

III. DEPT – Distortionless Enhancement by Polarization Transfer

(22-Jun-98)

A. Discussion of PT versus NOE experiments, and DEPT versus INEPT

Summarizing Derome (see Chap. 6 for very good discussion, p. 129ff): Polarization transfer experiments can offer sensitivity enhancements of:

$$\text{Polarization Transfer} \quad - \quad \left| \frac{g}{g_X} \right| \quad (1)$$

$$\text{NOE} \quad - \quad 1 + \frac{g}{2g_X} \quad (2)$$

where X is the nucleus being observed (e.g. ^{13}C or ^{29}Si), and I is the enhancing nucleus (usually ^1H , but could also be ^{19}F or ^{31}P). The following generalizations can be followed:

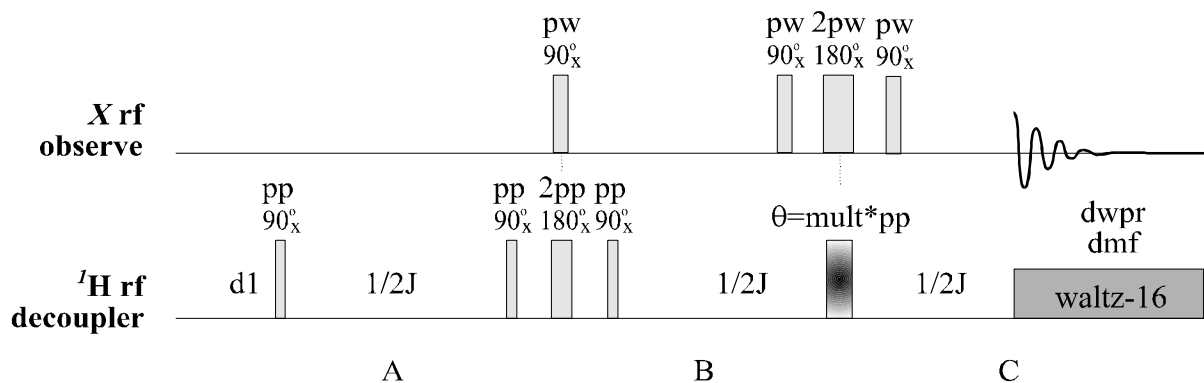
- Polarization transfer is always recommended for nuclei having negative γ values, ^{29}Si , ^{15}N , and ^{103}Rh being three examples. From eq (2) above, the NOE enhancement for these nuclei could result in 0 signal. PT is also always recommended for low- γ nuclei (e.g., starting ^{15}N and lower in frequency).
- DEPT is the best method for obtaining ^{13}C spectra, as well as spectra of other spin-1/2 X nuclei, of typically protonated compounds. DEPT is definitely preferred over INEPT if more than one J_{XI} value is involved for the nuclei you want to observe.
- DEPT should be used to obtain coupled spectra (turn the decoupler off during the acquisition: **dm='yyn'**); in general, DEPT will give better S/N than coupled NOE experiments.
- DEPT should be used even if no 1-bond coupling to protons are present for low- γ nuclei if long-range couplings can be used.
- INEPT should be used only if one J value is involved and it's size is known.
- typically, only a DEPT-135 is needed (**mult=1.5**), but vnmr makes fully edited spectra easy to obtain; accurate pulse widths are required for good methyl/methine differentiation
- For all these experiments, delays will be dependent on J_{XI} . The better the coupling is known, the better the experiment will work. Make every attempt to measure the couplings from the isotope splittings in the ^1H spectrum, or obtain good literature values. Lacking both, be prepared to run a series of experiments using different J_{XI} values to find the optimum parameters.
- For small J_{XI} couplings, a compromise between signal loss from T_2 (inverse natural line width)—especially for low-temp or high MW samples—and PT must be made. In some cases (mainly when $(T_1)_X$ is not too large), the non-NOE decoupled (Bruker's INVGATE) may be the preferred experiment.

B. Critical Parameters

- d1** – relaxation delay; typically = 1-2s
j = 140Hz; *change if you want to observe X with $J_{XH} > 180$ Hz or < 110 Hz*
pw, tpwr – observe X 90° pulse width **pw** at power level **tpwr**
pp, pplvl – high power ^1H 90° pulse width **pp** at power level **pplvl**

- mult** – determine type of DEPT; 0.5 = dept-45, 1.0 = dept-90, 1.5 = dept-135; see discussion below

1d DEPT (dept)



C. DEPT Acquisition

- for short runs, use facility calibrations for **pw**, **tpwr**, **pp**, **pplvl**, **dpwr** (**£46**) and **dmf**
- FILE SETUP SEQUENCES DEPT will setup Dept correctly, including for non-¹³C acquisitions
 - **mult** is set by the number of coupled protons
 - the interpulse delay is set according to **j**
- for overnights or longer runs, recalibrate (at least) observe and (best) decoupler pulse widths
- set **mult** as needed; dept-135 has **mult=1.5**; for full editing use array **mult=0.5,1.0,1.0,1.5**
- use **au** to acquire for full editing; **ga** is ok for dept-135

D. Calibration

- see ¹³C section for nominal ¹³C (X) and ¹H decoupler calibrations
- Often, the best way to calibrate the decoupler is to run a DEPT-90 on a compound having a known methylene; this carbon should be nulled in a DEPT-90. Change **pp** (can use an array) to obtain minimum signal at the methylene, and use on unknown or less concentrated sample.
- The delay **d2** and the final decoupler pulsewidth **mult*pp** are calculated by the DEPT macro as follows:

$$D2 = \frac{1}{2J} \quad [\text{use } J_{C-H} = 150 \text{ if olefinic present, } 130 \text{ otherwise}]$$

$$\theta \text{ pulse} \equiv \text{mult} * \text{pp} = \sin^{-1} \left(\frac{1}{\sqrt{n}} \right) (\text{in radians}) = \frac{\text{pp}}{90^\circ} \left[\sin^{-1} \left(\frac{1}{\sqrt{n}} \right) (\text{in deg}) \right]$$

$$\text{Thus } \mathbf{mult} = \frac{2}{\mathbf{p}} \left[\sin^{-1} \left(\frac{1}{\sqrt{n}} \right) \text{ (in radians)} \right] = \frac{1}{90^\circ} \left[\sin^{-1} \left(\frac{1}{\sqrt{n}} \right) \text{ (in deg)} \right]$$

For trimethyl-silyl ($J_{Si-H} = 2$ Hz),

$$\mathbf{d2} = 250 \text{ msec,}$$

$$\mathbf{mult} = \frac{19.47^\circ}{90^\circ} = 0.216$$

These values are calculated internal in the /vnmr/psglib/dept.c pulse sequence code.

E. Data Workup and Plotting

- for full editing, try **autodept** or **padept** macro;
- for dept-135, use **wft** and phase
- **s1** (s#) and **r1** (r#) are enormously useful for comparing data in different workspaces; use these in combination with **md(1,2)** for example to move the save regions in exp1 to exp2
- use **clradd spadd** to move a spectrum into exp5;
then **addi** to compare that spectrum with currently displayed spectrum
- use **dss** with proper **vo** and **ho** to give a stack
- **pl('all')** to plot the stack