

NMR spektroskopie

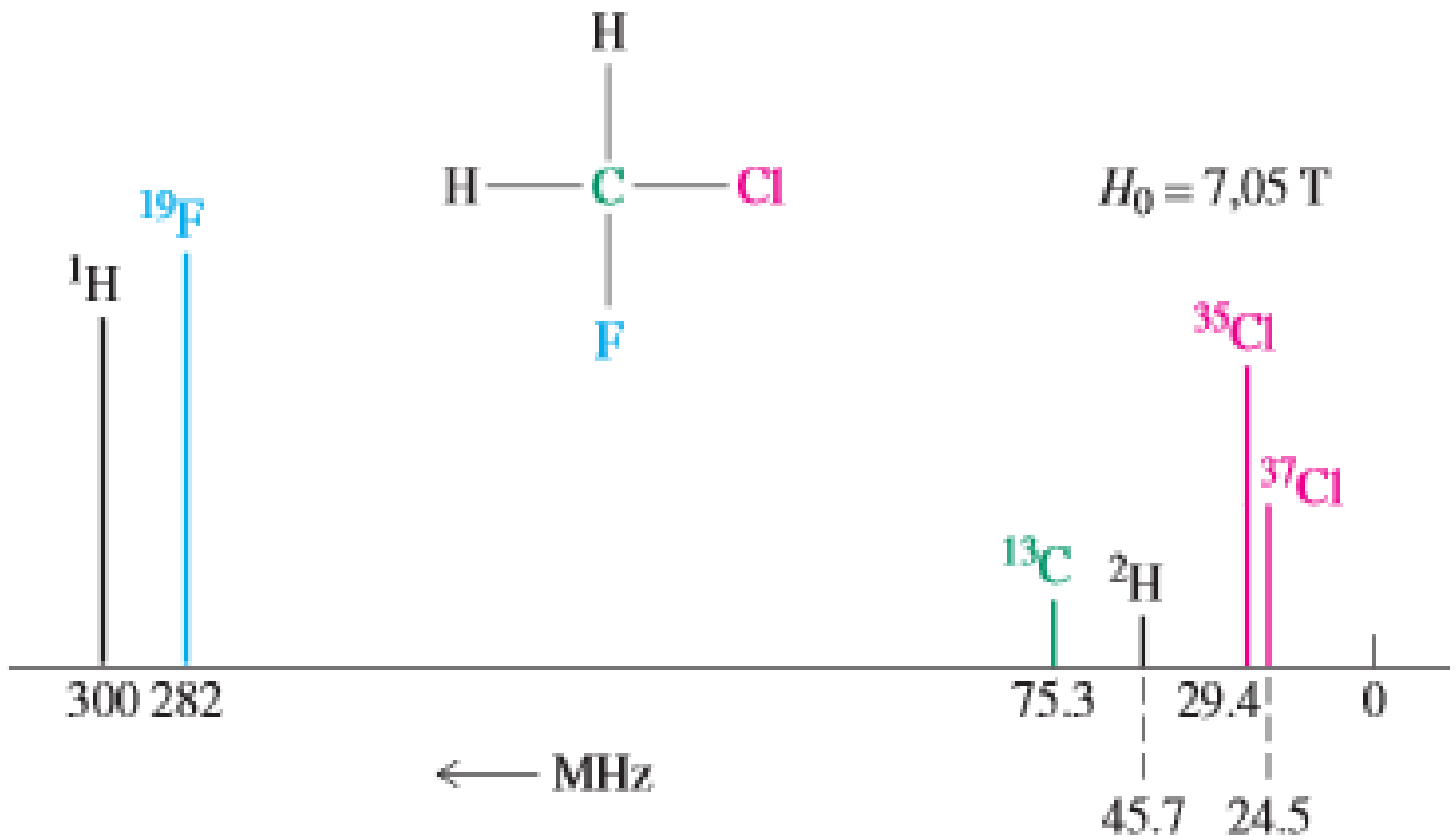


- spektroskopická metoda založená na měření absorpce elektromagnetického záření (rádiové frekvence od asi 4 do 900 MHz)
- spinová rezonance jader v silném magnetickém poli
- lze aplikovat pouze na atomy, jejichž jádro má spinový moment (lichý počet protonů nebo neutronů)

$I = 0$ (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





Increasing frequency ν

3000 Hz

2500

2000

1500

1000

500

0

^1H NMR

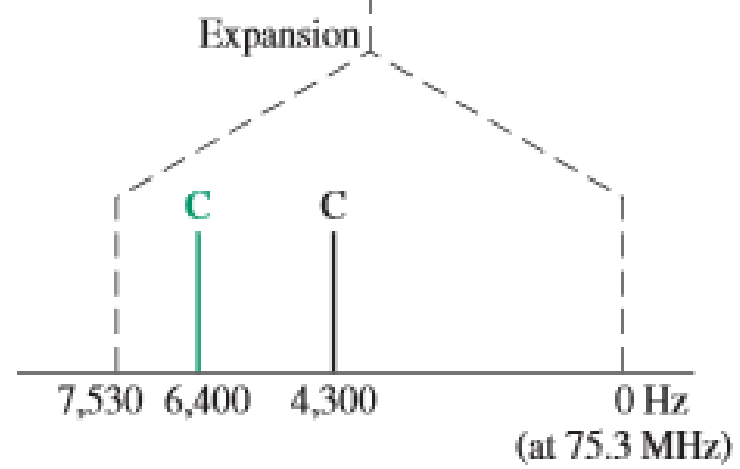
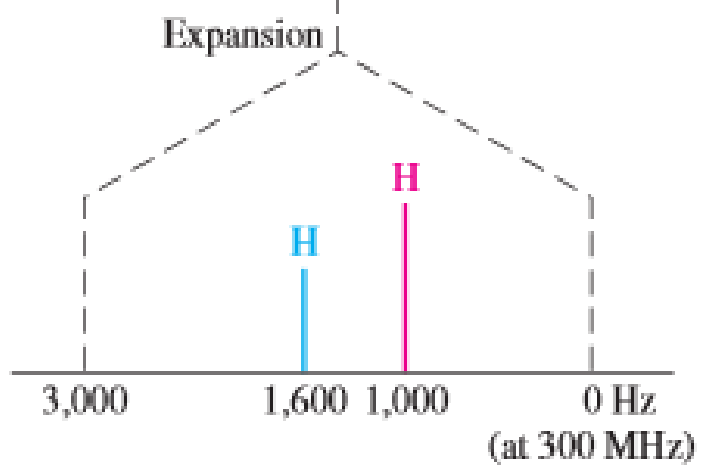
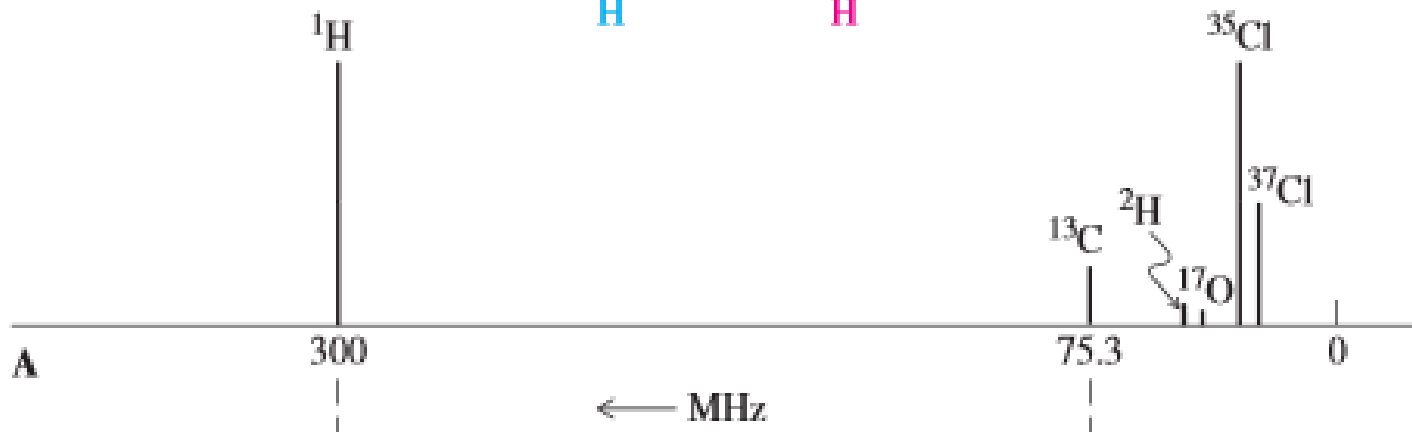
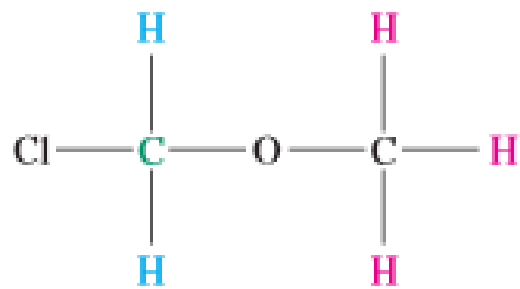
CH_3

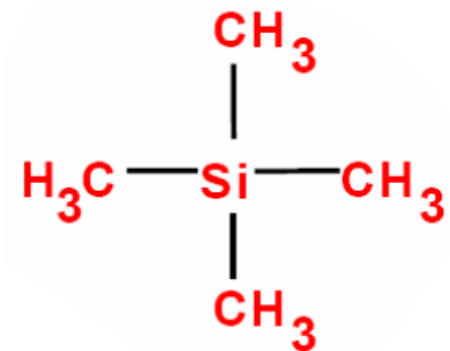


Two types of hydrogen:
two NMR-signals

CH_2



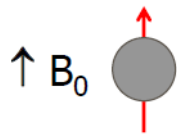




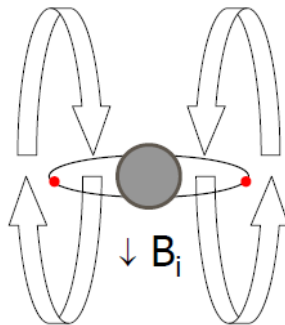
» Chemický posun

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

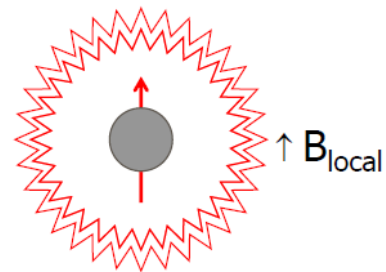




holé jádro (H^+)
bezezbytku cítí vliv
vnějšího pole (B_0)



elektrony vytváří
indukované pole (B_i)
orientované proti B_0



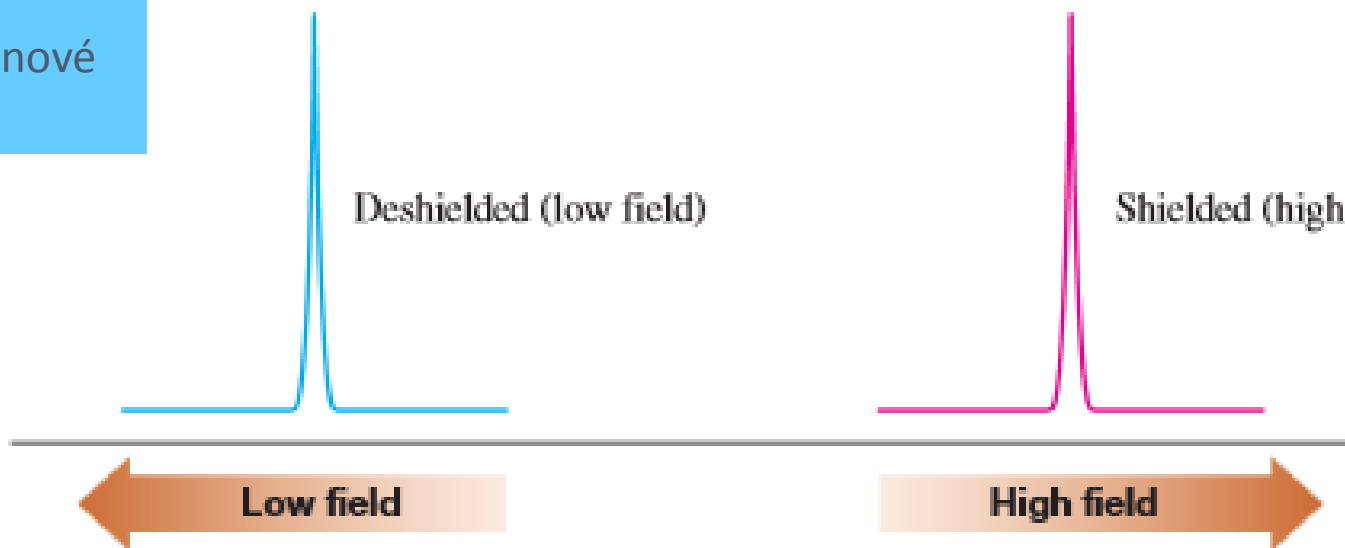
elektronová hustota částečně
odstiňuje jádro před
 B_0 takže to cítí B_{local}

Absorption for H^+

Absorption for $\begin{array}{c} | \\ -C-H \\ | \end{array}$

řídké
elektronové
okolí

husté
elektronové
okolí



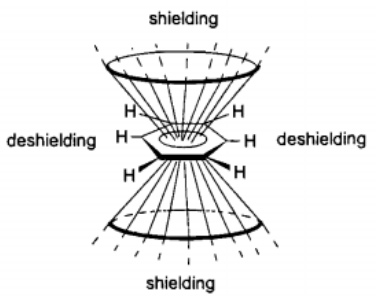
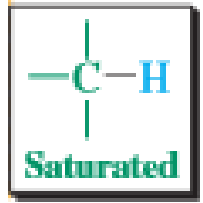
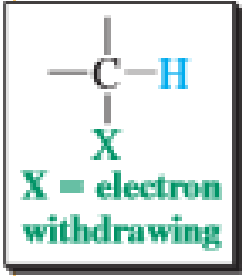
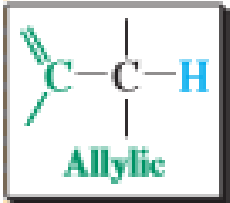
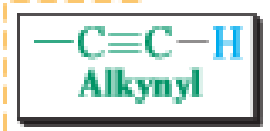
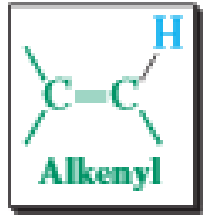
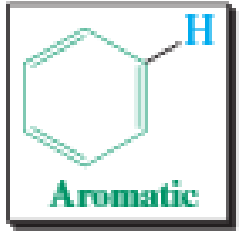
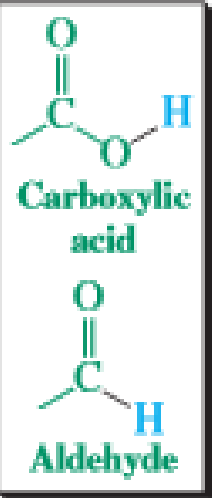
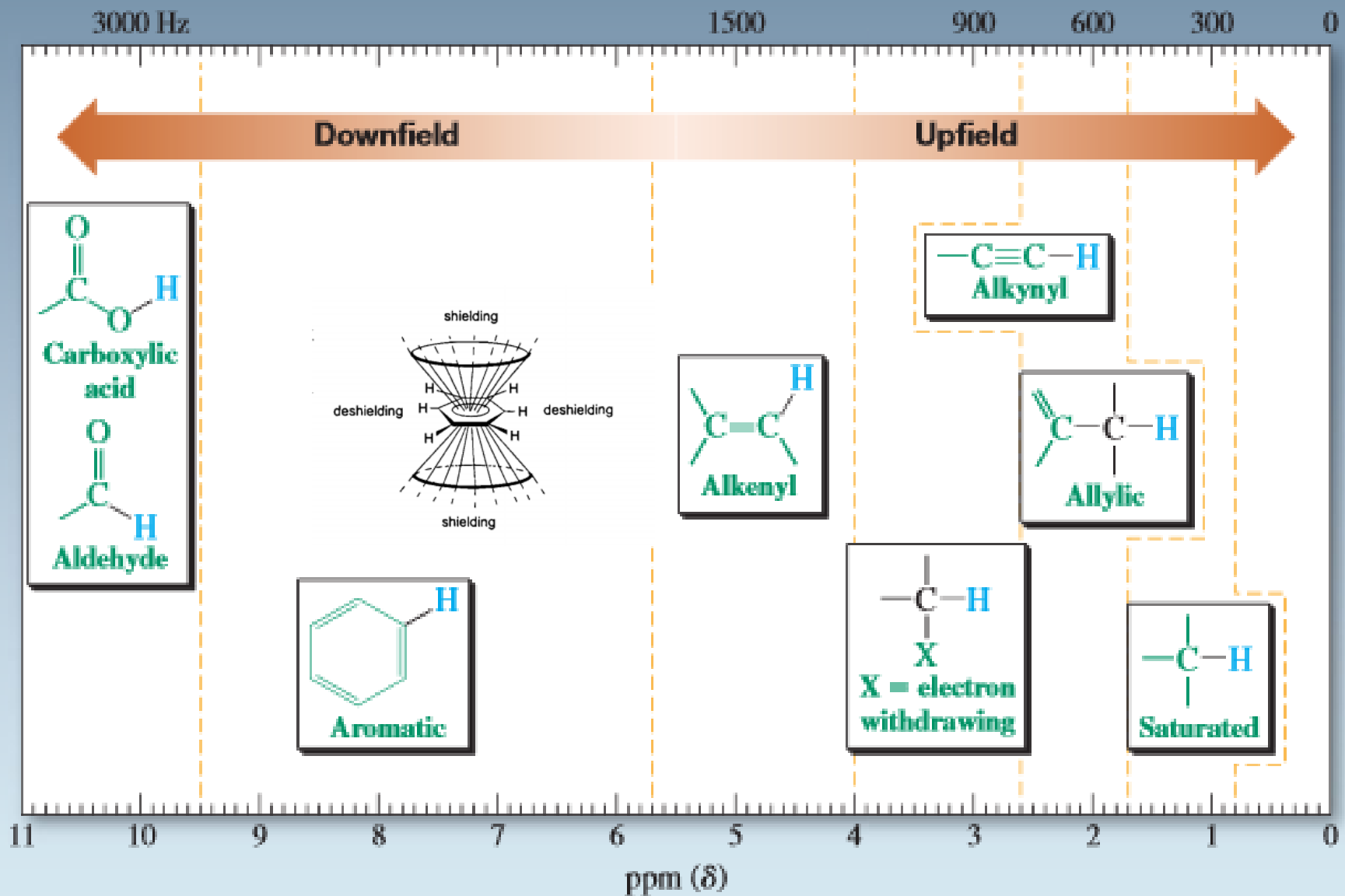



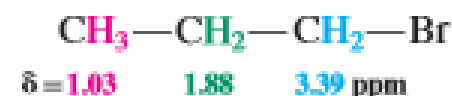
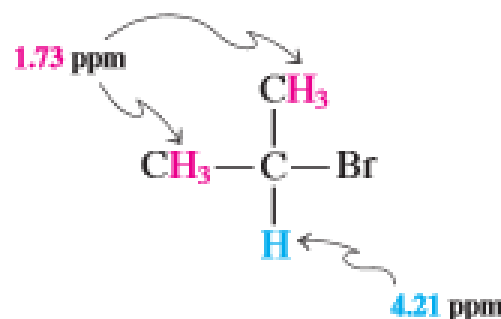
Table 10-3
The Deshielding Effect of Electronegative Atoms

CH_3X	Electronegativity of X (from Table 1-2)		Chemical shift δ (ppm) of CH_3 group
CH_3F	4.0	 Increasing electronegativity	4.26
CH_3OH	3.4		3.40
CH_3Cl	3.2		3.05
CH_3Br	3.0		2.68
CH_3I	2.7		2.16
CH_3H	2.2		0.23



Shielding



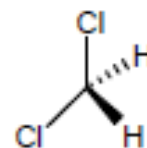
Deshielding


Symetrie molekuly pomáhá určit chemickou ekvivalenci



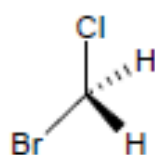
- NMR spektrum odráží symetrii molekuly
- o tom, zda dvojice atomů poskytne dva různé signály nebo jen jeden, rozhoduje jejich vzájemný vztah při operacích symetrie

Homotopické atomy

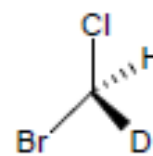
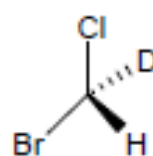


C_2 osa symetrie
ekvivalentní
1 signál ve spektru

Enantiotopické atomy



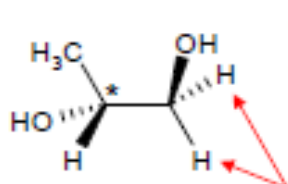
deuteriová
substituce
→



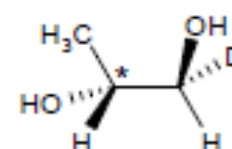
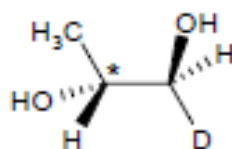
enantiomery

rovina symetrie
není osa symetrie
ekvivalentní
1 signál ve spektru

Diastereotopické atomy (molekuly s chirálním centrem)



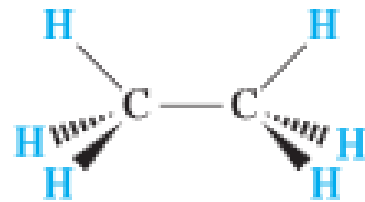
deuteriová
substituce
→



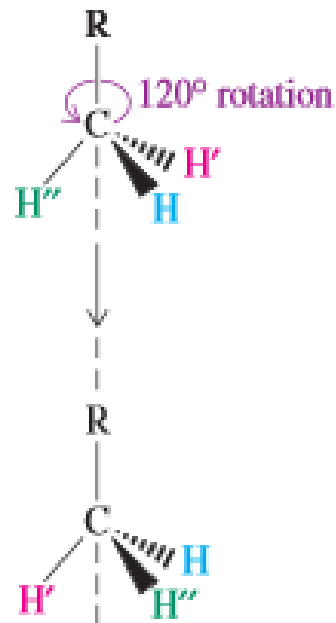
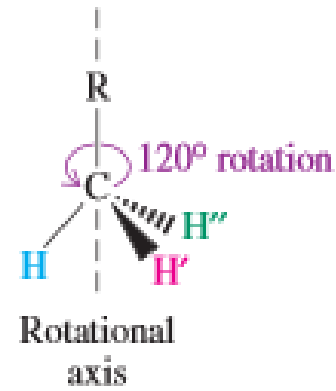
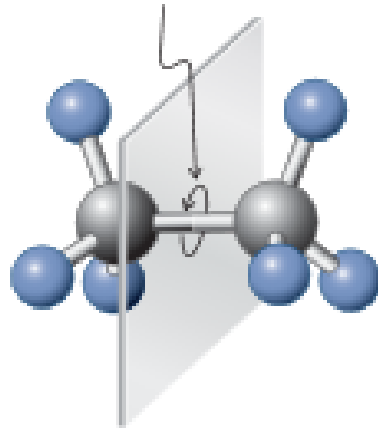
diastereomery

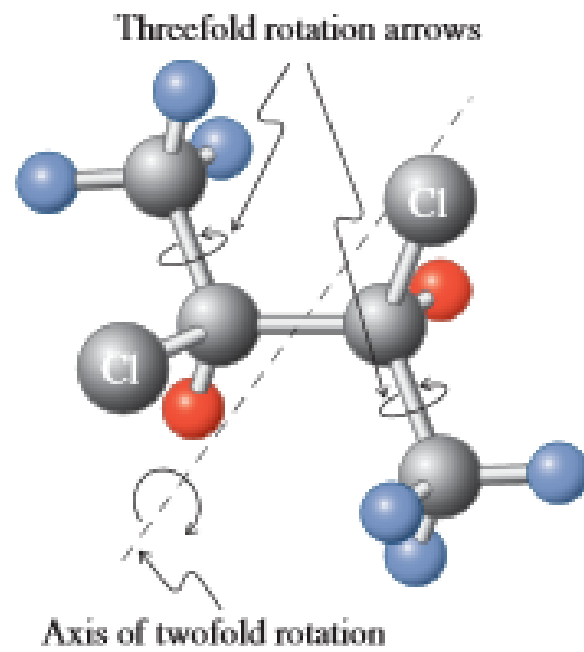
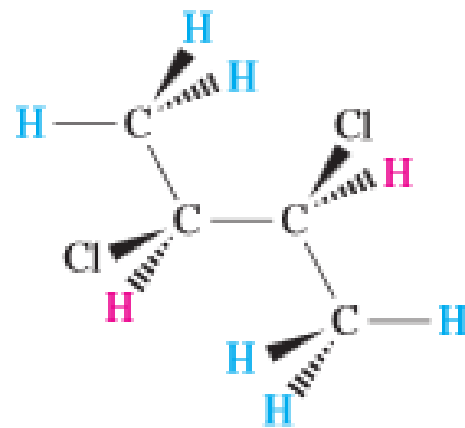
není osa symetrie
není rovina symetrie
neekvivalentní
rozišitelné ve spektru

diastereotopické
metylenové vodíky



Threefold rotation arrow





» 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

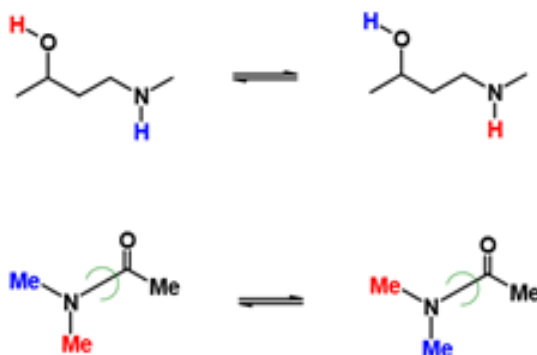
SH

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



Počet signálů - Chemická výměna

Buď se jedná o skutečný chemický proces (reakci) nebo se jedná změnu konformace, například v důsledku rotace kolem vazby.



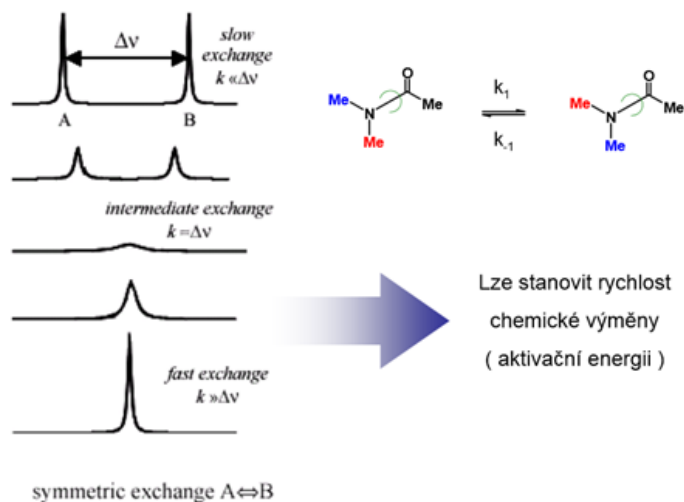
Chemická výměna je na časové škále NMR

a) Rychlá = pozorujeme průměrnou hodnotu

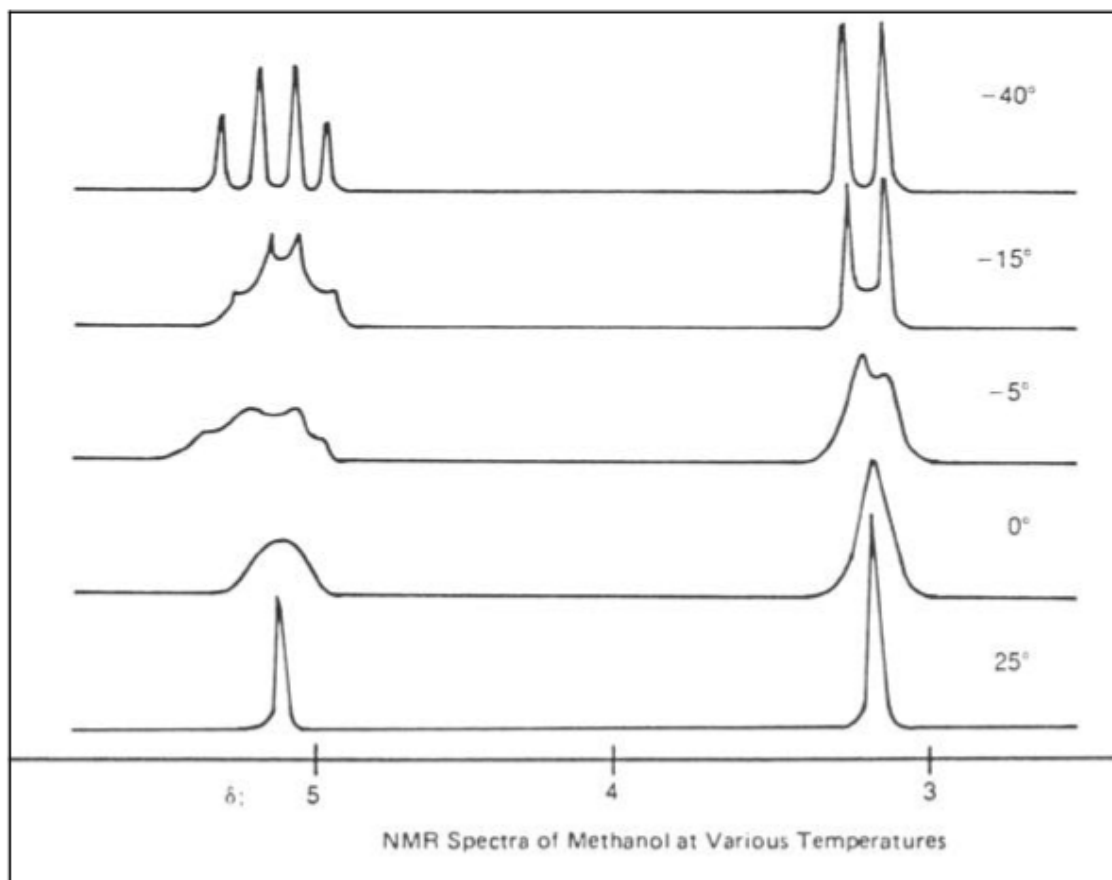
b) Střední = pozorujeme velmi široký signál

c) Pomalá = pozorujeme signály krajních stavů

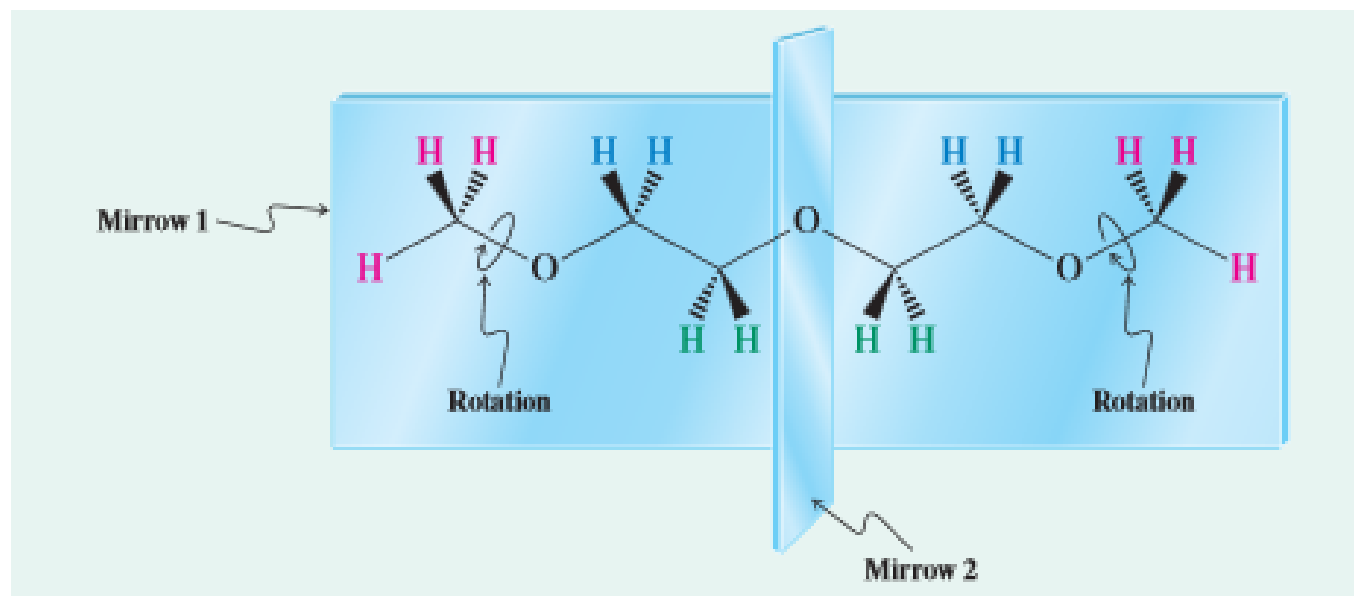
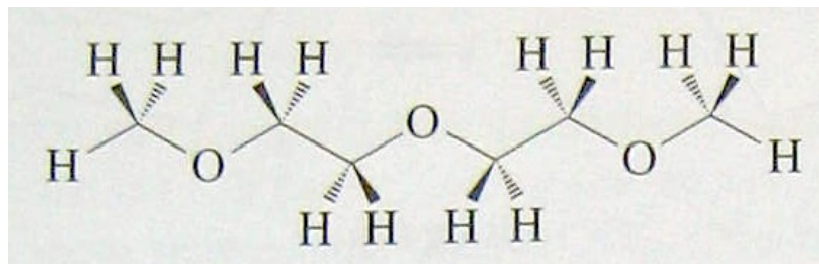
Počet signálů - Vliv teploty

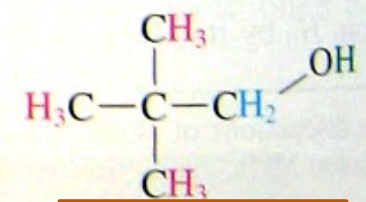
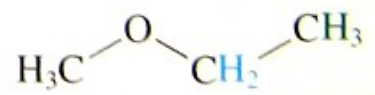
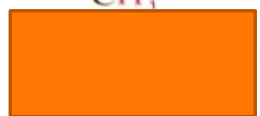
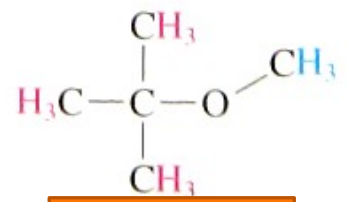
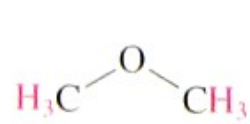
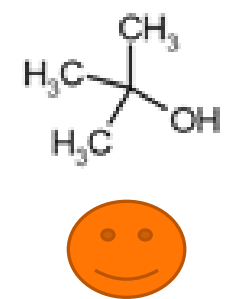
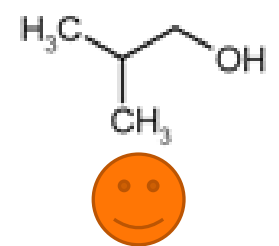
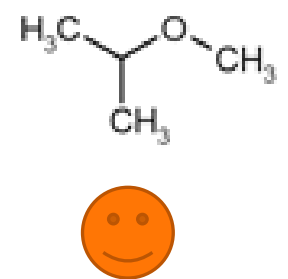


^1H NMR spektrum methanolu CH_3OH při různých teplotách

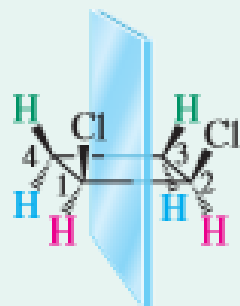


Kolik ^1H NMR signálů očekáváte u níže uvedené molekuly?





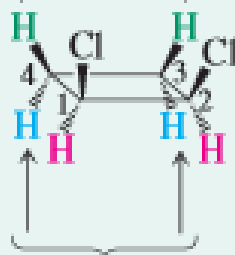
Kolik signálů očekáváte v ^1H NMR spektru *cis*- a *trans*-1,2-dichlorocyklobutanu?



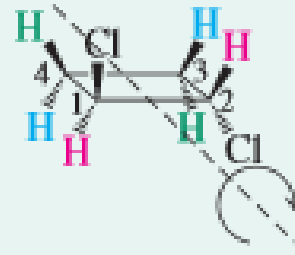
Mirror plane bisecting the molecule

cis-1,2-Dichlorocyclobutane

Cis to the chlorine atoms

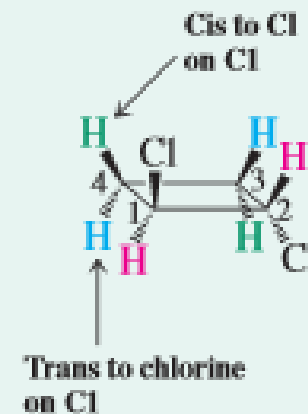


Trans to the chlorine atoms



Twofold rotational axis

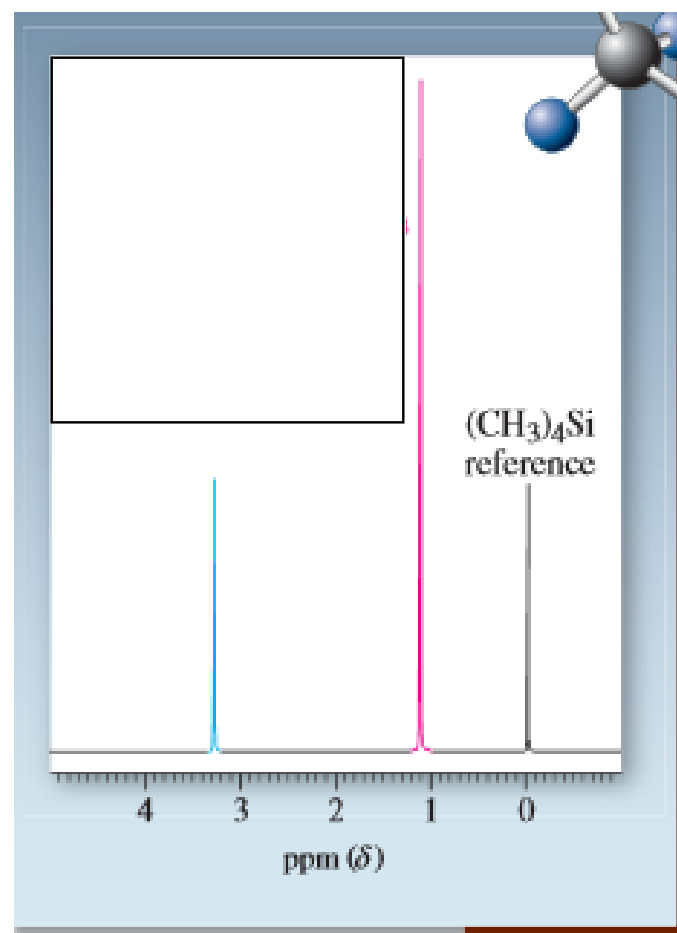
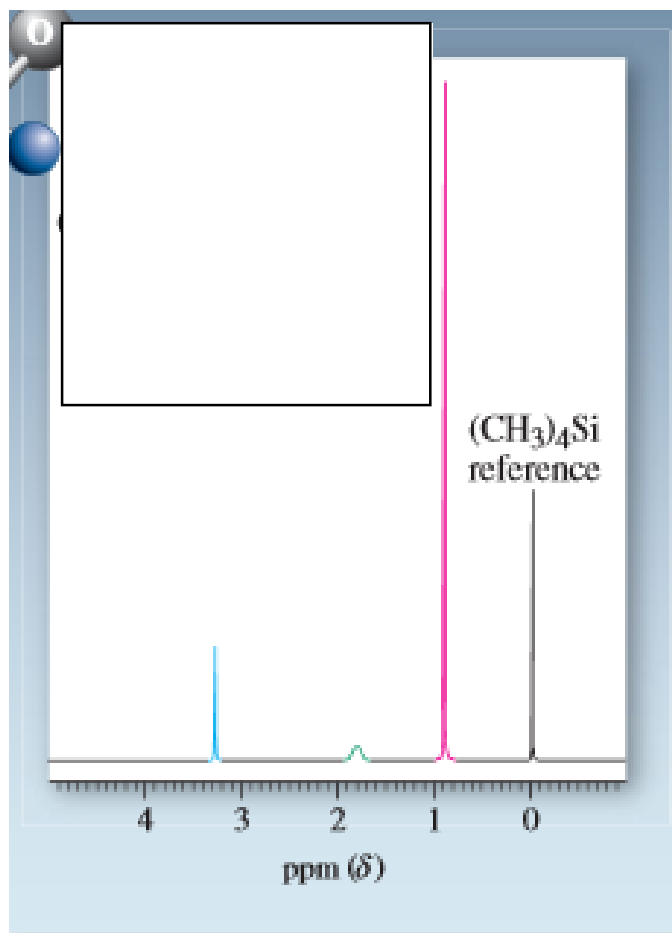
trans-1,2-Dichlorocyclobutane



Cis to Cl on Cl

Trans to chlorine on Cl





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



^1H NMR



15 mm
(equivalent to 6 H)

10 mm (equivalent to 4 H)

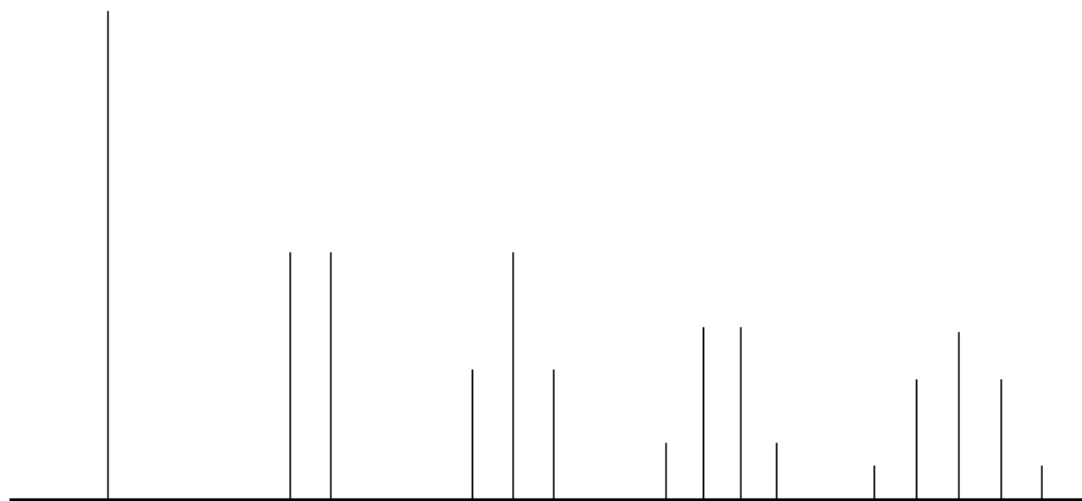
9 8 7 6 5 4 3 2 1 0

ppm (δ)

B



» Multiplicita signálů



singlet

dublet

triplet

kvartet

kvintet

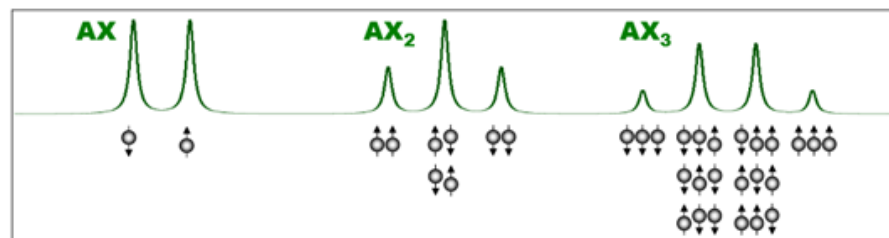
1 : 1

1 : 2 : 1

1 : 3 : 3 : 1

1 : 4 : 6 : 4 : 1

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



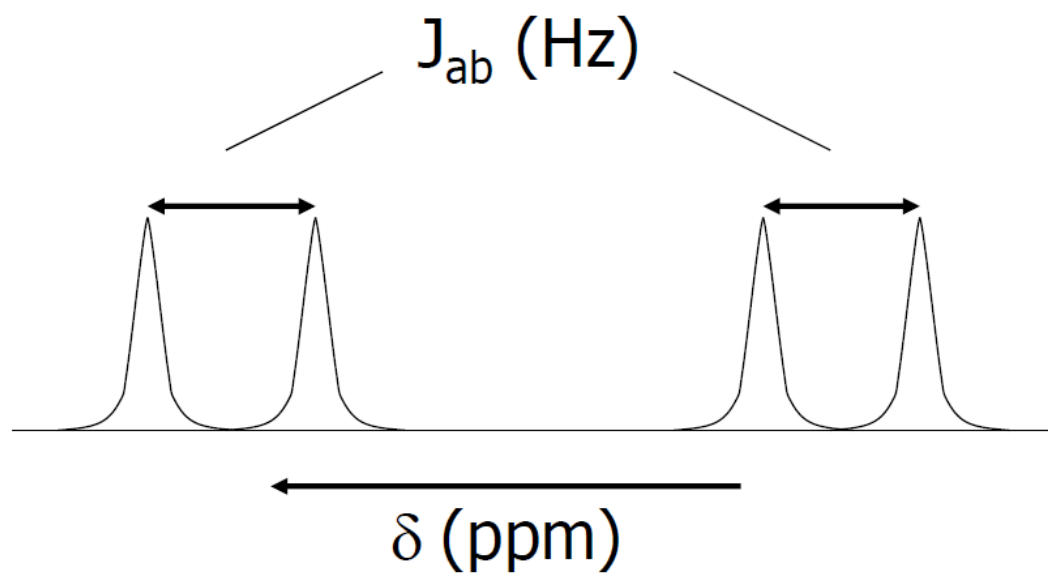
	Splitting pattern for H_a	Structure	Splitting pattern for H_b	
H_a has one neighbor H_b : 2 peaks or doublet				H_b has one neighbor H_a : 2 peaks or doublet
H_a has one neighbor H_b : 2 peaks or doublet				H_b has two neighbors H_a : 3 peaks or triplet
H_a has two neighbors H_b : 3 peaks or triplet				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.



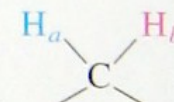
» Interakční konstanta

nezávisí na H_0 vnějšího magnetického pole

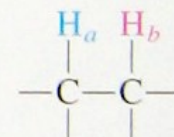


	$J(H,H)$ [Hz]	$J(C,H)$ [Hz]
geminální	1J	125 - 250
vicinální	2J	0 - 30
	3J	0 - 18
	$3+nJ$	1 - 10
dalekého dosahu (long range)		<1

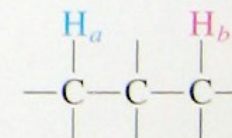
Coupling Between Close-Lying Hydrogens



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



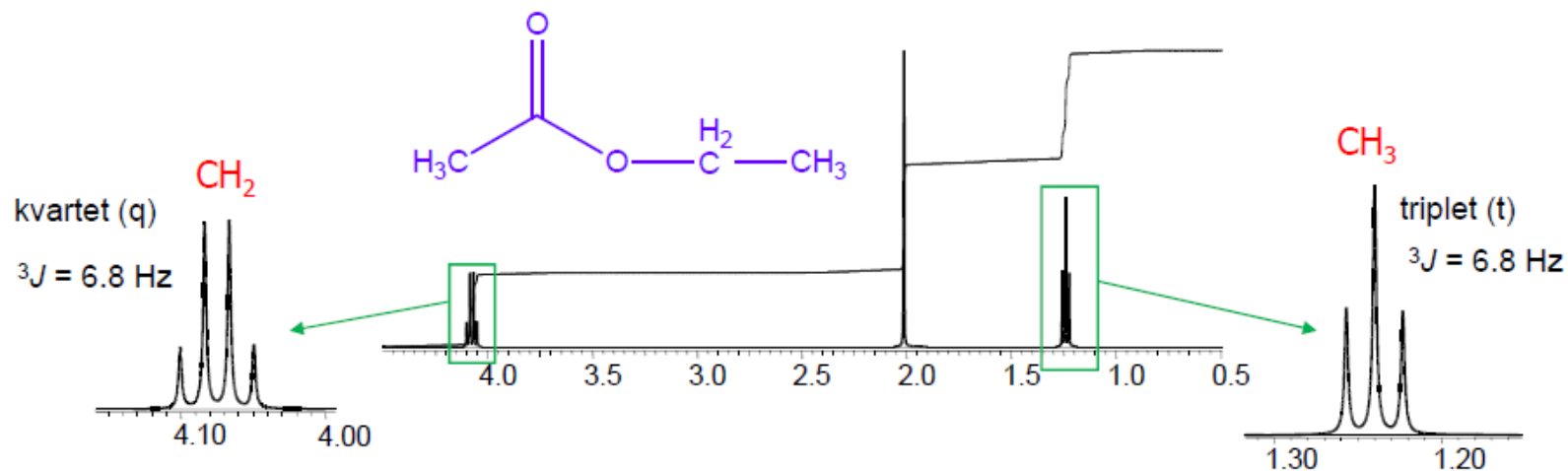
J_{ab} , vicinal coupling, typically 6-8 Hz



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



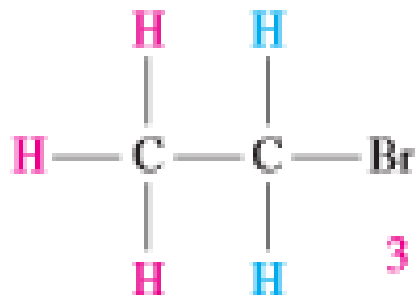
» ^1H NMR spektrum ethyl-acetátu



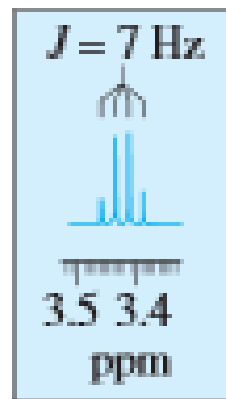
- spektrum 1. řádu: $\Delta\nu \gg J$, AX systém
- methylen vidí 4 různé stavy methylu (kvartet), methyl vidí 3 různé stavy methyleny (triplet)
- počet složek multipletu pro $I = 1/2$: $n+1$, n je počet interagujících jader v sousedním multipletu
- vzdálenost složek multipletu v Hz - interakční konstanta J
- střed multipletu - hodnota chemického posunu δ



^1H NMR



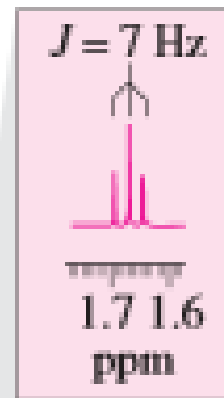
3 H neighbors:
quartet



2 H

3 H

2 H neighbors:
triplet



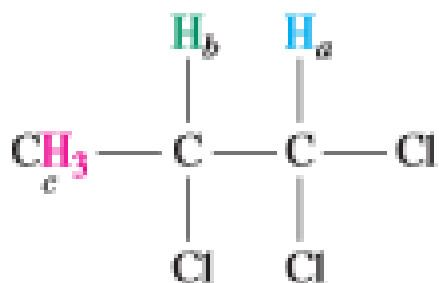
$(\text{CH}_3)_4\text{Si}$

9 8 7 6 5 4 3 2 1 0

ppm (δ)



$^1\text{H NMR}$



1 H neighbor:
doublet

$$J_{ab} = 3.6 \text{ Hz}$$



3 H neighbors: quartet
 $J_{bc} = 6.8 \text{ Hz}$

1 H neighbor: doublet
 $J_{ab} = 3.6 \text{ Hz}$

1 H

1 H

3 H

1 H neighbor:
doublet

$$J_{bc} = 6.8 \text{ Hz}$$



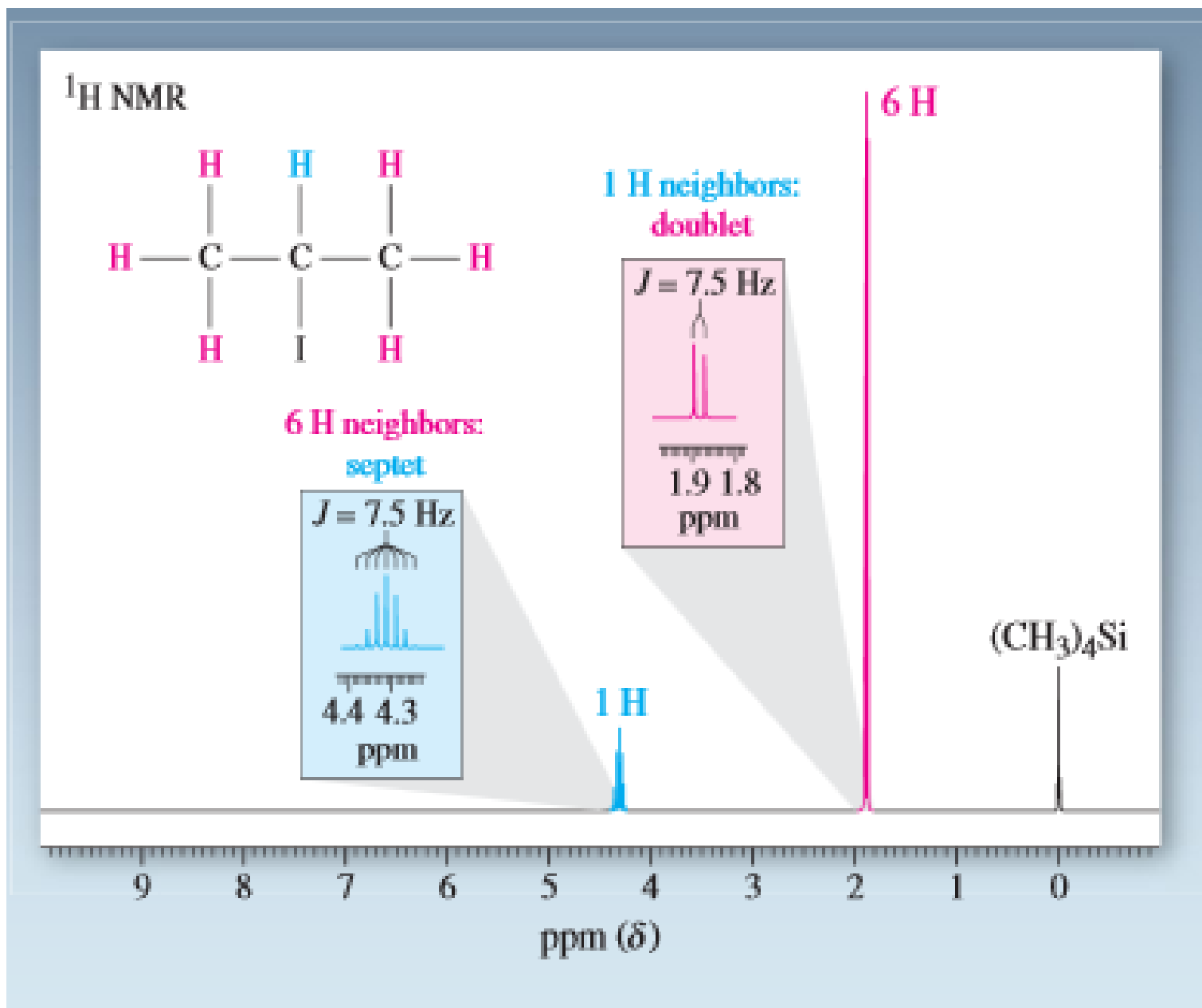
$(\text{CH}_3)_4\text{Si}$

9 8 7 6 5 4 3 2 1 0

ppm (δ)



Pokuste se navrhnout ^1H NMR spektrum 2-jodpropanu



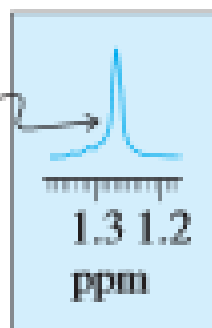
Pokuste se navrhnout ^1H NMR spektrum oktanu

^1H NMR

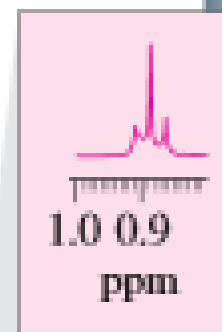


δ Values are close

Non-first-order



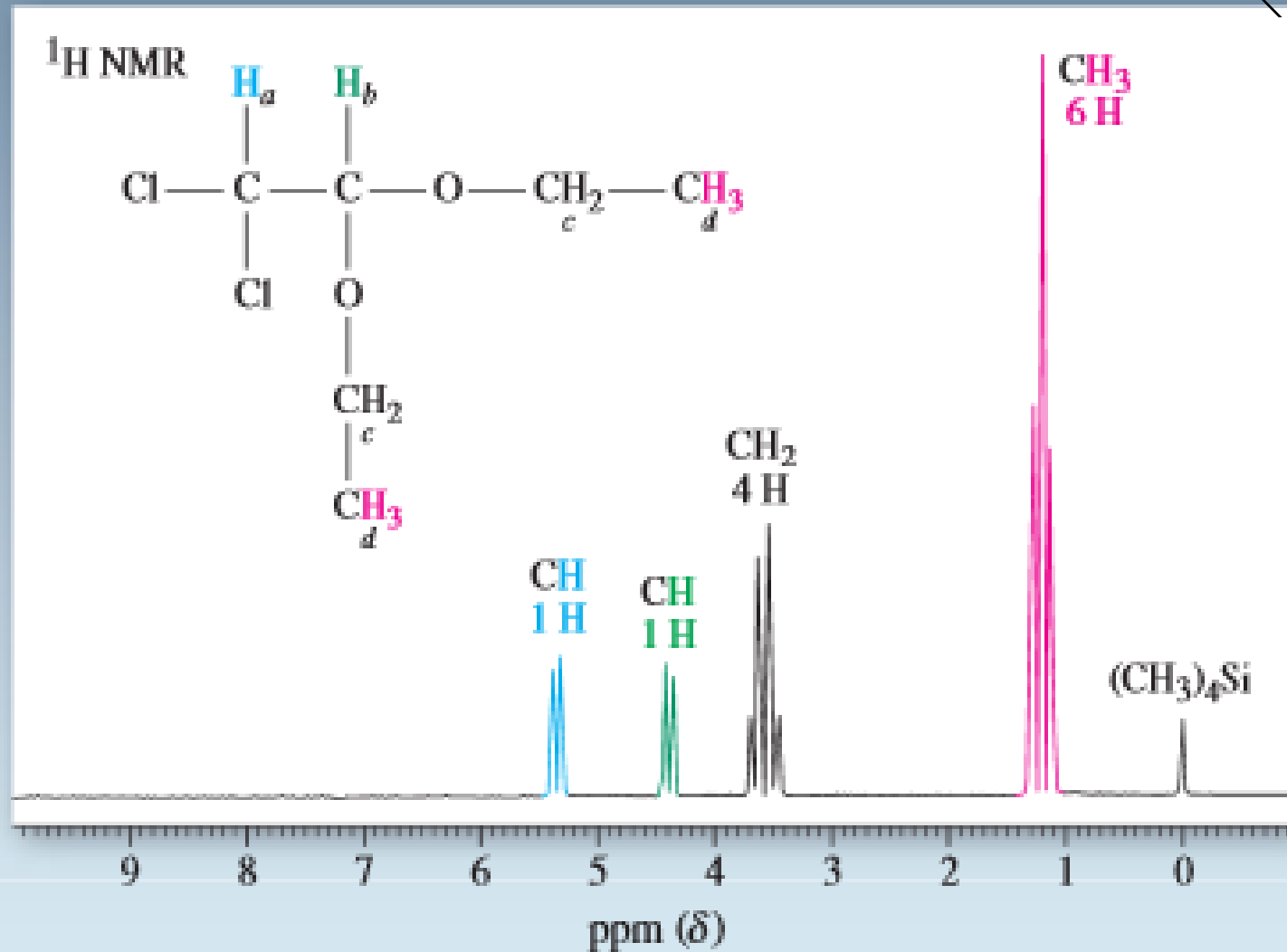
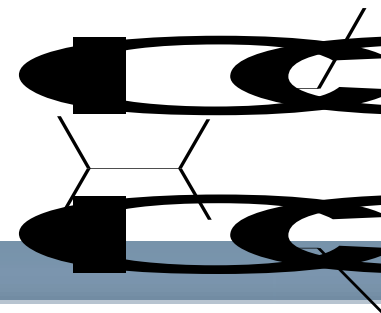
12 H
6 H



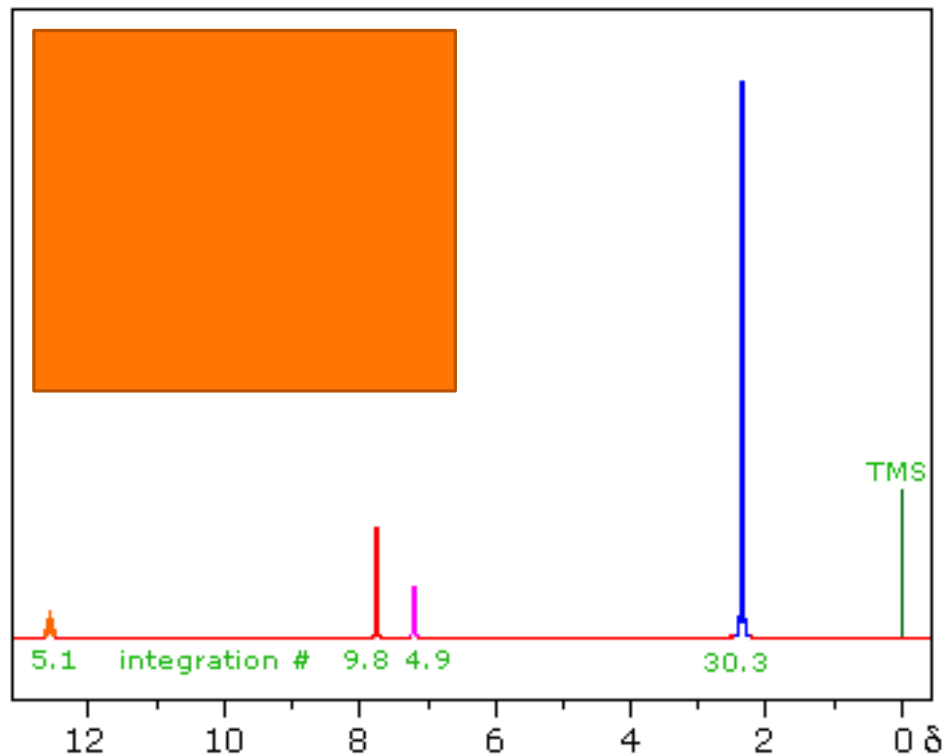
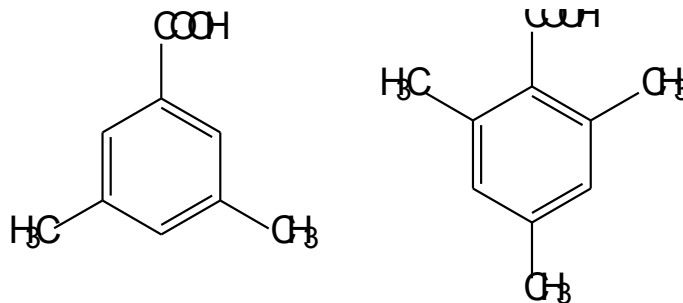
$(\text{CH}_3)_4\text{Si}$

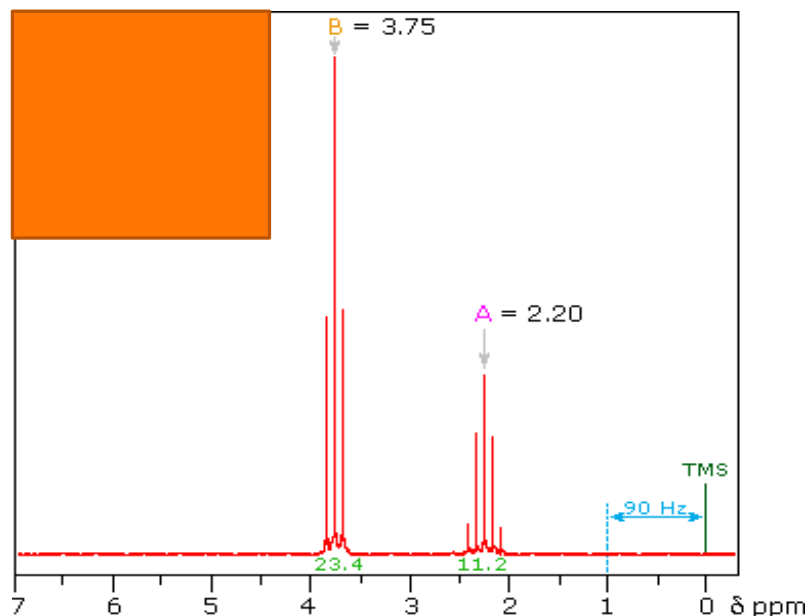


Pokuste se navrhnout ^1H NMR spektrum uvedené sloučeniny



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



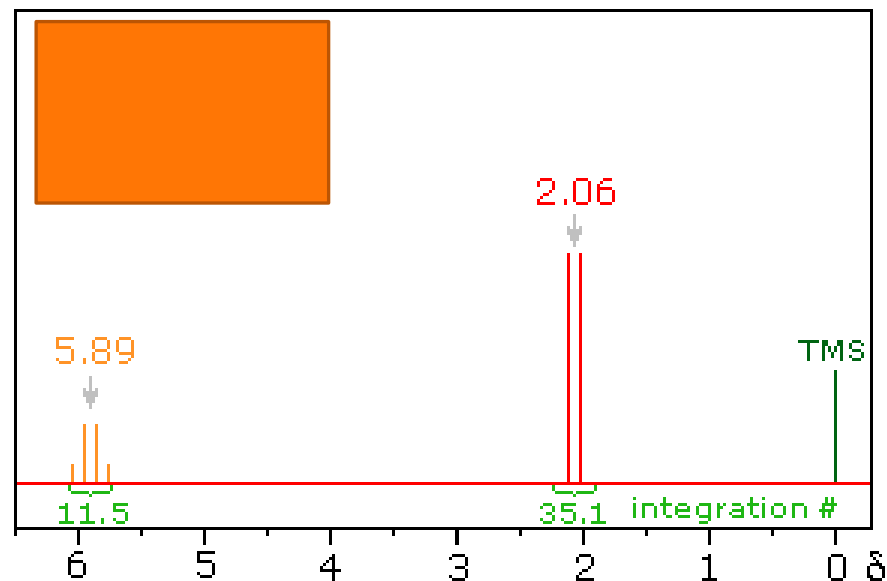
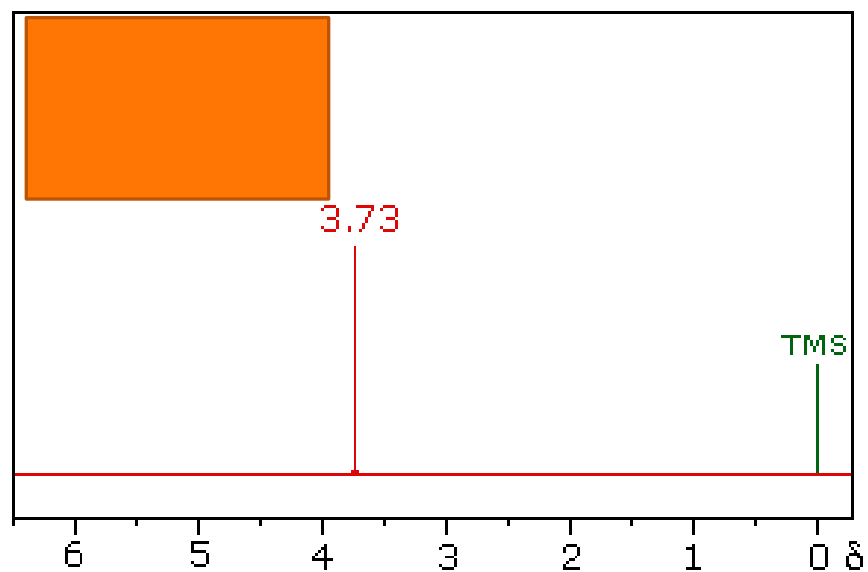


Přiřadte následující ^1H NMR spektra níže uvedeným sloučeninám:

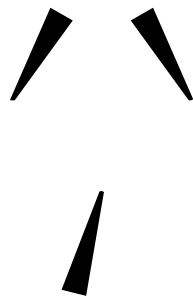
1,1-dichlorethan

1,2-dichlorethan

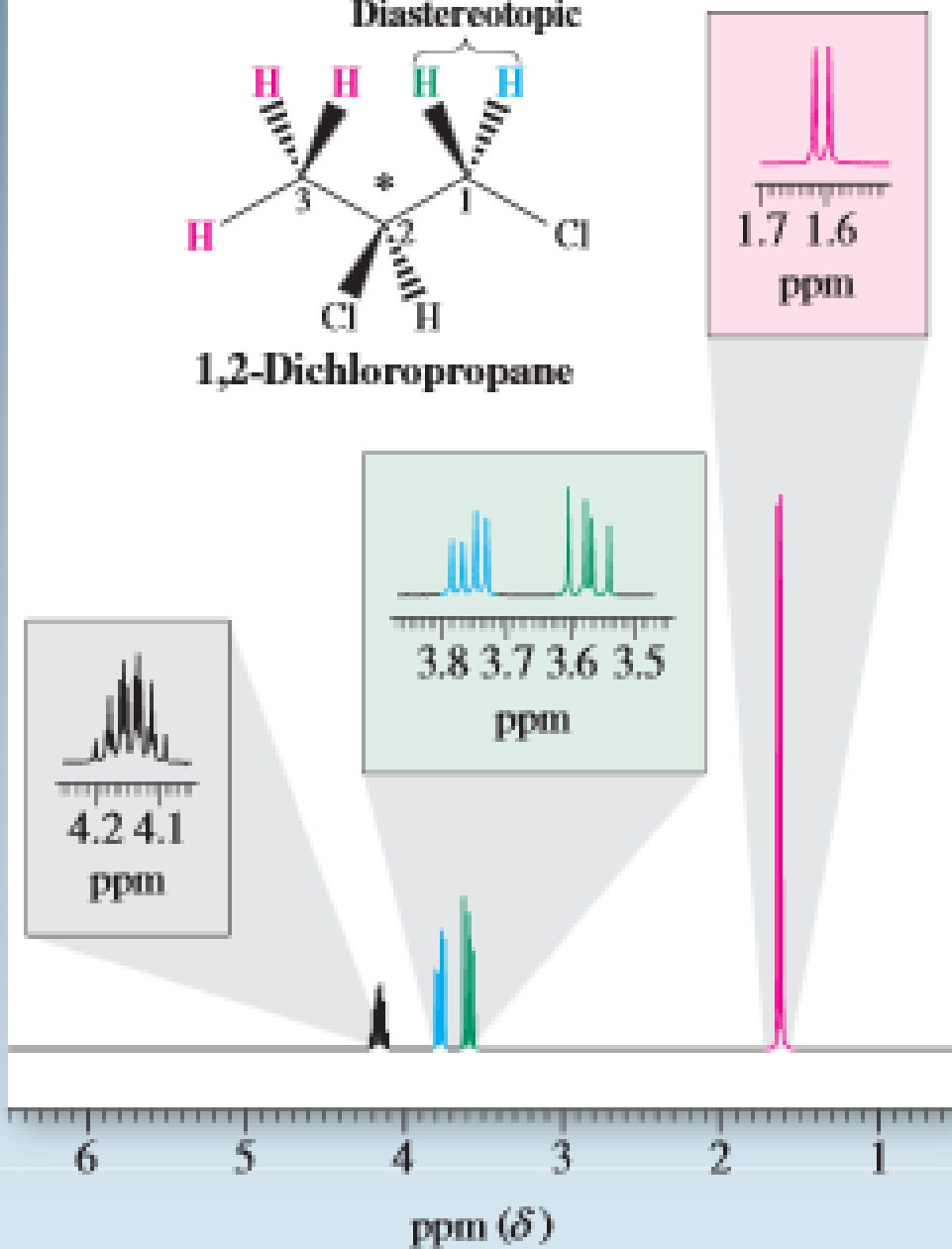
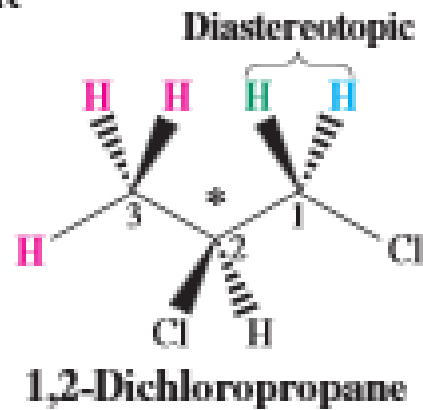
1,3-dichlorpropan



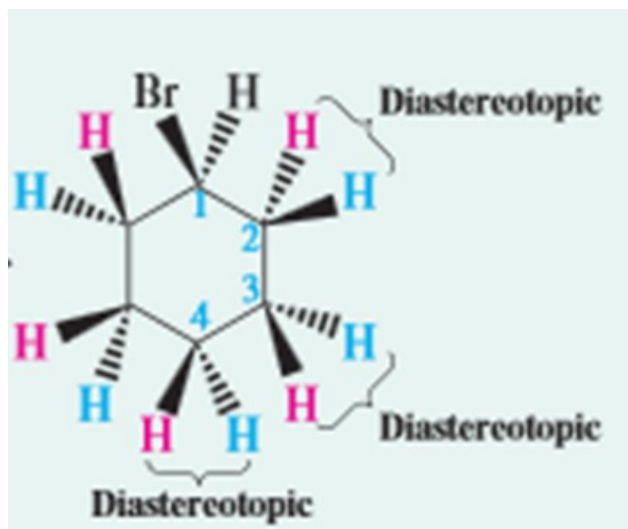
Pokuste se navrhnout, jak bude vypadat ^1H NMR spektrum uvedené sloučeniny



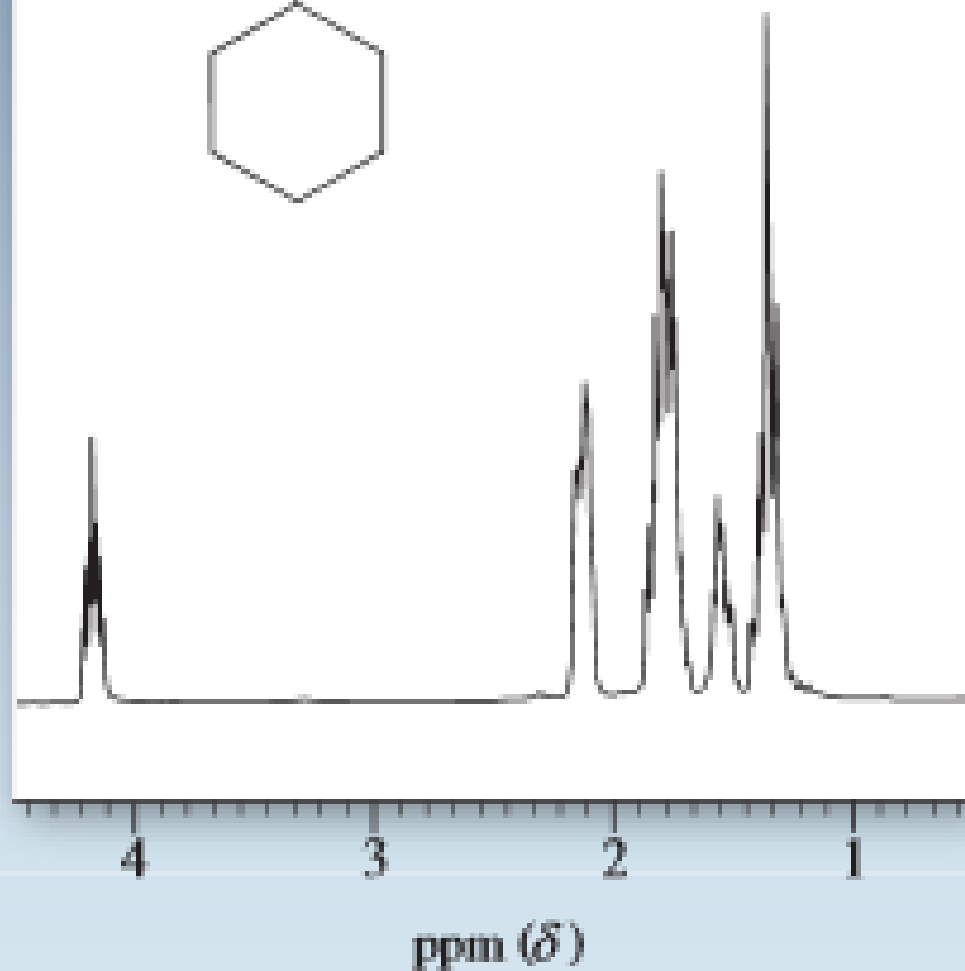
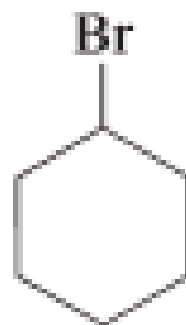
^1H NMR



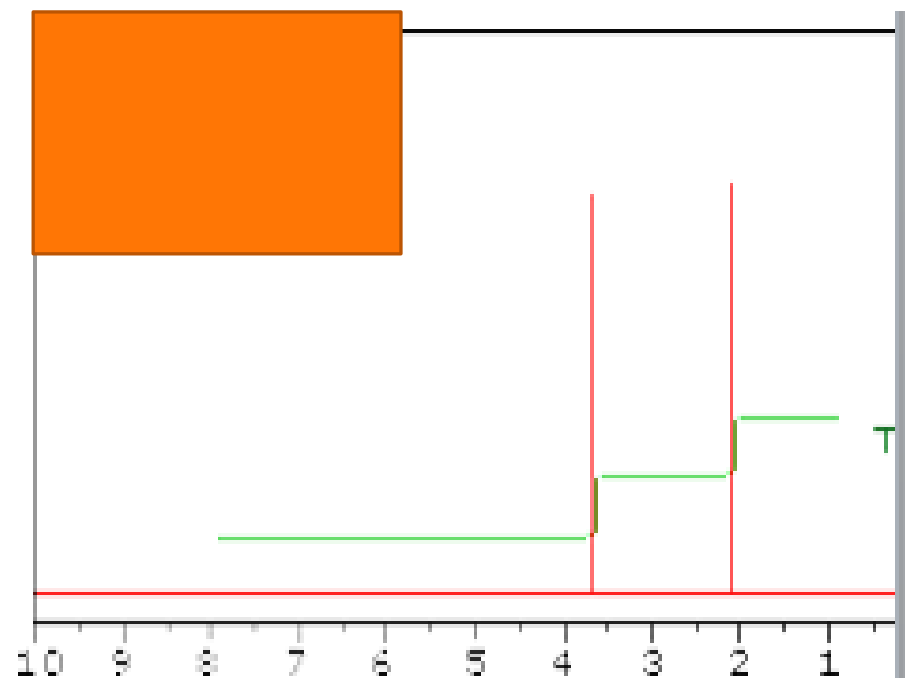
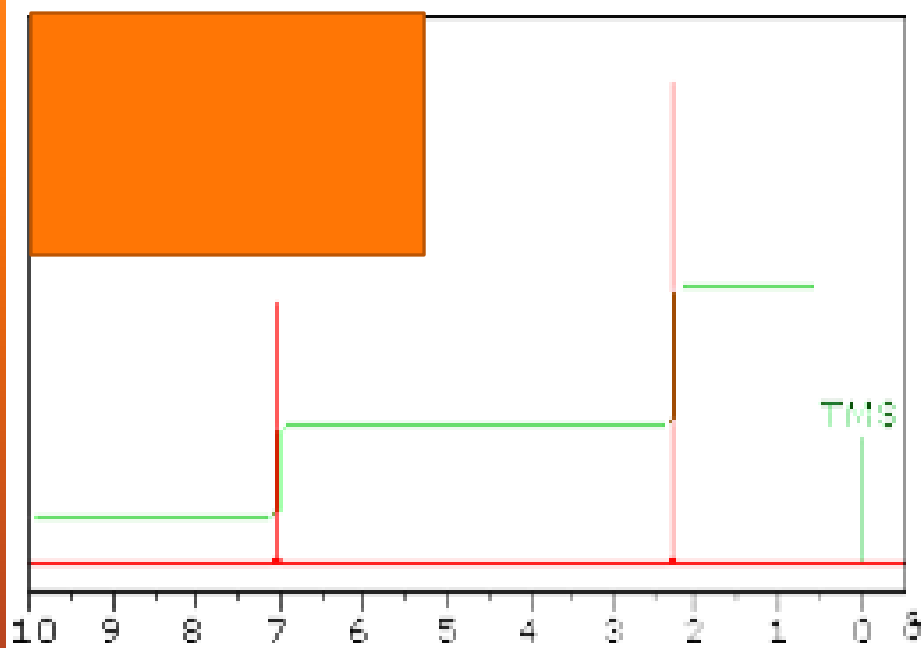
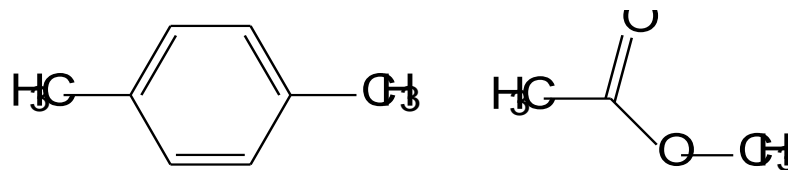
Pokuste se odhadnout,
jak bude vypadat ^1H NMR
spektrum bromcyklohexanu



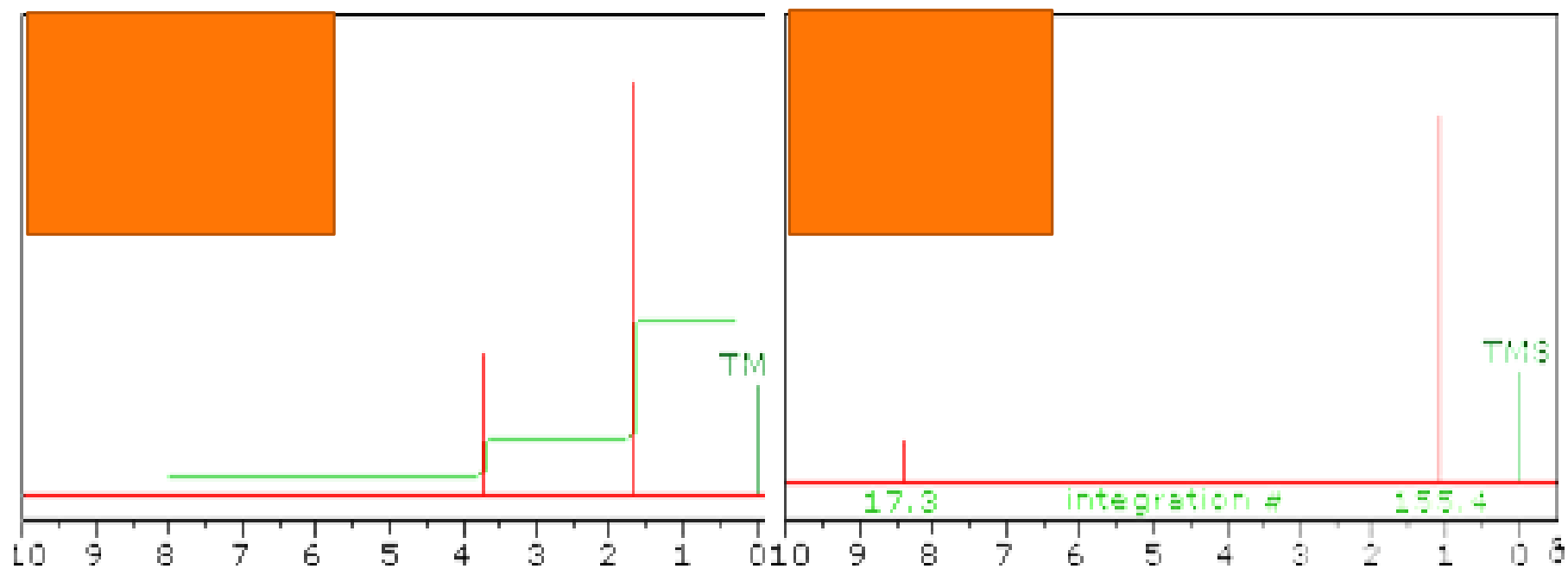
^1H NMR



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

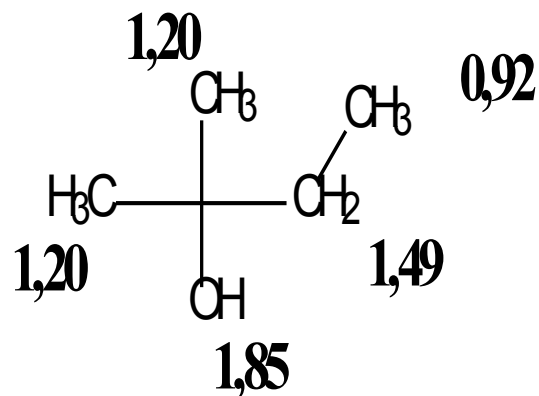
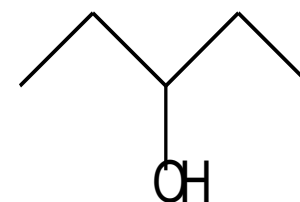
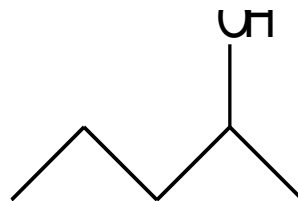


Rozhodněte, které z následujících sloučenin odpovídá níže uvedené ^1H NMR spektrum.



Pokuste se odhadnout, kterému z izomerních alkoholů sumárního vzorce $C_5H_{12}O$ odpovídá následující 1H NMR spektrum.

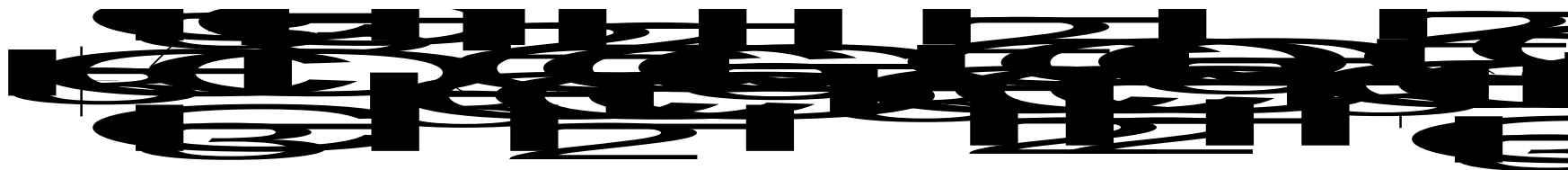
- » 0,92 (t, 3H)
- » 1,20 (s, 6H)
- » 1,49 (k, 2H)
- » 1,85 (š. s, 1H)



Pokuste se odhadnout, kterému z izomerní etherů sumárního vzorce $C_5H_{12}O$.
Odpovídá následující 1H NMR spektrum.

» 1,19 (s, 9H)

» 3,21 (s, 3H)



**Přiřadte následující signály
k jednotlivým vodíkovým
atomům**

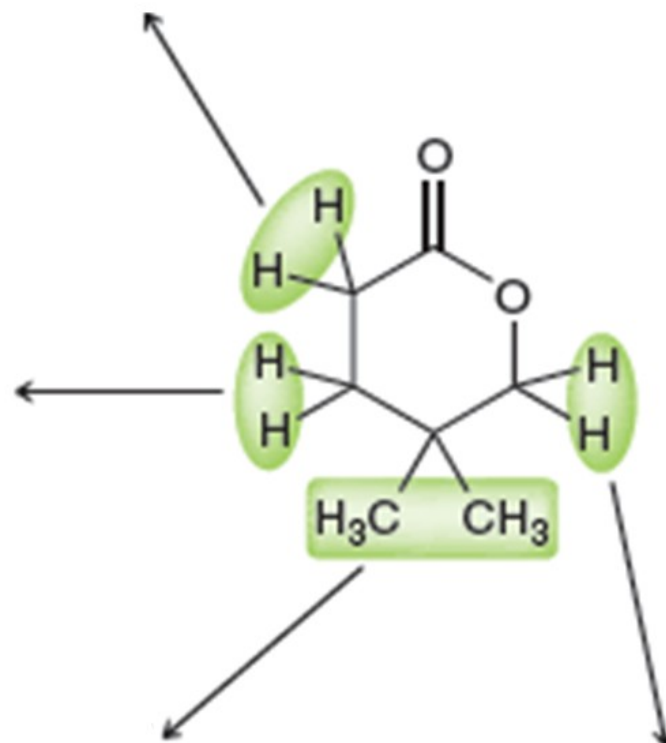
1,0 ppm, 6H, s
1,4 ppm, 2H, t
2,2 ppm, 2H, t
4,2 ppm, 2H, s

2,2 ppm, 2H, t

1,4 ppm, 2H, t

1,0 ppm, 6H, s

4,2 ppm, 2H, s

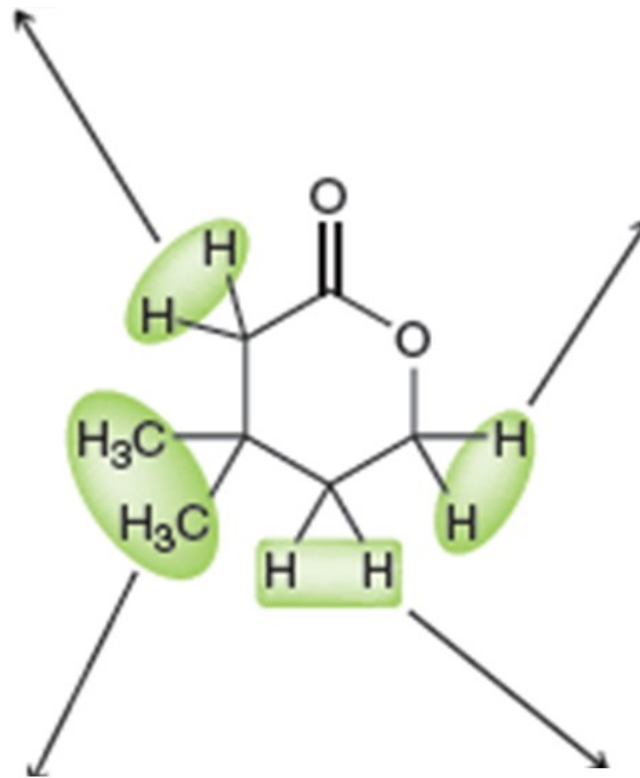


**Přiřadte následující signály
k jednotlivým vodíkovým
atomům**

0,9 ppm, 6H, s
1,8 ppm, 2H, t
2,2 ppm, 2H, s
4,2 ppm, 2H, t

2,2 ppm, 2H, s

m, 2H, t

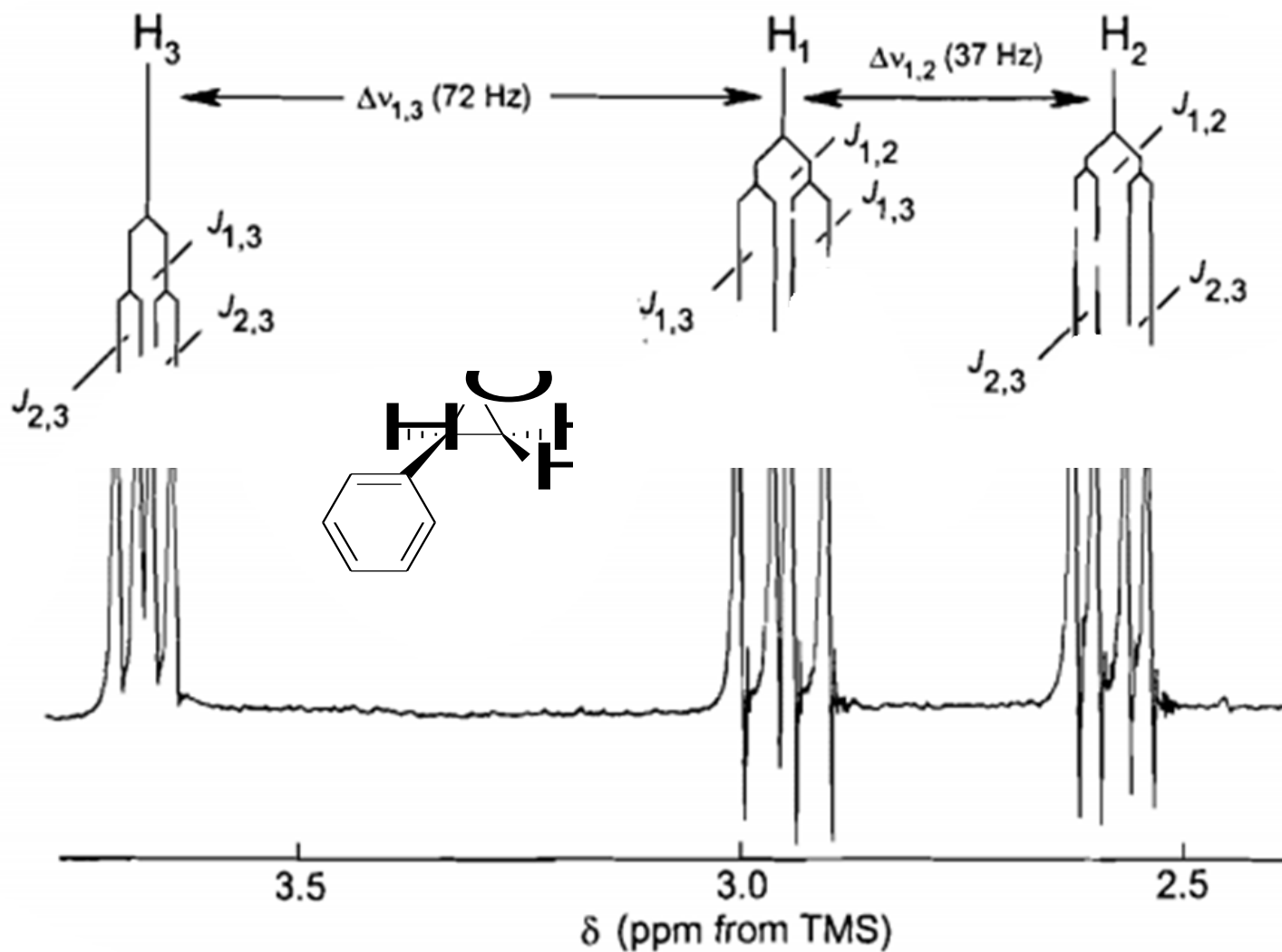


0,9 ppm, 6H, s

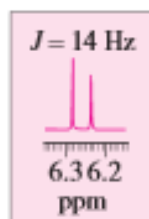
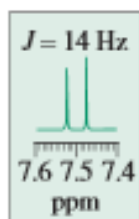
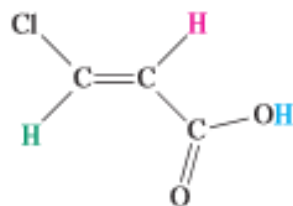
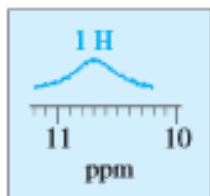
1,8 ppm, 2H, t



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



¹H NMR

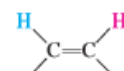


(CH₃)₄Si

1 H
1 H

ppm (δ)

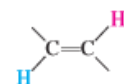
B



Vicinal, cis

6-14

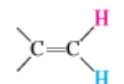
10



Vicinal, trans

11-18

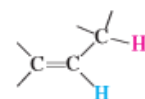
16



Geminal

0-3

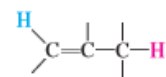
2



None

4-10

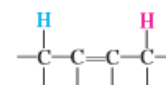
6



Allylic, (1,3)-cis or -trans

0.5-3.0

2

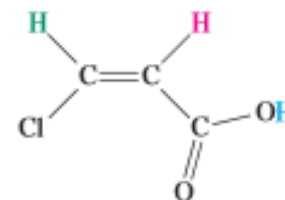
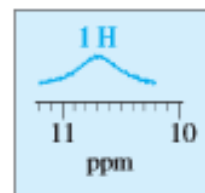


(1,4)- or long-range

0.0-1.6

1

¹H NMR



(CH₃)₄Si

1 H
1 H

ppm (δ)

A

^{13}C NMR spektroskopie

Stejná jako v ^1H NMR spektru, tj. odpovídá počtu ekvivalentních jader.

Ale značně závislá na způsobu měření neboť ^{13}C jádra mají velmi rozdílné relaxační časy ...


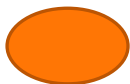
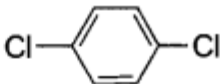
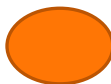
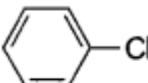

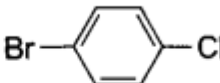

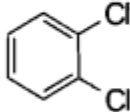

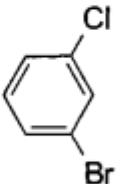

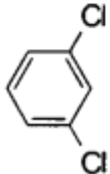
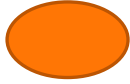
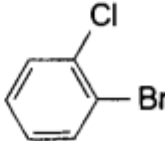
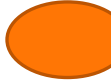
Obvykle tedy v ^{13}C neintegrujeme ... Ale!

Mají-li uhlíky blízké relaxační časy, pak je lze integrovat: např. fenyl skupina, směsi rotačních či konfiguračních izomerů, atp.

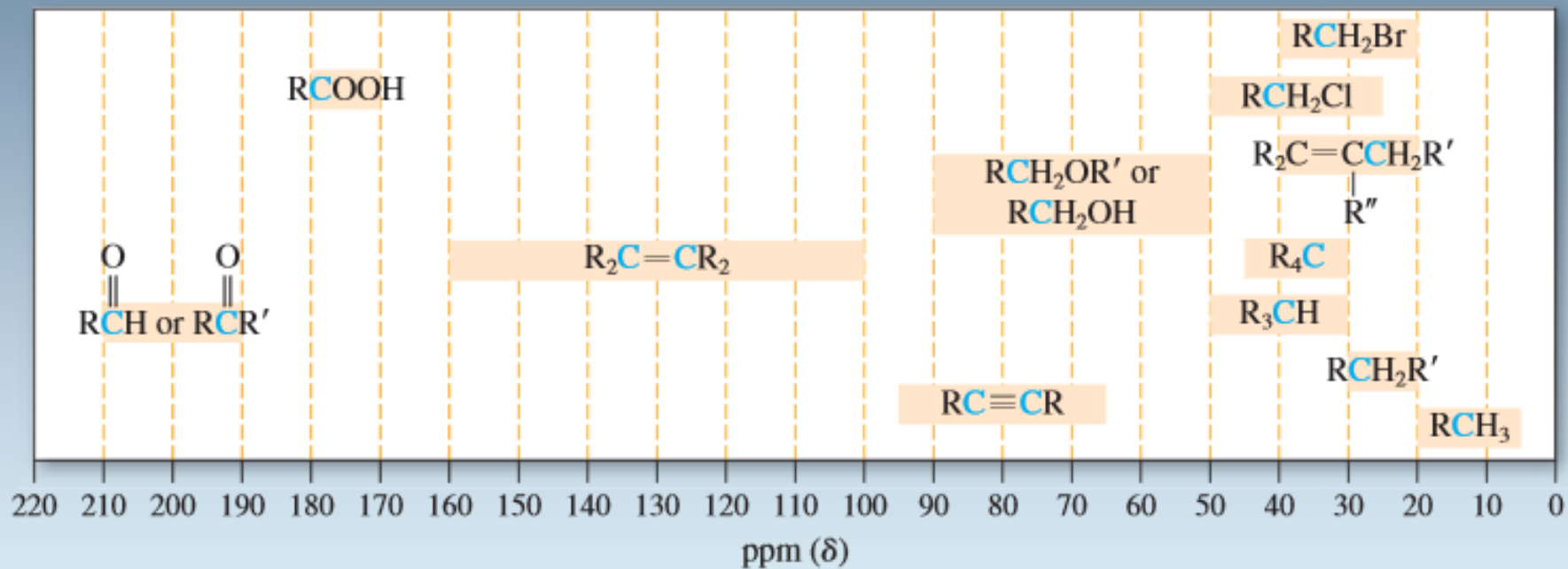
Počet vodíků, respektive množství spin-spin interakcí zrychluje relaxaci ^{13}C .



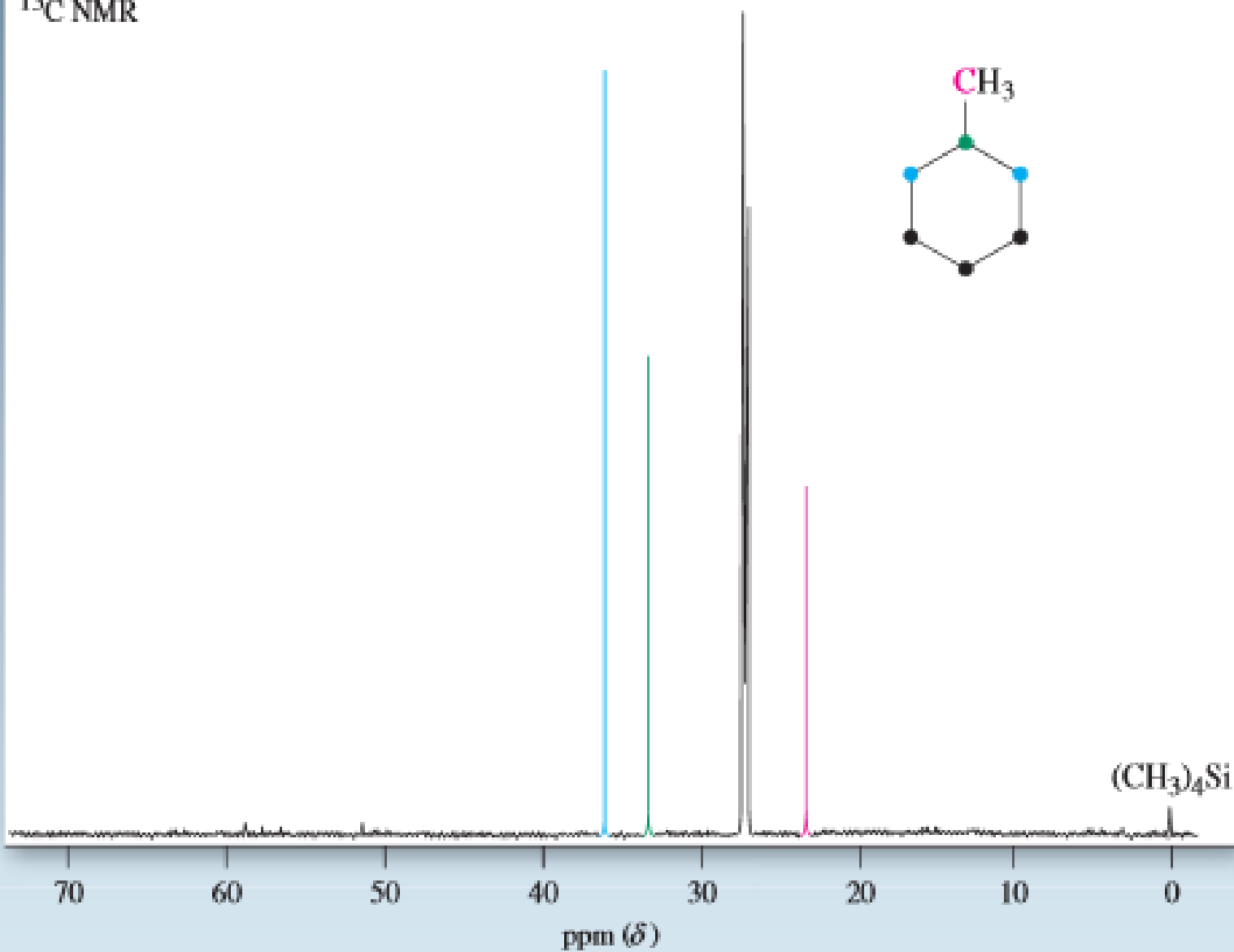
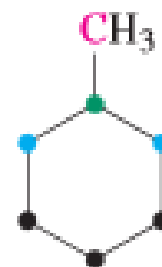
^{13}C NMR počet signálů

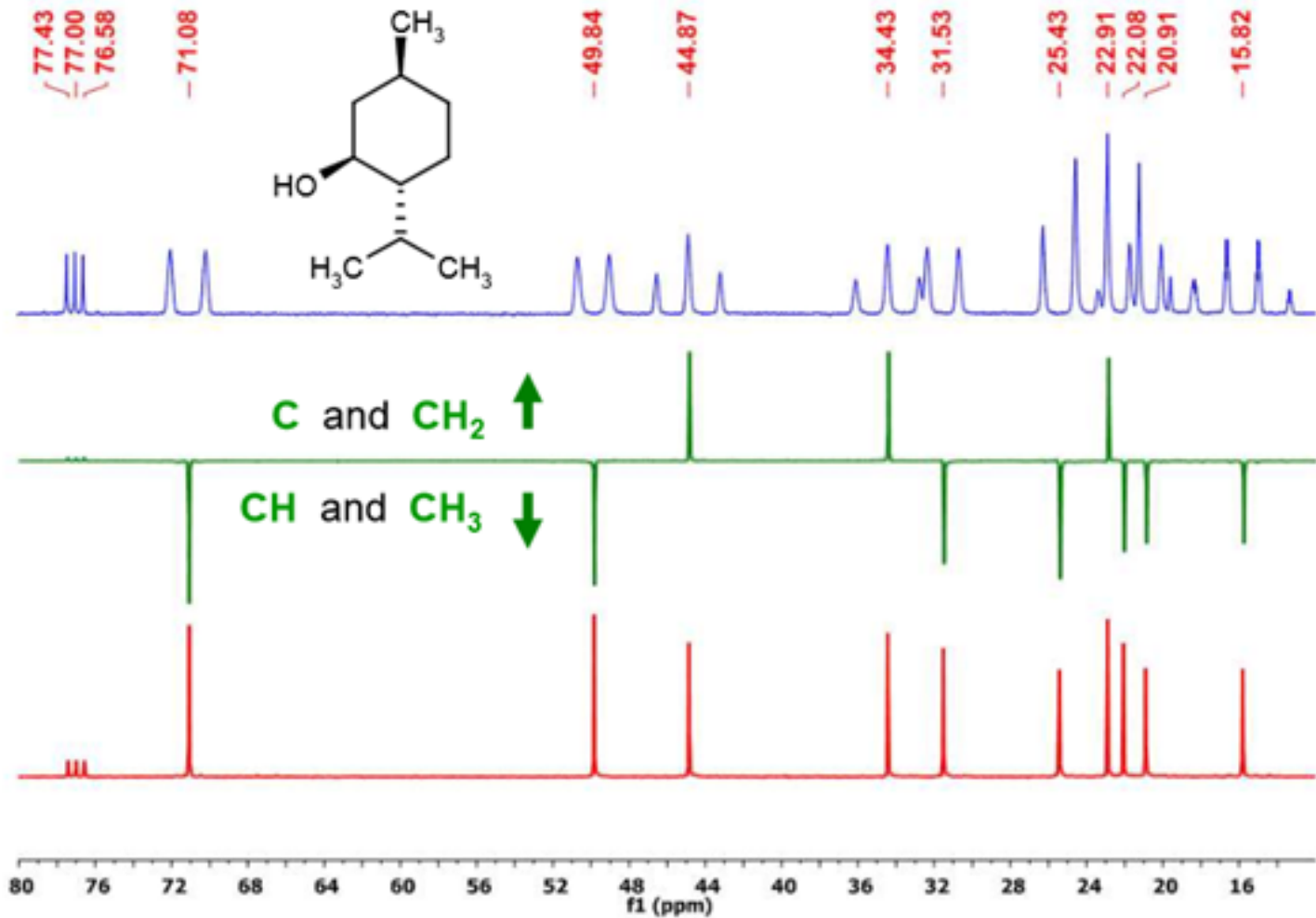




^{13}C NMR



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



<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

Použitá literatura

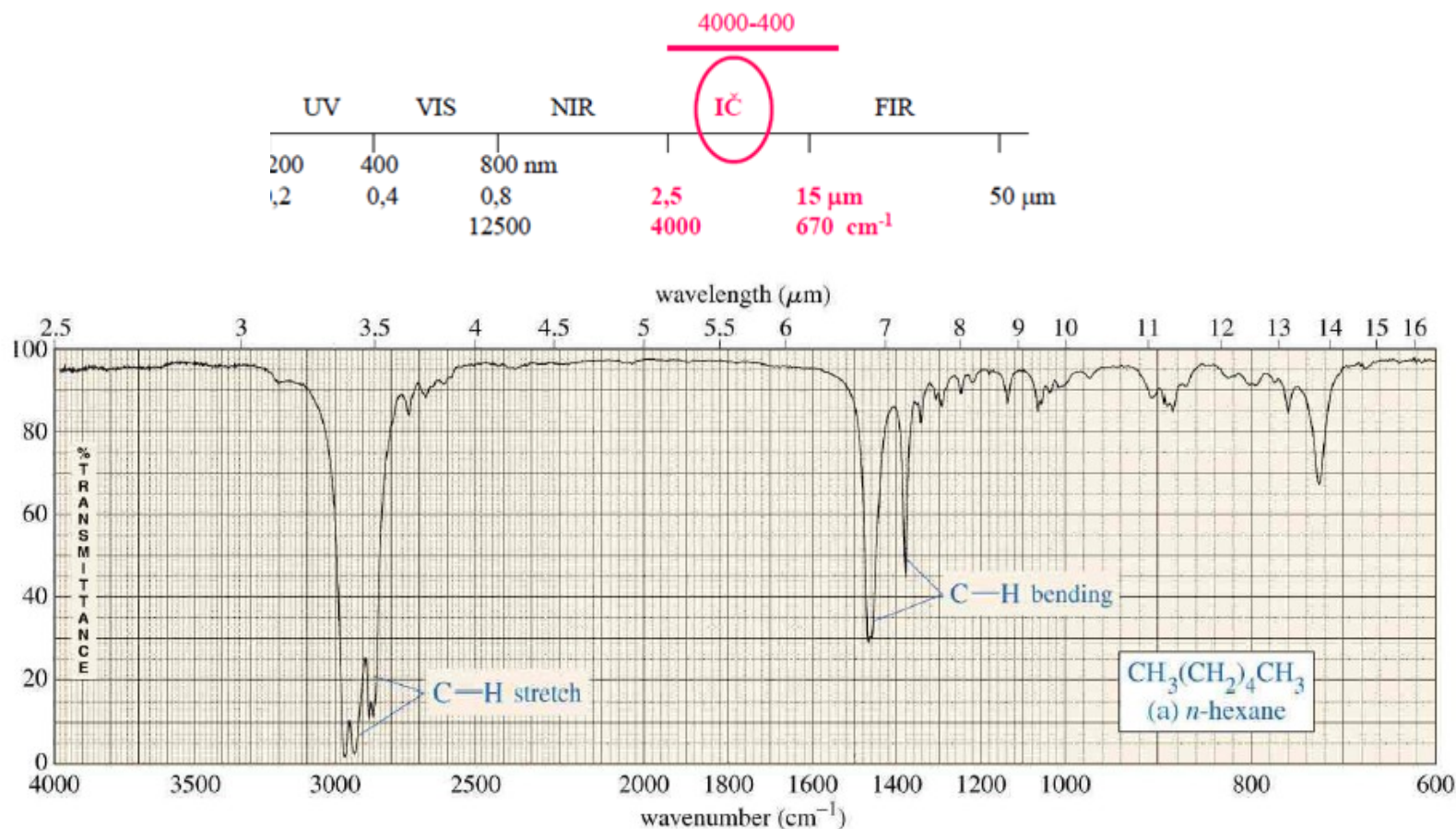


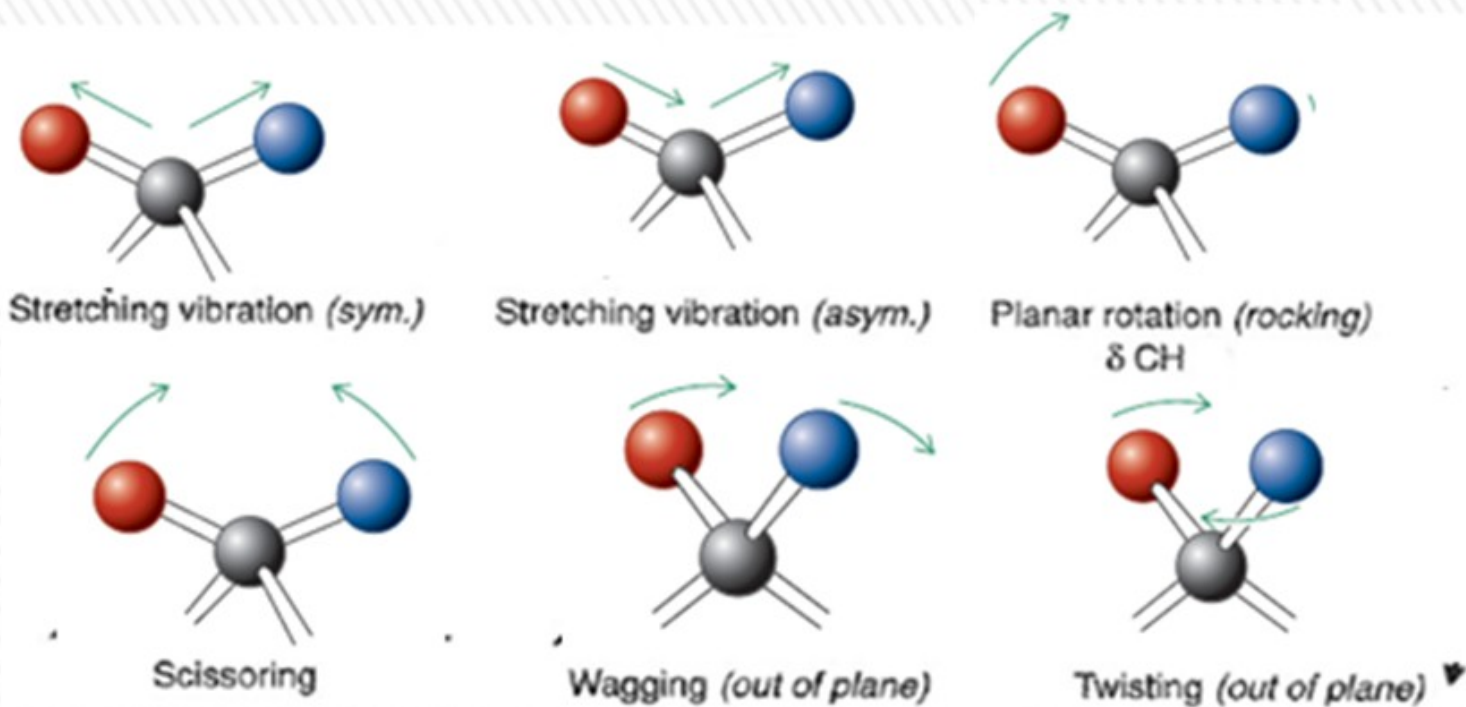


Infračervená spektroskopie

vibračně – rotační spektroskopie

v organické chemii – důkaz přítomnosti funkčních skupin



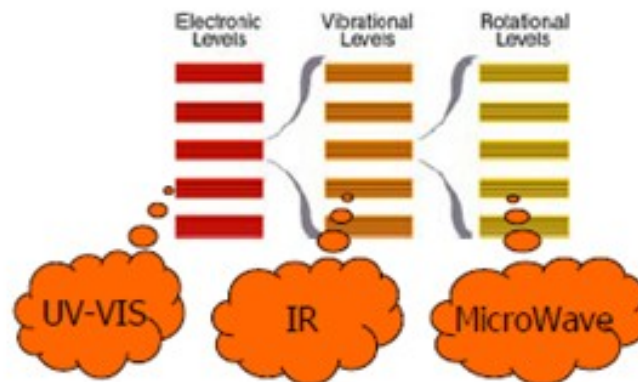
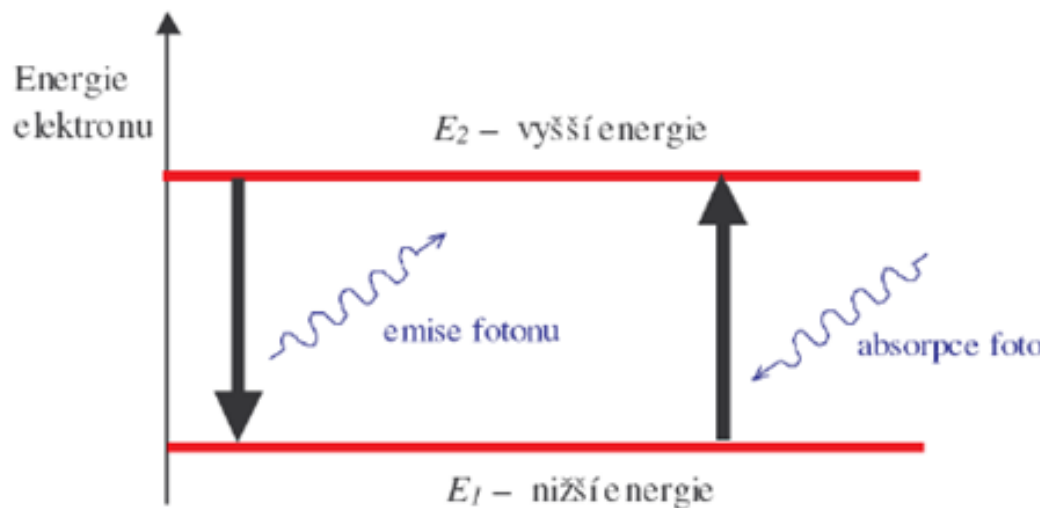


Valenční vibrace: stretching (symetrická a asymetrická) ν
Deformační rovinné: rocking – kyvadlová δ
 scissoring – nůžková
Deformační mimorovinné: wagging – vějířová γ
 twisting - krouťivá

w slabý **m** střední
s silný **v** různý
br široký **sh** ostrý



Aktivní jsou pouze ty vibrace v IČ spektru, při kterých se mění dipólový moment μ



$$h\nu = E_2 - E_1 = \frac{h \cdot c}{\lambda}$$

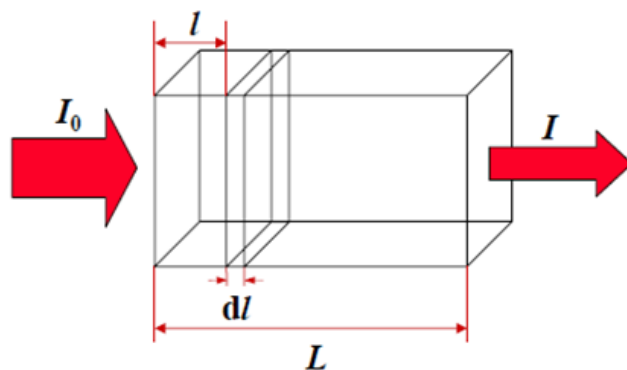


Transmittance T (propustnost) hodnoty 0 – 1 (0 – 100%)

$$T = I / I_0$$

T = 0 prostředí světlo nepropouští vůbec

T = 1 prostředí propouští všechno světlo



Absorbance

$$A = -\log T$$

$$A = \varepsilon \cdot l \cdot c$$



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



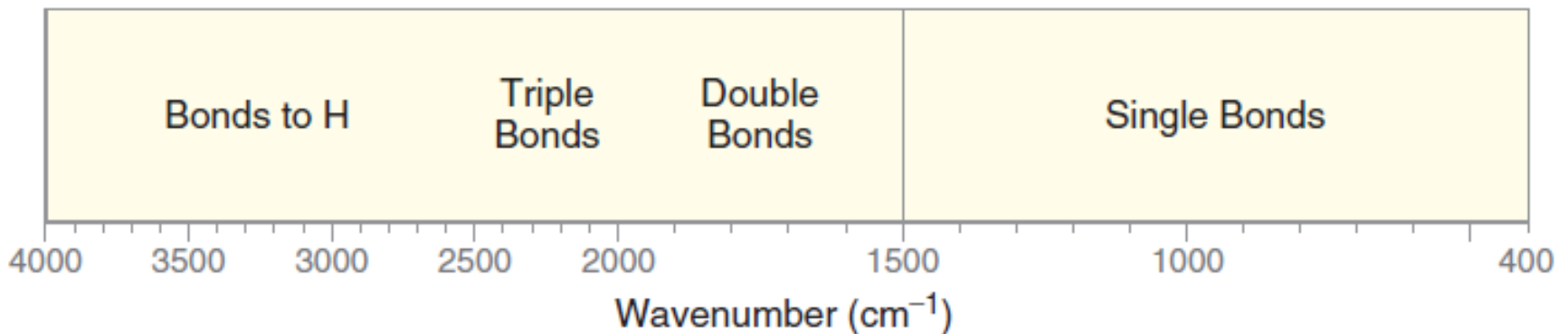
~1600 cm⁻¹

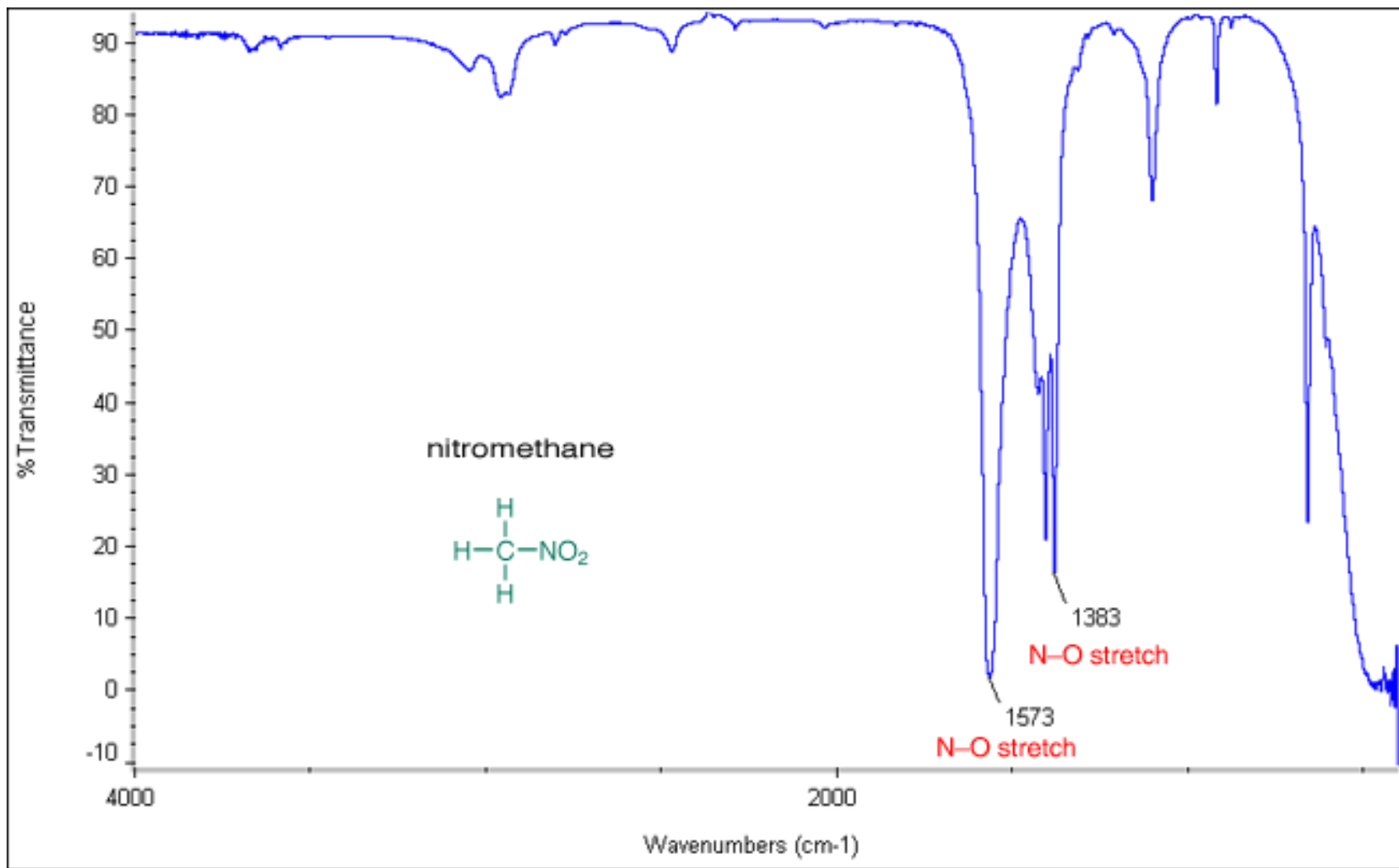


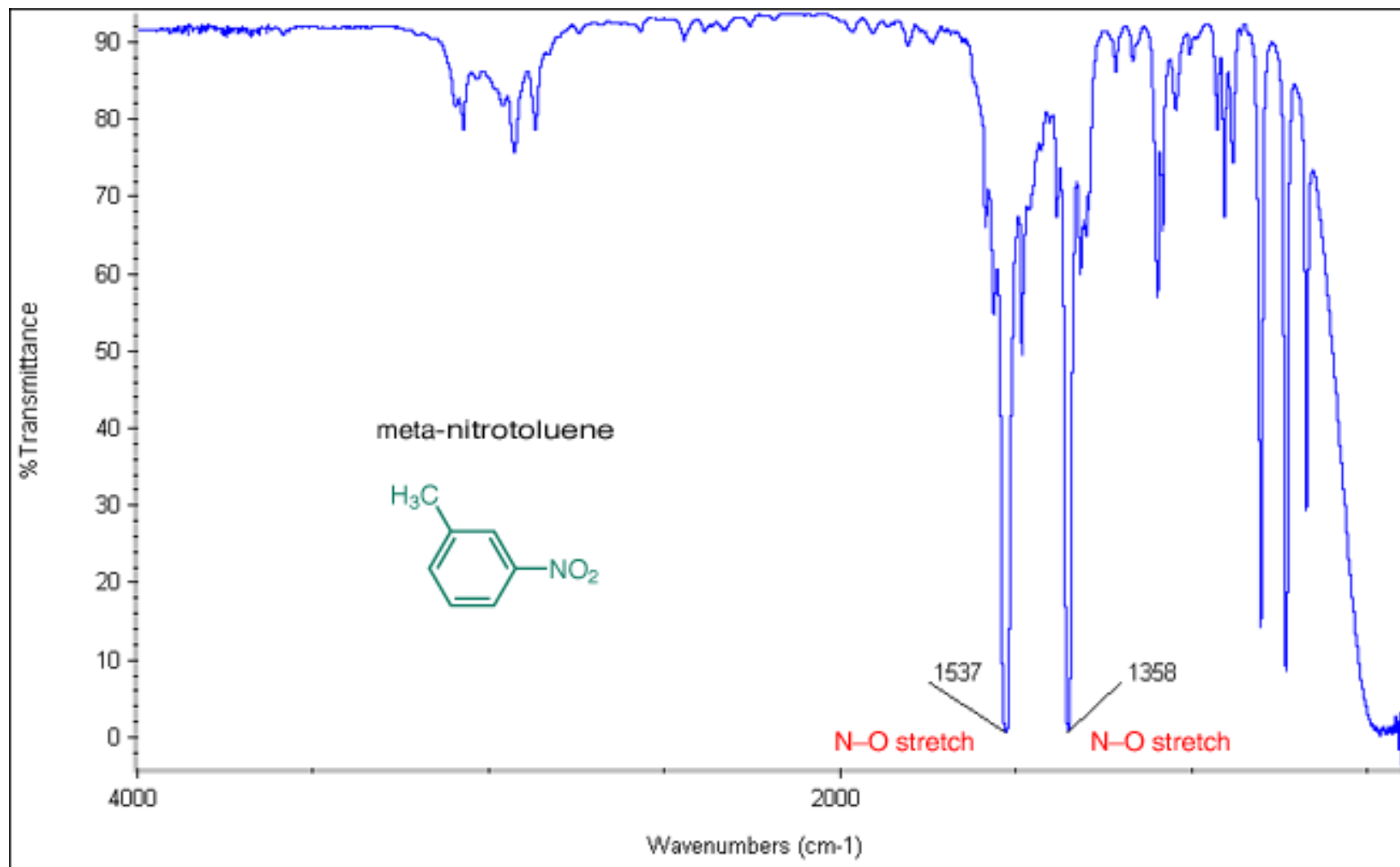
~1100 cm⁻¹

Diagnostic Region

Fingerprint Region

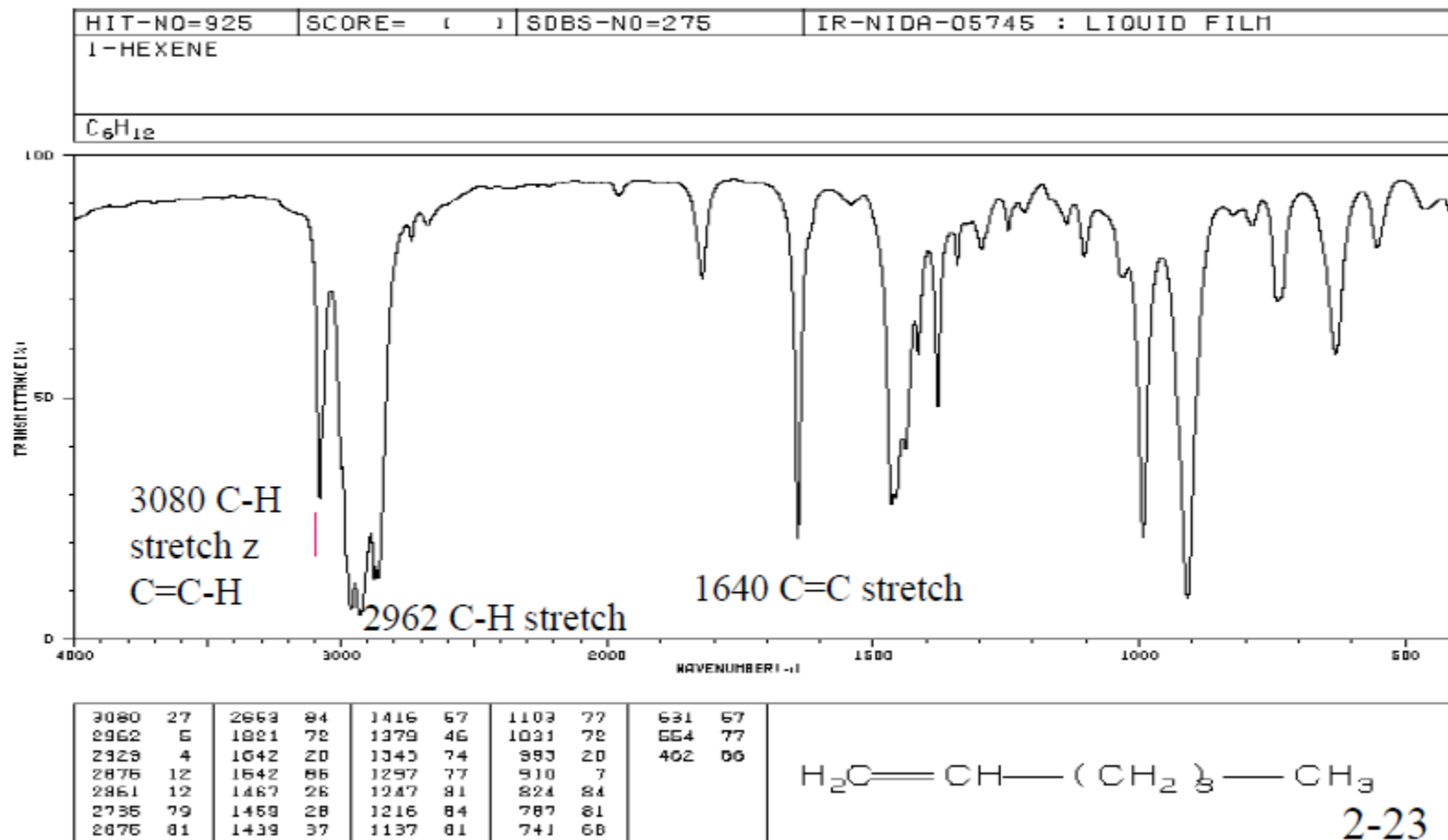




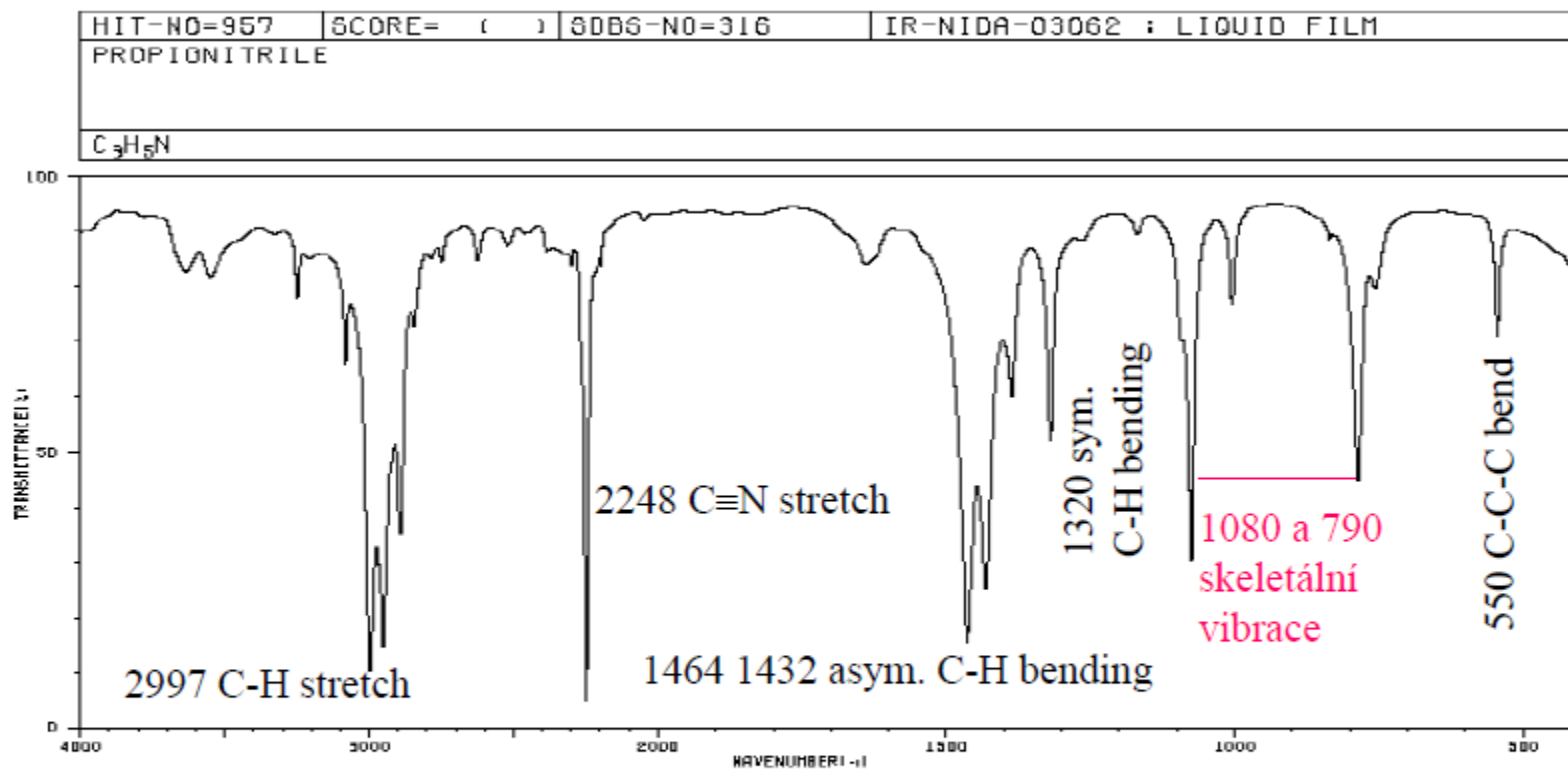


» 2000 – 1500 cm⁻¹

dvojn  vazby

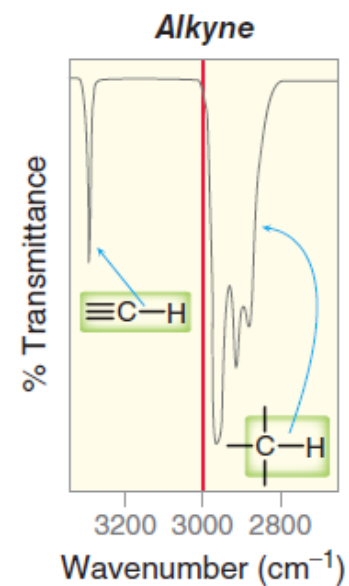
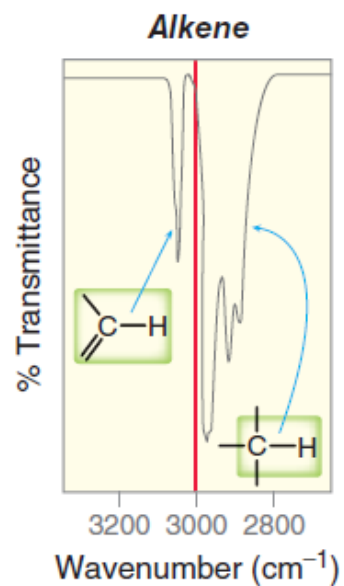
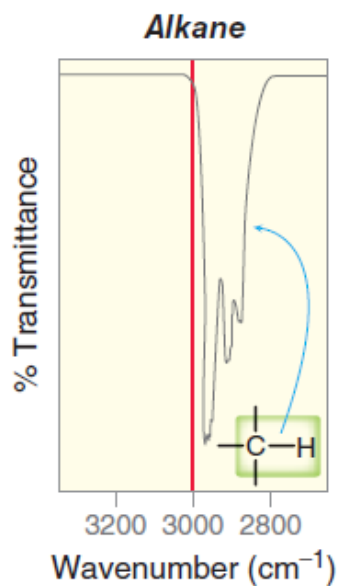
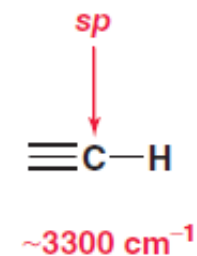
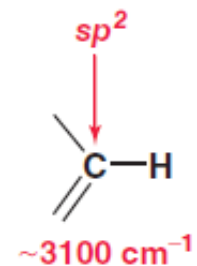
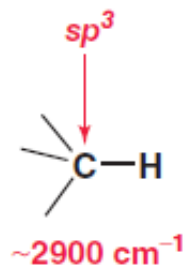
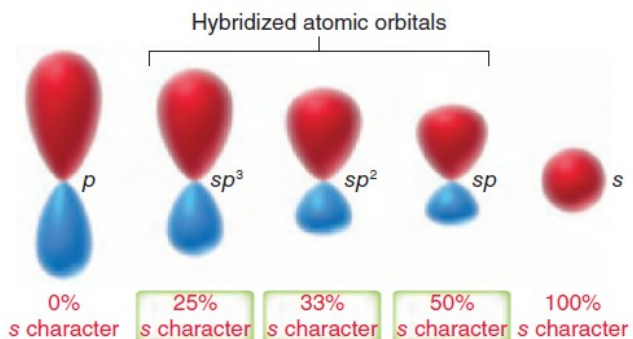


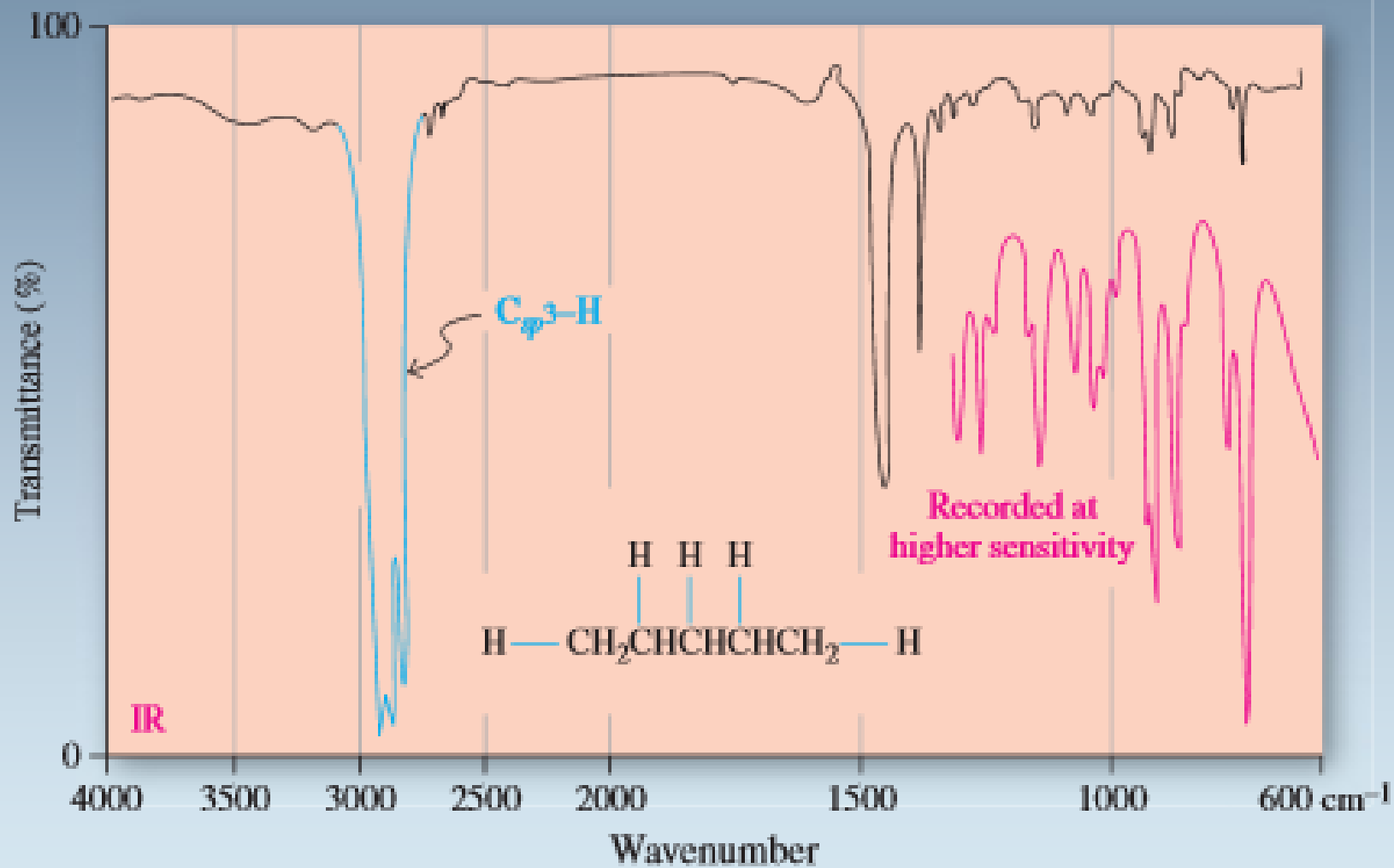
» trojná vazba - $\text{CH}_3\text{CH}_2\text{CN}$

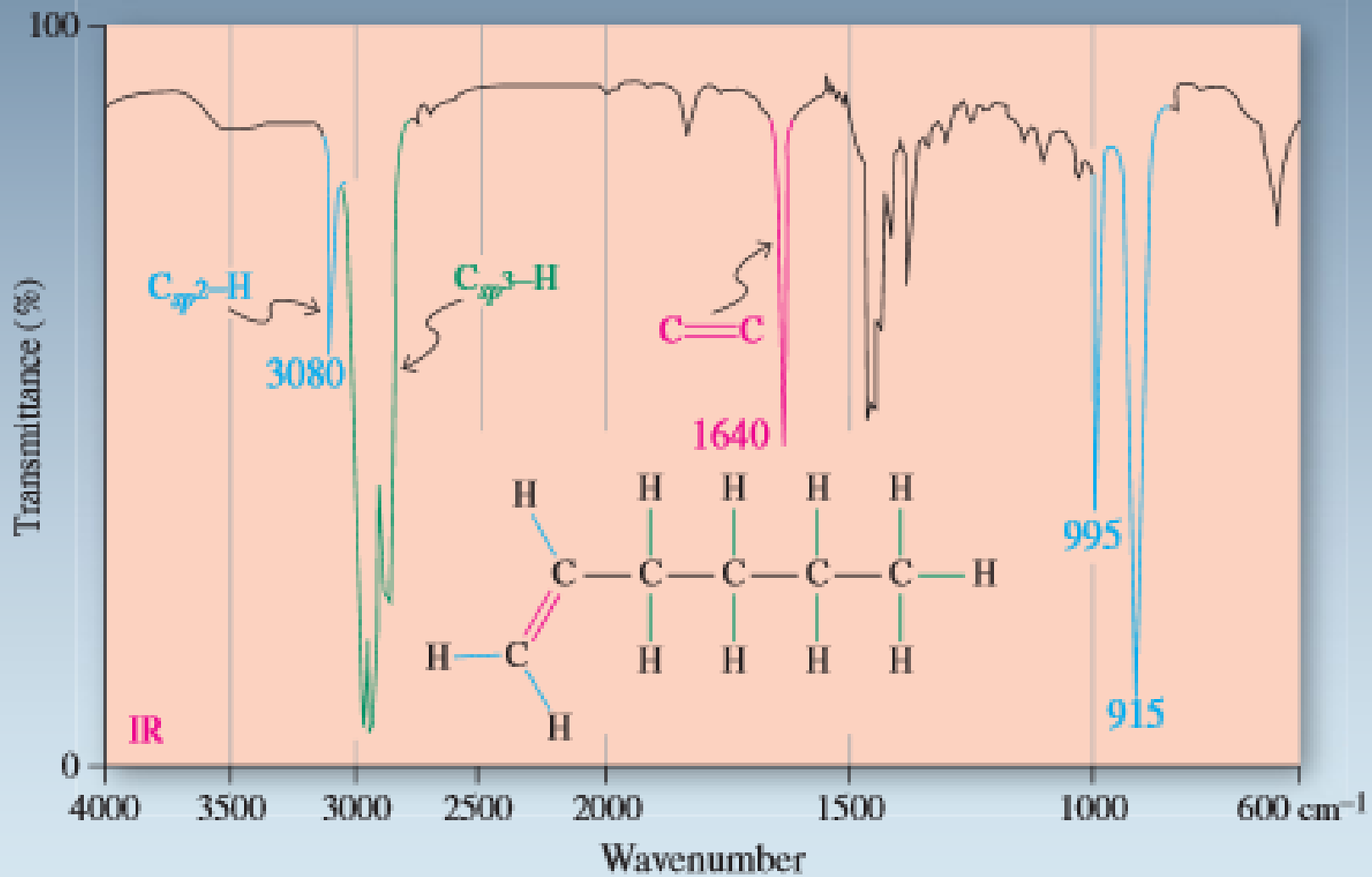


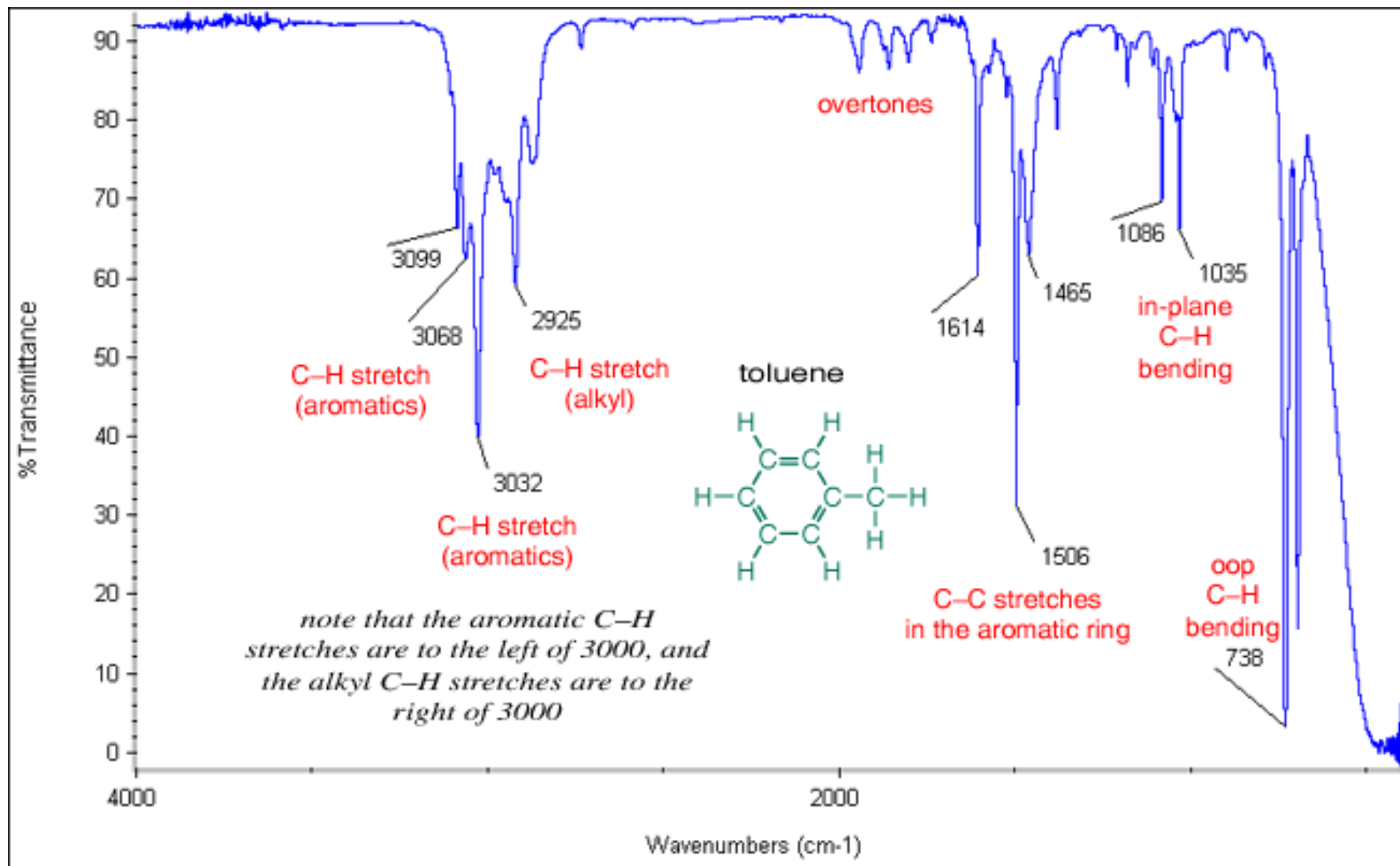
3632	79	2844	70	2299	81	1320	60	646	66
3548	70	2787	81	2248	4	1170	86		
3249	74	2749	81	2198	81	1075	29		
3082	64	2624	81	1639	81	1006	74		
2997	10	2521	84	1484	14	836	84		
2952	13	2461	86	1432	23	786	49		
2891	34	2460	86	1387	68	767	77		

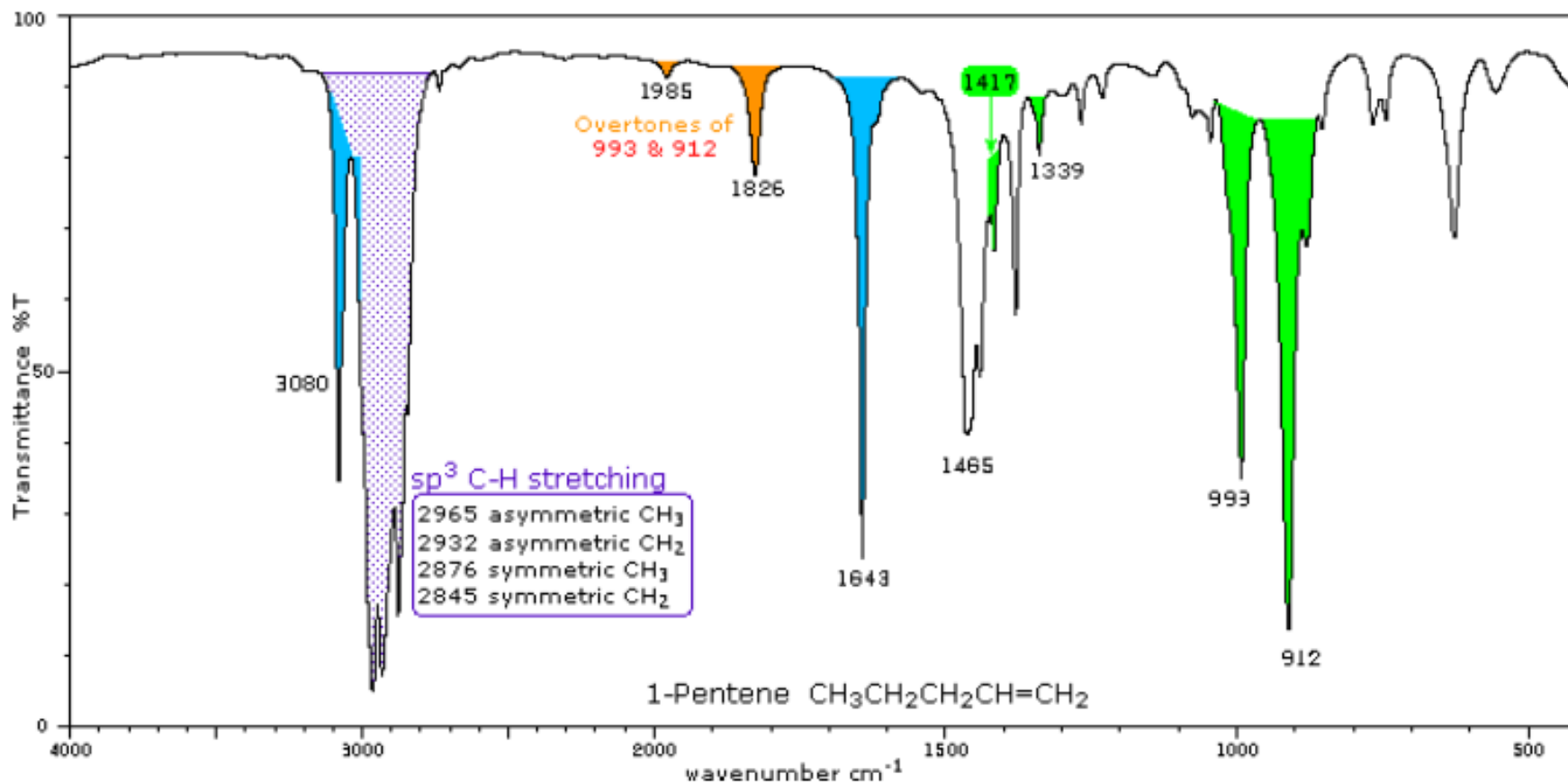
Efekt hybridizace



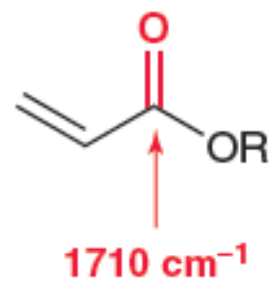
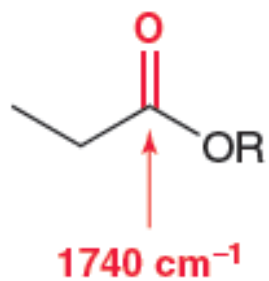
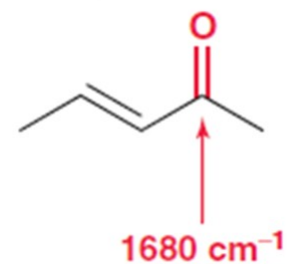
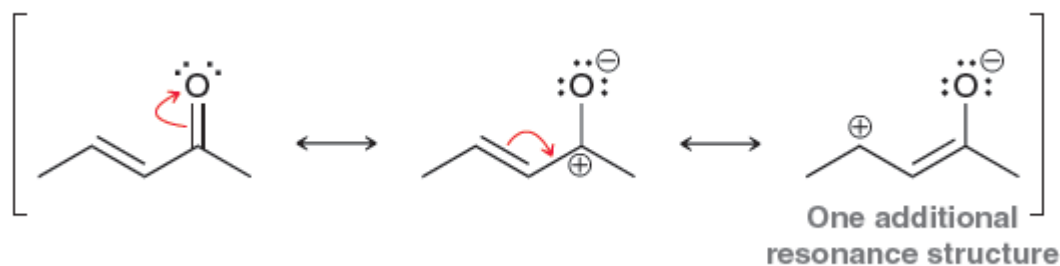
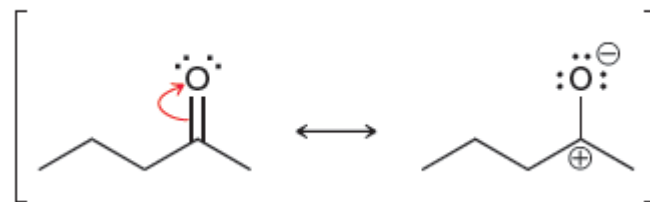
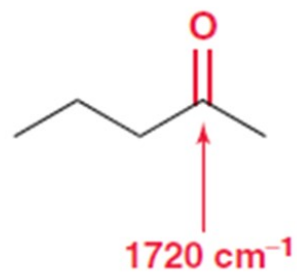




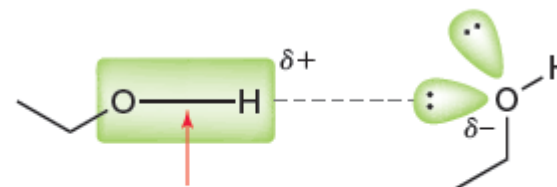




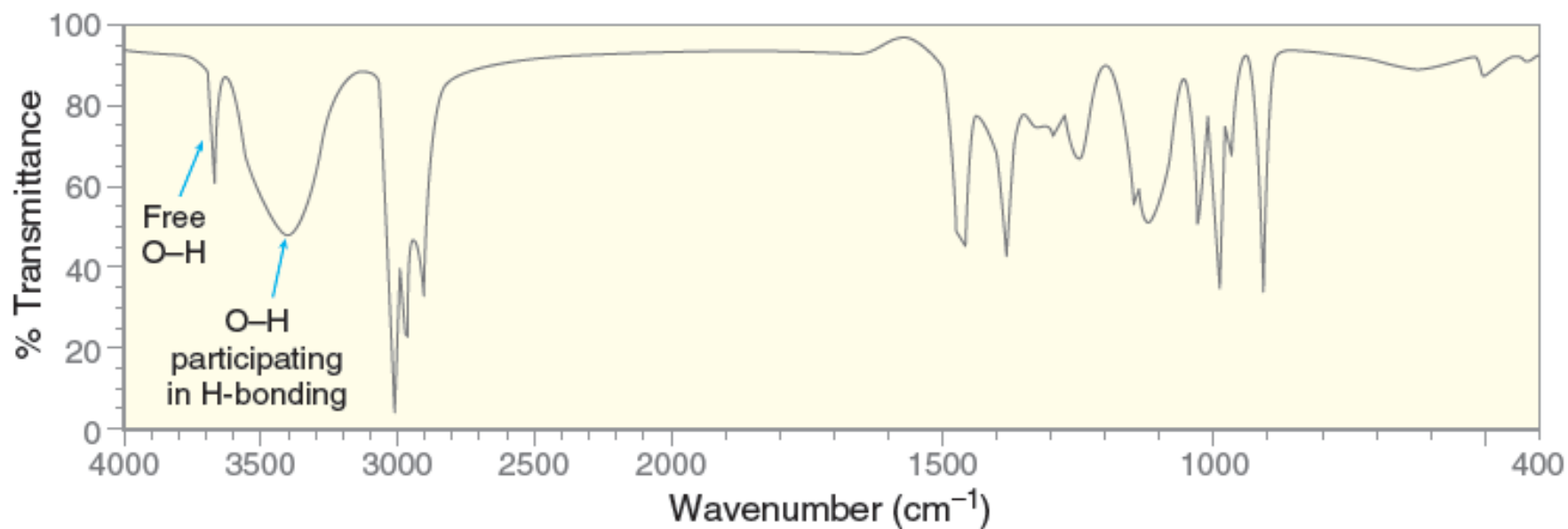
Efekt rezonance

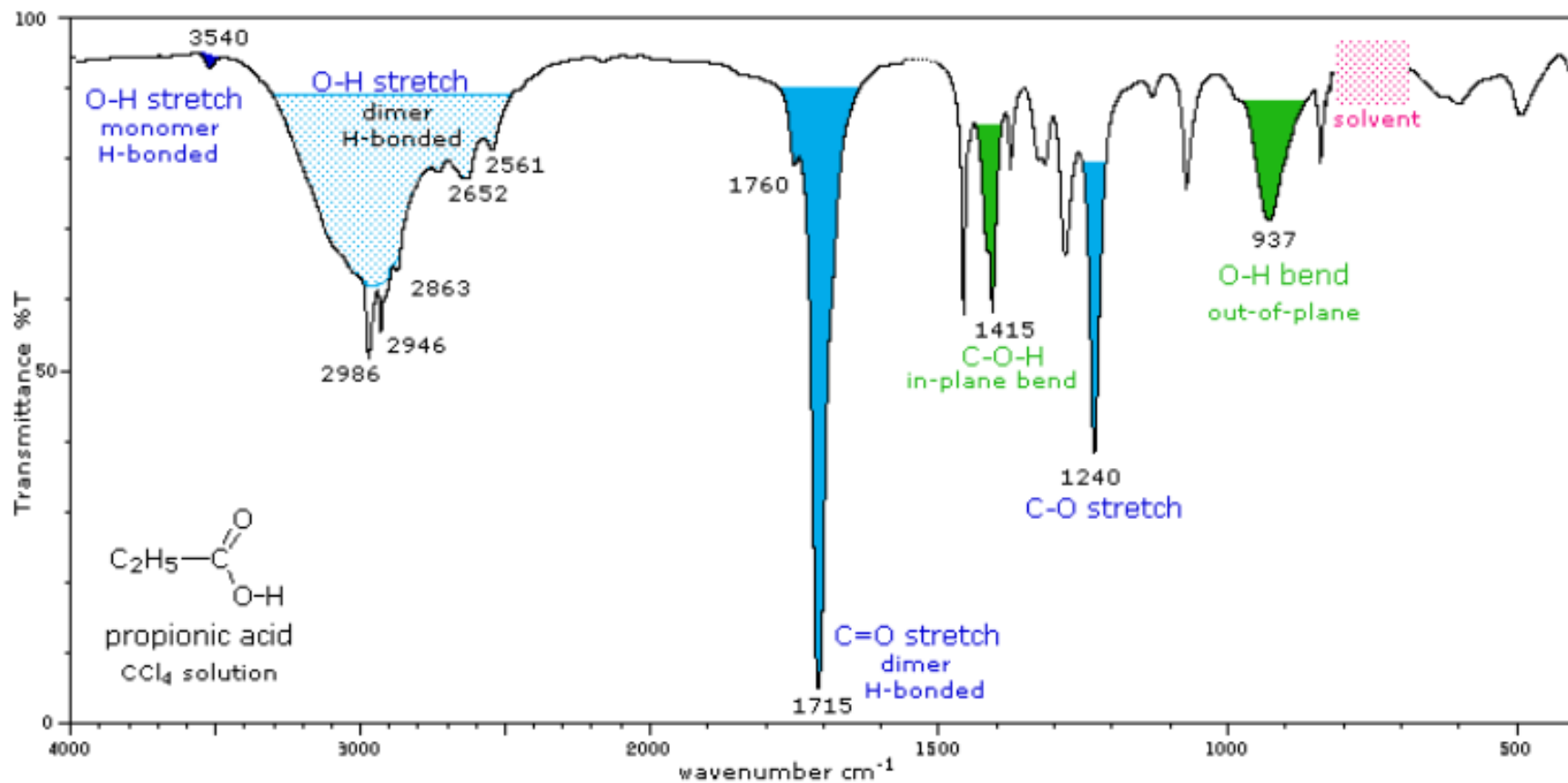
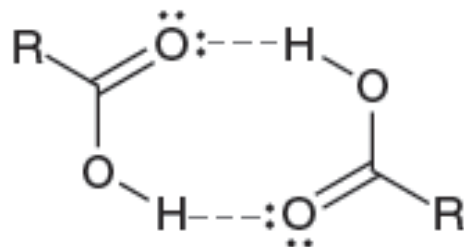


Efekt vodíkových vazeb



This bond is weakened as a result of H bonding

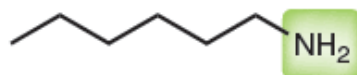




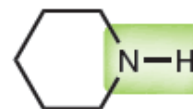
http://www.vscht.cz/anl/lach1/7_IC.pdf



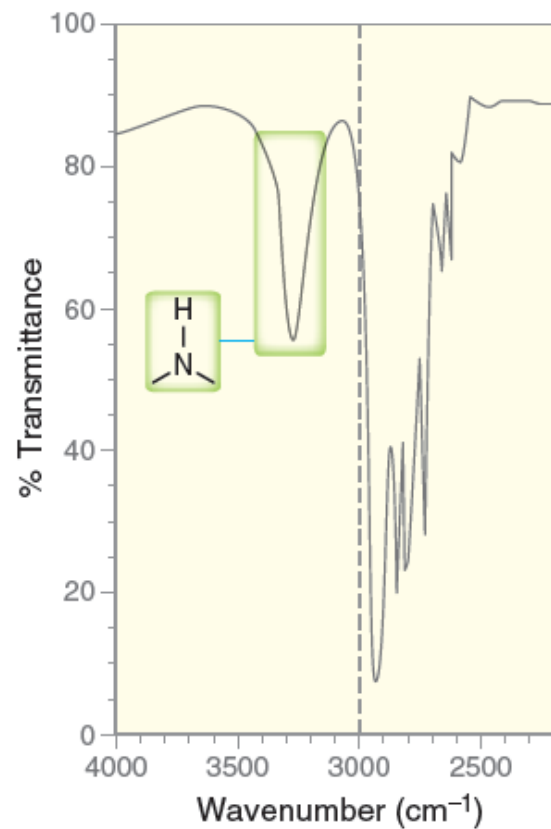
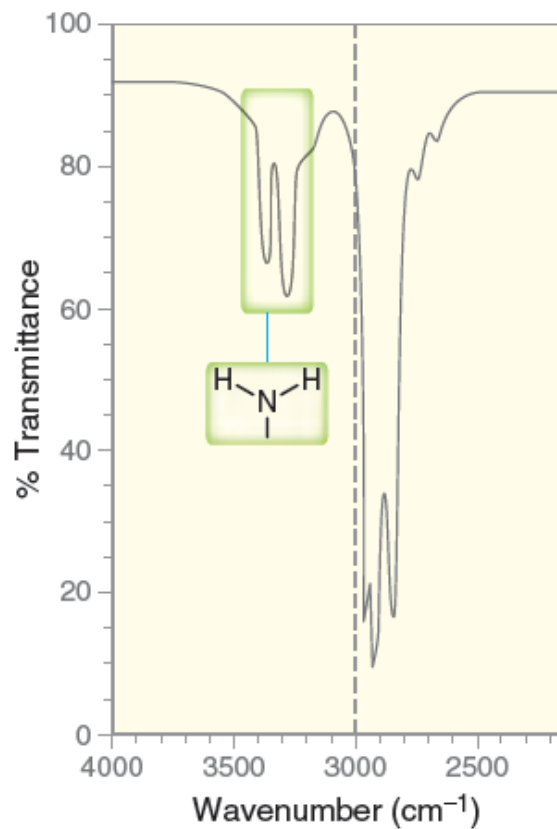
Aminy



Hexylamine
(a primary amine)



Piperidine
(a secondary amine)

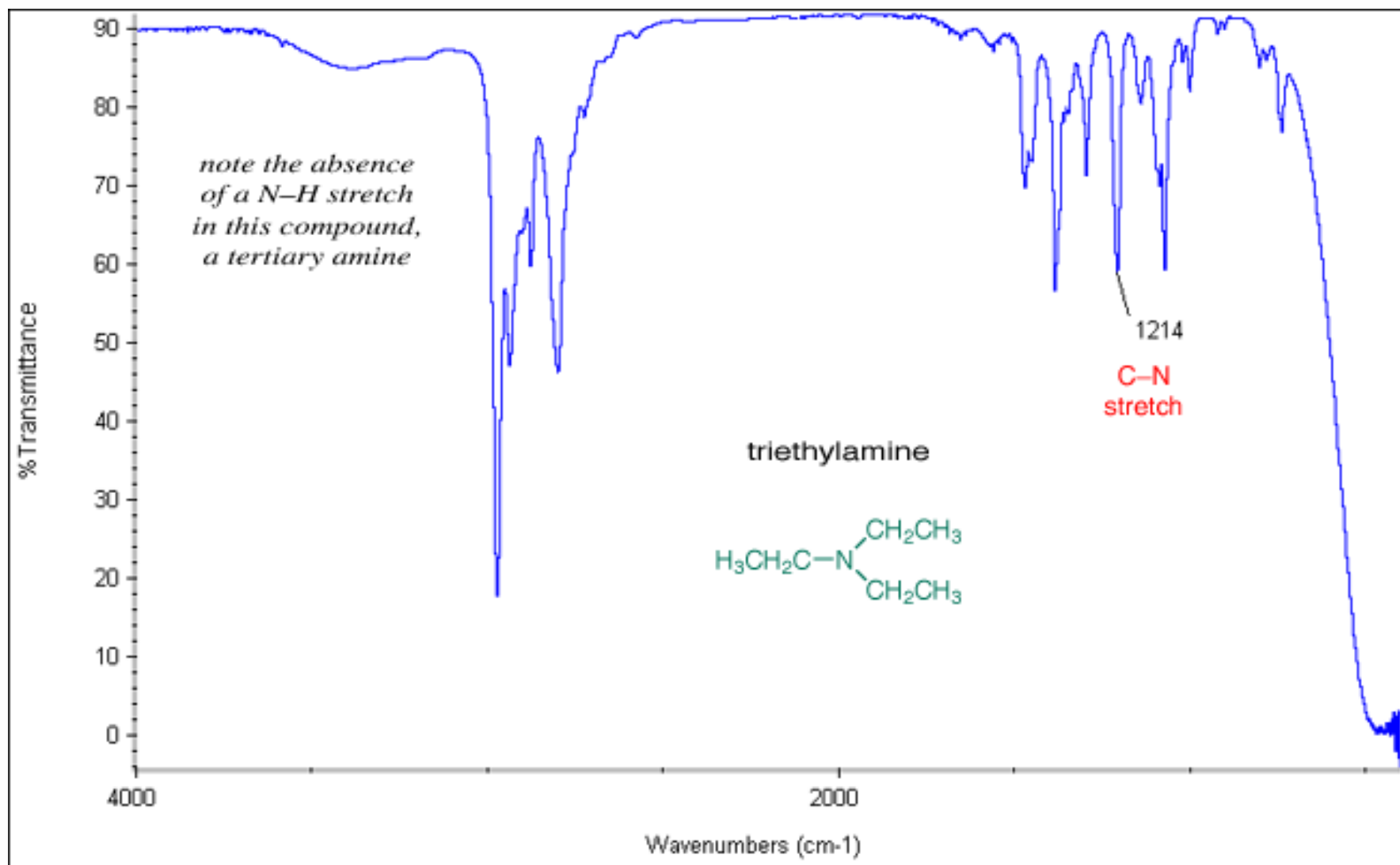


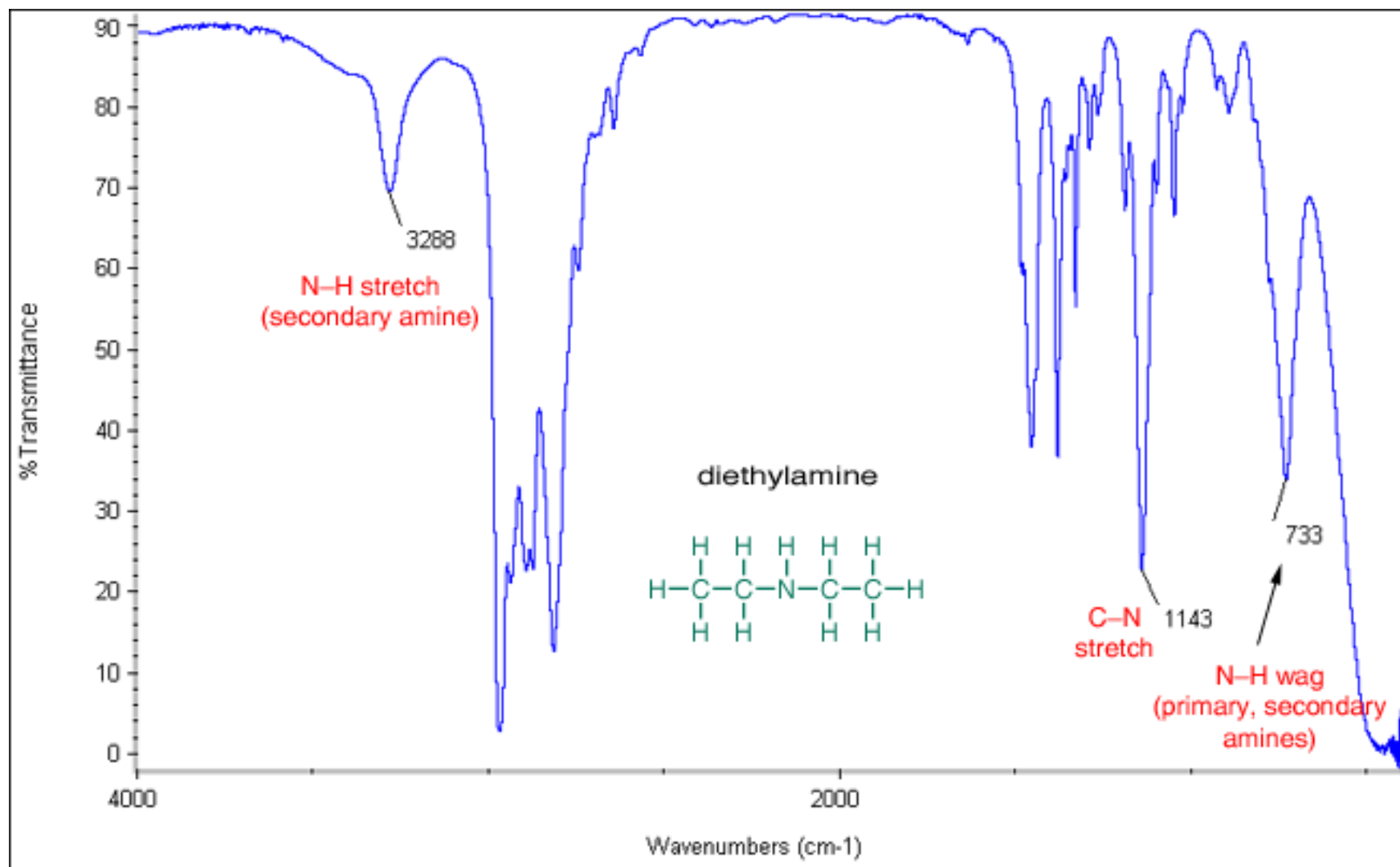
Symmetric stretching

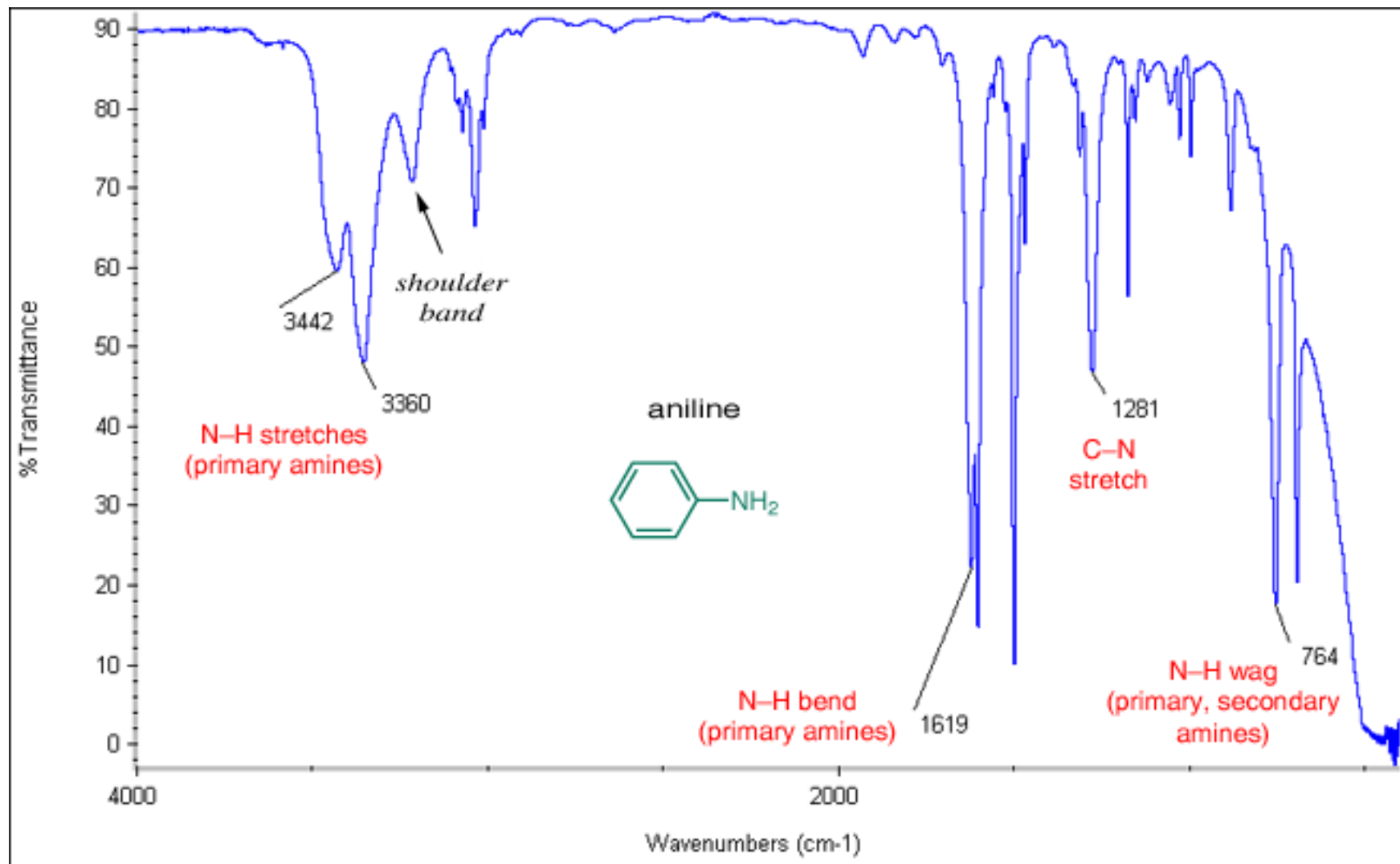


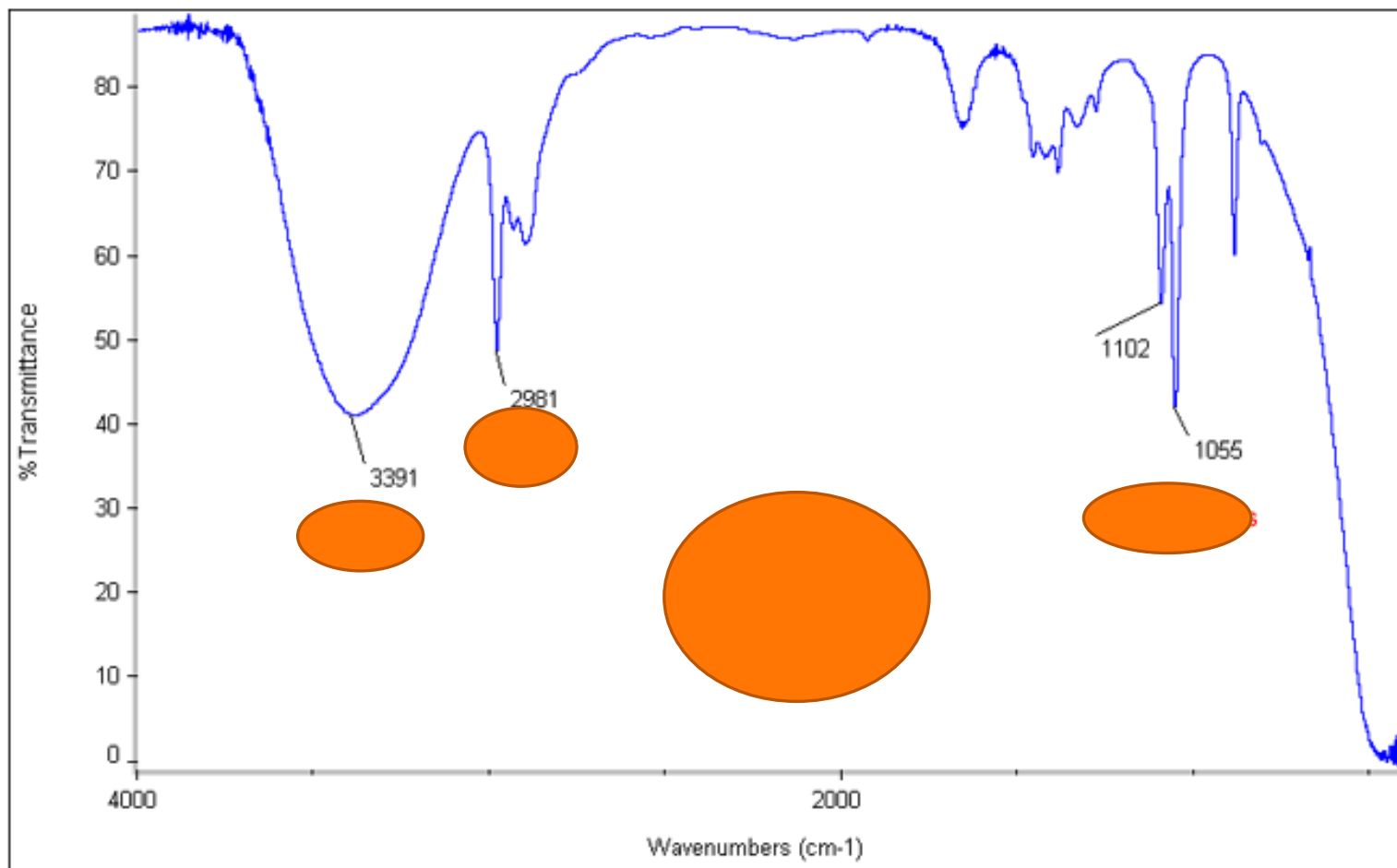
Asymmetric stretching

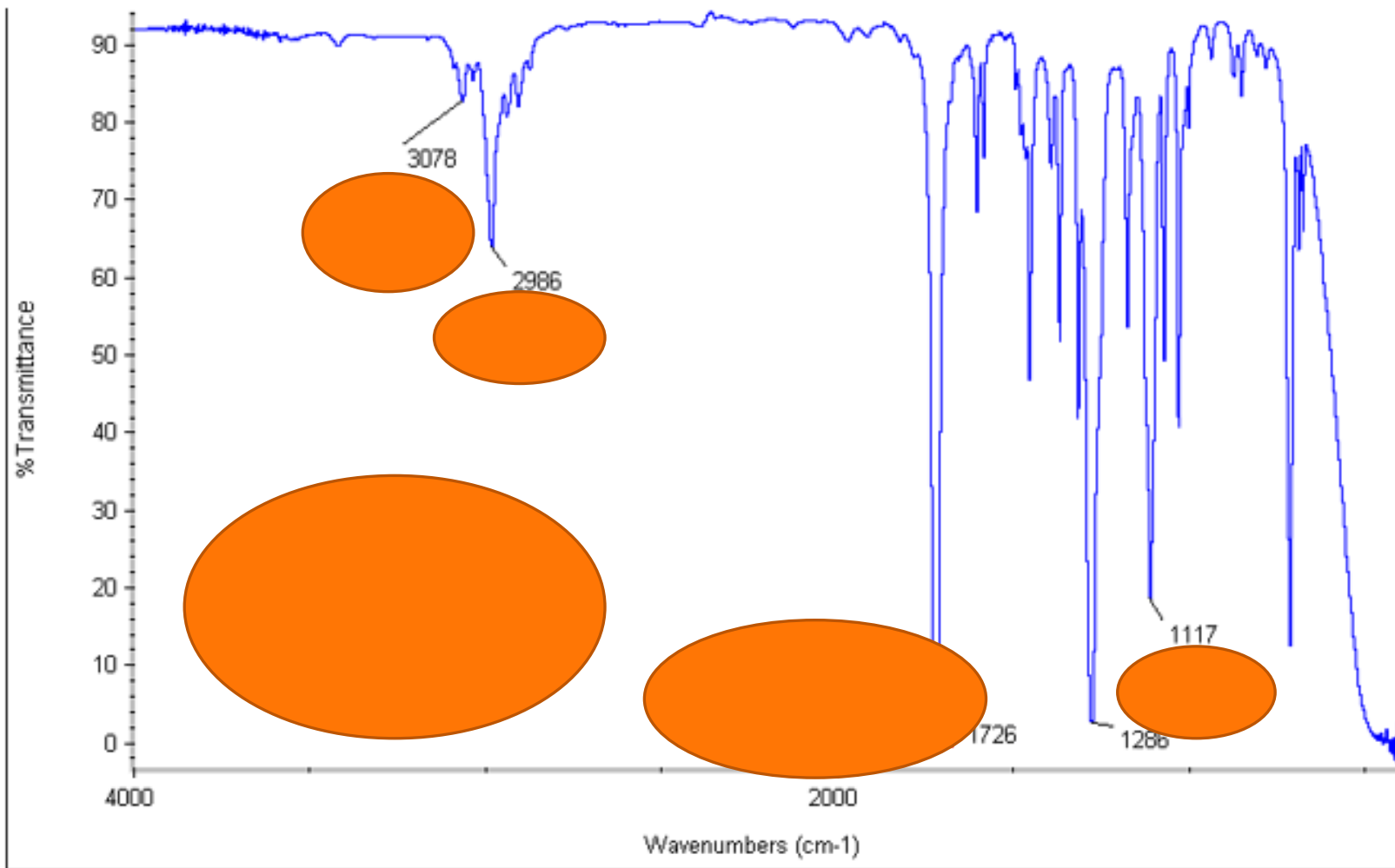


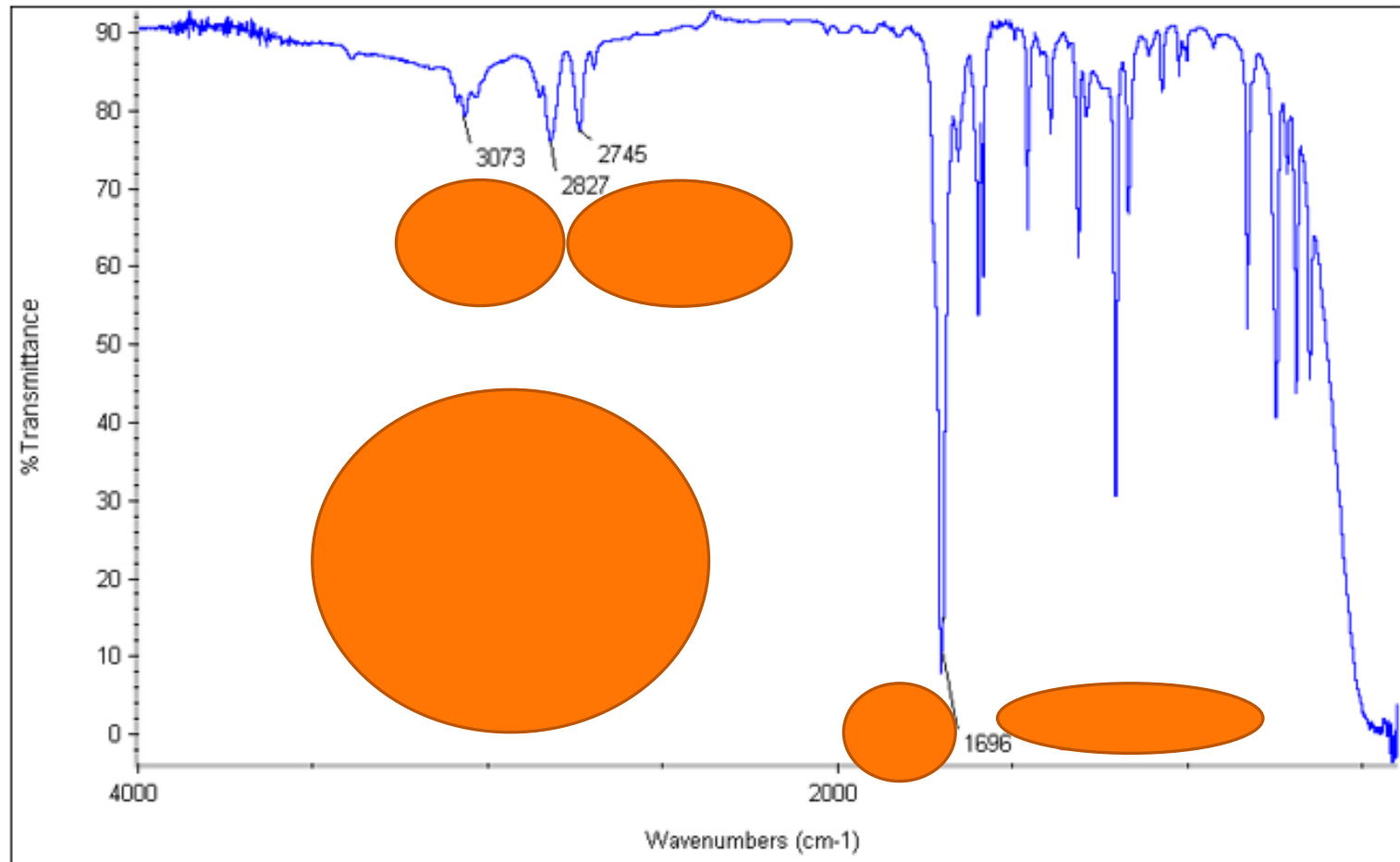


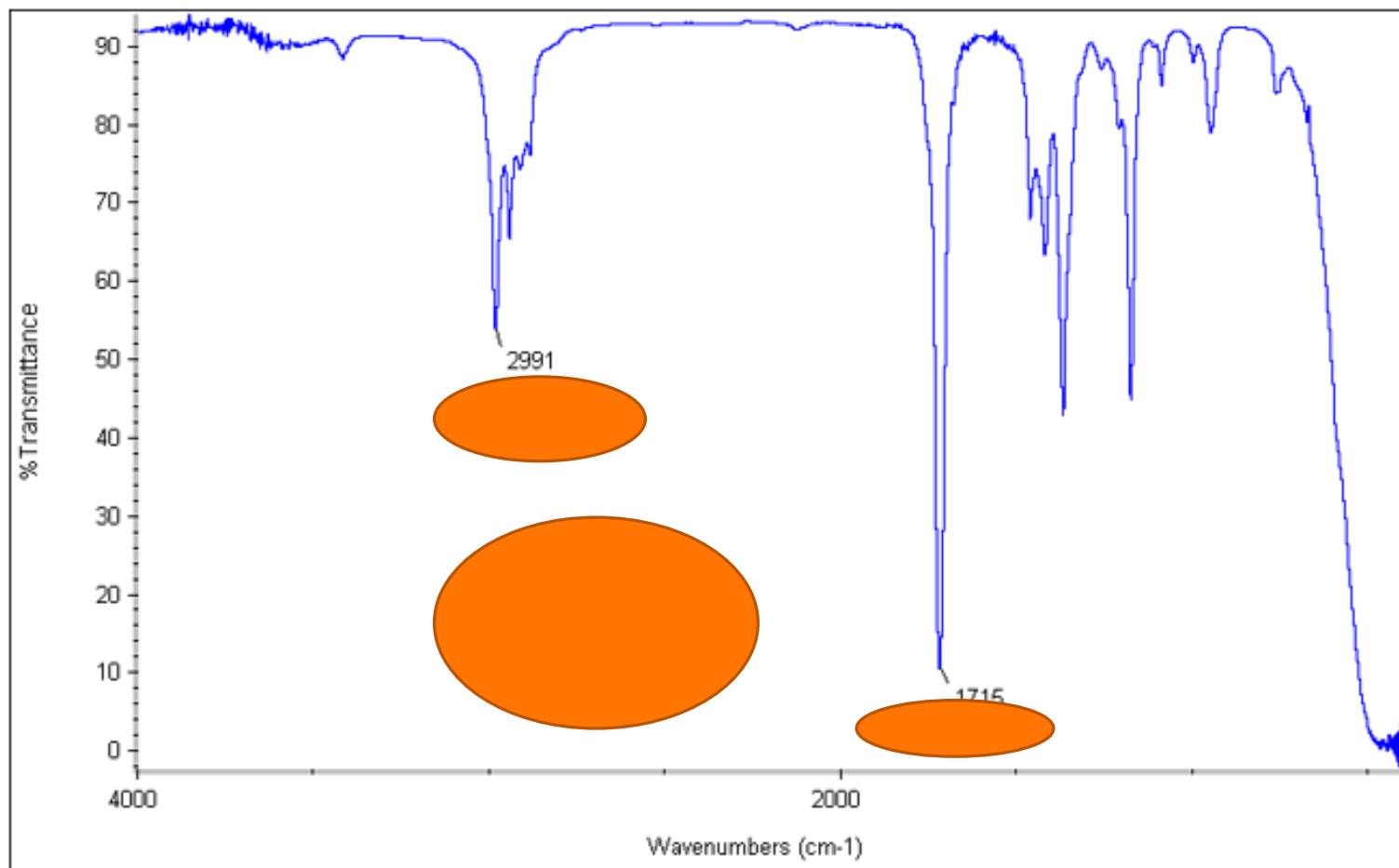


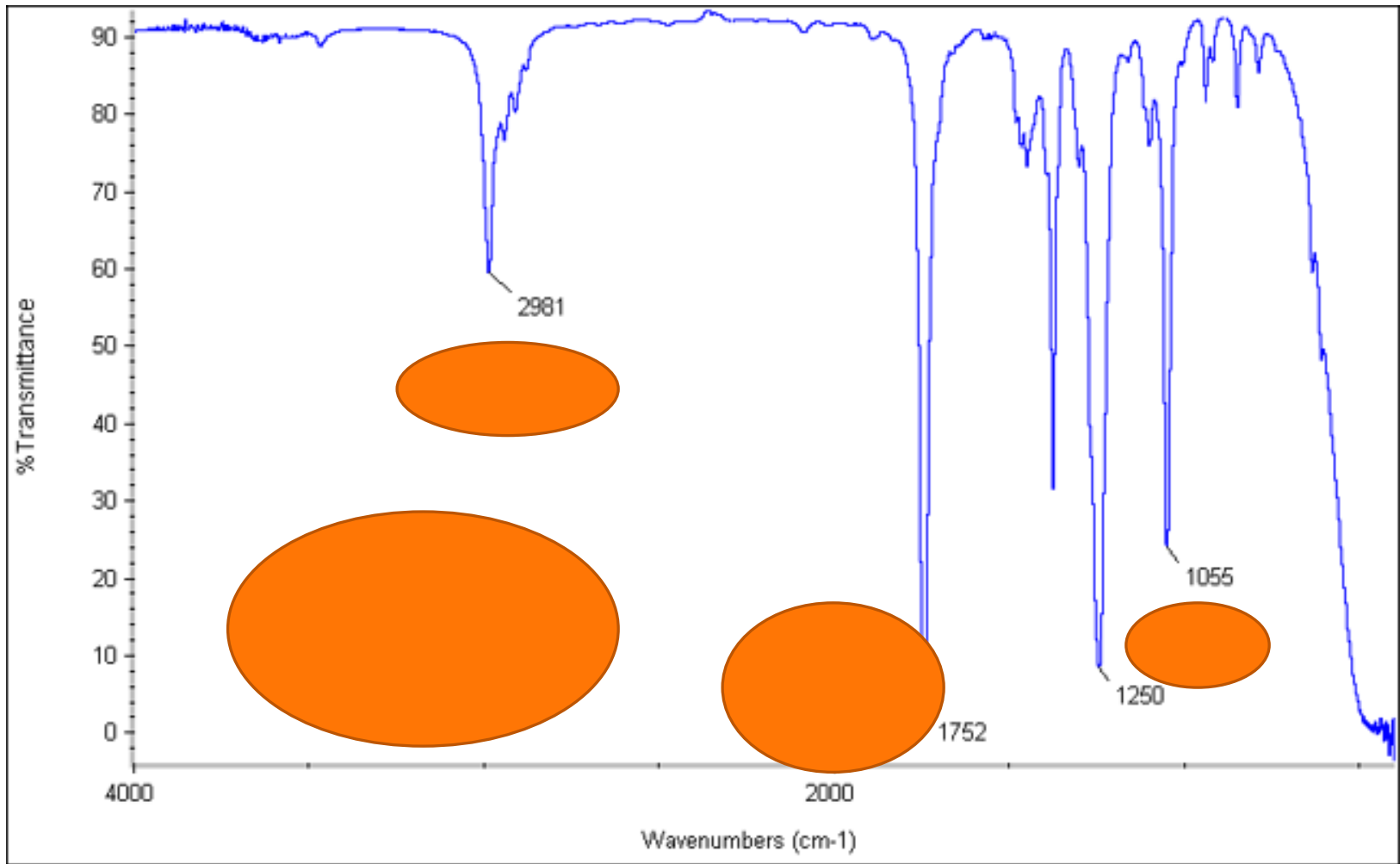


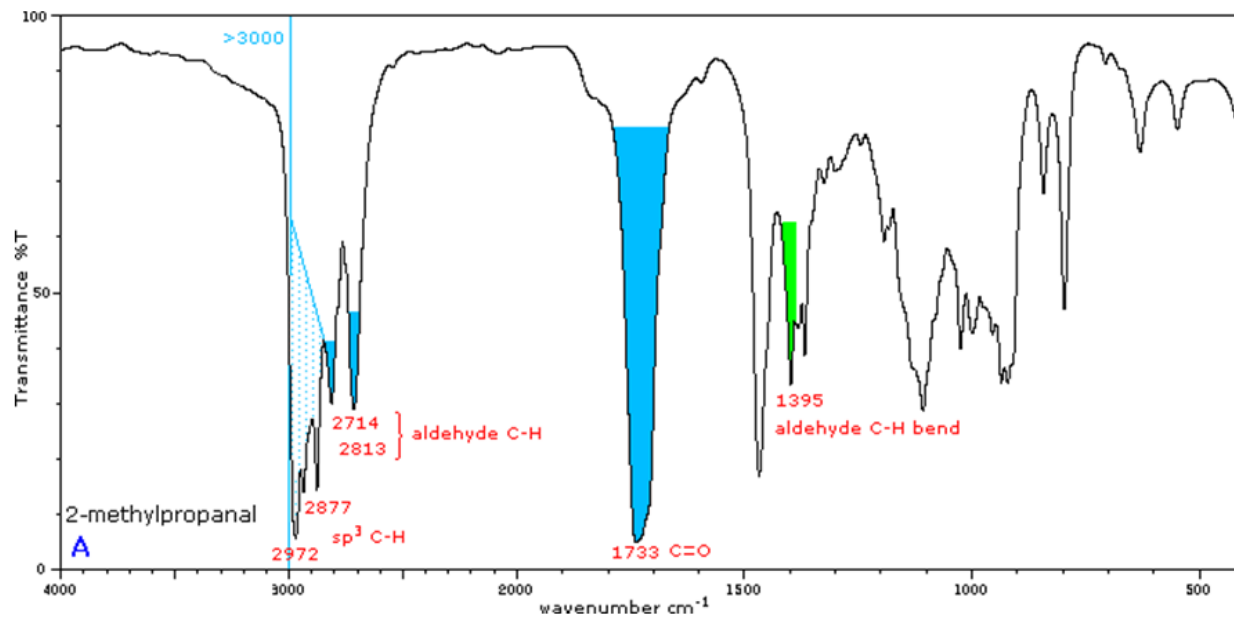
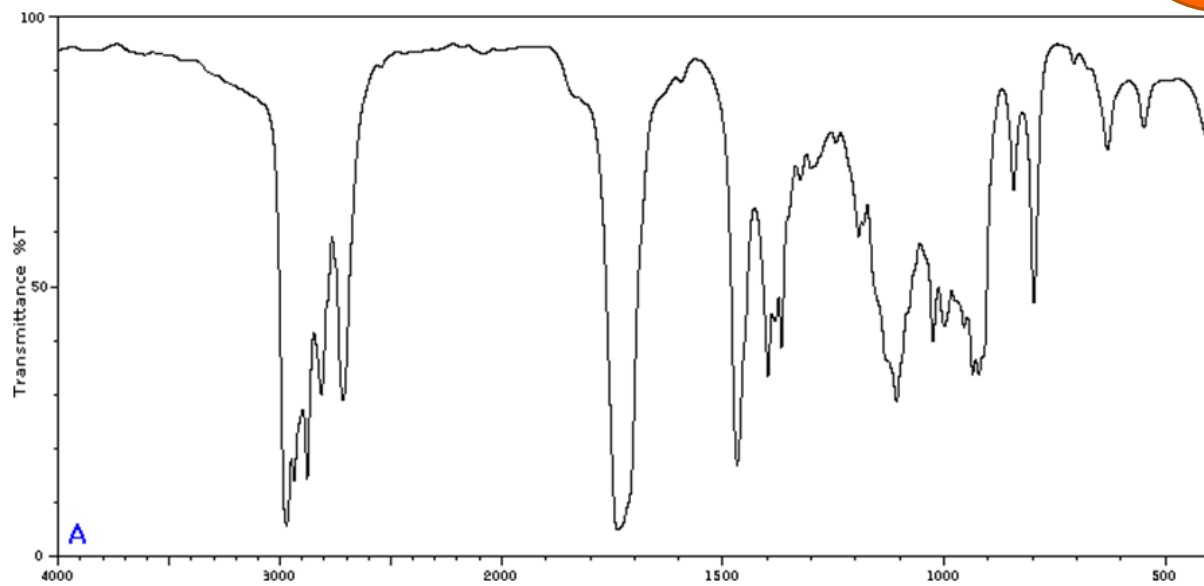
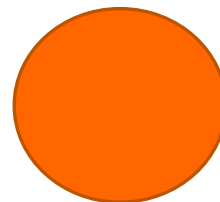
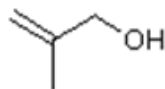
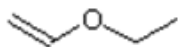
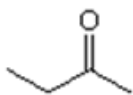
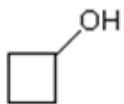


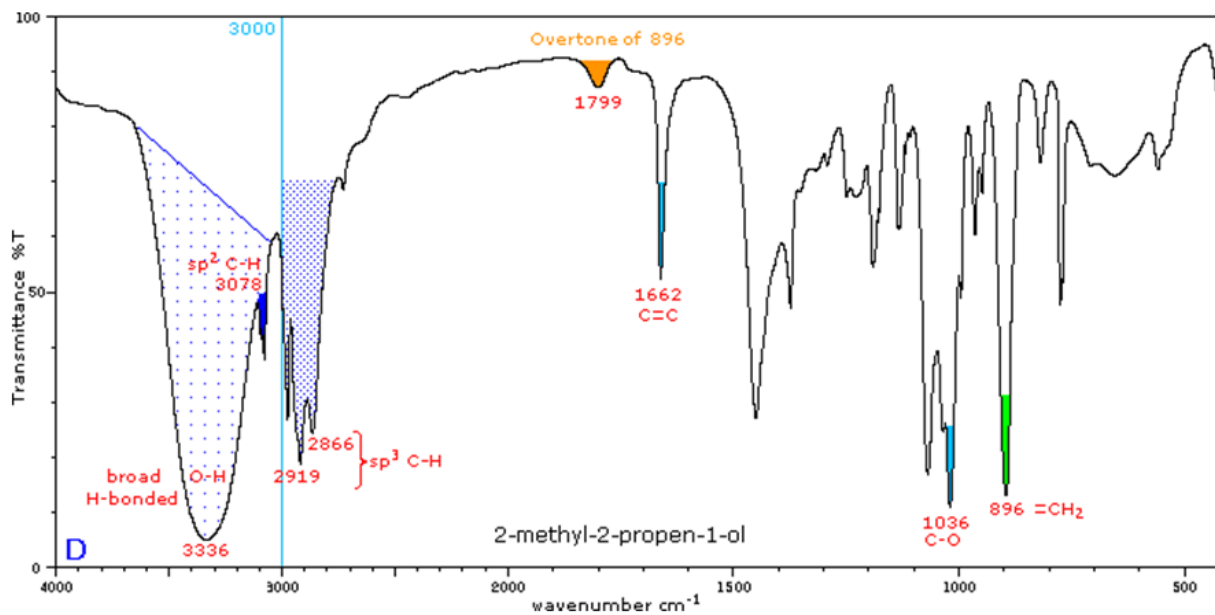
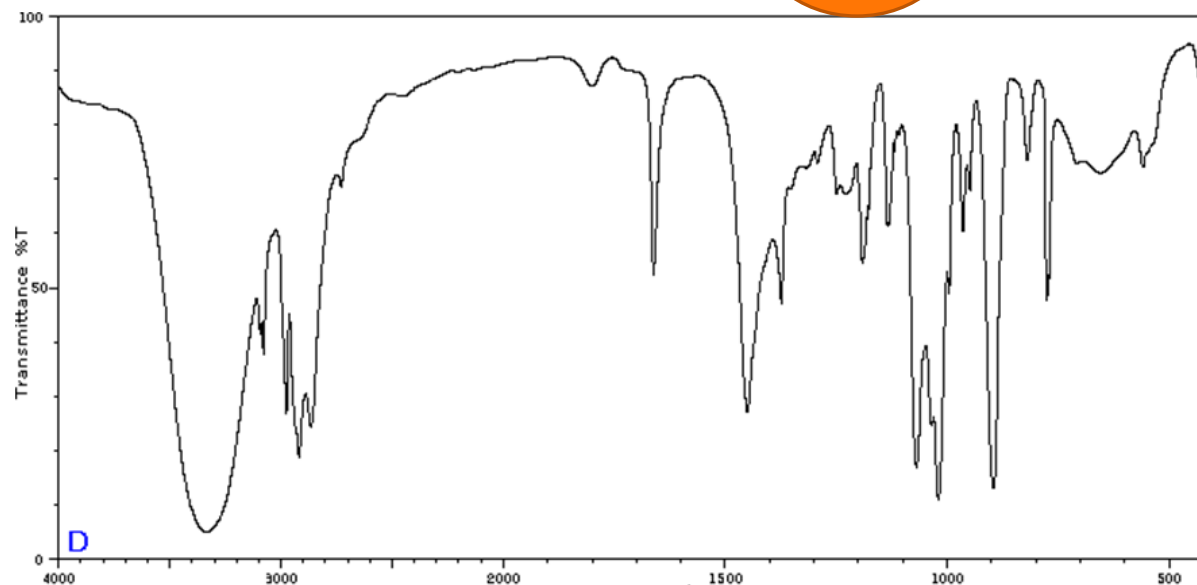
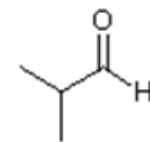
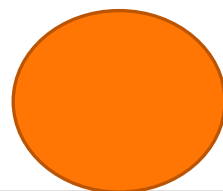
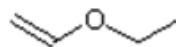
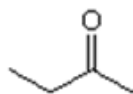
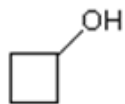


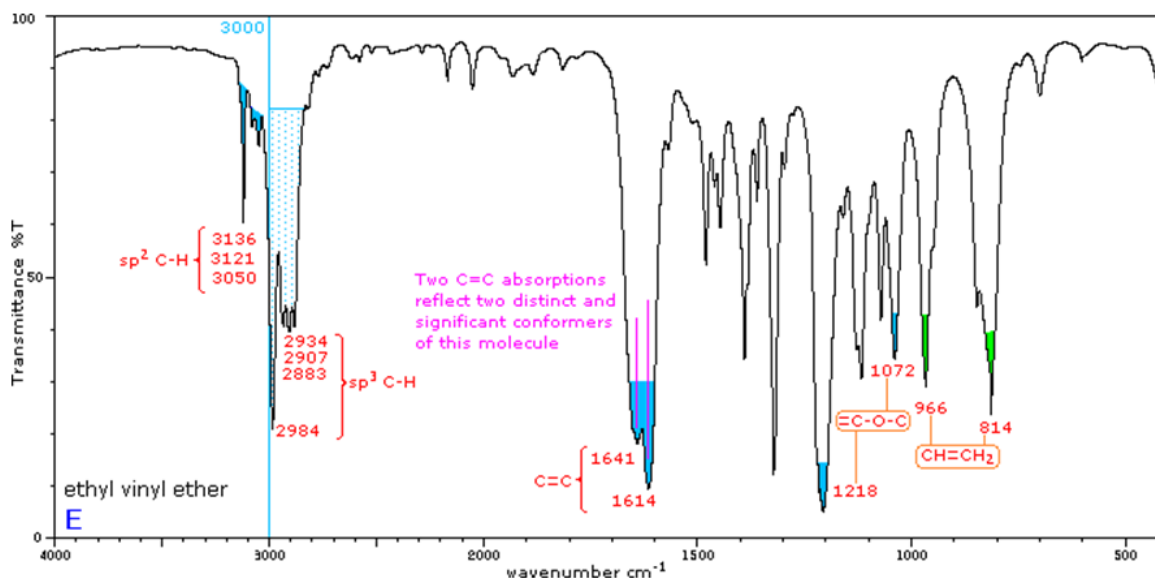
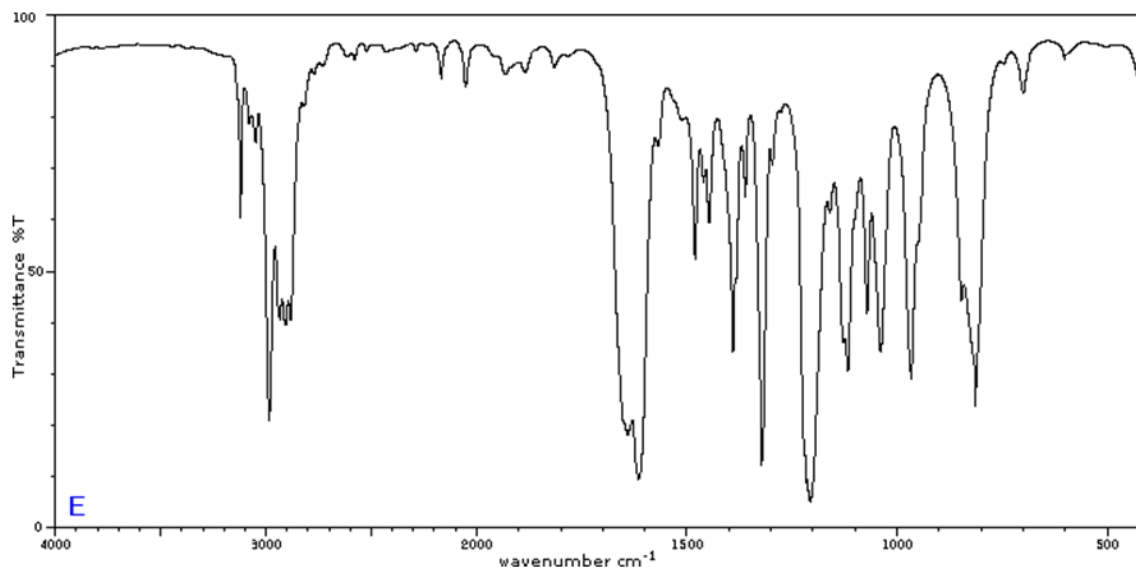
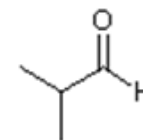
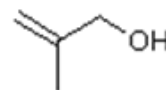
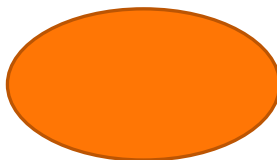
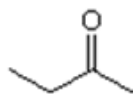
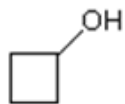


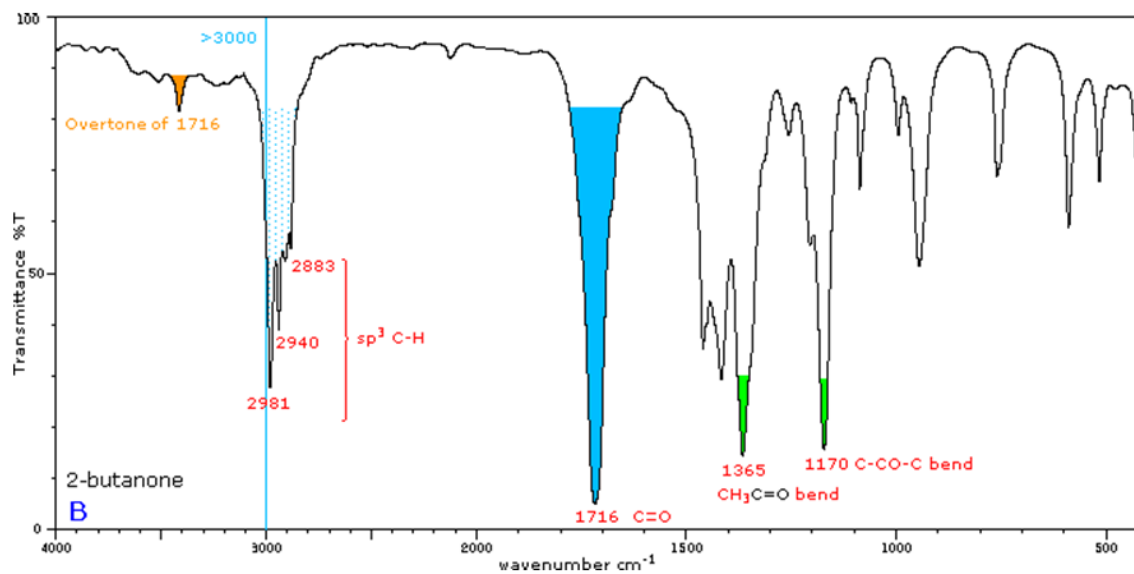
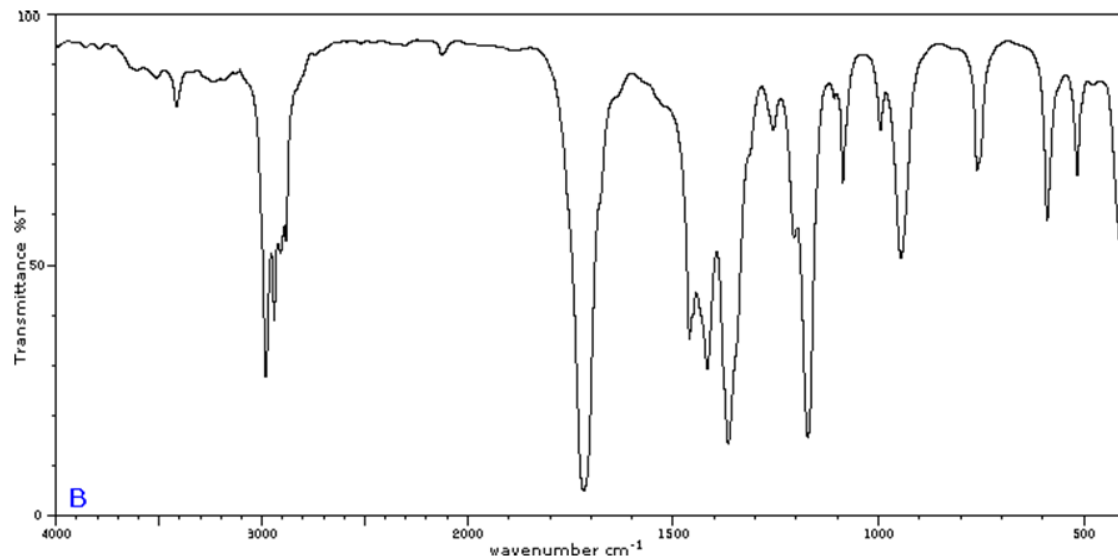
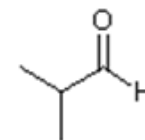
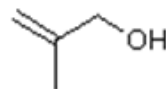
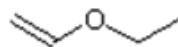
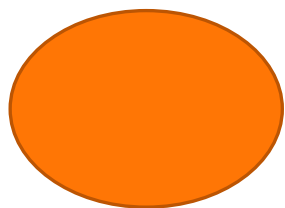
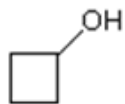


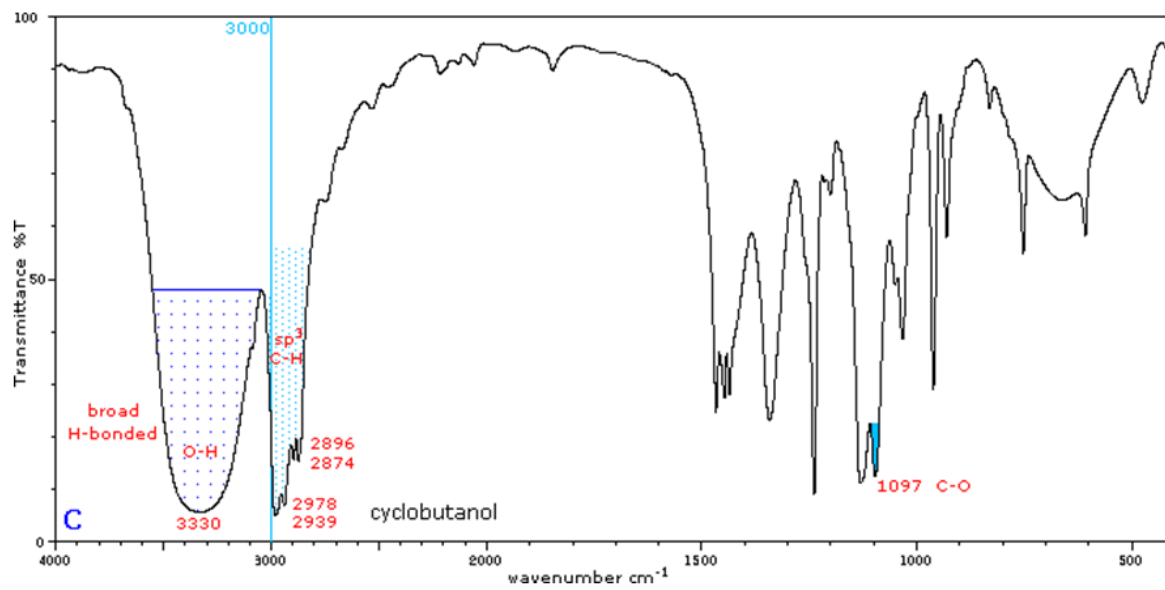
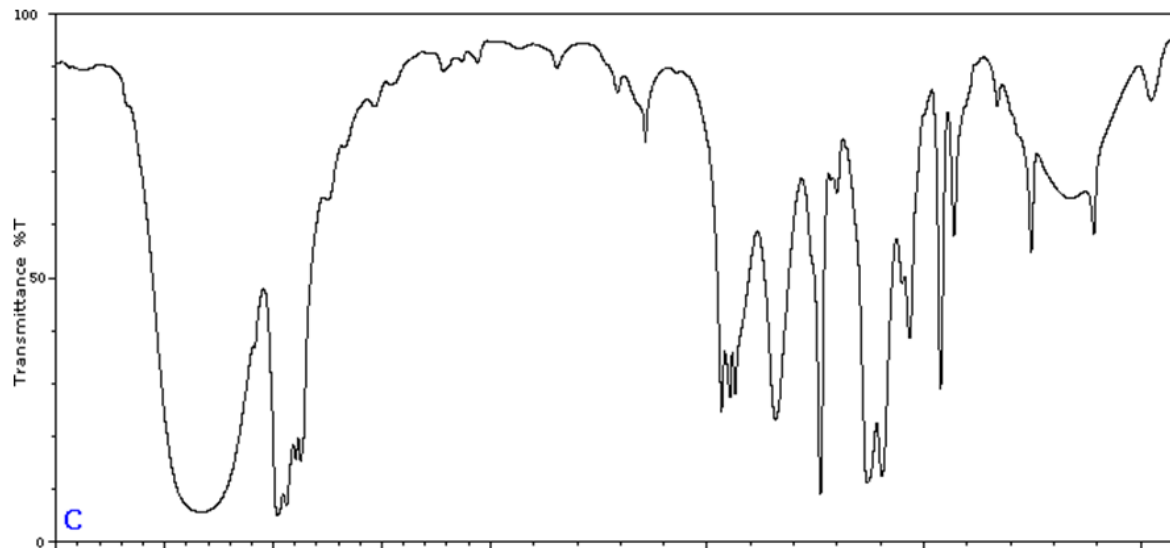
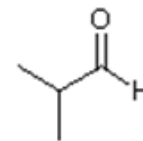
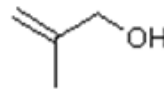
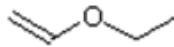
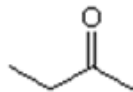
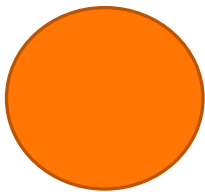












» HMOTNOSTNÍ SPEKTROMETRIE



primárně vzniká molekulární ion M^+
 fragmentací vznikají ionty dceřinné

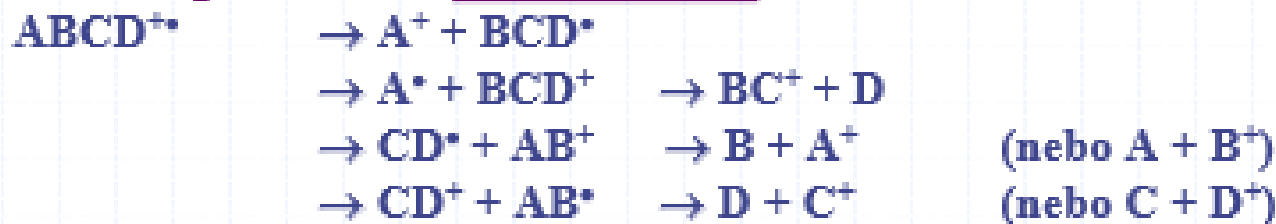
Ionization of a Molecule on Electron Impact



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

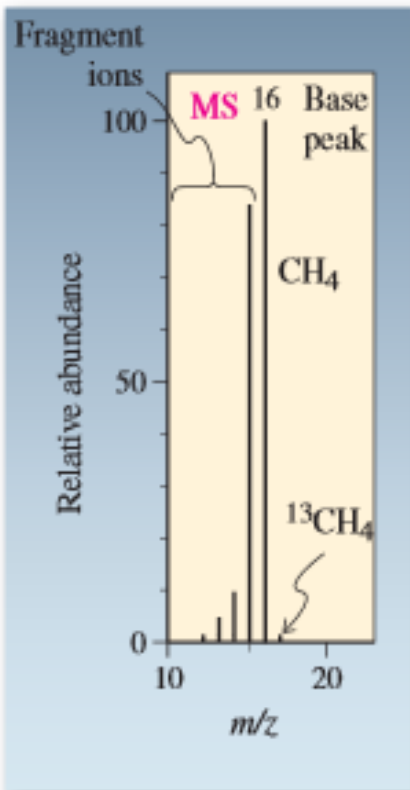


- Fragmentace \Rightarrow dceřinné ionty:



- Kolize + následná fragmentace:

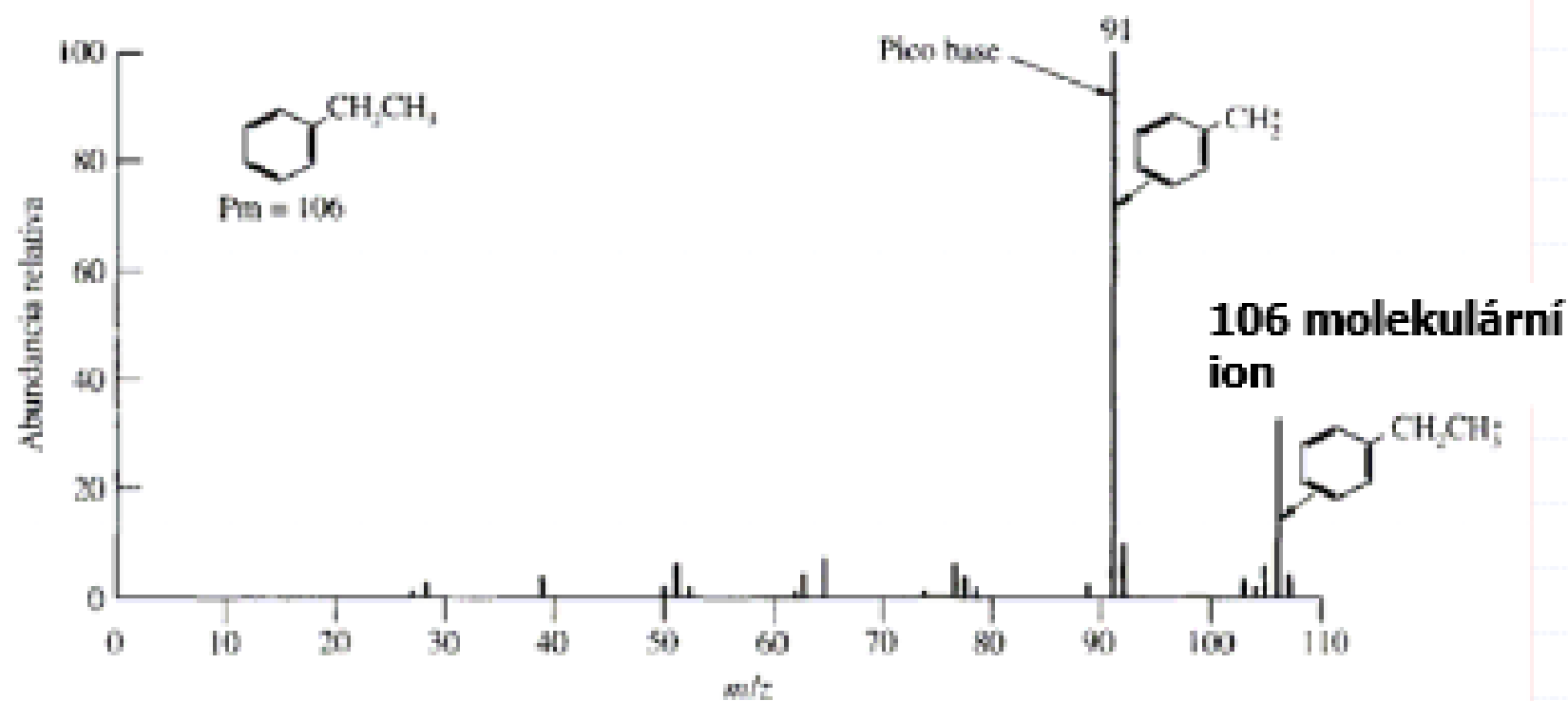




Tabulated Spectrum

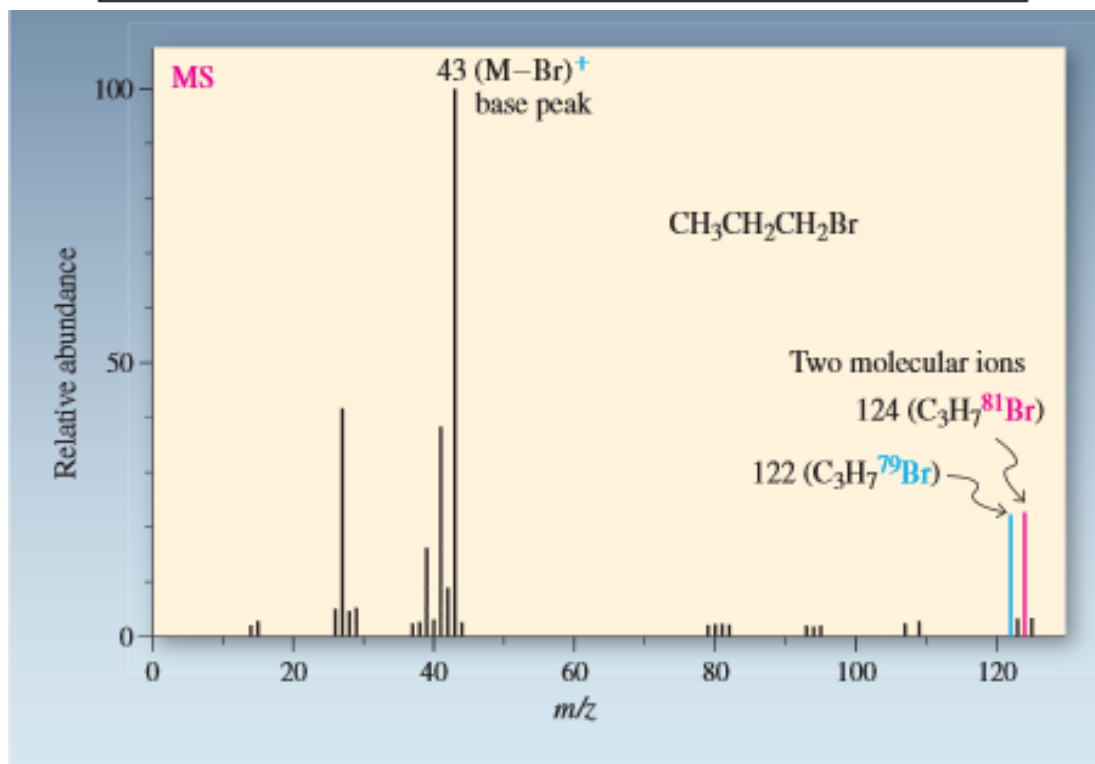
<i>m/z</i>	Relative Abundance (%)	Molecular or Fragment ion
17	1.1	(M + 1) ⁺
16	100.0 (base peak)	M ⁺ (parent ion)
15	85.0	(M - 1) ⁺
14	9.2	(M - 2) ⁺
13	3.9	(M - 3) ⁺
12	1.0	(M - 4) ⁺

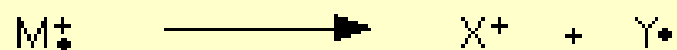




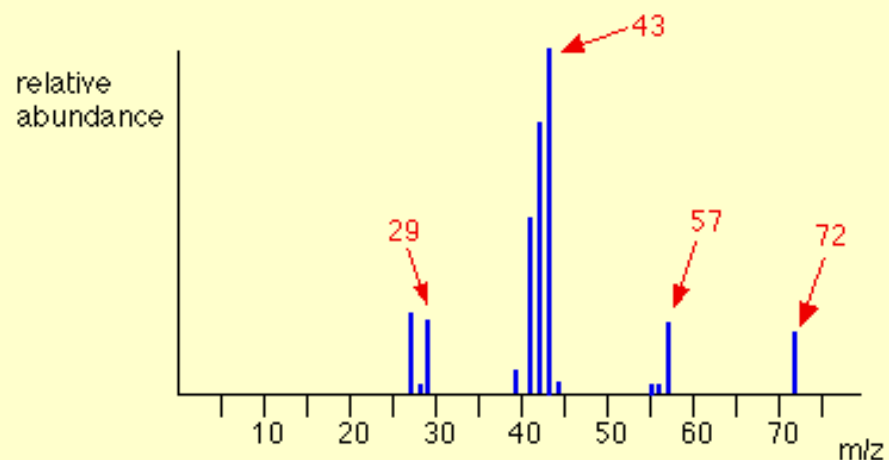
Přírodní zastoupení izotopů běžných organických prvků

Prvek	"M"		"M+1"		"M+2"		Typ prvku
	m/z	%	m/z	%	m/z	%	
H	1	100	2	0.015			"M"
C	12	100	13	1.1			"M+1"
N	14	100	15	0.37			"M+1"
O	16	100	17	0.04	18	0.2	"M+2"
F	19	100					"M"
Si	28	100	29	5.1	30	3.4	"M+2"
P	31	100					"M"
S	32	100	33	0.79	34	4.4	"M+2"
Cl	35	100			37	32	"M+2"
Br	79	100			81	97.3	"M+2"
I	127	100					"M"

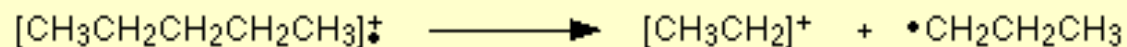
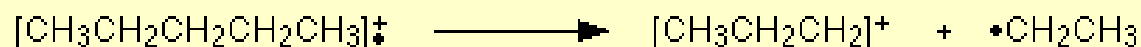
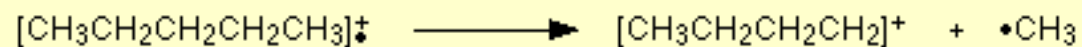
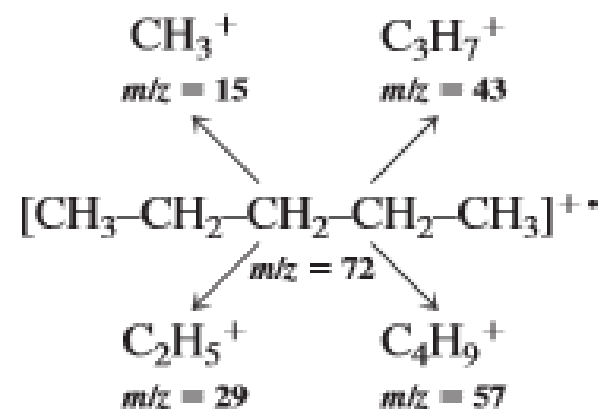




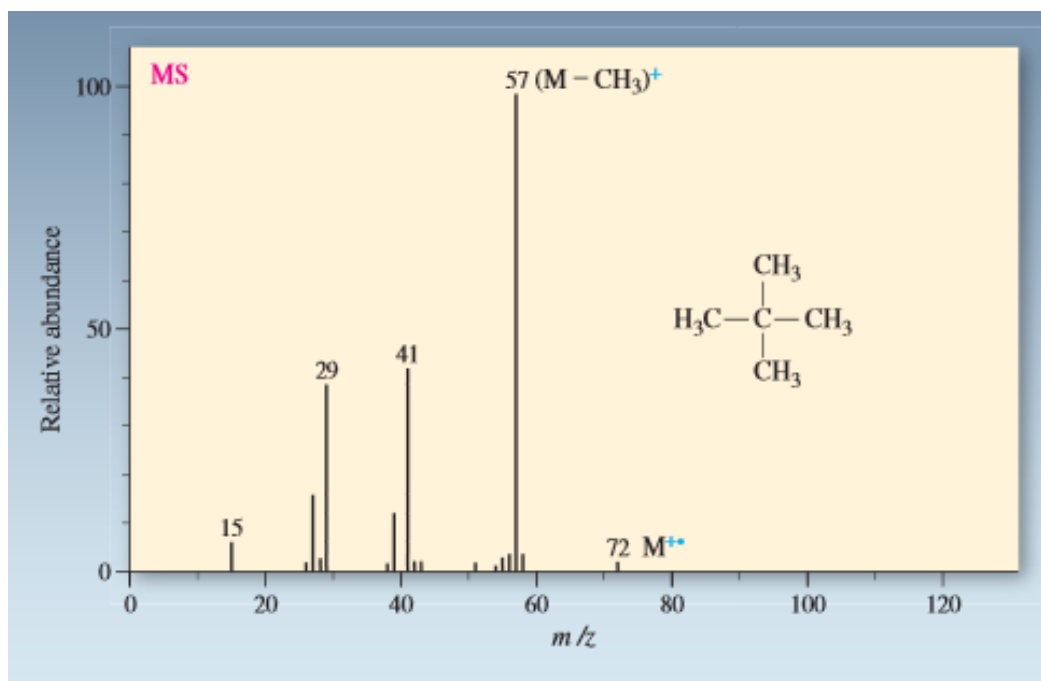
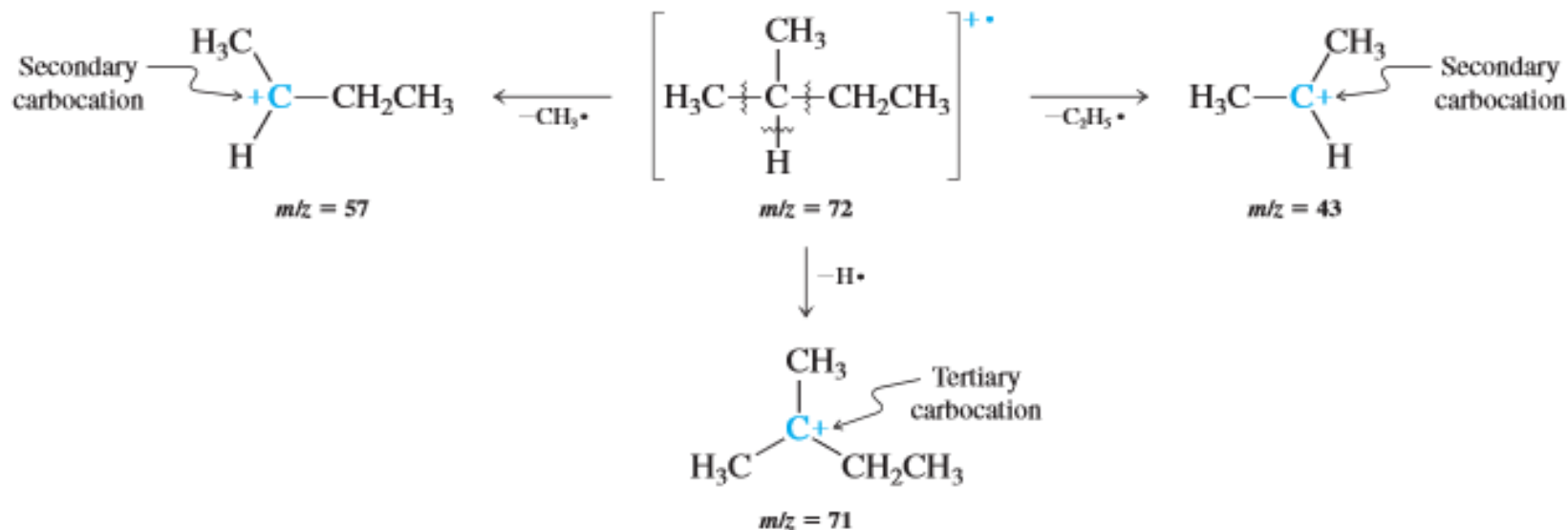
simplified mass spectrum of pentane - $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

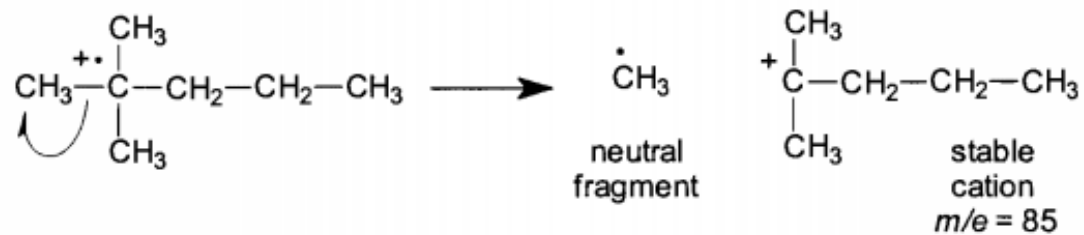


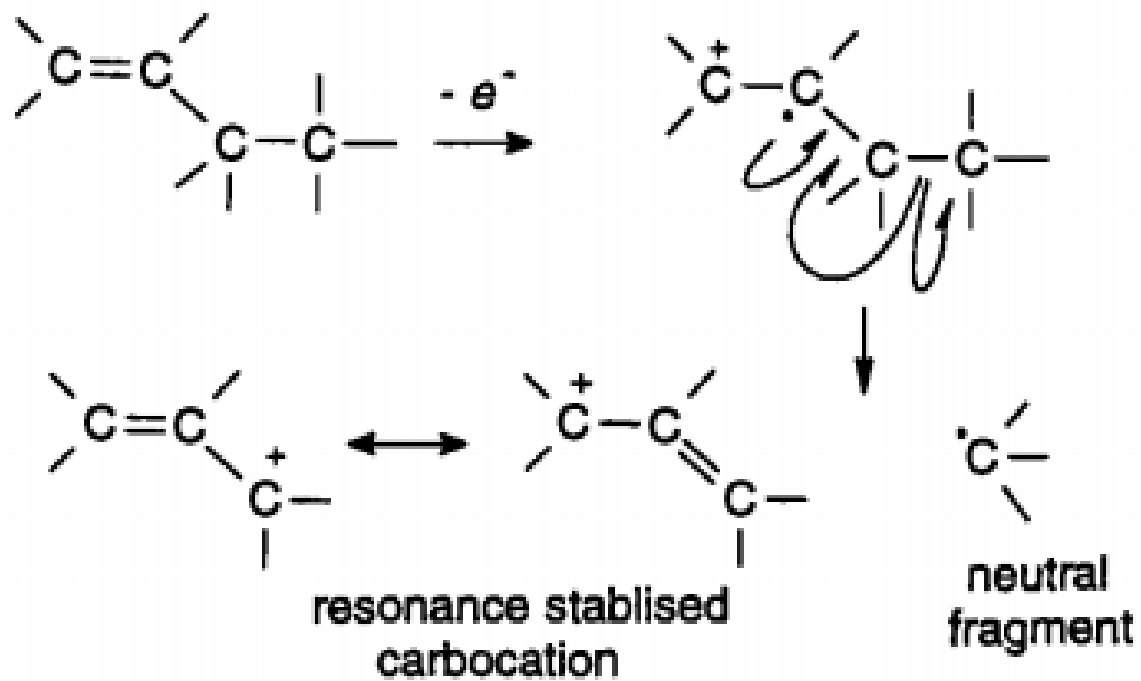
Fragment Ions from Pentane

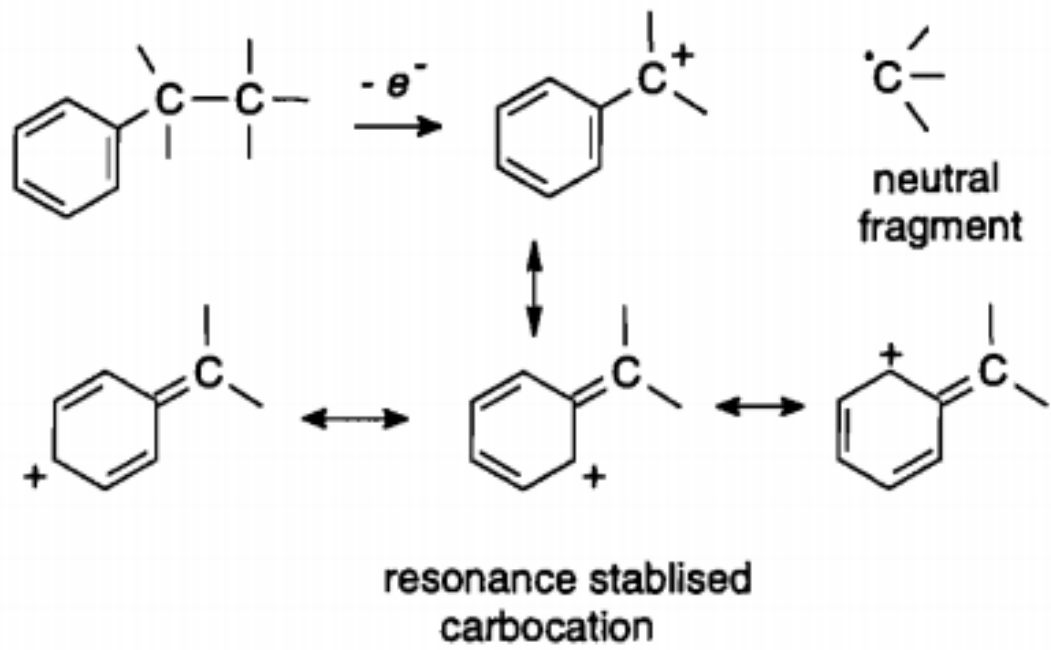


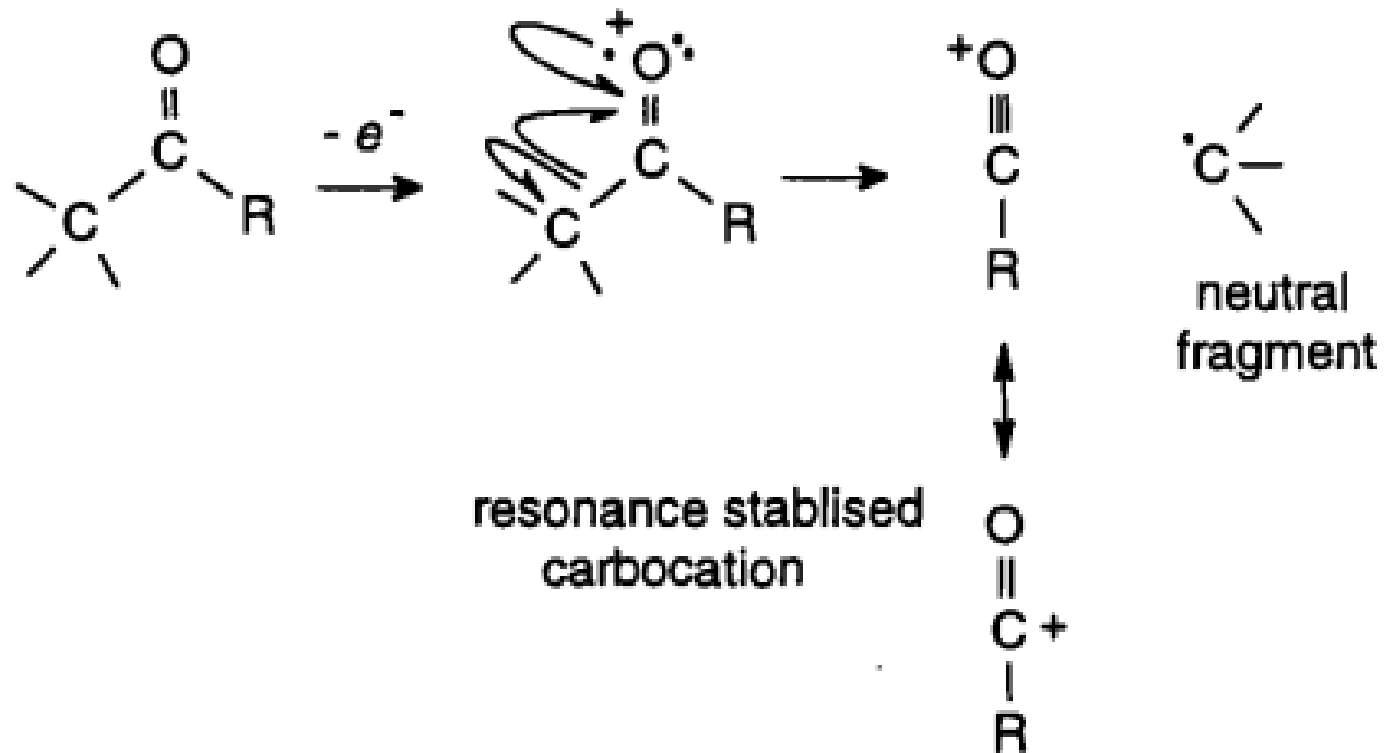
Preferred Fragmentation of 2-Methylbutane

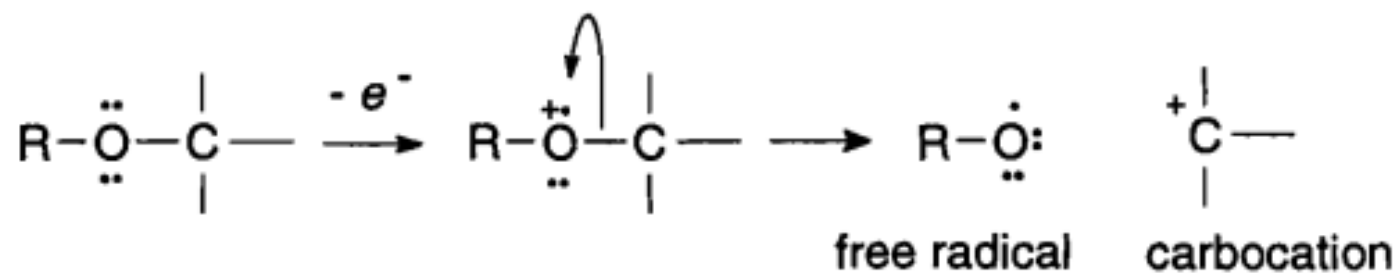


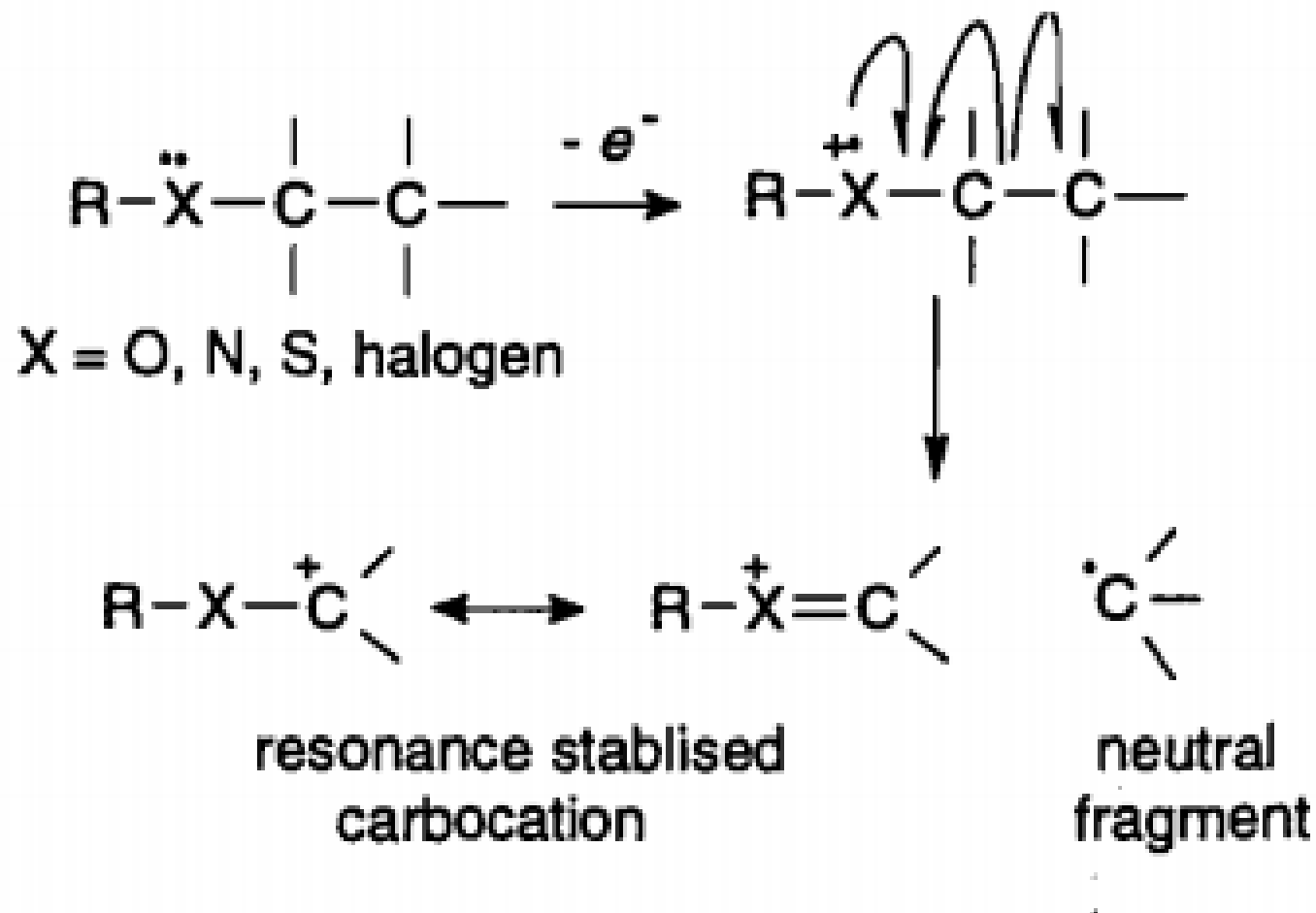




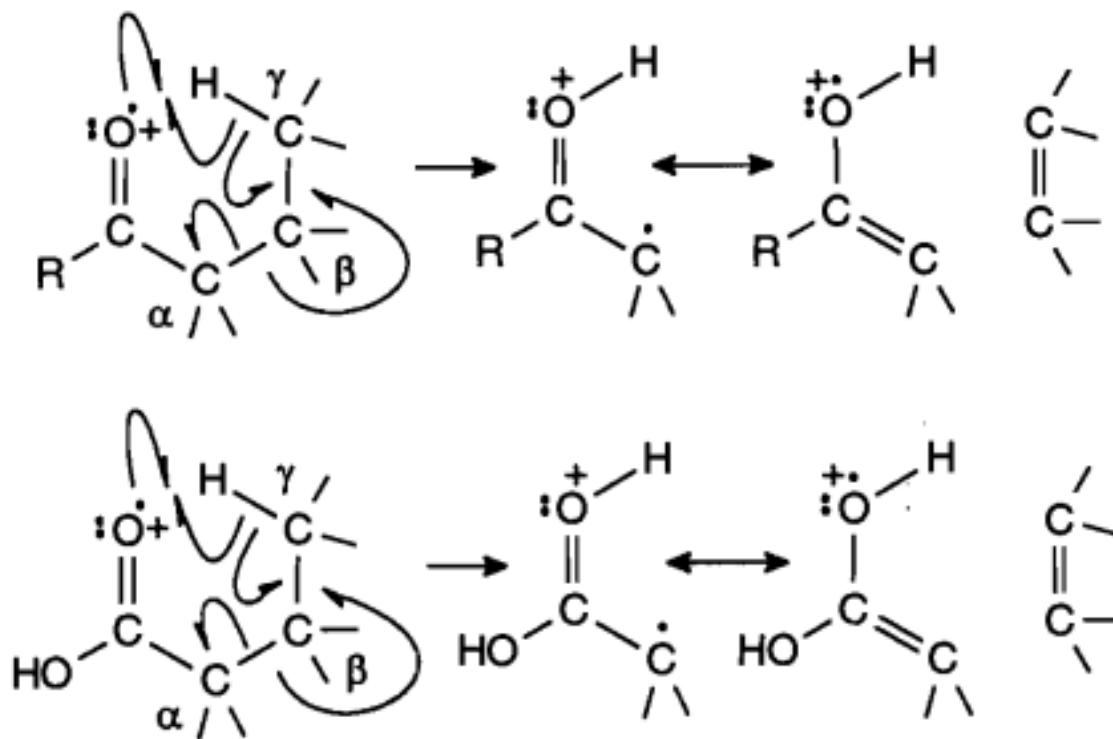


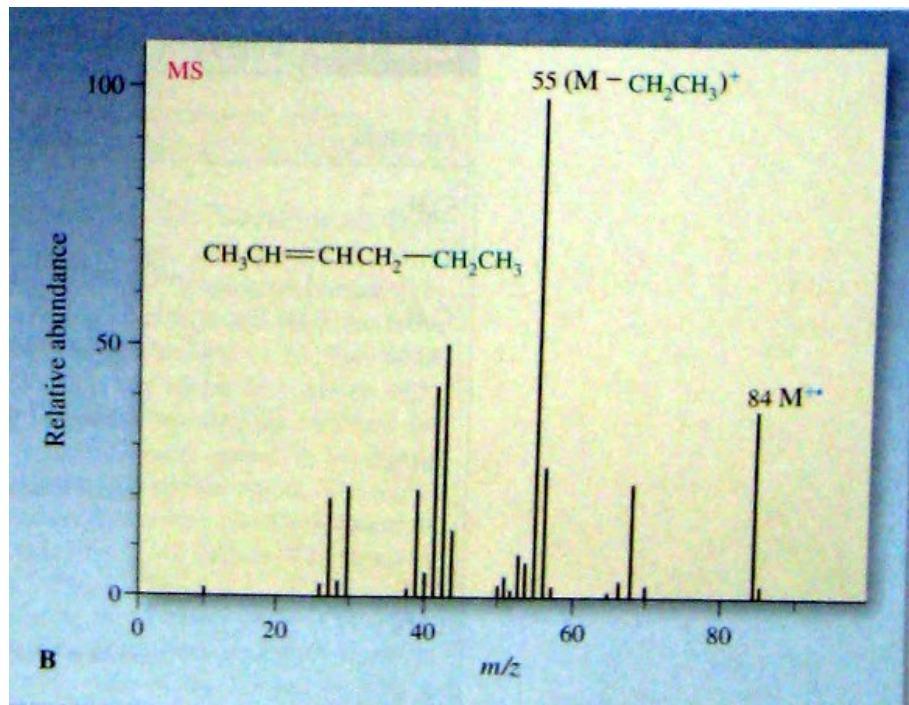
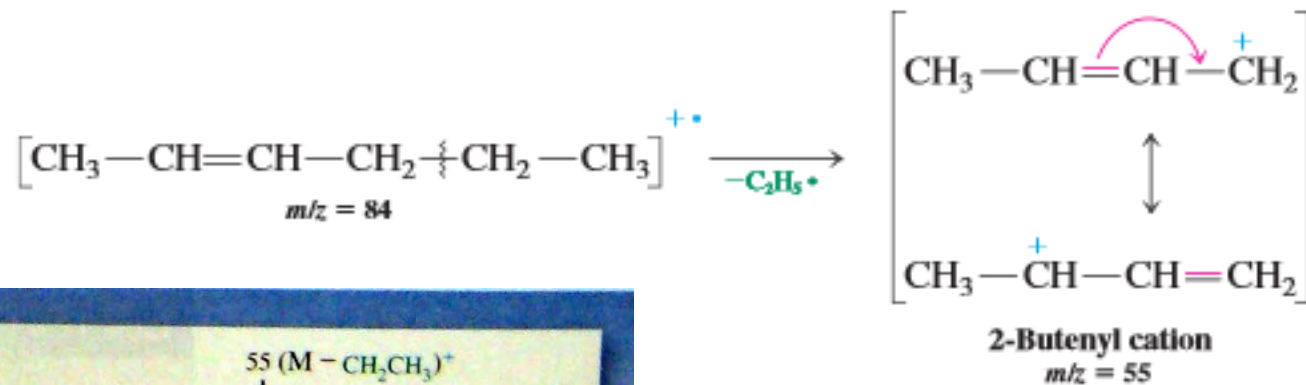
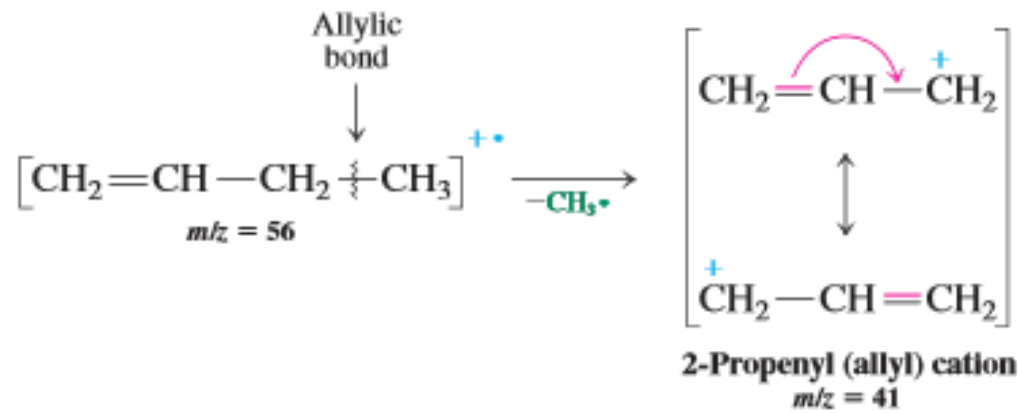




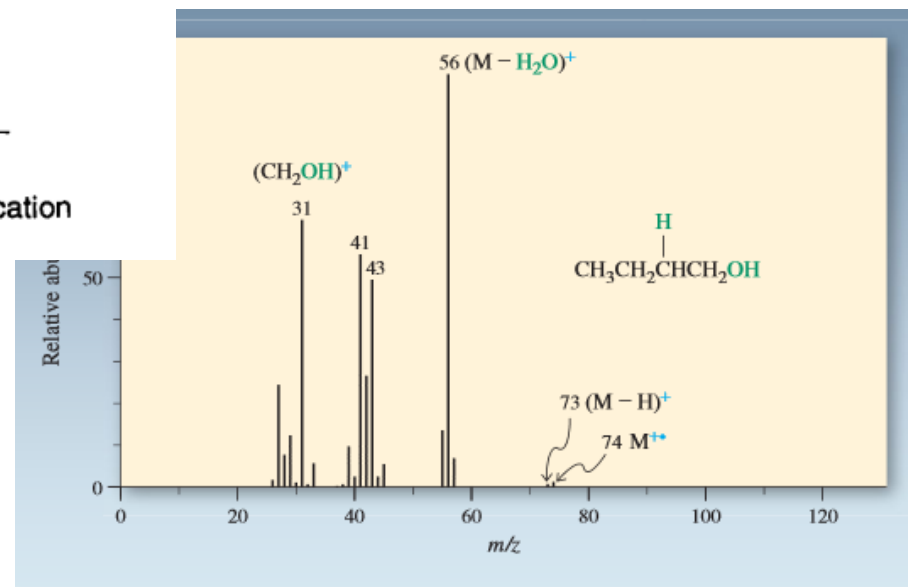
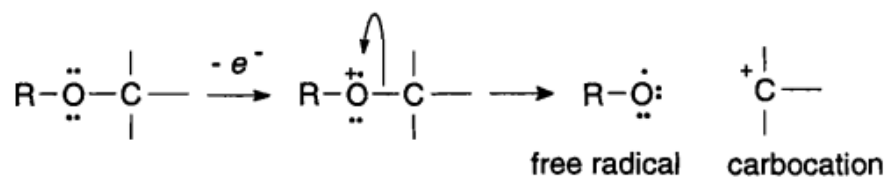


» Mc Laffertyho přesmyk

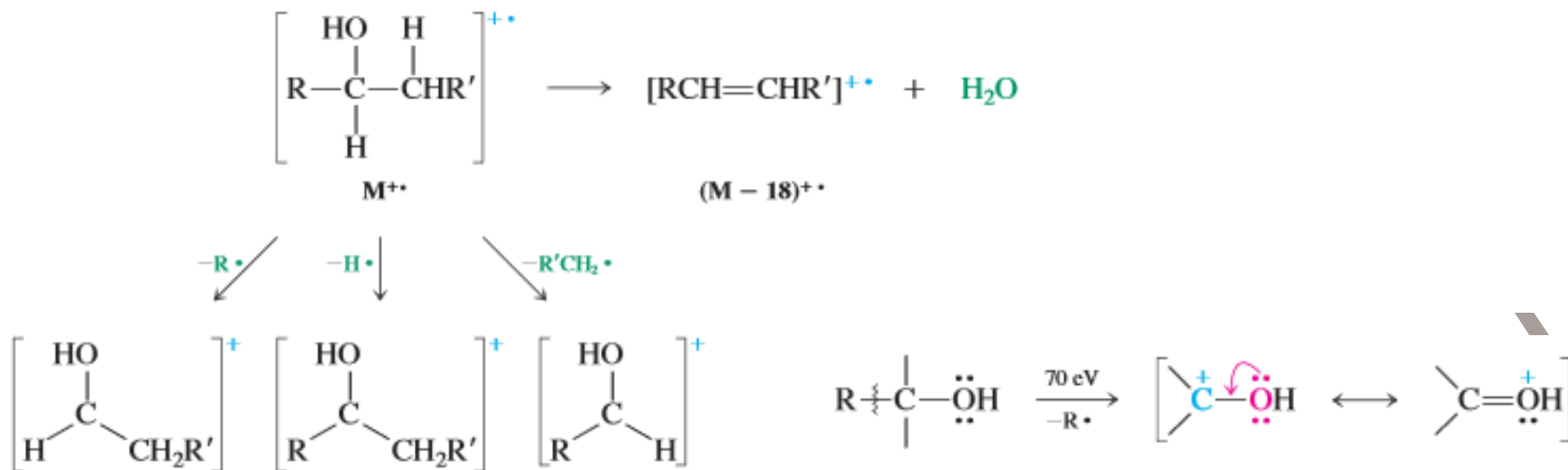




» štěpení alfa k heteroatomu



Alcohol Fragmentation by Dehydration and α Cleavage



» štěpení alfa ke karbonylu

simplified mass spectrum of pentan-3-one - $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$

