UNIT 5 INFRARED SPECTRA OF POLYATOMIC MOLECULES

Structure

5.1 INTRODUCTION

In the previous unit, we learnt the principles of vibrational spectra of diatomic molecules. We have explained the aspects like spacings between vibrational levels and also the concept of zero point energy. The vibration-rotation spectra of diatomic molecules have also been discussed.

In this unit, we will study the IR spectra of molecules containing more than two atoms, i.e., polyatomic molecules. First, we shall discuss the number of vibrational degrees of freedom for linear and nonlinear molecules. We will proceed to explain the energy level scheme for water molecule. Then we will learn to identify the presence of functional groups in organic compounds with the help of chart of group frequencies. We will also discuss how the isotopic substitution, inductive effect, resonance effect, hydrogen bonding and steric effect affect the group frequencies in IR spectra. Finally in the Appendix part, we shall outline the steps involved in the analysis of IR spectra of molecules.

Objectives

After studying this unit you should be able to:

- calculate the number of vibrational modes in polyatomic molecules,
- discuss the energy level scheme for water,

- explain the concept of group frequency and derive information about molecular structure using group frequencies,
- state how isotopic mass alters the frequencies of functional groups,
- explain how electronic factors affect the IR spectra of molecules,
- state the effect of hydrogen bonding and steric effect on the IR spectra of molecules, and
- discuss the steps involved in the analysis of IR spectra of simple molecules.

5.2 VIBRATIONAL DEGREES OF FREEDOM OF POLYATOMIC MOLECULES

For a nonlinear molecule, six coordinates (out of $3N$ coordinates) are accounted for by translational and rotational degrees of freedom. Hence a nonlinear molecule has $(3N-6)$ vibrational degrees of freedom. For a linear molecule, there are only two rotational degrees of freedom apart from three translational degrees of freedom. Hence the vibrational degrees of freedom for a linear molecule are $(3N-5)$.

We have already seen in Unit 4 that a diatomic molecule has only one fundamental vibration or one vibrational coordinate. This arises due to the stretching and compression of the bond connecting two atoms just like a spring (see Fig. 3.1 of Unit 3). Let us calculate the vibrational degrees of freedom of a polyatomic molecule. First let us assume that each atom is free to move in three perpendicular directions (along x, y, and z axes) and thus has three **degrees of freedom**. The degrees of freedom are the number of directions in which an atom can move freely independent of other atoms in the molecule. Hence, for a molecule containing N atoms, the total degrees of freedom is $3N$.

We know that a molecule has translational, rotational and vibrational motions. A molecule can have only three degrees of translational motion since centre of mass of the molecule can move only along three axial directions. That is, the whole molecule can move along the three axes. In addition, when the molecule is nonlinear, there are three degrees of freedom due to rotational motions about the three axes. Therefore, there remains $3N-(3+3) = (3N-6)$ coordinates which account for vibrational degrees of freedom for nonlinear polyatomic molecules.

(Total degrees of freedom) – (translational degrees of freedom + rotational degrees of freedom) = Vibrational degrees of freedom.

For a linear molecule, there are two rotational degrees of freedom as the rotations about two axes perpendicular to internuclear bond axis only are allowed. The rotation about the internuclear axis is not possible since the moment of inertia along the internuclear axis is zero. Therefore a linear molecule possesses $3N-(3+2) = (3N-5)$ vibrational degrees of freedom. The details of the number of degrees of freedom for linear and nonlinear molecules are presented in Table 5.1

Table 5.1 : Degrees of Freedom for Polyatomic Molecules

Degrees of Freedom	Linear	Nonlinear
Total	$3N$	$3N$
Translational	3	3
Rotational	2	3
Vibrational	$(3N-5)$	$(3N-6)$

Using Table 5.1, can you state the vibrational degrees of freedom of CO_2, H_2O and NH_3 molecules? It is worth recollecting that CO_2 is linear, H_2O is angular and NH_3 is pyramidal. CO_2 molecule has $(3 \times 3 - 5) = 4$ vibrational degrees of freedom; H_2O molecule has $(3 \times 3 - 6) = 3$ vibrational degrees of freedom and NH_3 molecule has $(3 \times 4 - 6) = 6$ vibrational degrees of freedom.

Normal Modes Vibrations

A molecule can vibrate only in certain modes, known as normal modes. Each normal mode corresponds to a vibrational degree of freedom. A normal mode is an independent simultaneous motion of atoms or group of atoms that may be excited without leading to the excitation of any other normal mode. **In general, a normal vibration is one in which all atoms in a molecule vibrate at the same frequency and in phase with each other.**

For a polyatomic molecule, the normal modes of vibration are of two types:

(i) stretching vibrations (ii) bending vibrations

The linear and nonlinear molecules have $(N-1)$ stretching vibrations. The bending vibrations for linear and nonlinear molecules are $(2N-4)$and$(2N-5)$, respectively.

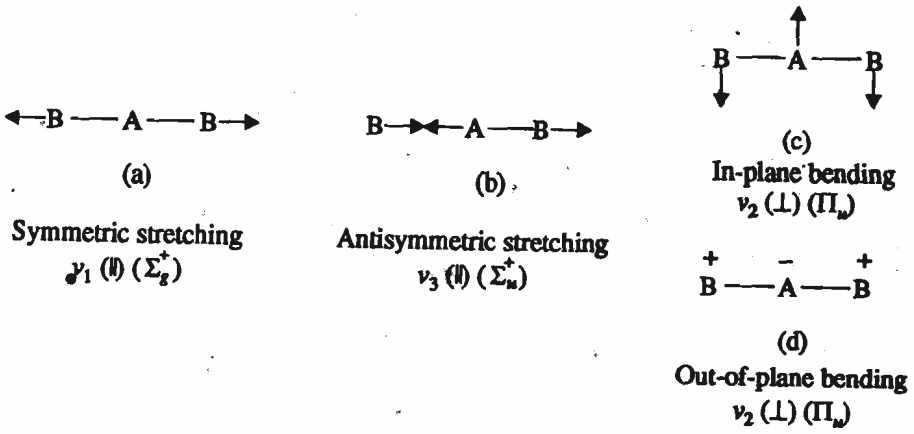

Fig.5.1: Normal modes of vibration of a triatomic linear molecule, AB_2 (e.g., CO_2). (a) symmetric stretching (ν_1) (b) antisymmetric stretching (ν_3) (c) in-plane bending and (d) out-of-plane bending ; both (c) and (d) are degenerate and hence these two give rise to only one band (ν_2);(+) sign shows that the atom is going above the plane while (−) sign indicates that the atom is going below the molecular plane. The ν_1 and ν_3 vibrations are parallel (||) vibrations whereas the degenerate vibration ν_2 is a perpendicular (⊥) vibration.

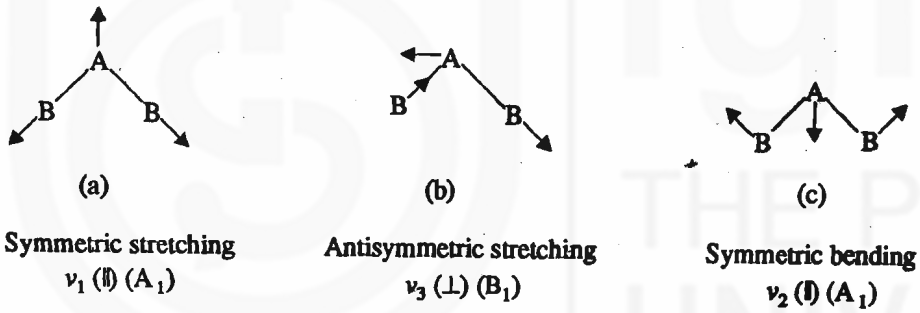

Fig.5.2: Normal modes of vibrations of a triatomic angular molecule, AB_2 (e.g., H_2O). (a) symmetric stretching (ν_1) (b) antisymmetric stretching (ν_3) (c) symmetric bending (ν_2). ν_1 and ν_2 are parallel vibrations whereas ν_3 is a perpendicular vibration.

In **stretching vibrations,** the atoms move along the bond axis so that the bond length increases or decreases at regular intervals. The stretching vibrations again are of two types. They are symmetric and antisymmetric stretchings. In symmetric stretching of a triatomic molecule, both the bonds connected to a common atom can simultaneously either elongate or contract. In the case of antisymmetric stretching, if one bond is lengthened, the other bond is shortened or vice versa. These stretchings are shown in Figs. 5.1a and b and Figs. 5.2a and b for linear and angular molecules of the type AB_2. **The arrows attached to each atom show the direction of its motion during half of the vibration.** In Figs. 5.1 and 5.2, we indicate the type of each vibration mode as parallel (||)or perpendicular (⊥). In a parallel vibration, the dipole change takes place along the line of the principal axis of symmetry. In a perpendicular vibration, the dipole change takes place perpendicular to the line of the principal axis of symmetry. The nature of vibration-rotation spectra of polyatomic molecules depends on the type of vibration – parallel or perpendicular. We shall discuss this in Sec. 5.3.4.

The **bending vibrations** occur when there is a change in bond angle between bonds connected to a common atom. In some cases, the movement of a group of atoms with respect to the remaining atoms in the molecule also causes bending vibrations for a polyatomic molecule. A linear triatomic molecule has two bending vibrations (Fig.5.1 c

The displacement of each atom during each normal mode of vibration is such that all atoms move with the same frequency and in phase but with different amplitude. The amplitudes of vibrations of atoms are such that the centre of mass does not move. In other words, there is no translational motion of the molecule as a result of vibration and also there is no rotational motion of the molecule.

The normal mode concept can facilitate the understanding of the vibrational excitation of a particular group depending on the frequency of incident radiation; this radiation has no effect on the other part of the molecule.

Vibrations are classified as parallel (||) or perpendicular (⊥) vibrations depending on whether the dipole moment change is parallel or perpendicular to the principal axis of the molecule.

Degeneracy of a vibrational mode is the number of normal modes which have same energy. For instance, the degeneracy of ν_2 mode of CO_2 is two since the two bending modes (in-plane and out-of-plane) have same energy.

and d) while a nonlinear triatomic molecule has only one bending vibration (5.2 c). Thus for a linear triatomic molecule (e.g., CO_2), we could expect four vibrational modes, two stretching and two bending. Both these bending vibrations are identical in all respects except the direction. Such vibrations have same frequency (and energy) and, are said to be degenerate. For instance, the two bending vibrations of CO_2 are degenerate. As a result of this, only three absorption bands are found for CO_2 - two corresponding to the stretching vibrations and one to the bending vibration. A nonlinear angular triatomic molecule (e.g., H_2O) also has three vibrational modes, two being due to the stretching modes and one due to the bending mode. The difference between the linear and nonlinear triatomic molecules lies in the degeneracy of the bending mode of the former.

Using the materials in this section, answer the following SAQ.

SAQ 1

State the number of stretching and bending modes of C_2H_2.

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5.3 IR SPECTRA OF SOME POLYATOMIC MOLECULES

First we shall discuss the IR spectrum of simple molecules like H_2O and CO_2.

5.3.1 IR Spectrum of H_2O Molecule

As mentioned in the last section, water, a nonlinear molecule, has three normal modes of vibrations. Fig.5.3 shows the IR spectrum of water in an inert solvent.

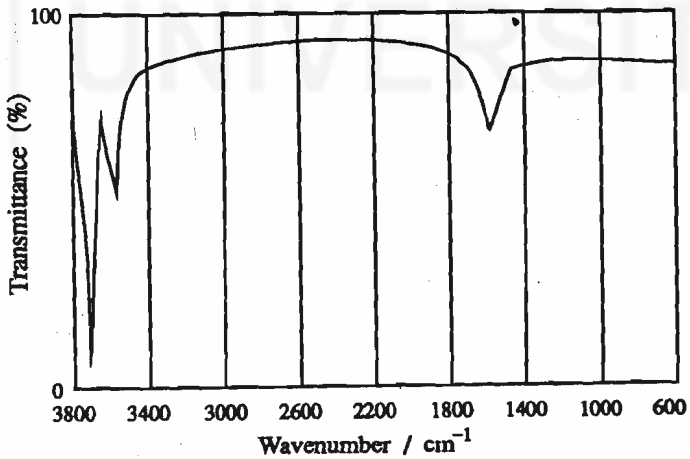


Fig.5.3 : Infrared spectrum (schematic) of H_2O in an inert solvent showing three dominant absorptions.

We can notice two sharp bands at higher frequency region (at 3756 cm^{-1} and 3652 cm^{-1}) and one sharp band at lower frequency region (at 1595 cm^{-1}). Group theory can be used in assigning vibrational modes to the observed IR absorption frequencies. Two examples (H_2O and NH_3) are discussed in the Appendix part of this unit. The frequencies at 3652 cm^{-1}, 1595 cm^{-1} and 3756 cm^{-1} are associated with symmetric stretching, symmetric bending and antisymmetric stretching modes,

respectively. All the three vibrations are associated with a change in dipole moment, which is a necessary condition for a vibration to be infrared active. It is also possible to draw vibrational energy level diagram corresponding to these three bands as in Fig. 5.4. The quantum numbers for each of the vibrational levels are shown below ν_1, ν_2 and ν_3. The quantum number notation is useful in identifying each of the energy sublevels. For instance, '000' means $\nu_1 = \nu_2 = \nu_3 = 0$; '010' means $\nu_1 = 0, \nu_2 = 1$ and $\nu_3 = 0$; '020' means $\nu_1 = 0, \nu_2 = 2$ and $\nu_3 = 0$ and so on. You can see that the wave number corresponding to the energy difference between $E(100)$ and $E(000)$ is $3652\,cm^{-1}$; the wave number corresponding to the energy difference between $E(010)$ and $E(000)$is $1595\ cm^{-1}$ and the wave number corresponding to the energy difference between $E(001)$and $E(000)$is $3756\ cm^{-1}$. The three vibrational modes which are associated with the three IR bands are similar to those shown in Fig.5.2.

The notation '000' means that the molecule is in the vibrational energy level given by the quantum numbers, $(\nu_1 \nu_2 \nu_3) = (000)$.

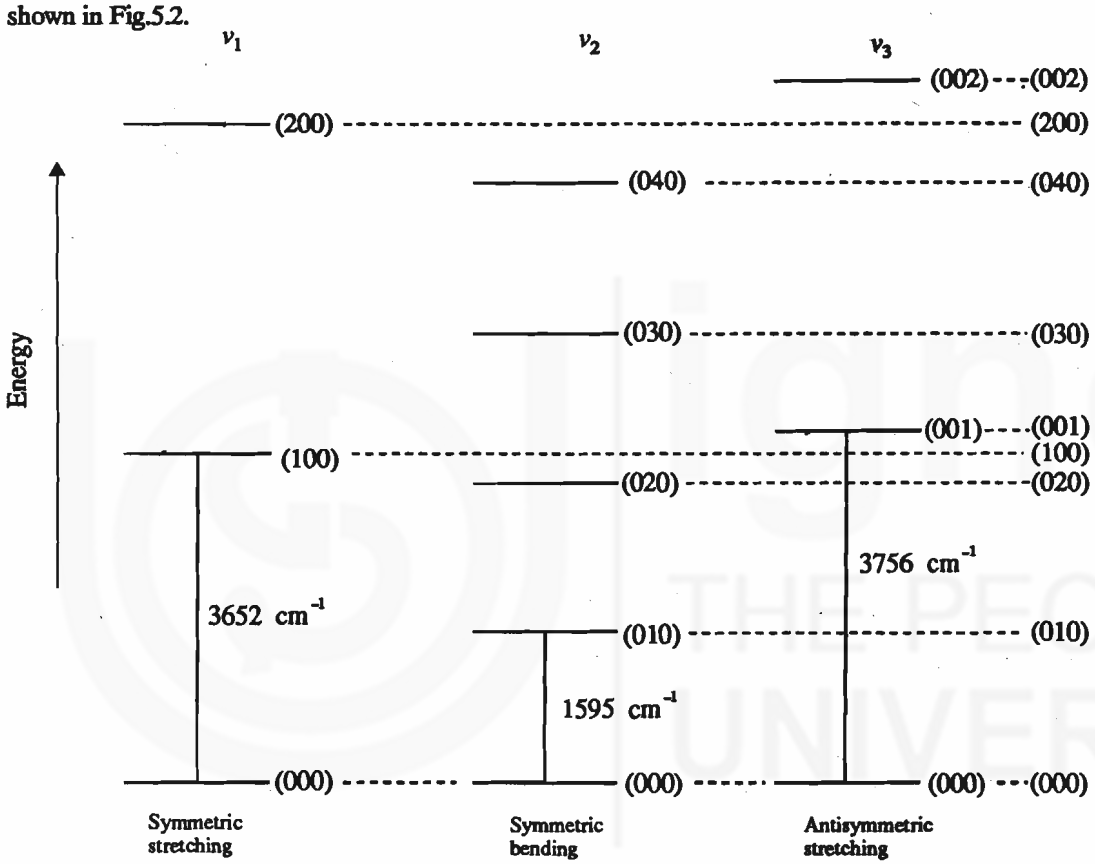


Fig. 5.4 : The three vibrational energy levels for water molecule.

The quantum mechanical vibrational energy of a polyatomic molecule containing N atoms is given by,

$$E(\nu_1 \nu_2 .....) = hc \sum (\nu_i + d_i/2)\,\bar{\nu}_i \quad \text{(summation over all } \nu_i\text{)}$$

where ν_i, d_i and $\bar{\nu}_i$ are the quantum number, degeneracy and fundamental frequency for a particular vibrational mode, ν_i. In case of H_2O, this equation can be written as

$$E(\nu_1\nu_2\nu_3) = hc\,[((\nu_1 + 1/2)\,3.652 \times 10^5) + ((\nu_2 + 1/2)\,1.595 \times 10^5) + ((\nu_3 + 1/2)\,3.756 \times 10^5)\,]\,J$$

Unit of E = units of $hc\bar{\nu}$
$= J\,s\,m\,s^{-1}\,m^{-1}$
$= J$

since degeneracy is 1 for each of the modes in H_2O molecule.

Using this equation, we can calculate the total zero point energy for H_2O molecule as shown below:

$$E(000) = hc\left(\left(\frac{1}{2}\times 3.652\times 10^{5}\right) + \left(\frac{1}{2}\times 1.595\times 10^{5}\right) + \left(\frac{1}{2}\times 3.756\times 10^{5}\right)\right) \text{ J}$$

$$= \frac{1}{2}\times 6.626\times 10^{-34}\times 3\times 10^{8}\times 10^{5}\,(3.652 + 1.595 + 3.756)\text{ J}$$

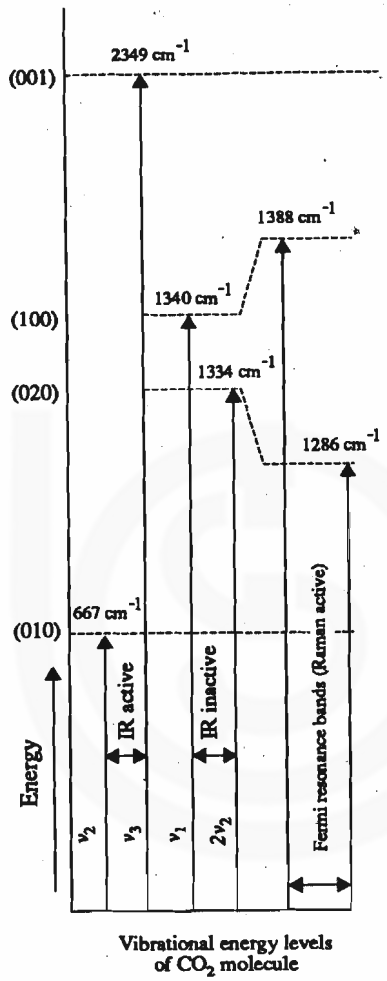
$$= 8.945\times 10^{-20}\text{ J}$$

Wave number in cm^{-1} to m^{-1} unit during calculation. Thus 3652 cm^{-1} is written as 3.652×10^{5} m^{-1}.
$1\ cm^{-1} = 10^{2}\ m^{-1}$

So far, we discussed the IR spectrum of H_2O which is an angular triatomic molecule. Let us now discuss the IR spectra of CO_2 which is a linear triatomic molecule.

5.3.2 IR Spectrum of CO_2 Molecule

Among the four vibrations shown in Fig.5.1 for a triatomic linear molecule such as CO_2, the IR active vibrations are antisymmetric stretching (ν_3) and bending (ν_2) but not the symmetric stretching(ν_1) since it does not cause any change in the dipole moment. The two IR bands of CO_2 at 2349 cm^{-1} and 667 cm^{-1} correspond to ν_3 and ν_2, respectively. The band due to symmetric stretching (ν_1) at 1340 cm^{-1} is not observed in IR spectrum. However the stretching band is Raman active. In the case of CO_2, the first overtone of ν_2 i.e., $2\nu_2$ ($2\times 667\ cm^{-1} = 1334\ cm^{-1}$) has the same symmetry as the symmetric stretching mode and hence interacts with this fundamental vibration due to **Fermi resonance** giving rise to two bands. These two bands are not observable in IR spectrum but both are observable in Raman spectrum which will be discussed in the next unit. In fact, the Raman spectrum shows two bands at 1388 and 1286 cm^{-1}; the mean of these two values (1337 cm^{-1}) is close to ν_1 and $2\nu_2$. The overtone $2\nu_2$ which would normally be weak borrows intensity from the fundamental ν_1, and hence, two bands are observable in Raman spectrum.



Vibrational energy levels of CO_2 molecule

Note that the bending mode of CO_2 has a perpendicular band symmetry whereas the overtone of the bending mode ($2\nu_2$) has parallel band symmetry like symmetric stretching mode.
Fig. 5.1 can be used for depicting the vibrational modes of CO_2. Note that the symmetric stretching mode is IR inactive whereas antisymmetric stretching and bending modes are IR active.

An overtone is an absorption band at twice, thrice, etc. the frequencies of the fundamental band.

Earlier we stated the formula for the quantum mechanical vibrational energy of poly - atomic molecules. We can calculate the quantum mechanical vibrational energy of a linear polyatomic molecule by carrying out summation over (3*N*–5)terms. But we leave it to you as an exercise in SAQ 2.

5.3.3 Complexity of the IR Spectra of Polyatomic Molecules

As we have discussed earlier, the infrared spectrum of a polyatomic molecule consists of an absorption band at each of the (3*N*–6) or (3*N*–5) fundamental frequencies for nonlinear and linear molecules, respectively. This is based on the assumption that each vibration is simple harmonic. But actually the vibrations are anharmonic, and therefore, we will have overtones of diminishing intensities at twice, thrice the fundamental frequency etc. In addition, we may have bands due to combination of two fundamentals (combination bands) or difference of two fundamentals (difference bands). These bands are weak. Also, a fundamental and an overtone may have frequencies very close to each other. The two close frequencies may resonate leading to higher and lower frequencies relative to the original. This is

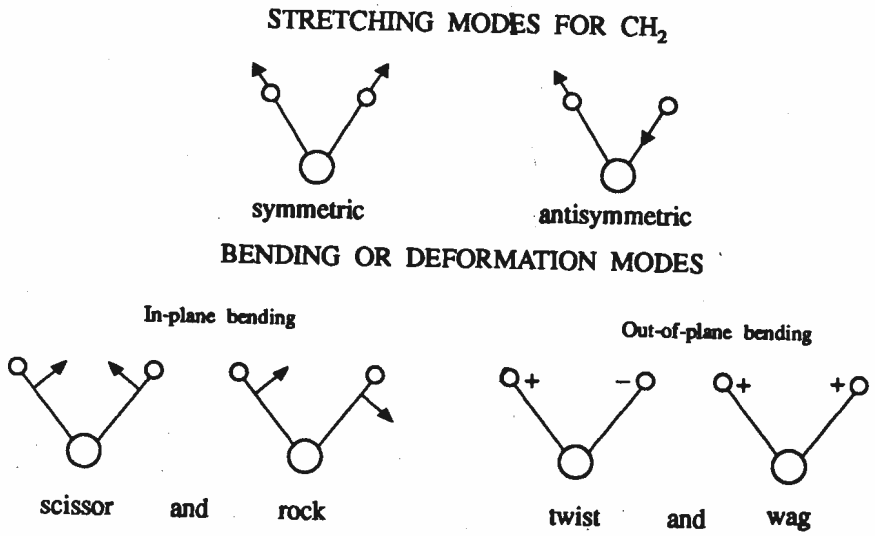


Fig. 5.5: Vibration modes in methylene group

called Fermi resonance and we have discussed it earlier. Thus an infrared spectrum of a compound will have strong fundamental absorptions and weak overtones, combination bands and Fermi resonance bands. As the number of atoms increase, the spectrum becomes complicated. In the case of polyatomic molecules, many out-of-plane bending vibrations also are responsible for the complexity of the IR spectra and a complete analysis of the IR spectrum becomes quite difficult. For instance, the stretching and bending modes of $>CH_2$ group are given in Fig.5.5.

The complexity of IR spectrum of even a simple molecule such as H_2O can be understood from the frequencies of the IR bands of water vapour given in Table 5.2.

Table 5.2 : Infrared Bands of H_2O Vapour

Wave number/cm^{-1}	Intensity*	Transition involved
1595	vs	(000) ⟶ (010)
3154	m	(000) ⟶ (020)
3652	s	(000) ⟶ (100)
3756	vs	(000) ⟶ (001)
5332	m	(000) ⟶ (011)
6874	w	(000) ⟶ (021)

* s = strong, m = medium, vs = very strong, w = weak.

In the next subsection, we shall examine the influence of rotational fine structure on the vibrational spectra of molecules. Generally, IR spectrum of a molecule is used for assigning the strongest bands and to identify the weaker ones as overtones or combination bands or difference bands. In fact, the detailed procedure involved in frequency assignment shall be illustrated in Sec. 6.7 of Unit 6 using the IR and Raman spectra of SO_2 molecule.

5.3.4 Vibration-Rotation Spectra of Polyatomic Molecules

In the last unit, we studied the effect of rotation on the vibration spectra of diatomic molecules. Now we briefly state some of the aspects of vibration-rotation spectra of polyatomic molecules having linear structure. Just for the purpose of having a simple treatment, we shall not be discussing nonlinear molecules.

It is interesting to note that the rotational fine structure of linear molecules depends on the way they undergo dipole change-parallel or perpendicular-with respect to principal axis of symmetry. We have illustrated these two types of vibrations for a linear triatomic molecule through Fig. 5.1. We shall state the selection rules for these two types separately.

Parallel vibrations of linear molecules

The selection rule for the parallel vibrations of linear molecules is stated below:

$\Delta J = \pm 1, \quad \Delta v = \pm 1$ for simple harmonic motion

$\Delta J = \pm 1, \quad \Delta v = \pm 1, \pm 2, \pm 3, ...$ for anharmonic motion

The spectra would be similar to diatomic molecules with P and R branches with equally spaced lines on either side of the band centre. There is no line corresponding to band centre. Fig.5.6 shows the P and R branches centering around 3310 cm^{-1} for HCN molecule which is linear.

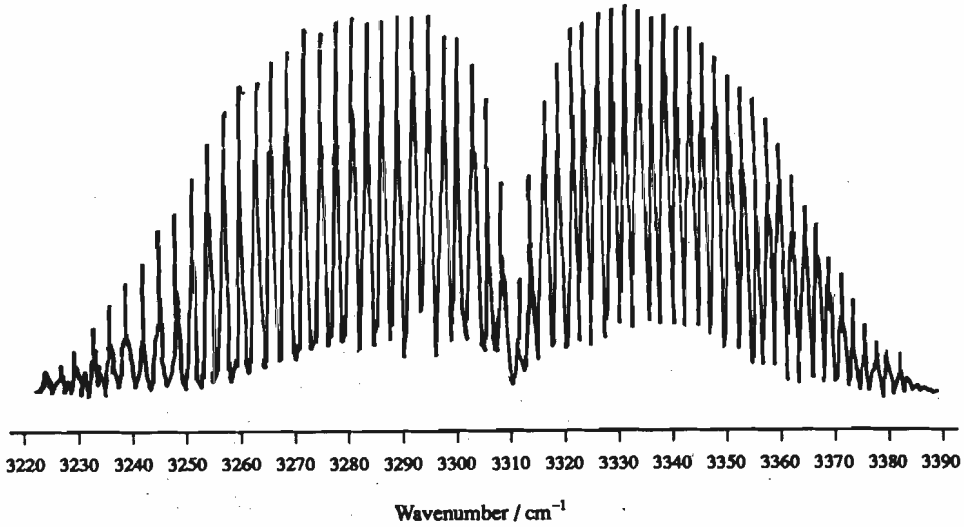


Fig.5.6 : Spectrum of symmetric stretching vibration of HCN molecule showing *P* and *R* branch lines.

For larger molecules, the value of *B* may be so small that separate lines can no longer be resolved in the *P* and *R* branches. In this case, rotational fine structure is lost and a typical *PR* contour is seen (Fig.5.7).

A nonlinear molecule cannot give rise to such a simple *PR* band and so, observation of *PR* band somewhere within a spectrum is a sufficient proof that the molecule is linear or nearly linear.

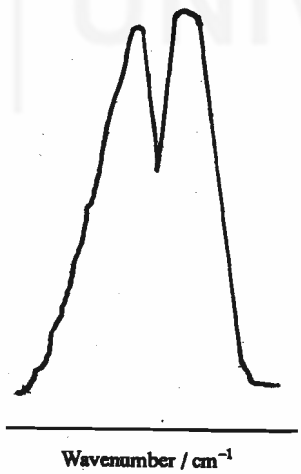


Fig.5.7 : Typical *PR* contour arising due to low resolution.

Perpendicular vibrations of linear molecules

The selection rule for these vibrations is given below:

$\Delta v = \pm 1, \quad \Delta J = 0, \pm 1$ for simple harmonic vibration

This means, a vibrational change could take place with no simultaneous rotational transition. You may remember that $\Delta J = 0$ corresponds to Q branch. The nature of the spectrum then depends on the difference between B values in the upper and lower levels. Normally these two values are not much different with the result that Q branch appears as a broad absorption band. If the rotational fine structure is unresolved, this band has the distinctive contour as shown in Fig. 5.8.

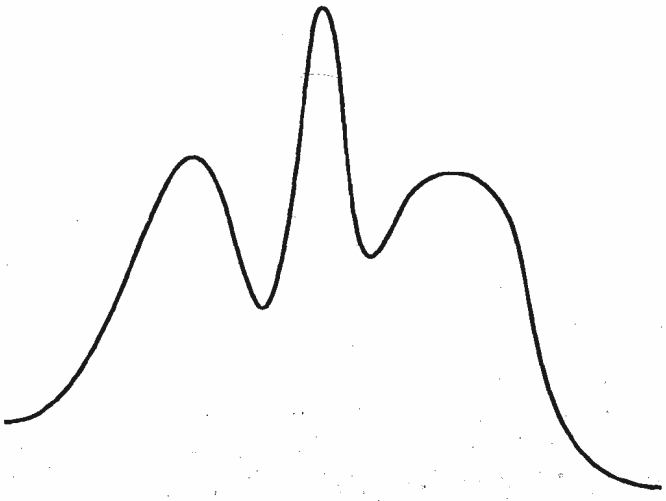


Fig. 5.8 : The contour of *PQR* band under low resolution.

The utility of studying vibration-rotation spectra is more for nonpolar molecules like CO_2, C_2H_2, CH_4 etc. for which dipole moment is zero. These molecules do not give rise to pure rotation spectra. These molecules however show infrared or Raman spectra. If these spectra exhibit resolved fine structure, the moment of inertia of the molecule can be obtained.

Although nuclear spin also has a significant effect on the rotational fine structure of vibration spectra, we do not intend studying the same.

Answer the following SAQ's.

SAQ 2

Assuming that $\bar{\nu}_1$, $\bar{\nu}_2$ and $\bar{\nu}_3$ of CO_2 are 1340 cm^{-1}, 667 cm^{-1} and 2349 cm^{-1}, calculate its zero point energy.
(**Hint :** Degeneracy (d_i) is 1 for ν_1 and ν_3 but 2 for ν_2).

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SAQ 3

Calculate the wavenumbers of the first and second overtones of ν_2 of CO_2. Use $\bar{\nu}_2$ from SAQ 2.

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5.4 GROUP FREQUENCY CONCEPT AND CHART OF GROUP FREQUENCIES

The normal modes of vibration can be divided into two types, namely, skeletal vibrations and the characteristic group vibrations. The skeletal vibrations involve displacements of all atoms to the same extent. The skeletal vibrations usually fall in the range 1400 – 700 cm^{-1}. The ether linkage, saturated hydrocarbon chain, aromatic rings etc. give rise to skeletal vibration bands. A complex pattern of bands may occur in the IR spectrum of a compound which could be identified as due to a particular skeletal structure. We shall discuss this later in this section.

The second type of normal modes known as the characteristic group vibrations involve the displacement of only a small portion of the molecule independent of the rest of the molecule. The absorption bands which arise due to the characteristic group vibrations are called **group frequencies.** The group frequencies are in general independent of the structure of the molecule as a whole. A few instances of the perturbation of group frequencies are discussed in the next section.

Many commonly occurring functional groups such as $-CH_3$, $>C=O$, $-NH_2$ etc. have characteristic group frequencies when they are present in a molecule. For example, all compounds containing a $-CH_3$ group possess absorption bands in the region of 2950 cm^{-1} (stretching) and 1400 cm^{-1} (bending). Similarly all compounds having the $>C=O$ group have a strong band at about 1700 cm^{-1}. Such group frequencies are listed in Table 5.3 which is also known as chart of group frequencies.

Table 5.3 : Group Frequencies

	Group	Intensity	Range/cm^{-1}	
A.	**Hydrocarbon chromophore**			
1.	**C – H STRETCHING**			
	a. Alkane	(m-s)	2962-2853	
	b. Alkene	(m)	3100-3000	
	c. Alkyne	(s)	3300	
	d. Aromatic	(v)	3030	
2.	**C – H BENDING**			
	a. Alkane, C–H	(w)	1340	
	Alkane, CH_2	(m)	1485-1445	
	Alkane, CH_3	(m) (s)	1470-1430 1380-1370	and
	Alkane, *gem*-dimethyl (doublet)	(s) (s)	1385-1380 1370-1365	and
	Alkane, *tert*-butyl (doublet)	(m) (s)	1395-1385 ~ 1365	and
	b. Alkene, monosubstituted (vinyl)	(s) (s) (s)	995-985 915-905 1420-1410	and
	Alkene, disubstituted, *cis*	(s)	690	
	Alkene, disubstituted, *trans*	(s) (m)	970-960 1310-1295	and

	Group	Intensity	Range/cm^{-1}	
	Alkene, disubstituted,	(s)	895-885	and
	gem	(s)	1420-1410	
	Alkene, trisubstituted	(s)	840-790	
c.	Alkyne	(s)	630	
d.	Aromatic substitution type:			
	Five adjacent hydrogen atoms	(v,s)	750	and
		(v,s)	700	
	four adjacent hydrogen atoms	(v,s)	750	
	three adjacent hydrogen atoms	(v,m)	780	
	two adjacent hydrogen atoms	(v,m)	830	
	one hydrogen atom	(v,w)	880	
3.	**C–C MULTIPLE BOND STRETCHING**			
a.	Alkene, nonconjugated	(v)	1680-1620	
	Alkene, monosubstituted (vinyl)	(m)	1645	
	Alkene, disubstituted, *cis*	(m)	1656	
	Alkene, disubstituted, *trans*	(m)	1675	
	Alkene, disubstituted, *gem*	(m)	1653	
	Alkene trisubstituted	(m)	1669	
	Alkene tetrasubstituted	(w)	1669	
b.	Alkyne, monosubstituted	(m)	2140-2100	
	Alkyne, disubstituted	(v,w)	2260-2190	
c.	Aromatic	(v)	1600	
		(v)	1580	
		(m)	1500	and
		(m)	1450	
B.	**Carbonyl chromophore**			
1.	**KETONES**			
a.	Saturated	(s)	1725-1705	
b	α,β–Unsaturated	(s)	1685-1665	
c.	Aryl	(s)	1700-1680	
2.	**ALDEHYDES**			
a.	Carbonyl stretching			
	Saturated, aliphatic,	(s)	1740-1720	
	α,β-Unsaturated, aliphatic	(s)	1705-1680	
	Aryl	(s)	1715-1695	
b.	C–H stretching	(w)	2900-2820	and
	(two bands)	(w)	2775-2700	

Group	Intensity	Range/cm^{-1}
3. ESTERS		
a. Carbonyl stretching		
Saturated, acyclic	(s)	1750-1735
Saturated, cyclic:		
δ-lactones (and larger rings)	(s)	1750-1735
γ- lactones	(s)	1780-1760
β-lactones	(s)	1820
Unsaturated:		
Vinyl ester type	(s)	1800-1770
α,β-unsaturated and aryl	(s)	1730-1717
α-ketoesters	(s)	1755-1740
β-ketoesters (enolic)	(s)	1650
b. C–O stretching		
All types of esters stated above; one or two bands	(s)	1300-1050
4. CARBOXYLIC ACIDS		
a. Carbonyl stretching:		
Saturated aliphatic	(s)	1725-1700
α,β –unsaturated aliphatic	(s)	1715-1690
Aryl	(s)	1700-1680
b. Hydroxyl stretching (bonded), several bands	(w)	2700-2500
c. Carboxylate anion stretching	(s) (s)	1610-1550 and 1400-1300
5. AMIDES		
a. Carbonyl stretching		
Primary, solid and concentrated solution	(s)	1650
Primary, dilute solution	(s)	1690
Secondary, solid and concentrated solution	(s)	1680-1630
Secondary, dilute solution	(s)	1700-1670
Tertiary, solid and all solutions	(s)	1670-1630
b. N – H stretching		
Primary, free: two bands	(m) (m)	3500 and 3400
Primary, bonded: two bands	(m) (m)	3350 and 3180
Secondary, free: one band	(m)	3430
Secondary,bonded: one band	(m)	3320-3140

Group	Intensity	Range/cm^{-1}	
c. N–H bending			
Primary amides, dilute solution	(s)	1620-1590	
Secondary amides, dilute solution	(s)	1550-1510	
C. Miscellaneous chromophoric groups			
1. ALCOHOLS AND PHENOLS			
a. O–H stretching			
Free O–H	(v, sh)	3700-3600	
Intermolecularly hydrogen bonded (changes on dilution)			
single bridge compounds	(v, sh)	3550-3450	
Polymeric association	(s, b)	3400-3300	
Intramolecularly hydrogen bonded (no change on dilution)			
Single bridge compounds	(v, sh)	3570-3450	
Chelate compounds	(w,b)	3200-2500	
b. O–H bending and C–O stretching			
Primary alcohols	(s) (s)	1050 1350-1260	and
Secondary alcohols	(s) (s)	1100 1350-1260	and
Tertiary alcohols	(s) (s)	1150 1410-1310	and
Phenols	(s) (s)	1200 1410-1310	and
2. Ethers			
C–O stretching			
Dialkyl ethers	(s)	1150-1070	
Alkyl vinyl ethers or alkyl phenyl ethers	(s) (s)	1275-1200 1075-1020	and
3. AMINES			
a. N–H stretching			
Primary, free; two bands	(m) (m)	3500 3400	and
Secondary, free; one band	(m)	3500-3310	
Imines (=N–H); one band	(m)	3400-3300	
b. N–H bending			
Primary	(s-m)	1650-1590	
Secondary	(w)	1650-1550	

	Group	Intensity	Range/cm^{-1}	
c.	C–N stretching			
	Aromatic, primary	(s)	1340-1250	
	Aromatic, secondary	(s)	1350-1280	
	Aromatic, tertiary	(s)	1360-1310	
	Aliphatic	(w) (w)	1220-1020 1410	and
4.	**UNSATURATED NITROGEN COMPOUNDS**			
a.	C≡N stretching Alkyl nitriles	(m)	2260-2240	
	α,β – Unsaturated alkyl nitriles	(m)	2235-2215	
	Aryl nitriles	(m)	2240-2220	
b.	C=N stretching (imines, oximes)			
	Alkyl compounds	(v)	1690-1640	
	α,β – Unsaturated compounds	(v)	1660-1630	
c.	C–NO_2, Nitro compounds			
	aromatic	(s) (s)	1570-1500 1370-1300	and
	aliphatic	(s) (s)	1570-1550 1380-1370	and
5.	**HALOGEN COMPOUNDS**			
	C–X stretching			
a.	C–F	(s)	1400-1000	
b.	C–Cl	(s)	800-600	
c.	C–Br	(s)	600-500	
d.	C–I	(s)	500	
6.	**SULFUR COMPOUNDS**			
a.	S–H stretching	(w)	2600-2550	
b.	C=S stretching	(s)	1200-1050	
c.	S=O stretching			
	Sulfonamides	(s) (s)	1180-1140 1350-1300	and
	Sulfonic acids	(s) (s) (s)	1210-1150 1060-1030 650	and

Abbreviations: s = strong, m = medium, w = weak, v = variable
b = broad, sh = sharp.

Now we will investigate in a detailed way the characteristic regions of IR absorption using which it is possible to identify the functional groups. We know that IR region falls between wavenumbers 4000 cm^{-1} and 600 cm^{-1}. The whole region can be divided

into **four distinct regions** to facilitate easy identification of functional groups in a polyatomic organic molecule. The four distinct regions of absorption are given below:

$4000 - 2500\ cm^{-1}$
$2500 - 2000\ cm^{-1}$
$2000 - 1500\ cm^{-1}$
$1500 - 600\ cm^{-1}$

$4000 - 2500\ cm^{-1}$ region

The absorption occurring due to stretching of X–H bond (X = O, N and C) falls in this region. For organic compounds, the stretching vibrations noticed in this region invariably point out the presence of O–H, N–H or C–H. This region extends upto $2500\ cm^{-1}$

The **O–H stretching** band occurs at $3700 - 3600\ cm^{-1}$ when not involved in hydrogen bonding. It is a relatively broad band. The O–H group of alcohols and phenols gives absorption in this region. Regarding the O–H stretching frequency of carboxylic acids, we shall discuss shortly under hydrogen bonding effect in Subsec. 5.5.3. The **N–H stretching** can be noticed between 3500 and $3100\ cm^{-1}$. The amines and amides give absorption in this region. The primary amines (having $-NH_2$ group) show a doublet structure (two sharp bands), while secondary amines, (having > N–H group) give only one sharp band. The tertiary amines understandably do not show absorption as these do not have N–H bond.

The **C–H stretching** from aliphatic compounds also occur in the range of 3300-2850 cm^{-1}. They are moderately broad. A little care has to be exercised while identifying C–H stretching, because C–H stretching of aromatic compounds occur as shoulder above $3000\ cm^{-1}$. To be precise, the shoulder of aromatic hydrogen atoms can be noticed around $3030\ cm^{-1}$. The antisymmetric and symmetric stretchings of methylene (> CH_2) and methyl ($-CH_3$) groups can be seen between 2965 and 2880 cm^{-1}. The C–H stretching vibrations of alkenes occur between 3100 and $3000\ cm^{-1}$ while those of alkynes occur around $3300\ cm^{-1}$.

$2500 - 2000\ cm^{-1}$ region

The compounds containing triple bond absorb in this region. The triple bond corresponds to bond order three. The strength of the bond and hence the force constant is high. Since the vibrational frequency is directly proportional to the square root of force constant, the triple bonds absorb at higher frequency as compared to double and single bonds.

The **carbon-carbon triple bond** ($-C\equiv C-$) absorbs between 2300 and $2100\ cm^{-1}$. The band is normally of weak intensity. The nitrile group absorbs between $2300 - 2200\ cm^{-1}$. Further the band due to nitrile group is of medium intensity. Only by the intensities of the bands, these two groups can be distinguished. The change involved in dipole moment is greater for $-C\equiv N$ group than for $-C\equiv C-$ group. This is the reason for greater intensity of band for $-C\equiv N$ than for $-C\equiv C-$ group.

2000 – 1500 cm^{-1} region

All compounds having double bond show absorption in this region. The groups which exhibit significant absorption in this region are >C = C< and >C = O. Among these two, the C = O stretching is easy to recognise in the IR spectra. It is an intense band observed between 1830 and 1650 cm^{-1}. This absorption helps in identifying carbonyl group in organic compounds.The C = C stretch is much weaker in character and can be noticed around 1650 cm^{-1}

1500 –600 cm^{-1} region

We have so far dealt with the groups which absorb above 1500 cm^{-1}. It is also easy to assign the bands above 1500 cm^{-1} to a particular group. But below 1500 cm^{-1}, it will not be easy to assign the bands. Especially in the region 1450-900 cm^{-1}, even structurally similar molecules give different absorption patterns. This is the reason for referring to this region as **fingerprint region.**

In this region, many of the single bonds such as C-C, C-N, C-O absorb, apart from absorptions due to **skeletal vibrations** mentioned at the beginning of this section. Further, there will also be coupling of vibrational bands. For example, C – C stretching frequencies can couple with C – H bending vibrations. Much useful information can be derived from the finger print region. We shall now see briefly the characteristic absorption in this region.

i) The C – H stretching is between 1400-1000 cm^{-1} and it is an intense band.

ii) The aromatic rings and alkenes in general give rise to out-of-plane C – H bending vibrations and can be seen between 1000-700 cm^{-1}.

iii) In substituted benzenes, the spectral pattern in this region give information whether it is monosubstituted or 1,2-,1,3- or 1,4- disubstituted. This is because C-H bonds adjacent to these substituted positions appear distinctively in 850-690 cm^{-1} region. The position of absorption band varies with respect to substitution pattern as shown below:

Monosubstituted	750 cm^{-1} and 700 cm^{-1}
o-disubstituted	750 cm^{-1}
m-disubstituted	780 cm^{-1}
p-disubstituted	830 cm^{-1}

iv) The compound containing *gem*-dimethyl groups ($>C(CH_3)_2$) has a doublet band at about 1375 cm^{-1}.

v) The compound containing a chain of at least four methylene groups shows band at 720 cm^{-1}.

We shall discuss the applications of IR spectra in structure determination in Sec 5.6.

SAQ 4

The infrared spectrum of 2-methyl propan-1-ol has the following absorption bands:

3400 cm^{-1}	(broad)
2960 cm^{-1}	(medium)

1450 cm^{-1} (medium)

1380 cm^{-1} } (sharp doublet)

1370 cm^{-1} }

1050 cm^{-1} (sharp)

Indicate the groups responsible for these bands.

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5.5 PERTURBATION OF GROUP FREQUENCIES

The frequency of a particular IR band can be altered due to isotopic substitution, electronic effects, hydrogen bonding or steric effect. These aspects are to be understood carefully in order to derive useful information from the infrared spectra of compounds.

5.5.1 Mass Effect

The isotopic substitution causes a change in the reduced mass of a functional group. Since the vibrational wavenumber is related to the masses of atoms, the change in reduced mass causes a change in the wavenumber of absorption. Let us illustrate this by seeing the effect of deuterium substitution on the wavenumber of absorption of C–H bond.

$$\frac{\bar{\nu}_{C-D}}{\bar{\nu}_{C-H}} = \left(\frac{\mu_{C-H}}{\mu_{C-D}}\right)^{1/2} = \left(\frac{m_C \cdot m_H}{N_A (m_C + m_H)} \cdot \frac{(m_C + m_D) N_A}{m_C \cdot m_D}\right)^{1/2}$$

$$= \left(\frac{m_H}{(m_C + m_H)} \cdot \frac{(m_C + m_D)}{m_D}\right)^{1/2}$$

$\bar{\nu}$ is proportional to $\mu^{1/2}$ since,

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

where m_C, m_H and m_D are the atomic masses of carbon, hydrogen and deuterium and N_A is the Avogadro constant.

$$\frac{\bar{\nu}_{C-D}}{\bar{\nu}_{C-H}} = \left(\frac{1 \times (12 + 2)}{(12 + 1) \times 2}\right)^{1/2}$$

$$= \left(\frac{14}{13 \times 2}\right)^{1/2} = 0.7338$$

Hence, $\bar{\nu}_{C-D} = 0.7338\ \bar{\nu}_{C-H}$

$= (0.7338 \times 2900)\ cm^{-1}$ (since $\bar{\nu}_{C-H} = 2900\ cm^{-1}$)

$= 2128\ cm^{-1}$

Thus, we see that the substitution of heavier isotope reduces the vibrational frequency of a bond. This aspect is of much value in the IR spectral analysis of compounds and in the assignment of IR frequencies to a particular mode of vibration. Two more examples of the effect of isotopic substitution on IR frequency are given below. The

observed and the calculated values given below are those obtained experimentally and calculated (using the relationship between $\bar{\nu}$ and $\mu^{1/2}$).

Stretching vibration :	O–H	3620 cm^{-1}	(observed)
	O–D	2634 cm^{-1}	(calculated)
	O–D	2630 cm^{-1}	(observed)
Bending vibration :	C=C–H	815 cm^{-1}	(observed)
	C=C–D	598 cm^{-1}	(calculated)
	C=C–D	678 cm^{-1}	(observed)

5.5.2 Electronic Effects

Let us see the effect of electron withdrawing or donating groups on the IR absorption frequency of a particular group. Before we study this, it is advisable to recapitulate what you may have studied in Unit 5 of Organic Chemistry (CHE-05) course regarding electronic effects.

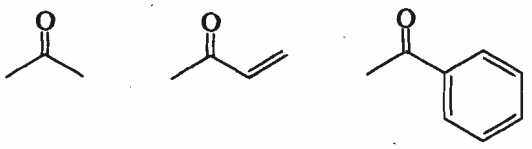
(i) Inductive effect

The inductive effect acts through the sigma (σ) electrons or bonds in a molecule. Inductive effect is felt only at short distances and it weakens as the length of the carbon chain increases. The groups which withdraw electron density from the neighbouring atoms in a saturated carbon chain are called $-I$ groups and those which enhance electron density, the $+I$ groups. A list of $-I$ and $+I$ groups are given in Table 5.2 in Unit 5 of CHE-05 course.

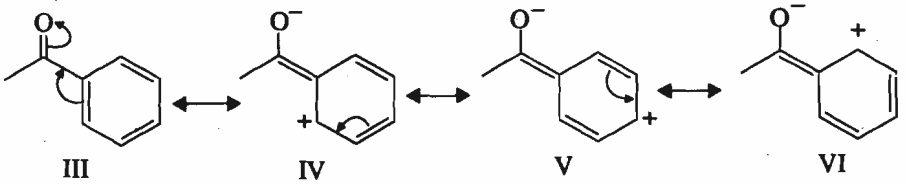
(ii) Resonance effect

In contrast to the inductive effect, the resonance effect acts through the *pi* bonds. The groups which withdraw electrons through *pi* bonds are $-R$ groups while those which donate electrons are $+R$ groups. A list of $+R$ and $-R$ groups are given in Table 5.6 of Unit 5 of CHE-05 course. While trying to see the influence of electronic effects on the IR frequency of a group, we have to bear in mind the following principles:

- Any substituent which enhances bond order (or shortens the bond length)in a group, causes an increase in IR frequency; if the substituent causes a decrease in bond order (or enhances the bond length), a decrease in IR frequency of the group results.
- If the inductive and resonance effects operate in opposite ways, then the one having predominant influence decides the IR frequency value.



Carbonyl frequency	1720 cm^{-1}	1700 cm^{-1}	1700 cm^{-1}
	I	II	III



III IV V VI

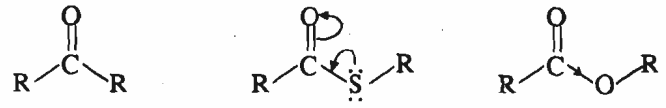
Let us consider a few examples. The carbonyl frequencies of I, II and III can be rationalised by realising that $+R$ nature of the vinyl ($-CH = CH_2$) and phenyl groups have a dominating influence over their $-I$ nature. For instance, the resonance effect in III operates to decrease the bond order of the carbonyl group as per structures IV, V and VI. This could explain the lower carbonyl frequency in III as compared to I.

As an example for the change in absorption frequency caused by the inductive effect, we can see that the aldehydes have higher carbonyl absorption frequency than ketones have. The additional alkyl group in ketones which has $+I$ nature causes a decrease in C = O frequency.

(R is alkyl group)

Carbonyl frequency	Around 1735 cm^{-1}	Around 1720 cm^{-1}
	VII	VIII

As another example, we can compare the carbonyl group frequencies of the ketone (VIII) with those of the thiol ester (IX) and the ester (X).



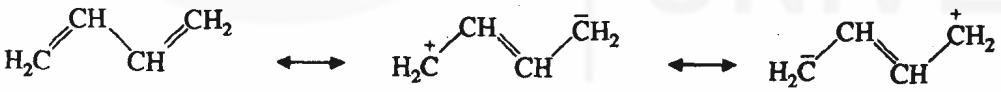
Carbonyl frequency	Around 1720 cm^{-1}	Around 1690 cm^{-1}	Around 1740 cm^{-1}	
	VIII	IX	X	(+R > −I of S) (+R < −I of O)

The $+R$ nature of sulphur atom is more than its $-I$ nature which leads to loss of double bond character of the carbonyl group in the thiol ester. This accounts for the lower frequency of the carbonyl group in the thiol ester IX as compared to VIII. On the other hand, in the case of ester X, the $-I$ effect of oxygen atom dominates over its $+R$ nature. This results in the shortening of the carbonyl bond in X and in the increase of carbonyl frequency as compared to VIII.

The role of conjugation in resonance effect can be illustrated using the IR frequency values of XI and XII.

C=C frequency	1650 cm^{-1}	1610 cm^{-1}
	XI	XII

The frequency of >C = C< group in XII decreases due to the following resonance structures (XIII and XIV)wherein the terminal bonds have bond order value between one and two.



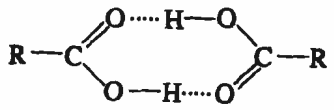
XII XIII XIV

5.5.3 Effect of Hydrogen Bonding

Hydrogen bonding can occur in any system containing a proton donor group (X – H) and a proton acceptor (Y), if the *s* oribital of the proton can overlap effectively with the *p* orbital of the acceptor group. Atoms X and Y are electronegative and, Y possesses lone pair of electrons.

The common proton donor groups in organic molecules are carboxyl, hydroxyl, amino or amido groups. Common proton acceptor atoms are oxygen, nitrogen and the halogens. Unsaturated groups like the ethylenic linkage can also function as proton acceptors. Hydrogen bonding alters the force constant of both the groups and, stretching and bending frequencies are altered. Because of hydrogen bonding, the X–H stretching bands move to lower frequencies with increased intensity and band widening. The stretching frequency of the acceptor group, for example, of the >C=O group is also reduced but to a lesser degree than the proton donor group. The X–H bending vibration usually shifts to higher frequency, when hydrogen bonding occurs.

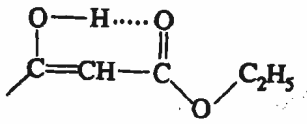
This shift is less pronounced compared to the stretching frequency shift.



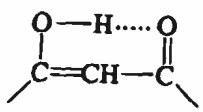
XV

There can be intermolecular or intramolecular hydrogen bonding. Intermolecular hydrogen bonding (or association)may result in dimer molecules or in polymers. For example, carboxylic acids form dimers (XV).

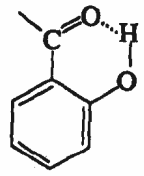
Intramolecular hydrogen bonding is possible in systems where 5 or 6 membered ring formation is possible as in XVI, XVII and XVIII.



XVI



XVII



XVIII

Intermolecular hydrogen bonding (or association)is affected by concentration change and temperature change, whereas these factors do not influence intramolecular hydrogen bonding. As a result of this, dilution or temperature change can alter the IR spectral pattern of associated molecules. For instance, dilution reduces the possibility of dimer or polymer formation. So at low concentrations, intermolecular hydrogen bonding possibility becomes less and the intensity of the corresponding absorption band also becomes less. This can be illustrated as follows:

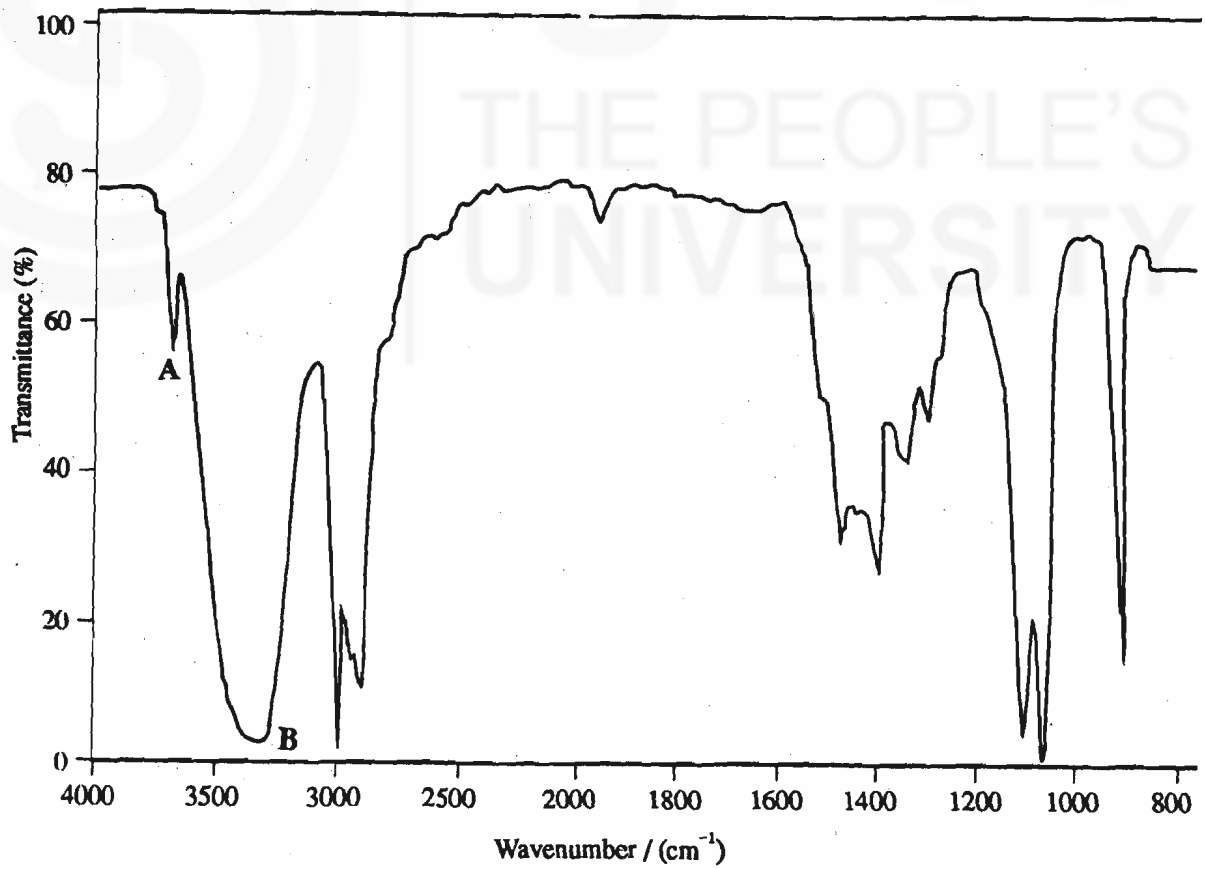


Fig.5.9 : Infrared spectrum of ethanol (10% *V/V* in CCl_4).

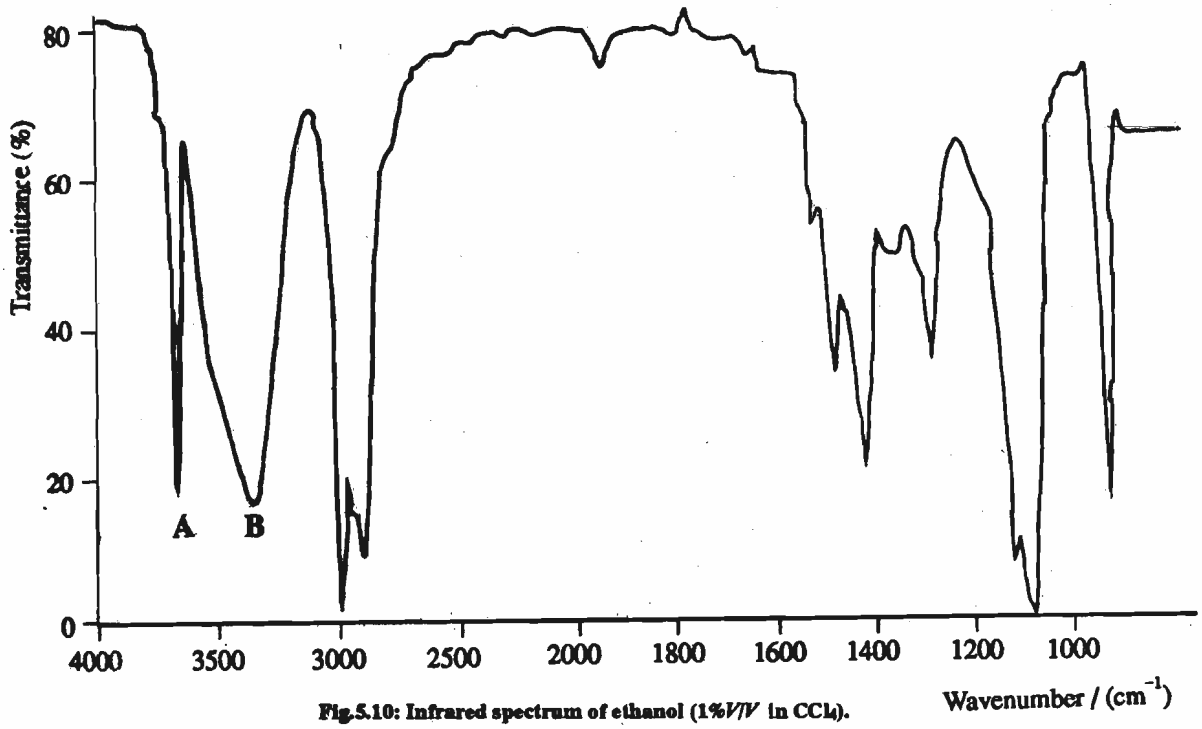


Fig.5.10: Infrared spectrum of ethanol (1%*V/V* in CCl_4).

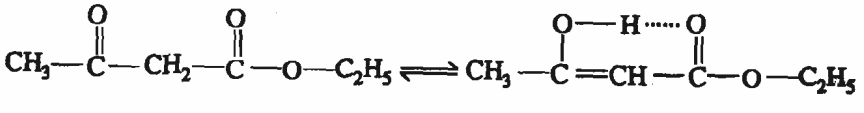
The IR spectra of both 10% and 1% ethanol in CCl_4 show the effect of concentration on intermolecular H-bonding. Figs.5.9 and 5.10 show these spectra. In Fig.5.9, the 10% ethanol solution has one sharp absorption at 3640 cm^{-1} (A) and a strong broad absorption at 3340 cm^{-1} (B). Two such peaks are also noticed in Fig.5.10 for 1% ethanol. However in 1% ethanol, the sharp band at 3640 cm^{-1} (A) has increased intensity and, to balance this, the intensity of the broad band at 3340 cm^{-1} is less. From these considerations, the sharp band has been taken to be due to monomeric form of ethanol (O–H bond unassociated) and broad band due to the polymeric form (O–H bond associated). The amount of monomer or unassociated alcohol has increased on dilution resulting in the gain of intensity of sharp band (at 3640 cm^{-1}) relative to the broad band (at 3340 cm^{-1}).

The effect of temperature on intermolecular H-bonding is similar to the one noticed in the case of concentration. The association of molecules is prevented at higher temperatures and so the increase in the intensity of sharp band at 3640 cm^{-1} is noticed. It is desirable to determine the spectra of a sample under different conditions of physical state or concentration. In very dilute solution or in the vapour phase, molecular association effects are minimised, whereas in solid state or in concentrated solution, molecular association effects are considerable. For example in the IR spectrum of pure liquid acetic acid, C = O stretching is seen at 1718 cm^{-1}; in the vapour phase, two carbonyl bands are seen at 1733 cm^{-1} and 1786 cm^{-1}. The C = O absorption in the liquid state is attributed to the dimer only, whereas, the two bands at 1733 cm^{-1} and 1786 cm^{-1} in the vapour state are due to the dimer and monomer, respectively. The absorption caused by free O–H stretching of a carboxylic acid is observed near 3550 cm^{-1} whereas the bonded O – H in the dimeric form absorbs in the region 2700-2500 cm^{-1}. Also when a carbonyl group is involved in intramolecular hydrogen bonding, it has lower stretching frequency. For instance, acetophenone (III) has carbonyl absorption at 1700 cm^{-1} whereas 2-hydroxyacetophenone (XVIII) which has intramolecular hydrogen bonding has carbonyl absorption band at 1635 cm^{-1}, showing a decrease of 65 cm^{-1}.

The existence of keto and enol forms can be understood in terms of the effect of hydrogen bonding on IR spectral frequencies. For instance, ethyl acetoacetate which has both keto and enol forms shows absorption characteristic of both the forms.

1724 cm^{-1} keto carbonyl } keto form (XIX)
1748 cm^{-1} ester carbonyl }

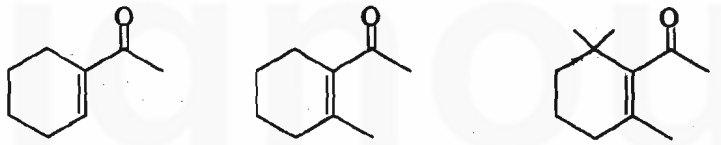
1650 cm^{-1} ester carbonyl enol form (XVI)



(XIX) (XVI)

5.5.4 Steric Effect

The steric effect arises due to spatial interactions between the groups. This has been discussed in detail in Subsec. 5.4.5 of Unit 5 of Block 1 of Organic Chemistry course. The most common instance of steric effect is that which arises when the bulky groups are present near a reactive group. Let us state an example. Generally, the resonance effect lowers the frequency of a carbonyl band as mentioned in the case of I, II and III in Subsec. 5.5.2 above. In order that the resonance forms may exist, there should be coplanarity between the >C = C< and >C = O groups. If the coplanarity is prevented due to steric effect, then the resonance structures (such as III to VI) may not be possible, which means interaction between >C=C< and >C=O groups is reduced. Consequently, the steric inhibition of resonance in XXI and (more so in) XXII causes the carbonyl frequency to be higher than that in XX.



Carbonyl frequency 1663 cm^{-1} 1686 cm^{-1} 1693 cm^{-1}

XX XXI XXII

Thus we have seen in this section the perturbation of group frequencies due to structural features. Answer the following SAQ's.

SAQ 5

Arrange the following compounds in the increasing order of carbonyl frequency:

Acetophenone, *p*-methoxyacetophenone and *p*-nitroacetophenone.

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SAQ 6

The infrared spectrum of 1-butanol (liquid film) has single broad band between 3500-3200 cm^{-1}; when it is diluted with CCl_4, it shows an additional band near 3650 cm^{-1}. Explain the reason.

Hint: 'Liquid film' means pure liquid is taken for spectral study without adding any solvent.

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5.6 APPLICATIONS OF IR SPECTRA IN STRUCTURE DETERMINATION

The infrared spectra find a wide range of applications. For instance, structure determination, quantitative analysis, hydrogen bonding studies and conformational studies are some of the fields where infrared spectra play a vital role. The method of determination of structure of simple inorganic compounds will be discussed in Unit 6 using IR and Raman spectral data. In this section, we shall discuss the role of IR spectra in arriving at the structure of organic compounds.

The matching of the IR spectrum of an unknown compound with those of known compounds provides the best means of structure identification of organic compounds. The finger print region could be particularly useful for this purpose. Infrared correlation charts such as Table 5.3 could be used to identify the hydrocarbon skeleton and the functional groups present in a molecule. To be sure of the structure of a compound, data from IR spectra should be supported by other evidences like its chemical, physical or other spectroscopic data (NMR,UV etc).

For instance in Unit 13 of this course, we shall come across many interesting problems of structure determination using a collection of spectral data. A preliminary assessment of structural details could be made using IR spectral data. For this you have to spend some time in finding the answers for the following questions.

I Hydrocarbon skeleton

Look for IR data indicating the presence of alkane, alkene, alkyne and aromatic residues. For doing this effectively, compare the IR spectral data of the compound with the entries under ' A. Hydrocarbon chromophore' of Table 5.3 and find the answers for the following questions:

(i) What is the type of hydrocarbon skeleton?

(ii) Is there any special features in the IR spectrum which throw light on substitution pattern?

You can arrive at the hydrocarbon skeleton using C–H stretching, C–H bending and C–C multiple bond stretching absorptions.

Look for specific indications regarding the type of aromatic substitution, *cis-trans* isomers, presence of *gem*-dimethyl groups etc.

II Functional groups

The nature of functional groups can be decided from the answers to the following questions.

(i) Does the compound have carbonyl group(s)?

Look for sharp IR band(s) in the region 1800-1600 cm^{-1}. If you find one such, answer the questions (a) to (e) given below.

(a) Does the spectrum have C–H stretching characteristic of an aldehyde?

(b) Does the spectrum have C–O stretching characteristic of an ester (or lactone)?

(c) Does the spectrum have O–H stretching characteristic of – COOH group?

(d) Does it show N–H stretching and bending vibrations characteristic of amides?

(e) Could it be a ketone only?

Remember that the compound could have two carbonyl groups even. Note down the inferences and find the answers for the following questions also.

(ii) Does it show O–H stretching, O–H bending and C–O stretching bands characteristic of alcohols or phenols?

(iii) Does it show only C–O absorption without O–H stretching band (which is characteristic of ethers)?

(iv) Does it show N–H stretching, N–H bending and C–N vibrations characteristic of amines?

(v) Does it have vibrations characteristic of $-C\equiv N$, $>C=N-$ or $-NO_2$ groups?

(vi) Does it have S–H, C = S or S = O vibrations characteristic of thiols, thioacids, sulphonyl derivatives etc.?

III Some special features regarding structure

The answer to the following question can throw light on some structural aspects:

Does the spectrum show any special features which bring out the presence of tautomers, intramolecular hydrogen bonding, intermolecular hydrogen bonding etc.?

The answers to the above questions provide us information regarding hydrocarbon skeleton and the functional groups present in the compound. Let us work out three problems using the above approach.

Example 1

A compound of molecular formula C_7H_8 has IR bands at the following frequencies:

3050 cm^{-1}

2900 cm^{-1}

1600 cm^{-1}

1500 cm^{-1}

1430 cm^{-1}

1380 cm^{-1}

750 cm^{-1}

700 cm^{-1}

Suggest a possible structure for the compound.

We have to look for the answers for only the questions relating to the hydrocarbon skeleton, since the molecular formula suggests that it is a hydrocarbon and it cannot have any specific functional group.

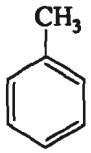
Hydrocarbon skeleton

The presence of aromatic ring is indicated by the presence of bands at 3050 cm^{-1} (aromatic C–H stretching) and at 1600 cm^{-1} and 1500 cm^{-1} (C–C multiple bond stretching of the aromatic ring). The presence of $-CH_3$ and or $>CH_2$ groups is hinted by the absorptions at 2900 cm^{-1} (aliphatic C–H stretching) and at 1430 cm^{-1} and 1380 cm^{-1} (aliphatic C – H bending).

Substitution type

The absorptions at 750 cm^{-1} and 700 cm^{-1} show the presence of monosubstituted benzene ring (C_6H_5-).

Since the molecular formula is C_7H_8 we can infer that it has a $-C_6H_5$ group and a $-CH_3$ group ($C_7H_8 - C_6H_5 = CH_3$). Hence, the possible structure of the compound is



This needs confirmation through NMR data.

Example 2

A compound has molecular formula C_4H_8O. The NMR spectrum shows the presence of two methyl groups and one methylene group. Further NMR spectrum excludes the possibility of aldehyde group. The IR spectrum shows the following prominent bands:

2941-2850 cm^{-1}	(medium)
1716 cm^{-1}	(sharp)
1459 cm^{-1}	(medium)

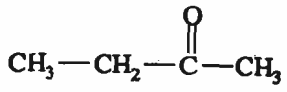
Arrive at the structure of the compound.

Hydrocarbon skeleton

The hydrocarbon skeleton is of alkane type since the C–H stretching (2941-2850 cm^{-1}) and bending vibrations (1459 cm^{-1}) indicate the presence of one or more $-CH_3$ and $>CH_2$ groups.

Functional group

The absorption at 1716 cm^{-1} shows the presence of $>C=O$ group. The molecular formula indicates the presence of only one oxygen atom and this, in conjunction with IR band at 1716 cm^{-1} indicates that the compound should be an aldehyde or a ketone. Since NMR spectrum excludes the presence of aldehyde group, the structure of the compound is



This structure is in line with NMR spectral data which show the presence of two $-CH_3$ groups and one $>CH_2$ group. This example will be discussed again with detailed NMR data in Unit 13 (as problem 1).

Example 3

A compound of molecular formula $C_9H_{10}O_2$ yields the following IR data:

3022 cm^{-1} (weak)

2940 cm^{-1} (weak)

1730 cm^{-1} (sharp)

1605 cm^{-1} and 1504 cm^{-1} (weak)

1060 cm^{-1} (sharp)

835 cm^{-1} (sharp)

NMR data provides information regarding the presence of two $-CH_3$ groups and one $>C_6H_4$ group. Suggest possible structures.

The structures can be arrived at as follows.

Hydrocarbon skeleton

The absorptions at 3022 cm^{-1}, 1605 cm^{-1} and 1504 cm^{-1} bring out the presence of aromatic ring. Further the absorption at 2940 cm^{-1} is suggestive of the presence of one or more $-CH_3$ and or $>CH_2$ groups.

Substitution type

The band at 835 cm^{-1} is indicative of *p*- disubstitution.

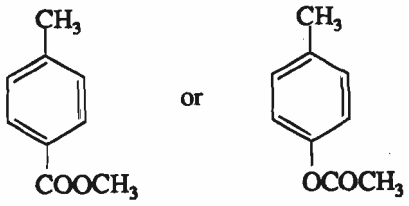
Functional group

The absorptions at 1730 cm^{-1} and 1060 cm^{-1} indicate the presence of ester group.

On the basis of available IR and NMR data, we can conclude that the compound has (i) $p-C_6H_4$ group (ii) two methyl groups and (iii) one ester group.

Possibly one of the methyl groups is attached directly to the benzene ring and another methyl group forms part of the ester group, i.e., either as $-COOCH_3$ or CH_3COO-

As it is, the two possible structures are:



More evidences are required to take a clear decision regarding structure.

From the above examples, you can understand that IR data could give vital clues regarding the hydrocarbon skeleton and the functional groups. For arriving at the exact structure, more spectral data are required.

Answer the following SAQ.

SAQ 7

A compound has the molecular formula C_7H_5N. It has the following absorption bands:

3050 cm^{-1}

2240 cm^{-1}

1600 cm^{-1}

1500 cm^{-1}

750 cm^{-1}

700 cm^{-1}

Arrive at the structure of the compound.

.....

.....

.....

5.7 SUMMARY

In this unit we discussed the method of calculation of vibrational degrees of freedom of linear and nonlinear polyatomic molecules. We explained the IR spectra of H_2O and CO_2. The use of the chart of group frequencies has been stated. The perturbation of group frequencies arising out of mass effect, electronic effects, hydrogen bonding and steric effect has been discussed. Finally the method of using IR spectra for determination of structure of organic compounds has been illustrated. In the Appendix portion, we have explained the steps involved in ascertaining the IR active vibrations. For this purpose, group theory is being made use of.

5.8 TERMINAL QUESTIONS

1. Calculate the number of stretching and bending modes of PF_3 and CH_4.
2. SiF_2 vapour is angular in shape and it belongs to C_{2v} group. The frequencies for its symmetric stretching, symmetric bending and antisymmetric stretching modes are 855 cm^{-1}, 345 cm^{-1} and 872 cm^{-1}, respectively. Calculate its total zero point energy.
3. The infrared spectrum of nonane has the following three prominent bands: 2960 cm^{-1}, 1450 cm^{-1} and 1370 cm^{-1}. Identify the groups responsible for these absorptions.
4. The infrared spectrum of $CH_3 - \overset{\overset{O}{\|}}{C} - SH$ has the following prominent bands:

2960 cm^{-1}
2500 cm^{-1}

1700 cm^{-1}

1450 cm^{-1}

1380 cm^{-1}

Indicate the groups responsible for these bands.

5. Explain the following:

   a) The C=O frequency in acyl chlorides is higher than that in alkyl esters.

   b) The C=O frequency in methyl acetate is less than that in phenyl acetate.

6. 2,4-Pentanedione shows a broad band stretching from 3400 cm^{-1} to 2400 cm^{-1} which is unchanged on dilution. Try to identify this band.

7. A compound has the molecular formula $C_4H_{10}O$. It has no prominent absorption bands above 3000 cm^{-1}, in the region 2900-1500 cm^{-1} or below 1000 cm^{-1}. The main absorption bands are given below:

2970 cm^{-1}	
1450 cm^{-1}	
1370 cm^{-1}	Separate bands - no doublet
1100 cm^{-1}	

Suggest possible structures for the compound.

5.9 ANSWERS

Self Assessment Questions

1. A linear molecule has $(N-1)$stretching and $(2N-4)$bending vibrations. Since N is four for C_2H_2, there are three stretching and four bending vibrations.

2. $E(000) = hc[(0 + 1/2)\bar{\nu}_1 + (0 + 1)\bar{\nu}_2 + (0 + 1/2)\bar{\nu}_3]\ J$

   $= 6.626 \times 10^{-34} \times 3 \times 10^8 \times 10^2\ [(1340 \times 1/2) + 667 + (2349 \times 1/2)]\ J$

   $= 4.992 \times 10^{-20}\ J$

   The factor 10^2 is used to convert cm^{-1} into m^{-1}.

3. The first and the second overtones of ν_2 appear at 1334 cm^{-1} and 2001 cm^{-1}.

4. | | | |
   |---|---|---|
   | 3400 cm^{-1} | | O – H stretching |
   | 2960 cm^{-1} | | C – H stretching of $-CH_3$ and $>CH_2$ groups |
   | 1450 cm^{-1} | | C – H bending of $>CH_2$ group |
   | 1380 cm^{-1} / 1370 cm^{-1} | and | C – H bending of *gem*-dimethyl groups |
   | 1050 cm^{-1} | | O – H bending and C – O stretching |

5. *p*-methoxyacetophenone < acetophenone < *p*-nitroacetophenone.

   The $+R$ nature of $-OCH_3$ group and $-R$ nature of *p*-nitro group which interact with the carbonyl group result in the change in the carbonyl frequency as mentioned above.

6. The single broad band of the pure alcohol is due to associated –O–H group. On dilution, the free –O–H group stretching also appears.

7. **Hydrocarbon skeleton**

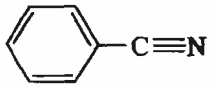
The presence of aromatic ring is brought out by the presence of bands at 3050 cm^{-1} (aromatic C – H stretching). The absorptions at 1600 cm^{-1} and 1500 cm^{-1} are due to C – C multiple bond stretching of the aromatic ring.

Substitution type

The bands at 750 cm^{-1} and 700 cm^{-1} (C – H bending) are characteristic of monosubstituted benzene ring.

Functional group

The absorption at 2240 cm^{-1} brings out the presence of – C ≡ N group. Keeping in mind the molecular formula (C_7H_5N), the structure assigned is



Terminal Questions

		Stretching	Bending
1.	PF_3	3	3
	CH_4	4	5

2. The degeneracy is 1 for each of the three modes.

$$E\,(000) = hc\,[(\bar{\nu}_1 \times 1/2) + (\bar{\nu}_2 \times 1/2) + (\bar{\nu}_3 \times 1/2)]\,J$$
$$= 6.626 \times 10^{-34} \times 3 \times 10^8 \times 10^2\,[(855 \times 1/2) + (345 \times 1/2) + (872 \times 1/2)]\,J$$
$$= 2.059 \times 10^{-20}\,J$$

3. 2960 cm^{-1} (C–H stretching of $-CH_3$ and $>CH_2$ groups)

1450 cm^{-1}, 1370 cm^{-1} (C–H bending of $-CH_3$ and $>CH_2$ groups)

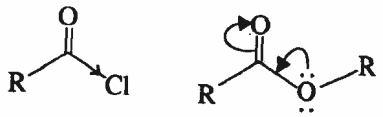
4. 2960 cm^{-1} C – H stretching of $-CH_3$ group

2500 cm^{-1} S – H stretching

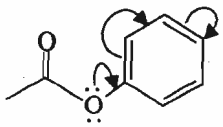
1700 cm^{-1} C = O stretching

1450 cm^{-1}, 1380 cm^{-1} and C – H bending of $-CH_3$ group

5. a) The dominance of *–I* nature over *+R* is more prominent in the case of chloro group than for –OR group. This may possibly be responsible for the higher carbonyl frequency in the case of acyl chlorides.



b) In phenyl acetate, the nonbonding pair on aryl oxygen is partly drawn into the ring and its conjugation with carbonyl group is diminished. When this happens in phenyl acetate, *–I* effect of oxygen becomes dominant and carbonyl group moves to higher frequency as compared to that in methyl acetate.



6. 2,4-Pentanedione exists in keto and enol forms. The broad band mentioned is due to the enolic O – H stretching which is involved in intramolecular hydrogen bonding.

7. **The carbon skeleton**

The C – H stretching absorption at 2970 cm^{-1}, and C – H bending absorptions at 1450 cm^{-1} and 1370 cm^{-1} indicate the presence of $-CH_3$ and $>CH_2$ groups. Absence of doublets around 1370 cm^{-1} rule out the possibility of *gem*-dimethyl or *t*-butyl branching.

Functional group

The absorption at 1100 cm^{-1} indicates ether linkage.

The two possible structures are given below:

$$CH_3 - CH_2 - O - CH_2 - CH_3$$

$$CH_3 - O - CH_2 - CH_2 - CH_3$$

5.10 APPENDIX

We can use group theory for finding the symmetry species of the normal modes of vibration of a molecule and also for determining the number of infrared active vibrations in a molecule. We can also associate the experimentally observed IR absorption bands with the vibrational modes. Using H_2O and NH_3 molecules as examples, we shall explain the steps involved in identifying the number of IR active vibrations of a molecule. In the Appendix of Unit 6, we shall explain how the assignment of frequencies to the vibrational modes is done by using IR and Raman spectra.

Analysis of IR spectra of molecules

You must recapitulate the group theory discussed in the Appendix of Unit 2 in order to understand the materials discussed here. Let us first state the steps involved in identifying the number of IR active vibrations of a molecule.

Step 1 : Find the reducible representation for all the symmetry operations of the molecule.

Step 2 : Obtaining the reducible representation of all the vibrations.

Step 3 : Obtain the symmetry species of the vibrational modes.

Step 4 : Identify the symmetry species of each vibrational mode.

Step 5 : Identify the infrared active vibrational modes.

Let us apply these steps to identify the IR active vibrations of H_2O molecule. You are aware that H_2O has the following symmetry operations :

$$E, C_2, \sigma_v(xz) \text{ and } \sigma'_v(yz).$$

Step 1 : Finding the reducible representation for all the symmetry operations of the molecule

We shall discuss a simple method to build the characters of a reducible representation

(R) of a molecule and then apply this to H_2O first and later to NH_3. The character $\chi_R^I(p)$ for a particular symmetry operation (p) in a reducible representation R is given by the product of

(i) The number of atoms (n_a) which are not shifted by the symmetry operation and

(ii) The contribution $\chi_R(p)$ that each unshifted atom makes to the character for a particular symmetry operation p in a reducible representation, R.

i.e., $$\chi_R^I(p) = n_a \cdot \chi_R(p) \quad \ldots(A.1)$$

n_a values

In case of water, n_a values for the symmetry operations, E, C_2, $\sigma_v(xz)$ and $\sigma_v'(yz)$ are given below:

(i) E does not shift any of the three atoms in H_2O and, $n_a = 3$.

(ii) C_2 rotation does not shift oxygen but interchanges two hydrogen atoms (see Fig.2.3 of Unit 2), i.e. $n_a = 1$.

(iii) $\sigma_v(xz)$ reflection does not shift any of the three atoms since this reflection is in the molecular plane (see Fig.2.7 of Unit 2), i.e., $n_a = 3$.

(iv) $\sigma_v'(yz)$ reflection does not shift oxygen atom whereas it shifts the two hydrogen atoms (see Fig. 2.7 of Unit 2), i.e., $n_a = 1$.

$\chi_R(p)$ values

The contribution $\chi_R(p)$ that each unshifted atom makes to the character for a particular symmetry operation p in a reducible representation can be obtained using Table A.1.

Table A.1 : $\chi_R(p)$ values

	Proper rotation		Improper rotation		
p	E	$C(\alpha)$	σ	$S(\alpha)$	i
$\chi_R(p)$	3	$1 + 2\cos\alpha$	1	$-1 + 2\cos\alpha$	-3

The proper rotation by $\alpha = 2\pi/n$ is denoted as $C(\alpha)$ while improper rotation by α is denoted as $S(\alpha)$. Note α is the minimum angle of rotation.

One must note that the identity operation E is equivalent to proper rotation through 2π and that the character $\chi_R(E)$ is a special case for proper rotation with $\alpha = 2\pi$. Similarly $\sigma = S(2\pi)$ with character $\chi_R(\sigma) = -1 + 2\cos 2\pi = 1$, and, $i = S(\pi)$ with character $\chi_R(i) = -1 + 2\cos\pi = -3$ are special cases of the general result for improper rotation, $S(\alpha)$. It is therefore only necessary to consider two kinds of symmetry operations, proper rotation $C(\alpha)$ and improper rotation, $S(\alpha)$. Further, the character, $\chi_R(C_2) = 1 + 2\cos\pi = -1$, since C_2 is proper rotation with $\alpha = \pi$.

The calculation of $\chi_R^I(p)$ for each symmetry operation can be done using Eq. A.1 as follows:

p	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	
$\chi_R(p)$	3	−1	1	1	
n_a	3	1	3	1	
$\chi_R^I(p)$ (using Eq. A.1)	9	−1	3	1	...(A.2)

Step 2: Obtaining the reducible representation of all the vibrations

In order to obtain the reducible representation of all the vibrational modes of H_2O molecule, we must subtract the characters of the symmetry operations in the irreducible representations of translations and rotations from the characters of symmetry operations given by Eq. A.2. The translations belong to B_1, B_2 and A_1 as per C_{2v} character table because they are influenced by the symmetry operations in the same way as x, y and z directions. Similarly the rotations belong to B_2, B_1 and A_2, since R_x, R_y and R_z belong to these three symmetry species as per C_{2v} character table.

Character Table of C_{2v} Group

	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$			Four classes of operations
A_1	1	1	1	1	z	x^2, y^2, z^2	
A_2	1	1	–1	–1		xy	R_z
B_1	1	–1	1	–1	x	xz	R_y
B_2	1	–1	–1	1	y	yz	R_x

Irreducible representations of C_{2v} group

From C_{2v} character table, the sum of the characters of the symmetry operations in the irreducible representations of translations is given by $B_1 + B_2 + A_1$.

	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$	
$B_1 + B_2 + A_1$	3	–1	1	1	...(A.3)

Similarly, the sum of the characters of the symmetry operations in the irreducible representations of rotations is given by $B_2 + B_1 + A_2$.

	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$	
$B_2 + B_1 + A_2$	3	–1	–1	–1	...(A.4)

Hence the characters of the symmetry operations in the reducible representation of vibrations (τ) is given by subtracting Eqs. A.3 and A.4 from Eq. A.2 as follows:

	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$	
$\chi^t_R(p)$	9	–1	3	1	
$-[(B_1 + B_2 + A_1)$	3	–1	1	1]	
$-[(B_2 + B_1 + A_2)$	3	–1	–1	–1]	
τ	3	1	3	1	...(A.5)

Eq. A.5 represents the characters of the symmetry operations ($\chi(p)$) in the reducible representation, τ.

Again τ represents the reducible representation of all the vibrational modes of H_2O molecule.

Step 3: Obtaining the symmetry species of the vibrational modes

In order to obtain the symmetry species of the vibrational modes, we have to split the reducible representation τ into various irreducible representations by using the reduction formula (Eq. A.6). Before stating the reduction formula, we should know the following:

Note that N is the number of operations in a class while h is the number of operations in a group.

(i) $\chi_I(p)$, the character for each symmetry operation in an irreducible representation I.

(ii) $\chi(p)$, the character for each symmetry operation in the reducible representation, τ.

(iii) N, the number of symmetry operations in a class (which is equal to the number of equivalent operations in the class).

The word 'class' will be explained shortly.

(iv) h, the order of the group (which is equal to the total number of operations in the group).

Obtaining the character $\chi_I(p)$ for each symmetry operation in an irreducible representation, I.

The entries below the operations, E, C_2, $\sigma_v(xz)$ and $\sigma'_v(yz)$ in the first row of the character table of C_{2v} group give the characters for these operations in the irreducible representation, A_1.

$$\chi_{A_1}(E) = 1$$

$$\chi_{A_1}(C_2) = 1$$

$$\chi_{A_1}(\sigma_v(xz)) = 1$$

$$\chi_{A_1}(\sigma'_v(yz)) = 1$$

You may revise the characteristics of the character tables A.2 and A.3 discussed in the Appendix part of Unit 2. Table A.2 of Unit 2 contains the sets of characters for the four symmetry operations, E, C_2, $\sigma_v(xz)$ and $\sigma'_v(yz)$ in the four irreducible representations, A_1, A_2, B_1 and B_2 of C_{2v} group. Table A.3 of Unit 2 contains the sets of characters for the three classes of symmetry operations in the three irreducible representations, A_1, A_2 and E of C_{3v} group.

Similarly the entries in the second row of the C_{2v} character table give the characters of the symmetry operations of C_{2v} group in the irreducible representation, A_2.

$$\chi_{A_2}(E) = 1$$

$$\chi_{A_2}(C_2) = 1$$

$$\chi_{A_2}(\sigma_v(xz)) = -1$$

$$\chi_{A_2}(\sigma'_v(yz)) = -1$$

The entries in the third and fourth rows of C_{2v} character table give the characters of the symmetry operations of C_{2v} group in the irreducible representations, B_1 and B_2, especively.

Obtaining the character $\chi(p)$ for each symmetry operation in the reducible representation τ.

In the reducible representation τ of C_{2v} group, the character for each symmetry operation is as indicated in Eq. A.5.

$$\left.\begin{aligned}\chi(E) &= 3\\ \chi(C_2) &= 1\\ \chi(\sigma_v(xz)) &= 3\\ \chi(\sigma'_v(yz)) &= 1\end{aligned}\right\} \qquad ...(A.5)$$

Obtaining the number of symmetry operations *(N)* in a Class

We denote the number of symmetry operations in a class as N. The term 'class' is better explained using the symmetry operations of C_{3v} group. We shall be presently using the materials of Secs. 2.4 and 2.5 of Unit 2. A set of operations are in the same class if they are equivalent operations. The word "equivalent operations" means that such operations lead to equivalent configurations of the molecule. For instance, C_3^1 and C_3^2 operations (mentioned in Sec. 2.4 of Unit 2) lead to equivalent configurations. Hence C_3^1 and C_3^2 are equivalent operations and these two operations belong to the same class. As mentioned in Sec. 2.5 of Unit 2, σ_v, σ'_v and σ''_v operations in NH_3 molecule are equivalent operations and each of these planes passes through nitrogen atom and a hydrogen atom and relates the other two hydrogen atoms as a mirror image of each other. Hence σ_v, σ'_v and σ''_v belong to the same class and $N = 3$ for this class. Also E is an operation which does not have any equivalent operation and hence E is a class in itself for which $N = 1$. Hence C_{3v} point group has three classes, E, $2C_3$ and $3\,\sigma_v$ with N values of 1, 2 and 3, respectively.

The characters of all elements in a class are same. Hence, only the characters of the classes are given in the character table. In C_{2v} character table, each element (i.e., symmetry operation) is a class . The four symmetry operations in C_{2v} group are four classes.

In C_{3v} group, E is a class in itself; the two C_3 operations, C_3^1 and C_3^2 constitute a class and are denoted as $2C_3$ in C_{3v} character table (given in Table A.3 in Unit 2 and also towards the end of this Appendix). Also the three operations, σ_v, σ'_v and σ''_v constitute another class and are denoted as $3\,\sigma_v$. Hence there are three classes in C_{3v} group.

In the case of H_2O (C_{2v} group), each of the four operations E, C_2, $\sigma_v(xz)$ and $\sigma'_v(yz)$ belongs to different class. Note that $\sigma_v(xz)$ in H_2O is in the molecular plane which contains both the hydrogen atoms and the oxygen atom while $\sigma'_v(yz)$ is perpendicular to $\sigma_v(xz)$ plane and it passes through only oxygen atom and relates the two hydrogen atoms as a mirror image of each other (Fig.2.7 of Unit 2). Hence there are four classes of operations in C_{2v} group each having $N = 1$.

Obtaining the order of the group *(h)*

Order of the group (h) is the total number of operations in a group. In C_{2v} group, there are four symmetry operations and hence, $h = 4$.

Having understood the terms required, we shall state the reduction formula which is useful in obtaining the symmetry species of the vibrational modes.

Reduction formula

$$\left.\begin{aligned}&\text{Number of times } (n_I) \text{ an}\\ &\text{irreducible representation } I\\ &\text{occurs in the reducible}\\ &\text{representation } (\tau)\end{aligned}\right\} = \frac{1}{h}\sum_{\substack{\text{over all}\\ \text{classes}}} \chi_I(p)\cdot\chi(p)\cdot N \qquad ...(A.6)$$

$\sum'$ means summation of the terms $\chi_I(p)\cdot\chi(p)\cdot N$ for all the classes of a point group.

Let us reduce the reducible representation τ of C_{2v} group into the irreducible representations, A_1, A_2, B_1 and B_2. Using the $\chi_I(p)$ values of A_1, A_2, B_1 and B_2 representations of C_{2v} group and knowing that (i) $h = 4$ for C_{2v} group and (ii) $N = 1$ for each of the four classes of operations in C_{2v} group, we can find out n_I for each of the four irreducible representations, I.

$$\left.\begin{aligned}&\text{Number of times } A_1 \text{ symmetry}\\ &\text{species occurs in}\\ &\text{representation } \tau\end{aligned}\right\} = n_{A_1}$$

$$= \frac{1}{4}\left[\underset{\downarrow}{\chi_{A_1}(E)}\ \underset{\downarrow}{\chi(E)}\ \underset{\downarrow}{N} \right.$$
$$\left. \underset{\leftarrow E \rightarrow}{(1 \times 3 \times 1)} + \underset{\leftarrow C_2 \rightarrow}{(1 \times 1 \times 1)} + \underset{\leftarrow \sigma_v(xz) \rightarrow}{(1 \times 3 \times 1)} + \underset{\leftarrow \sigma'_v(yz) \rightarrow}{(1 \times 1 \times 1)} \right]$$

$$= \frac{1}{4}[3 + 1 + 3 + 1] = 2$$

Hence, $n_{A_1} = 2$ or A_1 occurs twice in the reducible representation, τ.

Similarly,

$$n_{A_2} = \frac{1}{4}\left[\underset{\leftarrow E \rightarrow}{(1 \times 3 \times 1)} + \underset{\leftarrow C_2 \rightarrow}{(1 \times 1 \times 1)} + \underset{\leftarrow \sigma_v(xz) \rightarrow}{((-1) \times 3 \times 1)} + \underset{\leftarrow \sigma'_v(yz) \rightarrow}{((-1) \times 1 \times 1)}\right]$$

$$= \frac{1}{4}[3 + 1 - 3 - 1] = 0$$

i.e., A_2 does not occur in the reducible representation τ.

$$n_{B_1} = \frac{1}{4}\left[(1 \times 3 \times 1) + ((-1) \times 1 \times 1) + (1 \times 3 \times 1) + ((-1) \times 1 \times 1)\right]$$

$$= \frac{1}{4}[3 - 1 + 3 - 1] = 1$$

Hence, B_1 occurs once in the reducible representation, τ.

$$n_{B_2} = \frac{1}{4}\left[(1 \times 3 \times 1) + ((-1) \times 1 \times 1) + ((-1) \times 3 \times 1) + (1 \times 1 \times 1)\right]$$

$$= \frac{1}{4}[3 - 1 - 3 + 1] = 0$$

So, B_2 does not occur in the reducible representation, τ. In short τ can be split into $2A_1 + B_1$. In other words, symmetry species of vibrations = $2A_1 + B_1$.

In Sec. 5.2, we have mentioned that H_2O which is an angular triatomic molecule must have three vibrational modes, namely, symmetric stretching (ν_1) symmetric bending (ν_2) and antisymmetric stretching (ν_3).We now understand that two of these vibrations must belong to A_1 symmetry while the third one must belong to B_1 symmetry. In the next step, we shall identify the symmetry species of each mode of vibration.

Step 4 : Identifying the symmetry species of each vibrational mode

We arrive at the irreducible representations of symmetric stretching, symmetric bending and antisymmetric stretching modes by performance of the symmetry operations on the molecule.

Irreducible representation of symmetric stretching mode

We can identify the set of character values for each of the four operations E, C_2, $\sigma_v(xz)$ and $\sigma'_v(yz)$ over the symmetric stretching mode. If the performance of an operation does not change the direction of arrows in a stretching mode, 1 is given as the character value; but if the direction of arrows changes by the performance of an operation, –1 is given as the character value.

Note that there are four classes of operations in C_{2v} group. Hence there are four terms in the summation corresponding to four classes.

In the calculation of n_{A_1}, using Eq. A.6, there are four terms corresponding to E, C_2, $\sigma_v(xy)$ and $\sigma'_v(yz)$.

The first term marked,

$$\underset{\downarrow}{\chi_{A_1}(E)}\ \underset{\downarrow}{\chi(E)}\ \underset{\downarrow}{N}$$
$$\underset{\leftarrow E \rightarrow}{(1 \times 3 \times 1)}$$

stands for the application of the formula for the class of operation, E. This term is obtained using the relationships,

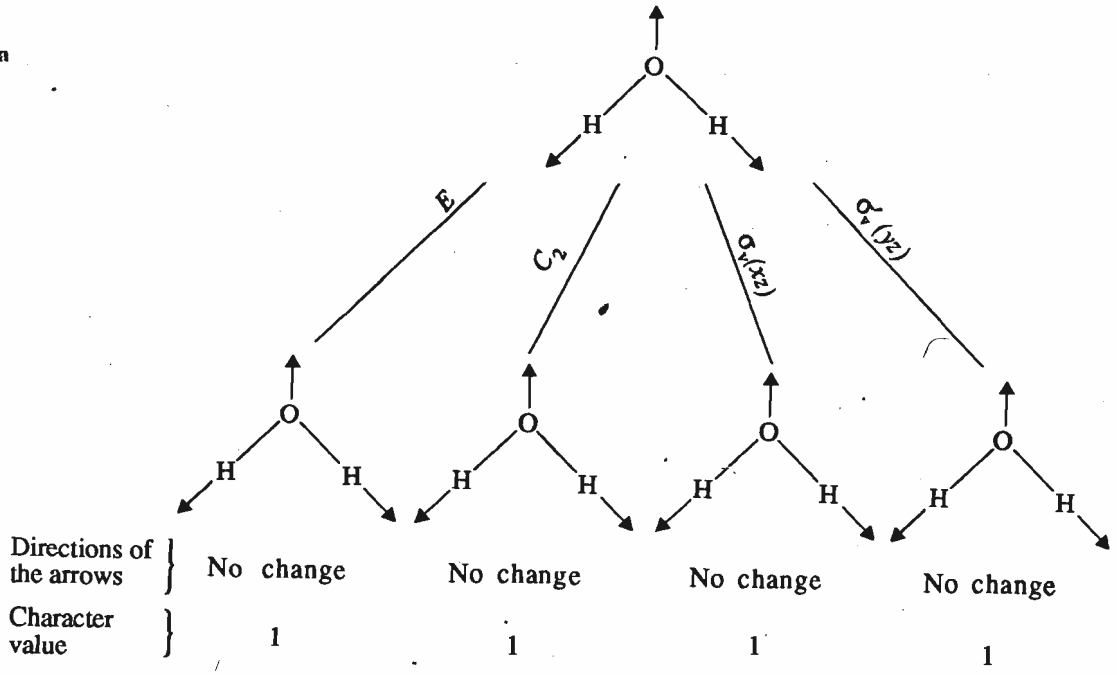
$\chi_{A_1}(E) = 1$,
$\chi(E) = 3$ and
$N = 1$

Similarly the second term stands for the application of formula for the class of operation, C_2.The third and fourth terms stand for the classes of operations, $\sigma_v(xz)$ and $\sigma'_v(yz)$, respectively.

As mentioned in Sec. 5.2, the arrows attached to each atom show the direction of its motion during half of the vibration. During the other half of the vibration, the movement will be in the opposite direction.

Hence, antisymmetric stretching vibration belongs to B_1 representation.

It is worth pointing out that



Symmetry species of symmetric stretching = A_1

You may remember that C_2 rotation is around z axis and because of C_2 rotation, the two H atoms change their positions; but again the directions of two arrows around these H atoms are similar to those of the initial configuration suggesting no change in the direction of the stretching mode. $\sigma_v(xz)$ does not bring about a change in the direction of the stretching mode since xz reflection takes place in the molecular plane. $\sigma'_v(yz)$ reflection takes place in a direction perpendicular to the molecular plane and it brings about the reflection of two H atoms; but again, there are two arrows with the direction similar to those of the original configuration which indicates that there is no change in the stretching mode. Hence the character value of 1 is obtained in each of the four operations, E, C_2, $\sigma_v(xz)$ and $\sigma'_v(yz)$, indicating that the symmetric stretching vibration belongs to A_1 representation.

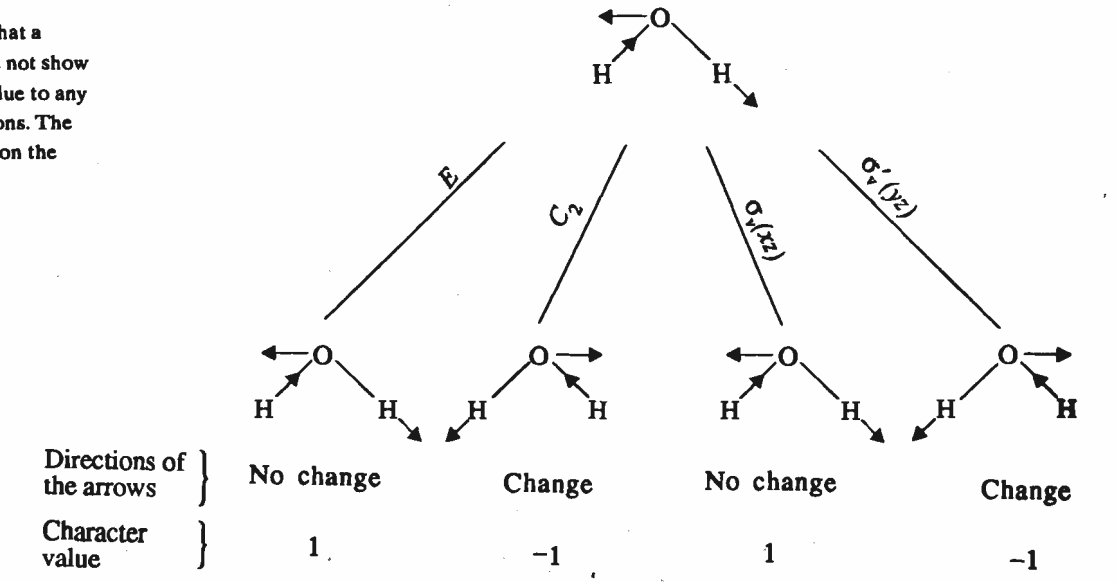
Irreducible representation of the symmetric bending mode

It can be shown using the diagrams that after performing each of the four symmetry operations, E, C_2, $\sigma_v(xz)$ and $\sigma'_v(yz)$, the arrows are in the same directions showing no change in the direction of the bending mode. You may try this as an exercise. So, the character values corresponding to these four operations are 1, 1, 1, 1 which indicates that the symmetric bending mode also belongs to A_1 representation.

Irreducible representation of the antisymmetric stretching mode

The effect of the four symmetry operations on the arrows drawn for the antisymmetric stretching is explained through the diagram as follows:

"Totally symmetric A_1 representation" means that a particular vibration does not show any change in direction due to any of the symmetry operations. The result of each operation on the vibration is + 1".



Symmetry species of antisymmetric stretching = B_1

Also C_3^1 and C_3^2 belong to one class, σ_v, σ'_v, σ''_v belong to another class

Hence, antisymmetric stretching vibration belongs to B_1 representation.

It is worth pointing out that symmetric stretching and symmetric bending modes derive their name from the fact that these two stretching modes belong to the **totally symmetric** A_1 representation. On the other hand, antisymmetric stretching mode owes its name to the fact that it is antisymmetric to at least two of the operations, C_2 and $\sigma'_v(yz)$.

Thus we have seen that two of the normal modes belong to A_1 representation while the third belongs to B_1 representation as mentioned earlier in Step 3.

Step 5: Identifying the infrared active vibrational modes

In the Appendix portion of Unit 2 and under the title, "uses of character tables", we have shown that for a spectral transition to occur from the state a to b, at least one of the components of the transition dipole moment (μ_x, μ_y, or μ_z) should be nonzero. We have explained that for an allowed spectral transition, the symmetry species of the product, $\psi_b \psi_a$ must be same as that of x, y or z coordinate. Such a spectral transition is symmetry allowed, since the product of the symmetry species of the functions ψ_b and ψ_a and that of one of the coordinates x, y or z becomes totally symmetric i.e., $\psi_b x \psi_a$ or $\psi_b y \psi_a$ or $\psi_b z \psi_a$, belongs to A_1 representation.

Using the procedure followed in Appendix of Unit 2 for obtaining the representation of the products $\psi_b x \psi_a$, $\psi_b y \psi_a$ or $\psi_b z \psi_a$ you can try to prove that

(i) the symmetric stretching and bending modes are IR active and are polarized in the z-direction and

(ii) the antisymmetric stretching mode is also IR active and is polarized in the x-direction.

To prove the above statements, the following hints also will be useful :

(i) For the symmetric stretching and bending modes, $\psi_b = A_1$, $\psi_a = A_1$ and $\psi_b \psi_a = A_1$; since, $z = A_1$, $(\psi_b \psi_a) z = A_1 A_1 = A_1$ and the z-component of the transition dipole moment (μ_z) is nonzero.

(ii) For the antisymmetric stretching mode, $\psi_b = B_1$, $\psi_a = A_1$ and $\psi_b \psi_a = B_1 A_1 = B_1$; since $x = B_1$, $(\psi_b \psi_a) x = B_1 B_1 = A_1$ and the x-component of the transition dipole moment (μ_x) is nonzero.

Note that the results (i) $\psi_b = A_1$ for symmetric stretching and bending modes, and (ii) $\psi_b = B_1$ for the antisymmetric stretching mode follow from our discussion on the irreducible representations of the vibrational modes in Step 4. Also the ground state belongs to A_1 i.e., $\psi_a = A_1$ for all these three modes.

Hence, all the three vibrational modes of H_2O are IR active.

Here it is worth making the generalisation:

A vibration will be IR active, if it belongs to the same symmetry species as a component of transition dipole moment, i.e., to the same symmetry species as x, y, or z.

We shall shortly apply this rule to NH_3 molecule which belongs to C_{3v} group.

In Sec. 6.7 of Unit 6, the assignment of vibrational modes to the experimentally observed IR absorption bands will be explained using IR and Raman spectra.

You are aware that NH_3 has the following symmetry operations :

$E, C_3^1, C_3^2, \sigma_v, \sigma'_v$ and σ''_v (See Secs. 2.4 and 2.5 of Unit 2).

Also C_3^1 and C_3^2 belong to one class, σ_v, σ'_v,σ''_v belong to another class while E is a class in itself. Hence the operations are grouped under **three classes:**

$$E, 2C_3 \text{ and } 3\sigma_v$$

The character table for C_{3v} is given below:

Character Table of C_{3v}

	Three classes in C_{3v}					
C_{3v}	E	$2C_3$	$3\sigma_v$			
A_1	1	1	1	z	z^2, x^2+y^2	
A_2	1	1	−1			R_z
E	2	−1	0	(x, y)	(xy, x^2-y^2) (xz, yz)	(R_x, R_y)

Irreducible representations of C_{3v} group

Step 1: Reducible representation for all the symmetry operations of NH_3

To find the characters of the reducible representation using Eq. A.1, we must know n_a and $\chi_R(p)$ for each of the symmetry operations. While arriving at n_a and $\chi_R(p)$ values, it is enough to consider only one member of each class. Hence, n_a, $\chi_R(p)$ and $\chi_R^t(p)$ of E, C_3 and σ_v are to be calculated for finding the reducible representation of the molecule.

You may be aware that operation E does not shift any of the four atoms in NH_3; hence $n_a = 4$ for E. During C_3 (C_3^1 or C_3^2) operation, nitrogen atom alone is not shifted; hence $n_a = 1$ for C_3. During any of the three σ_v operations, nitrogen atom and one of the H atoms are not shifted. Hence $n_a = 2$ for σ_v.

We can obtain $\chi_R(p)$ values of E, C_3 and σ_v using Table A.1 as follows:

	E	$C(120°)$	σ_v
$\chi_R(p)$	3	$1 + 2\cos 120°$	1
		$= 0$	

The calculation of $\chi_R^t(p)$ for each symmetry operation can be shown as follows:

p	E	$2C_3$	$3\sigma_v$	
$\chi_R(p)$	3	0	1	
n_a	4	1	2	
$\chi_R^t(p)$ (calculated as per Eq. A.1)	12	0	2	...(A.7)

For C_3 axis, the order of axis $(n) = 3$. Using Eq. 2.1 of Unit 2, minimum angle of rotation

$(\alpha) = 360°/3 = 120°$

Also $C(120°) = 1 + 2\cos 120°$

$= 1 - (2 \times 1/2)$

$= 0$

because $\cos 120° = -\sin 30°$

$= -1/2$

Step 2 : Obtaining the reducible representation of all the vibrations

As done in the case of H_2O molecule, we shall subtract the characters of symmetry operations in the irreducible representations of translations and rotations from the characters of symmetry operations given by Eq. A.7 so that we could obtain the reducible representation of all the vibrational modes of NH_3 molecule.

As per C_{3v} character table, the translations belong to E and A_1, because these are influenced by the symmetry operations in the same way as x, y and z directions. Similarly the rotations belong to E and A_2 since R_x, R_y and R_z belong to these symmetry species.

Hence the sum of the characters of the symmetry operations in the irreducible representations of translations is given by $E + A_1$ (Eq. A.8); and the sum of the characters of the symmetry operations in the irreducible representations of rotations is given by $E + A_2$ (Eq. A.9).

Using C_{3v} character table, $E + A_1$ and $E + A_2$ can be calculated. The characters of the symmetry operations in the reducible representation of vibrations (τ) is given by subtracting Eqs. A.8 and A.9 from Eq. A.7.

	E	$2C_3$	$3\sigma_v$	
$\chi_R^t(p)$	12	0	2	...(A.7)
$-[(E + A_1)$	3	0	1	...(A.8)]
$-[(E + A_2)$	3	0	–1	...(A.9)]
	6	0	2	...(A.10)

Eq. A.10 represents the characters of the symmetry operations ($\chi(p)$) in τ, the reducible representation of all vibrational modes of NH_3 molecule.

Step 3: Obtaining the symmetry species of the vibrational modes

We shall use Eq. A.6 to obtain the symmetry species of the vibrational modes of NH_3 molecule. We know that for C_{3v} group, $h = 6$, since there are six operations:

$$E, C_3^1, C_3^2, \sigma_v, \sigma'_v \text{ and } \sigma''_v$$

Also $N = 1$ for the class of operation, E; $N = 2$ for the class of operations C_3^1 and C_3^2 and $N = 3$ for the class of operations, σ_v, σ'_v and σ''_v

To get $\chi(p)$, we have to use Eq. A.10 and, to get $\chi_I(p)$, we have to use character table of C_{3v}.

Number of times A_1 symmetry species occurs in τ representation $= n_{A_1}$

$$= 1/6\,[(1 \times 6 \times 1) + (1 \times 0 \times 2) + (1 \times 2 \times 3)]$$

$$= 1/6\,[12] = 2$$

Similarly, $n_{A_2} = 1/6\,[(1 \times 6 \times 1) + (1 \times 0 \times 2) + ((-1) \times 2 \times 3)]$

$$= 1/6\,[6 - 6] = 0$$

$$n_E = 1/6\,[(2 \times 6 \times 1) + ((-1) \times 0 \times 2) + (0 \times 2 \times 3)]$$

$$= 2$$

Hence symmetry species of vibrations $= 2A_1 + 2E$.

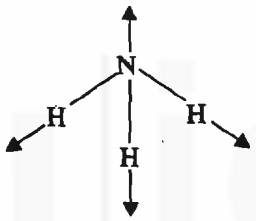
The two vibrations which belong to the symmetry species A_1 must be totally symmetric with respect to all symmetry operations, while two others belonging to E are antisymmetric and are doubly degenerate.

Step 4 : Identifying the symmetry species of each vibrational mode

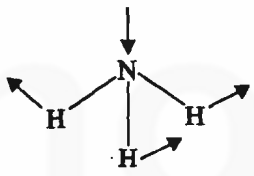
The four fundamental modes of NH_3 given below can be examined with respect to the symmetry operations E, C_3 and σ_v. The vibrational modes for which the directions of the arrows remain the same after performing each one of these three operations belong to the totally symmetric species, A_1. Those vibrational modes for which there is a change in the direction of arrows could be considered to belong to the symmetry species E through a process of elimination.

If you proceed correctly, you will find that one stretching vibration and one bending vibration belong to the totally symmetric species (A_1). Evidently the other two belong to the antisymmetric species (which are assumed to belong to E, the doubly degenerate mode).

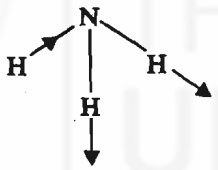
The four fundamental vibrational modes of NH_3 are given below:



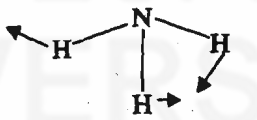
Symmetric stretching
A_1



Out-of-plane symmetric bending
A_1



Antisymmetric stretching
E



Antisymmetric bending
E

Step 5 : Identifying the infrared active vibrational modes

Using the method indicated for H_2O molecule, you may try to see whether the two vibrational modes with A_1 and the other two with E symmetry are IR active. By using the generalisation stated earlier regarding the infrared activity of vibration, we can conclude that all these are expected to be IR active since (i) two of the vibrational modes (symmetric stretching and out-of-plane symmetric bending) belong to A_1 to which z also belongs and (ii) the other two vibrational modes, (antisymmetric stretching and antisymmetric bending), belong to E to which x and y also belong. Hence all the four fundamental modes are expected to be IR active.