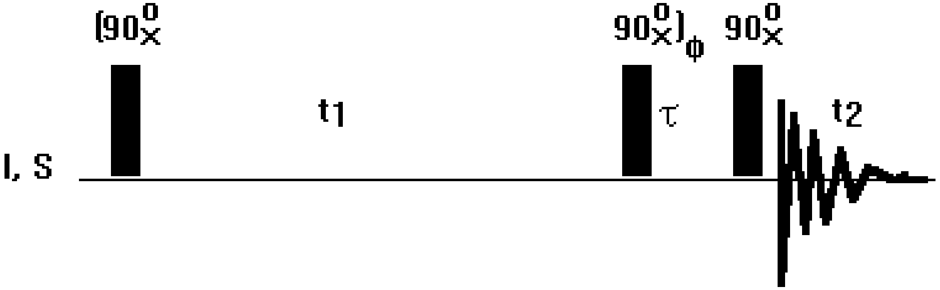
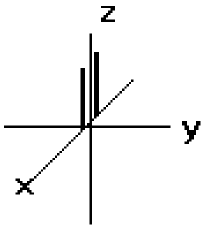
DQF-COSY = Double-Quantum Filtered-COrrelated SpectroscopY

The pulse sequence: $90°_{\phi}$ - t_1 - $90°_{\phi}$ - τ- $90°_{x}$ - t_2



Consider: Ω_I, Ω_S and $J_{I,S}$

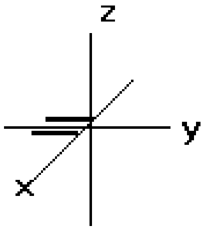
σ[eq.] — I_z and S_z



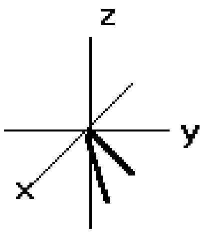
$\hat{H} = \pi/2\ \ (\hat{I}_x + \check{S}_x)$ $\downarrow 90°_x$

σ[0] — $-I_y$ and $-S_y$

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

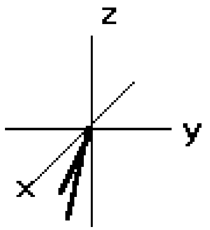


$-\mathbf{I}_y \cos(\Omega_I t_1)$
$+\mathbf{I}_x \sin(\Omega_I t_1)$
$-\mathbf{S}_y \cos(\Omega_S t_1)$
$+\mathbf{S}_x \sin(\Omega_S t_1)$



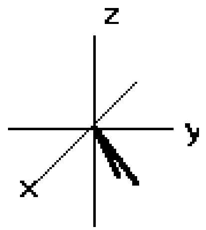
$\hat{H} = 2\hat{I}_z\check{S}_z(J_{IS}\pi t_1)$ $\downarrow$

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



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

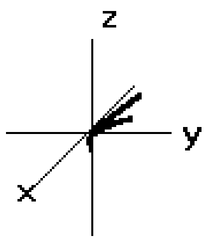
$-\mathbf{I}_y \cos(\Omega_I t_1)\cos(\pi J_{IS} t_1)$
$\quad +2\mathbf{I}_x\mathbf{S}_z \cos(\Omega_I t_1)\sin(\pi J_{IS} t_1)$
$+\mathbf{I}_x \sin(\Omega_I t_1)\cos(\pi J_{IS} t_1)$
$\quad +2\mathbf{I}_y\mathbf{S}_z \sin(\Omega_I t_1)\sin(\pi J_{IS} t_1)$
$-\mathbf{S}_y \cos(\Omega_S t_1)\cos(\pi J_{IS}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



$\sigma[t_1]$
$\hat{H} = \pi/2\ (\hat{I}_x + \check{S}_x)$

$\downarrow 90°_x$ *memo.* $= \cos(\pi/2) = 0, \sin(\pi/2) = 1$

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



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

$\sigma[t_1,0]$

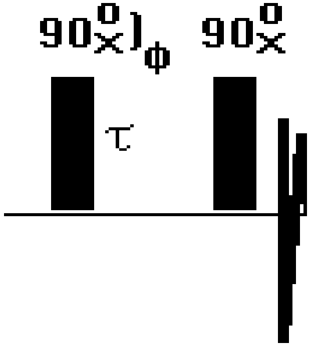
memo.

$\mathbf{I}_z$ *and* $\mathbf{S}_z$ (z magnetization)

$\mathbf{I}_x\mathbf{S}_y$ *and* $\mathbf{S}_x\mathbf{I}_y$ (double quant. coherence)

$\mathbf{I}_x$ *and* $\mathbf{S}_x$ (single quant. coherence)

$\mathbf{I}_z\mathbf{S}_y$ *and* $\mathbf{S}_z\mathbf{I}_y$ (single quant. coherence)



In DQF-COSY we preserve only double quant. coherences: $\mathbf{I}_x\mathbf{S}_y$ *and* $\mathbf{S}_x\mathbf{I}_y$
Therefore only two terms remain:

$$\sigma[t_1,0] \quad \begin{array}{l} -2\mathbf{I}_x\mathbf{S}_y \cos(\Omega_I t_1)\sin(\pi J_{IS} t_1) \\ -2\mathbf{S}_x\mathbf{I}_y \cos(\Omega_S t_1)\sin(\pi J_{IS} t_1) \end{array}$$

In reality $\mathbf{I}_x\mathbf{S}_y$ *and* $\mathbf{S}_x\mathbf{I}_y$ are still **mixtures of** zero-quantum and double-quantum coherences

memo :

$$I^+ = I_x + iI_y$$
$$I^- = I_x - iI_y$$
$$S^+ = S_x + iS_y$$
$$S^- = S_x - iS_y$$

consequently: $1/2\,[I^+ + I^-] = \mathbf{I_x}$ and $1/(2i)[S^+ - S^-] = \mathbf{S_y}$

Therefore:

$$-2\mathbf{I}_x\mathbf{S}_y = -2\{1/2\,[I^+ + I^-]1/(2i)[S^+ - S^-]\} = \mathbf{-1/(2i)\,\{I^+S^+ - I^+S^- + I^-S^+ - I^-S^-\}}$$

only I^+S^+ and I^-S^- are double quant. coh. (or coherence order 2),
I^+S^- and I^-S^+ are zero quant. coh. (or coherence order 0)

In reality *via* phase cycling the zero quantum coherences are removed and thus only
$\mathbf{-\,1/(2i)\,\{I^+S^+ - I^-S^-\}}$ terms remain.

In conclusion term **$-1/(2i)\ \{(I^+S^+)-(I^-S^-)\}$** is as follows:

$$-1/(2i)\ [\{(I_x + iI_y)(S_x + iS_y)\} - \{(I_x - iI_y)(S_x - iS_y)\}] =$$

$$-1/(2i)\ [I_xS_x + iI_yS_x + iI_xS_y - I_yS_y - I_xS_x + iI_yS_x + iI_xS_y + I_yS_y]$$

$$-1/(2i)\ [iI_yS_x + iI_xS_y + iI_yS_x + iI_xS_y]$$

$$\mathbf{-1/2\ [2I_yS_x + 2I_xS_y]}$$

In summary: $-2\mathbf{I}_x\mathbf{S}_y \Rightarrow -1/2\ [2I_yS_x + 2I_xS_y]$ (the 2 true double quant. parts of it)

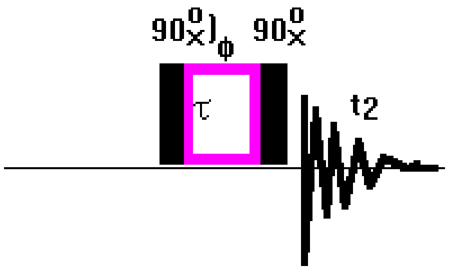
for the same reason: $-2\mathbf{S}_x\mathbf{I}_y \Rightarrow -1/2\ [2I_xS_y + 2I_yS_x]$

now

$$-2\mathbf{I}_x\mathbf{S}_y \cos(\Omega_I t_1)\sin(\pi J_{IS} t_1) \Rightarrow -1/2\ [2I_yS_x + 2I_xS_y] \cos(\Omega_I t_1)\sin(\pi J_{IS} t_1)$$

$$-2\mathbf{S}_x\mathbf{I}_y \cos(\Omega_S t_1)\sin(\pi J_{IS} t_1) \Rightarrow -1/2\ [2I_xS_y + 2I_yS_x] \cos(\Omega_S t_1)\sin(\pi J_{IS} t_1)$$

τ is set to be short and thus: - no evolution
- no coupling



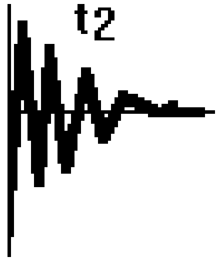
$$-I_yS_x \cos(\Omega_I t_1)\sin(\pi J_{IS} t_1) - I_xS_y \cos(\Omega_I t_1)\sin(\pi J_{IS} t_1)$$
$$-I_xS_y \cos(\Omega_S t_1)\sin(\pi J_{IS} t_1) - I_yS_x \cos(\Omega_S t_1)\sin(\pi J_{IS} t_1)$$

$\hat{H} = \pi/2\ (\hat{I}_x + \check{S}_x)$ $\downarrow 90°_x$

$$-I_zS_x \cos(\Omega_I t_1)\sin(\pi J_{IS} t_1) - I_xS_z \cos(\Omega_I t_1)\sin(\pi J_{IS} t_1)$$
$$-I_xS_z \cos(\Omega_S t_1)\sin(\pi J_{IS} t_1) - I_zS_x \cos(\Omega_S t_1)\sin(\pi J_{IS} t_1)$$

$-I_zS_x \cos(\Omega_I t_1)\sin(\pi J_{IS} t_1)$ $-I_xS_z \cos(\Omega_I t_1)\sin(\pi J_{IS} t_1)$

$-I_xS_z \cos(\Omega_S t_1)\sin(\pi J_{IS} t_1)$ $-I_zS_x \cos(\Omega_S t_1)\sin(\pi J_{IS} t_1)$



During acquisition (t_2):

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

the $-I_xS_z$ term during ACQ $\Rightarrow -\mathbf{I}_x\mathbf{S}_z \cos(\Omega_I t_1)\sin(\pi J_{IS} t_1)\cos(\Omega_I t_2)\cos(\pi J_{IS} t_2)$

$-1/2\mathbf{I}_y \cos(\Omega_I t_1)\sin(\pi J_{IS} t_1)\cos(\Omega_I t_2)\sin(\pi J_{IS} t_2)$

$+\mathbf{I}_y\mathbf{S}_z \cos(\Omega_I t_1)\sin(\pi J_{IS} t_1)\sin(\Omega_I t_2)\cos(\pi J_{IS} t_2)$

$-1/2\mathbf{I}_x \cos(\Omega_I t_1)\sin(\pi J_{IS} t_1)\sin(\Omega_I t_2)\sin(\pi J_{IS} t_2)$ ↵

the $-I_zS_x$ term during ACQ $\Rightarrow -\mathbf{I}_z\mathbf{S}_x \cos(\Omega_S t_1)\sin(\pi J_{IS} t_1)\cos(\Omega_S t_2)\cos(\pi J_{IS} t_2)$

$-1/2\mathbf{S}_y \cos(\Omega_S t_1)\sin(\pi J_{IS} t_1)\cos(\Omega_S t_2)\sin(\pi J_{IS} t_2)$

$+\mathbf{I}_z\mathbf{S}_y \cos(\Omega_S t_1)\sin(\pi J_{IS} t_1)\sin(\Omega_S t_2)\cos(\pi J_{IS} t_2)$

$-1/2\mathbf{S}_x \cos(\Omega_S t_1)\sin(\pi J_{IS} t_1)\sin(\Omega_S t_2)\sin(\pi J_{IS} t_2)$ ↵

the $-I_zS_x$ term during ACQ $\Rightarrow -\mathbf{I}_z\mathbf{S}_x \cos(\Omega_I t_1)\sin(\pi J_{IS} t_1)\cos(\Omega_S t_2)\cos(\pi J_{IS} t_2)$

$-1/2\mathbf{S}_y \cos(\Omega_I t_1)\sin(\pi J_{IS} t_1)\cos(\Omega_S t_2)\sin(\pi J_{IS} t_2)$

$+\mathbf{S}_y\mathbf{I}_z \cos(\Omega_I t_1)\sin(\pi J_{IS} t_1)\sin(\Omega_S t_2)\cos(\pi J_{IS} t_2)$

$-1/2\mathbf{S}_x \cos(\Omega_I t_1)\sin(\pi J_{IS} t_1)\sin(\Omega_S t_2)\sin(\pi J_{IS} t_2)$ ↵

the $-I_xS_z$ term during ACQ $\Rightarrow -\mathbf{I}_x\mathbf{S}_z \cos(\Omega_S t_1)\sin(\pi J_{IS} t_1)\cos(\Omega_I t_2)\cos(\pi J_{IS} t_2)$

$-1/2\mathbf{I}_y \cos(\Omega_S t_1)\sin(\pi J_{IS} t_1)\cos(\Omega_I t_2)\sin(\pi J_{IS} t_2)$

$+\mathbf{S}_z\mathbf{I}_y \cos(\Omega_S t_1)\sin(\pi J_{IS} t_1)\sin(\Omega_I t_2)\cos(\pi J_{IS} t_2)$

$-1/2\mathbf{I}_x \cos(\Omega_S t_1)\sin(\pi J_{IS} t_1)\sin(\Omega_I t_2)\sin(\pi J_{IS} t_2)$ ↵

memo 1: receiver on x

therefore only the four x term remain

$-1/2\mathbf{S}_x \cos(\Omega_S t_1)\sin(\pi J_{IS} t_1)\sin(\Omega_S t_2)\sin(\pi J_{IS} t_2)$

$-1/2\mathbf{S}_x \cos(\Omega_I t_1)\sin(\pi J_{IS} t_1)\sin(\Omega_S t_2)\sin(\pi J_{IS} t_2)$

$-1/2\mathbf{I}_x \cos(\Omega_I t_1)\sin(\pi J_{IS} t_1)\sin(\Omega_I t_2)\sin(\pi J_{IS} t_2)$

$-1/2\mathbf{I}_x \cos(\Omega_S t_1)\sin(\pi J_{IS} t_1)\sin(\Omega_I t_2)\sin(\pi J_{IS} t_2)$

memo 2:

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

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

therefore

$+1/8\mathbf{I}_x[+\sin\{(\Omega_I+\pi J_{IS})t_1\} - \sin\{(\Omega_I-\pi J_{IS})t_1\}]\ [+\cos\{(\Omega_I-\pi J_{IS})t_2\}- \cos\{(\Omega_I+\pi_{IS})t_2\}]$

$+1/8\mathbf{I}_x[+\sin\{(\Omega_S+\pi J_{IS})t_1\}- \sin\{(\Omega_S-\pi J_{IS})t_1\}]\ [+\cos\{(\Omega_I-\pi J_{IS})t_2 - \cos\{(\Omega_I+\pi J_{IS})t_2\}]$

$+1/8\mathbf{S}_x[+\sin\{(\Omega_S+\pi J_{IS})t_1\}-\sin\{(\Omega_S-\pi J_{IS})t_1\}]\ [+\cos\{(\Omega_S-\pi J_{IS})t_2\}- \cos\{(\Omega_S+\pi J_{IS})t_2\}]$

$+1/8\mathbf{S}_x[+\sin\{(\Omega_I+\pi J_{IS})t_1\}- \sin\{(\Omega_I-\pi J_{IS})t_1\}]\ [+\cos\{(\Omega_S-\pi J_{IS})t_2\}-\cos\{(\Omega_S+\pi J_{IS})t_2\}]$

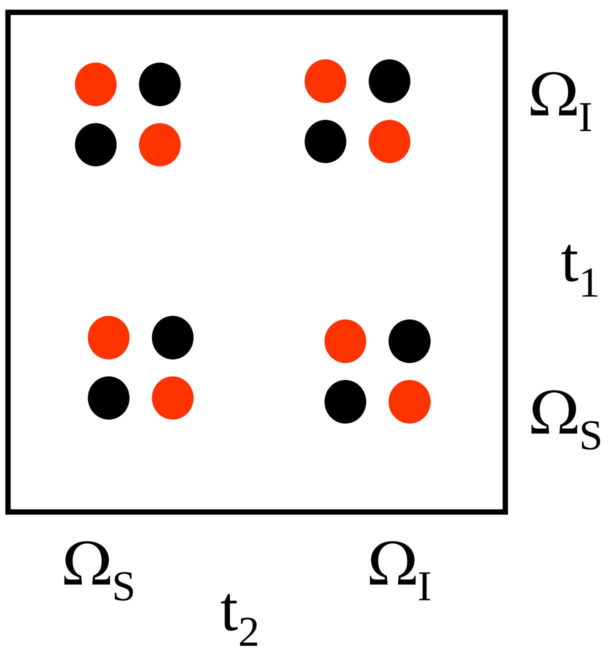
the following terms can be found

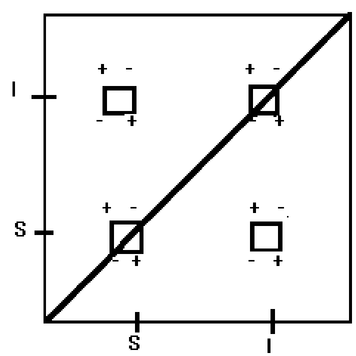
$\mathbf{I}_x$ [+ .. - .. + .. - ..] at Ω_I , Ω_I
$\mathbf{I}_x$ [+ .. - .. + .. - ..] at Ω_S , Ω_I
$\mathbf{S}_x$[+ .. - .. + .. - ..] at Ω_S , Ω_S
$\mathbf{S}_x$[+ .. - .. + .. - ..] at Ω_I , Ω_S

if one sets the phase that *sin is absorptive (a) in* t_1
cos is absorptive (d) in t_2

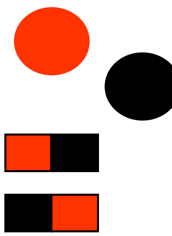
$\mathbf{I}_x$ [+a .. -a .. +a .. -a ..] at Ω_I , Ω_I
$\mathbf{I}_x$ [+a .. -a .. +a .. -a ..] at Ω_S , Ω_I
$\mathbf{S}_x$[+a .. -a.. +a .. -a ..] at Ω_S , Ω_S
$\mathbf{S}_x$[+a .. -a ..+a .. -a ..] at Ω_I , Ω_S

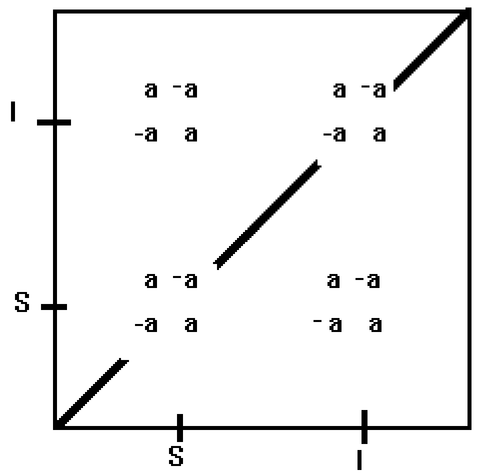
so the diagonals as well as all off-diagonals have absorptive line shape

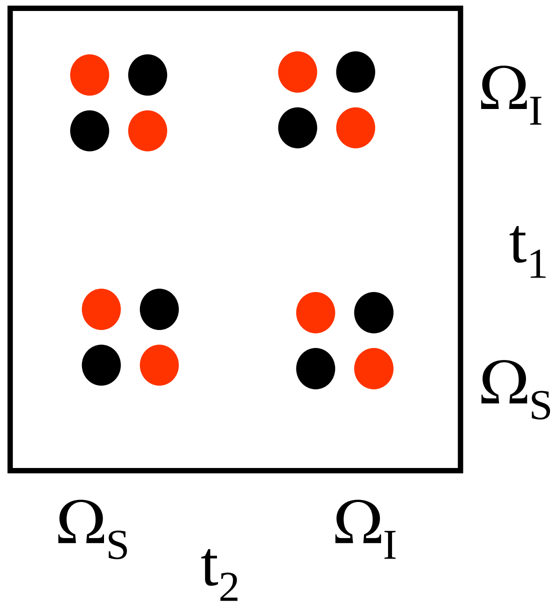




memo: line shapes
positive absorptive (+a),
negative absorptive (-a),
positive dispersive (+d),
negative dispersive (-d),







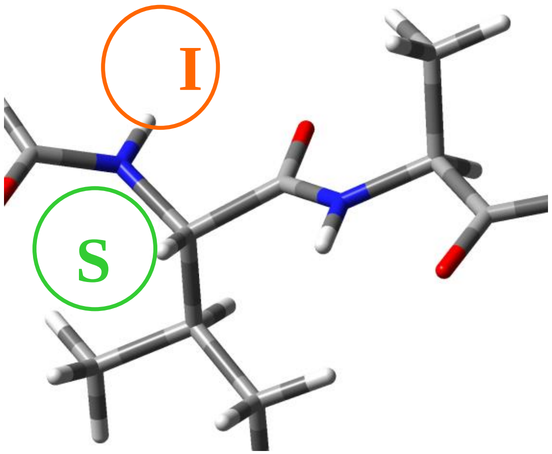
Comment:

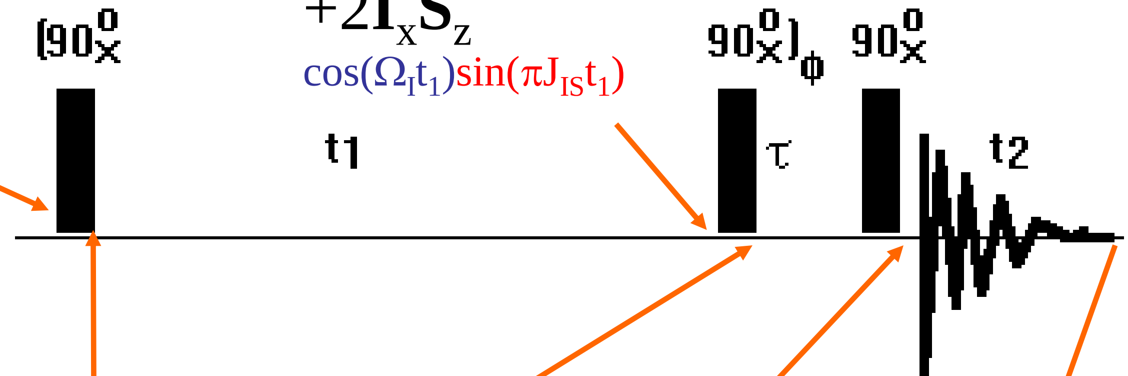
The intensity of the DQF-COSY peaks are half of the appropriate COSY peaks (1/8 -> 1/4)

Phase cycled DQF-COSY is 4 time longer than the appropriate COSY.

Note: If selection is made not by phase-cycling but by "gradient", then the time requirement of the two experiments are identical.

Summary: ¹H-¹H DQF-COSY the raise of an off-diagonal peak





I_z

$-I_y$

$+2I_xS_z$ $\cos(\Omega_I t_1)\sin(\pi J_{IS} t_1)$

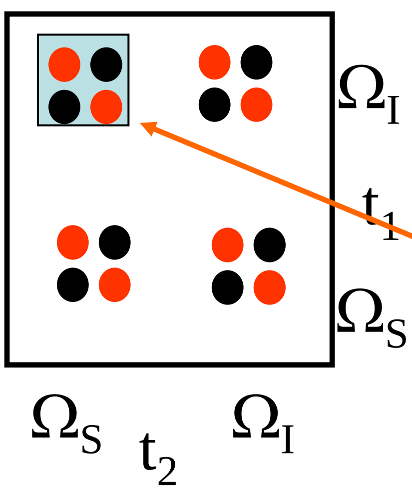
A DQ tagból a zQ tag kiemelését követően:

$-2S_xI_y \Rightarrow -1/2\,[2I_xS_y + 2I_yS_x]$

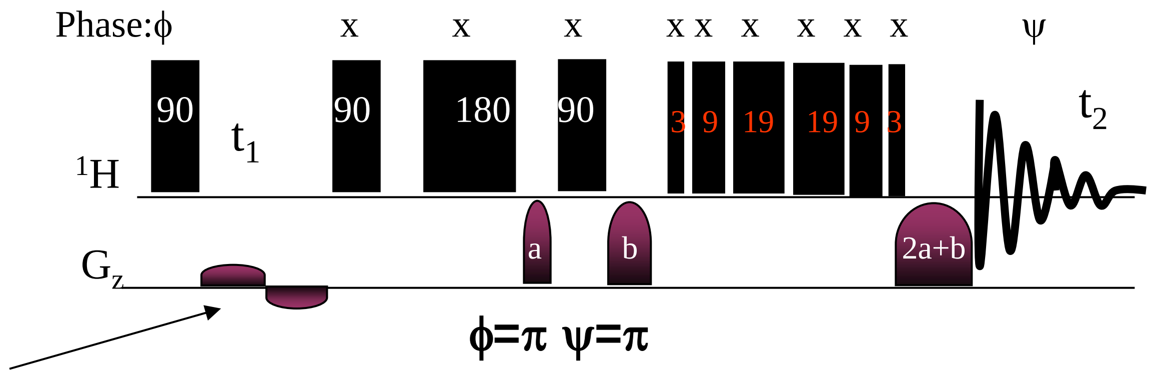
$-I_zS_x$ $\cos(\Omega_I t_1)\sin(\pi J_{IS} t_1)$

$-1/2S_x \cos(\Omega_I t_1)\sin(\pi J_{IS} t_1)$
$\sin(\Omega_S t_2)\sin(\pi J_{IS} t_2)$

$+1/8S_x[+\sin\{(\Omega_I+\pi J_{IS})t_1\} - \sin\{(\Omega_I-\pi J_{IS})t_1\}]$
$[+\cos\{(\Omega_S-\pi J_{IS})t_2\} - \cos\{(\Omega_S+\pi J_{IS})t_2\}]$



DQF-COSY with bipolar gradient and -3-9-19:



bipolar gradient is taking care of water during evolution:

a pair of gradients (typically of low power *e.g.* 0.5%) of increasing length covering the overall time of evolution (t_1). Radiation dumping is minimized since the otherwise bulk water, as well as any other signals, are dephased and rephased in a symmetric manner during evolution. (No uniform (big) water, no radiation dumping occurs.)

The 180 pulse of DQF (the one between the second and the third 90s):
It is there since a finite (ms!) time is required for the gradient under which time evolution of chemical shift will occur.
This unwanted evolution is eliminated by the refocusing effect of the 180^{o} pulse (*see echo*)

Two step phase cycling (0, π) is required to refocus axial peaks present because of quadrature detection (see phase cycling).

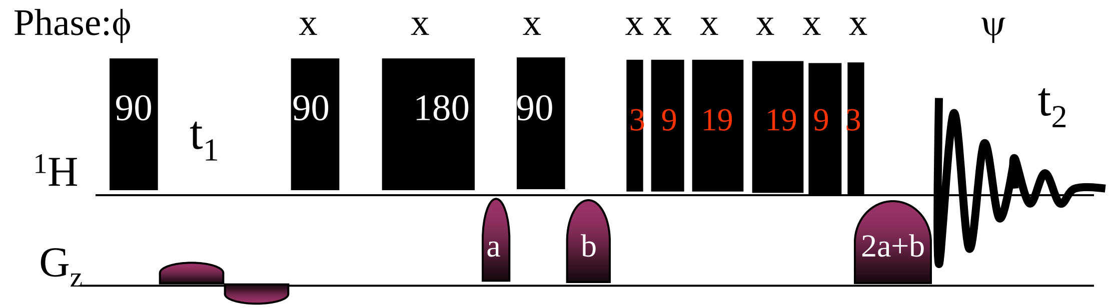
The 3-9-19 watergate or binominal water suppression is to remove water before acquisition

Gradient "a" dephases a double quantum coherence transferred subsequently to a single quantum coherence. When coherence is refocused by the second gradient before acquisition it has to have a length of 2*a.
Gradient "b" is that of the "standard" watergate.

And needs to be refocused

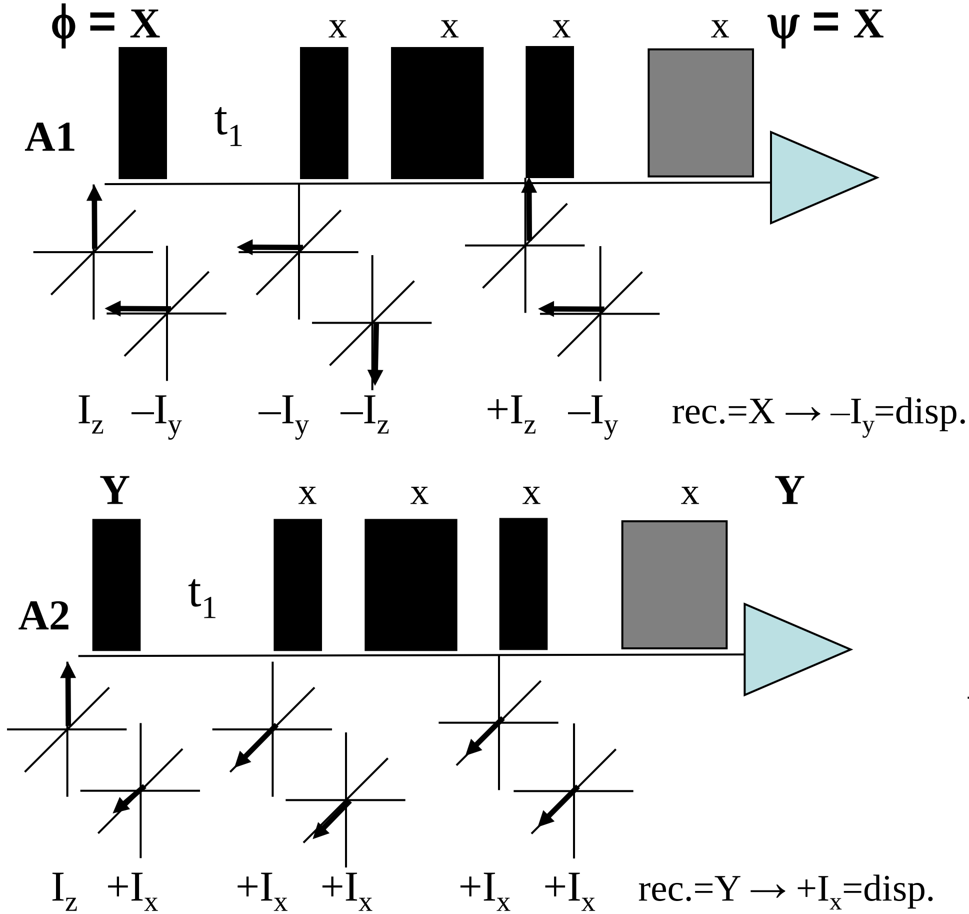
DQF-COSY-bipolar gradient and -3-9-19:

↑ Net magnetization form H_2O (on resonance)

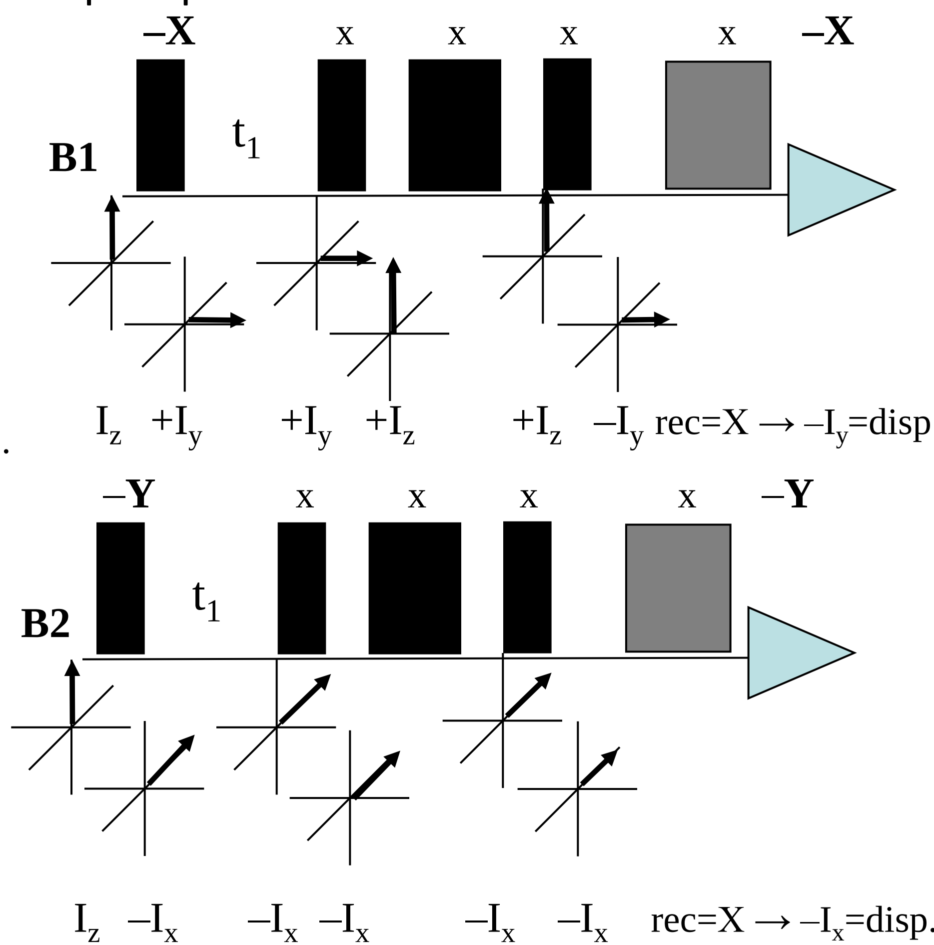


wo step phase cycling (0, π)
ith quadrature detection
refocus axial peaks:

ϕ=0 ψ=0



ϕ=π ψ=π



The constructive co-adding of A1 and A2 is possible. The constructive co-adding of B1 and B2 is possible.