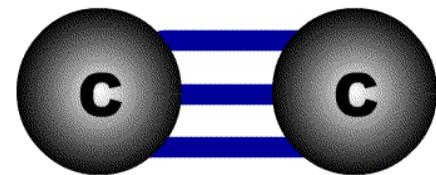


Infrared or Vibrational Spectroscopy

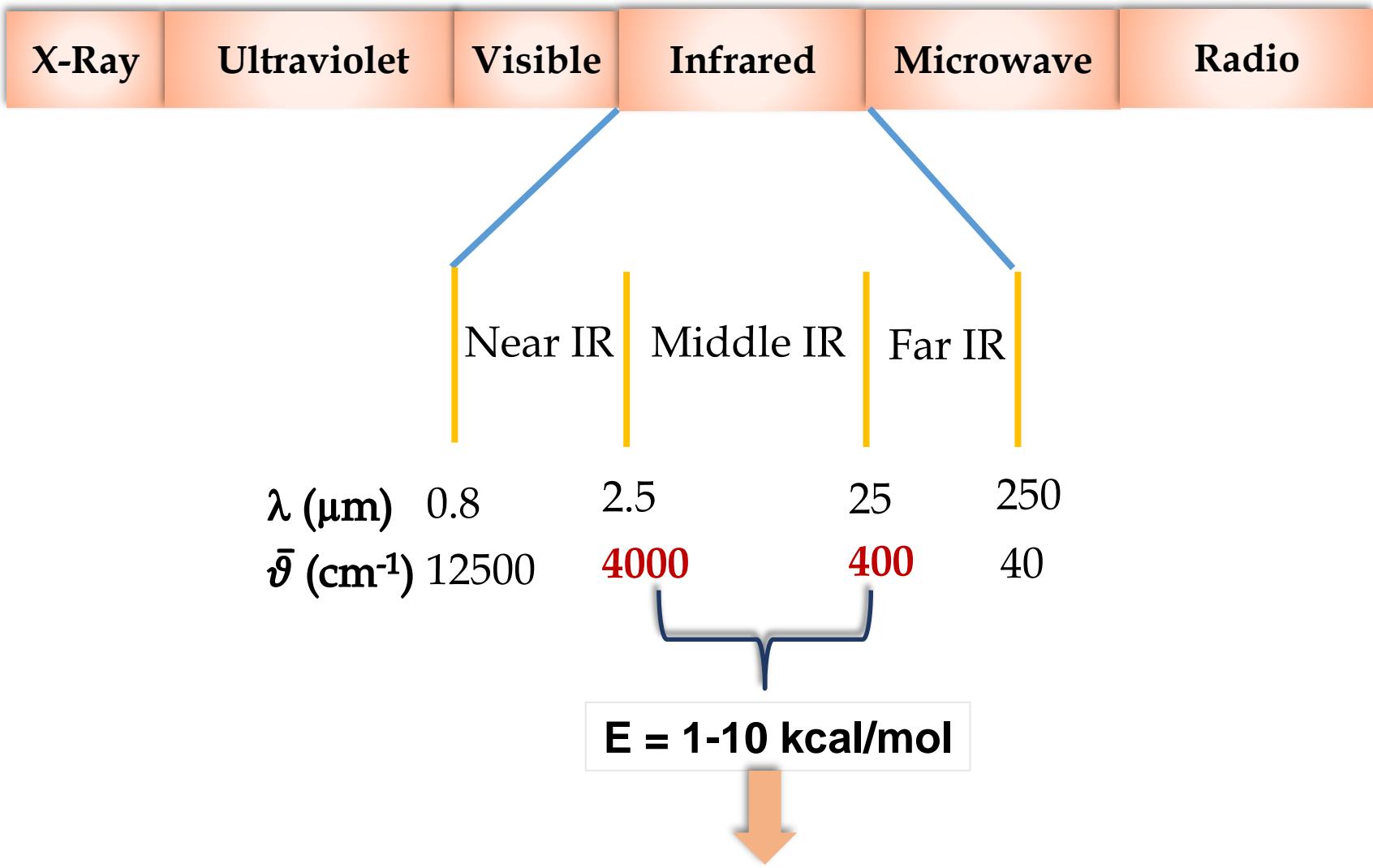


Dr. Janardhan B.
Assistant Professor
Department of Chemistry

Reference Books

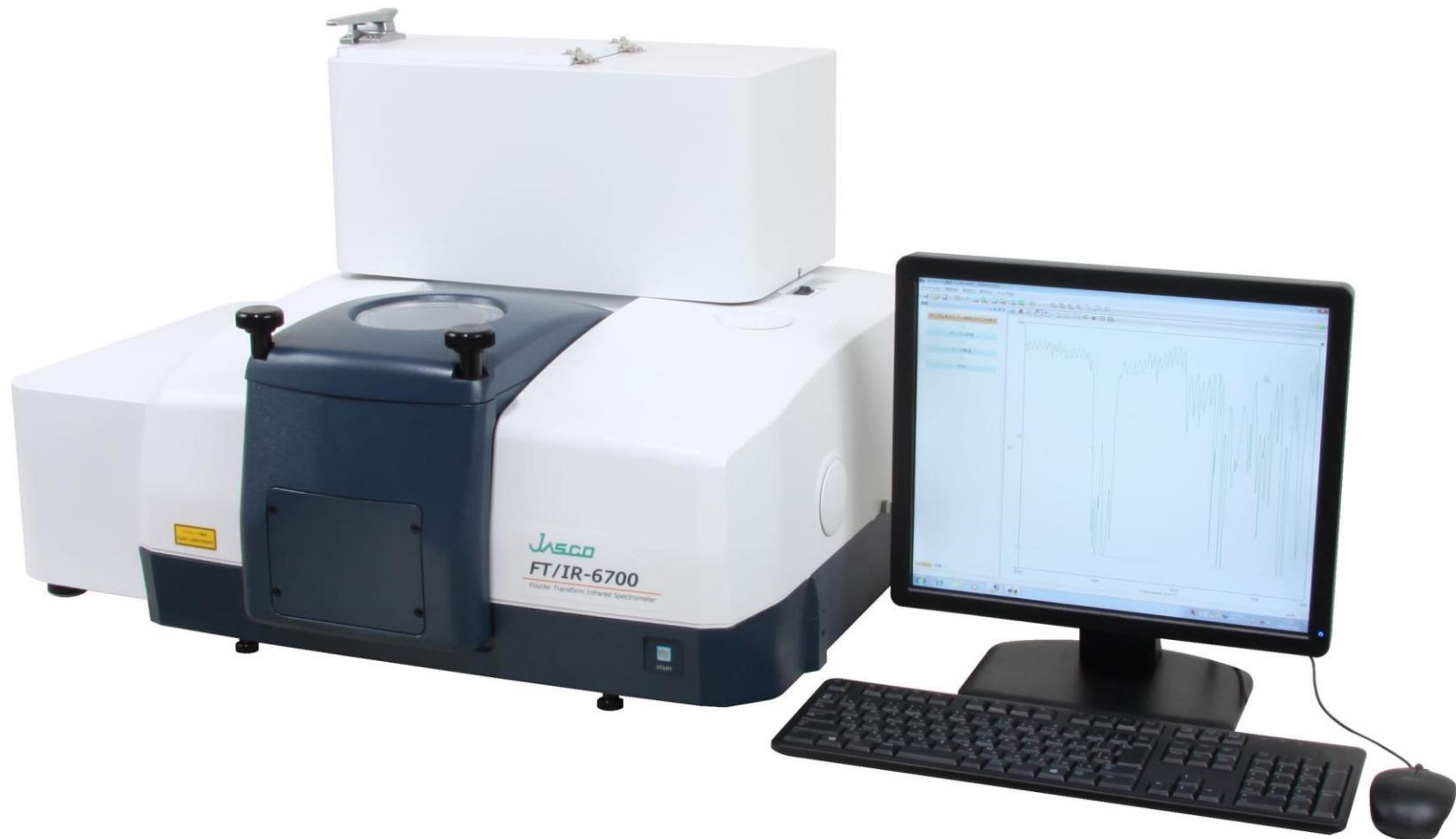
- 1. Fundamentals of Molecular Spectroscopy, 4th Edition,
by Colin N. Banwell and Elaine M. McCash**
- 2. Introduction to Spectroscopy, 5th Edition, Donald L.
Pavia, Gary M. Lampman, George S. Kriz**
- 3. Organic Spectroscopy By William Kemp**
- 4. Spectroscopy Of Organic Compounds By P S Kalsi**
- 5. Elementary Organic Spectroscopy By Y R Sharma**

IR Range of EM Spectrum

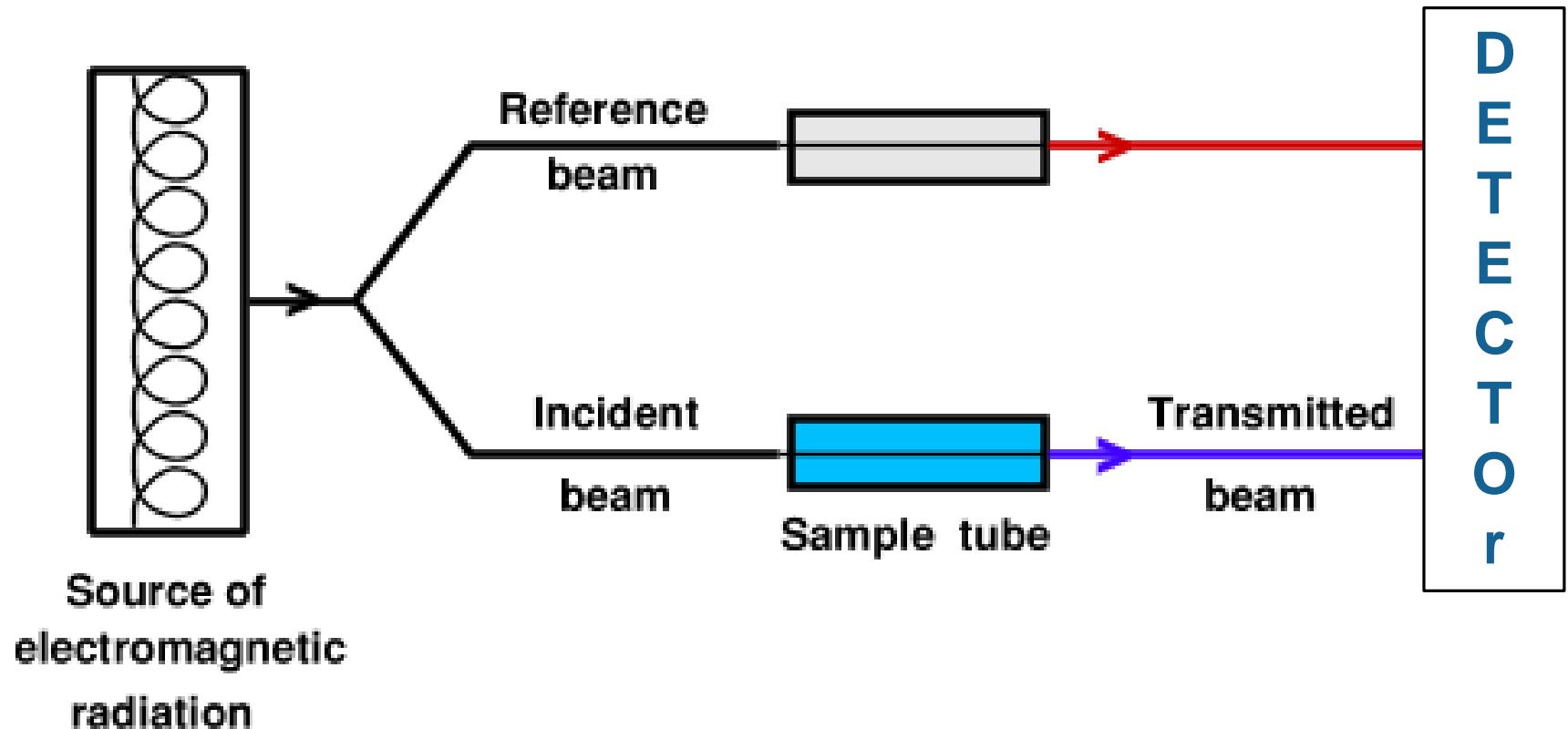


Bond Vibrations (most useful I.R. region)

IR SPECTROMETER



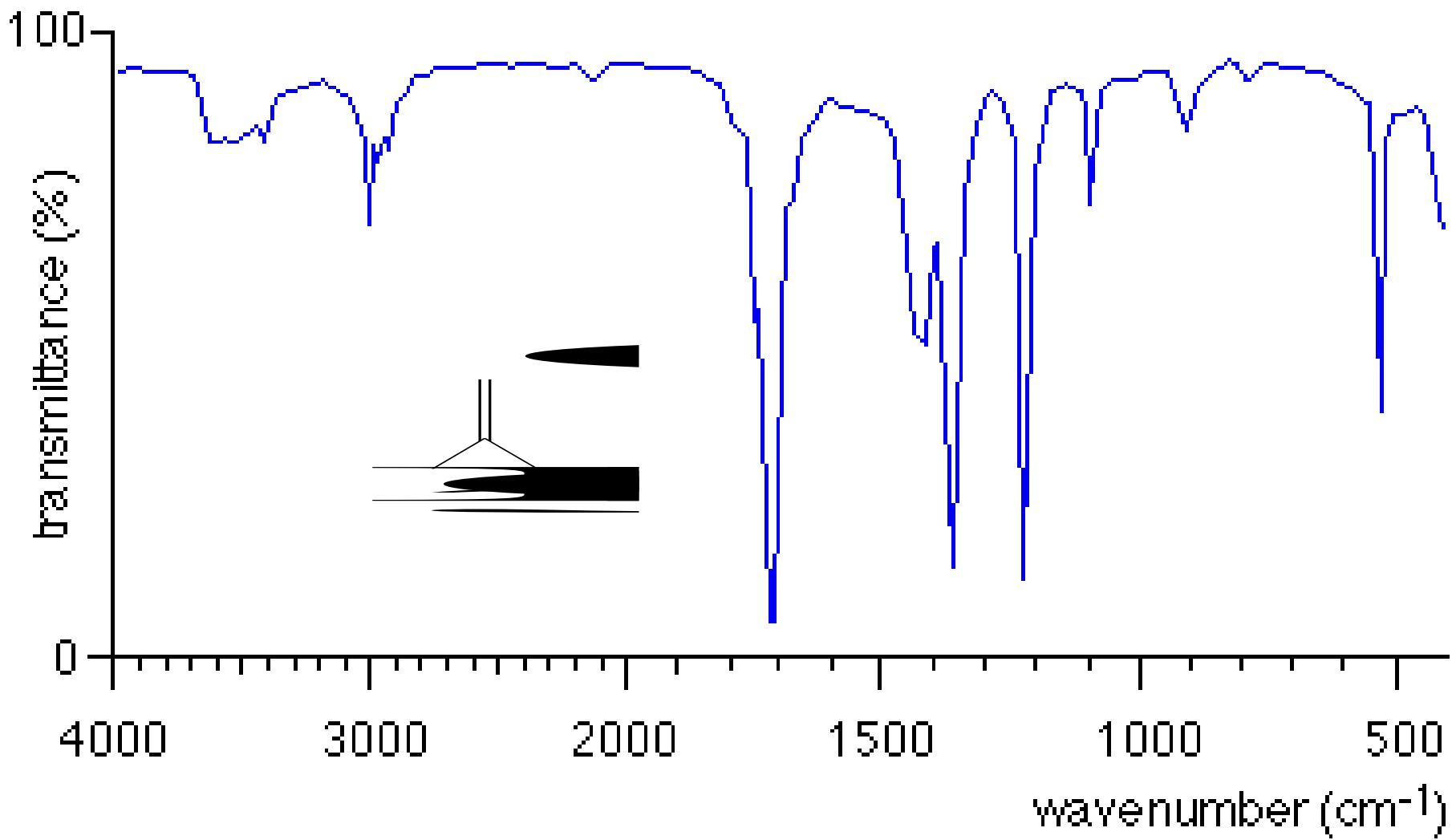
Schematic diagram of IR Spectrometer



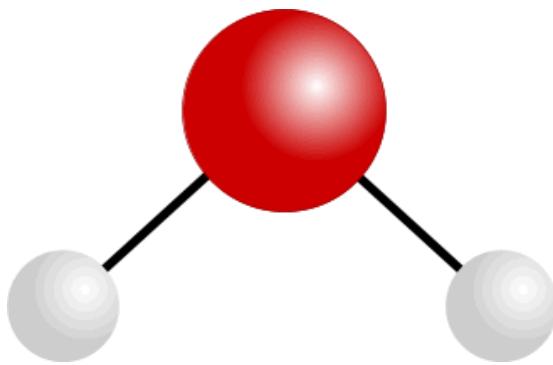
Principle of IR Spectroscopy

- ❖ IR Spectroscopy is concerned with the **study of absorption of IR radiation**, which causes vibrational transitions in the molecule due to the change in the dipole moment. Hence IR spectroscopy is also known as **Vibrational spectroscopy**.
- ❖ Used in structural elucidation to determine the functional groups.

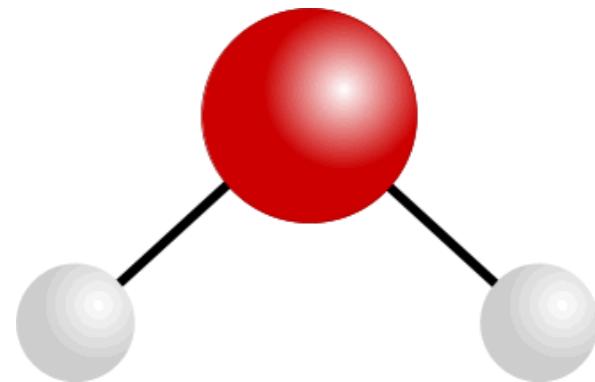
Representation of IR Spectra



Theory of IR Spectra - Vibrational Motion in Covalent Bond



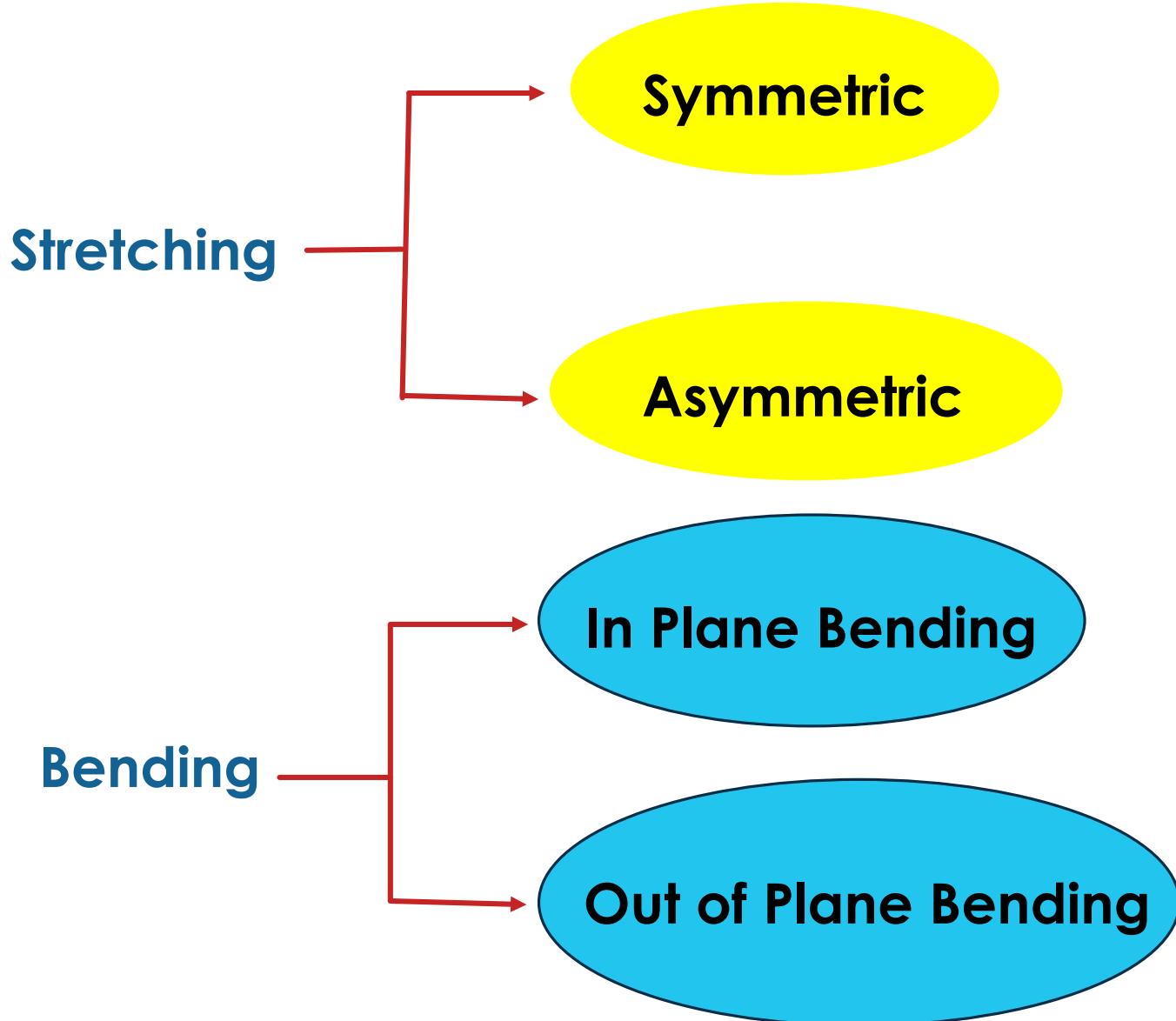
Normal Vibration



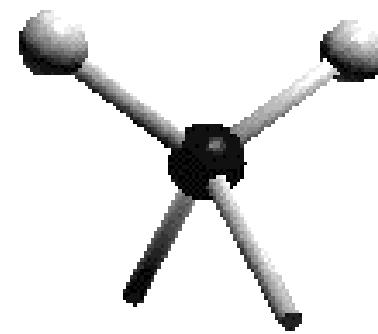
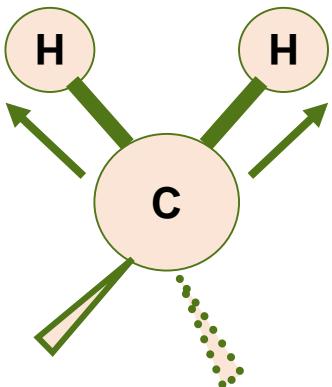
Vibration having Absorbed Energy

A bond will absorb radiation of a frequency similar to its vibration(s)

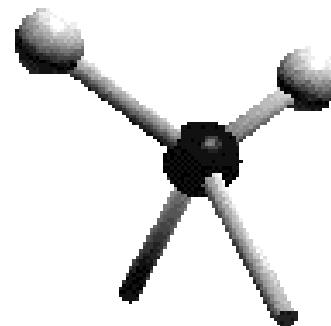
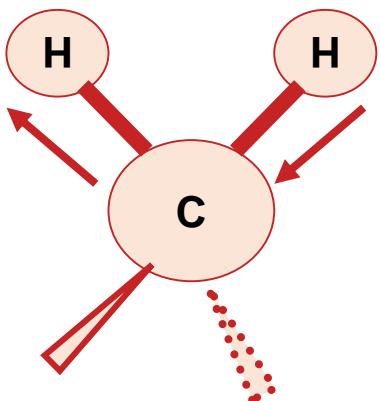
Types of Bond Motions



Symmetric Stretching



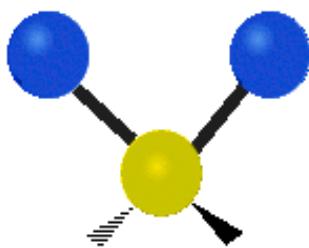
Asymmetric Stretching



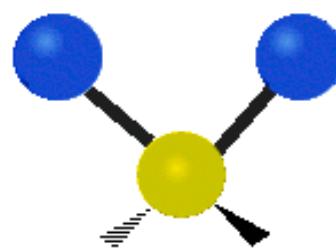
In Plane

Bending

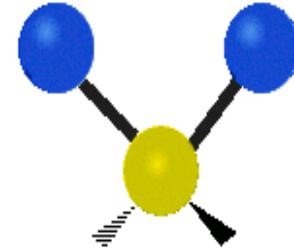
Out Of Plane



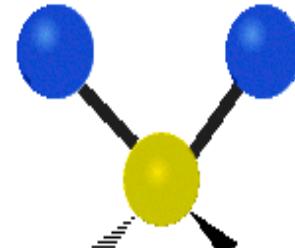
Scissoring



Rocking



Twisting



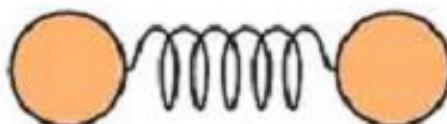
Wagging

Vibrating Diatomic Molecules

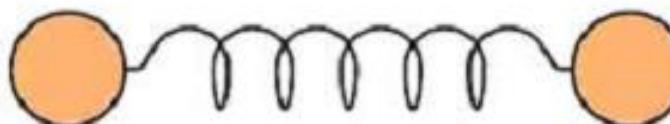
The energy of a diatomic molecule:

The two atoms in a molecule settle at a mean inter-nuclear distance such that these forces are just balanced and the total energy of the whole system is minimum.

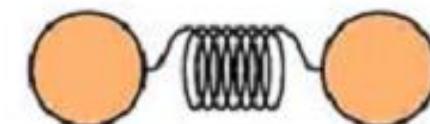
Specific bonds respond to (absorb) **specific** frequencies



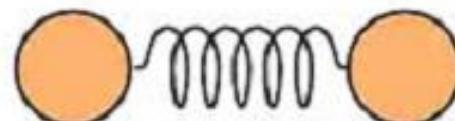
equilibrium
bond length



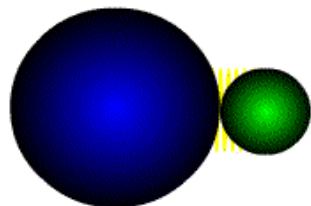
stretched



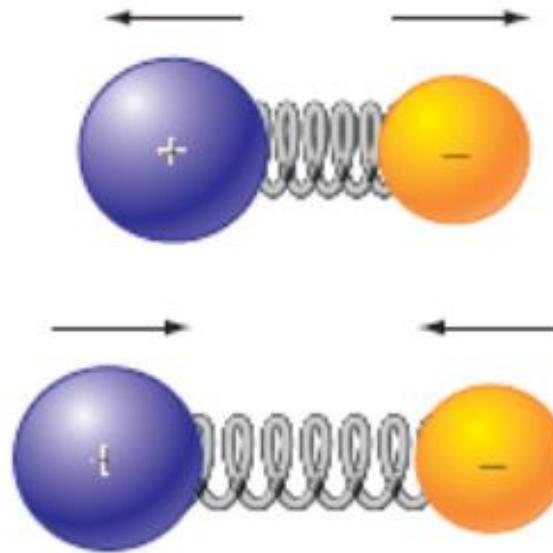
compressed



Stretching-Out



Fluctuating Dipole
of Polar Molecule



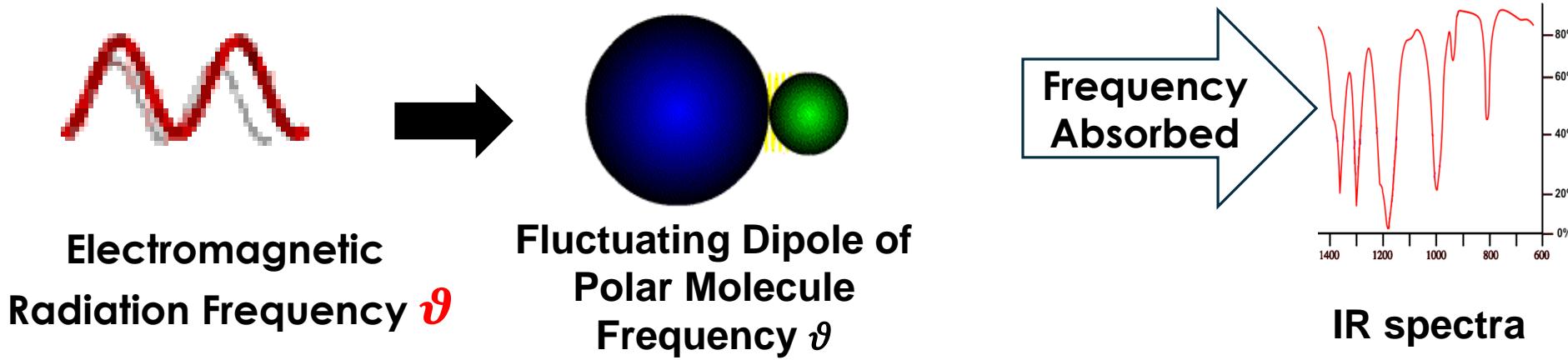
***Electric Field
Induced***



Stretching-In

Induced Electric Field Interacts with the EM Radiation

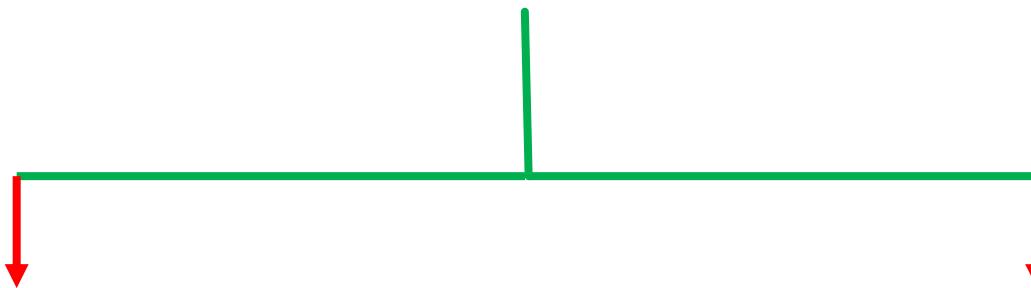
The vibrating bond will absorb EM radiation (in IR Range) only when its frequency is same as the frequency of the oscillating dipole.



Each Vibrational mode with change in dipole moment of the system leads to absorption of frequency in IR range

Criteria for IR Absorption

Dipole Moment of the bond must change during
Vibrational Motion



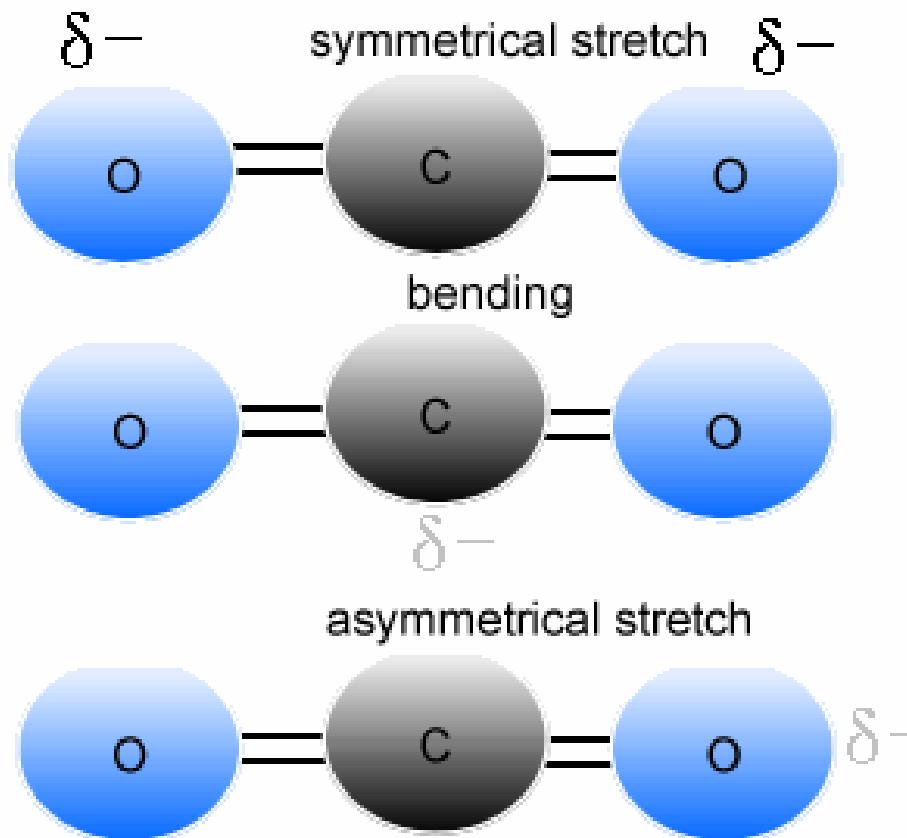
e.g. H_2 , N_2 , O_2

IR-Inactive

e.g. H_2O , SO_2 , HCl

IR-active

Example CO₂



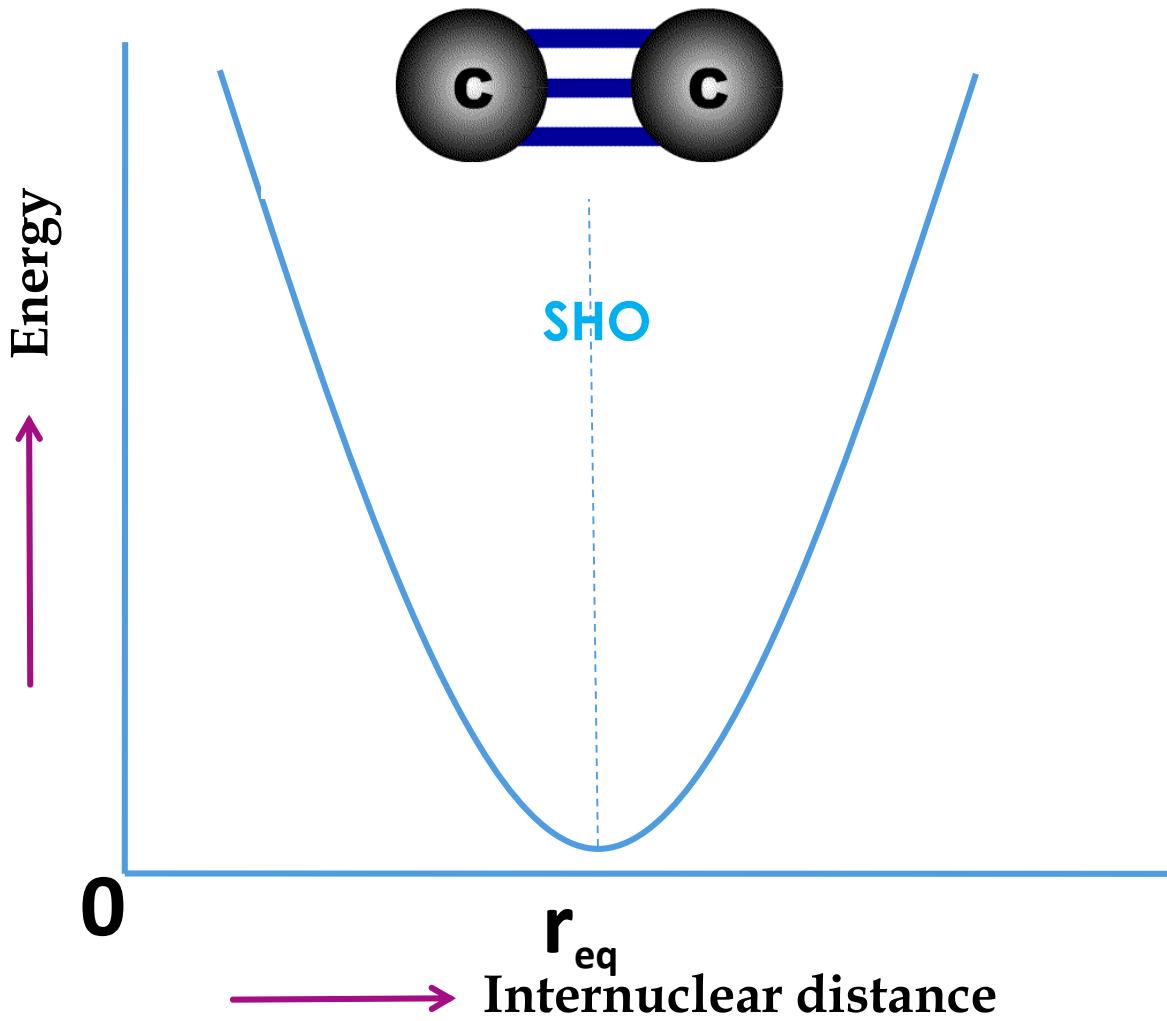
No Change in Dipole

Change in Dipole

Change in Dipole

Though CO₂ is non polar it is IR active

Simple Harmonic Oscillator (SHO)



Morse Energy Diagram

For diatomic molecule behaving as SHO

Frequency of a vibrational stretching

$$\bar{\vartheta} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

Where, k = Force constant

$\bar{\vartheta}$ = Wave number

c = Velocity

$$\mu = \text{Reduced Mass} = \frac{m_1 m_2}{m_1 + m_2}$$

$$\bar{\vartheta} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad \text{cm}^{-1}$$

Two conclusions can be drawn from the above equation:-

$$\bar{\vartheta} \propto \sqrt{k}$$

Means stronger bonds absorbs frequency in high range

$$\bar{\vartheta} \propto \sqrt{\frac{1}{\mu}}$$

Means heavier atoms absorb frequency in low wave number

Problems

1. What is the order of decreasing vibrational frequency for C — H & C — D?
2. What is the correct increasing order of stretching frequencies for C ≡ C, C = C and C — C?

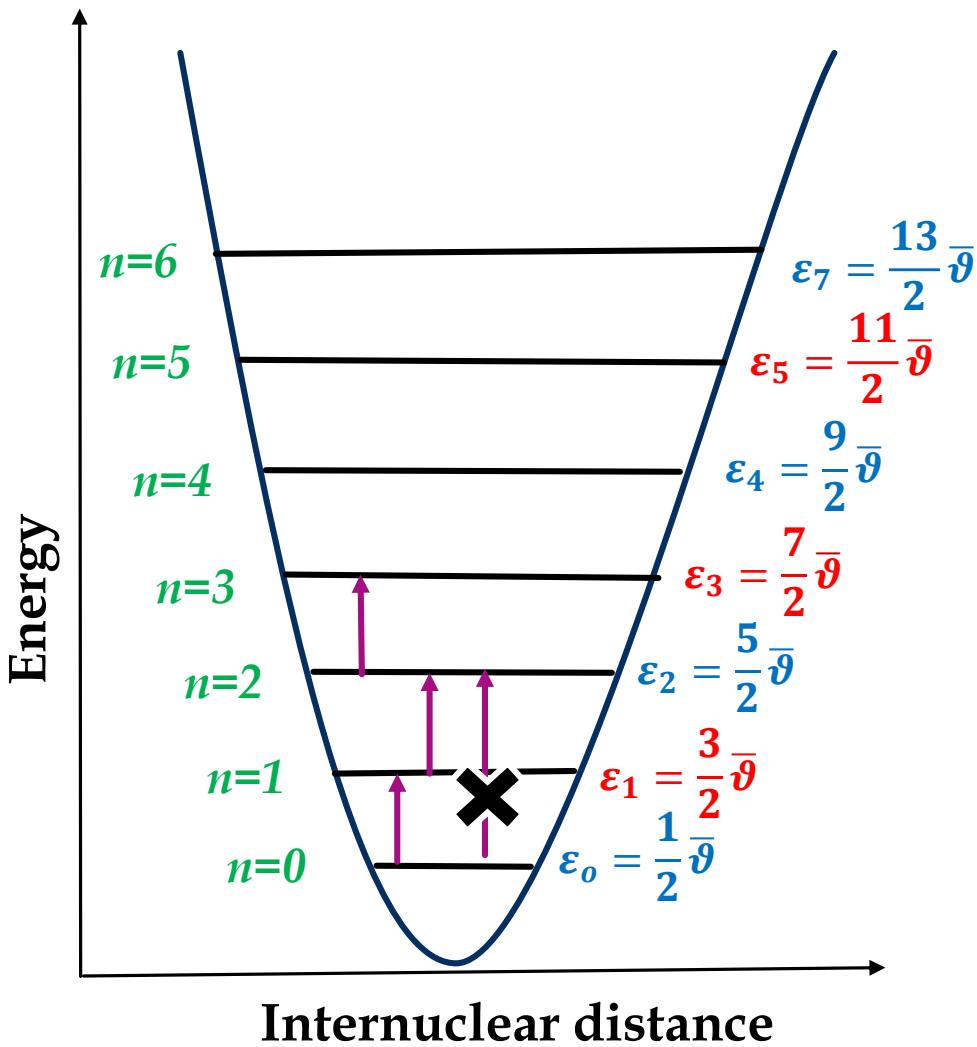
$$\bar{\vartheta} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad cm^{-1}$$

Energy of Vibrational Energy level is expressed as

$$E_n = \left(n + \frac{1}{2} \right) h\vartheta \quad Joules$$

$$\varepsilon_n = \frac{E}{hc} = \left(n + \frac{1}{2} \right) \bar{\vartheta} \quad cm^{-1}$$

Where, $n = vibrational\ quantum\ number = 0, 1, 2, 3, \dots \dots$



$$\epsilon_n = \frac{E}{hc} = \left(n + \frac{1}{2}\right) \bar{\vartheta} \text{ cm}^{-1}$$

At $n = 0$, $\epsilon_0 = \frac{1}{2} \bar{\vartheta} \text{ cm}^{-1}$

Zero Point Energy

At $n = 1$, $\epsilon_1 = \frac{3}{2} \bar{\vartheta} \text{ cm}^{-1}$

At $n = 2$, $\epsilon_2 = \frac{5}{2} \bar{\vartheta} \text{ cm}^{-1}$

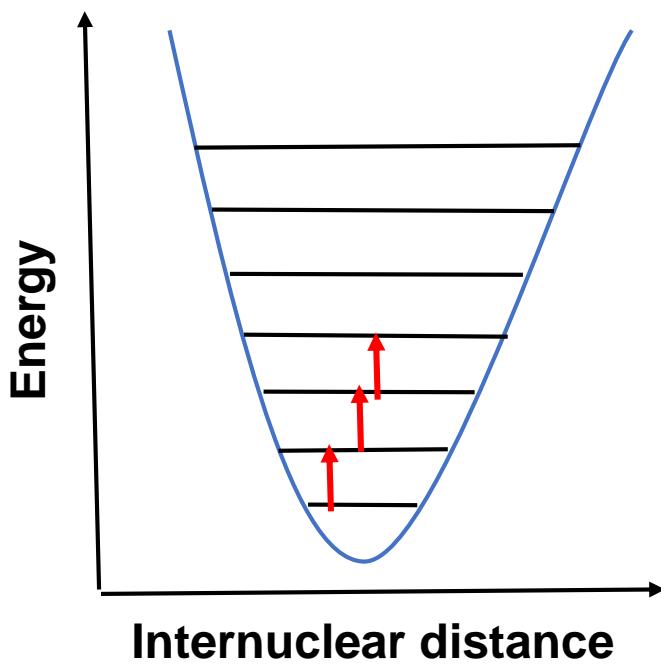
Selection rule for a SHO undergoing vibrational changes

$$\Delta n = \pm 1$$

Energy levels of SHO are equally spaced

- A molecule can never have zero vibrational energy.
- The energy of the molecule corresponding to $n = 0$ level is known as **Zero Point Energy**.

Energy between two adjacent levels



$$\varepsilon_{n \rightarrow n+1} = \left(n + 1 + \frac{1}{2} \right) \bar{\vartheta} - \left(n + \frac{1}{2} \right) \bar{\vartheta} \text{ cm}^{-1} = \bar{\vartheta} \text{ cm}^{-1}$$

The Anharmonic Oscillator (AHO)

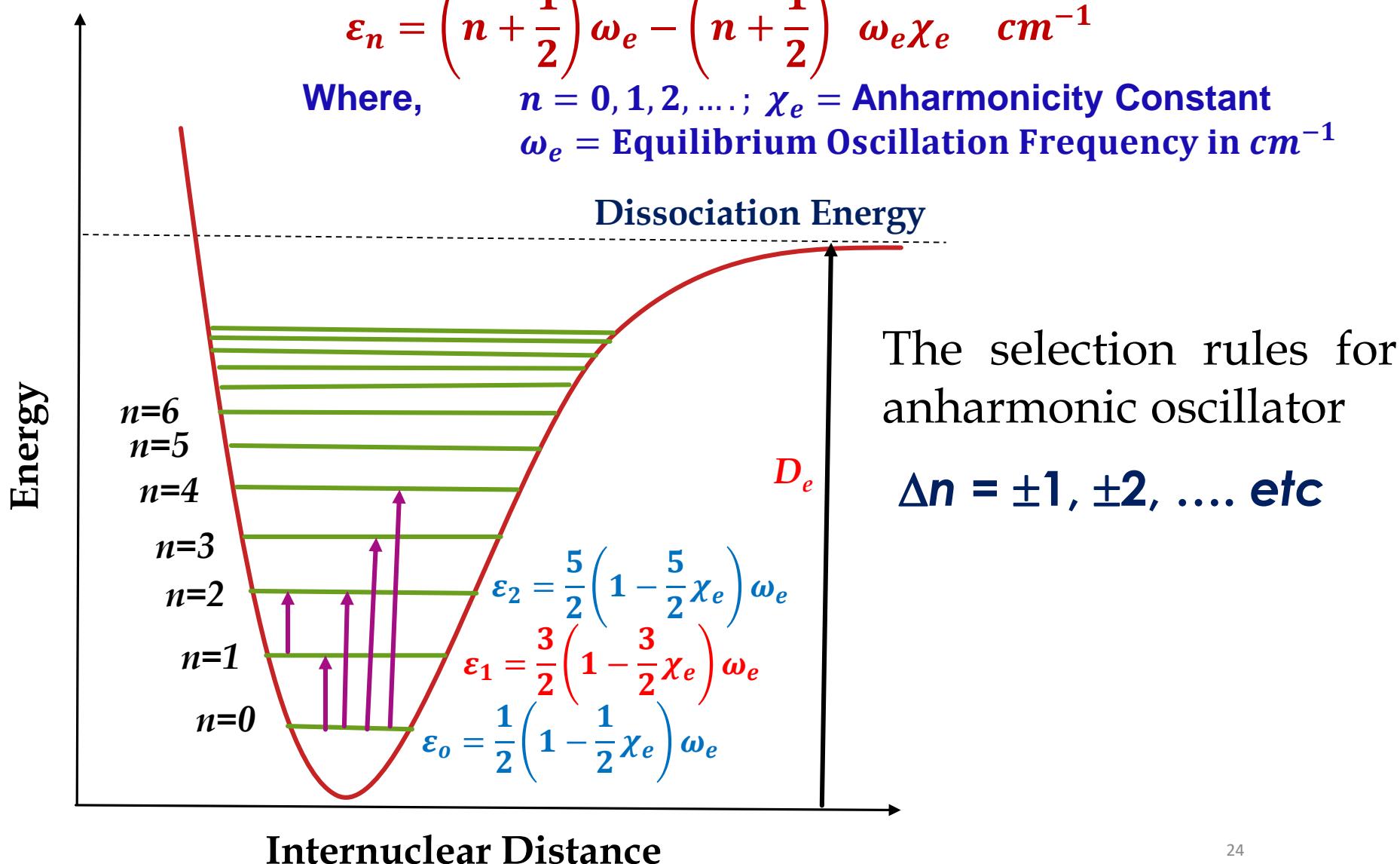
Real molecules do not obey laws of SHO for large amplitude of vibrations.

$$\varepsilon_n = \left(n + \frac{1}{2} \right) \omega_e - \left(n + \frac{1}{2} \right)^2 \omega_e \chi_e \text{ cm}^{-1}$$

Where,

$n = 0, 1, 2, \dots$; χ_e = Anharmonicity Constant

ω_e = Equilibrium Oscillation Frequency in cm^{-1}



$$\varepsilon_n = \left(n + \frac{1}{2}\right) \omega_e - \left(n + \frac{1}{2}\right)^2 \omega_e \chi_e \quad cm^{-1}$$

$$\varepsilon_n = \omega_e \left(n + \frac{1}{2}\right) \left\{1 - \chi_e \left(n + \frac{1}{2}\right)\right\} \quad cm^{-1}$$

Where, $n = 0, 1, 2, \dots$

χ_e = Anharmonicity Constant

ω_e = Equilibrium Oscillation Frequency in cm^{-1}

Calculate the Zero Point Energy?

Probable Transitions

- $n = 0 \rightarrow n = 1, \Delta n = 1$

Intense Absorption (Fundamental Absorption)

$$\Delta\epsilon = \omega_e (1 - 2\chi_e) \text{ cm}^{-1}$$

- $n = 0 \rightarrow n = 2, \Delta n = 2$

With Small Intensity (First overtone)

$$\Delta\epsilon = 2\omega_e (1 - 3\chi_e) \text{ cm}^{-1}$$

- $n = 0 \rightarrow n = 3, \Delta n = 3$

Negligible intensity (Second overtone)

$$\Delta\epsilon = 3\omega_e (1 - 4\chi_e) \text{ cm}^{-1}$$

Problems

Q1. The fundamental and first overtone transitions of NO are centred at 1876 cm^{-1} and 3724 cm^{-1} respectively. Evaluate the equilibrium vibrational frequency, the anharmonicity constant and the zero point energy.

Ans:

$$\Delta\varepsilon = \omega_e (1 - 2\chi_e) \text{ cm}^{-1}$$

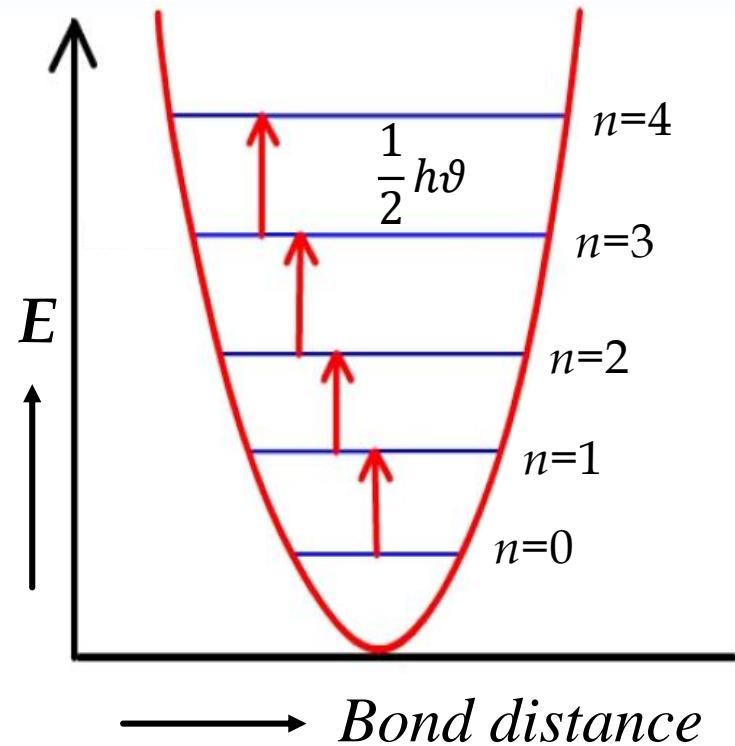
$$\Delta\varepsilon = 2\omega_e (1 - 3\chi_e) \text{ cm}^{-1}$$

$$\sim \omega_e = 1903\text{ cm}^{-1}, \chi_e = 7.3 \times 10^{-3}\text{ cm}^{-1}, \\ \text{zero point energy} = 949\text{ cm}^{-1}$$

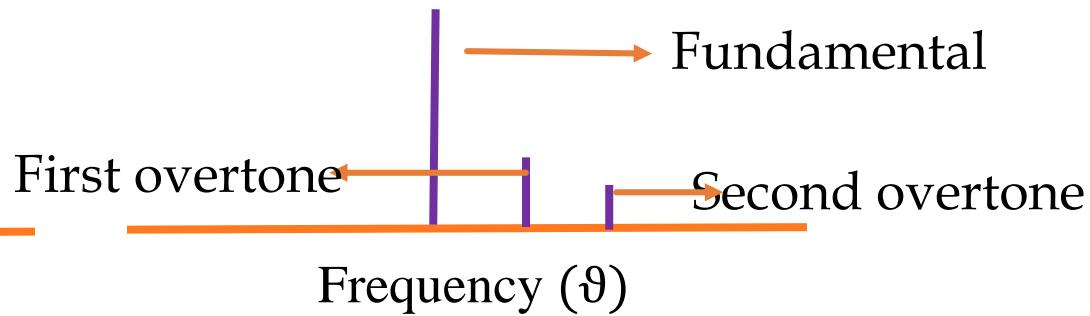
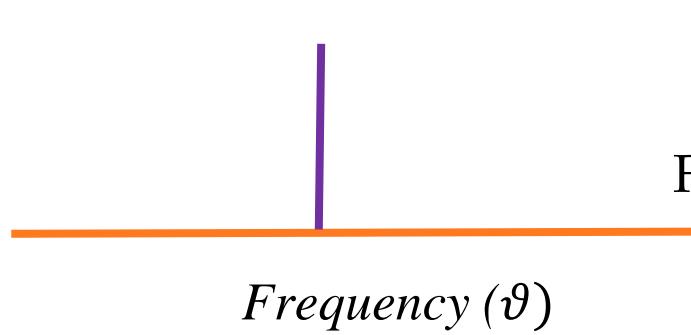
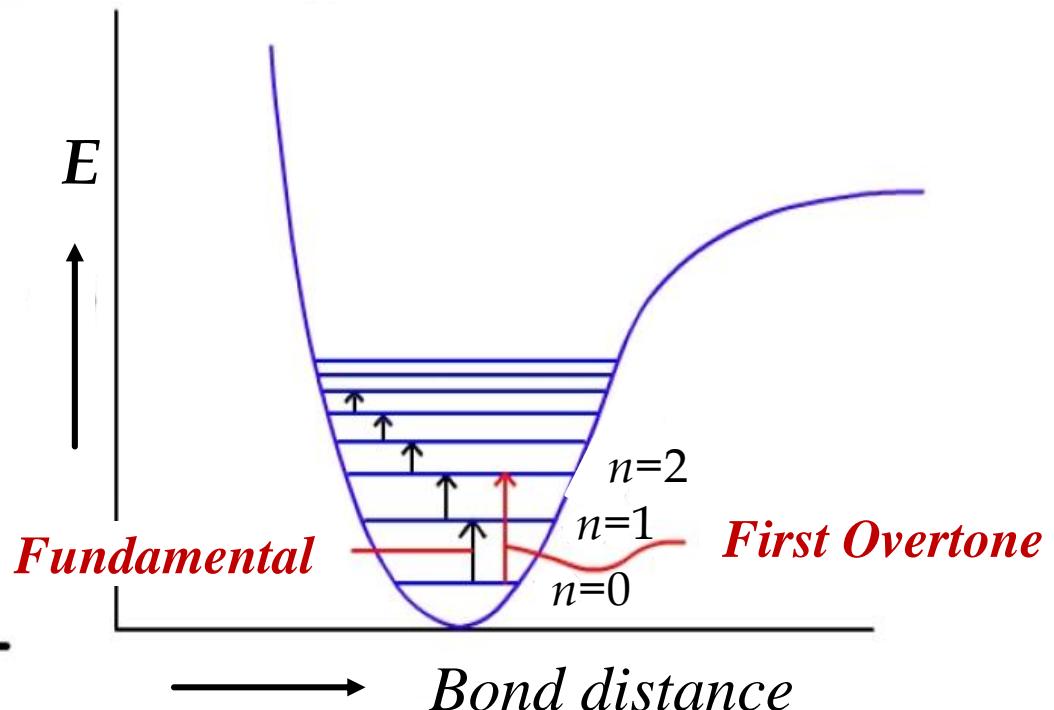
Q2. The spectrum of HCl, shows a very intense absorption at 2886 cm^{-1} a weak one at 5668 cm^{-1} and a very weak one at 8347 cm^{-1} . Calculate the equilibrium frequency (ω_e) and anharmonicity constant (χ_e).

Ans. $\chi_e = 0.0174$, $\omega_e = 2990\text{ cm}^{-1}$.

Harmonic oscillator



Anharmonic oscillator



Fundamental Vibrations: Polyatomic Molecules

Degree of freedom: The number of directions in which atom can move freely is defined as its degree of freedom.

A molecule composed of N atoms. The total number of coordinates to specify the locations of N atoms is $3N$ (e.g. x, y, z per atom). Says that the molecule has **3N** degree of freedom.

$3N = \text{degrees of freedom of translational} + \text{rotational} + \text{vibrational motions}$

For linear or non linear molecule – translational motions are 3

For linear molecules rotational motions = 2

For non linear molecule rotational motions = 3

The degree of freedom of vibrational motion

For linear molecule $3N-5$

Non-linear molecule $3N-6$

} Fundamental vibrations

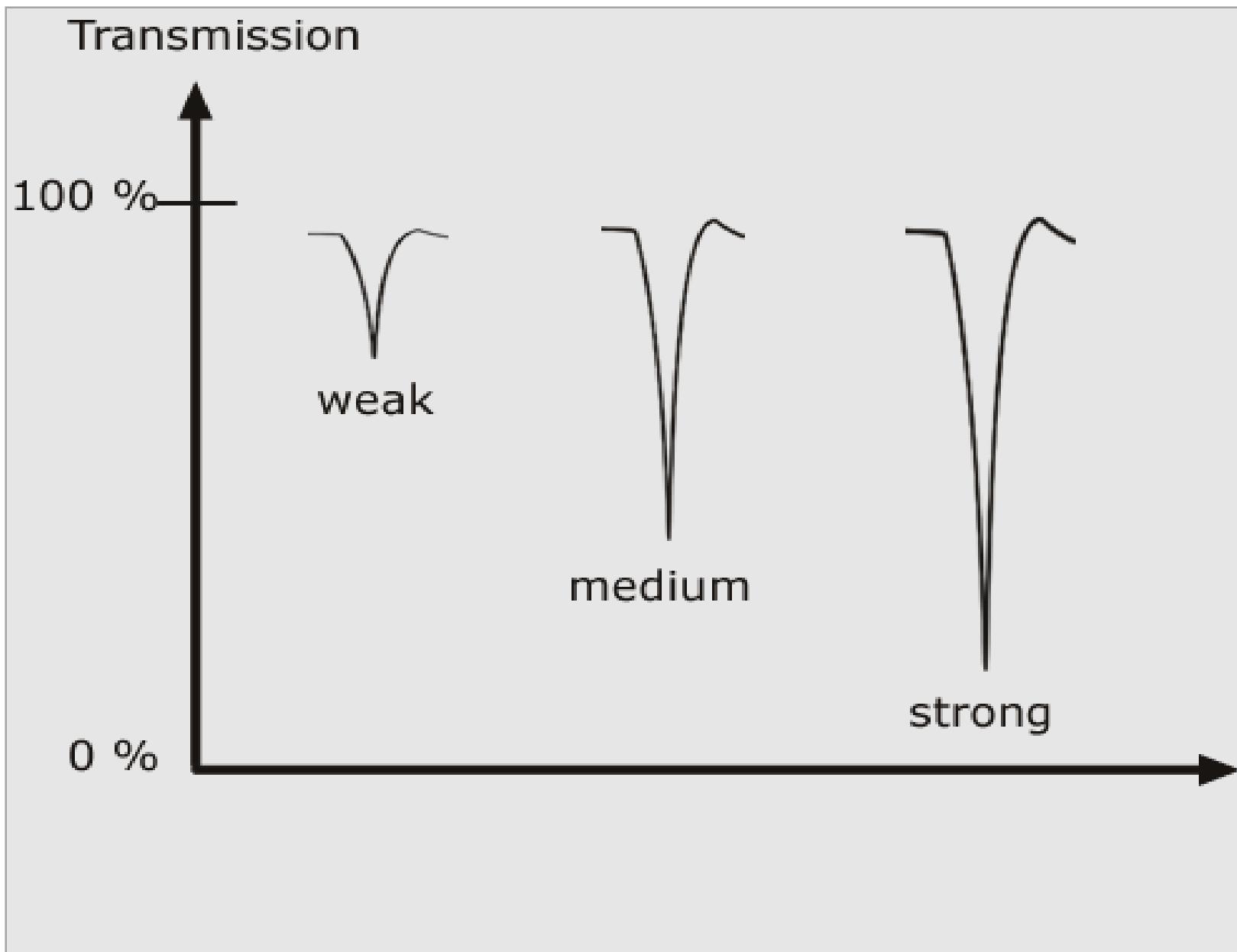
No. of stretching motions of linear or non linear molecule is $N-1$

No. of bending motions for

linear molecules = $2N-4$,

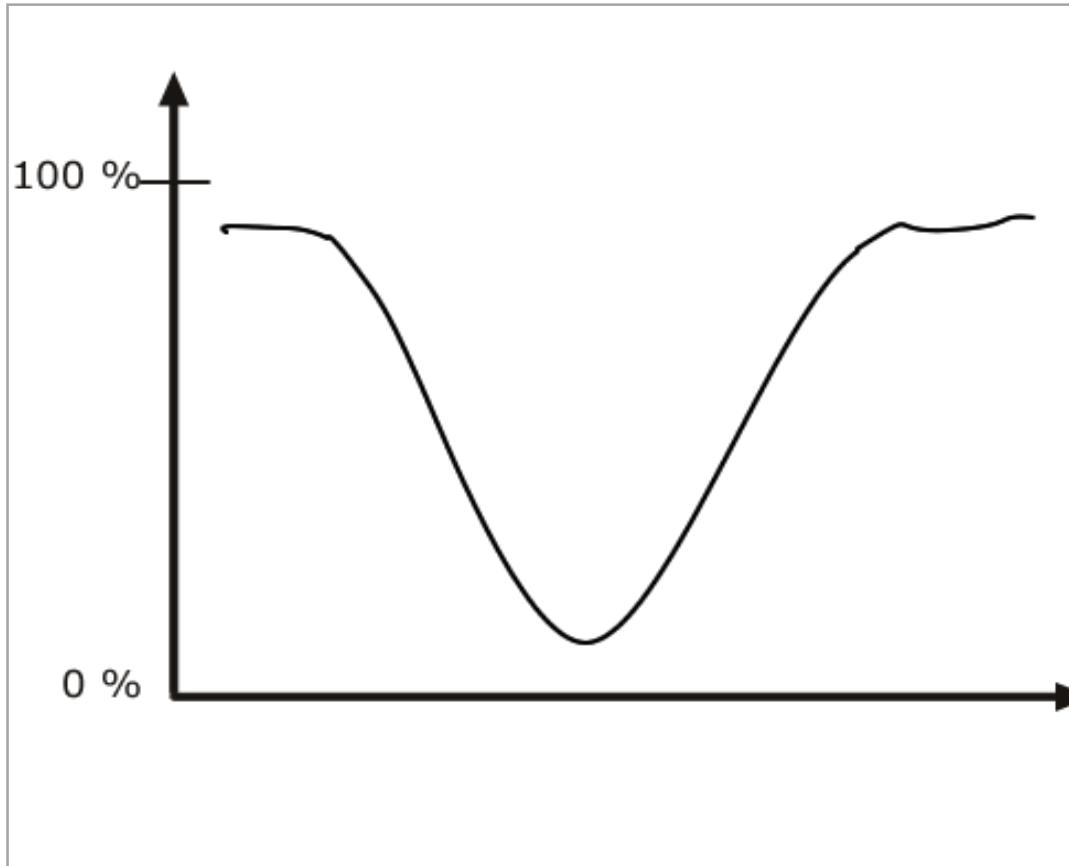
Non-linear molecules = $2N-5$

IR Spectrum - The detection of different bonds



IR Spectrum - Band Shapes

- ❖ IR band shapes come in various forms. Two of the most common are **narrow and broad**. Narrow bands are thin and pointed, like a dagger. Broad bands are wide and smoother.
- ❖ A typical example of a **broad band** is that displayed by O-H bonds, such as those found in alcohols and carboxylic acids, as shown below.



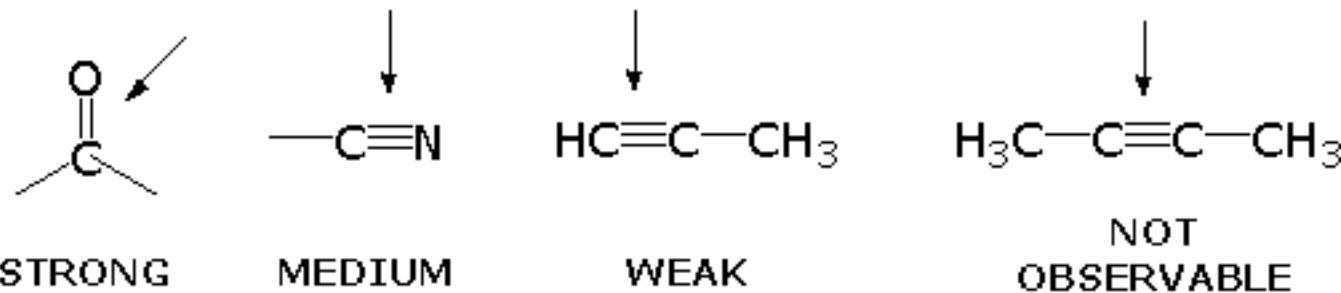
Absorptions in IR Spectra

Band	Depends on	Frequency
Position	Reduced mass of atoms	Lighter atoms – higher frequency
	Bond strength	Strong – higher frequency
Strength	Change in dipole moment	Large dipole moment gives strong absorption
Width	Hydrogen bonding	Strong H-bond gives wide peak

IR Active Bonds

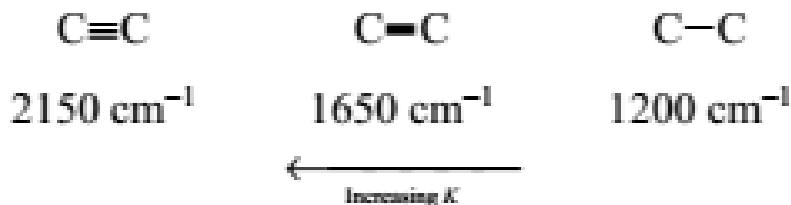
- Not all covalent bonds display bands in the IR spectrum. **Only polar bonds do so. These are referred to as IR active.**
- Strongly polar bonds such as carbonyl groups (C=O) produce strong bands.
- Medium polarity bonds and asymmetric bonds produce medium bands.
- Weakly polar bond and symmetric bonds produce weak or non observable bands.

Symmetric bond that has identical or nearly identical groups on each end will not absorb in the infrared

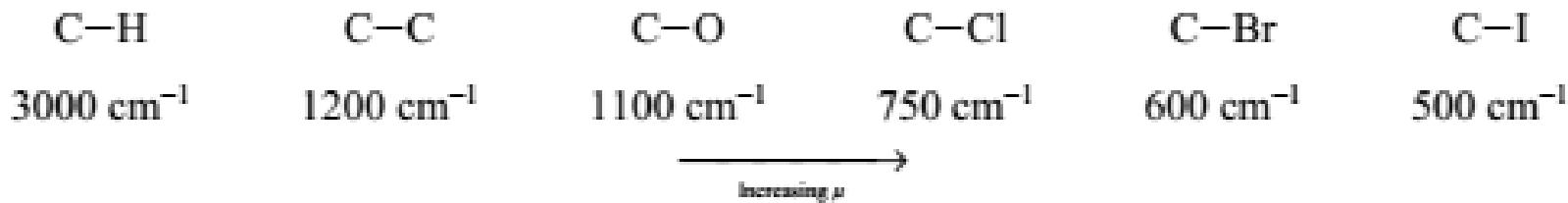


$$\bar{v} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}}$$

- Stronger bonds have a larger force constant K and vibrate at higher frequencies than weaker bonds.

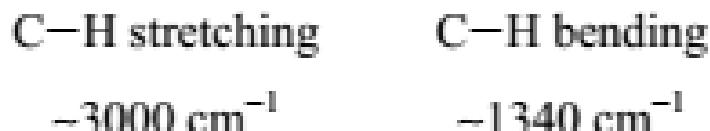


- bonds between atoms of higher masses (larger reduced mass) vibrate at lower frequencies than bonds between lighter atoms.

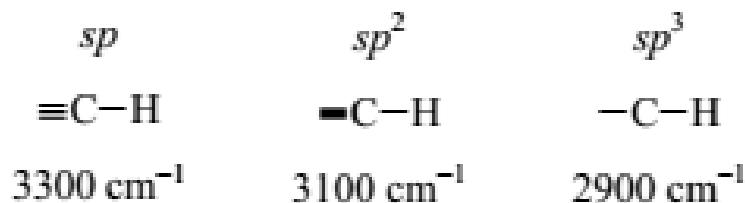


$$\bar{v} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}}$$

- Bending motions occur at lower energy (lower frequency) than the typical stretching motions because of the lower value for the bending force constant K.



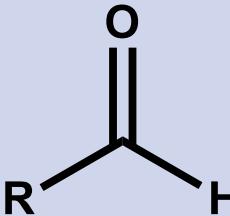
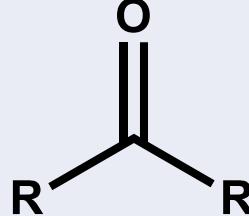
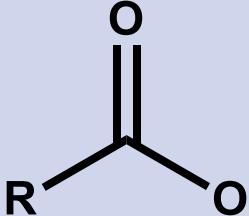
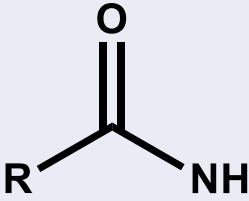
- Hybridization affects the force constant K, also $sp > sp^2 > sp^3$



Group Frequencies

Infrared Spectroscopy Table

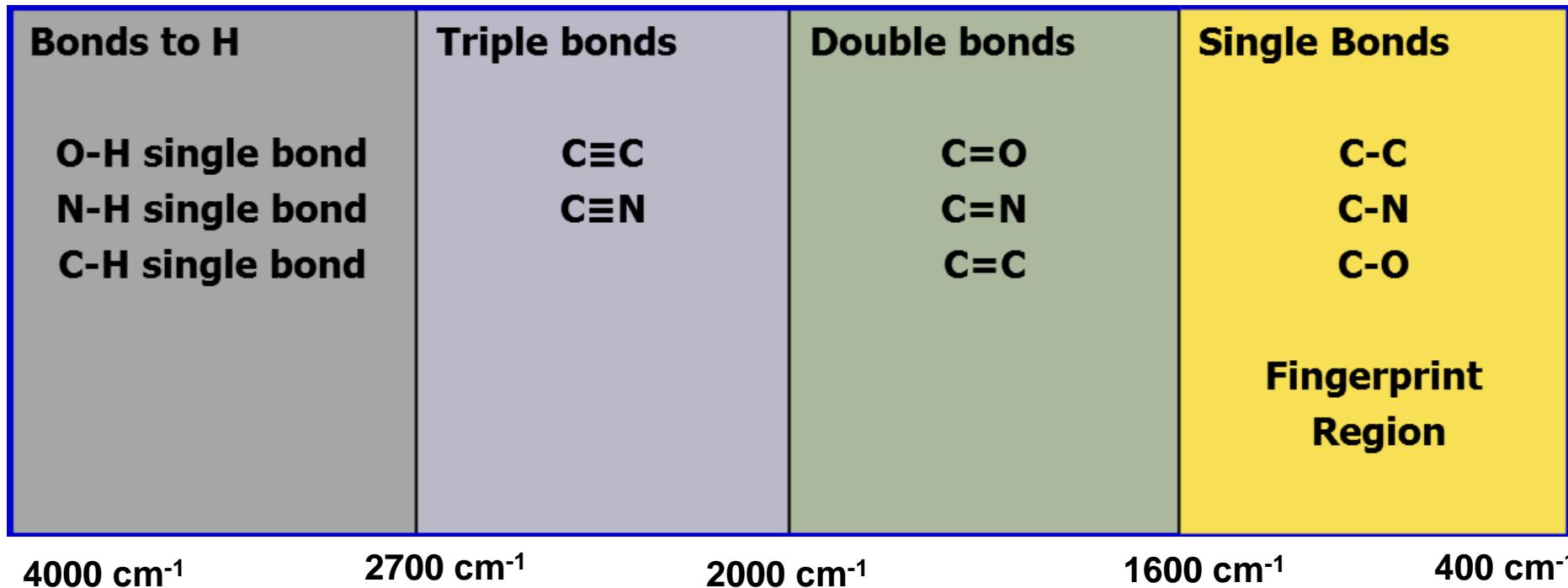
Bond	Class of compound	Range (cm ⁻¹)
C-C	Alkane	1200 - 700
C=C	Alkene	1680 - 1620
C ≡ C	Alkyne	2130 - 2150
C-H	Alkane (C-sp ³)	2965 - 2850
	Aromatic (C-sp ²)	> 3000

Bond	Class of compound	Range (cm^{-1})
	Aldehyde	1740 – 1720
	Ketone	1725 - 1705
	Carboxylic acid	1725 - 1700
	Amide	1700 - 1630

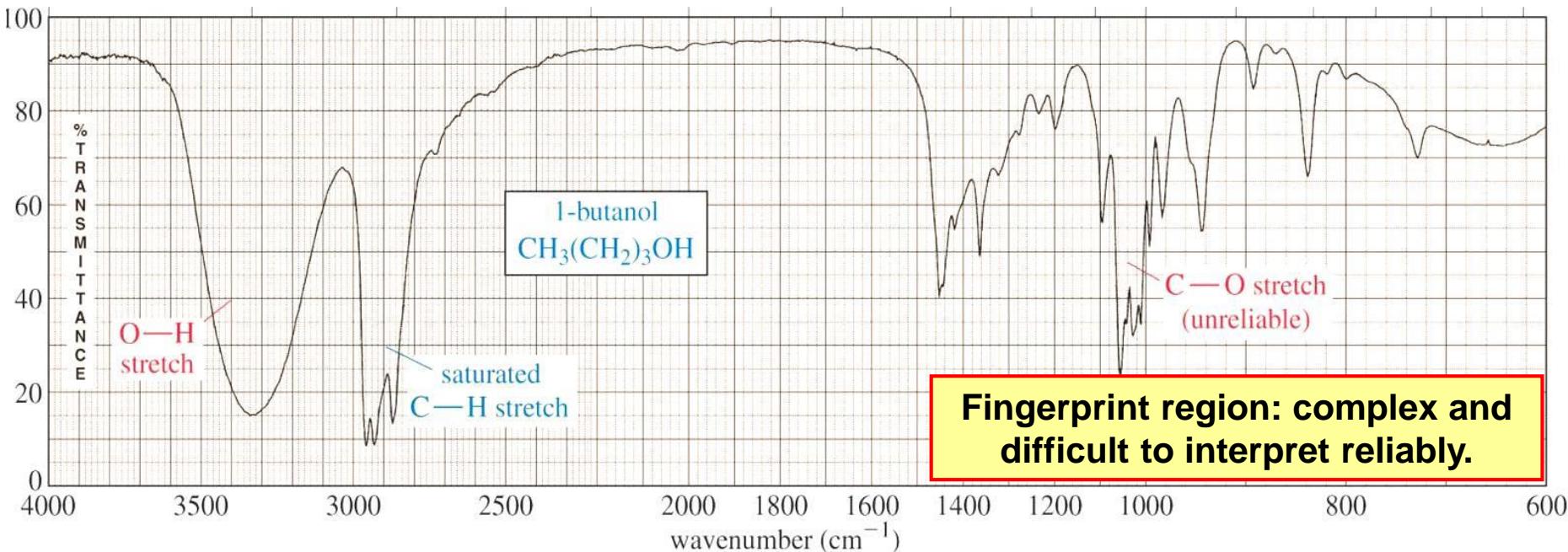
Bond	Class of compound	Range (cm ⁻¹)
O-H	Alcohol (monomer)	3650 - 3590
O-H...O	Alcohol (H-bonded)	3420 – 3200
O-H	Carboxylic acid (H-bonded)	3300 - 3250
C-O	Alcohols, Esters, Acids and Ethers	1300 - 1000

Bond	Class of compound	Range (cm ⁻¹)
N-H	Amine/Amide	3500 (approx.)
C≡N	Nitrile	2260 - 2240
C-X	X = Chloride	800 - 600
	X = Bromide	600 - 500
	X = Iodide	500 (approx.)

IR Absorption Range



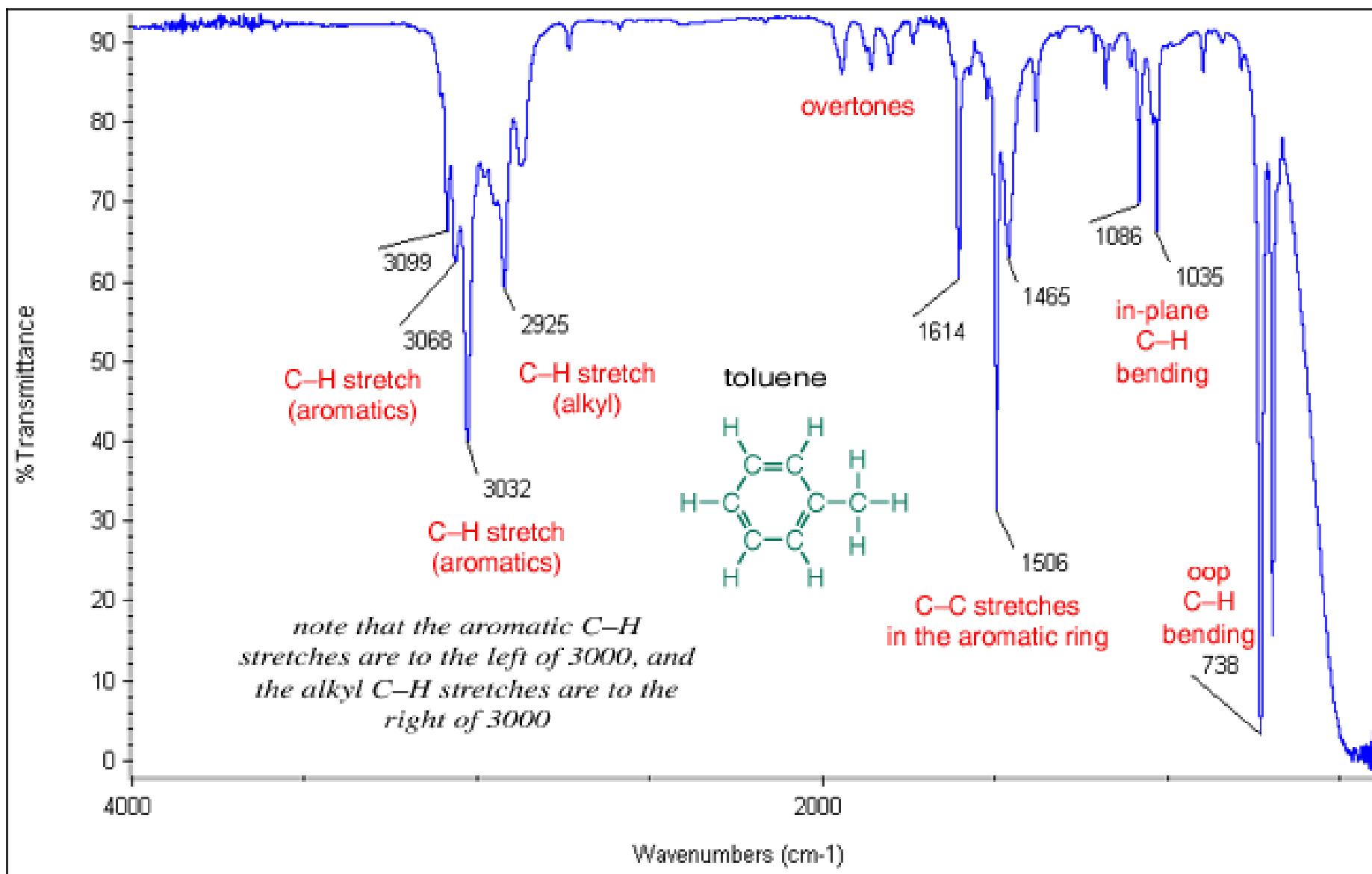
Looking at a Spectrum

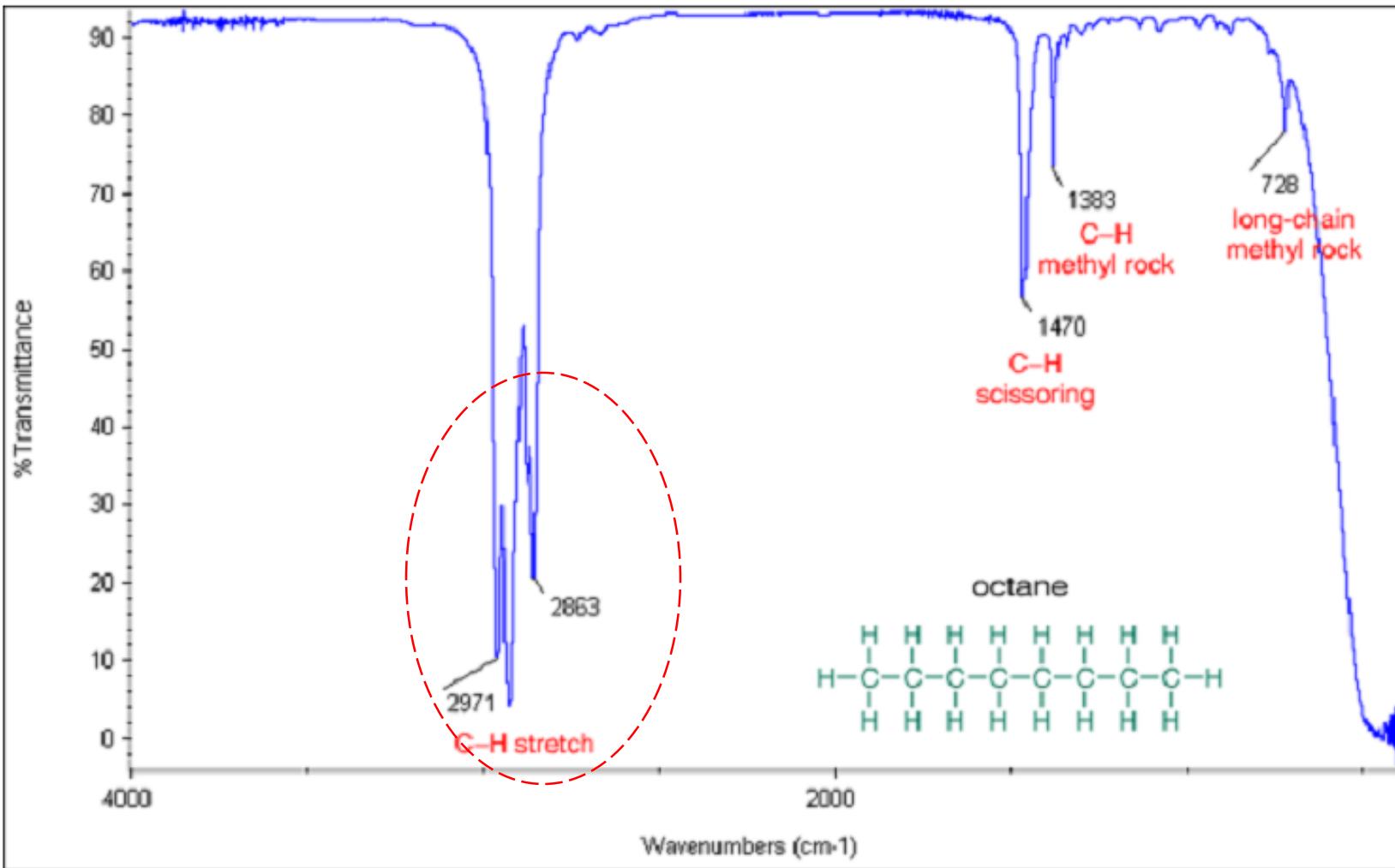


Focus your analysis on this region
(Functional group region). This is where
most stretching frequencies appear.

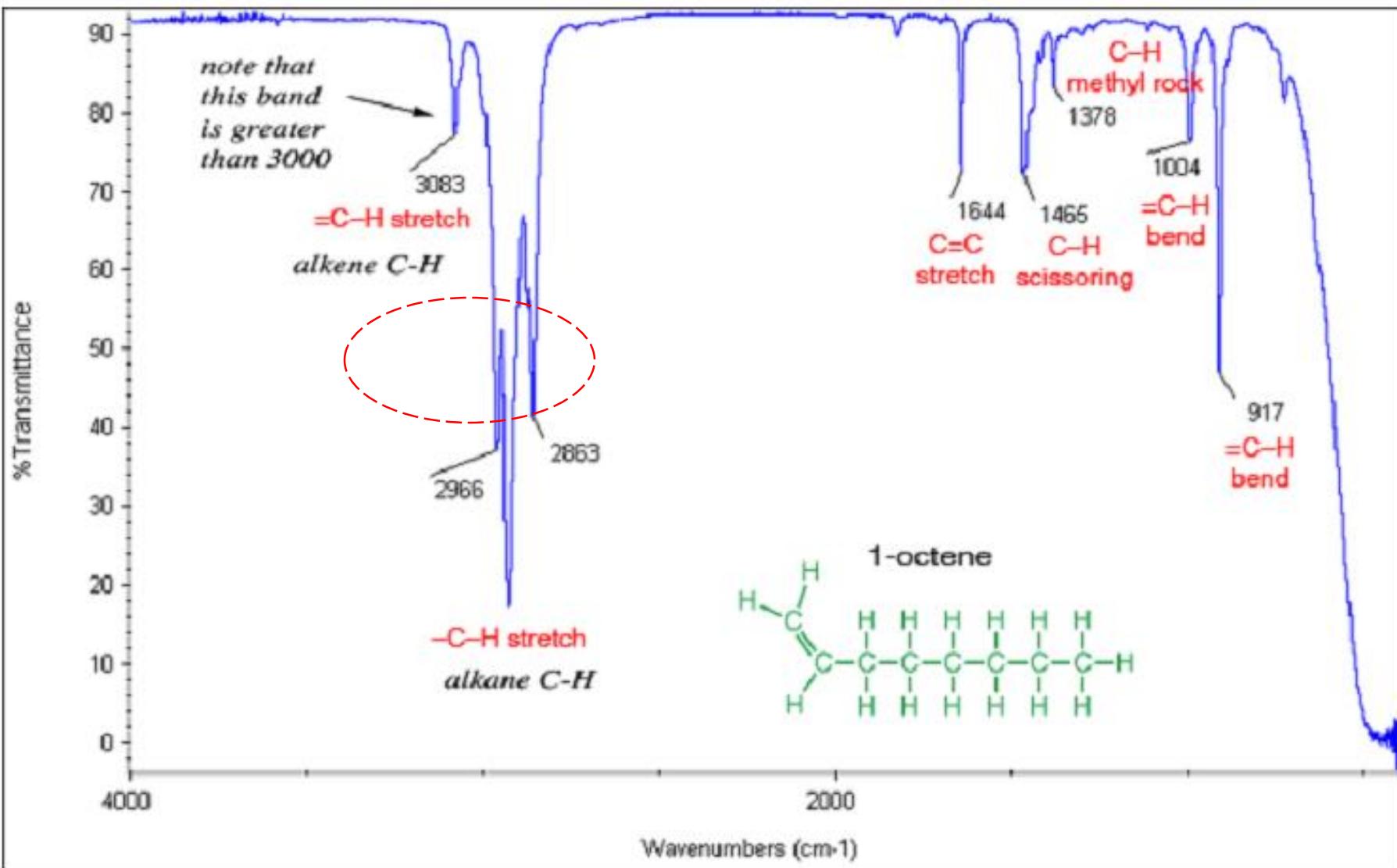
- Fingerprint region is rich in **Bending Vibration** of C-C, C-H, C-N, C-O etc.

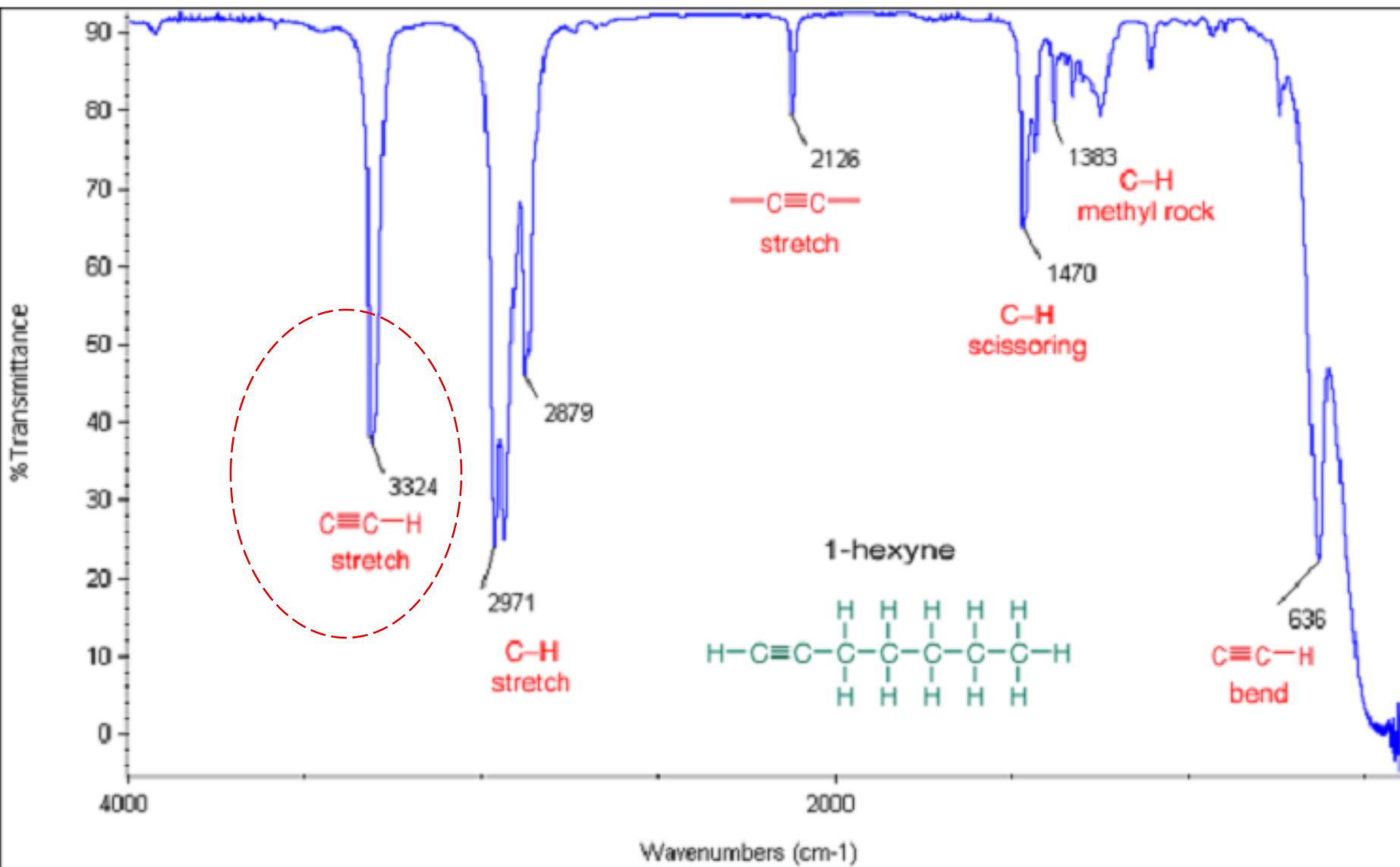
Hydrocarbons

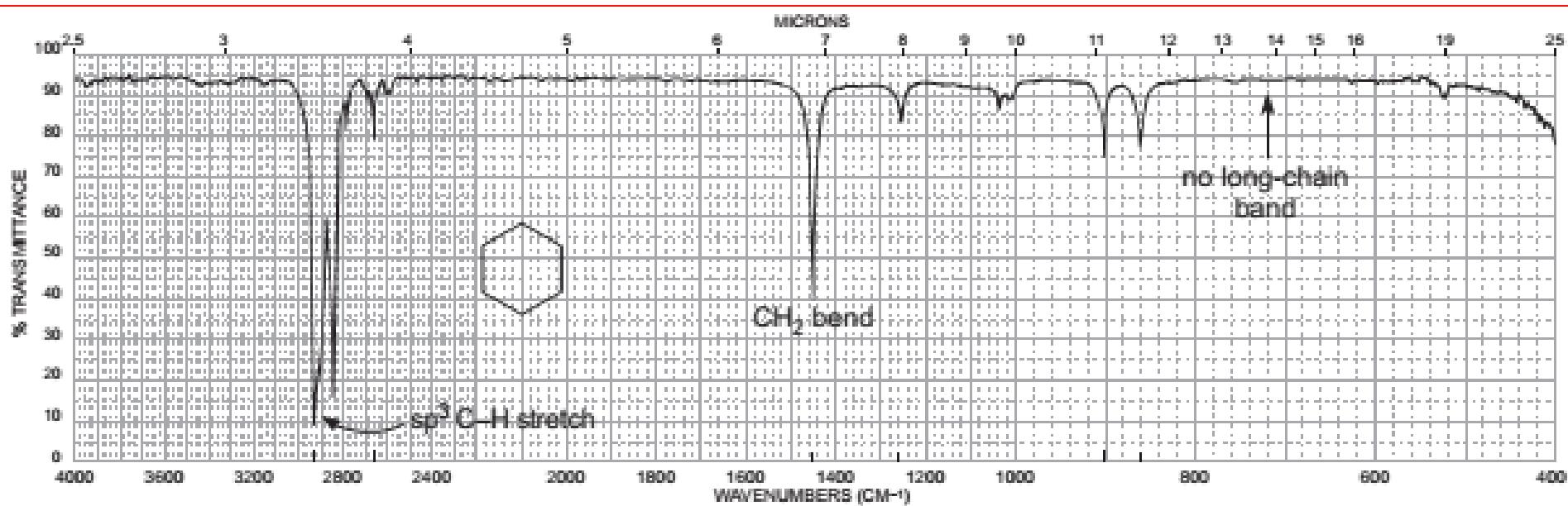
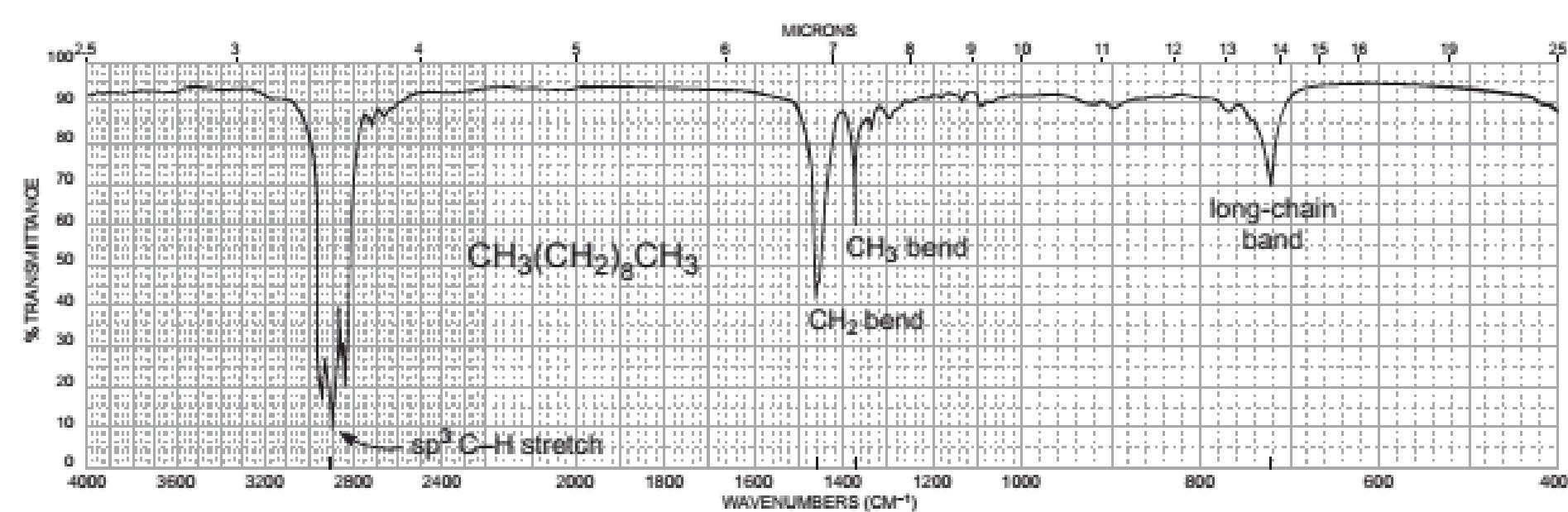




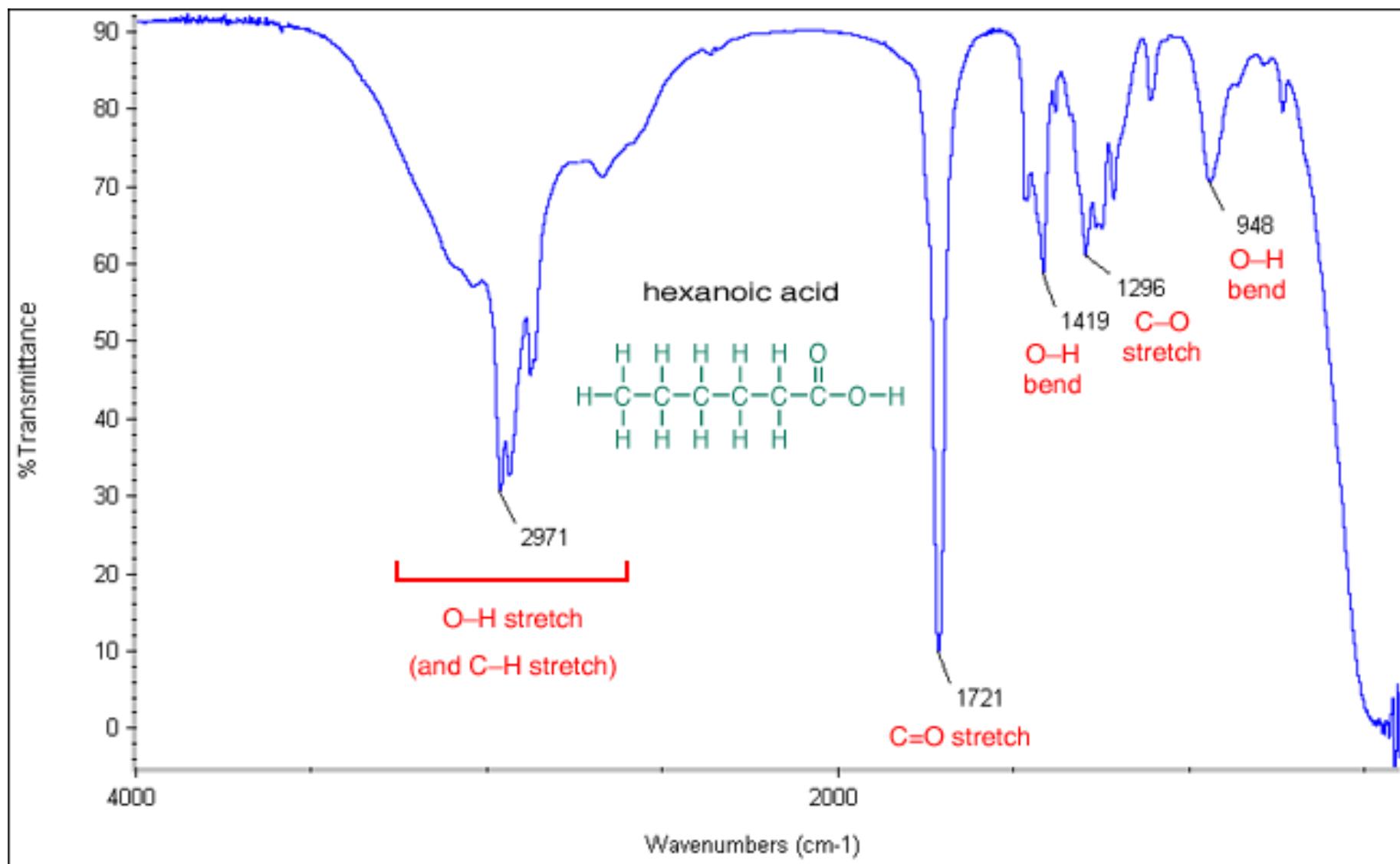
Note the strong bands in the $3000\text{-}2850 \text{ cm}^{-1}$ region due to C-H stretch.
 The C-H scissoring (1470 cm^{-1}), methyl rock (1383 cm^{-1}), and long-chain methyl rock (728 cm^{-1}) are noted on this spectrum.



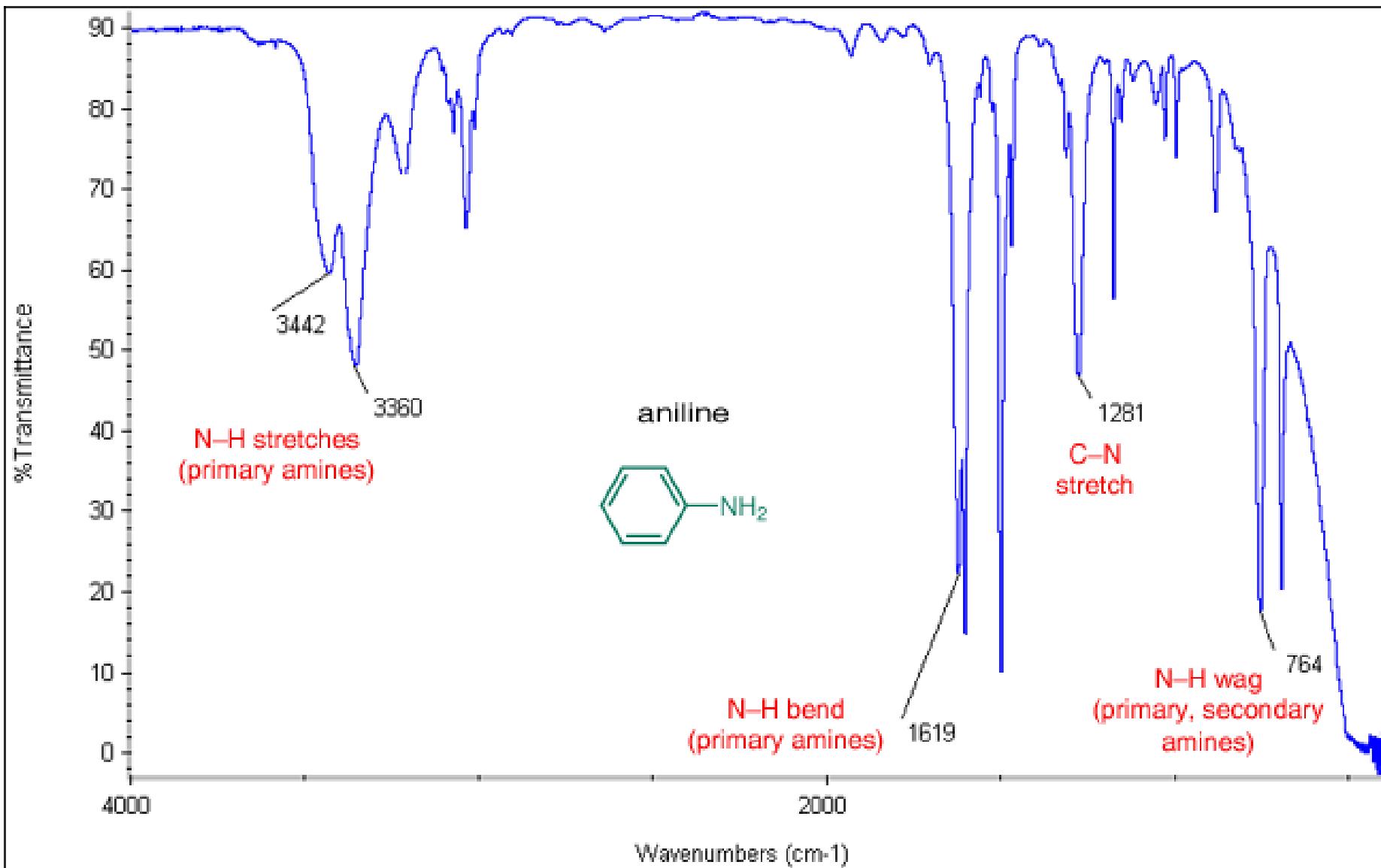


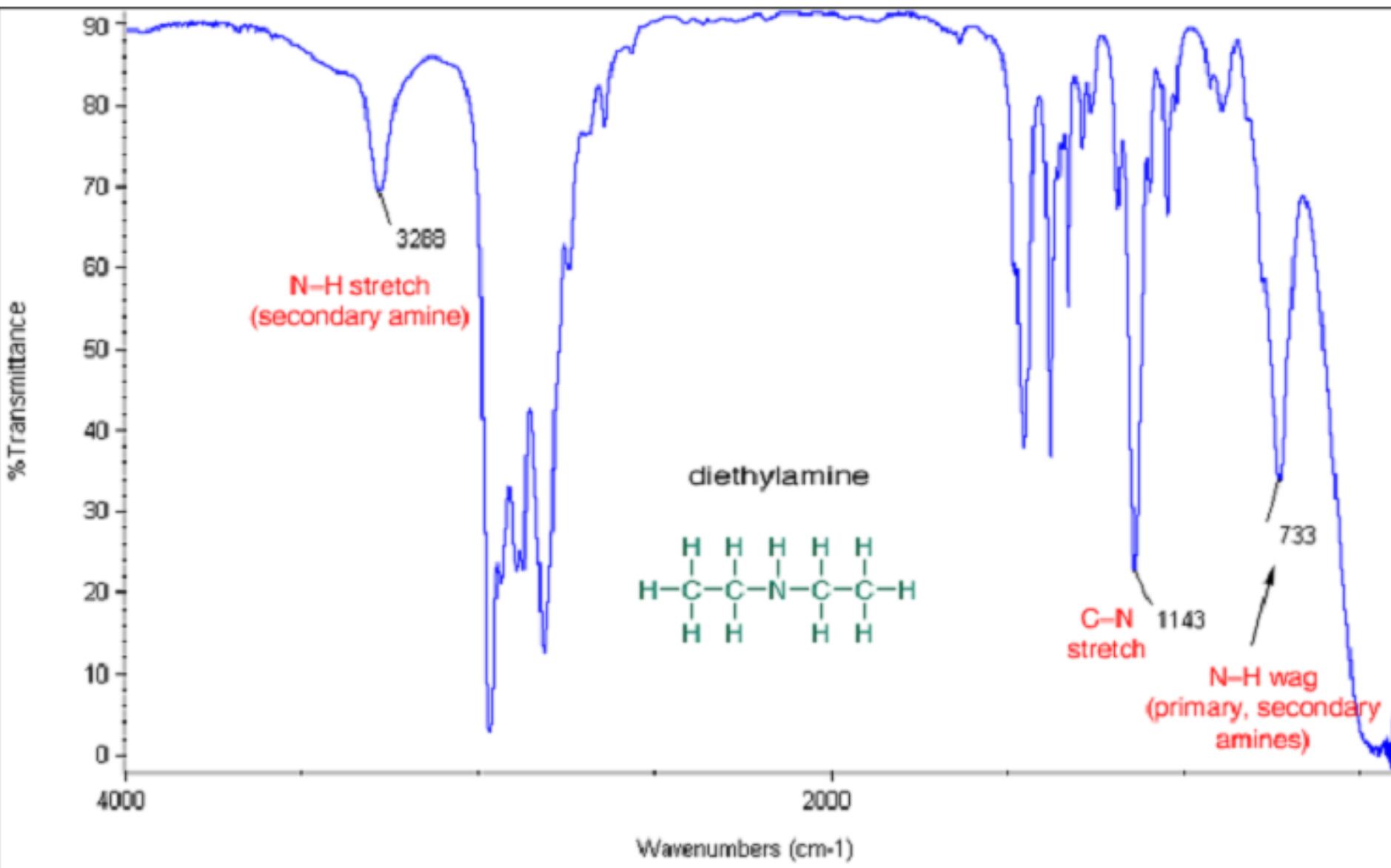


Carboxylic Acid



Amines

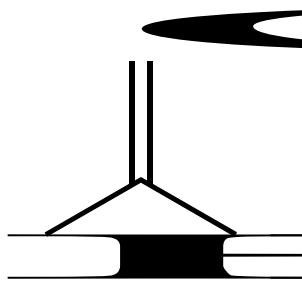




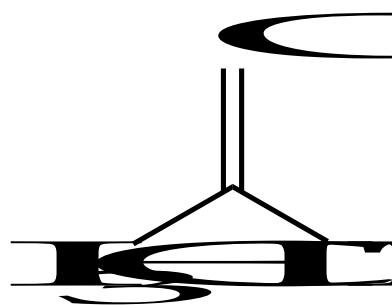
Factors Influencing the Vibrational Frequency of C=O Bond

Inductive Effect

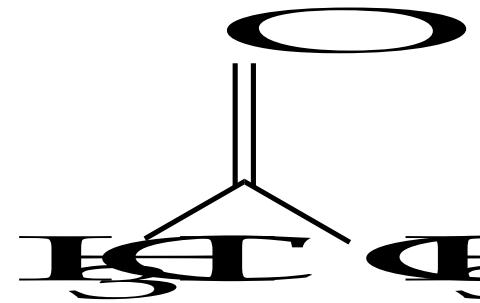
- ❖ Addition of +/ groups result in weakening of CO bond and the ϑ_{co} value decreases.



1750 cm⁻¹



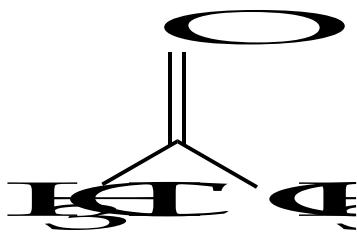
1745 cm⁻¹



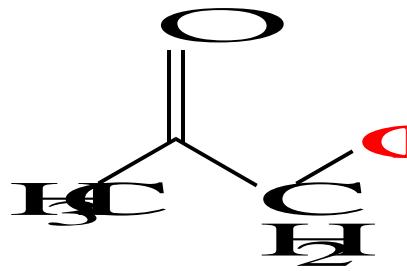
1715 cm⁻¹

Reason: Decrease in Bond Order and hence the Bond strength

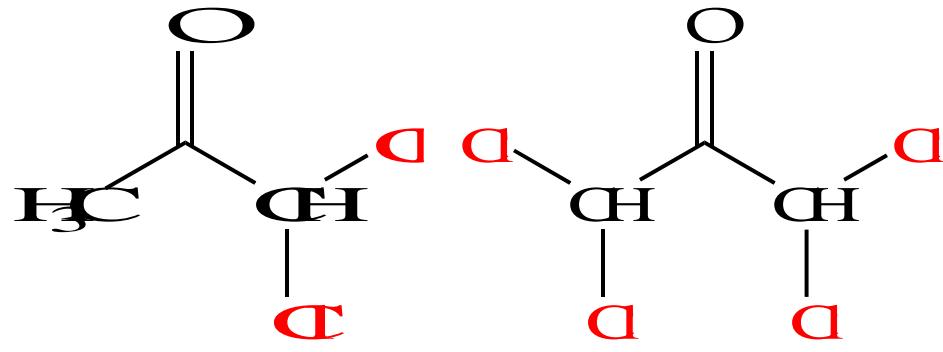
- ❖ Introduction of *-I*-groups results in increase in bond order of CO and hence the absorption frequency (ϑ value) increases.



1715 cm⁻¹



1725 cm⁻¹



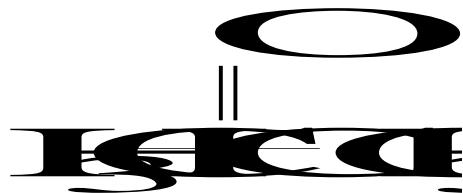
1740 cm⁻¹

1750 cm⁻¹

Mesomeric Effect

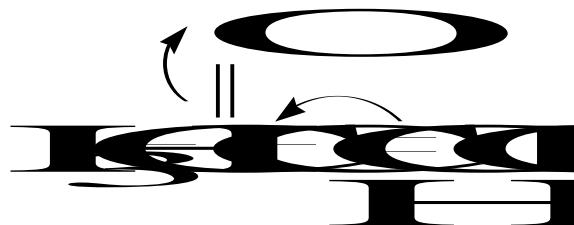
- ❖ Conjugation lowers the ϑ_{co} value by weakening the bond.
- ❖ Mode of conjugation enhances, the ϑ_{co} value further decreases.

No Conjugation



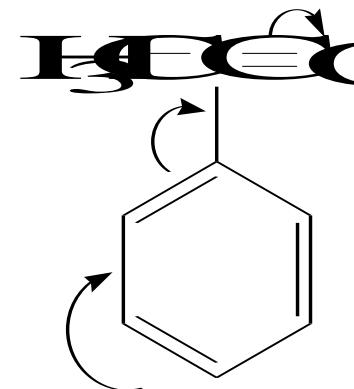
1715 cm^{-1}

Conjugation



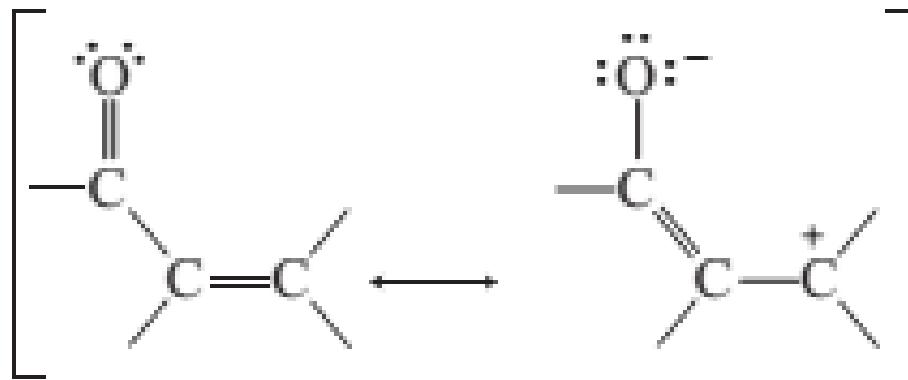
1706 cm^{-1}

Extension of Conjugation

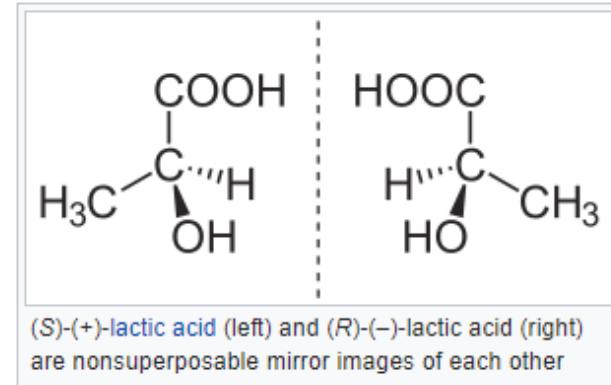


1693 cm^{-1}

- Resonance also affects the strength and length of a bond and hence its force constant K.
- Thus, whereas a normal ketone has its C=O stretching vibration at **1715 cm⁻¹**; a ketone that is conjugated with a C=C double bond absorbs at a lower frequency, near **1675** to **1680 cm⁻¹**
- That is because resonance lengthens the C=O bond distance and gives it more single-bond character.

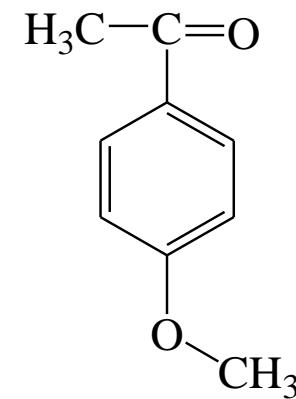
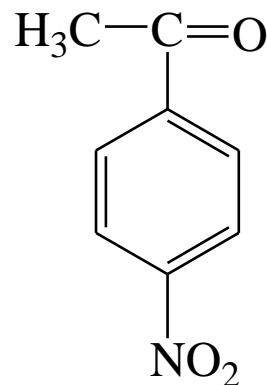
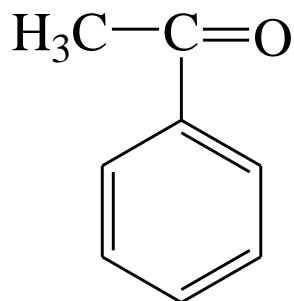


No two molecules will give exactly the same IR spectrum (except enantiomers).



1. Problem: In the IR spectra, Benzamide and Phenyl Acetate showed ϑ_{co} stretching frequency at 1663 cm^{-1} and 1730 cm^{-1} respectively. Explain the reason for difference in their peak position.

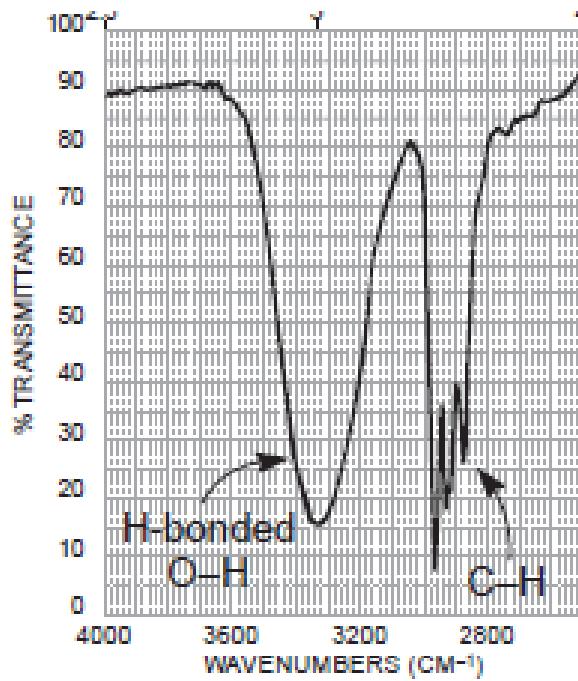
2. Problem: Arrange the following compounds according to their ϑ_{co} absorption frequency: 1677 cm^{-1} , 1700 cm^{-1} , 1770 cm^{-1} .



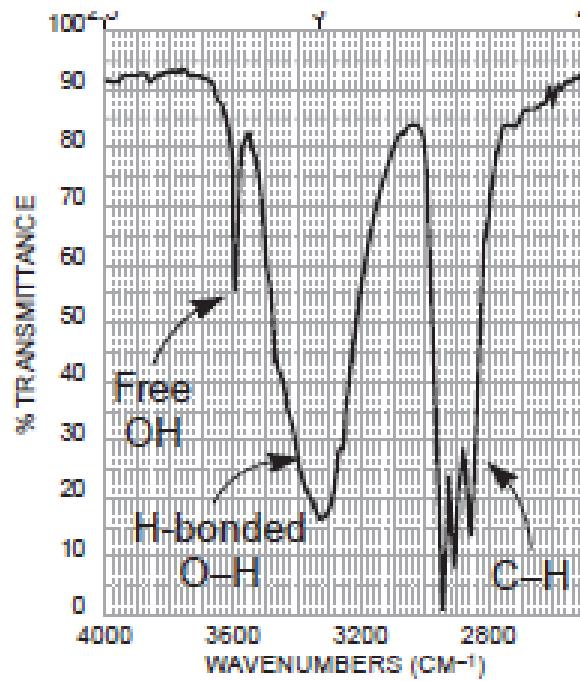
Hydrogen Bonding

- ❖ H-bonding brings downward frequency shifts.
- ❖ Stronger the H-bonding, greater is the absorption shift towards lower frequency.
- ❖ Inter-molecular H-bonding gives rise to broad band and strong peak.
- ❖ Intra-molecular H-bonding gives rise to sharp and defined peak.

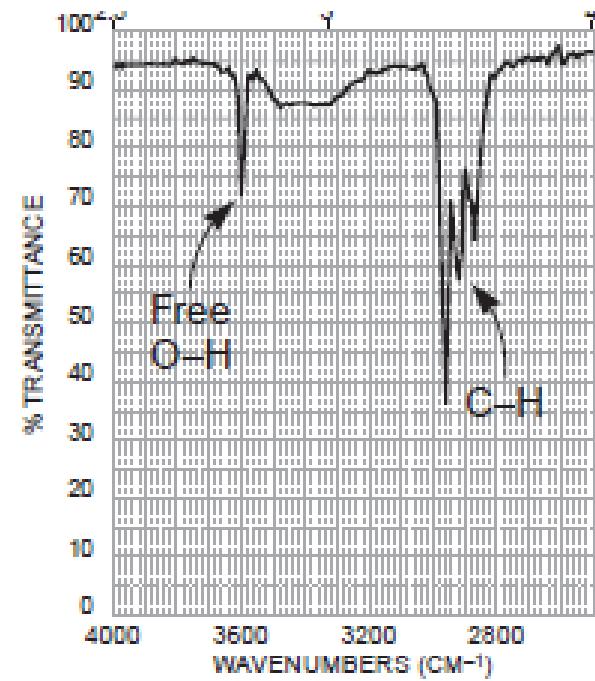
Intermolecular Hydrogen bonding



(a)



(b)

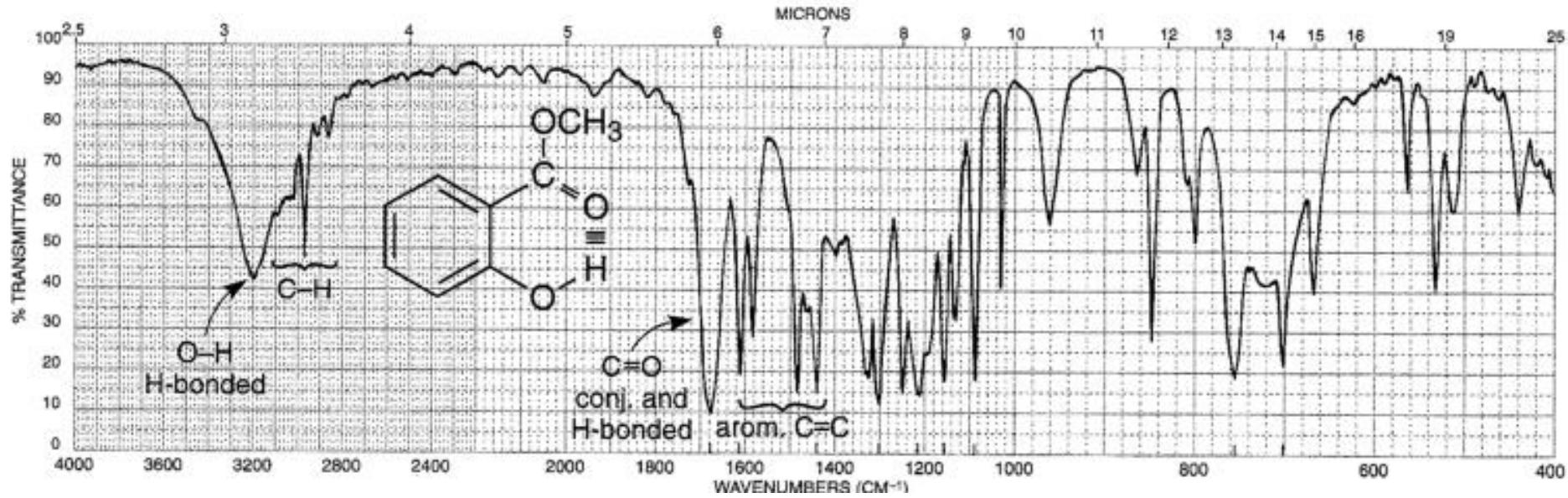


(c)

Effect of dilution on Hydrogen bonding - effect on O-H stretching

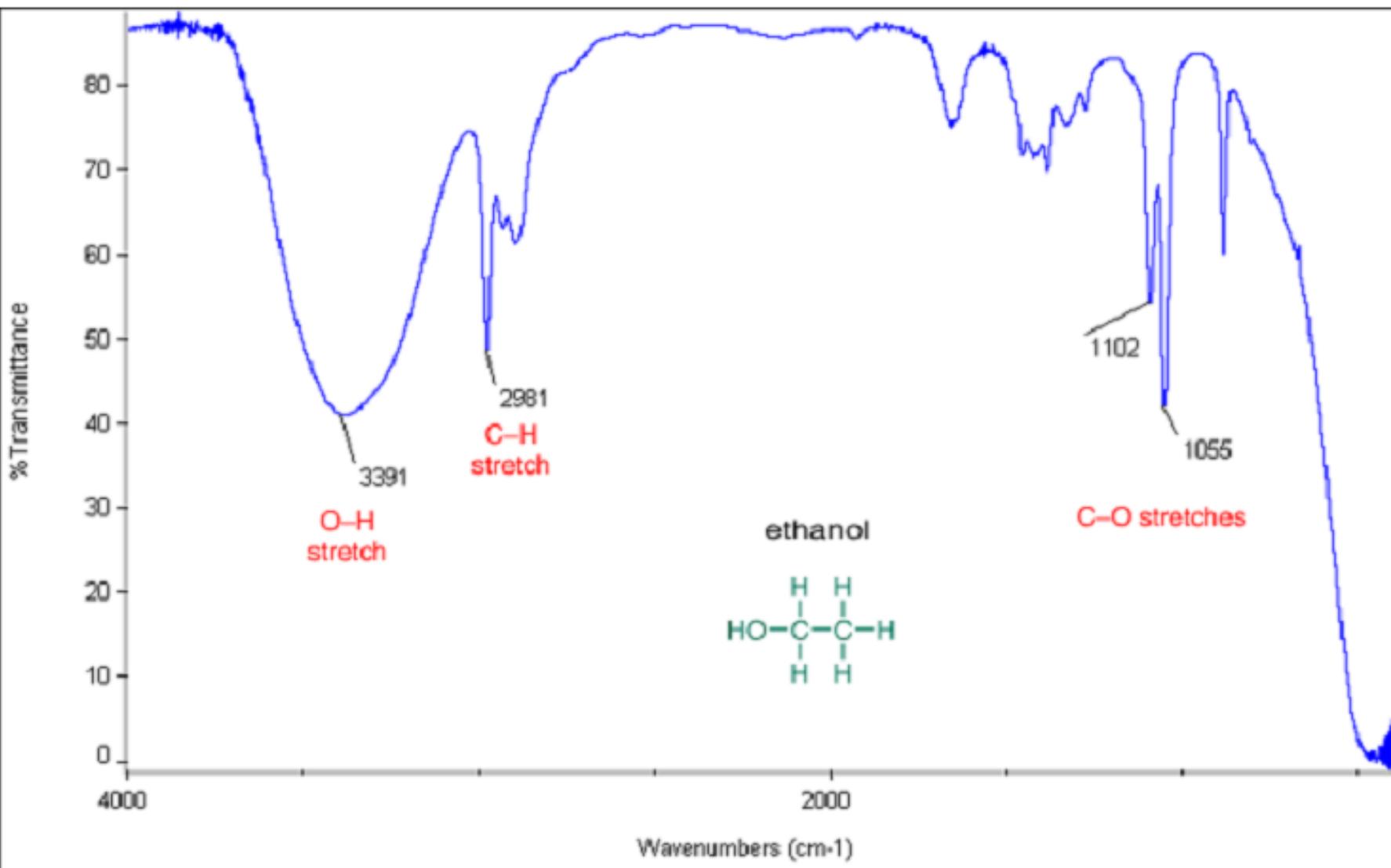
Intermolecular hydrogen bonding weaken the O-H bond, thereby shifting the band to lower frequency.

Intramolecular H bonding



Intramolecular-H bonding shifts the OH band to lower frequency

“Does not depend on the concentration”



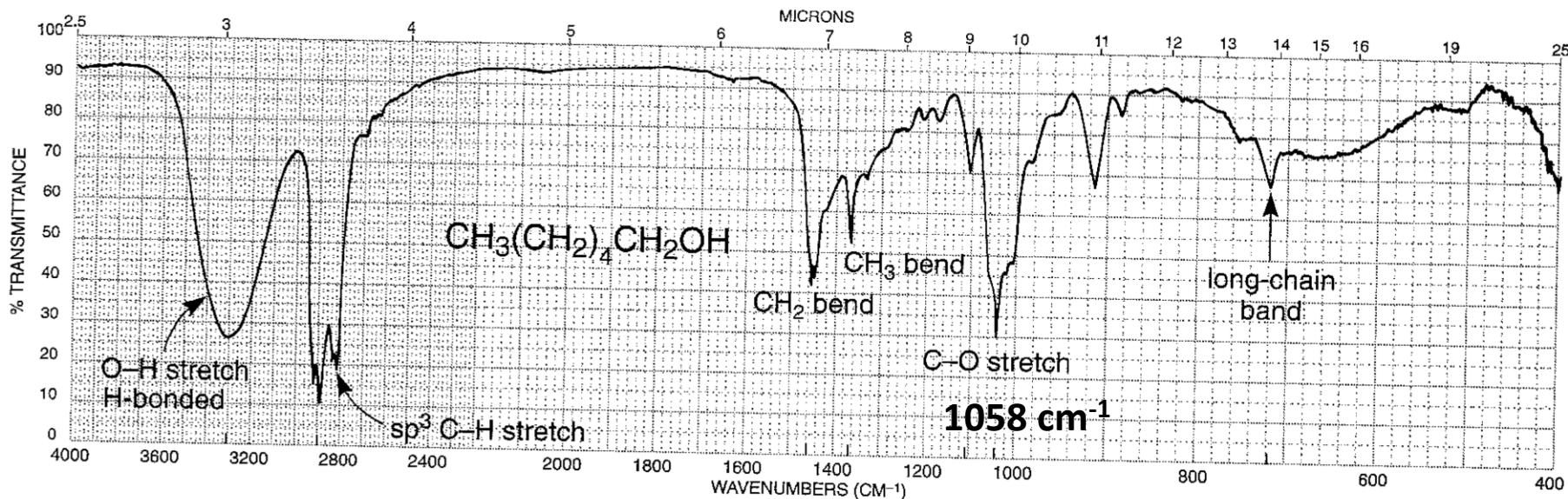


FIGURE 2.29 The infrared spectrum of 1-hexanol (neat liquid, KBr plates).

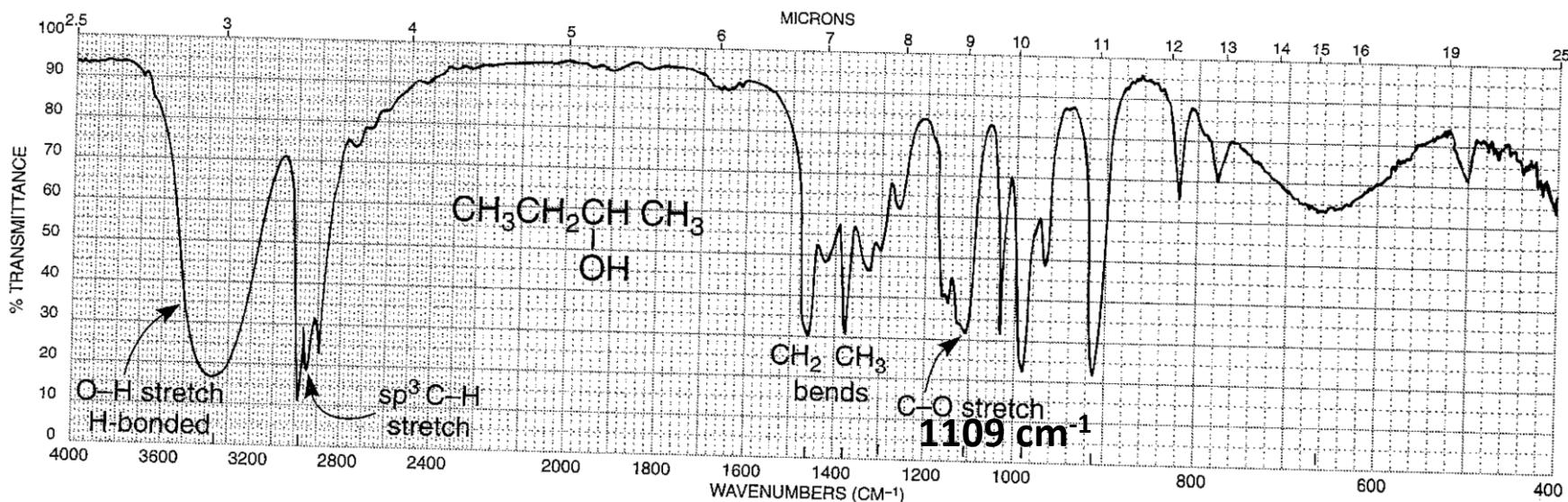


FIGURE 2.30 The infrared spectrum of 2-butanol (neat liquid, KBr plates).

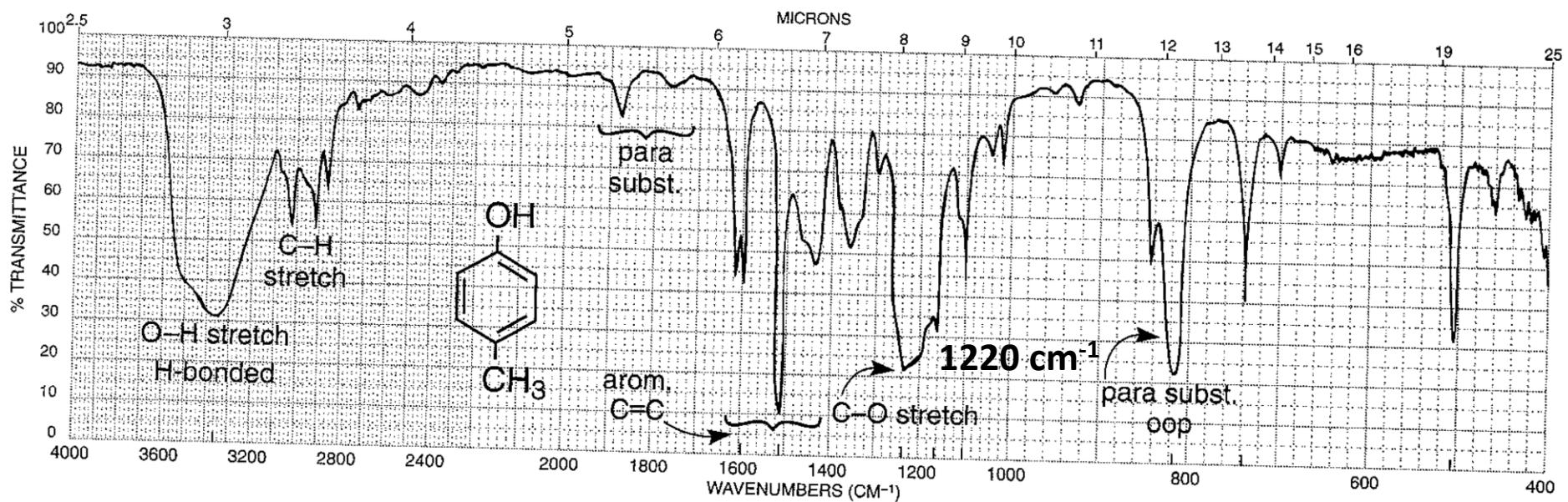


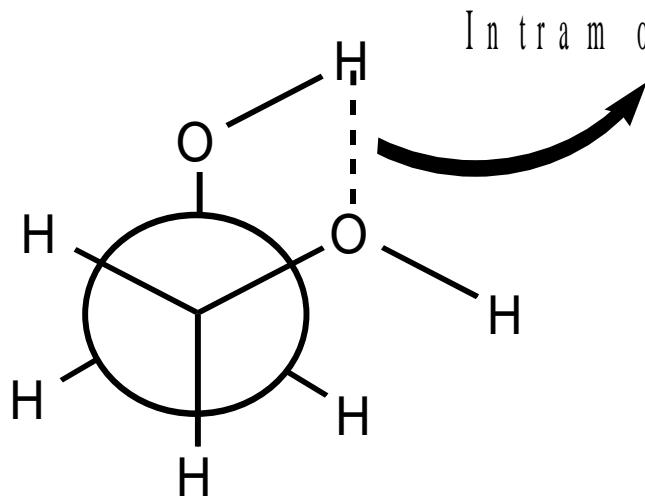
FIGURE 2.31 The infrared spectrum of *para*-cresol (neat liquid, KBr plates).

Explain why,

1. In dilute solution, Amines show stretching frequency at 3650 cm^{-1} , while a broad band is appeared at 3300 cm^{-1} in condense phase spectra.
Explain why?

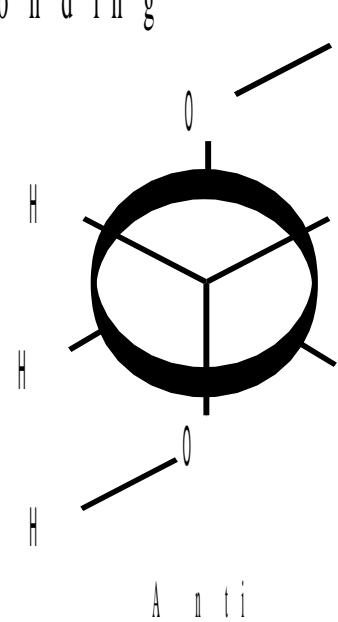
Explain why,

2. The spectrum of glycol in CCl_4 shows two peak at 3644 and 3612 cm^{-1} .



Syn

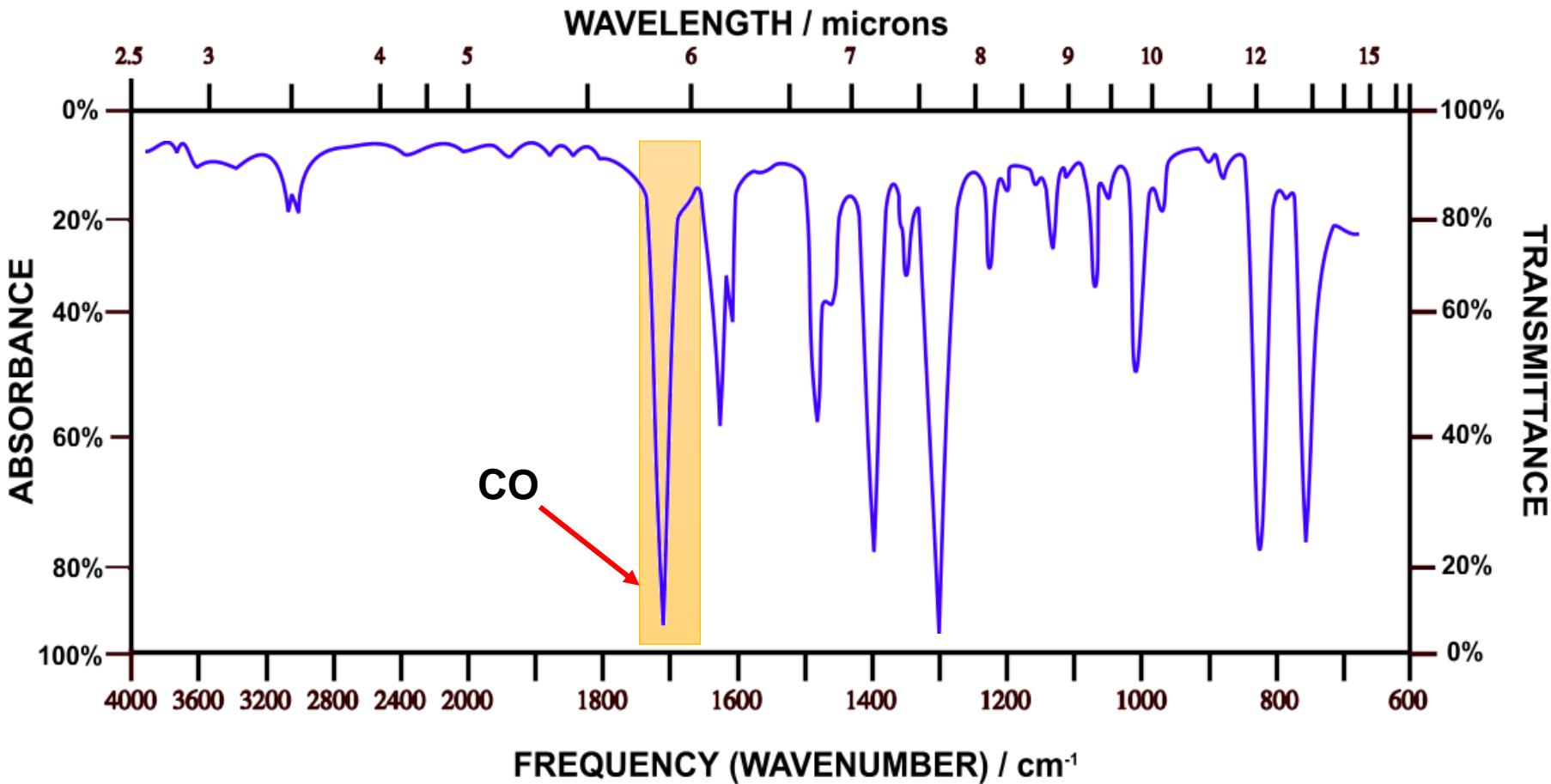
Intramolecular H-bonding



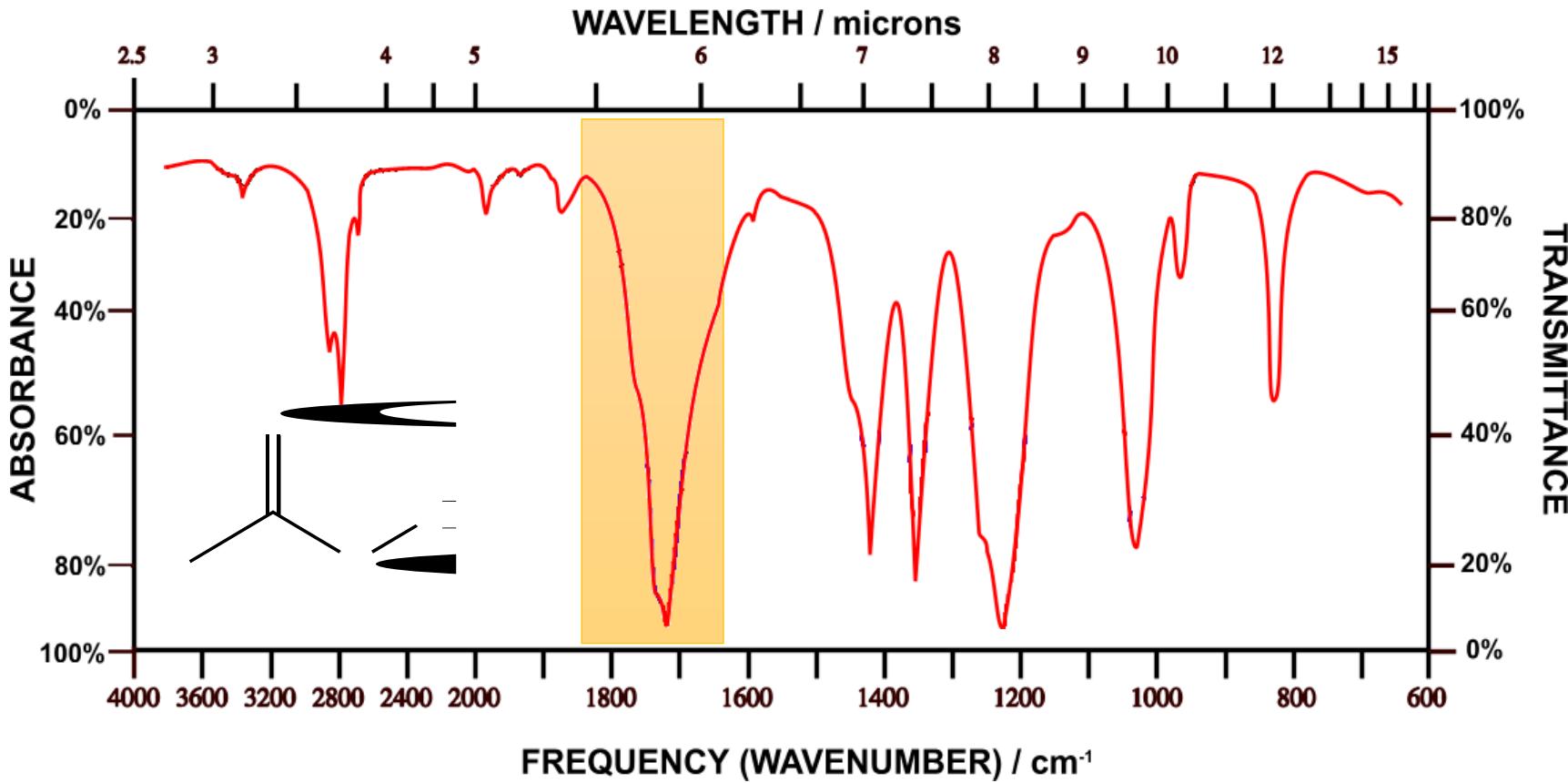
Anti

No Intermolecular H-bonding

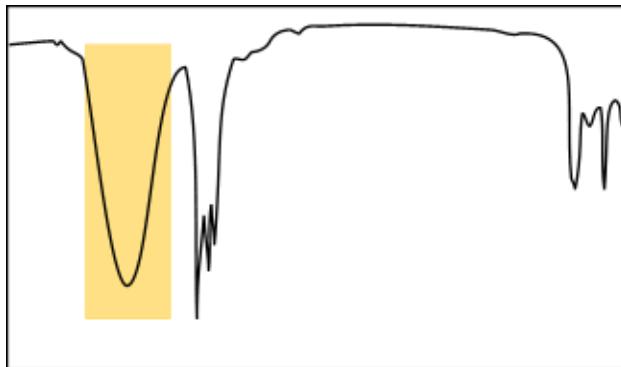
No Intra & Intermolecular H-bonding



$\vartheta_{\text{CO}} \sim 1700\text{-}1630 \text{ cm}^{-1}$ (Sharp & Strong) in aldehydes, ketones, carboxylic acids, esters, etc.



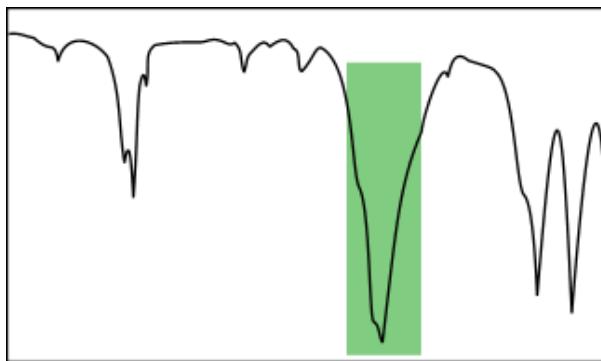
Esters show a strong absorption between **1750 - 1730 cm^{-1}** due to C=O bond stretching.



ALCOHOL

O-H STRETCH

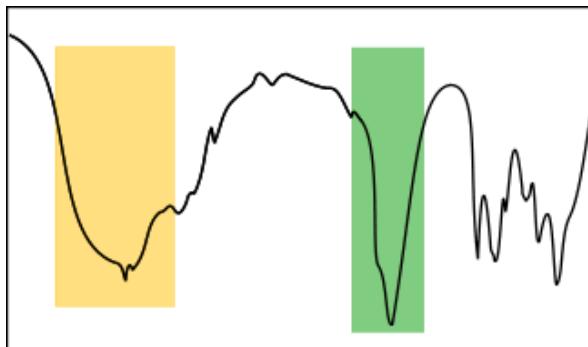
3300-2500 cm^{-1}



ALDEHYDE

C=O STRETCH

1725-1630 cm^{-1}



CARBOXYLIC
ACID

O-H STRETCH
AND
C=O STRETCH

3300-2500 cm^{-1}

1725-1630 cm^{-1}

A SIMPLIFIED CORRELATION CHART

		Type of Vibration	Frequency (cm ⁻¹)	Intensity
C—H	Alkanes	(stretch)	3000–2850	s
	—CH ₃	(bend)	1450 and 1375	m
	—CH ₂ —	(bend)	1465	m
	Alkenes	(stretch)	3100–3000	m
		(out-of-plane bend)	1000–650	s
	Aromatics	(stretch)	3150–3050	s
		(out-of-plane bend)	900–690	s
	Alkyne	(stretch)	ca. 3300	s
	Aldehyde		2900–2800	w
			2800–2700	w
C—C	Alkane		Not interpretatively useful	
C=C	Alkene		1680–1600	m-w
	Aromatic		1600 and 1475	m-w
C≡C	Alkyne		2250–2100	m-w
C=O	Aldehyde		1740–1720	s
	Ketone		1725–1705	s
	Carboxylic acid		1725–1700	s
	Ester		1750–1730	s
	Amide		1680–1630	s
	Anhydride		1810 and 1760	s
	Acid chloride		1800	s
C—O	Alcohols, ethers, esters, carboxylic acids, anhydrides		1300–1000	s

O—H	Alcohols, phenols		
	Free	3650–3600	m
	H-bonded	3400–3200	m
	Carboxylic acids	3400–2400	m
N—H	Primary and secondary amines and amides		
	(stretch)	3500–3100	m
	(bend)	1640–1550	m–s
C—N	Amines	1350–1000	m–s
C=N	Imines and oximes	1690–1640	w–s
C≡N	Nitriles	2260–2240	m
X=C=Y	Allenes, ketenes, isocyanates, isothiocyanates	2270–1940	m–s
N=O	Nitro (R—NO ₂)	1550 and 1350	s
S—H	Mercaptans	2550	w
S=O	Sulfoxides	1050	s
	Sulfones, sulfonyl chlorides, sulfates, sulfonamides	1375–1300 and 1350–1140	s
C—X	Fluoride	1400–1000	s
	Chloride	785–540	s
	Bromide, iodide	< 667	s

Look Again !!!!!!!

3500-3300 cm⁻¹	N–H stretch	amines
3500-3200 cm⁻¹	O–H stretch	alcohols, a broad, strong band
3100-3000 cm⁻¹	C–H stretch	alkenes
3000-2850 cm⁻¹	C–H stretch	alkanes
1760-1665 cm⁻¹	C=O stretch	ketones, aldehydes, esters
1680-1640 cm⁻¹	C=C stretch	alkenes

How to analyze IR spectra ???

Begin by looking in the region from 4000-1300. Look at the C–H stretching bands around 3000:

Indicates:

alkyl groups (present in most organic molecules)

a C=C bond or aromatic group in the molecule

Are any or all to the **right** of 3000?

Are any or all to the **left** of 3000?

How to analyze IR spectra ???

Look for a carbonyl in the region 1760-1690. If there is such a band:

Indicates:

Is an O–H band also present?

a carboxylic acid group

Is a C–O band also present?

an ester

Is an aldehydic C–H band also present?

an aldehyde

Is an N–H band also present?

an amide

Are none of the above present?

a ketone

(also **check the exact position of the carbonyl band** for clues as to the type of carbonyl compound it is)

Look for a broad O–H band in the region 3500-3200 cm⁻¹. If there is such a band:

Indicates:

Is an O–H band present?

an alcohol or phenol

Look for a single or double sharp N–H band in the region 3400-3250 cm⁻¹
If there is such a band

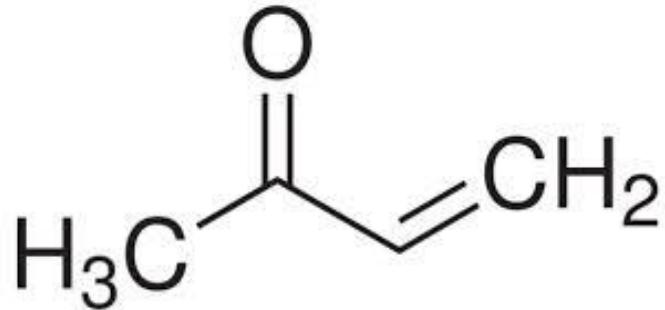
Are there two bands?

a primary amine

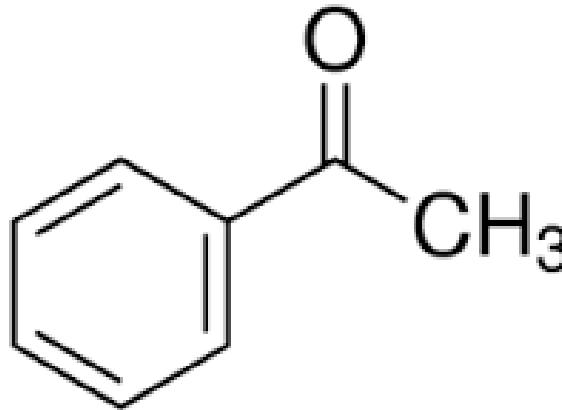
Is there only one band?

a secondary amine

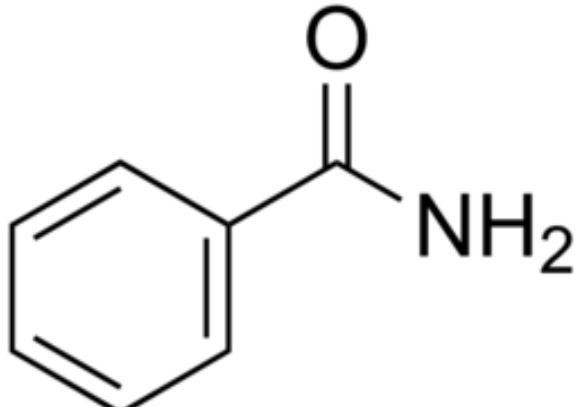
Explain why the C=O stretching vibration occurs at the following values compared to normal keto group ???



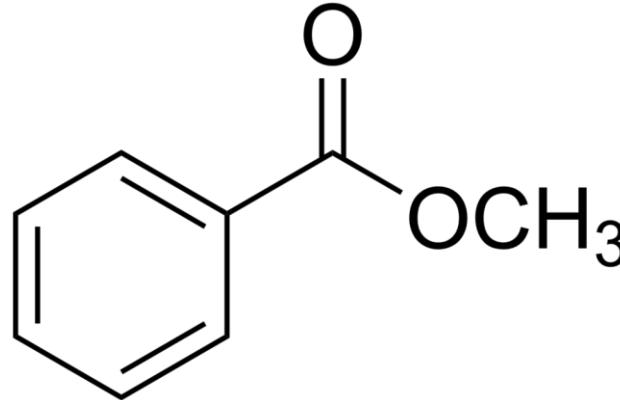
C=O 1706 cm⁻¹



C=O 1693 cm⁻¹



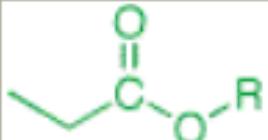
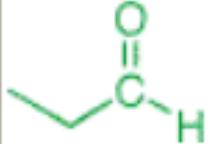
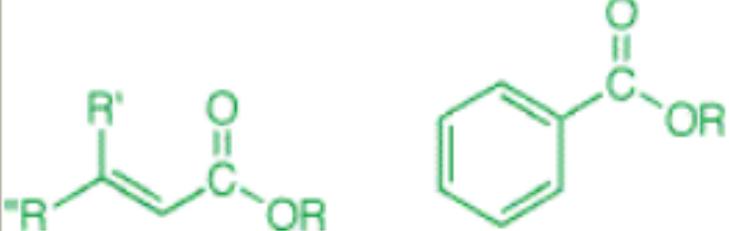
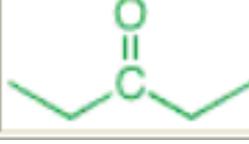
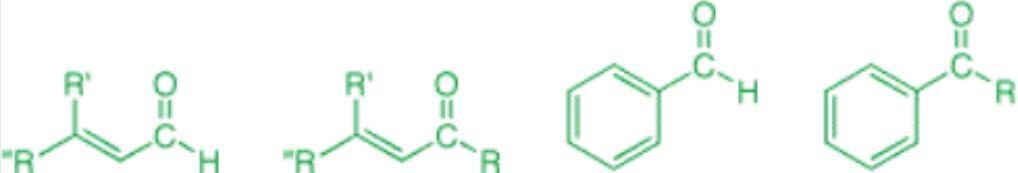
C=O 1695 cm⁻¹



C=O 1730 cm⁻¹

IR Spectroscopy : Carbonyl compounds

All carbonyl compounds absorb in the region **1760-1665 cm⁻¹** due to the stretching vibration of the C=O bond

range	type of compound	such as:
1750-1735 cm ⁻¹	saturated aliphatic esters	
1740-1720 cm ⁻¹	saturated aliphatic aldehydes	
1730-1715 cm ⁻¹	α, β -unsaturated esters	
1715 cm ⁻¹	saturated aliphatic ketones	
1710-1665 cm ⁻¹	α, β -unsaturated aldehydes and ketones	

Q The C–H stretching vibrations in dimethyl sulfoxide (Figure 3.18) occur at 2997 and 2909 cm^{-1} . Using Hooke's law, and assuming that the C–H bond is the same strength as the C–D bond (same force constant, k), calculate the stretching frequencies of the C–D bonds in dimethyl sulfoxide- d_6 .

Ans:

A Hooke's law: $\bar{v} = \frac{1}{2\pi c} \sqrt{k/\mu}$, where $\mu = (m_1 \times m_2)/(m_1 + m_2)$

$$\therefore \bar{v}_{\text{CH}} = \frac{1}{2\pi c} \sqrt{k_{\text{CH}}/\mu_{\text{CH}}} \text{ and } \bar{v}_{\text{CD}} = \frac{1}{2\pi c} \sqrt{k_{\text{CD}}/\mu_{\text{CD}}}$$

Since $k_{\text{CH}} = k_{\text{CD}}$, then:

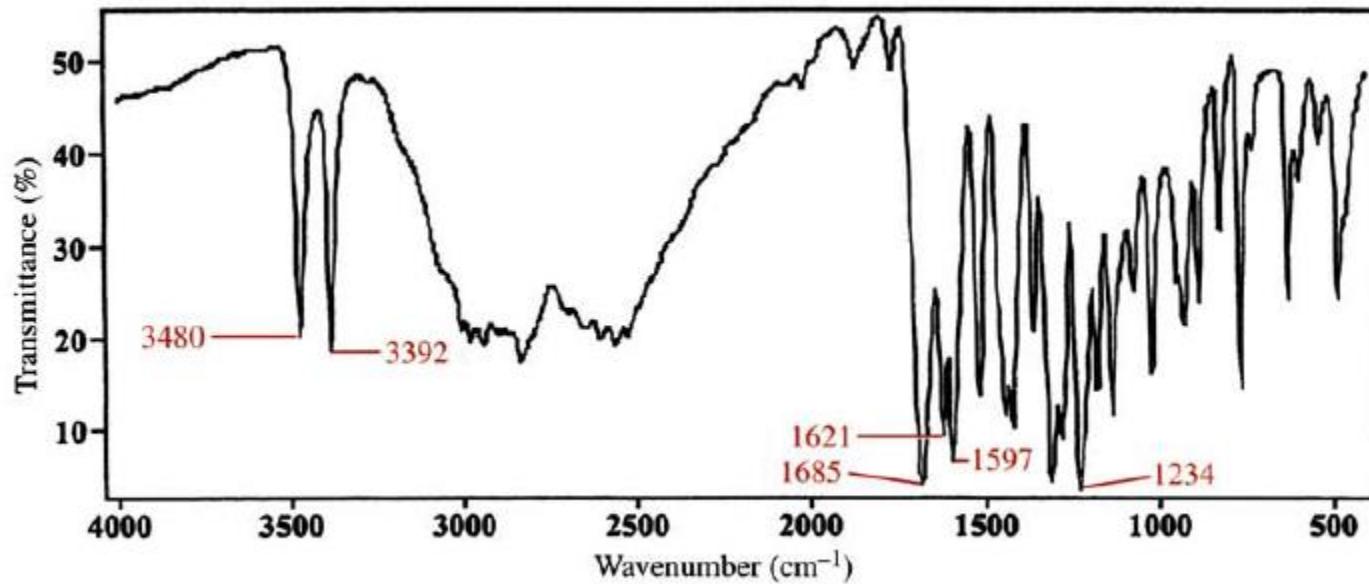
$$\bar{v}_{\text{CD}}/\bar{v}_{\text{CH}} = \sqrt{\mu_{\text{CH}}/\mu_{\text{CD}}}$$

$$\therefore \bar{v}_{\text{CD}} = \bar{v}_{\text{CH}} \sqrt{\mu_{\text{CH}}/\mu_{\text{CD}}}$$

Thus $\bar{v}_{\text{CD}} = 2997 \sqrt{0.92/1.71} = 2198 \text{ cm}^{-1}$ (actual 2250 cm^{-1})
and $\bar{v}_{\text{CD}} = 2909 \sqrt{0.92/1.71} = 2134 \text{ cm}^{-1}$ (actual 2124 cm^{-1})

You will find the actual values in Figure 3.21, and will also see that the replacement of H by D results in a slight decrease in the stretching frequency of the S=O bond. Remember that Hooke's law is really only applicable to a diatomic molecule, but we are using it to try to predict the stretching frequencies of something much more complex. It is little wonder that the calculated values do not quite match the actual values (although they are not bad!) and that the value for the S=O stretch is also affected.

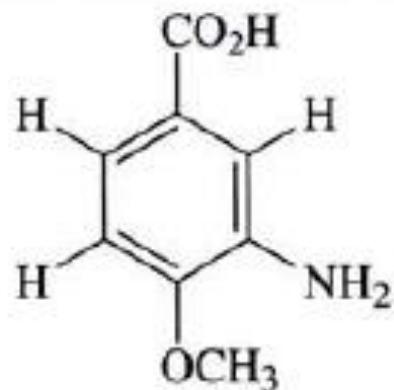
3.1. Unknown A has a molecular formula of $C_8H_9NO_3$. Calculate the number of double bond equivalents and, using the IR spectrum in Figure 3.22, suggest functional groups that might be present.



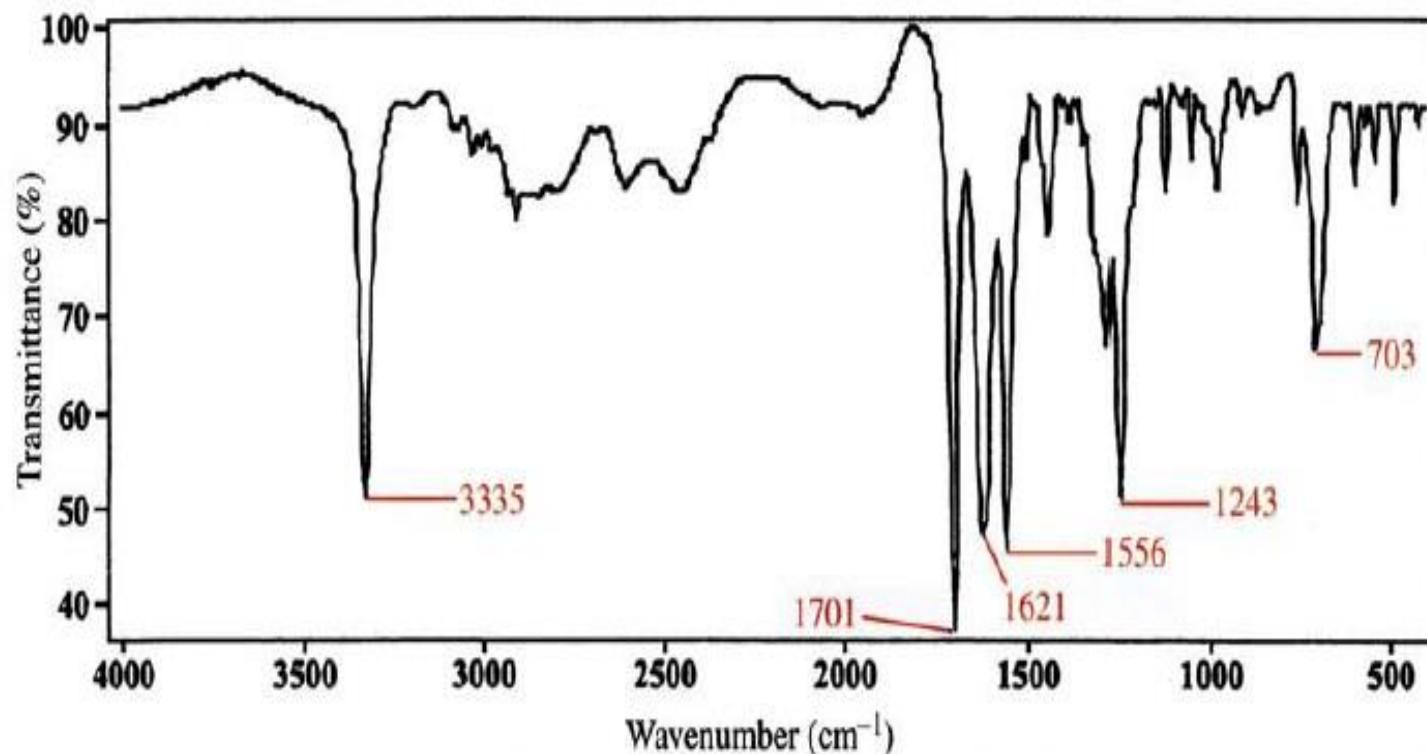
Ans: Double bond equivalents/Degree of unsaturation can be calculated using the following equation.

$$DBE = C - \frac{H}{2} + \frac{N}{2} + 1$$

3.1. Unknown A: 5 DBE; $-\text{NH}_2$, C=O , OH . Structure:

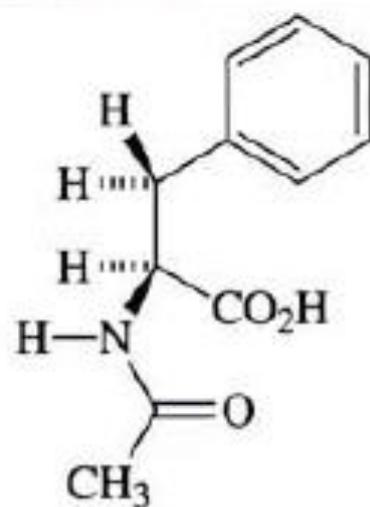


3.2. Unknown **B** has a molecular formula of $C_{11}H_{13}NO_3$. Calculate the number of double bond equivalents and, using the IR spectrum in Figure 3.23, suggest functional groups that might be present.



Ans:

3.2. Unknown B: 6 DBE; $-\text{NHCO}-$, CO_2H , $\text{C}=\text{C}$. Structure:



3.3. From an analysis of the IR spectrum of unknown C (Figure 3.24), suggest functional groups that may be present.

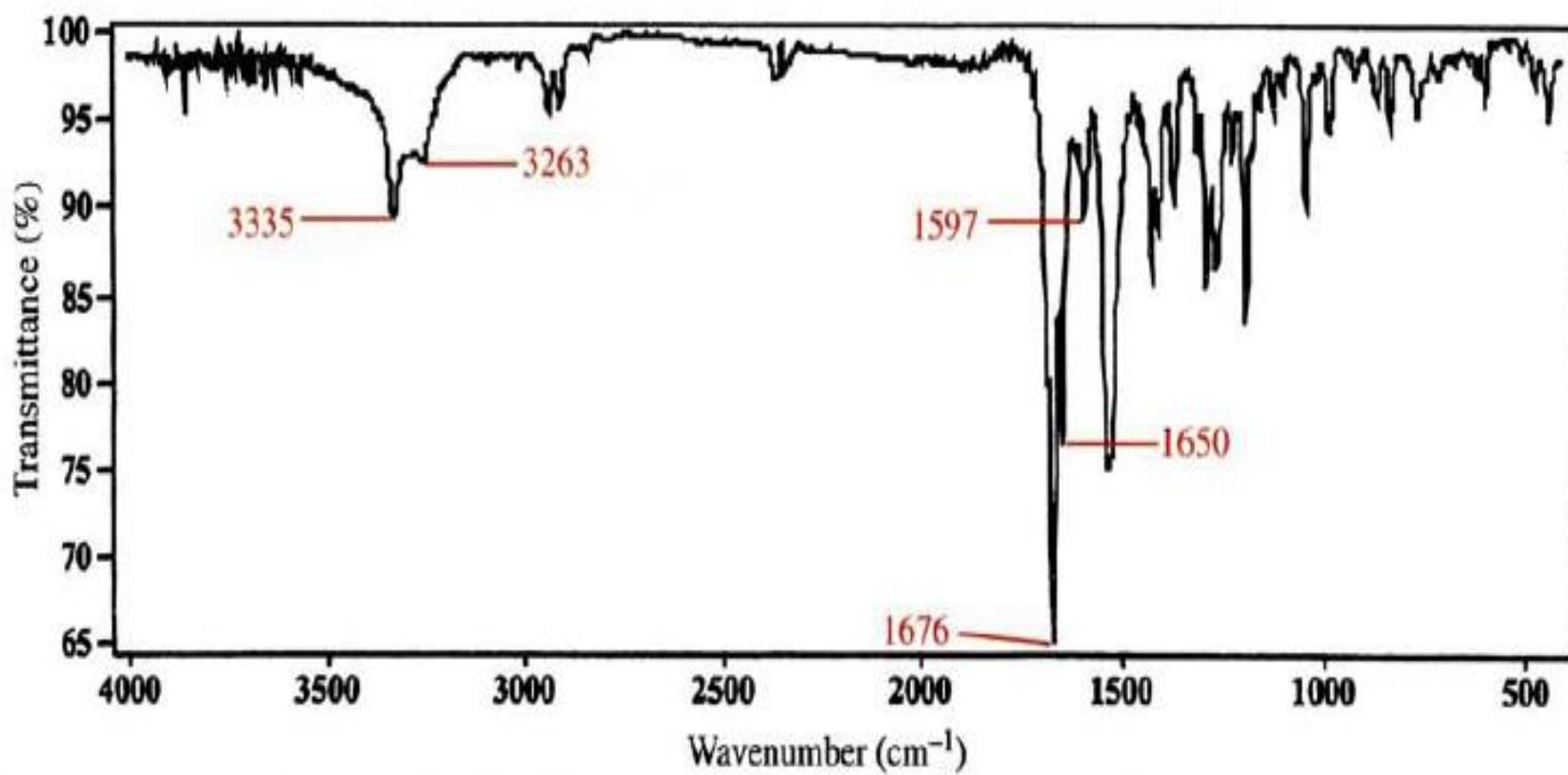
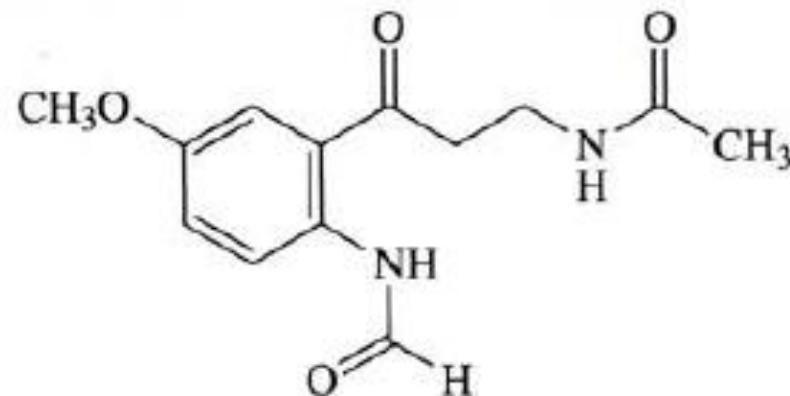


Figure 3.24 IR spectrum of unknown C (KBr disc)

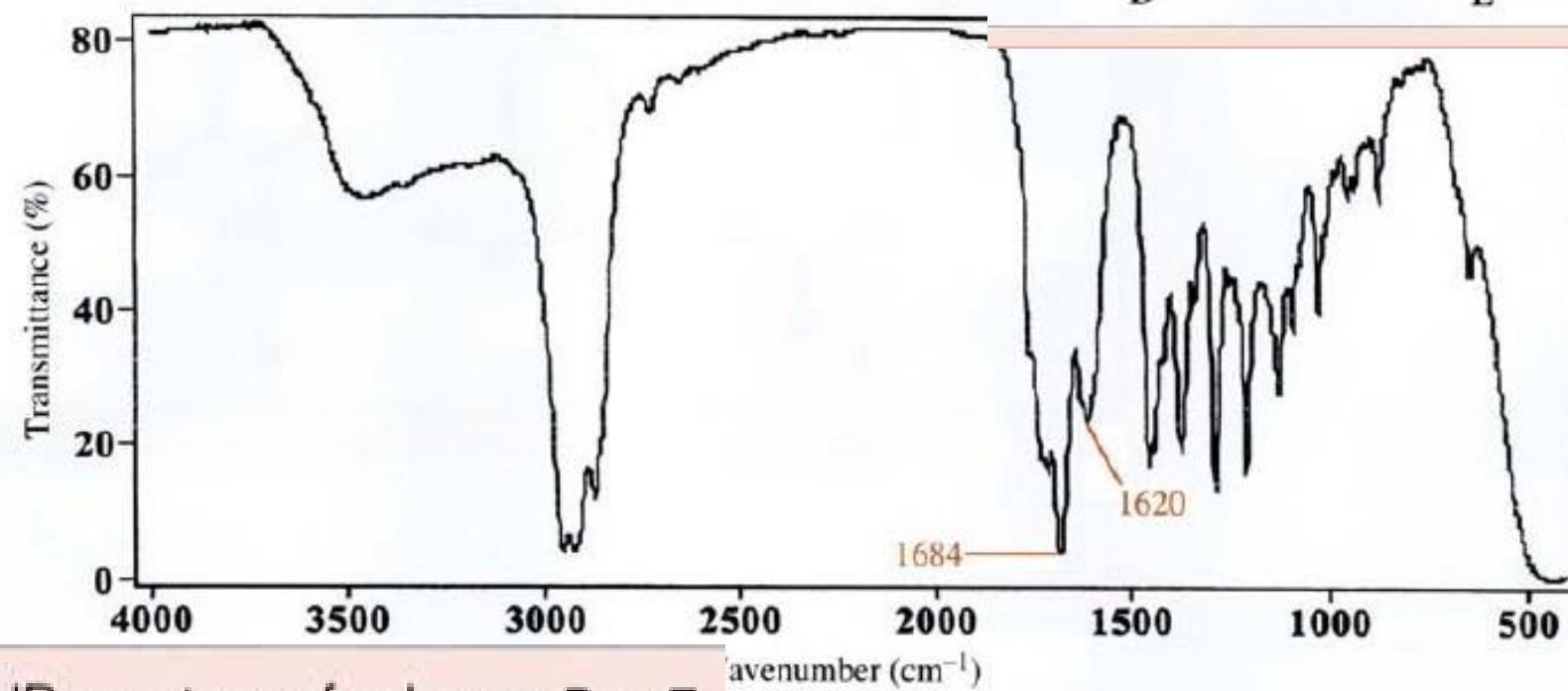
Ans:

3.3. Unknown C: -NHCO—, C=O, C=C. Structure:



3.4. The IR spectra of a pair of isomers, **D** and **E**, of molecular formula $C_{10}H_{16}O$ are given in Figures 3.25 and 3.26. Assign these spectra to the structures shown below.

Figure 3.25



IR spectrum of unknown **D** or **E**

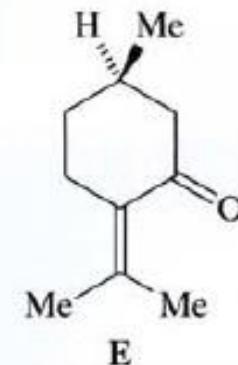
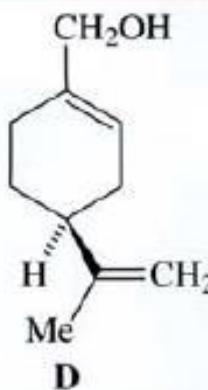
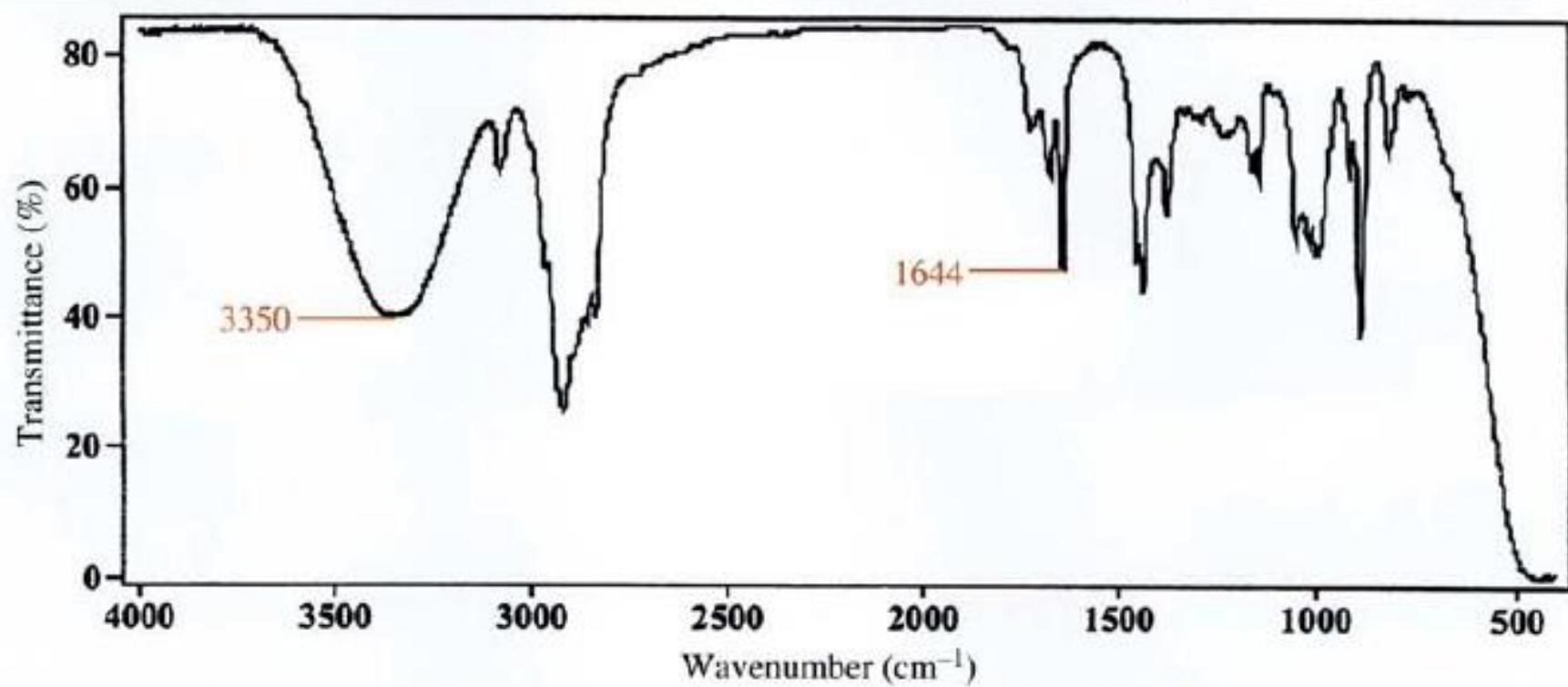


Figure 3.26

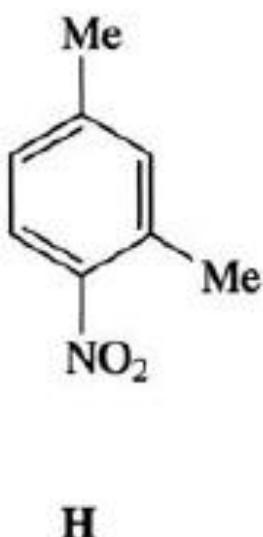
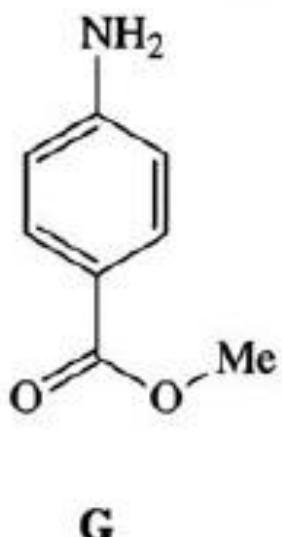
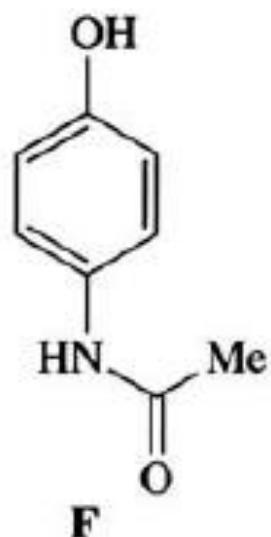


IR spectrum of unknown D or E

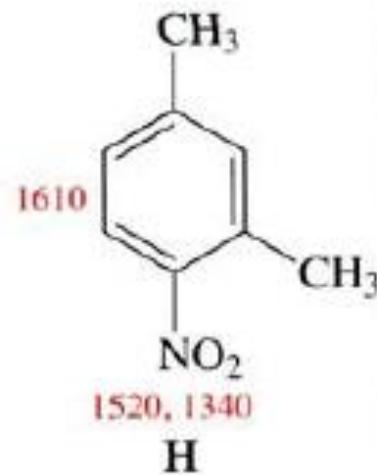
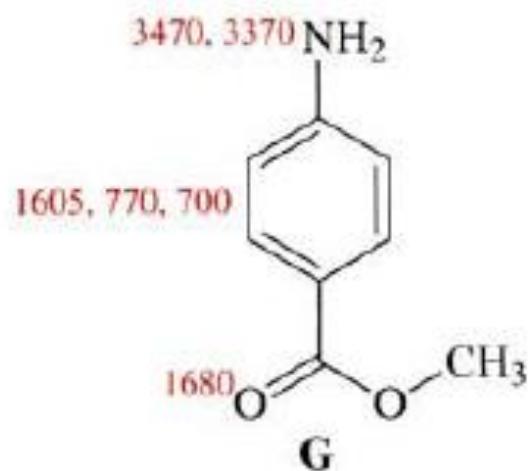
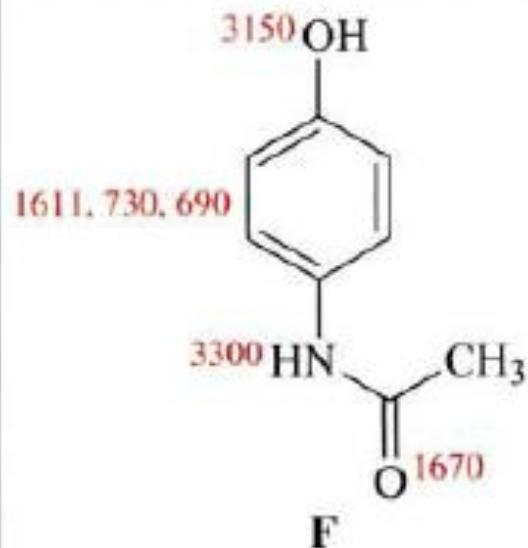
Ans:

3.4. E is Figure 3.25 and D is Figure 3.26.

3.5. Predict the main absorption bands in the IR spectra of isomers **F**, **G** and **H**.



Ans:



1. a) Define zero point energy. **(2 marks)**

Define with plot

b) The fundamental vibrational frequency of $^1\text{H}^{19}\text{F}$ is 8.67×10^{13} Hz. Calculate the fundamental vibrational frequency (in Hz) of $^2\text{D}^{19}\text{F}$ on the assumption that the force constants of both the bonds are equal. **(2 marks)**

By definition, the harmonic frequency ν_0 is given by

$$\nu_0 = \frac{1}{2\pi} \left(\frac{k}{\mu} \right)^{1/2}. \quad \textbf{(0.5 mark)}$$

Therefore, the ratio of frequencies can be written

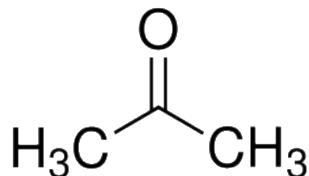
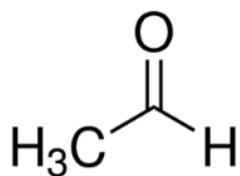
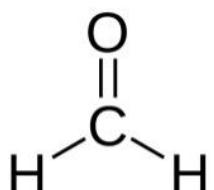
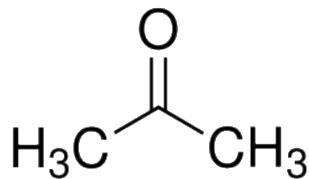
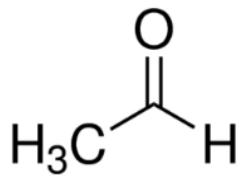
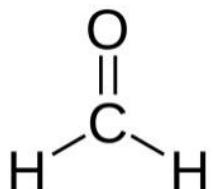
$$\frac{\nu_0(\text{HCl})}{\nu_0(\text{DCl})} = \frac{\frac{1}{2\pi} \left(\frac{k_{\text{HCl}}}{\mu_{\text{HCl}}} \right)^{1/2}}{\frac{1}{2\pi} \left(\frac{k_{\text{DCl}}}{\mu_{\text{DCl}}} \right)^{1/2}}.$$

Assuming that $k_{\text{HCl}} = k_{\text{DCl}}$, this equation simplifies to

$$\frac{\nu_0(\text{HCl})}{\nu_0(\text{DCl})} = \left(\frac{\mu_{\text{DCl}}}{\mu_{\text{HCl}}} \right)^{1/2}. \quad \text{(calculation of } \mu = 0.5\text{)}$$

$$\begin{aligned} \nu_{\text{DCl}} &= \nu_{\text{HCl}} / (\mu_{\text{DCl}}/\mu_{\text{HCl}})^{1/2} = 8.67 \times 10^{13} \text{ Hz} / (3.1411 \times 10^{-27} \text{ kg} / 1.61418 \times 10^{-27} \text{ kg})^{1/2} \quad \textbf{(0.5 mark)} \\ &= \mathbf{6.215 \times 10^{13} \text{ Hz}} \quad \textbf{(0.5 mark)} \end{aligned}$$

2. Arrange the following molecules in the increasing order of vibrational frequencies of C=O groups. Explain the reason. **(2 marks)**



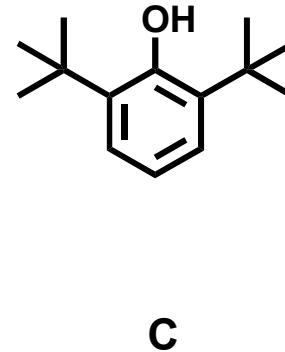
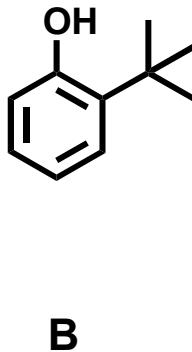
(A) 1750 cm^{-1}

(B) 1745 cm^{-1}

(C) 1715 cm^{-1}

The introduction of an atom or group causes –I effect which results in the enhancement of bond order and hence force constant. Consequently the wavenumber of absorption increases

4. The $-\text{OH}$ stretching frequencies in the following substituted phenols are observed at 3608 cm^{-1} (broad) for **A**, at 3605 cm^{-1} (broad) and 3643 cm^{-1} (sharp) for **B** and at 3643 cm^{-1} (sharp) for **C**. What is the reason for this shift of $-\text{OH}$ frequencies for A, B and C? (3 marks)



Answer:

Compound A: As the 3^0 -butyl group is in the para position, $-\text{OH}$ can participate in intermolecular H-bonding hence broader spectra around 3608 cm^{-1} is observed. (1 mark)

Compound B: broader peak (3605 cm^{-1}) is due to the intermolecular H-bonding while sharper band (3643 cm^{-1}) is due to the free $-\text{OH}$ group, steric hindrance offered by the 3^0 -butyl group at ortho position prevents some fraction of molecules from undergoing intermolecular H-bonding. (1 mark)

Compound C: steric hindrance offered by the 3^0 -butyl groups on either sides (ortho position) of $-\text{OH}$ group prevent association through intermolecular H-bonding, hence only one sharp peak (3643 cm^{-1}) due to the presence free $-\text{OH}$ group. (1 mark)

7. The fundamental and first overtone transitions for $^{14}\text{N}^{16}\text{O}$ are centered at 1876.06 cm^{-1} and 3724.20 cm^{-1} respectively. Evaluate (a) the equilibrium vibrational frequency, (b) the anharmonicity constant, (c) zero-point energy and (d) the force constant for $^{14}\text{N}^{16}\text{O}$. (Mass of $^{14}\text{N} = 23.25 \times 10^{-27}\text{ kg}$, Mass of $^{16}\text{O} = 26.56 \times 10^{-27}\text{ kg}$). (4 marks)

Answer:

$$\text{Frequency of fundamental} = \omega (1-2C_e) = 1876.06\text{ cm}^{-1}$$

$$\text{Frequency of first overtone} = 2\omega (1-3C_e) = 3724.20\text{ cm}^{-1}$$

$$\text{On solving these two liner equations we can get } \omega = 1903.98\text{ cm}^{-1} \text{ and } C_e = 7.332 \times 10^{-3} \quad (1+1 \text{ mark})$$

$$\text{Zero-point energy} = \frac{1}{2} \omega (1-1/2 C_e) = 945\text{ cm}^{-1} \quad (1 \text{ mark})$$

$$\text{Reduced mass} = m_1 m_2 / (m_1 + m_2) = 12.3975 \times 10^{-27}\text{ kg}$$

$$\text{Force constant} = 4p^2 c^2 \omega^2 \propto = 1598\text{ N/m} \quad (1 \text{ mark})$$