

13. PO TREATMENT OF DEPT (DISTORTIONLESS ENHANCEMENT POLARIZATION TRANSFER)

DEPT is a one-dimensional sequence used as a tool for unambiguous identification of the CH, CH₂, and CH₃ peaks in a proton decoupled ¹³C spectrum. It shares with INEPT the advantage of permitting a fast repetition rate. The recycle time has to be longer than the proton relaxation time but can be fairly shorter than the carbon T₁. The nonprotonated carbons will not show up in a DEPT spectrum.

The sequence is shown in Figure II.8.

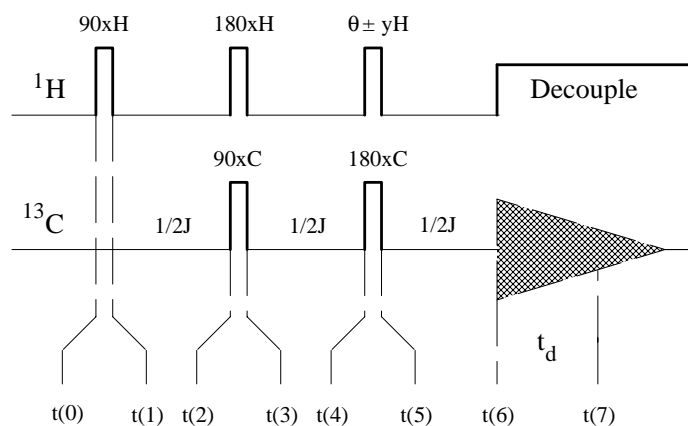


Figure II.8. The basic (one-dimensional) DEPT sequence: $90xH - 1/2J - 180xH - 90xC - 1/2J - 180xC - \theta \pm yH - 1/2J - \text{AT}(\text{dec})$.

The initial density matrix is

$$D(0) = -\lambda(p'/n)\{z1\} - q'\{1z\} \quad (\text{II.71})$$

where λ is a recovery factor for carbon [see (II.53)]

$$D(0) \xrightarrow{90xH} -\lambda(p'/n)\{z1\} + q'\{1y\} \quad (\text{II.72})$$

D(1)

For the evolution we use the notations

$$\begin{aligned} c &= \cos \Omega_C / 2J & c' &= \cos \Omega_H / 2J & C &= \cos \pi J / 2J = \cos \pi / 2 = 0 \\ s &= \sin \Omega_C / 2J & s' &= \sin \Omega_H / 2J & S &= \sin \pi J / 2J = \sin \pi / 2 = 1 \end{aligned} \quad (\text{II.73})$$

In treating the evolution, the shift and coupling may be handled in any order. Here, because of the particular values of C and S , we are better off by starting with the coupling.

$$\begin{aligned} D(1) &\xrightarrow{J_{\text{coupl.}}} -\lambda(p'/n)\{z1\} - q'\{zx\} \\ &\xrightarrow{\text{shiftH}} -\lambda(p'/n)\{z1\} - q'c'\{zx\} - q's'\{zy\} \end{aligned} \quad (\text{II.74})$$

D(2)

$$\begin{aligned} D(2) &\xrightarrow{180.xH} -\lambda(p'/n)\{z1\} - q'c'\{zx\} + q's'\{zy\} \\ &\xrightarrow{90.xC} \lambda(p'/n)\{y1\} + q'c'\{yx\} - q's'\{yy\} \end{aligned} \quad (\text{II.75})$$

D(3)

The multiplet formalism $\{ \}$ can help us only so far. It does not apply to the coupled evolution of terms like $\{zx\}$ or $\{yx\}$ since this coupled evolution is followed by some more pulses (cf. Rule #5 in Appendix L). We have to consider separately the CH, CH₂, and CH₃, using the corresponding subscripts 1,2,3. For completeness, we will also consider the case of the nonprotonated carbon (subscript zero).

$$\begin{aligned} D_0(3) &= \lambda p'[y] \\ D_1(3) &= \lambda p'[y1] + q'c'[yx] - q's'[yy] \\ D_2(3) &= \lambda p'[y11] + q'c'([yx1] + [y1x]) - q's'([yy1] + [y1y]) \\ D_3(3) &= \lambda p'[y111] + q'c'([yx11] + [y1x1] + [y11x]) \\ &\quad - q's'([yy11] + [y1y1] + [y11y]) \end{aligned} \quad (\text{II.76})$$

The evolution from $t(3)$ to $t(4)$ leads to

$$\begin{aligned}
D_0(3) &\xrightarrow{\text{shift C}} \lambda p'(c[y] - s[x]) = D_0(4) && \text{(no coupling)} \\
D_1(3) &\xrightarrow{J^{\text{coupl.}}} -\lambda p'[xz] + q'(c'[yx] - s'[yy]) \\
&\xrightarrow{\text{shift H}} -\lambda p'[xz] + q'(c'^2[yx] + c's'[yy] - s'c'[yy] + s'^2[yx]) \\
&= -\lambda p'[xz] + q'[yx] \\
&\xrightarrow{\text{shift C}} -\lambda p'(c[xz] + s[yz]) + q'(c[yx] - s[xx]) = D_1(4)
\end{aligned}$$

In processing the evolution of $D_2(3)$ we have to treat separately the coupling of the carbon with the first and with the second proton.

$$\begin{aligned}
D_2(3) &\xrightarrow{\text{cpl AX1}} -\lambda p'[xzl] + q'c'([yx1] - [xzx]) - q's'([yy1] - [xzy]) \\
&\xrightarrow{\text{cpl AX2}} -\lambda p'[yzz] + q'c'(-[xxz] - [xzx]) - q's'([xyz] - [xzy]) \\
&\xrightarrow{\text{shift H}} -\lambda p'[yzz] + q'c'^2(-[xxz] - [xzx]) + q'c's'(-[xyz] - [xzy]) \\
&\quad - q's'c'(-[xyz] - [xzy]) - q's'^2([xxz] + [xzx]) \\
&= -\lambda p'[yzz] - q'([xxz] + [xzx]) \xrightarrow{\text{shift C}} -\lambda p'(c[yzz] - s[xzz]) \\
&\quad - q'c'([xxz] + [xzx]) - q's'([yxz] + [yzx]) = D_2(4)
\end{aligned}$$

We were allowed to handle the evolution of both protons in one step only because none of the POs had x or y for both protons, i.e., only one proton was affected by the evolution in each PO.

Similar calculations will produce $D_3(4)$. Summarizing the results at $t(4)$ we have:

$$\begin{aligned}
D_0(4) &= \lambda p'(c[y] - s[x]) \\
D_1(4) &= \lambda p'(-c[xz] - s[yz]) + q'c[yx] - q's[xx] && \text{(II.77)} \\
D_2(4) &= \lambda p'(-c[yzz] + s[xzz]) - q'c'([xxz] + [xzx]) - q's'([yxz] + [yzx]) \\
D_3(4) &= \lambda p'(c[xzzz] + s[yzzz]) - q'c'([yxzz] + [yzxz] + [yzzx]) \\
&\quad + q's'([xxzz] + [xzxz] + [xzzx])
\end{aligned}$$

The $\theta \pm y$ pulse is mathematically equivalent to a $\pm\theta y$ pulse. Therefore, we will treat it as a rotation about the y-axis with alternate signs of θ . We take also into account that

$$\begin{aligned} \cos(-\theta) &= \cos\theta & ; & & \sin(-\theta) &= -\sin\theta \\ \cos(\pm\theta) &= \cos\theta & ; & & \sin(\pm\theta) &= \pm\sin\theta \end{aligned}$$

$$D_o(4) \xrightarrow{180_x C} \lambda p'(-c[y] - s[x]) = D_o(5)$$

(the proton pulse has no effect).

$$\begin{aligned} D_1(4) &\xrightarrow{180_x C} \lambda p'(-c[xz] + s[yz]) - q'c[yx] - q's[xx] \\ &\xrightarrow{\pm\theta_y H} \lambda p' \cos\theta(-c[xz] + s[yz]) \pm q' \sin\theta(c[yz] + q's[xz]) + \text{NOT} \\ &= D_1(5) \end{aligned}$$

In the last calculation we have retained only the observable terms ($[x1],[y1]$) and the potentially observable terms ($[xz],[yz]$). We have relegated terms as $[xx], [xy], [yx], [yy]$ to the NOT bunch (non-observable terms), as described in Appendix K.

In processing $D_2(4)$ we have to calculate the effect of the proton pulse, which is neither 90° nor 180° , separately on the two protons (see end of Section II.6).

$$\begin{aligned} D_2(4) &\xrightarrow{180_x C} \\ &\longrightarrow \lambda p'(c[yzz] + s[xzz]) - q'c([xxz] + [xzx]) + q's([yxz] + [yzx]) \\ &\xrightarrow{\pm\theta_y X1} \lambda p' \cos\theta(c[yzz] + s[xzz]) + q' \cos\theta(-c[xzx] + s[yzx]) \\ &\quad \pm q' \sin\theta(c[xzz] - s[yzz]) + \text{NOT} \\ &\xrightarrow{\pm\theta_y X2} \lambda p' \cos^2\theta(c[yzz] + s[xzz]) \pm q' \cos\theta \sin\theta(c[xzz] - s[yzz]) \\ &\quad \pm q' \sin\theta \cos\theta(c[xzz] - s[yzz]) + \text{NOT} \\ &= \lambda p' \cos^2\theta(c[yzz] + s[xzz]) \pm 2q' \cos\theta \sin\theta(c[xzz] - s[yzz]) + \text{NOT} \\ &= D_2(5) \end{aligned}$$

Similar calculations have to be performed on $D_3(4)$ and the situation at $t(5)$ is

$$\begin{aligned}
 D_0(5) &= \lambda p'(-c[y] - s[x]) \\
 D_1(5) &= \lambda p' \cos \theta(-c[xz] + s[yz]) \pm q' \sin \theta(c[yz] + q' s[xz]) + \text{NOT} \\
 D_2(5) &= \lambda p' \cos^2 \theta(c[yzz] + s[xzz]) \\
 &\quad \pm 2q' \cos \theta \sin \theta(c[xzz] - s[yzz]) + \text{NOT} \\
 D_3(5) &= \lambda p' \cos^3 \theta(c[xzzz] - s[yzzz]) \\
 &\quad \pm 3q' \cos^2 \theta \sin \theta(-c[yzzz] - s[xzzz]) + \text{NOT}
 \end{aligned} \tag{II.78}$$

Follows now the last $1/2J$ coupled evolution. We will retain only the observable terms, having x or y for carbon and 1 for all protons.

$$\begin{aligned}
 D_0(5) &\xrightarrow{\text{shift C}} \lambda p'(-c^2[y] + cs[x] - sc[x] - s^2[y]) = -\lambda p'[y] \\
 &= -\lambda p'[y] = D_0(6) \\
 D_1(5) &\xrightarrow{\text{coupl.}} \lambda p' \cos \theta(-c[y1] - s[x1]) \pm q' \sin \theta(-c[x1] + s[y1]) + \text{NOT} \\
 &\quad \xrightarrow{\text{shift C}} \lambda p' \cos \theta(-c^2[y1] + cs[x1] - sc[x1] - s^2[y1]) \\
 &\quad \pm q' \sin \theta(-c^2[x1] - cs[y1] + sc[y1] - s^2[x1]) + \text{NOT} \\
 &= -\lambda p' \cos \theta[y1] - (\pm q' \sin \theta[x1]) + \text{NOT} = D_1(6)
 \end{aligned}$$

After performing similar calculations for $D_2(5)$ and $D_3(5)$, we can summarize the results at $t(6)$ as follows

$$\begin{aligned}
 D_0(6) &= -\lambda p'[y] \\
 D_1(6) &= -(\lambda p' \cos \theta[y1] \pm q' \sin \theta[x1]) + \text{NOT} \\
 D_2(6) &= -(\lambda p' \cos^2 \theta[y11] \pm 2q' \sin \theta \cos \theta[x11]) + \text{NOT} \\
 D_3(6) &= -(\lambda p' \cos^3 \theta[y111] \pm 3q' \sin \theta \cos^2 \theta[x111]) + \text{NOT}
 \end{aligned} \tag{II.79}$$

As a remarkable achievement of the DEPT sequence, we notice that no chemical shift (proton or carbon) is expressed in the density matrix at time $t(6)$, when the acquisition begins. We will not have any frequency dependent phase shift. This alone can justify the "distortionless" claim in the name of the sequence.

The term containing λ can be relatively small when a high repetition rate is used. We are interested in the second term, which does not contain the factor λ and is also polarization enhanced (has q' rather than p').

The first term can be edited out by phase cycling. The $\pm \sin \theta$ factor in the expression of the density matrix corresponds to the last proton pulse (see Figure II.8) being applied along the $+y$ and $-y$ axis, respectively. If we take a scan with the phase $+y$ and subtract it from the one with phase $-y$, the first term is cancelled and we are left with

$$\begin{aligned} D_1(6) &= q' \sin \theta [x1] + \text{NOT} \\ D_2(6) &= 2q' \sin \theta \cos \theta [x11] + \text{NOT} \\ D_3(6) &= 3q' \sin \theta \cos^2 \theta [x111] + \text{NOT} \end{aligned} \quad (\text{II.80})$$

The subtraction is performed by a 180° shift in the receiver phase. Theoretically, a two-step phase cycling is enough, in which the phase of the last proton pulse is

$$-y \qquad +y$$

and the receiver phase is

$$0^\circ \qquad 180^\circ$$

Additional phase cycling is commonly used to cancel radio-frequency interferences and the effect of pulse imperfections.

The nonprotonated carbons do not appear in the phase-cycled spectrum. The discrimination between CH, CH₂, and CH₃ is done by running the sequence three times, with different values of the flip angle θ , namely 90° , 45° and 135° .

When $\theta = 90^\circ$, then $\cos \theta = 0$, $\sin \theta = 1$ and (II.80) becomes

$$\begin{aligned} D_1(6) &= q'[x1] + \text{NOT} \\ D_2(6) &= \text{NOT} \\ D_3(6) &= \text{NOT} \end{aligned}$$

This is a ¹³C spectrum in which only the CH lines appear. When θ is slightly larger or smaller than 90° , a CH₂ will appear as a small singlet, negative or positive, respectively. That is why DEPT is a good method for calibrating the 90° proton pulse in a spectrometer configured for observing carbon.

When $\theta = 45^\circ$, $\cos\theta = 1/\sqrt{2}$, $\sin\theta = 1/\sqrt{2}$ and (II.80) becomes

$$D_1(6) = (1/\sqrt{2})q'[x1]) + \text{NOT}$$

$$D_2(6) = q'[x11] + \text{NOT}$$

$$D_3(6) = (3/2\sqrt{2}) q'[x111]) + \text{NOT}$$

All CH, CH₂, and CH₃ appear as positive singlets.

When $\theta = 135^\circ$, then $\cos\theta = -1/\sqrt{2}$, $\sin\theta = 1/\sqrt{2}$ and (II.80) becomes

$$D_1(6) = (1/\sqrt{2})q'[x1]) + \text{NOT}$$

$$D_2(6) = -q'[x11] + \text{NOT}$$

$$D_3(6) = (3/2\sqrt{2}) q'[x111]) + \text{NOT}$$

This is the same situation as for 45° , but CH₂ peaks appear negative.

We have discussed all the features of DEPT using the expression of the density matrix at time $t(6)$, when the acquisition begins. The ¹³C magnetization, which is oriented along x at $t(6)$, will precess during the acquisition with the Larmor frequency corresponding to the respective line and will appear as a singlet.

In principle only the 90° and the 135° runs are sufficient for an unambiguous identification of the CH, CH₂, and CH₃ peaks. The 45° run is necessary when one wants to do spectral editing. For the nonprotonated carbons, a normal run is needed with a long recycle time.

Modern instruments offer the possibility to edit DEPT spectra in order to select only the peaks of one group (e.g., CH) while eliminating the peaks of the other two groups (CH₂ and CH₃). This is theoretically based on linear combinations of the spectra obtained with different values of θ (45° , 90° , 135°).

Table II.2 contains the relative amplitudes of CH, CH₂, and CH₃ peaks for each of the three angles.

Table II.2. Relative peak amplitudes in the raw DEPT spectra.

Spectrum	θ	CH	CH ₂	CH ₃
A	45°	$1/\sqrt{2}$ (0.707)	1	$3/(2\sqrt{2})$ (1.06)
B	90°	1	0	0
C	135°	$1/\sqrt{2}$ (0.707)	-1	$3/(2\sqrt{2})$ (1.06)

Table II.3 shows the operations necessary to obtain spectra of only one of the three groups or all of them together (note that the spectrum taken at 45° also shows the peaks of all groups, but not their true amplitudes).

Table II.3. Linear combinations of the raw DEPT spectra, necessary in order to obtain only one of the three groups or all of them together.

Combination	CH	CH ₂	CH ₃
B	1	0	0
(A - C)/2	0	1	0
(A+C - 1.41B)/2.12	0	0	1
Sum of the above	1	1	1

Some instrument softwares make it possible to alter the theoretical coefficients in order to compensate for hardware imperfections.