2 | Learning Goals for Today

In this lecture, we will:

- Discuss basic building blocks for heteronuclear polarisation transfer

At the end, you will

- Understand the product operator theory of polarisation transfer;
- Be able to recognise polarisation transfer steps in complex pulse sequences;
- Be familiar with the important INEPT pulse sequence element.
NMR Sensitivity

\[ \text{SNR} \propto |\gamma|^{\frac{5}{2}} (B_0)^{\frac{3}{2}} \]

Example: $^{15}$N vs $^1$H;

\[ \gamma_H \approx -10 \gamma_N \]

Idea: transfer polarisation from the high-$\gamma$ nuclei to the ones with low $\gamma$.

Advantages:
- Higher SNR ($\gamma_H / \gamma_N$)
- Shorter relaxation time of H vs N: faster repetition times

How can this be accomplished?

Polarisation transfer requires *interactions* between the spin types in question.
Density operator terms

- Large $\gamma$: $I = (I_x, I_y, I_z)$
- Low $\gamma$: $S = (S_x, S_y, S_z)$

Hamiltonian

$$H = -\gamma I B_0 I_z - \gamma S B_0 S_z + 2\pi J_{IS} I_z S_z$$

\footnote{Drawings from M.H. Levitt, Spin Dynamics, J. Wiley and Sons, 2003}
5 | Insensitive Nuclei Enhanced by Polarisation Transfer

\[ \begin{align*}
  & \text{(\(\pi/2\))}_x \quad \text{(\(\pi\))}_x \quad \text{(\(\pi/2\))}_y \\
  & \quad \tau/2 \quad \tau/2 \quad \tau/2 \\
  & I \quad S
\end{align*} \]
6 | INEPT equivalent pulse sequence

\[ \rho_1 = \frac{1}{4} + \frac{1}{4} B_I I_z + \frac{1}{4} B_S S_z \]

\[ \rho_2 = \frac{1}{4} + \frac{1}{4} B_I I_y - \frac{1}{4} B_S S_z \]

\[ \rho_3 = \frac{1}{4} + \frac{1}{4} B_I 2I_x S_z - \frac{1}{4} B_S S_z \]

\[ \rho_4 = \frac{1}{4} + \frac{1}{4} B_I 2I_z S_y + \frac{1}{4} B_S S_y \]
7 | INEPT Spectrum

\[ \rho_4 = \frac{1}{4} + \frac{1}{4} B_I 2I_z S_y + \frac{1}{4} B_S S_y \]

- **transferred**
- **non-transferred**
- **total**

(a) (b) (c) (d)
INEPT cannot be directly combined with decoupling:

\[ \Omega \]

INEPT-enhanced

\[ \Omega \]

decoupled

Solution: additional delay before acquisition:

\[ \frac{\pi}{2} \]

\[ x \]

\[ \pi \]

\[ x \]

\[ \frac{\pi}{2} \]

decoupled

\[ \frac{\pi}{2} \]

\[ y \]

\[ \pi \]

\[ y \]

\[ \frac{\pi}{2} \]

DECouple
Refocussed INEPT: Product operators

\[ \rho_1 = \frac{1}{4} + \frac{1}{4} B_I I_z + \frac{1}{4} B_S S_z \]
\[ \rho_2 = \frac{1}{4} + \frac{1}{4} B_I I_y - \frac{1}{4} B_S S_z \]
\[ \rho_3 = \frac{1}{4} + \frac{1}{4} B_I 2I_x S_z - \frac{1}{4} B_S S_z \]
\[ \rho_4 = \frac{1}{4} + \frac{1}{4} B_I 2I_z S_x + \frac{1}{4} B_S S_x \]
\[ \rho_5 = \frac{1}{4} - \frac{1}{4} B_I 2I_z S_x + \frac{1}{4} B_S S_x \]
\[ \rho_6 = \frac{1}{4} + \frac{1}{4} B_I S_y - \frac{1}{4} B_S I_z S_y \]
10 | INEPT and Refocussed INEPT subspectra

**INEPT (without decoupling)**

\[
\rho_4 = \frac{1}{4} + \frac{1}{4} B_I 2 I_z S_y + \frac{1}{4} B_S S_y
\]

\[\begin{array}{c}
\beta^- \\
\alpha^-
\end{array}\]

transferred

\[\begin{array}{c}
\Omega \\
\Omega
\end{array}\]

non-transferred

\[\begin{array}{c}
\Omega
\end{array}\]

total

**Refocussed INEPT**

\[
\rho_6 = \frac{1}{4} + \frac{1}{4} B_I S_y - \frac{1}{4} B_S I_z S_y
\]

\[\begin{array}{c}
\beta^- \\
\alpha^-
\end{array}\]

transferred

\[\begin{array}{c}
\beta^- \\
\alpha^-
\end{array}\]

non-transferred
Fig. 6. A quantitative $^{13}$C spectrum compared to Q-INEPT-CT spectrum, showing the signal-rich upfield portion of the spectrum, obtained from the sample #1 (ethylbenzene and cholesterol). Quaternary carbon signals are marked by an asterisk in the quantitative $^{13}$C spectrum (note that at ∼42.5 ppm, the signals of quaternary carbon C8 and protonated carbon C7 overlap).
Take-home messages from today:

- Heteronuclear polarisation transfer can boost sensitivity for low-γ nuclei;
- polarisation transfer requires spin-spin interactions;
- in weakly coupled spin systems, the evolution under chemical shifts can be separated from that under $J$-couplings;
- the INEPT pulse sequence leads to antiphase doublet signals for CH and NH systems;
- refocussing produces absorption signals that can be decoupled;
- INEPT is an important building block in many advanced pulse sequences.