III. X-Nucleus Acquisitions—Example Session

- See "XwinNMR Acquisition Manual," Sections 1.4, 1.5 (see list of acquistion parameter descriptions starting 1.5.2.4, pg. A-39), 1.6

a) General Theme for X-Acquisitions

- Setup normally (edc, edhead, edte, lock, shim) until need to read in parameters.
- Choose a parameter set matching observe nucleus, e.g. rpar P31CPD .
- Use eda, ased, or pulprog↵ to change to desired pulsesequence, then SAVE.
- Use eda → PROSOL → TRUE → SAVE (or equivalently gpro) to read in ***some*** but not necessarily all probe dependent parameters.
- Check parameters carefully with ased then eda comparing to listing of pulsesequence (using **cdpp → jot** or edpul).
- Check probe tuning with wob .
- Acquire data, using tr to check signal-to-noise.

b) Detailed Setup for X-Acquisitions

1. Use the Console window to start up xwinnmr: **xwinnmr -r↵**
   ; **-r** removes hung sessions

2. edc or iexpno – edit the current data set name

3. edhead – check that correct probe is defined

4. To set the temperature, use:
   edte↵ brings up temp window; usually you will leave this open

☞ use ii to initialize interface (if error messages appear, redo ii until they go away)

5. Enter lockdisp to open the lock display window. Lock using lock . Select the solvent, and the spectrometer should lock up.

6. Shim normally; best to check shims in a 1H spectrum. Poor shims will reduce sensitivity of any X-nucleas experiments, so good line shape is still highly desired.

7. Parameter sets can be read in rather than starting with a base sequence:

   rpar *cgf (lists just subset written by cgfry)
   rpar (lists all parameters sets saved by any user)

wpar will save your parameters; all files from all users go into a common directory, **/u/exp/stan/nmr/par** (use **cdpar** in UNIX to move to this directory), so append the suffix initials so you can isolate just your files with the first rpar command above.

☞ all Bruker parameter sets use UPPER CASE letters; ***never*** use upper case for your parameter sets, and ***always*** use your initials as the suffix; that way the Bruker sets will be obvious, and you will have a simple method of finding your parameters

8. The following are known, good parameter sets:

PROTON	standard proton parameters using zg30
C13CPD	standard carbon parameters using zgpg30
C13DEPT*	standard ^{13}C dept parameters
P31CPD	standard ^{31}P parameters using zgpg30 (o1 not checked)
N15IG	standard ^{15}N parameters using zgig (o1 not checked)
N15INEPT	standard ^{15}N parameters using ineptrd (o1 not checked)
SI29IG.UW	UW ^{29}Si parameters starting with zgig
H2.UW	UW ^{2}H parameters
LI6.UW	UW ^{6}Li parameters
LI7.UW	UW ^{7}Li parameters
COSYGS.UW	UW 2d gradient COSY
COSY90SW	2d non-gradient COSY (for 10mm probe)
ghsqcse.UW	UW 2d sensitivity-enhanced 1H-13C 1-bond hsqc experiment
gChsqc.UW	UW 2d gradient 1H-13C 1-bond hsqc
gNhsqc.UW	UW 2d gradient 1H-15N hsqc (long-range probably next?)
ghmbc.UW	UW 2d 1H-13C long-range hmbc experiment

Listings of parameters sets in Unix can be accomplished with the **-d** qualifier:

cdpar
dir -d C13* or
ls -d S*

9. Old data sets can be read in by typing dir and clicking on the desired set.
In Unix, you can get to your dataset by typing: **cddata (/u/data/cgfry/nmr**)
Make new datasets, or new experiment numbers with: edc

10. Use an Xshell window to look at pulse sequences:
cdpp equivalent to **cd /u/exp/stan/nmr/lists/pp**

cp *pulsesequence pulsesequence.cgf*
jot *pulsesequence.cgf*

- ☞ always copy the sequence to your initials if you want to make changes or add comments; you will not have privileges to change the standard sequences)
- you do not need to copy sequences if you just want to see the listing
- all Bruker original sequences are kept in **/u/exp/stan/nmr/lists/pp.orig**
- you can also use editors within xwinnmr by typing: edpul *pulsesequence.cgf*

11. The most important sequences for X-nucleus acquisitions are:

zg30 ; not recommended, with no decoupling, no NOE, no PT

☞ zgpg30 ; standard decoupling sequence → with 30° pulse and NOE growth during d1

zgpg ; same as zgpg30 except with 90° pulse

zg0pg ; same as zgpg expect uses p0 @ pl1 for variable angle flip

zgdc30 ; same as zgpg30 except with a single power level for decoupling

zggd30 ; gated decoupling → with 30° pulse, coupled spectrum with NOE buildup during d1

☞ zgig30 ; inverse gated → with 30° pulse, for quantitative observation of decoupled X-nuclei, no NOE buildup; d1 ≥ $3\times T_1(X)$

☞ ineptrd ; inept+ → with decoupling:
cnst2 = J(XH)
cnst11 = $2\pi[\sin^{-1}(1/\sqrt{n})]^{-1}$ (rad)
= $360°[[\sin^{-1}(1/\sqrt{n})]^{-1}$ (deg)
where n=# ^1H involved in J(XH)
see http://cic.chem.wisc.edu/nmr/Guides/BUG/PT.pdf

☞ ineptpnd ; coupled inept+ → same as ineptrd with no decoupling during acquisition

ineptnd ; coupled inept → similar to ineptpnd but shorter; use if T_2's are short

☞ dept ; standard dept → p0 controls PT via last pulse on ^1H channel
cnst2 = J(XH)
p0 is set relative to p1 @ pl1 (^1H 90° pulse)
p0 = $\sin^{-1}(1/\sqrt{n})$ (rad or deg)
= p1/90° × [$\sin^{-1}(1/\sqrt{n})$ (deg)] (μs)
where n=# ^1H involved in J(XH)
see http://cic.chem.wisc.edu/nmr/Guides/BUG/PT.pdf

dept45 ; standard dept with final 45° pulse preset

dept90 ; standard dept with final 90° pulse preset

☞ dept135 ; standard dept with final 135° pulse preset

deptcp ; same as dept but with ^1H composite 180° pulse

☞ deptnd ; same as dept but no decoupling during acquisition, best for short T_2's

deptppnd ; dept++ with no decoupling during acquisition; less distortion than deptnd

☞ decp90 ; sequence to calibrate decoupler 90° pulsewidths
or use dept90 and minimize a CH_2 group

12. Chose the pulsesequence you need to use:

zgpg30	; for standard decoupled spectra with nuclei having positive γ (e.g., ^{13}C, ^{31}P, ^{19}F, ^{2}H) do not use for nuclei with negative γ (e.g., ^{29}Si, ^{15}N)
zgig30	; for quantitative spectra, or when no ^{1}H couplings or NOEs are available
zggd30	; simple coupled spectra; **deptnd** or **ineptpnd** should work better for coupled spectra
dept	; for ^{13}C reduces distortions arising from range of J_{XH}'s
ineptrd	; for ^{29}Si (seems to work better than dept?)

Make the change by going into the ased or eda window and clicking on the down arrow next to the pulsesequence. You can also change it directly by typing pulprog↵ and typing in the new name.

13. Use PROSOL → TRUE → SAVE or gpro to read in probe dependent parameters.

14. The facility will keep the most up-to-date pulsewidth calibrations in the probe-solvent files which can be viewed with solvloop. We will also keep a log of calibrations, which will include dates and temps for the calibration in a file:

probe-calibrations.txt

in the shims directory at: **/u/exp/stan/lists/bsms** (**cdshims** alias to move there).

15. Check the acquisition parameters by using: ased

Then check other parameters not included in ased using: eda

It is recommended that the pulse sequence be open and checked while going through the parameters for the first time (e.g., **cdpp jot *pulsesequence*** in UNIX window).

☞ use ii to initialize interface

16. Check the probe tuning with wob

Always tune the X-channel first, then the 1H channel afterward.

17. Perform any parameter optimization required.

18. Check all parameters, especially following the comments at the bottom of the pulseprogram listing. Note that Bruker may not be consistent in their use of pulse, delay or constant definitions. Do NOT assume similar named sequences are written the same!!

    expt gives experiment time; typically aq d1 ns and td1 (for 2d exps) dominate times

19. For now, use rga to set the receiver gain. Note that on other Bruker and Varian spectrometers, rga can lead to very wrong settings of the receiver gain, so use with care!

20. Use zg and acqu (to observe 1st fid) to start acquisition. Transformation will not occur automatically; note the *finished* message in the bottom info bar.

    efp to transform and phase.

    tr to push data to disk to allow transformation during acquisition

21. Use edp to process the data in xwinnmr. For 2d data, the comments in the pulse program will tell whether the data was acquired TPPI, States-TPPI, or States.

    xfb will transform in both directions keeping all quadrants of the data.
    xfb n will transform, but not keep the imaginary components; much faster, but you won't be able to phase without retransforming here.

    Use the +/- buttons to turn on negative and both signs of 2d sets.

    1d: use PHASE CUR and click middle button to define the toggle point, then click-hold the left button on PH0 and phase at the toggle point. Click-hold the left button on PH1 to 1st-order phase far away from the toggle point. pk will apply the previous phase correction.

    2d: use PHASE CUR ROW and click middle button in 2d set; click on 1 to place in the 1 window; repeat for 2 and 3 windows. Then do PH0 and PH1.
    Repeat complete process for CUR COL if F1 needs phasing.