

IR SPECTROSCOPY

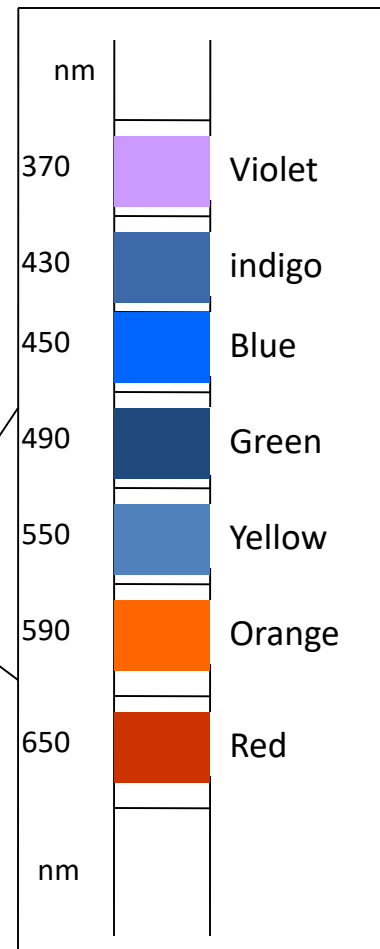
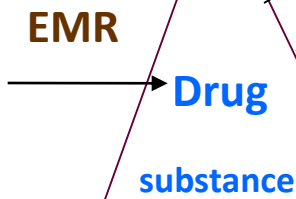
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THE ELECTROMAGNETIC SPECTRUM

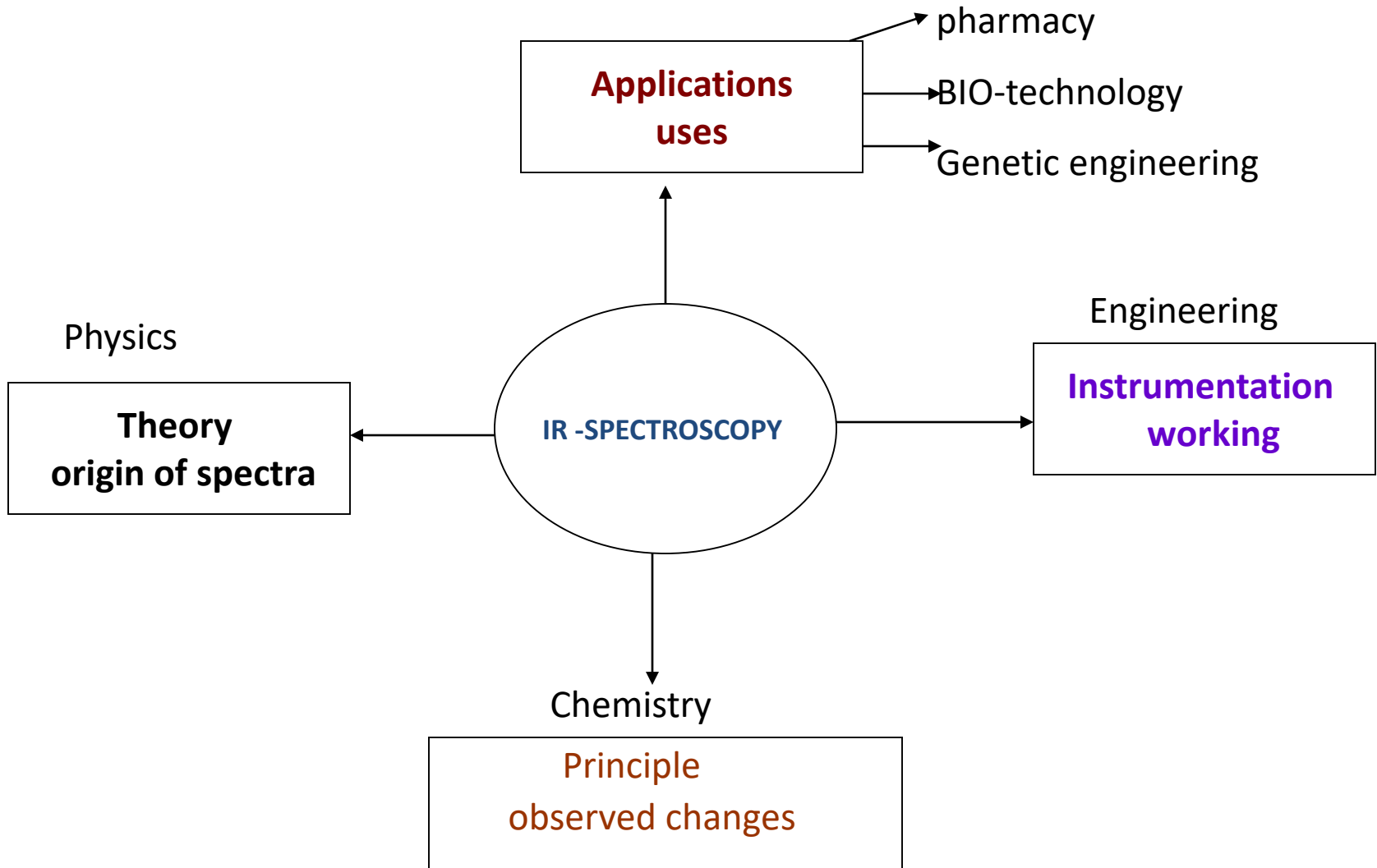
Characteristics of radiations

Absorbing radiations	Energy Kcal/mol	$\Delta \text{ } ^\circ\text{A}$	Frequency (Hz)	Type of spectroscopy
Gamma rays	9.4×10^7	1	10^{21}	Emission
X rays	9.4×10^3	15 0	10^{17}	Both E & Abs
UV	9.4×10^1	3 8 0 0	10^{15}	Absorption
Visible	9.4×10^{-1}	7 6 0 0	10^{13}	Absorption
Infra-Red	9.4×10^{-3}	6×10^6	10^{11}	Absorption
Micro waves	9.4×10^{-5}	3×10^9	10^9	Absorption
Radio waves	9.4×10^{-7}	3×10^{13}	10^7	NMR Abs



Resulting spectrum

Multidisciplinary of IR spectroscopy



IR-REGION: 12,800 - 10 cm⁻¹

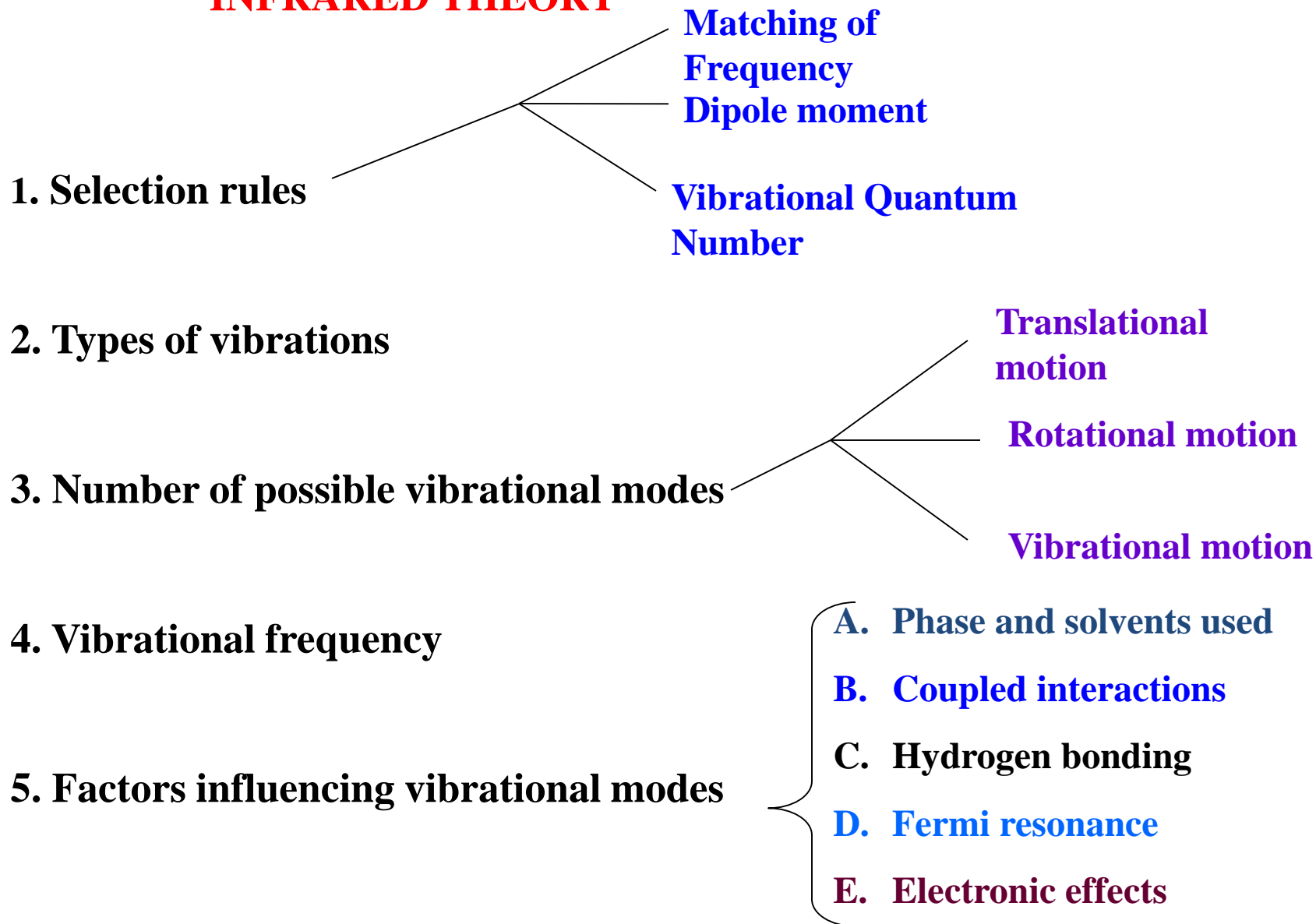
REGION	WAVE LENGTH λ (μm)	WAVE NUMBER ν (cm⁻¹)	FREQUENCY RANGE Hz
NEAR	0.78 - 2.5	12800 - 4000	3.8x10¹⁴-1.2x10¹⁴
MIDDLE	2.5 - 50	4000 - 200	1.2x10¹⁴ - 6x10¹²
FAR	50 - 1000	200 - 10	6x10¹²- 30x10¹¹
MOST USED	2.5 - 15	4000 - 670	1.2x10¹⁴-2x10¹³

1. Near IR----carbohydrates and proteins
2. Middle IR-----organic molecules—functional groups
3. Far IR—in-organic –co-ordination bonds& quaternary ammonium compounds

Differences between various types of IR spectra

Character	Electronic band spectra ^a	Vibration- rotational spectra ^b	Rotational spectra ^c
1. IR region	Near IR	Middle IR	Far IR
2. Energy required	Higher	less	very less
3. Dipole moment	less induced	Definite dipole	Intense dipole
4. Sample state	Solids	Liquids / gases	Only gases
5. Theory supporting	Frank codon principle	Harmonic oscillator principle	Rigid rotor principle
6. Changes observed	Excitation, vibration	Vibration , rotation	Only rotation
7. Highly feasible for	single bonds	double bonds	Triple bonds

INFRARED THEORY



- For a molecule to absorb IR, the vibrations within a molecule must cause a net change in the dipole moment of the molecule. The alternating electrical field of the radiation (remember that electromagnetic radiation consists of an oscillating electrical field and an oscillating magnetic field, perpendicular to each other) interacts with fluctuations in the dipole moment of the molecule.
- If the frequency of the radiation matches the vibrational frequency of the molecule then radiation will be absorbed, causing a change in the amplitude of molecular vibration.

Molecular vibration induced by IR adsorption

The stretching frequency of a bond can be approximated by Hooke's Law. Two atoms and the connecting bond are treated as a simple harmonic oscillator composed of 2 masses (atoms) joined by a spring:

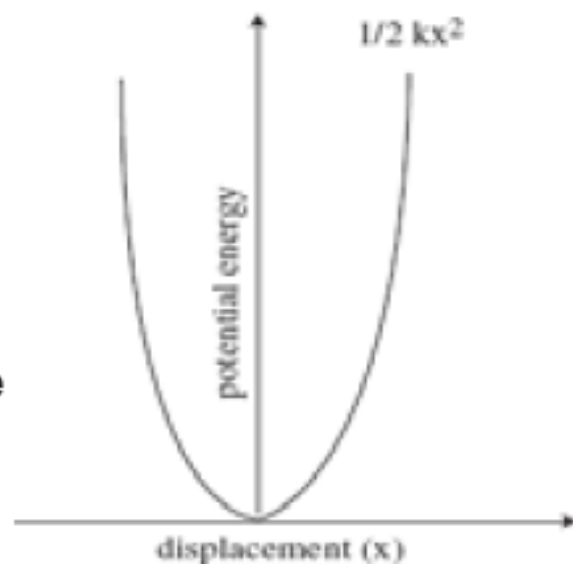
According to Hooke's law, the vibration frequency of the spring is expressed by:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$



where k is the force constant, m is the mass, ν is the vibration frequency

In the classical harmonic oscillator, $E = 1/2kx^2 = h\nu$, where x is the displacement of the spring. Thus, the energy or frequency is dependent on how far one stretches or compresses the spring, which can be any value. If this simple model were true, a molecule could absorb energy of any wavelength.



Molecular vibration induced by IR adsorption

The following formula has been derived from Hooke's law. For the case of a diatomic molecule,

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{f(m_1 + m_2)}{m_1 m_2}}$$



$$\text{recall: } \nu = \frac{c}{\lambda} \text{ and } \lambda = \frac{c}{\nu}$$
$$\bar{\nu} = \frac{1}{\lambda} \quad \nu = c\bar{\nu}$$

where $\bar{\nu}$ is the wavenumber (cm^{-1}), m_1 and m_2 are the mass of atoms 1 and 2, respectively, c is the velocity of light (cm/s), f is the force constant of the bond (dyne/cm)

Equation shows the relationship of bond strength and atomic mass to the wavenumber (vibration frequency) at which a molecule will absorb IR radiation. As the force constant increases, the wavenumber increases.

$$V(r) = \frac{1}{2} k \cdot \Delta r^2 = 2\pi^2 \cdot \mu \nu_{osc}^2 \Delta r^2$$

$$\mu = \frac{m_1 \cdot m_2}{m_1 + m_2} \quad (\text{reduced mass})$$

$$\nu_{osc} = \frac{1}{2\pi} \cdot \sqrt{\frac{f}{\mu}}$$

Vibrations – relative positions of the atoms change while the average position and orientation of the molecule remain fixed.

Fundamental Vibrations

Degrees of freedom	linear	non-linear
Translational	3	3
Rotational	2	3
Vibrational	$3N-5$	$3N-6$
Total	$3N$	$3N$

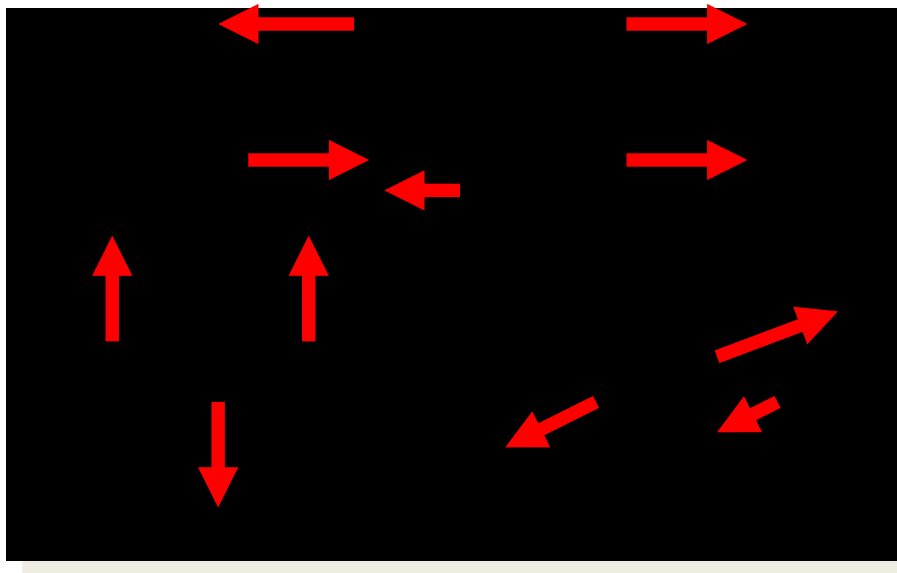
N = number of atoms in molecule

prerequisites for Infrared active

- 1) The frequency of the infrared light must be identical to the frequency of the vibration (resonance).
 - 2) The dipole of the molecule must change during vibration.
 - 3) The direction of the dipole change must be the same as the direction of the electric field vector
- That is, the molecules can interact with light and lead to infrared absorption only when all the following requirements are met:

INFRARED SPECTROSCOPY

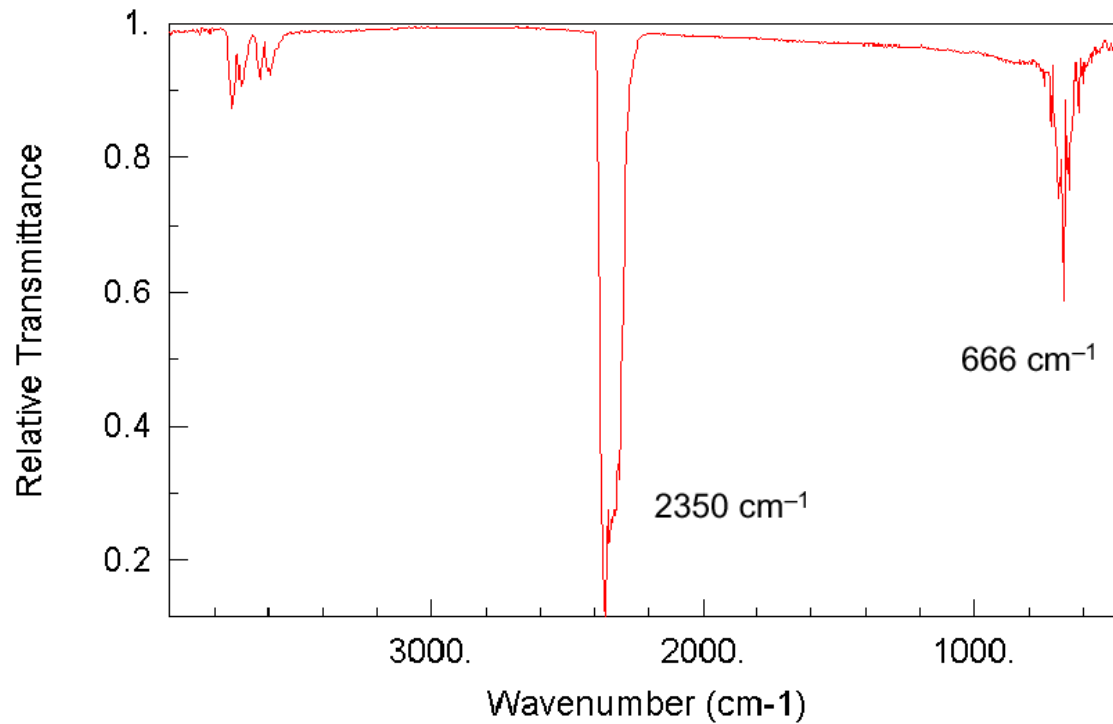
- Only vibrations that cause a change in 'polarity' give rise to bands in IR spectra – which of the vibrations for CO₂ are infrared active?



Symmetric stretch

Asymmetric stretch

Bending (doubly degenerate)



Infrared Spectrum of Carbon Dioxide

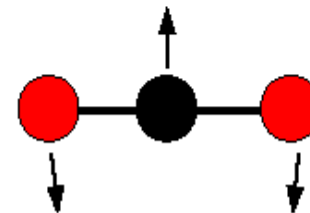
Example: CO₂

symmetrical stretching
1340 cm⁻¹



asymmetrical stretching
2350 cm⁻¹

scissoring bending
666 cm⁻¹



scissoring bending
666 cm⁻¹

Selection Rules

The energy associated with a quantum of light may be transferred to the molecule if work can be performed on the molecule in the form of displacement of charge.

Selection rule:

A molecule will absorb infrared radiation if the change in vibrational states is associated with a change in the dipole moment (μ) of the molecule.

$$\mu = qr$$

q: electrical charge, r: directed distance of that charge from some defined origin of coordinates from the molecule.

Dipole moment is greater when electronegativity difference between the atoms in a bond is greater. Some electronegativity values are:

H 2.2; C 2.55; N 3.04; O 3.44; F 3.98; P 2.19; S 2.58; Cl 3.16

- Vibrations which do not change the dipole moment are *Infrared Inactive* (homonuclear diatomics).

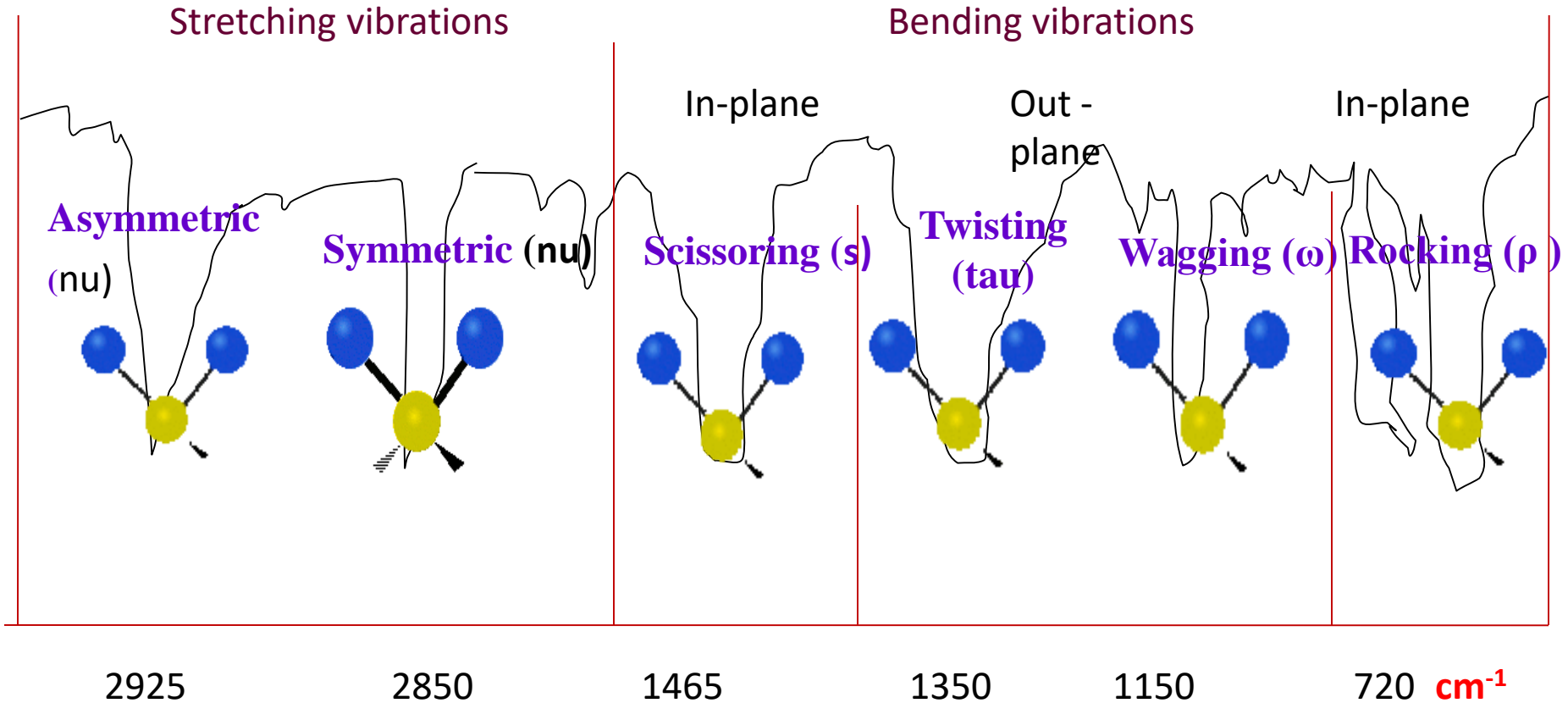
Types of vibrations

For stretching vibration = $N - 1$

For bending vibration

$[(3N - 6) - (N - 1)] = 2N - 5$ for non-linear

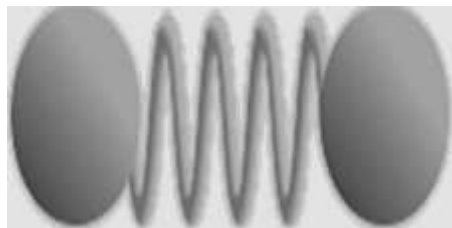
$[(3N - 5) - (N - 1)] = 2N - 4$ for linear 'N' is the number of atoms in the bond.



Vibrational energy depends on :-

1. masses of the atoms
2. strength of bonds
3. arrangement of atoms within the molecule

Vibrational frequency



M1 Force constant, k M2

■ Ball and spring representation of 2 atom of molecule vibrating in the direction of bond

Hooke's law :

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}}$$

$\bar{\nu}$: Frequency in cm^{-1}
 c : Velocity of light $\Rightarrow 3 \times 10^{10}$ cm/s
 K : Force constant \Rightarrow dynes/cm
 $\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{M_1 M_2}{M_1 + M_2} (6.02 \times 10^{23})$

Factors influencing absorption frequency

● **Masses of attached atoms.** As masses increase, wave number decreases.

C-H	C-C	C-O	C-Cl	C-Br	C-I
3000 cm^{-1}	1200 cm^{-1}	1100 cm^{-1}	750 cm^{-1}	600 cm^{-1}	500 cm^{-1}

● **Strength of chemical bond.** As bond strength increases, wave number increases.

C \equiv C	C=C	C-C
2150 cm^{-1}	1650 cm^{-1}	1200 cm^{-1}

● **Hybridization.** Bonds are stronger in the order $sp > sp^2 > sp^3$.

C-H (sp)	C-H (sp^2)	C-H (sp^3)
3300 cm^{-1}	3100 cm^{-1}	2900 cm^{-1}

● **Resonance.** Conjugation lowers the energy to vibrate bond.

isolated ketones	α, β -unsaturated ketone	$\alpha, \beta, \gamma, \delta$ -unsaturated ketone
1715 cm^{-1}	1690 cm^{-1}	1675 cm^{-1}

Factors influencing vibrational modes

A. Phase and solvents used

Phase and solvents may bring the changes in IR in the aspects of

1. Band frequency shifts

2. Band splitting

e.g.:- the effect of phase and solvents in Acetone.

>c=o in acetone -----1742 **cm⁻¹ in vapor state**
-----1718 **cm⁻¹ in liquid state**

Dipole-dipole lowers wave number

Acetone interactions with some solvents

-----1726 **cm⁻¹ in a solution of Hexane**

-----1713 **cm⁻¹ in chloroform**

-----1709 **cm⁻¹ in ethanol**

B. Coupled interactions

Extent of coupling influenced by

- 1. stretching vibrations with two vibrations have common atom**
- 2. bending vibrations with a common bond b/t vibrating groups.**
- 3. coupled groups of identical energies.**
- 4. groups separated by two/more bonds, little or no interaction occur.**
- 6. vibrations of symmetrical species.**

Factors influencing vibrational modes

C.. Hydrogen bonding

Strength of H-bond effected by

1. ring strain
2. molecular geometry
3. relative acidity and basicity of proton donor and acceptor

Types of hydrogen bonding :-

1. intermolecular hydrogen bonding

2. intramolecular hydrogen bonding

extent of bonding
depends on Temp.

D. Fermi resonance

Factors leads to Fermi resonance

- a) vibrational levels are same for symmetrical compounds.
- b) interacting groups located in the molecule for an appreciable mechanical coupling to occur.

e.g.:-

1. CO_2 actual absorption frequencies at 1286, 1388 cm^{-1} the splitting caused by coupling b/t fundamental $\text{C}=\text{O}$ stre. near 1340 cm^{-1} and 667 cm^{-1} ----- 1344 cm^{-1} 1st overtone
2. lactones, lactims, lactums, aldehydes.

Factors influencing vibrational modes

E. Electronic effects

1. Inductive effect—introduction of alkyl group →

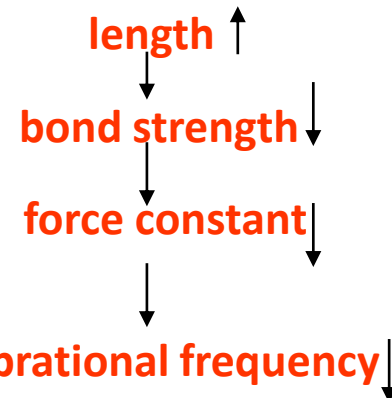
2. Mesomeric effect

3. Field effect.

HCHO----1750 cm⁻¹

CH₃CHO---1745 cm⁻¹

CH₃COCH₃---1715 cm⁻¹



- ▶ Lone pair of electrons
- ▶ conjugation lowers absorption
- ▶ Mesomeric effect dominate inductive effect for some time and vice versa

Introduction of electronegative atoms → ↑ Bond strength → ↑ Force constant

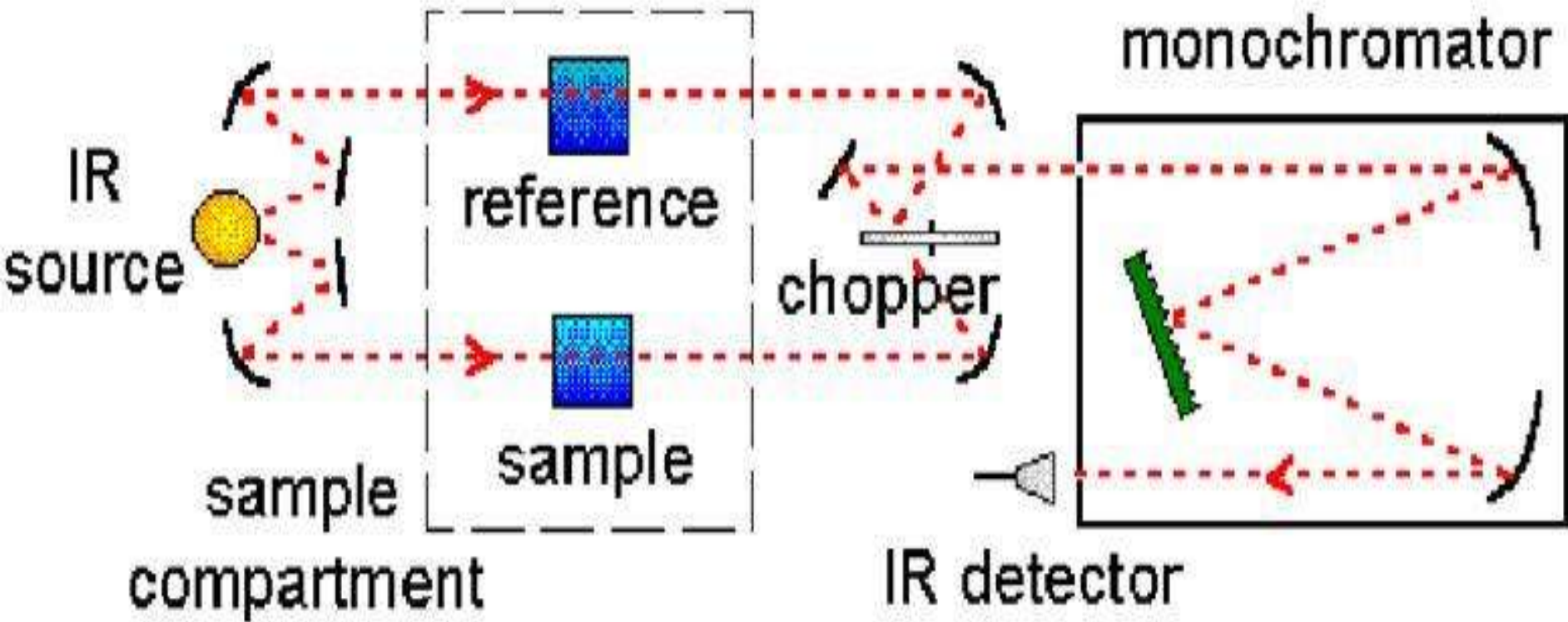
CH₃COCH₃---1715 cm⁻¹

ClCH₂COCH₃--1725 cm⁻¹

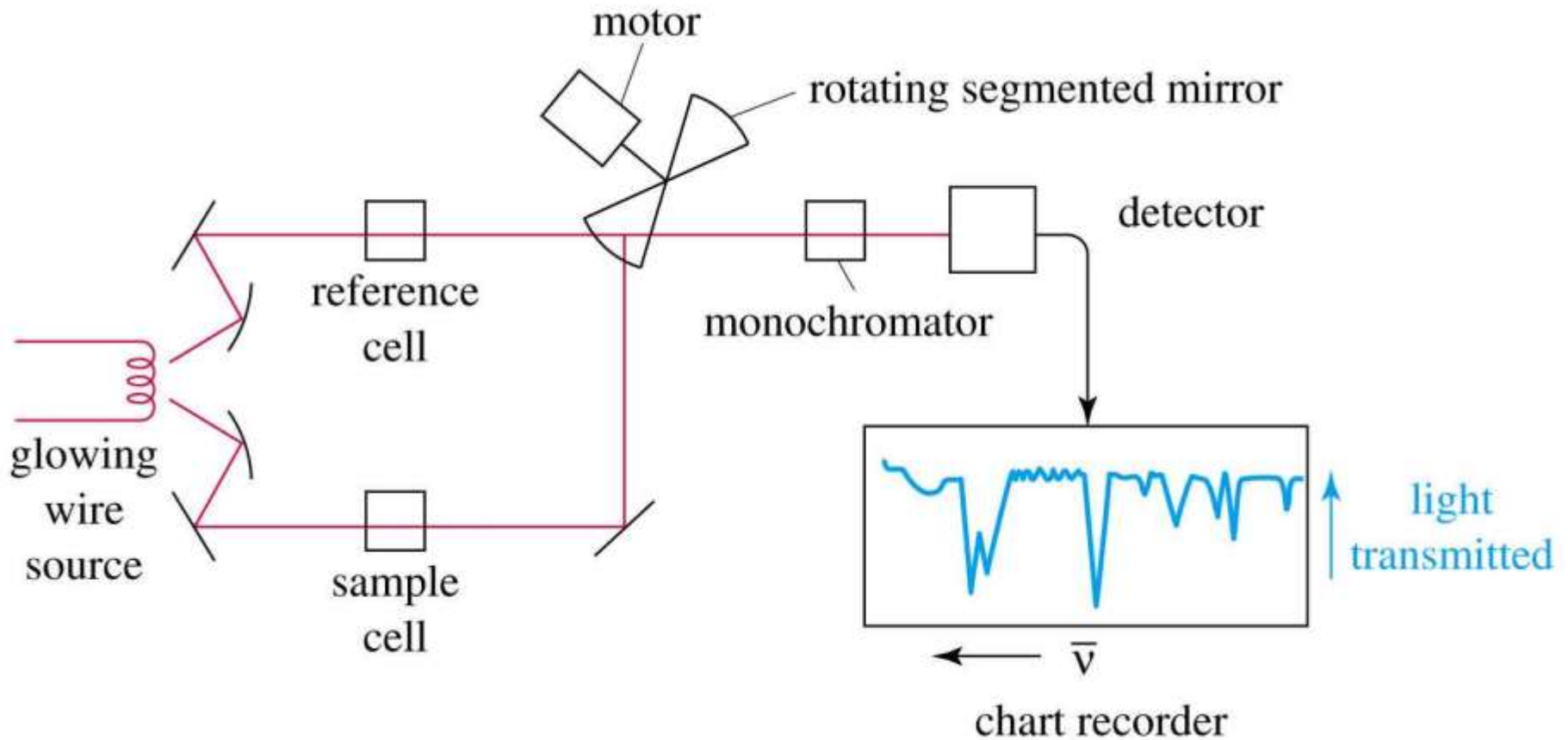
Cl₂CHCOCH₃----1740 cm⁻¹

↓
↑ Vibrational frequency

INSTRUMENTATION



An Infrared Spectrometer



INFRARED SOURCES

S.NO	Character	Nernst glower	Globar	Incandescent	Mercury arc	Tungsten lamp	Co ₂ laser
1.	Composition	Rare earth oxides	Silicone carbide	Nichrome wire	High (Hg) pressure	Tungsten – Halogen	Tunable Co ₂ laser.
2.	Operating temp.	1200 — 2200K	1300 --- 1500 K	1100K	1000K	3500K	-----
3.	Radiations produced O.P	12,800-4000cm ⁻¹	5200 cm ⁻¹	10,800--8000cm ⁻¹	< 665 cm ⁻¹	10,100—4000 cm ⁻¹	1100-900cm ⁻¹
4.	IR region used	Near / visible	Middle	Near	Far	Middle	Middle /near
5.	Intensity of radiation	More intense	As equal to Nernst	Less but longer life.	Greater	Mild	More effective
6.	Out put significant (λ)	>2μm	>5μm	2-4μm	10μm	2-4μm	5 μm
7.	Used for	Carbohydrate , protein	Simple Functional groups	complex organic molecules.	In- organic complexes.	Most organic functional groups	NH ₃ C ₆ H ₆ , C ₂ H ₅ OH

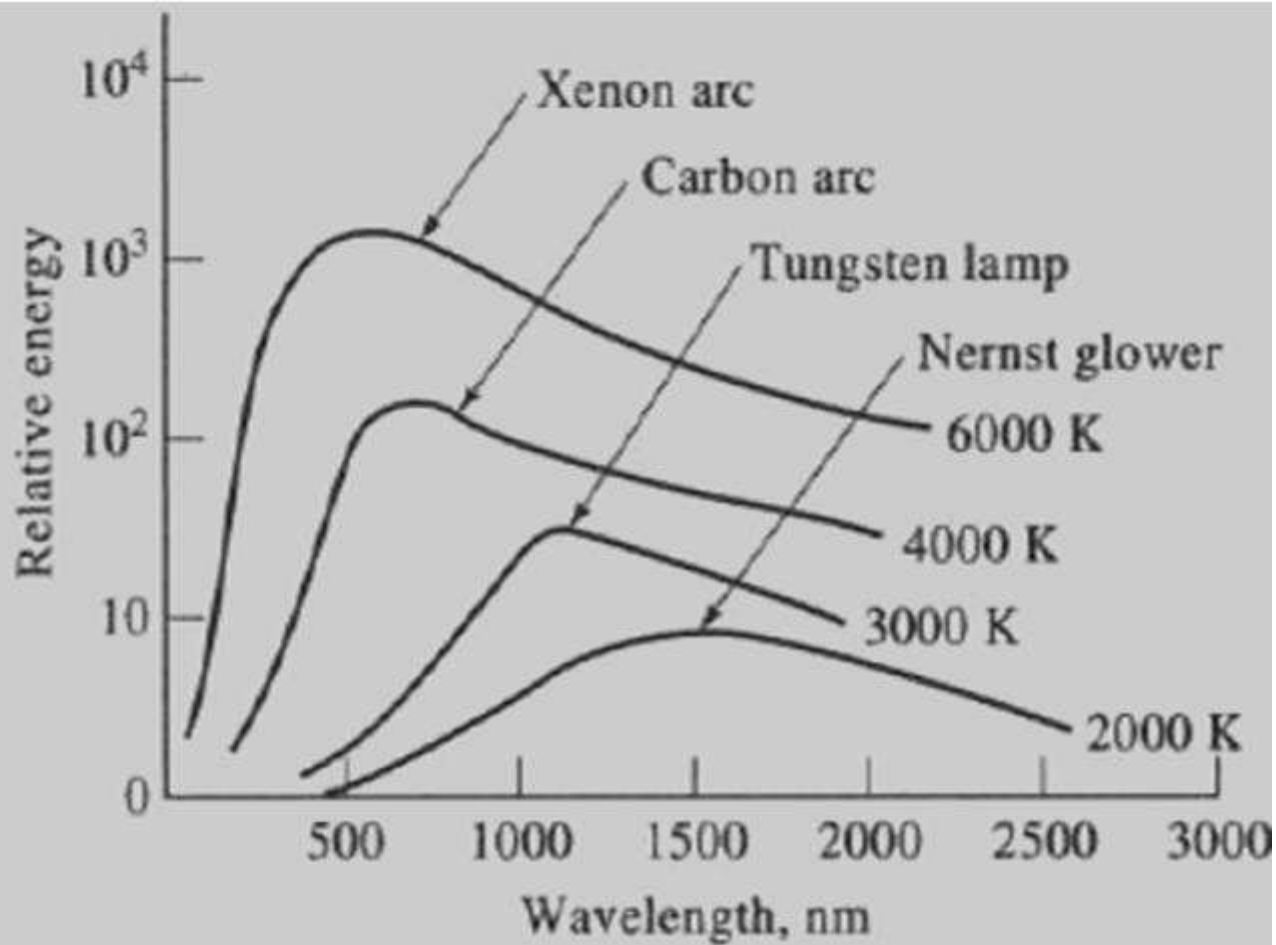
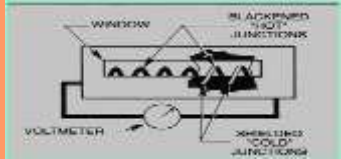
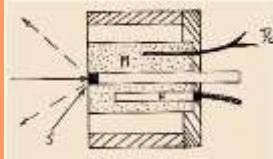
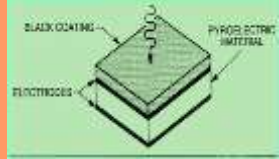
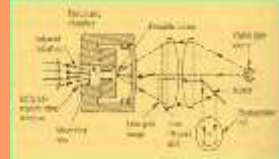


Figure 6-18 Blackbody radiation curves.

DETECTORS or TRANSDUCERS

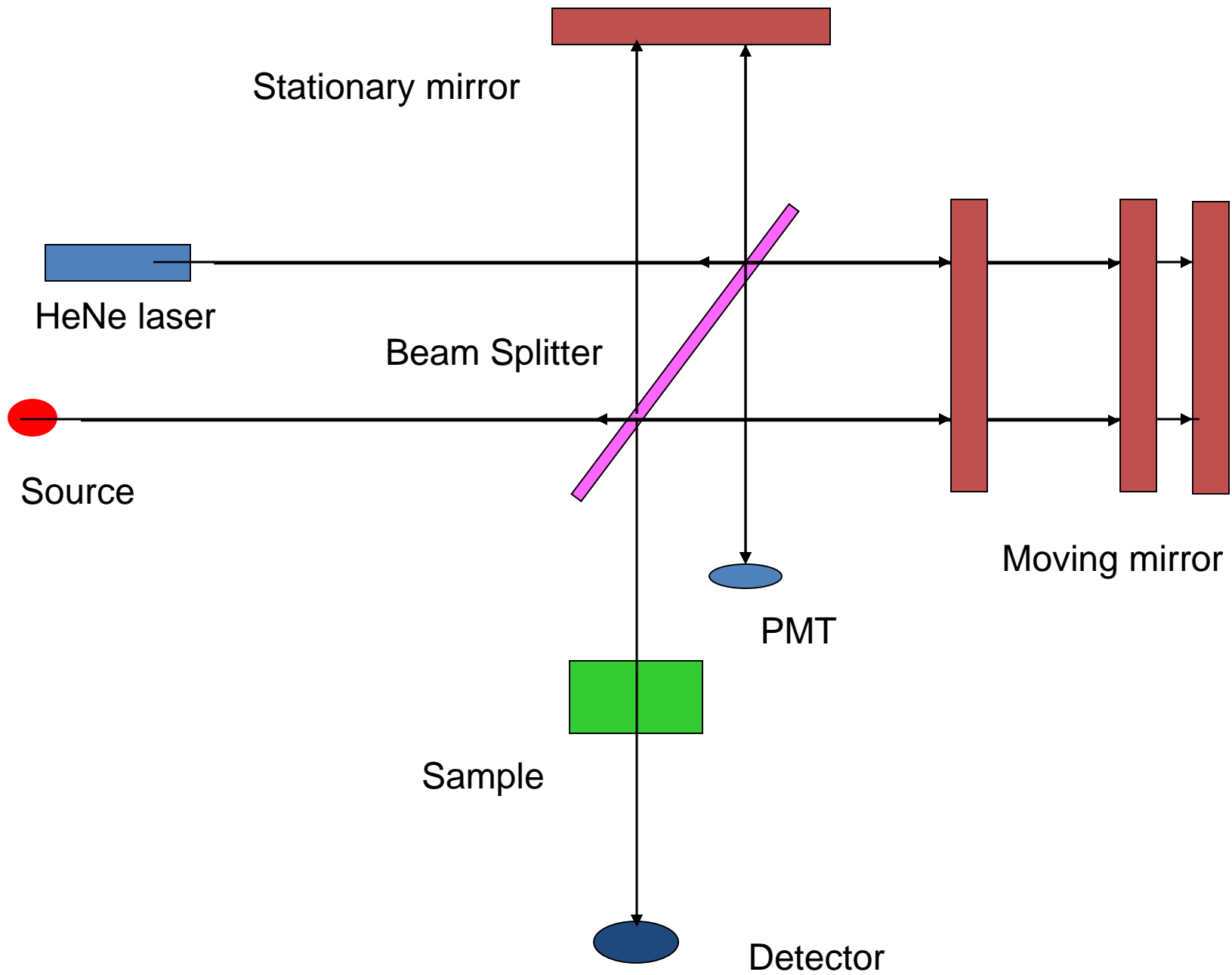
S.No	Character	Thermocouple 	Thermister 	Pyroelectric 	Golay 
1.	Principle	Pelletier effect	Whetstone bridge	Electric polarization	Expansion of gases
2.	Materials used	Bismuth & Antimony, coated by metal oxides	Sintered oxides of Mn, co, Ni	TGS, DTGS, LiTGO ₃ , LiTubO ₃	generally CO ₂
3.	Material should be	Thermally active	Thermally sensitive resistors	Non-center symmetric crystal	Inert nature
4.	Description	Half -junction- hot Alternate -junction -cold	-----	-----	Metal cylinder closed in b/t metal plate & Ag
5.	Conversion unit	Radiant to Electric signal ---measured	Change in resistance - Q	Thermal alteration to E.polarization	Expansion of gas to pressure to e.signal
6.	Used	Photocoustic spectroscopy	Diffusive reflectance	FTIR	Non –dispersive IR
7.	Response time	30 sec	4 sec	multiple scanning	0.01sec

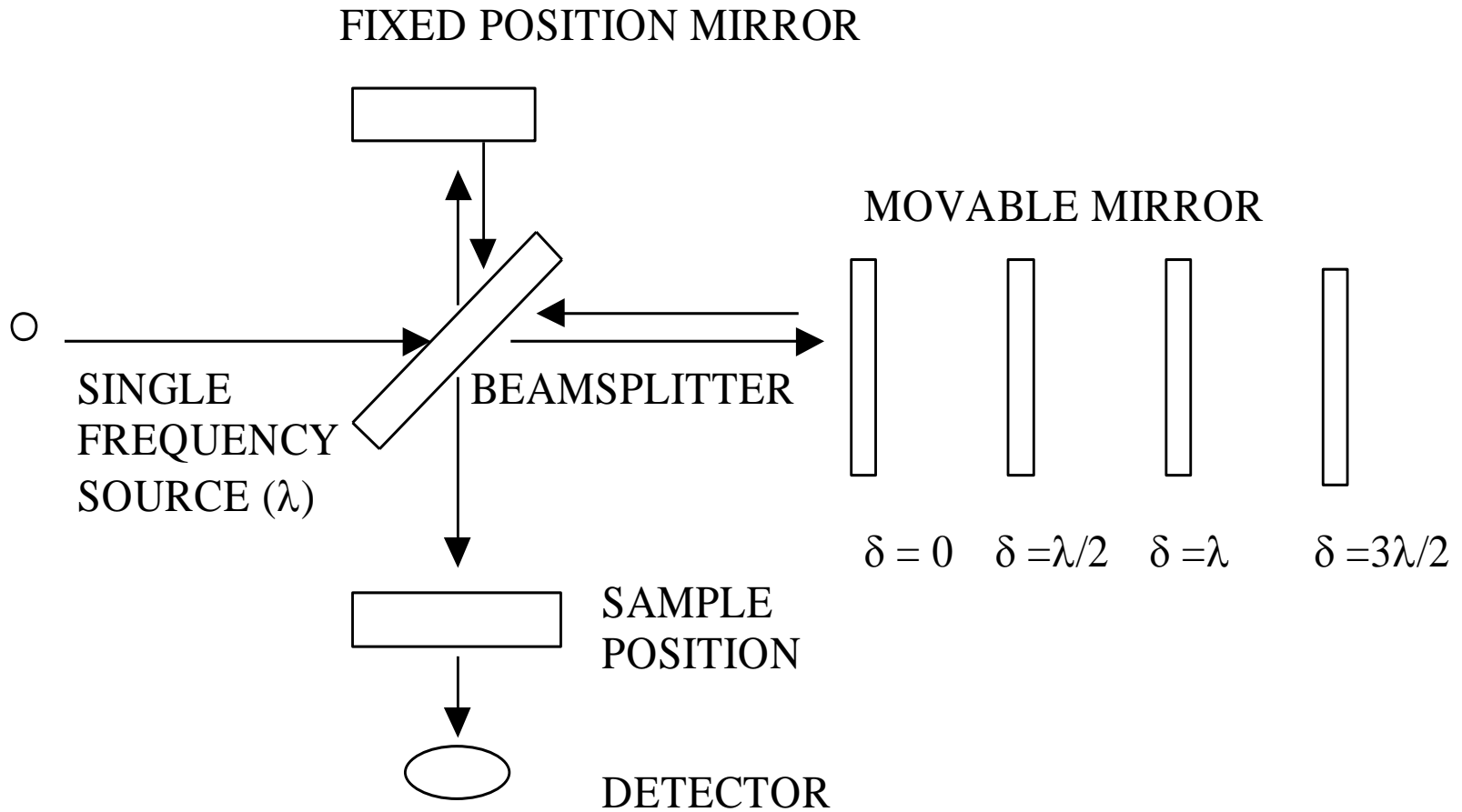
FT – IR spectrophotometer

- *Fourier transform infrared spectroscopy is preferred over dispersive or filter methods of infrared spectral analysis for several reasons:*
 - It is a non-destructive technique
 - It provides a precise measurement method which requires no external calibration
 - It can increase speed, collecting a scan every second
 - It can increase sensitivity – one second scans can be co-added together to ratio out random noise
 - It has greater optical throughput
 - It is mechanically simple with only one moving part

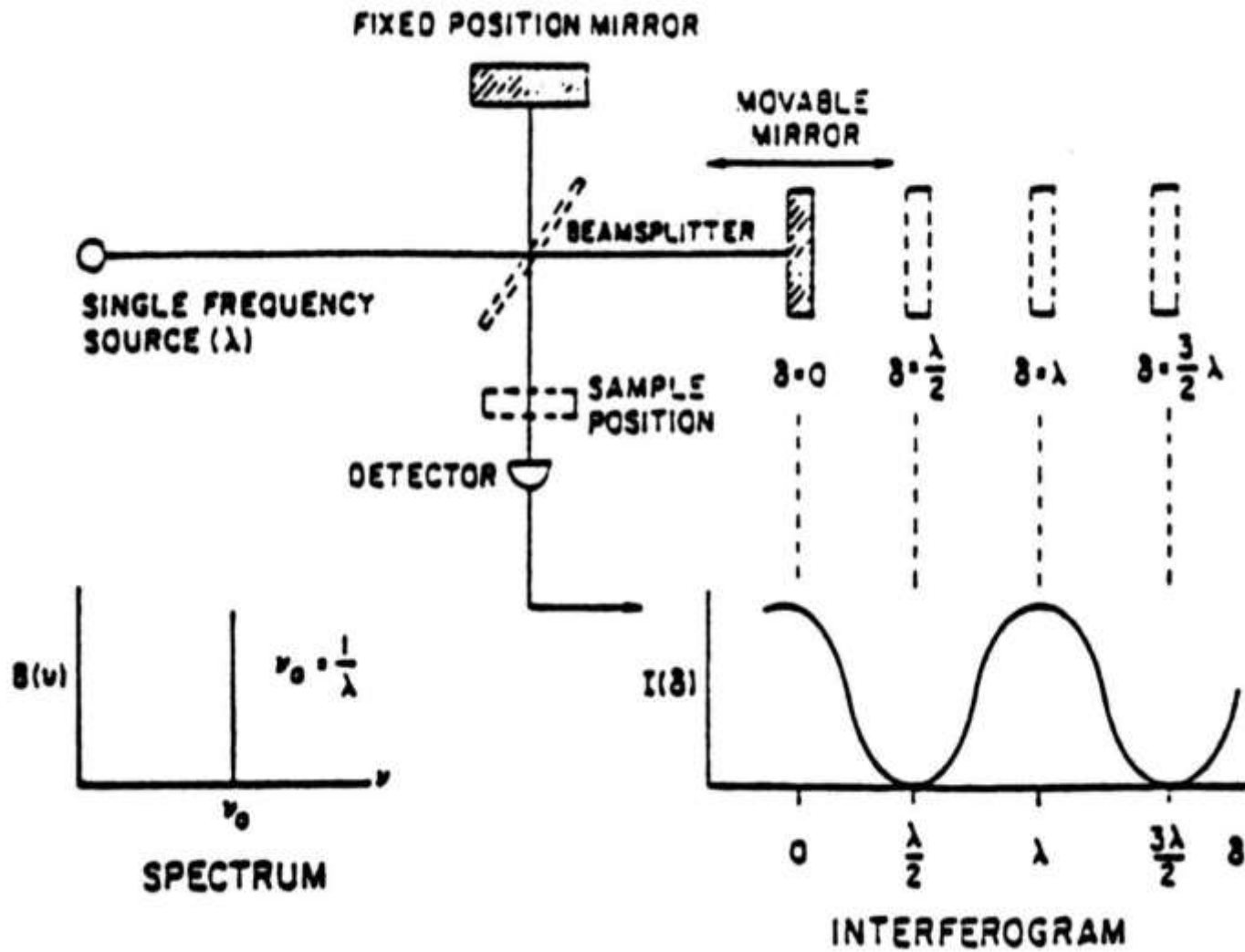
Why FT-IR?

- Fourier Transform Infrared (FT-IR) spectrometry was developed in order to overcome the limitations encountered with dispersive instruments. The main difficulty was the slow scanning process. A method for measuring all of the infrared frequencies **simultaneously**, rather than individually, was needed.
- A solution was developed which employed a very simple optical device called an **interferometer**.
- The interferometer produces a unique type of signal which has all of the infrared frequencies “encoded” into it.
- The signal can be measured very quickly, usually on the order of **one second** or so.
- Thus, the time element per sample is reduced to a matter of a few seconds rather than several minutes.





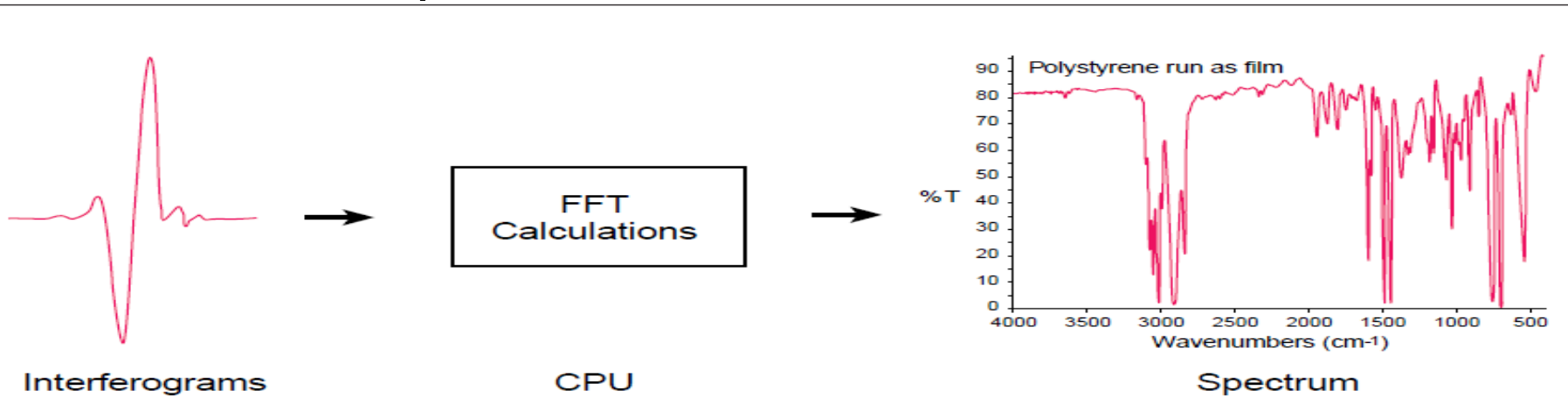
THE MICHELSON INTERFEROMETER



Schematic of a Michelson Interferometer.

- Most interferometers employ a **beamsplitter** which takes the incoming infrared beam and divides it into two optical beams. One beam reflects off of a flat mirror which is fixed in place.
- The other beam reflects off of a flat mirror which is on a mechanism which allows this mirror to move a very short distance (typically a few millimeters) away from the beamsplitter.
- The two beams reflect off of their respective mirrors and are recombined when they meet back at the beamsplitter. Because the path that one beam travels is a fixed length and the other is constantly changing as its mirror moves, the signal which exits the interferometer is the result of these two beams “interfering” with each other. The resulting signal is called an **interferogram** which has the unique property that every data point (a function of the moving mirror position) which makes up the signal has information about every infrared frequency which comes from the source.
- This means that as the interferogram is measured, all frequencies are being measured **simultaneously**. Thus, the use of the interferometer results in extremely fast measurements.

- Because the analyst requires a **frequency spectrum** (a plot of the intensity at each individual frequency) in order to make an identification, the measured interferogram signal can not be interpreted directly.
- A means of “decoding” the individual frequencies is required. This can be accomplished via a well-known mathematical technique called the **Fourier transformation**.
- This transformation is performed by the computer which then presents the user with the desired



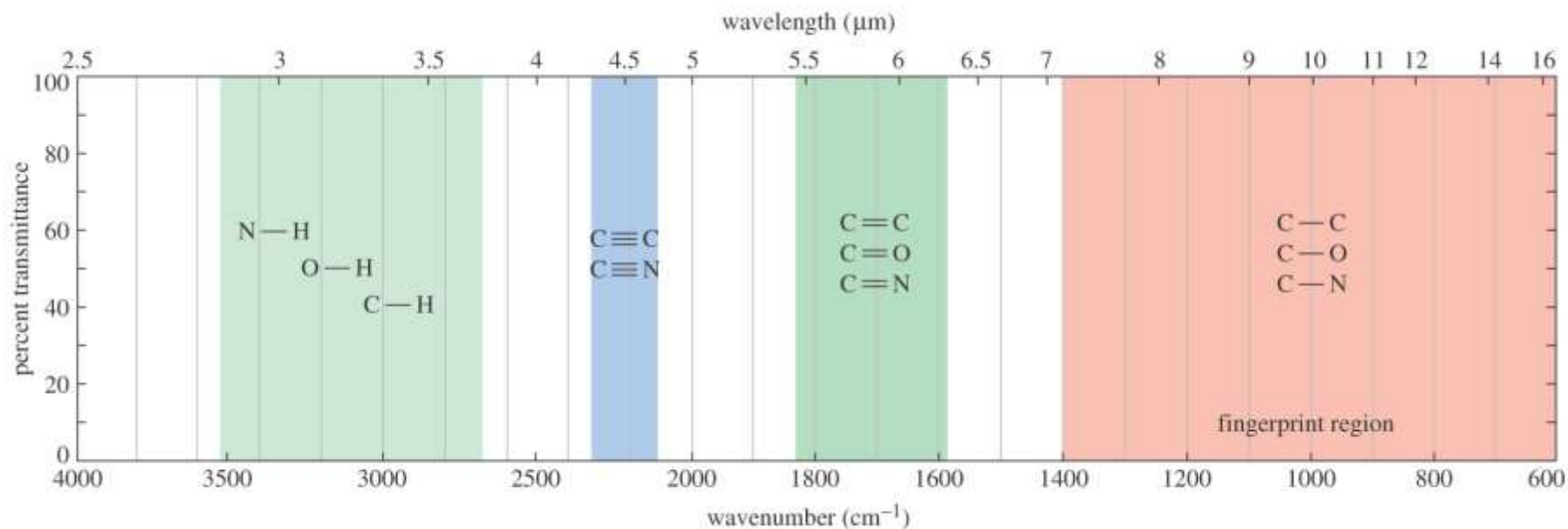
Advantages of FT-IR

- Some of the major advantages of FT-IR over the dispersive technique include:
 - **Speed:** Because all of the frequencies are measured simultaneously, most measurements by FT-IR are made in a matter of seconds rather than several minutes. This is sometimes referred to as the **Felgett Advantage**.
 - **Sensitivity:** Sensitivity is dramatically improved with FT-IR for many reasons. The detectors employed are much more sensitive, the optical throughput is much higher (referred to as the **Jacquinot Advantage**) which results in much lower noise levels, and the fast scans enable the coaddition of several scans in order to reduce the random measurement noise to any desired level (referred to as **signal averaging**).
 - **Mechanical Simplicity:** The moving mirror in the interferometer is the only continuously moving part in the instrument. Thus, there is very little possibility of mechanical breakdown.
 - **Internally Calibrated:** These instruments employ a HeNe laser as an internal wavelength calibration standard (referred to as the **Connes Advantage**). These instruments are self-calibrating and never need to be calibrated by the user.

Ranges of IR

O-H	C-H	C≡C C≡N	Very few Bands	C=O	C=C Alkene, Aromatic	C-N	C-O	C-Cl
N-H					C=N	C-C		
					(N=O O=N)			
4000	2500	2000	1800	1650	1550			650

Summary of IR Absorptions



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TABLE 17-3 Abbreviated Table of Group Frequencies for Organic Functional Groups

Bond	Type of Compound	Frequency Range, cm^{-1}	Intensity
C—H	Alkanes	2850–2970	Strong
		1340–1470	Strong
C—H	Alkenes (>C=C<H)	3010–3095	Medium
		675–995	Strong
C—H	Alkynes ($\text{—C}\equiv\text{C—H}$)	3300	Strong
C—H	Aromatic rings	3010–3100	Medium
		690–900	Strong
O—H	Monomeric alcohols, phenols	3590–3650	Variable
	Hydrogen-bonded alcohols, phenols	3200–3600	Variable, sometimes broad
	Monomeric carboxylic acids	3500–3650	Medium
	Hydrogen-bonded carboxylic acids	2500–2700	Broad
N—H	Amines, amides	3300–3500	Medium
C=C	Alkenes	1610–1680	Variable
C=C	Aromatic rings	1500–1600	Variable
C≡C	Alkynes	2100–2260	Variable
C—N	Amines, amides	1180–1360	Strong
C≡N	Nitriles	2210–2280	Strong
C—O	Alcohols, ethers, carboxylic acids, esters	1050–1300	Strong
C=O	Aldehydes, ketones, carboxylic acids, esters	1690–1760	Strong
NO ₂	Nitro compounds	1500–1570	Strong
		1300–1370	Strong

Carbon-Carbon Bond Stretching

- Stronger bonds absorb at higher frequencies:
 - C-C 1200 cm^{-1}
 - C=C 1660 cm^{-1}
 - C \equiv C 2200 cm^{-1} (weak or absent if internal)
- Conjugation lowers the frequency:
 - isolated C=C 1640-1680 cm^{-1}
 - conjugated C=C 1620-1640 cm^{-1}
 - aromatic C=C approx. 1600 cm^{-1} =>

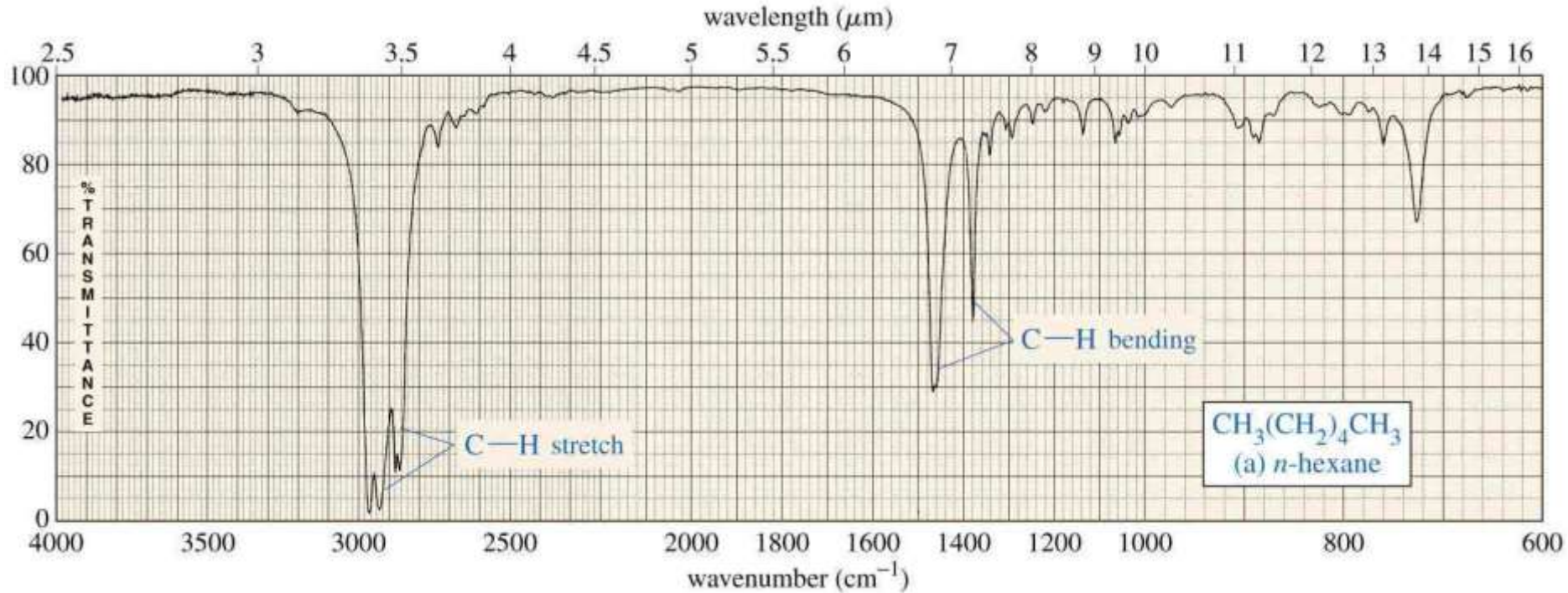
Carbon-Hydrogen Stretching

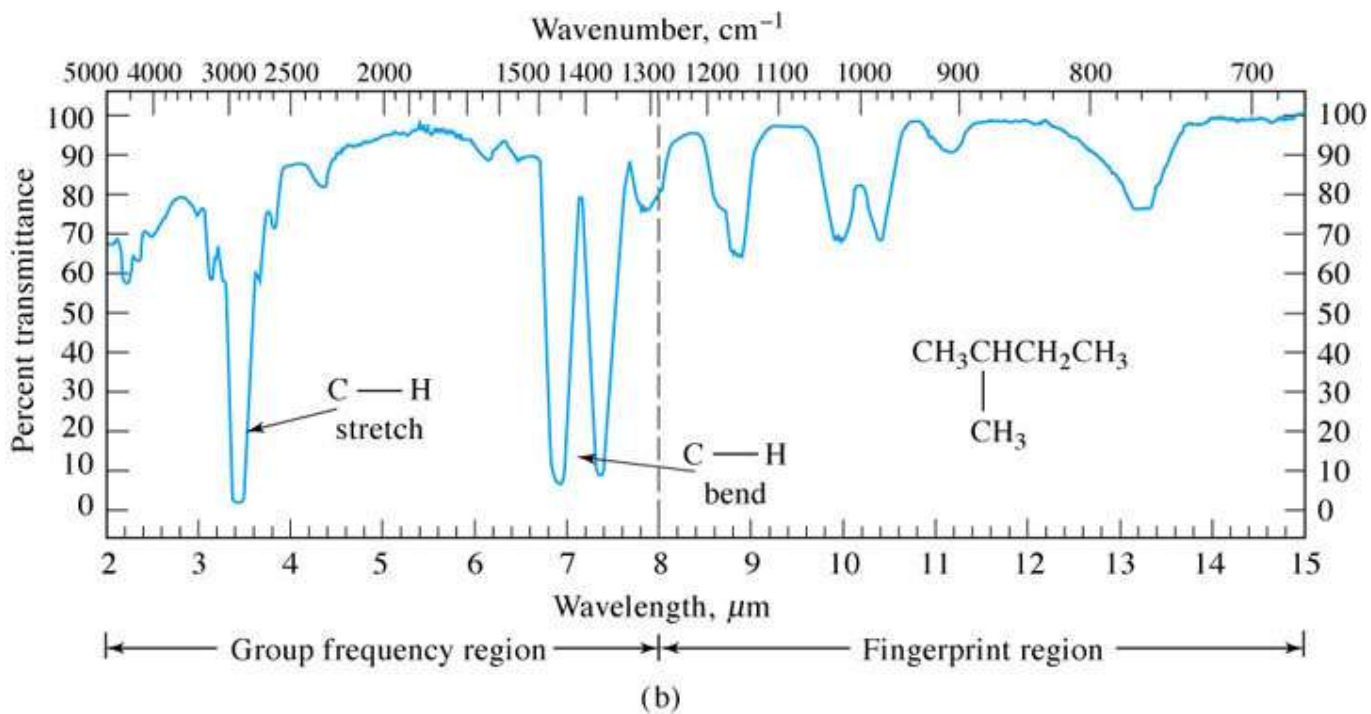
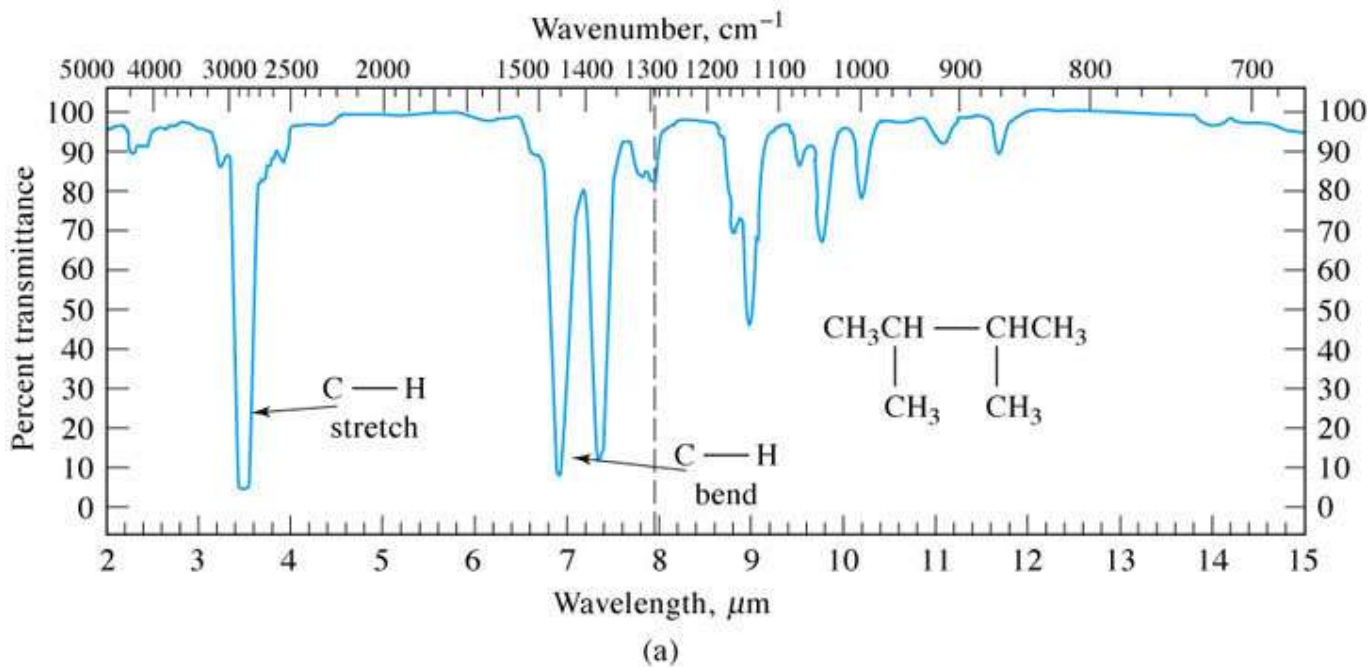
Bonds with more *s* character absorb at a higher frequency.

- sp^3 C-H, just below 3000 cm^{-1} (to the right)
- sp^2 C-H, just above 3000 cm^{-1} (to the left)
- sp C-H, at 3300 cm^{-1}

=>

An Alkane IR Spectrum





N-Alkanes

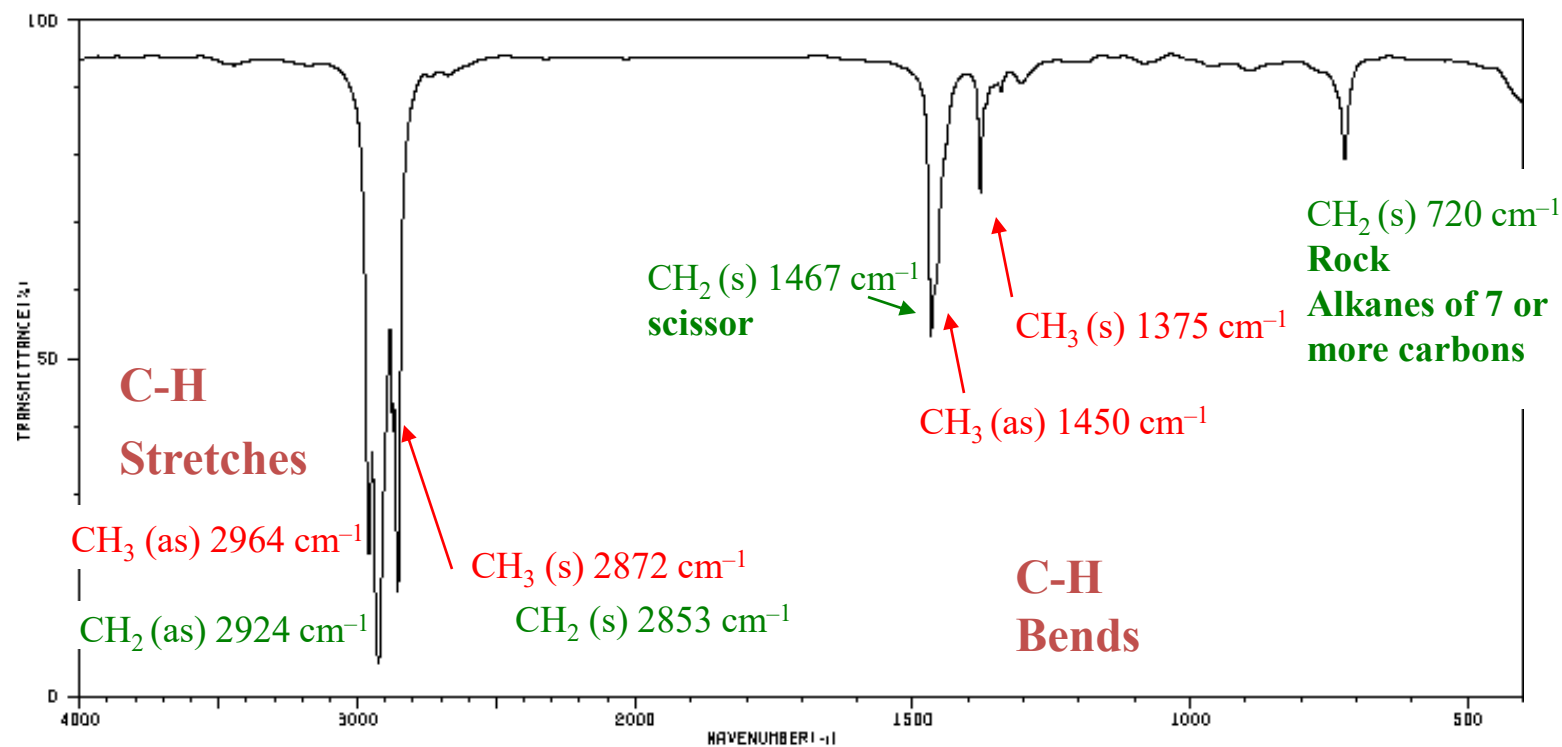
- interpreted in terms of 4 vibrations:
 - stretching and bending of C–H and C–C bonds
 - C–C bends: ca. 500 cm^{-1} (out of spectral window)
 - C–C stretches: $1200\text{--}800\text{ cm}^{-1}$, weak bands
not of value for interpretation (fingerprint)

more characteristic

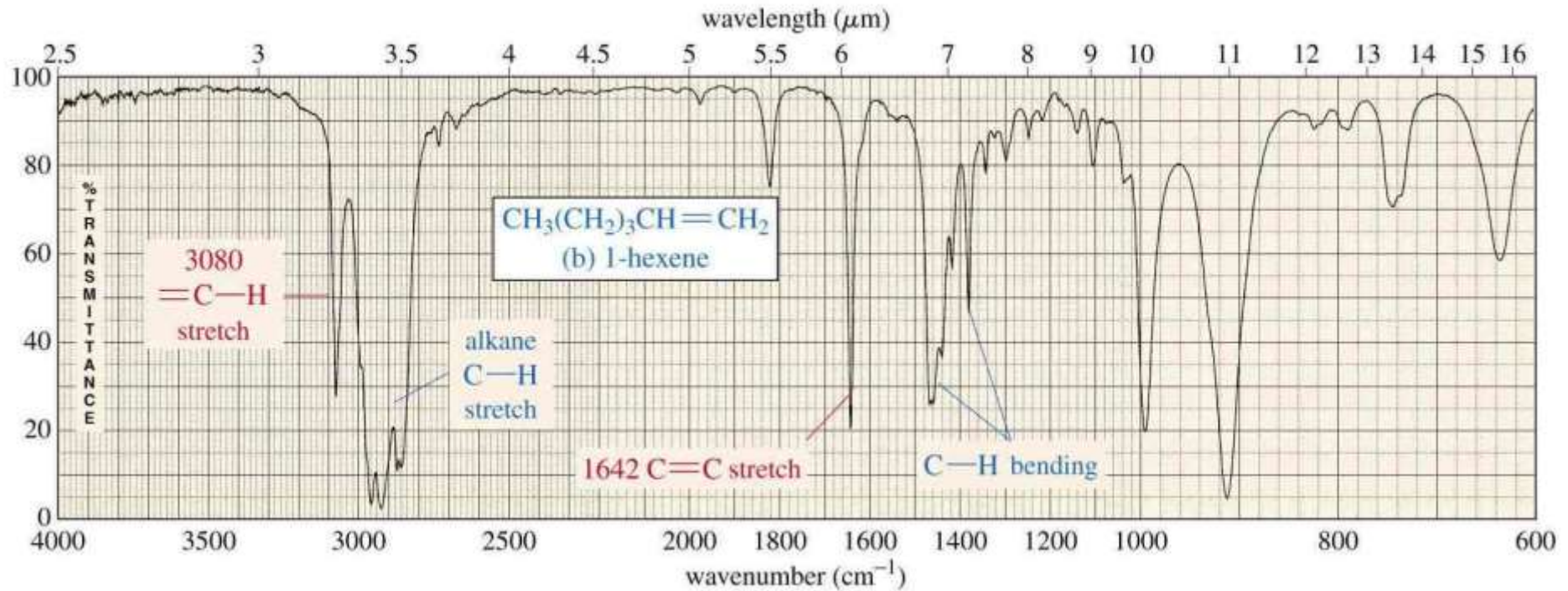
- C–H stretches: occurs from $3000\text{--}2840\text{ cm}^{-1}$
 - CH₃: 2962 cm^{-1} , asymmetrical stretch
 2872 cm^{-1} , symmetrical stretch
 - CH₂: 2926 cm^{-1} , asymmetrical stretch
 2853 cm^{-1} , symmetrical stretch

Note precision!

n-alkanes

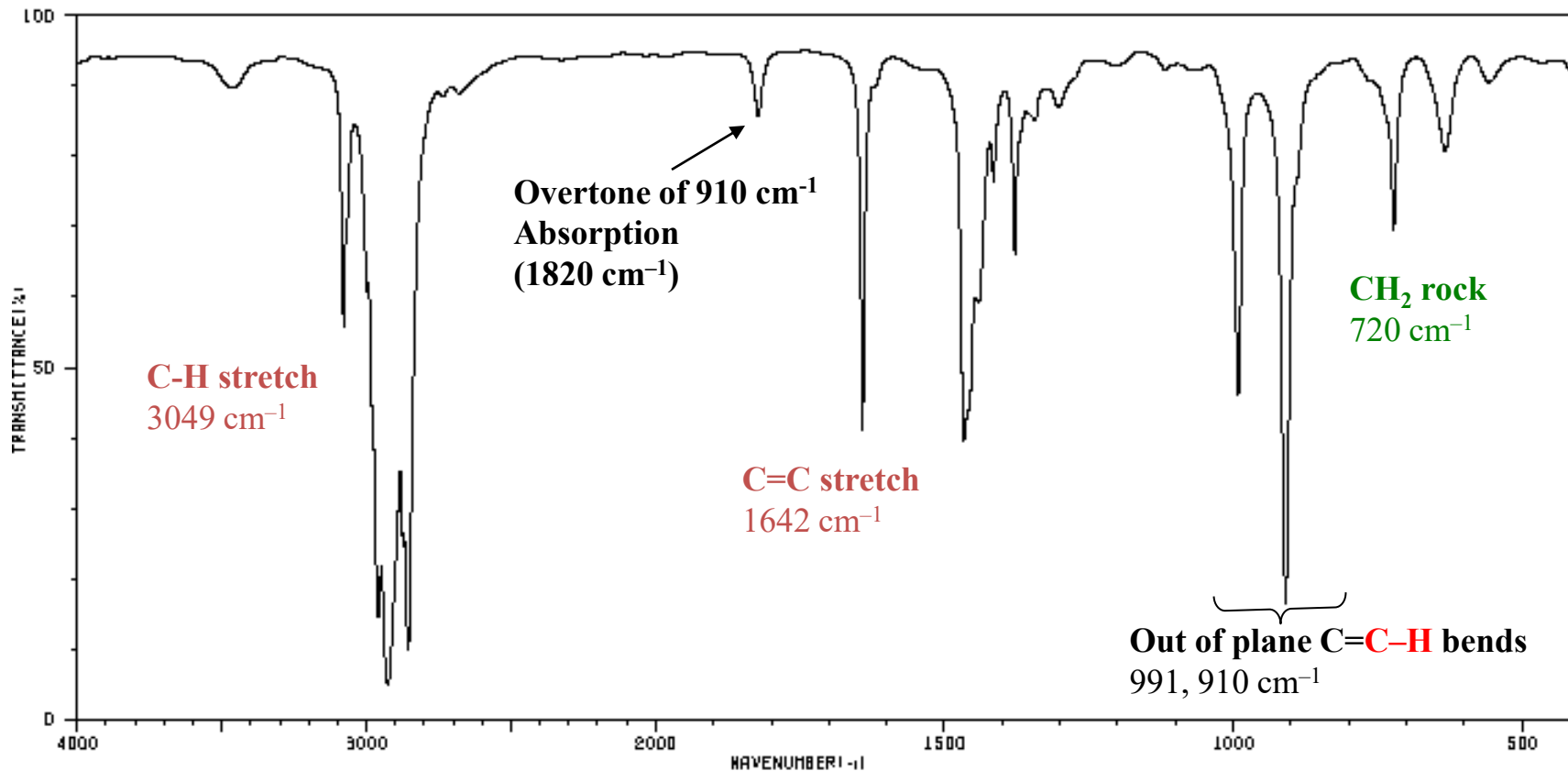


An Alkene IR Spectrum

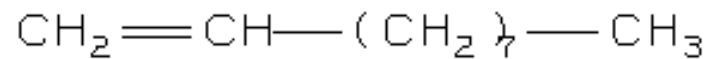


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Unconjugated Alkenes



1-decene



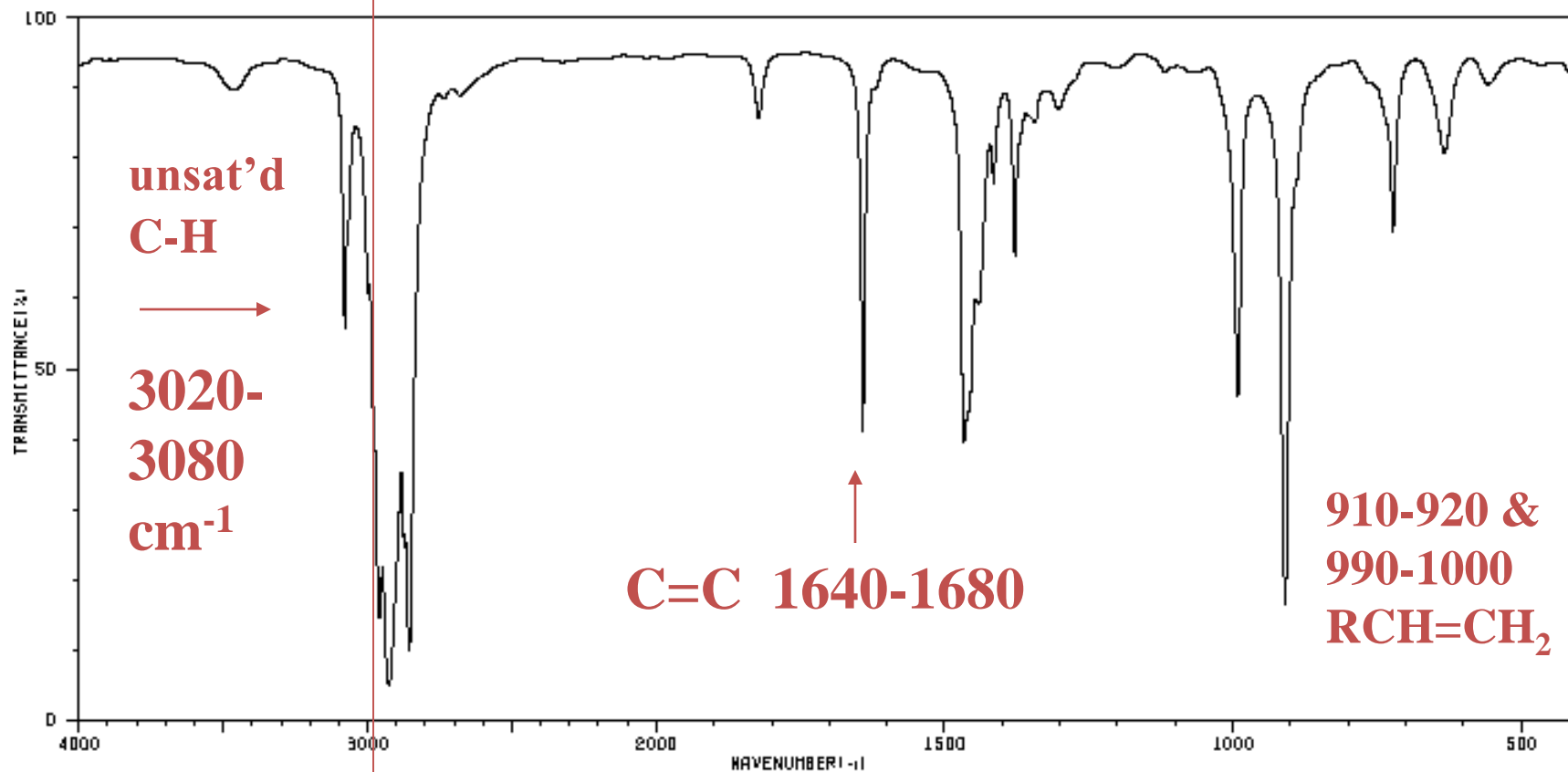
HIT-NO=1698

SCORE= ()

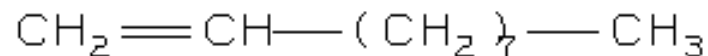
SDBS-NO=2024

IR-NIDA-04854 : LIQUID FILM

1-DECENE

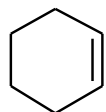
1-decene $C_{10}H_{20}$ 

3467	86	2874	29	1379	64
3457	86	2858	9	1343	81
3079	53	2678	86	1303	84
3068	68	1822	81	991	44
2998	58	1642	39	910	15
2958	13	1467	38	723	86
2926	4	1416	72	633	77



- cyclic alkenes:

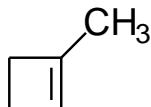
- C=C stretch: sensitive to ring strain



1650 cm⁻¹



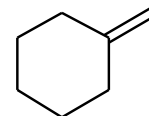
1566 cm⁻¹



1641 cm⁻¹



1640 cm⁻¹



1650 cm⁻¹



1781 cm⁻¹

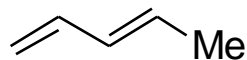
- cumulated alkenes:

- C=C=C stretch (asymmetric): 2000–1900 cm⁻¹

- conjugated alkenes:

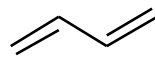
- the alkene bond stretching vibrations in alkenes w/o a center of symmetry give rise to two C=C stretches

- for symmetrical molecules, e.g. butadiene, only the asymmetric stretch is observed

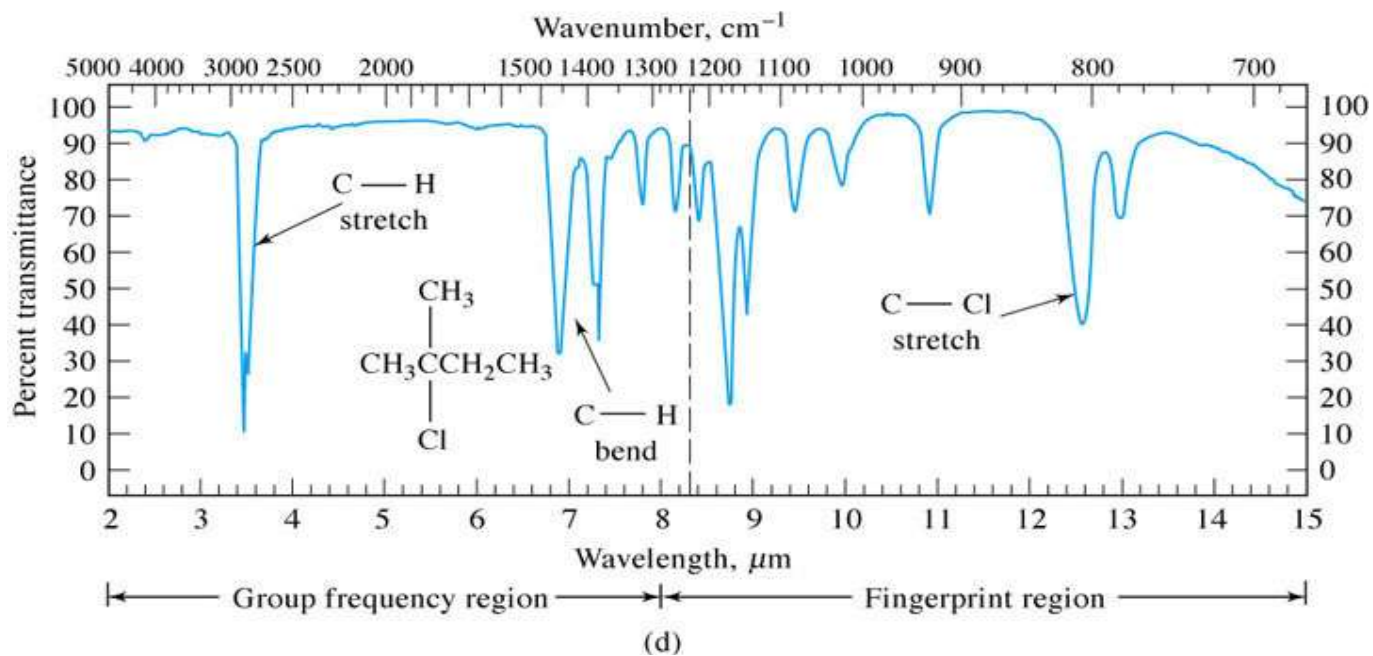
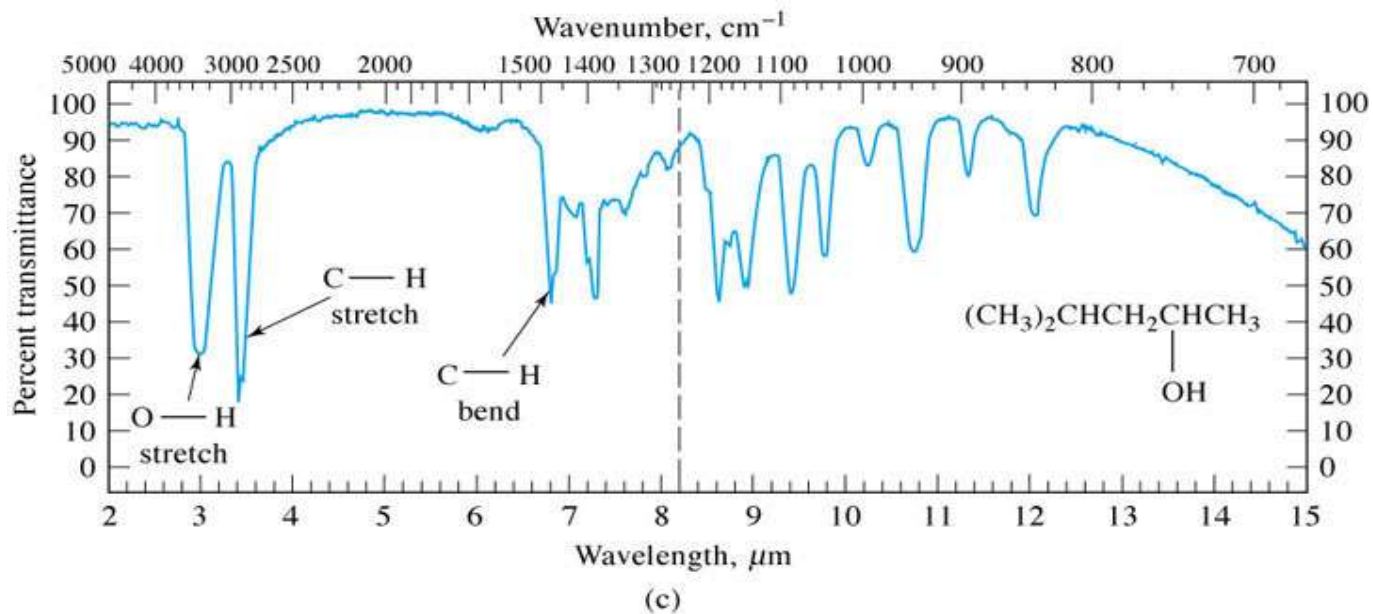


1650 cm⁻¹ (as)

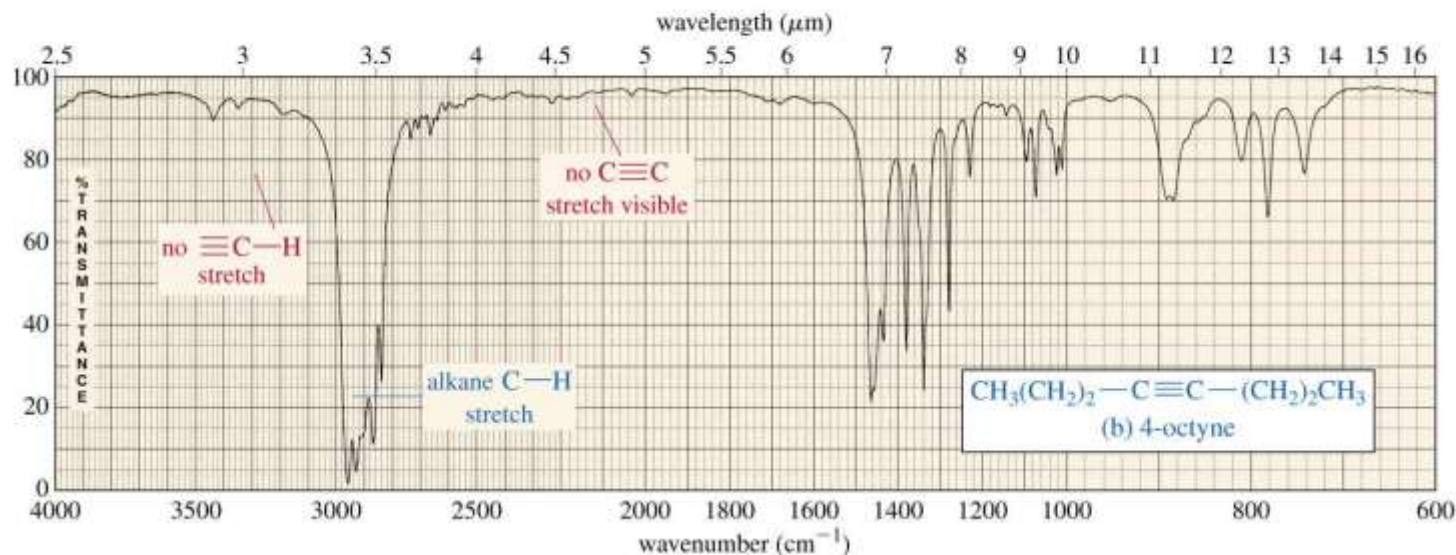
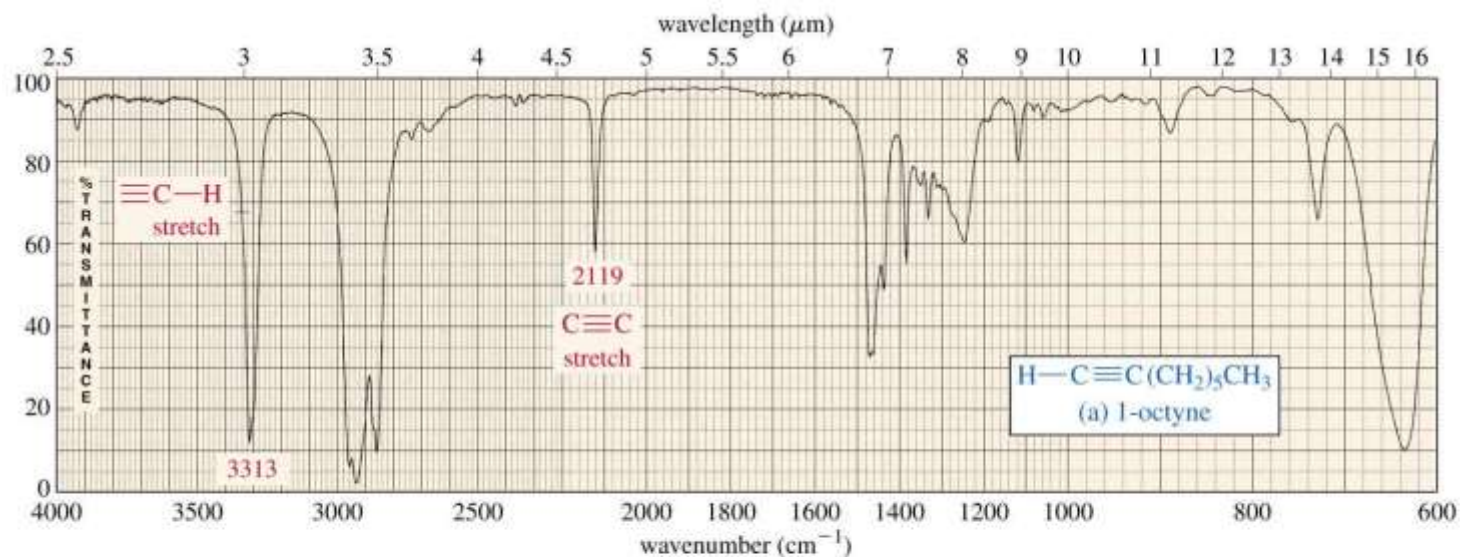
1600 cm⁻¹ (s)



1600 cm⁻¹ (as)



An Alkyne IR Spectrum



O-H and N-H Stretching

- Both of these occur around 3300 cm^{-1} , but they look different.
 - Alcohol O-H, broad with rounded tip.
 - Secondary amine (R_2NH), broad with one sharp spike.
 - Primary amine (RNH_2), broad with two sharp spikes.
 - No signal for a tertiary amine (R_3N) \Rightarrow

Region 4000-2500 cm⁻¹

O-H

C-H

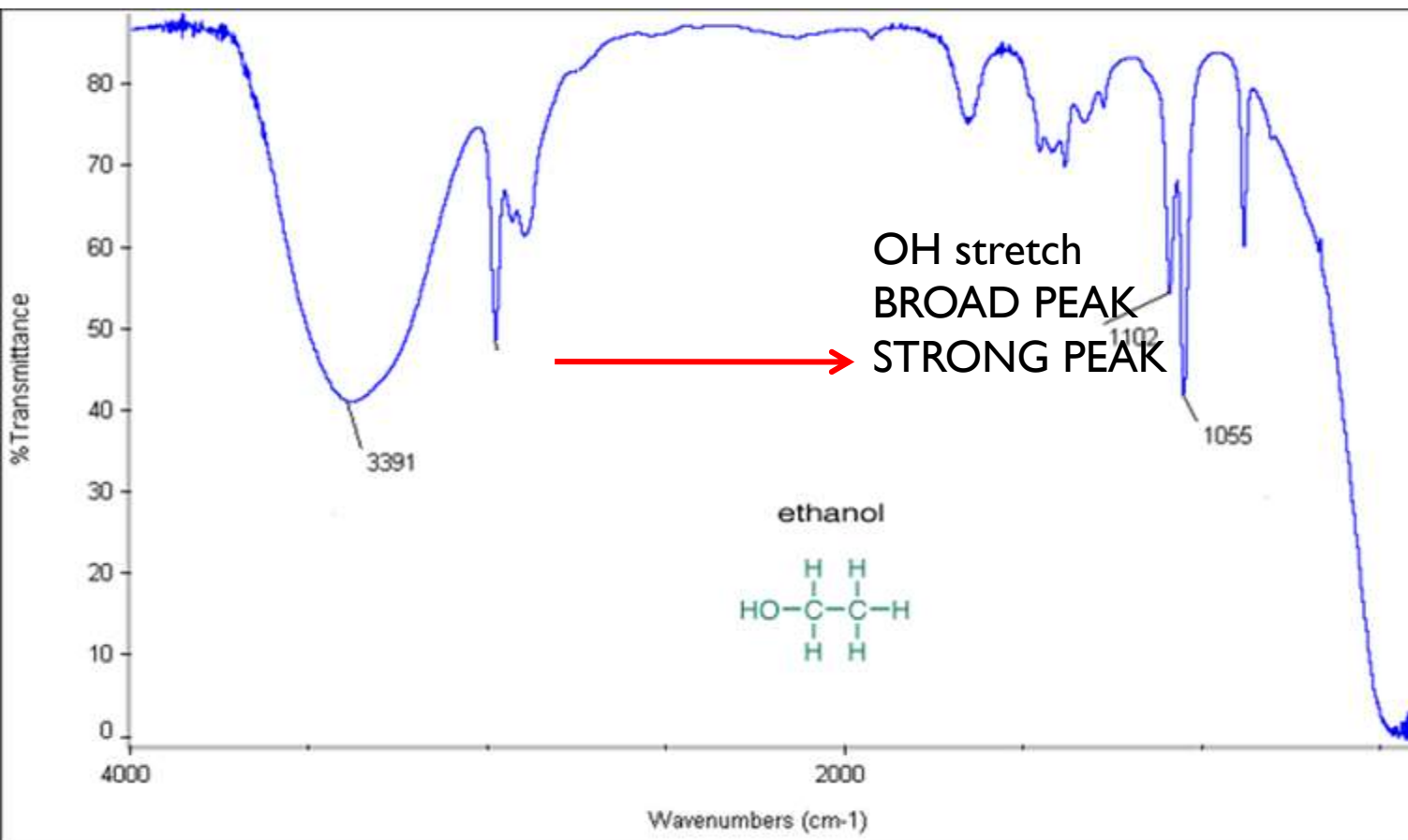
N-H

4000

2500

O-H (*alcohols
and phenols*)
3650-3200 cm⁻¹
Strong, Broad Peak in
the range around 3400
..
Could **NOT** be
confused with another
peak

Alcoholic and phenolic OH



Region 4000-2500 cm^{-1}

O-H

C-H

N-H

4000

2500

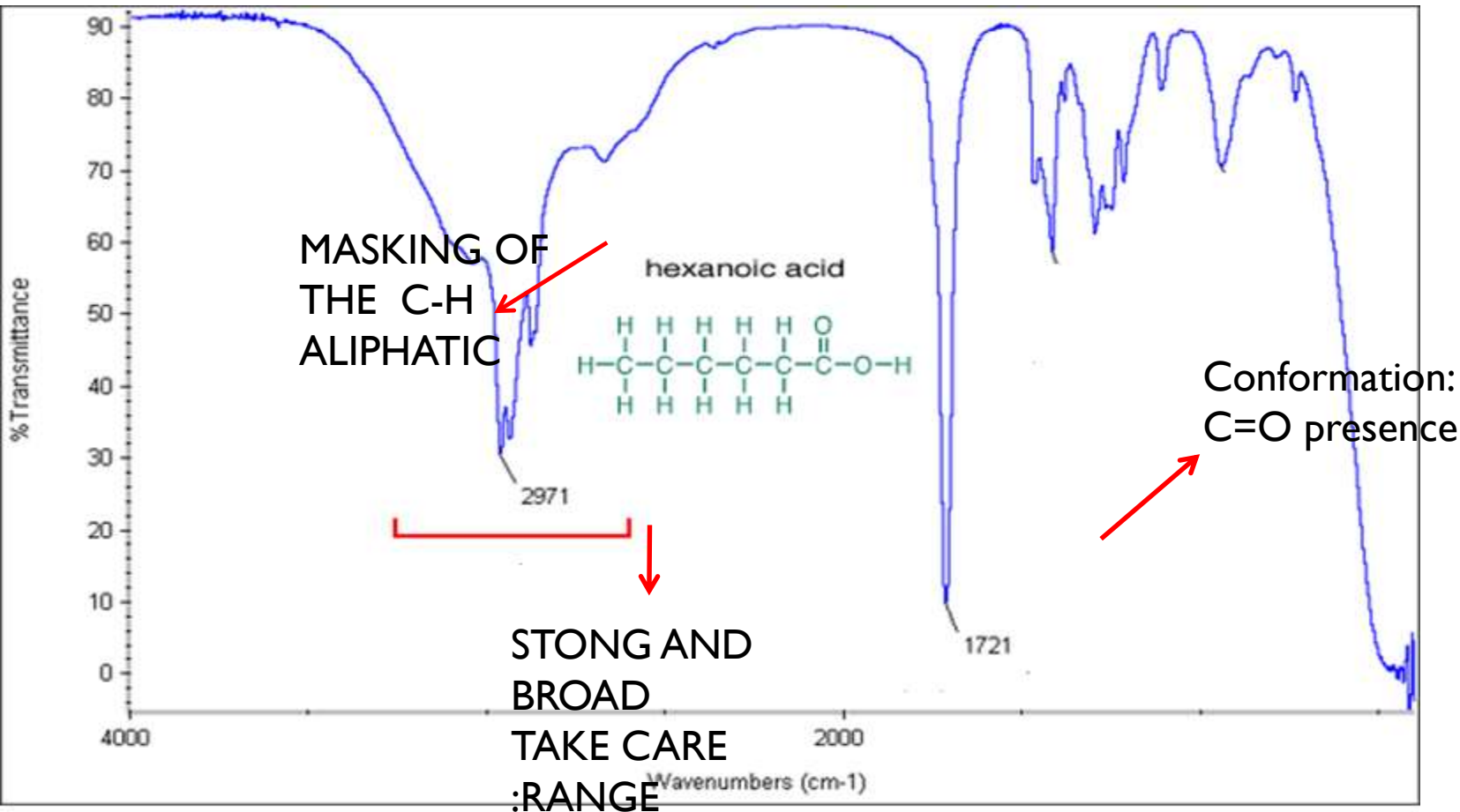
- Strong .. but **MUCH BROADER** than O-H of alcohols and phenols

- Notice the range **3400-2400 cm^{-1}**

- Could **NOT** be confused with O-H alcoholic or phenolic

- Easy to **confirm** by looking for C=O of acid

Carboxylic acid OH



Region 4000-2500 cm^{-1}

O-H

C-H

N-H

4000

2500

3500-3100 cm^{-1}

N-H (stretching)

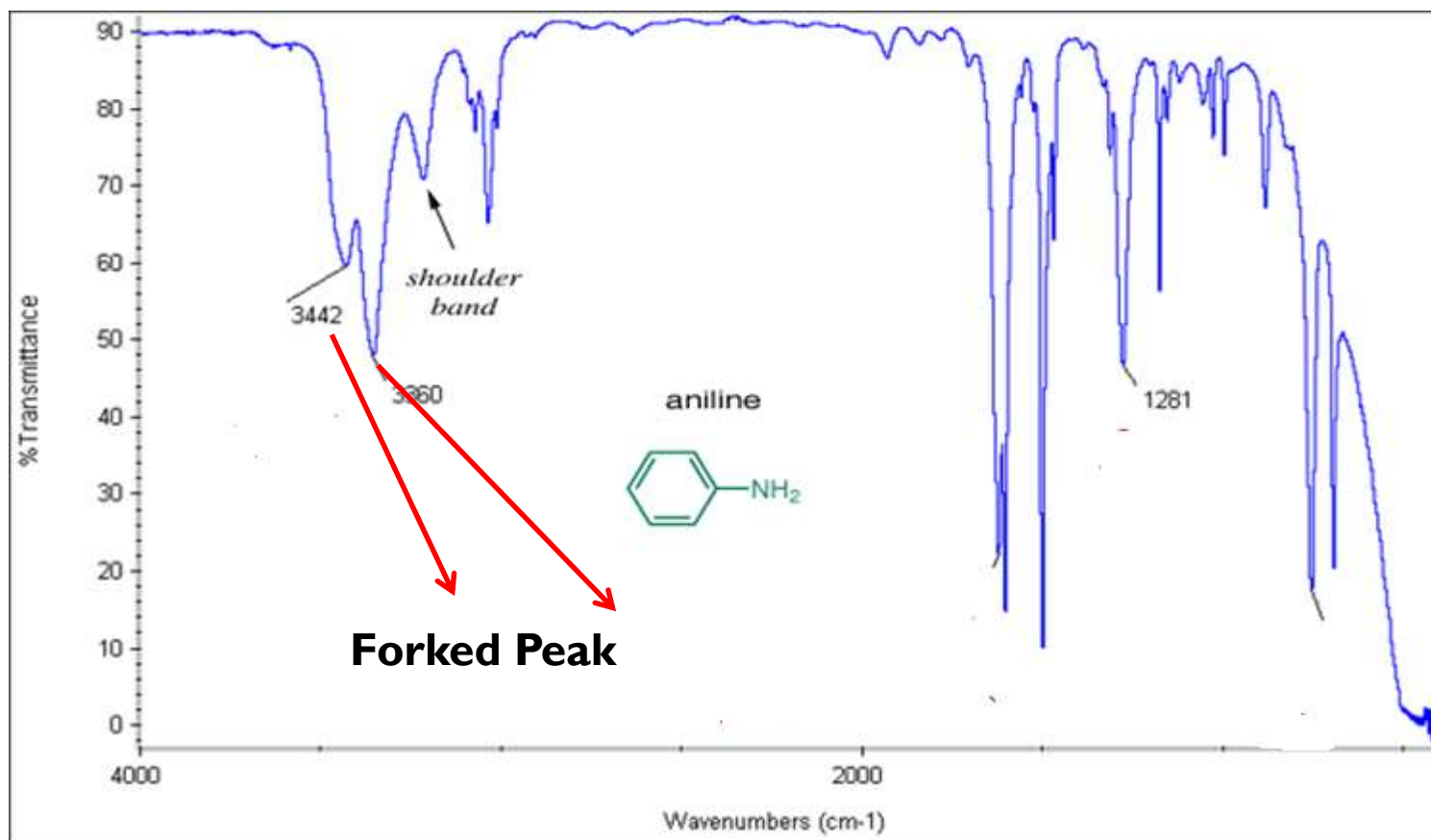
LESS strong .. LESS broad than O-H, **although in the same range!!**

Primary amines (R-NH_2) give **Forked Peak**

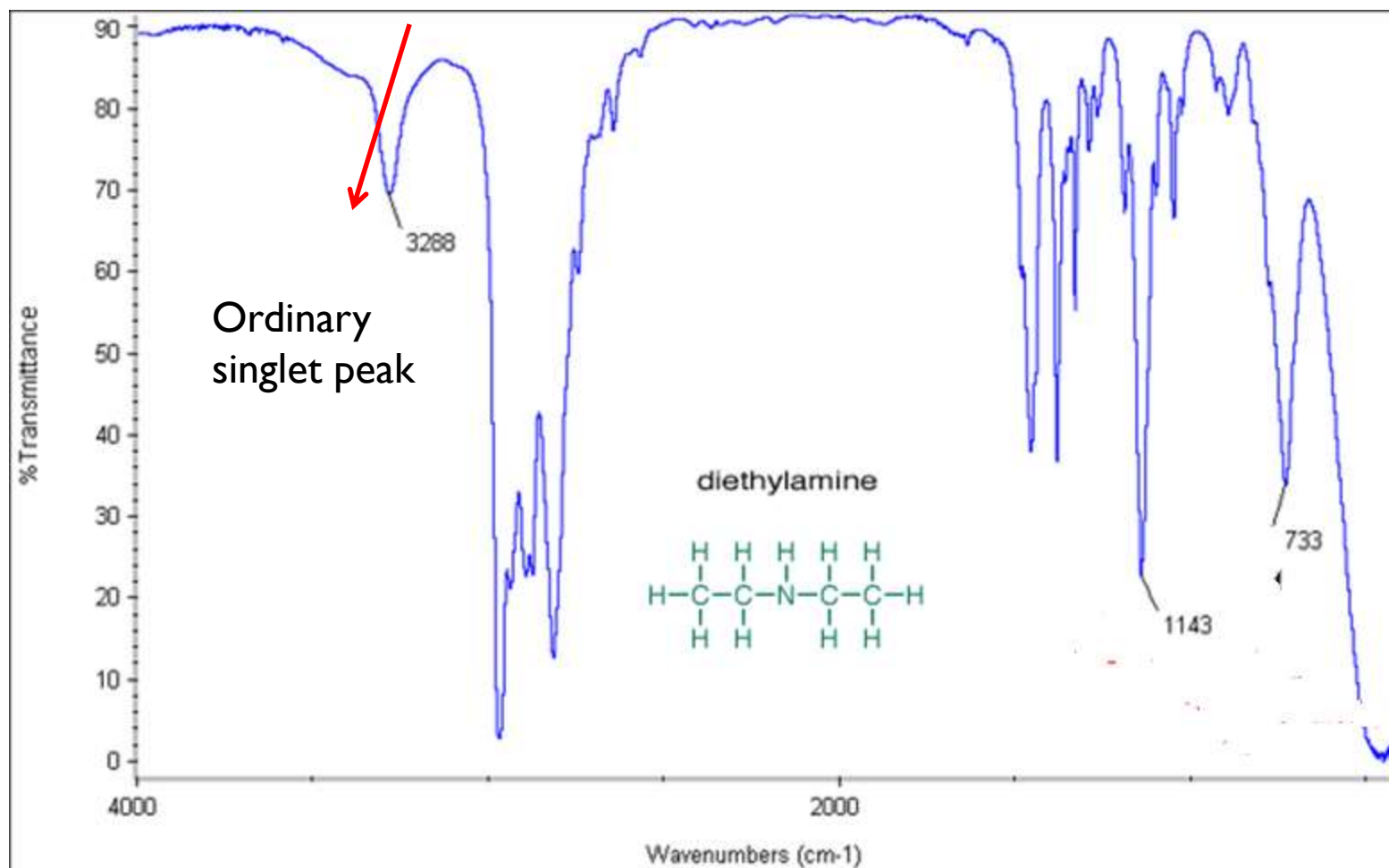
Secondary amines ($\text{R-NH-R}'$) give and ordinary singlet peak

Tertiary amines ($\text{R}_3\text{-N}$) show no peaks in this region .. simply because they donNOT possess any N-H !!!

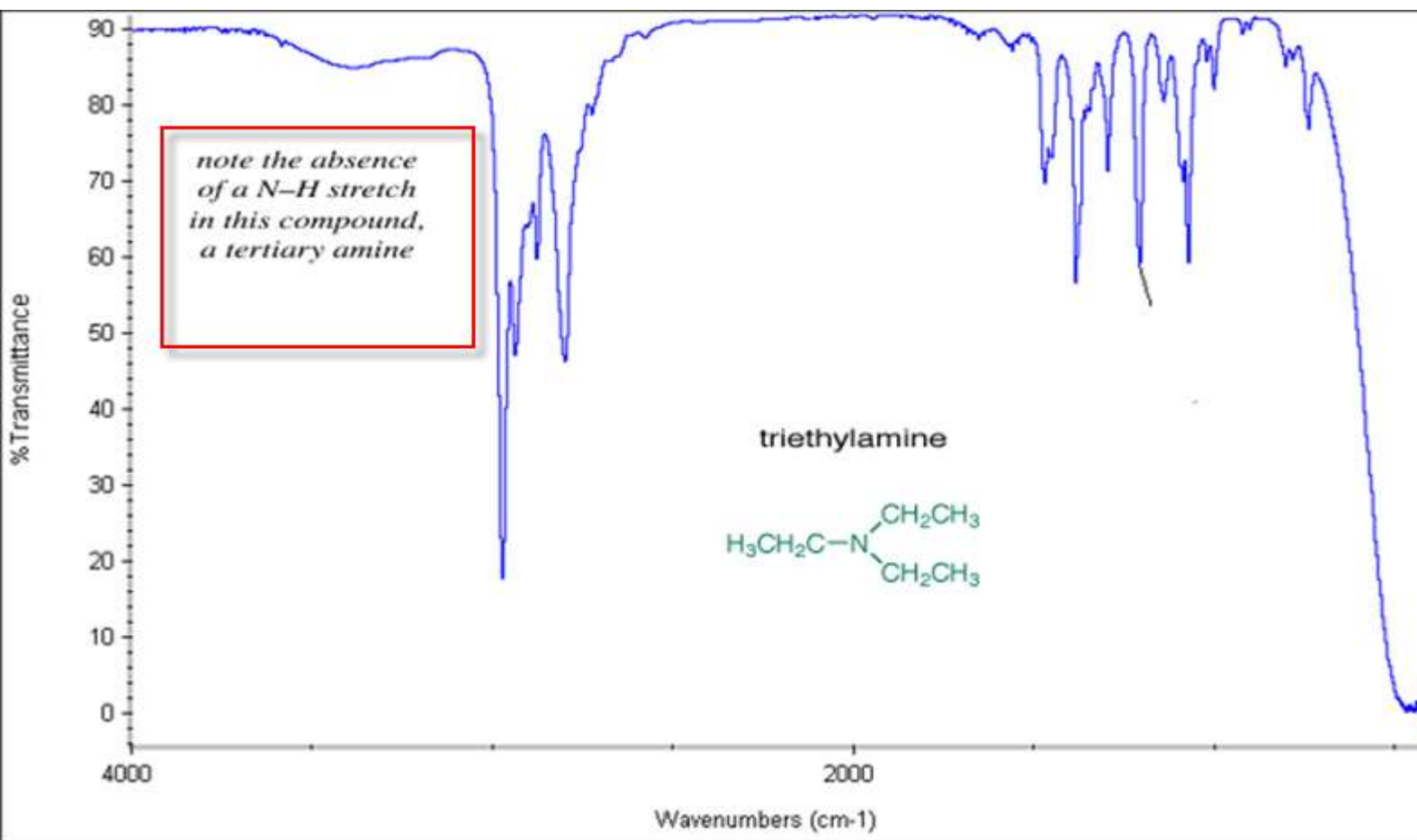
Amines (primary amines)



Amine (secondary amines)



Amines (Tertiary amines)



Region 4000-2500 cm^{-1}

O-H

C-H

N-H

ALKYNE

SHARP, medium

peak around 3300

cm^{-1}

AND

AROMATIC

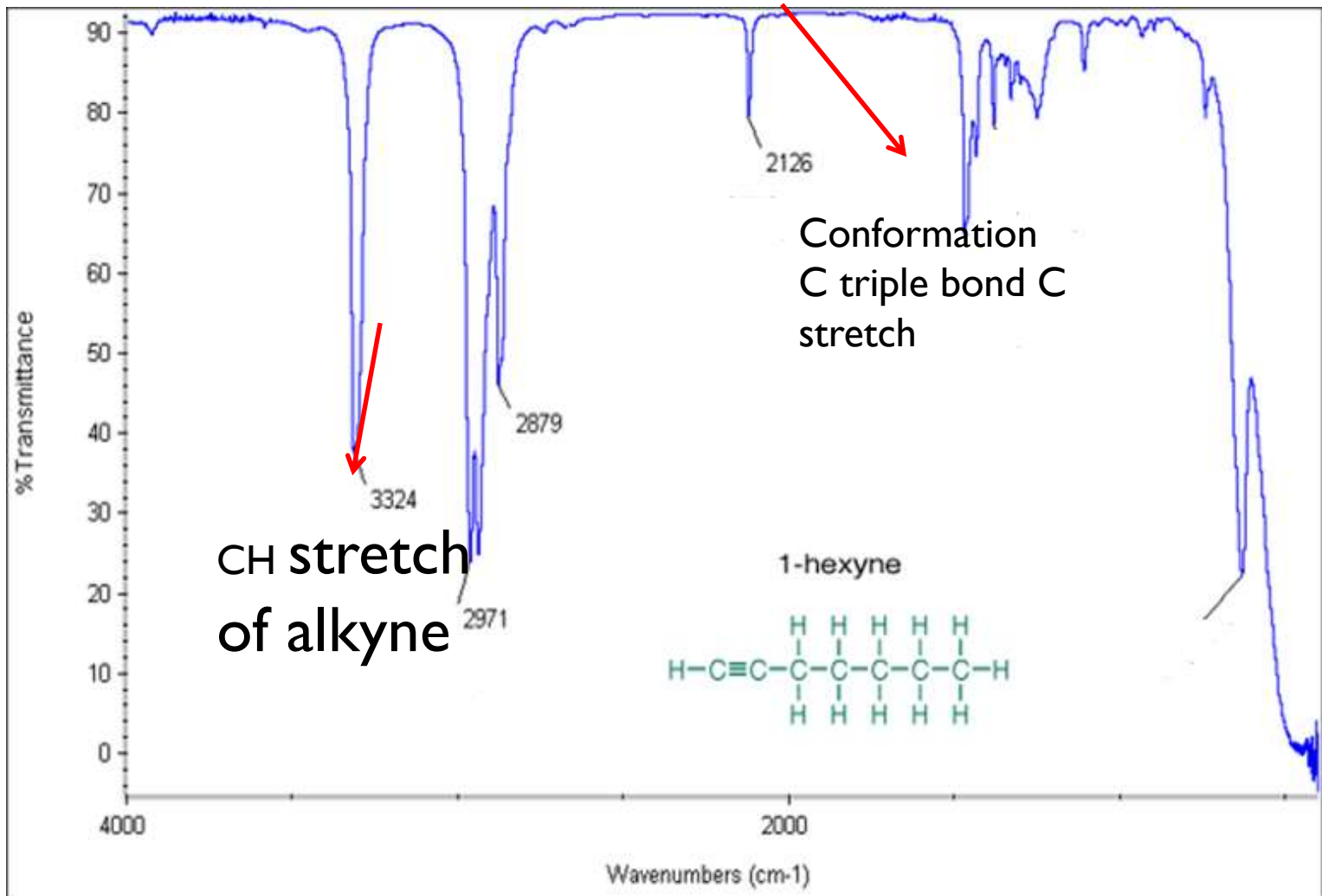
3-ALKANE

4-ALDEHYDIC

4000

2500

C-H ALKYNE



Region 4000-2500 cm^{-1}

O-H

C-H

N-H

4000

2500

2-Alkene and

Aromatic

3100-3000 cm^{-1}

2-Alkene and

Simply to the

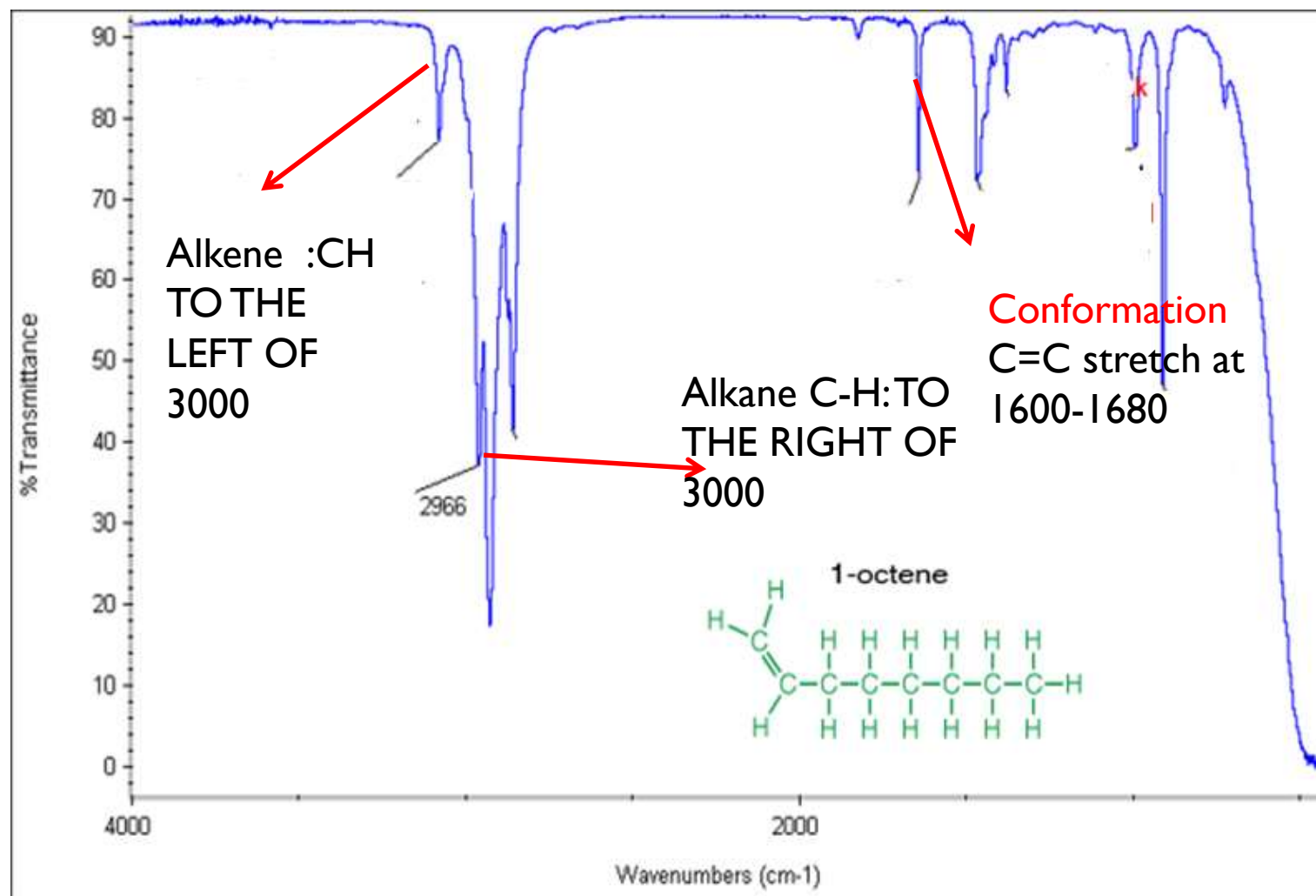
Aromatic

LEFT of 3000

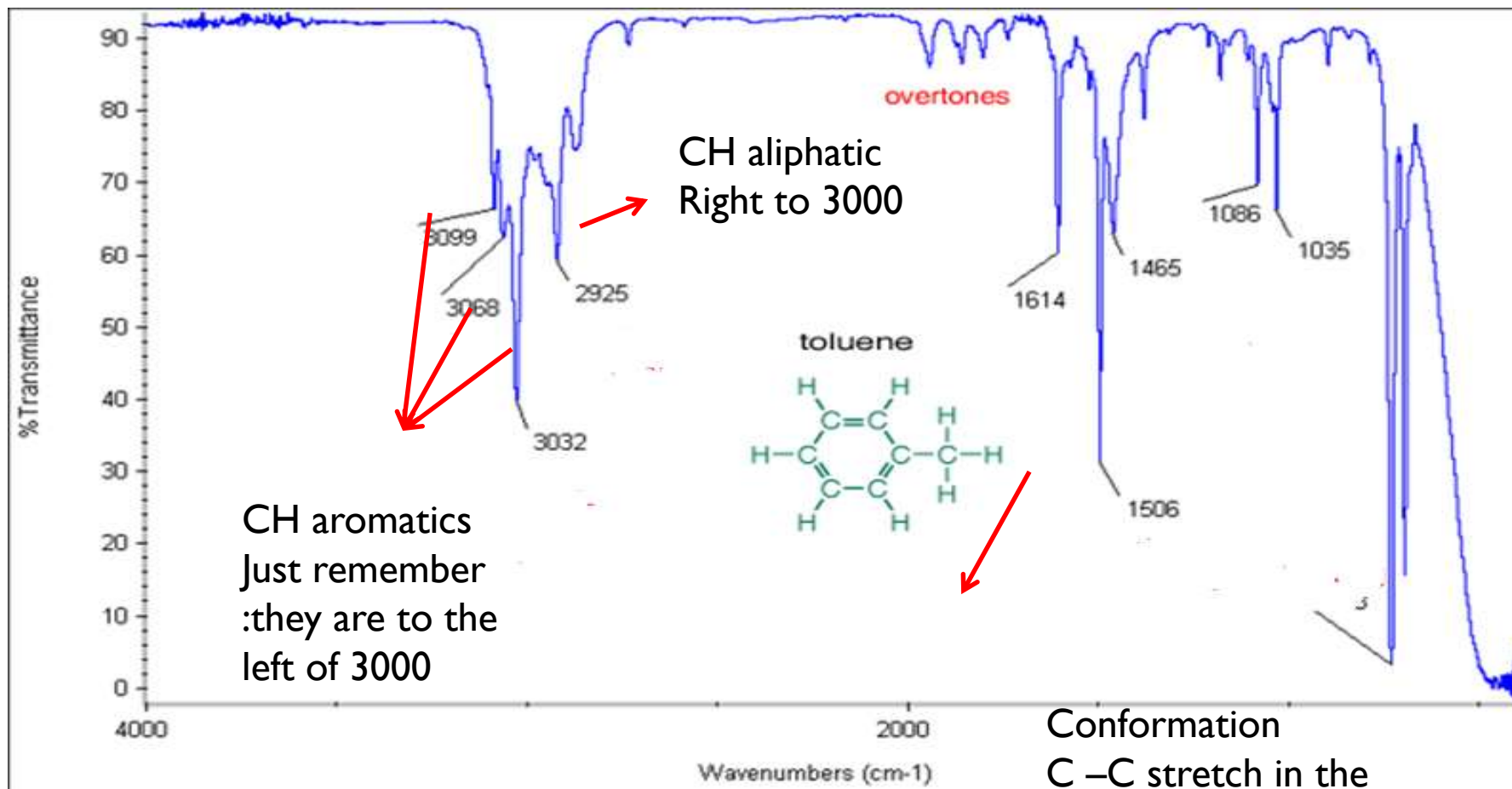
3-Alkane

4-Aldehydic

C-H Alkene



C-H aromatic

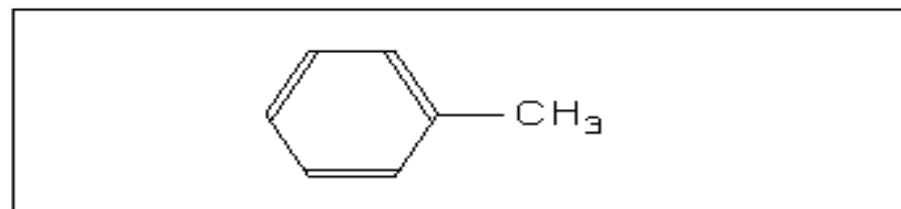
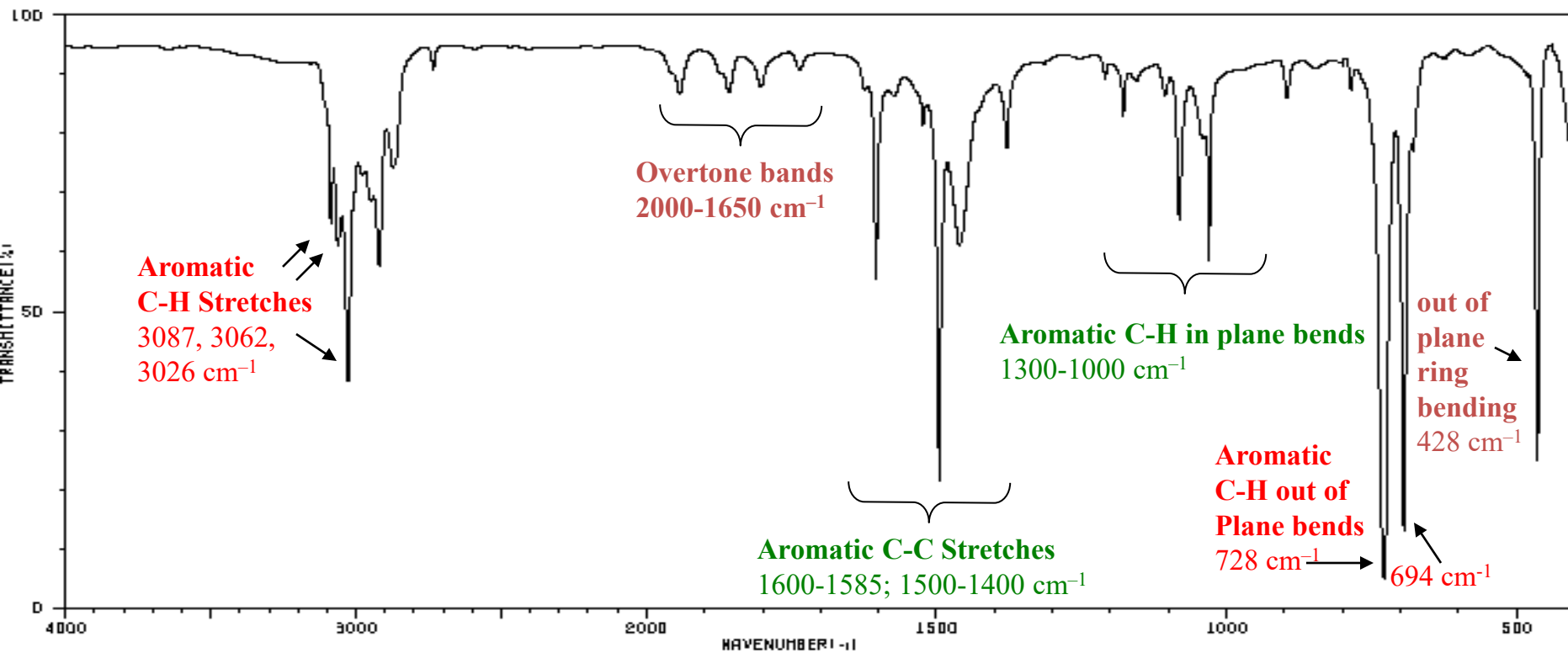


CH aliphatic
Right to 3000

CH aromatics
Just remember
:they are to the
left of 3000

Conformation
C -C stretch in the
ring (two peaks)
1600 and 1475

Mononuclear Aromatics



Region 4000-2500 cm^{-1}

O-H

C-H

N-H

4000

2500

3-ALKANE

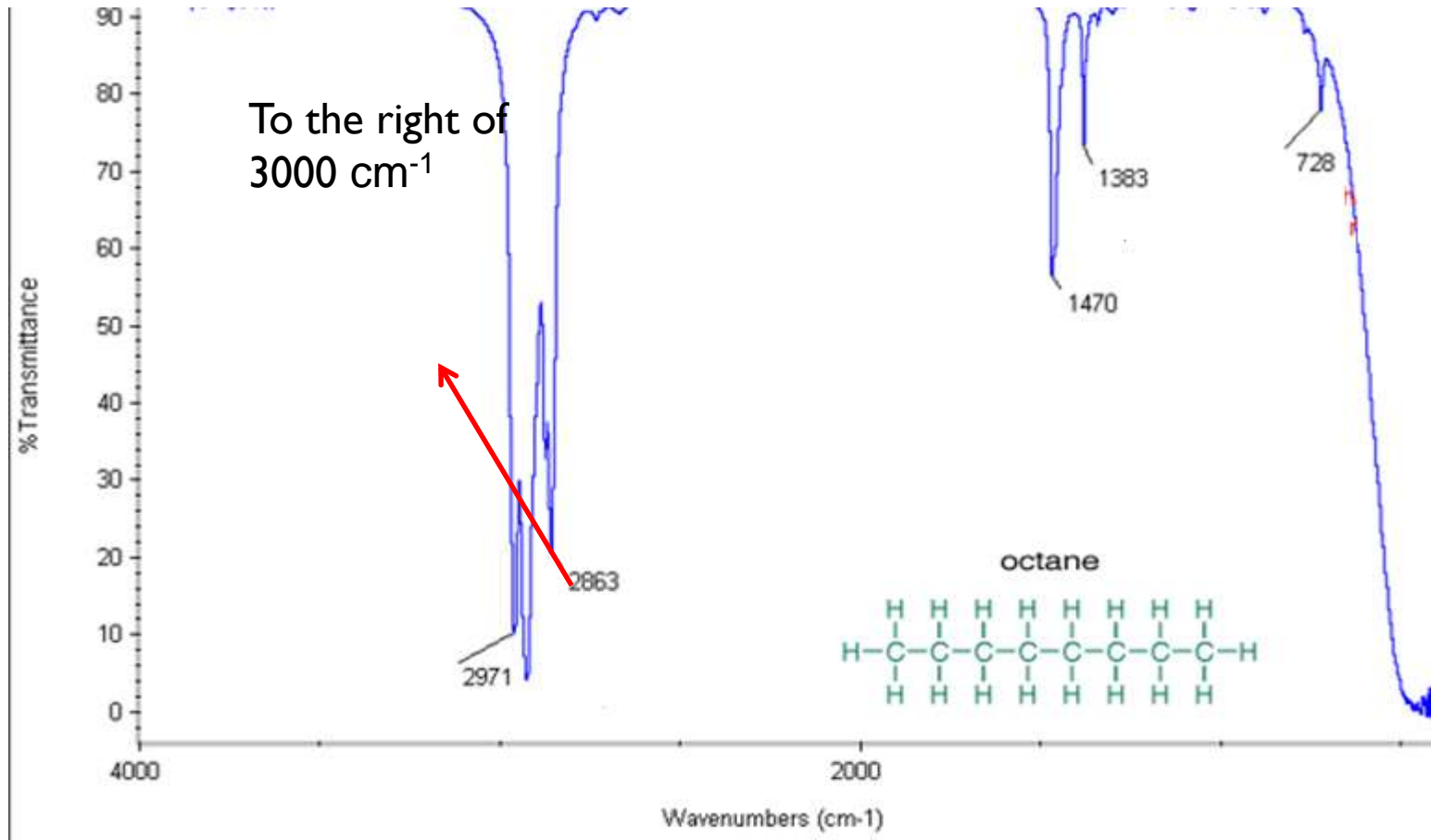
3000-2900 cm^{-1}
Alkyne

Simply to the **RIGHT**
2-Alkene and
of 3000 cm^{-1}
Aromatic

3-Alkane

4-Aldehydic

C-H alkane



Region 4000-2500 cm^{-1}

O-H

C-H

N-H

Aldehydic hydrogen

Two peaks

2900-2800 cm^{-1}

AND

2800-2700 cm^{-1}

1-Alkyne

2-Alkene and

Aromatic

3-Alkane

4-Aldehydic

Note:

First peak is indistinguishable from alkane peaks which is in the same range.

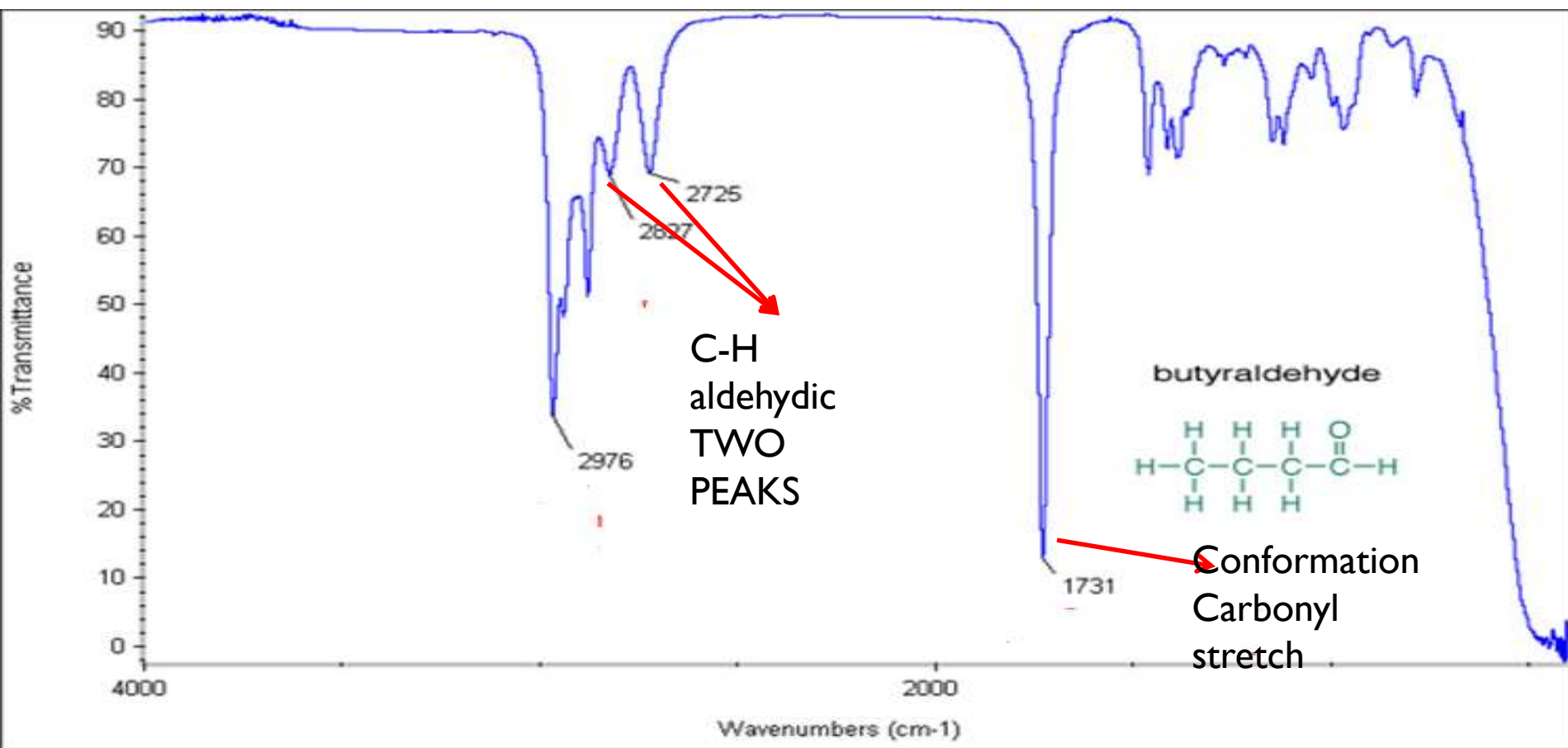
Note :

Second peak appears as a shoulder-type peak just to the right of the alkyl C-H

4000

2500

Aldehydic hydrogen



Region 2500-2000 cm^{-1}



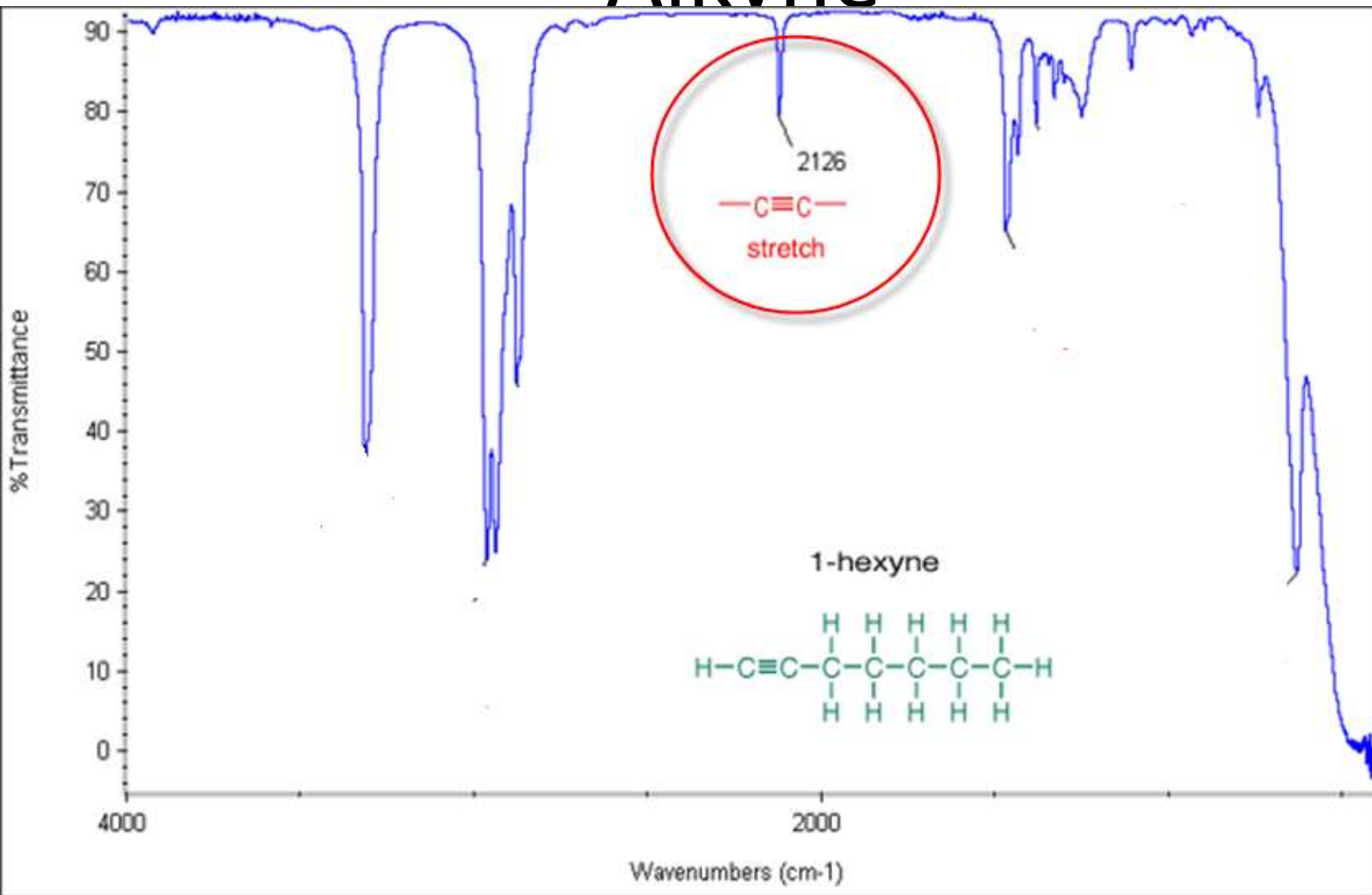
**SHARP, medium peak
around 2150 cm^{-1}** ■
**DoNOT forget to look
also for C-H alkyne
peak, *although not
necessarily present***

■ **SHARP, medium peak
around 2250 cm^{-1}**
**DoNOT confuse with $\text{C}\equiv\text{C}$
(alkyne)**

2500

2000

Alkyne



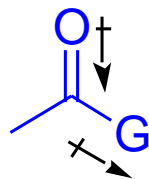
Carbonyls

C=O stretch— easily recognized, intense band

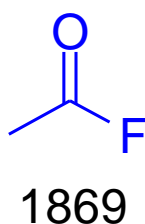
- Ketones, aldehydes, acids, esters, lactones, acid halides, anhydrides, amides and lactams all show C=O stretching in the region 1870-1540 cm^{-1} .
- Position is determined by (1) physical state (2) electronic and mass of neighboring groups (3) conjugation (4) hydrogen bonding (5) ring strain

Ketones

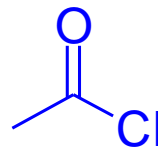
- **aliphatic**: 'normal' position of a neat aliphatic ketone is 1715 cm^{-1}
- **competing effects**



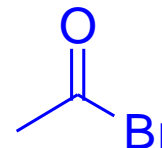
inductive: increases $\bar{\nu}$



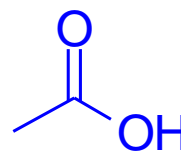
1869



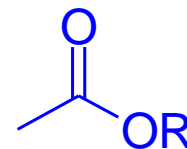
1815–1785



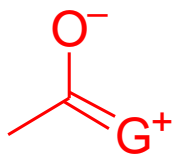
1812



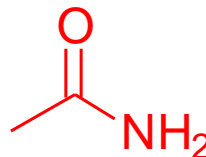
1760 (monomer)



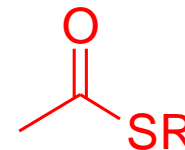
1750-1735



resonance: decreases $\bar{\nu}$



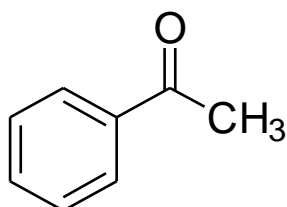
1695-1650



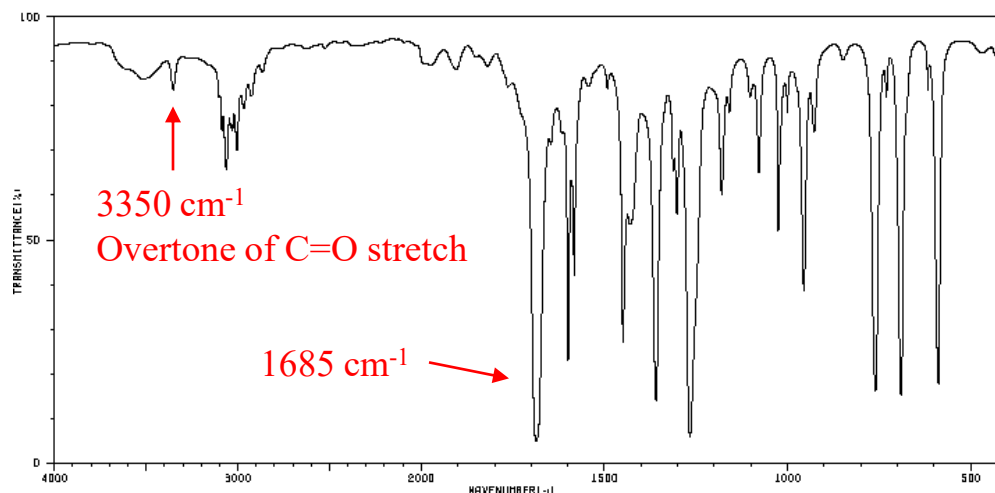
1720-1690

Ketones

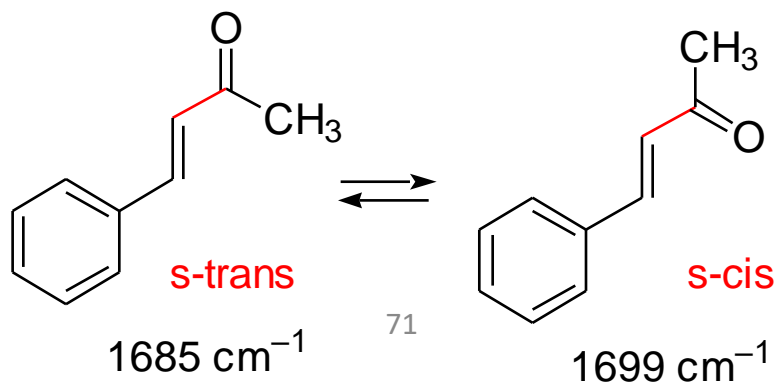
- **conjugation**: shifts position to lower frequency
alkene or phenyl group causes absorption in the 1685-1666 cm^{-1} region. For α,β -unsaturated carbonyls, 2 absorptions may be observed



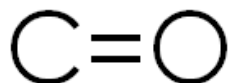
1685 cm^{-1}



- For α,β -unsaturated carbonyls, 2 absorptions may be observed



Region 1800-1650 cm^{-1}



Is N-H also present?!

Medium absorption near 3400 cm^{-1}

← cm^{-1} →

1810

1800

1760

1735

1725

1715

1710

1690

Anyhdride
(Band 1)

Acid
Chloride

Anyhdride
(Band 2)

Ester

Aldehyde

Ketone

Carboxylic
Acid

Amide

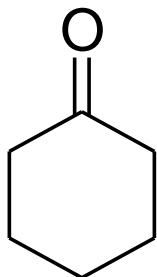
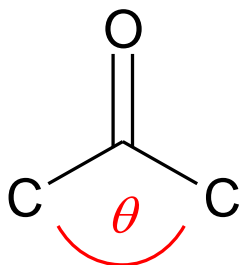
1800

1650

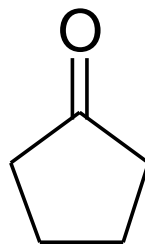
Cyclic Ketones

The bond angle influences the absorption frequency of the C=O

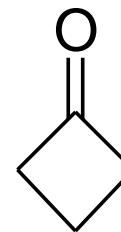
In strained rings, interaction with the adjacent C-C bonds increases the frequency of C=O stretching



1715 cm^{-1}



1751 cm^{-1}

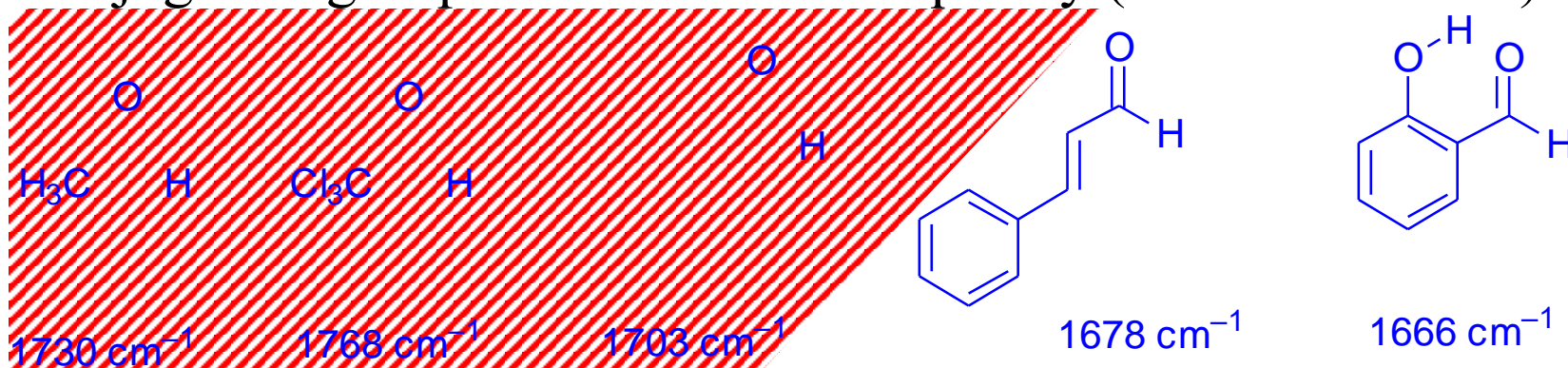


1775 cm^{-1}

Aldehydes

C=O stretch

- Aliphatic aldehydes: C=O stretch at 1740-1720 cm^{-1}
- Electron withdrawing groups shift to higher frequency
- Conjugative groups shift to lower frequency (1710-1685 cm^{-1})



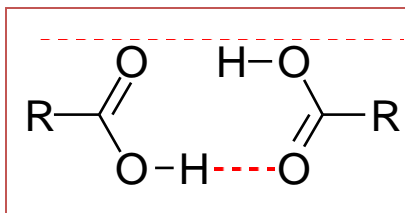
C–H stretch

2830–2695 cm^{-1} Often, two bands are observed (the other is a result of an overtone of the C–H bend of the aldehyde)

Carboxylic Acids

OH stretch

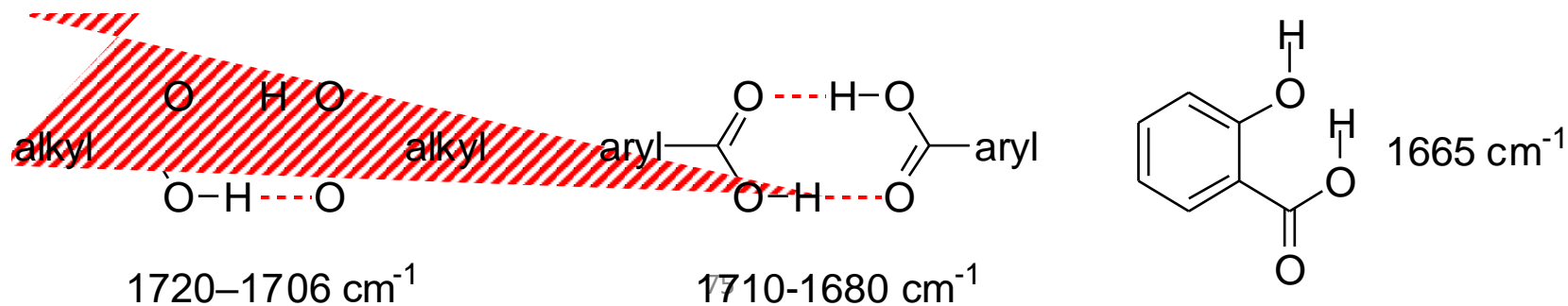
- 'free' OH (ca. 3520 cm^{-1}) is observed only in the vapor phase or in very dilute ($<0.01\text{ M}$) solution in a non-polar solvent
- Otherwise, acids exist as dimers



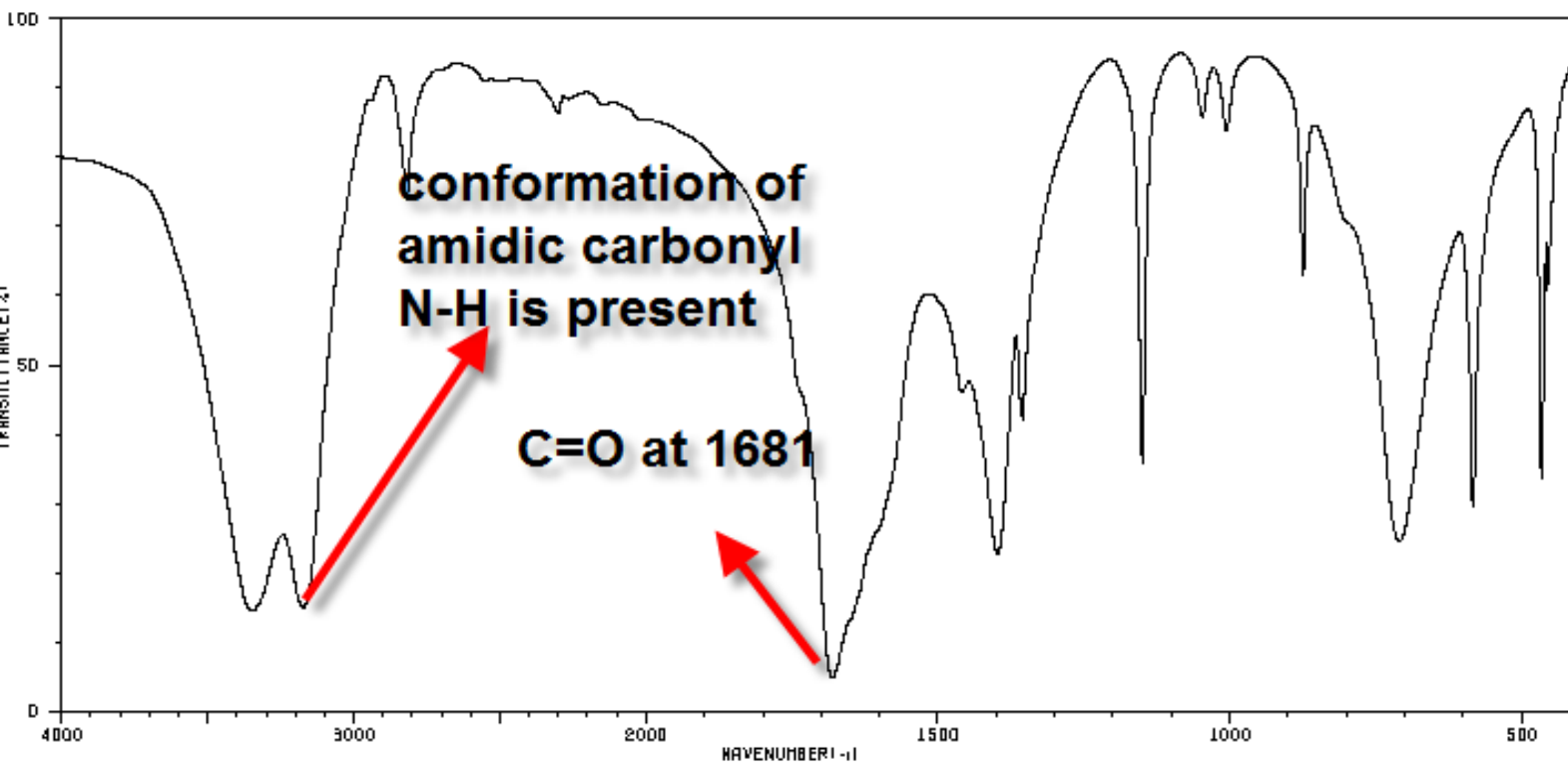
Intense, OH stretching in the $3300\text{--}2500\text{ cm}^{-1}$ region centered near 3000 cm^{-1}

C=O stretch

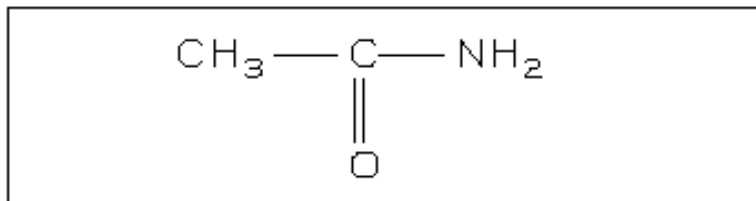
- monomer: 1760 cm^{-1} for aliphatic acids
- dimer: Hydrogen bonding reduces the frequency of the asymmetric C=O stretch, especially when intramolecular



Amide

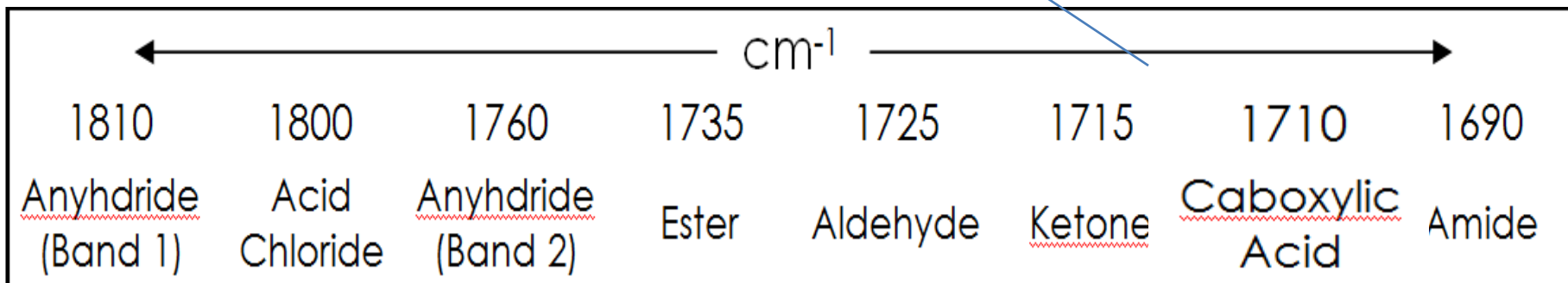
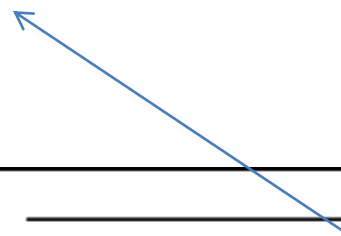


3348	13	1366	41	467	32
3173	14	1151	34	457	58
2819	70	1047	81		
2301	84	1006	81		
1681	4	874	60		
1460	44	710	29		
1398	21	684	28		

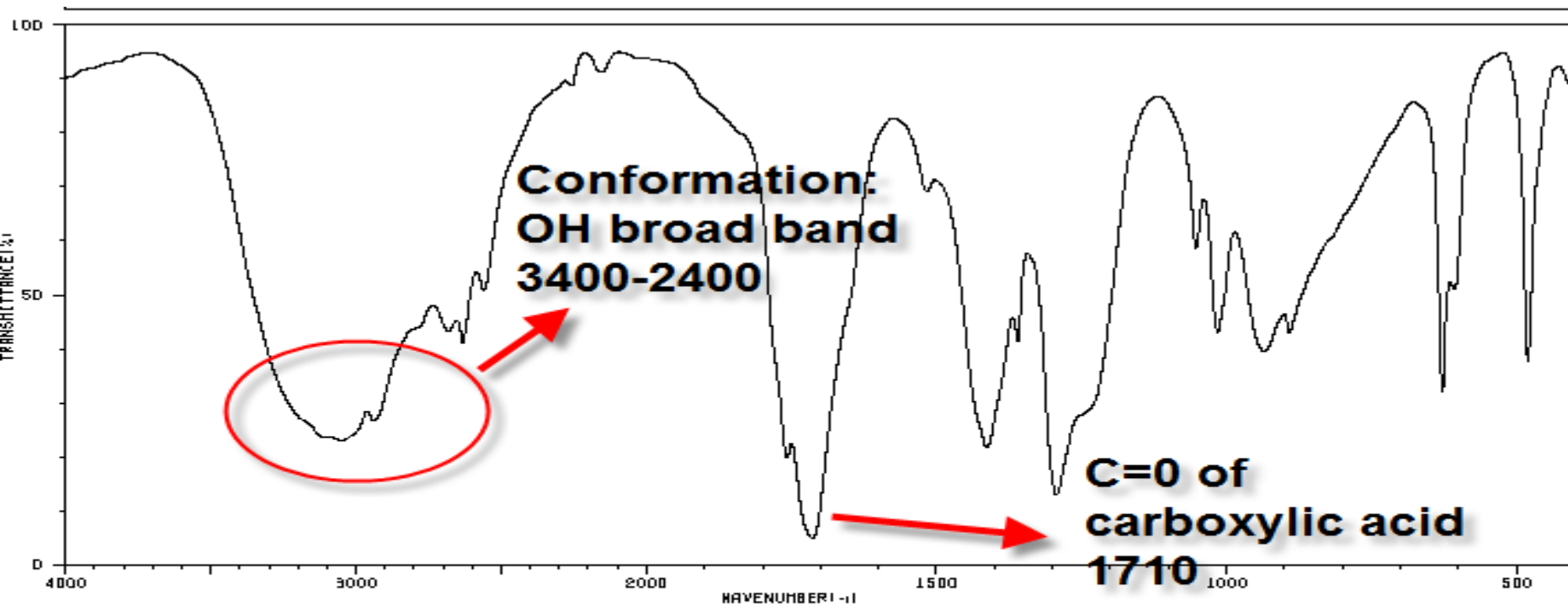


Region 1800-1650 cm^{-1}

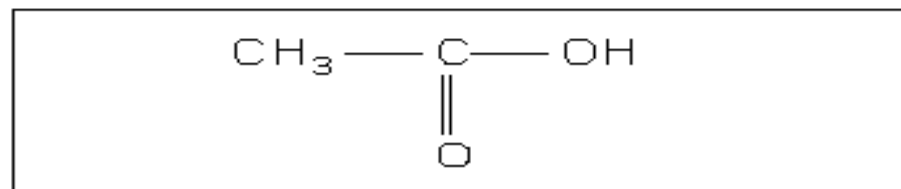
Is O-H also present?!
Broad absorption near
3400-2400 cm^{-1} (usually
overlap C-H)



Carboxylic acid



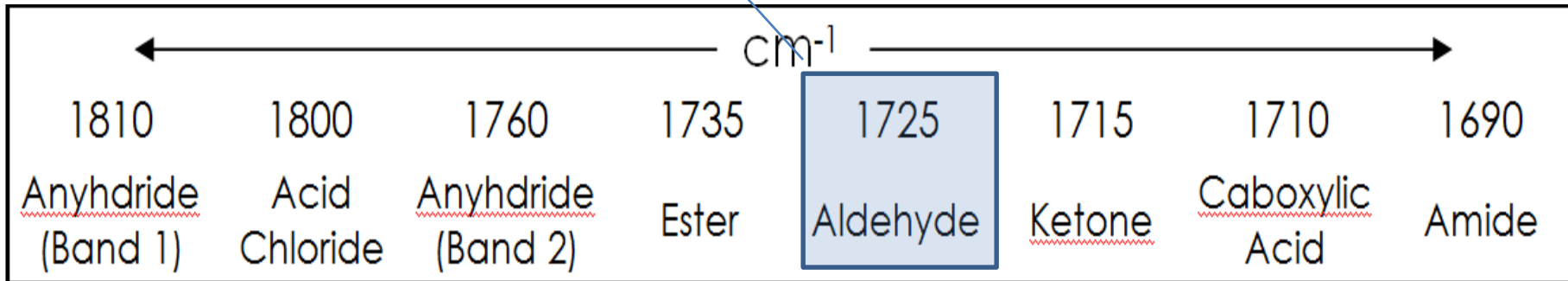
2937	26	1414	20	629	31
2884	41	1360	39	607	49
2831	39	1294	12	481	36
2669	49	1063	67	473	62
1758	19	1016	41		
1714	4	935	37		
1617	66	892	41		



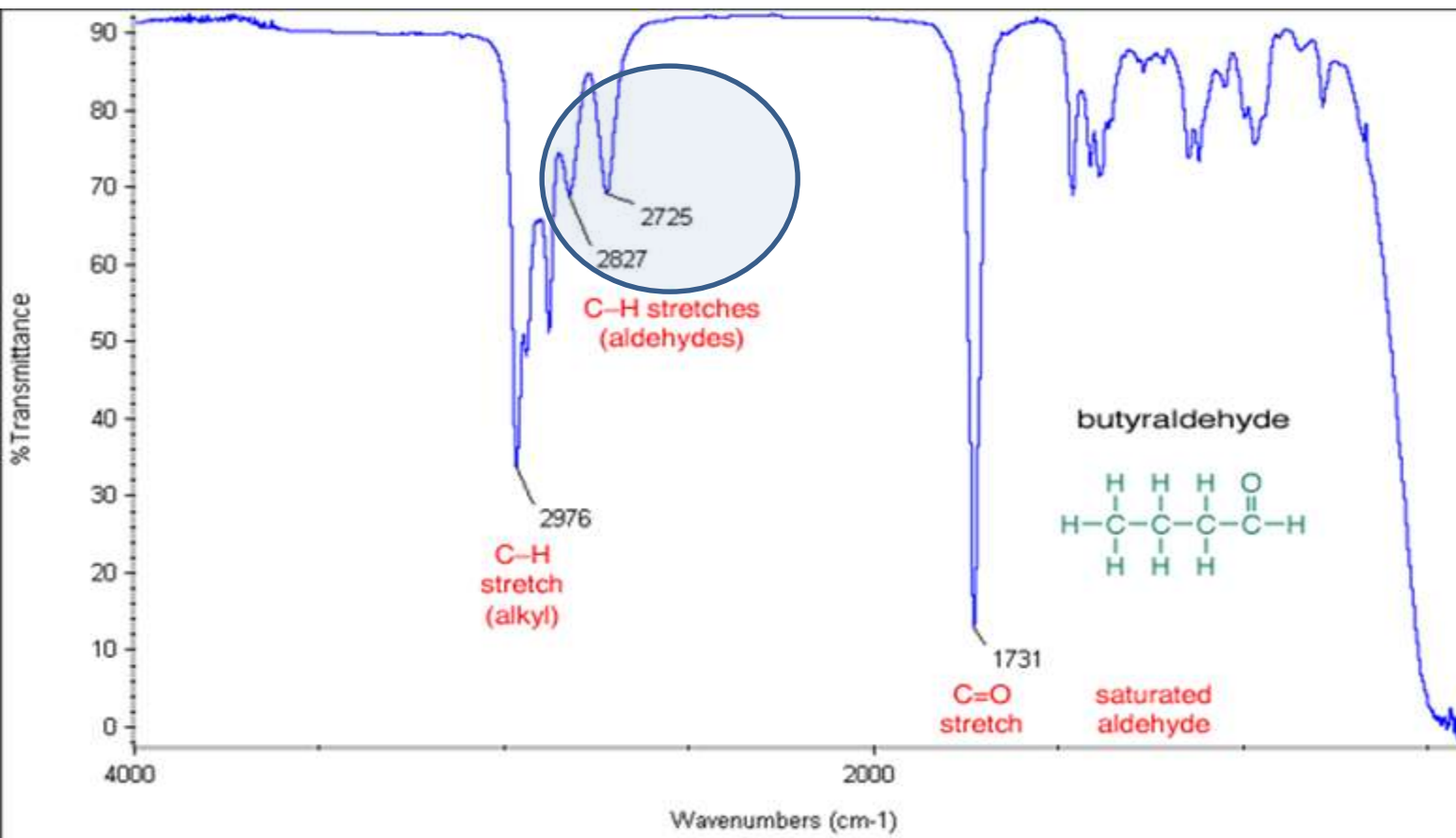
Region 1800-1650 cm^{-1}

Is aldehyde C-H present?!

Two weak absorptions near 2850 and 2750 cm^{-1} on the right side of the aliphatic C-H absorptions



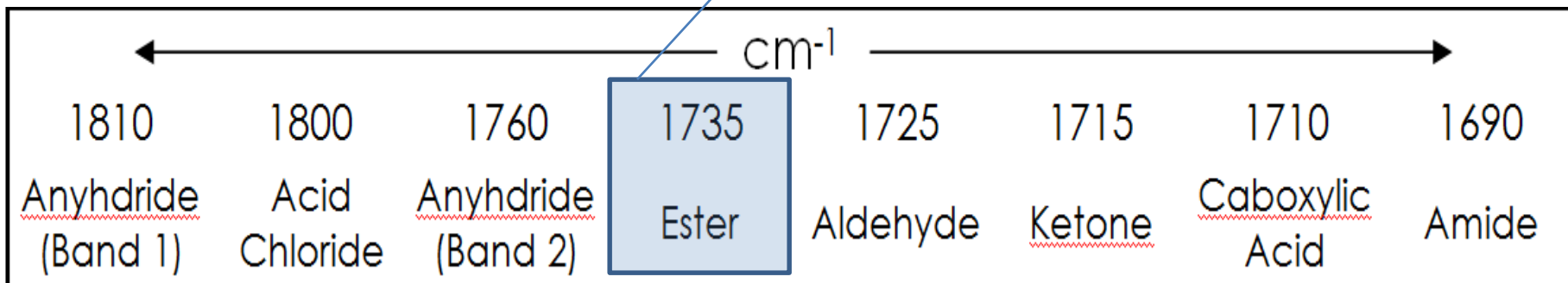
Aldehyde



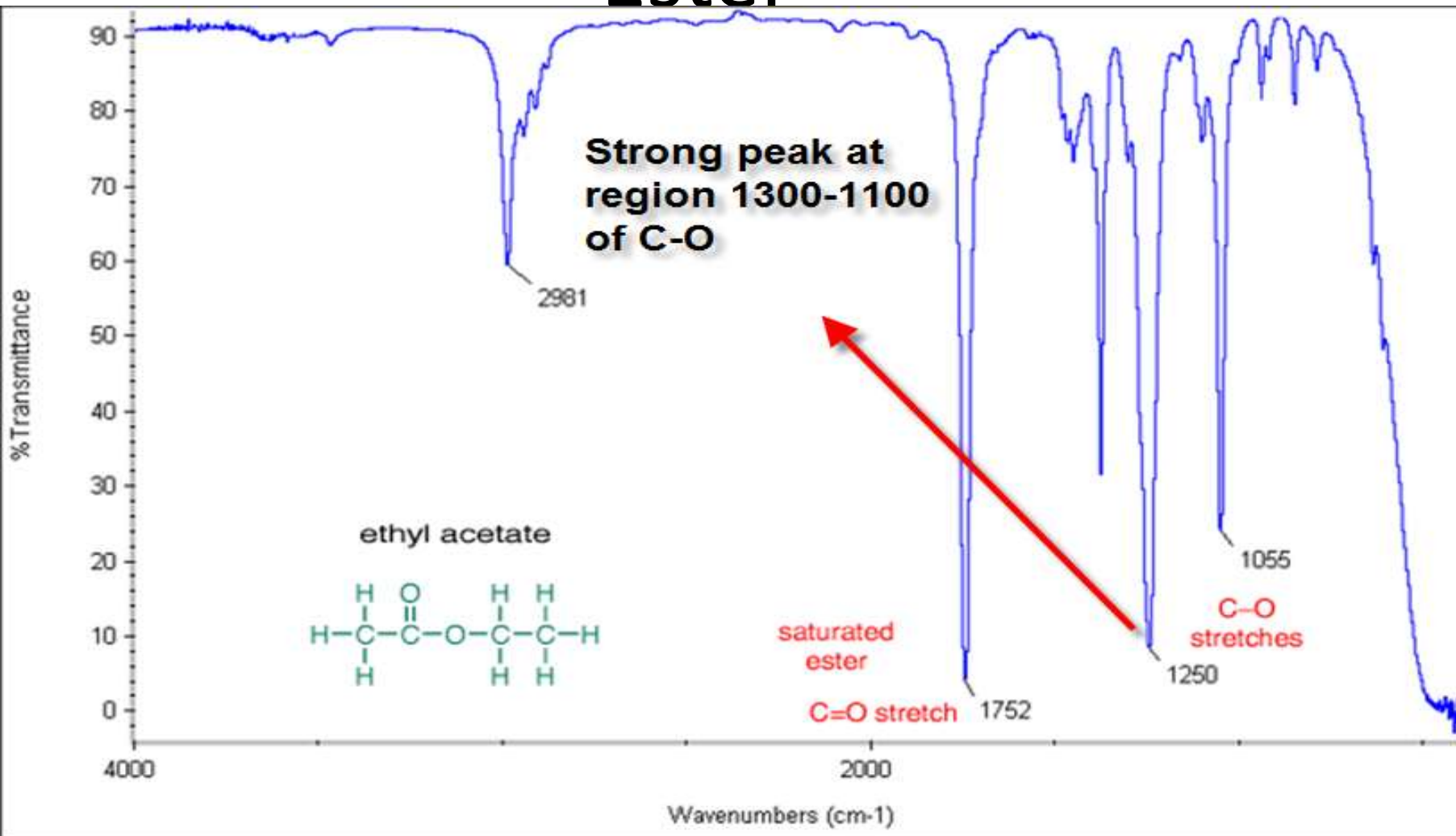
Region 1800-1650 cm^{-1}

Is C-O also present?!

Strong intensity absorption near 1300-1000 cm^{-1}



Ester

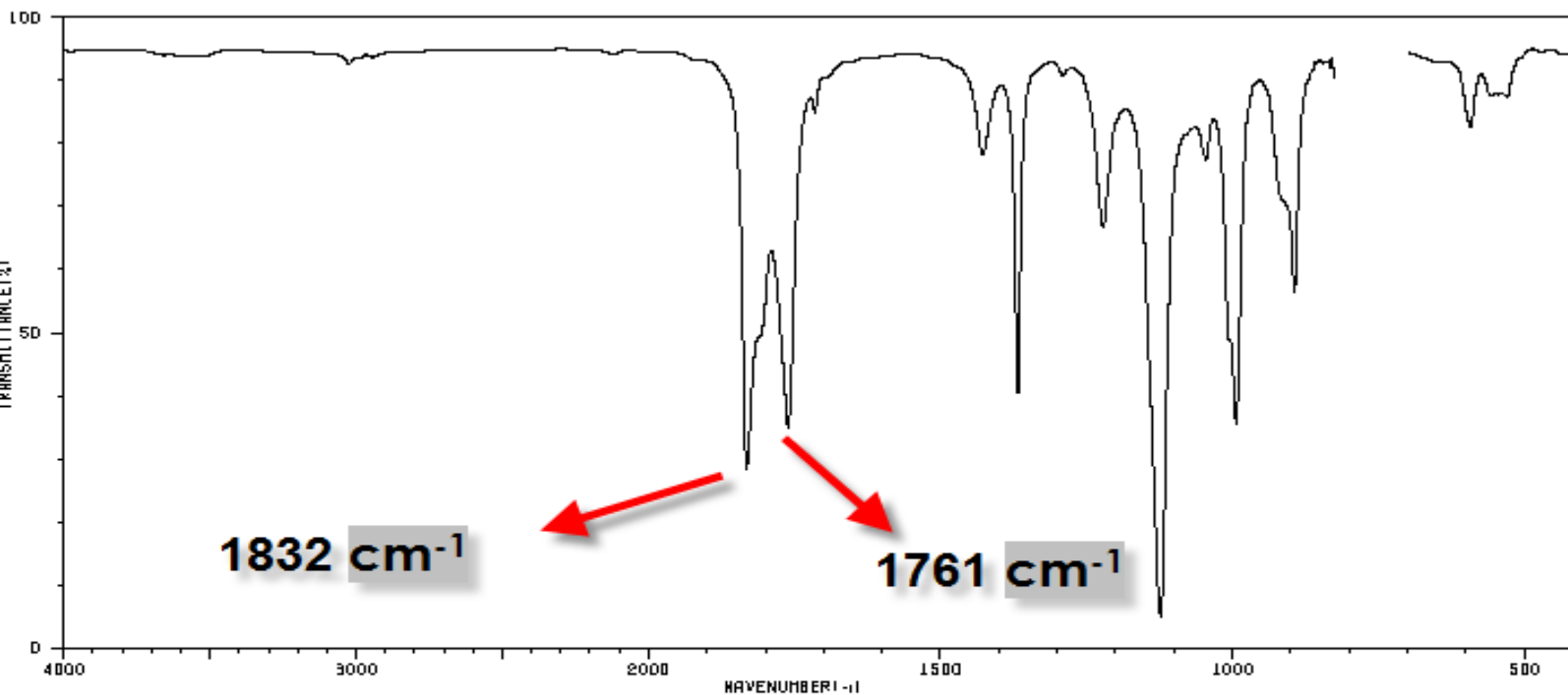


Region 1800-1650 cm^{-1}

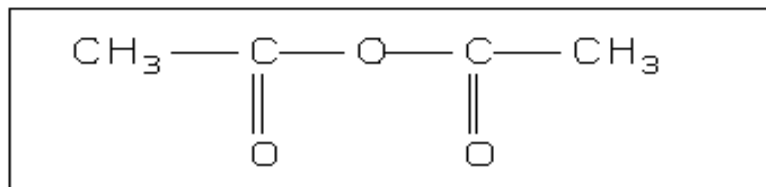
Two C=O absorptions near 1810 and 1760 cm^{-1}



Anhydride



1832	26	1046	74	540	84
1761	33	1005	46		
1715	81	994	34		
1428	74	894	53		
1368	38	603	84		
1222	84	593	79		
1124	4	547	84		

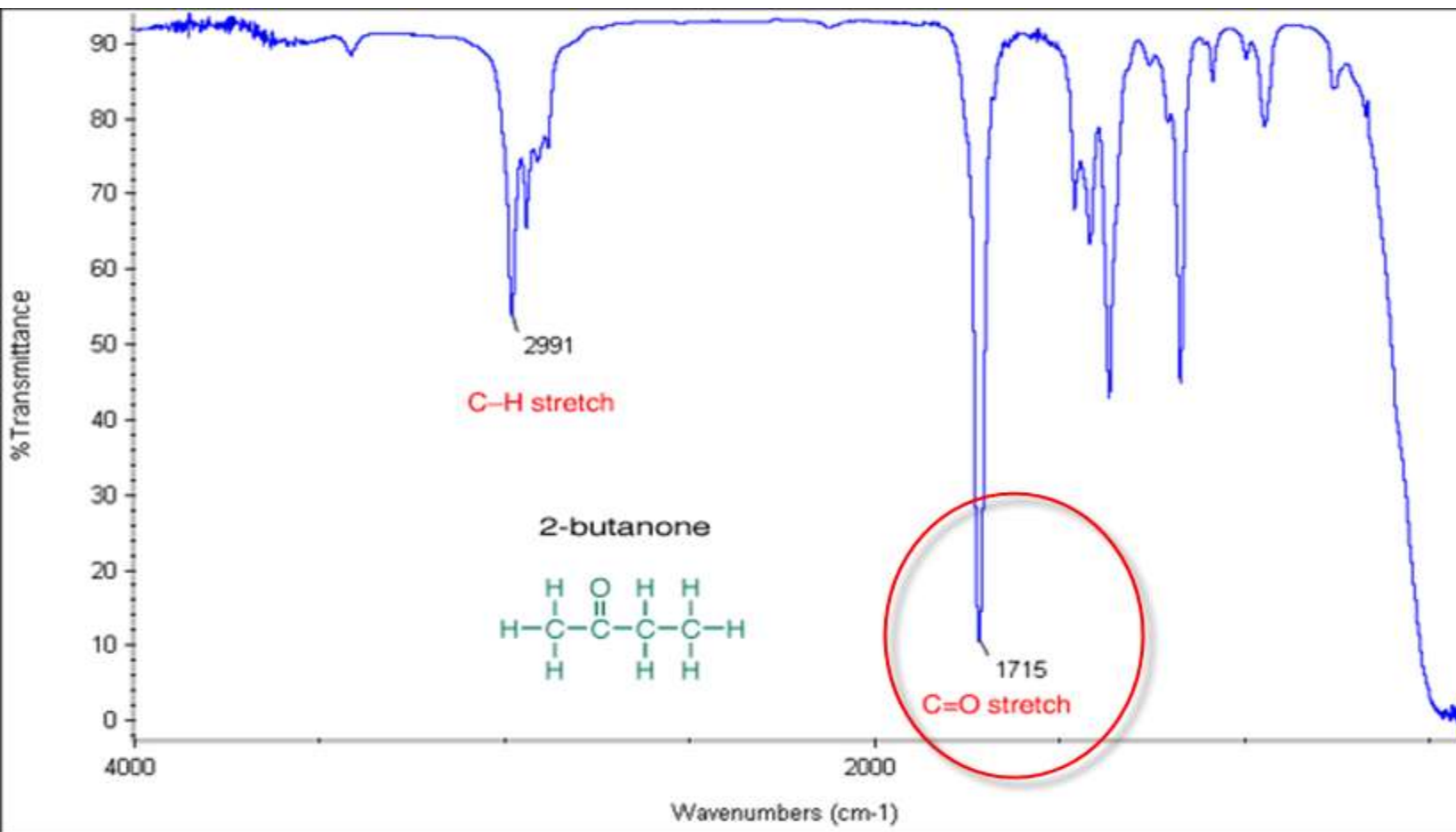


Region 1800-1650 cm^{-1}

The preceding five choices have been eliminated



Ketone



Region 1650-1550 cm^{-1}

	$\text{C}=\text{C}$ Alkene, Aromatic	
	$\text{C}=\text{N}$	
1650	(N=O O=N)	1550

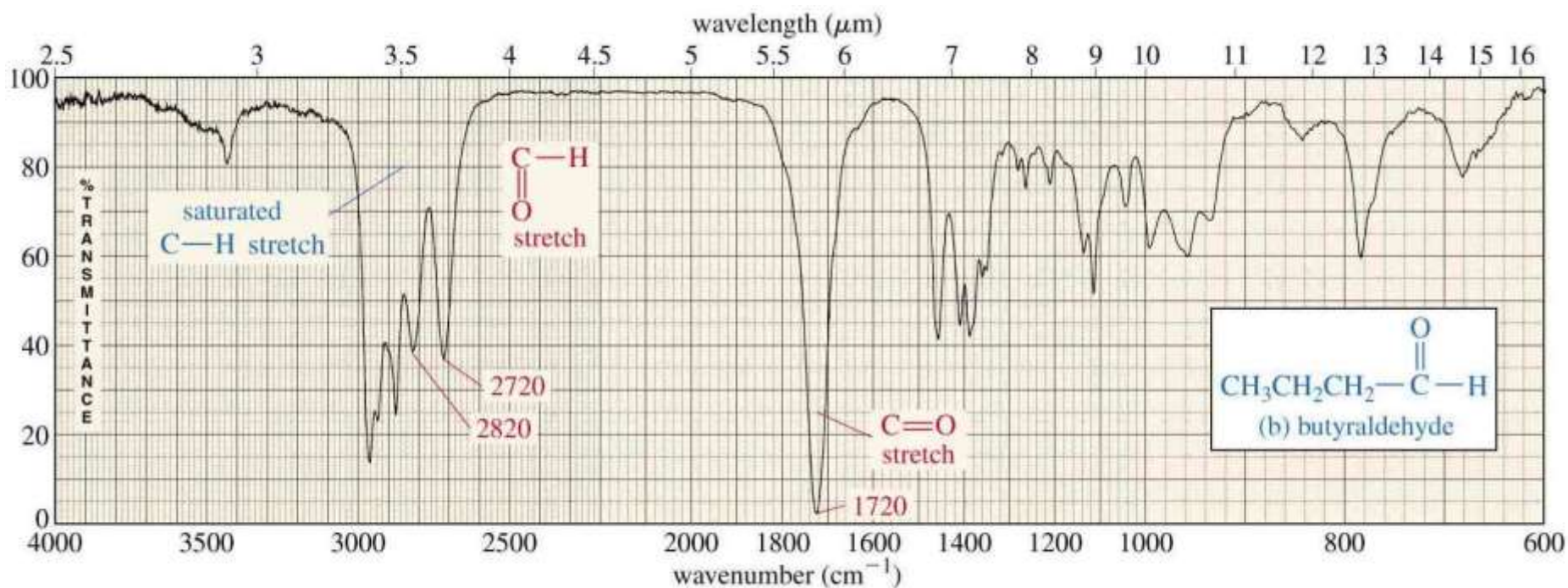
1680-1600 cm^{-1}

Shows **ONLY ONE PEAK** around 1600 cm^{-1}
DoNOT confuse with C=O, which NEVER
appears below 1650 cm^{-1}
DoNOT confuse with C=C (*aromatic*)..

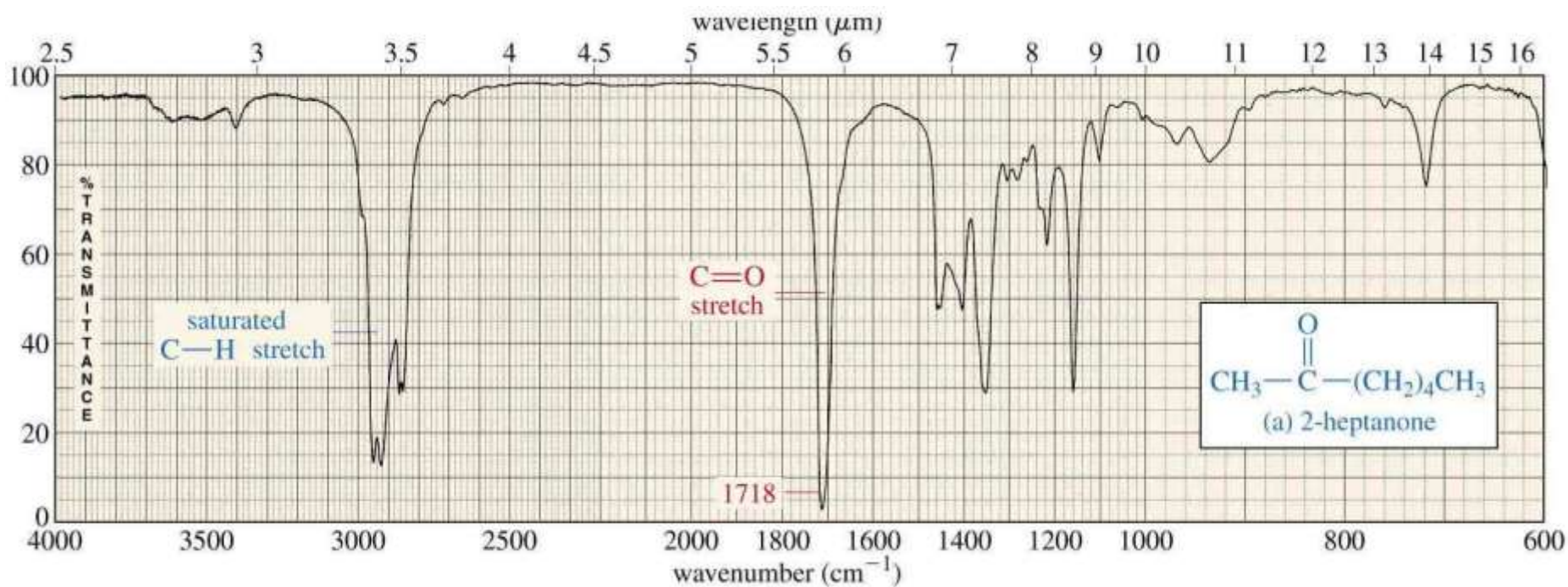
1600 AND 1475 cm^{-1}

Shows **TWO PEAKS**,
the first just before 1600 cm^{-1} ,
the second just before
1500 cm^{-1}

An Aldehyde IR Spectrum

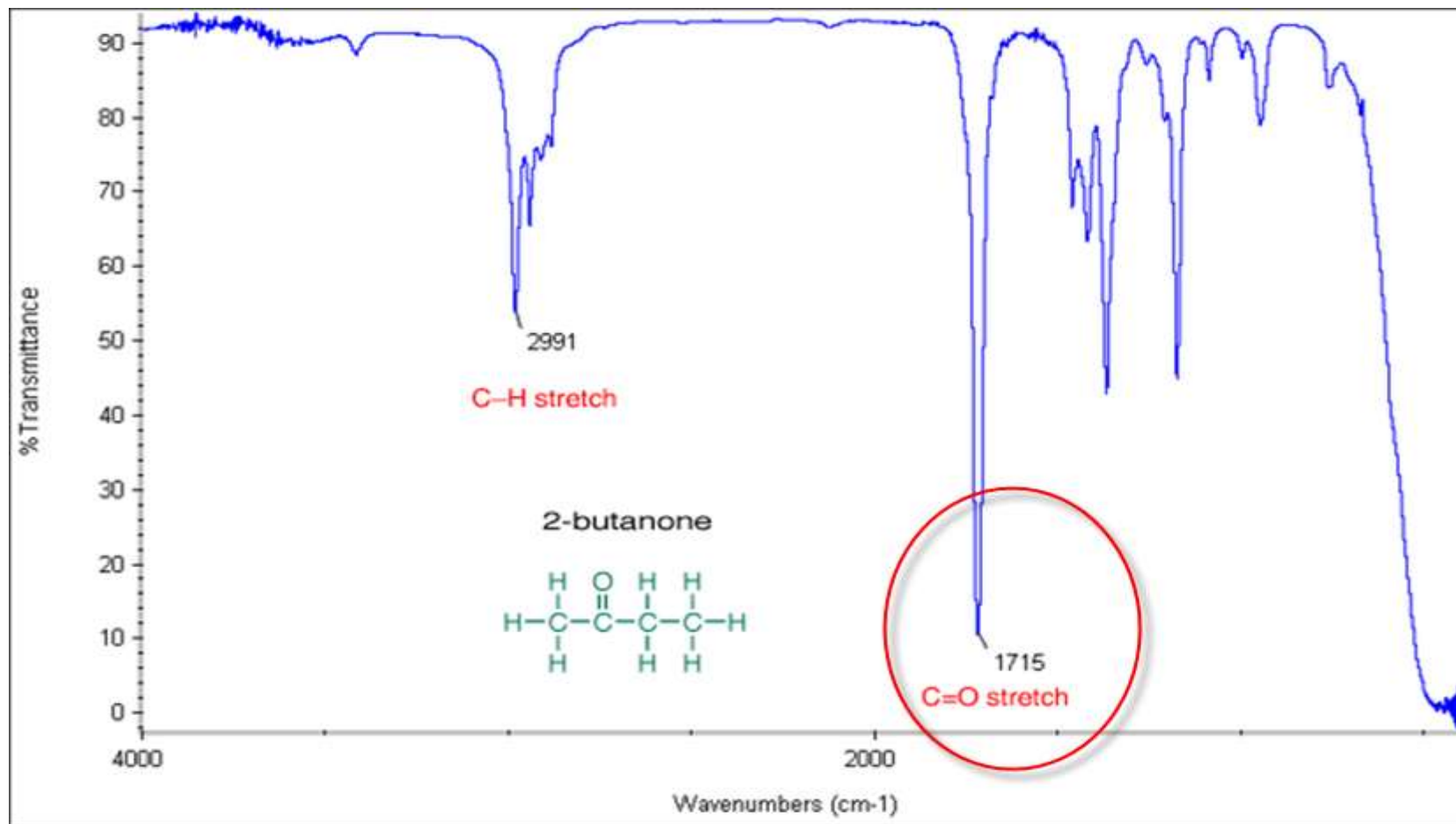


A Ketone IR Spectrum



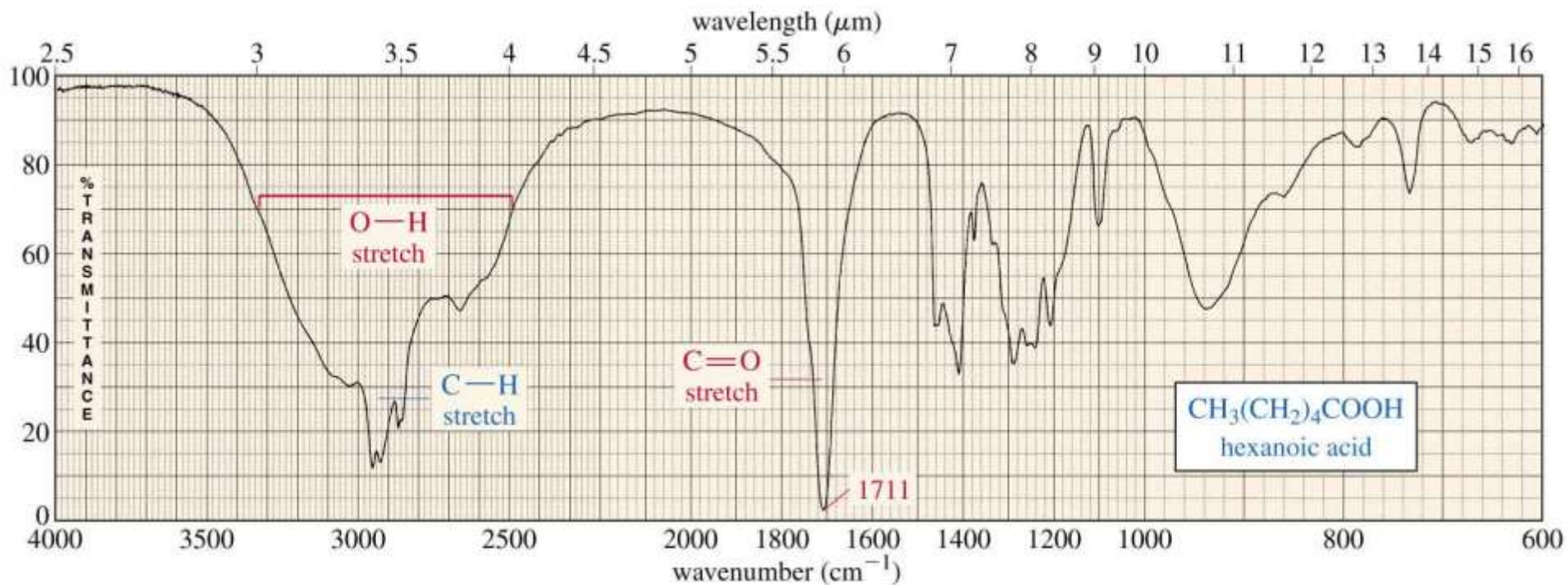
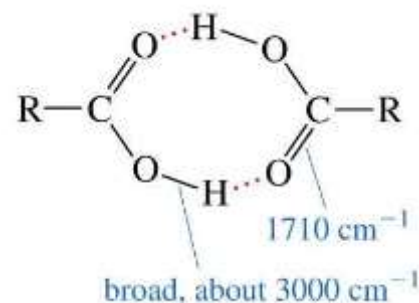
=>

Ketone



O-H Stretch of a Carboxylic Acid

This O-H absorbs broadly, 2500-3500 cm^{-1} , due to strong hydrogen bonding.



Variations in C=O Absorption

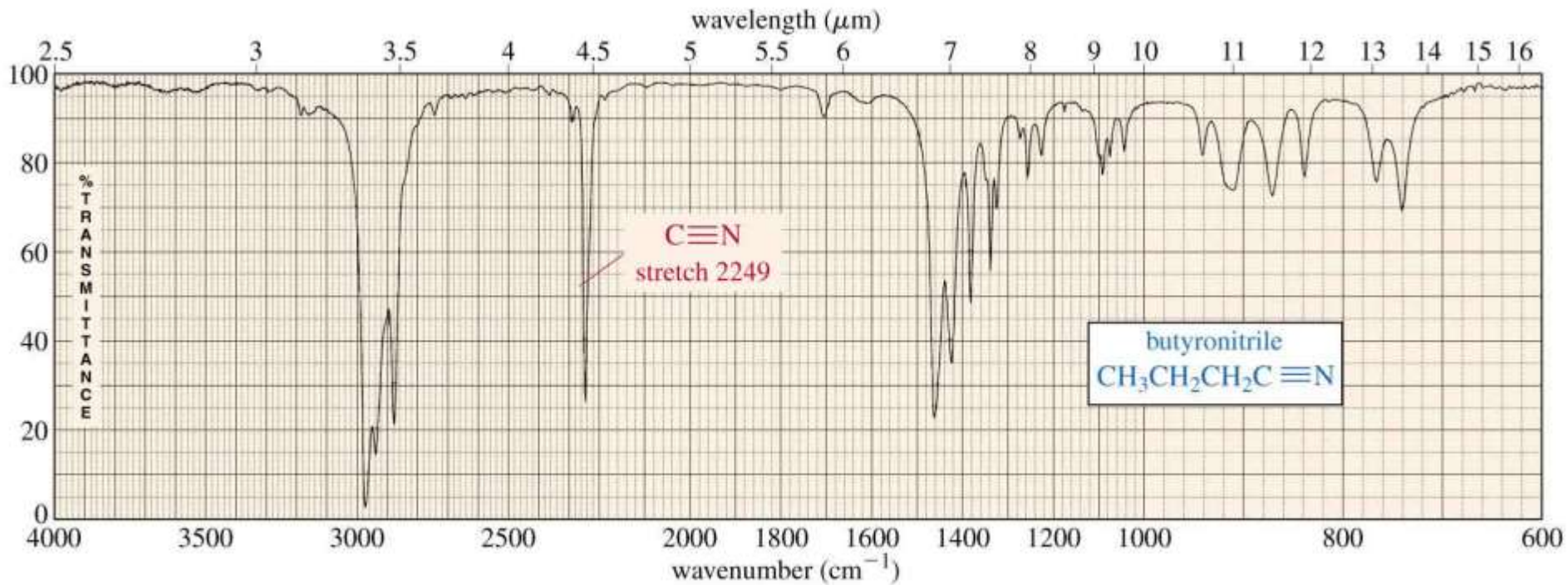
- Conjugation of C=O with C=C lowers the stretching frequency to $\sim 1680 \text{ cm}^{-1}$.
- The C=O group of an amide absorbs at an even lower frequency, $1640\text{-}1680 \text{ cm}^{-1}$.
- The C=O of an ester absorbs at a higher frequency, $\sim 1730\text{-}1740 \text{ cm}^{-1}$.
- Carbonyl groups in small rings (5 C's or less) absorb at an even higher frequency. =>

Carbon - Nitrogen Stretching

- C - N absorbs around 1200 cm^{-1} .
- C = N absorbs around 1660 cm^{-1} and is much stronger than the C = C absorption in the same region.
- C \equiv N absorbs strongly just *above* 2200 cm^{-1} . The alkyne C \equiv C signal is much weaker and is just *below* 2200 cm^{-1} .

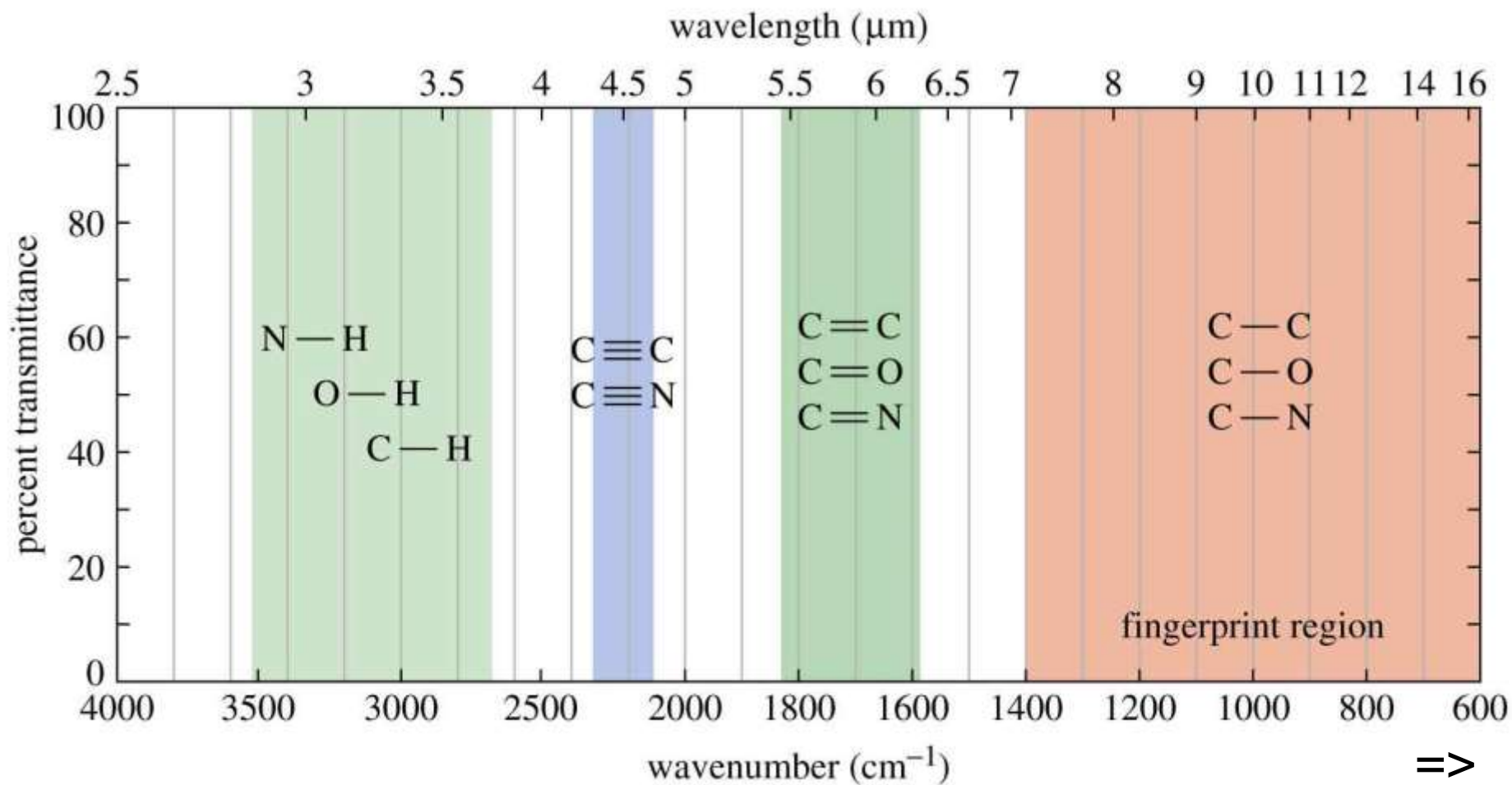
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A Nitrile IR Spectrum



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Summary of IR Absorptions



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A wooden easel with a white canvas stands in a vibrant green field. The canvas displays the text "Thank u" in a bold, green, serif font. In the background, a large, leafy green tree stands against a clear blue sky. The scene is bright and cheerful, suggesting an outdoor setting.

Thank u