Pulse Width Calibrations

- We will expect you check 90° ^{1}H pulsewidth if problems occur with sensitivity
- For long *X*-nucleus experiments, you should always use up-to-date calibrations
  - a month is a reasonable length calibrations will last
  - you must know how to perform your own calibrations, including **decp90**
- 90° calibrations are absolutely necessary for proper use of equipment

Pulse Width Calibrations

Sensitivity of Experiments to Calibrations

Experiment	Sensitivity	Comments
1d ^1H spectra	little to none	provides check of correct probe operation
1d ^1H quantitative studies	little to none	d1 and inter-experiment delays are critical!!
1d ^1H relaxation studies	strong	corrections can be made for minor missettings of 180°
1d dynamic studies	strong	temp changes affect probe tuning
1d kinetic studies	little	d1 and inter-experiment delays are critical!!
1d *X*-nucleus (NOE-based)	moderate	*X* calibration not important ^1H decoupler must be well-tuned
1d *X*-nucleus (PT-based)	strong	*X* calibration and high-power ^1H calibrations are critical *X* by normal 180°/360° null checks ^1H on f2-channel by **decp90** (90° null) or **dept90** (CH2 null) checks
1d *X*-nucleus (quantitative)	moderate	d1 delay setting is critical!! *X* calibration not important ^1H decoupler must be well-tuned
2d cosy, cosy-45	little/moderate	pretty tolerant of missets
2d dq-cosy	moderate	must calibrate ^1H 90°; d1 setting is critical
2d tocsy	moderate	must calibrate ^1H 90°, spin-lock must be reasonably set
2d noesy/roesy	moderate	must calibrate ^1H 90°, spin-lock must be reasonably set
2d X-nucleus experiments	strong	must calibrate ^1H 90°, length of experiment very dependent

Pulse Width Calibrations

Parameter optimization can be done in three ways:

a) Use gs and then acqu to start the go setup routine. An icon will appear that provides a sliding bar that can be used to adjust o1 or rg, for example. You can exit or stop the gs by click on the **STOP** button.

b) Manually change p1 for ns 1 acquisitions and look for nulls in FIDs of FTs.

c) Use paropt (Bruker's semi-equivalent to vnmr's array command) as follows:

- Take a single scan and phase and expand properly.
- Click on the DP1 button and hit return through the three query screens.
- Now enter paropt and answer the queries properly: e.g., p1 3 3 30 for a pulsewidth optimization using the sequence zg. Note that for zg30 you would need to use p1 9 9 30 to get equivalent results, since zg30 multiplies p1 by 0.33.
- paropt places results into procno 999. To return to your original experiment (assume it's in expno 1), enter re 1 1

Proper Use of decp90

- need either very concentrated sample (e.g., 80% benzene in 20% acetone-d_6) or labeled sample
- check J-coupling in ^1H or in coupled *X*-experiment
- center *X*-multiplet in spectrum (UTILITIES → O1 buttons); write down o1
- calibrate proper 90° (180°/360° null) for *X*-nucleus (watch zg30-type pp's)
- center ^1H "multiplet" in spectrum (UTILITIES → O1 buttons); write down o1 as o2 (for X-observe experiments
- edc from *X*-expno; change pp to decp90
- check o1 (from *X*-experiment)
  o2 (from o1 of ^1H experiment)
  p1 (from calibration of *X*-nucleas 90°)
- set p3 to 1μs initially; should antiphase multiplet
- paropt p3 to see null; that will be 90° length at power (attenuation) pl2
- change pl2 (e.g., to 16) to calibrate lower power decoupling
  – pulsewidth ×2 for every 6dB additional attenuation

Stacked 1d, and 2d Experiments

- multizg ; experiments must be in a group

  ; parameters will copy correctly 1st time only, later changes will not!

  multiefp

  stack1d

- PARMODE in eda changes 1D ↔ 2D
- must set correctly:
  - nd0 (# of d0 delays; but cannot trust matches actual # d0's in sequence!)
  - ns ≥ minimum phase cycle
  - td1 matches any loop counter criteria (e.g., some roesy and tocsy sequences)
  - MC2 (can be corrected after acquisition in edp)
- see first lecture notes for some simple 2d processing commands

Suggested practice prior to final check-out:

1. Acquire a ^{13}C spectrum on a sample of your choice at 300K.

   You should have prior knowledge (from similar acquisitions on the ACs or other) that the sample is concentrated enough to be observable with ≤ 10 mins acquisition time.

2. Now acquire a ^{31}P spectrum on a sample you choose, or the sample we have placed in the lab. Use Bruker's P31CPD parameter file, but make sure you check that PROSOL TRUE sets up parameters correctly.

3. Calibrate the ^{31}P 90° pulsewidth. Write down the information you obtain in a detailed manner so we can see how you came to the final 90° calibration numbers.

4. Change the temperature to a setting of your choice, but within the range -50°C ≤ te ≤ +50°C [setting te in xwinnmr, and changing with the command teset is a better choice than using the Change button in the edte window; teset insures the parameter te matches the actual setpoint temperature].

5. Calibrate the temperature with the methanol sample in the lab. You must run this sample unlocked (note: sweep with _no_ light; backwards from the ACs). Submit your temp calibration with the homework.

6. Reacquire the ^{31}P spectrum, and recalibrate the ^{31}P pulsewidth. List the new calibration numbers.

7. Use the thump tube to check the LN2 level, and write this down appropriately. Refill the dewar(s) as needed.

8. Leave the spectrometer at 300K.