Indira Gandhi National
Open University
School of Sciences

BCHET-147

ORGANOMETALLICS, BIOINORGANIC CHEMISTRY, POLYNUCLEAR HYDROCARBONS AND UV, IR SPECTROSCOPY

Block

4

APPLICATIONS OF SPECTROSCOPY TO SIMPLE ORGANIC MOLECULES

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BLOCK-4: APPLICATIONS OF SPECTROSCOPY TO SIMPLE ORGANIC MOLECULES

In the previous block of this course you have learnt about methylene, polynuclear aromatic and heteroaromatic compounds. You have been also introduced to the synthesis of these compounds.

In this block you will study about the applications of spectroscopy to simple organic molecules. This block has 4 Units.

Unit 11 deals with ultraviolet-visible spectroscopy which is a consequence of interaction of electromagnetic radiation in the ultraviolet–visible range with the molecules constituting matter. The different types of transitions possible in the electronic spectra of polyatomic molecules, λ_{max} and ε_{max} and the various important terms have been defined.

Unit 12 deals with small organic compounds, specially those with conjugated dienes, with the help of UV-visible spectroscopy. Discussions on the Woodward rules to predict absorption maxima in conjugated simple organic compounds have been included and problems based on these have also been discussed.

In Unit 13 the concepts of the spectroscopic tool IR spectroscopy and how it helps in the determination of the structure of simple organic molecules have been discussed.

Unit 14 discusses in detail about the identification of organic molecules using IR spectra. The structural features of various classes of organic compounds have been corrected with the bands in their IR spectra. Thus, the analysis of the IR spectra helps in the identification of organic compounds.

Expected Learning Outcomes

After studying this block, you should be able to:

- explain electromagnetic radiations and its wave nature;
- define important terms used in electronic spectra;
- list the applications of electronic spectroscopy and apply Woodward rules to predict the absorption maximum for unsaturated organic compounds;
- discuss the different types of molecular vibrations;
- explain the important features of IR spectra of simple molecules belonging to various classes of organic compounds;
- correlate the important bands in IR spectrum with the structural units present in the molecule; and
- arrive at the structure of a molecule from its spectral data and also predict the spectral data for a given molecule from its structure.

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UNIT 11

UV–VISIBLE ABSORPTION SPECTROSCOPY

Structure

11.1 INTRODUCTION

In the previous block of this course you have learnt about the aromatic, heteroaromatic and active methylene compounds. This block is on "Applications of Spectroscopy to Simple Organic Molecules".

In this unit, we will start our discussions on electromagnetic radiations. Then you will learn about ultraviolet-visible spectroscopy which is a consequence of interaction of electromagnetic radiation in the ultraviolet – visible range with the molecules constituting matter. The different types of transitions possible in the electronic spectra of polyatomic molecules, λ_{max} and ε_{max} will then be discussed. The terms chromophore, auxochrome, hypsochromic and bathochromic effects, hyperchromic and hypochromic effects will be defined. In the next unit, you will actually learn how to identify small organic compounds, specially those with conjugated dienes, with the help of UV-visible spectroscopy.

Expected Learning Outcomes

After studying this unit and having performed the experiments, you should be able to:

- ❖ explain electromagnetic radiations and its wave nature;
- ❖ explain using diagrams the $n - \pi^*$, $n - \sigma^*$, $\sigma - \sigma^*$, and $\pi - \pi^*$ transitions;
- ❖ define chromophore, auxochrome, hypsochromic and bathochromic effects, hyperchromic and hypochromic effects in electronic spectra;

11.2 ELECTROMAGNETIC RADIATIONS

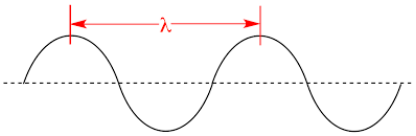
Now, the question is 'why certain substances are coloured? For example, the green colour of vegetation is due to a compound chlorophyll. Transition metal complexes, such as $[Ti(H_2O)_6]^{3+}$, are coloured. The answer to the origin of colours in substances and information about excited states of molecules can be obtained from a study of their electronic spectra which occur in the visible (400-800 nm) and ultraviolet (200-400 nm) regions of electromagnetic spectrum. The spectra are obtained from spectroscopy which is a powerful tool to investigate the interaction of electromagnetic field with matter. It is utilized by researchers to conduct analysis in research laboratories and industries.

Spectroscopy is the study of interaction of electromagnetic radiation with matter.

An electromagnetic radiation may be defined as the radiant energy which is transmitted through space at enormous velocities. It does not require any medium for transmission. In previous courses you must have studied the characteristic of light, a form of electromagnetic radiation, and we will provide only a summary here. Gamma rays, X-rays, ultraviolet light, visible light, infrared radiation, microwaves and radio waves are all examples of **electromagnetic radiation** and part of the electromagnetic spectrum. Because electromagnetic radiation behaves as a wave travelling at the speed of light, it is described in terms of its wavelength and frequency.

Wavelength is the linear distance between any two consecutive equivalent points on the wave (for examples, crest to crest or trough to trough). Wavelength is given the symbol λ (Greek letter *lambda*) and is usually expressed in the SI base unit of meters. Other derived units commonly used to express wavelength are given in Table 11.1.

Table 11.1: Common units used to express wavelength (λ)

Unit	Relation of meter	
millimeter (mm)	1 mm = 10^{-3} m	
Micrometer (μm)	1 μm = 10^{-6} m	
nanometer (nm)	1 nm = 10^{-9} m	

The **frequency** of a wave is the number of full cycles of the wave that pass a given point in a second. Frequency is given the symbol ν (Greek letter *nu*) and is reported in second inverse or per second, s^{-1} (also called H**ertz, Hz**). Wavelength and frequency are inversely proportional, and we can calculate one from the other using the relationship:

$$c = \nu\lambda$$

where ν is frequency in s^{-1}, c is the velocity of light (3.0×10^{-8} m s^{-1}), and λ is the wavelength in meters.

The wave number is the number of waves per centimeter per unit distance. It is expressed in units of nu bar $(\bar{\nu})$ and is equal to the reciprocal of the wavelength expressed in meters (m). Thus the unit of wave number will be meter inverse (m^{-1}). If the wavelength is expressed as cm then wave number will be cm^{-1}.

$$\bar{\nu} = \frac{1}{\lambda}$$

An alternative way to describe electromagnetic radiation is in terms of particles. We call these particles as photons. The energy of a photon and the frequency of radiation are related by the equation.

$$E = h\nu = h(c/\lambda)$$

Where E is the energy in kJ and h is Planck's constant, 6.626×10^{-34} J s. This equation tells us that high-energy radiation corresponds to short wavelengths, and vice versa. Thus, ultraviolet light (higher energy) has a shorter wavelength (approximately 10^{-7} m) than infrared radiation (lower energy), which has a wavelength of approximately 10^{-5} m.

1 cm = 10^{-2} m

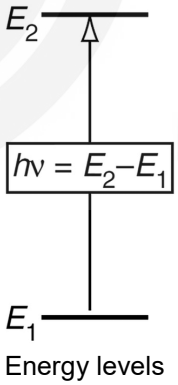
1 μm = 10^{-6} m

1 nm = 10^{-9} m

1 Å = 10^{-10} m

An atom or molecule undergoes a transition from lower energy state E_1 to a higher energy state E_2 by irradiating it with electromagnetic radiation corresponding to the energy difference between states E_1 and E_2 as illustrated schematically in Fig.11.1. Absorption of photon results in electronic transition of a molecule, and electrons are promoted from ground state to higher electronic states.

In UV-visible spectra, nanometer is usually used as unit for wavelength.



Energy levels

Fig. 11.1: Electromagnetic radiation.

When the excited atom or molecule returns to the ground state, an equivalent amount of energy is emitted. When a compound is irradiated with electromagnetic radiation of various wavelengths, it absorbs energy of particular wavelengths, while the wavelengths not absorbed simply pass through or are reflected from the sample unchanged. The structure of electronic spectra, involves the change of at least three quantum numbers simultaneously, namely electronic, vibrational and rotational quantum numbers. Since it involves an electron excitation phenomenon, so, UV-visible Spectroscopy is also called as Electronic Spectroscopy.

Fig. 11.2 summarises the wavelengths and frequencies of some regions of the electromagnetic spectrum.

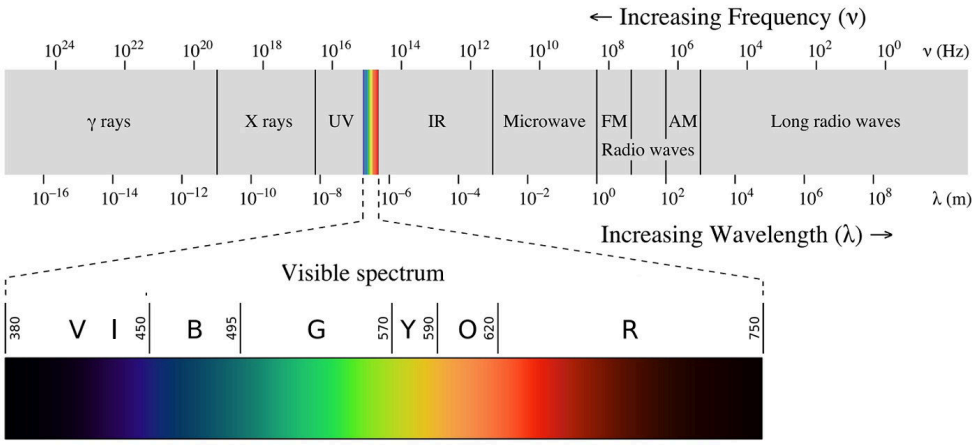


Fig. 11.2: The wavelengths and frequencies of some regions of the electromagnetic spectrum.

If you look at the electromagnetic spectrum as in Fig. 11.2 you can see that the spectrum is divided into γ-rays, x-rays, ultraviolet, visible, infrared, microwave and radio waves, etc. as the wavelength increases.

We can sense only the visible region of the spectrum with the help of human eye. Before going to the next section, try to answer the following SAQ.

SAQ 1

Which region of the electromagnetic region is the UV-visible region?

11.3 ELECTRONIC TRANSITIONS

In an atom, various electronic states can arise from a given electronic configuration due to coupling of orbital angular momentum and spin angular momentum of electron. The atomic spectra arise due to transition between different electronic energy states. Similarly for molecules various electronic states can arise from a given electronic configuration of a molecule. The electronic configuration of a molecule can be derived on the basis of molecular orbital theory which you studied in Unit 9 of the BCHCT131 course. Please recapitulate the Molecular Orbital Treatment of molecules in that unit, especially the LCAO method. You also have to remember that the rules of filling up electrons in molecular orbitals are same as the filling of atomic orbitals. That is

i) the electrons occupy the available molecular orbitals one at a time, the lowest energy orbital being filled first (**aufbau principle**),

ii) each molecular orbital can accommodate a maximum of two electrons, provided their spins are opposite (**Pauli's exclusion principle**),

iii) no pairing of electrons in orbitals of equal energy will take place unless there is at least one electron in each of them (**Hund's rule of maximum multiplicity**).

The electronic structure of the absorbing species, like, atoms, molecules, ions or complexes, which absorb in the UV-visible region of the spectrum, influence the absorption of radiation.

The structure of electronic spectra, involves the change of at least three quantum numbers simultaneously, namely electronic, vibrational and rotational quantum numbers. This follows the Born-Oppenheimer approximation that rotational (E_R), vibrational (E_v) and electronic (E_e) energy levels are independent of one another. The total energy E is written as

$$E = E_e + E_v + E_R$$

and therefore the change in the total energy as a result of electronic transition, in a molecule is given by

$$\Delta E = \Delta E_e + \Delta E_v + \Delta E_R$$

Thus each electronic level comprises a number of vibrational levels and each vibrational level consists of several rotational levels, as is shown in Fig. 11.3.

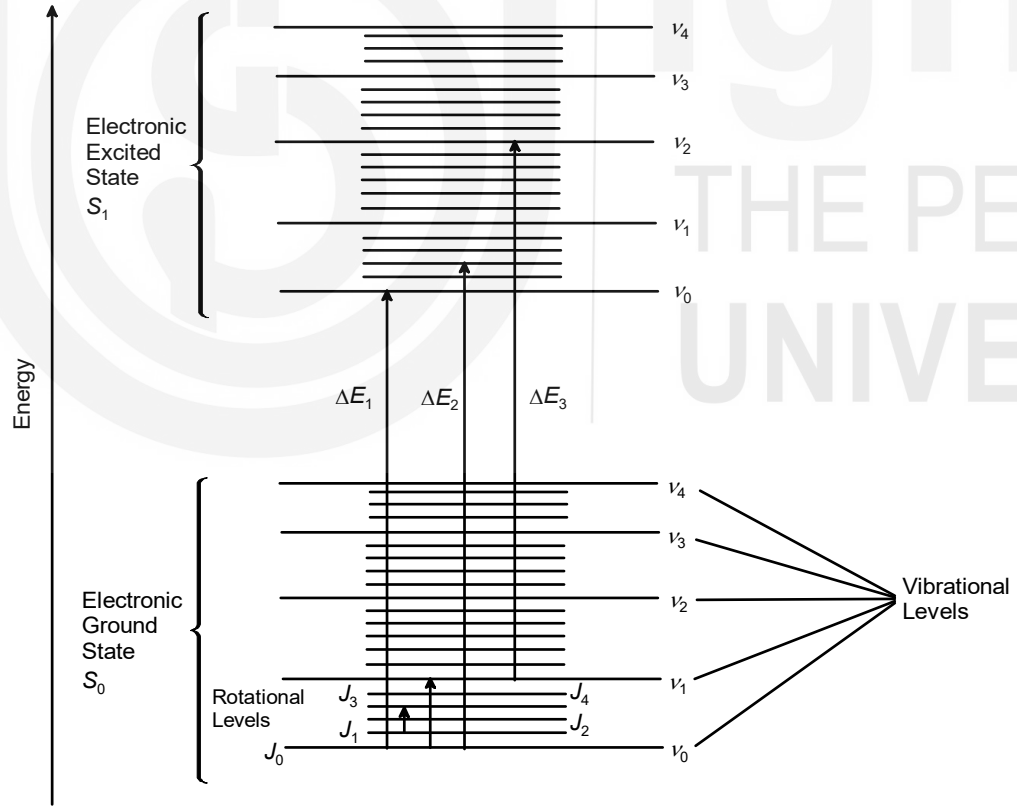


Fig. 11.3: Rotational, vibrational and electronic energy levels in a molecule.

The UV-visible radiations cause transition of electrons from the low energy electronic states to the higher energy states. But IR (discussed in Units 13 and 14) radiations cause transitions among vibrational and rotational energy levels.

You see that every electronic level has several vibrational levels. Again, each vibrational level is associated with several rotational energy levels. So there

are several vibrational and rotational transitions associated in the transitions caused by UV-visible radiation. From these values of relative order of energies, as we see in Fig. 11.3, we find that the vibrational changes give a 'coarse structure' and the smaller rotational changes give a 'fine structure' to the electronic spectra. Since rotational energy changes are minimum, these energy changes are neglected and electronic band system is considered in terms of transitions between electronic levels each consisting of a series of vibronic levels of the same kind. So the molecular spectra becomes very complex due to such large number of transitions. This results in band spectrum due to electronic absorptions. The bands for molecules are found to be quite broad.

Absorption of ultraviolet and visible radiation in organic molecules is restricted to certain functional groups (chromophores) that contain valence electrons of low excitation energy.

Spectra of small organic molecules provides important information about electronic structure. We make use of molecular orbital theory to understand theoretical aspects of spectra of these. In electronic transitions of such molecules, we encounter three types of molecular orbitals: σ and σ^*, π and π^*, and n (nonbonding) orbitals. Orbitals without * are bonding orbitals and those with * are antibonding orbitals. The energy levels of these molecular orbitals, in increasing order of energy, are shown in Fig.11.4.

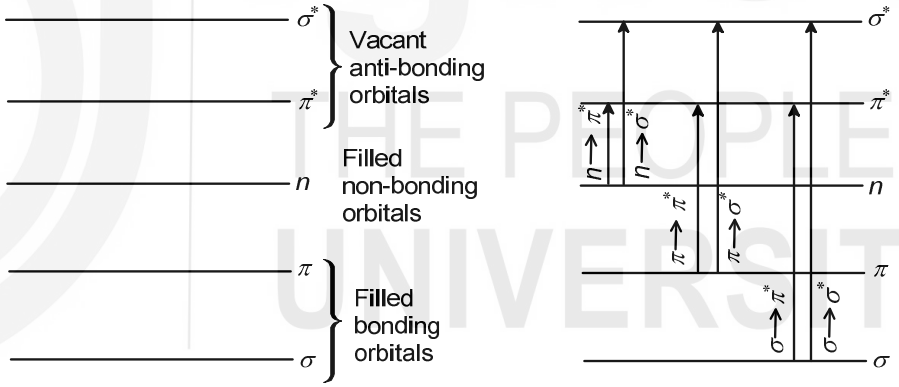


Fig. 11.4: Schematic diagram of (a) order of molecular orbital energies (b) possible electronic transitions.

When a molecule absorbs energy in the UV or visible region, an electron from a specific MO is excited to another MO of higher energy. The possible transitions of the electron between the MOs are:

$$\sigma - \sigma^*, n - \sigma^*, n - \pi^*, \pi - \pi^*, \pi - \sigma^* \text{ and } \sigma - \pi^*,$$

The order of decreasing energy for these transitions is as follows:

$$\sigma - \sigma^* > \sigma - \pi^* \approx \pi - \sigma^* > \pi - \pi^* \approx n - \sigma^* > n - \pi^*$$

Of all the possible transitions, the last three are responsible for absorptions in the region 200-800 nm, whereas others require much higher energy.

σ– σ^* transition: Fig. 11.4 reveals that this transition requires very high energy. The absorption spectra obtained appears in the far ultraviolet region

(< < 200 nm). Molecules which give this type of spectrum are saturated hydrocarbons and other compounds in which all valence electrons are involved in single bond formation. Since a spectrometer generally cannot measure below 185 nm, the region involving $\sigma - \sigma^*$ transitions is relatively of little importance for chemical analysis.

***n* – σ^* transition:** The spectra corresponding to $n - \sigma^*$ transition appears in the near UV or visible region. Compounds containing non-bonding or lone-pair electrons show this transition. For example, methyl alcohol vapour shows an absorption maximum at 183 nm. Methyl chloride and methyl amine show absorption maxima at 173 nm and 213 nm, respectively.

***n* – π^* transition:** This type of transition requires least energy and is exhibited by unsaturated molecules containing non bonding electrons. Certain organic groups like $\rangle C-N-$, $-N=O$, $\rangle C=O$ show this type of transition and we observe absorption maxima for these systems at wavelengths greater than 280 nm. Groups such as $\rangle C-N-$, $-N=O$, $\rangle C=O$, $-COOH$ causing absorption at wavelengths greater than 175 nm are referred to as chromophores. More information on chromophores will be presented a little later.

$\pi - \pi^*$ transition: Bands due to $\pi - \pi^*$ transition appear in the spectra of compounds containing $\rangle C-C\langle$, $-C\equiv C-$, $\rangle C=O$, and $\rangle C-N-$ functional groups. Ethylene and acetone exhibit $\pi - \pi^*$ transition at 165 and 150 nm, respectively. The $\pi - \pi^*$ transition is highly affected by conjugation.

You have already done experiment (Job's Method) based on UV-visible spectroscopy in the previous laboratory course BCHCL138 . Recapitulating some concepts here is also very important. The absorption bands in ultraviolet and visible spectra are characterised by two main parameters which are

i) λ_{max} Value: The value of the wavelength at which absorption maximum occurs is called the λ_{max} value. This corresponds to the wavelength of the radiation whose energy is equal to that required for an electronic transition. As different transitions require different energies, their λ_{max} values are different.

ii) ε_{max} Value : ε value, which is known as molar absorptivity or molar extinction coefficient, is a measure of extent of absorption or intensity of absorption. The ε value is characteristic of a particular compound at a given wavelength. Usually for the wavelength of maximum absorption (λ_{max}), molar absorptivity is expressed as ε_{max}.

The intensity of absorption can be expressed as transmittance (T), which is defined as the ratio of the intensity of the radiation transmitted from the sample (I) to that of the radiation incident on the sample (I_o), i.e.,

$$T = I / I_o$$

Intensity of absorption is more conveniently expressed in terms of absorbance (A), which is the logarithm of reciprocal of transmittance (T), i.e.,

$$A = \log_{10} (1/T) = \log_{10} (I_o/I)$$

Absorbance of a band is related to the sample thickness and the concentration of the absorbing species. The relationship is expressed in the form of Beer-Lambert law as shown below:

$$A = \varepsilon cl = \log_{10} (I_o/I)$$

or $$\varepsilon = \frac{A}{cl}$$

where ε = molar absorptivity or molar absorption constant; c = concentration of solute; l = sample thickness or path length through the sample

Absorbance is a dimensionless quantity. Concentration (c) is usually expressed in mol dm^{-3} and path length (l) in cm, hence ε has the units of dm^3 mol^{-1} cm^{-1}. If we use SI units of mol m^{-3} for concentration and m for path length, the units of ε will be m^2 mol^{-1}. We can obtain the values of ε in m^2 mol^{-1} units from those in dm^3 mol^{-1} cm^{-1} units in the following manner: ε = dm^3 mol^{-1} cm^{-1} =10^{-3} m^3 mol^{-1} $(10^{-2}\ m)^{-1}$ = 10^{-1} m^2 mol^{-1}.

Values of ε in SI units can, therefore, easily be obtained from published values in dm^3 mol^{-1} cm^{-1} by dividing the numerical quantity in latter units by 10.

Absorption bands with ε_{max} value > 10^3 m^2 mol^{-1} are considered to be high intensity or strong bands, whereas those with ε_{max} values < 10^2 m^2 mol^{-1} are known as low intensity or weak bands.

The process of scanning is said to be done when a single wavelength (in the UV-visible region) is employed on the sample. This way the UV-visible spectrum is obtained over a range of wavelength. The amount of radiation absorbed at each wavelength is measured and plotted against the wavelength or frequency (in nm) in the x-axis and the intensity of absorption (absorbance) in the y axis. Such UV-visible spectroscopy is used extensively in teaching, research and analytical laboratories for the quantitative analysis of molecules that absorb ultraviolet and visible electromagnetic radiation and therefore it is important for you to know the basics of this powerful tool. The kind of data that we generally see in UV-visible spectroscopy is shown in the following Fig.11.5:

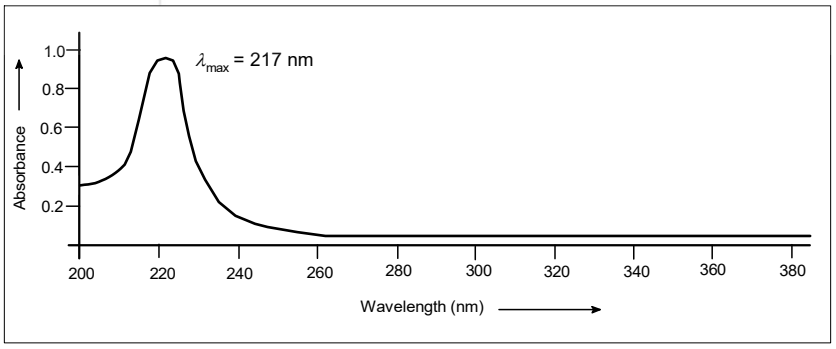


Fig. 11.5: Sample graph obtained in UV-visible spectroscopy.

Now try out the following SAQ before moving to the next section.

SAQ 2

Which are the two main parameters on which the absorption bands in ultraviolet and visible spectra are measured?

11.4 SOME IMPORTANT TERMS USED IN ELECTRONIC SPECTROCOPY

Chromophore:

In a number of molecules, the absorption of a photon can be traced to the electrons of certain covalently bonded unsaturated groups. Such groups, for example, carbonyl in aldehydes or ketones which are responsible for electronic absorption, are referred to as chromophores. Other examples of chromophores are $\diagup C{=}C \diagdown$, $-C{\equiv}C-$,$-COOH, -N{=}O, -NO_2, -N{=}N-$ etc. Chromophore in Greek means colour bringer and the presence of a chromophore often accounts for colours of substances. The following table lists the absorption maxima for some typical chromophores.

Table 11.2: Absorption Data for Isolated Chromophores

Chromophoric Group	System	Example	Transition	$\frac{\lambda_{max}}{nm}$	$\frac{\varepsilon_{max}}{m^2mol^{-1}}$	Solvent
Ethylenic	RCH=CHR	Ethylene	$\pi \rightarrow \pi^*$	165	1500	Vapour
Acetylenic	R–C≡C–R	Acetylene	$\pi \rightarrow \pi^*$	173	6000	Vapour
Carbonyl	RR′C=O	Acetone	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	188 279	900 1.5	n-Hexane
Carbonyl	RHC=O	Acetald-ehyde	$n \rightarrow \pi^*$	290	1.6	Heptane
Carbonyl	RCOOH	Acetic acid	$n \rightarrow \pi^*$	204	6.0	Water
Amido	$RCONH_2$	Acetamide	$n \rightarrow \pi^*$	< 208	–	–
Azomethine	$\diagup C{=}N-$	Acetoxime	$\pi \rightarrow \pi^*$	190	5000	Water
Nitrile	–C≡N	Acetonitrile	$\pi \rightarrow \pi^*$	< 160	–	–
Azo	–N=N–	Azomethane	$n \rightarrow \pi^*$	347	0.45	Dioxane
Nitroso	–N=O	Nitroso-butane	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	300 665	10 2.0	Ether
Nitrate	$-ONO_2$	Ethyl nitrate	$n \rightarrow \pi^*$	270	1.2	Dioxane
Nitro	$-NO_2$	Nitromethane	$n \rightarrow \pi^*$	271	1.86	Alcohol
Nitrite	–ONO	Amyl nitrite	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	218.5 346.5	112	Petroleum ether

Auxochrome

A saturated group with nonbonded electrons which, when attached to a chromophore, alters both the wavelength and the intensity of the absorption band is called an auxochrome, e.g., OH, NH_2 and Cl. The auxochrome by itself is unable to impart colour to a compound. The auxochromic effect depends on the ability of the chemical group to donate electrons into conjugated system.

This has been most studied with aromatic systems and the band shifts of monosubstituted aromatic compounds have been correlated with electron donating power of auxochromes. The electron donating power of some common auxochromes decreases in the order

$$O^- > NHCH_3 > NH_2 > OH > Cl > CH_3 > NH_3^+ = H$$

In this list, the effect of protonating the NH_2 group should be noted. The proton binds to the nonbonding (lone pair) electrons on the nitrogen of the amino group and thus prevents them from interacting with the benzene π-electron system. Thus, the λ_{max} value for aniline ($C_6H_5NH_2$) and the anilinium ion ($C_6H_5NH_3^+$) is 230 nm and 203 nm, respectively as compared to 204 nm for benzene.

Bathochromic or red shift: A shift of the absorption maximum towards longer wavelength (lower frequency) produced by a change of medium or by the presence of an auxochrome, is called bathochromic shift or red shift. The $\pi \rightarrow \pi^*$ transition in carbonyl compounds experiences bathochromic shift when polarity of the solvent is decreased.

Hypsochromic shift or Blue shift: A shift towards shorter wavelength (higher frequency) caused by a change of medium or by removal of conjugation is referred to as hypsochromic shift or blue shift. For example, the conjugation of the lone pair of electrons on the nitrogen atom of aniline with the π-bond system of the benzene ring is removed by protonation. Aniline absorbs at 230 nm, but in acid solution the main peak is shifted to 203 nm due to the presence of anilinium ions.

Hypochromic effect: An effect leading to decreased absorption intensity is called hypochromic effect.

Hyperchromic effect: An effect leading to increased absorption intensity is called hyperchromic effect.

You may now try to answer the following SAQ.

SAQ 3

Why the λ_{max} value for aniline ($C_6H_5NH_2$) is 230 nm whereas that of benzene is 204 nm?

11.5 SUMMARY

In this unit, you have first learnt about electromagnetic radiations. Then different types of transitions possible in the electronic spectra of polyatomic molecules, λ_{max} and ε_{max} were discussed. Lastly, you have learnt some important definitions of terms used in electronic spectroscopy. In the next unit, you will be actually studying how to apply the UV-visible spectroscopy as a tool to identify small organic compounds, specially those with conjugated dienes.

11.6 TERMINAL QUESTIONS

1. How can a molecule absorb and emit electromagnetic radiation? Explain with a suitable diagram.
2. Which electronic transitions in small organic molecules are responsible for absorptions in the region 200-800 nm?
3. What are the expected transitions for amido and azomethine chromophore?
4. What information does UV-visible spectroscopy give about small organic molecules?
5. What sort of shift may be observed in chloroethylene, CH_2=CHCl?

11.7 ANSWERS

Self-Assessment Questions

1. The visible region of the electromagnetic spectrum is 400-800 nm and ultraviolet region is 200-400 nm.
2. λ_{max} and ε_{max}
3. The auxochromes, e.g., OH, NH_2 and Cl can donate electrons into conjugated system. This has been most studied with aromatic systems and the spectral shifts of monosubstituted aromatic compounds have been correlated with electron donating power of auxochromes. The electron donating power of NH_2 is much more than that of H. So the observation of greater value of λ_{max} in aniline.

Terminal Questions

1. We can cause an atom or molecule to undergo a transition from lower energy state to a higher energy state by irradiating it with electromagnetic radiation corresponding to the energy difference between the states (give Fig. 11.2). When the atom or molecule in excited state returns to the ground state, an equivalent amount of energy is emitted. When a compound is irradiated with electromagnetic radiation of various wavelengths, it absorbs energy of particular wavelengths, while the wavelengths not absorbed simply pass through or are reflected from the sample unchanged.
2. Of the four possible transitions given below, the last three are responsible for absorptions in the region 200-800 nm, whereas the first one requires much higher energy:

   $\pi - \sigma^*$ transition, $n - \sigma^*$ transition, $n - \pi^*$ transition and $\pi - \pi^*$ transition.
3. Please see Table 11.3.
4. UV-Visible spectroscopy involves the valance electron transitions and thus gives information about π-bonds and conjugated systems of small organic

molecules.

5. In chloroethylene, CH_2=CHCl, C=C is a chromophore. Cl is an auxochrome. Substitution of a hydrogen atom in ethylene by a halogen atom causes a bathochromic shift and a hyperchromic effect.

UNIT 12

IDENTIFICATION OF COMPOUNDS USING UV SPECTROSCOPY

Structure

12.1 INTRODUCTION

In the previous unit, you have learnt about an introduction to UV-visible spectroscopy along with the basics of electromagnetic radiation. Also you have learnt about some important terms used in this context. In this unit, you will actually learn how to identify small organic compounds, specially those with conjugated dienes, with the help of UV-visible spectroscopy. The rules to predict the position of absorption maxima in conjugated dienes and enones will then be presented. The unit will conclude with a discussion of effect of solvents on $n - \pi^*$ and $\pi - \pi^*$ transitions in carbonyl and unsaturated compounds and some representative problems based on these.

Expected Learning Outcomes

After studying this unit you should be able to:

- understand the applications of Electronic Spectroscopy and Woodward rules to predict the absorption maximum for *α, β* –unsaturated compounds;

- explain the effect of solvent on $n - \pi^*$ and $\pi - \pi^*$ transitions in electronic spectra; and
- be able to solve problems on UV-vis spectroscopy for small organic molecules.

12.2 APPLICATION OF ELECTRONIC SPECTROSCOPY AND WOODWARD RULES FOR CALCULATING λ_{max} OF α, β - CONJUGATED DIENES

In the previous unit, you have learnt about the term chromophore. In this section, we shall discuss the applications of electronic absorptions of only two of the more important chromophores in more detail. These are the ethylenic and the carbonyl chromophores. We will also look into the Woodward rules for calculating λ_{max} of conjugated dienes. In addition, we shall have a brief look at the absorptions of the acetylenic and the benzenoid chromophores.

12.2.1 Ethylenic Chromophore

As you know ethylene has five σ bonds (four C–H and one C–C) and one π bond. If we denote σ molecular orbitals as σ_1, σ_2 etc., and consider only the twelve valence electrons, the ground state electronic configuration of ethylene is $(\sigma_1)^2(\sigma_2^*)^2(\sigma_3)^2(\sigma_4^*)^2\ (\sigma_5)^2\ \ (\pi)^2$. If we consider only the highest σ orbital, the ordering of the molecular orbitals is as shown in Fig. 12.1.

In ethylene only four electronic transitions are possible which are $\pi - \pi^*, \sigma - \sigma^*, \pi - \sigma^*$ and $\sigma - \pi^*$. Out of these the latter two are symmetry forbidden. Of the other two, you can see from the Fig. 12.1, the $\pi - \pi^*$ transition requires less energy. In ethylene in the vapour phase the $\pi - \pi^*$ transition appears at 165 nm (ε_{max} = 1000 $m^2\ mol^{-1}$). The transition is out of the normal range of most spectrometers.

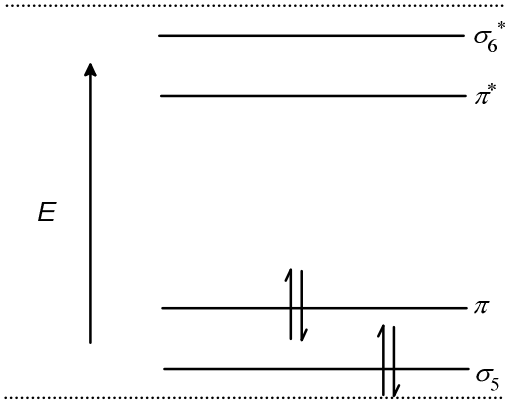
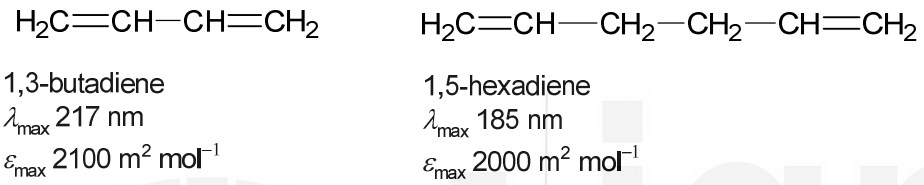


Fig. 12.1: Orbital energy diagram for ethylene.

Alkyl substitution of the ethylenic compound moves the absorption to longer wavelengths (bathochromic shift). The effect is progressive as the number of alkyl groups increases. Attachment of a heteroatom (bearing nonbonded electrons) to the ethylenic linkage also gives rise to a red or bathochromic

shift. Nitrogen and sulphur are the most effective heteroatoms shifting the absorption well into the near ultraviolet region. For example methyl vinyl sulphide ($CH_3SCH=CH_2$) absorbs at 228 nm. The absorptions of cyclic monoolefins resemble those of the open chain olefins and the absorption has no relationship to ring size. When there are two or more isolated ethylenic bonds in a molecule, it absorbs at the same position as the single ethylenic chromophore. The intensity of absorption, however, is proportional to the number of isolated chromophoric groups in the molecule.

As the absorption due to isolated ethylenic chromophore takes place in far ultraviolet region, electronic spectroscopy has thus little use in detecting isolated double bond. Conjugation markedly affects the position of absorption due to the $\diagup C{=}C \diagdown$ chromophore giving rise to a bathochromic shift. Thus, the λ_{max} value for $\pi - \pi^*$ transition for the 1, 3-butadiene is 217 nm as compared to 185 nm for the 1,5-hexadiene.



This relatively large increase in the wavelength of absorption due to conjugation can be explained as follows. In ethylene, the two 2*p* atomic orbitals combine to form a set of π and π^* molecular orbitals. In conjugated dienes such as 1,3-butadiene, when π and π^* molecular orbitals of two ethylenic linkages are close enough, overlap can occur. As a result, a combination of two π molecular orbitals gives two delocalized orbitals of lower and higher energy (π_1 and π_2). Similarly the two π^* orbitals give rise to two delocalized π^* orbitals of different energies (π_3^* and π_4^*) (Fig.12.2). Thus, the lowest energy $\pi_2 - \pi_3$ transition in 1,3-butadiene occurs at a longer wavelength (217nm) as compared to the lowest energy $\pi - \pi^*$ transition of 1,5-hexadiene (185 nm).

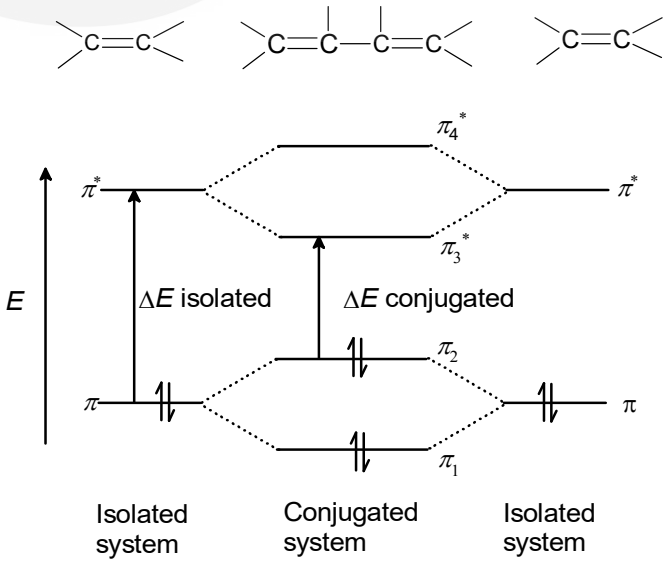


Fig. 12.2: Molecular orbital energy relationship between π-orbitals of isolated and conjugated dienes.

As the extent of conjugation increases, it lowers still further the energy of transition from the highest occupied π orbital to the lowest unoccupied π^* orbital, thereby the λ_{max} value increases.

Table 12.1 gives the wavelengths of some conjugated polyenes that demonstrate this effect.

Table 12.1: Absorption bands of conjugated polyenes $H(CH=CH)_nH$

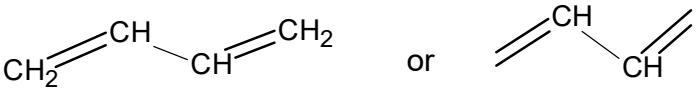
n	λ_{max}/nm
2	217
3	268
4	304
5	334
6	364
11	390
8	410

The effects of substituents and geometry on the absorption bands of conjugated dienes are fairly consistent. A set of empirical rules has been formulated by Woodward to predict the absorption of open chain (acyclic) and six-membered ring dienes. These rules have been modified by Feiser and Scott. The rules are summarised in Table 12.2.

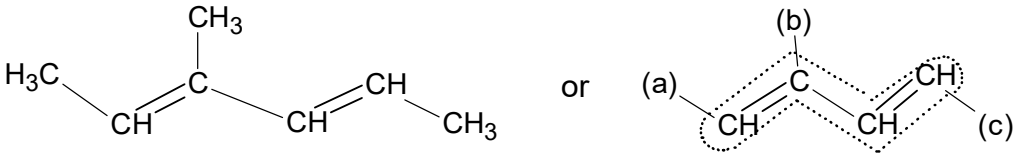
Table 12.2: Woodward Rules for predicting $\pi - \pi^*$ Absorption in Dienes

Value assigned to parent open chain diene			217 nm
Value assigned to parent heteroannualar diene			214 nm
Value assigned to parent homoannualar diene			253 nm
Increments for			
a)	each alkyl substituent or ring residue		5 nm
b)	each exocyclic double bond		5 nm
c)	Each double bond extending conjugation		30 nm
d)	auxochrome	– O(acyl)	0 nm
		–O(alkyl)	6 nm
		–S(alkyl)	30 nm
		–Cl, –Br	5 nm
		$-N(alkyl)_2$	60 nm
		Calculated λ_{max} =	Total

In order to be able to apply these rules you must be able to identify the type of structures referred to in Table 12.2. The basic chromophore unit is a 1,3-butadiene which is considered the parent acyclic (or non-cyclic) diene:



If saturated alkyl groups are attached to the diene, then an additional contribution for each group is added, e.g., $\pi - \pi^*$ absorption in 1,2,4-trimethylbutadiene(I) is analysed in terms of the rules as follows:



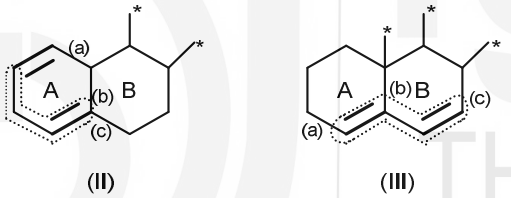
Base value for acyclic diene (I) = 217 nm

For three methyl groups, add 3×5 = + 15 nm

Predicted λ_{max} for $\pi - \pi^*$ transition = 232 nm

Observed λ_{max} for $\pi - \pi^*$ transition = 231 nm

If the diene system is contained in a single ring, it is termed homoannular, e.g., compound (II). On the other hand if it is spread over two rings, it is said to be heteroannular, e.g., compound (III).



For compound (II) we have a base value of = 253 nm

For three ring residues (a), (b) and (c): add 3×5 nm = + 15 nm

The lower double bond in A is attached to but is outside ring B, i.e., it is exocyclic to ring B: add 5 nm = + 5

Predicted λ_{max} value = 273 nm

Observed λ_{max} value = 275 nm

Note that the groups marked with a * do not contribute as they are not directly attached to the diene system.

For compound (III) we have a base value of = 214 nm

For three ring residues (a), (b) and (c): add 3×5 nm = + 15 nm

The double bond in ring A is in exocyclic position to ring B: add 5 nm = + 5

Predicted λ_{max} value = 234 nm

Observed λ_{max} value = 235 nm

Thus in all the three cases, the predicted λ_{max} values are in very good agreement with the observed values.

SAQ 1

Why the λ_{max} value for $\pi - \pi^*$ transition for the 1, 3-butadiene is 217 nm as compared to 185 nm for the 1,5-hexadiene?

12.2.2 Acetylenic and Benzenoid Chromophore

The electronic spectra of the acetylenic and benzenoid chromophores are more complex than those of the ethylenic chromophore. These cannot be explained by following the model presented for the ethylenic chromophore. They exhibit three absorption bands each as shown below.

Acetylene: 152 nm (strong), 182 nm (moderate), 220 nm(weak)

Benzene: 184 nm (strong), 204 nm (strong), 254 nm (weak).

In each case, you can see, the lowest energy absorption band is weak, which is characteristic of a forbidden transition, e.g., $n - \pi^*$. But there are no non-bonding electrons in these molecules. Thus all the three transitions arise from $\pi - \pi^*$ transitions. Acetylene and benzene are highly symmetrical molecules having degenerate molecular orbitals. Transitions between degenerate orbitals in these cases give rise to the complexity in their electronic spectra.

12.2.3 Carbonyl Chromophore

You know that the carbonyl group contains, in addition to a pair of σ electrons, a pair of π electrons and two pairs of nonbonding electrons. Saturated aldehydes and ketones exhibit three absorption bands due to $\pi - \pi^*$, $n - \sigma^*$ and $n - \pi^*$ transitions (Fig. 12.3)

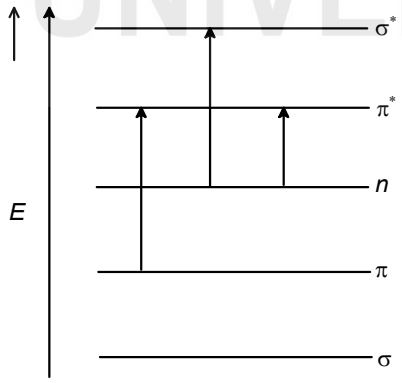


Fig. 12.3: Electronic transitions of a carbonyl group in aldehyde and ketones.

Two bands appear in the far ultraviolet region near 150 nm and 190 nm region and are due to the $\pi - \pi^*$ and $n - \sigma^*$ transitions, respectively. The third band is due to the forbidden $n - \pi^*$ transition which appears as a weak band (ε_{max} < 3.0 m^2 mol^{-1}) in the near ultraviolet region in the 270-300 nm region. In formaldehyde the $n - \pi^*$ absorption band is found at 310 nm. In contrast to the situation in alkenes, alkyl substitution moves this absorption to higher energy. Thus in acetaldehyde and acetone this band appears at 290 nm and 279 nm,

respectively. Auxochromes such as Cl, OH and NH_2 cause a larger shift in the carbonyl $n - \pi^*$ absorption to shorter wavelengths. The shift in absorption results from a combination of resonance and inductive effects. The resonance effect (π-electron release) of the lone pair of the substituent raises the energy of the π^* orbital, but leaves the nonbonding electrons of the carbonyl group unchanged in energy (Fig. 12.4 (a)). The negative inductive effect (σ-electron withdrawal) lowers the energy of the nonbonding orbital by making the carbon atom of the group more positive (Fig. 12.4 (b)). The overall shift arises from the sum of these two effects.

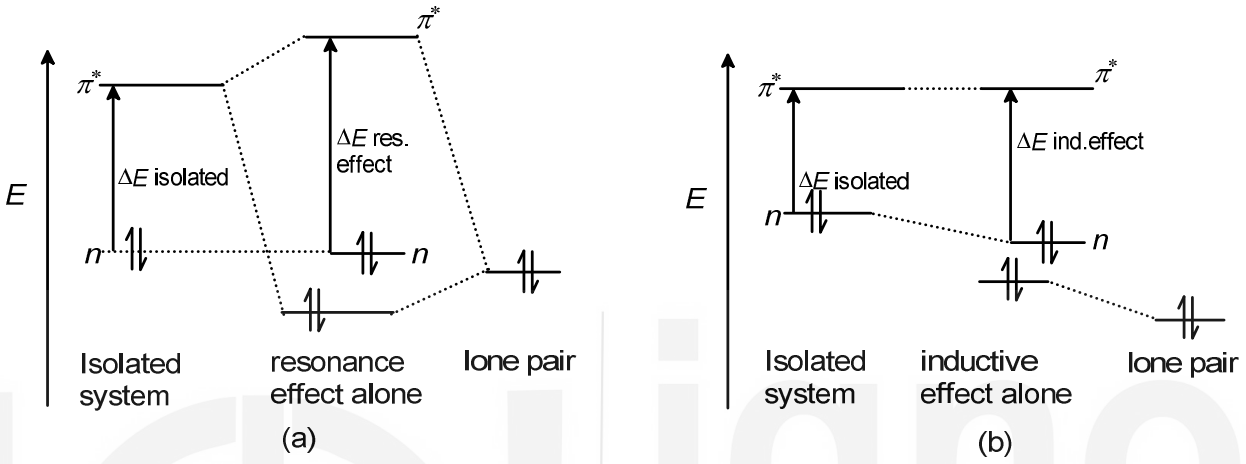


Fig. 12.4: Schematic diagram of a) the resonance effect alone and b) the inductive effect alone of a substituent on the $n - \pi^*$ transition of a carbonyl group.

When a carbonyl group of a ketone is conjugated with a carbon-carbon double bond ($\diagdown C{=}C \diagup$), the compound is known as an enone or α, β-unsaturated ketone, e.g., methyl vinyl ketone ($CH_3COCH{=}CH_2$). Conjugation has an effect on the energy of $\pi - \pi^*$ transition similar to that in alkenes. As the energy of the π^* orbital is lowered by conjugation (Fig.12.5), the $\pi - \pi^*$ and $n - \pi^*$ absorptions move to longer wavelengths. Thus for propenal ($CH_2{=}CH{-}CHO$), the $\pi - \pi^*$ and $n - \pi^*$ absorptions occur at 202 nm and 336 nm, respectively.

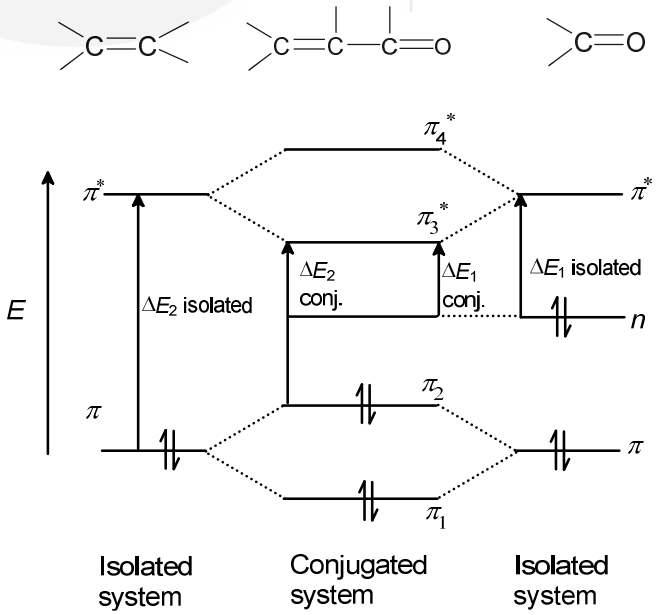
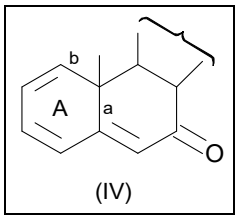


Fig. 12.5: Orbital energy relationships between isolated and conjugated C=C and C=O groups.

As with the conjugated dienes, there are empirical rules to predict the position of the $\pi - \pi^*$ band in enones. These rules were put forth by Woodward and modified by Feiser and Scott. These rules are summarised in Table 12.3.

We will now apply the rules for α, β-unsaturated ketones to predict the absorption maximum in compound IV.



(IV)

Value for α, β-unsaturated ketones	=	215 nm
for β-substituent (marked a); add 12 nm	=	+ 12 nm
for α-substituent (marked b); add 18 nm	=	+ 18 nm
for two double bonds extending conjugation; add 2 × 30 nm	=	+ 60 nm
for homoannular diene component; add 39 nm	=	+ 39 nm
For exocyclic double bond; add 5 nm	=	+ 5 nm
calculated λ_{max} value	=	349 nm

Three λ_{max} values have been observed for this compound and these are 230 nm, 278 nm and 348 nm. The longest wavelength peak is in excellent agreement with the calculated value.

Table 12.3: Feiser and Scott rules for predicting $\pi - \pi^*$ absorption in α, β-unsaturated ketones (enones) and aldehydes

Value for parent acyclic ketone					215 nm
Value for parent six-membered ring ketone					215 nm
Value for parent five-membered ring ketone					202 nm
Value for parent unsaturated aldehyde					207 nm
Increments for					
a)	each of double bond extending the conjugation				30 nm
b)	each alkyl group or ring residue			α	10 nm
				β	12 nm
				γ and higher	18 nm
c)	auxochromes	(i)	–OH	α	35 nm
				β	30 nm
				δ	50 nm
		(ii)	–OAc	α, β, δ	6 nm
		(iii)	–OMe	α	35 nm
				β	30 nm
				γ	17 nm
				δ	31 nm
		(iv)	–Salk		85 nm
		(v)	–Cl	α	15 nm
				β	12 nm
		(vi)	–Br	α	25 nm
				β	30 nm
		(vii)	NR_2	β	95 nm

d)	exocyclic double bond	5 nm
e)	homodiene component	39 nm
	Calculated λ_{max} value	= Total

The next section describes the effect of solvent on electronic spectra.

SAQ 2

Explain with the help of a diagram the orbital energy relationships between isolated and conjugated C=C and C=O groups.

12.3 SOLVENT EFFECTS ON ELECTRONIC SPECTRA

As with vibrational spectra, the phase of the sample or the solvent used while measuring the spectrum can make a marked difference to the electronic spectra. Broadly, there are two extremes; the vapour phase and non-polar solvents on the one hand, and polar and hydroxylic solvents on the other. Let us consider the effect of solvents on $\pi - \pi^*$ and $n - \pi^*$ transitions one by one.

$\pi - \pi^*$ transitions

When a polar solvent is used, the dipole-dipole interaction with the solvent molecules lowers the energy of the excited state more than that of the ground state (Fig. 12.6). This is due to the fact that excited states are more polar than ground states. The energy difference between the excited and ground states is reduced. This leads to a small red shift of the absorption maximum in polar solvents. Thus the $\pi - \pi^*$ transition shows a red shift of the order of 10-20 nm when the solvent is changed from hexane to ethanol.

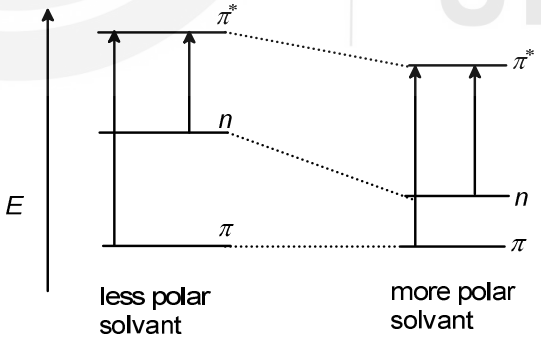


Fig. 12.6: Solvent effects on $n - \pi^*$ and $\pi - \pi^*$ transition.

$n - \pi^*$ transitions

Solvent effect for $n - \pi^*$ transitions is opposite to that found for $\pi - \pi^*$ transitions. Polar solvents cause a shift to lower wavelengths (blue shift) relative to non-polar solvents or the vapour phase. The effect is particularly pronounced in hydroxylic solvents. The lone-pair electrons in the non-bonding orbital hydrogen bond or otherwise interact strongly with the polar solvent, leading to a lowering in energy of the non-bonding orbital whereas π^* orbital is

affected much less (Fig.12.6). The result is an increase in the transition energy on going from a less polar to a more polar solvent. For example, in hexane solution, acetone shows absorption maximum at 279 nm whereas in aqueous solution, the absorption maximum is at 264.5 nm.

SAQ 3

Fill in the blanks in the following statements using the words given below:

Polar, red, increased, decreased

a) The $\pi - \pi^*$ transition shows a _____ shift in more polar solvents.

b) The $\pi - \pi^*$ transition shows a blue shift in more _____ solvents.

c) Hyperchromic effect means that the intensity of an absorption is _____

d) Hypochromic effect means that the intensity of an absorption is _____

12.4 REPRESENTATIVE PROBLEMS

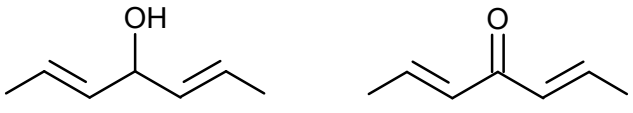
In this section there are some representative problems based on UV-visible spectroscopy. Try to solve them on your own and then verify the solution.

Example 12.1: Which molecule absorbs at the longer wavelength, 1,3-hexadiene or 1,4-hexadiene?

1,3-hexadiene 1,4-hexadiene

Solution: 1,3 hexadiene is conjugated and so absorbs at longest wavelength.

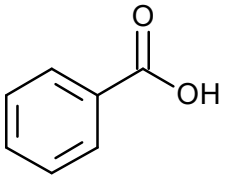
Example 12.2: Which of the following two molecules absorbs at the longer wavelength?



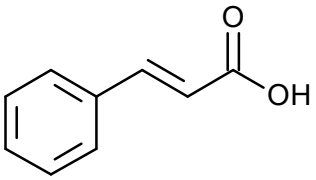
A B

Solution: Generally, the more the conjugation length, the higher the λ_{max}. B (the ketone participates in conjugation, while the carbon with the alcohol (A) does not), so B will absorb at longer wavelength.

Example 12.3: Benzoic acid has an absorption maximum at 230 nm. Where do you expect to see the absorption maximum in cinnamic acid?



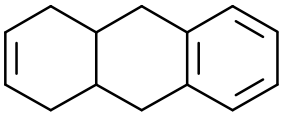
benzoic acid

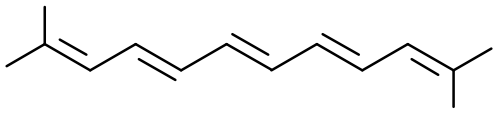


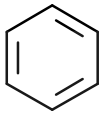
cinnamic acid

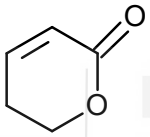
Solution: Add another 30 or 40 nm due to conjugation and you get 260 or 270 nm.

Example 12.4: Which of the following compounds is most likely to absorb the visible region of the electromagnetic spectrum?

a) 

b) 

c) 

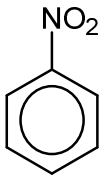
d) 

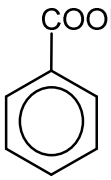
e) 

Solution: B as the length of its conjugation is quite large.

Example 12.5: Which of the following compounds absorbs UV radiation? Heptane, benzene, butadiene, water, 1-heptene, nitrobenzene, benzoic acid.

Solution:

S. No.	Name	Structure	Type of Transmission
1.	Heptane	$CH_3–(CH_2)_3–CH_3$	$\sigma \rightarrow \sigma^*$ transition (No absorption, need very high energy)
2.	Benzene		$\pi \rightarrow \pi^*$ transition
3.	Butadiene	$CH_2=CH–XH=CH_2$	$\pi \rightarrow \pi^*$ transition
4.	Water	H_2O	$\sigma \rightarrow \sigma^*$ transition
5.	1-heptene	$CH_3–(CH_2)_4–CH=CH_2$	$\pi \rightarrow \pi^*$ transition
6.	Nitrobenzene		$\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition

7.	Benzoic acid		$\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition

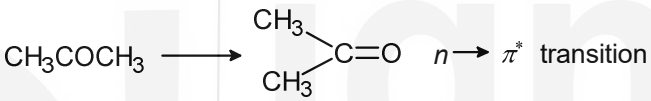
Example 12.6: UV spectrum of acetone (CH_3COCH_3) shows two peaks at λ_{max} = 189 nm and λ_{max} =273 nm. Identify the electronic transitions for each peak.

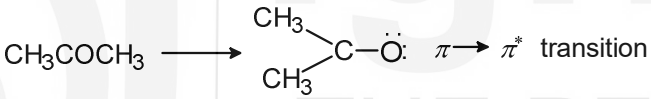
Solution:

1. Higher wavelength, have less energy, show $n \rightarrow \pi$ transition (λ_{max} = 273 nm).
2. Lower wavelength, have high energy, show $\pi \rightarrow \pi^*$ transition (λ_{max} = 189 nm).

We know that

$\pi \rightarrow \pi^* > n \rightarrow \pi^*$



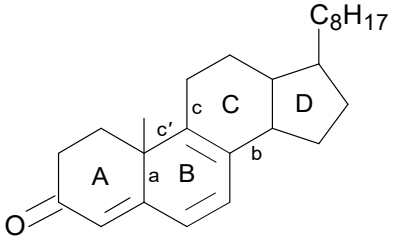


12.5 SUMMARY

In this unit, you have learnt how to identify small organic compounds, specially those with conjugated dienes, with the help of UV-visible spectroscopy. Discussions on the Woodward rules to predict absorption maxima in conjugated dienes, trienes and α, β-unsaturated aldehydes and ketones have been included. Lastly the effect of solvent on $n - \pi^*$ and $\pi - \pi^*$ transitions in carbonyl and unsaturated compounds and problems based on these have also been discussed.

12.6 TERMINAL QUESTION

1. Most spectrometers cannot detect the wavelength of ethylene but can do so when there is an alkyl substitution of the ethylenic compound , why?
2. Expalin with the help of a diagram the resonance and the inductive effect of a substituent on the $n - \pi^*$ transition of a carbonyl group.
3. Will nitrobenzene absorb UV radiations? Justify.
4. Calculate the λ_{max} for the unsaturated ketone (V).



(V)

12.7 ANSWERS

Self-Assessment Questions

1. This relatively large increase in the wavelength of absorption is due to conjugation and can be explained as follows. In ethylene, the two 2*p* atomic orbitals combine to form a set of π and π^* molecular orbitals. In conjugated dienes such as 1,3-butadiene, when π and π^* molecular orbitals of two ethylenic linkages are close enough, overlap can occur. LCAO of two π molecular orbitals gives two delocalized orbitals of lower and higher energy (π_1 and π_2). Similarly the two π^* orbitals give rise to two delocalized π^* orbitals of different energies (π_3^* and π_4^*) (Fig.12.2). Thus, the lowest energy $\pi_2 - \pi_3^*$ transition in 1,3-butadiene occurs at a longer wavelength (217nm) as compared to the lowest energy $\pi - \pi^*$ transition of 1,5-hexadiene (185 nm).

2. When a carbonyl group of a ketone is conjugated with a carbon-carbon double bond ($\diagdown C{=}C \diagup$), the compound is known as an enone or α, β-unsaturated ketone, e.g., methyl vinyl ketone ($CH_3COCH{=}CH_2$). Conjugation has an effect on the energy of $\pi - \pi^*$ transition similar to that in alkenes. As the energy of the π^* orbital is lowered by conjugation (Give Fig.12.5), the $\pi - \pi^*$ and $n - \pi^*$ absorptions move to longer wavelengths. Thus for propenal ($CH_2{=}CH{-}CHO$), the $\pi - \pi^*$ and $n - \pi^*$ absorptions occur at 202 nm and 336 nm, respectively.

3. a) red b) polar c) increased d) decreased

Terminal Questions

1. Alkyl substitution of the ethylenic compound moves the absorption to longer wavelengths (bathochromic shift) which is detectable by most spectrophotometers.

2. Auxochromes such as Cl, OH and NH_2 cause a larger shift in the carbonyl $n - \pi^*$ absorption to shorter wavelengths. The shift in absorption results from a combination of resonance and inductive effects. The resonance effect (π-electron release) of the lone pair of the substituent raises the energy of the π^* orbital, but leaves the nonbonding electrons of the carbonyl group unchanged in energy (give Fig. 12.4 (a)). The negative inductive effect (σ-electron withdrawal) lowers the energy of the nonbonding orbital by making the carbon atom of the group more positive (give Fig. 12.4 (b)). The overall shift arises from the sum of these two effects.

3. Yes. Nitrobenzene will absorb UV radiations as it shows $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.

4.

Base value for α, β-unsaturated ketone	= 215 nm
for two double bonds extending conjugation, add (2×30)	= + 60 nm
for ring residue β (marked a), add 1 × 12 nm	= + 12 nm
for ring residue (marked b), add 1 × 18 nm	= + 18 nm
for ring residue (marked c and c′), add 2 × 18 nm	= + 36 nm
for one exocyclic double bond in ring marked A, add 1×5 nm	= + 5 nm
for homodiene component, add 1 × 39 nm	= + 39 nm
Calculated λ_{max}	= 385 nm

UNIT 13

IR SPECTROSCOPY

Structure

13.1 INTRODUCTION

Scientists have done extensive research on utilizing infrared (IR) spectroscopy to characterize numerous compounds. Infrared spectroscopy is an analytical technique which is based on the vibrational transitions of a molecule. In this unit and in the next unit you are going to mainly learn how IR spectroscopy helps in the determination of the structure of simple organic molecules. In the next unit you are going to learn more about how to use IR spectroscopy to identify simple organic molecules for both known and unknown simple organic compounds. In this way, with the help of units 13 and 14 of this block, you will be able to understand how to use IR spectroscopy as a powerful tool to identify simple organic molecules.

Expected Learning Outcomes

After studying this unit, you should be able to:

- understand the range of IR Radiation as well as that of the Fingerprint Region;
- discuss the different types of molecular vibrations; and
- gain knowledge about the characteristic frequencies of functional groups.

13.2 RANGE OF IR RADIATION (FINGERPRINT REGION)

While identifying a simple organic molecule, it is very important to understand the following:

- How the atoms are connected together?
- Which bonds are single, double, or triple?
- What functional groups exist in the molecule?
- Do we have a specific stereoisomer?

The answers to these questions can be found to a large extent from IR spectroscopy of the compounds which we are going to discuss now.

Infrared spectroscopy

The IR spectroscopy involves in triggering molecular vibrations through irradiation with infrared light. Infrared radiation is largely thermal energy. It induces strong molecular vibrations in covalent bonds, which are almost the same as springs holding together two masses, or atoms as shown in Fig. 13.1 below.

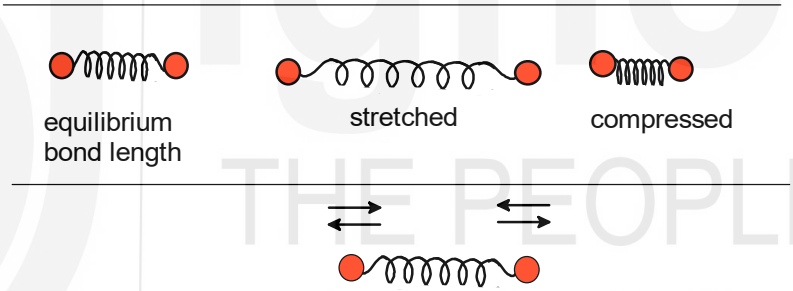


Fig. 13.1: Springs holding together two masses, or atoms.

IR spectroscopy provides mostly information about the presence or absence of certain functional groups. Specific bonds respond to (absorb) specific frequencies. Upon irradiation with infrared light, certain bonds respond by vibrating faster. This response can be detected and translated into a visual representation called a spectrum as shown in Fig. 13.2.

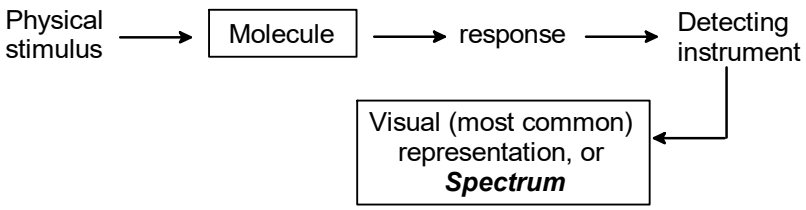


Fig.13.2: Spectral information as obtained from spectroscopy.

Spectroscopic techniques, including, infrared (IR) spectroscopy, involve the interaction of molecules with electromagnetic radiation. Thus, to understand the fundamentals of spectroscopy, you must recapitulate the fundamentals of electromagnetic radiation.

In previous Unit 11 of this course, you have recapitulated about electromagnetic radiation, and we will provide only a summary here. Gamma rays, X-rays, ultraviolet light, visible light, **infrared radiation**, microwaves and radio waves are all examples of **electromagnetic radiation** and part of the electromagnetic spectrum. Because electromagnetic radiation behaves as a wave travelling at the speed of light, it is described in terms of its wavelength and frequency. Fig. 13.3 shows the electromagnetic spectrum where the IR region has been highlighted.

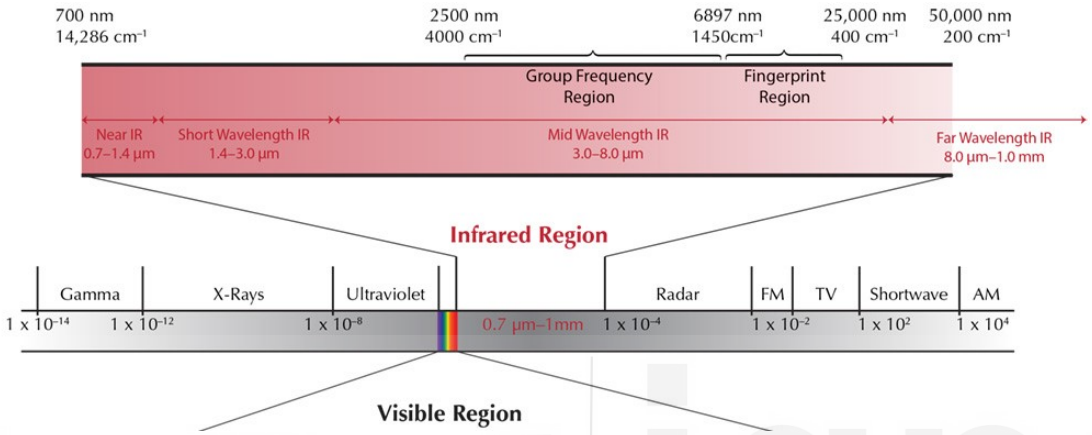


Fig. 13.3: The electromagnetic spectrum where the IR region has been highlighted.

In Unit 11 you have also recapitulated about wavelength λ and it SI base unit of meters and its relation with the **frequency** ν in s^{-1} (also called **hertz, Hz**). Alternatively, the electromagnetic radiations in terms of particles have also been discussed there.

You have already studied that molecules are flexible structures with atoms and groups of atoms able to rotate around covalent single bonds. Covalent bonds stretch and bend just as if the atoms were joined by flexible springs as shown earlier in Fig. 13.1. We know from experimental observations and from theories of molecular structure that all energy changes within a molecule are quantized; that is, they are subdivided into small, but well-defined, increments. For example, vibrations of bonds within a molecule can undergo transitions only between allowed vibrational energy levels.

We can cause an atom or molecule to undergo a transition from energy state E_1 to a higher energy state E_2 by irradiating it with electromagnetic radiation corresponding to the energy difference between states E_1 and E_2 as illustrated schematically in Fig. 11.1 in Unit 11 of this block.

When the atom or molecule returns to the ground state from excited state, equivalent amount of energy is emitted. When a compound is irradiated with electromagnetic radiation of various wavelengths, it absorbs energy of particular wavelengths, while the wavelengths not absorbed simply pass through or are reflected from the sample unchanged. In infrared (IR) spectroscopy, when we irradiate a compound with infrared radiation, this radiation is absorbed when its energy (frequency) is exactly equal to the energy required to excite a molecule to a higher energy state. Because different functional groups have different bond strengths, the energy required

to bring about these transitions varies from one functional group to another. Thus, in infrared spectroscopy, we can detect functional groups by the vibrations of their bonds.

The infrared region of the electromagnetic spectrum (Fig. 13.3) covers the range of wave lengths from 7.8 x 10^{-7} m (just longer than the visible region) to 2.0 x 10^{-3} m (just shorter than the microwave region). In chemistry, however, we routinely use only the portion that extends from 2.5 x 10^{-6} to 2.5 x 10^{5} m. This region is often called the **vibrational infrared** region and we commonly refer to radiation in this region by its **wavenumber** $(\bar{\nu})$, the number of waves per centimeter which you have already learnt in section 11.2 of Unit 11. For molecular vibrations, the frequency value is very large, so it is convenient to use wave number for IR spectroscopy.

$$\bar{\nu} = \frac{1}{\lambda}$$

So we can say,

$$\bar{\nu} = \frac{\nu}{c} \text{ (Frequency/Velocity of light)}$$

e.g., For ν = 3 x 10^{13} s^{-1}, the wave number is

$$\bar{\nu} = \frac{3x10^{13}s^{-1}}{3x10^{10}cms^{-1}}$$

$$\bar{\nu} = 1000 \text{ cm}^{-1}$$

Expressed in wavenumbers, the vibrational region of the infrared spectrum extends from 4000 to 400 cm^{-1} (the unit cm^{-1} is read 'reciprocal centimeter'). An advantage of using wavenumbers is that they are directly proportional to energy: the higher the wavenumber, the higher the energy of radiation.

Now, let us understand what is meant by absorption of IR light and what is meant by transmission? Well, when a chemical sample is exposed to the infrared light, some of the frequencies can be absorbed while the rest may be transmitted. Even some of the light may be reflected back to the source as shown in Fig. 13.4 below. The detector detects the transmitted frequencies, and by doing so also reveals the values of the absorbed frequencies.

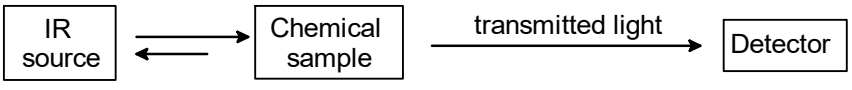


Fig. 13.4: Transmission and absorption of IR light by a chemical sample.

Next let us understand the situation when the we see the IR spectrum in the absorption mode. The absorption of radiation corresponds to trough or valley. Strange as it may seem, we commonly refer to infrared absorptions as peaks, even though they are actually troughs.

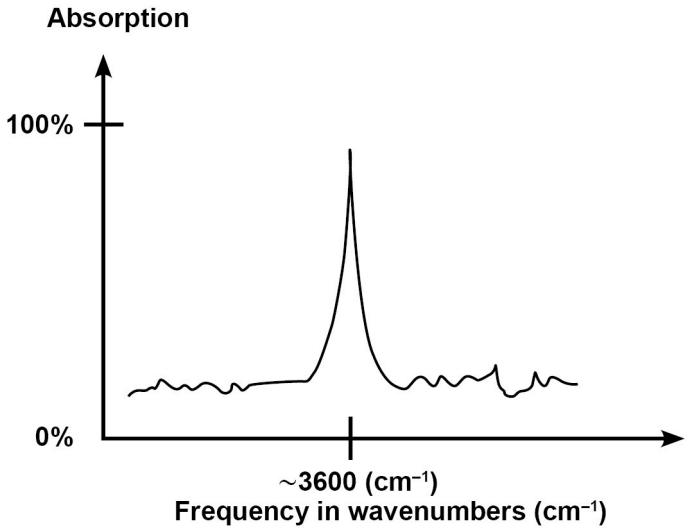


Fig. 13.5: An IR spectrum in the absorption mode.

The IR spectrum is actually the plot of transmitted (or absorbed) frequencies versus the intensity of the transmission (or absorption). Frequencies are given in units of inverse centimeters (wavenumbers) and is in the x-axis. The intensities are plotted in the y-axis in percentage units. The graph in Fig. 13.5 shows the IR spectrum in the absorption mode. The vertical axis measures transmittance, with 100% transmittance at the top and 0% transmittance at the bottom. Thus, the baseline for an infrared spectrum (100% transmittance of radiation through the sample = 0% absorption) is at the top of the chart.

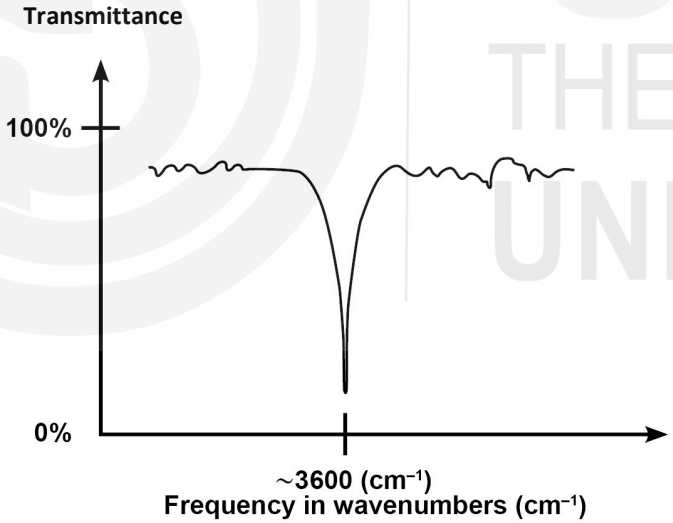


Fig. 13.6 An IR spectrum in the transmittance mode.

The graph in Fig.13.6 shows the IR spectrum in the transmittance mode (this transmittance mode graph). You will find in most chemistry and spectroscopy books and is widely used. Henceforth we will use this transmittance mode representation only.

You must also know that the IR bands may be classified as strong(s), medium (m), or weak (w), depending on their relative intensities in the infrared spectrum. Almost the whole of y-axis is covered by a strong band whereas, at about half of the y-axis falls the medium band. At almost one-third or less of the y-axis falls the weak band. Fig.13.7 shows the relative intensities in the IR spectrum of weak, medium and strong bands.

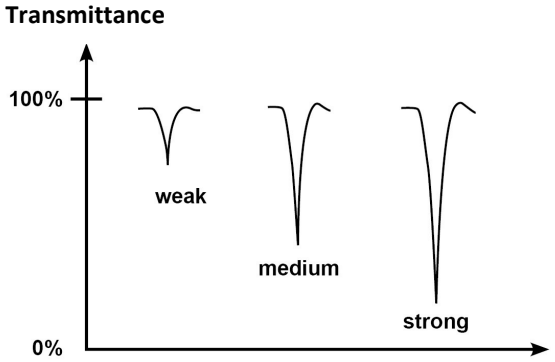


Fig. 13.7: Relative intensities in the IR spectrum of weak, medium and strong bands.

The IR region falls between wavenumbers 4000 cm^{-1} and 600 cm^{-1}. But here you must note specially the **1500 - 600 cm^{-1} region**. Above 1500 cm^{-1}, it is the diagnostic region and all the functional groups may be detected in this region. 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**.

Below in Fig. 13.8 is given a sample IR spectrum where the diagnostic part and the fingerprint regions are labelled. It is clear that you must focus your analysis on the left marked part which is the diagnostic part and not bother about the complicated fingerprint region on the right side of the spectrum.

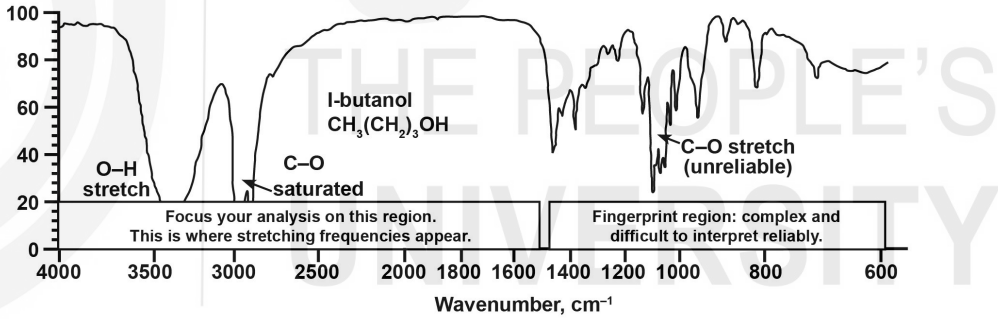
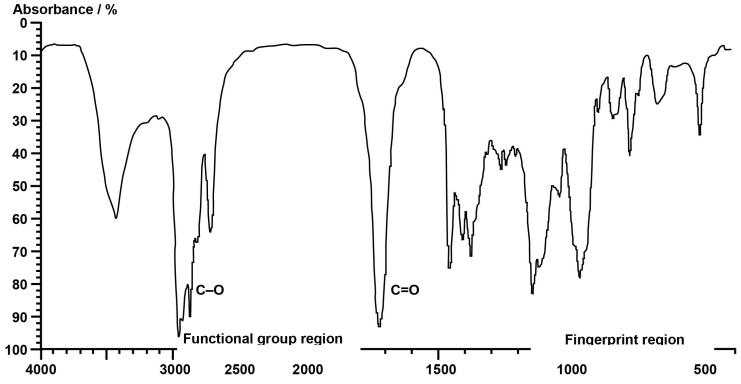


Fig. 13.8: The diagnostic and the fingerprint region of a sample IR spectrum.

SAQ 1

Based on the IR spectrum given below, what interpretations you can derive? Label the functional group region and the fingerprint region in it.



13.3 TYPES OF MOLECULAR VIBRATIONS

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

For a molecule to absorb infrared radiation, the bond undergoing vibration must be polar, and its vibration must cause a periodic change in the bond dipole. The greater the polarity of the bond, the is the cause a periodic change in the bond dipole; the greater the polarity of the bond, the more intense is the absorption. Any vibration that meets these criteria is said to be infrared active. Covalent bonds in homonuclear diatomic molecules, such as H_2 and Br_2, and some carbon-carbon double or triple bonds in symmetrical alkenes and alkynes do not absorb infrared radiation because they are not polar bonds. The multiple bonds in the following two molecules, for example, do not have a dipole moment so are not infrared active. For a molecule as simple as ethanol, CH_3CH_2OH, there are 21 fundamental vibrations, and for hexanoic acid, $CH_3(CH_2)_4COOH$, there are 54. Thus, even for relatively simple molecules, a large number of vibrational energy levels exist, and the patterns of energy absorption for these and larger molecules are quite complex.

Looking at a diatomic molecule you can say that it 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. 13.1). 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 in 3*N*.

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 3*N* - (3+3) = (3*N*-6) coordinates which account for vibrational degrees of freedom for nonlinear polyatomic molecules.

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 3*N* - (3+2) = (3*N*-5) vibrational degrees of freedom. The details of the number of degrees of freedom for linear and nonlinear molecules are presented in Table 13.1.

Table 13.1: Degrees of Freedom for Polyatomic Molecules

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

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 radiations; this radiation has no effect on the other part of the molecule.

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

Using Table 13.1, 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 x 3 – 5) = 4 vibrational degrees of freedom; H_2O molecule has (3 x 3 – 6) = 3 vibrational degrees of freedom and NH_3 molecule has (3 x 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.

In **stretching vibrations,** the atoms move along the bond axis so that the bond length increases or decrerases at regular intervals. The stretching vibrations again are of two types. They are symmetric and antisymmetric stretching. 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 stretching are shown in Figs. 13.9a and b and Figs. 13.10a 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. 13.9 and 13.10, we indicate the type of each vibration mode as parallel **(II)** 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.

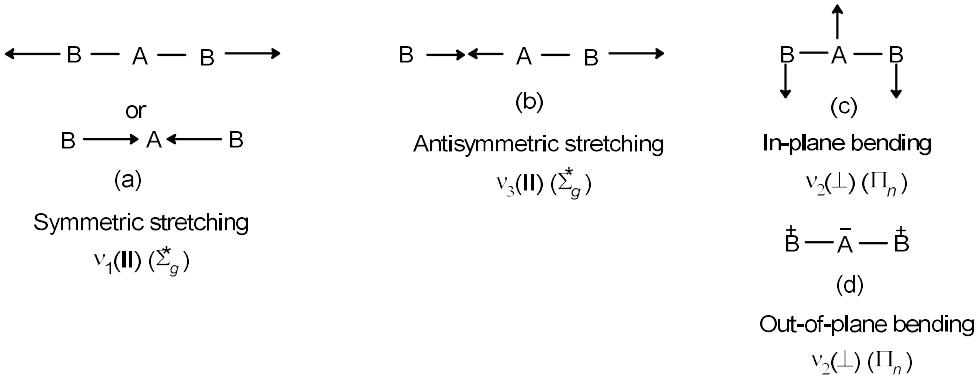
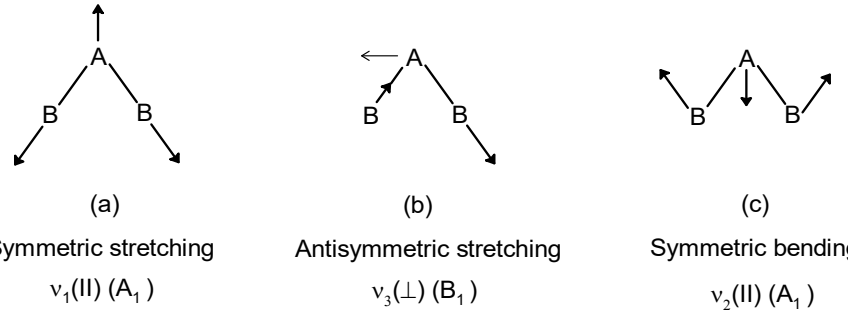


Fig. 13.9: Normal modes of a triatomic linear molecule, AB_2 (e.g., CO_2). (a) symmetric stretching (ν_1) (b) antisymmetric stretching (ν_3) (c) in-plane bending and (d) out of plane bending; both (c) and (d) are degenerate and hence these two give rise to only one band (ν_2); (+) sign shows that the 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 (II) vibrations whereas the degenerate vibration ν_2 is a perpendicular ($\perp$) vibration.



(a) Symmetric stretching ν_1(II) (A_1)

(b) Antisymmetric stretching $\nu_3(\perp)$ (B_1)

(c) Symmetric bending ν_2(II) (A_1)

Degeneracy of a vibrational mode is the number of normal modes which have same energy. For instance, the degeneracy of v_2 mode of CO_2 is two since the two bending modes (in-plane and out-of-plane) have same energy.

Fig. 13.10: 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.

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 vibrations for a polyatomic molecule. A linear triatomic molecule has two bending vibrations (Fig. 13.9c and d) while a nonlinear triatomic molecule has only bending vibration (13.10 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 2

State the number of stretching and bending modes of C_2H_2.

13.4 CHARACTERISTIC FREQUENCIES OF FUNCTIONAL GROUPS

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 chains, aromatic rings etc. give rise to skeletal vibraton 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 the next unit.

The second type of normal modes which are 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 indepdndent of the structure of the molecule as a whole. A few instances of the perturbation of group frequencies are discussed in the next unit.

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). Such group frequencies are listed in Table 13.2 which is also known as chart of group frequencies.

Table 13.2: 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)	1470-1430 and
	(s)	1380-1370
Alkane, gem-dimethyl (doublet)	(s)	1385-1380 and
	(s)	1370-1365
Alkane, tert-butyl (doublet)	(m)	1395-1385 and
	(s)	~ 1365
b. Alkene, monosubstituted	(s)	995-985
(vinyl)	(s)	915-905 and
	(s)	1420-1410
Alkene, disubstituted, *cis*	(s)	690
Alkene, disubstituted, *trans*	(s)	970-960 and
	(m)	1310-1295
Alkene, disubstituted, *gem*	(s)	895-885 and
	(s)	1420-1410
Alkene, trisubstituted	(s)	840-790
c. Alkyne	(s)	630
d. Aromatic substitution type:		
Five adjacent hydrogen atoms (monosubstituted)	(v,s)	750 and
	(v,s)	700

Three adjacent hydrogen atoms (1,2,3-trisubstituted)	(v,m)	780	
Two adjacent hydrogen atoms (1,2,3,4-tetrasubstituted)	(v,m)	830	
One hydrogen atom (pentasubstituted)	(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, disubsituted, *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)	2900-2920	and
(two bands)	(w)	2775-2700	
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		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	(w)	2700-2500
	(bonded), several bands		
c.	Carboxylate anion stretching	(s)	1610-1550 and 1400-1300
5.	**AMIDES**		
a.	Carbonyl stretching		
	Primary, solid and concentrated	(s)	1650
	Solution		
	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
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)	1050 and
	(s)	1350-1260
Secondary alcohols	(s)	1100 and
	(s)	1350-1260
Tertiary alcohols	(s)	1150 and
	(s)	1410-1310
Phenols	(s)	1200 and
	(s)	1410-1310
2. Ethers		
C-O stretching		
Dialkyl ethers	(s)	1150-1070
Alkyl vinyl ethers or	(s)	1275-1200
Alkyl phenyl ethers	(s)	1075-1020
3. AMINES		
a. N-H stretching		
Primary, free; two bands	(m)	3500 and
	(m)	3400
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
c. C-N stretching		
Aromatic, primary	(s)	1340-1250
Aromatic, secondary	(s)	1350-1280
Aromatic, tertiary	(s)	1360-1310
Aliphatic	(w)	1220-1020 and
	(w)	1410
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)	1570-1500 and
	(s)	1370-1300
Aliphatic	(s)	1570-1550 and
	(s)	1380-1370
5. HALOGEN COMPOUNDS		
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)	1180-1140 and
	(s)	1350-1300
Sulfonic acids	(s)	1210-1150
	(s)	1060-1030 and 650

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

Now we will study the characteristic regions of IR absorption using which it is possible to identify the functional groups in detail. 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 the next unit 14. 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 ($\diagdown CH_2 \diagup$) 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 akynes occur around 3300 cm^{-1}.

2500 - 2000 cm^{-1} region

The compounds conlaining 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 $\diagdown C{=}C \diagup$ and $\diagdown C{=}O \diagup$. 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} because 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 Unit 14.

SAQ 3

Give the reason for greater intensity of band for –C≡N than for –C≡C– group in the 2500 – 2000 cm^{-1} region of the IR spectrum.

13.5 SUMMARY

In this unit you have been introduced to the spectroscopic tool IR spectroscopy and how it helps in the determination of the structure of simple organic molecules. You have learnt about the range of IR radiation as well as that of the Fingerprint Region. Also the different types of molecular vibrations possible in small molecules have been discussed in detail. Lastly, the characteristic frequencies of functional groups have been given in a tabular form and introductory discussions in detail have been done on the different regions of the IR spectrum. In the next unit you are going to learn more about how to use IR spectroscopy to identify simple organic molecules in more details with the help of problems.

13.6 TERMINAL QUESTION

1. What information is obtained from the functional group region of a IR spectrum? What is its difference from the fingerprint region of the spectrum?

2. What are the normal modes if vibrations? Explain diagrammatically with a suitable example.

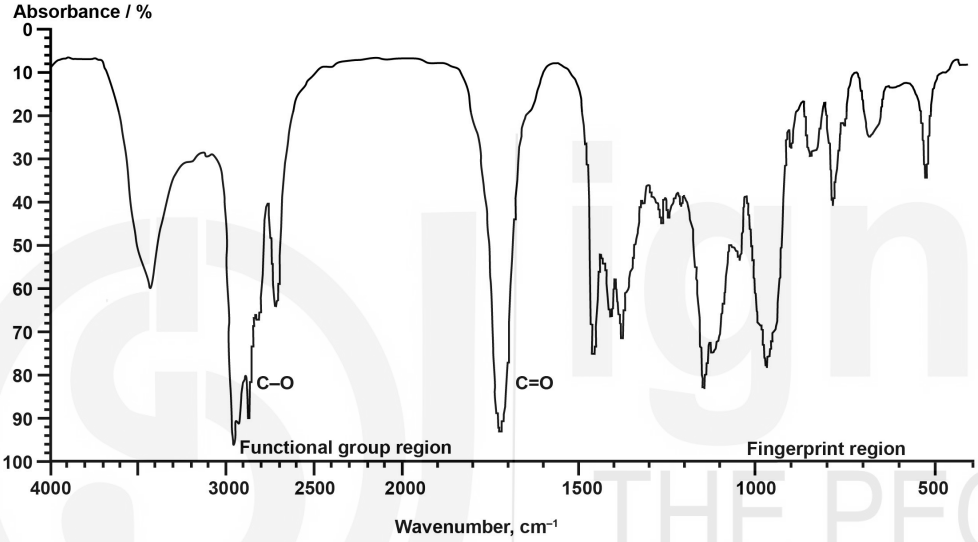
3. What are the requirements for a compound to absorb IR radiation?

4. Refer to Table 13.2 and give the stretching frequencies observed in alkyl and aryl nitriles. What is the strength of the bands?

13.7 ANSWERS

Self Assessment Questions

1. The given IR spectrum shows the x-axis as wavenumbers and the IR region falls between wavenumbers 4000 cm^{-1} and 600 cm^{-1}. The graph is in the transmittance mode which is commonly shown in most textbooks.



2. 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.

3. In the 2500 - 2000 cm^{-1} region the compounds conlaining triple bond absorb whose strength and hence the force constant is high. The carbon-carbon triple bond ($-C \equiv C-$) absorbs between 2300 and 2100 cm^{-1} and is of weak intensity. The nitrile group absorbs between 2300-2200 $cm^{-1}$and is of medium intensity. 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.

Terminal Questions

1. Most of the information that is used to interpret an IR spectrum is obtained from the functional group region. In practice, it is the polar covalent bonds than are IR "active" and whose excitation can be observed in an IR spectrum. In organic molecules these polar covalent bonds represent the functional groups. Hence, the most useful information obtained from an IR spectrum is what functional groups are present within the molecule. In the fingerprint region, the spectra tend to be more complex and much harder to assign.

2. 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.

3. The following are the requirements for a compound to absorb IR radiation:

   i) Correct wavelength of radiation - A molecule absorbs radiation when the frequency of vibrations of some part of a molecule is the same as the frequency of incident radiation.

   ii) Change in dipole moment - A molecule can only absorb IR radiations when its absorption causes a change in its electric dipole. A polar bond is usually IR active whereas non polar bond in a symmetrical molecule will absorb weakly or not at all

4. C=N stretching

Alkyl nitriles	(m)	2260-2240
α,β-unsaturated alkyl nitriles	(m)	2235-2215
Aryl nitriles	(m)	2240-2220

   The bands are all medium in strength.

UNIT 14

IDENTIFICATION OF SIMPLE ORGANIC MOLECULES

Structure

14.1 INTRODUCTION

This is the last unit of this course and Block 4 also. In the earlier units of Block 4, you have studied about the spectroscopy and identification of compounds using UV spectroscopy. In the last unit, we dealt with the basic aspects of IR spectroscopy. After understanding the fundamental aspects of IR spectroscopy, in this unit, you will study about the characteristic features of IR spectra of simple organic compounds.

We will be explaining the important features of IR spectra of various classes of organic compounds such as alkanes, alkenes, alkynes, simple alcohols, aldehydes and ketones and carboxylic acids and their derivatives.

After the detailed discussion of the IR spectra of above mentioned classes of organic compounds, we will be solving the integrated problems involving the spectral data of simple organic molecules.

Expected Learning Outcomes

After studying this unit, you should be able to:

- explain the important features of IR spectra of simple molecules belonging to various classes of organic compounds;
- correlate the important bands in IR spectrum with the structural units present in the molecule;
- solve simple problems related to the structure of the organic compounds by using their spectral data; and
- arrive at the structure of a molecule from its spectral data and also predict the spectral data for a given molecule from its structure.

14.2 SOME BASIC ASPECTS OF IR SPECTRA

Before actually discussing the important aspects of infrared spectra of simple organic molecules belonging to different classes, let us deliberate on some features listed below on which we will be focussing our attention while discussing these spectra.

(a) Position of the IR band

(b) Intensity of the IR band

The following factors determine the position of the IR band:

(i) Strength of the bond

(ii) Masses of the atoms involved in the formation of the bond

(iii) The type of vibration being observed.

From Hooke's law which you studied in Unit 13, you can say that the **stronger the bond, higher will be its vibration (IR) frequently**. Also, the **lower the atoms in the mass, the lesser will be the vibration frequency**.

Since the lesser energy is required in bending (in analogy to spring i.e., the bond holding the two balls as atoms), as compared to stretching it; the bending vibrations occur at lower frequency than the stretching vibrations. Factors which govern the intensity of a particular sample are:

(i) Concentration of the compound in sample.

(ii) The number of particular bonds in the molecule leading to that particular frequency.

(iii) The change in dipole moment involved in that particular mode of vibration being observed.

For example, if no change of dipole moment is observed in a symmetrical molecule for a particular stretching mode of a structural unit, the infrared frequency for that mode will **not be observed** in the IR spectrum. Hence, that particular vibration will be **IR inactive**.

Please note that when we say that a particular mode of vibration is IR inactive, it **does not** indicate that the particular vibration is **not** occurring the molecule. It is occurring is the molecule but not being observed in the IR spectrum due to *no change in the dipole moment* and hence, stated as **IR inactive**.

Also, the **greater the change in the dipole moment, the more intense will be** the absorption band. The intensities of the IR bands are expressed as strong, weak, medium etc. according to the observed bands.

In addition to the fundamentals bands, some overtones and coupled absorptions, though weak in nature, also appear in the IR spectra and this makes its appearance sometimes very complex. Hence, one needs to focus on the important and intense bands when the IR spectrum of a molecule is analysed and correlated to its structure.

14.3 IR SPECTRA OF ALKANES, ALKENES AND ALKYNES

In Unit 13, you have already studied about the characteristic frequencies of various functional groups. Alkanes, alkenes and alkynes have only carbon-carbon and carbon-hydrogen bonds present in their molecules. Let us now understand about the IR spectra of each of these classes of hydrocarbons.

14.3.1 IR Spectra of Alkanes

Since in alkane molecules, only C–C and C–H single bonds are present. The C–C stretching vibration is infrared **inactive** (or *nearly inactive*) as it does not involve any change (or *little change*) in the dipole moment.

However, the C–H stretching absorptions are exhibited in the 2850-2960 cm^{-1} region of infrared spectrum as intense bands as many C–H bonds are present in alkanes. For example, C–H stretching bands appear in the IR spectrum of pentane at 2961, 2928 and 2875 cm^{-1}, see Fig. 14.1.

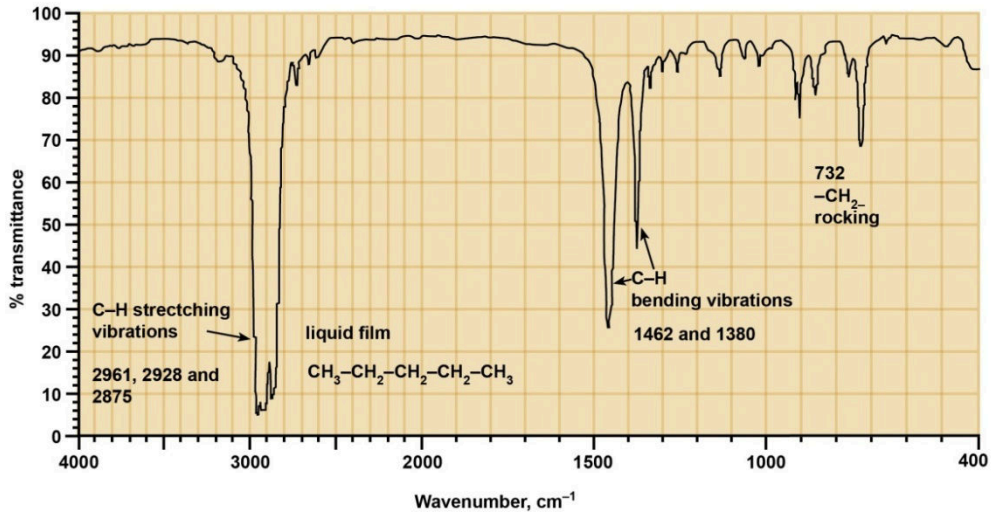


Fig. 14.1: IR Spectrum of pentane.

In addition to the C–H stretching vibrations, there are C–H bending vibrations which are observed in case of IR spectrum of pentane at 1462, 1380 and 732 cm^{-1}. Remember that the 1462 and 1380 cm^{-1} bending vibrations appear in the **finger print region**. The band at 1462 cm^{-1} is due to methylene bending (scissoring) vibration and that at 1380 cm^{-1} is due to methyl (CH_3) bending (rocking) vibration. The absorption at 732 cm^{-1} is due to another bending mode of $-CH_2-$, called rocking.

Such $C_{sp^3}-H$ stretching and C–H bending absorptions occur not only in alkanes but in many other compounds which contain CH_3- and $-CH_2-$ groups. Hence, in such compounds, these are also observed is the IR spectra as bands. But these are to be attributed to $C_{sp^3}-H$ stretching and bending modes while analysing their spectra.

SAQ 1

The IR spectrum of nonane shows bands near 2920 cm^{-1}, 1470 and 1380 cm^{-1}. Explain the origin of these bands.

Let us now study about the infrared spectra of alkenes.

14.3.2 Infrared Spectra of Alkenes

The characteristic structural feature of alkenes is the presence of a **double bond** in their molecules. But around the double bond, a lot of structural features are to be observed when we interpret the infrared spectrum of an alkene. The infrared spectrum of alkenes also give very important information about the substitution pattern of the $-\overset{|}{C}=\overset{|}{C}-$ double bond. The $C_{sp^3}-H$ stretching absorption appears between 3000 and 3200 cm^{-1}, i.e., at higher frequency as compared to $C_{sp^3}-H$ stretching which appears below 3000 cm^{-1}. Can you guess the reason for this difference?

The reason for this is that $C_{sp^2}-H$ bond is stronger than $C_{sp^3}-H$ bond; hence, the greater absorption frequency for $C_{sp^2}-H$ bond according to Hooke's law as explained in Sec. 14.2.

Alkenes show typical $\diagdown C=C \diagup$ stretching absorptions in the range of 1620 – 1680 cm^{-1}. The terminal vinyl, i.e., $-CH=CH_2$ shows C=C stretching at 1640 cm^{-1}, while the terminal methylene group i.e., $\diagdown C=CH_2$ appears at 1655 cm^{-1}.

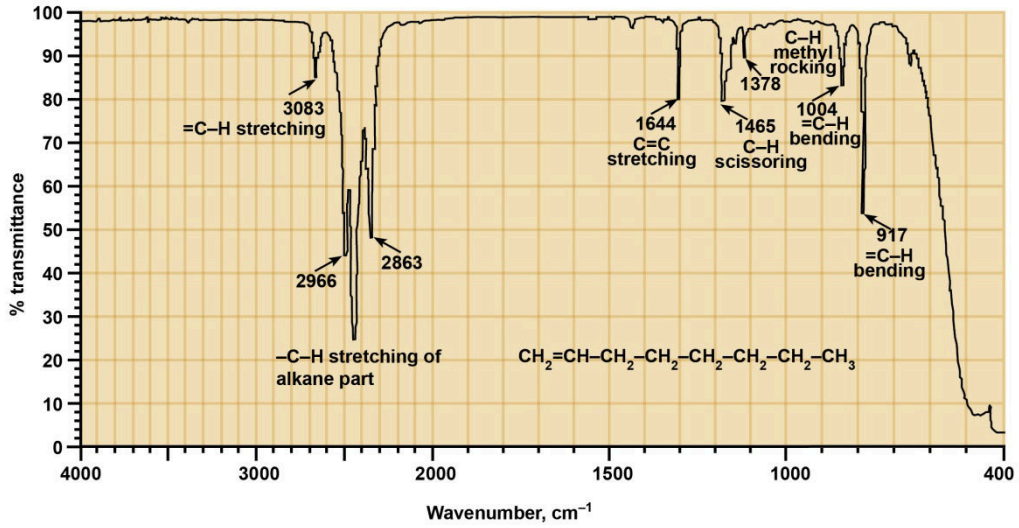
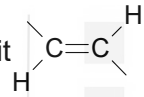
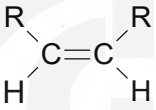


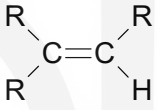
Fig. 14.2: IR spectrum of 1-octene.

The symmetrical *trans* alkenes do not exhibit  stretching absorption.

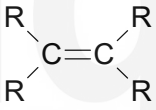
The other patterns of substitution in alkenes, are shown below:



cis-alkene



Trisubstituted alkene



Tetrasubstituted alkene

In these alkenes also, the C=C stretching is often weak or absent. This absorption, if present, occurs in the region 1660–1675 cm^{-1}.The reason being that there is no change in the dipole moment. Also, *the more the substitution at the double, the lesser the intensity and greater the frequency of absorption*. See Fig. 14.2 and 14.3 for the IR spectra of l-octene and *trans*-3-hexene, respectively.

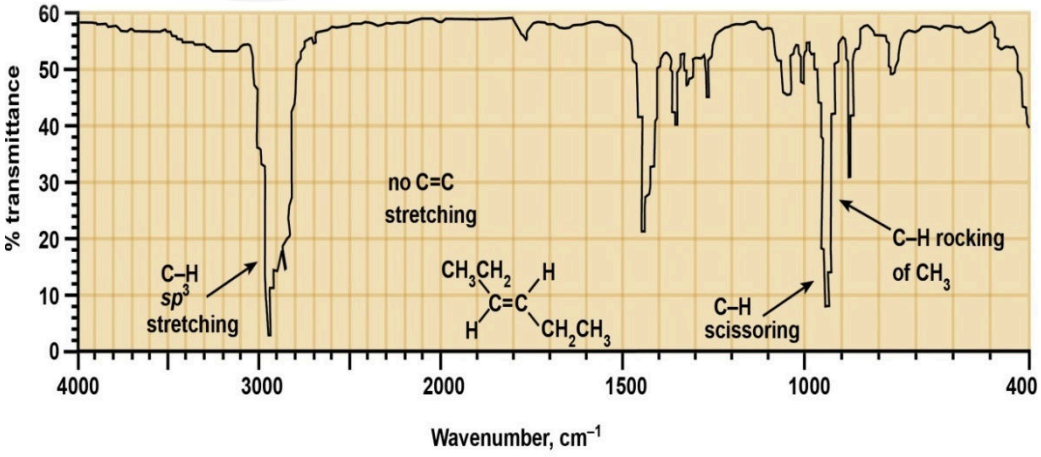
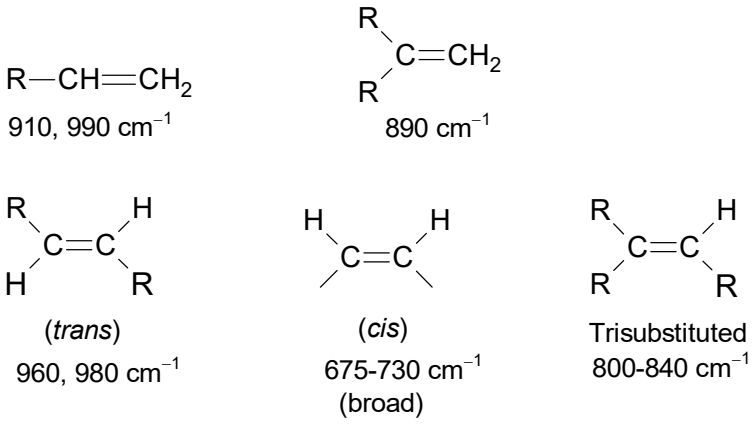


Fig. 14.3: IR spectra of *trans*-3-hexene.

The =C-H bending absorptions of alkenes appear as strong bands at lower frequencies and indicates the substitution pattern at the double bond. Some substitution patterns along with their range of absorptions are given below:



SAQ 2

An alkene having molecular formula ,C_6H_{12} shows prominent absorptions at 3080, 1640, 995 and 915 cm^{-1}. What could be its structure? Explain.

14.3.3 Infrared Spectra of Alkynes

The characteristic structural feature in alkynes is a –C≡C– unit, i.e., a triple bond between the two carbon atoms. On the basis of location of the triple bond, the alkynes can be either *terminal alkynes* when the triple bond is present between the carbon atoms at the end of the carbon chain or an *internal alkynes* when the triple bond is present at the position in between the carbon chain.

$R - CH_2 - C \equiv CH$ — A terminal alkyne

$R - C \equiv C - R$ — An internal alkyne

The characteristic – C ≡ C – absorption occurs in the range of 2100-2260 cm^{-1}. Fig. 14.4 shows the IR spectrum of 1-hexyne.

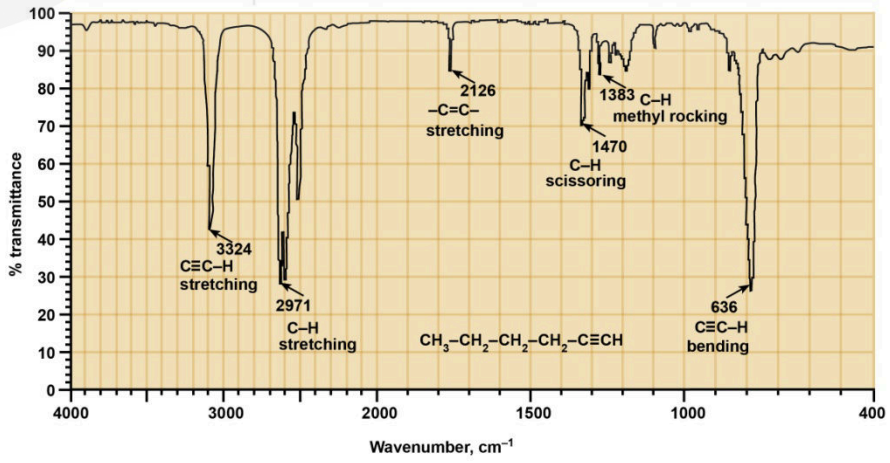


Fig. 14.4: IR spectrum of 1-hexyne

Fig. 14.4: IR spectrum of 1-hexyne.

The terminal alkynes absorb in the range 2120-2150 cm^{-1} while the internal alkynes exhibit absorption in the range of 2190-2260 cm^{-1}. The absorptions in internal alkynes are very weak and generally not observed as the change in dipole moment is almost nil. Thus, symmetrical or nearly symmetrical alkynes

do not exhibit the absorption. In terminal alkynes, the $C_{sp}-H$ stretching absorption appears at 3260-3300 cm^{-1} and the $C_{sp}-H$ bending absorption is exhibited at 636 cm^{-1}.

SAQ 3

Why IR spectroscopy cannot be used to identify symmetrical alkynes?

14.4 IR SPECTRA OF ALCOHOLS

The characteristic functional group in alcohols, –OH group exhibits O–H stretching absorption. The position and the intensity of this stretching vibration depends upon the extent of hydrogen bonding. The broad intense bands in the region 3200-3500 cm^{-1} indicate the hydrogen bonded alcohol molecules. You can see the same in the IR spectrum of ethanol shown below in Fig. 14.5.

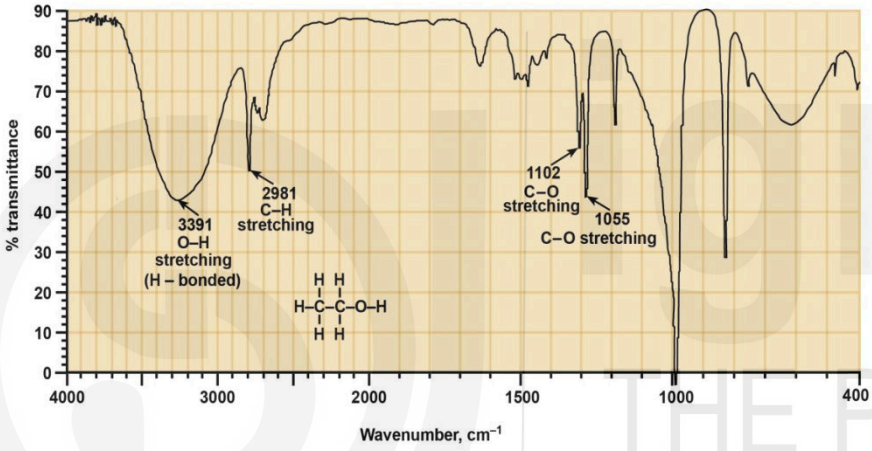


Fig. 14.5: IR spectrum of ethanol.

For example, in 1-hexanol, the hydrogen bonded stretching of O–H appears at 3340 cm^{-1} while it is observed at 3391 cm^{-1} in case of ethanol.

However, in dry alcohols or in very dilute solution (in non-hydrogen bonding solvents when hydrogen bonding is not there), the O–H stretching absorption appears at 3650 cm^{-1} as a sharp narrow band. See Fig. 14.6 below for the IR spectrum of dry ethanol.

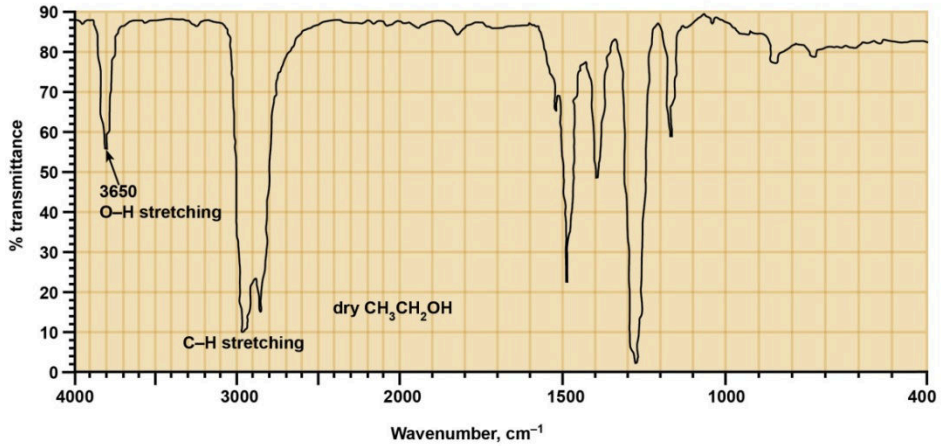


Fig. 14.6: IR spectrum of dry ethanol.

The other characteristic absoprtion of alcohols is C–O stertching absoprtion exhibited in the range 1050-1200 cm^{-1}. The primary alcohols such as I-hexanol show this absorption at 1060 cm^{-1} and they absorb at the lower end of the frequency range. However, the tertiary alcohols absorb near the higher end of this absorption range of frequencies.

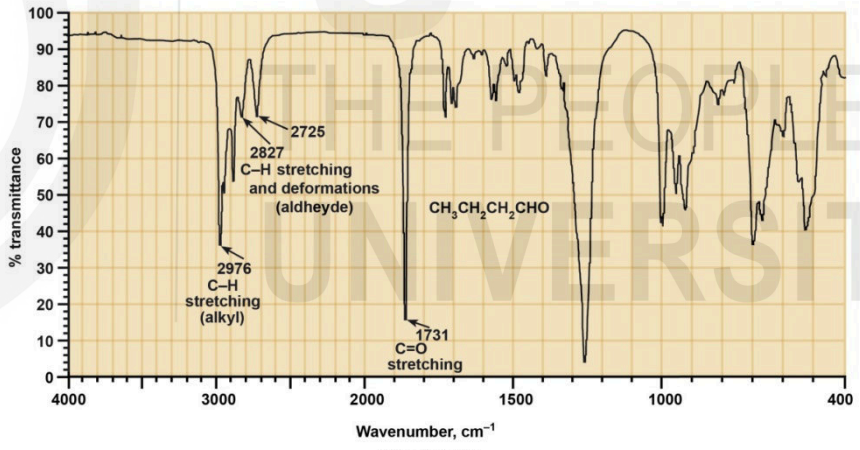
SAQ 4

You are given a sample of cyclohexanol and you get its IR spectrum recorded. Which major absorption bands you would be looking for in the spectrum?

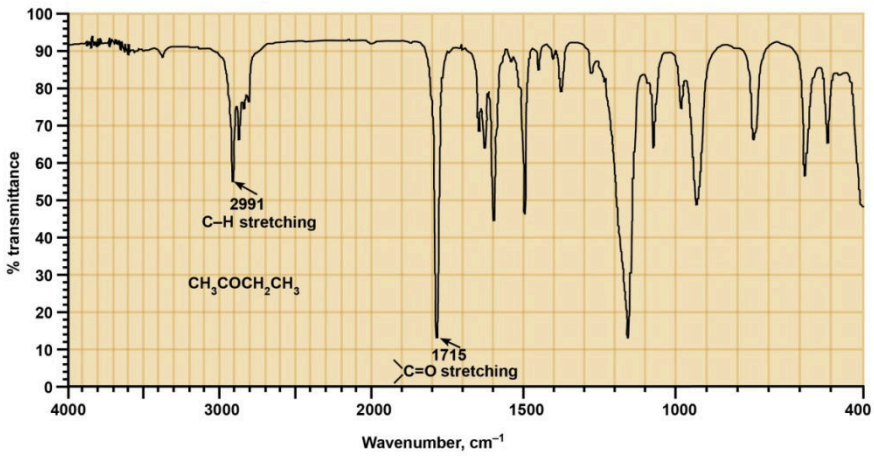
14.5 IR SPECTRA OF ALDEHYDES AND KETONES

The main absorption in the IR spectra of aldehydes and ketones is $\rangle C{=}O$ stretching absorption. It appears as a strong absorption in the region near 1700 cm^{-1}.

Simple aldehydes absorb around 1720-1725 cm^{-1} while simple ketones show this absorption near 1715 cm^{-1}, see Fig. 14.7 for IR specta of butanal and 2-butanone. Also, in aldehydes C–H stretching absorption of $-\overset{O}{\overset{\|}{C}}-H$ group appears near 2710 cm^{-1} as a weak band. The presence of such an aldehydic hydrogen is, however, confirmed by its signal in the NMR spectrum.



a)



b)

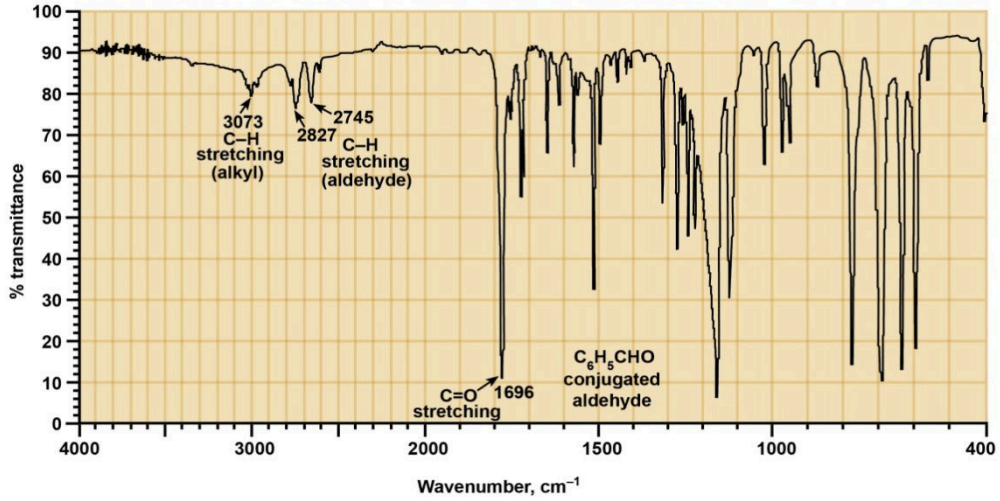
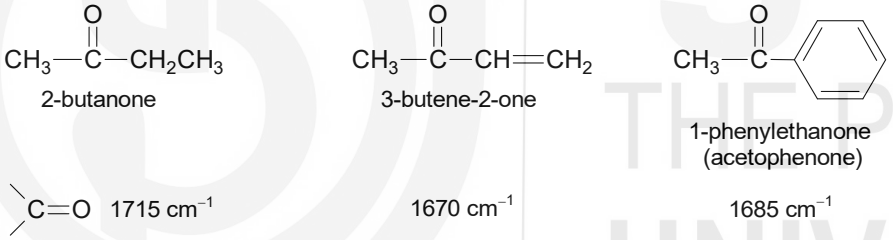


Fig. 14.7: IR spectrum of a)1-butanal, b) 2-butanone and c) benzenecabaldehyde (benzaldehyde)

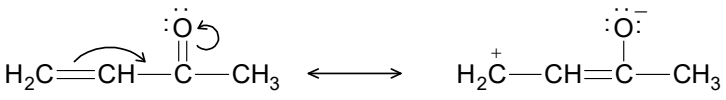
Effect of Conjugation

When the carbonyl group in an aldehyde or ketone is conjugated with a double bond or a triple bond or a phenyl ring, the >C=O stretching absorption frequency gets lowered by about 30-40 cm^{-1}. This is shown below with examples.



You can see a decrease the >C=O stretching frequency is observed when the carbonyl group is conjugated in 3-butene-2-one with a double bond and also in 1-phenylethanone when it is conjugated with the phenyl ring. Similar lowering of >C=O stretching is observed in benzaldehyde also in which the absorption appears at 1696 cm^{-1}, see Fig. 14.7 c). Note that in benzaldehyde, the carbonyl group is conjugated to the phenyl ring.

It may be intersting to note here that when such a conjugated system is present, then the corresponding C=C stretching frequencies also appear at lower values as compared to their normal values in the non-conjugated systems. The reason for this being the existance of following resonance structures in such systems.



Thus, some single bond character is present in both the C=C and C=O bonds, reducing their normal C=C and C=O double bond character. This leads to their lower strength and hence, lowering of frequencies in the IR spectra.

Thus, the IR C=C absorption appears in 1-butene at 1642 cm^{-1} and its value decreases to 1631 cm^{-1} and 1600 cm^{-1} (in the conjugated systems). in 3-butene-2-one and 1-phenylethanone ,respectively.

SAQ 5

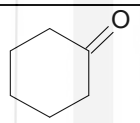
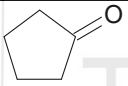
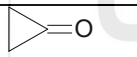
Why is the $\backslash C{=}O$ absorption intense in the IR spectra of aldehydes and ketones ?

Effect of ring size and angle strain

In case of cyclic ketones, when there is increase in the angle strain, when the ring size decreases, the $\backslash C{=}O$ stretching absorption frequencies increase.

This is illustrated below in Table 14.1 for the cyclic ketones of different ring sizes.

Table 14.1: Carbonyl stretching absorption frequencies in IR spectra for some cyclic ketones

Cyclic Ketone	>C=O Absorption Frequency
 cyclohexanone	1715 cm^{-1}
 cyclopentanone	1745 cm^{-1}
 cyclobutanone	1780 cm^{-1}
 cyclopropanone	1850 cm^{-1}

SAQ 6

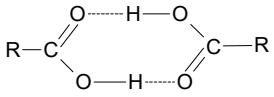
Differentiate between cyclohexanone and hexanal using their IR spectra.

14.6 IR SPECTRA OF CARBOXYLIC ACIDS AND THEIR DERIVATIVES

The carboxylic acids having the carboxy functional group $(-\overset{O}{\overset{\|}{C}}-OH)$ show the absorption in their IR spectra due to stretching vibrations of $-\overset{O}{\overset{\|}{C}}-$ (carbonyl) and – O – H bonds.

The O – H stretching vibration absorption shows a very broad band ranging from 2500-3300 cm^{-1}, see Fig. 14.8 for IR spectrum of ethanoic acid.

The absorption is broad due to hydrogen bonding and overlaps even with the C – H stretching absorption frequencies.



Dimer of carboxylic acid showing hydrogen bonding

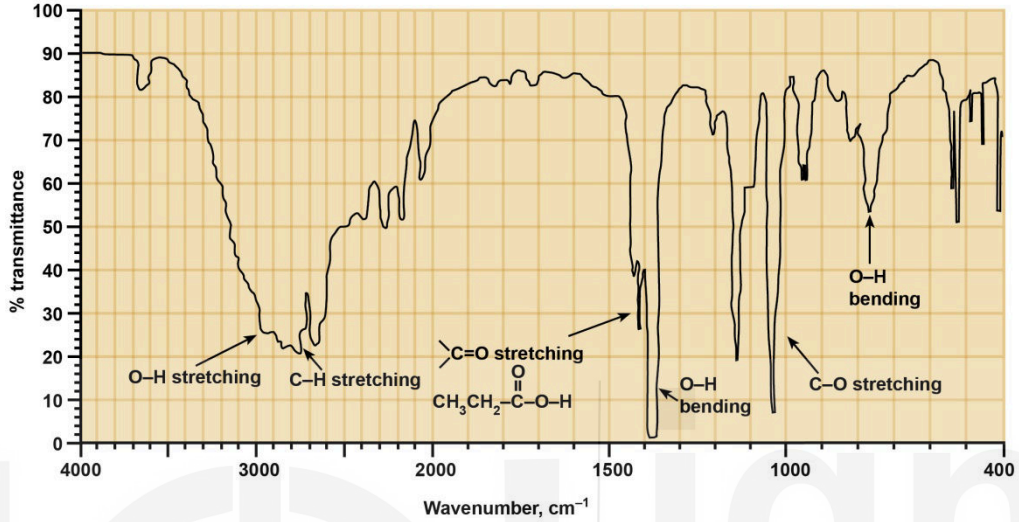


Fig. 14.8: IR spectrum of ethanoic acid.

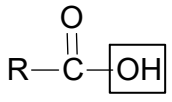
The monomer forms exhibit carbonyl stretching frequency at about 1760 cm^{-1} but these are normally not observed.

The stretching vibration of carbonyl group appears in the region of 1700-1725 cm^{-1} in the infrared spectra of the carboxylic acids which normally exist in the dimer form. Although aldehydes and ketones also exhibit the carbonyl stretching absorption in the similar range but due to the intermolecular hydrogen bonding, the absorption signal of carbonyl stretching in carboxylic acids is broader.

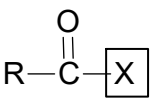
Let us now understand the absorption exhibited by carboxylic acid derivatives in their IR spectra.

14.6.1 Effect of Substitution on Carbonyl Stretching Absorption

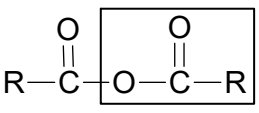
In carboxylic acid derivatives, the –OH group of the $-\overset{O}{\overset{\|}{C}}-OH$ carboxy functional group is replaced by another group say L. The carboxylic acid derivatives so obtained as shown below:



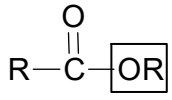
A carboxylic acid



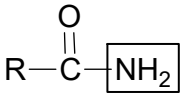
A carboxylic acid halide
X = Halogen



A carboxylic acid anhyldride



An ester



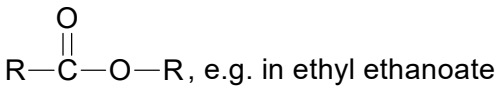
An amide

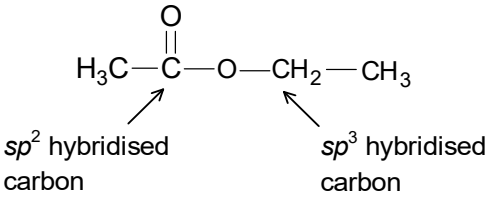
R – C ≡ N
Nitriles are also considered as carboxylic acid derivatives but we are not .discussing their IR spectra here.

Let us focus our attention on the characteristic IR spectral features of these carboxylic acid derivatives one by one.

(i) IR spectra of Carboxylic Acid Esters

In esters,





the >C=O frequency in esters appears between 1735-1750 cm^{-1}.

The two carbons present in C–O–C part are having two types of hybridisations – one carbon is sp^3 hybridised while the other one is sp^2 hybridised. The sp^3 C – O stretching absorption occurs at 1000-1100 cm^{-1} while the sp^2 C – O stretching band appears in the range 1200-1250 cm^{-1}, see Fig. 14.9.

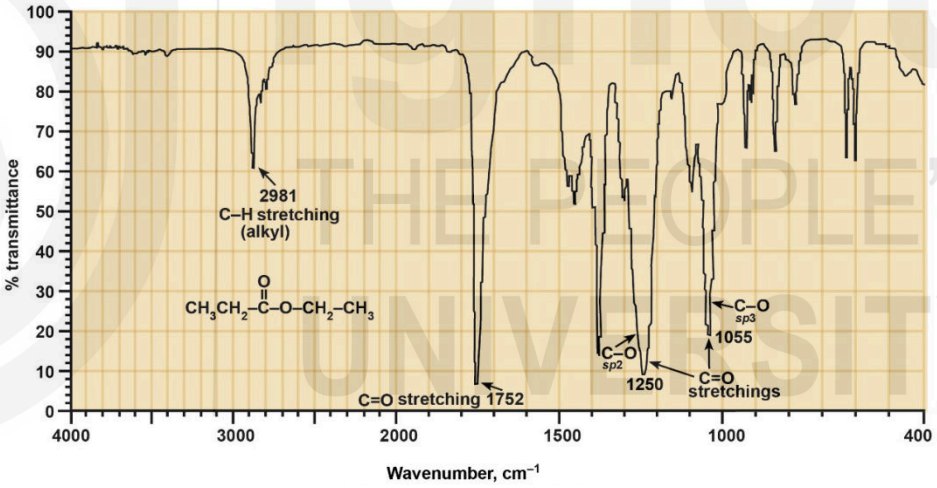


Fig. 14.9: for IR spectrum of ethyl ethanoate.

All these three absorptions appear as strong signals. The effects of conjugation, and when the cyclic esters are involved, are similar to those observed for the carbonyl frequencies in case of ketones as explained in Sec. 14.5 above.

(ii) IR Spectra of Carboxylic Acid Anhydrides

Carboxylic acid anhydrides exhibit two carbonyl stretching absorptions in their IR spectra – one at around 1740-1760 cm^{-1} while the other appears in the region 1800-1850 cm^{-1}. These arise due to symmetric and antisymmetric stretching of the entire anhydride group. The C – O stretching absorptions in anhydrides are observed in the range of 900-1300 cm^{-1}, see Fig. 14.10.

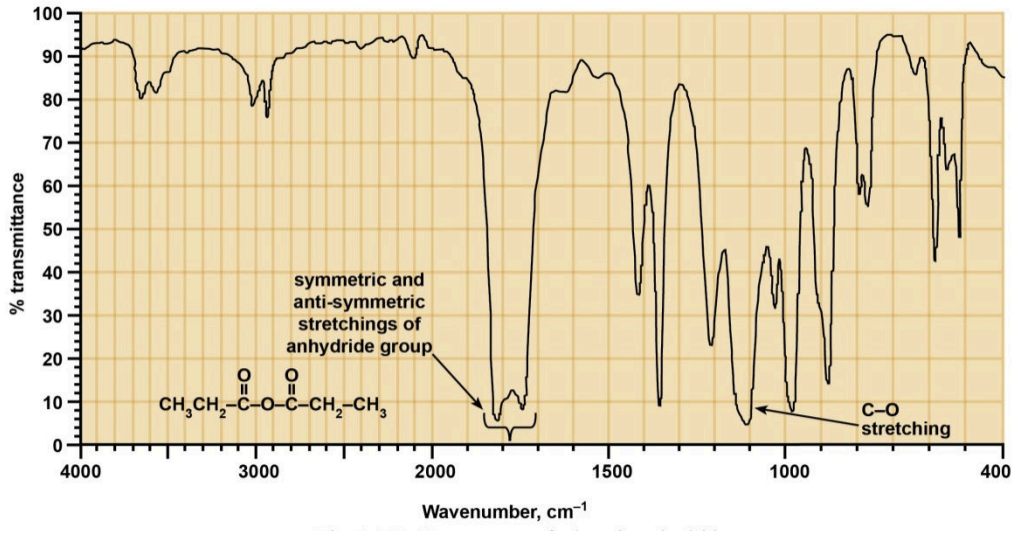


Fig. 14.10: IR spectrum of ethanoic anhydride.

(iii) IR Spectra of Carboxylic Acid Halides

The carboxylic acid halides e.g. alkanonyl halides exhibit the carbonyl stretching absorption in the range of 1790-1815 cm^{-1}, see Fig. 14.11. Some acid chlorides show two absorptions for the carbonyl stretching (additional band in C=O region is a result of Fermi resonance of C-Cl and C=O).

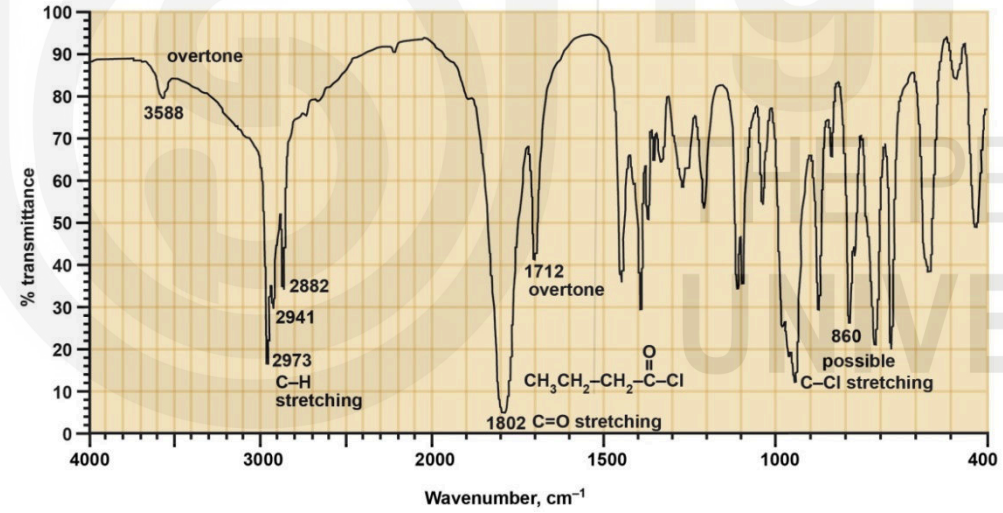
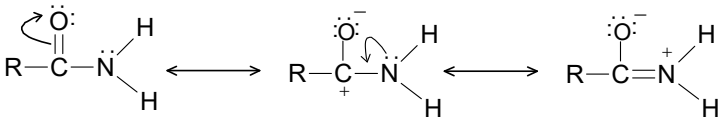


Fig. 14.11: IR Spectrum of Butanoyl Chloride

(iv) IR Spectra of Carboxylic Acid Amides

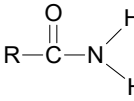
Carboxylic acid amides exhibit the following resonance structures:

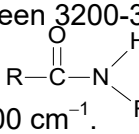


Thus, the carbonyl group is having single bond in two resonance structures out of three shown above. Hence, the carbonyl stretching frequency is lower as compared to other carboxylic acid derivatives and appears in the range of 1630-1680 cm^{-1}.

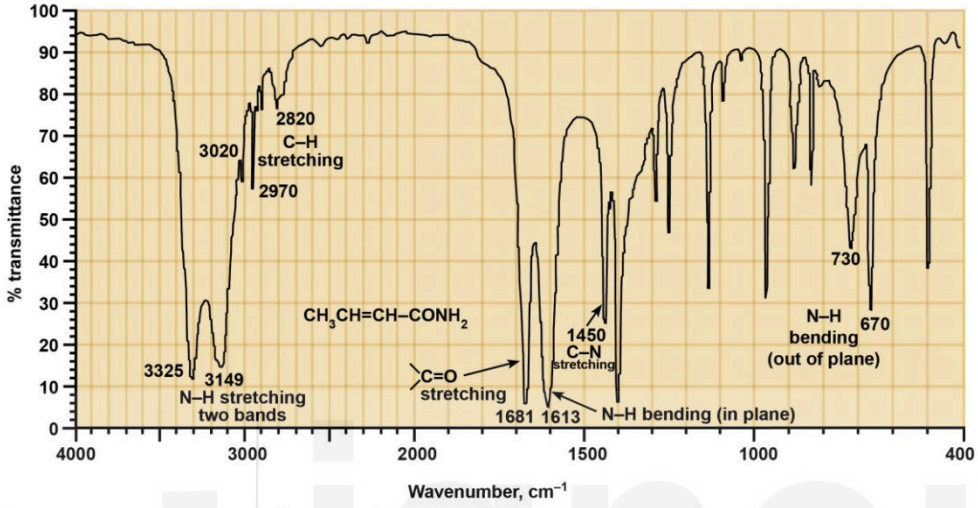
In addition to the carbonyl stretching absorption, amides also exhibit N – H stretching absorptions in the range 3200-3400 cm^{-1}. The *primary amides*,

Primary amides show carbonyl absorption in the range of 1700-1685 cm^{-1}, secondary amides exhibit carbonyl absorption in the region 1700-1670 cm^{-1} while tertiary amides absorb in the lower frequency range of 1670-1630 cm^{-1}.

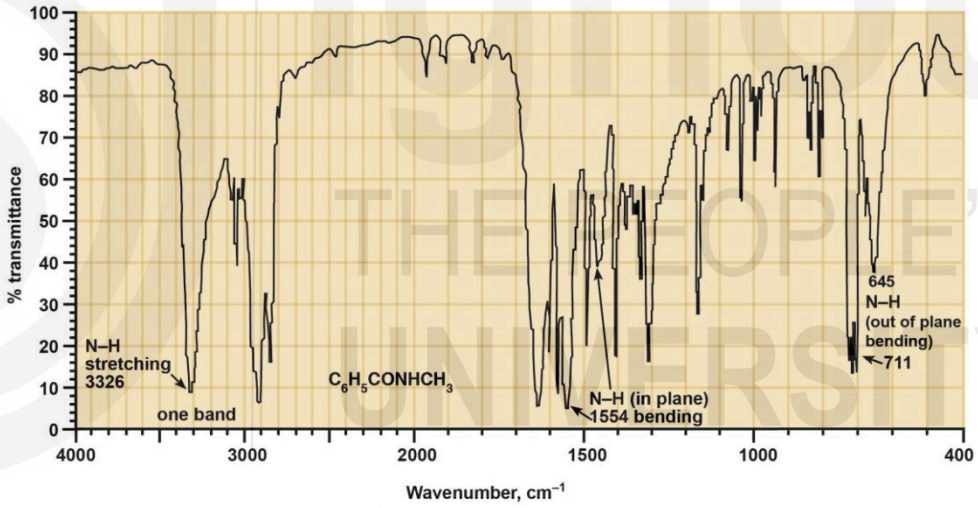


show *two* N – H absorptions between 3200-3400 cm^{-1} while the substituted amides, i.e. *secondary amides*,  show *only one* N – H stretching absorption in the region 3200-3400 cm^{-1}.

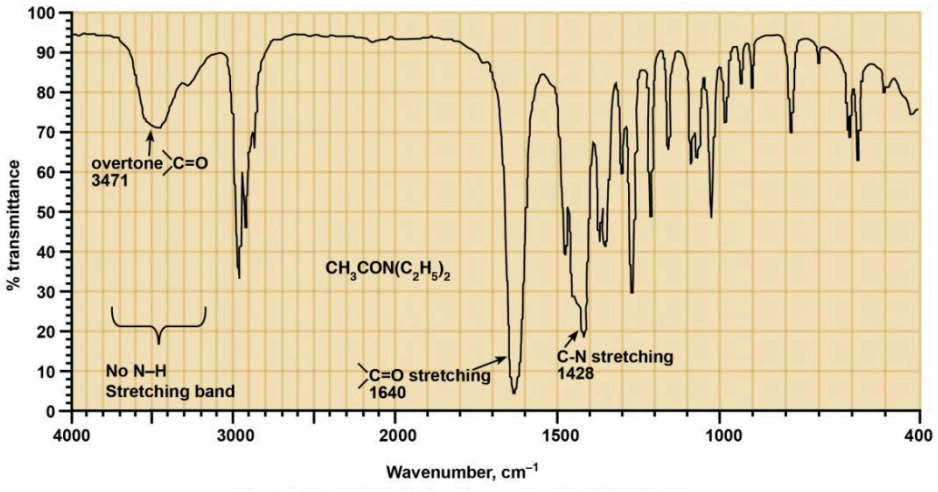
See Fig. 14.12 for IR spectra of primary and secondary amides i.e. ethanamide and *N*-methylethanamide, respectively.



a) **Crotonamide ($CH_3CH=CH-CONH_2$)**

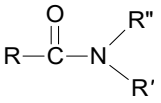


b) N-methylbenzamide, $C_6H_5CONHCH_3$



c) N, N-diethyethanamide, $CH_3CON(C_2H_5)_2$

Fig. 14.12: IR spectra of a) primary b) secondary and c) tertiary amides.

The tertiary amides which are disubstituted amides, i.e., 

do not have any N – H bond and hence no such absorption is present in their IR spectra.

SAQ 7

Arrange the carboxylic acid derivatives in the increasing order of their carbonyl stretching frequencies observed in their IR spectra.

The N – H bending absorption in amides can be seen in their IR spectra near 1640 cm^{-1} which appear as a shoulder to the lower frequency side of the carbonyl stretching.

14.7 SOME INTEGRATED PROBLEMS

So far you have studied about the IR spectra of organic compounds containing one functional group. Now we will consider only one functional group. But there are many natural as well as synthetic organic compounds which contain more than one functional group. In fact, more than three or four functional groups may also be present in a compound.

Here, we will discuss one example of a compound containing two functional groups i.e., a double bond and a hydroxyl group. The IR spectra of such a compound; but-2-ene-1-ol is shown below in Fig. 14.13.

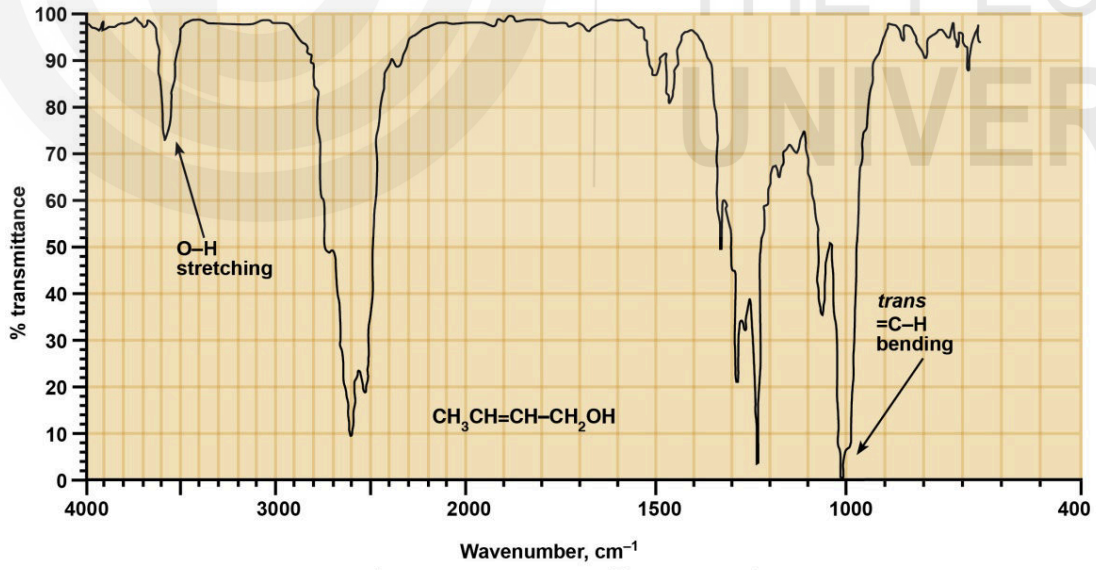
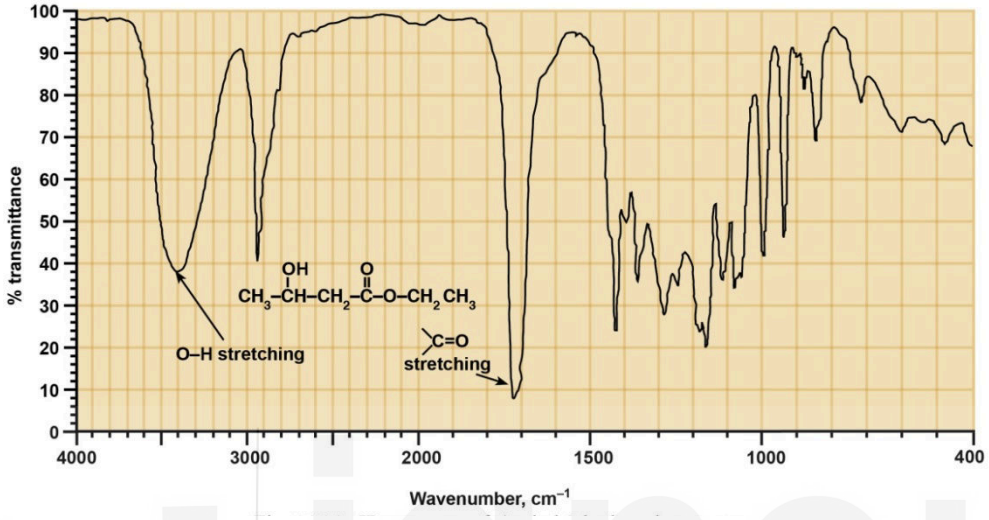


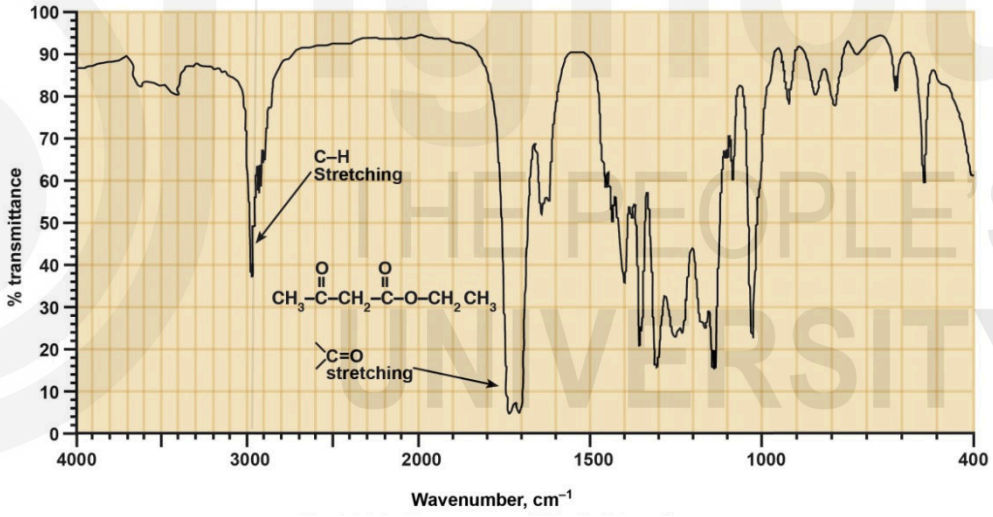
Fig. 14.13: IR spectrum of but-2-ene-1-ol

You can see that in the IR spectrum the band for the hydroxyl group i.e., O – H stretching appears at 3300-3500 cm^{-1}. The absorption for the C = C in the region 1620-1680 cm^{-1} is not exhibited in the spectra as the compound has *trans* arrangement around the double bond. Therefore, it should give a band in the region 960-980 cm^{-1} characteristic of a trans double bond. Such a band is visible in this range.

Let us consider two more compounds - ethyl 3-hydroxybutanoate and ethyl 3-oxobutanoate.Their IR spectra are shown in Fig.14.14 a) and b) .You can see the bands corresponding to the ester functional groups in both these compounds. Also, in ethyl 3-hydroxybutanoate, the band for O-H stretching is clearly identified while in ethyl 3-oxobutanoate, the carbonyl frequency of the keto and the ester groups are present.



a) ethyl 3-hydroxybutanoate



b) ethyl 3-oxobutanoate

Fig. 14.14: IR spectrum of a) ethyl 3-hydroxybutanoate and b) ethyl 3-oxobutanoate

Therefore, in the compounds having many functional groups, one has to look for the characteristics absorption for each of the functional groups in their respective regions, to get a complete picture about the structure of the compound.

14.8 SUMMARY

In this Unit, you have learnt that

- Absorption due to various vibrational modes of a molecule in the IR spectra occur if there is a change in the dipole moment of the bonds or groups under consideration.

- The absorption frequencies of the vibrations are directly proportional to the strength of the bond but are inversely related to the masses of the atoms involved in the bond formation.
- The functional groups present in a molecule exhibit characteristic absorption frequencies in the IR spectra and such characteristic frequencies help in the identification of the compounds.

  Besides correlating the functional group absorptions, the fingerprint region also shows characteristic absorptions in the IR spectra which can be correlated for identification of compounds.
- Alkanes exhibit C–H stretching absorption in the range 2850-2960 cm^{-1} and C–H bending vibrations occur in the range 1450-1475 cm^{-1} and 1375-1450 cm^{-1}.
- In alkanes, the C–H stretching vibration is observed above 3000 cm^{-1} while terminal alkynes exhibit the C–H stretching in the range 3260-3300 cm^{-1}.
- The C=C stretching in alkenes occurs in the range of 1620-1680 cm^{-1} while in alkynes, C≡C stretching appears at 2100-2260 cm^{-1}. *Trans* alkenes and symmetrical alkynes do not exhibit any such absorption.
- The bending absorption of =C–H in alkenes helps in the identification of substitution pattern of the alkenes.
- Alcohols show O–H stretching vibration in the range 3200-3500 for hydrogen bonded samples while in non-hydrogen bonded samples, it appears around 3650 cm^{-1}. The C–O stretching in alcohols is exhibited in the range 1050-1200 cm^{-1}.
- The carbonyl stretching absorption in aldehydes and ketones occur in the region near 1700 cm^{-1}. In aldehydes, additional C–H stretching is observed near 2710 cm^{-1}.

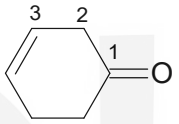
  Conjugation to a double/triple bond or benzene ring lowers the C=O stretching frequency by 30-40 cm^{-1}. Also the corresponding C=C and C≡C frequencies are observed at lower frequencies in such situations.

  In cyclic ketones, increase in the ring strain increases the carbonyl stretching absorption frequency.
- The carboxylic acids exhibit carbonyl stretching between 1735-1800 cm^{-1}. The C-O stretching absorptions occur in the range 1700-1725 cm^{-1}. While the O–H stretching frequency is observed as a very broad band in the range of 2500-3300 cm^{-1}.
- Esters show carbonyl stretching between 1735-1800 cm^{-1}. The C–O stretching absorptions occur at 1000-1100 cm^{-1} and 1200-1250 cm^{-1}.
- The carboxylic acid anhydrides show carbonyl stretching absorption frequencies at 1740-1760 cm^{-1} and 1800-1850 cm^{-1}. However, C–O stretching absorption is seen between 900-1300 cm^{-1}.
- Carboxylic acid halides exhibit carbonyl stretching absorption in the range 1790-1815 cm^{-1}.

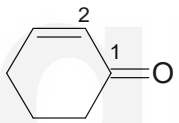
- Carboxylic acid amides exhibit carbonyl stretching frequency at lower values between 1630-1680 cm^{-1}. Also two N–H stretching absorptions for primary amides and one N–H stretching absorption is seen for secondary amides in the region 3200-3400 cm^{-1}. The N–H bending in amides appears as a shoulder near 1640 cm^{-1}.

14.9 TERMINAL QUESTIONS

1. Why 4-octyne does not exhibit –C≡C– stretching vibration?
2. Arrange the $\equiv C_{sp} - H$ stretching, $\equiv C_{sp^2} - H$ stretching and $\equiv C_{sp^3} - H$ stretching vibrations in the increasing order of their absorption frequencies observed in the IR spectra. Also give reason for your answer.
3. Why the C – O stretching in the infrared spectrum cannot be taken as a confirmatory evidence for presence of an alcohol group?
4. How will you differentiate between 3-cyclohexenone and 2-cyclohexenone using IR spectra?



3-cyclohexenone



2-cyclohexenone

14.8 ANSWERS

Self Assessment Questions

1. The bends near 2920 cm^{-1} are due to C–H stretching absorptions and those at 1470 and 1380 cm^{-1} are exhibited due to C–H bending vibrations.
2. The 3080 cm^{-1} absorption is due to C_{sp^2}–H and that at 1640 indicates C=C stretches due to terminal vinyl (–CH=CH_2). The terminal vinyl is also confirmed by two absorptions at 915 and 995 cm^{-1} due to =C–H bonding. Hence the alkene is I-hexene.

   CH_3– CH_2– CH_2– CH_2– CH= CH_2
3. The symmetrical alkynes do not exhibit – C ≡ C – stretching absorptions in the IR spectroscopy as there is no change in the depth moment. Hence, IR spectroscopy cannot be used to identify symmetrical alkynes.
4. O–H stretching vibration in the range near 3200-3500 cm^{-1} and C–O stretching vibration is the range near 1050 cm^{-1}.
5. Because of large electronegativity difference between carbon and oxygen, the change in dipole moment is large during this stretching; hence a strong absorption bond in IR spectra of aldehydes and ketones.
6. Cyclohexane shows C=O stretching absorption at 1715 cm^{-1} whereas hexanal shows absorption for C=O stretching at 1730 cm^{-1}. Also, in Haxanal, the C-H stretching of $-\overset{\overset{O}{\|}}{C}-H$ is present at 2719 cm^{-1}.

7. We can arrange the carbonyl stretching absorption in their increasing order as follows:

	Amides		Esters		Anhydrides		Acid chlorides
>C = O stretching absorption	1630-1680	<	1735-1800	<	1740-1760	<	1790-1815

Terminal Questions

1. $H_3C-CH_2-CH_2-C\equiv C-CH_2-CH_2-CH_3$

   4-octyne

   The structure of 4-octyne shows that it is a symmetrical alkyne. Hence, $-C\equiv C-$ stretching vibration does not involve any change in the dipole moment. Hence, the absorption corresponding to it is not observed.

2. $-C_{sp^3}-H$ < $-C_{sp^2}-H$ < $-C_{sp}-H$

   2850-2960 cm^{-1} 3000-3200 cm^{-1} 3260-3300 cm^{-1}

   Reason: The more the *s*-character of hybridisation of carbon, the stronger will be the C – H bond and hence, the greater will be the stretching frequency.

3. Because other functional groups such as carboxylic acids and esters also absorb in the range near 1100 cm^{-1} which is similar to that for alcohols.

4. Since 2-cyclohexenone is a conjugated ketone, both the C=O and C=C stretching absorption frequencies will be lower in the IR spectrum as compared to the corresponding frequencies in the IR spectrum of 3-cyclohexenone.