NMR I

Základní princip, ^{13}C NMR

Jaderný spin I (spinové číslo)

Protonové číslo sudé, nukleonové číslo sudé: spin = 0 (^{12}C, ^{16}O)

Protonové číslo liché, nukleonové číslo sudé: spin celočíselný (^{2}H)

Nukleonové číslo liché: spin = 1/2, 3/2, 5/2, .. (^{1}H, ^{13}C)

Magnetické kvantové číslo m

$$\boldsymbol{m = I, (I - 1), (I - 2), \ldots, -I}$$

Nejdůležitější jádra: I = 1/2 m = 1/2, -1/2

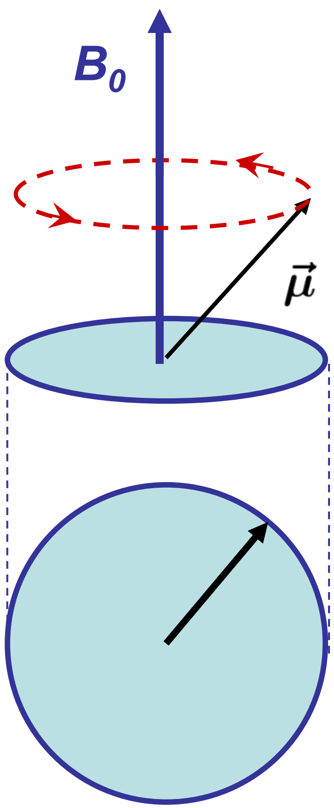
Jaderný magnetický moment

$$\vec{\mu} = \gamma \sqrt{I(I+1)}\, h / 2\pi \qquad \vec{\mu}_z = \gamma\, m\, h / 2\pi$$

γ – gyromagnetický poměr

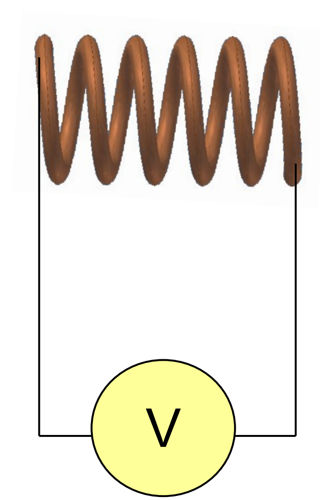
Larmorova precese

P. Callaghan video: http://www.youtube.com/watch?v=7aRKAXD4dAg



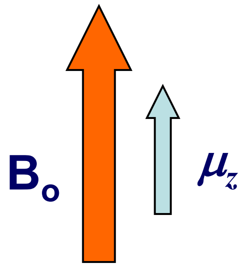
$$\nu = -\frac{\gamma}{2\pi} B_0$$

NMR měří frekvenci
Larmorovy precese
pro různá jádra
(jejich mag. momenty)

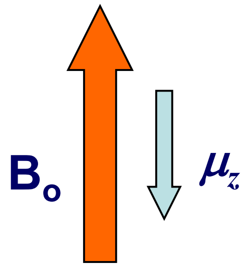


Proměnný magnetický tok indukuje signál v cívce

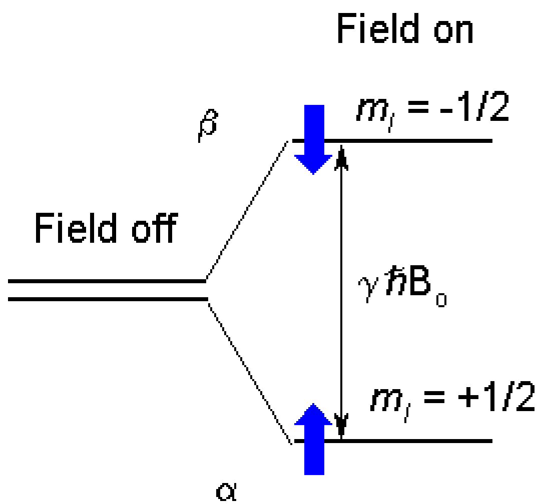
$$E = -\mu_z \cdot B_o$$



$$E_\alpha = -\gamma h B_o / 4\pi$$



$$E_\beta = \gamma h B_o / 4\pi$$



$$\Delta E = \gamma h B_o / 2\pi$$

$$h\nu = \Delta E = \gamma h B_o / 2\pi$$

$$\nu = \gamma B_o / 2\pi$$

Boltzmannův zákon

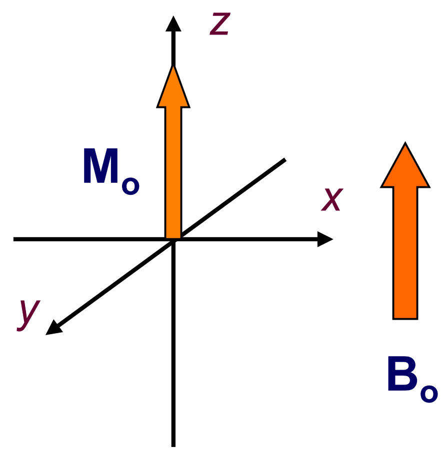
$$N_\alpha / N_\beta = e^{\Delta E / k_b T}$$

$\Delta E = \gamma h B_0 / 2\pi$

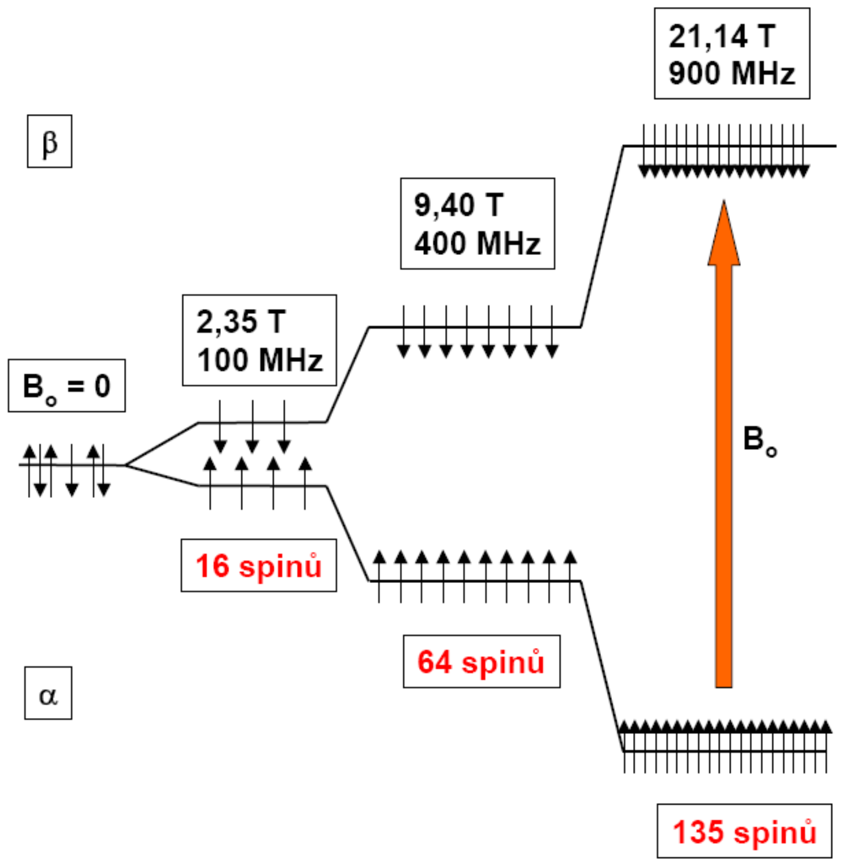
Příklad: $T = 300$ K, $B_0 = 7{,}05$ T (300 MHz)

$N\beta = 0{,}99995\ N\alpha$

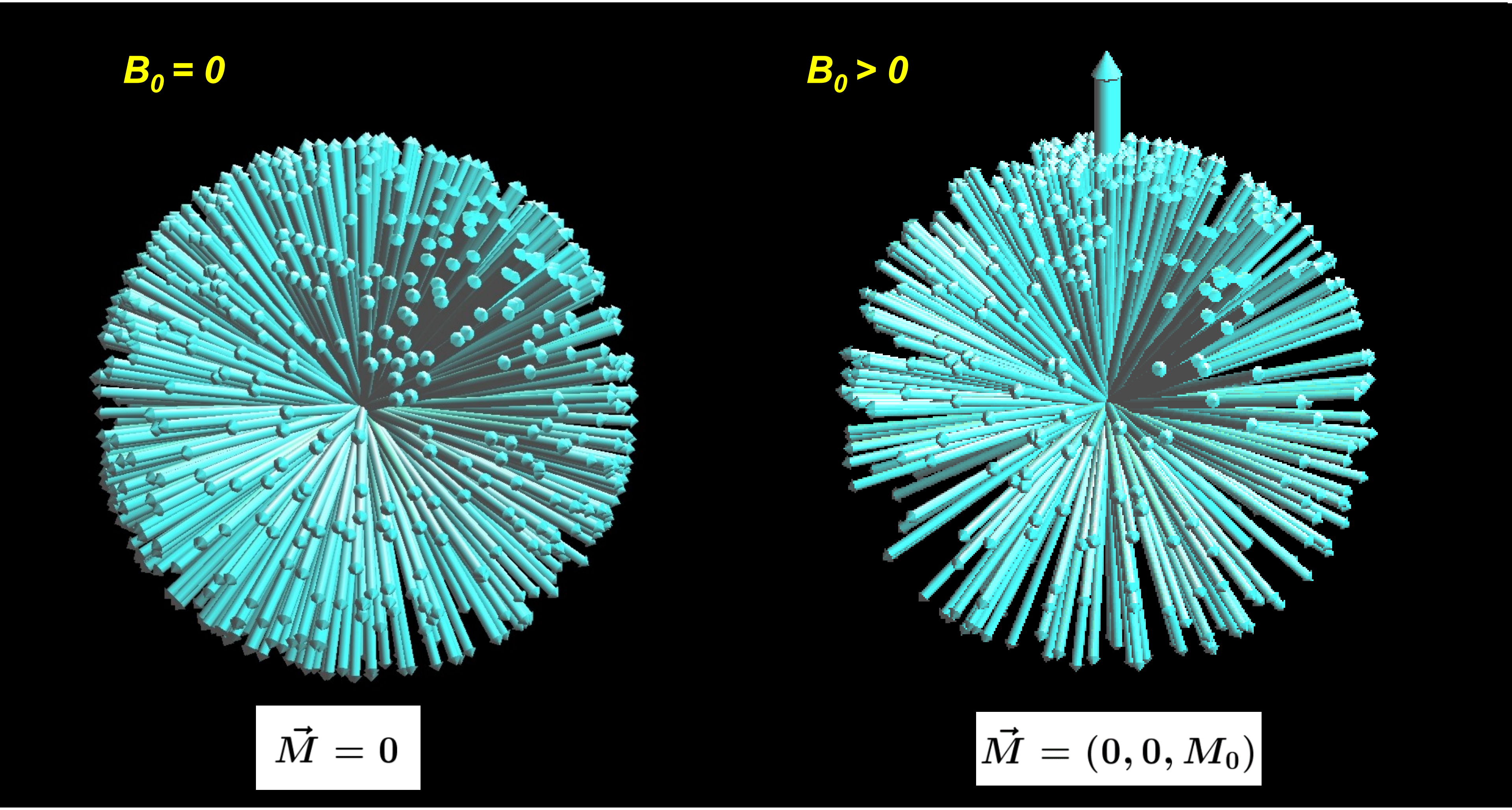
Magnetizace – makroskopická veličina



Je-li stav β obsazen 10^6 spinů, stav α obsahuje 10^6+přebytek.



Soubor spinů

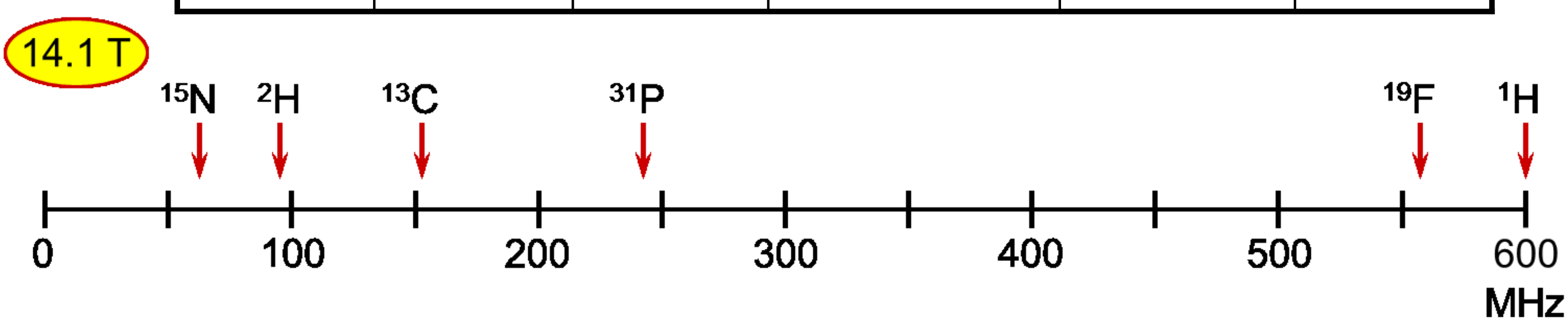


náhodné orientace

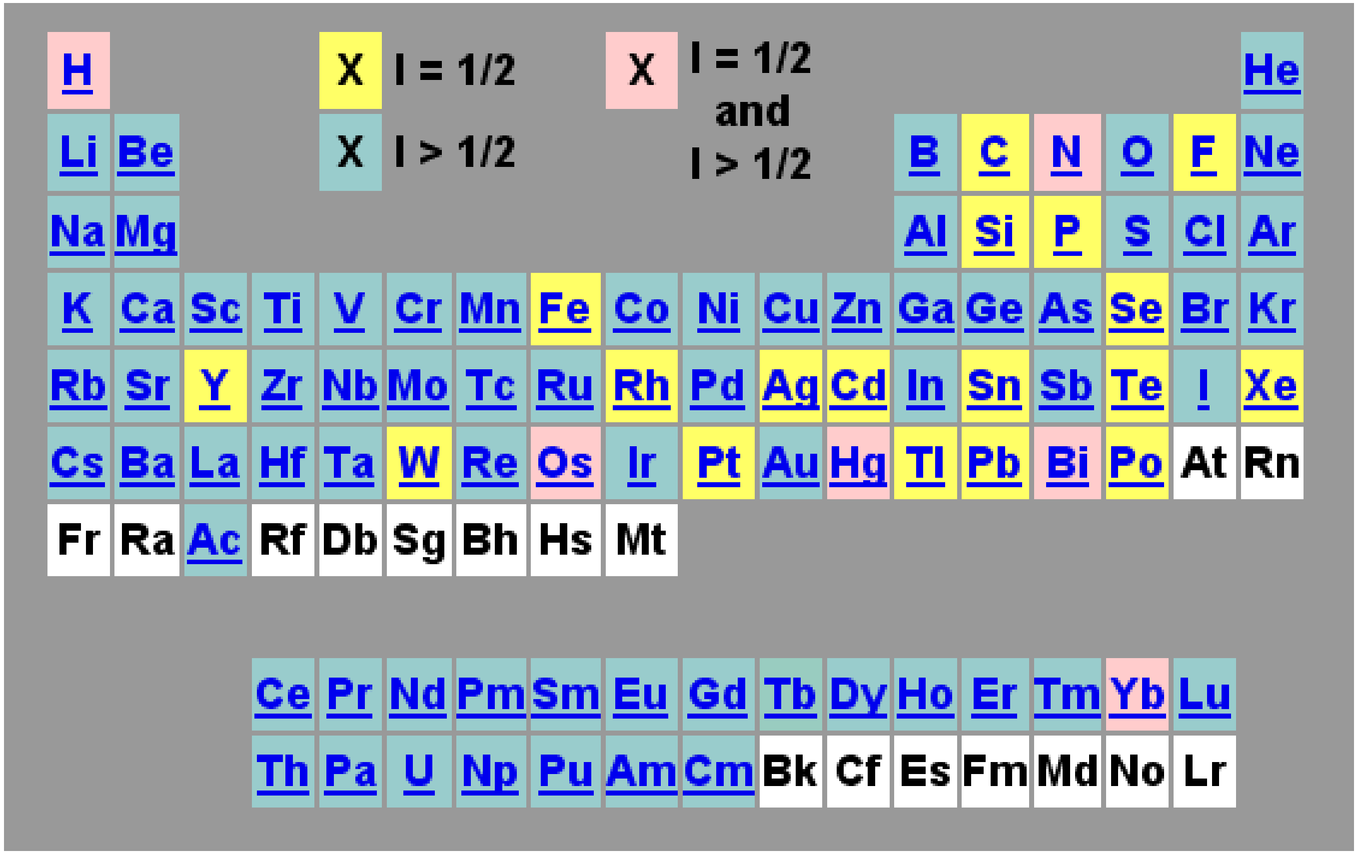
precese a polarizace

náhodná počáteční fáze

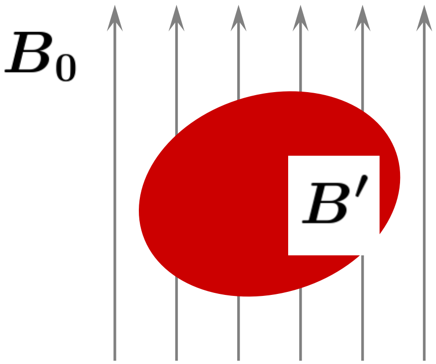
Jádro	Spin	Výskyt	γ [$10^7 rad T^{-1} s^{-1}$]	NMR frek. (11,74 T)	Citlivost
^1H	½	99,99	26,75	500,0	100
^2H	1	0,01	4,11	76,8	0,0001
^{12}C	0	98,93	-	-	-
^{13}C	½	1,07	6,73	125,7	0,02
^{14}N	1	99,63	1,93	36,1	0,1
^{15}N	½	0,37	-2,71	50,7	0,0004
^{16}O	0	99,96	-	-	-
^{19}F	½	100	25,18	470,4	83
^{31}P	½	100	10,84	202,4	6,6



Jádra a jejich spin



Stínění elektrony



Stínění jádra elektrony

lokální magnetické pole

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

pozměněná frekvence precese

$$\boxed{\delta = 10^6 \, \frac{\nu - \nu_{ref}}{\nu_{ref}}}$$

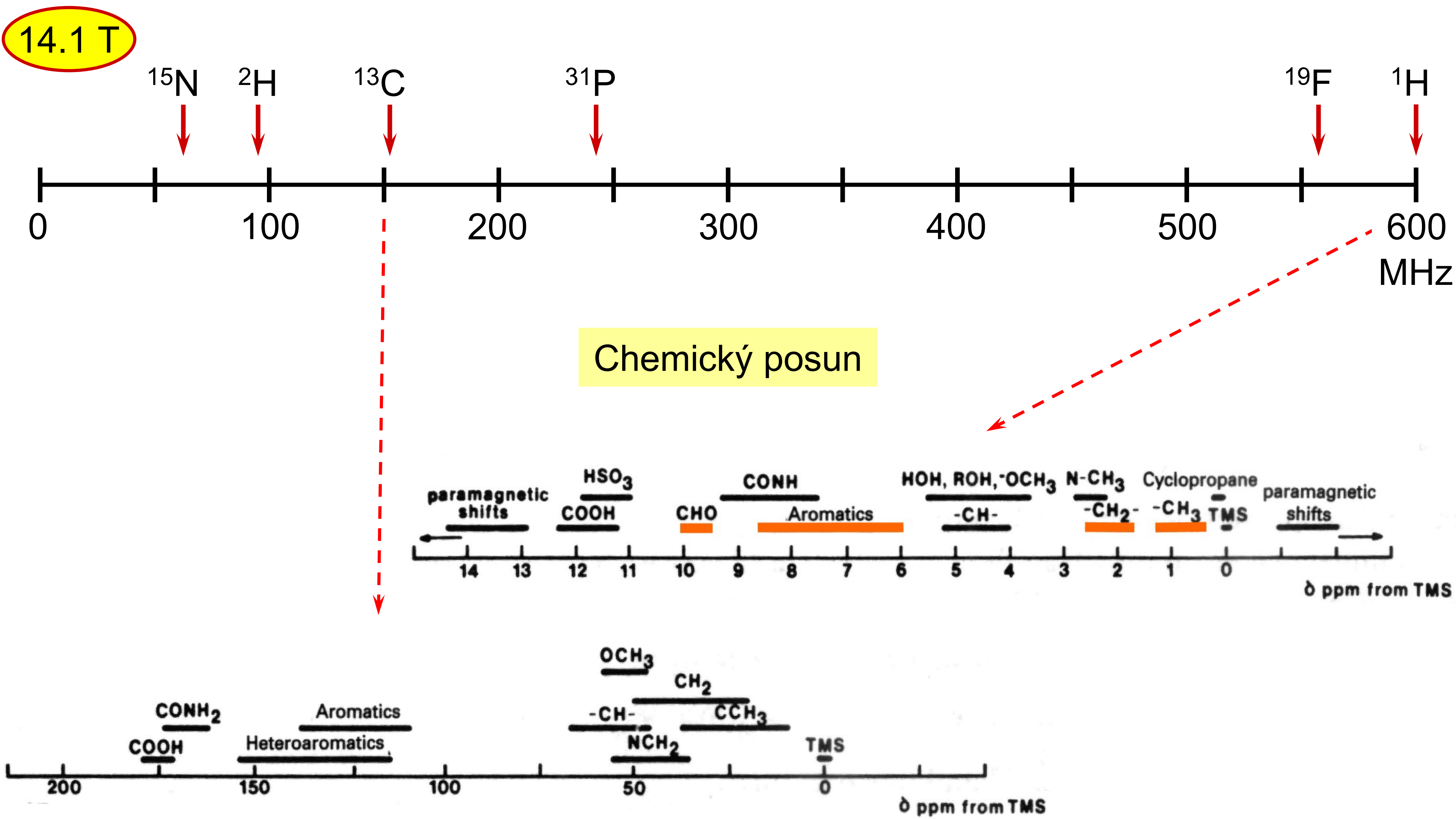
ppm

parts per milion

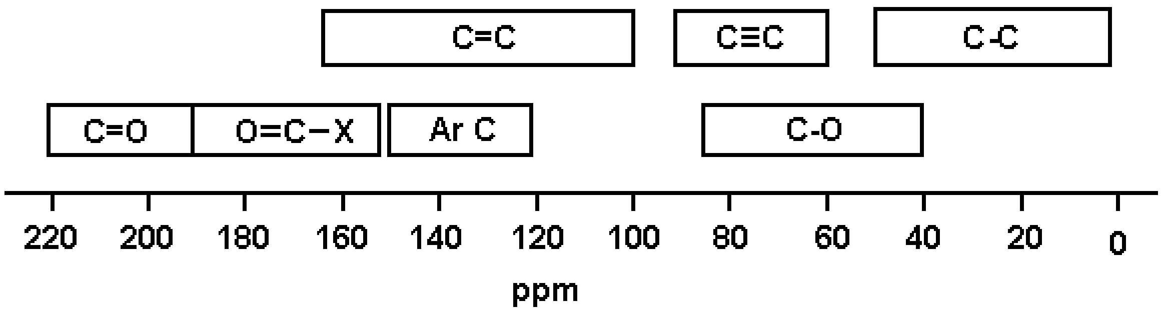
<u>Příklad pro ^{1}H</u>

TMS	500 000 000 Hz	0 ppm
MeOH	500 001 650 Hz	3,3 ppm
Benzen	500 003 635 Hz	7.27 ppm

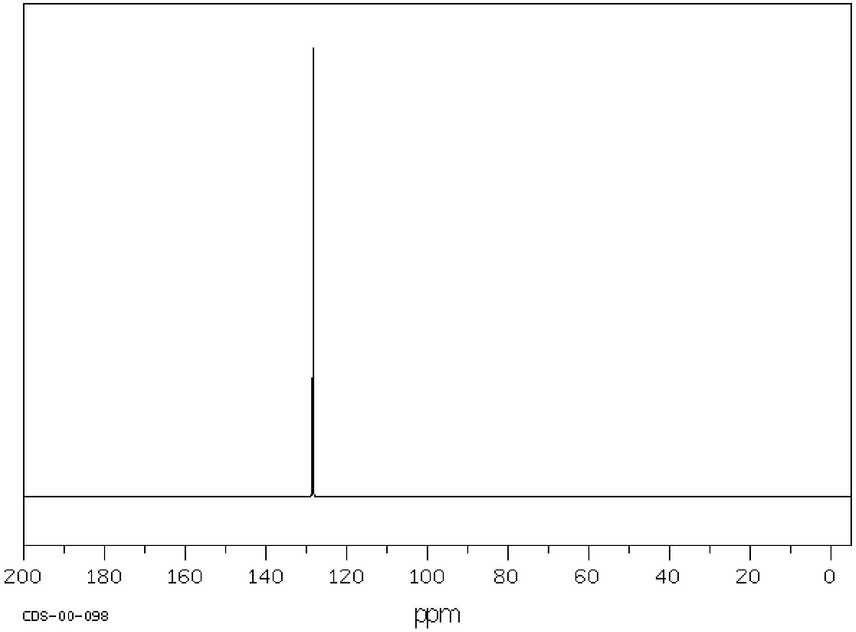
Stínění elektrony

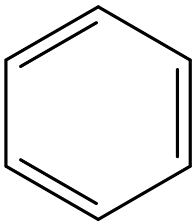


^{13}C NMR spektroskopie



Obecný princip: ***více elektronů kolem jádra = nižší*** δ





stejné chemické okolí

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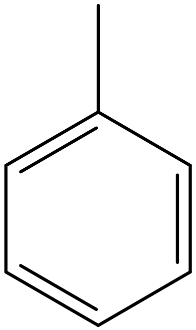
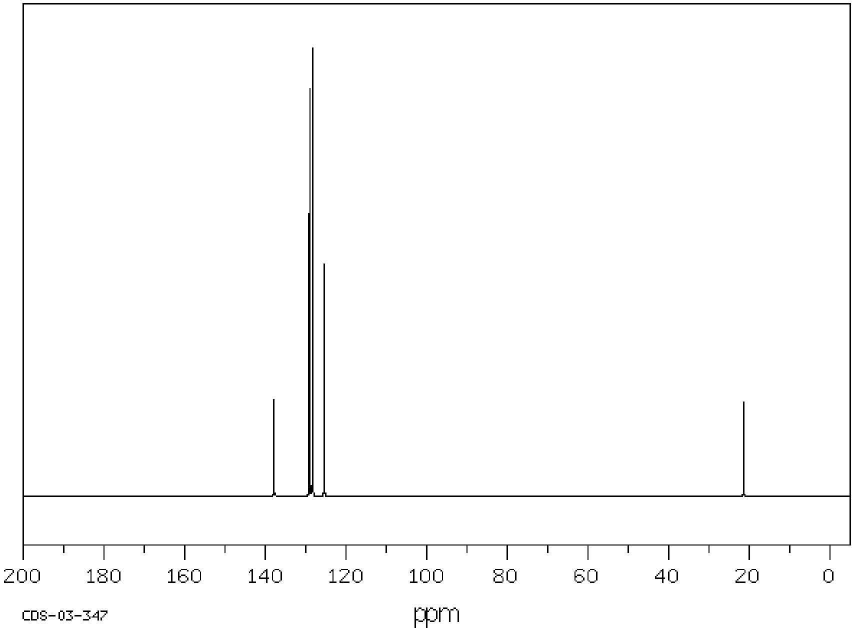
stejné stínění elektrony





počet signálů

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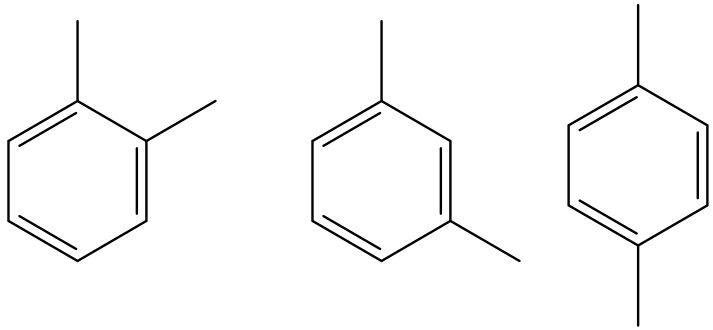
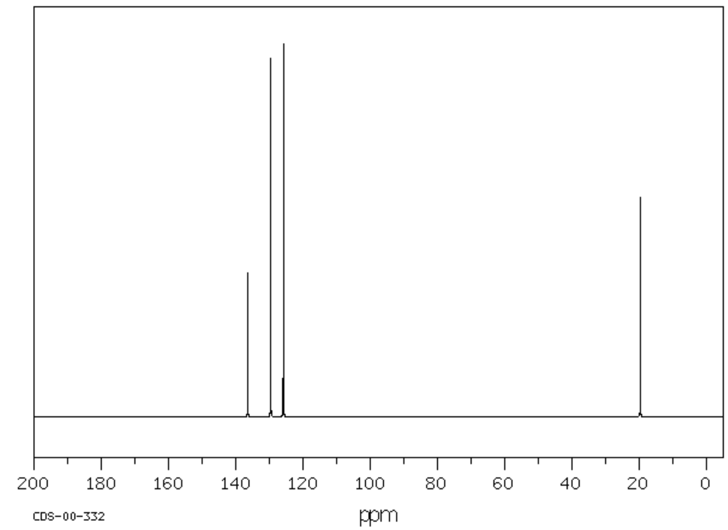
počet neekvivalentních jader





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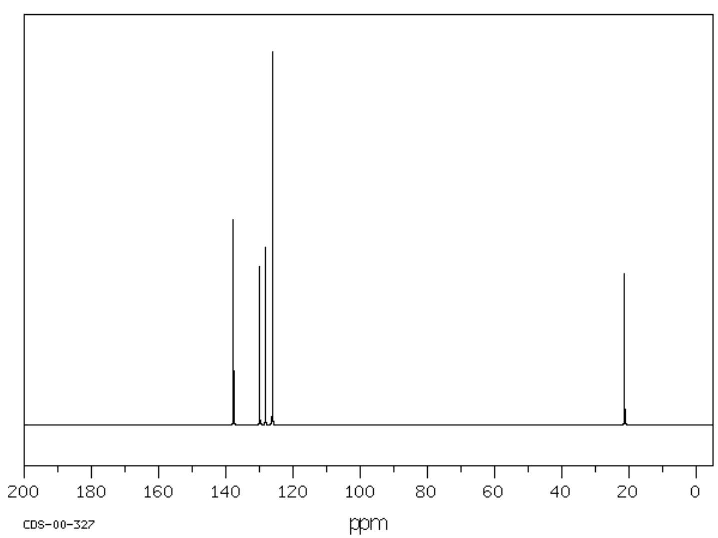
160
140
120
100
80
60
40
20
0
CDS-00-332
ppm



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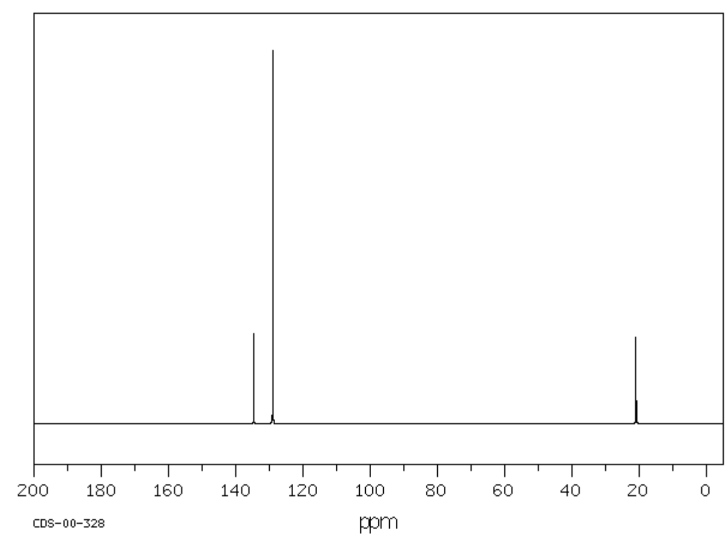
ppm



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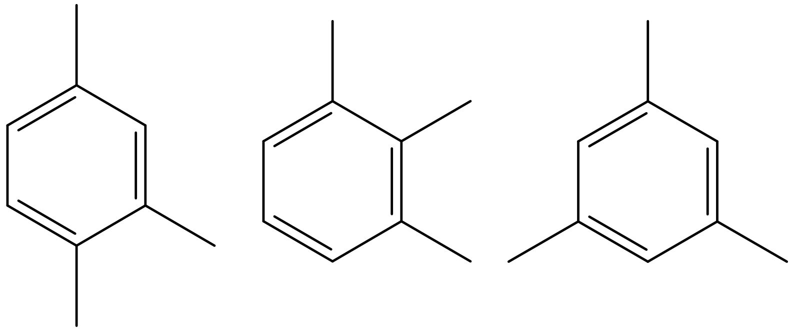
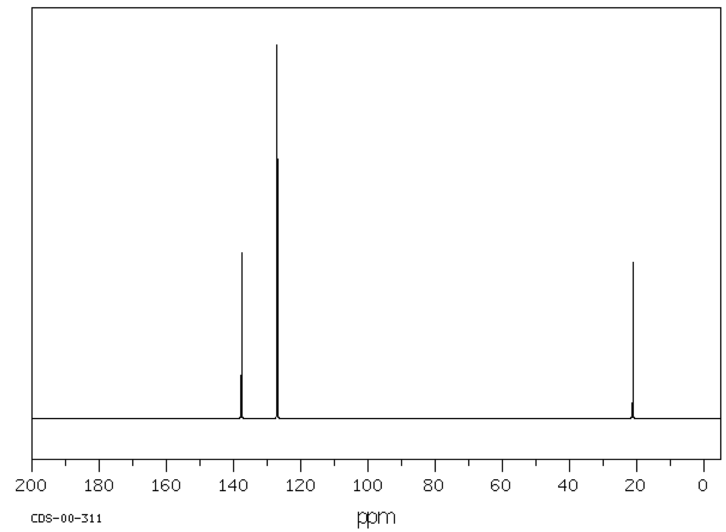
ppm

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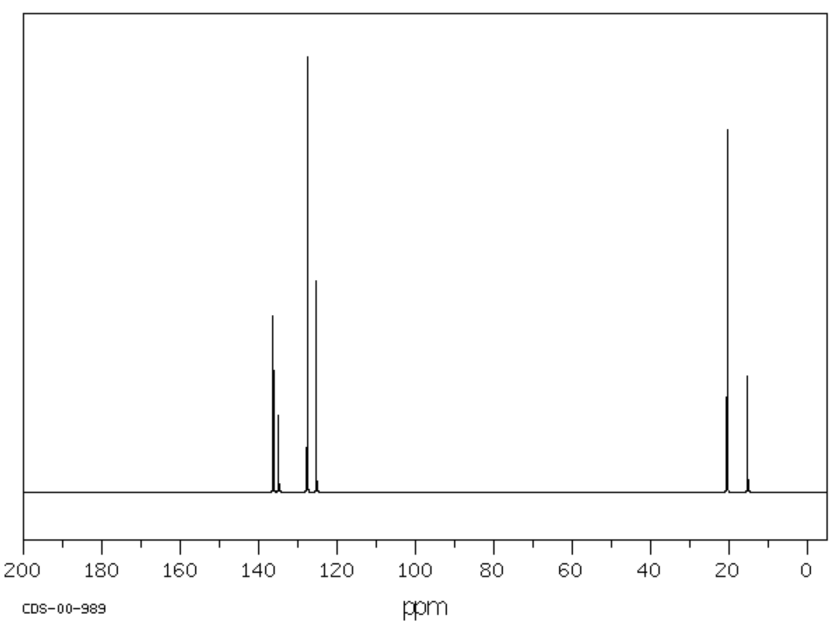
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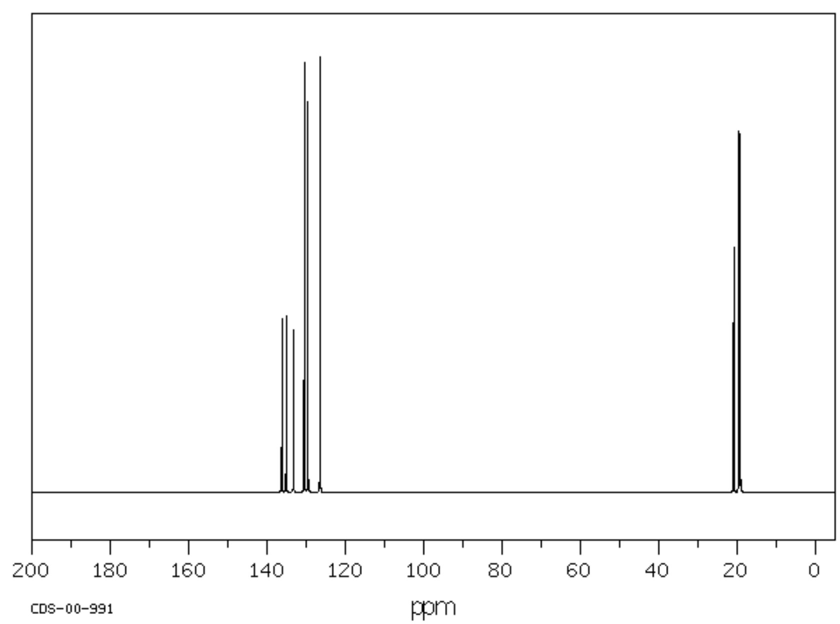
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ppm

4 izomery $C_4H_{10}O$