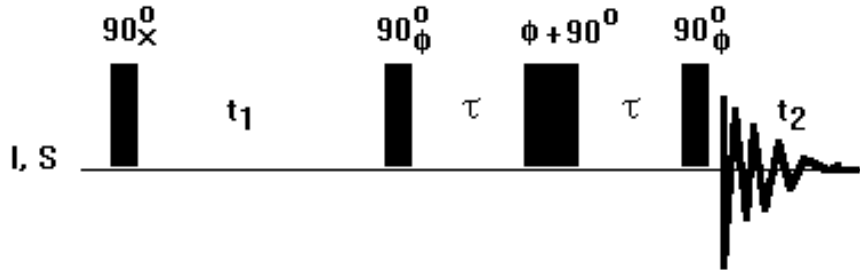


RELAY = RELAYed correlation spectroscopy

The pulse sequence:

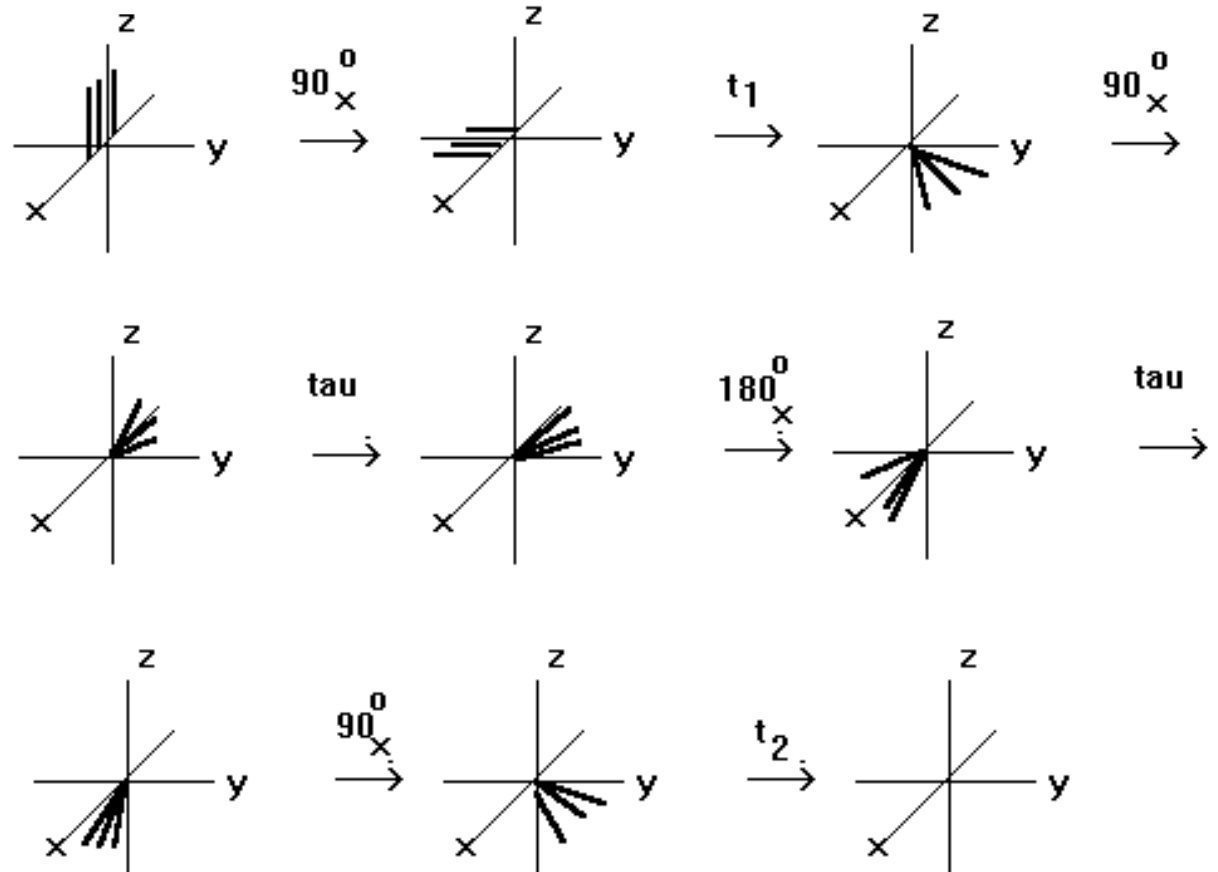
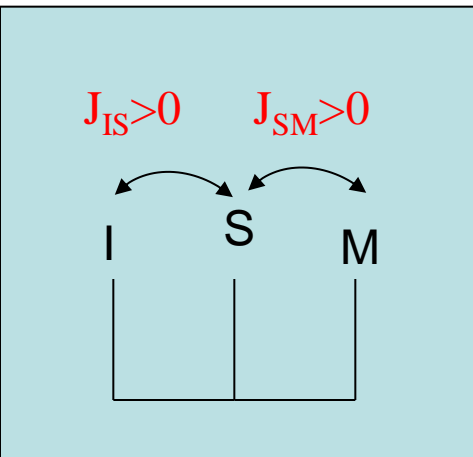
$$90_x^0 - t_1 - [90_\phi^0 - \tau - (90_{\phi+90}^0) - \tau - 90_\phi^0] - t_2$$



It can be phase-cycled but not essential.
If not phase-cycled then:

$$90_x^0 - t_1 - 90_x^0 - \tau - 180_x^0 - \tau - 90_x^0 - t_2$$

Consider: $\Omega_I, \Omega_S, \Omega_M$
and $J_{IS} > 0, J_{SM} > 0$
but $J_{IM} = 0$



$$\sigma[\text{eq.}]$$

$$\hat{H} = \pi/2 (\hat{I}_x + M_x + \check{S}_x)$$

$$\mathbf{I}_z, \mathbf{M}_z \text{ and } \mathbf{S}_z$$

$$\downarrow 90^\circ_x$$

$$\sigma[0]$$

$$\hat{H} = \hat{I}_z(\Omega_I t_1) + M_z(\Omega_M t_1) + \check{S}_z(\Omega_S t_1)$$

$$-\mathbf{I}_y, -\mathbf{M}_y \text{ and } -\mathbf{S}_y$$

$$\downarrow t_1$$

$$-\mathbf{I}_y \cos(\Omega_I t_1) + \mathbf{I}_x \sin(\Omega_I t_1)$$

$$-\mathbf{M}_y \cos(\Omega_M t_1) + \mathbf{M}_x \sin(\Omega_M t_1)$$

$$-\mathbf{S}_y \cos(\Omega_S t_1) + \mathbf{S}_x \sin(\Omega_S t_1)$$

$$\hat{H} = 2\hat{I}_z \check{S}_z (J_{IS} \pi t_1)$$

$$\downarrow$$

$$-\mathbf{I}_y \cos(\Omega_I t_1) \cos(\pi J_{IS} t_1)$$

$$+ 2\mathbf{I}_x \mathbf{S}_z \cos(\Omega_I t_1) \sin(\pi J_{IS} t_1)$$

$$+ \mathbf{I}_x \sin(\Omega_I t_1) \cos(\pi J_{IS} t_1)$$

$$+ 2\mathbf{I}_y \mathbf{S}_z \sin(\Omega_I t_1) \sin(\pi J_{IS} t_1)$$

$$-\mathbf{S}_y \cos(\Omega_S t_1) \cos(\pi J_{IS} t_1)$$

$$+ 2\mathbf{S}_x \mathbf{I}_z \cos(\Omega_S t_1) \sin(\pi J_{IS} t_1)$$

$$+ \mathbf{S}_x \sin(\Omega_S t_1) \cos(\pi J_{IS} t_1)$$

$$+ 2\mathbf{S}_y \mathbf{I}_z \sin(\Omega_S t_1) \sin(\pi J_{IS} t_1)$$

$$-\mathbf{M}_y \cos(\Omega_M t_1)$$

$$+\mathbf{M}_x \sin(\Omega_M t_1)$$

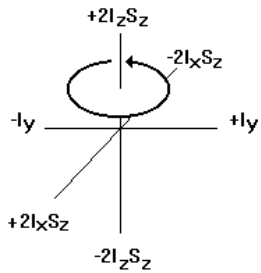
$$\begin{aligned}
& -\mathbf{I}_y \cos(\Omega_I t_1) \cos(\pi \mathbf{J}_{IS} t_1) + 2\mathbf{I}_x \mathbf{S}_z \cos(\Omega_I t_1) \sin(\pi \mathbf{J}_{IS} t_1) \\
& + \mathbf{I}_x \sin(\Omega_I t_1) \cos(\pi \mathbf{J}_{IS} t_1) + 2\mathbf{I}_y \mathbf{S}_z \sin(\Omega_I t_1) \sin(\pi \mathbf{J}_{IS} t_1) \\
& - \mathbf{S}_y \cos(\Omega_S t_1) \cos(\pi \mathbf{J}_{IS} t_1) + 2\mathbf{S}_x \mathbf{I}_z \cos(\Omega_S t_1) \sin(\pi \mathbf{J}_{IS} t_1) \\
& + \mathbf{S}_x \sin(\Omega_S t_1) \cos(\pi \mathbf{J}_{IS} t_1) + 2\mathbf{S}_y \mathbf{I}_z \sin(\Omega_S t_1) \sin(\pi \mathbf{J}_{IS} t_1) \\
& - \mathbf{M}_y \cos(\Omega_M t_1) + \mathbf{M}_x \sin(\Omega_M t_1)
\end{aligned}$$

$$\hat{\mathbf{H}} = 2\mathbf{S}_z \mathbf{M}_z (\mathbf{J}_{SM} \pi t_1)$$

↓

$$\begin{aligned}
& -\mathbf{I}_y \cos(\Omega_I t_1) \cos(\pi \mathbf{J}_{IS} t_1) + 2\mathbf{I}_x \mathbf{S}_z \cos(\Omega_I t_1) \sin(\pi \mathbf{J}_{IS} t_1) \\
& + \mathbf{I}_x \sin(\Omega_I t_1) \cos(\pi \mathbf{J}_{IS} t_1) + 2\mathbf{I}_y \mathbf{S}_z \sin(\Omega_I t_1) \sin(\pi \mathbf{J}_{IS} t_1)
\end{aligned}$$

and



$$\begin{aligned}
& -\mathbf{S}_y \cos(\Omega_S t_1) \cos(\pi \mathbf{J}_{IS} t_1) \cos(\pi \mathbf{J}_{SM} t_1) \\
& \quad + 2\mathbf{S}_x \mathbf{M}_z \cos(\Omega_S t_1) \cos(\pi \mathbf{J}_{IS} t_1) \sin(\pi \mathbf{J}_{SM} t_1) \\
& + 2\mathbf{S}_x \mathbf{I}_z \cos(\Omega_S t_1) \sin(\pi \mathbf{J}_{IS} t_1) \cos(\pi \mathbf{J}_{SM} t_1) \\
& \quad + 4\mathbf{S}_y \mathbf{M}_z \mathbf{I}_z \cos(\Omega_S t_1) \sin(\pi \mathbf{J}_{IS} t_1) \sin(\pi \mathbf{J}_{SM} t_1) \\
& + \mathbf{S}_x \sin(\Omega_S t_1) \cos(\pi \mathbf{J}_{IS} t_1) \cos(\pi \mathbf{J}_{SM} t_1) \\
& \quad + 2\mathbf{S}_y \mathbf{M}_z \sin(\Omega_S t_1) \cos(\pi \mathbf{J}_{IS} t_1) \sin(\pi \mathbf{J}_{SM} t_1) \\
& + 2\mathbf{S}_y \mathbf{I}_z \sin(\Omega_S t_1) \sin(\pi \mathbf{J}_{IS} t_1) \cos(\pi \mathbf{J}_{SM} t_1) \\
& \quad + 4\mathbf{S}_x \mathbf{M}_z \mathbf{I}_z \sin(\Omega_S t_1) \sin(\pi \mathbf{J}_{IS} t_1) \sin(\pi \mathbf{J}_{SM} t_1)
\end{aligned}$$

and

$$\begin{aligned}
& -\mathbf{M}_y \cos(\Omega_M t_1) \cos(\pi \mathbf{J}_{SM} t_1) \\
& \quad + 2\mathbf{S}_z \mathbf{M}_x \cos(\Omega_M t_1) \sin(\pi \mathbf{J}_{SM} t_1) \\
& + \mathbf{M}_x \sin(\Omega_M t_1) \cos(\pi \mathbf{J}_{SM} t_1) \\
& \quad + 2\mathbf{S}_z \mathbf{M}_y \sin(\Omega_M t_1) \sin(\pi \mathbf{J}_{SM} t_1)
\end{aligned}$$

$$\begin{aligned}
& -\mathbf{I}_y \cos(\Omega_I t_1) \cos(\pi J_{IS} t_1) + 2\mathbf{I}_x \mathbf{S}_z \cos(\Omega_I t_1) \sin(\pi J_{IS} t_1) \\
& + \mathbf{I}_x \sin(\Omega_I t_1) \cos(\pi J_{IS} t_1) + 2\mathbf{I}_y \mathbf{S}_z \sin(\Omega_I t_1) \sin(\pi J_{IS} t_1) \\
& - \mathbf{S}_y \cos(\Omega_S t_1) \cos(\pi J_{IS} t_1) \cos(\pi J_{SM} t_1) + 2\mathbf{S}_x \mathbf{M}_z \cos(\Omega_S t_1) \cos(\pi J_{IS} t_1) \sin(\pi J_{SM} t_1) \\
& + 2\mathbf{S}_x \mathbf{I}_z \cos(\Omega_S t_1) \sin(\pi J_{IS} t_1) \cos(\pi J_{SM} t_1) + 4\mathbf{S}_y \mathbf{M}_z \mathbf{I}_z \cos(\Omega_S t_1) \sin(\pi J_{IS} t_1) \sin(\pi J_{SM} t_1) \\
& + \mathbf{S}_x \sin(\Omega_S t_1) \cos(\pi J_{IS} t_1) \cos(\pi J_{SM} t_1) + 2\mathbf{S}_y \mathbf{M}_z \sin(\Omega_S t_1) \cos(\pi J_{IS} t_1) \sin(\pi J_{SM} t_1) \\
& + 2\mathbf{S}_y \mathbf{I}_z \sin(\Omega_S t_1) \sin(\pi J_{IS} t_1) \cos(\pi J_{SM} t_1) + 4\mathbf{S}_x \mathbf{M}_z \mathbf{I}_z \sin(\Omega_S t_1) \sin(\pi J_{IS} t_1) \sin(\pi J_{SM} t_1) \\
& - \mathbf{M}_y \cos(\Omega_M t_1) \cos(\pi J_{SM} t_1) + 2\mathbf{S}_z \mathbf{M}_x \cos(\Omega_M t_1) \sin(\pi J_{SM} t_1) \\
& + \mathbf{M}_x \sin(\Omega_M t_1) \cos(\pi J_{SM} t_1) + 2\mathbf{S}_z \mathbf{M}_y \sin(\Omega_M t_1) \sin(\pi J_{SM} t_1)
\end{aligned}$$

$$\hat{H} = \pi/2 (\hat{I}_x + \mathbf{M}_x + \check{S}_x)$$

$$\downarrow 90^\circ_x \text{ memo.} = \cos(\pi/2) = 0, \sin(\pi/2) = 1$$

$$\begin{aligned}
& -\mathbf{I}_z \cos(\Omega_I t_1) \cos(\pi J_{IS} t_1) \\
& \quad - 2\mathbf{I}_x \mathbf{S}_y \cos(\Omega_I t_1) \sin(\pi J_{IS} t_1) \\
& \quad + \mathbf{I}_x \sin(\Omega_I t_1) \cos(\pi J_{IS} t_1) \\
& \quad \quad - 2\mathbf{I}_z \mathbf{S}_y \sin(\Omega_I t_1) \sin(\pi J_{IS} t_1) \\
& - \mathbf{S}_z \cos(\Omega_S t_1) \cos(\pi J_{IS} t_1) \cos(\pi J_{SM} t_1) \\
& \quad - 2\mathbf{S}_x \mathbf{M}_y \cos(\Omega_S t_1) \cos(\pi J_{IS} t_1) \sin(\pi J_{SM} t_1) \\
& \quad - 2\mathbf{S}_x \mathbf{I}_y \cos(\Omega_S t_1) \sin(\pi J_{IS} t_1) \cos(\pi J_{SM} t_1) \\
& \quad \quad + 4\mathbf{S}_z \mathbf{M}_z \mathbf{I}_z \cos(\Omega_S t_1) \sin(\pi J_{IS} t_1) \sin(\pi J_{SM} t_1) \\
& + \mathbf{S}_x \sin(\Omega_S t_1) \cos(\pi J_{IS} t_1) \cos(\pi J_{SM} t_1) \\
& \quad - 2\mathbf{S}_z \mathbf{M}_y \sin(\Omega_S t_1) \cos(\pi J_{IS} t_1) \sin(\pi J_{SM} t_1) \\
& \quad - 2\mathbf{S}_z \mathbf{I}_y \sin(\Omega_S t_1) \sin(\pi J_{IS} t_1) \cos(\pi J_{SM} t_1) \\
& \quad \quad + 4\mathbf{S}_x \mathbf{M}_y \mathbf{I}_y \sin(\Omega_S t_1) \sin(\pi J_{IS} t_1) \sin(\pi J_{SM} t_1) \\
& - \mathbf{M}_z \cos(\Omega_M t_1) \cos(\pi J_{SM} t_1) \\
& \quad - 2\mathbf{S}_y \mathbf{M}_x \cos(\Omega_M t_1) \sin(\pi J_{SM} t_1) \\
& \quad + \mathbf{M}_x \sin(\Omega_M t_1) \cos(\pi J_{SM} t_1) \\
& \quad \quad - 2\mathbf{S}_y \mathbf{M}_z \sin(\Omega_M t_1) \sin(\pi J_{SM} t_1)
\end{aligned}$$

$$\sigma[t_1, 0]$$

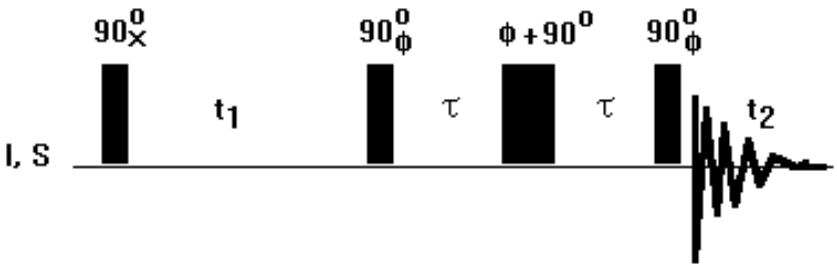
Among these 16 terms only the following 7 describe single quantum coherences

Among these 16 terms only the following 7 describe single quantum coherences

<i>in-phase I</i>	$+I_x \sin(\Omega_I t_1) \cos(\pi J_{IS} t_1)$	↙
<i>anti-phase S</i>	$-2I_z S_y \sin(\Omega_I t_1) \sin(\pi J_{IS} t_1)$	↙
<i>in-phase S</i>	$+S_x \sin(\Omega_S t_1) \cos(\pi J_{IS} t_1) \cos(\pi J_{SM} t_1)$	
<i>anti-phase M</i>	$-2S_z M_y \sin(\Omega_S t_1) \cos(\pi J_{IS} t_1) \sin(\pi J_{SM} t_1)$	
<i>anti-phase I</i>	$-2S_z I_y \sin(\Omega_S t_1) \sin(\pi J_{IS} t_1) \cos(\pi J_{SM} t_1)$	
<i>in-phase M</i>	$+M_x \sin(\Omega_M t_1) \cos(\pi J_{SM} t_1)$	↙
<i>anti-phase S</i>	$-2S_y M_z \sin(\Omega_M t_1) \sin(\pi J_{SM} t_1)$	↙

As we are interested in transfer from **I to M via S** and thus we keep only the **in-phase and the anti-phase I and M** coherences:

$$\begin{aligned}
 &+I_x \sin(\Omega_I t_1) \cos(\pi J_{IS} t_1) \\
 &\quad -2I_z S_y \sin(\Omega_I t_1) \sin(\pi J_{IS} t_1) \\
 &+M_x \sin(\Omega_M t_1) \cos(\pi J_{SM} t_1) \\
 &\quad -2S_y M_z \sin(\Omega_M t_1) \sin(\pi J_{SM} t_1)
 \end{aligned}$$



During the $[90^\circ_\phi - \tau - (90^\circ + \phi) - \tau - 90^\circ_\phi]$, when an echo is inserted, **only coupling** is effective while chemical shift is refocused.

if $\phi = x$, and the effective pulse is $[90^\circ_x - \tau - 180^\circ_x - \tau - 90^\circ_x]$ then only the following two terms evolve:

- A:** $-2I_z S_y \sin(\Omega_I t_1) \sin(\pi J_{IS} t_1)$
- B:** $-2S_y M_z \sin(\Omega_M t_1) \sin(\pi J_{SM} t_1)$.

memo: the "echo time" is 2τ

A: the first term evolves during 2τ such as:

$$\hat{H} = 2\hat{I}_z\check{S}_z(J_{IS}\pi 2\tau) \quad \begin{array}{l} -2\mathbf{I}_z\mathbf{S}_y \sin(\Omega_I t_1) \sin(\pi J_{IS} t_1) \\ \downarrow \end{array}$$

$$\hat{H} = 2\check{S}_z\mathbf{M}_z(J_{SM}\pi 2\tau) \quad \begin{array}{l} -2\mathbf{I}_z\mathbf{S}_y \sin(\Omega_I t_1) \sin(\pi J_{IS} t_1) \cos(\pi J_{IS} 2\tau) \\ +\mathbf{S}_x \sin(\Omega_I t_1) \sin(\pi J_{IS} t_1) \sin(\pi J_{IS} 2\tau) \\ \downarrow \end{array}$$

$$\begin{array}{l} -2\mathbf{I}_z\mathbf{S}_y \sin(\Omega_I t_1) \sin(\pi J_{IS} t_1) \cos(\pi J_{IS} 2\tau) \cos(\pi J_{SM} 2\tau) \\ +4\mathbf{I}_z\mathbf{S}_x\mathbf{M}_z \sin(\Omega_I t_1) \sin(\pi J_{IS} t_1) \cos(\pi J_{IS} 2\tau) \sin(\pi J_{SM} 2\tau) \\ +\mathbf{S}_x \sin(\Omega_I t_1) \sin(\pi J_{IS} t_1) \sin(\pi J_{IS} 2\tau) \cos(\pi J_{SM} 2\tau) \\ -2\mathbf{M}_y\mathbf{S}_z \sin(\Omega_I t_1) \sin(\pi J_{IS} t_1) \sin(\pi J_{IS} 2\tau) \sin(\pi J_{SM} 2\tau) \quad \ominus \end{array}$$

$-2\mathbf{M}_y\mathbf{S}_z$ is an anti-phased magnetization on M; a term originating from **I** and *via* S is now transfer. to **M**.

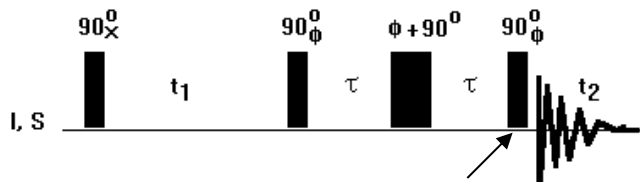
B: the second term under the same condition evolves such as :

$$\hat{H} = 2\check{S}_z\mathbf{M}_z(J_{SM}\pi 2\tau) \quad \begin{array}{l} -2\mathbf{M}_z\mathbf{S}_y \sin(\Omega_M t_1) \sin(\pi J_{SM} t_1) \\ \downarrow \end{array}$$

$$\hat{H} = 2\hat{I}_z\check{S}_z(J_{IS}\pi 2\tau) \quad \begin{array}{l} -2\mathbf{M}_z\mathbf{S}_y \sin(\Omega_M t_1) \sin(\pi J_{SM} t_1) \cos(\pi J_{SM} 2\tau) \\ +\mathbf{S}_x \sin(\Omega_M t_1) \sin(\pi J_{SM} t_1) \sin(\pi J_{SM} 2\tau) \\ \downarrow \end{array}$$

$$\begin{array}{l} -2\mathbf{M}_z\mathbf{S}_y \sin(\Omega_M t_1) \sin(\pi J_{SM} t_1) \cos(\pi J_{SM} 2\tau) \cos(\pi J_{IS} 2\tau) \\ +4\mathbf{M}_z\mathbf{S}_x\mathbf{I}_z \sin(\Omega_M t_1) \sin(\pi J_{SM} t_1) \cos(\pi J_{SM} 2\tau) \sin(\pi J_{IS} 2\tau) \\ +\mathbf{S}_x \sin(\Omega_M t_1) \sin(\pi J_{SM} t_1) \sin(\pi J_{SM} 2\tau) \cos(\pi J_{IS} 2\tau) \\ -2\mathbf{I}_y\mathbf{S}_z \sin(\Omega_M t_1) \sin(\pi J_{SM} t_1) \sin(\pi J_{SM} 2\tau) \sin(\pi J_{IS} 2\tau) \quad \ominus \end{array}$$

$-2\mathbf{I}_y\mathbf{S}_z$ is an anti-phased magnetization on I; a term originating from **M** and *via* S is now transfer. to **I**.



Before the last 90°_x (the reading pulse) beside the two unchanged terms:

$$+I_x \sin(\Omega_I t_1) \cos(\pi J_{IS} t_1) \\ +M_x \sin(\Omega_M t_1) \cos(\pi J_{SM} t_1),$$

The evolution of these two is important:

$$-2I_y S_z \sin(\Omega_M t_1) \sin(\pi J_{SM} t_1) \sin(\pi J_{SM} 2\tau) \sin(\pi J_{IS} 2\tau) \text{ and} \\ -2M_y S_z \sin(\Omega_I t_1) \sin(\pi J_{IS} t_1) \sin(\pi J_{IS} 2\tau) \sin(\pi J_{SM} 2\tau).$$

$$\hat{H} = \pi/2 (\hat{I}_x + M_x + \check{S}_x)$$

$$\downarrow 90^\circ_x \text{ memo.} = \cos(\pi/2) = 0, \sin(\pi/2) = 1$$

During the reading pulse:

$$+I_x \sin(\Omega_I t_1) \cos(\pi J_{IS} t_1) \\ +M_x \sin(\Omega_M t_1) \cos(\pi J_{SM} t_1) \\ -2S_z I_y \sin(\Omega_M t_1) \sin(\pi J_{SM} t_1) \sin(\pi J_{SM} 2\tau) \sin(\pi J_{IS} 2\tau) \\ -2S_z M_y \sin(\Omega_I t_1) \sin(\pi J_{IS} t_1) \sin(\pi J_{IS} 2\tau) \sin(\pi J_{SM} 2\tau)$$

During ACQ.

$$\text{Hem} = \hat{I}_z(\Omega_I t_2)$$

$$\hat{H} = 2\hat{I}_z \check{S}_z (J_{IS} \pi t_2)$$

$$+I_x \sin(\Omega_I t_1) \cos(\pi J_{IS} t_1)$$



$$+I_x \sin(\Omega_I t_1) \cos(\pi J_{IS} t_1) \cos(\Omega_I t_2) \quad +I_y \sin(\Omega_I t_1) \cos(\pi J_{IS} t_1) \sin(\Omega_I t_2)$$



$$+I_x \sin(\Omega_I t_1) \cos(\pi J_{IS} t_1) \cos(\Omega_I t_2) \cos(\pi J_{IS} t_2) \quad \odot \\ +2I_y S_z \sin(\Omega_I t_1) \cos(\pi J_{IS} t_1) \cos(\Omega_I t_2) \sin(\pi J_{IS} t_2) \\ +I_y \sin(\Omega_I t_1) \cos(\pi J_{IS} t_1) \sin(\Omega_I t_2) \cos(\pi J_{IS} t_2) \\ -2I_x S_z \sin(\Omega_I t_1) \cos(\pi J_{IS} t_1) \sin(\Omega_I t_2) \sin(\pi J_{IS} t_2)$$

During ACQ.

$$\text{Hem} = M_z(\Omega_M t_2)$$

$$\hat{H} = 2\check{S}_z M_z(J_{SM}\pi t_2)$$

$$+M_x \sin(\Omega_M t_1) \cos(\pi J_{SM} t_1) \cos(\Omega_M t_2) \quad +M_y \sin(\Omega_M t_1) \cos(\pi J_{SM} t_1) \sin(\Omega_M t_2)$$

$$+M_x \sin(\Omega_M t_1) \cos(\pi J_{SM} t_1) \cos(\Omega_M t_2) \cos(\pi J_{SM} t_2) \quad \text{☺}$$

$$+2M_y S_z \sin(\Omega_M t_1) \cos(\pi J_{SM} t_1) \cos(\Omega_M t_2) \sin(\pi J_{SM} t_2)$$

$$+M_y \sin(\Omega_M t_1) \cos(\pi J_{SM} t_1) \sin(\Omega_M t_2) \cos(\pi J_{SM} t_2)$$

$$-2M_x S_z \sin(\Omega_M t_1) \cos(\pi J_{SM} t_1) \sin(\Omega_M t_2) \sin(\pi J_{SM} t_2)$$

During ACQ.

$$\text{Hem} = I_z(\Omega_I t_2)$$

$$-2S_z I_y \sin(\Omega_M t_1) \sin(\pi J_{SM} t_1) \sin(\pi J_{SM} 2\tau) \sin(\pi J_{IS} 2\tau)$$

$$\hat{H} = 2\hat{I}_z \check{S}_z(J_{IS}\pi t_2)$$

$$-2S_z I_y \sin(\Omega_M t_1) \sin(\pi J_{SM} t_1) \sin(\pi J_{SM} 2\tau) \sin(\pi J_{IS} 2\tau) \cos(\Omega_I t_2)$$

$$+2S_z I_x \sin(\Omega_M t_1) \sin(\pi J_{SM} t_1) \sin(\pi J_{SM} 2\tau) \sin(\pi J_{IS} 2\tau) \sin(\Omega_I t_2)$$

$$-2S_z I_y \sin(\Omega_M t_1) \sin(\pi J_{SM} t_1) \sin(\pi J_{SM} 2\tau) \sin(\pi J_{IS} 2\tau) \cos(\Omega_I t_2) \cos(\pi J_{IS} t_2)$$

$$+I_x \sin(\Omega_M t_1) \sin(\pi J_{SM} t_1) \sin(\pi J_{SM} 2\tau) \sin(\pi J_{IS} 2\tau) \cos(\Omega_I t_2) \sin(\pi J_{IS} t_2) \quad \text{☺}$$

$$+2S_z I_x \sin(\Omega_M t_1) \sin(\pi J_{SM} t_1) \sin(\pi J_{SM} 2\tau) \sin(\pi J_{IS} 2\tau) \sin(\Omega_I t_2) \cos(\pi J_{IS} t_2)$$

$$+I_y \sin(\Omega_M t_1) \sin(\pi J_{SM} t_1) \sin(\pi J_{SM} 2\tau) \sin(\pi J_{IS} 2\tau) \sin(\Omega_I t_2) \sin(\pi J_{IS} t_2)$$

During ACQ.

$$\text{Hem} = M_z(\Omega_M t_2)$$

$$-2S_z M_y \sin(\Omega_I t_1) \sin(\pi J_{IS} t_1) \sin(\pi J_{IS} 2\tau) \sin(\pi J_{SM} 2\tau)$$



$$\begin{aligned} & -2S_z M_y \sin(\Omega_I t_1) \sin(\pi J_{IS} t_1) \sin(\pi J_{IS} 2\tau) \sin(\pi J_{SM} 2\tau) \cos(\Omega_M t_2) \\ & + 2S_z M_x \sin(\Omega_I t_1) \sin(\pi J_{IS} t_1) \sin(\pi J_{IS} 2\tau) \sin(\pi J_{SM} 2\tau) \sin(\Omega_M t_2) \end{aligned}$$

$$\hat{H} = 2M_z \check{S}_z(J_{SM} \pi t_2)$$



$$\begin{aligned} & -2S_z M_y \sin(\Omega_I t_1) \sin(\pi J_{IS} t_1) \sin(\pi J_{IS} 2\tau) \sin(\pi J_{SM} 2\tau) \cos(\Omega_M t_2) \cos(\pi J_{SM} t_2) \\ & \quad + M_x \sin(\Omega_I t_1) \sin(\pi J_{IS} t_1) \sin(\pi J_{IS} 2\tau) \sin(\pi J_{SM} 2\tau) \cos(\Omega_M t_2) \sin(\pi J_{SM} t_2) \\ & + 2S_z M_x \sin(\Omega_I t_1) \sin(\pi J_{IS} t_1) \sin(\pi J_{IS} 2\tau) \sin(\pi J_{SM} 2\tau) \sin(\Omega_M t_2) \cos(\pi J_{SM} t_2) \\ & \quad + M_y \sin(\Omega_I t_1) \sin(\pi J_{IS} t_1) \sin(\pi J_{IS} 2\tau) \sin(\pi J_{SM} 2\tau) \sin(\Omega_M t_2) \sin(\pi J_{SM} t_2) \end{aligned}$$



memo 1: receiver on x

therefore only the four x term remain:

$$\begin{aligned} & +I_x \sin(\Omega_I t_1) \cos(\pi J_{IS} t_1) \cos(\Omega_I t_2) \cos(\pi J_{IS} t_2) \\ & +M_x \sin(\Omega_M t_1) \cos(\pi J_{SM} t_1) \cos(\Omega_M t_2) \cos(\pi J_{SM} t_2) \\ & +I_x \sin(\Omega_M t_1) \sin(\pi J_{SM} t_1) \sin(\pi J_{SM} 2\tau) \sin(\pi J_{IS} 2\tau) \cos(\Omega_I t_2) \sin(\pi J_{IS} t_2) \\ & +M_x \sin(\Omega_I t_1) \sin(\pi J_{IS} t_1) \sin(\pi J_{IS} 2\tau) \sin(\pi J_{SM} 2\tau) \cos(\Omega_M t_2) \sin(\pi J_{SM} t_2) \end{aligned}$$

The term $\alpha = \sin(\pi J_{SM} 2\tau) \sin(\pi J_{IS} 2\tau)$ is the transfer function between I and M. Now:

$$\begin{aligned} & +I_x \sin(\Omega_I t_1) \cos(\pi J_{IS} t_1) \cos(\Omega_I t_2) \cos(\pi J_{IS} t_2) \\ & +M_x \sin(\Omega_M t_1) \cos(\pi J_{SM} t_1) \cos(\Omega_M t_2) \cos(\pi J_{SM} t_2) \\ & +I_x \alpha \sin(\Omega_M t_1) \sin(\pi J_{SM} t_1) \cos(\Omega_I t_2) \sin(\pi J_{IS} t_2) \\ & +M_x \alpha \sin(\Omega_I t_1) \sin(\pi J_{IS} t_1) \cos(\Omega_M t_2) \sin(\pi J_{SM} t_2) \end{aligned}$$

memo 2:

$$\sin(A)\cos(B) = 1/2[\sin(A+B)+\sin(A-B)]$$

$$\cos(A)\sin(B) = 1/2[\sin(A+B)-\sin(A-B)]$$

$$\sin(A)\sin(B) = 1/2[\cos(A-B)-\cos(A+B)]$$

$$\cos(A)\cos(B) = 1/2[\cos(A+B)+\cos(A-B)]$$

therefore:

$$\begin{aligned} &+1/4\mathbf{I}_x \quad [+ \sin\{(\Omega_I + \pi\mathbf{J}_{IS})t_1\} + \sin\{(\Omega_I - \pi\mathbf{J}_{IS})t_1\}] [+ \cos\{(\Omega_I + \pi\mathbf{J}_{IS})t_2\} + \cos\{(\Omega_I - \pi\mathbf{J}_{IS})t_2\}] \\ &+1/4\mathbf{M}_x \quad [+ \sin\{(\Omega_M + \pi\mathbf{J}_{SM})t_1\} + \sin\{(\Omega_M - \pi\mathbf{J}_{SM})t_1\}] [+ \cos\{(\Omega_M + \pi\mathbf{J}_{SM})t_2\} + \cos\{(\Omega_M - \pi\mathbf{J}_{SM})t_2\}] \\ &+1/4\mathbf{I}_x \alpha \quad [+ \cos\{(\Omega_M - \pi\mathbf{J}_{SM})t_1\} - \cos\{(\Omega_M + \pi\mathbf{J}_{SM})t_1\}] [+ \sin\{(\Omega_I + \pi\mathbf{J}_{IS})t_2\} - \sin\{(\Omega_I - \pi\mathbf{J}_{IS})t_2\}] \\ &+1/4\mathbf{M}_x \alpha \quad [+ \cos\{(\Omega_I - \pi\mathbf{J}_{IS})t_1\} - \cos\{(\Omega_I + \pi\mathbf{J}_{IS})t_1\}] [+ \sin\{(\Omega_M + \pi\mathbf{J}_{SM})t_2\} - \sin\{(\Omega_M - \pi\mathbf{J}_{SM})t_2\}] \end{aligned}$$

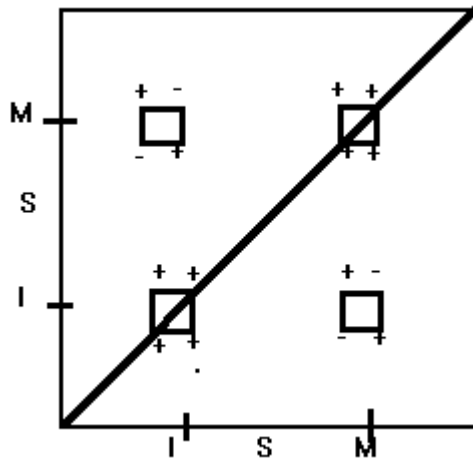
the following terms can be found

$$\mathbf{I}_x \quad [+ \dots + \dots + \dots + \dots] \text{ at } \Omega_I, \Omega_I$$

$$\mathbf{M}_x \quad [+ \dots + \dots + \dots + \dots] \text{ at } \Omega_M, \Omega_M$$

$$\mathbf{I}_x \quad [+ \dots - \dots + \dots - \dots] \text{ at } \Omega_M, \Omega_I$$

$$\mathbf{M}_x \quad [+ \dots - \dots + \dots - \dots] \text{ at } \Omega_I, \Omega_M$$



memo: line shapes

positive absorptive (+a),

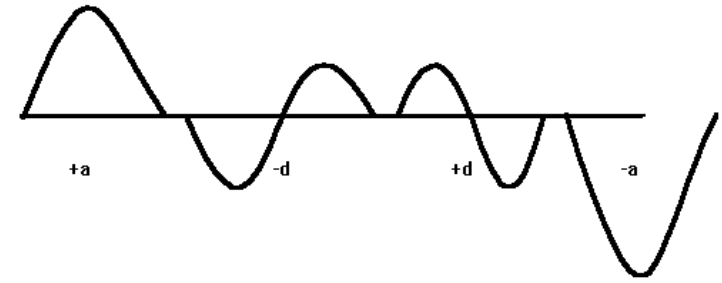
negative absorptive (-a),

positive dispersive (+d),

negative dispersive (-d),

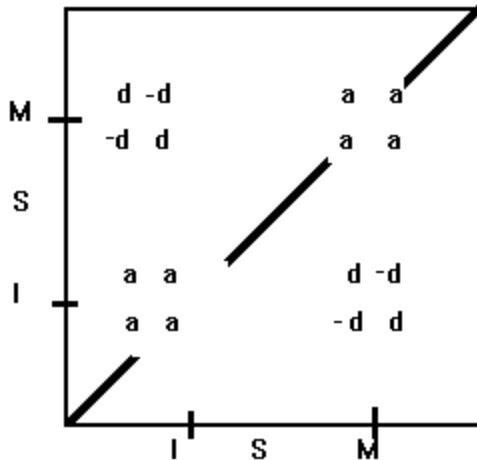
if one sets the phase that

sin is absorptive (*a*) in t_1
cos is absorptive (*d*) in t_2



\mathbf{I}_x [+a .. +a .. +a .. +a ..] at Ω_I, Ω_I
 \mathbf{M}_x [+a .. +a.. +a .. +a ..] at Ω_M, Ω_M
 \mathbf{I}_x [+d .. -d .. +d .. -d .] at Ω_M, Ω_I
 \mathbf{M}_x [+d .. -d .. +d .. -d .] at Ω_I, Ω_M

so the diagonals have absorptive and all off-diagonals have dispersive line shape. As expected for a COSY type spectrum.



The term $\alpha = \sin(\pi J_{SM}2\tau)\sin(\pi J_{IS}2\tau)$ term can be maximised if $\tau = 1/(4J_{IS})$ as well as $\tau = 1/(4J_{SM})$. but in general $J_{IS} \neq J_{SM}$