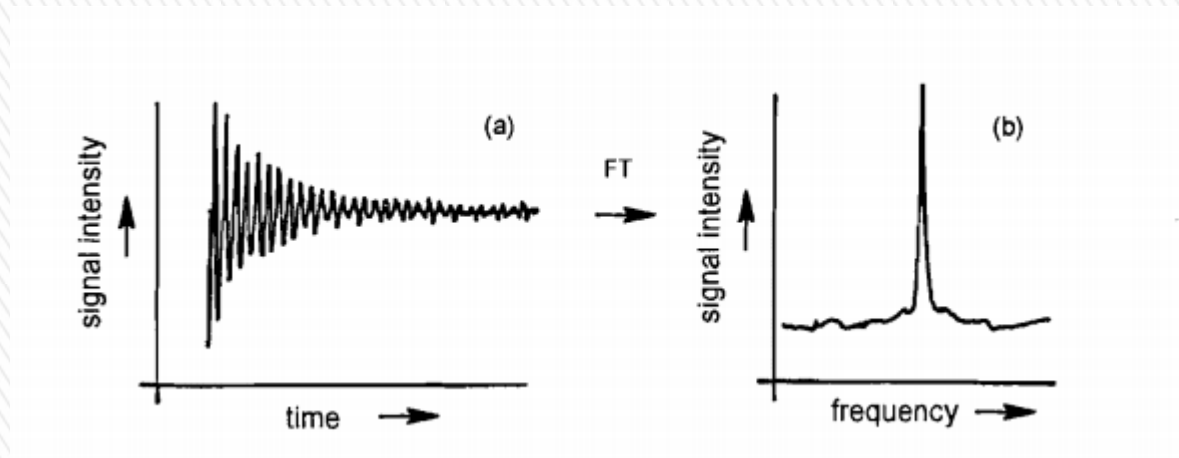
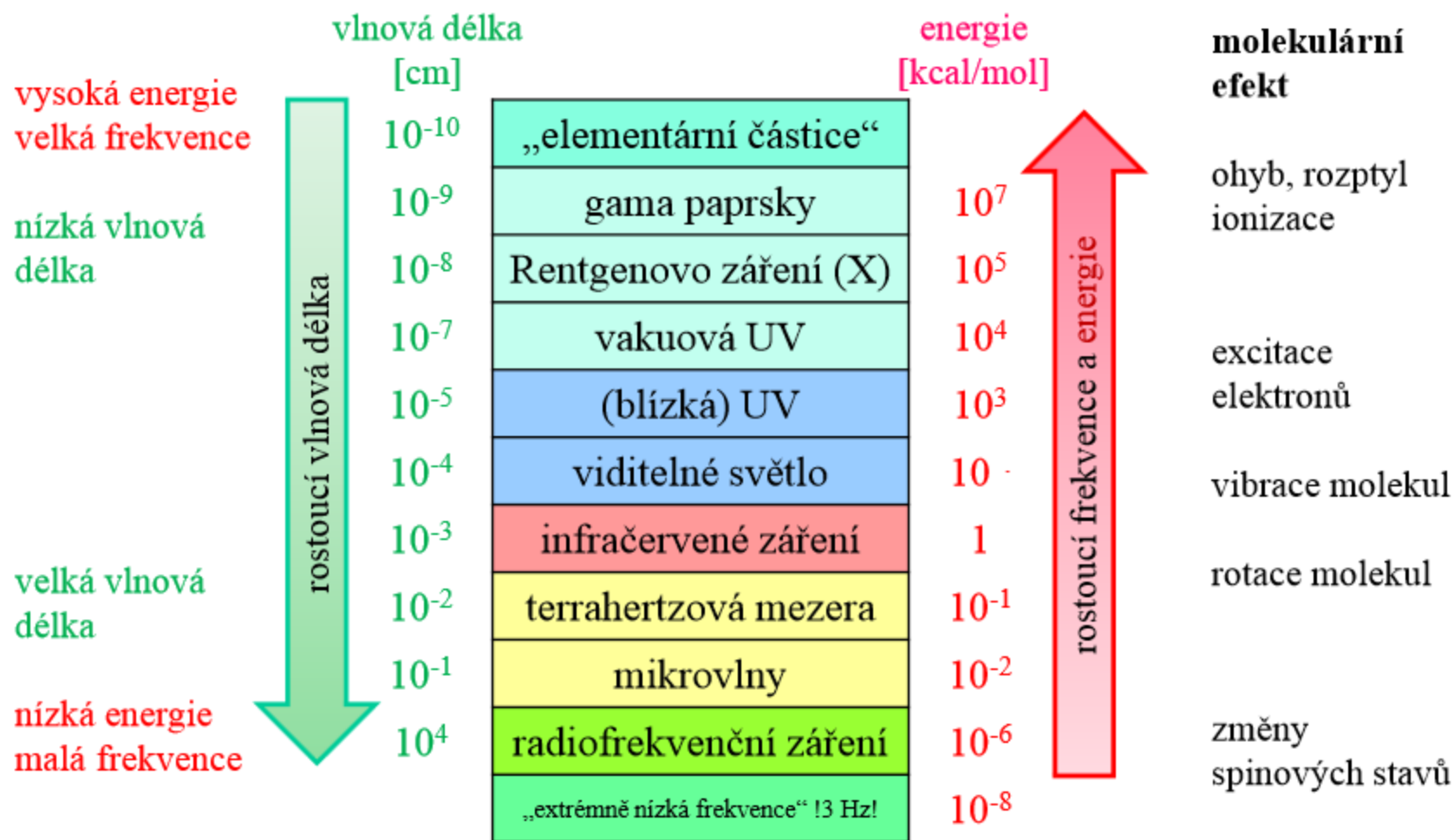


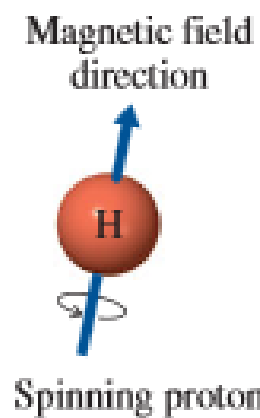
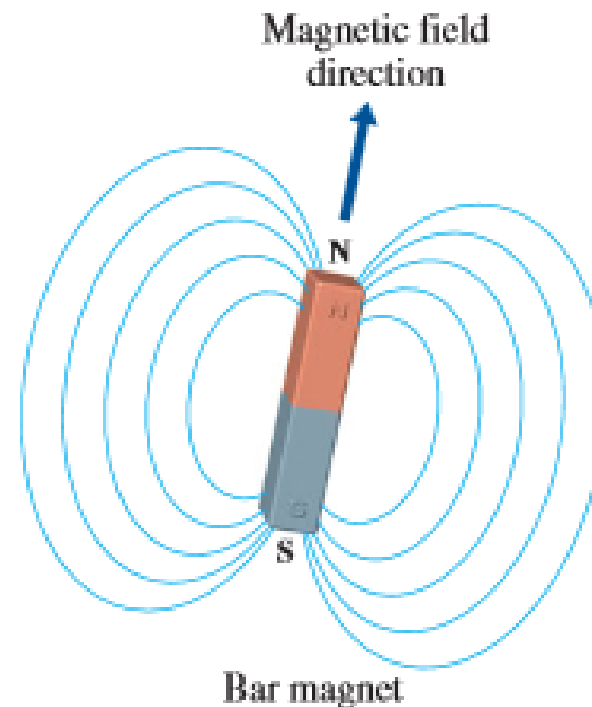
^1H NMR spektroskopie

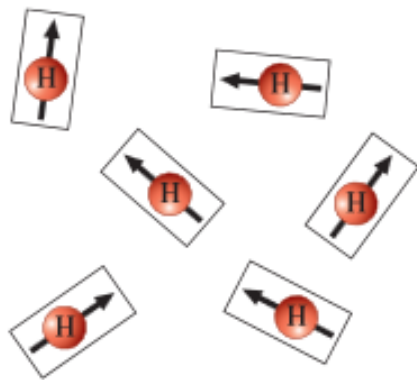


Spektrum elektromagnetického záření a jeho molekulární efekty



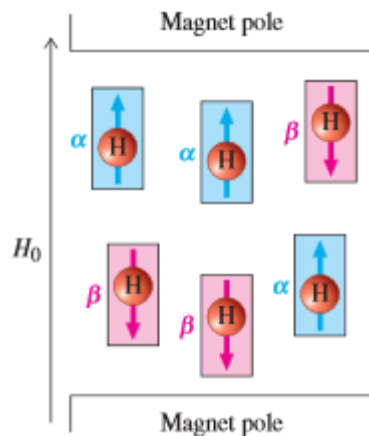
Vlastnosti NMR spektroskopie			
	^1H	^2H	^3H
Spin jadra	1/2	1	-1/2





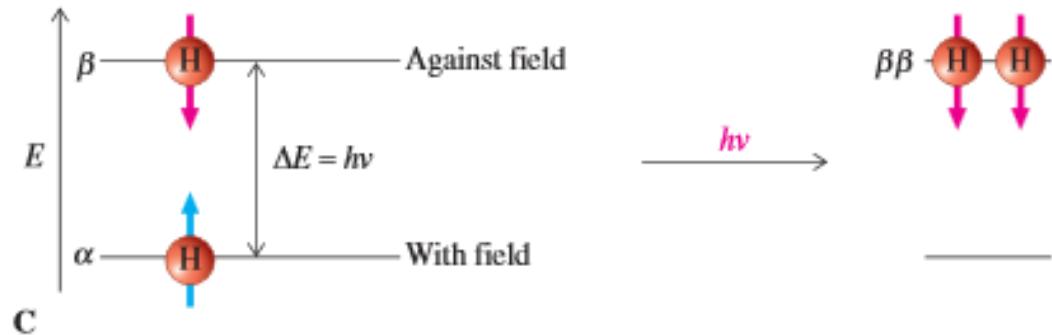
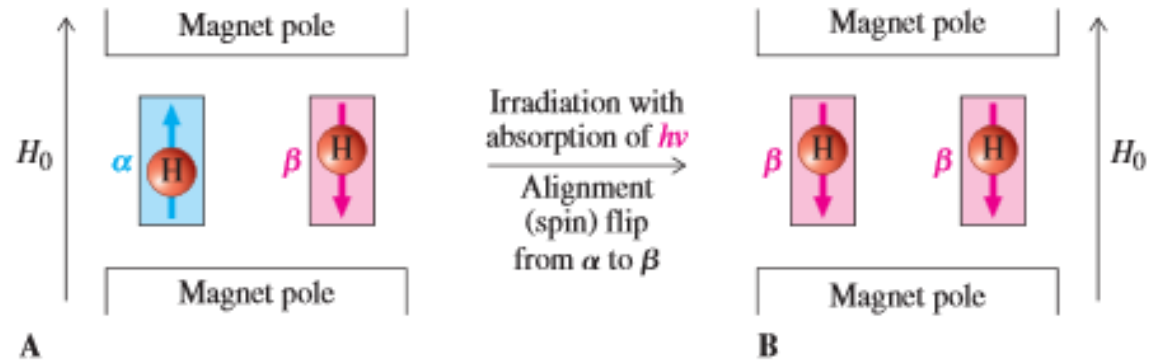
A

No external magnetic field: random orientation



B

In an external magnetic field: alignment with (α) or against (β) H_0



Magnetic Field Strength Is Proportional to Resonance Frequency

Increasing H_0

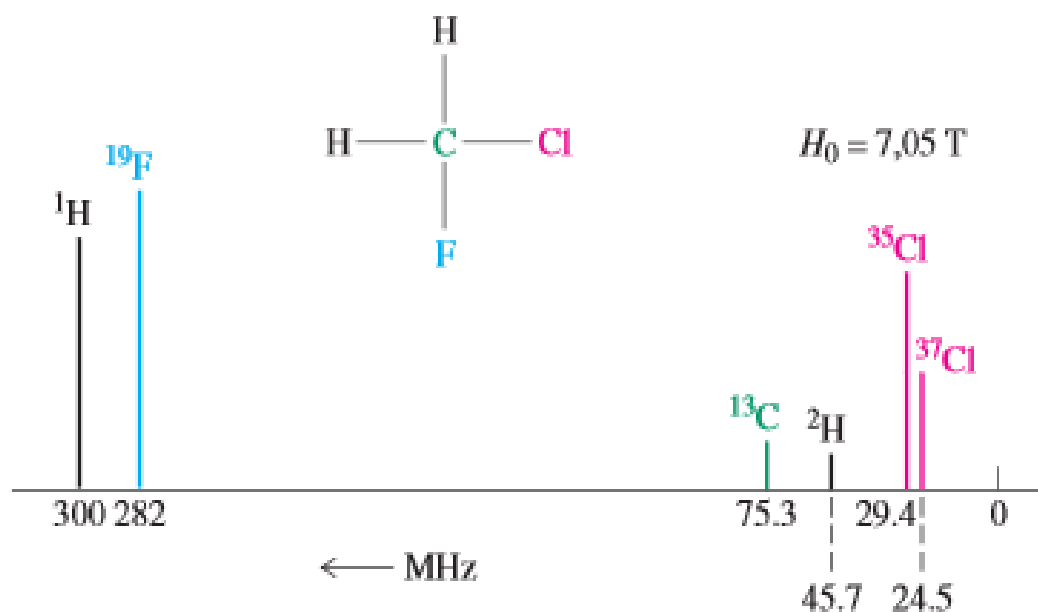
Magnetic field strength H_0 (tesla):	2.11	4.23	7.05	11.8	14.1	21.1	T
Hydrogen resonance frequency ν (megahertz):	90	180	300	500	600	900	MHz

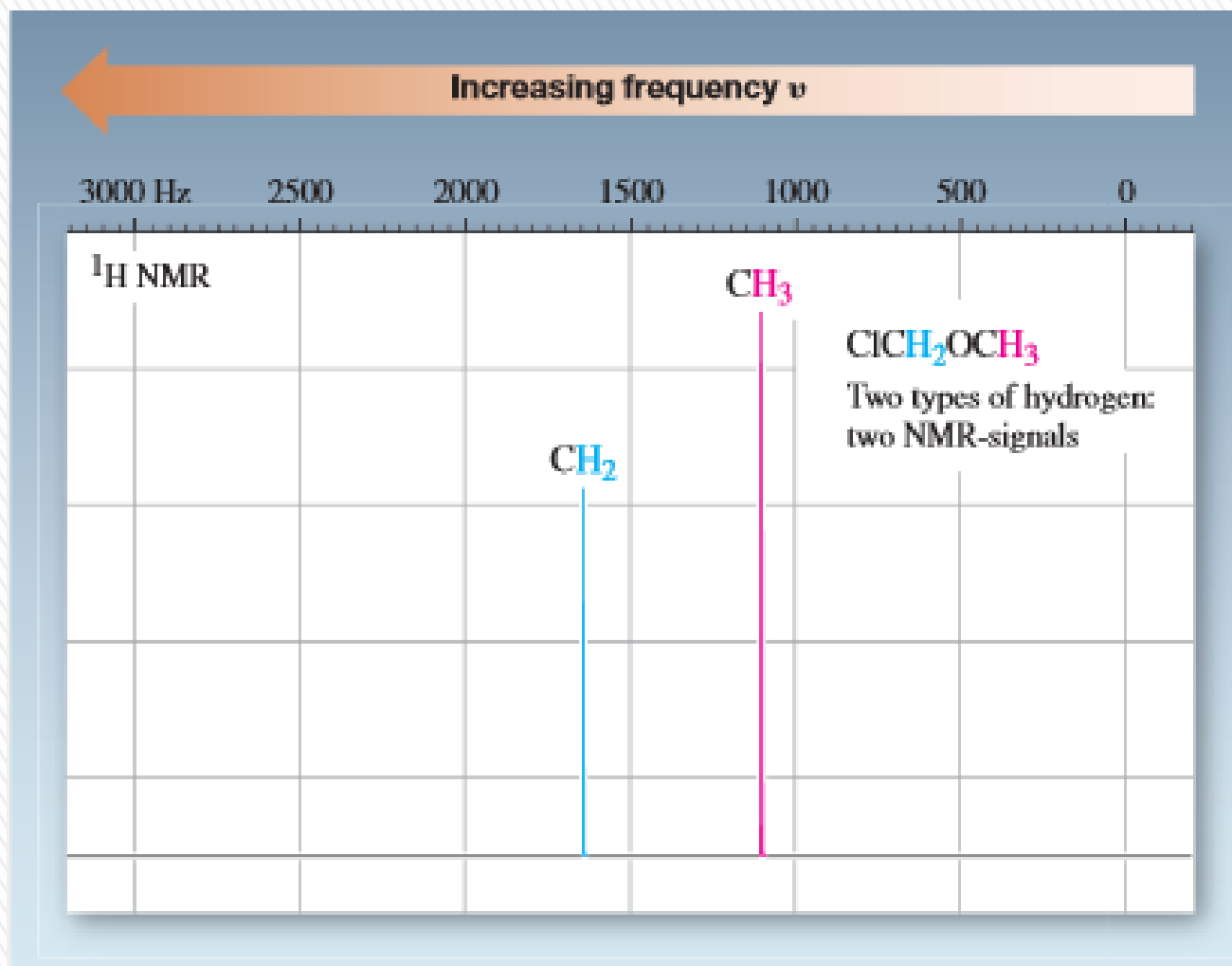
Increasing ν

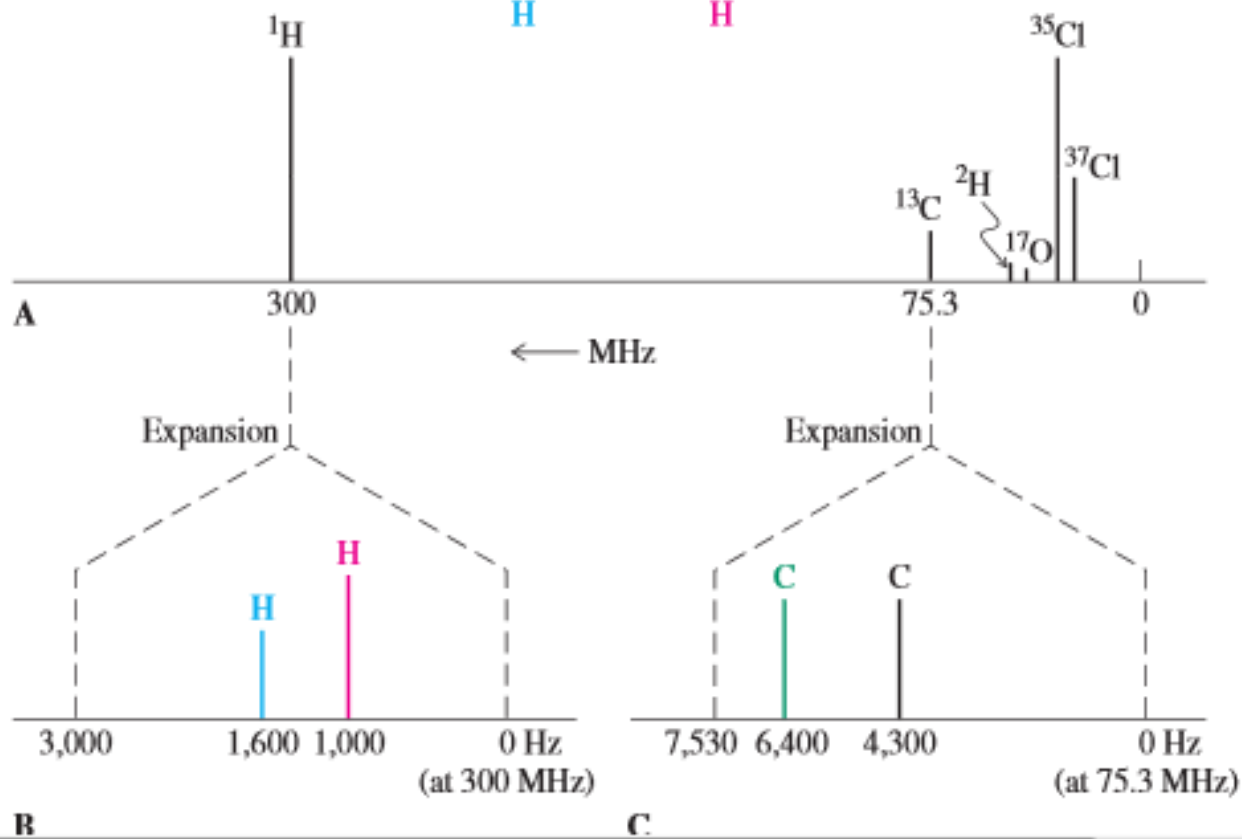
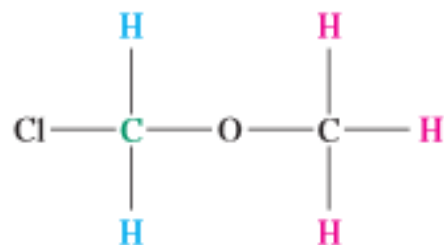
Table 10-1 NMR Activity and Natural Abundance of Selected Nuclei

Nucleus	NMR activity	Natural abundance (%)	Nucleus	NMR activity	Natural abundance (%)
^1H	Active	99.985	^{16}O	Inactive	99.759
^2H (D)	Active	0.015	^{17}O	Active	0.037
^3H (T)	Active	0	^{18}O	Inactive	0.204
^{12}C	Inactive	98.89	^{19}F	Active	100
^{13}C	Active	1.11	^{31}P	Active	100
^{14}N	Active	99.63	^{35}Cl	Active	75.53
^{15}N	Active	0.37	^{37}Cl	Active	24.47

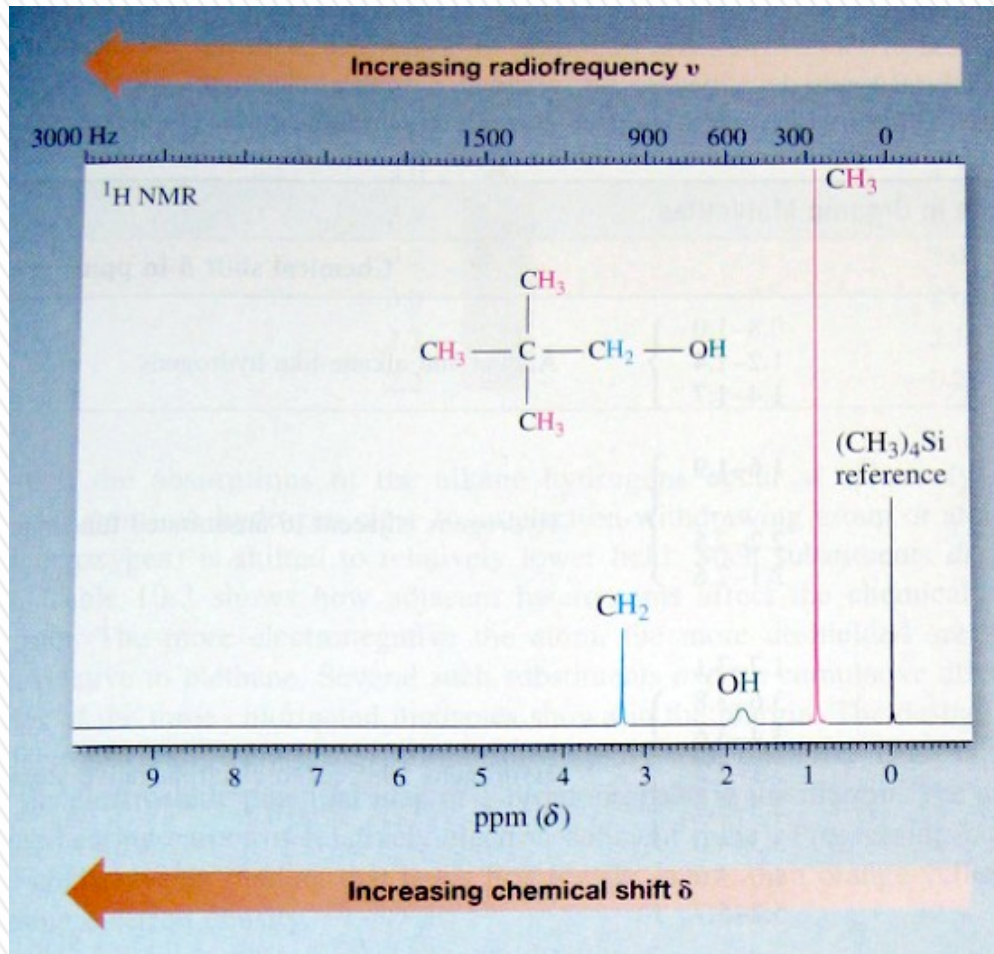
Abbreviations: D, deuterium; T, tritium.





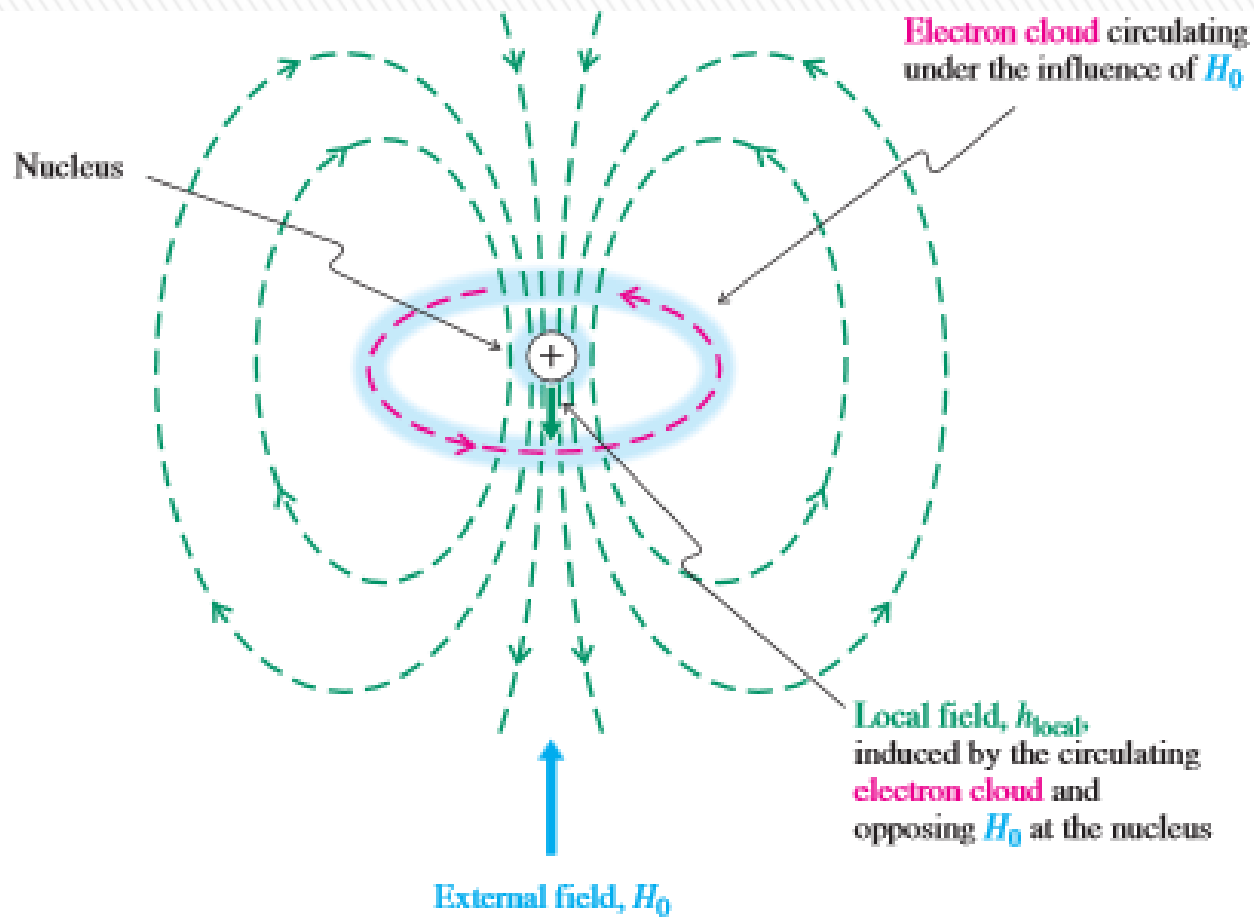


Chemický posun >>>

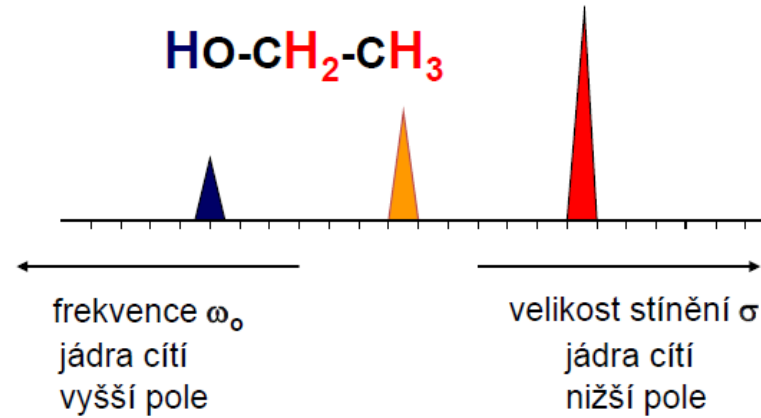


chemický posun

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

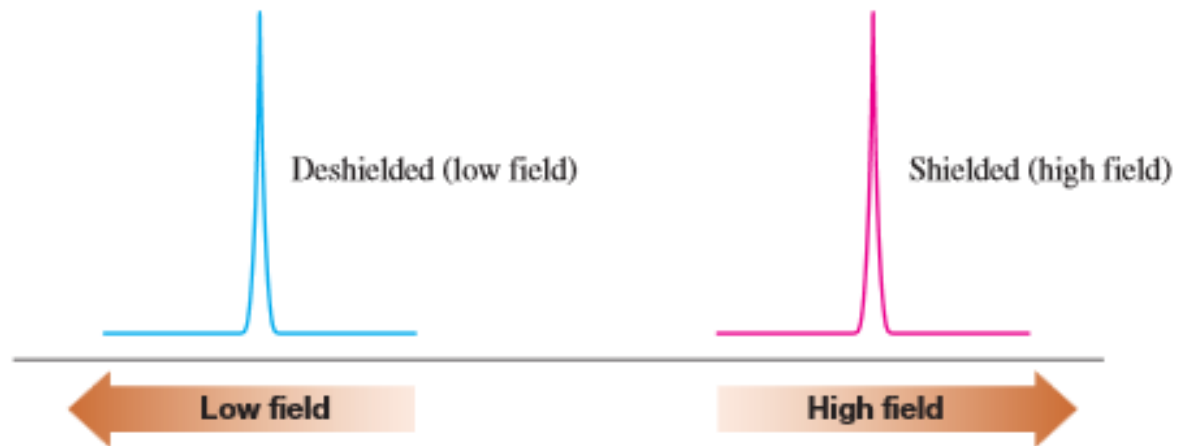


Vyšší pole vs. nižší pole



Absorption for **H⁺**

Absorption for $\text{—}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{—}$



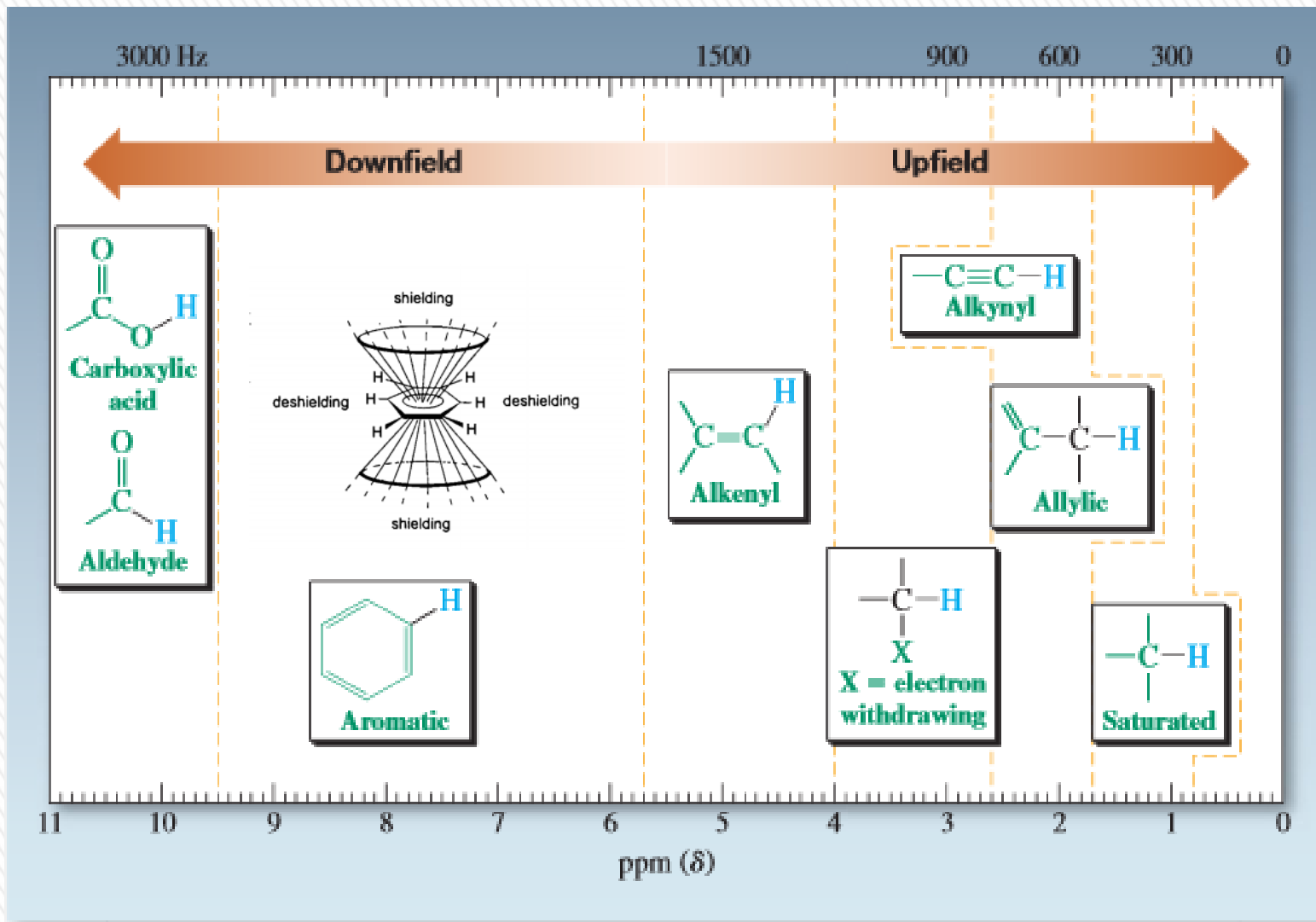
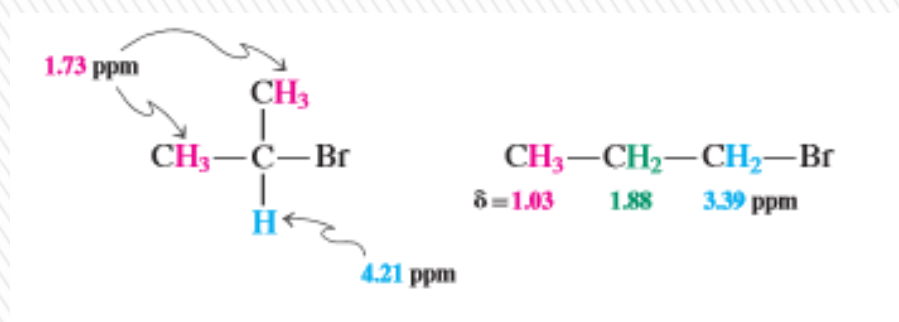
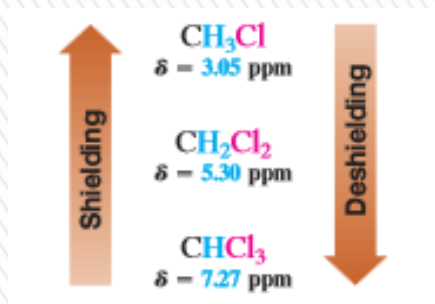


Table 10-3 The Deshielding Effect of Electronegative Atoms

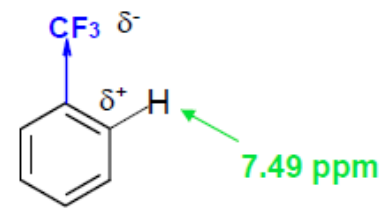
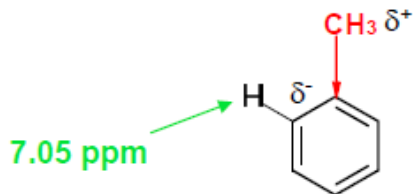
CH_3X	Electronegativity of X (from Table 1-2)	Chemical shift δ (ppm) of CH_3 group
CH_3F	4.0	4.26
CH_3OH	3.4	3.40
CH_3Cl	3.2	3.05
CH_3Br	3.0	2.68
CH_3I	2.7	2.16
CH_3H	2.2	0.23



Indukční a mezomerní efekty

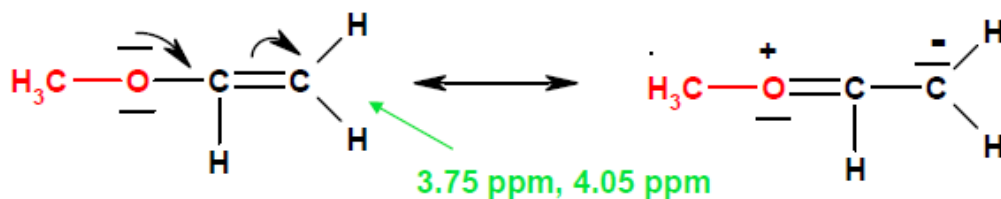
Indukční efekt (I-efekt) se týká posunu elektronů na σ vazbách.

I⁺ je způsoben
elektrondonorními
substituenty.

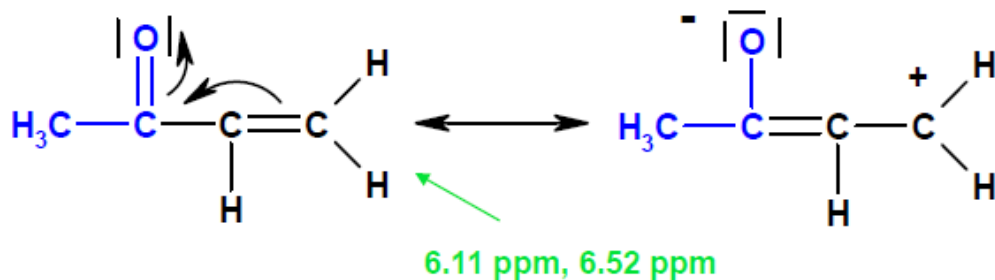


I⁻ je způsoben
elektronakceptorními
substituenty.

Mezomerní efekt (M-efekt) se týká posunu elektronů na konjugovaných vazbách π nebo interakcí ne vazebných elektronových párů s násobnou vazbou.



M⁺ způsobují substituenty
poskytující ne vazebné
elektrony.



M⁻ způsobují
substituenty přitahující
elektrony.

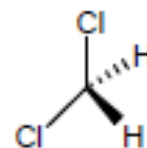


Symetrie molekuly pomáhá určit chemickou ekvivalenci



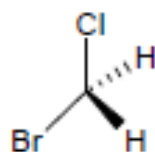
- NMR spektrum odráží symetrii molekuly
- o tom, zda dvojice atomů poskytne dva různé signály nebo jen jeden, rozhoduje jejich vzájemný vztah při operacích symetrie

Homotopické atomy

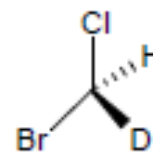
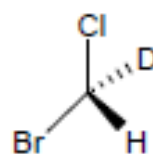


C_2 osa symetrie
ekvivalentní
1 signál ve spektru

Enantiotopické atomy



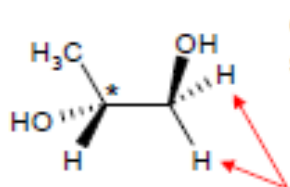
deuteriová
substituce



enantiomery

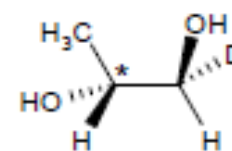
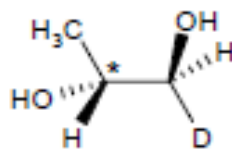
rovina symetrie
není osa symetrie
ekvivalentní
1 signál ve spektru

Diastereotopické atomy (molekuly s chirálním centrem)



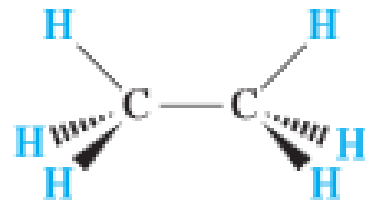
diastereotopické
metylenové vodíky

deuteriová
substituce

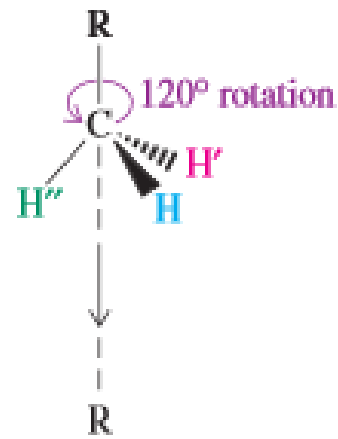
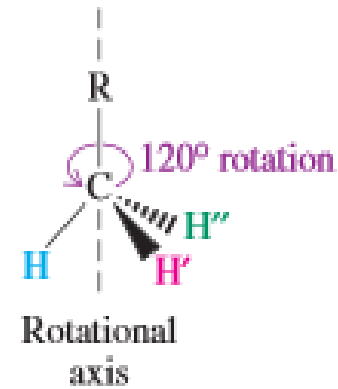
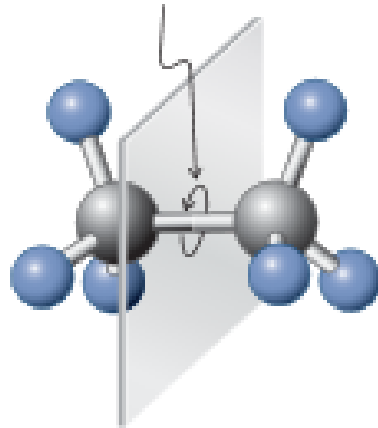


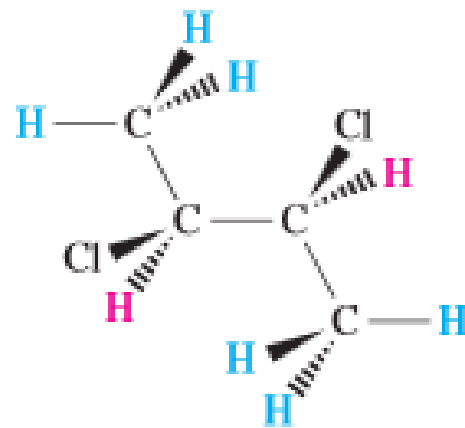
diastereomery

není osa symetrie
není rovina symetrie
neekvivalentní
rozišitelné ve spektru

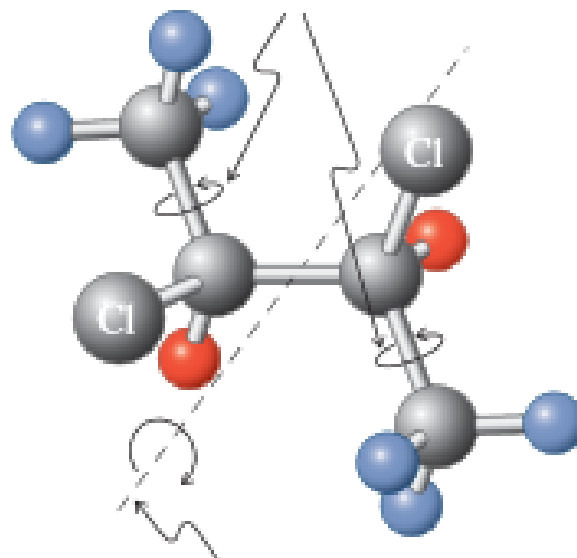


Threefold rotation arrow





Threefold rotation arrows

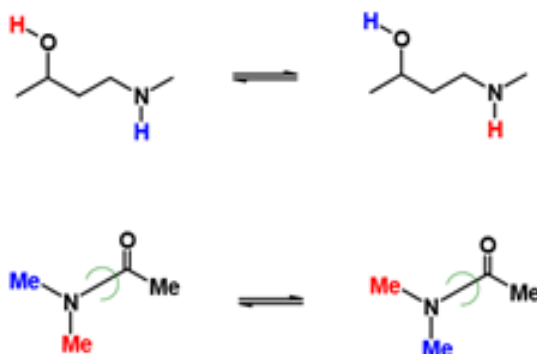


Axis of twofold rotation



Počet signálů - Chemická výměna

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



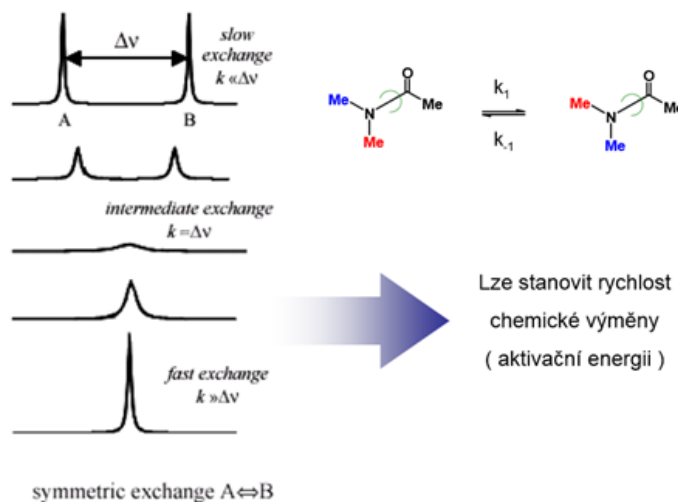
Chemická výměna je na časové škále NMR

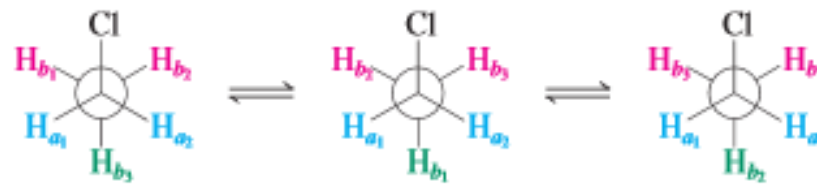
a) Rychlá = pozorujeme průměrnou hodnotu

b) Střední = pozorujeme velmi široký signál

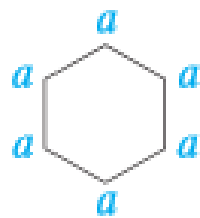
c) Pomalá = pozorujeme signály krajních stavů

Počet signálů - Vliv teploty

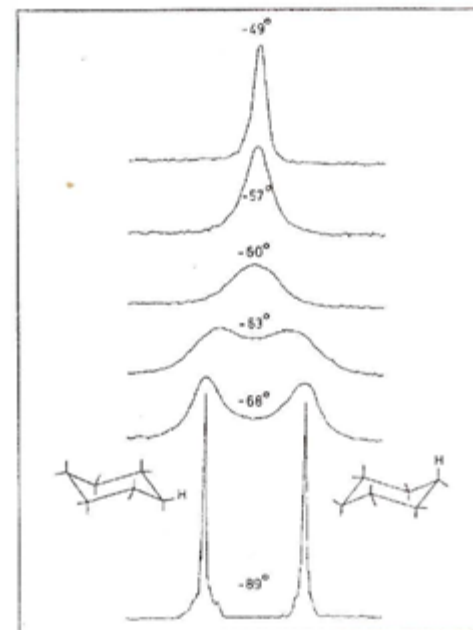




A Rotation of the methyl group, located in the back



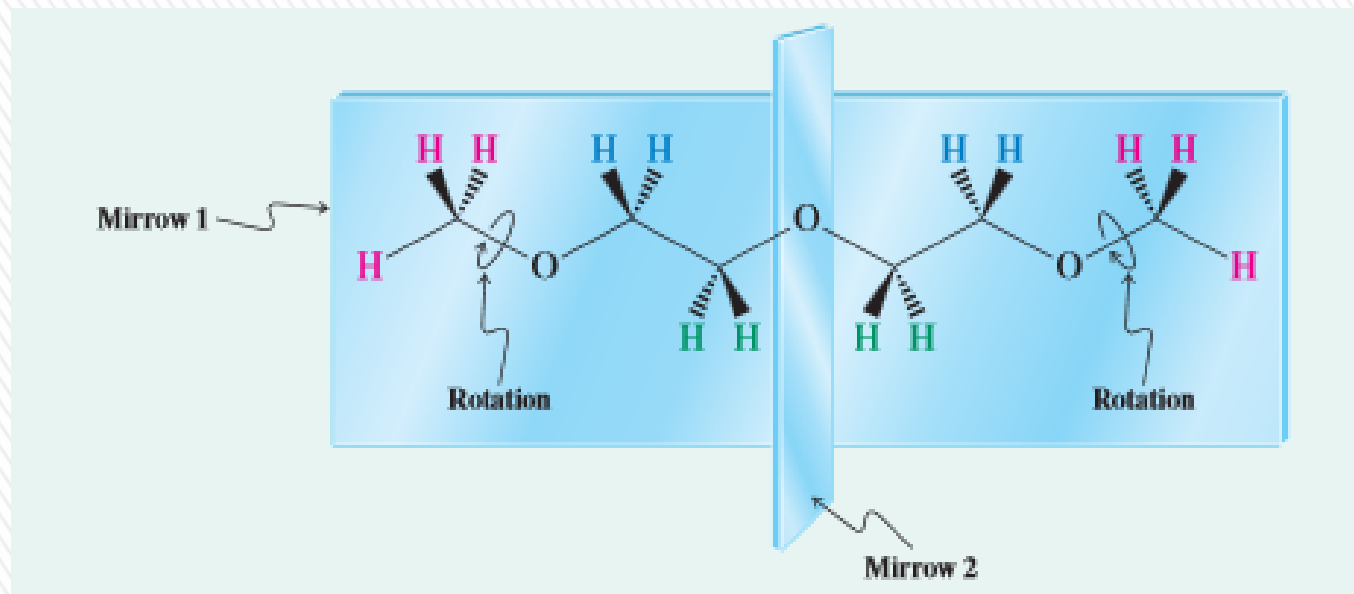
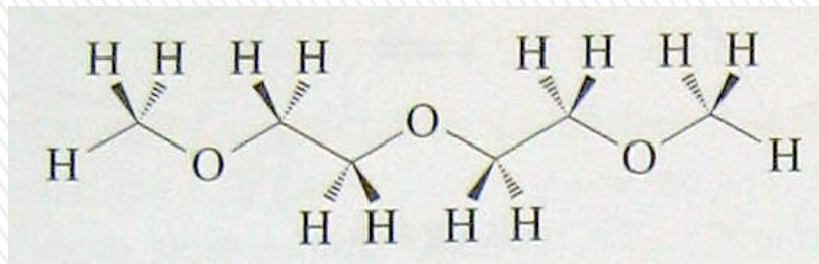
B Ring flip

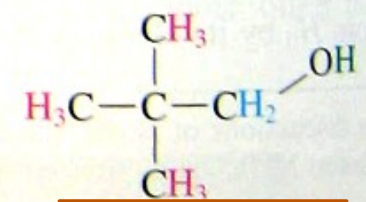
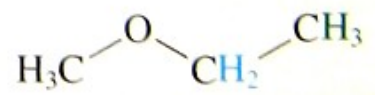
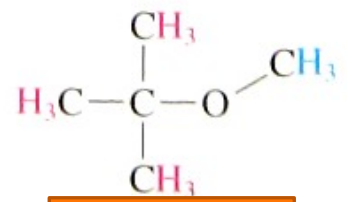
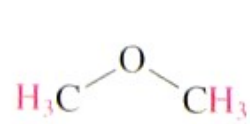
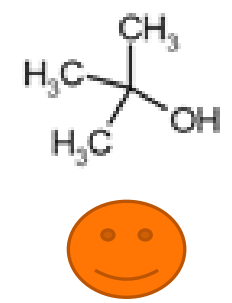
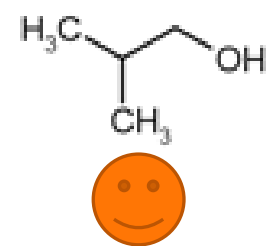
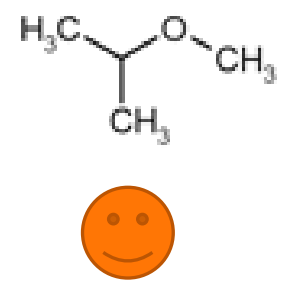
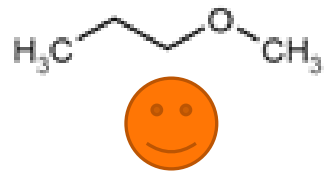


Obr. 31-3 ^1H NMR spektrum (60 MHz) jediného vodíku cyklohexanu- d_{11} v závislosti na teplote.

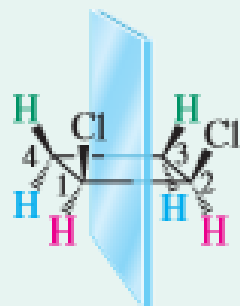


Kolik ^1H NMR signálů očekáváte u níže uvedené molekuly?





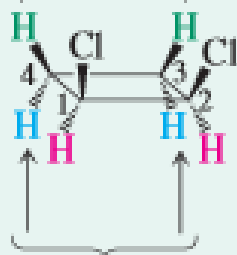
Kolik signálů očekáváte v ^1H NMR spektru *cis*- a *trans*-1,2-dichlorocyklobutanu?



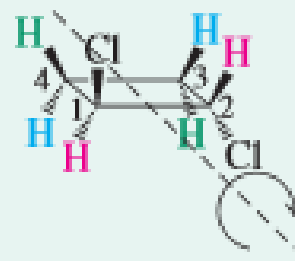
Mirror plane bisecting the molecule

cis-1,2-Dichlorocyclobutane

Cis to the chlorine atoms

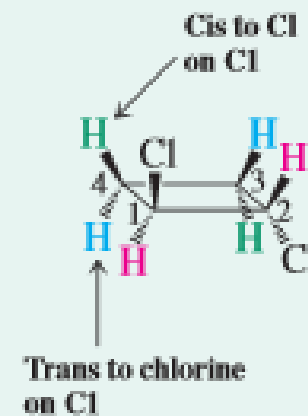


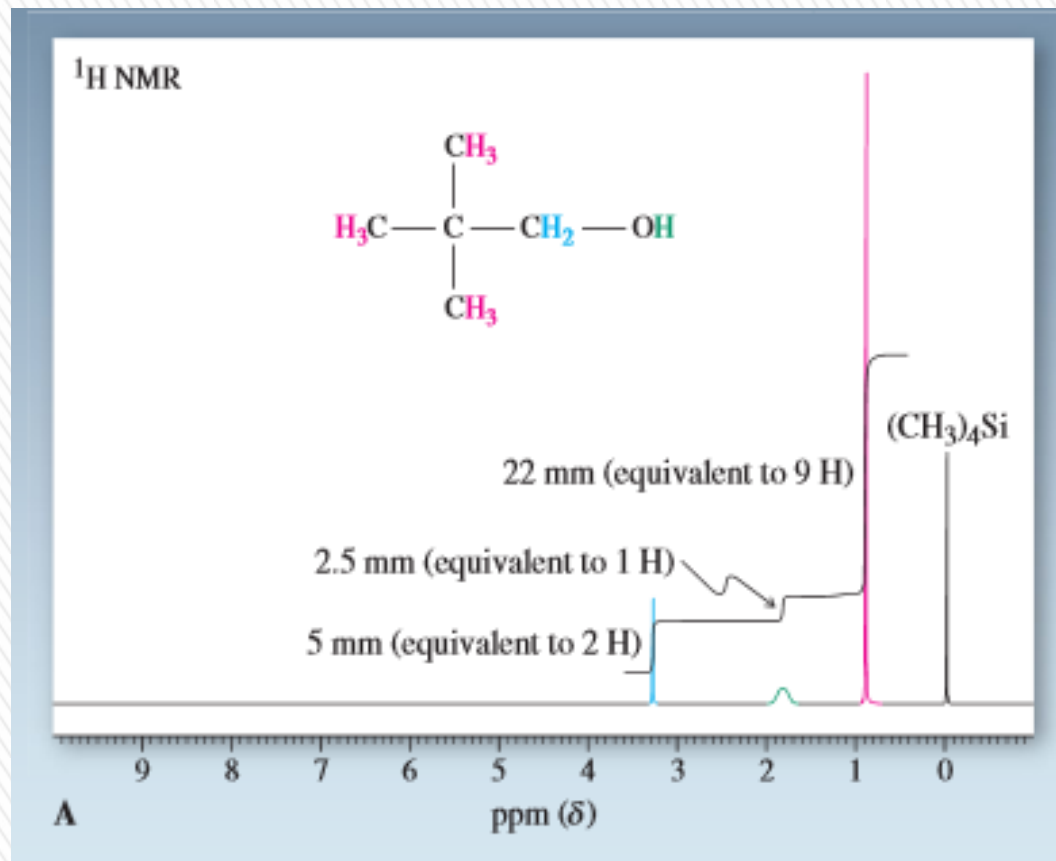
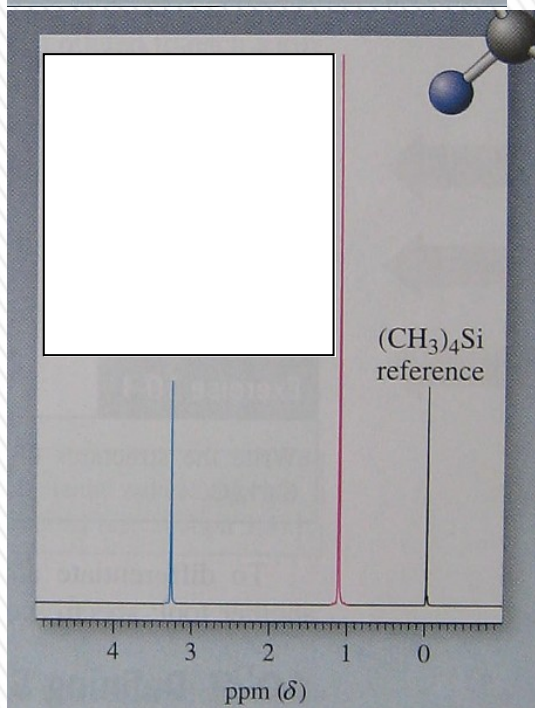
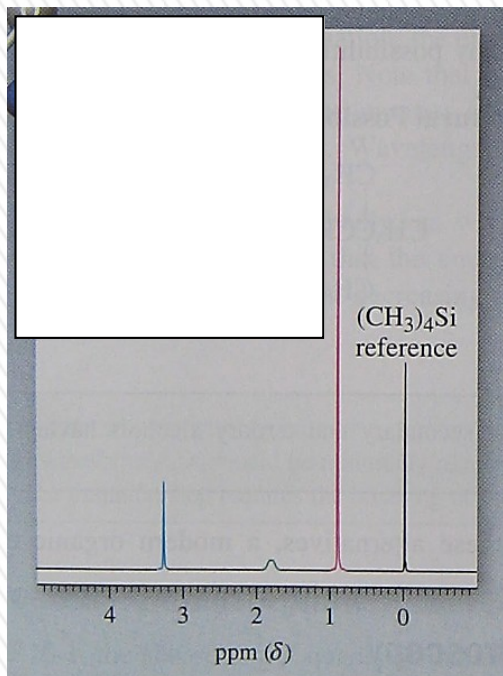
Trans to the chlorine atoms



Twofold rotational axis

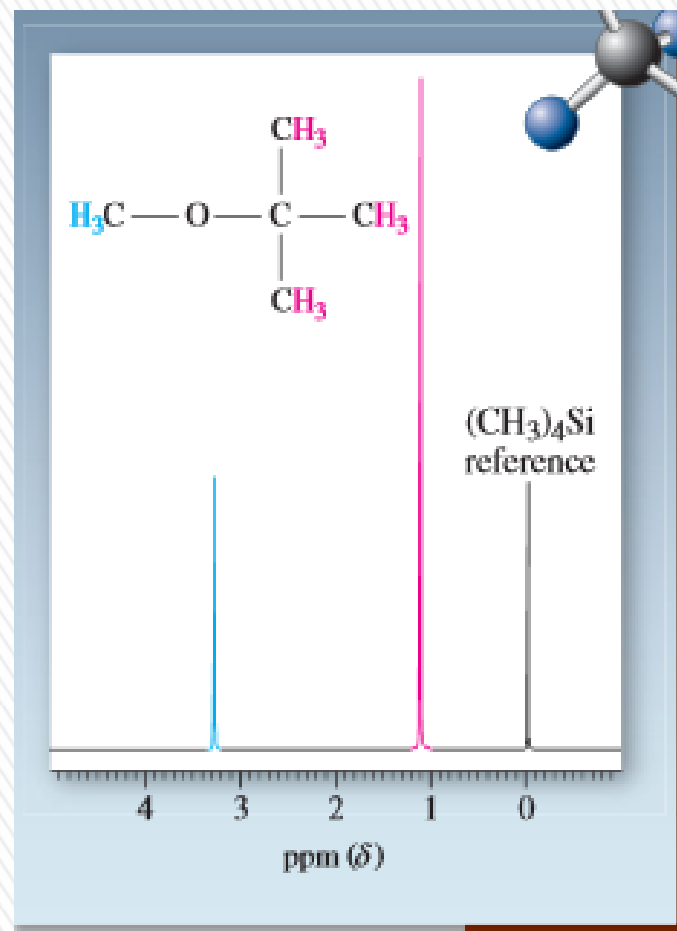
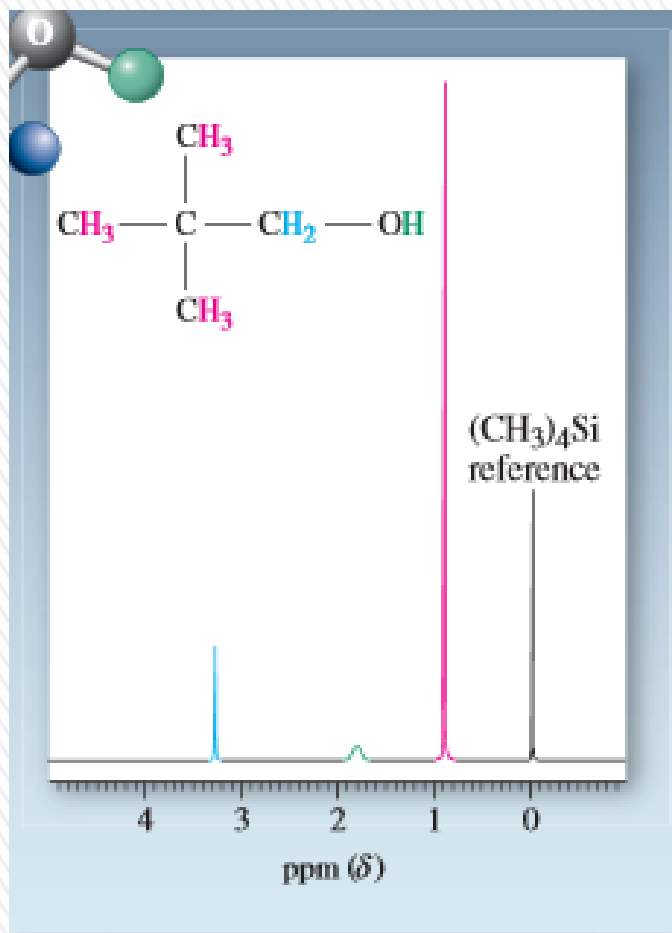
trans-1,2-Dichlorocyclobutane



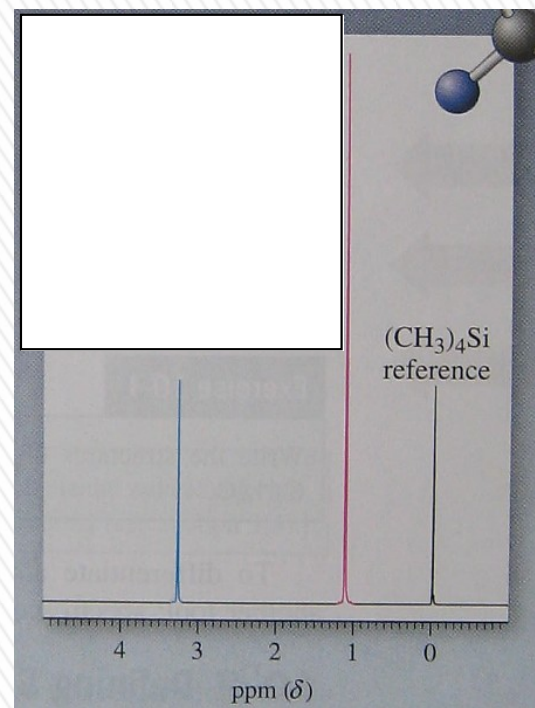
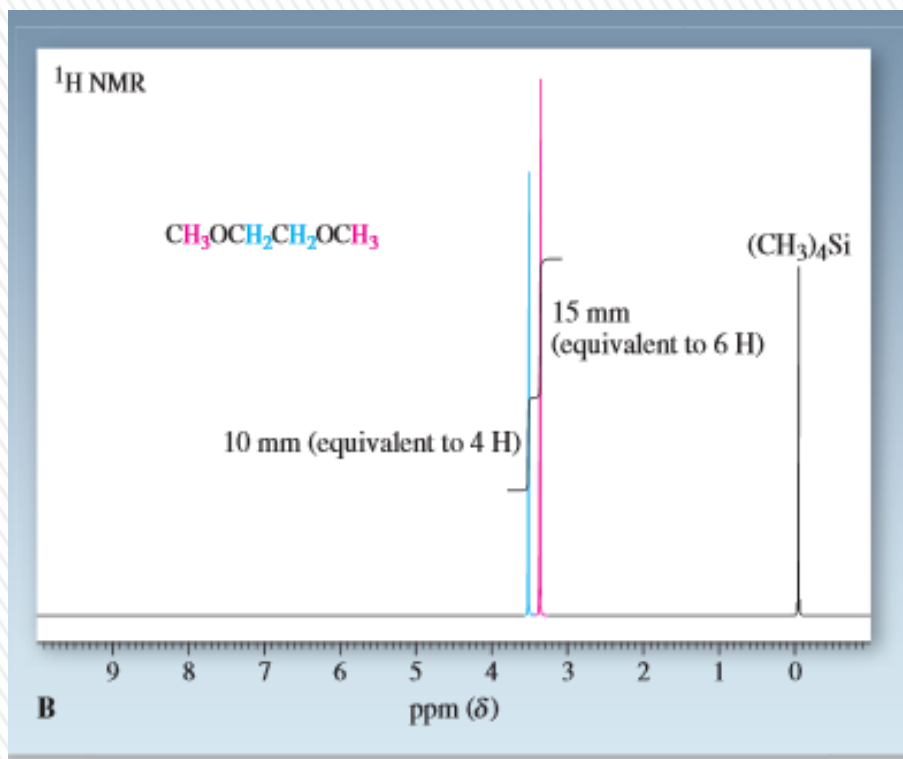


Rozhodněte, které spektrum náleží molekule (t-butyl)(methyl)etheru a které molekule 2,2-dimethylpropanolu?

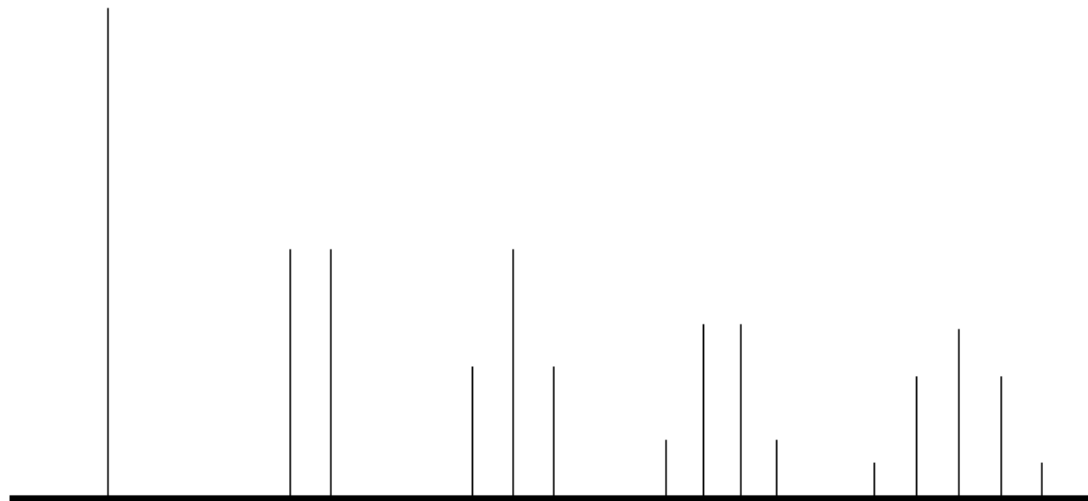




Rozhodněte, které spektrum náleží molekule
(*t*-butyl)(methyl)etheru a které molekule 1,2-dimethoxyethanu.



» Multiplicita signálů



singlet

dublet

triplet

kvartet

kvintet

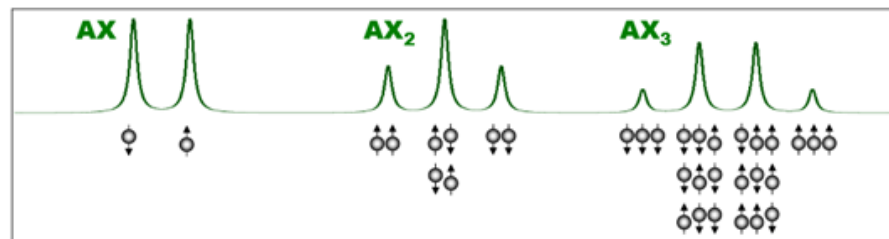
1 : 1

1 : 2 : 1

1 : 3 : 3 : 1

1 : 4 : 6 : 4 : 1

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



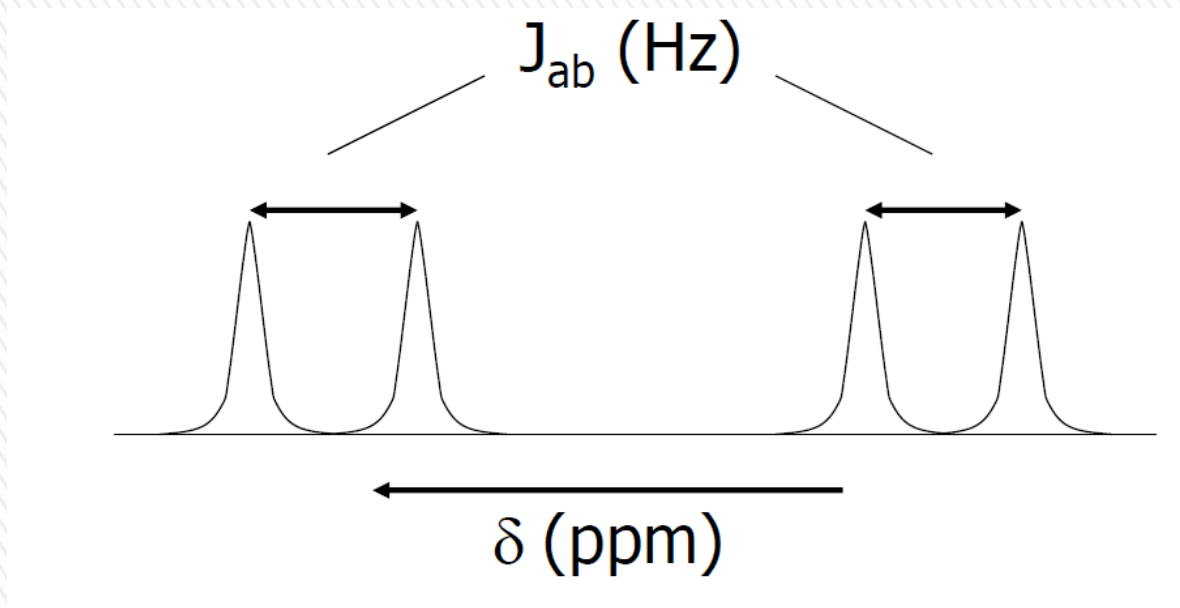
	Splitting pattern for H_a	Structure	Splitting pattern for H_b	
H_a has one neighbor H_b : 2 peaks or doublet				H_b has one neighbor H_a : 2 peaks or doublet
H_a has one neighbor H_b : 2 peaks or doublet				H_b has two neighbors H_a : 3 peaks or triplet
H_a has two neighbors H_b : 3 peaks or triplet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

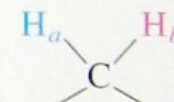


» Interakční konstanta

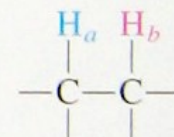
nezávisí na H_0 vnějšího magnetického pole



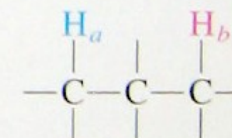
Coupling Between Close-Lying Hydrogens



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



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

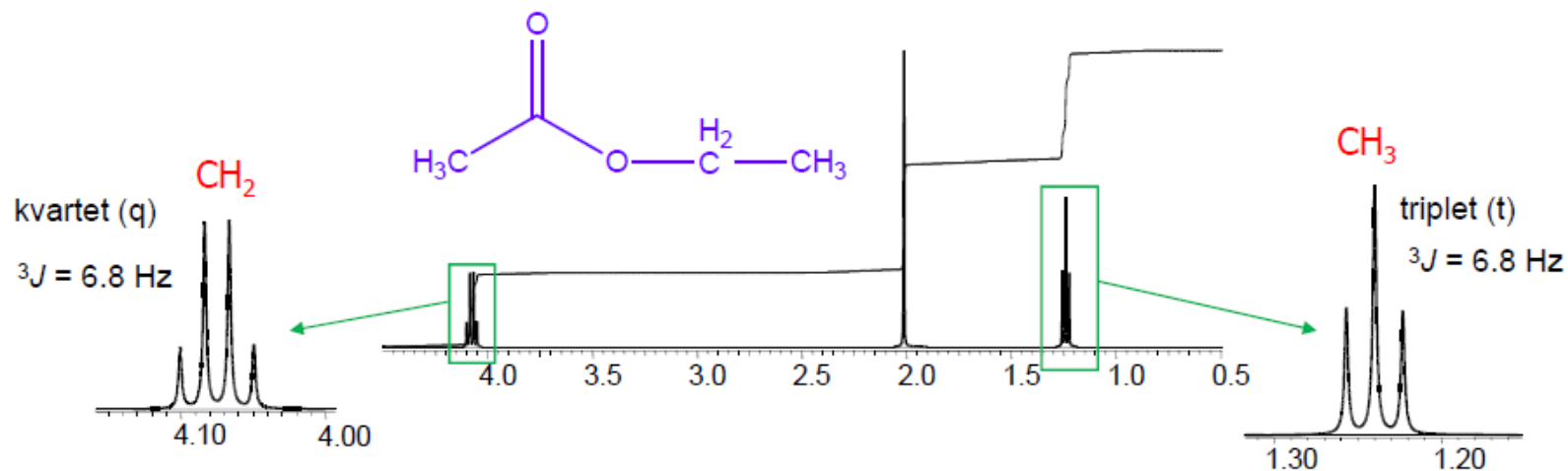


J_{ab} , 1,3-coupling, usually negligible

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



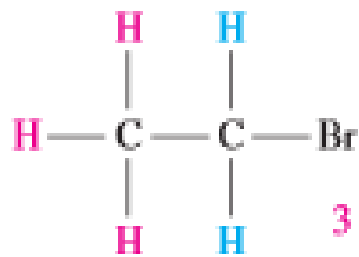
» ^1H NMR spektrum ethyl-acetátu



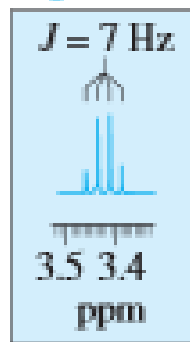
- spektrum 1. řádu: $\Delta\nu \gg J$, AX systém
- methylen vidí 4 různé stavy methylu (kvartet), methyl vidí 3 různé stavy methyleny (triplet)
- počet složek multipletu pro $I = 1/2$: $n+1$, n je počet interagujících jader v sousedním multipletu
- vzdálenost složek multipletu v Hz - interakční konstanta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



^1H NMR



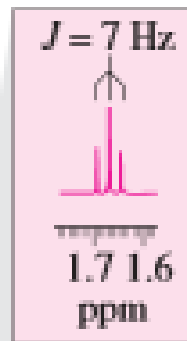
3 H neighbors:
quartet



2 H

2 H neighbors:
triplet

3 H



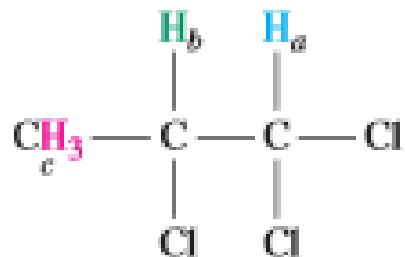
$(\text{CH}_3)_4\text{Si}$

9 8 7 6 5 4 3 2 1 0

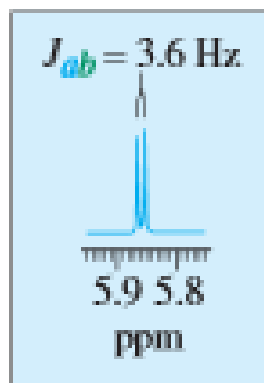
ppm (δ)



^1H NMR

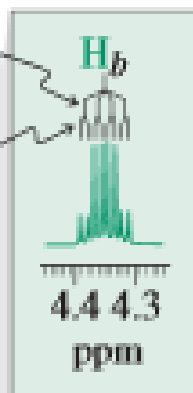


1 H neighbor:
doublet



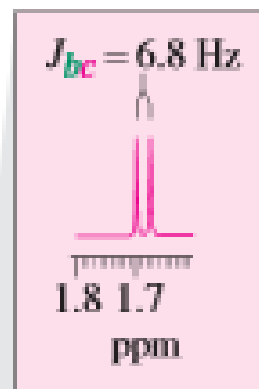
3 H neighbors: quartet
 $J_{bc} = 6.8 \text{ Hz}$

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



3 H

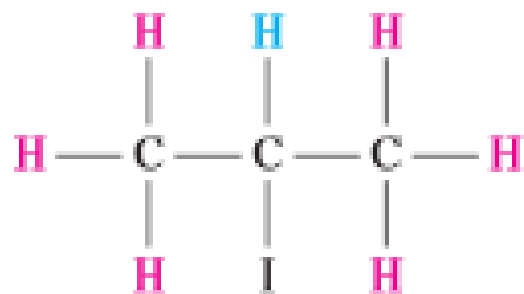
1 H neighbor:
doublet



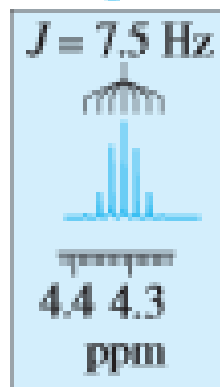
$(\text{CH}_3)_4\text{Si}$



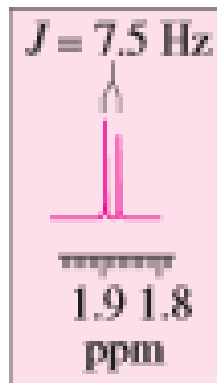
^1H NMR



6 H neighbors:
septet



1 H neighbors:
doublet



6 H

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

1 H



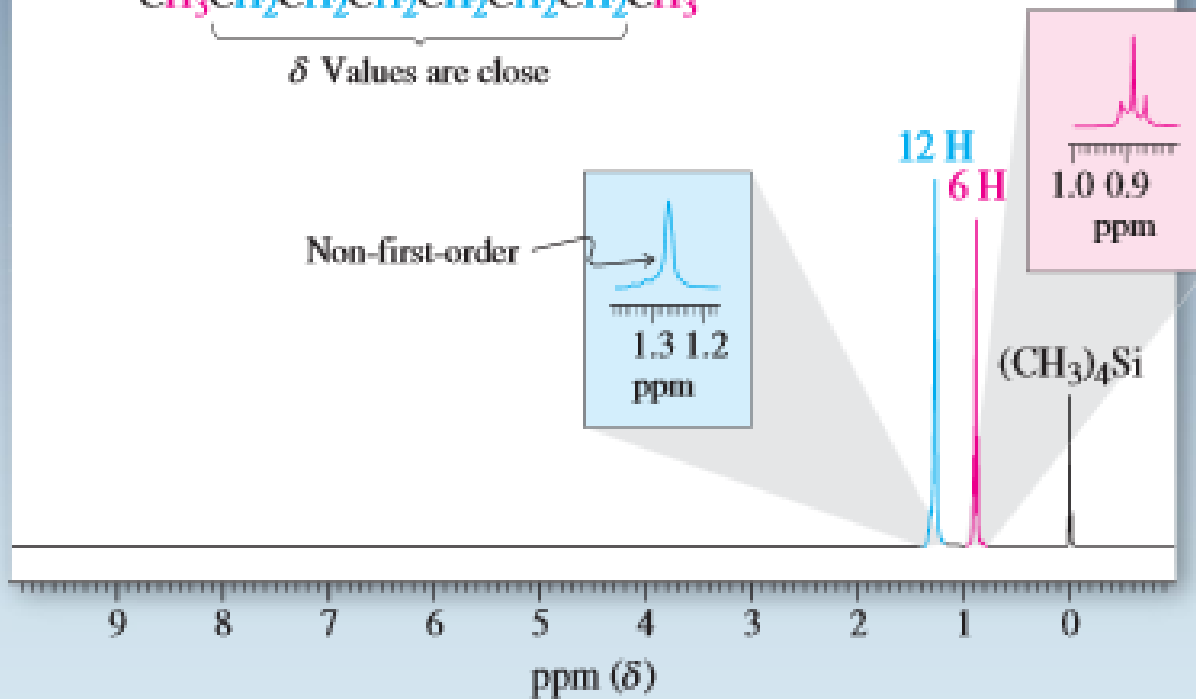
ppm (δ)

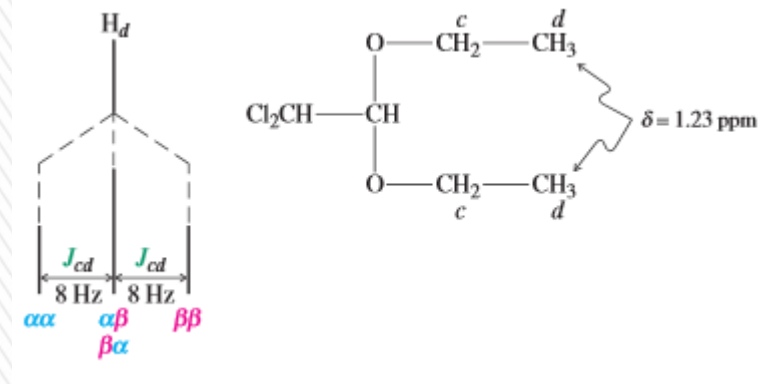
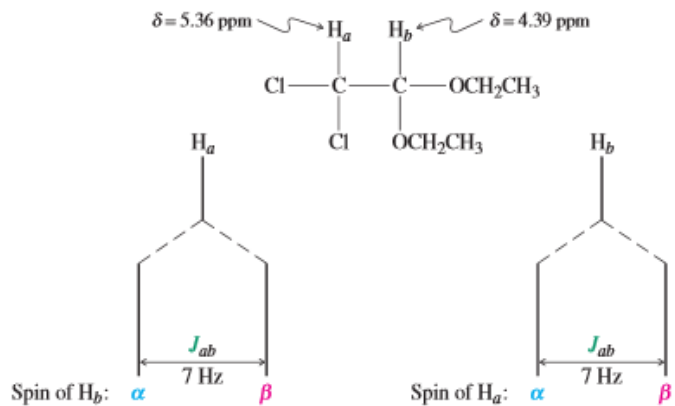
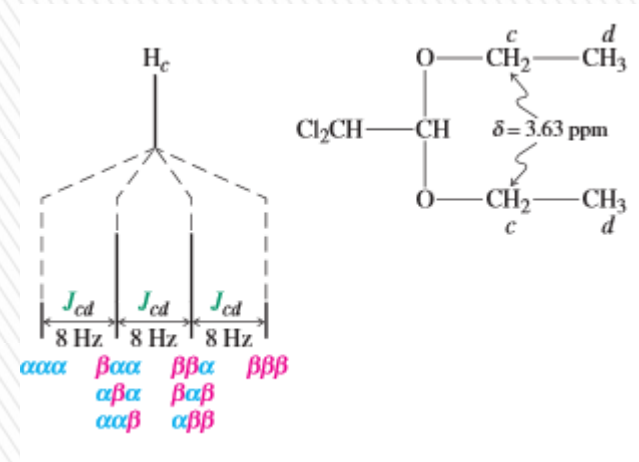
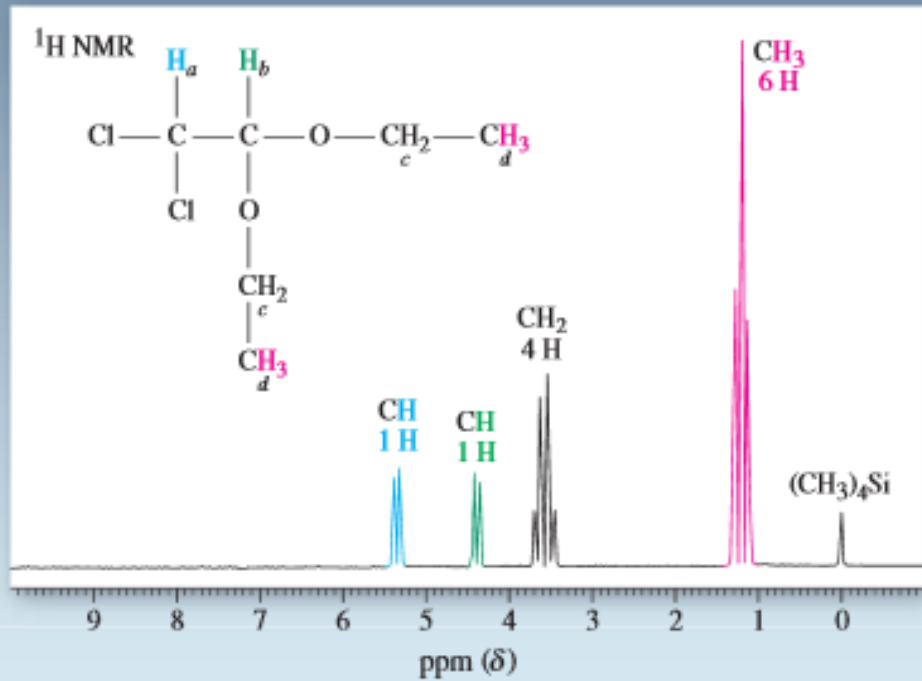


^1H NMR



δ Values are close

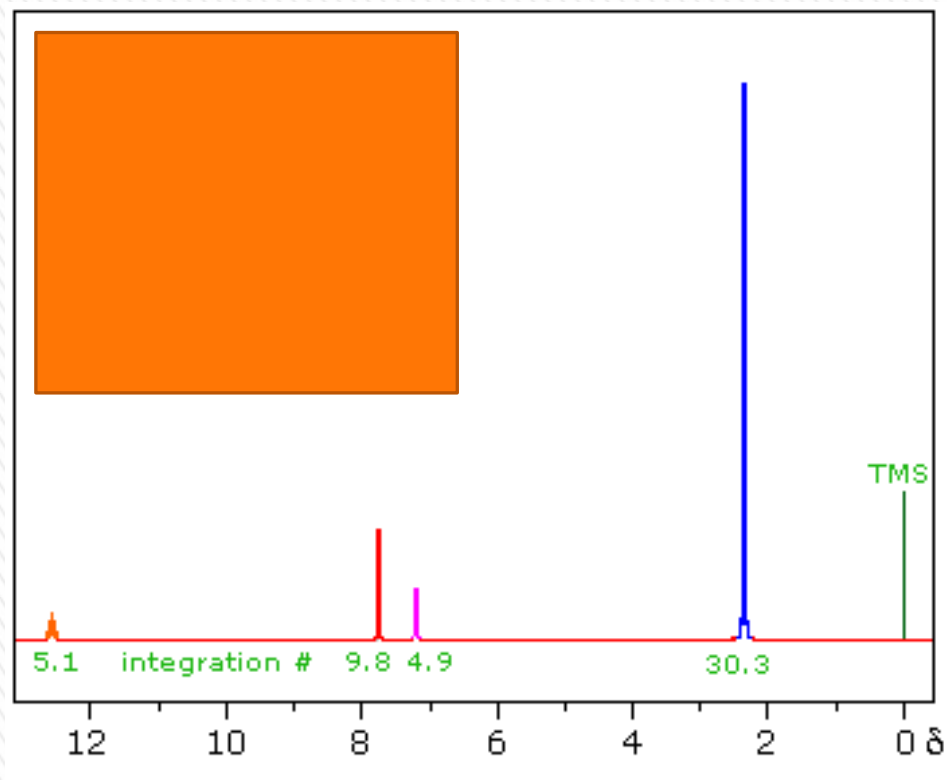
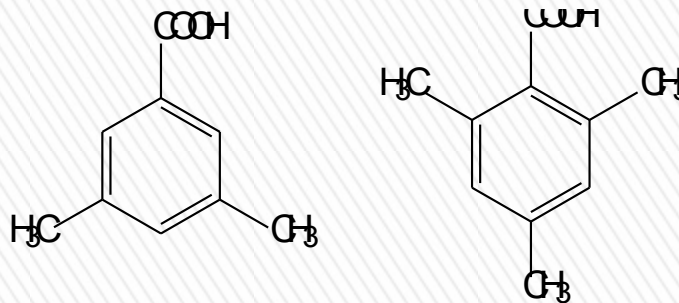


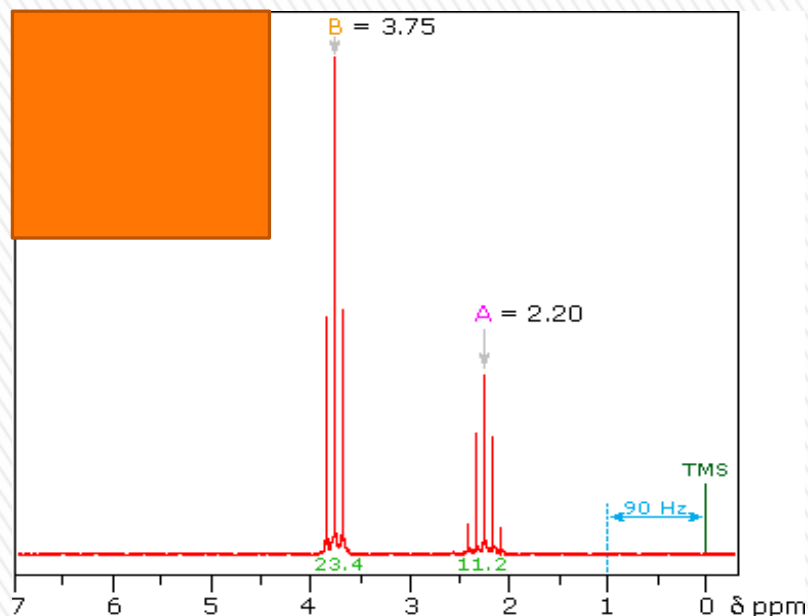


Štěpení signálů:
1,1-dichlor-2,2-diethoxyethan



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



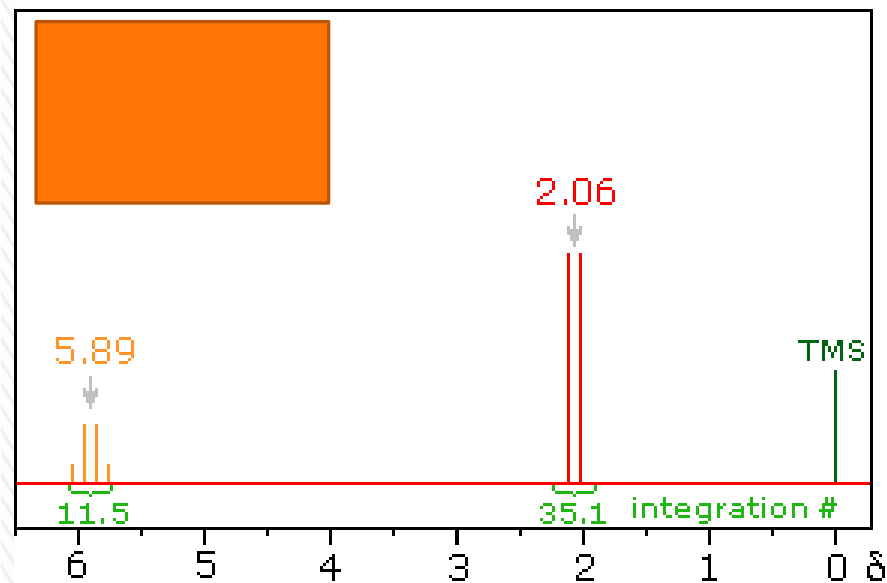
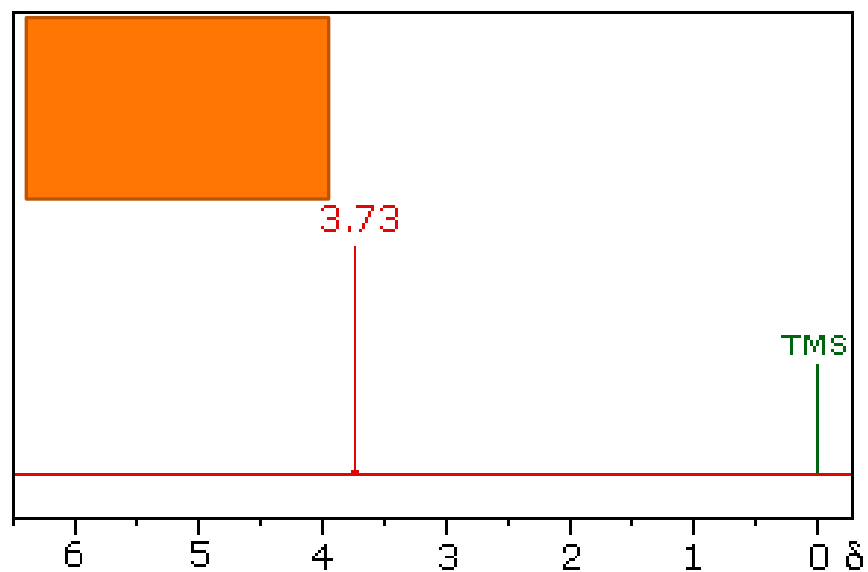


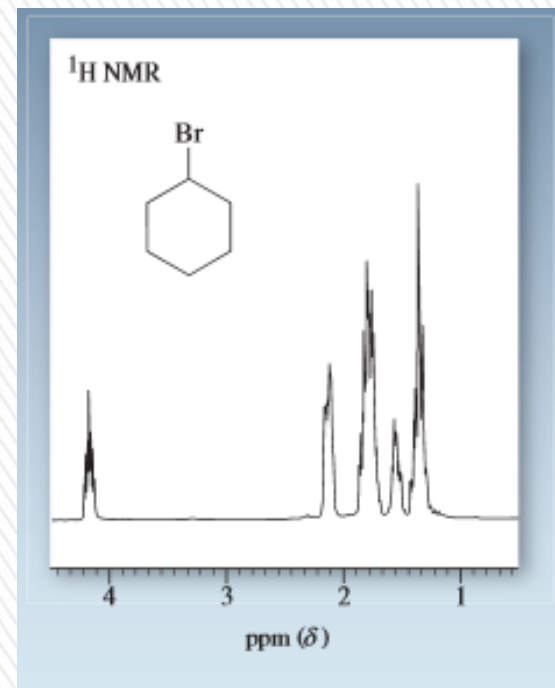
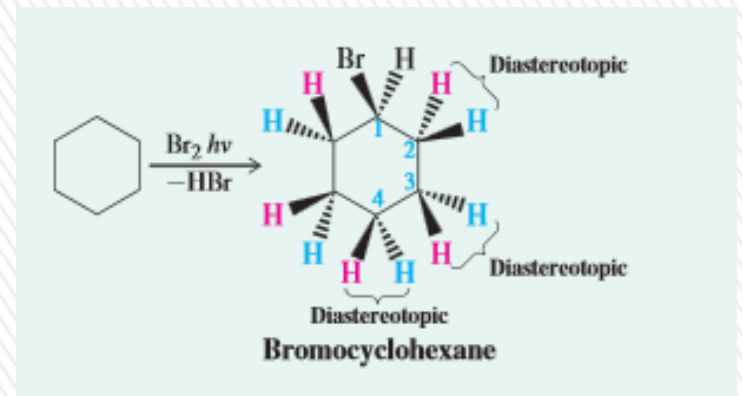
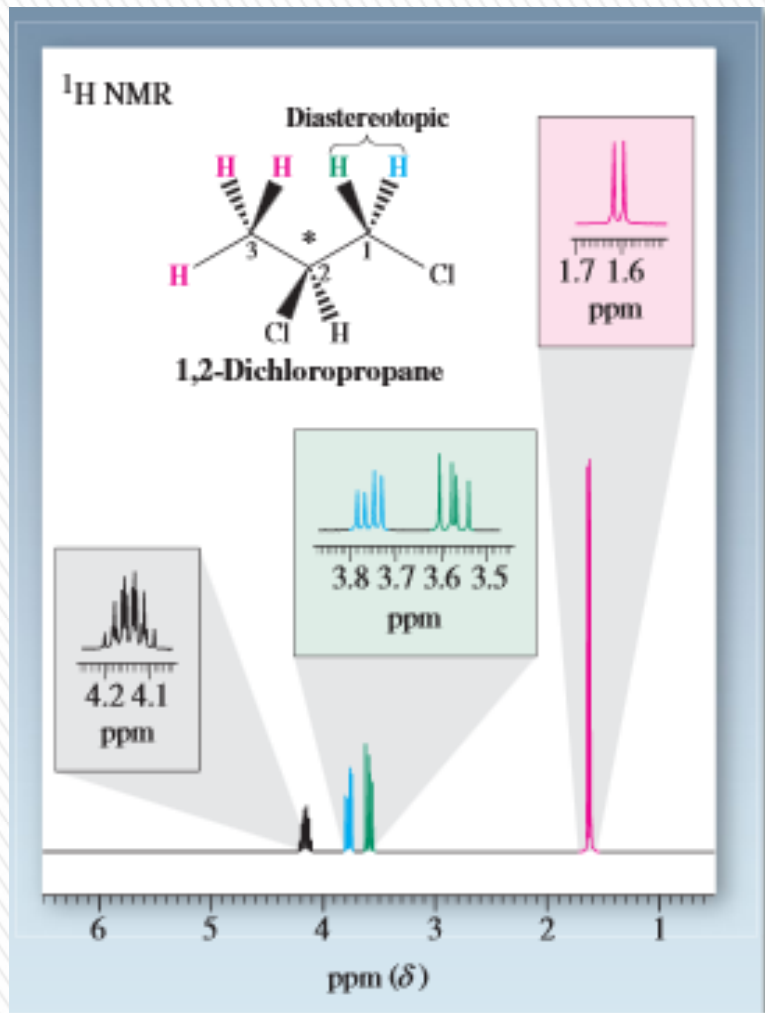
Přiřadte následující ^1H NMR spektra níže uvedeným sloučeninám:

1,1-dichlorethan

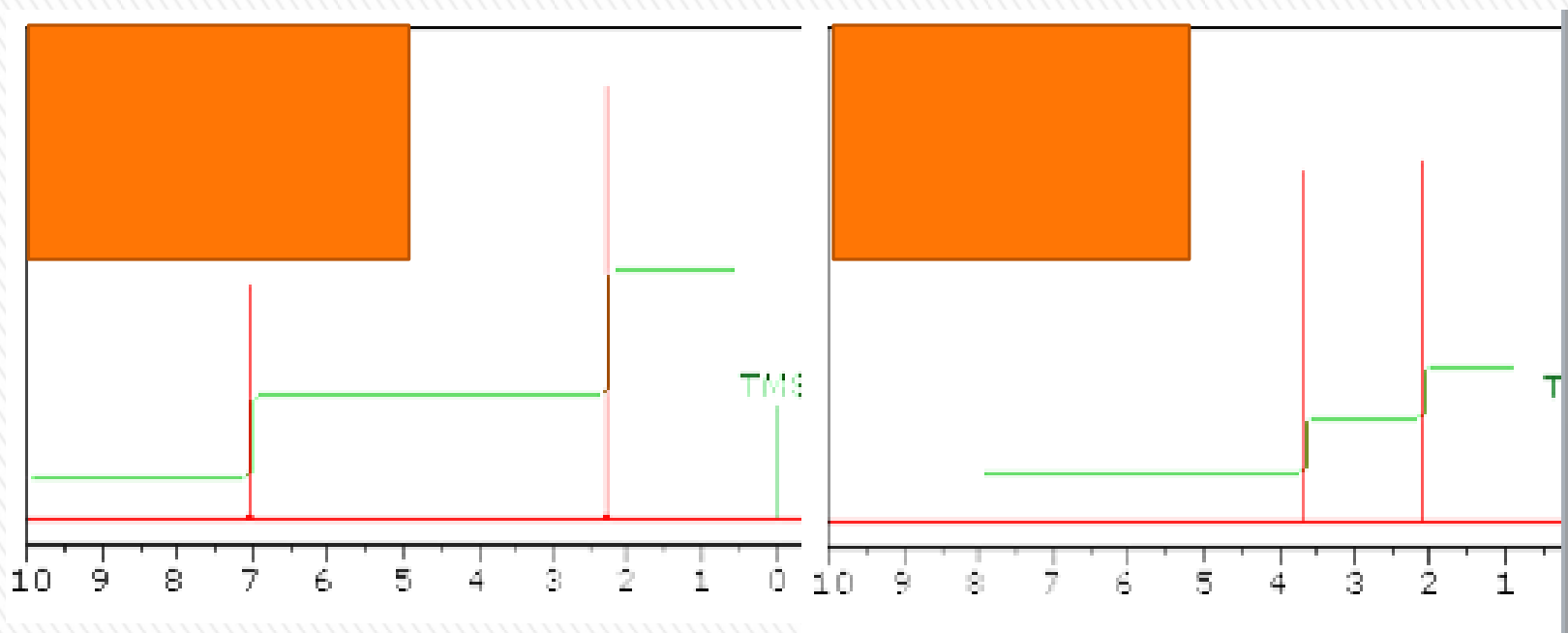
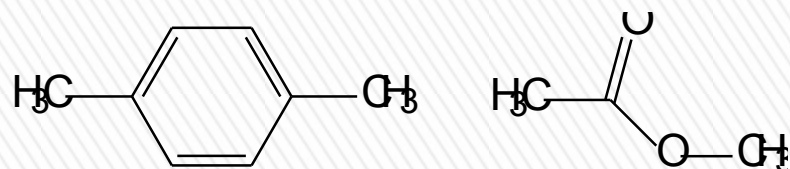
1,2-dichlorethan

1,3-dichlorpropan

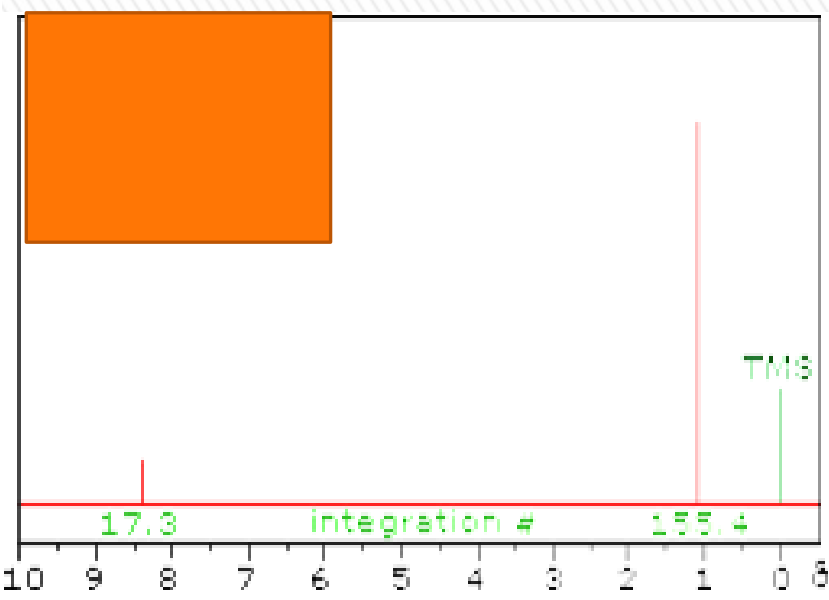
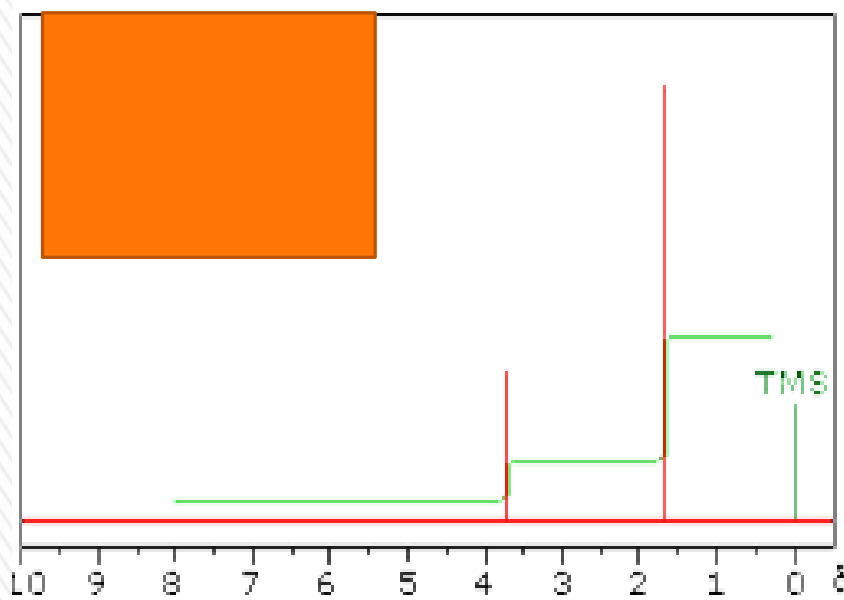
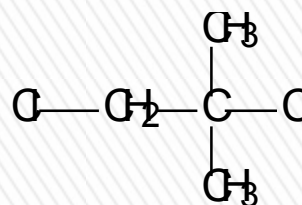
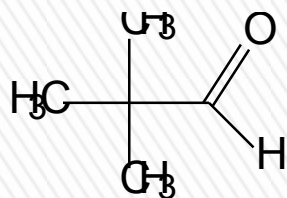




Rozhodněte, které z následujících sloučenin odpovídá níže uvedené ^1H NMR spektrum.

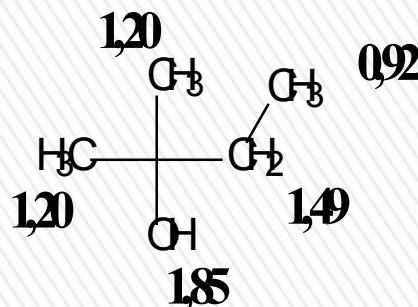
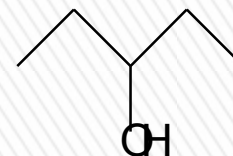
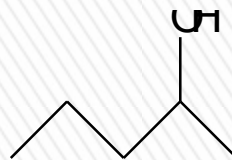


Rozhodněte, které z následujících sloučenin odpovídá níže uvedené ^1H NMR spektrum.

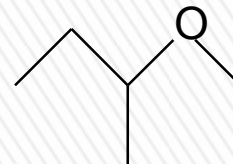
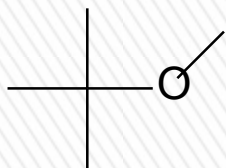


Pokuste se odhadnout, kterému z izomerních alkoholů sumárního vzorce $C_5H_{12}O$ odpovídá následující 1H NMR spektrum.

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



Pokuste se odhadnout, jak byste na základě ^1H NMR spekter rozlišili izomerní ethery sumárního vzorce $\text{C}_5\text{H}_{12}\text{O}$.



» 1,19 (s, 9H)

» 3,21 (s, 3H)

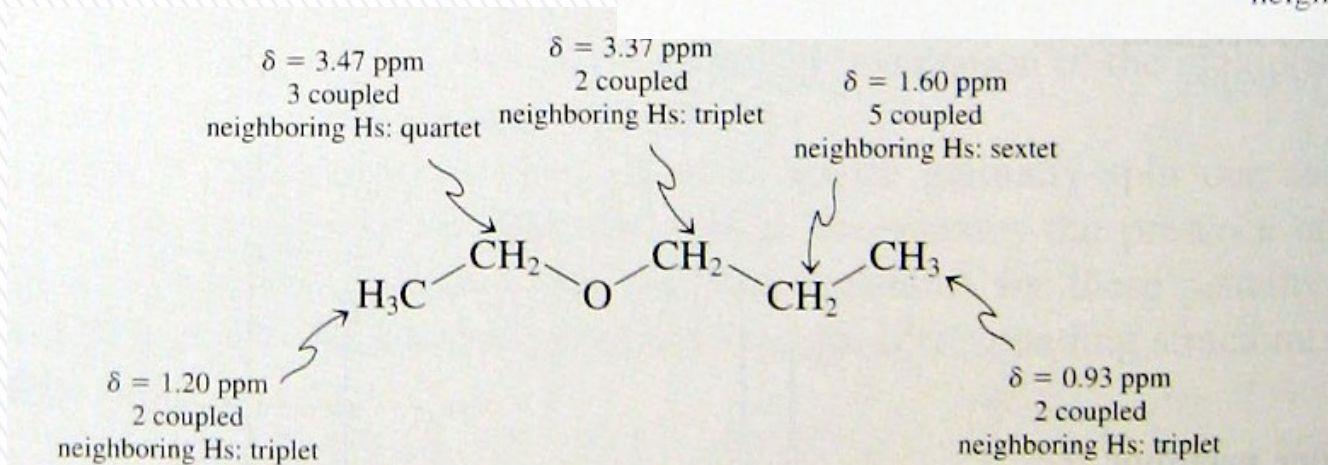
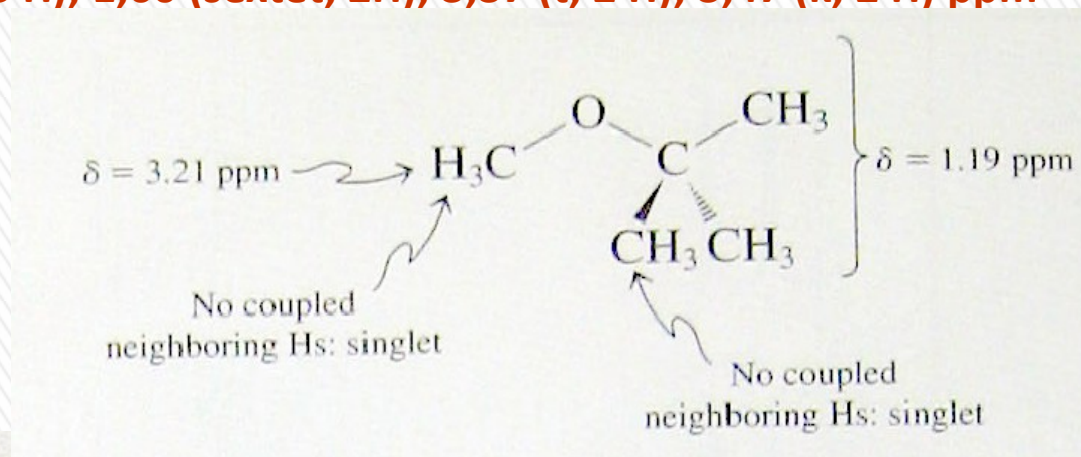


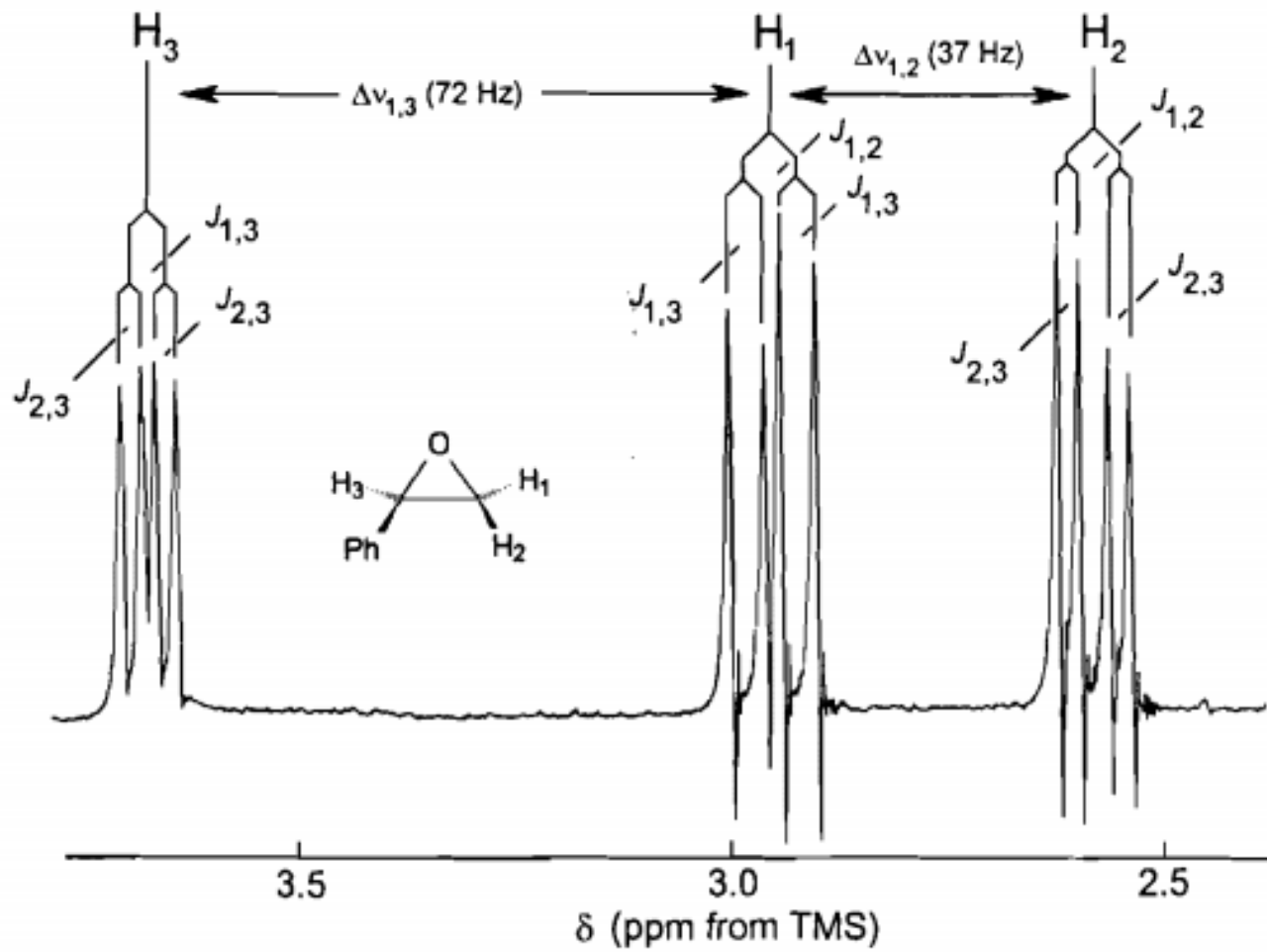
Pokuste se zjistit strukturu dvou izomerů A a B se sumárním vzorcem $C_5H_{12}O$, která mají následující 1H NMR spektra:

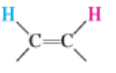
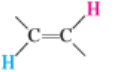
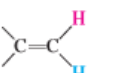
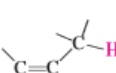
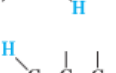

Pokuste se zjistit strukturu dvou izomerů A a B se sumárním vzorcem $C_5H_{12}O$, která mají následující 1H NMR spektra:

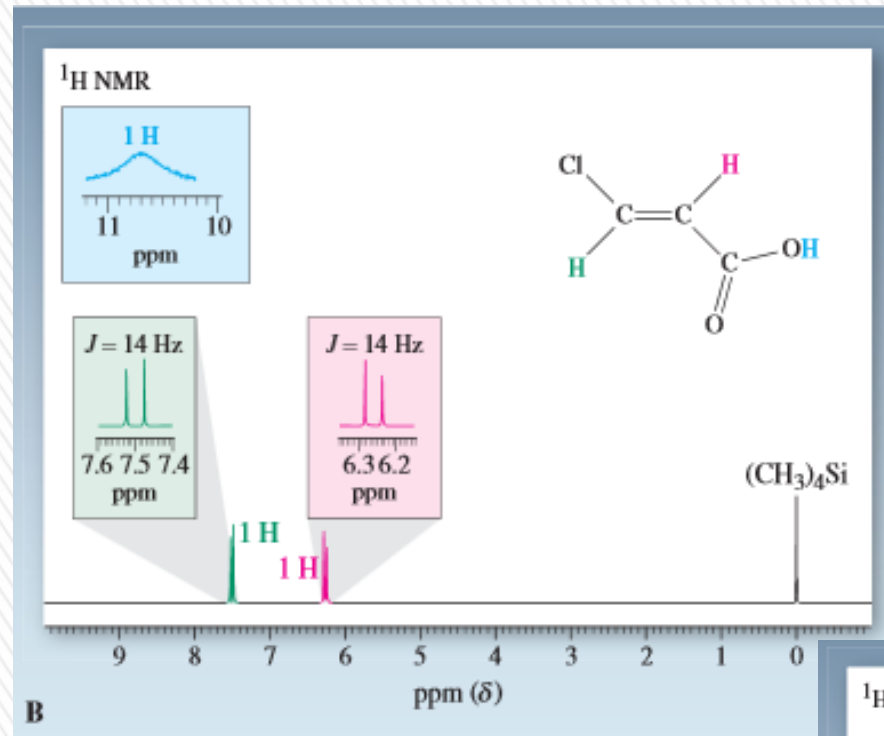
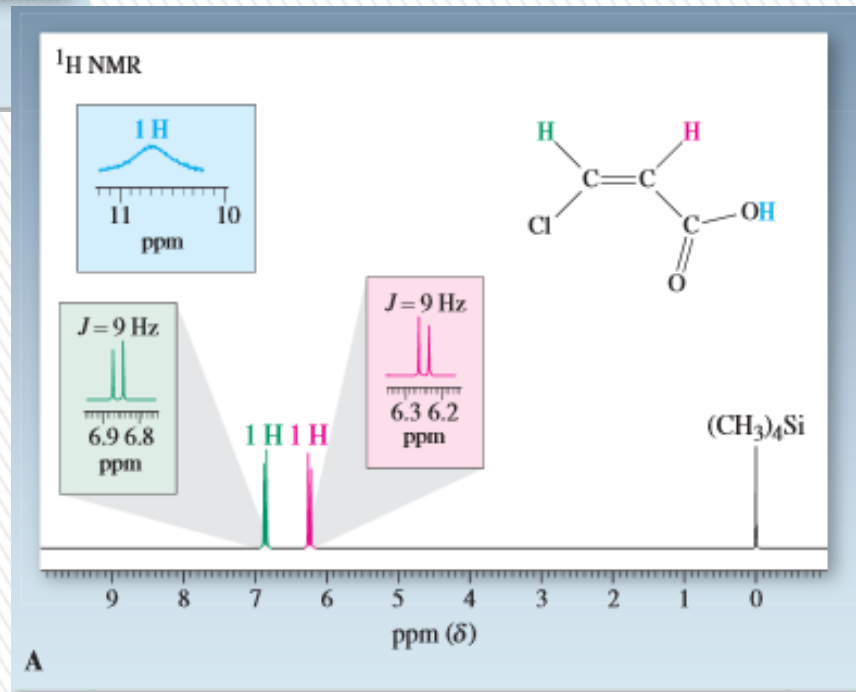
A: $\delta = 1,19$ (s, 9 H); 3,21 (s, 3 H) ppm

B: $\delta = 0,93$ (t, 3 H); 1,20 (t, 3 H); 1,60 (sextet, 2H); 3,37 (t, 2 H); 3,47 (k, 2 H) ppm





	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



^{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 ...


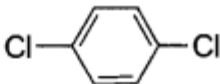
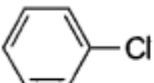
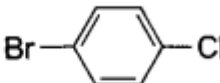
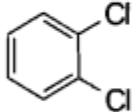
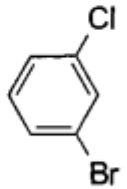
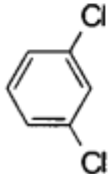
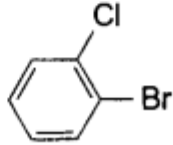
Obvykle tedy v ^{13}C neintegrujeme ... Ale!

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

	1		2
	4		4
	3		6
	4		6



Jaké nepřímé spin-spinové interakce lze očekávat?

Pouze s jádry mající významné přirozené zastoupení izotopů mající jaderný magnetický spin $I = \frac{1}{2}$.

Pozor na izotopově obohacené látky.

Jádro	Spin	Přirozený výskyt	Způsobí multiplicitu signálů ^{13}C jader ?
^1H	1/2	99,99	ANO
^2H	1	0,01	NE (DEUTEROVANÁ ROZPOUŠTĚDLA ANO)
^3H	1/2	-	NE (NEPATRNÝ VÝSKYT)
^{12}C	0	98,93	NE (NULOVÝ JADERNÝ MAGNETICKÝ SPIN)
^{13}C	1/2	1,07	NE (NÍZKÝ VÝSKYT)
^{14}N	1	99,63	NE (KVADRUPÓLOVÝ MOMENT)
^{15}N	1/2	0,37	NE (NÍZKÝ VÝSKYT)
^{16}O	0	99,96	NE (NULOVÝ JADERNÝ MAGNETICKÝ SPIN)
^{19}F	1/2	100	ANO
^{31}P	1/2	100	ANO

$\text{CH}_3 \rightarrow$ kvartet

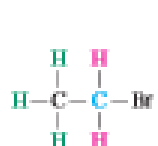
$\text{CH}_2 \rightarrow$ triplet (dublet dubletů)

$\text{CH} \rightarrow$ dublet

$\text{C} \rightarrow$ singlet

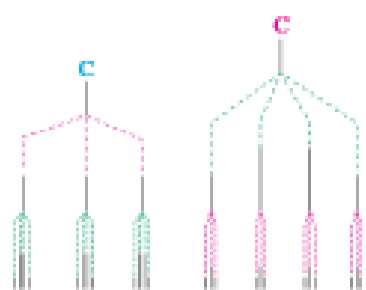


¹³C NMR



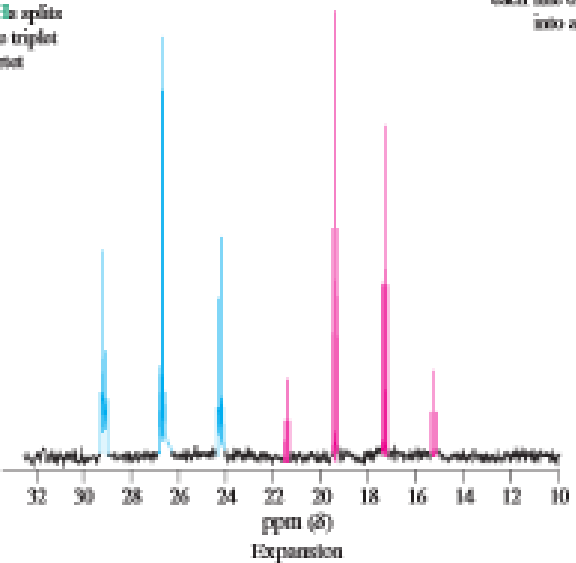
C is coupled to 2 attached **H**: triplet with a large *J*

A second, smaller coupling to the neighboring 3 **H**s splits each line of the triplet into a quartet

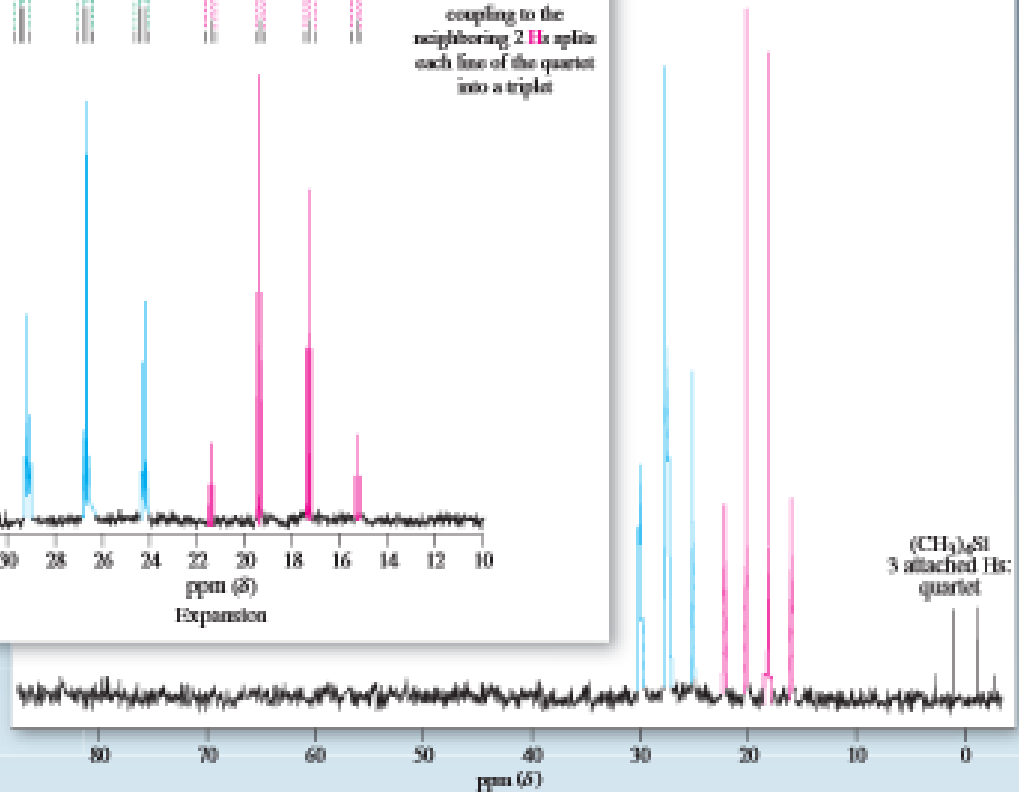


C is coupled to 3 attached **H**: quartet with a large *J*

A second, smaller coupling to the neighboring 2 **H**s splits each line of the quartet into a triplet



CH3CH2Br





A Normal ^{13}C NMR spectrum

B Spectrum showing only CH_3 peaks

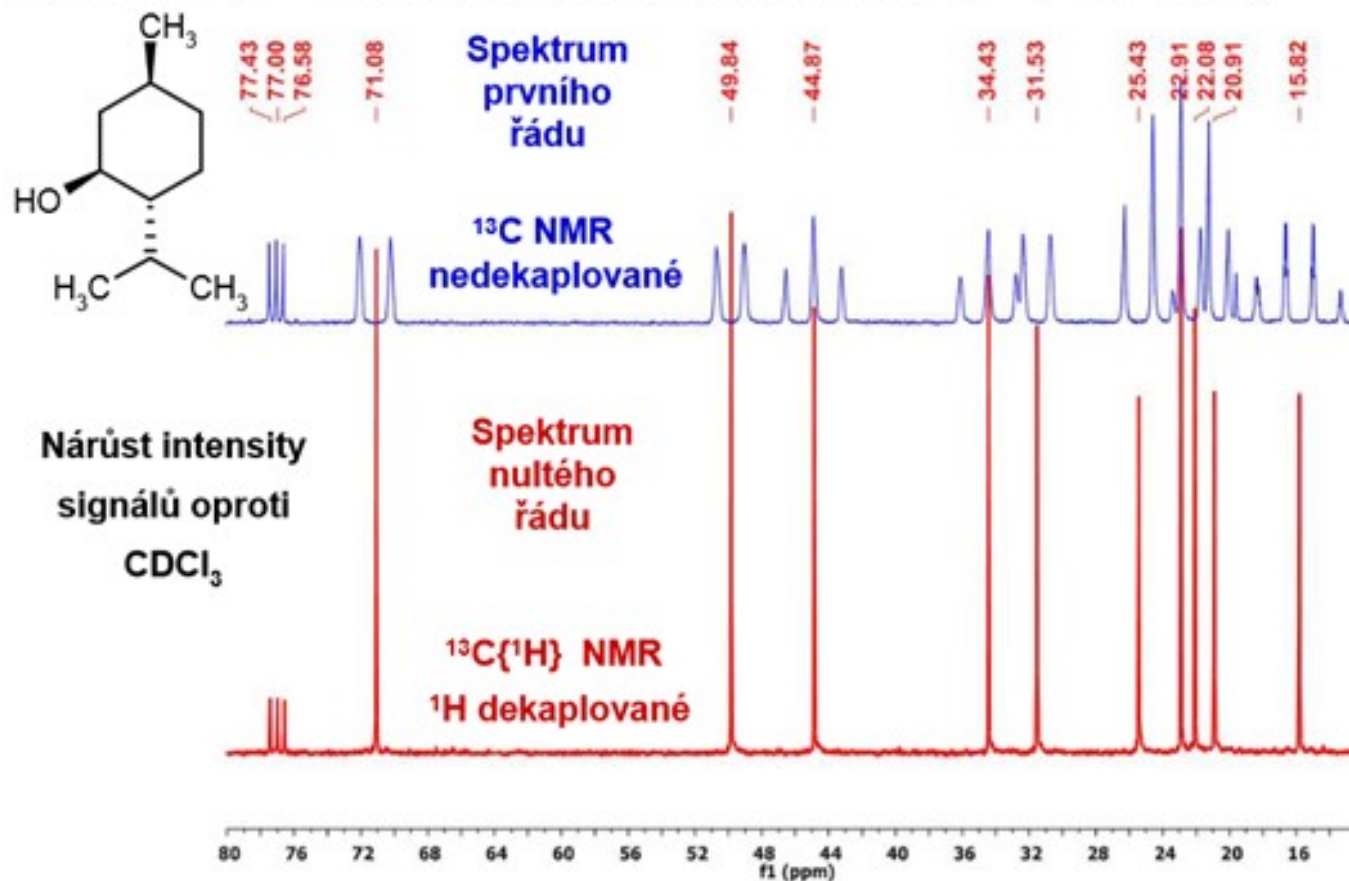
C Spectrum showing only CH_2 peaks

D Spectrum showing only CH peaks

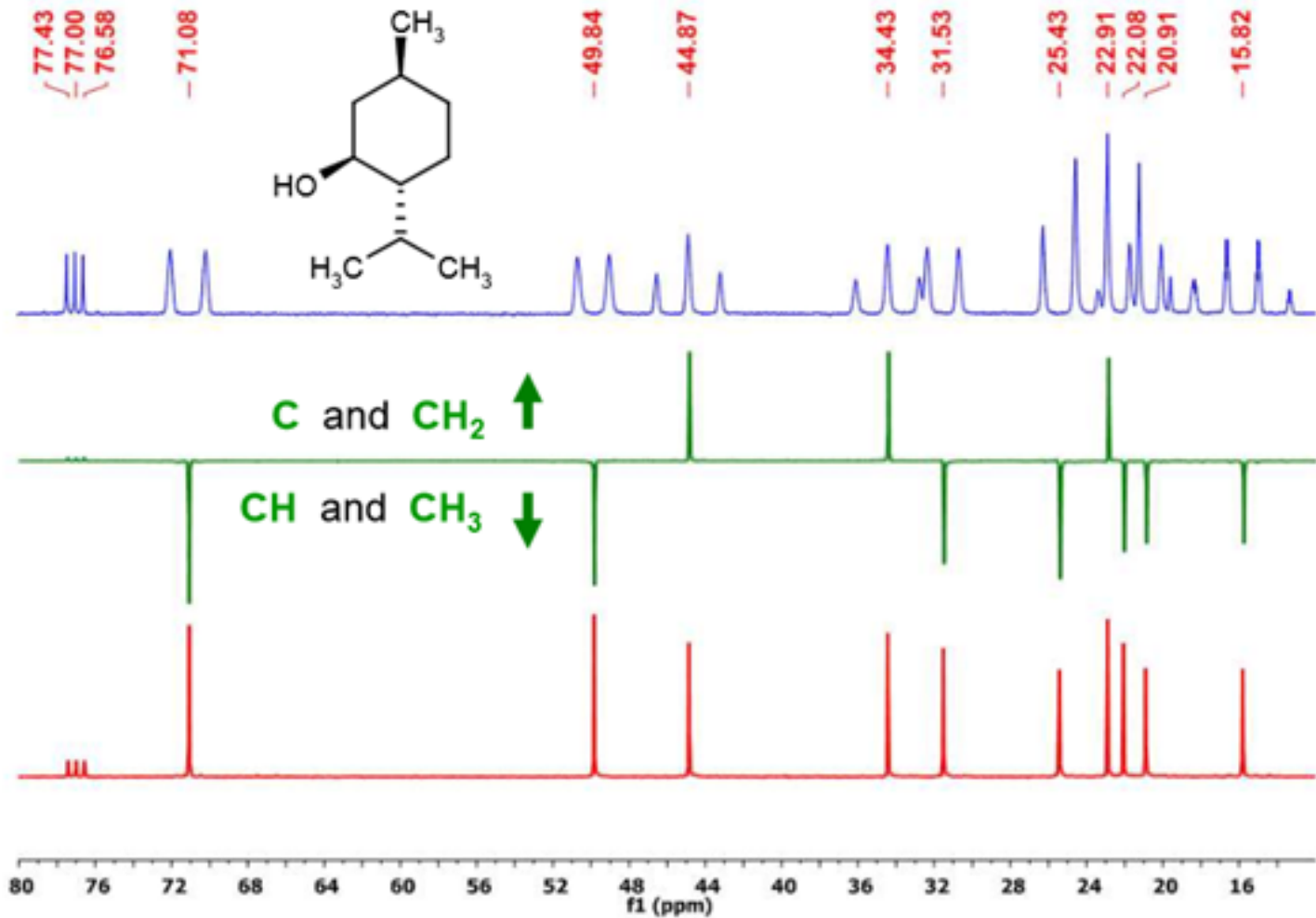


^{13}C NMR ... Šumový (širokopásmový) dekapling

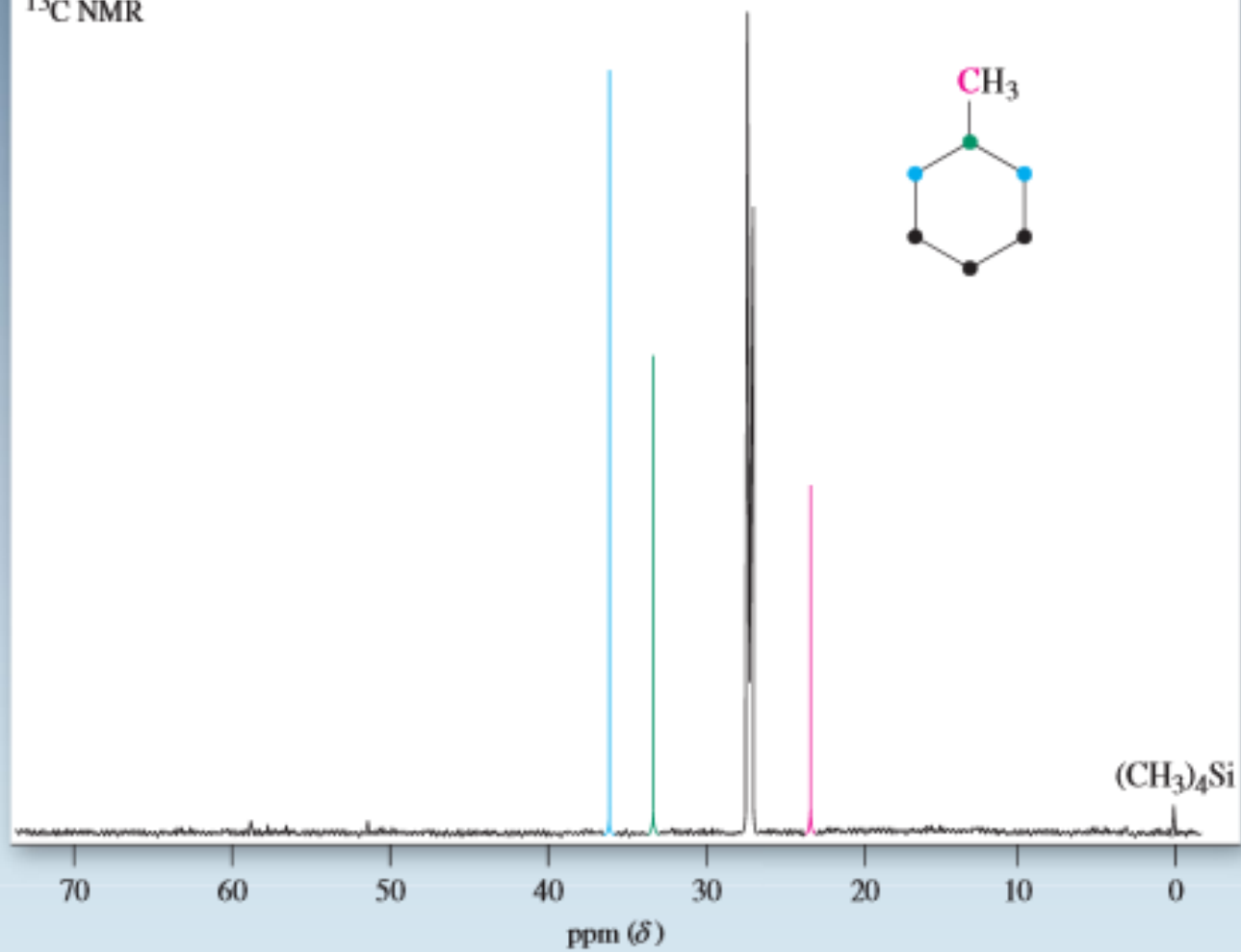
Standardně se ^{13}C NMR spektra měří s dekaplingem ^1H (^{19}F , ^{15}N , ...)

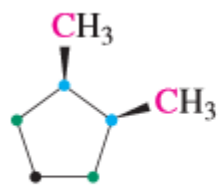
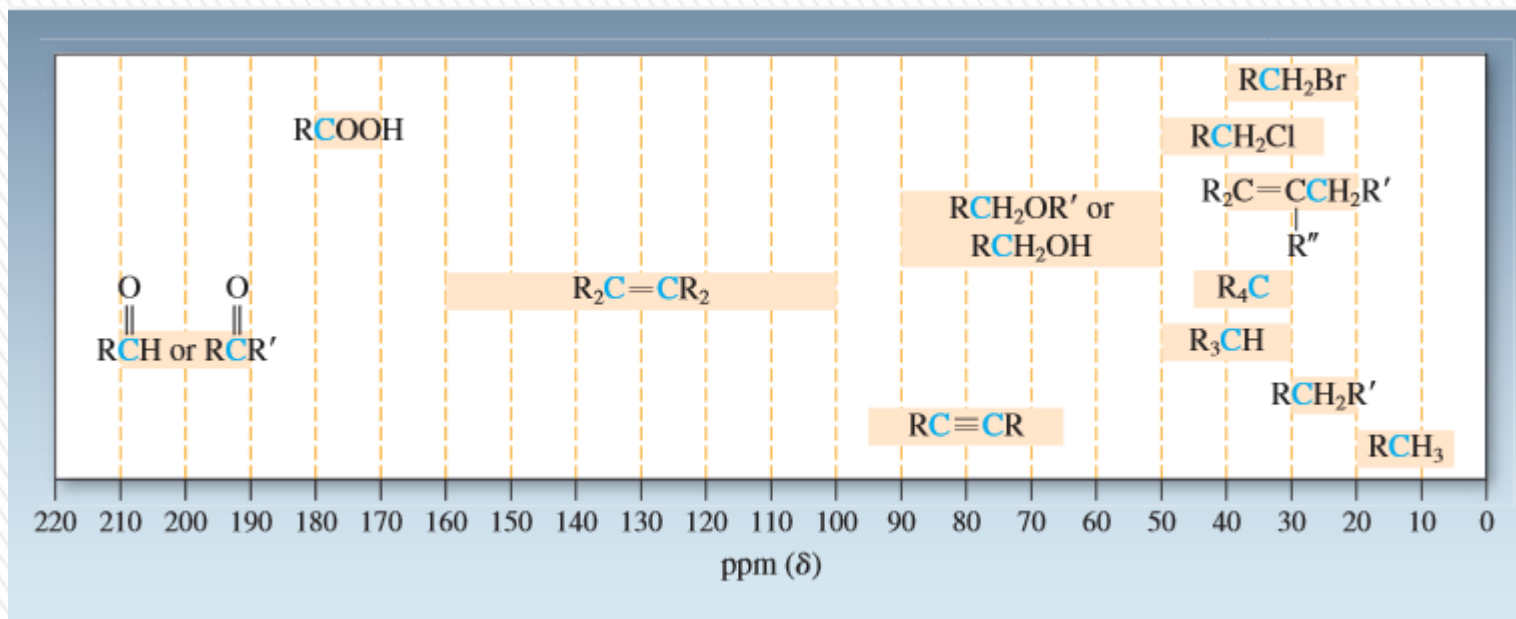


^{13}C NMR decoupling OFF or ON, and APT

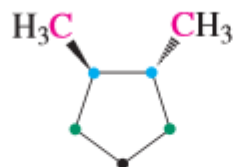


^{13}C NMR

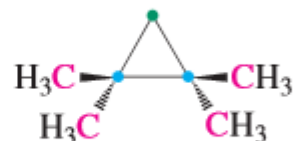




Four peaks



Four peaks

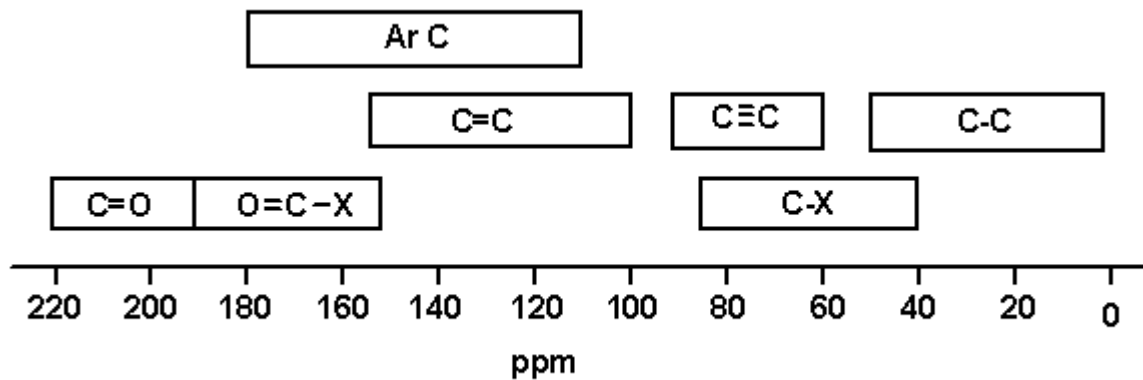


Three peaks

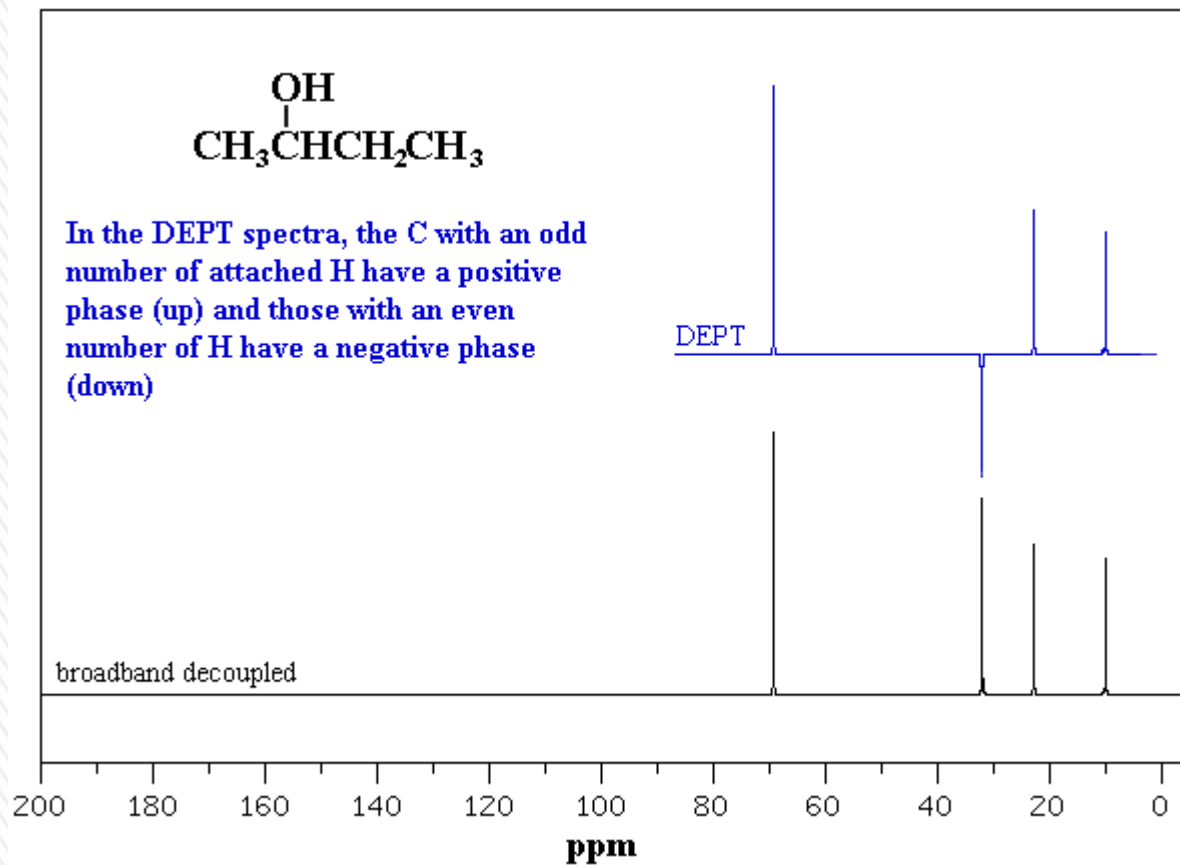


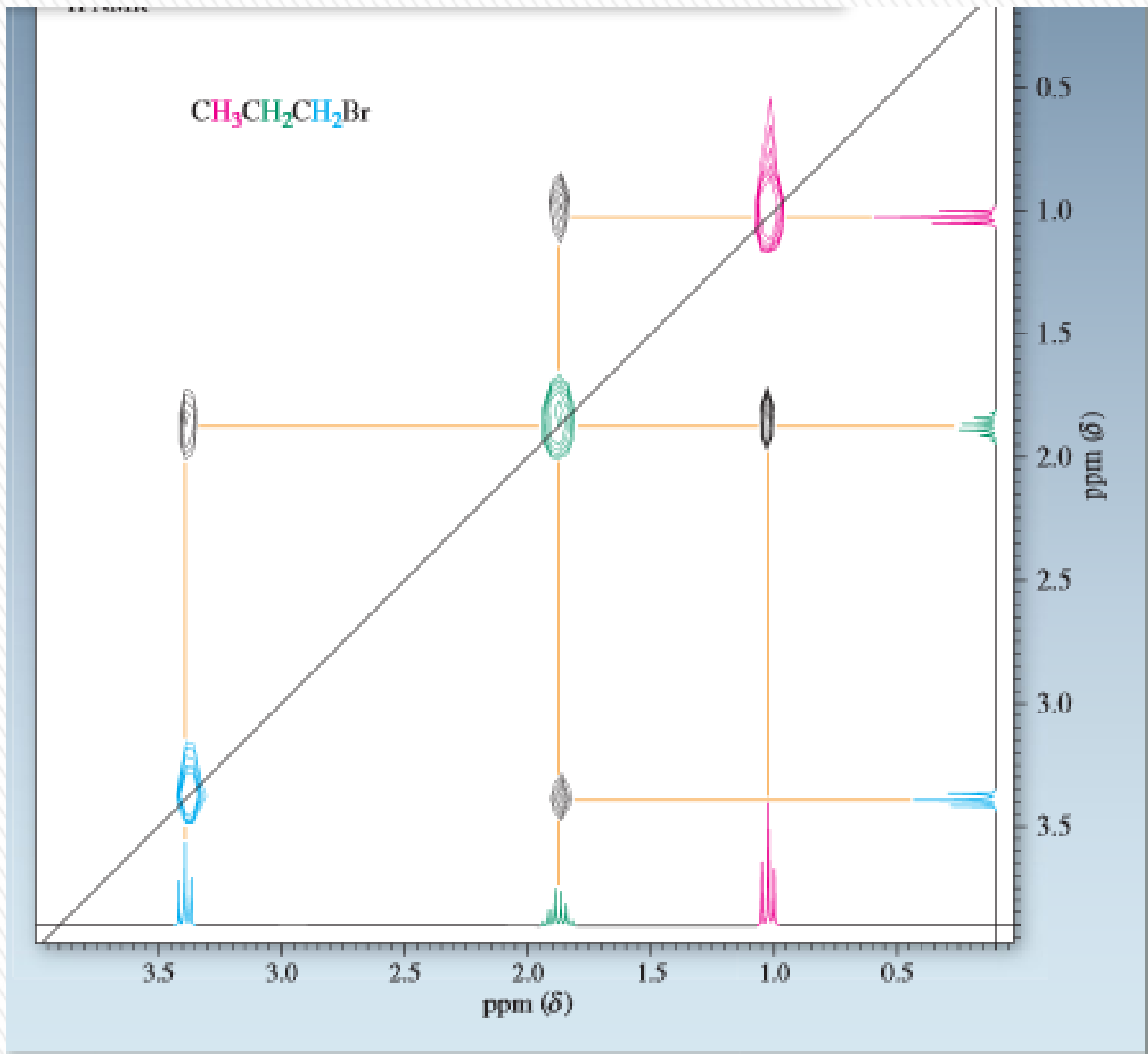
One peak





In the DEPT spectra, the C with an odd number of attached H have a positive phase (up) and those with an even number of H have a negative phase (down)



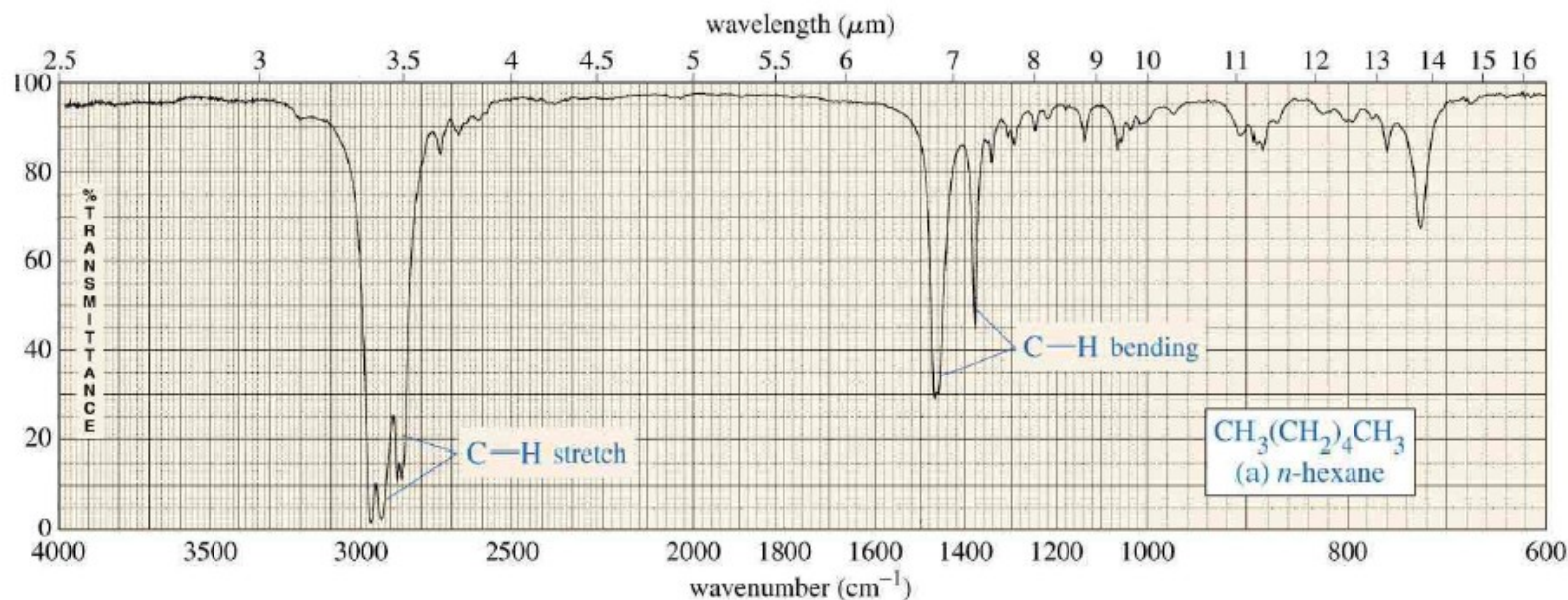
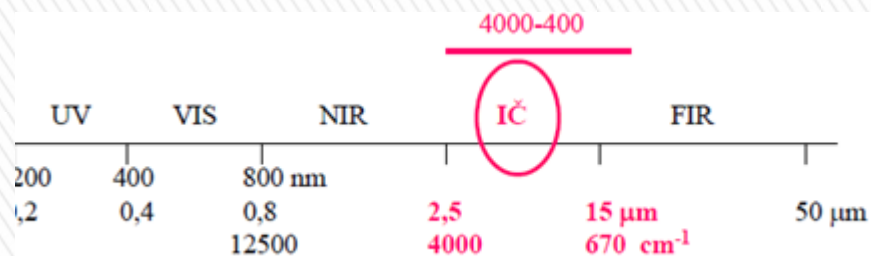




Infračervená spektroskopie

vibračně – rotační spektroskopie

v organické chemii – důkaz přítomnosti funkčních skupin



valenční ν - změna délky vazby

symetrická ν_s

antisymetrická ν_{as}

deformační δ - změna valenčního úhlu

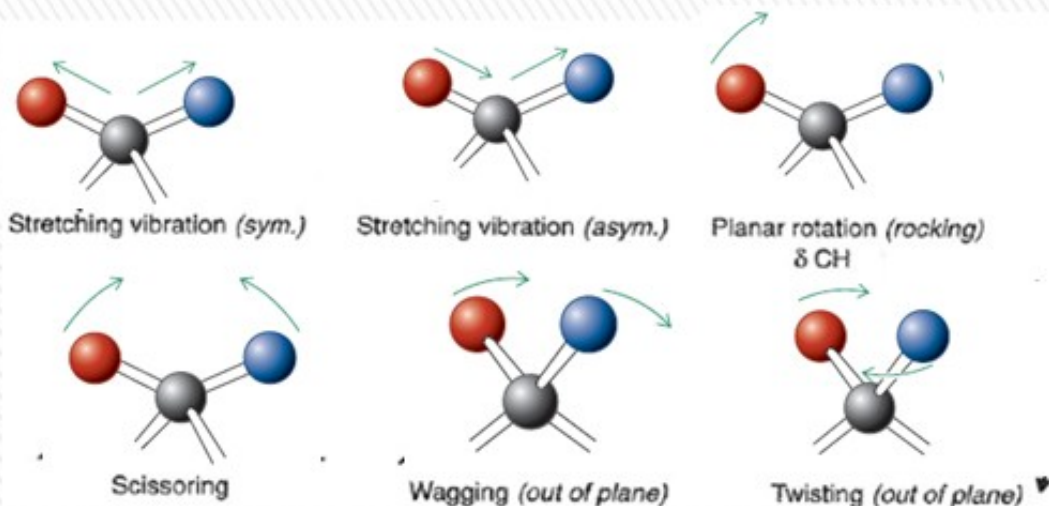
mají nižší energii

ve spektru leží při nižších frekvencích než vibrace

valenční

Vibrace lokalizované do určité části molekuly, která vibruje relativně nezávisle na zbytku molekuly se nazývají **charakteristické vibrace** →

charakteristické frekvence



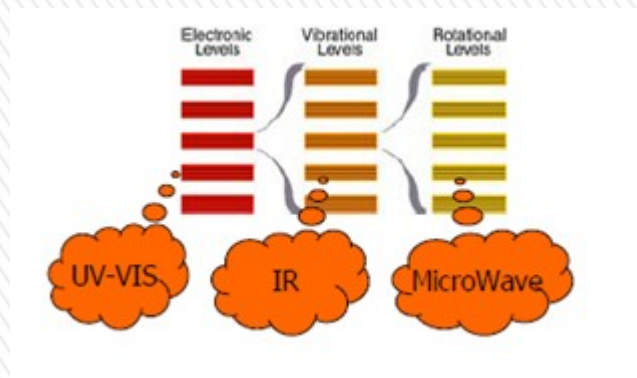
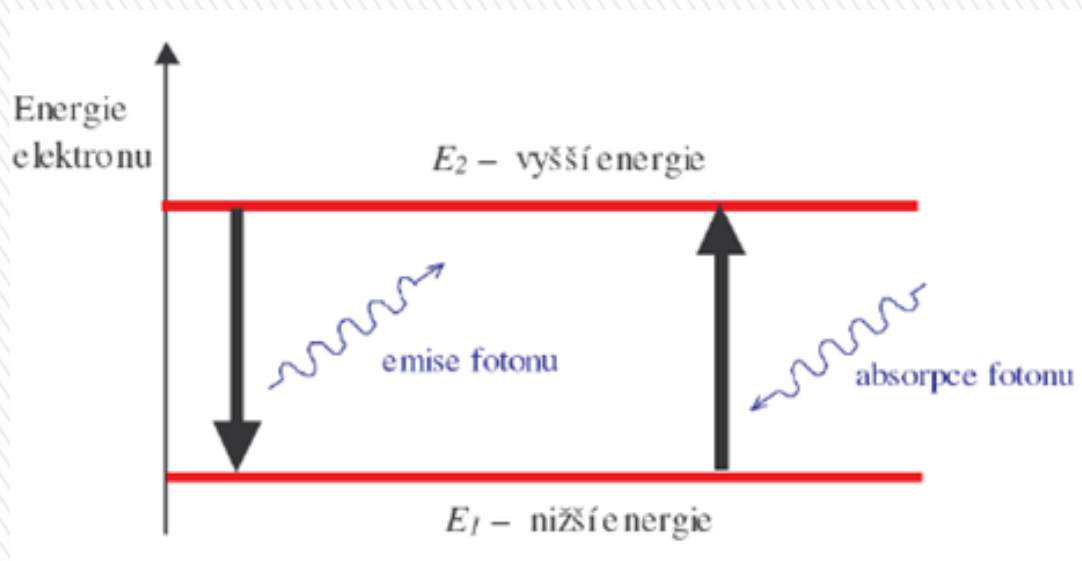
Valenční vibrace (ν): stretching – symetrická a asymetrická

Deformační rovinné (δ): rocking – kyvadlová; scissoring – nůžková

Deformační mimorovinné (γ): wagging – vějířová; twisting – krouživá



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



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

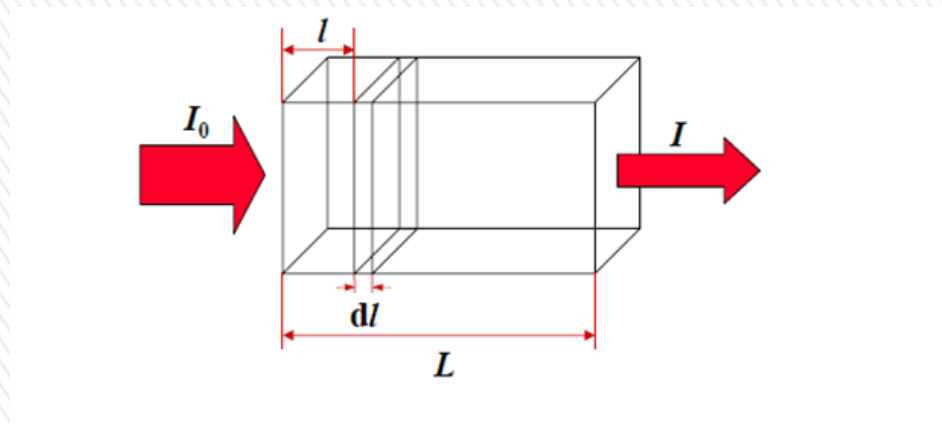


Transmittance T (propustnost) hodnoty 0 – 1 (0 – 100%)

$$T = I / I_0$$

T = 0 prostředí světlo nepropouští vůbec

T = 1 prostředí propouští všechno světlo



Absorbance

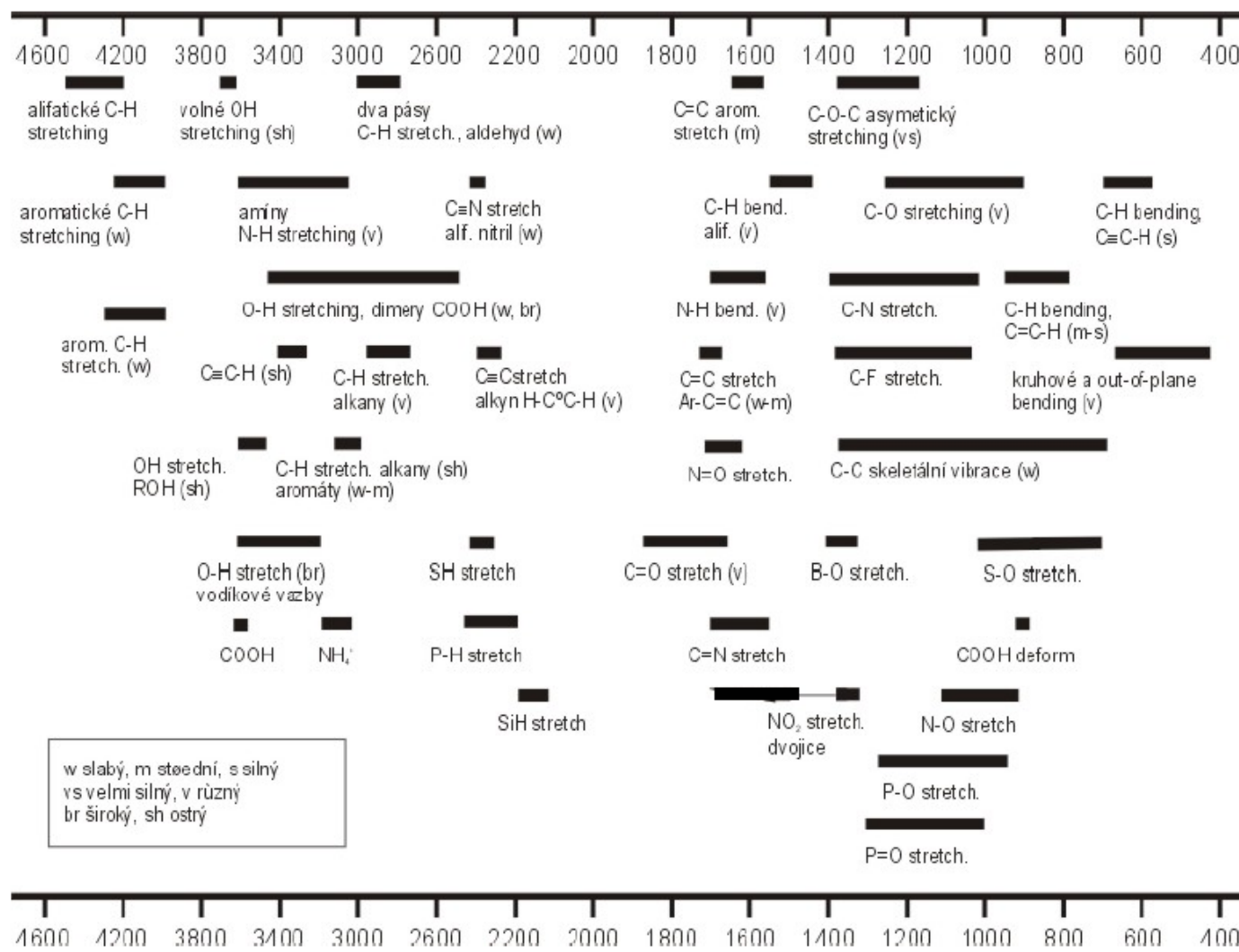
$$A = -\log T$$

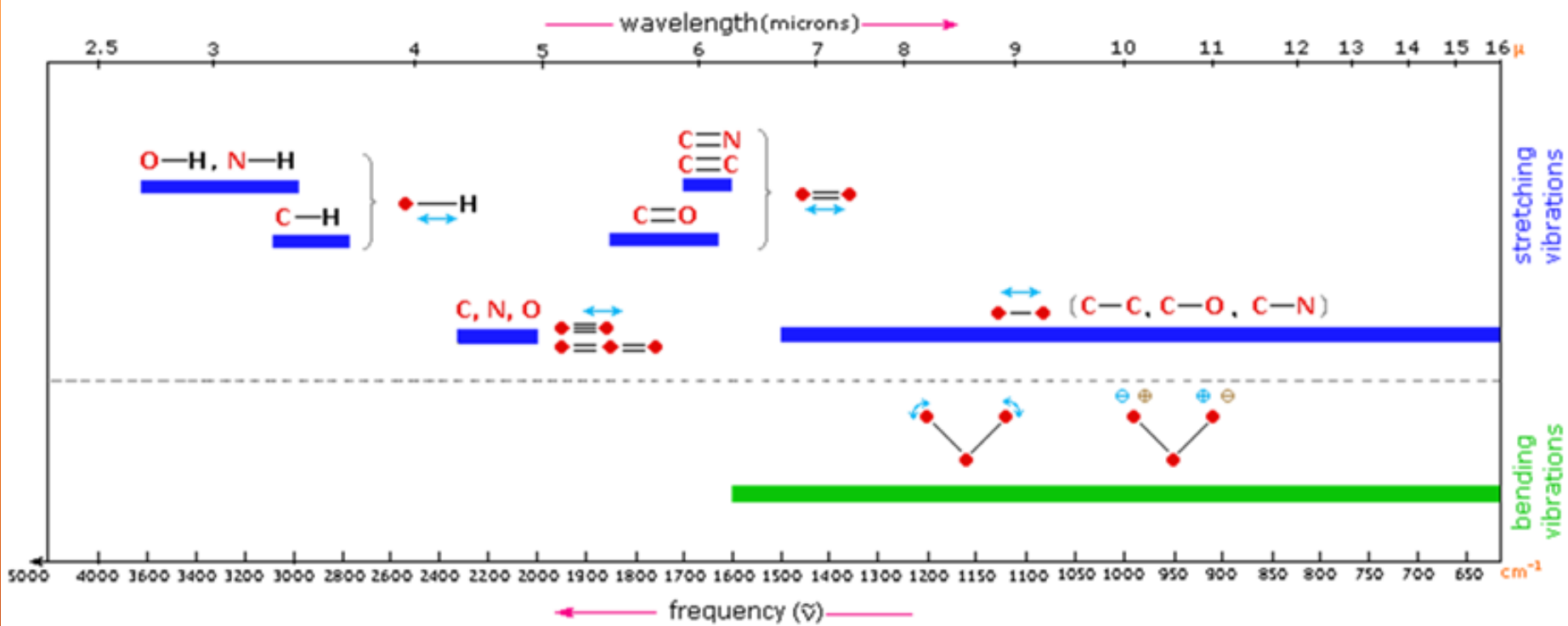
$$A = \epsilon \cdot l \cdot c$$

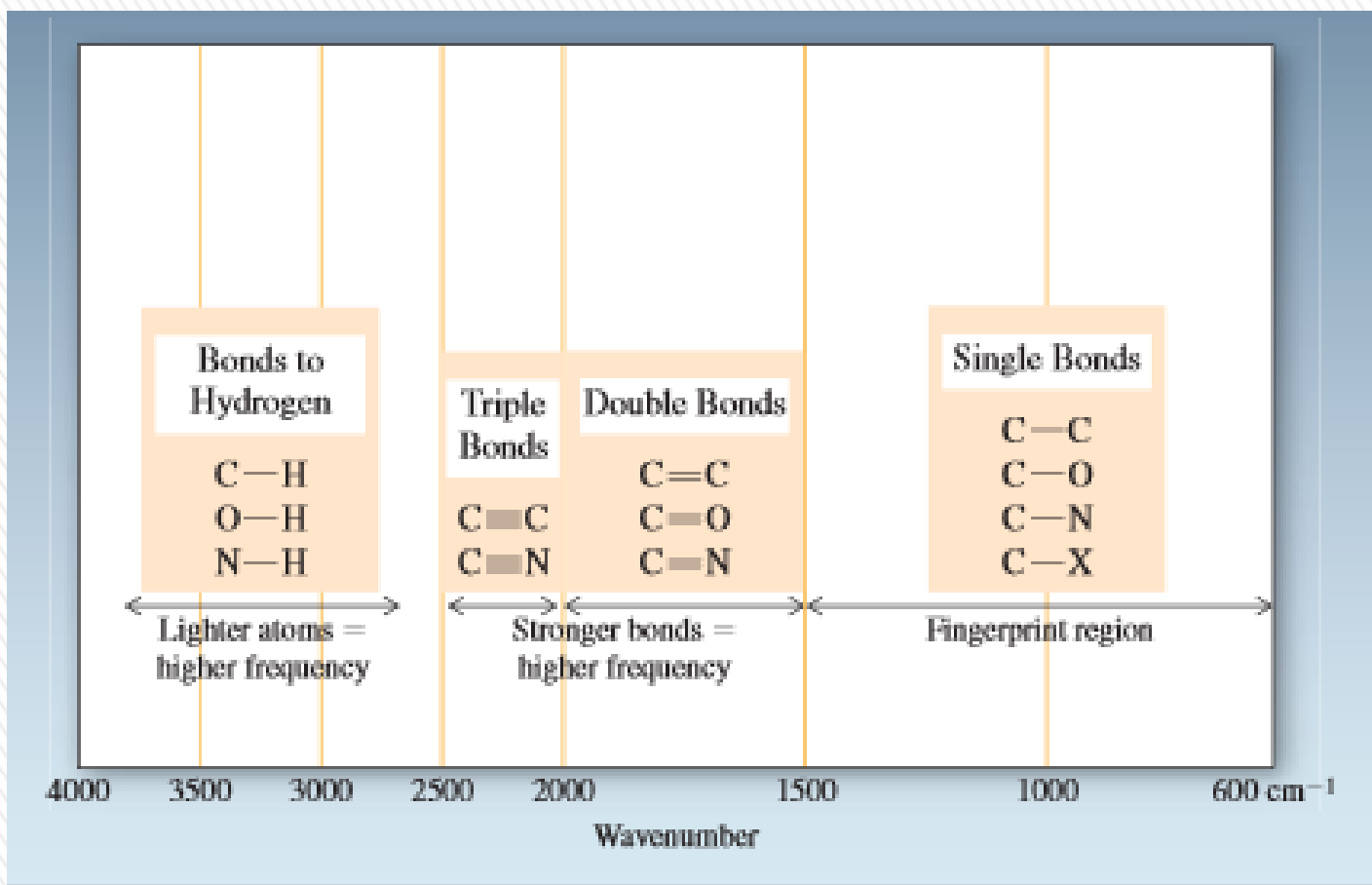


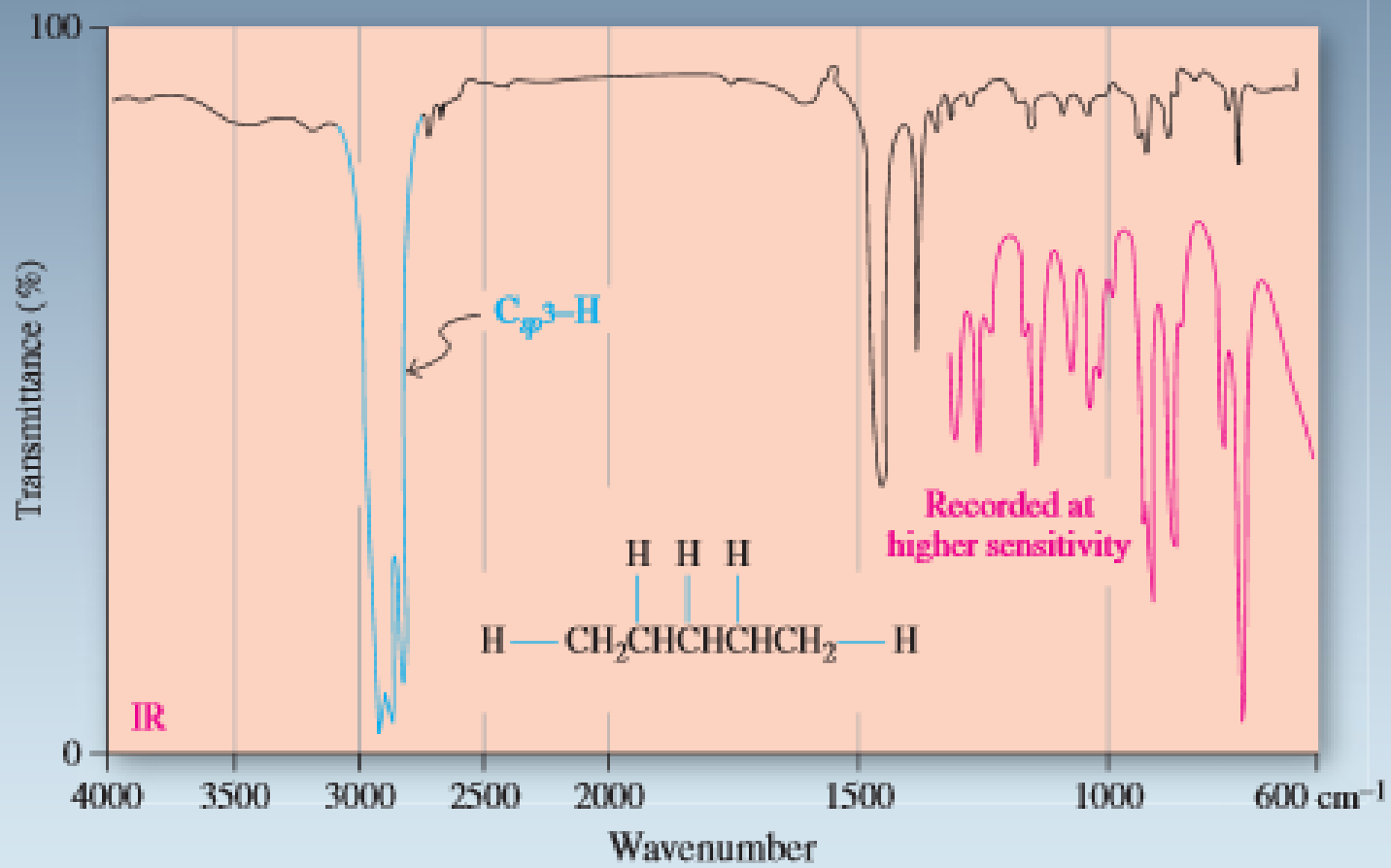
» Charakteristické vibrace

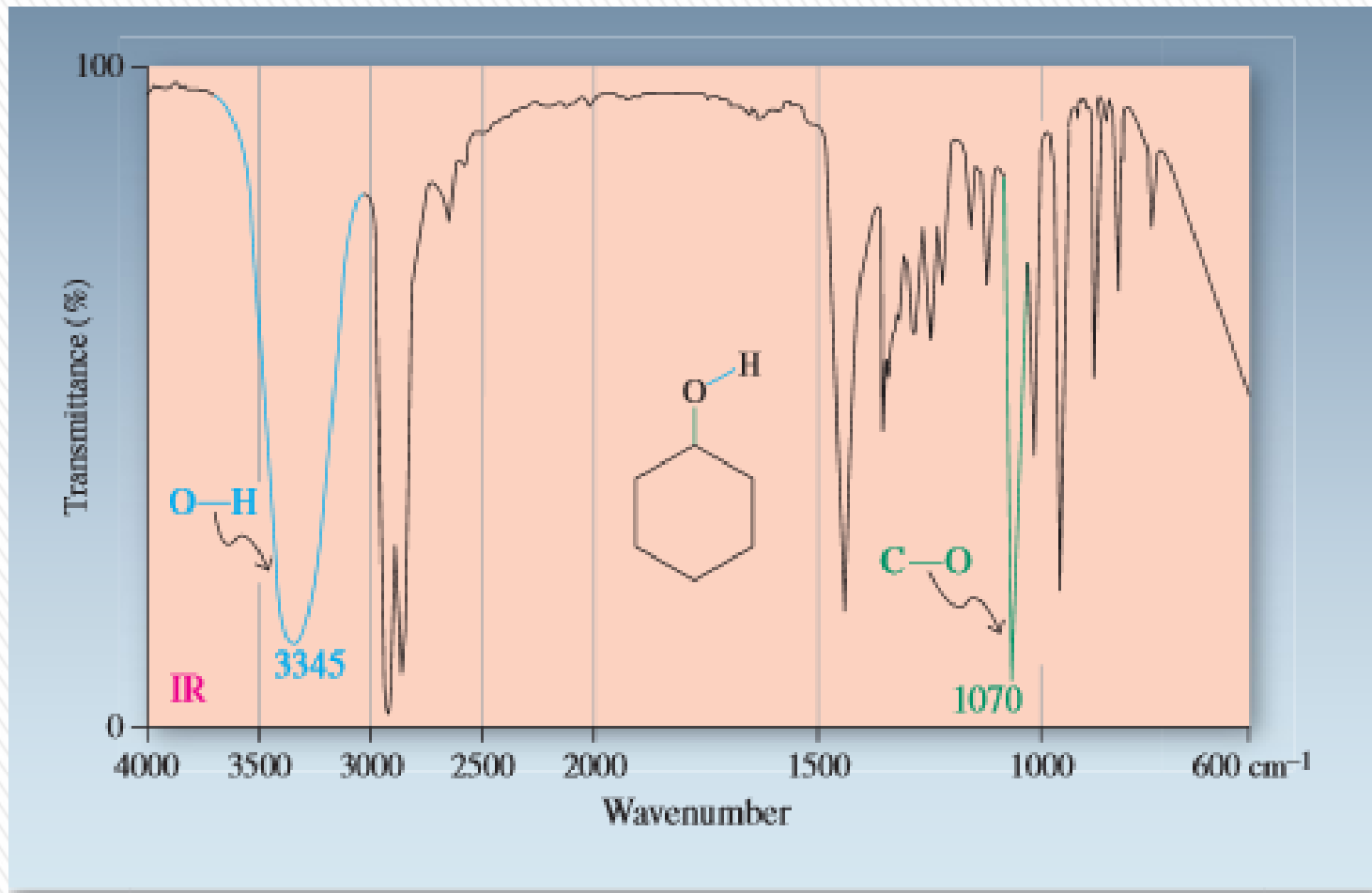
cm⁻¹

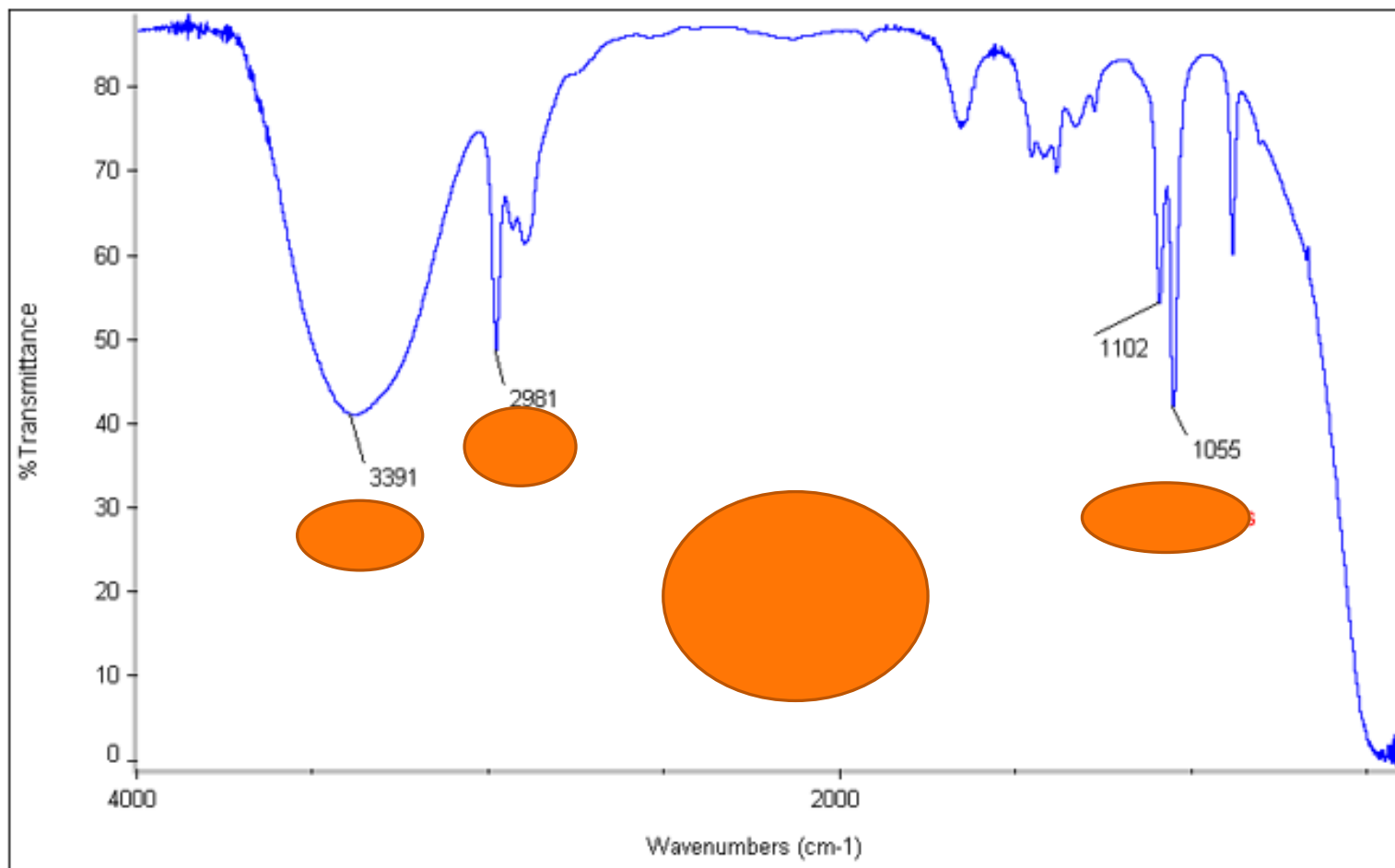


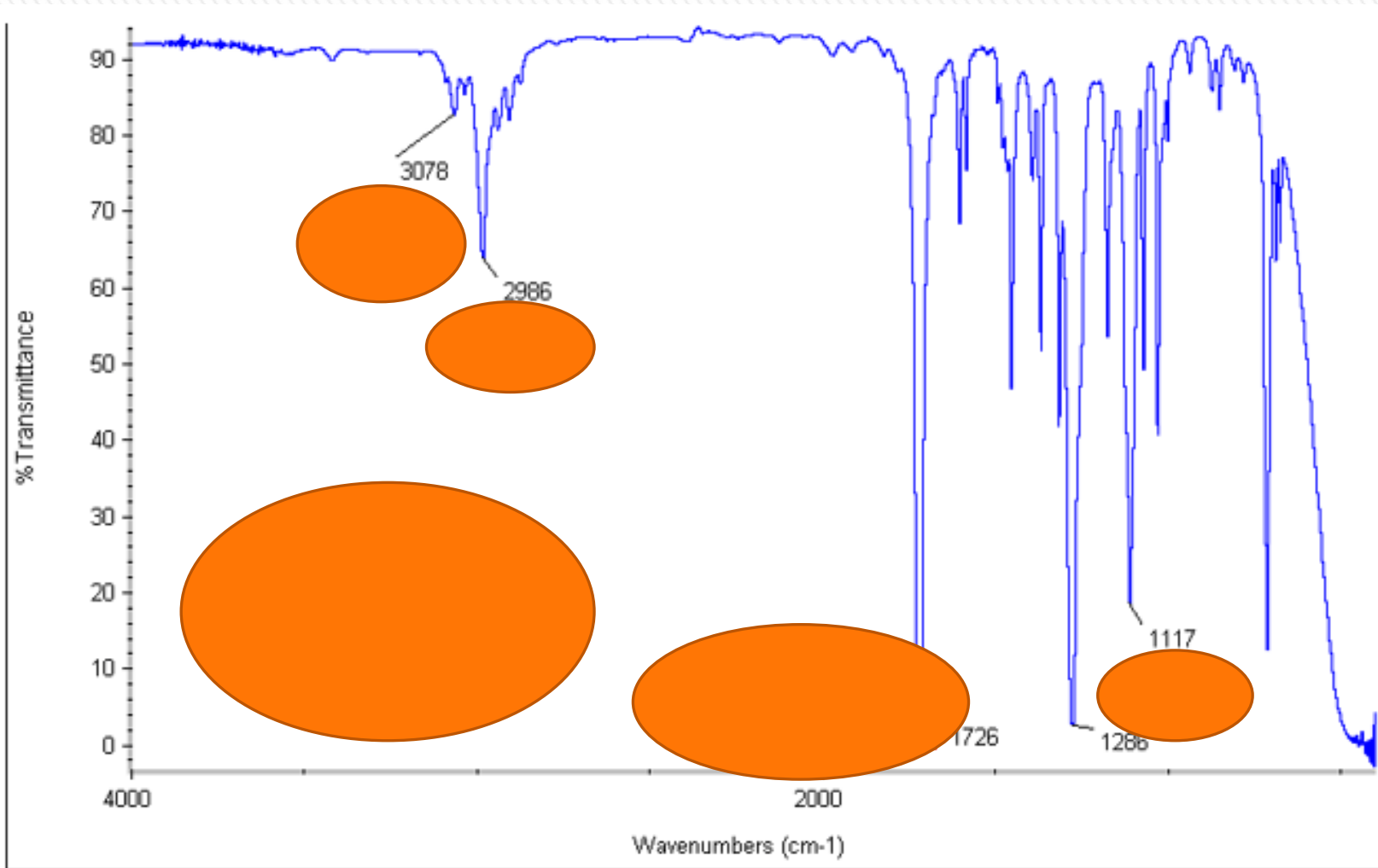


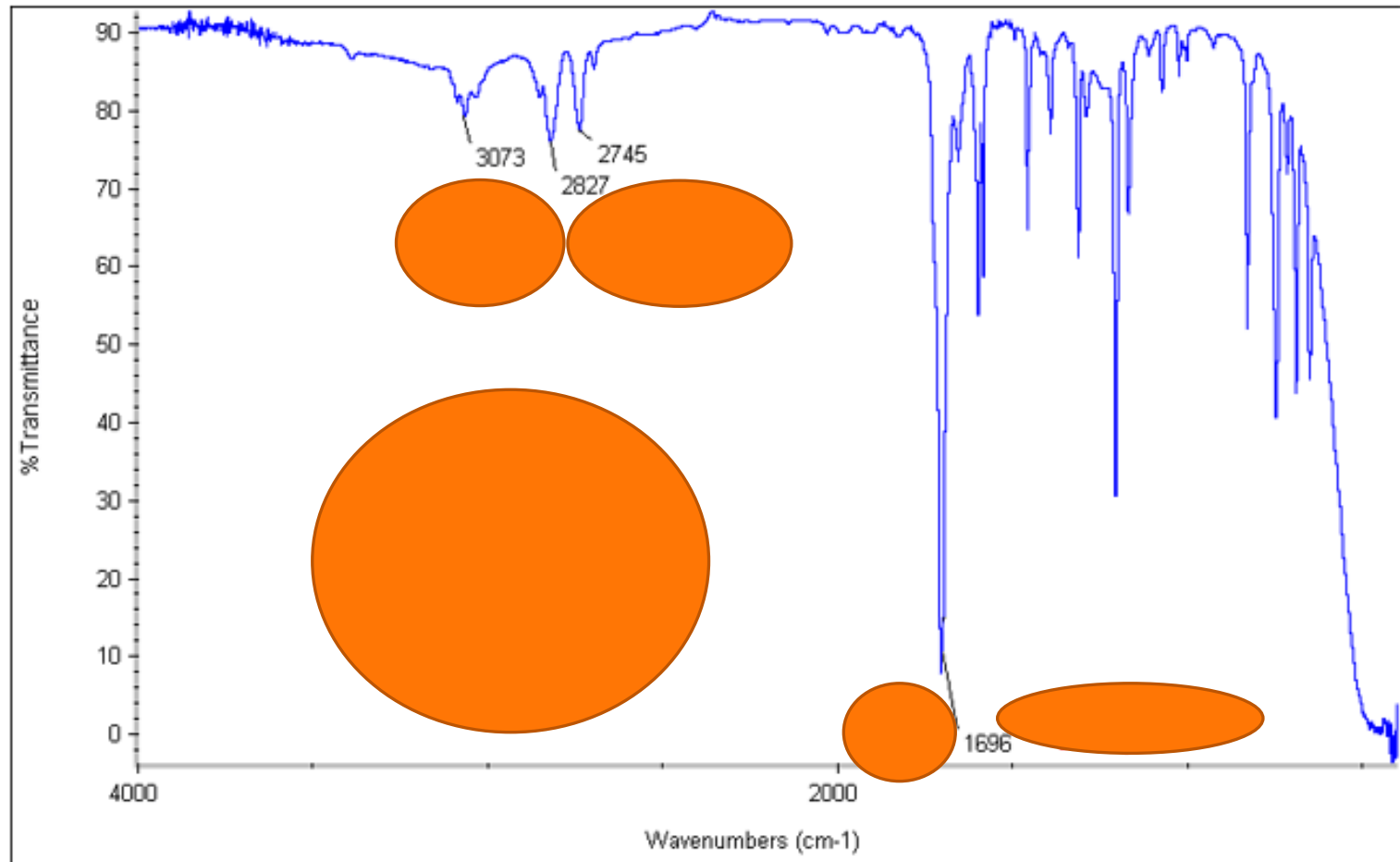


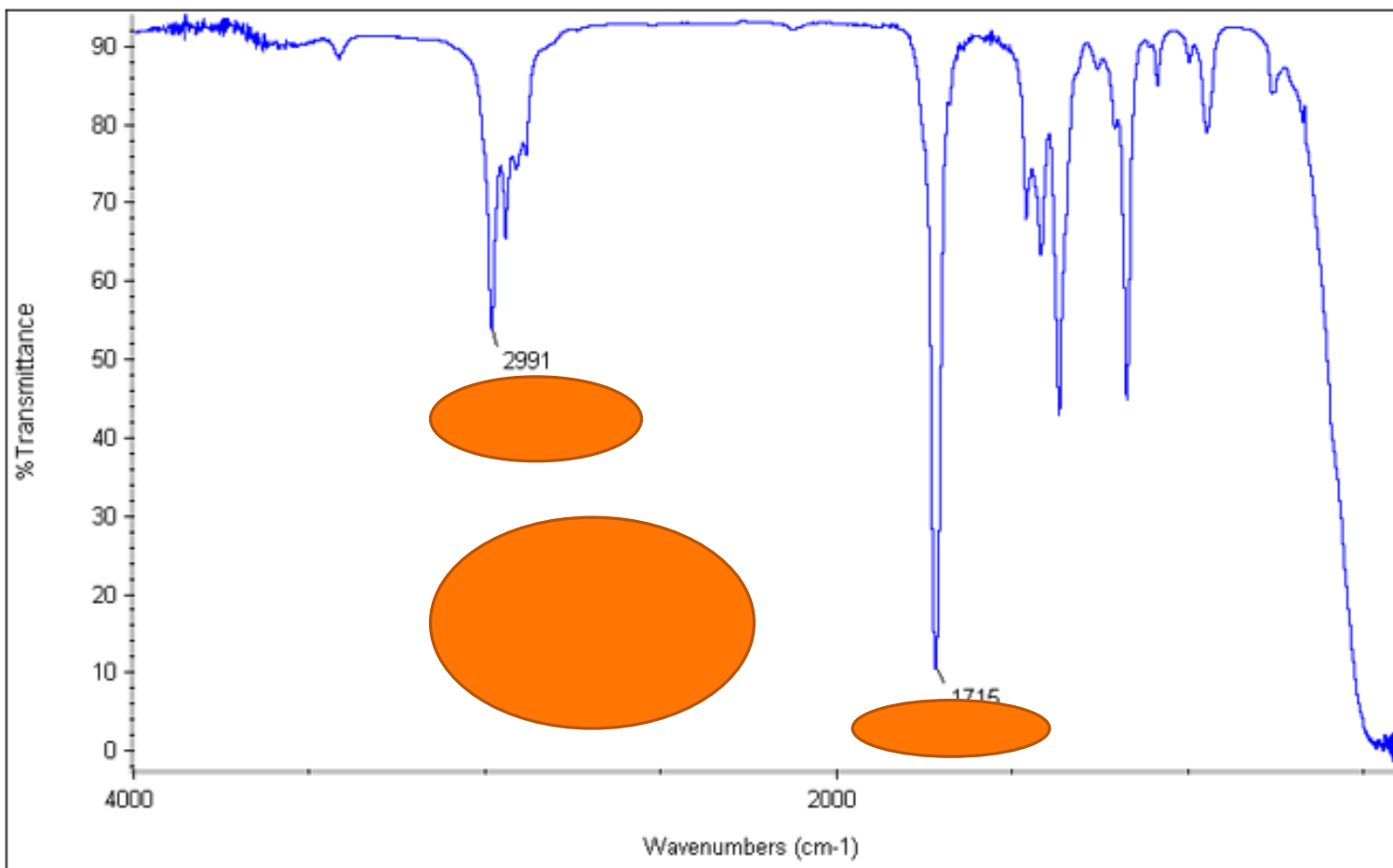


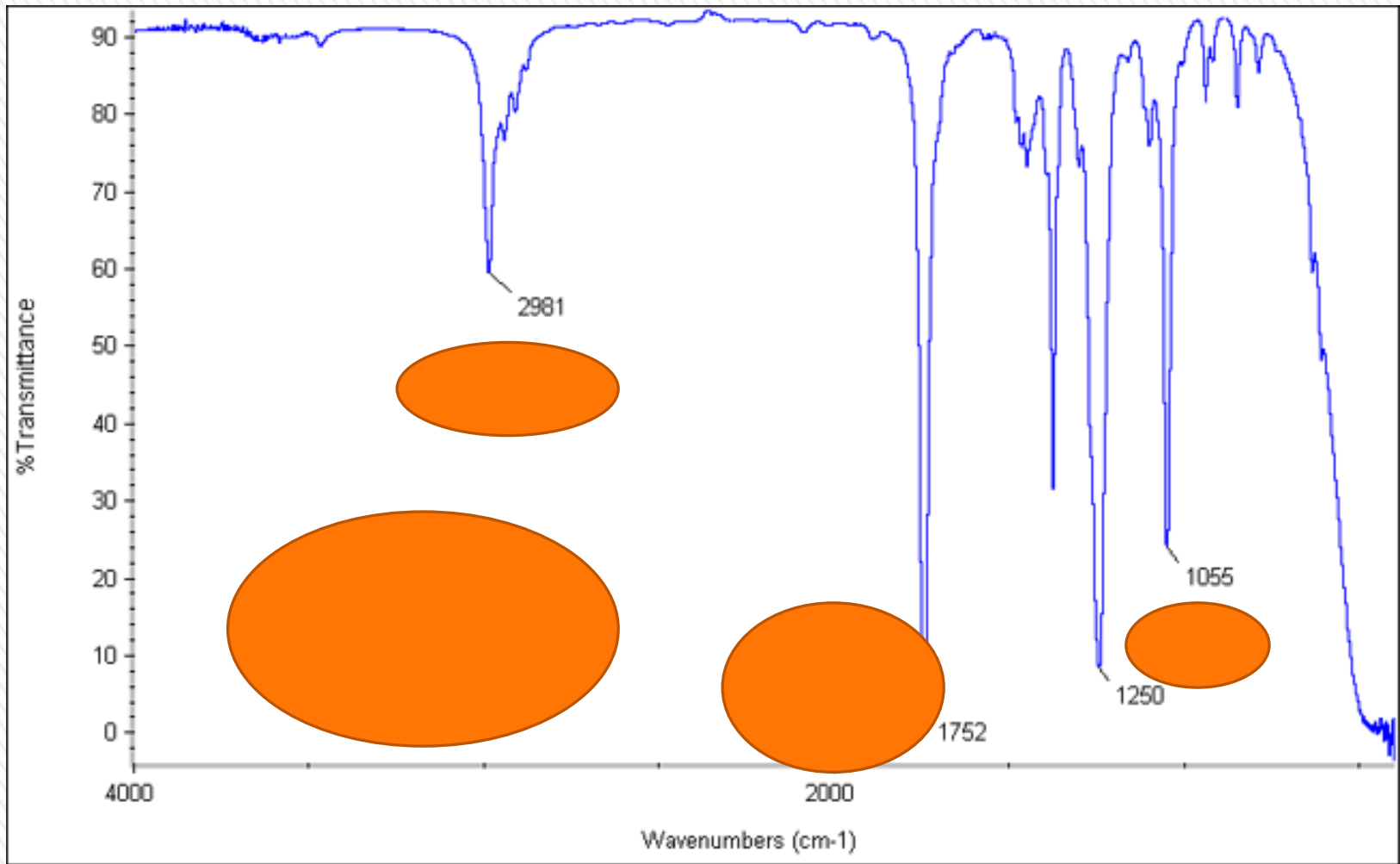


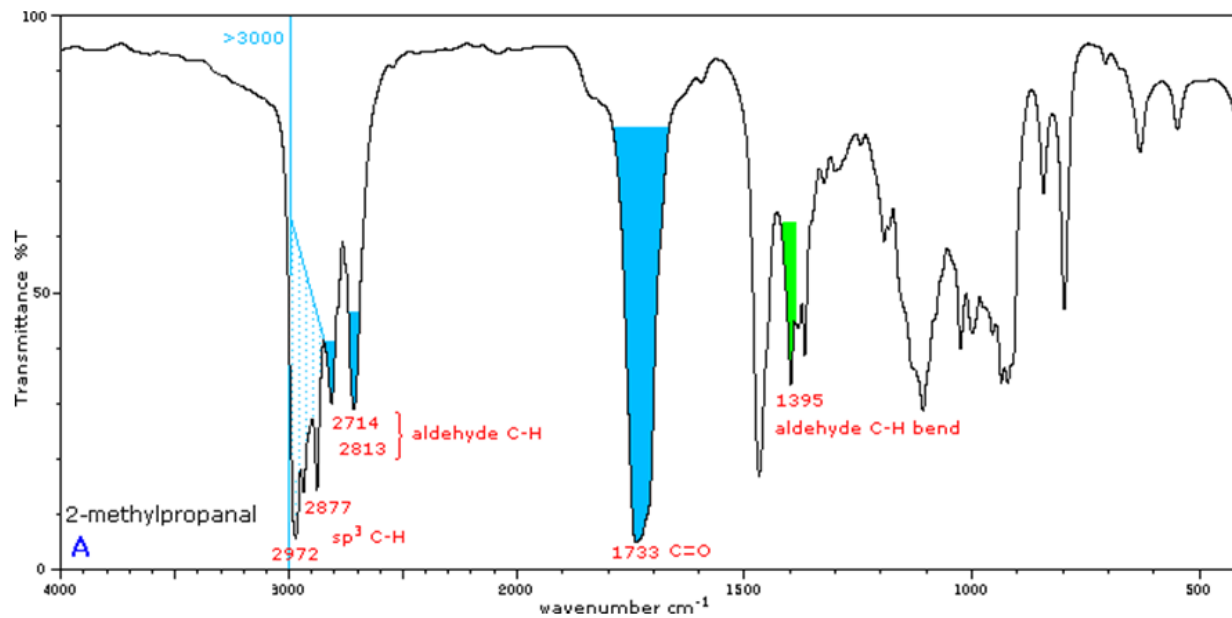
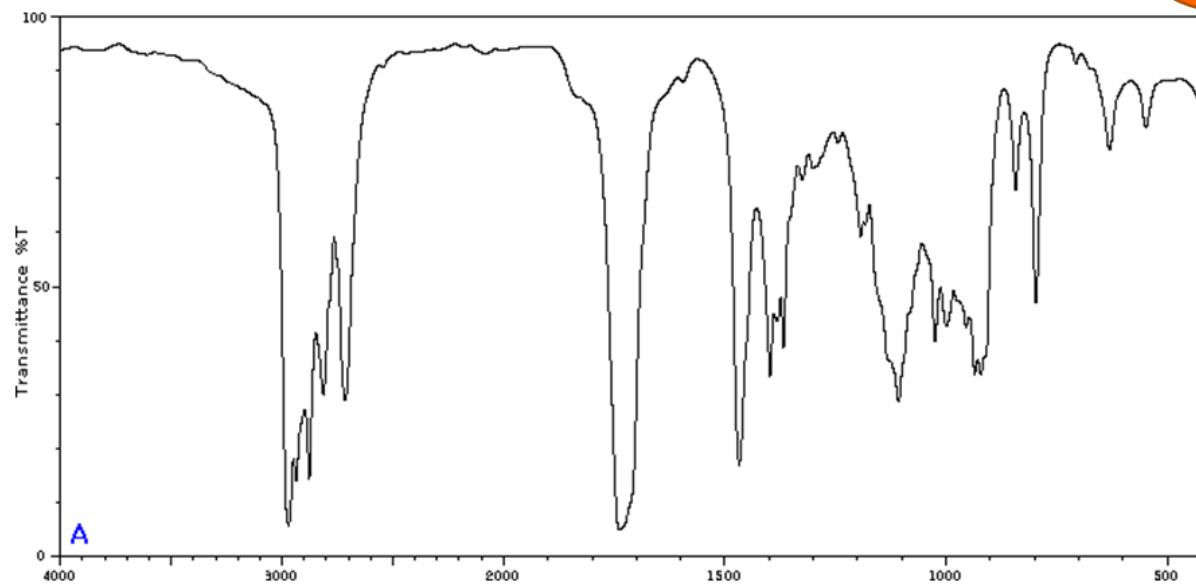
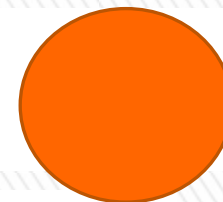
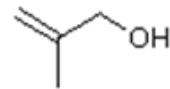
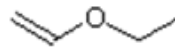
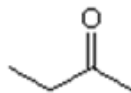
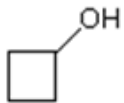


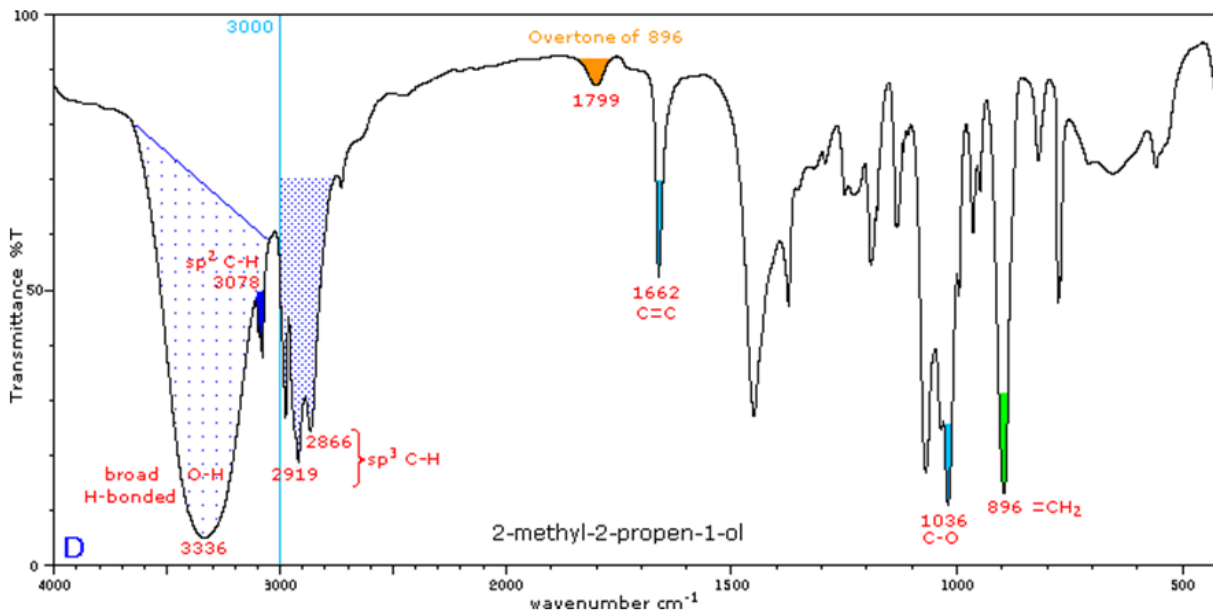
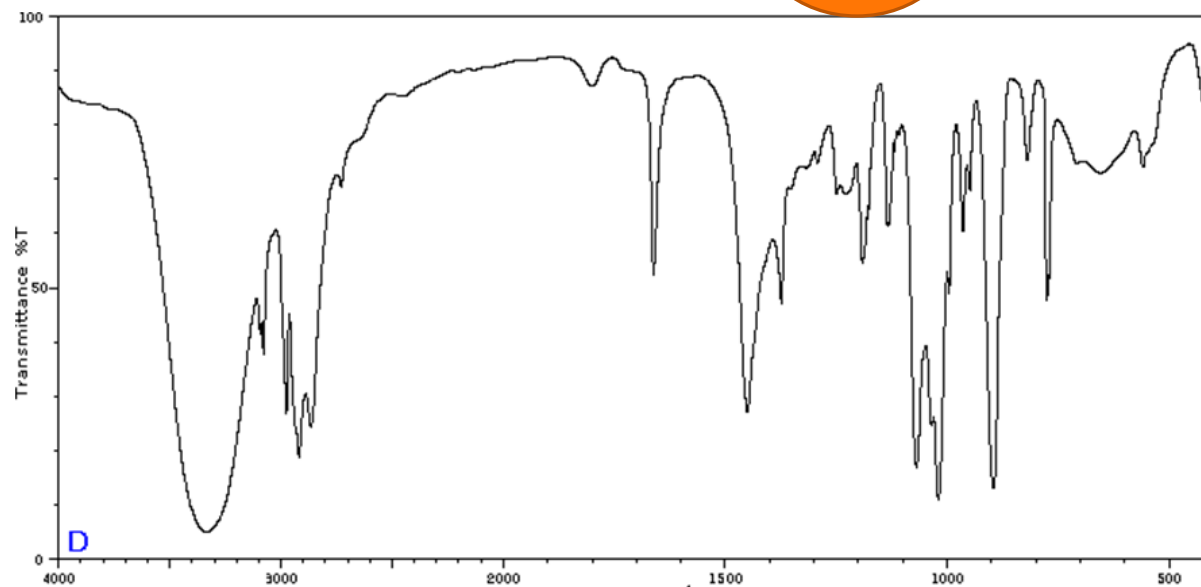
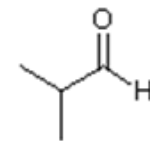
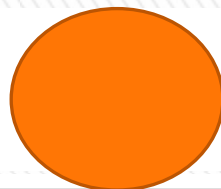
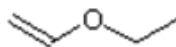
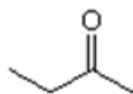
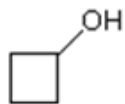


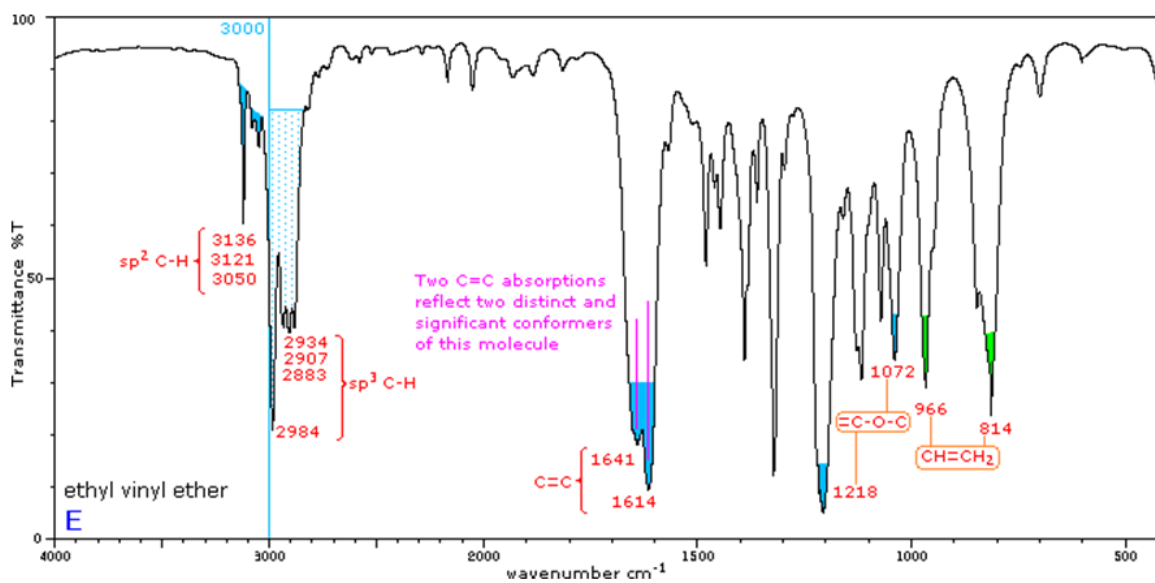
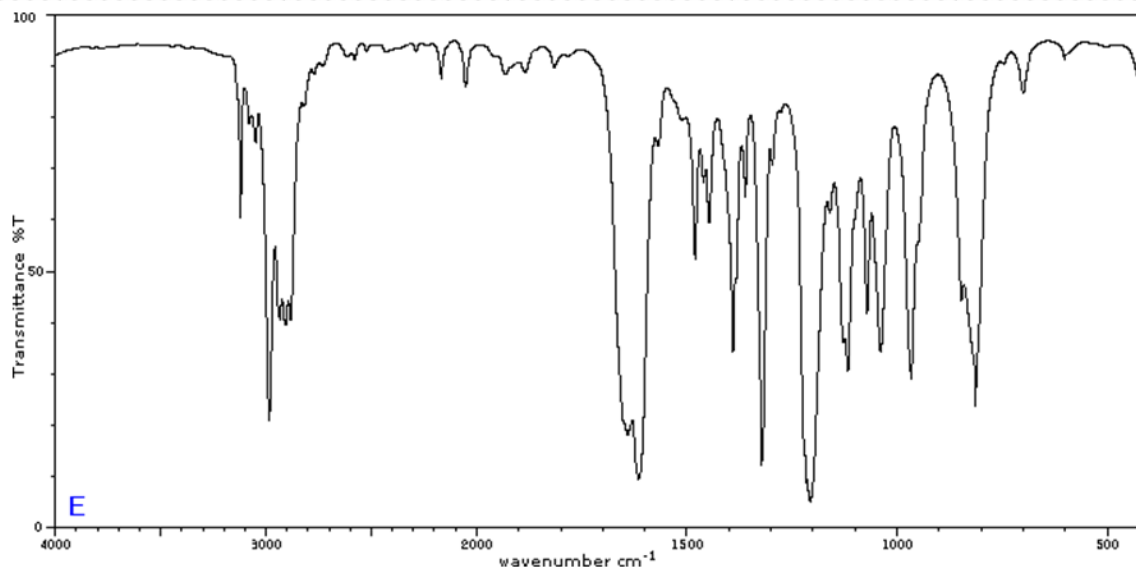
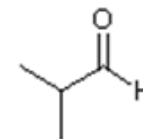
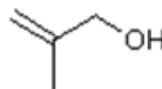
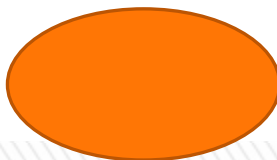
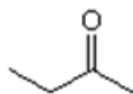
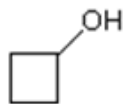


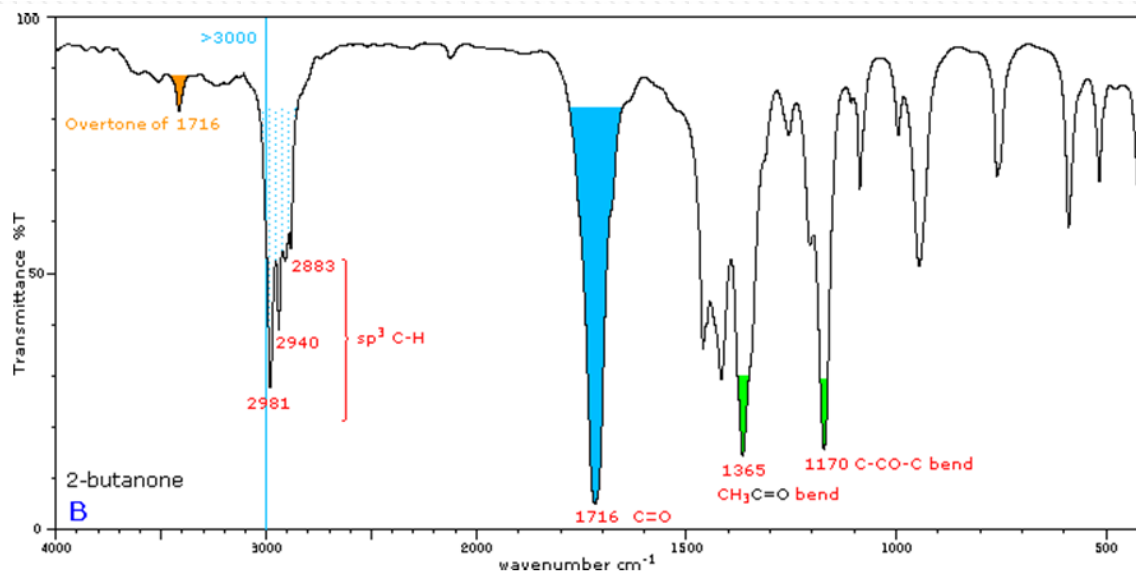
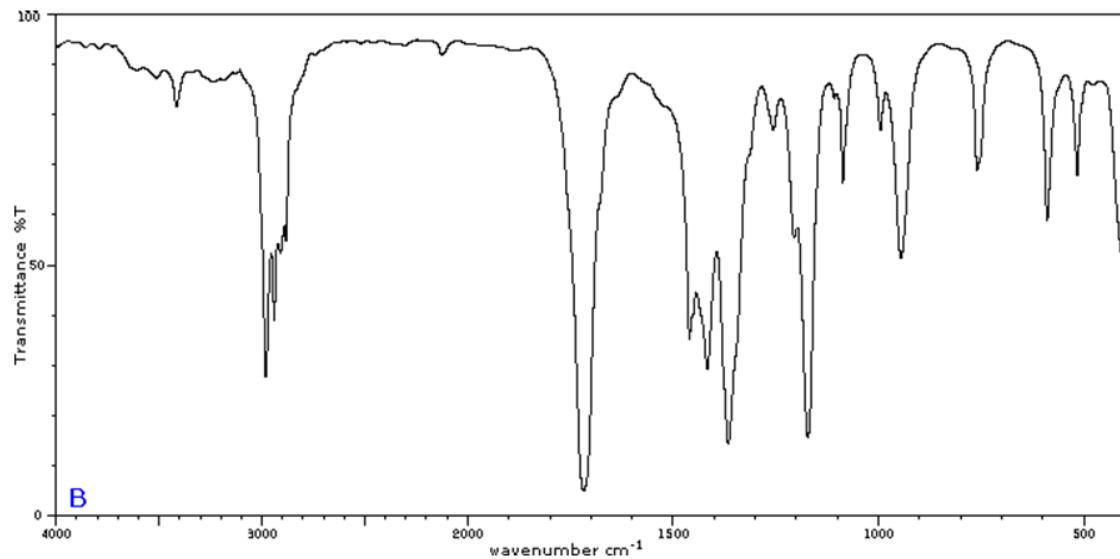
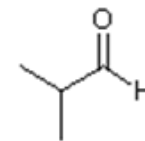
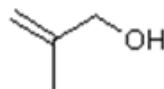
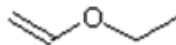
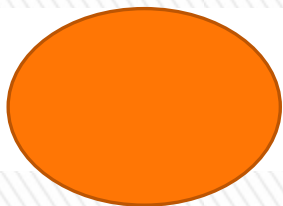
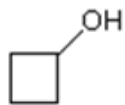


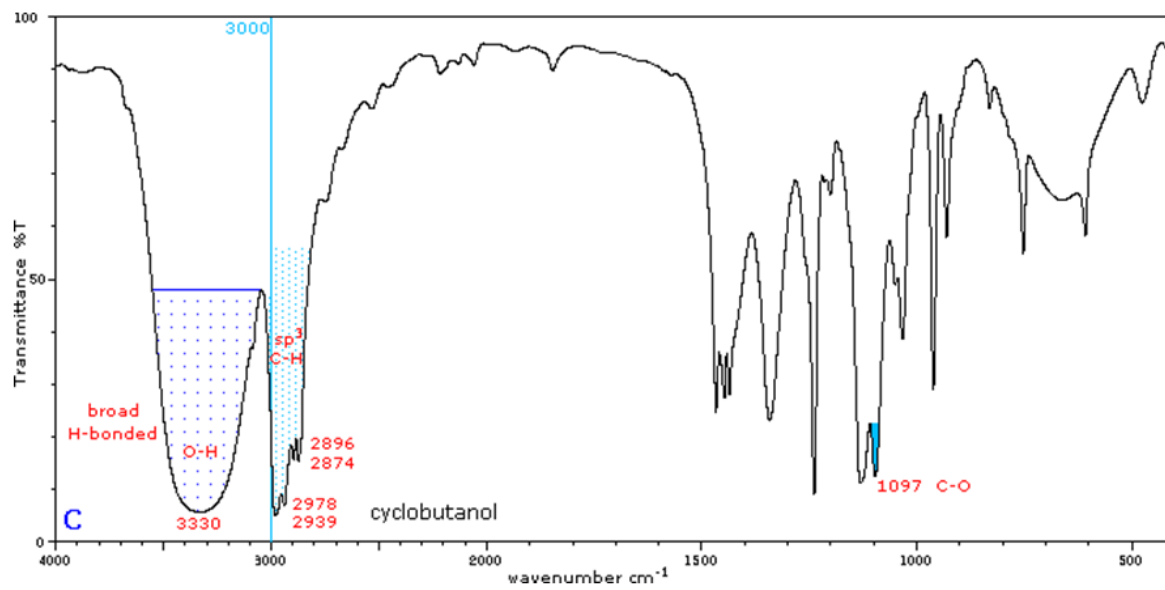
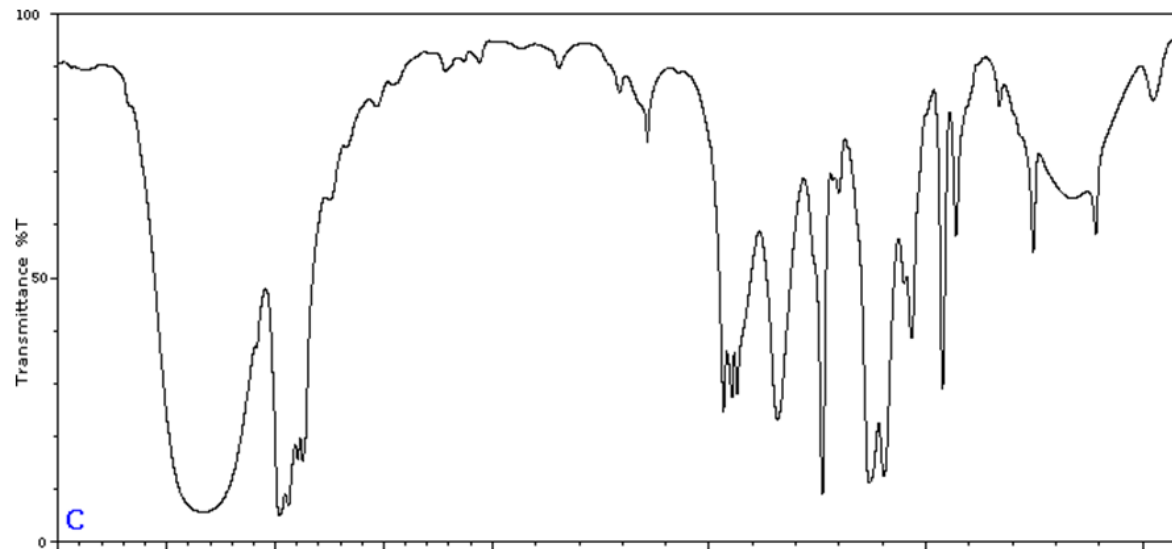
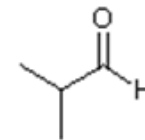
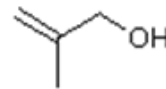
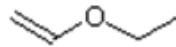
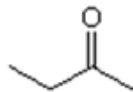












» HMOTNOSTNÍ SPEKTROMETRIE

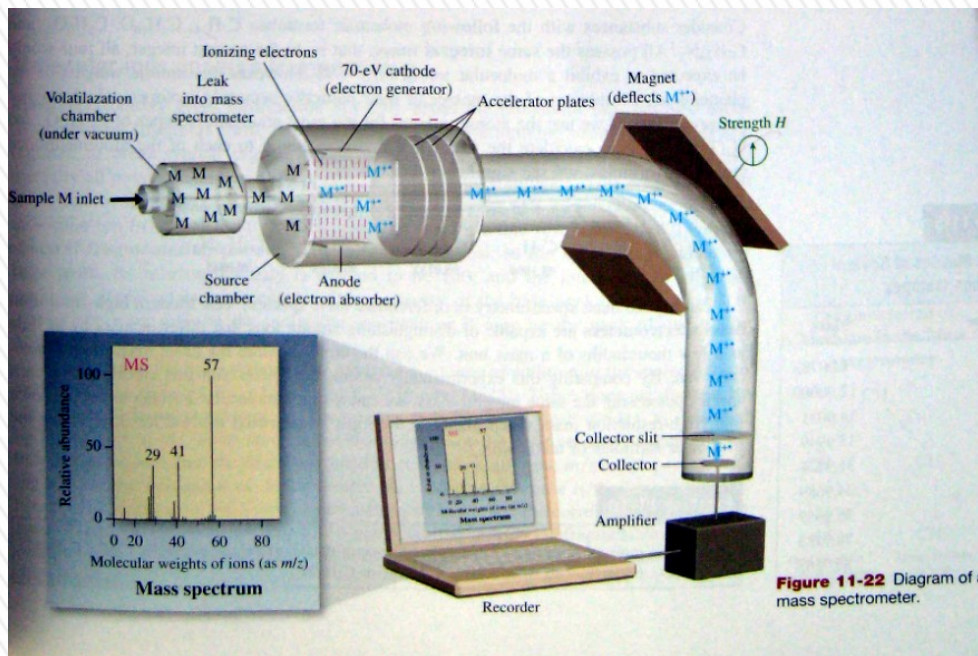


Figure 11-22 Diagram of a mass spectrometer.



primárně vzniká molekulární ion M^+
 fragmentací vznikají ionty dceřinné

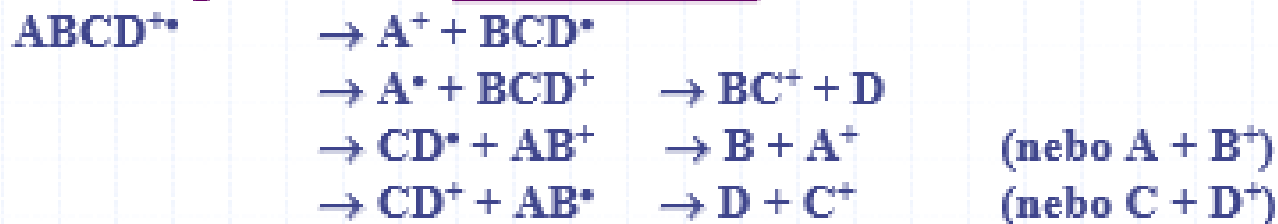
Ionization of a Molecule on Electron Impact



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

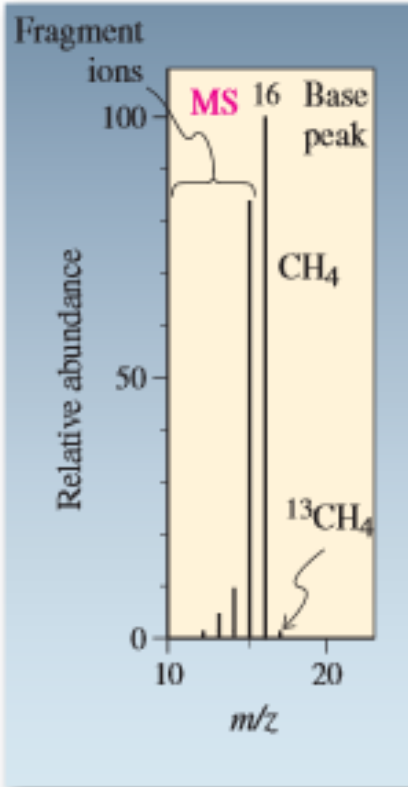


- Fragmentace \Rightarrow dceřinné ionty:



- Kolize + následná fragmentace:





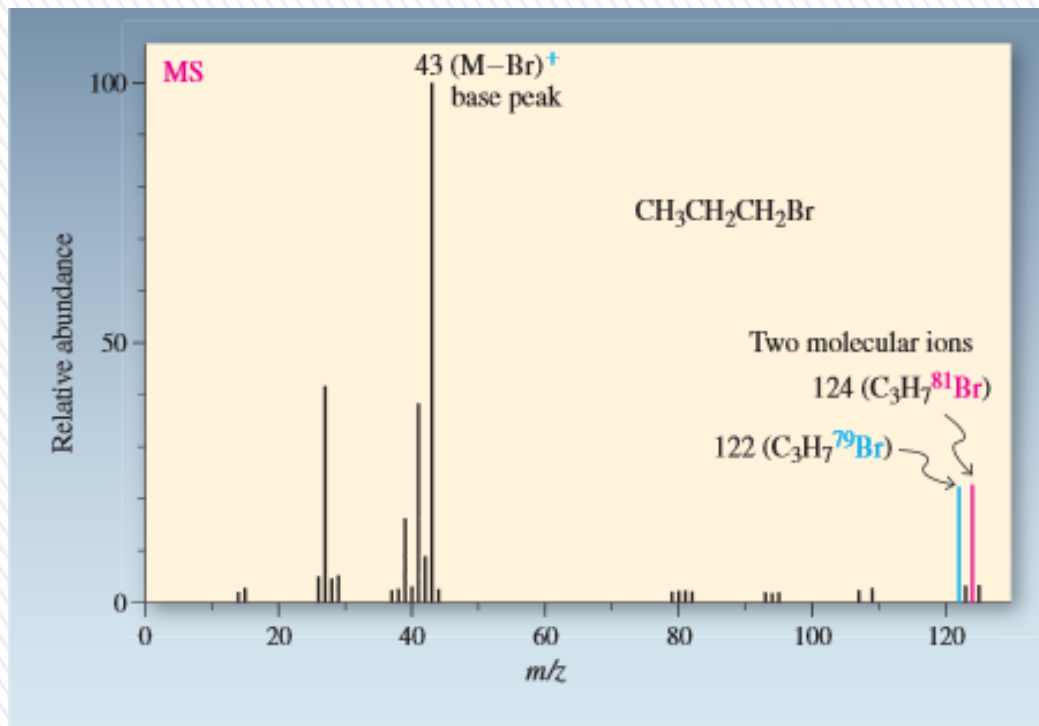
Tabulated Spectrum

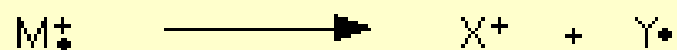
<i>m/z</i>	Relative Abundance (%)	Molecular or Fragment ion
17	1.1	(M + 1) ⁺
16	100.0 (base peak)	M ⁺ (parent ion)
15	85.0	(M - 1) ⁺
14	9.2	(M - 2) ⁺
13	3.9	(M - 3) ⁺
12	1.0	(M - 4) ⁺



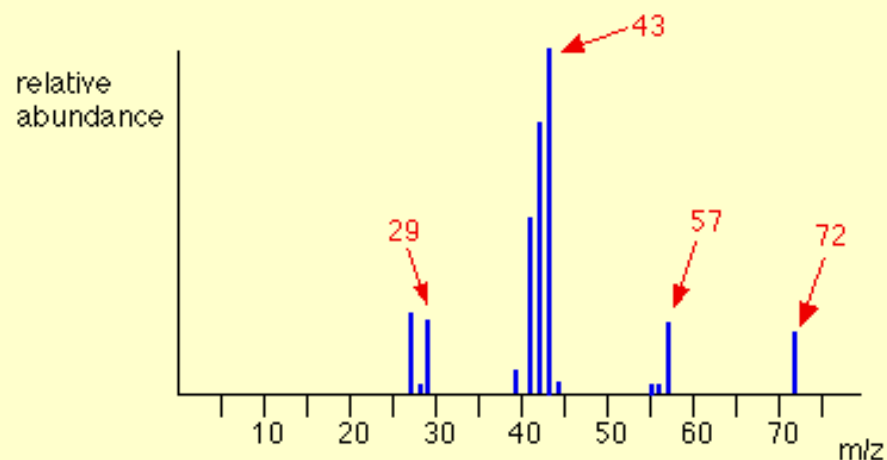
Přírodní zastoupení izotopů běžných organických prvků

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"

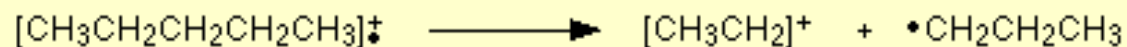
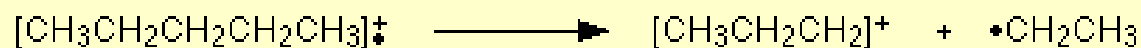
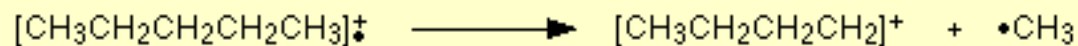
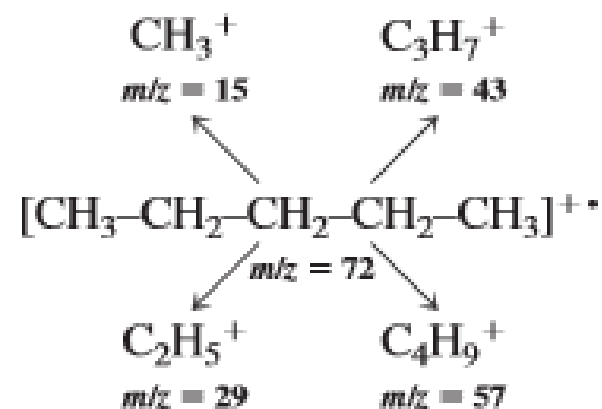




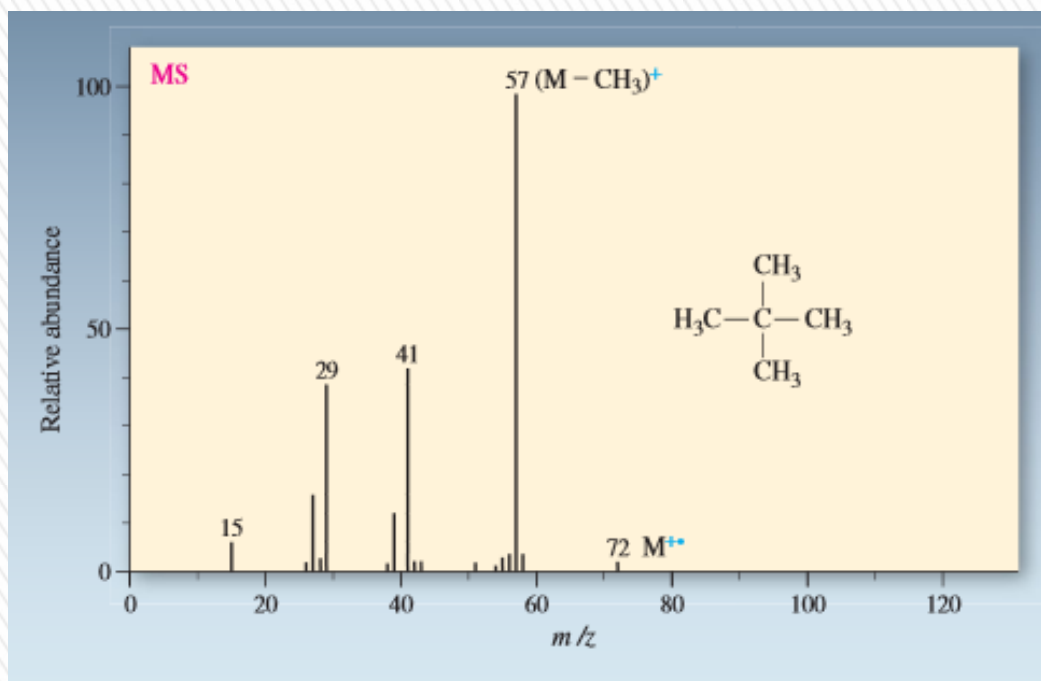
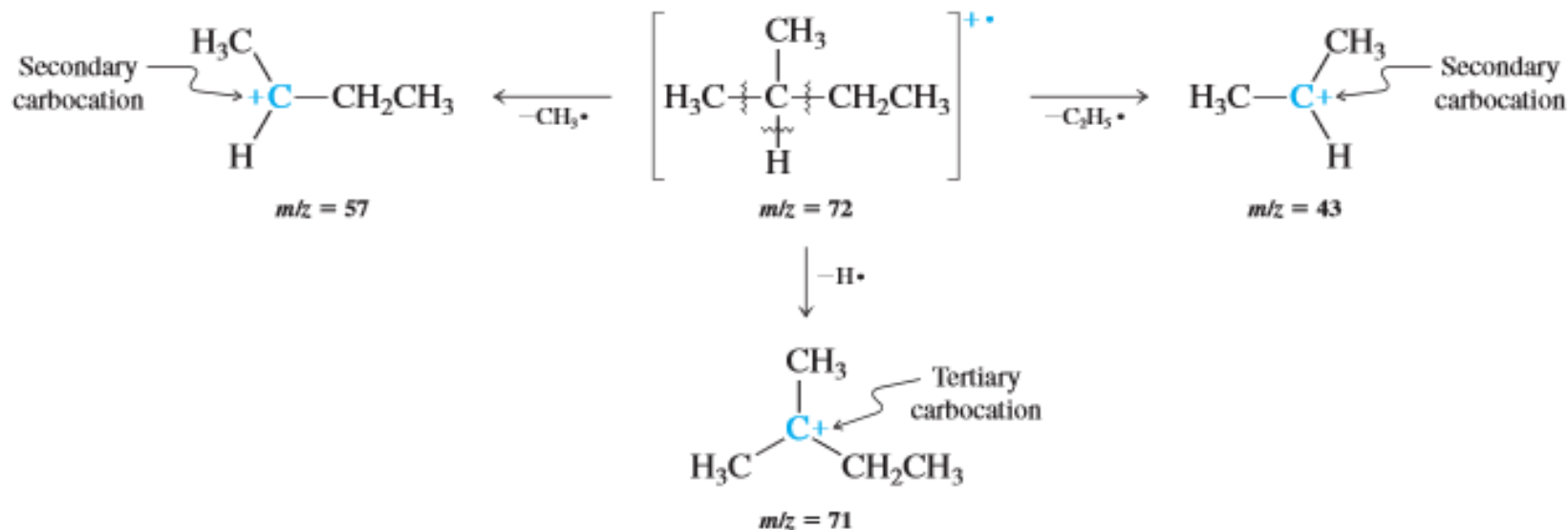
simplified mass spectrum of pentane - $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

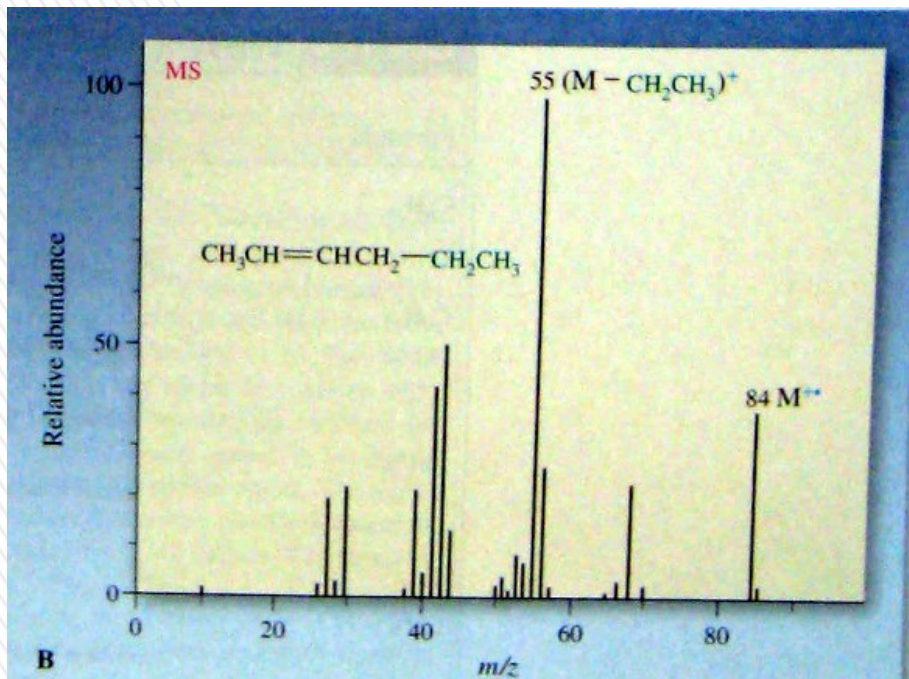
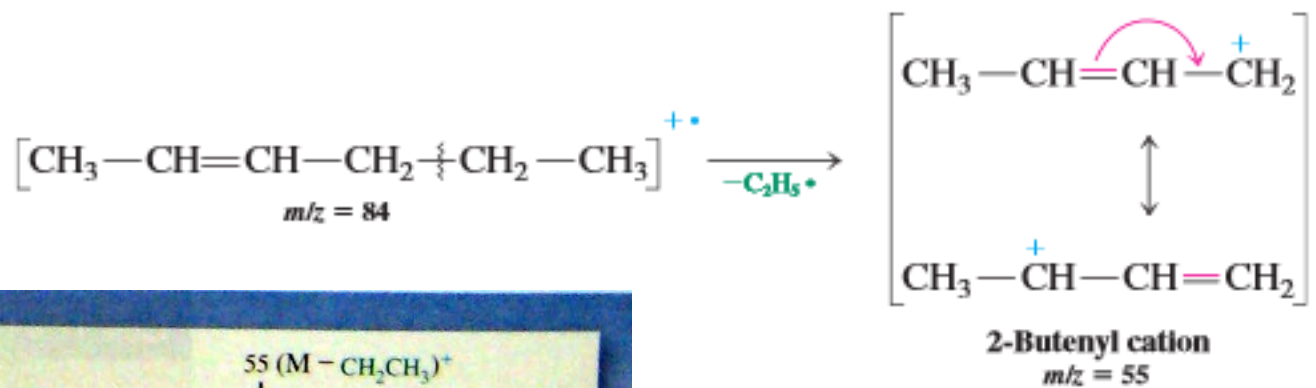
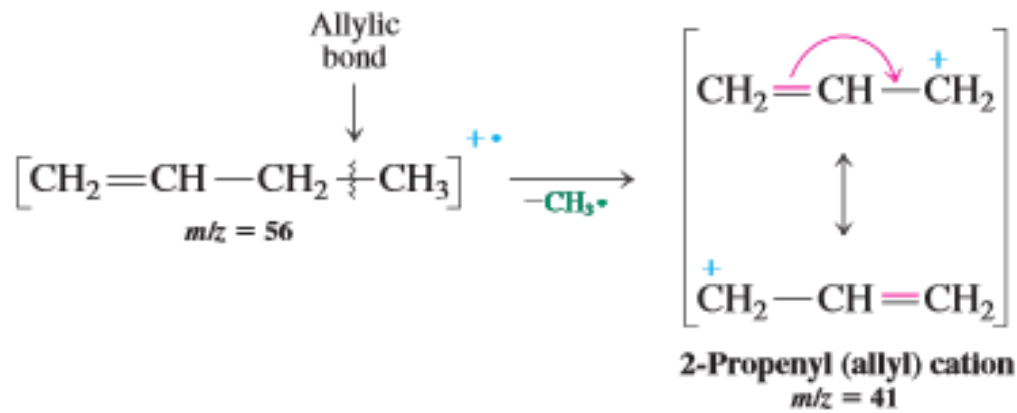


Fragment Ions from Pentane

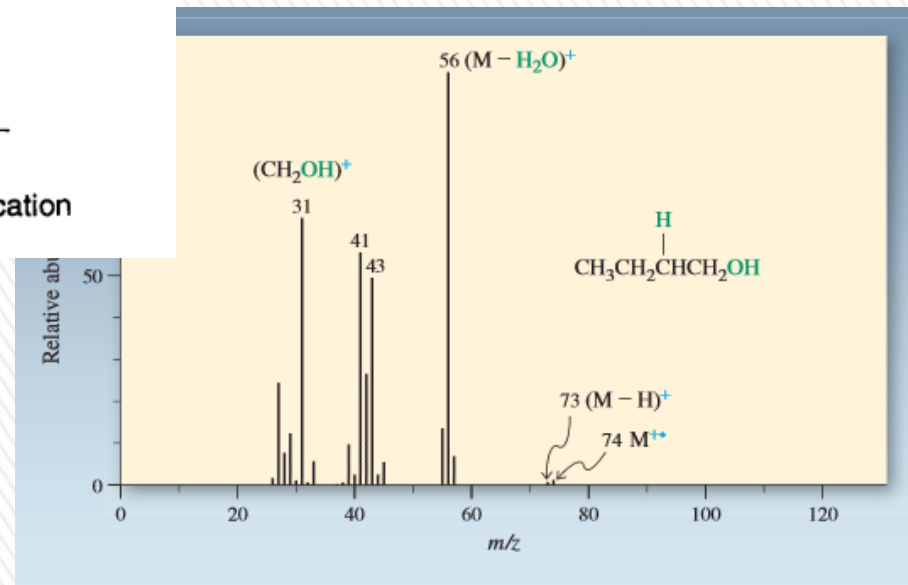
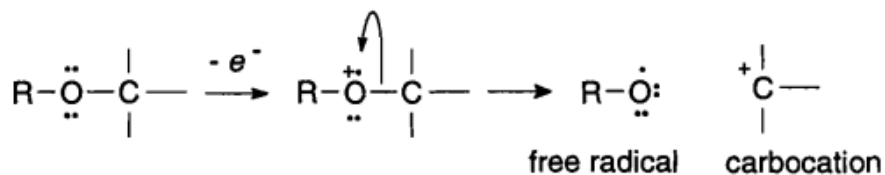


Preferred Fragmentation of 2-Methylbutane

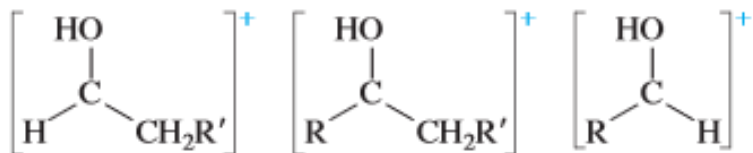
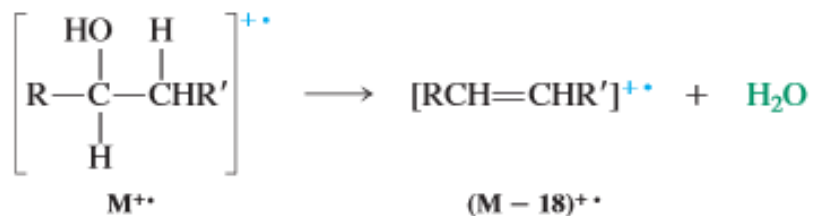




» štěpení alfa k heteroatomu



Alcohol Fragmentation by Dehydration and α Cleavage



» štěpení alfa ke karbonylu

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

