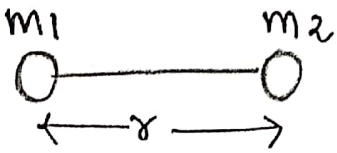
ROTATIONAL (OR MICROWAVE) SPECTROSCOPY OF DIATOMIC MOLECULE

* Absorption spectrum in microwave Region (3 to 300cm) correspond to promotion of molecule from lower Rotational level to Higher Rotational level

A gaseous diatomic molecule is Represented via a rigid bar at the end of which Two masses of m_1 & m_2 are connected seprated by distance r.



μ = Reduced mass = $\frac{m_1 m_2}{m_1 + m_2}$

moment of Inertia ← $I = \mu r^2$

Energy of this molecule is given by ⇒ $E = \frac{h^2}{8\pi^2 I} J(J+1)$

$$F = \frac{E}{hc} = BJ(J+1)$$

$F = BJ(J+1)$ in wave No.

J = Rotational Quantum No.

$B = \frac{h}{8\pi^2 I c}$ = Rotational Constant

SELECTION Rule

Transistion from one Rotational level to another occurs with condition

$$\Delta J = \pm 1$$

J = Rotational Quantum Number

Appearance of Rotational spectrum

$$F = BJ(J+1)$$

Difference between Two Rotational Level

$$\Delta F = BJ'(J'+1) - BJ''(J''+1)$$

J' → Higher, J'' → Lower

$$\boxed{\Delta F = 2B(J''+1)}$$

$J' = J'' + 1$ i.e. J'' = Lower Rotational Level

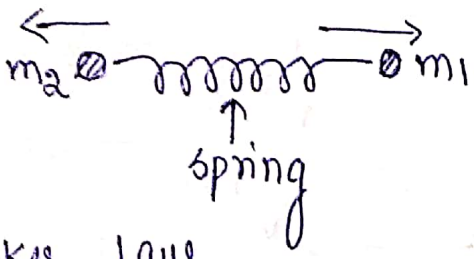
J' = Higher " "

What is criteria for Diatomic molecule to exhibit Rotational Spectrum

* Molecule should Have Permanent Dipole Moment
* Molecules having Permanent Dipole Moment are called Microwave Active Molecules (like H_2O, H_2S, etc)
* Molecules with Not Permanent Dipole moment are known as Microwave In active Molecules Example (H_2, O_2, Cl_2, CO_2, CS_2 etc) They does not exhibit Rotational Spectrum

Vibrational Frequency

* Vibration are simply Based on HOOKE LAW.
* Diatomic molecule are considered as two atoms connected by elastic spring



According to Hookes Law

Restoring Force $= -Kx$ $\quad x =$ displacement of atom from respective position

$K =$ Force constant

So during Osillation fundamental Vibration is given by

Fundamental Vibration frequency $=$

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}} \ cm^{-1} \qquad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

The force constant K may be defined as Restoring force per unit displacement of Harmonic osillar

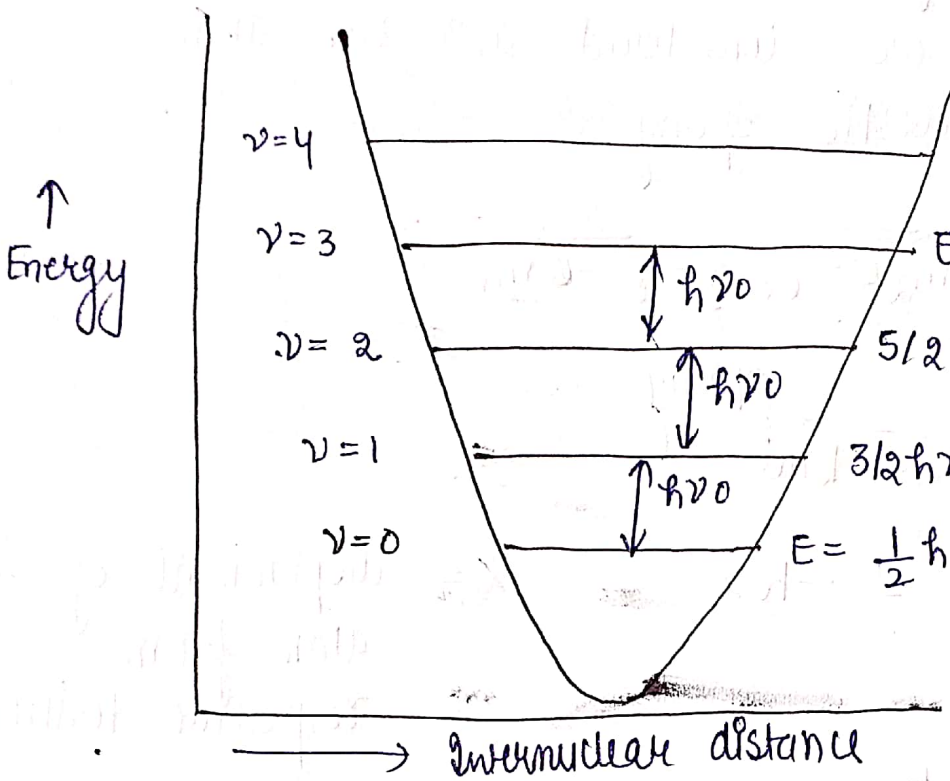
Energy of Vibration $=$ Evib $= \left(v + \frac{1}{2}\right) h\nu_0$

$\nu_0 =$ Classical frequency of vibration

$v =$ Vibrational Quantum Number

Value of $v = 0, 1, 2, 3, 4 \ldots\ldots$

Vibrational level for simple Harmonic Oscillator (SHO)



Vibrational levels are equally spaced

($E = \frac{1}{2} h\nu_0$ = zero point Energy)

Selection Rule of IR Spectroscopy (YMCA)

$$\boxed{\Delta v = \pm 1}$$

v = Vibrational Quantum Number

Change in Vibrational Quantum No. Should be ± 1.

INFRA-RED SPECTROSCOPY

OR

(VIBRATIONAL-ROTATIONAL SPECTROSCOPY)

Ques- What is IR-spectroscopy (1mark)

→ In this spectroscopy Transistion occurs in Vibrational energy level due to absorption of IR Radiations by molecules.

→ Since it involves Transistion in both Vibrational and Rotational level so it is also called Rotational-Vibrational Spectroscopy.

Most useful IR-Region 4000 - 670cm^{-1}

What is criteria for molecule to be IR-active?

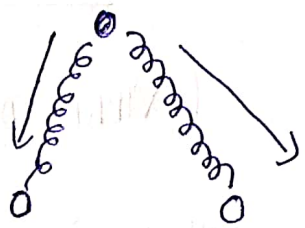
There should be a "NET CHANGE IN DIPOLE MOMENT"

THEORY OF IR Absorption

→ The alternating electrical field of Radiation interact with fluctuation in Dipole moment of molecule. When the frequency of Radiation matches Vibrational frequency of molecule then Radiation will be absorbed causing Change in Amplitude of molecular Vibrations

TYPES OF MOLECULAR VIBRATIONS

Molecule may be visualised as balls consisting of springs of varying length.



(a) STRETCHING VIBRATIONS

Distance between two atom increase or decrease equally and central atom remains at same position

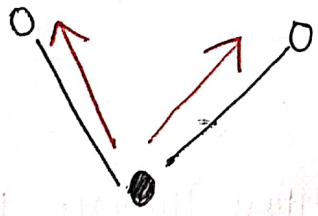
Stretching Vibration are of Two Types

(a) Symmetric stretching → Bonds move in same direction (opposite or towards central atom)

(b) Assymetric stretching

↓

one Bond atom approaches central atom while other departs from it



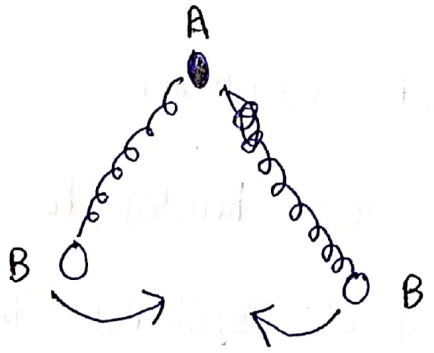
Symmetric stretching

Assymetric stretching

(b) BENDING VIBRATIONS { They Require Less energy as compared to stretching vibration }

In this type of vibration the position of atom change with Respect to orignal bond axis leading to change in Bond Angles.

For AB_2 molecule



There are four Types of Bending Vibration.

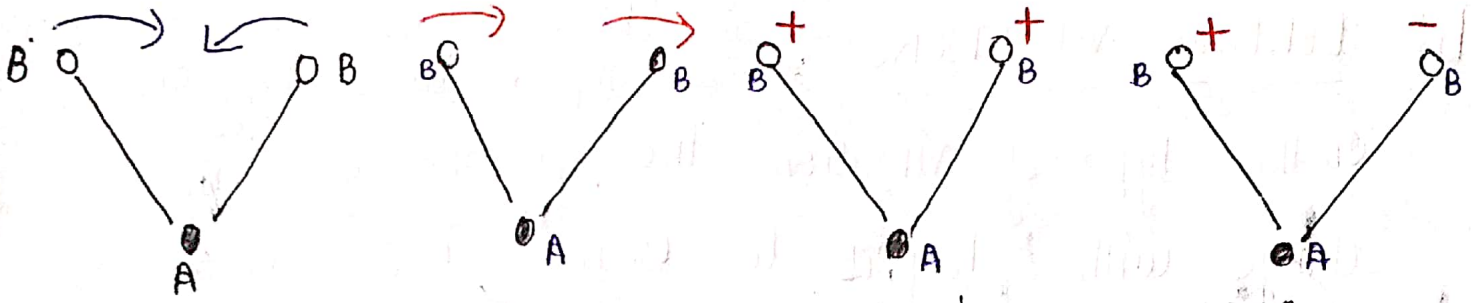
(i) Scissoring → Two atoms (B) approach to each other

(ii) Rocking → Two atoms (B) move in same direction

(iii) Wagging → Two atoms (B) moves up and down the plane and central atom (A) Remains fixed

(iv) Twisting : one of atom moves up the plane while the other moves down the plane with respect to central atom

* Scissoring and Rocking are In-Plane-Bending
* Wagging and Twisting are out of plane Bending



Scissoring Rocking Wagging Twisting

FUNDAMENTAL MODES OF VIBRATION

→ These fundamental Band are Related to Degrees of freedom

→ Degree of freedom = Sum of coordinates to locate all atom of molecules in space.

→ A molecule is made up of Rotational, Vibrational and Translational Degrees of freedom.

3n Degrees of freedom = Translational + Rot. + Vib.

For Linear Polyatomic Molecule

Vibrational Degree of freedom = $3n - 5$

n = no. of atoms (Total)

for example CO_2 ⇒ linear molecule O=C=O

No. of vibrational Degrees = $3*3 - 5 = 9 - 5 = \boxed{4}$

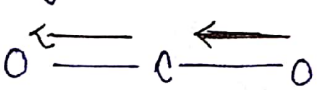
Ques- What are Normal Vibration modes of CO_2

Ans- Since CO_2 is a Linear Molecule [O=C=O]

Vibrational Degrees = $3*3-5 = 9-5$

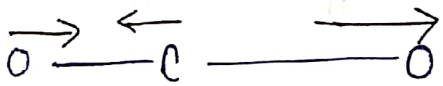
= 4 Vibrational Modes

① Symmetric Stretching



1300 cm^{-1}

② Assymetric Stretching



2349

③

BENDING Modes [Degenerate Pair]

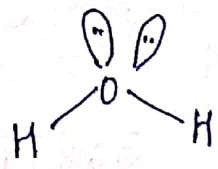
Vibration Modes for NON-LINEAR MOLECULE

Vibrational Modes = $3n-6$

Example Includes ⇒ H_2O molecule, H_2S molecul etc.

Ques- Find out Normal Vibrational Modes for H_2O molecule

Ans- Since H_2O is a NON Linear Molecul

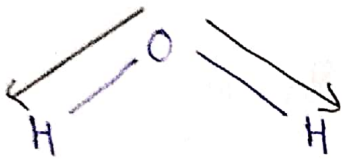


We will use formula = $3N-6$

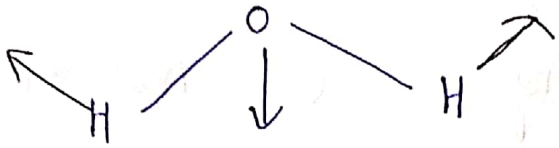
Since there are Total 3 atoms

Vibrational Modes = $3N-6$

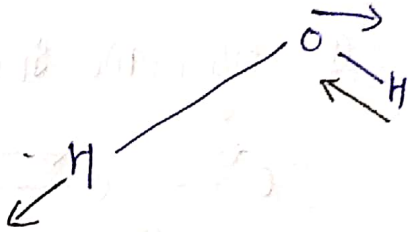
$= 3*3-6 = 9-6 = 3$



Symmetric Stretching



Symmetric Bending

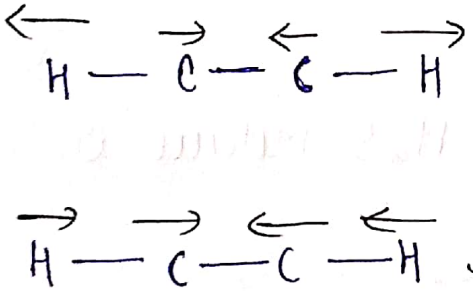


Assymetric Stretching

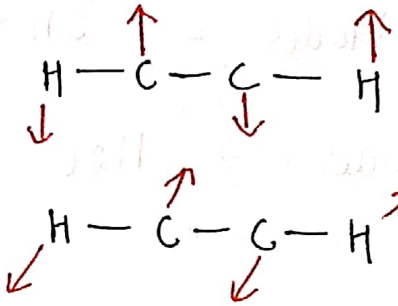
Not Imp

Q- for acetylene molecule

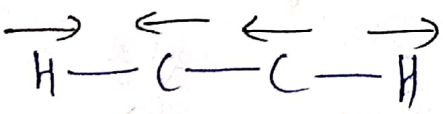
$3N-5 = 3*4-5 = 7$



Symmetric Stretching

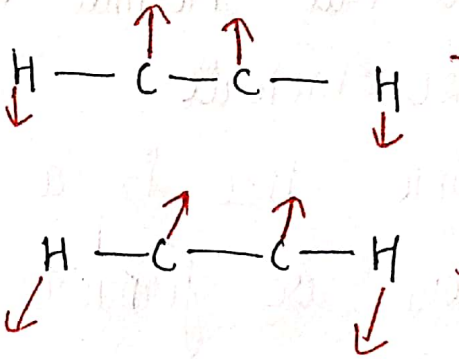


Degenerate 612



3287 cm-1

Assymetric Stretching



729 Degenerate Pair

729 cm-1

What do you Understand by Overtones. (YMCA)

Overtones occurs at multiples of given fundamental frequency. For example if molecule has fundamental frequency at $\bar{\nu}$ Then owtone occur at $2\bar{\nu}$, $3\bar{\nu}$, $4\bar{\nu}$ etc.

$2\bar{\nu}$ = First Overtone

$3\bar{\nu}$ = Second Overtone

$4\bar{\nu}$ = Third overtone

They Have low intensities as compared to fundamental vibrations.

What do you understand by Combination Bands.

** Combination Bands are sum of Two fundamental frequencies or Overtones

$$\bar{\nu}_{combination} = \bar{\nu}_1 + \bar{\nu}_2$$

Two vibrational frequny couple to give rise to new frequny ($\bar{\nu}_{combination}$) within molecule.

Qus- What do You understand by difference Band

These are differnces of Two or more fundamental frequencies or Overtones $\bar{\nu}_{diff} = \bar{\nu}_1 - \nu_2$

What do you mean by Fermi- Resonance ?

When fundamental mode of vibration becomes accidentally degenerate [couples] with overtone or combination Band . As a Result Intensity of overtone or combination Band which is otherwise low is Enhanced by Resonance This phenomena is called Fermi Resonance .

What is fingerprint Region ? What is it Importance . [YMCA]

The Region below 1500 cm^{-1} is rich in many absorptions due to bending as well as stretching vibrations of C–C bond, C–O and C–N Bonds .

There are more bending vibrations as compared to stretching vibrations so Region below 1500 cm^{-1} (1500 cm^{-1} to 600 cm^{-1}) is Rich in absorption band & Shoulders and Therefore called finger print Region . It is unique for every molecule .

Importance :* Used to Identify identical compounds which show Similar absorption above 1500 cm^{-1}

* Each compound has different spectra in finger print Region . So it is very useful for Identification of compounds .

Finger Print Region Have characteristic absorption of different functional group, cis-Trans configuration and also for mono/disubstituted Benzene.

APPLICATION OF IR SPECTROSCOPY

1.) Identification of organic compounds

→ Fingerprint Region Help in Identification of Identical compounds.

2.) Structure Determination

→ different functional group exhibit different Bands in IR Spectra.

3.) Detection of Impurities.

4.) Distinction b/w Inter and Intramolecular H-Bonding.

Intramolecular H Bonding has no effect on dilution while absorption pattern changes for Intermolecular H-Bonding on dilution.

5.) To Study Kinetics of Reaction.

6.) To find what kind of Isomers are present

7.) Whether Compound is Aromatic or Aliphatic

TABLE 2.3
A SIMPLIFIED CORRELATION CHART

	Type of Vibration		Frequency (cm^{-1})	Intensity	Page Reference
C–H	Alkanes	(stretch)	3000–2850	s	31
	$-CH_3$	(bend)	1450 and 1375	m	
	$-CH_2-$	(bend)	1465	m	
	Alkenes	(stretch)	3100–3000	m	33
		(out-of-plane bend)	1000–650	s	
	Aromatics	(stretch)	3150–3050	s	43
		(out-of-plane bend)	900–690	s	
	Alkyne	(stretch)	ca. 3300	s	35
	Aldehyde		2900–2800	w	56
			2800–2700	w	
C–C	Alkane		Not interpretatively useful		
C=C	Alkene		1680–1600	m–w	33
	Aromatic		1600 and 1475	m–w	43
C≡C	Alkyne		2250–2100	m–w	35
C=O	Aldehyde		1740–1720	s	56
	Ketone		1725–1705	s	58
	Carboxylic acid		1725–1700	s	62
	Ester		1750–1730	s	64
	Amide		1700–1640	s	70
	Anhydride		1810 and 1760	s	73
	Acid chloride		1800	s	72
C–O	Alcohols, ethers, esters, carboxylic acids, anhydrides		1300–1000	s	47, 50, 62, 64, and 73
O–H	Alcohols, phenols				
	Free		3650–3600	m	47
	H-bonded		3400–3200	m	47
	Carboxylic acids		3400–2400	m	62
N–H	Primary and secondary amines and amides				
	(stretch)		3500–3100	m	74
	(bend)		1640–1550	m–s	74
C–N	Amines		1350–1000	m–s	74
C=N	Imines and oximes		1690–1640	w–s	77
C≡N	Nitriles		2260–2240	m	77
X=C=Y	Allenes, ketenes, isocyanates, isothiocyanates		2270–1940	m–s	77
N=O	Nitro ($R-NO_2$)		1550 and 1350	s	79
S–H	Mercaptans		2550	w	81
S=O	Sulfoxides		1050	s	81
	Sulfones, sulfonyl chlorides, sulfates, sulfonamides		1375–1300 and 1350–1140	s	82
C–X	Fluoride		1400–1000	s	85
	Chloride		785–540	s	85
	Bromide, iodide		< 667	s	85

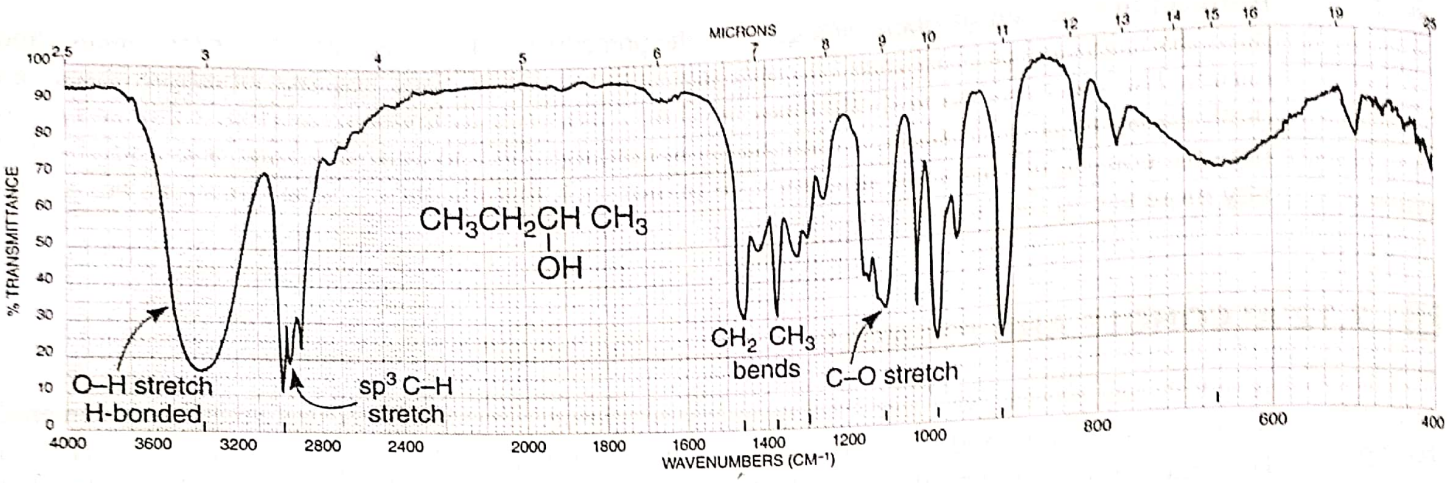


FIGURE 2.30 The infrared spectrum of 2-butanol (neat liquid, KBr plates).

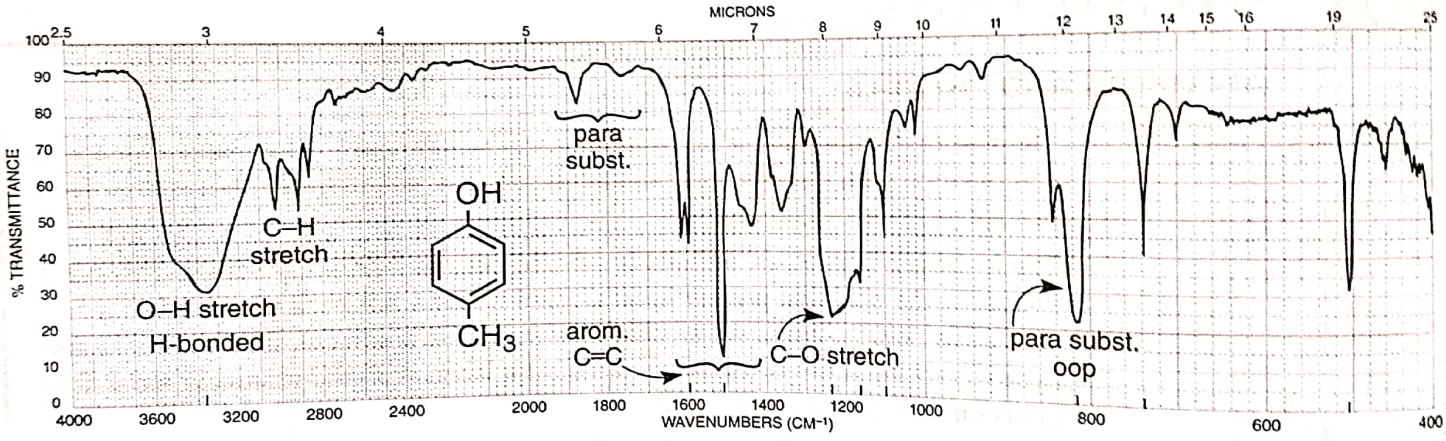


FIGURE 2.31 The infrared spectrum of *para*-cresol (neat liquid, KBr plates).

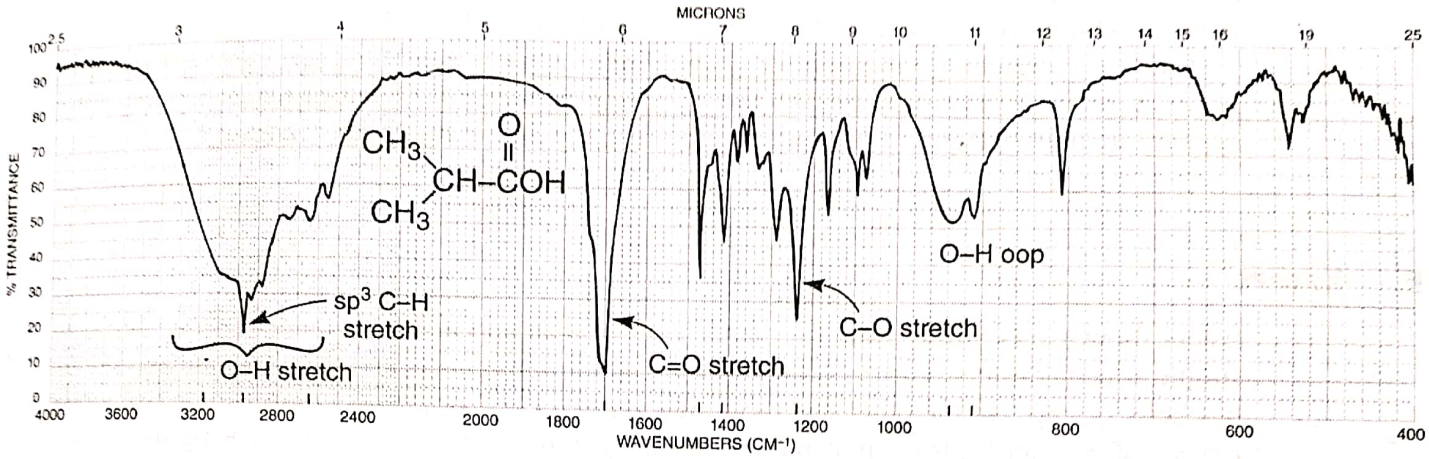


FIGURE 2.45 The infrared spectrum of isobutyric acid (neat liquid, KBr plates).

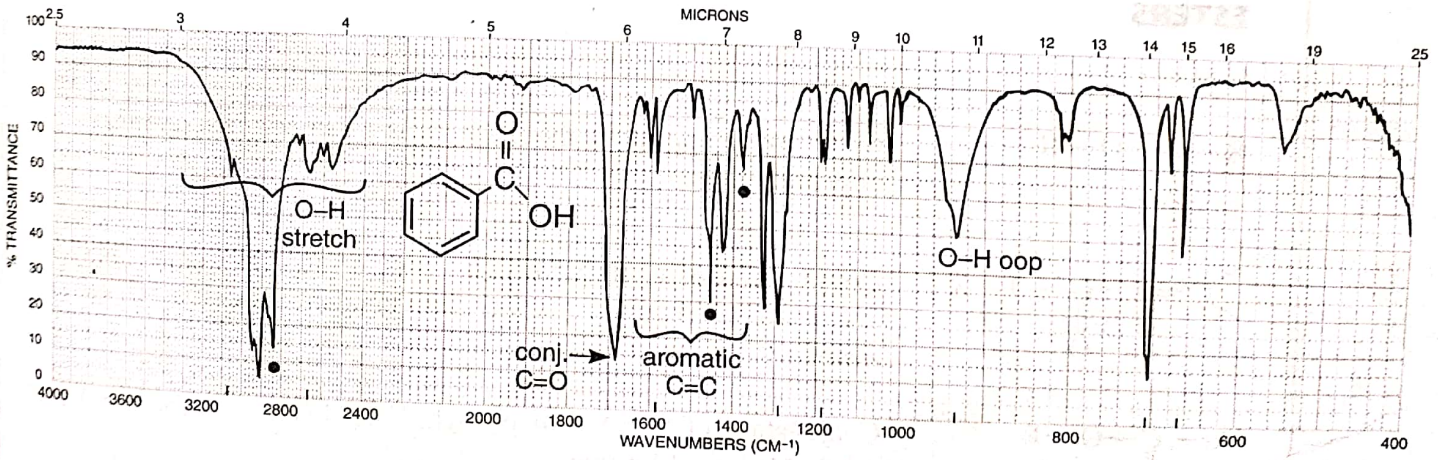


FIGURE 2.46 The infrared spectrum of benzoic acid (Nujol mull, KBr plates). Dots indicate the Nujol (mineral oil) absorption bands (see Fig. 2.8).

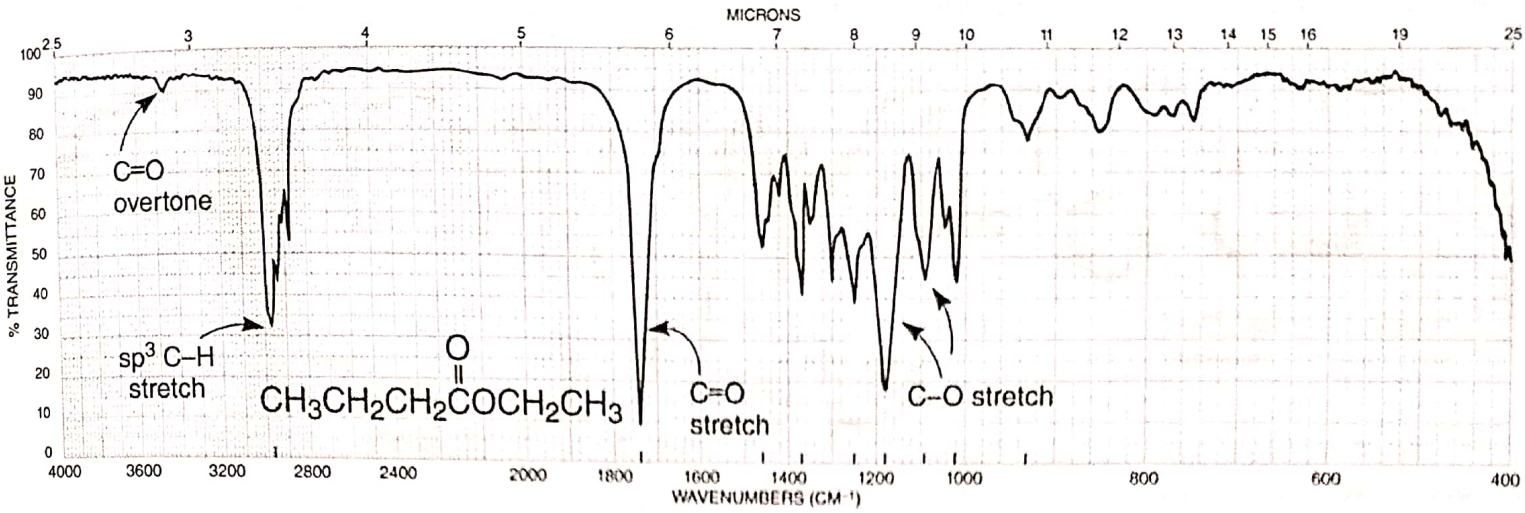


FIGURE 2.47 The infrared spectrum of ethyl butyrate (neat liquid, KBr plates).

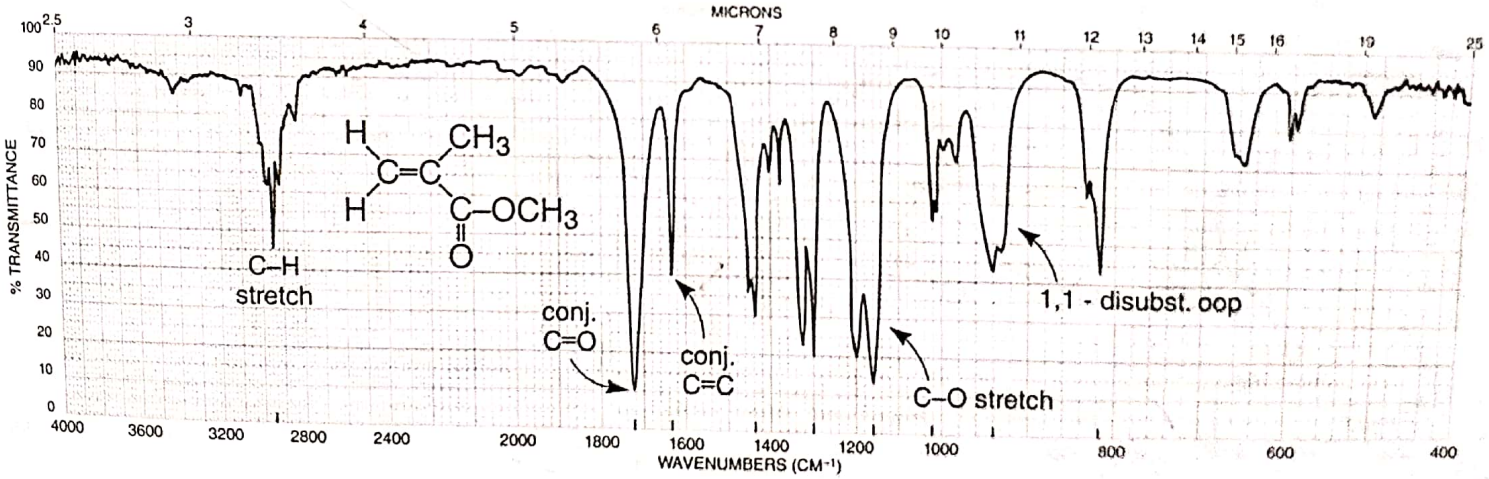


FIGURE 2.48 The infrared spectrum of methyl methacrylate (neat liquid, KBr plates).