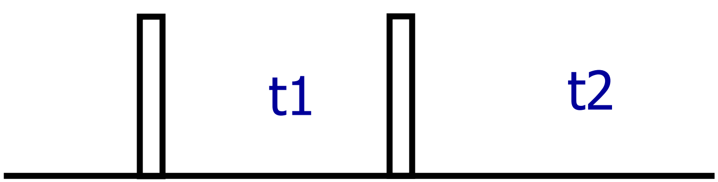
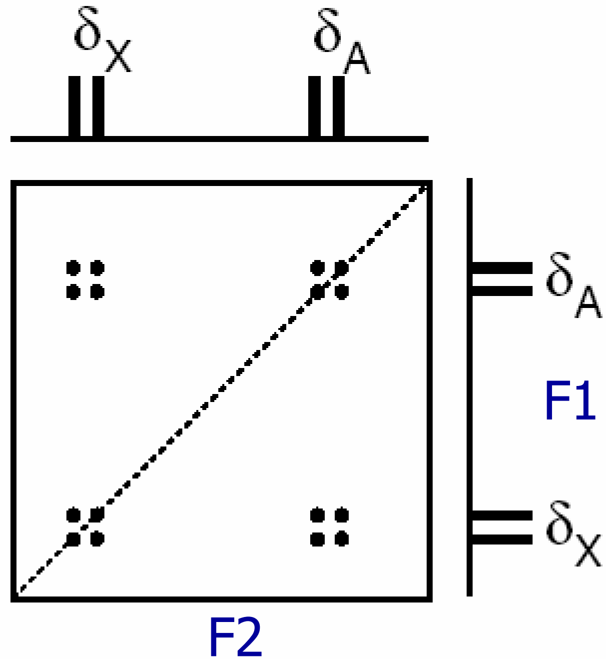
Metody 2D FT NMR spektroskopie

Elementární základy

Two-spin system AX

COSY – COrrelated SpectroscopY





Schematic COSY spectrum for two coupled spins, A and X

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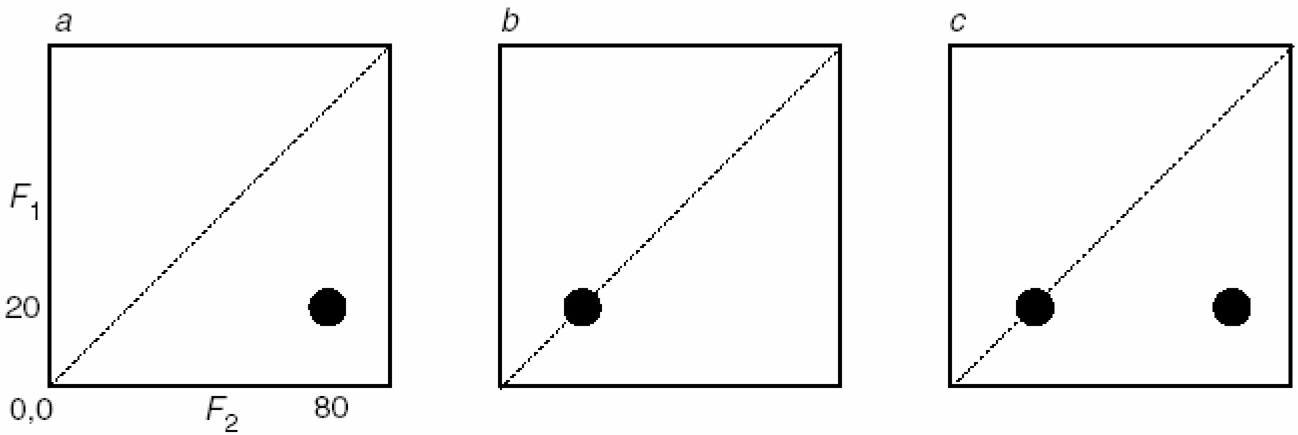
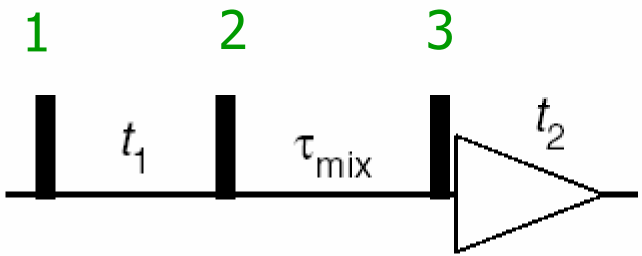


Metody 2D FT NMR spektroskopie

NOE SpectroscopY a EXchange SpectroscopY



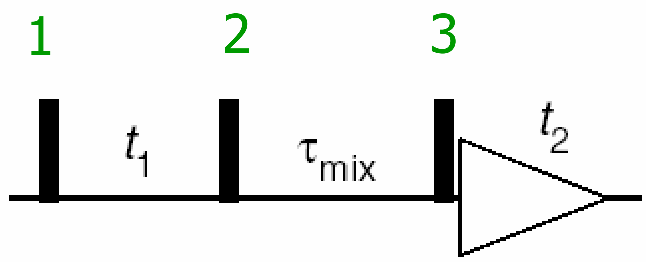
1. pulz: $$I_{1z} \xrightarrow{\pi/2\, I_{1x}} \xrightarrow{\pi/2\, I_{2x}} -I_{1y}$$

t1: $$-I_{1y} \xrightarrow{\Omega_1 t_1 I_{1z}} \xrightarrow{\Omega_2 t_1 I_{2z}} -\cos\Omega_1 t_1\; I_{1y} + \sin\Omega_1 t_1\; I_{1x}$$

2. pulz:
$$-\cos\Omega_1 t_1\; I_{1y} \xrightarrow{\pi/2\, I_{1x}} \xrightarrow{\pi/2\, I_{2x}} -\cos\Omega_1 t_1\; I_{1z}$$
$$\sin\Omega_1 t_1\; I_{1x} \xrightarrow{\pi/2\, I_{1x}} \xrightarrow{\pi/2\, I_{2x}} \sin\Omega_1 t_1\; I_{1x}$$

Metody 2D FT NMR spektroskopie

NOE SpectroscopY a EXchange SpectroscopY



směšování: I_{1z} <-> I_{2z}
chemická výměna

$$-\cos\Omega_1 t_1\ I_{1z} \xrightarrow{\text{mixing}} -(1-f)\cos\Omega_1 t_1\ I_{1z} - f\cos\Omega_1 t_1\ I_{2z}$$

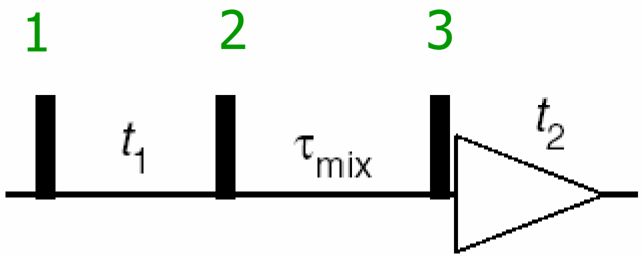
3. pulz:

$$-(1-f)\cos\Omega_1 t_1\ I_{1z} \xrightarrow{\pi/2\, I_{1x}} \xrightarrow{\pi/2\, I_{2x}} (1-f)\cos\Omega_1 t_1\ I_{1y}$$

$$-f\cos\Omega_1 t_1\ I_{2z} \xrightarrow{\pi/2\, I_{1x}} \xrightarrow{\pi/2\, I_{2x}} f\cos\Omega_1 t_1\ I_{2y}$$

Metody 2D FT NMR spektroskopie

NOE SpectroscopY a EXchange SpectroscopY



t2:

$$(1-f)\cos\Omega_1 t_1\; I_{1y} \xrightarrow{\Omega_1 t_2\, I_{1z}} \xrightarrow{\Omega_2 t_2\, I_{2z}}$$

$$(1-f)\cos\Omega_1 t_2 \cos\Omega_1 t_1\; I_{1y} - (1-f)\sin\Omega_1 t_2 \cos\Omega_1 t_1\; I_{1x}$$

$$f\cos\Omega_1 t_1\; I_{2y} \xrightarrow{\Omega_1 t_2\, I_{1z}} \xrightarrow{\Omega_2 t_2\, I_{2z}}$$

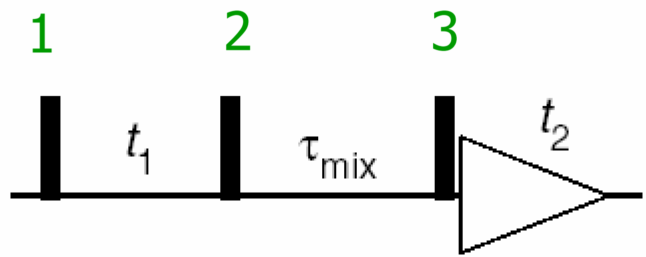
$$f\cos\Omega_2 t_2 \cos\Omega_1 t_1\; I_{2y} - f\sin\Omega_2 t_2 \cos\Omega_1 t_1\; I_{2x}$$

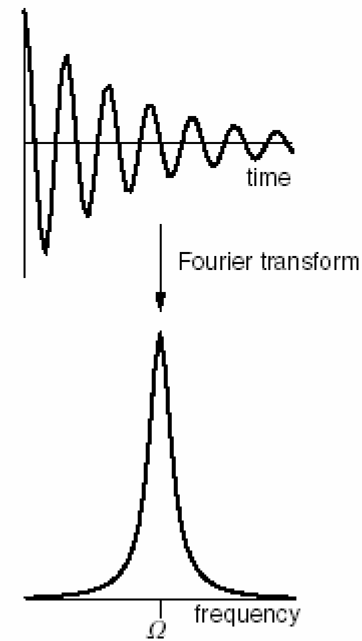
detekce $F = I_y$:

$$(1-f)\cos\Omega_1 t_2 \cos\Omega_1 t_1 + f\cos\Omega_2 t_2 \cos\Omega_1 t_1$$

Metody 2D FT NMR spektroskopie

NOE SpectroscopY a EXchange SpectroscopY





FT zpracování t_2

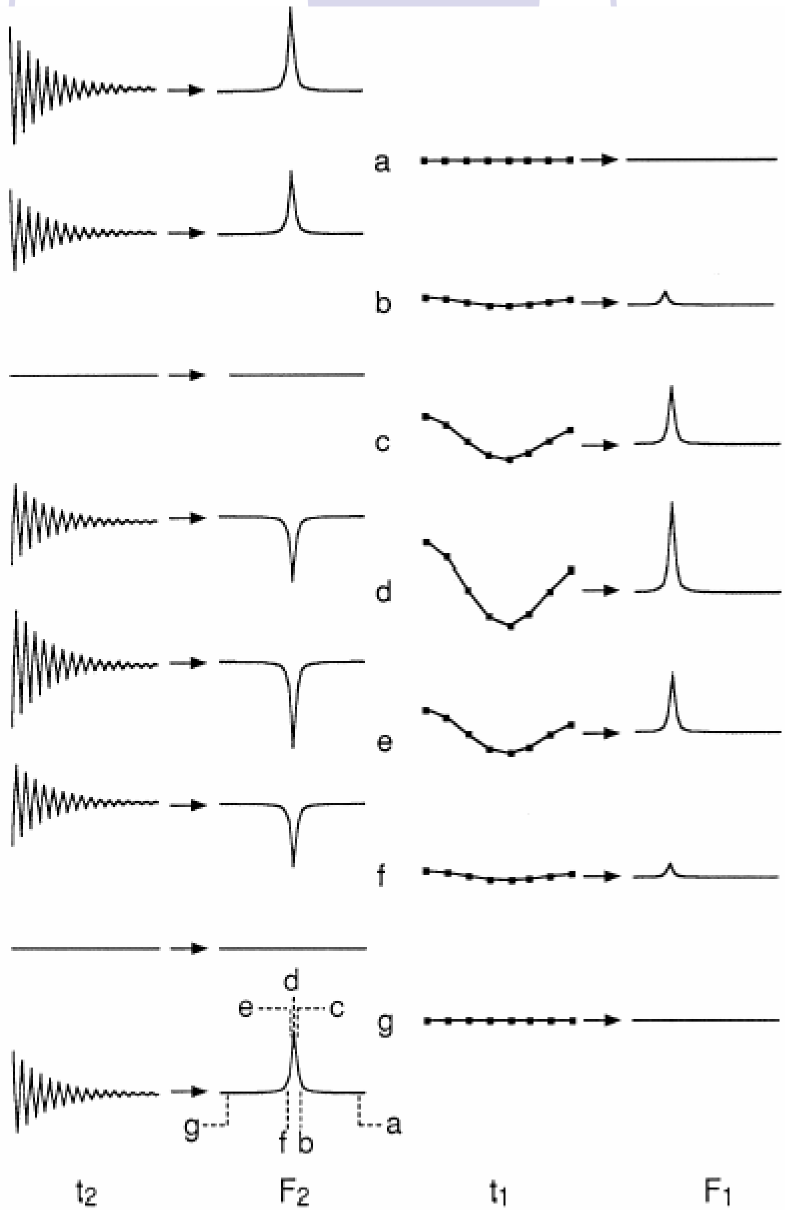
$$(1-f)A_1^{(2)}\cos\Omega_1 t_1 + fA_2^{(2)}\cos\Omega_1 t_1$$

FT zpracování t_1

$$(1-f)A_1^{(2)}A_1^{(1)} + fA_2^{(2)}A_1^{(1)}$$

Metody 2D FT NMR spektroskopie

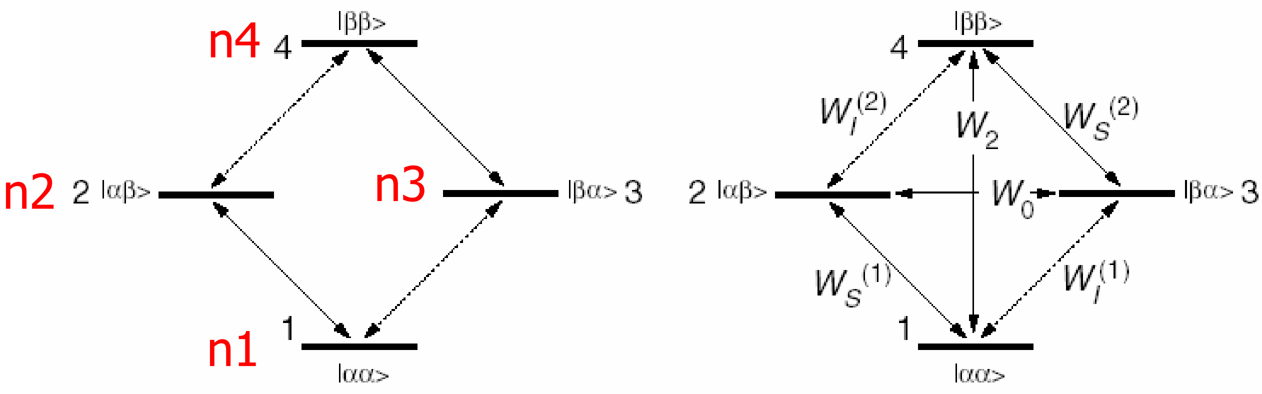
Modulace signálů



Metody 2D FT NMR spektroskopie

NOE SpectroscopY a EXchange SpectroscopY

Dvouspinový systém IS



(a) (b)

$$S_z = n_1 - n_2 + n_3 - n_4$$

$$I_z = n_1 - n_3 + n_2 - n_4$$

$$n_1 = \tfrac{1}{4}\left(E + I_z + S_z + 2I_zS_z\right)$$

$$n_2 = \tfrac{1}{4}\left(E + I_z - S_z - 2I_zS_z\right)$$

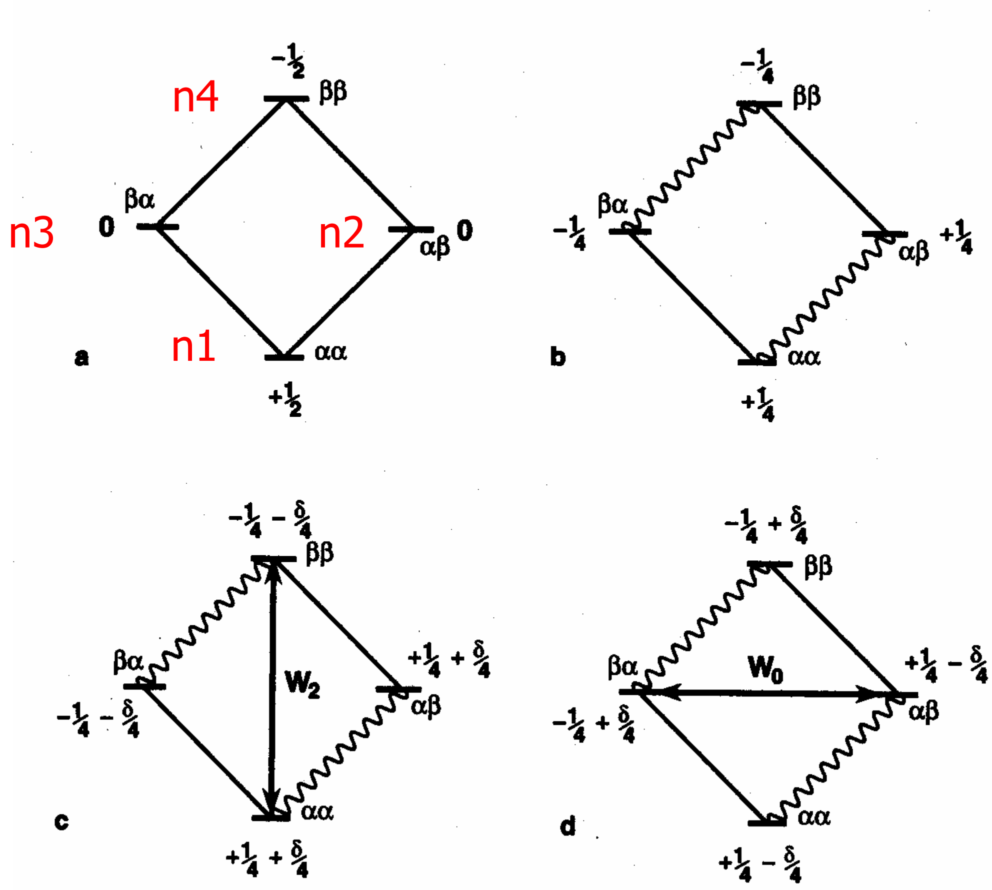
$$n_3 = \tfrac{1}{4}\left(E - I_z + S_z - 2I_zS_z\right)$$

$$n_4 = \tfrac{1}{4}\left(E - I_z - S_z + 2I_zS_z\right)$$

Metody 2D FT NMR spektroskopie

NOE SpectroscopY a EXchange SpectroscopY

Dvouspinový systém IS



S – je saturován

I -Pozitivní NOE

$\Delta = 1 + \delta$

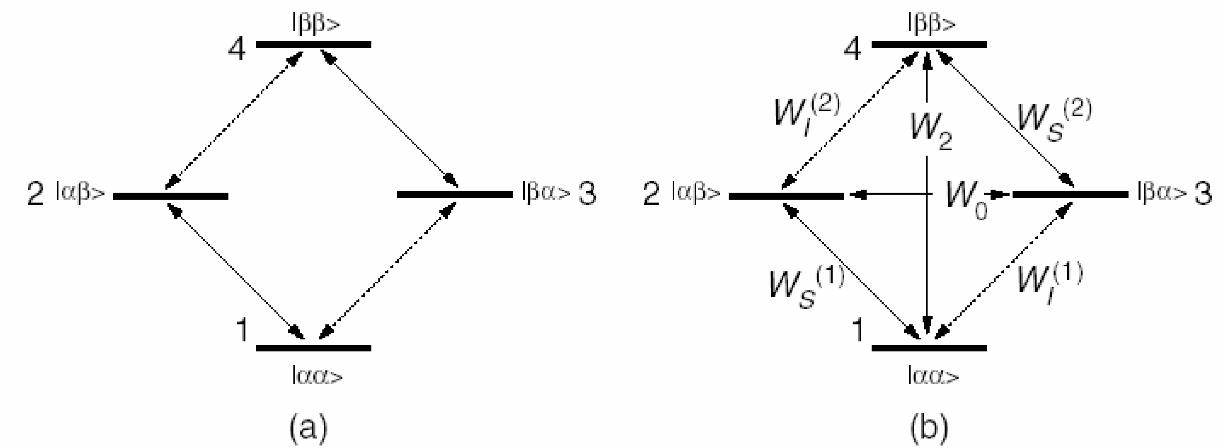
I -Negativní NOE

$\Delta = 1 - \delta$

n1 - n3 + n2 – n4

Metody 2D FT NMR spektroskopie

NOE SpectroscopY a EXchange SpectroscopY



$$\frac{dI_z}{dt} = -\left(W_I^{(1)} + W_I^{(2)} + W_2 + W_0\right)I_z - \left(W_2 - W_0\right)S_z - \left(W_I^{(1)} - W_I^{(2)}\right)2I_zS_z$$

$$\frac{dS_z}{dt} = -\left(W_2 - W_0\right)I_z - \left(W_S^{(1)} + W_S^{(2)} + W_2 + W_0\right)S_z - \left(W_S^{(1)} - W_S^{(2)}\right)2I_zS_z$$

$$\frac{d2I_zS_z}{dt} = -\left(W_I^{(1)} - W_I^{(2)}\right)I_z - \left(W_S^{(1)} - W_S^{(2)}\right)S_z - \left(W_I^{(1)} + W_I^{(2)} + W_S^{(1)} + W_S^{(2)}\right)2I_zS_z$$

Solomonovy rovnice

Metody 2D FT NMR spektroskopie

NOE SpectroscopY a EXchange SpectroscopY

Solomonovy rovnice - řešení

S_z^o, I_z^o rovnovážný velikost

I_z velikost při ozařování S

Ustálený stav

$$0 = -(I_z - I_z^o)(W_{0IS} + 2W_{1I} + W_{2IS}) + S_z^o\,(W_{2IS} - W_{0IS})$$

$$\frac{I_z - I_z^o}{S_z^o} = \frac{W_{2IS} - W_{0IS}}{(W_{0IS} + 2W_{1I} + W_{2IS})}$$

$$S_z^o = (\gamma_S/\gamma_I)I_z^o$$

NOE $$f_I\{S\} = \frac{I_z - I_z^o}{I_z^o} = (\gamma_S/\gamma_I)\frac{W_{2IS} - W_{0IS}}{(W_{0IS} + 2W_{1I} + W_{2IS})}$$

Rychlost DD příčné relaxace $(W_{2IS} - W_{0IS}) = \sigma_{IS}$

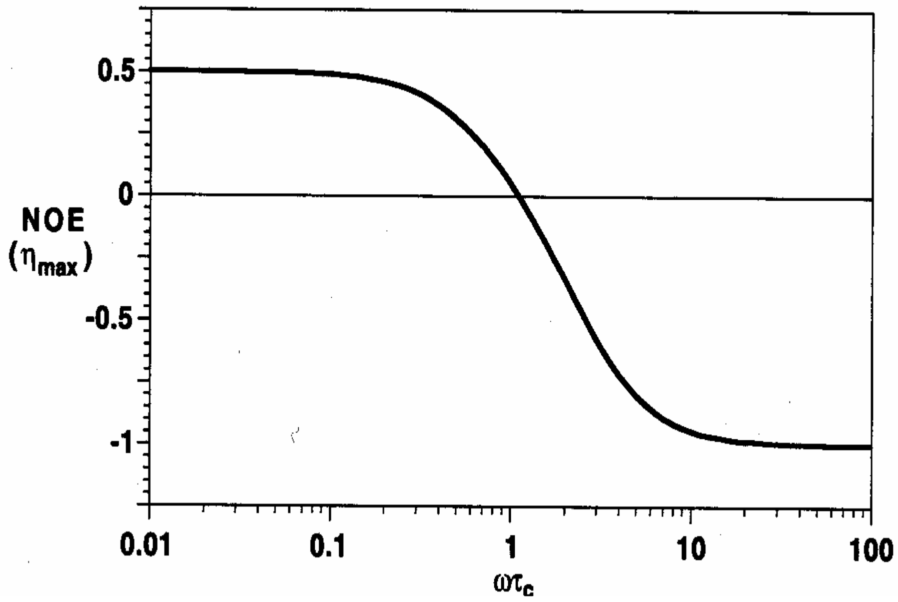
Rychlost DD podélné relaxace $(W_{0IS} + 2W_{1I} + W_{2IS}) = \rho_{IS}$

Metody 2D FT NMR spektroskopie

NOE SpectroscopY a EXchange SpectroscopY

NOE $f_I\{S\}$ =

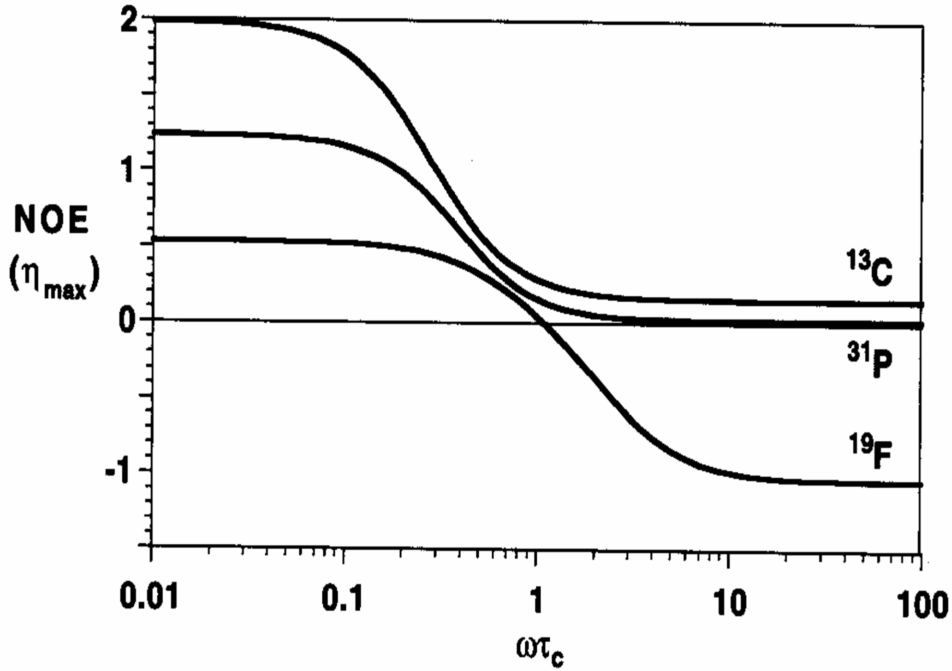
NOE max = $\gamma_S/2\gamma_I$



Metody 2D FT NMR spektroskopie

NOE SpectroscopY a EXchange SpectroscopY

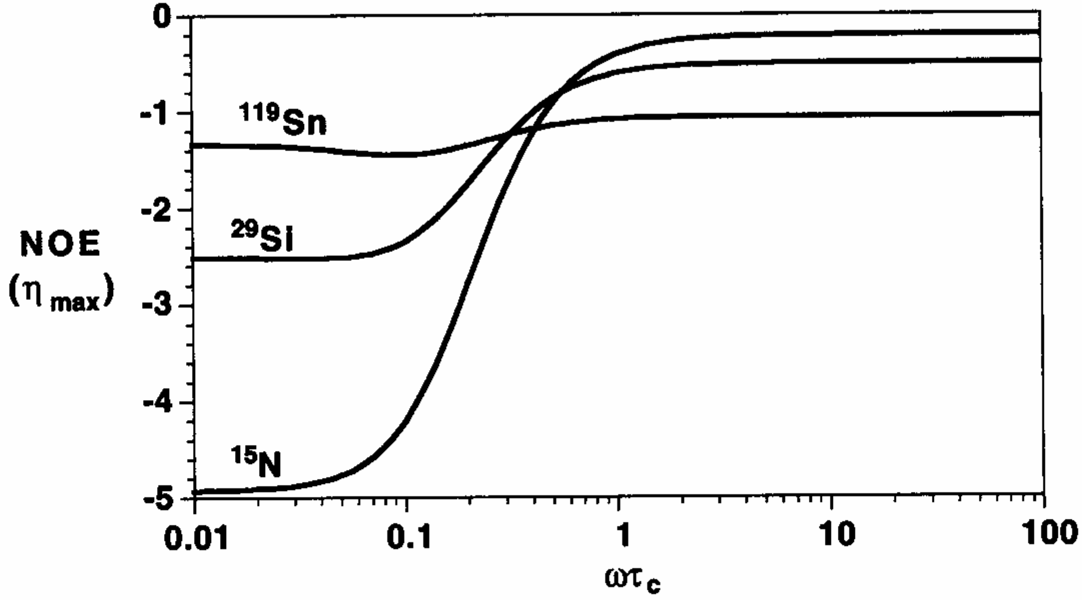
NOE max = $\gamma_S/2\gamma_I$



Metody 2D FT NMR spektroskopie

NOE SpectroscopY a EXchange SpectroscopY

NOE max = $\gamma_S/2\gamma_I$

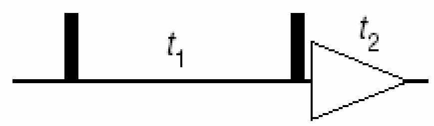


Metody 2D FT NMR spektroskopie

Experimenty s přenosem koherence - homonukleární

$$I_{1x} \xrightarrow{\text{coupling}} \underset{\text{spin 1}}{2I_{1y}I_{2z}} \xrightarrow{90°(x) \text{ to both spins}} \underset{\text{spin 2}}{2I_{1z}I_{2y}}$$

COSY



1. Pulz – spin I_1:

$$I_{1z} \xrightarrow{\pi/2\, I_{1x}} \xrightarrow{\pi/2\, I_{2x}} -I_{1y}$$

t1: - spin I_1 vliv Ω_I

$$-I_{1y} \xrightarrow{\Omega_1 t_1 I_{1z}} -\cos\Omega_1 t_1\, I_{1y} + \sin\Omega_1 t_1\, I_{1x}$$

t1: - spin I_1 vliv J_{12}

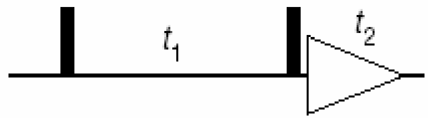
$$-\cos\Omega_1 t_1\, I_{1y} \xrightarrow{2\pi J_{12} t_1 I_{1z} I_{2z}} -\cos\pi J_{12} t_1 \cos\Omega_1 t_1\, I_{1y} + \sin\pi J_{12} t_1 \cos\Omega_1 t_1\, 2I_{1x}I$$

$$\sin\Omega_1 t_1\, I_{1x} \xrightarrow{2\pi J_{12} t_1 I_{1z} I_{2z}} \cos\pi J_{12} t_1 \sin\Omega_1 t_1\, I_{1x} + \sin\pi J_{12} t_1 \sin\Omega_1 t_1\, 2I_{1y}I_{2z}$$

Metody 2D FT NMR spektroskopie

Experimenty s přenosem koherence - homonukleární

COSY



$$-\cos \pi J_{12} t_1 \cos \Omega_1 t_1 \, I_{1y} \xrightarrow{\pi/2\, I_{1x}} \xrightarrow{\pi/2\, I_{2x}} -\cos \pi J_{12} t_1 \cos \Omega_1 t_1 \, I_{1z} \qquad \{1\}$$

$$\sin \pi J_{12} t_1 \cos \Omega_1 t_1 \, 2 I_{1x} I_{2z} \xrightarrow{\pi/2\, I_{1x}} \xrightarrow{\pi/2\, I_{2x}} -\sin \pi J_{12} t_1 \cos \Omega_1 t_1 \, 2 I_{1x} I_{2y} \qquad \{2\}$$

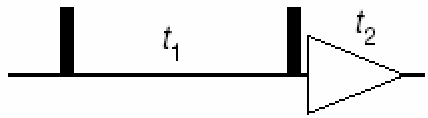
$$\cos \pi J_{12} t_1 \sin \Omega_1 t_1 \, I_{1x} \xrightarrow{\pi/2\, I_{1x}} \xrightarrow{\pi/2\, I_{2x}} \cos \pi J_{12} t_1 \sin \Omega_1 t_1 \, I_{1x} \qquad \{3\}$$

$$\sin \pi J_{12} t_1 \sin \Omega_1 t_1 \, 2 I_{1y} I_{2z} \xrightarrow{\pi/2\, I_{1x}} \xrightarrow{\pi/2\, I_{2x}} -\sin \pi J_{12} t_1 \sin \Omega_1 t_1 \, 2 I_{1z} I_{2y} \qquad \{4\}$$

Metody 2D FT NMR spektroskopie

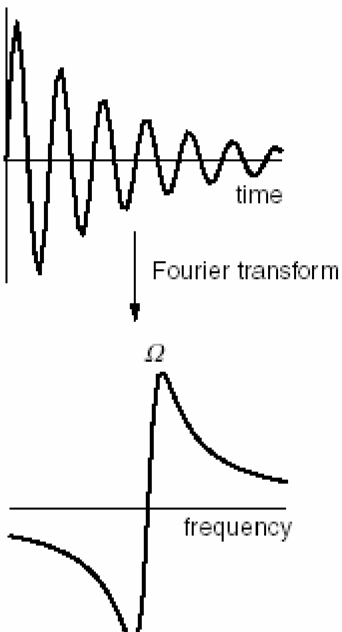
Experimenty s přenosem koherence - homonukleární

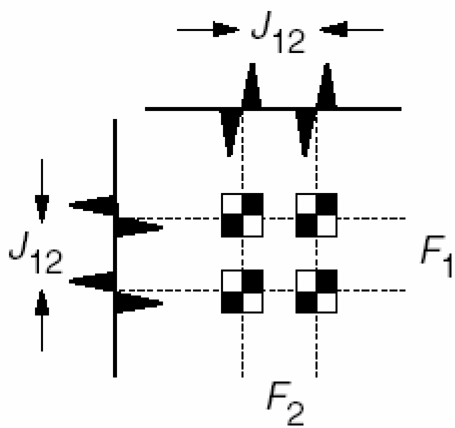
COSY



{3} $$\cos A \sin B = \tfrac{1}{2}\{\sin(B+A)+\sin(B-A)\}$$

$$\cos \pi J_{12} t_1 \sin \Omega_1 t_1 = \tfrac{1}{2}\left\{\sin\left(\Omega_1 t_1 + \pi J_{12} t_1\right) + \sin\left(\Omega_1 t_1 - \pi J_{12} t\right)\right\}$$

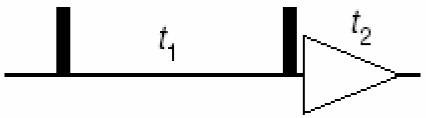


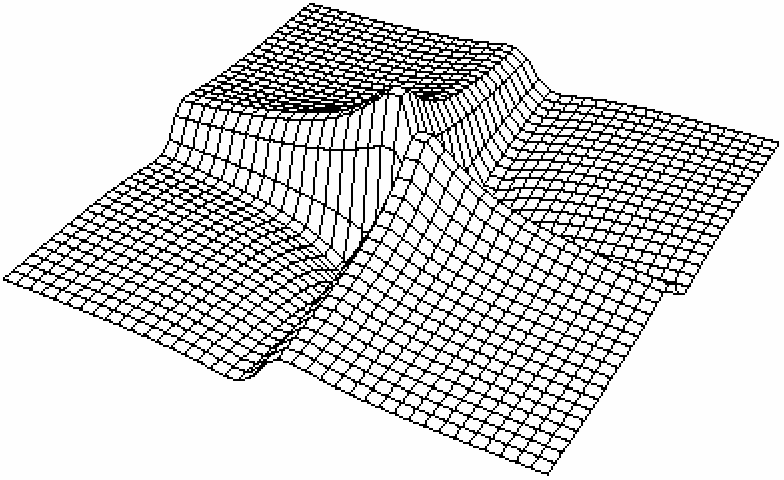


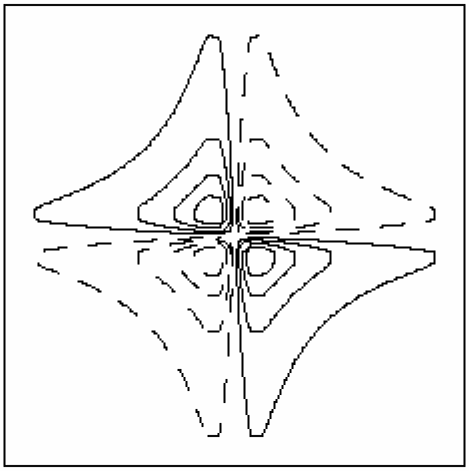
Metody 2D FT NMR spektroskopie

Experimenty s přenosem koherence - homonukleární

COSY



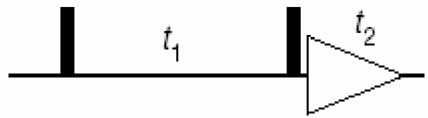




Metody 2D FT NMR spektroskopie

Experimenty s přenosem koherence - homonukleární

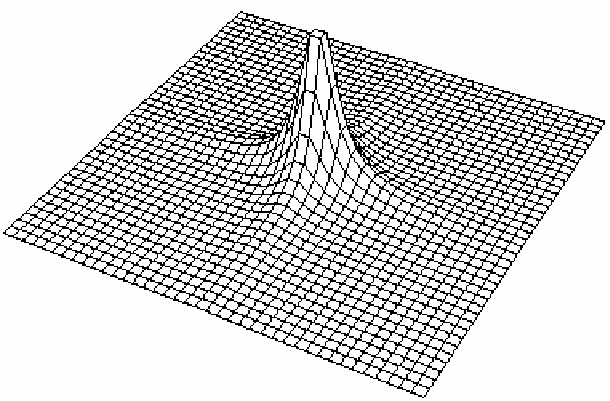
COSY

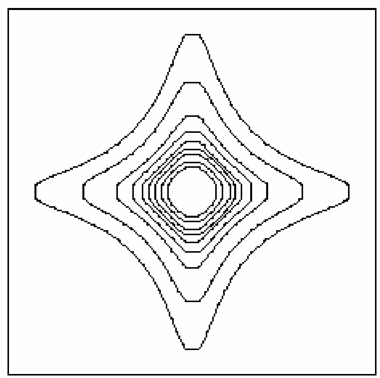


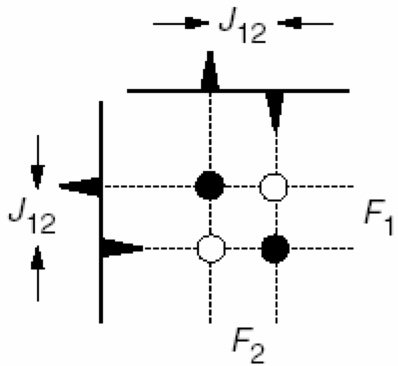
{4}

$$\sin B \sin A = \tfrac{1}{2}\left\{-\cos(B+A)+\cos(B-A)\right\}$$

$$\sin \pi J_{12}t_1 \sin \Omega_1 t = \tfrac{1}{2}\left\{-\cos\left(\Omega_1 t_1 + \pi J_{12}t_1\right)+\cos\left(\Omega_1 t_1 - \pi J_{12}t\right)\right\}$$



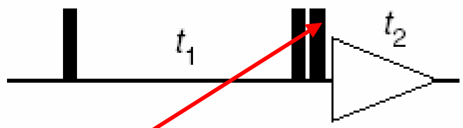




Metody 2D FT NMR spektroskopie

Experimenty s přenosem koherence - homonukleární

2 DQF COSY



{2}

$$2I_{1x}I_{2y} = 2\times\tfrac{1}{2}\left(I_{1+}+I_{1-}\right)\times\tfrac{1}{2i}\left(I_{2+}-I_{2-}\right)$$

$$= \tfrac{1}{2i}\left(I_{1+}I_{2+}-I_{1-}I_{2-}\right)+\tfrac{1}{2i}\left(-I_{1+}I_{2-}+I_{1-}I_{2+}\right)$$

$$\tfrac{1}{2i}\left(I_{1+}I_{2+}-I_{1-}I_{2-}\right)=\tfrac{1}{2i}\left[\left(I_{1x}+iI_{1y}\right)\left(I_{1x}+iI_{1y}\right)+\left(I_{2x}-iI_{2y}\right)\left(I_{2x}-iI_{2y}\right)\right]$$

$$=\tfrac{1}{2}\left[2I_{1x}I_{2y}+2I_{1y}I_{2x}\right]$$

90°(x)

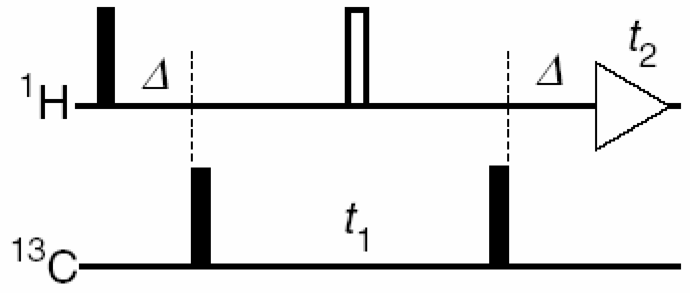
$$-\tfrac{1}{2}\sin\pi J_{12}t_1\cos\Omega_1 t_1\left(2I_{1x}I_{2y}+2I_{1y}I_{2x}\right)\xrightarrow{\pi/2 I_{1x}}\xrightarrow{\pi/2 I_{2x}}$$

$$-\tfrac{1}{2}\sin\pi J_{12}t_1\cos\Omega_1 t_1\left(2I_{1x}I_{2z}+2I_{1z}I_{2x}\right)$$

Metody 2D FT NMR spektroskopie

Experimenty s přenosem koherence - heteronukleární

HMQC -Heteronuclear Multiple-Quantum Correlation



Δ – spin I_1 (J): $$-\cos \pi J_{12}\Delta\ I_{1y} + \sin \pi J_{12}\Delta\ 2I_{1x}I_{2z}$$

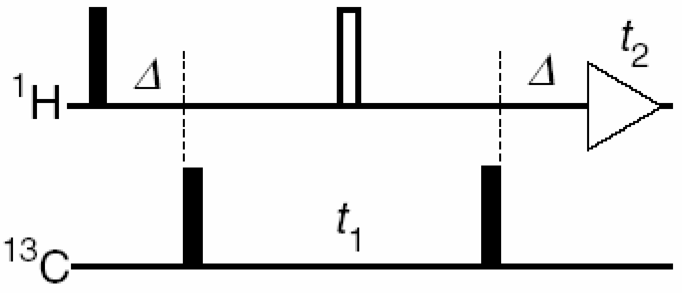
2. Pulz – spin I_2: $$2I_{1x}I_{2z} \xrightarrow{\pi/2\,I_{2x}} -2I_{1x}I_{2y}$$

t1 – vývoj spin I_2 (Ω_2): $$-2I_{1x}I_{2y} \xrightarrow{\Omega_2 t_1 I_{2z}} -\cos \Omega_2 t_1\ 2I_{1x}I_{2y} + \sin \Omega_2 t_1\ 2I_{1x}I_{2x}$$

Metody 2D FT NMR spektroskopie

Experimenty s přenosem koherence - heteronukleární

HMQC -Heteronuclear Multiple-Quantum Correlation

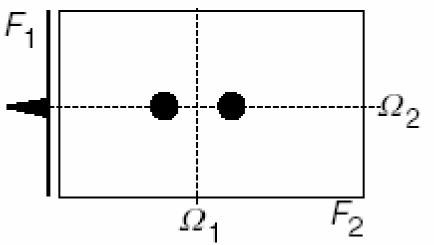


3. Pulz – spin I_2:

$$-\cos\Omega_2 t_1\; 2I_{1x}I_{2y} \xrightarrow{\pi/2\, I_{2x}} -\cos\Omega_2 t_1\; 2I_{1x}I_{2z}$$

Δ=1/2J – spin I_1 (J):

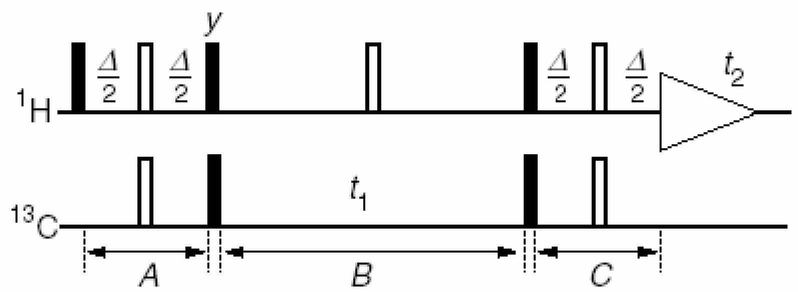
$$-\cos\Omega_2 t_1\; 2I_{1x}I_{2z} \xrightarrow{2\pi J_{12}\Delta I_{1z}I_{2z},\ \Delta=1/(2J_{12})} -\cos\Omega_2 t_1\; I_{1y}$$



Metody 2D FT NMR spektroskopie

Experimenty s přenosem koherence - heteronukleární

HSQC -Heteronuclear Single-Quantum Correlation



B: t1 – vývoj spin I_2 (Ω_2):

$$-2I_{1z}I_{2y} \xrightarrow{\Omega_2 t_1 \; I_{2z}} -\cos\Omega_2 t_1 \; 2I_{1z}I_{2y} + \sin\Omega_2 t_1 \; 2I_{1z}I_{2x}$$

90° Pulzy – spiny I_1 a I_2:

$$-\cos\Omega_2 t_1 \; 2I_{1z}I_{2y} + \sin\Omega_2 t_1 \; 2I_{1z}I_{2x} \xrightarrow{\pi/2(I_{1x}+I_{2x})}$$

$$-\cos\Omega_2 t_1 \; 2I_{1y}I_{2z} - \sin\Omega_2 t_1 \; 2I_{1y}I_{2x}$$

C: $\Delta = 1/2J$ – vývoj spin I_1 (J):

$$\cos\Omega_2 t_1 \; I_{1x}.$$

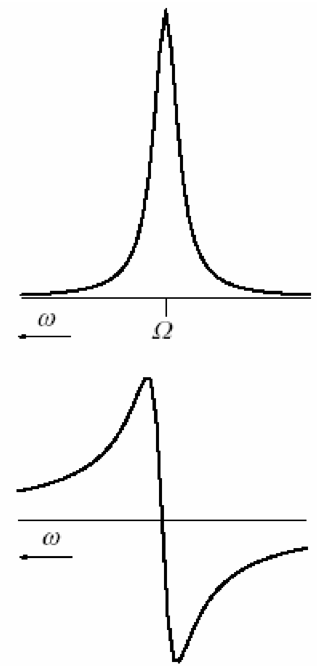
Metody 2D FT NMR spektroskopie

Tvar čar a diskriminace frekvencí – 1D spektrum

$$S_x(t) = \gamma \cos \Omega t \exp(-t/T_2) \quad S_y(t) = \gamma \sin \Omega t \exp(-t/T_2)$$

$$\begin{aligned} S(t) &= S_x(t) + iS_y(t) \\ &= \gamma(\cos \Omega t + i \sin \Omega t)\exp(-t/T_2) \\ &= \gamma \exp(i\Omega t)\exp(-t/T_2) \end{aligned}$$

$$\begin{aligned} S(\omega) &= FT[S(t)] \\ &= \gamma\{A(\omega) + iD(\omega)\} \end{aligned}$$



$$A(\omega) = \frac{1}{(\omega - \Omega)^2 T_2^2 + 1} \qquad D(\omega) = \frac{(\omega - \Omega)T_2}{(\omega - \Omega)^2 T_2^2 + 1}$$

Metody 2D FT NMR spektroskopie

Fáze

Vliv spektrometru

$$S(t) = \gamma \exp(i\phi_{instr}) \exp(i\Omega t) \exp(-t/T_2)$$

$$\mathrm{Re}[S(t)] = \gamma(\cos\phi_{instr} \cos\Omega t - \sin\phi_{instr} \sin\Omega t) \exp(-t/T_2)$$

$$\mathrm{Im}[S(t)] = \gamma(\cos\phi_{instr} \sin\Omega t + \sin\phi_{instr} \cos\Omega t) \exp(-t/T_2)$$

FT

$$S(\omega) = \gamma \exp(i\phi_{instr})\{A(\omega) + iD(\omega)\}$$

$$\mathrm{Re}[S(\omega)] = \gamma(\cos\phi_{instr} A(\omega) - \sin\phi_{instr} D(\omega))$$

$$\mathrm{Im}[S(\omega)] = \gamma(\cos\phi_{instr} D(\omega) + \sin\phi_{instr} A(\omega))$$

$(\phi_{corr} + \phi_{inst}) = 0$ (*i.e.* $\phi_{corr} = -\phi_{instr}$)

$$S(\omega)\exp(i\phi_{corr}) = \gamma \exp(i\phi_{corr}) \exp(i\phi_{instr})\{A(\omega) + iD(\omega)\}$$

$$= \gamma \exp(i(\phi_{corr} + \phi_{instr}))\{A(\omega) + iD(\omega)\}$$

Metody 2D FT NMR spektroskopie

Fáze je libovolná

Změna fáze excitačního pulzu 90_x -> 90_y

$$S_x(t) = \gamma \sin \Omega t \exp(-t/T_2) \quad S_y(t) = -\gamma \cos \Omega t \exp(-t/T_2)$$

$$\begin{aligned} S(t) &= S_x(t) + iS_y(t) \\ &= \gamma(\sin \Omega t - i \cos \Omega t)\exp(-t/T_2) \\ &= \gamma(-i)(\cos \Omega t + i \sin \Omega t)\exp(-t/T_2) \\ &= \gamma(-i)\exp(i\Omega t)\exp(-t/T_2) \\ &= \gamma \exp(i\phi_{\text{exp}})\exp(i\Omega t)\exp(-t/T_2) \end{aligned}$$

Pro Φ = -90° platí, že: $\exp(i\phi) = \cos\phi + i \sin\phi$, so that $\exp(-i\,\pi/2) = -i$.

$$S(\omega) = \gamma(-i)\{A(\omega) + iD(\omega)\}$$

$$\mathrm{Re}[S(\omega)] = \gamma D(\omega) \qquad \mathrm{Im}[S(\omega)] = -\gamma A(\omega)$$

Diskriminace frekvencí – 1D spektrum

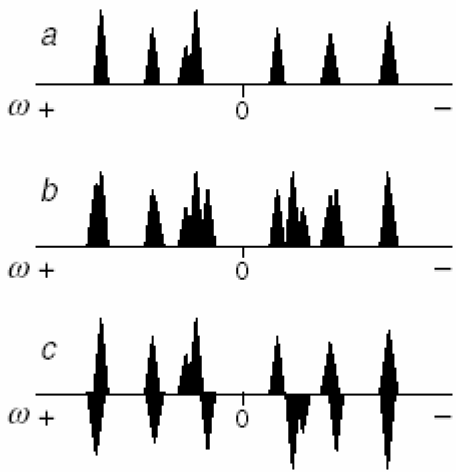
Detekce v jedné ose - x
(jedním detektorem)

$$S(t) = \gamma \cos \Omega t \exp(-t/T_2)$$

$$S(t) = \tfrac{1}{2}\gamma[\exp(i\Omega t) + \exp(-i\Omega t)]\exp(-t/T_2)$$

$$= \tfrac{1}{2}\gamma \exp(i\Omega t)\exp(-t/T_2) + \tfrac{1}{2}\gamma \exp(-i\Omega t)\exp(-t/T_2)$$

$$\mathrm{Re}[S(\omega)] = \tfrac{1}{2}\gamma A_+ + \tfrac{1}{2}\gamma A_-$$



+

$$S(t) = i\gamma \sin \Omega t \exp(-t/T_2)$$

$$S(t) = \tfrac{1}{2}\gamma[\exp(i\Omega t) - \exp(-i\Omega t)]\exp(-t/T_2)$$

$$= \tfrac{1}{2}\gamma \exp(i\Omega t)\exp(-t/T_2) - \tfrac{1}{2}\gamma \exp(-i\Omega t)\exp(-t/T_2)$$

$$\mathrm{Re}[S(\omega)] = \tfrac{1}{2}\gamma A_+ - \tfrac{1}{2}\gamma A_-$$

Detekce v jedné ose - y
(jedním detektorem)

Metody 2D FT NMR spektroskopie

Fázová a amplitufová modulace – 2D spektra

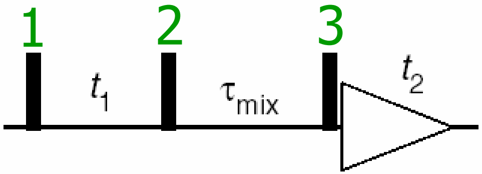
fázová modulace

$$S(t_1,t_2)_{\text{phase}} = \gamma \exp(i\Omega_1 t_1)\exp\left(-t_1/T_2^{(1)}\right)\exp(i\Omega_2 t_2)\exp\left(-t_2/T_2^{(2)}\right)$$

amplitudová modulace

$$S(t)_c = \gamma \cos(\Omega_1 t_1)\exp\left(-t_1/T_2^{(1)}\right)\exp(i\Omega_2 t_2)\exp\left(-t_2/T_2^{(2)}\right)$$

$$S(t)_s = \gamma \sin(\Omega_1 t_1)\exp\left(-t_1/T_2^{(1)}\right)\exp(i\Omega_2 t_2)\exp\left(-t_2/T_2^{(2)}\right)$$



1. pulz: 90x $\quad (1-f)\cos\Omega_1 t_1\ I_{1y} + f\cos\Omega_1 t_1\ I_{2y}$

1. pulz: 90y $\quad -(1-f)\sin\Omega_1 t_1\ I_{1y} - f\sin\Omega_1 t_1\ I_{2y}$

Metody 2D FT NMR spektroskopie

Tvar čar – 2D spektra

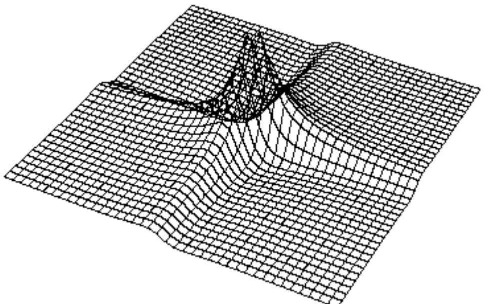
$$FT\left[\exp(i\Omega t)\exp(-t/T_2)\right] = \{A(\omega) + iD(\omega)\}$$

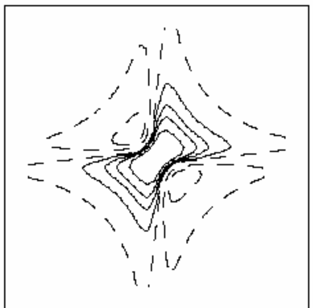
fázová modulace

$$S(t_1,\omega_2)_{\text{phase}} = \gamma \exp(i\Omega_1 t_1)\exp\left(-t_1/T_2^{(1)}\right)\left[A_+^{(2)} + iD_+^{(2)}\right]$$

$$S(\omega_1,\omega_2)_{\text{phase}} = \gamma\left[A_+^{(1)} + iD_+^{(1)}\right]\left[A_+^{(2)} + iD_+^{(2)}\right]$$

$$\text{Re}\left[S(\omega_1,\omega_2)_{\text{phase}}\right] = \gamma\left(A_+^{(1)}A_+^{(2)} - D_+^{(1)}D_+^{(2)}\right)$$





Metody 2D FT NMR spektroskopie

Tvar čar – 2D spektra

amplitudová modulace
kosinový člen

$$S(t_1,\omega_2)_c = \gamma\cos(\Omega_1 t_1)\exp\left(-t_1/T_2^{(1)}\right)\left[A_+^{(2)} + iD_+^{(2)}\right]$$

$$S(t_1,\omega_2)_c = \tfrac{1}{2}\gamma\left[\exp(i\Omega_1 t_1) + \exp(-i\Omega_1 t_1)\right]\exp\left(-t_1/T_2^{(1)}\right)\left[A_+^{(2)} + iD_+^{(2)}\right]$$

$$S(\omega_1,\omega_2)_c = \tfrac{1}{2}\gamma\left[\left\{A_+^{(1)} + iD_+^{(1)}\right\} + \left\{A_-^{(1)} - iD_-^{(1)}\right\}\right]\left[A_+^{(2)} + iD_+^{(2)}\right]$$

$$\mathrm{Re}\left[S(\omega_1,\omega_2)_c\right] = \tfrac{1}{2}\gamma\left(A_+^{(1)}A_+^{(2)} - D_+^{(1)}D_+^{(2)}\right) + \tfrac{1}{2}\gamma\left(A_-^{(1)}A_+^{(2)} - D_-^{(1)}D_+^{(2)}\right)$$

$$S(t_1,\omega_2)_c^{\mathrm{Re}} = \mathrm{Re}\left[S(t_1,\omega_2)_c\right] = \gamma\cos(\Omega_1 t_1)\exp\left(-t_1/T_2^{(1)}\right)A_+^{(2)}$$

Metody 2D FT NMR spektroskopie

Tvar čar – 2D spektra

$$S(t_1,\omega_2)_c^{\mathrm{Re}} = \mathrm{Re}\left[S(t_1,\omega_2)_c\right]$$
$$= \gamma \cos(\Omega_1 t_1)\exp\left(-t_1/T_2^{(1)}\right)A_+^{(2)}$$

$$S(t_1,\omega_2)_c^{\mathrm{Re}} = \tfrac{1}{2}\gamma\left[\exp(i\Omega_1 t_1)+\exp(-i\Omega_1 t_1)\right]\exp\left(-t_1/T_2^{(1)}\right)A_+^{(2)}$$

$$S(\omega_1,\omega_2)_c^{\mathrm{Re}} = \tfrac{1}{2}\gamma\left[\left\{A_+^{(1)}+iD_+^{(1)}\right\}+\left\{A_-^{(1)}+iD_-^{(1)}\right\}\right]A_+^{(2)}$$

$$\mathrm{Re}\left[S(\omega_1,\omega_2)_c^{\mathrm{Re}}\right] = \tfrac{1}{2}\gamma A_+^{(1)}A_+^{(2)} + \tfrac{1}{2}\gamma A_-^{(1)}A_+^{(2)}$$

Metody 2D FT NMR spektroskopie

Tvar čar – 2D spektra

amplitudová modulace
sinový člen

$$S(t_1,\omega_2)_s = \gamma \sin(\Omega_1 t_1)\exp\left(-t_1/T_2^{(1)}\right)\left[A_+^{(2)} + iD_+^{(2)}\right]$$

$$S(t_1,\omega_2)_s = \tfrac{1}{2i}\gamma\left[\exp(i\Omega_1 t_1) - \exp(-i\Omega_1 t_1)\right]\exp\left(-t_1/T_2^{(1)}\right)\left[A_+^{(2)} + iD_+^{(2)}\right]$$

$$S(\omega_1,\omega_2)_s = \tfrac{1}{2i}\gamma\left[\left\{A_+^{(1)} + iD_+^{(1)}\right\} - \left\{A_-^{(1)} - iD_-^{(1)}\right\}\right]\left[A_+^{(2)} + iD_+^{(2)}\right]$$

$$\mathrm{Im}\left[S(\omega_1,\omega_2)_s\right] = -\tfrac{1}{2}\gamma\left(A_+^{(1)}A_+^{(2)} - D_+^{(1)}D_+^{(2)}\right) + \tfrac{1}{2}\gamma\left(A_-^{(1)}A_+^{(2)} - D_-^{(1)}D_+^{(2)}\right)$$

$$S(t_1,\omega_2)_s^{\mathrm{Re}} = \mathrm{Re}\left[S(t_1,\omega_2)_s\right]$$
$$= \gamma \sin(\Omega_1 t_1)\exp\left(-t_1/T_2^{(1)}\right)A_+^{(2)}$$

Metody 2D FT NMR spektroskopie

Tvar čar – 2D spektra

$$S(t_1,\omega_2)_s^{\mathrm{Re}} = \mathrm{Re}\left[S(t_1,\omega_2)_s\right]$$
$$= \gamma \sin(\Omega_1 t_1)\exp\left(-t_1/T_2^{(1)}\right)A_+^{(2)}$$

$$S(t_1,\omega_2)_s^{\mathrm{Re}} = \tfrac{1}{2i}\gamma\left[\exp(i\Omega_1 t_1) - \exp(-i\Omega_1 t_1)\right]\exp\left(-t_1/T_2^{(1)}\right)A_+^{(2)}$$

$$S(\omega_1,\omega_2)_s^{\mathrm{Re}} = \tfrac{1}{2i}\gamma\left[\left\{A_+^{(1)} + iD_+^{(1)}\right\} - \left\{A_-^{(1)} + iD_-^{(1)}\right\}\right]A_+^{(2)}$$

$$\mathrm{Im}\left[S(\omega_1,\omega_2)_s^{\mathrm{Re}}\right] = -\tfrac{1}{2}\gamma A_+^{(1)}A_+^{(2)} + \tfrac{1}{2}\gamma A_-^{(1)}A_+^{(2)}$$

Metody 2D FT NMR spektroskopie

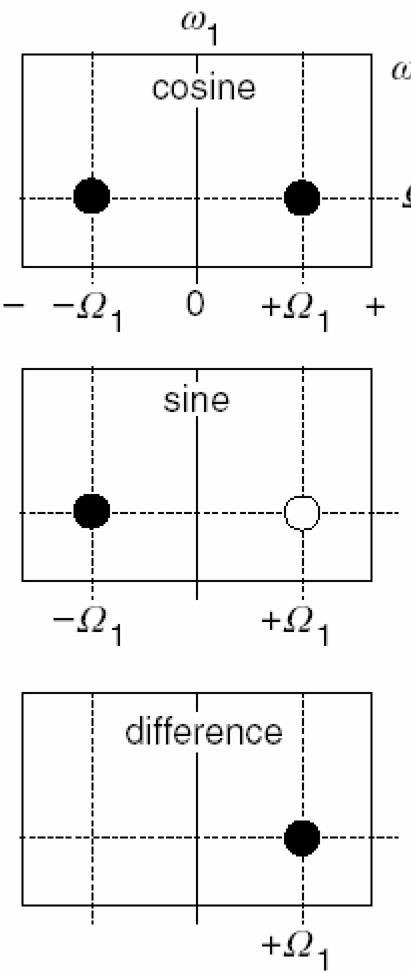
Frekvenční diskriminace a zachování absorpčího tvaru čar

Metoda States-Haberkorn a Rubenova (SHR)

$$\mathrm{Re}\left[S(\omega_1,\omega_2)_{c}^{\mathrm{Re}}\right]-\mathrm{Im}\left[S(\omega_1,\omega_2)_{s}^{\mathrm{Re}}\right]$$
$$=\left[\tfrac{1}{2}\gamma A_{+}^{(1)}A_{+}^{(2)}+\tfrac{1}{2}\gamma A_{-}^{(1)}A_{+}^{(2)}\right]-\left[-\tfrac{1}{2}\gamma A_{+}^{(1)}A_{+}^{(2)}+\tfrac{1}{2}\gamma A_{-}^{(1)}A_{+}^{(2)}\right]$$
$$=\gamma A_{+}^{(1)}A_{+}^{(2)}$$

$$(t_1,\omega_2)_{\mathrm{SHR}}=S(t_1,\omega_2)_{c}^{\mathrm{Re}}+iS(t_1,\omega_2)_{s}^{\mathrm{Re}}$$
$$=\gamma\cos(\Omega_1 t_1)\exp\left(-t_1/T_2^{(1)}\right)A_{+}^{(2)}+i\gamma\sin(\Omega_1 t_1)\exp\left(-t_1/T_2^{(1)}\right)A_{+}^{(2)}$$
$$=\gamma\exp(i\Omega_1 t_1)\exp\left(-t_1/T_2^{(1)}\right)A_{+}^{(2)}$$

$$S(\omega_1,\omega_2)_{\mathrm{SHR}}=\gamma\left[A_{+}^{(1)}+iD_{+}^{(1)}\right]A_{+}^{(2)}$$
$$=\gamma A_{+}^{(1)}A_{+}^{(2)}+iD_{+}^{(1)}A_{+}^{(2)}$$



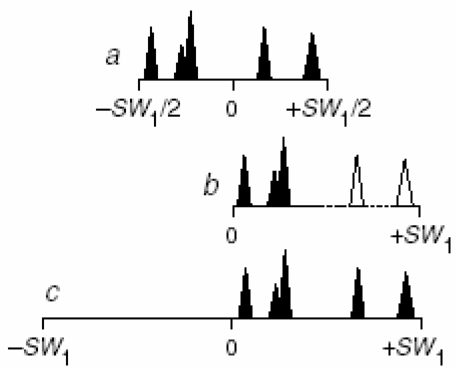
Metody 2D FT NMR spektroskopie

Frekvenční diskriminace a zachování absorpčího tvaru čar

Metoda TPPI –
Time Proportional Phase Incrementation

$$\cos(\Omega_1 t_1 + \phi) = \cos\Omega_1 t\cos\phi - \sin\Omega_1 t\sin\phi$$

$$\cos(\Omega_1 t_1 + \pi/2) = \cos\Omega_1 t\cos\pi/2 - \sin\Omega_1 t\sin\pi/2$$
$$= -\sin\Omega_1 t$$



$$\phi(t_1) = \omega_{\text{additional}} t_1$$

of $\omega_{\text{additional}}$ are radians s^{-1}, that is $\omega_{\text{additiona}}$

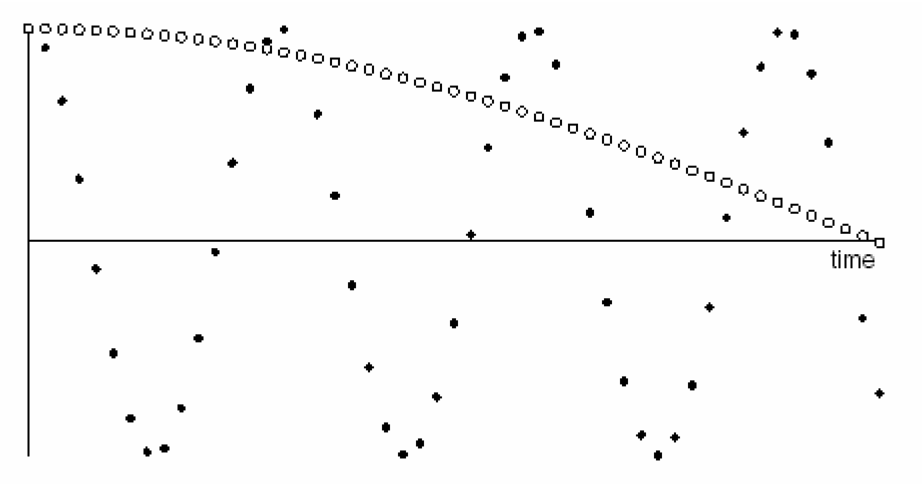
$$\cos(\Omega_1 t_1 + \phi(t_1)) = \cos(\Omega_1 t_1 + \omega_{\text{additional}} t_1)$$
$$= \cos(\Omega_1 + \omega_{\text{additional}})t_1$$

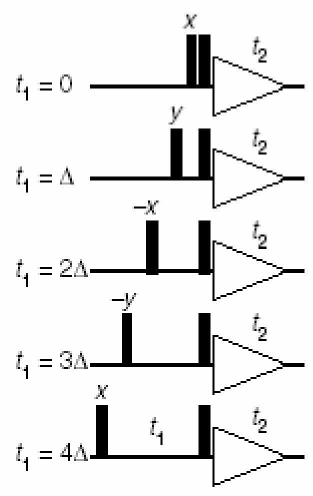
Metody 2D FT NMR spektroskopie

Frekvenční diskriminace a zachování absorpčího tvaru čar

Metoda TPPI – Time Proportional Phase Incrementation

$$\omega_{\text{additional}} t_1 = 2\pi \left(\frac{SW_1}{2} \right) (n\Delta_1)$$
$$= 2\pi \left(\frac{SW_1}{2} \right) \left(n \frac{1}{2\,SW_1} \right)$$
$$= n \frac{\pi}{2}$$





Metody 2D FT NMR spektroskopie

Frekvenční diskriminace a zachování absorpčího tvaru čar

Metoda Echo-Antiecho

P-spektrum - antiecho

$$S(t_1,t_2)_{\mathrm{P}} = \gamma \exp(i\Omega_1 t_1)\exp\left(-t_1/T_2^{(1)}\right)\exp(i\Omega_2 t_2)\exp\left(-t_2/T_2^{(2)}\right)$$

N-spektrum - echo

$$S(t_1,t_2)_{\mathrm{N}} = \gamma \exp(-i\Omega_1 t_1)\exp\left(-t_1/T_2^{(1)}\right)\exp(i\Omega_2 t_2)\exp\left(-t_2/T_2^{(2)}\right)$$

$$\tfrac{1}{2}\left[S(t_1,t_2)_{\mathrm{P}} + S(t_1,t_2)_{\mathrm{N}}\right] =$$

$$\tfrac{1}{2}\gamma\left[\exp(i\Omega_1 t_1) + \exp(-i\Omega_1 t_1)\right]\exp\left(-t_1/T_2^{(1)}\right)\exp(i\Omega_2 t_2)\exp\left(-t_2/T_2^{(2)}\right)$$

Kosinová modulace

$$= \gamma \cos(\Omega_1 t_1)\exp\left(-t_1/T_2^{(1)}\right)\exp(i\Omega_2 t_2)\exp\left(-t_2/T_2^{(2)}\right)$$

$$\tfrac{1}{2i}\left[S(t_1,t_2)_{\mathrm{P}} - S(t_1,t_2)_{\mathrm{N}}\right] =$$

$$\tfrac{1}{2i}\gamma\left[\exp(i\Omega_1 t_1) - \exp(-i\Omega_1 t_1)\right]\exp\left(-t_1/T_2^{(1)}\right)\exp(i\Omega_2 t_2)\exp\left(-t_2/T_2^{(2}\right.$$

Sinová modulace

$$= \gamma \sin(\Omega_1 t_1)\exp\left(-t_1/T_2^{(1)}\right)\exp(i\Omega_2 t_2)\exp\left(-t_2/T_2^{(2)}\right)$$

Metoda SHR