Pulse Width Calibrations

- We will expect you to check $90^\circ$ $^1H$ pulse width 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 deep90.
- $90^\circ$ calibrations are absolutely necessary for proper use of equipment.
## Pulse Width Calibrations

### Sensitivity of Experiments to Calibrations

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Sensitivity</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1d $^1$H spectra</td>
<td>little to none</td>
<td>provides check of correct probe operation</td>
</tr>
<tr>
<td>1d $^1$H quantitative studies</td>
<td>little to none</td>
<td>$d_1$ and inter-experiment delays are critical!!</td>
</tr>
<tr>
<td>1d $^1$H relaxation studies</td>
<td>strong</td>
<td>corrections can be made for minor missettings of $180^\circ$</td>
</tr>
<tr>
<td>1d dynamic studies</td>
<td>strong</td>
<td>temp changes affect probe tuning</td>
</tr>
<tr>
<td>1d kinetic studies</td>
<td>little</td>
<td>$d_1$ and inter-experiment delays are critical!!</td>
</tr>
<tr>
<td>1d X-nucleus (NOE-based)</td>
<td>moderate</td>
<td>$X$ calibration not important, $^1$H decoupler must be well-tuned</td>
</tr>
<tr>
<td>1d X-nucleus (PT-based)</td>
<td>strong</td>
<td>$X$ calibration and high-power $^1$H calibrations are critical $X$ by normal $180^\circ/360^\circ$ null checks $^1$H on f2-channel by <strong>decp90</strong> (90° null) or <strong>dept90</strong> (CH2 null) checks</td>
</tr>
<tr>
<td>1d X-nucleus (quantitative)</td>
<td>moderate</td>
<td>$X$ calibration not important, $^1$H decoupler must be well-tuned</td>
</tr>
<tr>
<td>2d cosy, cosy-45</td>
<td>little/moderate</td>
<td>pretty tolerant of missets</td>
</tr>
<tr>
<td>2d dq-cosy</td>
<td>moderate</td>
<td>must calibrate $^1$H 90°; $d_1$ setting is critical</td>
</tr>
<tr>
<td>2d tocsy</td>
<td>moderate</td>
<td>must calibrate $^1$H 90°, spin-lock must be reasonably set</td>
</tr>
<tr>
<td>2d noesy/roesy</td>
<td>moderate</td>
<td>must calibrate $^1$H 90°, spin-lock must be reasonably set</td>
</tr>
<tr>
<td>2d X-nucleus experiments</td>
<td>strong</td>
<td>must calibrate $^1$H 90°, length of experiment very dependent</td>
</tr>
</tbody>
</table>
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-d₆) or labeled sample
- check J-coupling in \(^1\text{H}\) 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 \(^1\text{H}\) “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 \(^1\text{H}\) 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 $\leq 10$ 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 $-50^{\circ}C \leq te \leq +50^{\circ}C$ [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.