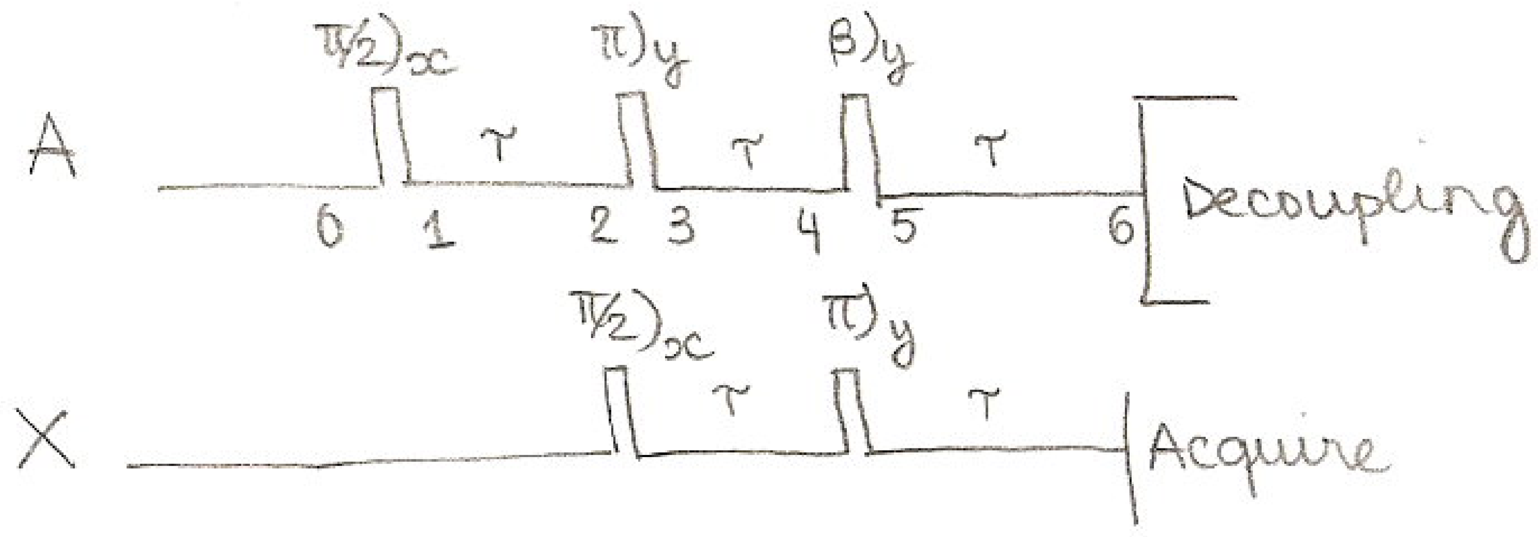
DEPT – Distortionless enhancement by polarization transfer



τ: (initially) arbitrary. We set it to $1/2J$ at the end.

<u>0</u>: $I_z^A + I_z^X$

$\downarrow \pi/2)_x^A$

<u>1</u>: $-I_y^A + I_z^X$

$\downarrow$ scalar coupling τ

$$-I_y^A \cos(\pi J\tau) + 2I_x^A I_z^X \sin(\pi J\tau) + I_z^X$$

$\downarrow$ chemical shifts A, X

<u>2</u>: $-I_y^A \cos(\pi J\tau)\cos(\omega_A\tau) + I_x^A\cos(\pi J\tau)\sin(\omega_A\tau) + 2I_z^X \sin(\pi J\tau)\cdot(I_x^A\cos(\omega_A\tau) + I_y^A\sin(\omega_A\tau)) + I_z^X$

$\downarrow \pi)_y^A$

$$-I_y^A\cos(\pi J\tau)\cos(\omega_A\tau) - I_x^A\cos(\pi J\tau)\sin(\omega_A\tau) + 2I_z^X\sin(\pi J\tau)\cdot(-I_x^A\cos(\omega_A\tau) + I_y^A\sin(\omega_A\tau)) + I_z^X$$

$\downarrow \pi/2)_x^X$

<u>3</u>: $-I_y^A\cos(\pi J\tau)\cos(\omega_A\tau) - I_x^A\cos(\pi J\tau)\sin(\omega_A\tau) - 2I_y^X\sin(\pi J\tau)\cdot(-I_x^A\cos(\omega_A\tau) + I_y^A\sin(\omega_A\tau)) - I_y^X$

$\downarrow$ scalar coupling τ

$\cos(\pi J\tau)\cos(\omega_A\tau)[-I_y^A\cos(\pi J\tau) + 2I_x^A I_z^X\sin(\pi J\tau) +$

$\cos(\pi J\tau)\sin(\omega_A\tau)[-I_x^A\cos(\pi J\tau) - 2I_y^A I_z^X\sin(\pi J\tau)] +$

$2\sin(\pi J\tau)\cos(\omega_A\tau)[I_y^X I_x^A] +$

$2\sin(\pi J\tau)\sin(\omega_A\tau)[-I_y^X I_y^A] +$

$-I_y^X\cos(\pi J\tau) + 2I_x^X I_z^A\sin(\pi J\tau)$

$\downarrow$ chemical shifts A, X

<u>4</u>: $\cos(\pi J\tau)\sin(\omega_A\tau)\{\cos(\pi J\tau)[-\cos(\omega_A\tau)I_y^A + \sin(\omega_A\tau)I_x^A] + 2\sin(\pi J\tau)[[I_x^A\cos(\omega_A\tau) + I_y^A\sin(\omega_A\tau)]\cdot I_z^X]\} +$

$\cos(\pi J\tau)\sin(\omega_A\tau)\{\cos(\pi J\tau)[-\cos(\omega_A\tau)I_x^A - \sin(\omega_A\tau)I_y^A] - 2\sin(\pi J\tau)[[I_y^A\cos(\omega_A\tau) - I_x^A\sin(\omega_A\tau)]\cdot I_z^X]\} +$

$2\sin(\pi J\tau)\cos(\omega_A\tau)\{[I_y^X\cos(\omega_X\tau) - I_x^X\sin(\omega_X\tau)]\cdot[I_x^A\cos(\omega_A\tau) + I_y^A\sin(\omega_A\tau)]\} +$

$2\sin(\pi J\tau)\cos(\omega_A\tau)\{[-I_y^X\cos(\omega_X\tau) + I_x^X\sin(\omega_X\tau)]\cdot[I_y^A\cos(\omega_A\tau) - I_x^A\sin(\omega_A\tau)]\} +$

$\cos(\pi J\tau)[-I_y^X\cos(\omega_X\tau) + I_x^X\sin(\omega_X\tau)] + 2\sin(\pi J\tau)[I_x^X\cos(\omega_X\tau) + I_y^X\sin(\omega_X\tau)]\cdot I_z^A$

$$\downarrow \beta)_y^A$$

$$\cos(\pi J\tau)\sin(\omega_A\tau)\cdot\Big\{\cos(\pi J\tau)\big[-\cos(\omega_A\tau)I_y^A + \sin(\omega_A\tau)[I_x^A\cos\beta - I_z^A\sin\beta]\big] +$$
$$2\sin(\pi J\tau)\big[[\cos(\omega_A\tau)[I_x^A\cos\beta - I_z^A\sin\beta]]\,I_y^A\sin(\omega_A\tau)\,I_z^x\big]\Big\} +$$

$$\cos(\pi J\tau)\sin(\omega_A\tau)\cdot\Big\{\cos(\pi J\tau)\big[-\cos(\omega_A\tau)\cdot[I_x^A\cos\beta - I_z^A\sin\beta] - \sin(\omega_A\tau)I_y^A\big]$$
$$-2\sin(\pi J\tau)\big[[I_y^A\cos(\omega_A\tau) - \sin(\omega_A\tau)[I_x^A\cos\beta - I_z^A\sin\beta]]\,I_z^x\big]\Big\} +$$

$$2\sin(\pi J\tau)\cos(\omega_A\tau)\Big\{[I_y^x\cos(\omega_x\tau) - I_x^x\sin(\omega_x\tau)]\cdot[\cos(\omega_A\tau)[I_x^A\cos\beta - I_z^A\sin\beta] + I_y^A\sin(\omega_A\tau)]\Big\} +$$

$$2\sin(\pi J\tau)\cos(\omega_A\tau)\Big\{[-I_y^x\cos(\omega_x\tau) + I_x^x\sin(\omega_x\tau)]\cdot[\cos(\omega_A\tau)\cdot I_y^A - \sin(\omega_A\tau)[I_x^A\cos\beta - I_z^A\sin\beta]]\Big\} +$$

$$\cos(\pi J\tau)\big[-I_y^x\cos(\omega_x\tau) + I_x^x\sin(\omega_x\tau)\big] + 2\sin(\pi J\tau)[I_x^x\cos(\omega_x\tau) + I_y^x\sin(\omega_x\tau)][I_z^A\cos\beta + I_x^A\sin\beta]$$

$$\downarrow \pi)_y^x$$

5: $$\cos(\pi J\tau)\sin(\omega_A\tau)\cdot\Big\{\cos(\pi J\tau)\big[-\cos(\omega_A\tau)I_y^A + \sin(\omega_A\tau)[I_x^A\cos\beta - I_z^A\sin\beta]\big] +$$
$$2\sin(\pi J\tau)\big[[\cos(\omega_A\tau)[I_x^A\cos\beta - I_z^A\sin\beta]]\,I_y^A\sin(\omega_A\tau)\cdot[-I_z^x]\big]\Big\} +$$

$$\cos(\pi J\tau)\sin(\omega_A\tau)\cdot\Big\{\cos(\pi J\tau)\big[-\cos(\omega_A\tau)\cdot[I_x^A\cos\beta - I_z^A\sin\beta] - \sin(\omega_A\tau)I_y^A\big]$$
$$-2\sin(\pi J\tau)\big[[I_y^A\cos(\omega_A\tau) - \sin(\omega_A\tau)[I_x^A\cos\beta - I_z^A\sin\beta]][-I_z^x]\big]\Big\} +$$

$$2\sin(\pi J\tau)\cos(\omega_A\tau)\Big\{[I_y^x\cos(\omega_x\tau) + \sin(\omega_x\tau)\cdot I_x^x]\cdot$$
$$[\cos(\omega_A\tau)[I_x^A\cos\beta - I_z^A\sin\beta] + I_y^A\sin(\omega_A\tau)]\Big\} +$$

$$2\sin(\pi J\tau)\cos(\omega_A\tau)\Big\{[-I_y^x\cos(\omega_x\tau) - \sin(\omega_x\tau)I_x^x]\cdot$$
$$[\cos(\omega_A\tau)I_y^A - \sin(\omega_A\tau)[I_x^A\cos\beta - I_z^A\sin\beta]]\Big\} +$$

$$\cos(\pi J\tau)\big[-I_y^x\cos(\omega_x\tau) - I_x^x\sin(\omega_x\tau)\big] + 2\sin(\pi J\tau)[-I_x^x\cos(\omega_x\tau) + I_y^x\sin(\omega_x\tau)][I_z^A\cos\beta + I_x^A\sin\beta]$$

$\downarrow$ scalar coupling τ

$$\cos(\pi J T)\sin(\omega_A T)\Big\{\cos(\pi J T)\Big[-\cos(\omega_A T)\cdot[I_y^A\cos(\pi J T)-2I_x^A I_z^x\sin(\pi J T)]+$$

$$+\sin(\omega_A T)[\cos\beta(I_x^A\cos(\pi J T)+2I_y^A I_z^x\sin(\pi J T))-\sin\beta I_z^A]+$$

$$+2\sin(\pi J T)\Big[\Big[\cos(\omega_A T)[\cos\beta(I_x^A\cos(\pi J T)+2I_y^A I_z^x\sin(\pi J T))-\sin\beta I_z^A]\cdot$$

$$[I_y^A\cos(\pi J T)-2I_x^A I_z^x\sin(\pi J T)]\cdot(-I_z^x)\Big]\Big]\Big\}+$$

$$\cos(\pi J T)\sin(\omega_A T)\cdot\Big\{\cos(\pi J T)\Big[-\cos(\omega_A T)[\cos\beta(I_x^A\cos(\pi J T)+2I_y^A I_z^x\sin(\pi J T))-\sin\beta I_z^A]$$

$$-\sin(\omega_A T)[I_y^A\cos(\pi J T)-2I_x^A I_z^x\sin(\pi J T)]$$

$$-2\sin(\pi J T)\Big[\Big[\cos(\omega_A T)[I_y^A\cos(\pi J T)-2I_x^A I_z^x\sin(\pi J T)]$$

$$+\sin(\omega_A T)[\cos\beta(I_x^A\cos(\pi J T)+2I_y^A I_z^x\sin(\pi J T))-\sin\beta I_z^A]\cdot I_z^x\Big\}+$$

$$2\sin(\pi J T)\cos(\omega_A T)\Big\{\Big[\cos(\omega_x T)[I_y^x\cos(\pi J T)-2I_x^x I_z^A\sin(\pi J T)]+\sin(\omega_x T)[I_x^x\cos(\pi J T)+2I_y^x I_z^A\sin(\pi J T)]\Big]\cdot$$

$$\Big[\cos(\omega_A T)[\cos\beta[I_x^A\cos(\pi J T)+2I_y^A I_z^x\sin(\pi J T)]-\sin\beta I_z^A]+$$

$$+\sin(\omega_A T)\cdot[I_y^A\cos(\pi J T)-2I_x^A I_z^x\sin(\pi J T)]\Big]\Big\}+$$

$$2\sin(\pi J T)\cos(\omega_A T)\Big\{\Big[-\cos(\omega_x T)\cdot[I_y^x\cos(\pi J T)-2I_x^x I_z^A\sin(\pi J T)]-\sin(\omega_x T)[I_x^x\cos(\pi J T)+2I_y^x I_z^A\sin(\pi J T)]\Big]\cdot$$

$$\Big[\cos(\omega_A T)[I_y^A\cos(\pi J T)-2I_x^A I_z^x\sin(\pi J T)]$$

$$-\sin(\omega_A T)[\cos\beta[I_x^A\cos(\pi J T)+2I_y^A I_z^x\sin(\pi J T)]-\sin\beta I_z^A]\Big]\Big\}+$$

$$\cos(\pi J T)\cdot\Big[-\cos(\omega_x T)[I_y^x\cos(\pi J T)-2I_x^x I_z^A\sin(\pi J T)]-\sin(\omega_x T)[I_x^x\cos(\pi J T)+2I_y^x I_z^A\sin(\pi J T)]\Big]$$

$$+2\sin(\pi J T)\Big[-\cos(\omega_x T)[I_x^x\cos(\pi J T)+2I_y^x I_z^A\sin(\pi J T)]$$

$$+\sin(\omega_x T)[I_y^x\cos(\pi J T)-2I_x^x I_z^A\sin(\pi J T)]\Big]\cdot$$

$$\Big[\cos\beta I_z^A+\sin\beta[I_x^A\cos(\pi J T)+2I_y^A I_z^x\sin(\pi J T)]\Big]$$

Now it is getting very long and I give in and set $\tau = 1/2J$:

$$2\cos(\omega_A\tau)\Big\{\big[\cos(\omega_x\tau)[-2I_x^x I_z^A] + \sin(\omega_x\tau)[2I_y^x I_z^A]\big]\cdot\big[\cos(\omega_A\tau)[\cos\beta\, 2I_y^A I_z^x - \sin\beta\, I_z^A] + \sin(\omega_A\tau)[-2I_x^A I_z^x]\big]\Big\} +$$

$$2\cos(\omega_A\tau)\Big\{\big[-\cos(\omega_x\tau)[-2I_x^x I_z^A] - \sin(\omega_x\tau)[2I_y^x I_z^A]\big]\cdot\big[\cos(\omega_A\tau)[-2I_x^A I_z^x] - \sin(\omega_A\tau)[\cos\beta\, 2I_y^A I_z^x - \sin\beta\, I_z^A]\big]\Big\} +$$

$$2\big[-\cos(\omega_x\tau)[2I_y^x I_z^A] + \sin(\omega_x\tau)[-2I_x^x I_z^A]\big]\cdot\big[\cos\beta\, I_z^A + \sin\beta\, 2I_y^A I_z^x\big]$$

↓ chemical shifts A, X (we expect them to be refocussed)

6: $$2\cos(\omega_A\tau)\Big\{\big[\cos(\omega_x\tau)[-2I_z^A(I_x^x\cos(\omega_x\tau) + I_y^x\sin(\omega_x\tau))] + \sin(\omega_x\tau)[2I_z^A(I_y^x\cos(\omega_x\tau) - I_x^x\sin(\omega_x\tau))]\big]\cdot$$
$$\big[\cos(\omega_A\tau)[\cos\beta\, 2I_z^x(I_y^A\cos(\omega_A\tau) - I_x^A\sin(\omega_A\tau)) - \sin\beta\, I_z^A] + \sin(\omega_A\tau)[-2I_z^x(I_x^A\cos(\omega_A\tau) + I_y^A\sin(\omega_A\tau))]\big]\Big\} +$$

$$2\cos(\omega_A\tau)\Big\{\big[+\cos(\omega_x\tau)[2I_z^A(I_x^x\cos(\omega_x\tau) + I_y^x\sin(\omega_x\tau))] - \sin(\omega_x\tau)[2I_z^A(I_y^x\cos(\omega_x\tau) - I_x^x\sin(\omega_x\tau))]\big]\cdot$$
$$\big[-\cos(\omega_A\tau)[2I_z^x(I_x^A\cos(\omega_A\tau) + I_y^A\sin(\omega_A\tau))] - \sin(\omega_A\tau)[\cos\beta\, 2I_z^x(I_y^A\sin(\omega_A\tau) - I_x^A\cos(\omega_A\tau)) - \sin\beta\, I_z^A]\big]\Big\} +$$

$$2\big[-\cos(\omega_x\tau)[2I_z^A(I_y^x\cos(\omega_x\tau) - I_x^x\sin(\omega_x\tau))] + - \sin(\omega_x\tau)[2I_z^A(I_x^x\cos(\omega_x\tau) + I_y^x\sin(\omega_x\tau))]\big]\cdot\big[\cos\beta\, I_z^A + \sin\beta\, 2I_z^x(I_y^A\cos(\omega_A\tau) - I_x^A\sin(\omega_A\tau))\big]$$

Except for potential mistakes, the density operator, simplified, should look like this at step 6:

THIS is CORRECT { $\boxed{+4 I_x^x \sin\beta}$ ← only one contributing to signal acquired!

$+$

THIS IS NOT LIKELY TO BE 100% CORRECT

$$2 I_z^A \cos(w_A T) \sin\beta \left(\sin(w_A T) - \cos(w_A T)\right)$$

$$+$$

$$8 I_z^A I_z^x \sin\beta \left(I_x^A I_x^x \sin(w_A T) - I_y^A I_y^x \cos(w_A T)\right)$$

$$+$$

$$4 I_z^x I_x^A \left[\cos^2(w_A T)\left(\sin(w_A T)\sin\beta - \cos(w_A T) - \sin(w_A T) - \sin(w_A T)\cos\beta\right)\right]$$

$$+$$

$$4 I_z^x I_y^A \left[\cos(w_A T)\left[\cos^2(w_A T)\cos\beta - \sin^2(w_A T) - \sin^2(w_A T)\cos\beta + \cos(w_A T)\sin(w_A T)\right]\right]$$

One sees that the flip angle that maximizes this spectrum is $\beta = \pi/2$.

The DEPT experiment is conceived to make the difference between AX, A_2X, A_3X systems because they can be shown to give rise to spectra w/ ≠ dependencies on β:

	signal	
AX	$\propto$	$I_x^x \sin\beta$
A_2X	$\propto$	$I_x^x \sin 2\beta$
A_3X	$\propto$	$I_x^x\, 3 \sin\beta \cos^2\beta$