

Fyzikálně-chemické základy nukleární magnetické rezonance

NMR a elektromagnetické spektrum

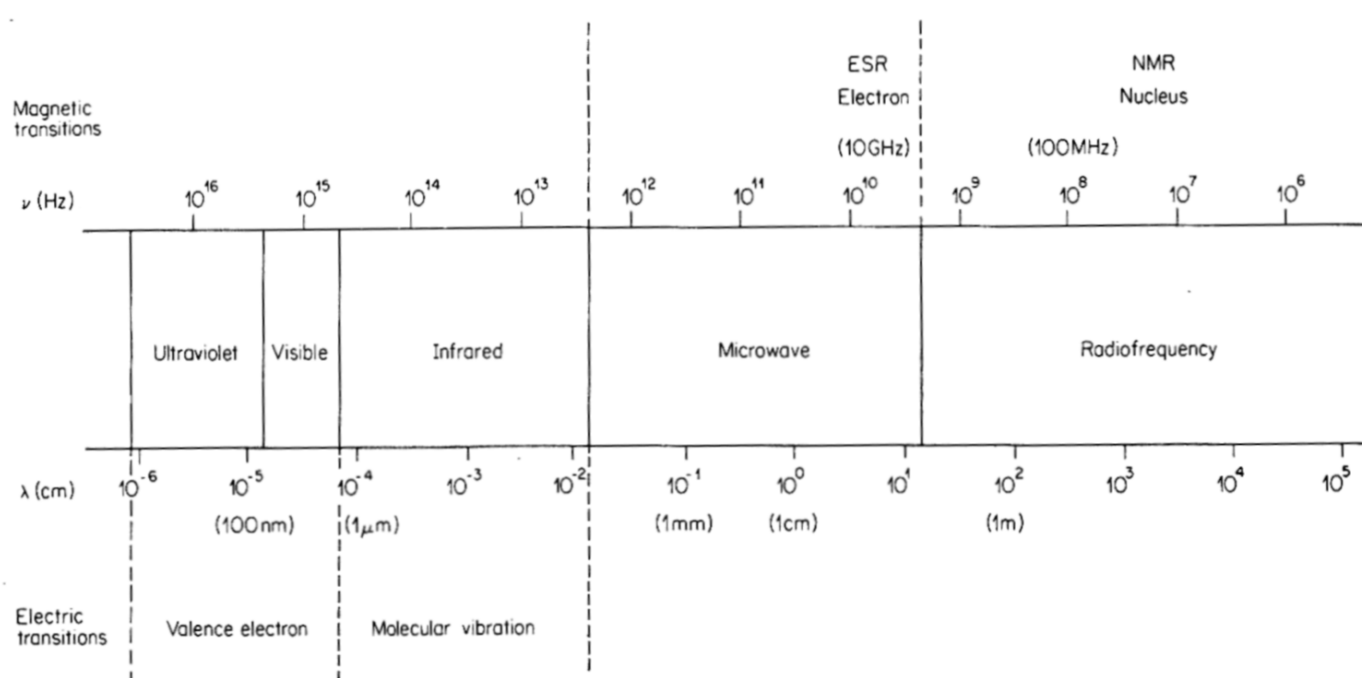
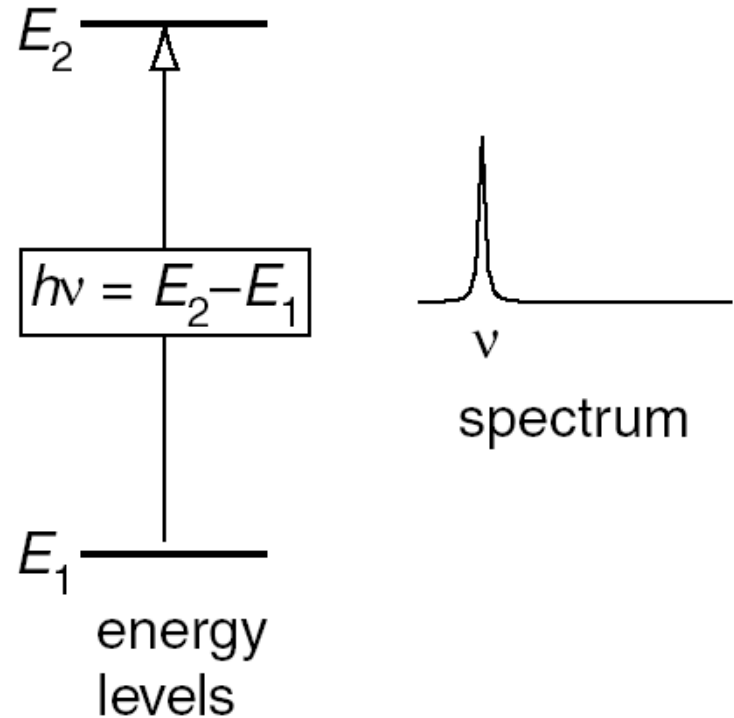


Figure 1.2 Spectral regions of the electromagnetic spectrum of interest in biological investigations

NMR a energiové hladiny

$$\Delta E = h\nu$$

h - Planckova konstanta = $6,626 \cdot 10^{-34}$ J.s



NMR a energiové hladiny

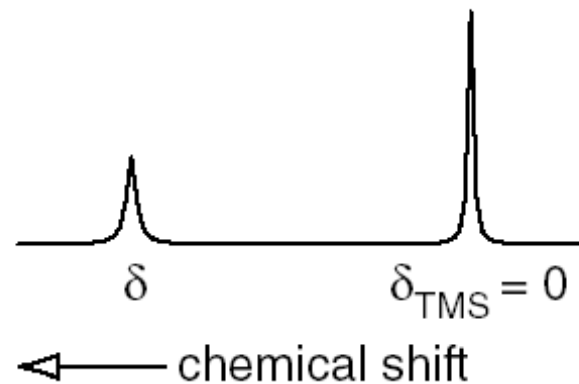
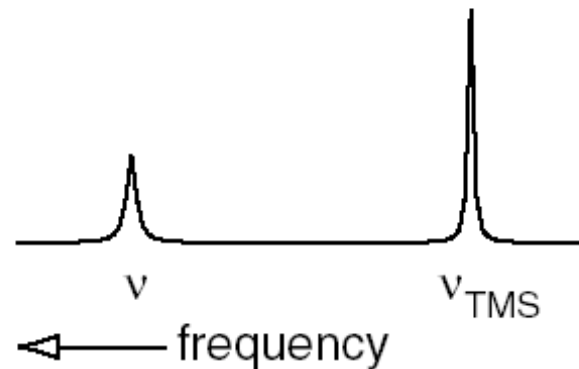
Chemický posun

$$\delta = \frac{\nu - \nu_{\text{TMS}}}{\nu_{\text{TMS}}}$$

$$\delta_{\text{ppm}} = 10^6 \times \frac{\nu - \nu_{\text{TMS}}}{\nu_{\text{TMS}}}$$

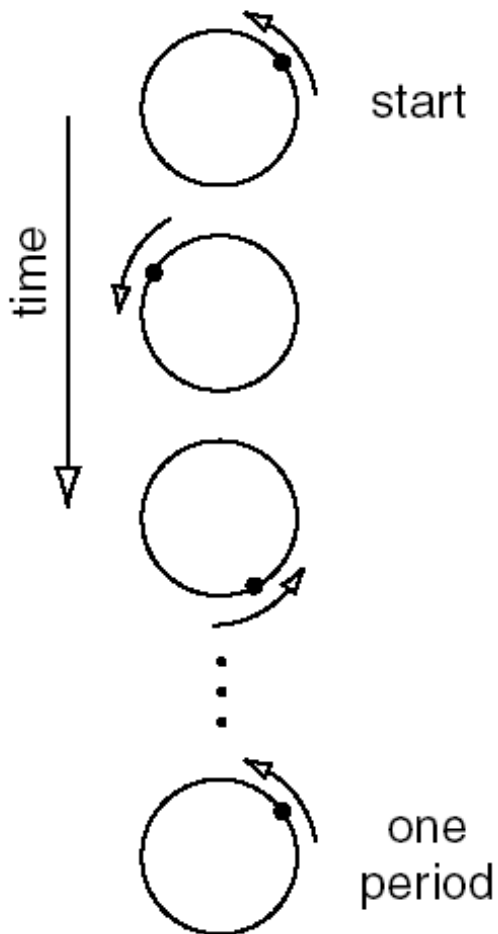
$$\begin{aligned}(\delta_2 - \delta_1) &= 10^6 \times \frac{\nu_2 - \nu_{\text{TMS}}}{\nu_{\text{TMS}}} - 10^6 \times \frac{\nu_1 - \nu_{\text{TMS}}}{\nu_{\text{TMS}}} \\ &= 10^6 \times \frac{\nu_2 - \nu_1}{\nu_{\text{TMS}}}\end{aligned}$$

$$(\nu_2 - \nu_1) = 10^{-6} \times \nu_{\text{TMS}} \times (\delta_2 - \delta_1)$$



NMR a energiové hladiny

Rotační frekvence a energie



$$\nu = \frac{1}{\tau}$$

$$\omega = \frac{2\pi}{\tau}$$

$$\nu = \frac{\omega}{2\pi} \quad \text{or} \quad \omega = 2\pi\nu$$

$$E = h \frac{\omega}{2\pi}$$
$$= \hbar\omega$$

The slide features five light purple circles arranged horizontally. The second circle from the left is outlined in white and contains the main title. The other four circles are solid light purple.

NMR a energiové hladiny

Nukleární spin a spinové stavy

$I = k * \frac{1}{2}$, k je celé číslo 0, 1, 2 spinové kvantové číslo

$m = -I, -I+1, -I+2 \dots I-2, I-1, I$ magnetické kvantové číslo

pro $I = \frac{1}{2}$ $m = \frac{1}{2}$ α stav
 $m = -\frac{1}{2}$ β stav

Pro 2 spiny s $I = \frac{1}{2}$ existují 4 možné kombinace stavů $\alpha\alpha$, $\alpha\beta$, $\beta\alpha$ a $\beta\beta$

Pro 3 spiny s $I = \frac{1}{2}$ existuje 8 možností kombinace stavů

$\alpha\alpha\alpha$, $\alpha\alpha\beta$, $\alpha\beta\alpha$, $\beta\alpha\alpha$, $\alpha\beta\beta$, $\beta\alpha\beta$, $\beta\beta\alpha$, a $\beta\beta\beta$

Animated course – Basic concepts

<..\..\QSU NMR course animated\webcourse\basic.htm>



NMR a energiové hladiny

$$E_m = m * \nu_{0,1}$$

pořadové číslo spinu

$$\nu_0 - \text{Larmorova frekvence}$$

$$E_\alpha = + 1/2 * \nu_{0,1} \quad E_\beta = - 1/2 * \nu_{0,1}$$

$$\nu_{0,1} = -\frac{1}{2\pi} \gamma_1 (1 + \delta_1) B_0$$

$$\omega_0 = -\gamma (1 + \delta) B_0$$

γ - magnetogyrická konstanta (poměr) [rad. s⁻¹.T⁻¹]

pro ¹H $\gamma = +2,67 \times 10^8 \text{ rad. s}^{-1}.\text{T}^{-1} = 42\,494\,369 \text{ s}^{-1}.\text{T}^{-1}$

Při $B_0 = 4.7 \text{ T}$

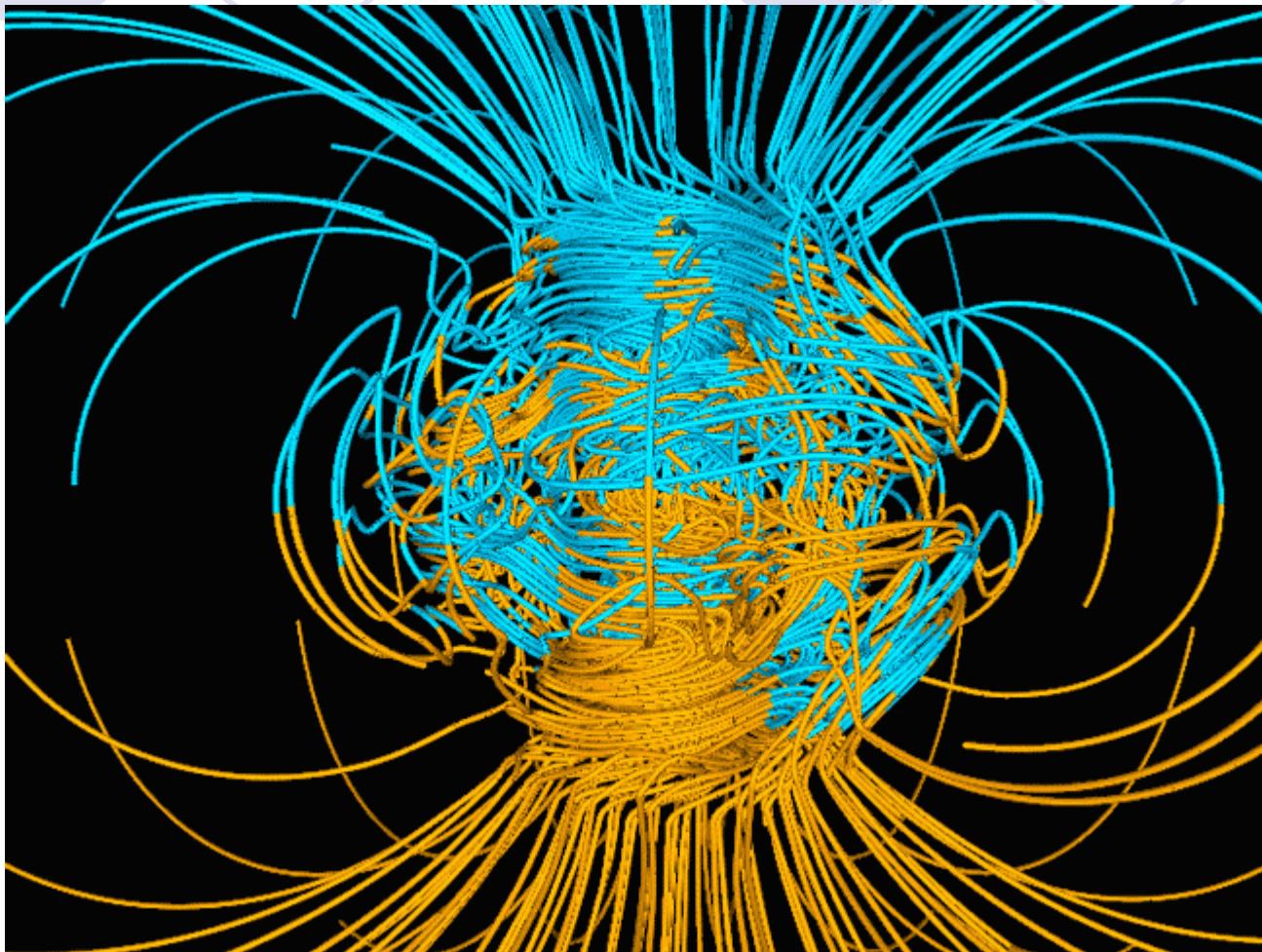
$$\nu_0 = -200 \times 10^6 \text{ Hz}$$

a

$$\omega_0 = -1,225 \times 10^9 \text{ rad.s}^{-1}$$

Zemské magnetické pole $B_0 = 40 \mu\text{T}$, $\nu_0 = -1.7 \text{ kHz}$

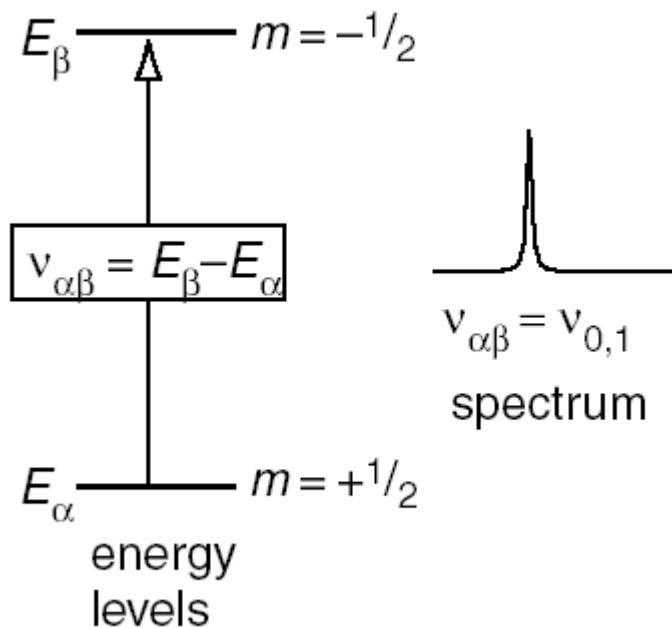
The strength of the field at the Earth's surface at this time ranges from less than 30 microteslas (0.3 gauss) in an area including most of South America and South Africa to over 60 microteslas (0.6 gauss) around the magnetic poles in northern Canada and south of Australia, and in part of Siberia.



NMR a energiové hladiny

Spektrum

Výběrové pravidlo



$$\Delta m = m(\text{initial state}) - m(\text{final state}) = \pm 1.$$

$$\begin{aligned} \nu_{\alpha\beta} &= E_\beta - E_\alpha \\ &= -\frac{1}{2}\nu_{0,1} - \left(+\frac{1}{2}\nu_{0,1}\right) \\ &= -\nu_{0,1}. \end{aligned}$$

NMR a energiové hladiny

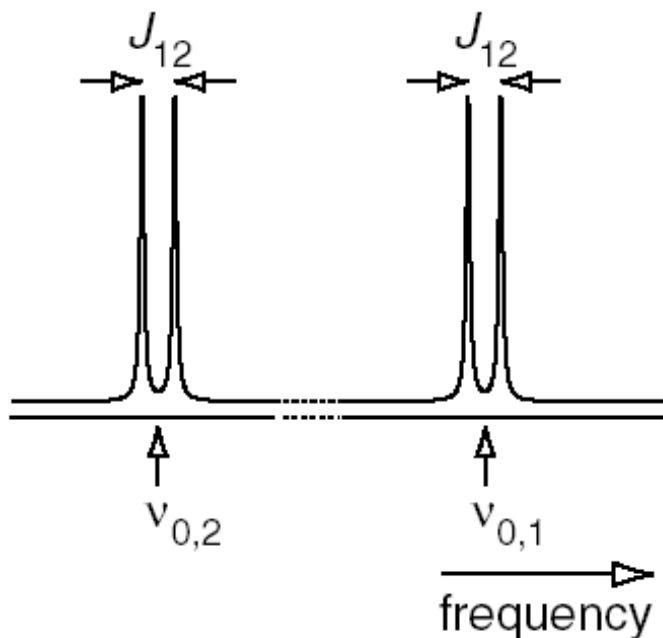
Dva spiny

Larmorova frekvence

$$\nu_{0,1} = -\frac{1}{2\pi} \gamma_1 (1 + \delta_1) B_0$$

$$\nu_{0,2} = -\frac{1}{2\pi} \gamma_2 (1 + \delta_2) B_0.$$

$\gamma_1 = \gamma_2$ homonukleární systém
 $\gamma_1 \neq \gamma_2$ heteronukleární systém

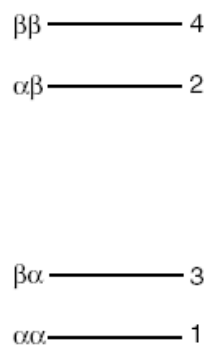
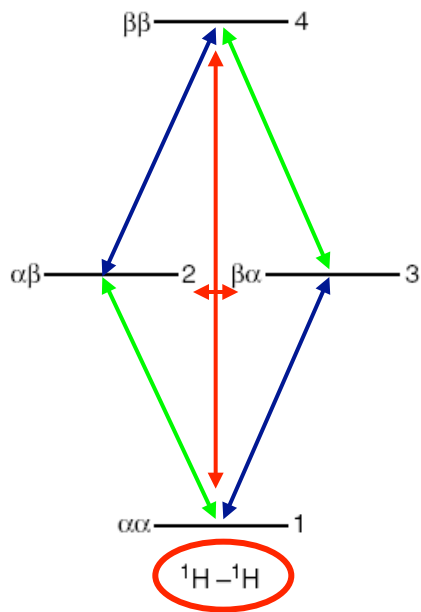


number	spin states	energy
1	$\alpha\alpha$	$+\frac{1}{2}\nu_{0,1} + \frac{1}{2}\nu_{0,2} + \frac{1}{4}J_{12}$
2	$\alpha\beta$	$+\frac{1}{2}\nu_{0,1} - \frac{1}{2}\nu_{0,2} - \frac{1}{4}J_{12}$
3	$\beta\alpha$	$-\frac{1}{2}\nu_{0,1} + \frac{1}{2}\nu_{0,2} - \frac{1}{4}J_{12}$
4	$\beta\beta$	$-\frac{1}{2}\nu_{0,1} - \frac{1}{2}\nu_{0,2} + \frac{1}{4}J_{12}$

$$E_{m_1 m_2} = m_1 \nu_{0,1} + m_2 \nu_{0,2} + m_1 m_2 J_{12}$$

NMR a energiové hladiny

Dva spiny



$^{13}\text{C}-^1\text{H}$

$$M = m_1 + m_2.$$

number	spin states	M
1	$\alpha\alpha$	1
2	$\alpha\beta$	0
3	$\beta\alpha$	0
4	$\beta\beta$	-1

Výběrové pravidlo $\Delta M = \pm 1$
 Dovolené přechody mezi
 1-3 a 2-4, 1-2 a 3-4,

NMR a energiové hladiny

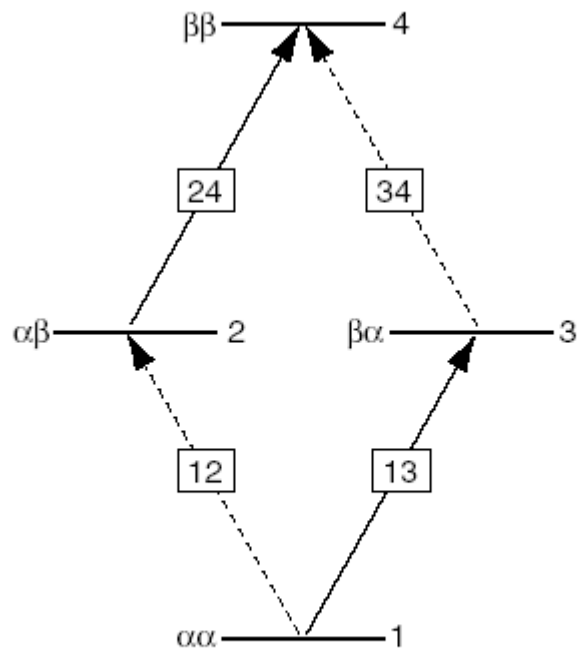
Dva spiny

$$\begin{aligned}\nu_{12} &= E_2 - E_1 \\ &= +\frac{1}{2}\nu_{0,1} - \frac{1}{2}\nu_{0,2} - \frac{1}{4}J_{12} - \left(\frac{1}{2}\nu_{0,1} + \frac{1}{2}\nu_{0,2} + \frac{1}{4}J_{12}\right) \\ &= -\nu_{0,2} - \frac{1}{2}J_{12}.\end{aligned}$$

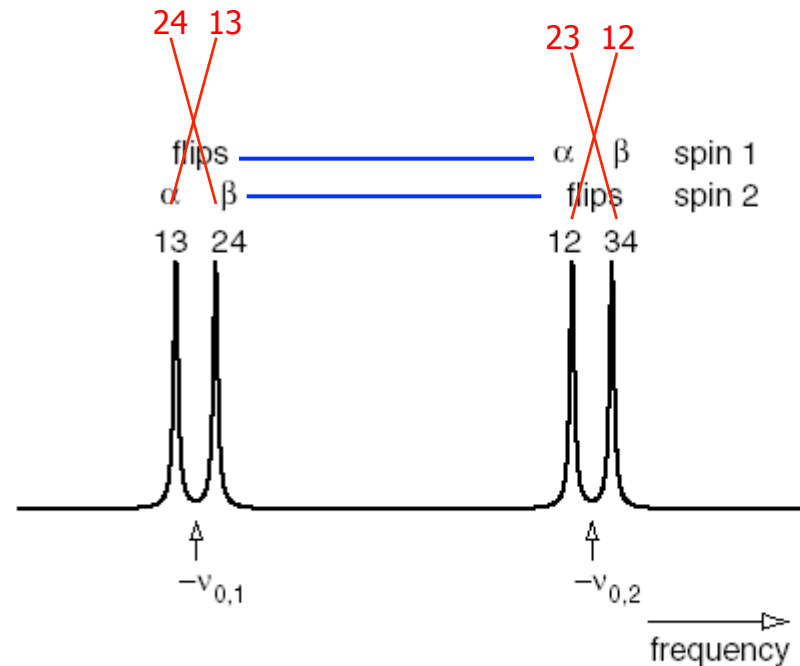
transition	spin states	frequency
1 \rightarrow 2	$\alpha\alpha \rightarrow \alpha\beta$	$-\nu_{0,2} - \frac{1}{2}J_{12}$
3 \rightarrow 4	$\beta\alpha \rightarrow \beta\beta$	$-\nu_{0,2} + \frac{1}{2}J_{12}$
1 \rightarrow 3	$\alpha\alpha \rightarrow \beta\alpha$	$-\nu_{0,1} - \frac{1}{2}J_{12}$
2 \rightarrow 4	$\alpha\beta \rightarrow \beta\beta$	$-\nu_{0,1} + \frac{1}{2}J_{12}$

NMR a energiové hladiny

Dva spiny – jedno-kvantové přechody



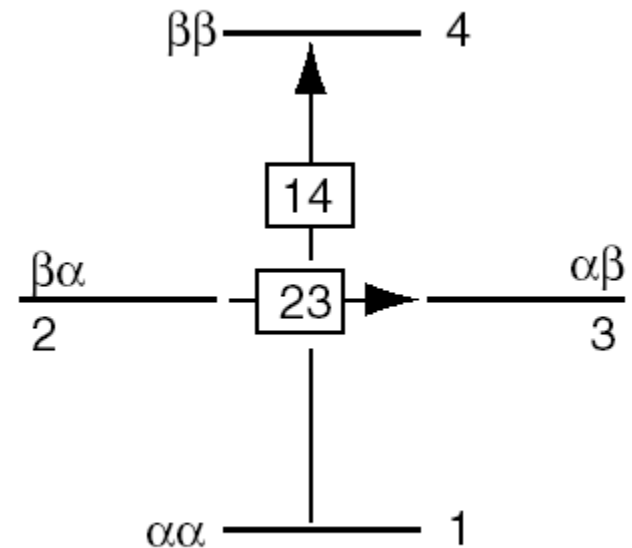
Pro $J < 0$



NMR a energiové hladiny

Dva spiny – více-kvantové přechody

number	spin states	M
1	$\alpha\alpha$	1
2	$\alpha\beta$	0
3	$\beta\alpha$	0
4	$\beta\beta$	-1



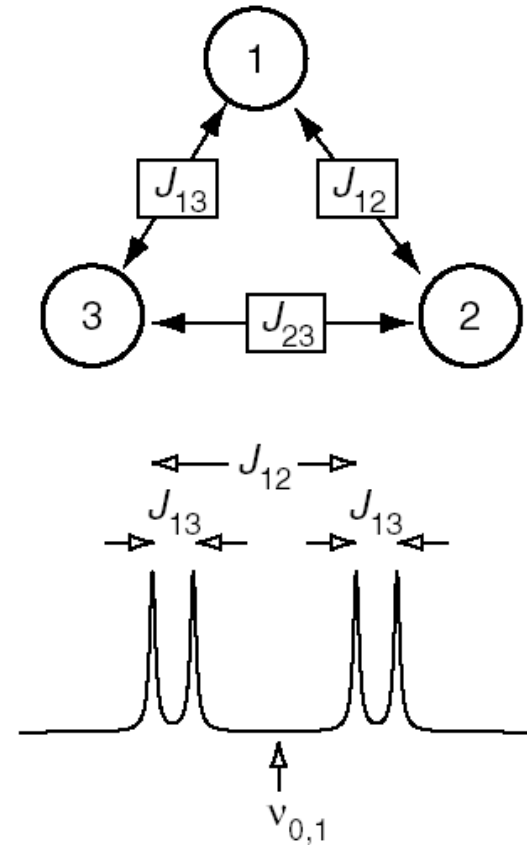
14 – dvou-kvantový přechod
23 – nul-kvantový přechod

NMR a energiové hladiny

Tři spiny

$$E_{m_1 m_2 m_3} = m_1 \nu_{0,1} + m_2 \nu_{0,2} + m_3 \nu_{0,3} + m_1 m_2 J_{12} + m_1 m_3 J_{13} + m_2 m_3 J_{23}$$

number	spin states	M	energy
1	$\alpha\alpha\alpha$	$\frac{3}{2}$	$+\frac{1}{2}\nu_{0,1} + \frac{1}{2}\nu_{0,2} + \frac{1}{2}\nu_{0,3} + \frac{1}{4}J_{12} + \frac{1}{4}J_{13} + \frac{1}{4}J_{23}$
2	$\alpha\beta\alpha$	$\frac{1}{2}$	$+\frac{1}{2}\nu_{0,1} - \frac{1}{2}\nu_{0,2} + \frac{1}{2}\nu_{0,3} - \frac{1}{4}J_{12} + \frac{1}{4}J_{13} - \frac{1}{4}J_{23}$
3	$\beta\alpha\alpha$	$\frac{1}{2}$	$-\frac{1}{2}\nu_{0,1} + \frac{1}{2}\nu_{0,2} + \frac{1}{2}\nu_{0,3} - \frac{1}{4}J_{12} - \frac{1}{4}J_{13} + \frac{1}{4}J_{23}$
4	$\beta\beta\alpha$	$-\frac{1}{2}$	$-\frac{1}{2}\nu_{0,1} - \frac{1}{2}\nu_{0,2} + \frac{1}{2}\nu_{0,3} + \frac{1}{4}J_{12} - \frac{1}{4}J_{13} - \frac{1}{4}J_{23}$
5	$\alpha\alpha\beta$	$\frac{1}{2}$	$+\frac{1}{2}\nu_{0,1} + \frac{1}{2}\nu_{0,2} - \frac{1}{2}\nu_{0,3} + \frac{1}{4}J_{12} - \frac{1}{4}J_{13} - \frac{1}{4}J_{23}$
6	$\alpha\beta\beta$	$-\frac{1}{2}$	$+\frac{1}{2}\nu_{0,1} - \frac{1}{2}\nu_{0,2} - \frac{1}{2}\nu_{0,3} - \frac{1}{4}J_{12} - \frac{1}{4}J_{13} + \frac{1}{4}J_{23}$
7	$\beta\alpha\beta$	$-\frac{1}{2}$	$-\frac{1}{2}\nu_{0,1} + \frac{1}{2}\nu_{0,2} - \frac{1}{2}\nu_{0,3} - \frac{1}{4}J_{12} + \frac{1}{4}J_{13} - \frac{1}{4}J_{23}$
8	$\beta\beta\beta$	$-\frac{3}{2}$	$-\frac{1}{2}\nu_{0,1} - \frac{1}{2}\nu_{0,2} - \frac{1}{2}\nu_{0,3} + \frac{1}{4}J_{12} + \frac{1}{4}J_{13} + \frac{1}{4}J_{23}$





NMR a energiové hladiny

Tři spiny

Spin 3 β

$\beta\beta\beta$ ----- 8

Spin 3 α

$\beta\beta\alpha$ ----- 4

$\alpha\beta\beta$ ----- 6 $\beta\alpha\beta$ ----- 7

$\alpha\beta\alpha$ ----- 2 $\beta\alpha\alpha$ ----- 3

$\alpha\alpha\beta$ ----- 5

$\alpha\alpha\alpha$ ----- 1

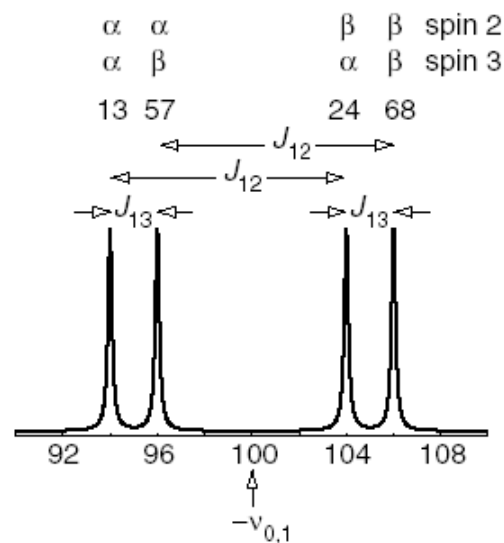
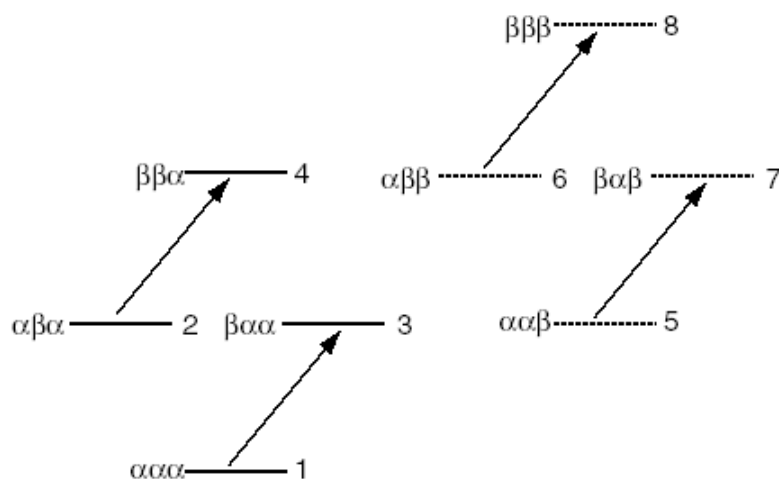
NMR a energiové hladiny

Tři spiny

transition	state of spin 2	state of spin 3	frequency
1-3	α	α	$-\nu_{0,1} - \frac{1}{2}J_{12} - \frac{1}{2}J_{13}$
2-4	β	α	$-\nu_{0,1} + \frac{1}{2}J_{12} - \frac{1}{2}J_{13}$
5-7	α	β	$-\nu_{0,1} - \frac{1}{2}J_{12} + \frac{1}{2}J_{13}$
6-8	β	β	$-\nu_{0,1} + \frac{1}{2}J_{12} + \frac{1}{2}J_{13}$

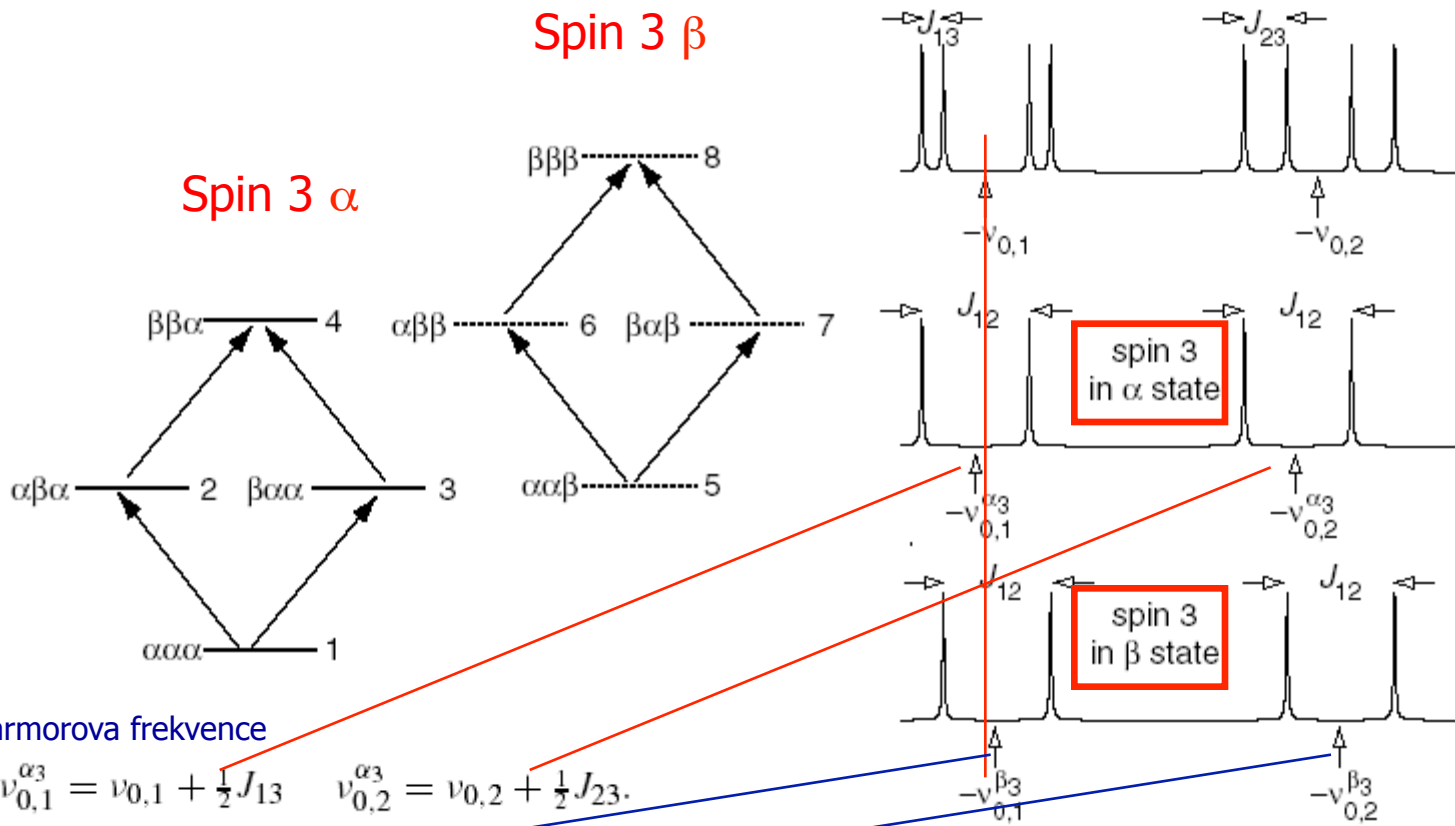
Výběrové pravidlo $\Delta M = \pm 1$

ale jen jeden spin může změnit svůj stav



NMR a energiové hladiny

Tři spiny - subspektra

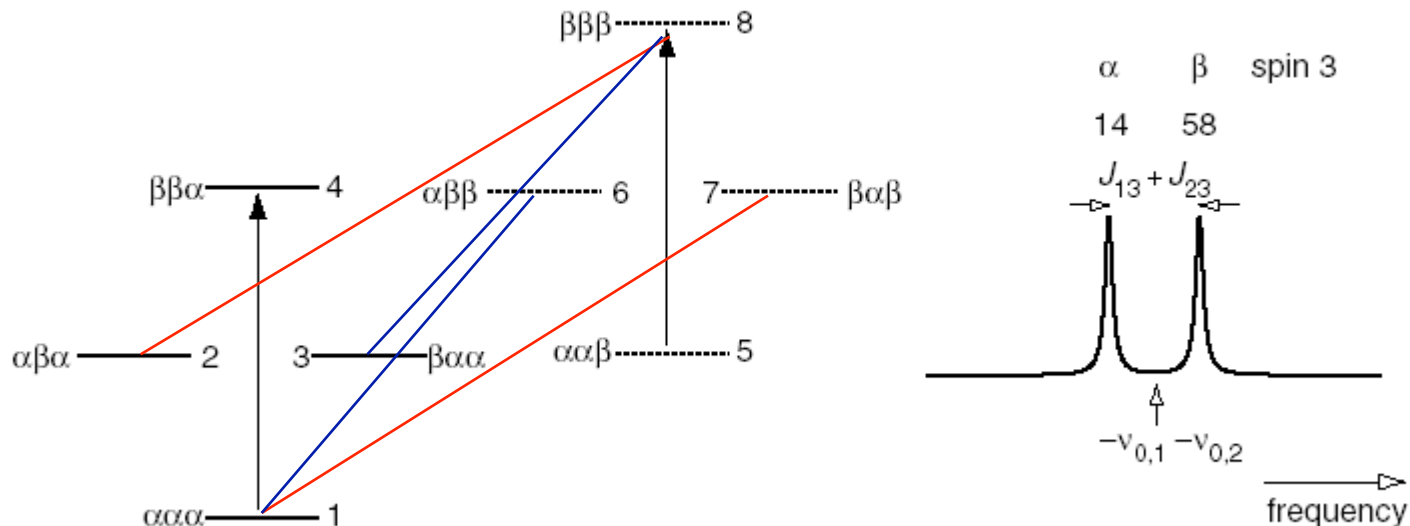


Efektivní Larmorova frekvence

NMR a energiové hladiny

Tři spiny – více-kvantové přechody

	transition	initial state	final state	frequency
1-2	1-4	$\alpha\alpha\alpha$	$\beta\beta\alpha$	$-\nu_{0,1} - \nu_{0,2} - \frac{1}{2}J_{13} - \frac{1}{2}J_{23}$
	5-8	$\alpha\alpha\beta$	$\beta\beta\beta$	$-\nu_{0,1} - \nu_{0,2} + \frac{1}{2}J_{13} + \frac{1}{2}J_{23}$
1-3	1-7	$\alpha\alpha\alpha$	$\beta\alpha\beta$	$-\nu_{0,1} - \nu_{0,3} - \frac{1}{2}J_{12} - \frac{1}{2}J_{23}$
	2-8	$\alpha\beta\alpha$	$\beta\beta\beta$	$-\nu_{0,1} - \nu_{0,3} + \frac{1}{2}J_{12} + \frac{1}{2}J_{23}$
2-3	1-6	$\alpha\alpha\alpha$	$\alpha\beta\beta$	$-\nu_{0,2} - \nu_{0,3} - \frac{1}{2}J_{12} - \frac{1}{2}J_{13}$
	3-8	$\beta\alpha\alpha$	$\beta\beta\beta$	$-\nu_{0,2} - \nu_{0,3} + \frac{1}{2}J_{12} + \frac{1}{2}J_{13}$



NMR a energiové hladiny

Dva spiny – silná interakce

$$\Delta\delta_{12} = (\nu_{0,1} - \nu_{0,2}) < 7 \cdot J_{12}$$

transition	frequency	intensity
1-2	$\frac{1}{2}D - \frac{1}{2}\Sigma - \frac{1}{2}J_{12}$	$(1 + \sin 2\theta)$
3-4	$\frac{1}{2}D - \frac{1}{2}\Sigma + \frac{1}{2}J_{12}$	$(1 - \sin 2\theta)$
1-3	$-\frac{1}{2}D - \frac{1}{2}\Sigma - \frac{1}{2}J_{12}$	$(1 - \sin 2\theta)$
2-4	$-\frac{1}{2}D - \frac{1}{2}\Sigma + \frac{1}{2}J_{12}$	$(1 + \sin 2\theta)$

$$\Sigma = \nu_{0,1} + \nu_{0,2} \quad D^2 = (\nu_{0,1} - \nu_{0,2})^2 + J_{12}^2. \quad \sin 2\theta = \frac{J_{12}}{D}.$$

$$D^2 = (\nu_{0,1} - \nu_{0,2})^2 + J_{12}^2$$
$$\approx (\nu_{0,1} - \nu_{0,2})^2 \quad \leftarrow \text{slabá interakce}$$

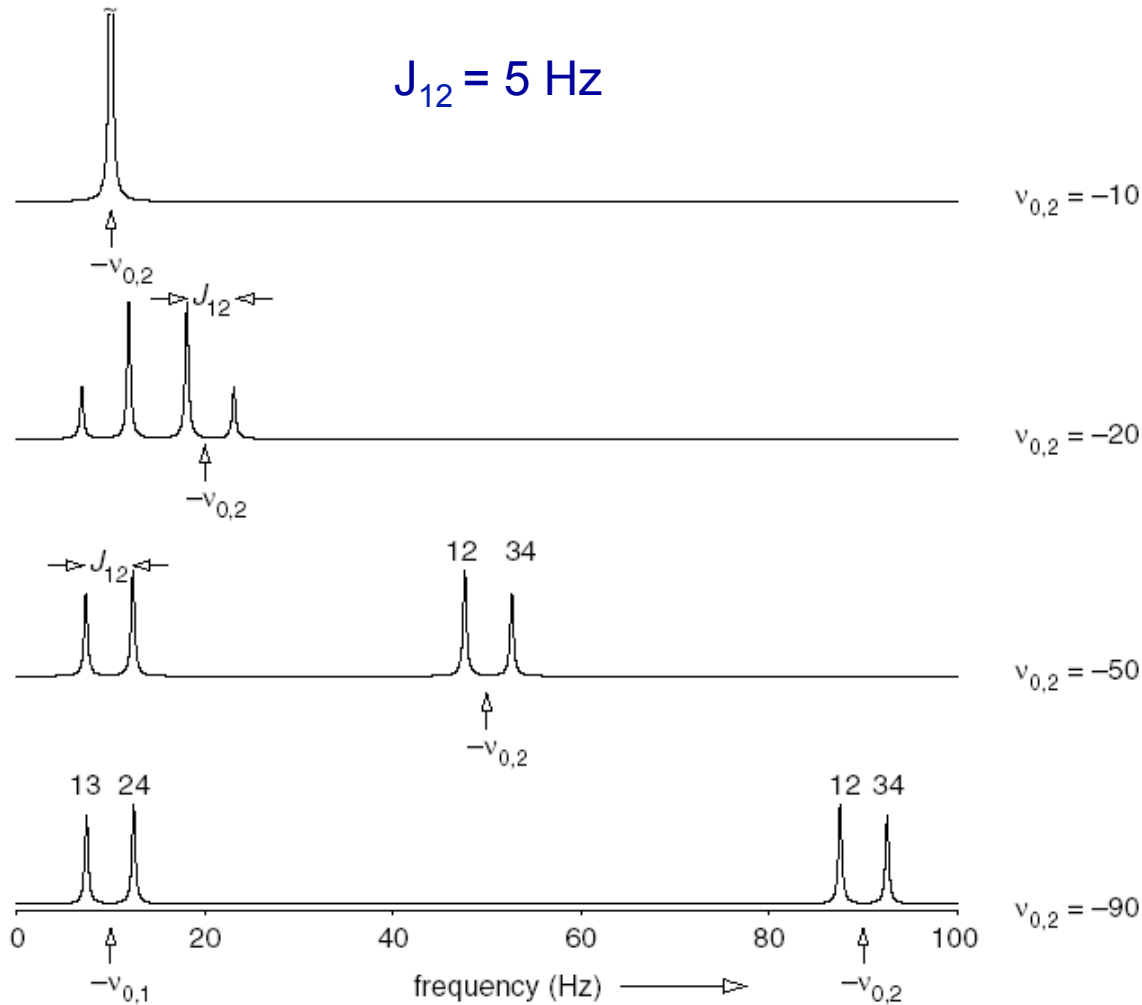
$$\text{pro } (\nu_{0,1} - \nu_{0,2}) = 7 \cdot J_{12} \quad \sin 2\theta = 0.143, \theta = 4.1$$

NMR a energiové hladiny

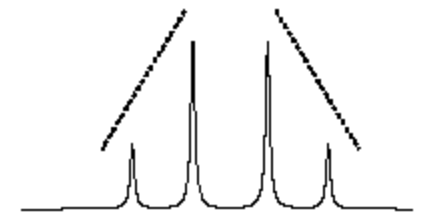
Dva spiny – silná interakce

$$\Delta\delta_{12} < 7 \cdot J_{12}$$

$$J_{12} = 5 \text{ Hz}$$



Stříškový efekt

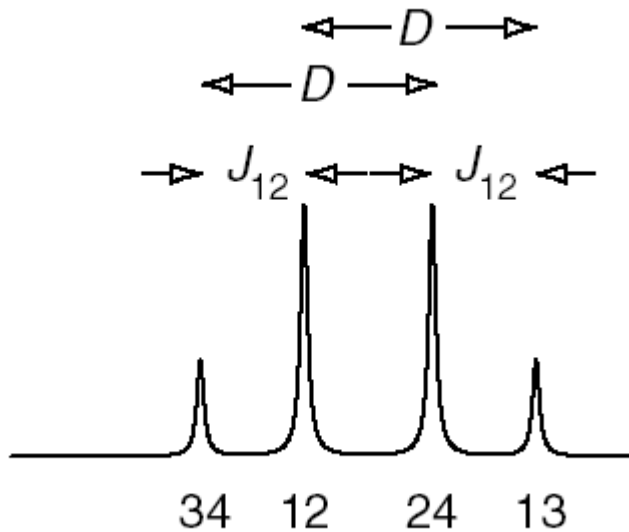


2.10.2012 RF

NMR a energiové hladiny

Dva spiny – silná interakce

$$\Delta\delta_{12} < 7 \cdot J_{12}$$



$$\begin{aligned} \nu_{34} - \nu_{24} &= \left(\frac{1}{2}D - \frac{1}{2}\Sigma + \frac{1}{2}J_{12}\right) - \left(-\frac{1}{2}D - \frac{1}{2}\Sigma + \frac{1}{2}J_{12}\right) \\ &= D. \end{aligned}$$

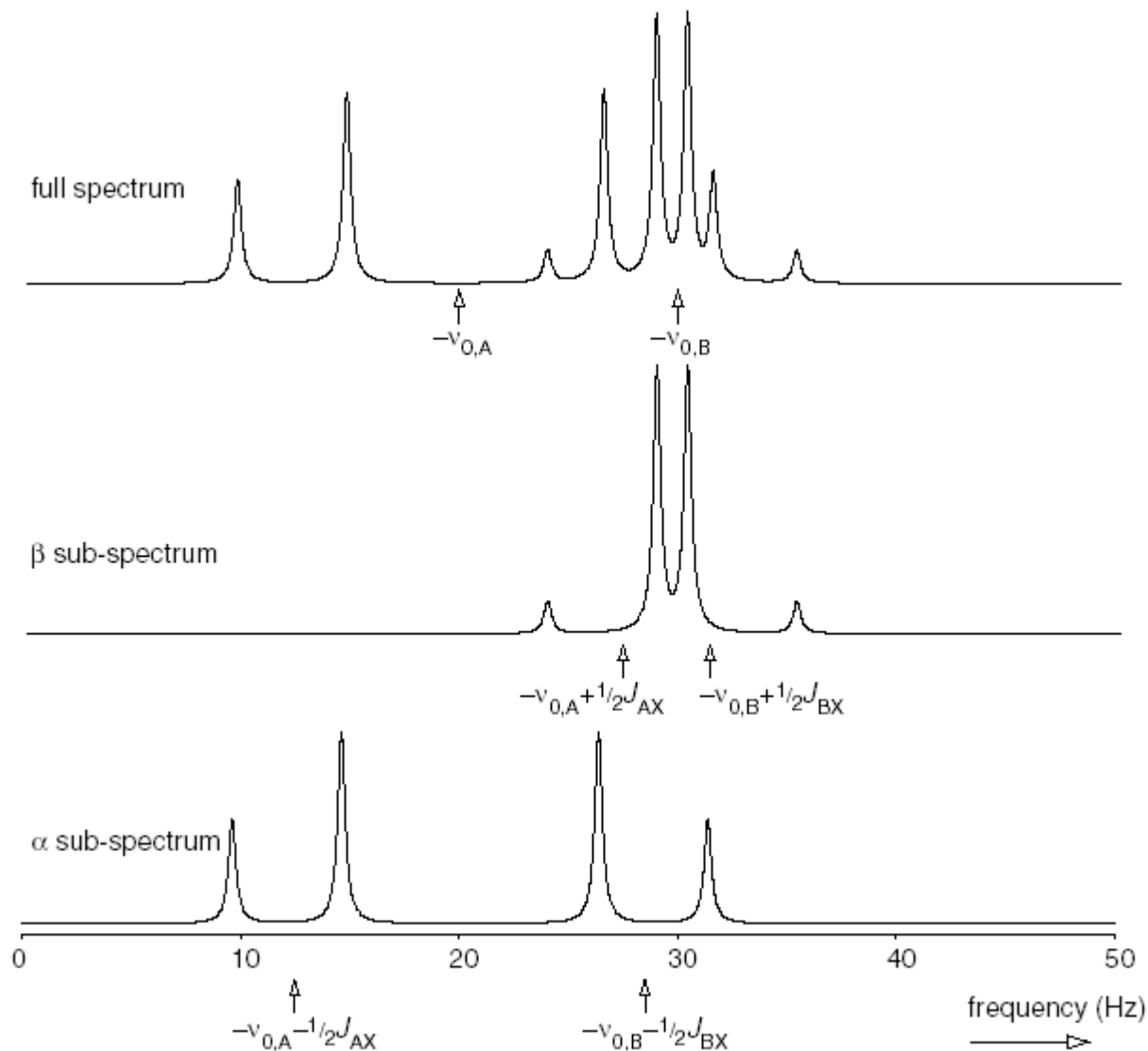
$$D^2 = (\nu_{0,1} - \nu_{0,2})^2 + J_{12}^2$$

$$\begin{aligned} \nu_{12} + \nu_{24} &= \left(\frac{1}{2}D - \frac{1}{2}\Sigma - \frac{1}{2}J_{12}\right) + \left(-\frac{1}{2}D - \frac{1}{2}\Sigma + \frac{1}{2}J_{12}\right) \\ &= -\Sigma. \end{aligned}$$

$$\nu_{0,1} = \frac{1}{2}(\Sigma + (\nu_{0,1} - \nu_{0,2})) \quad \nu_{0,2} = \frac{1}{2}(\Sigma - (\nu_{0,1} - \nu_{0,2})).$$

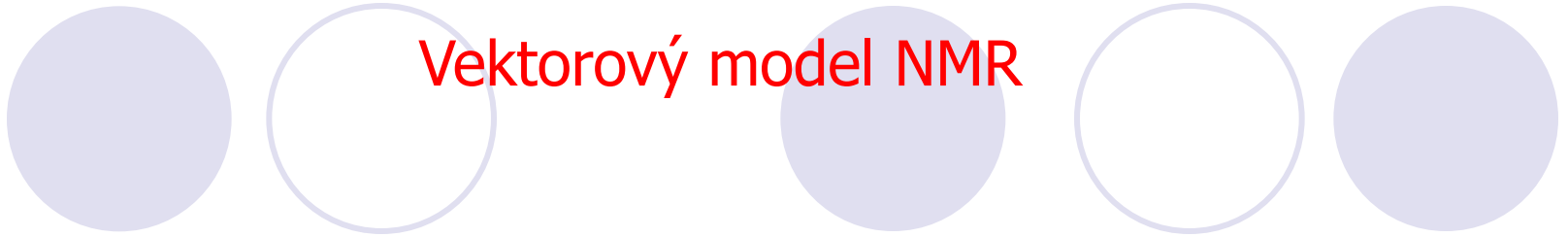
NMR a energiové hladiny

Tři spiny – ABX systém - subspektra

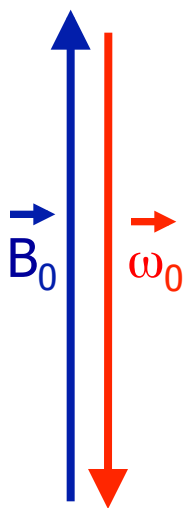


4.10.2009

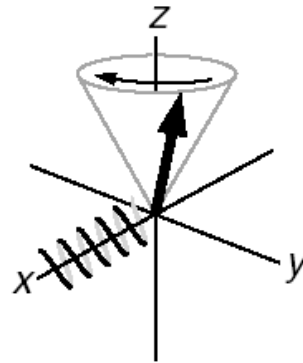
Vektorový model NMR



Larmorova precesní frekvence



$$\vec{\omega}_0 = -\gamma \vec{B}_0$$



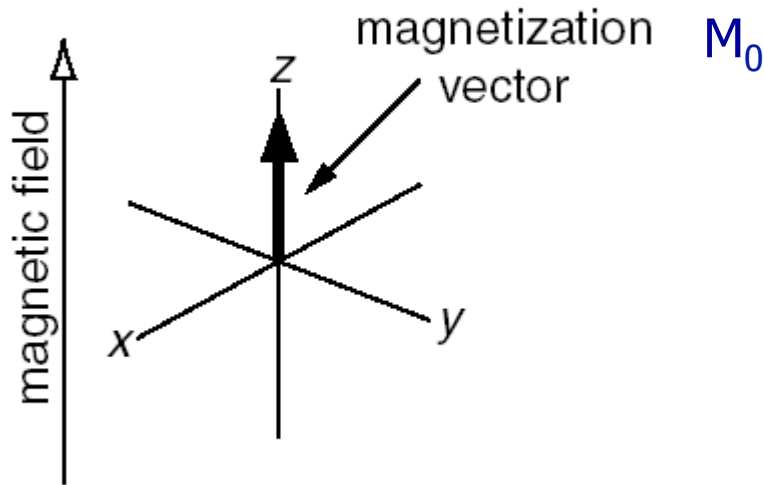
$$\vec{\nu}_0 = -\frac{1}{2\pi} \gamma \vec{B}_0$$

Pravidlo pravé ruky
Pozor na znaménko γ !

Vektorový model NMR

Makroskopická magnetizace

Směr rotace je negativní – $+x \rightarrow -y!!$

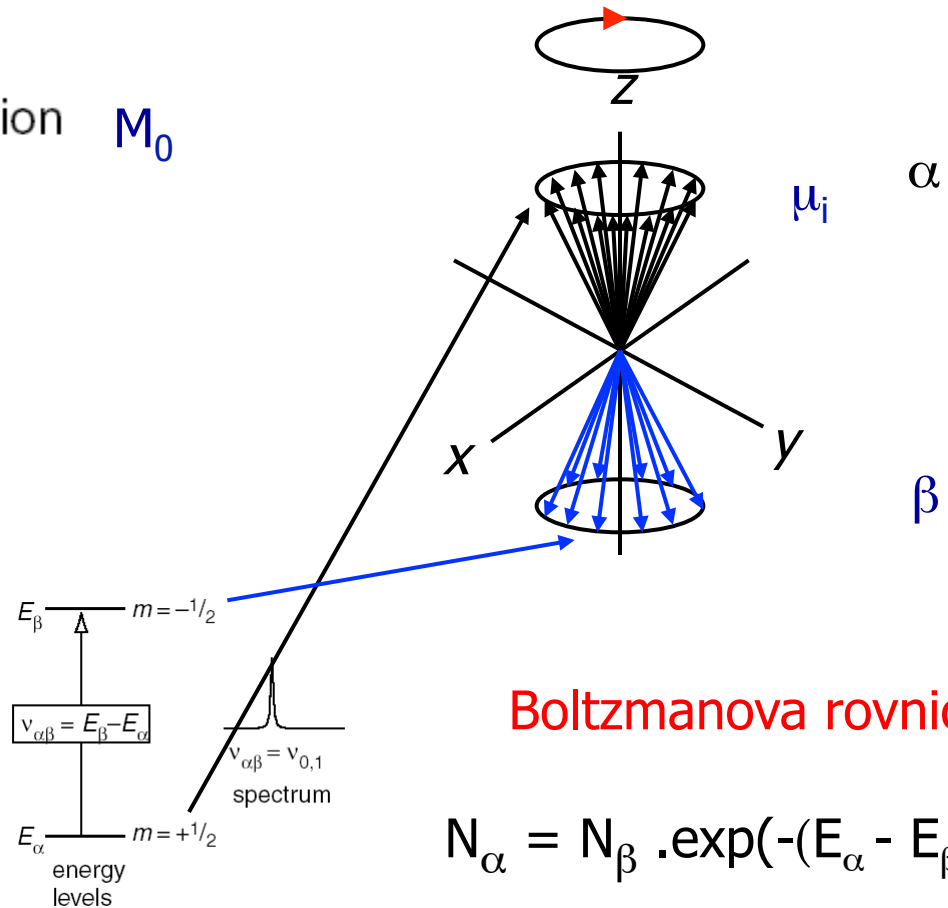


$$M(M_x, M_y, M_z) = \Sigma (\mu_i)$$

Curieho zákon

$$M_0 = N \cdot \gamma \cdot h^2 I(I+1) / 3kT \cdot H_0$$

$$N = N_\alpha - N_\beta$$



Boltzmanova rovnice

$$N_\alpha = N_\beta \cdot \exp(-(E_\alpha - E_\beta) / kT)$$

Vektorový model NMR

Makroskopická magnetizace

Výpočet obsazení spinových hladin

Boltzmanova rovnice

$$N_{\alpha} = N_{\beta} \cdot \exp(-(E_{\alpha} - E_{\beta}/kT)$$

$$\nu_{\alpha} - \nu_{\beta} = -500 \text{ MHz} \quad E_{\alpha} - E_{\beta} = -500 \ 000 \ 000 \cdot 6,626 \cdot 10^{-34} = -3,313 \cdot 10^{-25} \text{ J}$$

$$k = 1,38 \cdot 10^{-23} \text{ J.deg}^{-1} \quad T=303 \text{ K}$$

$$\begin{aligned} N_{\alpha} &= N_{\beta} \cdot \exp(3.13/(1.38 \times 303) \times 10^{-2}) = N_{\beta} \cdot \exp(0.0000749) \\ &= N_{\beta} \cdot 1.0000749 \end{aligned}$$

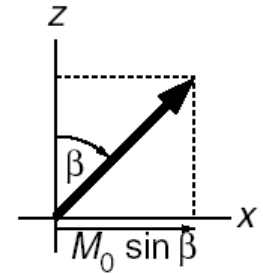
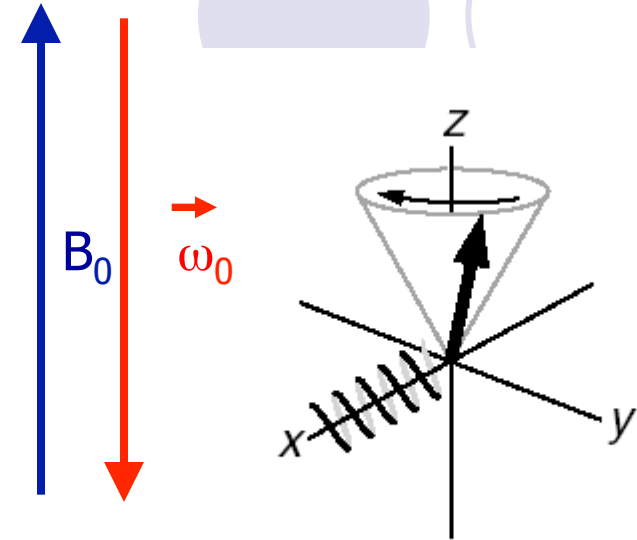
Vektorový model NMR

Detekce

Pohyb vektoru magnetizace

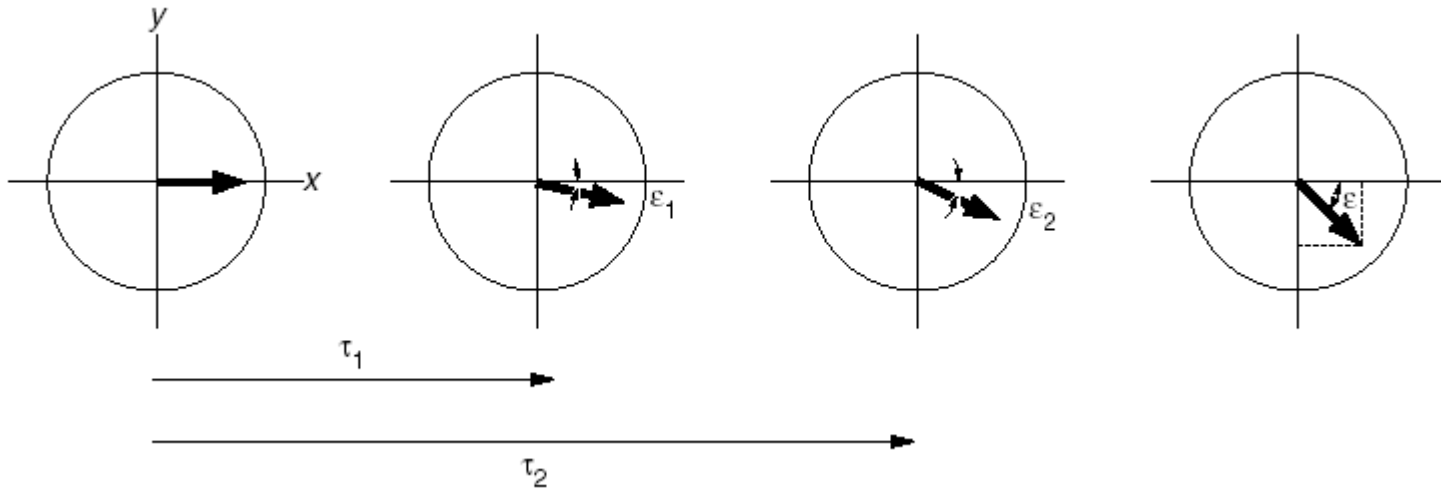
$$\frac{d\vec{\mu}}{dt} = -\gamma \cdot \vec{B}_0 \times \vec{\mu}$$

(klasická pohybová rovnice)



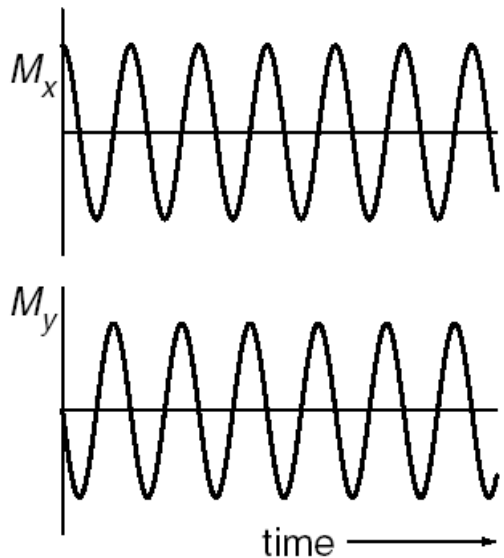
$$\vec{M}(M_x, M_y, M_z) = \sum (\vec{\mu}_i)$$

$$\frac{d\vec{M}}{dt} = -\gamma \cdot \vec{B}_0 \times \vec{M} = \vec{\omega} \times \vec{M}$$



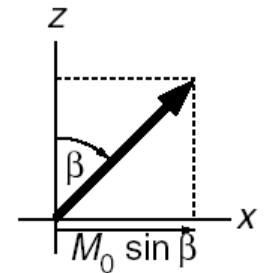
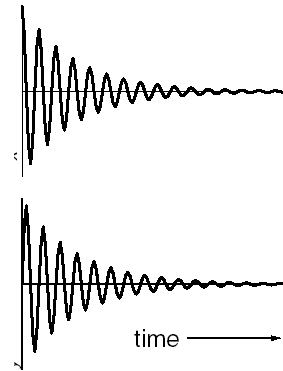
Vektorový model NMR

Detekce



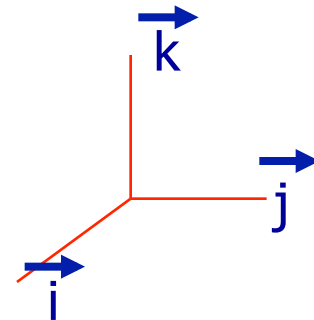
$$M_x = M_0 \sin \beta \cos(\omega_0 t)$$

$$M_y = -M_0 \sin \beta \sin(\omega_0 t).$$



RELAXACE => Blochova rovnice

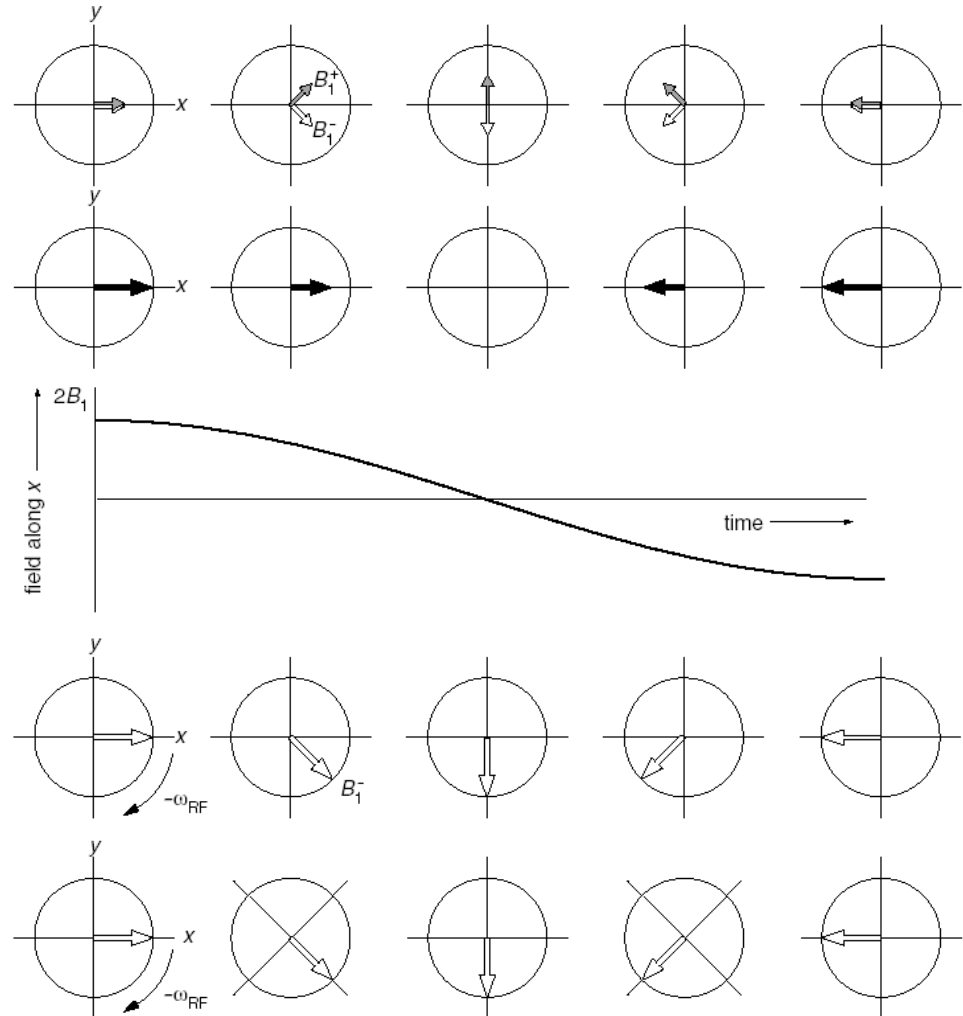
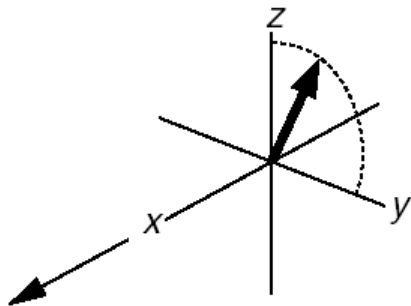
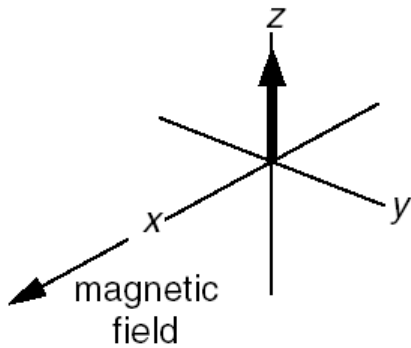
$$\frac{d\vec{M}}{dt} = -\gamma \cdot \vec{B}_0 \times \vec{M} - M_x/T_2 \cdot \vec{i} - M_y/T_2 \cdot \vec{j} - (M_z - M_0)/T_1 \cdot \vec{k}$$



Vektorový model NMR

Rotující souřadná soustava

RF pulzy



Směr rotace je negativní – $+x \rightarrow -y!!$

Vektorový model NMR

Larmorova frekvence v rotující souřadné soustavě – efektivní pole

Offset $\Omega = \omega_0 - \omega_{\text{rot. fram.}}$

$$\omega = -\gamma B.$$

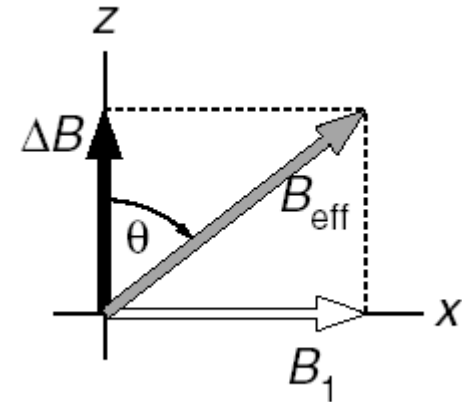
$$\omega_1 = +\gamma B_1$$

$$\Omega = -\gamma \Delta B$$

$$\Delta B = -\frac{\Omega}{\gamma}$$

$$\Omega = \omega_0 - (-\omega_{\text{RF}})$$

$$= \omega_0 + \omega_{\text{RF}}.$$



$$B_{\text{eff}} = \sqrt{B_1^2 + \Delta B^2}.$$

$$\omega_{\text{eff}} = \gamma B_{\text{eff}}$$

$$\sin \theta = \frac{B_1}{B_{\text{eff}}} \quad \cos \theta = \frac{\Delta B}{B_{\text{eff}}} \quad \tan \theta = \frac{B_1}{\Delta B}.$$

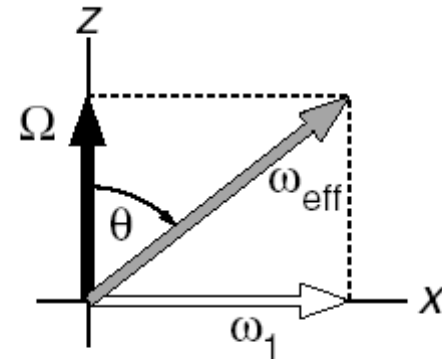
Vektorový model NMR

Larmorova frekvence v rotující souřadné soustavě – efektivní pole

$$\Omega = -\gamma \Delta B.$$

$$\omega_1 = \gamma B_1$$

$$\omega_{\text{eff}} = \gamma B_{\text{eff}}.$$

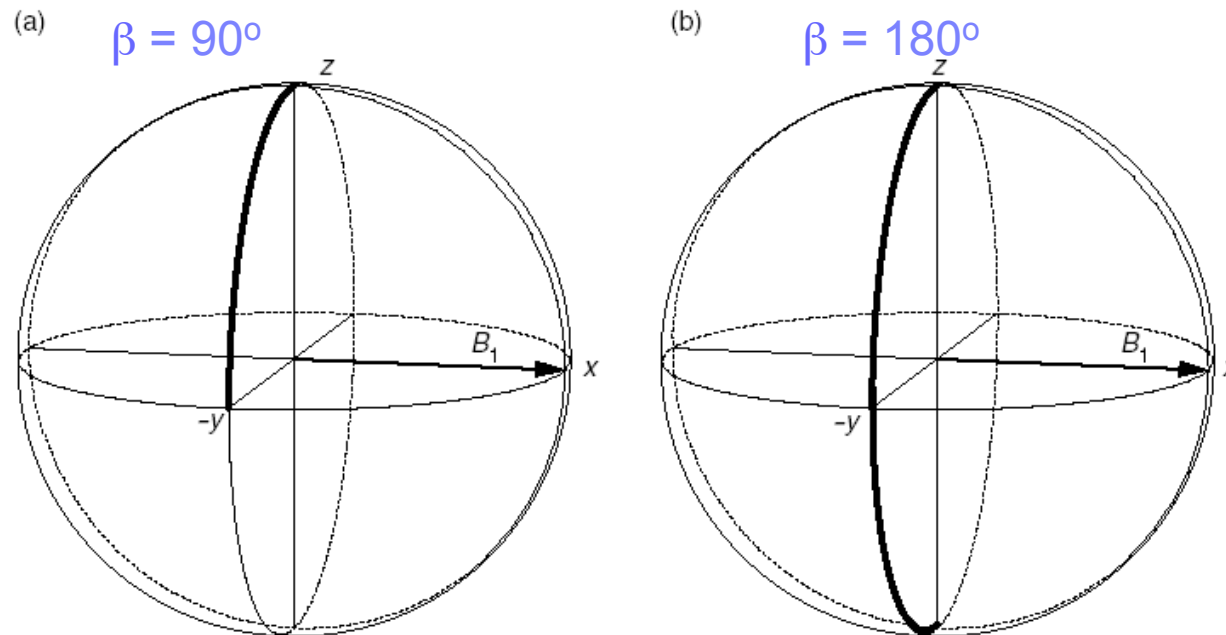


$$\omega_{\text{eff}} = \sqrt{\omega_1^2 + \Omega^2}.$$

$$\sin \theta = \frac{\omega_1}{\omega_{\text{eff}}} \quad \cos \theta = \frac{\Omega}{\omega_{\text{eff}}} \quad \tan \theta = \frac{\omega_1}{\Omega}.$$

Vektorový model NMR

RF pulzy – působení v rezonanci – offset $\Omega = \Delta B = 0$



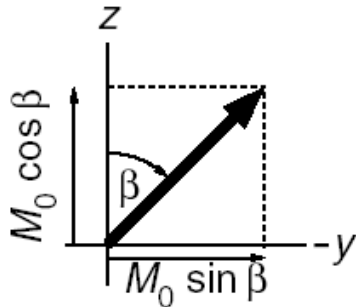
$$\beta = \omega_1 t_p$$

$$\beta = \nu_1 \cdot t_p \cdot 360^\circ$$

$$M_z = M_0 \cos \beta \quad M_y = -M_0 \sin \beta;$$

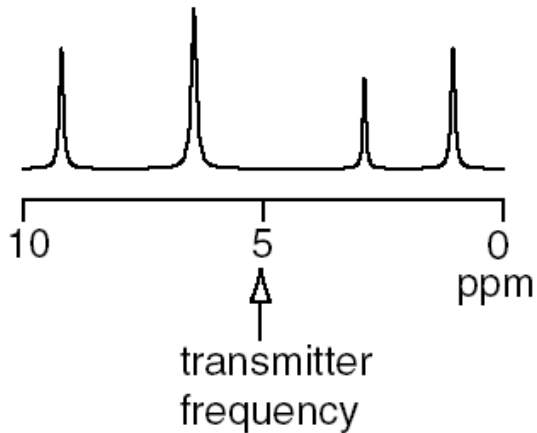
Vektorový model NMR

RF pulzy – 'tvrdé pulzy'



$$\beta = \omega_1 t_p \text{ hence } \omega_1 = \frac{\beta}{t_p}.$$

Je-li $\beta = 90^\circ$ pro $t_p = 12 \mu\text{s}$ potom

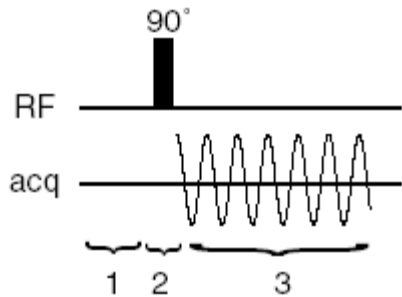


$$\begin{aligned} \omega_1 &= \frac{\pi/2}{12 \times 10^{-6}} \\ &= 1.3 \times 10^5 \text{ rad s}^{-1}. \end{aligned}$$

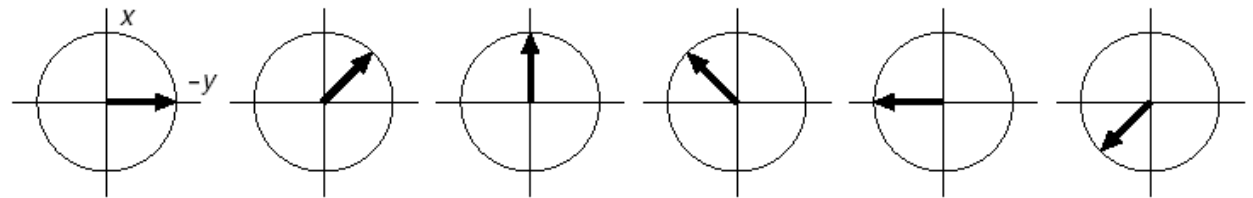
$$\nu_1 = 20\,833,333 \text{ Hz}$$

Vektorový model NMR

Detekce v rotující souřadné soustavě

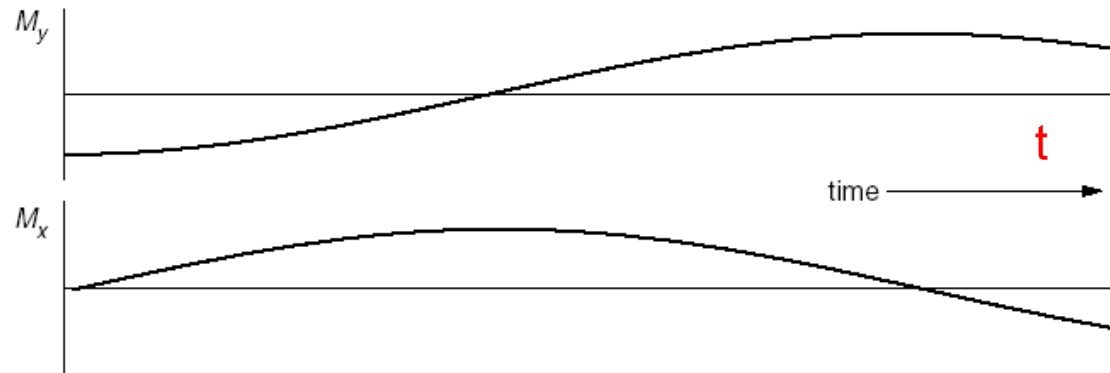


$$\varphi = \Omega t$$



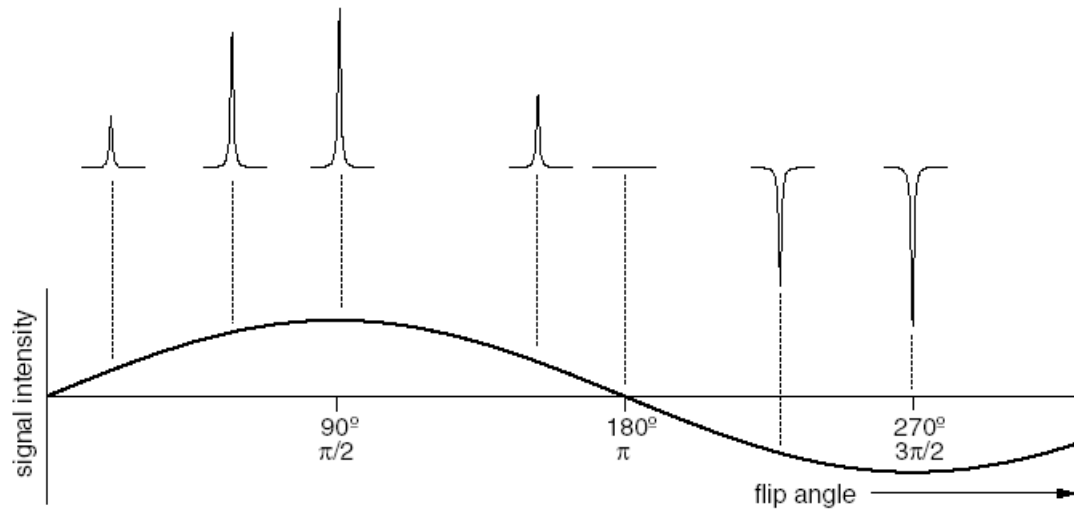
$$M_y = -M_0 \cos(\Omega t)$$

$$M_x = M_0 \sin(\Omega t).$$



Vektorový model NMR

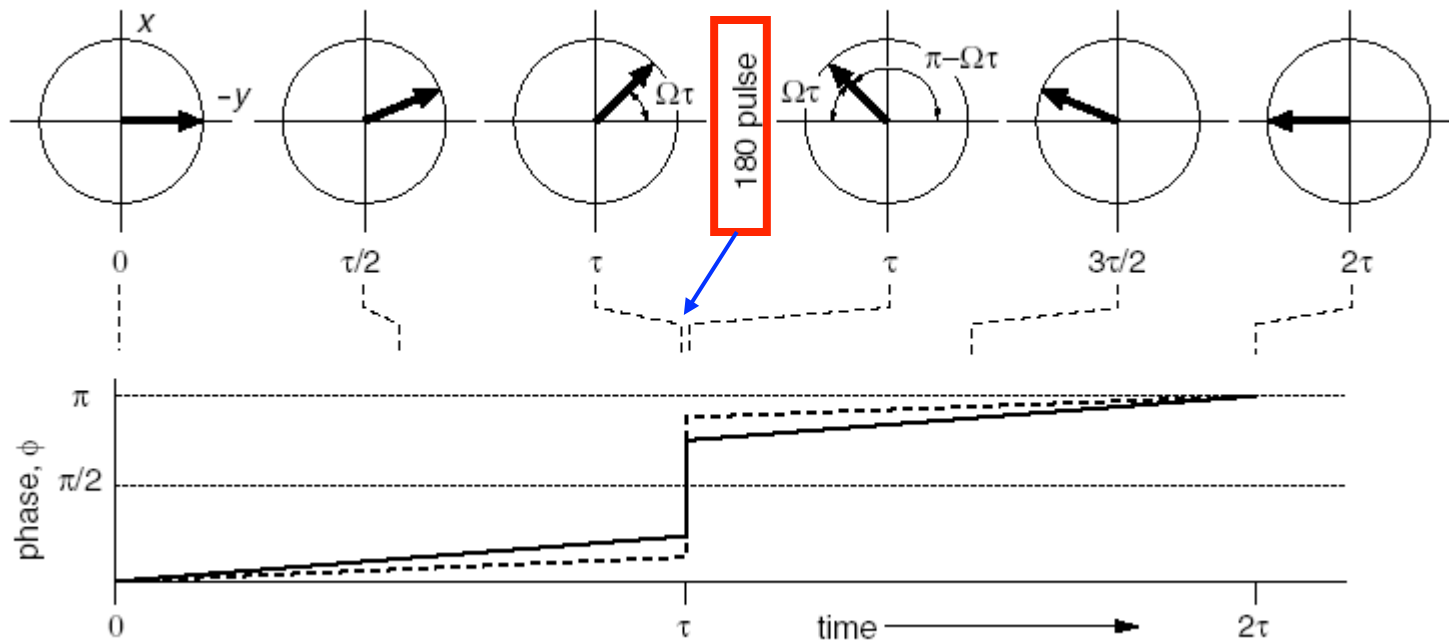
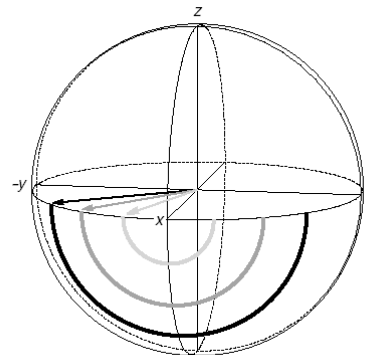
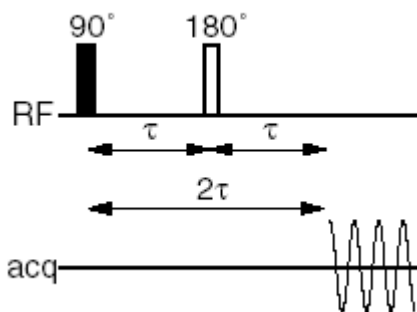
Kalibrace rf pulzů



$$\pi = \omega_1 t_{180}$$
$$\omega_1 = \frac{\pi}{t_{180}}$$
$$(\omega_1/2\pi) = \frac{1}{2t_{180}} \text{ Hz}$$
$$\omega_1 = \frac{\pi}{15.5 \times 10^{-6}} = 2.03 \times 10^5 \text{ rad s}^{-1}$$
$$(\omega_1/2\pi) = \frac{1}{2 \times 15.5 \times 10^{-6}} = 32.3 \text{ kHz}$$

Vektorový model NMR

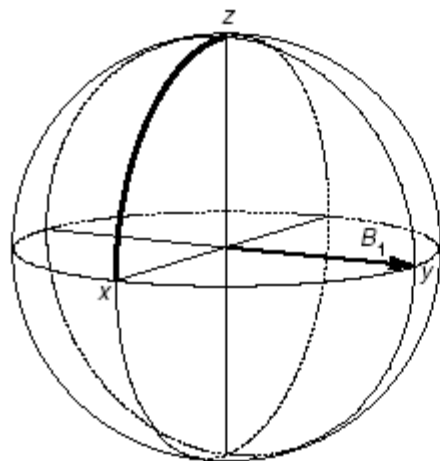
Spinové echo



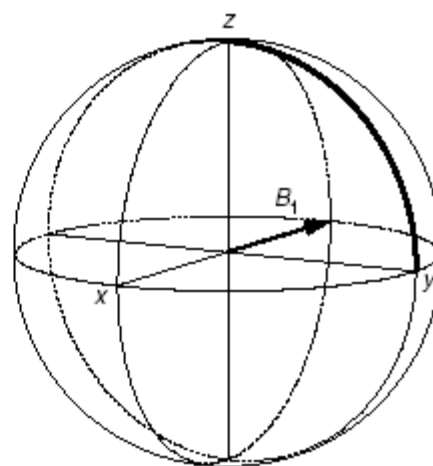
Vektorový model NMR

Fáze rf pulzů

(a)

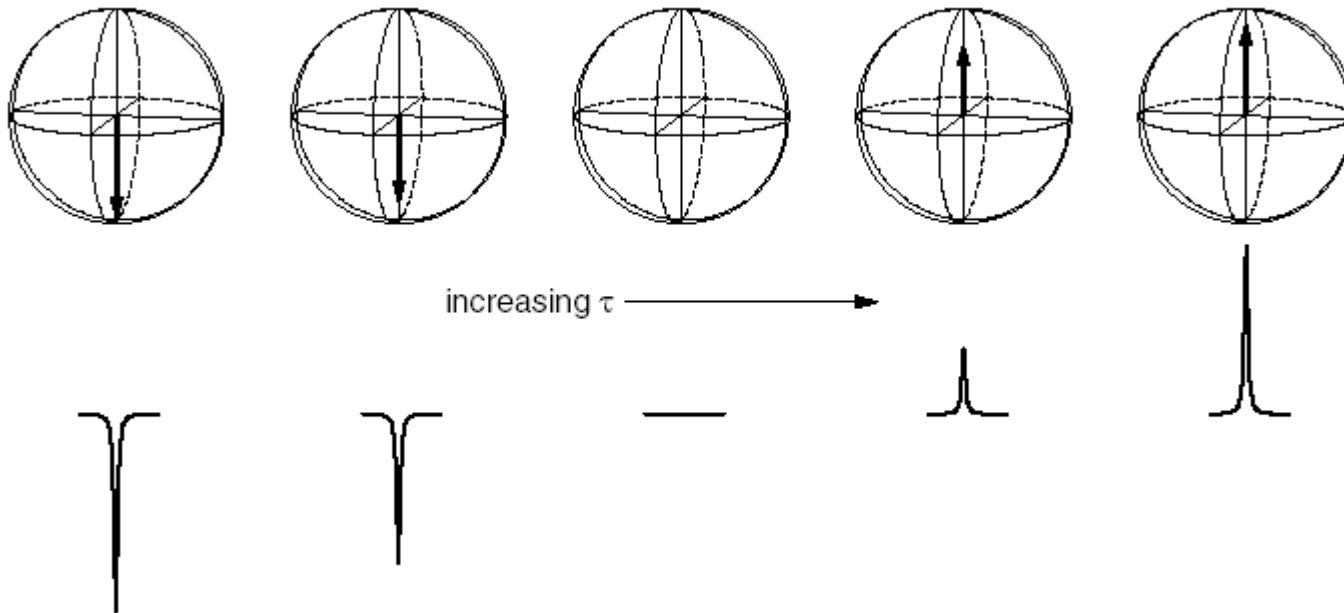
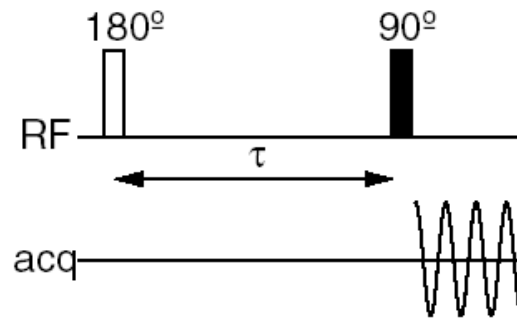


(b)



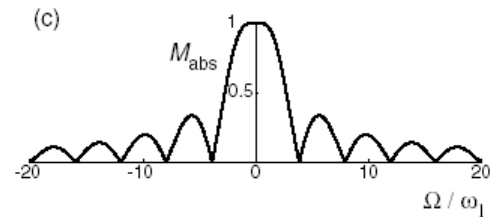
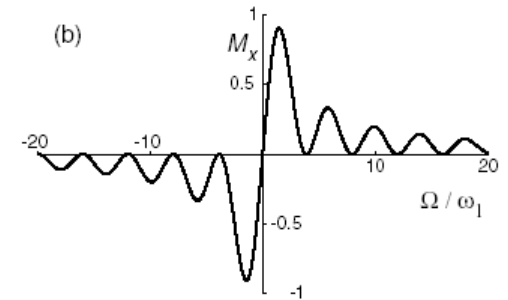
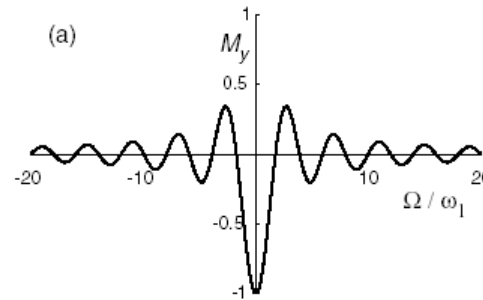
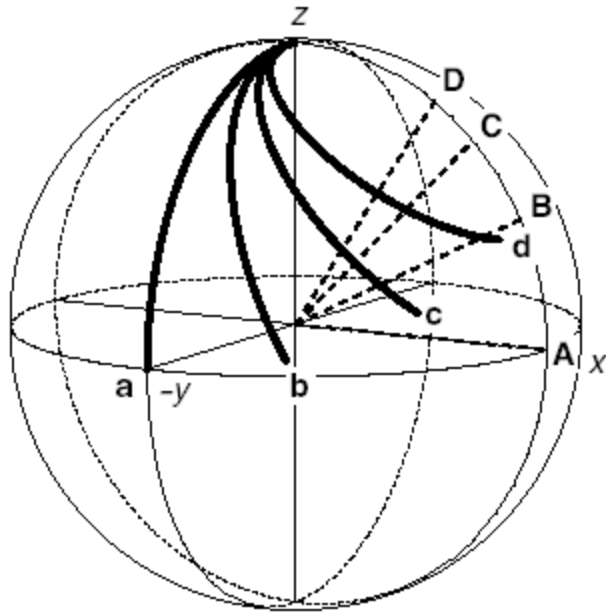
Vektorový model NMR

Relaxace



Vektorový model NMR

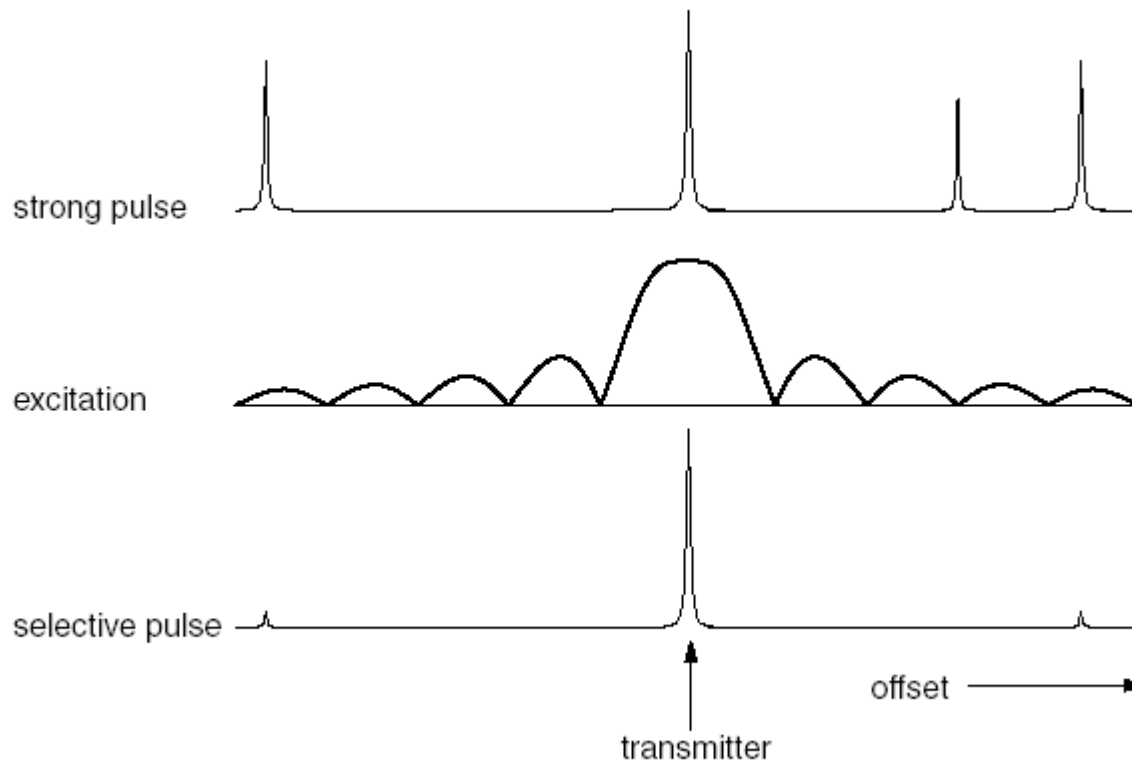
Off-rezonanční vlivy a slabé pulzy



$$M_{\text{abs}} = \sqrt{M_x^2 + M_y^2}.$$

Vektorový model NMR

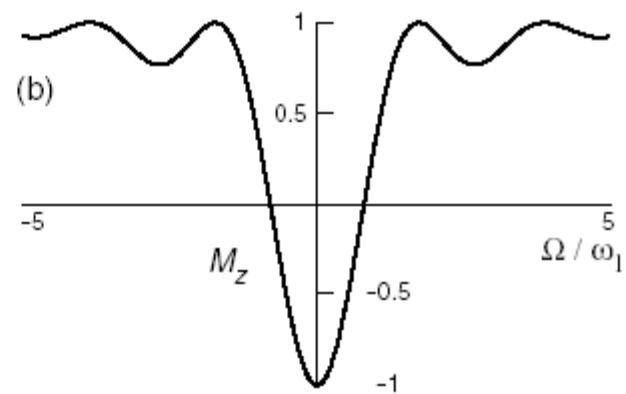
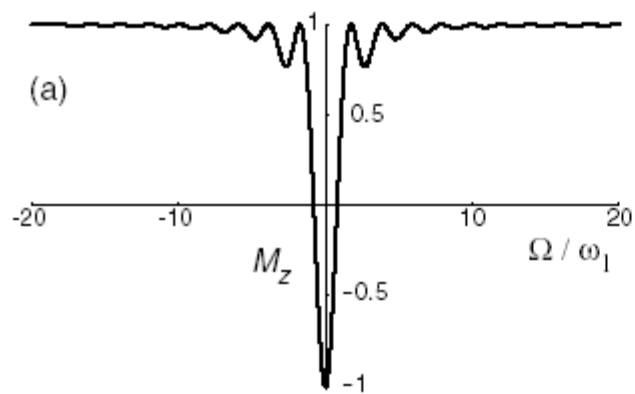
Selektivní excitace a slabé pulzy



NMRSim demo

Vektorový model NMR

Selektivní inverze a slabé pulzy



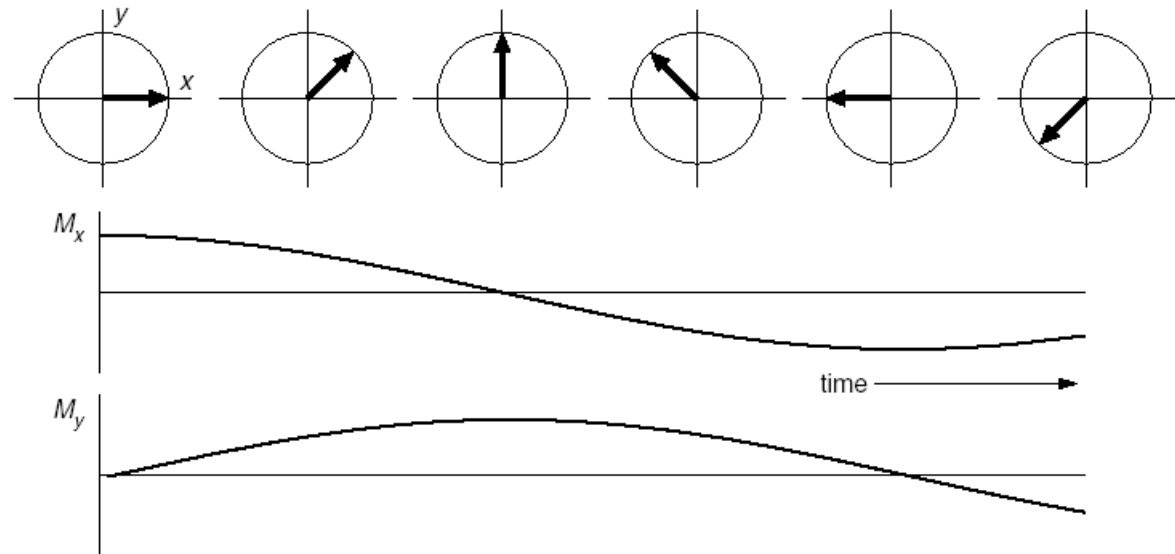
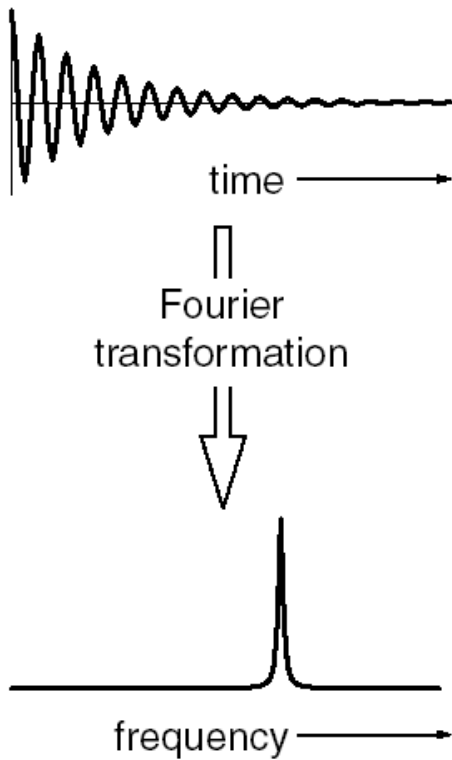


Vektorový model NMR - shrnutí

- Vysokofrekvenční výkon vytváří ve snímací cívce okolo měřeného vzorku oscilující magnetické pole B_1 v definované směru kolmém na směr statického magnetického pole.
- Toto lineárně oscilující pole může být rozloženo na dvě protisměrně rotující magnetická pole. Pouze jedno z nich, mající shodnou frekvenci a směr s frekvencí Larmorovou, se bere v úvahu.
- Rotující pole se zavedením rotující souřadně soustavy (rss) s vhodnou frekvencí stane statickým.
- V rss jsou rezonanční frekvence modifikovány. Rozdílová frekvence mezi frekvencí rss a rezonančním Larmorovým kmitočtem nazývaná offset Ω potom odpovídá redukovanému magnetickému poli
$$\Delta B = -\Omega / \gamma.$$
- Vektor magnetizace rotuje kolem efektivního magnetického pole, které je vektorovým součtem $\Delta B + B_1$.
- Efektivní pole je orientováno blízko ose pole B_1 pokud je rezonanční ofset malý.

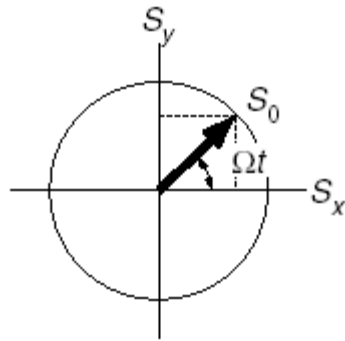
Fourierova transformace a zpracování dat

FID – free induction decay



Fourierova transformace a zpracování dat

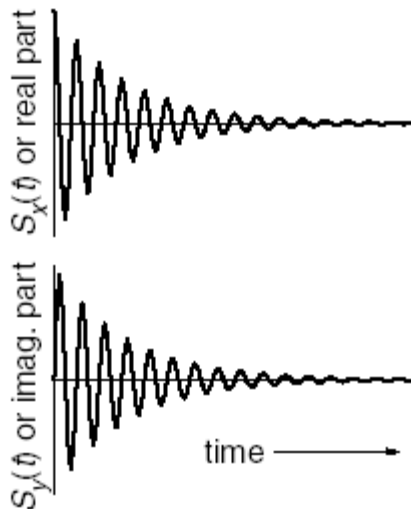
FID – free induction decay



$$M_x = M_0 \cos \Omega t$$

$$M_y = M_0 \sin \Omega t.$$

$$S_x(t) = S_0 \cos \Omega t \quad \text{and} \quad S_y(t) = S_0 \sin \Omega t$$

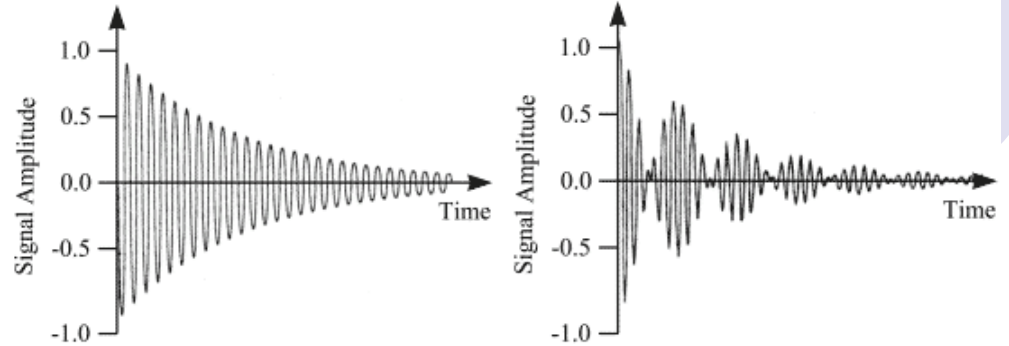


$$\begin{aligned} S(t) &= S_x(t) + i S_y(t) \\ &= S_0 \cos \Omega t + i S_0 \sin \Omega t \\ &= S_0 \exp(i \Omega t). \end{aligned}$$

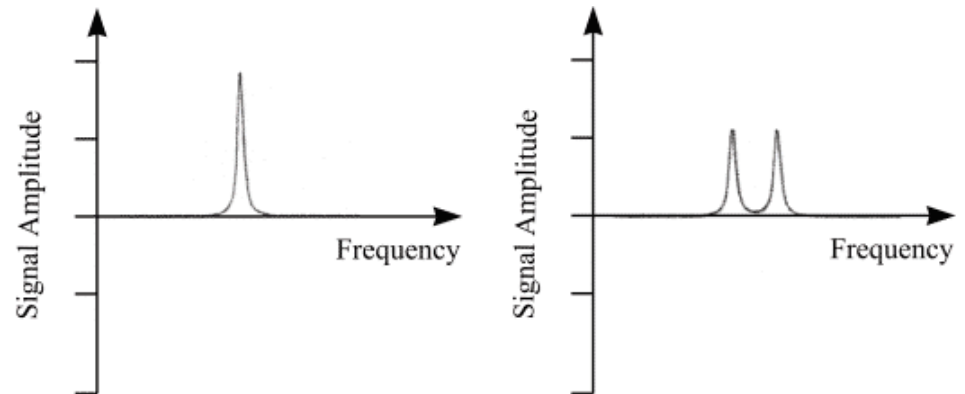
$$S(t) = S_0 \exp(i \Omega t) \exp\left(\frac{-t}{T_2}\right).$$



Joseph Fourier
(1768 – 1830)



Fourier Transform



Jean Baptiste Joseph Fourier
born Auxerre, March 21, 1768
died, Paris, May 16, 1830

He took a prominent part in his own district in promoting the revolution, and was rewarded by an appointment in 1795 in the Normal school, and subsequently by a chair in the Polytechnic school.

Fourier went with Napoleon on his Eastern expedition in 1798, and was made governor of Lower Egypt.

After the British victories and the capitulation of the French under General Menou in 1801, Fourier returned to France, and was made prefect of Grenoble, and it was while there that he made his experiments on the propagation of heat. He moved to Paris in 1816. In 1822 he published his *Théorie analytique de la chaleur*, in which he shows that any functions of a variable, whether continuous or discontinuous, can be expanded in a series of sines of multiples of the variable - a result which is constantly used in modern analysis.



J.W.Cooley and J.W.Tukey, *Math. Comp.* 1965, 19, 297
Fast Fourier Transform

Fourierova transformace a zpracování dat

Fourierova transformace – základní vlastnosti

FT

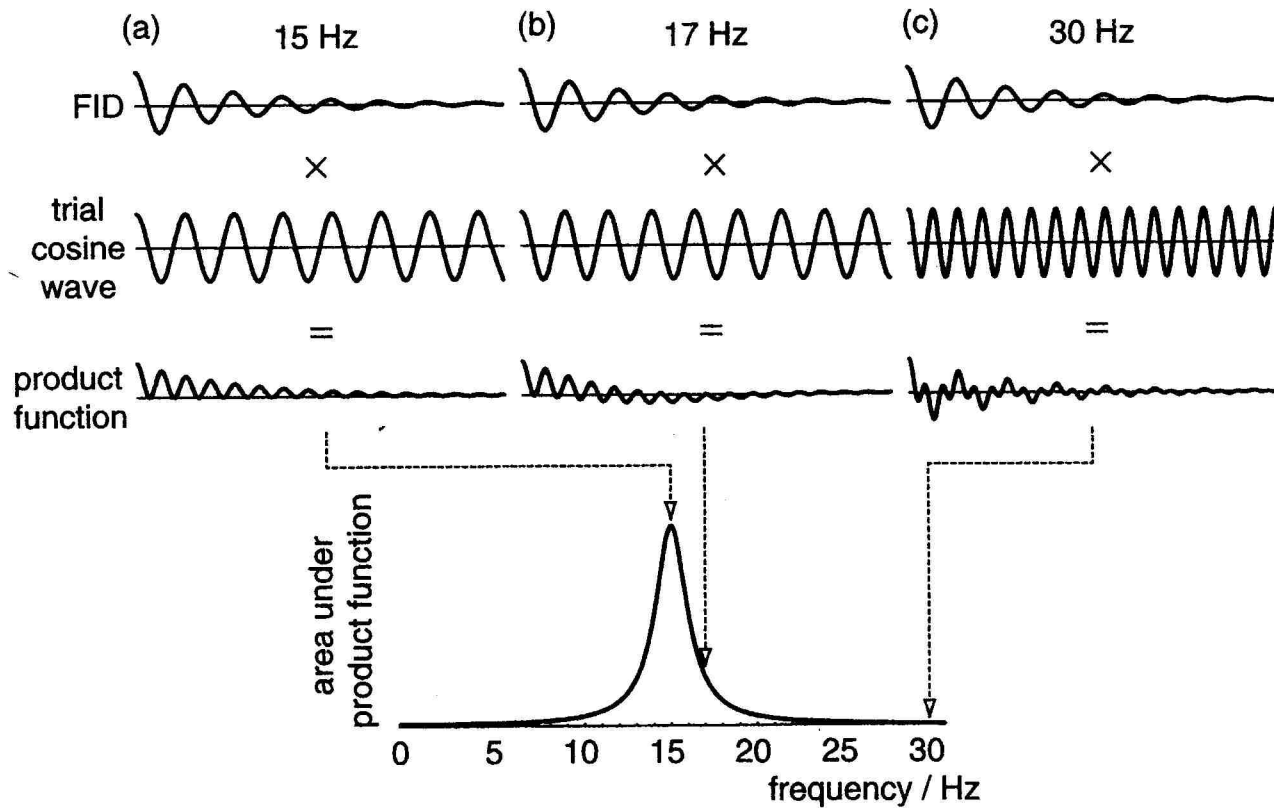
$$S(\nu) = \int_{-\infty}^{+\infty} S(t) \cdot \exp(-i \cdot 2\pi \cdot \nu \cdot t) dt$$

iFT

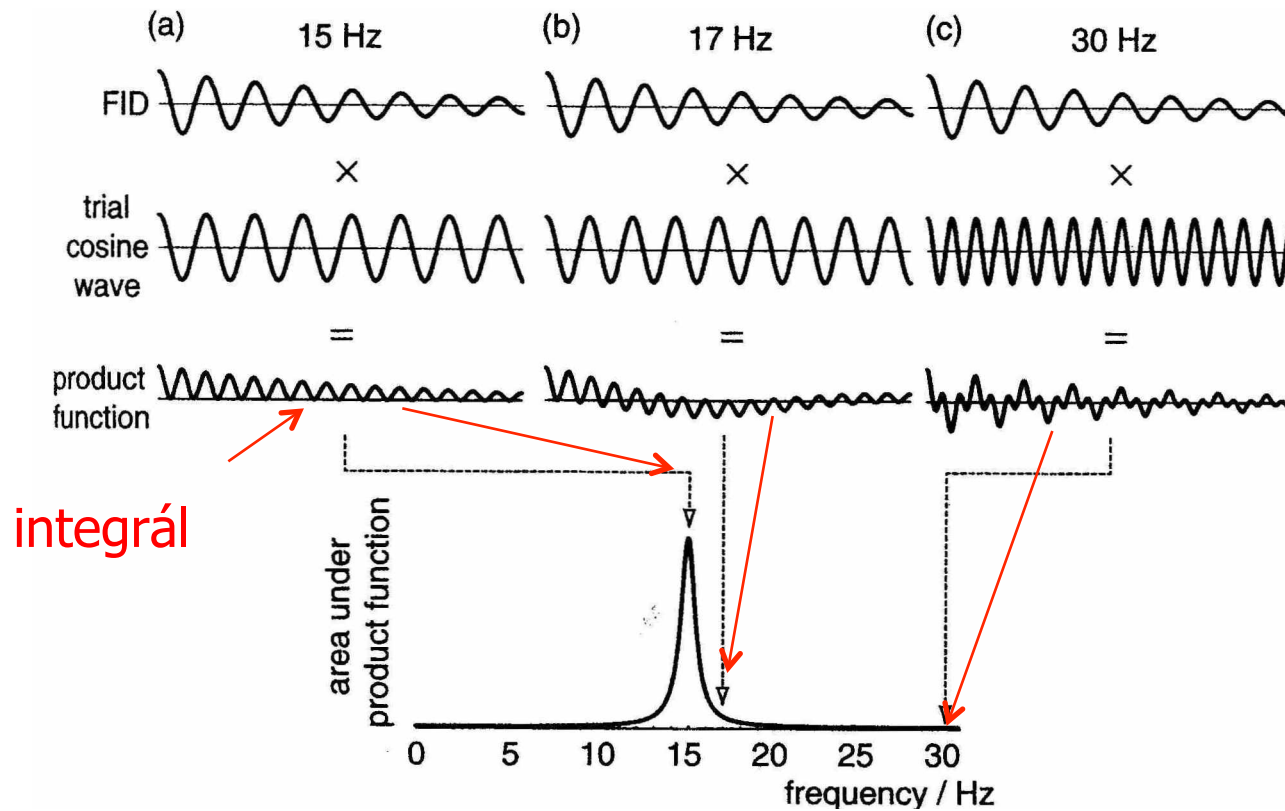
$$S(t) = \int_{-\infty}^{+\infty} S(\nu) \cdot \exp(+i \cdot 2\pi \cdot \nu \cdot t) d\nu$$

Diskrétní Fourierova transformace – algoritmus Cooley a Tukey, 1966

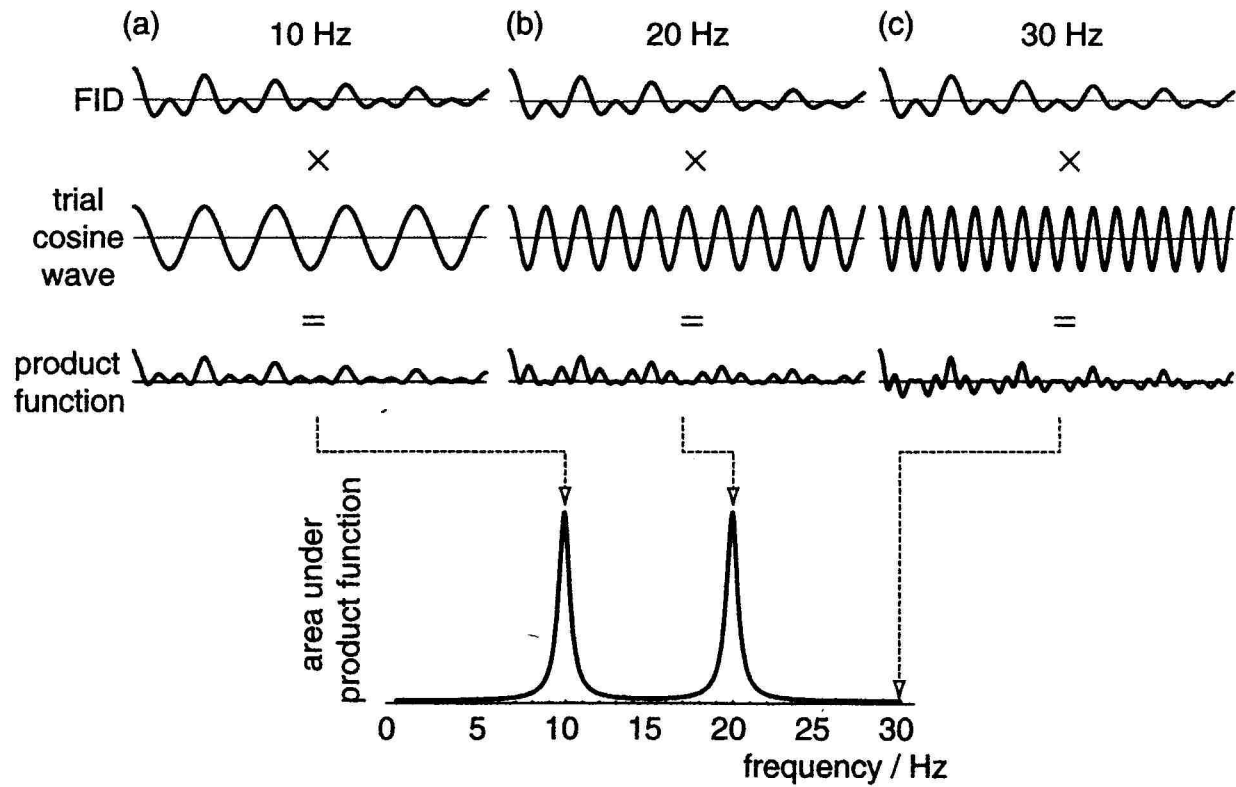
Fourierova transformace a zpracování dat



Fourierova transformace a zpracování dat



Fourierova transformace a zpracování dat



Fourierova transformace a zpracování dat

Fourierova řada

$$s(x) = \sum C_n e^{in\omega x}$$

Koeficienty Fourierovy řady

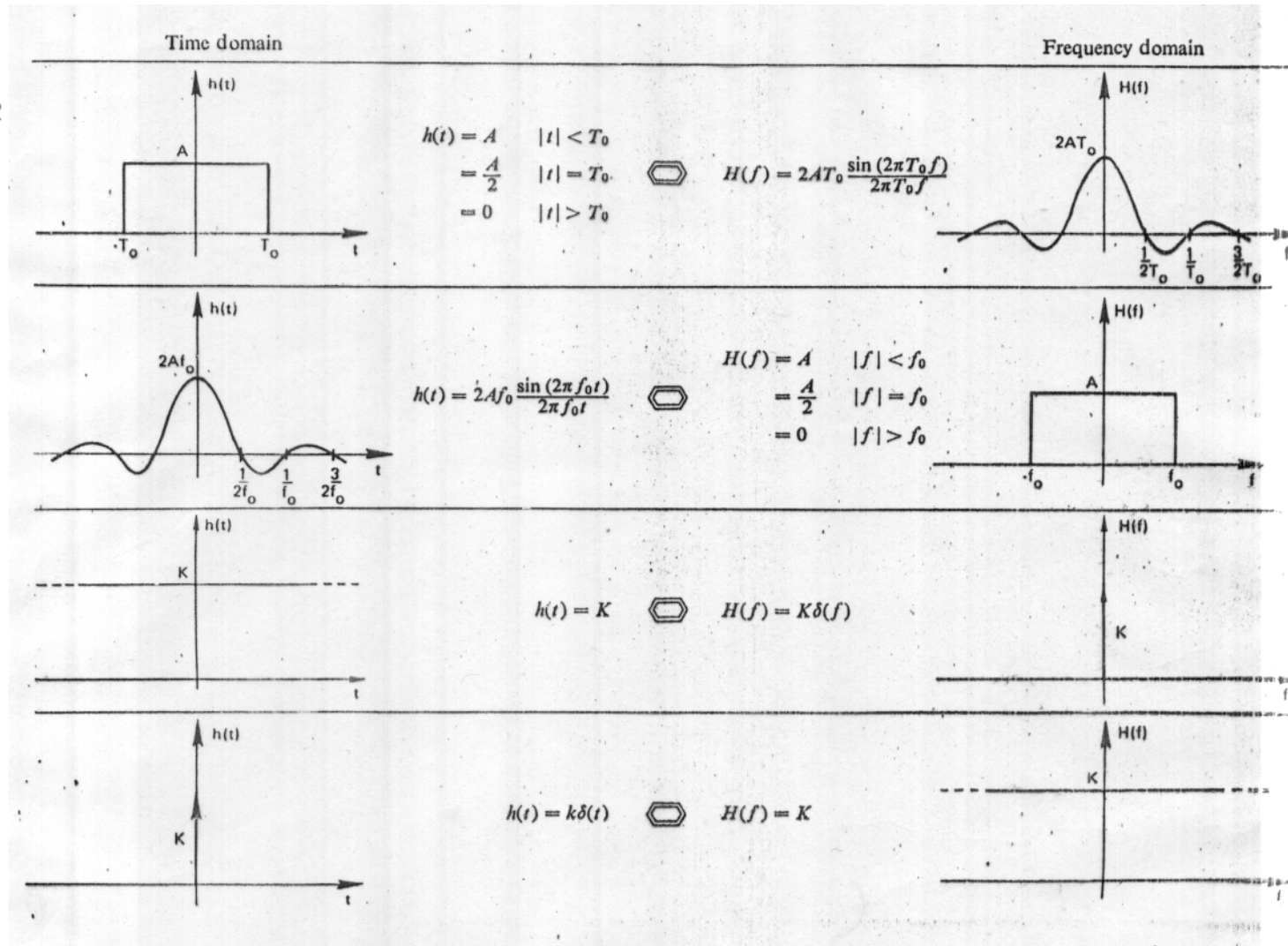
$$C_n = 1/T \int f(x) e^{-in\omega x} dx$$

Nalezení koeficientů Fourierovy řady \equiv harmonická analýza

Fourierova transformace a zpracování dat

Fourierova transformace – základní vlastnosti

24



Fourierova transformace a zpracování dat

Fourierova transformace – základní vlastnosti

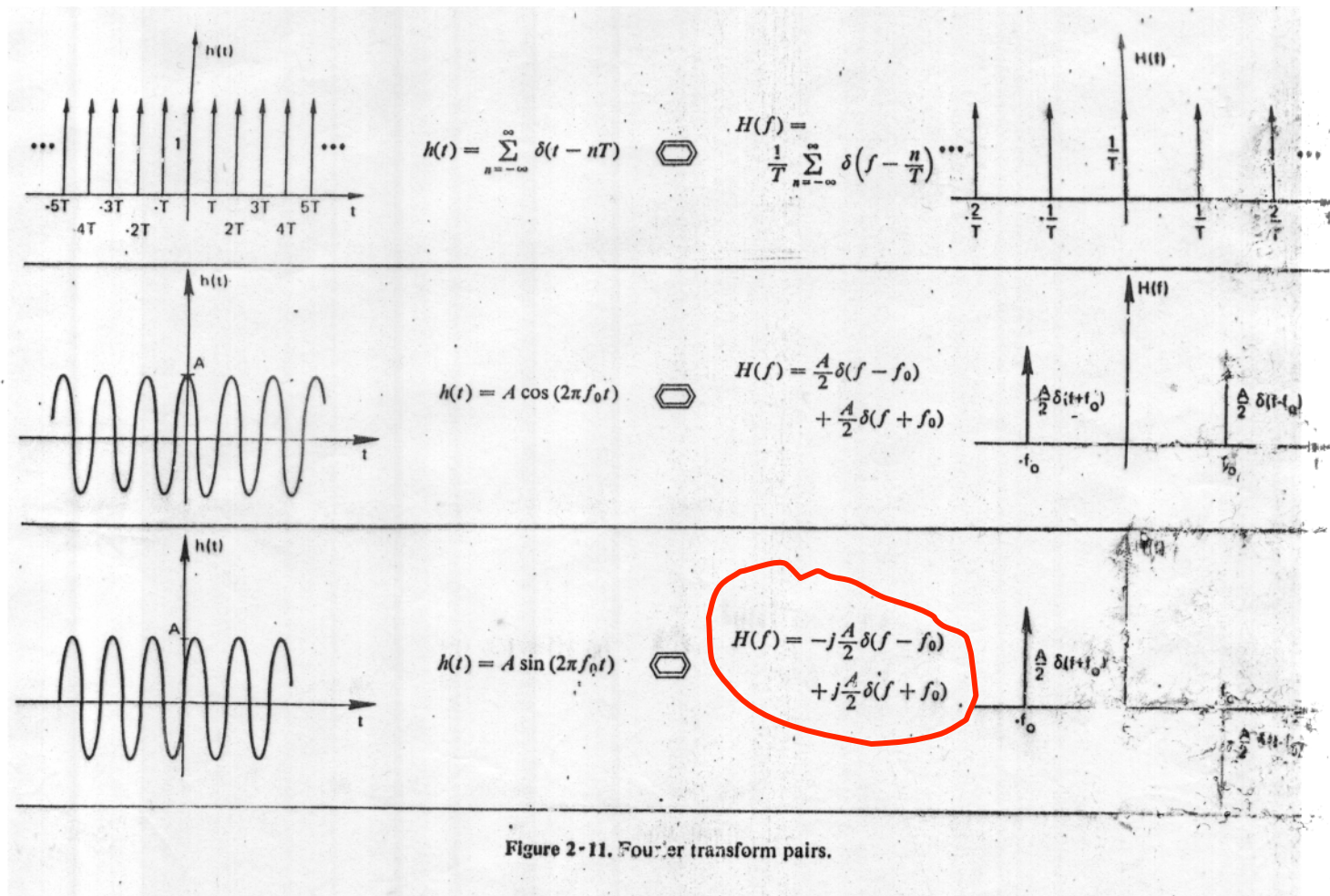
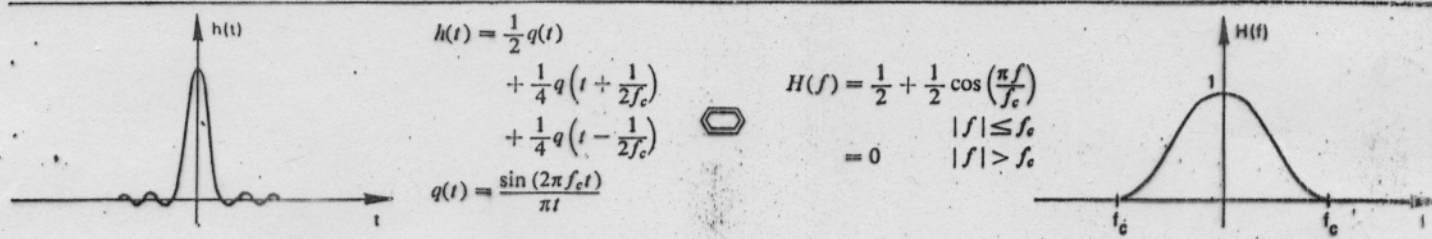
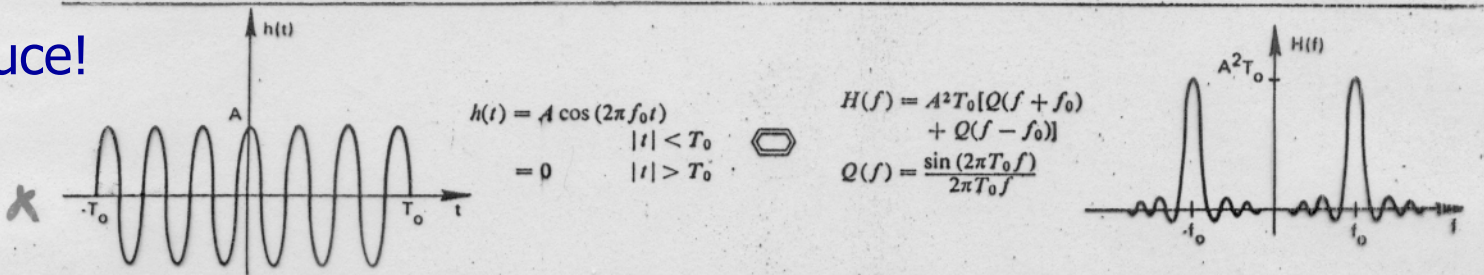
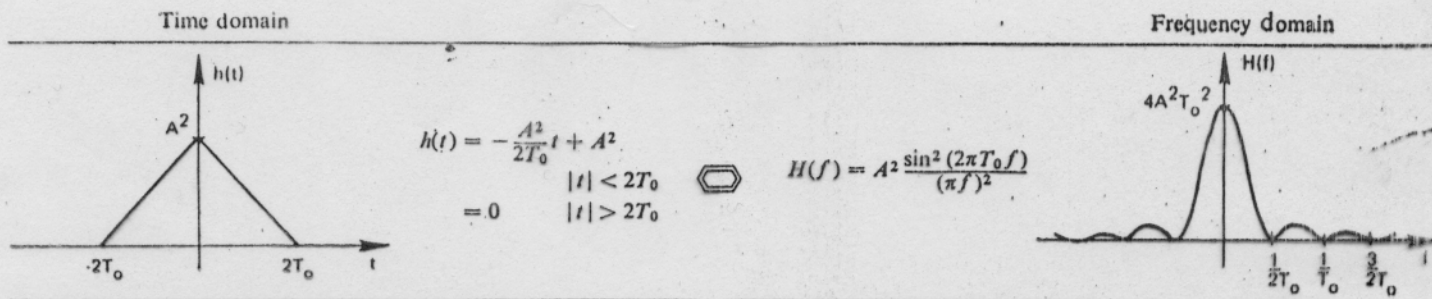


Figure 2-11. Fourier transform pairs.

Fourierova transformace a zpracování dat

Fourierova transformace – základní vlastnosti

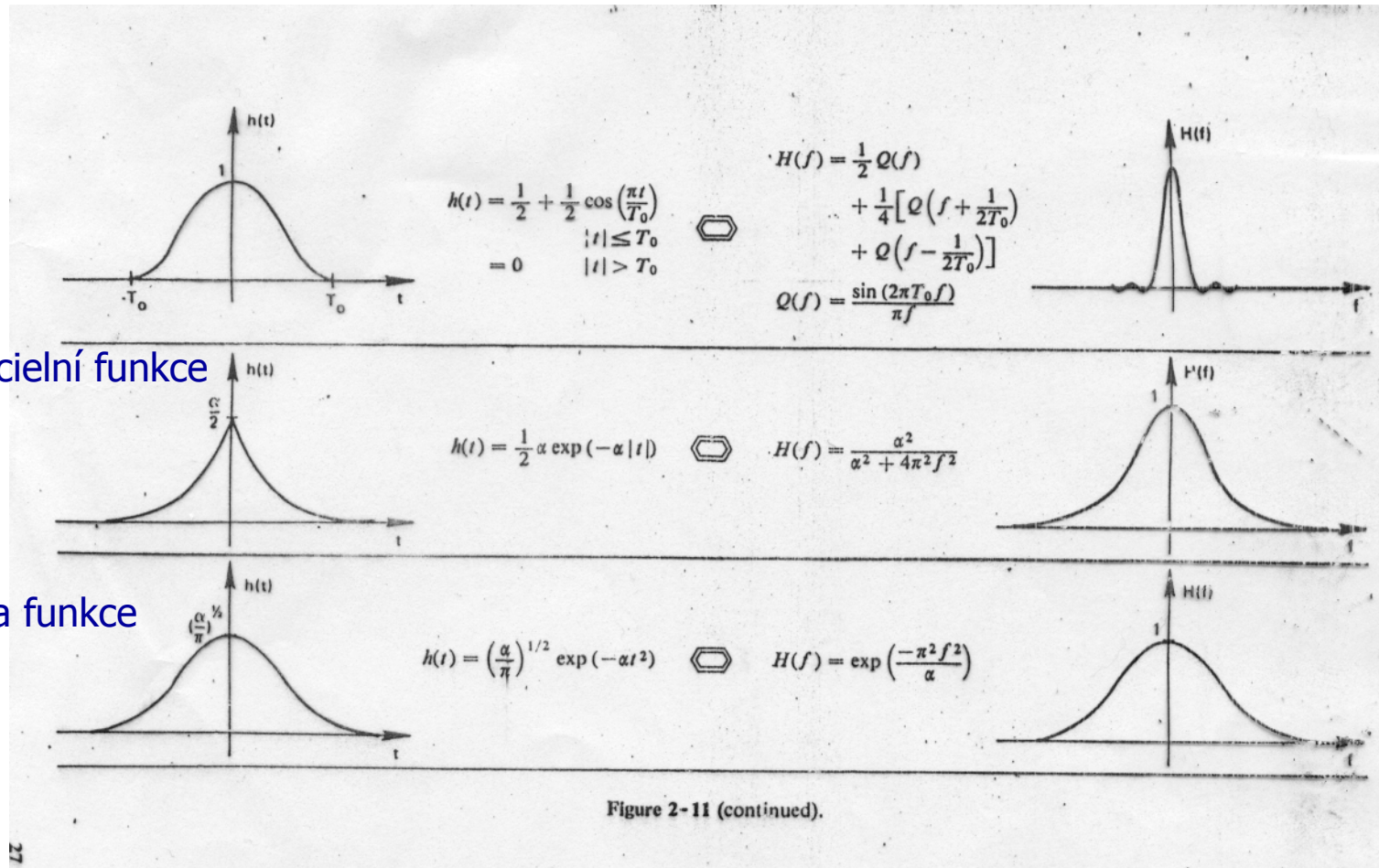
26



Konvoluce!

Fourierova transformace a zpracování dat

Fourierova transformace – základní vlastnosti



exponenciální funkce

Gaussova funkce

Fourierova transformace a zpracování dat

Fourierova transformace – základní teorémy

linearita	$x(t) + y(t)$	\Leftrightarrow	$X(\nu) + Y(\nu)$
časové škálování	$x(kt)$	\Leftrightarrow	$1/k \cdot X(\nu/k)$
časový posun	$x(t - t_0)$	\Leftrightarrow	$X(\nu)\exp(-i2\pi\nu t_0)$
modulace	$x(t) \cdot \exp(i2\pi\nu_0 t)$	\Leftrightarrow	$X(\nu - \nu_0)$
sudá funkce	$x_E(t)$	\Leftrightarrow	$X_E(\nu) = R_E(\nu)$ sudá a reálná
lichá funkce	$x_O(t)$	\Leftrightarrow	$i \cdot X_O(\nu) = i I_O(\nu)$ lichá a imaginární
reálná funkce	$x_R(t)$	\Leftrightarrow	$X(\nu) = R_E(\nu) + i I_O(\nu)$

Fourierova transformace a zpracování dat

Fourierova transformace – základní vlastnosti

Konvoluční integrál

$$r(t) * s(t) = \int_{-\infty}^{+\infty} r(\tau) \cdot s(t - \tau) d\tau$$

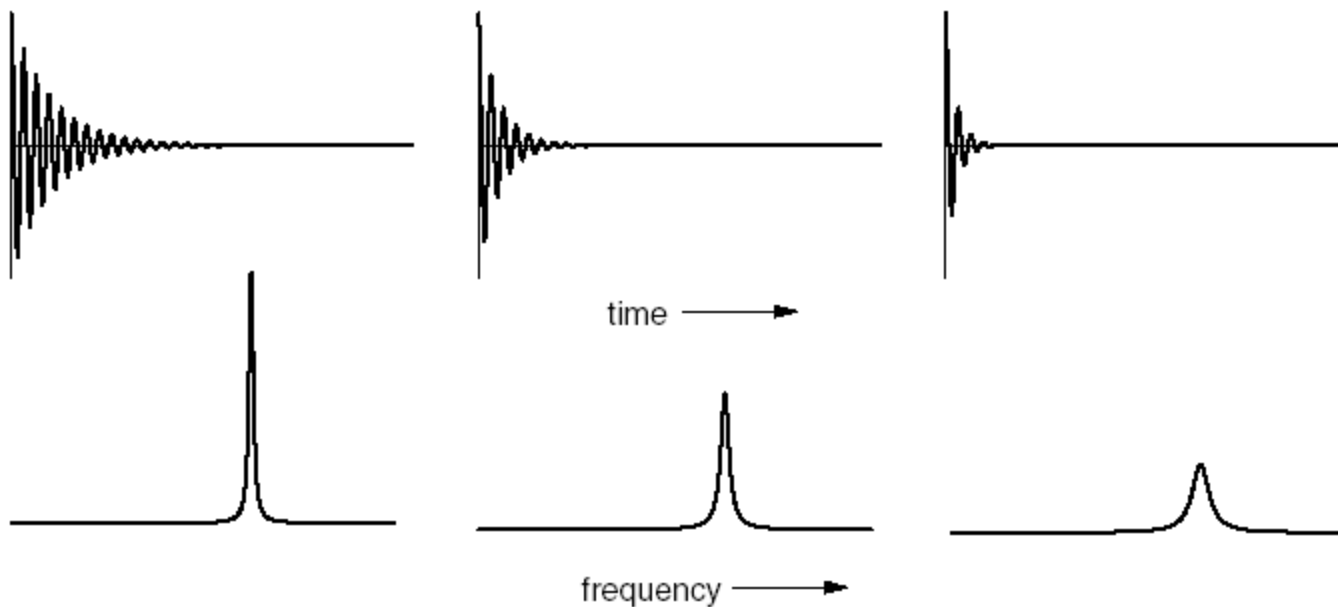
FT konv. integrálu

$$\mathfrak{F}(r(t) * s(t)) = R(\nu) \cdot S(\nu)$$

příklady

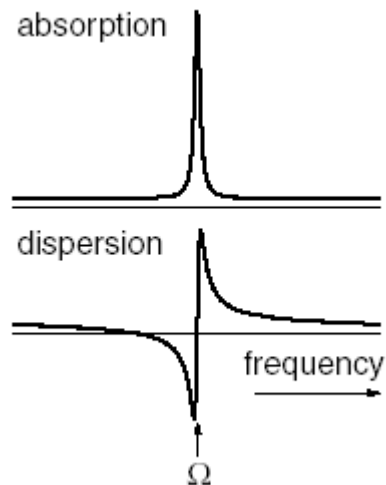
Fourierova transformace a zpracování dat

Fourierova transformace



Fourierova transformace a zpracování dat

Fourierova transformace



Spektrum s více čarami

$$S(t) = S_{0,1} \exp(i\Omega_1 t) \exp\left(\frac{-t}{T_2^{(1)}}\right) + S_{0,2} \exp(i\Omega_2 t) \exp\left(\frac{-t}{T_2^{(2)}}\right) + S_{0,3} \exp(i\Omega_3 t) \exp\left(\frac{-t}{T_2^{(3)}}\right).$$

Fourierova transformace a zpracování dat

Fáze spektra

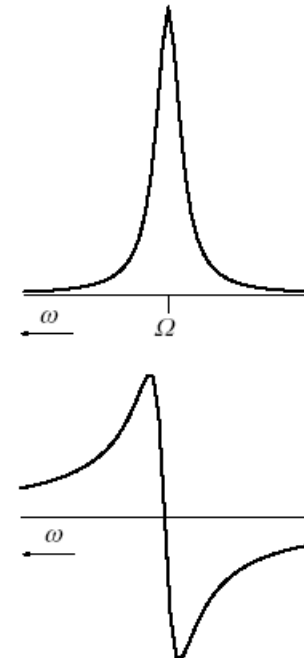
$$S_x(t) = \gamma \cos \Omega t \exp(-t/T_2) \quad S_y(t) = \gamma \sin \Omega t \exp(-t/T_2)$$

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

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

γ – amplituda signálu

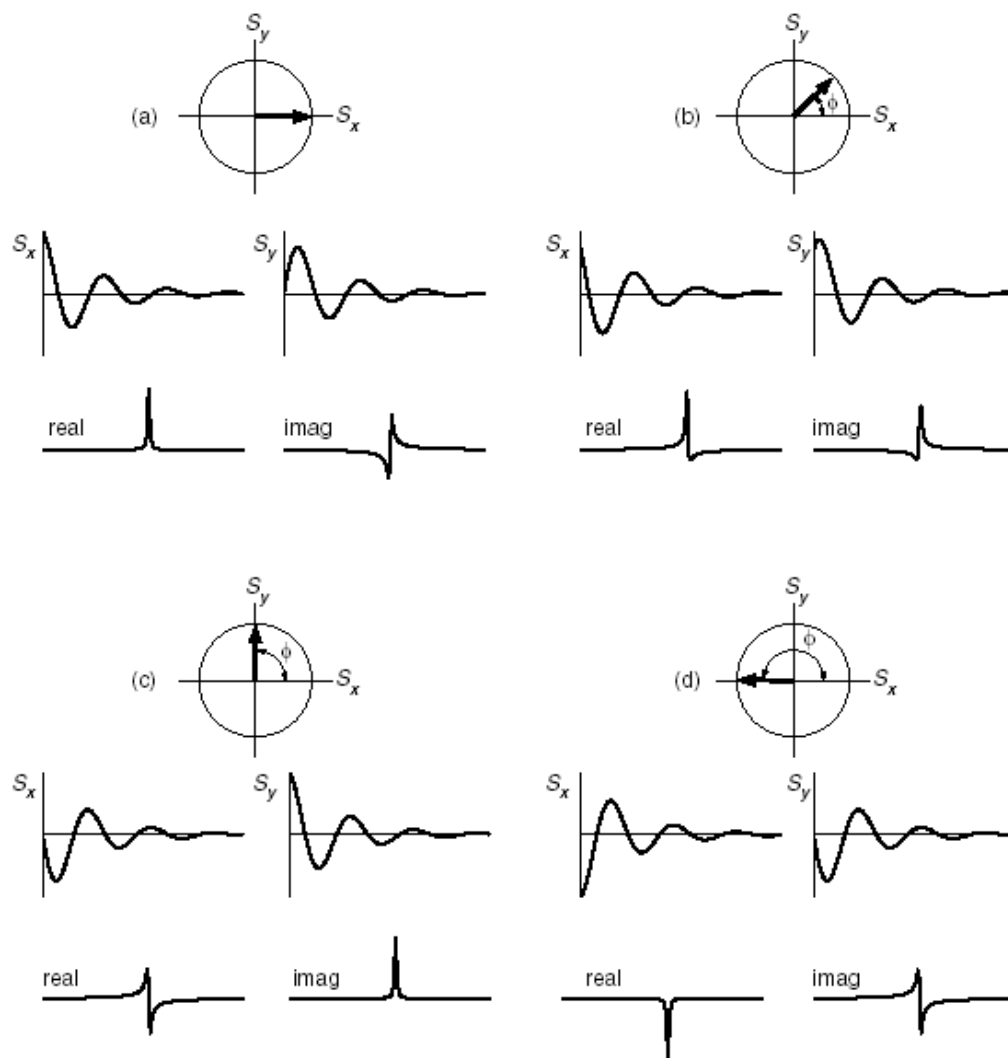
$$A(\omega) = \frac{1}{(\omega - \Omega)^2 T_2^2 + 1} \quad D(\omega) = \frac{(\omega - \Omega)T_2}{(\omega - \Omega)^2 T_2^2 + 1}$$



Lorentzův tvar spektrálních čar

Fourierova transformace a zpracování dat

Fáze spektra



Fourierova transformace a zpracování dat

Fáze spektra

fázová korekce

fázově posunutý signál

$$\exp(i\phi_{\text{corr}})S(t) = \exp(i\phi_{\text{corr}}) \times \left[S_0 \exp(i\phi) \exp(i\Omega t) \exp\left(\frac{-t}{T_2}\right) \right].$$

$$\exp(i\phi_{\text{corr}})S(t) = \exp(i(\phi_{\text{corr}} + \phi)) \left[S_0 \exp(i\Omega t) \exp\left(\frac{-t}{T_2}\right) \right].$$

je-li $\phi_{\text{corr}} = -\phi$, pak $\exp(i(\phi + \phi_{\text{corr}})) = 1$

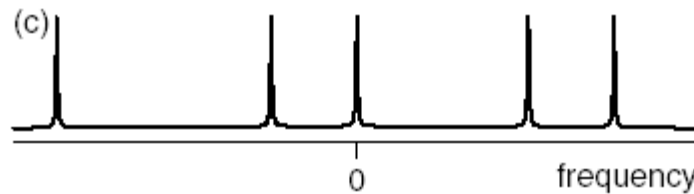
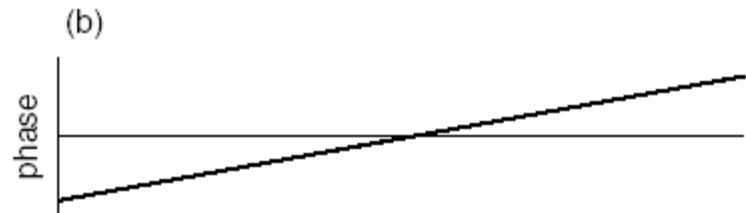
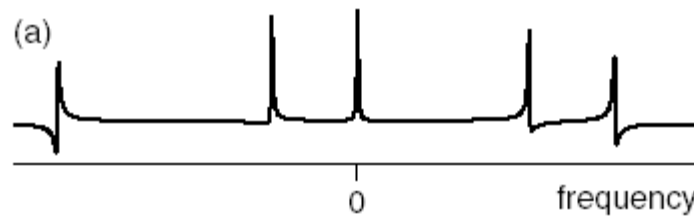
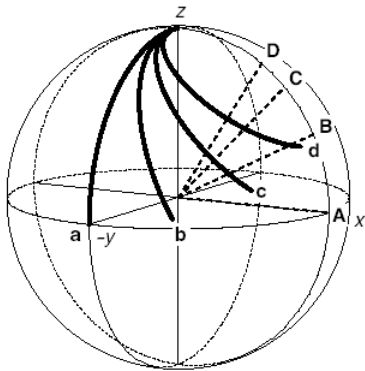
$$\exp(i\phi_{\text{corr}})S(t) = S_0 \exp(i\Omega t) \exp\left(\frac{-t}{T_2}\right).$$

Analogicky, korekce platí i ve frekvenční doméně

$$\exp(i\phi_{\text{corr}})S(\omega).$$

Fourierova transformace a zpracování dat

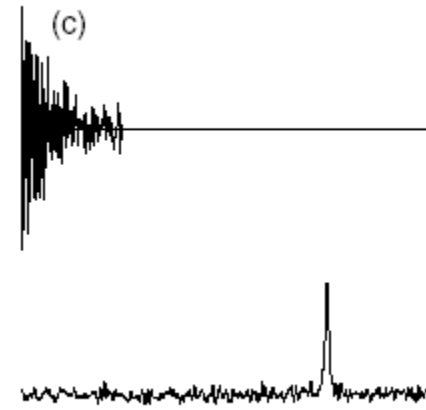
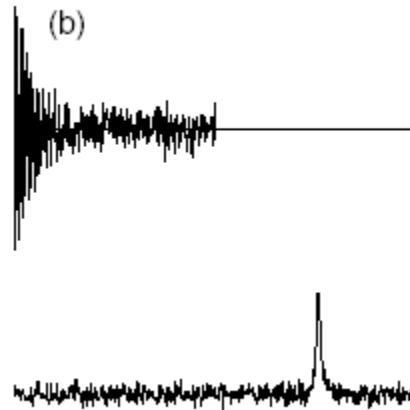
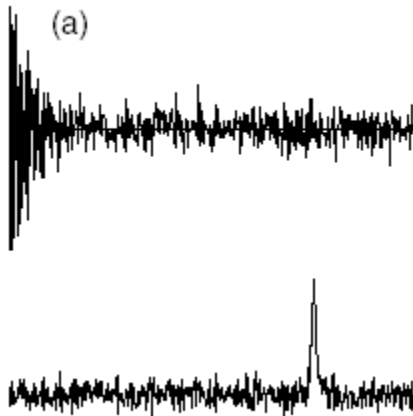
Fáze spektra – frekvenčně závislá chyba



fázová chyba lineárně závislá na ofsetu

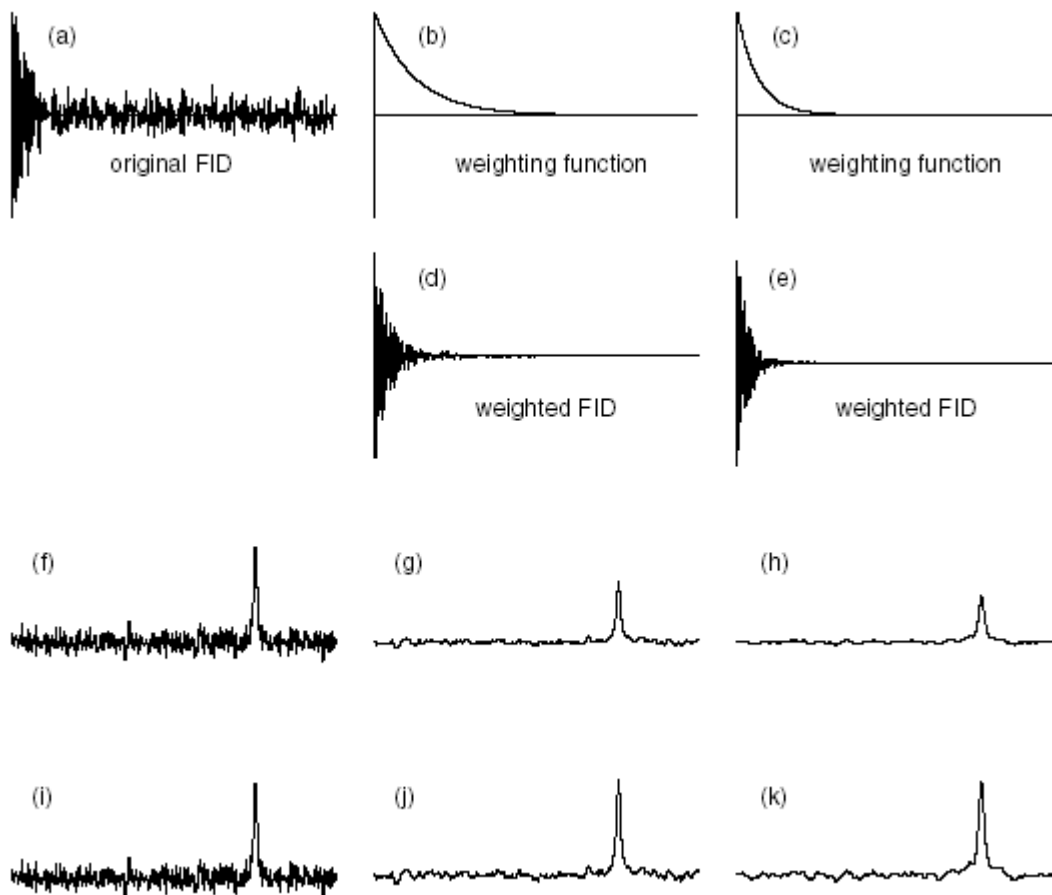
Fourierova transformace a zpracování dat

Zvýšení citlivosti



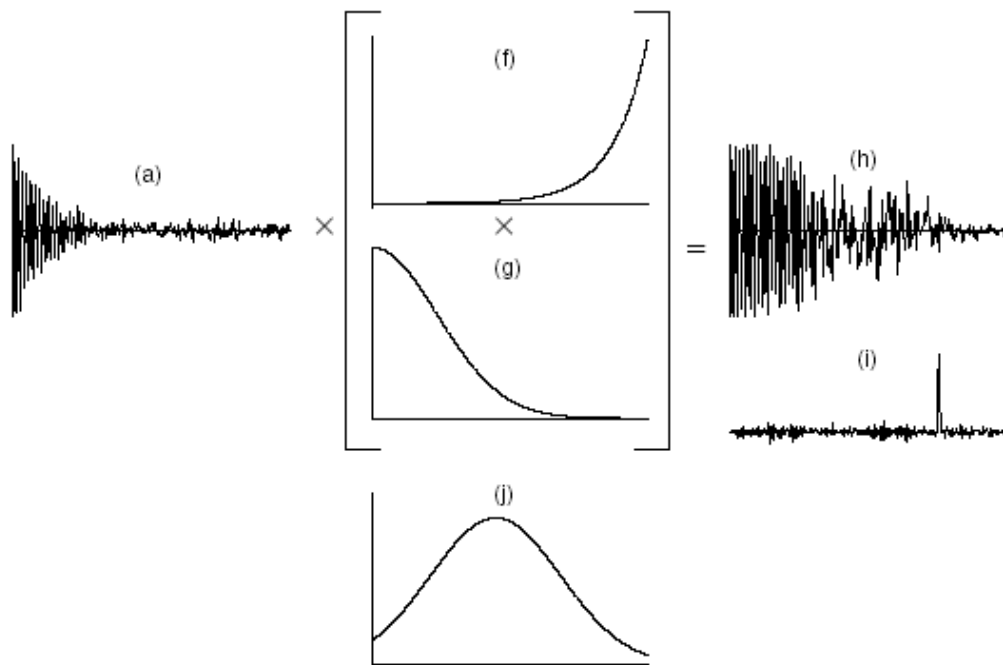
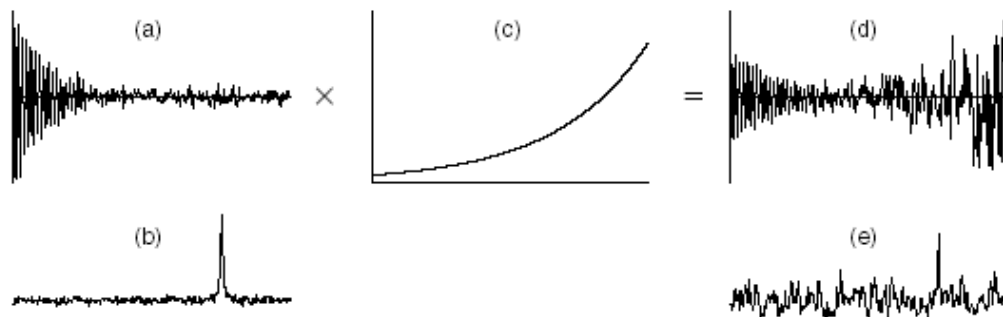
Fourierova transformace a zpracování dat

Zvýšení citlivosti



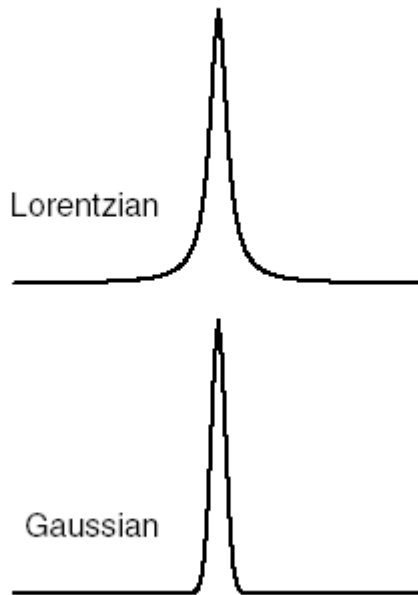
Fourierova transformace a zpracování dat

Zvýšení rozlišení



Fourierova transformace a zpracování dat

Zvýšení rozlišení



$$W(t) = \exp(-R_{LB}t)$$

Řízený filtr (matched filter) $R_{LB} = R_2^*$

$$\Delta\nu_{1/2} = 2 \Delta\nu_{1/2}^*$$

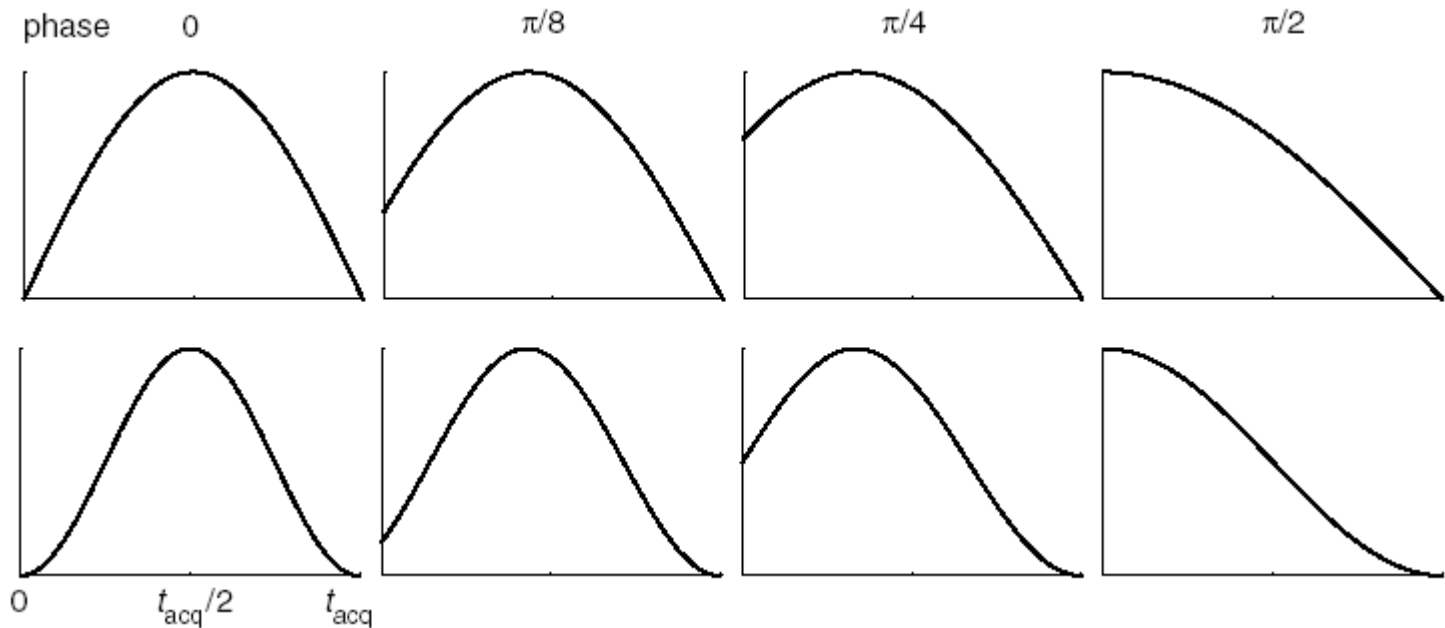
$$W(t) = \exp(-\alpha t^2),$$

Řízený filtr (matched filter) $\alpha = R_2^*$

$$\Delta\nu_{1/2} = 2^{1/2} \Delta\nu_{1/2}^*$$

Fourierova transformace a zpracování dat

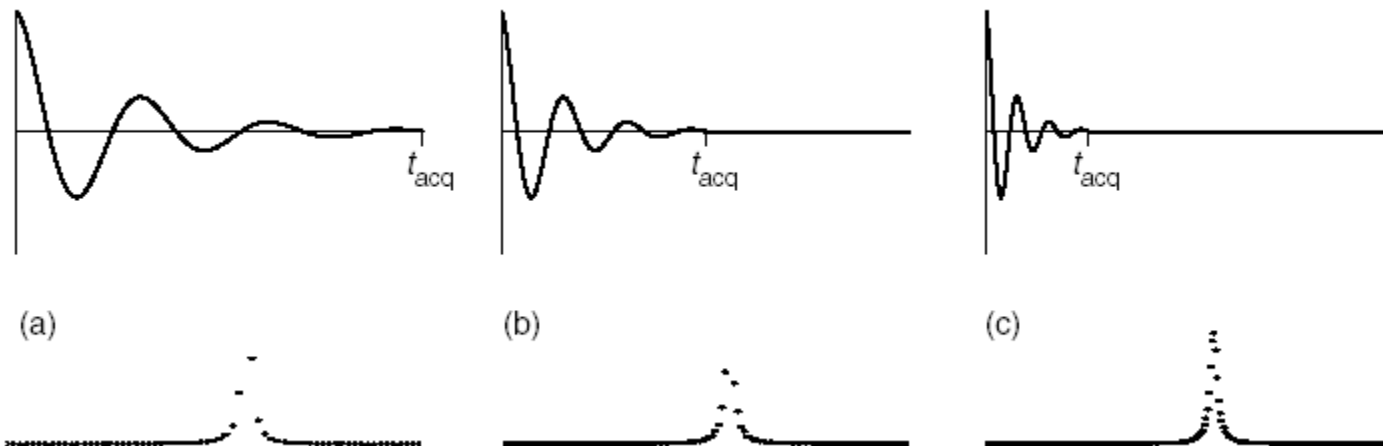
Zvýšení rozlišení



$$W(t) = \sin\left(\frac{\pi t}{t_{acq}}\right), \quad W(t) = \sin\left(\frac{(\pi - \phi)t}{t_{acq}} + \phi\right), \quad W(t) = \sin^2\left(\frac{(\pi - \phi)t}{t_{acq}} + \phi\right).$$

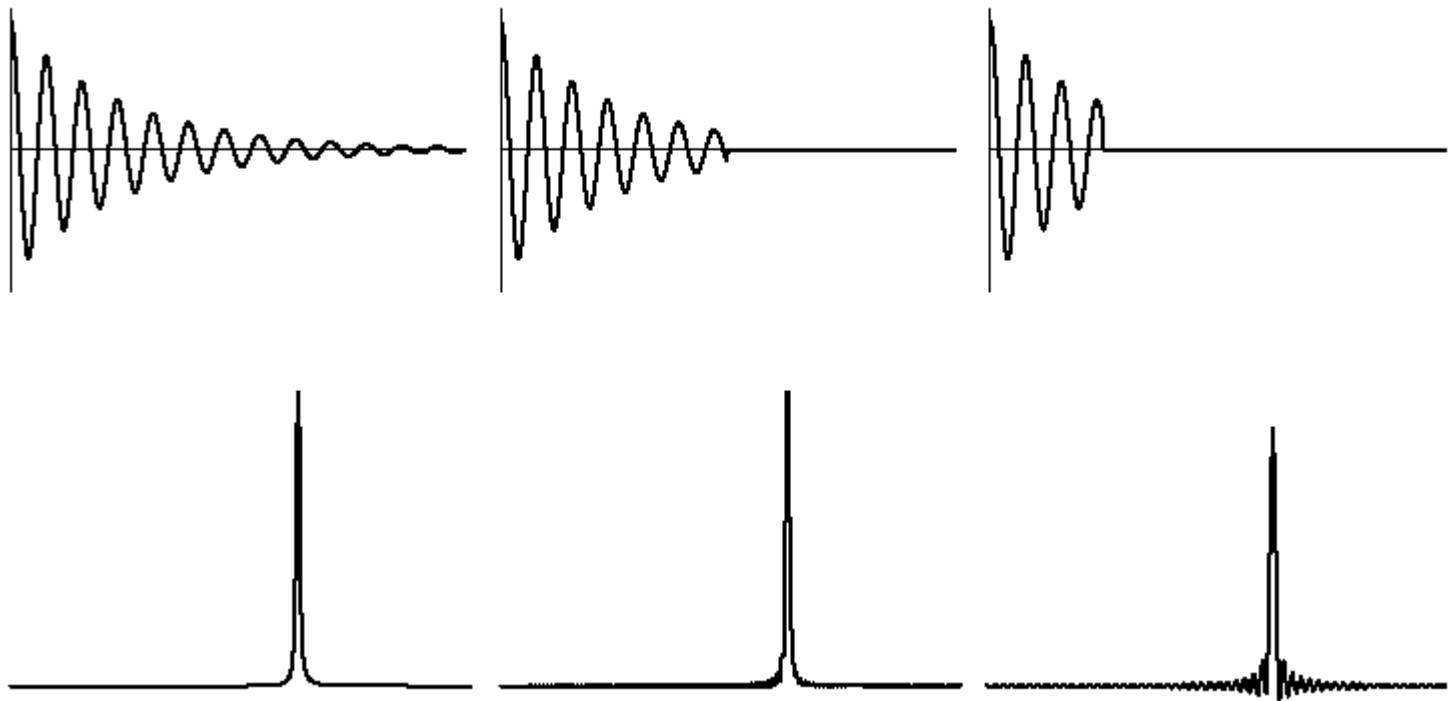
Fourierova transformace a zpracování dat

Doplňování nulami



Fourierova transformace a zpracování dat

Zkrácení signálu (truncation)



Jak pracuje spektrometr

Jednotlivé části

- Magnet
- Sonda
- Vysílač
- Přijímač
- Převodník
- Pulsní programátor
- Počítač



Jak prauje spektrometr

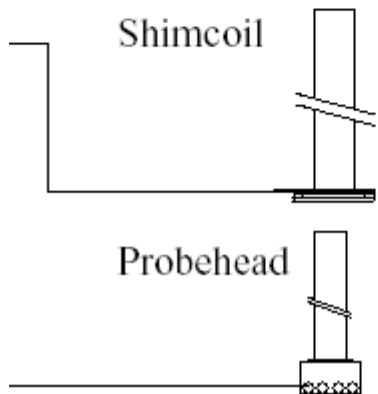
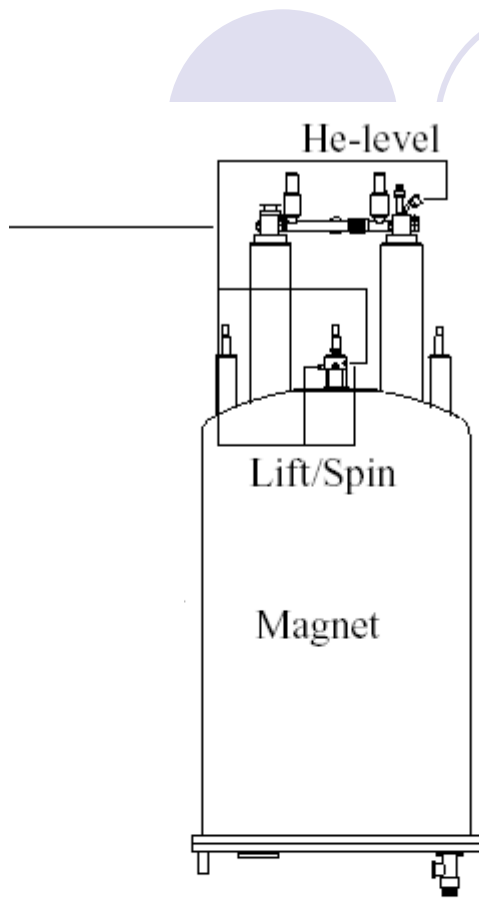
Magnet



Properties	Nitrogen	Helium
Molecular weight	28	4
Normal boiling point	[°C] -196	-269
	[°K] 77	4.2
Approximate expansion ration (volume of gas at 15°C and atmospheric pressure produced by unit volume of liquid at normal boiling point).	680	740
Density of liquid at normal boiling point	[kg m ⁻³] 810	125
Color (liquid)	none	none
Color (gas)	none	none
Odour (gas)	none	none
Toxicity	very low	very low
Explosion hazard with combustible material	no	no
Pressure rupture if liquid or cold gas is trapped	yes	yes
Fire hazard: combustible	no	no
Fire hazard: promotes ignition directly	no	no
Fire hazard: liquefies oxygen and promotes ignition	yes	yes

Jak pracuje spektrometr

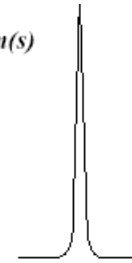
Magnet – korekce (shims)



Spectrum before Adjustment

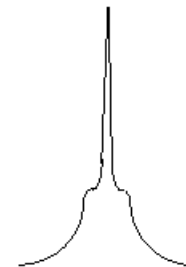


*Adjusted shim(s)
Z*

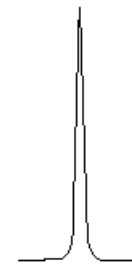


Adjusted Spectrum

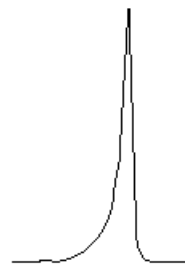
Spectrum before Adjustment



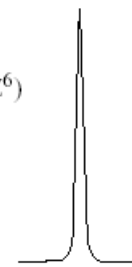
Z³, Z⁵



Spectrum before Adjustment

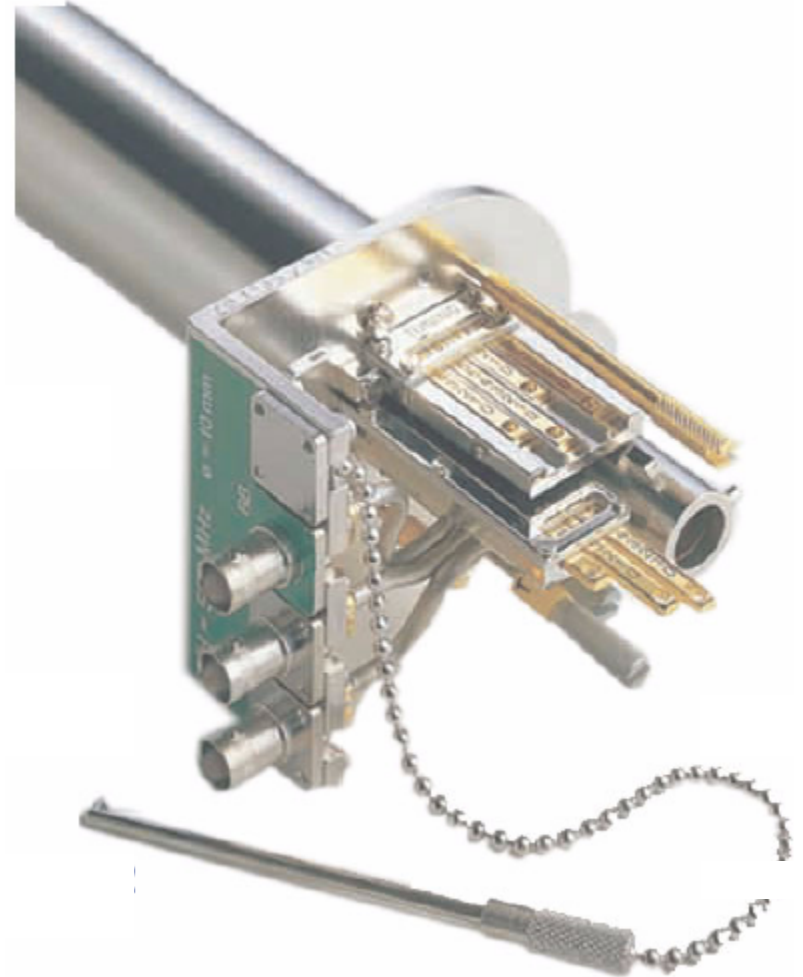
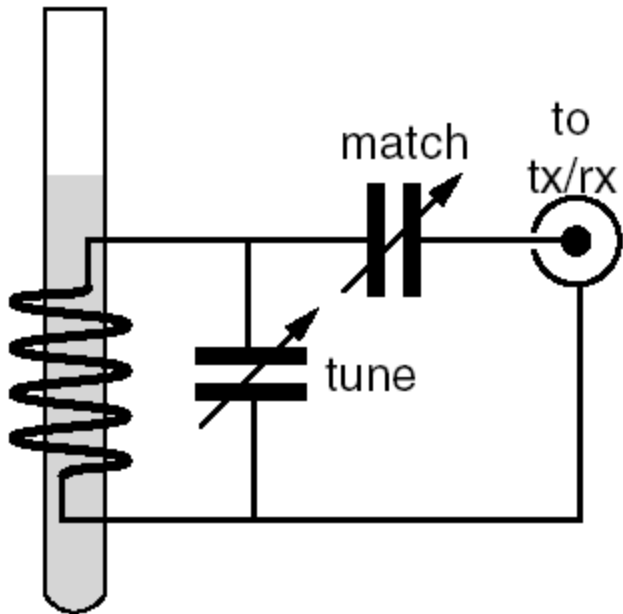


-Z², -Z⁴, (-Z⁶)



Jak prauje spektrometr

Sonda



Jak pracuje spektrometr

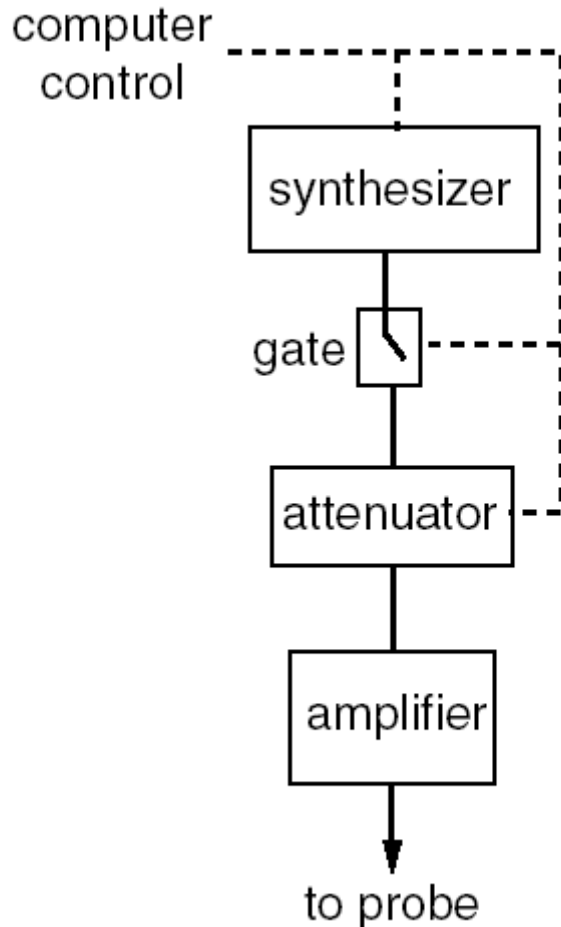
Vysílač – výkon *vers.* indukce rf pole

$$L_p = 10 \times \log_{10} \frac{P_{out}}{P_{in}}; \quad [\text{dB}]$$

$$10 \times \log_{10} \frac{P_{out}}{P_{in}} = 10 \times \log_{10} \frac{1}{2} = -3.0$$

Relativní hodnota výkonu se vyjadřuje v decibelech
1 dB: $P_1/P_2 = 1.2589254$

!!!!!!! $B_1 \sim I \sim P^{1/2}$ (P=RI²)!!!!!!!



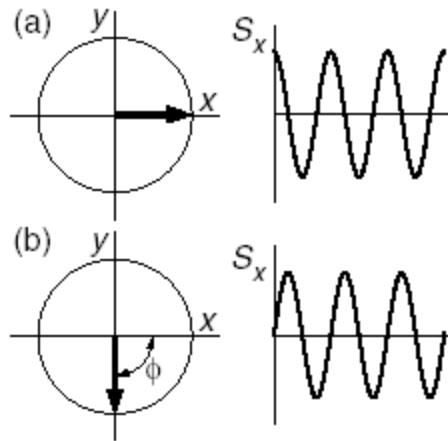
$$\text{power ratio} = \left(\frac{\omega_1^{\text{new}}/2\pi}{\omega_1^{\text{init}}/2\pi} \right)^2$$

$$\begin{aligned} \text{power ratio in dB} &= 10 \log_{10} \left(\frac{\omega_1^{\text{new}}/2\pi}{\omega_1^{\text{init}}/2\pi} \right)^2 \\ &= 20 \log_{10} \left(\frac{\omega_1^{\text{new}}/2\pi}{\omega_1^{\text{init}}/2\pi} \right) \end{aligned}$$

Relativní hodnota rf pole vyjádřená v decibelech
1 dB: $\omega_1/\omega_2 = 1.120185$

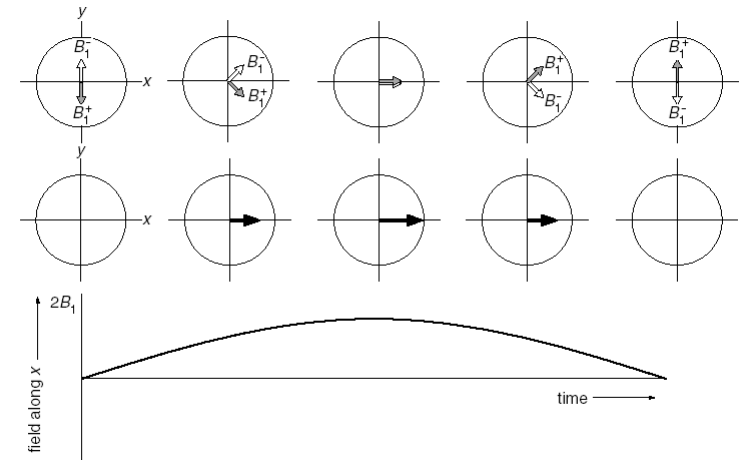
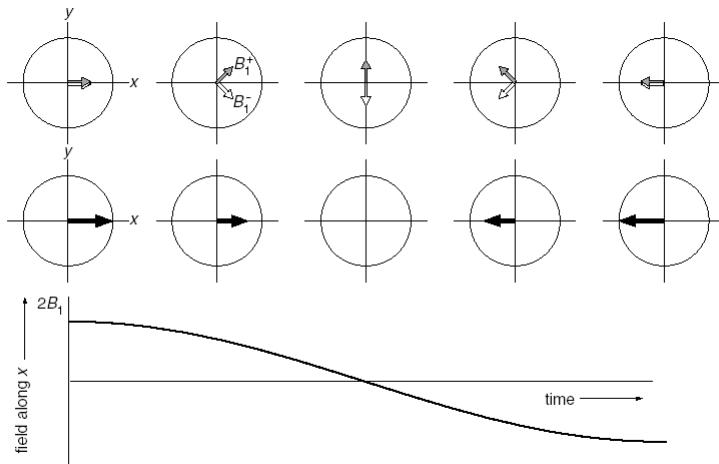
Jak pracuje spektrometr

Vysílač – fázově posunuté pulzy



$$2B_1 \cos \omega_{RF}t.$$

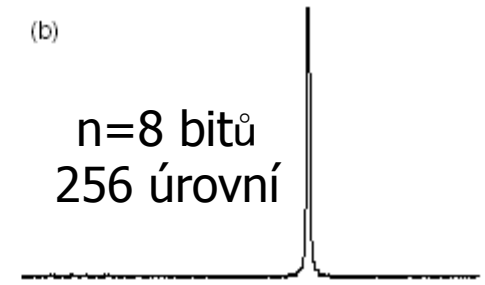
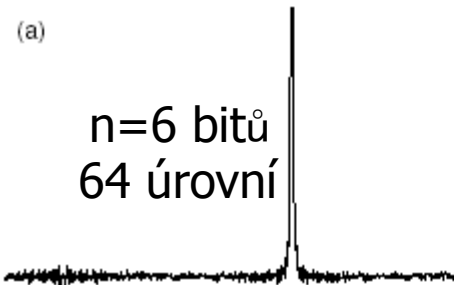
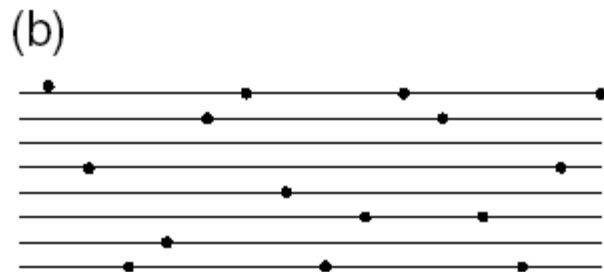
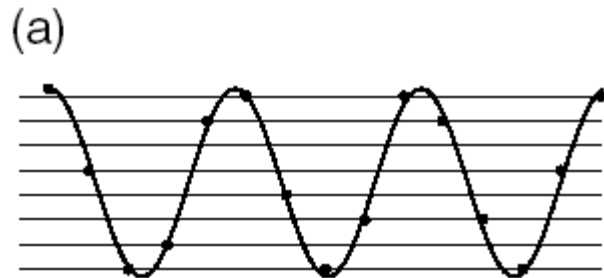
$$2B_1 \sin \omega_{RF}t.$$



Jak pracuje spektrometr

3bitový A/D převodník (8 úrovní)
 $2^n = 8$

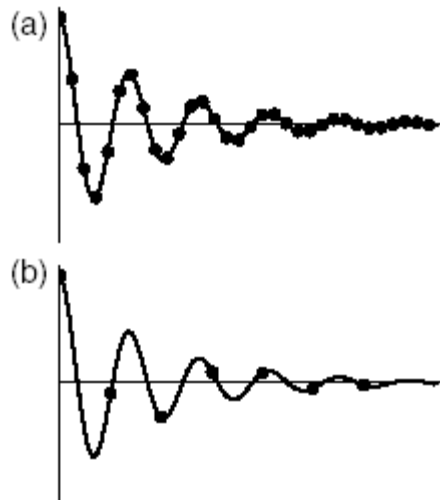
A/D převodník



Typický A/D převodník 16 bitů
tj. 65 536 úrovní
32 bitů
Tj. 4 294 967 296 úrovní

Jak pracuje spektrometr

A/D převodník – vzorkovací rychlost



Nyquistova frekvence

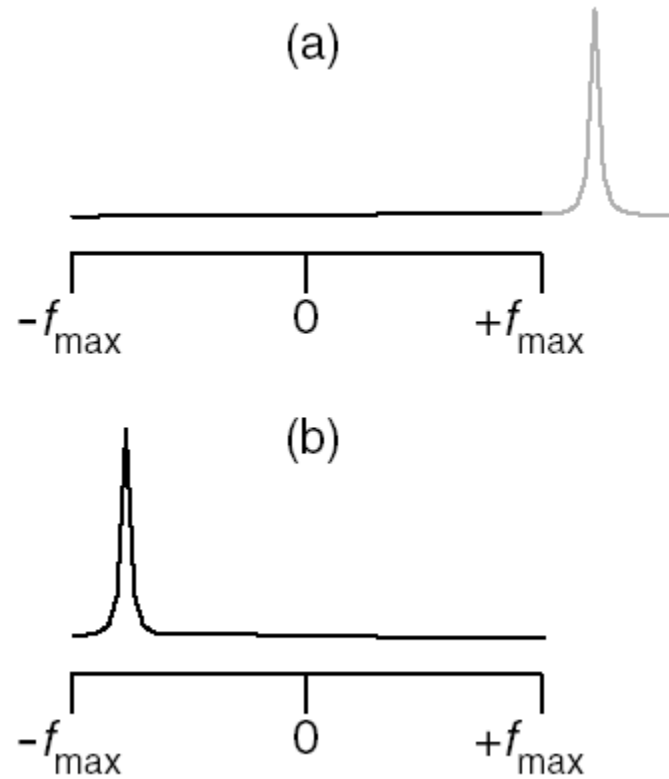
$$f_{\max} = \frac{1}{2\Delta};$$

$$\Delta = \frac{1}{2f_{\max}}.$$

$$f_{\max} = 1 \text{ kHz} \Rightarrow \Delta = 500 \text{ } \mu\text{s}$$

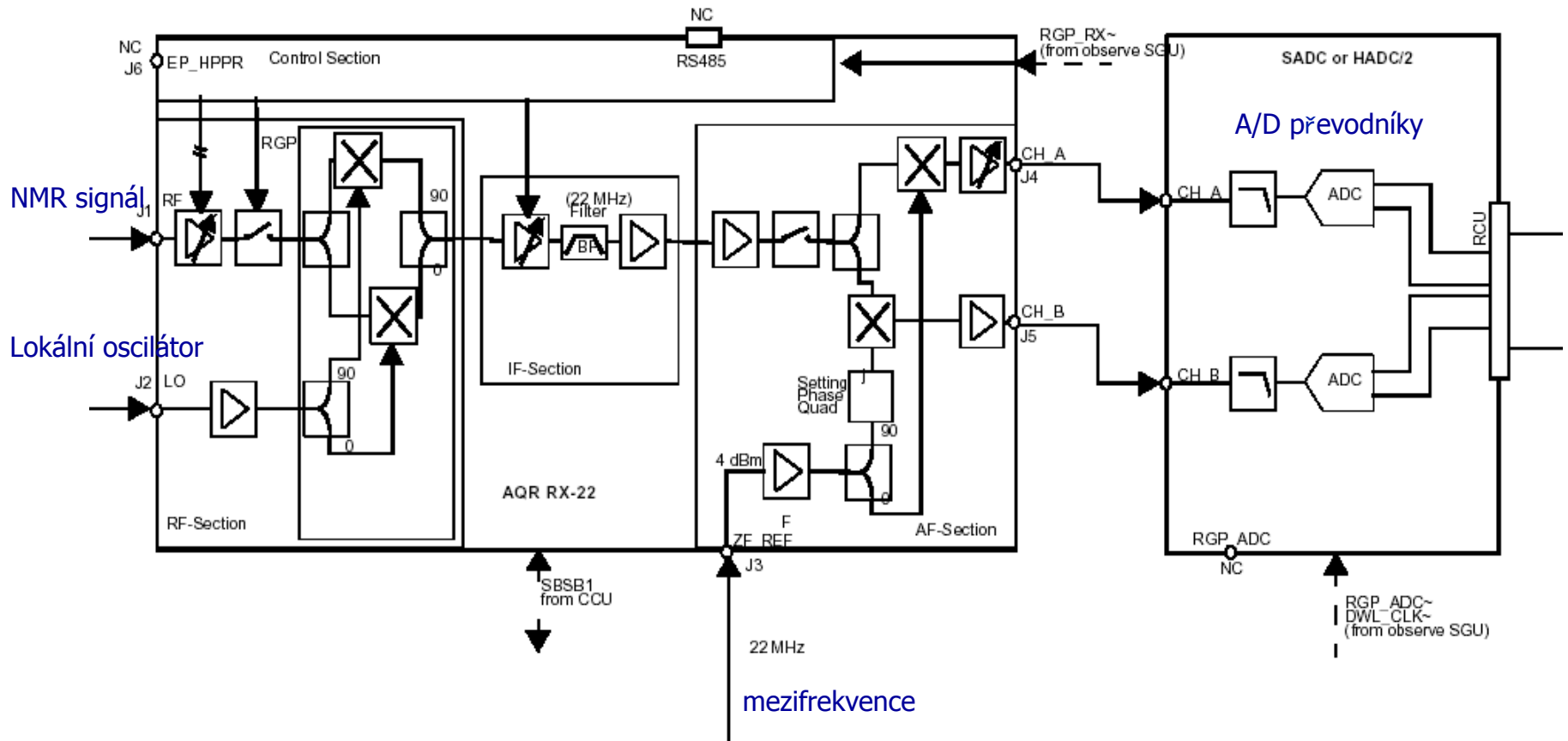
Jak pracuje spektrometr

A/D-převodník – překládání signálů



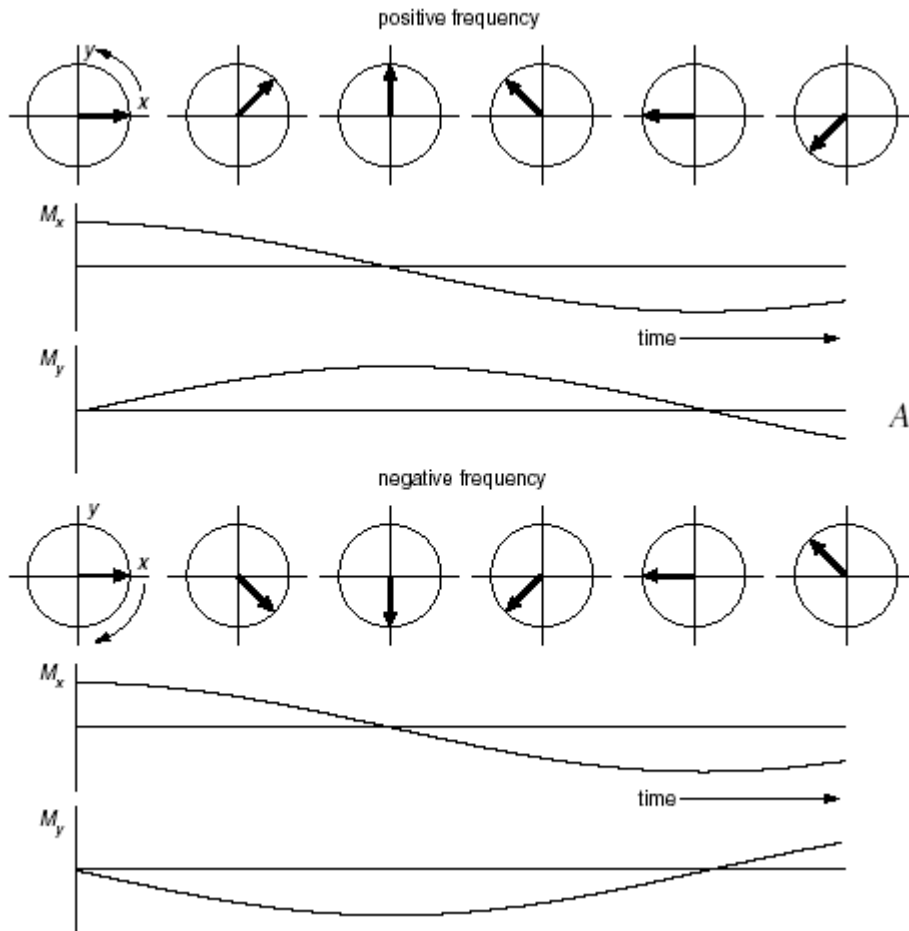
Jak pracuje spektrometr

Přijímač

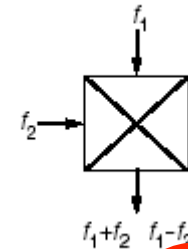


Jak pracuje spektrometr

Kvadrurní detekce



směšovač



$$A \cos \omega_0 t \times \cos \omega_{rx} t = \frac{1}{2} A [\cos(\omega_0 + \omega_{rx})t + \cos(\omega_0 - \omega_{rx})t]$$

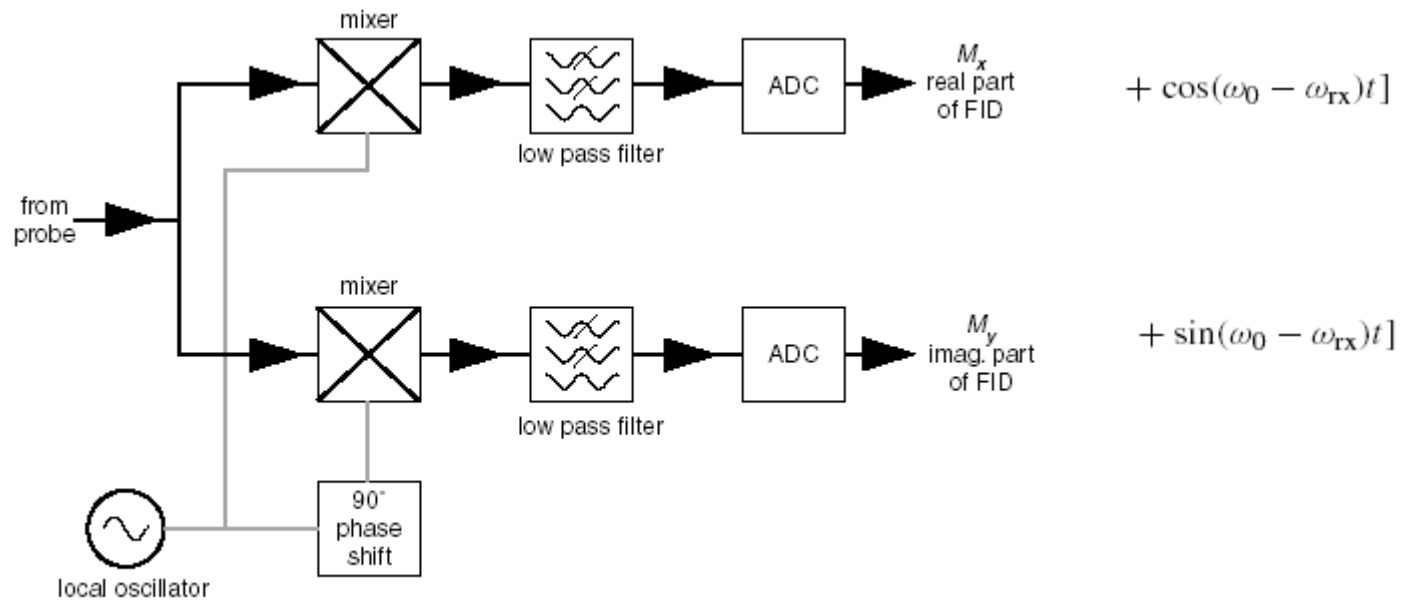
$$A \cos \omega_0 t \times (-\sin \omega_{rx} t) = \frac{1}{2} A [-\sin(\omega_0 + \omega_{rx})t + \sin(\omega_0 - \omega_{rx})t]$$

$$\cos A \cdot \cos B = \frac{1}{2} (\cos(A+B) + \cos(A-B))$$

$$\cos A \cdot \sin B = \frac{1}{2} (\sin(A+B) - \sin(A-B))$$

Jak pracuje spektrometr

Kvadrurní detekce



mezifrekvence

filter odstraní frekvence $\omega_0 + \omega_{rx}$

Jak pracuje spektrometr

Kvadrurní detekce – čas *vers.* frekvence

Šířka spektra f_{sw}

Akviziční čas t_{acq}

N – počet akvizických bodů

$$\Delta = \frac{1}{f_{sw}}$$

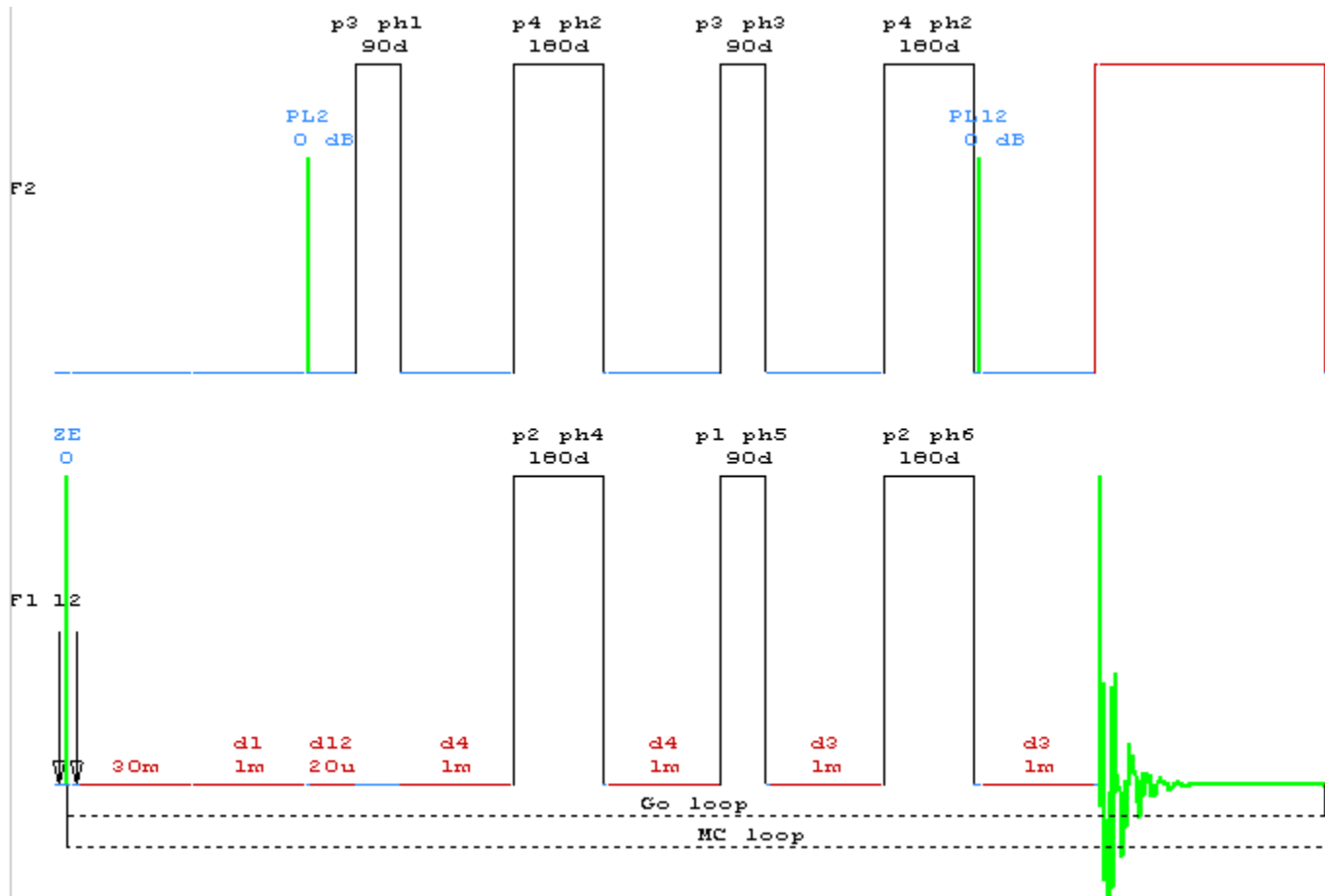
$$N = \frac{t_{acq}}{\Delta}$$

Δ – vzorkovací interval

Jak pracuje spektrometr

Pulzní programátor

INEPT s refokusací



Jak pracuje spektrometr

Pulzní programátor

```
;ineptrd
;avance-version (02/05/31)
;INEPT for non-selective polarization transfer
;with decoupling during acquisition
```

```
#include <Avance.incl>
```

```
"p2=p1*2"
"p4=p3*2"
"d3=1s/(cnst2*cnst11)"
"d4=1s/(cnst2*4)"
"d12=20u"
```

```
1 ze
2 30m do:f2
  d1
  d12 pl2:f2
  (p3 ph1):f2
  d4
  (center (p4 ph2):f2 (p2 ph4) )
  d4
  (p3 ph3):f2 (p1 ph5)
  d3
  (center (p4 ph2):f2 (p2 ph6) )
  d3 pl12:f2
  go=2 ph31 cpd2:f2
  30m do:f2 mc #0 to 2 F0(zd)
exit
```

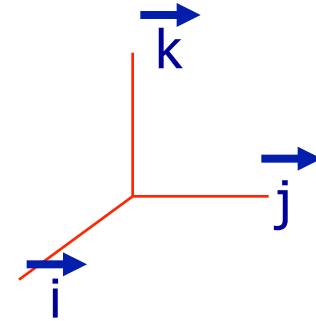
```
ph1=0 0 0 0 0 0 0 2 2 2 2 2 2 2 2
ph2=0 2
ph3=1 1 3 3
ph4=0 2
ph5=0 0 0 0 1 1 1 1 2 2 2 2 3 3 3 3
ph6=0 2 0 2 1 3 1 3
ph31=0 0 2 2 1 1 3 3
```

```
;pl1 : f1 channel - power level for pulse (default)
;pl2 : f2 channel - power level for pulse (default)
;pl12: f2 channel - power level for CPD/BB decoupling
;p1 : f1 channel - 90 degree high power pulse
;p2 : f1 channel - 180 degree high power pulse
;p3 : f2 channel - 90 degree high power pulse
;p4 : f2 channel - 180 degree high power pulse
;d1 : relaxation delay; 1-5 * T1
;d3 : 1/(6J(XH)) XH, XH2, XH3 positive
; 1/(4J(XH)) XH only
; 1/(3J(XH)) XH, XH3 positive, XH2 negative
;d4 : 1/(4J(XH))
;d12: delay for power switching [20 usec]
;cnst2: = J(XH)
;cnst11: 6 XH, XH2, XH3 positive
; 4 XH only
; 3 XH, XH3 positive, XH2 negative
;NS: 4 * n, total number of scans: NS * TD0
;DS: 16
;cpd2: decoupling according to sequence defined by cpdprg2
;pcpd2: f2 channel - 90 degree pulse for decoupling sequence
```

Vektorový model = Blochova rovnice

$$\frac{d\vec{M}}{dt} = -\gamma \cdot \vec{B}_0 \times \vec{M} - M_x/T_2 \cdot \vec{i} - M_y/T_2 \cdot \vec{j} - (M_z - M_0)/T_1 \cdot \vec{k}$$

$$\vec{M}(t) = M_x(t)\vec{i} + M_y(t)\vec{j} + M_z(t)\vec{k} = a(t)\vec{i} + b(t)\vec{j} + c(t)\vec{k}$$



Numerické řešení

$$d\vec{M}/dt = \begin{bmatrix} R11 & R12 & R13 \\ R21 & R22 & R23 \\ R31 & R32 & R33 \end{bmatrix} \times \begin{bmatrix} M_x(0) \\ M_y(0) \\ M_z(0) \end{bmatrix} = \begin{bmatrix} M_x(t) = R11 \cdot M_x(0) + R12 \cdot M_y(0) + R13 \cdot M_z(0) \\ M_y(t) = R21 \cdot M_x(0) + R22 \cdot M_y(0) + R23 \cdot M_z(0) \\ M_z(t) = R31 \cdot M_x(0) + R32 \cdot M_y(0) + R33 \cdot M_z(0) \end{bmatrix}$$

Vektorový model = rotační matice

$$R_x(\theta) = \begin{array}{|c|c|c|} \hline 1 & 0 & 0 \\ \hline 0 & \cos \theta & \sin \theta \\ \hline 0 & -\sin \theta & \cos \theta \\ \hline \end{array}$$

$$R_y(\chi) = \begin{array}{|c|c|c|} \hline \cos \chi & 0 & -\sin \chi \\ \hline 0 & 1 & 0 \\ \hline \sin \chi & 0 & \cos \chi \\ \hline \end{array}$$

$$R_z(\phi) = \begin{array}{|c|c|c|} \hline \cos \phi & \sin \phi & 0 \\ \hline -\sin \phi & \cos \phi & 0 \\ \hline 0 & 0 & 1 \\ \hline \end{array}$$

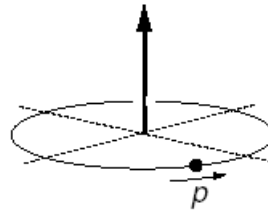
Součinový operátorový formalismus

Přestručné opakování základů kvantové mechaniky

Operátor

Operátor x funkce = nová funkce; $d/dx(\sin x) = \cos x$

Rotační moment hybnosti



Spinový operátor

I_x , I_y a I_z – Pauliho spinové matice

Hamiltonián

Operátor energie

Vlastní hodnoty operátorů, vlastní funkce

Součinný operátorový formalismus

Přestručné opakování základů kvantové mechaniky

Matice hustoty (operátor)

Operátor hustoty (též *matice hustoty* nebo *statistický operátor*) je operátor používaný pro popis kvantového stavu systému. Na rozdíl od vlnové funkce je obecnější, protože kromě čistých kvantových stavů popisuje i měřitelné vlastnosti statistických souborů kvantových stavů, tedy případ, kdy pracujeme se směsí různých kvantových stavů, které jsou zastoupeny s jistými pravděpodobnostmi. Takové statistické soubory se nazývají *smíšenými stavy*.

Operátor hustoty se široce používá v teorii dekoherence a obecně v teorii otevřených kvantových systémů, kdy se systém nevyvíjí koherentně, tj. podle Schrödingerovy rovnice, ale je průběžně měřen svým okolím. V takovém případě nelze formalismus vlnové funkce využít, protože systém je procesem měření z čistého kvantového stavu pomalu přeměňován na stav smíšený.

Hamiltonián pulzů a vývojových intervalů

$$\sigma(t) = a(t)I_x + b(t)I_y + c(t)I_z$$

$$H_{\text{free}} = \Omega I_z$$

$$H_{\text{pulse},x} = \omega_1 I_x$$

$$H_{\text{pulse},y} = \omega_1 I_y$$

Součinový operátorový formalismus

Přestručné opakování základů kvantové mechaniky

Pohybová rovnice – Liouville-von Neumanova rovnice

$$\sigma(t)/dt = -i \cdot [H(t), \sigma(t)]$$

$$\sigma(t) = \exp(-i H t) \sigma(0) \exp(i H t)$$

$$H = \omega_1 I_x \quad \sigma(0) = I_z$$

$$\sigma(t_p) = \exp\left(-i \underbrace{\omega_1 t_p}_{\beta} I_x\right) I_z \exp(i \omega_1 t_p I_x)$$

Součinový operátorový formalismus

Přestručné opakování základů kvantové mechaniky

$$\exp(-i\beta I_x) I_z \exp(i\beta I_x) \equiv \cos \beta I_z - \sin \beta I_y$$

$$\sigma(t_p) = \cos \omega_1 t_p I_z - \sin \omega_1 t_p I_y$$

Součinový operátorový formalismus

Standardní rotace

1. příklad

$$\exp(-i\theta I_x) I_y \exp(i\theta I_x) \quad \exp(-i\theta I_x) I_y \exp(i\theta I_x) \equiv \cos\theta I_y + \sin\theta I_z$$

2. příklad

$$\exp(-i\theta I_y) \{-I_z\} \exp(i\theta I_y)$$

$$\begin{aligned} \exp(-i\theta I_y) \{-I_z\} \exp(i\theta I_y) &\equiv \cos\theta \{-I_z\} + \sin\theta \{-I_x\} \\ &\equiv -\cos\theta I_z - \sin\theta I_x \end{aligned}$$

Zkrácená notace

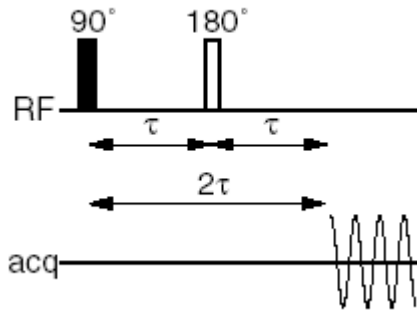
$$\sigma(t_p) = \exp(-i\omega_1 t_p I_x) \sigma(0) \exp(i\omega_1 t_p I_x)$$

$$\sigma(0) \xrightarrow{\omega_1 t_p I_x} \sigma(t_p)$$

$$I_z \xrightarrow{\omega_1 t_p I_x} \cos\omega_1 t_p I_z - \sin\omega_1 t_p I_y$$

Součinný operátorový formalismus

Spinové echo – příklad výpočtu



$$90^\circ(x) \xrightarrow{a} \text{delay } \tau \xrightarrow{b} 180^\circ(x) \xrightarrow{e} \text{delay } \tau \xrightarrow{f} \text{acquire}$$

$$-I_y \xrightarrow{\Omega t_z} \sigma(b)$$

$$-I_y \xrightarrow{\Omega t_z} -\cos \Omega \tau I_y + \sin \Omega \tau I_x$$

$$-\cos \Omega \tau I_y + \sin \Omega \tau I_x \xrightarrow{\omega_1 t_p I_x} \sigma(e)$$

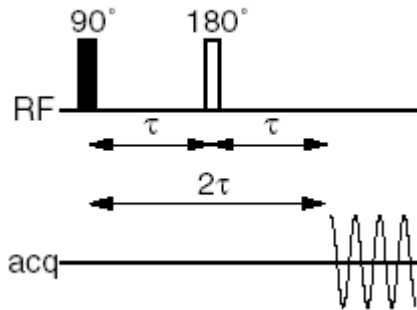
$$-\cos \Omega \tau I_y \xrightarrow{\omega_1 t_p I_x} -\cos \Omega \tau \cos \omega_1 t_p I_y - \cos \Omega \tau \sin \omega_1 t_p I_z$$

$$-\cos \Omega \tau I_y \xrightarrow{\pi I_x} \cos \Omega \tau I_y$$

$$-\cos \Omega \tau I_y + \sin \Omega \tau I_x \xrightarrow{\pi I_x} \cos \Omega \tau I_y + \sin \Omega \tau I_x$$

Součinný operátorový formalismus

Spinové echo – příklad výpočtu



$$90^\circ(x) \xrightarrow{a} \text{delay } \tau \xrightarrow{b} 180^\circ(x) \xrightarrow{e} \text{delay } \tau \xrightarrow{f} \text{acquire}$$

$$\begin{aligned} \cos \Omega \tau I_y &\xrightarrow{\Omega t_z} \cos \Omega \tau \cos \Omega \tau I_y - \sin \Omega \tau \cos \Omega \tau I_x \\ \sin \Omega \tau I_x &\xrightarrow{\Omega t_z} \cos \Omega \tau \sin \Omega \tau I_x + \sin \Omega \tau \sin \Omega \tau I_y \\ &(\cos \Omega \tau \cos \Omega \tau + \sin \Omega \tau \sin \Omega \tau) I_y + (\cos \Omega \tau \sin \Omega \tau - \sin \Omega \tau \cos \Omega \tau) I_x \end{aligned}$$

1
0

Celkový výsledek

$$I_z \xrightarrow{90^\circ(x)-\tau-180^\circ(x)-\tau-} I_y$$

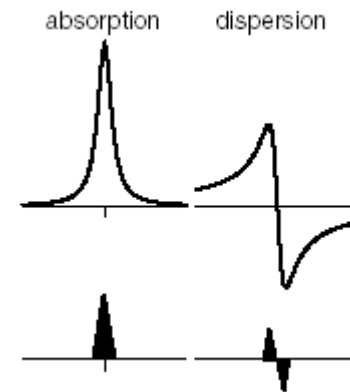
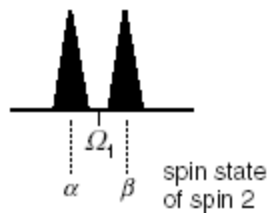
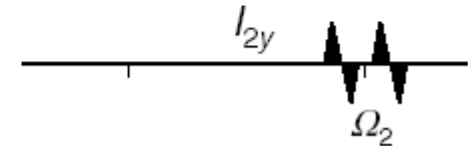
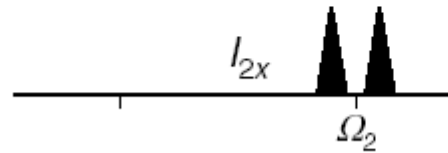
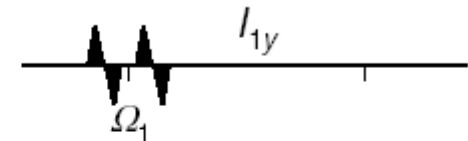
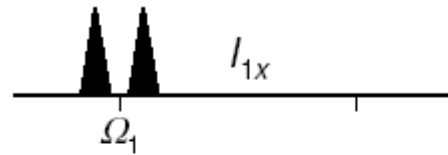
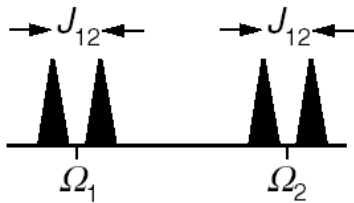
Součinný operátorový formalismus

Dvouspinové operátory

Soufázové (in-phase) operátory - 6

spin 1 : I_{1x} I_{1y} I_{1z}

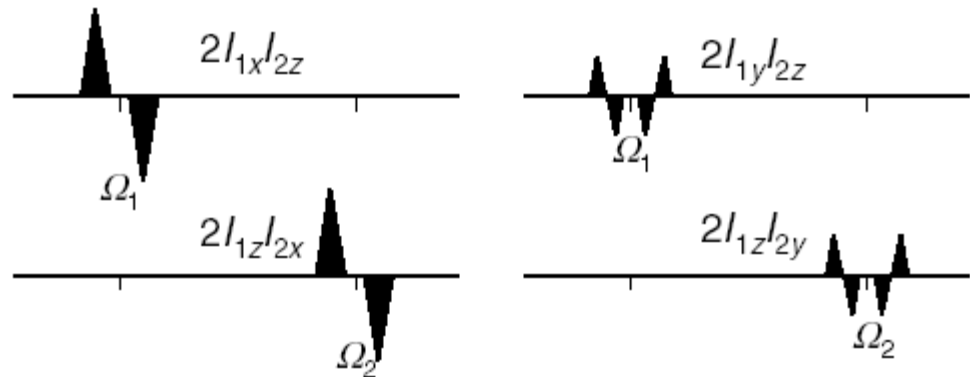
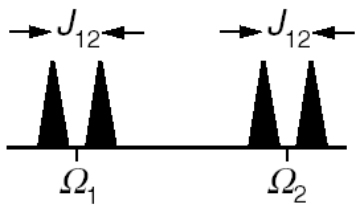
spin 2 : I_{2x} I_{2y} I_{2z}



Součinový operátorový formalismus

Dvouspinové operátory

Antifázové (anti-phase) operátory - 4



Celkový počet operátorů
 4^N (N je počet spinů)
 pro N=2 tedy 16

Více-kvantové operátory - 4

multiple quantum : $2I_{1x}I_{2y}$ $2I_{1y}I_{2x}$ $2I_{1x}I_{2x}$ $2I_{1y}I_{2y}$

Zbývající operátory - 2

E - jednotkový operátor, $2I_{1z}I_{2z}$

Součinový operátorový formalismus

Popis vlivu chemického posunu a rf pulzů na vývoj matice hustoty

Dvou spinový systém – vliv chemického posunu na I_{1x}

$$H_{\text{free}} = \Omega_1 I_{1z} + \Omega_2 I_{2z}$$

$$I_{1x} \xrightarrow{H_{\text{free}} t}$$

$$I_{1x} \xrightarrow{\Omega_1 t I_{1z} + \Omega_2 t I_{2z}}$$

$$I_{1x} \xrightarrow{\Omega_1 t I_{1z}} \xrightarrow{\Omega_2 t I_{2z}}$$

$$I_{1x} \xrightarrow{\Omega_1 t I_{1z}} \cos \Omega_1 t I_{1x} + \sin \Omega_1 t I_{1y} \xrightarrow{\Omega_2 t I_{2z}}$$

$$I_{1x} \xrightarrow{\Omega_1 t I_{1z} + \Omega_2 t I_{2z}} \cos \Omega_1 t I_{1x} + \sin \Omega_1 t I_{1y}$$

Dvou spinový systém – vliv rf pulzu v ose y na $2I_{1x}I_{2z}$

$$H = \omega_1 I_{1y} + \omega_1 I_{2y}$$

$$2I_{1x}I_{2z} \xrightarrow{\omega_1 t I_{1y}} \xrightarrow{\omega_1 t I_{2y}}$$

$$2I_{1x}I_{2z} \xrightarrow{\omega_1 t I_{1y}} \cos \omega_1 t 2I_{1x}I_{2z} - \sin \omega_1 t 2I_{1z}I_{2z} \xrightarrow{\omega_1 t I_{2y}}$$

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

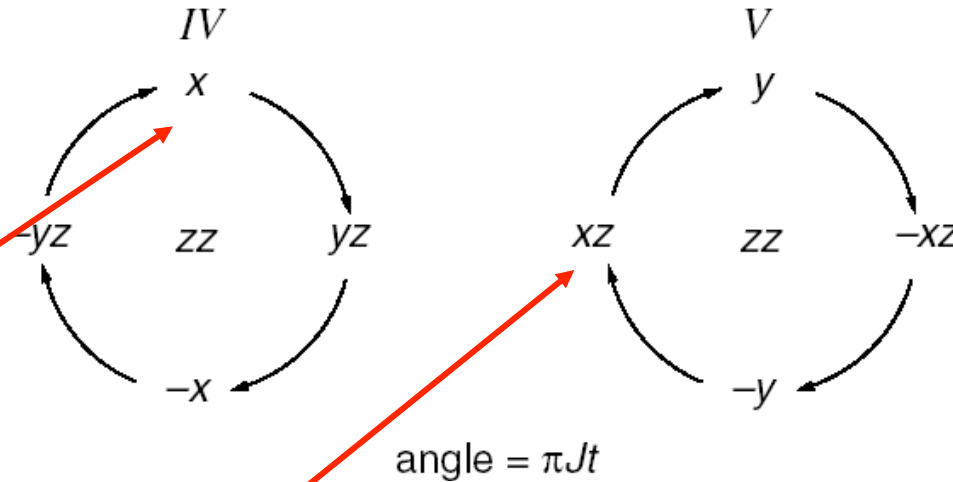
$$2I_{1x}I_{2z} \xrightarrow{\pi/2 I_{1y}} -2I_{1z}I_{2z} \xrightarrow{\pi/2 I_{2y}} -2I_{1z}I_{2x}$$

Součinový operátorový formalismus

Popis vlivu spin-spinové skalární interakce na vývoj matice hustoty

Hamiltonián

$$H_J = 2\pi J_{12} I_{1z} I_{2z}$$



Záměna indexů
– rotace proti směru hr

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

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

Součinový operátorový formalismus

Popis vlivu spin-spinové skalární interakce na vývoj matice hustoty

Hamiltonián

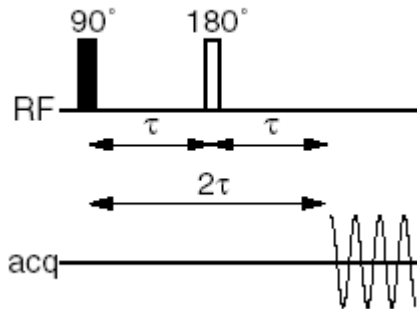
$$H_J = 2\pi J_{12} I_{1z} I_{2z}$$

$$I_{1x} \xrightarrow[2\pi J_{12} t I_{1z} I_{2z}]{t=1/2 J_{12}} 2I_{1y} I_{2z}$$

$$I_{2y} \xrightarrow[2\pi J_{12} t I_{1z} I_{2z}]{t=1/J_{12}} -I_{2y}$$

Součinný operátorový formalismus

Popis spinového echa ve dvouspinovém systému s J interakcí



Homonukleární systém

– τ – 180°(x, to spin 1 and spin 2) – τ –

Chemický posun je refokusován (viz obrázek č. 36)

1. interval τ

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

180° pulz

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

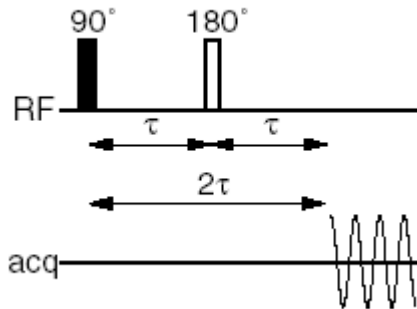
$$\begin{aligned} & \cos \pi J_{12}\tau I_{1x} + \sin \pi J_{12}\tau 2I_{1y}I_{2z} \xrightarrow{\pi I_{1x}} \cos \pi J_{12}\tau I_{1x} - \sin \pi J_{12}\tau 2I_{1y}I_{2z} \\ & \xrightarrow{\pi I_{2x}} \cos \pi J_{12}\tau I_{1x} + \sin \pi J_{12}\tau 2I_{1y}I_{2z} \end{aligned}$$

Spinové echo v homonukleárním systému nemá žádný vliv na vývoj J

$$I_{1x} \xrightarrow{\tau-180^\circ(x)-\tau} \cos 2\pi J_{12}\tau I_{1x} + \sin 2\pi J_{12}\tau 2I_{1y}I_{2z}$$

Součinný operátorový formalismus

Popis spinového echa ve dvouspinovém systému s J interakcí



Homonukleární systém

– τ – 180°(x, to spin 1 and spin 2) – τ –

Chemický posun je refokusován (viz obrázek č. 87/88)

Interkonverze soufázové a antifázové magnetizace

$$\tau = 1/4J \quad - 1/(4J_{12}) - 180^\circ(x) - 1/(4J_{12}) -$$

$$I_{1x} \xrightarrow{\tau-180^\circ(x)-\tau} \cos 2\pi J_{12}\tau I_{1x} + \sin 2\pi J_{12}\tau 2I_{1y}I_{2z}$$

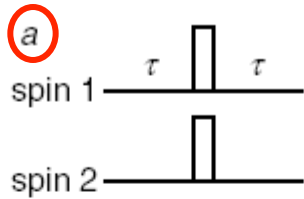
$$I_{1x} \rightarrow 2I_{1y}I_{2z}$$

$$2I_{1x}I_{2z} \rightarrow I_{1y}$$

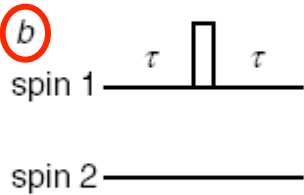
Součinný operátorový formalismus

Popis spinového echa ve dvouspinovém systému s J interakcí

Heteronukleární systém



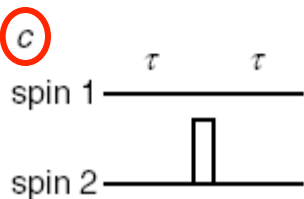
Sekvence a – viz homonukleární systém



Sekvence b

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

$$\cos \pi J_{12}\tau I_{1x} + \sin \pi J_{12}\tau 2I_{1y}I_{2z} \xrightarrow{\pi I_{1x}} \cos \pi J_{12}\tau I_{1x} - \sin \pi J_{12}\tau 2I_{1y}I_{2z}$$



$$\cos \pi J_{12}\tau I_{1x} \xrightarrow{2\pi J_{12}\tau I_{1z}I_{2z}}$$

$$\cos \pi J_{12}\tau \cos \pi J_{12}\tau I_{1x} + \sin \pi J_{12}\tau \cos \pi J_{12}\tau 2I_{1y}I_{2z}$$

$$- \sin \pi J_{12}\tau 2I_{1y}I_{2z} \xrightarrow{2\pi J_{12}\tau I_{1z}I_{2z}}$$

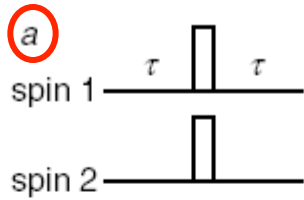
$$- \cos \pi J_{12}\tau \sin \pi J_{12}\tau 2I_{1y}I_{2z} + \sin \pi J_{12}\tau \sin \pi J_{12}\tau I_{1x}$$

$$\longrightarrow I_{1x}$$

Součinný operátorový formalismus

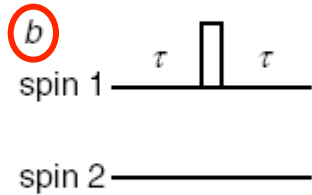
Popis spinového echa ve dvouspinovém systému s J interakcí

Heteronukleární systém

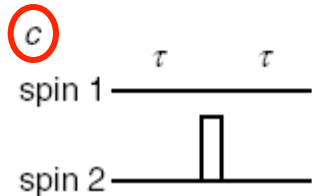


Sekvence c

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



$$\cos \pi J_{12}\tau I_{1x} + \sin \pi J_{12}\tau 2I_{1y}I_{2z} \xrightarrow{\pi I_{2x}} \cos \pi J_{12}\tau I_{1x} - \sin \pi J_{12}\tau 2I_{1y}I_{2z}$$



$$\longrightarrow I_{1x}: (I_x \cos 2\Omega_1\tau + I_y \cos 2\Omega_1\tau)$$

Ale vývoj v důsledku chemického posunu spinu I_1 zůstává zachován

Součinový operátorový formalismus

Více-kvantové členy

Řád koherence - p

$$I_{x'}, 2I_{1y}I_{2z} \quad p = \pm 1$$

$$I_{z'}, 2I_{1z}I_{2z} \quad p = 0$$

$$2I_{1x}I_{2y} \quad p = 0 \text{ i } p = \pm 2$$

Zdvihové operátory (raising and lowering operators)

$$I_+ \quad p = + 1$$

$$I_+ = I_x + iI_y$$

$$I_- = I_x - iI_y$$

$$I_- \quad p = - 1$$

$$I_x = \frac{1}{2}(I_+ + I_-)$$

$$I_y = \frac{1}{2i}(I_+ - I_-)$$

$$2I_{1x}I_{2x} = 2 \times \frac{1}{2}(I_{1+} + I_{1-}) \times \frac{1}{2}(I_{2+} + I_{2-})$$

$$= \frac{1}{2}(I_{1+}I_{2+} + I_{1-}I_{2-}) + \frac{1}{2}(I_{1+}I_{2-} + I_{1-}I_{2+})$$

$$p = + 2$$

$$p = - 2$$

$$p = 0$$

$$p = 0$$

Součinový operátorový formalismus

Více-kvantové členy

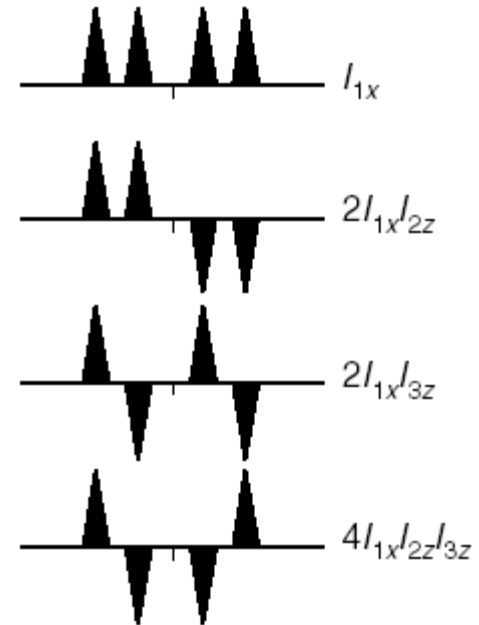
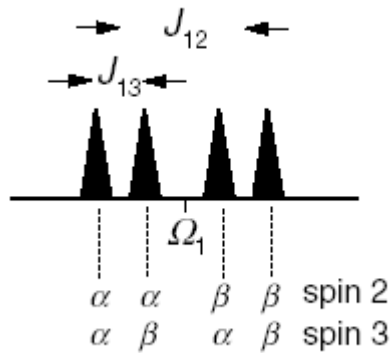
Řád koherence - p

$$\text{double quantum part}[2I_{1x}I_{2x}] = \frac{1}{2}(I_{1+}I_{2+} + I_{1-}I_{2-})$$

$$\begin{aligned} \frac{1}{2}(I_{1+}I_{2+} + I_{1-}I_{2-}) &= \frac{1}{2}\left[(I_{1x} + iI_{1y})(I_{2x} + iI_{2y}) + (I_{1x} - iI_{1y})(I_{2x} - iI_{2y})\right] \\ &= \frac{1}{2}\left[2I_{1x}I_{2x} + 2I_{1y}I_{2y}\right] \end{aligned}$$

Součinový operátorový formalismus

Tříspinové operátory



Celkový počet operátorů
 4^N (N je počet spinů)
pro N=3 tedy 64

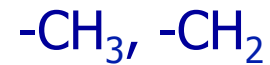
Součinný operátorový formalismus

Alternativní notace

IS spinový systém

$$2I_{1y}I_{2z} \quad 2I_yS_z$$

I_n S spinový systém



Součinný operátorový formalismus

Více-kvantové členy - vývoj

double quantum, $p = \pm 2$

$$DQ_x^{(ij)} \equiv \frac{1}{2}(2I_{ix}I_{jx} - 2I_{iy}I_{jy}) \equiv \frac{1}{2}(I_{i+}I_{j+} + I_{i-}I_{j-})$$

$$DQ_y^{(ij)} \equiv \frac{1}{2}(2I_{ix}I_{jy} + 2I_{iy}I_{jx}) \equiv \frac{1}{2i}(I_{i+}I_{j+} - I_{i-}I_{j-})$$

zero quantum, $p = 0$

$$ZQ_x^{(ij)} \equiv \frac{1}{2}(2I_{ix}I_{jx} + 2I_{iy}I_{jy}) \equiv \frac{1}{2}(I_{i+}I_{j-} + I_{i-}I_{j+})$$

$$ZQ_y^{(ij)} \equiv \frac{1}{2}(2I_{iy}I_{jx} - 2I_{ix}I_{jy}) \equiv \frac{1}{2i}(I_{i+}I_{j-} - I_{i-}I_{j+})$$

Popis vlivu chemického posunu

$$DQ_x^{(ij)} \xrightarrow{\Omega_i I_{iz} + \Omega_j I_{jz}} \cos(\Omega_i + \Omega_j)t DQ_x^{(ij)} + \sin(\Omega_i + \Omega_j)t DQ_y^{(ij)}$$

$$DQ_y^{(ij)} \xrightarrow{\Omega_i I_{iz} + \Omega_j I_{jz}} \cos(\Omega_i + \Omega_j)t DQ_y^{(ij)} - \sin(\Omega_i + \Omega_j)t DQ_x^{(ij)}$$

$$ZQ_x^{(ij)} \xrightarrow{\Omega_i I_{iz} + \Omega_j I_{jz}} \cos(\Omega_i - \Omega_j)t ZQ_x^{(ij)} + \sin(\Omega_i - \Omega_j)t ZQ_y^{(ij)}$$

$$ZQ_y^{(ij)} \xrightarrow{\Omega_i I_{iz} + \Omega_j I_{jz}} \cos(\Omega_i - \Omega_j)t ZQ_y^{(ij)} - \sin(\Omega_i - \Omega_j)t ZQ_x^{(ij)}$$

Součinný operátorový formalismus

Více-kvantové členy - vývoj

Popis vlivu spin-spinové interakce

$$DQ_x^{(ij)} \longrightarrow \cos \pi J_{DQ,eff} t DQ_x^{(ij)} + \sin \pi J_{DQ,eff} t 2I_{kz} DQ_y^{(ij)}$$

$$DQ_y^{(ij)} \longrightarrow \cos \pi J_{DQ,eff} t DQ_y^{(ij)} - \sin \pi J_{DQ,eff} t 2I_{kz} DQ_x^{(ij)}$$

$$ZQ_x^{(ij)} \longrightarrow \cos \pi J_{ZQ,eff} t ZQ_x^{(ij)} + \sin \pi J_{ZQ,eff} t 2I_{kz} ZQ_y^{(ij)}$$

$$ZQ_y^{(ij)} \longrightarrow \cos \pi J_{ZQ,eff} t ZQ_y^{(ij)} - \sin \pi J_{ZQ,eff} t 2I_{kz} ZQ_x^{(ij)}$$

$J_{DQ,eff}$ – součet J mezi spinem i a všemi ostatními *plus*
součet mezi spinem j a všemi ostatními

$J_{ZQ,eff}$ – součet J mezi spinem i a všemi ostatními *mínus*
součet mezi spinem j a všemi ostatními

2 spiny - CH

	$\cos(\pi J\tau)$	$\sin(\pi J\tau)$
$2I_{1Z}S_X$	$2I_{1Z}S_X$	S_Y
$2I_{1X}S_Z$	$2I_{1X}S_Z$	I_Y
I_X	I_X	$2I_Y S_Z$
S_X	S_X	$2I_Z S_Y$

3 spiny - CH₂

	$\cos^2(\pi J\tau)$	$\cos(\pi J\tau)$	$\cos(\pi J\tau) \sin(\pi J\tau)$	$\sin(\pi J\tau)$	$\sin^2(\pi J\tau)$
$4I_{1Z}I_{2Z}S_X$	$4I_{1Z}I_{2Z}S_X$		$2[I_{1Z}+I_{2Z}]S_Y$		$-S_X$
$4I_{1Z}I_{2X}S_X$		$4I_{1Z}I_{2X}S_X$		$2I_{2X}S_Y$	
$4I_{1X}I_{2X}S_Z$	$4I_{1X}I_{2X}S_Z$		$2[I_{1X}I_{2Y}+I_{1Y}I_{2X}]$		$4[I_{1Y}I_{2Y}]S_Z$
$4I_{1Z}I_{2X}S_Z$		$4I_{1Z}I_{2X}S_Z$		$2I_{1Z}I_{2Y}$	
$2I_{2X}S_X$		$2I_{2X}S_X$		$4I_{1Z}I_{2X}S_Y$	
			S_Y		
$2I_{2Z}S_X$	$2I_{2Z}S_X$		$+4I_{1Z}I_{2Z}S_Y$		$-2I_{1Z}S_X$
$2I_{2X}S_Z$		$2I_{2X}S_Z$		I_{2Y}	
S_X	S_X		$2[I_{1Z}+I_{2Z}]S_Y$		$-4I_{1Z}I_{2Z}S_X$
$2I_{1X}I_{2X}$	$2I_{1X}I_{2X}$		$4[I_{1X}I_{2Y}+I_{1Y}I_{2X}]S_Z$		$2I_{1Y}I_{2Y}$
$2I_{1Z}I_{2X}$		$2I_{1Z}I_{2X}$		$4I_{1Z}I_{2Y}S_Z$	
I_{2X}		I_{2X}^1		$2I_{2Y}S_Z$	

4 spiny - CH₃

	$\cos^2(\pi J_T)$	$\cos^2(\pi J_T)$	$\cos(\pi J_T)$	$\cos^2(\pi J_T) \sin(\pi J_T)$	$\cos(\pi J_T) \sin(\pi J_T)$	$\cos(\pi J_T) \sin^2(\pi J_T)$	$\sin(\pi J_T)$	$\sin^2(\pi J_T)$	$\sin^2(\pi J_T)$
$8I_{1Z}I_{2Z}I_{3Z}S_X$	$8I_{1Z}I_{2Z}I_{3Z}S_X$			$4[I_{1Z}I_{2Z}+I_{1Z}I_{2Z}+I_{2Z}I_{3Z}]S_Y$		$-2[I_{1Z}+I_{2Z}+I_{2Z}]S_X$			$-8Y$
$8I_{1Z}I_{2Z}I_{3X}S_X$		$8I_{1Z}I_{2Z}I_{3X}S_X$			$[I_{1Z}+I_{2Z}]I_{3X}S_Y$			$-I_{3X}S_X$	
$8I_{1Z}I_{2X}I_{3X}S_X$			$8I_{1Z}I_{2X}I_{3X}S_X$				$4I_{2X}I_{3X}S_Y$		
$8I_{1X}I_{2X}I_{3X}S_Z$	$8I_{1X}I_{2X}I_{3X}S_Z$			$4[I_{1X}I_{2X}I_{3Y}+I_{1X}I_{2Y}I_{3X}+I_{1Y}I_{2X}I_{3X}]$		$8[I_{1X}I_{2Y}I_{3Y}+I_{1Y}I_{2X}I_{3Y}+I_{1Y}I_{2Y}I_{3X}]S_Z$			$4I_{1Y}I_{2Y}I_{3Y}$
$8I_{1Z}I_{2X}I_{3X}S_Z$	$8I_{1Z}I_{2X}I_{3X}S_Z$				$4I_{1Z}[I_{2X}I_{3Y}+I_{2Y}I_{3X}]$			$8I_{1Z}I_{2Y}I_{3Y}S_Z$	
$8I_{1Z}I_{2Z}I_{3X}S_Z$			$8I_{1Z}I_{2Z}I_{3X}S_Z$				$4I_{1Z}I_{2Z}I_{3Y}$		
$4I_{2X}I_{3X}S_X$			$4I_{2X}I_{3X}S_X$				$8I_{1Z}I_{2X}I_{3X}S_Y$		
$4I_{2Z}I_{3X}S_X$		$4I_{2Z}I_{3X}S_X$			$8I_{1Z}I_{2Z}I_{3X}S_Y$			$-4I_{1Z}I_{3X}S_X$	
$4I_{2Z}I_{3Z}S_X$	$4I_{2Z}I_{3Z}S_X$			$8I_{1Z}I_{2Z}I_{3Z}S_Y+2[I_{2Z}+I_{3Z}]S_Y$		$-4[I_{1Z}I_{2Z}+I_{1Z}I_{2Z}]S_X$			$-2I_{1Z}S_Y$
$4I_{2X}I_{3X}S_Z$		$4I_{2X}I_{3X}S_Z$			$2I_{2X}I_{3Y}+2I_{2Y}I_{3X}$			$4I_{2Y}I_{3Y}S_Z$	
$4I_{2Z}I_{3X}S_Z$			$4I_{2Z}I_{3X}S_Z$				$2I_{2Z}I_{3Y}$		
$2I_{3X}S_X$		$2I_{3X}S_X$			$4[I_{1Z}I_{3X}+I_{2Z}I_{3X}]S_Y$			$-8I_{1Z}I_{2Z}I_{3X}S_X$	
$2I_{2Z}S_X$	$2I_{2Z}S_X$			$4[I_{1Z}I_{2Z}+I_{2Z}I_{3Z}]S_Y+8Y$		$-2[4I_{1Z}I_{2Z}I_{3Z}+I_{1Z}+I_{2Z}]S_X$			$-4I_{1Z}I_{2Z}S_Y$
$2I_{3X}S_Z$			$2I_{3X}S_Z$				I_{3Y}		
S_X	$8X$			$2[I_{1Z}+I_{2Z}+I_{3Z}]S_Y$		$-4[I_{1Z}I_{2Z}+I_{1Z}I_{2Z}+I_{2Z}I_{3Z}]S_X$			$-8I_{1Z}I_{2Z}I_{3Z}S_Y$
$4I_{1X}I_{2X}I_{3X}$	$4I_{1X}I_{2X}I_{3X}$			$8[I_{1X}I_{2X}I_{3Y}+I_{1X}I_{2Y}I_{3X}+I_{1Y}I_{2X}I_{3X}]S_Z$		$4[I_{1X}I_{2Y}I_{3Y}+I_{1Y}I_{2X}I_{3Y}+I_{1Y}I_{2Y}I_{3X}]$			$8I_{1Y}I_{2Y}I_{3Y}S_Z$
$4I_{1Z}I_{2X}I_{3X}$		$4I_{1Z}I_{2X}I_{3X}$			$8[I_{1Z}I_{2X}I_{3Y}+I_{1Z}I_{2Y}I_{3X}]S_Z$			$4I_{1Z}I_{2Y}I_{3Y}$	
$4I_{1Z}I_{2Z}I_{3X}$			$4I_{1Z}I_{2Z}I_{3X}$				$4I_{1Z}I_{2Z}I_{3Y}S_Z$		
$2I_{2X}I_{3X}$		$2I_{2X}I_{3X}$			$4[I_{2X}I_{3Y}+I_{2Y}I_{3X}]S_Z$			$2I_{2Y}I_{3Y}$	
$2I_{2Z}I_{3X}$			$2I_{2Z}I_{3X}$				$2I_{2Z}I_{3Y}S_Z$		
I_X			I_X				$2I_Y S_Z$		

Metody 1D FT NMR spektroskopie

Širokopásmový dekaplink

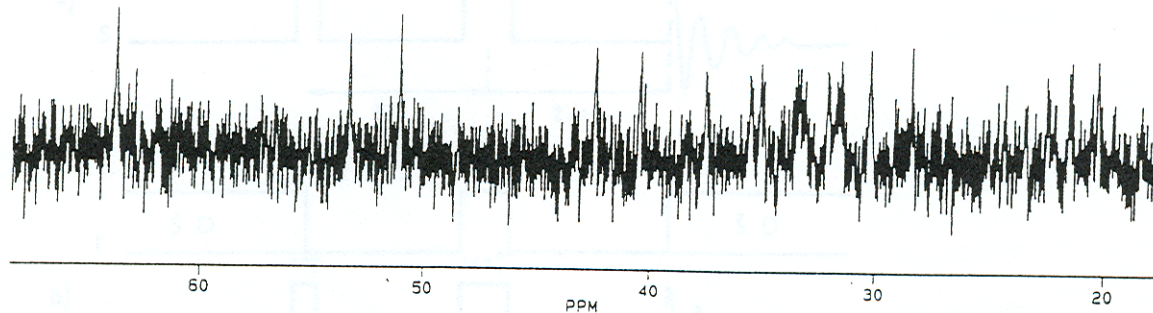


Figure 4.1: Coupled ^{13}C spectrum of sucrose obtained in 64 scans

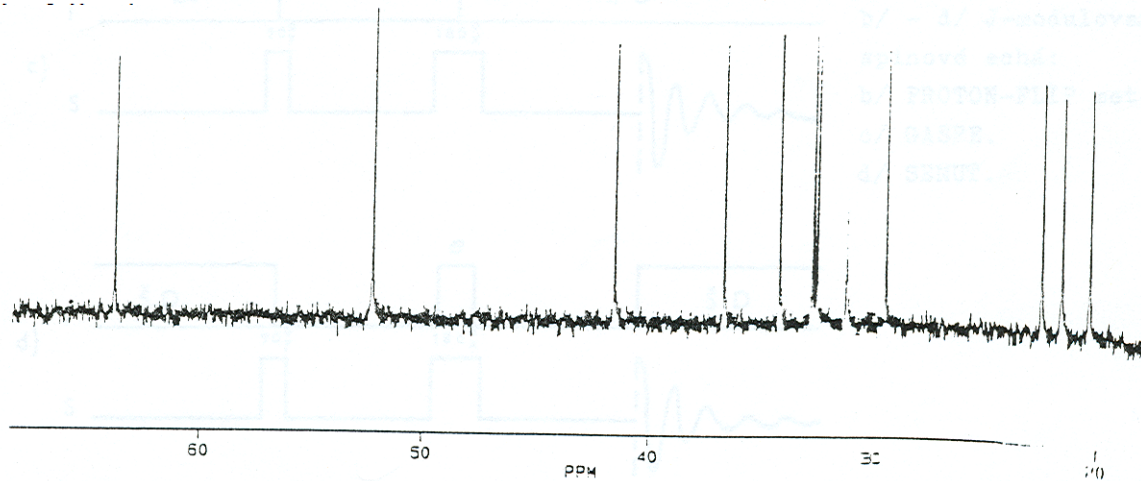
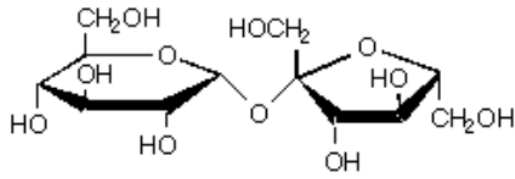


Figure 4.2: Broadband decoupled ^{13}C spectrum of sucrose obtained in 64 scans

Metody 1D FT NMR spektroskopie

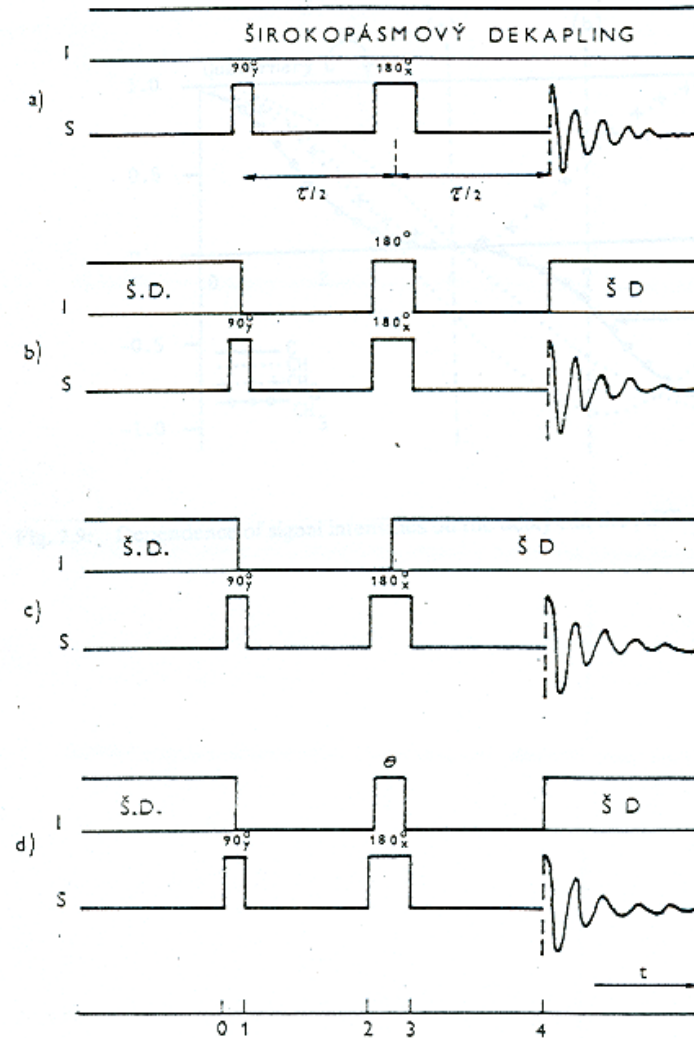
Pulzní sekvence – editace spekter

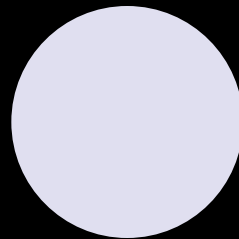
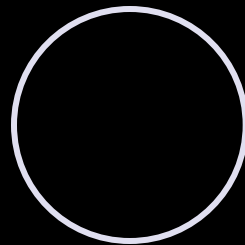
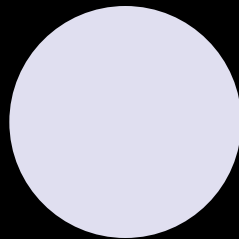
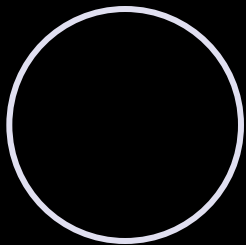
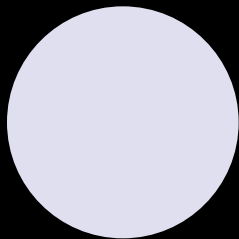
SE

APT

GASPE

SEMUT





Metody 1D FT NMR spektroskopie

APT

APT

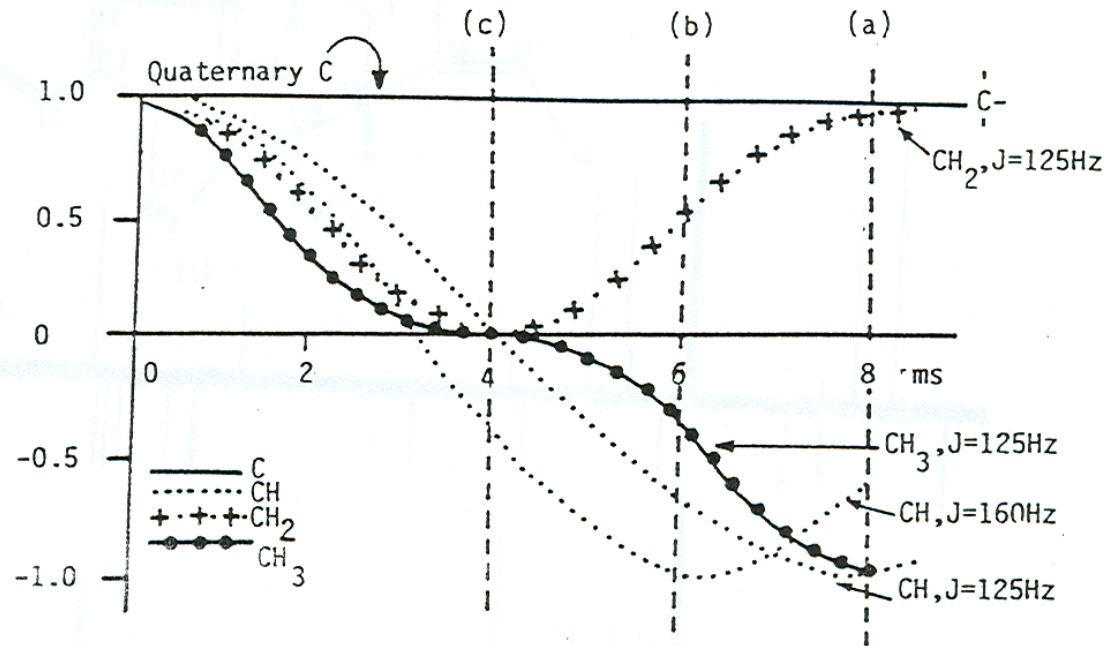
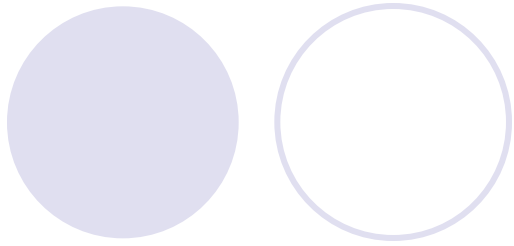
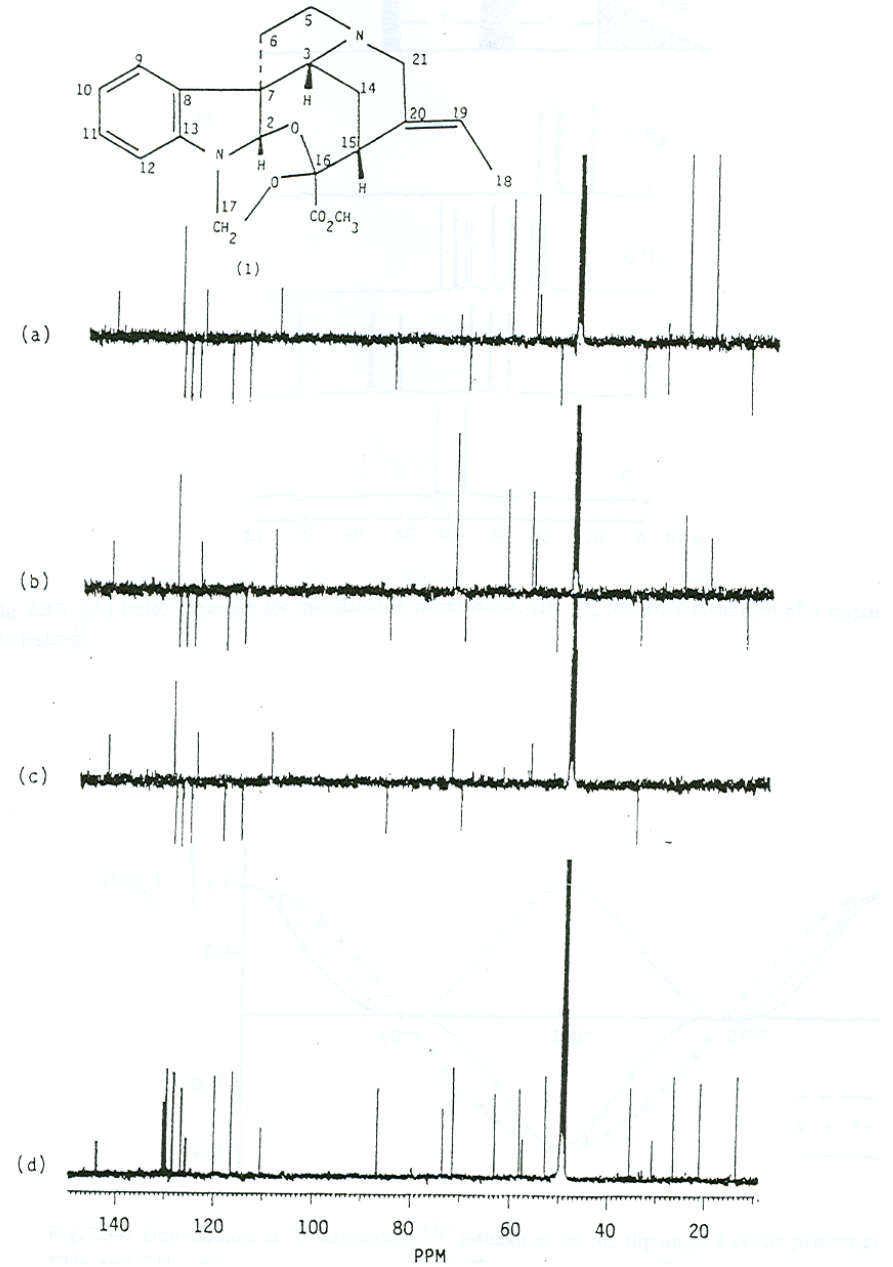


Fig. 2.9: Dependence of signal intensities on the delay τ in the APT experiment.

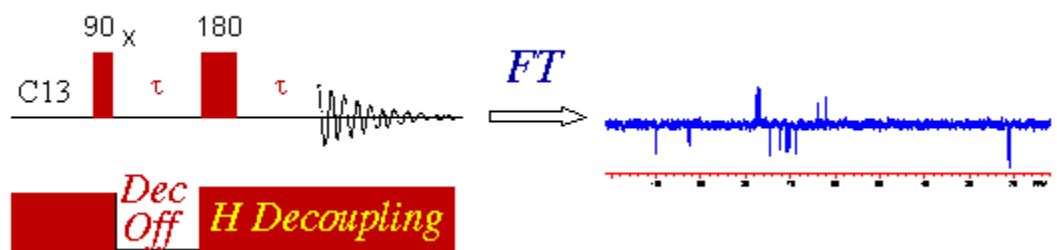


Metody 1D FT NMR spektroskopie

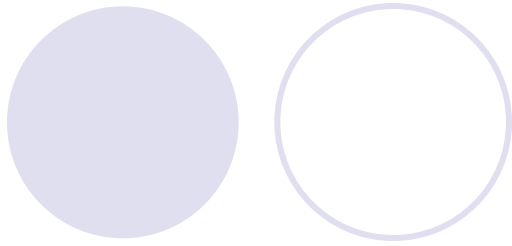
APT



GASPE



Delay	t (in msec) (J=130)	δ_{CH}	δ_{CH_2}	δ_{CH_3}	Carbon-13 Spectra
1/(4J)	1.92	$+J/2$ $-J/2$	$+J$ $-J$	$+3J/2$ $-3J/2$ $+J/2$ $-J/2$	all carbons showing with positive amplitude
1/(2J)	3.85				only quaternary carbons showing up
1/J	7.69				CH ₂ & C CH ₃ & CH



Metody 1D FT NMR spektroskopie

SEMUT

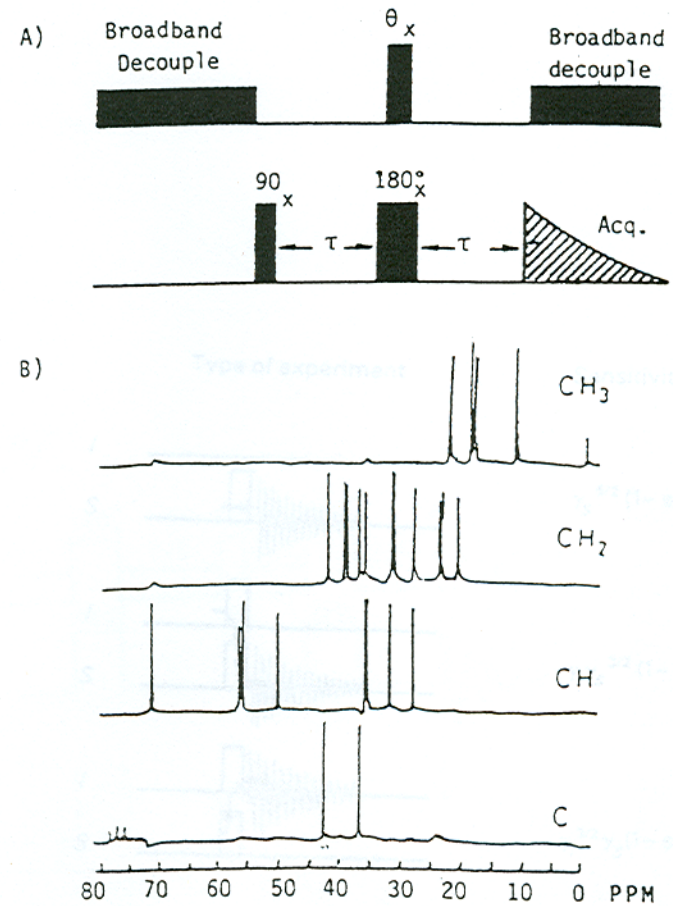
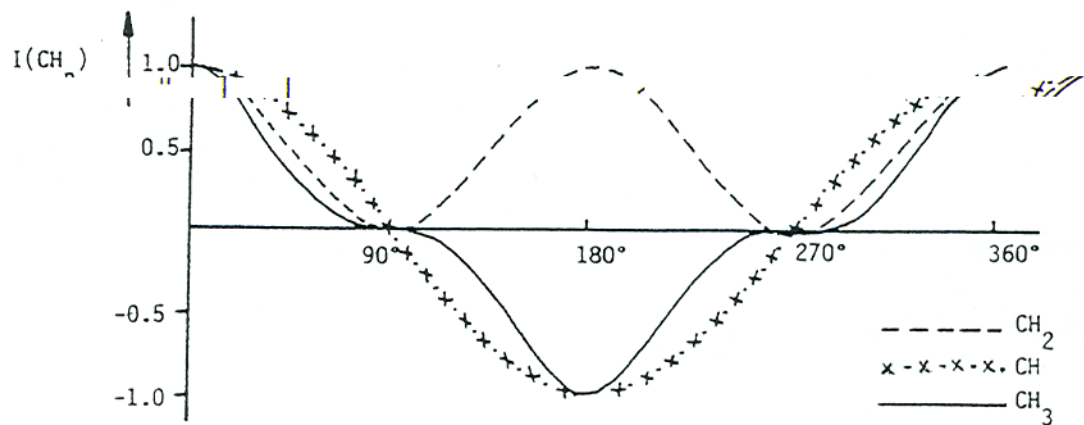


Fig. 2.33: (A) Pulse sequence for the SEMUT experiment. (B) ^{13}C SEMUT spectrum of a region of cholesterol.





Metody 1D FT NMR spektroskopie

SEMUT



Metody 1D FT NMR spektroskopie

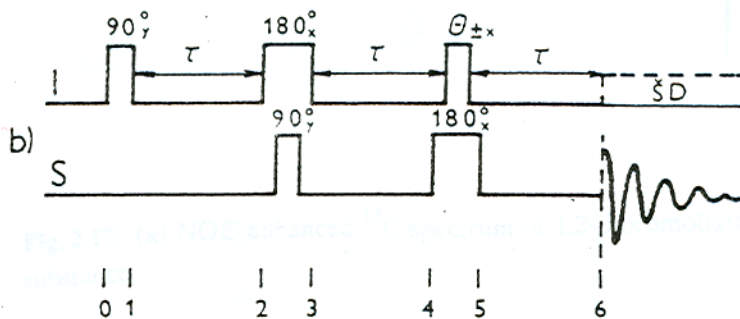
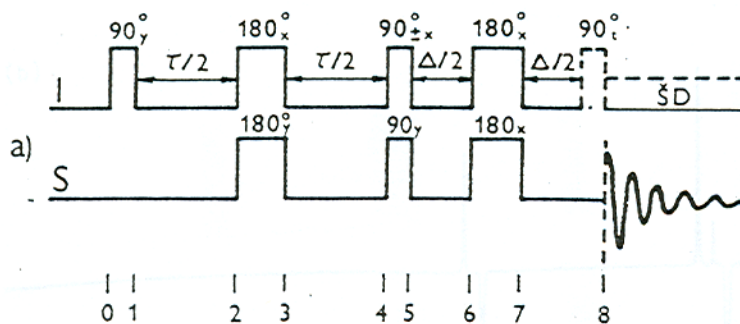
Relativní citlivost

Type of experiment	Sensitivity	C-13	N-15
	$\gamma_S^{5/2} (1 - e^{-T/T_1^S})$	1	1
	$\gamma_I \gamma_S^{3/2} (1 - e^{-T/T_1^I})$	4	10
	$\gamma_I^{3/2} \gamma_S (1 - e^{-T/T_1^S})$	8	31.6
	$\gamma_I^{5/2} (1 - e^{-T/T_1^I})$	32	316

Metody 1D FT NMR spektroskopie

Přenos polarizace

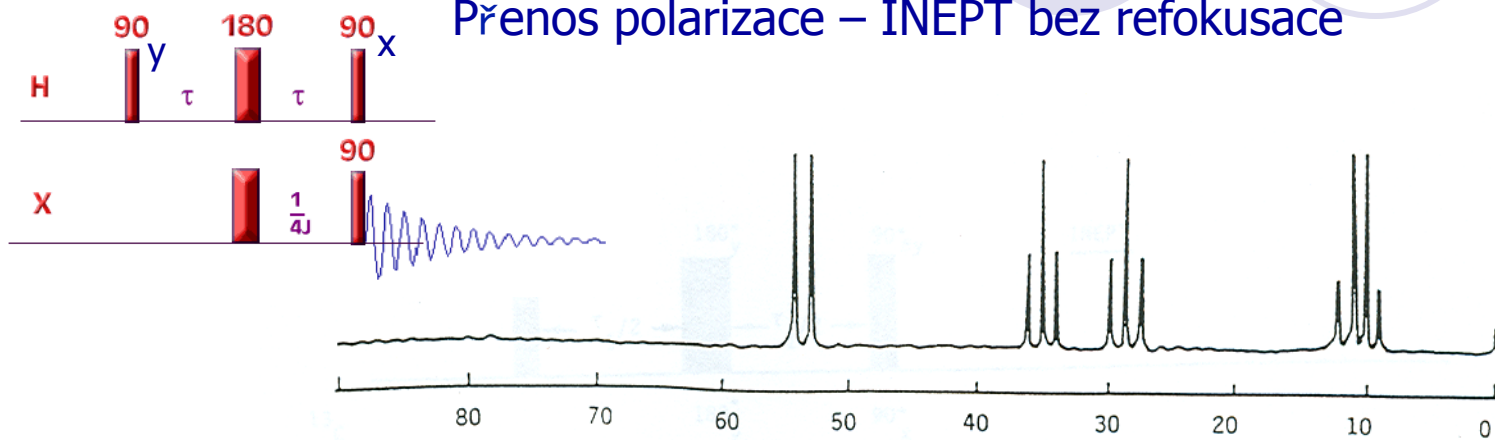
INEPT



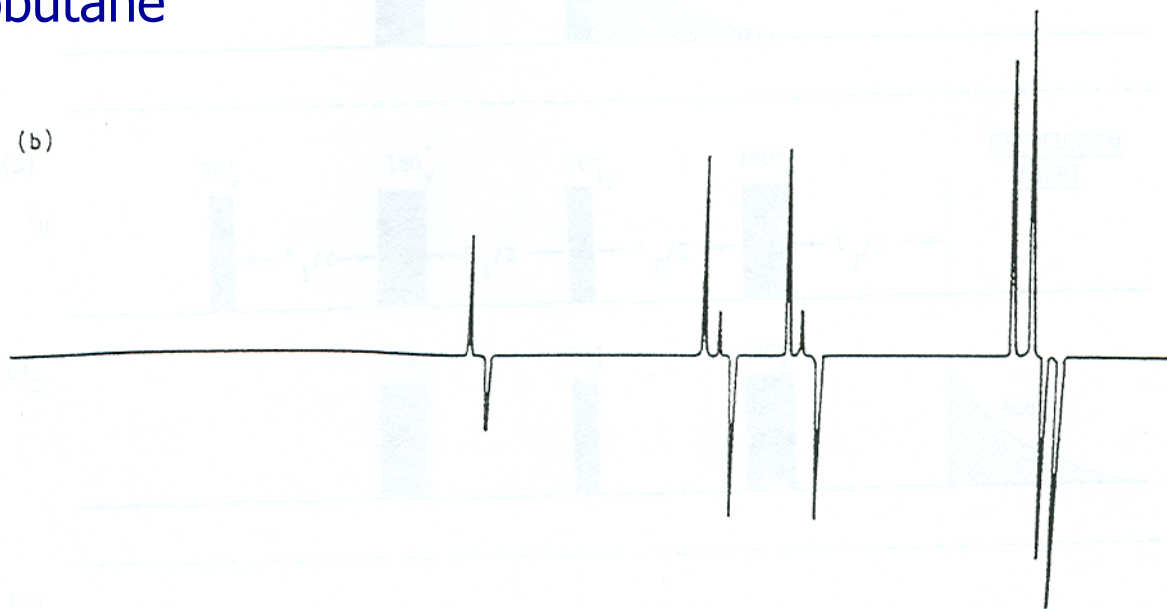
DEPT

Metody 1D FT NMR spektroskopie

Přenos polarizace – INEPT bez refokusace

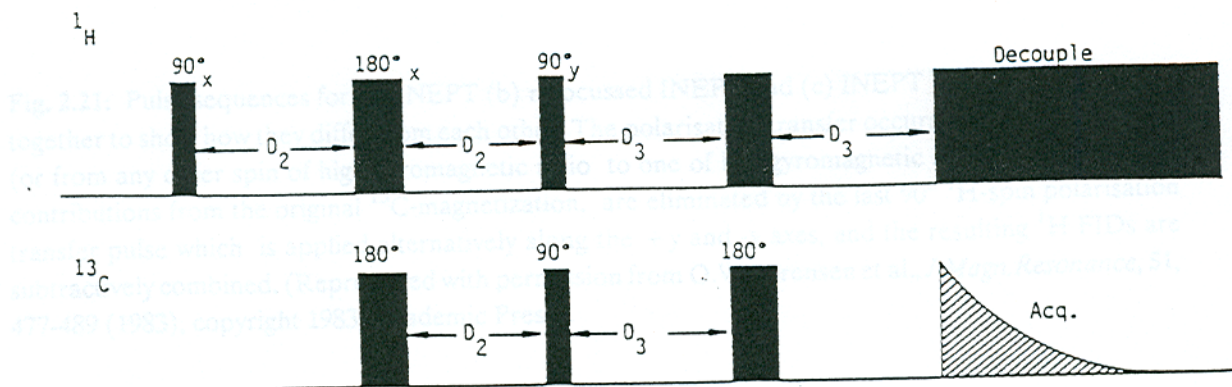


1,2-dibromobutane



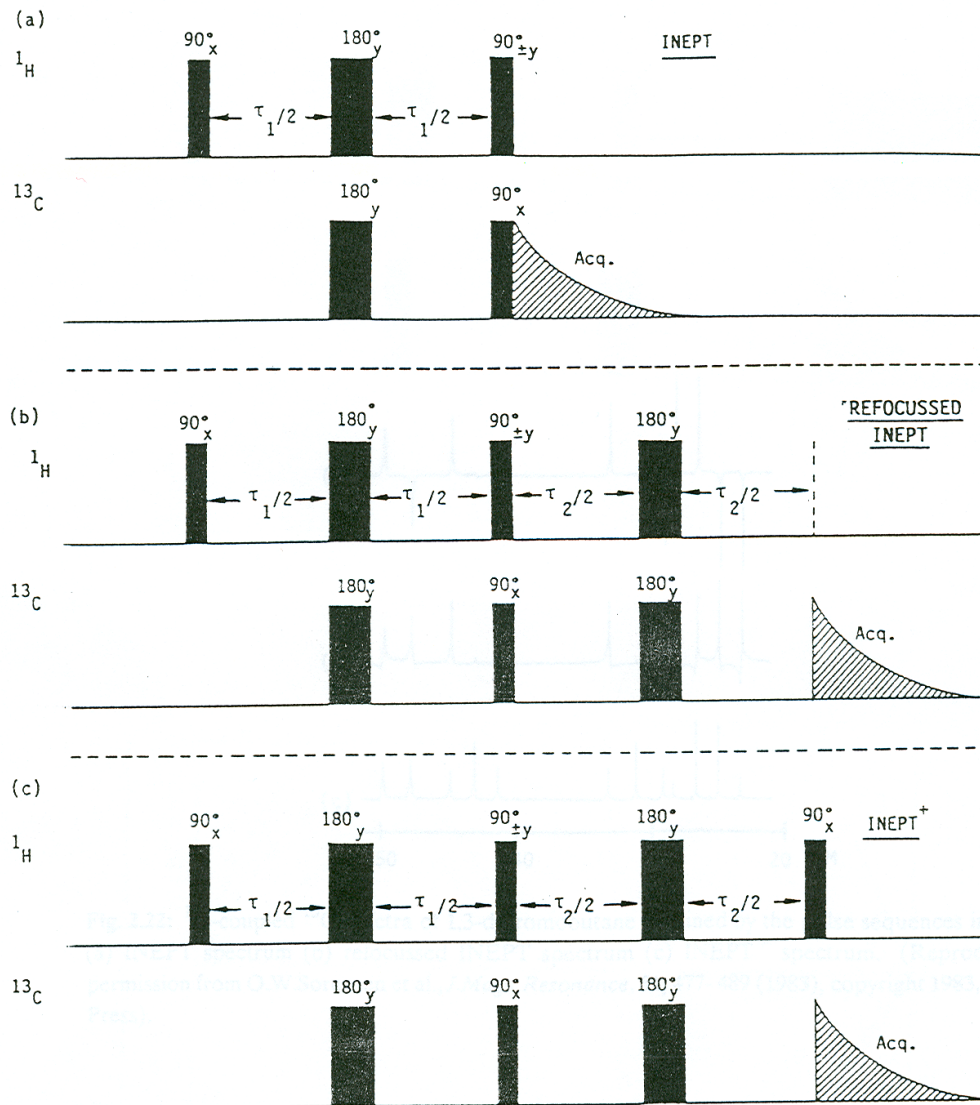
Metody 1D FT NMR spektroskopie

Přenos polarizace – INEPT s refokusací



Metody 1D FT NMR spektroskopie

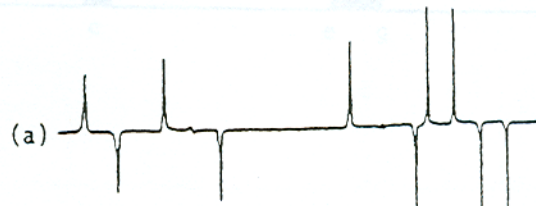
Přenos polarizace – INEPT – různé varianty



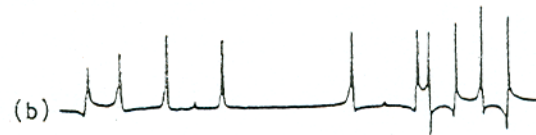
Metody 1D FT NMR spektroskopie

Přenos polarizace – INEPT – různé varianty

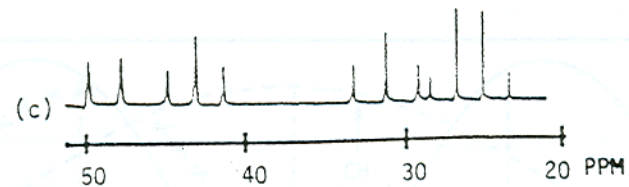
INEPT



INEPT s refokusací

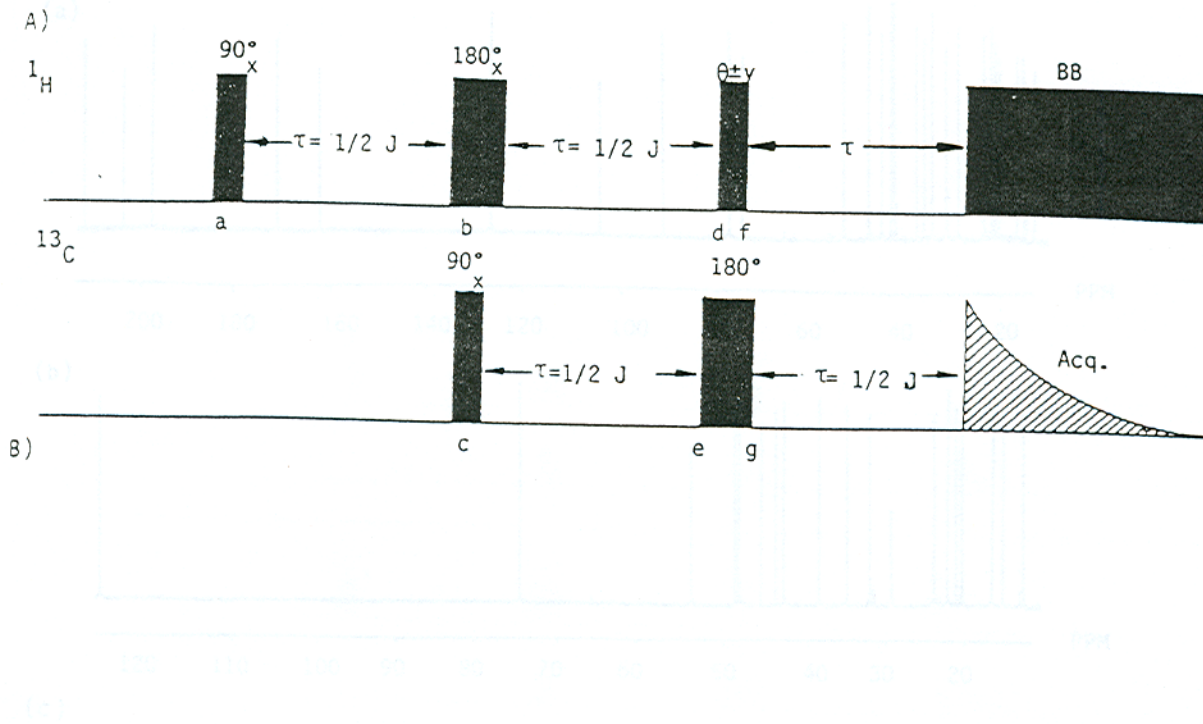


INEPT+



Metody 1D FT NMR spektroskopie

Přenos polarizace – DEPT



Metody 1D FT NMR spektroskopie

Přenos polarizace – DEPT vers. INEPT

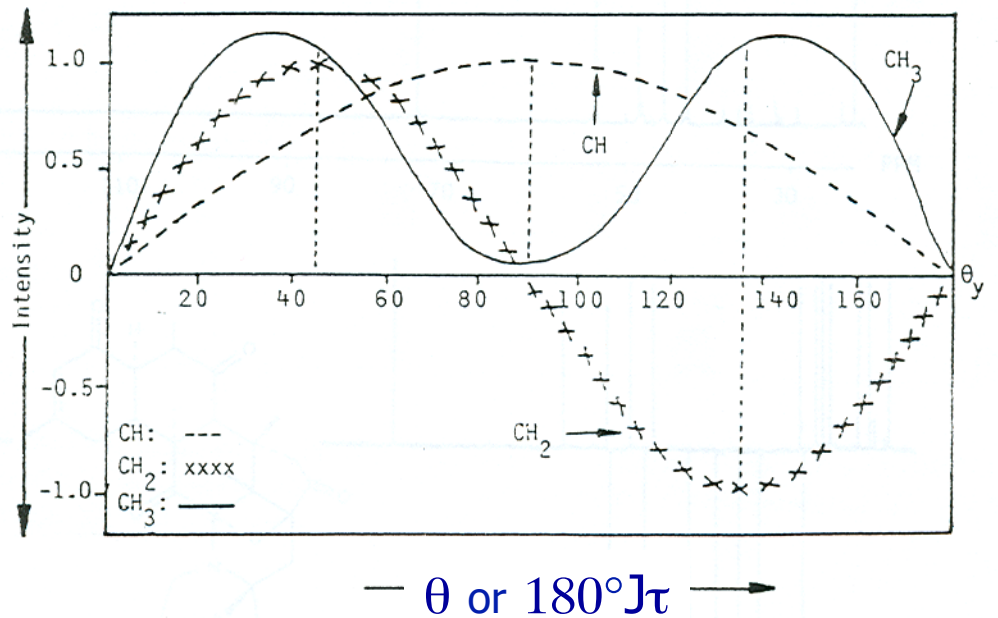
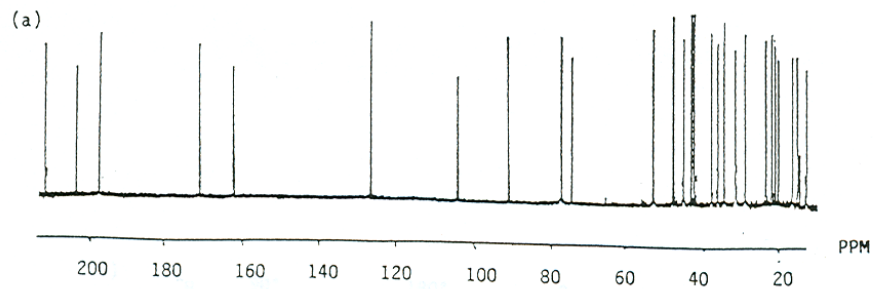


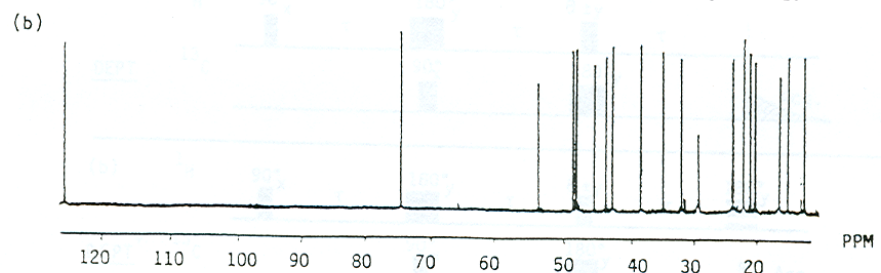
Fig. 2.26: Dependence of signal intensities of CH_3 , CH_2 and CH carbons in the DEPT experiment on the angle θ_y of the last polarisation pulse.

1D C-13 spektrum



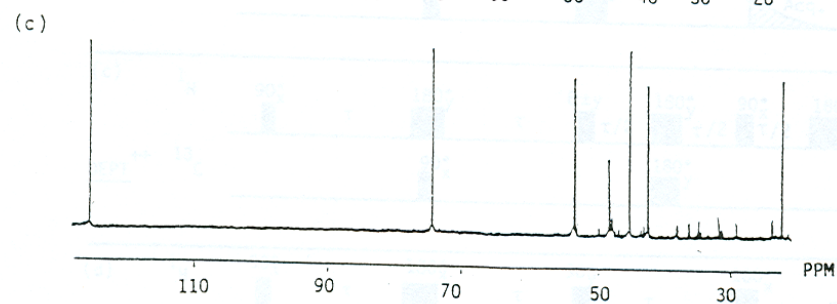
C, CH, CH₂ CH₃

DEPT - $\theta=45^\circ$



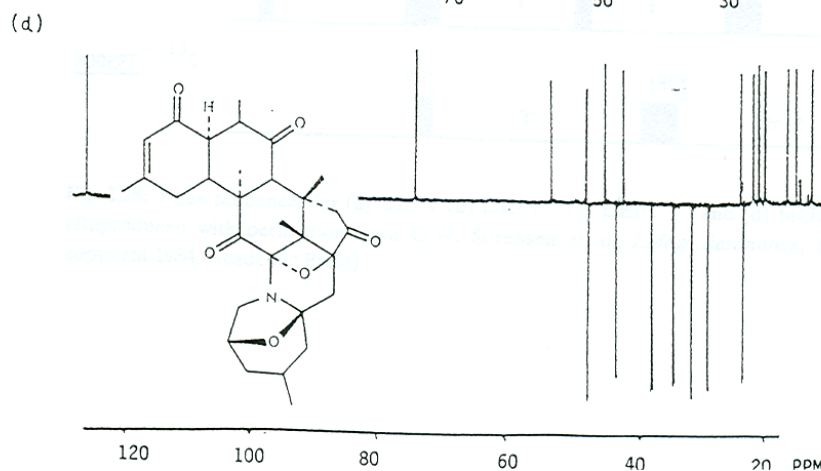
CH, CH₂ CH₃

DEPT - $\theta=90^\circ$



CH

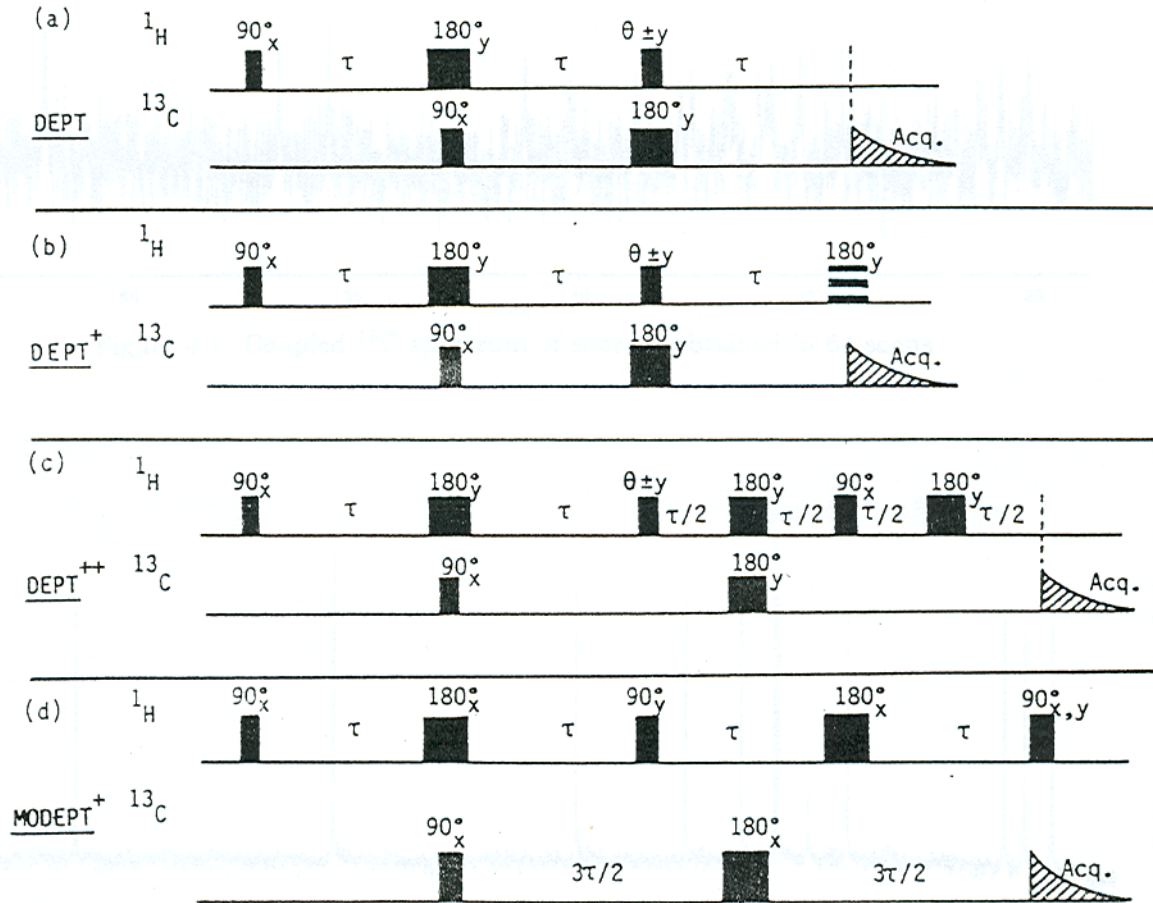
DEPT - $\theta=135^\circ$



CH⁺, CH₂⁻, CH₃⁺

Metody 1D FT NMR spektroskopie

Přenos polarizace – DEPT – různé varianty



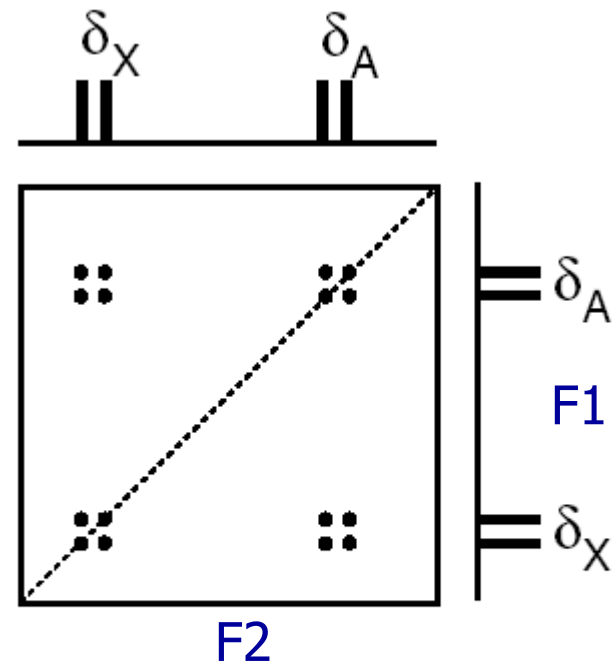
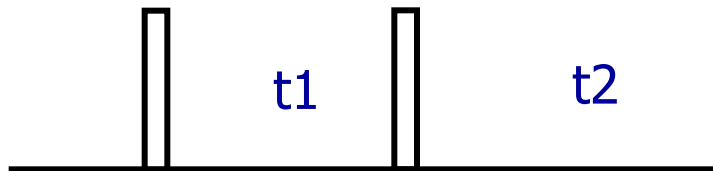
27.11.2012

Metody 2D FT NMR spektroskopie

Elementární základy

Two-spin system AX

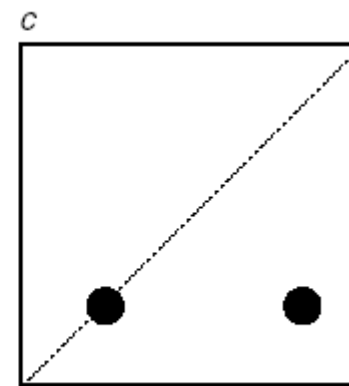
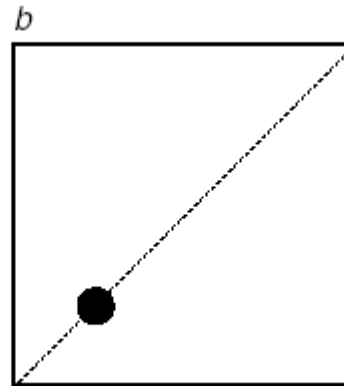
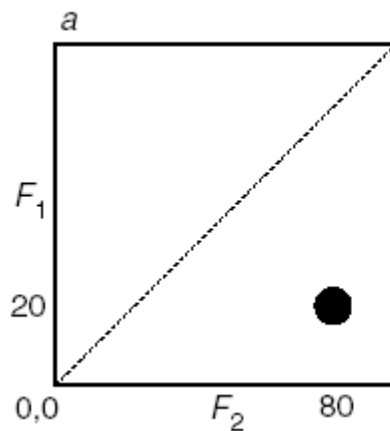
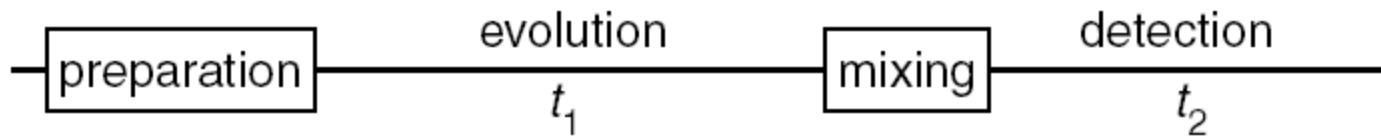
COSY – COrelated SpectroscopY



Schematic COSY spectrum for two coupled spins, A and X

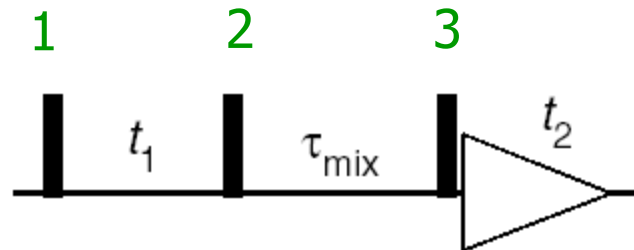
Metody 2D FT NMR spektroskopie

Elementární základy



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

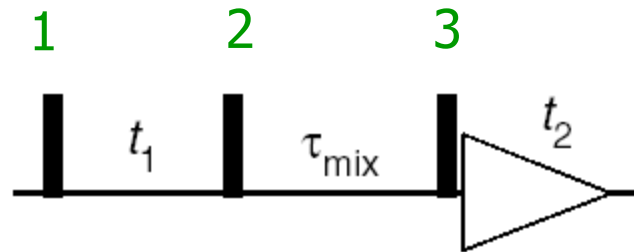
2. pulz:

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

$$\sin \Omega_1 t_1 I_{1x} \xrightarrow{\pi/2 I_{1x}} \xrightarrow{\pi/2 I_{2x}} \sin \Omega_1 t_1 I_{1x}$$

Metody 2D FT NMR spektroskopie

NOE Spectroscopy a EXchange Spectroscopy



směšování: $I_{1z} \leftrightarrow I_{2z}$
chemická výměna

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

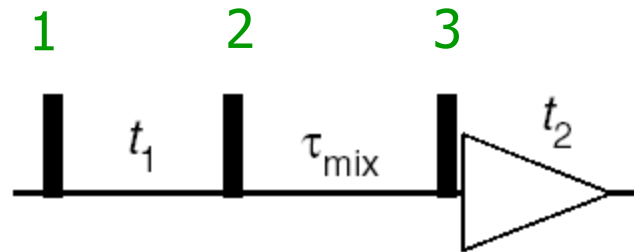
3. pulz:

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

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

Metody 2D FT NMR spektroskopie

NOE Spectroscopy a EXchange Spectroscopy



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

t2:

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

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

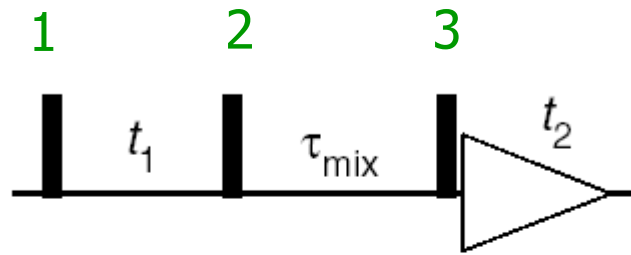
$$f \cos \Omega_2 t_2 \cos \Omega_1 t_1 I_{2y} - f \sin \Omega_2 t_2 \cos \Omega_1 t_1 I_{2x}$$

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

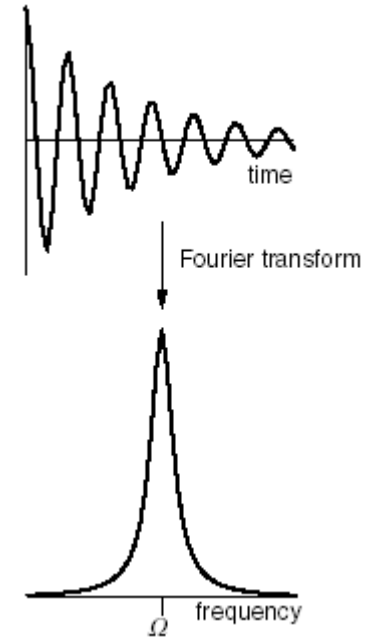


FT zpracování t_2

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

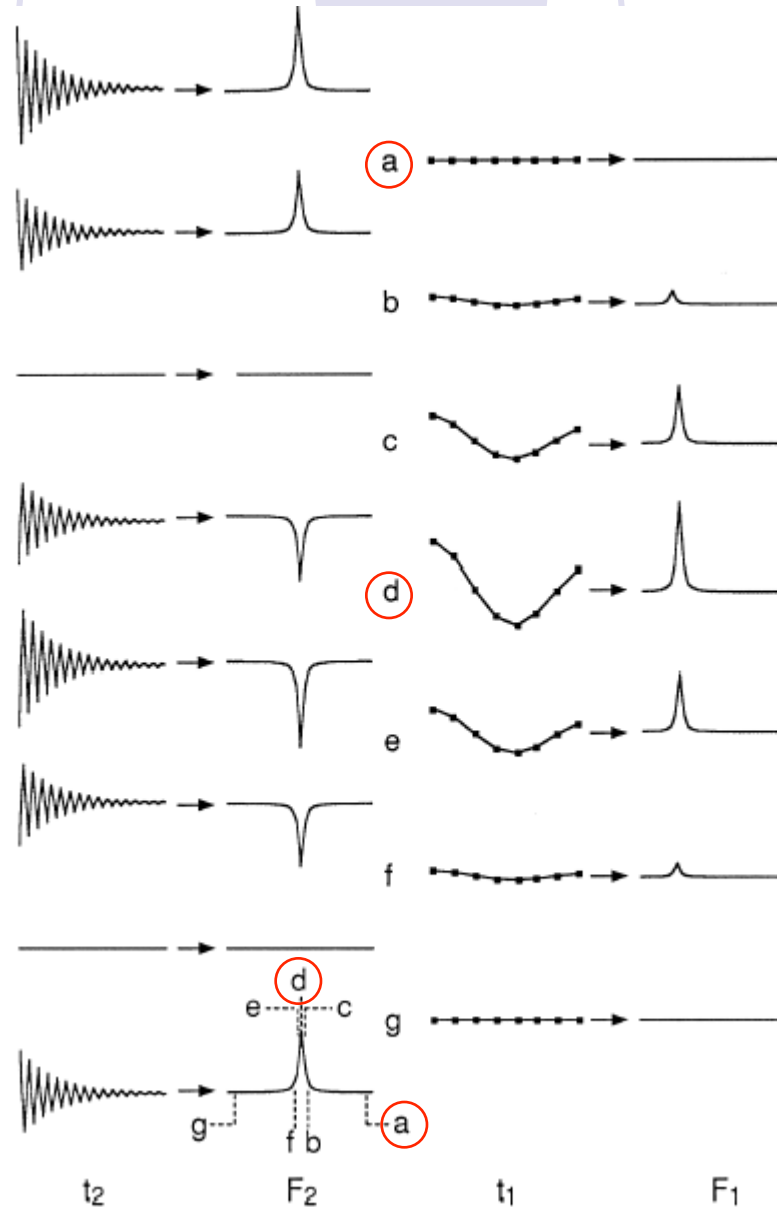
FT zpracování t_1

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



Metody 2D FT NMR spektroskopie

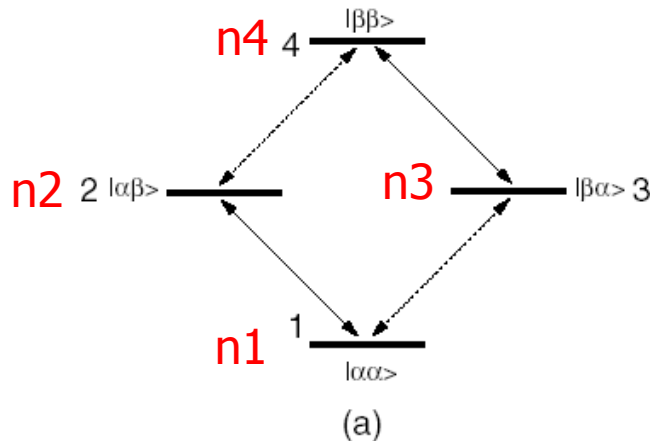
Modulace signálů



Metody 2D FT NMR spektroskopie

NOE Spectroscopy a EXchange Spectroscopy

Dvouspinový systém IS

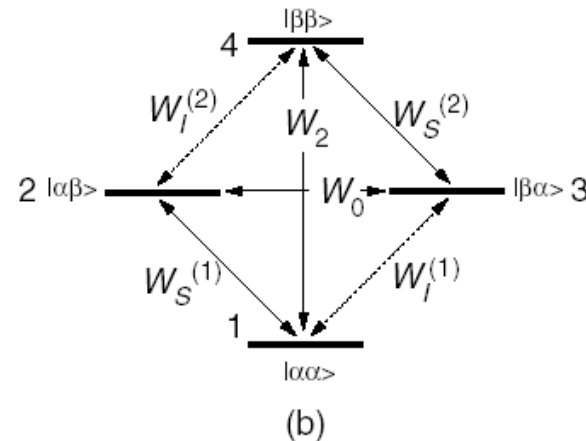


$$S_z = n_1 - n_2 + n_3 - n_4$$

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

$$2I_z S_z = n_1 - n_3 - n_2 + n_4$$

$$E = n_1 + n_2 + n_3 + n_4$$



$$n_1 = \frac{1}{4}(E + I_z + S_z + 2I_z S_z)$$

$$n_2 = \frac{1}{4}(E + I_z - S_z - 2I_z S_z)$$

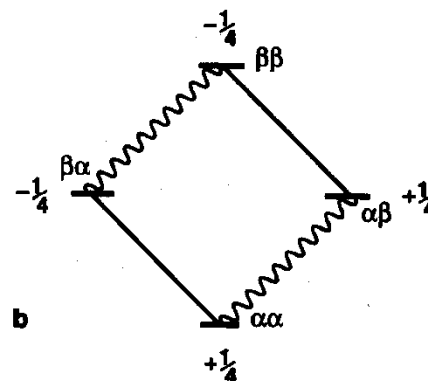
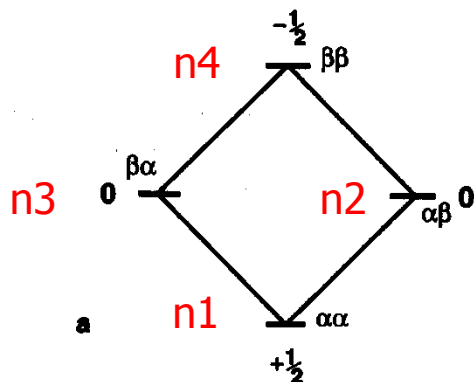
$$n_3 = \frac{1}{4}(E - I_z + S_z - 2I_z S_z)$$

$$n_4 = \frac{1}{4}(E - I_z - S_z + 2I_z S_z)$$

Metody 2D FT NMR spektroskopie

NOE Spectroscopy a EXchange Spectroscopy

Dvouspinový systém IS

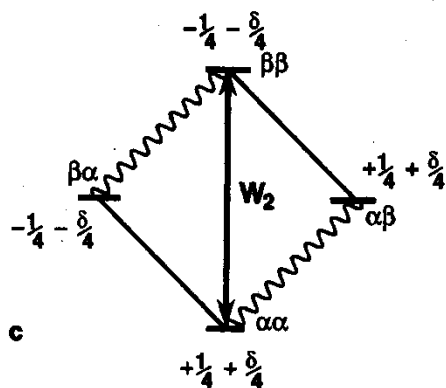


S – je saturován

I -Pozitivní NOE

$$\Delta = 1 + \delta$$

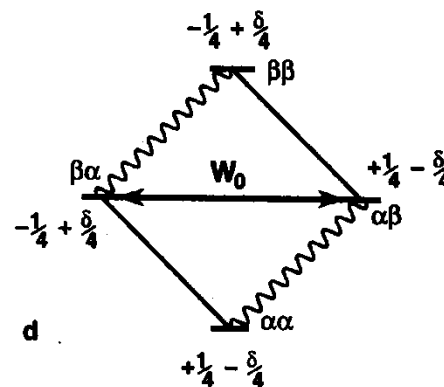
W_2 přechod generuje pozitivní NOE



I -Negativní NOE

$$\Delta = 1 - \delta$$

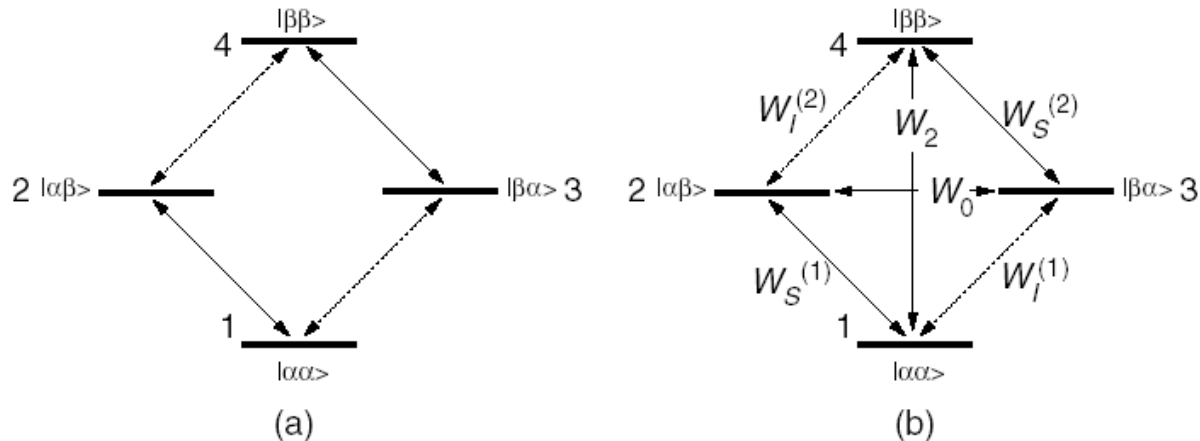
W_0 přechod generuje negativní NOE



$$n1 - n3 + n2 - n4$$

Metody 2D FT NMR spektroskopie

NOE Spectroscopy a EXchange Spectroscopy



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

$$-(W_2 - W_0)S_z - (W_I^{(1)} - W_I^{(2)})2I_zS_z$$

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

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

$$-(W_I^{(1)} + W_I^{(2)} + W_S^{(1)} + W_S^{(2)})2I_zS_z$$

Solomonovy rovnice

Metody 2D FT NMR spektroskopie

NOE Spectroscopy a EXchange Spectroscopy

Solomonovy rovnice - řešení

S_z^o , I_z^o rovnovážná velikost
 I_z velikost při ozařování S

Ustálený stav

$$0 = -(I_z - I_z^o)(W_{OIS} + 2W_{II} + W_{2IS}) + S_z^o (W_{2IS} - W_{OIS})$$

$$\frac{I_z - I_z^o}{S_z^o} = \frac{W_{2IS} - W_{OIS}}{(W_{OIS} + 2W_{II} + W_{2IS})}$$

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

$$\text{NOE } f_1\{S\} = \frac{I_z - I_z^o}{I_z^o} = (\gamma_S/\gamma_I) \frac{W_{2IS} - W_{OIS}}{(W_{OIS} + 2W_{II} + W_{2IS})} = (\gamma_S/\gamma_I) \frac{\sigma_{IS}}{\rho_{IS}}$$

Rychlost DD příčné relaxace ($W_{2IS} - W_{OIS}$) = σ_{IS}

Rychlost DD podélné relaxace ($W_{OIS} + 2W_{II} + W_{2IS}$) = ρ_{IS}

Metody 2D FT NMR spektroskopie NOE Spectroscopy a EXchange Spectroscopy

Dvospinový systém IS

$$\begin{aligned}\sigma_{IS} &= W_{2IS} - W_{0IS} \\ &= \frac{1}{10} K^2 \tau_c \left[\frac{6}{1 + (\omega_I + \omega_S)^2 \tau_c^2} - \frac{1}{1 + (\omega_I - \omega_S)^2 \tau_c^2} \right]\end{aligned}$$

and

$$\begin{aligned}\rho_{IS} &= W_{0IS} + 2W_{1IS} + W_{2IS} \\ &= \frac{1}{10} K^2 \tau_c \left[\frac{1}{1 + (\omega_I - \omega_S)^2 \tau_c^2} + \frac{3}{1 + \omega_I^2 \tau_c^2} + \frac{6}{1 + (\omega_I + \omega_S)^2 \tau_c^2} \right]\end{aligned}$$

$$K = (\mu_o/4\pi)h/2\pi \cdot \gamma_I \cdot \gamma_S \cdot r^{-3}_{IS}$$

Metody 2D FT NMR spektroskopie NOE Spectroscopy a EXchange Spectroscopy

Dvouspinový heteronukleární systém IS

$$f_I\{S\} = \left(\frac{\gamma_S}{\gamma_I} \right) \left[\frac{6}{1 + (\omega_I + \omega_S)^2 \tau_c^2} - \frac{1}{1 + (\omega_I - \omega_S)^2 \tau_c^2} \right] \\ / \left[\frac{1}{1 + (\omega_I - \omega_S)^2 \tau_c^2} + \frac{3}{1 + \omega_I^2 \tau_c^2} + \frac{6}{1 + (\omega_I + \omega_S)^2 \tau_c^2} \right]$$

Metody 2D FT NMR spektroskopie NOE Spectroscopy a EXchange Spectroscopy

Dvospinový systém IS

Dvospinový HOMONUKLEÁRNÍ systém IS

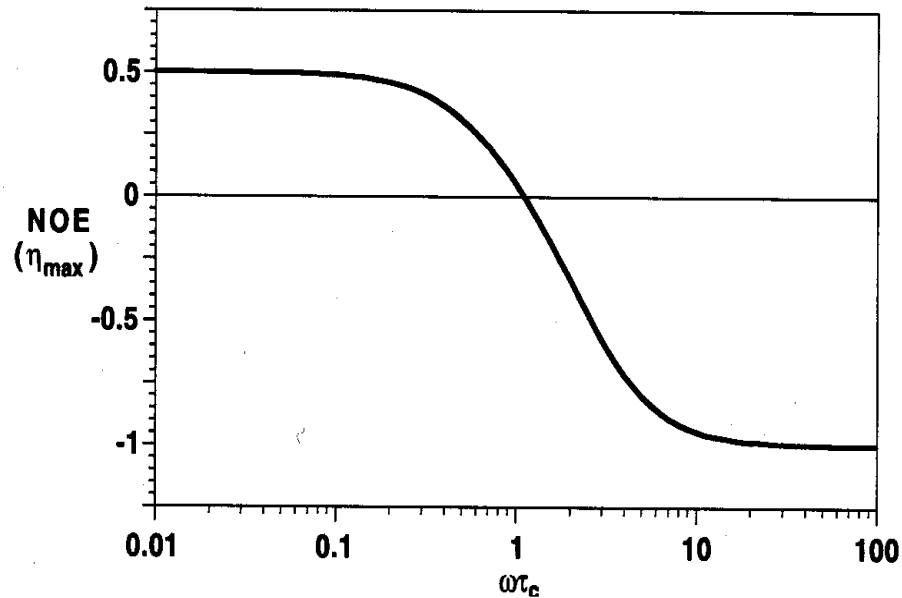
$$f_I\{S\} = \eta_{\max} = \frac{5 + \omega^2\tau_c^2 - 4\omega^4\tau_c^4}{10 + 23\omega^2\tau_c^2 + 4\omega^4\tau_c^4}$$

Metody 2D FT NMR spektroskopie

NOE Spectroscopy a EXchange Spectroscopy

NOE $f_I\{S\} =$

NOE max = $\gamma_I/2\gamma_I = 1/2$

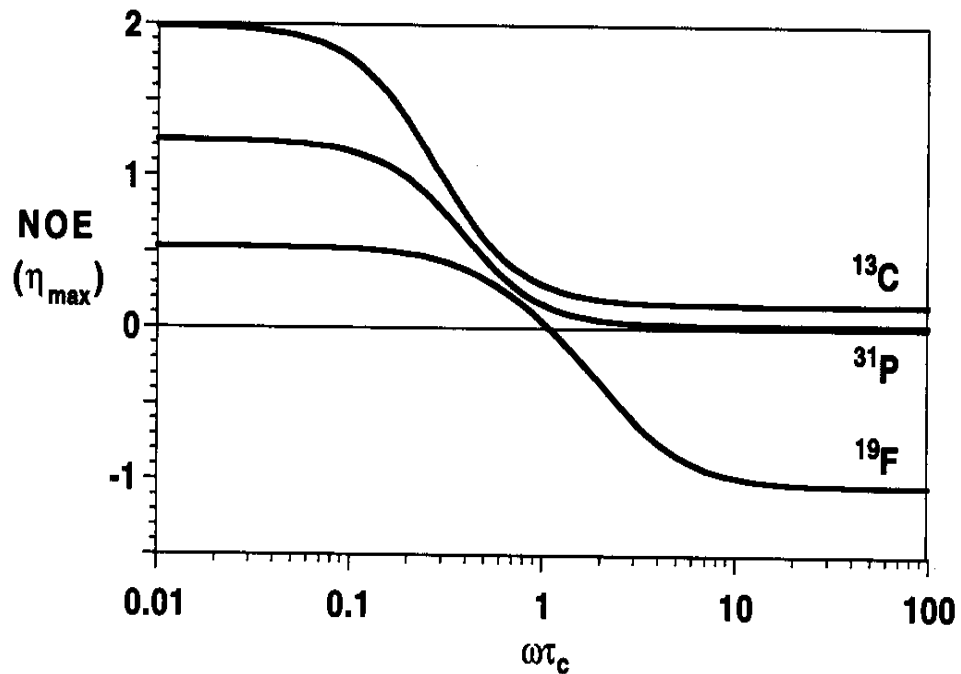


Metody 2D FT NMR spektroskopie

NOE Spectroscopy a EXchange Spectroscopy

$$\text{NOE } f_I\{S\} =$$

$$\text{NOE max} = \gamma_S/2\gamma_I$$

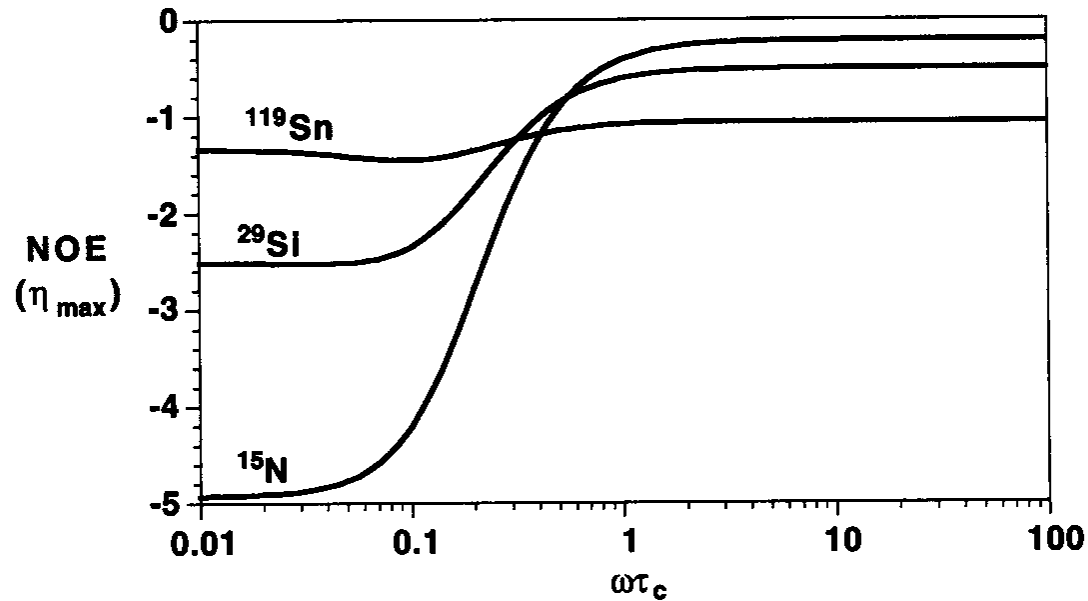


Metody 2D FT NMR spektroskopie

NOE Spectroscopy a EXchange Spectroscopy

NOE $f_I\{S\} =$

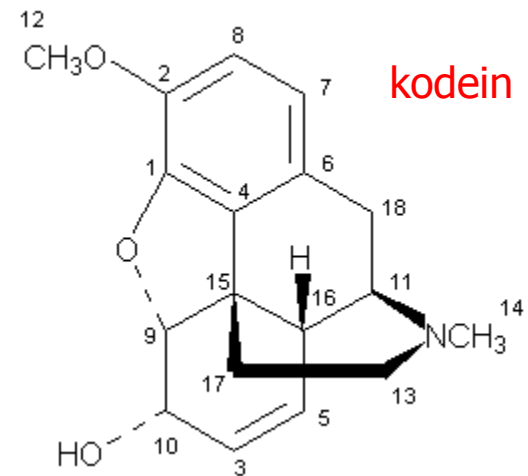
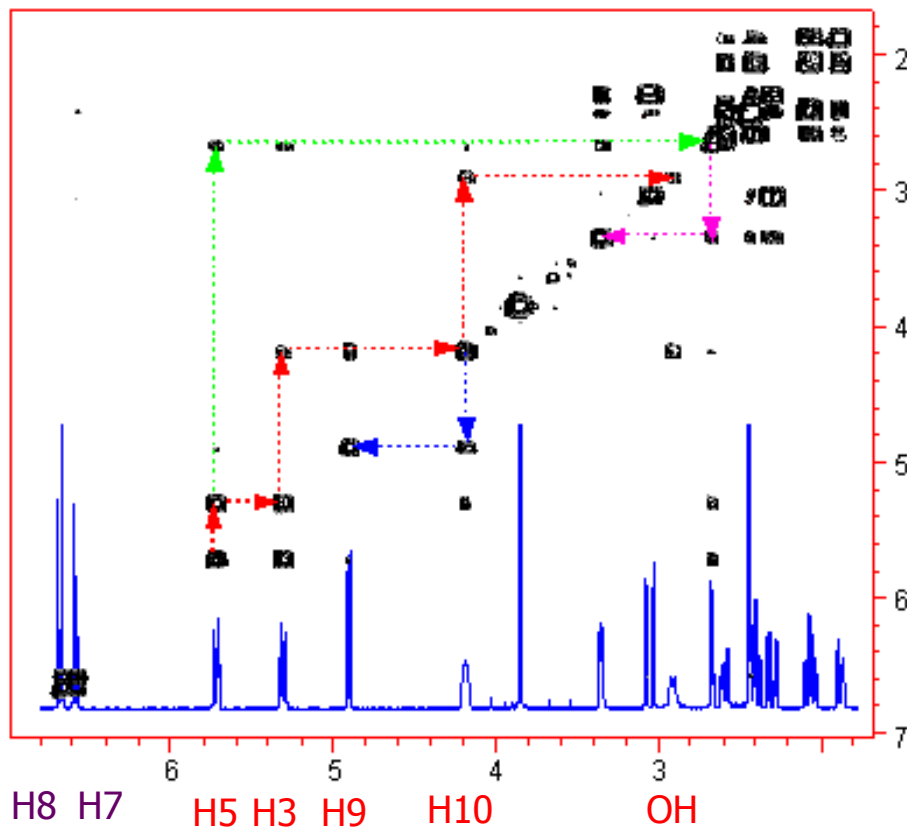
$$\text{NOE max} = \gamma_S / 2\gamma_I$$



Negativní γ_I

Metody 2D FT NMR spektroskopie

Experimenty s přenosem koherence - homonukleární



H-5 → H-3 → H-10 → OH

H-10 → H-9

H-5 → H16

H-16 → H-11

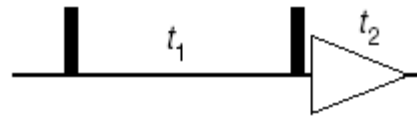
Metody 2D FT NMR spektroskopie

Experimenty s přenosem koherence - homonukleární

$$I_{1x} \xrightarrow{\text{coupling}} 2I_{1y}I_{2z} \xrightarrow{90^\circ(x) \text{ to both spins}} 2I_{1z}I_{2y}$$

spin 1 spin 2

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}

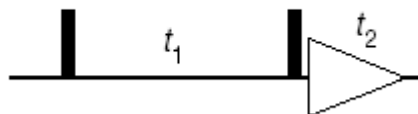
$$-\cos \Omega_1 t_1 I_{1y} \xrightarrow{2\pi J_{12} t_1 I_{1z} I_{2z}} -\cos \pi J_{12} t_1 \cos \Omega_1 t_1 I_{1y} + \sin \pi J_{12} t_1 \cos \Omega_1 t_1 2I_{1x} I_{2z}$$

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

Metody 2D FT NMR spektroskopie

Experimenty s přenosem koherence - homonukleární

COSY



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

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

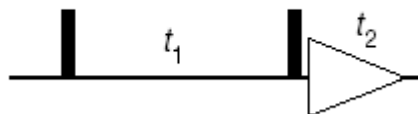
$$\cos \pi J_{12} t_1 \sin \Omega_1 t_1 I_{1x} \xrightarrow{\pi/2 I_{1x}} \xrightarrow{\pi/2 I_{2x}} \cos \pi J_{12} t_1 \sin \Omega_1 t_1 I_{1x} \quad \{3\}$$

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

Metody 2D FT NMR spektroskopie

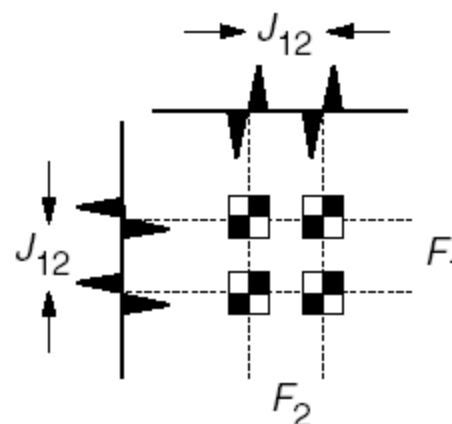
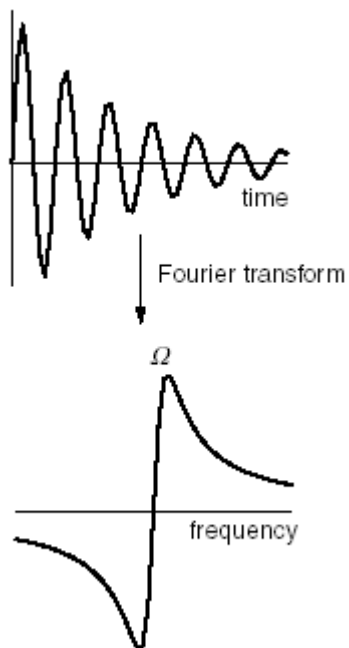
Experimenty s přenosem koherence - homonukleární

COSY



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

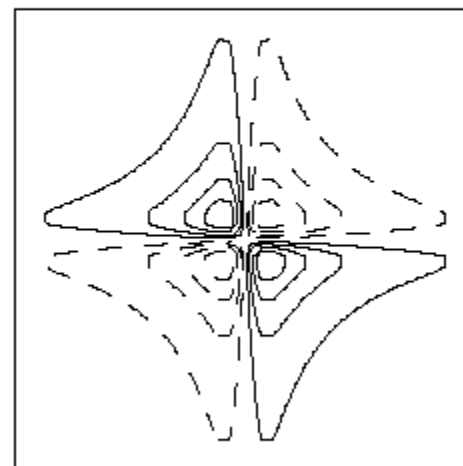
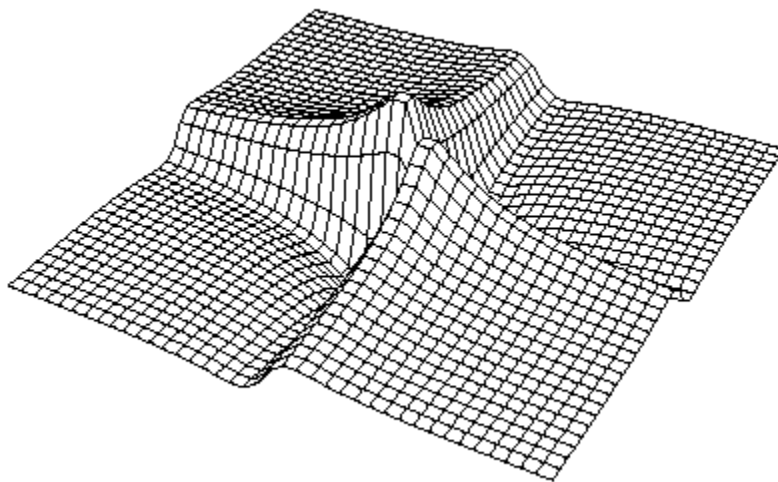
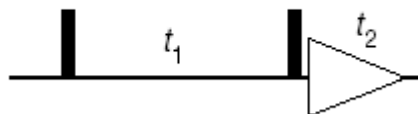
$$\cos \pi J_{12} t_1 \sin \Omega_1 t_1 = \frac{1}{2} \{ \sin(\Omega_1 t_1 + \pi J_{12} t_1) + \sin(\Omega_1 t_1 - \pi J_{12} t_1) \}$$



Metody 2D FT NMR spektroskopie

Experimenty s přenosem koherence - homonukleární

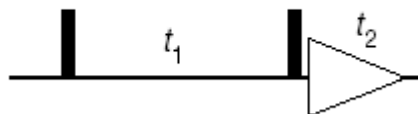
COSY



Metody 2D FT NMR spektroskopie

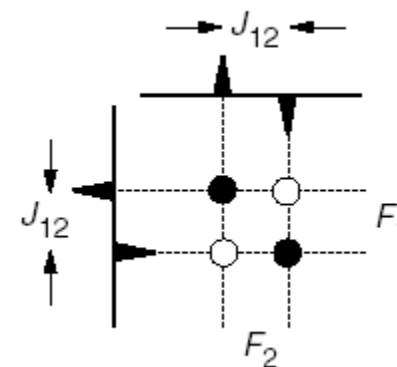
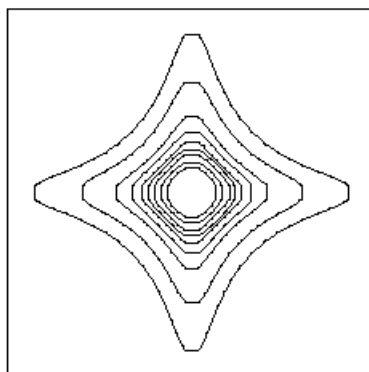
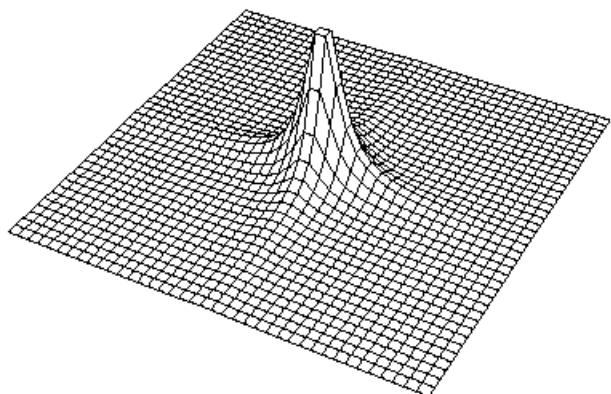
Experimenty s přenosem koherence - homonukleární

COSY



$$\{4\} \quad \sin B \sin A = \frac{1}{2} \{-\cos(B + A) + \cos(B - A)\}$$

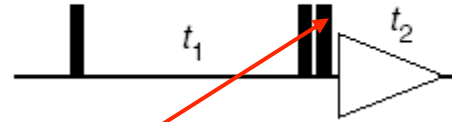
$$\sin \pi J_{12} t_1 \sin \Omega_1 t = \frac{1}{2} \{-\cos(\Omega_1 t_1 + \pi J_{12} t_1) + \cos(\Omega_1 t_1 - \pi J_{12} t_1)\}$$



Metody 2D FT NMR spektroskopie

Experimenty s přenosem koherence - homonukleární

2 DQF COSY



$$\{2\} \quad 2I_{1x}I_{2y} = 2 \times \frac{1}{2}(I_{1+} + I_{1-}) \times \frac{1}{2i}(I_{2+} - I_{2-})$$

$$= \frac{1}{2i}(I_{1+}I_{2+} - I_{1-}I_{2-}) + \frac{1}{2i}(-I_{1+}I_{2-} + I_{1-}I_{2+})$$

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

$$= \frac{1}{2}[2I_{1x}I_{2y} + 2I_{1y}I_{2x}]$$

$90^\circ(x)$

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

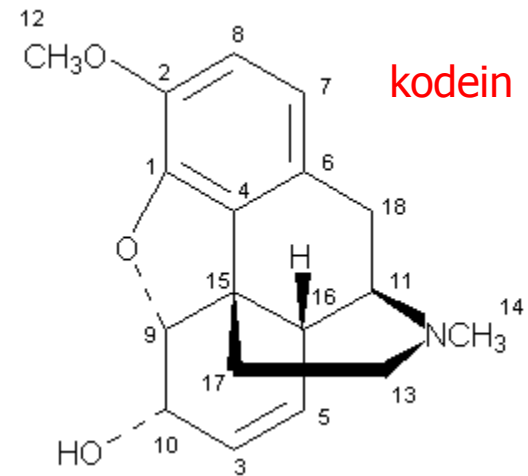
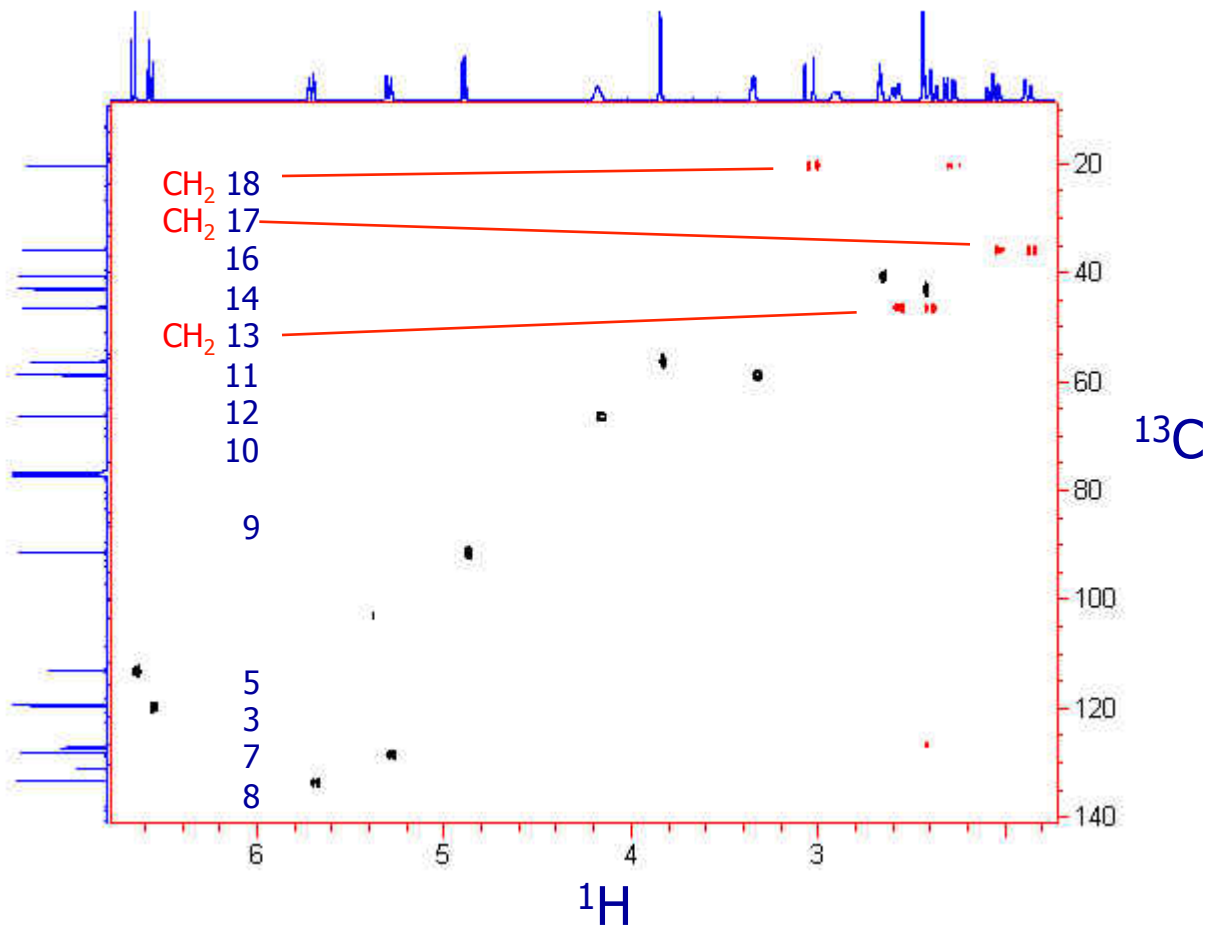
$$-\frac{1}{2} \sin \pi J_{12} t_1 \cos \Omega_1 t_1 (2I_{1x}I_{2z} + 2I_{1z}I_{2x})$$

↑
diagonální pík

↑
interakční pík

Metody 2D FT NMR spektroskopie

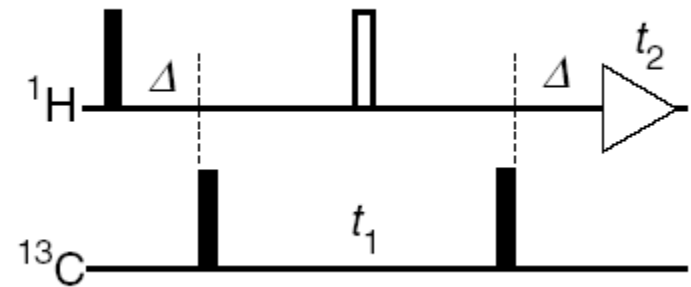
Experimenty s přenosem koherence – heteronukleární



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 :

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

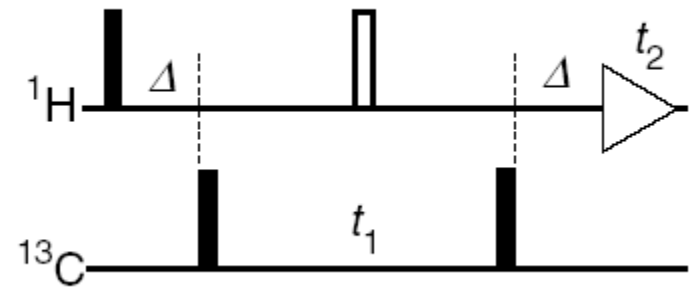
t_1 – vývoj spin I_2 (Ω_2):

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

Metody 2D FT NMR spektroskopie

Experimenty s přenosem koherence - heteronukleární

HMQC - Heteronuclear Multiple-Quantum Correlation



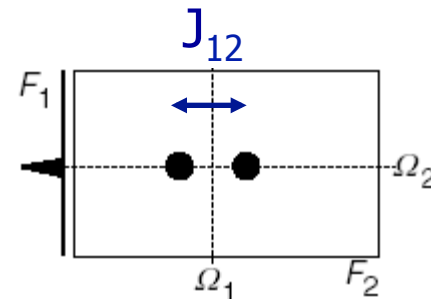
3. Pulz – spin I_2 :

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

$\Delta = 1/2J$ – spin I_1 (J):

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

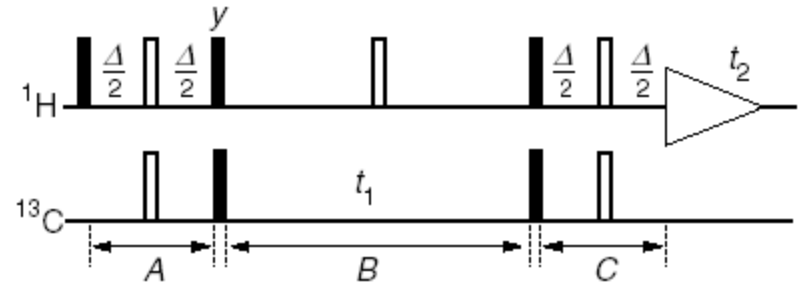
!!!!!!!!!!!!!! $^1\text{H}-^{12}\text{C}$ vers. $^1\text{H}-^{13}\text{C}$!!!!!!!!!!!!!!



Metody 2D FT NMR spektroskopie

Experimenty s přenosem koherence - heteronukleární

HSQC -Heteronuclear Single-Quantum
Correlation



B: t_1 – 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

Praktické aplikace

[QSU webcourse](#)

Metody 2D FT NMR spektroskopie

Tvar čar a diskriminace frekvencí – 1D spektrum

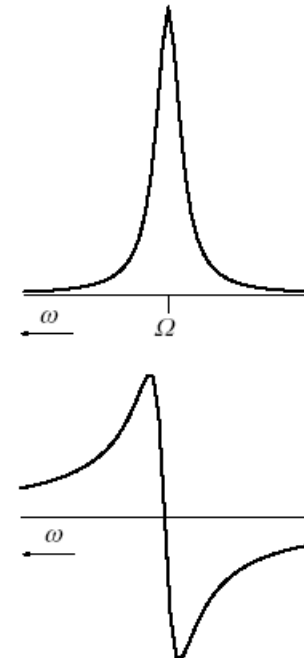
$$S_x(t) = \gamma \cos \Omega t \exp(-t/T_2) \quad S_y(t) = \gamma \sin \Omega t \exp(-t/T_2)$$

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

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

γ – amplituda signálu

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



Lorentzův tvar spektrálních čar

Metody 2D FT NMR spektroskopie

Fáze

Vliv spektrometru
(časové zpoždění během detekce)

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

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

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

↓ FT

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

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

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

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

$$\begin{aligned} S(\omega) \exp(i\phi_{\text{corr}}) &= \gamma \exp(i\phi_{\text{corr}}) \exp(i\phi_{\text{instr}}) \{A(\omega) + iD(\omega)\} \\ &= \gamma \exp(i(\phi_{\text{corr}} + \phi_{\text{instr}})) \{A(\omega) + iD(\omega)\} \end{aligned}$$

Metody 2D FT NMR spektroskopie

Fáze je libovolná

Změna fáze excitačního pulzu $90_y \rightarrow 90_x$

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

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

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

$$\begin{aligned} S(\omega) &= \gamma(-i)\{A(\omega) + iD(\omega)\} \\ \text{Re}[S(\omega)] &= \gamma D(\omega) \quad \text{Im}[S(\omega)] = -\gamma A(\omega) \end{aligned}$$

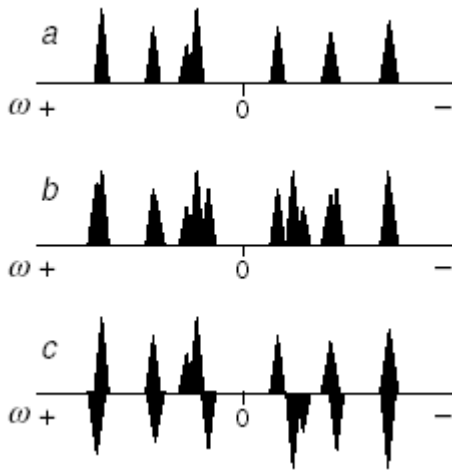
Metody 2D FT NMR spektroskopie

Diskriminace frekvencí – 1D spektrum

Detekce v jedné ose - x
(jediným detektorem)

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

$$\begin{aligned} S(t) &= \frac{1}{2} \gamma [\exp(i\Omega t) + \exp(-i\Omega t)] \exp(-t/T_2) \\ &= \frac{1}{2} \gamma \exp(i\Omega t) \exp(-t/T_2) + \frac{1}{2} \gamma \exp(-i\Omega t) \exp(-t/T_2) \end{aligned}$$



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

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

$$\begin{aligned} S(t) &= \frac{1}{2} \gamma [\exp(i\Omega t) - \exp(-i\Omega t)] \exp(-t/T_2) \\ &= \frac{1}{2} \gamma \exp(i\Omega t) \exp(-t/T_2) - \frac{1}{2} \gamma \exp(-i\Omega t) \exp(-t/T_2) \end{aligned}$$

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

Detekce v jedné ose - y
(jediným detektorem)

Metody 2D FT NMR spektroskopie

Fázová a amplitufová modulace – 2D spektra

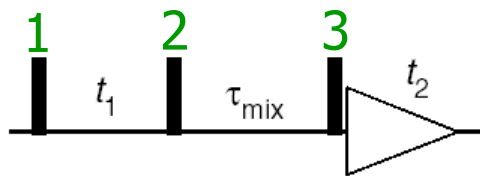
fázová modulace

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

amplitudová modulace

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

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



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

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

Metody 2D FT NMR spektroskopie

Tvar čar – 2D spektra

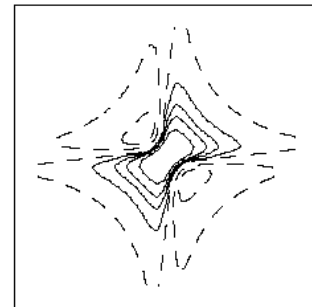
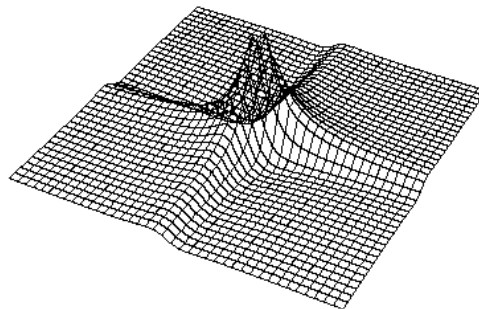
$$FT[\exp(i\Omega t)\exp(-t/T_2)] = \{A(\omega) + iD(\omega)\}$$

fázová modulace

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

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

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



Metody 2D FT NMR spektroskopie

Tvar čar – 2D spektra

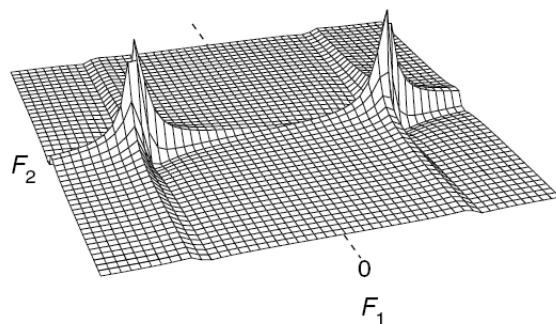
amplitudová modulace
kosinový člen

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

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

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

$$\text{Re}[S(\omega_1, \omega_2)_c] = \frac{1}{2} \gamma (A_+^{(1)} A_+^{(2)} - D_+^{(1)} D_+^{(2)}) + \frac{1}{2} \gamma (A_-^{(1)} A_+^{(2)} - D_-^{(1)} D_+^{(2)})$$



Metody 2D FT NMR spektroskopie

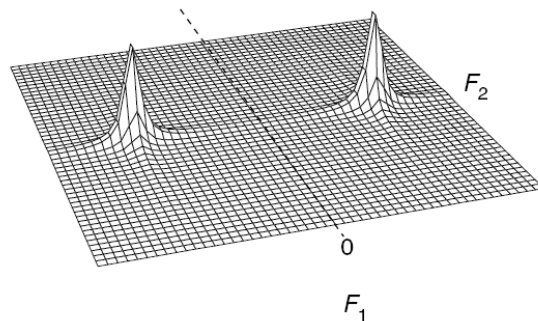
Tvar čar – 2D spektra

$$\begin{aligned} S(t_1, \omega_2)_c^{\text{Re}} &= \text{Re}[S(t_1, \omega_2)_c] \\ &= \gamma \cos(\Omega_1 t_1) \exp(-t_1/T_2^{(1)}) A_+^{(2)} \end{aligned}$$

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

$$S(\omega_1, \omega_2)_c^{\text{Re}} = \frac{1}{2} \gamma [\{A_+^{(1)} + iD_+^{(1)}\} + \{A_-^{(1)} + iD_-^{(1)}\}] A_+^{(2)}$$

$$\text{Re}[S(\omega_1, \omega_2)_c^{\text{Re}}] = \frac{1}{2} \gamma A_+^{(1)} A_+^{(2)} + \frac{1}{2} \gamma A_-^{(1)} A_+^{(2)}$$



Metody 2D FT NMR spektroskopie

Tvar čar – 2D spektra

amplitudová modulace
sinový člen

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

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

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

$$\text{Im}[S(\omega_1, \omega_2)_s] = -\frac{1}{2} \gamma (A_+^{(1)} A_+^{(2)} - D_+^{(1)} D_+^{(2)}) + \frac{1}{2} \gamma (A_-^{(1)} A_+^{(2)} - D_-^{(1)} D_+^{(2)})$$

$$\begin{aligned} S(t_1, \omega_2)_s^{\text{Re}} &= \text{Re}[S(t_1, \omega_2)_s] \\ &= \gamma \sin(\Omega_1 t_1) \exp(-t_1/T_2^{(1)}) A_+^{(2)} \end{aligned}$$

Metody 2D FT NMR spektroskopie

Tvar čar – 2D spektra

$$\begin{aligned} S(t_1, \omega_2)_s^{\text{Re}} &= \text{Re}[S(t_1, \omega_2)_s] \\ &= \gamma \sin(\Omega_1 t_1) \exp(-t_1/T_2^{(1)}) A_+^{(2)} \end{aligned}$$

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

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

$$\text{Im}[S(\omega_1, \omega_2)_s^{\text{Re}}] = -\frac{1}{2} \gamma A_+^{(1)} A_+^{(2)} + \frac{1}{2} \gamma A_-^{(1)} A_+^{(2)}$$

Metody 2D FT NMR spektroskopie

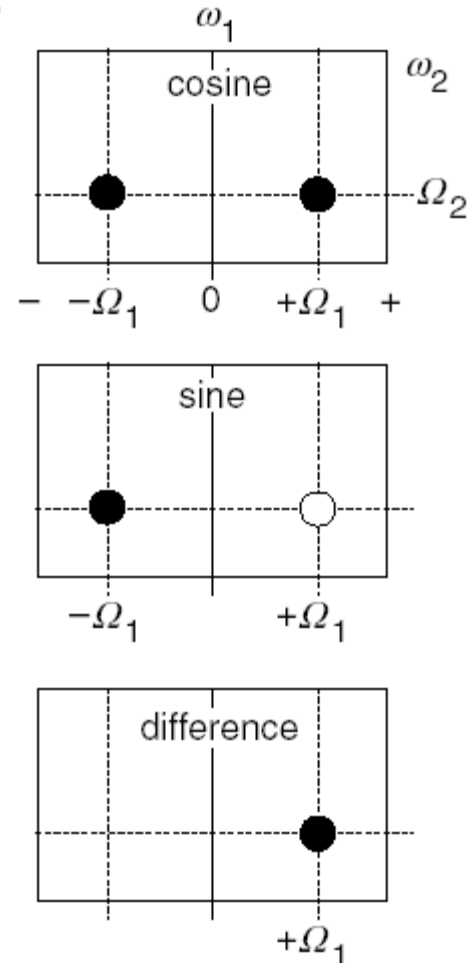
Frekvenční diskriminace a zachování absorpčního tvaru čar

Metoda States-Haberhorn a Rubenova (SHR)

$$\begin{aligned} \operatorname{Re}\left[S(\omega_1, \omega_2)_c^{\operatorname{Re}}\right] - \operatorname{Im}\left[S(\omega_1, \omega_2)_s^{\operatorname{Re}}\right] \\ = \left[\frac{1}{2}\gamma A_+^{(1)} A_+^{(2)} + \frac{1}{2}\gamma A_-^{(1)} A_+^{(2)}\right] - \left[-\frac{1}{2}\gamma A_+^{(1)} A_+^{(2)} + \frac{1}{2}\gamma A_-^{(1)} A_+^{(2)}\right] \\ = \gamma A_+^{(1)} A_+^{(2)} \end{aligned}$$

$$\begin{aligned} S(t_1, \omega_2)_{\text{SHR}} &= S(t_1, \omega_2)_c^{\operatorname{Re}} + iS(t_1, \omega_2)_s^{\operatorname{Re}} \\ &= \gamma \cos(\Omega_1 t_1) \exp(-t_1/T_2^{(1)}) A_+^{(2)} + i\gamma \sin(\Omega_1 t_1) \exp(-t_1/T_2^{(1)}) A_+^{(2)} \\ &= \gamma \exp(i\Omega_1 t_1) \exp(-t_1/T_2^{(1)}) A_+^{(2)} \end{aligned}$$

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



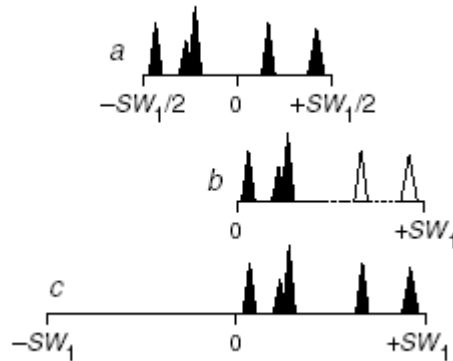
Metody 2D FT NMR spektroskopie

Frekvenční diskriminace a zachování absorpčního tvaru čar

Metoda TPPI – Time Proportional Phase Incrementation

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

$$\begin{aligned} \cos(\Omega_1 t_1 + \pi/2) &= \cos \Omega_1 t \cos \pi/2 - \sin \Omega_1 t \sin \pi/2 \\ &= -\sin \Omega_1 t \end{aligned}$$



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

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

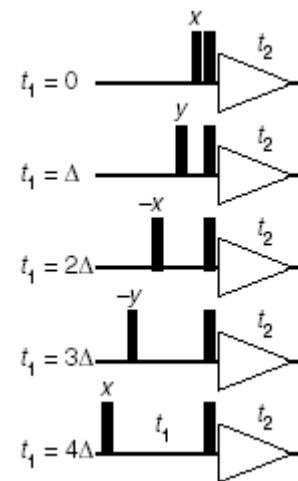
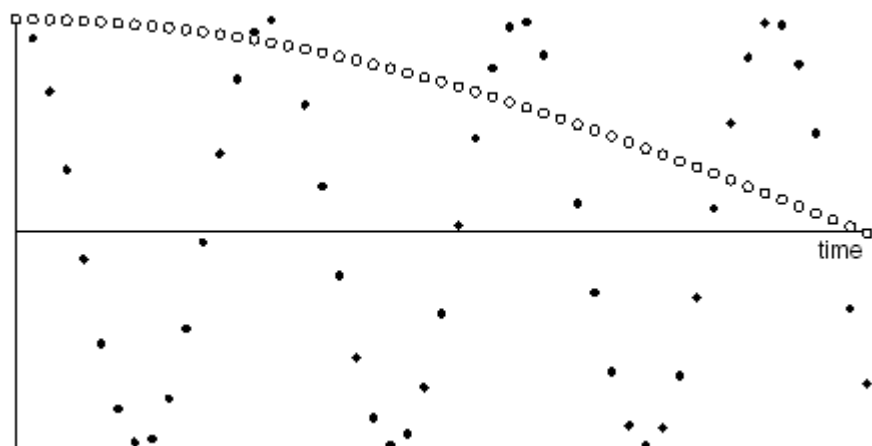
$$\begin{aligned} \cos(\Omega_1 t_1 + \phi(t_1)) &= \cos(\Omega_1 t_1 + \omega_{\text{additional}} t_1) \\ &= \cos(\Omega_1 + \omega_{\text{additional}}) t_1 \end{aligned}$$

Metody 2D FT NMR spektroskopie

Frekvenční diskriminace a zachování absorpčního tvaru čar

Metoda TPPI –
Time Proportional Phase Incrementation

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



Metody 2D FT NMR spektroskopie

Frekvenční diskriminace a zachování absorpčního tvaru čar

Metoda Echo-Antiecho

P-spektrum - antiecho $S(t_1, t_2)_P = \gamma \exp(i\Omega_1 t_1) \exp(-t_1/T_2^{(1)}) \exp(i\Omega_2 t_2) \exp(-t_2/T_2^{(2)})$

N-spektrum - echo $S(t_1, t_2)_N = \gamma \exp(-i\Omega_1 t_1) \exp(-t_1/T_2^{(1)}) \exp(i\Omega_2 t_2) \exp(-t_2/T_2^{(2)})$

Kosinová modulace $\frac{1}{2} [S(t_1, t_2)_P + S(t_1, t_2)_N] =$
 $\frac{1}{2} \gamma [\exp(i\Omega_1 t_1) + \exp(-i\Omega_1 t_1)] \exp(-t_1/T_2^{(1)}) \exp(i\Omega_2 t_2) \exp(-t_2/T_2^{(2)})$
 $= \gamma \cos(\Omega_1 t_1) \exp(-t_1/T_2^{(1)}) \exp(i\Omega_2 t_2) \exp(-t_2/T_2^{(2)})$

Sinová modulace $\frac{1}{2i} [S(t_1, t_2)_P - S(t_1, t_2)_N] =$
 $\frac{1}{2i} \gamma [\exp(i\Omega_1 t_1) - \exp(-i\Omega_1 t_1)] \exp(-t_1/T_2^{(1)}) \exp(i\Omega_2 t_2) \exp(-t_2/T_2^{(2)})$
 $= \gamma \sin(\Omega_1 t_1) \exp(-t_1/T_2^{(1)}) \exp(i\Omega_2 t_2) \exp(-t_2/T_2^{(2)})$

Metoda SHR