

# Az NMR spektroszkópia jelentősége

## Szerkezeti kémia

Szerves kémia: Minőségi analízis. Új vegyületek szerkezetvizsgálata. Enantiomer tisztaság vizsgálata.

Természetes vegyületek szerkezetvizsgálata.

Metabolitok vizsgálata

## Fizikai-kémiai vizsgálatok:

Gazda-vendég kölcsönhatások.

Reakciókinetika

## Makromolekulák háromdimenziós szerkezete:

Peptidek, fehérjék, enzimek

DNS/RNS, DNS/RNS komplexek

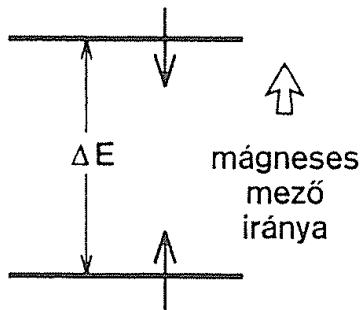
Poliszaharidok

## Gyógyszerkutató: Receptor kötődési vizsgálatok

## Orvostudomány: diagnosztika (Magnetic Resonance Imaging (MRI))

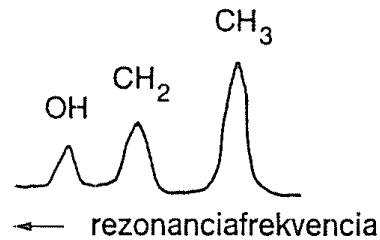
# Mágneses atommag viselkedése mágneses térben

1.1. ábra A hidrogénatommag energiaszintjei mágneses mezőben. A mag mágneses momentumának a mágneses mezőhöz viszonyított két lehetséges beállása közötti energiakülönbség:  $\Delta E$ .

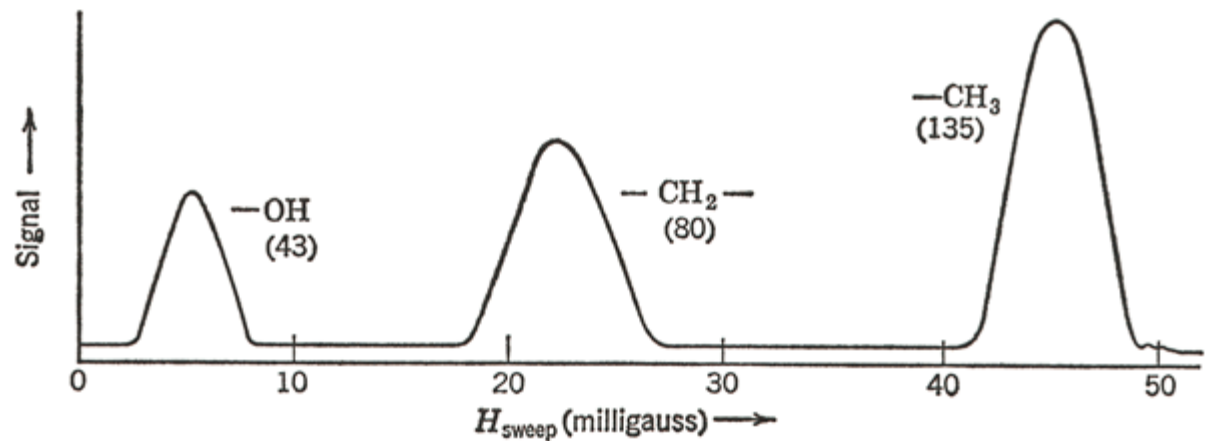
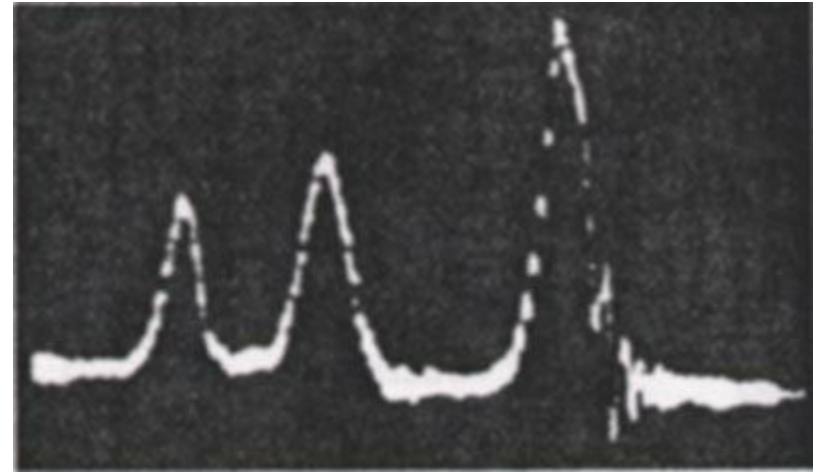


$$\Delta E = h\nu$$

$$h = 6.626 \times 10^{-34} \text{ Js}$$



1.2. ábra Az etanol (CH3CH2OH) <sup>1</sup>H-NMR-spektruma folyadékfázisban.  
(J. T. Arnold, S. S. Dharmatti és M. E. Packard után: *J. Chem. Phys.*, 1951, 19, 507).



# Mágneses atommag viselkedése mágneses térben

$$|\mathbf{I}| = [I(I+1)]^{1/2}\hbar$$

$$I_z = m\hbar$$

$$(m = -I, -I+1, \dots, I-1, +I)$$

$$\boldsymbol{\mu} = \gamma\mathbf{I}$$

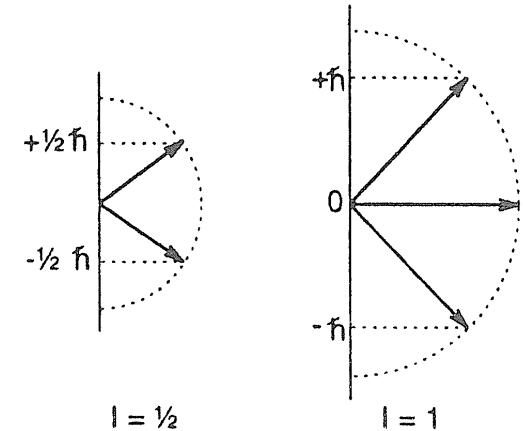
$$\mathbf{E} = -\boldsymbol{\mu}\mathbf{B} = -\mu_z\mathbf{B}$$

$$\mathbf{E} = -m\hbar\gamma\mathbf{B}$$

$$\Delta E = \hbar\gamma B = h\nu$$

$$\nu = \frac{\gamma B}{2\pi}$$

$I$	Atommag
0	$^{12}\text{C}, ^{16}\text{O}$
$\frac{1}{2}$	$^1\text{H}, ^{13}\text{C}, ^{15}\text{N}, ^{19}\text{F}, ^{29}\text{Si}, ^{31}\text{P}$
1	$^2\text{H}, ^{14}\text{N}$
$\frac{3}{2}$	$^{11}\text{B}, ^{23}\text{Na}, ^{35}\text{Cl}, ^{37}\text{Cl}$
$\frac{5}{2}$	$^{17}\text{O}, ^{27}\text{Al}$
3	$^{10}\text{B}$



Protonok száma	Neutronok száma	$I$
páros	páros	0
páratlan	páratlan	1 vagy 2 vagy 3 vagy ...
páros	páratlan	$\frac{1}{2}$ vagy $\frac{3}{2}$ vagy $\frac{5}{2}$ vagy ...
páratlan	páros	$\frac{1}{2}$ vagy $\frac{3}{2}$ vagy $\frac{5}{2}$ vagy ...

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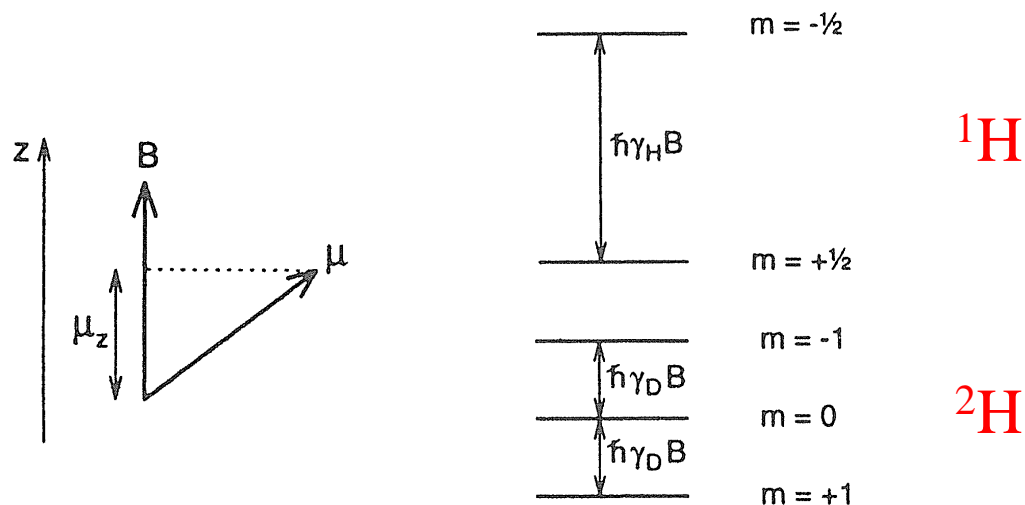
$$E = -\boldsymbol{\mu}\mathbf{B} = -\mu_z B$$

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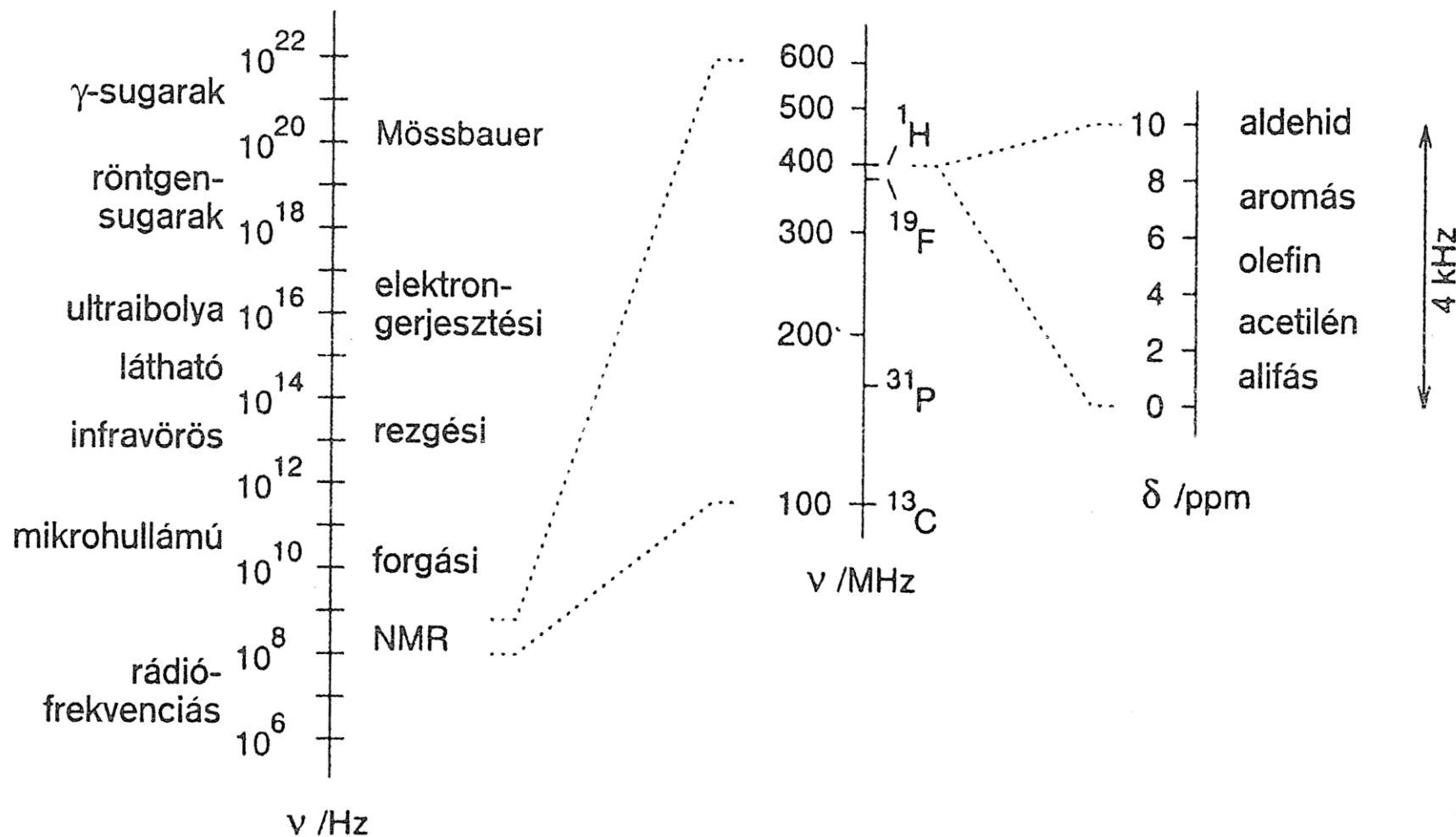
$$\Delta E = \hbar\gamma B = h\nu$$

$$\nu = \frac{\gamma B}{2\pi}$$

	$\gamma/10^7\text{T}^{-1}\text{s}^{-1}$	$\nu/\text{MHz}$	Természetes gyakoriság %
$^1\text{H}$	26,75	400,0	99,985
$^2\text{H}$	4,11	61,4	0,015
$^{13}\text{C}$	6,73	100,6	1,108
$^{14}\text{N}$	1,93	28,9	99,63
$^{15}\text{N}$	-2,71	40,5	0,37
$^{17}\text{O}$	-3,63	54,3	0,037
$^{19}\text{F}$	25,18	376,5	100,0
$^{29}\text{Si}$	-5,32	79,6	4,70
$^{31}\text{P}$	10,84	162,1	100,0



# Rezonanciafrekvenciák az NMR spektroszkópiában



## Az energiaszintek betöltöttsége

$$\frac{n_{\text{felső}}}{n_{\text{alsó}}} = e^{-\Delta E/kT}$$

**NMR:**  $\Delta E = \hbar\gamma B = 2.65 \times 10^{-25} \text{ J}$ , ha  $B = 9.4 \text{ T}$

$$k = 1.3807 \times 10^{-23} \text{ J/K}$$

$$\Delta E/kT = 6.4 \times 10^{-5}, \text{ ha } T = 300 \text{ K}$$

$$\frac{n_{\text{felső}}}{n_{\text{alsó}}} = 1 - \frac{\Delta E}{kT}$$

### Elektronrgerjesztési spektroszkópia:

$$\Delta E = h\nu = 3.976 \times 10^{-17} \text{ J}, \text{ ha } \nu = 6 \times 10^{16} \text{ Hz}$$

$$\Delta E/kT = 9598, \text{ ha } T = 300 \text{ K}$$

$$\frac{\Delta E}{kT} = 1 - \frac{n_{\text{felső}}}{n_{\text{alsó}}} = \frac{n_{\text{alsó}} - n_{\text{felső}}}{n_{\text{alsó}}}$$

$$\frac{\Delta E}{2kT} = \frac{n_{\text{alsó}} - n_{\text{felső}}}{2n_{\text{alsó}}} \approx \frac{n_{\text{alsó}} - n_{\text{felső}}}{n_{\text{alsó}} + n_{\text{felső}}} = 3.2 \times 10^{-5}$$

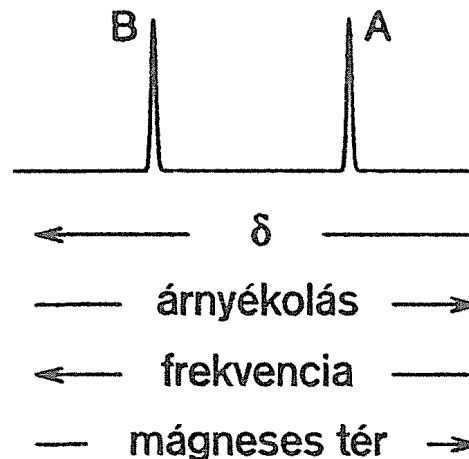
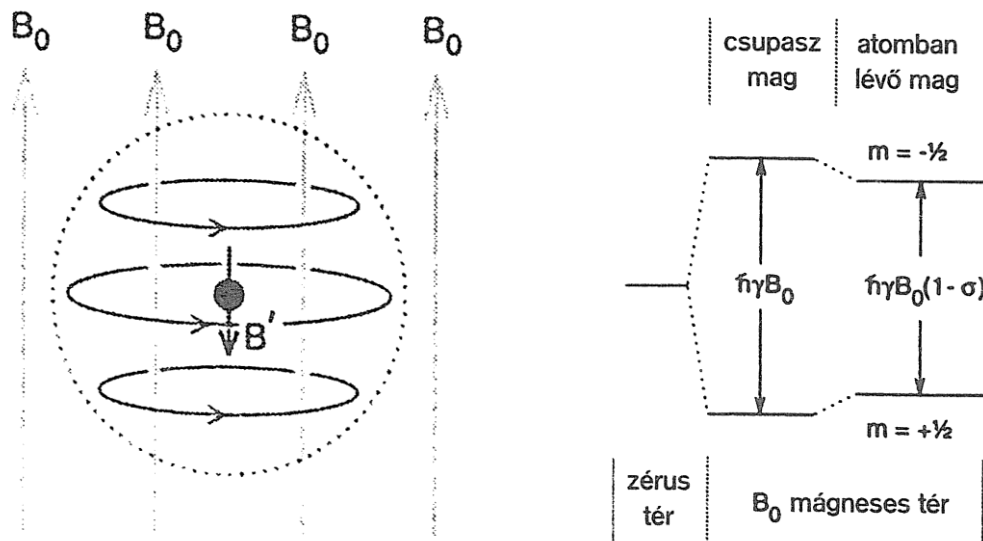
# Az atommagok árnyékolása és a kémiai eltolódás

$$B = B_0 - B' = B_0(1 - \sigma)$$

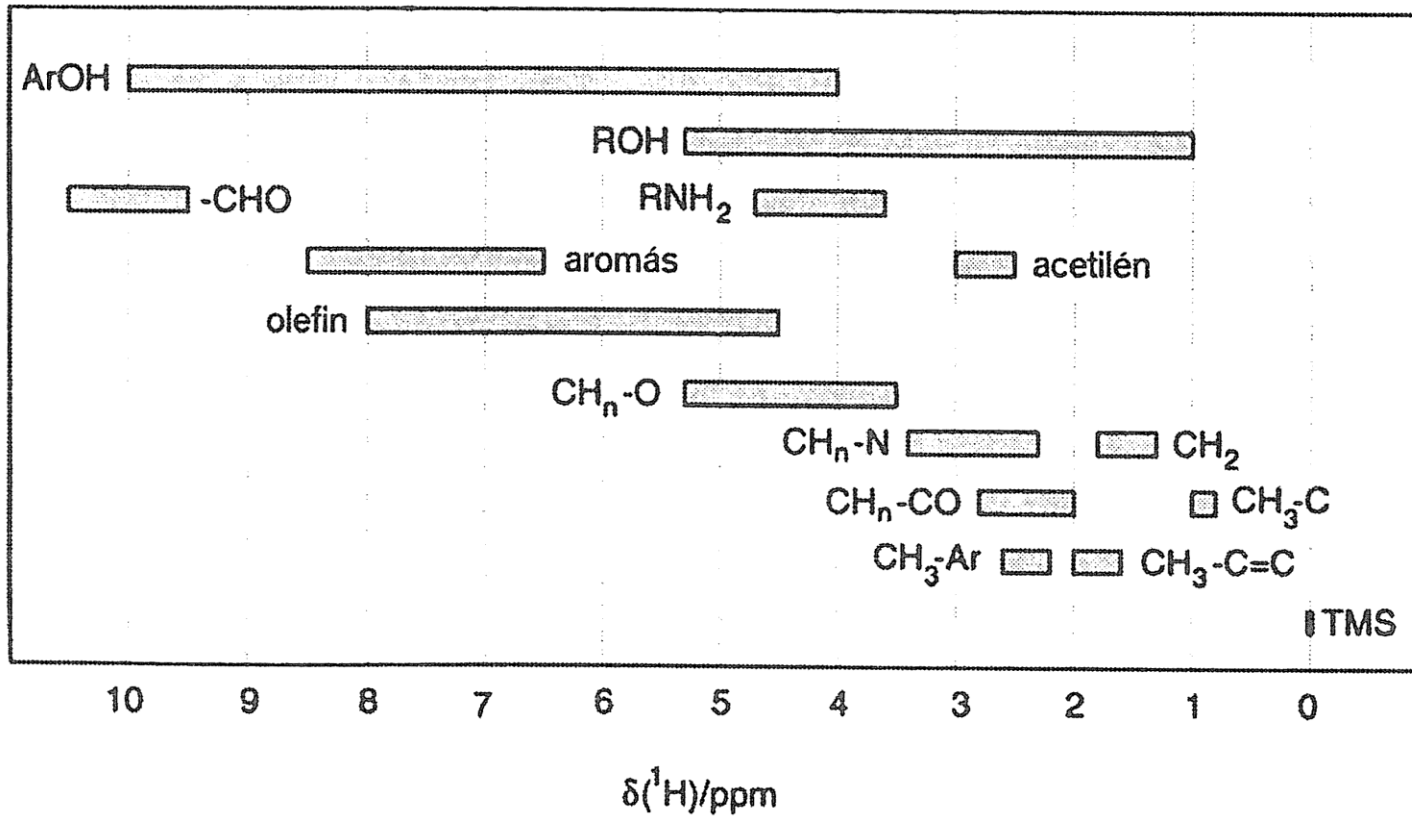
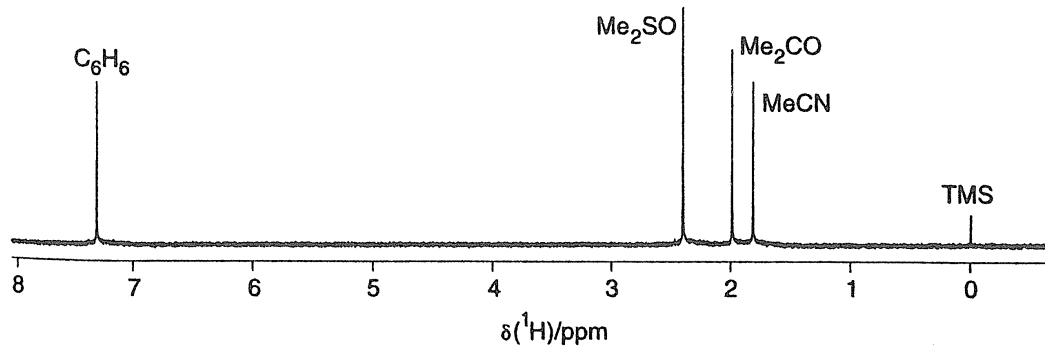
$$\nu = \frac{\gamma B_0(1 - \sigma)}{2\pi}$$

$$\delta = 10^6 \frac{(\nu - \nu_{\text{ref}})}{\nu_{\text{ref}}}$$

$$\delta = 10^6 \frac{(\sigma_{\text{ref}} - \sigma)}{1 - \sigma_{\text{ref}}} \approx 10^6 (\sigma_{\text{ref}} - \sigma)$$

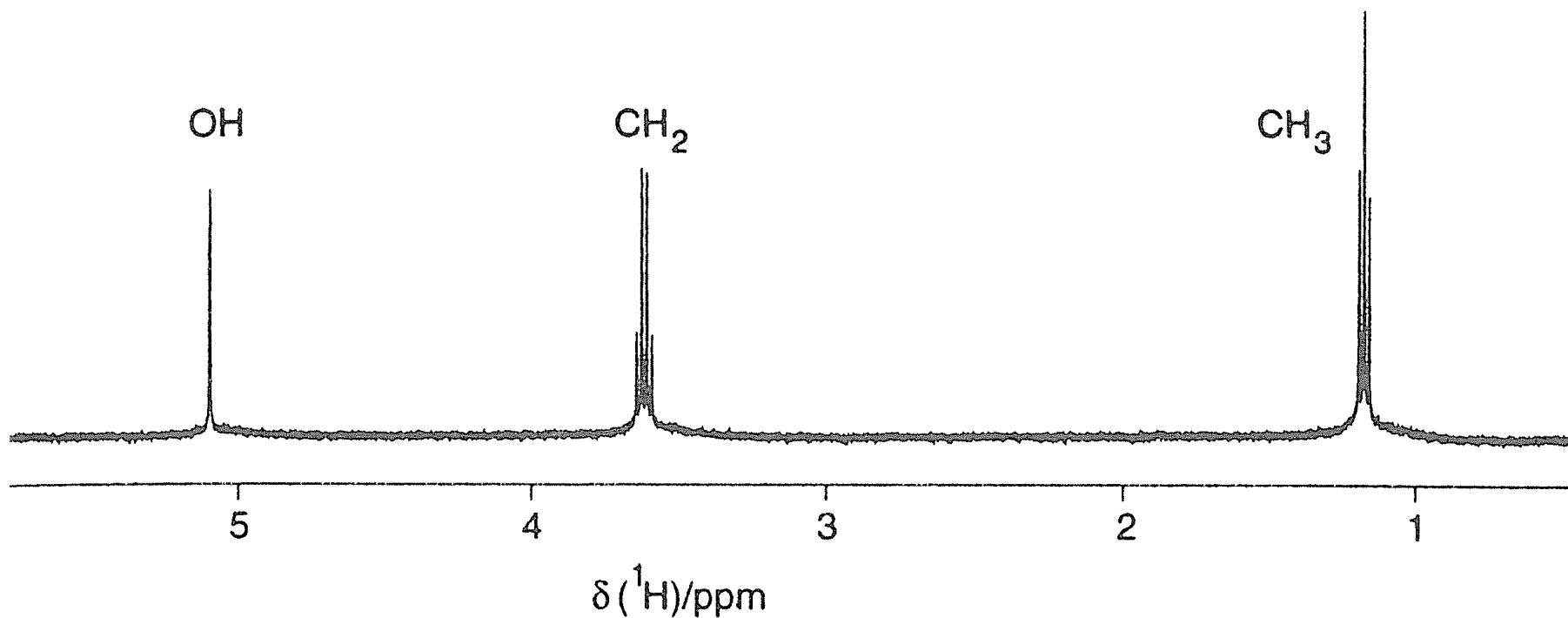
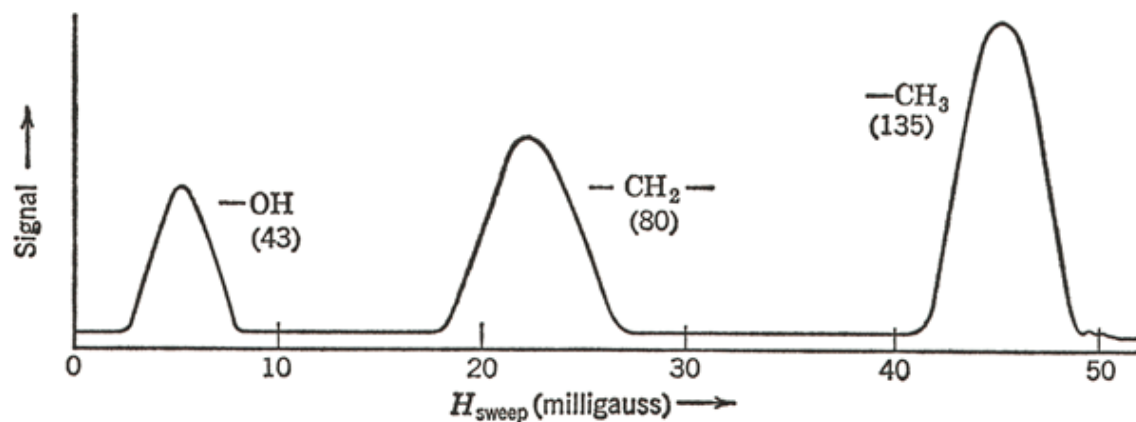
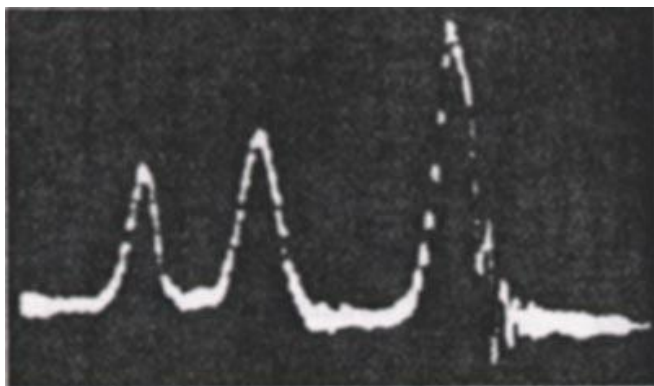


# Kémiai eltolódás, példák





# A spin-spin csatolás (skaláris csatolás, $J$ -csatolás)



# Spin-spin csatolás, az $AM_nX_m$ rendszerek spektrumai ( $I = 1/2$ )

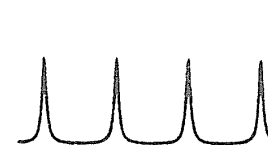
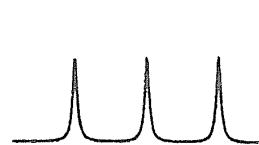
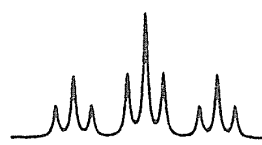
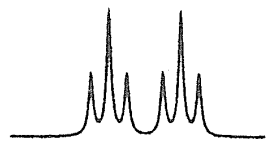
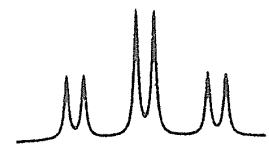
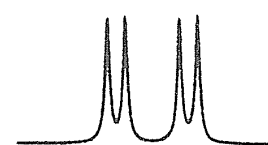
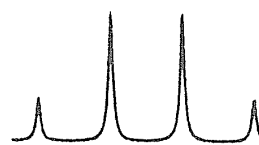
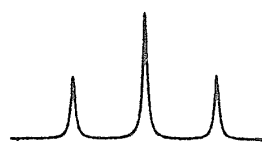
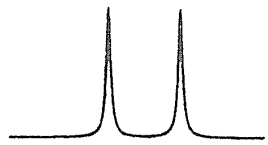
A

AX

$AX_2$

$AX_3$

AMX



$AMX_2$

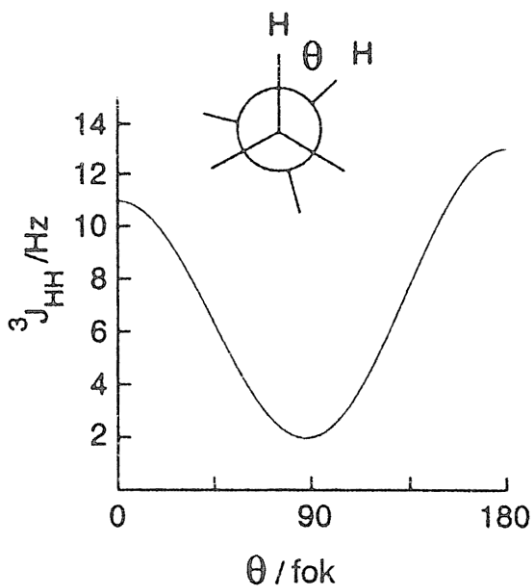
$AM_2X$

$AM_2X_2$

AX ( $I=1$ )

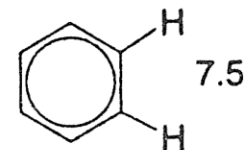
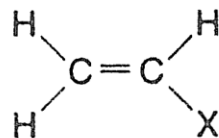
AX ( $I=3/2$ )

# Háromkötéses skaláris csatolások



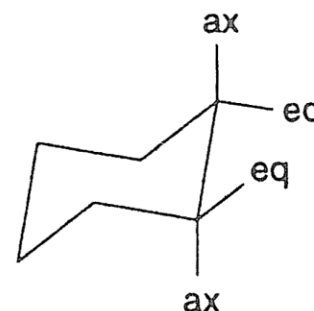
Karplus összefüggés:

$${}^3J = A + B \cos \Theta + C \cos^2 \Theta$$



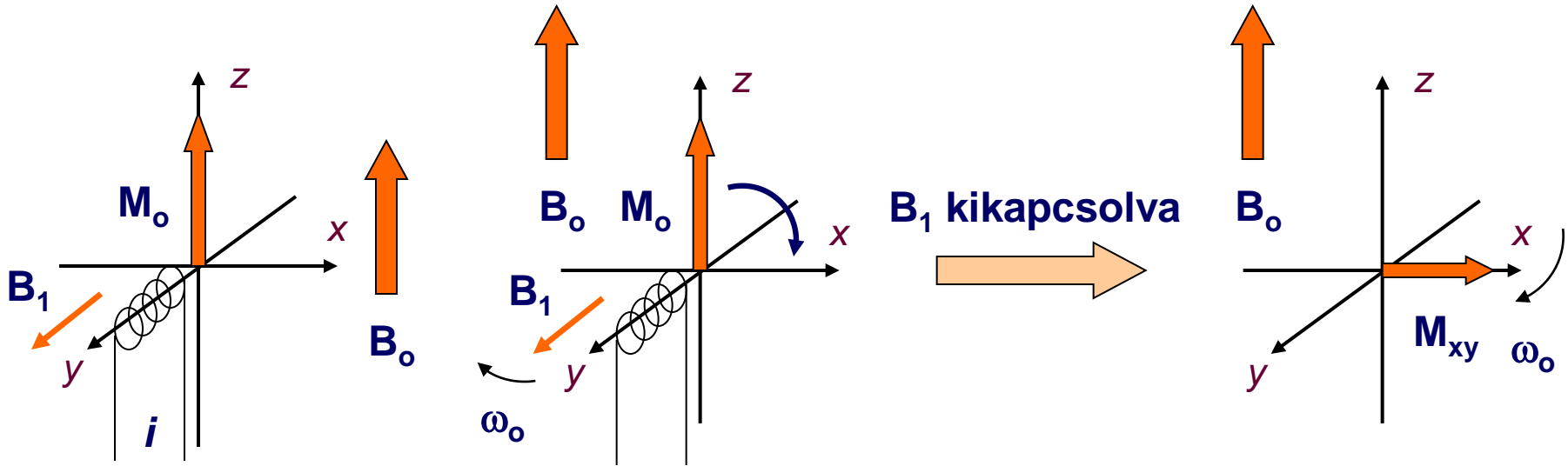
cisz      transz

X = H	+11.5	+19.0	+8.0
X = Ph	+10.7	+17.5	+7.6
X = Cl	+7.4	+14.8	+7.2
X = CN	+11.8	+17.9	+7.6

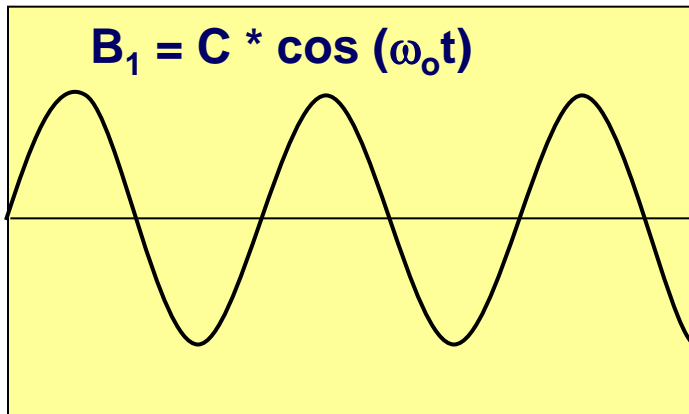


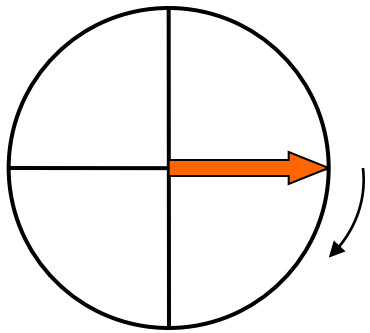
		$\theta$
ax-ax	11.8	$180^\circ$
ax-eq	3.9	$60^\circ$
eq-eq	3.9	$60^\circ$

# NMR jel észlelése



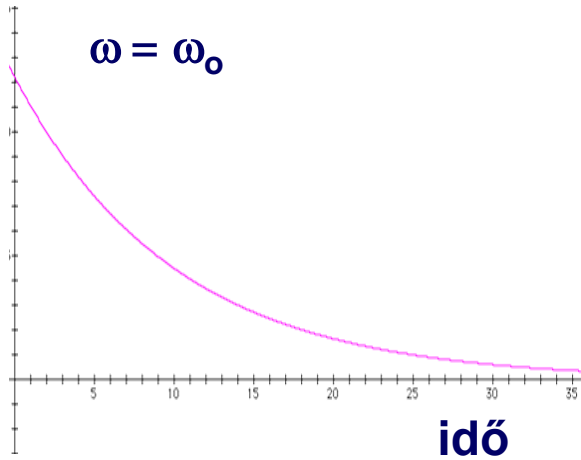
adótekercs (y)



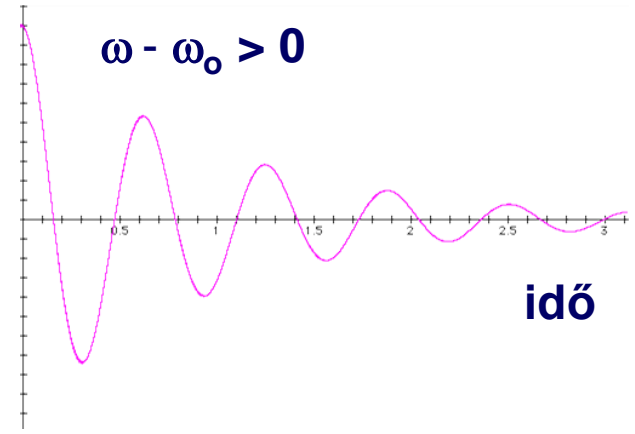


$M_{xy}$

$\omega = \omega_0$

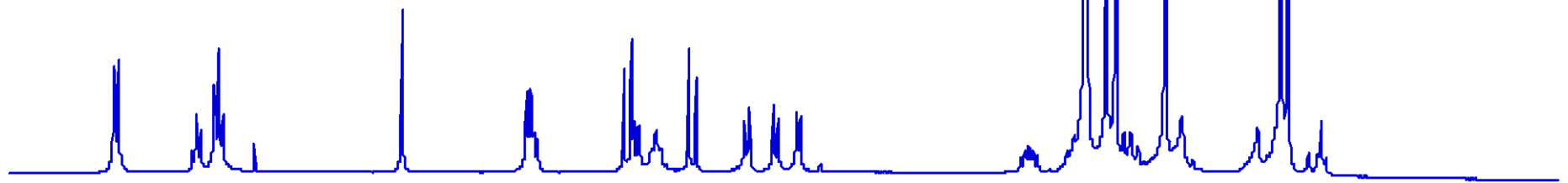
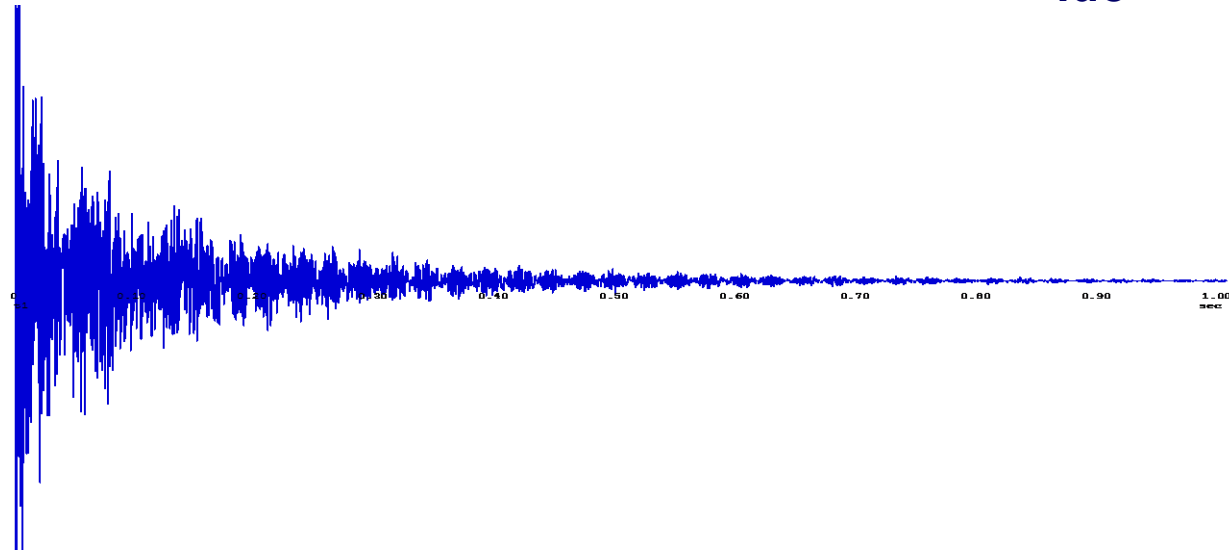


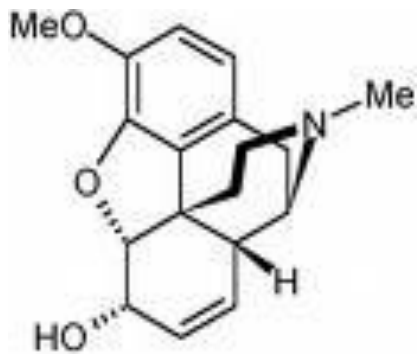
$\omega - \omega_0 > 0$



idő

idő

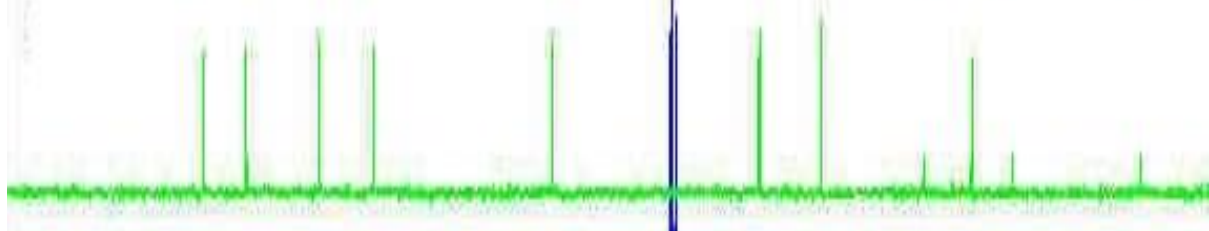




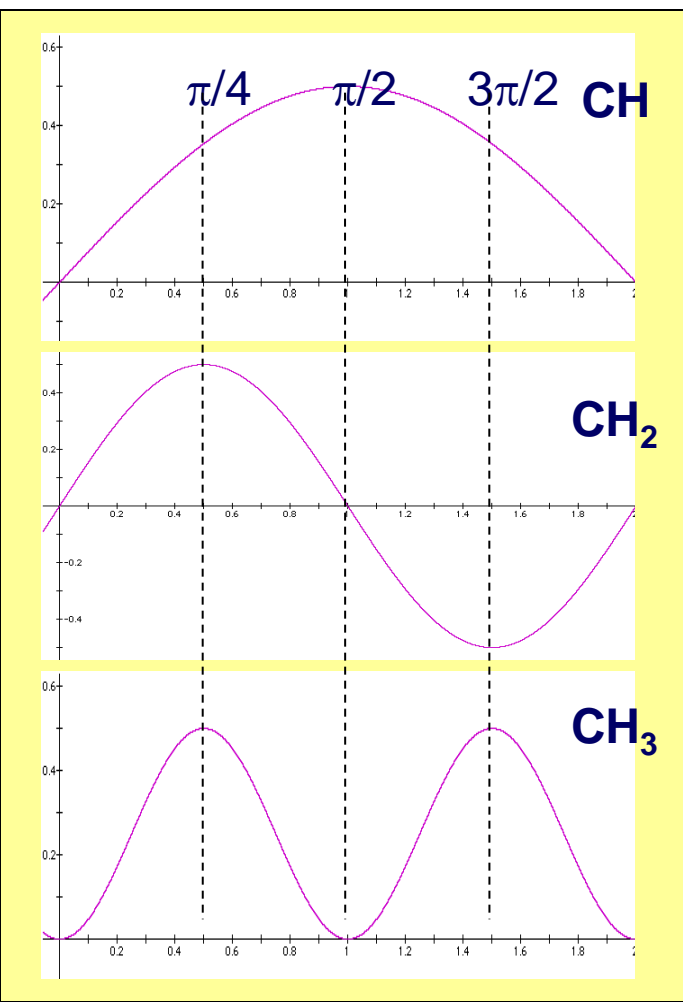
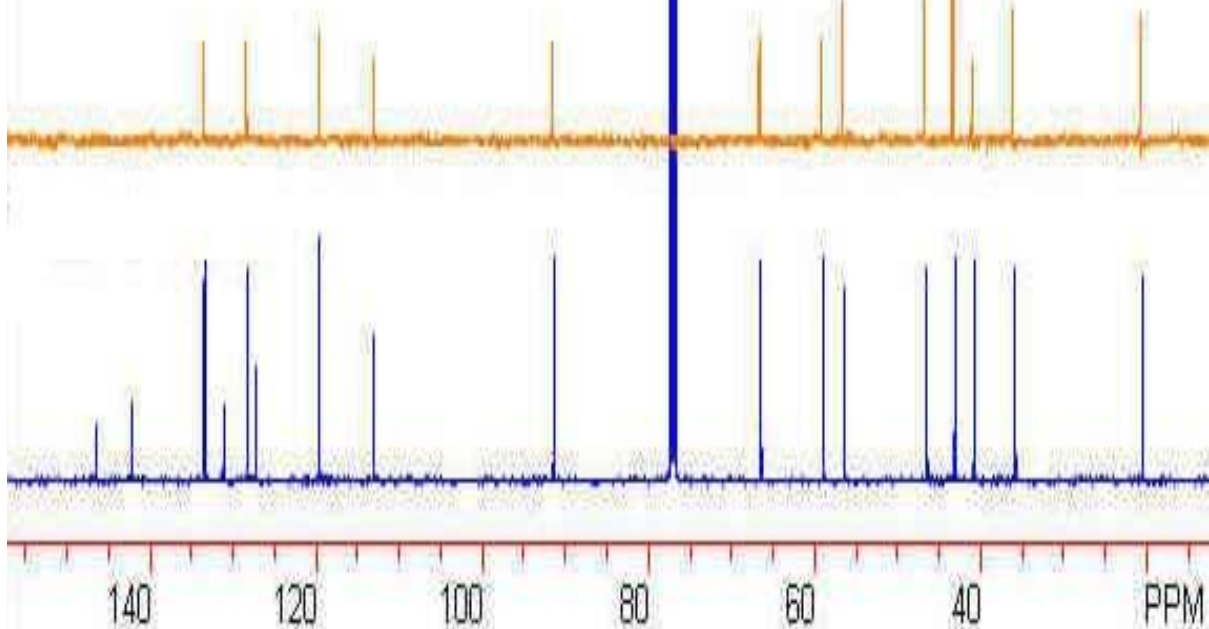
DEPT-135



DEPT-90



DEPT-45





# NMR spektrométerek egykor és ma





## A térerő hatása a spektrumra

