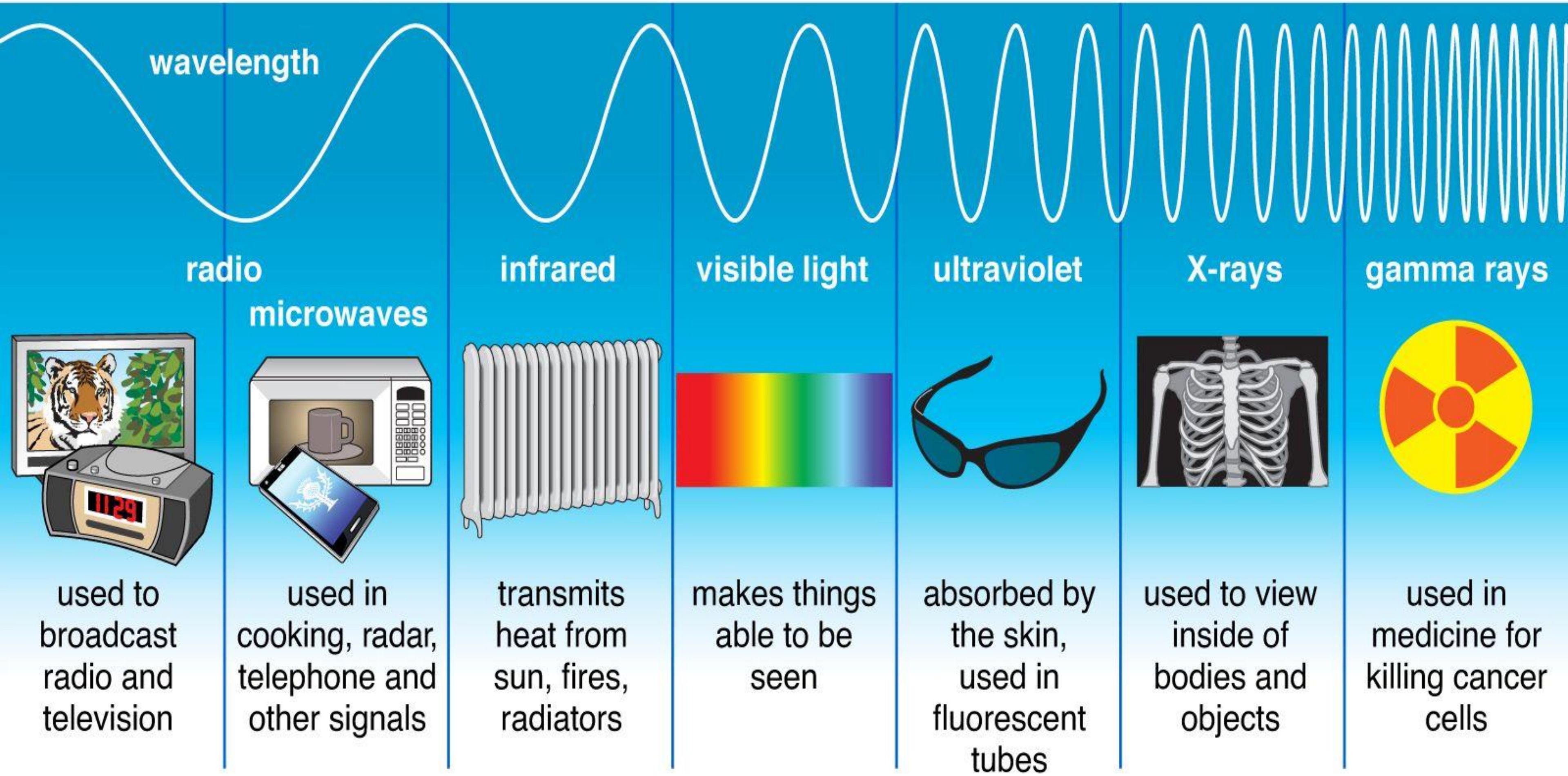
Λ. Χατζηαράπογλου

Φάσματα Υπερύθρου

Types of Electromagnetic Radiation



wavelength

radio

used to broadcast radio and television

microwaves

used in cooking, radar, telephone and other signals

infrared

transmits heat from sun, fires, radiators

visible light

makes things able to be seen

ultraviolet

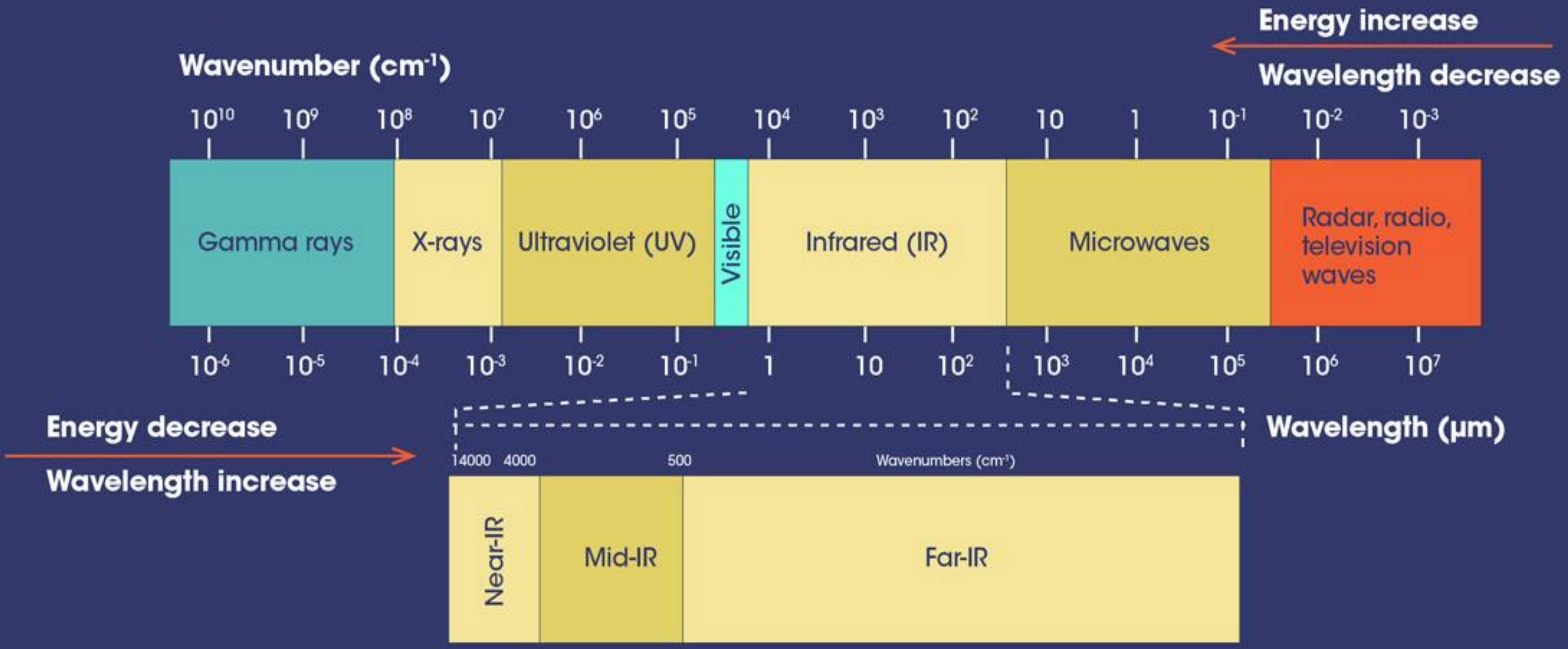
absorbed by the skin, used in fluorescent tubes

X-rays

used to view inside of bodies and objects

gamma rays

used in medicine for killing cancer cells



Energy increase

Wavelength decrease

Wavenumber (cm^{-1})	10^{10}	10^{9}	10^{8}	10^{7}	10^{6}	10^{5}	10^{4}	10^{3}	10^{2}	10	1	10^{-1}	10^{-2}	10^{-3}
Wavelength (µm)	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	1	10	10^{2}	10^{3}	10^{4}	10^{5}	10^{6}	10^{7}

Gamma rays

X-rays

Ultraviolet (UV)

Visible

Infrared (IR)

Microwaves

Radar, radio, television waves

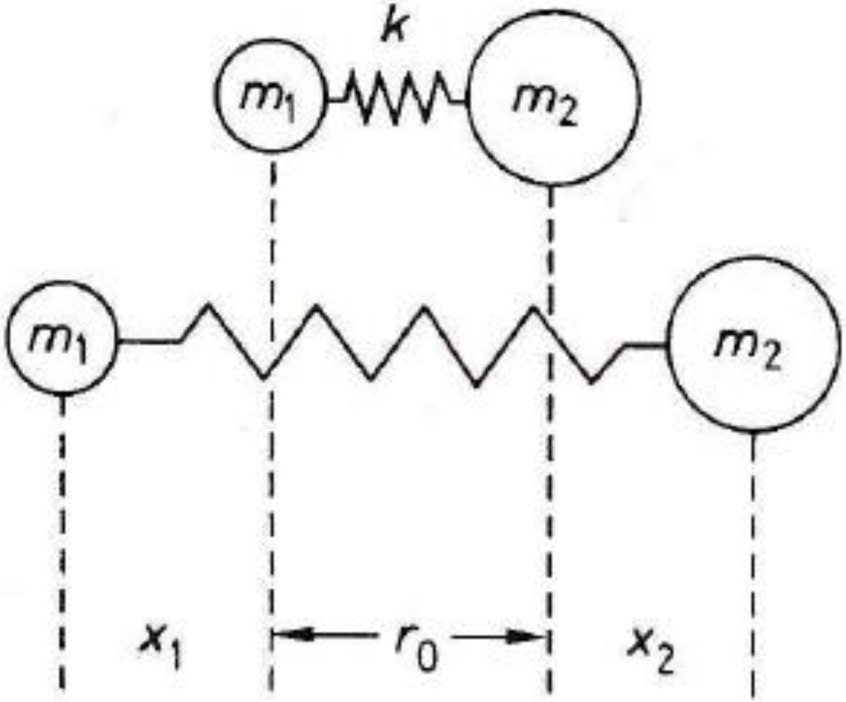
Energy decrease

Wavelength increase

Near-IR

Mid-IR

Far-IR


k
m_1
m_2
m_1
m_2
x_1
r_0
x_2

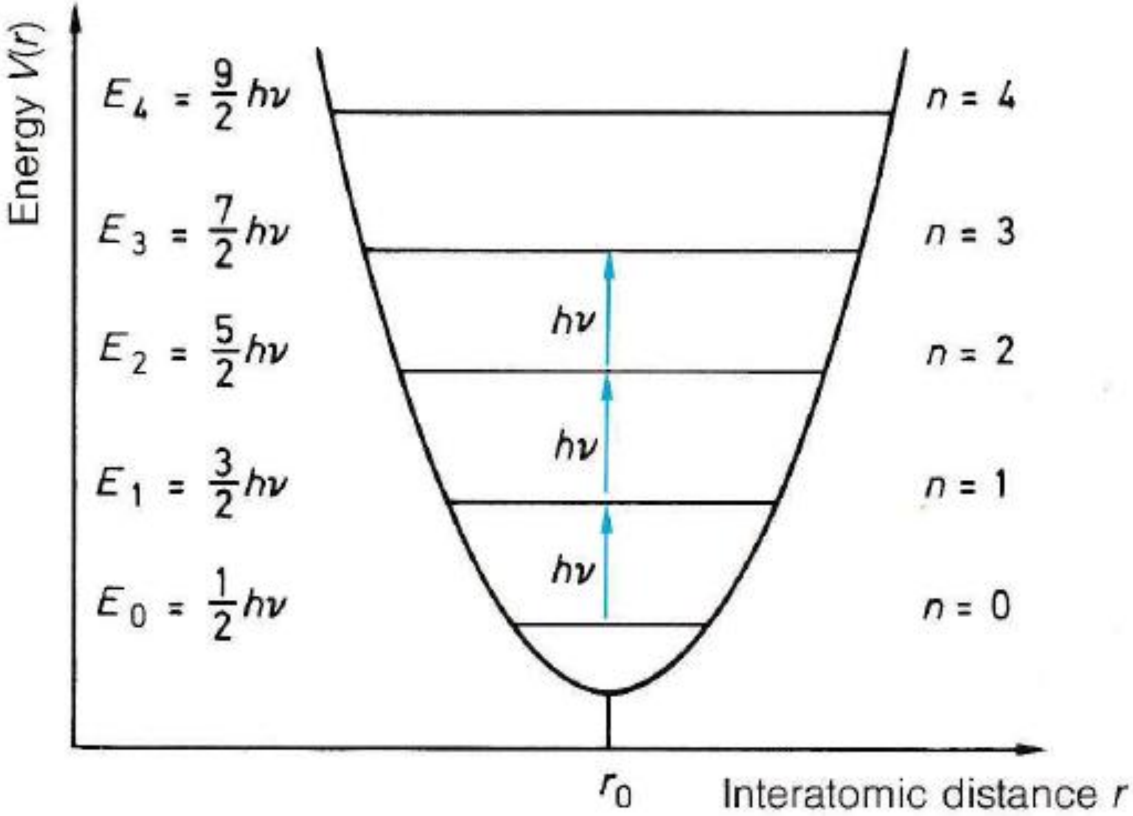
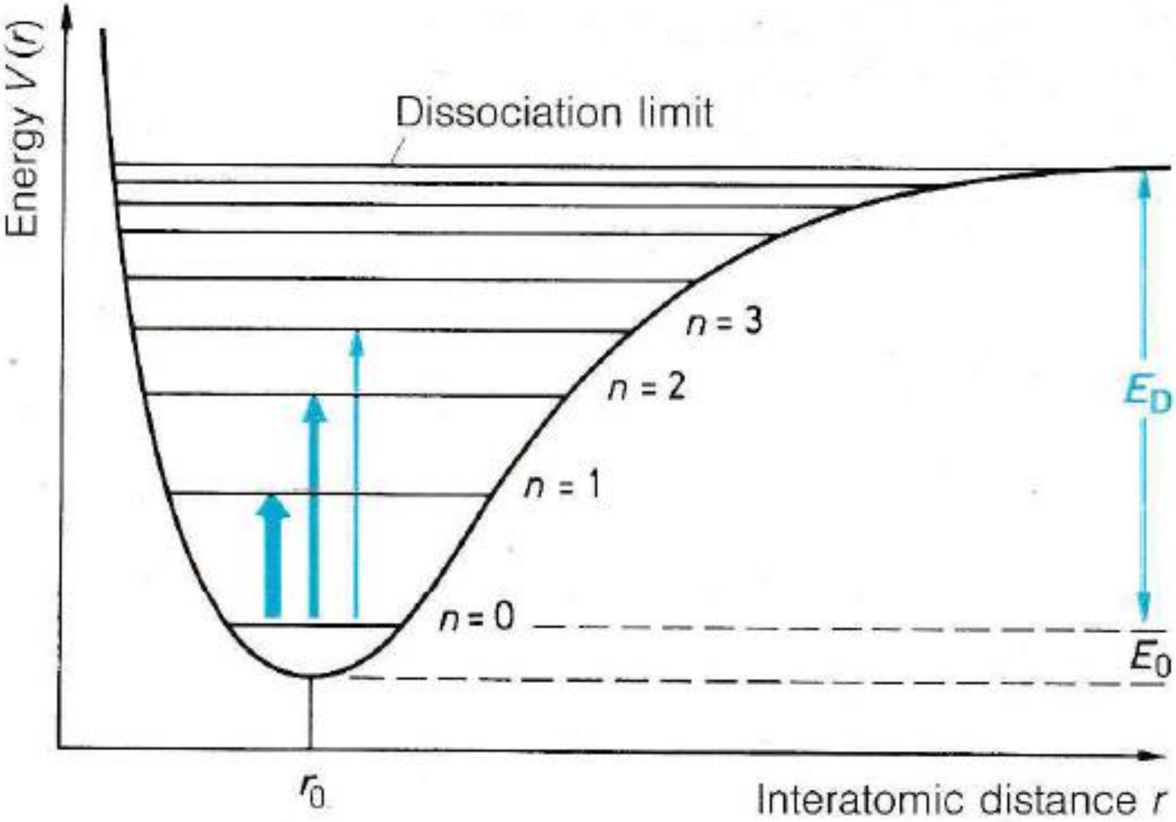
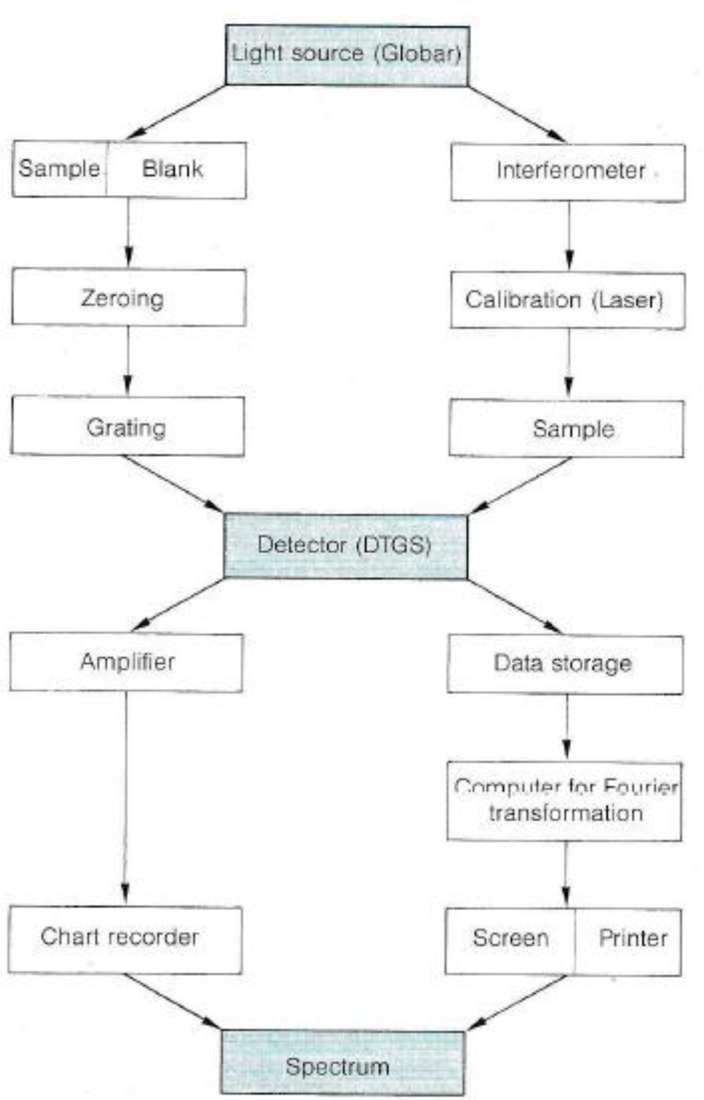
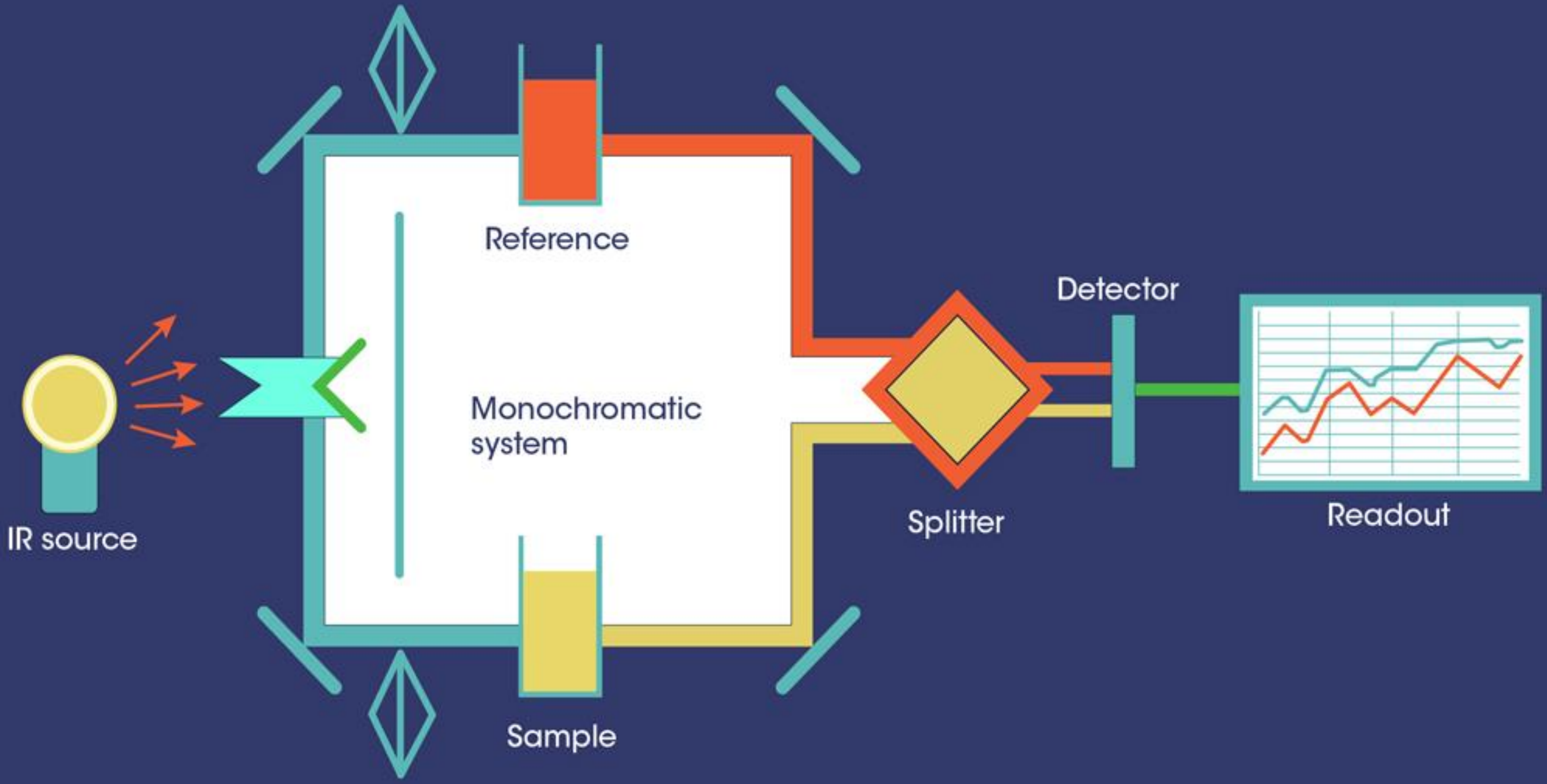


Fig. 2.2 Potential energy curve of a harmonic oscillator with discrete vibrational levels E_i

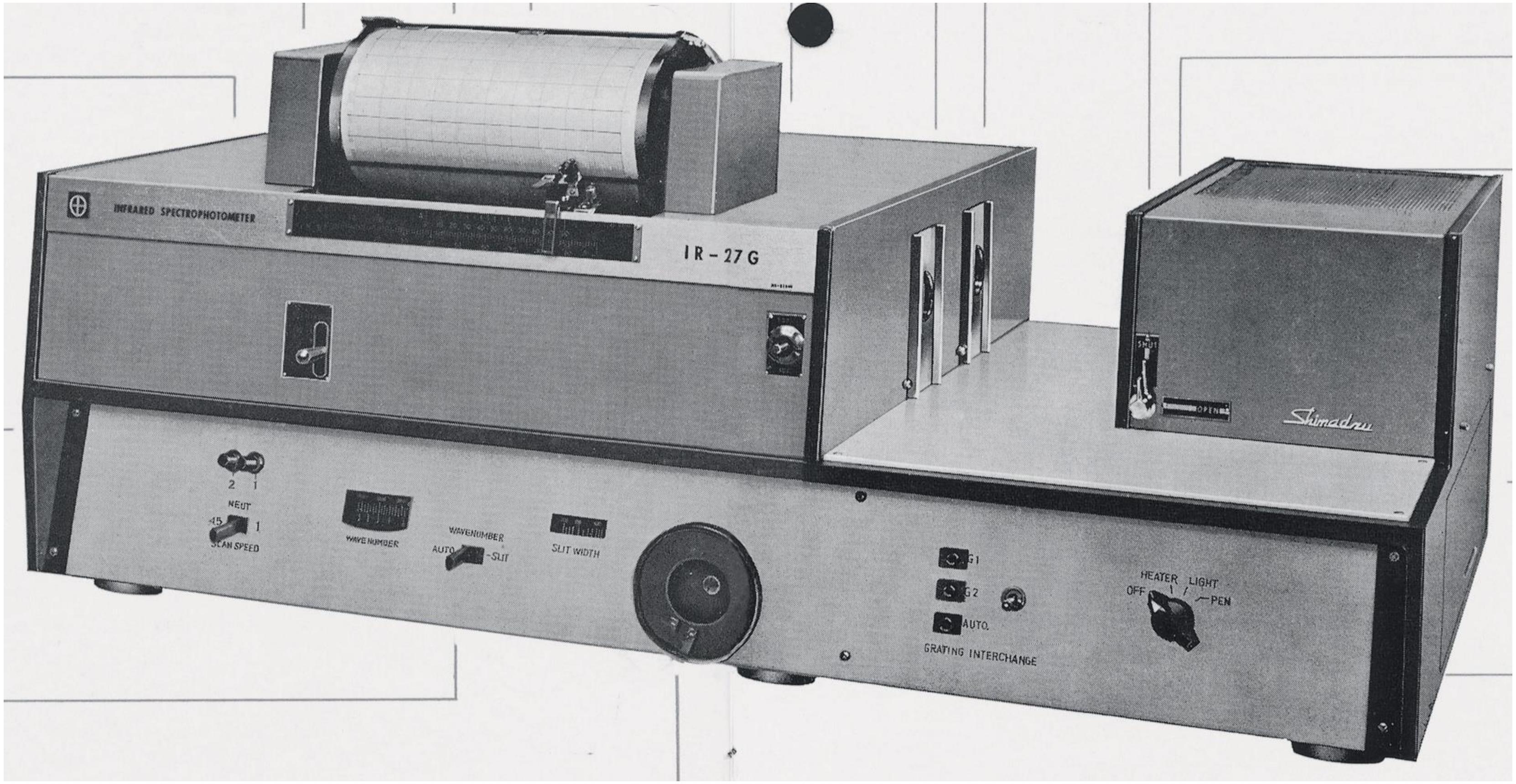

Energy V(r)
Dissociation limit
n = 3
n = 2
n = 1
n = 0
E_D
E_0
r_0
Interatomic distance r

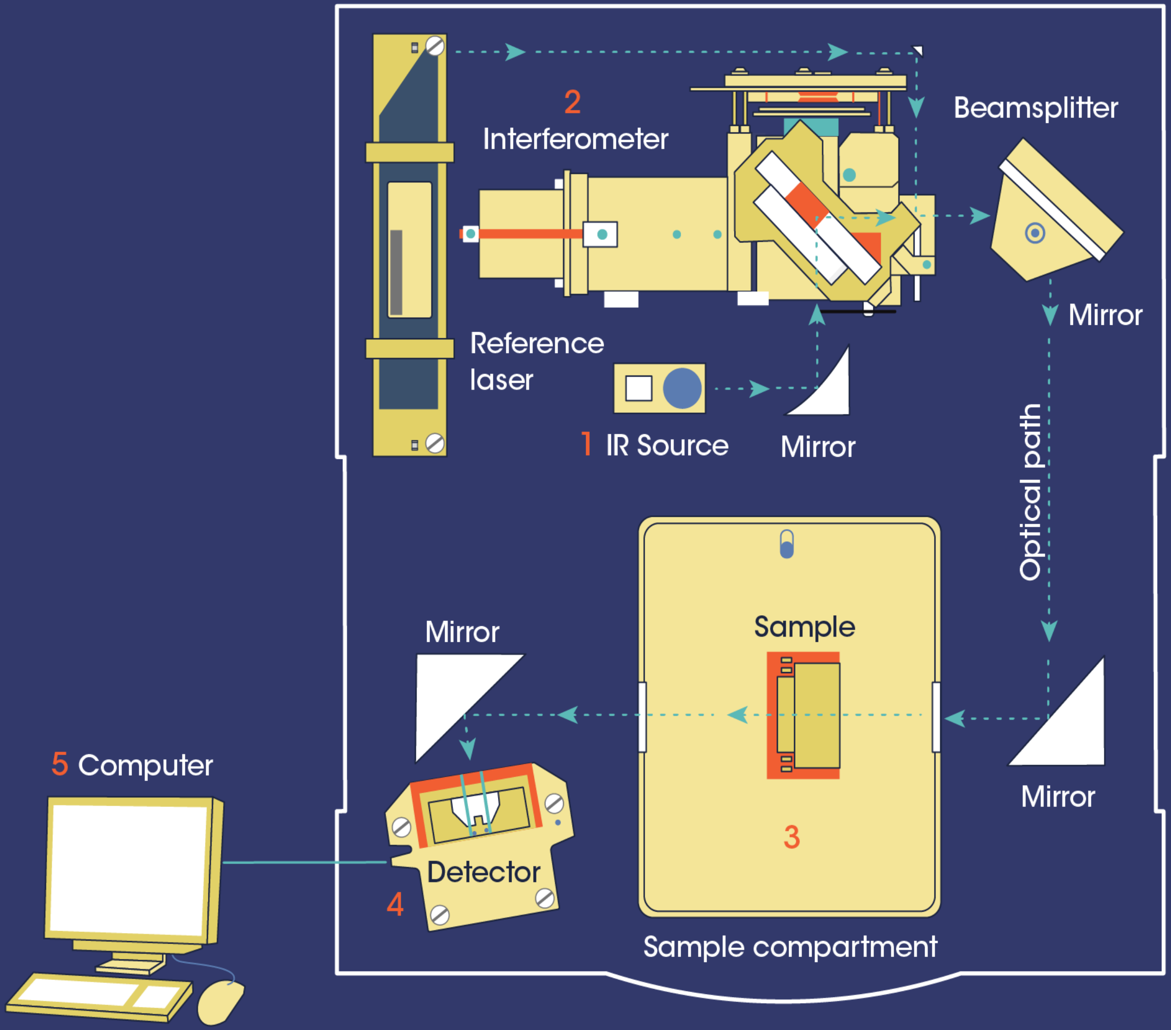

Light source (Globar)
Sample
Blank
Interferometer
Zeroing
Calibration (Laser)
Grating
Sample
Detector (DTGS)
Amplifier
Data storage
Computer for Fourier transformation
Chart recorder
Screen
Printer
Spectrum

Φασματόμετρο Υπερύθρου

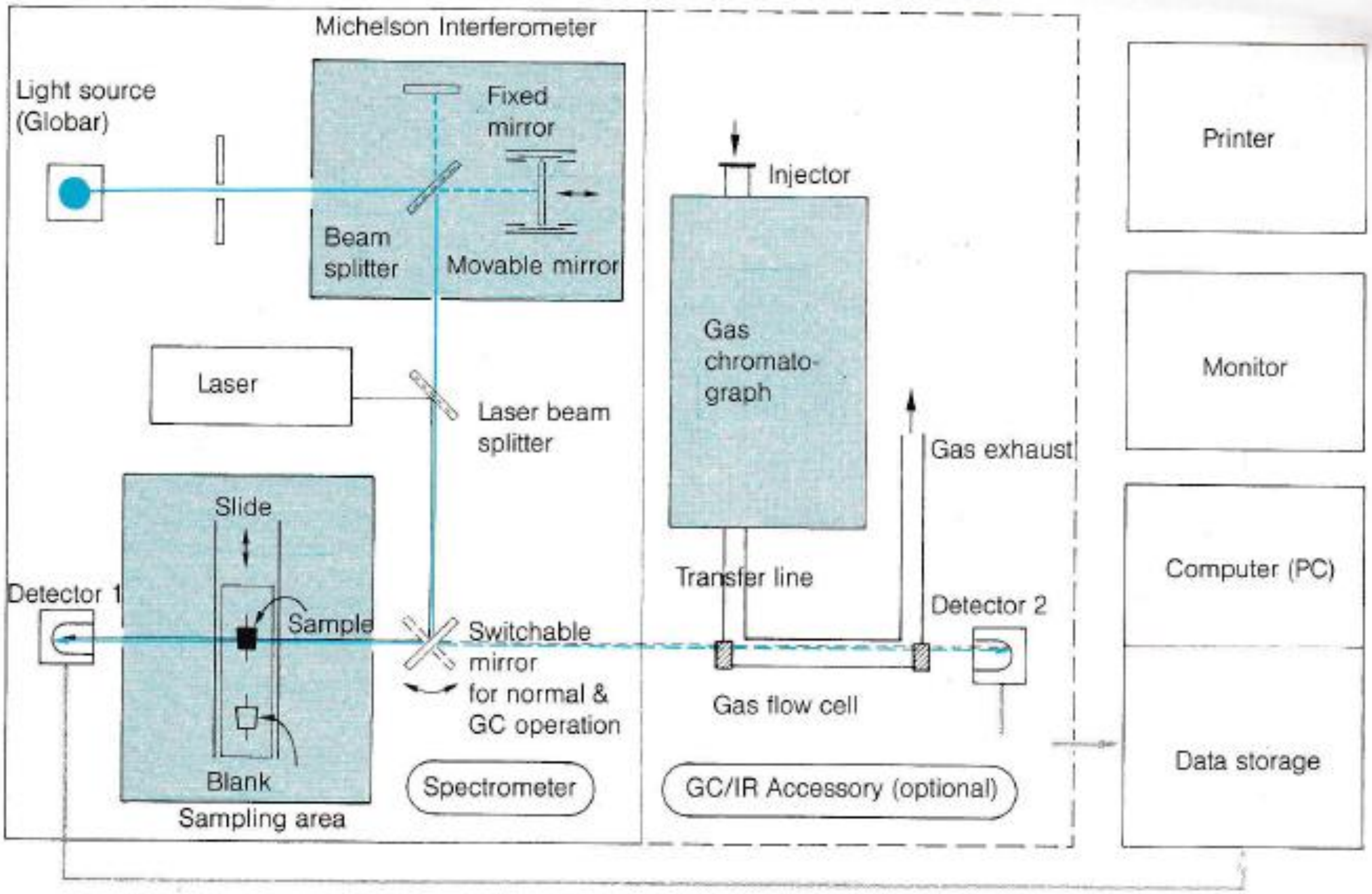


Shimadzu, IR-27G, 1959




2
Interferometer
Beamsplitter
Mirror
Reference
laser
1 IR Source
Mirror
Optical path
Sample
3
Sample compartment
Mirror
Mirror
Detector
4
5 Computer


Thermo
iS50 ABX
iS50 FT-IR


Michelson Interferometer
Light source (Globar)
Fixed mirror
Beam splitter
Movable mirror
Laser
Laser beam splitter
Slide
Detector 1
Sample
Switchable mirror for normal & GC operation
Blank
Sampling area
Spectrometer
Injector
Gas chromatograph
Gas exhaust
Transfer line
Detector 2
Gas flow cell
GC/IR Accessory (optional)
Printer
Monitor
Computer (PC)
Data storage

NaCl , KCl, KBr, CaF_2, BaF_2, AgCl

NaCl	KCl	KBr	CaF_2	BaF_2	AgCl
$42.00	$44.00	$46.00	$80.00	$107.00	$337.00

$164.00

$134.00

3mm Die Set

$1,430.00

13mm Die Set

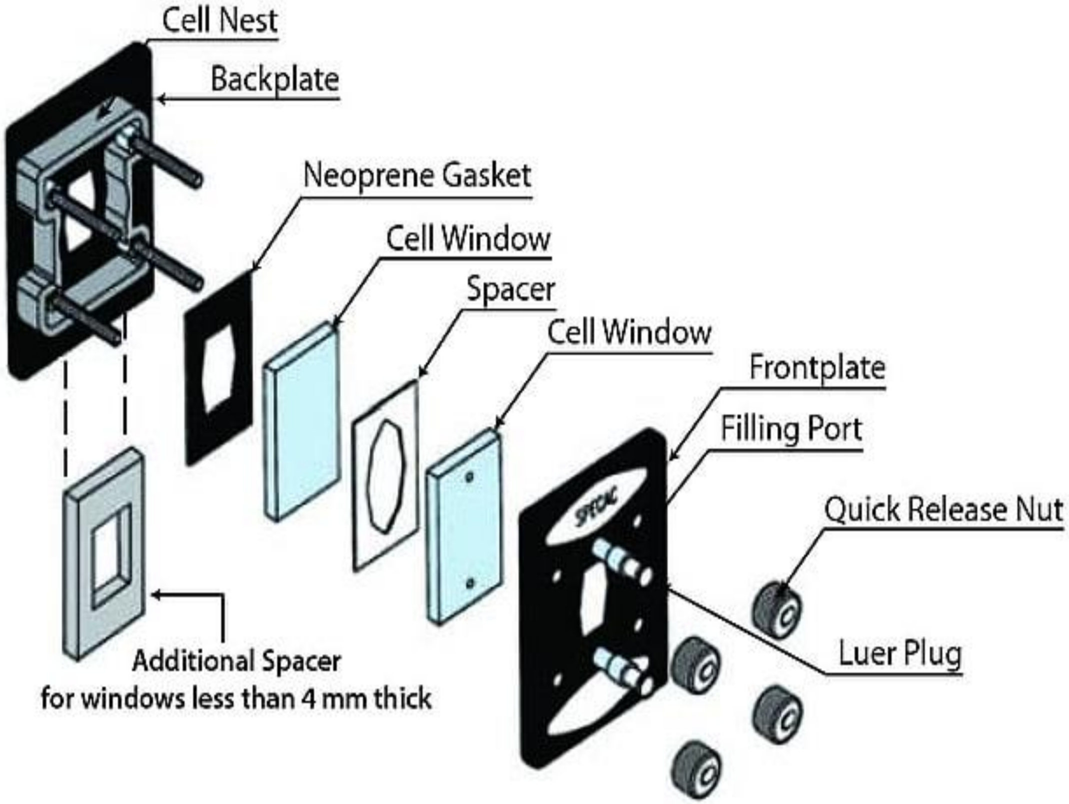
$900.00

32mm Die Set

$2,222.00

$229.00


OMNI-CELL
SPECAC

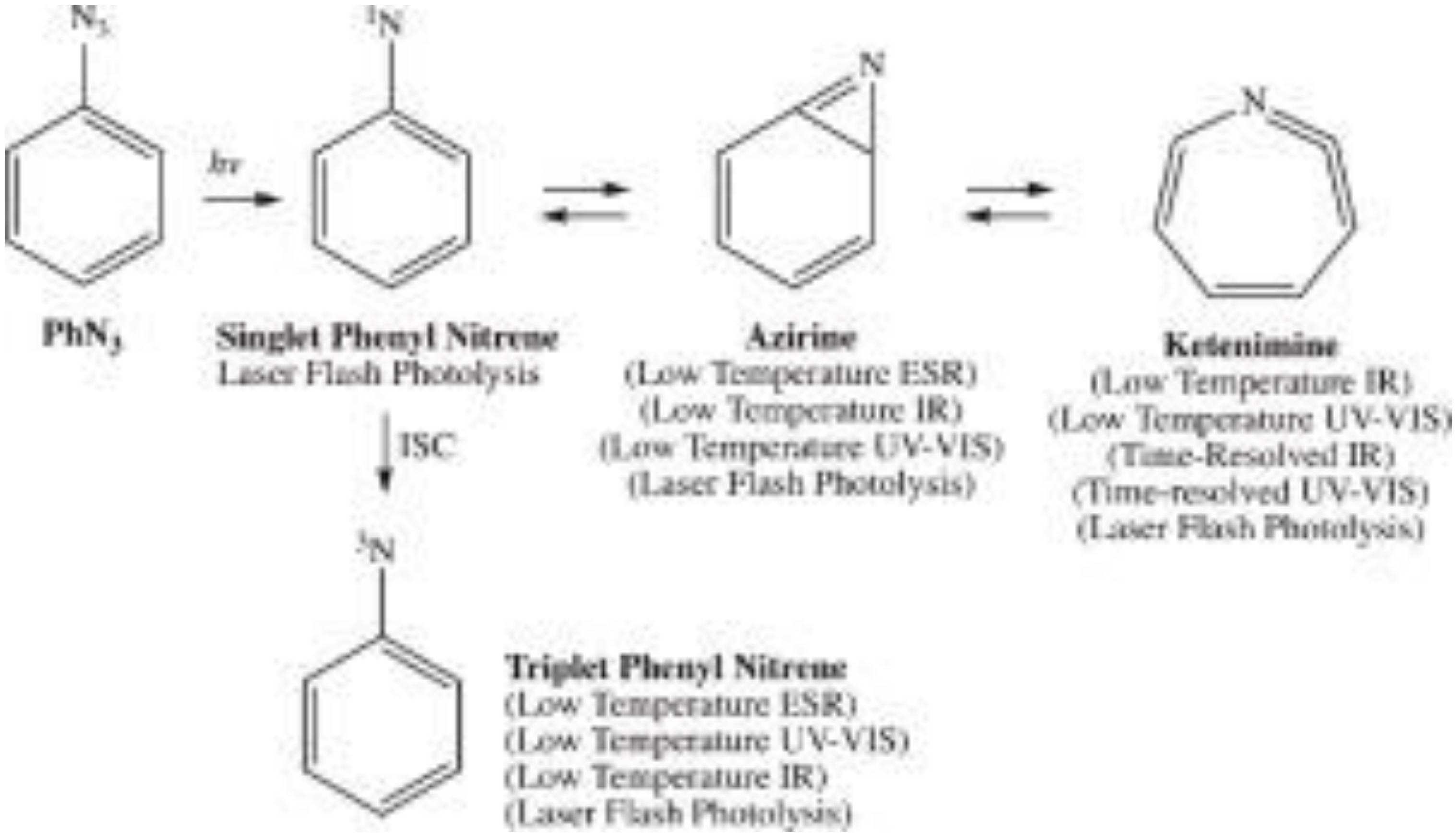

Cell Nest
Backplate
Neoprene Gasket
Cell Window
Spacer
Cell Window
Frontplate
Filling Port
Quick Release Nut
Luer Plug
SPECAC
Additional Spacer
for windows less than 4 mm thick

$550.00

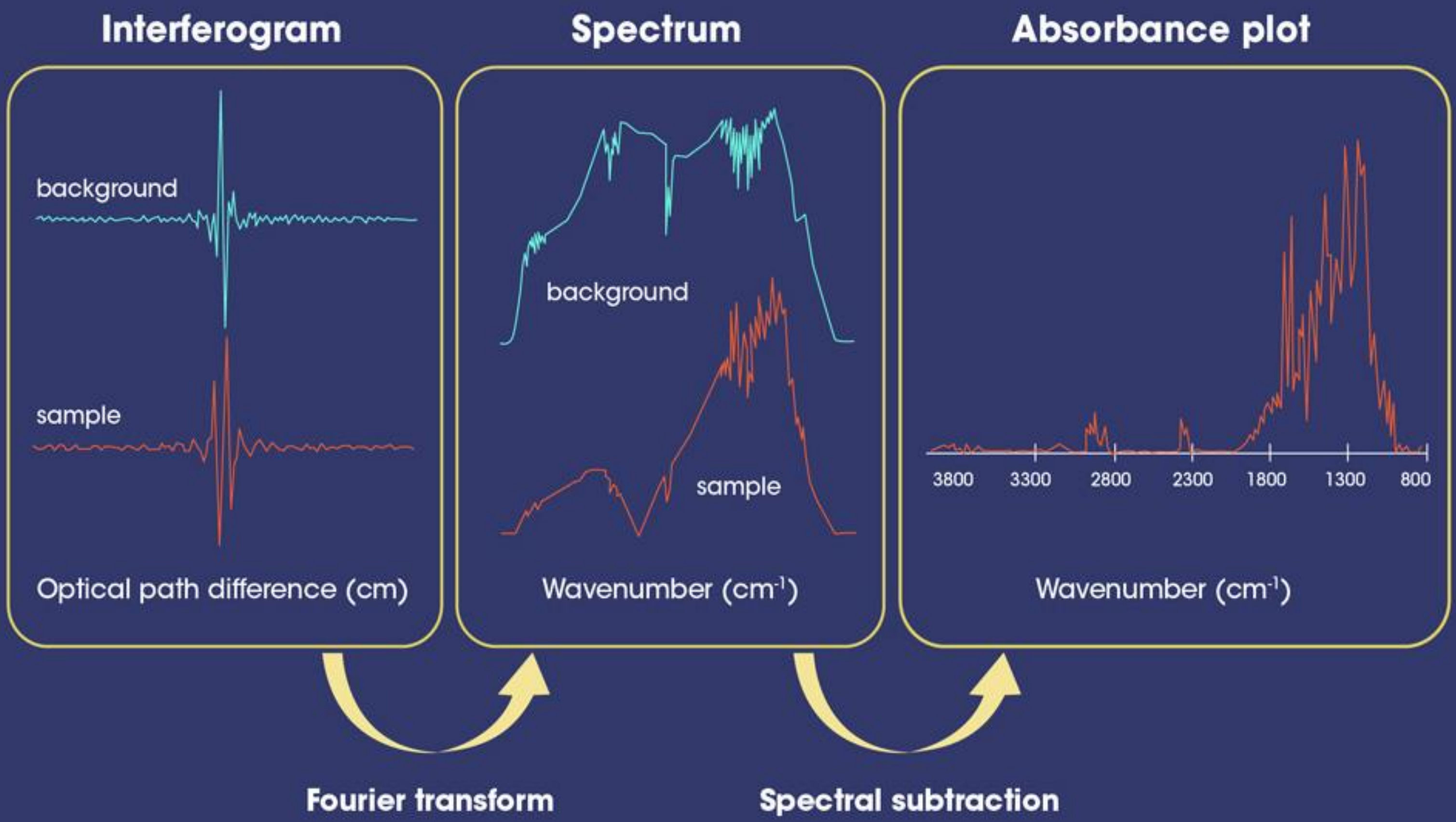
$7,350.00


©International Crystal Laboratories


Specac



N3
PhN3
hν
1N
Singlet Phenyl Nitrene
Laser Flash Photolysis
ISC
3N
Triplet Phenyl Nitrene
(Low Temperature ESR)
(Low Temperature UV-VIS)
(Low Temperature IR)
(Laser Flash Photolysis)
N
Azirine
(Low Temperature ESR)
(Low Temperature IR)
(Low Temperature UV-VIS)
(Laser Flash Photolysis)
N
Ketenimine
(Low Temperature IR)
(Low Temperature UV-VIS)
(Time-Resolved IR)
(Time-resolved UV-VIS)
(Laser Flash Photolysis)



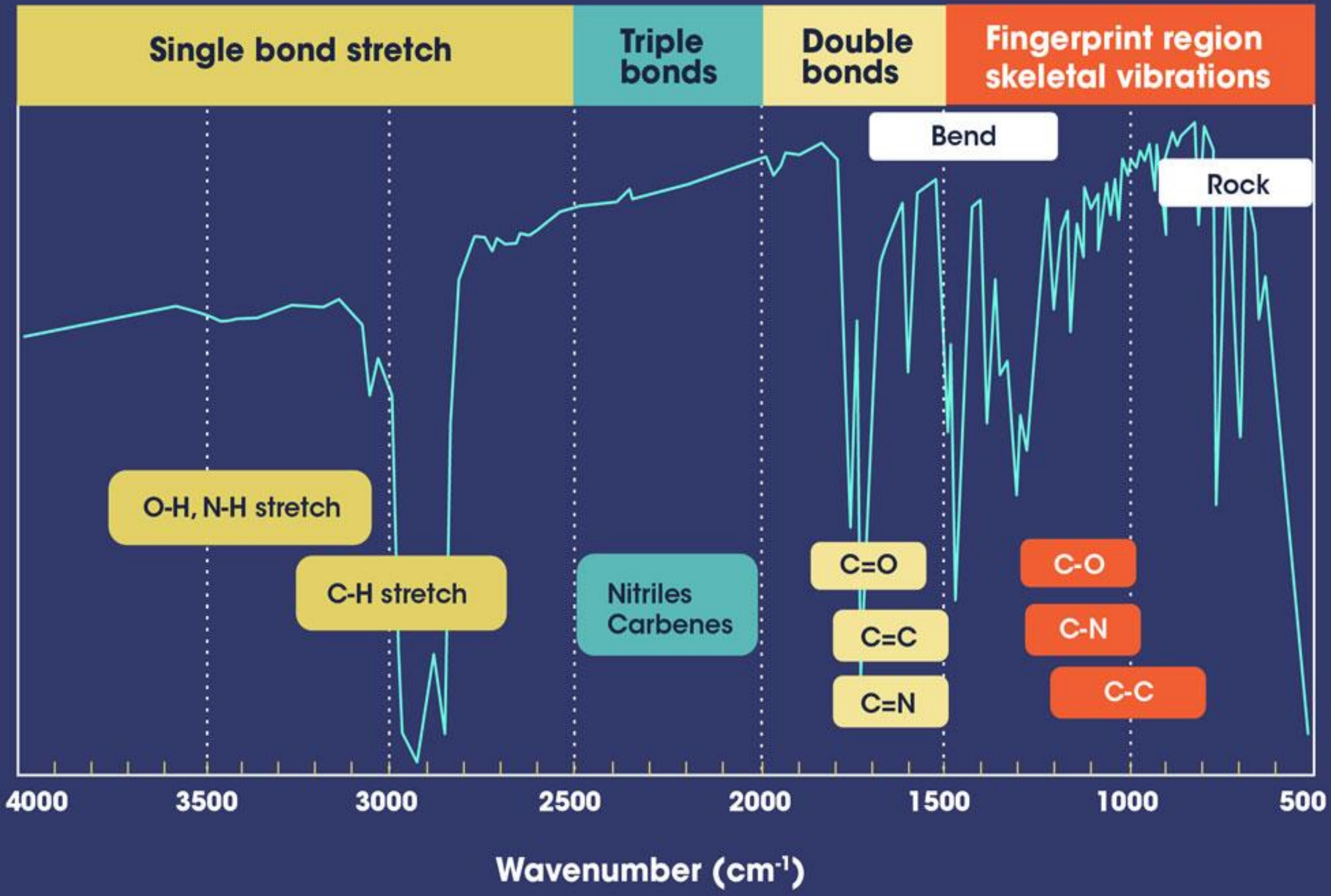
Interferogram

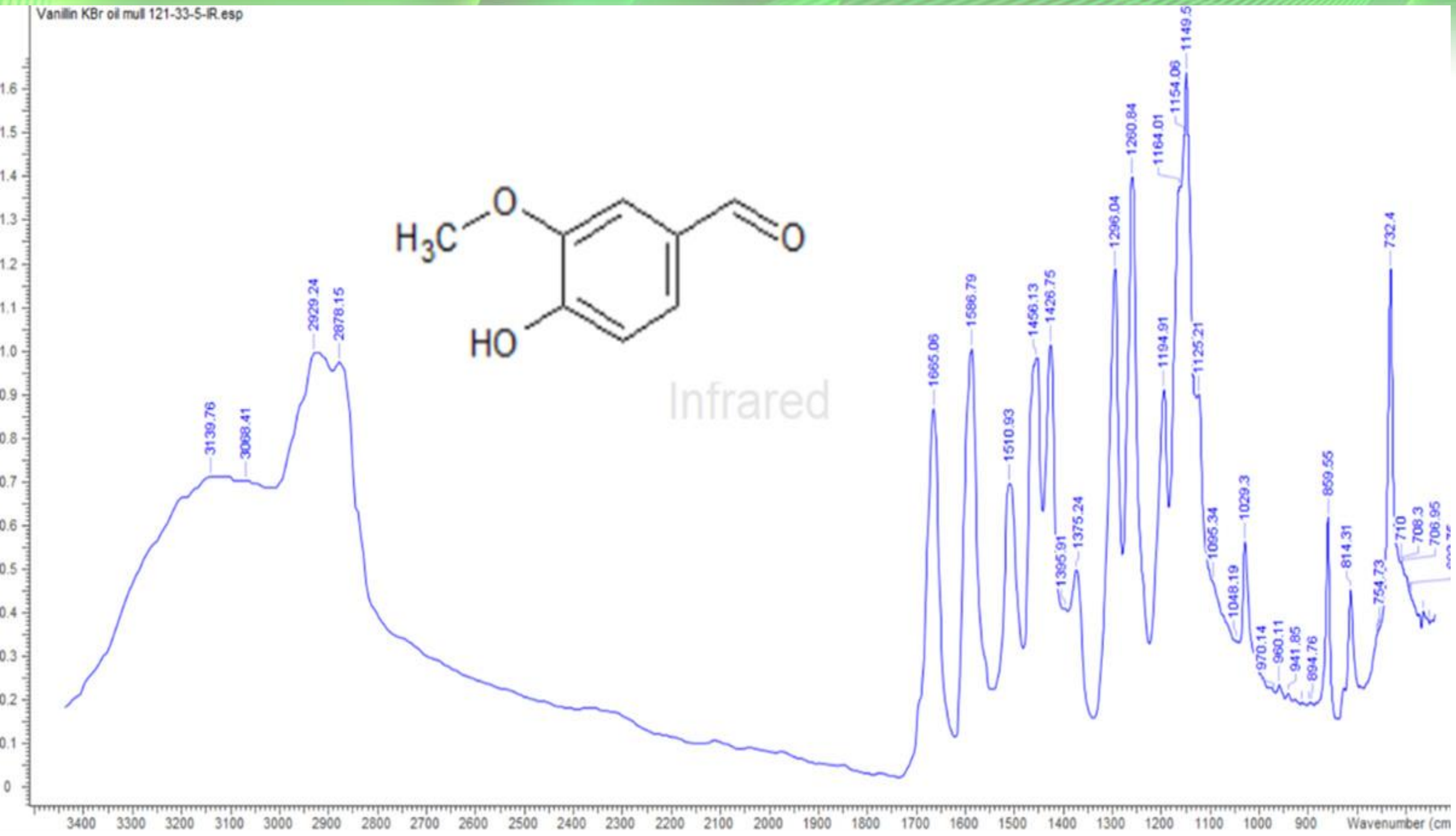
Spectrum

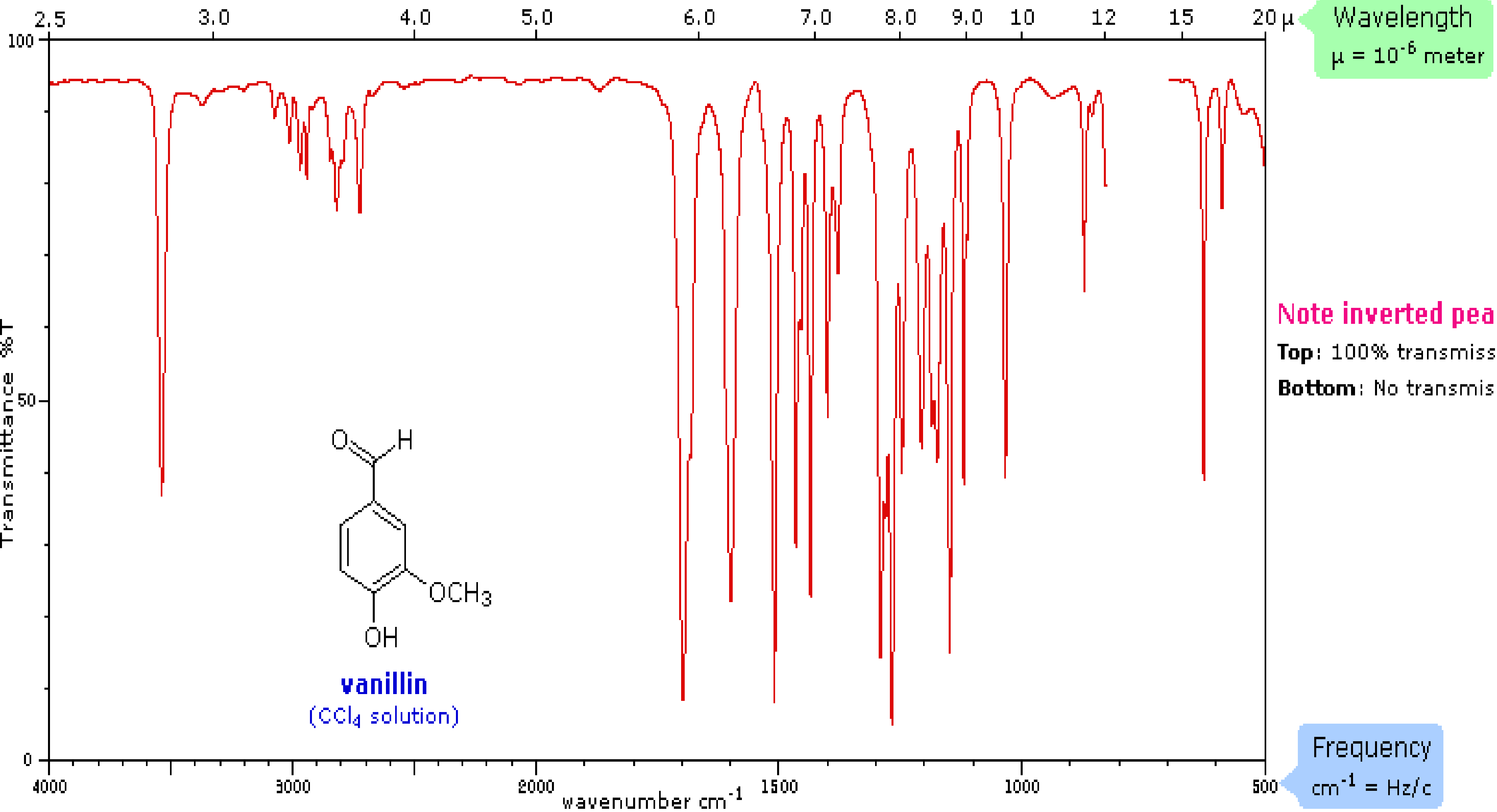
Absorbance plot

Fourier transform

Spectral subtraction


Single bond stretch
Triple bonds
Double bonds
Fingerprint region skeletal vibrations
Bend
Rock
O-H, N-H stretch
C-H stretch
Nitriles
Carbenes
C=O
C=C
C=N
C-O
C-N
C-C
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm⁻¹)


Vanillin KBr oil mull 121-33-5-IR.esp
H3C
O
O
HO
Infrared
3139.76
3068.41
2929.24
2878.15
1665.06
1586.79
1510.93
1456.13
1426.75
1395.91
1375.24
1296.04
1260.84
1194.91
1164.01
1154.06
1149.5
1125.21
1095.34
1048.19
1029.3
970.14
960.11
941.85
894.76
859.55
814.31
754.73
732.4
710
708.3
706.95
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
3400
3300
3200
3100
3000
2900
2800
2700
2600
2500
2400
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
Wavenumber (cm

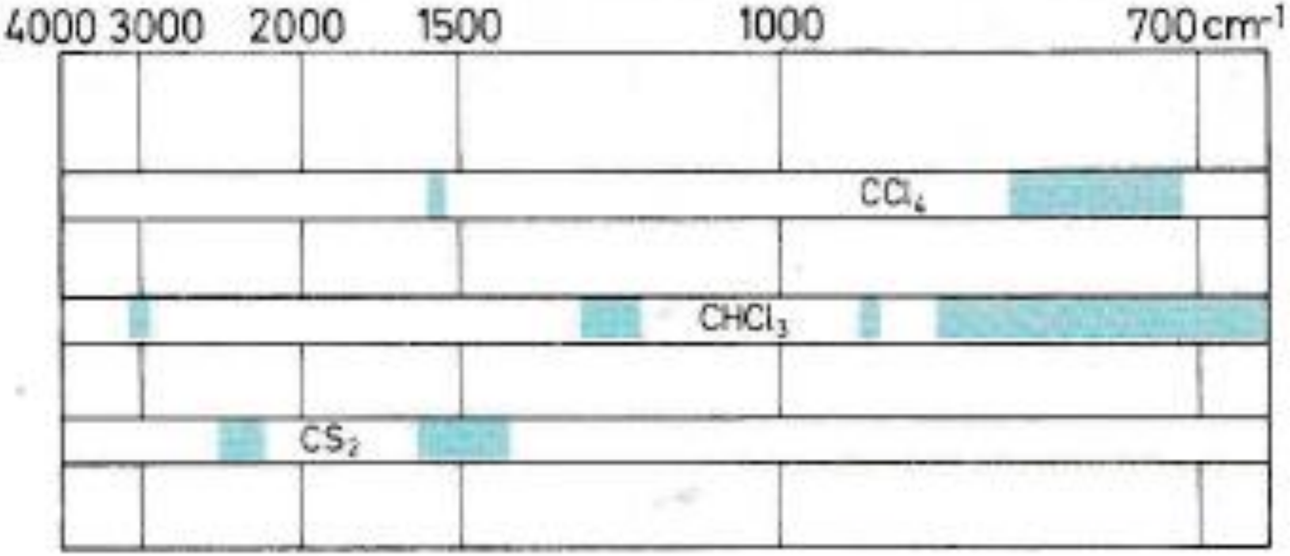


vanillin
(CCl_4 solution)

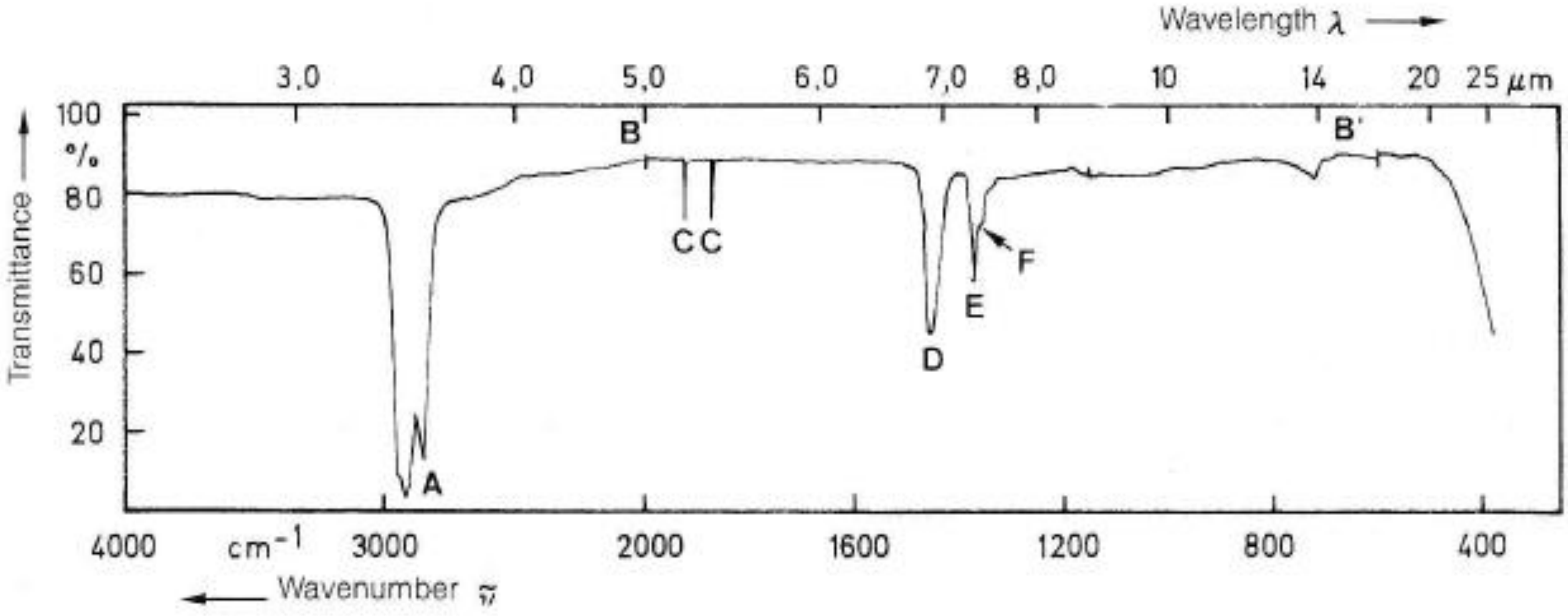
Note inverted peaks

Top: 100% transmission

Bottom: No transmission

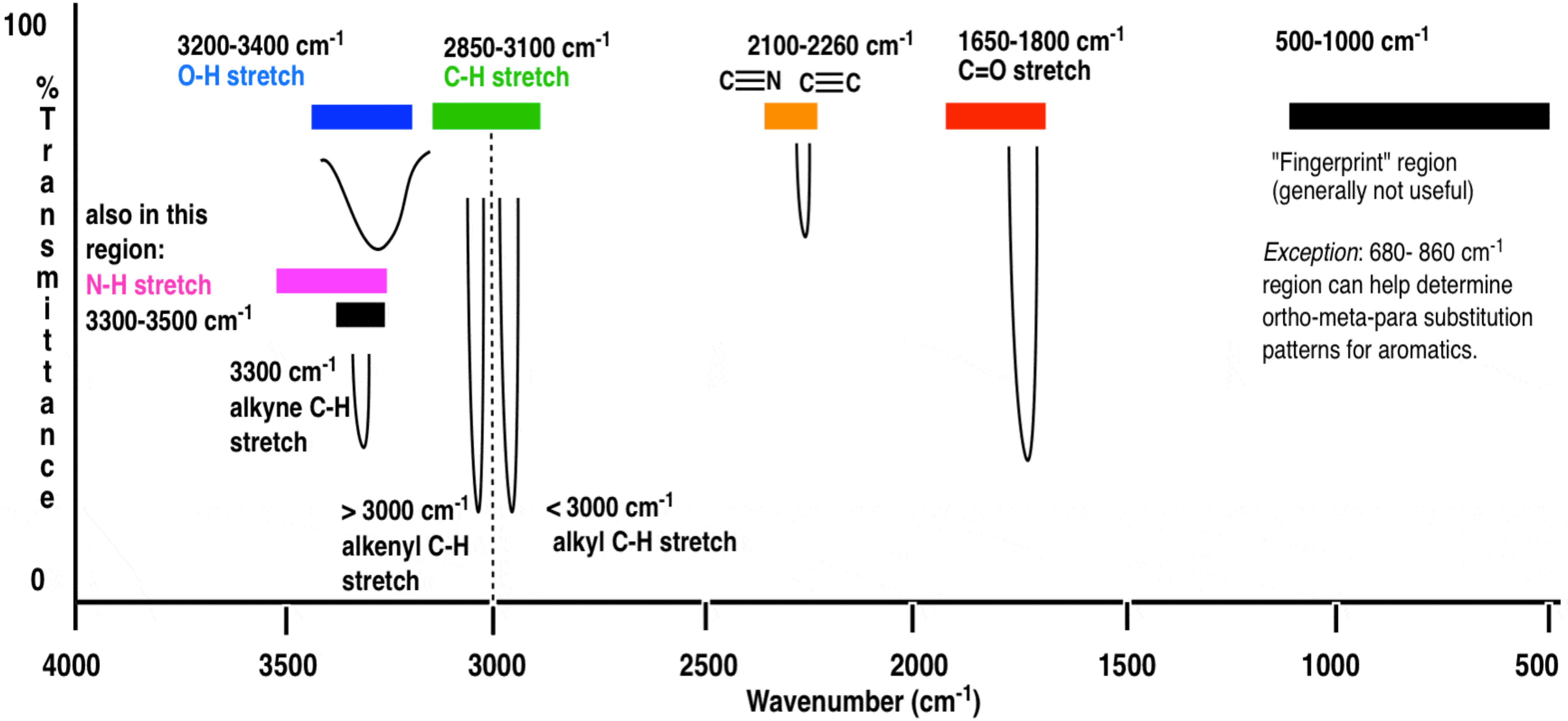

4000
3000
2000
1500
1000
700 cm^{-1}
CCl_4
$CHCl_3$
CS_2

Nujol



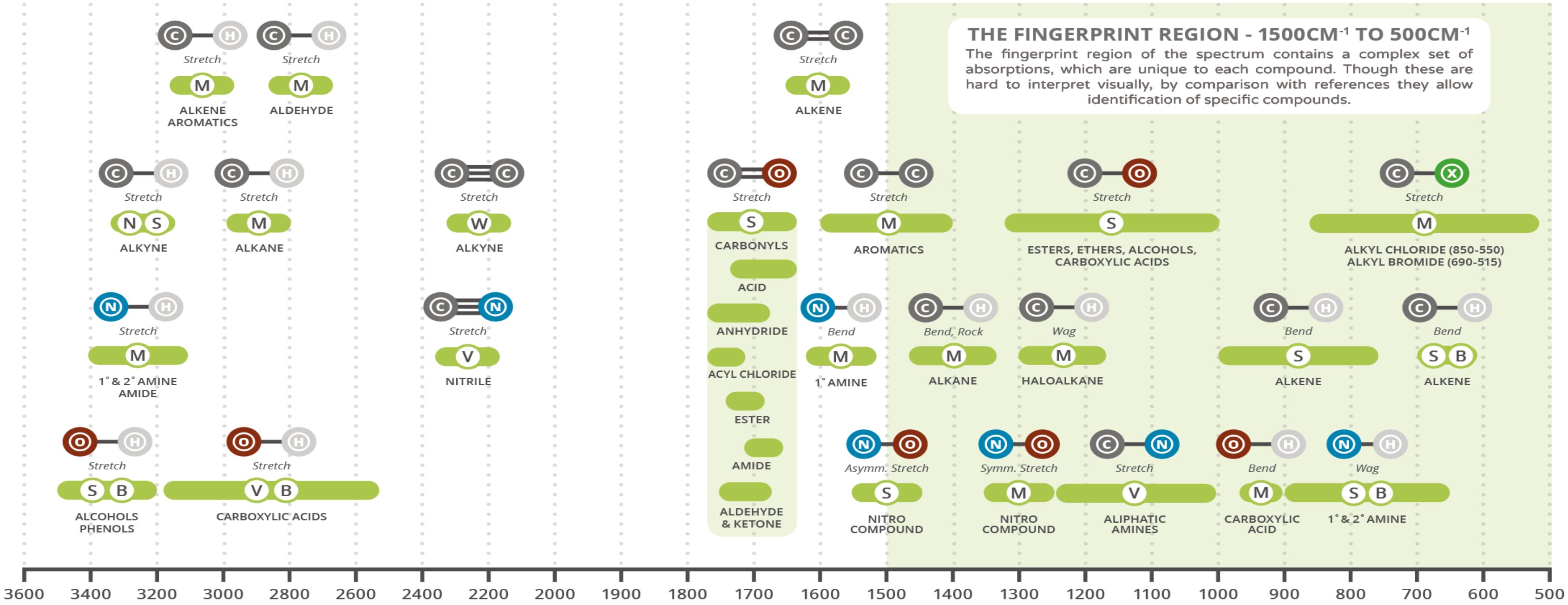
Wavelength λ
3,0
4,0
5,0
6,0
7,0
8,0
10
14
20
25 μm
100
%
80
60
40
20
Transmittance
B
B'
C C
D
E
F
A
4000
cm⁻¹
3000
2000
1600
1200
800
400
Wavenumber ṽ

Typical Infrared Absorption Values For Various Types of Bonds



ANALYTICAL CHEMISTRY - INFRARED SPECTROSCOPY

Commonly referred to as IR spectroscopy, this technique allows chemists to identify characteristic groups of atoms (functional groups) present in molecules.



THE FINGERPRINT REGION - 1500CM^{-1} TO 500CM^{-1}

The fingerprint region of the spectrum contains a complex set of absorptions, which are unique to each compound. Though these are hard to interpret visually, by comparison with references they allow identification of specific compounds.

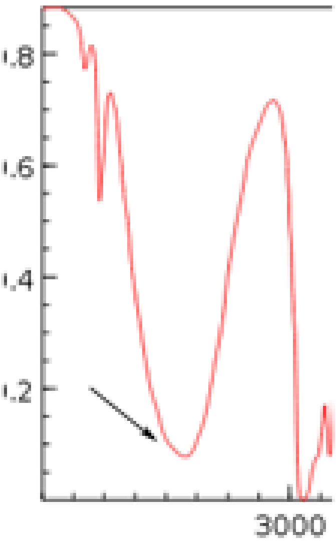
FREQUENCY/WAVENUMBER OF ABSORPTION (CM^{-1})

Key: S STRONG M MEDIUM W WEAK B BROAD N NARROW V VARIABLE

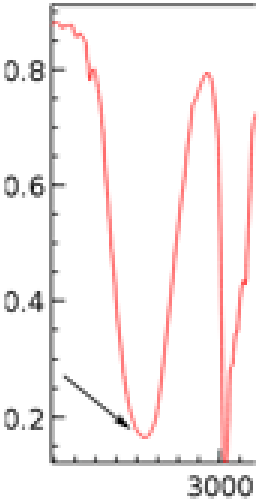
Infrared frequencies make up a portion of the electromagnetic spectrum. If a range of infrared frequencies are shone through an organic compound, some of the frequencies are absorbed by the chemical bonds within the compound. Different chemical bonds absorb different frequencies of infrared radiation. There are a number of characteristic absorptions which allow functional groups (the parts of a compound which give it its particular reactivity) to be identified. This graphic shows a number of these absorptions.

A collection of “tongues” - the O-H stretch around 3400-3200 cm^{-1}

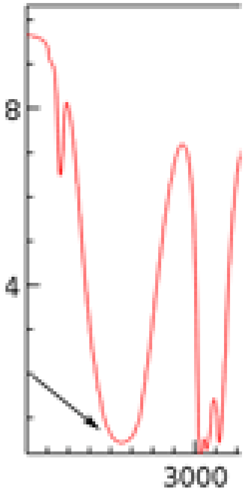
Example 1



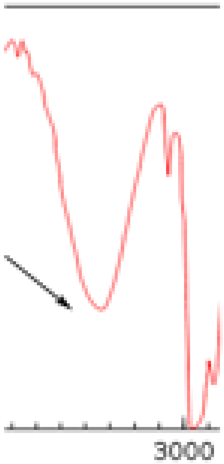
Example 2



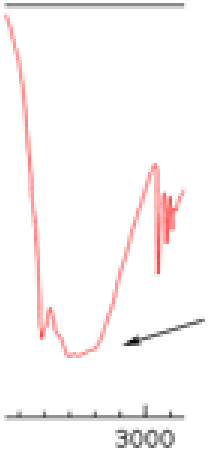
Example 3



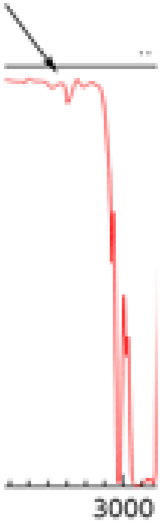
Example 4



Example 5

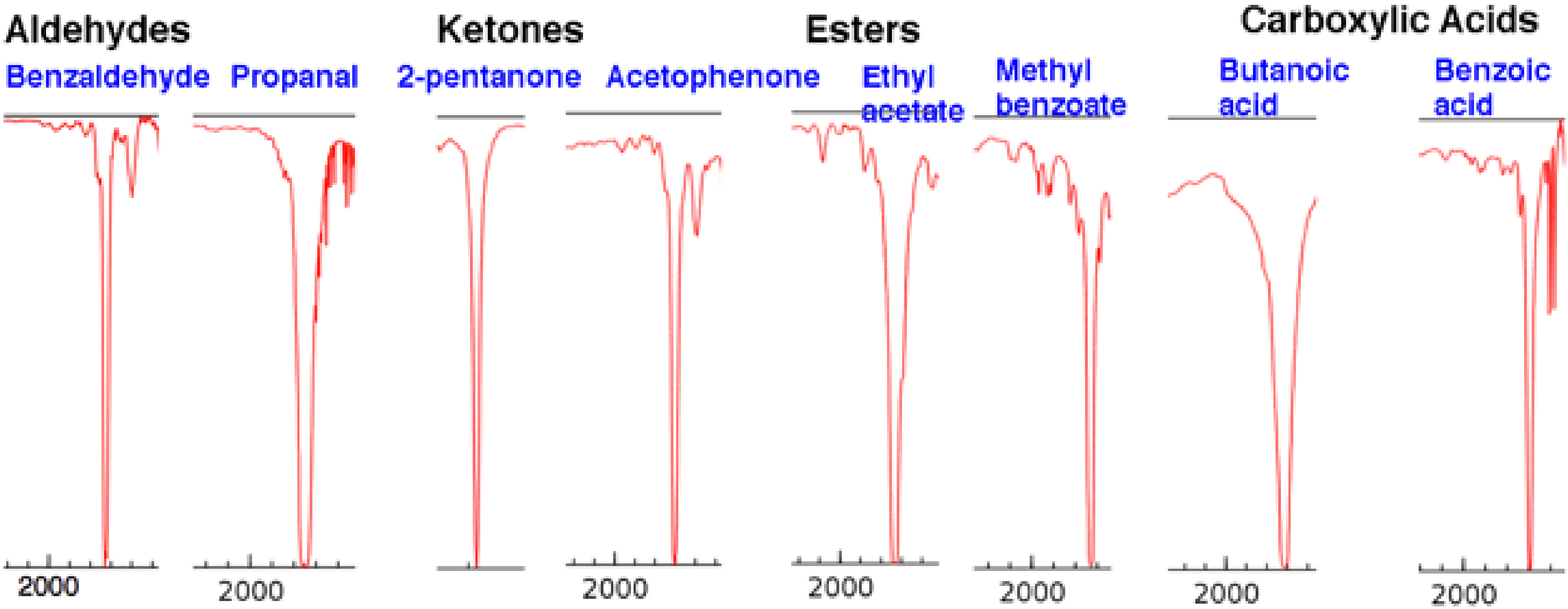


NOT an OH stretch!



With the exception of the last example, each of these “blobs” represents the OH stretch of an alcohol

A collection of “swords” - the C=O stretch around 1700 cm



Aldehydes: 1740-1720 cm^{-1}

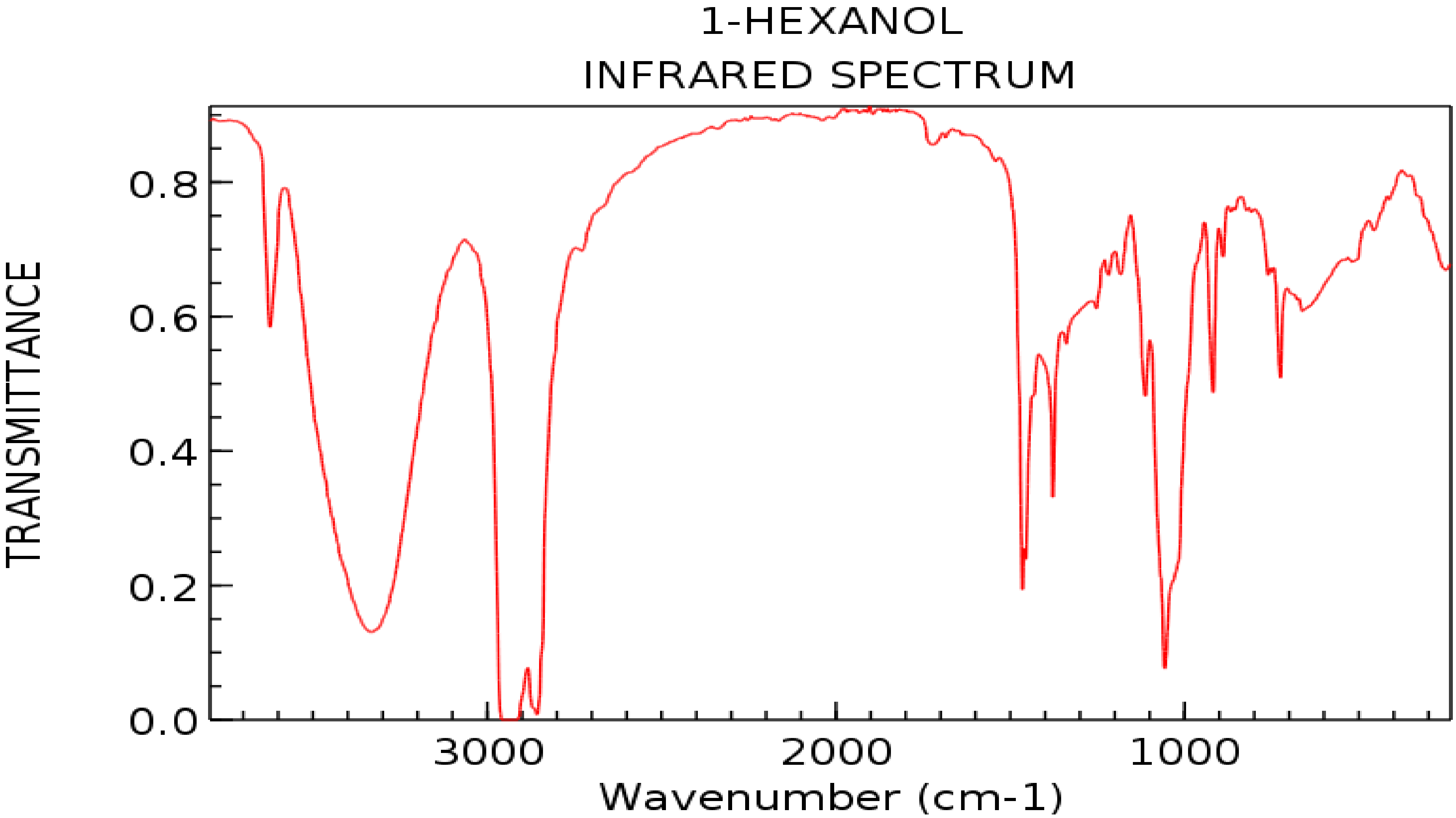
Ketones: 1750-1715 cm^{-1}

Esters: 1750-1735 cm^{-1}

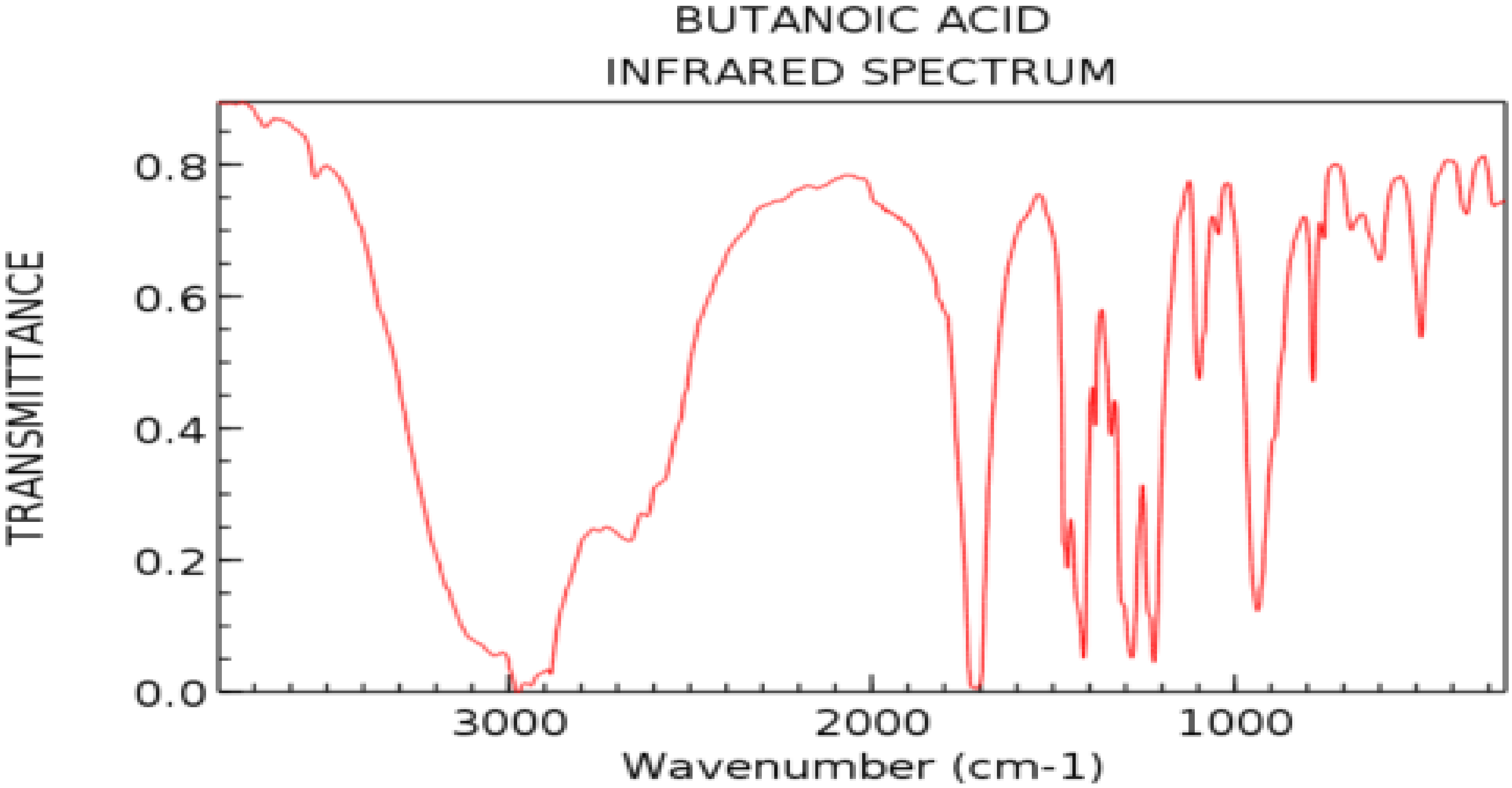
Carboxylic Acids: 1725-1700 cm^{-1}

(less if conjugated)

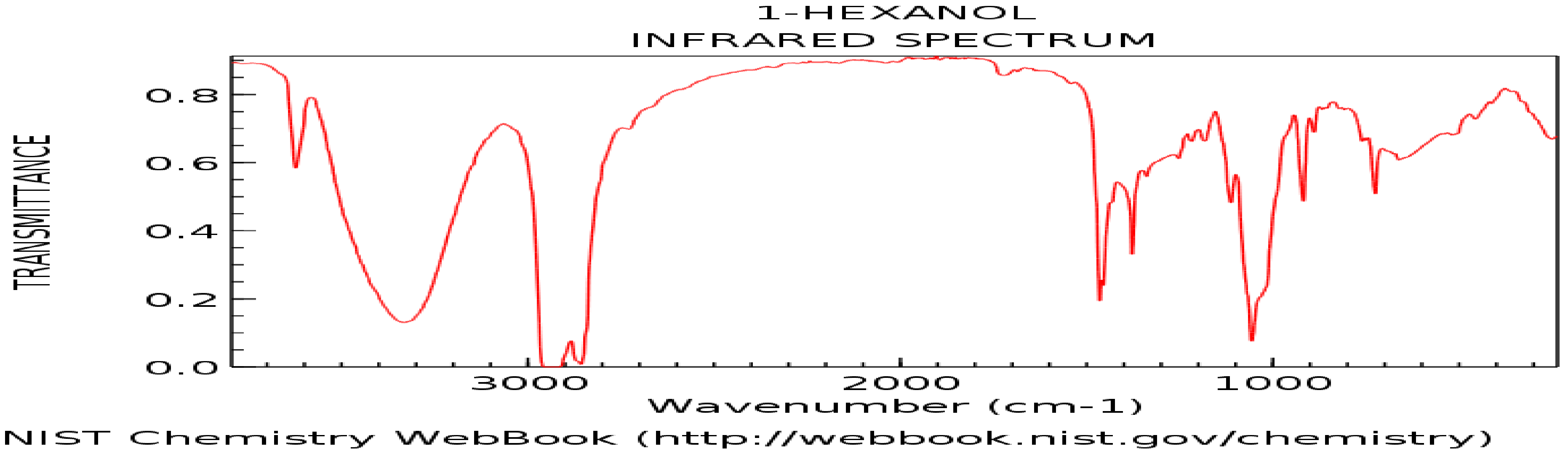
Almost always the strongest peak on the spectrum

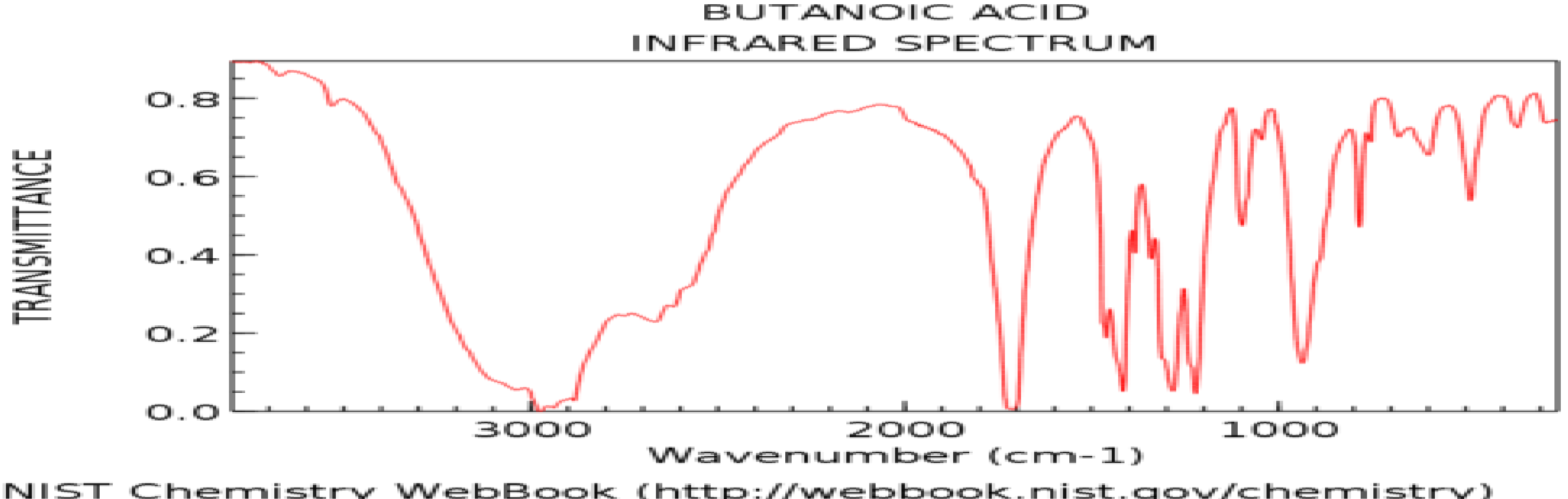


NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)



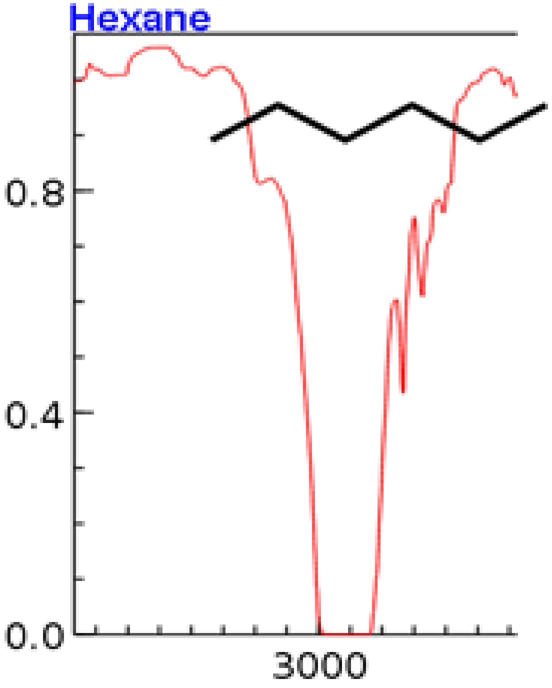
NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)


1-HEXANOL
INFRARED SPECTRUM
TRANSMITTANCE
0.8
0.6
0.4
0.2
0.0
3000
2000
1000
Wavenumber (cm-1)
NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)


BUTANOIC ACID
INFRARED SPECTRUM
TRANSMITTANCE
0.8
0.6
0.4
0.2
0.0
3000
2000
1000
Wavenumber (cm-1)
NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

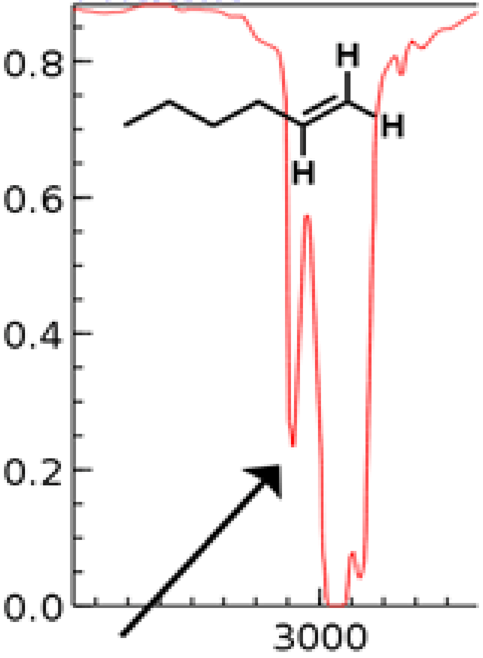
The 3000 cm^{-1} “Dividing Line” Between sp^3 C–H and sp^2 C–H

Hexane



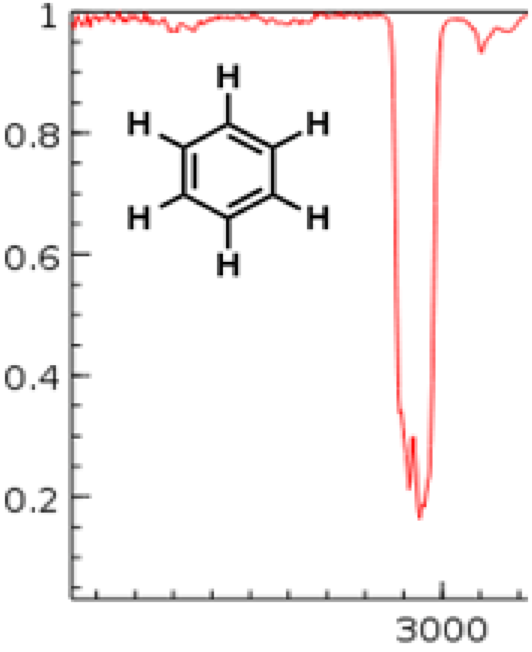
All peaks below 3000 cm^{-1}
(all sp^3 C–H)

1-Hexene



Note single peak above 3000 cm^{-1}
(corresponds to sp^2 C–H)

Benzene



All peaks above 3000 cm^{-1}
(all sp^2 C–H)

Peaks slightly above 3000 cm^{-1} can indicate presence of alkenes

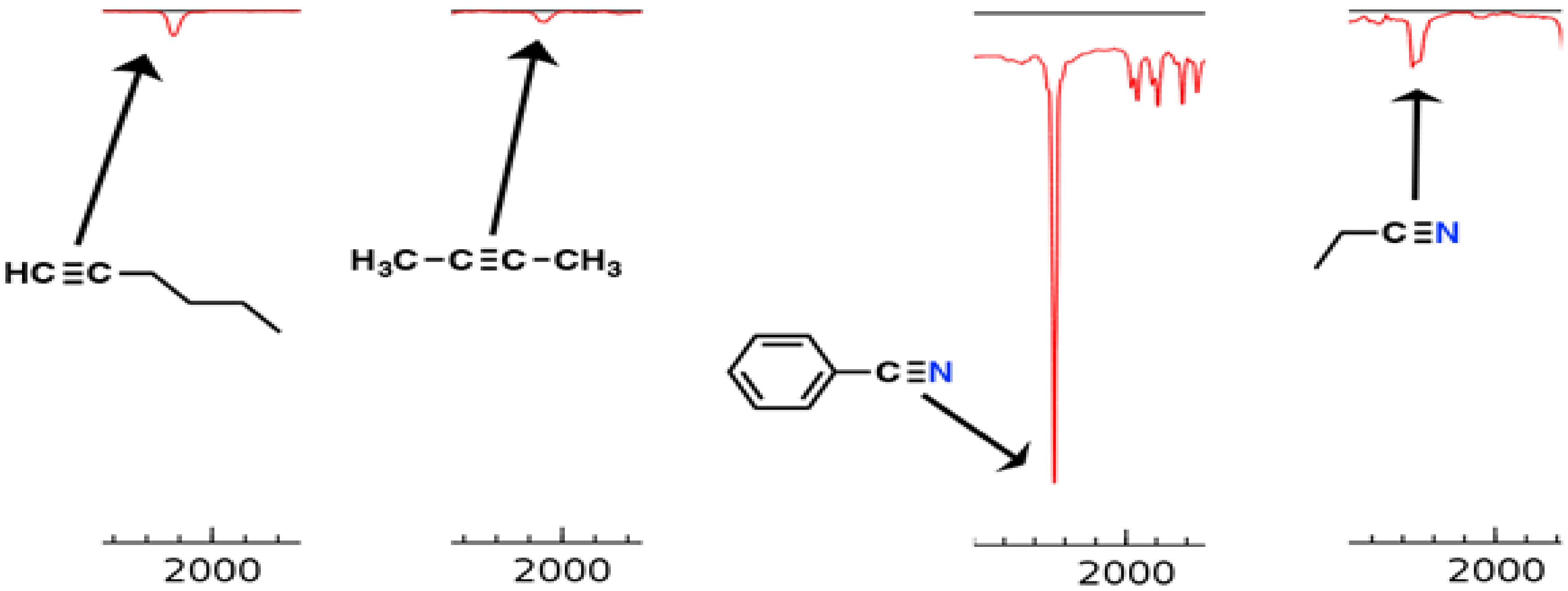
Triple Bonds Show Up Around 2050-2250 cm^{-1}

Alkynes

1-Hexyne **2-Butyne**

Nitriles

Benzonitrile **Propanenitrile**

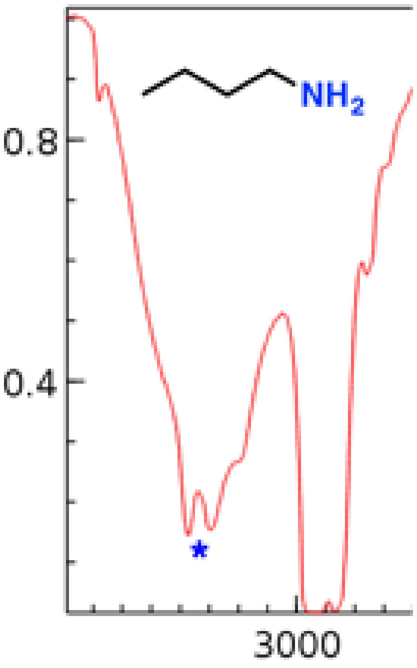


Alkyne CC stretch: very weak,
but nothing else in this region

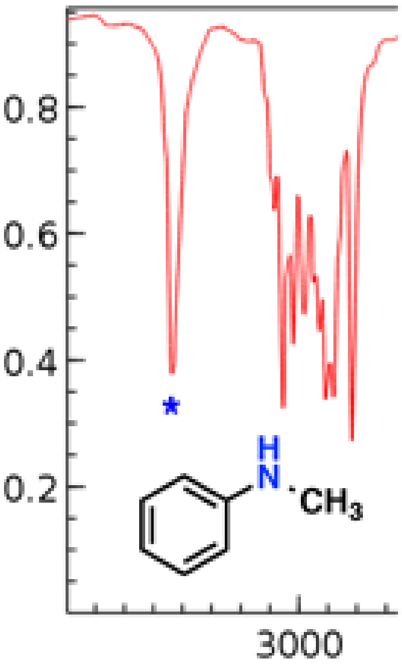
Nitrile CN stretch: around 2250 cm^{-1}

One of the few examples of weak peaks being useful

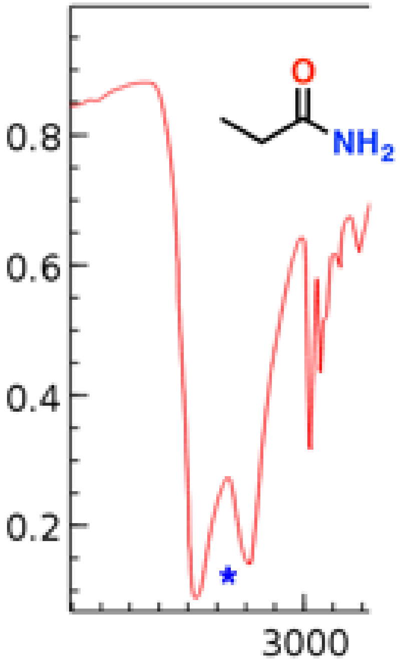
Primary amine



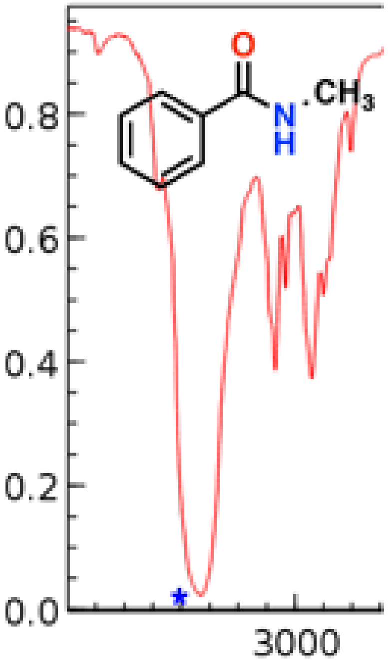
Secondary amine

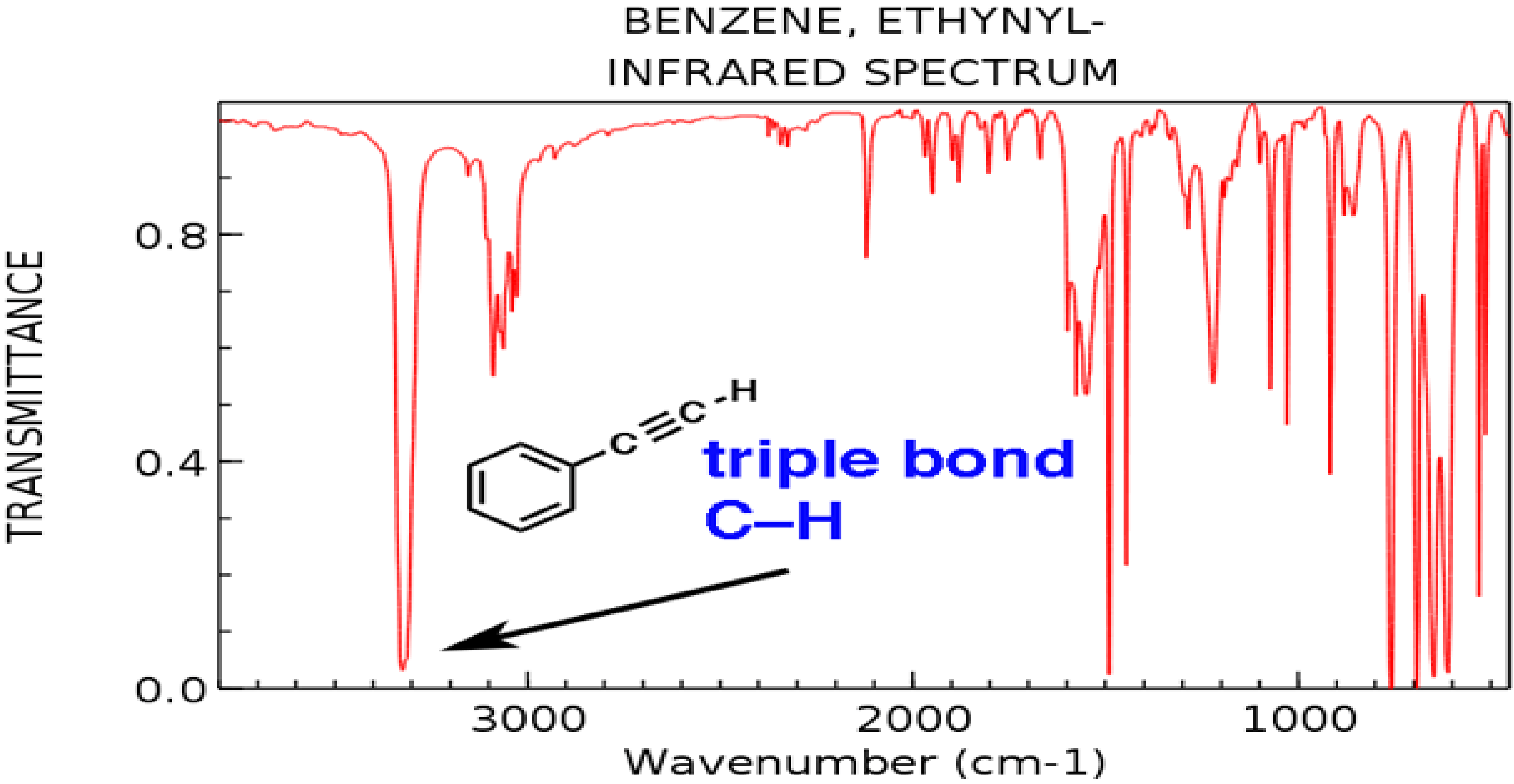


Primary amide



Secondary amide





NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

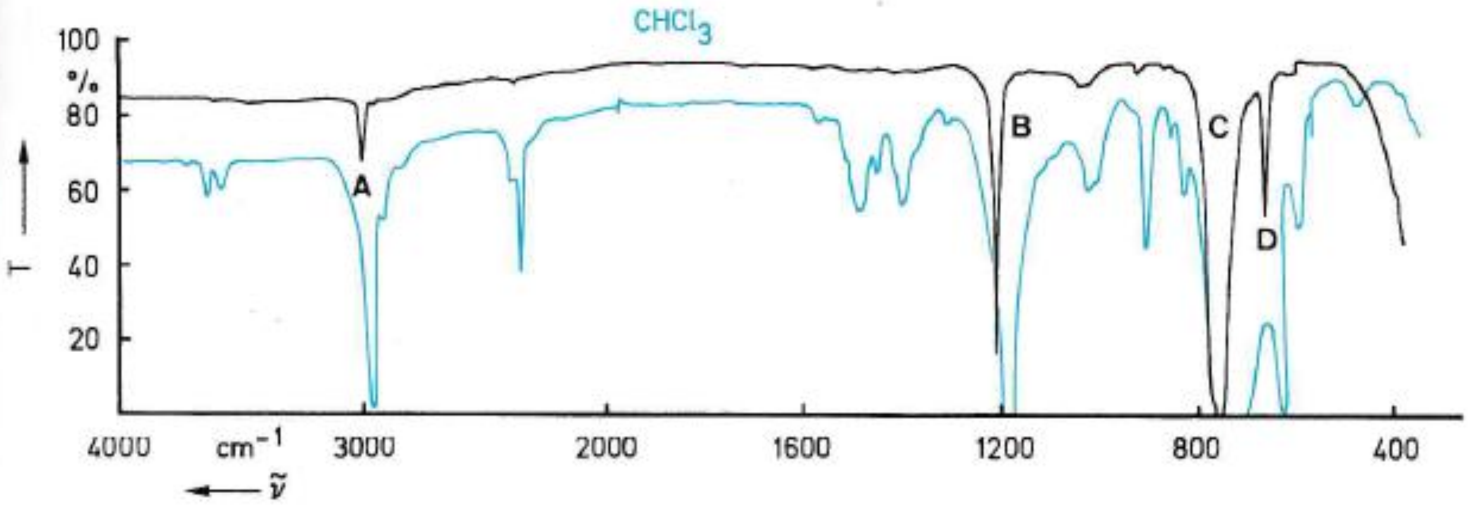


Fig. 2.15 Chloroform (as liquid film); black spectrum: 9 µm film thickness, blue spectrum: 100 µm. The figure shows the dependence of the strength of the bands on the thickness of the film for a commonly used solvent. In the regions of strong absorption the transparency using thick cells (>0.2 mm film thickness) is no longer sufficient for the detector to operate properly

A 3030 cm^{-1} (C–H) stretching vibration ν (CH)
B 1215 cm^{-1} (C–H) bending vibration δ (CH)
C 760 cm^{-1} asymmetric (C–Cl) stretching vibration
D 670 cm^{-1} symmetric (C–Cl) stretching vibration

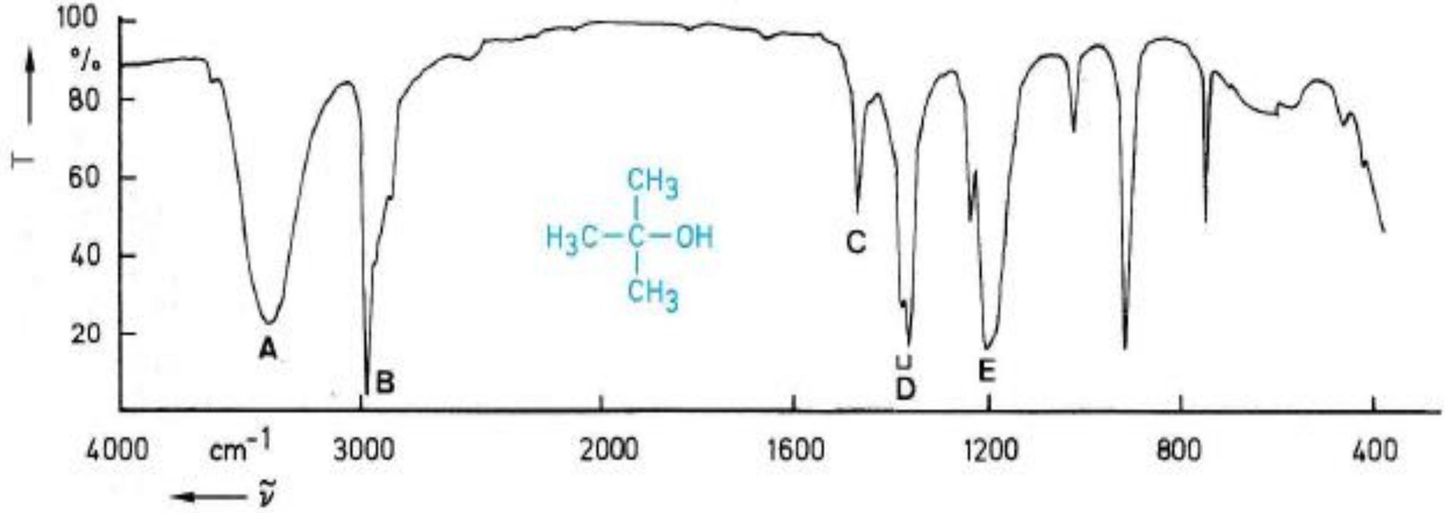


Fig. 2.16 *tert*-Butanol (as liquid film)
Alcohols are easily identified by the strong OH-band (A) and an intense and broad absorption between 1250–1000 cm^{-1} (E)

A	≈ 3400 cm^{-1}	hydrogen bonded (O–H) stretching vibration; the preceding shoulder at 3605 cm^{-1} is presumably due to non-associated O–H
B	2975 cm^{-1}	(C–H) stretching vibration $\nu_{as}(CH_3)$
C	1470 cm^{-1}	asymmetric (C–H) bending vibration
D	1380 cm^{-1}	characteristic double band for *t*-butyl groups
	1365 cm^{-1}	δ_s (C(CH$_3$)$_3$
E	1200 cm^{-1}	(C–O) stretching vibration ν (C–O)

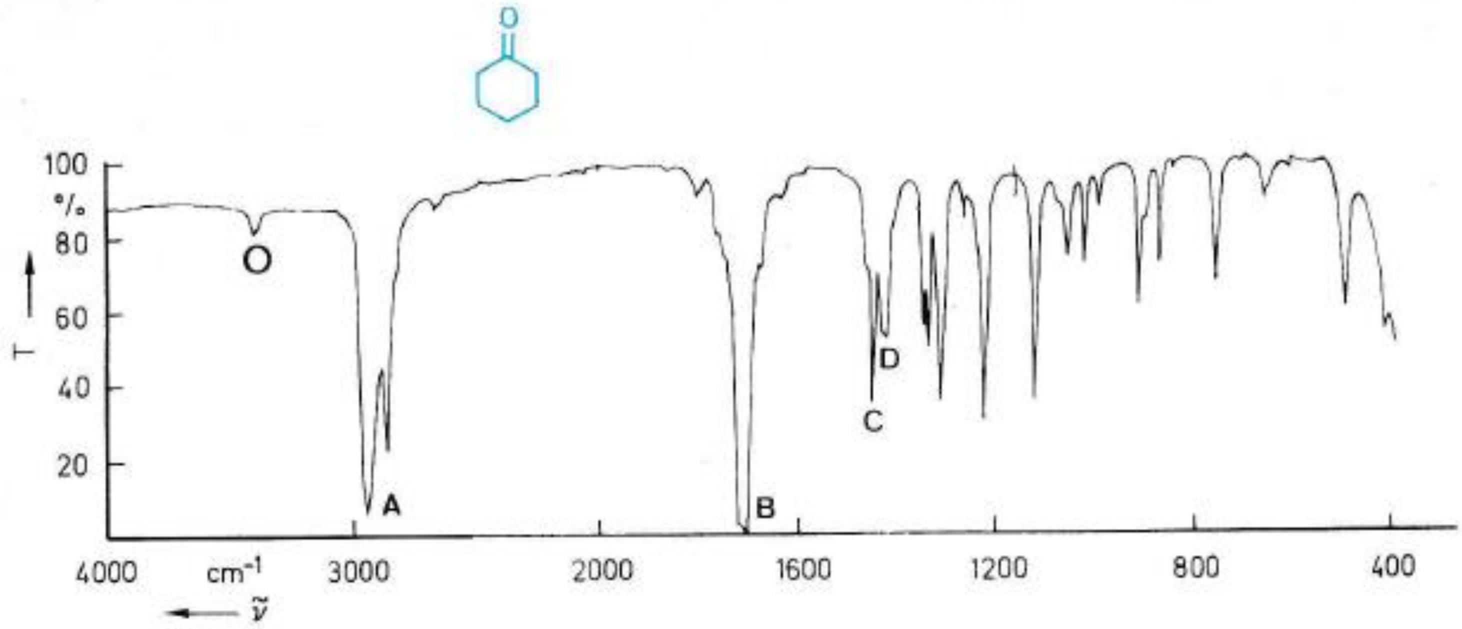


Fig. 2.17 Cyclohexanone (as liquid film)

O 3400 cm^{-1} overtone vibration of the carbonyl group (see also Fig. 2.20 and 2.9, p. 57 and 38)
A (C–H) stretching vibration $\nu_{as,s}(CH_3)$
B 1710 cm^{-1} (C=O) stretching vibration ν (C=O)
C 1450 cm^{-1} (C–H) bending vibration δ (CH_2)
D 1420 cm^{-1} (C–H) bending vibration next to C=O

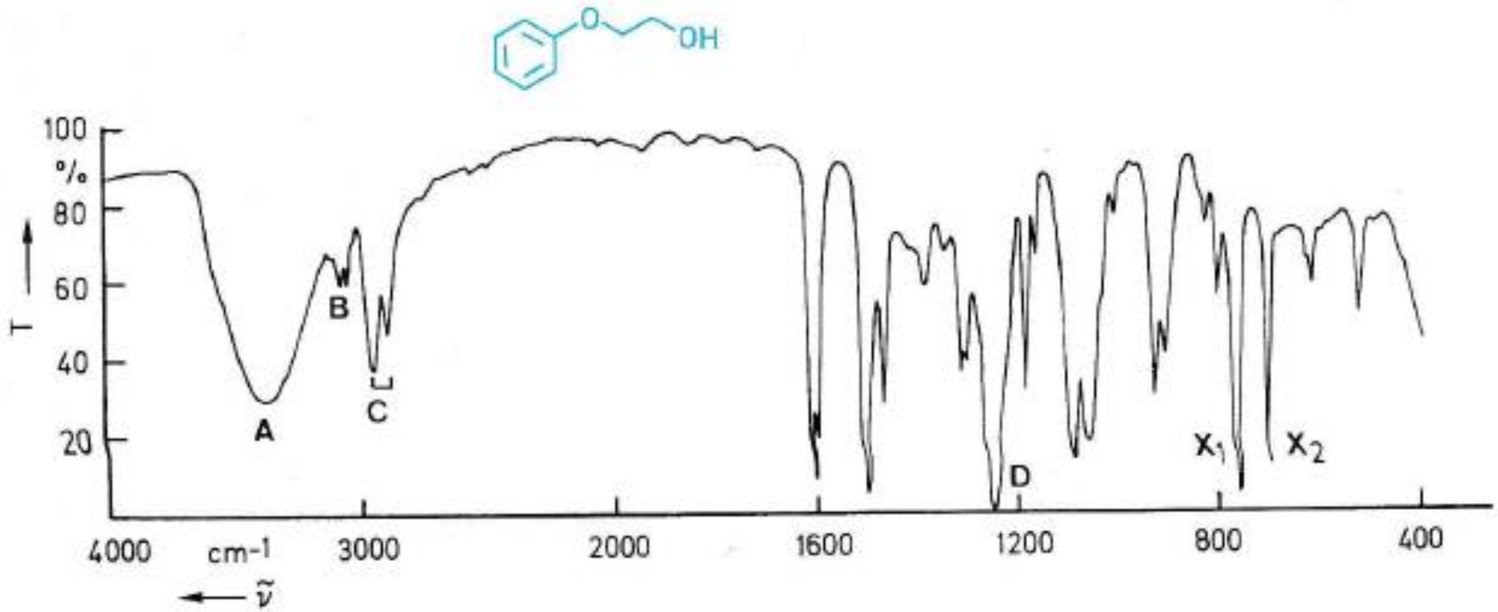


Fig. 2.18 2-Phenoxyethanol (as liquid film)
This example shows characteristic bands for an alcohol, an ether, and a monosubstituted aromatic ring

A	*≈ 3350 cm^{-1}*	*hydrogen bonded (O–H) stretching vibration*
B		(C–H) stretching vibration of the benzene ring
C		(C–H) stretching vibration of the CH_2 groups
D	1250 cm^{-1}	(C–O) stretching vibration in aryl alkyl ethers; dialkyl ether bands lie at lower frequency (Tab. 2.19)
X_1	760 cm^{-1}	monosubstituted aromatic, i.e. five neighbouring H-atoms
X_2	695 cm^{-1}	(cf. toluene, Fig. 2.23)

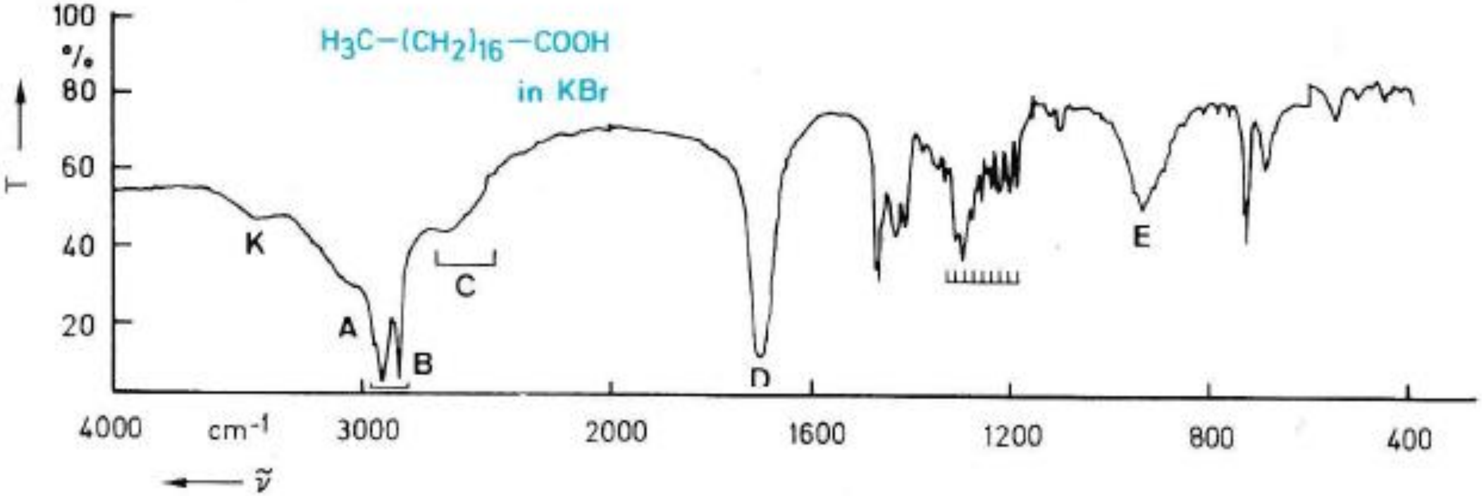


Fig. 2.19 Octadecanoic acid (stearic acid; in KBr)
Carboxylic acids associate by formation of hydrogen bonds (broad band for the dimeric form at 3000 cm^{-1}). The bending vibration of the hydrogen bonded complex at 930 cm^{-1} is also characteristic. In longer chains ($>C_{12}$) **progression bands** are observed in the solid state; these are equidistant bands between 1350 and 1200 cm^{-1}, which arise from the (*E*)-oriented CH$_2$ groups (**twisting** and **rocking** vibrations).

A	≈3000 cm^{-1}	very broad OH band from hydrogen bonds
B		overlapping (C–H) stretching vibrations $\nu_{as,s}$(CH$_2$, CH$_3$)
C	2700 to 2500 cm^{-1}	characteristic shoulders, arising from overtones and combination vibrations
D	1700 cm^{-1}	(C=O) stretching vibration
E	930 cm^{-1}	(O–H) bending vibration from hydrogen bonds
		O–H from traces of water in the KBr

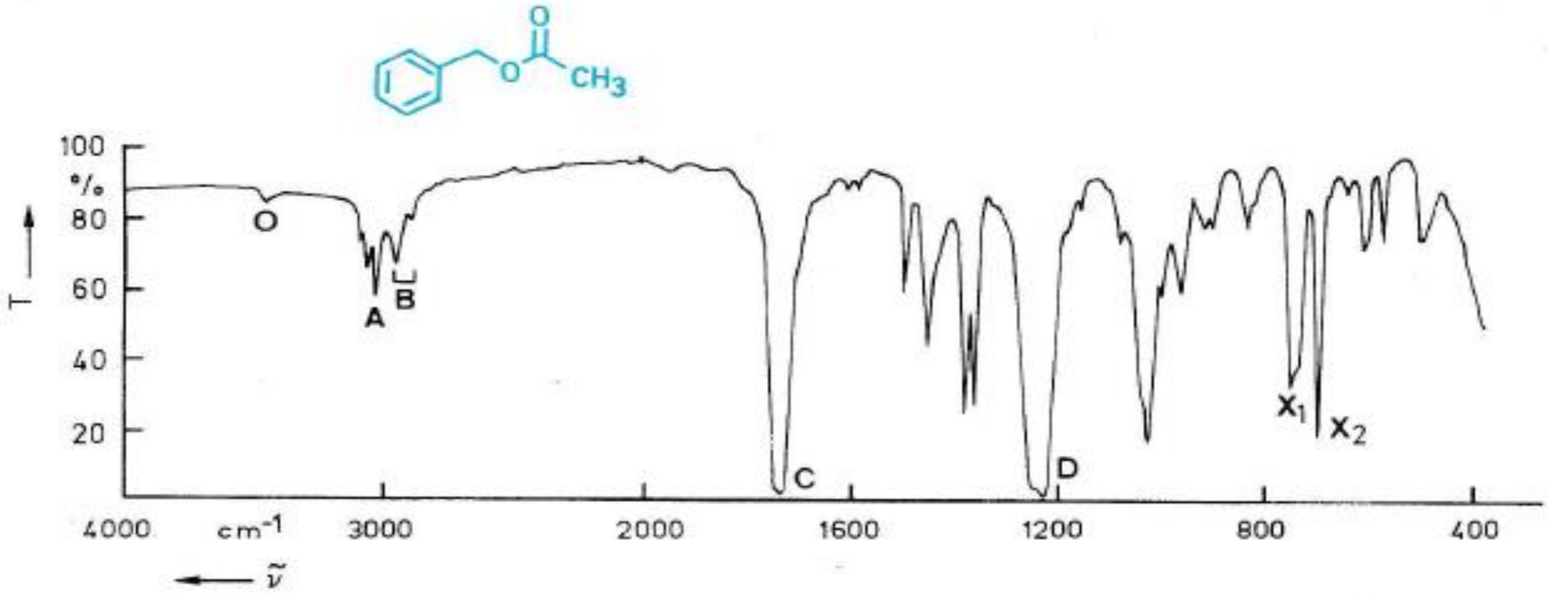


Fig. 2.20 Benzyl acetate (as liquid film)

O	3450 cm^{-1}	probably not traces of water, but overtone vibration of the carbonyl group (cf. Fig. 2.17)
A	3050 to 3020 cm^{-1}	(C–H) stretching vibration of the benzene ring
B	2960 to 2880 cm^{-1}	(C–H) stretching vibration of the CH_3 group
C	1740 cm^{-1}	(C=O) stretching vibration
D	1230 cm^{-1}	(C–O) stretching vibration; position is characteristic for the acetyl group
X_1	750 cm^{-1}	monosubstituted aromatic
X_2	700 cm^{-1}	(cf. toluene, Fig. 2.23)

$H_3C{-}CH_2{-}C{\equiv}N$

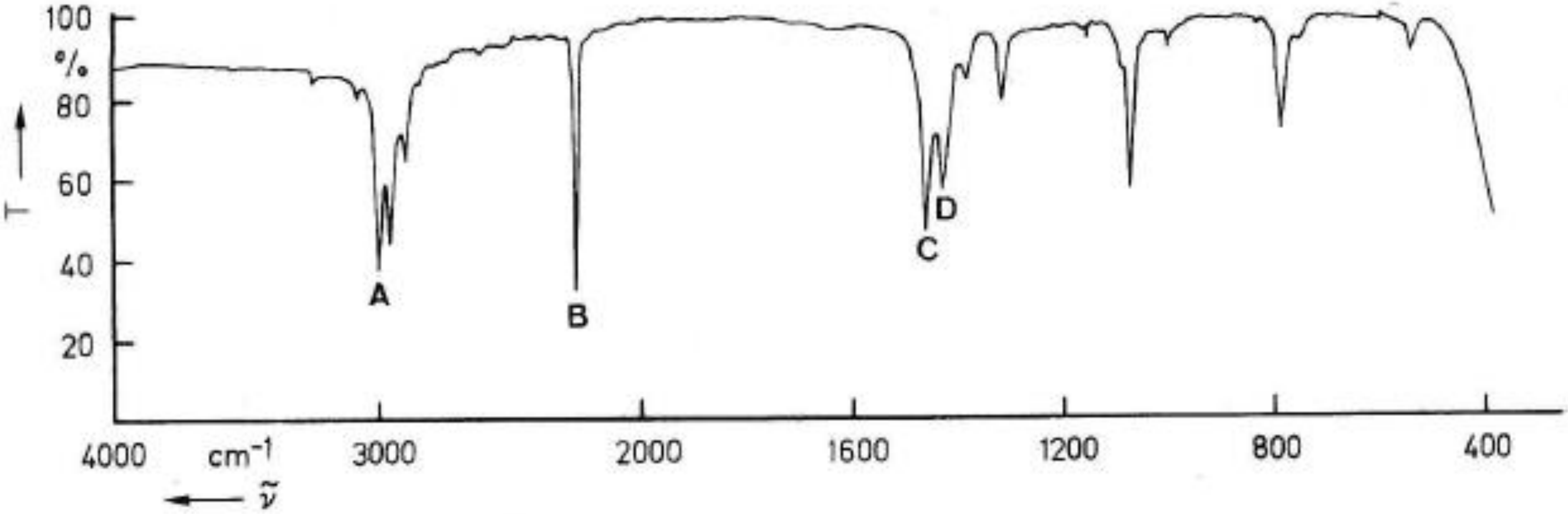


Fig. 2.21 Propionitrile (as liquid film)
Absorption bands in the region 2300–2000 cm⁻¹ are almost certain indicators of triple bonds (see Tab. 2.8, p. 47)

A (C–H) stretching vibrations $\nu_{as,s}(CH_2, CH_3)$
B 2250 cm⁻¹ ($C{\equiv}N$) stretching vibration
C 1460 cm⁻¹ (C–H) bending vibration
D 1430 cm⁻¹ (C–H) bending vibration next to $C{\equiv}N$

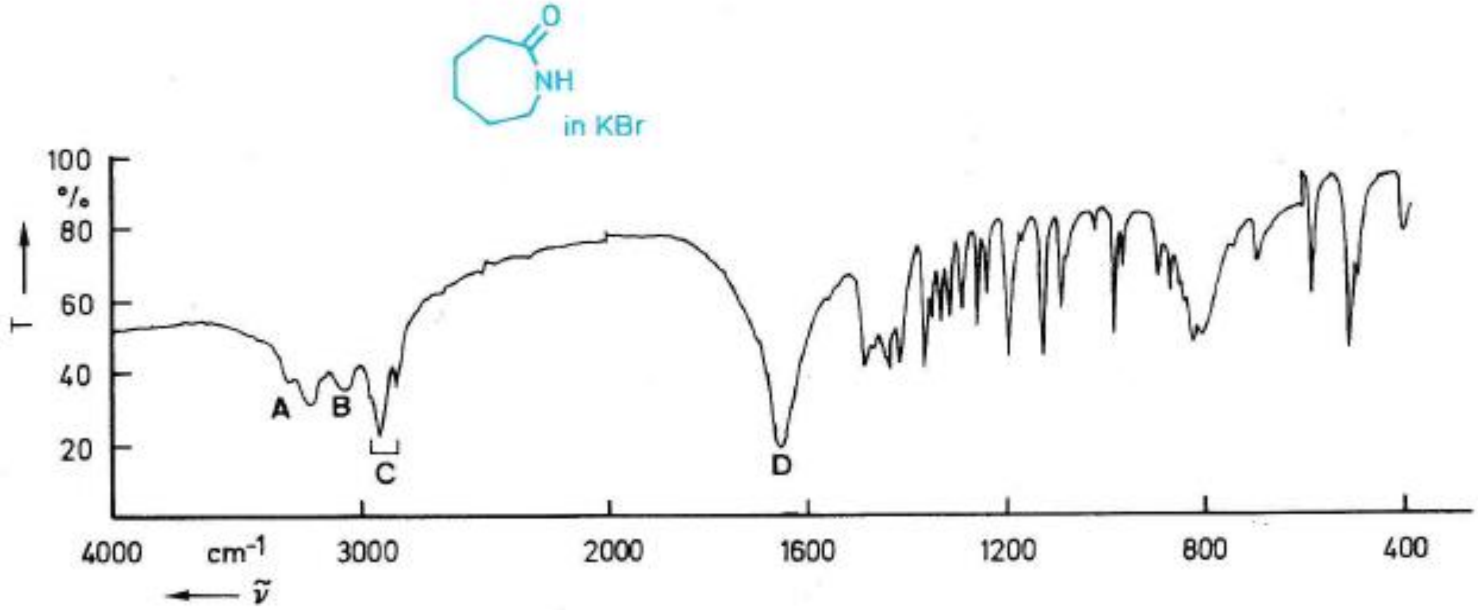


Fig. 2.22 ε-Caprolactam (hexahydro-2*H*-azepin-2-one) (in KBr)
Example of a cyclic carboxylic acid amide with absence of the amide II band (cf. Fig. 2.28a, p. 62). The many sharp bands in the fingerprint region are typical for aliphatic rings

A 3295 cm^{-1} (N–H) stretching vibrations in N-monosubstituted amides
3210 cm^{-1}
B 3100 cm^{-1} combination band ν(C=O) + δ (N–H)
C (C–H) stretching vibration $\nu_{as,s}(CH_2)$
D 1660 cm^{-1} (C=O) stretching vibration

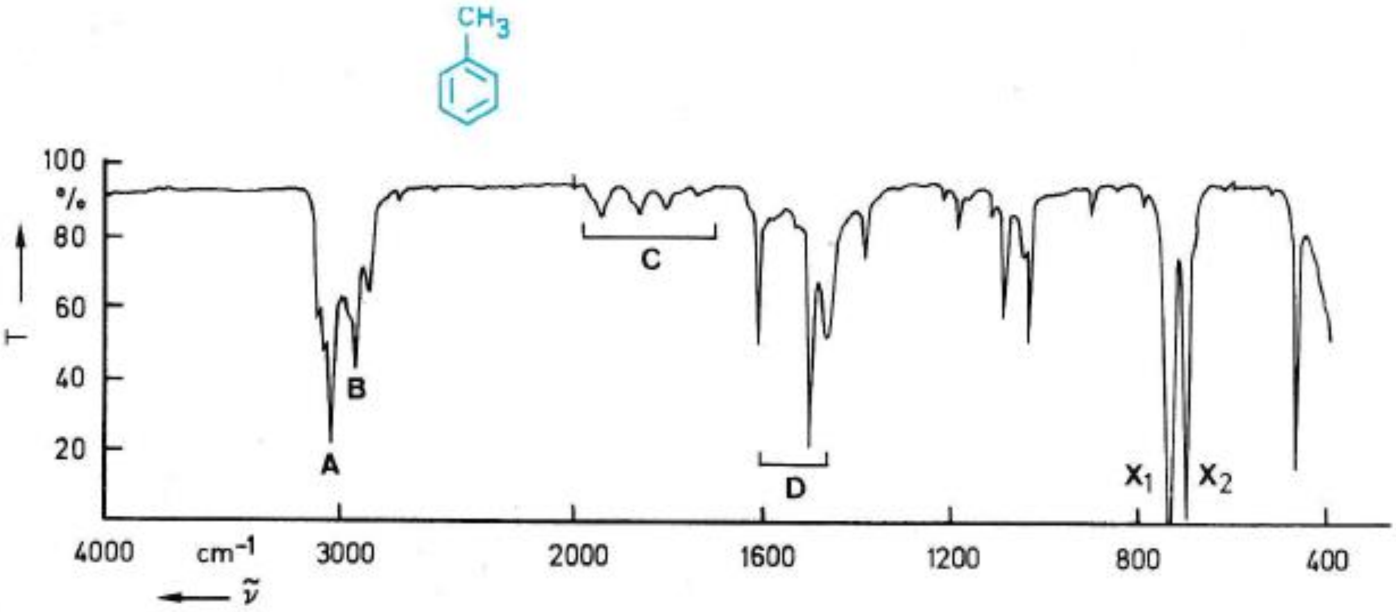


Fig. 2.23 Toluene (as liquid film)

A		aromatic (C–H) stretching vibrations
B		aliphatic (C–H) stretching vibrations
C		overtones and combination vibrations of aromatics
D		(C=C) stretching vibrations, typical of aromatics
$\mathbf{X}_1$	730 cm^{-1}	monosubstituted aromatic (five neighbouring H-atoms); H bending vibration (out of plane); (see Tab. 2.16, p. 53)
$\mathbf{X}_2$	695 cm^{-1}	ring bending vibration, also characteristic for a monosubstituted benzene

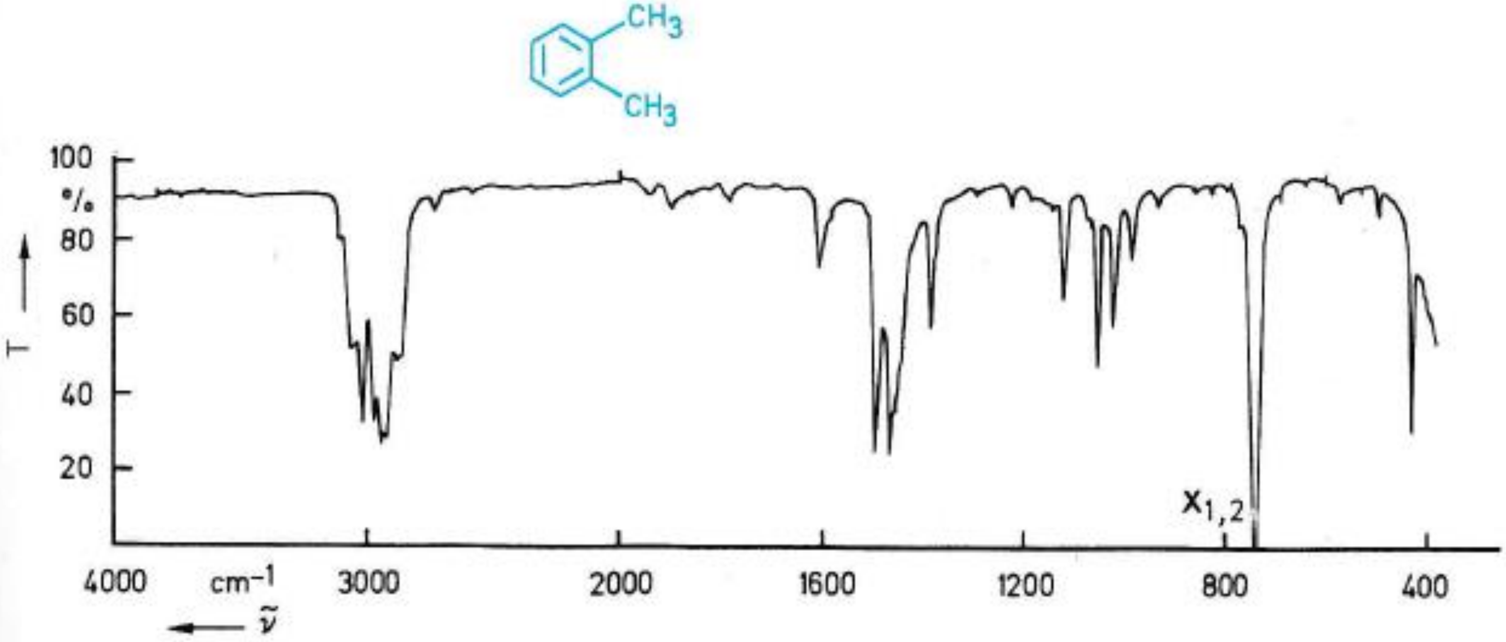


Fig. 2.24a 1,2-Dimethylbenzene (*o*-xylene) (as liquid film)

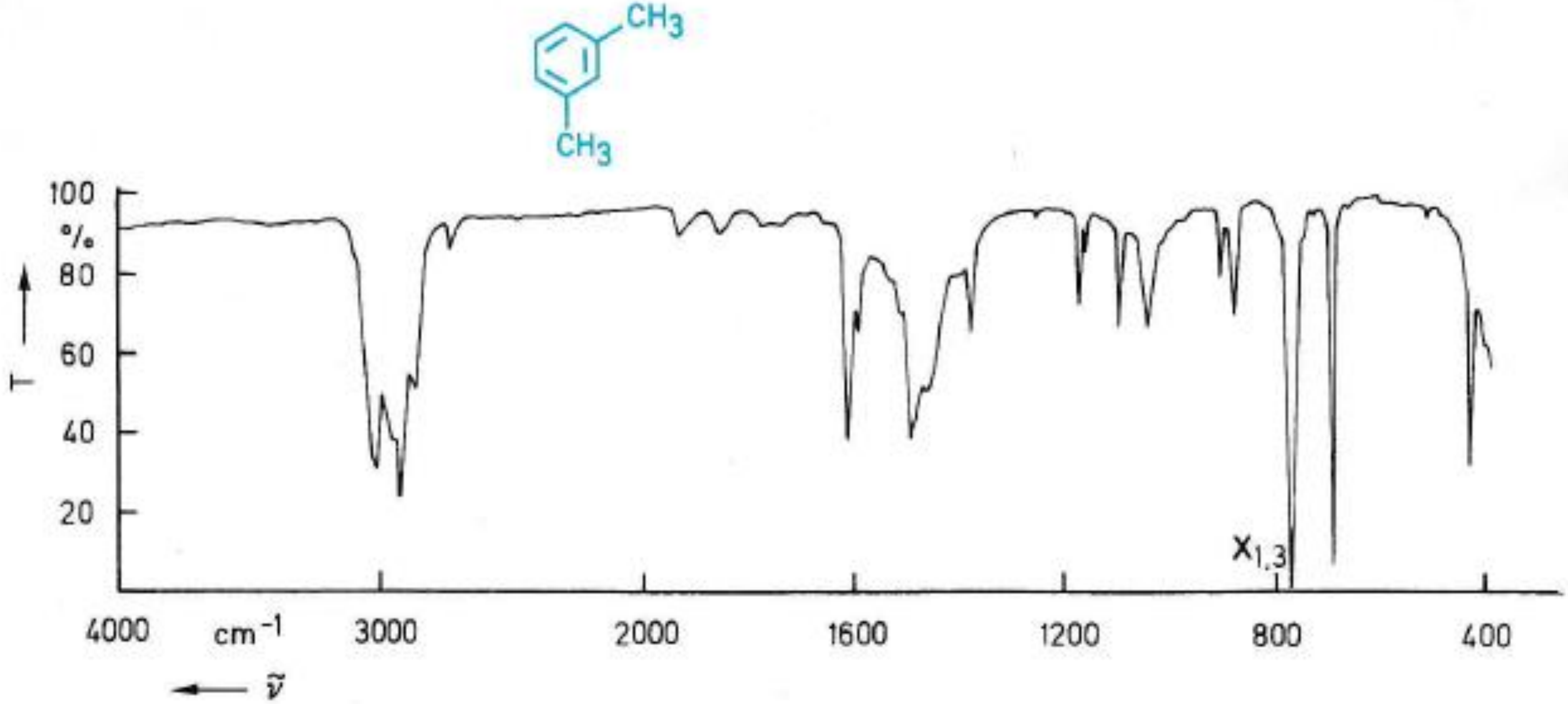


Fig. 2.24b 1,3-Dimethylbenzene (*m*-xylene) (as liquid film)

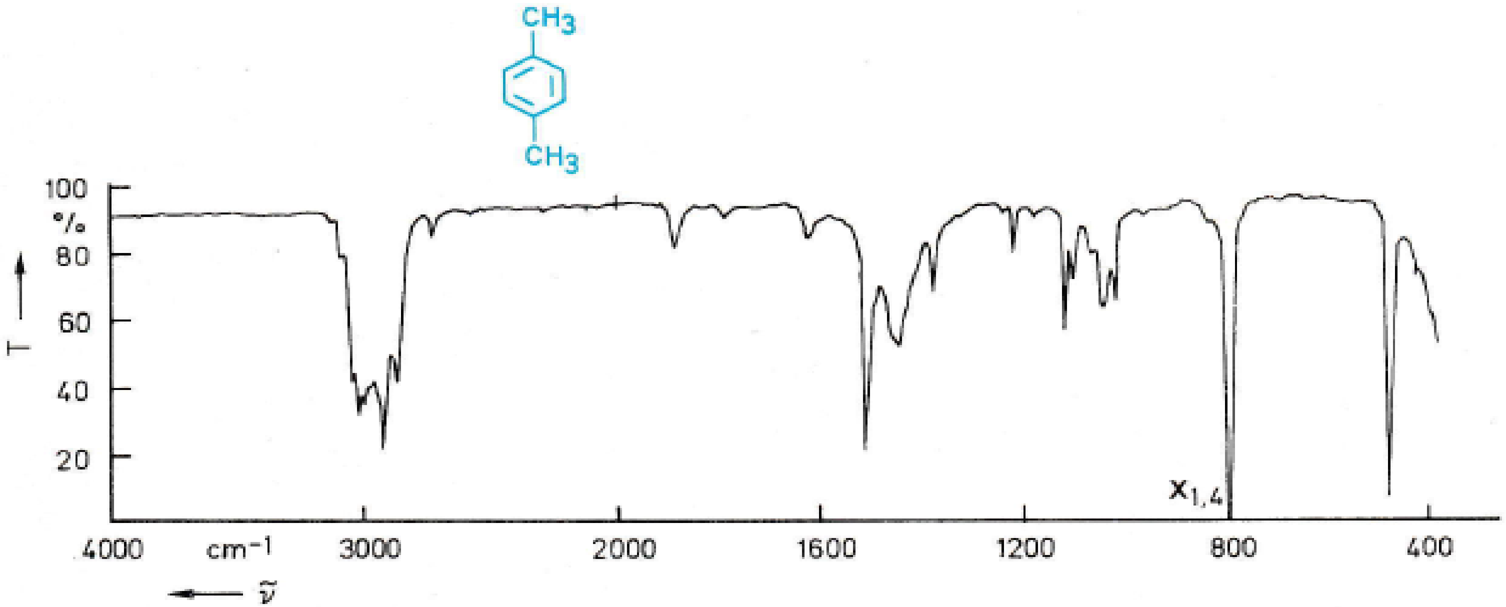


Fig. 2.24c 1,4-Dimethylbenzene (*p*-xylene) (as liquid film)

Determination of the substitution pattern from Tab. 2.16 (p. 53)

$X_{1,2}$ 740 cm^{-1} typical of four neighbouring H on an aromatic (1,2-disubstitution)
$X_{1,3}$ 770 cm^{-1} three neighbouring H (1,3-disubstitution).
$X_{1,4}$ 770 cm^{-1} two neighbouring H (1,4-disubstitution)
For the assignment of the remaining bands compare with the spectrum of toluene (see Fig. 2.23)

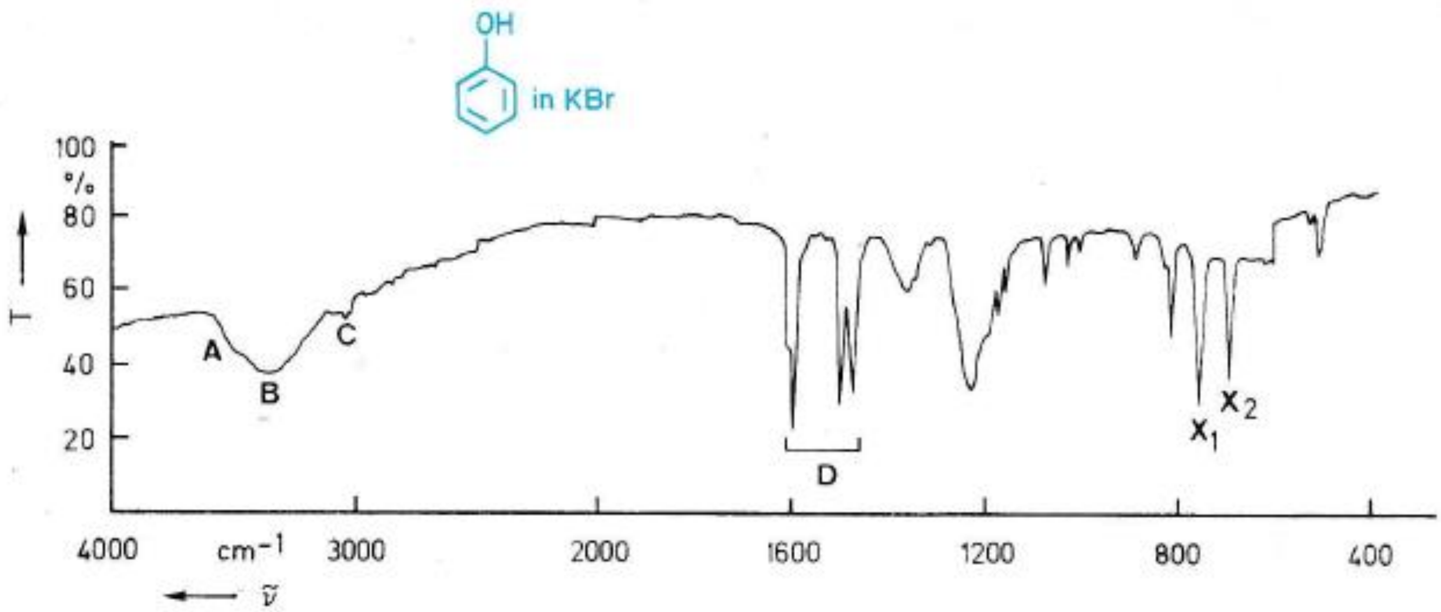


Fig. 2.25 Phenol (in KBr)

A 3500 cm^{-1} (O–H) stretching vibration in hydrogen bonded dimer
B 3360 cm^{-1} (O–H) stretching vibration in hydrogen bonded polymer
C 3040 cm^{-1} (C–H) stretching vibration in aromatic
D (C=C) stretching vibrations, typical of aromatics (cf. Fig. 2.33)
X_1 755 cm^{-1}
X_2 690 cm^{-1} monosubstituted aromatic (see Tab. 2.16, p. 53)

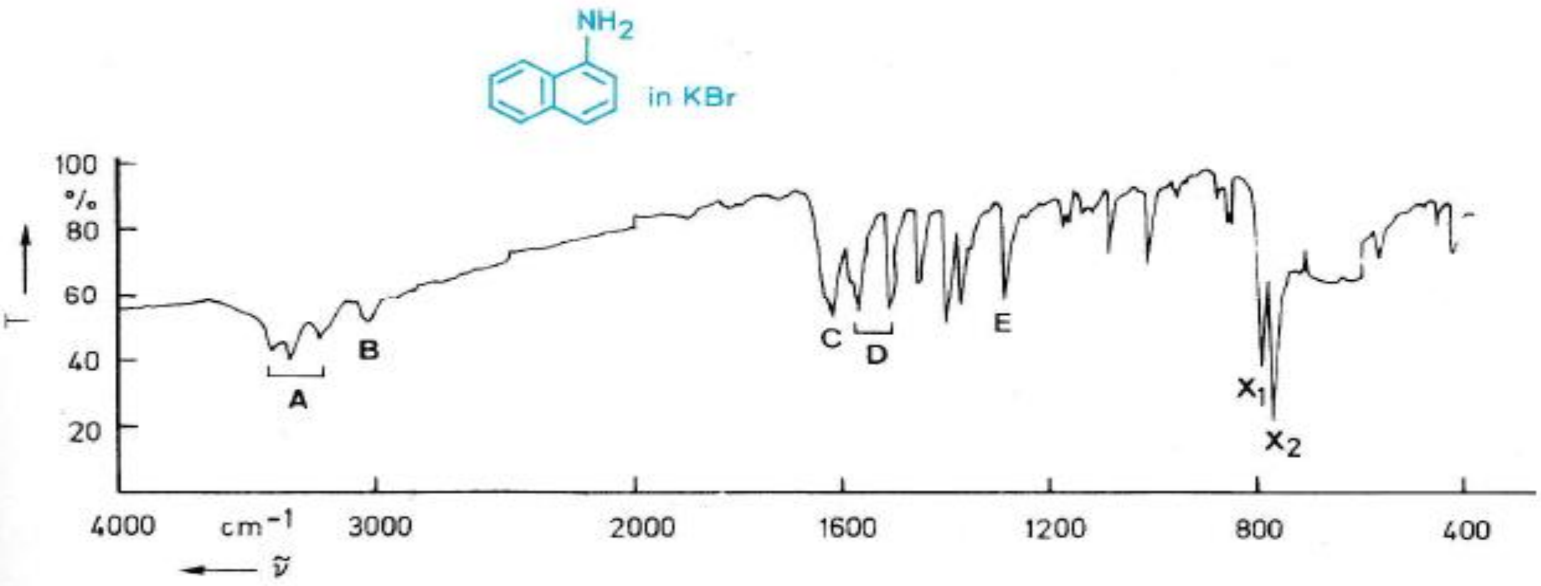


Fig. 2.26 1-Naphthylamine (in KBr)

A		(N–H) stretching vibration (various degrees of association)
B	3040 cm^{-1}	(C–H) stretching vibration in aromatic
C	1620 cm^{-1}	(N–H) bending vibration
D	1570 cm^{-1} 1510 cm^{-1}	aromatic (C=C) stretching vibrations
E	1290 cm^{-1}	(C–N) stretching vibration
X_1	795 cm^{-1}	monosubstituted aromatic (the values in Tab. 2.16 apply approximately to naphthalenes)
X_2	770 cm^{-1}	

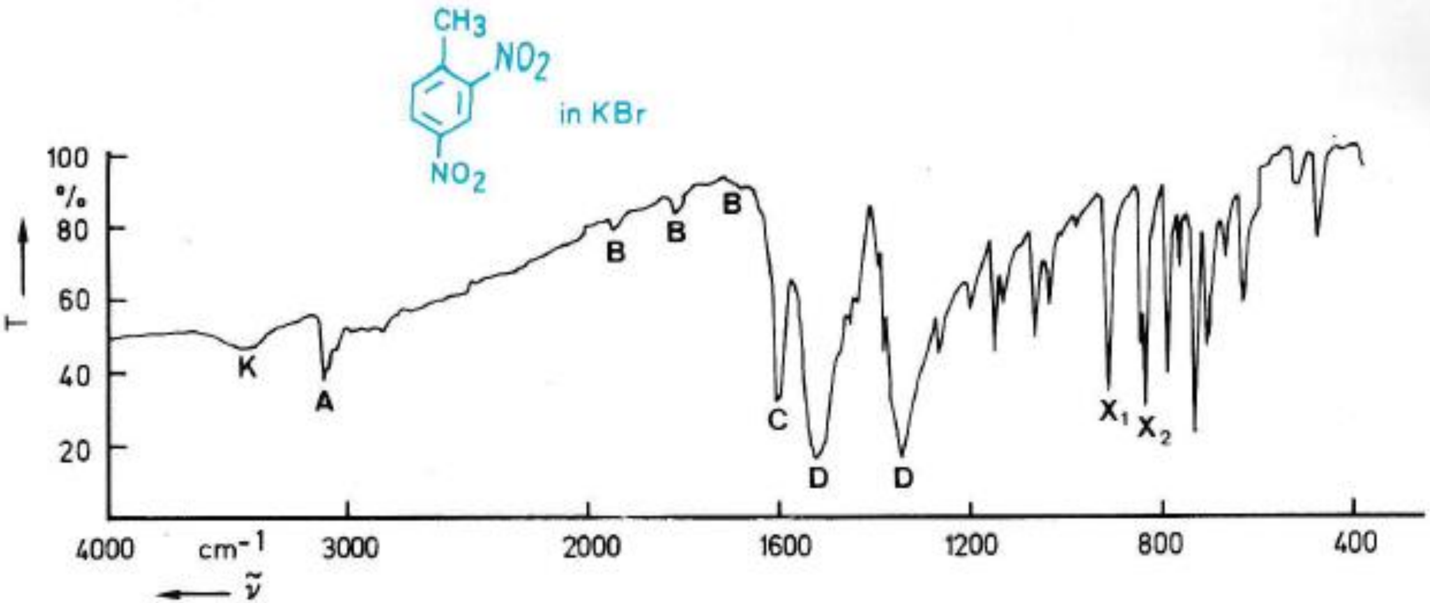


Fig. 2.27 2,4-Dinitrotoluene (in KBr)

A	3100 cm^{-1}	aromatic (C–H) stretching vibration
B		aromatic overtone vibrations
C	1600 cm^{-1}	aromatic (C=C) stretching vibrations
D	1520 cm^{-1}	asymmetric and symmetric N=O stretching vibration
	1340 cm^{-1}	(conjugated to aromatic system)
X_1	915 cm^{-1}	probably the two bands of the out-of-plane (C–H) bending vibrations
X_2	840 cm^{-1}	indicative of 1,2,4-substitution
K		traces of water in the KBr disc

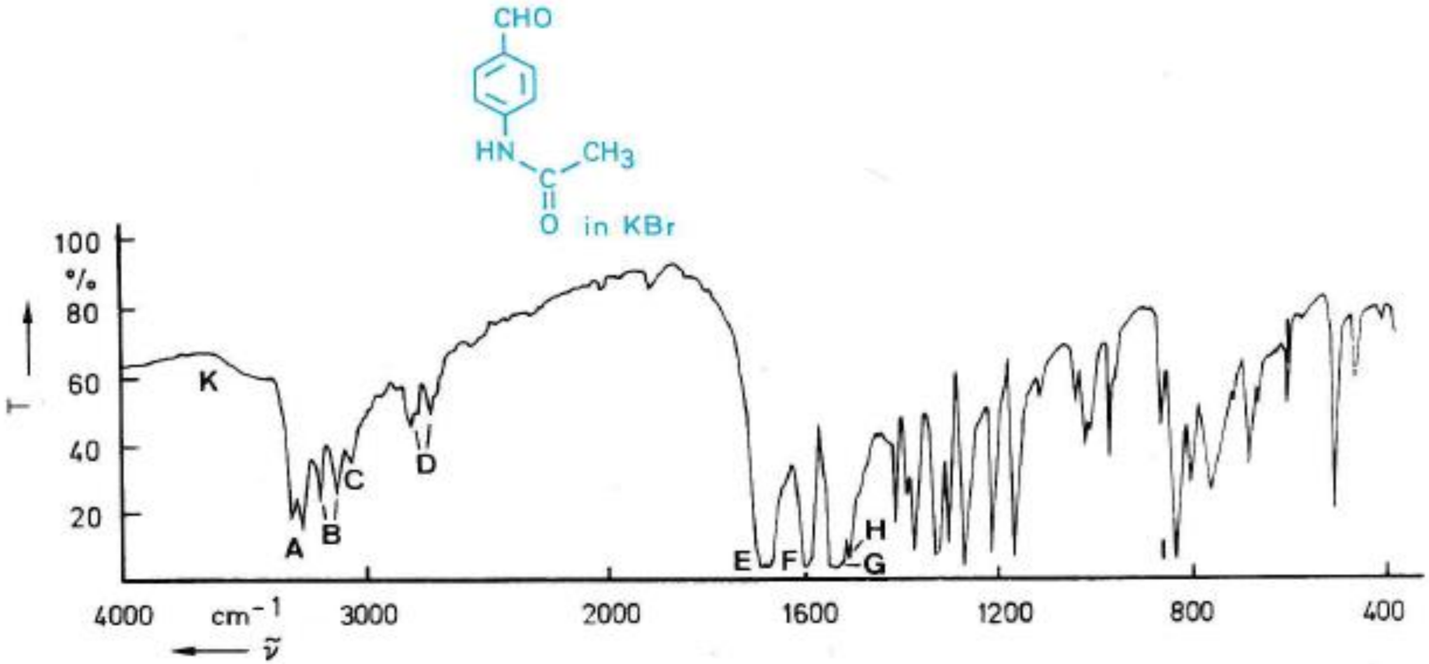


Fig. 2.28a 4-Acetylaminobenzaldehyde (in KBr)

A 3300 and 3260 cm^{-1} N–H in N-monosubstituted amides
B 3190 and 3110 cm^{-1} amide bands of unknown origin
C 3060 cm^{-1} aromatic C–H
D 2810 and 2730 cm^{-1} C–H in aldehydes
E 1690 and 1670 cm^{-1} aldehyde-carbonyl and amide I
F 1600 cm^{-1} benzene ring
G 1535 cm^{-1} amide II
H 1515 cm^{-1} benzene ring
I 835 cm^{-1} *p*-disubstituted benzene ring
K shoulder of an OH band from traces of water in the KBr disc

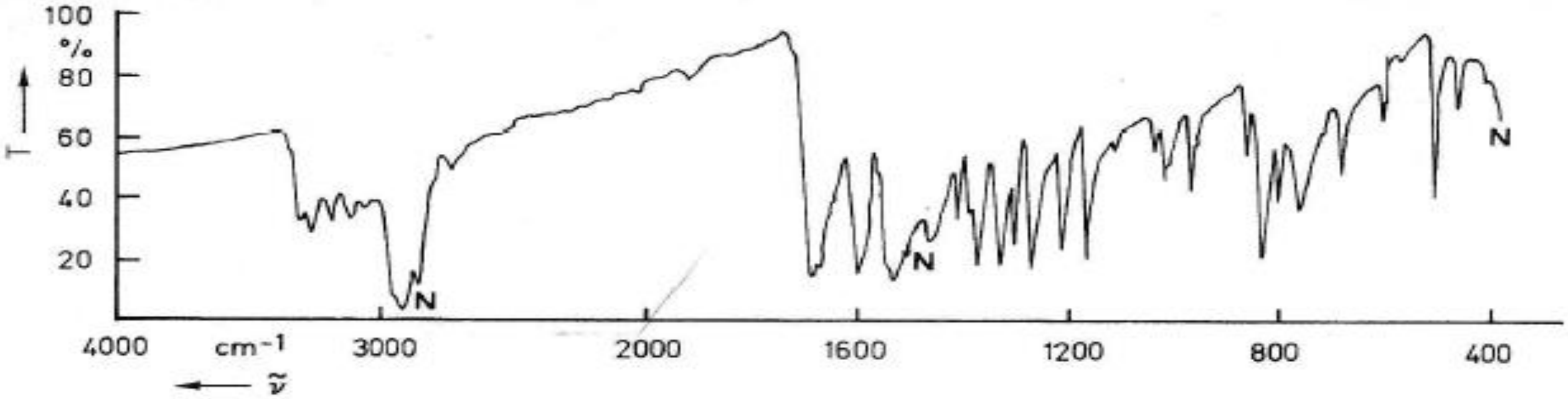


Fig. 2.28b 4-Acetylaminobenzaldehyde (in Nujol)

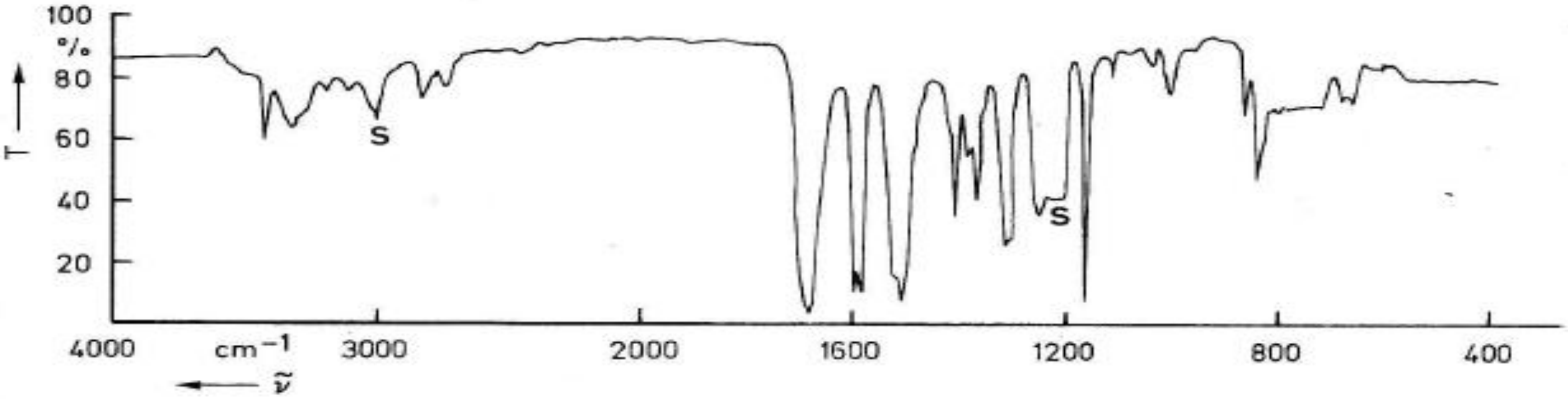


Fig. 2.28c 4-Acetylaminobenzaldehyde (in $CHCl_3$)

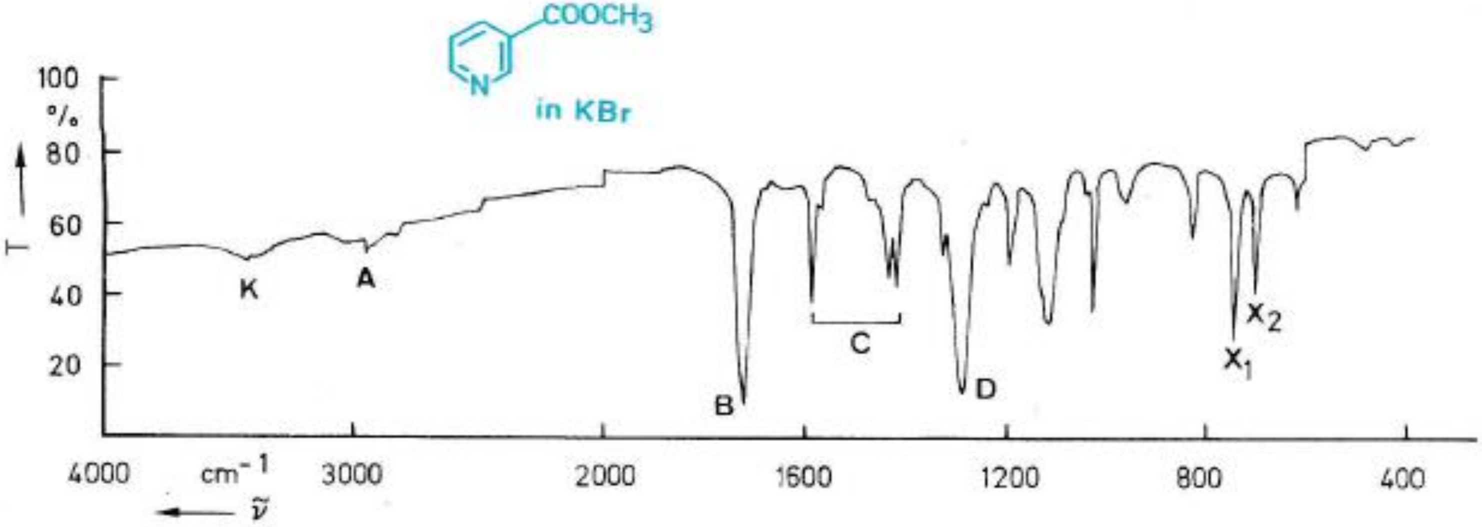


Fig. 2.29 Nicotinic acid methyl ester (in KBr)

A 2950 cm^{-1} (C–H) stretching vibration ν (CH_3); the aromatic (C–H) stretching vibration is only weakly visible (above 3000 cm^{-1})
B 1725 cm^{-1} (C=O) stretching vibration; (C=C) and (C=N) stretching vibration
D 1290 cm^{-1} (C–O) stretching vibration
X_1 745 cm^{-1} monosubstituted aromatic (the values in Tab. 2.16 apply approximately to pyridines)
X_2 705 cm^{-1}
K traces of water in the KBr disc

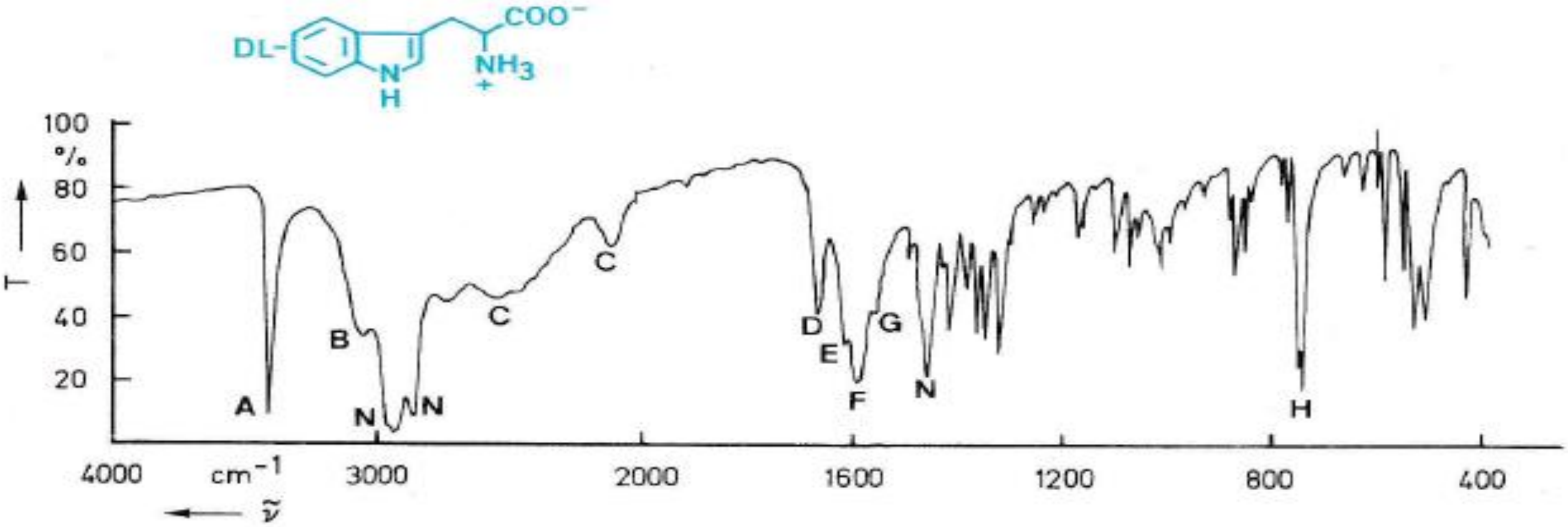


Fig. 2.30 D,L-Tryptophan (in Nujol)

A	3400 cm^{-1}	indole (N–H) stretching vibration
B	3030 cm^{-1}	broad "ammonium" band from $-NH_3^+$
C	≈2500 and ≈2100 cm^{-1}	two bands, very common in amino acids, also appear in primary ammonium salts
D	1665 cm^{-1}	amino acid I; unusually strong
E	1610 cm^{-1}	probably aryl group
F	1585 cm^{-1}	amino acid II; ionised carboxyl group $-COO^-$
G	1555 cm^{-1}	$-NH_3^+$ bending vibration
H	755 or 745 cm^{-1}	(C–H) out-of-plane bending vibrations of a 1,2-disubstituted benzene ring
N		Nujol bands

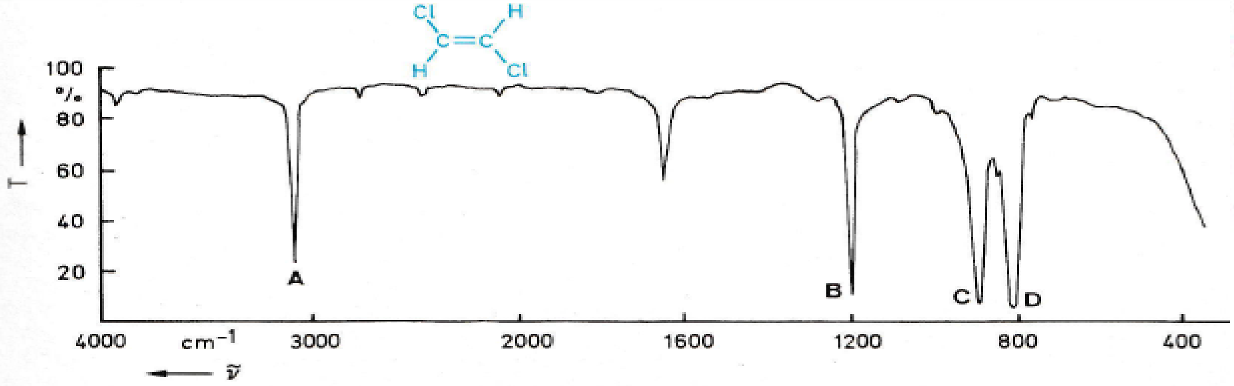


Fig. 2.34 IR spectrum of dichloroethylene

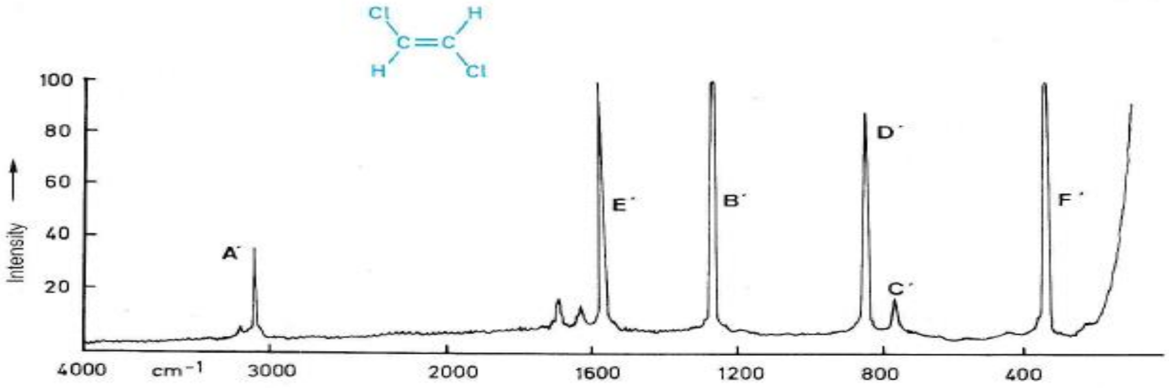
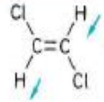
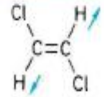
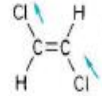
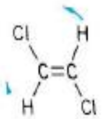
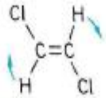
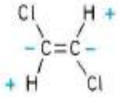
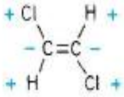
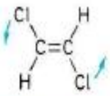


Fig. 2.35 Laser Raman spectrum of (*E*)-dichloroethylene

Tab. 2.22 Assignment of the bands in Figs. 2.34 and 2.35

vibration type	anti-symmetric vibration (IR active)	IR band Fig. 2.34 (cm⁻¹)	symmetric vibration (Raman active)	Raman band Fig. 2.35 (cm⁻¹)
ν(C—H)		3090 (**A**)		3070 (**A'**)
ν(C—Cl)		817 (**D**)		844 (**D'**)
δ(C—H)		1200 (**B**)		1270 (**B'**)
γ(C—H)		895 (**C**)		760 (**C'**)
ν(C=C)	–	–		1576 (**E'**)
δ(C—Cl)	below 300 cm⁻¹ in IR	–		350 (**F'**)