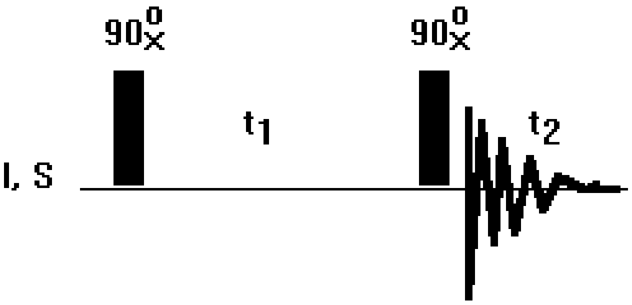
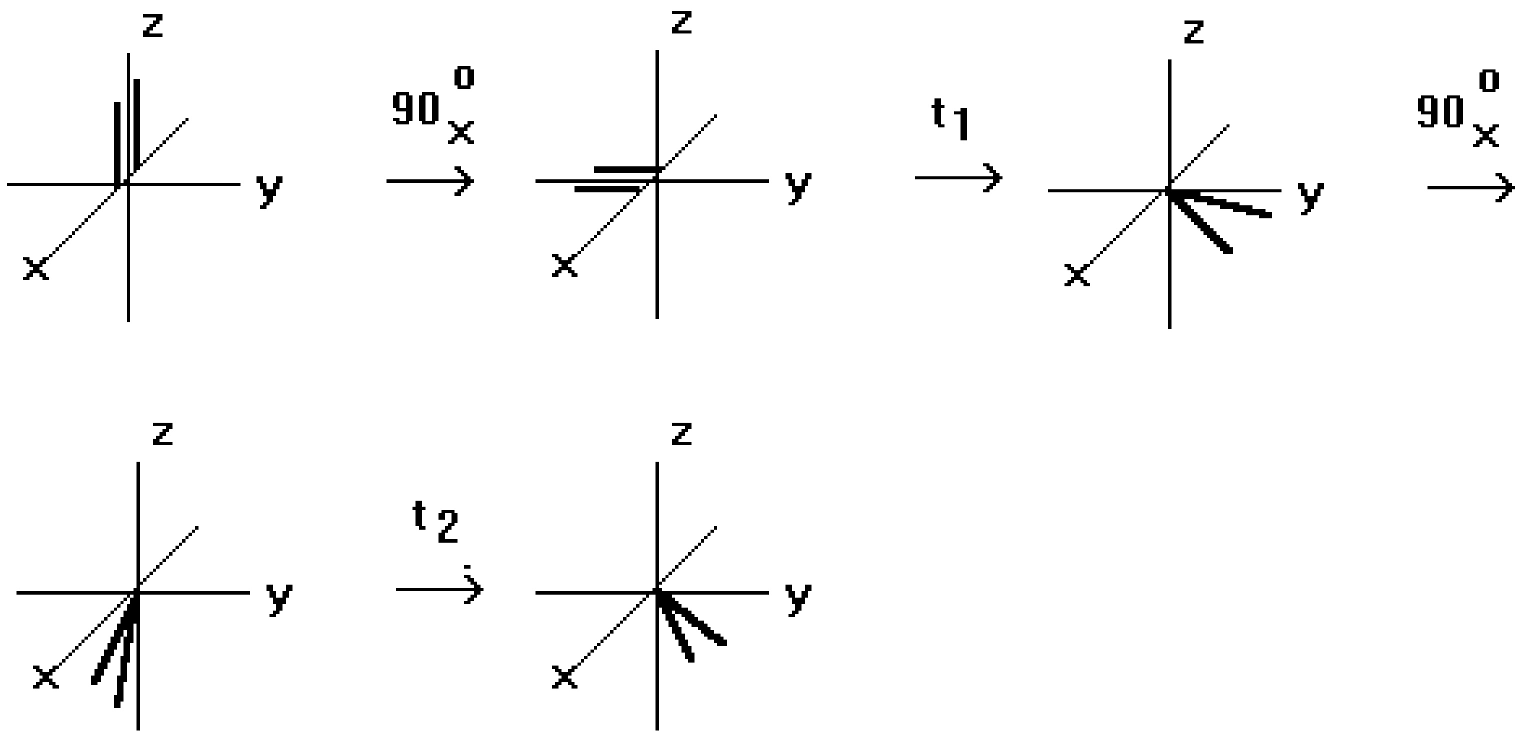
COSY = COrrelated SpectroscopY

The pulse sequence: $90°_x$ - t_1 - $90°_x$ - t_2



Consider: Ω_I, Ω_S and J_{IS}



σ[eq.] $\hat{H} = \pi/2 \ (\hat{I}_x + \check{S}_x)$

$\mathbf{I}_z$ and $\mathbf{S}_z$

↓ $90°_x$

σ[0] $\hat{H} = \hat{I}_z(\Omega_I t_1) + \check{S}_z(\Omega_S t_1)$

$-\mathbf{I}_y$ and $-\mathbf{S}_y$

↓ t_1

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

and

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

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

↓

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

and

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

σ[t_1]

$\hat{H} = \pi/2 \; (\hat{I}_x + \hat{S}_x)$ $\downarrow 90°_x$ *memo.=cos(π/2) = 0, sin(π/2) = 1*

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

and

$$-\mathbf{S}_z \cos(\Omega_S t_1)\cos(\pi J_{IS} t_1)$$
$$-2\mathbf{S}_x\mathbf{I}_y \cos(\Omega_S t_1)\sin(\pi J_{IS} t_1)$$
$$+\mathbf{S}_x \sin(\Omega_S t_1)\cos(\pi J_{IS} t_1)$$
$$\sigma[t_1,0] \qquad -2\mathbf{S}_z\mathbf{I}_y \sin(\Omega_S t_1)\sin(\pi J_{IS} t_1)$$

memo.= Both $\mathbf{I}_z$ *and* $\mathbf{S}_z$ (z magnetization) as well as $\mathbf{I}_x\mathbf{S}_y$ *and* $\mathbf{S}_x\mathbf{I}_y$ (zero-double quant. coherences) will not result in observable signal, thus these 4 terms are ignored.

Therefore, the following 4 terms remain only :

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

and

$$+\mathbf{S}_x \sin(\Omega_S t_1)\cos(\pi J_{IS} t_1)$$
$$\sigma[t_1,0] \qquad -2\mathbf{S}_z\mathbf{I}_y \sin(\Omega_S t_1)\sin(\pi J_{IS} t_1)$$

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

the $\mathbf{I}_x$ term during ACQ $\Rightarrow$

$$+\mathbf{I}_x \sin(\Omega_I t_1)\cos(\pi J_{IS} t_1)\cos(\Omega_I t_2)\cos(\pi J_{IS} t_2) \quad \hookleftarrow$$
$$+2\mathbf{I}_y\mathbf{S}_z \sin(\Omega_I t_1)\cos(\pi J_{IS} t_1)\cos(\Omega_I t_2)\sin(\pi J_{IS} t_2)$$
$$+\mathbf{I}_y \sin(\Omega_I t_1)\cos(\pi J_{IS} t_1)\sin(\Omega_I t_2)\cos(\pi J_{IS} t_2)$$
$$-2\mathbf{I}_x\mathbf{S}_z \sin(\Omega_I t_1)\cos(\pi J_{IS} t_1)\sin(\Omega_I t_2)\sin(\pi J_{IS} t_2)$$

the $\mathbf{S}_x$ term during ACQ $\Rightarrow$

$$+\mathbf{S}_x \sin(\Omega_S t_1)\cos(\pi J_{IS} t_1)\cos(\Omega_S t_2)\cos(\pi J_{IS} t_2) \quad \hookleftarrow$$
$$+2\mathbf{I}_z\mathbf{S}_y \sin(\Omega_S t_1)\cos(\pi J_{IS} t_1)\cos(\Omega_S t_2)\sin(\pi J_{IS} t_2)$$
$$+\mathbf{S}_y \sin(\Omega_S t_1)\cos(\pi J_{IS} t_1)\sin(\Omega_S t_2)\cos(\pi J_{IS} t_2)$$
$$-2\mathbf{I}_z\mathbf{S}_x \sin(\Omega_S t_1)\cos(\pi J_{IS} t_1)\sin(\Omega_S t_2)\sin(\pi J_{IS} t_2)$$

the $-2\mathbf{I}_y\mathbf{S}_z$ term during ACQ $\Rightarrow$

$$-2\mathbf{I}_y\mathbf{S}_z \sin(\Omega_S t_1)\sin(\pi J_{IS} t_1)\cos(\Omega_I t_2)\cos(\pi J_{IS} t_2)$$
$$+\mathbf{I}_x \sin(\Omega_S t_1)\sin(\pi J_{IS} t_1)\cos(\Omega_I t_2)\sin(\pi J_{IS} t_2) \quad \hookleftarrow$$
$$+2\mathbf{I}_x\mathbf{S}_z \sin(\Omega_S t_1)\sin(\pi J_{IS} t_1)\sin(\Omega_I t_2)\cos(\pi J_{IS} t_2)$$
$$+\mathbf{I}_y \sin(\Omega_S t_1)\sin(\pi J_{IS} t_1)\sin(\Omega_I t_2)\sin(\pi J_{IS} t_2)$$

the $-2\mathbf{I}_z\mathbf{S}_y$ term during ACQ $\Rightarrow$

$$-2\mathbf{I}_z\mathbf{S}_y \sin(\Omega_I t_1)\sin(\pi J_{IS} t_1)\cos(\Omega_S t_2)\cos(\pi J_{IS} t_2)$$
$$+\mathbf{S}_x \sin(\Omega_I t_1)\sin(\pi J_{IS} t_1)\cos(\Omega_S t_2)\sin(\pi J_{IS} t_2) \quad \hookleftarrow$$
$$+2\mathbf{I}_z\mathbf{S}_x \sin(\Omega_I t_1)\sin(\pi J_{IS} t_1)\sin(\Omega_S t_2)\cos(\pi J_{IS} t_2)$$
$$+\mathbf{S}_y \sin(\Omega_I t_1)\sin(\pi J_{IS} t_1)\sin(\Omega_S t_2)\sin(\pi J_{IS} t_2)$$

memo 1: if receiver is on x axis
the following four x terms remain:

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

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

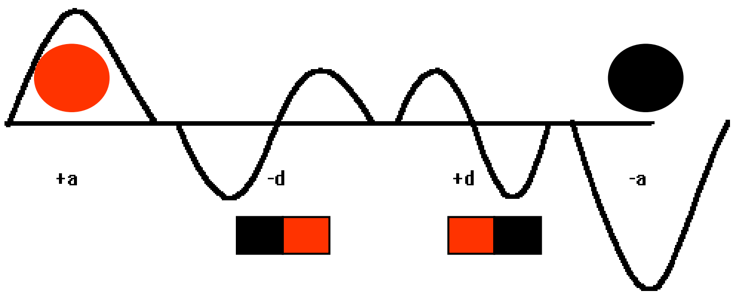
$$+1/4\mathbf{I}_x[+\sin\{(\Omega_I+\pi J_{IS})t_1\}+\sin\{(\Omega_I-\pi J_{IS})t_1\}][+\cos\{(\Omega_I+\pi J_{IS})t_2\}+\cos\{(\Omega_I-\pi J_{IS})t_2\}]$$
$$+1/4\mathbf{S}_x[+\sin\{(\Omega_S+\pi J_{IS})t_1\}+\sin\{(\Omega_S-\pi J_{IS})t_1\}][+\cos\{(\Omega_S+\pi J_{IS})t_2\}+\cos\{(\Omega_S-\pi_{IS})t_2\}]$$
$$+1/4\mathbf{I}_x[+\cos\{(\Omega_S-\pi J_{IS})t_1\}-\cos\{(\Omega_S+\pi J_{IS})t_1\}][+\sin\{(\Omega_I+\pi J_{IS})t_2\}-\sin\{(\Omega_I-\pi J_{IS})t_2\}]$$
$$+1/4\mathbf{S}_x[+\cos\{(\Omega_I-\pi J_{IS})t_1\}-\cos\{(\Omega_I+\pi J_{IS})t_1\}][+\sin\{(\Omega_S+\pi J_{IS})t_2\}-\sin\{(\Omega_S-\pi J_{IS})t_2\}]$$

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

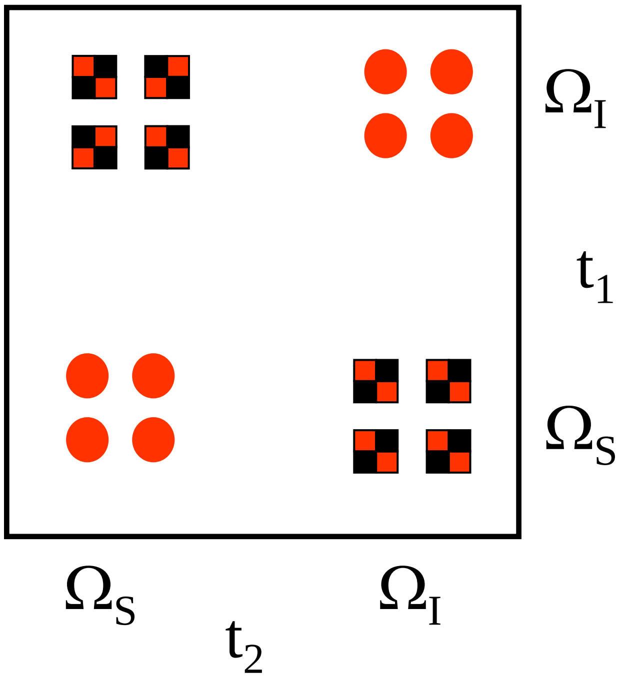
$$+1/4\mathbf{I}_x[+\sin\{(\Omega_I+\pi J_{IS})t_1\}+\sin\{(\Omega_I-\pi J_{IS})t_1\}]\ [+\cos\{(\Omega_I+\pi J_{IS})t_2\}+\cos\{(\Omega_I-\pi J_{IS})t_2\}]$$
$$+1/4\mathbf{I}_x[+\cos\{(\Omega_S-\pi J_{IS})t_1\}-\cos\{(\Omega_S+\pi J_{IS})t_1\}][+\sin\{(\Omega_I+\pi J_{IS})t_2\}-\sin\{(\Omega_I-\pi J_{IS})t_2\}]$$
$$+1/4\mathbf{S}_x[+\sin\{(\Omega_S+\pi J_{IS})t_1\}+\sin\{(\Omega_S-\pi J_{IS})t_1\}][+\cos\{(\Omega_S+\pi J_{IS})t_2\}+\cos\{(\Omega_S-\pi_{IS})t_2\}]$$
$$+1/4\mathbf{S}_x[+\cos\{(\Omega_I-\pi J_{IS})t_1\}-\cos\{(\Omega_I+\pi J_{IS})t_1\}]\ [+\sin\{(\Omega_S+\pi J_{IS})t_2\}-\sin\{(\Omega_S-\pi J_{IS})t_2\}]$$

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

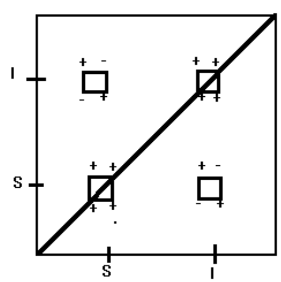


if one sets the phase that **sin** is **absorptive** (a) in t_1 and **cos** is **absorptiv**e (a) in t_2 **then:**

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

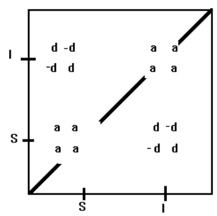


so the diagonals peaks have absorptive and all the off-diagonals have dispersive line shape.

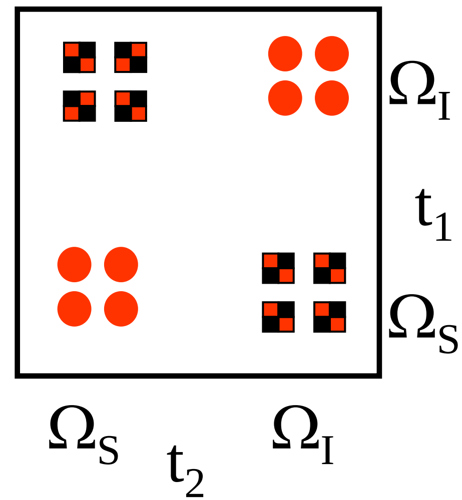


$$+1/4\mathbf{I}_x[+\sin\{(\Omega_I+\pi J_{IS})t_1\}+\sin\{(\Omega_I-\pi J_{IS})t_1\}]\ [+\cos\{(\Omega_I+\pi J_{IS})t_2\}+\cos\{(\Omega_I-\pi J_{IS})t_2\}]$$
$$+1/4\mathbf{I}_x[+\cos\{(\Omega_S-\pi J_{IS})t_1\}-\cos\{(\Omega_S+\pi J_{IS})t_1\}][+\sin\{(\Omega_I+\pi J_{IS})t_2\}-\sin\{(\Omega_I-\pi J_{IS})t_2\}]$$
$$+1/4\mathbf{S}_x[+\sin\{(\Omega_S+\pi J_{IS})t_1\}+\sin\{(\Omega_S-\pi J_{IS})t_1\}][+\cos\{(\Omega_S+\pi J_{IS})t_2\}+\cos\{(\Omega_S-\pi_{IS})t_2\}]$$
$$+1/4\mathbf{S}_x[+\cos\{(\Omega_I-\pi J_{IS})t_1\}-\cos\{(\Omega_I+\pi J_{IS})t_1\}]\ [+\sin\{(\Omega_S+\pi J_{IS})t_2\}-\sin\{(\Omega_S-\pi J_{IS})t_2\}]$$

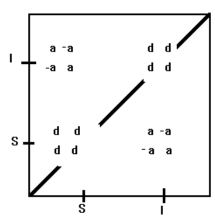
if one sets the phase that sin is absorptive (a) in t_1 and cos is absorptive (a) in $t_{2:}$



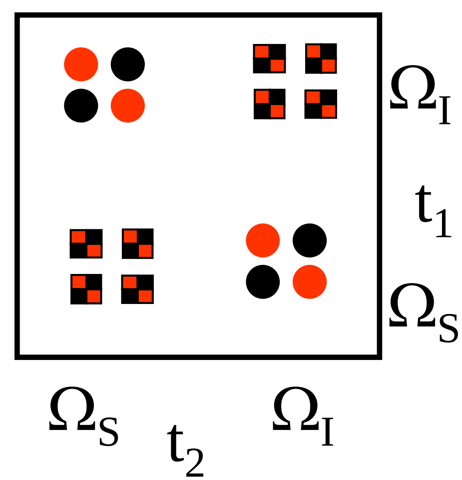
$\mathbf{I}_x$ [+a .. +a .. +a .. +a ..] at Ω_I , Ω_I
$\mathbf{I}_x$ [+d .. –d .. +d .. –d ..] at Ω_S , Ω_I
$\mathbf{S}_x$[+a . . +a.. +a . . +a ..] at Ω_S , Ω_S
$\mathbf{S}_x$[+d .. –d .. +d .. –d ..] at Ω_I , Ω_S



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



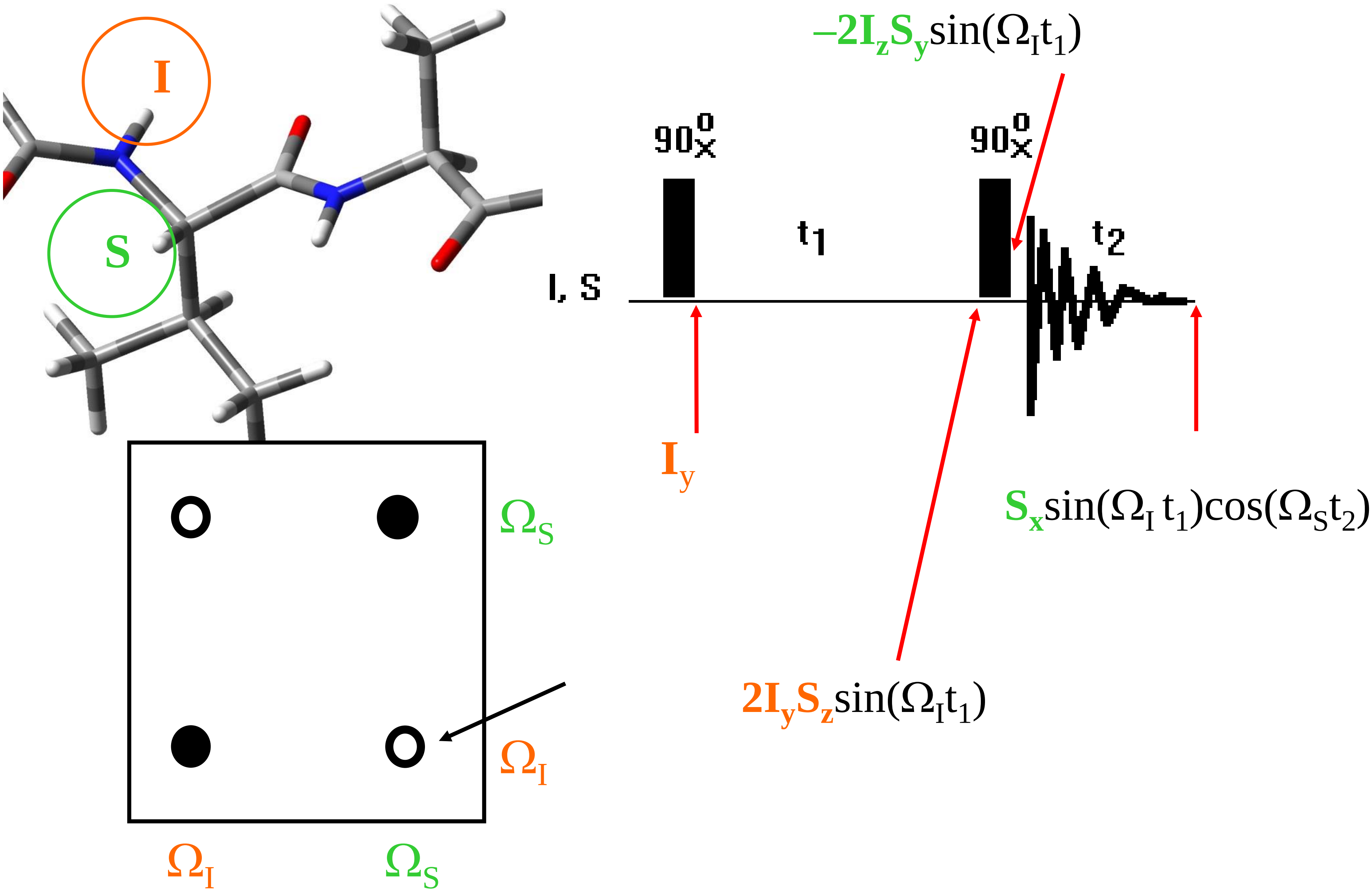
$\mathbf{I}_x$ [+d .. +d .. +d .. +d ..] at Ω_I , Ω_I
$\mathbf{I}_x$ [+a .. –a .. +a .. –a ..] at Ω_S , Ω_I
$\mathbf{S}_x$[+d .. +d.. +d .. +d ..] at Ω_S , Ω_S
$\mathbf{S}_x$[+a .. –a .. +a .. –a ..] at Ω_I , Ω_S

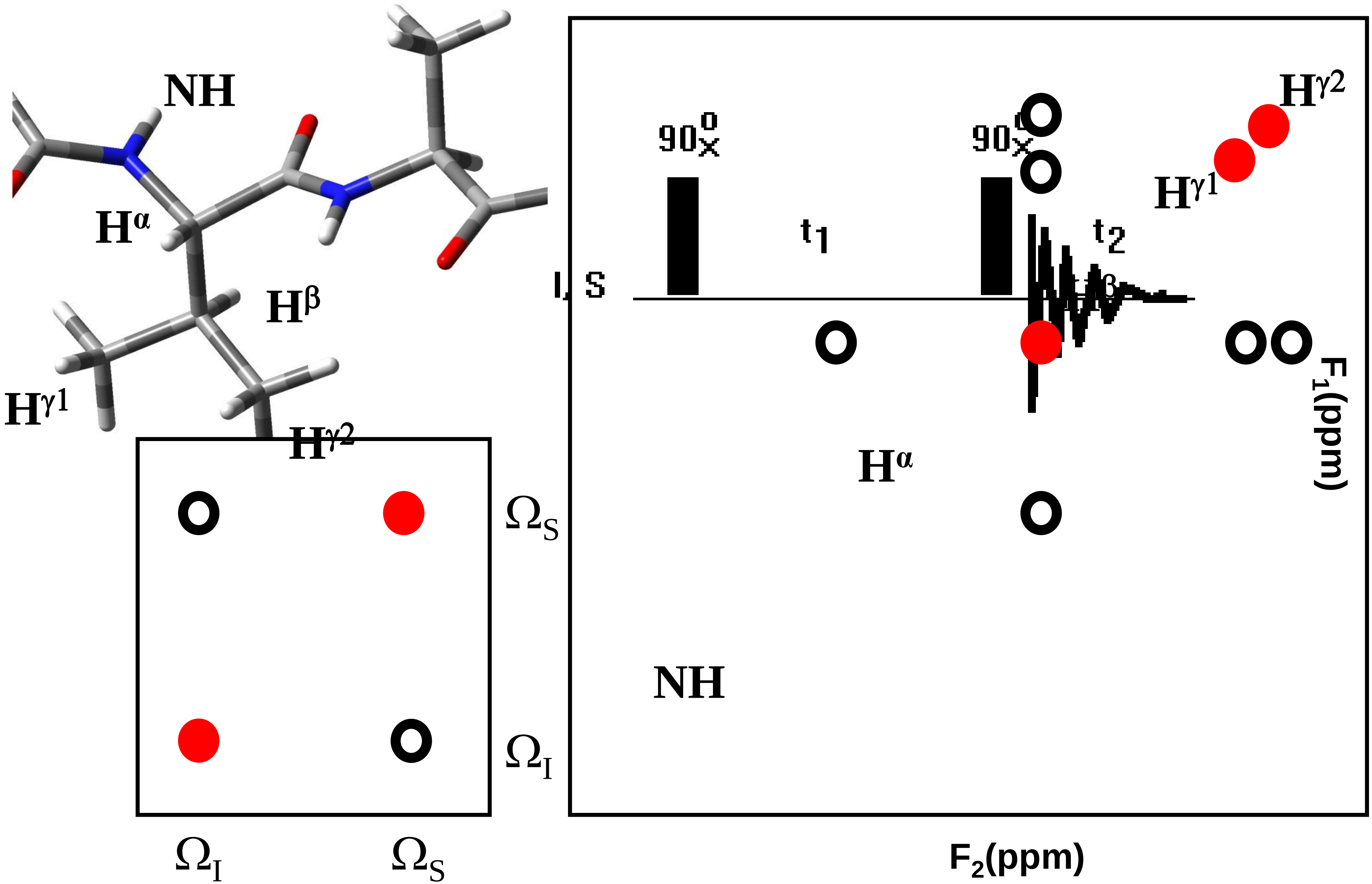


so now the diagonals have dispersive and all off-diagonals have absorptive line shape

Comment : even if the diagonals have dispersive and the off-diagonal peaks have absorptive line-shape, the off-diagonal peaks near the diagonal will have poor resolution because of the poor base line.

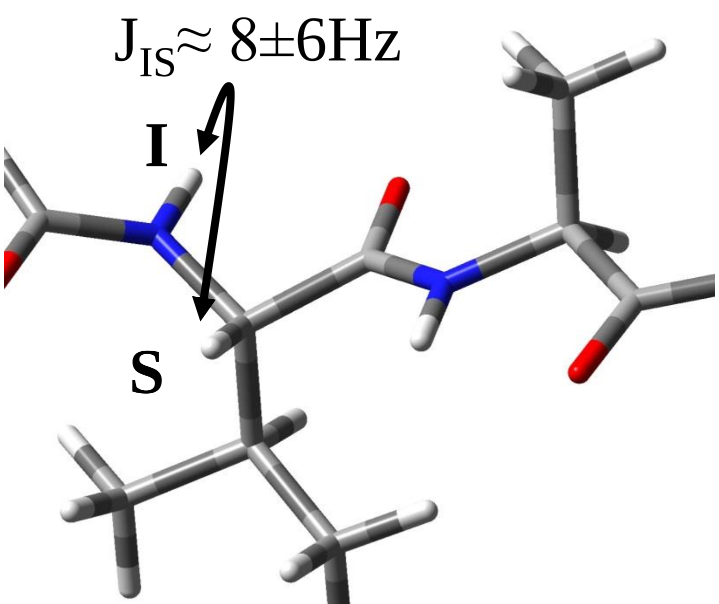
Összefoglaló I: ^{1}H-^{1}H COSY (homonukleáris korrelációs spektrum)



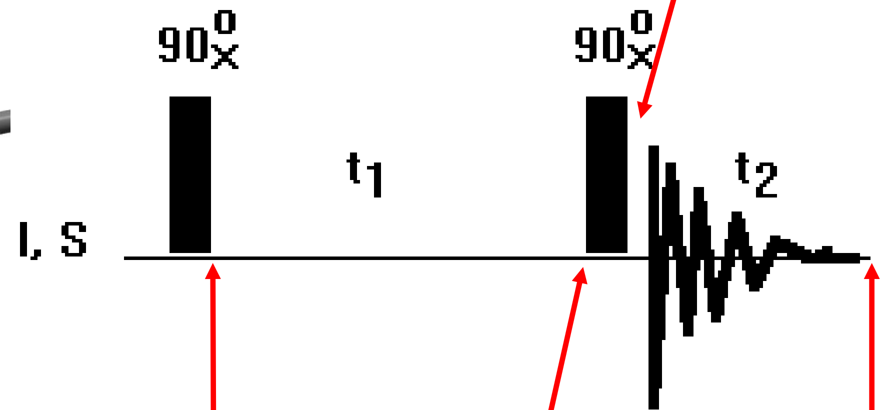


A spektrumban a J_{IS} okozta modulációtól eltekintünk

Összefoglaló II: ¹H-¹H COSY (homonukleáris korrelációs spektrum)



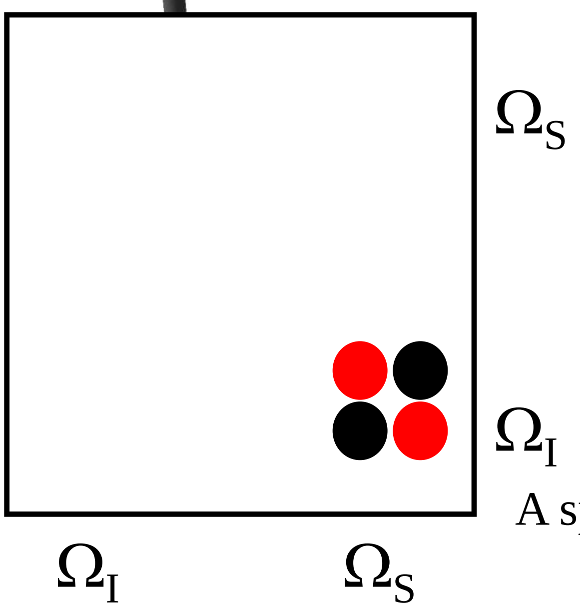
$-\mathbf{2I_zS_y}\sin(\Omega_I t_1)\sin(\pi J_{IS} t_1)$



$\mathbf{I}_x$

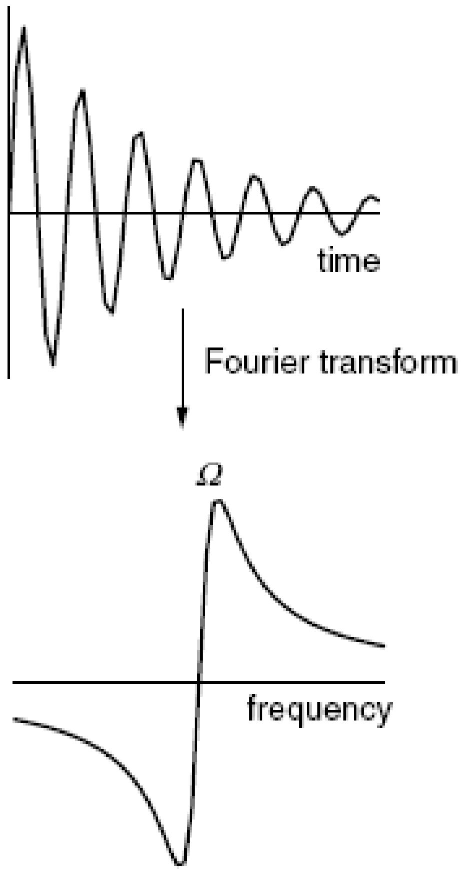
$\mathbf{S_x}\sin(\Omega_I\, t_1)\sin(\pi J_{IS} t_1)$
$\cos(\Omega_S t_2)\sin(\pi J_{IS} t_2)$

$\mathbf{2I_yS_z}\sin(\Omega_I t_1)\sin(\pi J_{IS} t_1)$

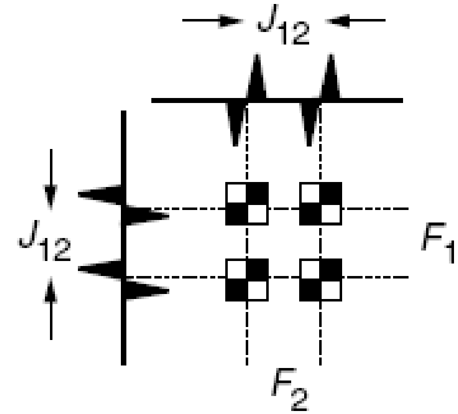


A spektrumban a J_{IS} okozta modulációt **figyelembe vesszük**

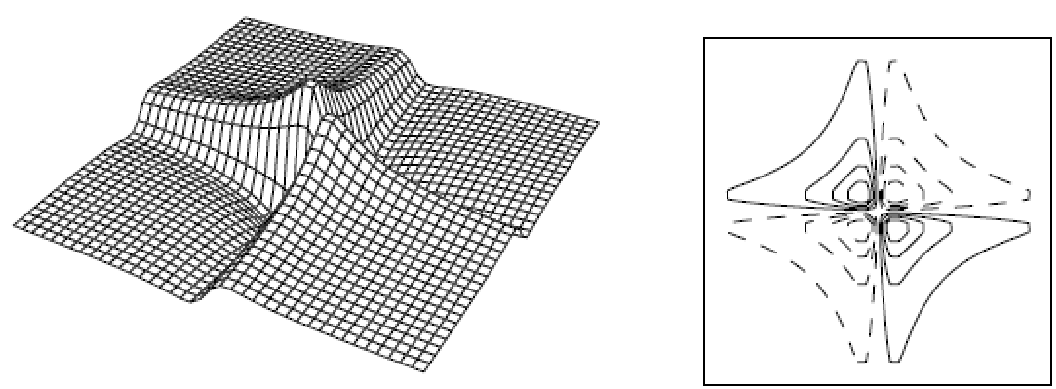
$+1/4\mathbf{S}_x[+\cos\{(\Omega_I-\pi J_{IS})t_1\}-\cos\{(\Omega_I+\pi J_{IS})t_1\}][+\sin\{(\Omega_S+\pi J_{IS})t_2\}-\sin\{(\Omega_S-\pi J_{IS})t_2\}]$



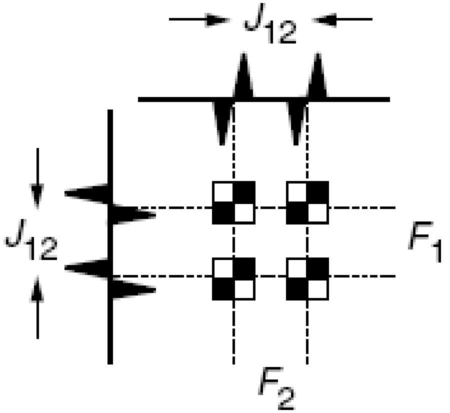
The Fourier transform of a decaying sine function $\sin\Omega t \exp(-t/T_2)$ is a dispersion mode Lorentzian centred at frequency Ω.



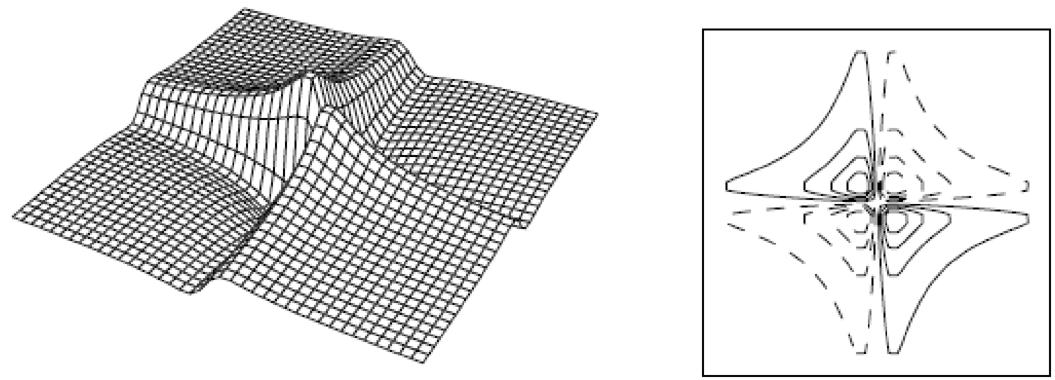
Schematic view of the diagonal peak from a COSY spectrum. The squares are supposed to indicate the two-dimensional double dispersion lineshape illustrated below



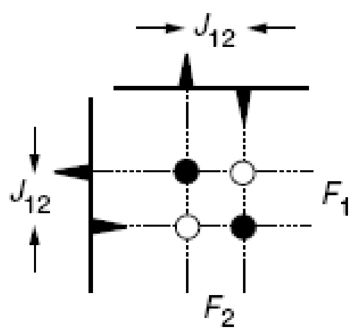
The double dispersion lineshape seen in pseudo 3D and as a contour plot; negative contours are indicated by dashed lines.



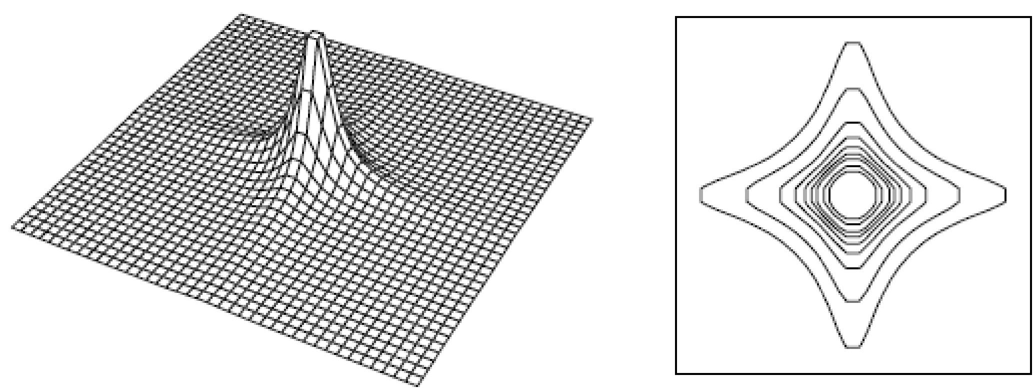
Schematic view of the diagonal peak from a COSY spectrum. The squares are supposed to indicate the two-dimensional double dispersion lineshape illustrated below



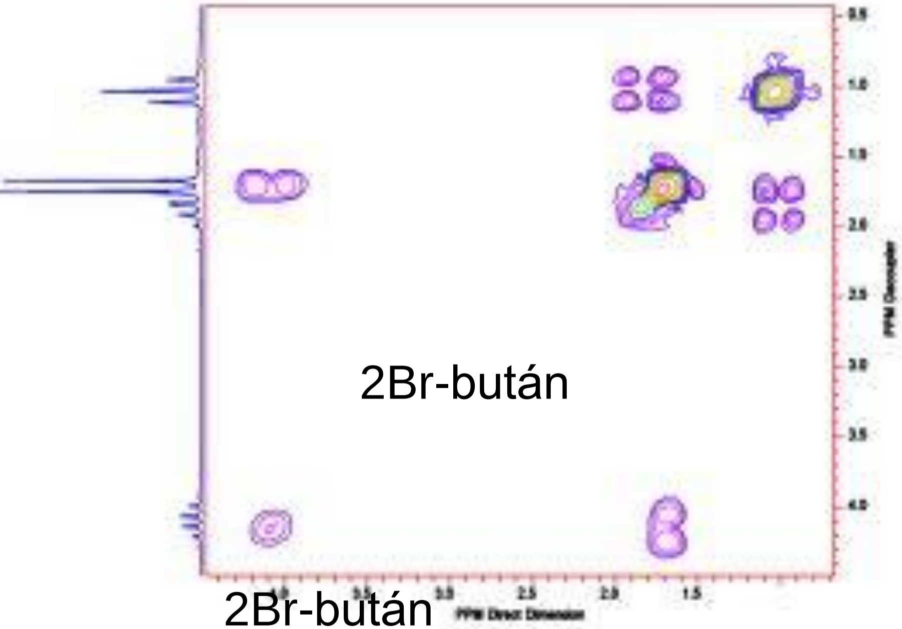
The double dispersion lineshape seen in pseudo 3D and as a contour plot; negative contours are indicated by dashed lines.

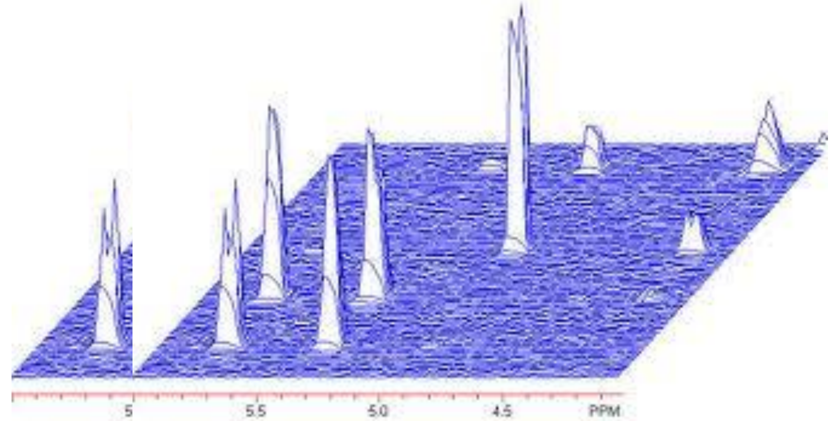


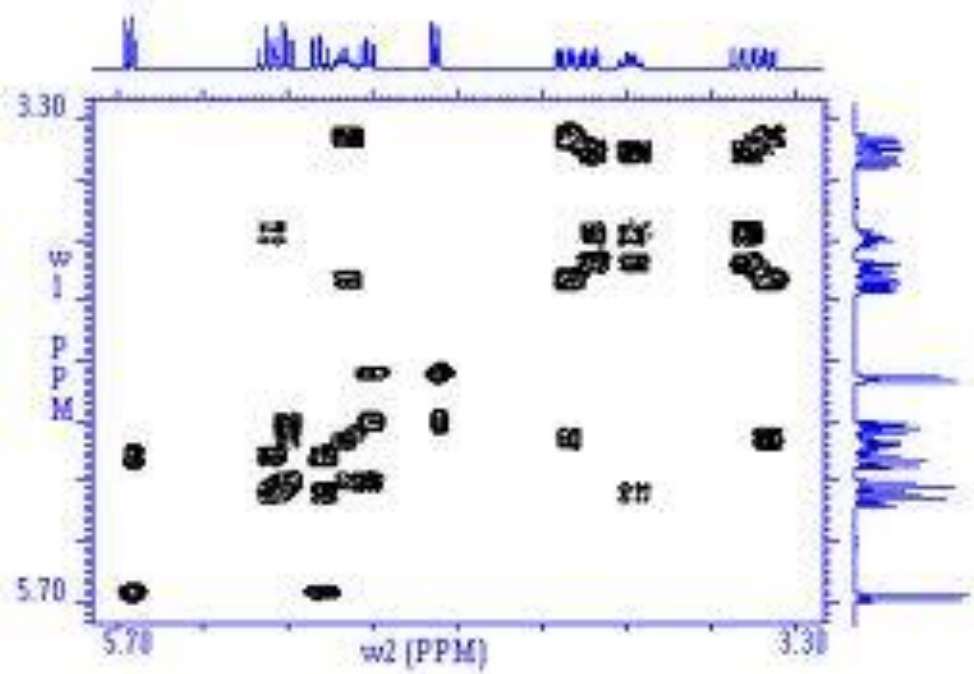
Schematic view of the cross-peak multiplet from a COSY spectrum. The circles are supposed to indicate the two-dimensional double absorption lineshape illustrated below; filled circles represent positive intensity, open represent negative intensity.

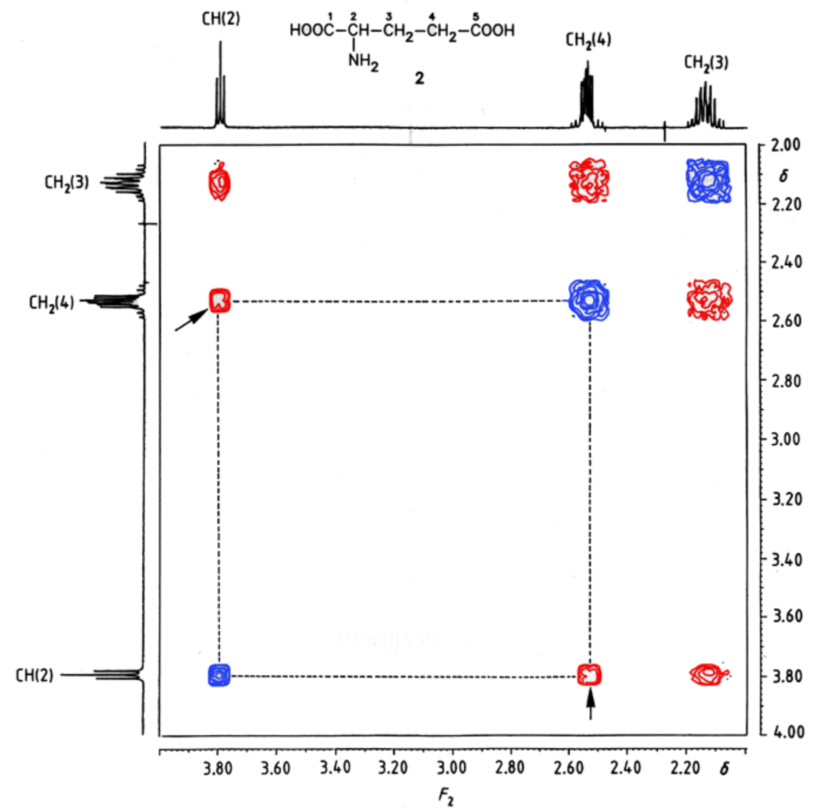


The double absorption lineshape seen in pseudo 3D and as a contour plot.


2Br-bután
2Br-bután
PPM Direct Dimension


5
5.5
5.0
4.5
PPM


3.30
5.70
w1 PPM
w2 (PPM)
5.70
3.30


CH(2)
HOOC–CH–CH2–CH2–COOH
NH2
2
CH2(4)
CH2(3)
CH2(3)
CH2(4)
CH(2)
F1
F2
δ