# **19.** Polarization Transfer Experiments (INEPT and DEPT)

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## I. General Discussion

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

**Polarization Transfer** - 
$$\frac{\gamma_I}{\gamma_X}$$
 (1)

**NOE** 
$$- 1 + \frac{\gamma_I}{2\gamma_X}$$
 (2)

where X is the nucleus being observed (e.g.  ${}^{13}C$  or  ${}^{29}Si$ ), and I is the enhancing nucleus (usually  ${}^{1}H$ , but could also be  ${}^{19}F$  or  ${}^{31}P$ ). PT enchancements are 4 for  ${}^{13}C$  and ~10 for  ${}^{15}N$ , compared to the NOE enhancements of 3 for  ${}^{13}C$ , and –4 for  ${}^{15}N$ . Thus, PT improvements are most dramatic as  $\gamma$  decreases. The following generalizations can be followed:

- Polarization transfer is always recommended for nuclei having negative  $\gamma$  values, <sup>29</sup>Si, <sup>15</sup>N, and <sup>103</sup>Rh being three examples. NOE enhancement for these nuclei could result in 0 signal.
- Polarization transfer is recommended for X nuclei having long relaxation times, as PT experiments have recycle delays determined by the relaxation of the I nuclei (typically  ${}^{1}H$  or  ${}^{31}P$ ).
- In general, DEPT is preferred over INEPT experiments. DEPT removes distortions that occur in INEPT spectra when many *different* J-coupling are present. One-bond carbon-hydrogen J-couplings in typical organic compounds fit this discription: aliphatic  $J_{CH} = 110-130$ Hz, whereas aromatic  $J_{CH} = 160-180$  Hz. Selection of a compromise  $J_{CH} \sim 145$  Hz presents errors of 20% or more from that actual value. DEPT does much better under these circumstances than INEPT, and is recommended for  ${}^{13}C$  spectra for standard multiplicity analysis.
- 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 <sup>1</sup>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 coupled spectra, DEPT+ is the preferred experiment (use either DEPTC.AU or DEPTPP.AU).
- 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. INEPT often is the preferred sequence in these cases, running total delays half that of DEPT. In some cases (mainly when  $(T_I)_X$  is not too large, and  $T_2$  is very small), INVGATE may be the preferred experiment.



#### **II.** Setting Up INEPT Experiments

Practical details for  ${}^{13}C$  experiments are simple for our Bruker-AC 300 spectrometers (Homer and Athena):

- 1. Read in a DEPT jobfile (e.g., RJ DEPTC6D6.1DJ for a compound in CDCl<sub>3</sub>.
- 2. Check all parameters using **AS INEPTRD.AU** (or similar .AU, as required), and adjust the critical parameters **D2** and **D3** (and **D1**) as discussed below.
- 3. Acquire the data using AU INEPTRD.AU .

For other nuclei (e.g.,  ${}^{31}P$ ), read in the appropriate jobfile, and adjust the critical parameters (**P3**, **P4**, **D2**, **D3**, **D1**) appropriately for the observe PW90 (=**P3**) of that nucleus, and coupling constants relevant for that compound. Note that long-range coupling constants can be utilized down to ~ 3 Hz (depending on the relaxation properties for nucleus/compound).

#### A. Critical Parameters

• The most important parameter is  $J_{XI}$  (e.g.,  $J_{CH}$ ); DEPT is recommended for compounds having multiple different *J*-couplings, i.e. for typical organic compounds where  ${}^{13}C$  is being observed.

• 
$$D2 = \frac{1}{4J}$$
 echo period involving two D2 delays creates <sup>1</sup>H antiphase state

• 
$$D3 = \frac{\Delta}{2} = \frac{1}{2\pi J} \left[ \sin^{-1} \left( \frac{1}{\sqrt{n}} \right) (\operatorname{rad}) \right] = \frac{1}{360^{\circ} J} \left[ \sin^{-1} \left( \frac{1}{\sqrt{n}} \right) (\operatorname{deg}) \right]$$

where n = # I nuclei

example: suppose have triethylsilyl, and want to detect  ${}^{29}Si$ , and  $J^{2}_{Si-C-H} = 3.1$  Hz,

then 
$$D2 = 1/(4 \times 3.1 \text{ Hz}) = 81 \text{ msec}$$

and 
$$D3 = \frac{1}{360^{\circ} \times 3.1 \text{Hz}} \sin^{-1} \left(\frac{1}{\sqrt{9}}\right) = \frac{19.47^{\circ}}{360^{\circ} \times 3.1 \text{Hz}} = 17 \text{m sec}$$

- D1 = repetition delay; should > 3  $T_I({}^{I}H)$ ; is a primary advantage over NOE-based acquisition where repetition delay relies on  $T_I(X)$
- all pulse widths, P1 thru P4, must be reasonably correct (within 10% or so)

#### **B.** Coupled Experiments

• Use Bruker's INEPTP.AU automation routine. Setup is identical to INEPTRD.AU.

# Distortionless Enhancement by Polarization Transfer - DEPT (Bruker's DEPT.AU)



### **III. Setting Up DEPT Experiments**

Practical details for  ${}^{13}C$  experiments are simple for our Bruker-AC 300 spectrometers (Homer and Athena):

- 1. Read in a DEPT jobfile (e.g., **RJ DEPTC6D6.1DJ** for a compound in CDCl<sub>3</sub>.
- 2. Check all parameters using **AS DEPT.AU** (or similar .AU, as required), and adjust the critical parameter **P0** (and **D1**) as discussed below.
- 3. Acquire the data using AU DEPT.AU .

For other nuclei (e.g.,  ${}^{31}P$ ), read in the appropriate jobfile, and adjust the critical parameters (**P3**, **P4**, **D1**) appropriately for the observe PW90 (=**P3**) of that nucleus, and coupling constants relevant for that compound. Note that long-range coupling constants can be utilized down to ~ 3 Hz (depending on the relaxation properties for nucleus/compound).

#### A. Critical Parameters

Most spectrometers have DEPT jobfiles present, so a RJ DEPTD20.1DJ will setup all standard parameters (D2O, ACET, C6D6 simply changes the decoupler to be centered— ~ 4.5 ppm —in <sup>1</sup>H spectrum for different solvents).

- The most important is  $J_{XI}$  (e.g.,  $J_{CH}$ ):
- D2 =  $\frac{1}{2J}$  [use  $J_{C-H}$  = 150 if olefinic present, 130 otherwise]
- $\theta$  pulse  $\equiv$  P0 =  $\sin^{-1}\left(\frac{1}{\sqrt{n}}\right) = \frac{P1}{90^{\circ}}\left[\sin^{-1}\left(\frac{1}{\sqrt{n}}\right) (\text{deg})\right]$

for the triethyl-silyl example above ( $J_{Si-H} = 3.1 \text{ Hz}$ ),

D2 = 161 msec,

$$P0 = \frac{19.47^{\circ}}{90^{\circ}} \times P1 = 0.216 \times P1$$

- D1 = repetition delay; should > 3  $T_I({}^IH)$ ; is a primary advantage over NOE-based acquisition where repetition delay relies on  $T_I(X)$
- all pulse widths, P0 thru P4, must be reasonably correct (within 10% or so)

# **B.** Coupled Experiments

- Use Bruker's DEPTC.AU automation routine. Setup is identical to DEPT.AU.
- Could try DEPTPP.AU if confident of pulse widths, and see distortion on multiplets; DEPTPP.AU has an additional delay, D3 = D2.