

# Fyzikálně-chemické základy nukleární magnetické rezonance

# NMR a elektromagnetické spektrum

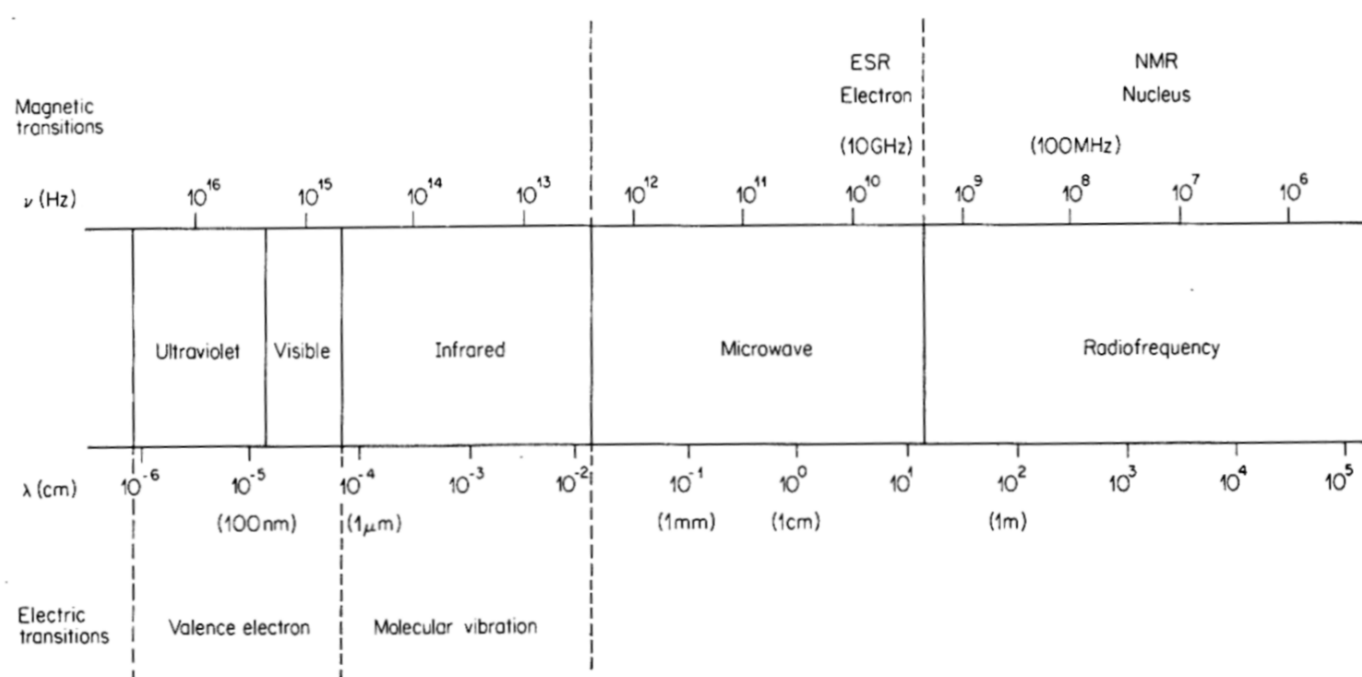
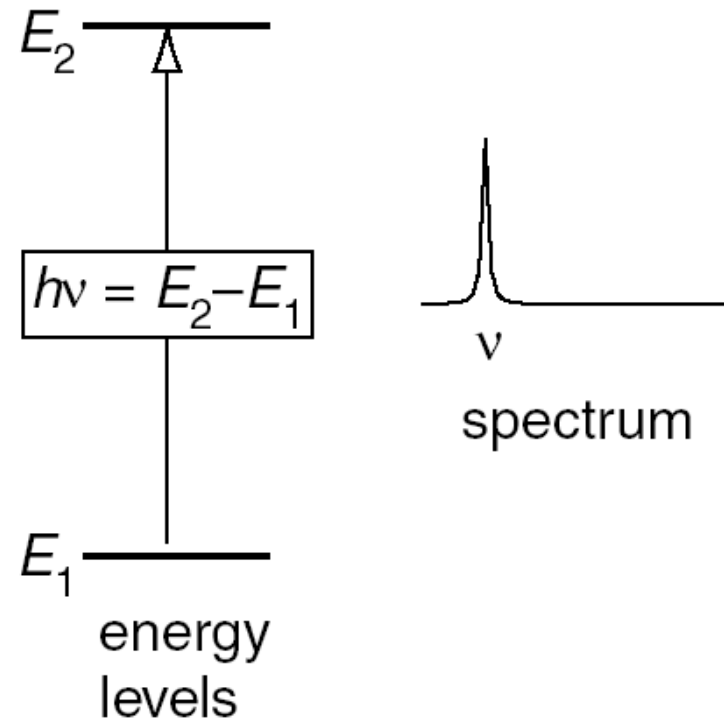


Figure 1.2 Spectral regions of the electromagnetic spectrum of interest in biological investigations

# NMR a energiové hladiny

$$\Delta E = h\nu$$



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

# NMR a energiové hladiny

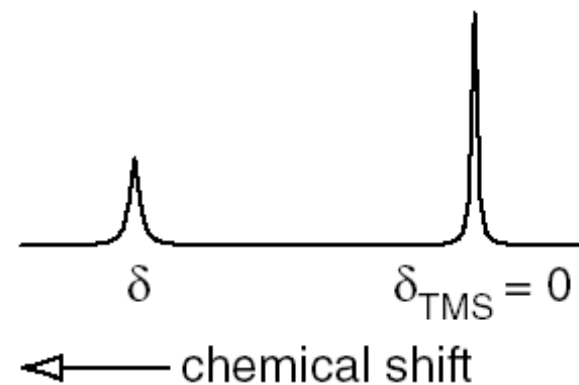
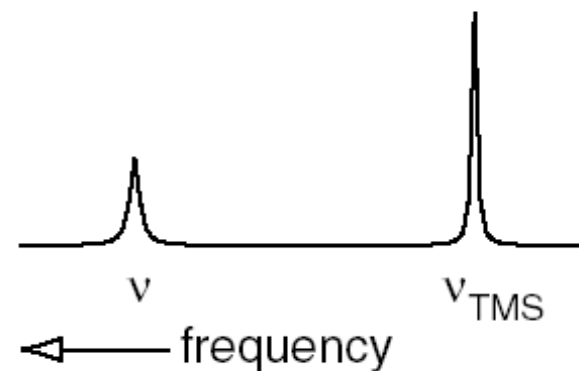
## Chemický posun

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

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

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

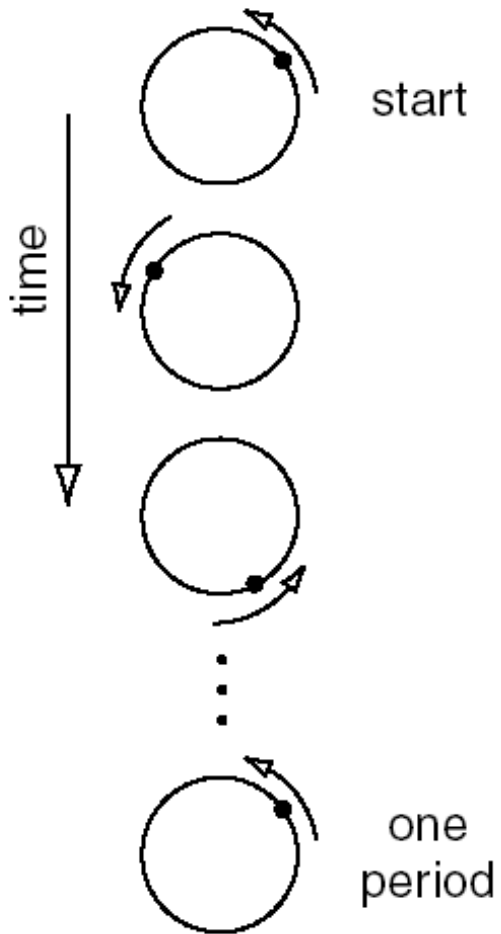
$$(\nu_2 - \nu_1) = 10^{-6} \times \nu_{\text{TMS}} \times (\delta_2 - \delta_1)$$





# NMR a energiové hladiny

## Rotační frekvence a energie



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

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

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

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



# 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  $I = \frac{1}{2}$        $m = \frac{1}{2}$   $\alpha$  stav  
 $m = -\frac{1}{2}$   $\beta$  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

$\alpha\alpha\alpha, \alpha\alpha\beta, \alpha\beta\alpha, \beta\alpha\alpha, \alpha\beta\beta, \beta\alpha\beta, \beta\beta\alpha, \text{ a } \beta\beta\beta$

**Animated course – Basic concepts**

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



## NMR a energiové hladiny

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

←  
pořadové číslo spinu

$\nu_0$  - Larmorova frekvence

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

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

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

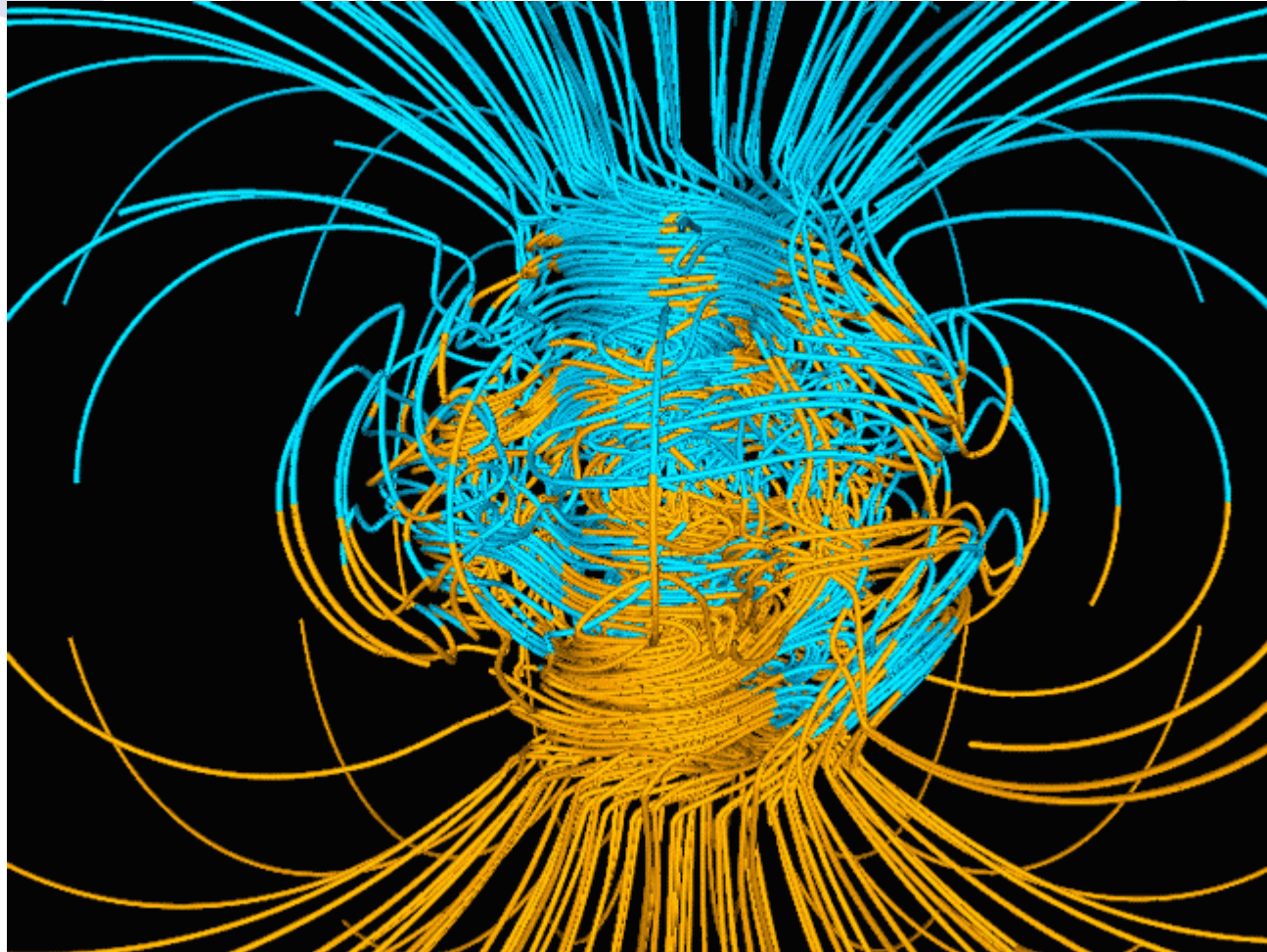
$\gamma$  - magnetogyrická konstanta (poměr) [rad. s<sup>-1</sup>.T<sup>-1</sup>]

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

|                                       |                           |  |
|---------------------------------------|---------------------------|--|
| $\nu_0 = -200 \times 10^6 \text{ Hz}$ | Při $B_0 = 4.7 \text{ T}$ |  |
|                                       | a                         | $\omega_0 = -1,225 \times 10^9 \text{ rad.s}^{-1}$ |

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

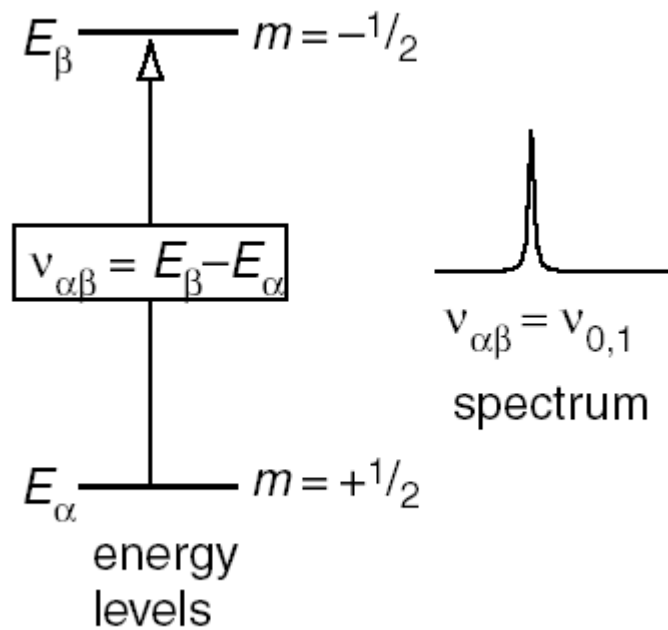
The strength of the field at the Earth's surface at this time ranges from less than 30 microteslas (0.3 gauss) in an area including most of South America and South Africa to over 60 microteslas (0.6 gauss) around the magnetic poles in northern Canada and south of Australia, and in part of Siberia.



# 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

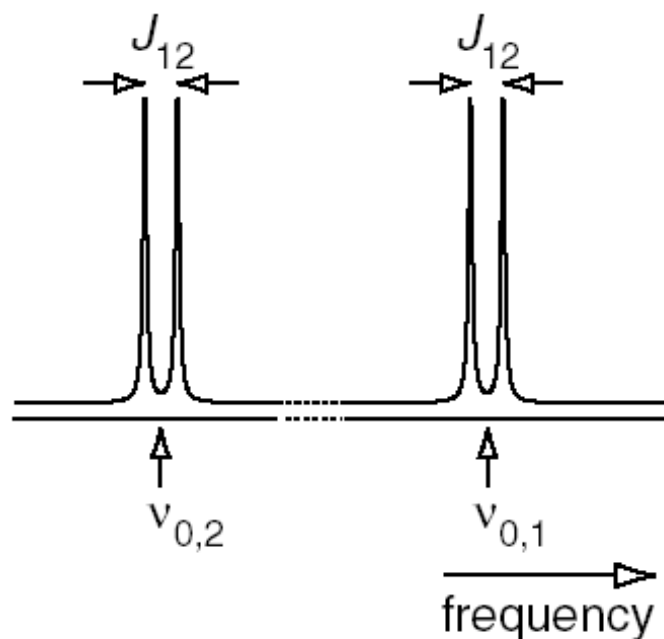
## Dva spiny

### 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

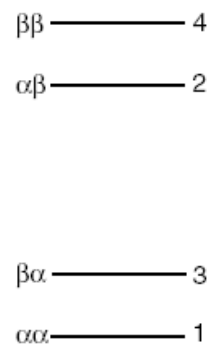
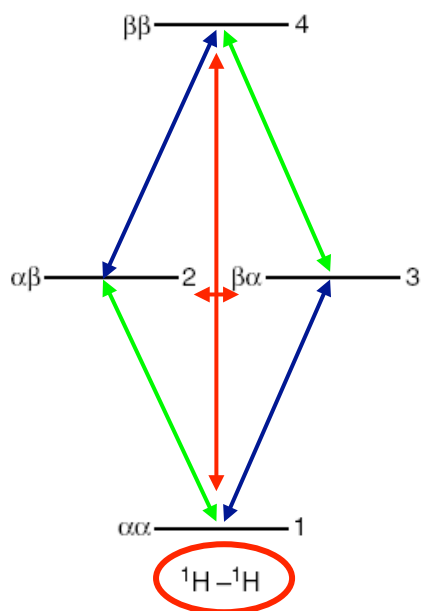


| number | spin states    | energy   |
|--------|----------------|--|
| 1      | $\alpha\alpha$ | $+\frac{1}{2}\nu_{0,1} + \frac{1}{2}\nu_{0,2} + \frac{1}{4}J_{12}$ |
| 2      | $\alpha\beta$  | $+\frac{1}{2}\nu_{0,1} - \frac{1}{2}\nu_{0,2} - \frac{1}{4}J_{12}$ |
| 3      | $\beta\alpha$  | $-\frac{1}{2}\nu_{0,1}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



$$M = m_1 + m_2.$$

| 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,



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

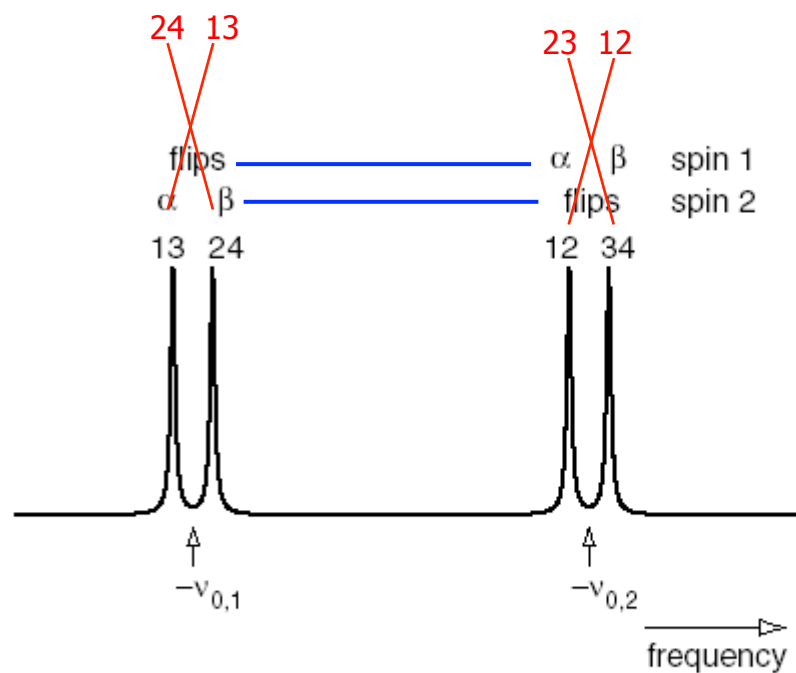
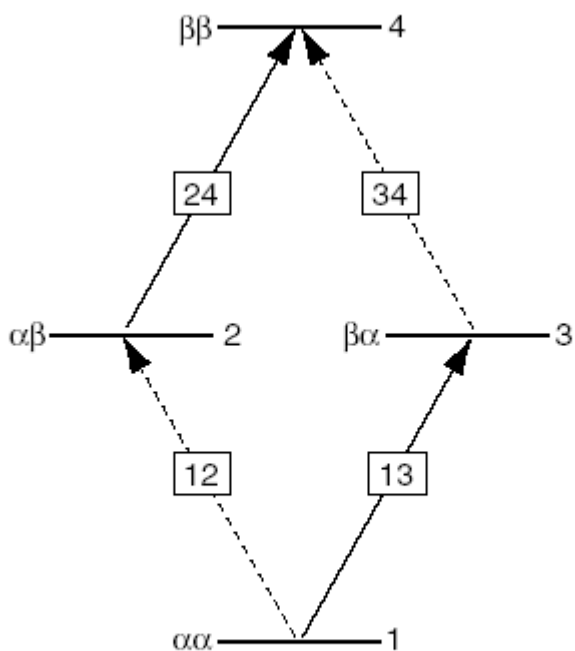
| transition | spin states                            | frequency                        |
|------------|--|----------------------------------|
| 1 → 2      | $\alpha\alpha \rightarrow \alpha\beta$ | $-\nu_{0,2} - \frac{1}{2}J_{12}$ |
| 3 → 4      | $\beta\alpha \rightarrow \beta\beta$   | $-\nu_{0,2}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



# NMR a energiové hladiny

## Dva spiny – jedno-kvantové přechody

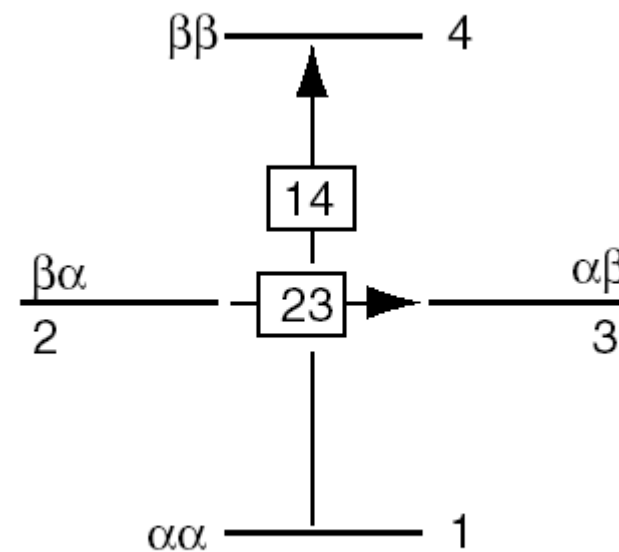
Pro  $J < 0$



# 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  |



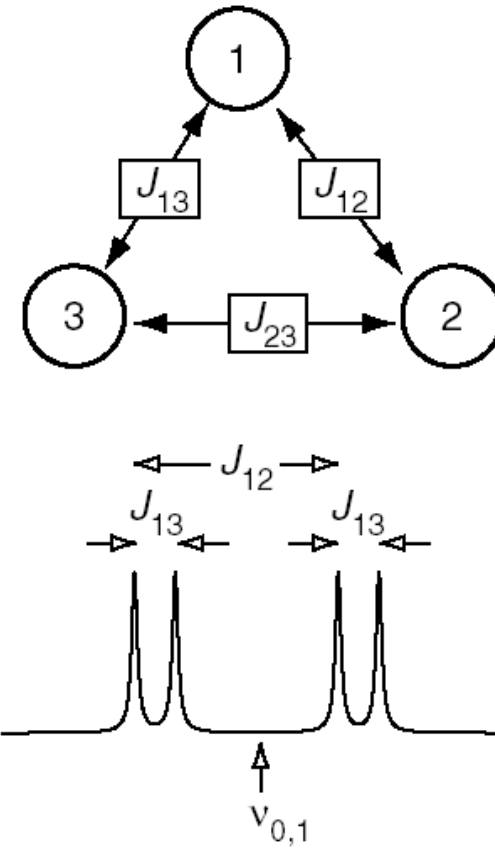
14 – dvou-kvantový přechod  
23 – nul-kvantový přechod

# 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 $\beta$

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

### Spin 3 $\alpha$

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

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

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

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

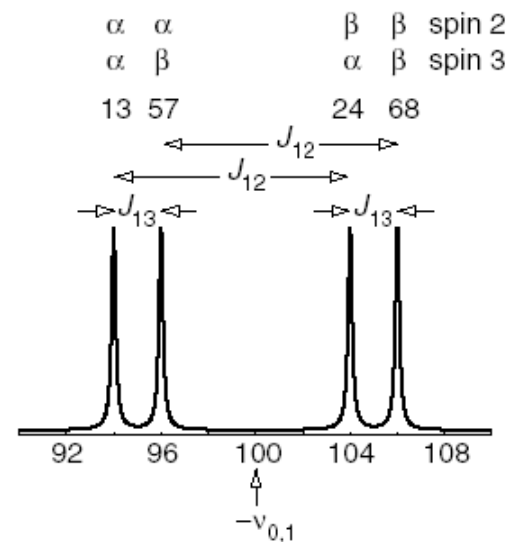
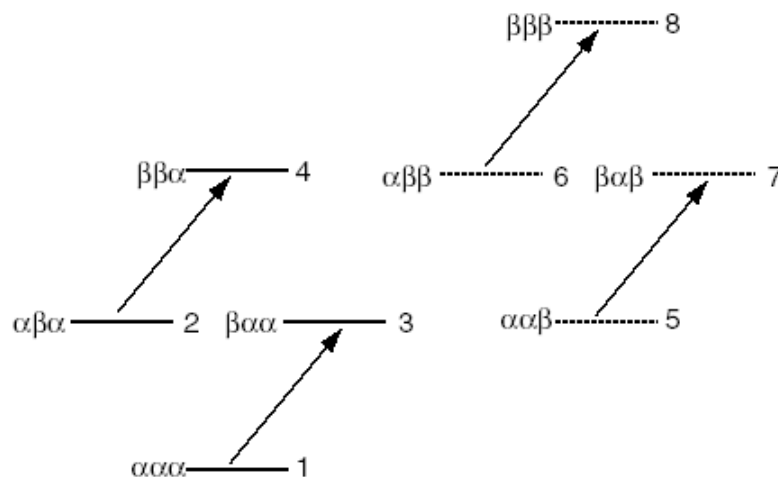
$\alpha\alpha\alpha$  ----- 1

# NMR a energiové hladiny

## Tři spiny

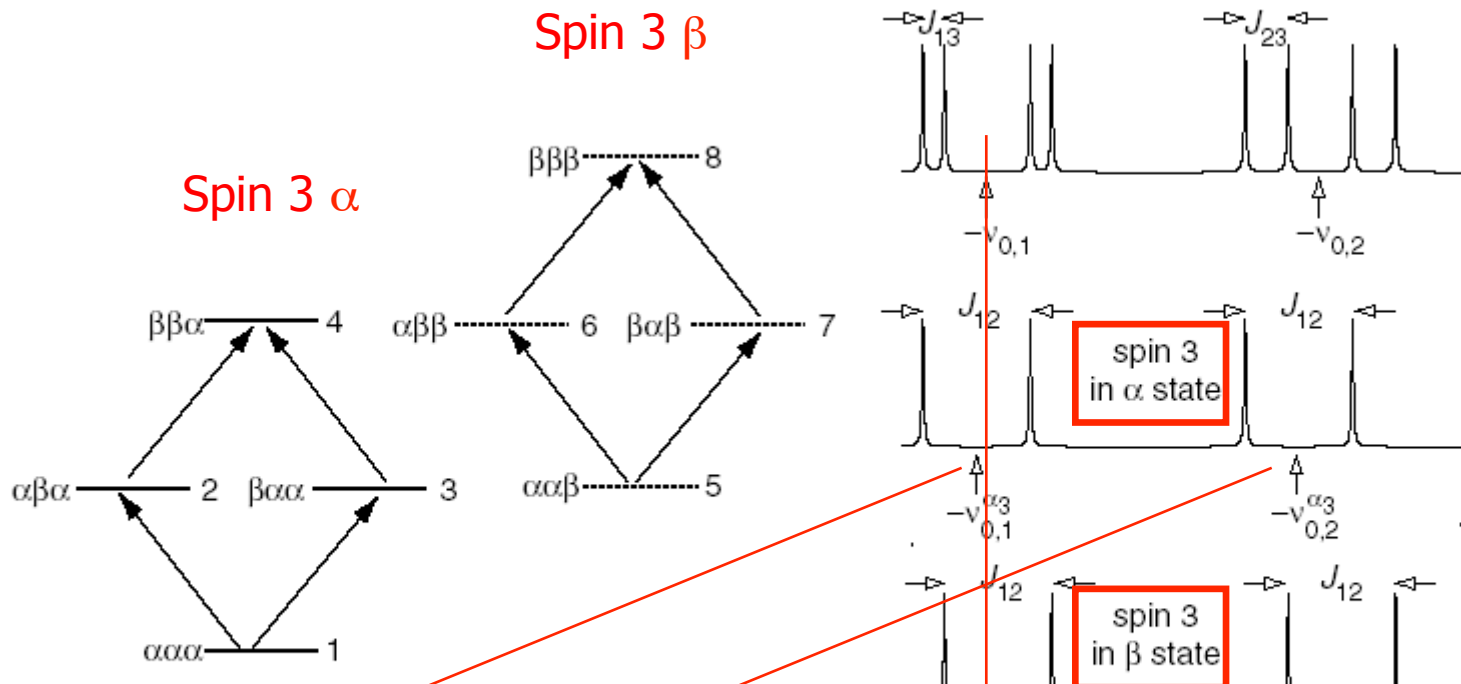
| transition | state of spin 2 | state of spin 3 | frequency  |
|------------|-----------------|-----------------|--|
| 1-3        | $\alpha$        | $\alpha$        | $-\nu_{0,1} - \frac{1}{2}J_{12} - \frac{1}{2}J_{13}$ |
| 2-4        | $\beta$         | $\alpha$        | $-\nu_{0,1} + \frac{1}{2}J_{12}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

Výběrové pravidlo  $\Delta M = \pm 1$   
 ale jen jeden spin může změnit svůj stav



# NMR a energetické hladiny

## Tři spiny - subspektra



Efektivní Larmorova frekvence

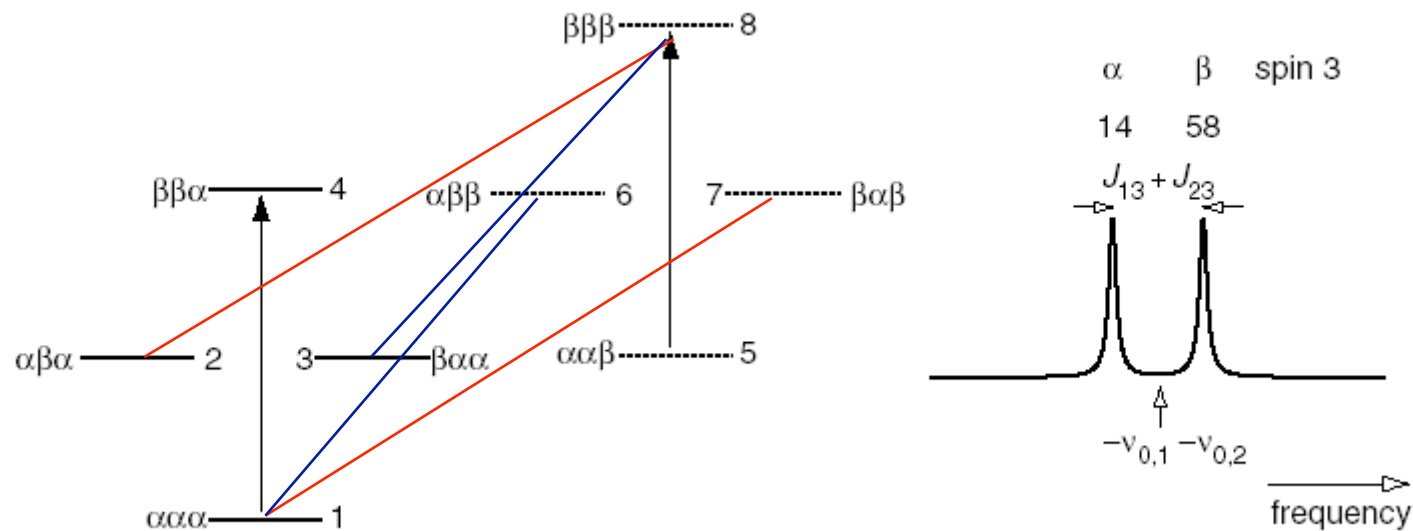
$$\nu_{0,1}^{\alpha_3} = \nu_{0,1} + \frac{1}{2}J_{13} \quad \nu_{0,2}^{\alpha_3} = \nu_{0,2} + \frac{1}{2}J_{23}$$

$$\nu_{0,1}^{\beta_3} = \nu_{0,1} - \frac{1}{2}J_{13} \quad \nu_{0,2}^{\beta_3} = \nu_{0,2} - \frac{1}{2}J_{23}$$

# 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        | $-\frac{1}{2}D - \frac{1}{2}\Sigma + \frac{1}{2}J_{12}$ | $(1 + \sin 2\theta)$ |

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

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

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



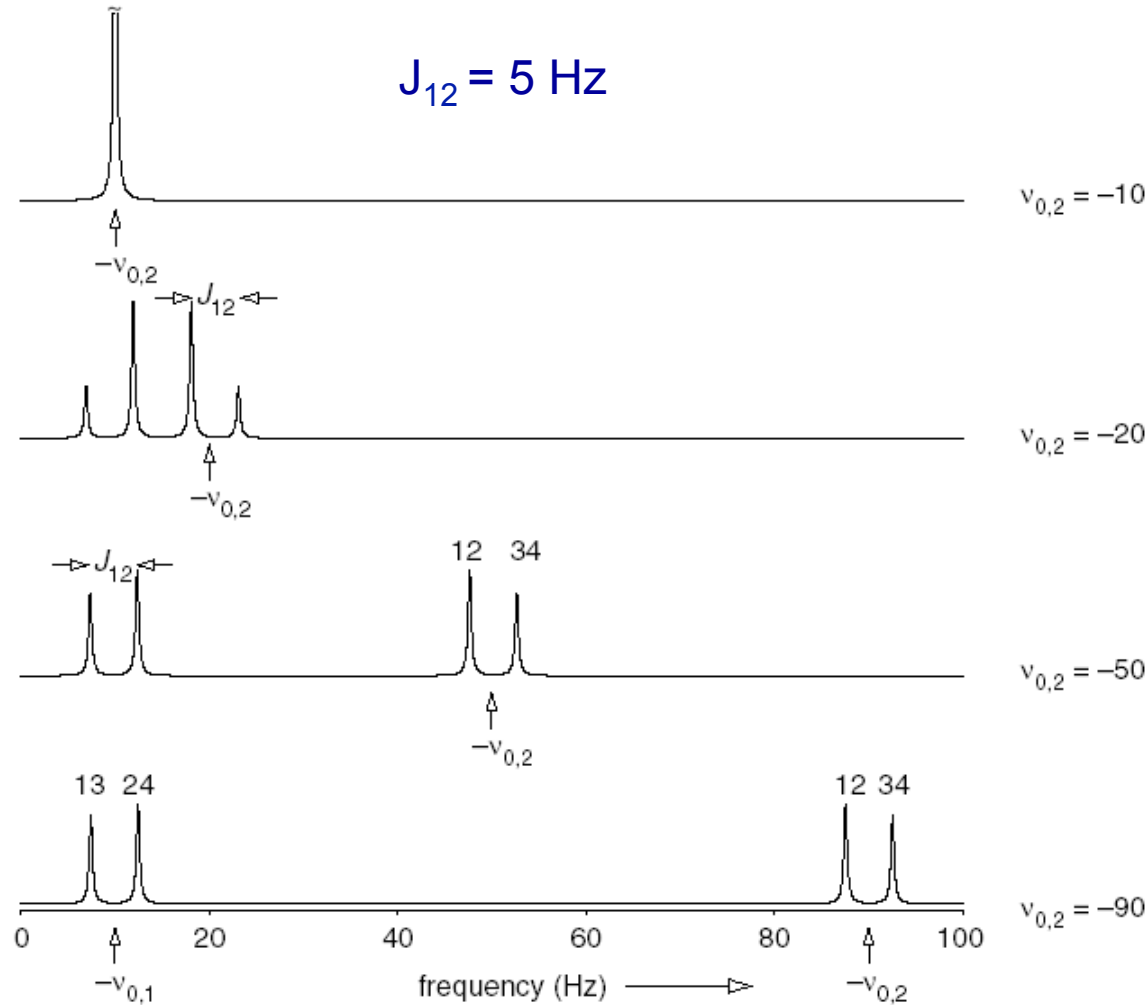
# NMR a energiové hladiny

## Dva spiny – silná interakce

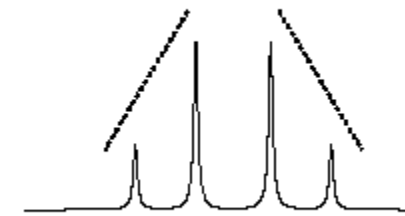
$$\Delta\delta_{12} < 7 \cdot J_{12}$$

$$\sin 2\theta = \frac{J_{12}}{D}$$

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



Střížkový efekt

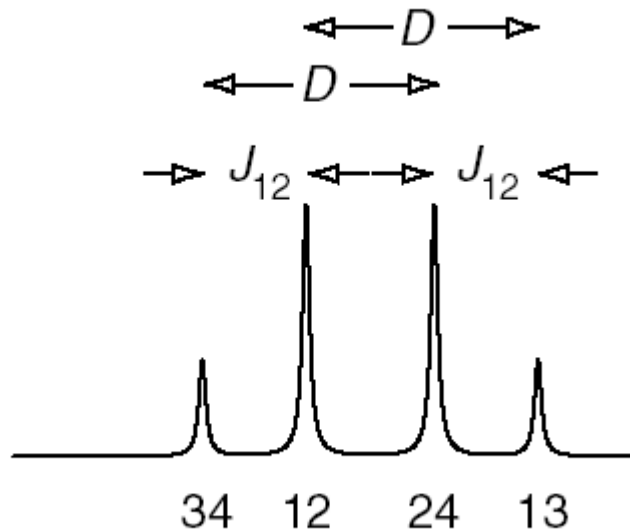


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# NMR a energiové hladiny

## Dva spiny – silná interakce

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



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

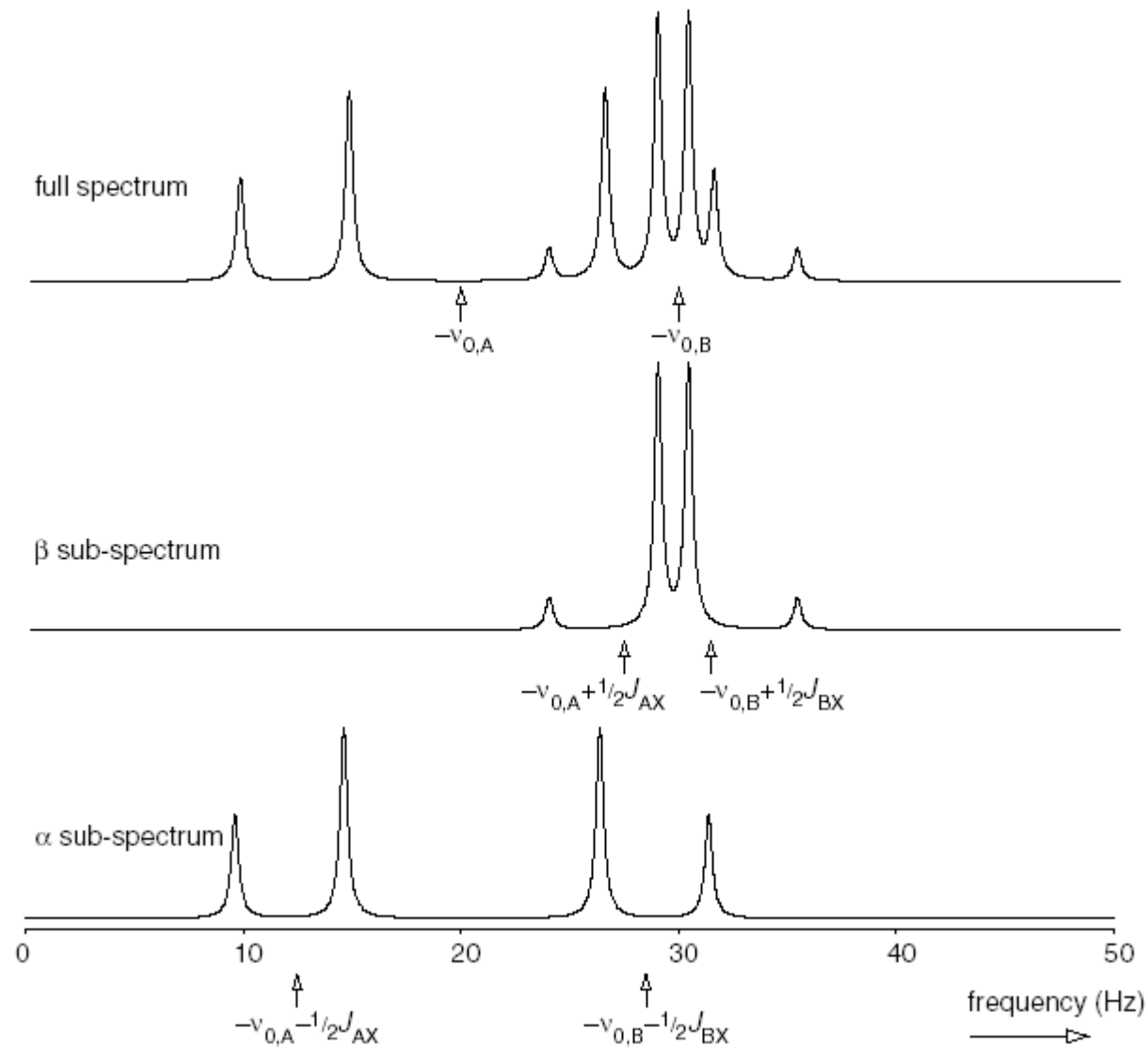
$$D^2 = (\nu_{0,1} - \nu_{0,2})^2 + J_{12}^2$$

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

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

# NMR a energiové hladiny

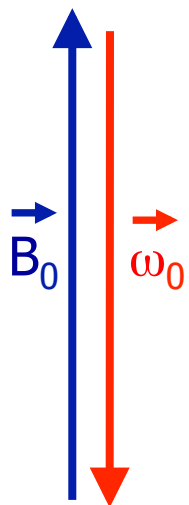
## Tři spiny – ABX systém - subspektra



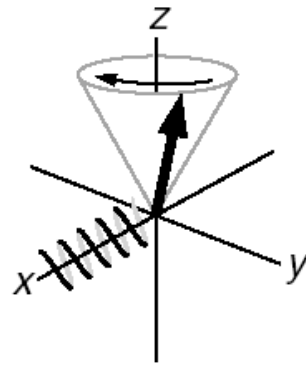
# Vektorový model NMR

## Larmorova precesní frekvence

Směr rotace je negativní – +x → -y!!



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



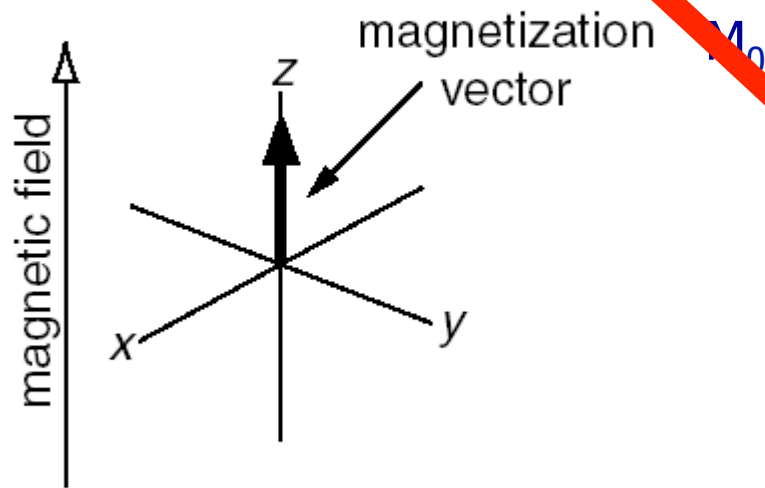
$$\vec{\nu}_0 = -\frac{1}{2\pi} \gamma \vec{B}_0$$

Pravidlo pravé ruky  
Pozor na znaménko  $\gamma$  !

# Vektorový model NMR

## Makroskopická magnetizace

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

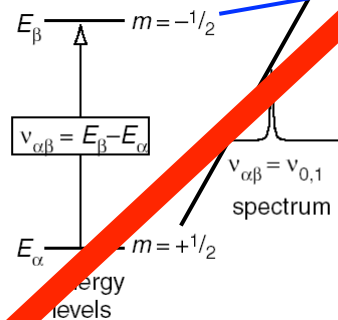
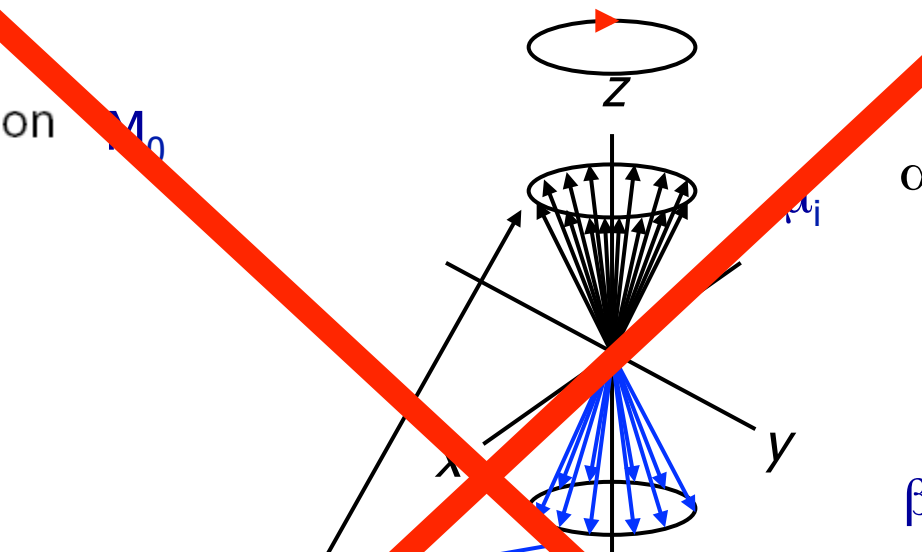


$$M(M_x, M_y, M_z) = \sum (\mu_j)$$

Curieho zákon

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

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

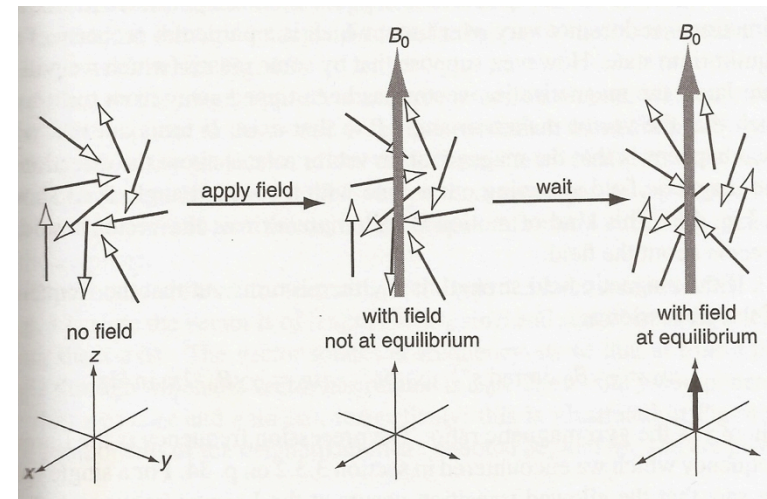
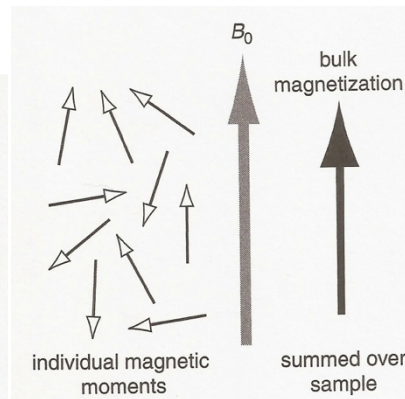
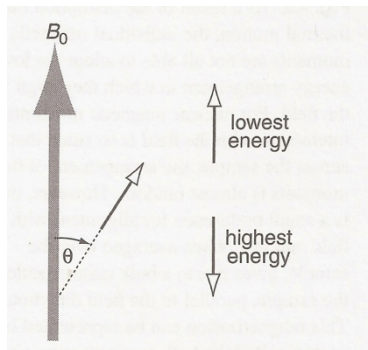


Boltzmanova rovnice

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

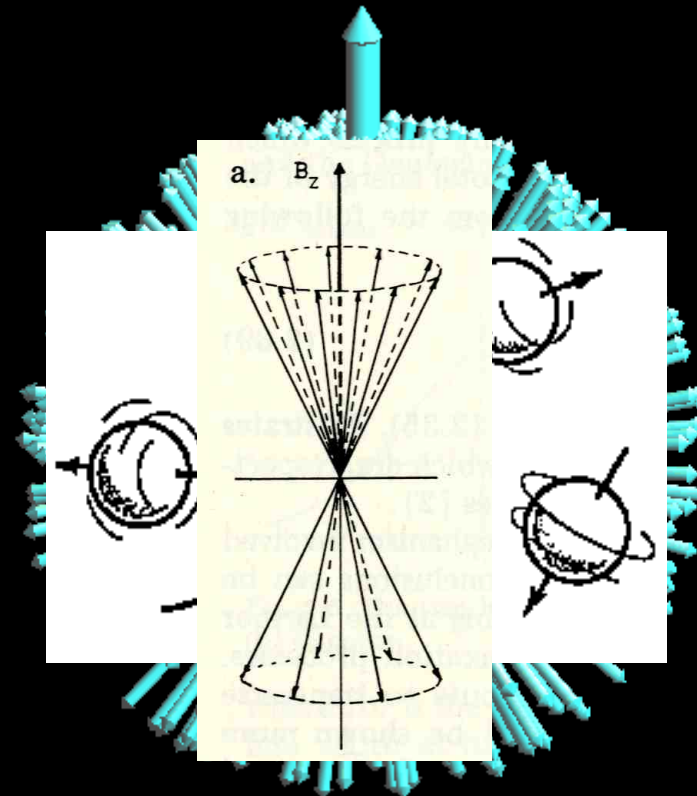
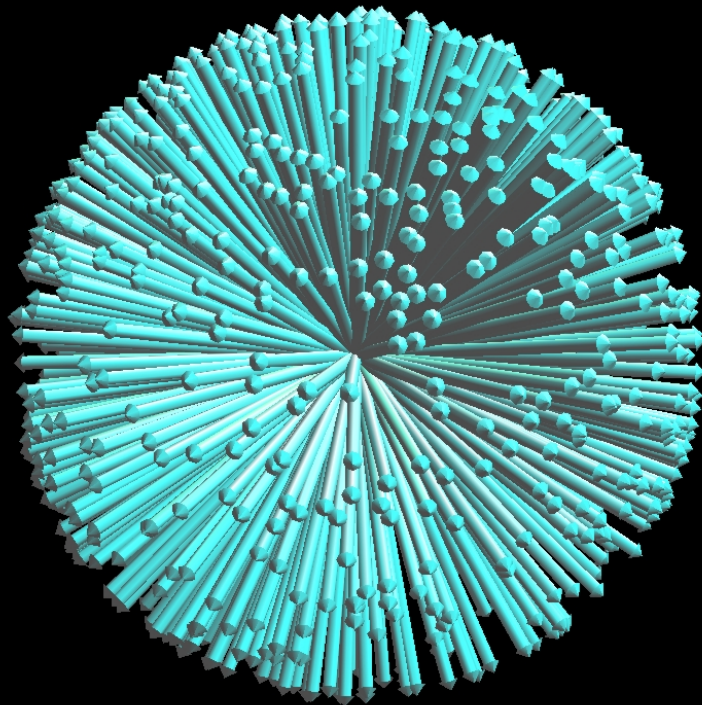
# Vektorový model NMR

## Makroskopická magnetizace



Malcolm H. Levitt: Spin Dynamics, Basics of Nuclear Magnetic Resonance  
Wiley 2008, ISBN-10: 0470511176, ISBN-13: 978-0470511176, Edition: 2  
Chapter 2.4 Spin Precession, p. 27-38.

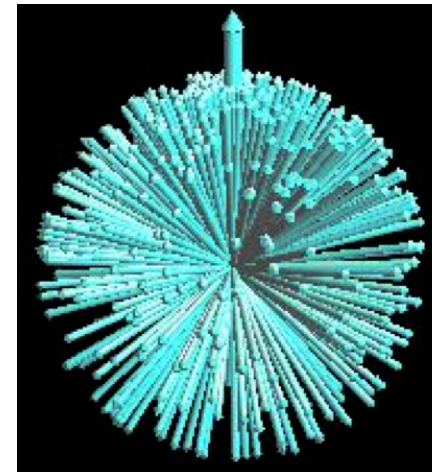
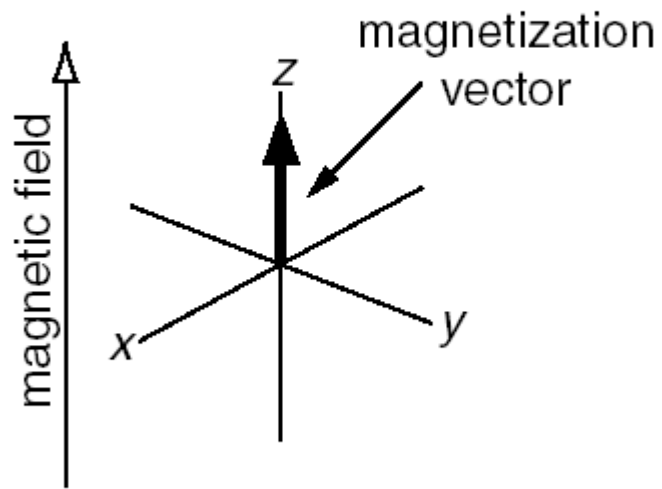
# The polarisation process



- Field causes precession and alignment,..
  - ...but nuclear interactions randomise orientations

# Vektorový model NMR

## Makroskopická magnetizace



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

Curieho zákon

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

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

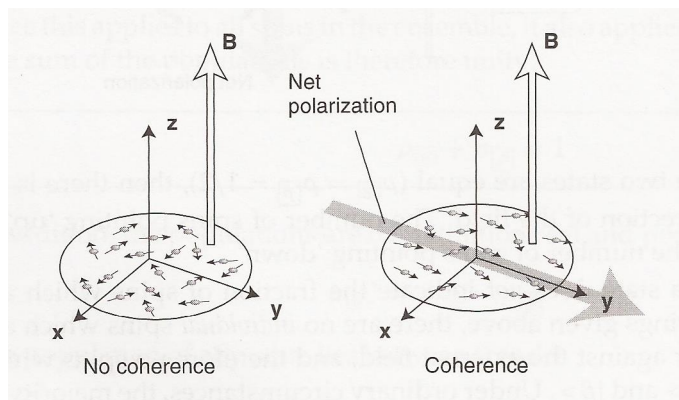
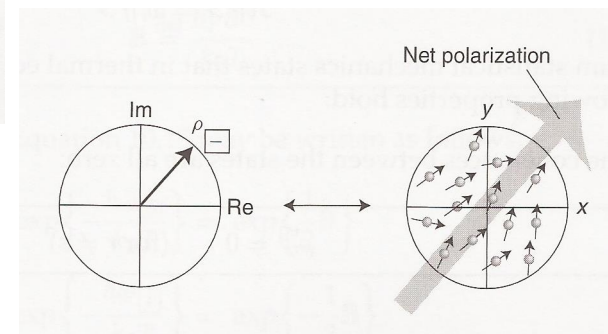
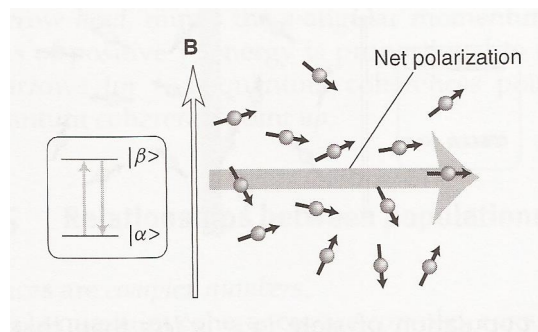
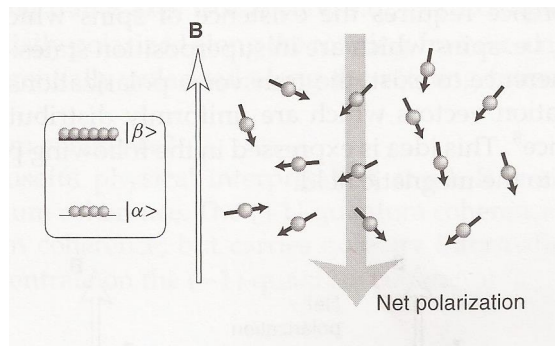
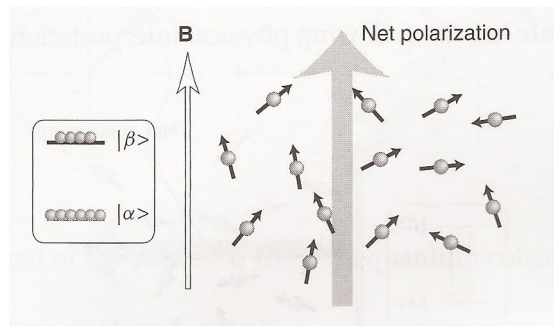
Boltzmanova rovnice

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



# Vektorový model NMR

## Makroskopická magnetizace



# Vektorový model NMR

## Makroskopická magnetizace

Výpočet obsazení spinových hladin

### Boltzmanova rovnice

Energie termálního pohybu  
 $E = k \cdot T = 4,18 \cdot 10^{-21}$

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

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

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

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

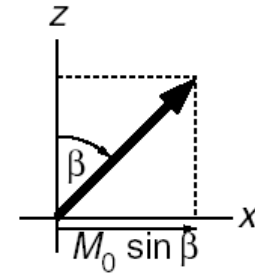
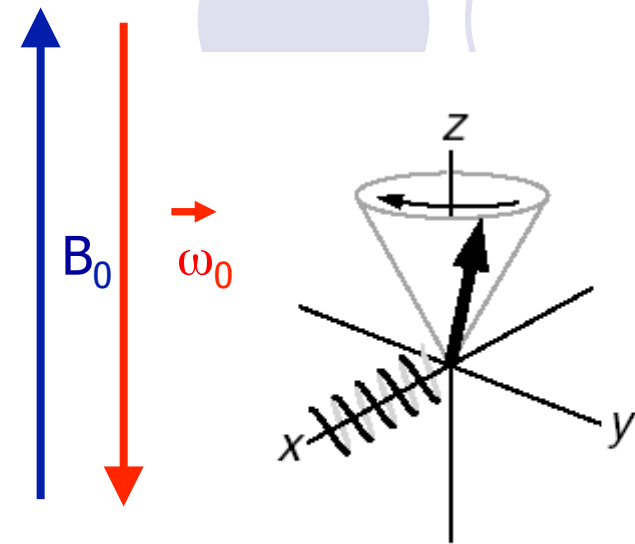
# Vektorový model NMR

Detekce

Pohyb vektoru magnetizace

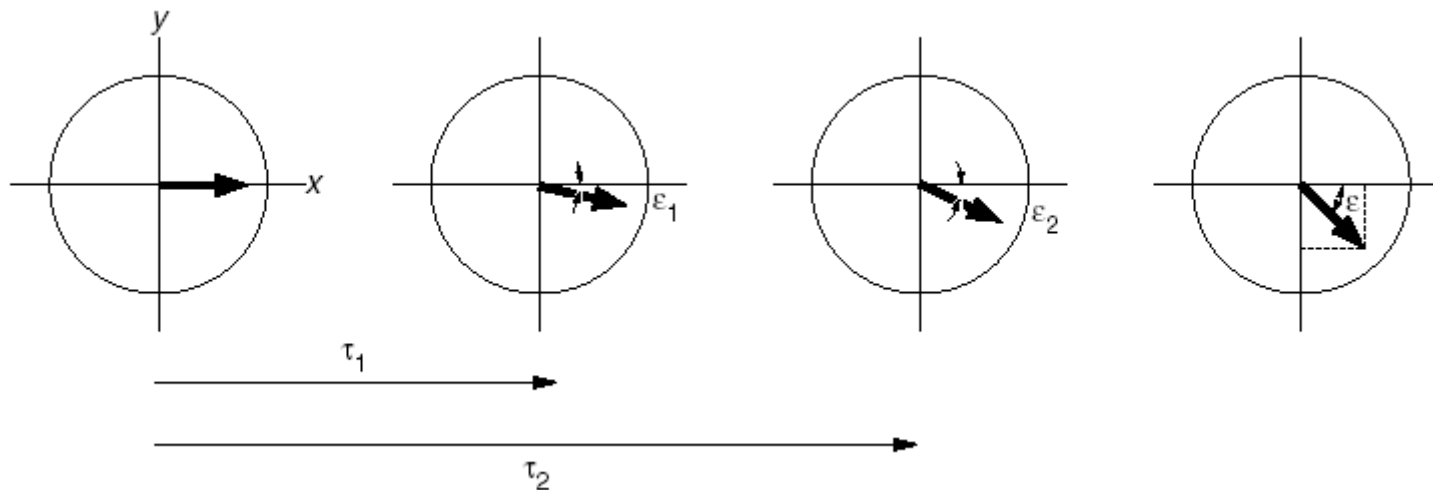
$$\frac{d\vec{\mu}}{dt} = -\gamma \cdot \vec{B}_0 \times \vec{\mu}$$

(klasická pohybová rovnice)



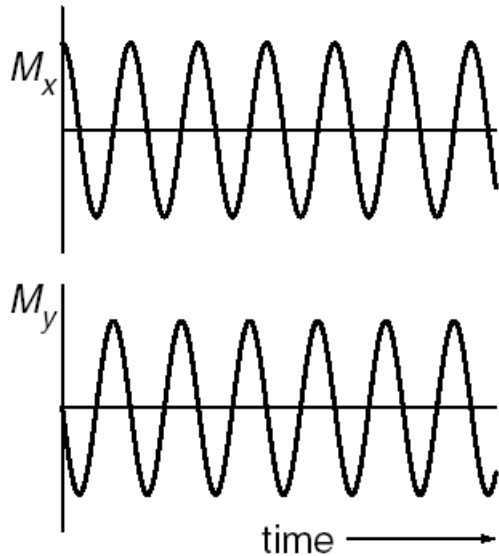
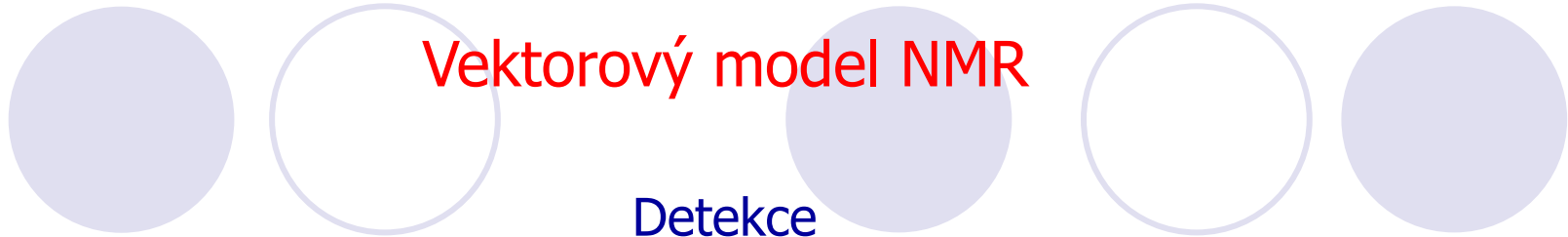
$$\vec{M}(M_x, M_y, M_z) = \sum (\vec{\mu}_i)$$

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



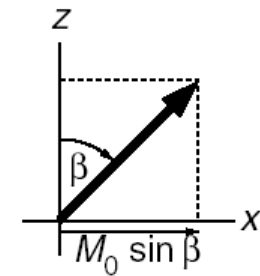
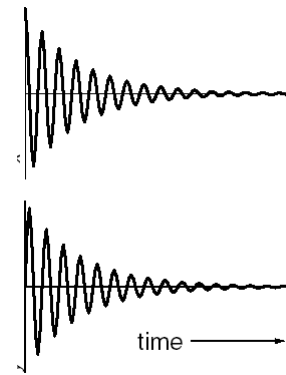
# Vektorový model NMR

Detekce



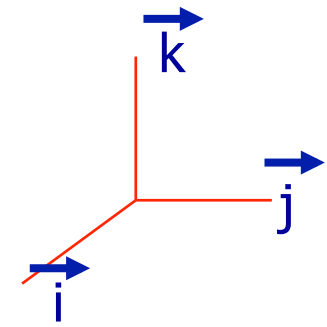
$$M_x = M_0 \sin \beta \cos(\omega_0 t)$$

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



RELAXACE => Blochova rovnice

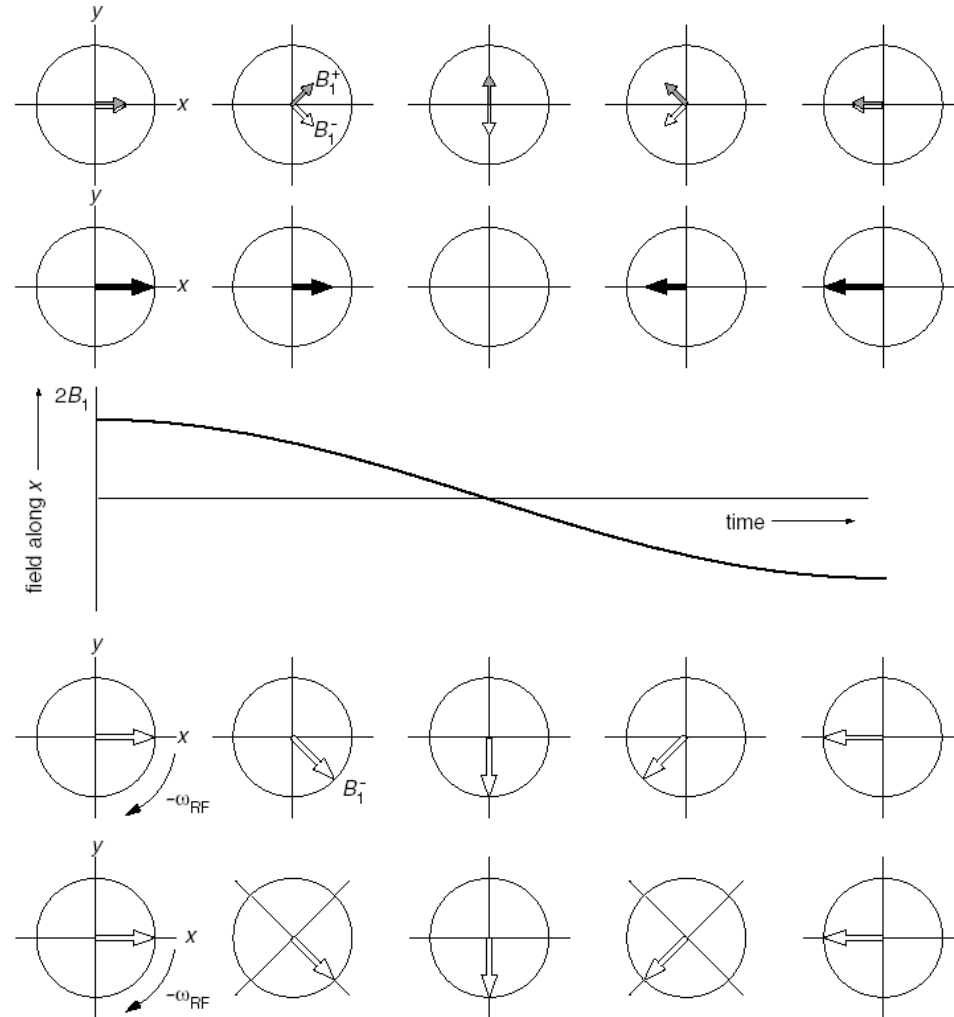
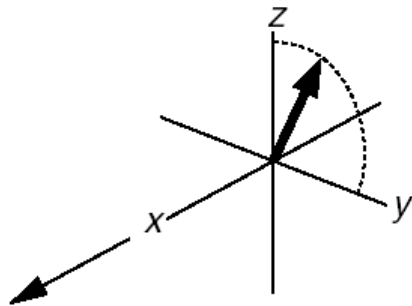
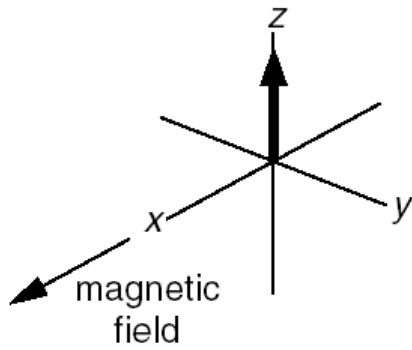
$$\frac{d\vec{M}}{dt} = -\gamma \cdot \vec{B}_0 \times \vec{M} - \frac{M_x}{T_2} \cdot \vec{i} - \frac{M_y}{T_2} \cdot \vec{j} - \frac{(M_z - M_0)}{T_1} \cdot \vec{k}$$



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

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

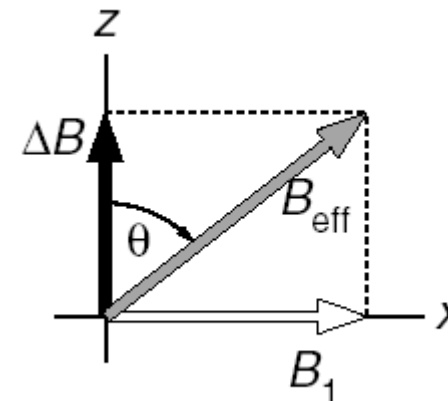
$$\omega_1 = +\gamma B_1$$

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

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

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

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



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

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

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

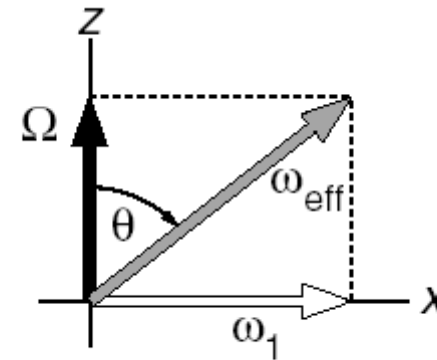
## Vektorový model NMR

Larmorova frekvence v rotující souřadné soustavě – efektivní pole

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

$$\omega_1 = \gamma B_1$$

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

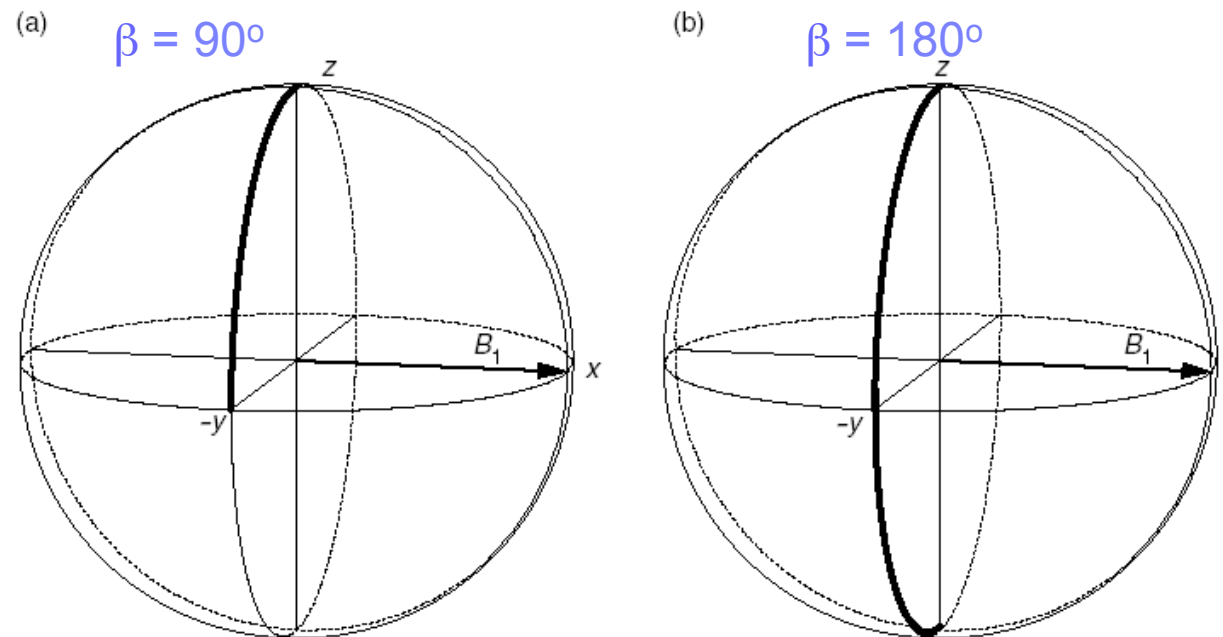


$$\omega_{\text{eff}} = \sqrt{\omega_1^2 + \Omega^2}.$$

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

## Vektorový model NMR

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



$$\beta = \omega_1 t_p$$

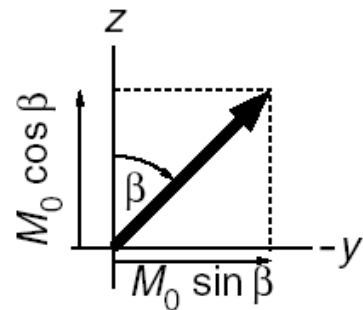
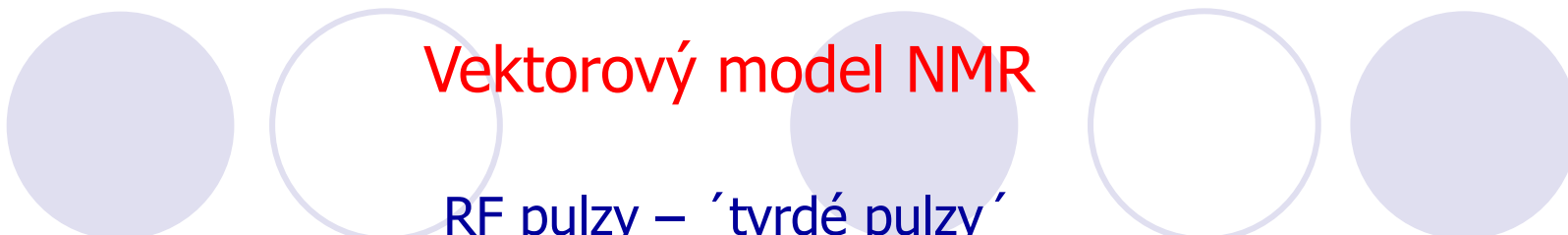
$$\beta = \nu_1 \cdot t_p \cdot 360^\circ$$

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



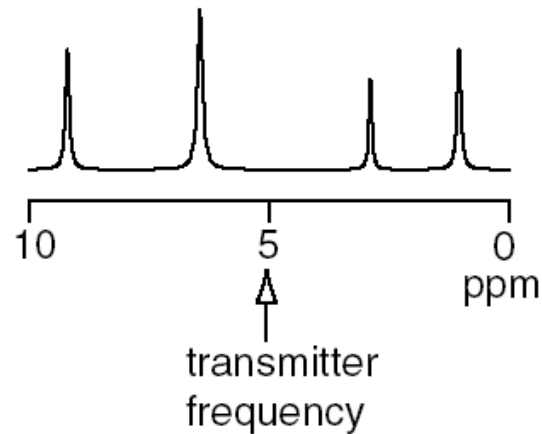
# Vektorový model NMR

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

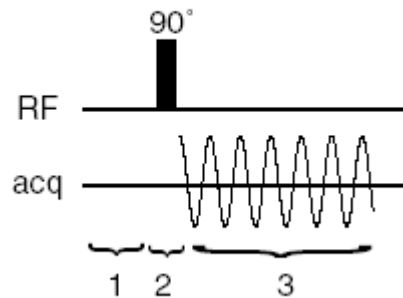


$$\begin{aligned} \omega_1 &= \frac{\pi/2}{12 \times 10^{-6}} \\ &= 1.3 \times 10^5 \text{ rad s}^{-1}. \end{aligned}$$

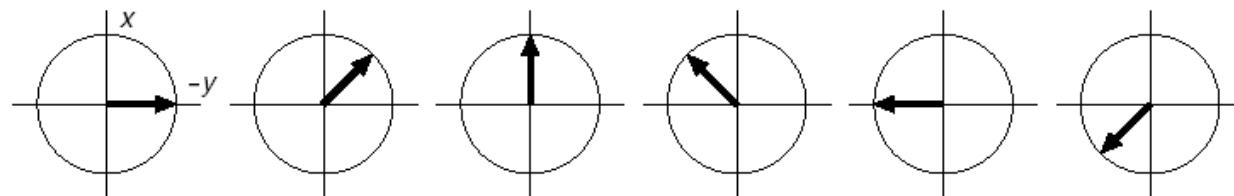
$$\nu_1 = 20\,833,333 \text{ Hz}$$

# Vektorový model NMR

## Detekce v rotující souřadné soustavě

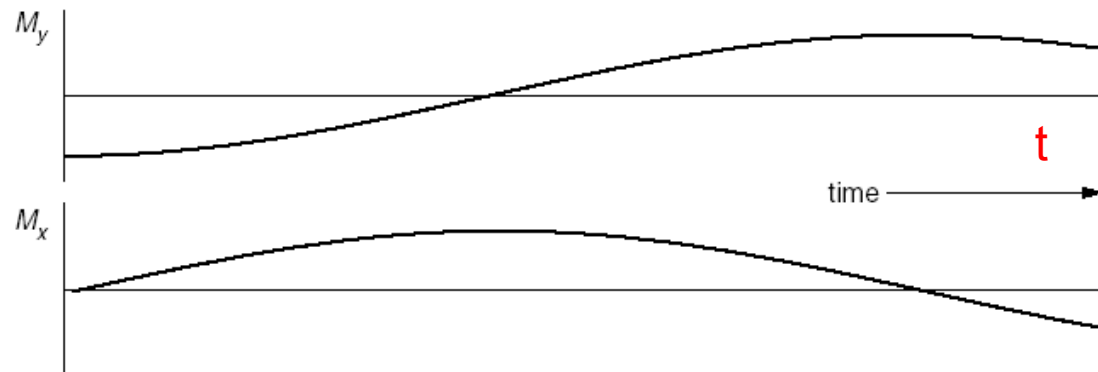


$$\varphi = \Omega t$$



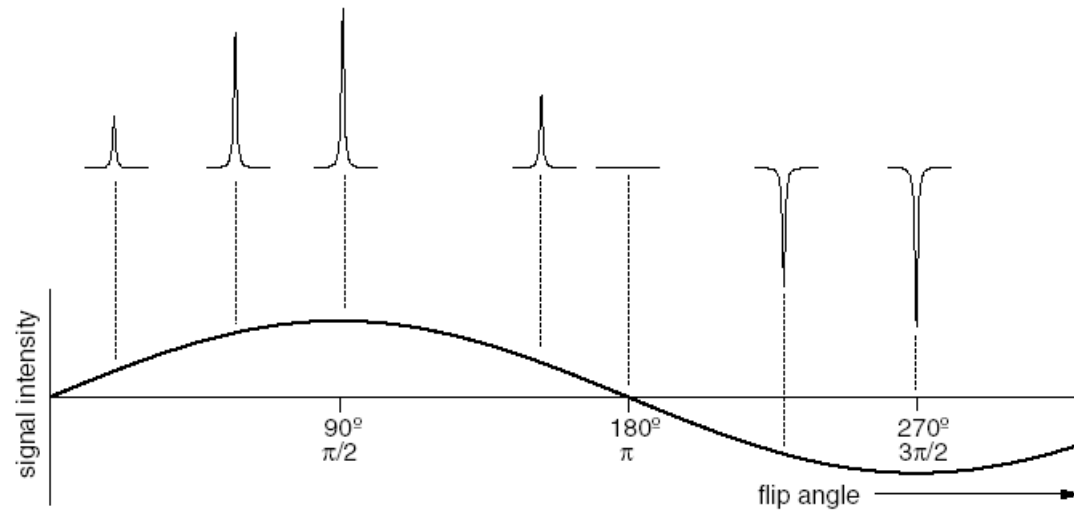
$$M_y = -M_0 \cos(\Omega t)$$

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



# Vektorový model NMR

## Kalibrace rf pulzů



$$\pi = \omega_1 t_{180}$$
$$\omega_1 = \frac{\pi}{t_{180}}$$

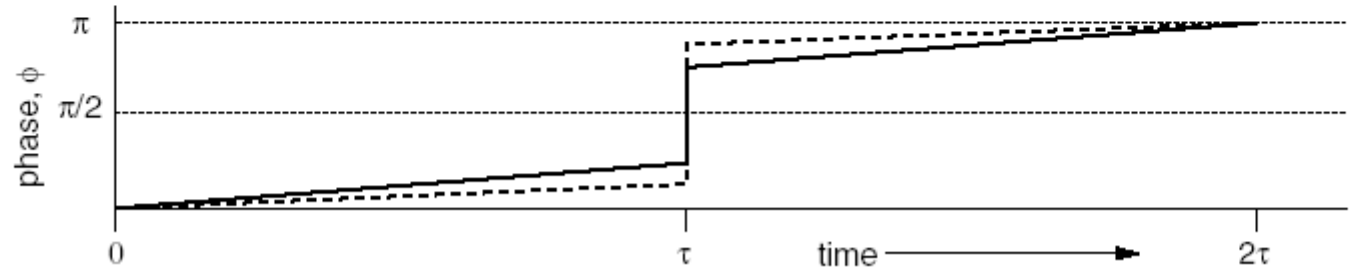
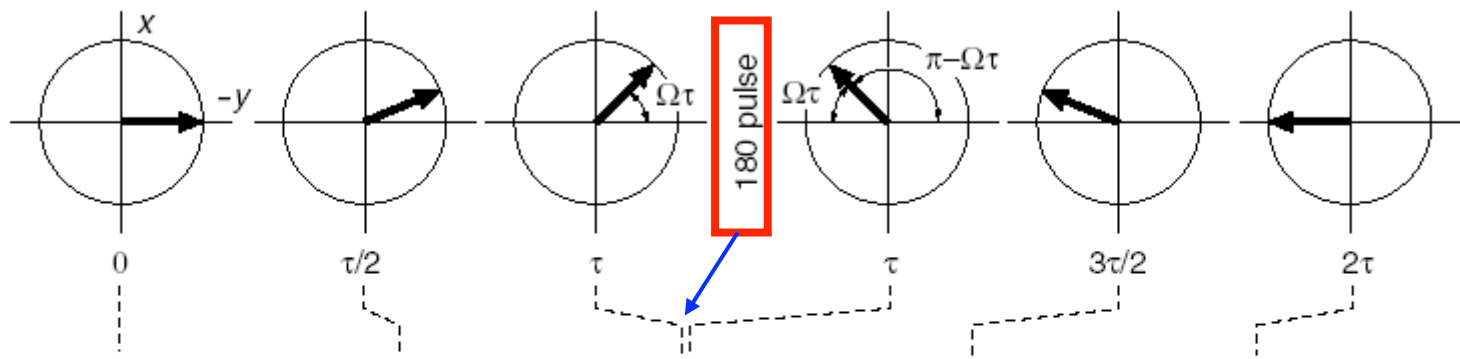
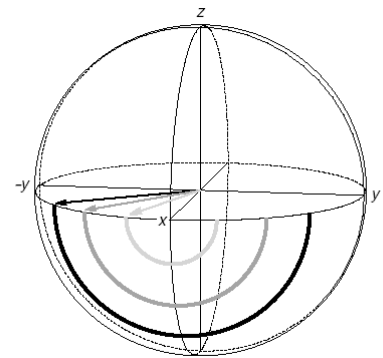
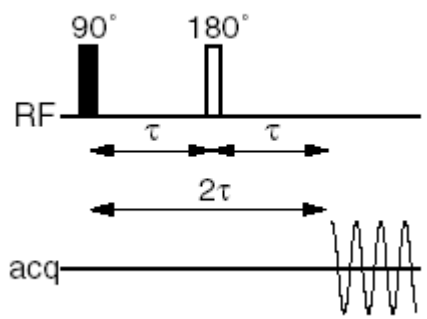
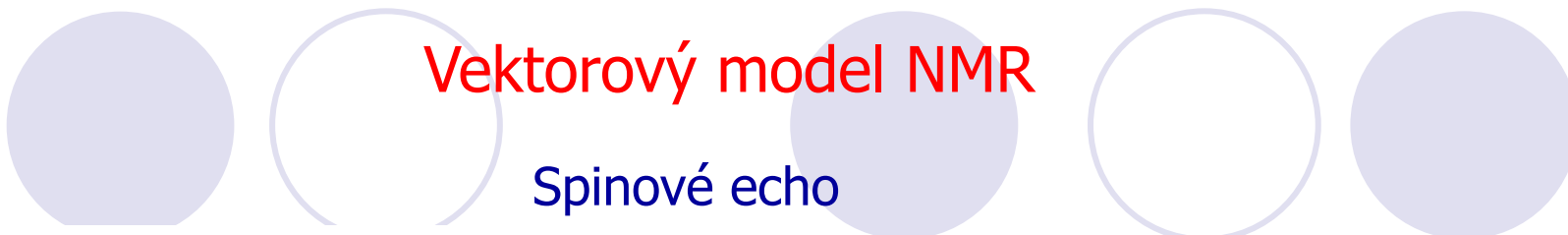
$$(\omega_1/2\pi) = \frac{1}{2t_{180}} \text{ Hz}$$

$$\omega_1 = \frac{\pi}{t_{180}} = \frac{\pi}{15.5 \times 10^{-6}} = 2.03 \times 10^5 \text{ rad s}^{-1}$$

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

# Vektorový model NMR

## Spinové echo

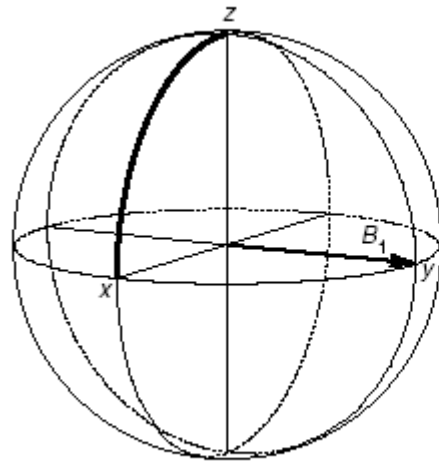


2.10.2014

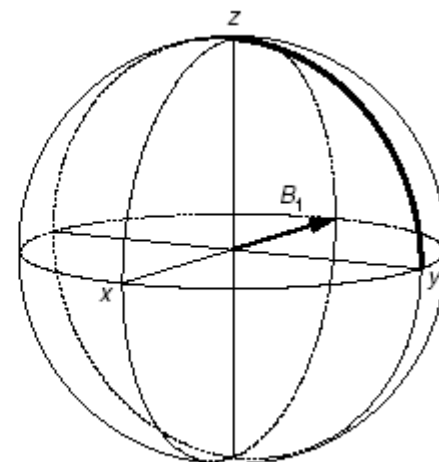
# Vektorový model NMR

## Fáze rf pulzů

(a)

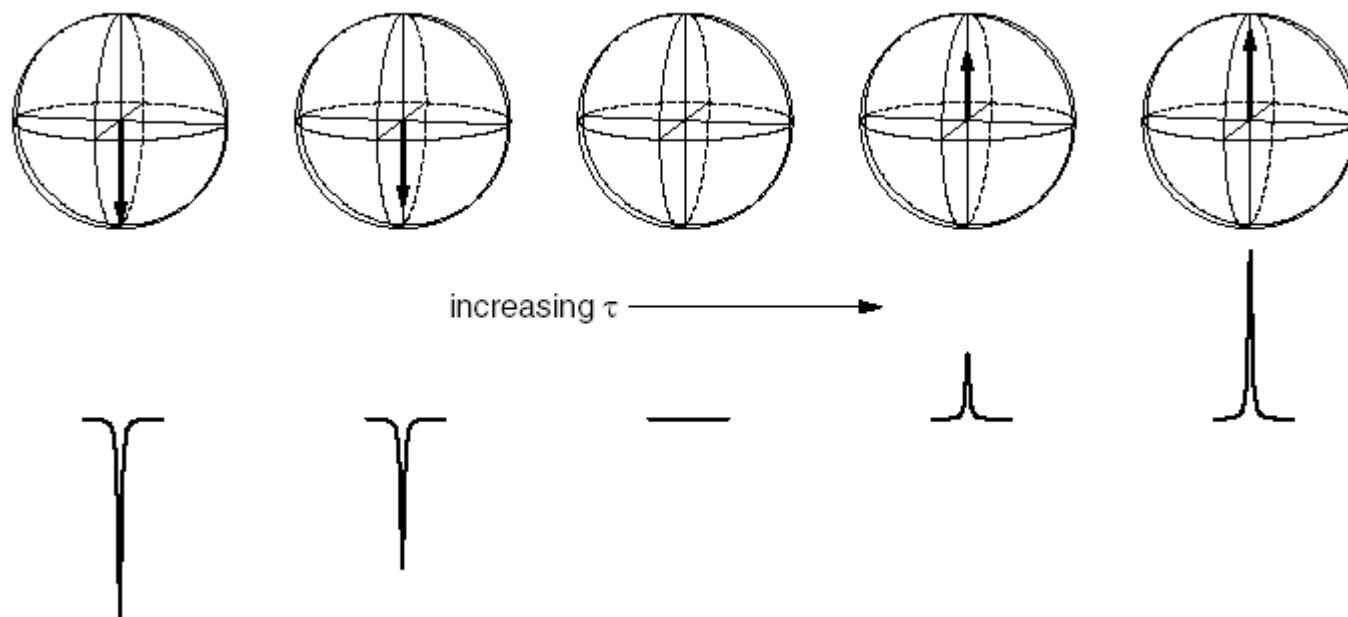
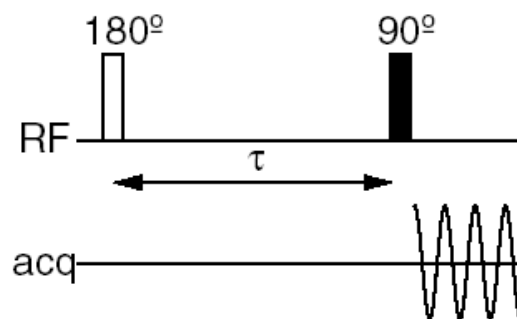


(b)



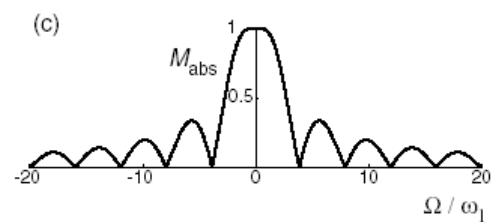
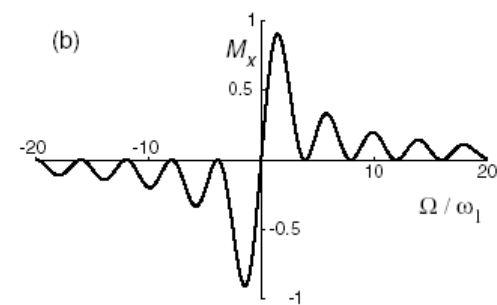
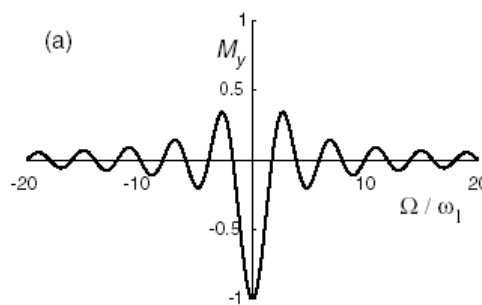
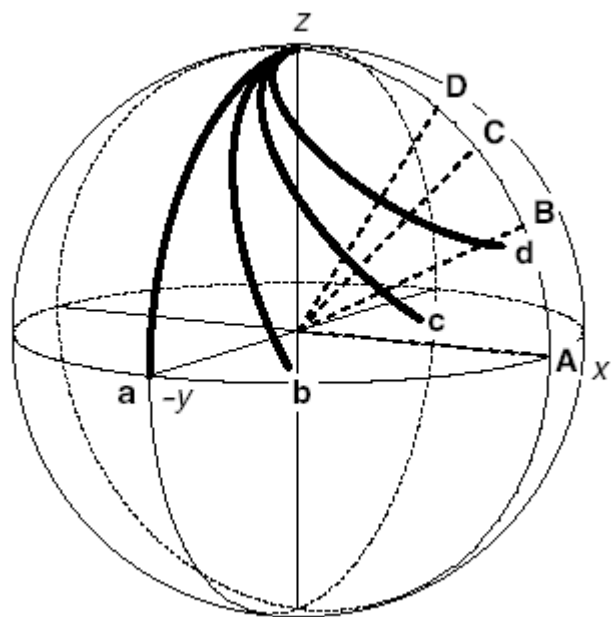
# Vektorový model NMR

## Relaxace



# Vektorový model NMR

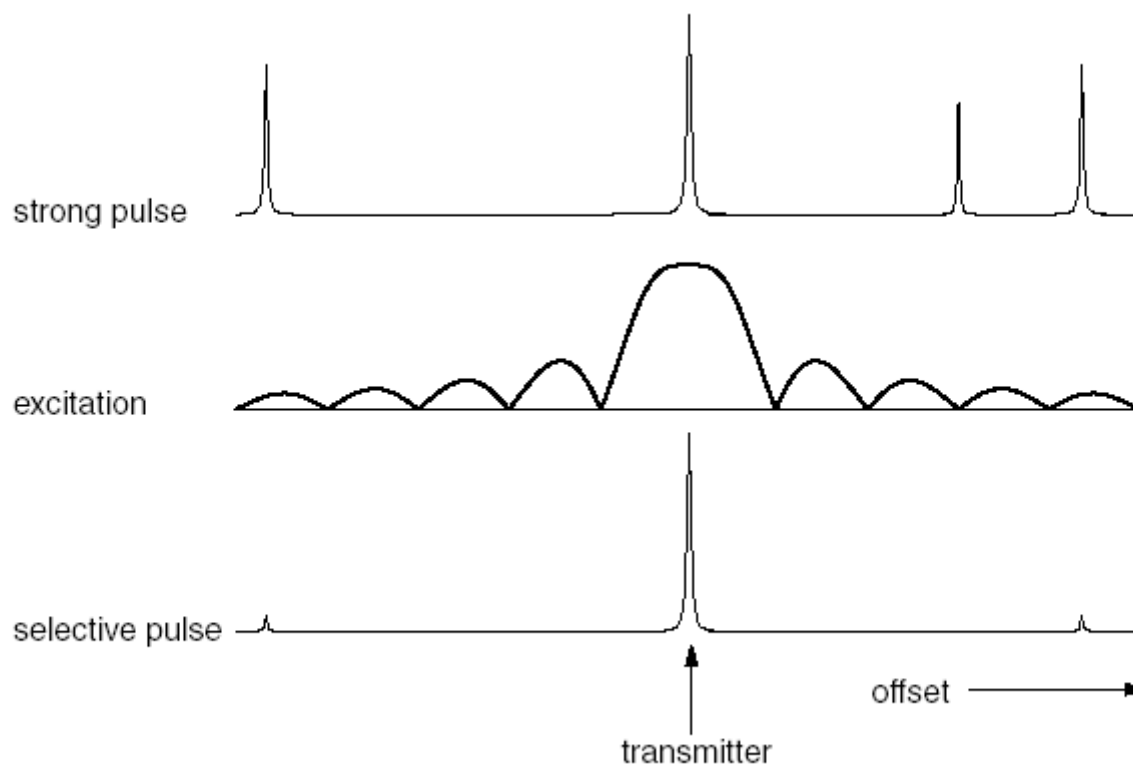
## Off-rezonanční vlivy a slabé pulzy



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

# Vektorový model NMR

Selektivní excitace a slabé pulzy

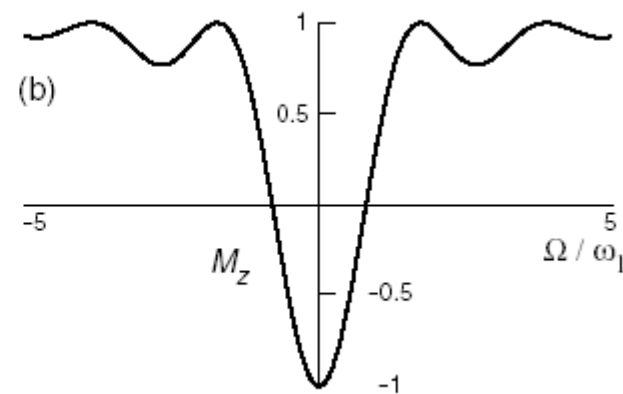
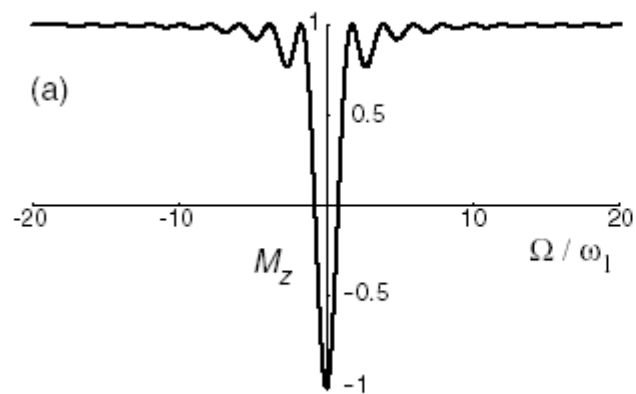


**NMRSim demo**



# Vektorový model NMR

## Selektivní inverze a slabé pulzy



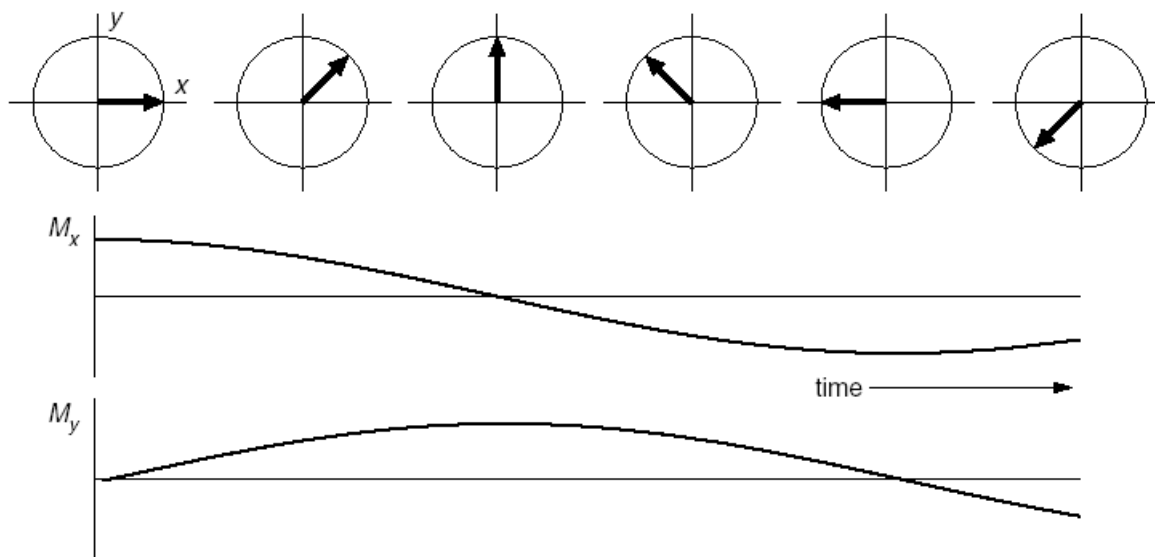
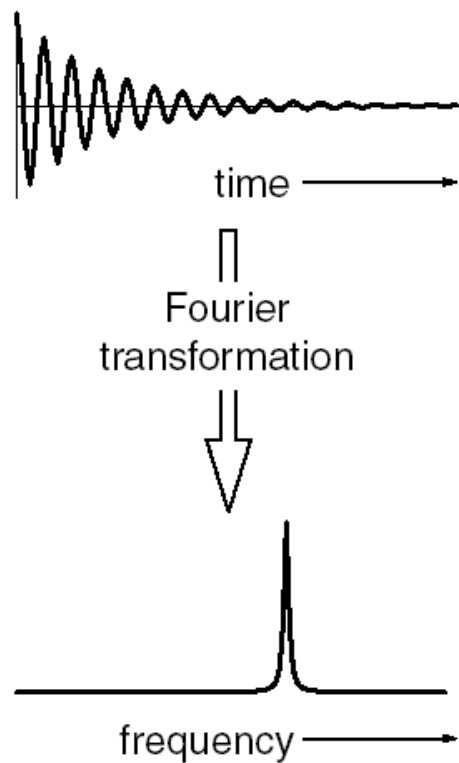


## Vektorový model NMR - shrnutí

- 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  $\Omega$  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.

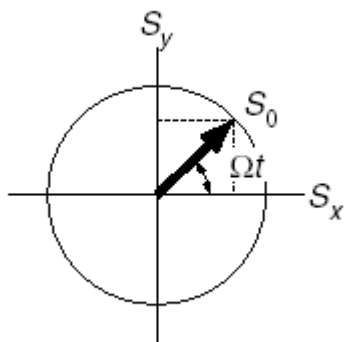
# Fourierova transformace a zpracování dat

FID – free induction decay



# Fourierova transformace a zpracování dat

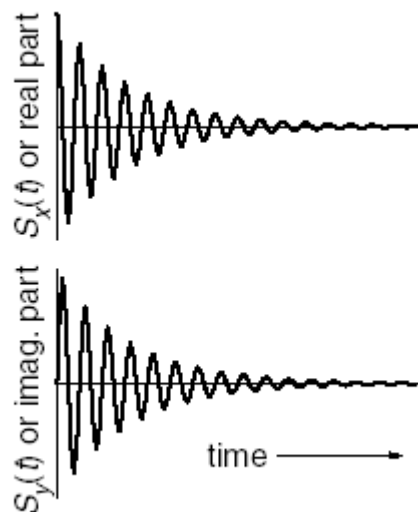
## FID – free induction decay



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

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

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

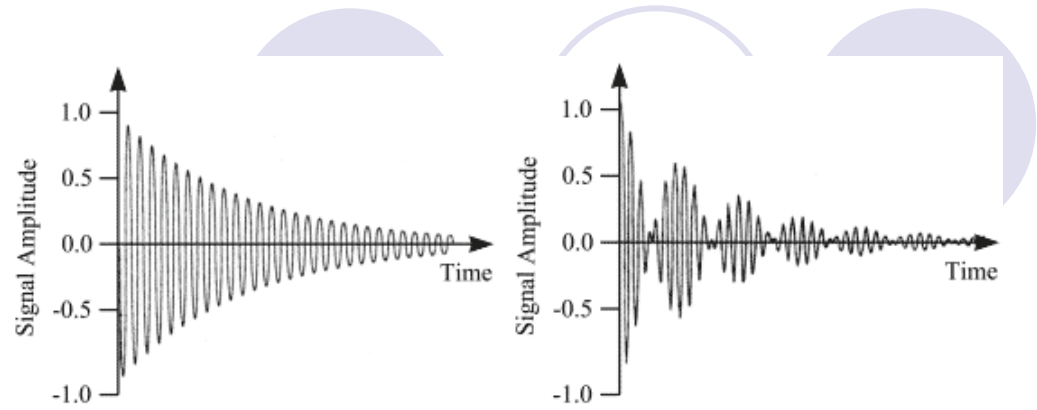


$$\begin{aligned} S(t) &= S_x(t) + i S_y(t) \\ &= S_0 \cos \Omega t + i S_0 \sin \Omega t \\ &= S_0 \exp(i \Omega t). \end{aligned}$$

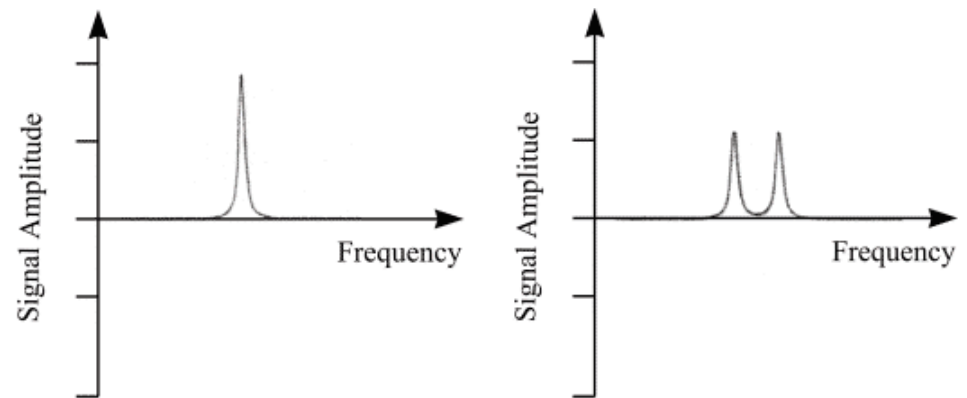
$$S(t) = S_0 \exp(i \Omega t) \exp\left(\frac{-t}{T_2}\right).$$



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 as a scientific advisor, 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

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

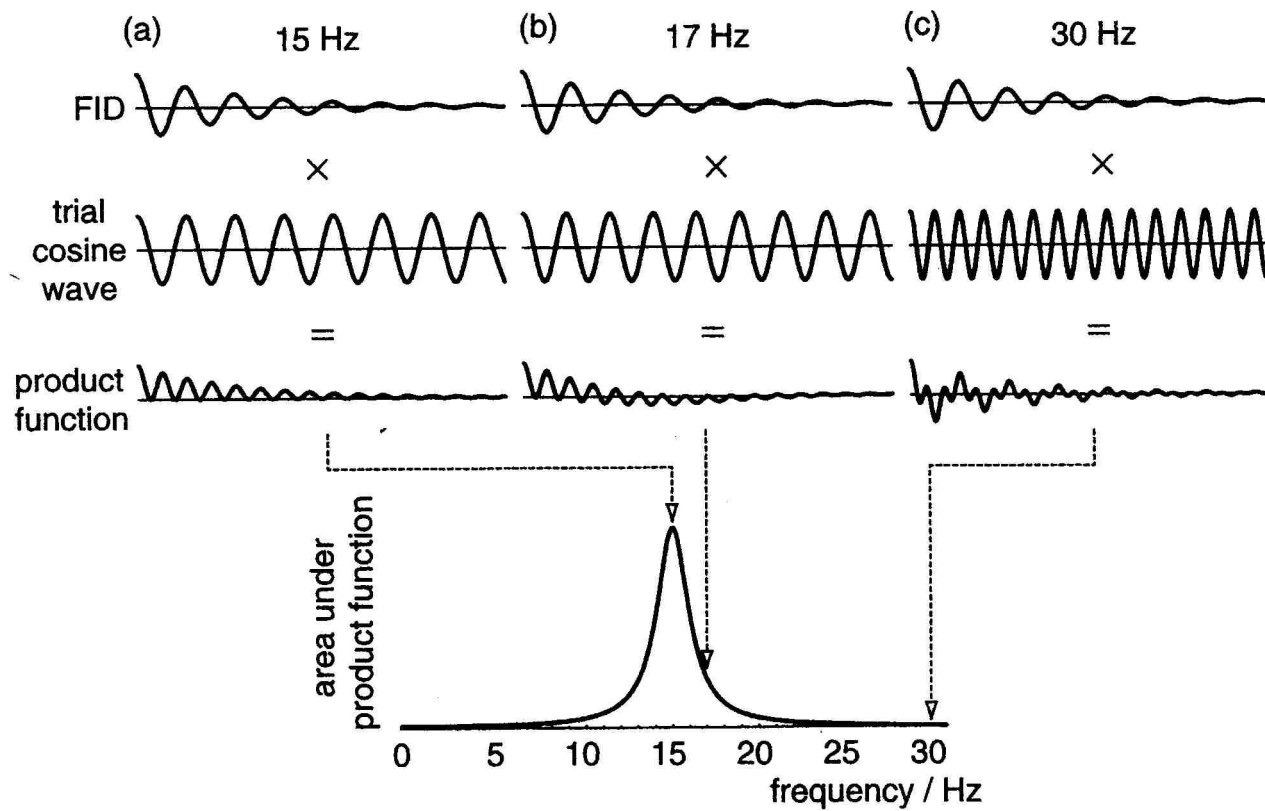
$$\text{iFT} \quad S(t) = \int_{-\infty}^{+\infty} S(\nu) \cdot \exp(+i \cdot 2\pi \cdot \nu \cdot t) d\nu$$

## Diskrétní Fourierova transformace – algoritmus Cooley a Tukey, 1966

Cooley-Tukey algoritmus je nejpoužívanější variantou FFT algoritmu.

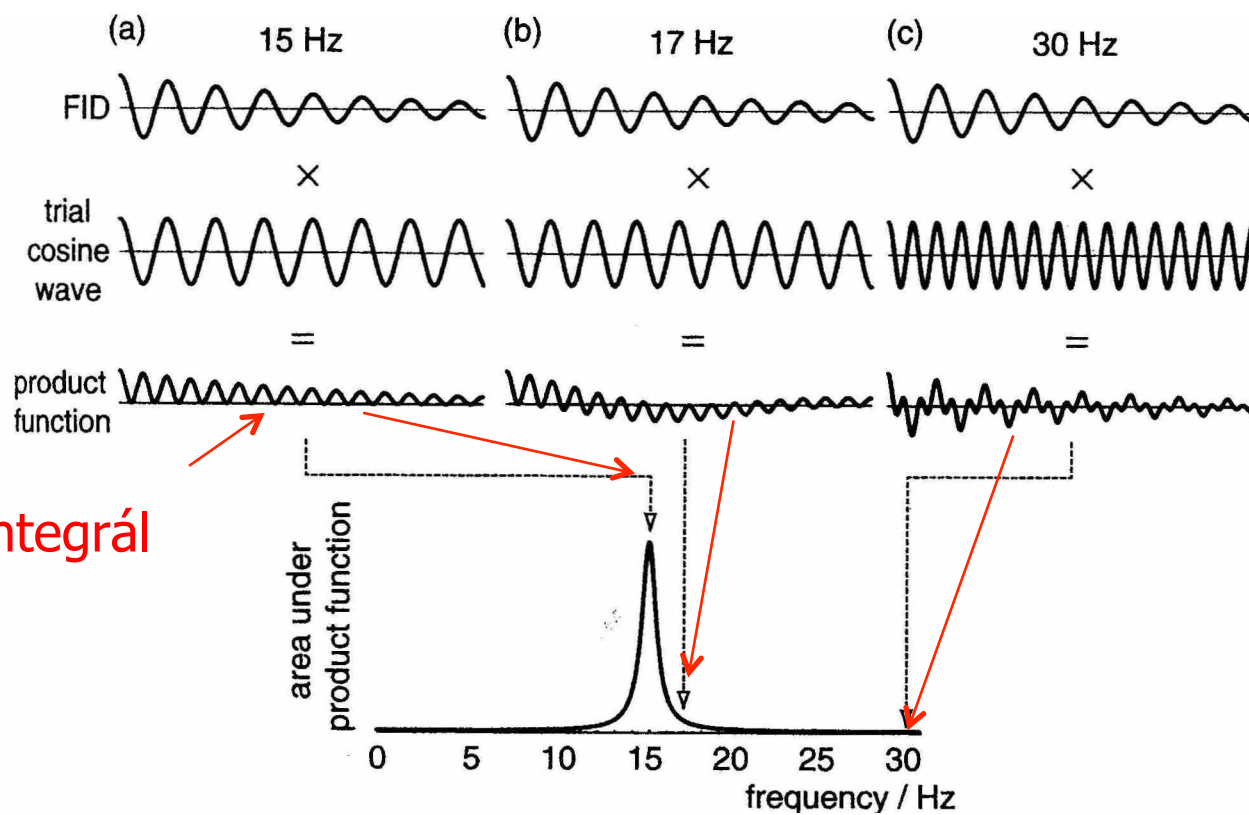
Tato metoda (a obecně myšlenka FFT) byla popularizována v práci [J. W. Cooleye](#) a [J. W. Tukeye](#) z roku [1965](#), nicméně později se přišlo na to, že tito autoři pouze znovuobjevili algoritmus známý již [Gaussovi](#) kolem roku [1805](#) (který byl poté v omezené podobě několikrát znovu objeven).

# Fourierova transformace a zpracování dat

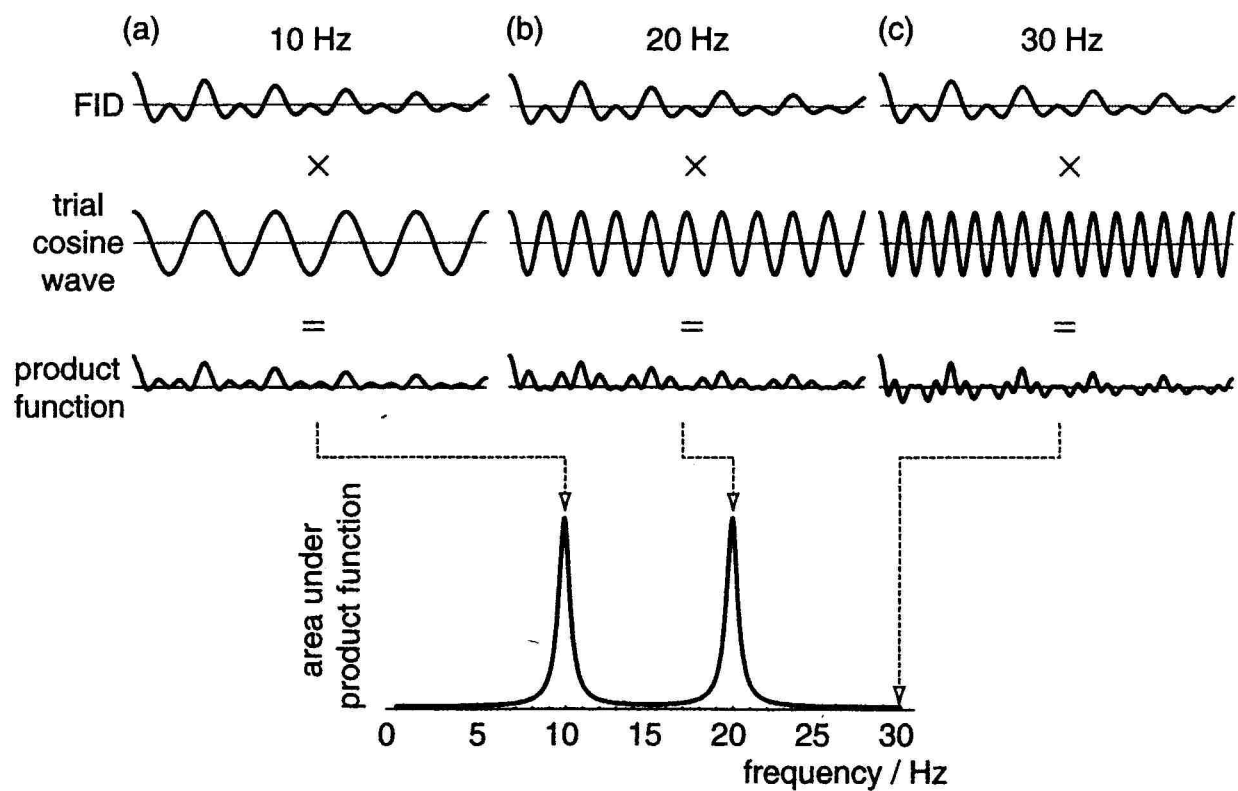




# Fourierova transformace a zpracování dat



# Fourierova transformace a zpracování dat





# Fourierova transformace a zpracování dat

Fourierova řada

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

Koeficienty Fourierovy řady

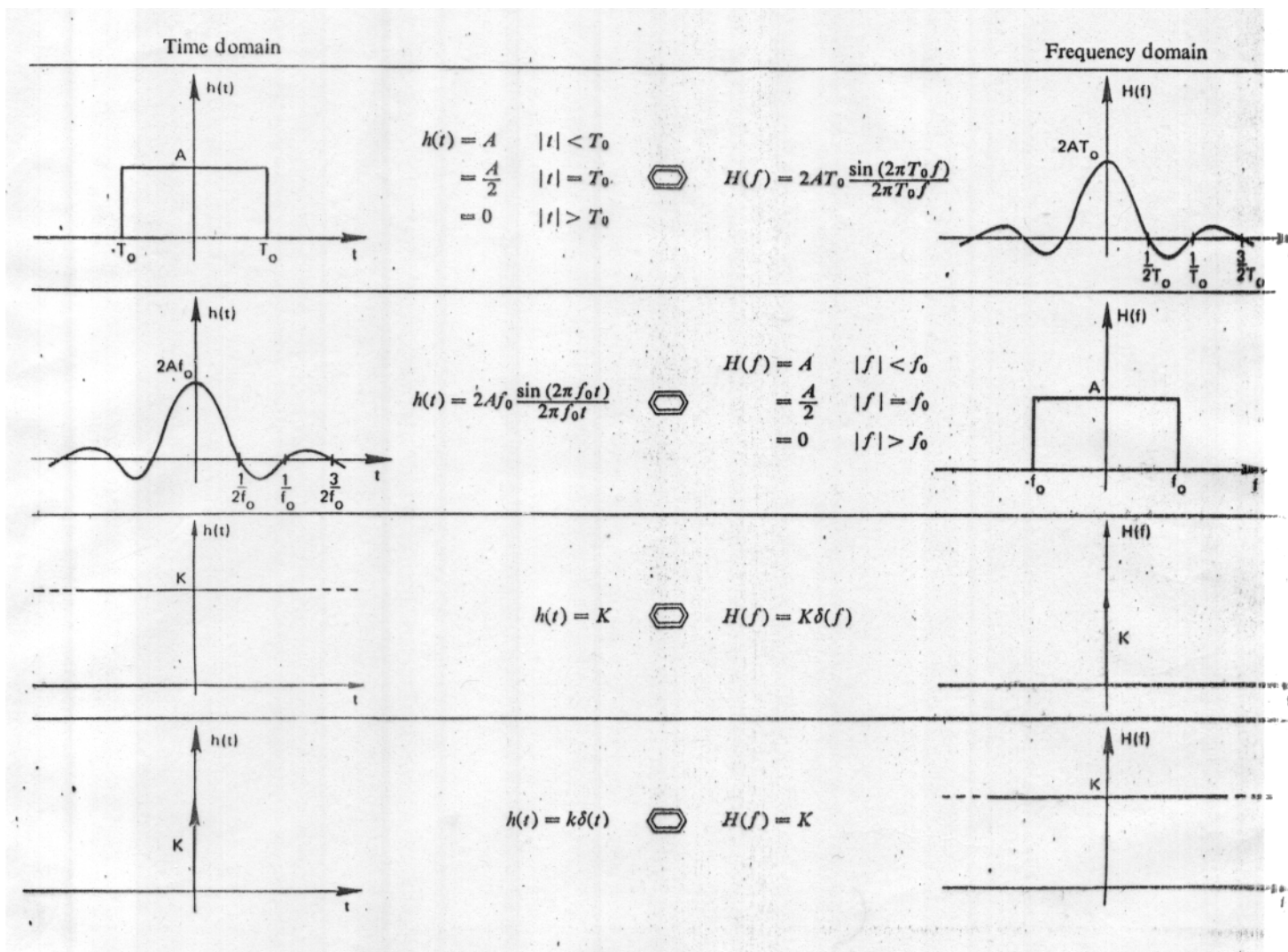
$$C_n = 1/T \int f(x) e^{-in\omega x} dx$$

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

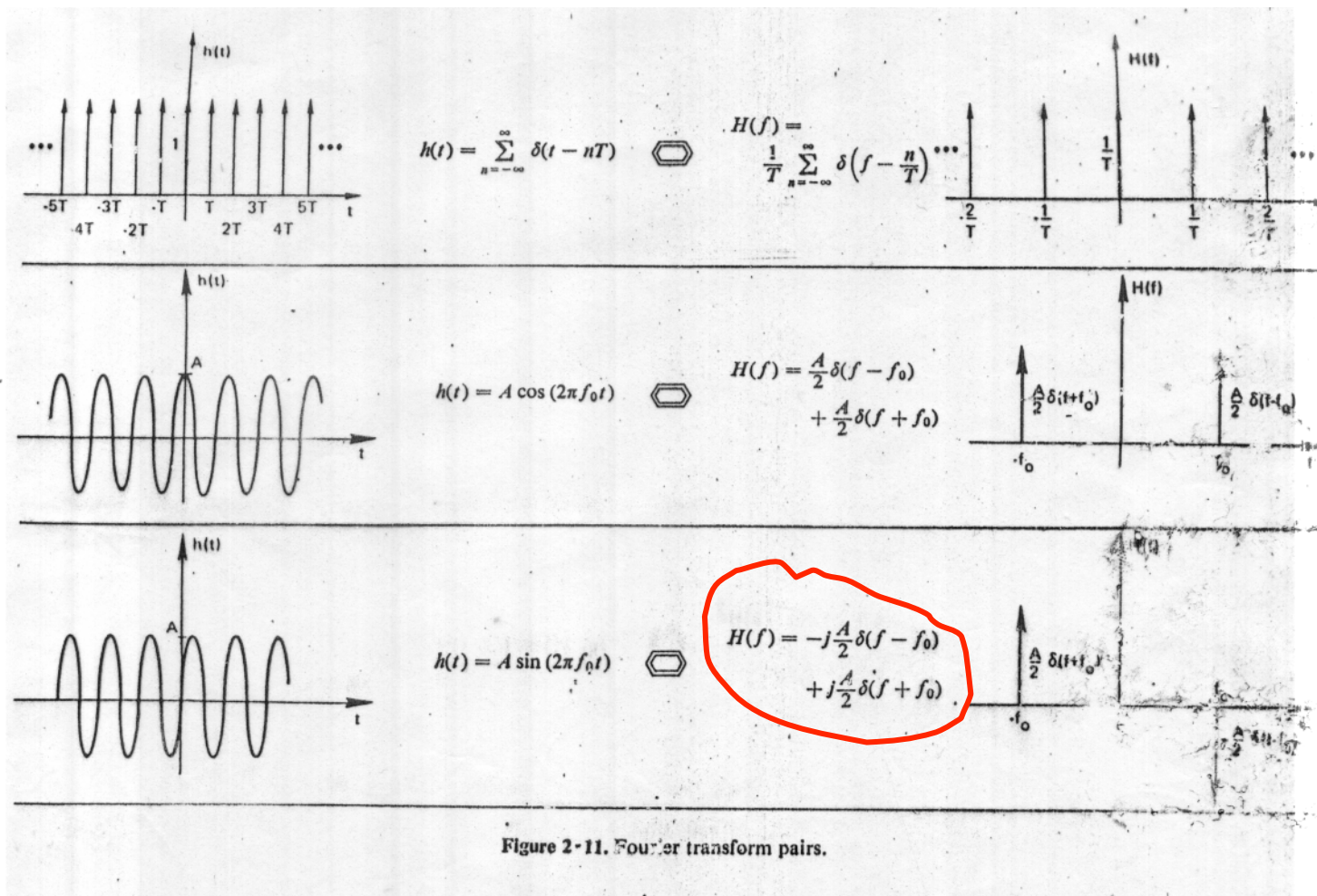
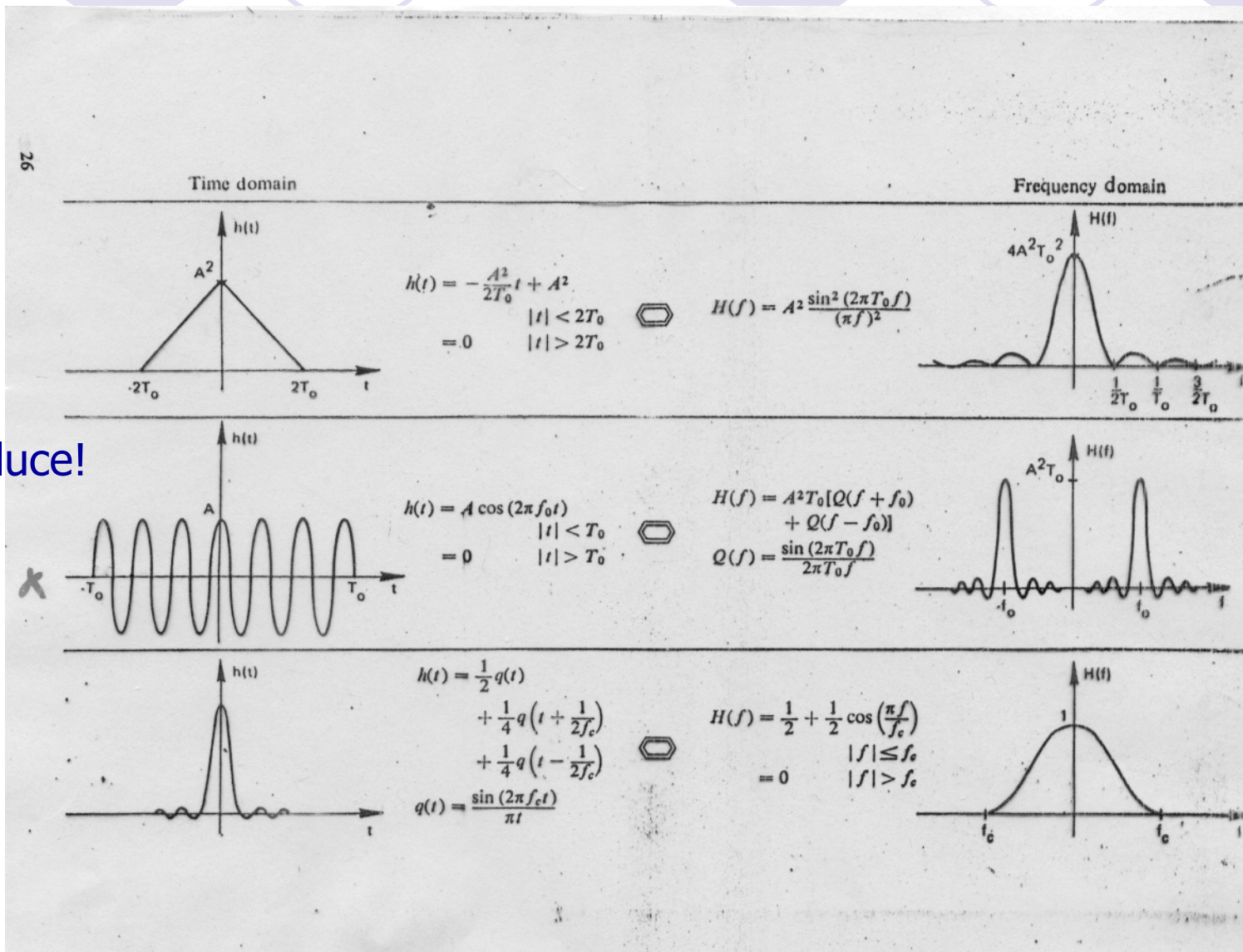


Figure 2-11. Fourier transform pairs.



# Fourierova transformace a zpracování dat

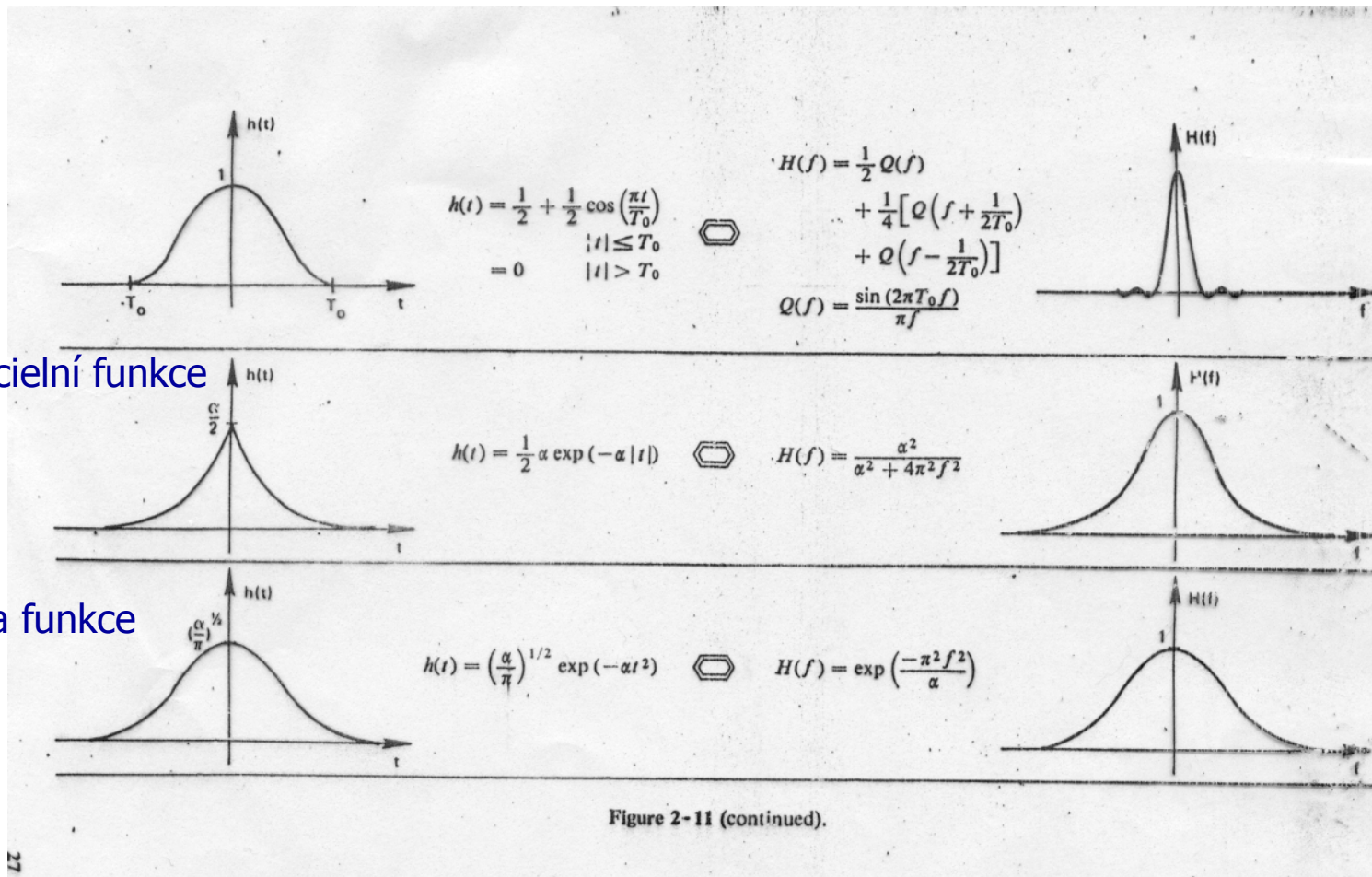
## Fourierova transformace – základní vlastnosti



Konvoluce!

# Fourierova transformace a zpracování dat

## Fourierova transformace – základní vlastnosti



# 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 – základní vlastnosti

$$\text{FT}(f(t).g(t)) = \int_{-\infty}^{+\infty} F(\nu).G(\mu - \nu).d\nu$$

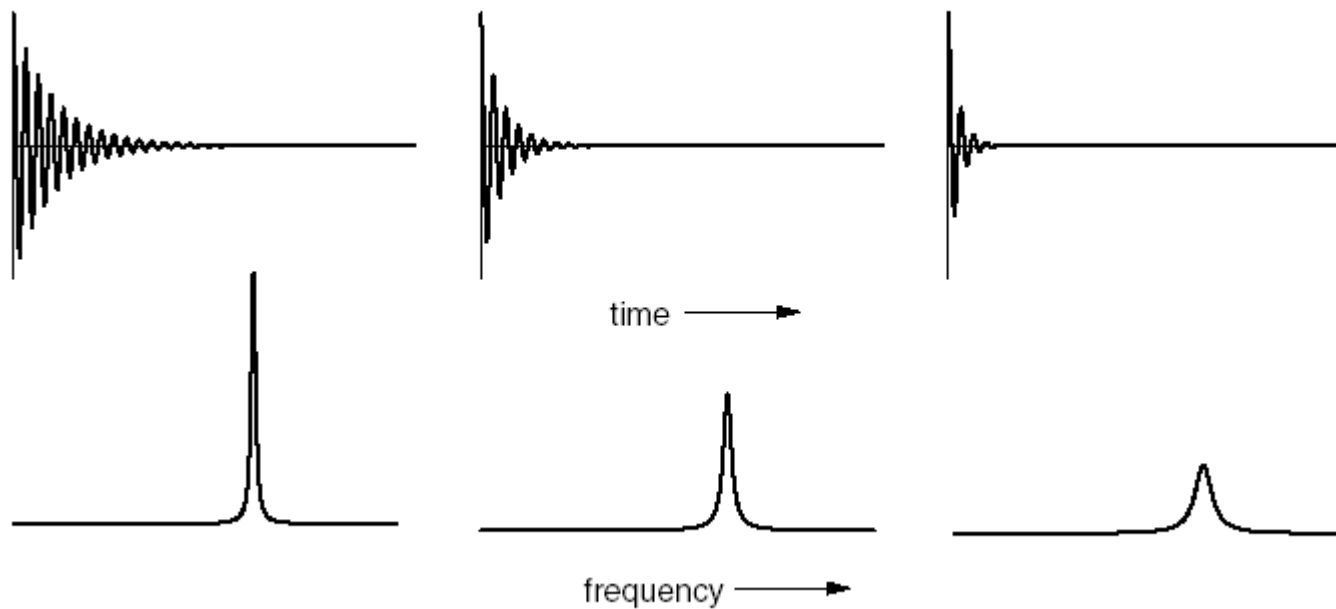
$$F(\nu) = \text{FT}(f(t))$$

$$G(\nu) = \text{FT}(g(t))$$

příklady

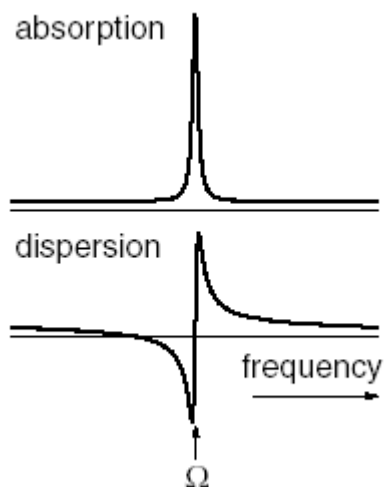
# Fourierova transformace a zpracování dat

## 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

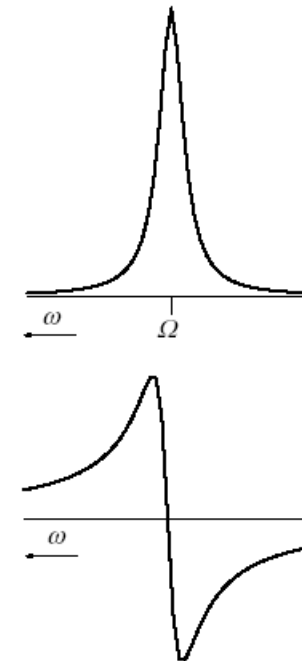
$$S_x(t) = \gamma \cos \Omega t \exp(-t/T_2) \quad S_y(t) = \gamma \sin \Omega t \exp(-t/T_2)$$

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

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

$\gamma$  – amplituda signálu

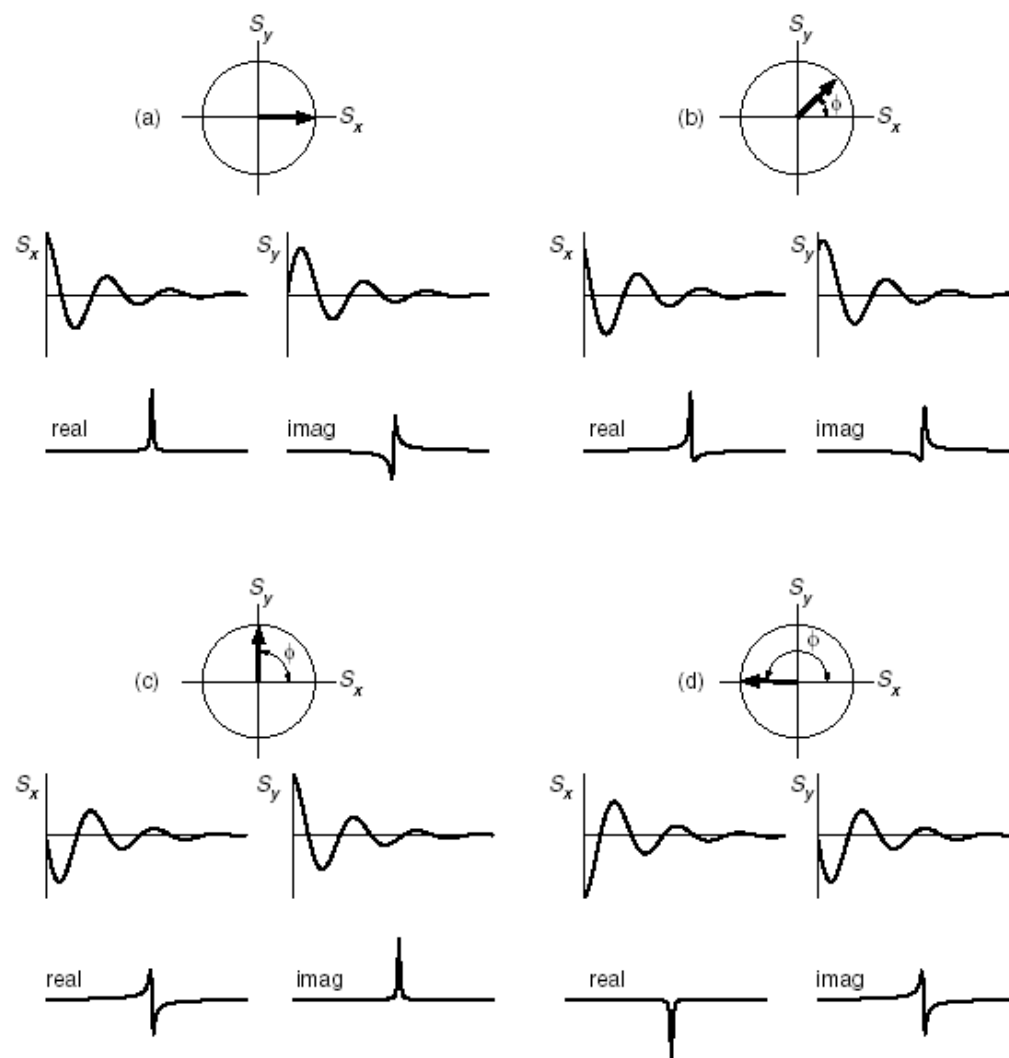
$$A(\omega) = \frac{1}{(\omega - \Omega)^2 T_2^2 + 1} \quad D(\omega) = \frac{(\omega - \Omega)T_2}{(\omega - \Omega)^2 T_2^2 + 1}$$



Lorentzův tvar spektrálních čar

# Fourierova transformace a zpracování dat

## Fáze spektra



# Fourierova transformace a zpracování dat

Fáze spektra

$$S(t) = S_o \exp(i\Omega t) \exp\left(-\frac{t}{T_2}\right) \cdot \exp(i\varphi)$$

↓ FT

$$S_o [A(\omega) + iD(\omega)] \cdot \exp(i\varphi) =$$

$$S_o [A(\omega) + iD(\omega)] \cdot [\cos\varphi + i \cdot \sin\varphi] =$$

$$S_o [\cos\varphi \cdot A - \sin\varphi \cdot D(\omega)] + i S_o [\sin\varphi \cdot A(\omega) + \cos\varphi \cdot D(\omega)]$$

real

imaginary

# 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  $\exp(i(\phi + \phi_{\text{corr}})) = 1$

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

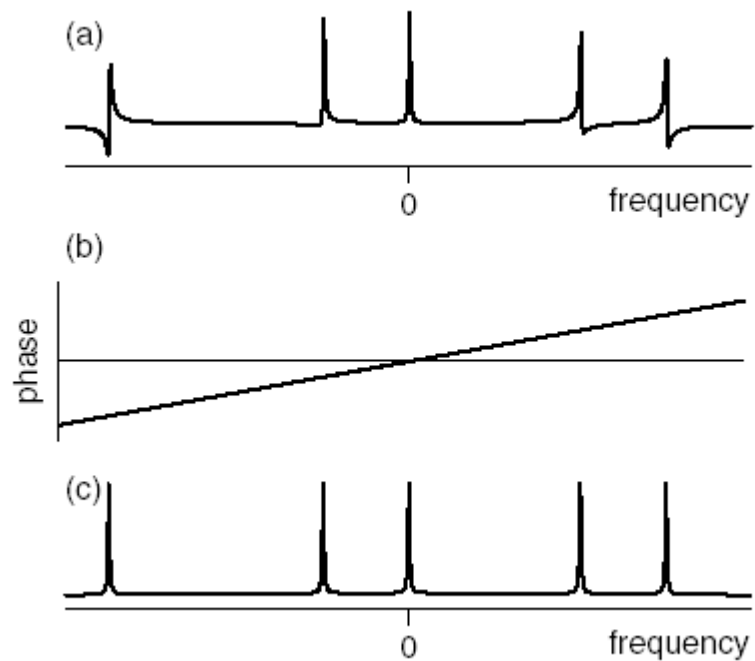
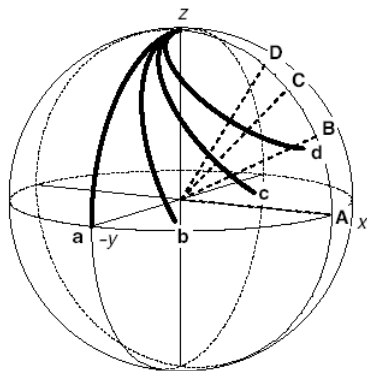
Analogicky, korekce platí i ve frekvenční doméně

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



# Fourierova transformace a zpracování dat

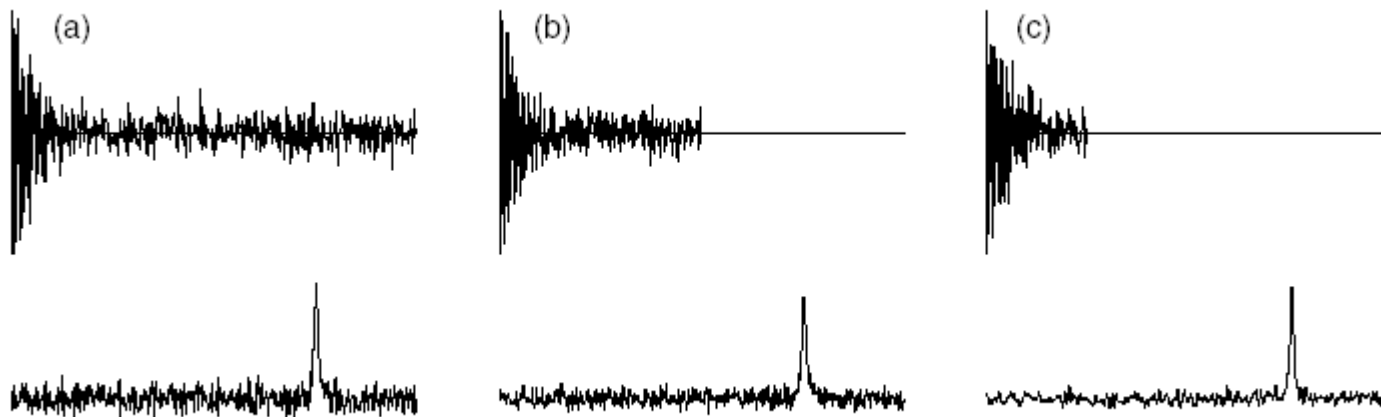
## Fáze spektra – frekvenčně závislá chyba



fázová chyba lineárně závislá na ofsetu

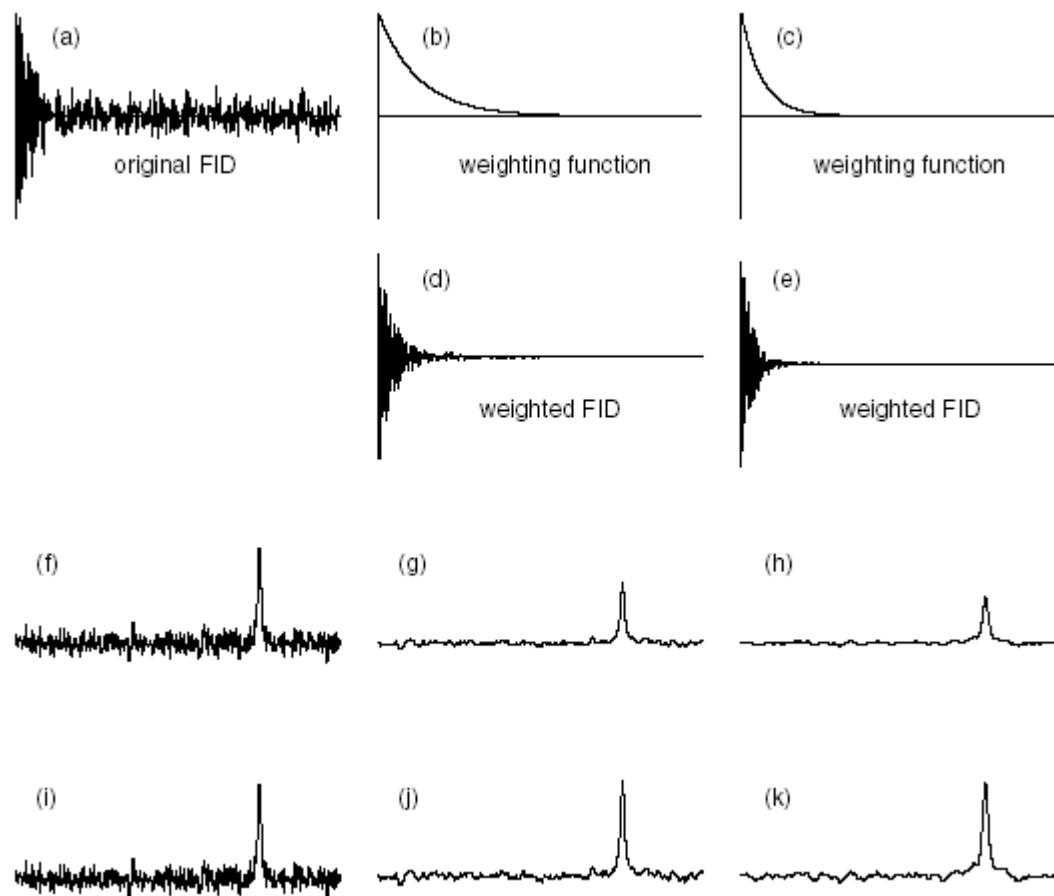
# Fourierova transformace a zpracování dat

Zvýšení citlivosti



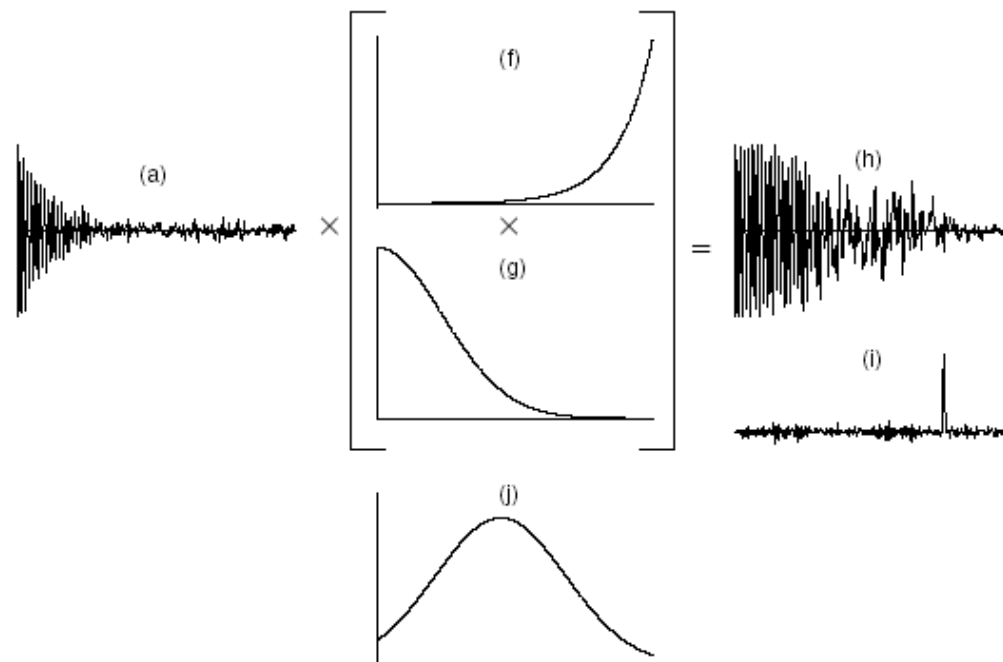
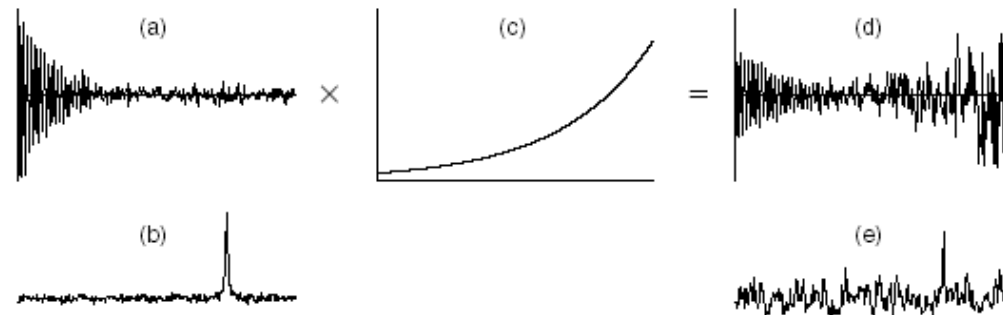
# Fourierova transformace a zpracování dat

## Zvýšení citlivosti



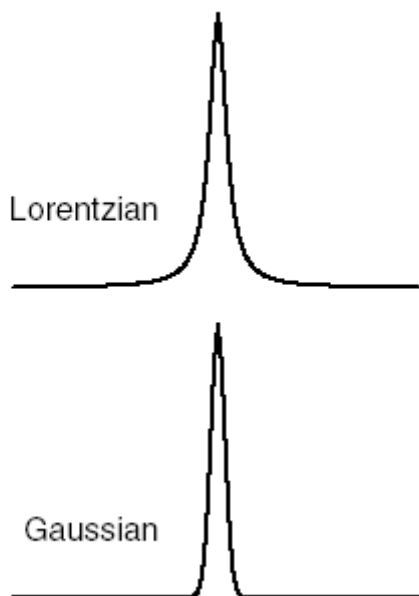
# Fourierova transformace a zpracování dat

## Zvýšení rozlišení



# Fourierova transformace a zpracování dat

## Zvýšení rozlišení



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

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

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

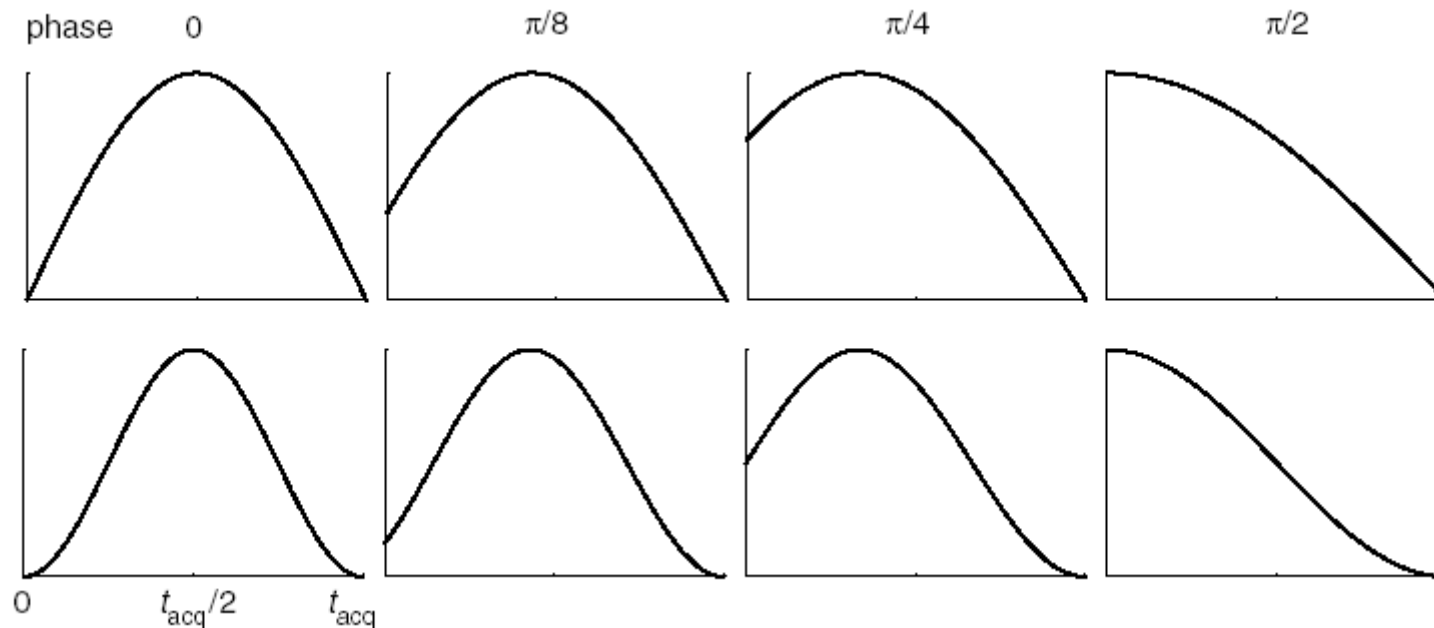
$$W(t) = \exp(-\alpha t^2),$$

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

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

# Fourierova transformace a zpracování dat

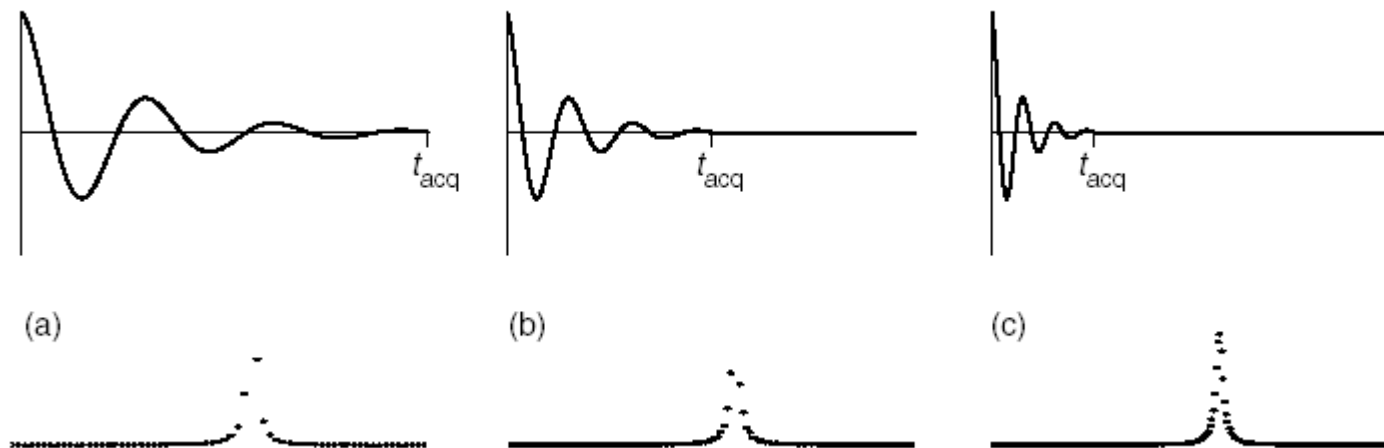
## Zvýšení rozlišení



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

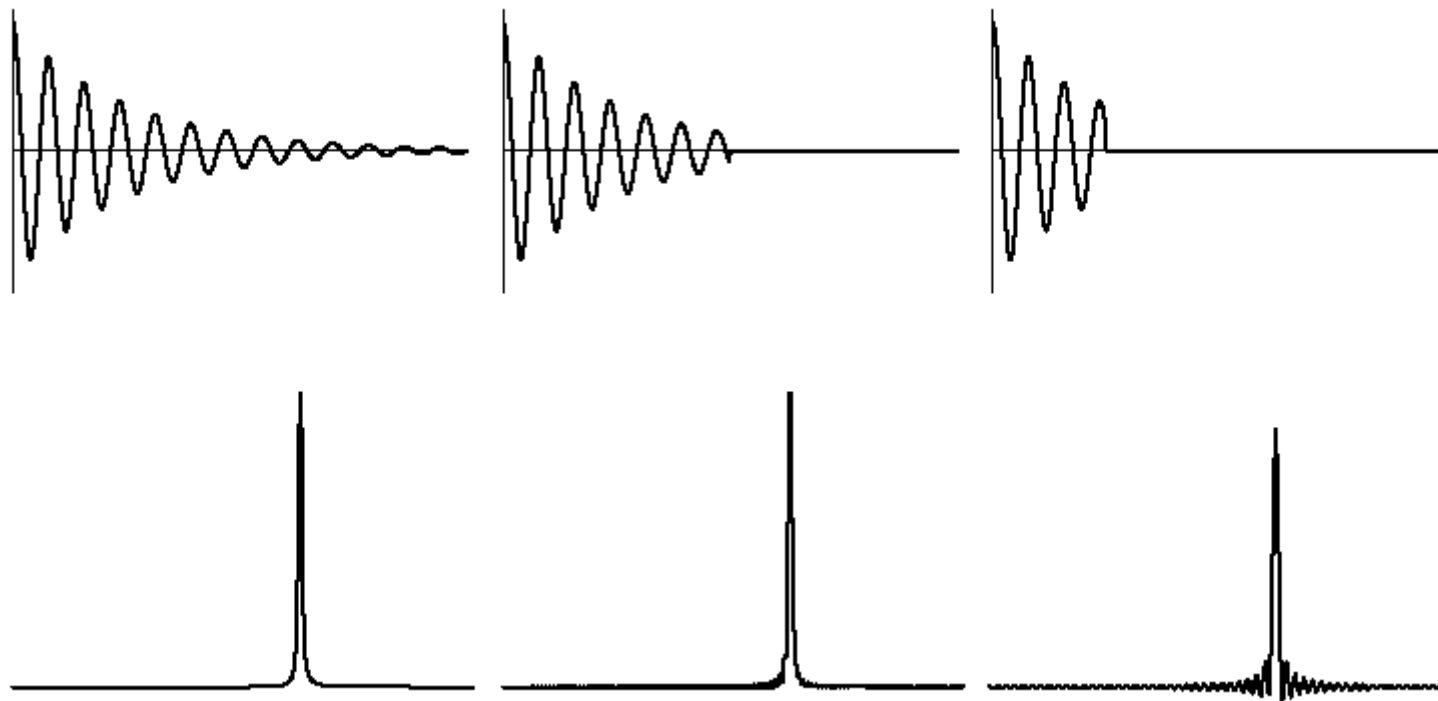
# Fourierova transformace a zpracování dat

## 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

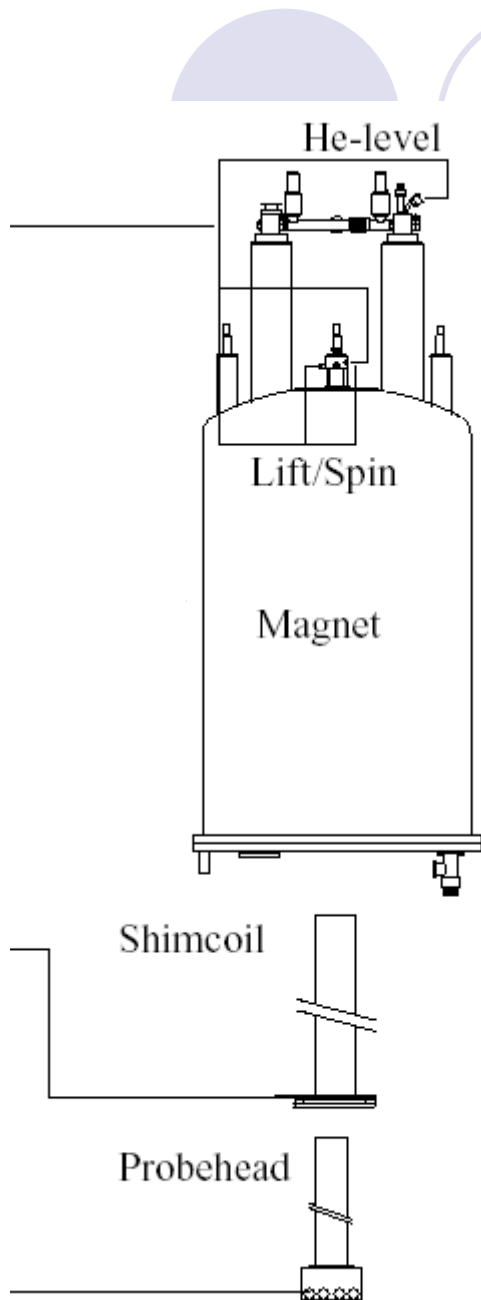
## Magnet



| Properties   | Nitrogen                     | Helium   |
|--|------------------------------|----------|
| Molecular weight   | 28                           | 4        |
| Normal boiling point   | [°C]<br>-196                 | -269     |
|  | [°K]<br>77                   | 4.2      |
| Approximate expansion ration<br>(volume of gas at 15°C and atmospheric pressure produced<br>by unit volume of liquid at normal boiling point). | 680                          | 740      |
| Density of liquid at normal boiling point  | [kg m <sup>-3</sup> ]<br>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)



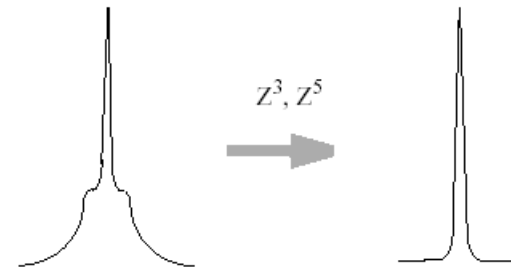
*Spectrum before Adjustment*

*Adjusted shim(s)*  
 $Z$

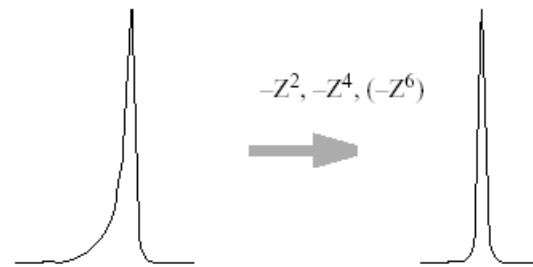
*Adjusted Spectrum*



$Z^3, Z^5$

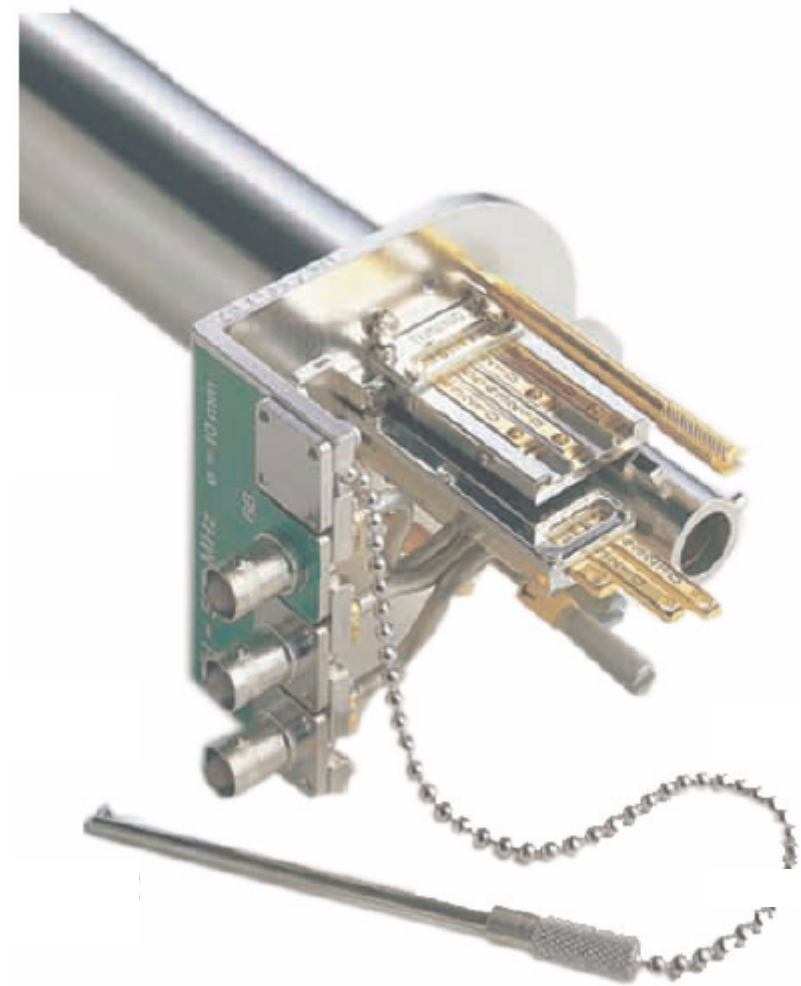
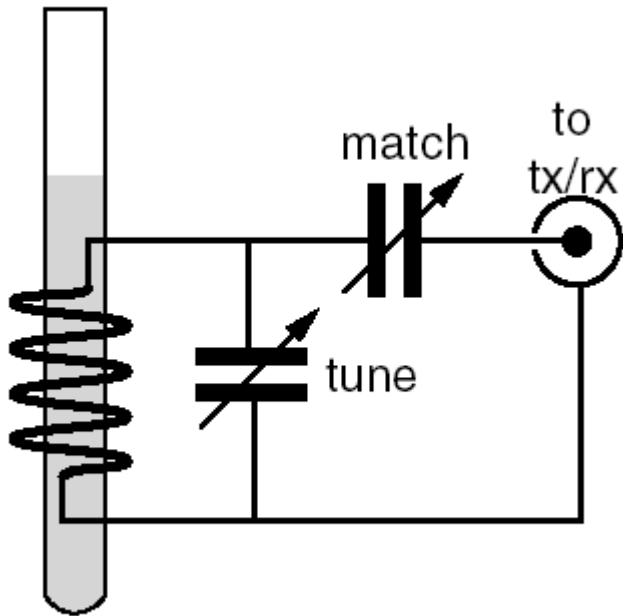


$-Z^2, -Z^4, (-Z^6)$



# Jak prauje spektrometr

Sonda



# Jak pracuje spektrometr

## Vysílač – výkon *vers.* indukce rf pole

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

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

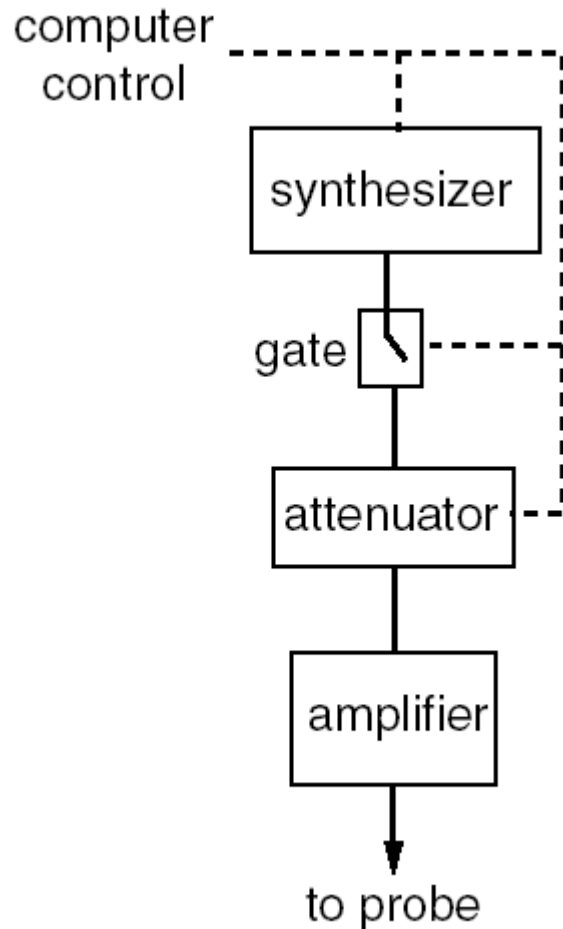
**Relativní hodnota výkonu se vyjadřuje v decibelech**  
**1 dB:  $P_1/P_2 = 1.2589254$**

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

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

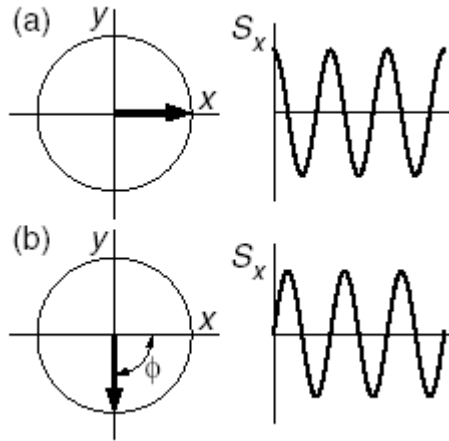
$$\begin{aligned} \text{power ratio in dB} &= 10 \log_{10} \left( \frac{\omega_1^{\text{new}}/2\pi}{\omega_1^{\text{init}}/2\pi} \right)^2 \\ &= 20 \log_{10} \left( \frac{\omega_1^{\text{new}}/2\pi}{\omega_1^{\text{init}}/2\pi} \right) \end{aligned}$$

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



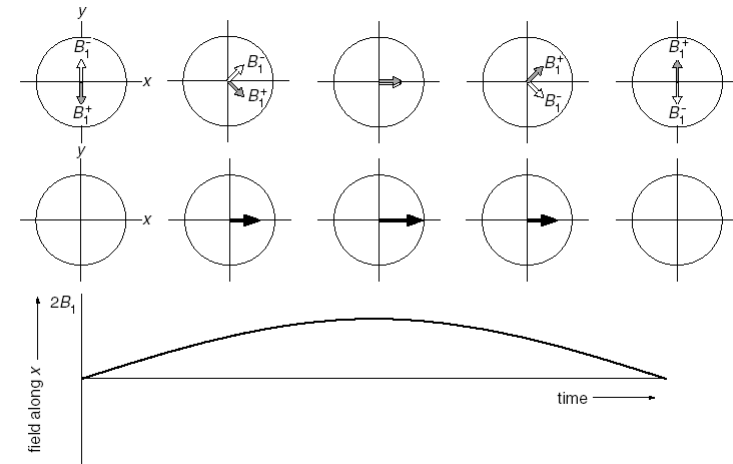
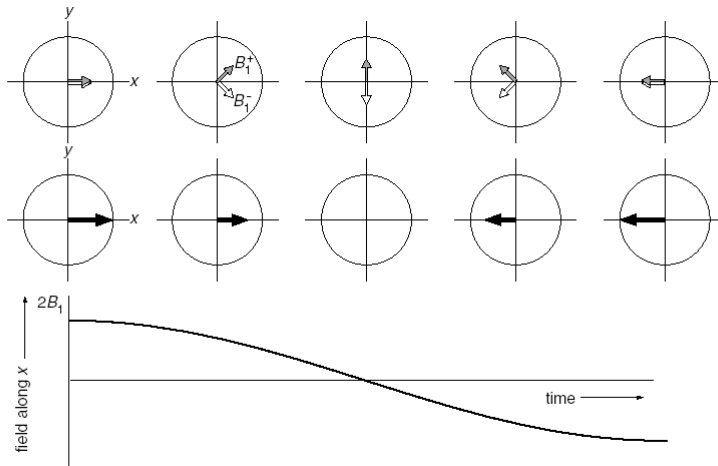
# Jak pracuje spektrometr

Vysílač – fázově posunuté pulzy



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

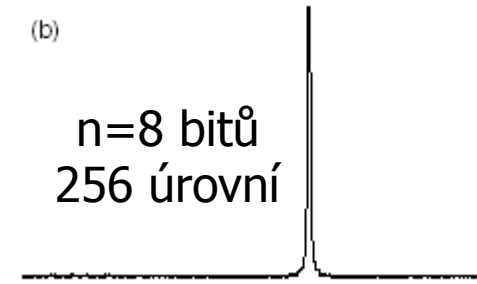
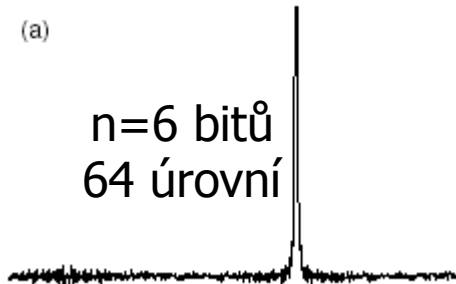
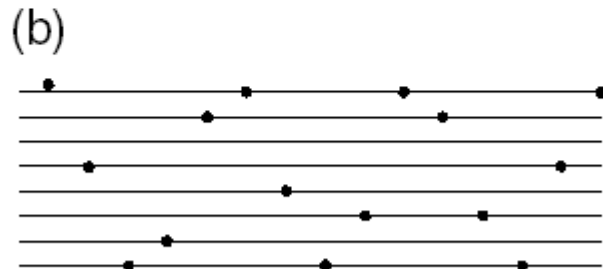
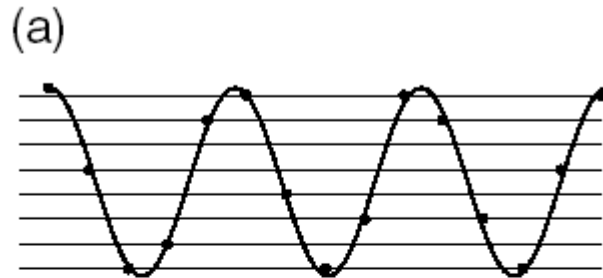
$$2B_1 \sin \omega_{RF}t.$$



# Jak pracuje spektrometr

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

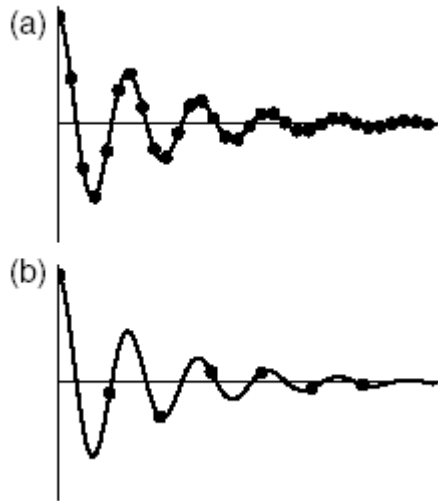
A/D převodník



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

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

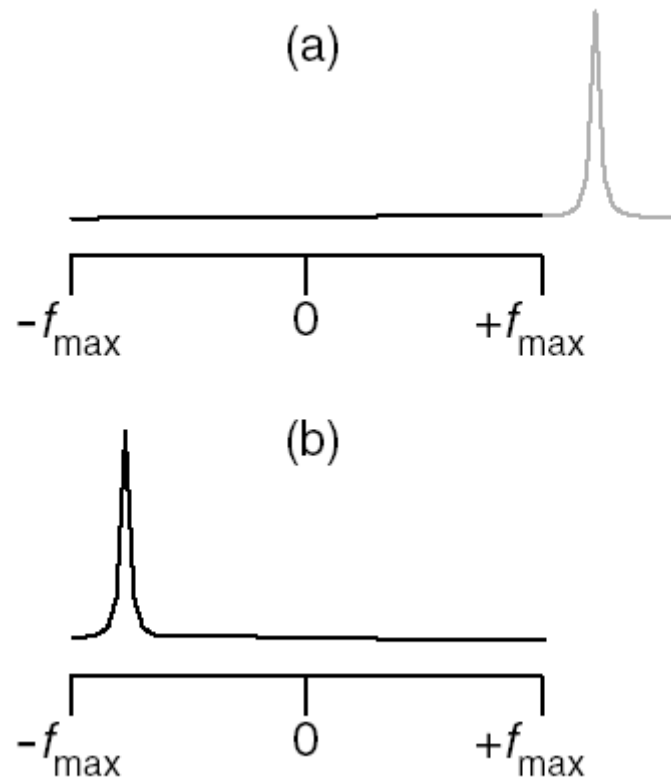
$$\Delta = \frac{1}{2f_{\max}}.$$

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



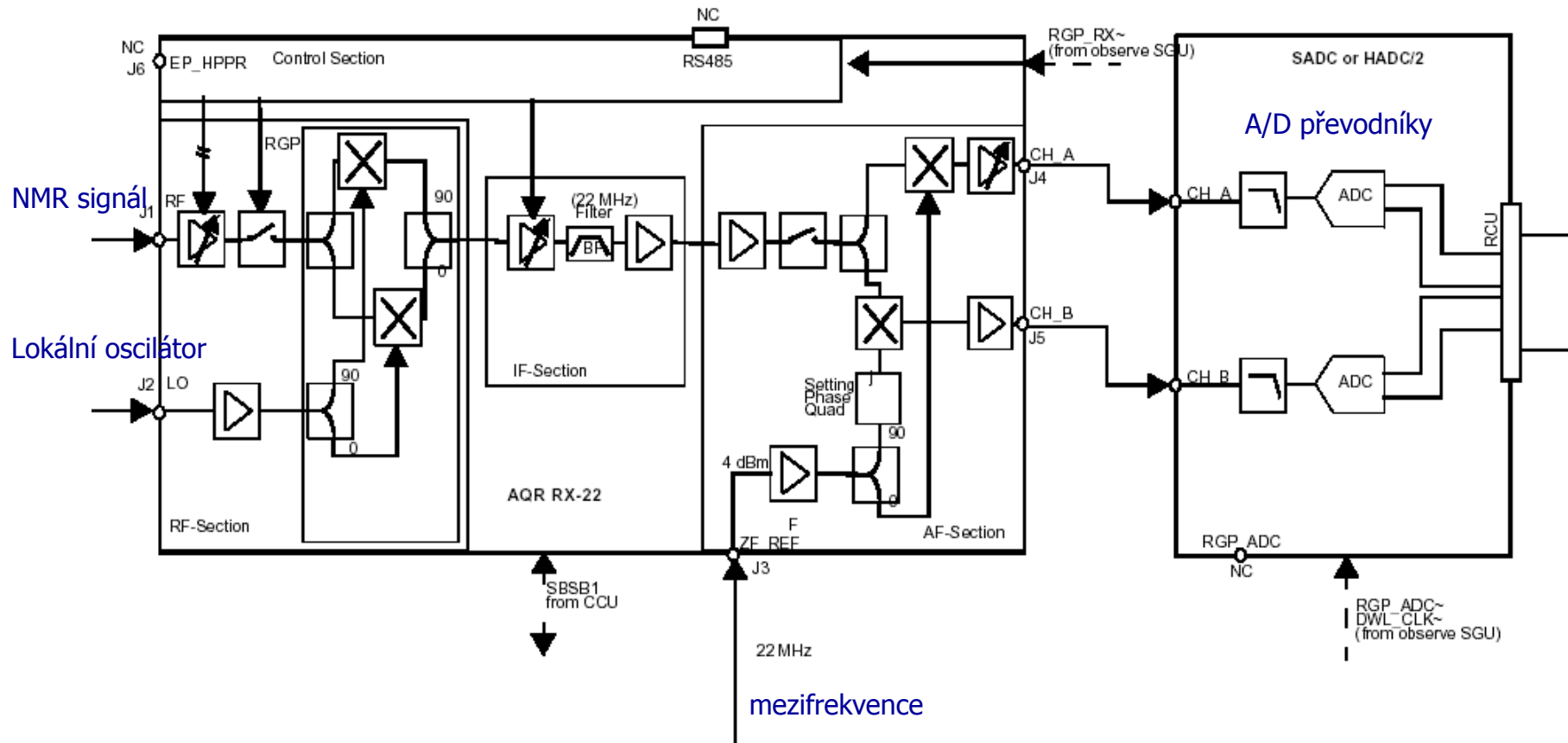
# Jak pracuje spektrometr

A/D-převodník – překládání signálů



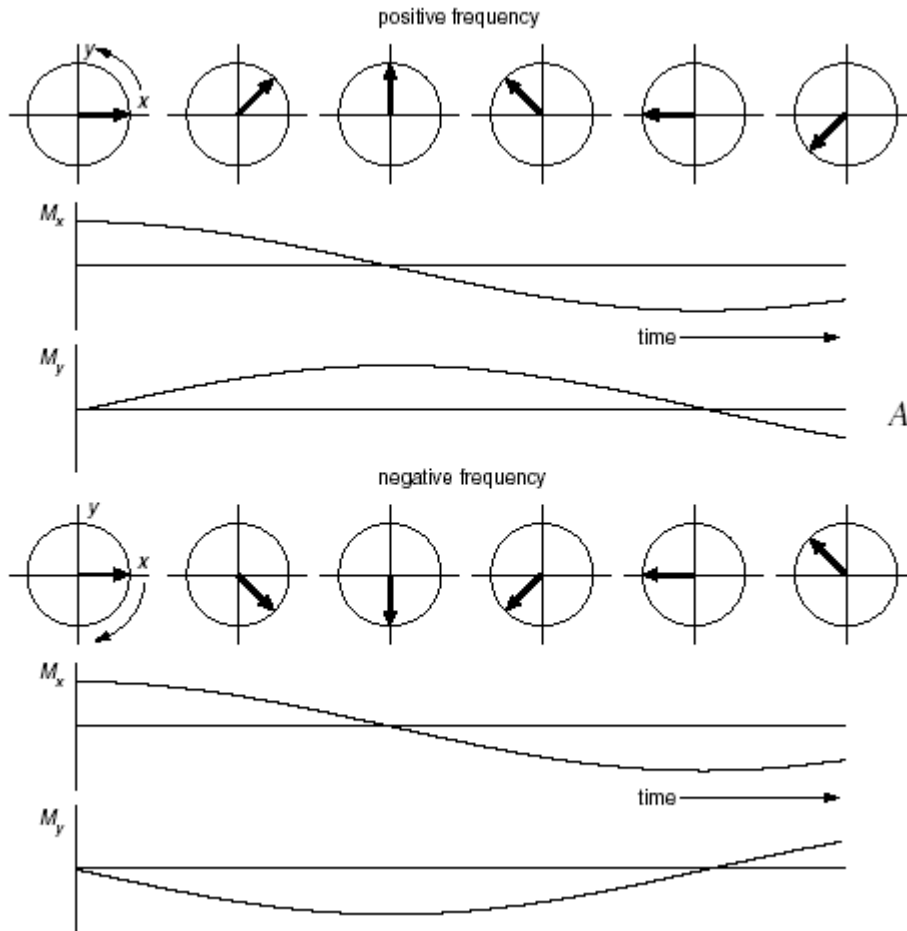
# Jak pracuje spektrometr

## Přijímač

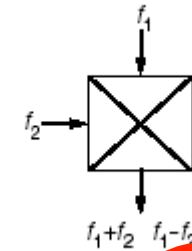


# Jak pracuje spektrometr

## Kvadrurní detekce



směšovač



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

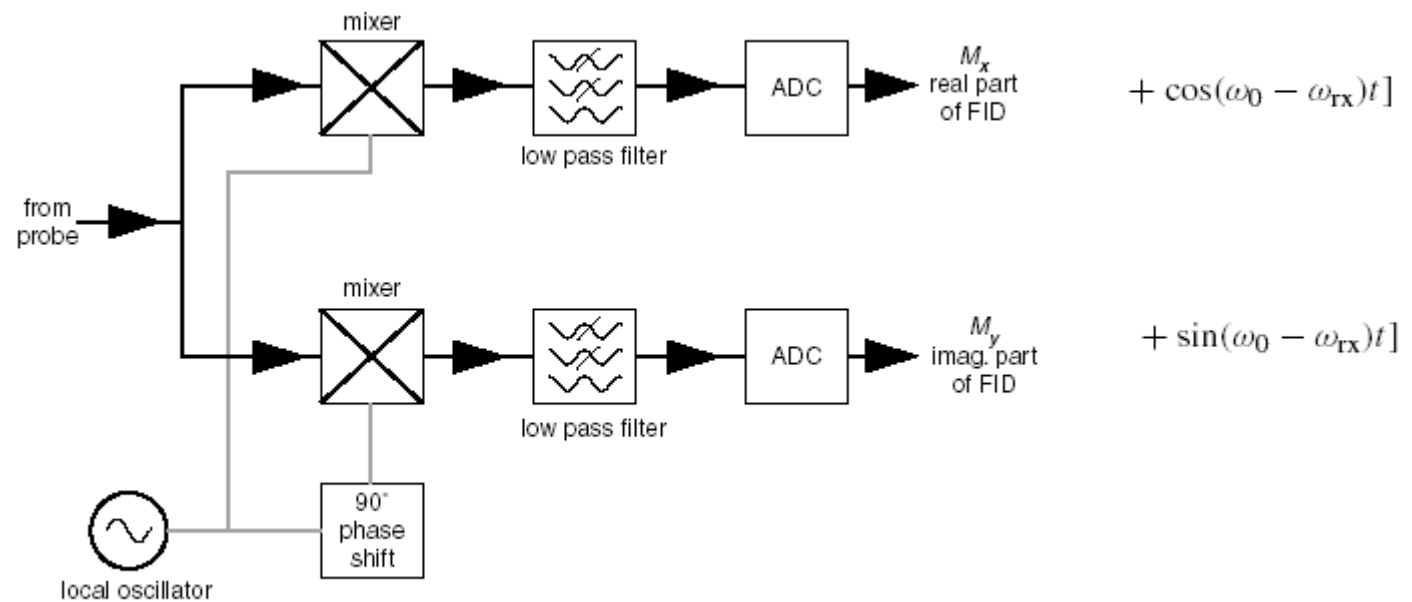
$$A \cos \omega_0 t \times (-\sin \omega_{rx} t) = \frac{1}{2} A [-\sin(\omega_0 + \omega_{rx})t + \sin(\omega_0 - \omega_{rx})t]$$

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

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

# 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 akvizičních bodů

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

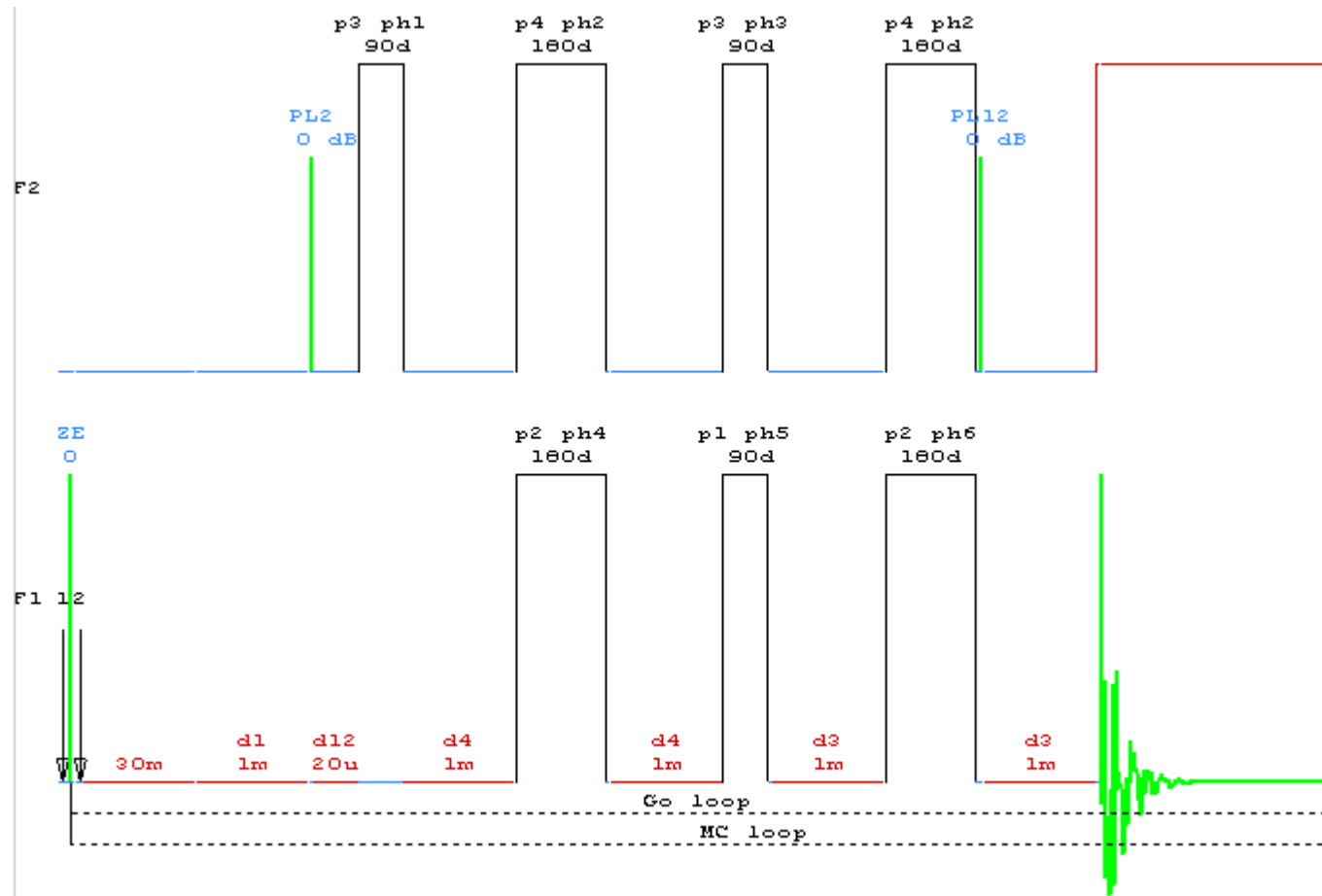
$$N = \frac{t_{acq}}{\Delta}$$

$\Delta$  – 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"
```

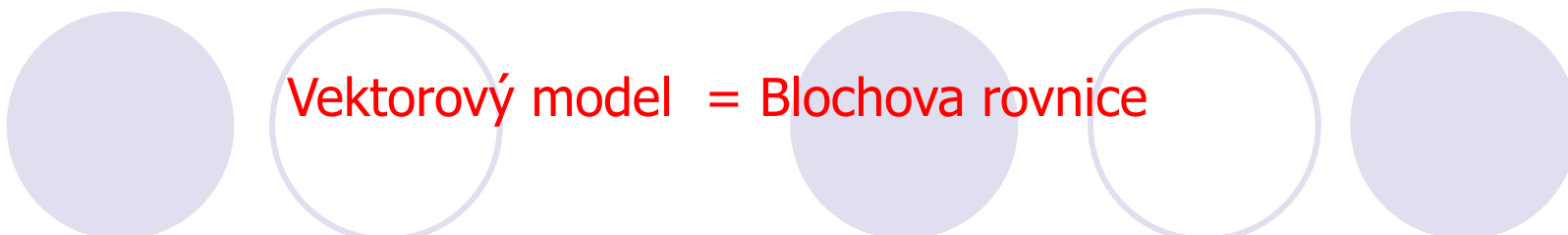
```
1 ze
2 30m do:f2
  d1
  d12 pl2:f2
  (p3 ph1):f2
  d4
  (center (p4 ph2):f2 (p2 ph4) )
  d4
  (p3 ph3):f2 (p1 ph5)
  d3
  (center (p4 ph2):f2 (p2 ph6) )
  d3 pl12:f2
  go=2 ph31 cpd2:f2
  30m do:f2 mc #0 to 2 F0(zd)
exit
```

15.10.2014

```
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
```

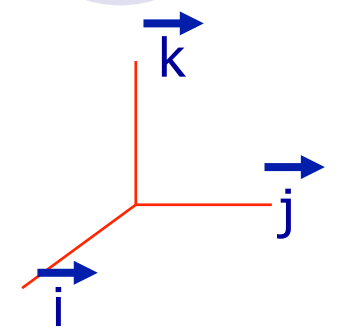
```
;$Id: ineptrd,v 1.8 2002/06/12 09:05:00 ber Exp $
```



Vektorový model = Blochova rovnice

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

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



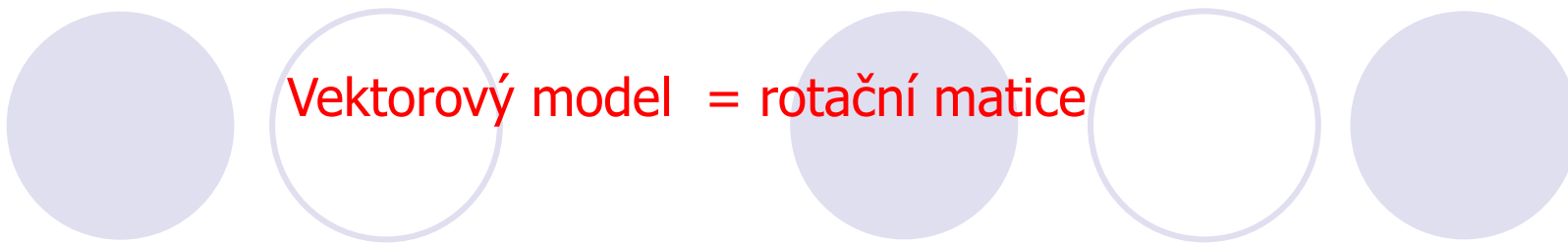
92

### Numerické řešení

$$dM/dt = \begin{matrix} R11 & R12 & R13 \\ R21 & R22 & R23 \\ R31 & R32 & R33 \end{matrix} \otimes \begin{matrix} Mx(0) \\ My(0) \\ Mz(0) \end{matrix} = \begin{matrix} Mx(t) = R11 \cdot Mx(0) + R12 \cdot My(0) + R13 \cdot Mz(0) \\ My(t) = R21 \cdot Mx(0) + R22 \cdot My(0) + R23 \cdot Mz(0) \\ Mz(t) = R31 \cdot Mx(0) + R32 \cdot My(0) + R33 \cdot Mz(0) \end{matrix}$$

92





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

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

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

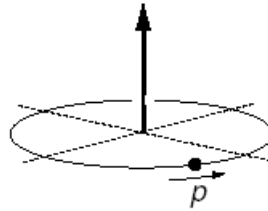
# Součinný operátorový formalismus

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

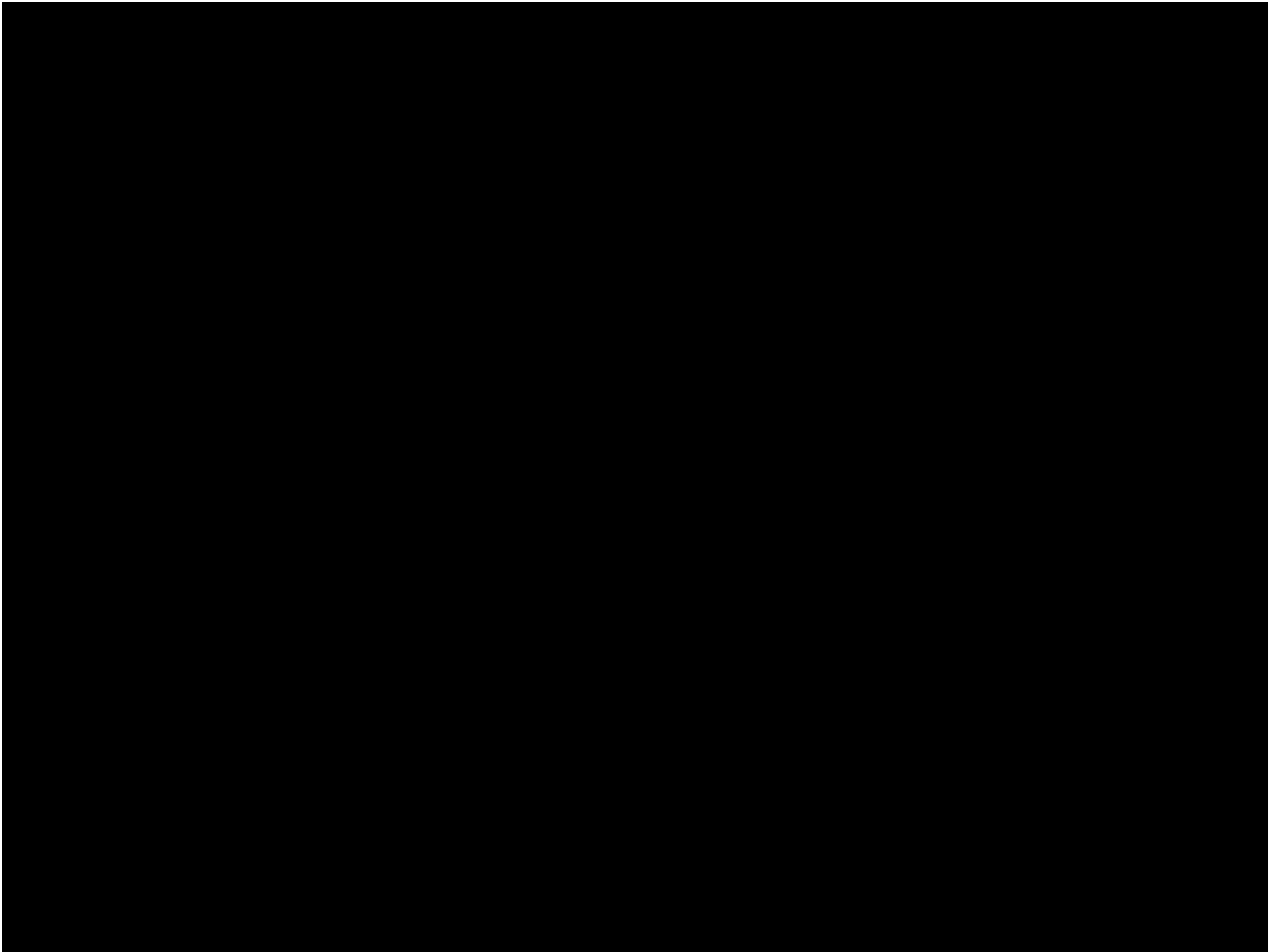
Pohybová rovnice – Liouville-von Neumanova rovnice

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

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

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

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



# Součinový operátorový formalismus

Přestručné opakování základů kvantové mechaniky

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

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

22.10.2013  
29.10.2013

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

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

Zkrácená notace

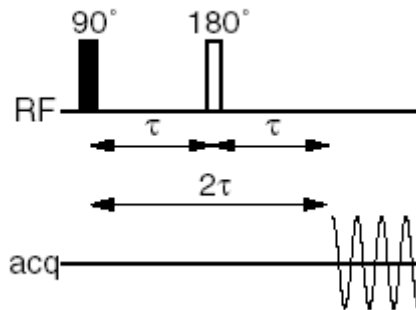
$$\sigma(t_p) = \exp(-i\omega_1 t_p I_x) \sigma(0) \exp(i\omega_1 t_p I_x)$$

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

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

# Součinový operátorový formalismus

## Spinové echo – příklad výpočtu



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

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

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

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

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

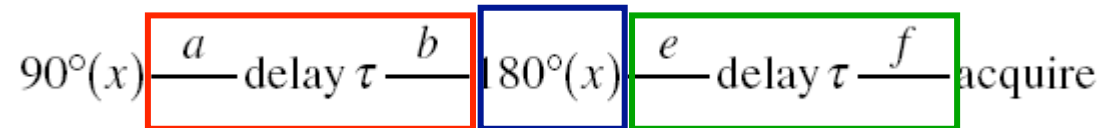
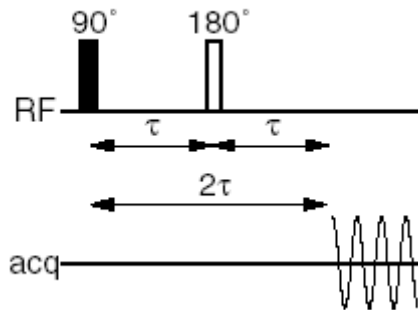
$$-\cos \Omega \tau I_y \xrightarrow{\pi I_x} \cos \Omega \tau I_y$$

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



# Součinový operátorový formalismus

## Spinové echo – příklad výpočtu



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

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

$$(\cos \Omega \tau \cos \Omega \tau + \sin \Omega \tau \sin \Omega \tau) I_y + (\cos \Omega \tau \sin \Omega \tau - \sin \Omega \tau \cos \Omega \tau) I_x$$

1

0

Celkový výsledek

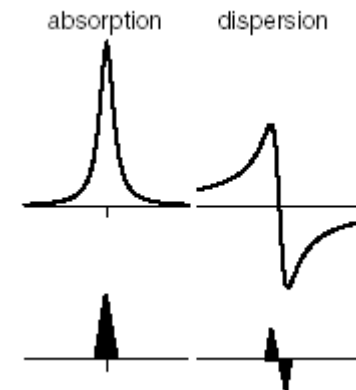
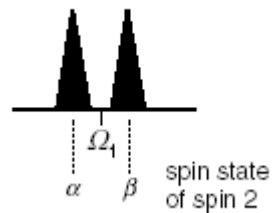
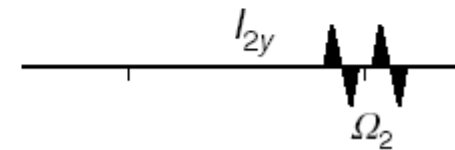
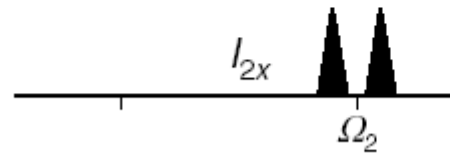
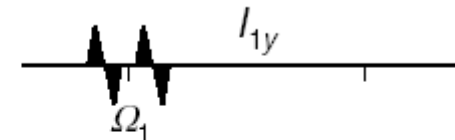
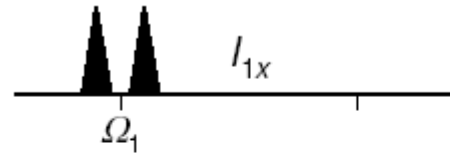
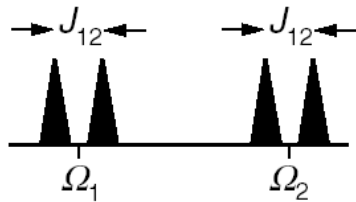
$$I_z \xrightarrow{90^\circ(x)-\tau-180^\circ(x)-\tau-} I_y$$

# Součinný operátorový formalismus

## Dvouspinové operátory

Soufázové (in-phase) operátory - 6

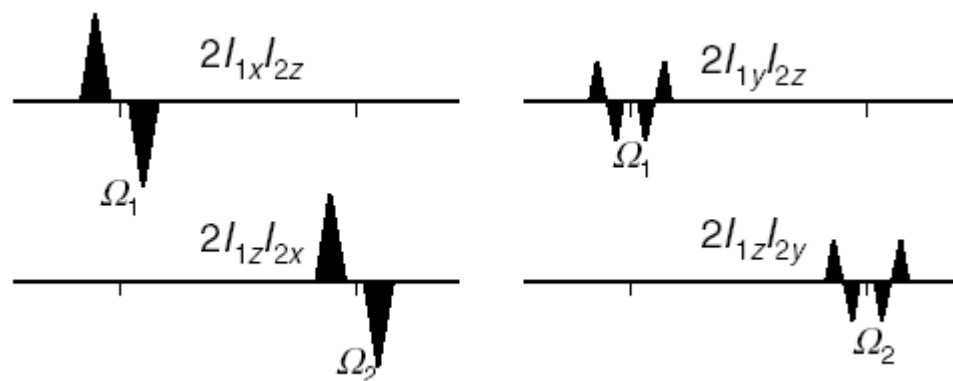
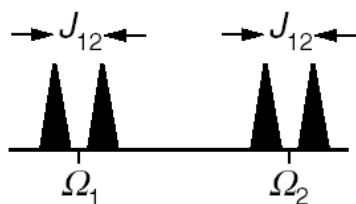
spin 1 :  $I_{1x}$   $I_{1y}$   $I_{1z}$     spin 2 :  $I_{2x}$   $I_{2y}$   $I_{2z}$



# Součinný 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  $2I_{1x}I_{2z}$

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

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

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

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

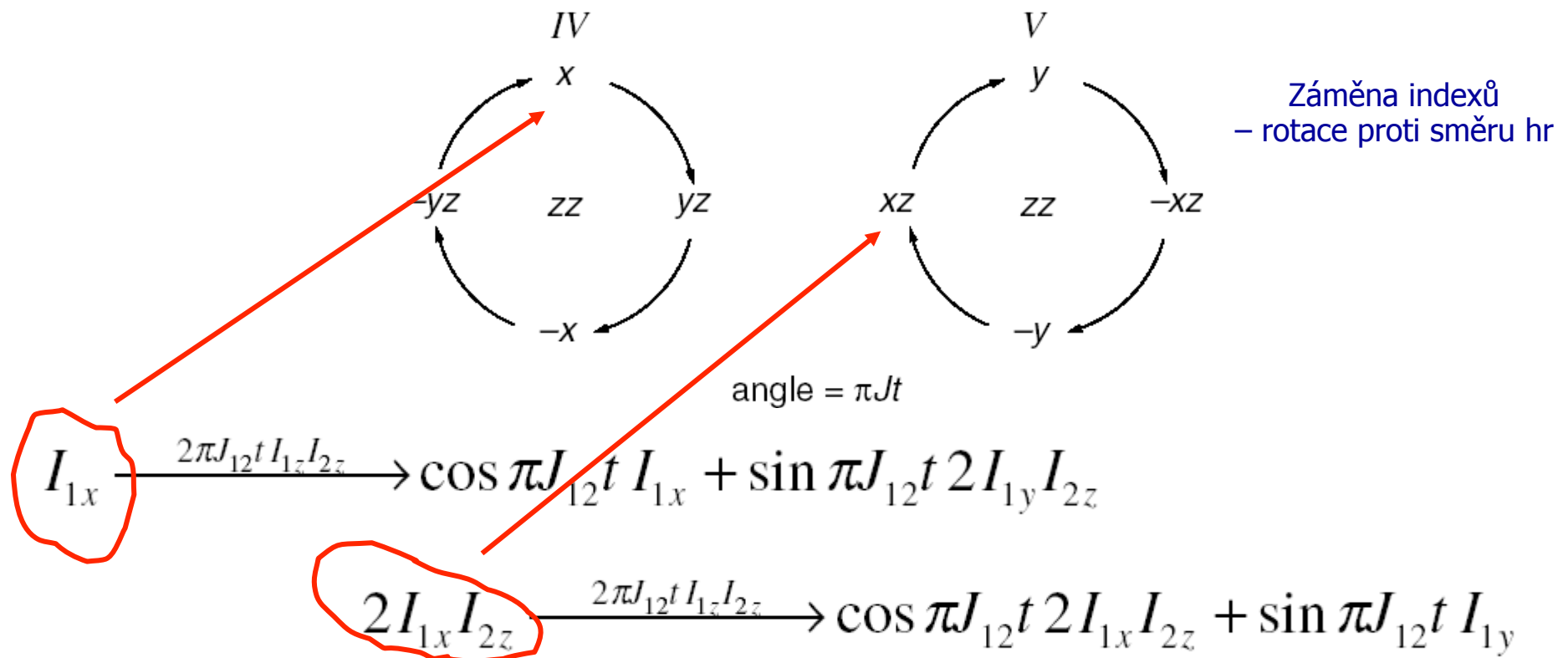
$$2I_{1x}I_{2z} \xrightarrow{\pi/2 I_{1y}} -2I_{1z}I_{2z} \xrightarrow{\pi/2 I_{2y}} -2I_{1z}I_{2x}$$

# Součinový operátorový formalismus

Popis vlivu spin-spinové skalární interakce na vývoj matice hustoty

Hamiltonián

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



# Součinový operátorový formalismus

Popis vlivu spin-spinové skalární interakce na vývoj matice hustoty

Hamiltonián

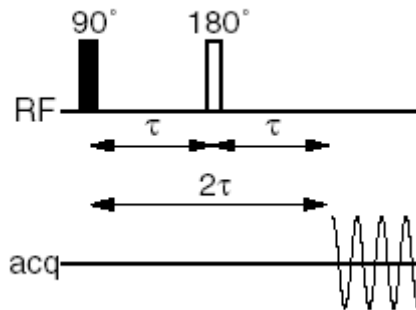
$$H_J = 2\pi J_{12} I_{1z} I_{2z}$$

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

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

# Součinný operátorový formalismus

Popis spinového echa ve dvouspinovém systému s J interakcí



## Homonukleární systém

–  $\tau$  –  $180^\circ(x, \text{ to spin 1 and spin 2})$  –  $\tau$  –

Chemický posun je refokusován (viz obrázek č. 36)

1. interval  $\tau$

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

180° pulz

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

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

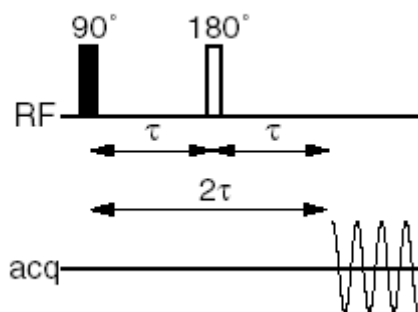
$$\xrightarrow{\pi I_{2x}} \cos \pi J_{12}\tau I_{1x} + \sin \pi J_{12}\tau 2I_{1y}I_{2z}$$

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

–  $\tau$  –  $180^\circ(x, \text{ to spin 1 and spin 2})$  –  $\tau$  –

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

Interkonverze soufázové a antifázové magnetizace

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

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

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

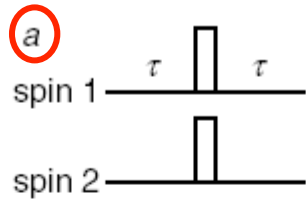
$$2I_{1x}I_{2z} \rightarrow I_{1y}$$



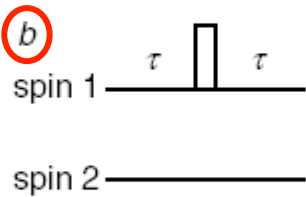
# Součinový operátorový formalismus

Popis spinového echa ve dvouspinovém systému s J interakcí

## Heteronukleární systém



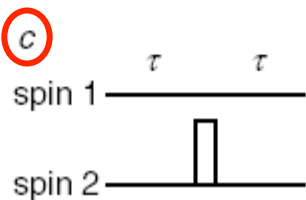
Sekvence a – viz homonukleární systém



Sekvence b

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

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



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

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

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

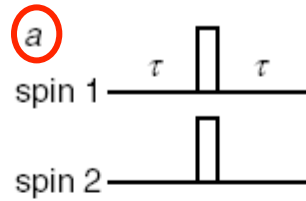
$$- \cos \pi J_{12}\tau \sin \pi J_{12}\tau 2I_{1y}I_{2z} + \sin \pi J_{12}\tau \sin \pi J_{12}\tau I_{1x}$$

$$\longrightarrow I_{1x}$$

# Součinový operátorový formalismus

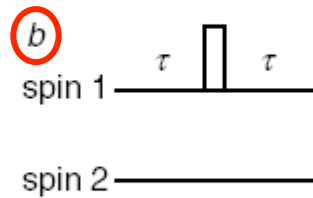
Popis spinového echa ve dvouspinovém systému s J interakcí

## Heteronukleární systém

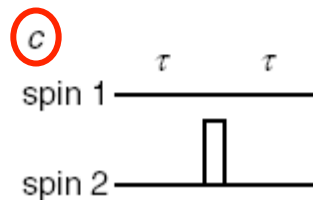


Sekvence c

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



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



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

Ale vývoj v důsledku chemického posunu spinu  $I_1$  zůstává zachován

# Součinný 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)

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

$$I_+ = I_x + iI_y$$

$$I_- = I_x - iI_y$$

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

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

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

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

$$p = + 2$$

$$p = - 2$$

$$p = 0$$

$$p = 0$$

# Součinný operátorový formalismus

Více-kvantové členy

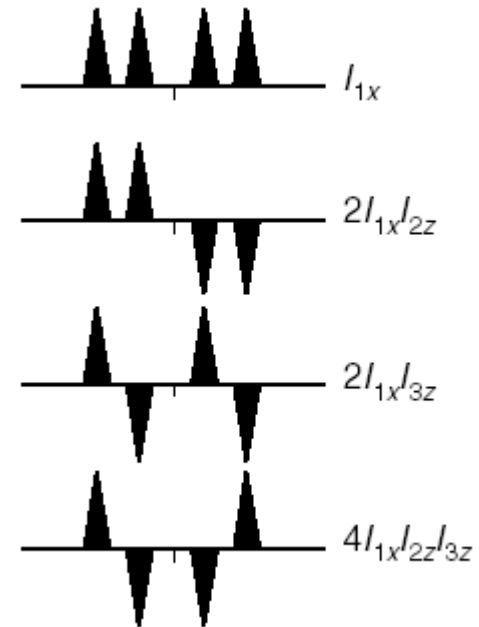
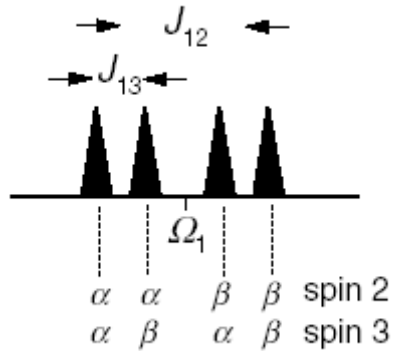
Řád koherence - p

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

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

# Součinný operátorový formalismus

## Tříspinové operátory



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

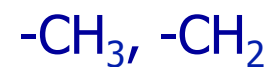
# Součinový operátorový formalismus

Alternativní notace

IS spinový systém

$$2I_{1y}I_{2z} \quad 2I_y S_z$$

$I_n$ S spinový systém



# Součinový 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 *minus*  
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 - CH<sub>2</sub>

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

# 4 spiny - CH<sub>3</sub>

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

# Metody 1D FT NMR spektroskopie

## Širokopásmový dekaplink

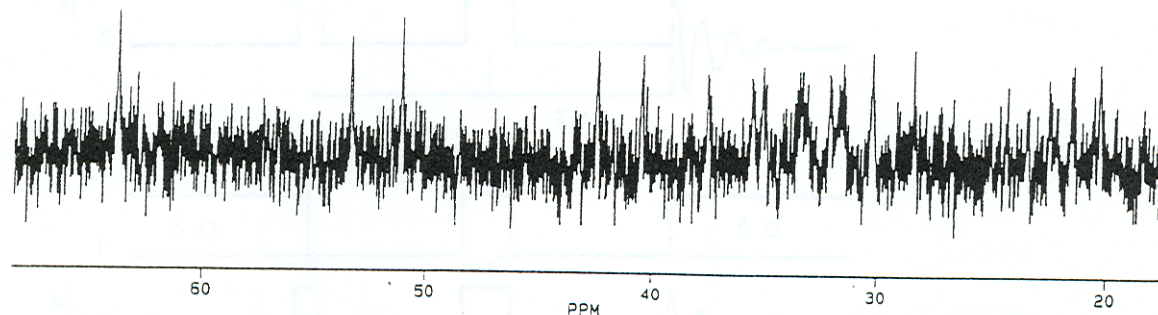


Figure 4.1: Coupled  $^{13}\text{C}$  spectrum of sucrose obtained in 64 scans

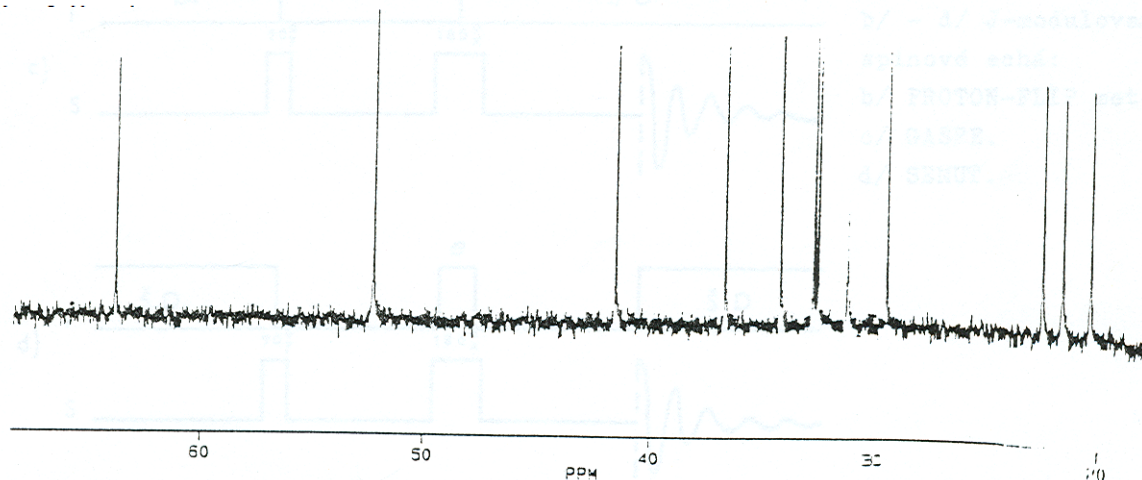
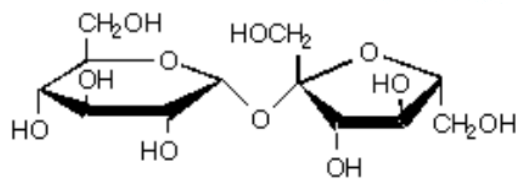


Figure 4.2: Broadband decoupled  $^{13}\text{C}$  spectrum of sucrose obtained in 64 scans

# Metody 1D FT NMR spektroskopie

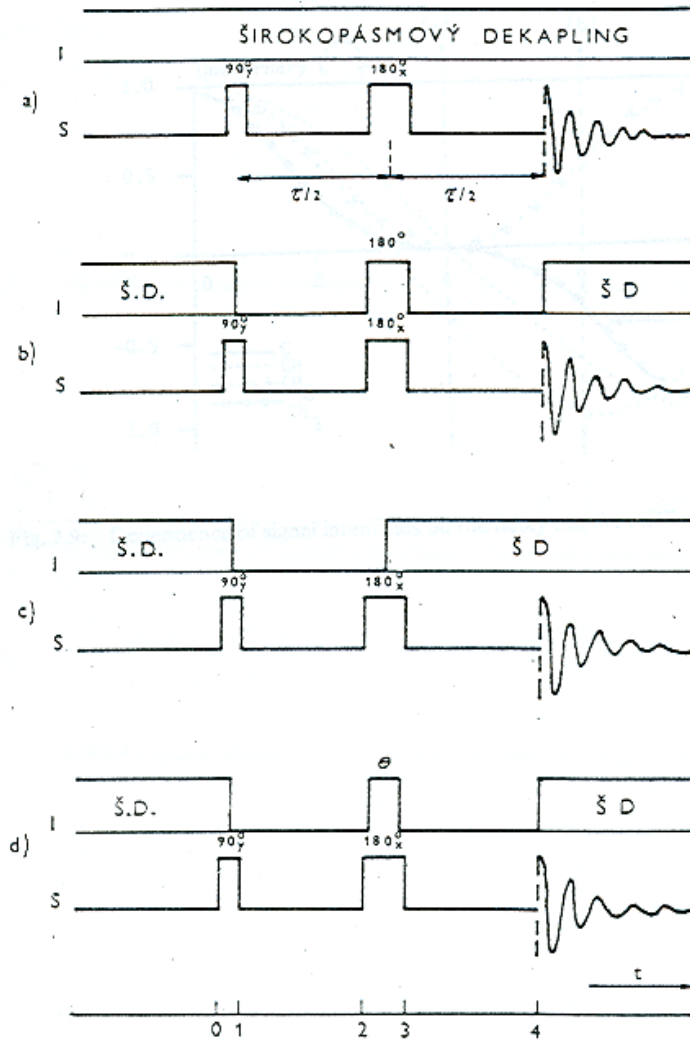
## Pulzní sekvence – editace spekter

SE

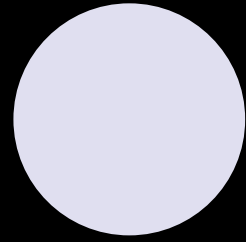
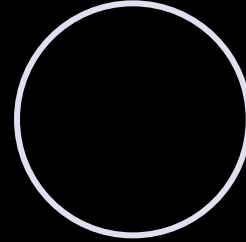
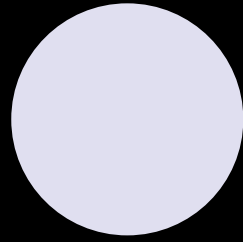
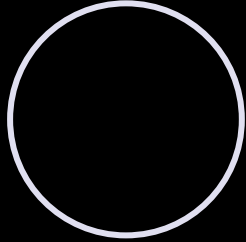
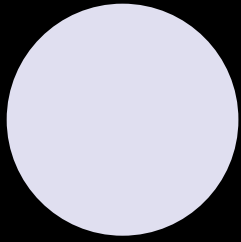
APT

GASPE

SEMUT



5.11.2014



# Metody 1D FT NMR spektroskopie

APT

APT

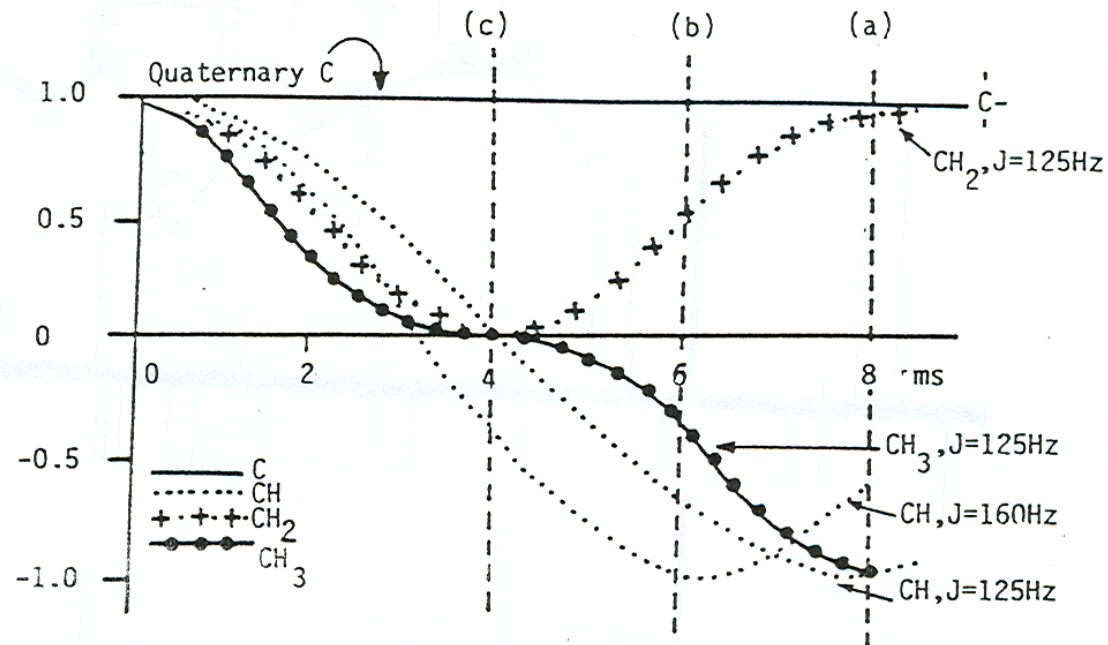
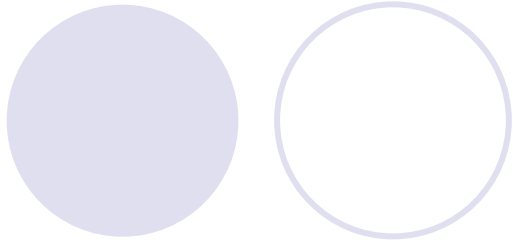
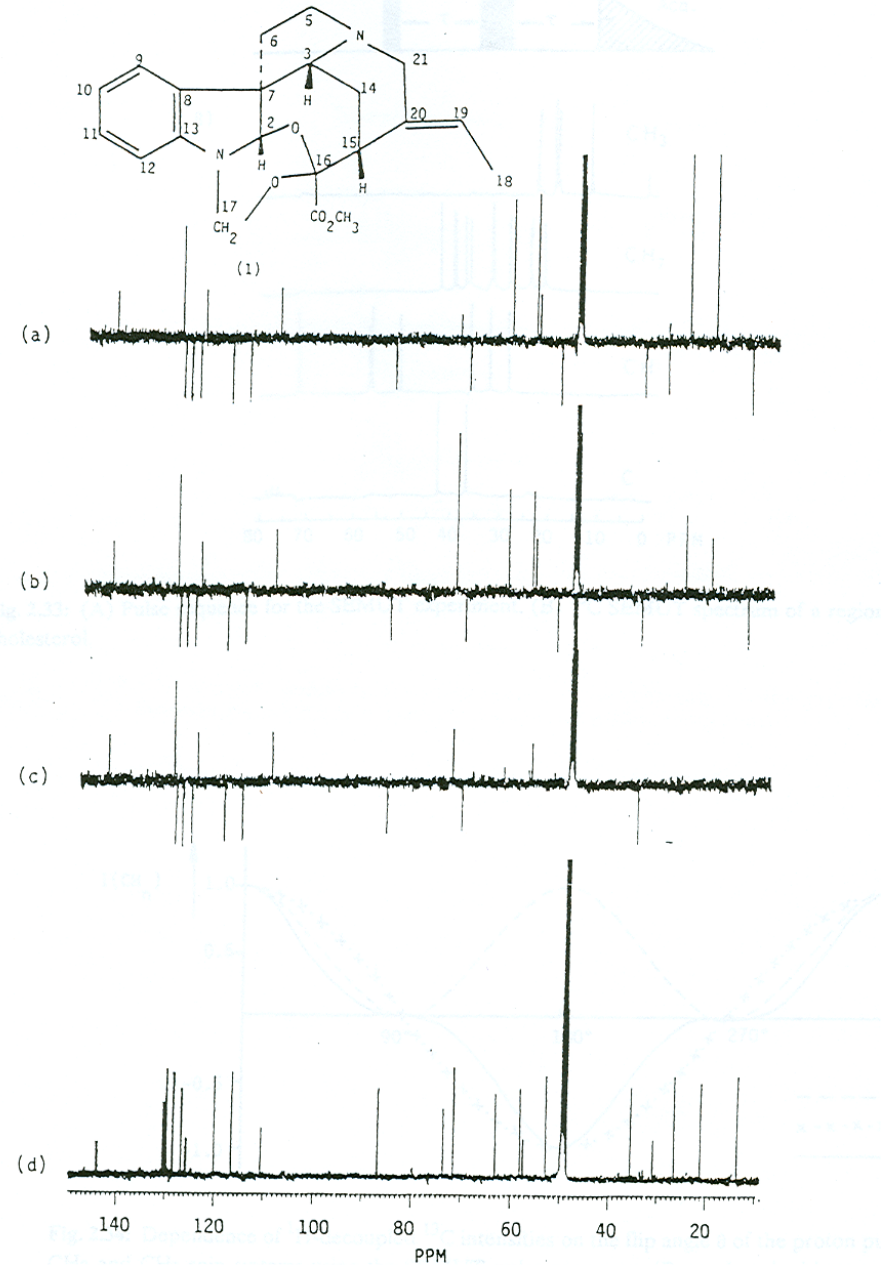


Fig. 2.9: Dependence of signal intensities on the delay  $\tau$  in the APT experiment.

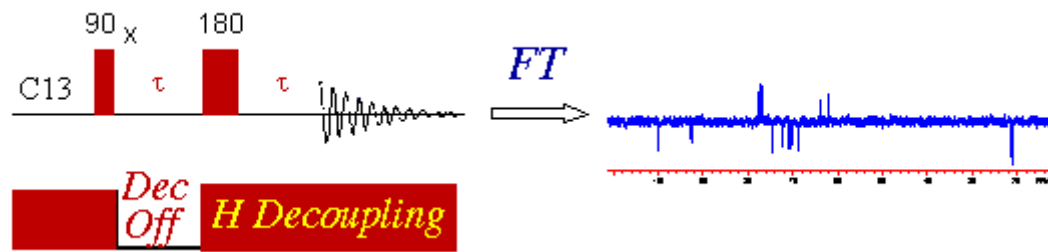


# Metody 1D FT NMR spektroskopie

APT

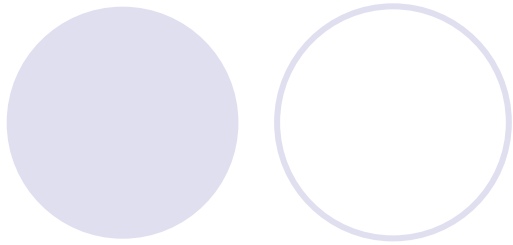


# GASPE



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





# Metody 1D FT NMR spektroskopie

## SEMUT

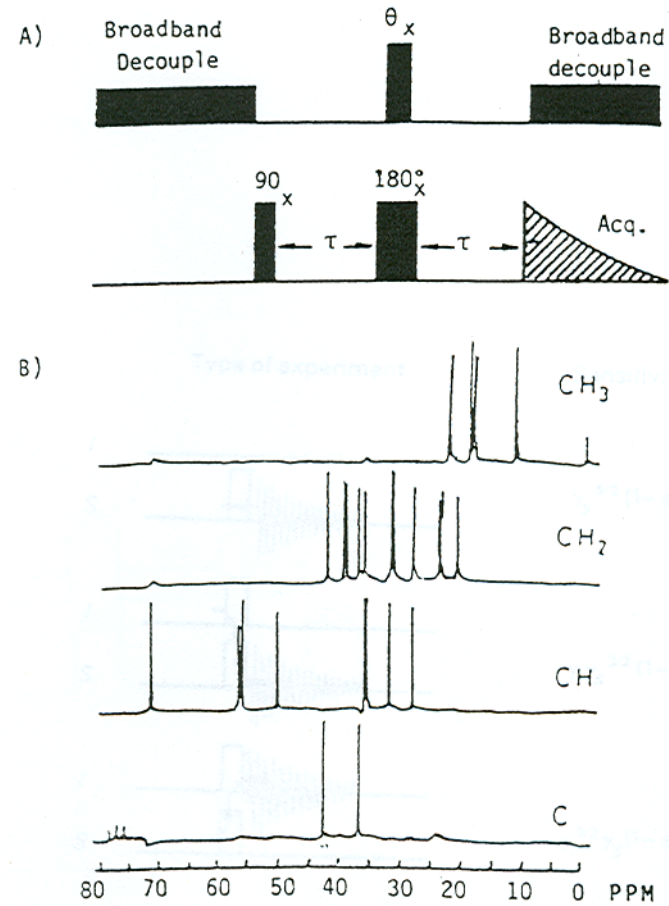
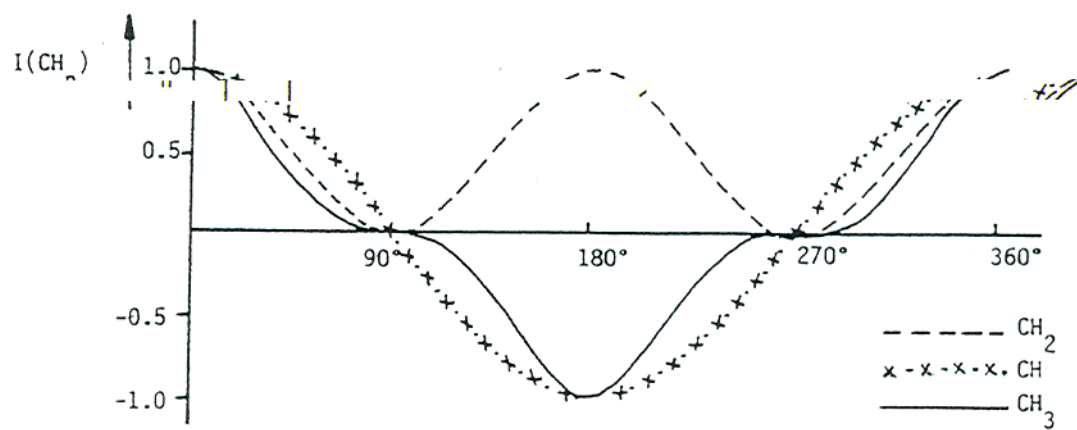


Fig. 2.33: (A) Pulse sequence for the SEMUT experiment. (B)  $^{13}\text{C}$  SEMUT spectrum of a region of cholesterol.



# Metody 1D FT NMR spektroskopie

## SEMUT



# Metody 1D FT NMR spektroskopie

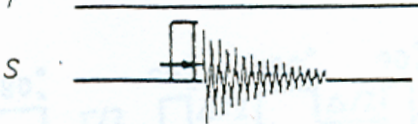



## Relativní citlivost

Examples

$T = 1.5 \text{ s}$

$T_1^I = 2 \text{ s}$

$T_1^S = 5 \text{ s}$

| 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  |

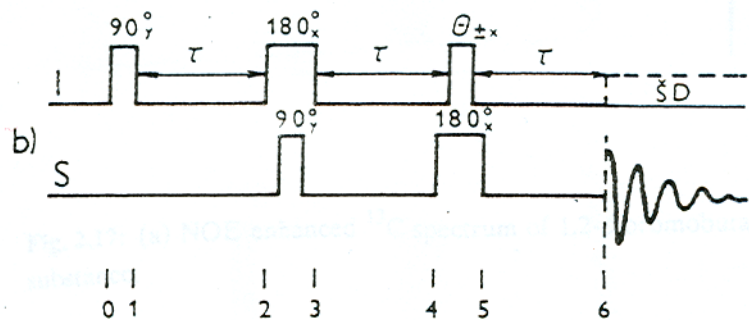
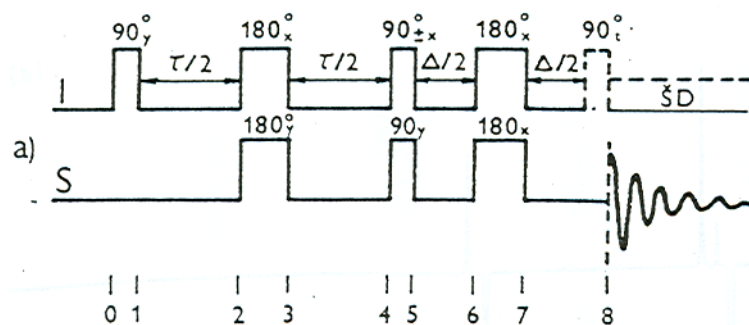
$$S / N \propto \gamma_{exc} \gamma_{obs}^{3/2} (1 - \exp(-T / T_1^{exc}))$$

$T$  – relaxation interval,  $T_1^S$ ,  $T_1^I$  – relaxation times

# Metody 1D FT NMR spektroskopie

## Přenos polarizace

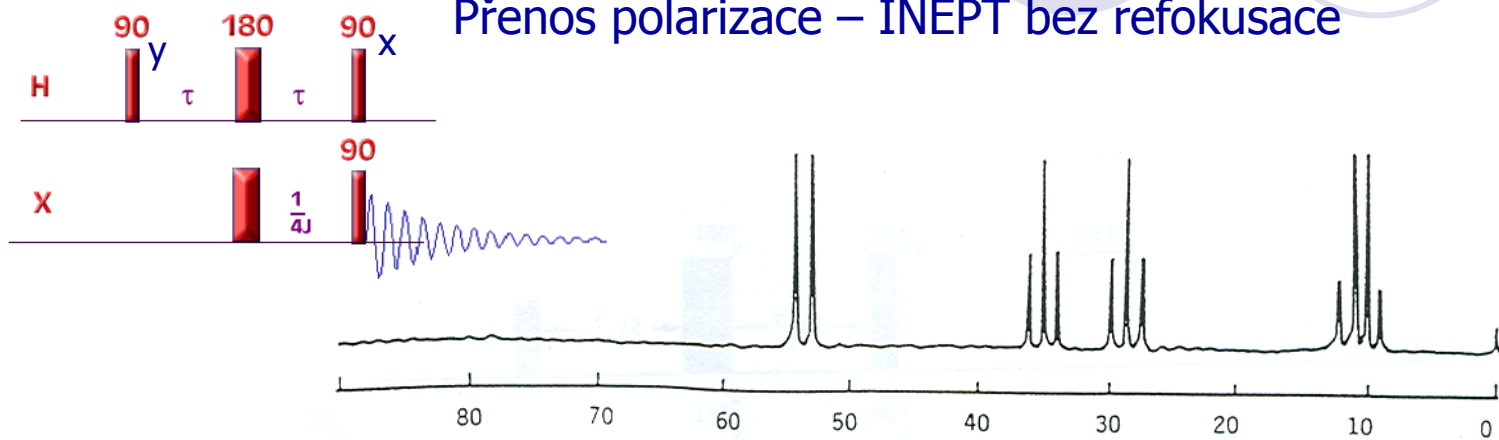
INEPT



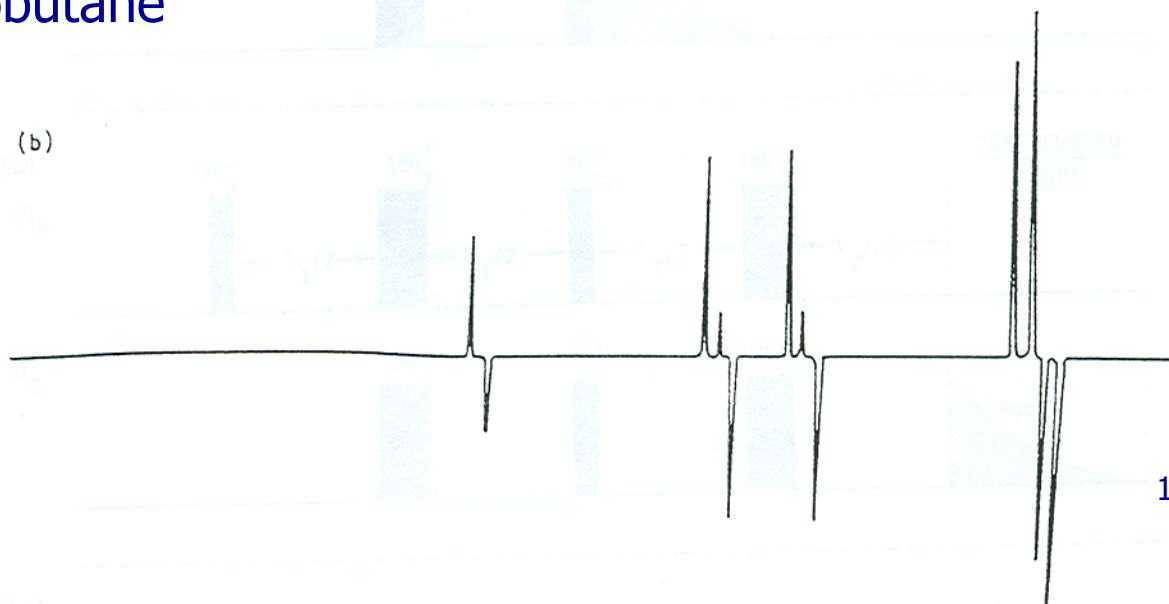
DEPT

# Metody 1D FT NMR spektroskopie

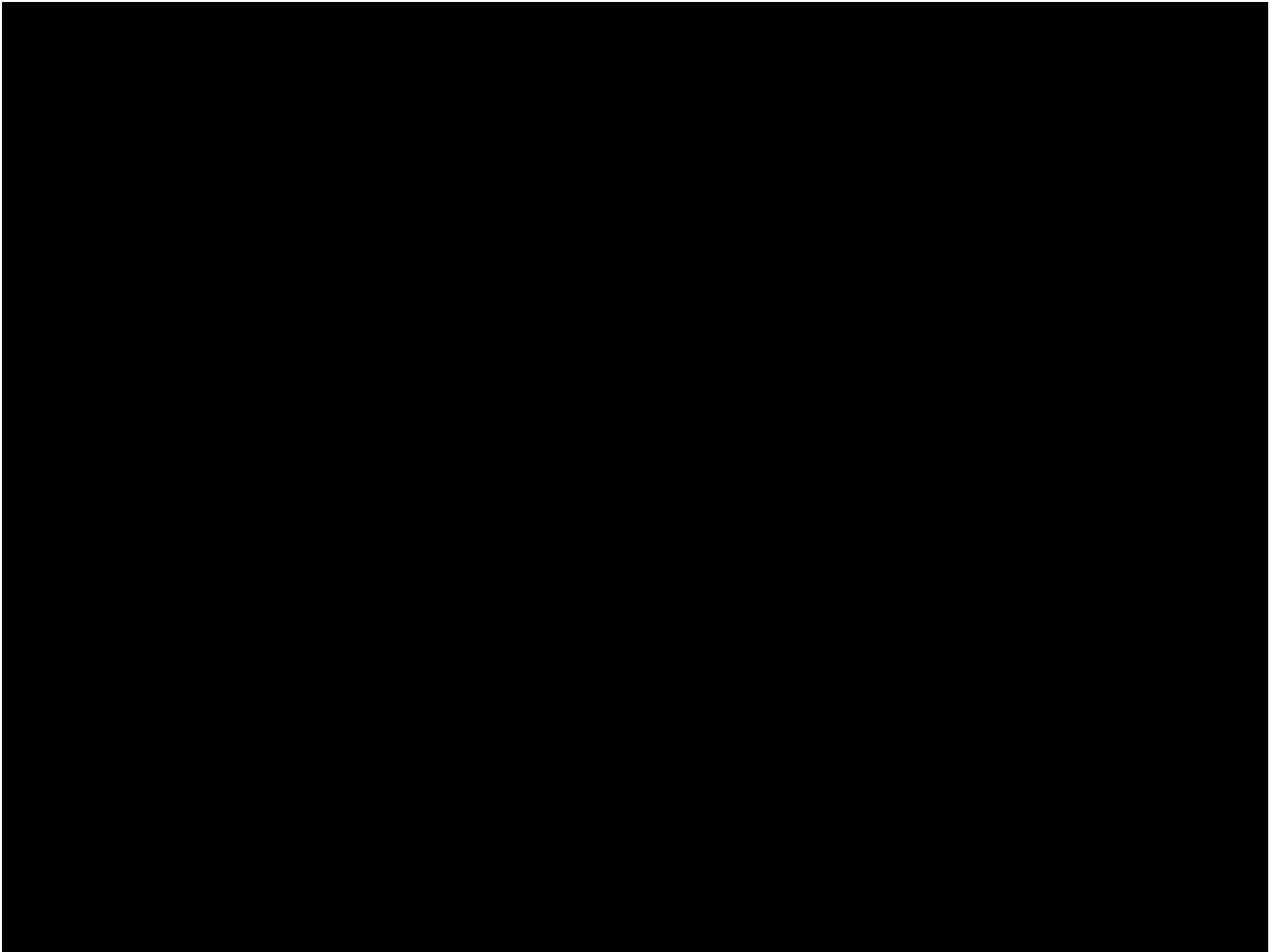
Přenos polarizace – INEPT bez refokusace



1,2-dibromobutane

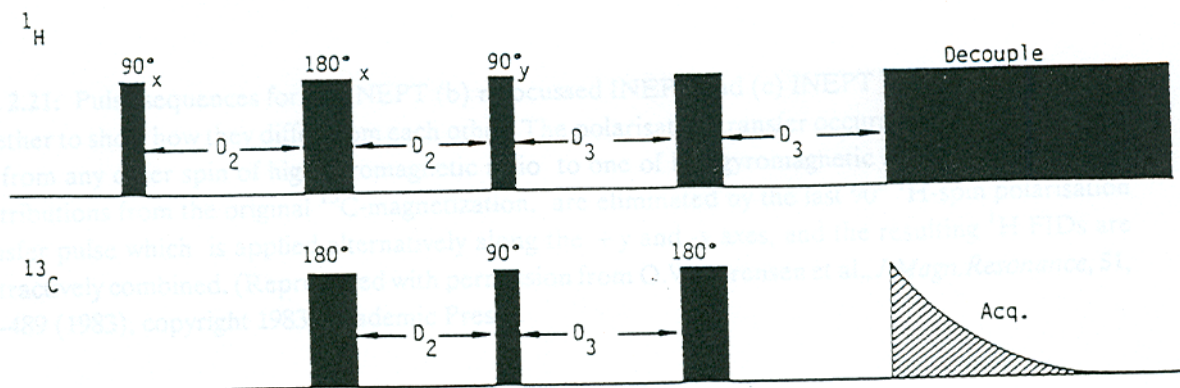


12.11.2014



# Metody 1D FT NMR spektroskopie

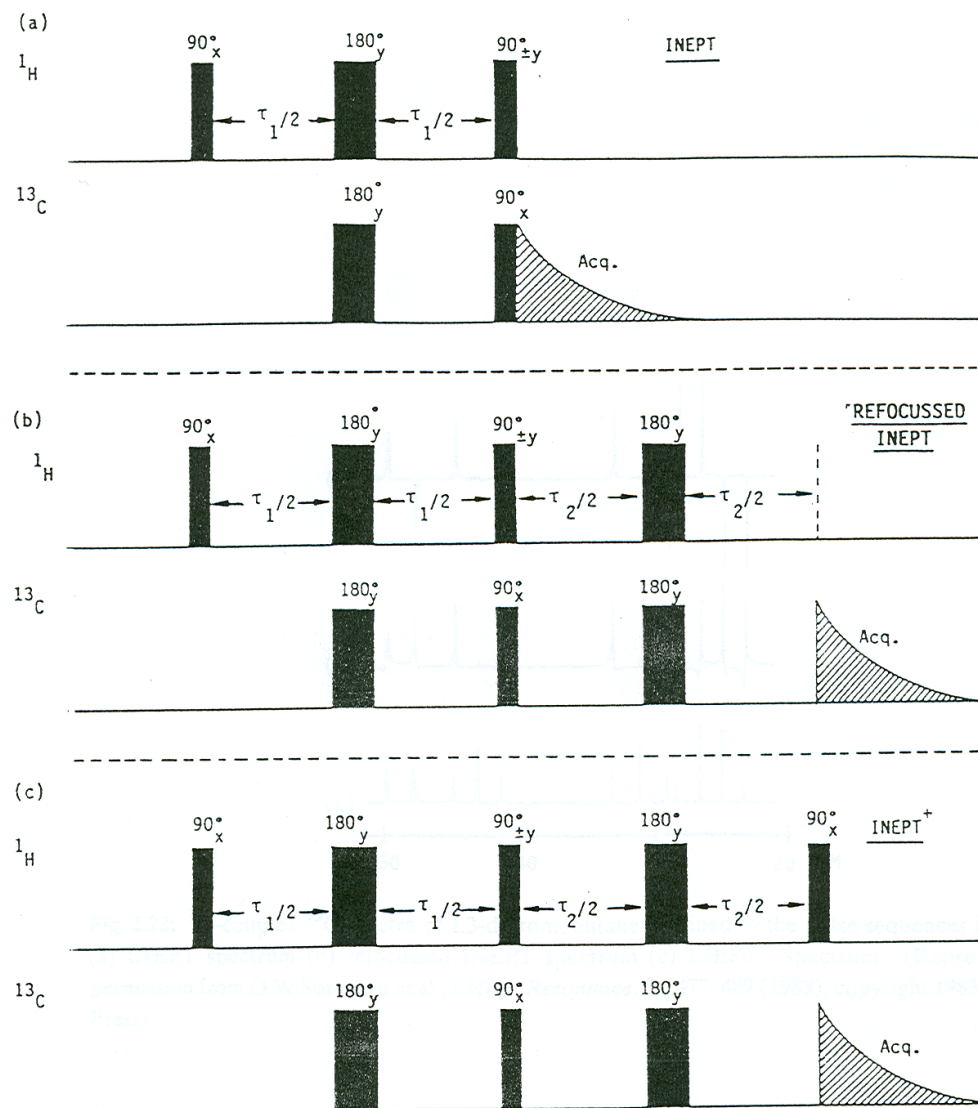
## Přenos polarizace – INEPT s refokusací





# Metody 1D FT NMR spektroskopie

## Přenos polarizace – INEPT – různé varianty



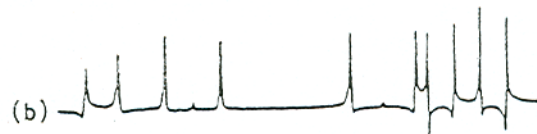
# Metody 1D FT NMR spektroskopie

## Přenos polarizace – INEPT – různé varianty

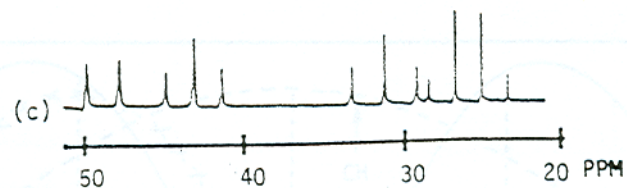
INEPT



INEPT s refokusací

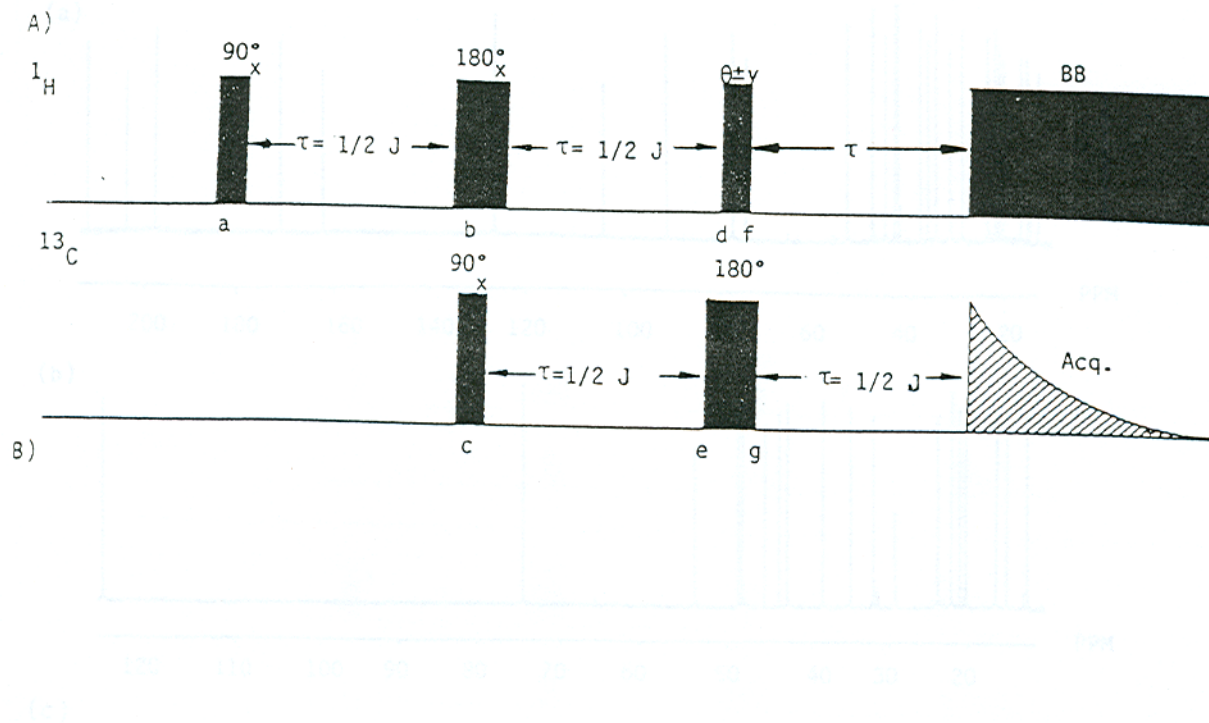


INEPT+



# Metody 1D FT NMR spektroskopie

## Přenos polarizace – DEPT





# Metody 1D FT NMR spektroskopie

## Přenos polarizace – DEPT vers. INEPT

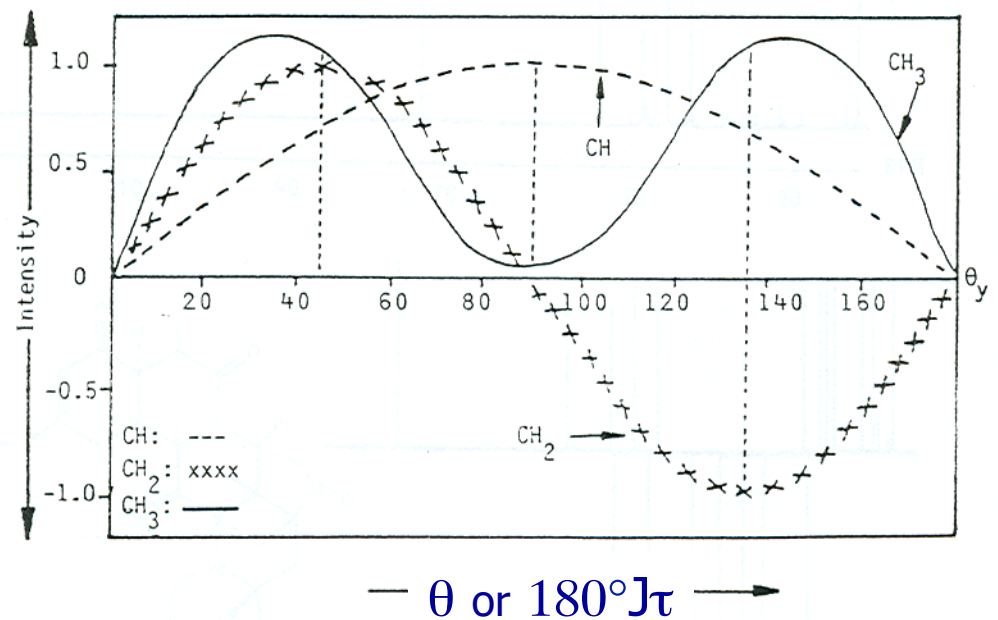


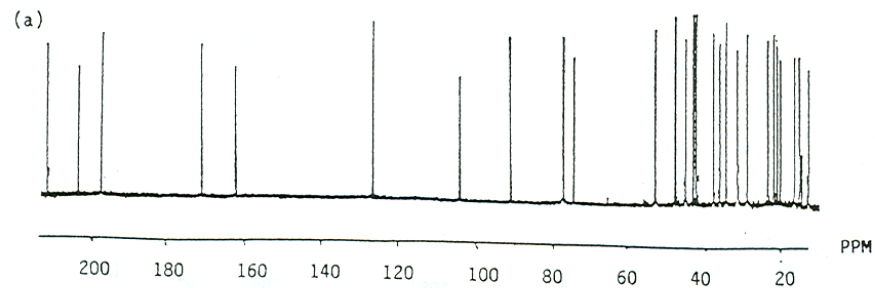
Fig. 2.26: Dependence of signal intensities of CH<sub>3</sub>, CH<sub>2</sub> and CH carbons in the DEPT experiment on the angle  $\theta_y$  of the last polarisation pulse.

1D C-13 spektrum

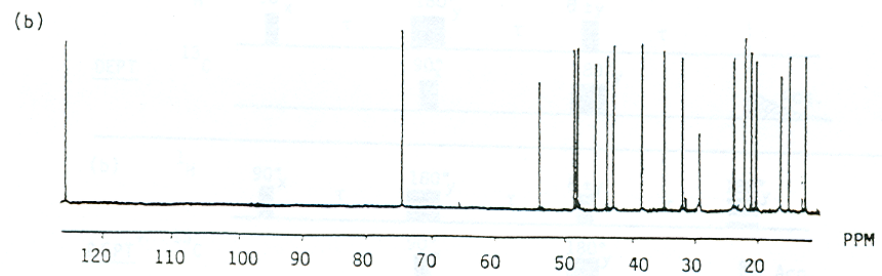
DEPT –  $\theta=45^\circ$

DEPT –  $\theta=90^\circ$

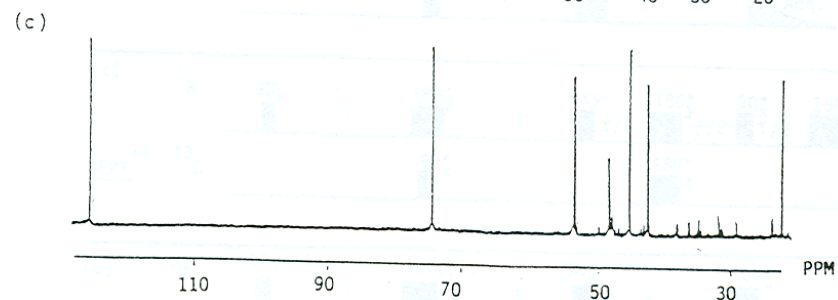
DEPT –  $\theta=135^\circ$



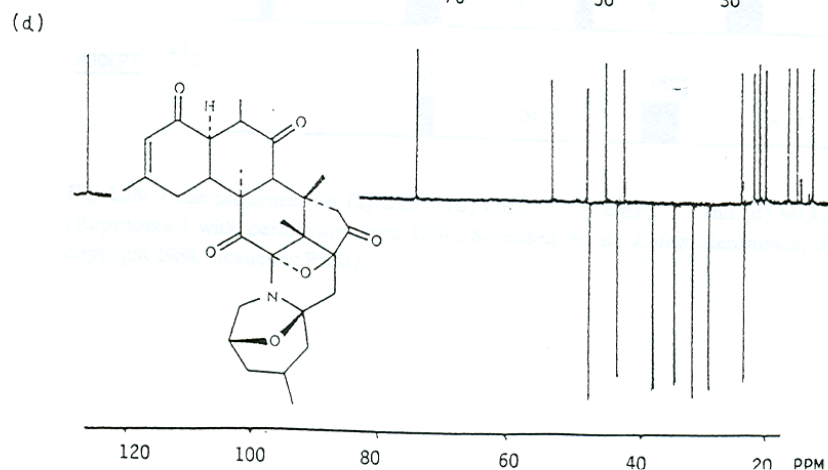
C, CH, CH<sub>2</sub> CH<sub>3</sub>



CH, CH<sub>2</sub> CH<sub>3</sub>



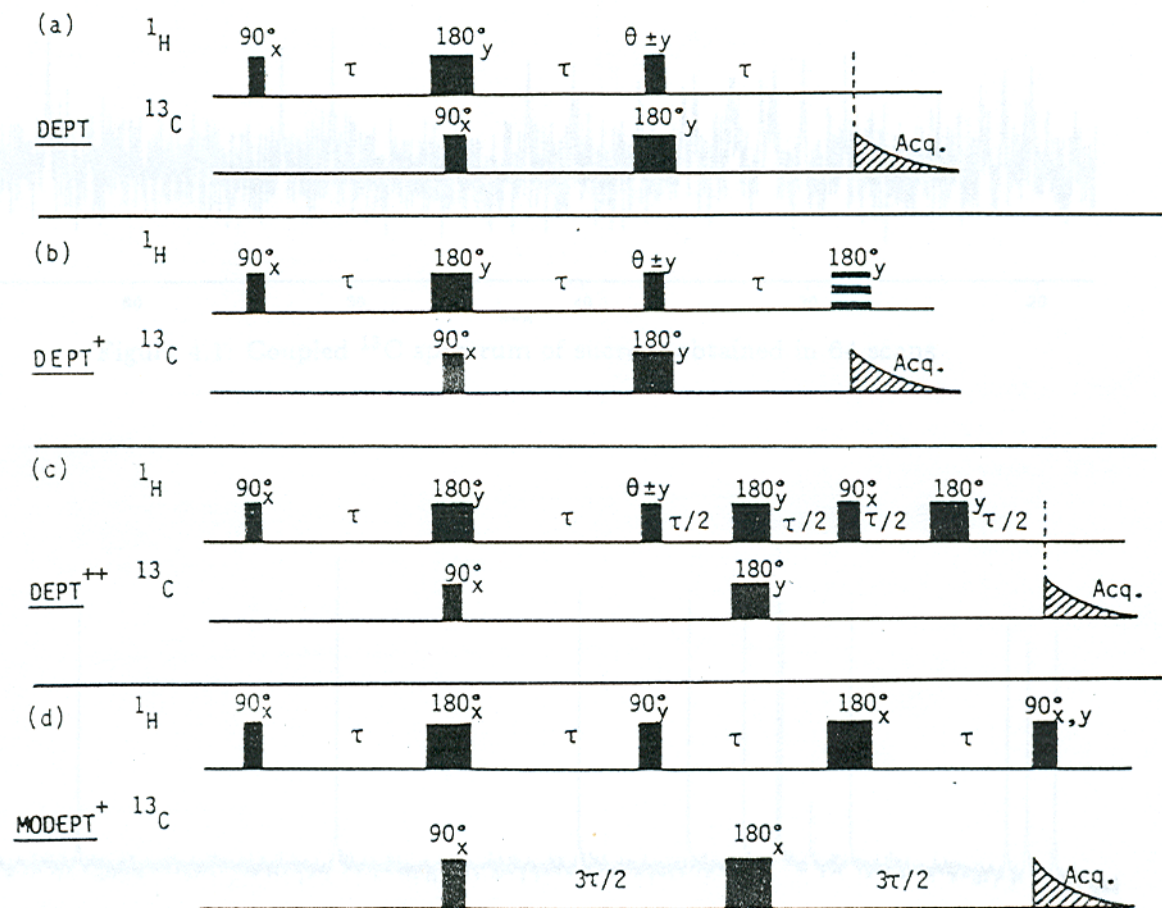
CH



CH<sup>+</sup>, CH<sub>2</sub><sup>-</sup>, CH<sub>3</sub><sup>+</sup>

# Metody 1D FT NMR spektroskopie

## Přenos polarizace – DEPT – různé varianty



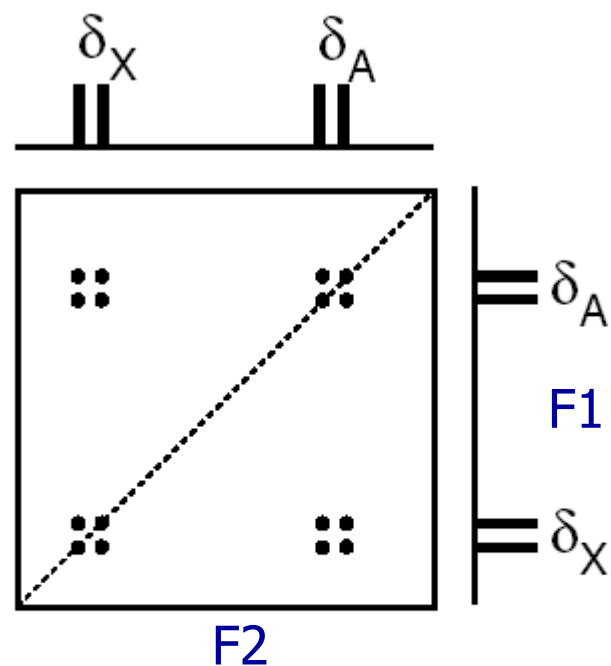
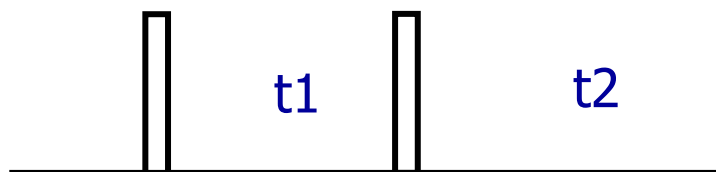
19.11.2014

# Metody 2D FT NMR spektroskopie

Elementární základy

Two-spin system AX

COSY – COrelated SpectroscopY

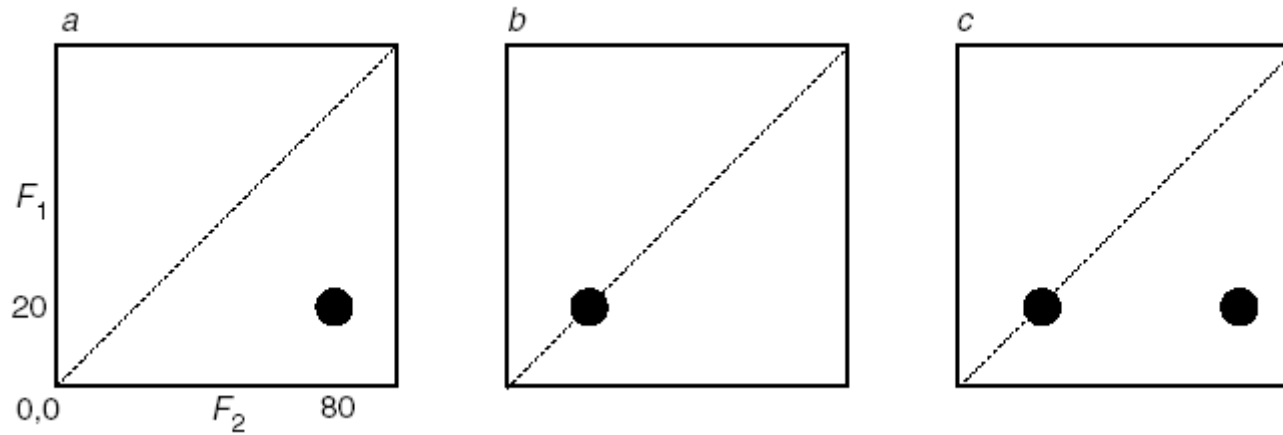
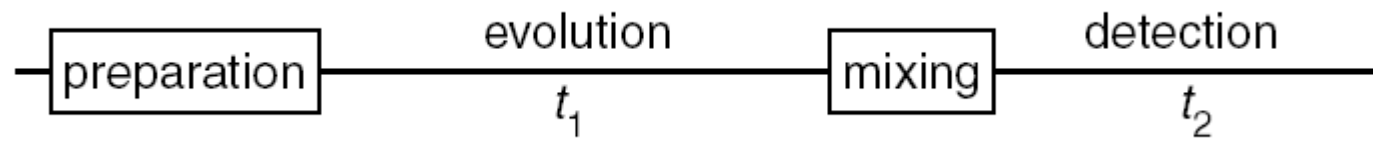


Schematic COSY spectrum for two coupled spins, A and X



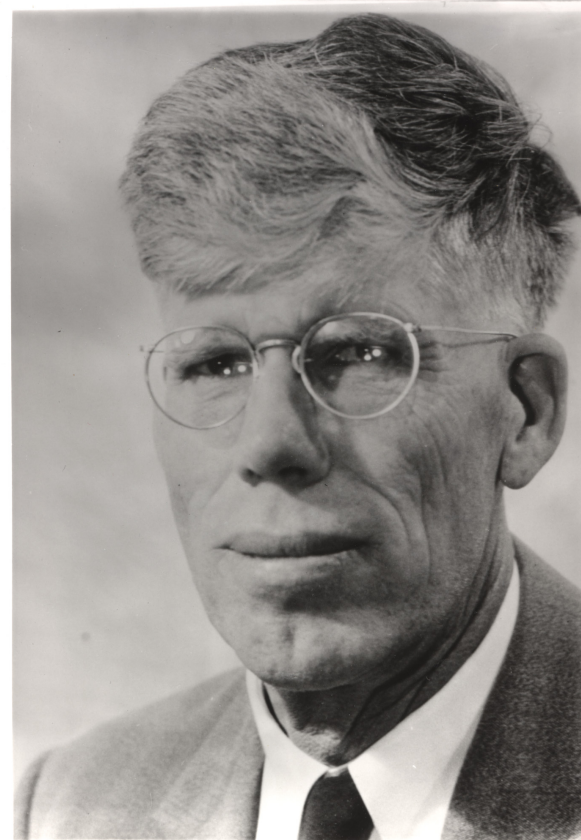
# Metody 2D FT NMR spektroskopie

## Elementární základy



# Russell Varian Prize

The Russell Varian prize honors the memory of the pioneer behind the first commercial Nuclear Magnetic Resonance spectrometers and co-founder of Varian Associates.



# Rules for the Russell Varian Prize

The Russell Varian Prize is awarded to a researcher based on **a single innovative contribution** (a single paper, patent, lecture or piece of hardware) **that has proven of high and broad impact on state-of-the-art NMR technology**. The prize is sponsored by Varian Inc., carries a monetary award of 15,000 Euro and was awarded for the first time in 2002.

Only single pieces of work are considered (a paper, a lecture, a patent, etc).

## Prize Committee 2009

Martin Billeter (EUROMAR Organizing Committee), Christian Griesinger, Jean Jeener (Chair), Ēriks Kupče, Vladimír Sklenář (Secretary), and Ole W. Sørensen.

# LAUREATE 2009

## Albert W. Overhauser (1925-2011)



|             |   |
|-------------|---|
| 1948        | UC Berkley, Physics and Mathematics         |
| 1951        | UC Berkley, Ph.D., Physics                  |
| 1951 - 1953 | postdoctoral fellow, University of Illinois |
| 1953 - 1958 | Cornell University                          |
| 1958 – 1973 | Ford Motor Company                          |
| 1973 – now  | Purdue University                           |

### **Purdue University**

Stuart Distinguished Professor of Physics

### **Awards and Honors**

National Medal of Science 1994

(the highest honor the United States bestows on its citizens for scientific achievement)

Elected to the National Academy of Sciences 1976

Oliver E. Buckley Solid State Physics Prize, 1975

Fellow of the American Academy of Arts and Sciences

Alexander von Humboldt Senior Scientist Award, 1979-80

Honorary Doctor of Laws Degree, Simon Fraser University, 1998

Honorary Doctor of Science Degree, University of Chicago, 1979

Honorary Doctor of Science Degree, Purdue University, 2005

# Awarded contribution

**The talk given by Albert Overhauser at the American Physical Society meeting on May 1, 1953, of which an abstract appeared as Albert W. Overhauser, Polarization of Nuclei in Metals, Phys. Rev. 91, 476 (1953), and full detail as Albert W. Overhauser, Polarization of Nuclei in Metals, Phys. Rev. 92, 411-415 (1953).**

This contribution is the seed of two important techniques in modern NMR: the Nuclear Overhauser Effect (NOE) and Dynamic Nuclear Polarization (DNP).

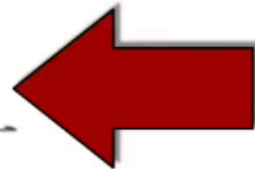
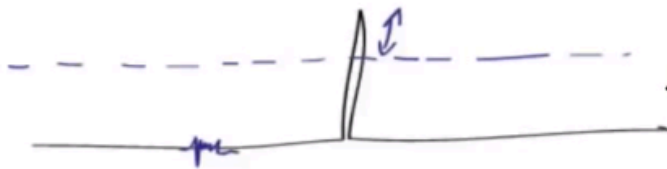
NOE describes the mutual influence of the polarizations of two spin species by spin-lattice relaxation. Originally, the spins were those of the nuclei of a metal and those of its conduction electrons. Soon after Overhauser's prediction, the effect was demonstrated by C. P. Slichter on metallic lithium, and was shown by Ionel Solomon to also exist between different nuclei in ordinary liquids. The NOE has played a key role in liquid state NMR over several decades, notably in establishing the overall structure of biological macromolecules in solution

DNP describes the often impressive enhancement of the nuclear polarization by strong irradiation of an electron resonance in the sample. Particularly within recent years, DNP technology has evolved considerably to a powerful sensitivity enhancement method in a growing variety of NMR.

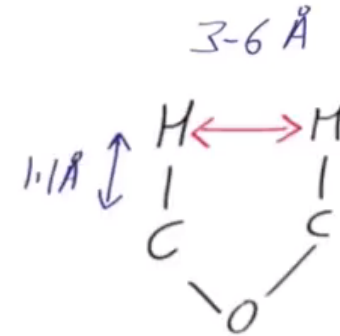
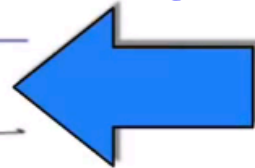
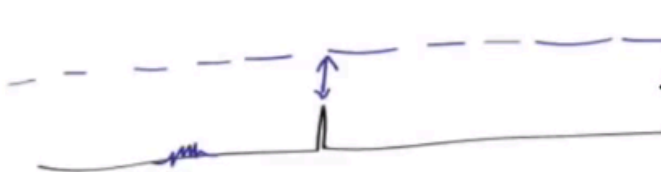
# NOE



**Positive**



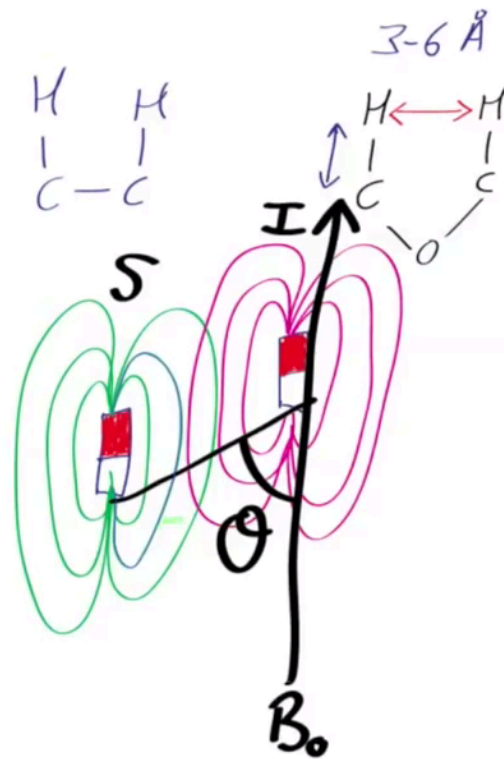
**Negative**



Through  
Space

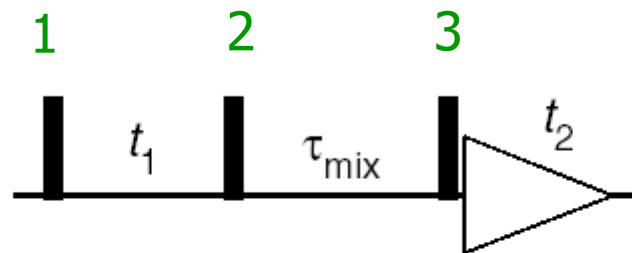
DIPOLAR  
COUPLING

# NOE



# 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:

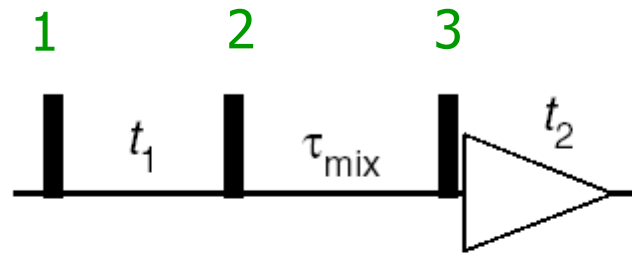
$$-\cos \Omega_1 t_1 I_{1y} \xrightarrow{\pi/2 I_{1x}} \xrightarrow{\pi/2 I_{2x}} -\cos \Omega_1 t_1 I_{1z}$$

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



# Metody 2D FT NMR spektroskopie

## NOE Spectroscopy a EXchange Spectroscopy



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

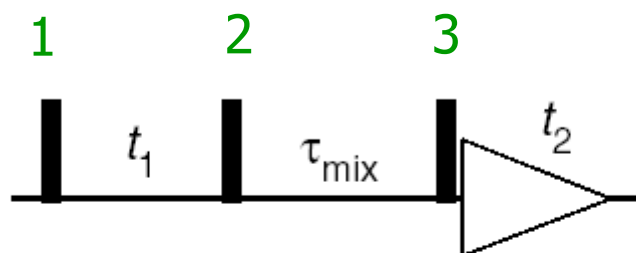
$$-\cos \Omega_1 t_1 I_{1z} \xrightarrow{\text{mixing}} -(1-f) \cos \Omega_1 t_1 I_{1z} - f \cos \Omega_1 t_1 I_{2z}$$

3. pulz:

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

# 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:

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

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

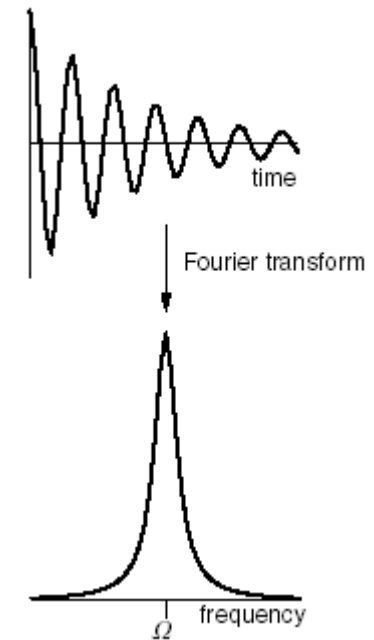
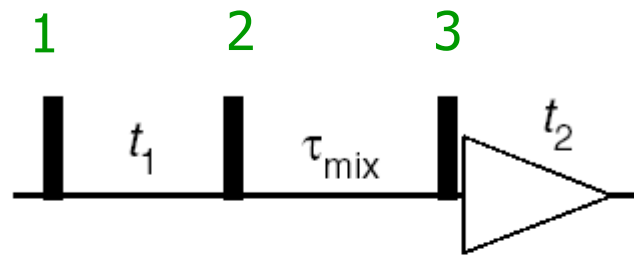
$$f \cos \Omega_2 t_2 \cos \Omega_1 t_1 I_{2y} - f \sin \Omega_2 t_2 \cos \Omega_1 t_1 I_{2x}$$

detekce F = I<sub>y</sub>:

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

# Metody 2D FT NMR spektroskopie

NOE Spectroscopy a EXchange Spectroscopy



FT zpracování  $t_2$

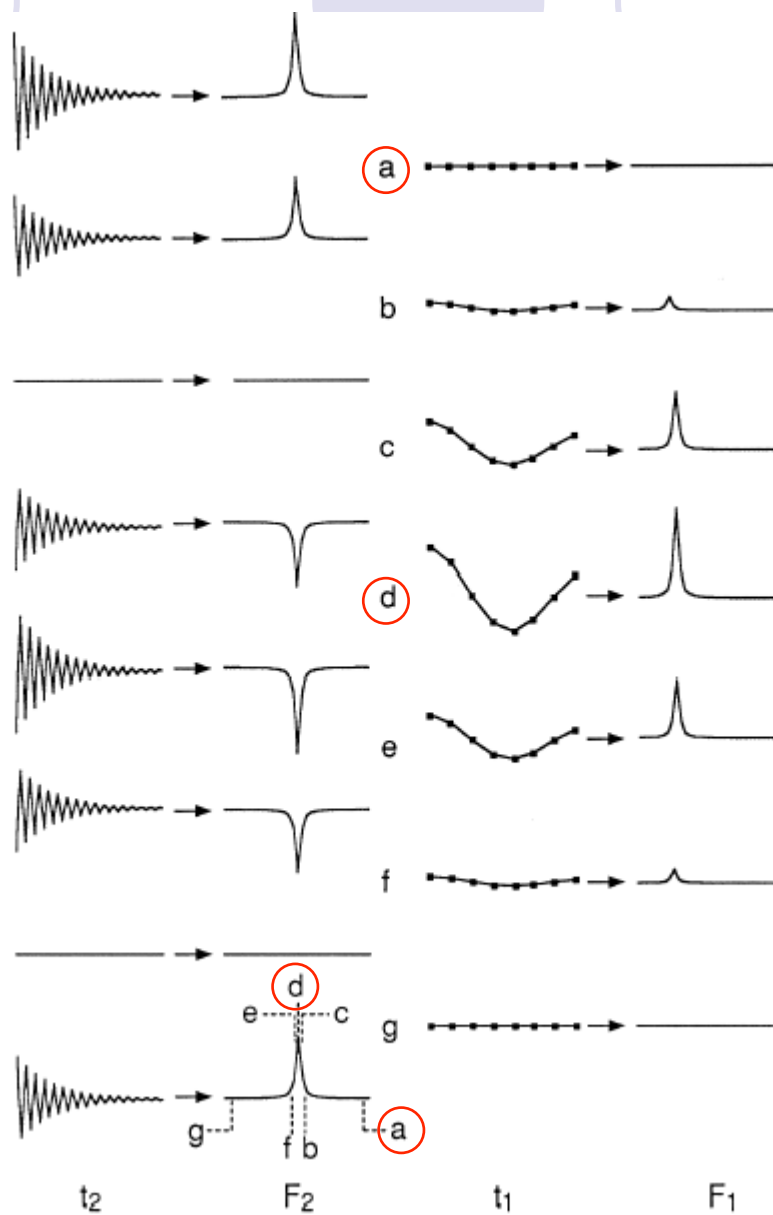
$$(1 - f)A_1^{(2)} \cos \Omega_1 t_1 + fA_2^{(2)} \cos \Omega_1 t_1$$

FT zpracování  $t_1$

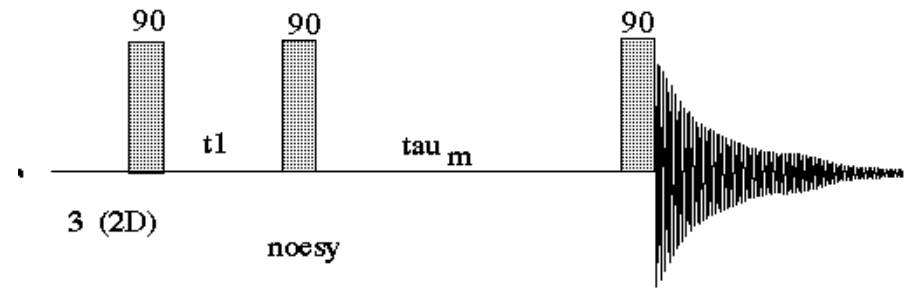
$$(1 - f)A_1^{(2)} A_1^{(1)} + fA_2^{(2)} A_1^{(1)}$$

# Metody 2D FT NMR spektroskopie

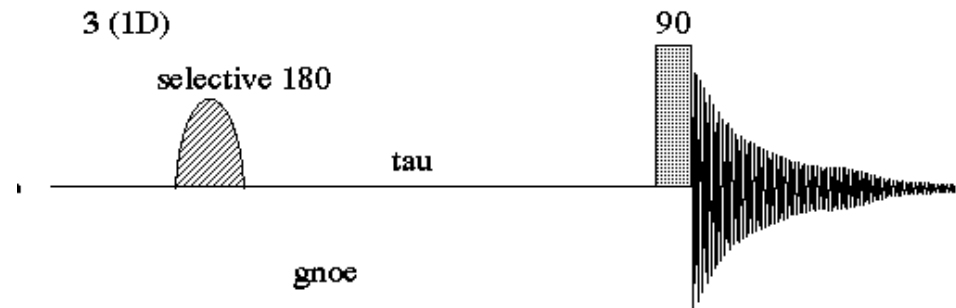
Modulace signálů



## 2D NOE – transient NOE



## 1D transient NOE

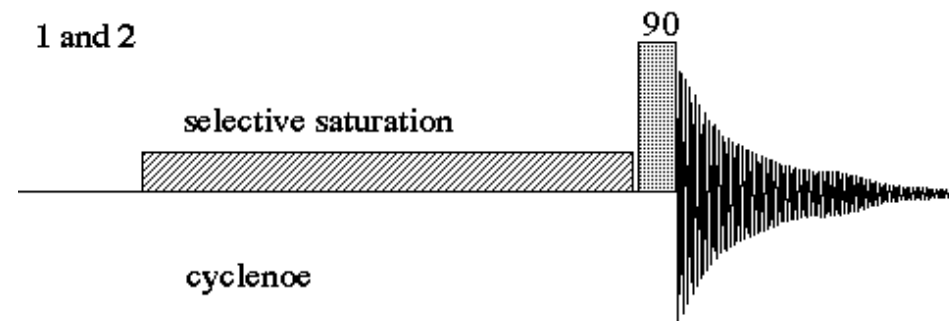


## 1D steady-state NOE

$$\tau_{irr.} > 5T_1$$

## 1D truncated-driven NOE (TOE)

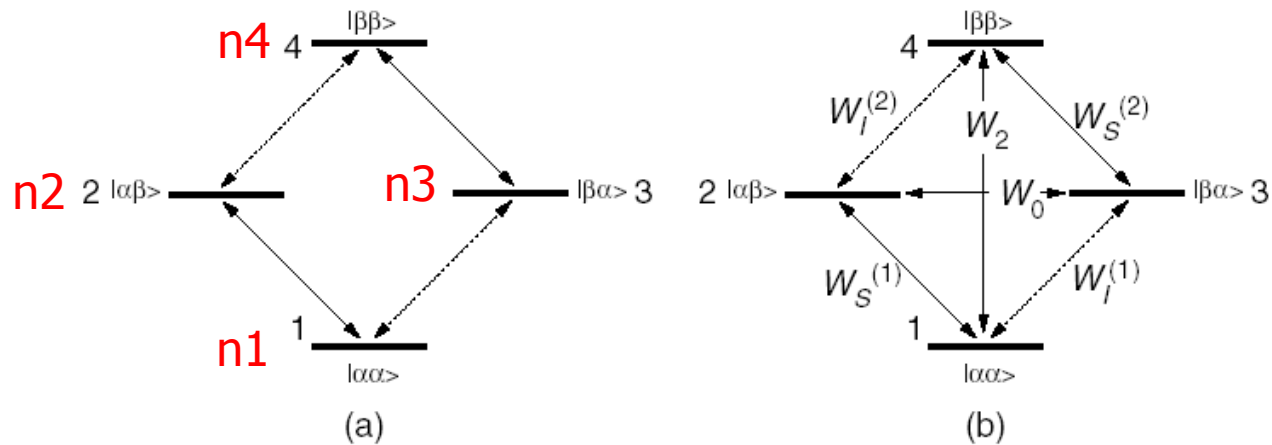
$$\tau_{irr.} \text{ variable}$$



# Metody 2D FT NMR spektroskopie

## NOE Spectroscopy a EXchange Spectroscopy

### Dvouspinový systém IS



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

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

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

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

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

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

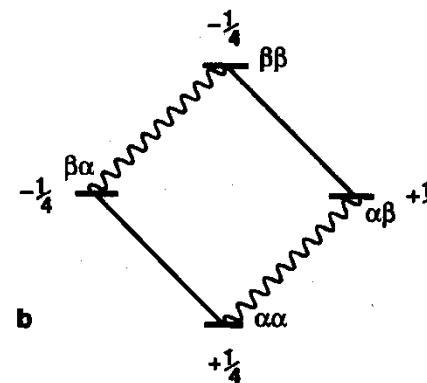
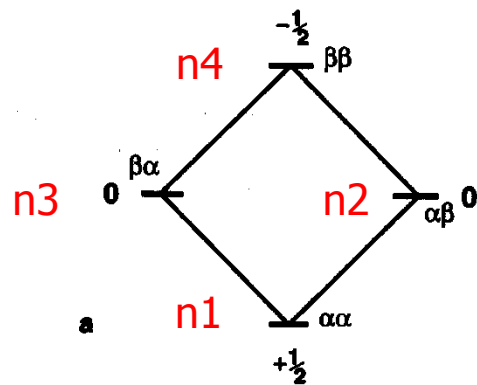
$$n_4 = \frac{1}{4}(E - I_z - S_z + 2I_z S_z)$$

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

# Metody 2D FT NMR spektroskopie

## NOE Spectroscopy a EXchange Spectroscopy

### Dvouspinový systém IS

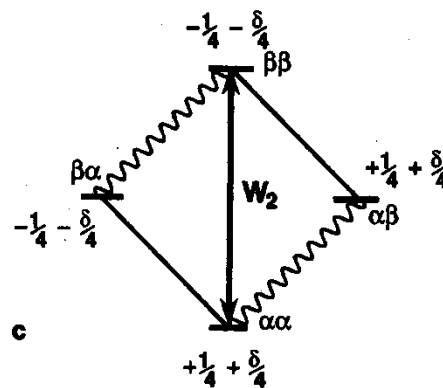


S – je saturován

I -Pozitivní NOE

$$\Delta = 1 + \delta$$

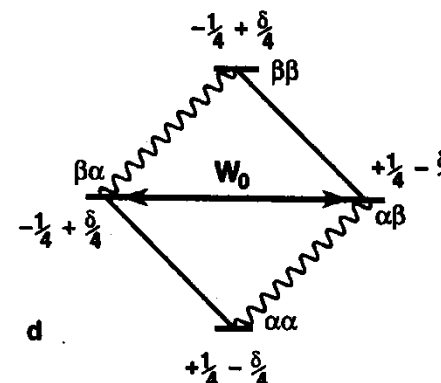
$W_2$  přechod generuje pozitivní NOE



I -Negativní NOE

$$\Delta = 1 - \delta$$

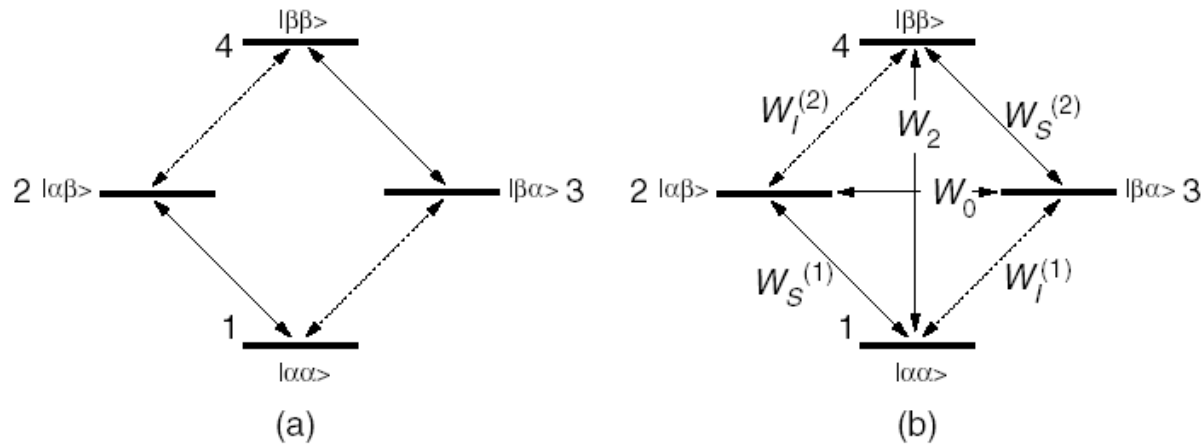
$W_0$  přechod generuje negativní NOE



$$I_z = n1 - n3 + n2 - n4$$

# 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

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

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

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

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

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

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



# Korelační čas

korelační funkce

$$g(\tau) = \overline{f(t)f(t + \tau)}$$

korelační čas

$$g(\tau) = \exp(-\tau/\tau_c)$$

Debye

$$\tau_c = 4\pi\eta a^3/3kT$$

$\eta$  – viskozita,  $a$  – poloměr molekuly

$$\tau_c \approx 10^{-12} W_M$$

$W_M$  molekulová hmotnost v Daltonech

$$\tau_c \approx 0.4 \cdot 10^{-12} W_M$$

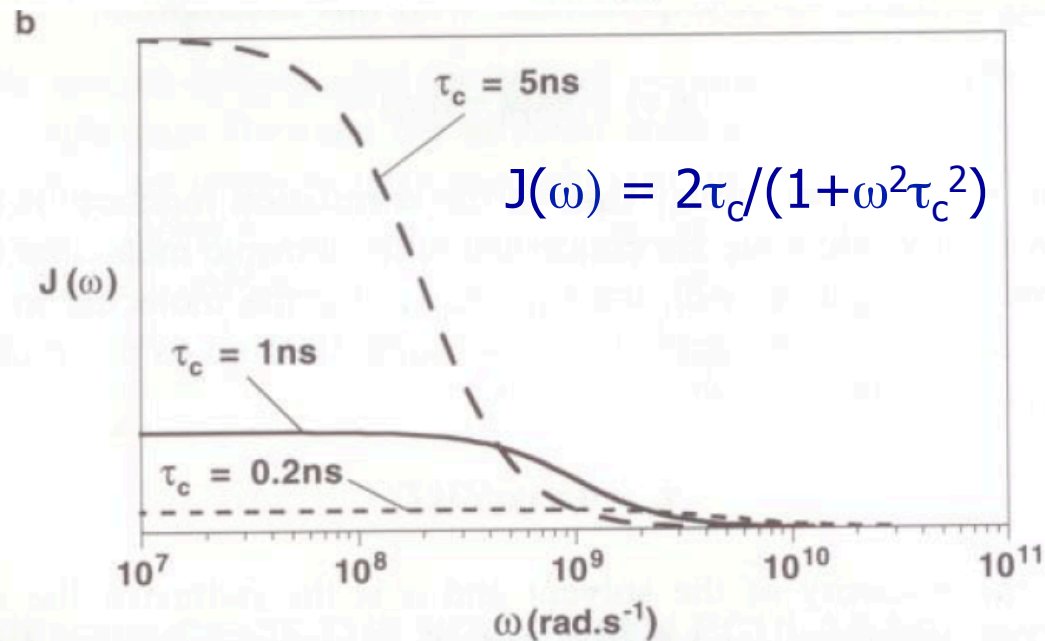
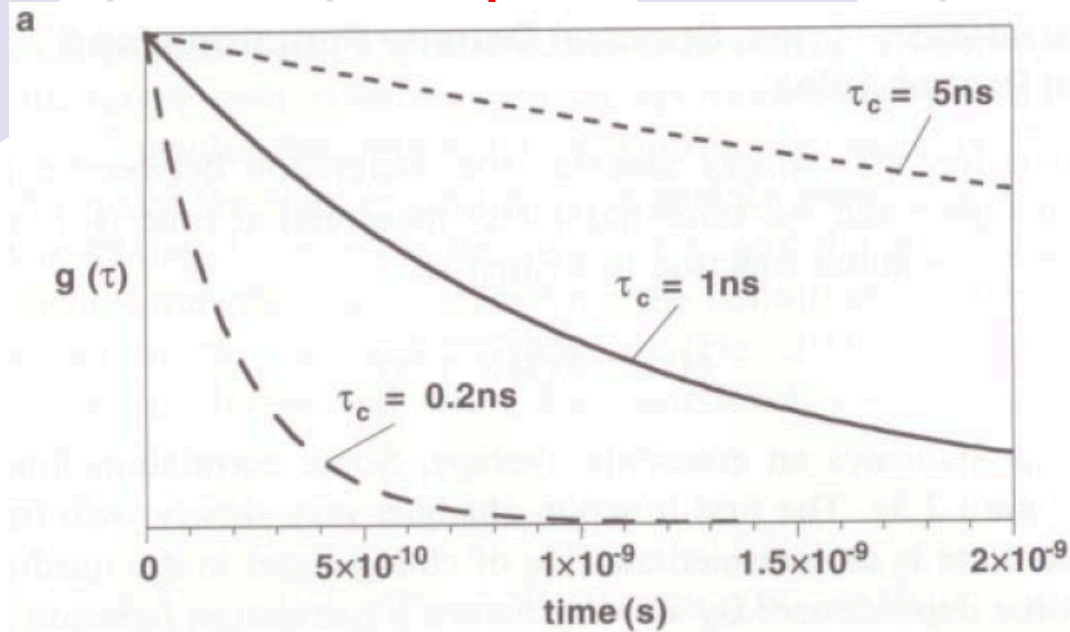
pro globulární proteiny

měření korelačního času

$$\frac{1}{T_1(^{13}\text{C})} = \left(\frac{\mu_0}{4\pi}\right)^2 \frac{N\gamma_H^2\gamma_C^2\hbar^2\tau_c}{r_{\text{CH}}^6}$$

# Korelační funkce a spektrální funkce hustoty

Fourier Transform



! logaritmická škála

# Metody 2D FT NMR spektroskopie

## NOE Spectroscopy a EXchange Spectroscopy

### Dvouspinový 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

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

$$K = (\mu_0/4\pi)h/2\pi \cdot \gamma_I \cdot \gamma_S \cdot r_{IS}^{-3}$$

# 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

Dvouspinový systém IS

Dvouspinový HOMONUKLEÁRNÍ systém IS

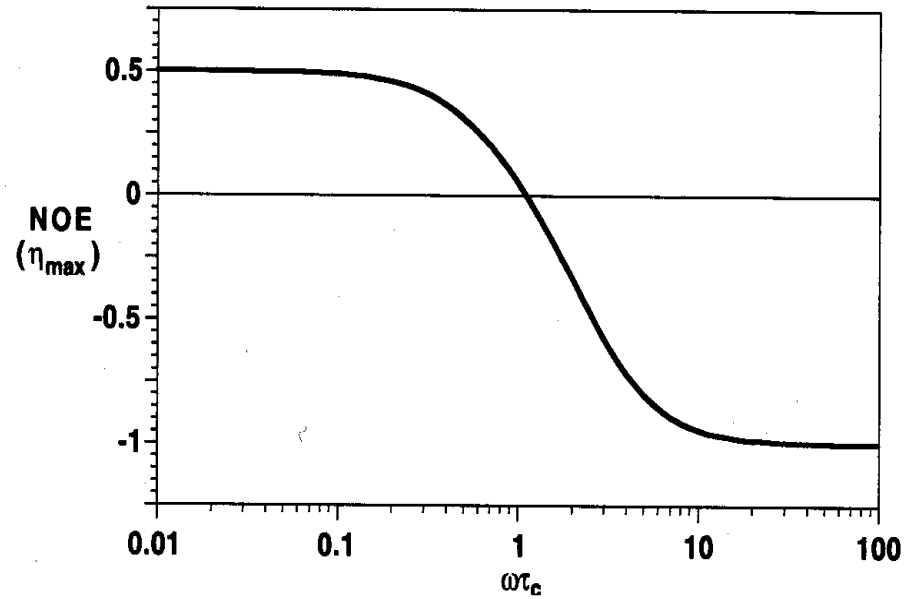
$$f_I\{S\} = \eta_{\max} = \frac{5 + \omega^2\tau_c^2 - 4\omega^4\tau_c^4}{10 + 23\omega^2\tau_c^2 + 4\omega^4\tau_c^4}$$

# Metody 2D FT NMR spektroskopie

NOE Spectroscopy a EXchange Spectroscopy

NOE  $f_I\{S\} =$

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

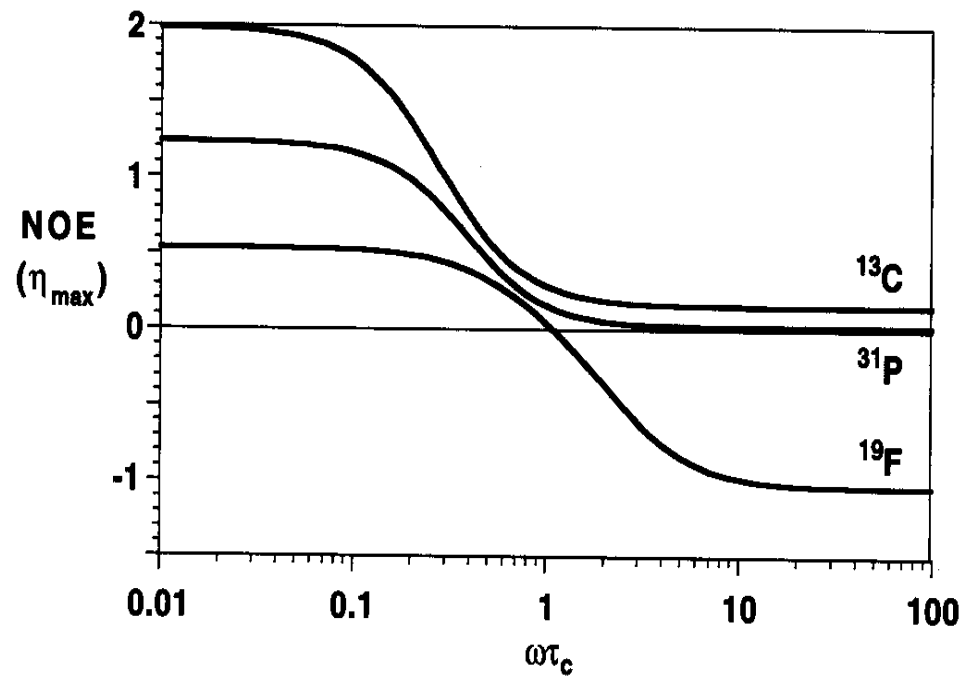


# Metody 2D FT NMR spektroskopie

NOE Spectroscopy a EXchange Spectroscopy

NOE  $f_I\{S\} =$

NOE max =  $\gamma_S/2\gamma_I$



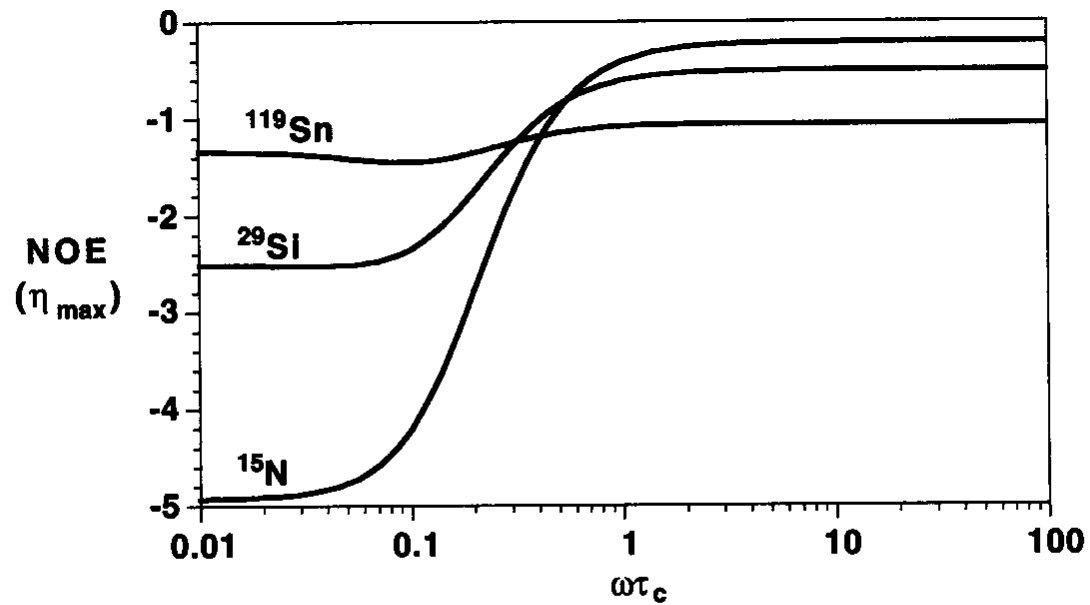


# Metody 2D FT NMR spektroskopie

## NOE Spectroscopy a EXchange Spectroscopy

NOE  $f_I\{S\} =$

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



Negativní  $\gamma_I$

# 2D NOE – transient NOE

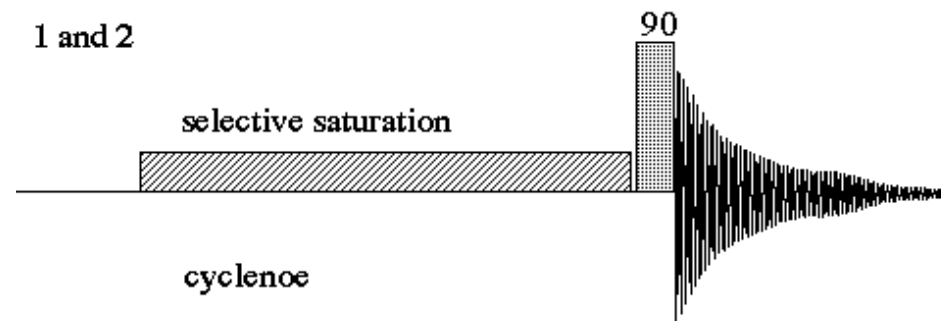
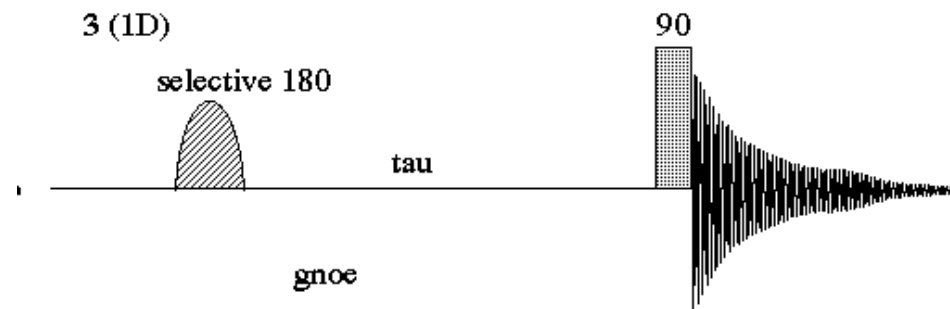
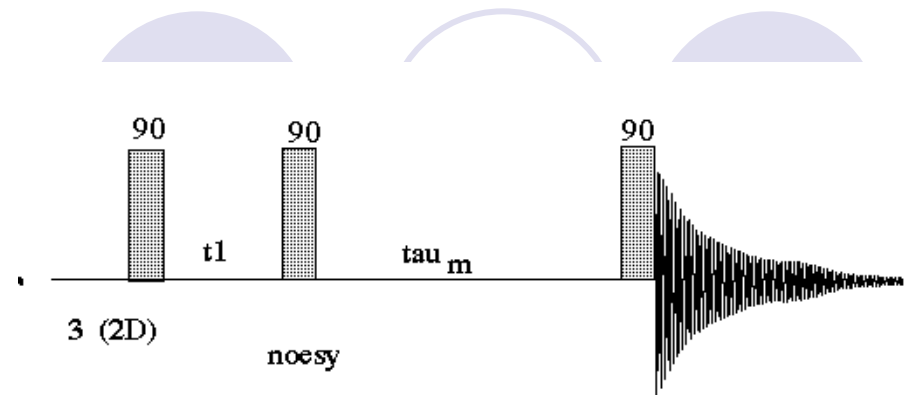
## 1D transient NOE

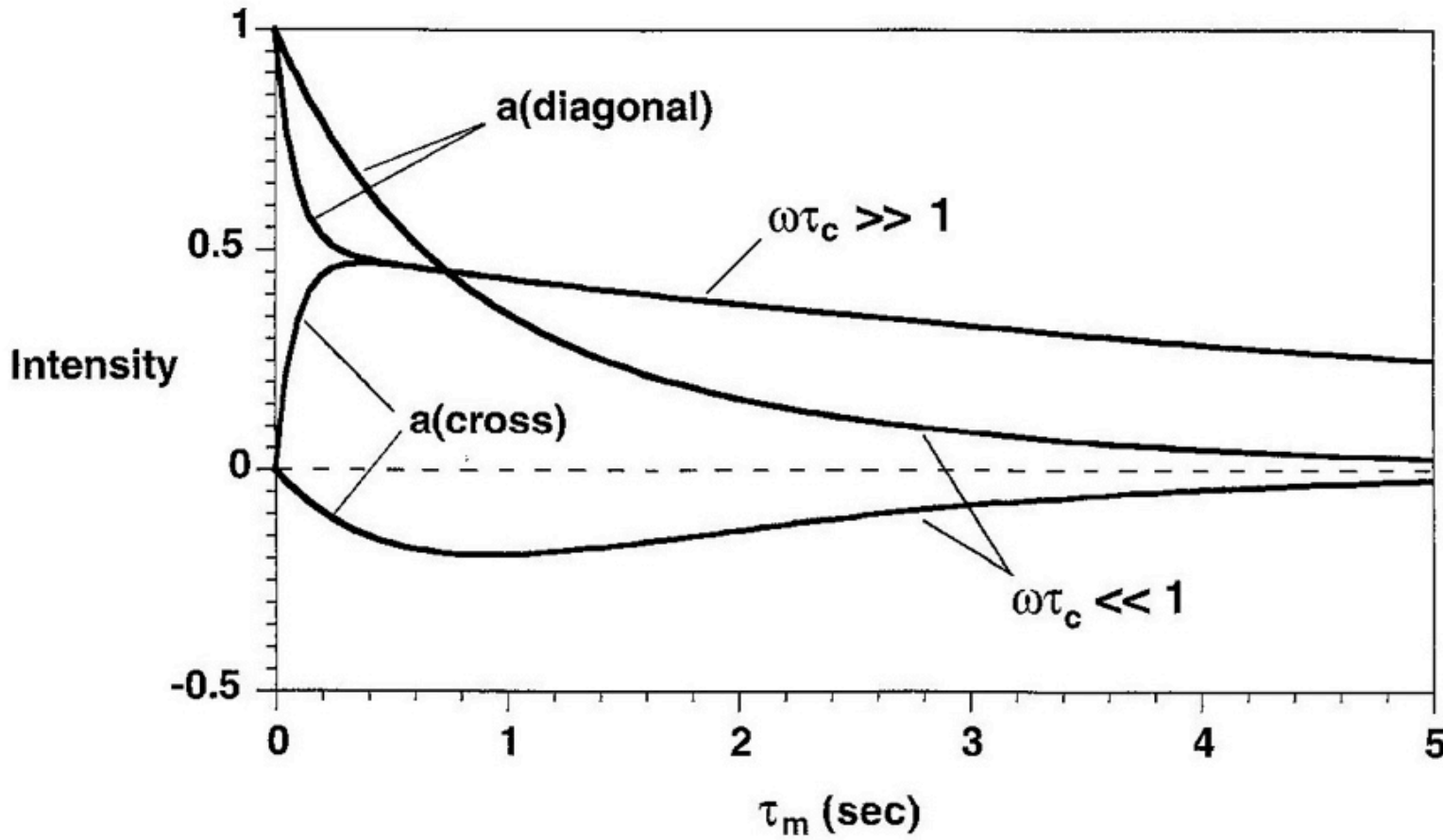
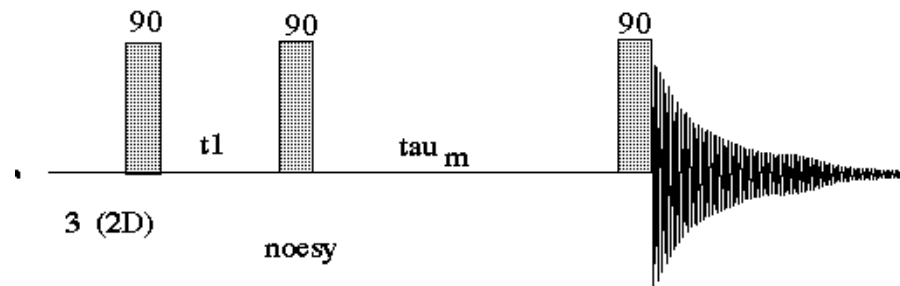
## 1D steady-state NOE

$$\tau_{irr.} > 5T_1$$

## 1D truncated-driven NOE (TOE)

$$\tau_{irr.} \text{ variable}$$



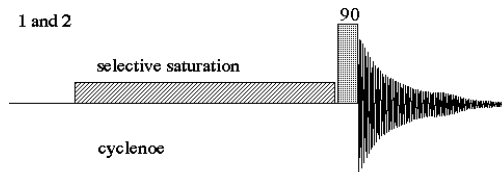


1D steady-state NOE

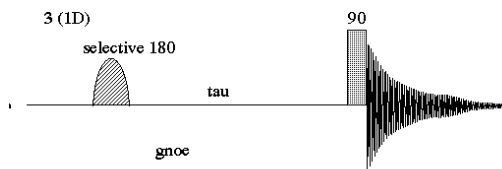
$\tau_{irr.} > 5T_1$

1D truncated-driven NOE  
(TOE)

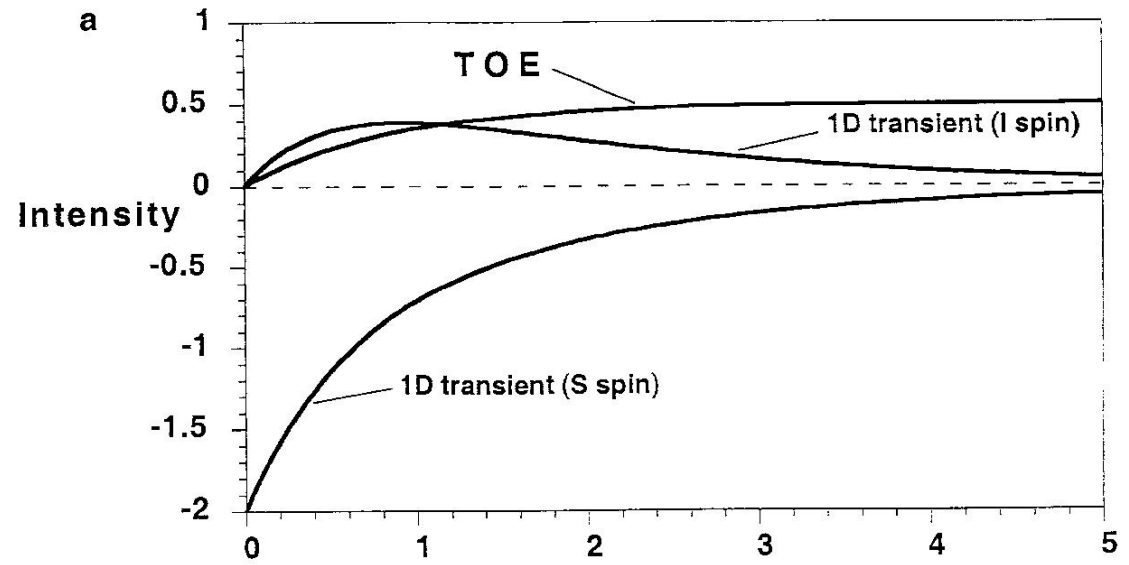
$\tau_{irr.}$  variable



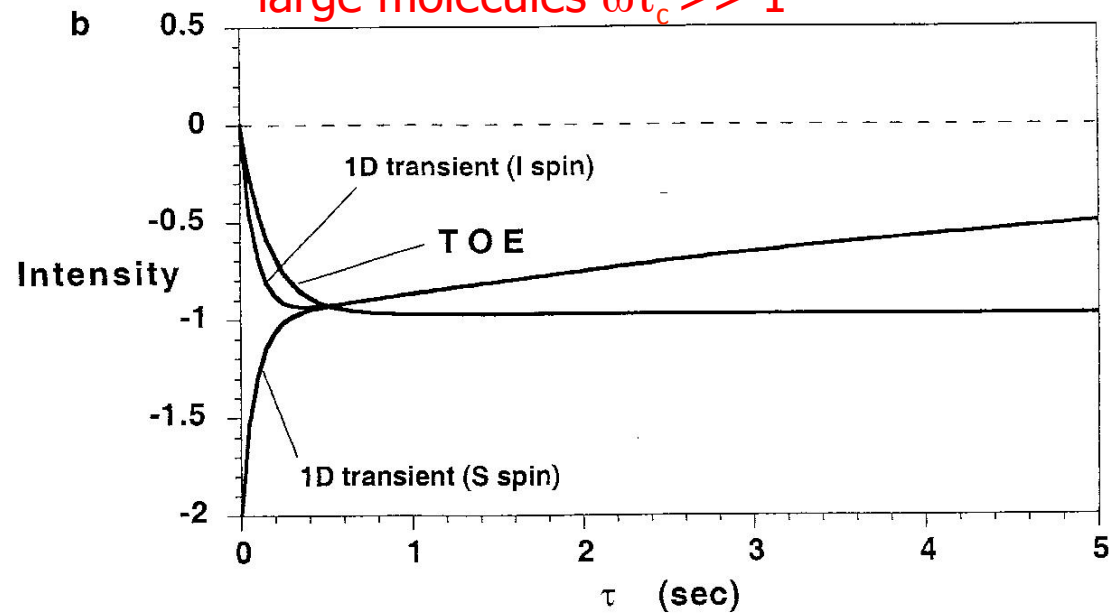
1D transient NOE



small molecules  $\omega\tau_c \ll 1$



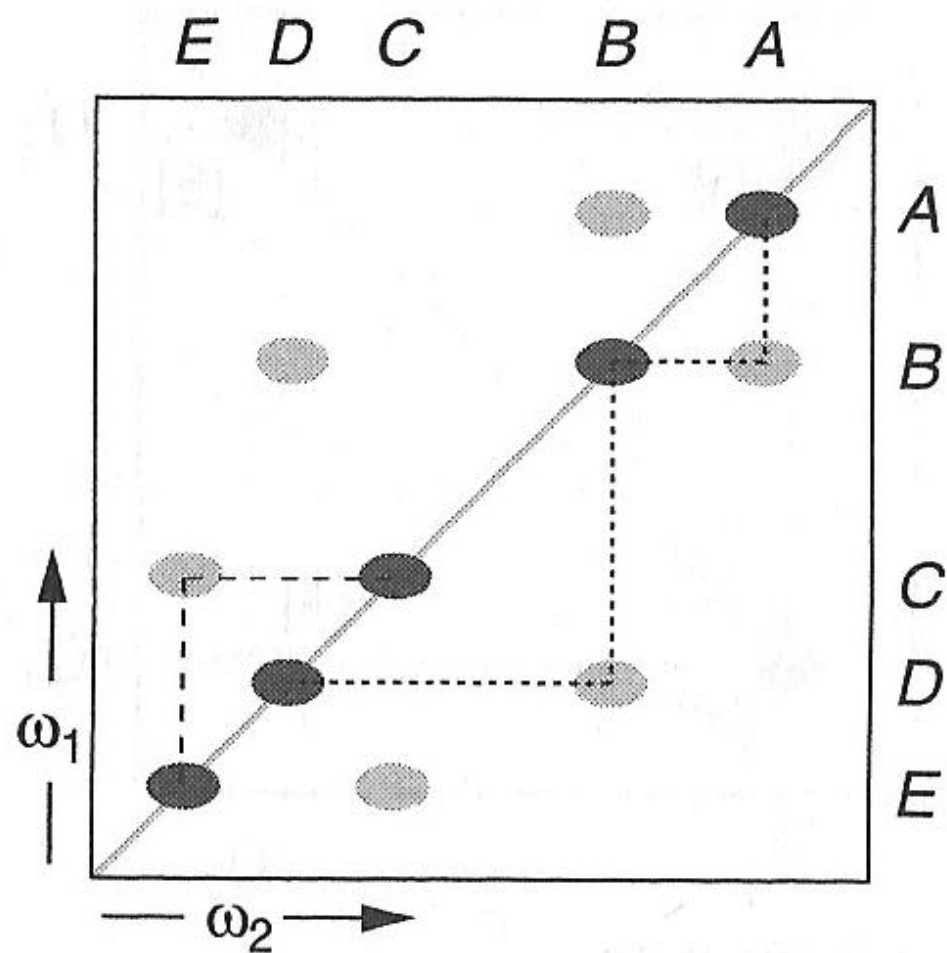
large molecules  $\omega\tau_c \gg 1$



# Metody 2D FT NMR spektroskopie

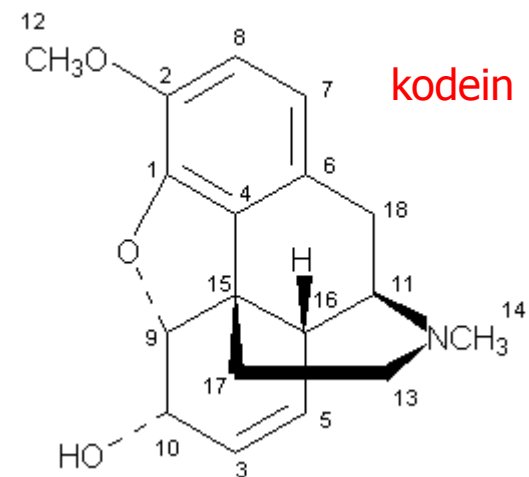
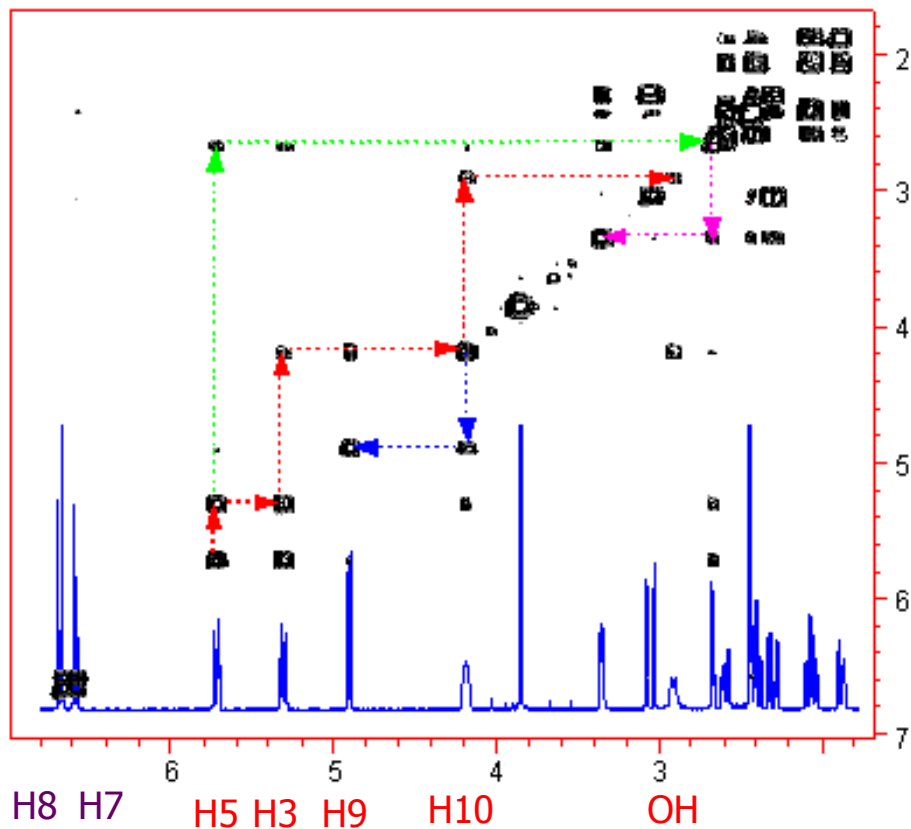
Experimenty s přenosem koherence - homonukleární

COSY



# Metody 2D FT NMR spektroskopie

Experimenty s přenosem koherence - homonukleární



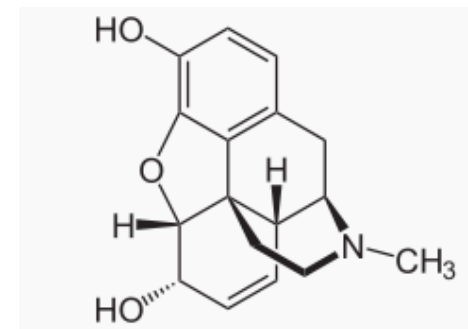
H-5 -> H-3 -> H-10 -> OH

H-10 -> H-9

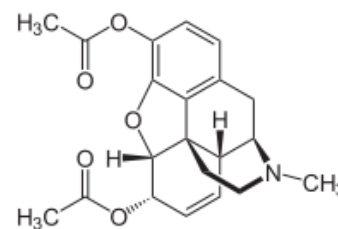
H-5 -> H16

H-16 -> H-11

**morfin**



**heroin**



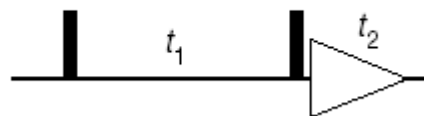
# Metody 2D FT NMR spektroskopie

## 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  $\Omega_1$

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

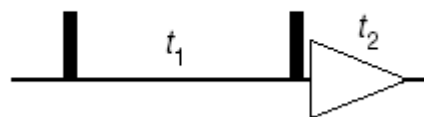
t1: - spin  $I_1$  vliv  $J_{12}$

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

# Metody 2D FT NMR spektroskopie

Experimenty s přenosem koherence - homonukleární

COSY



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

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

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

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

$$\{3\} \rightarrow I_{1x} \cos \pi J_{12} t_1 \sin \Omega_1 t_1 \cos \pi J_{12} t_2 \cos \Omega_1 t_2 \propto f(\Omega_1 \Omega_1) \quad \text{diagonální peak}$$

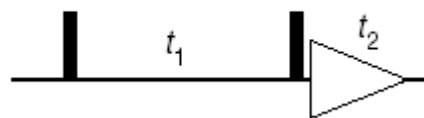
$$\{4\} \rightarrow I_{2x} \sin \pi J_{12} t_1 \sin \Omega_1 t_1 \sin \pi J_{12} t_2 \cos \Omega_2 t_2 \propto f(\Omega_1 \Omega_2) \quad \text{interakční peak}$$



# Metody 2D FT NMR spektroskopie

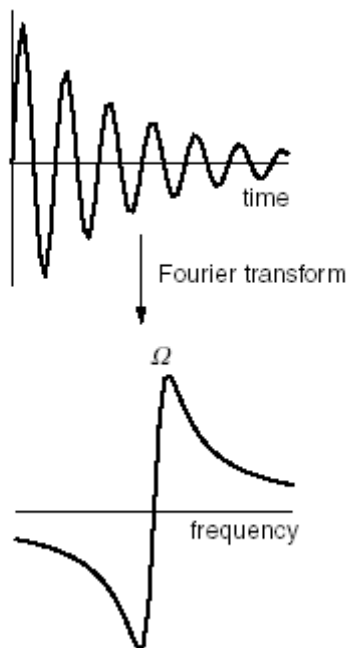
## Experimenty s přenosem koherence - homonukleární

COSY



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

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

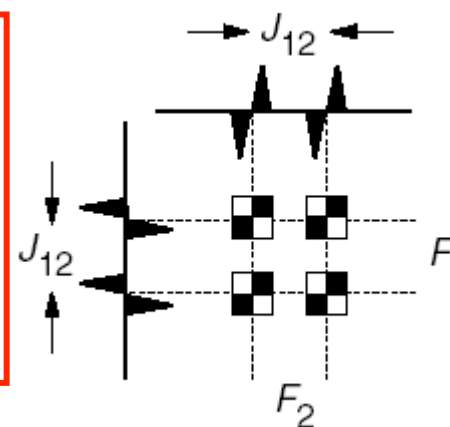


absorpce vers. disperse

$\sin^n$  v každé dimenzi separátně

$n$  sudé – absorpce (0,2,4,...)

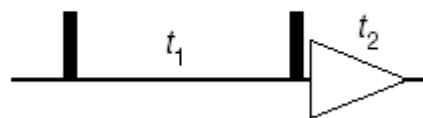
$n$  liché – disperse (1,3,5,...)



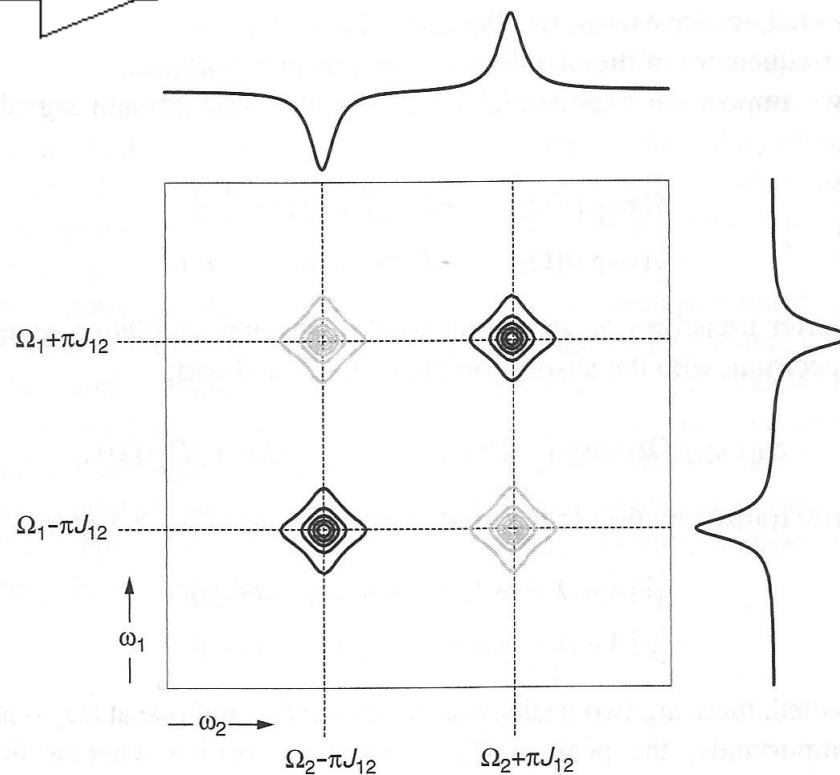
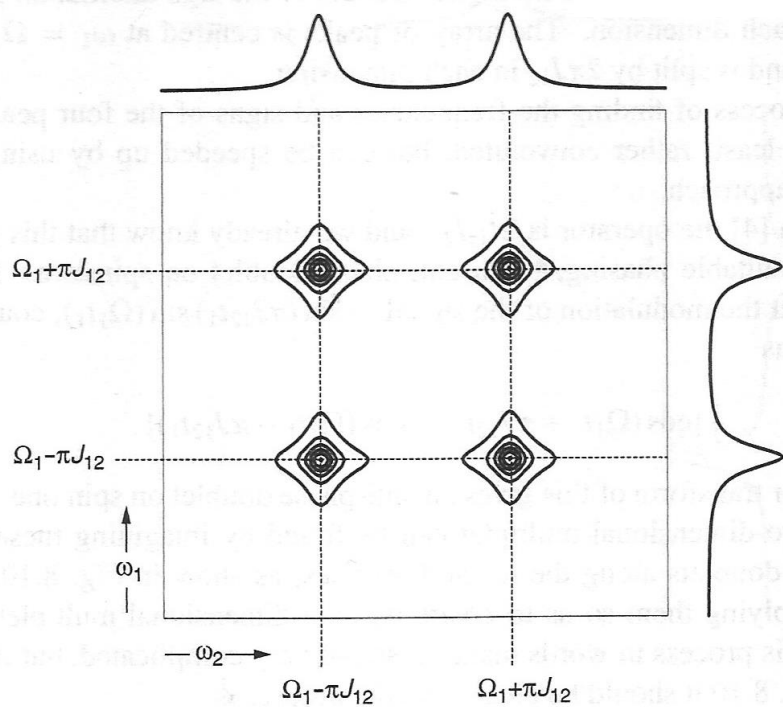
# Metody 2D FT NMR spektroskopie

Experimenty s přenosem koherence - homonukleární

COSY



vliv zpracování spekter



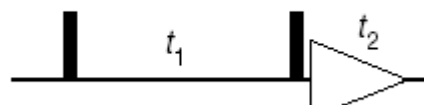
diagonální signál

interakční signál

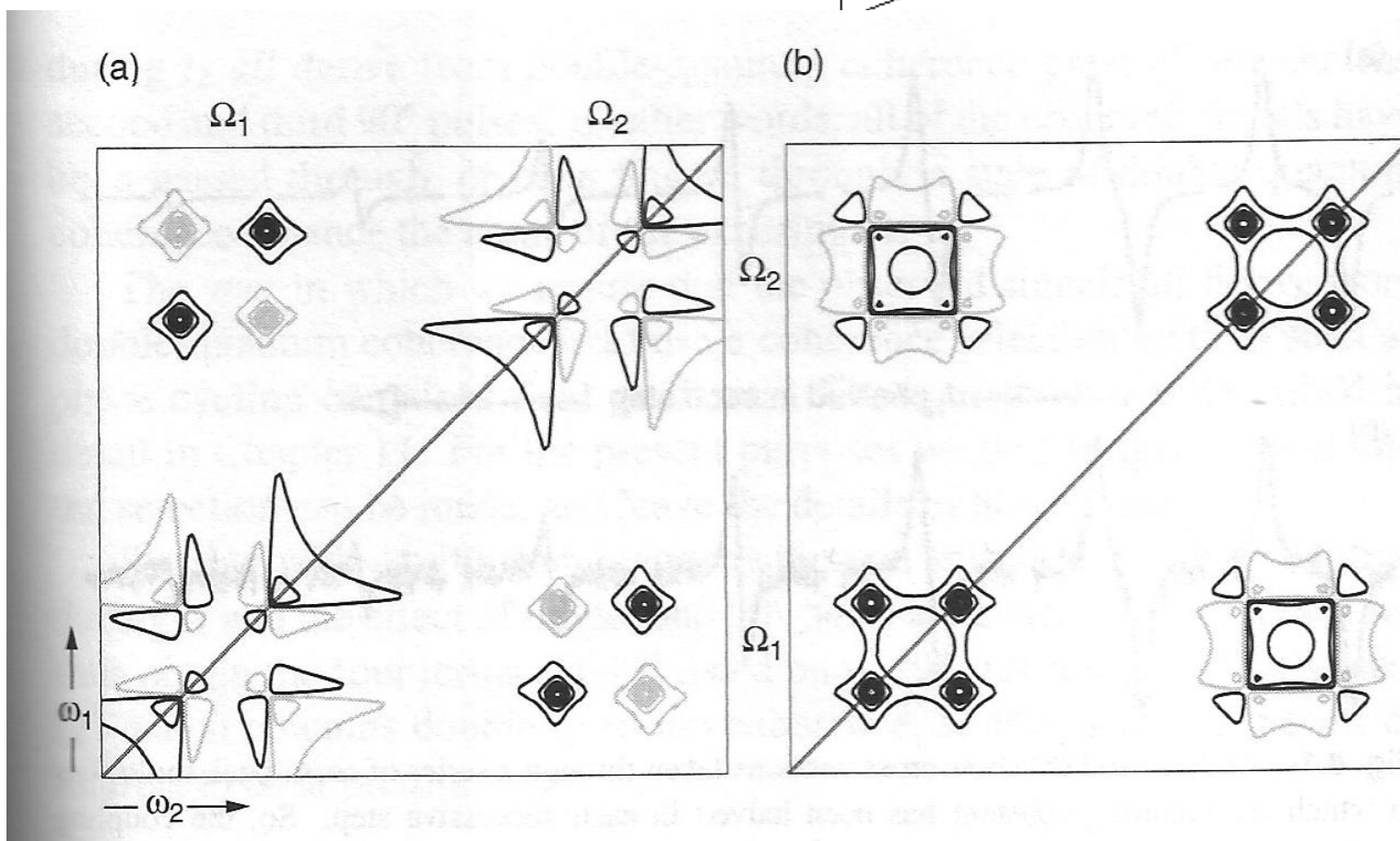
# Metody 2D FT NMR spektroskopie

Experimenty s přenosem koherence - homonukleární

COSY



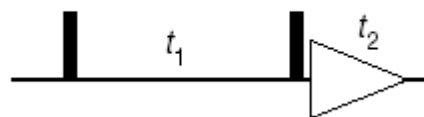
vliv zpracování spekter



# Metody 2D FT NMR spektroskopie

Experimenty s přenosem koherence - homonukleární

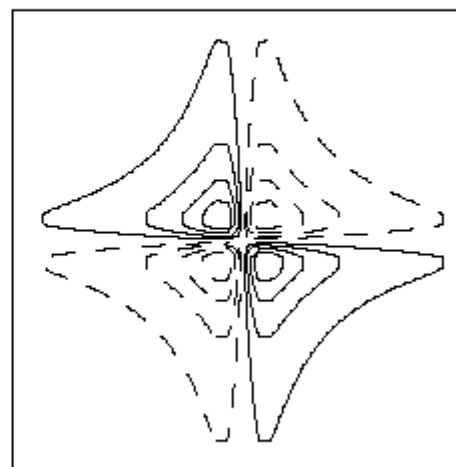
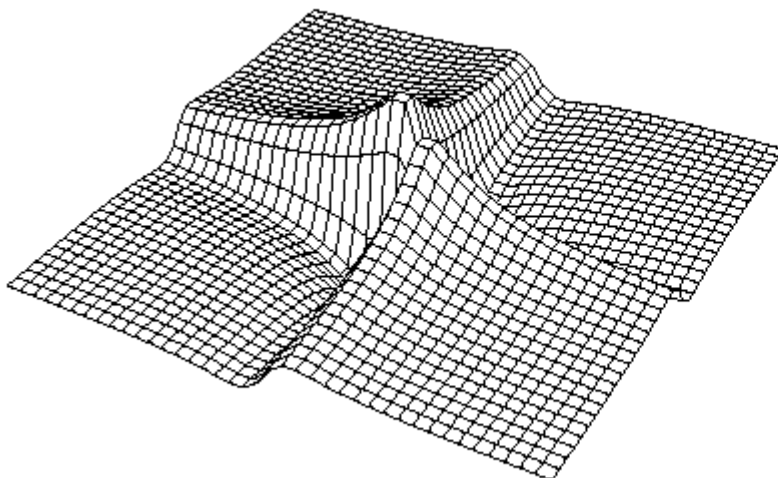
COSY



diagonální signál

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

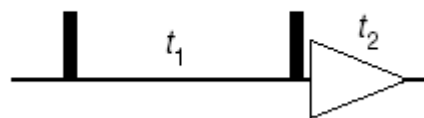
$$\cos \pi J_{12} t_1 \sin \Omega_1 t_1 = \frac{1}{2} \{ \sin(\Omega_1 t_1 + \pi J_{12} t_1) + \sin(\Omega_1 t_1 - \pi J_{12} t_1) \}$$



# Metody 2D FT NMR spektroskopie

Experimenty s přenosem koherence - homonukleární

COSY

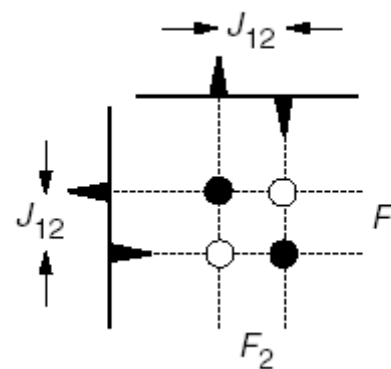
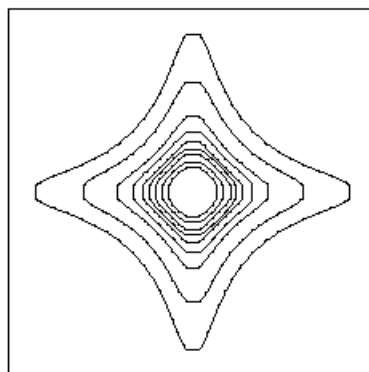
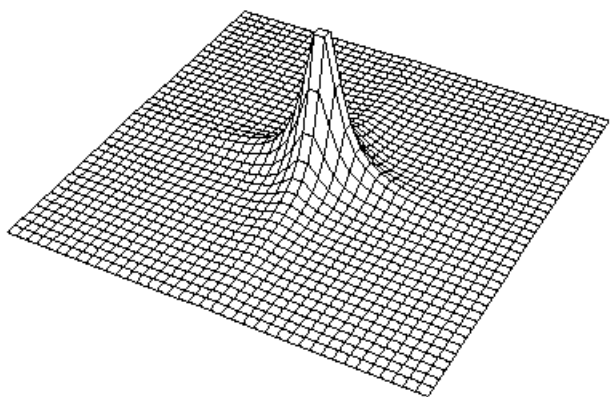


interakční signál

{ 4 }

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

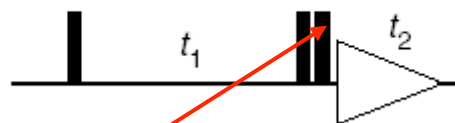
$$\sin \pi J_{12} t_1 \sin \Omega_1 t = \frac{1}{2} \{ -\cos(\Omega_1 t_1 + \pi J_{12} t_1) + \cos(\Omega_1 t_1 - \pi J_{12} t_1) \}$$



# Metody 2D FT NMR spektroskopie

Experimenty s přenosem koherence - homonukleární

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°(x)

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

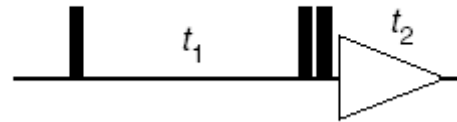
$$-\frac{1}{2} \sin \pi J_{12} t_1 \cos \Omega_1 t_1 (2I_{1x}I_{2z} + 2I_{1z}I_{2x})$$

diagonální pík    interakční pík

# Metody 2D FT NMR spektroskopie

Experimenty s přenosem koherence - homonukleární

DQF COSY



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

$$\frac{1}{2} I_{1y} \sin \pi J_{12} t_1 \cos \Omega_1 t_1 \sin \pi J_{12} t_2 \cos \Omega_1 t_2 \propto f(\Omega_1, \Omega_1)$$

diagonální peak

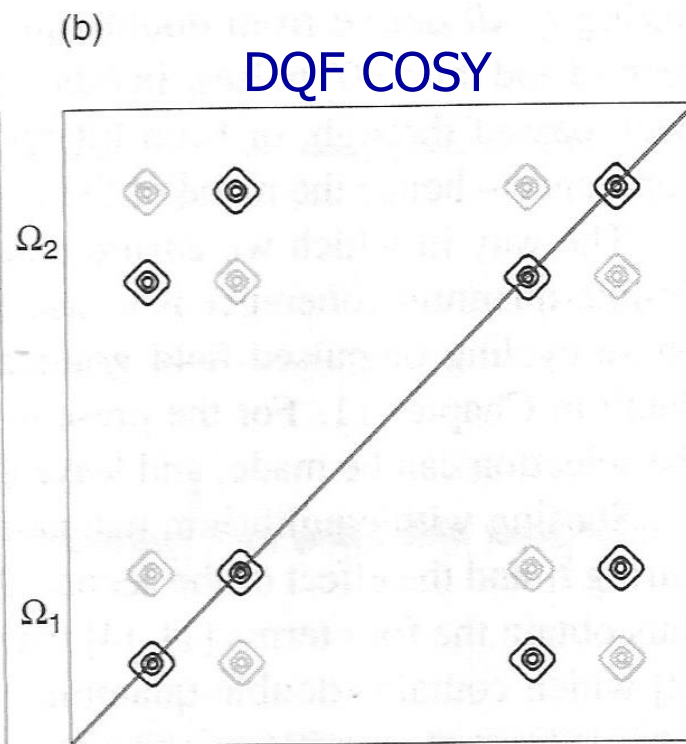
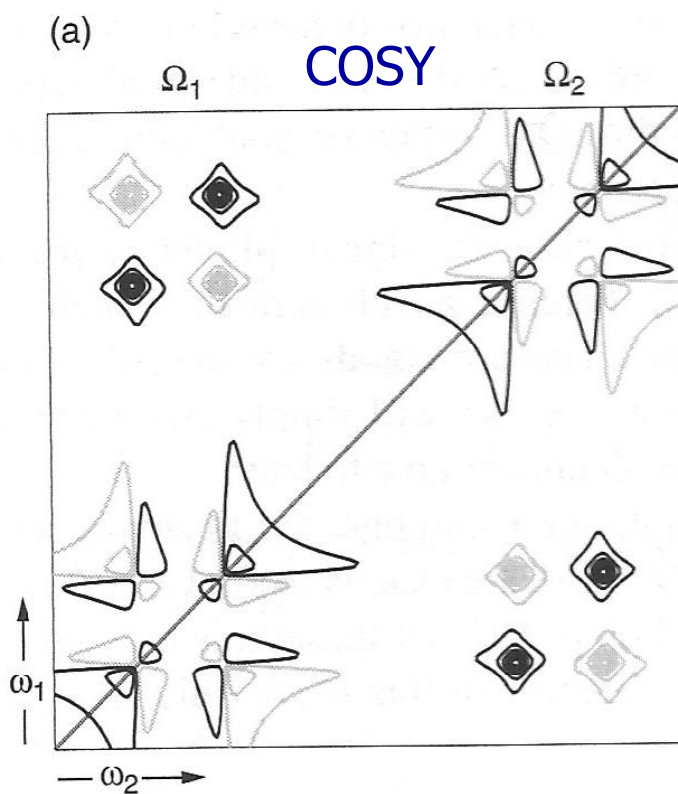
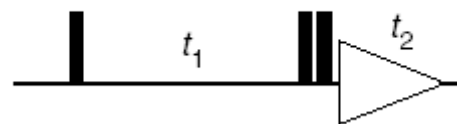
$$\frac{1}{2} I_{2y} \sin \pi J_{12} t_1 \cos \Omega_1 t_1 \sin \pi J_{12} t_2 \cos \Omega_2 t_2 \propto f(\Omega_1, \Omega_2)$$

interakční peak

poloviční citlivost

# Metody 2D FT NMR spektroskopie

Experimenty s přenosem koherence - homonukleární

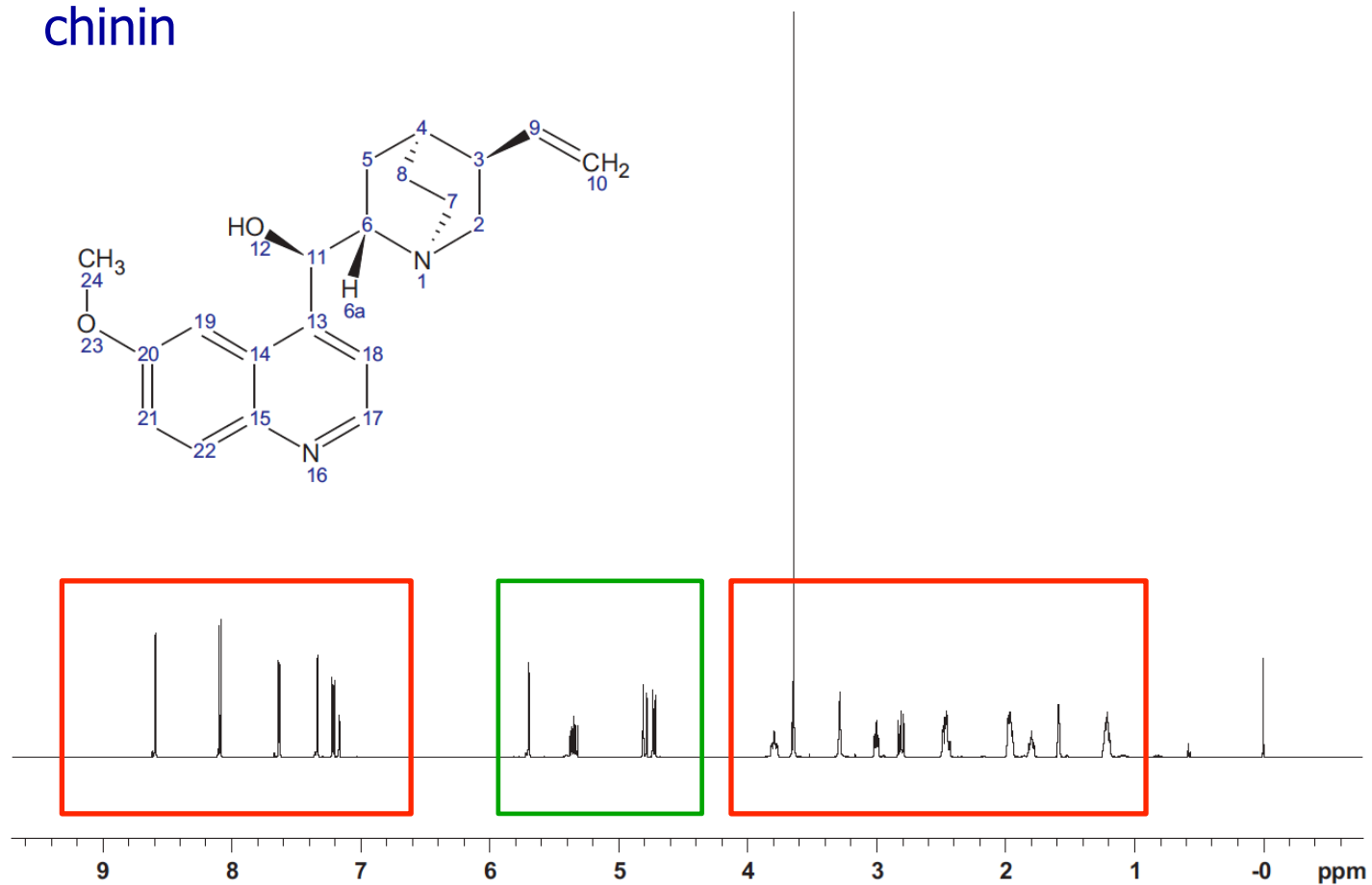




# Metody 2D FT NMR spektroskopie

Experimenty s přenosem koherence - homonukleární

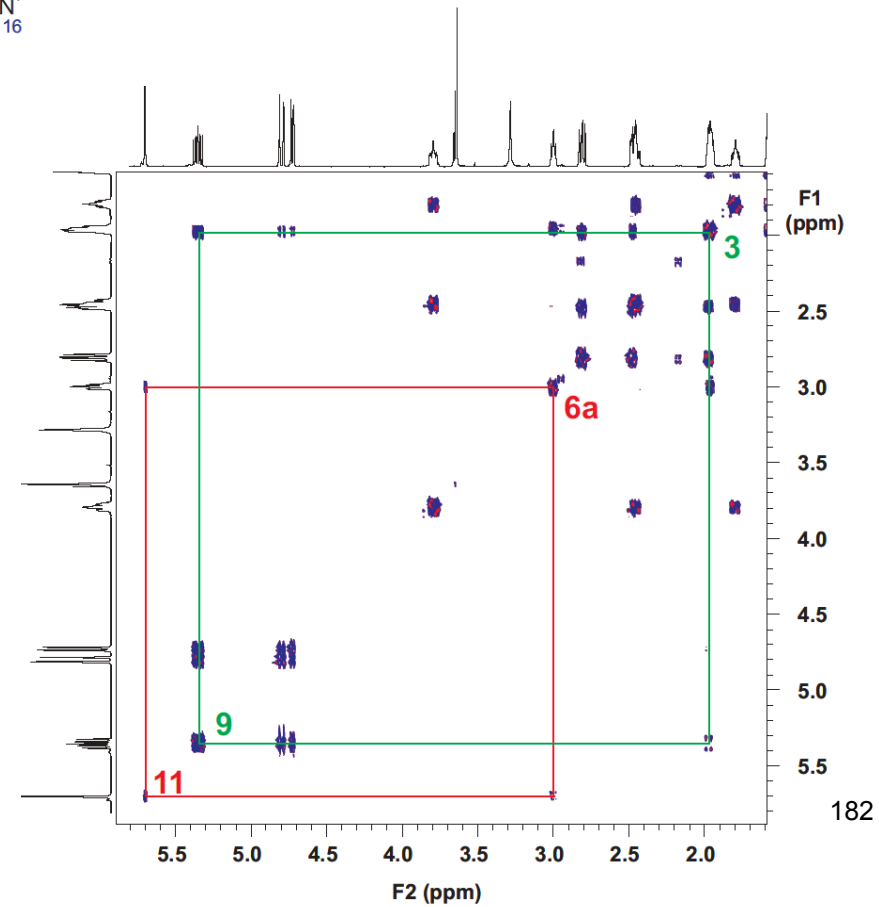
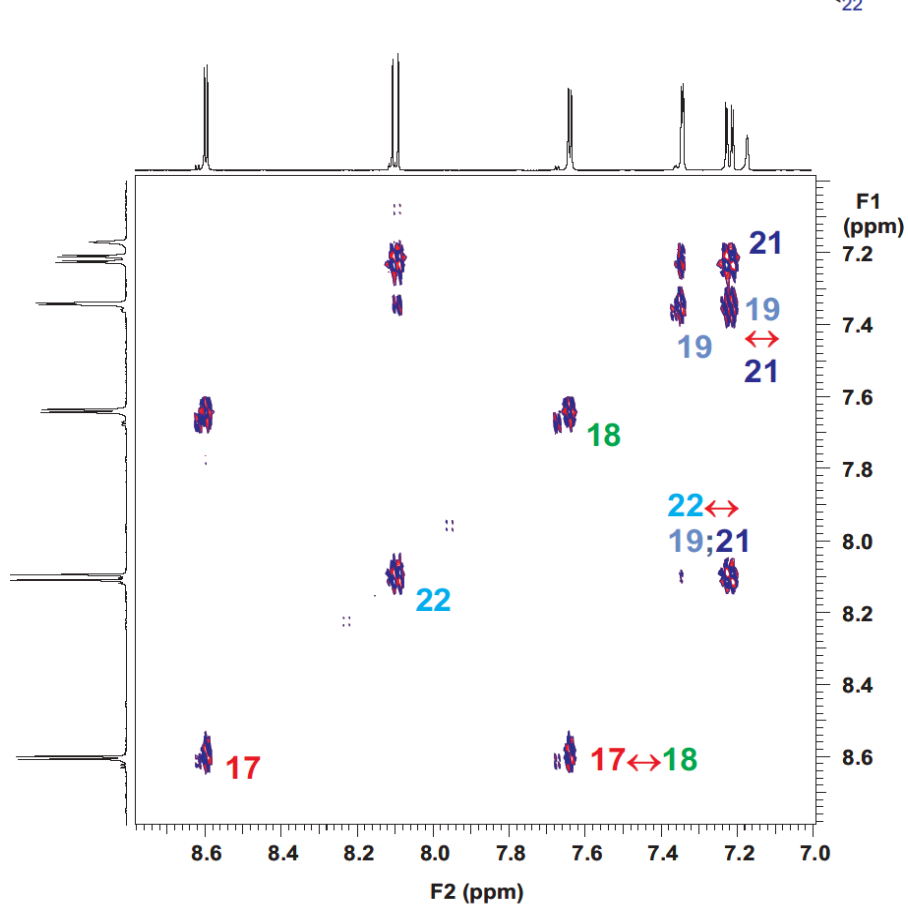
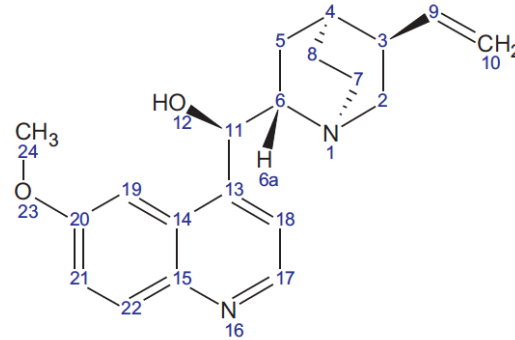
chinin



# Metody 2D FT NMR spektroskopie

## Experimenty s přenosem koherence - homonukleární

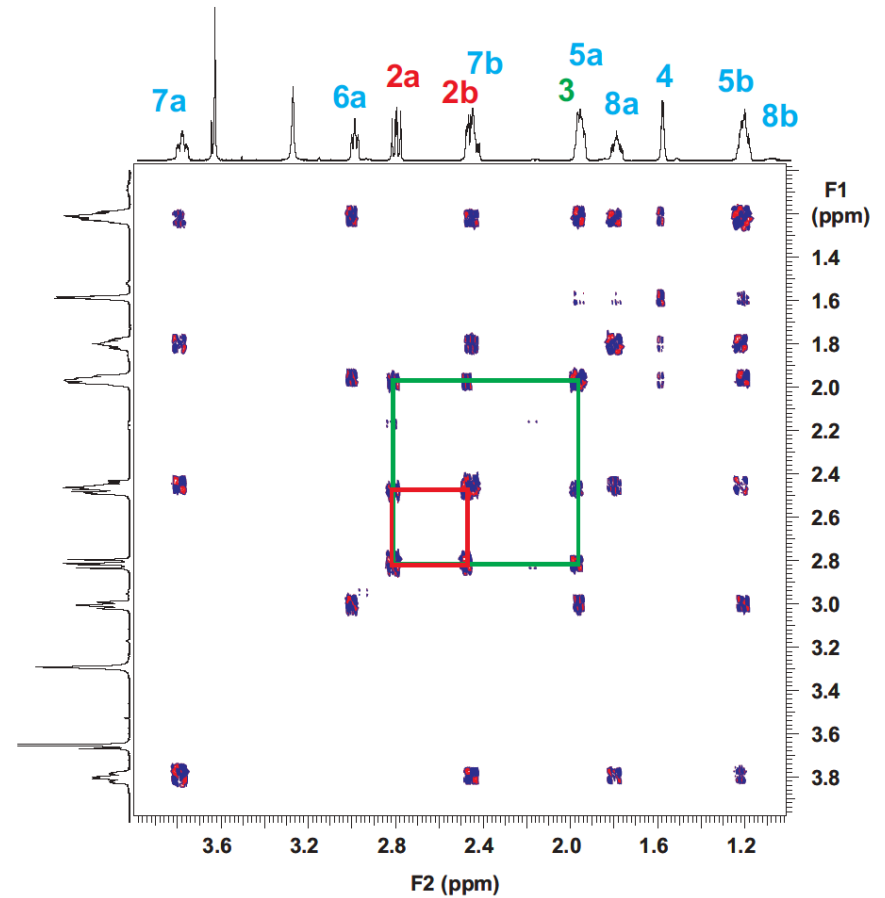
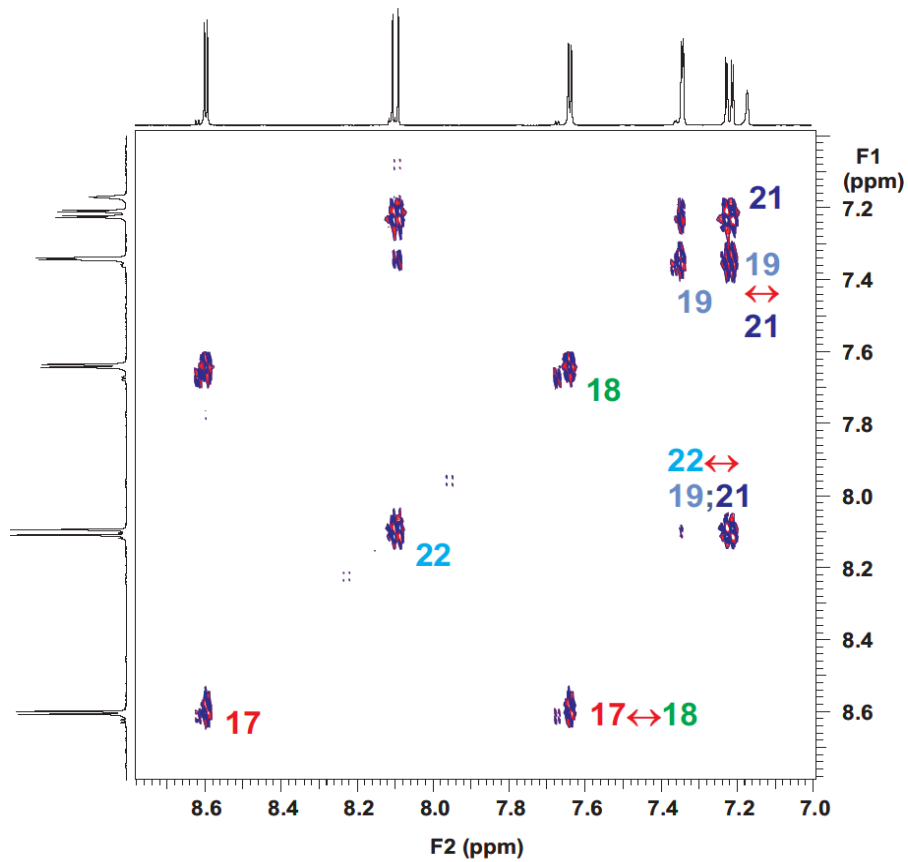
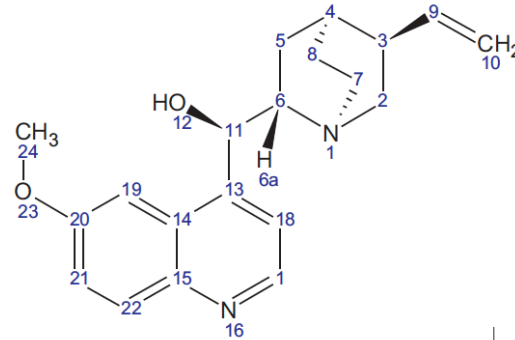
DQF COSY



# Metody 2D FT NMR spektroskopie

## Experimenty s přenosem koherence - homonukleární

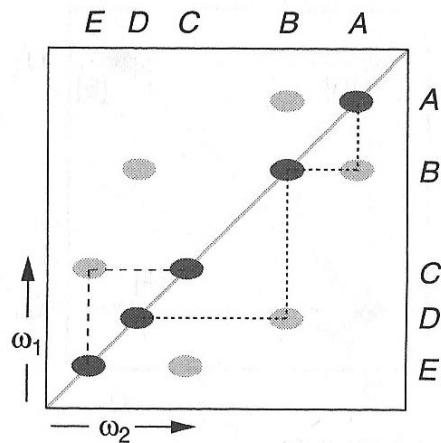
DQF COSY



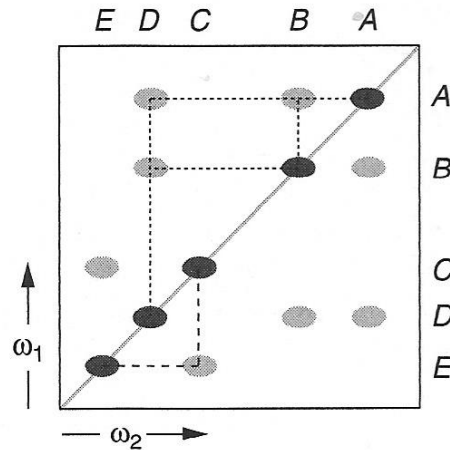
# Metody 2D FT NMR spektroskopie

## Experimenty s přenosem koherence - homonukleární

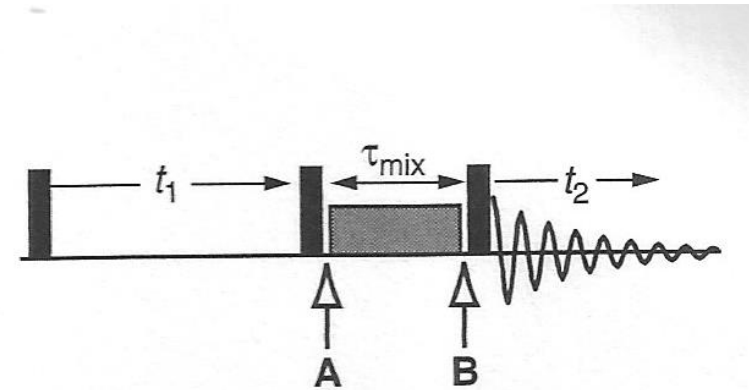
### TOCSY - **T**otal **C**orrelation **S**pectroscop**Y**



COSY



TOCSY



isotropní směšování  
(DIPSI-2, MLEV-17, WALTZ, etc.)

$$I_{1z} \rightarrow \frac{1}{2}(1 + \cos 2\pi J_{12} \tau_{mix}) I_{1z} + \frac{1}{2}(1 - \cos 2\pi J_{12} \tau_{mix}) I_{2z} - \sin(2\pi J_{12} \tau_{mix}) \frac{1}{2}(2I_{1y} I_{2x} - 2I_{1x} I_{2y})$$

diagonální pík    interakční pík    ZQ

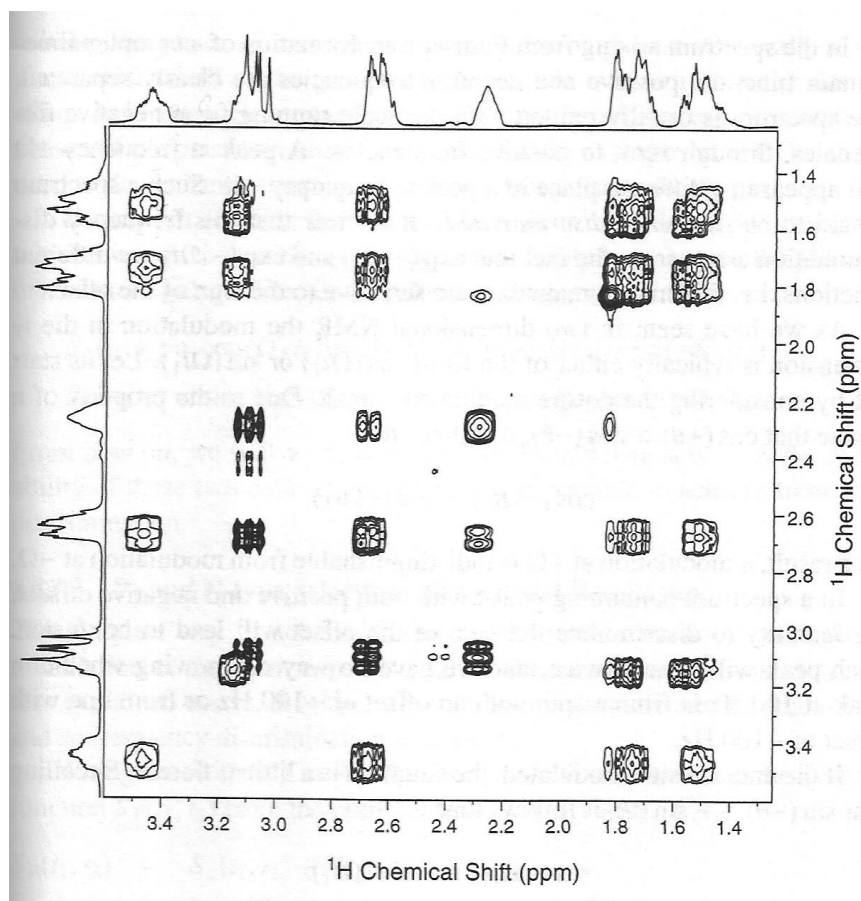
$$I_{1x} \rightarrow \frac{1}{2}(1 + \cos 2\pi J_{12} \tau_{mix}) I_{1x} + \frac{1}{2}(1 - \cos 2\pi J_{12} \tau_{mix}) I_{2x} - \sin(2\pi J_{12} \tau_{mix}) \frac{1}{2}(2I_{1z} I_{2y} - 2I_{1y} I_{2z})$$

# Metody 2D FT NMR spektroskopie

Experimenty s přenosem koherence - homonukleární

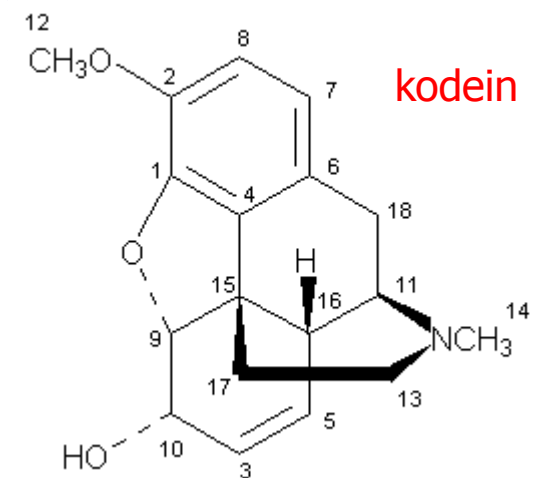
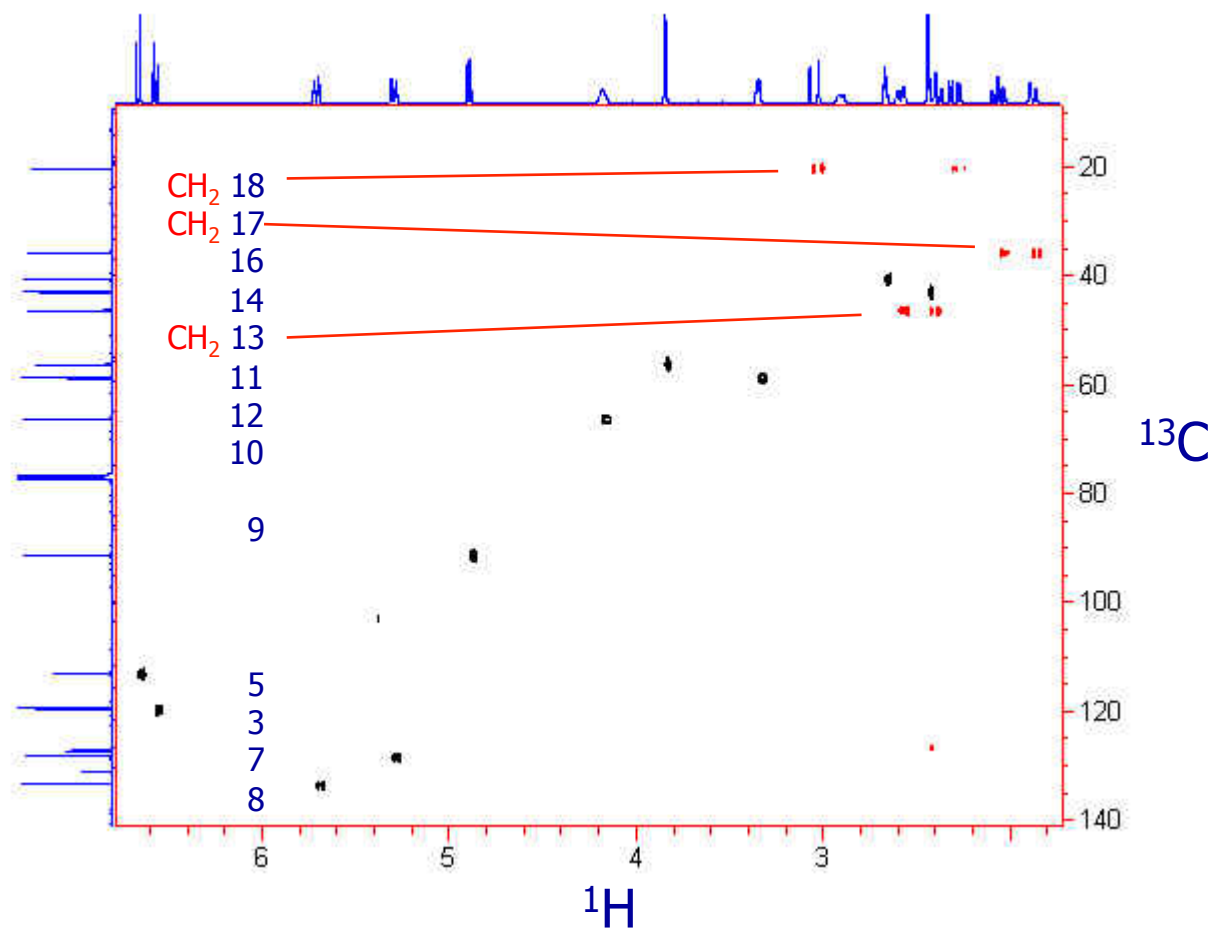
## TOCSY - **T**otal **C**orrelation **S**pectroscop**Y**

chinin



# Metody 2D FT NMR spektroskopie

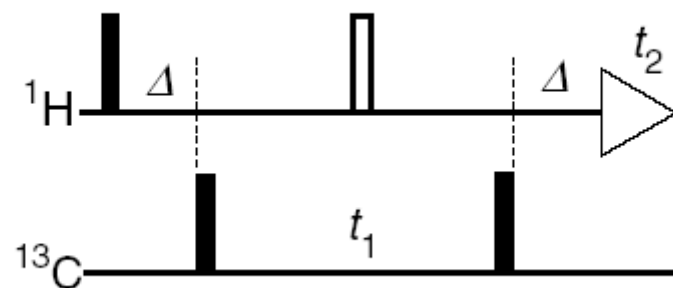
Experimenty s přenosem koherence – heteronukleární



# Metody 2D FT NMR spektroskopie

Experimenty s přenosem koherence - heteronukleární

## HMQC -Heteronuclear Multiple-Quantum Correlation



$\Delta$  – spin  $I_1$  (J):

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

2. Pulz – spin  $I_2$ :

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

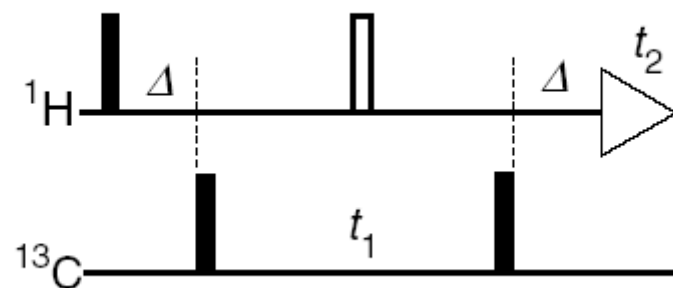
$t_1$  – vývoj spin  $I_2$  ( $\Omega_2$ ):

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

# Metody 2D FT NMR spektroskopie

Experimenty s přenosem koherence - heteronukleární

HMQC -Heteronuclear Multiple-Quantum  
Correlation



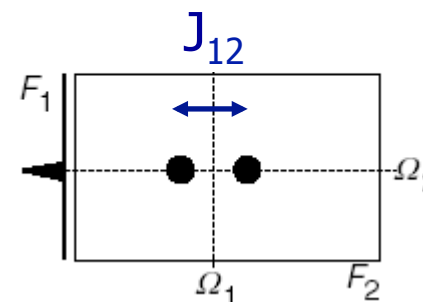
3. Pulz – spin  $I_2$ :

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

$\Delta = 1/2J$  – spin  $I_1$  (J):

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

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

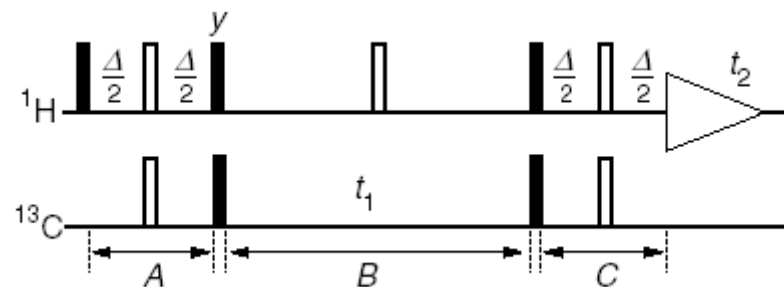




# Metody 2D FT NMR spektroskopie

Experimenty s přenosem koherence - heteronukleární

HSQC -Heteronuclear Single-Quantum Correlation



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

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):

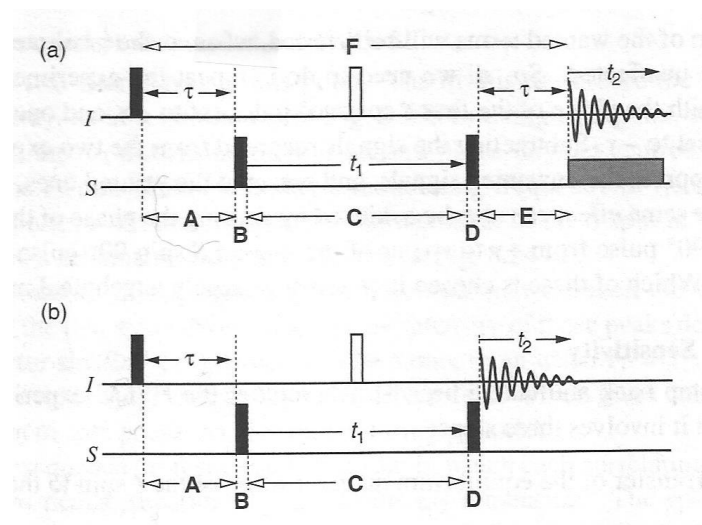
$$\cos \Omega_2 t_1 I_{1x}$$

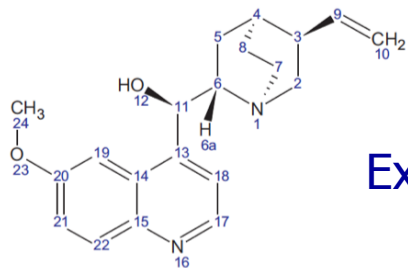
# Metody 2D FT NMR spektroskopie

Experimenty s přenosem koherence - heteronukleární

HMQC – Heteronuclear Multiple-Quantum  
Correlation

HMBC – Heteronuclear Multiple-Bond  
Correlation





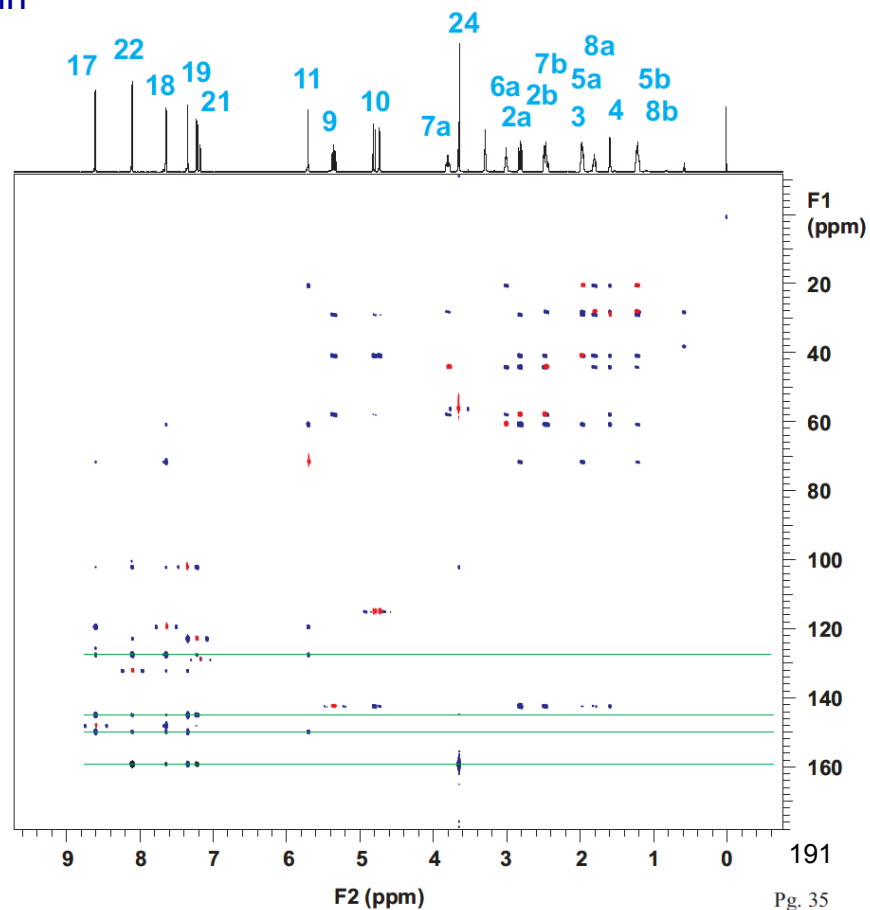
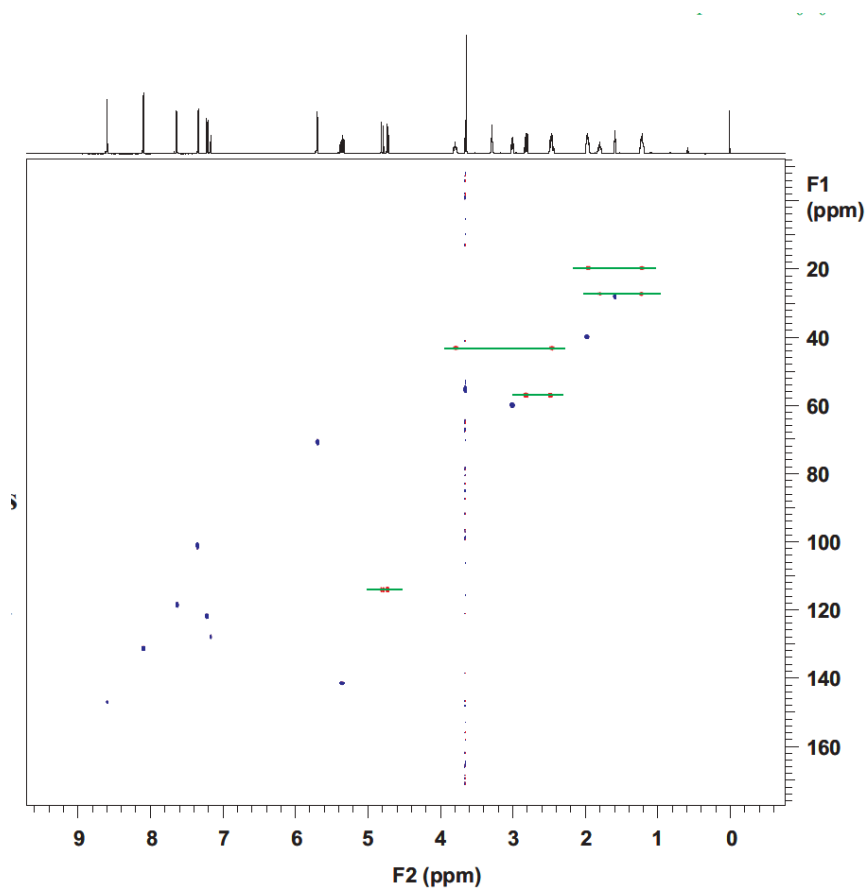
# Metody 2D FT NMR spektroskopie

Experimenty s přenosem koherence - heteronukleární

**HSQC** -Heteronuclear Single-Quantum Correlation

**HMBC** -Heteronuclear Multiple-Bond Correlation

chinin





# Metody 2D FT NMR spektroskopie

Praktické aplikace

[QSU webcourse](#)

# Metody 2D FT NMR spektroskopie

## Tvar čar a diskriminace frekvencí – 1D spektrum

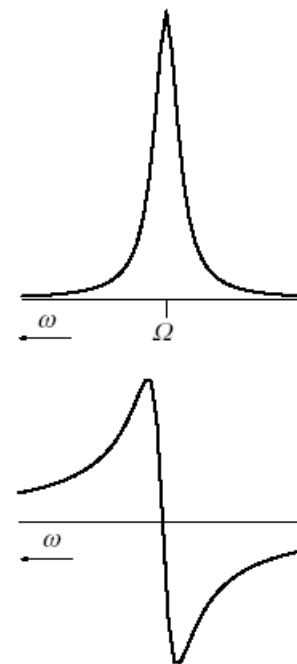
$$S_x(t) = \gamma \cos \Omega t \exp(-t/T_2) \quad S_y(t) = \gamma \sin \Omega t \exp(-t/T_2)$$

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

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

$\gamma$  – 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

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

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

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

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

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

## 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  $\exp(-i \pi/2) = -i$ .

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

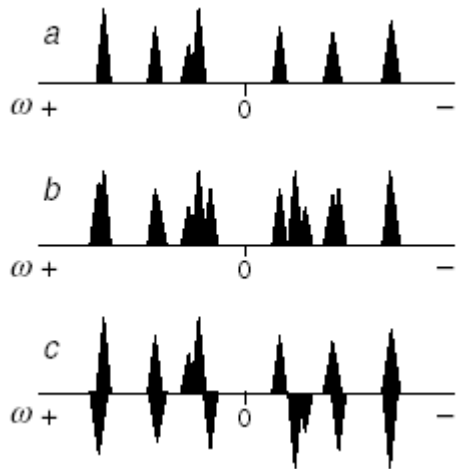
# Metody 2D FT NMR spektroskopie

## 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

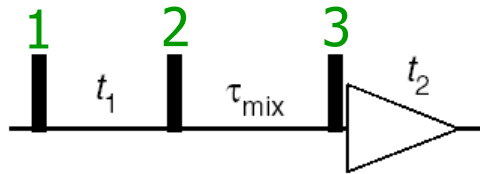
fázová modulace

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

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

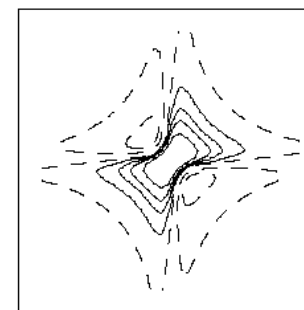
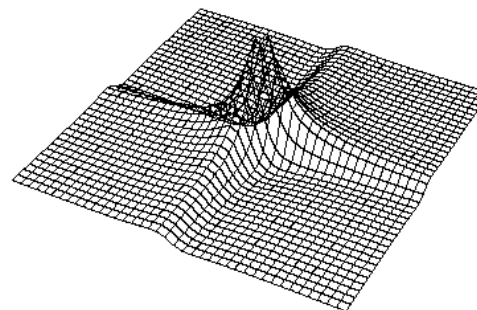
$$FT[\exp(i\Omega t)\exp(-t/T_2)] = \{A(\omega) + iD(\omega)\}$$

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

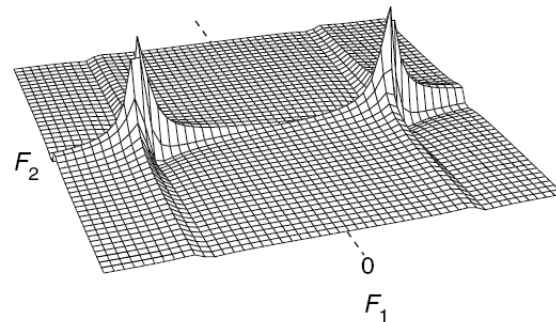
amplitudová modulace  
kosinový člen

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

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

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

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



# Metody 2D FT NMR spektroskopie

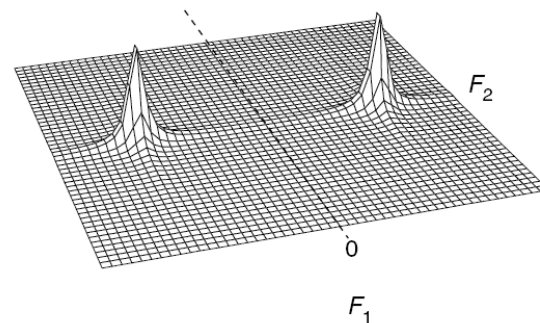
## Tvar čar – 2D spektra

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

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

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

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



# 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

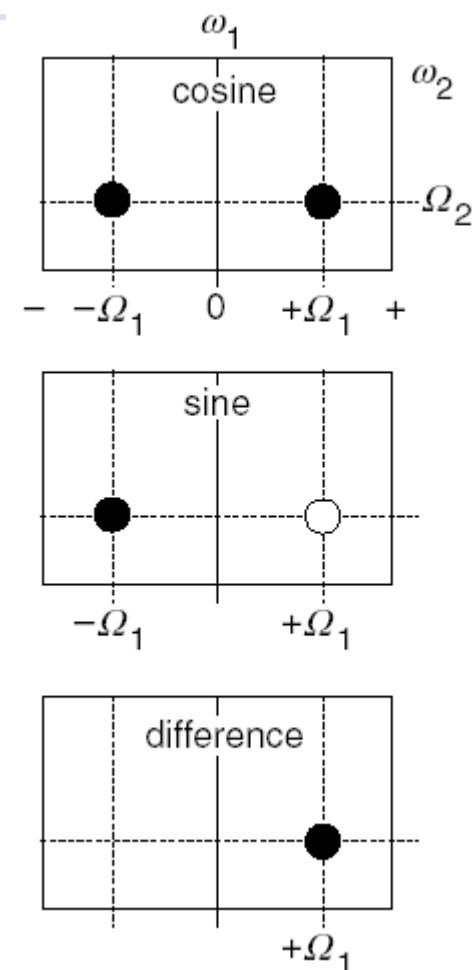
Frekvenční diskriminace a zachování absorpčního tvaru čar

## Metoda States-Haberhorn a Rubenova (SHR)

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

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

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



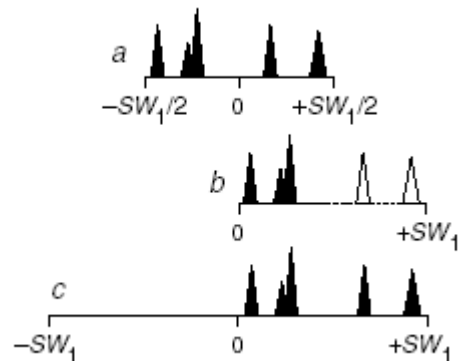
# Metody 2D FT NMR spektroskopie

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  $\omega_{\text{additional}}$

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

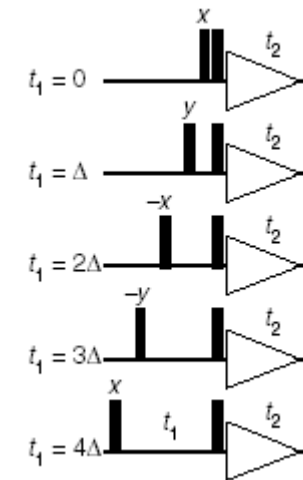
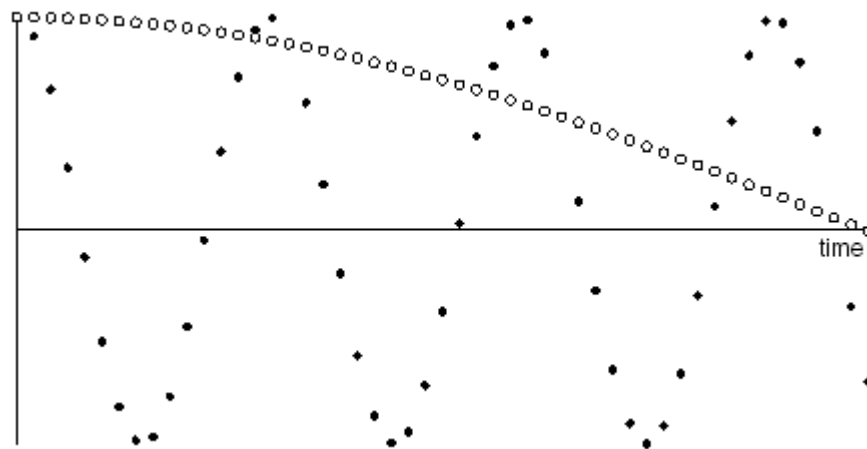


# Metody 2D FT NMR spektroskopie

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

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

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

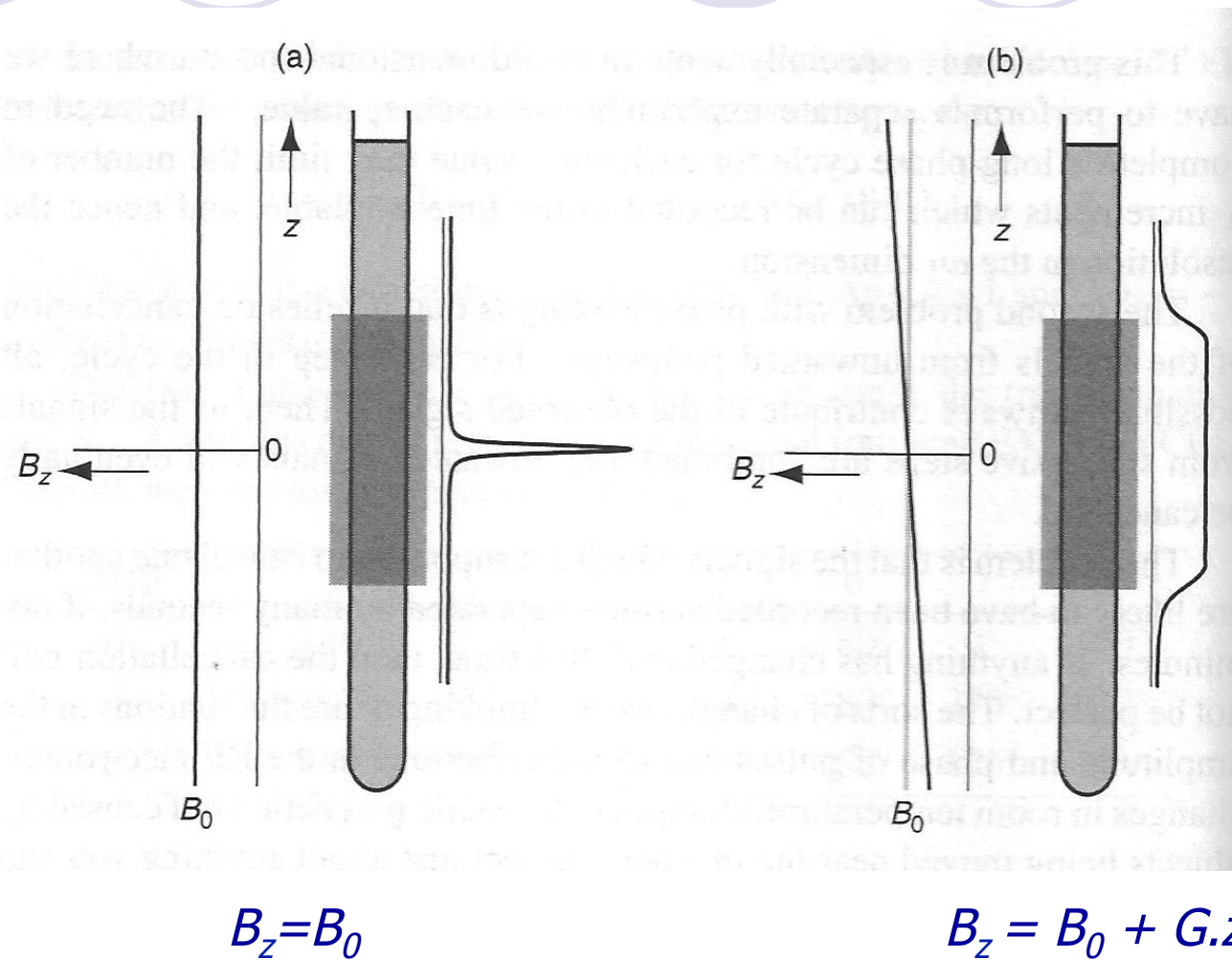
$$\frac{1}{2i} [S(t_1, t_2)_P - S(t_1, t_2)_N] =$$
$$\frac{1}{2i} \gamma [\exp(i\Omega_1 t_1) - \exp(-i\Omega_1 t_1)] \exp(-t_1/T_2^{(1)}) \exp(i\Omega_2 t_2) \exp(-t_2/T_2^{(2)})$$

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

## Metoda SHR

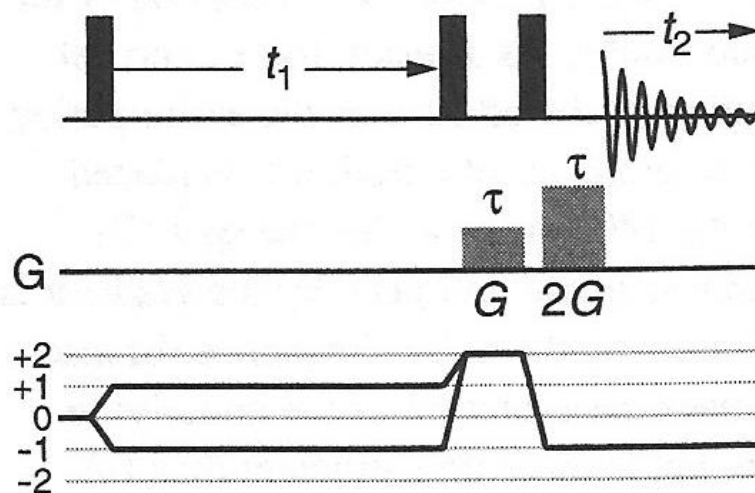
# Metody 2D FT NMR spektroskopie

## Gradients magnetického pole



# Metody 2D FT NMR spektroskopie

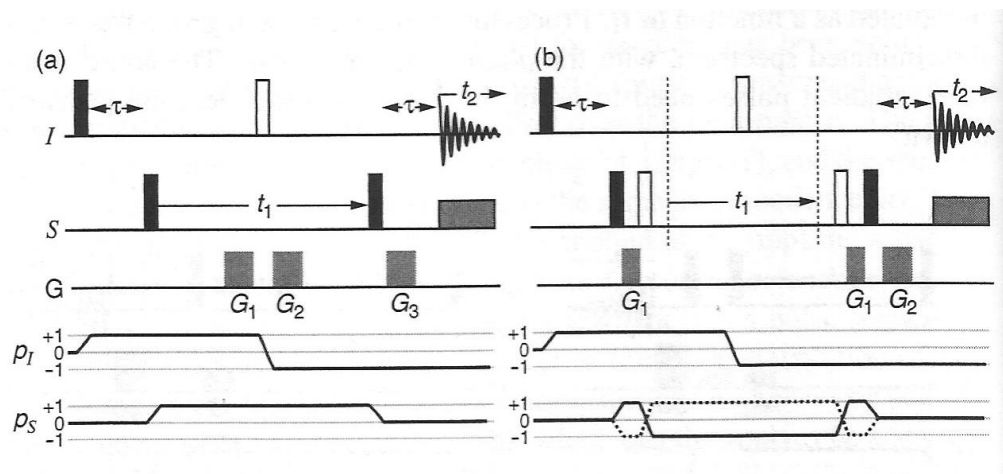
## Gradienty magnetického pole



# Metody 2D FT NMR spektroskopie

## Gradients magnetického pole

HMQC



HSQC

