Lecture #12
POF practice: Polarization Transfer

- Topics
  - POF practice
  - INEPT, INEPT-R,
  - pulsed field gradients
- References
  - van de Ven, sections 3.6, 4.8, pages 119-127, 211-223

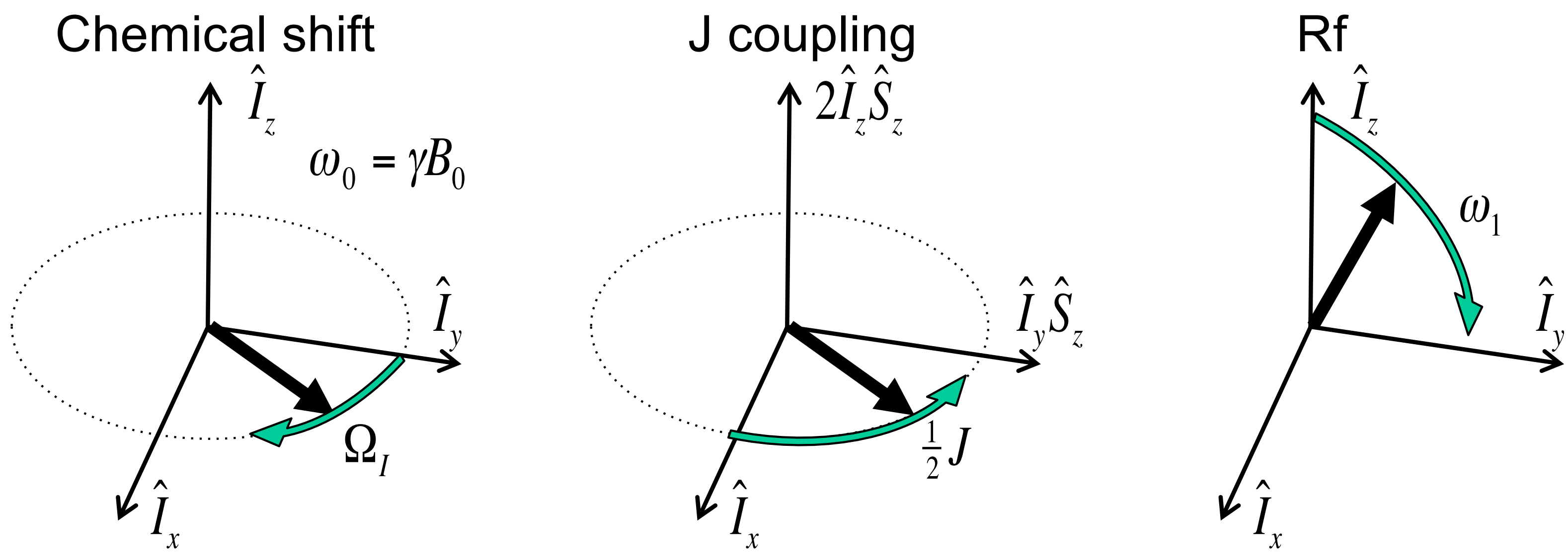
Branch Diagrams

- The branch diagram equation for product operators is

$$\hat{C}_p \xrightarrow{\hat{C}_q(\theta)} \begin{cases} \hat{C}_p & \Leftarrow \text{“cosine” branch} \\ -i[\hat{C}_q, \hat{C}_p] & \Leftarrow \text{“sine” branch} \end{cases}$$

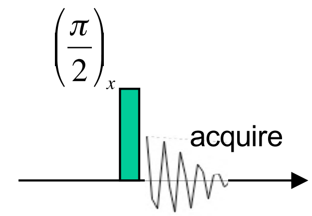
where $\hat{C}_p$ and $\hat{C}_q$ are any pair of product operator coherences.

- Use commutator tables or just remember these sign conventions:



Polarization Transfer

- The SNR for a simple pulse and acquire sequence:



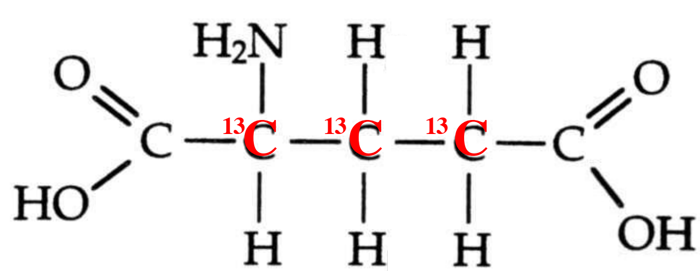
$$^{1}\text{H:}\quad \text{SNR}_H = \underset{\#\text{ of spins}}{N}\underbrace{\frac{\hbar\gamma_H}{2}}_{\text{Magnetic moment}}\underbrace{\left(\frac{\hbar\gamma_H B_0}{2kT}\right)}_{\text{Polarization}}$$

$$^{13}\text{C:}\quad \text{SNR}_C = N\frac{\hbar\gamma_C}{2}\left(\frac{\hbar\gamma_C B_0}{2kT}\right)$$

$$\text{Given } \gamma_H \approx 4\gamma_C \quad \Rightarrow \quad \text{SNR}_H \approx 16\ \text{SNR}_C$$

- Often desirable to enhance the SNR of the ^{13}C signal by exploiting the higher ^{1}H polarization.

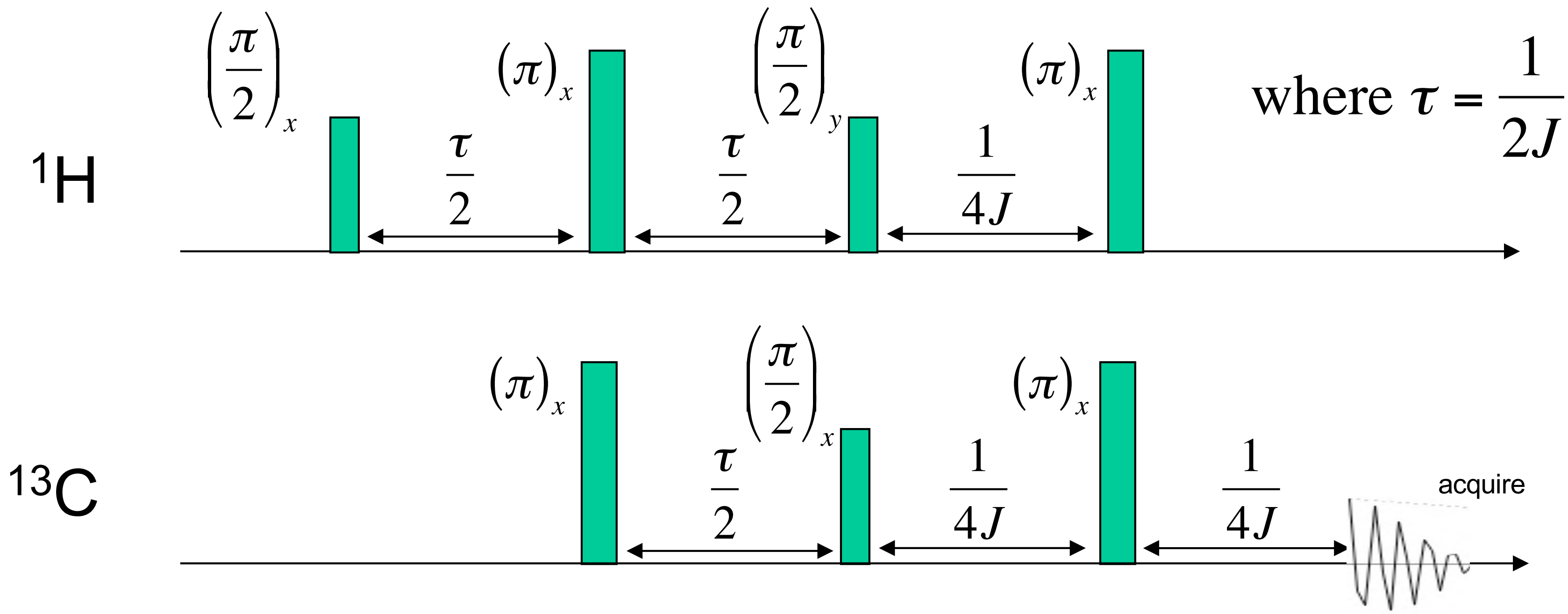
Example: ^{13}C-glutamate



Note: Glutamate is the brain's primary excitatory neurotransmitter.

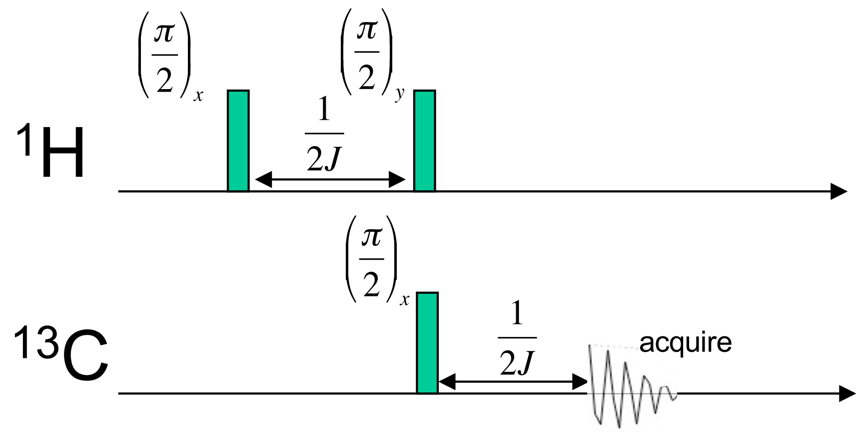
INEPT

- Insensitive Nuclei Enhanced by Polarization Transfer



- Gradient-enhanced INEPT

Consider a simple sequence…



- For now, let's assume that the chemical shift evolution during 1/2J is negligible, and the ^{1}H and ^{13}C spins are weakly J-coupled.
- Letting I = ^{1}H and S = ^{13}C, then the initial density operator is:

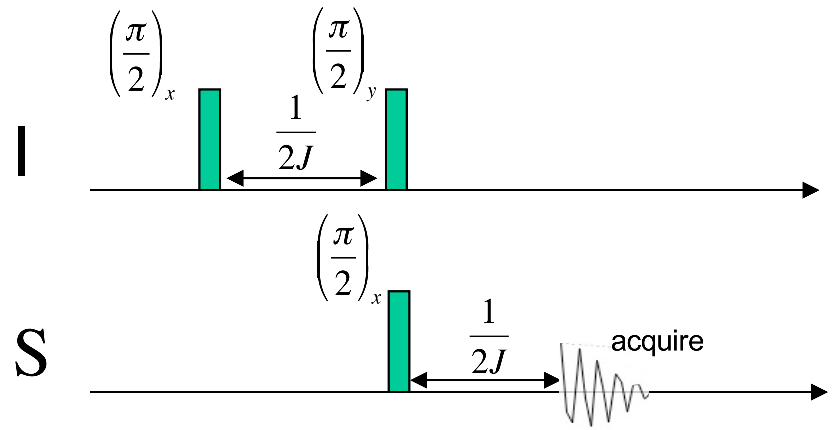
$$\hat{\sigma}(0) = \frac{\hbar B_0}{4kT}\left(\gamma_I \hat{I}_z + \gamma_S \hat{S}_z\right)$$

- The Hamiltonian during free precession is:

During 1/2J intervals: $\hat{H}_{\text{free}} \approx 2\pi J \hat{I}_z \hat{S}_z$ During acquisition: $\hat{H}_{\text{free}} = -\Omega_I \hat{I}_z - \Omega_S \hat{S}_z + 2\pi J \hat{I}_z \hat{S}_z$

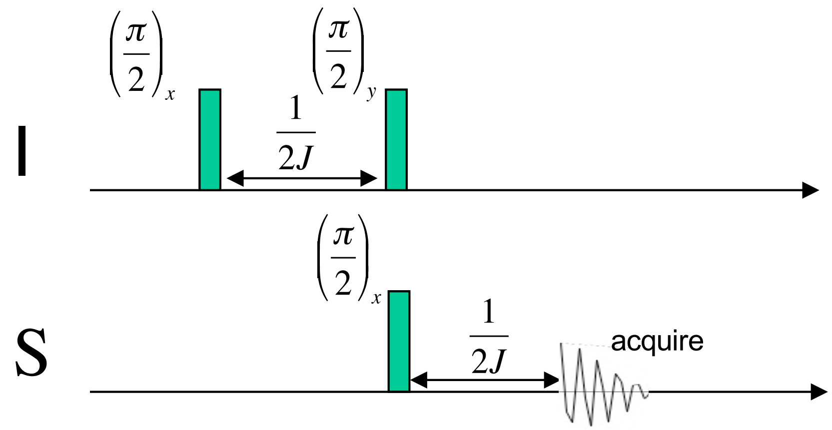
- We now wish to compute the branch diagram.

Branch Diagram



- Starting with the I spin…

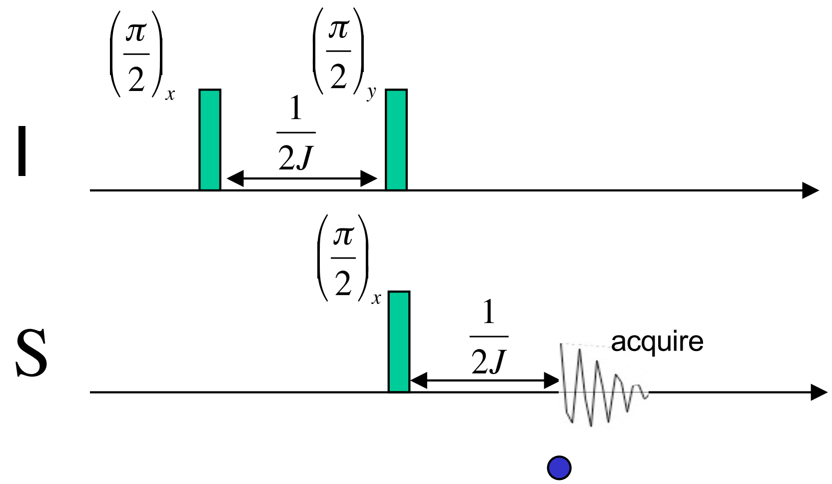
Branch Diagram



- Starting with the I spin…

$$\hat{I}_z \xrightarrow{\left(\frac{\pi}{2}\right)_x^I} \hat{I}_y \xrightarrow{-\pi J(\tau)} \begin{cases} \hat{I}_y \xrightarrow{\left(\frac{\pi}{2}\right)_y^I} \ldots \\ -2\hat{I}_x\hat{S}_z \xrightarrow{\left(\frac{\pi}{2}\right)_y^I} -2\hat{I}_z\hat{S}_z \xrightarrow{\left(\frac{\pi}{2}\right)_x^S} -2\hat{I}_z\hat{S}_y \xrightarrow{-\pi J\left(\frac{1}{2J}\right)} \hat{S}_x \end{cases}$$

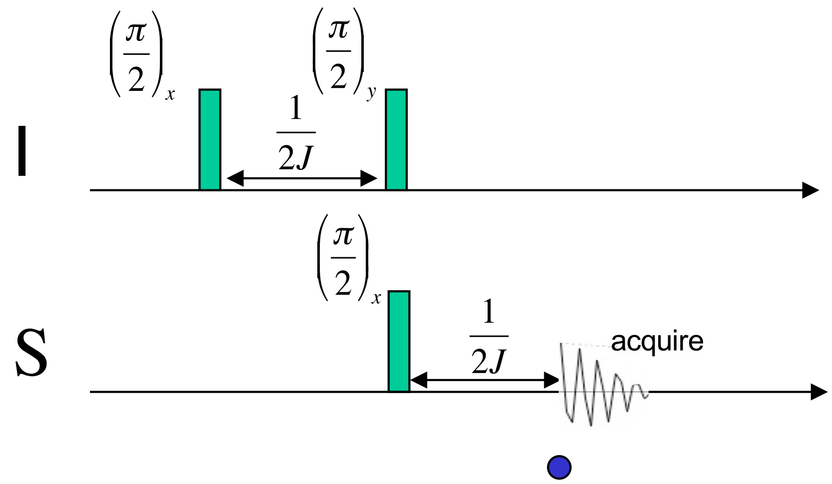
Branch Diagram



- During acquisition…

Fill in branch diagram

Branch Diagram



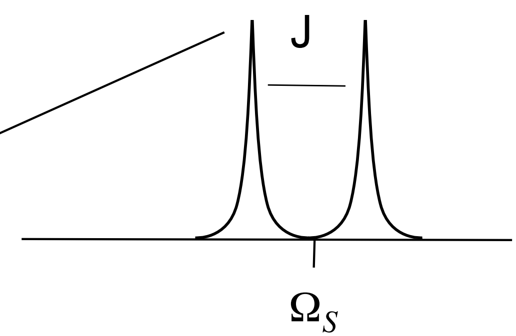
- During acquisition…

$$\hat{I}_z \longrightarrow \ldots \longrightarrow \hat{S}_x \xrightarrow{-\pi J t} \begin{cases} \hat{S}_x \xrightarrow{\Omega_S t} \begin{cases} \hat{S}_x \leftarrow M_x \\ -\hat{S}_y \leftarrow M_y \end{cases} \\ 2\hat{I}_z\hat{S}_y \xrightarrow{\Omega_S t} \begin{cases} 2\hat{I}_z\hat{S}_y \\ 2\hat{I}_z\hat{S}_x \end{cases} \end{cases}$$

$$M_x \propto \cos(\Omega_S t)\cos(\pi J t)$$

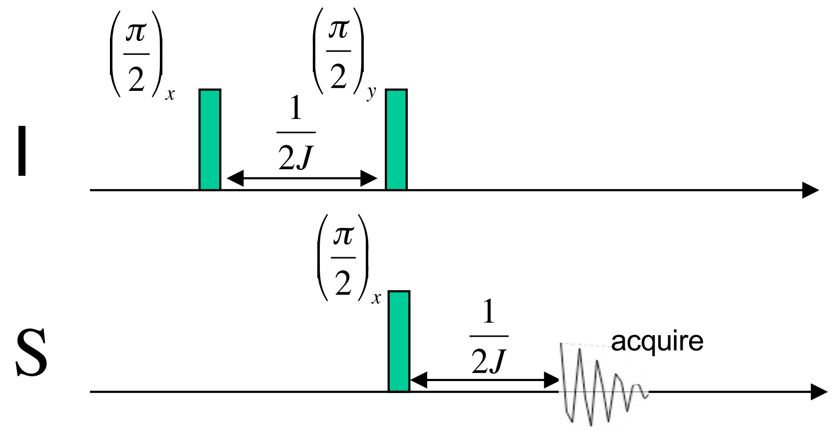
$$M_y \propto -\sin(\Omega_S t)\cos(\pi J t)$$

$$\omega_0 M_{xy} = \gamma_C B_0 M_{xy} = \frac{N\gamma_C^2 \gamma_H \hbar^2 B_0^2}{8kT}$$



This yields a factor of $\gamma_H/\gamma_C \approx 4$ SNR gain over direct ^{13}C detection.

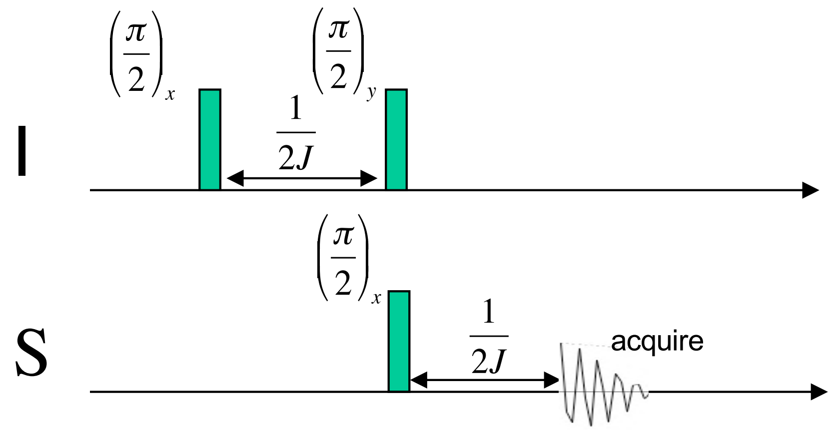
Branch Diagram



- What about the S spin?

Fill in branch diagram

Branch Diagram



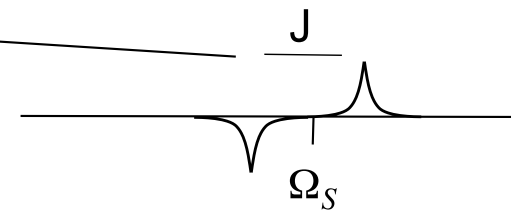
- What about the S spin?

$$\hat{S}_z \xrightarrow{\left(\frac{\pi}{2}\right)_x^S} \hat{S}_y \xrightarrow{-\pi Jt} -2\hat{I}_z\hat{S}_x \xrightarrow{-\pi Jt} \begin{cases} -2\hat{I}_z\hat{S}_x \xrightarrow{\Omega_S t} \begin{cases} -2\hat{I}_z\hat{S}_x \\ 2\hat{I}_z\hat{S}_y \end{cases} \\ -\hat{S}_y \xrightarrow{\Omega_S t} \begin{cases} -\hat{S}_y & \Leftarrow M_y \\ \hat{S}_x & \Leftarrow M_x \end{cases} \end{cases}$$

$$M_y \propto -\cos\left(\Omega_S t\right)\sin\left(\pi Jt\right)$$

$$M_x \propto \sin\left(\Omega_S t\right)\sin\left(\pi Jt\right)$$

$$\omega_0 M_{xy} = \gamma_C B_0 M_{xy} = \frac{N\gamma_C^2\gamma_C\hbar^2 B_0^2}{8kT}$$

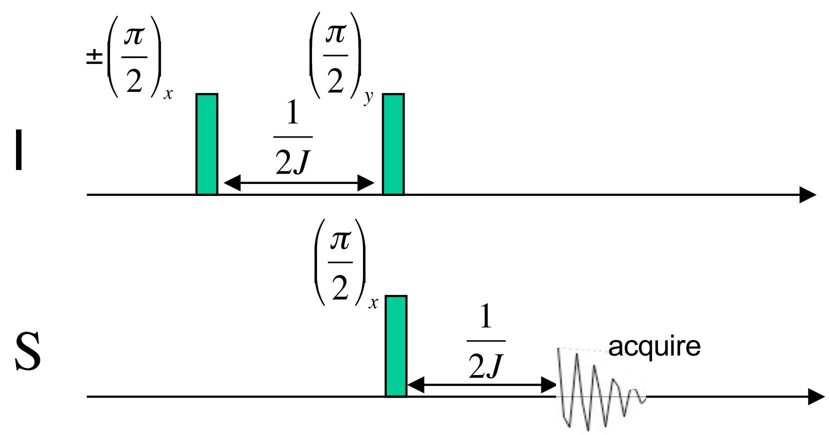


- We usually want to get rid of this "antiphase" doublet as well as any uncoupled ^{13}C spins.

Phase cycling

- Unwanted coherences can be eliminated by making multiple acquisitions while cycling the phase of the Rf pulses.

- For example, Rf1 = $\pm 90_x$

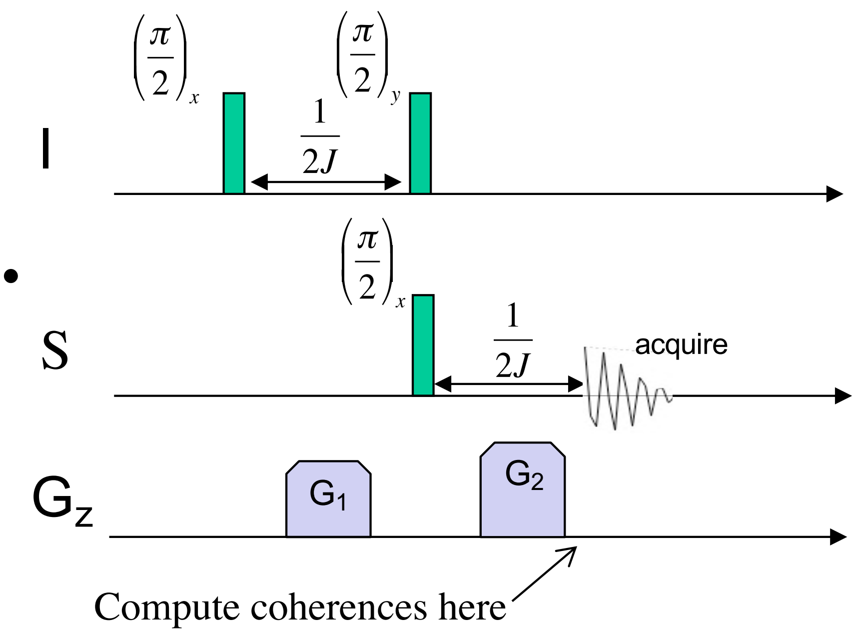


Alternatively, let's add gradients…

- Free precession Hamiltonian

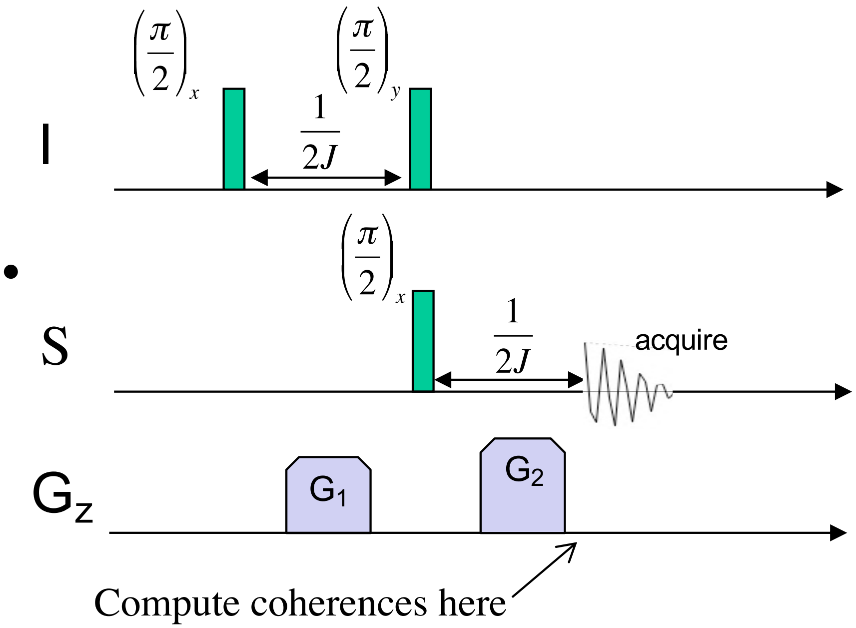
$$\hat{H}_{\text{free}} = -\Omega_I \hat{I}_z - \Omega_S \hat{S}_z + 2\pi J \hat{I}_z \hat{S}_z - \gamma_I G_z z \hat{I}_z - \gamma_S G_z z \hat{S}_z$$

- Find areas G_1 and G_2



Fill in branch diagram

Alternatively, let's add gradients…



- Free precession Hamiltonian

$$\hat{H}_{\text{free}} = -\Omega_I \hat{I}_z - \Omega_S \hat{S}_z + 2\pi J \hat{I}_z \hat{S}_z - \gamma_I G_z z \hat{I}_z - \gamma_S G_z z \hat{S}_z$$

- Find areas G_1 and G_2

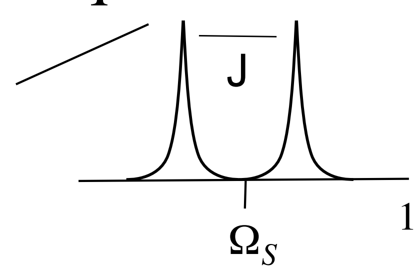
$$\hat{I}_z \xrightarrow{\left(\frac{\pi}{2}\right)_x^I} \hat{I}_y \xrightarrow{-\pi J(1/2J)} -2\hat{I}_x\hat{S}_z \xrightarrow{\gamma_I G_1 z} \begin{cases} -2\hat{I}_x\hat{S}_z \xrightarrow{\left(\frac{\pi}{2}\right)_y^I} -2\hat{I}_z\hat{S}_z \xrightarrow{\left(\frac{\pi}{2}\right)_x^S} -2\hat{I}_z\hat{S}_y \xrightarrow{\gamma_S G_2 z} \begin{cases} -2\hat{I}_z\hat{S}_y \xrightarrow{-\pi J(1/2J)} \hat{S}_x \\ -2\hat{I}_z\hat{S}_x \xrightarrow{-\pi J(1/2J)} -\hat{S}_y \end{cases} \\ 2\hat{I}_y\hat{S}_z \xrightarrow{\left(\frac{\pi}{2}\right)_y^I} 2\hat{I}_y\hat{S}_z \xrightarrow{\left(\frac{\pi}{2}\right)_x^S} \ldots \end{cases}$$

What happened to this coherence?
The unwanted antiphase doublet?

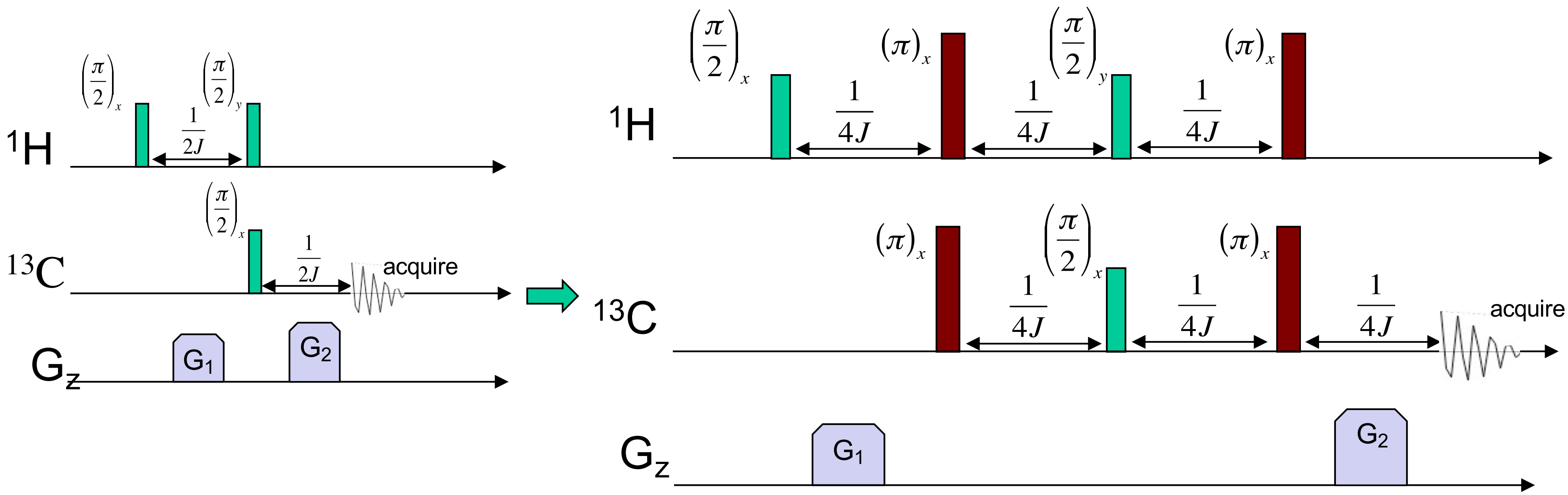
$$M_x \propto \cos(\gamma_C G_2 z)\cos(\gamma_H G_1 z) \Longrightarrow \underbrace{M_{xy}(t)}_{\text{aquired signal}} \propto e^{-i\Omega_S t}\cos(\pi J t)\underbrace{\int_z \cos(\gamma_C G_2 z)\cos(\gamma_H G_1 z)\,dz}_{\text{Integration due to RF coil}}$$

- Letting $G_2 = \frac{\gamma_H}{\gamma_C} G_1 \approx 4G_1$, yields a received signal during acquisition of:

$$M_{xy}(t) \propto e^{-i\Omega_S t}\cos(\pi J t)\int_z \cos^2(\gamma_H G_1 z)\,dz \Rightarrow \frac{N\gamma_C^2\gamma_H \hbar^2 B_0^2}{16kT}$$



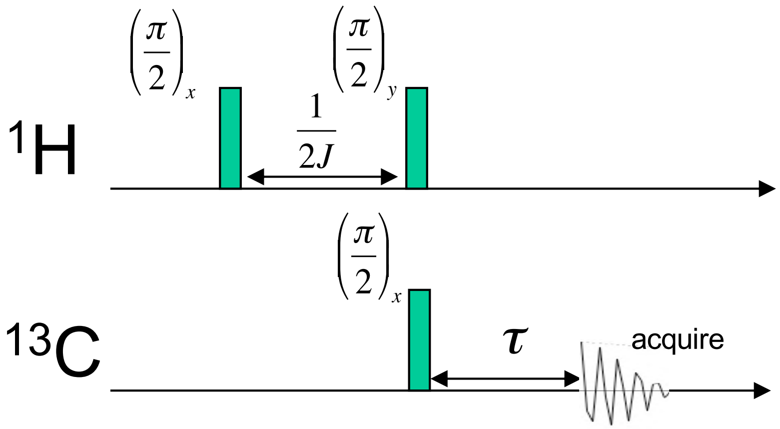
Refocusing chemical shift…

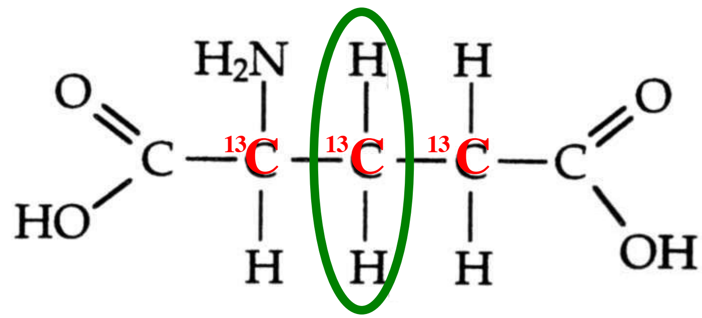


Gradient-enhanced INEPT-R

- 180° Rf pulses refocus chemical shift for both I and S spins.
- J-coupling unaffected.

What about an I_2S spin system…





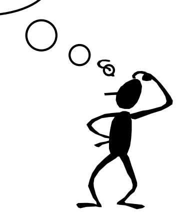
Example: ^{13}C-glutamate

- Letting $I_1 = {}^1H$, $I_2 = {}^1H$, and $S = {}^{13}C$, then the initial density operator is:

$$\hat{\sigma}(0) = \frac{\hbar B_0}{4kT}\left(\gamma_I \hat{I}_{1z} + \gamma_I \hat{I}_{2z} + \gamma_S \hat{S}_z\right)$$

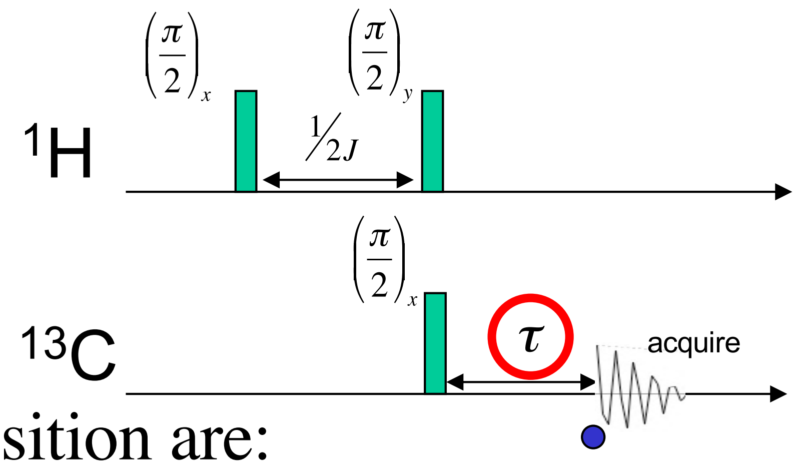
- The Hamiltonian during free precession is:

$$\hat{H}_{\text{free}} = -\Omega_I \hat{I}_{1z} - \Omega_I \hat{I}_{2z} - \Omega_S \hat{S}_z + 2\pi J \hat{I}_{1z}\hat{S}_z + 2\pi J \hat{I}_{2z}\hat{S}_z + 2\pi J_{HH} \hat{I}_{1z}\hat{I}_{2z}\,?$$



I_2S spin system…

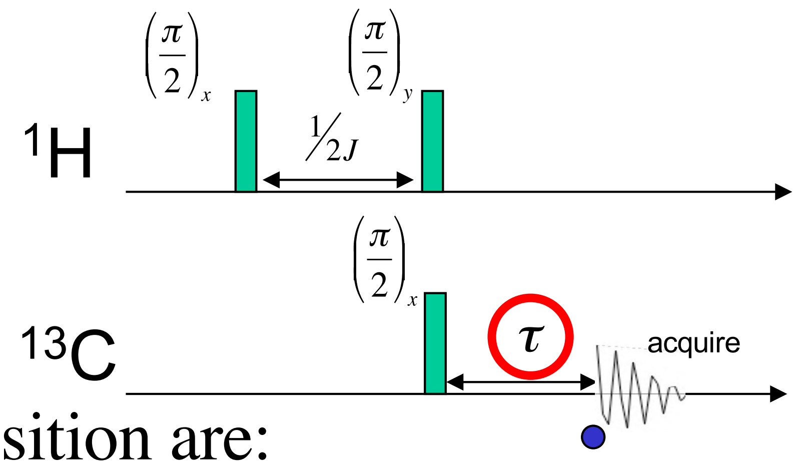
- As before, we are going to ignore chemical shift evolution during the 1/2J and τ time intervals (can always add 180ºs later)



- The coherences just before data acquisition are:

Fill in branch diagram

I_2S spin system…



- As before, we are going to ignore chemical shift evolution during the 1/2J and τ time intervals (can always add 180°s later)
- The coherences just before data acquisition are:

$$\hat{I}_{1z} \xrightarrow{\left(\frac{\pi}{2}\right)_x^{I_1},\,-\pi J_{I_1S}\left(\frac{1}{2J}\right)} -2\hat{I}_{1x}\hat{S}_z \xrightarrow{\left(\frac{\pi}{2}\right)_y^{I_1},\,\left(\frac{\pi}{2}\right)_x^{S}} -2\hat{I}_{1z}\hat{S}_y \xrightarrow{-\pi J_{I_1S}\tau} \begin{cases} -2\hat{I}_{1z}\hat{S}_y \xrightarrow{-\pi J_{I_2S}\tau} \begin{cases} -2\hat{I}_{1z}\hat{S}_y \\ 4\hat{I}_{1z}\hat{I}_{2z}\hat{S}_x \end{cases} \\ \hat{S}_x \xrightarrow{-\pi J_{I_2S}\tau} \begin{cases} \hat{S}_x \\ 2\hat{I}_{2z}\hat{S}_y \end{cases} \end{cases}$$

Normalization factor for 3-spin operators.

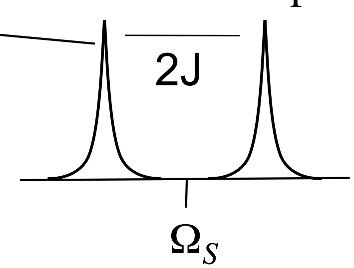
$$M_x \propto \sin(\pi J\tau)\cos(\pi J\tau)$$

Similarly $\hat{I}_{2z} \longrightarrow \ldots \longrightarrow \hat{S}_x \sin(\pi J\tau)\cos(\pi J\tau)$

Total: $M_x \propto 2\sin(\pi J\tau)\cos(\pi J\tau)$

Why is this not a 1-2-1 triplet?

$$\frac{N\gamma_C^2\gamma_H\hbar^2B_0^2}{8kT}$$



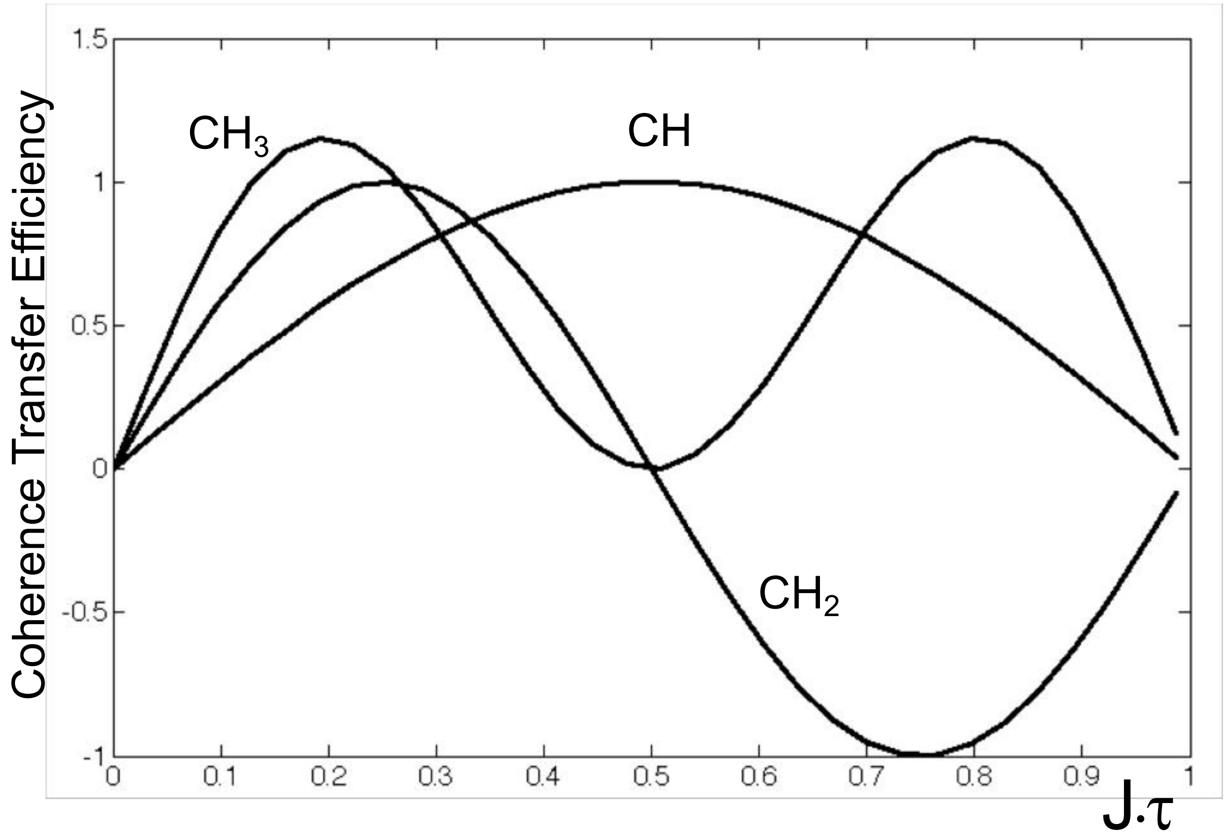
INEPT-R

- In general, the value of τ in an INEPT-R sequence needs to be optimized for different spin systems.

CH : $\sin(\pi J\tau)$

CH_2: $2\sin(\pi J\tau)\cos(\pi J\tau)$

CH_3: $3\sin(\pi J\tau)\cos^2(\pi J\tau)$



Summary

- Rotations in 16-dimensional space are really not that hard.
- In fact, for the CH_2 spin system, we were actually computing rotations in a 64-dimensional vector space. Try a CH_3 system for a 256-dimensional adventure!
- POF is a very convenient way of tracking spin coherences. It is particularly useful for weakly coupled spin systems.
- Next lecture: Spectral Editing