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Molekulska spektroskopija

Prof. dr. sc. Irena Škorić

Izvedbeni program kolegija

✓ ***IR spektroskopija***: primjena IR spektroskopije u detekciji karakterističnih funkcionalnih skupina u organskoj kemiji

✓ ***UV/Vis spektrofotometrija i fluorescencija***: instrumentacija, prezentacija spektara, otapala, kromofori, efekt konjugacije, Woodvardovo pravilo za enone, aromatski spojevi, vidljivi spektar, boja u spojevima

✓ ***Masena (MS) spektrometrija***: maseni spektrometar, GC/MS, maseni spektar, određivanje molekulske mase i formule, utjecaj izotopa, fragmentacija

- ***NMR spektroskopija***: osnovni pristupi, nuklearni magnetski moment. ^{1}H NMR spektri: kemijski pomak i zaklanjanje, integrali, kemijska okolina i kemijski pomak, magnetska anizotropija, konstanta sprege, ^{13}C NMR spektri: kemijski pomaci ugljika-13, integriranje u ^{13}C NMR spektru, NOE efekt, heteronuklearno sprezanje ugljika s deuterijem, fluorom-19 i fosforom-31

- ***NMR spektroskopija***. Spin-spin sprezanje: mehanizam sprezanja, konstante sprege spektra prvog i drugog reda, sprege dalekog dosega. Dodatna poglavlja u jednodimenzionalnom NMR-u: izmjena protona u vodi i D_2O, tautomerija, protoni na dušikovom atomu, utjecaj otapala na kemijski pomak; Napredne NMR tehnike: DEPT, dvodimenzijske spektroskopske metode: COSY, LR COSY, HETCOR, HSQC, HMBC, NOESY, TOCSY

Literatura:

1. D. L. Pavia, G. M. Lampman, G. S. Kriz: "*Introduction to Spectroscopy*", Third Edition, Brooks/Cole Thomson Learning, Australia, 2001.

2. R. M. Silverstein, F. X. Webster, D. J. Kiemle: "*Spectrometric Identification of Organic Compounds*", Seventh Edition, John Wiley & Sons, Inc., New York, USA, 2005.

3. R. M. Silverstein, G. C. Bassler, T. C. Morrill: "*Spectrometric Identification of Organic Compounds*", Fifth Edition, John Wiley & Sons, Inc., New York, USA, 1991.

Infracrvena (IR) spektroskopija

Infracrvena (IR) spektroskopija

- **Infracrvena spektroskopija:** Instrumentalna metoda detekcije funkcionalnih skupina!

IR spektroskopija

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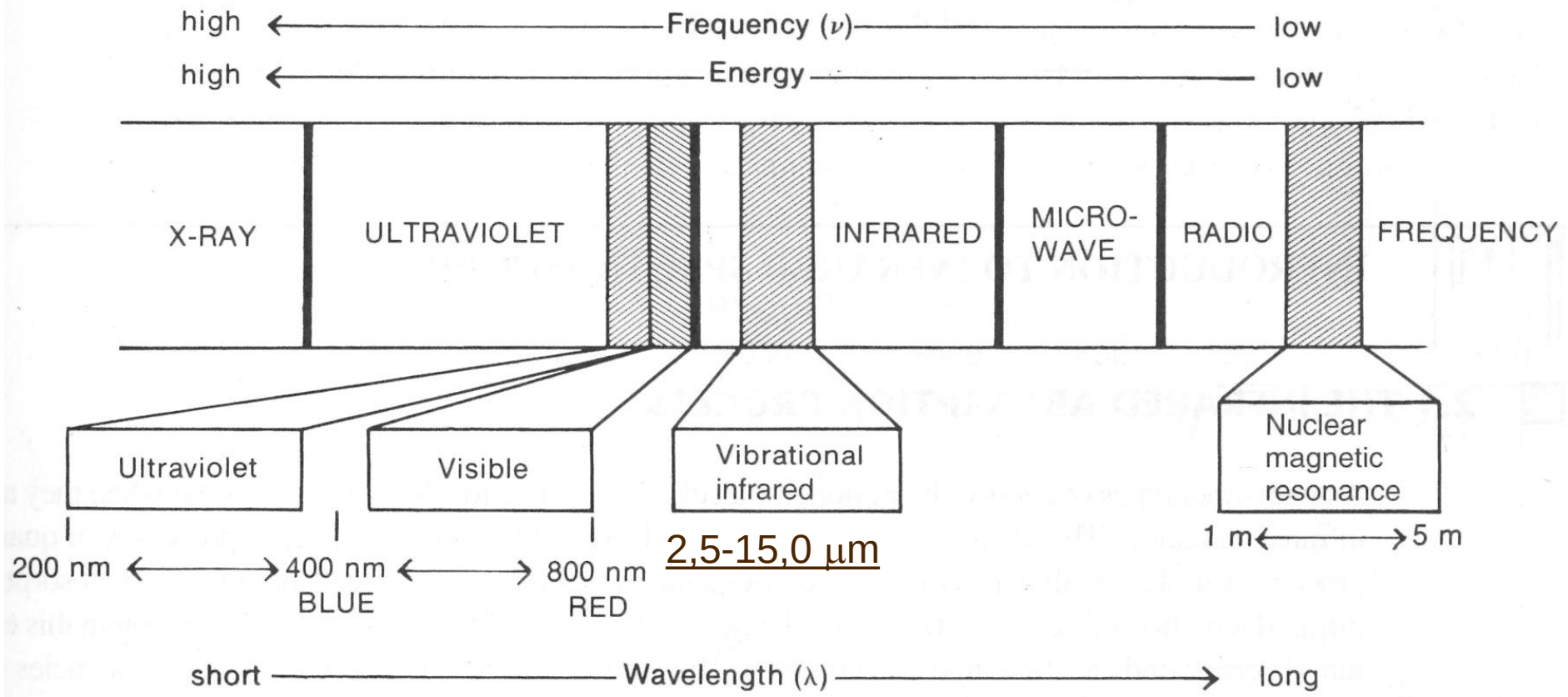
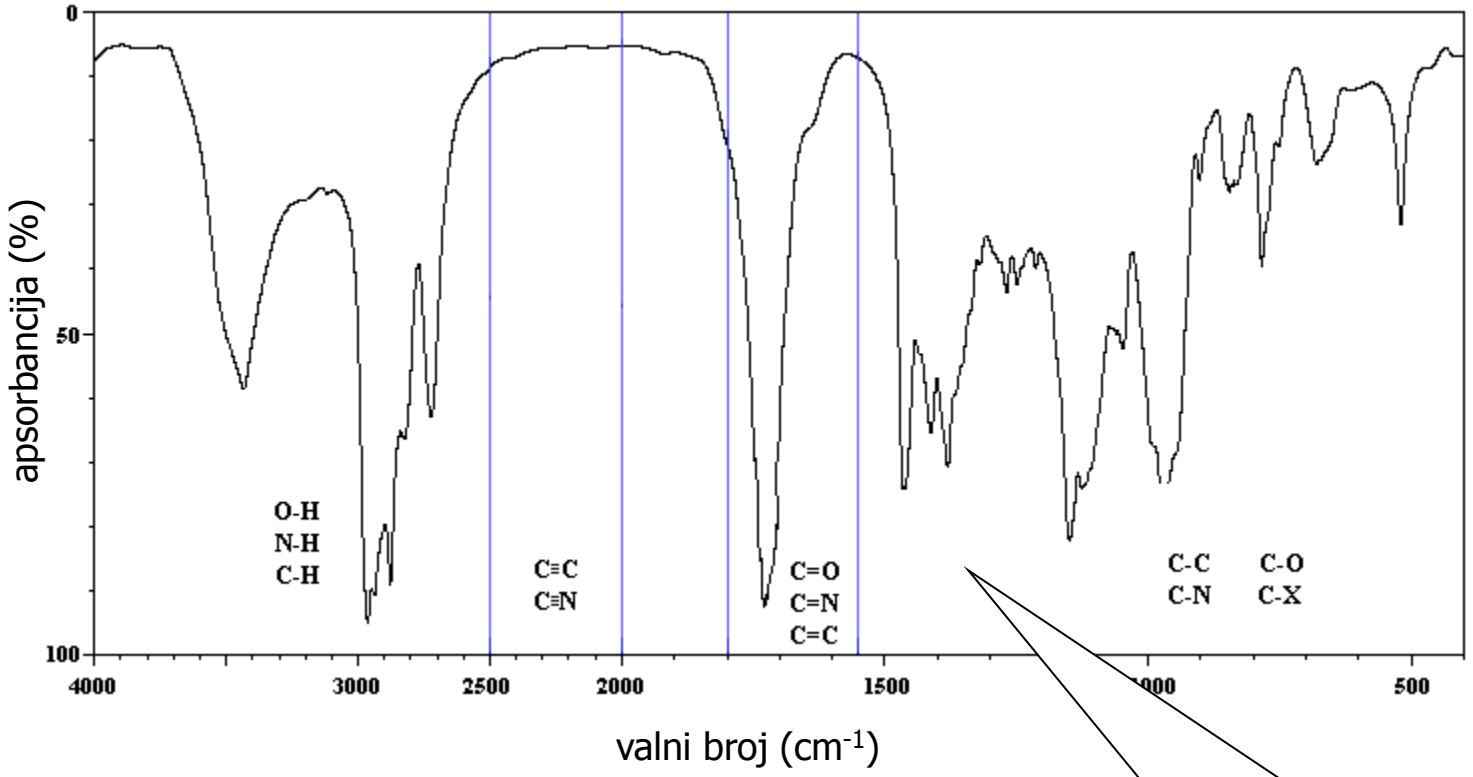
- Zanima nas područje od 2,5-15,0 μm



IR spektar

(**funkcionalne skupine** i njihove vrpce u određenim područjima valnih brojeva)



"otisak prsta" (fingerprint region)

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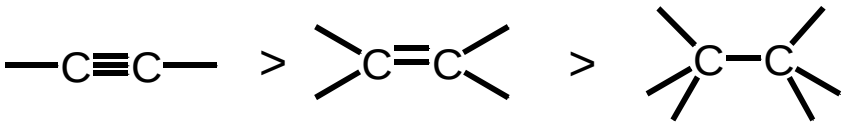
- IR spektar je snimka apsorbiranog svjetla kao funkcija valne duljine
- Apsorbira se samo svjetlo čija se frekvencija podudara s frekvencijom vibracija veze u molekuli tj. frekvencije radijacije i vibracije moraju biti iste da bi došlo do apsorpcije

- IR spektroskopija prvenstveno služi za identifikaciju funkcionalnih skupina prisutnih u molekuli

- Faktori koji određuju apsorpcijsku poziciju su jačina veze, masa atoma u vezi (uz istu jakost veze) i vrsta vibracije

- Jačinu veze određujemo iz energija disocijacije molekule



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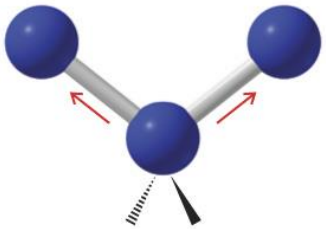
- VRSTE VIBRACIJA:

  - RASTEZANJE (STRETCHING) - veće vrijednosti valnog broja

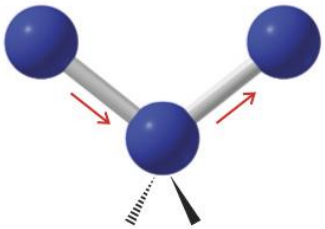
  - SVIJANJE (BENDING; deformacijske vibracije) - niži valni brojevi; simetrične i asimetrične

Rastezanje

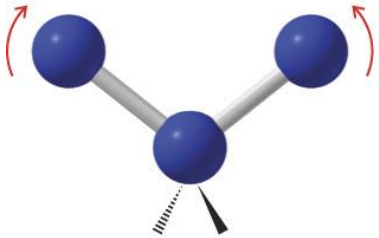
rastezne vibracije



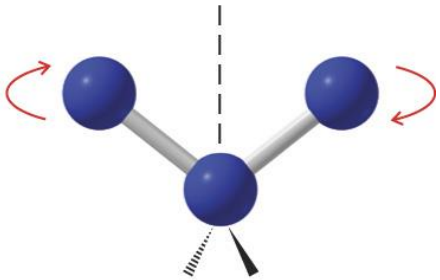
Simetrično rastezanje



Asimetrično rastezanje



Vibracije svijanja
u ravnini ("scissoring"
ili ravninska ***strižna*** vibr.)
Postoji i r. ***njihajna*** vibr.!



Vibracije svijanja
izvan ravnine; izvijanje ("twisting"
ili neravninska ***uvojna*** vibr.)
Postoji i n. ***njihajna*** vibracija!

vibracije svijanja

Karakteristične vrpce

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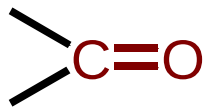
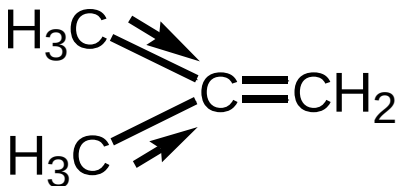
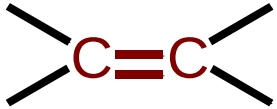


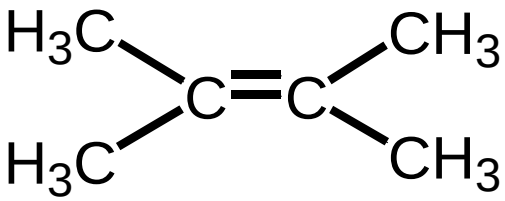
Izrazito jak signal u IR spektru posljedica je promjene dipolnog momenta molekule



Induktivni efekt CH_3 skupina dovodi do polarizacije veze. Rastezanjem dolazi do promjene dipolnog momenta kao funkcije udaljenosti



U IR spektru veza je aktivna na 1640 cm^{-1}



Nema dipolnog momenta niti njegove promjene; IR vrpca je inaktivna; iako vibracije postoje one se ne vide

- Postoje različite vrste vibracija rastezanja i svijanja uzrokovanih apsorpcijom energije infracrvenog spektra

- Stvarne relativne frekvencije vibracija mogu se predvidjeti
  - Veze s “lakšim” atomima vibriraju brže od onih s “težim” atomima

GROUP	BOND	FREQUENCY RANGE (CM^{-1})
Alkyl	C—H	2853–2962
Alcohol	O—H	3590–3650
Amine	N—H	3300–3500

- Trostruke veze (koje su jače) vibriraju pri višim frekvencijama od dvostrukih veza
  - Dvostruke veze vibriraju pri višim frekvencijama od jednostrukih veza

BOND	FREQUENCY RANGE (CM^{-1})
C≡C	2100 – 2260
C≡N	2220 – 2260
C=C	1620 – 1680
C=O	1630 – 1780

- IR spektar molekule obično sadrži veliki broj pikova
  - Dodatni pikovi rezultat su preklopljenih (overtone, harmonic) pikova koji su slabiji i niže frekvencije
  - IR je “fingerprint” molekule jer je jedinstven za pojedinu molekulu

Group		Frequency Range (cm^{-1})	Intensity[a]
A. Alkyl			
C—H (stretching)		2853–2962	(m–s)
Isopropyl, —$CH(CH_3)_2$		1380–1385	(s)
	and	1365–1370	(s)
tert-Butyl, —$C(CH_3)_3$		1385–1395	(m)
	and	~1365	(s)
B. Alkenyl			
C—H (stretching)		3010–3095	(m)
C=C (stretching)		1620–1680	(v)
R—CH=CH_2		985–1000	(s)
	and	905–920	(s)
$R_2C=CH_2$		880–900	(s)
cis-RCH=CHR		675–730	(s)
trans-RCH=CHR		960–975	(s)
C. Alkynyl			
≡C—H (stretching)		~3300	(s)
C≡C (stretching)		2100–2260	(v)

(out-of-plane C—H bendings)

D. Aromatic			
Ar—H (stretching)		~3030	(v)
Aromatic substitution type			
(C—H out-of-plane bendings)			
Monosubstituted		690–710	(very s)
o-Disubstituted	and	730–770	(very s)
m-Disubstituted		735–770	(s)
		680–725	(s)
	and	750–810	(very s)
p-Disubstituted		800–860	(very s)
E. Alcohols, Phenols, and Carboxylic Acids			
O—H (stretching)			
Alcohols, phenols (dilute solutions)		3590–3650	(sharp, v)
Alcohols, phenols (hydrogen bonded)		3200–3550	(broad, s)
Carboxylic acids (hydrogen bonded)		2500–3000	(broad, v)

F. Aldehydes, Ketones, Esters, and Carboxylic Acids		
C═O (stretching)	1630–1780	(s)
Aldehydes	1690–1740	(s)
Ketones	1680–1750	(s)
Esters	1735–1750	(s)
Carboxylic acids	1710–1780	(s)
Amides	1630–1690	(s)
G. Amines		
N—H	3300–3500	(m)
H. Nitriles		
C≡N	2220–2260	(m)

[a]Abbreviations: s = strong, m = medium, w = weak, v = variable, ~ = approximately.

Interpretacija IR spektara

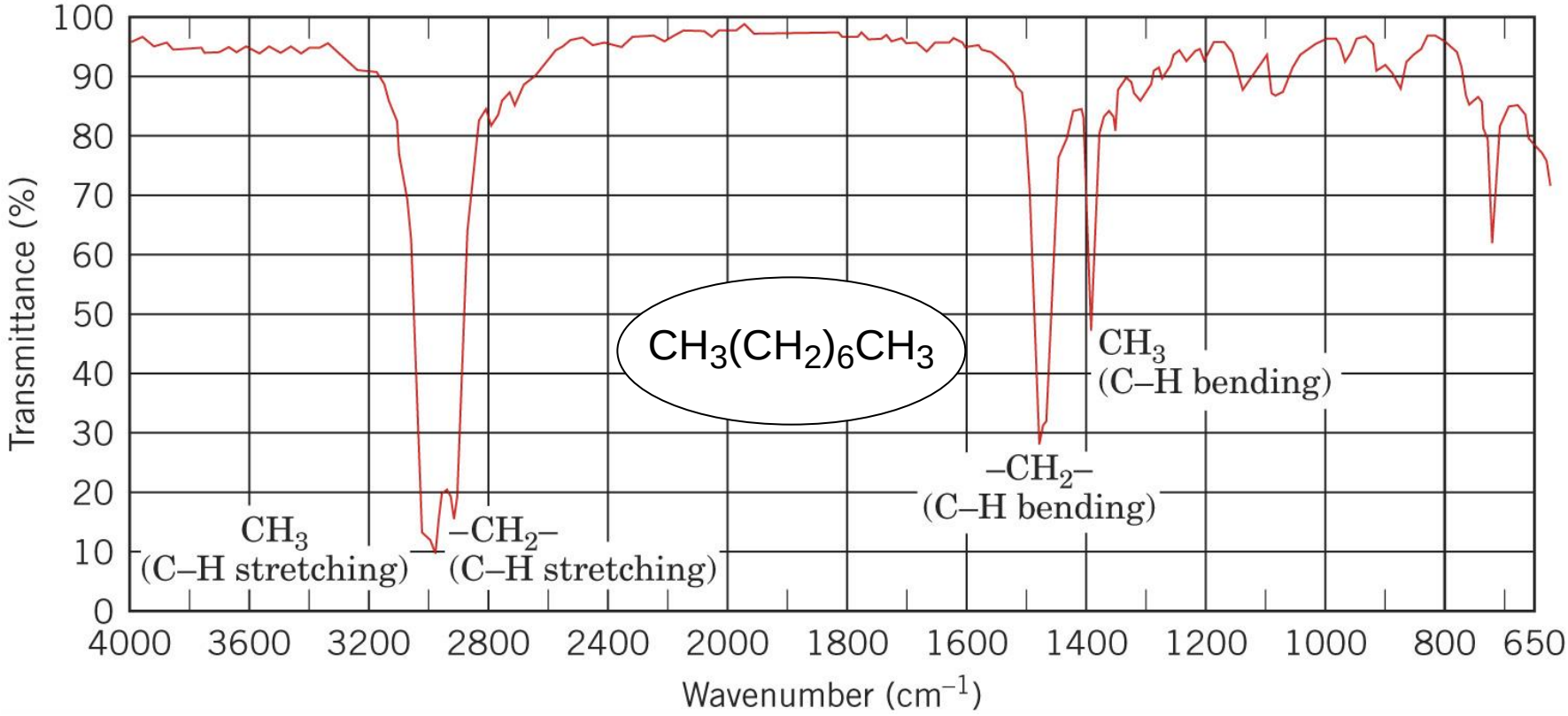
- Općenito se samo određeni signali interpretiraju u IR spektrima

Ugljikovodici

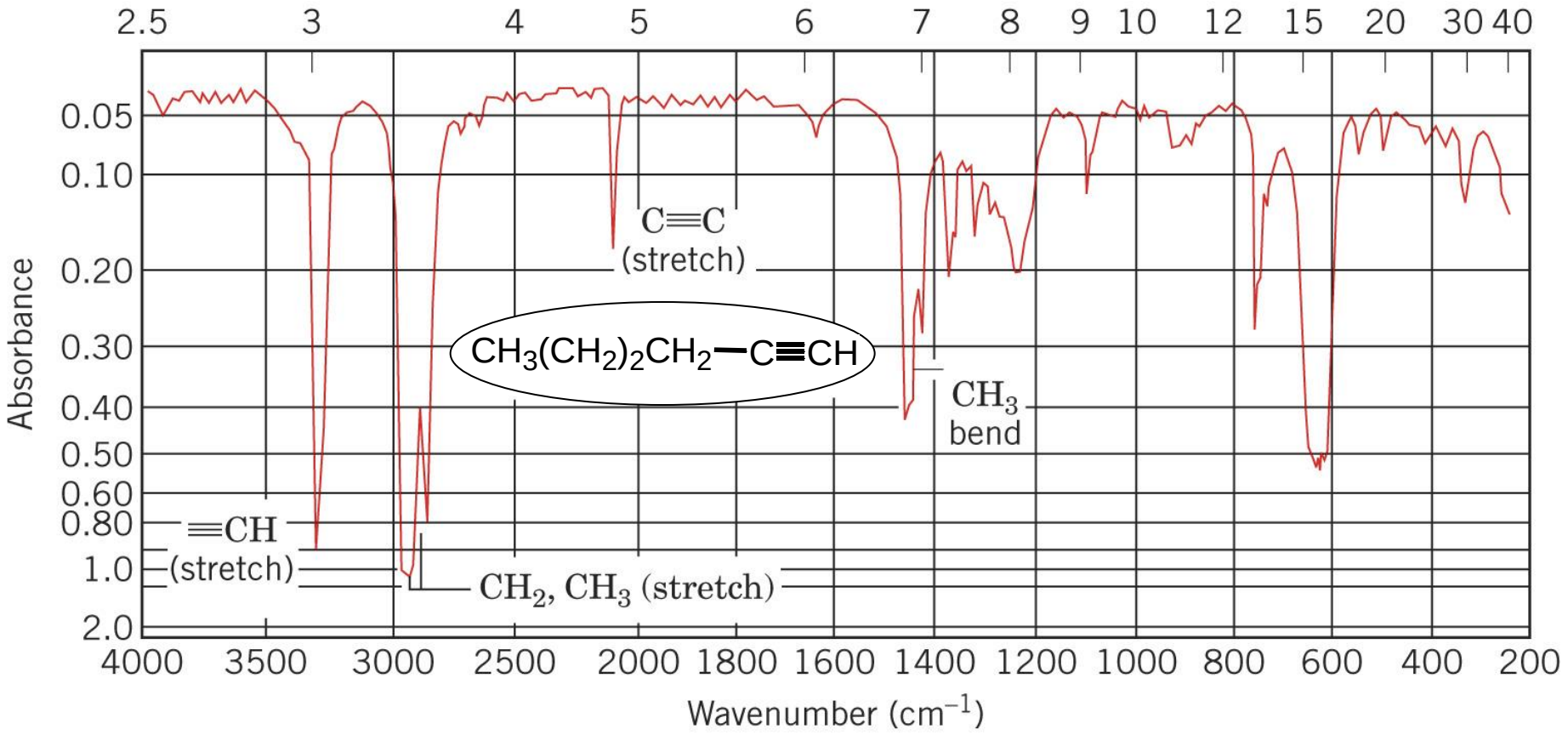
- Karakteristične vibracije C-H rastezanja su u području 2800-3300 cm^{-1}

- C-H veze u kojima je veći udio *s* karaktera veze su kraće, jače i pokazuju vibracije pri višim frekvencijama:
  - C-H veze na *sp* centrima su kod 3000-3100 cm^{-1}
  - C-H veze na sp^2 centrima javljaju se kod 3080 cm^{-1}
  - C-H veze na sp^3 centrima su kod ~ 2800-3000 cm^{-1}
- Frekvencije vibracija rastezanja C-C veze su jedine korisne za višestruke veze
  - C-C dvostruke veze pokazuju signale pri 1620-1680 cm^{-1}
  - C-C trostruke veze pokazuju signale pri 2100-2260 cm^{-1}
  - Ovi signali su odsutni u simetričnim dvostrukim i trostrukim vezama

- Primjer: oktan

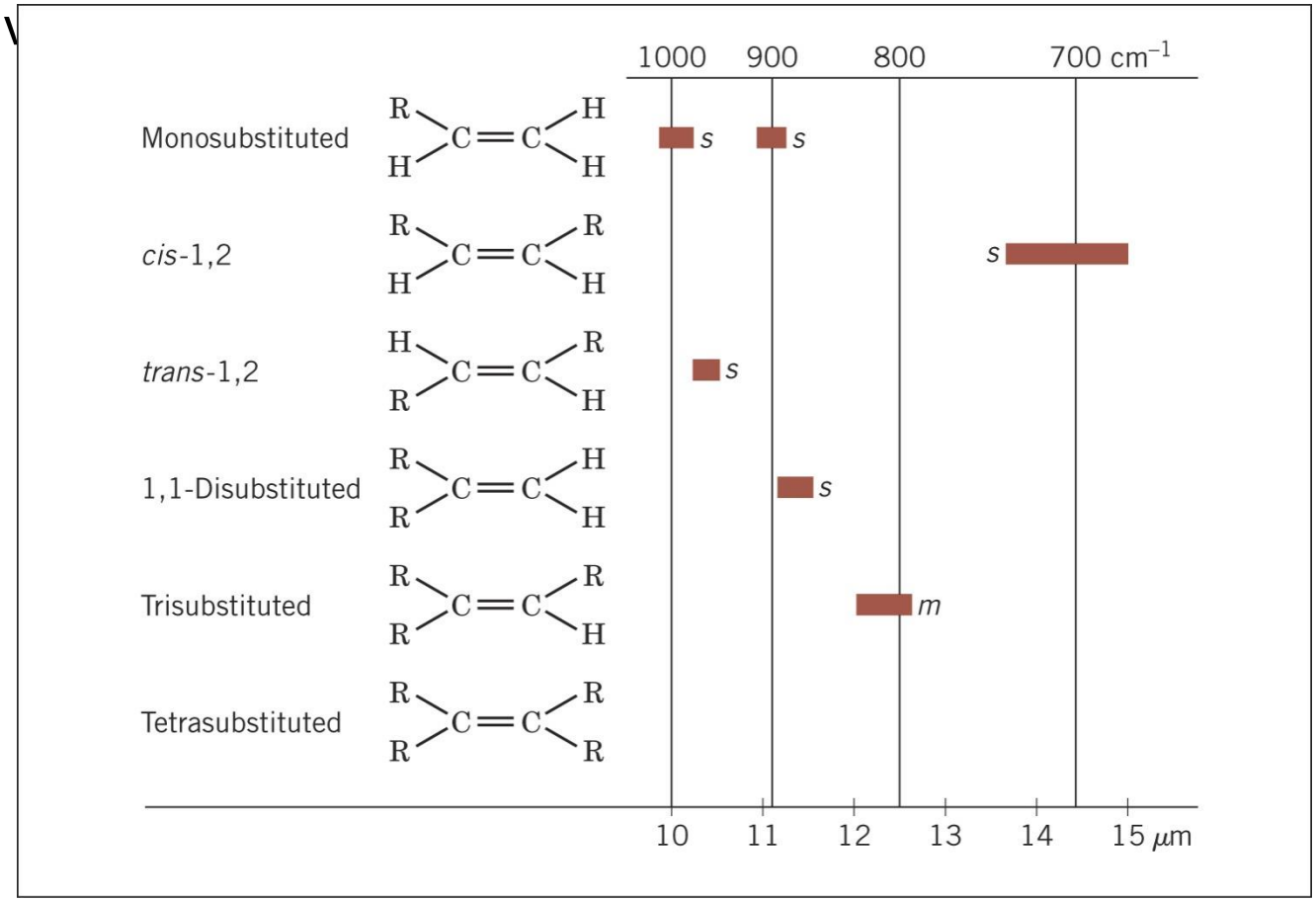


- Primjer: 1-heksin



Alkeni

- Signali za deformacijske vibracije C-H veza smještene kod 600-1000 cm^{-1} mogu se koristiti za određivanje supstitucijskog karaktera dvostruke



Primjer: 1-heksen

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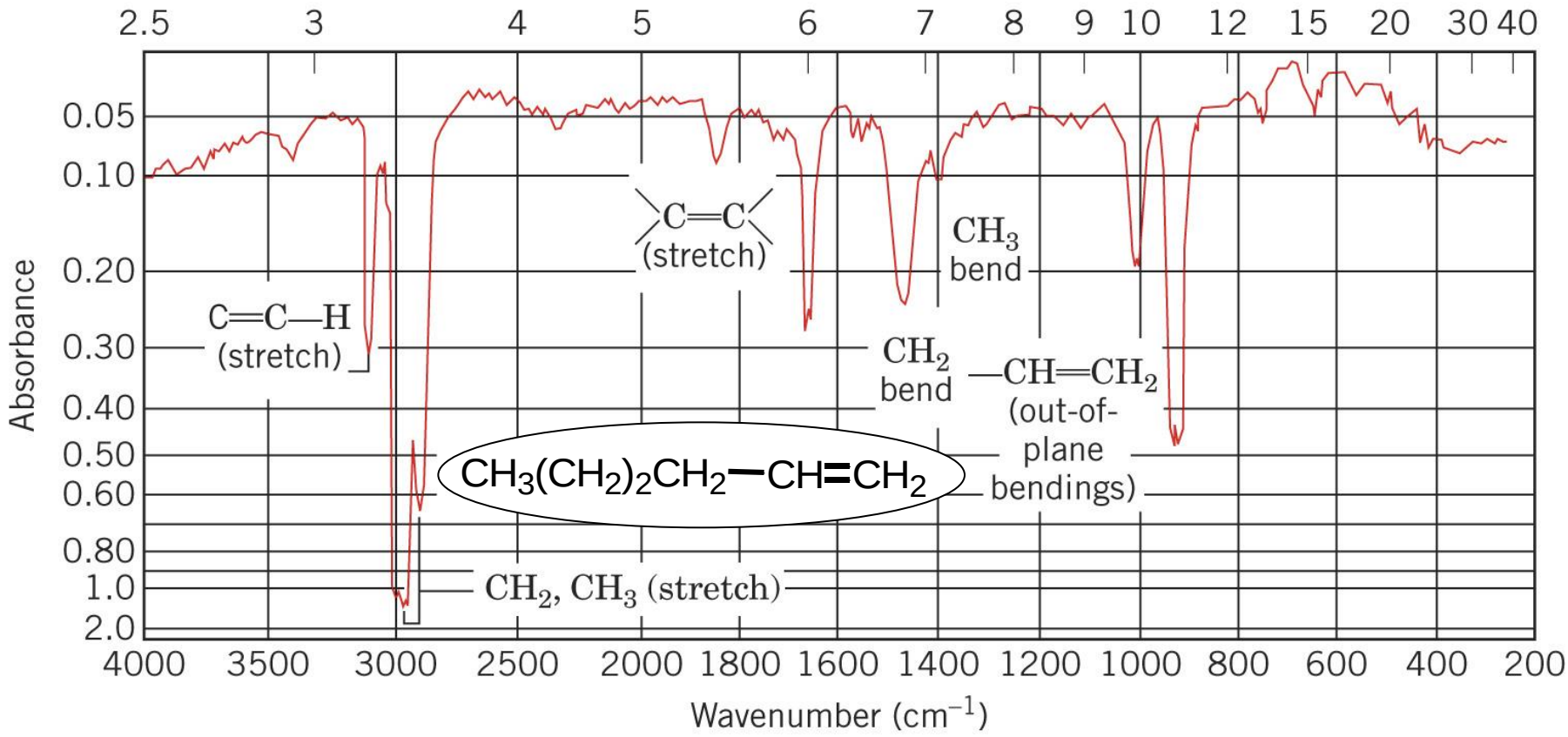
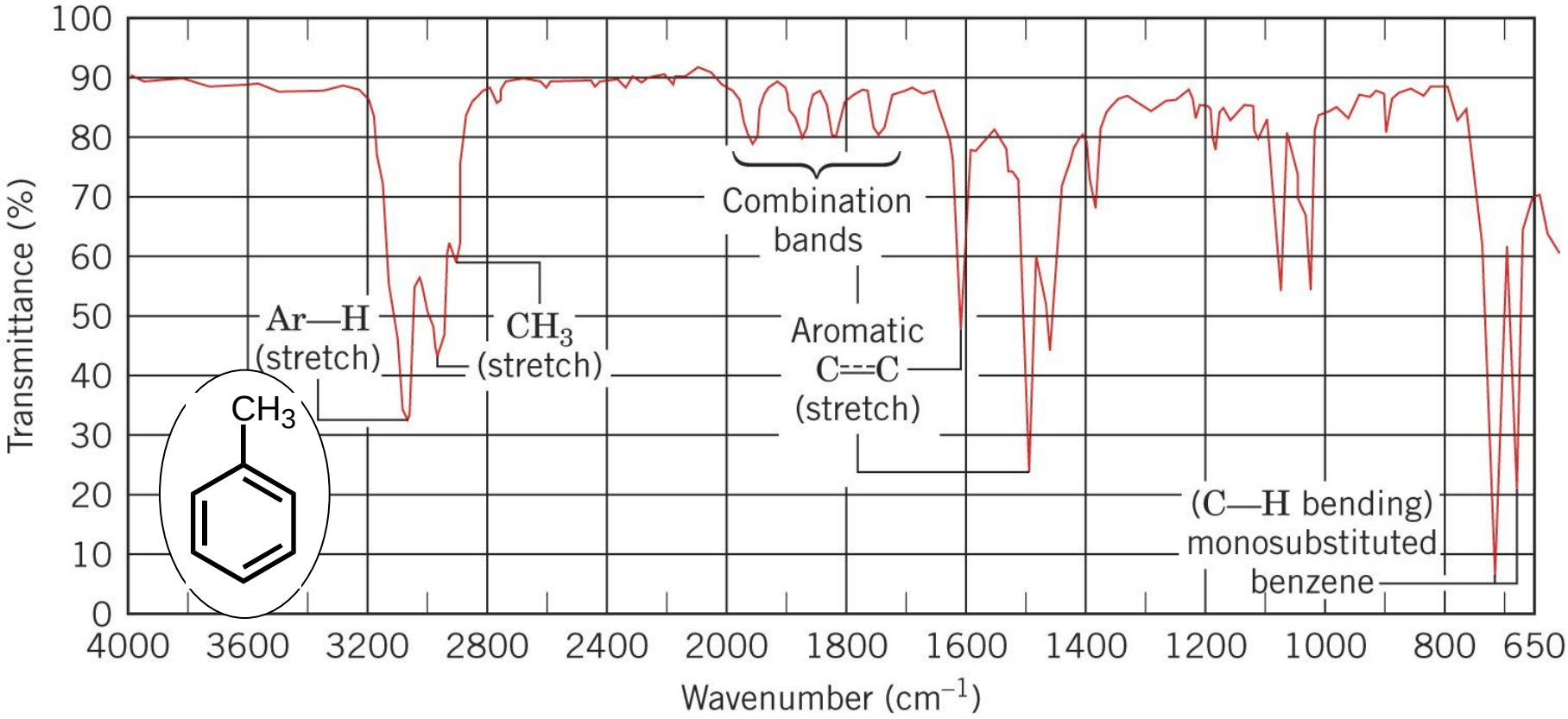


Aromatski spojevi

- Vibracije istezanja C-C veze daju set karakterističnih oštrih pikova između 1450-1600 cm^{-1}
- Primjer: toluen



Druge funkcionalne skupine

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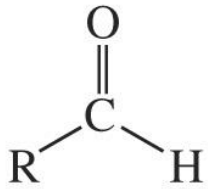
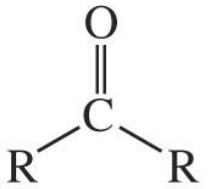
Karbonilna funkcionalna skupina

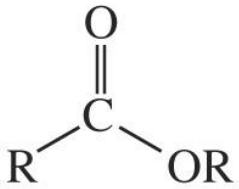
- Općenito karbonilna skupina daje jaki signal rastezanja koji se pojavljuje na 1630-1780 cm^{-1}
  - Potpuno precizno mjesto signala ovisi o stvarnoj prisutnoj funkcionalnoj skupini



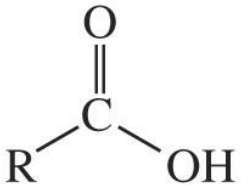
ALDEHID
1690 – 1740 cm^{-1}



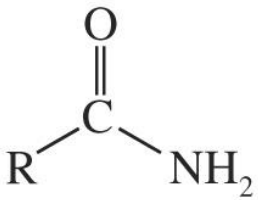
KETON
1680 – 1750 cm^{-1}



ESTER
1735 – 1750 cm^{-1}

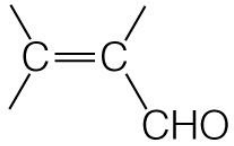
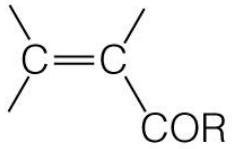


KARBOKSILNA KISELINA
1710 – 1780 cm^{-1}



AMID
1630 – 1690 cm^{-1}

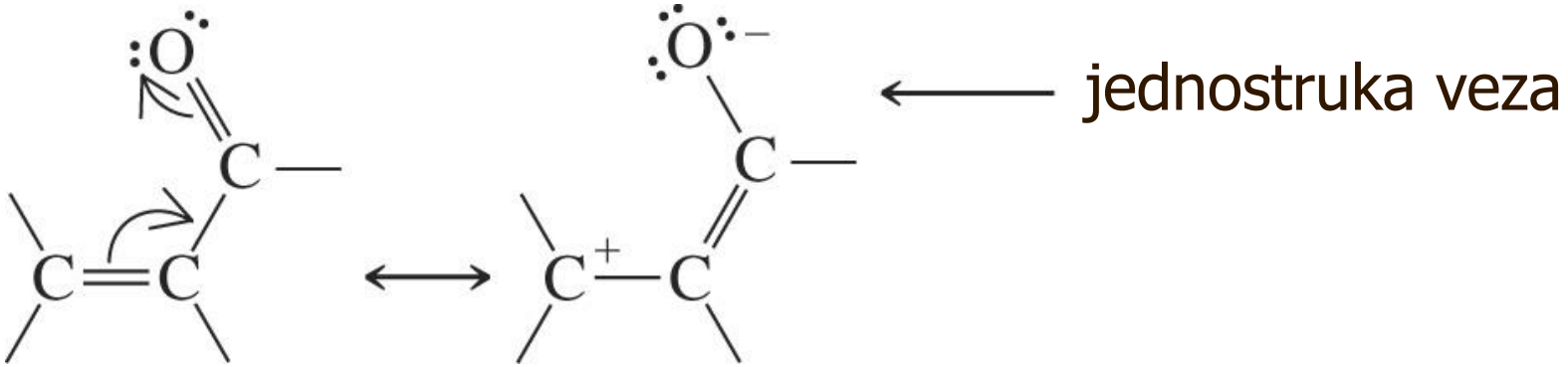
Aldehidi i ketoni

C=O Stretching Frequencies			
Compound	**Range (cm^{-1})**	**Compound**	**Range (cm^{-1})**
R—CHO	1720–1740	RCOR	1705–1720
Ar—CHO	1695–1715	ArCOR	1680–1700
	1680–1690		1665–1680
		Cyclohexanone	1715
		Cyclopentanone	1751
		Cyclobutanone	1785

Aldehidi i ketoni

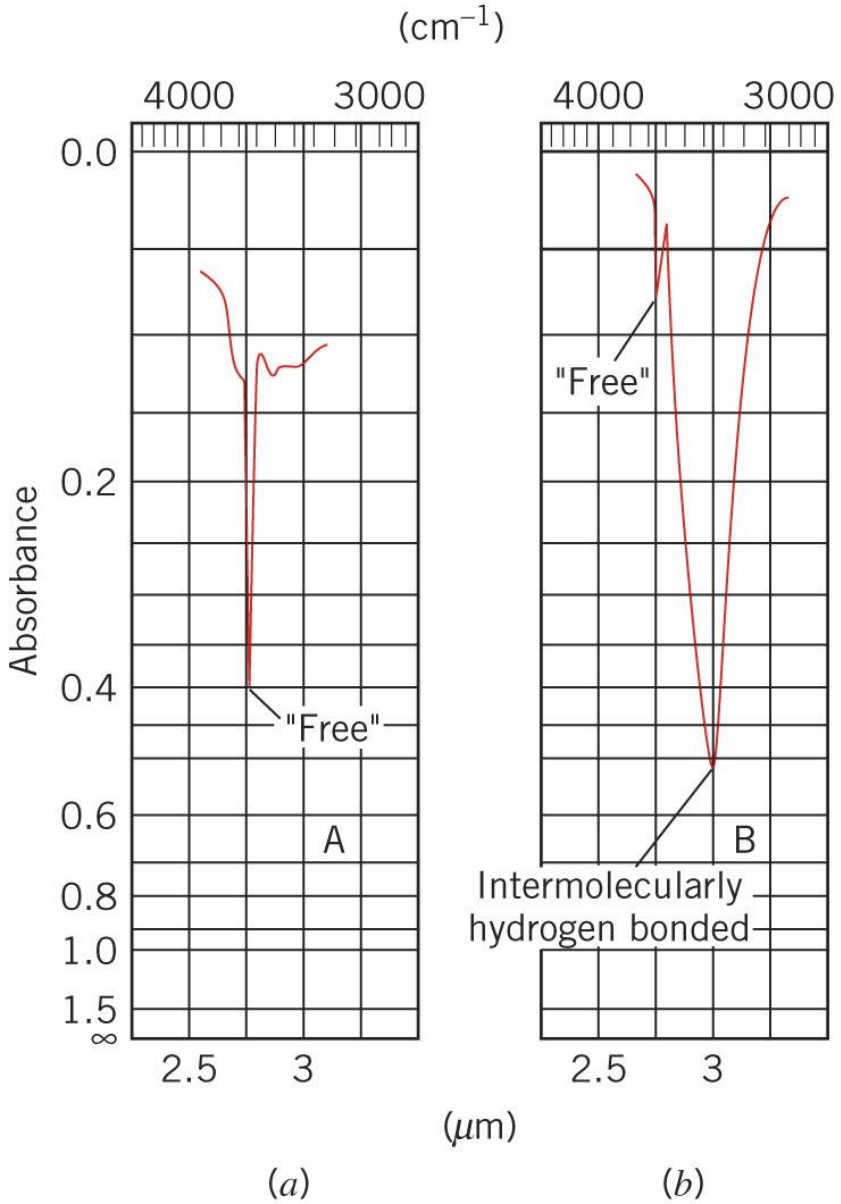
- Konjugacija pomiče frekvenciju u IR spektru prema približno 40 cm^{-1} nižim vrijednostima kako karbonilna skupina ima manji karakter dvostruke veze
  - Jednostruke veze se istežu puno lakše u odnosu na dvostruke veze

- Vibracije C-H veze aldehida daju dva slaba ali karakteristična signala kod 2700-2775 i 2820-2900 cm^{-1}



Alkoholi i fenoli

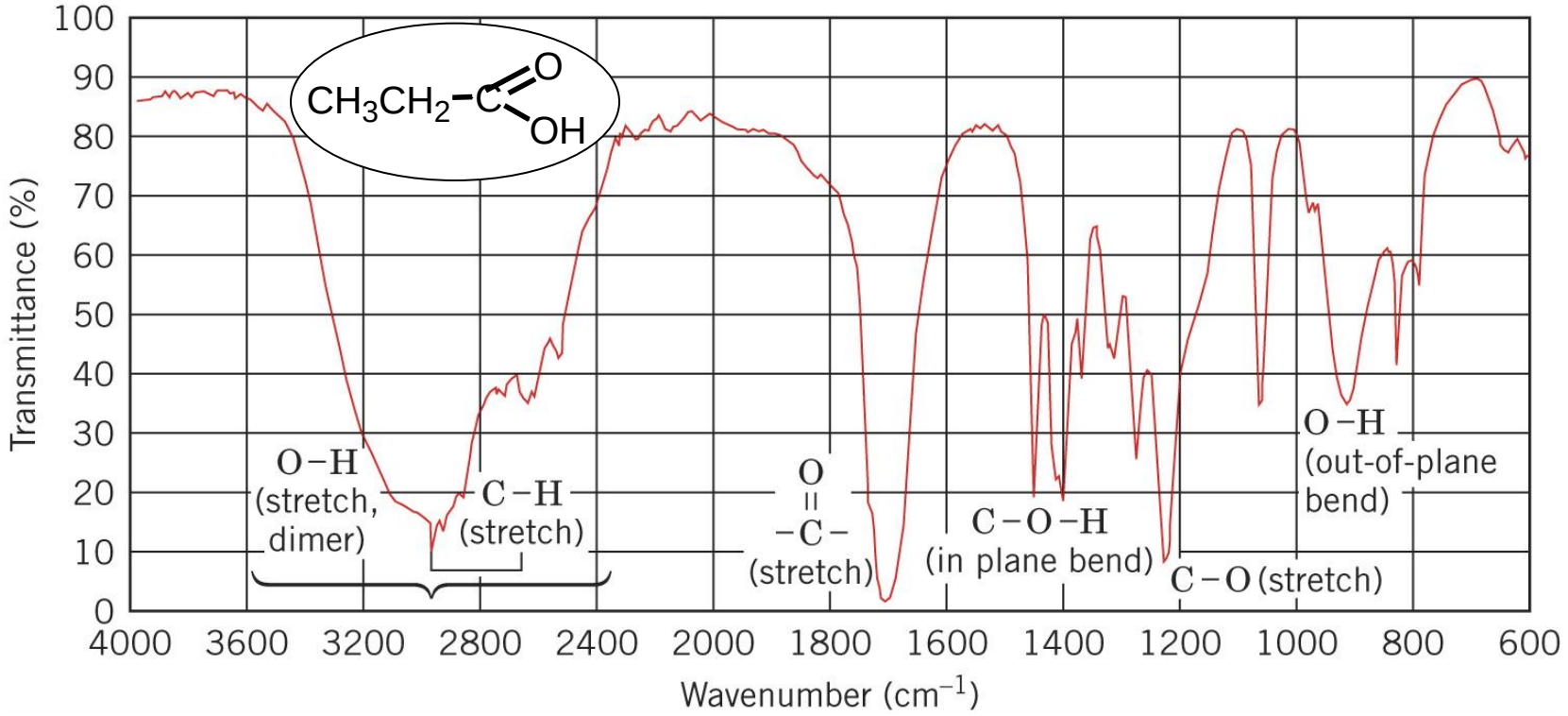
- Apsorpcija vibracija O-H rastezanja veoma je karakteristična
  - U vrlo razrijeđenim otopinama, vodikove veze su odsutne te se javlja jako oštar signal kod 3590-3650 cm^{-1} (*a*)
  - U koncentriranijim otopinama, hidroksilne skupine su vodikovim vezama povezane jedna s drugom, te se javlja veoma širok i velik signal kod 3200-3550 cm^{-1} (*b*)
  - Fenol ima hidroksilnu skupinu direktno vezanu na aromatski prsten



Karboksilne kiseline

- Karbonilni pik kod 1710-1780 cm^{-1} je vrlo specifičan
- Prisutnost signala vibracija dvije skupine, i karbonilne i O-H skupine, dovoljan je dokaz prisutnosti karboksilne kiseline

Primjer: propanska kiselina

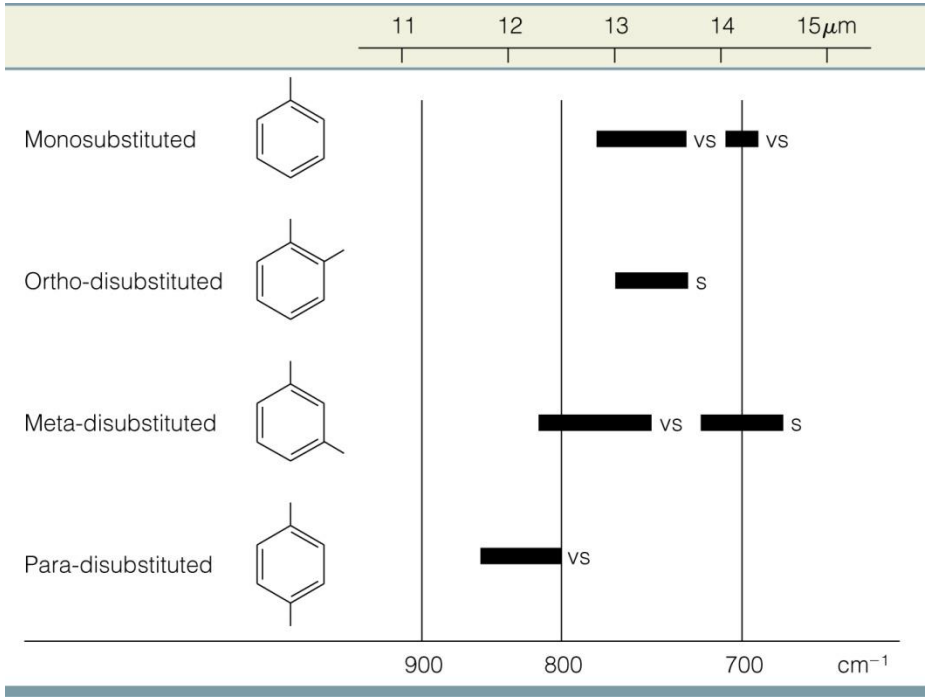


Amini i amidi

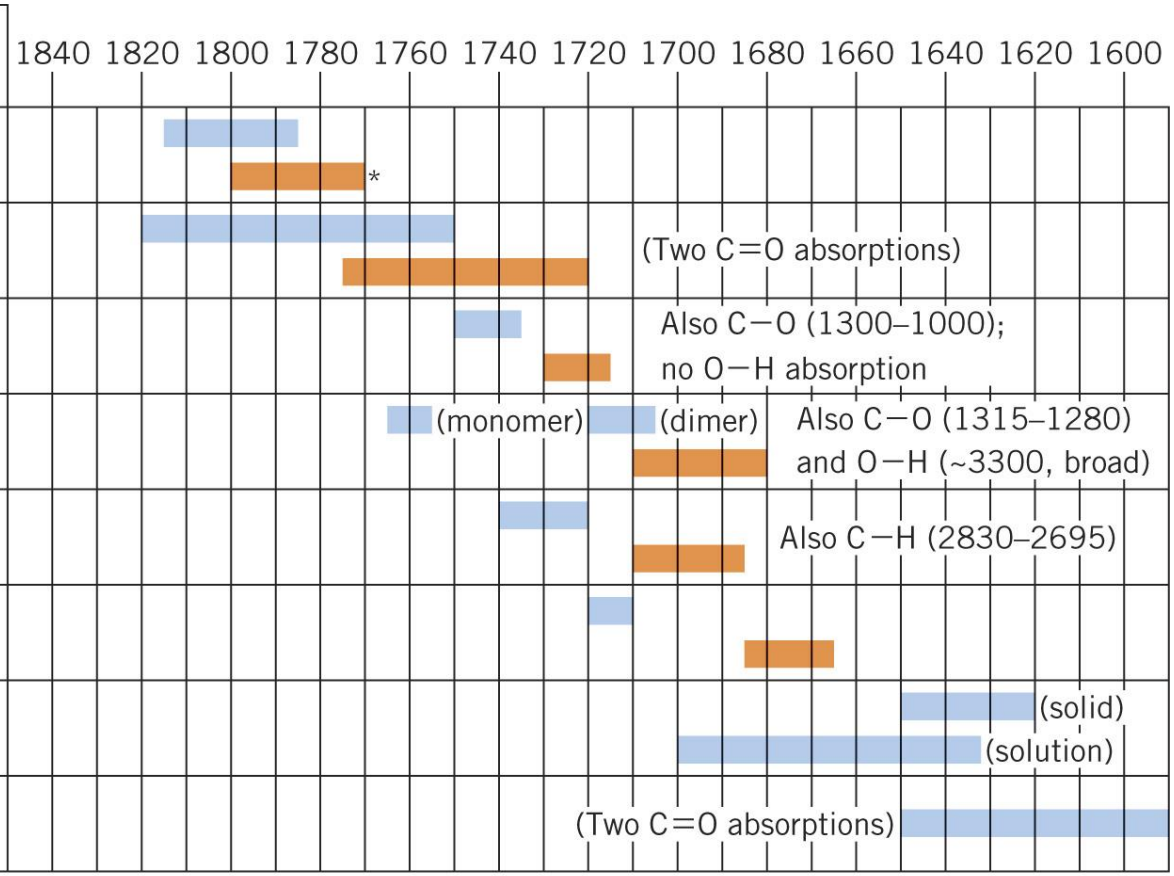
- Veoma razrijeđena otopina 1^{o} i 2^{o} amina pokazuje oštre signale kod 3300-3500 cm^{-1} za vibracije istezanja N-H veza
  - 1^{o} amini daju dva signala dok 2^{o} amini jedan pik
  - 3^{o} amini nemaju N-H veze te ne apsorbiraju u ovom području
- Koncentriranije otopine amina pokazuju šire signale
- Amidi imaju signale za vibracije istezanja N-H skupine i karbonilni pik

IR spektar supstituiranih benzena

- Derivati benzena pokazuju nekoliko karakterističnih frekvencija
  - C-H rastezanja detektiraju se kod 3030 cm^{-1}
  - Rezultat rastezanja aromatskog prstena su vrpce kod 1450-1600 cm^{-1} i dva signala blizu 1500 i 1600 cm^{-1}
- Monosupstituirani benzeni pokazuju dvije jake apsorpcijske vrpce kod 690-710 cm^{-1} i 730-770 cm^{-1}
- Disupstituirani benzeni pokazuju sljedeće apsorpcije:



Functional Group	Approximate Frequency Range (cm^{-1})
Acid chloride	1815–1785 1800–1770 (conj.)
Acid anhydride	1820–1750 1775–1720 (conj.)
Ester/Lactone	1750–1735 1730–1715 (conj.)
Carboxylic acid	~1760 or 1720–1705 1710–1680 (conj.)
Aldehyde	1740–1720 1710–1685 (conj.)
Ketone	1720–1710 1685–1665 (conj.)
Amide/lactam	1650–1640
Carboxylate salt	1650–1550



*Orange bars represent absorption ranges for conjugated species.

Alkani

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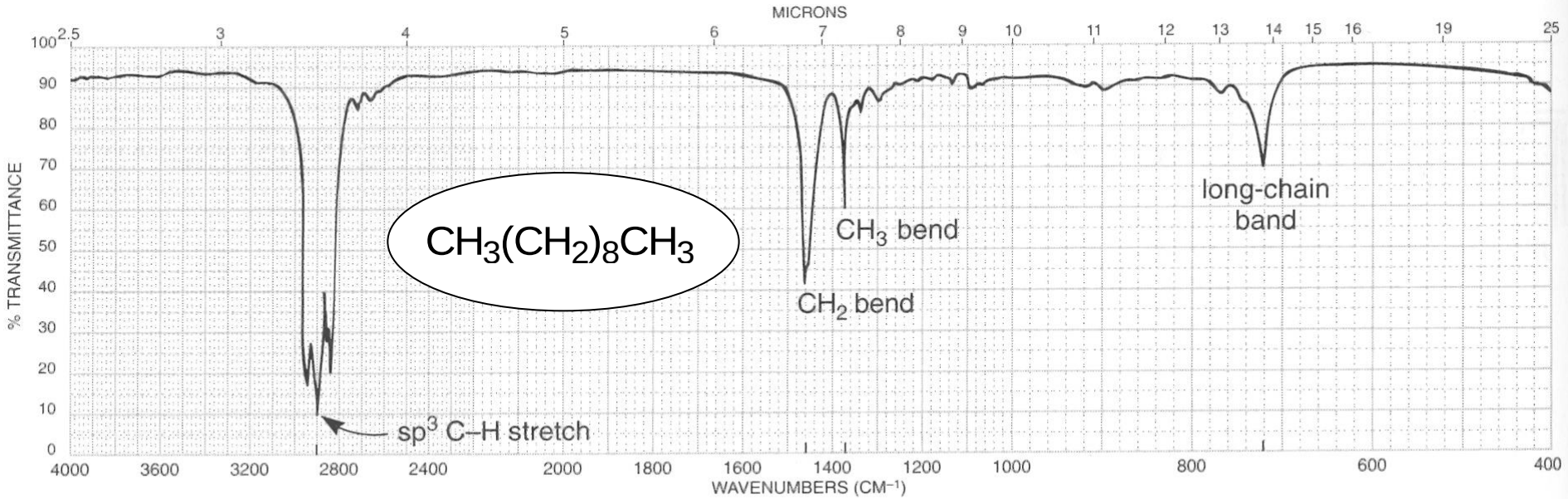
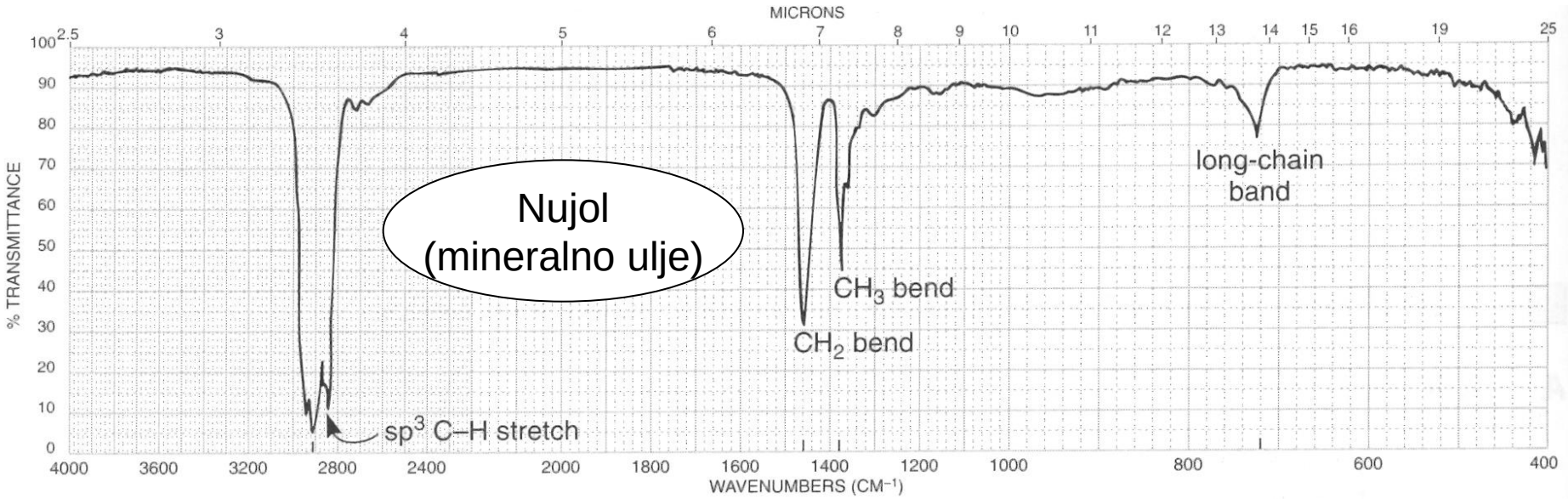


Infracrveni spektar dekana (KBr pločica)

Alkani



Infracrveni spektar mineralnog ulja (KBr pločica)

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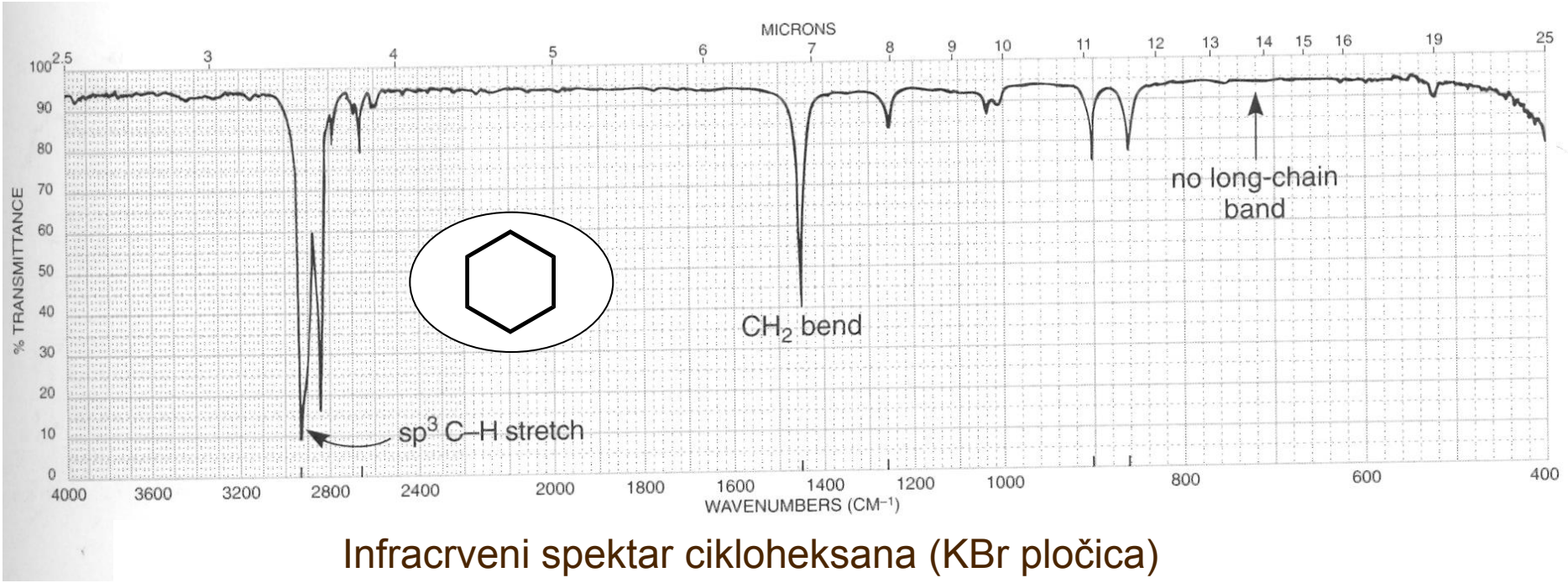

Infracrveni spektar cikloheksana (KBr pločica)

Alkeni

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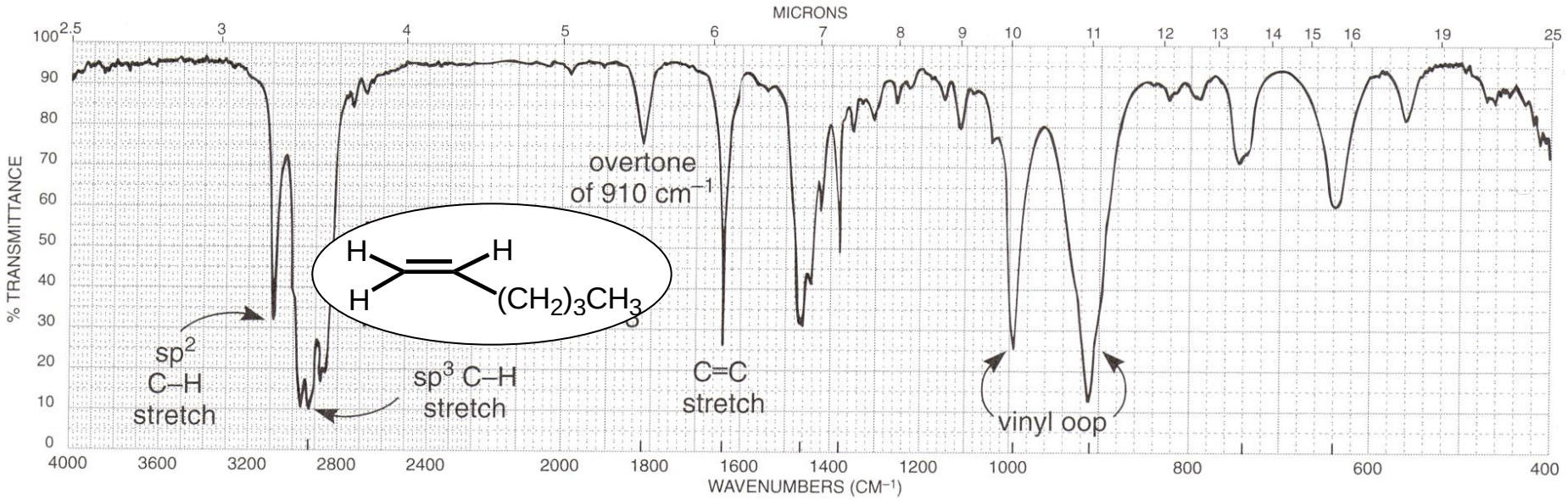

Infracrveni spektar heks-1-ena (KBr pločica)

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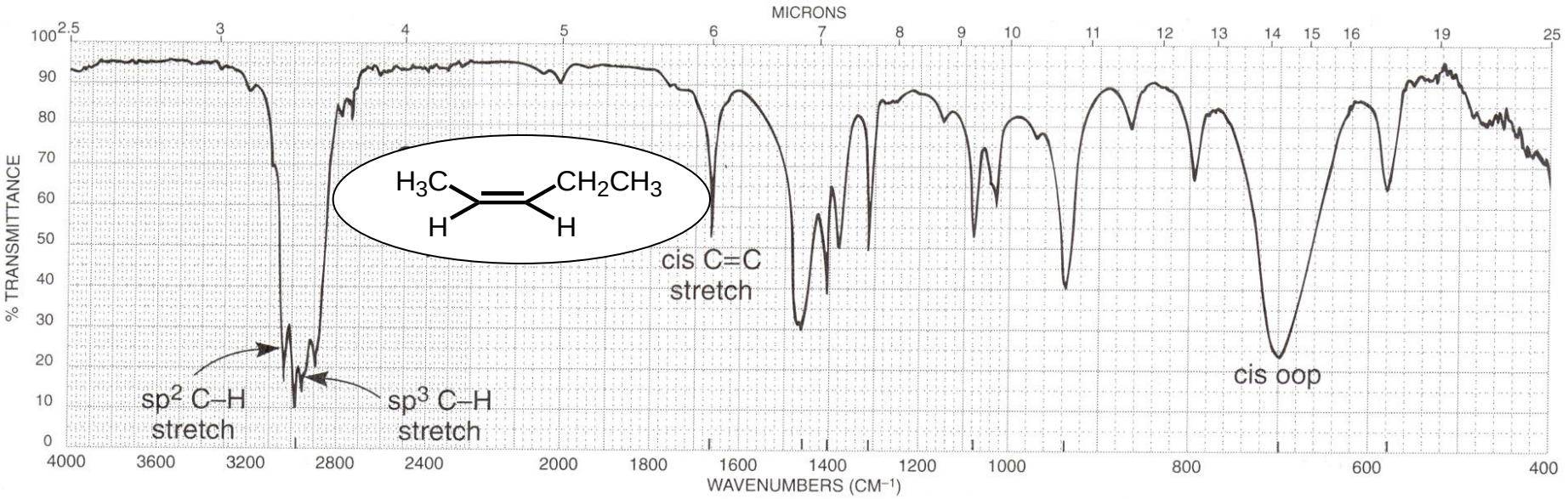

IR spektar *cis*-pent-2-ena (KBr pločica)

Alkeni

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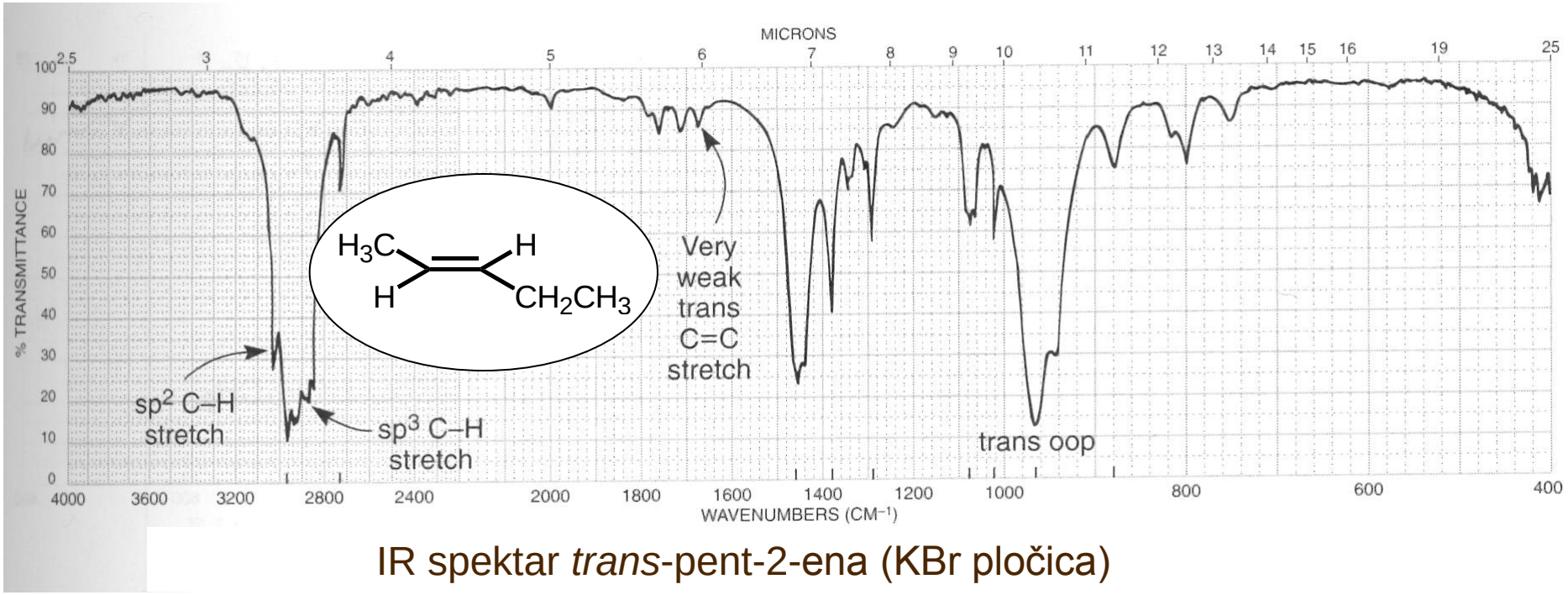

IR spektar *trans*-pent-2-ena (KBr pločica)

Cikloalkeni

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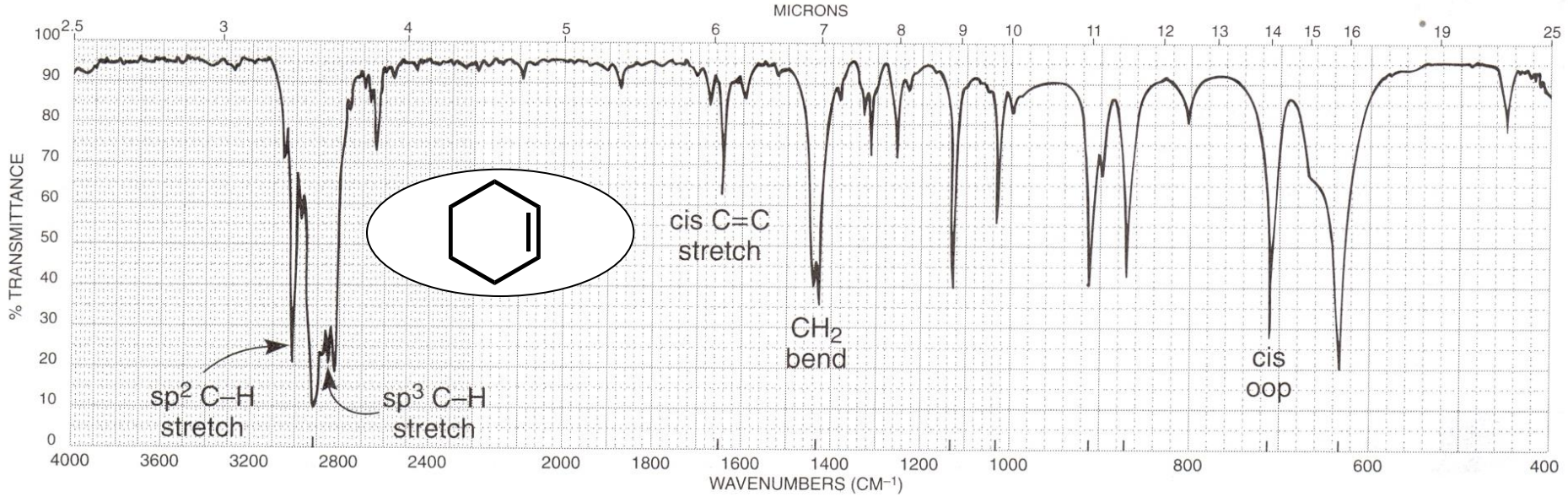

Infracrveni spektar cikloheksena (KBr pločica)

Alkini

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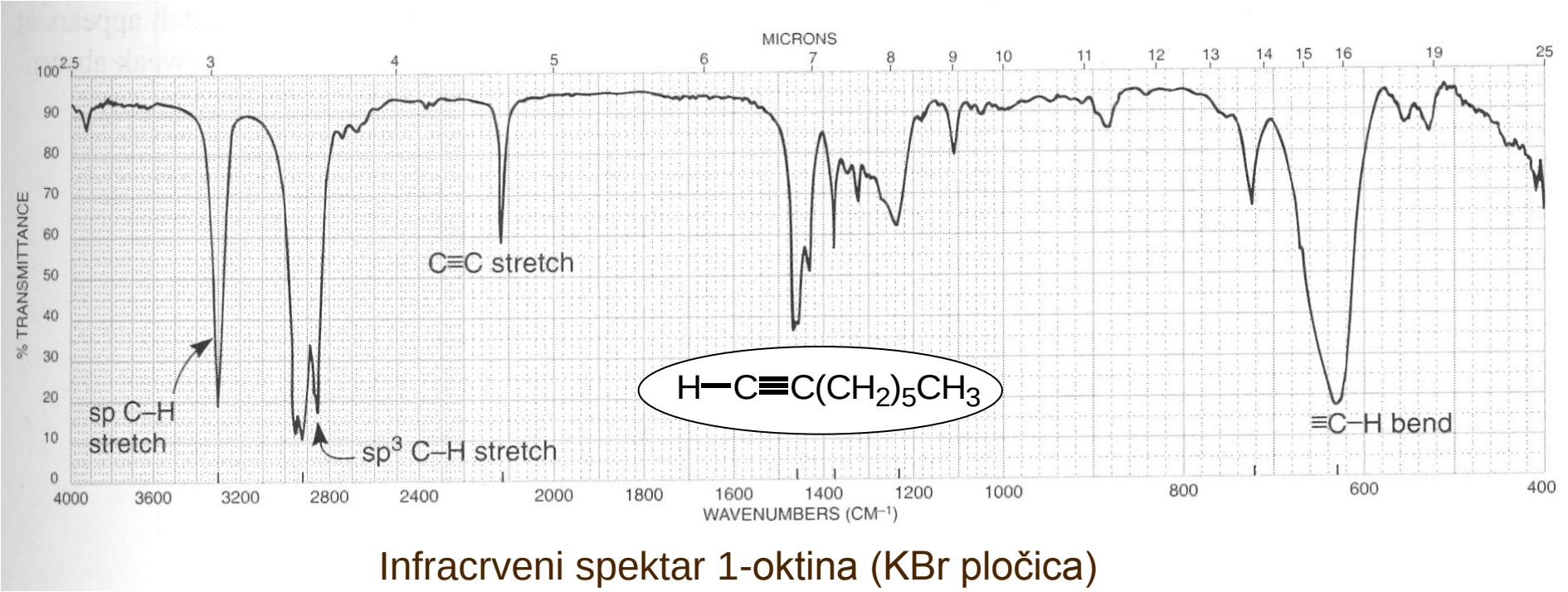
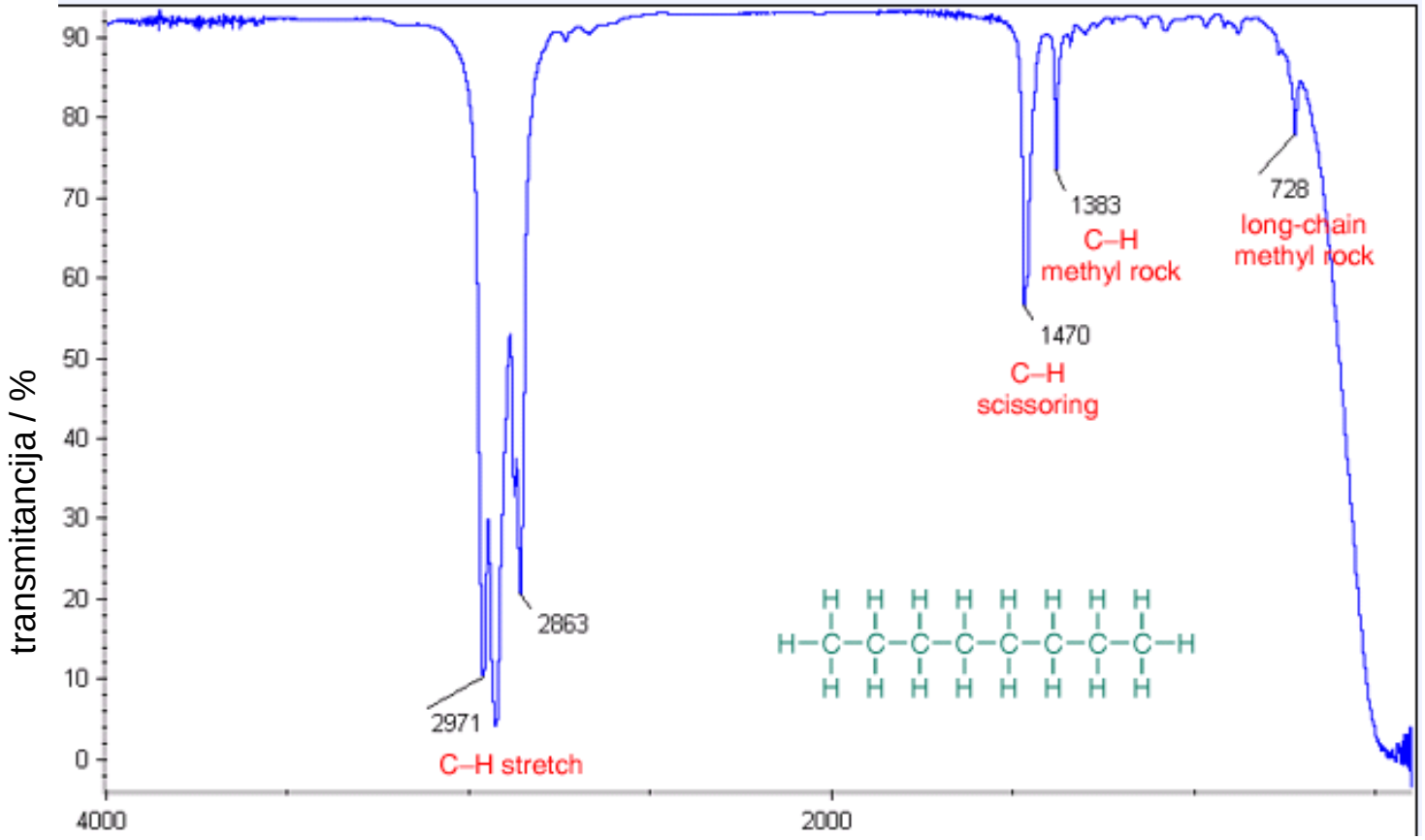


Infracrveni spektar 1-oktina (KBr pločica)

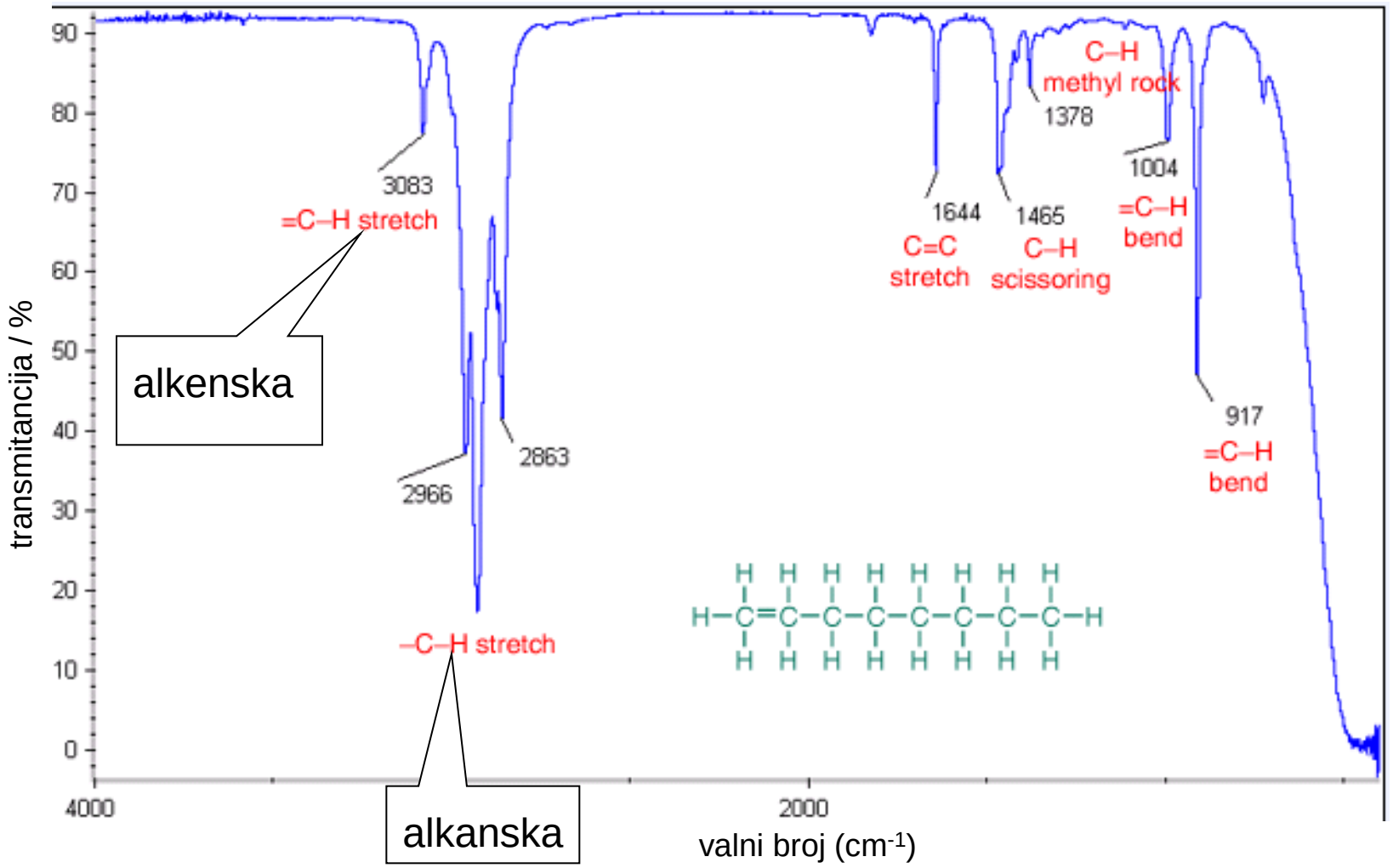
Dodatni primjeri

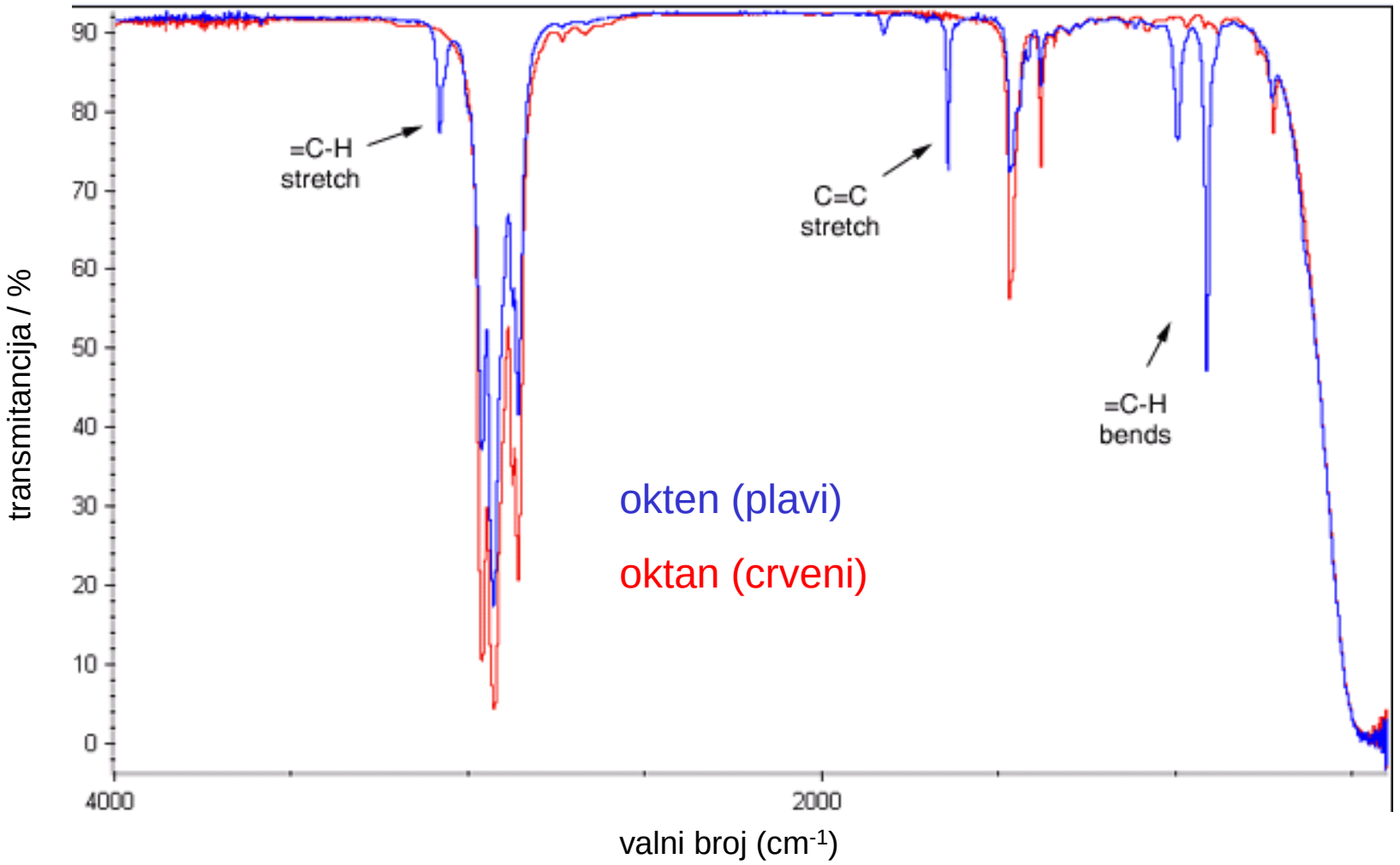
Alkani (oktan)



C-H rastezne: 3000-2850
C-H svijanja : 1470-1450
1370-1350
725-720
C-C (rast. i svij. se ne vide-slabe ili su izvan)

Alkeni (okten)




transmitancija / %
90
80
70
60
50
40
30
20
10
0
4000
2000
valni broj (cm-1)
=C-H
stretch
C=C
stretch
=C-H
bends
okten (plavi)
oktan (crveni)

Alkini (heptin)

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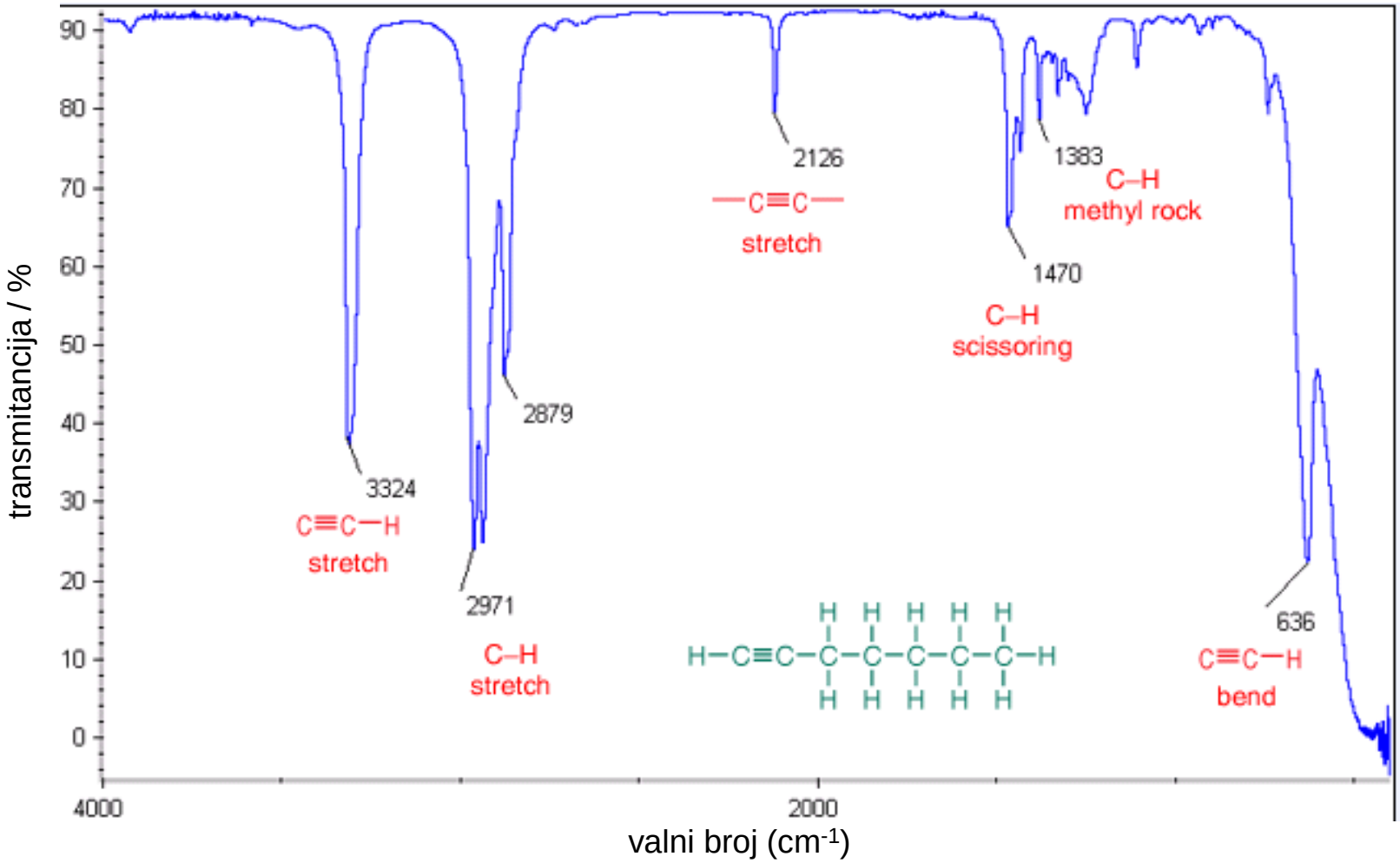

Alkil-halogenidi

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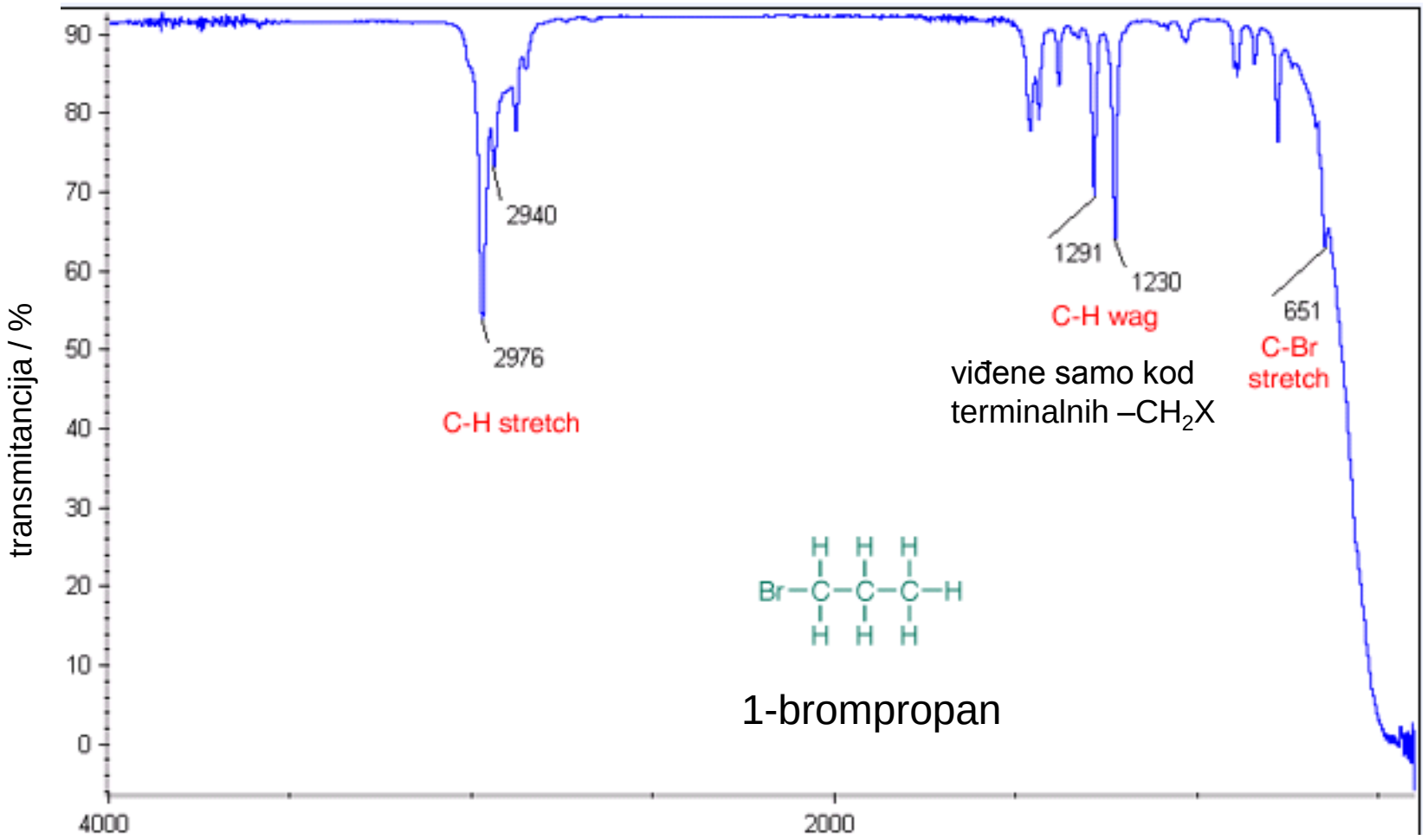
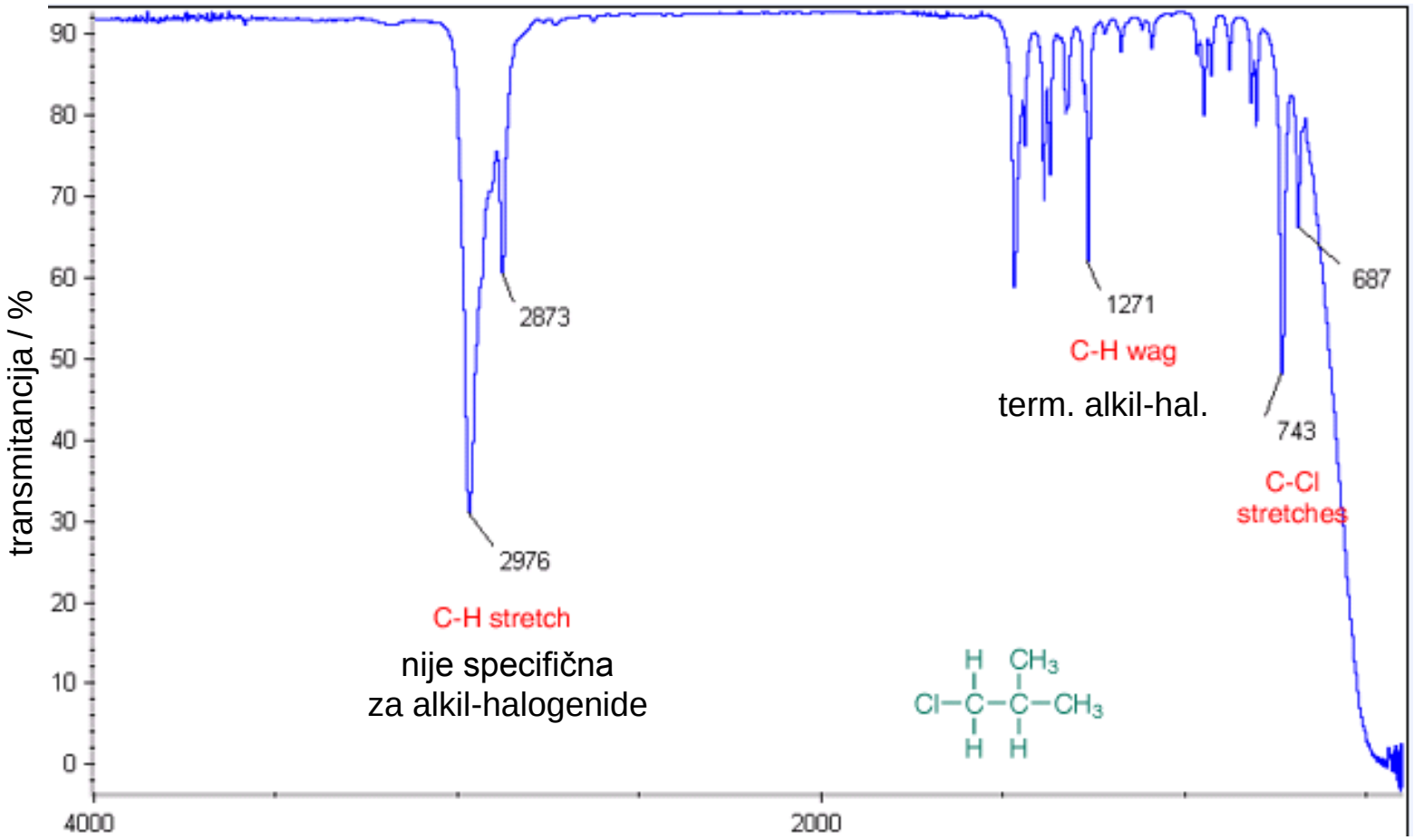
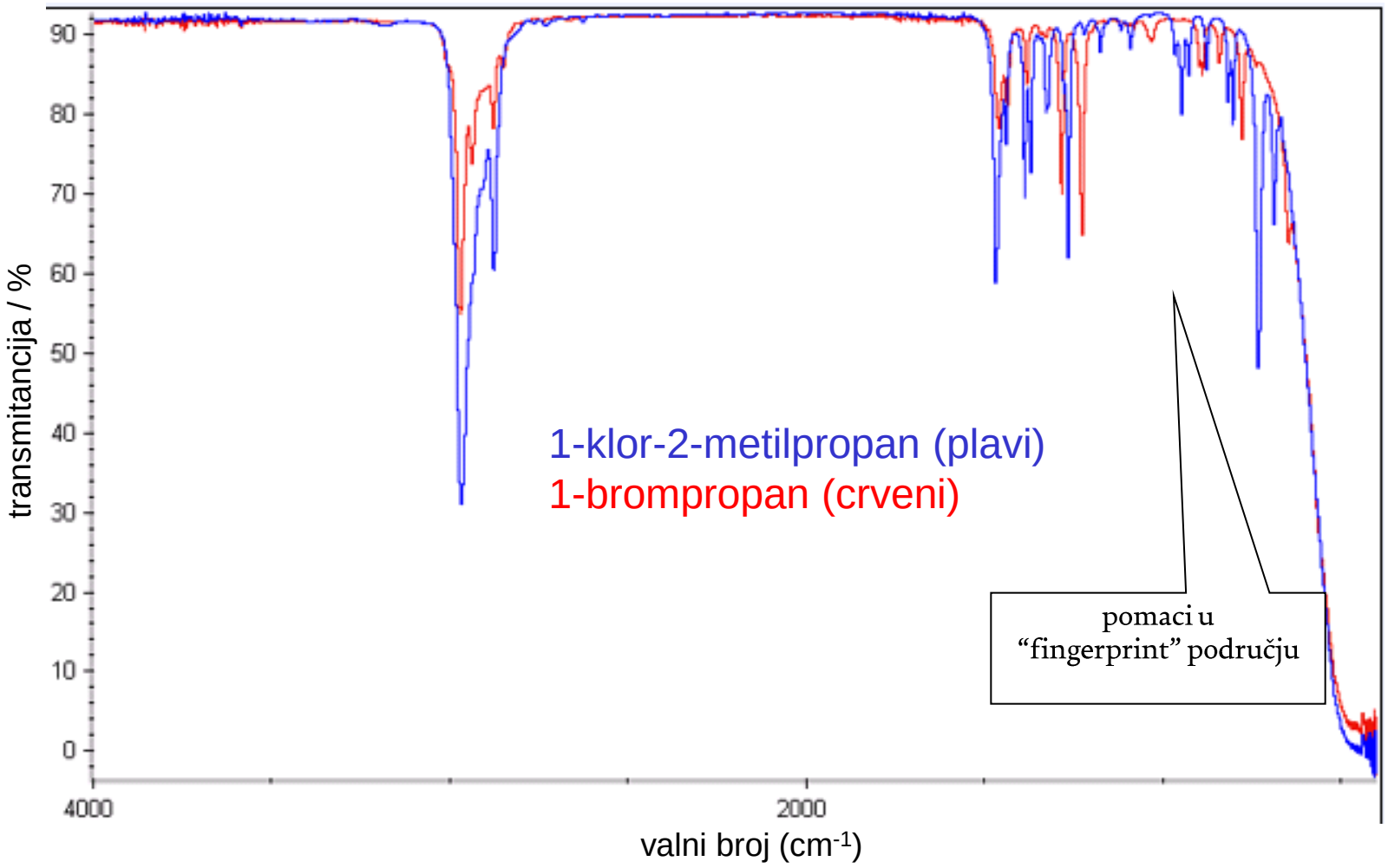


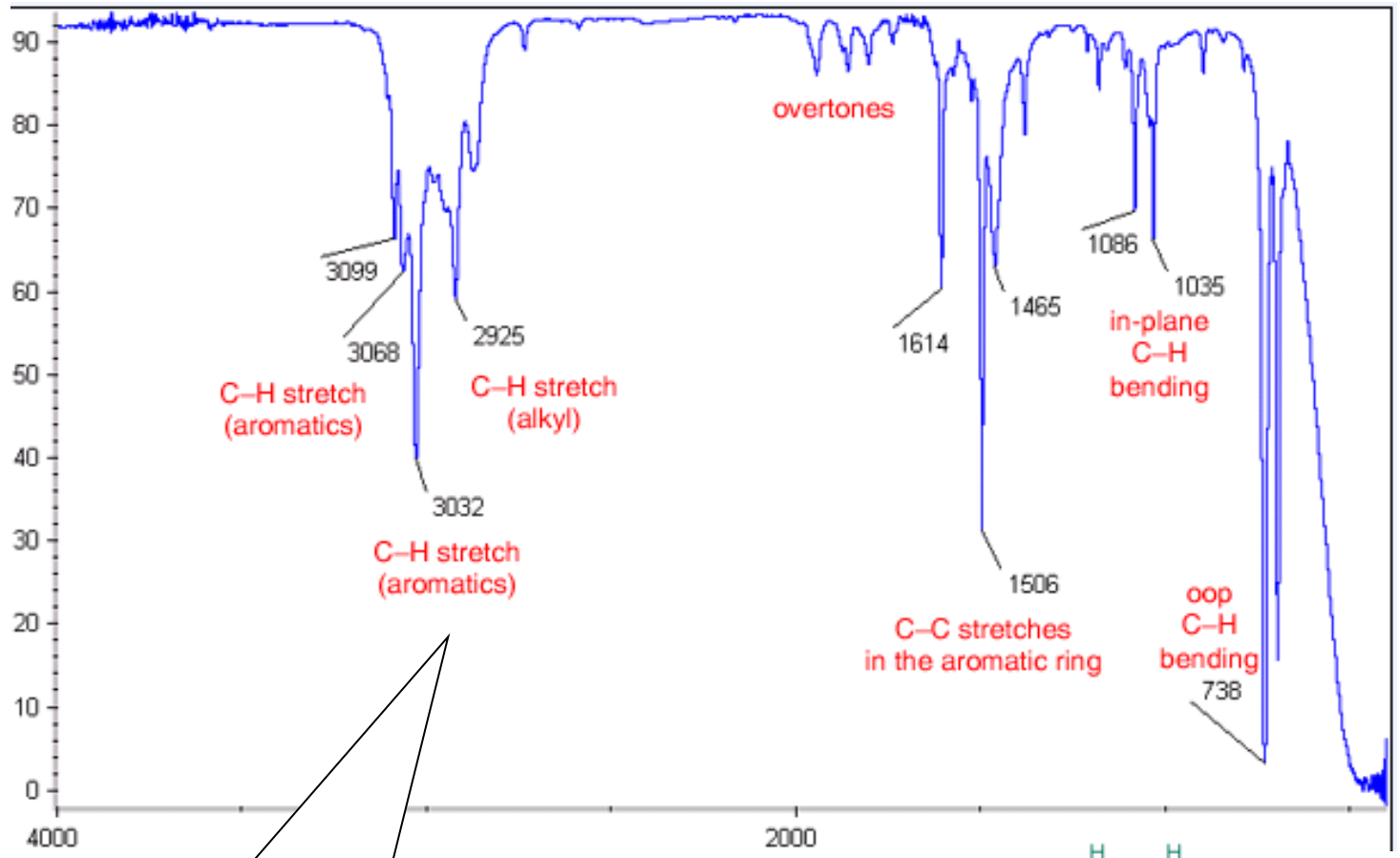


valni broj (cm-1)

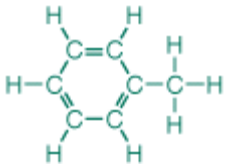
1-klor-2-metilpropan


transmitancija / %
90
80
70
60
50
40
30
20
10
0
4000
2000
valni broj (cm-1)
1-klor-2-metilpropan (plavi)
1-brompropan (crveni)
pomaci u
“fingerprint” području

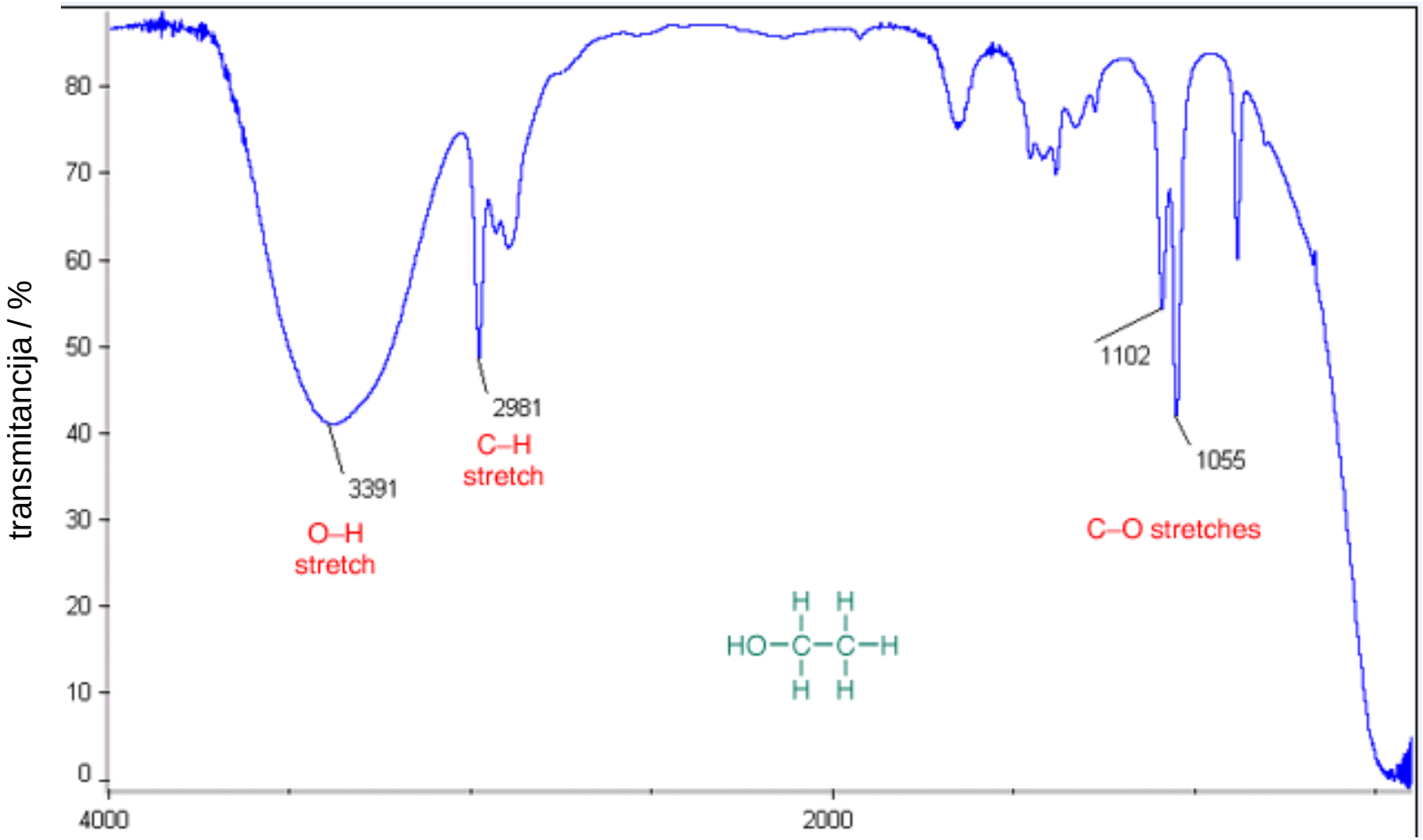
Aromati



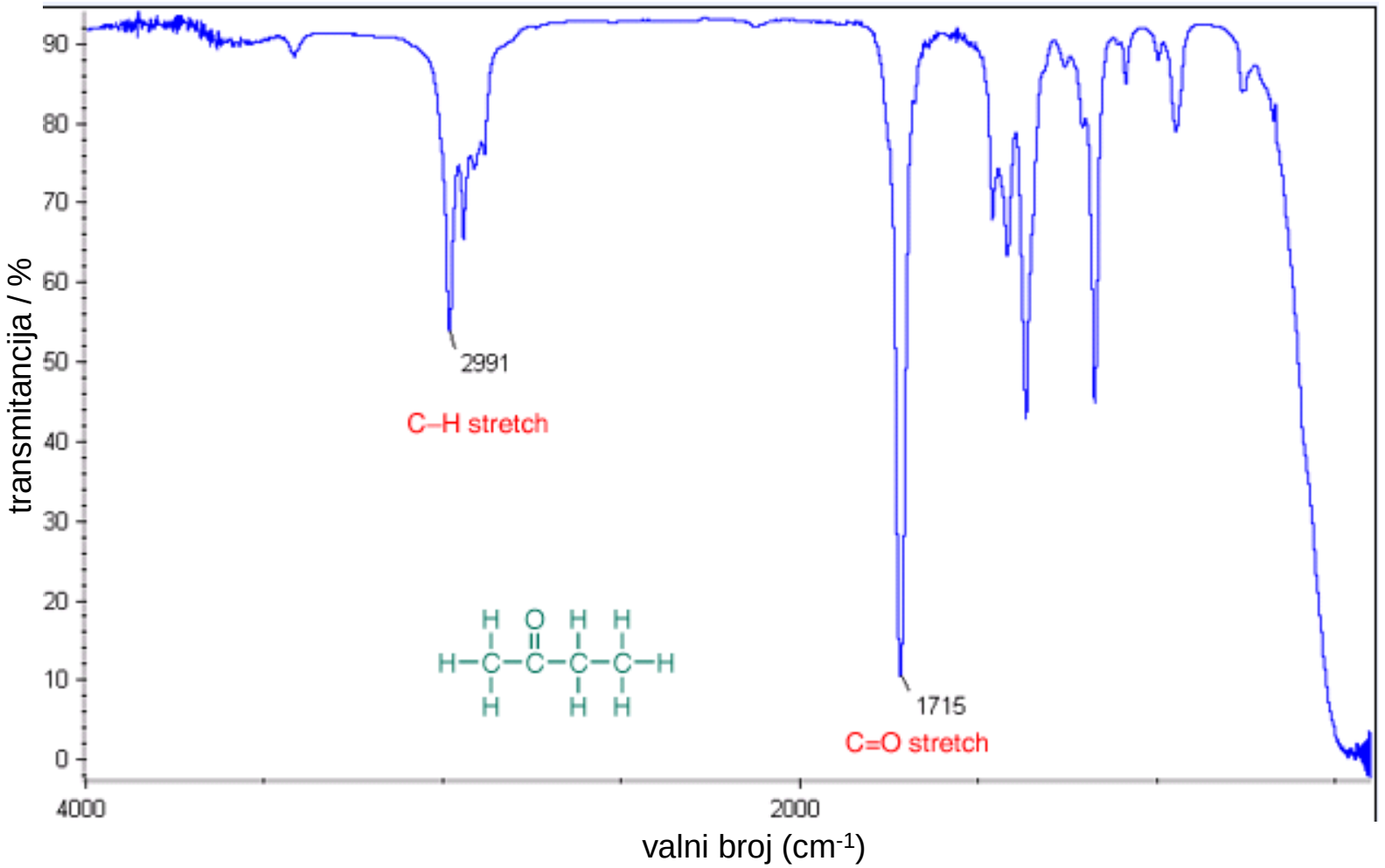
aromatske C-H su iznad 3000
alifatske su ispod 3000



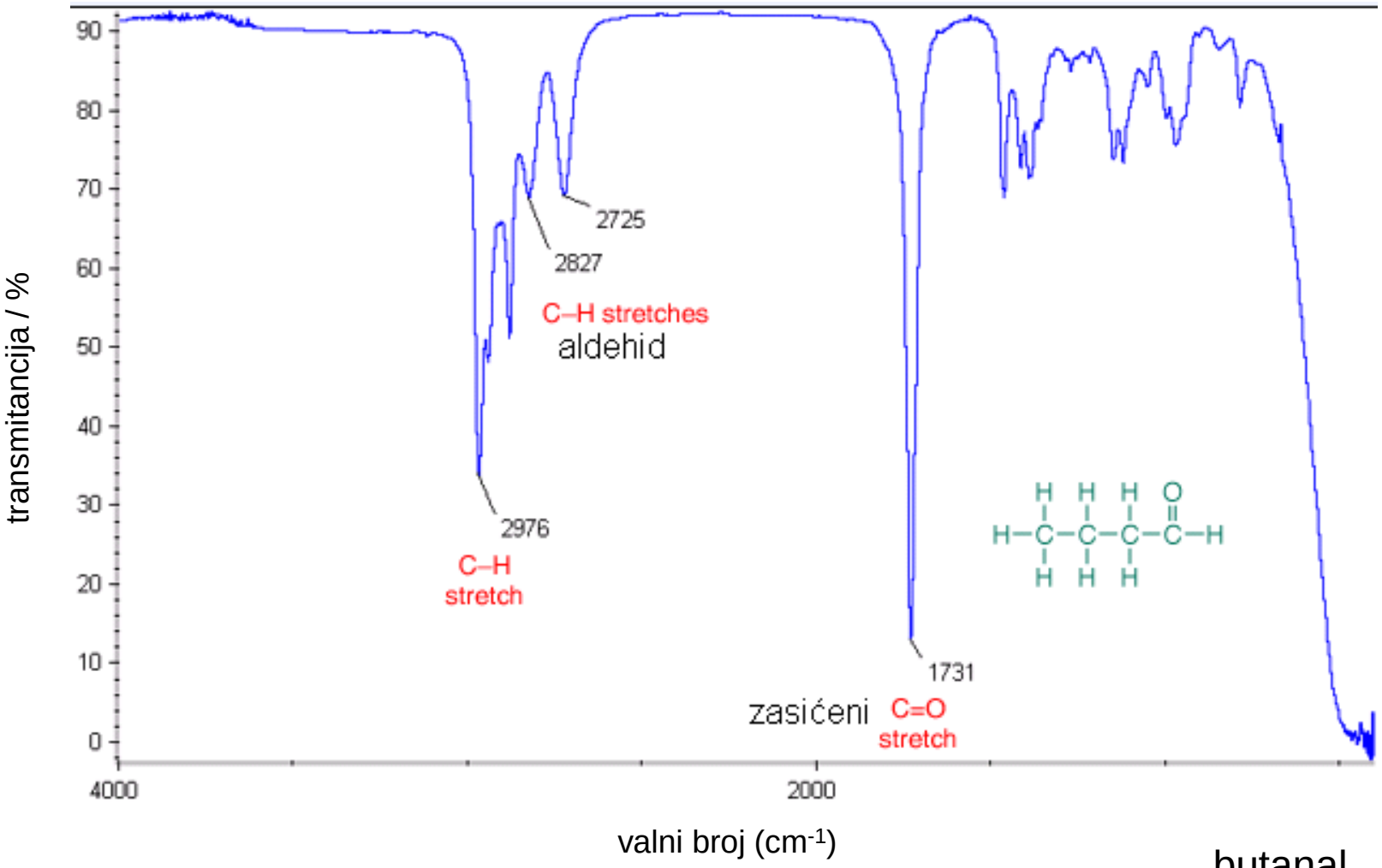
Alkoholi


transmitancija / %
80
70
60
50
40
30
20
10
0
4000
2000
valni broj (cm-1)
3391
O–H
stretch
2981
C–H
stretch
1102
1055
C–O stretches
HO–C–C–H

Ketoni


transmitancija / %
90
80
70
60
50
40
30
20
10
0
4000
2000
valni broj (cm-1)
2991
C–H stretch
1715
C=O stretch

Aldehidi


transmitancija / %
90
80
70
60
50
40
30
20
10
0
4000
2000
valni broj (cm-1)
2725
2827
C–H stretches
aldehid
2976
C–H
stretch
1731
zasićeni
C=O
stretch
butanal

Karboksilne kiseline

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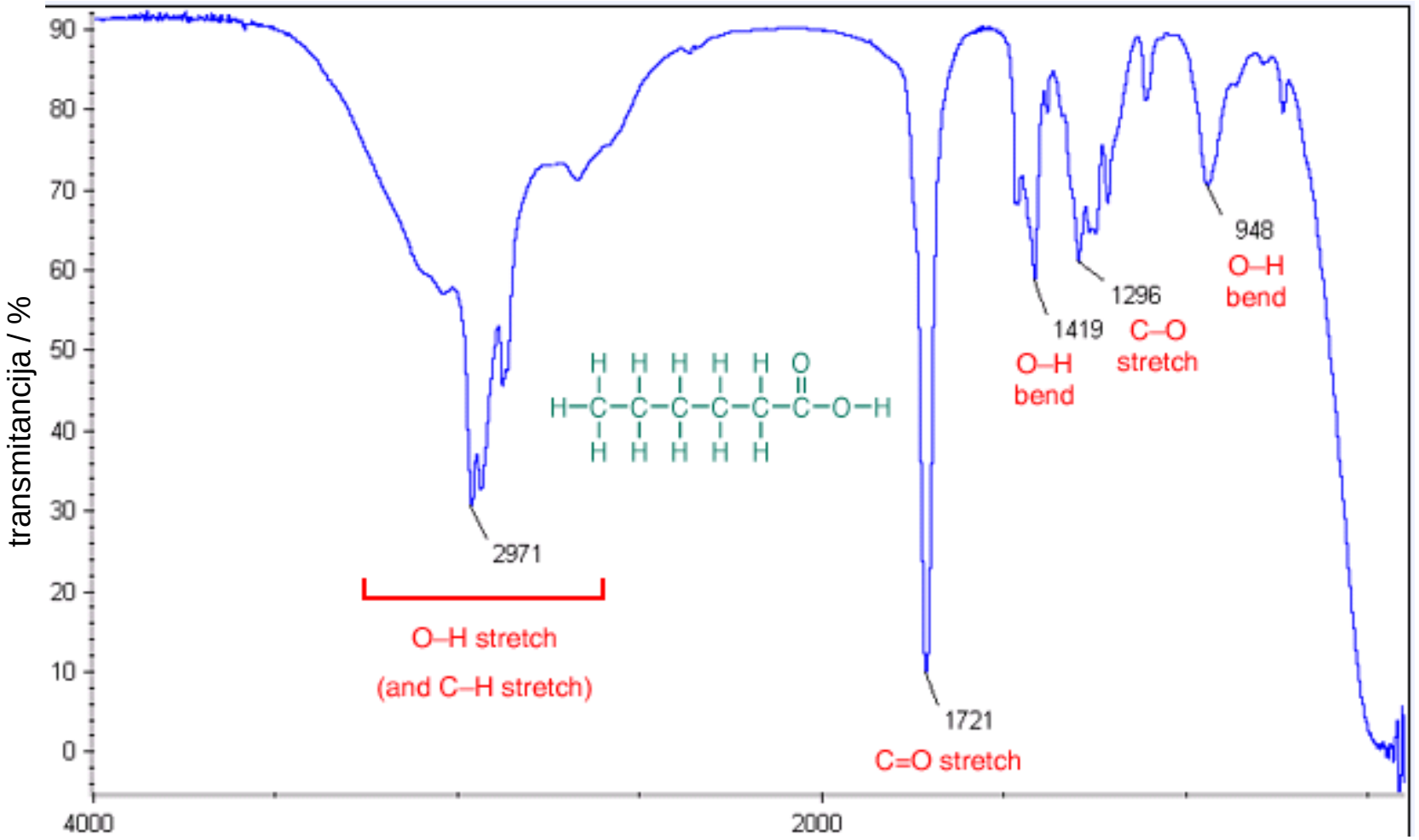

heksan-kiselina

Esteri

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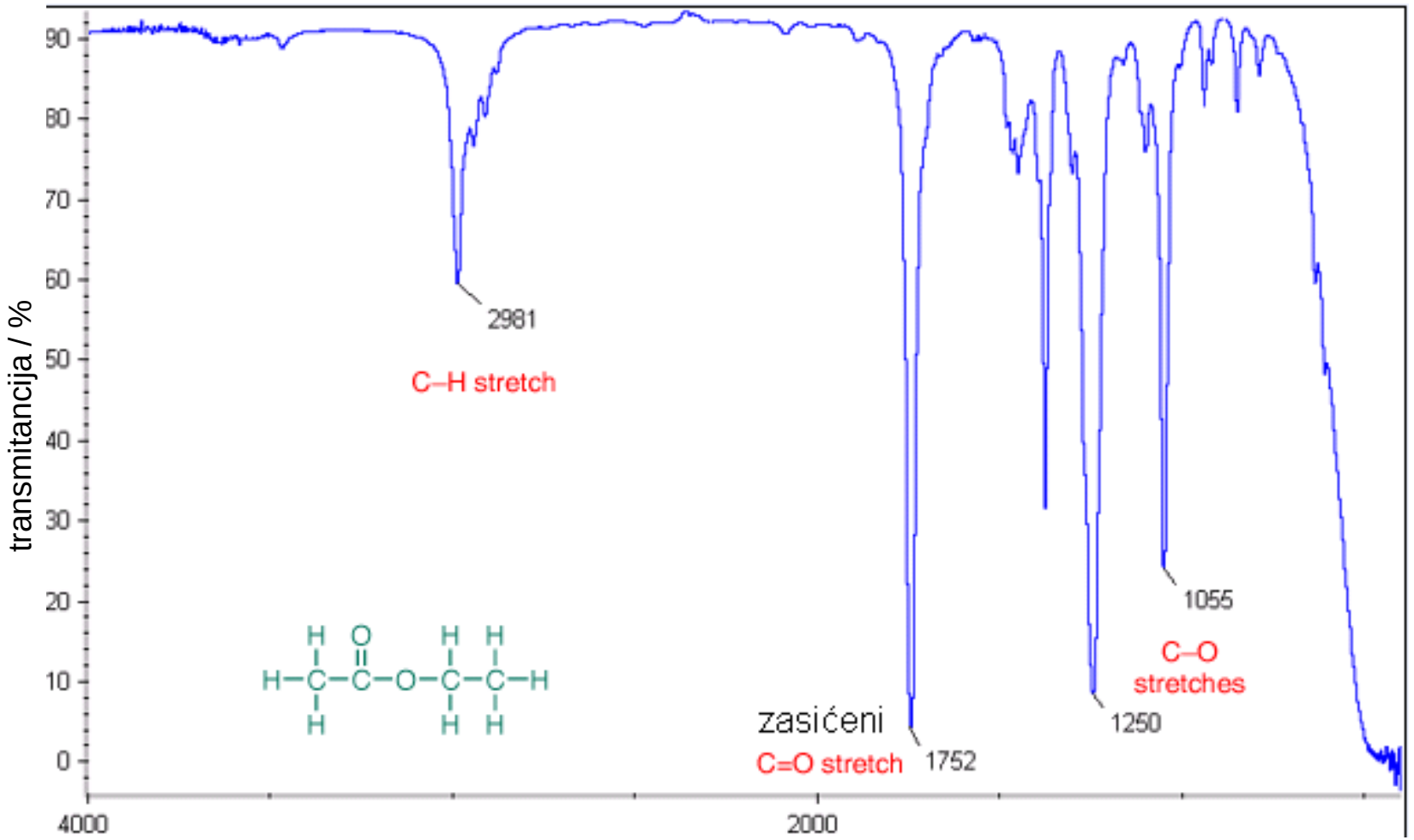
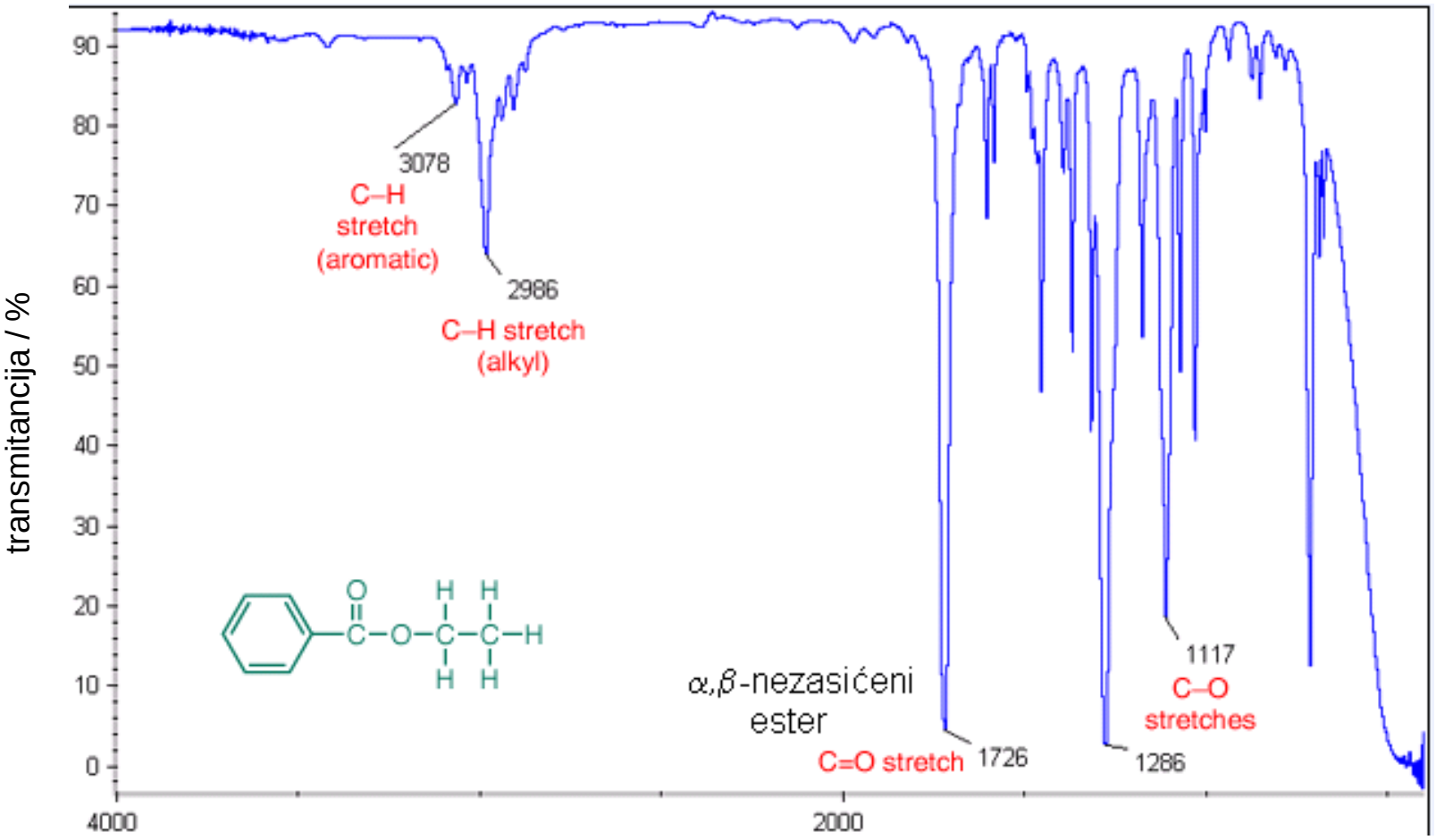
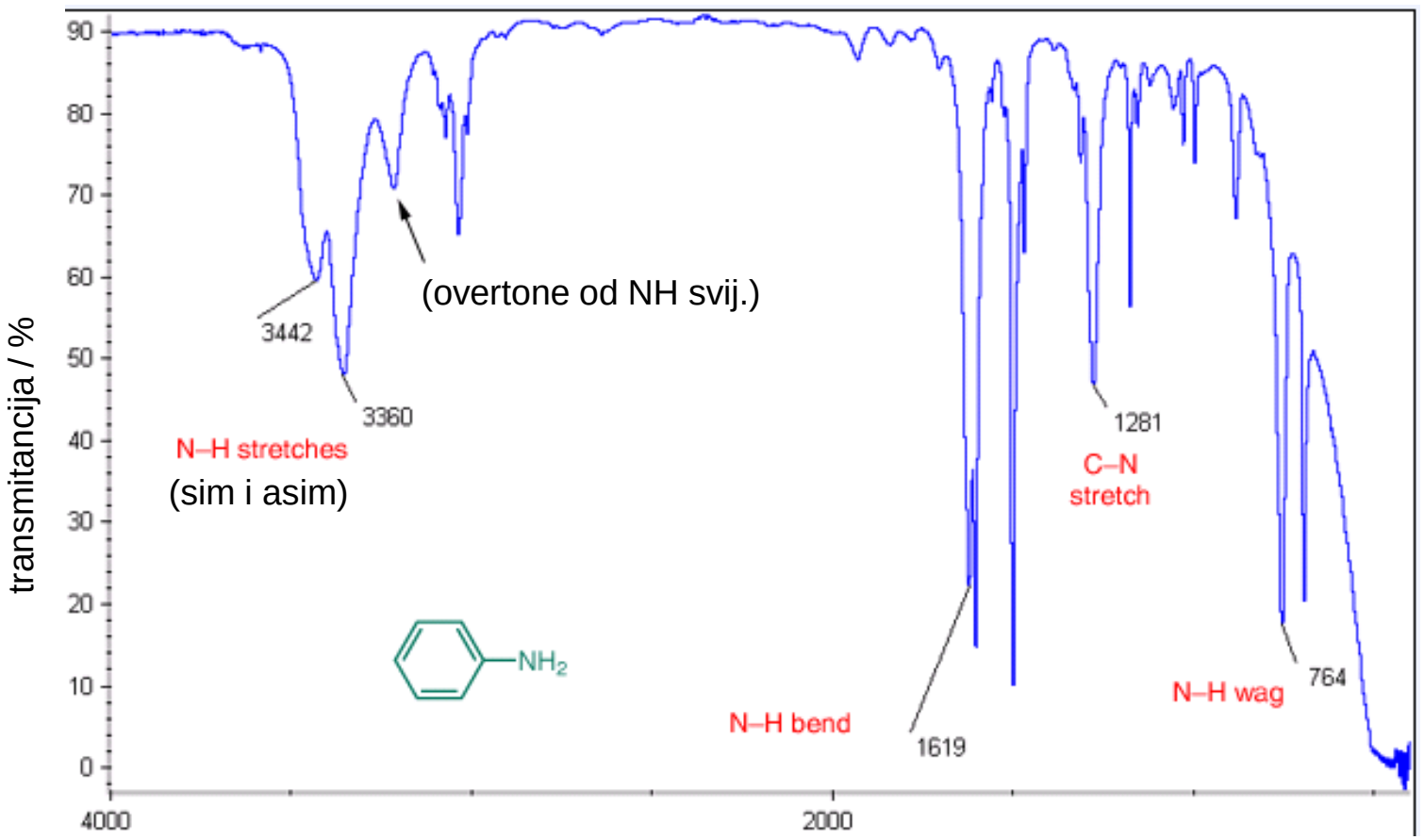


etilacetat

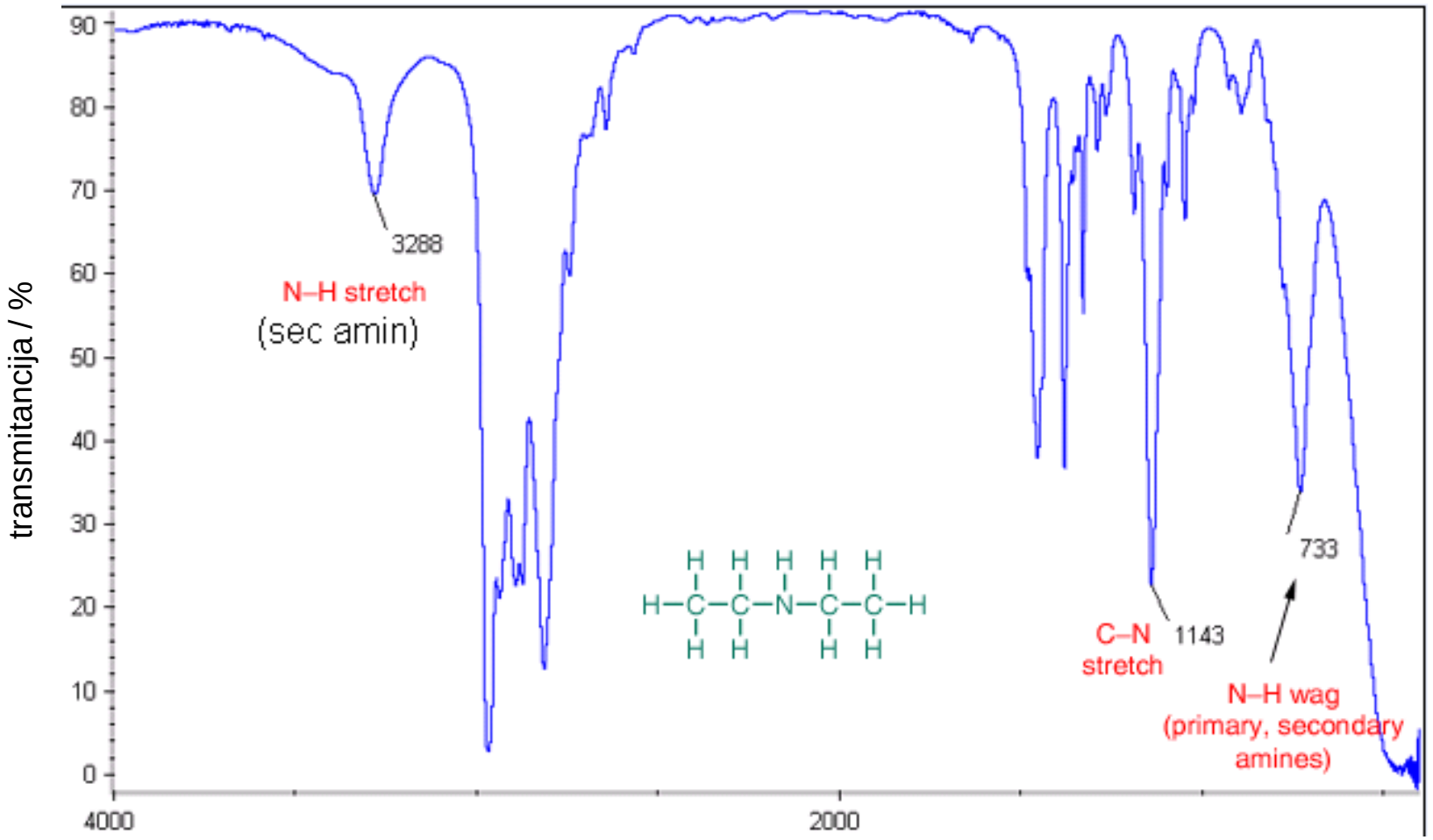


etilabenzoat

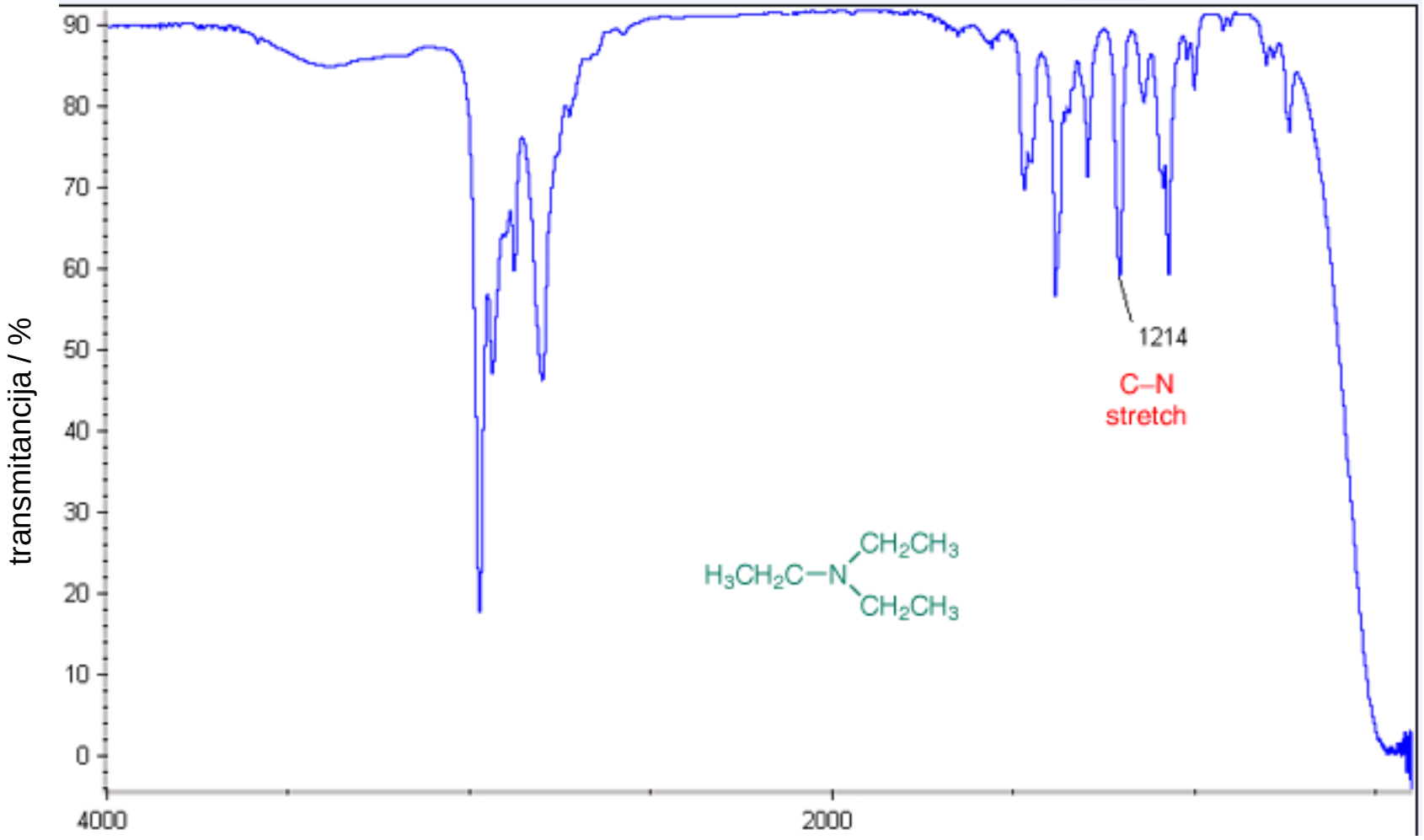
Amini



anilin (primarni amin)

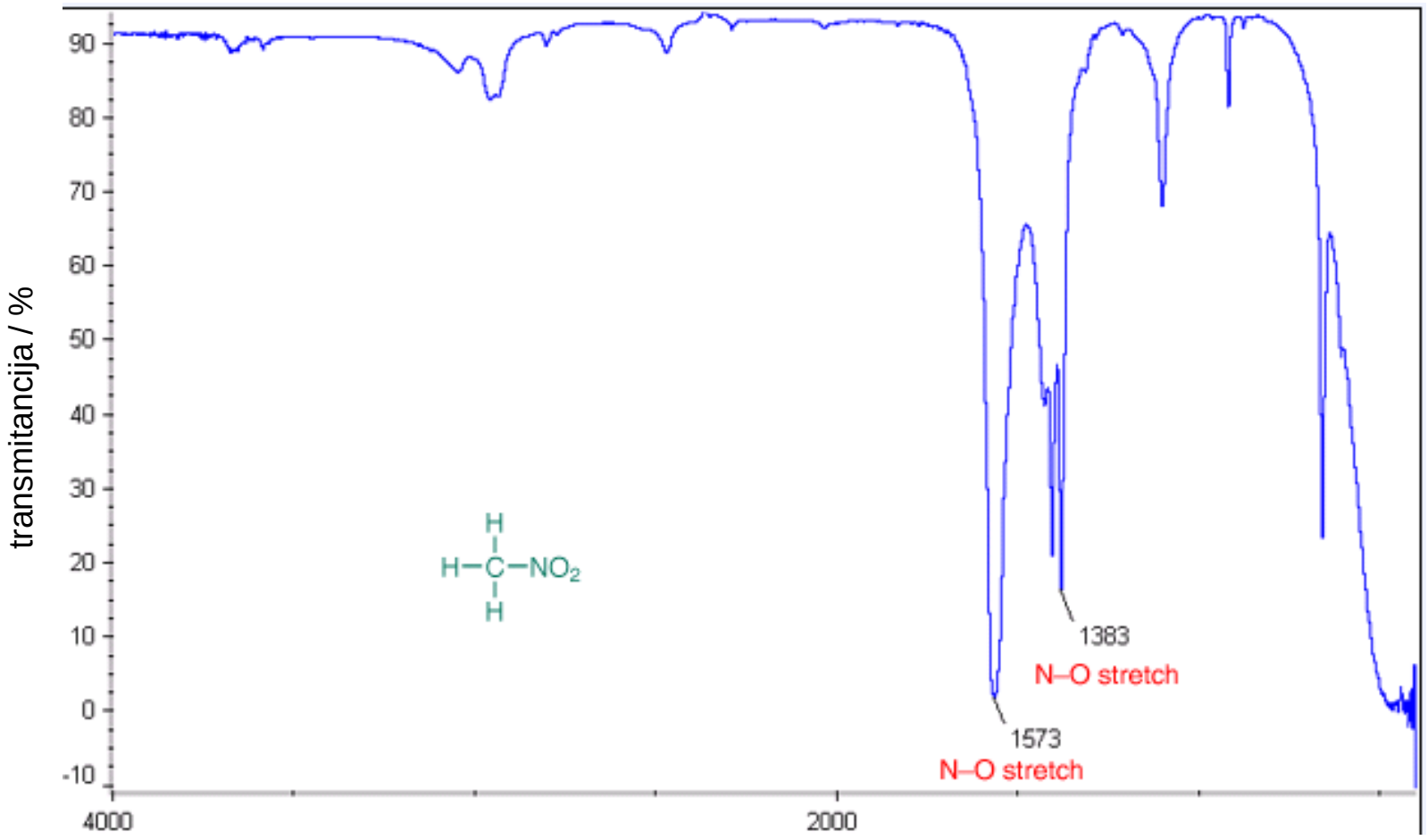


dietilamin (sekundarni amin)

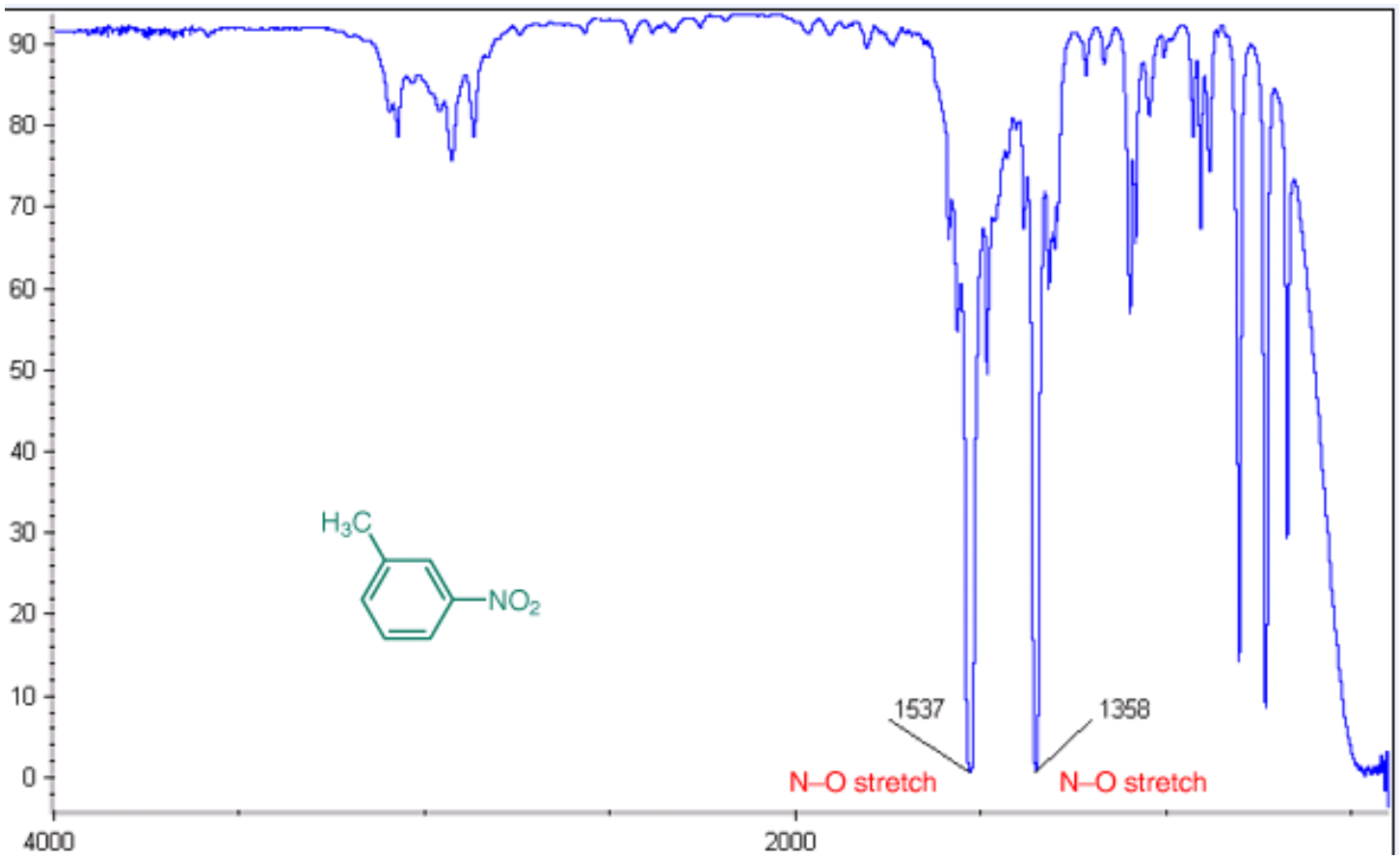


trietilamin (tercijarni amin)

Nitro-spojevi



nitrometan

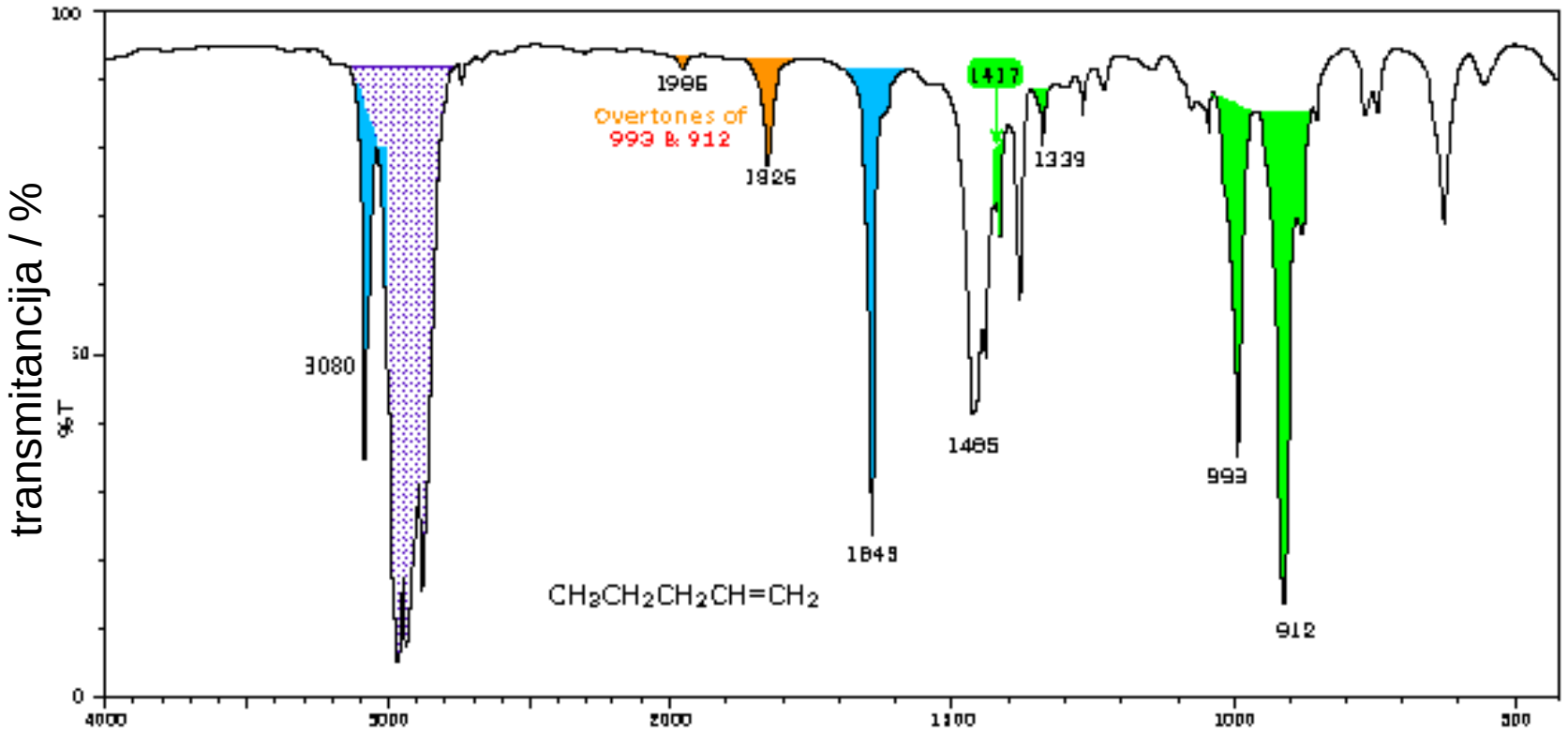


valni broj (cm^{-1})

m-nitrotoluen

Razrađeni primjeri

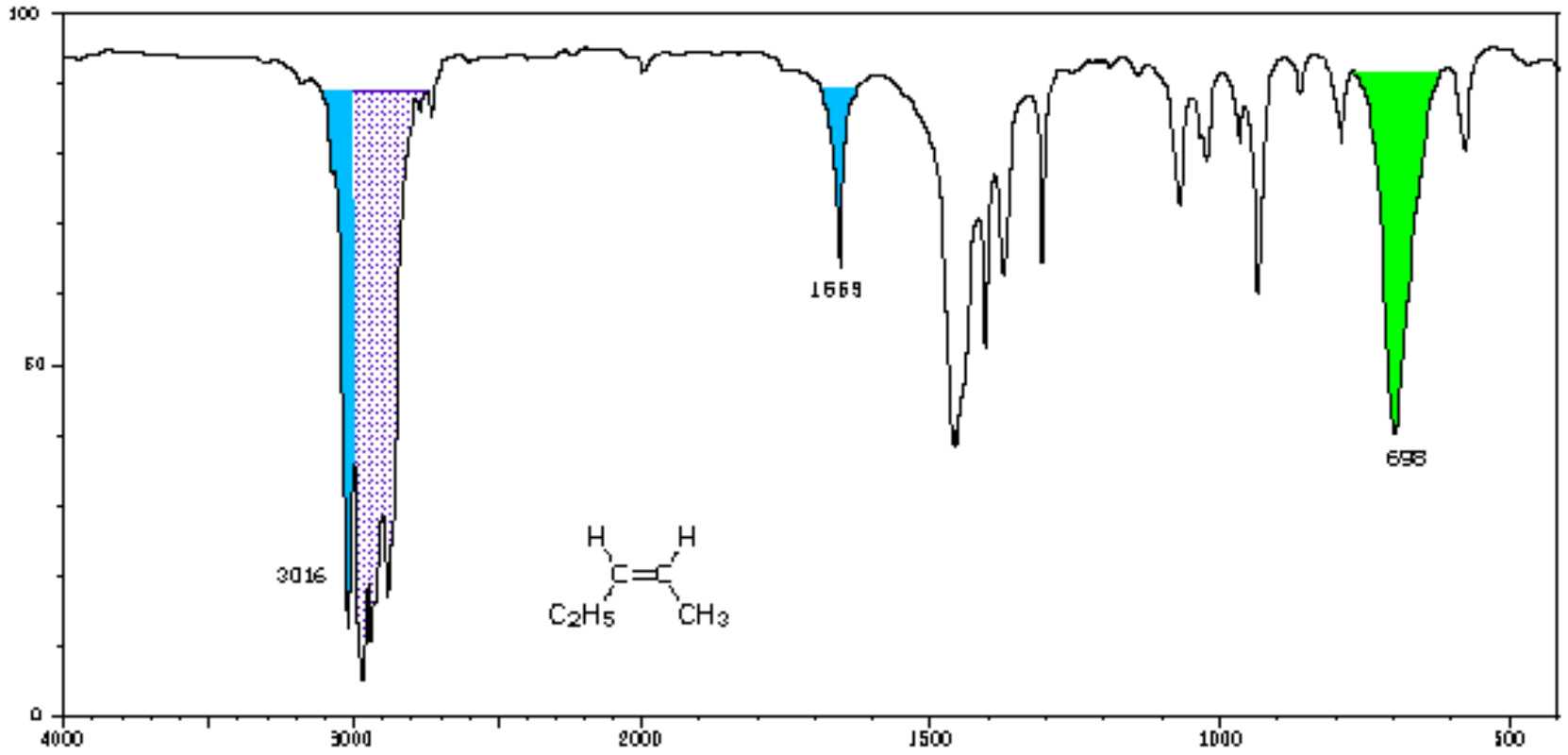
pent-1-en



sp^3 C-H rastezanja valni broj (cm^{-1})

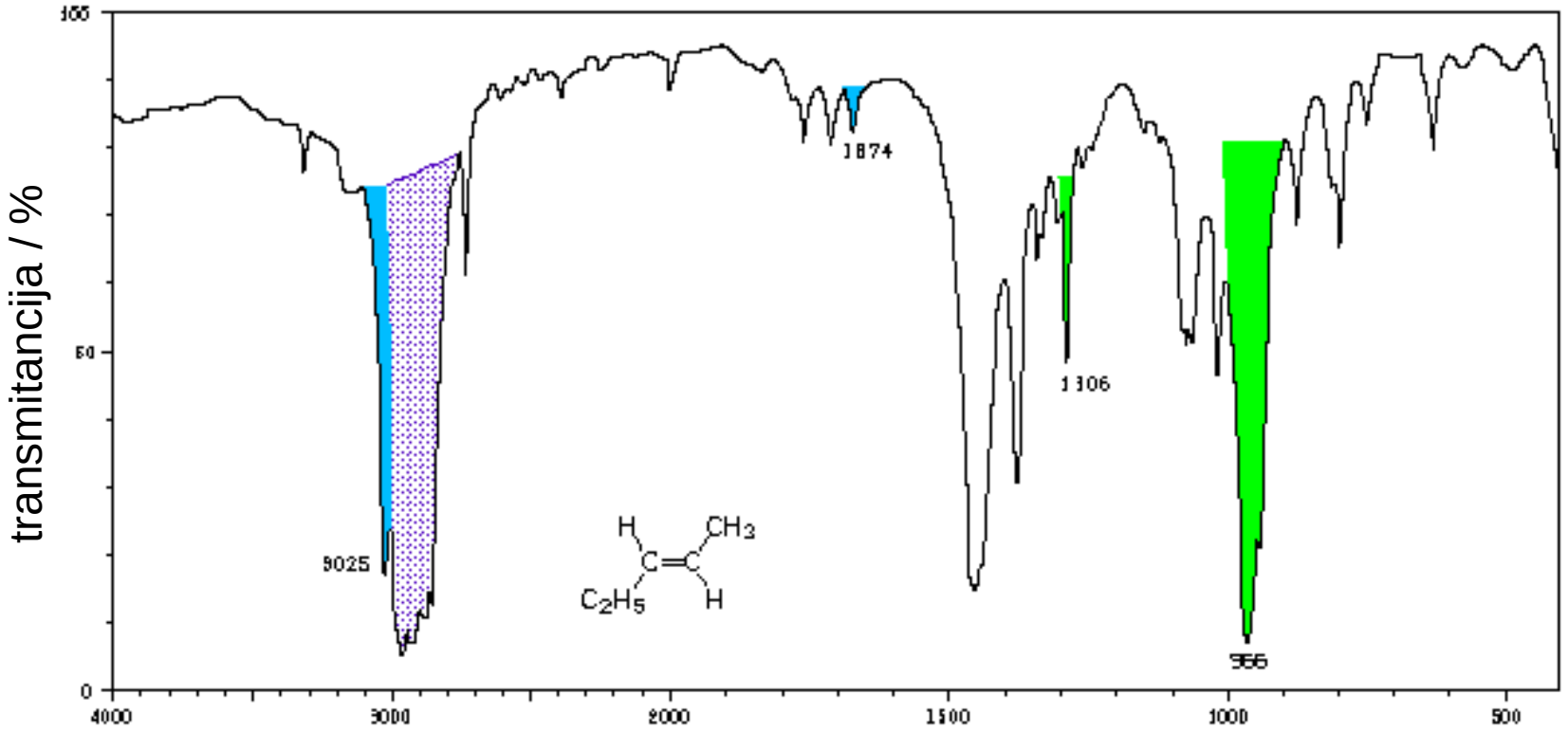
2965 asim CH_3
2932 asim CH_2
2876 sim CH_3
2845 sim CH_2

cis-pent-2-en



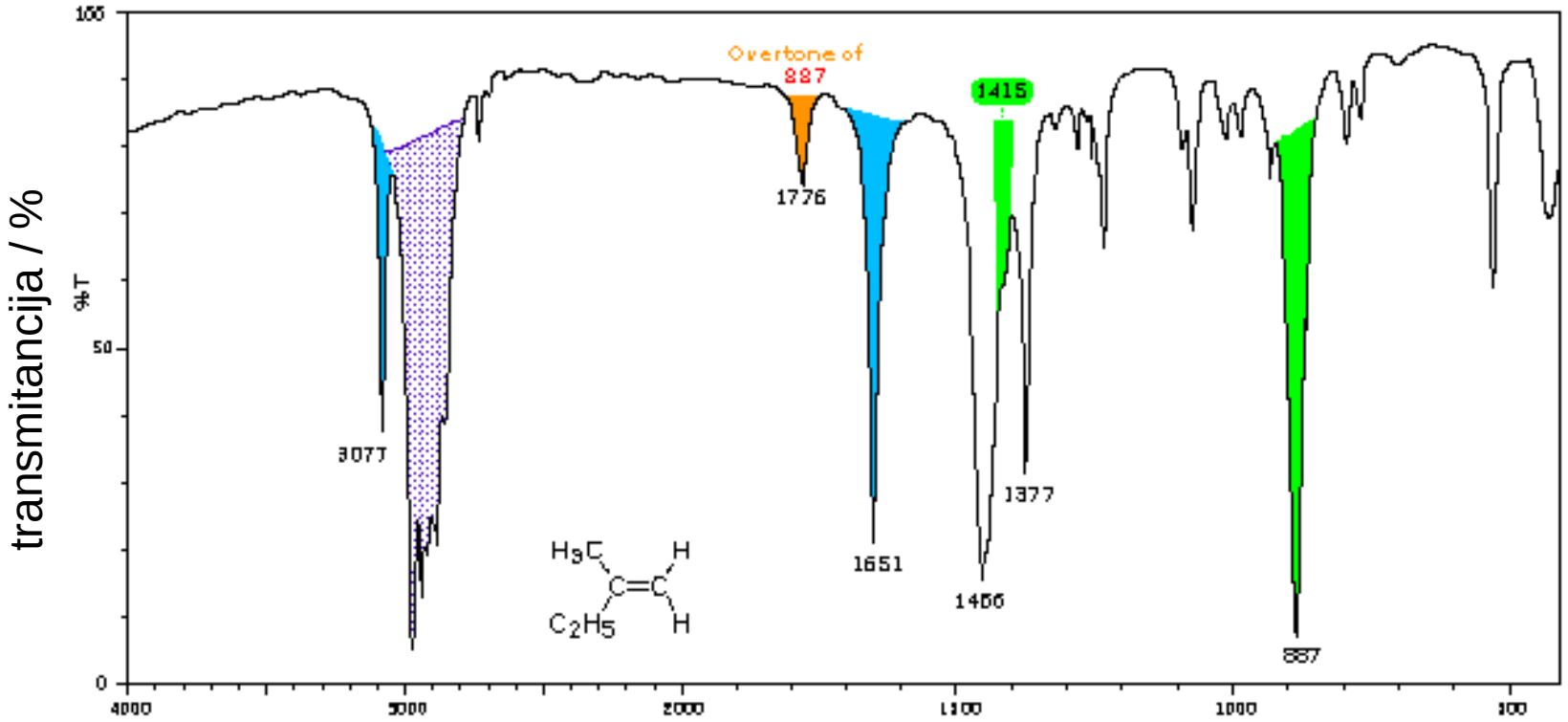
sp^3 C-H rastezanja	valni broj (cm^{-1})
2967 asim CH_3	
2937 asim CH_2	
2923 sim CH_3	
2878 sim CH_2	

trans-pent-2-en



sp^3 C-H rastezanja	valni broj (cm^{-1})
2965 asim CH_3	
2937 asim CH_2	
2922 sim CH_3	
2877 sim CH_2	

2-metilbut-1-en



sp^3 C-H rastezanja	valni broj (cm^{-1})
2970 asim CH_3	
2929 asim CH_3	
2919 sim CH_2	
2885 sim CH_2	

2-metilbut-2-en

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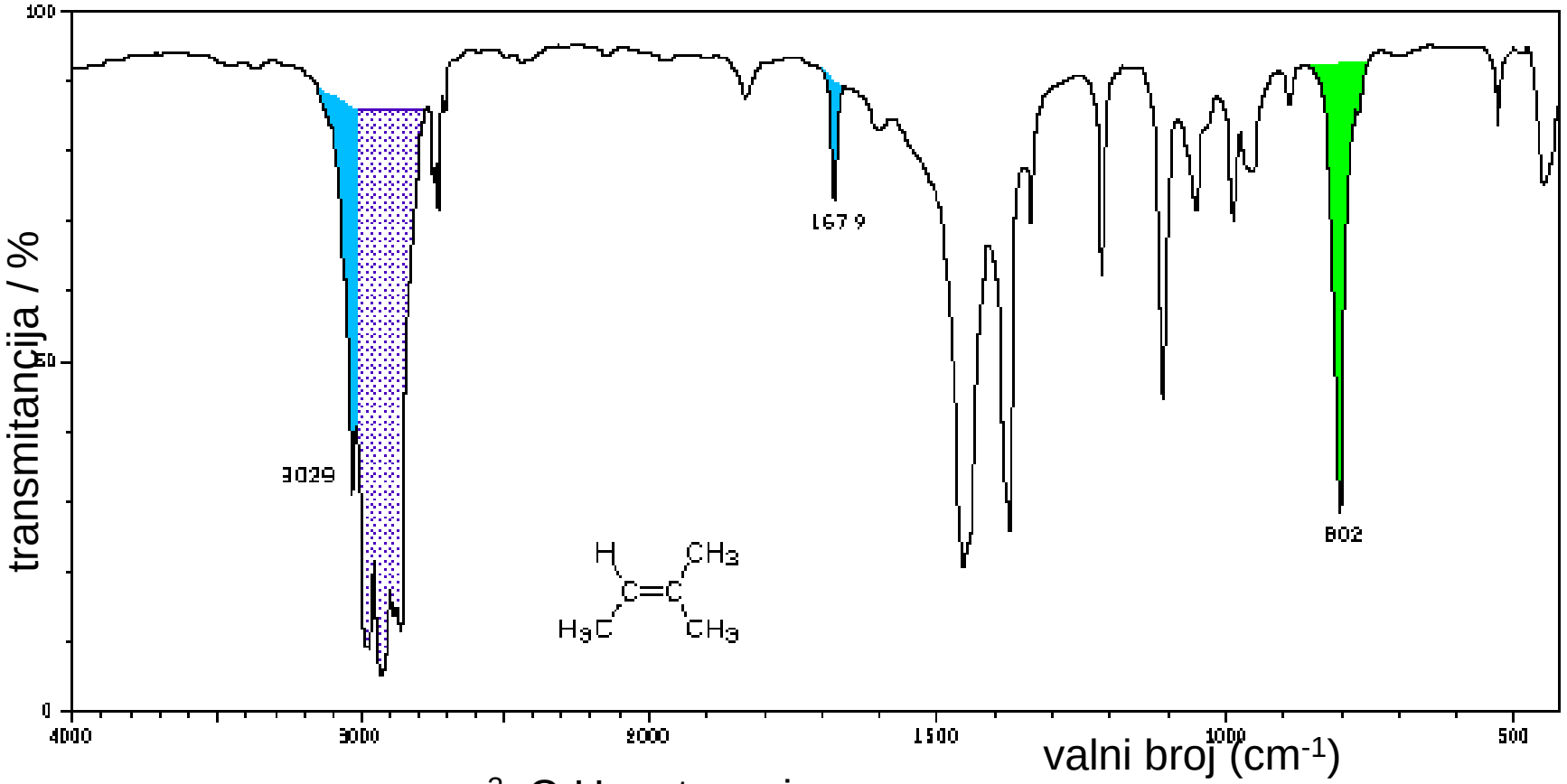
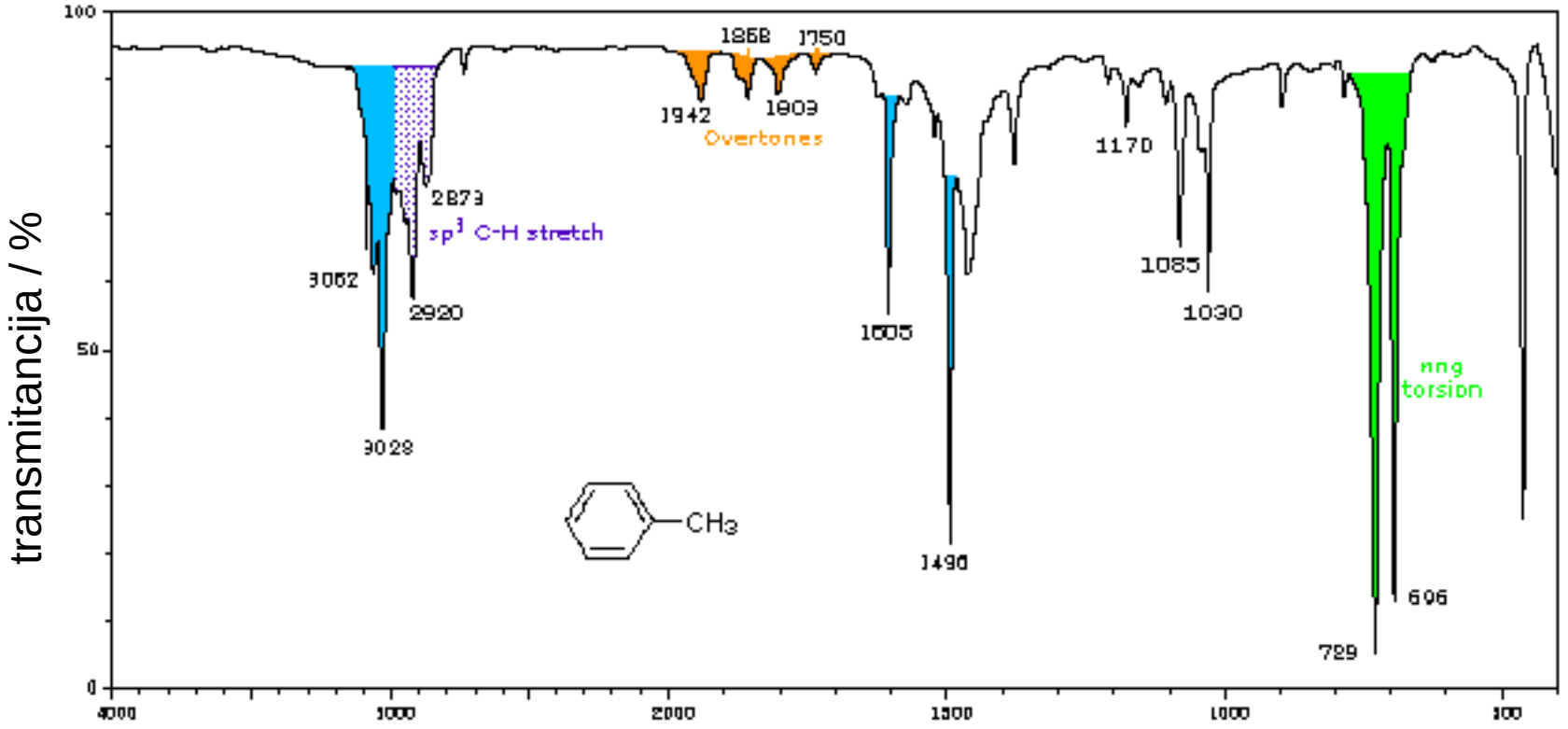
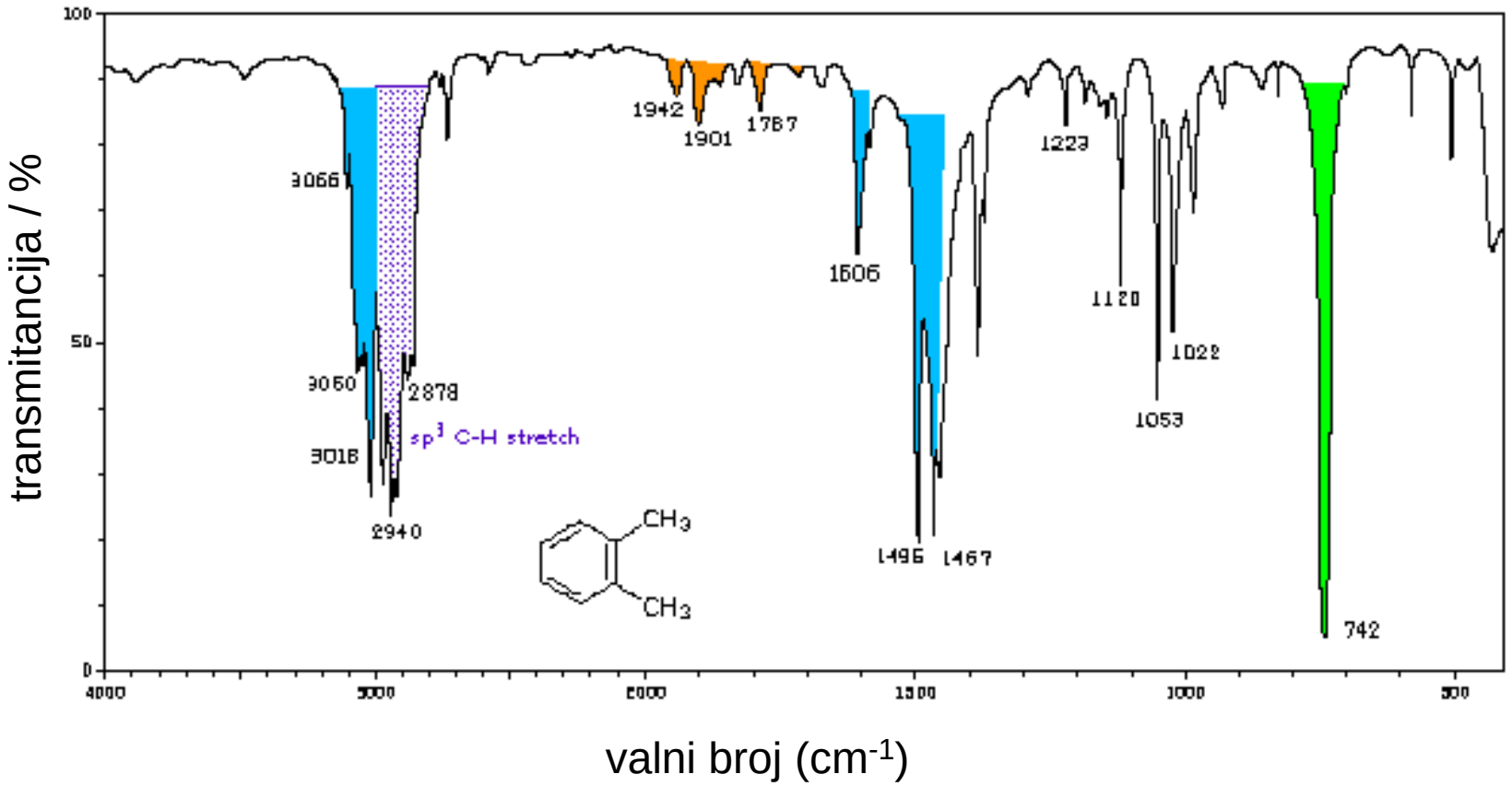


sp^3 C-H rastezanja
2974 asim CH_3
2929 asim CH_3
2883 sim CH_3
2864 sim CH_3

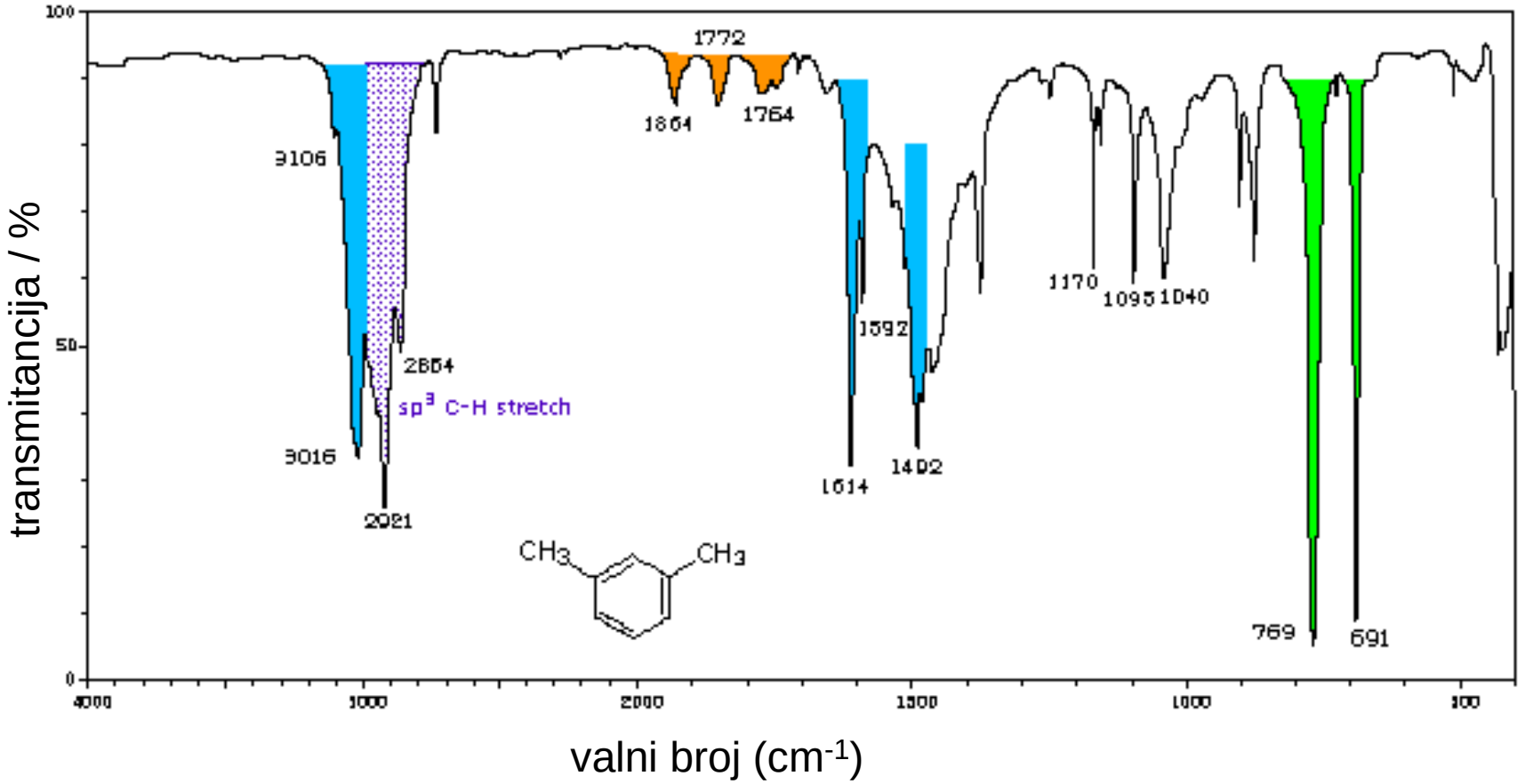
toluen


100
50
0
4000
3000
2000
1500
1000
500
transmitancija / %
valni broj (cm-1)
3062
3028
2920
2873
sp3 C-H stretch
1942
1868
1809
1750
Overtones
1605
1496
1170
1085
1030
729
696
ring
torsion
CH3

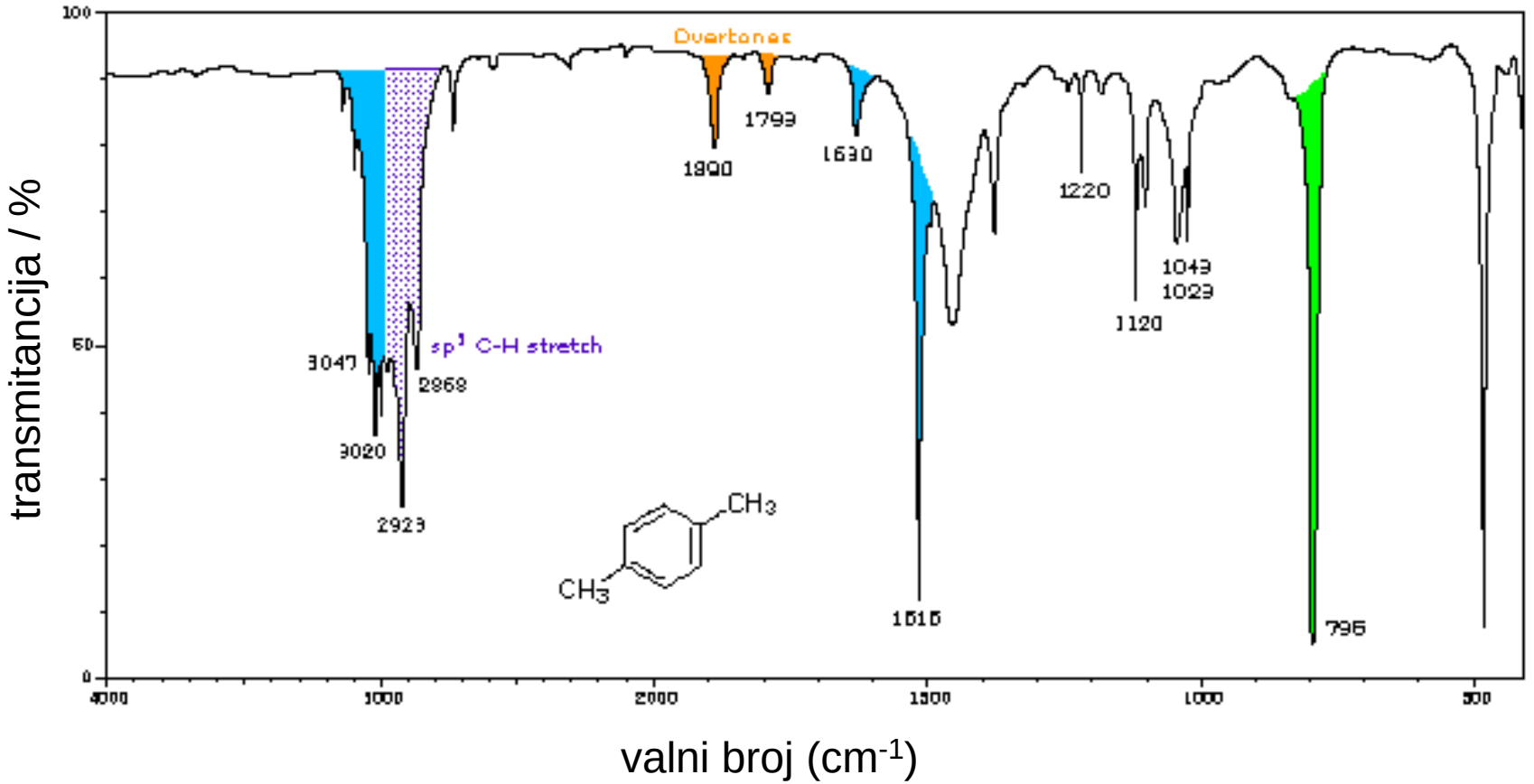
o-ksilen


transmitancija / %
100
50
0
4000
3000
2000
1500
1000
500
3066
3060
3018
2940
2878
sp3 C-H stretch
1942
1901
1787
1606
1496
1467
1223
1120
1053
1022
742
CH3
CH3
valni broj (cm-1)

m-ksilen


100
50
0
transmitancija / %
3106
3016
2921
2864
sp³ C-H stretch
1772
1864
1764
1614
1592
1492
1170
1095
1040
769
691
CH3
CH3
4000
3000
2000
1500
1000
500
valni broj (cm-1)

p-ksilen


transmitancija / %
100
50
0
4000
3000
2000
1500
1000
500
valni broj (cm-1)
Overtones
1990
1799
1630
1220
1120
1049
1029
3047
3020
2923
2868
sp3 C-H stretch
1515
796
CH3
CH3

1,2,3-trimetilbenzen

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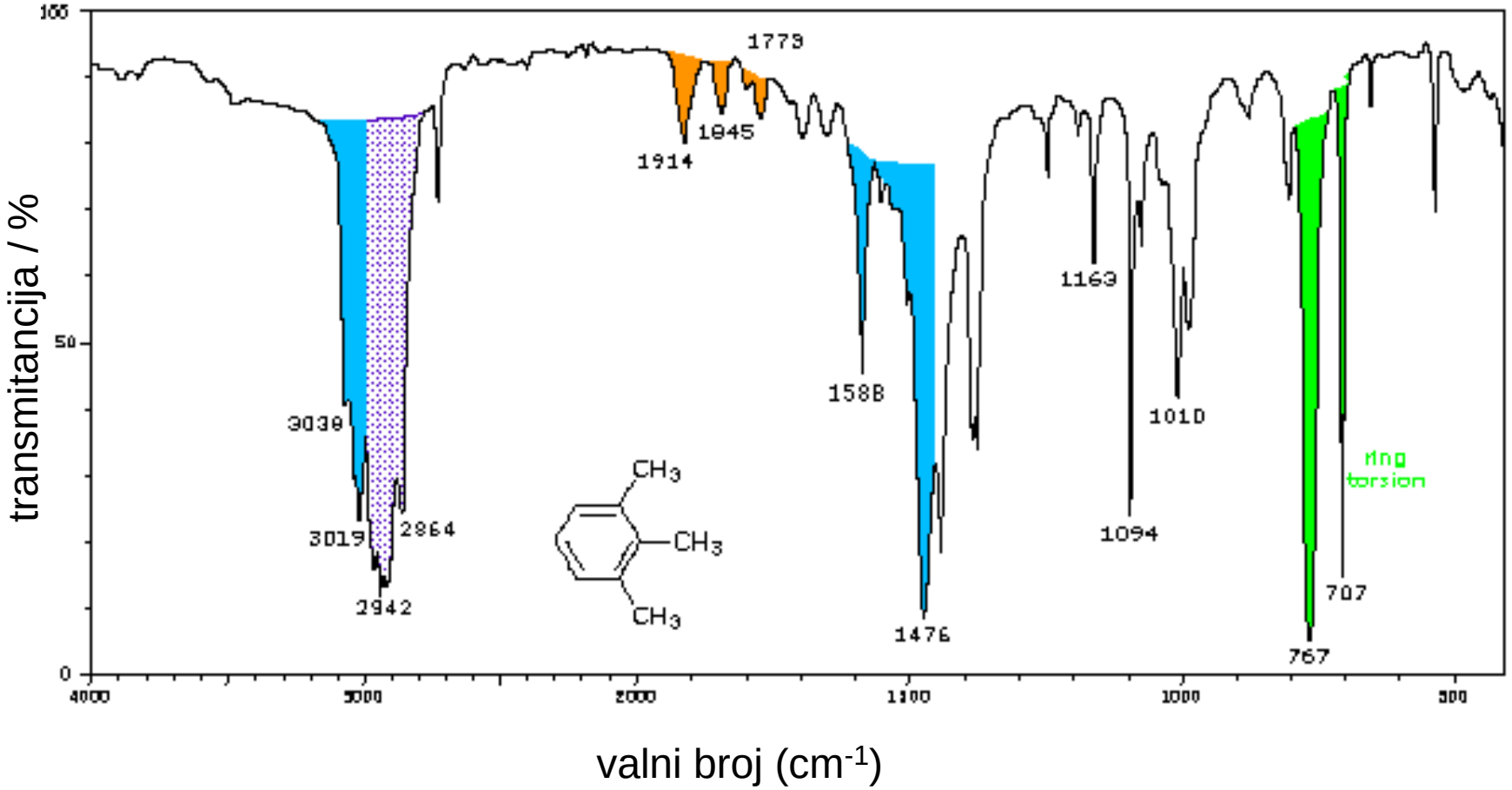
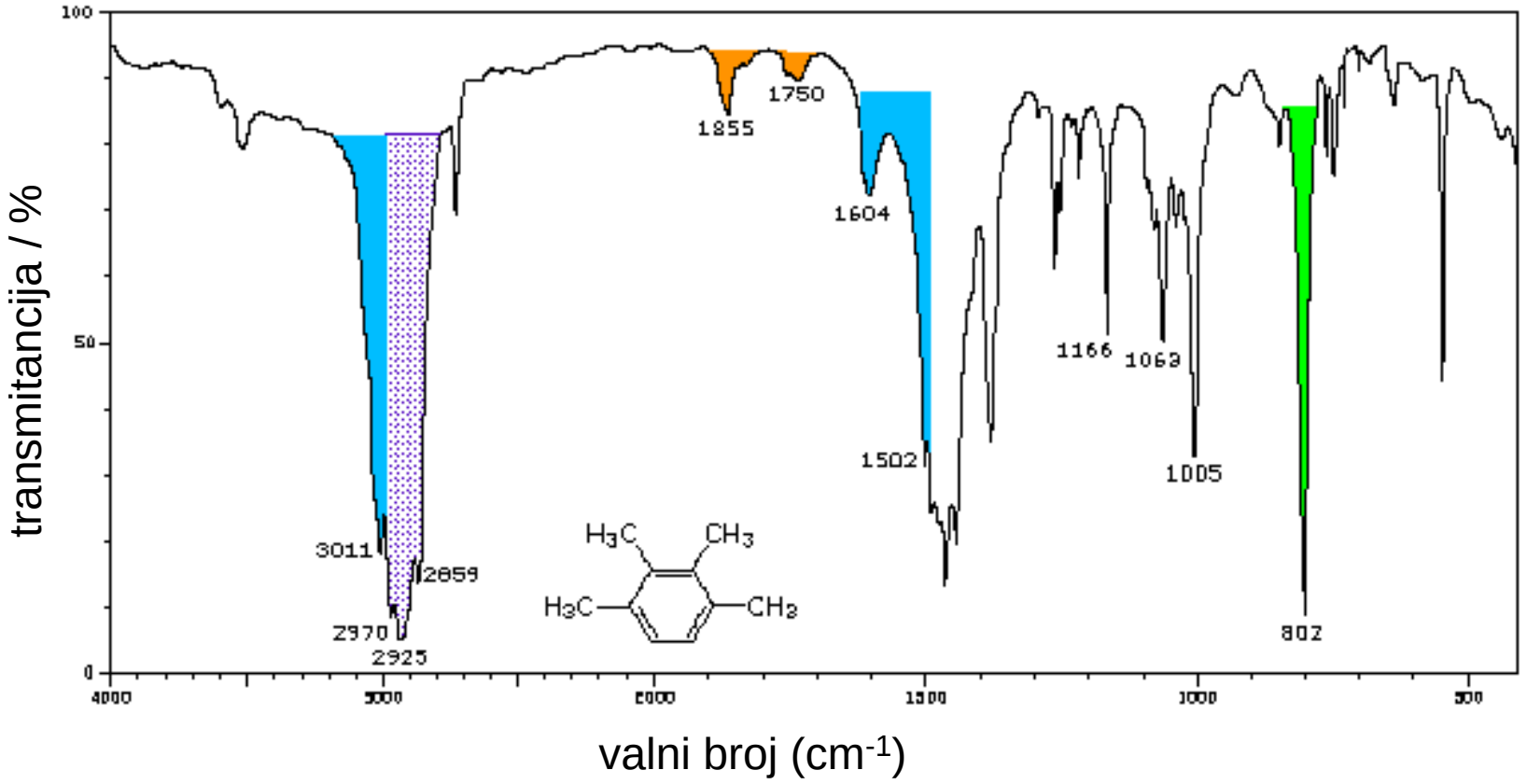
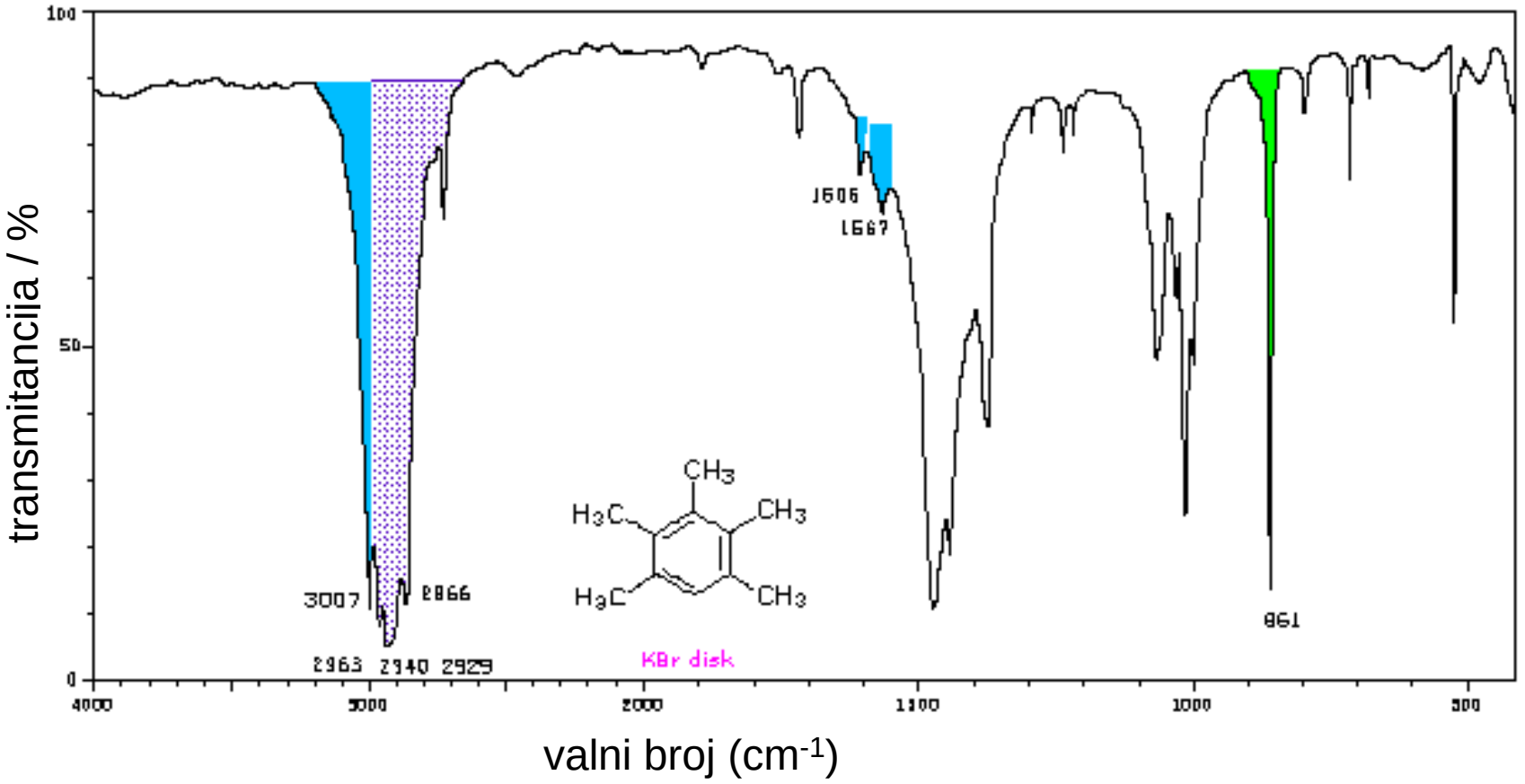


valni broj (cm^{-1})

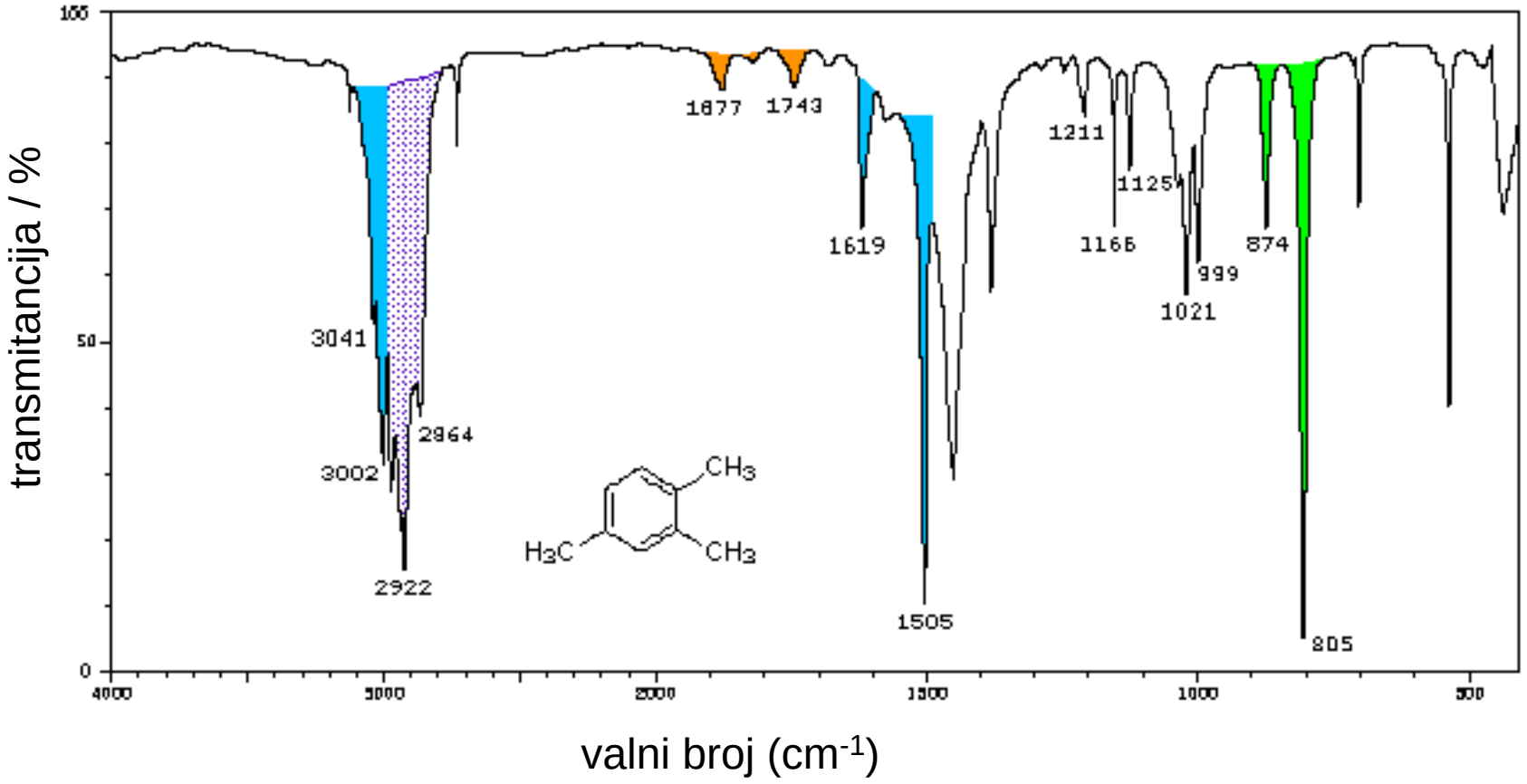
1,2,3,4-tetrametilbenzen



pentametilbenzen

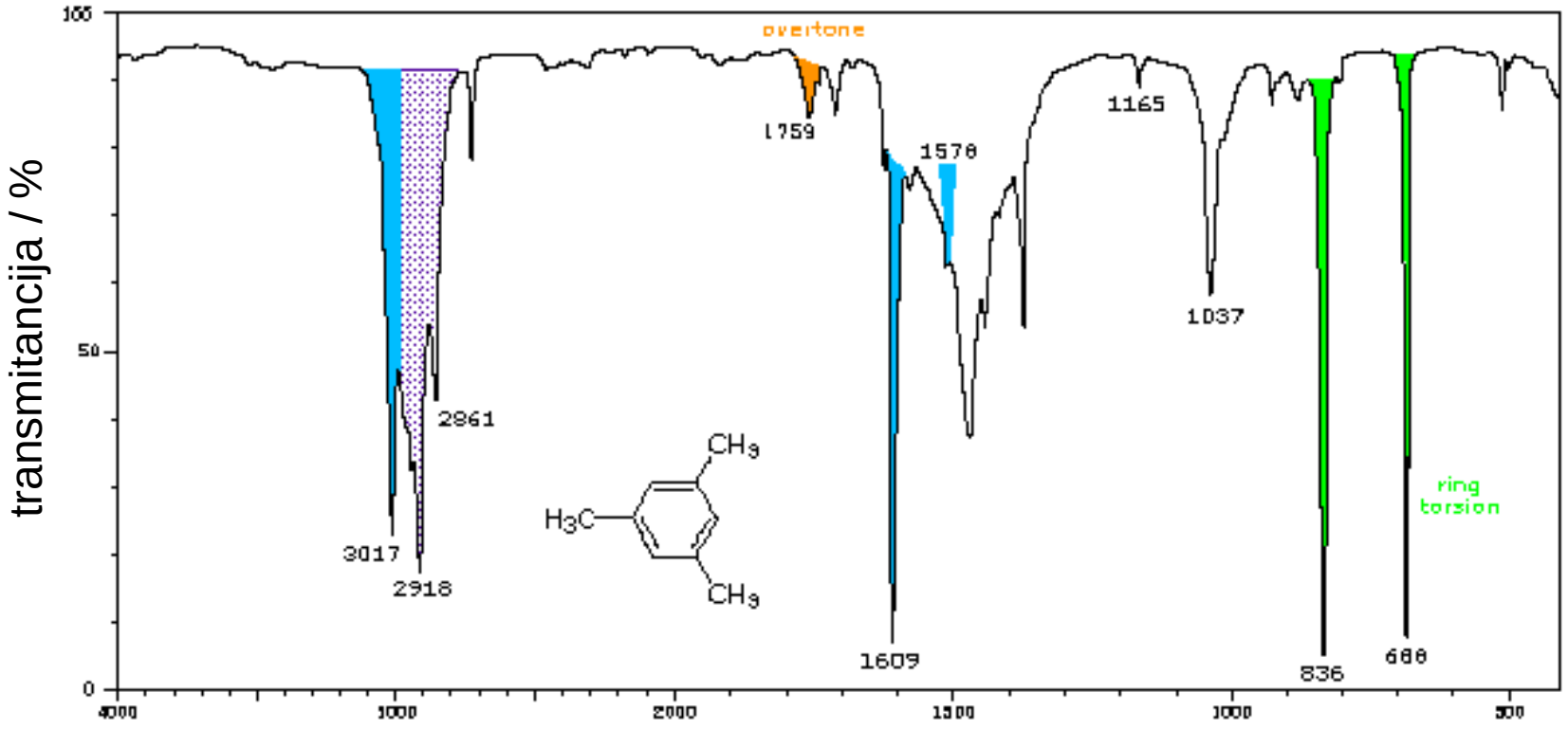


1,2,4-trimetilbenzen



valni broj (cm^{-1})

1,3,5-trimetilbenzen



valni broj (cm^{-1})

1,2,3,5-tetrametilbenzen

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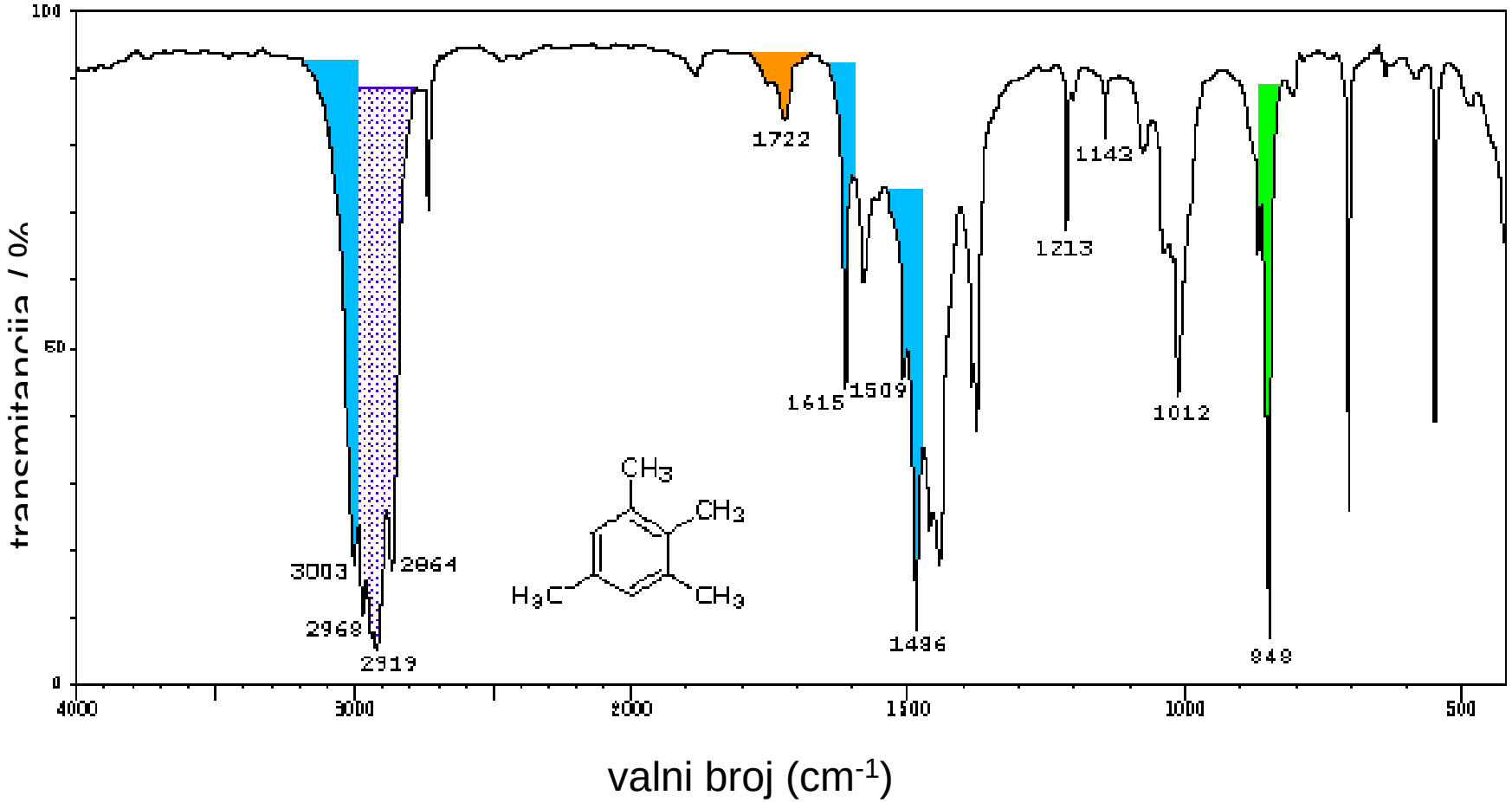
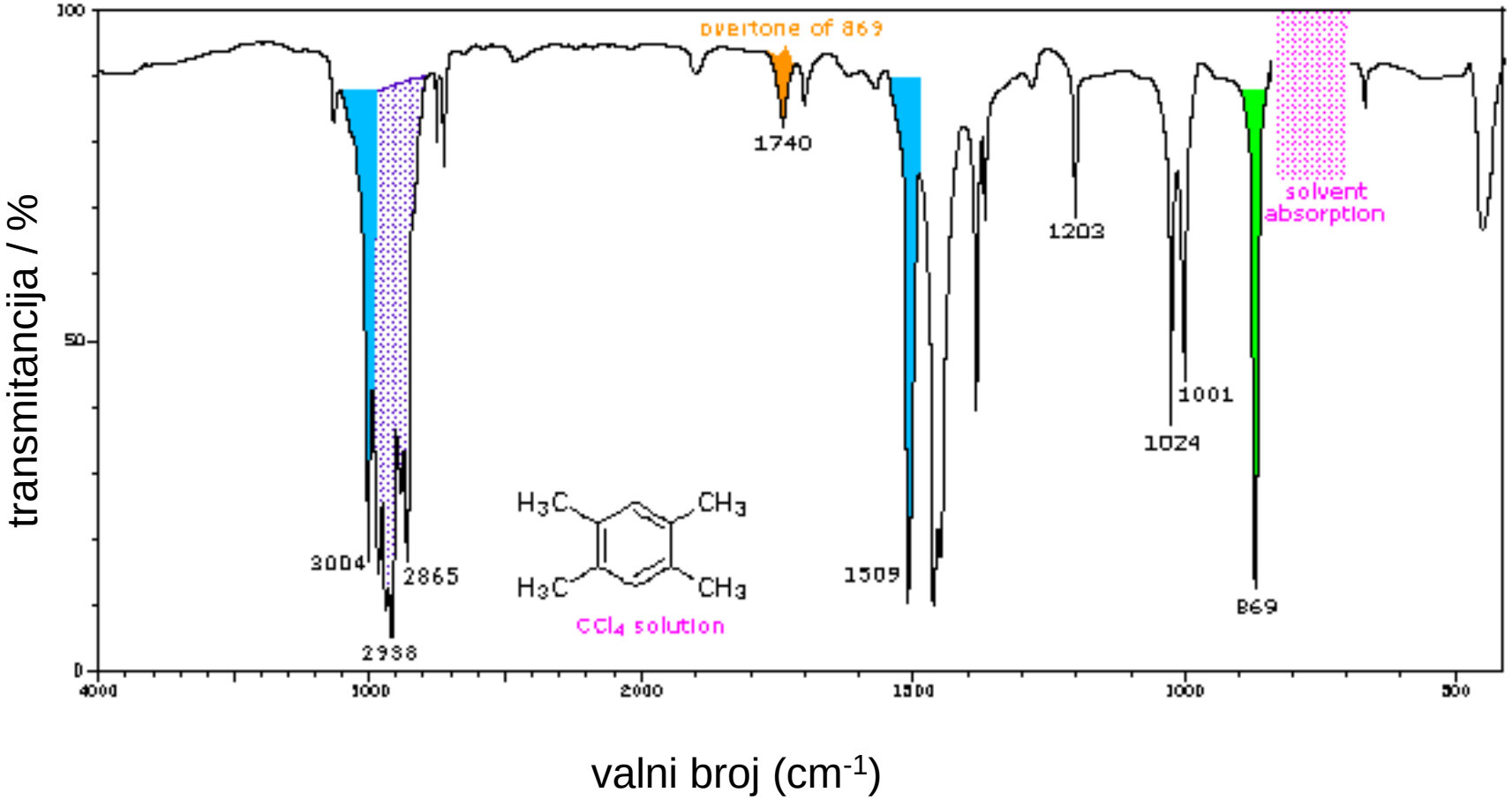


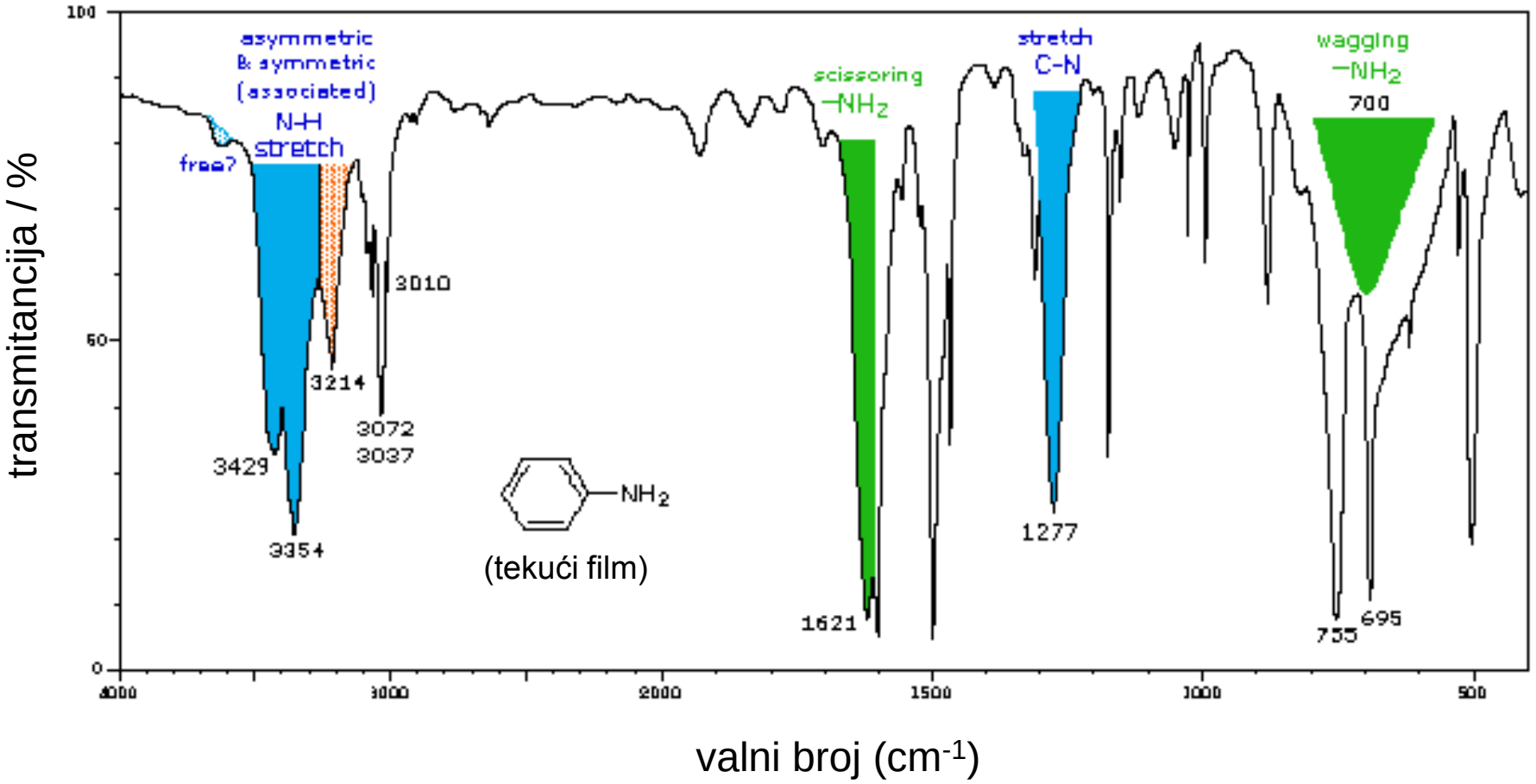
valni broj (cm^{-1})

1,2,4,5-tetrametilbenzen

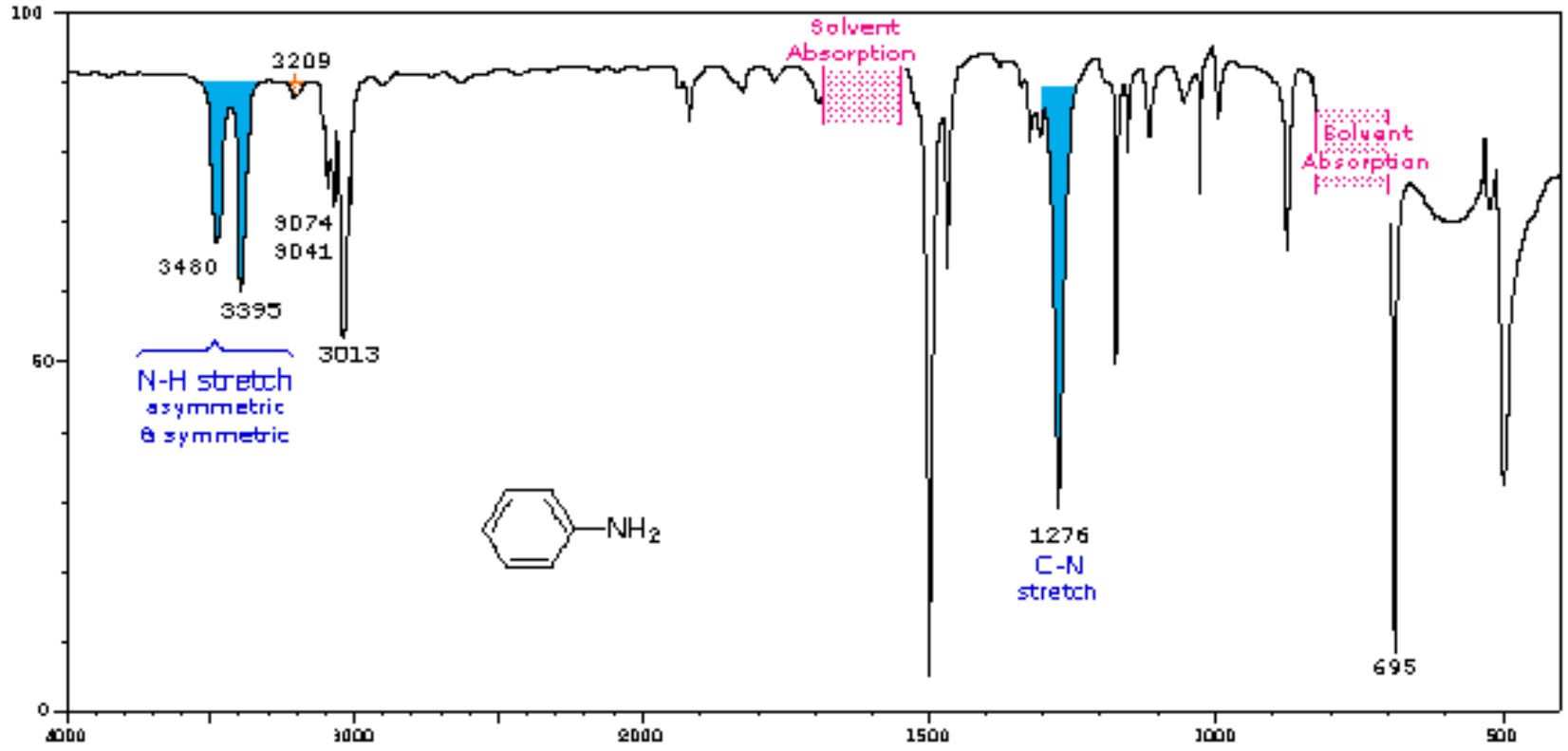
University of Zagreb
Faculty of Chemical
Engineering and Technology
FKITMCMXIX



anilin

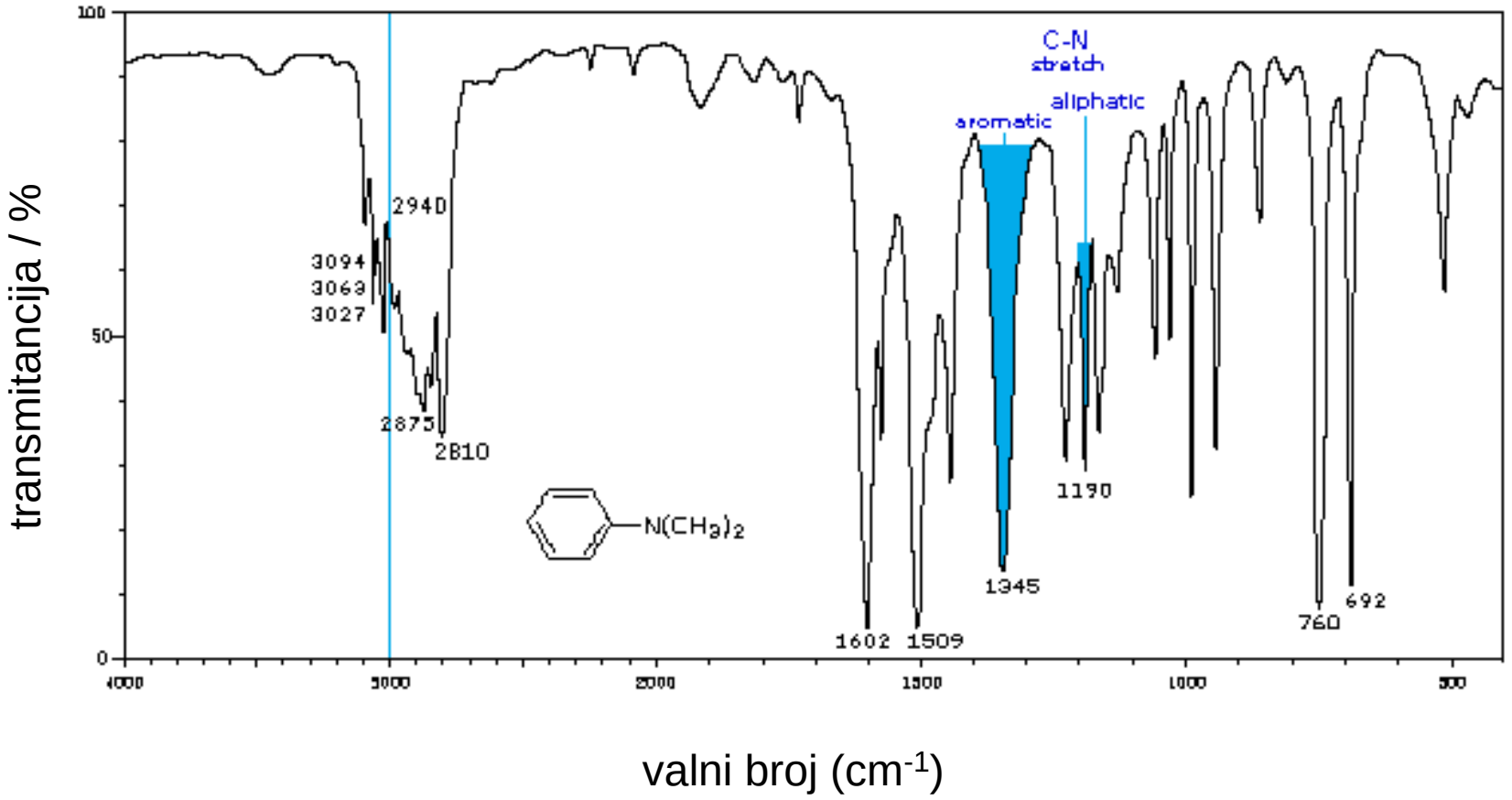

transmitancija / %
100
60
0
asymmetric
& symmetric
(associated)
N-H
stretch
free?
3429
3354
3214
3072
3037
3010
scissoring
–NH2
1621
stretch
C-N
1277
wagging
–NH2
700
755
695
NH2
(tekući film)
4000
3000
2000
1500
1000
500
valni broj (cm-1)

anilin (u CCl_4)



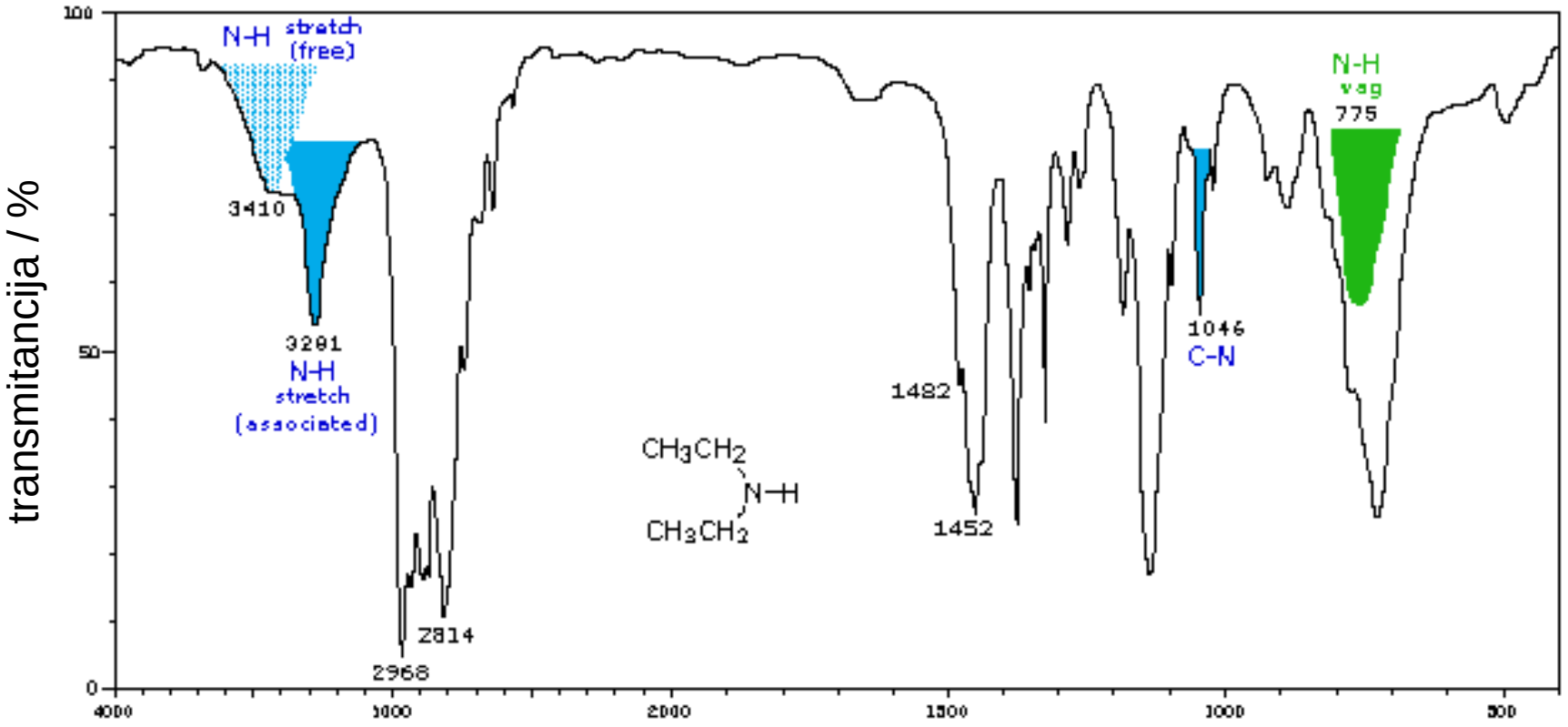
valni broj (cm^{-1})

N,N-dimetilanilin (tekući film)

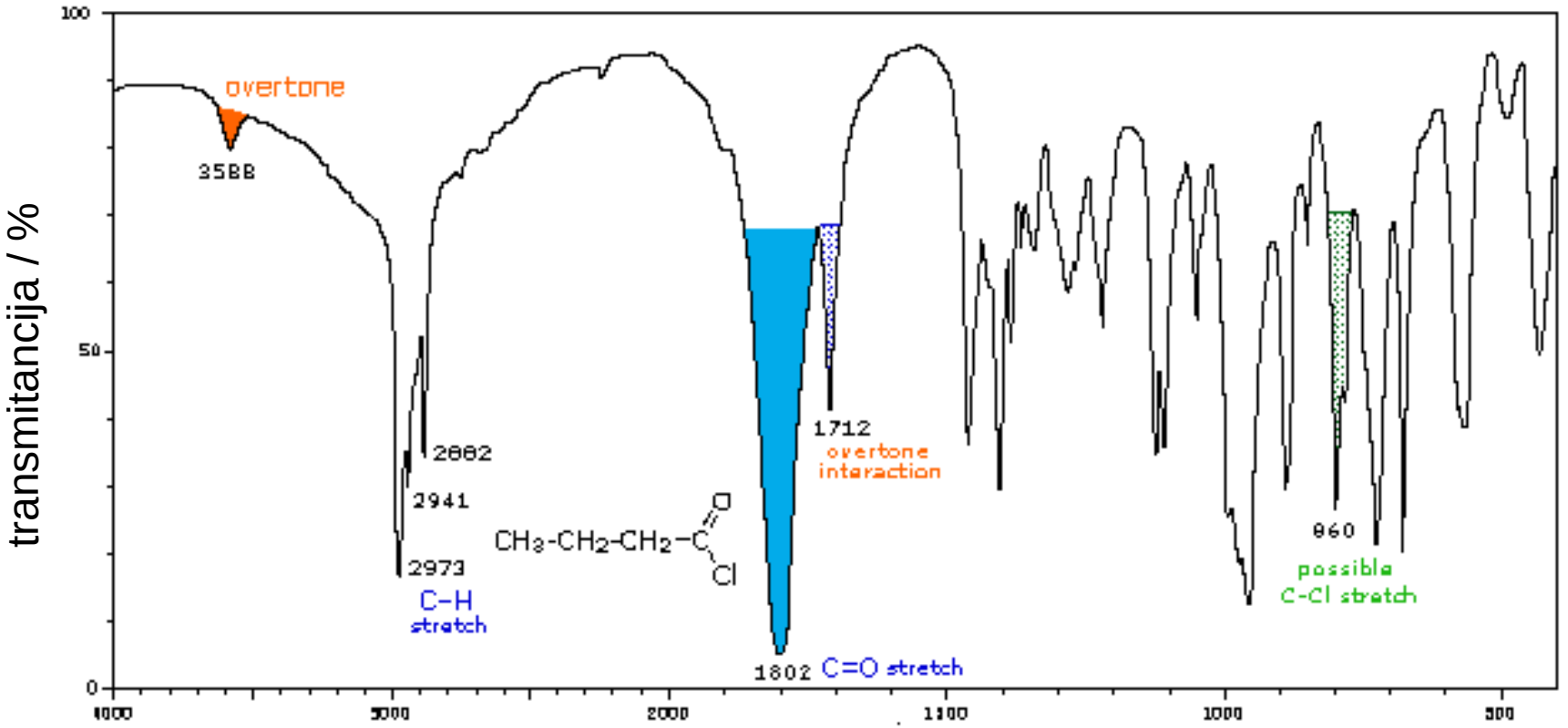


valni broj (cm^{-1})

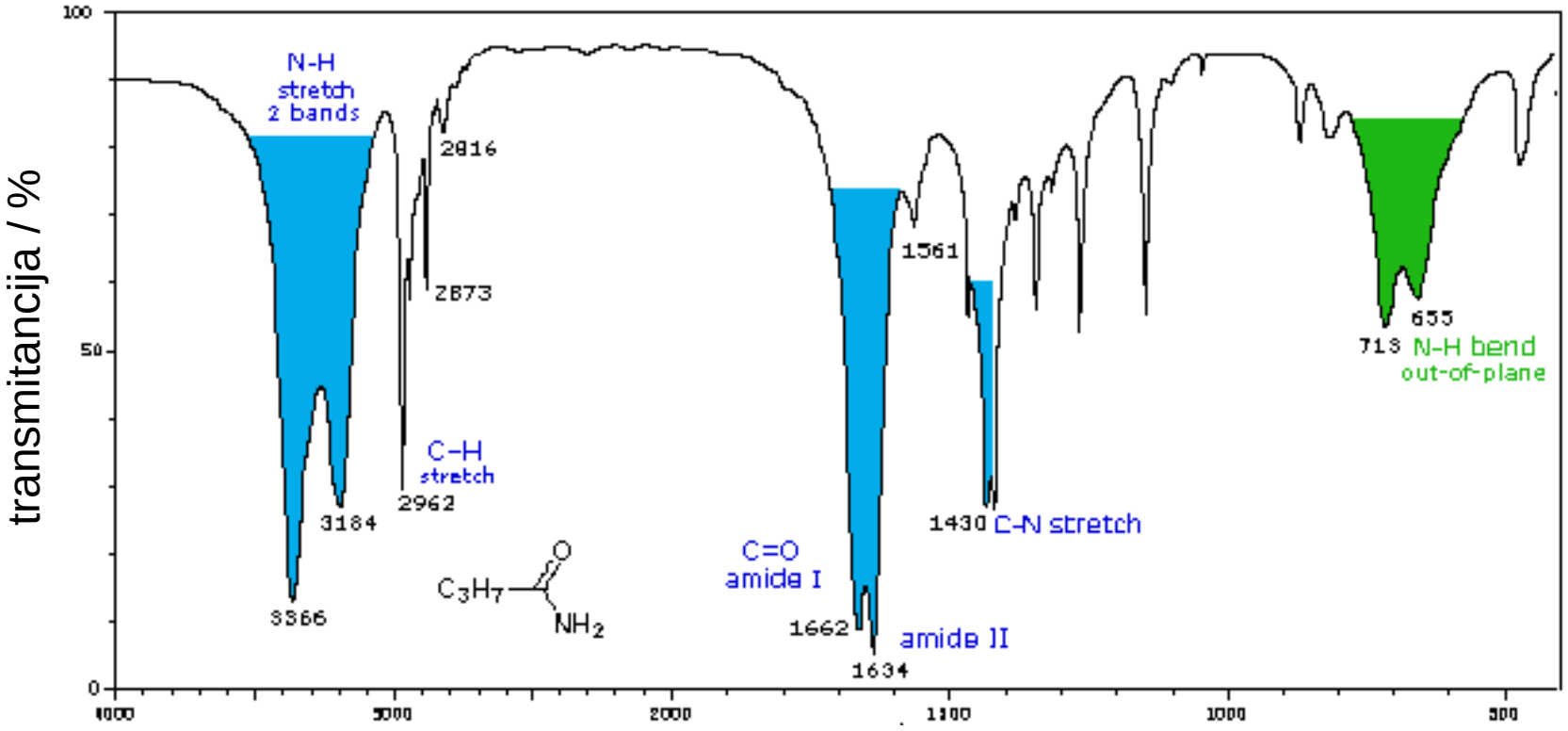
dietilamin (tekući film)



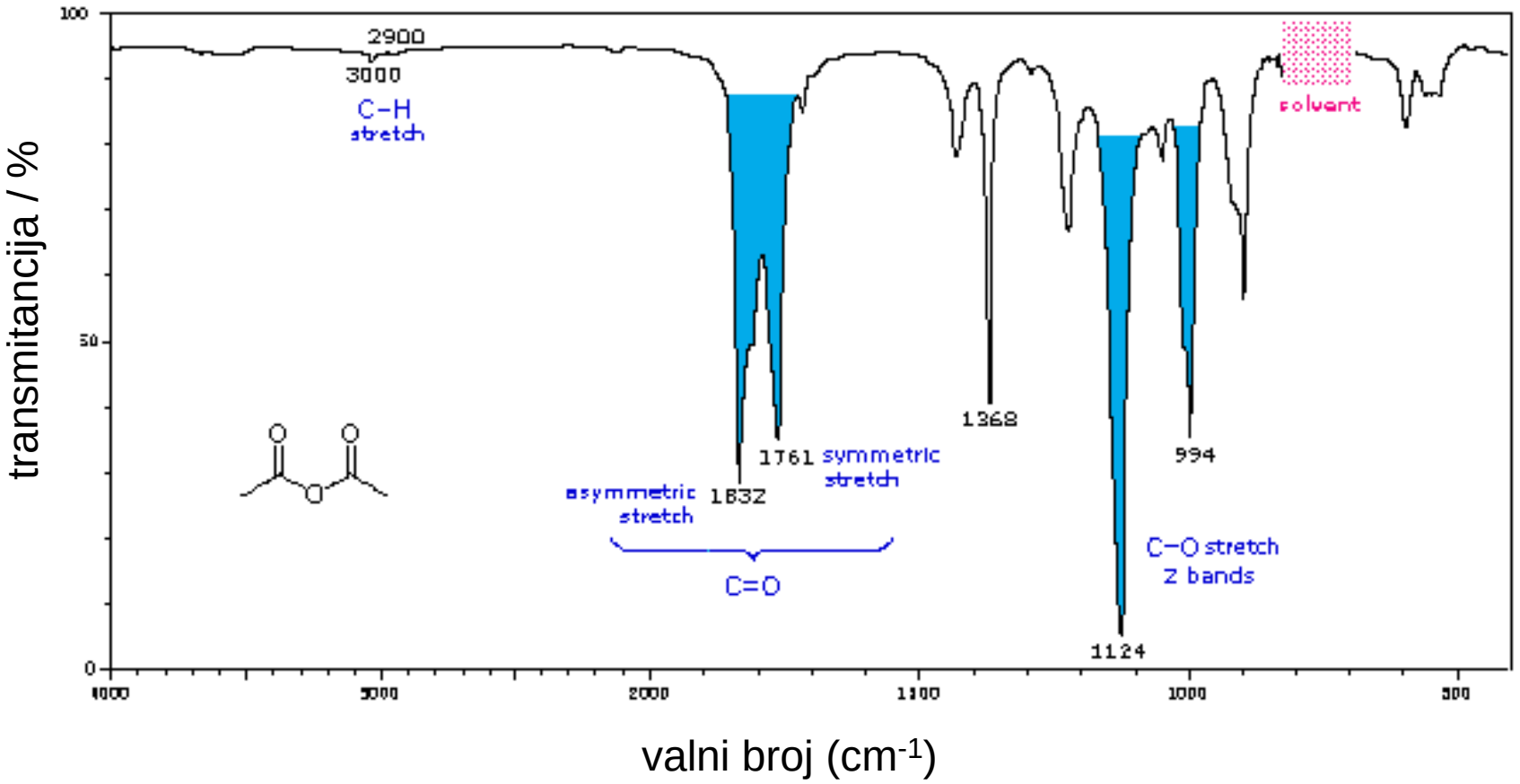
butanoil-klorid



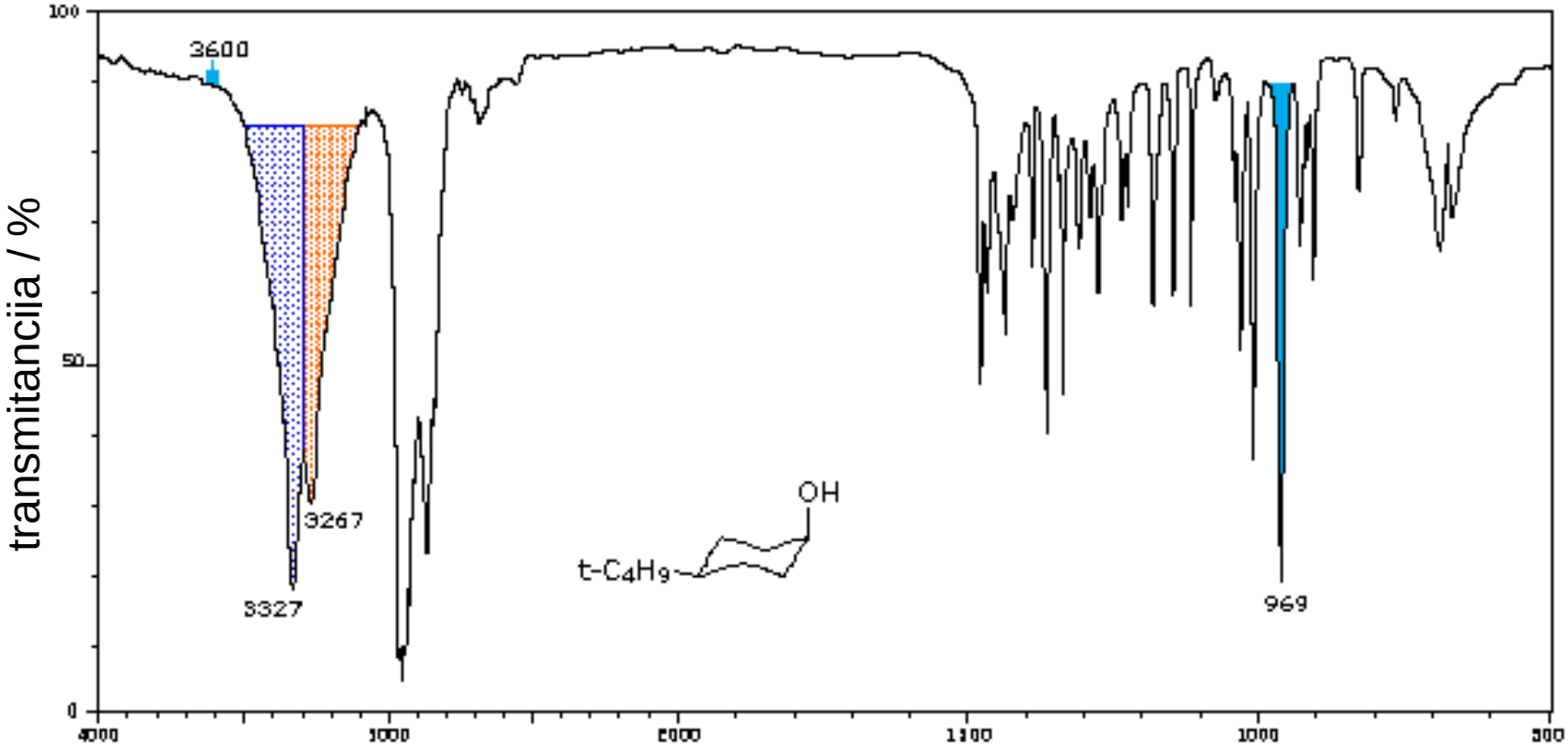
amid maslačne kiseline (KBr pločica)



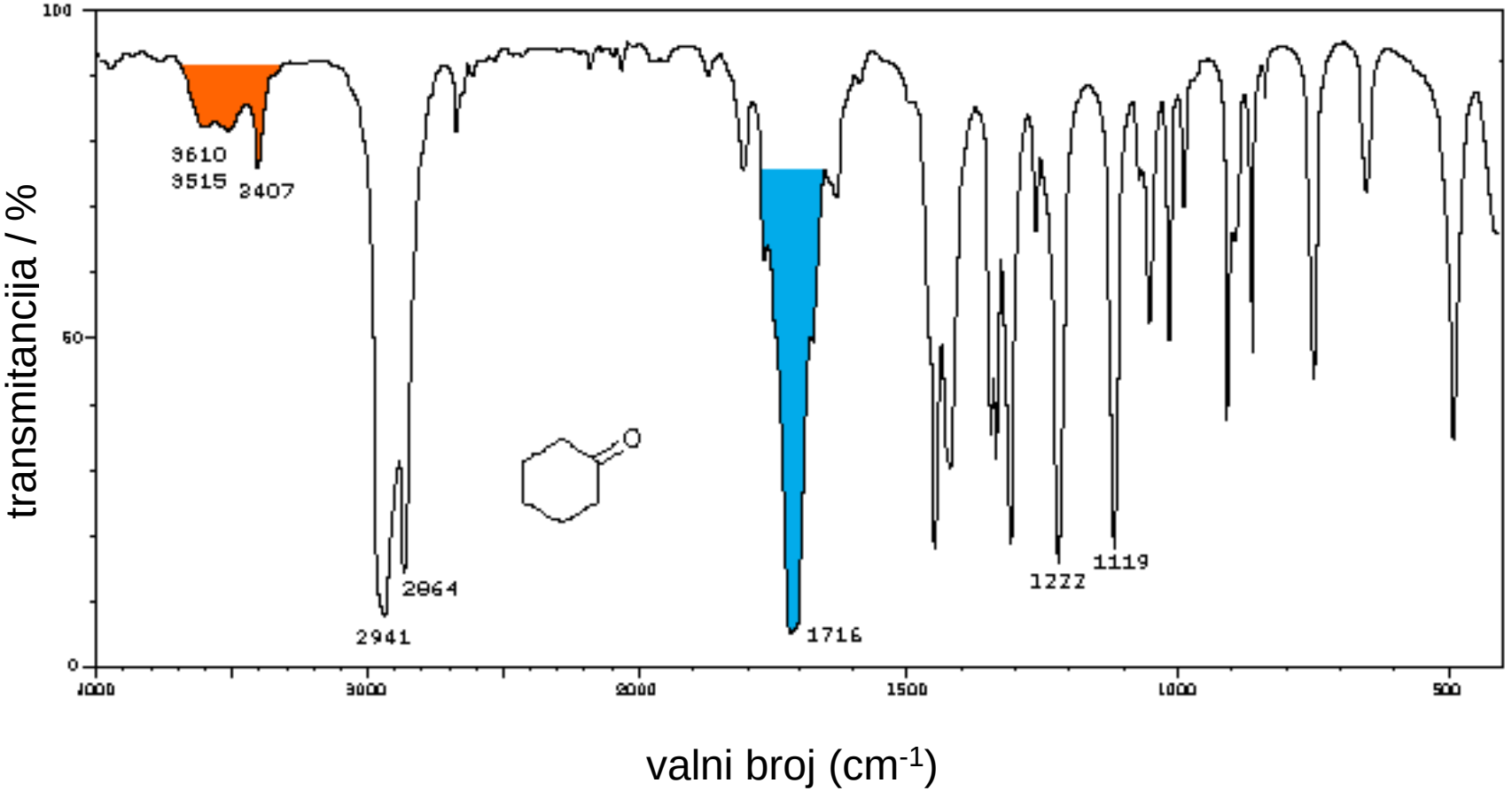
anhidrid octene kiseline (CCl_4)



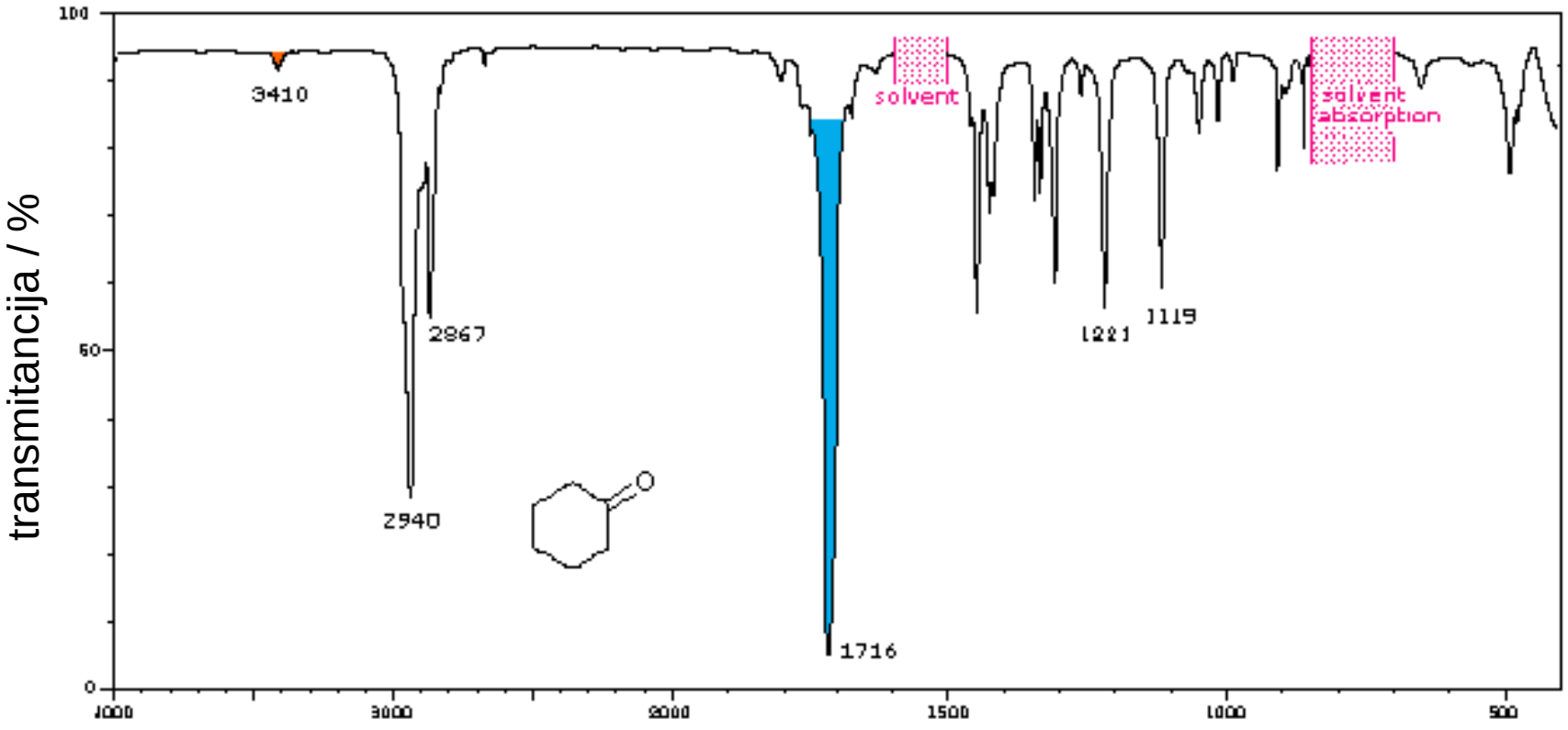
cis-4-tert-butilcikloheksanol (KBr pločica)



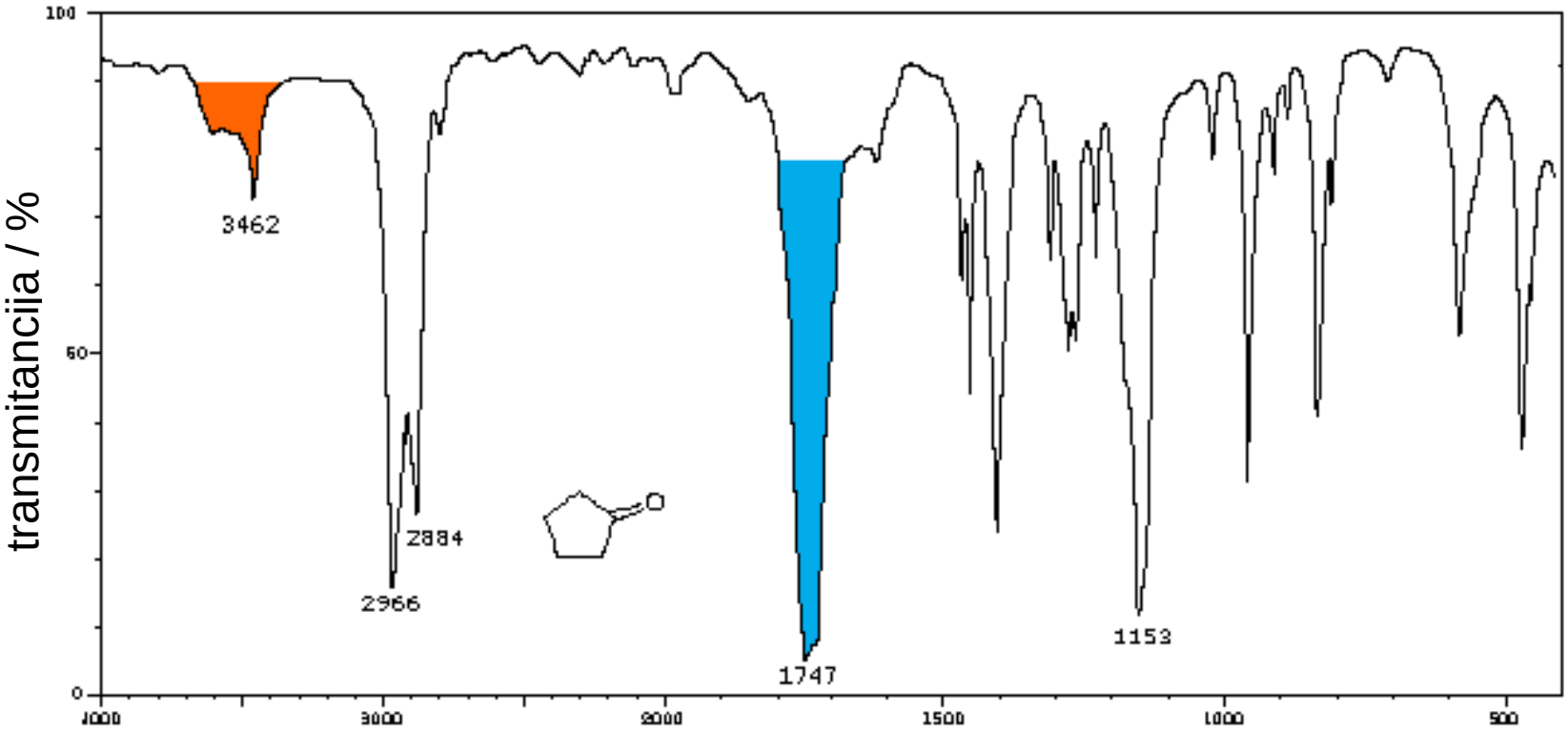
cikloheksanon (tekući film)



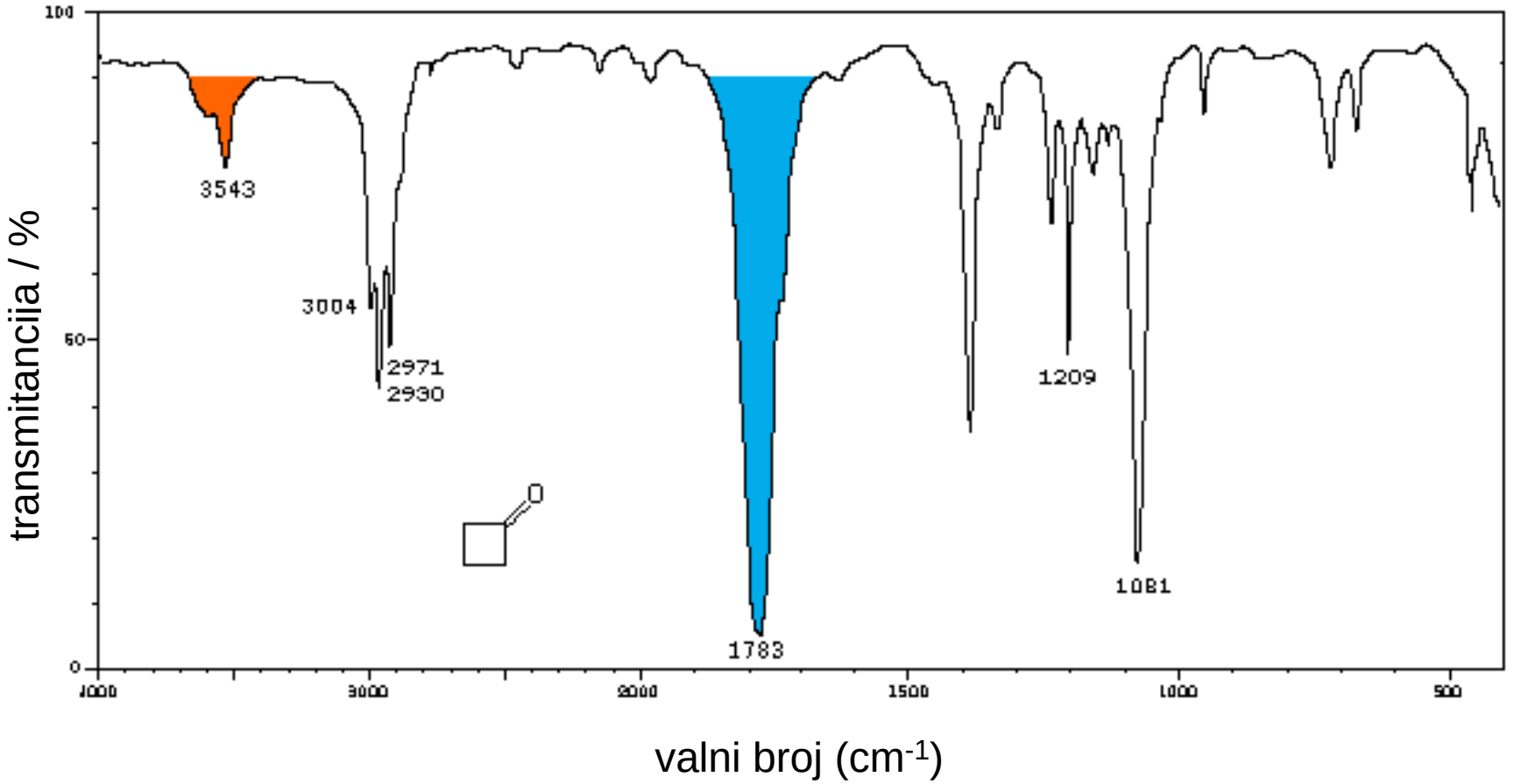
cikloheksanon (CCl_4)



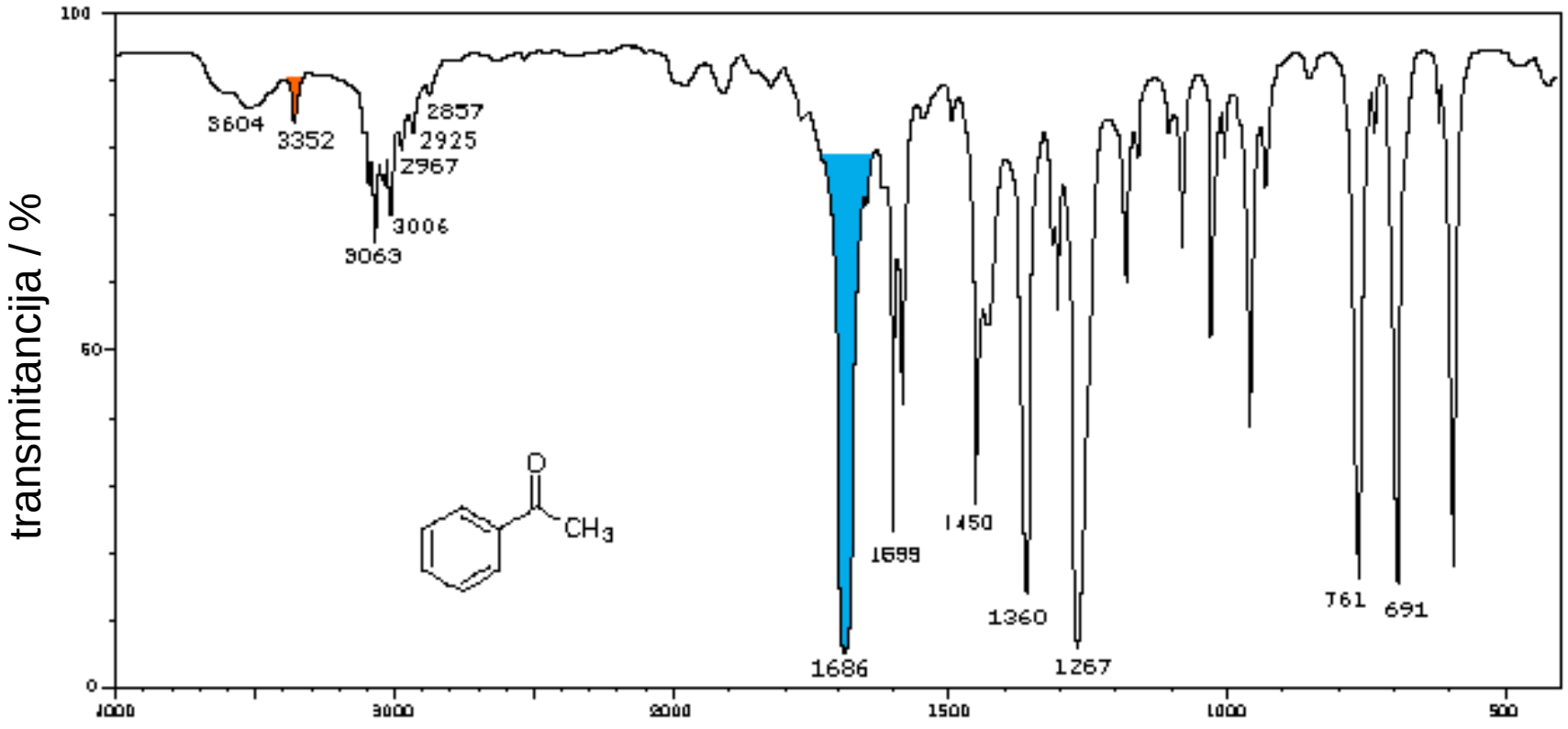
ciklopentanon (tekući film)



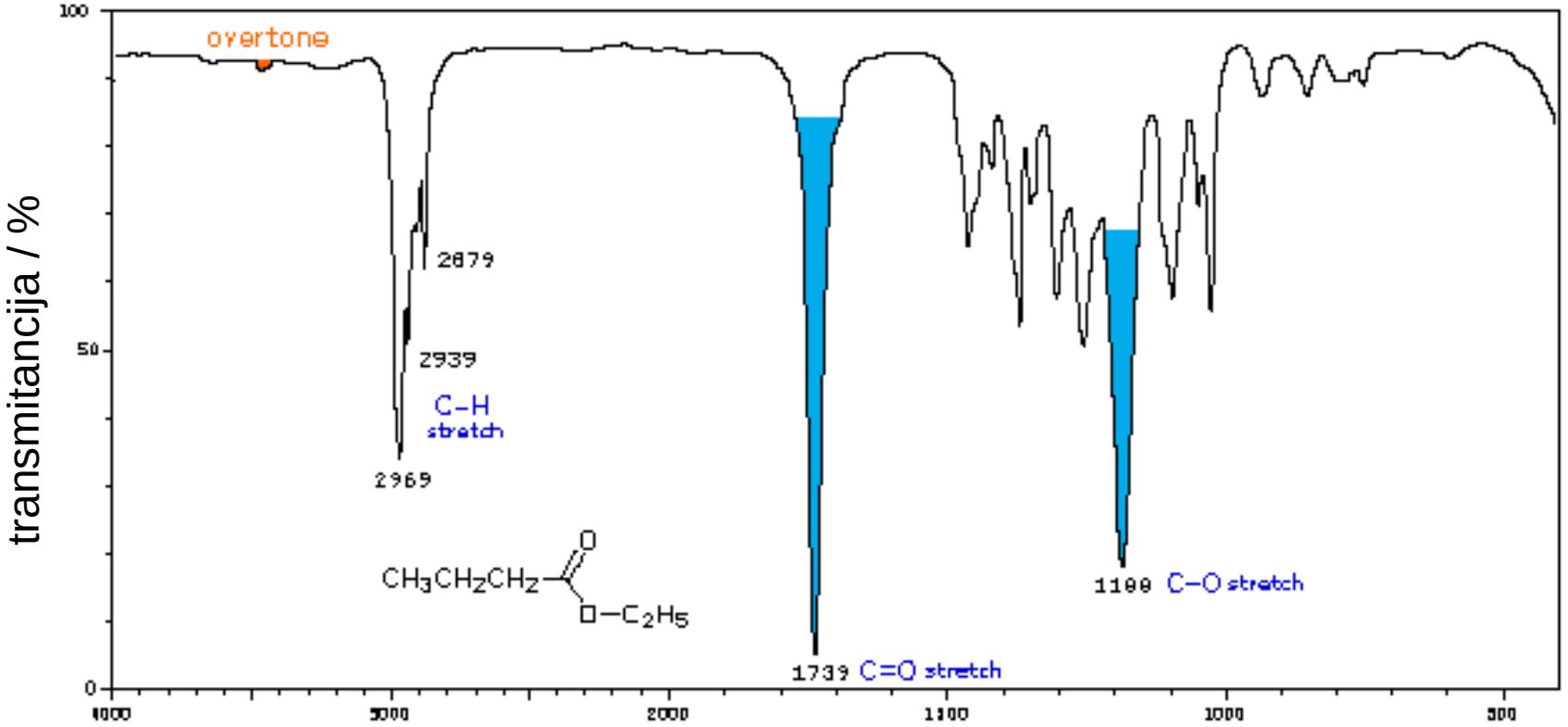
ciklobutanon (tekući film)



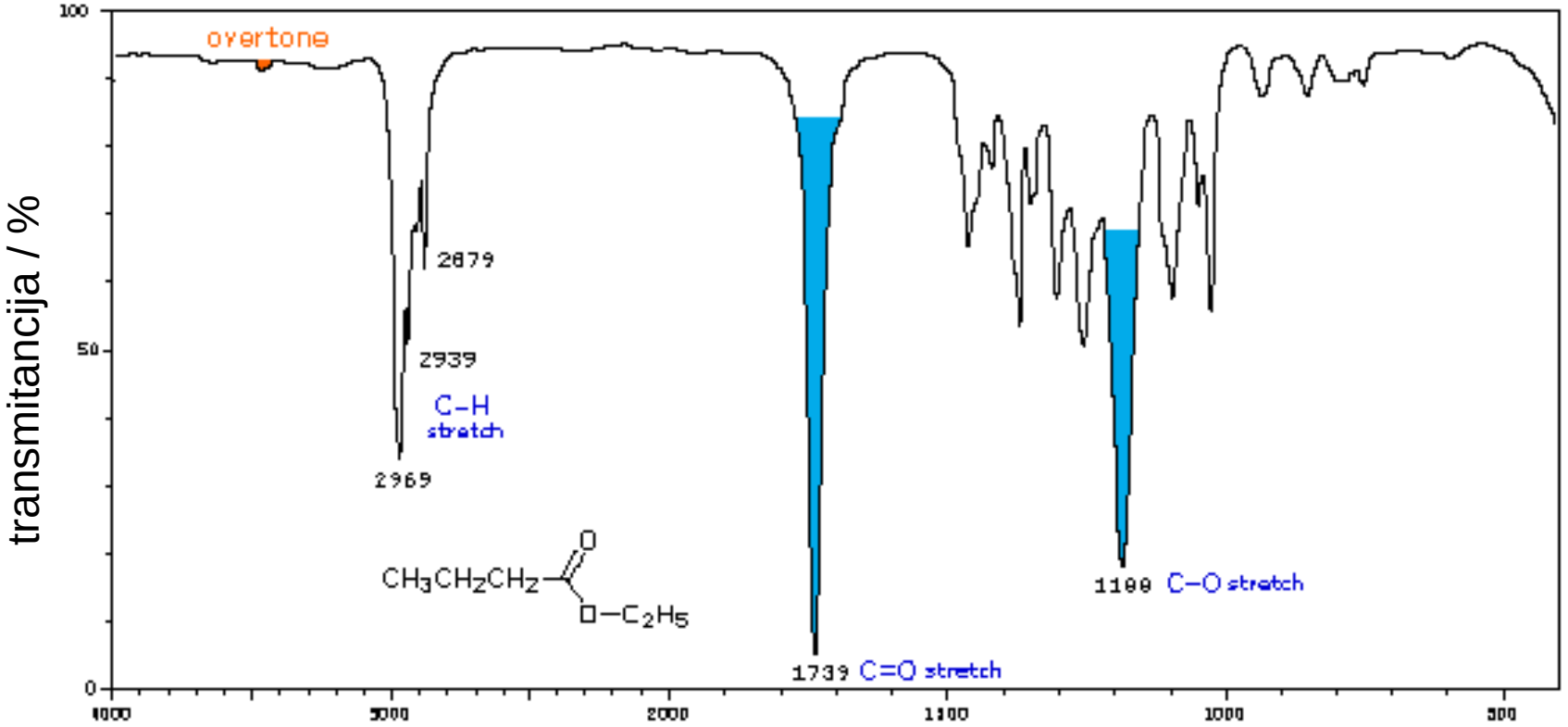
acetofenon (tekući film)



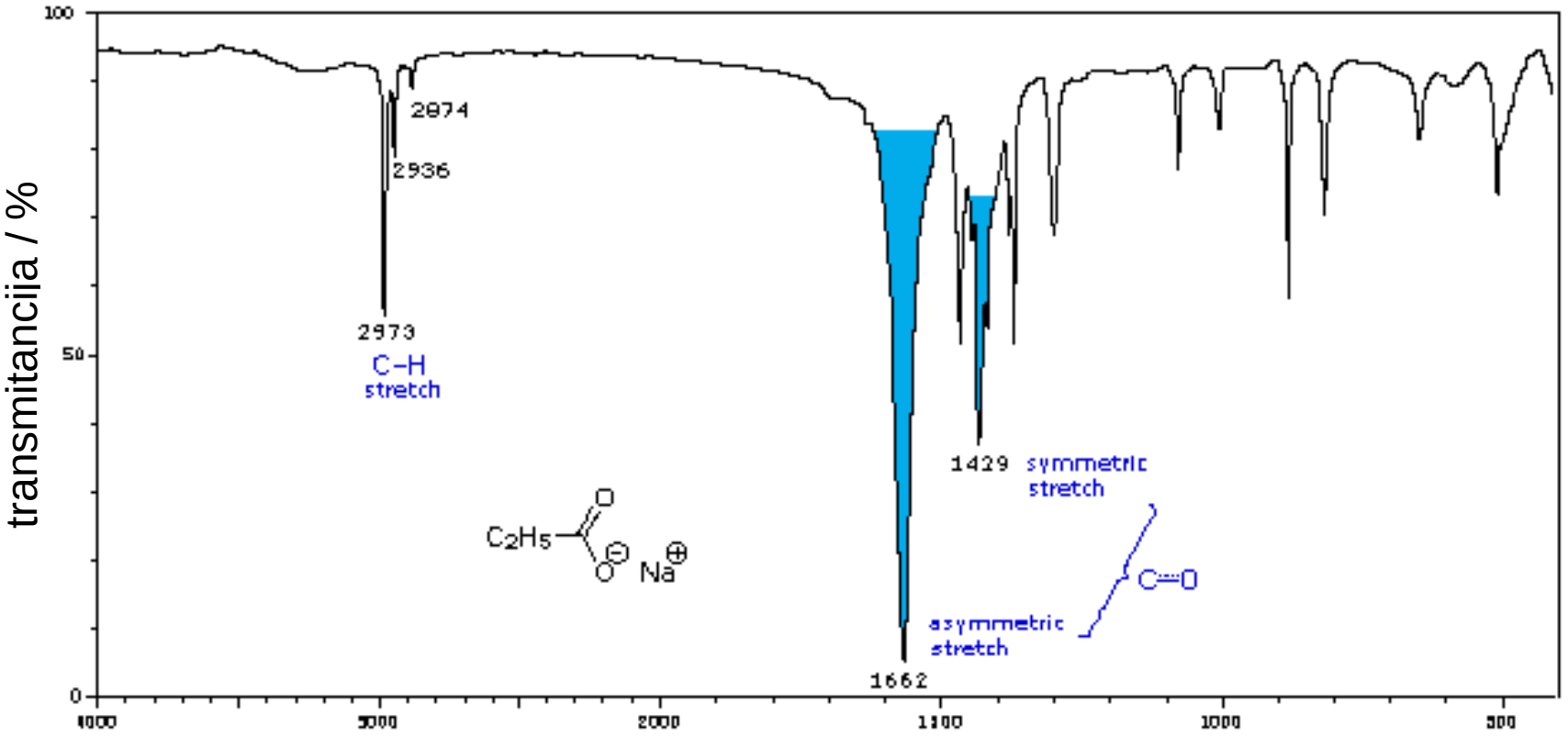
etil-butirat (tekući film)



etil-butirat (tekući film)

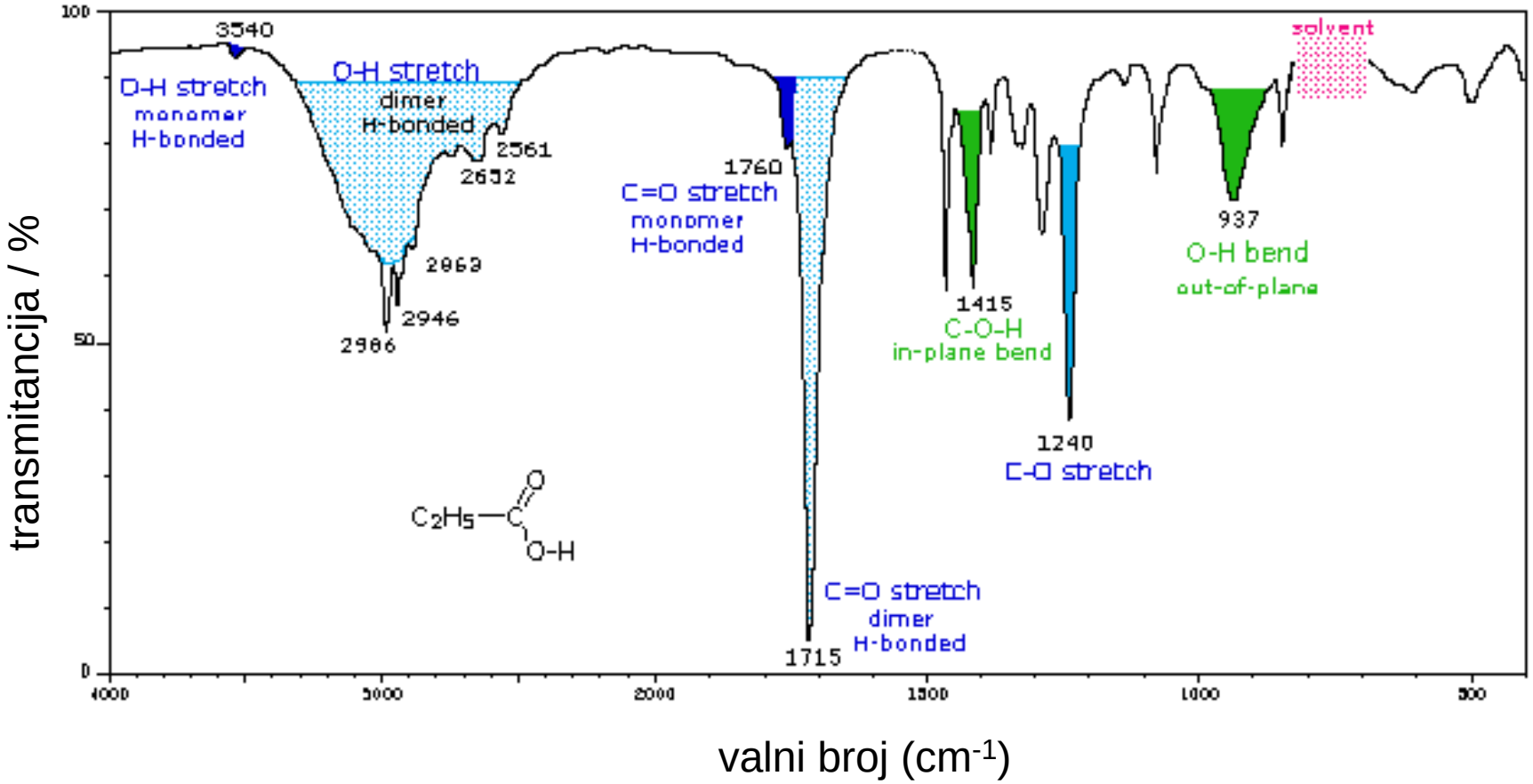


natrijev propionat (KBr pločica)

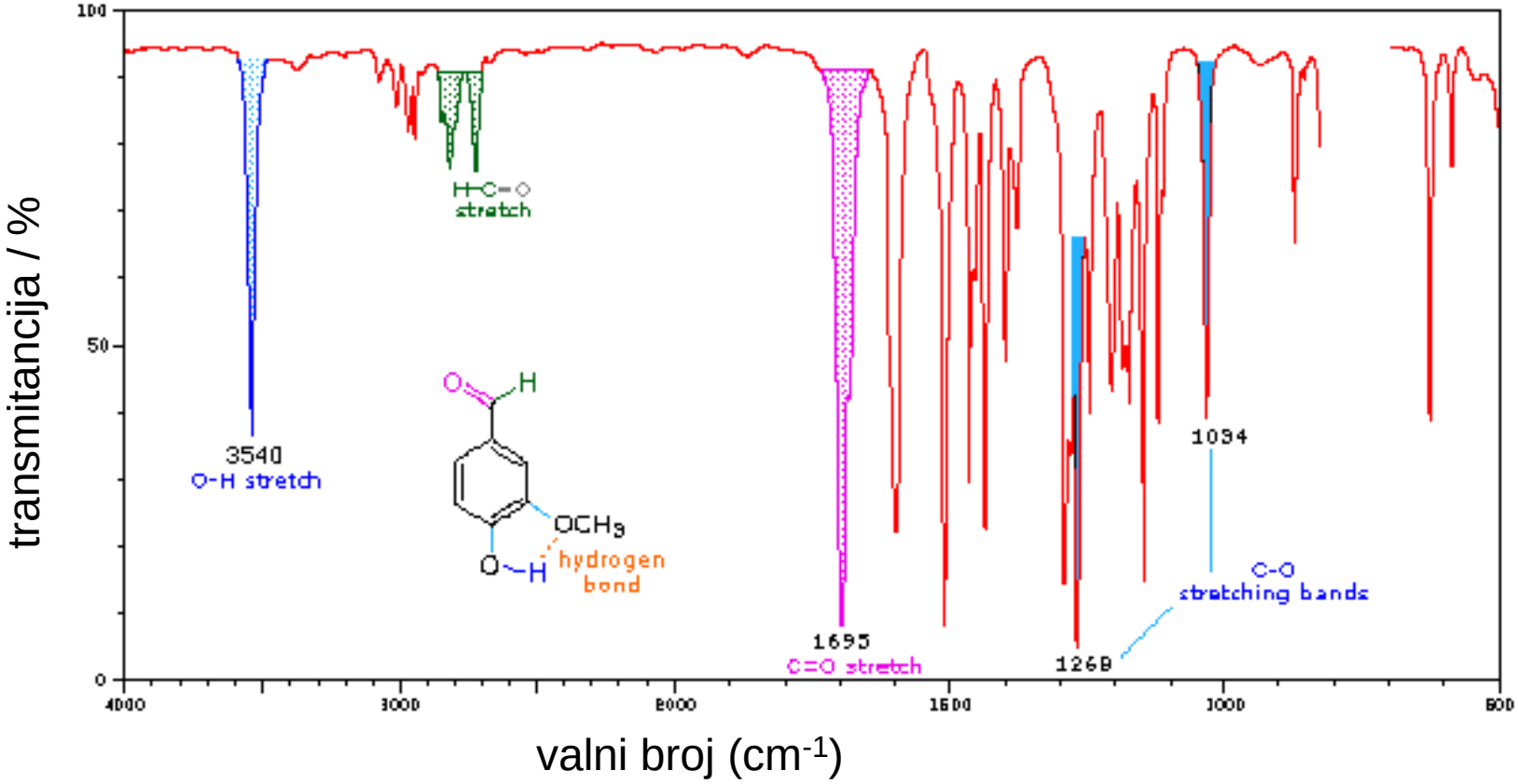


valni broj (cm^{-1})

propionska kiselina (CCl_4)

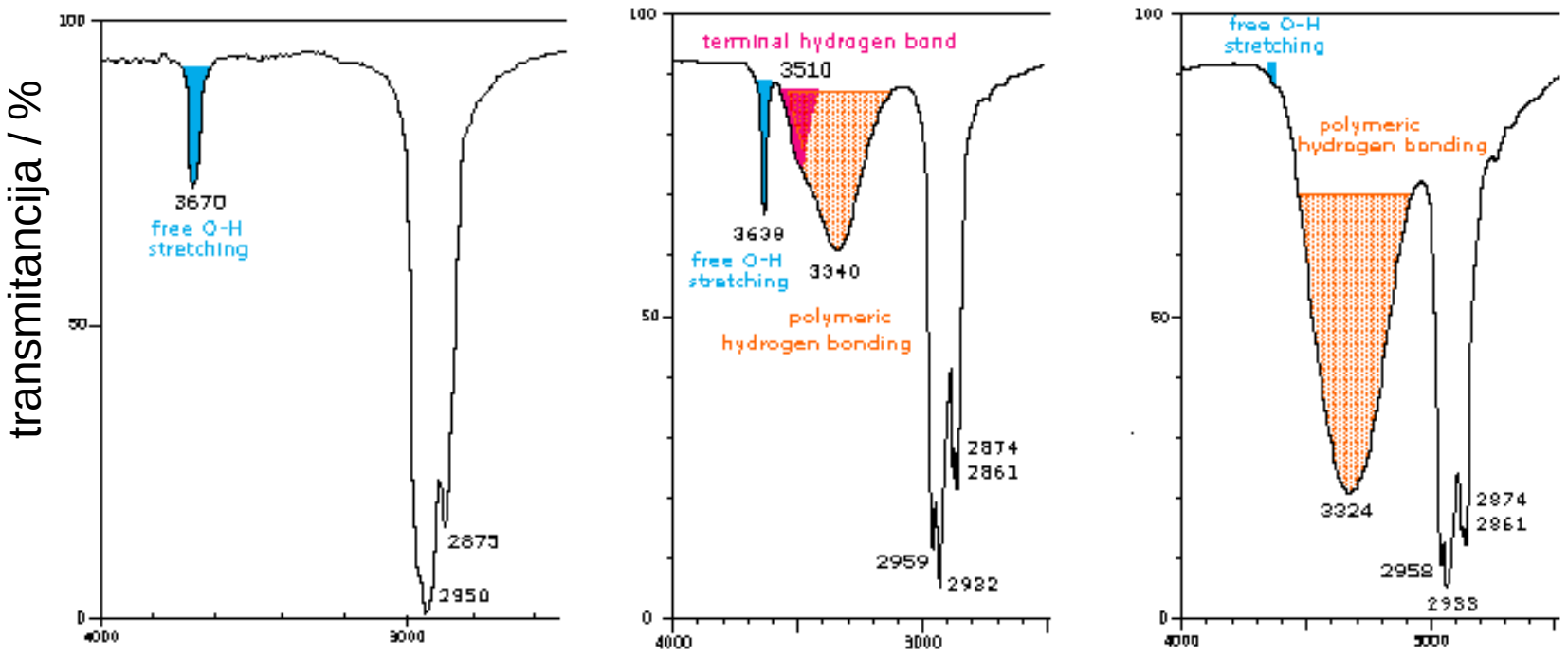


vanilin (CCl_4)



1-heksanol: dio spektra (različiti uvjeti snimanja)

CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-**OH**



plinska faza | CCl_4 | tekući film