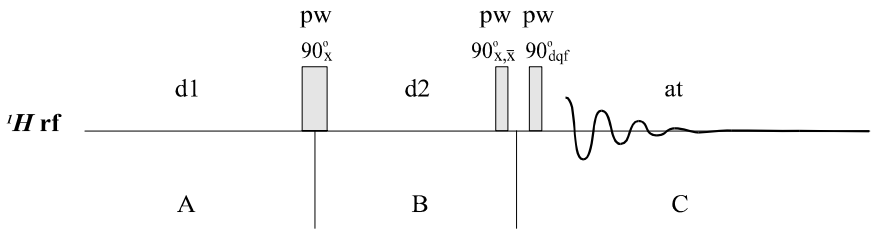
VIII. DQ-COSY – Double-Quantum Filtered COSY (Phase-Sensitive)

(17-Jul-00); see also **sbs** note from Chem637 class

A. Discussion

- DQCOSY is currently accepted by most in the NMR community as the most powerful form of COSY; it is recommended for any experiment beyond the FAST-COSY or GCOSY
- removes singlets (important for strong solvent peaks)
- diagonal in pure adsorption mode with crosspeaks (cleans diagonal for close-in crosspeaks)
- direct coupling (for crosspeak at ν_1,ν_2 is $J_{1,2}$) is anti-phase, whereas indirect coupling (at ν_1,ν_2 is $J_{1,3}$ or $J_{1,4}$, for example) is in-phase, allowing for J assignments in complex molecules
- alternative experiment is E. COSY (see section X)

2d Double-Quantum Filtered COSY (dqfcosy)



B. Critical Parameters

pw, tpwr	= 90° pulse width at power **tpwr**; recalibrate this parameter for all dqcosy experiments
d1	= relaxation delay; set 2-3*T_1 (artifacts will result if **d1** is too small)
ni	= number experiments, or number of points in t_1 ; should be set ok by macro, time allowing; want F1 digital resolution ≤ 6 Hz/pt = sw1/(2ni)
np	= number of points in t_2, usually want ≥ 2048 since costs nothing but disk space and gives better resolution in F2
fn fn1	= usual to not zerofill in F2 (**fn=np**), and give one zerofill in F1 (**fn1=2ni**); **fn1≠fn** is ok for DQCOSY, but to baseline correct in both dimensions set **fn1=fn**
nt	= multiple of 8
sspul	= 'y' gives homospoil-90-homospoil preceding **d1**

C. dqcosy Acquisition

- DQCOSY is setup essentially the same as COSY (use **dqcosy** macro) except want **fn=np**≥2048 and typically **ni** ≥ 350 (**ni** is set up by macro; check that F1 dig resol ≤ 6 Hz/pt = **sw1**/(2**ni**))

D. Calibration

- always recalibrate **pw90** (90° pulse) for dqcosy (experiment is sensitive to quality of this easily-calibrated parameter—see ^1H section for instructions); macro uses **pw90** to set **pw**
- with high-res 1d, or perhaps better **ni**=2 run, carefully baseline correct, then run **calfa**

E. Phase-Sensitive 2d Data Workup and Plotting

- Often should not need to phase DQCOSY data at all.
- ***phase sensitive*** data should be processed something like the following:
  - Set **pmode='full'** ; allows phasing along F2 in 2d spectrum
  - **wft(1)** ; transform just first spectrum
  - **wtia** ; interactive phasing; middle button scales, left sets **lb**
  - **wft1da** ; perform first transform (on t_2 dimension)
  - If integrals have been setup (best on high-res 1d done prior to setting up dqcosy), then **bc('f2')** can work wonders here.
  - Click on **TRACE** and select strong intensity trace.
    ; trace='f1' changes columns→rows, trace='f2' goes back
  - **wtia** ; interactive phasing on t_1 trace, left button sets **lb**/**gf**
  - **wft2da** ; performs second (or both) transform(s)
  - Pick off two (or 3) traces that have crosspeaks ; downfield trace save number as **r1**
    ; upfield trace save number as **r2**
  - **ds(r1)** do 0-order phase only
  - **ds(r2)** do 1st-order phase only (click left mouse button on downfield position sets toggle pt)
  - Iterate between **ds(r1)** and **ds(r2)** (and often useful, a 3rd trace) to get good phase.
  - **dconi** ; should now have good phasing

    → **trace='f2' dconi** allows phasing along F2 (similar to above) if needed
  - If integrals have been setup (as above), and only if **fn1=fn**, then **bc('f1')** can sometimes work wonders here
  - To plot, **plot2dhr** is a new macro that works quite well; if you want 1d projections, load the
  - **rl(..p)** references the F2 axis, **rl1(..p)** references the F1 axis.
  - To plot, **plot2dhr** is a macro that works quite well; if you want 1d projections, load the high-resolution 1d spectra into separate experiments before issuing the macro command. Otherwise, the parameters: **wc=130 wc2=wc sc=0** work well; this leaves room for a vertical projection or to print parameters on the page (use **disp2d** to set these).
  - **plot2dps** is exactly the same as plot2dhr, but it does not issue a **page** at the end; give a

    page('*filename*') to plot postscript or hpgl (preferred), depending on plotter selected.
  - **pconpos** or **pconneg** can have additional utility for plotting phase sensitive spectra (or just see **pcon** description in the Varian documentation.
  - Maximum printable parameters on 8.5×11 paper are **wc=230 wc2=150** ; square plots then use **wc=wc2=150**. **sc** will shift the plot from full right (**sc**=0) to the left by **sc** mm.