INFRA-RED SPECTROSCOPY

Infrared spectroscopy (**IR spectroscopy**) deals with the interaction of infrared radiation with matter. It is used to identify the functional groups present in an organic compound. In this technique, an instrument called infrared spectrometer is used to produce an infrared spectrum which gives characteristic absorbance (or transmittance) bands to get informations about the sample under observation. To analyze a sample by IR spectroscopy, the IR spectrum of the sample is recorded by passing IR radiation through the sample. A **silicon carbide** rod (5-10 mm width and 20-50 mm length), known as **Globar** (Glow and bar) is usually used as thermal light source for infrared spectroscopy. It is electrically heated upto 1000-1650^0 C to emit radiation. An IR spectrum is basically a graph of infrared light absorbance (or transmittance) on the Y- axis vs. wavenumber (or frequency) on the X- axis. Fourier Transform Infra-Red (FT-IR) spectrometer is usually used in the laboratories for the analysis of different samples.

In electromagnetic spectrum the infrared portion is usually divided into three regions –

Near Infra red region: The wavenumber in this region lies in the range 13000–4000 cm^{-1} (corresponding wavelength range 0.8–2.5 μm) (approximately). The IR radiation in this region has high energy and are suitable to excite overtone or harmonic vibrations.

Mid Infra red region: The wavenumber in this region lies in the range 4000–400 cm^{-1} (corresponding wavelength range 2.5–25 μm) (approximately). The energy of the IR radiation lying in this region is suitable for the study of fundamental vibrations.

Far Infra red region: The wavenumber in this region lies in the range 400–10 cm^{-1} (corresponding wavelength range 25–1000 μm) (approximately). The IR radiation in this region has low energy and may be used for rotational spectroscopy.

Samples having covalent bonds are mainly analyzed by IR spectroscopy. During analysis the sample should be used with high level of purity. This is because samples with high purity will have fewer IR active bonds and as a result the spectra observed will be simple. On the other hand, if the sample is impure then due to the presence of higher IR active bonds the spectra will be complex, which will be less useful for a synthetic chemist.

Principle

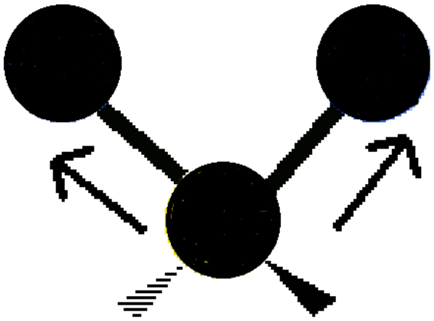
Infrared photons correspond to the quantum energy in the range 10^{-3} to 1.7 eV. This energy range is suitable for generating molecular vibration and cannot induce electronic transitions as in case of UV radiations. Moreover, a molecule can absorb IR radiation only if the vibrations (or rotations) within the molecule are accompanied by a net change in the dipole moment of the molecule. The alternating electrical field of the IR radiation (which is a constituent of electromagnetic radiation) interacts with fluctuations in the dipole moment of the molecule. During interaction, if the frequency of the radiation matches the vibrational frequency of the molecule then radiation will be absorbed which results in a change of the amplitude of molecular vibration. Under this condition an absorbance band will be observed.

Molecular vibrations

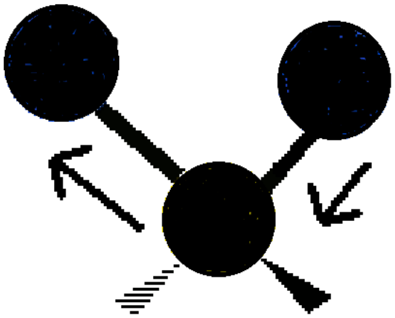
The atoms in a molecule encounter a number of different types of vibrations, as a result the positions of atoms in a molecule are not fixed but changes periodically. Broadly, molecular vibrations can be classified into two categories –

(i) **Stretching Vibration:** In this type of vibrations the distance between the two atoms changes i.e. the distance between the atoms either increases or decreases but the atoms remains in the same bond axis. There are two types of stretching vibrations –

- **Symmetric Stretching:** In this type of stretching vibrations, the movement of the atoms with respect to a particular central atom takes place in the same direction.



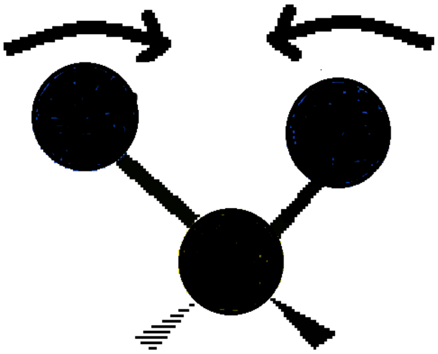
Symmetric Stretching



Asymmetric Stretching

- **Asymmetric Stretching:** In this type of stretching vibrations, the movement of the atoms with respect to a particular central atom takes place in opposite direction i.e. one atom approaches towards the central atom while the other atom moves away from it.

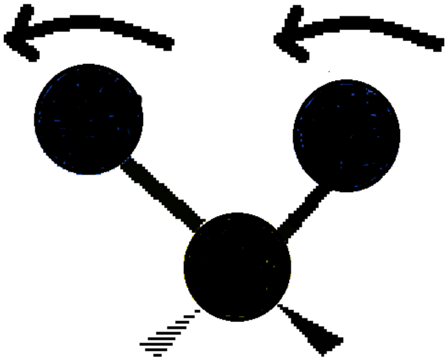
(ii) Bending Vibrations: In this type of vibrations, the angle between the bonded atoms changes i.e. the positions of the atoms changes with respect to the original bond axis. Bending vibrations are of four types –



Scissoring

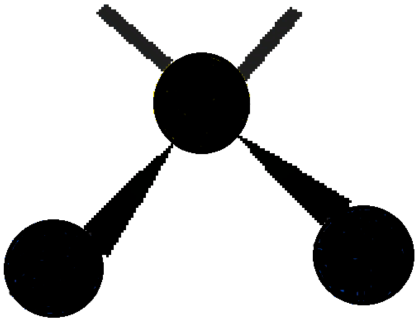
- **Scissoring:** In this type of bending vibrations, two atoms either move away from each other or move towards each other with respect to a central atom i.e. they operate like a scissor. In this type of bending vibration, the operation takes place in plane.

- **Rocking:** In this type of bending vibrations, two atoms move in the same direction with respect to a central atom. In this type of bending vibration, the operation takes place in plane.



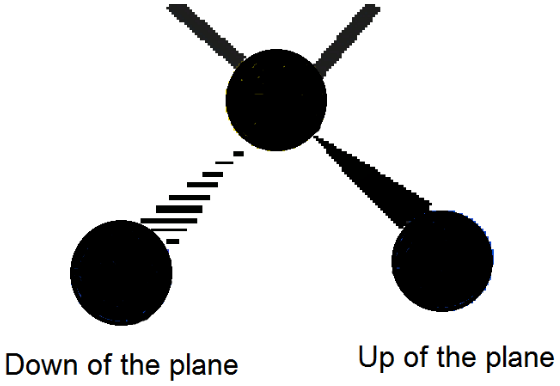
Rocking

- **Wagging:** In this type of bending vibrations, two atoms either move up of the plane or move down of the plane with respect to the plane containing the central atom. In this type of bending vibration, the operation takes place out-of-plane.



Wagging

- **Twisting:** In this type of bending vibrations, one atom move up of the plane while other atom move down of the plane with respect to the plane containing the central atom. In this type of bending vibration, the operation takes place out-of-plane.



Twisting

Infra-Red Active or Inactive

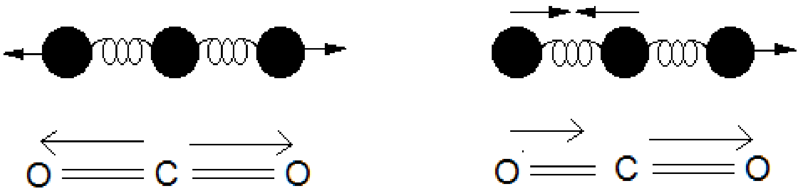
Molecules whose vibrational motions are accompanied by a change in dipole moment are infra red active. Let us consider CO_2 molecule to know whether a particular mode of vibration of a molecule is active or inactive towards IR radiation. Since CO_2 molecule is linear, so, it has 4 normal modes of vibration [(3n-5) modes of vibration for Linear a molecule].

The four normal modes of vibration of CO_2 are –

Symmetric stretching vibration: In this mode of vibration, both the C=O bonds lengthen and contract together (in-phase), as a result, during vibration no change in dipole moment of the molecule takes place. Hence, this mode of vibration is IR inactive.

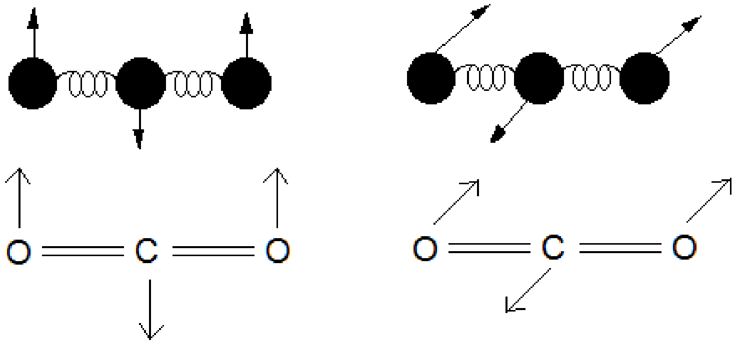
Asymmetric stretching vibration: In this mode of vibration, one C=O bond lengthen while other the other C=O bond contract, as a result, during vibration change in dipole moment of the molecule takes place. Hence, this mode of vibration is IR active.

Bending vibration: There are two bending mode of vibrations which are of equal energy. But one bending mode is in the plane of the paper while the other is perpendicular to the plane of the paper. Both these bending vibrations are IR active, as their vibrations are accompanied by change in dipole moment. All these four normal modes of vibrations of CO_2 are shown in **figure 2.1**.



Symmetric Stretching
IR Inactive

Asymmetric Stretching
IR Active



Bending (in plane of paper)
IR Active

Bending (in perpendicular plane of paper)
IR Active

Fig 2.1 IR active and inactive modes of vibrations of CO_2

Finger Print Region

In the IR spectrum, the region below 1500 cm^{-1}(usually 1500 cm^{-1}- 500 cm^{-1}) is very rich in much absorption which are caused mainly due to the bending vibrations within the molecule. Since in a spectrum, the numbers of bending vibrations are usually more than the number of stretching vibrations, so, this region gives a large number of information about the structure of the molecule. This region is known as finger print region in IR spectrum.

Organic compounds that contain same functional group, show similar characteristic absorptions above 1500 cm^{-1}, but their IR spectra differ in the region below 1500 cm^{-1}. Thus, comparing the spectra of such compounds below 1500 cm^{-1}, it is possible to distinguish the structures of the two compounds.

To understand this fact clearly, let us compare the IR spectra of propan-1-ol and propan-2-ol. Due to the presence of alcoholic -OH group (as functional group), both the molecules will show an absorbance band at ~ 3400 cm^{-1}, so, in order to differentiate between the two, we must compare the spectra in the region below 1500 cm^{-1}, which is quite different for both the molecules. The spectrum of propan-1-ol and propan-2-ol is shown in **figure 2.2**. Thus this region of the spectrum is important for differentiating between two organic compounds containing the same functional group by considering the fact that each compound produces a different pattern of troughs in this region of the spectrum.

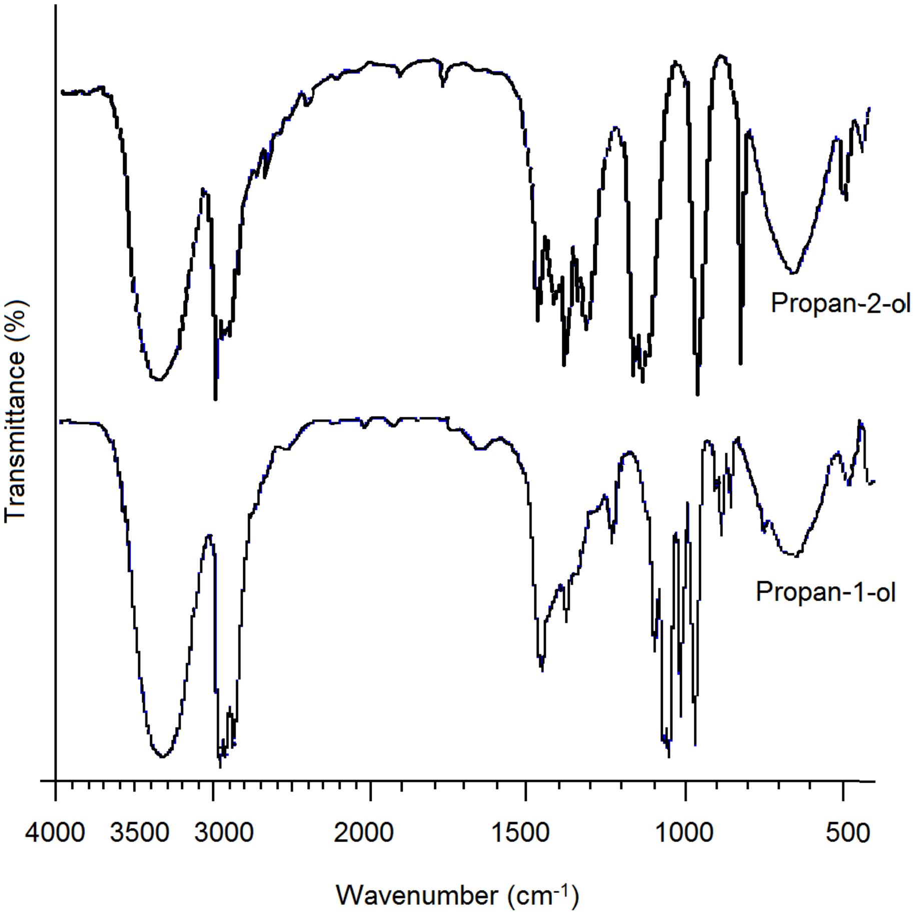


Fig. 2.2 IR Spectrum of Propan-1-ol and Propan-2-ol

Group Frequencies

Vibrations those are associated with certain fixed structural units viz. –OH, - C≡N, - NH_2 etc. appear in fairly constant regions (i.e. approximately at constant wavenumbers) as characteristic absorbance bands in the spectrum, such wavenumbers at which the absorbance bands appear are known as **group frequencies**.

Characteristic IR Absorbance Bands (Absorption Frequencies), type of vibration and intensities of some organic functional groups are shown in **table 2.1**.

Table 2.1 Absorbance Bands, type of vibration and intensities of some organic functional group

Functional Group	Type of vibration	Wavenumber (cm^{-1})	Intensity
Alcohol, Phenol			
O-H	Stretch, free	3500 - 3650	sharp, strong
O-H	Stretch, H-bonded	3200-3400	broad, strong
C-O	Stretch	1000-1200	strong
Alkane			
-C - H	Stretch	2850-3000	strong
$-CH_2-$	Bend	1365-1480	medium
Alkene			
=C-H	Stretch	3000-3100	medium
=C-H	Bend	675-1000	strong
C=C	Stretch	1600-1680	variable (m-w)
Alkyne			
-C-H	stretch	3300	strong, sharp
- C≡C-	stretch	2100-2250	variable (m-w)
Alkyl halide			
C-F	stretch	1000-1400	strong
C- Cl	stretch	550-800	strong
C-Br, C-I	stretch	500-660	strong
Amine			
N-H	stretch	3200-3500	medium
N-H	bend	1550-1650	medium
C-N	stretch	1000-1350	medium
Aldehyde			
C=O	stretch	1720-1740	strong
=C-H	stretch	2800-2850	medium
Ketone			

C=O (acyclic)	stretch	1700-1725	strong
C=O (cyclic)	stretch	1850 (3-membered) 1780 (4-membered) 1745 (5-membered) 1715 (6-membered) 1705 (7-membered)	strong
C=O (α, β-unsaturated)	stretch	1660-1685	strong
C=O (aryl)	stretch	1680-1700	strong
Ether			
C-O	stretch	1000-1300	strong
Nitrile			
- C≡N	stretch	2220-2260	medium
Nitro			
N=O	stretch	1350-1550	strong
Amide			
C=O	stretch	1630-1690	strong
N-H	stretch	3200-3500	medium
N-H	bend	1550-1650	medium
Acid Anhydride			
C=O	stretch	1800-1830 & 1740-1775	two bands (strong)
Ester			
C=O	stretch	1730-1750	strong
C-O	stretch	1000-1300	strong
Aromatic			
C-H	stretch	3000-3150	medium
C=C	stretch	1475-1600	medium-weak, multiple bands
Carboxylic acid			
C=O	stretch	1700-1725	strong
O-H	stretch	2400-3400	medium
C-O	stretch	1000-1300	strong

Effect of Hydrogen Bonding

Hydrogen bonding results in a slight weakening of the A-H bond (where A may be N, O or F) and as a result the A-H bond distance slightly increases. Due to weakening of the bond, the frequency of the A-H stretching vibration decreases. Thus, hydrogen bonding brings about downward frequency shift. In absence of the H- bonding, the A-H bond being polar, show sharp IR absorption band while the presence of H-bonding shifts the band towards lower frequency side and at the same time the band also becomes broader.

IR spectroscopy is a very important tool for distinguishing between intermolecular and intramolecular H-bonding. Intermolecular H-bonding weakens the A-H bond, thereby shifting the band towards lower frequency side in the spectra. Intermolecular H-bonds depend on concentration of the solution. To understand the dependence of the intermolecular H-bonds on concentration of the solution, let us consider the IR spectra of haxan-1-ol at different dilutions. In case of pure haxan-1-ol sample a broad band is observed in the wavenumber range 3300 – 3400 cm^{-1}, here the formation of intermolecular H-bonding takes place among the haxan-1-ol molecules. On dilution haxan-1-ol with a solvent like CCl_4 (i.e. with a solvent that is unable to form H-bonding), a sharp non H-bonded O-H stretching band appears at ~ 3600 cm^{-1} and at the same time the broad H-bonded band reduces considerably. On further dilution, the broad H-bonded band vanishes and the free O-H

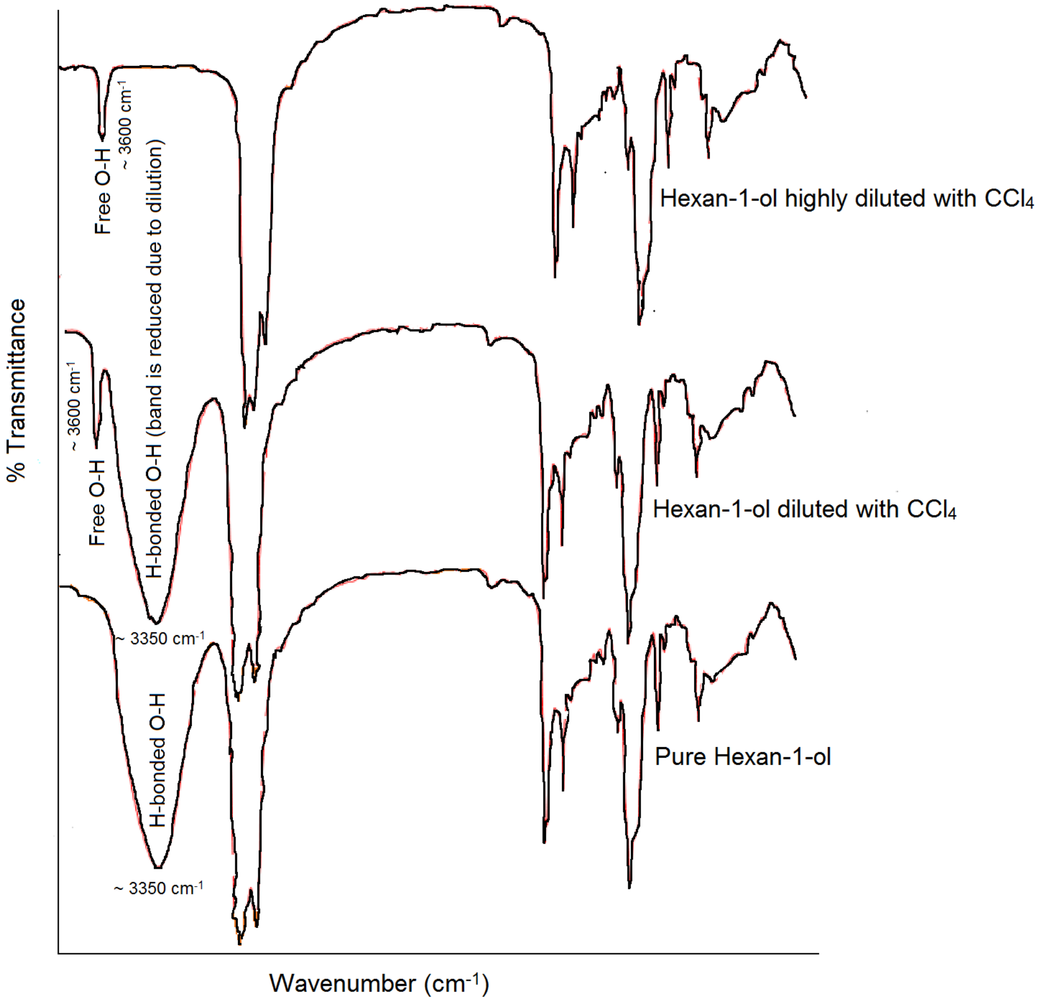


Fig. 2.3 IR Spectra of Hexan-1-ol showing the effect of intermolecular H-bonding

stretching band appears as the major band. IR spectra of hexan-1-ol showing the effect of intermolecular H-bonding is shown in **figure 2.3**. Intramolecular H-bonds are independent on the concentration of the solution and in such cases the band does not change its position significantly even at a very high dilution, this is because the internal bonding is not changed by a change in concentration. For example, in the IR spectrum of phenol, the O-H band appears as a broad band with centre at ~ 3350 cm^{-1}, on the other hand, due to the presence of intramolecular H-bonding, the O-H band for methyl salicylate shifts towards lower wavenumber and appears as a broad band with centre at ~ 3200 cm^{-1}. However, this shift of absorbance band remains same at all dilution.

Problem 2.1: In the IR spectrum of pure butan-1-ol, a broadband is observed within the range 3500-3200 cm^{-1}, but a dilute solution of the compound in CCl_4 shows an additional band at 3650 cm^{-1}. Explain the observation. [**GU 2016**]

NB:

(I) IR absorption bands depend on the masses of the two atoms involved in bonding. The higher the mass of the bonded atoms, the lower is the absorbance band. For example, if we compare the IR spectra of $CHCl_3$ and $CDCl_3$, we observe the following differences –

- The band observed for C-H stretching (3020 cm^{-1}) and bending (1220 cm^{-1}) in case of $CHCl_3$ is not seen in case of $CDCl_3$.
- In case of $CDCl_3$ the absorbance bands shift towards lower wavenumber by about 20 cm^{-1} in comparison to $CHCl_3$.

(II) As the bond order increases, bond strength also increases and as a result absorbance bands shift towards higher wavenumber. For example, C≡C bond stretches at ~2100 cm^{-1} while C=C bond stretches at ~1650 cm^{-1}. Similarly, C=O bond stretches at ~1700 cm^{-1} while C - O bond stretches at ~1100 cm^{-1}.

Problem 2.2: Arrange the following bonds in increasing order of their IR absorbance bands

C≡N, C=N, C - N

Problem2.3: Using IR spectra, how will you distinguish between ethanol and ethanal ? [**GU 2014**].

Solution:

The IR spectrum of ethanol shows the following absorbance bands (shown in **Figure 2.4**)

$\nu_{O\text{-}H}$ = 3391 cm^{-1} (broad band due to the formation of H- bonding)

$\nu_{C\text{-}H}$ = 2981 cm^{-1}

$\nu_{C\text{-}O}$ = 1055 cm^{-1} and 1102 cm^{-1}

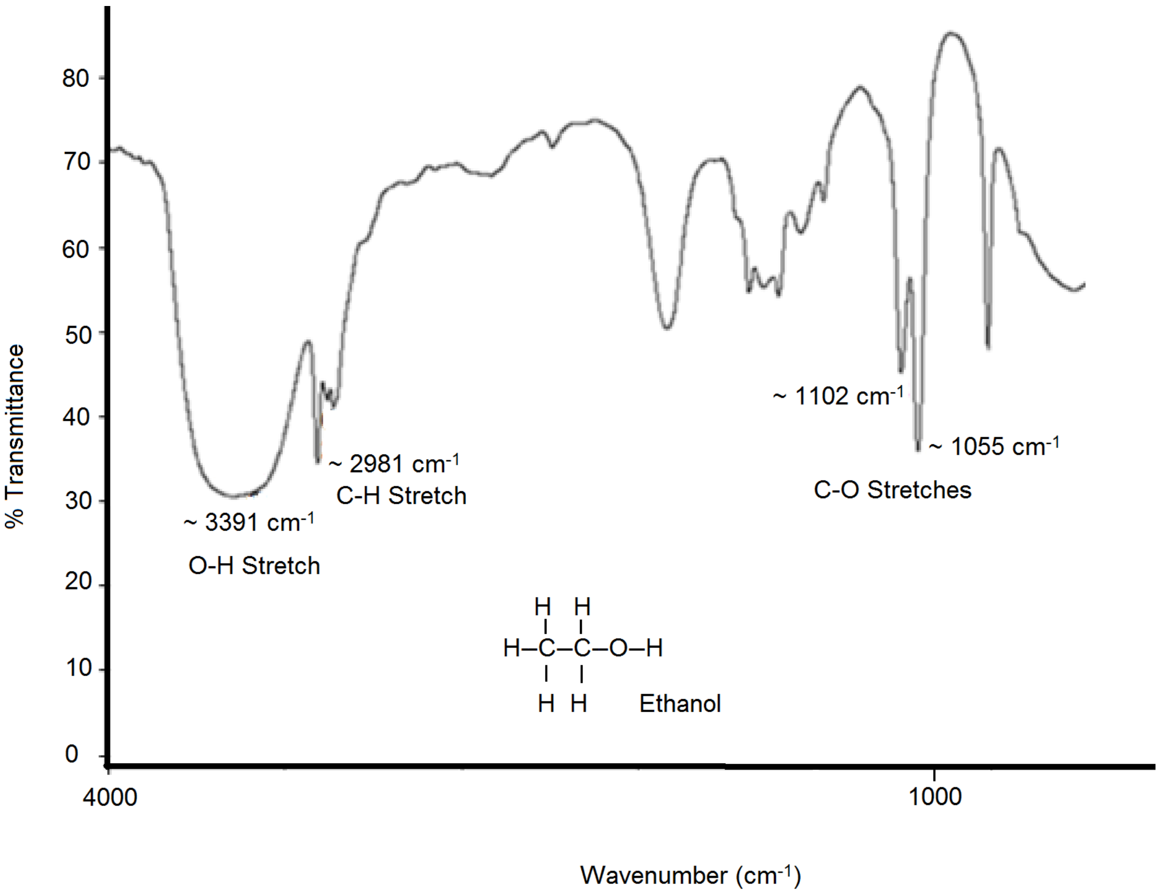


Fig. 2.4 IR Spectrum of Ethanol

On the other hand IR spectrum of ethanal shows the following absorbance bands (shown in **Figure 2.5**).

$\nu_{C=O} = 1730\ cm^{-1}$

$\nu_{C-H} = 2820\ cm^{-1}$

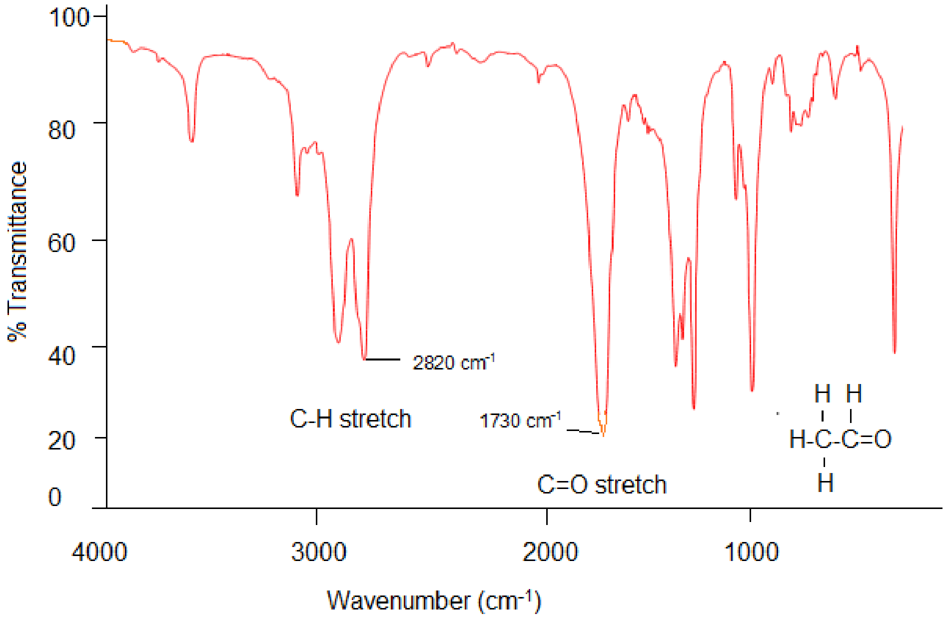


Fig. 2.5 IR spectra of ethanal

Thus, by comparing the two spectra it is possible to distinguish between ethanol and ethanal.

Problem 2.4 : The IR spectra of an organic compound ($C_7H_6O_2$) show the following absorbance bands 1150 cm^{-1}, 1520 cm^{-1}, 1700 cm^{-1}, 3050 cm^{-1} and 3350 cm^{-1}. Predict the probable structure of the compound ?

Solution:

The bands may be assigned as –

1150 cm^{-1} for C – O (stretch)

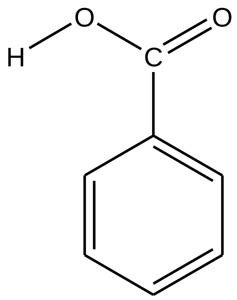
1520 cm^{-1} for C = C (stretch) (aromatic)

1700 cm^{-1} for C = O (stretch)

3050 cm^{-1} for C - H (stretch) (aromatic)

3350 cm^{-1} for O - H (stretch)

Thus from the above assignments, it may be predicted that the organic compound may be benzoic acid.



Problem 2.5: A compound with molecular formula C_7H_5N shows the following prominent IR bands:

3050, 2240,1600, 1500,750,700 (all in cm^{-1})

Predict the structure of the molecule. [**GU 2014**]

Solution:

The bands may be assigned as –

700 cm^{-1} for =C –H (bend)

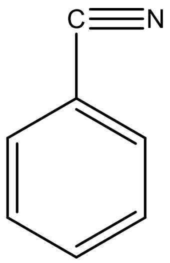
750 cm^{-1} for =C –H (bend)

1500 cm^{-1} for C = C (stretch) (aromatic)

1600 cm^{-1} for C = C (stretch) (aromatic)

2240 cm^{-1} for C ≡ N (stretch)

3050 cm^{-1} for C - H (stretch) (aromatic)



Thus from the above assignments, it may be predicted that the organic compound may be benzonitrile. The IR spectrum of benzonitrile is shown in **figure 2.6**.

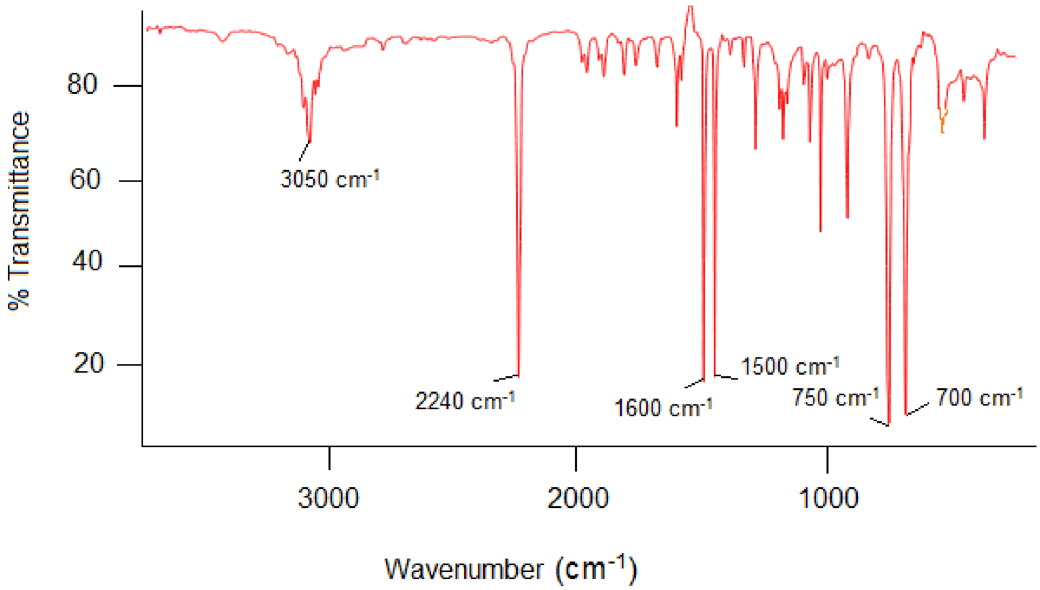


Fig. 2.6 IR spectrum of benzonitrile