

INFRARED SPECTROSCOPY

Infra red region can be divided into three sections:

Region	Wavelength range (mm)	Wavenumber range (cm⁻¹)
Near	0.78 - 2.5	12800 - 4000
Middle	2.5 - 50	4000 - 200
Far	50 - 1000	200 - 10

The most useful I.R. region lies between 4000 - 670cm⁻¹.

MOLECULAR VIBRATION

NUMBER OF VIBRATIONAL MODES

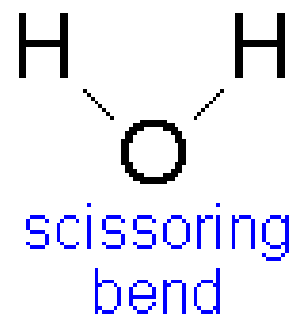
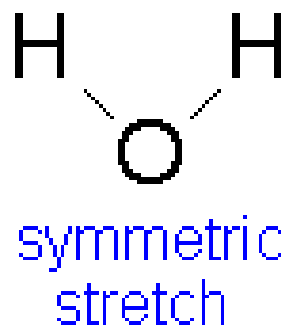
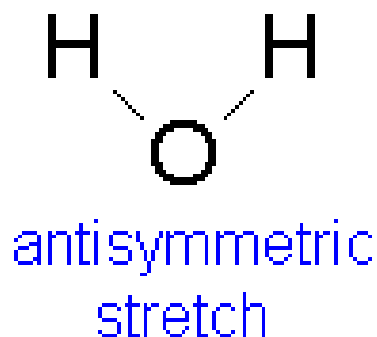
Degree of freedom for molecule = Total number of degrees of freedom of component atoms

If a molecule has N number of atoms then degree of freedom = $3N$

Non-linear molecule = $3N-6$ degrees of freedom for vibration

Linear molecule = $3N-5$ degrees of freedom for vibration

VIBRATIONAL MODES OF H₂O



VIBRATIONAL MODES OF CO₂



symmetric
stretch

inactive
no dipole
change



antisymmetric
stretch

active



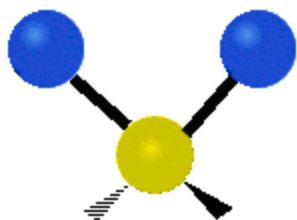
δ_{xz}



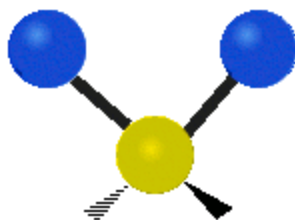
δ_y

degenerate
same energy
one band

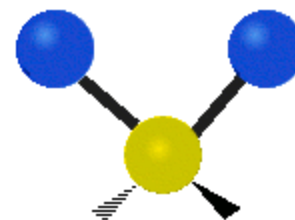
Polyatomic Molecular Vibration



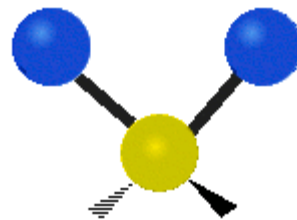
Symmetric Stretch



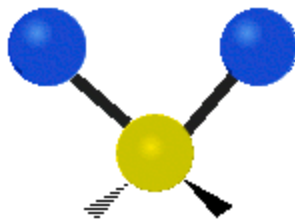
Asymmetric Stretch



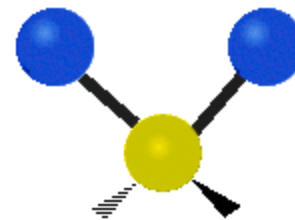
Twisting



Wagging



Scissoring



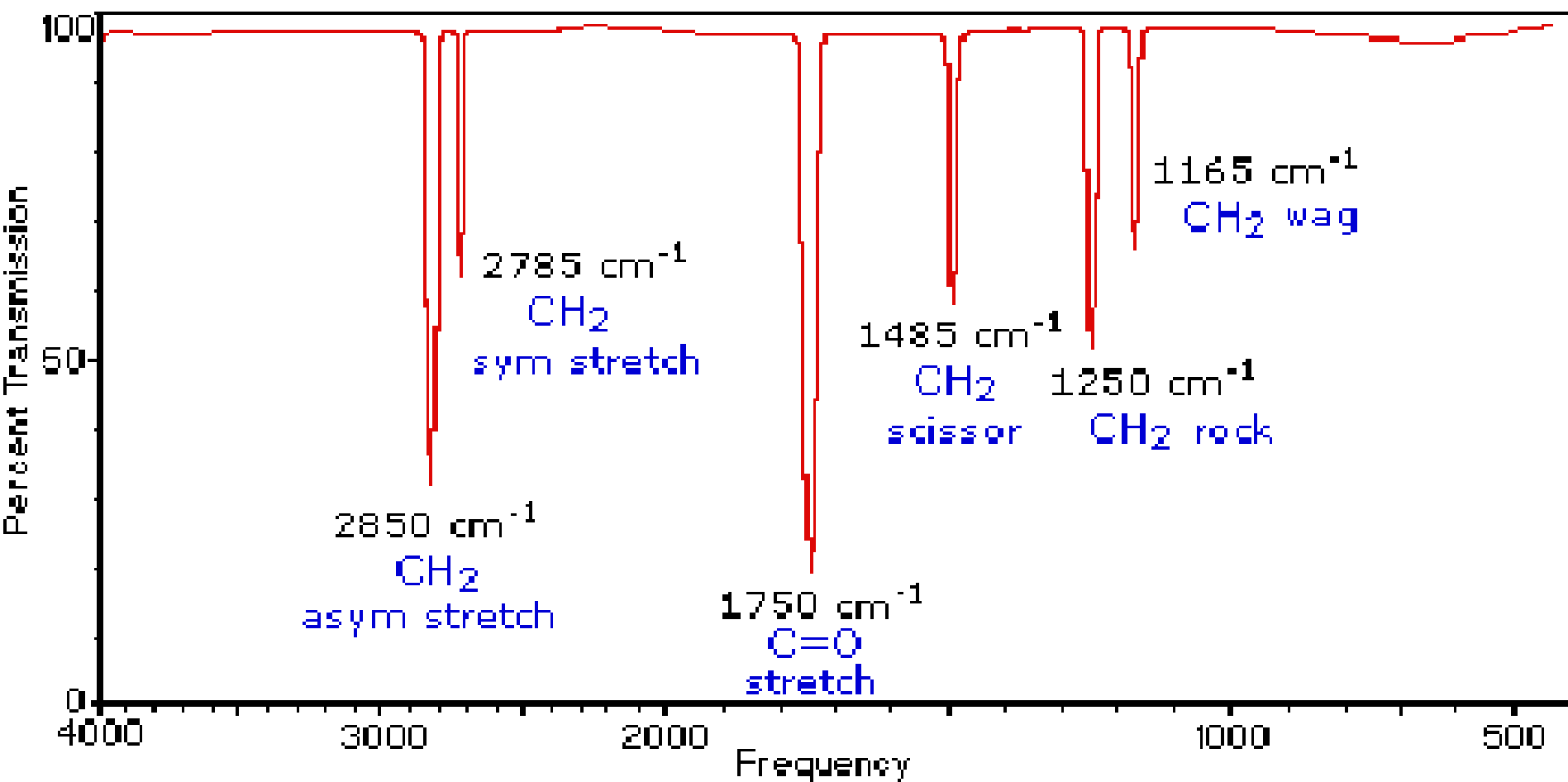
Rocking

For a molecule to be IR active following criteria has to be met

1. The natural frequency of vibration of the molecule should equal the vibration of IR radiation.

2. There should be a net change in dipole moment as the molecule vibrates.

FORMALDEHYDE



Important parameters in all IR spectra:

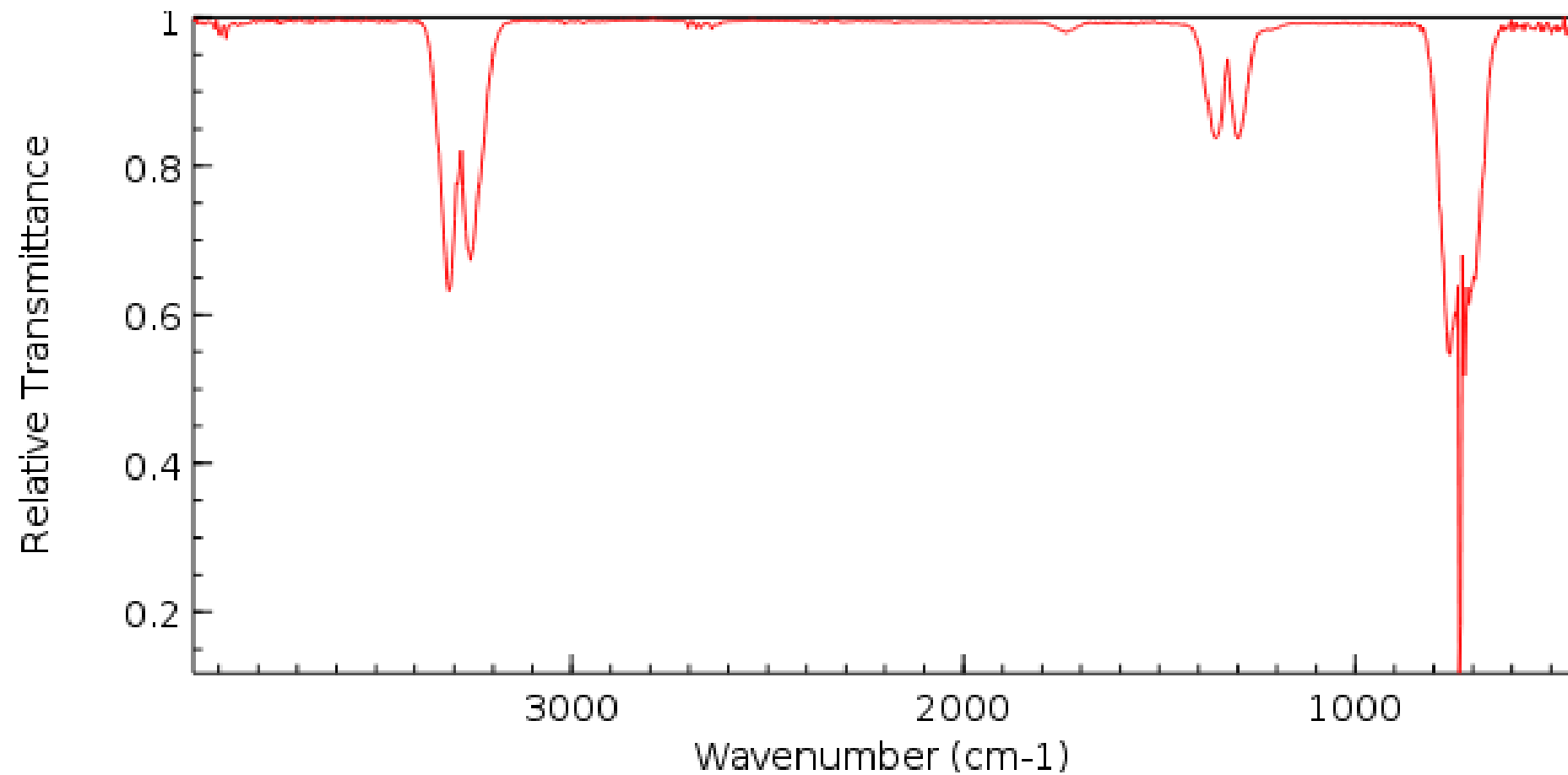
The frequency of the signal, ν

The intensity of the signal, I

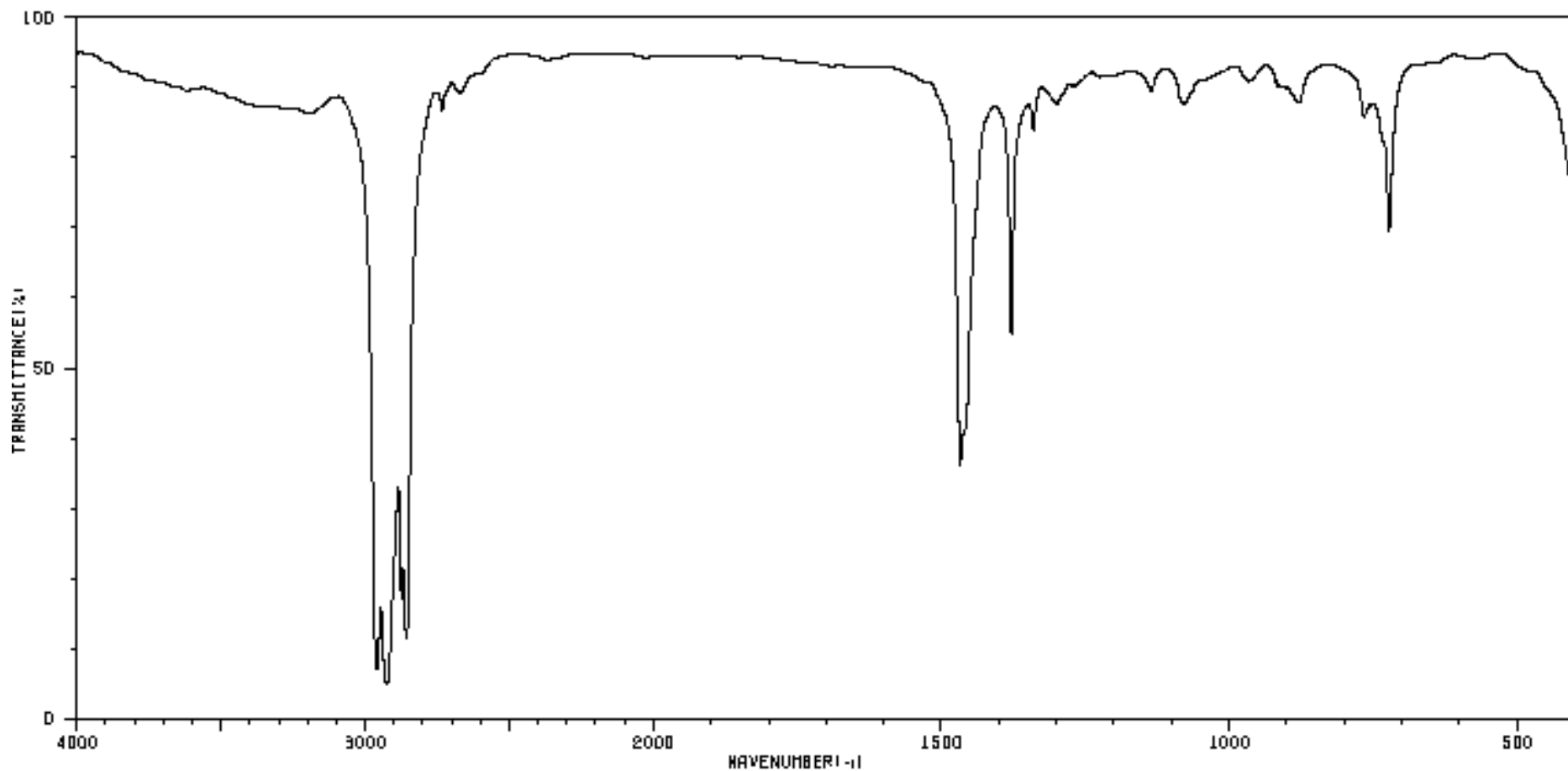
The width of the signal, w

The frequency of the signal, ν

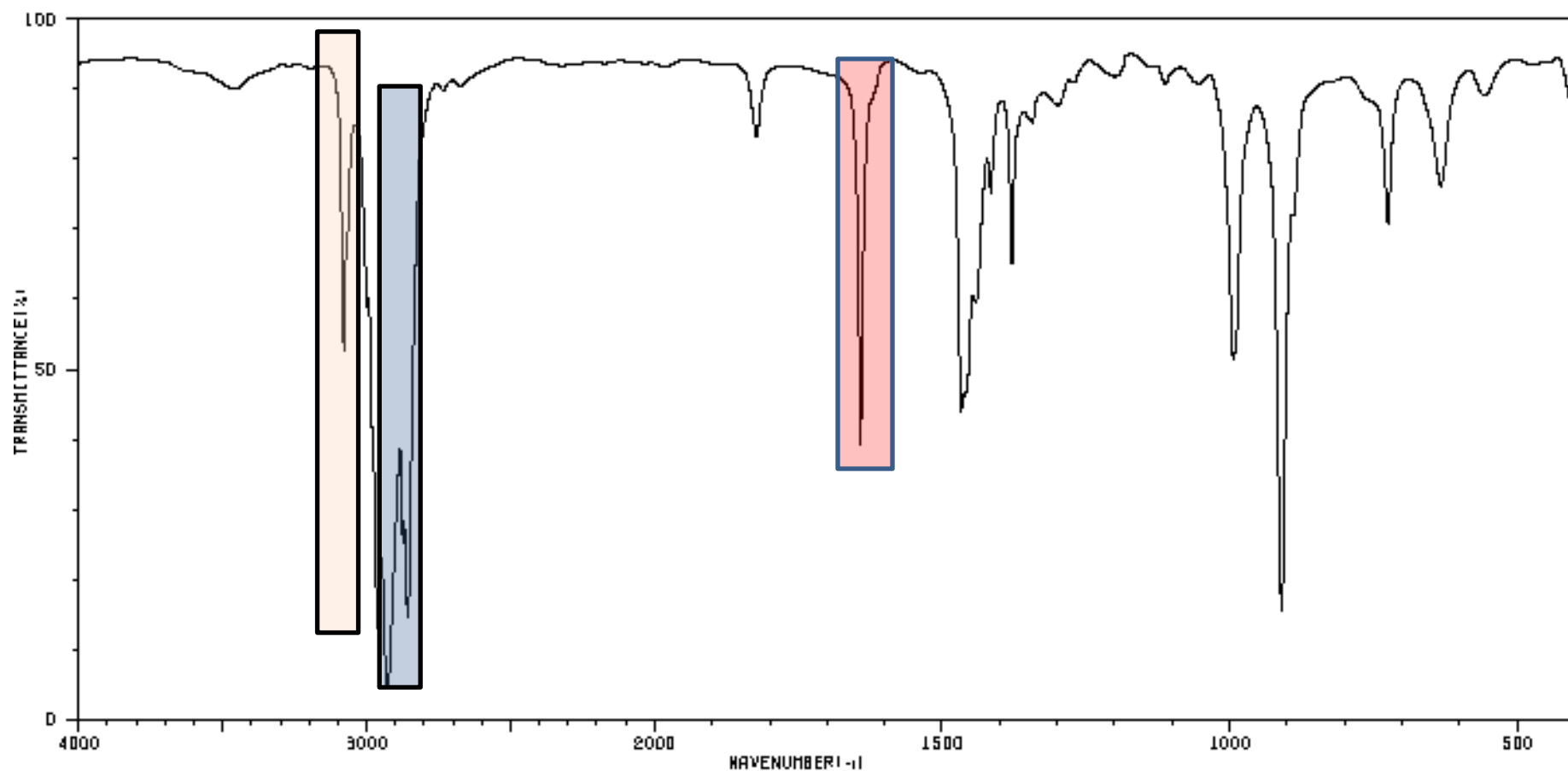
ACETYLENE



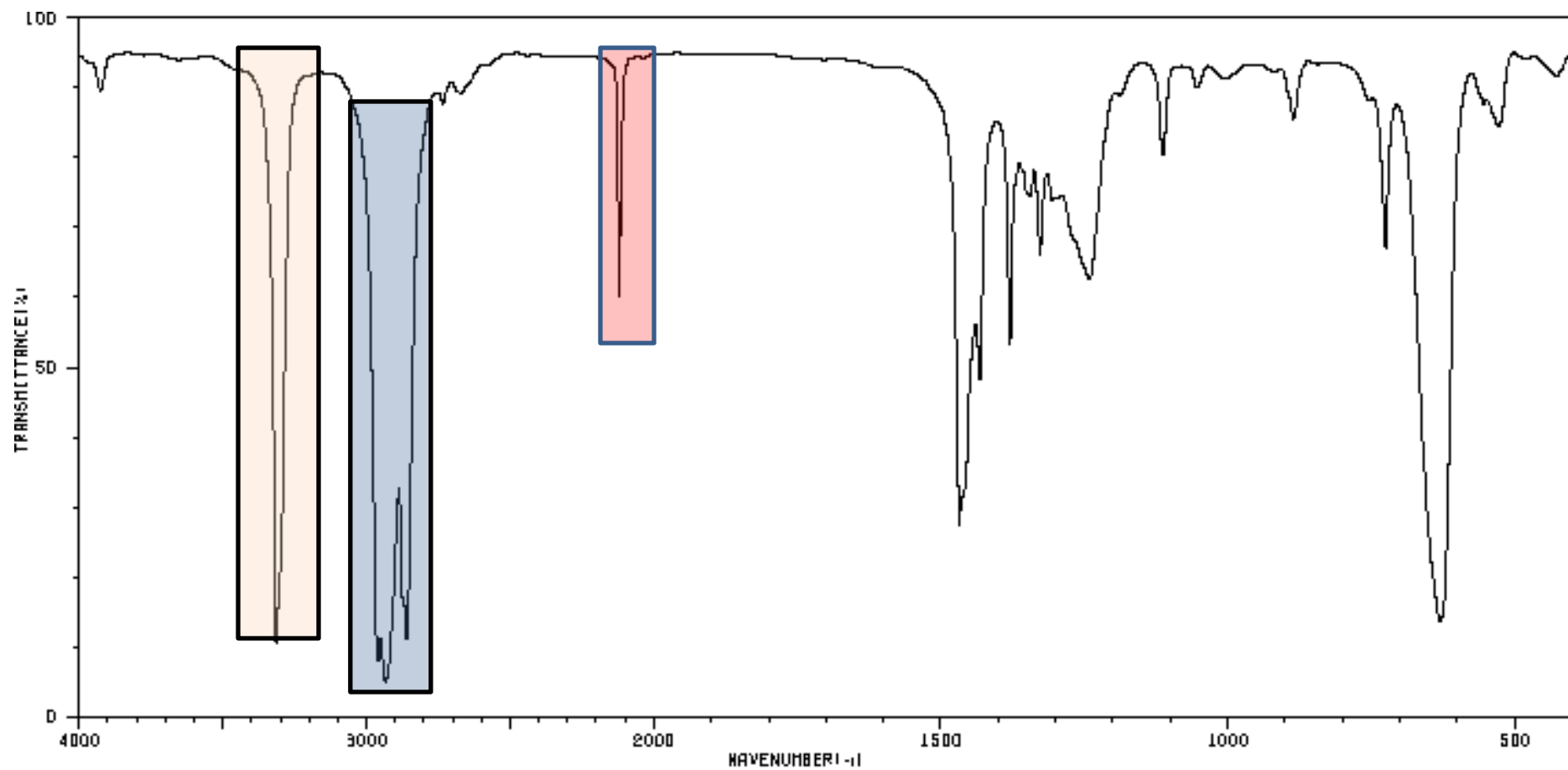
OCTANE



1-OCTENE

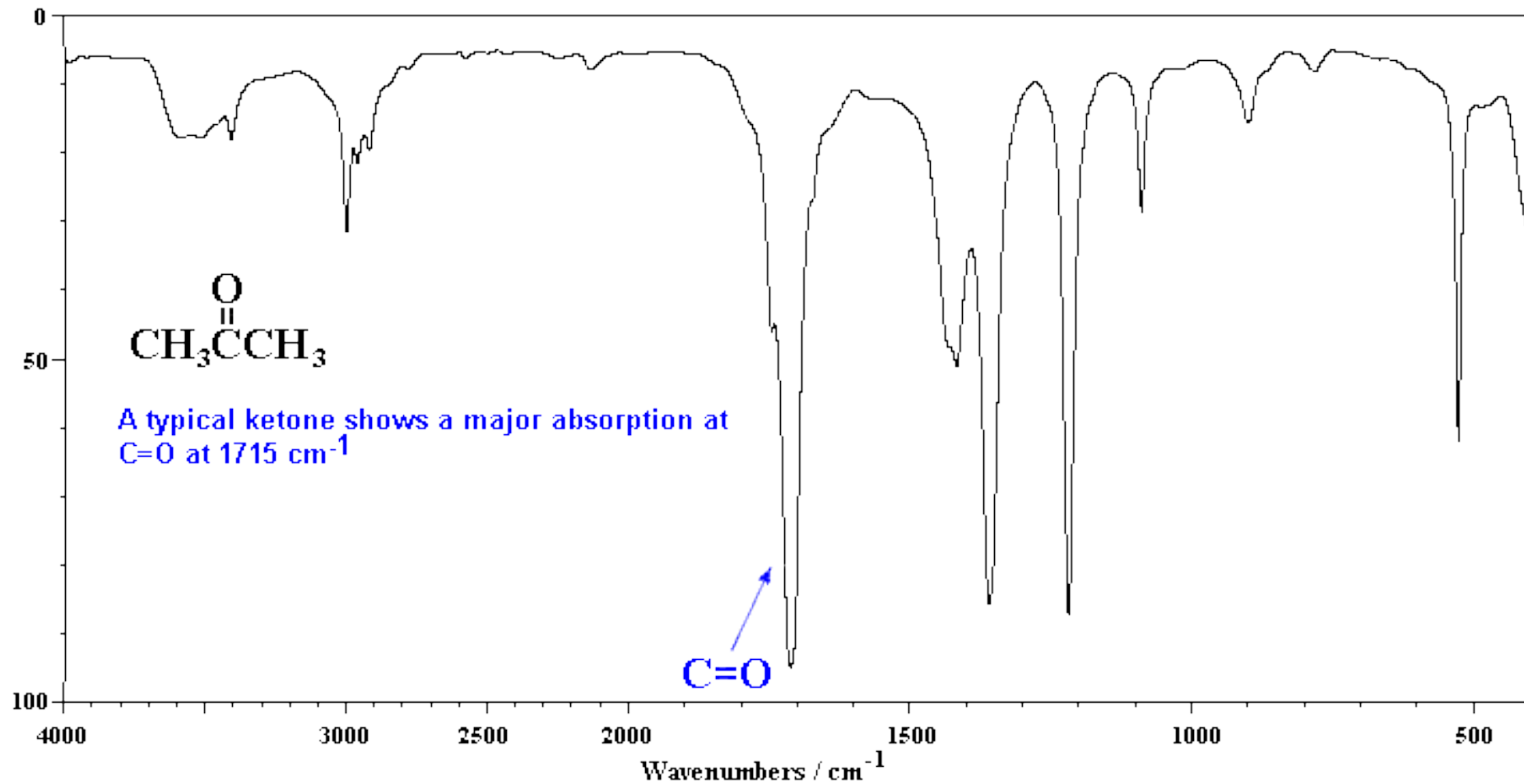


1-OCTYNE

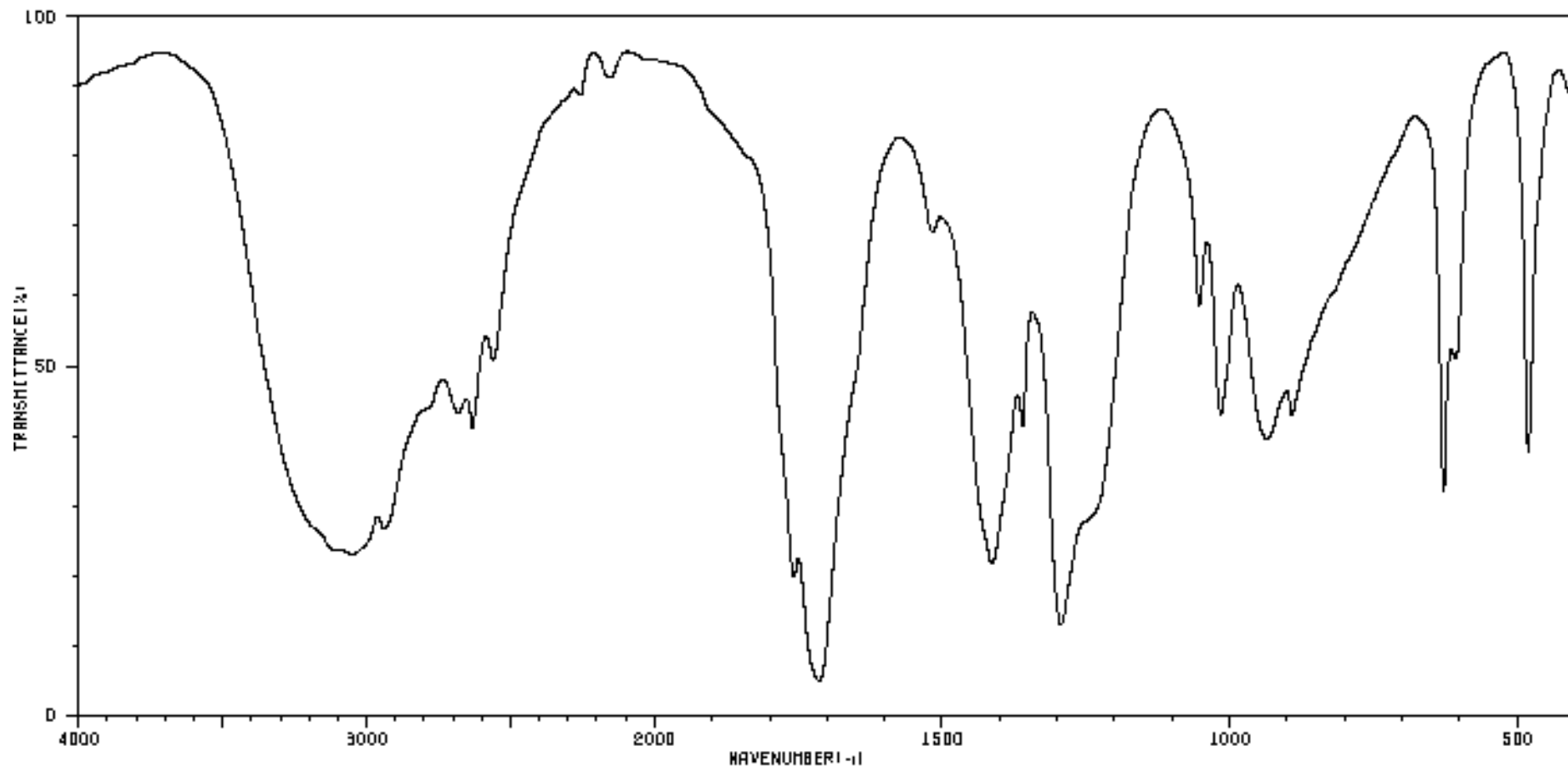


ACETONE

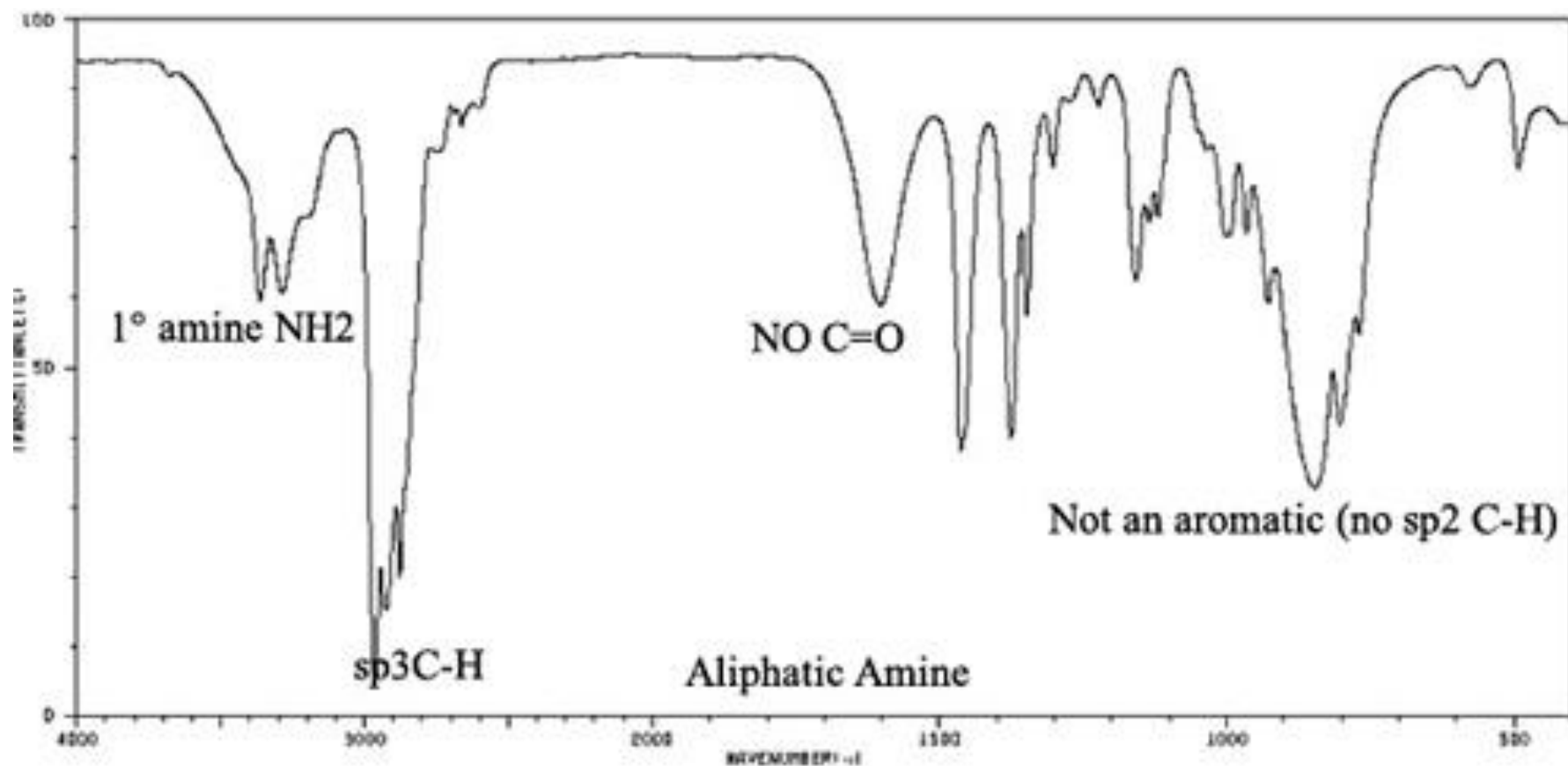
Absorbance / %



ACETIC ACID



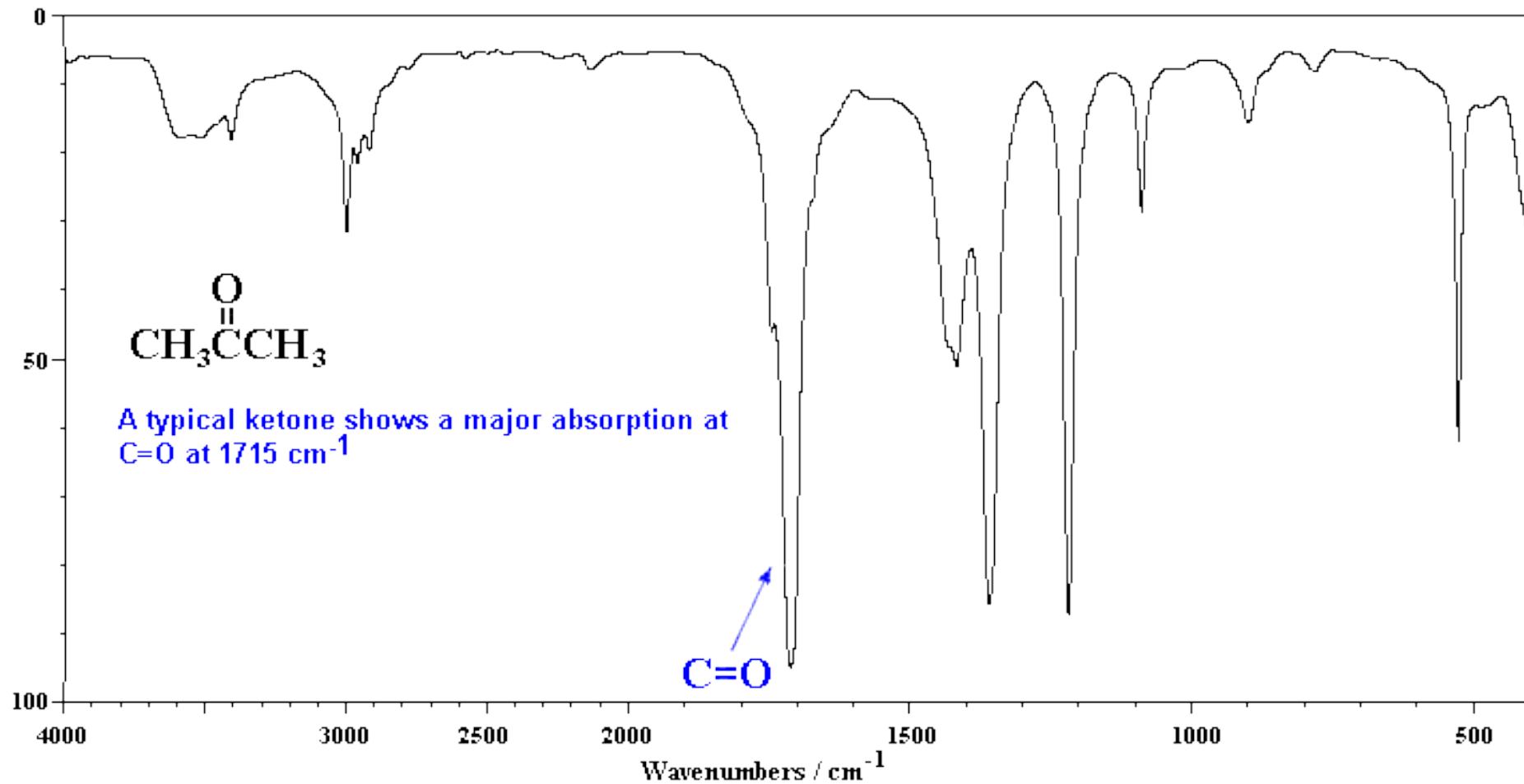
PRIMARY AMINE



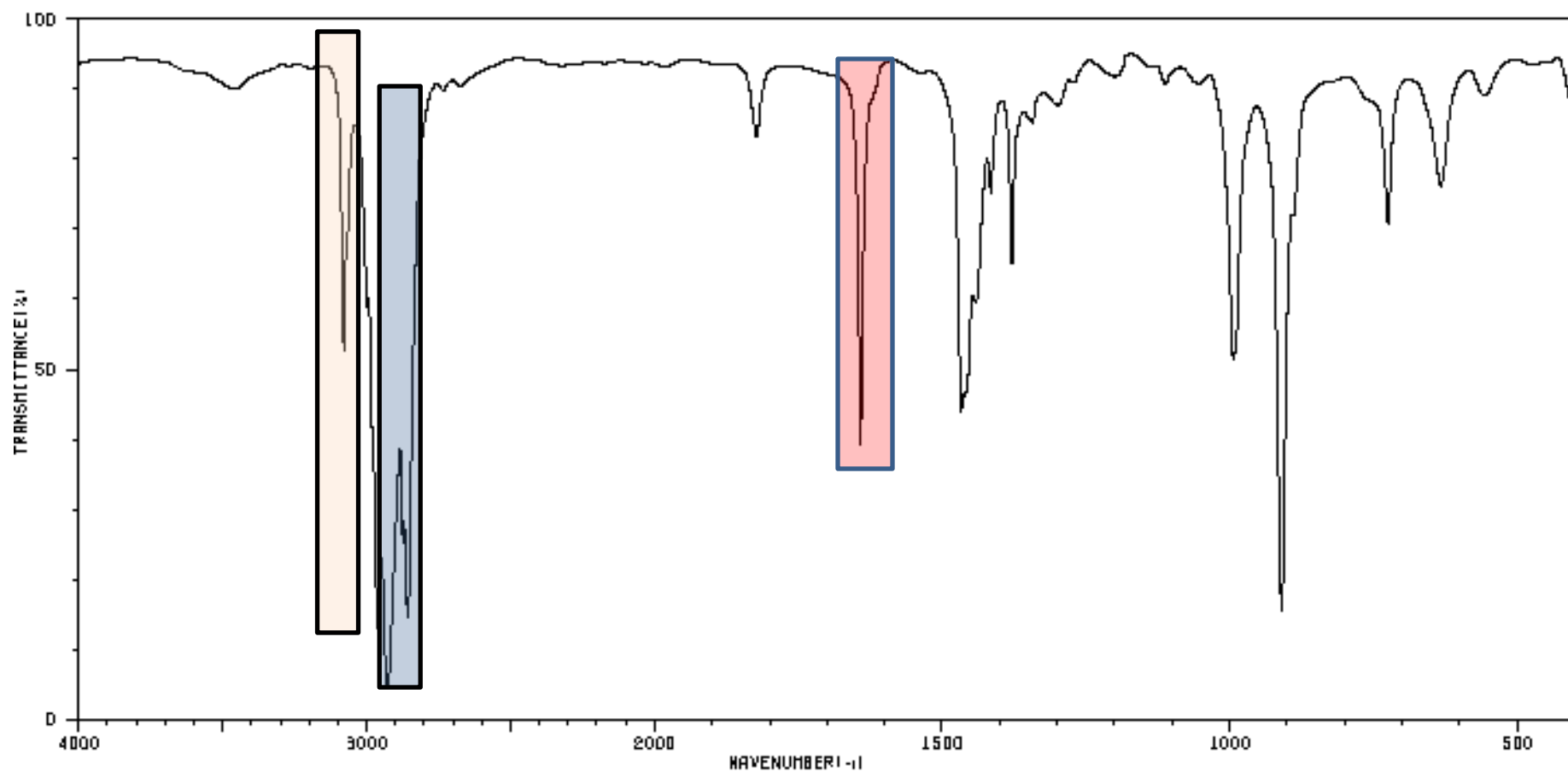
The intensity of the signal, I

ACETONE

Absorbance / %



1-OCTENE



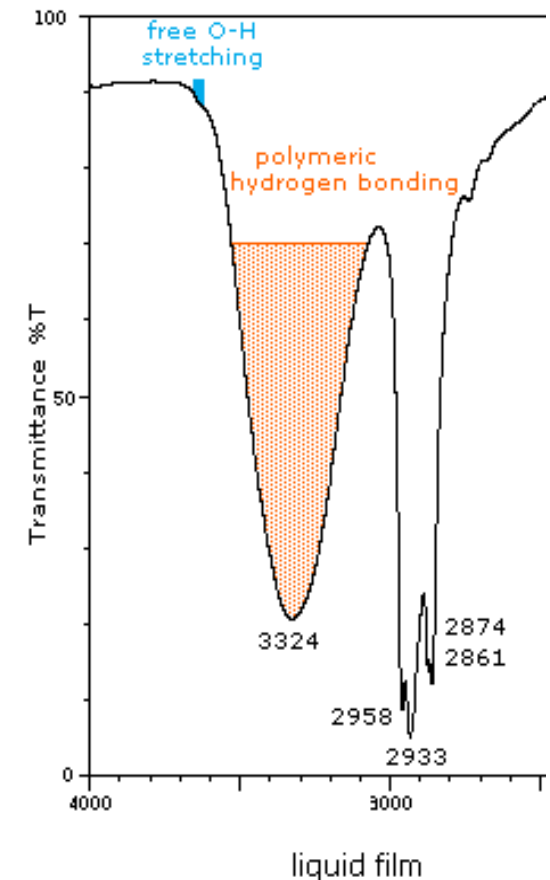
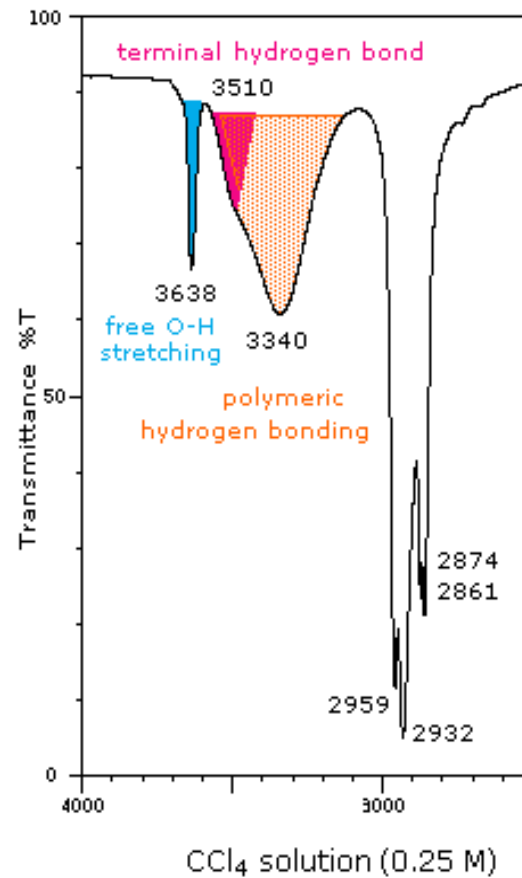
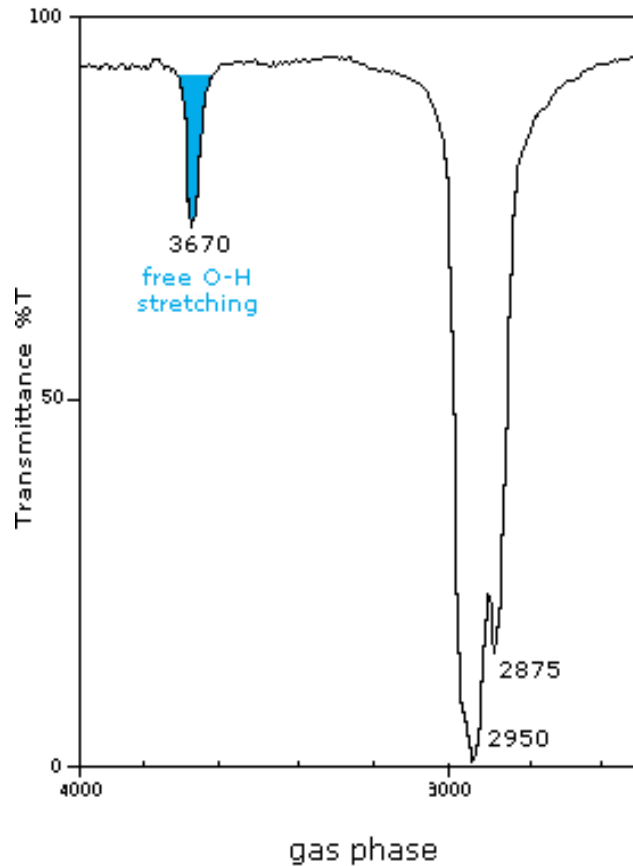
The width of the signal, w

Hydrogen Bonding

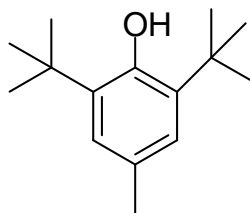
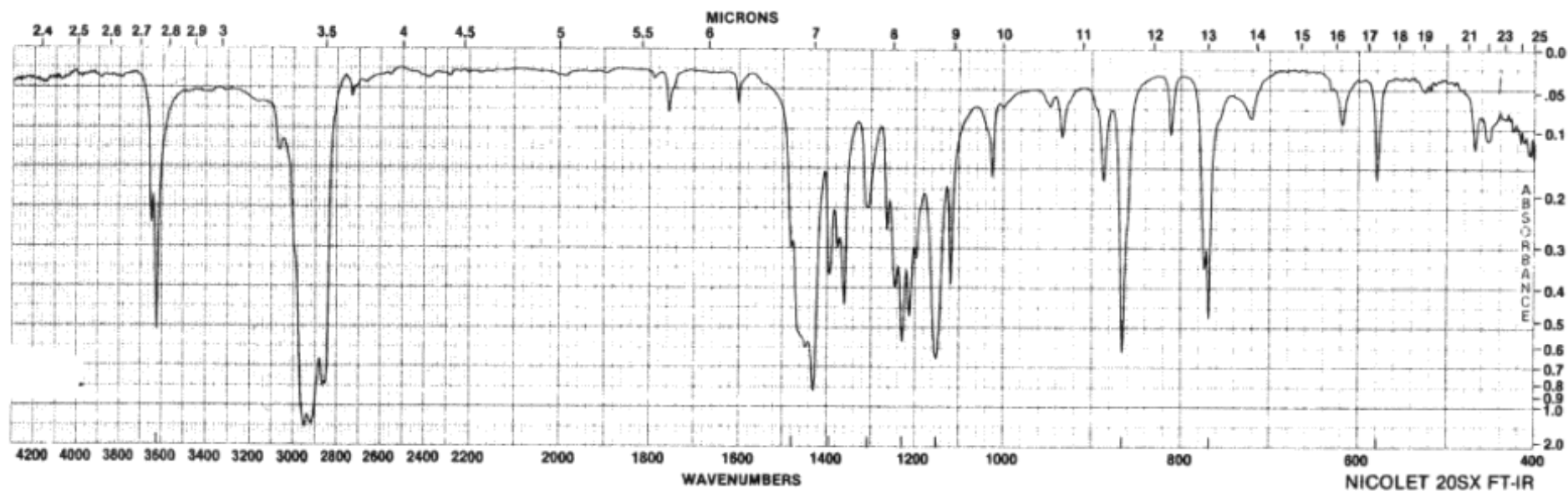
- Hydrogen bonding can occur in any system containing a proton donor and a proton acceptor group.
- Common proton donor groups: carboxyl, hydroxyl, amine or amide
- Common proton acceptor atoms: oxygen and halogens
- Strength of hydrogen bond decreases as distance between acceptor and donor increases
- Hydrogen bonding alters the strength of bond and hence stretching/bending frequencies are altered

Intermolecular Hydrogen bonding

1-hexanol $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-OH}$

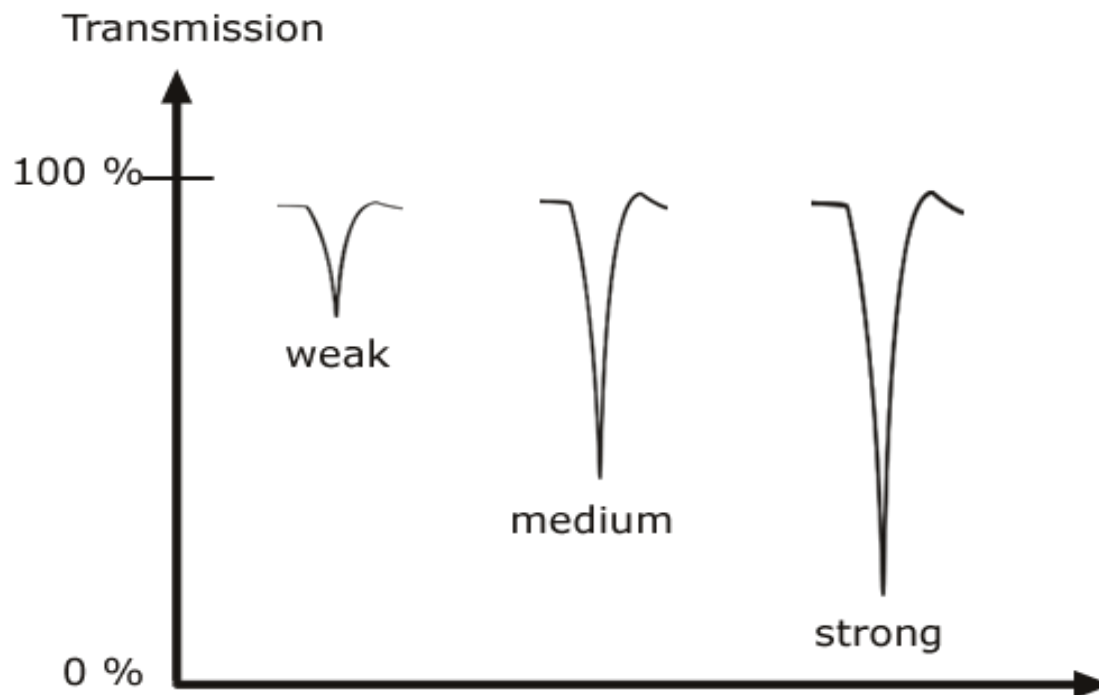


Steric hindrance to Hydrogen bonding



CLASSIFICATION OF IR BANDS

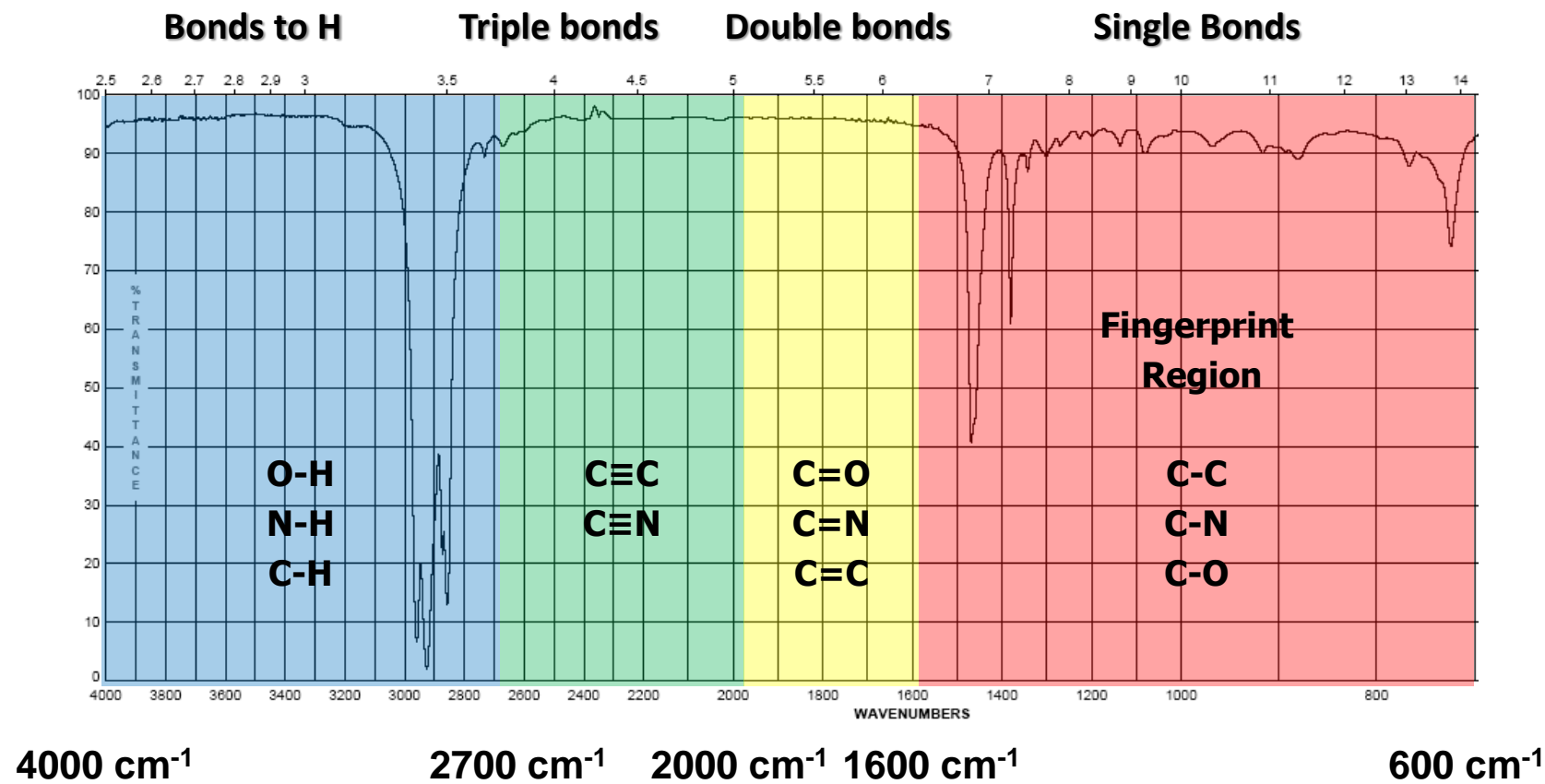
IR bands can be classified as **strong** (s), **medium** (m), or **weak** (w), depending on their relative intensities in the infrared spectrum. A strong band covers most of the y-axis. A medium band falls to about half of the y-axis, and a weak band falls to about one third or less of the y-axis.




Infrared Spectroscopy

Infrared Group Analysis

The four primary regions of the IR spectrum



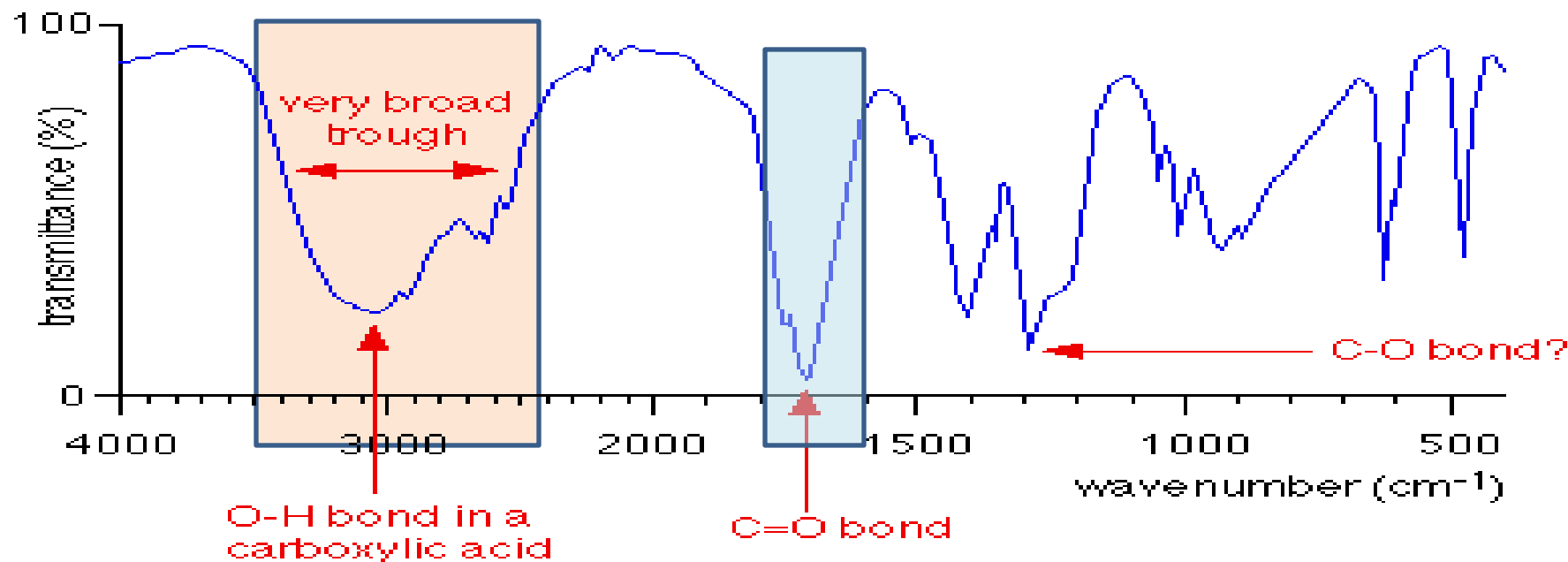
Characteristic infrared absorption in organic molecules

bond	location	wavenumber/cm ⁻¹	intensity
C—H	alkanes	2850–2950	M–S
	alkenes, arenes	3000–3100	M–S
	alkynes	ca. 3300	S * hydrogen bonded
C=C	alkenes	1620–1680	M
	arenes	several peaks in range 1450–1650	variable
C≡C	alkynes	2100–2260	M
C=O	aldehydes	1720–1740	S
	ketones	1705–1725	S
	carboxylic acids	1700–1725	S
	esters	1735–1750	S
	amides	1630–1700	M
C—O	alcohols, ethers, esters	1050–1300	S
C≡N	nitriles	2200–2260	M
C—F	fluoroalkanes	1000–1400	S
	chloroalkanes	600–800	S
	bromoalkanes	500–600	S
O—H	alcohols, phenols	3600–3640	S
	*alcohols, phenols	3200–3600	S (broad)
	*carboxylic acids	2500–3200	M (broad)
N—H	primary amines	3300–3500	M–S
	amides	ca. 3500	M

SPECTRAL INTERPRETATION

CARBOXYLIC ACID

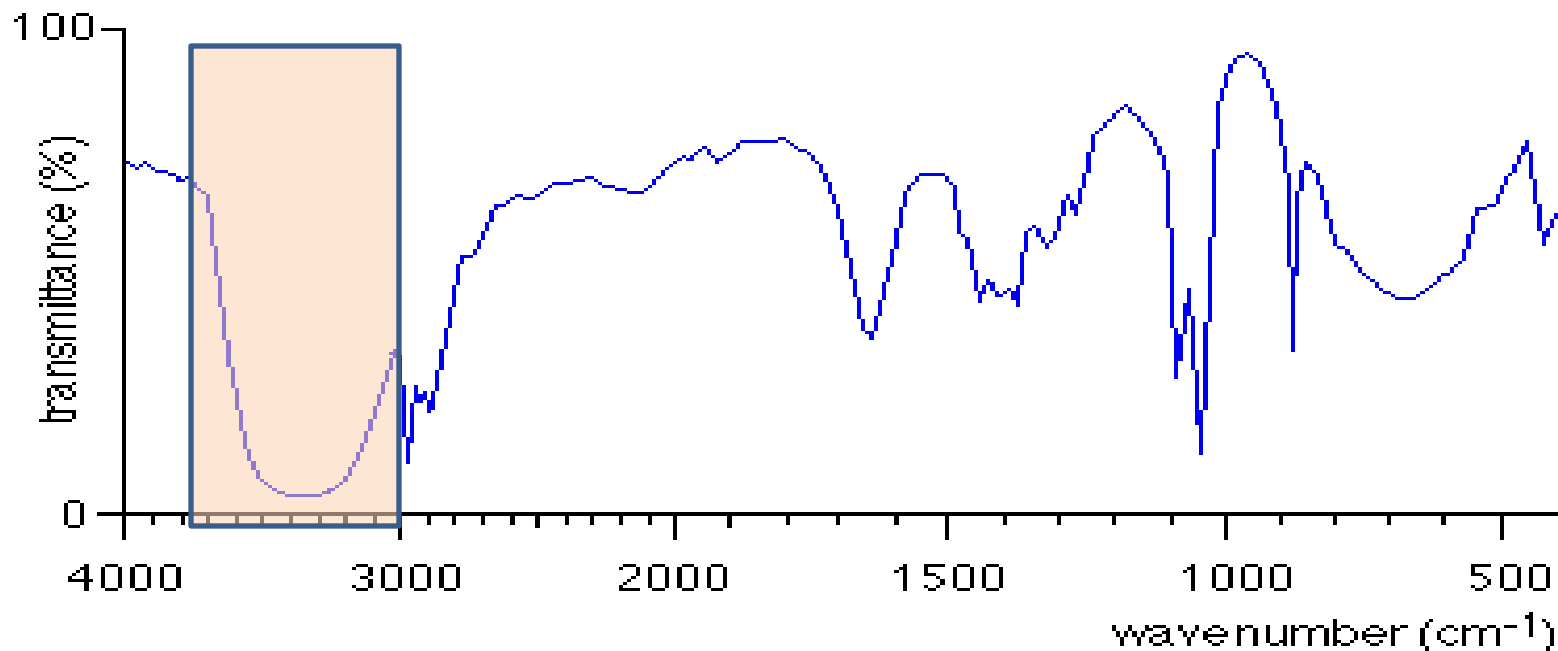
infra-red spectrum of ethanoic acid, CH_3COOH



- Strong C=O stretch in 1680 -1750 cm^{-1} .
- Typical -OH band producing a trough between 2500 – 3300 cm^{-1} .
- C – O (single bond) stretch is in finger print region and considered only if specifically mentioned.

ALCOHOLS

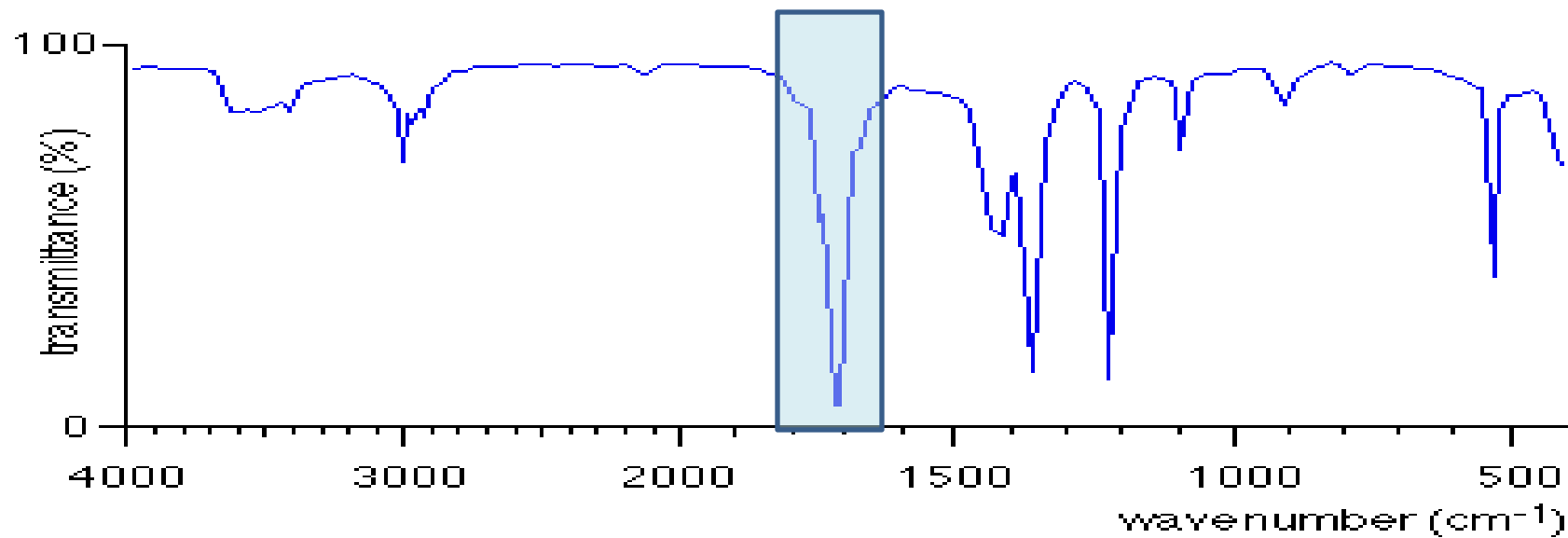
infra-red spectrum of ethanol, $\text{CH}_3\text{CH}_2\text{OH}$



- Typical strong broad -OH band between $3230 - 3550\text{cm}^{-1}$ (higher than acid).
- Absence of strong C=O stretch.

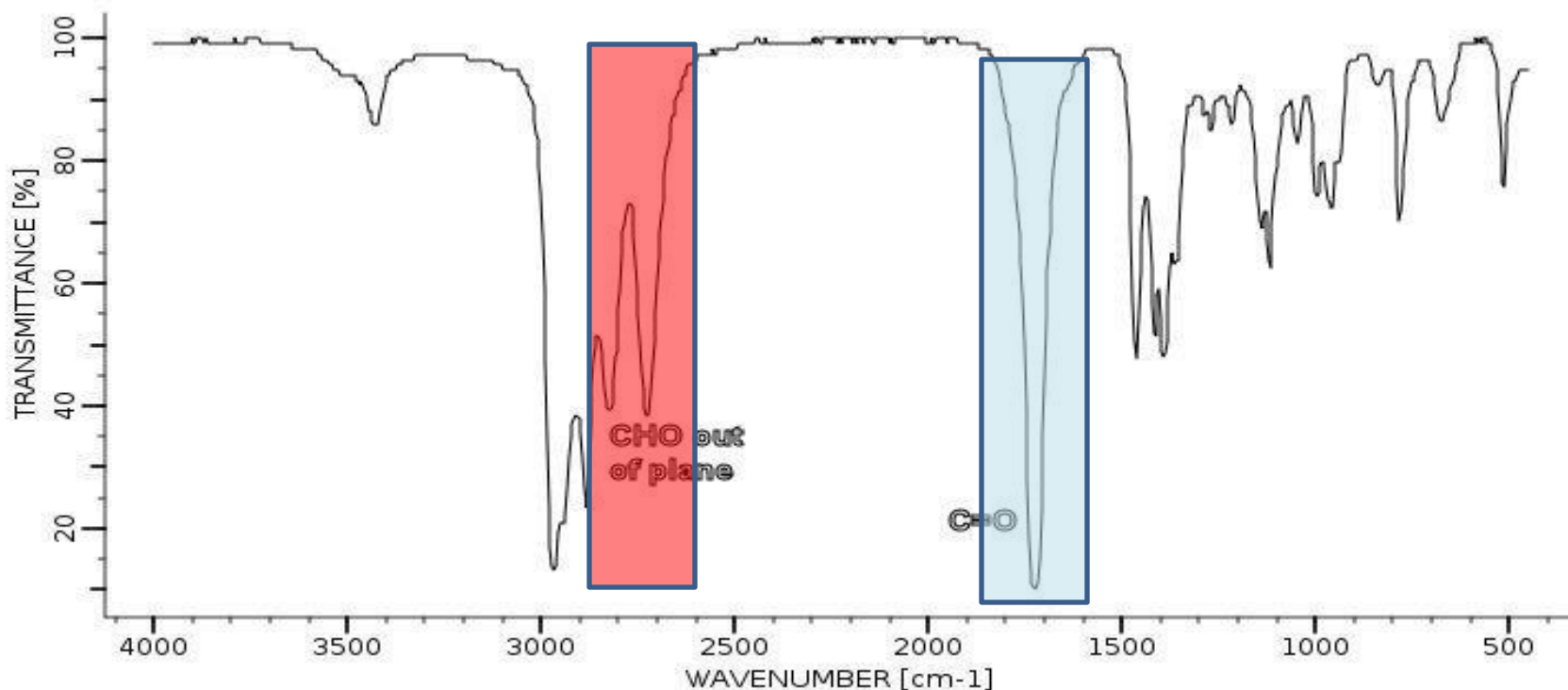
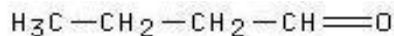
KETONES

infra-red spectrum of propanone, $\text{CH}_3\text{C}(=\text{O})\text{CH}_3$



- Strong C=O stretch in 1680 -1750 cm⁻¹.
- Absence of -OH band.

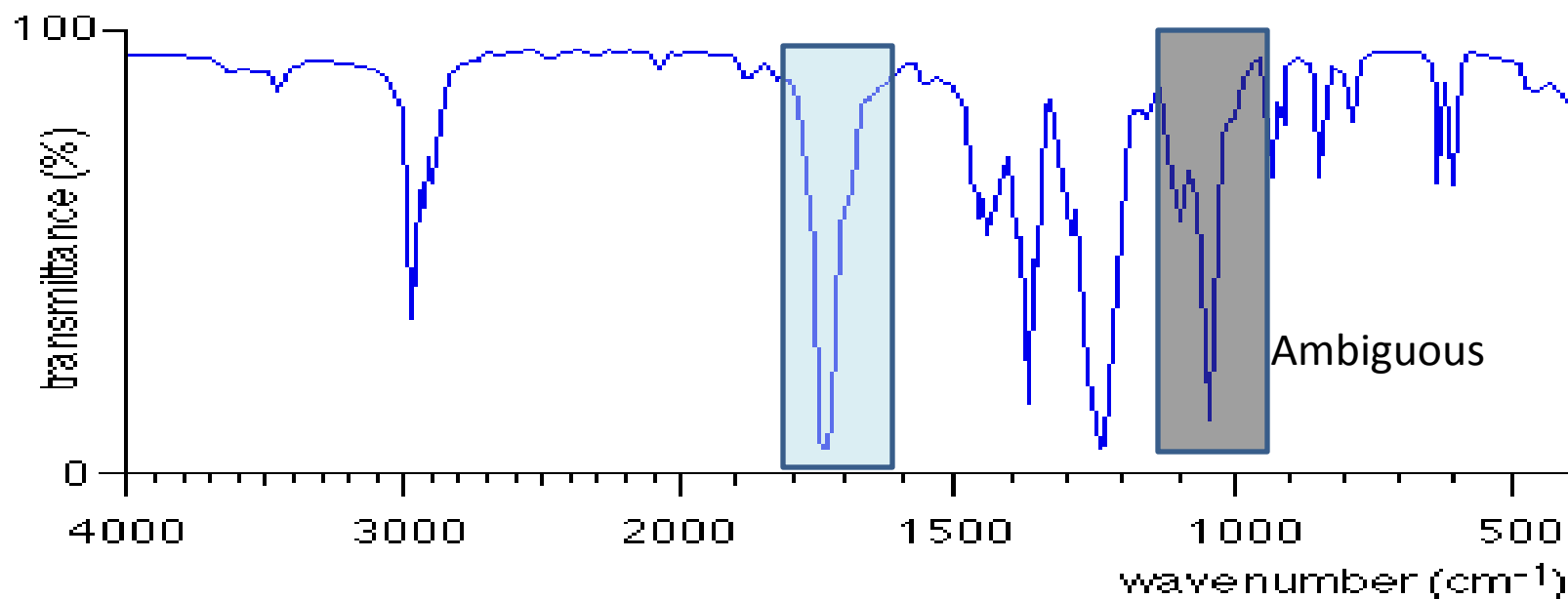
ALDEHYDES



- Strong C=O stretch in 1680 -1750 cm^{-1} .
- Absence of -OH band.
- Presence of C-H stretch along with C=O indicates a possibility of aldehyde

ESTER

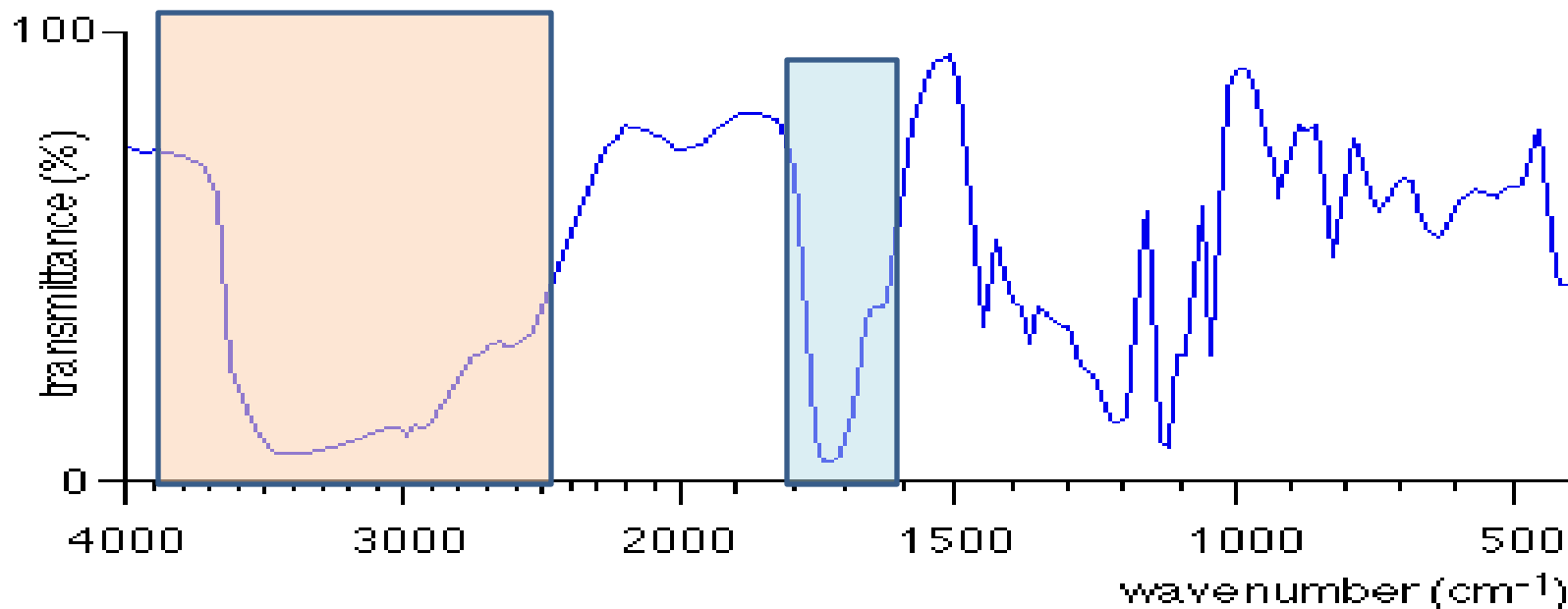
infra-red spectrum of ethyl ethanoate, $\text{CH}_3\text{C}(=\text{O})\text{OCH}_2\text{CH}_3$



- Strong C=O stretch in 1680 -1750 cm⁻¹.
- Absence of -OH band.
- Consider “C – O” (~1100 cm⁻¹) with ambiguity.

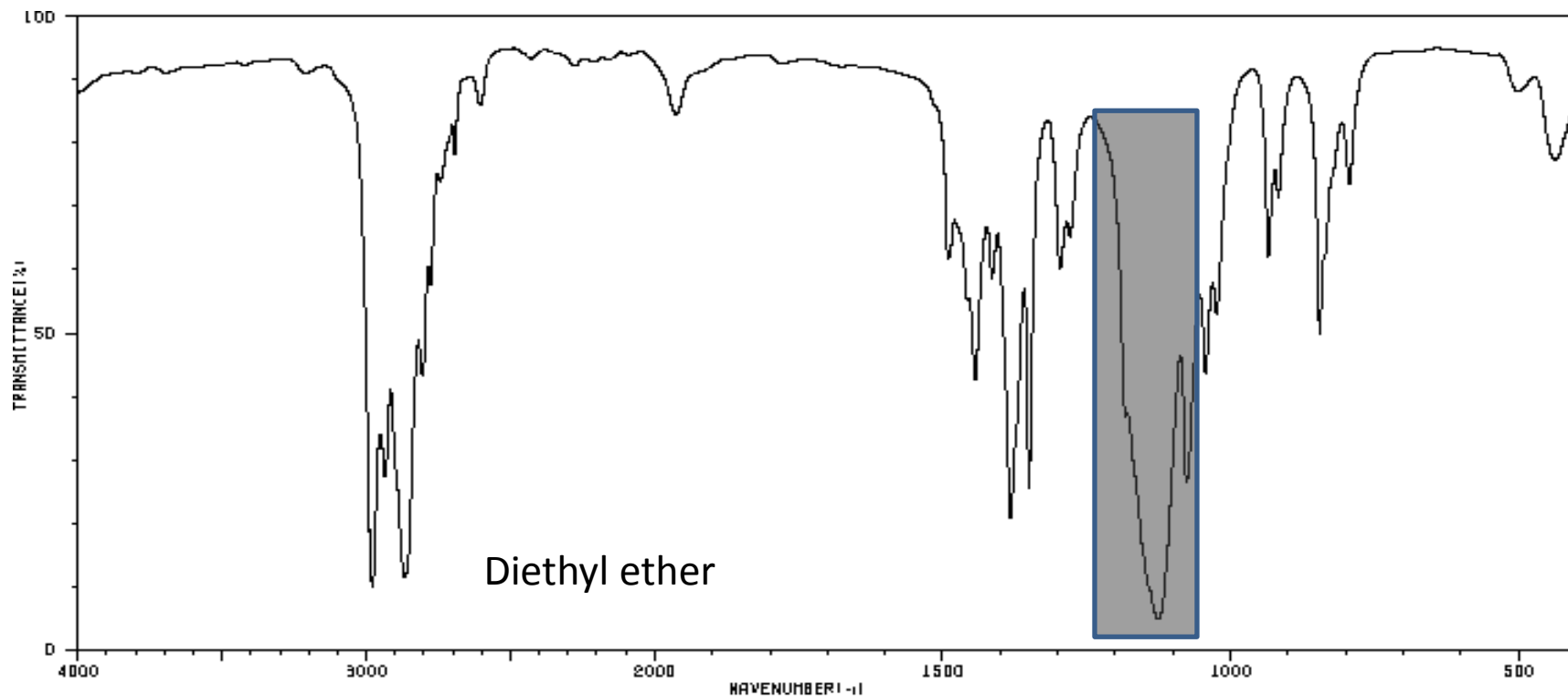
HYDROXY ACID

infra-red spectrum of 2-hydroxypropanoic acid, $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$



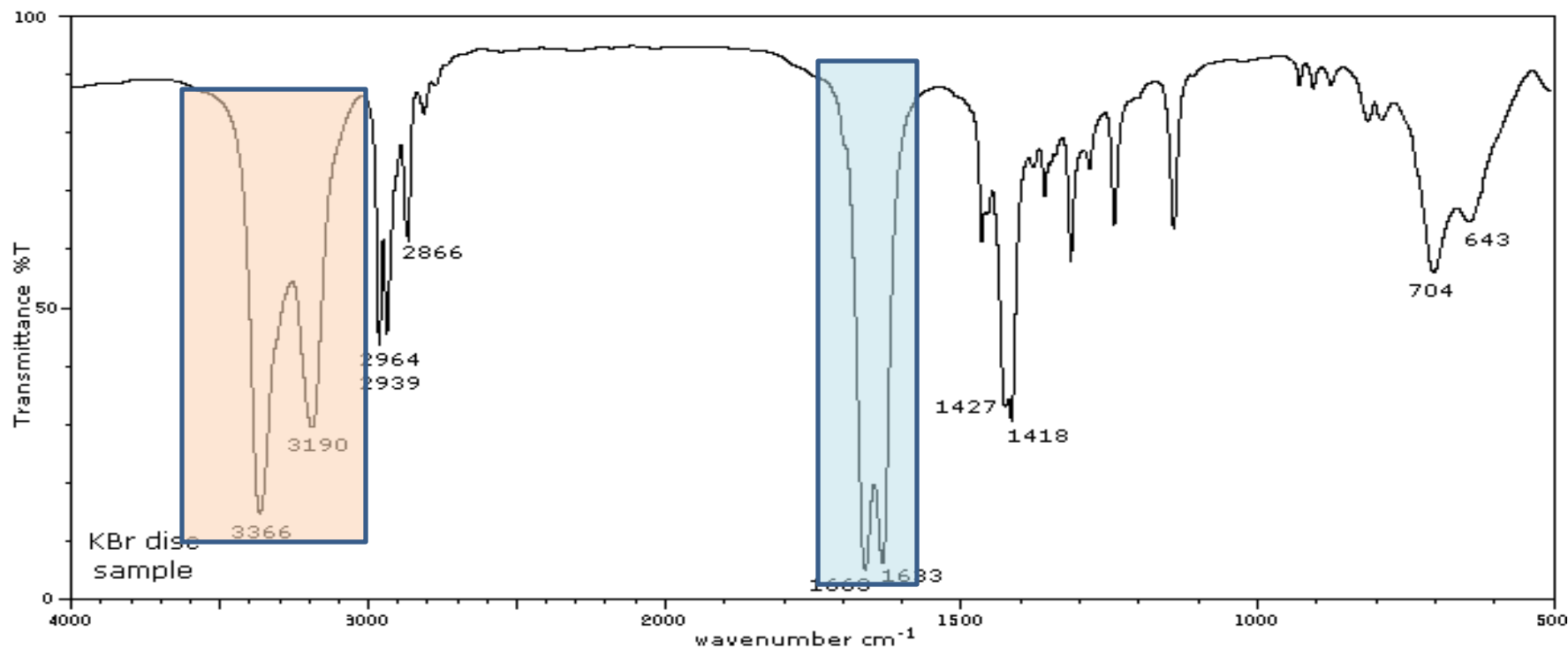
- Strong C=O stretch in 1680 -1750 cm^{-1} .
- Typical -OH band producing a trough between 2500 – 3600 cm^{-1} .

ETHER



- Can look for C – O ($\sim 1100\text{ cm}^{-1}$) stretch but cannot be sure since it is in finger print region.

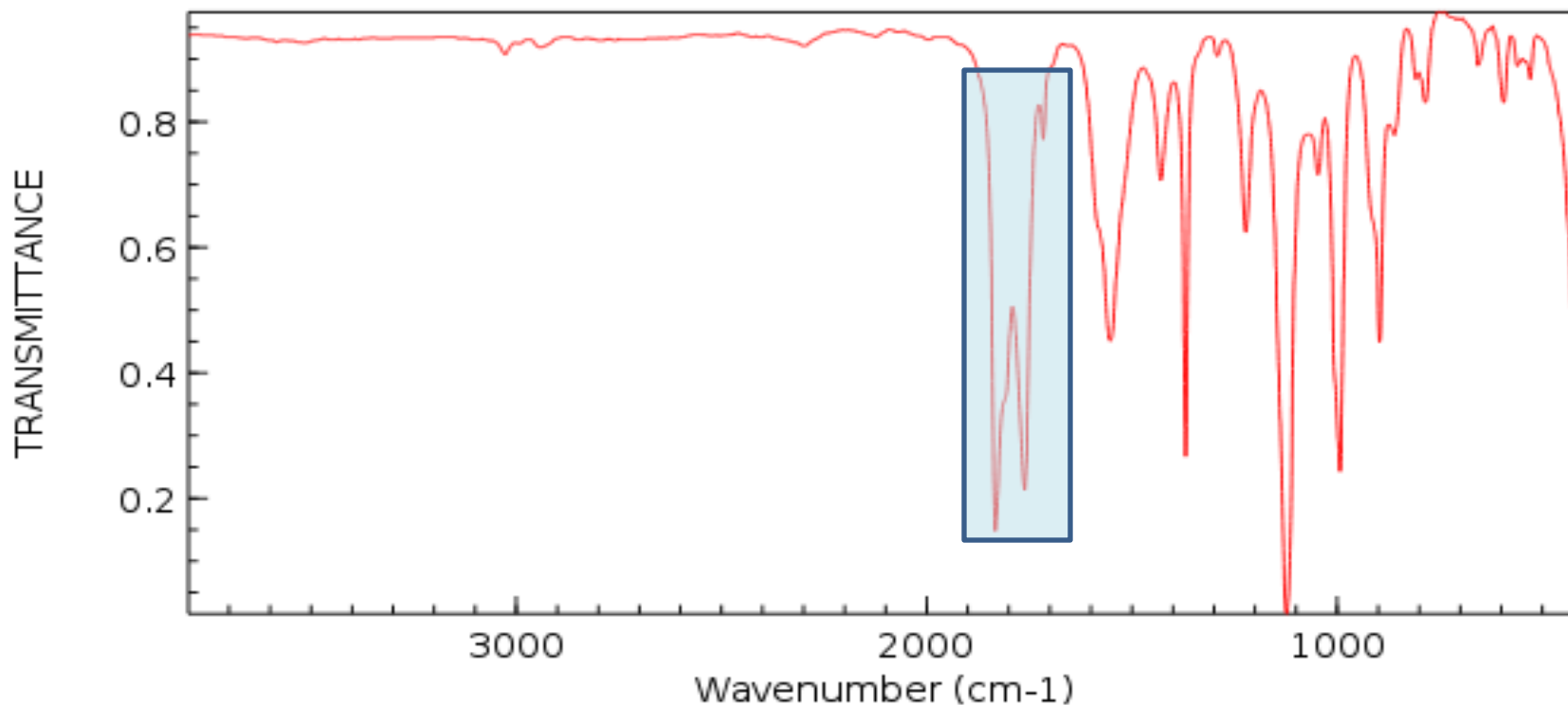
AMIDES



- **TWO** Strong C=O stretch in 1680 -1750 cm^{-1} .
- Presence of -NH band (excludes anhydride).

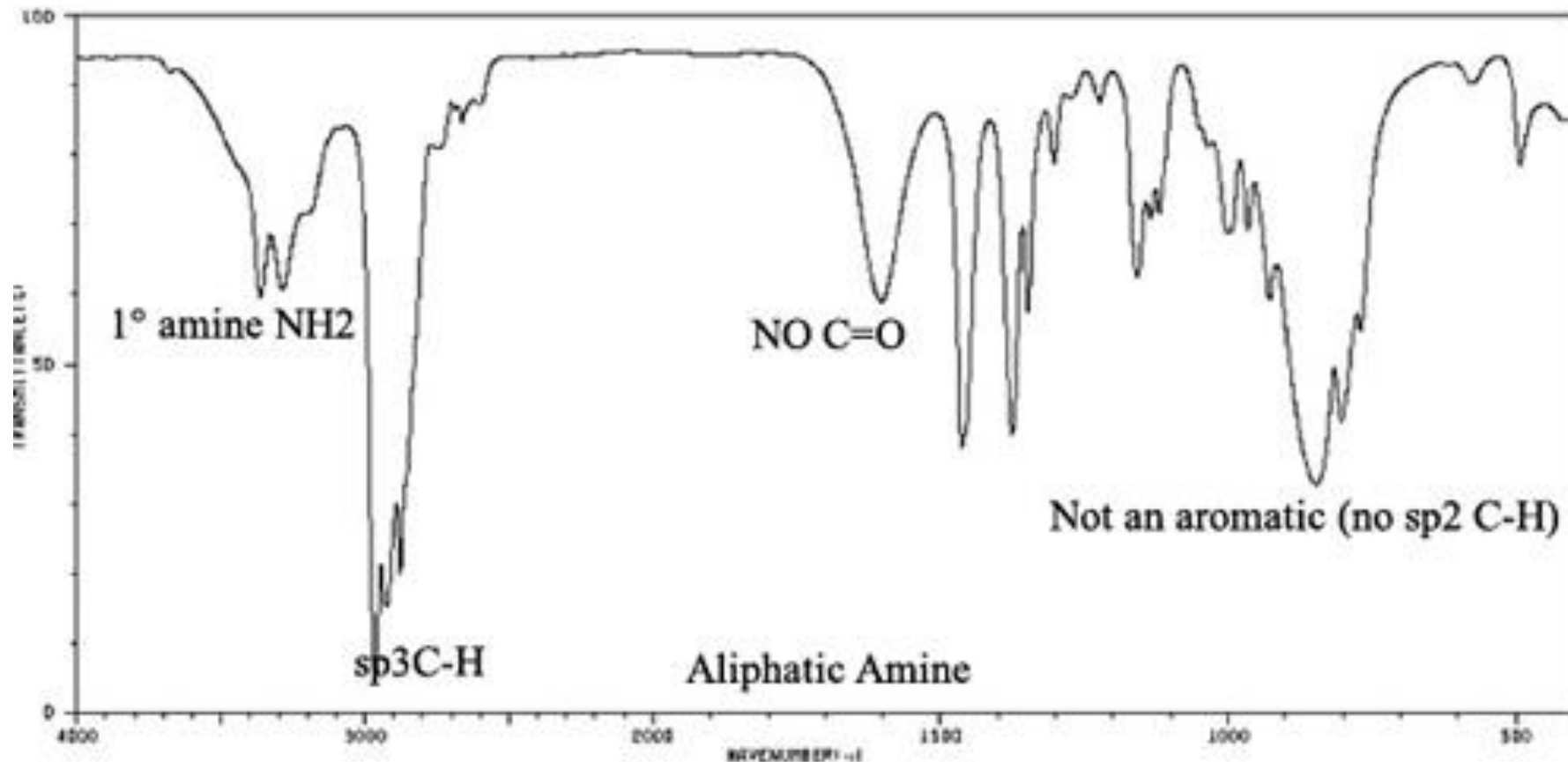
ACID ANHYDRIDE

ACETIC ACID ANHYDRIDE
INFRARED SPECTRUM



- **TWO** Strong C=O stretch in 1680 -1750 cm⁻¹.
- Absence of –NH band (excludes amide).

PRIMARY- AMINES



SECONDARY- AMINES

