

NMR spektroskopie



- spektroskopická metoda založená na měření absorpce elektromagnetického záření (rádiové frekvence od asi 4 do 900 MHz)
- spinová rezonance jader v silném magnetickém poli
- lze aplikovat pouze na atomy, jejichž jádro má spinový moment (lichý počet protonů nebo neutronů)

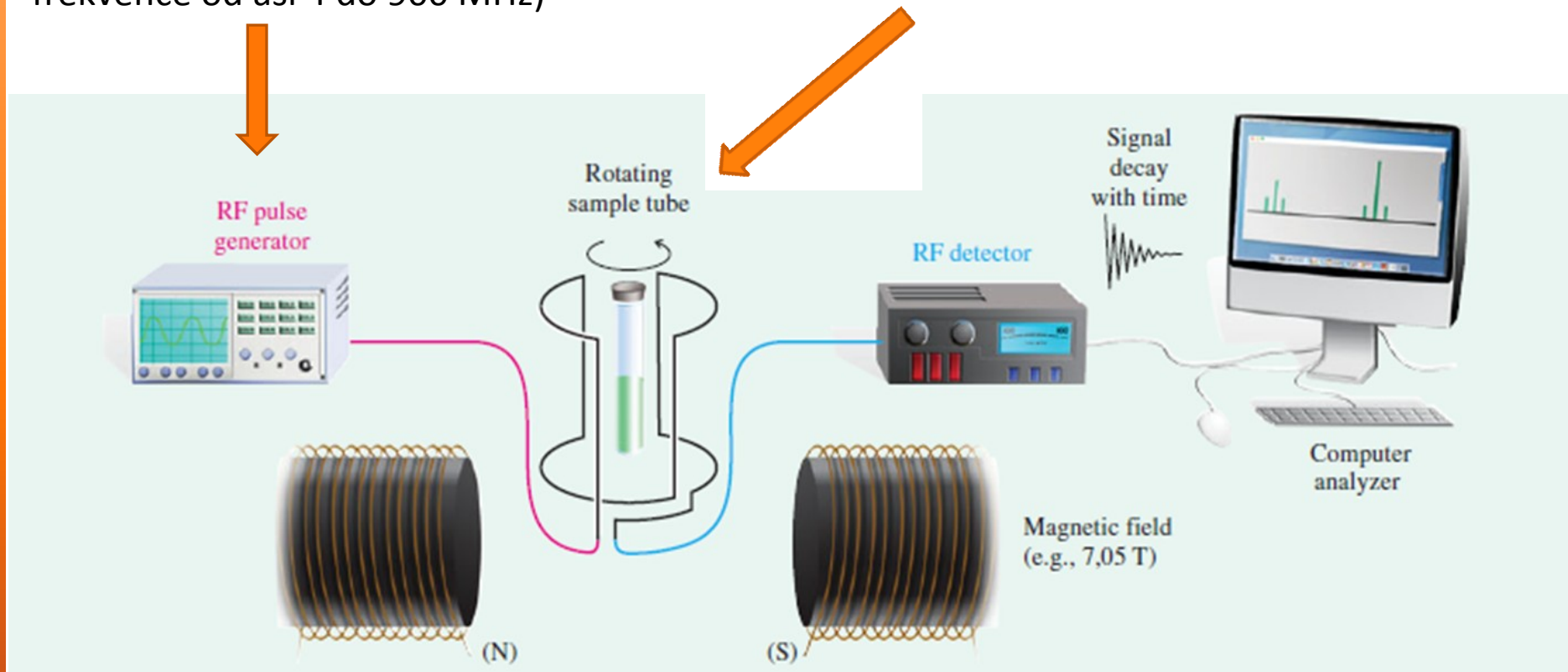
$I = 0$ (sudý počet protonů i neutronů) ^{12}C , ^{16}O , ^{32}S

$I = 1/2$ snadno měřitelná ^{15}N , ^{19}F , ^{31}P

je-li $I > 1/2$, jádra mají vedle jaderného magnetického momentu i kvadrupólový moment – obtížně měřitelná

spektroskopická metoda založená na měření absorpce elektromagnetického záření (rádiové frekvence od asi 4 do 900 MHz)

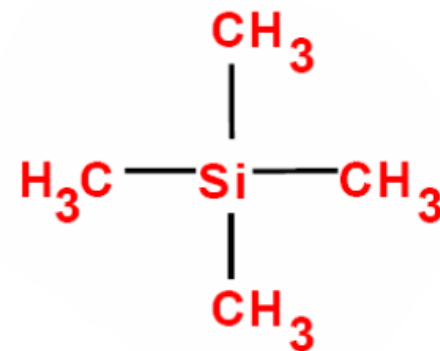
lze aplikovat pouze na atomy, jejichž jádro má spinový moment (lichý počet protonů nebo neutronů)



spinová rezonance jader v silném magnetickém poli

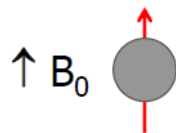


» Chemický posun

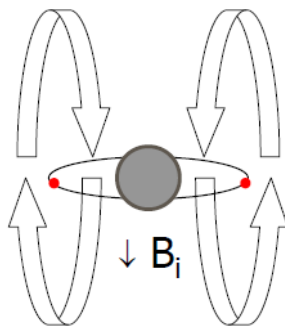


$$\delta = \frac{\text{vzdálenost píku od } (\text{CH}_3)_4\text{Si v Hz}}{\text{frekvence spektrometru v MHz}}$$

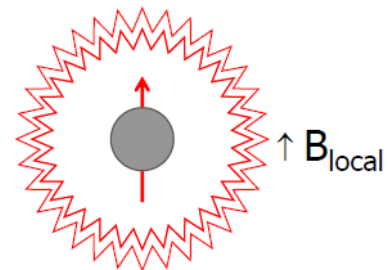




holé jádro (H^+)
bezebytku cítí vliv
vnějšího pole (B_0)



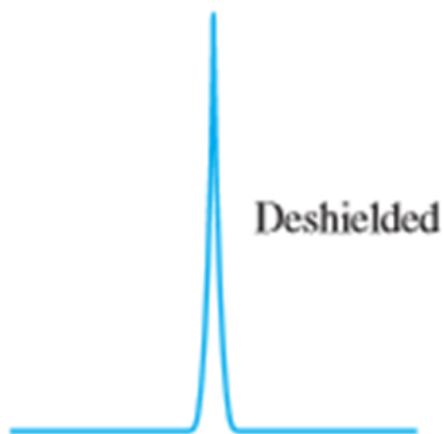
elektrony vytváří
indukované pole (B_i)
orientované proti B_0



elektronová hustota částečně
odstiňuje jádro před
 B_0 takže to cítí B_{local}

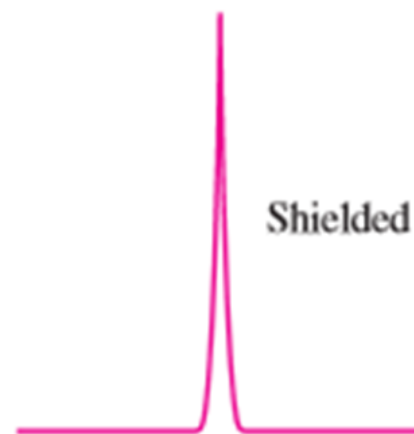
Absorption for H^+

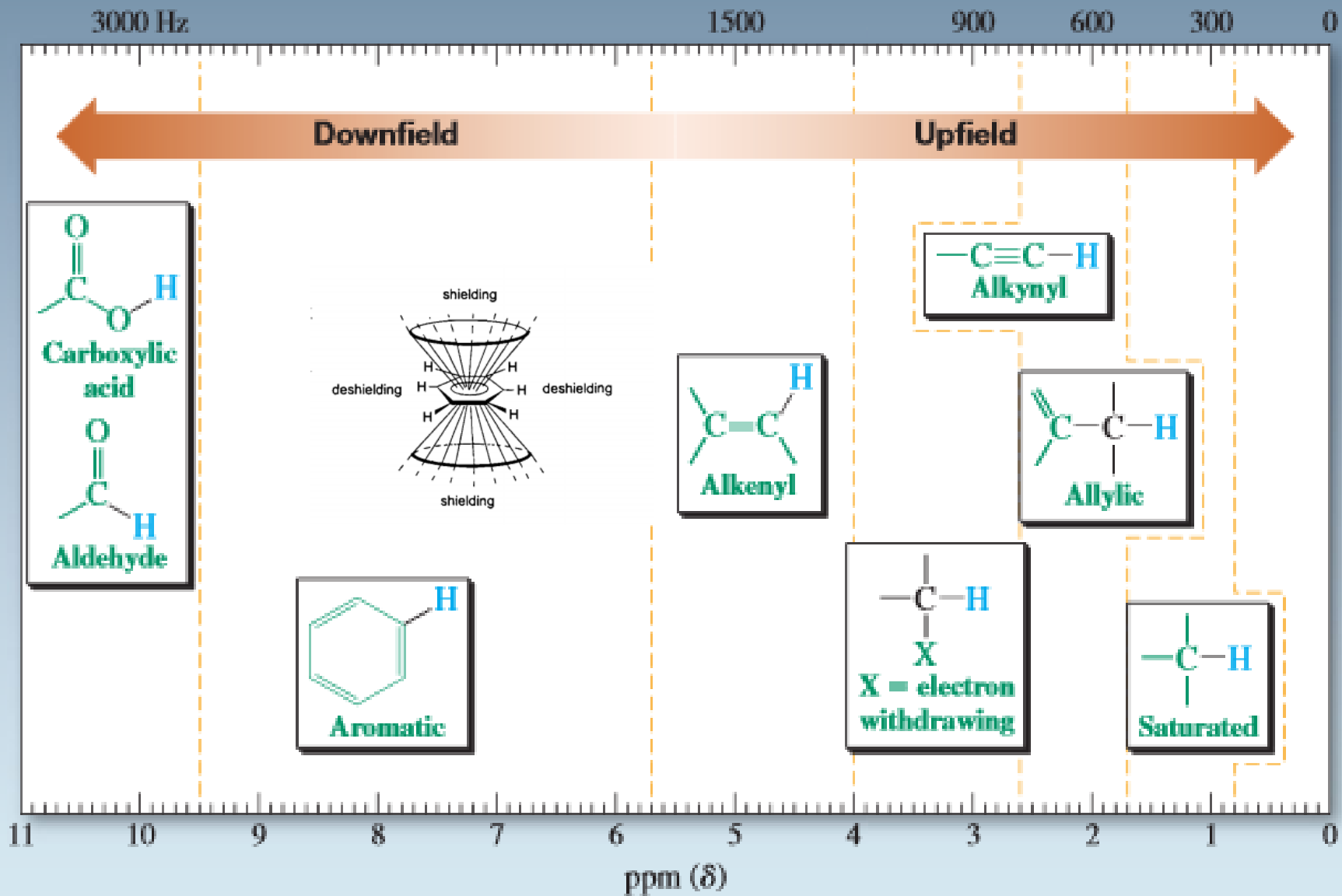
řidké
elektronové
okolí



Absorption for ---C---H

husté
elektronové
okolí

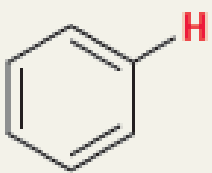
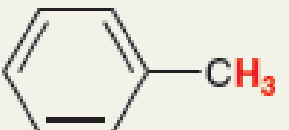




Použitá literatura (spektra)

Vollhardt, Peter K and Neil E. Schore. *Organic Chemistry Structure and Function*. Ed. Clancy Marshall. New York: W.H. Freeman and Company, 2007.

TABLE 16.2 CHEMICAL SHIFTS FOR PROTONS IN DIFFERENT ELECTRONIC ENVIRONMENTS

TYPE OF PROTON	CHEMICAL SHIFT (δ)	TYPE OF PROTON	CHEMICAL SHIFT (δ)		
Methyl	$R-CH_3$	~ 0.9	Alkyl halide	$\begin{array}{c} H \\ \\ R-C-X \\ \\ R \end{array}$	2-4
Methylene	$\text{>}CH_2$	~ 1.2	Alcohol	$R-O-H$	2-5
Methine	$\begin{array}{c} \\ -CH \\ \end{array}$	~ 1.7	Vinylic	$\begin{array}{c} H \\ \\ =C \end{array}$	4.5-6.5
Allylic	$\begin{array}{c} \text{>}C=C \\ \\ -CH_2-H \end{array}$	~ 2	Aryl		6.5-8
Alkynyl	$R-C\equiv C-H$	~ 2.5	Aldehyde	$\begin{array}{c} O \\ \\ R-C-H \end{array}$	~ 10
Aromatic methyl		~ 2.5	Carboxylic acid	$\begin{array}{c} O \\ \\ R-C-O-H \end{array}$	~ 12

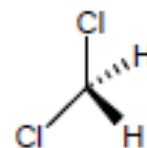


Symetrie molekuly pomáhá určit chemickou ekvivalenci



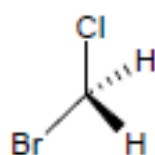
- NMR spektrum odráží symetrii molekuly
- o tom, zda dvojice atomů poskytne dva různé signály nebo jen jeden, rozhoduje jejich vzájemný vztah při operacích symetrie

Homotopické atomy

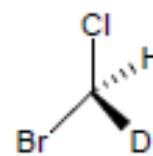
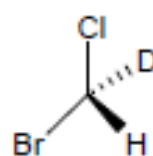


C_2 osa symetrie
ekvivalentní
1 signál ve spektru

Enantiotopické atomy



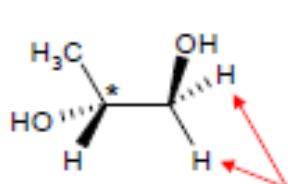
deuteriová
substituce
→



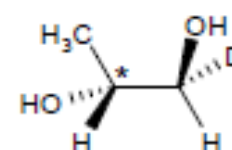
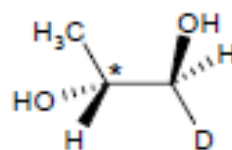
enantiomery

rovina symetrie
není osa symetrie
ekvivalentní
1 signál ve spektru

Diastereotopické atomy (molekuly s chirálním centrem)



deuteriová
substituce
→

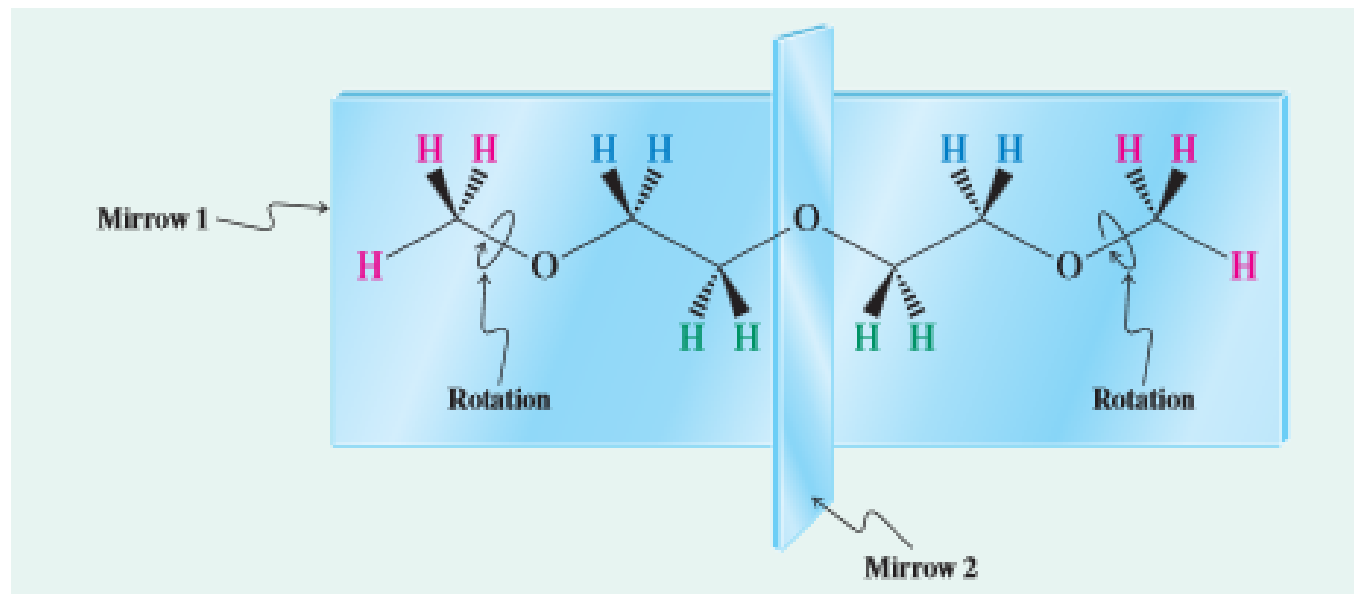
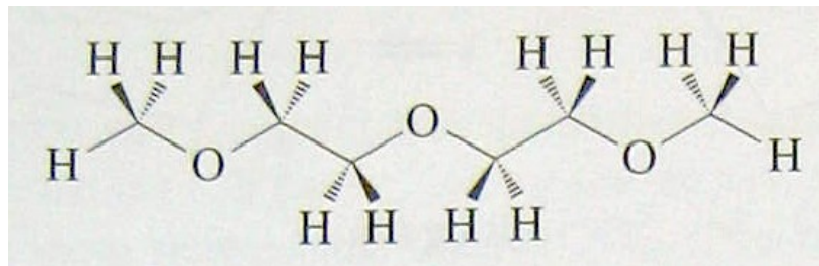


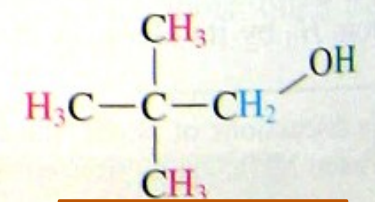
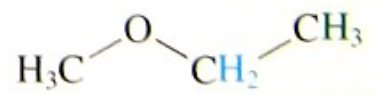
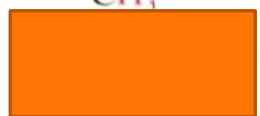
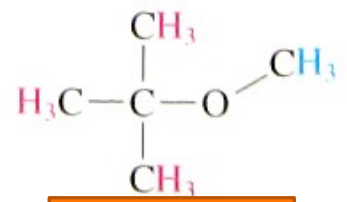
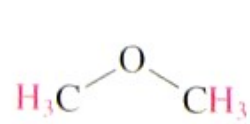
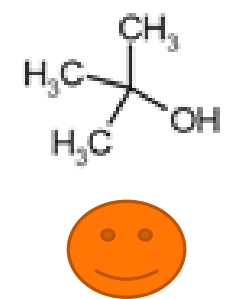
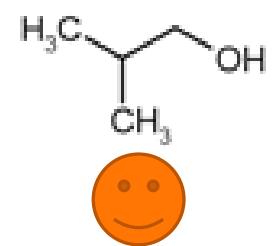
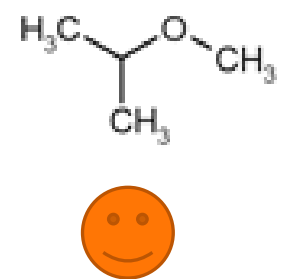
diastereomery

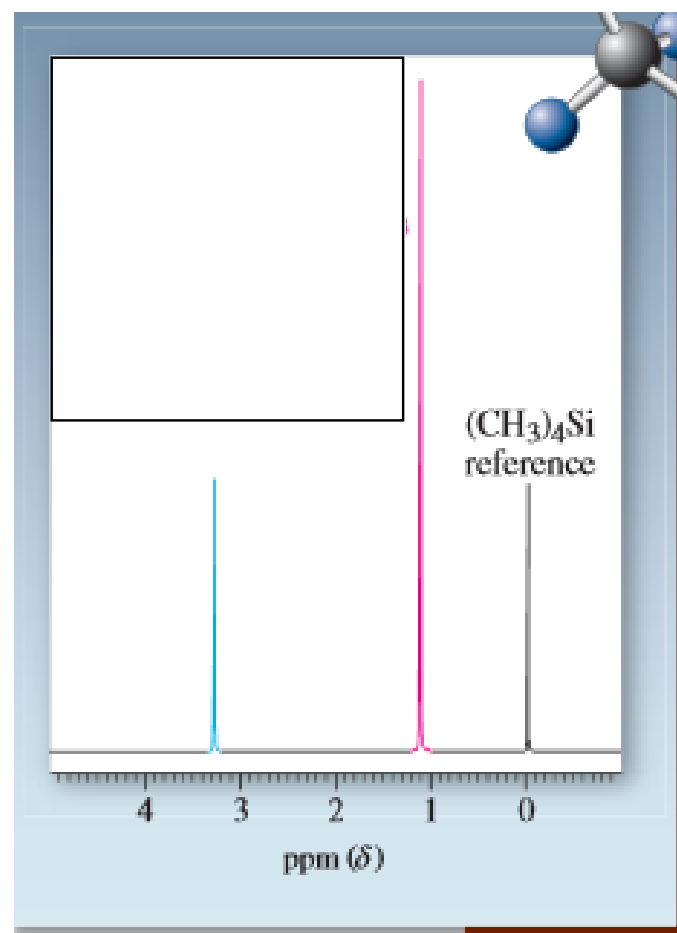
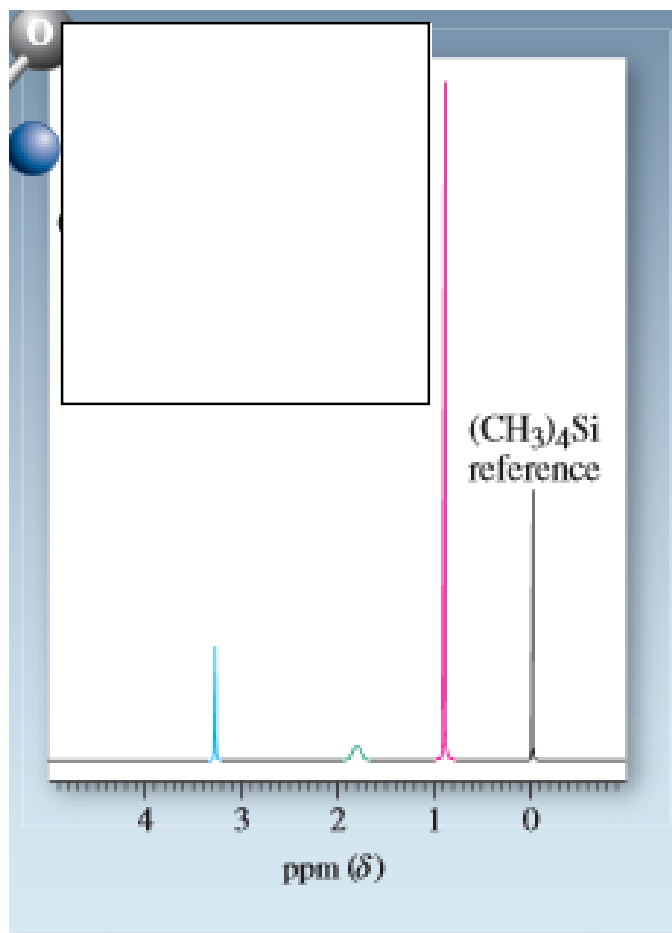
není osa symetrie
není rovina symetrie
neekvivalentní
rozišitelné ve spektru

diastereotopické
metylenové vodíky

Kolik ^1H NMR signálů očekáváte u níže uvedené molekuly?







Rozhodněte, které spektrum náleží molekule *(terc-butyl)(methyl)etheru* a které molekule 2,2-dimethylpropanolu?



» Vyměnitelné protony

- protony v **OH**, **NH**, **SH**: proměnlivé chemické posuny
- kyselý charakter
- H můstky, chemická výměna
- závislost na koncentraci, teplotě, rozpouštědle atd.
- chem. posuny reprodukovatelné pouze za přesně definovaných podmínek
- multiplety nebo široké singlety (v závislosti na rychlosti chemické výměny)
- přítomnost více vyměnitelných protonů: inter- nebo intramolekulární chemická výměna
- praktické využití výměny protonů za deuterium (D_2O , CD_3COOD)

OH

alkoholy 1 - 5 ppm
fenoly 4 - 10 ppm
kyseliny 9 - 13 ppm
enoly 10 - 17 ppm

NH

aminy 1 - 5 ppm
amidy 5 - 6.5 ppm
amidické skupiny v peptidech 7 - 10 ppm

SH

alifatické thioly 1 - 2.5 ppm
aromatické thioly 3 - 4 ppm



^1H NMR



15 mm
(equivalent to 6 H)

10 mm (equivalent to 4 H)

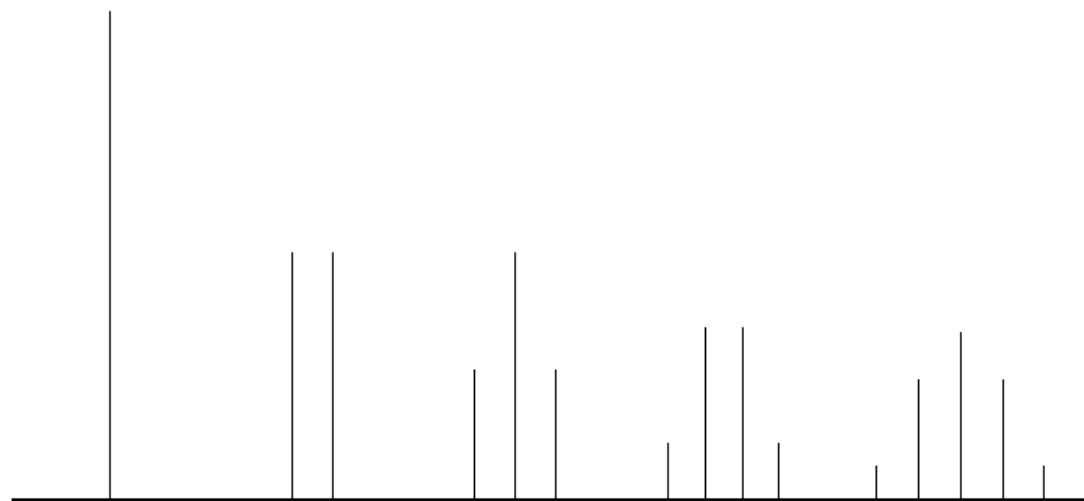
9 8 7 6 5 4 3 2 1 0

ppm (δ)

B



» Multiplicita signálů



singlet

dublet

triplet

kvartet

kvintet

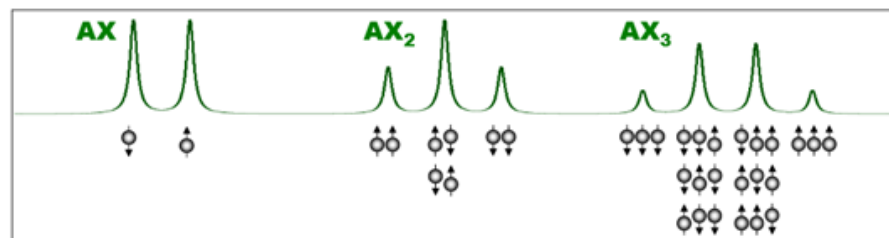
1 : 1

1 : 2 : 1

1 : 3 : 3 : 1

1 : 4 : 6 : 4 : 1

Multiplicita signálu – Počet linií pro $I = \frac{1}{2}$



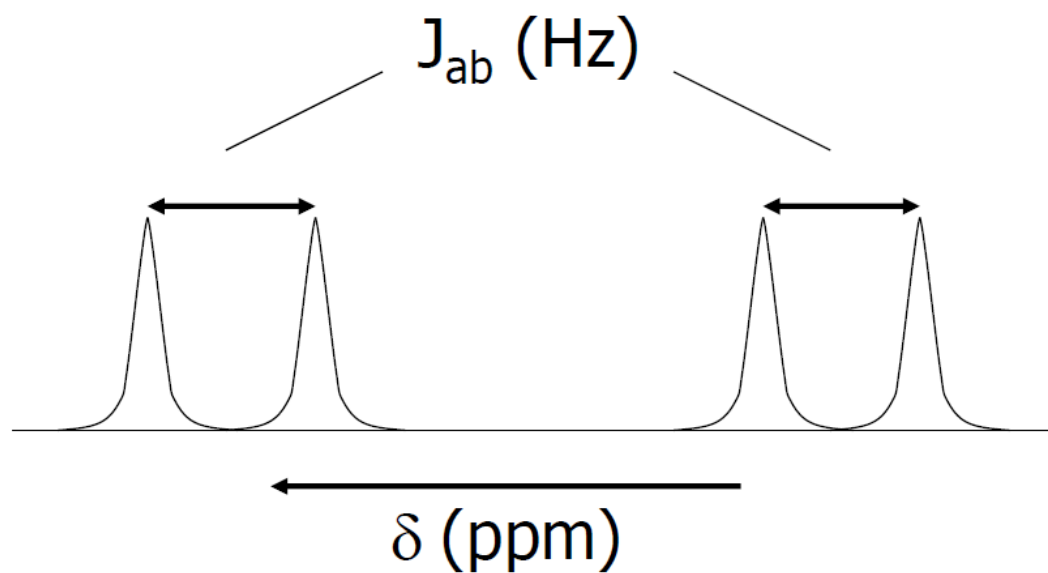
	Splitting pattern for H_a	Structure	Splitting pattern for H_b	
H_a has one neighbor H_b : 2 peaks or doublet				H_b has one neighbor H_a : 2 peaks or doublet
H_a has one neighbor H_b : 2 peaks or doublet				H_b has two neighbors H_a : 3 peaks or triplet
H_a has two neighbors H_b : 3 peaks or triplet				H_b has two neighbors H_a : 3 peaks or triplet
H_a has one neighbor H_b : 2 peaks or doublet				H_b has three neighbors H_a : 4 peaks or quartet
H_a has two neighbors H_b : 3 peaks or triplet				H_b has three neighbors H_a : 4 peaks or quartet
H_a has one neighbor H_b : 2 peaks or doublet				H_b has six neighbors H_a : 7 peaks or septet

Note: H_a and H_b are not equivalent and have no other coupled nuclei in their vicinity.



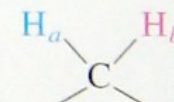
» Interakční konstanta

nezávisí na H_0 vnějšího magnetického pole

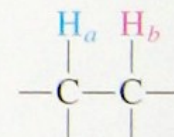


	$J(H,H)$ [Hz]	$J(C,H)$ [Hz]
geminální	1J	125 - 250
vicinální	2J	0 - 30
	3J	-10 až 20
dalekého dosahu (long range)	$3+nJ$	1 - 10
		<1

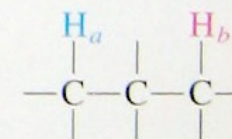
Coupling Between Close-Lying Hydrogens



J_{ab} , geminal coupling, variable 0-18 Hz



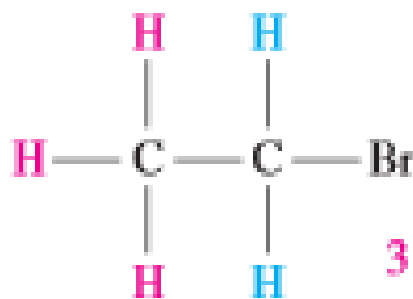
J_{ab} , vicinal coupling, typically 6-8 Hz



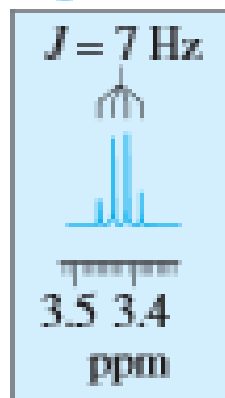
J_{ab} , 1,3-coupling, usually negligible



^1H NMR



3 H neighbors:
quartet



2 H

2 H neighbors:
triplet

3 H

$J = 7 \text{ Hz}$



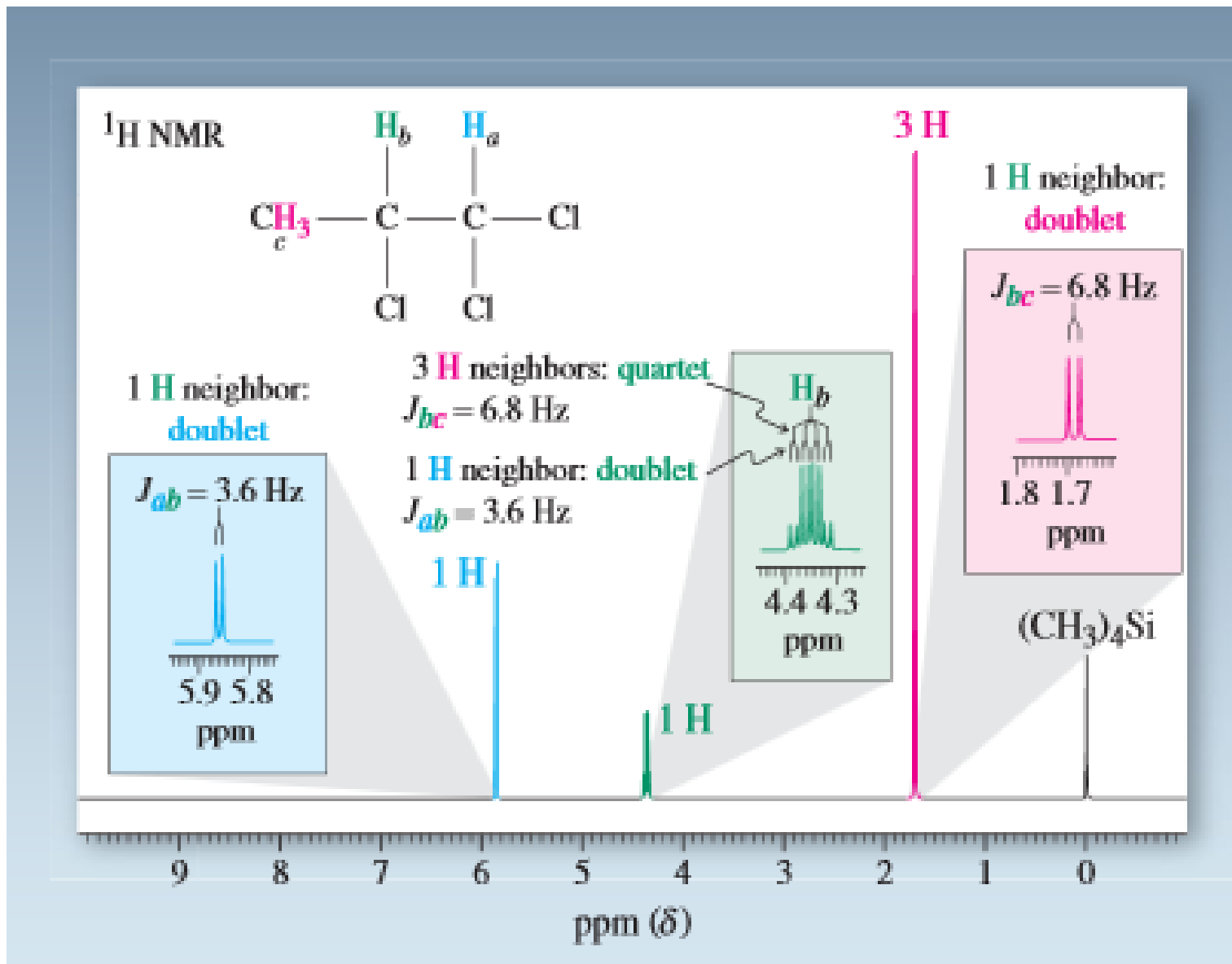
$(\text{CH}_3)_4\text{Si}$

9 8 7 6 5 4 3 2 1 0

ppm (δ)

Použitá literatura (spektra)

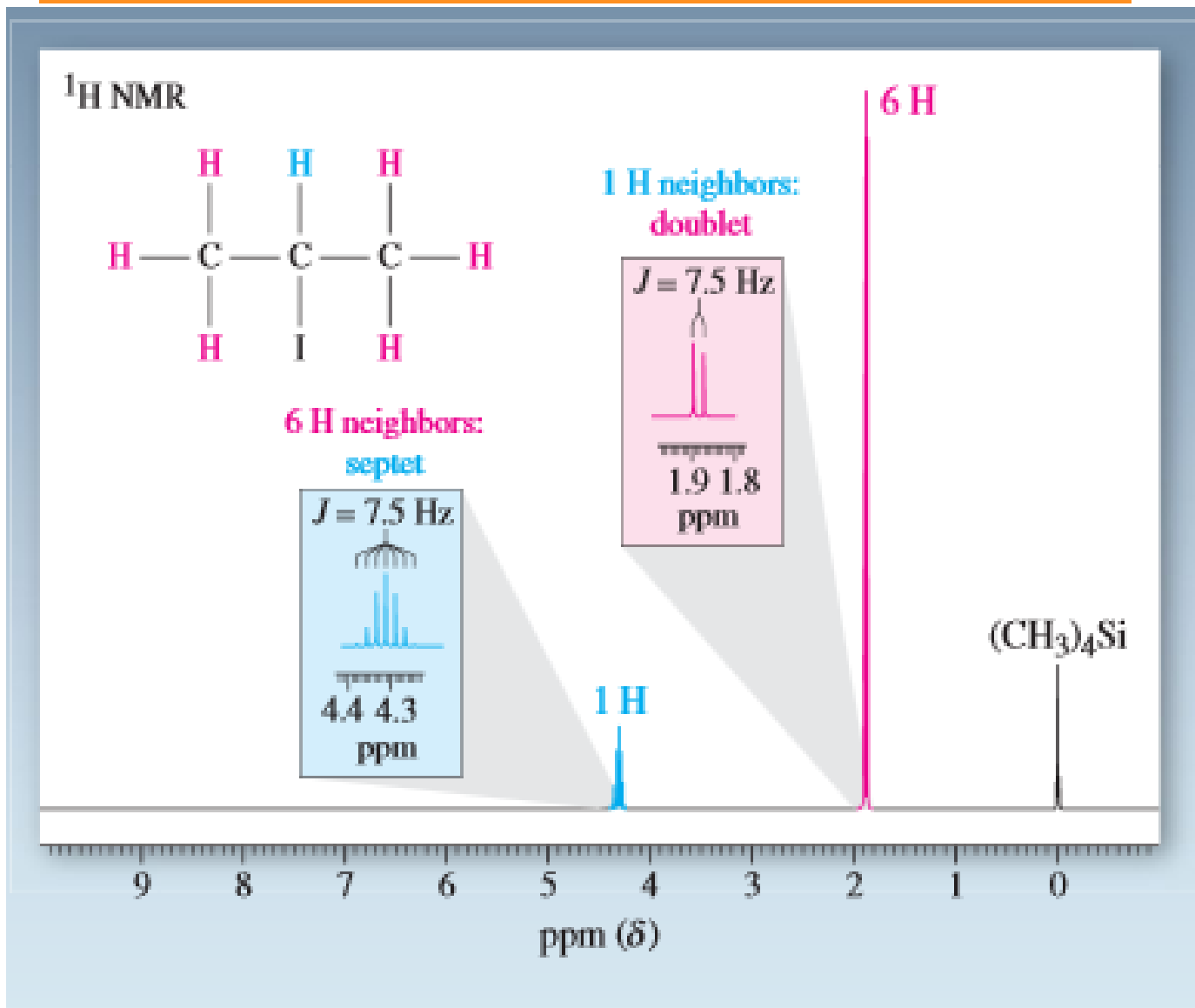
Vollhardt, Peter K and Neil E. Schore. Organic Chemistry Structure and Function. Ed. Clancy Marshall. New York: W.H. Freeman and Company, 2007.



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Vollhardt, Peter K and Neil E. Schore. *Organic Chemistry Structure and Function*. Ed. Clancy Marshall. New York: W.H. Freeman and Company, 2007.

Pokuste se navrhnout ^1H NMR spektrum 2-jodpropanu

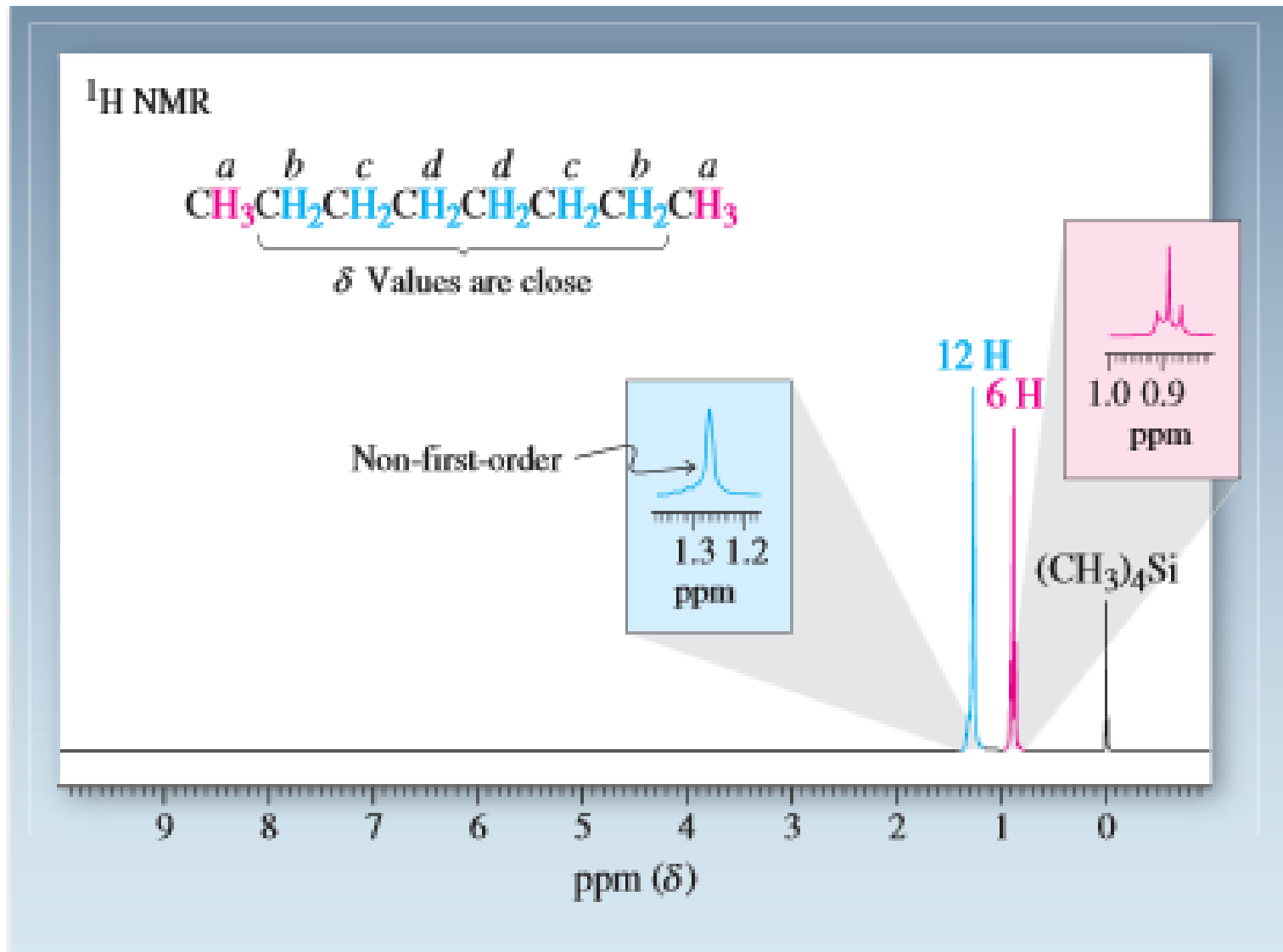


Použitá literatura (spektra)

Vollhardt, Peter K and Neil E. Schore. *Organic Chemistry Structure and Function*. Ed. Clancy Marshall. New York: W.H. Freeman and Company, 2007.



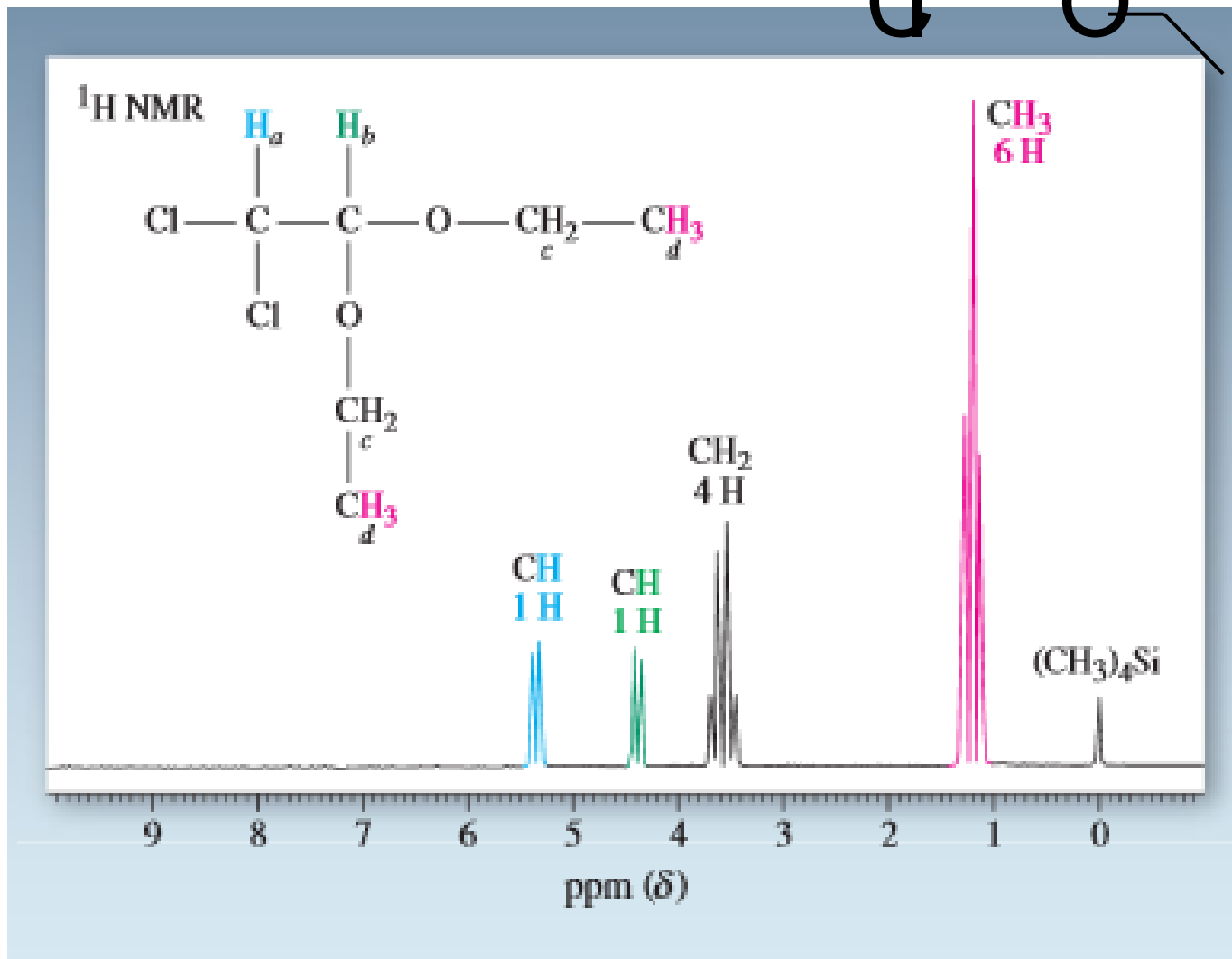
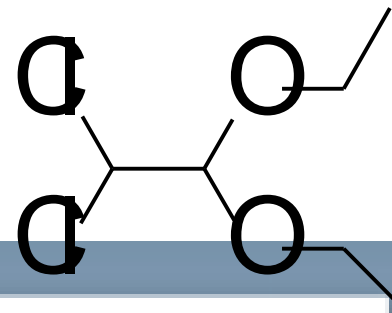
Pokuste se navrhnout ^1H NMR spektrum oktanu



Použitá literatura (spektra)

Vollhardt, Peter K and Neil E. Schore. Organic Chemistry Structure and Function. Ed. Clancy Marshall. New York: W.H. Freeman and Company, 2007.

Pokuste se navrhnout ^1H NMR spektrum uvedené sloučeniny

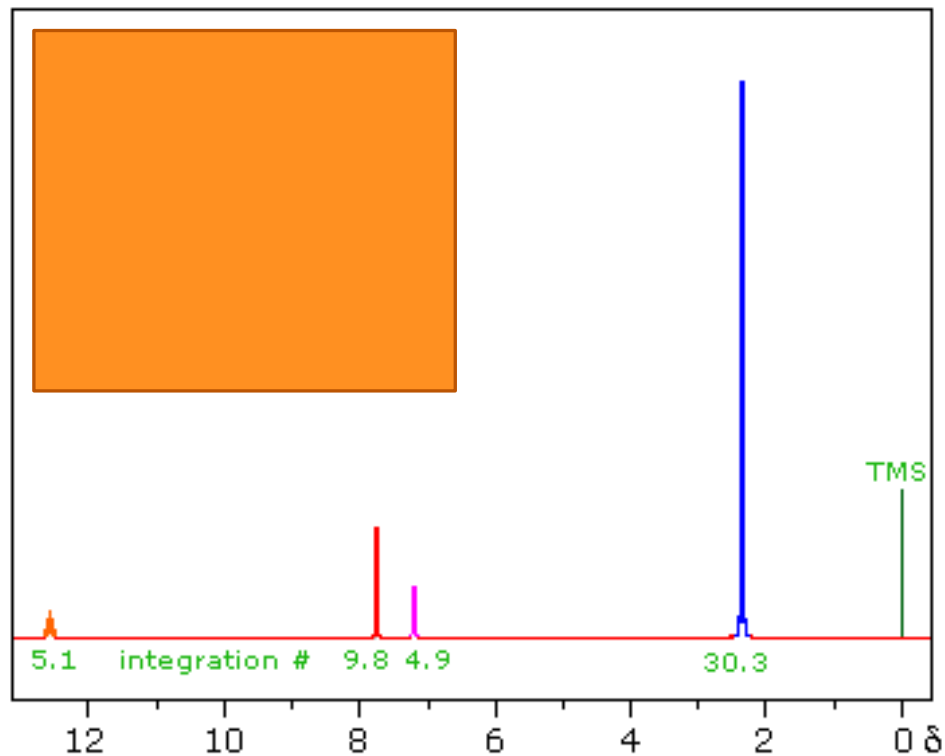
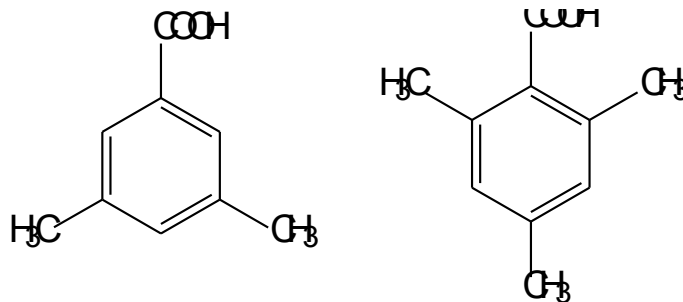


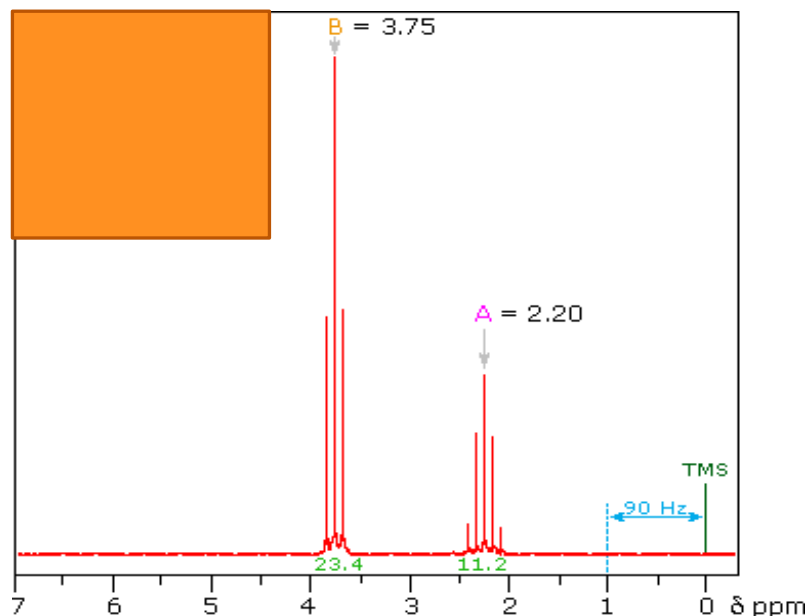
Použitá literatura (spektra)

Vollhardt, Peter K and Neil E. Schore. [Organic Chemistry Structure and Function](#). Ed. Clancy Marshall. New York: W.H. Freeman and Company, 2007.



Rozhodněte, které z následujících sloučenin odpovídá níže uvedené ^1H NMR spektrum.



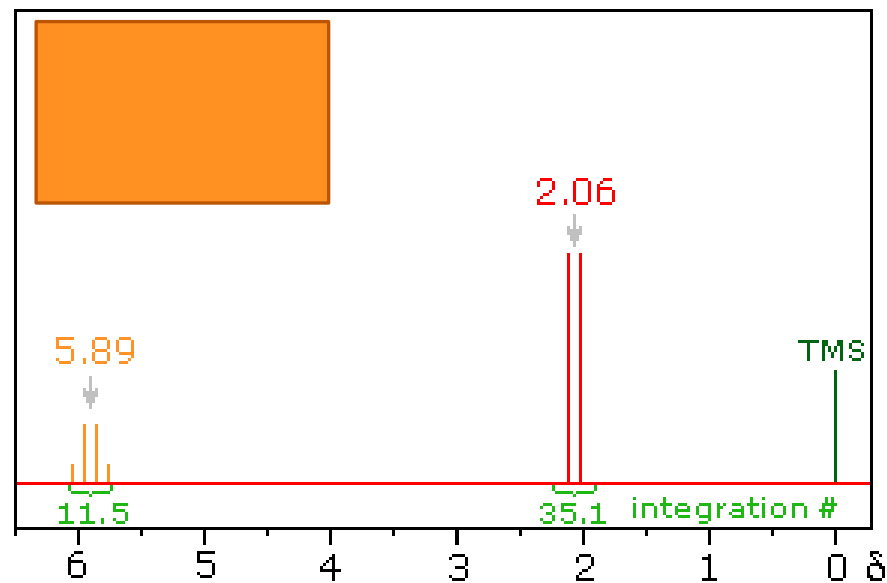
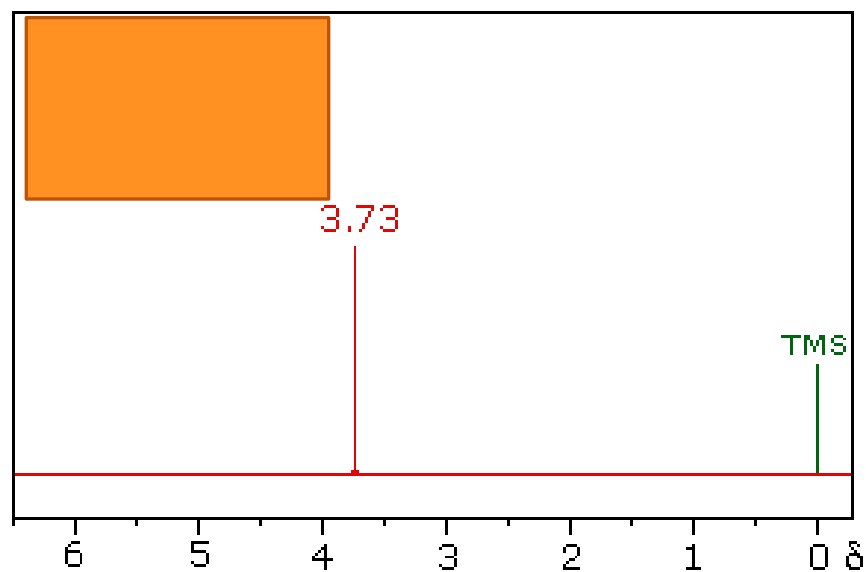


Přiřaďte následující ^1H NMR spektra níže uvedeným sloučeninám:

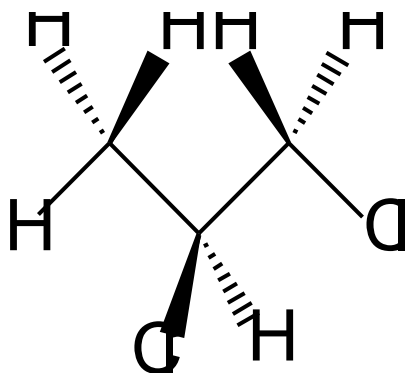
1,1-dichlorethan

1,2-dichlorethan

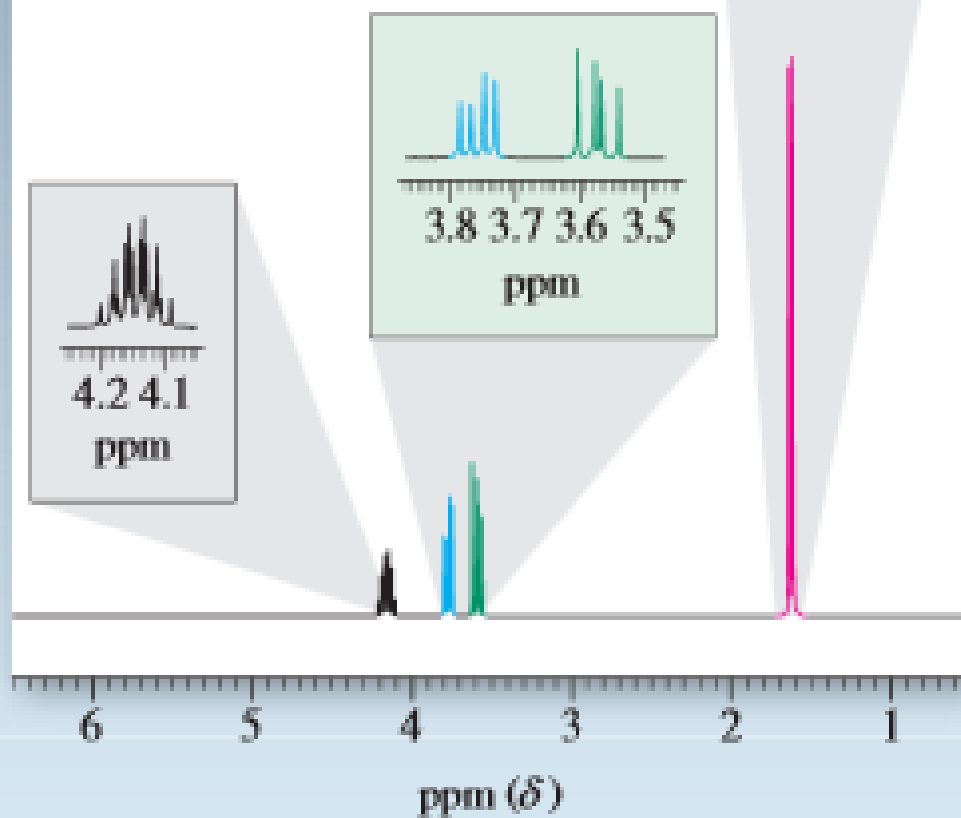
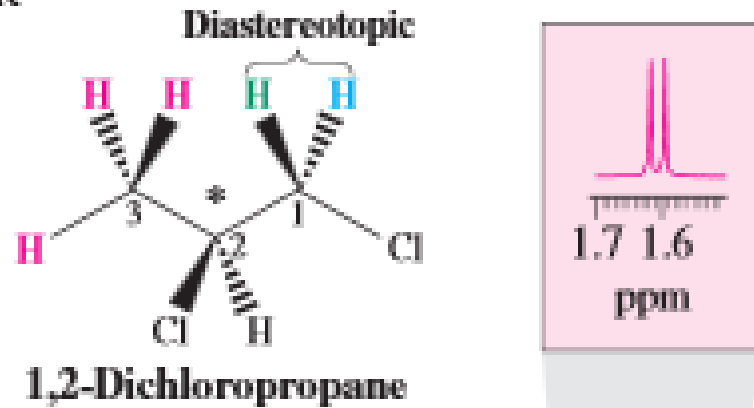
1,3-dichlorpropan



Pokuste se navrhnout, jak bude vypadat ^1H NMR spektrum uvedené sloučeniny



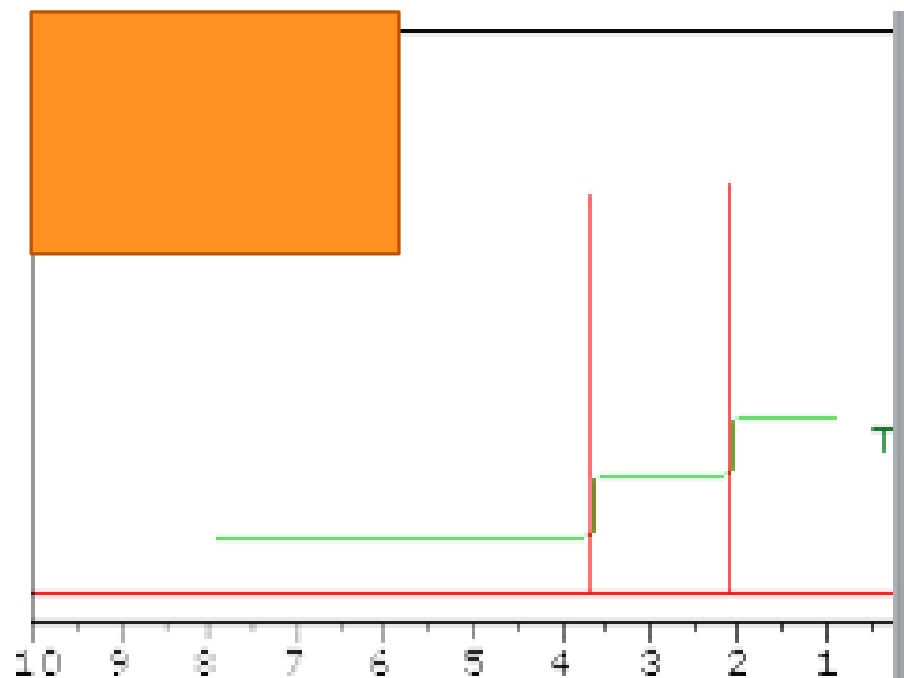
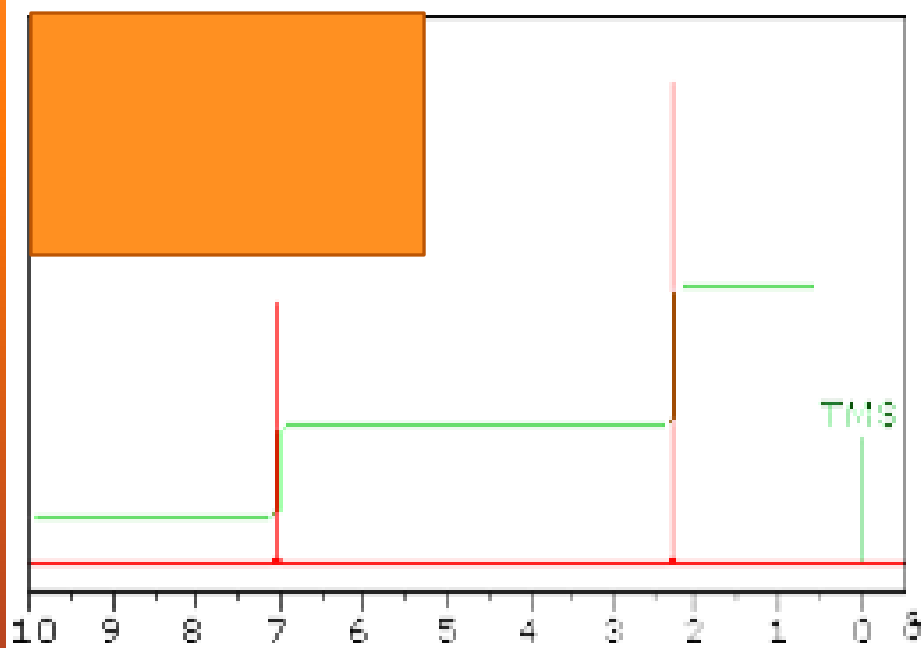
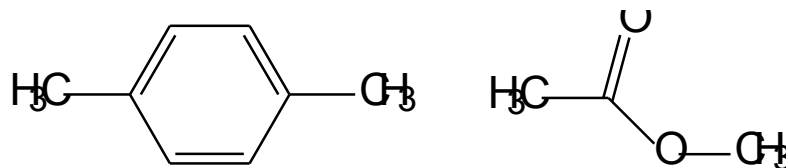
^1H NMR



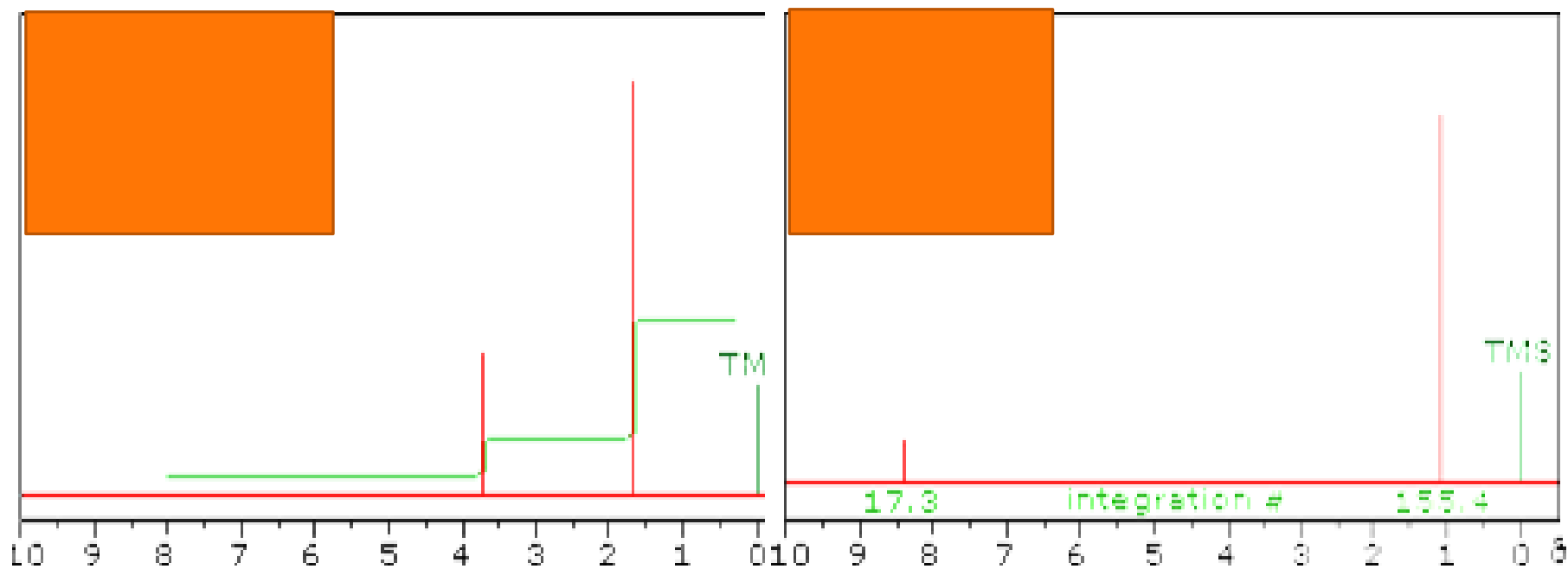
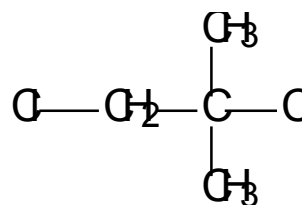
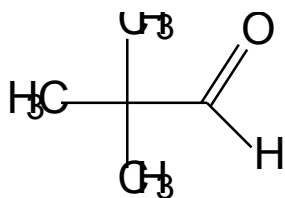
Použitá literatura (spektra)

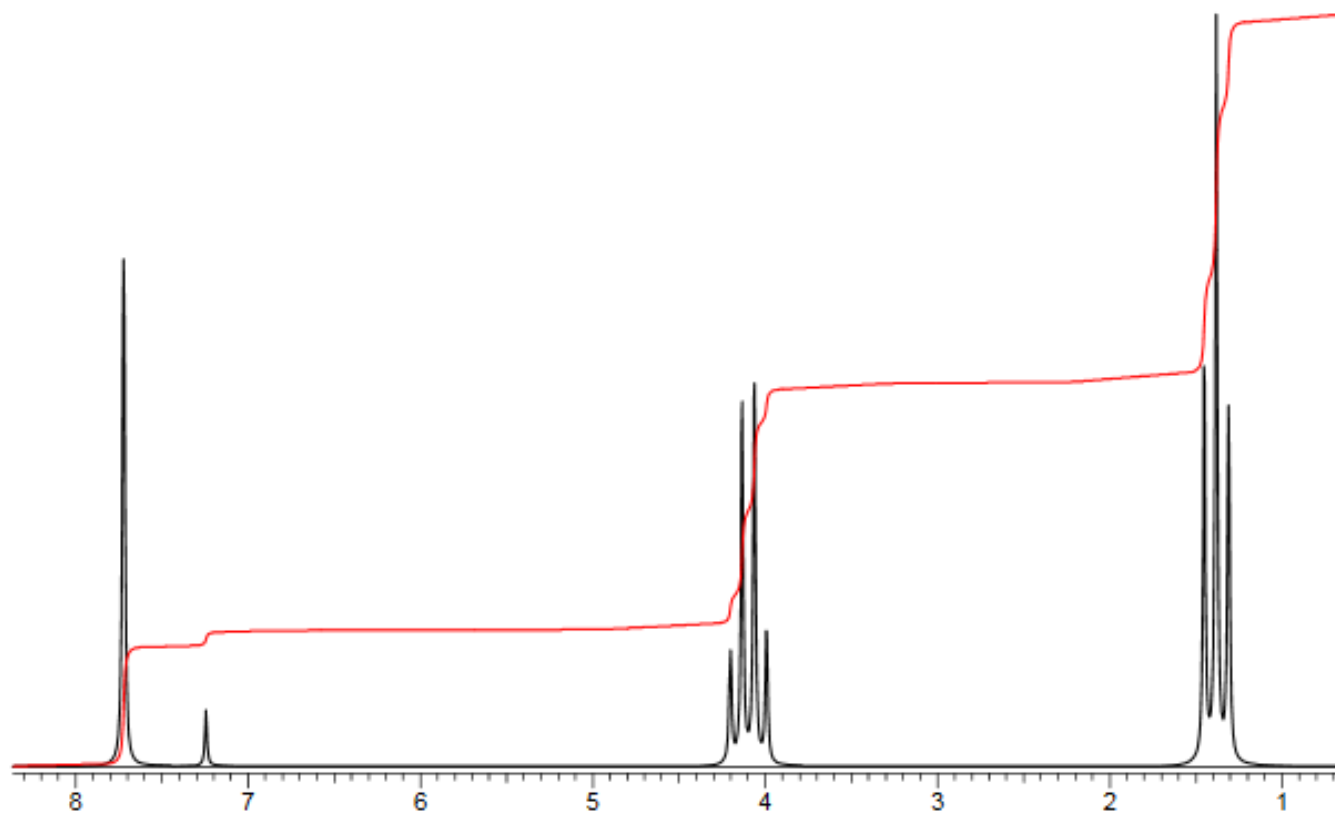
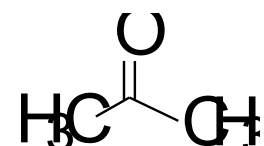
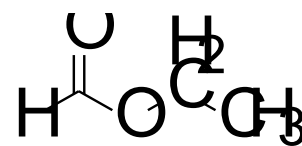
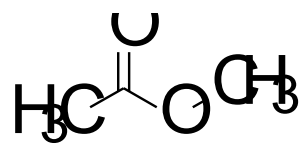
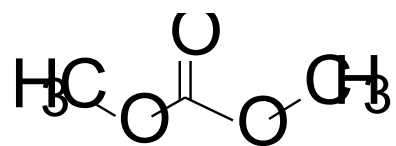
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Rozhodněte, které z následujících sloučenin odpovídá níže uvedené ^1H NMR spektrum.



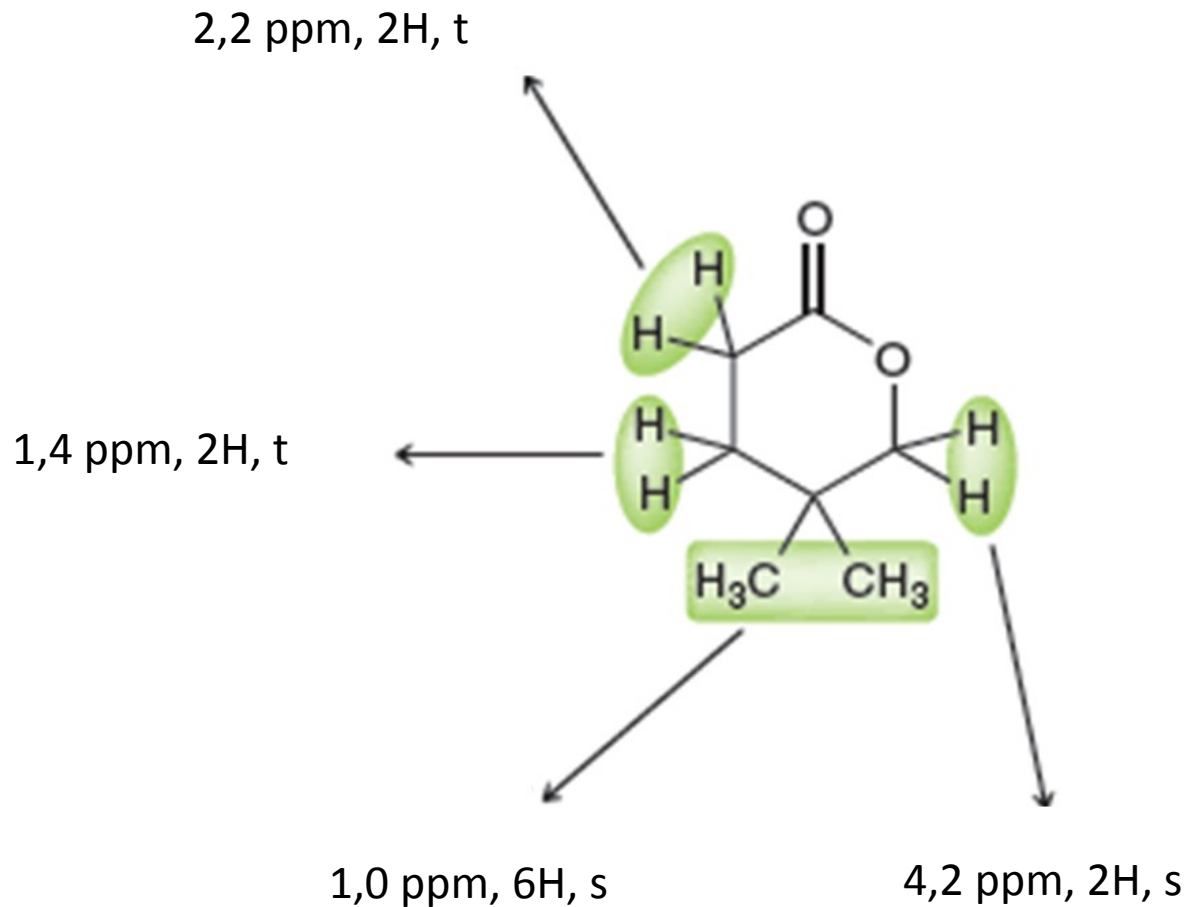
Rozhodněte, které z následujících sloučenin odpovídá níže uvedené ^1H NMR spektrum.

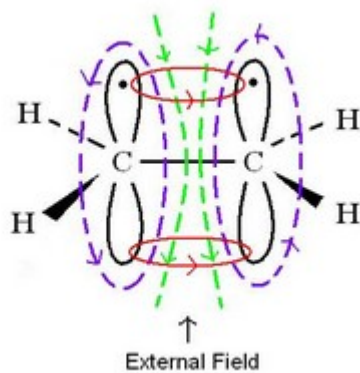


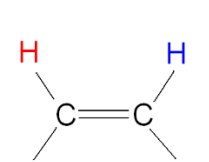
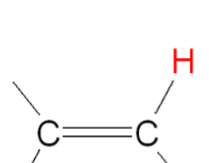
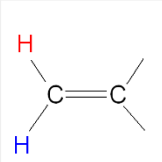
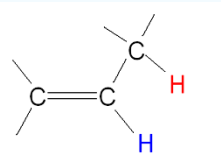


Přiřadte následující signály k jednotlivým vodíkovým atomům

1,0 ppm, 6H, s
1,4 ppm, 2H, t
2,2 ppm, 2H, t
4,2 ppm, 2H, s





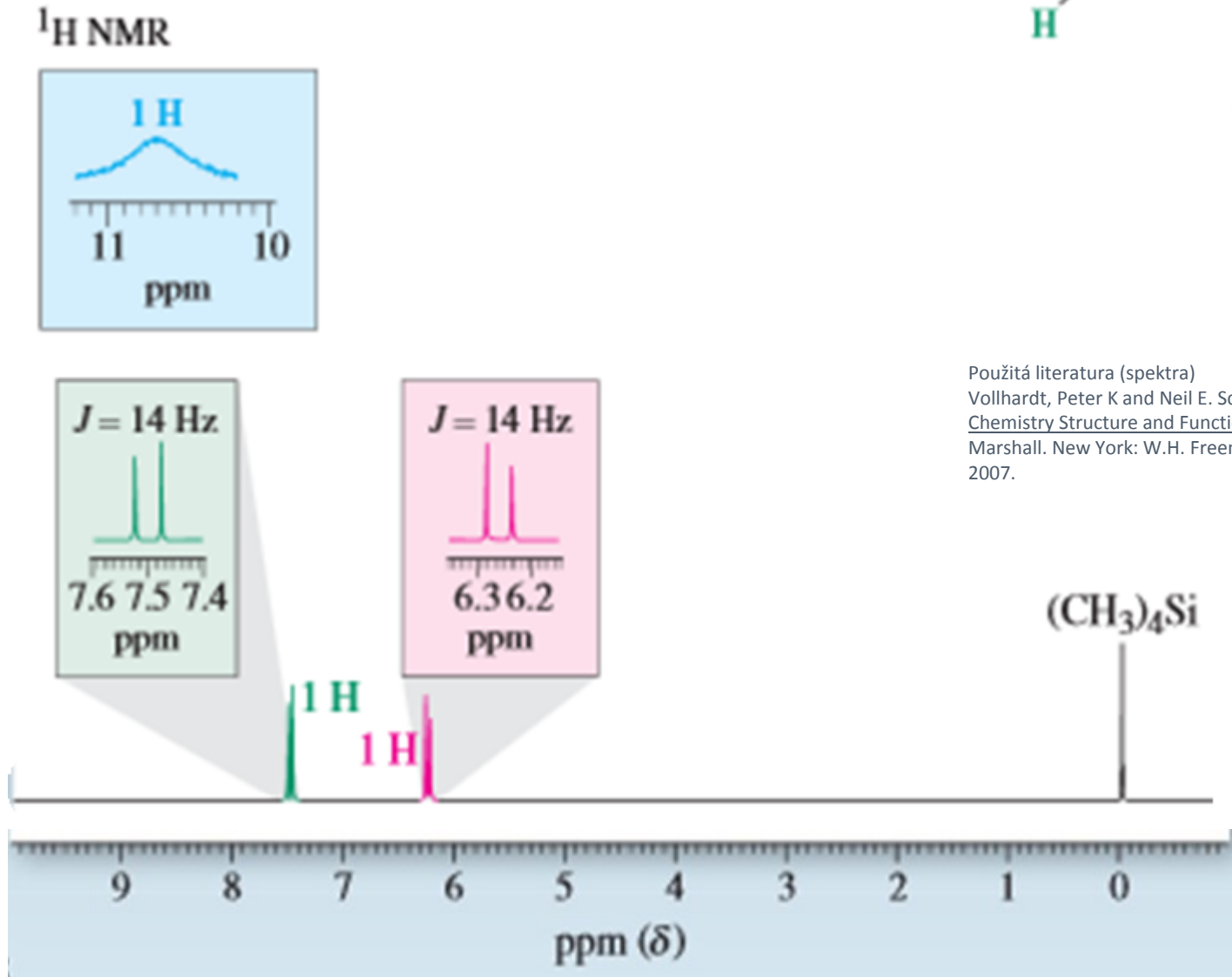
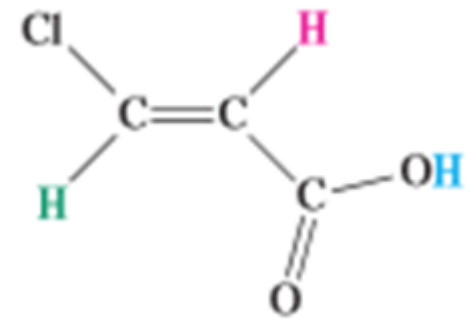
Type of coupling	Name	Range (Hz)	Typical (Hz)
 <p>Vicinal, cis</p>	Vicinal, cis	6-14	10
 <p>Vicinal, trans</p>	Vicinal, trans	11-18	16
 <p>Geminal</p>	Geminal	0-3	2
	None	4-10	6

<https://chem.libretexts.org/>

[https://chem.libretexts.org/Bookshelves/Organic_Chemistry/Supplemental_Modules_\(Organic_Chemistry\)/Alkenes/Properties_of_Alkenes/Nuclear_Magnetic_Resonance_\(NMR\)_of_Alkenes](https://chem.libretexts.org/Bookshelves/Organic_Chemistry/Supplemental_Modules_(Organic_Chemistry)/Alkenes/Properties_of_Alkenes/Nuclear_Magnetic_Resonance_(NMR)_of_Alkenes)



Pokuste se přiřadit jednotlivé píky v následující ^1H NMR spektrum vodíkovým atomům v níže uvedené sloučenině




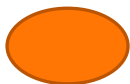
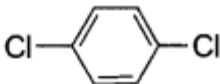
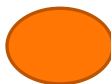
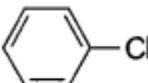

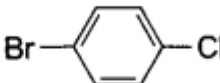

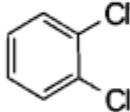

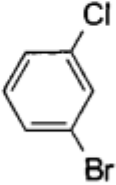

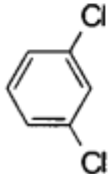
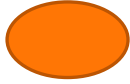
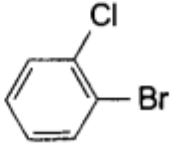
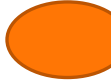
Použitá literatura (spektra)
Vollhardt, Peter K and Neil E. Schore. *Organic Chemistry Structure and Function*. Ed. Clancy Marshall. New York: W.H. Freeman and Company, 2007.



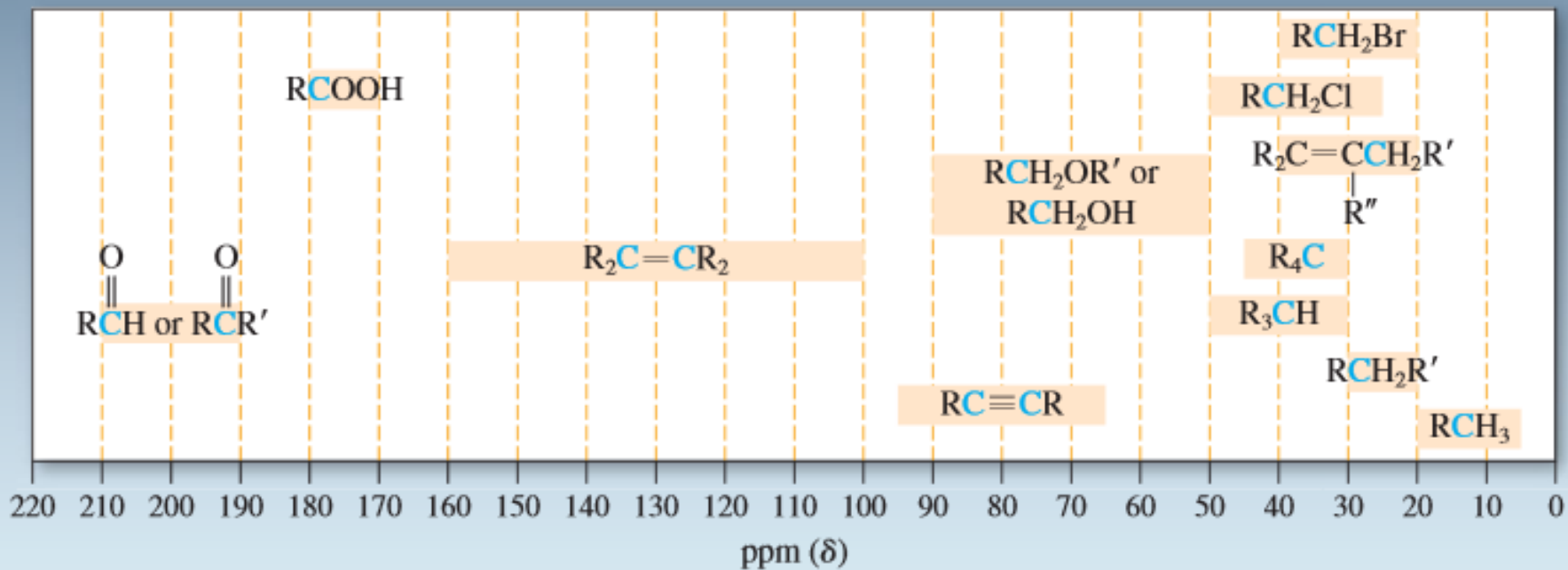
^{13}C NMR spektroskopie



^{13}C NMR počet signálů



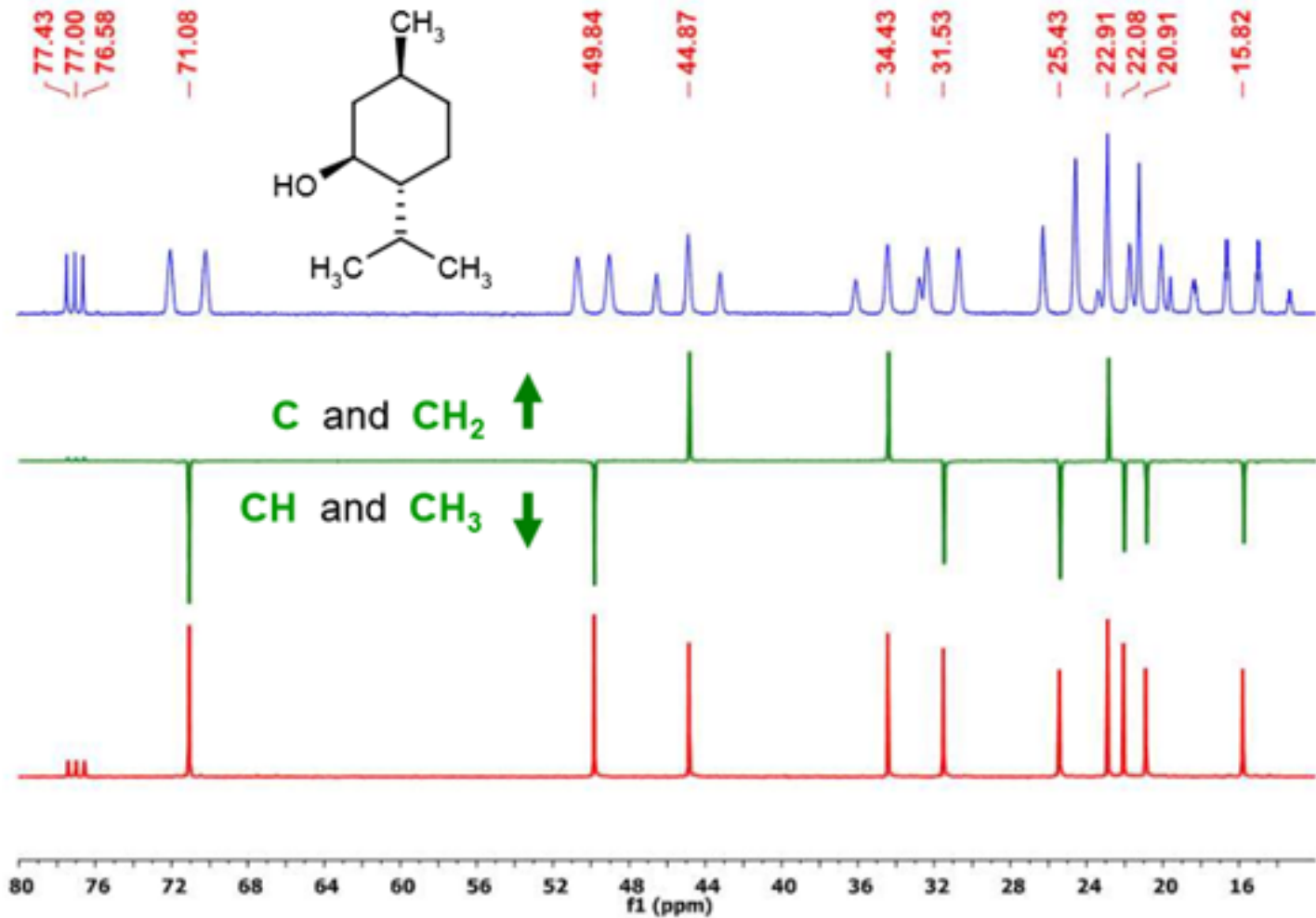


Použitá literatura (spektra)

Vollhardt, Peter K and Neil E. Schore. Organic Chemistry Structure and Function. Ed. Clancy Marshall. New York: W.H. Freeman and Company, 2007.



^{13}C NMR decoupling OFF or ON, and APT

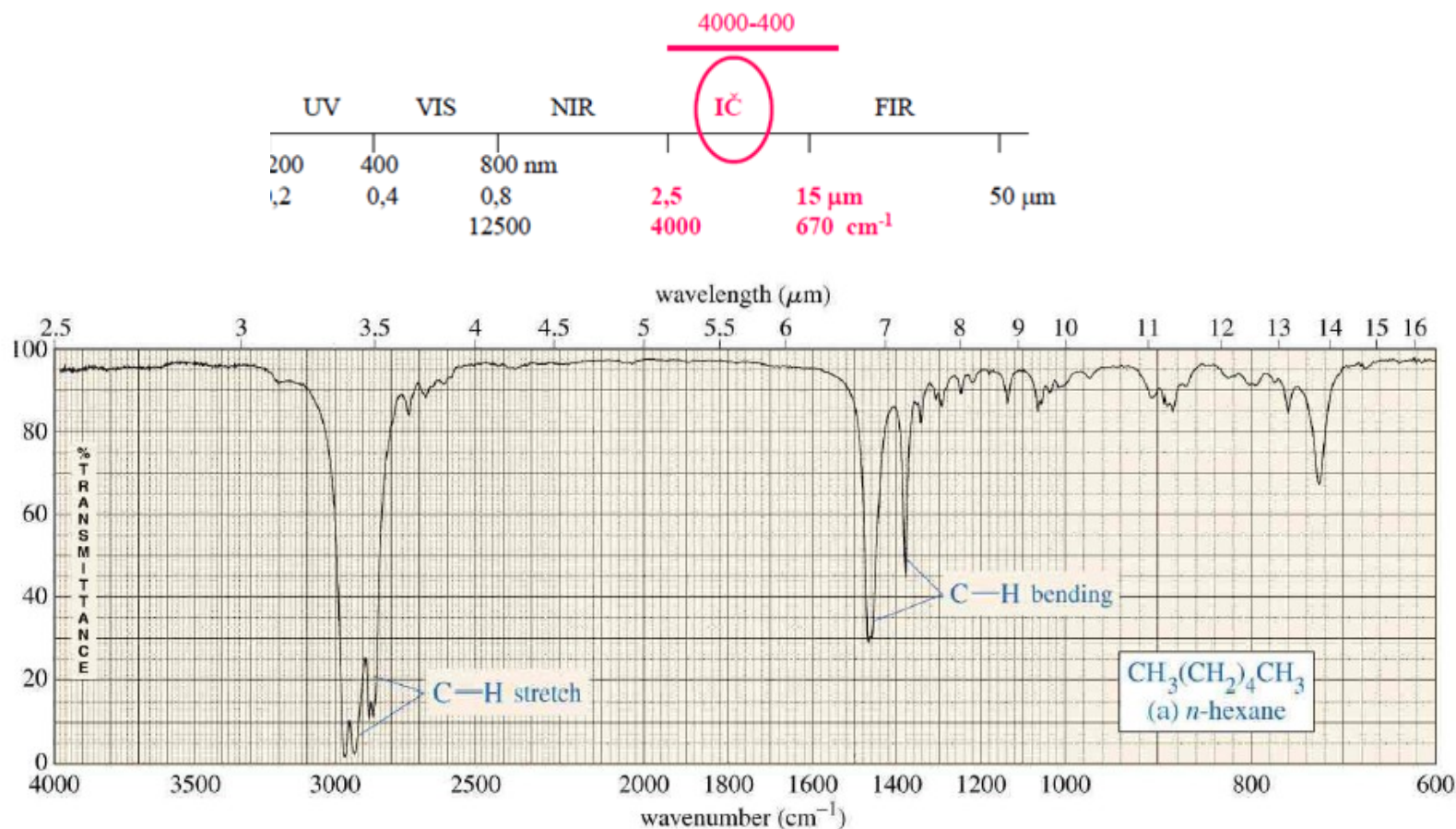




Infračervená spektroskopie

vibračně – rotační spektroskopie

v organické chemii – důkaz přítomnosti funkčních skupin



Hookův zákon

$$\tilde{\nu} = \left(\frac{1}{2\pi c} \right) \left(\frac{f}{m_{\text{red}}} \right)^{\frac{1}{2}}$$

force constant (bond strength)

reduced mass = $\left(\frac{m_1 m_2}{m_1 + m_2} \right)$



~3000 cm⁻¹



~2200 cm⁻¹



~1100 cm⁻¹



~700 cm⁻¹



~2200 cm⁻¹



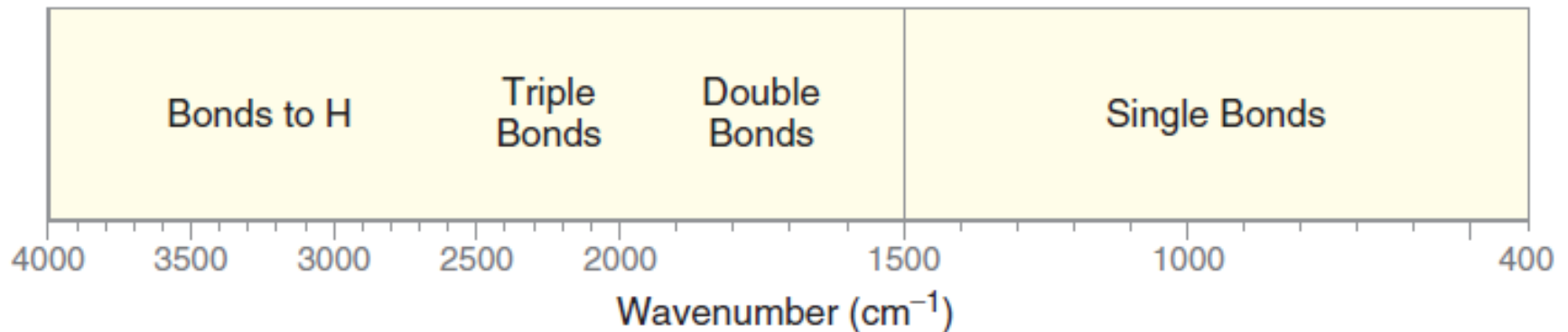
~1600 cm⁻¹



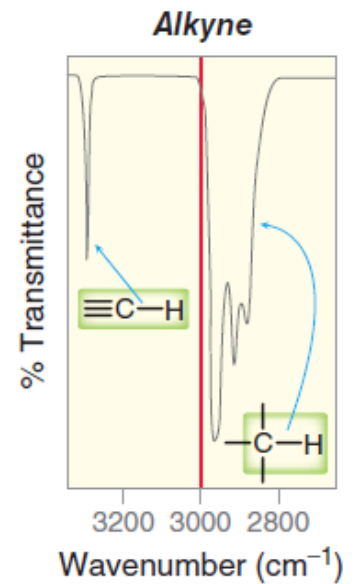
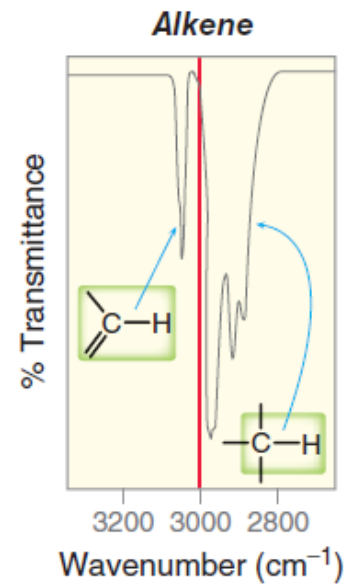
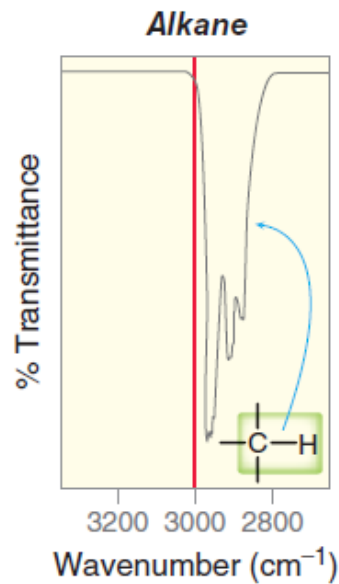
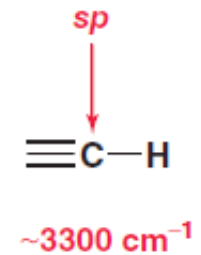
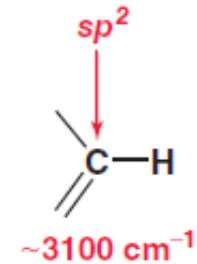
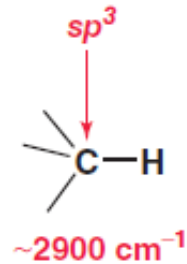
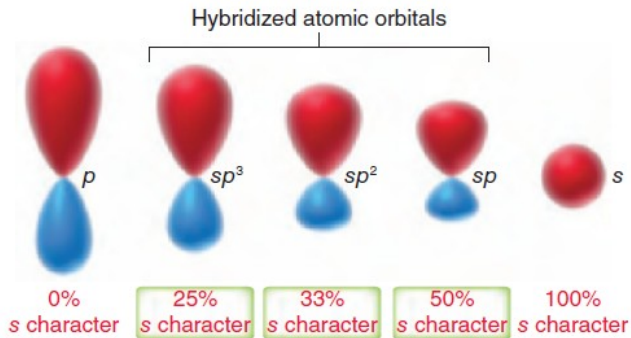
~1100 cm⁻¹

Diagnostic Region

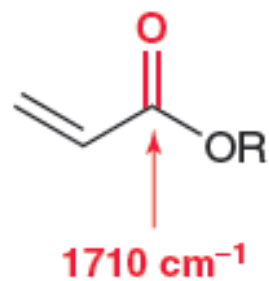
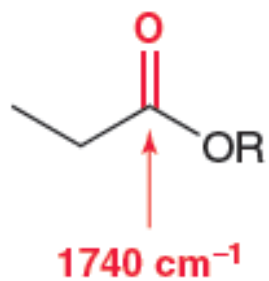
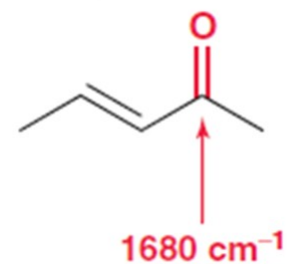
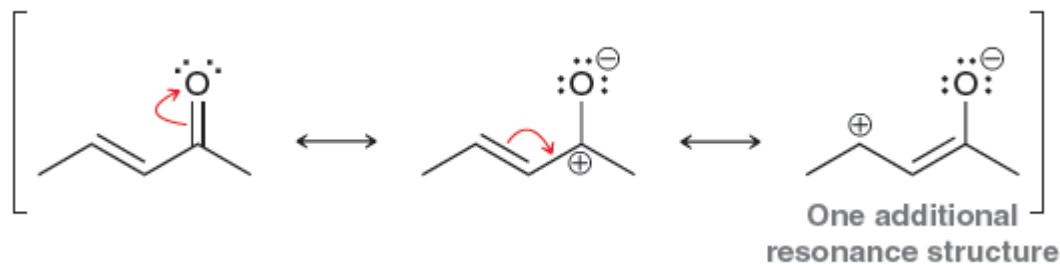
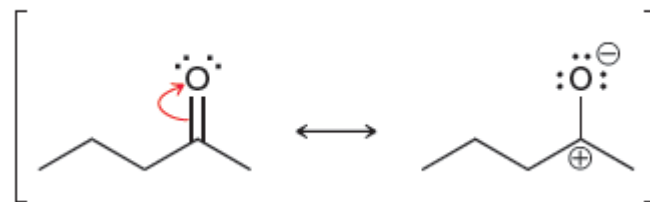
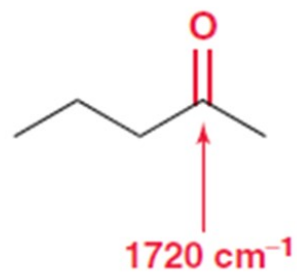
Fingerprint Region



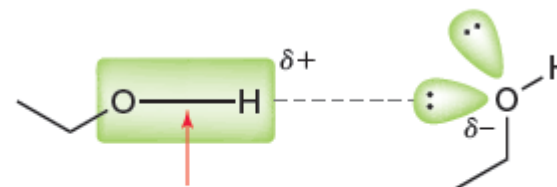
Efekt hybridizace



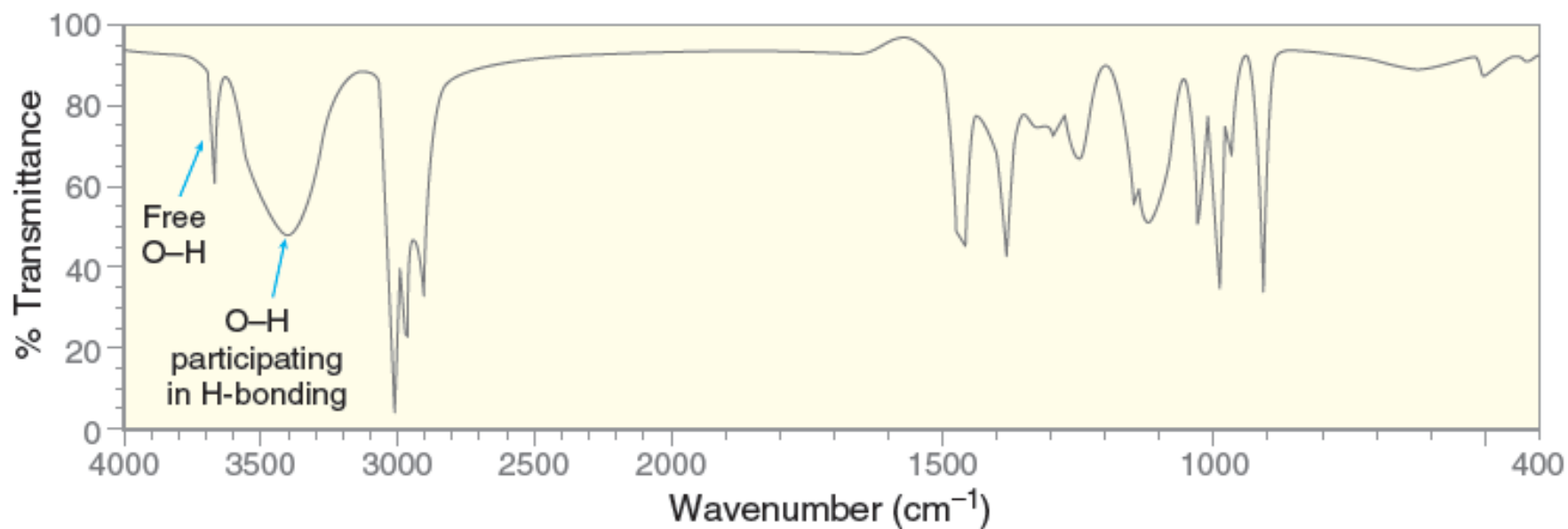
Efekt rezonance



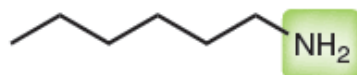
Efekt vodíkových vazeb



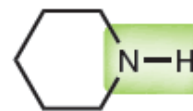
This bond is weakened as a result of H bonding



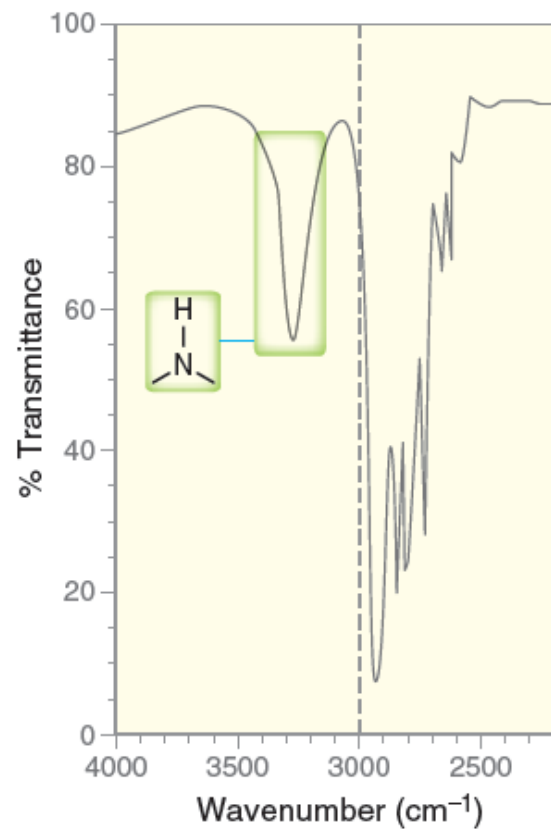
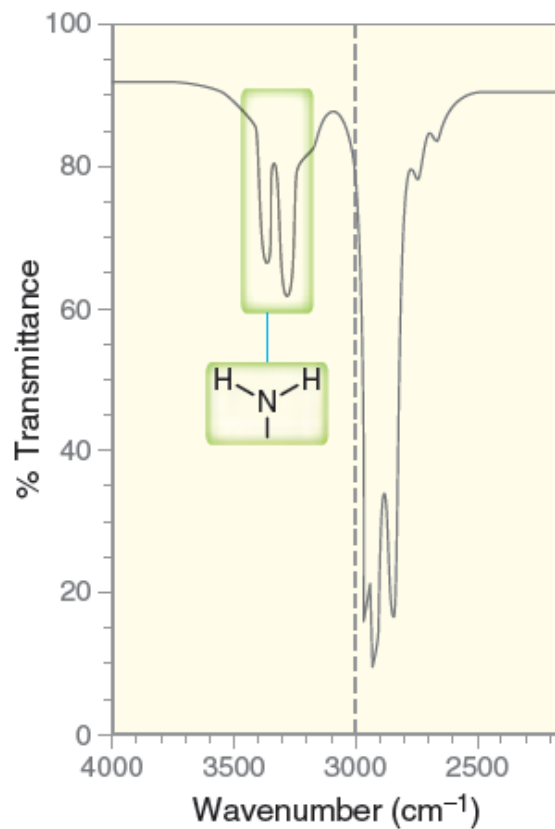
Aminy



Hexylamine
(a primary amine)



Piperidine
(a secondary amine)

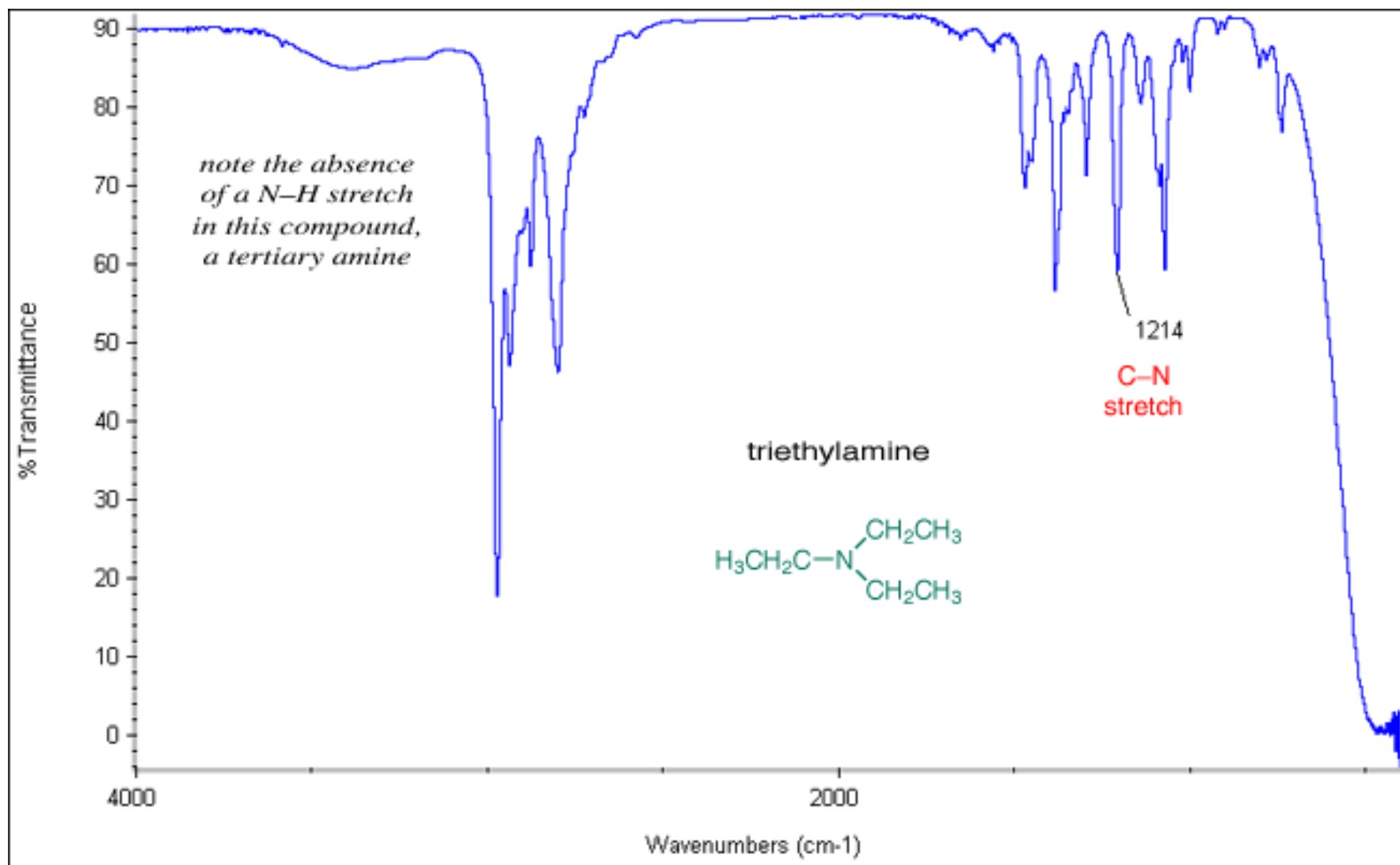


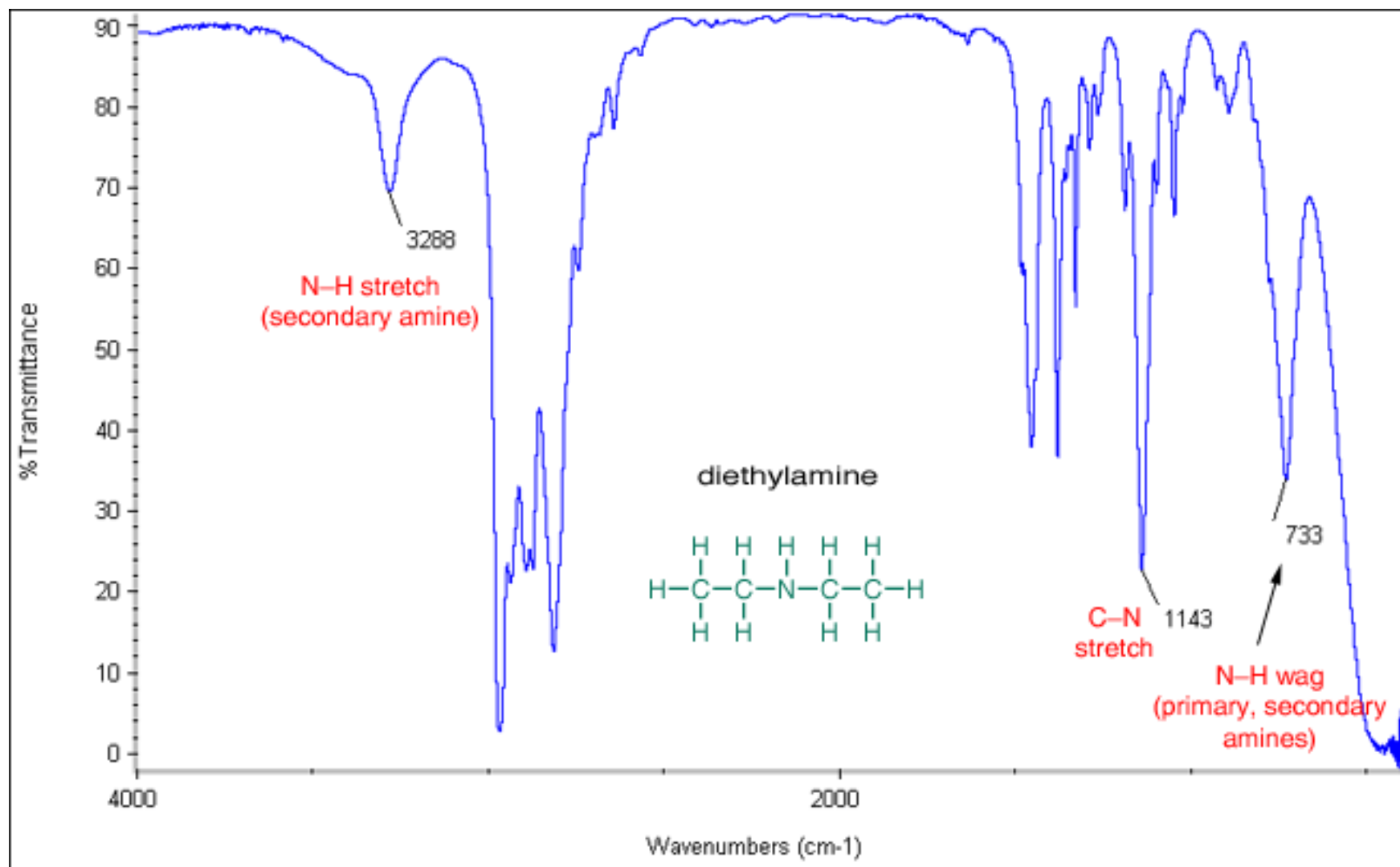
Symmetric stretching

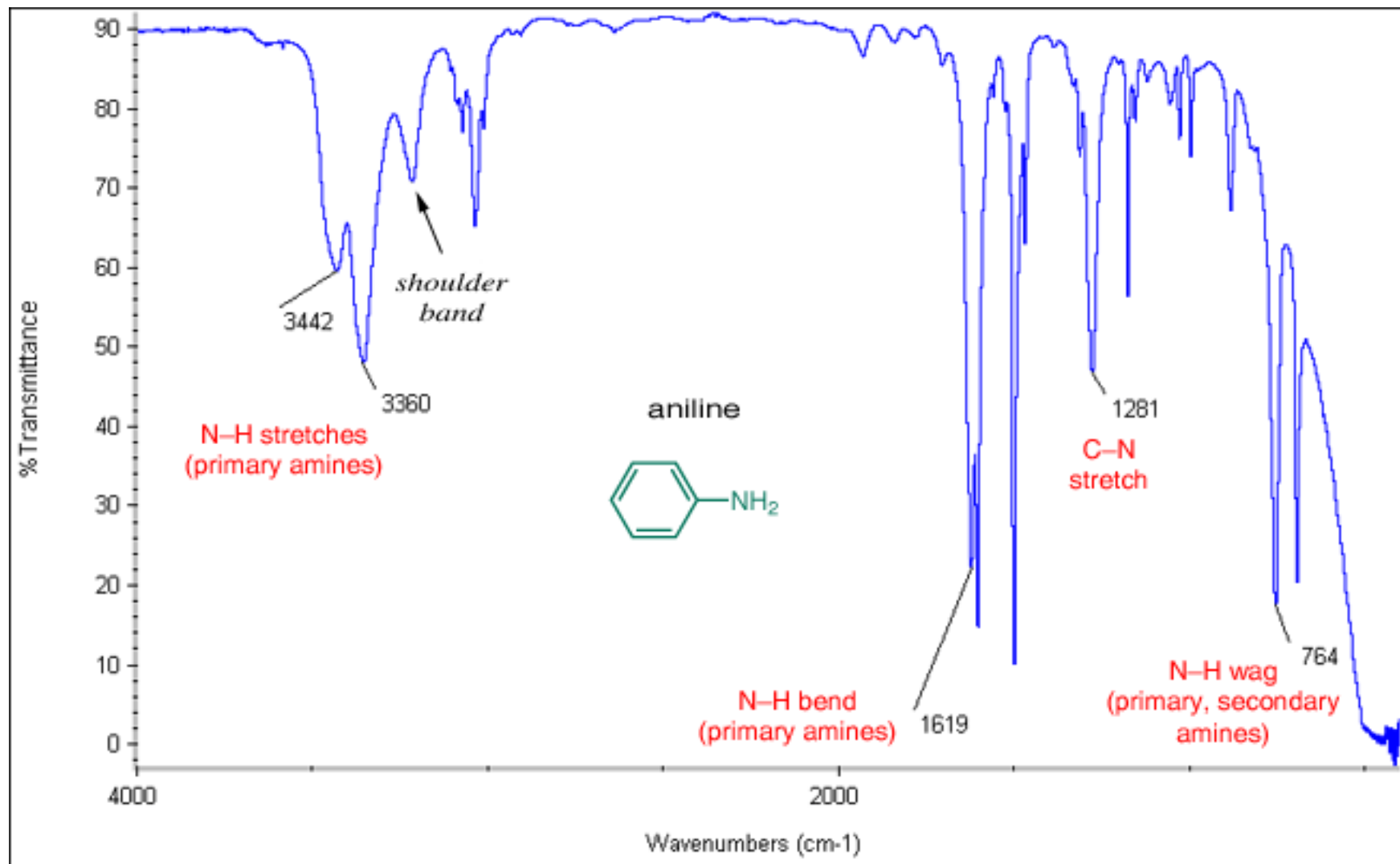


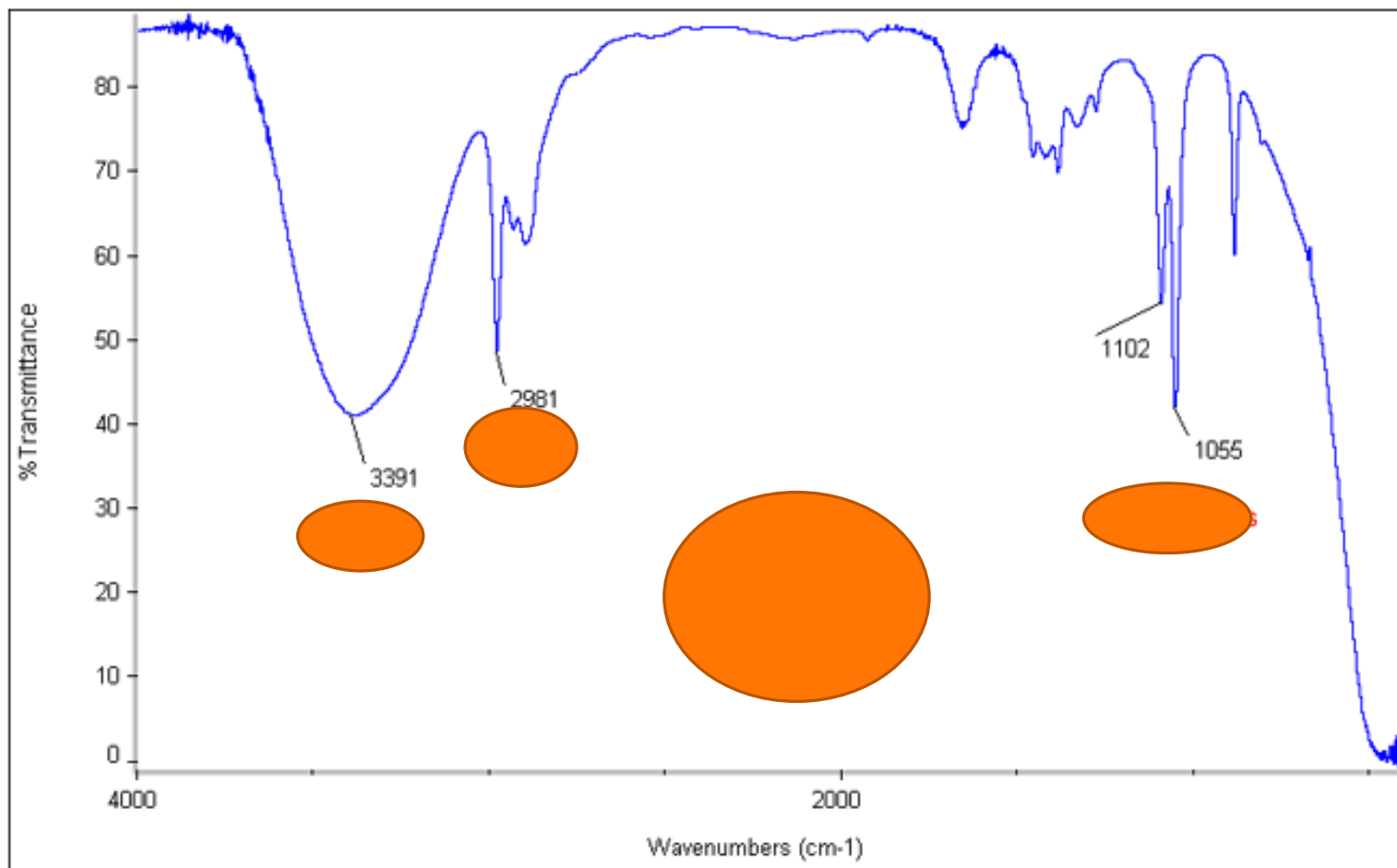
Asymmetric stretching

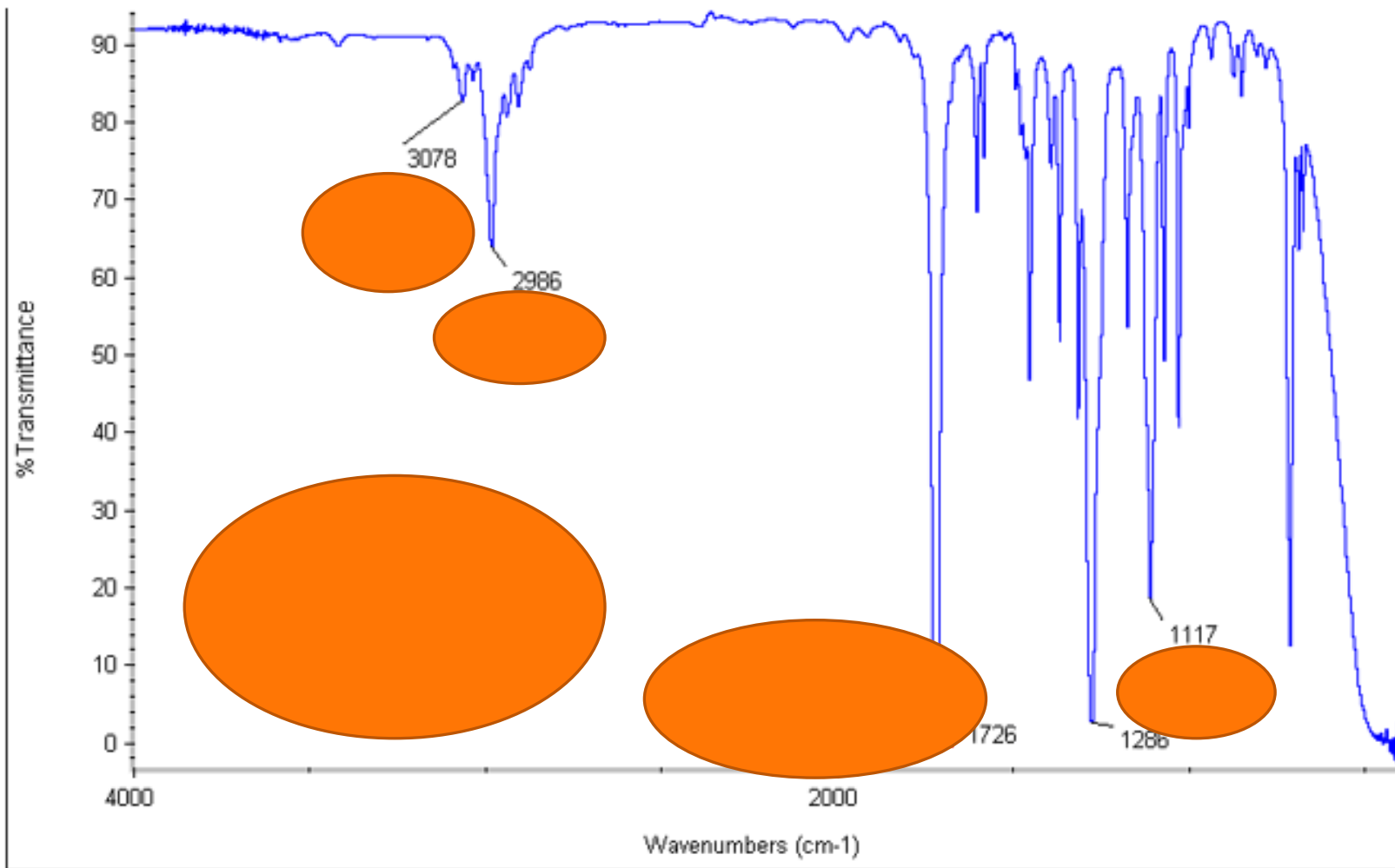


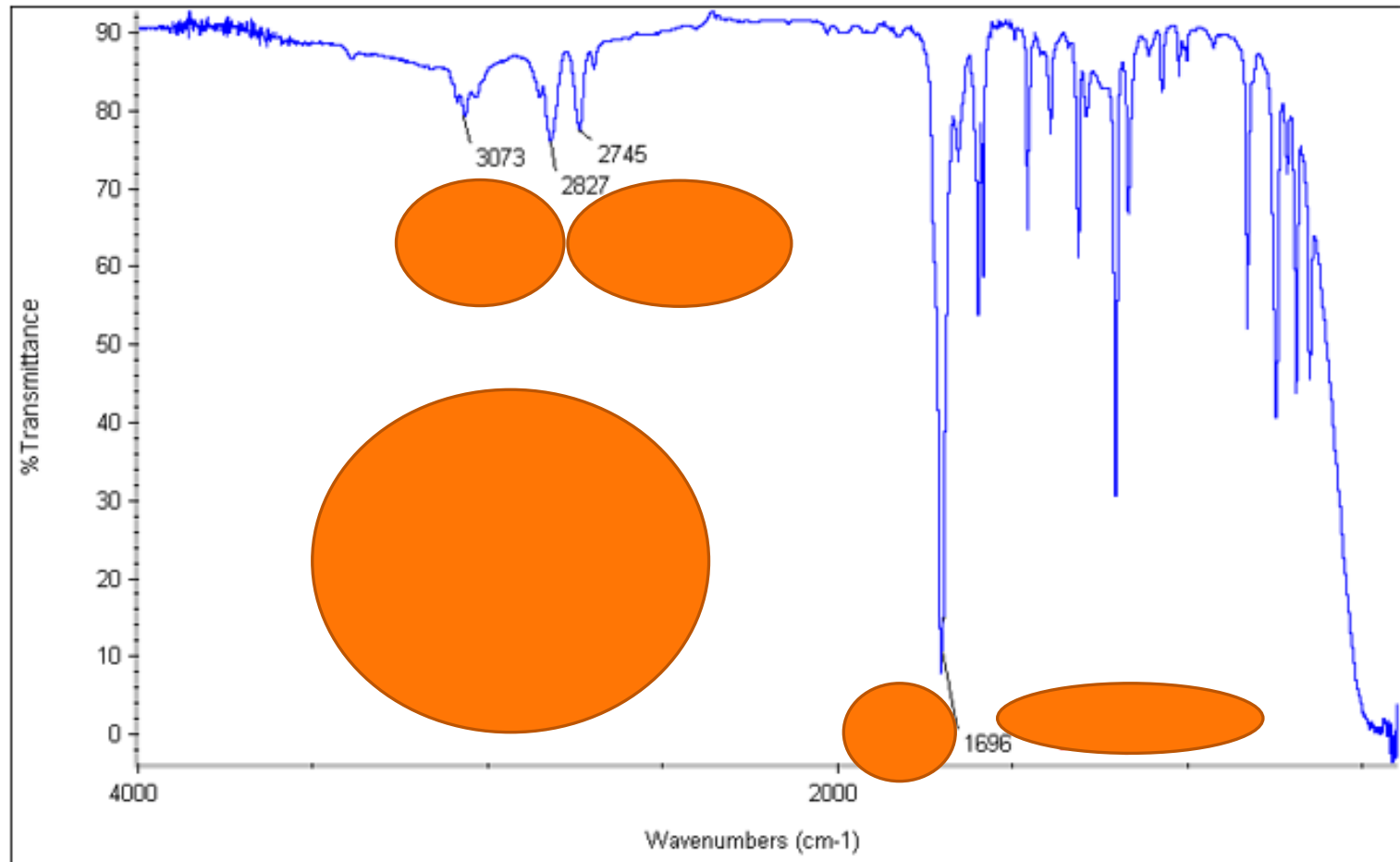


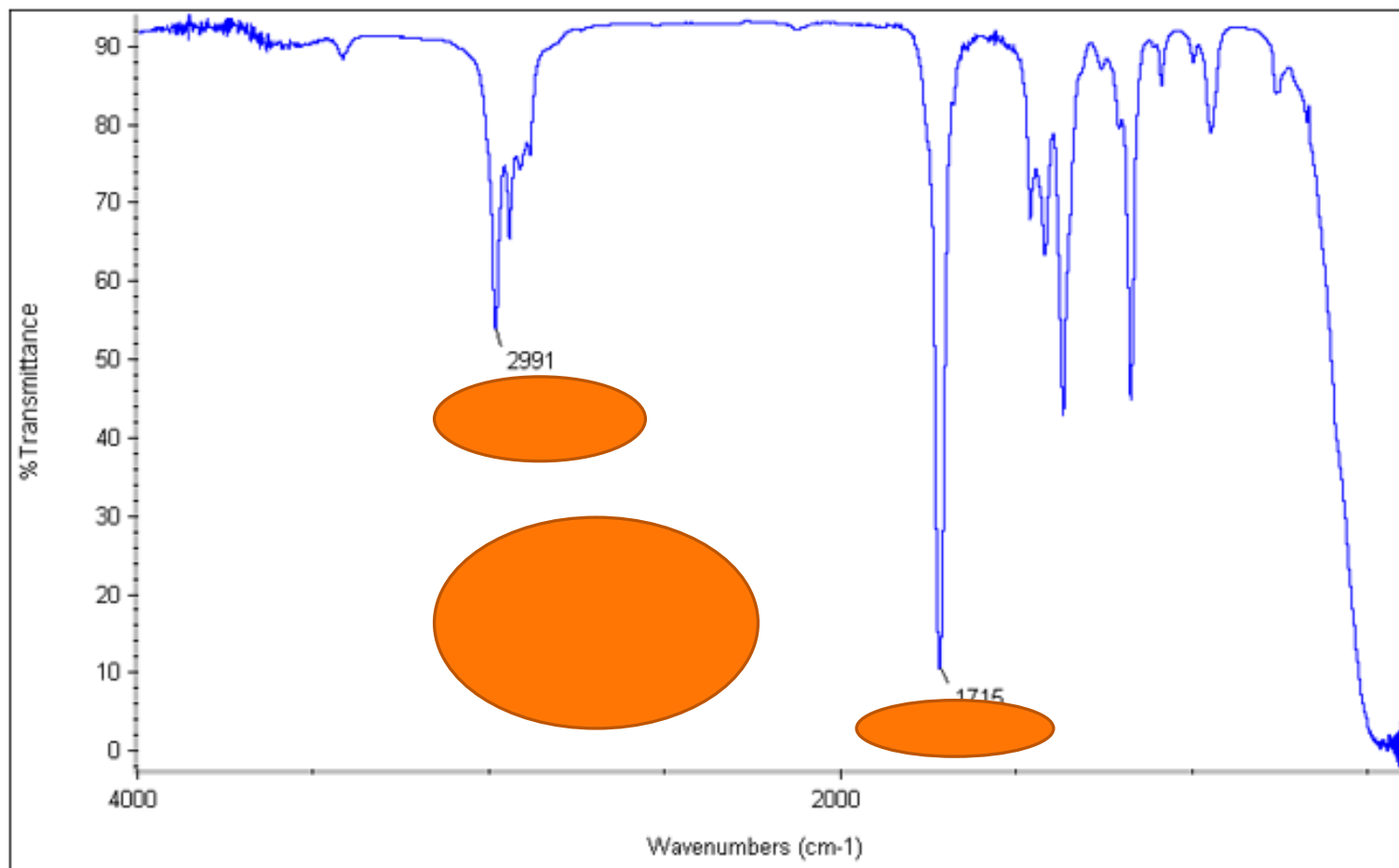


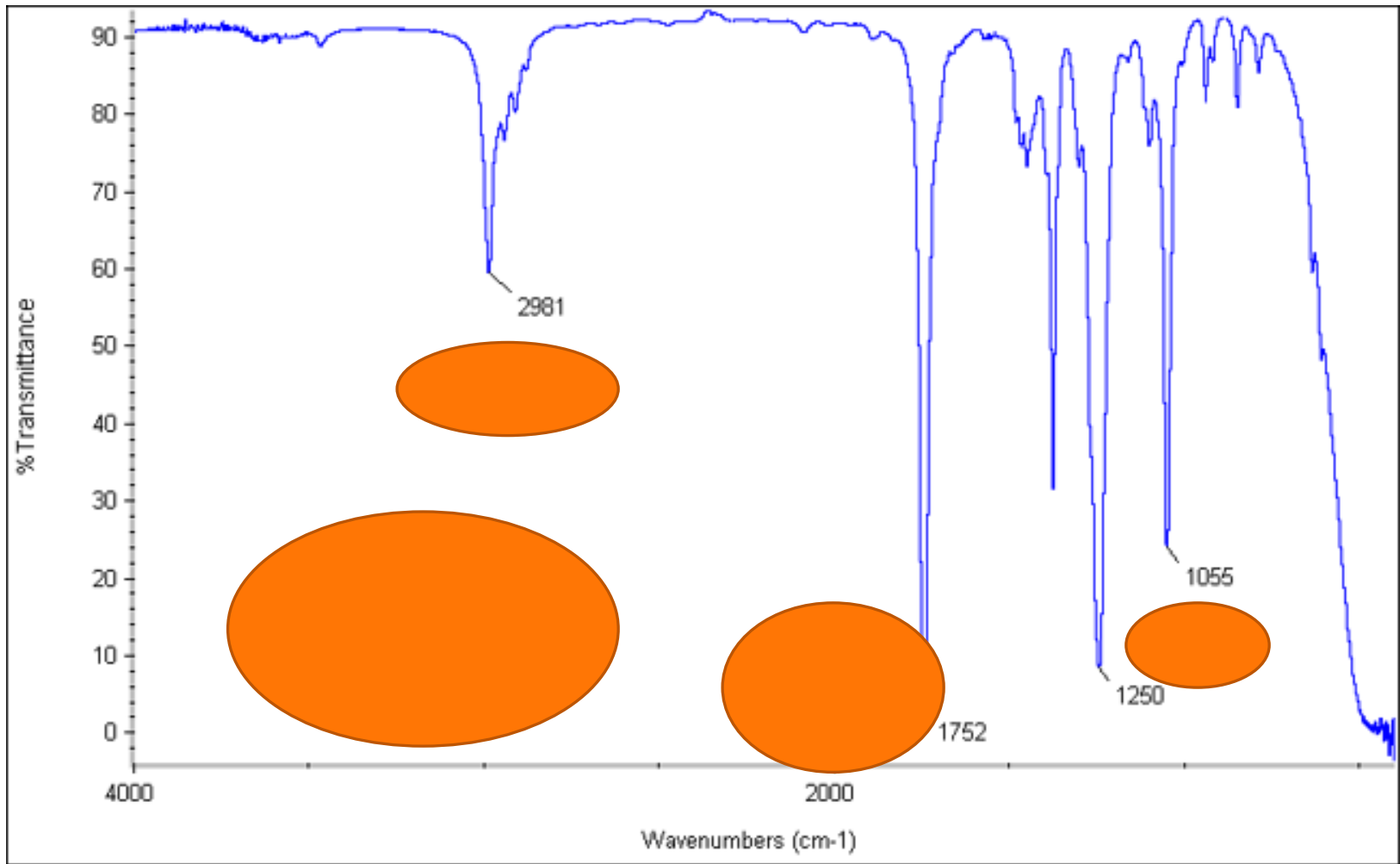












» HMOTNOSTNÍ SPEKTROMETRIE

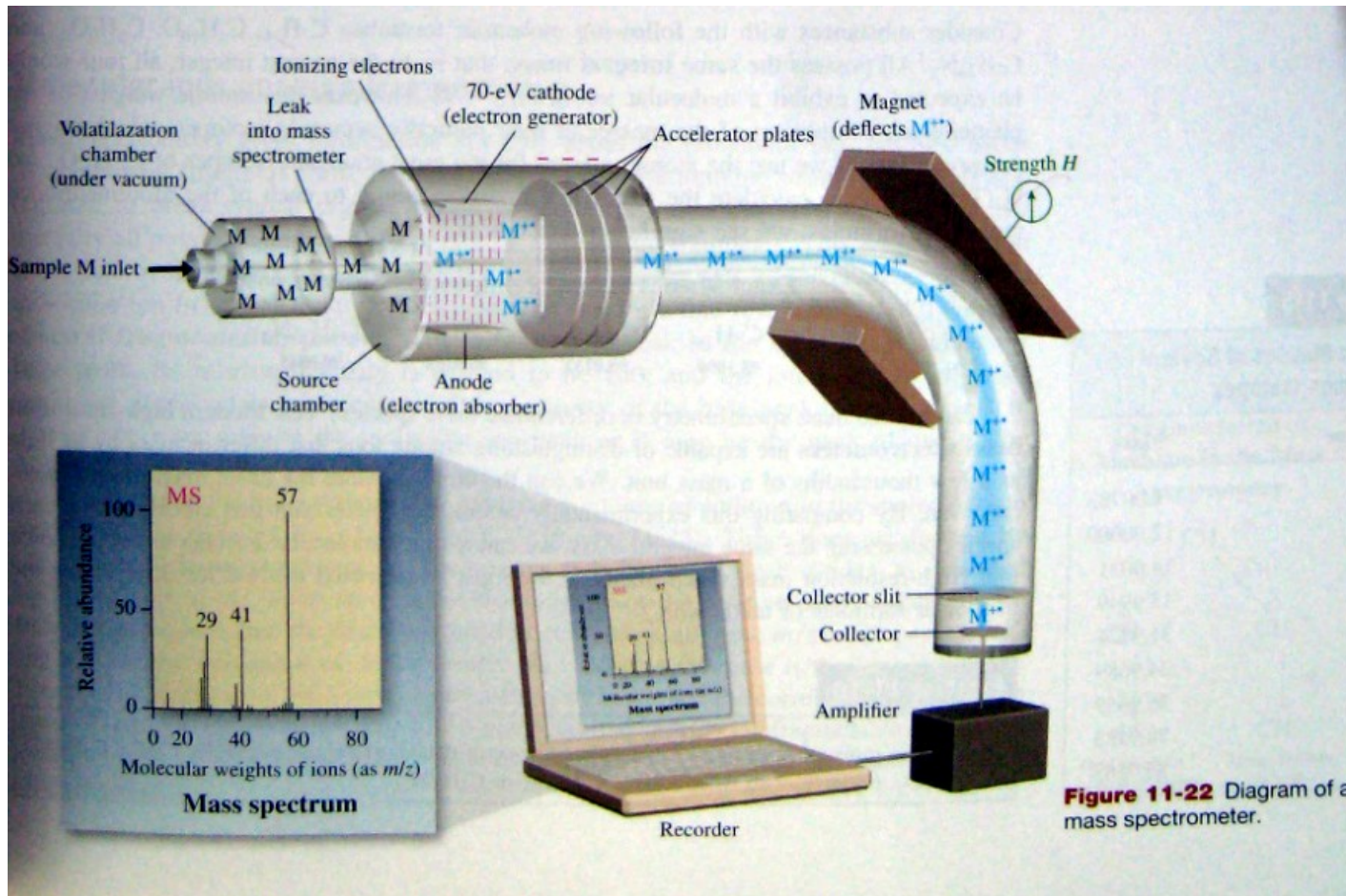
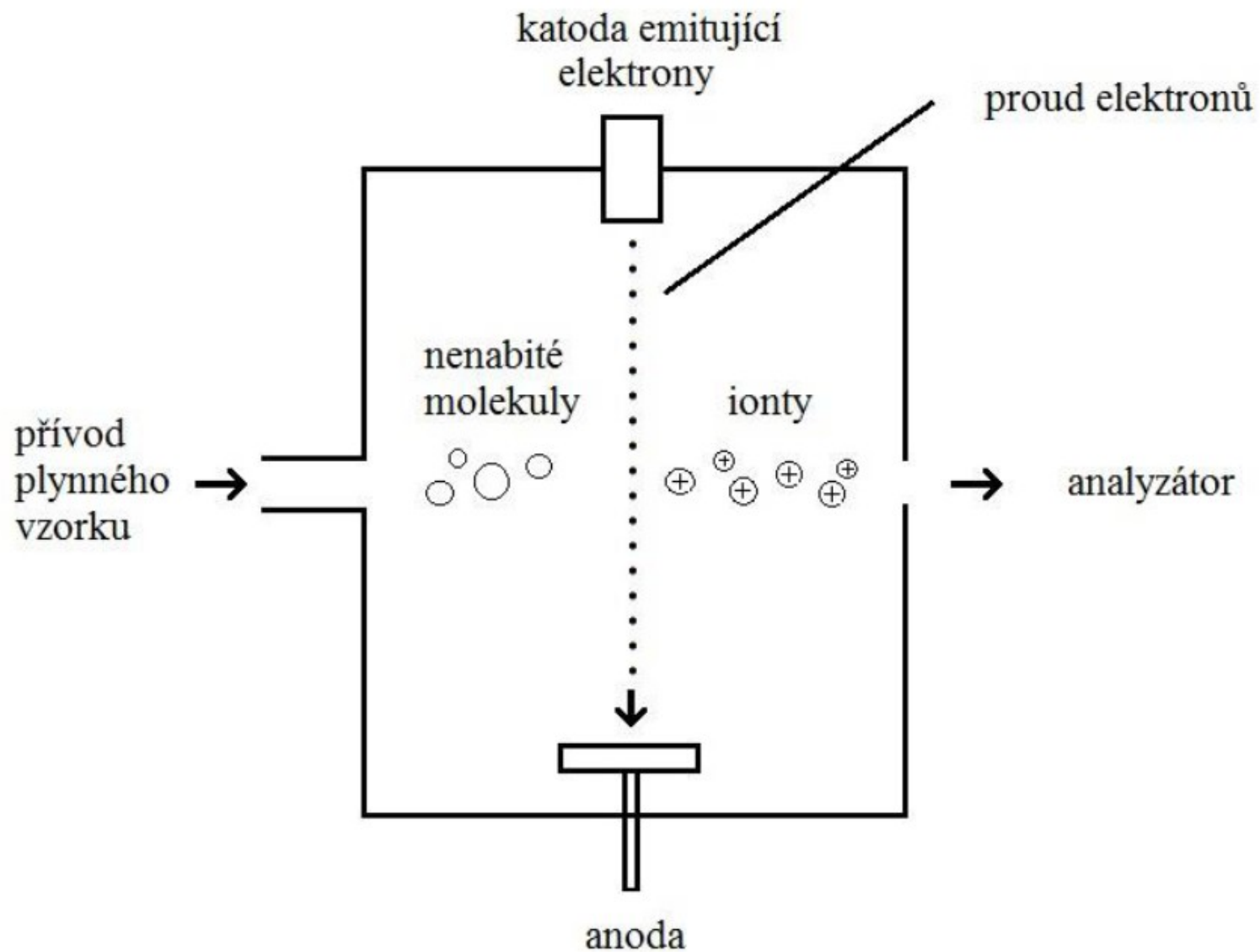
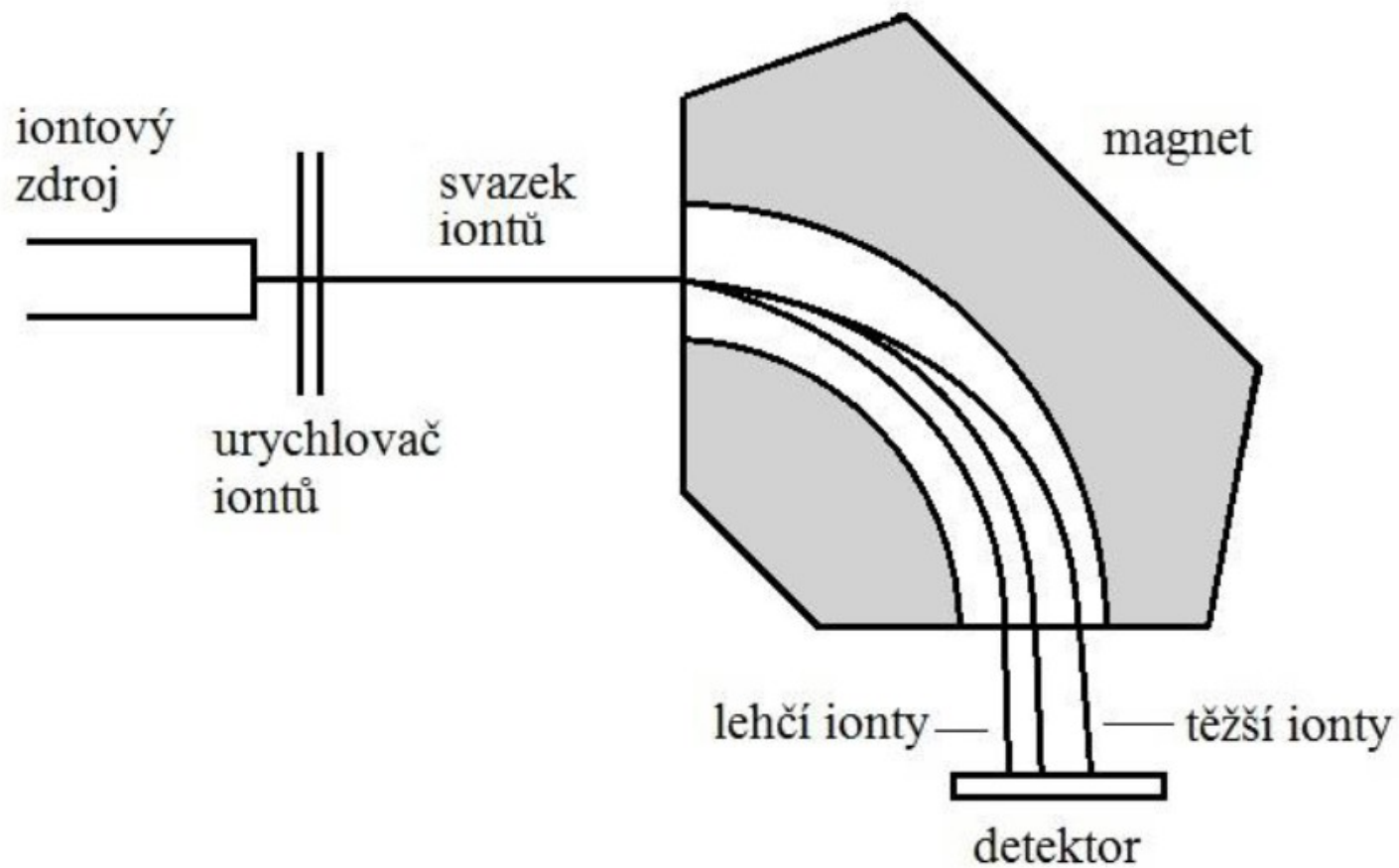


Figure 11-22 Diagram of a mass spectrometer.







primárně vzniká molekulární ion M^+
 fragmentací vznikají ionty dceřinné

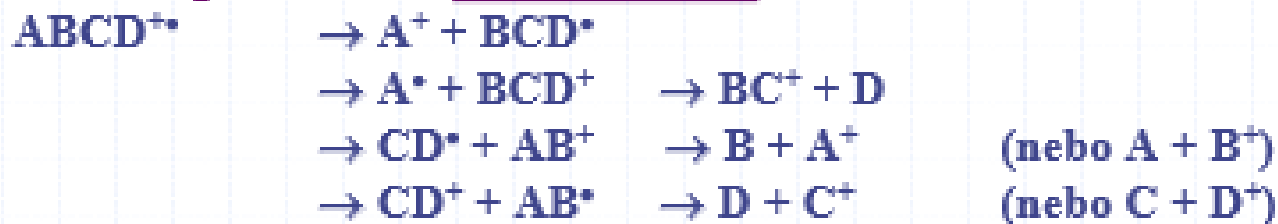
Ionization of a Molecule on Electron Impact



- Vznik molekulárního iontu (radikál ion!!!):



- Fragmentace \Rightarrow dceřinné ionty:



- Kolize + následná fragmentace:



<http://www.vscht.cz/nmr/predmet/lekce/NMR-lekce6.pdf> (26.2.2014)

<http://www.nmrdb.org/predictornew> (Simulace NMR spekter)

http://www.vscht.cz/anl/dolensky/technmr/soubory/2013_Techniky_MereniInterpretaceNMR_INTRO.pdf

Vollhardt, Peter K and Neil E. Schore. Organic Chemistry Structure and Function. Ed. Clancy Marshall. New York: W.H. Freeman and Company, 2007.

Použitá literatura

