Polarisation Transfer: INEPT, DEPT, and Friends

CHEM 6154 – Nuclear Magnetic Resonance

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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.

3 | Polarisation transfer can enhance sensitivity

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-γ nuclei to the ones with low γ.
Advantages:

- Higher SNR (γ_H/γ_N)
- Shorter relaxation time of H vs N: faster repetition times

How can this be accomplished?

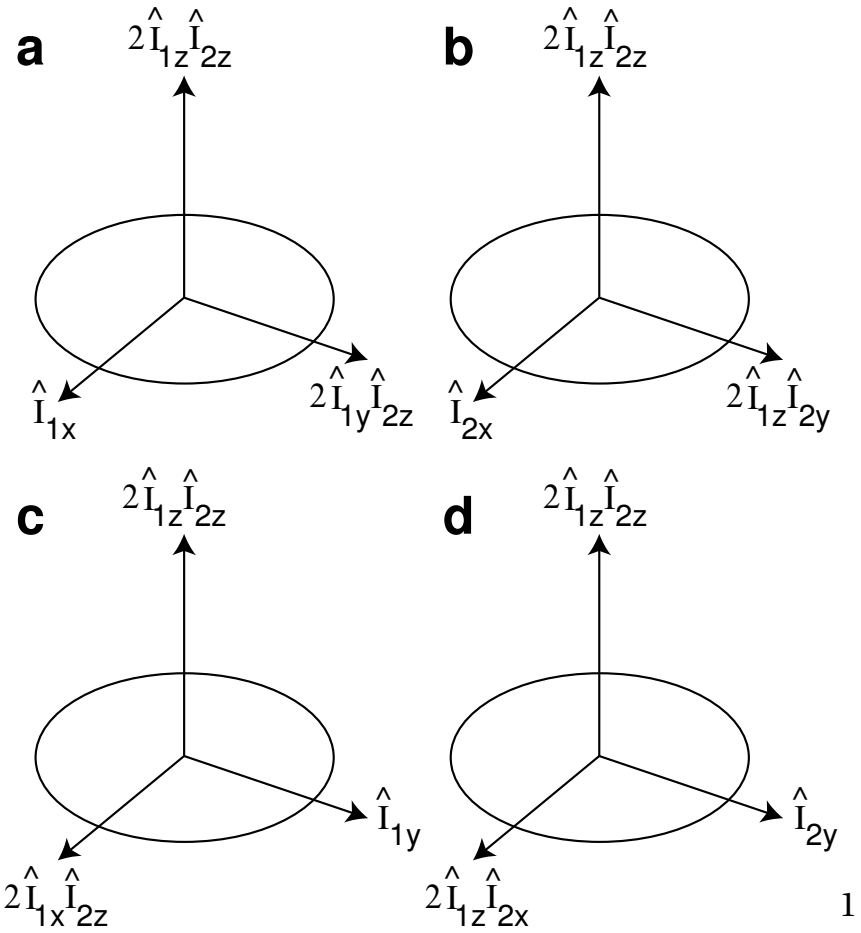
Polarisation transfer requires *interactions* between the spin types in question.

4 | Density operator terms

- Large γ: $\mathbf{I} = (I_x, I_y, I_z)$
- Low γ: $\mathbf{S} = (S_x, S_y, S_z)$

Hamiltonian

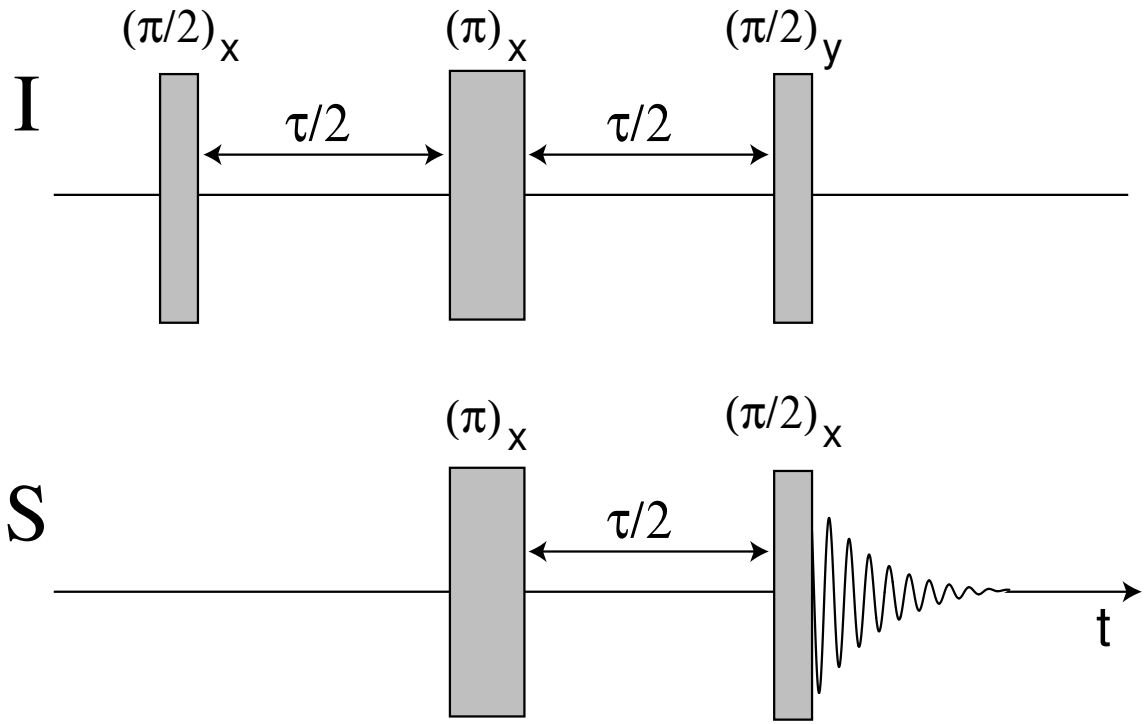
$$H = -\gamma_I B_0 I_z - \gamma_S B_0 S_z + 2\pi J_{IS} I_z S_z$$



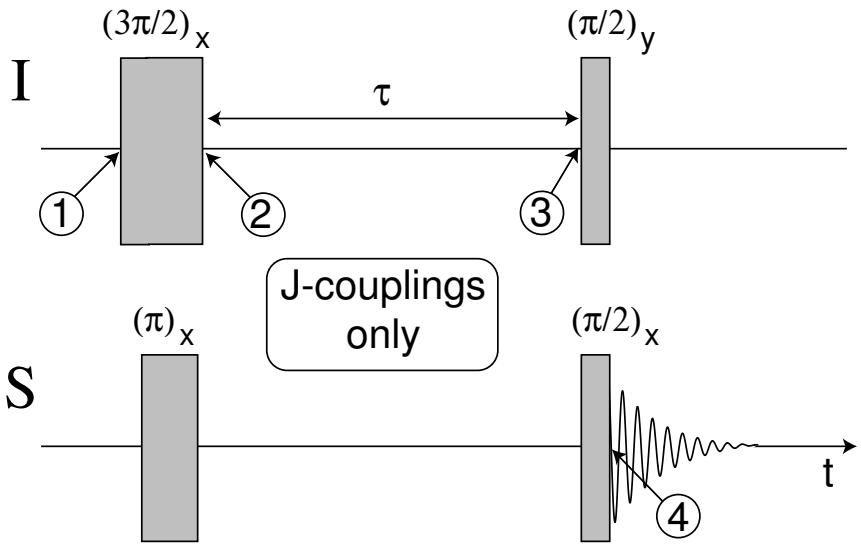
[1]

[1] Drawings from M.H. Levitt, Spin Dynamics, J. Wiley and Sons, 2003

5 | Insensitive Nuclei Enhanced by Polarisation Transfer



6 | INEPT equivalent pulse sequence



$$\rho_{①} = \frac{1}{4} + \frac{1}{4}\mathbb{B}_I\, I_z + \frac{1}{4}\mathbb{B}_S\, S_z$$

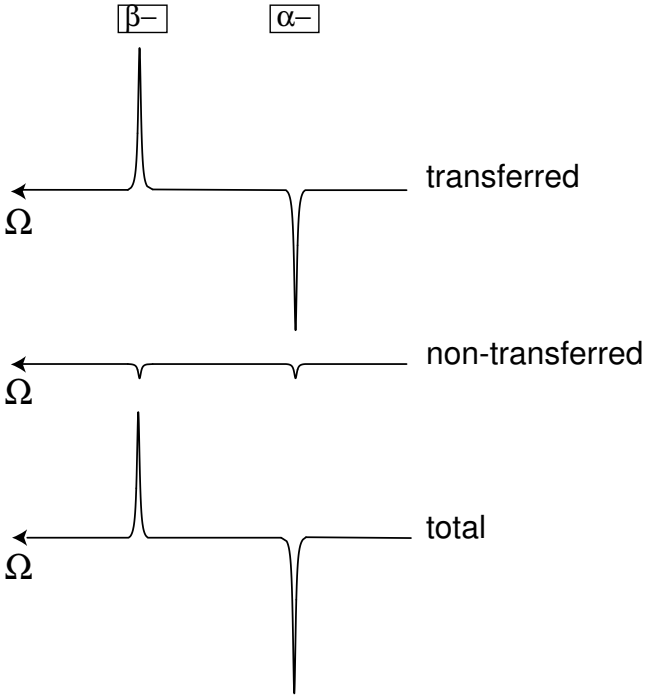
$$\rho_{②} = \frac{1}{4} + \frac{1}{4}\mathbb{B}_I\, I_y - \frac{1}{4}\mathbb{B}_S\, S_z$$

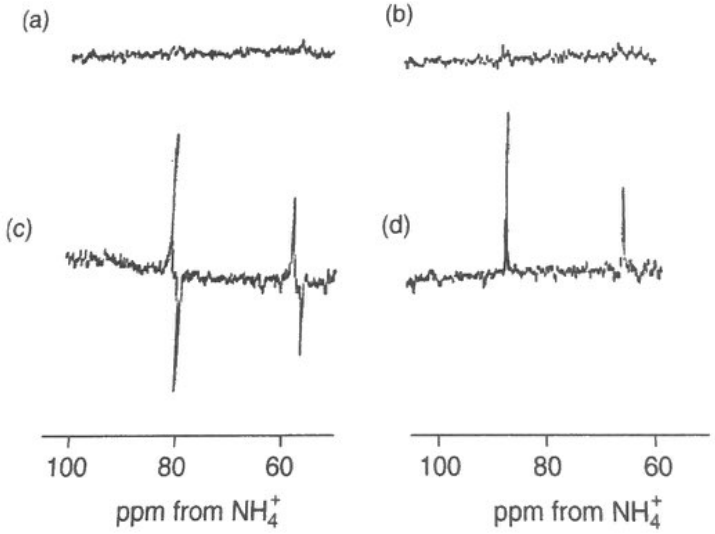
$$\rho_{③} = \frac{1}{4} + \frac{1}{4}\mathbb{B}_I\, 2I_x S_z - \frac{1}{4}\mathbb{B}_S\, S_z$$

$$\rho_{④} = \frac{1}{4} + \frac{1}{4}\mathbb{B}_I\, 2I_z S_y + \frac{1}{4}\mathbb{B}_S\, S_y$$

7 | INEPT Spectrum

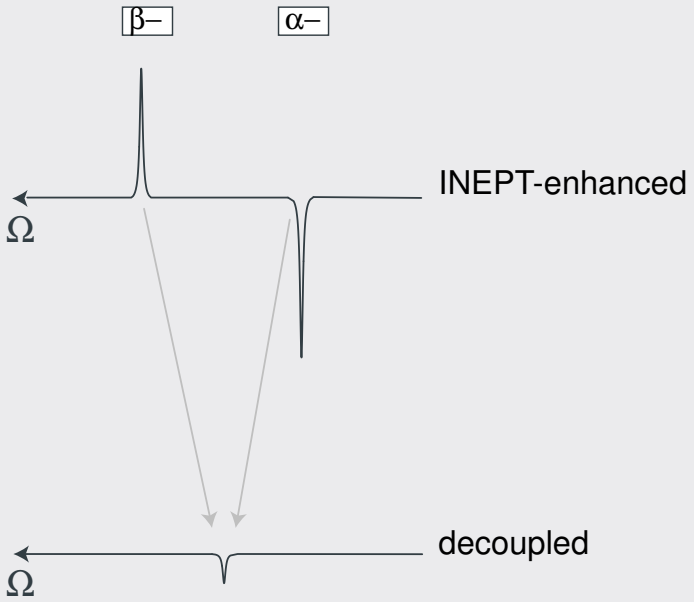
$$\rho_{④} = \frac{1}{4} + \frac{1}{4}\mathbb{B}_I\, 2I_z S_y + \frac{1}{4}\mathbb{B}_S\, S_y$$



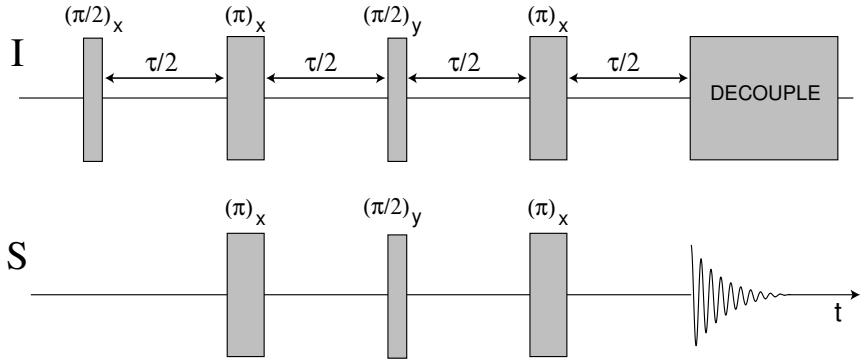


8 | Refocused INEPT

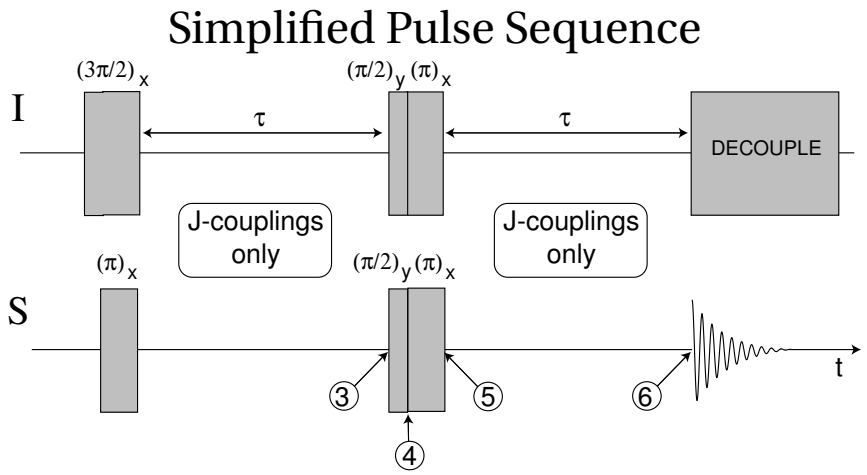
INEPT cannot be directly combined with decoupling:



Solution: additional delay before acquisition:



9 | Refocussed INEPT: Product operators



$$\rho_{①} = \frac{1}{4} + \frac{1}{4}\mathbb{B}_I\, I_z + \frac{1}{4}\mathbb{B}_S\, S_z$$

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$$\rho_{④} = \frac{1}{4} + \frac{1}{4}\mathbb{B}_I\, 2I_z S_x + \frac{1}{4}\mathbb{B}_S\, S_x$$

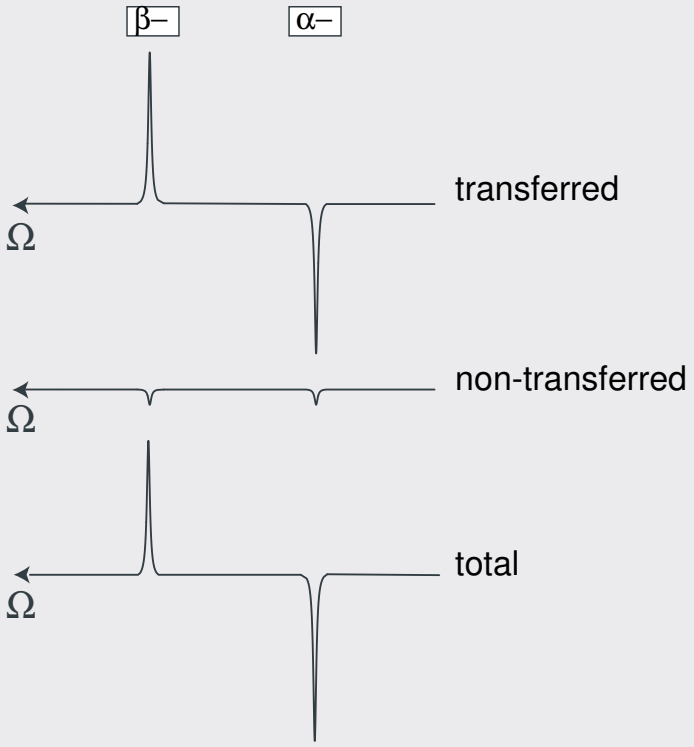
$$\rho_{⑤} = \frac{1}{4} - \frac{1}{4}\mathbb{B}_I\, 2I_z S_x + \frac{1}{4}\mathbb{B}_S\, S_x$$

$$\rho_{⑥} = \frac{1}{4} + \frac{1}{4}\mathbb{B}_I\, S_y - \frac{1}{4}\mathbb{B}_S\, I_z S_y$$

10 | INEPT and Refocussed INEPT subspectra

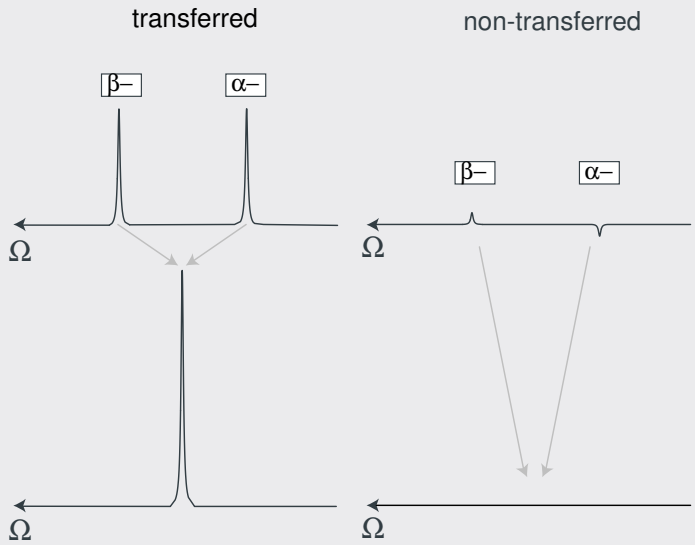
INEPT (without decoupling)

$$\rho_{④} = \frac{1}{4} + \frac{1}{4}\mathbb{B}_I\, 2I_z S_y + \frac{1}{4}\mathbb{B}_S\, S_y$$



Refocussed INEPT

$$\rho_{⑥} = \frac{1}{4} + \frac{1}{4}\mathbb{B}_I\, S_y - \frac{1}{4}\mathbb{B}_S\, I_z S_y$$



11 | INEPT: A recent example

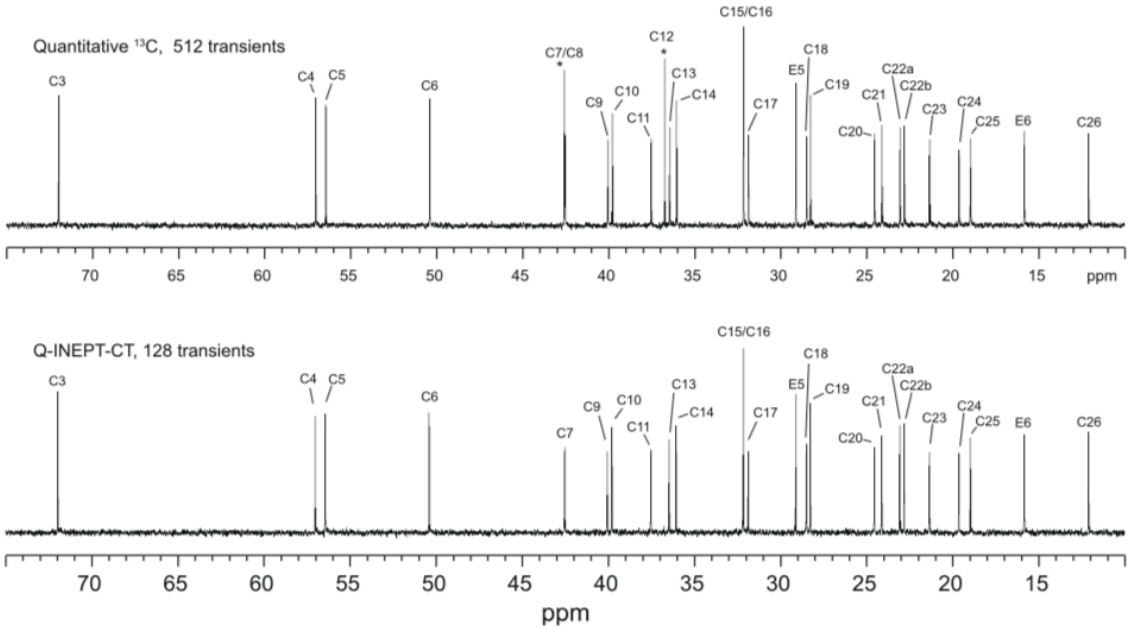
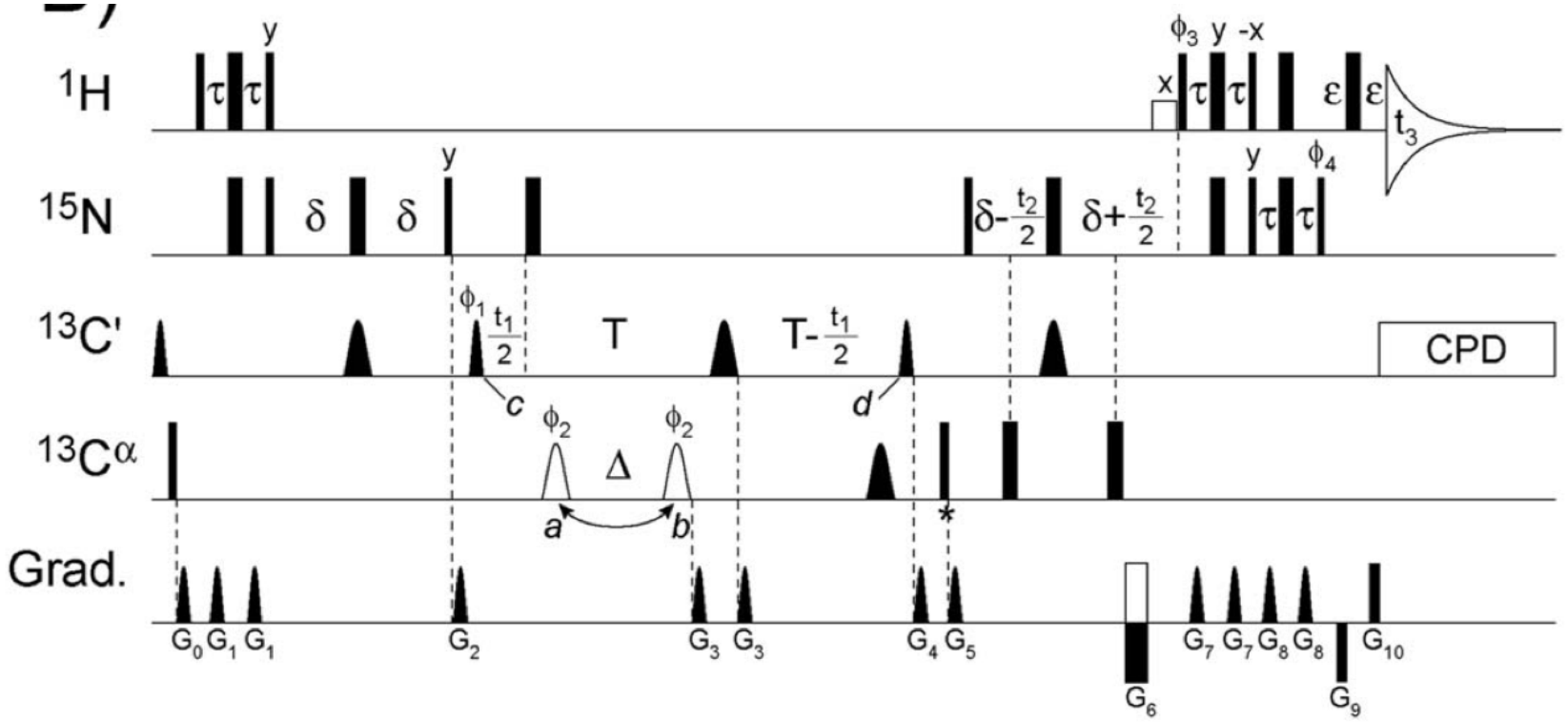


Fig. 6. A quantitative ^{13}C spectrum compared to Q-INEPT-CT spectrum, showing the signal-rich upfield portion of the spectrum, obtained from the sample #1 (ethylbenzene and cholesterol). Quaternary carbon signals are marked by an asterisk in the quantitative ^{13}C spectrum (note that at ~42.5 ppm,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

12 | INEPT as a building block in advanced experiments



Jaroniec, C. P., Ulmer, T. S., & Bax, A. (n.d.). Quantitative *J* correlation methods for the accurate measurement of $^{13}C'$-$^{13}C^{\alpha}$ dipolar couplings in proteins. *Journal of Biomolecular NMR*, **30**, 181–194.

13 | Recapitulation

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.