.00
Advanced CP Experiments

- TOSS

$\text{Excitation}$ $\text{p}_3 \text{p}_1 \text{p}_{12}$ $\text{p}_{15} : \text{spf}_0 \text{p}_2$ $\text{TPPM, p}_{31} \text{p}_1 \text{p}_{12}$

$\text{p}_{15} \text{p}_1$ $\text{p}_2 \text{p}_1 \text{p}_{11}$

$\text{1H}$ $\text{13C}$

$\text{Evolution, decoupling}$ $2\tau_r$
• Androstene TOSS

CP only
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

<table>
<thead>
<tr>
<th>Variable delay list</th>
<th>Variable pulse list</th>
</tr>
</thead>
<tbody>
<tr>
<td>4m</td>
<td>400u</td>
</tr>
<tr>
<td>16m</td>
<td>1600u</td>
</tr>
<tr>
<td>10m</td>
<td>1m</td>
</tr>
<tr>
<td>10m</td>
<td>3m</td>
</tr>
<tr>
<td>6m</td>
<td>5m</td>
</tr>
<tr>
<td>4m</td>
<td>10m</td>
</tr>
<tr>
<td>17m</td>
<td>15m</td>
</tr>
<tr>
<td>11m</td>
<td>18m</td>
</tr>
<tr>
<td>18m</td>
<td>30m</td>
</tr>
<tr>
<td>12m</td>
<td></td>
</tr>
</tbody>
</table>
• $T_1$ relaxation experiment $^{13}$C:

Excitation polarization relaxation delay evolution, transfer (PT) decoupling
### Relaxation Experiments

**edpar**

<table>
<thead>
<tr>
<th>Acquisition Parameters</th>
<th>F2</th>
<th>F1</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1LPROG</td>
<td>cp xt1.av</td>
<td></td>
</tr>
<tr>
<td>AQ_mod</td>
<td>qsim</td>
<td></td>
</tr>
<tr>
<td>F1NMODE</td>
<td></td>
<td>undefined</td>
</tr>
<tr>
<td>TD</td>
<td>1624</td>
<td>10</td>
</tr>
<tr>
<td>PARMODE</td>
<td>2D</td>
<td></td>
</tr>
<tr>
<td>NS</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>DS</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>TDO</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>** Array **</td>
<td>sec</td>
</tr>
<tr>
<td>P</td>
<td>** Array **</td>
<td>usec</td>
</tr>
<tr>
<td>NDO</td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>INO</td>
<td></td>
<td>0.00006300</td>
</tr>
<tr>
<td>SW</td>
<td>199.5381</td>
<td>42.1247</td>
</tr>
<tr>
<td>SWH</td>
<td>25062.656</td>
<td>5291.006</td>
</tr>
<tr>
<td>FIDRES</td>
<td>24.475250</td>
<td>529,100525</td>
</tr>
</tbody>
</table>

**SAVE**   **Parameter**   **Next**   **CANCEL**
$T_1$ Relaxation Experiment on PE
$T_1$ Relaxation Experiment on PE
$T_1$ Relaxation Experiment on PE
**T₁ Relaxation Experiment on PE**

<table>
<thead>
<tr>
<th>Dataset:</th>
<th>Title:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Setup t1 parameters</td>
<td>[edt1]</td>
</tr>
<tr>
<td>Multi-component fit</td>
<td>[simfit]</td>
</tr>
<tr>
<td>Multi-component fit (all peaks)</td>
<td>[simfit all]</td>
</tr>
<tr>
<td>Fit data from ASCII file t1ascii</td>
<td>[simfit asc]</td>
</tr>
<tr>
<td>Fit all peaks read from ASCII file</td>
<td>[simfit asc all]</td>
</tr>
</tbody>
</table>

- Calculate the t1 value: [ctl1]
- Calculate the t2 value: [ct2]
- Calculate t1 for all peaks: [dat1]
- Calculate t2 for all peaks: [dat2]
- Eliminate a point from the fit: [elim]
- Display the next peak: [nxtp]
- List data for the current peak: [lstp]
- List data for all peaks: [lsta]
- Peak pick a series of spectra: [pd]
- Pick intensities exactly at point: [pd0]
- Pick points from a serial file: [pf]
- Pick points from a t2 fid: [pft2]
- Print the x,y pairs: [prxy]
- Include all eliminated points: [rstp]
- Read SER slice for point selection: [rfid]
- Read SMX slice for peak selection: [rscp]
### T1 Relaxation Experiment on PE

#### T1 Parameters

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

- **SAVE**
- **2-COL**
- **Parameter**
- **Next**
- **CANCEL**
### T₁ Relaxation Experiment on PE

<table>
<thead>
<tr>
<th>Dataset:</th>
<th>Title:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Setup t₁ parameters</td>
</tr>
<tr>
<td></td>
<td>Multi-component fit</td>
</tr>
<tr>
<td></td>
<td>Multi-component fit (all peaks)</td>
</tr>
<tr>
<td></td>
<td>Fit data from ASCII file t₁asci</td>
</tr>
<tr>
<td></td>
<td>Fit all peaks read from ASCII file</td>
</tr>
<tr>
<td></td>
<td>Calculate the t₁ value</td>
</tr>
<tr>
<td></td>
<td>Calculate the t₂ value</td>
</tr>
<tr>
<td></td>
<td>Calculate t₁ for all peaks</td>
</tr>
<tr>
<td></td>
<td>Calculate t₂ for all peaks</td>
</tr>
<tr>
<td></td>
<td>Eliminate a point from the fit</td>
</tr>
<tr>
<td></td>
<td>Display the next peak</td>
</tr>
<tr>
<td></td>
<td>List data for the current peak</td>
</tr>
<tr>
<td></td>
<td>List data for all peaks</td>
</tr>
<tr>
<td></td>
<td>Peak pick a series of spectra</td>
</tr>
<tr>
<td></td>
<td>Pick intensities exactly at point</td>
</tr>
<tr>
<td></td>
<td>Pick points from a serial file</td>
</tr>
<tr>
<td></td>
<td>Pick points from a t₂ fid</td>
</tr>
<tr>
<td></td>
<td>Print the x,y pairs</td>
</tr>
<tr>
<td></td>
<td>Include all eliminated points</td>
</tr>
<tr>
<td></td>
<td>Read SER slice for point selection</td>
</tr>
<tr>
<td></td>
<td>Read SMX slice for peak selection</td>
</tr>
</tbody>
</table>

**Additional Details:**
- **XWIN NMR Version 3.1 on PINE5 started by Administrator**
- **Point 1020, 500.23 Hz, 31.610 ppm**
$T_1$ Relaxation Experiment on PE

Dataset: <class 'zoo2002 21 I C: \
jo50502'>

Title:

Return
$T_1$ Relaxation Experiment on PE

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

Peak No. 1 at 131.772 ppm, $t_1/t_2$, $I[0] = 3.010e-01$, $P = -1.187e+00$, $T = 127.437s$
$T_1$ Relaxation Experiment on Adamantane

Peak No. 2 at 131.772 ppm, $t_1/t_2$, $I[0] = 9.982 \times 10^{-1}$, $P = -1.707 \times 10^0$, $T = 1.389$ s
• Variable contact, increment p15 or use vp-list

\[ \text{p}_3 \text{pl}_{12} \quad \text{p}_{15} \text{ or vp pl}_2 \quad \text{TPPM, p}_3 \text{ pl}_{12} \]

Excitation  polarization  transfer (PT)  evolution, acquisition  decoupling
Variable Contact Experiment

Class 2001
Variable Contact HH PE

- PE
Advanced CP Experiments

- Glycine variable contact

[Graph showing the comparison between Carbonyl and Aliphatic signals over time]
• $T_{1\rho}$ relaxation experiment $^1H$

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

$^1H$

$^13C$

$T_{1\rho}$ relaxation experiment $^1H$
Cross Polarization Experiments

- PE

$^1\text{H} \ T_{1\rho}$ experiment
Triple Resonance Experiments

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

- $^{15}\text{N}$ setup

```
bf1 50.6136950 50.6136950
sfo1 50.6136950
ofsx1 0.000
bf2 499.5000000
sfo2 499.5009990
ofsh1 999.000
bf3 125.593750
sfo3 125.6119749
ofsx2 12599.930
```

```
preferred output for 19f:
- 19f
- x
```
Triple Resonance Experiments

- $^{13}\text{C}$ setup
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

- Homo
  - J
  - DD
  - CSA
  - 2Q
  - ZQ

- Hetero
  - X-(^1H)
  - X-Y
  - DDC

- DDC
Triple Resonance Experiments

- Rotational Echo Double Resonance (REDOR)

Excitation, PT, rotor synchronized evolution, heteronuclear decoupling, dipolar recoupling
Triple Resonance Experiments

- Rotational Echo Double Resonance (REDOR)
• Rotational Echo Double Resonance (REDOR)
FSLG Experiments Setup

Basic experimental scheme: Measures J coupling

\[ \begin{align*}
\^{1}\text{H}: f2 & \quad \text{Excitation} \\
p3, pl12, p15, \text{spnam0, pl2} & \quad \text{Polarization Transfer} \\
pl12, p31 (TPPM), pl13, p10, \text{spnam1 (FSLG)} & \quad \text{Acquisition / Homonuclear Decoupling} \\
\^{13}\text{C}: f1 & \\
p15, pl1 &
\end{align*} \]
Phases: 2 0 2 0

Nutation angle: 2\pi - 2\pi 2\pi -2\pi

Frequency switch: +\Delta f -\Delta f +\Delta f -\Delta f

1 LG cycle 1 LG cycle
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

- **Phases:**
  - 2
  - 0
  - 2
  - 0

- **Nutation angle:**
  - 2π
  - -2π
  - 2π
  - -2π

- **Frequency switch:**
  - p5
  - p5
  - p5
  - p5

  **1 LG cycle**

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

![Diagram showing pulse sequence with labels: $^1$H Excitation, $^1$H evolution, $^1$H-13C polarization transfer, acquisition, CP, TPPM decoupling.](image-url)
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

TPPM decoupling

$\phi_1 \cdots \phi_7 \phi_{10}$

$^{1}H$

$^{13}C$

$\phi_2 \phi_{\text{rec}}$

Graph showing $^{1}H$ and $^{13}C$ transitions with TPPM decoupling.
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 \((x,x_{\text{bar}})\)
  - Time reversed blocks \((x_{\text{bar}},x)\)

\[(xx)_n (x\overline{x})_n\]

PMLG Experiments

• Typical PMLG shapes

\[(xxx)(xx)\] \[(xxx)\cdot (xx)\cdot (xx)\cdot (xx)\]
PMLG Experiments

Pulse Program using normal shape: lghetshape.av

Pulse Program using fast shape: lghetloop.av
Experiments using FSLG or PMLG

- Attached Proton Test in Solid State NMR

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

- **MAS-J- HMQC**

![Diagram](image)

- **Excitation**: $^1H$
- **PT**: $^1H$-$^13C$
- **$S_x$**: antiphase coherence evolution
- **$2I_zS_y$**: DQ evolution
- **$I_z S_y$**: antiphase coherence reconvert
- **$S_x$**: acquisition

$t_1$: Time for $S_x$ evolution
$t_2$: Time for acquisition
- Avance 500 WB
- 4 mm DVT probe
  - $^1\text{H}/^{13}\text{C}$, 1 ms contact
  - $\pm 80.6$ kHz frequency switch
  - $^{13}\text{C}$ rf field: 67 kHz
  - $^1\text{H}$ rf field:
    - 67 kHz contact
    - 114 kHz TPPM
    and FSLG
  - 96 scans
  - 2.5 s recycle delay
Experiments using FSLG or PMLG

- **PISEMA**

\[ \pi/2, X, -X \quad 35.3, -X, X \quad 2\pi \quad 3\pi \quad 2\pi \]

- **1H**
  - \( 1H \)
  - \(-Y\)
  - \(Y+LG\)
  - \(-Y-LG\)
  - \(Y+LG\)
  - \(-Y-LG\)
  - **TPPM decoupling**

- **15N**
  - \( ^{15}N \)
  - \(X\)
  - \(X\)
  - \(-X\)
  - \(X\)
  - \(-X\)

- **Evolution period of**
  - Excitation polarisation transfer
  - Heteronuclear dipolar coupling
  - Acquisition
  - Spin systems in HH contact
  - \(^1H\) spin system spin-locked at Magic angle
Experiments using FSLG or PMLG

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

Alternatively:
- Measure $^1\text{H}$ pulses and power levels
- Calculate LG frequency assuming $^1\text{H} B_1$ field is effective field. Calculate required power level change for $^1\text{H}$
- Set LG frequency and calculated power level for $^1\text{H}$
- optimize HH contact by variation of power level for $^1\text{H}$ during spin lock.
Experiments using FSLG or PMLG

- **Version 1**
  - $^1\text{H}$
    - 0
    - 3
    - 2
    - 1+LG
    - 3-LG
    - DEC
  - $^{15}\text{N}$
    - 0
    - 0
    - 2

- **Version 2**
  - $^1\text{H}$
    - 0
    - 3
    - 2
    - 1+LG
    - 3-LG
    - DEC
  - $^{15}\text{N}$
    - 0
    - 0
    - 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 $^{15}\text{N}$ -
    - No oscillation of $^{15}\text{N}$ magnetization during spin lock
Experiments using FSLG or PMLG

- PISEMA setup
  - Test spin lock $^1$H

• Avance 500 WB
• 4 mm DVT probe
  - $^1\text{H}/^{15}\text{N}$, 5 ms contact
  - ±46600 Hz frequency switch
  - $^{15}\text{N}$ rf field: 80.5 kHz
  - $^1\text{H}$ 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

3,1 0  
TPPM  CWLG  TPPM decoupling

$^1\text{H}$

$^{13}\text{C}$

$^{15}\text{N}$

$t_1$  $t_2$

Excitation  PT evolution  PT acquisition
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 optimize 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

Arginine uniformly $^{15}$N $^{13}$C labeled

- Avance 500 WB
- 4 mm probe
- $^{1}H/^{15}$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
- $^{1}H$ 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

\[ H_{DD} = d_{is} I_z S_z + I_y \cos(\theta(t)) + 2I_x S_z \sin(\theta(t)) \]

\[ H_{DD} = d_{is} I_z S_z + I_y \cos(\theta(t)) + 2I_x S_z \sin(\theta(t)) \]

1H, 13C

Redor Block
\[ I_x S_z \text{ excitation through spin pair} \]
Dipole dipole interaction

2I_x S_z evolution

Inverted Redor Block
\[ S_y \text{ reconversion from } I_z S_x \]
Antiphase coherence

tppm
Recoupled Polarization Transfer HSQC

Preparation: 1H

Excitation: 13C

Evolution: 1H

Reconversion: 13C

Detection: tppm

N_{exc\tau_r}

N_{rec\tau_r}

t_1

t_2
- 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
- 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+dipole dipole interaction with dipole dipole interaction in $f_1$.

Gabriela Leu and D. Cory see poster

Dipolar evolution, time independent susceptibility fields refocused

MQ filter evolution under dipolar and susceptibility fields
Separated local field spectroscopy