Electromagnetic radiation

- frequency (ν): how many waves in 1s [Hz]

- wavelength (λ): distance between two neighbouring maxima of the wave (nm)

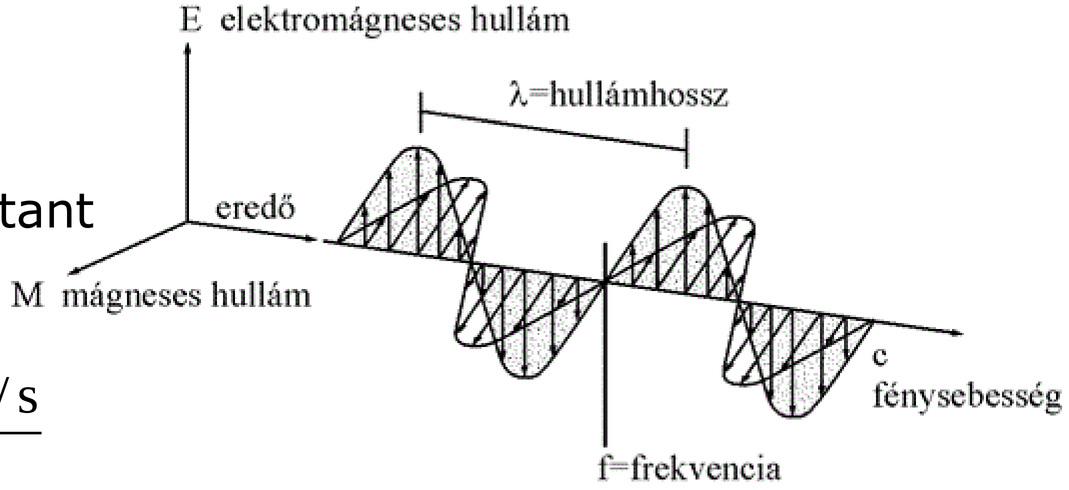
- wavenumber ($\tilde{\nu}$): how many waves are in one meter

$$\nu = \frac{c}{\lambda}$$

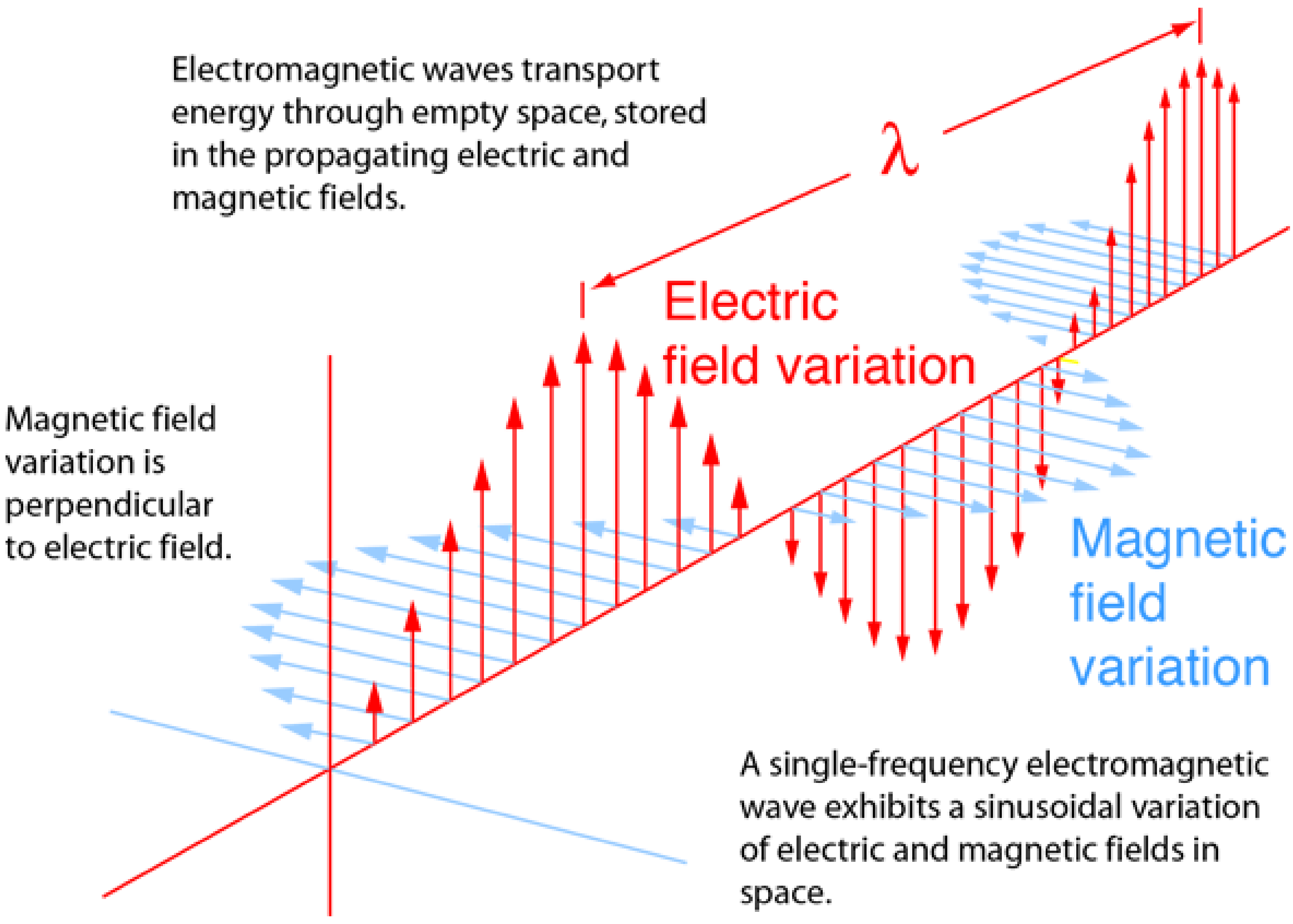
$c = 3 \cdot 10^8$ m/s speed of light in vacuo

$E = h\nu$ [J]

$h = 6.63 \cdot 10^{-34}$ Js Planck constant

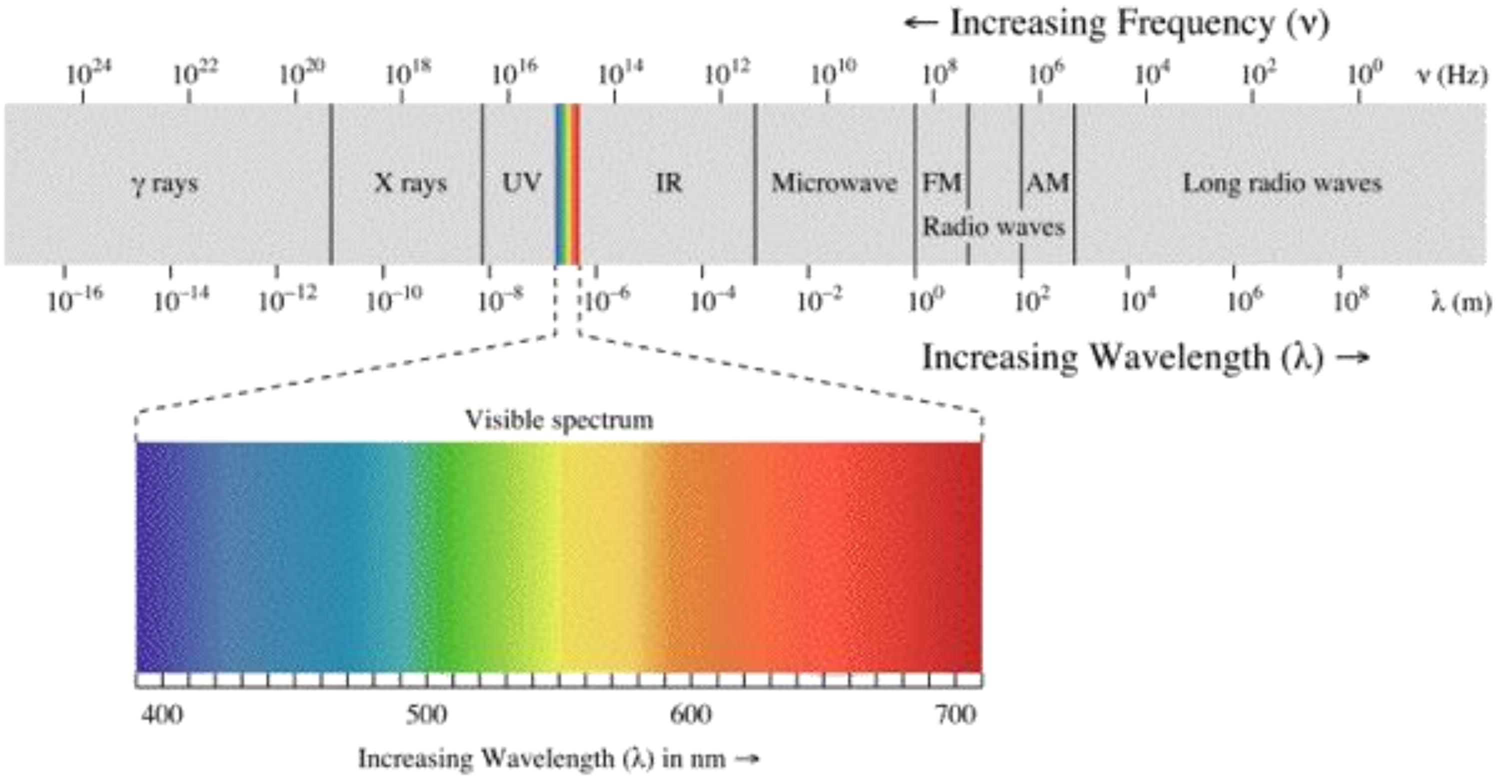


$$E = \frac{hc}{\lambda} = \frac{6.63 \cdot 10^{-34}\,\mathrm{Js} \cdot 3 \cdot 10^{8}\,\mathrm{m/s}}{\lambda}$$


Electromagnetic waves transport energy through empty space, stored in the propagating electric and magnetic fields.
λ
Electric field variation
Magnetic field variation is perpendicular to electric field.
Magnetic field variation
A single-frequency electromagnetic wave exhibits a sinusoidal variation of electric and magnetic fields in space.

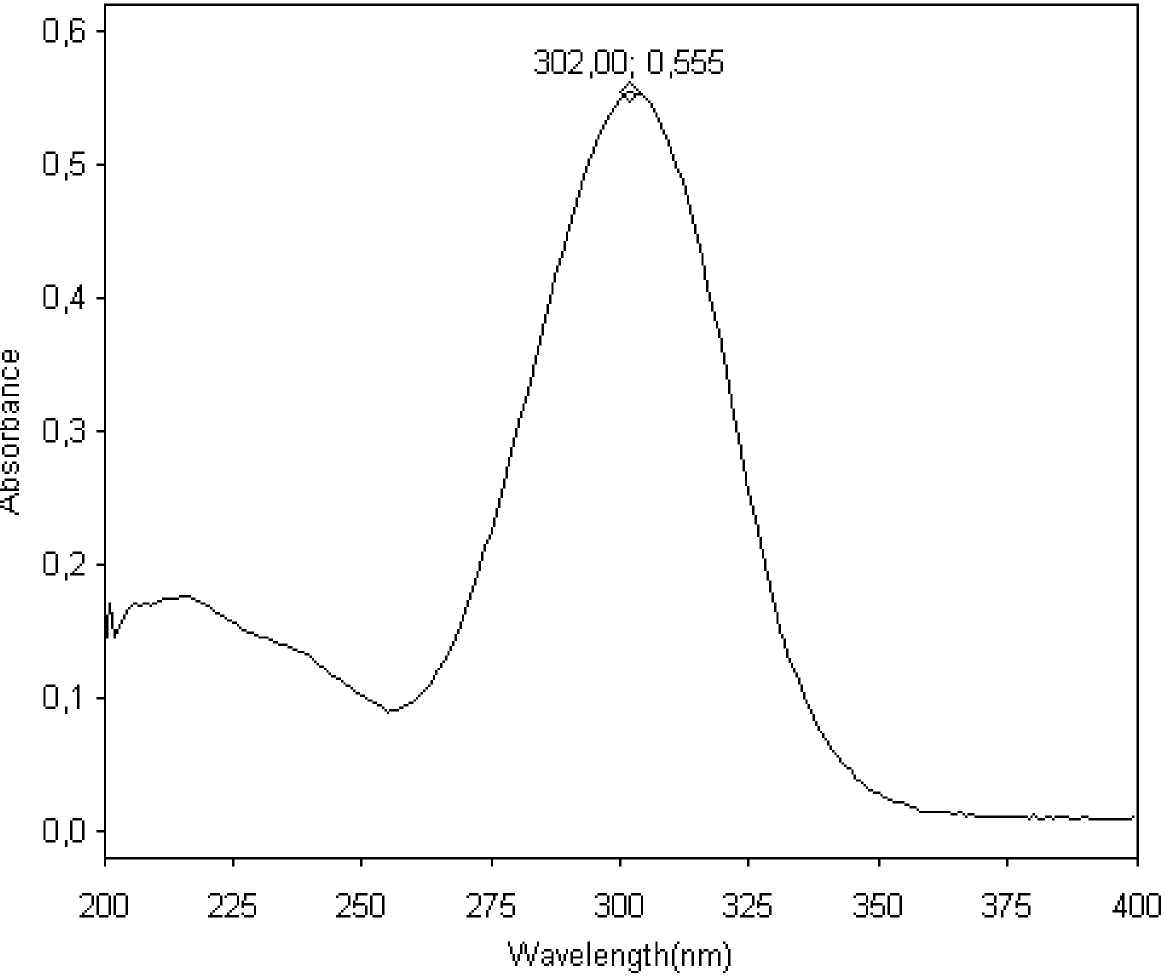
Interaction of electromagnetic radiation with molecules

M + ν	$\rightarrow$	M*	absorption
M*	$\rightarrow$	M + ν	emission
M + ν	$\rightarrow$	M* + ν'	Raman-scattering
M* + ν	$\rightarrow$	M + 2ν	stimulated emission



Spectral region	VHF	UHF	Microwave	Infrared	Visible	Ultraviolet	X-rays	γ-rays
Common usage	NMR	EPR	rotational transitions	vibrational transitions	electronic transitions		ionisation	nuclear effects
Frequency (Hz)	5×10^{8}	3×10^{10}	3×10^{11}	3×10^{13}	6×10^{14}	1.2×10^{15}	3.0×10^{17}	1.5×10^{19}
Wavelength	0.6 m	1 cm	1 mm	10 μm	500 nm	250 nm	1 nm	20 pm
Wavenumber (cm^{-1})	0.017	1.0	10.0	1000	20,000	40,000	1.0×10^{7}	5.0×10^{8}
Single photon energy (eV)	2.07×10^{-6}	1.24×10^{-4}	1.24×10^{-3}	1.24×10^{-1}	2.5	5.0	1.24×10^{3}	6.2×10^{4}
Photon energy (kJ mol^{-1})	2.03×10^{-4}	1.20×10^{-2}	1.20×10^{-1}	12.0	239	479	1.2×10^{5}	6×10^{6}

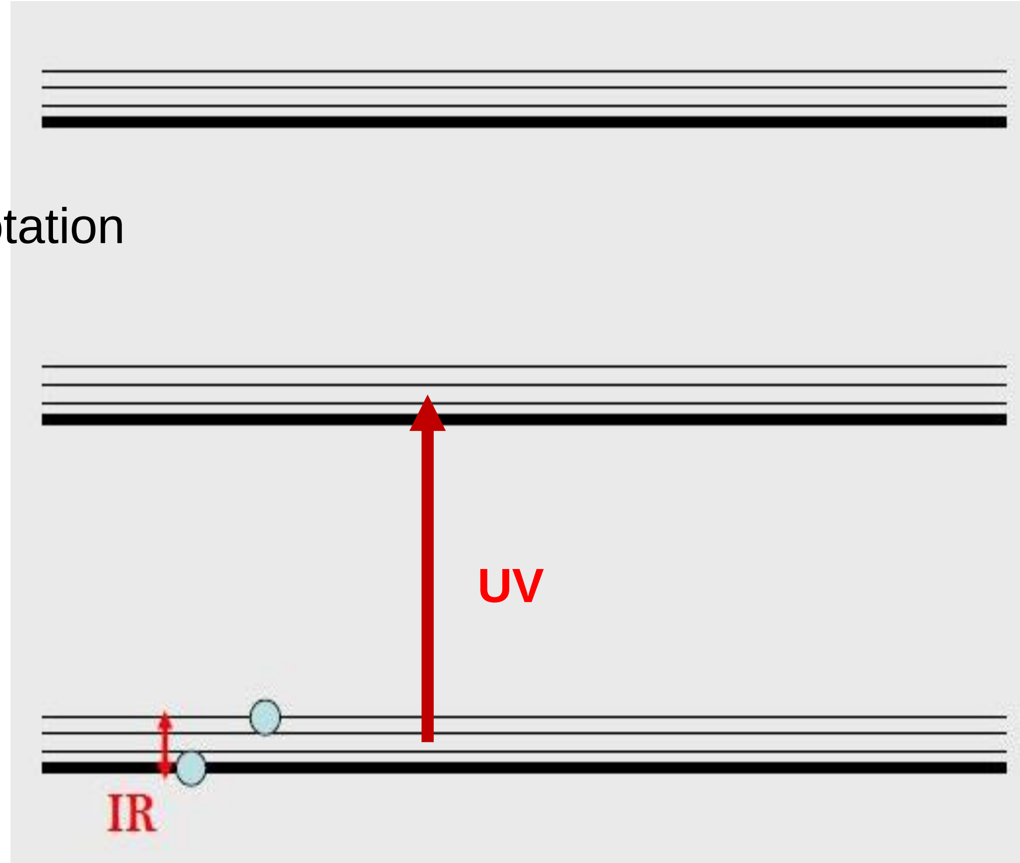
UV spectrum



Structure??????

Transititions

$$E = E_{electron} + E_{vibration} + E_{rotation}$$



HOMO

Highest occupied

UV absorption →

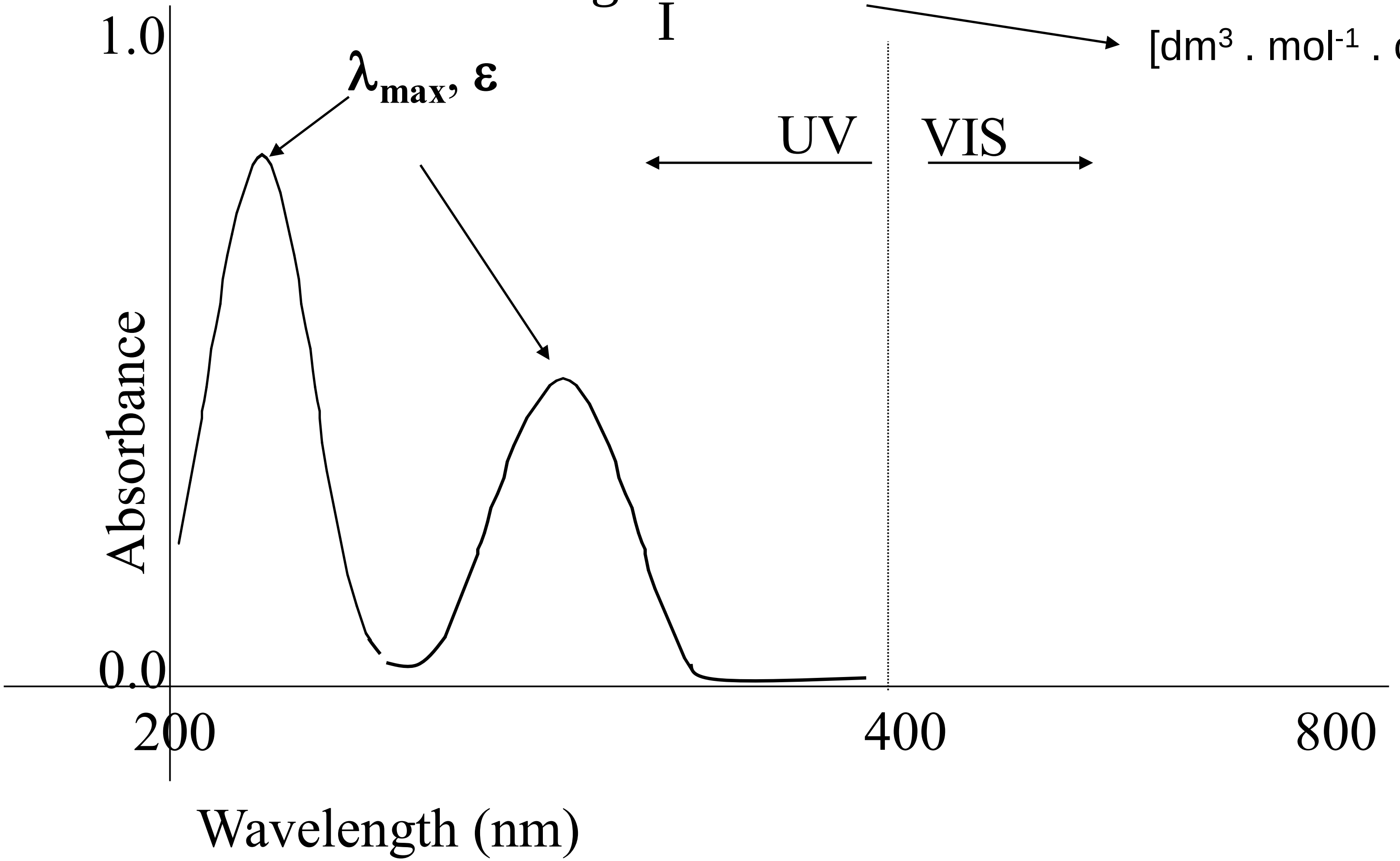
LUMO

Lowest unoccupied

How does a UV spectrum look like?

$$\log \frac{I_o}{I} = A = \varepsilon \cdot l \cdot c$$

[$dm^3 . mol^{-1} . cm^{-1}$]



What is seen in a UV/VIS spectrum

•$\sigma \rightarrow \sigma^*$ and $\sigma \rightarrow \pi^*$ transitions: too high energy, only in vacuo, λ_{max} <150 nm. Not used in practice.

•$\pi \rightarrow \sigma^*$ transitions: λ_{max} 150-250 nm

•n $\rightarrow \sigma^*$ nonbonding electrons, λ_{max} 150-250 nm (eg: C-I)

•n $\rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions : mostly observed. λ_{max} = 200-600 nm.

Cromophor groups

Double bond	**λ [nm]**	**ε**	
C=C	190	9000	π→π*
C=O	280 190 160	20 2000	n →π* n →σ* π →π*
COOR	205 165	50 2000	n →π* π →π*
C=N	250	200	n →π*
C=N–OH	193	2000	n →π*
C=S	500 240	10 9000	n →π* π →π*
$C=N_2$	350	5	n →π*
–N=N–	340 240	10	n →π*
>S=O–	210	2000	

Double bond	**λ [nm]**	**ε**	
N=O	673 300	20 100	n →π* n →π*
–ONO	310-390 220	30 1000	n →π*
NO_2	330 280	10 20	n →π*
$–ONO_2$	260	20	n →π*
–SCN	245	100	n →π*
–NCS	250	1000	
$–C–N_3$	280 220	30 150	n →π*

Triple bond	**λ [nm]**	**ε**	
–C≡C–	175	8000	π →π*

Usually in liquid phase, the solvent should not absorb in the region

Most important UV/VIS solvents (minimum possible wavelength)

Water	191	THF	220
Acetonitrile	190	CH_2Cl_2	235
Cycohexane	195	$CHCl_3$	245
Diethyl ether	215	CCl_4	265
Ethanol	204	Acetone	300
Hexane	195		
Methanol	201		
Dioxane	220		

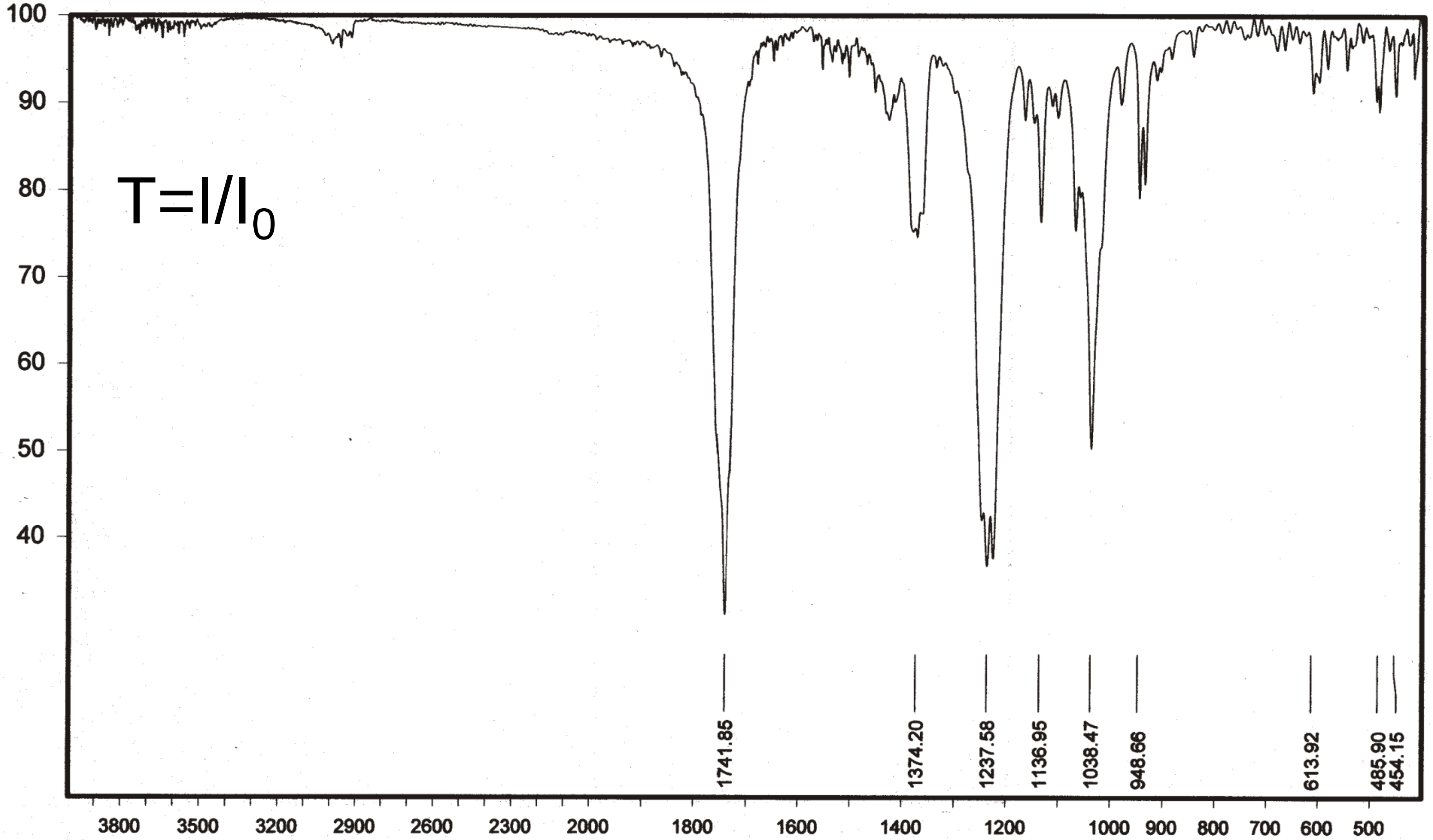
Used for detection, **verification**, quantification, first assumptions of possible functionalties, following reactions

high sensitivity (small amount of material needed)

noninvasive

IR

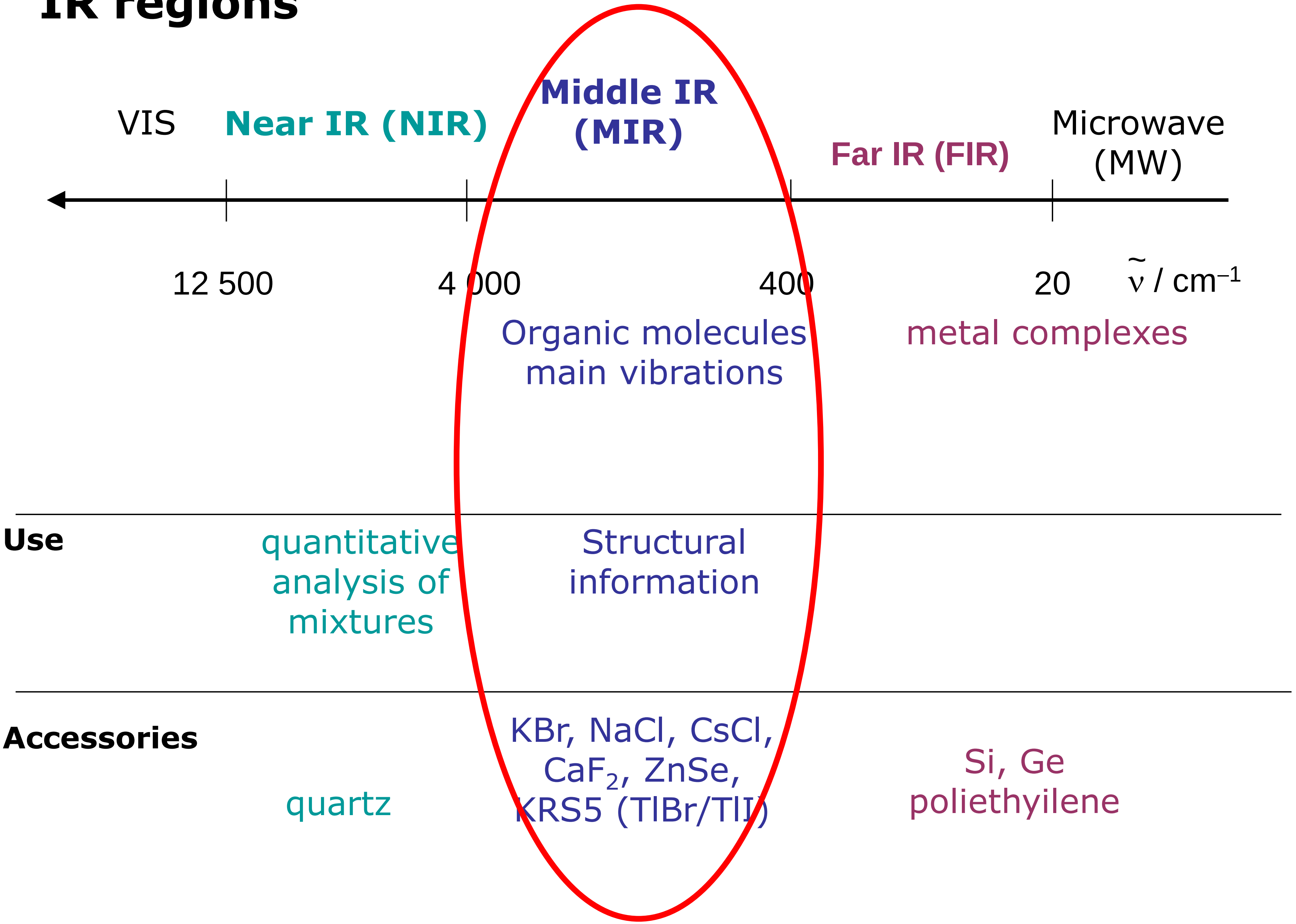
$$E = E_{electron} + E_{vibration} + E_{rotation}$$



$T = I/I_0$

1/cm

IR regions



VIS
Near IR (NIR)
Middle IR (MIR)
Far IR (FIR)
Microwave (MW)
12 500
4 000
400
20
$\tilde{\nu}$ / cm^{-1}
Organic molecules main vibrations
metal complexes
Use
quantitative analysis of mixtures
Structural information
Accessories
quartz
KBr, NaCl, CsCl, CaF_2, ZnSe, KRS5 (TlBr/TlI)
Si, Ge poliethyilene

The frequency of the absorbed radiation must be equal to a vibrational frequency of the molecule. Observable only if the dipolmomentum is changed.

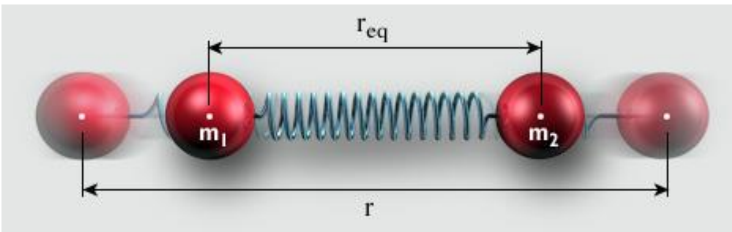
Question: Does IR absorbance of O_2 exist?

NO, because there is no change in dipolmomentum

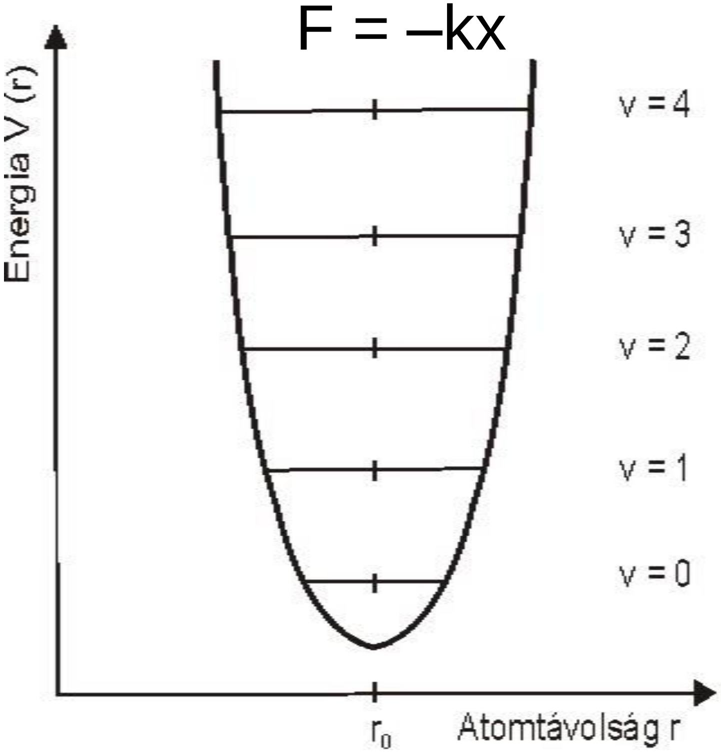
Two atomic molecule

$$\nu = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \qquad \mu = \frac{m_1 \cdot m_2}{m_1 + m_2}$$

Harmonic oscillator



F = –kx

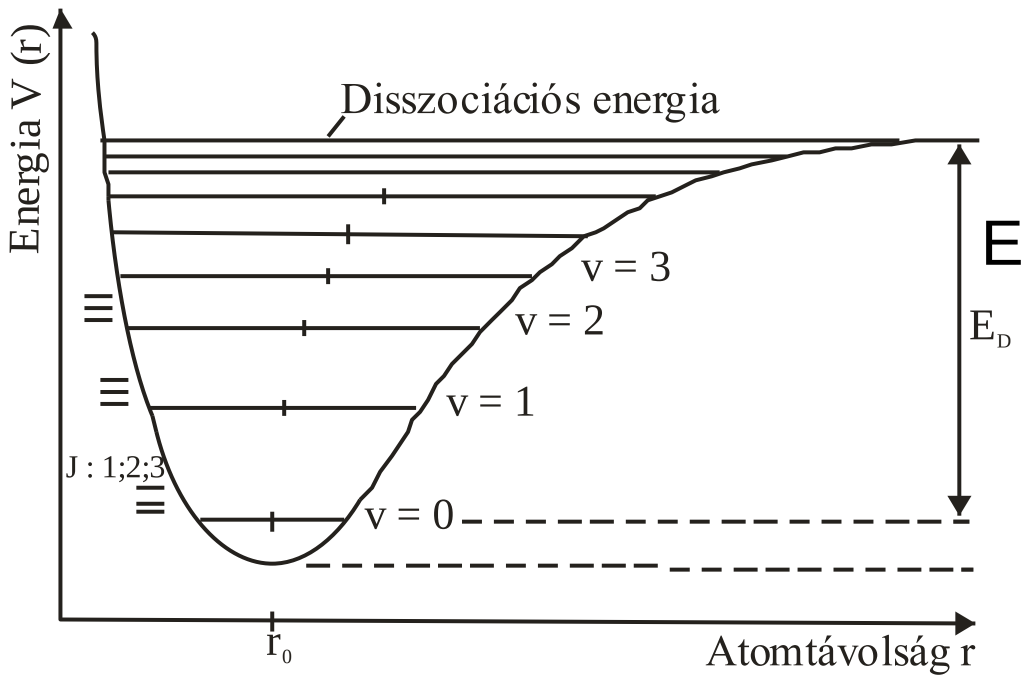


$E = h\nu_f(v+1/2)$

$\Delta v = \pm 1$

During excitation, the frequency does not change!

2. Anharmonic oscillator



anharmonikus oszcillátor

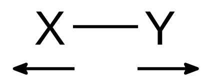
$\Delta v = \pm 1, \pm 2, \pm 3$

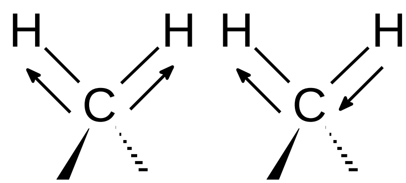
Energy levels not equidistant

3N-6 (linear:3N-5) different vibrational modes

Type of vibrations

stretching: length of the bond changes

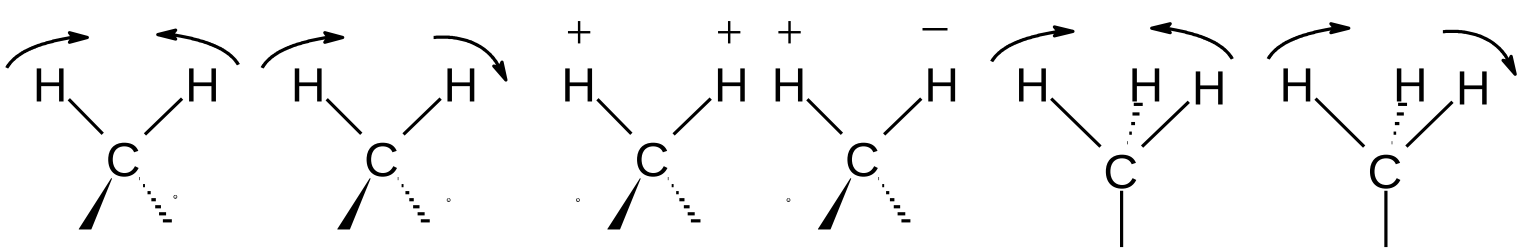




ν_s ν_{as}

deformations: bending: rocking, twisting, wagging, scissoring

In plane perpendicular other



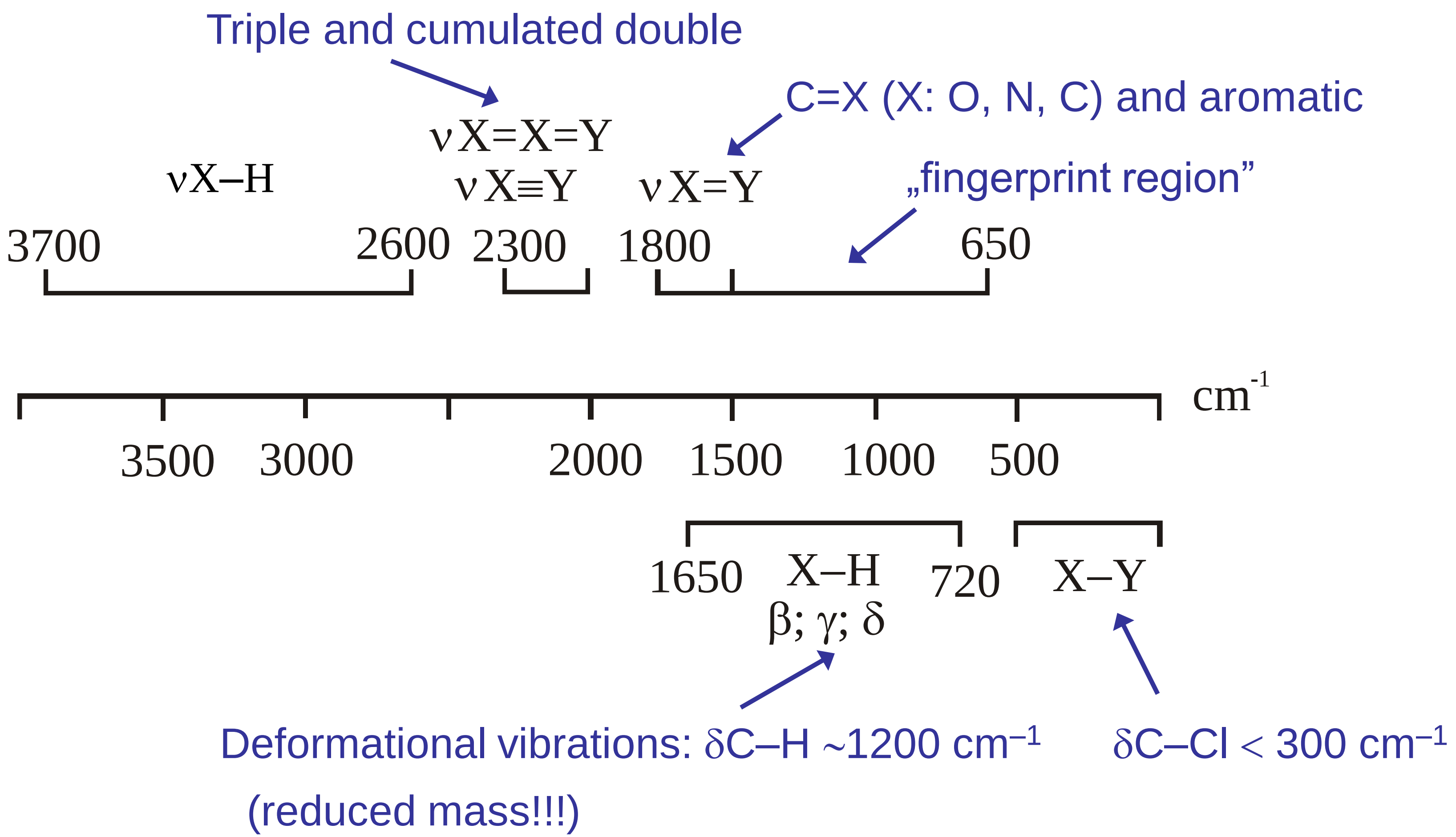
β_s β_{as} γ_s γ_{as} $\delta_{s\,CH_3}$ $\delta_{as\,CH_3}$

scissoring rocking wagging twisting

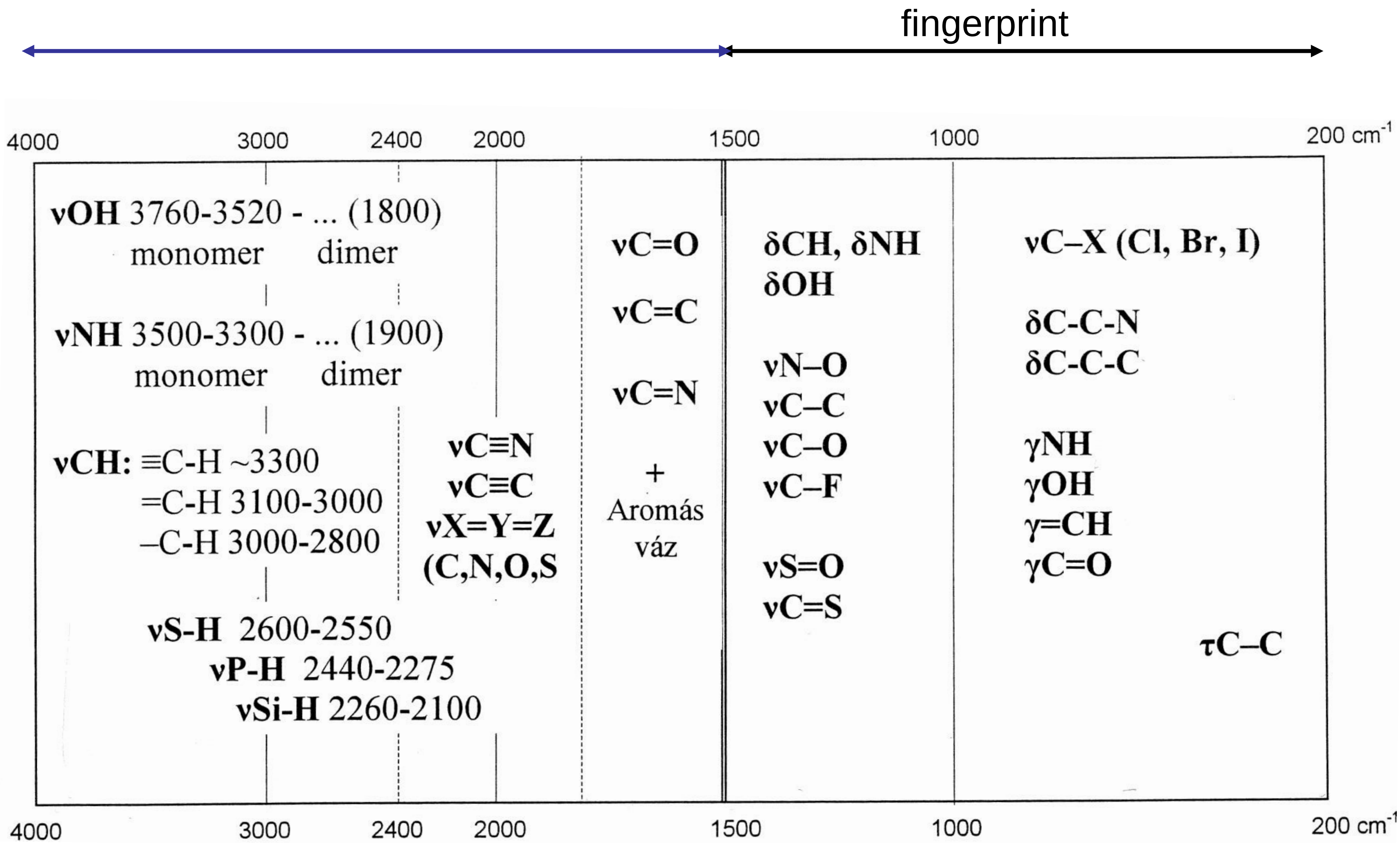
https://www.youtube.com/watch?v=1PQqDfJKXvA

IR regions

Characteristic is a region if a given vibrational mode resonates with a typical frequency and no other types



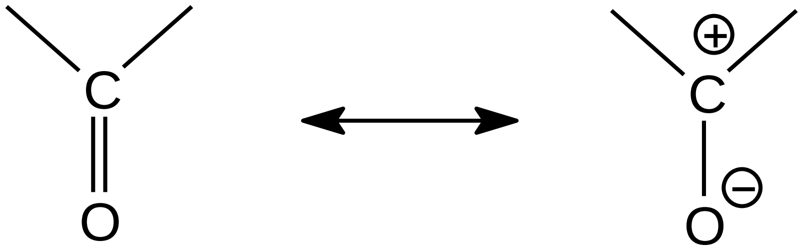
Chararcteristic regions



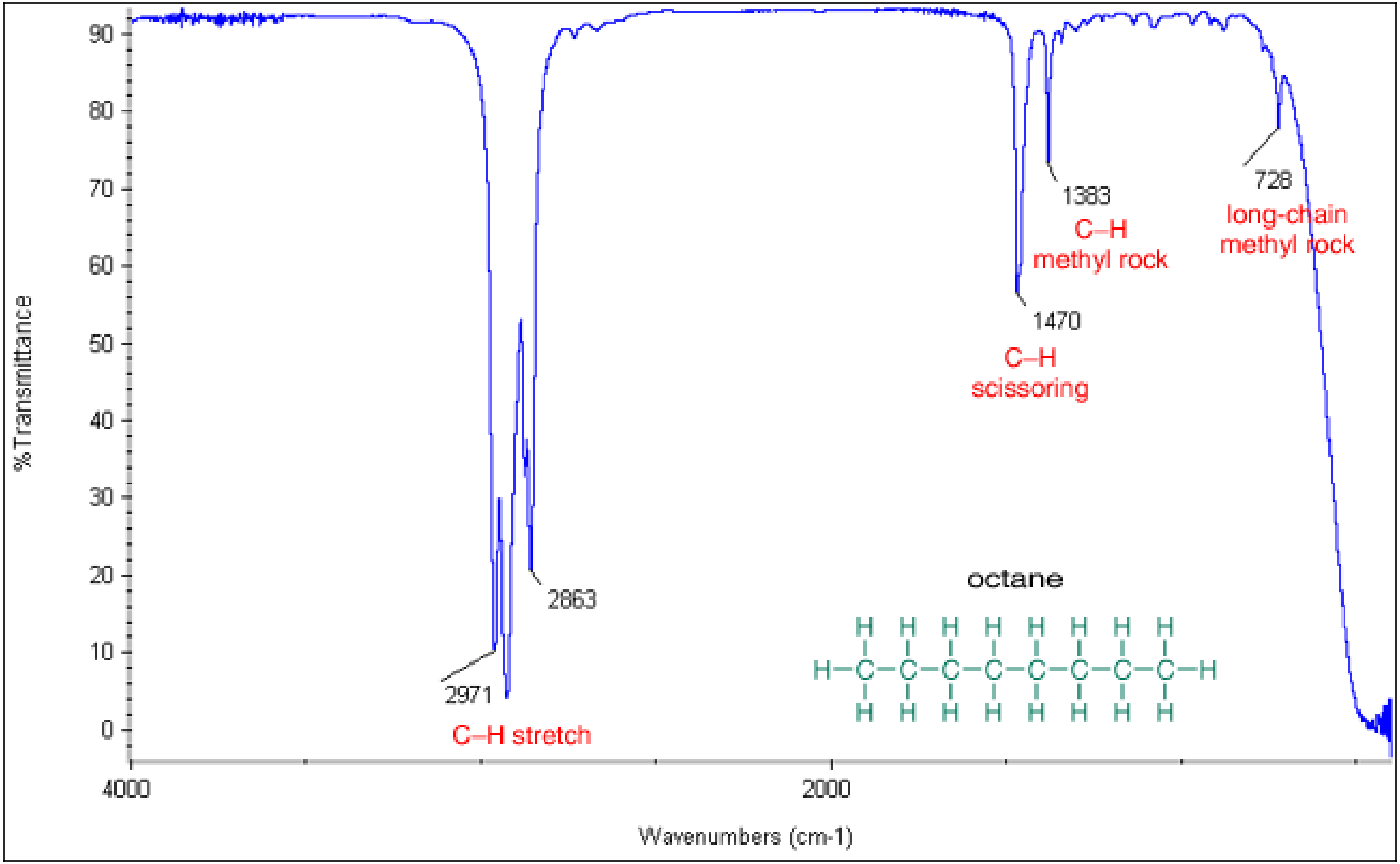
IR spectroscopy table

Vibrational mode	σ (cm^{-1})	Intensity
alcohol O—H (stretching)	3600-3200	strong
carboxylic acid O—H (stretching)	3600-2500	strong
N—H (stretching)	3500-3350	strong
≡C—H (stretching)	3300	strong
=C—H (stretching)	3100-3000	weak
C—H (stretching)	2950-2840	weak
–(CO)—H (stretching)	2900-2800	weak
C≡N (stretching)	2250	strong
C≡C (stretching)	2260-2100	variable
aldehyde C=O (stretching)	1740-1720	strong
anhydride C=O (stretching)	1840-1800; 1780-1740	weak; strong
ester C=O (stretching)	1750-1720	strong
ketone C=O (stretching)	1745-1715	strong
amide C=O (stretching)	1700-1500	strong
alkene C=C (stretching)	1680-1600	weak
aromatic C=C (stretching)	1600-1400	weak
CH_2 (bending)	1480-1440	medium
CH_3 (bending)	1465-1440; 1390-1365	medium
C—O—C (stretching)	1250-1050 (several)	strong
C—OH (stretching)	1200-1020	strong
NO_2 (stretching)	1600-1500; 1400-1300	strong

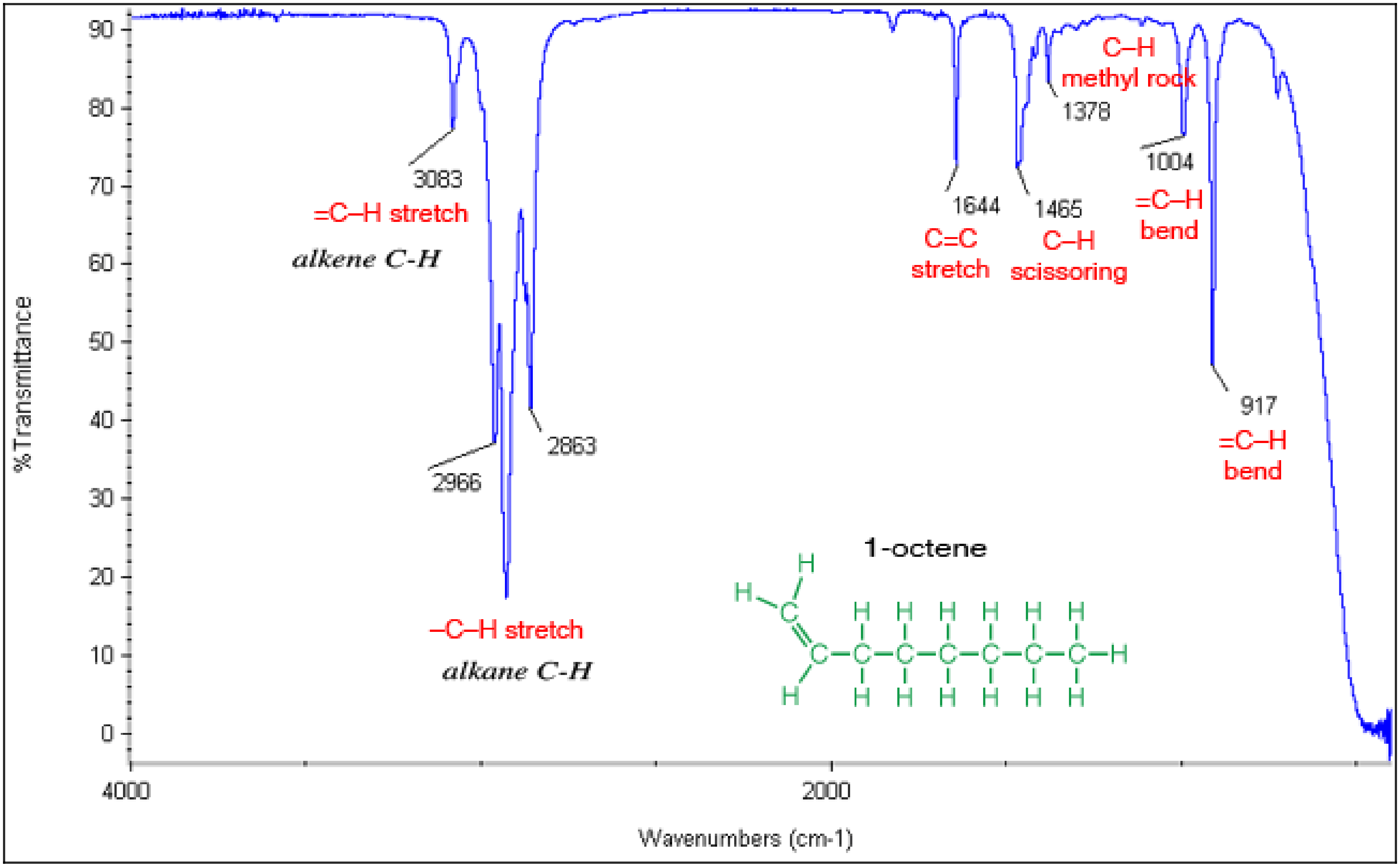
k↑ ν↑



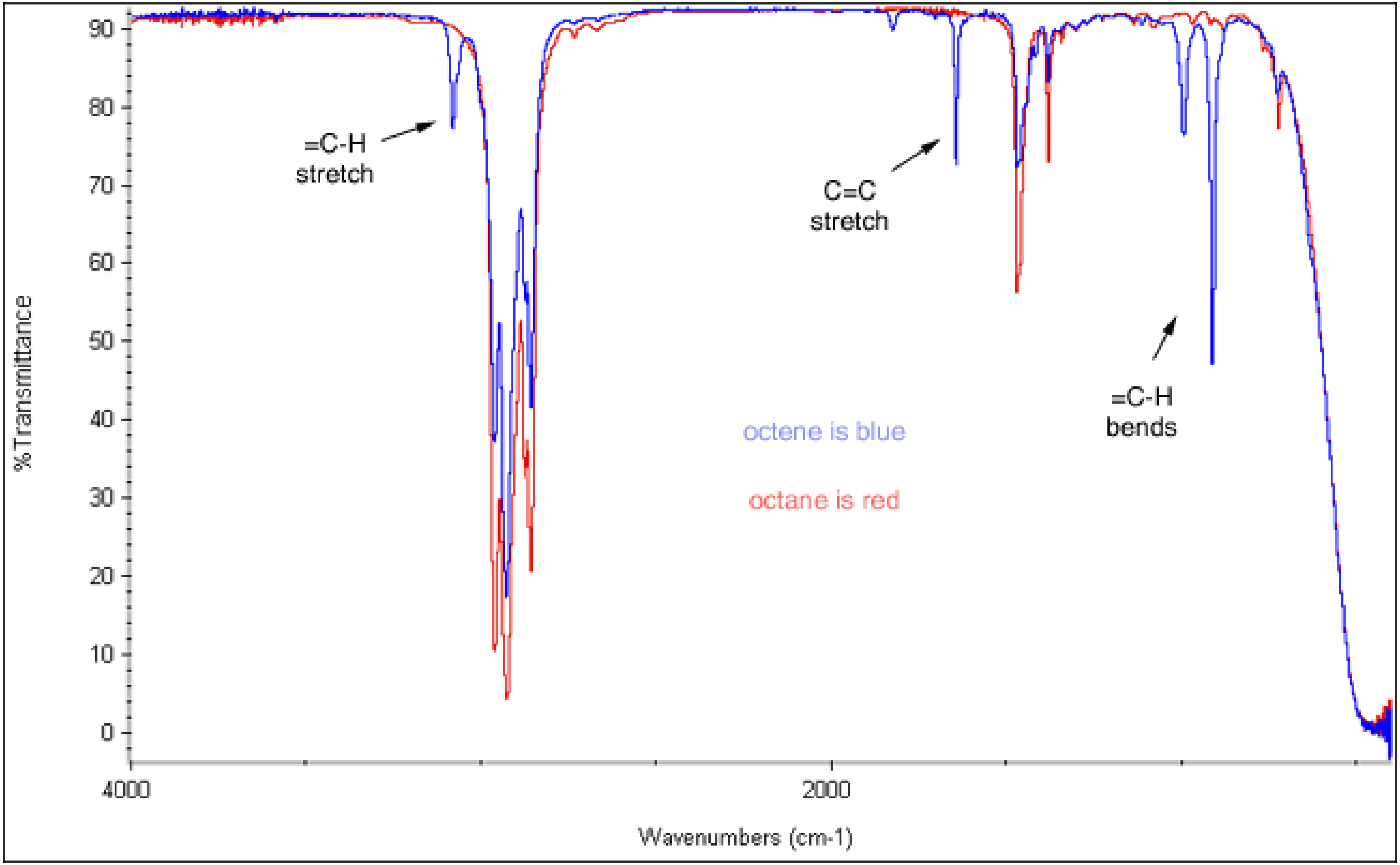
bond: 2	bond: 1
ν↑	ν↓
Electron withdrawing subst.	Conjugation, electron sending substituents

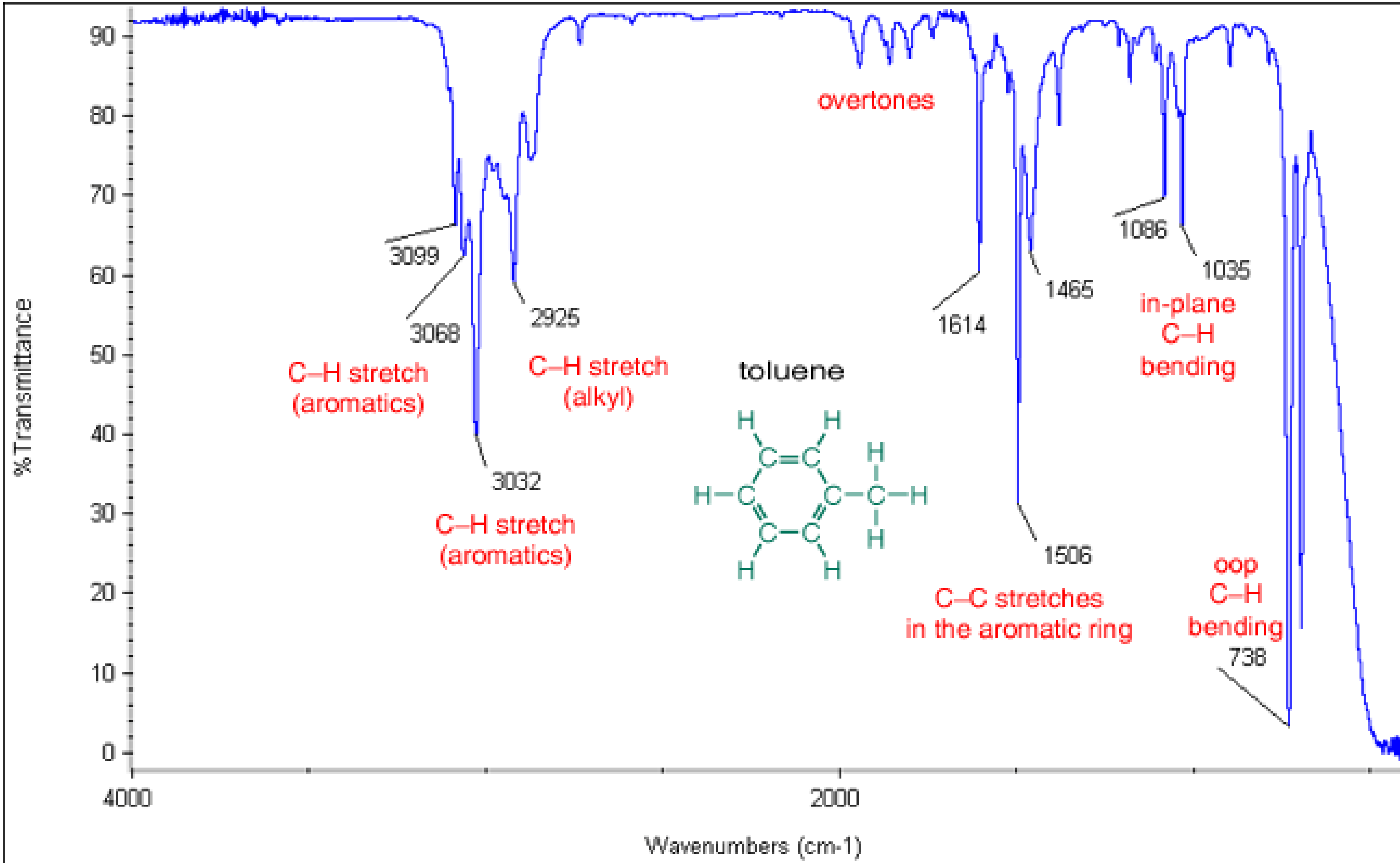


90
80
70
60
50
40
30
20
10
0
%Transmittance
4000
2000
Wavenumbers (cm-1)
2971
2863
C–H stretch
1470
C–H
scissoring
1383
C–H
methyl rock
728
long-chain
methyl rock
octane
H H H H H H H H
H–C–C–C–C–C–C–C–C–H
H H H H H H H H

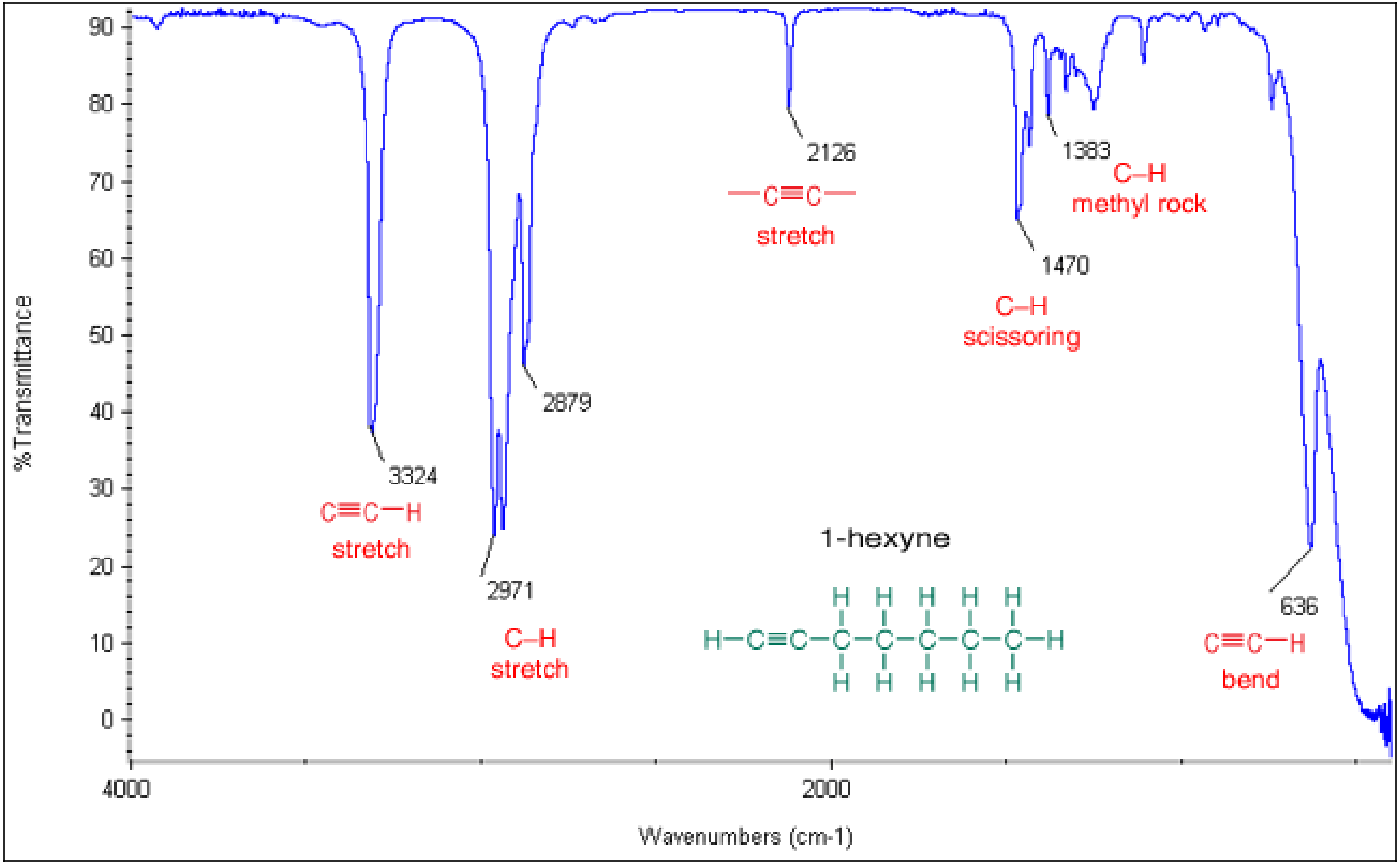


%Transmittance
90
80
70
60
50
40
30
20
10
0
4000
2000
Wavenumbers (cm-1)
3083
=C–H stretch
alkene C-H
2966
2863
–C–H stretch
alkane C-H
1644
C=C
stretch
1465
C–H
scissoring
1378
C–H
methyl rock
1004
=C–H
bend
917
=C–H
bend
1-octene

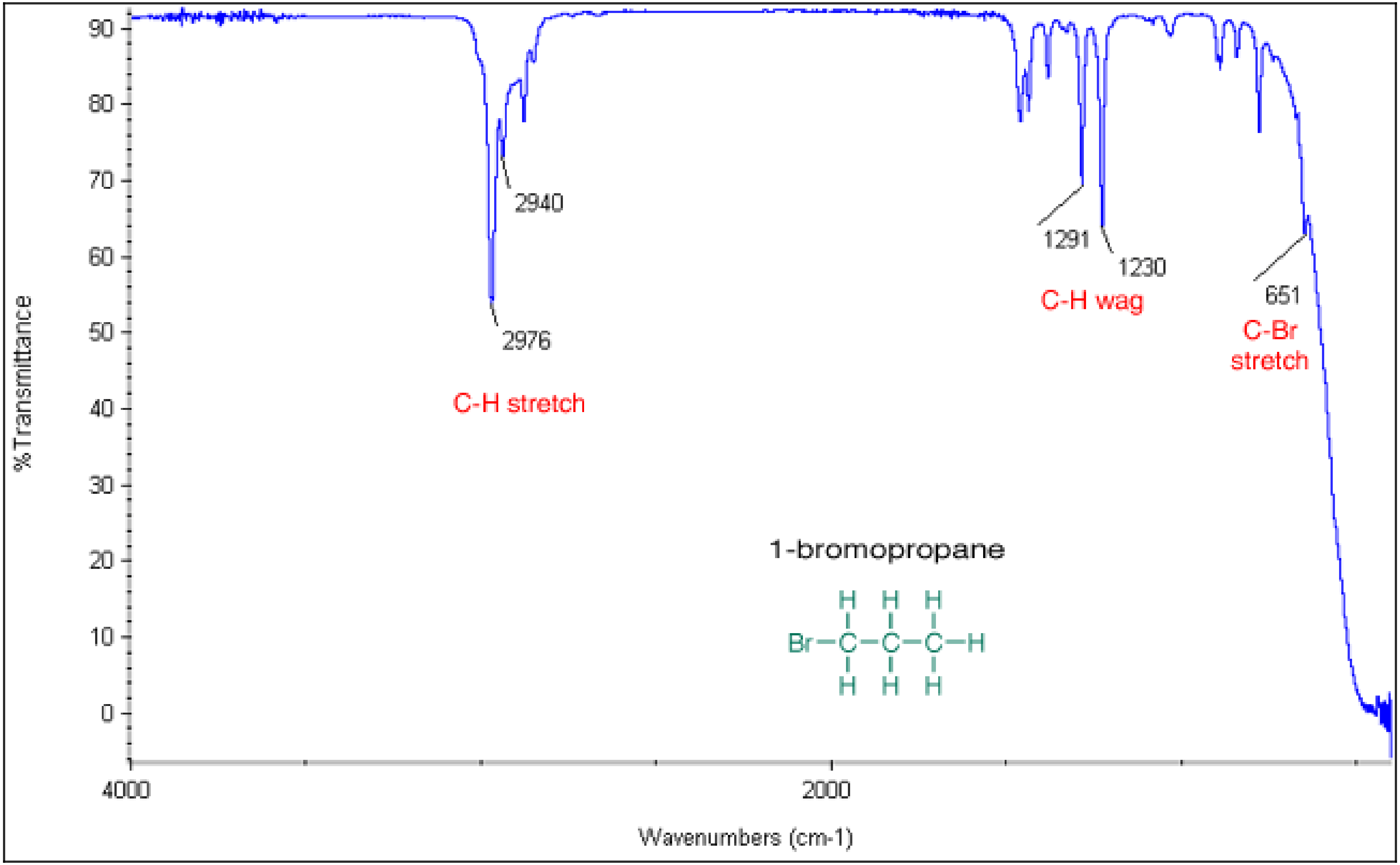

90
80
70
60
50
40
30
20
10
0
%Transmittance
4000
2000
Wavenumbers (cm-1)
=C-H
stretch
C=C
stretch
=C-H
bends
octene is blue
octane is red



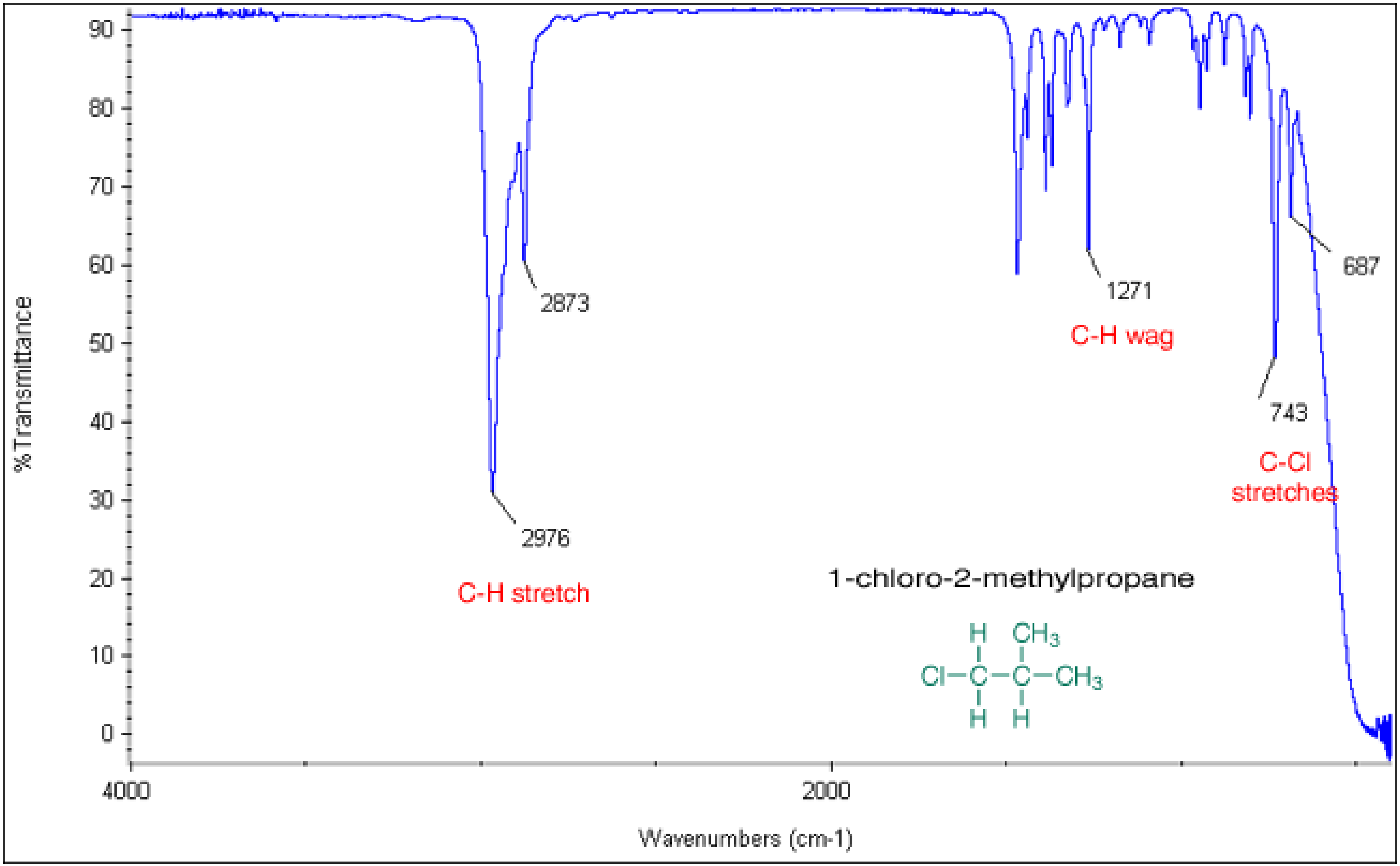
%Transmittance
Wavenumbers (cm-1)
4000
2000
90
80
70
60
50
40
30
20
10
0
3099
3068
3032
2925
C–H stretch (aromatics)
C–H stretch (alkyl)
C–H stretch (aromatics)
toluene
overtones
1614
1506
1465
1086
1035
in-plane C–H bending
C–C stretches in the aromatic ring
oop C–H bending
738

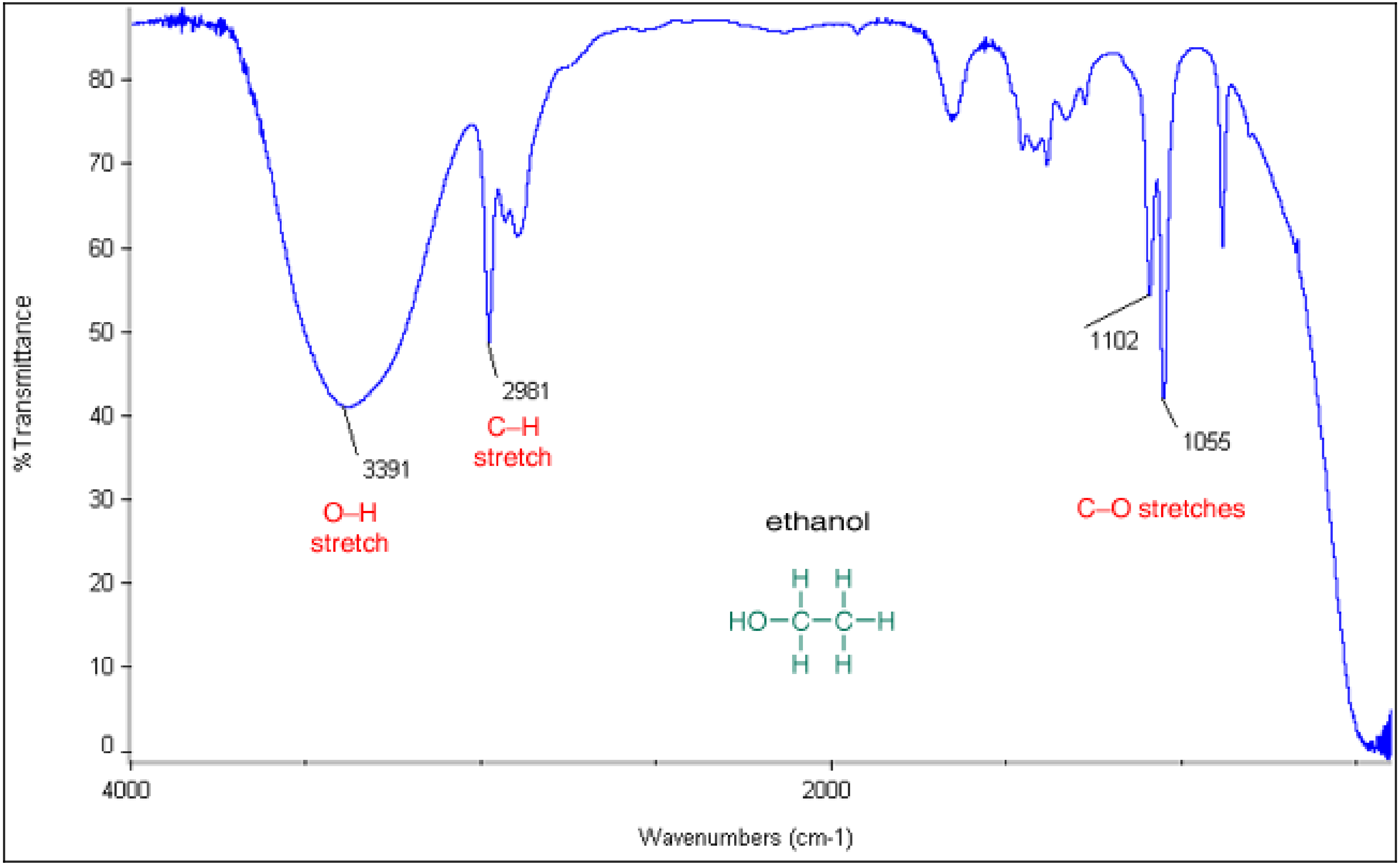


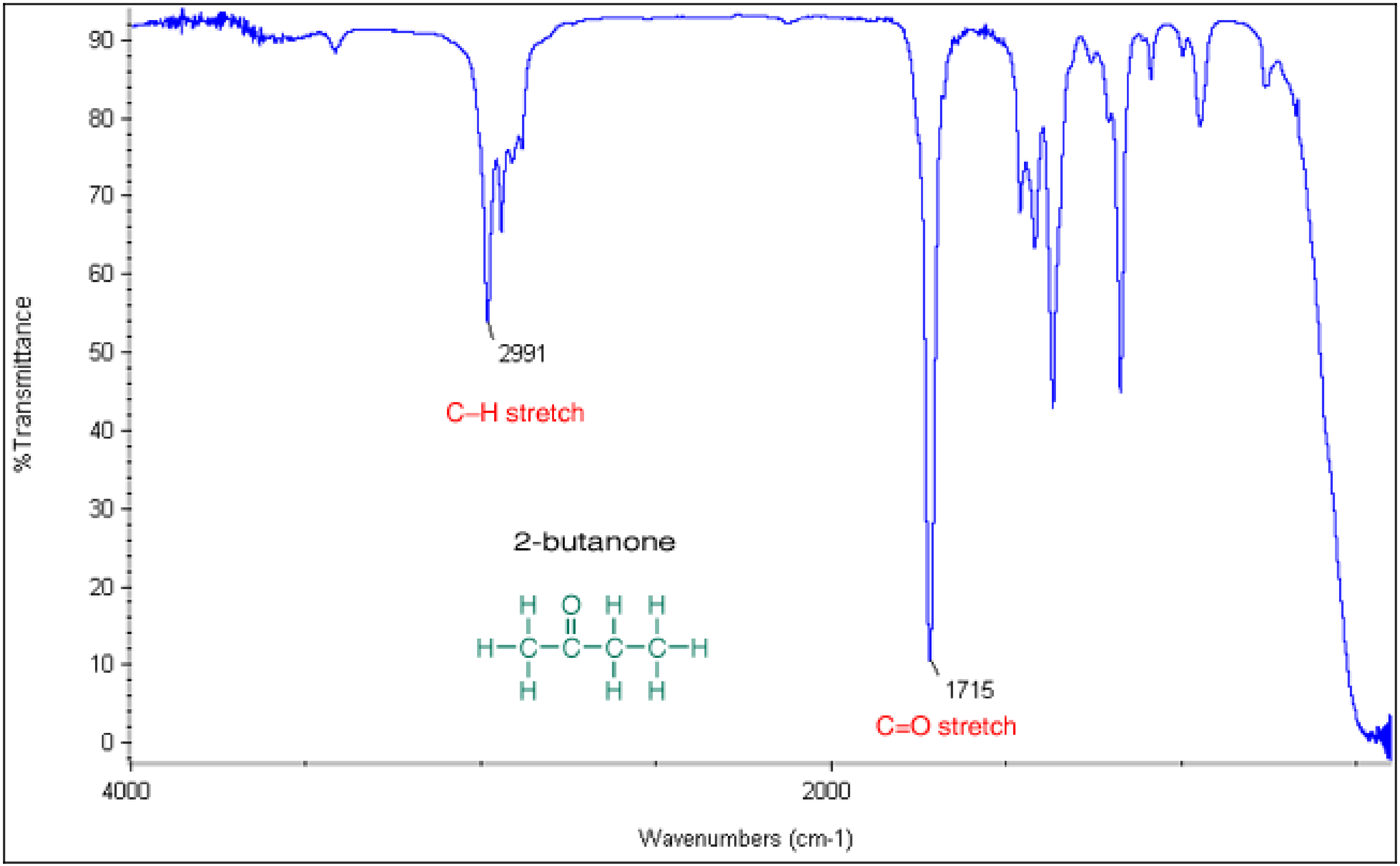
90
80
70
60
50
40
30
20
10
0
%Transmittance
4000
2000
Wavenumbers (cm-1)
3324
C≡C—H
stretch
2971
C–H
stretch
2879
2126
—C≡C—
stretch
1470
C–H
scissoring
1383
C–H
methyl rock
636
C≡C—H
bend
1-hexyne
H—C≡C—C—C—C—C—C—H



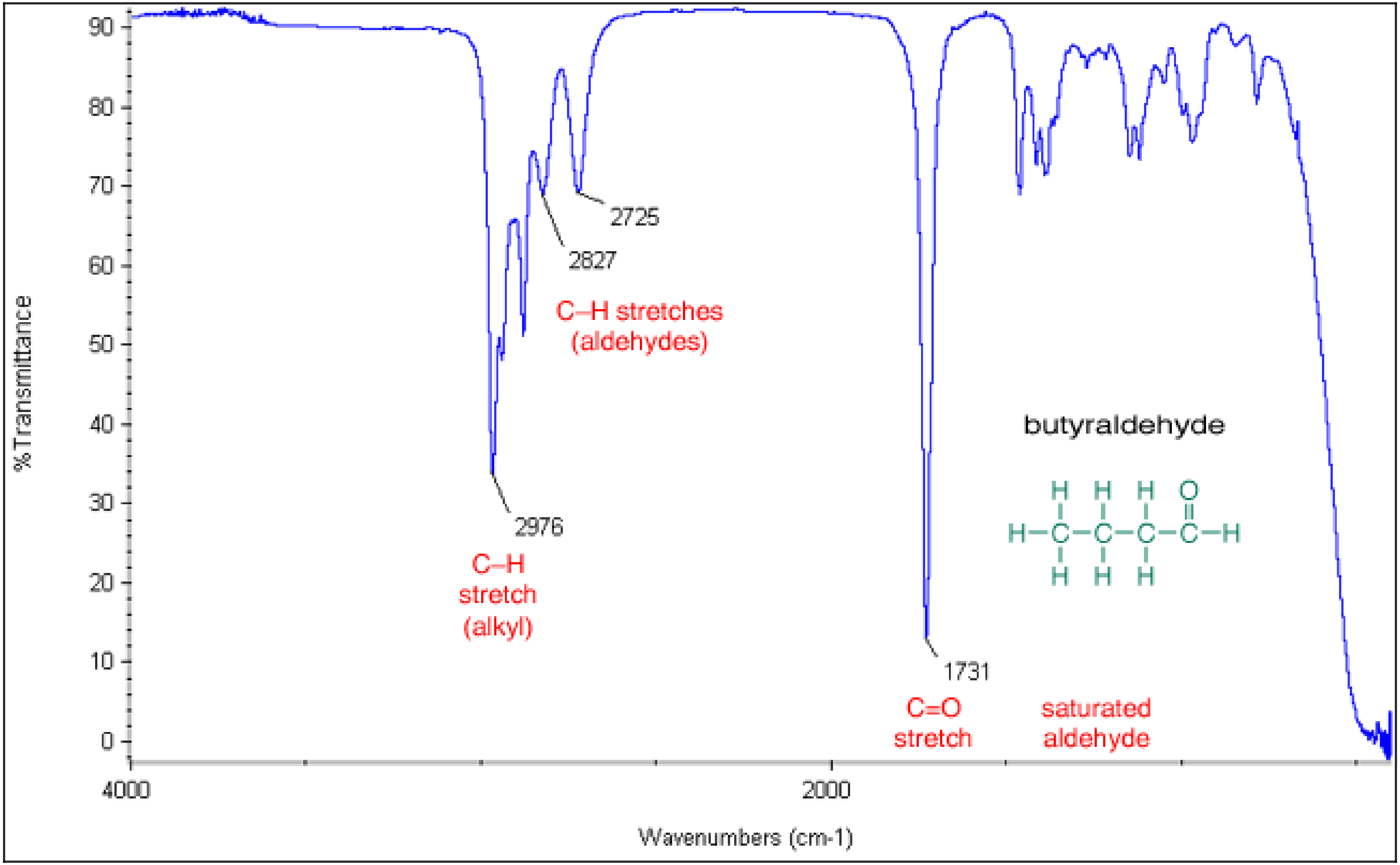
%Transmittance
90
80
70
60
50
40
30
20
10
0
2940
2976
C-H stretch
1291
1230
C-H wag
651
C-Br
stretch
1-bromopropane
Br—C—C—C—H
4000
2000
Wavenumbers (cm-1)


%Transmittance
90
80
70
60
50
40
30
20
10
0
4000
2000
Wavenumbers (cm-1)
2976
2873
C-H stretch
1271
C-H wag
743
687
C-Cl
stretches
1-chloro-2-methylpropane
H CH3
Cl-C-C-CH3
H H

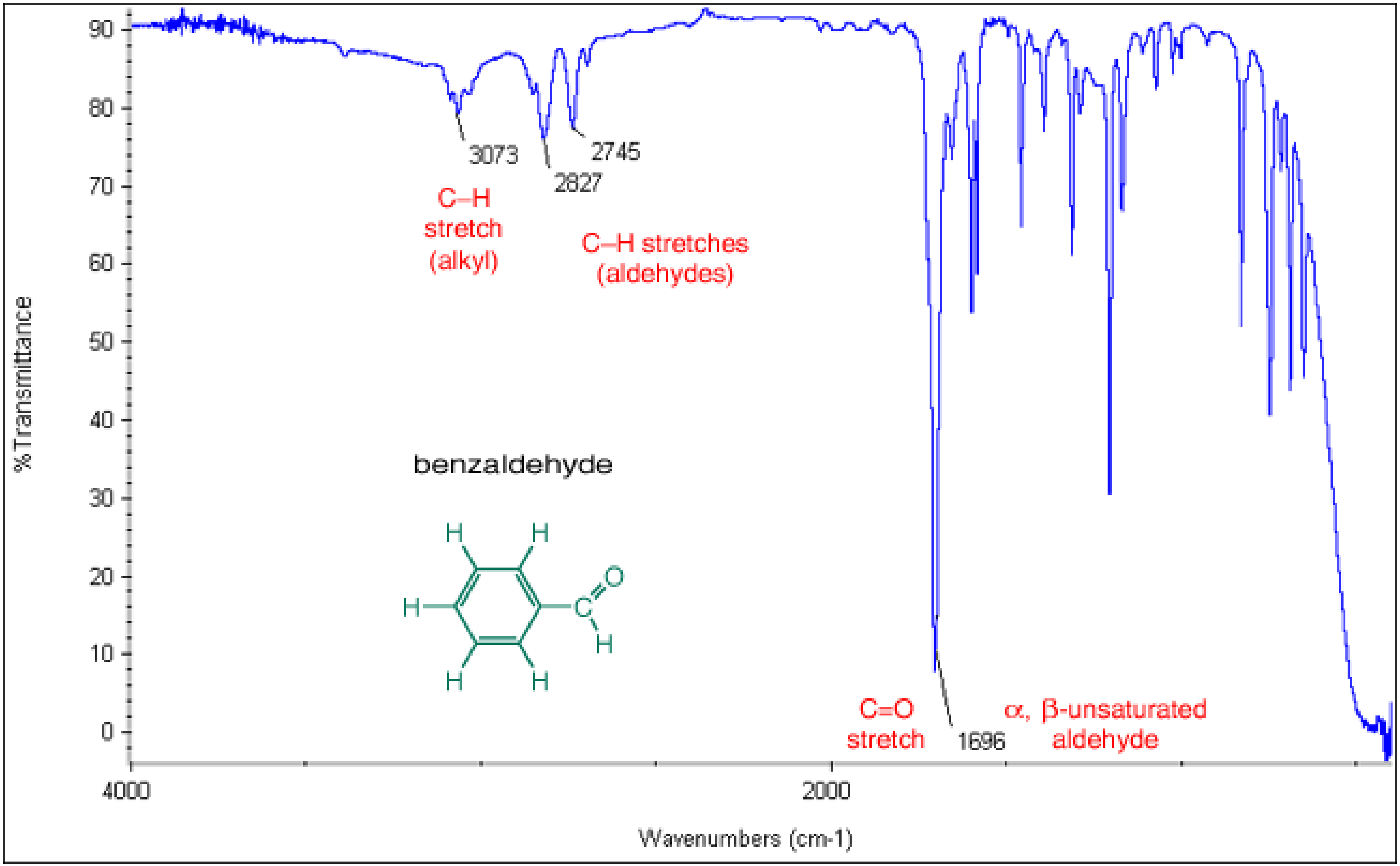

80
70
60
50
40
30
20
10
0
% Transmittance
4000
2000
Wavenumbers (cm-1)
3391
O–H
stretch
2981
C–H
stretch
ethanol
HO–C–C–H
1102
1055
C–O stretches



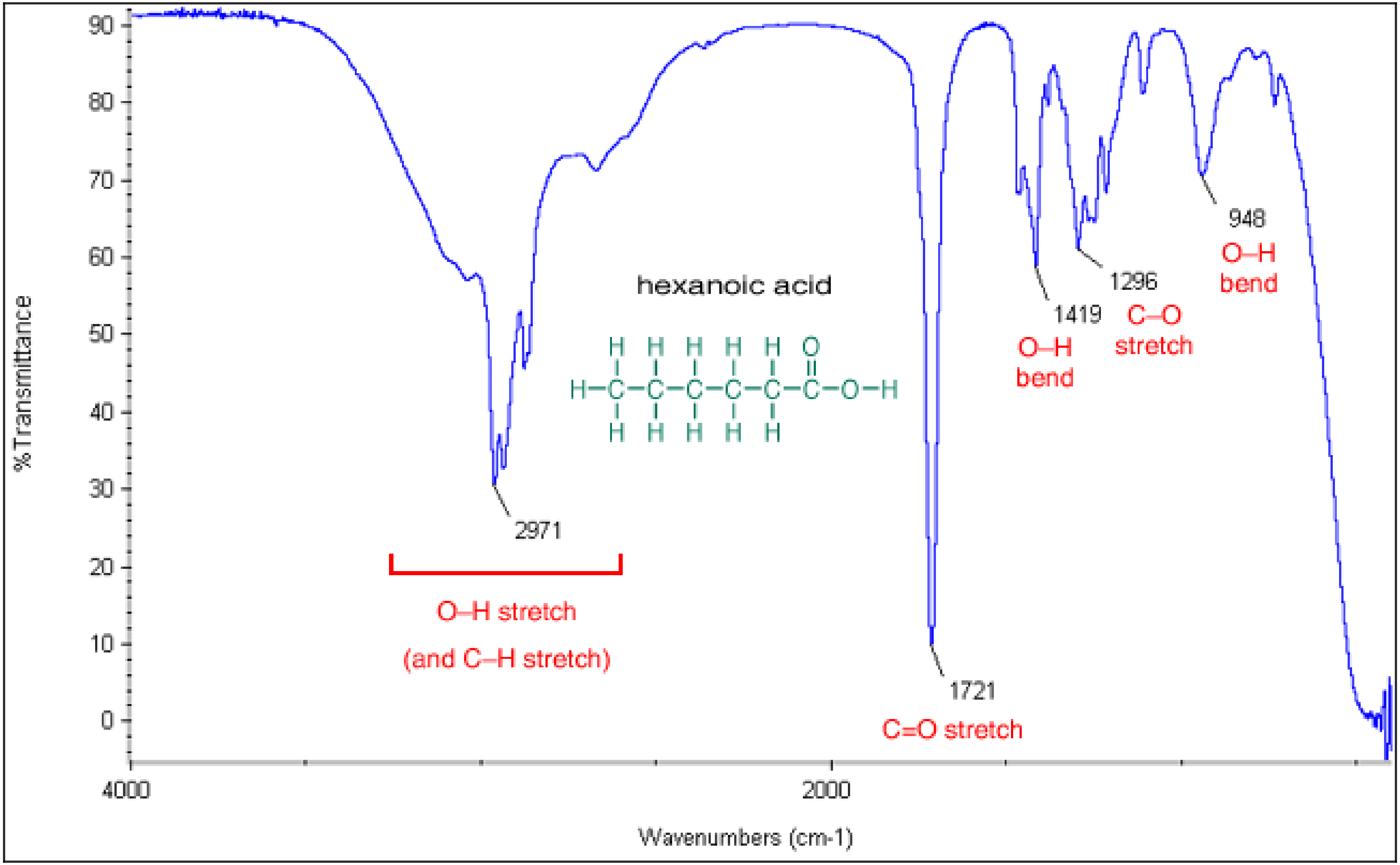
% Transmittance
90
80
70
60
50
40
30
20
10
0
4000
2000
Wavenumbers (cm-1)
2991
C–H stretch
2-butanone
1715
C=O stretch



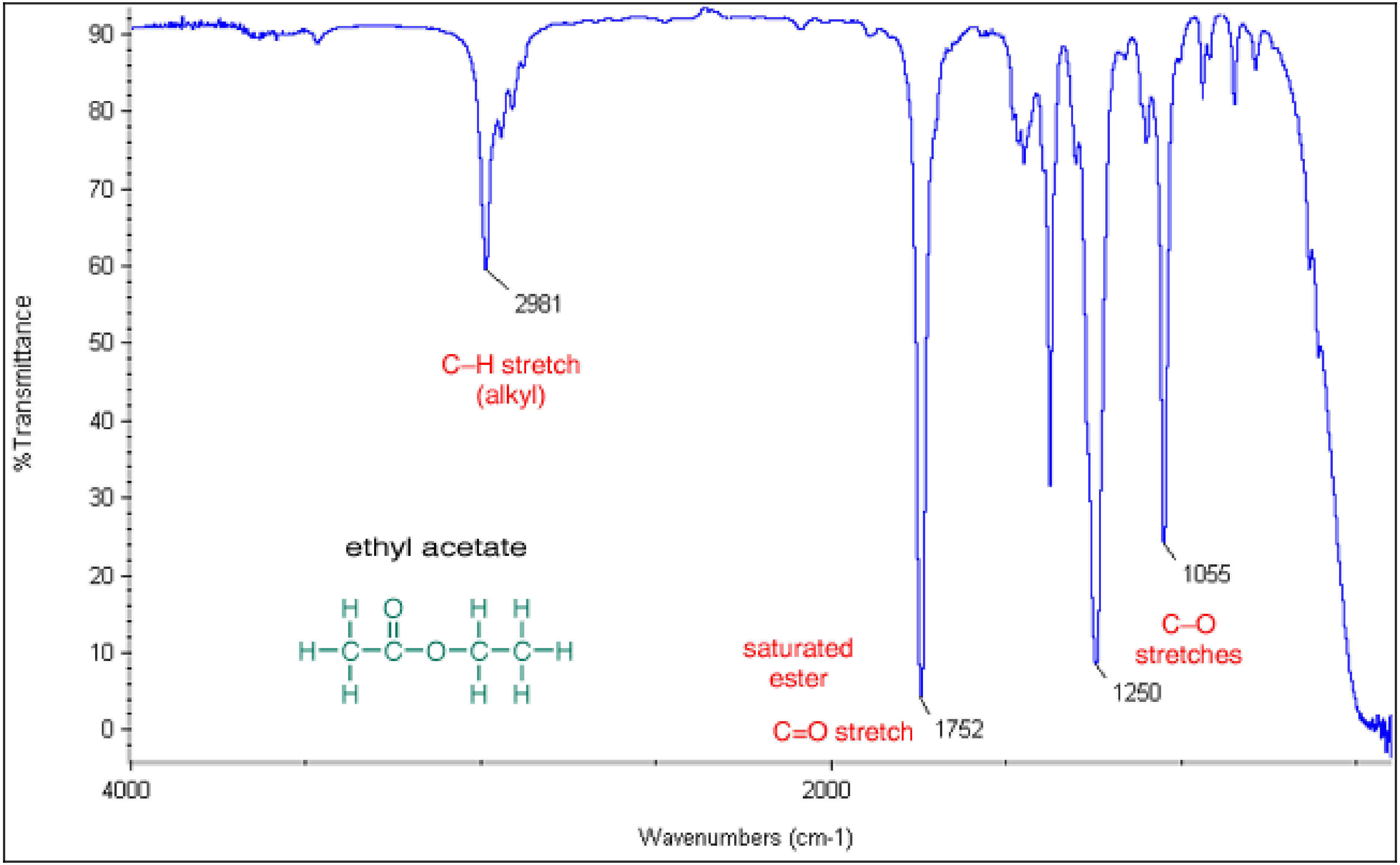
%Transmittance
90
80
70
60
50
40
30
20
10
0
4000
2000
Wavenumbers (cm-1)
2976
C–H stretch (alkyl)
2827
2725
C–H stretches (aldehydes)
1731
C=O stretch
saturated aldehyde
butyraldehyde



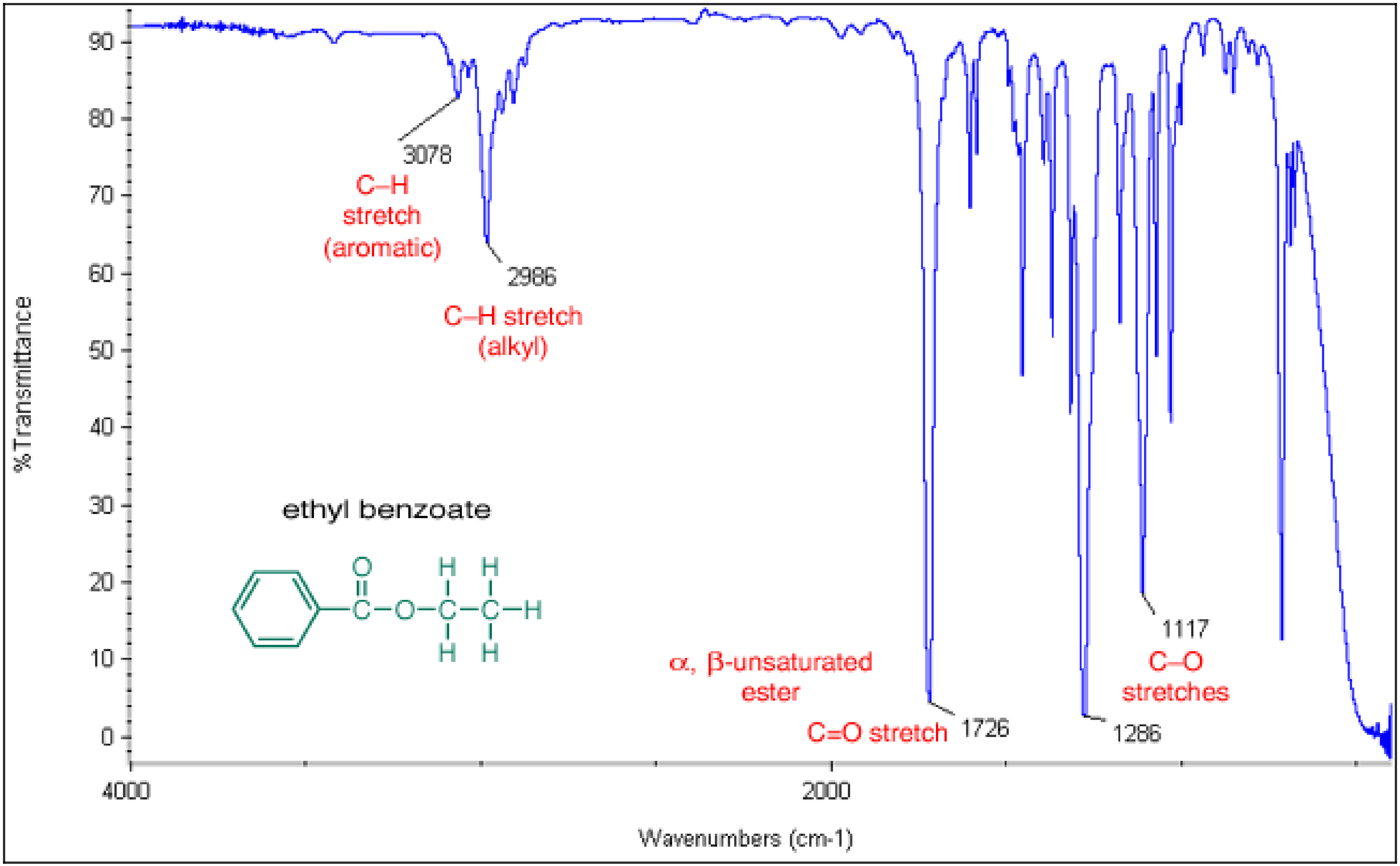
90
80
70
60
50
40
30
20
10
0
% Transmittance
3073
2827
2745
C–H
stretch
(alkyl)
C–H stretches
(aldehydes)
benzaldehyde
H
H
H
H
H
C
O
H
C=O
stretch
1696
α, β-unsaturated
aldehyde
4000
2000
Wavenumbers (cm-1)



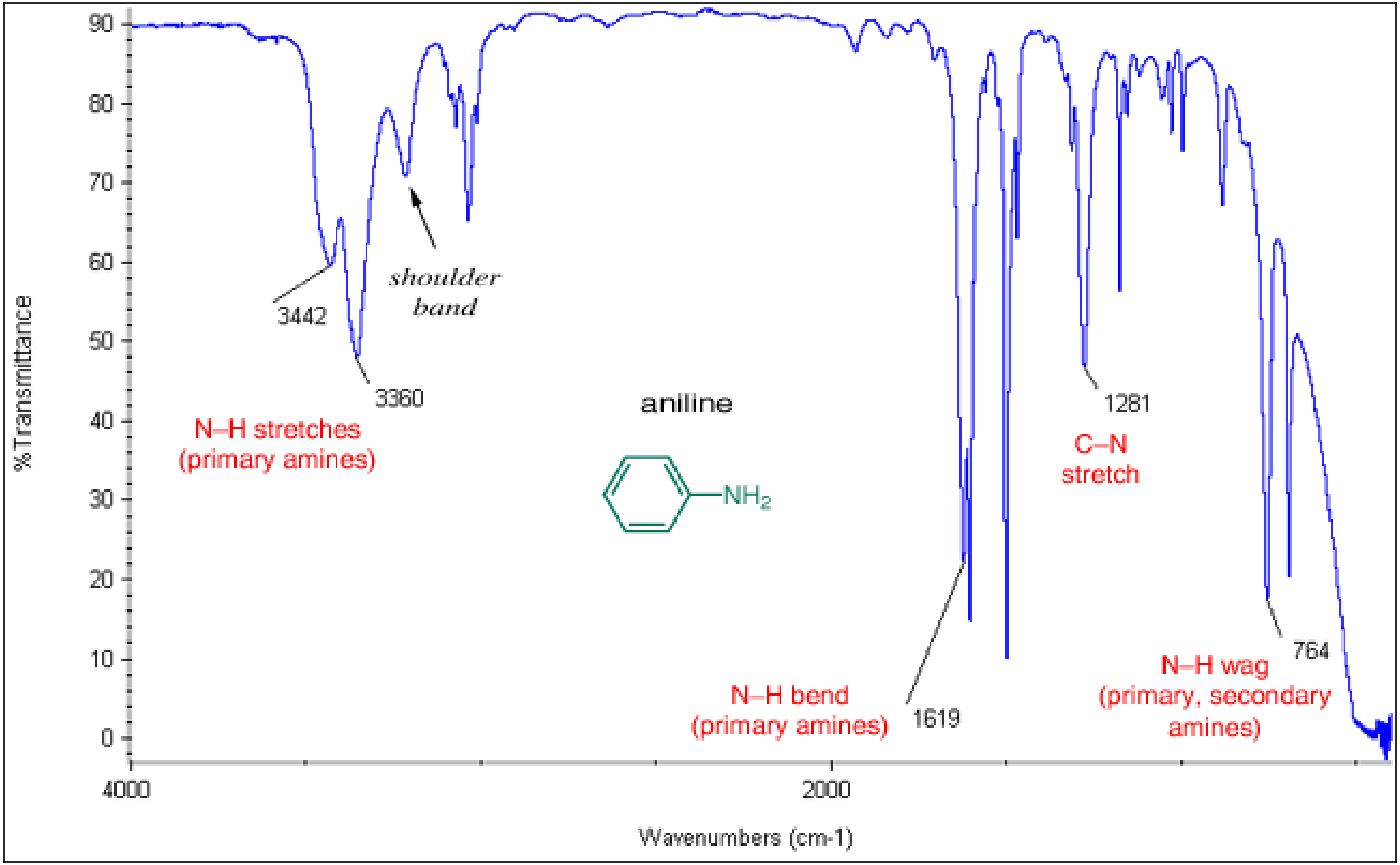
90
80
70
60
50
40
30
20
10
0
%Transmittance
4000
2000
Wavenumbers (cm-1)
hexanoic acid
2971
O–H stretch
(and C–H stretch)
1721
C=O stretch
1419
O–H
bend
1296
C–O
stretch
948
O–H
bend

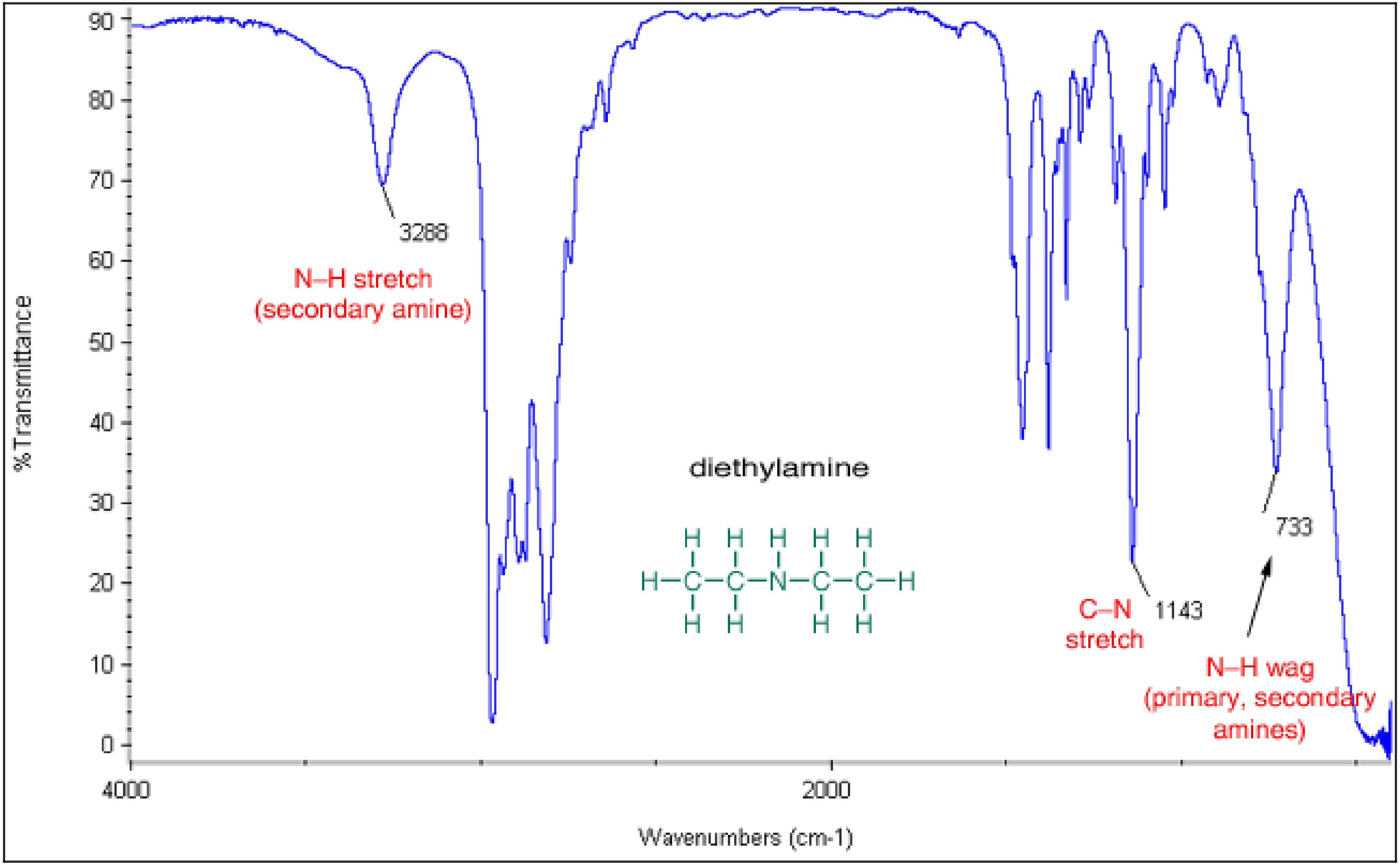


%Transmittance
90
80
70
60
50
40
30
20
10
0
2981
C–H stretch
(alkyl)
ethyl acetate
saturated
ester
C=O stretch
1752
1250
1055
C–O
stretches
4000
2000
Wavenumbers (cm-1)

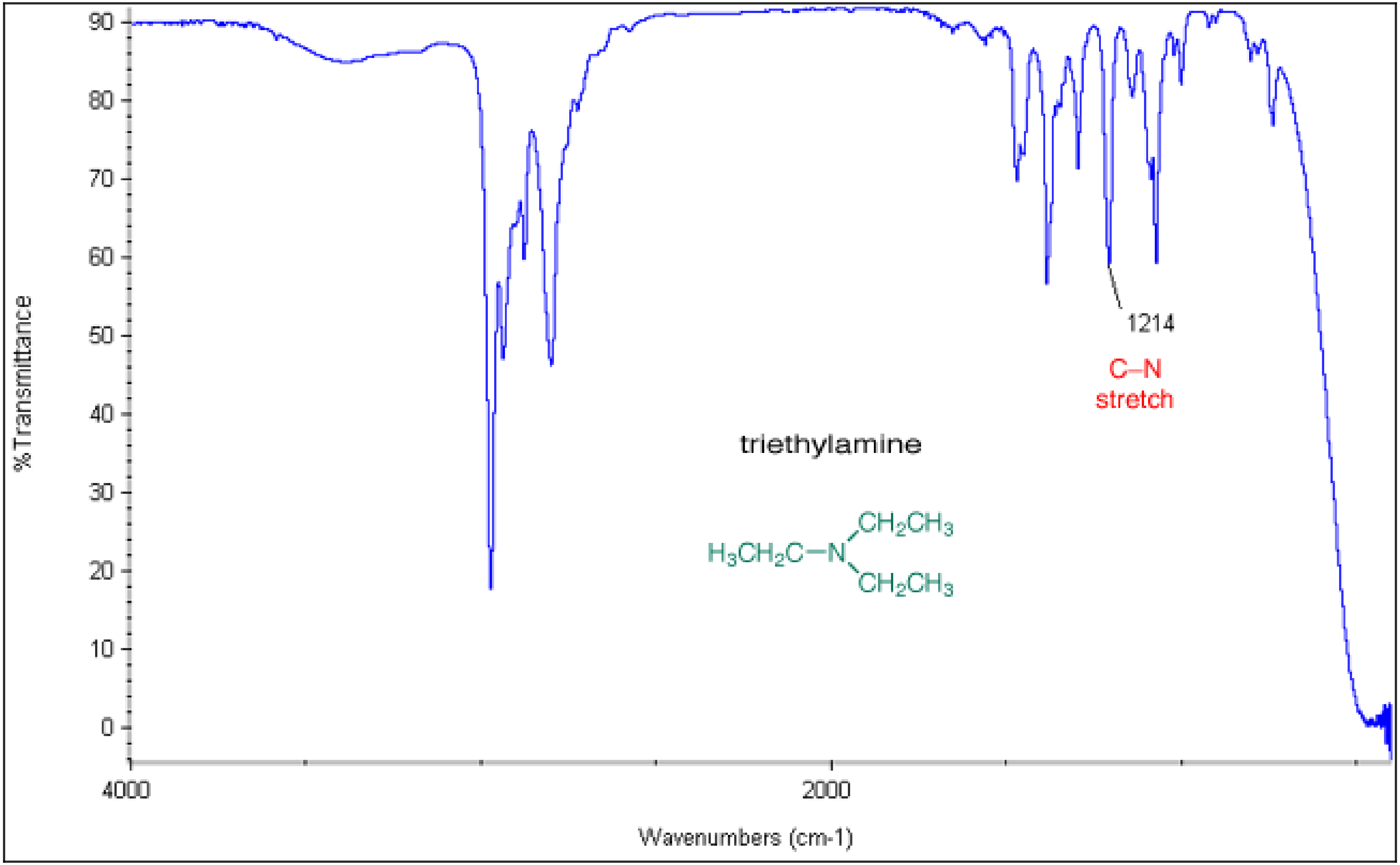


90
80
70
60
50
40
30
20
10
0
%Transmittance
3078
C–H
stretch
(aromatic)
2986
C–H stretch
(alkyl)
ethyl benzoate
O
C
O
C
C
H
α, β-unsaturated
ester
C=O stretch
1726
1286
1117
C–O
stretches
4000
2000
Wavenumbers (cm-1)

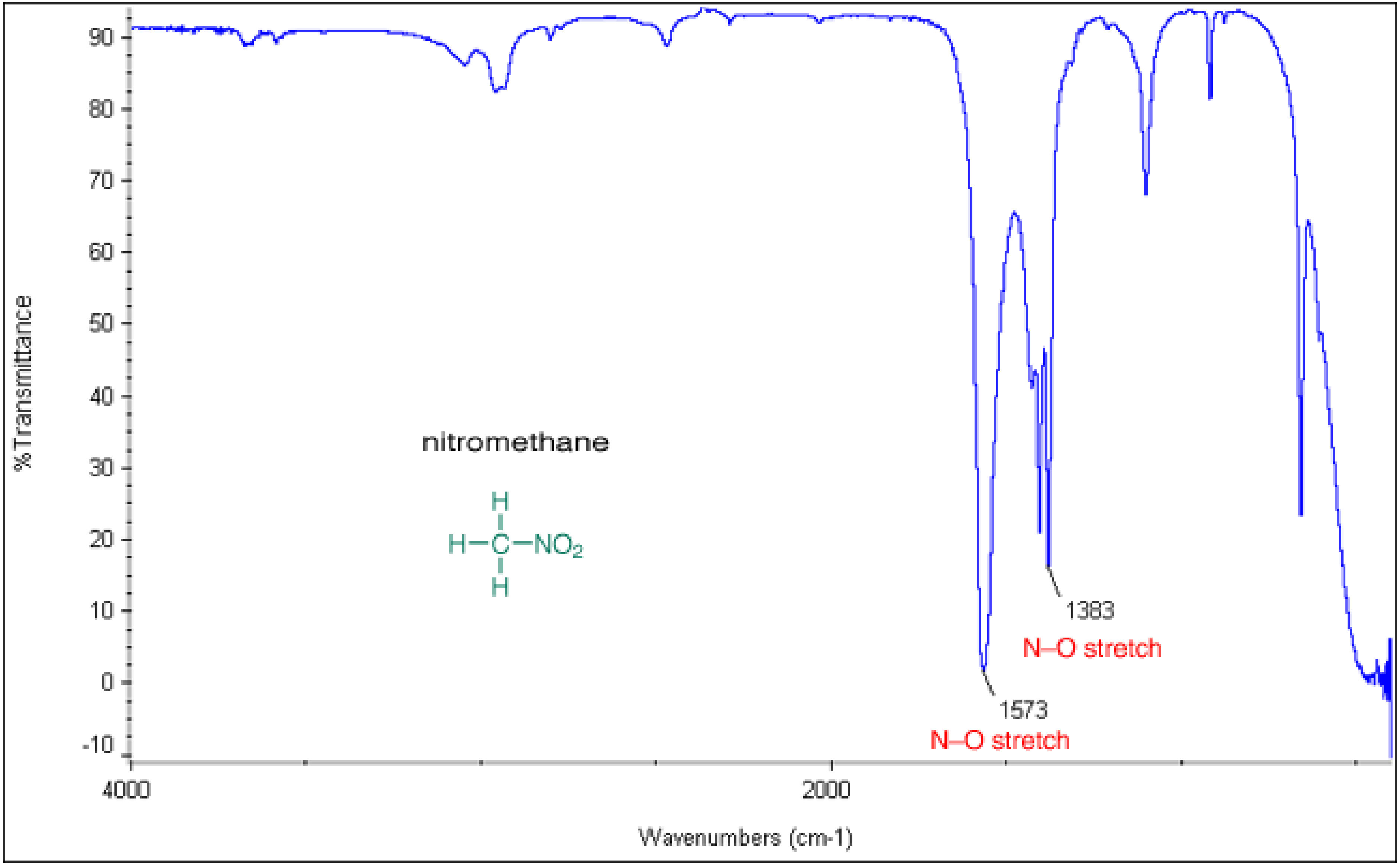

%Transmittance
90
80
70
60
50
40
30
20
10
0
4000
2000
Wavenumbers (cm-1)
3442
3360
shoulder band
N–H stretches (primary amines)
aniline
NH2
1619
N–H bend (primary amines)
1281
C–N stretch
764
N–H wag (primary, secondary amines)



%Transmittance
90
80
70
60
50
40
30
20
10
0
4000
2000
Wavenumbers (cm-1)
3288
N–H stretch
(secondary amine)
diethylamine
H H H H H
H–C–C–N–C–C–H
H H H H
C–N
stretch
1143
733
N–H wag
(primary, secondary
amines)

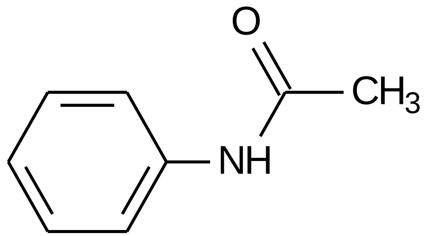


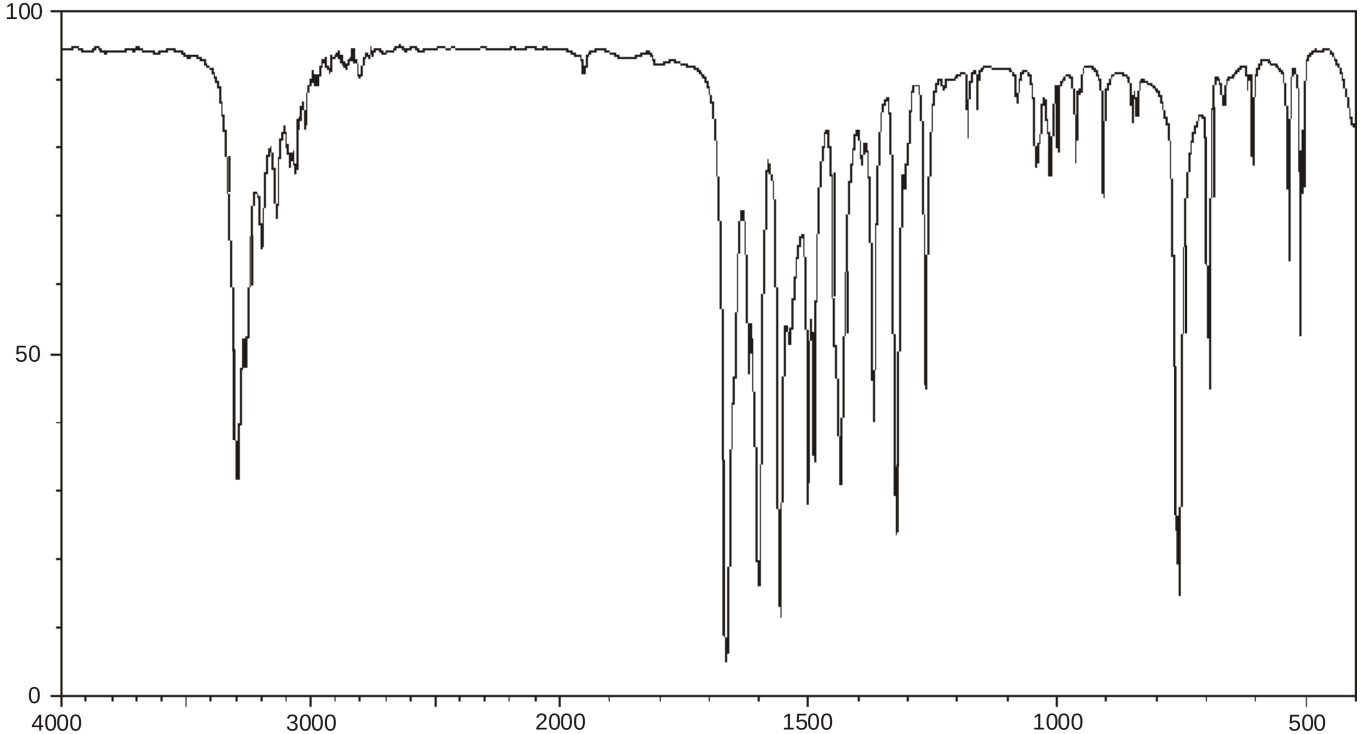
%Transmittance
90
80
70
60
50
40
30
20
10
0
4000
2000
Wavenumbers (cm-1)
1214
C–N
stretch
triethylamine
$H_3CH_2C-N(CH_2CH_3)_2$



%Transmittance
90
80
70
60
50
40
30
20
10
0
-10
4000
2000
Wavenumbers (cm-1)
nitromethane
H
H—C—NO2
H
1383
N–O stretch
1573
N–O stretch

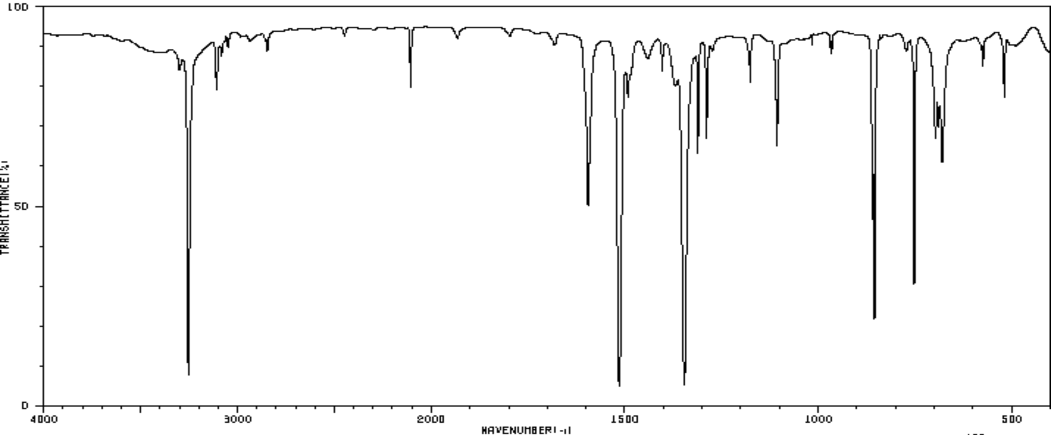
acetanilid

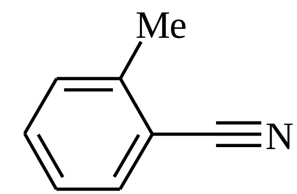


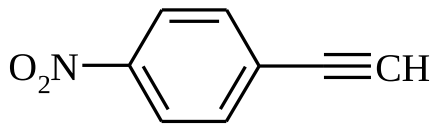


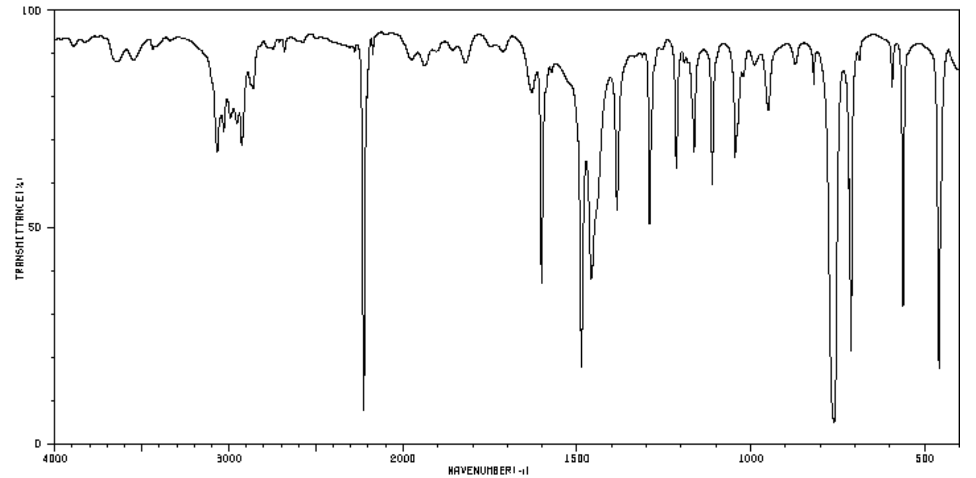
3294	30
3196	62
3137	66
3059	74
1665	4
1620	44
1599	15
1557	10
1501	28
1489	33
1436	29
1369	38
1324	22
1266	43
754	13
694	43

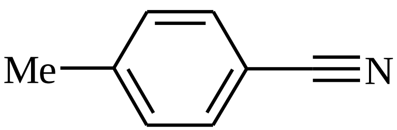
νNH 3294, νNH_{assz} 3137; Ar νCH 3059; amid-I 1665; amid-II 1557; Ar νC=C 1620;1599, 1501 és 1489; Amid-III 1324; Ar (mono-) γCH és γCC 754 és 694 cm^{-1}.

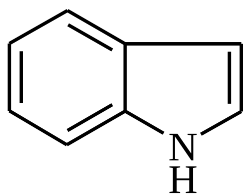


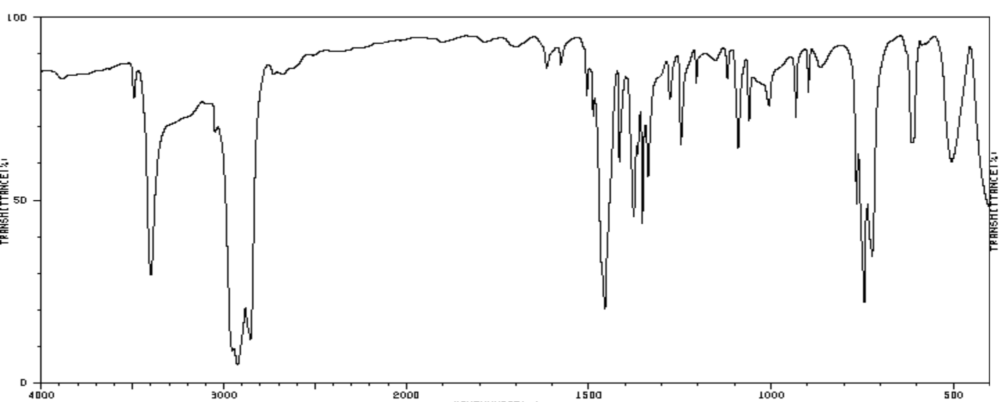

Me
N

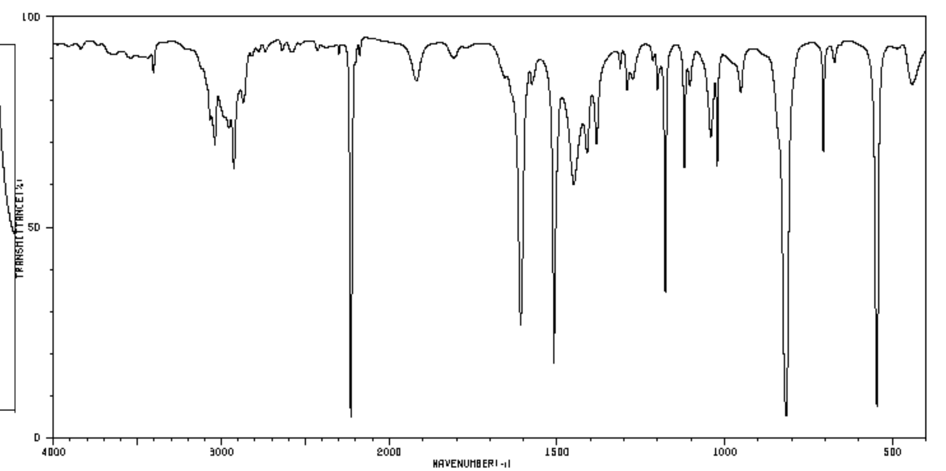

O2N
CH

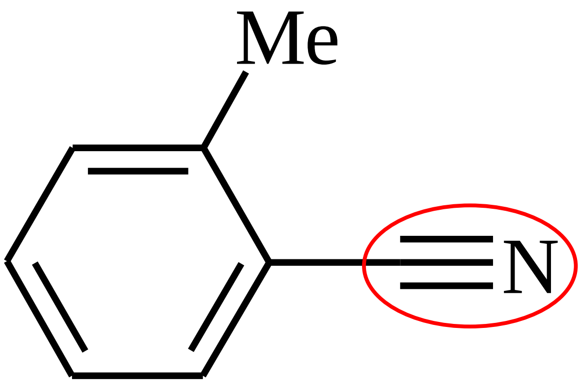



Me
N

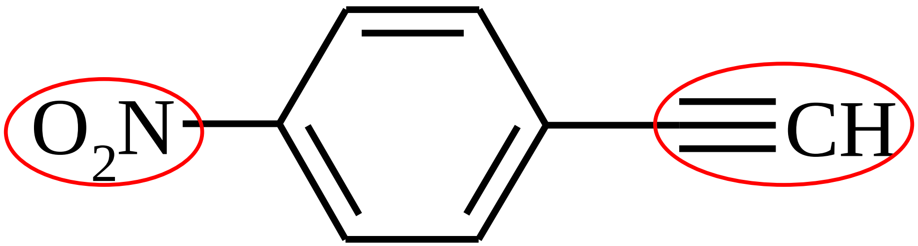

N
H



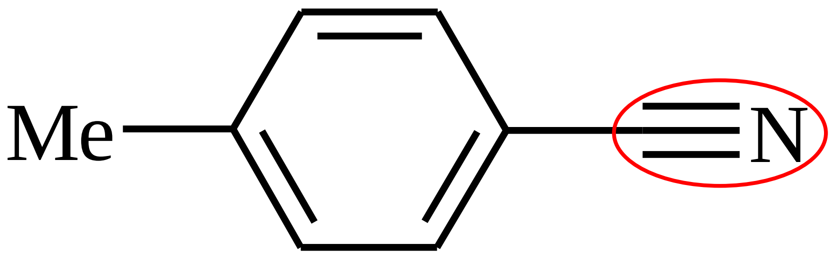




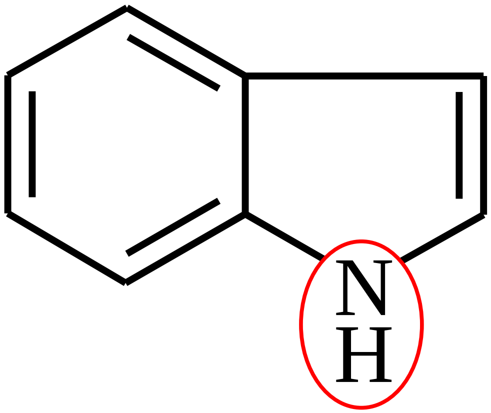
o-metil-benzonitril



(*p*-nitrofenil)-acetilén



p-metil-benzonitril



indol

Hármas kötések

–C≡C–H	νC≡C	2140 - 2100	ν≡CH 3300
–C≡C–	νC≡C	2260 - 2190	
$–CH_2–C≡N$	νC≡N	2260 - 2240	
–C=C–C≡N	νC≡N	2235 - 2215	
Ar–C≡N	νC≡N	2240 - 2220	
$–N^+≡C^–$	νC≡N	2165 - 2110	
–C≡N→O	νC≡N	2300 - 2290	
R–S–C≡N	νC≡N	2140	
Ar–S–C≡N	νC≡N	2175 - 2160	
>N–C≡N	νC≡N	2225 - 2175	
$C≡N^+$	νC≡N	2200 - 2070	
$–N^+≡N$	νN≡N	2260 ± 20	

–NO_2, –NO csoportok

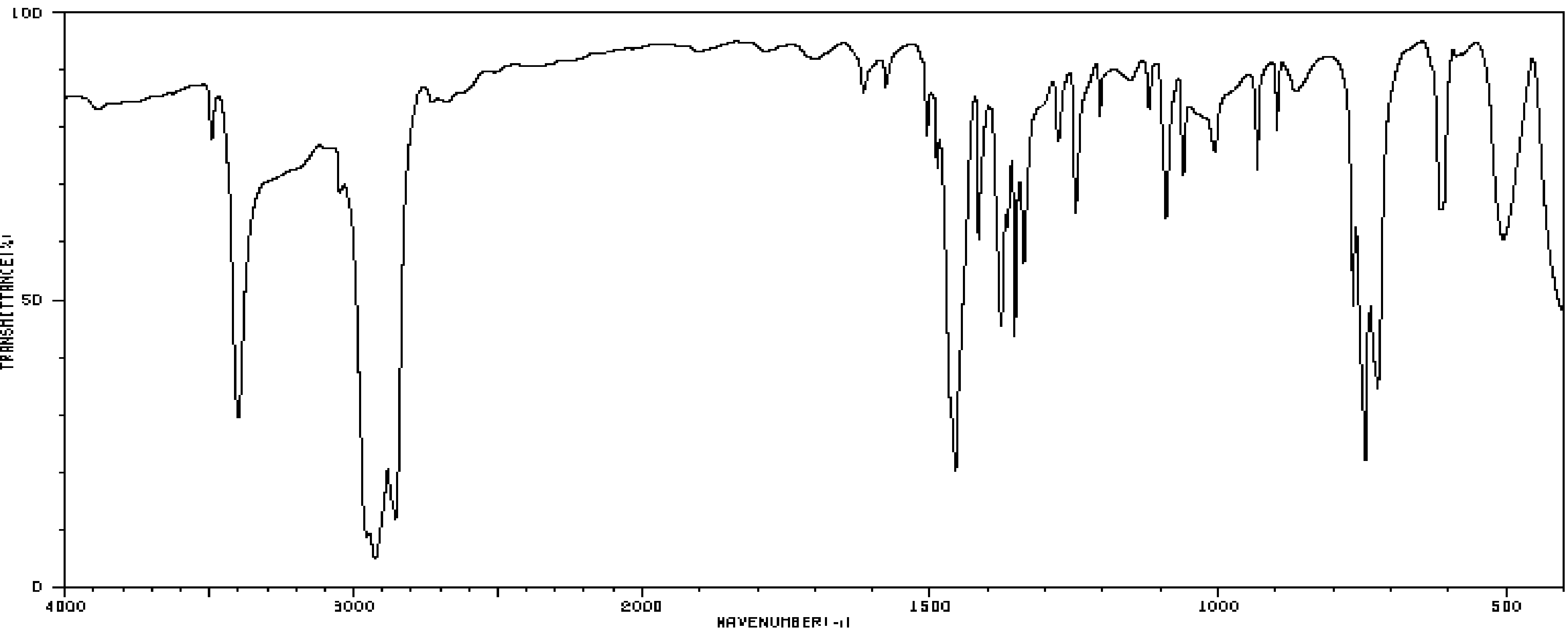
C–NO_2	$\nu_{as}NO_2$ ~1560	ν_sNO_2 ~1350
O–NO_2	$\nu_{as}NO_2$ ~1630	ν_sNO_2 ~1280
N–NO_2	$\nu_{as}NO_2$ ~1600	ν_sNO_2 ~1270
C–N=O	νN=O 1600 - 1500	
O–N=O_{transz}	νN=O 1680 - 1650	
O–N=O_{cisz}	νN=O 1625 - 1610	
N–N=O	νN=O 1460 - 1430	
R–$N^+ \rightarrow O^-$	νN–O 970 - 950	
Ar–$N^+ \rightarrow O^-$	νN–O 1300 - 1200	
NO_2^-	νNO_2^- 1250 - 1230	
NO_3^-	νNO_3^- 1410 - 1340	

Aromások

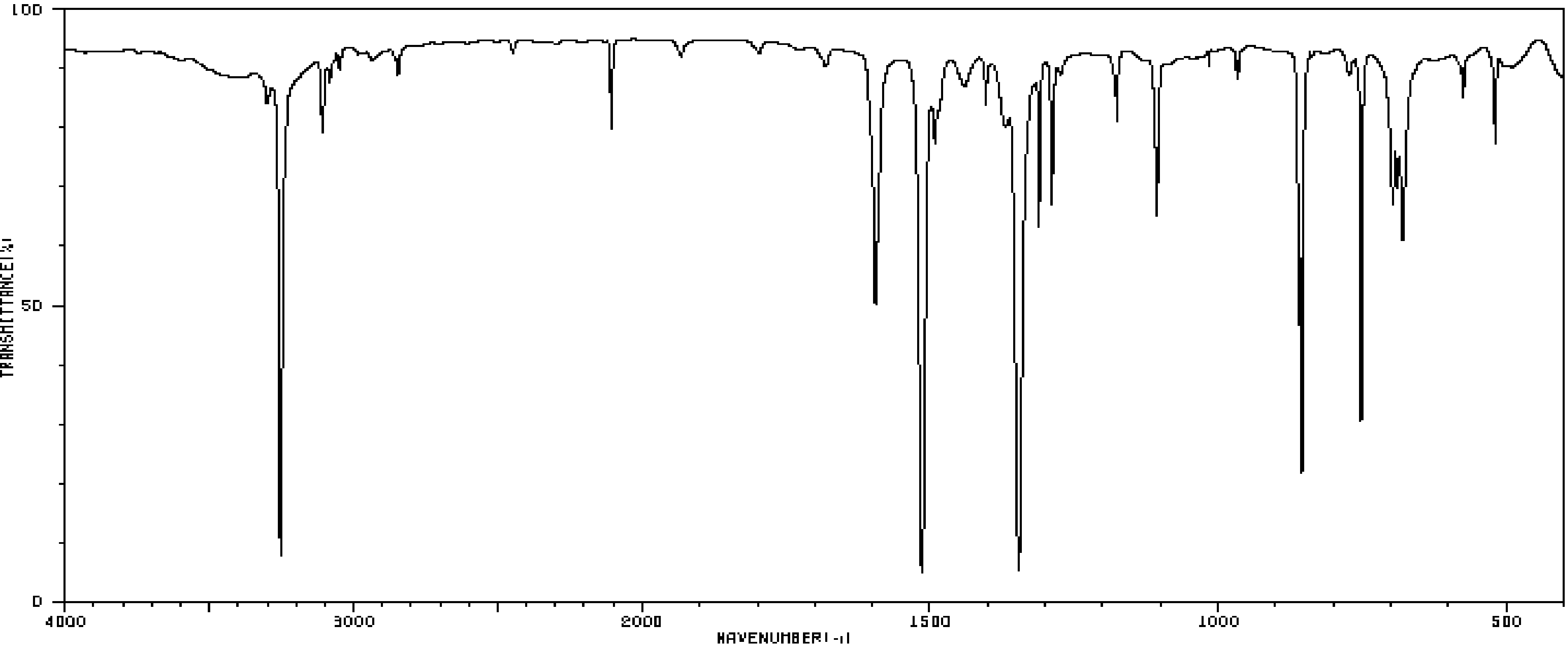
νCH		3030
νC=C vázrezgés		1600; 1500
konjugált		1580; 1450
β=CH		1225-950 több jel
γCH és γC–C		
monoszubsztituált		690-710; 730-770
diszubsztituált		
orto		735-770
meta		690-710; 750-810
para		810-840
triszubsztituált		
1,2,3		705-745; 760-780
1,2,4		805-825; 870-885
1,3,5		675-730; 810-865
pentaszubsztituált		870

–OH, –NH, –SH, –PH csoportok

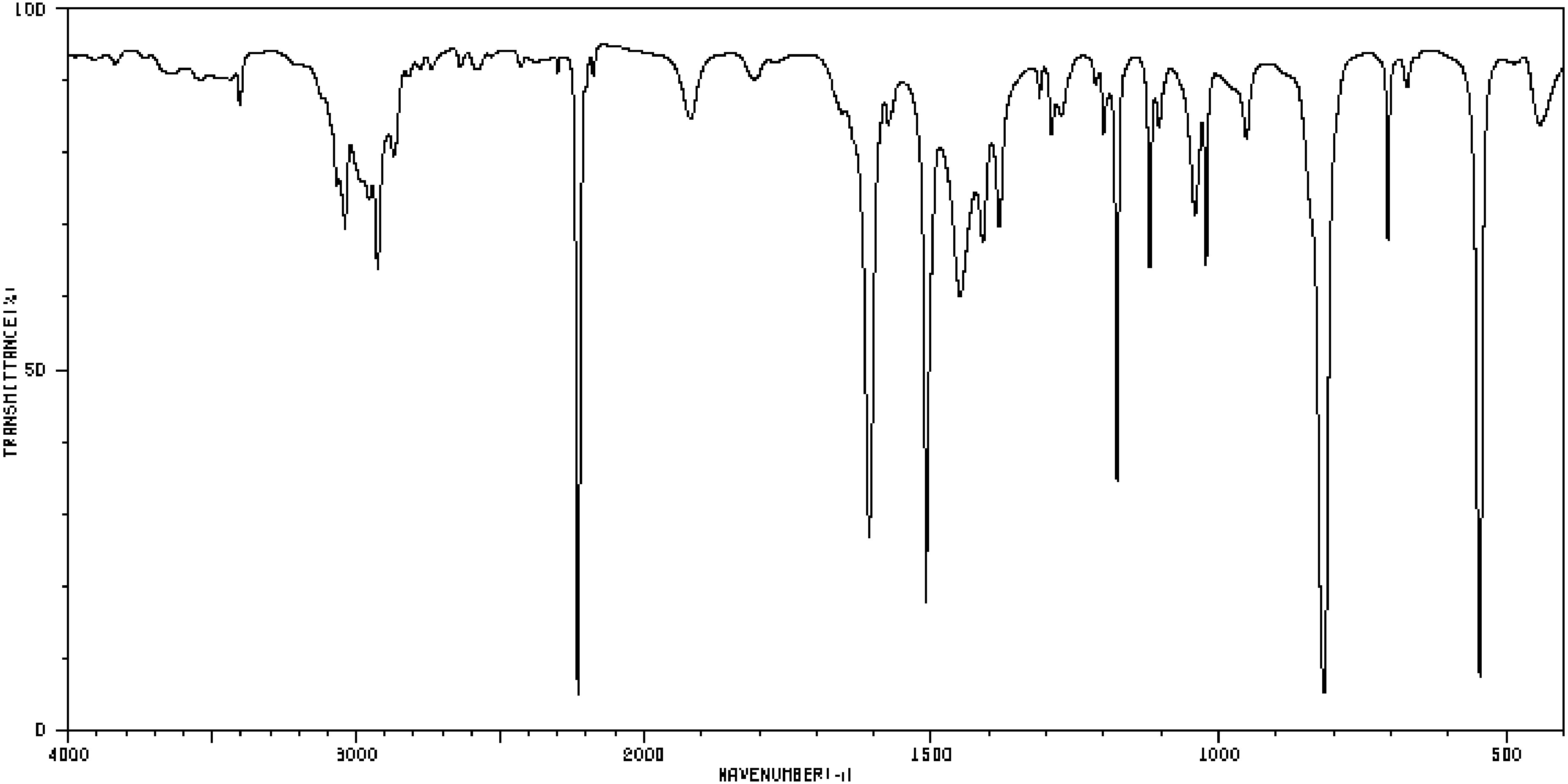
–OH	νOH	3650 - 3200	νC–O, νC–N
	monomer		
	primer	3640	~1050
	szek.	3630	~1100
	terc.	3620	~1150
	fenolos	3610	~1200
	asszociált	3600 - 3200	
	COOH, kelát	3200 - 2500	
$–NH_2$	$\nu_{as}NH_2$	~3500	βNH_2 ~1600
	$\nu_s NH_2$	~3400	
–NH	νNH	3350 - 3300	~1550
=NH	ν=NH	3350 - 3300	
$–N^+H_3$	νNH_3	~3000	~1500
$–N^+H_2$	νNH_2	2700 -2250	~1500
$–N^+H$	νNH	2700 -2250	~1500
–SH	νSH	2600 - 2550	
>PH	νPH	2440 - 2350	



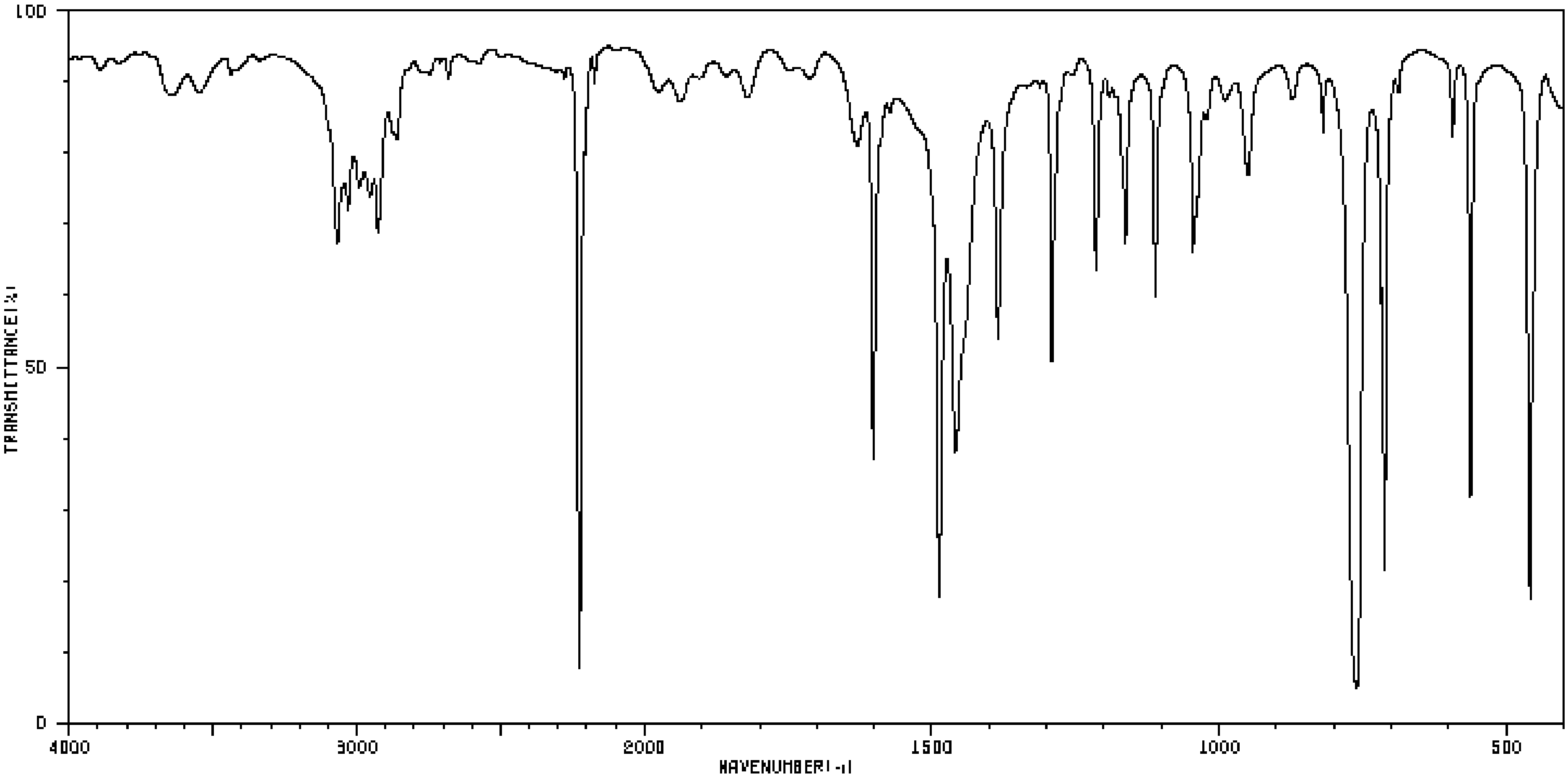
3886	79	1616	84	1366	60	1091	62	870	84
3403	74	1577	84	1353	42	1061	68	765	47
3400	26	1505	74	1338	53	1021	79	745	21
3060	86	1488	70	1278	74	1011	74	738	43
2954	8	1456	19	1248	62	1005	72	723	33
2924	4	1418	58	1206	79	932	70	612	62
2866	11	1377	49	1120	79	898	77	606	68



3301	81	1596	49	1311	60	866	21	620	74
3253	7	1514	4	1289	64	772	86		
3106	77	1492	74	1274	86	752	29		
3084	84	1441	84	1176	77	697	64		
3049	86	1404	81	1107	62	690	66		
2846	86	1359	77	965	84	680	58		
2107	77	1347	6	860	44	676	81		

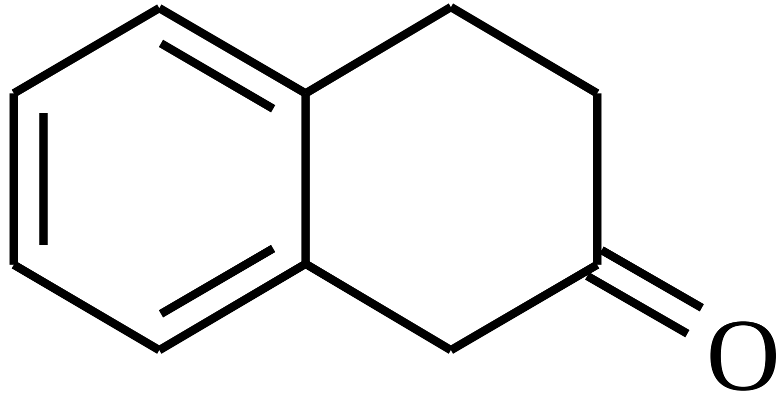


3404	84	2201	86	1411	64	1190	84	817	6
3068	72	1919	81	1383	68	1178	33	706	66
3039	86	1609	26	1312	84	1120	62	673	66
2966	70	1676	81	1291	79	1104	79	646	7
2926	62	1568	81	1274	81	1041	68	441	81
2869	77	1509	17	1215	86	1022	62		
2229	4	1460	68	1201	79	962	78		

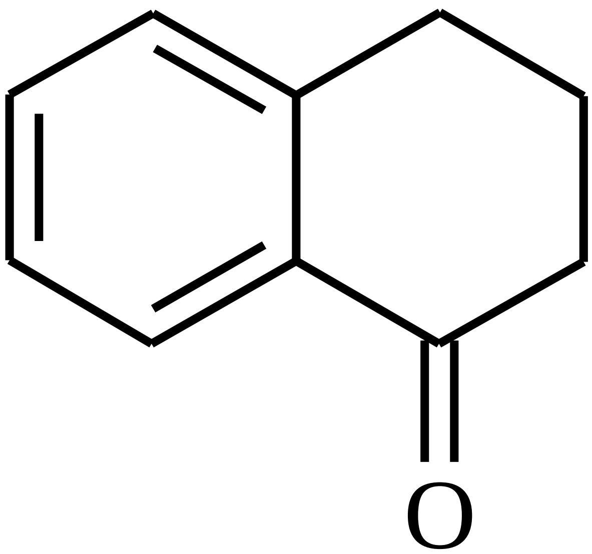


3644	84	2860	79	1602	36	1214	60	761	4
3547	84	2226	7	1591	79	1163	64	719	57
3067	84	2206	77	1574	81	1111	57	712	20
3030	70	1976	84	1487	17	1046	64	688	84
2991	72	1938	84	1460	36	990	84	594	79
2954	70	1820	84	1385	52	950	74	563	30
2926	66	1630	78	1291	49	819	78	469	16

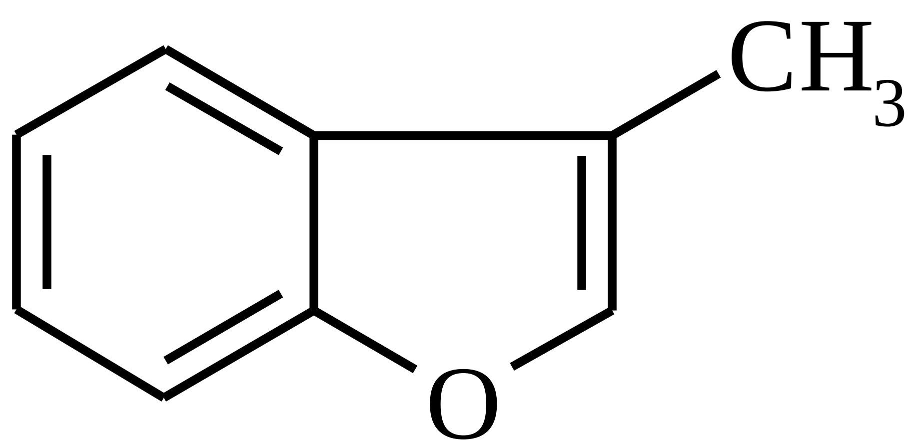
Homework



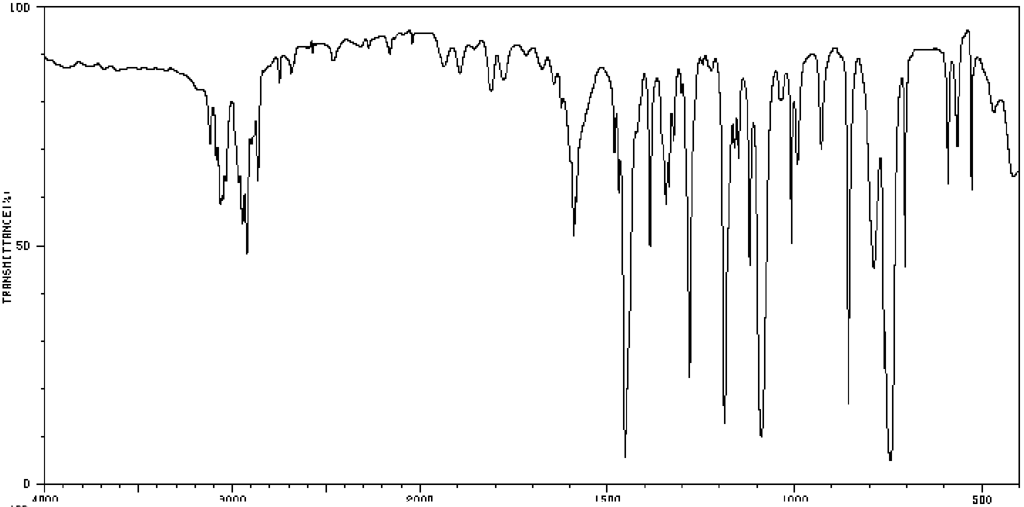
2-tetralone

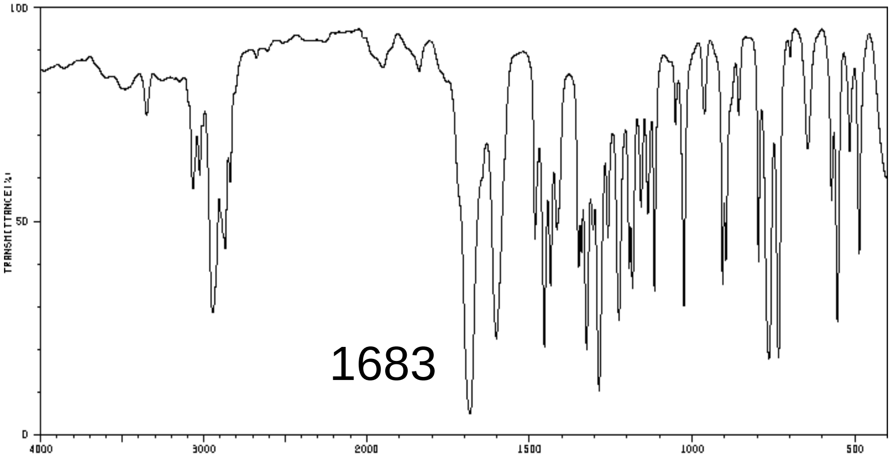


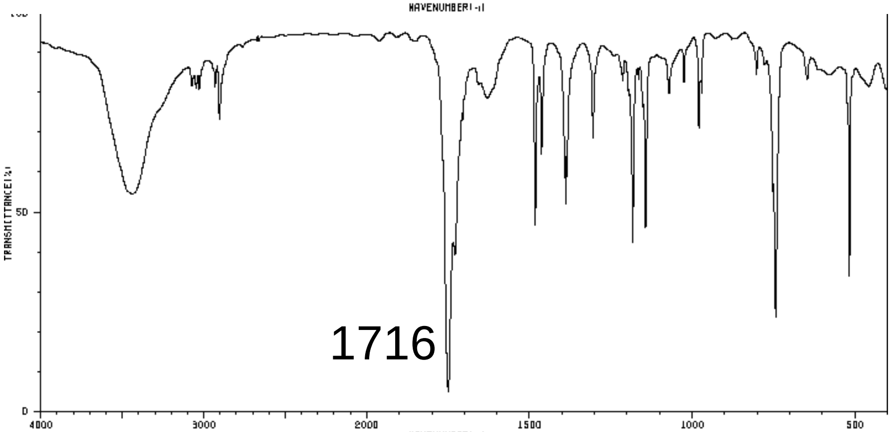
1-tetralone



3-methyl-benzofurane


TRANSMITTANCE(%)
100
50
0
4000
3000
2000
1500
1000
500


TRANSMITTANCE(%)
100
50
0
1683
4000
3000
2000
1500
1000
500
WAVENUMBER(-1)


TRANSMITTANCE(%)
50
0
1716
4000
3000
2000
1500
1000
500
WAVENUMBER(-1)