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:

\[
Polarization \text{ Transfer} = \frac{\gamma_I}{\gamma_X} \quad (1)
\]

\[
\text{NOE} = 1 + \frac{\gamma_I}{2\gamma_X} \quad (2)
\]

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

- Polarization transfer is always recommended for nuclei having negative \(\gamma\) values, \(^{29}\text{Si}\), \(^{15}\text{N}\), and \(^{103}\text{Rh}\) 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-\(\gamma\) nuclei (e.g., starting \(^{15}\text{N}\) and lower in frequency).

- DEPT is the best method for obtaining \(^{13}\text{C}\) 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: \(dm='ynn'\)); 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-\(\gamma\) 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 (\text{mult}=1.5), but vnmr makes fully edited spectra easy to obtain; accurate pulse widths are required for good methyl/methylene 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 \(^1\text{H}\) 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 \(J_{XI}>180\) Hz or <110 Hz
- \(pw, tpwr\) – observe \(X\) 90° pulse width \(pw\) at power level \(tpwr\)
- \(pp, pplvl\) – high power \(^1\text{H}\) 90° pulse width \(pp\) at power level \(pplvl\)
**C. DEPT Acquisition**

- for short runs, use facility calibrations for \( \text{pw, tpwr, pp, pplvl, dpwr} \) \((\leq 46)\) and \( \text{dmf} \)
- FILE SETUP SEQUENCES DEPT will setup Dept correctly, including for non-\(^{13}\text{C}\) acquisitions
  - \( \text{mult} \) 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 \( \text{mult} \) as needed; dept-135 has \( \text{mult}=1.5 \); for full editing use array \( \text{mult}=0.5, 1.0, 1.0, 1.5 \)
- use \( \text{au} \) to acquire for full editing; \( \text{ga} \) is ok for dept-135

**D. Calibration**

- see \(^{13}\text{C}\) section for nominal \(^{13}\text{C} \,(X)\) and \(^1\text{H}\) 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 \( \text{pp} \) (can use an array) to obtain minimum signal at the methylene, and use on unknown or less concentrated sample.
- The delay \( \text{d2} \) and the final decoupler pulsewidth \( \text{mult} \times \text{pp} \) are calculated by the DEPT macro as follows:

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

\[
\theta \text{ pulse} = \text{mult} \times \text{pp} = \sin^{-1}\left(\frac{1}{\sqrt{n}}\right) \text{ (in radians)} = \frac{\text{pp}}{90^\circ} \left[ \sin^{-1}\left(\frac{1}{\sqrt{n}}\right) \right] \text{ (in deg)}
\]
Thus \[ \text{mult} = \frac{2}{\pi} \left[ \sin^{-1} \left( \frac{1}{\sqrt{n}} \right) \right] \text{ (in radians)} = \frac{1}{90^\circ} \left[ \sin^{-1} \left( \frac{1}{\sqrt{n}} \right) \right] \text{ (in deg)} \]

For trimethyl-silyl \( (J_{Si-H} = 2 \text{ Hz}) \),
\[ d2 = 250 \text{ msec}, \]
\[ \text{mult} = \frac{19.47^\circ}{90^\circ} = 0.216 \]

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