11. PO TREATMENT OF A POLARIZATION TRANSFER SEQUENCE: INEPT (INSENSITIVE NUCLEI ENHANCEMENT BY POLARIZATION TRANSFER) WITH DECOUPLING

We discuss first the decoupled INEPT sequence shown in Figure II.5. Its goal, an increased sensitivity of ^{13}C spectra, is achieved in two ways: by increasing the peak intensities for the protonated carbons, and by allowing a larger number of scans in a given experiment time.

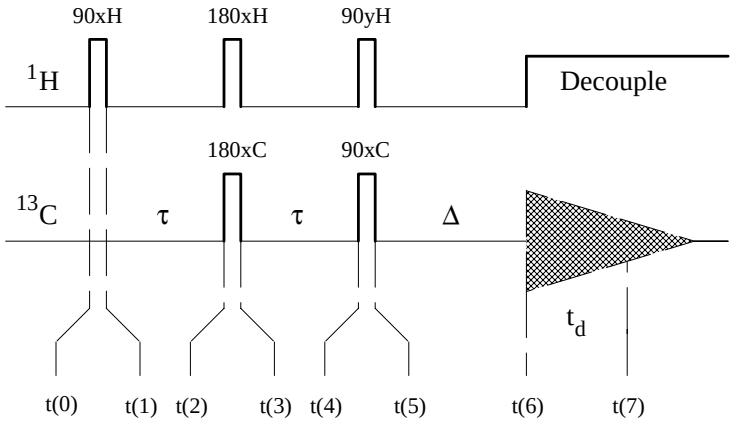

Figure II.5 The INEPT sequence: $90xH - \tau - 180xCH - \tau - 90yH - 90xC - \Delta - AT$

We treat the CH_n case with n = 1,2 or 3. The density matrix at thermal equilibrium is:

$$D = -(p'/n)\{z1\} - q'\{1z\} \qquad \text{(II.52)}$$

One of the advantages of INEPT is that it allows fast scanning, (limited by the proton relaxation only). In order to emphasize this feature we will assume that only the protons have fully relaxed in the interval between sequences and will write the initial density matrix as

$$D(0) = -\lambda(p'/n)\{z1\} - q'\{1z\} \qquad \text{(II.53)}$$

where λ is a recovery factor for carbon $(0 \le \lambda \le 1)$.

The effect of the first pulse is

$$D(0) \xrightarrow{90xH} -\lambda(p'/n)\{z1\} + q'\{1y\} \qquad \text{(II.54)}$$

D(1)

See Appendix L for the meaning of { } (multiplet formalism). We treat now the portion from $t(1)$ to $t(4)$ as a shift-refocusing routine (see Section II.8). We will apply a nonselective 180xCH pulse followed by a 2τ evolution in which the coupling only is expressed and this will bring us to $t(4)$.

$$\begin{aligned} D(1) &\xrightarrow{180xCH} +\lambda(p'/n)\{z1\} - q'\{1y\} \xrightarrow{2\tau\ (J\ coupl.)} \\ &\longrightarrow \lambda(p'/n)\{z1\} - q'\{1y\}\cos 2\pi J\tau + q'\{zx\}\sin 2\pi J\tau \end{aligned} \qquad \text{(II.55)}$$

D(4)

The next two pulses have to be treated successively because one of the terms in $D(4)$ is affected by both the proton and the carbon pulse.

$$\begin{aligned} D(4) &\xrightarrow{90yH} \lambda(p'/n)\{z1\} - q'\{1y\}\cos 2\pi J\tau - q'\{zz\}\sin 2\pi J\tau \\ &\xrightarrow{90xC} -\lambda(p'/n)\{y1\} - q'\{1y\}\cos 2\pi J\tau + q'\{yz\}\sin 2\pi J\tau \end{aligned}$$

D(5) (II.56)

After $t(5)$ no pulse follows and we can concentrate on the observable terms, keeping in mind that our observe nucleus is ^{13}C.

$$D(5) = -\lambda(p'/n)\{y1\} + q'\{yz\}\sin 2\pi J\tau + \text{NOT} \qquad \text{(II.57)}$$

The second term is enhanced by polarization transfer and it does not depend on λ. This means the pulse repetition rate is limited only by the proton relaxation as far as the second term is concerned. The optimum value for τ is 1/4J which leads to $\sin 2\pi J\tau = 1$. With this assumption:

$$D(5) = -\lambda(p'/n)\{y1\} + q'\{yz\} + \text{NOT} \qquad \text{(II.58)}$$

In $D(5)$ the second term is still not an observable; hence, the necessity of Δ. Using rule #5 in Appendix L we obtain:

$$\begin{aligned} D(5) &\xrightarrow{\Delta} -\lambda(p'/n)C^n(c\{y1\} - s\{x1\}) \\ &+ q'SC^{n-1}(-c\{x1\} - s\{y1\}) + \text{NOT} \end{aligned} \qquad \text{(II.59)}$$

D(6)

Where

$$c = \cos\Omega_C\Delta \qquad C = \cos\pi J\Delta$$
$$s = \sin\Omega_C\Delta \qquad S = \sin\pi J\Delta$$

The expression (II.59) has much in common with (II.48), with the difference that the proton frequency Ω_H is not to be seen. This is not alarming since INEPT is not intended as a 2D sequence. Going through the same steps as from (II.48) to (II.50) we get:

$$M_{TC}(6) = M_{oC}[-i\lambda C^n - n(q'/p')SC^{n-1}]\exp(i\Omega_C\Delta) \qquad \text{(II.60)}$$
$$M_{TC}(7) = M_{oC}[-i\lambda C^n - n(q'/p')SC^{n-1}]\exp[i\Omega_C(t_d+\Delta)] \qquad \text{(II.61)}$$

We focus on the second term in the brackets (polarization transfer and fast scanning). The optimum value of Δ is selected according to Figure II.4 and relations (II.51), leading to $nSC^{n-1} \geq 0.8$. The enhancement factor is therefore $\geq 0.8\gamma_H/\gamma_C$.

12. COUPLED INEPT

The coupled INEPT (Figure II.6) is used for spectra editing.

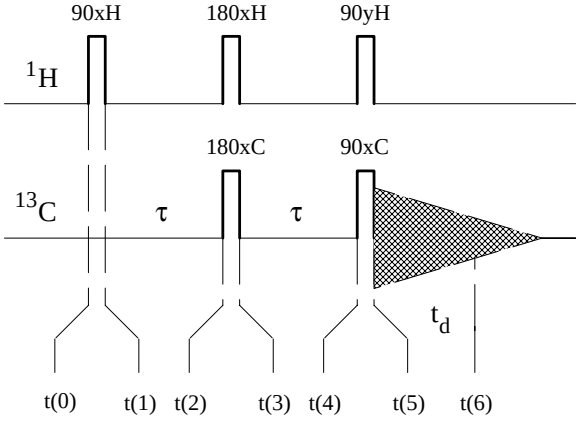

Figure II.6 The coupled INEPT sequence: $90xH - \tau - 180xCH - \tau - 90yH - 90xC - AT$

The magnetization at *t*(6) can be written by taking its expression from the previous sequence (II.60) and replacing Δ by t_d :

$$M_{TC}(6) = M_{oC}[-i\lambda C^n - n(q'/p')SC^{n-1}]\exp(i\Omega_C t_d) \qquad \text{(II.62)}$$

with $$C = \cos\pi J t_d \qquad S = \sin\pi J t_d \qquad \text{(II.63)}$$

The resemblance with (II.61) is only formal. In (II.61) we had:

$$C = \cos\pi J\Delta \qquad S = \sin\pi J\Delta$$

and the detection time t_d appeared only in the exponential factor outside the brackets. The signal was a singlet. In (II.62) the variable t_d is also contained in C and S and the Fourier transform exhibits a multiplet. In order to see how this multiplet looks like, we have to discuss the expression (II.62) for n = 1, 2, and 3. We split M_{TC}(6) into two terms

$$\begin{aligned} M_{TC}(6) &= -M_{oC}(q'/p')nSC^{n-1}\exp(i\Omega_C t_d) - iM_{oC}\lambda C^n\exp(i\Omega_C t_d) \\ &= M_A + M_B \end{aligned} \qquad \text{(II.64)}$$

and discuss these two terms separately, while keeping in mind that *C* and *S* have the meanings in (II.63).

A) Polarization enhanced multiplet (term M_A)

We discuss separately the CH, CH_2, and CH_3 cases.

n = 1 (CH case)

$$M_A = -M_{oC}(q'/p')S\exp(i\Omega_C t_d)$$

Using (A28) we have

$$S = \frac{\exp(i\pi J t_d) - \exp(-i\pi J t_d)}{2i}$$

and this leads to

$$M_A = M_{oC}(q'/p')(\frac{1}{2i})[-e^{i(\Omega_C+\pi J)t_d} + e^{i(\Omega_C-\pi J)t_d}] \qquad \text{(II.65)}$$

This is the up-down doublet of Figure II.7a .

For a methylene

$n = 2$ (CH_2 case)

$$M_A = -M_{oC}(q'/p')2SC\exp(i\Omega_C t_d)$$

Using (A36) we have

$$SC = \frac{\exp(2i\pi Jt_d) - \exp(-2i\pi Jt_d)}{4i}$$

and

$$M_A = M_{oC}(q'/p')(\frac{1}{2i})[-e^{i(\Omega_C + 2\pi J)t_d} + e^{i(\Omega_C - 2\pi J)t_d}] \qquad \text{(II.66)}$$

This is a triplet with the central line missing and the other two lines one up and one down (see Figure II.7b).

$n = 3$ (CH_3 case)

$$M_A = -M_{oC}(q'/p')3SC^2\exp(i\Omega_C t_d)$$

We use (A38) and obtain

$$M_A = M_{oC}(q'/p')(\frac{3}{8i})[-e^{i(\Omega_C + 3\pi J)t_d} - e^{i(\Omega_C + \pi J)t_d} + e^{i(\Omega_C - \pi J)t_d} + e^{i(\Omega_C - 3\pi J)t_d}] \qquad \text{(II.67)}$$

This is the peculiar quartet in Figure II.7c: four lines of equal intensities, two up and two down.

B) Residual nonenhanced multiplet (term M_B)

The term M_B in (II.64) is smaller than M_A (no polarization enhancement and $\lambda < 1$). We will show that it represents a conventional multiplet.

$n = 1$ (CH case)

$$M_B = -iM_{oC}\lambda C\exp(i\Omega_C t_d)$$

Using (A27) and $-i = 1/i$ we obtain

$$M_B = M_{oC}\lambda(\frac{1}{2i})[e^{i(\Omega_C+\pi J)t_d} + e^{i(\Omega_C-\pi J)t_d}] \qquad \text{(II.68)}$$

the regular doublet in Figure II.7d .

n = 2 (CH_2 case)

$$M_B = -iM_{oC}\lambda C^2 \exp(i\Omega_C t_d)$$

Using (A35) we obtain the triplet

$$M_B = M_{oC}\lambda(\frac{1}{4i})[e^{i(\Omega_C+2\pi J)t_d} + 2e^{i\Omega_C t_d} + e^{i(\Omega_C-2\pi J)t_d}] \qquad \text{(II.69)}$$

as in Figure II.7e .

n = 3 (CH_3 case)

$$M_B = -iM_{oC}\lambda C^3 \exp(i\Omega_C t_d)$$

We use (A37) and obtain

$$M_B = M_{oC}\lambda(\frac{1}{8i})[e^{i(\Omega_C+3\pi J)t_d} + 3e^{i(\Omega_C+\pi J)t_d} + 3e^{i(\Omega_C-\pi J)t_d} + e^{i(\Omega_C-3\pi J)t_d}] \qquad \text{(II.70)}$$

a regular looking quartet (see Figure II.7f).

We notice that all the expressions (II.65) through (II.70) contain the factor $1/i$ (or $-i$) , indicating that the respective magnetizations are along the $-y$ axis.

When the term M_B is not vanishingly small, it breaks the symmetry of the multiplet, as shown in Figure II.7 (g through i). This drawback can be eliminated by means of an appropriate phase cycling. It is shown in Section II.13 that we have a similar situation with the DEPT sequence and a two step phase cycling is sufficient to cancel the residual nonenhanced signal.

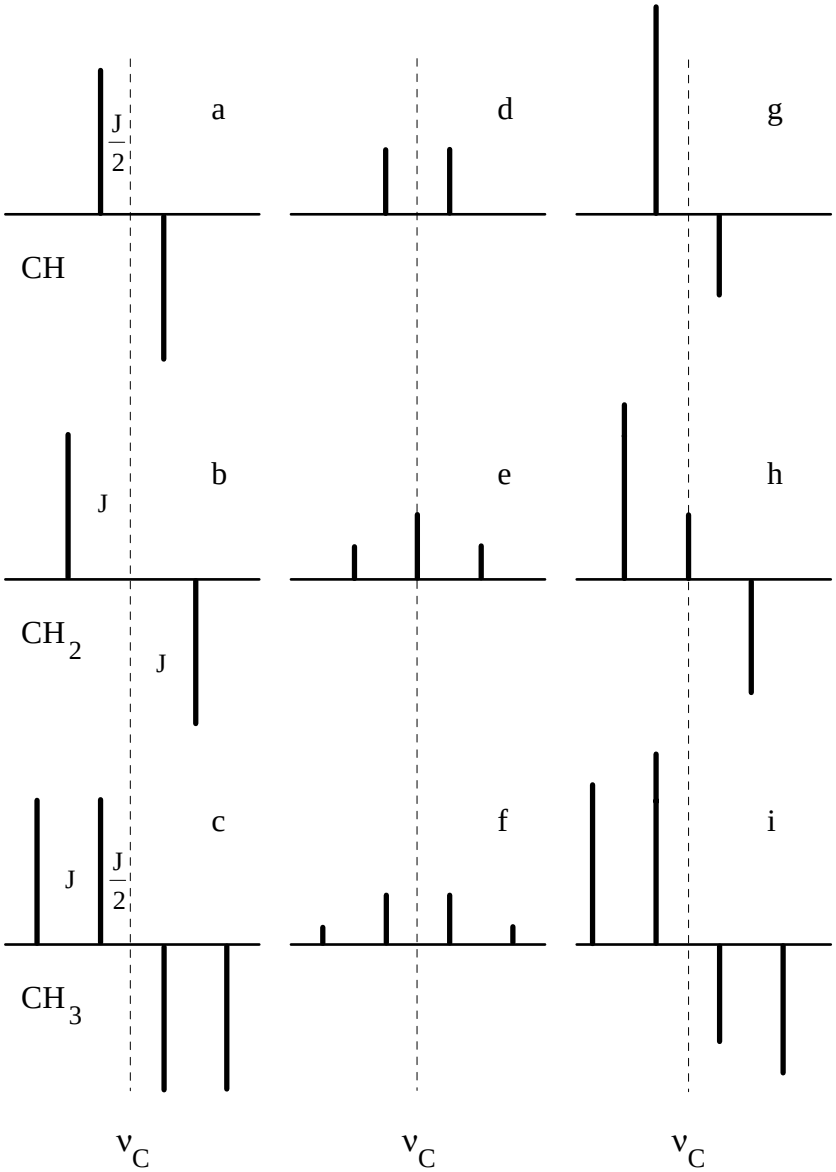

Figure II.7. Coupled INEPT; a,b,c − Polarization enhanced multiplet (term M_A); d,e,f − Residual non-enhanced multiplet (term M_B); g,h,i − Actual spectrum $(\text{term}\, M_A + M_B)$