Chapter 1

SPECTROSCOPY

1.1 Introduction

Structure elucidation of organic compounds by classical methods is a tedious and time consuming process. Further, large quantity of compound is needed. This makes the structural elucidation of many organic compounds more difficult. However, with the development in spectroscopic methods, particularly ultraviolet (UV), infrared (IR), nuclear magnetic resonance (NMR) and mass (MS) the task has become relatively easier. Thus fundamental to modern techniques of structure determination is the field of **spectroscopy:** *the study of the interaction of matter and electromagnetic radiation.* In fact, spectroscopy is the measurement of the amount of light absorbed by a compound as a function of the wavelength of light. In general, the sample is irradiated by a light source, and the amount of light transmitted at various wavelengths is measured by a detector. Unlike chemical tests, spectroscopic techniques are **nondestructive**; that is, none of the sample is destroyed.

1.2. Electromagnetic Spectrum

Visible light is one form of energy generally known as electromagnetic radiation. Other common forms of electromagnetic radiation are *X*-rays; ultraviolet radiation (UV, the radiation from the sun); infrared radiation (IR, the radiation from a heat source); microwaves (used in radar and in the microwave oven); and radio waves (used to carry radio and television signals). Electromagnetic radiations can be characterised by their **frequency** or **wavelength.** The wavelength is a more convenient description of waves with higher frequencies. The wavelength (λ) of a wave is defined by the equation

$$\lambda = \frac{c}{\nu} \qquad \ldots \text{(i)}$$

in which c = the velocity of light = 3×10^{10} cm/sec, and ν = frequency of radiation.

The energy associated with a particular electromagnetic radiation is given by the expression:

$$E = h\nu = \frac{hc}{\lambda} \qquad \ldots \text{(ii)}$$

where E = energy of radiation in ergs

h = Planck's constant (6.62×10^{-27} ergs sec)

ν = frequency of radiation (in hertz or cps)

Equation (ii) shows that the energy, frequency and wavelength of electromagnetic radiation are simply related. Thus, when the frequency or wavelength of electromagnetic radiation is known, its energy is also known. The total range of electromagnetic radiation is called the **electromagnetic spectrum.** The types of radiation within the electromagnetic spectrum are shown in Fig. 1.1. All electromagnetic radiations are fundamentally the same, the various forms differ only in energy.

Wavelength (λ)		**Energy per mole**	**Molecular effects**
10^{-10} meter	gamma rays	10^{6} kcal	
10^{-8} meter	*X*-rays	10^{4} kcal	ionization
	vacuum UV	10^{2} kcal	
	near UV		electronic transitions
10^{-6} meter	visible	10 kcal	
10^{-4} meter	infrared (IR)	1 kcal	molecular vibrations
10^{-2} meter	microwave	10^{-2} kcal 10^{-4} kcal	rotational motion
10^{0} (1 meter) 10^{2} meters	radio	10^{-6} kcal	nuclear spin transitions

Fig. 1.1 Electromagnetic spectrum

1.3 Absorption Spectroscopy

The most common type of sepctroscopy used for structure determination is **absorption spectroscopy.** The basis of absorption spectroscopy is that substance can absorb energy from certain wavelengths of electromagnetic radiation. In an absorption spectroscopy experiment, this absorption is determined as a function of wavelength, frequency or energy in an instrument called **spectrophotometer** or **spectrometer** (Fig. 1.2).

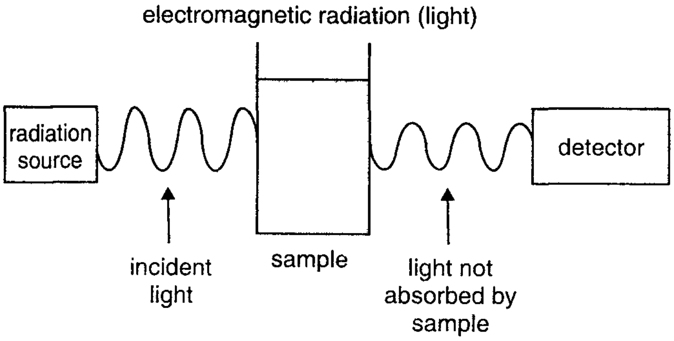


Fig. 1.2 An absorption spectroscopy experiment

The experiment requires, first a source of electromagnetic radiation. We place the material to be examined (known as *sample*), in the radiation beam. A detector measures the intensity of radiation that passes through the sample unabsorbed; when this intensity is subtracted from the intensity of the source, the amount of radiation absorbed by the sample is known. We then vary the wavelength of the radiation falling on the sample, and the radiation observed at each wavelength is recorded as a graph of either radiation transmitted or radiation absorbed versus wavelength or frequency. This graph is commonly known as a **spectrum** of the sample (Figs. 1.3 and 1.4).

There are many types of spectroscopy. The three types of greatest use to organic chemists for structure determination are NMR, IR and UV-visible spectroscopy. These types of spectroscopy differ conceptually only in the type of radiation used, although the kinds of spectrometers required for each are quite different. Mass spectrometry is fourth physical technique but it is not a type of absorption spectroscopy and is thus fundamentally different from NMR, IR and UV spectroscopy.

1.4 Origin of Absorption Spectra

The energy (E) of molecule, besides translational and nuclear energies (which do not interfere in spectroscopic analysis) can be considered to be made up of:

(i) Electronic or transitional energy: This is the energy which is associated with motion of electrons in the molecule.

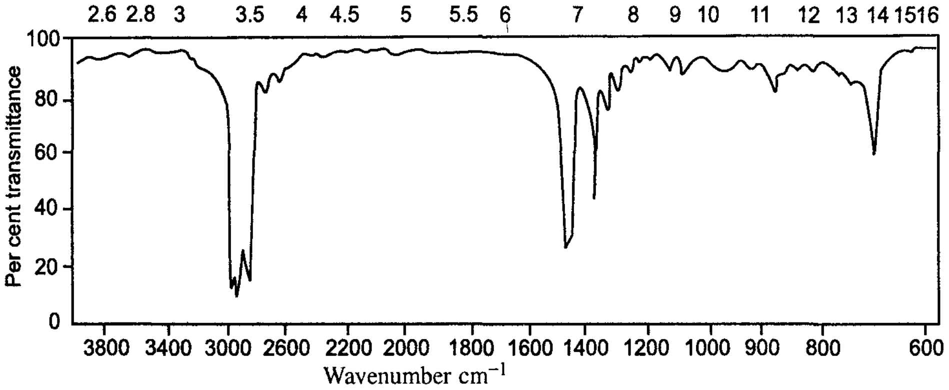


Fig. 1.3 Infrared spectrum of nonane

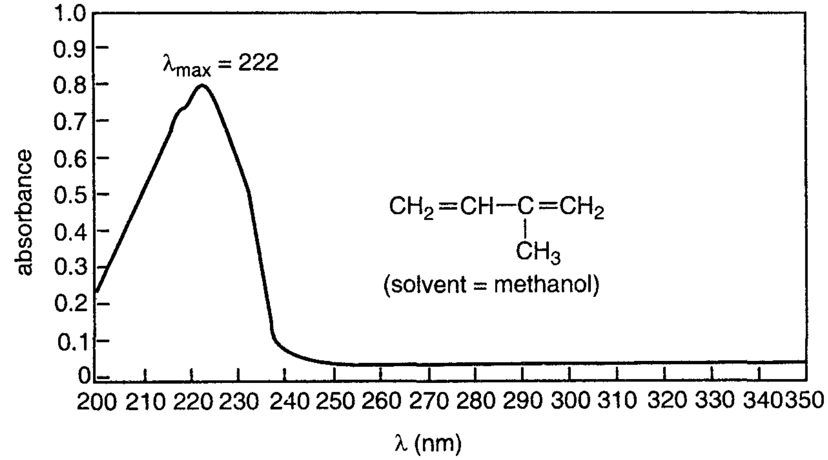


Fig. 1.4 The UV spectrum of isoprene dissolved in methanol shows λ_{max} = **222 nm**, ε = **20,000**

(ii) Vibrational energy: This is the energy which is associated with the vibrations of the constituent atom in the molecule.

(iii) Rotational energy: This is the energy which is associated with the rotation of the molecule as a whole.

Thus the total energy of the molecule for spectoscpic purpose can be written as:

$$E_{total} = E_{electronic} + E_{vibrational} + E_{rotational}$$

Each of these energies is quantised and can exist with some discrete values. This means that these energies have to follow quantum restrictions. The discrete values (quantised) of these energies depend on the properties of the moleculs, *i.e.*, shape, size, flexibility as well as on the type of the motion.

If a molecule is placed in an electromagnetic radiation, a transfer of energy from the electromagnetic radiation to the molecule occurs when,

$$\Delta E = h\nu$$

where h = Planck's constant

ν = frequency of light

ΔE = Difference in energy between two quantised states.

The molecule absorbs energy when it is excited from the lower energy state E_1 to higher energy state E_2. Hence,

$$\Delta E = E_1 - E_2$$

when molecule absorbs energy, there may be three types of changes in the molecule.

(i) There may be change in rotational levels.

(ii) There may also be a change in vibrational levels on which rotational change may be superimposed.

(iii) An electronic state may change simultaneously with changes in both vibrational and rotational energies.

As a result, even with a simple diatomic molecule, there is posibility of a large number of changes in energy states producing many spectral lines.

The various energy levels in the molecule are shown in Fig. 1.5. Suppose A and B are two electronic states (energy state n) of a molecule. In each electronic state there are vibrational energy levels, indicated by virbational quantum number $V (= 0, 1, 2, 3, 4, 5, ...)$. Again, for each vibrational state (energy level), there exist several rotational energy levels, indicated by quantum number $J (= 0, 1, 2, 3, 4, 5, ...)$. A possible transition in any one of these energy levels will lead to a charge in energy content and hence give rise to spectral lines.

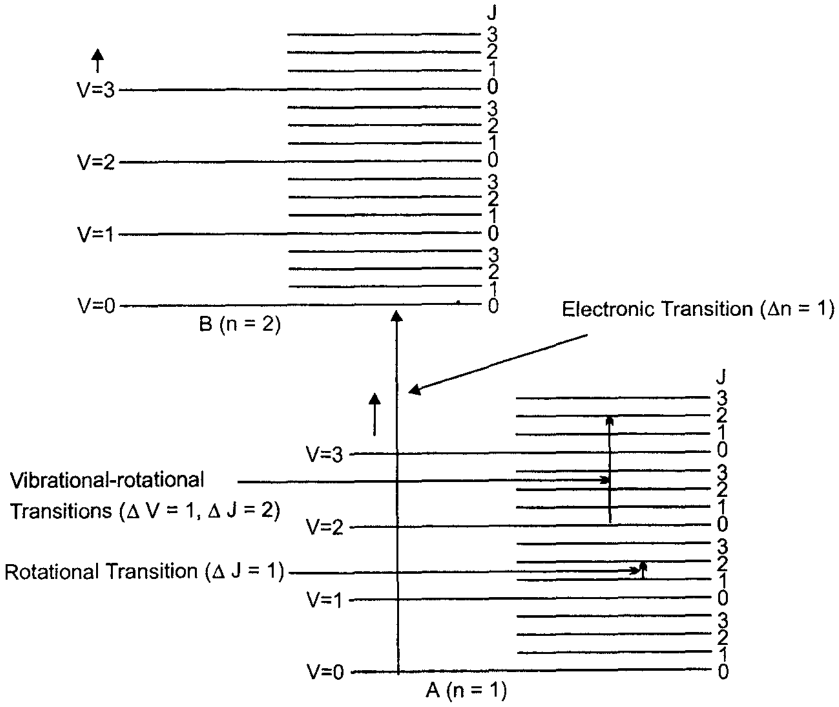


Fig. 1.5 Molecular energy level diagram

1.5 Classification of Molecular Spectra

There are following types of molecular spectra, correspnding to the types of energy changes in a molecule.

(1) **Rotational Spectra:** Rotational spectra are produced due to change in energy in rotational quantum levels within a vibrational level. The rotational energy levels are relatively close to each other and hence energy changes taking place in rotational transitions are of small amounts. That is why pure rotational spectra appear in far infrared and microwave region (*i.e.*, 10^4 μ to 10^2 μ range).

(2) **Vibrational-Rotational Spectra:** The separation of vibrational energy levels is greater as compared to the rotational levels. Thus the vibrational spectra would appear in the mid-infrared regions (10^2 μ to 1 μ range). During a vibrational change, the rotational energy also changes and the energy absorbed is the sum of two energy changes.

(3) **Electronic Spectra:** The electronic energy levels (denoted by the quantum number n) are far apart. Hence a change in electronic state is associated with a larger difference in energy. The electronic spectra appear in the visible and ultraviolet region (1 μ to 0.1 μ range). That is why electronic spectra are also called ultraviolet and visible spectroscopy.

(4) **Nuclear Magnetic Resonance (NMR) Spectra:** Nuclear magnetic resonance spectroscopy is concerned with the study of interaction of electromagnetic radiation in the radio frequency region (3 MHz to 30,000 MHz) with spinning nuclei. NMR spectroscopy measures the energy necessary to bring about transitions between spin states of nuclei in molecules. This depends on the magnetic property of atomic nuclei. The absorption of electromagnetic radiation takes place under the influence of an applied magnetic field.

(5) **Electron Spin Resonance (ESR) Spectra:** ESR spectroscopy is an absorption spectroscopy which involves the absorption of radiation in the microwave region ($10^4 - 10^6$ MHz) by substances containing one or more unpaired electrons which display characteristic magnetic properties arising from the spin properties of unpaired electrons. This absorption of microwave radiation takes place under the influence of an applied magnetic field. The substances with one or more unpaired electrons are paramagnetic and exihibit ESR, thus ESR spectroscopy is also called electron paramagnetic resonance (EPR) spectroscopy or electron magnetic resonance spectroscopy.

(6) **Mass Spectrometry (MS):** Besides the above types of spectroscopic techniques using electromagnetic radiations, another technique is mass spectrometry which has major structural and analytic applications. It is not a type of absorption spectroscopy and is thus fundamentally different from UV, IR, NMR and ESR spectroscopy. Mass spectrometry is based on the principle that molecules in the vapour phase are converted, by bombarding with high energy electron beams, into parent (initial formula) and daughter (fragment) positive (or less often negative) ions which are sorted and recorded according to their m/e (m = mass, e = charge) by passing through a combination of magnetic and/or electric fields.

1.6 Ultraviolet and Visible Spectroscopy

Ultraviolet spectroscopy measures the absorption of ultraviolet light by a sample. Dienes and other conjugated compounds give useful UV spectra. Thus, before discussing this technique we will first discuss molecular orbital picture of conjugated polyenes.

1.6.1 Construction of *pi* molecular orbitals of polyenes

A conjugated polyene contains either $4n$ or $(4n + 2)\,\pi$ electrons. The simplest $4n$ system is 1, 3-butadiene where $n = 1$. The simplest $(4n + 2)\,\pi$ electron system is 1, 3, 5-hexatriene where $n = 1$. The *pi* molecular orbitals of conjugated molecules can be constructed according to following generalisations:

(1) A *pi* electron system derived from the interaction of say m p-atomic orbitals contains m

molecular orbitals that differ in energy. Thus the number of *pi* molecular orbitals is the same as the number of *p*-atomic orbitals overlapping in the conjugated system.

(2) Half of the molecular orbitals (*i.e.*, half of $m = m/2$) have lower energy than the isolated *p*-orbitals. These are called bonding molecular orbitals and are represented by π or ψ. The remaining half (*i.e.*, $m/2$) have higher energy than the isolated *p*-orbitals. These are called antibonding molecular orbitals and are represented by π^* or ψ^*.

(3) The bonding molecular orbital of lowest energy, ψ_1 or π_1 has *no* nodes. Each molecular orbital of increasingly higher energy has one additional node. In 1, 3-butadiene ψ_1 has no node, ψ_2 has one node, ψ_3^* has two nodes and ψ_4^* has three nodes.

(4) The nodes occur between atoms and are arranged symmetrically with respect to the centre of the π electron system.

1.6.2 Construction of molecular orbitals of ethylene and 1,3-butadiene

Pi molecular orbitals of ethylene from the two *p* atomic orbitals of the two carbons can be constructed as follows:

Each *p* orbital consists of two lobes, with opposite phases of the wave function of the two lobes. The plus and minus signs used in drawing these orbitals indicate the phase of the wave function.

In the bonding orbital of ethylene, there is overlap of similar signs (+ with + and – with –) in the bonding region between the nuclei. This reinforcement of the wave function is called **constructive overlap**. In the antibonding orbital there is cancelling of opposite signs (+ and –) in the bonding region. This cancelling of the wave function is called **destructive overlap**. (Fig. 1.6).

In butadiene, we have a system of four *p* orbitals on four adjacent carbons. These four atomic *p* orbitals will overlap to produce four π molecular orbitals. We can get four new MO's in a number of equivalent ways. One of the ways to obtain four new molecular orbitals is by linear combination of two molecular orbitals of ethylene. Linear combination always takes place between two orbitals having minimum energy difference. This means that we need to look only at the result of the $\pi \pm \pi$ and $\pi^* + \pi^*$ interactions and do not have to consider $\pi \pm \pi^*$ (Fig. 1.7).

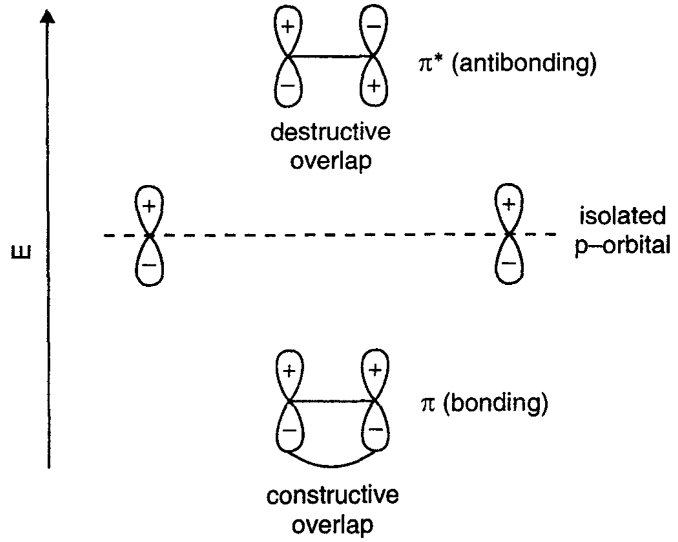


Fig. 1.6 The combination of two *p* orbitals results in the formation of two molecular orbitals

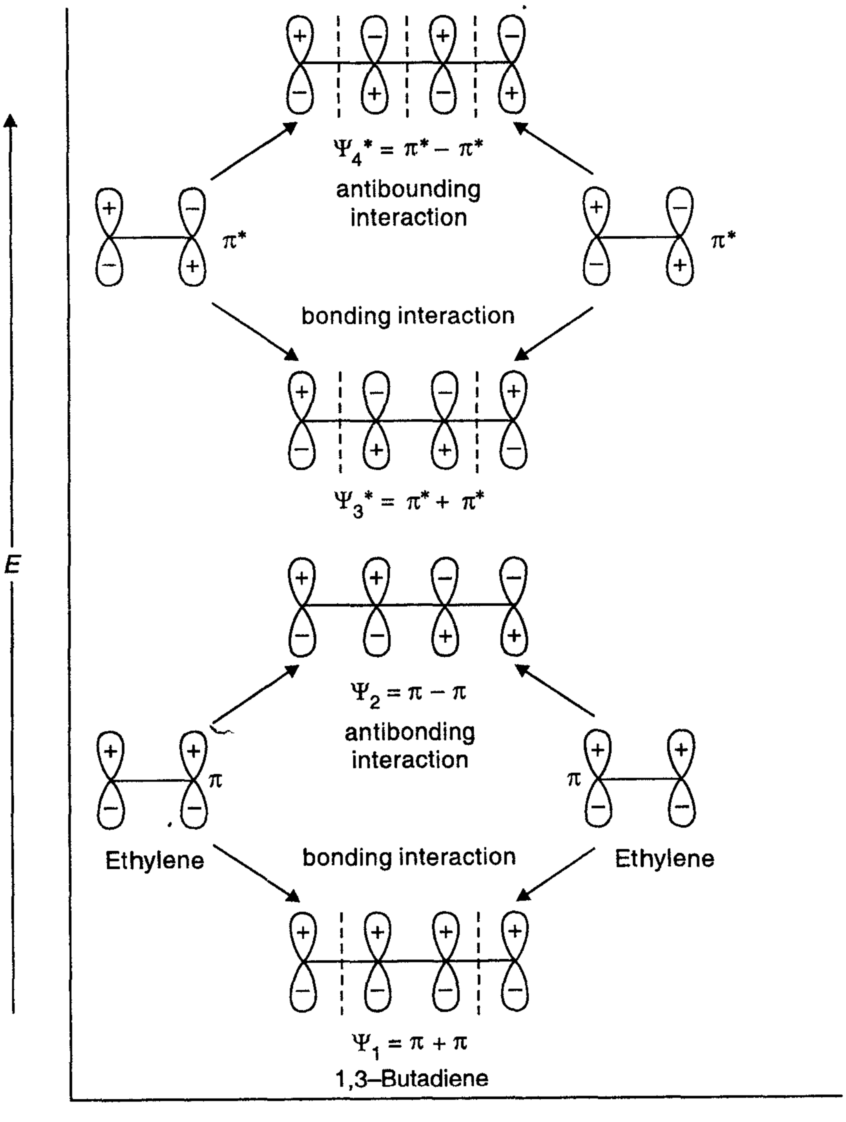
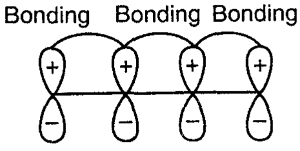


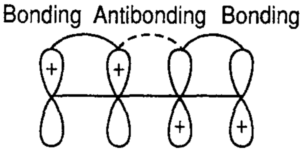
Fig. 1.7 The schematic formation of the π molecular orbitals of 1,3-butadiene from the π molecular orbitals of ethylene

The lowest energy orbital (ψ_1) of 1, 3-butadiene is exceptionally stable for two reasons: there are three bonding interactions, and the electrons are delocalised over four nuclei.



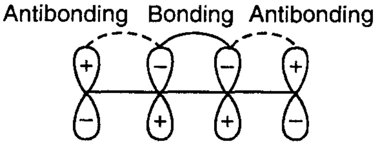
$\psi_1 = \pi + \pi$ (bonding interaction between two ethylene bonding MO's)

The second molecular orbital (ψ_2) of 1, 3-butadiene is obtained from the antibonding interaction between two bonding molecular orbitals of ethylene. The ψ_2 orbital has two bonding and one antibonding interaction, so we would expect it to be a bonding orbital (two bonding-one antibonding = one bonding). Thus energy of ψ_2 is more than that of ψ_1. ψ_2 molecular orbital has one node between $c_2 - c_3$. A node is a plane where the wave function drops to zero.



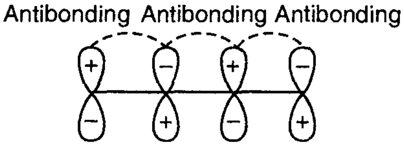
$\psi_2 = \pi - \pi$ (antibonding interaction between two ethylene π molecular orbitals)

The third butadiene MO, ψ_3* has two nodes. This molecular orbital is obtained from the bonding interaction between π* and π* of two ethylene molecules. There is a bonding interaction at the $c_2 - c_3$ bond and there are two antibonding interactions: one at $c_1 - c_2$ bond and the other at the $c_3 - c_4$ bond. This is an antibonding orbital (one bonding-two antibonding = one antibonding MO) having two nodes. Thus energy of this orbital is more than the energy of ψ_2 MO.



$\psi_3^* = \pi^* + \pi^*$ (bonding interaction between two antibonding MO's of ethylene)

The fourth molecular orbital (ψ_4*) is obtained from the antibonding interaction between π* and π* of two ethylene molecules. This molecular orbital has three nodes and is totally antibonding. This MO has the highest energy.



$\psi_4^* = \pi^* - \pi^*$ (antibonding interaction between π* and π* of ethylene)

Two π molecular orbitals are of particular importance in understanding UV spectroscopy. One is the occupied molecular orbital of highest energy, known as highest occupied molecular orbital (**HOMO**). The other is the unoccupied molecular orbital of lowest energy known as lowest unoccupied molecular orbital (LUMO). The energy difference between HOMO and LUMO is minimum. (Fig. 1.8 on next page)

1.7 The UV Spectrum

Absorption of radiations in UV-visible range (λ 1 nm to 800 nm) causes electronic excitations. The electrons are excited from their ground state to higher excitation states by absorbing the proper radiations. Since *UV-visible spectroscopy involves electronic transitions, it is often called* **electronic spectroscopy**. The intensity of absorption of radiations as a function of wavelength of light absorbed is plotted and the graph gives an idea of electronic transitions taking place in the molecule. From these electronic transitions information is obtained about the structure of the molecule.

Most of the organic compounds absorb UV light having wave length of 200-400 nm. The coloured compounds usually absorb the light of wavelength 400-800 nm but they may also absorb the

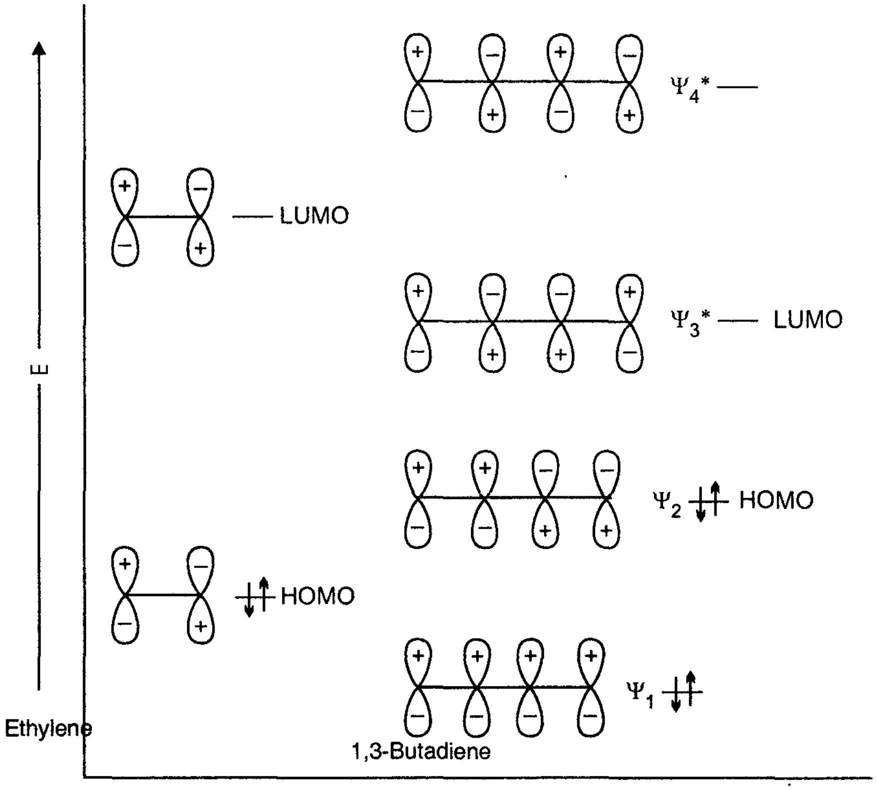


Fig. 1.8 HOMO and LUMO of ethylene and 1,3-butadiene

light of shorter wavelengths, the radiations having wavelength shorter than 200 nm are also absorbed by atmospheric gases. Therefore, in order to study the transitions brought about by these radiations in a molecule, the study should be conducted in vacuum.

Most UV-visible spectrophotometers are double beam instruments as shown schematically in Fig. 1.9. The caption of this figure briefly describes the working of the spectrophotometer. For recording an UV spectrum. The sample is dissolved in a suitable organic solvent and placed in a cell while pure solvent is placed in another similar cell called the reference cell. The most common solvents used for recording UV spectra are methanol, ethanol, hexane and water, which are transparent to UV

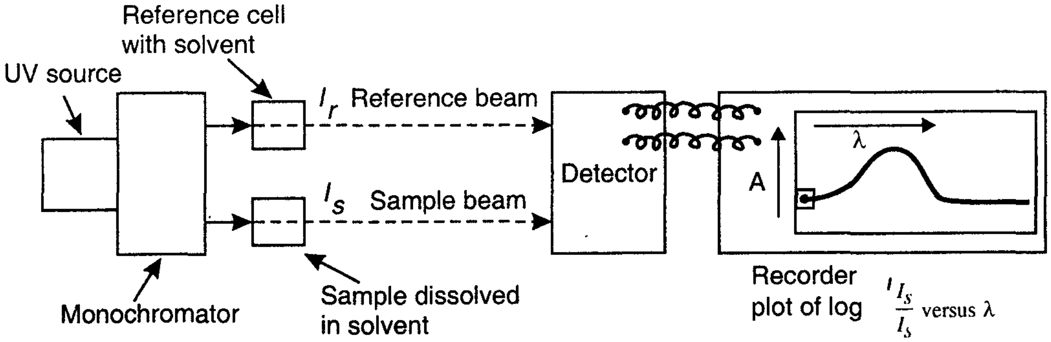


Fig. 1.9 In the ultraviolet spectrometer, the UV source produces a continuum of light in the UV region. The monochromator selects one wavelength of light, which is split into two beams. One beam passes through the sample cell, while the other passes through the reference cell. The detector measures the ratio of the two beams, and the chart recorder plots this ratio as a function of wavelength.

radiation. The light source is usually a hydrogen lamp, and the opticals and cells are made of quartz because most other clear materials absorb UV radiation.

The absorption of energy is recorded as absorbance (not transmittance).

Two empirical laws have been formulated about absorption intensity.

(1) Lambert's Law: Lambert's law states that the fraction of the incident monochromatic radiation absorbed by a homogeneous medium is independent of the intensity of the incident radiation.

(2) Beer's Law: Beer's law states that the absorption of a monochromatic radiation by a homogeneous medium is proportional to the number of absorbing molecules.

The absorption at a particular wavelength is defined by the equation:

$$A = \log \frac{I_r}{I_s}$$

where A = absorbance

I_r = intensity of the reference radiation

I_s = intensity of the beam coming out of sample cell.

The absorbance by a compound at a particular wavelength increases with an increasing number of molecules undergoing transitions. Therefore, absorbance depends upon the electronic structure of the compound and also upon the concentration of the sample and the length of the sample cell. For this reason energy absorption is reported as molar asborptivity ε, also known as molar extinction coeffcient, rather than as the actual absorbance. Often UV spectra are reported to show ε or $\log \varepsilon$ instead of A, as the ordinate. The $\log \varepsilon$ value is specially useful when values for ε are very large.

$$A \propto C$$

$$A \propto l$$

Therefore:

$$A \propto Cl$$

$$A = \text{constant } Cl$$

$$A = \varepsilon \,.\, Cl$$

$$\varepsilon = \frac{A}{Cl}$$

where ε = molar absorptivity

A = absorbance

C = concentration in mole/litre

l = cell length in cm

If absorbance, concentration and cell length are known, the molar absorptivity can be calculated. It is a valuable information that can be used in connection with UV spectra. Spectra are often redrawn by plotting ε against λ, expressed in nm. (One nanometer equals to 10^{-9} meter). The molar absorptivity ranges from 10 to 100,000. The typical UV spectrum plot is shown in Fig. 1.10. UV absorption bands are thus characterised by the wavelength of the absorption maxima (λ_{max}) and ε.

1.8 Types of Electronic Transitions

Let us consider the different types of electronic transitions which take place on absorption of light in UV-visible range. The ground state of organic molecule contains valence electrons in three principal types of molecular orbitals : *Sigma* (σ) orbitals. *pi* (π) orbitals and filled, but nonbonded orbitals (n). Both σ and π orbitals are formed from the overlapping of two atomic or hybrid orbitals. Each of these molecular orbitals, therefore, has an antibonding σ^* to π^* orbital associated with it. An orbital containing nonbonding (n) electrons does not have an antibonding orbital because nonbonding

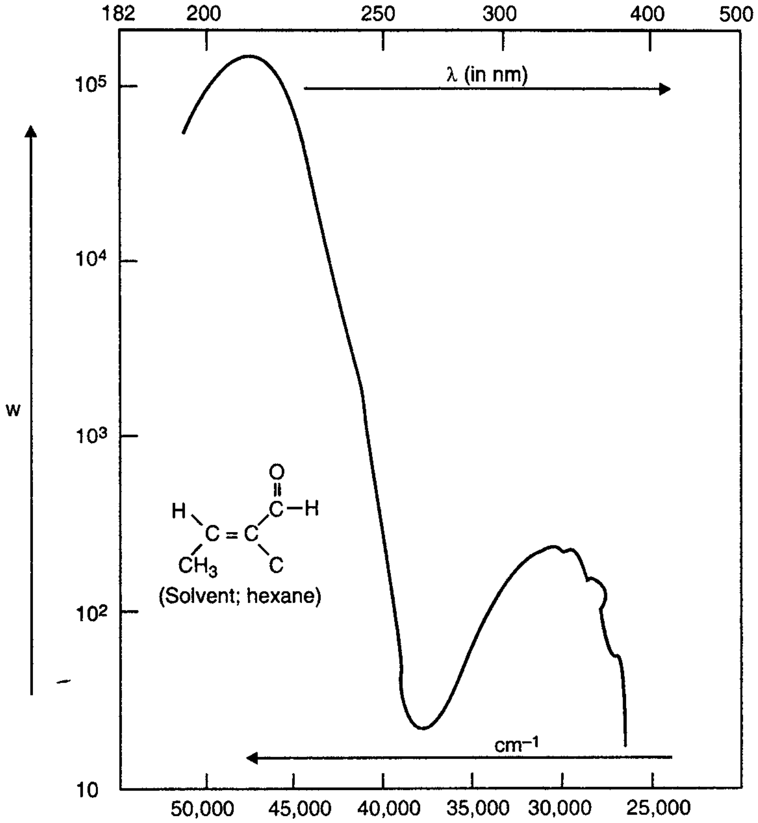


Fig. 1.10 Typical UV spectrum

electrons present in them do not form bonds. Electron transitions involve the promotion of an electron from one of the three ground states $(\sigma, \pi$ or $n)$ to one of the two excited states $(\sigma^*$ or $\pi^*)$. The four important transitions and their relative energies are shown in Fig. 1.11.

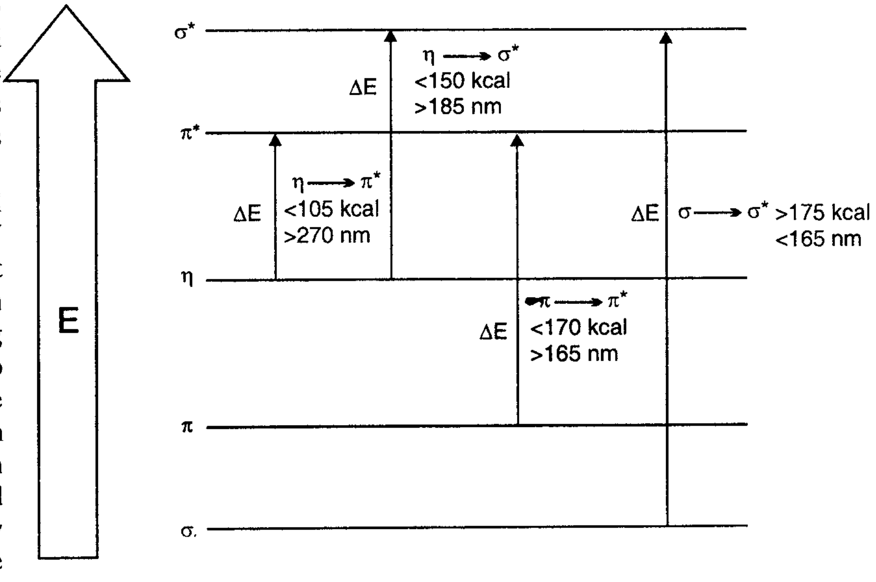


Fig. 1.11 Energy requirement for different electronic transitions

The most useful region of the UV spectrum is at wavelengths longer than 200 nm. The following transitions give rise to absorption in the non-useful 100-200 nm range: $\pi \rightarrow \pi^*$ for an isolated double bond and $\sigma \rightarrow \sigma^*$ for an ordinary carbon-carbon bond. The useful transitions

(200-400 nm) are $\pi \rightarrow \pi^*$ for compound with conjugated double bonds and some $n \rightarrow \sigma^*$ and $n \rightarrow \pi^*$ transitions.

1.9 Formation of Absorption Bands

Since the energy required for each electronic transition is quantised, the UV spectrum is expected to exhibit a single, discrete line corresponding to each electronic transition. In practice, broad absorption bands are usually observed. In a molecule, each electronic energy level (either in ground state or in excited state) is accompanied by large number of vibrational (*e.g.*, V_0, V_1, V_2, . . .etc.) and rotational (*e.g.*, J_0, J_1, J_2, J_3 . . .etc.) energy levels which are also quantised (Fig. 1.5). In complex molecules having many atoms, there are still a large number of closer vibrational energy levels.

The radiation energy that passes through a sample is sufficient to induce various electronic transitions as well as transitions in accompanying vibrational and rotational energy levels. However, these transitions have very small energy difference, but the energy. required to induce an electronic transition is larger than that required to cause transition in the accomparying vibrational and rotational energy levels. Thus, electronic absorption is superimposed upon the accompanying vibrational and rotational absorptions resulting in the formation of broad bands. In other words, not only a single but a large number of very close wavelengths are absorbed and the closeness of the resulting discrete lines causes them to coalesce to give broad absorption bands in case of complex molecules.

1.10 Designation of Absorption Bands

UV-visible absorption bands may be designated by the type of electronic transition from which they originate, *e.g.*, $\sigma \rightarrow \sigma^*$ band, $\pi \rightarrow \pi^*$ band, etc., or by the letter designation. The following letter designation was proposed because more than one band may arise due to the same type of electronic transition.

(1) ***K*-bands** (German: *Konjugierte* = conjugated): These bands originate from $\pi - \pi^*$ transitions in compounds having a $\pi - \pi$ conjugated system. The intensity of *K*-band is usually 10^4. *K*-band is exihibited by conjugated enes and enones. Some *K* bonds attributed to $\pi \rightarrow \pi^*$ transitions are given in Table 1.1.

TABLE 1.1 ***K* Bands attributed to $\pi \rightarrow \pi^*$ transitions**

Compound	λ_{max} nm	ε_{max}
1, 3-Butadiene	217	21,000
Acrolein	210	11,500
Acetophenone	240	13,000
2, 3-Dimethylbutadiene	226	21,400
Styrene	244	12,000
1, 3, 5-Hexatriene	258	35,000

(2) ***R*-Bands** (German: *Radikalartig* = Radical-like): These bands originate from $n \rightarrow \pi^*$ transitions of a single chromophoric group, *e.g.*, carbonyl or nitro group. These bands are also called forbidden bands. *R* bands are less intense with ε_{max} value below 100. Some *R* bands attributed to $n \rightarrow \pi^*$ transitions are given in the Table 1.2.

TABLE 1.2 ***R Bands attributed to n → π* transitions***

Compound	λ_{max}, nm	ε_{max}
Acetaldehyde	290	17
Acetone	279	15
Acrolein	315	14
Methyl vinyl ketone	320	14
Acetophenone	319	50

(3) ***B*-Bands** (Benzenoid bands): These bands originate from π → π* transitions in aromatic or hetero aromatic compounds. Some *B* bands due to π → π* transitions are given in the Table 1.3.

TABLE 1.3 ***B-Bands due to π → π* transitions***

Compound	λ_{max}, nm	ε_{max}
Benzene	256	200
Toluene	262	174
Naphthalene	312	289
Phenol	270	1450

(4) ***E* or Ethylenic Bands:** Such bands originate due to the electronic transitions in the benzenoid system of three ethylenic bands which are in closed cyclic conjugation. These are further characterised as E_1 and E_2 bands. The E_1 band of benzene, which appears at lower wavelength (180 nm) is more intense than E_2 band that occurs at longer wavelength (200 nm). Some E_1 and E_2 bands due to π → π* transitions are given in Table 1.4.

TABLE 1.4 ***E-Bands due to π → π* transitions***

Compound	E_1 band		E_2 band	
	λ_{max}	ε_{max}	λ_{max}	ε_{max}
Benzene	180	60,000	200	7,900
Naphthalene	221	133,000	286	9,300
Anthracene	256	180,000	375	9,000

1.11 Transition Probability: Allowed and Forbidden Transitions

On exposure to UV or visible radiation a molecule may or may not absorb the radiation, *i.e.*, it may or may not undergo electronic excitation. The molar absorptivity at maximum absorption has been found to be:

$$\varepsilon_{max} = 0.87 \times 10^{20} P.a.$$

where P = transition probability with value from 0 to 1

a = Target area of the absorbing system, *i.e.*, a chromophore

A chromophore with a length of the order of 10 Å or 10^{-7} cm and with unit probability will have ε_{max} value of ≈ 10^5. Thus there is a direct relationship between the area of chromophore and its absorption intensity (ε_{max}). Transitions with ε_{max} values greater than 10^4 are called allowed transitions.

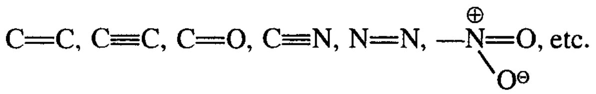
These are generally caused by $\pi \rightarrow \pi^*$ transtions, *e.g.*, in 1, 3-butadiene, the absorption at 217 nm, ε_{max} 21,000 results from the allowed transitions. Transitions with ε_{max} less than 10^4 are called forbidden transitions. These are generally caused by $n \rightarrow \pi^*$ transitions, *e.g.*, in carbonyl compounds, the absorption near 300 nm with ε_{max} values 10-100 results from the forbidden transition.

In addition to the area of a chromophore, there are some other factors also which govern the transition probability. However, the prediction of their effects on the transition probability is complicated because they involve geometries of the lower and higher energy molecular orbitals as well as symmetry of the molecule as a whole. Symmetrical molecules have more restrictions on their transitions than comparatively less symmetrical molecules. Consequently, symmetrical molecules like benzene have simple electronic absorption spectra as compared to less symmetrical molecules. There is much less symmetry restriction for a highly unsymmetrical molecule, thus it will exhibit a complex electronic absorption spectrum.

1.12 Terminology used in UV Spectroscopy

The following terms are commonly used in UV spectroscopy:

1.12.1 Chromophore: A covalently unsaturated group responsible for absorption in the UV or visible region is known as a chromophore. For example:



$$\mathrm{C{=}C,\ C{\equiv}C,\ C{=}O,\ C{\equiv}N,\ N{=}N,\ -\overset{\oplus}{N}({=}O)O^{\ominus},\ etc.}$$

Molecules containing the same chromophores can usually be expected to have similar UV spectra.

1.12.2 Auxochrome (Auxilliary chromophore): A covalently saturated group, which, when attached to a chromophore, changes both the wavelength and intensity of the absorption maximum is known as an **auxochrome.** Generally auxochromes are atoms or groups with one or more lone pairs, *e.g.*, $-\overset{..}{\underset{..}{\mathrm{O}}}\mathrm{H}$, $-\overset{..}{\underset{..}{\mathrm{O}}}\mathrm{R}$, $-\overset{..}{\underset{..}{\mathrm{S}}}\mathrm{H}$, $-\overset{..}{\mathrm{N}}\mathrm{H_2}$, $-\overset{..}{\mathrm{N}}\mathrm{R_2}$, $-\overset{..}{\underset{..}{\mathrm{X}}}\!:$, etc.

1.12.3 Bathochromic shift or Effect: The shift of the absorption maximum to longer wavelength caused by either substitution on to the chromophore (by an auxochrome), or by a change in the solvent is called a **bathochromic shift or red shift.**

For example, benzene shows λ_{max} 256 nm and aniline shows λ_{max} 280 nm. Thus there is a bathochromic shift of 24 nm in the λ_{max} of benzene due to the presence of the auxochrome $-\overset{..}{\mathrm{N}}\mathrm{H_2}$. Similarly, a bathochromic shift of $n \rightarrow \pi^*$ band is observed in carbonyl compounds on decreasing solvent polarity, *e.g.*, λ_{max} of acetone is at 264.5 nn is water as compared to 279 nm in hexane.

1.12.4 Hypsochromic shift or Effect: The shift of an absorption maximum to a shorter wavelength as a result of removal of conjugation, or change in solvent polarity. For example, aniline shows λ_{max} 280 nm, whereas anilinium ion (acidic solution of aniline) shows λ_{max} 254 nm. This hypsochromic shift is due to the removal of $n - \pi$ conjugation of the lone pair of electrons of the nitrogen atom of aniline with the π-bonded system of the benzene ring on protonation because the protonated aniline (anilinium ion) has no lone pair of electrons for conjugation. Similarly, there is a hyprochromic shift of 10-20 nm in the λ_{max} of $\pi \rightarrow \pi^*$ bands of carbonyl compounds on going from ethanol as solvent to hexane, *i.e.*, on decreasing solvent polarity.

1.12.5 Hyperchromic Effect: An effect which leads to an increase in absorption intensity (ε_{max}) is called hyperchromic effect (Fig. 1.12). The introduction of an auxochrome usually causes hyperchromic shift. For example, benezene shows *B*-band at 256 nm, ε_{max} 200, whereas aniline shows *B*-band at 280 nm, ε_{max} 1430. The increase of 1230 in the value ε_{max} of aniline compared to that of benzene is due to the hyperchromic effect of the auxochrome NH_2.

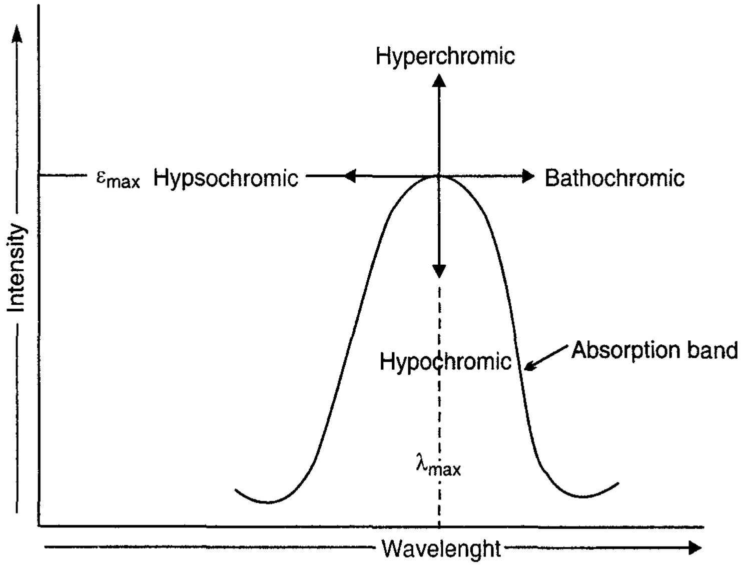


Fig. 1.12 Shifts in absorption position and intensity

1.12.6 Hypochromic effect: An effect which leads to a decrease in absorption intensity, (ε_{max}) is called hypochromic effect (Fig. 1.12). This is caused by reduction in conjugation. For example, aniline shows λ_{max} 280 nm and ε_{max} 1430 whereas the anilinium ion shows λ_{max} 254 nm and ε_{max} 160.

λ_{max} of some isolated chromophoric groups are given in Table 1.5.

TABLE 1.5 ***λ_{max} of some isolated chromophoric groups***

Chromophore	Example	λ_{max}	ε_{max}	Transition	Solvent
>C=C<	Ethylene	171	15,530	$\pi \rightarrow \pi^*$	Vapour
—C≡C—	Acetylene	150	10,000	$\pi \rightarrow \pi^*$	Hexame
>C=O	Acetaldehyde	160	20,000	$n \rightarrow \sigma^*$	Vapour
		180	10,000	$\pi \rightarrow \pi^*$	Vapour
		290	17	$n \rightarrow \pi^*$	Hexane
	Acetone	166	16,000	$n \rightarrow \sigma^*$	Vapour
		188	900	$\pi \rightarrow \pi^*$	Hexane
		279	15	$n \rightarrow \pi^*$	Hexane
—COOH	Acetic acid	204	60	$n \rightarrow \pi^*$	Water
—COOR	Ethyl acetate	211	57	$n \rightarrow \pi^*$	Ethanol
—$CONH_2$	Acetamide	178	9500	$\pi \rightarrow \pi^*$	Hexane
		220	63	$n \rightarrow \pi^*$	Water
—C≡N	Acetonitrile	167	Weak	$\pi \rightarrow \pi^*$	Vapour

1.13 Effect of Conjugation on Absorption Maximum

The $\pi - \pi^*$ transition of ethylene requires absorption of light at 171 nm (164 kcal/mole), slightly into the vacuum ultraviolet region. In conjugated system, however, there are electronic transtitions with lower energies that correspond to wavelengths longer than 200 nm. Let us compare the energy levels of ethylene and 1, 3-butadiene.

In ethylene there is only one occupied MO and only one unoccupied MO. The only possible transition is the excitation of an electron from the occupied MO to the unoccupied MO. In butadiene there are four possible transitions, involving excitation of an electron from either of the field orbitals into either of the empty ones. The lowest energy transition, corresponding to absorption of light of the longest wavelength, is the excitation of an electron from the HOMO to the LUMO. This is a $\pi_2 \rightarrow \pi_3^*$ transition.

Notice in Fig. 1.13 that the HOMO of butadiene is higher in energy than the HOMO of ethylene. Also, the LUMO of butadiene is lower in energy than the LUMO of ethylene. Both of these differences reduce the relative energy of the $\pi \rightarrow \pi^*$ transition in butadiene. The resulting absorption is at 217 nm (129 kcal (mole).

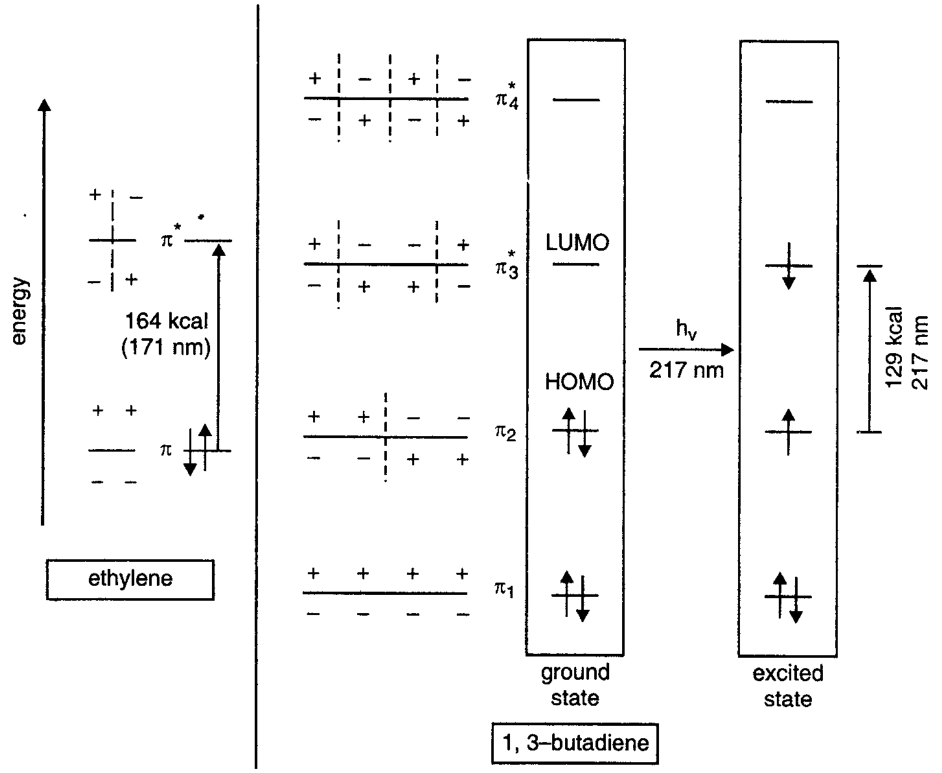


Fig. 1.13 In 1,3-butadiene, the $\pi \rightarrow \pi^*$ transition absorbs at a wavelength of 217 nm (129 kcal/mole or 540 kJ/mole), compared with 171 nm (164 kcal/mole or 686 kJ/mole) for ethylene. This longer-wavelength (lower-energy) absorption results from a smaller energy difference between the HOMO and LUMO in butadiene than in ethylene

Just as conjugated dienes absorb at longer wavelengths than simple alkenes, the conjugated trienes absorb at even longer wavelengths. In 1,3,5-hexatriene, for example, (Fig. 1.14), the HOMO is π_3 and the LUMO is π_4^*. The lowest energy transition is the excitation of an electron from π_3 into π_4^*. The HOMO in 1,3,5-hexatriene is slightly higher in energy than that for 1, 3-butadiene, and the hexatriene LUMO is slightly lower in energy. Once again, the narrowing of the energy between the HOMO and the LUMO gives a lower energy, longer wavelength absorption. The principal $\pi \rightarrow \pi^*$ transition in 1,3,5-hexatriene occurs at 258 nm (108 kcal/mole).

Similar to the conjugated alkenes, other conjugated compounds such as aldehydes, ketones, etc. also absorb at longer wavelengths as compared to the simple unconjugated compounds.

Another way to point out the narrowing of the HOMO-LUMO energy as the conjugated system grows is to look at the number of nodes in the molecular orbitals. In general, the HOMO of a

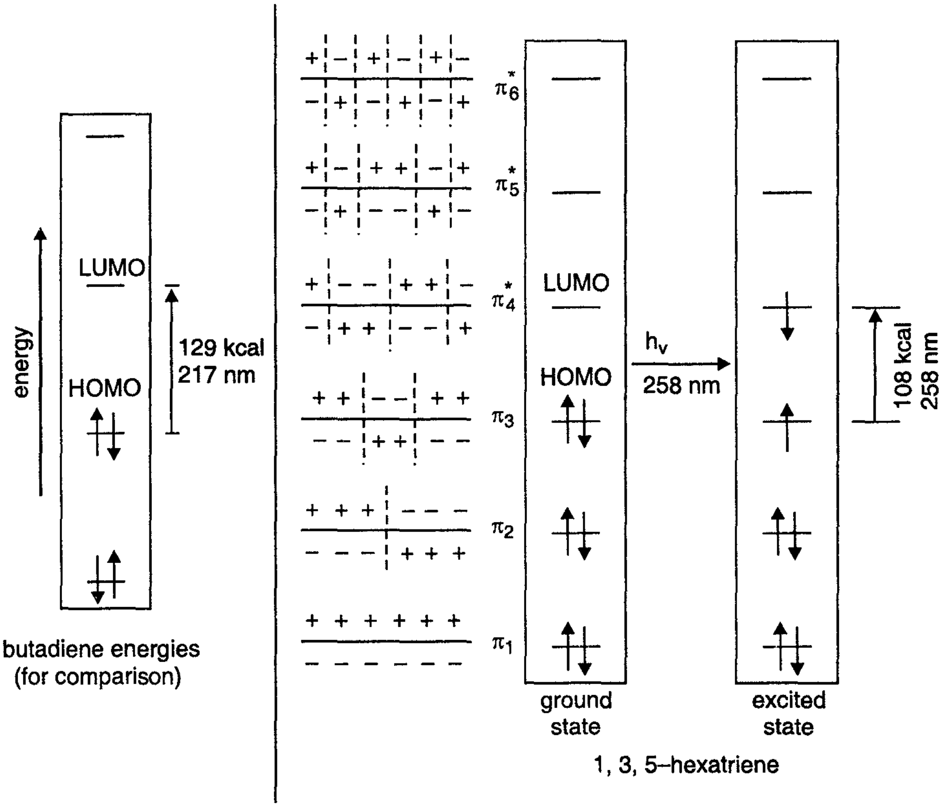


Fig. 1.14 1,3,5-hexatriene has a smaller energy difference (108 kcal/mole or 452 kJ/mole) between its HOMO and LUMO than does 1,3-butadiene (129 kcal/mole or 540 kJ/mole). The $\pi \rightarrow \pi^*$ transition corresponding to this energy difference absorbs at a longer wavelength: 228 nm, compared with 217 nm for 1,3-butadiene

conjugated system with N *pi* electrons has N/2 – 1 nodes: none for ethylene, one for butadiene, two for 1,3,5-hexatriene and so on. The LUMO always has one more node. Usually the more nodes an orbital already has, the less additional energy is involved in adding one more node. **In other words, the longer the conjugated system, lesser is the difference between HOMO and LUMO energy and hence the higher are the values of λ_{max} and ε_{max}.**

In general, *the longer the conjugated system, the higher are the values of* λ_{max} *and* ε_{max}.

1.14 Solvent Effects

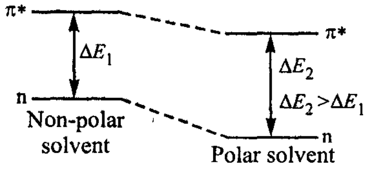
The polarity of the solvent has a significant influence on the position as well as intensity of absorption. Compounds like dienes and conjugated polyenes do not experience any appreciable shift on increasing the polarity of the solvent. In general, the absorption maximum for the non-polar compounds is same in polar (like alcohol) as well as in non-polar (like hexane) solvents. The absorption maximum for the polar compounds is usually shifted with the change in polarity of the solvent. Following two rules are used for the effect of solvents on the absorption maxima.

(a) If the absorbing substance is non-polar, the effect of solvent is mainly determined by the refractive index of the solvent.

(b) For polar light absorbing substances in polar solvents, the dipole moment of the solvent is mainly responsible for the change in the position of the absorption band.

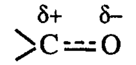
These rules are, however, not valid in cases where complex formation occurs between solvent and solute because in such cases the band may appear in an entirely new position. Moreover, polar solvents such as water, alcohols, ketones and esters tend to obliterate spectral fine structure arising from vibrational effects. Let us consider solvents' effects in the following transitions:

(i) $n \rightarrow \pi^*$ transitions: If a group is more polar in the ground state than in the excited state; the non-bonded electrons in the ground state are stabilised relative to the excited state due to hydrogen bonding or dipole-dipole interactions with the polar solvents. As a result, the energy difference between the excited state and the ground state increases and hence the absorption shifts towards shorter wave length as shown below:



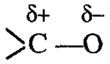
Effect of polarity of solvent on $n \rightarrow \pi^*$ transition

A carbonyl group is more polar in the ground state than in the excited state.



$$\overset{\delta+}{>C}\overset{\delta-}{\overline{\underline{\quad}}O}$$

Ground state
more polar



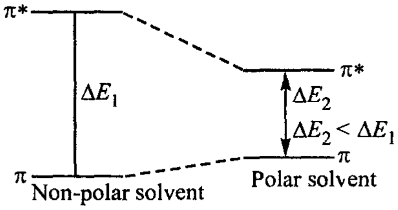
$$\overset{\delta+}{>C}-\overset{\delta-}{O}$$

Excited state
(less polar)

As a result hydrogen bonding or dipole-dipole interactions will lower the energy of the ground state more than that of the excited state and hence the absorption shifted to shorter wavelength. For example, the absorption maximum of acetone which appears at 279 nm in hexane (non-polar solvent) shifts to shorter wave length as the polarity of the solvent increases.

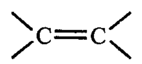
Solvent	C_6H_{14}	$CHCl_3$	C_2H_5OH	CH_3OH	H_2O
λ_{max} (nm)	279 .	277	272	270	265

(ii) $\pi \rightarrow \pi$ transition: If a group is more polar in the excited state than in the ground state, the hydrogen bonding and dipole-dipole interactions with the solvent will stabilise the excited state more than the ground. As a result, the energy gap between the ground state and the excited state decreases and the absorption shifted towards longer wavelength as shown below:

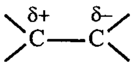


Effect of polarity of solvent on $\pi \rightarrow \pi^*$ transition

Consider for example, ethylene molecule. In the ground state, the molecule is non-polar. But in the excited state, one of the carbon atoms becomes electron deficient and the other electron rich. As a result, the molecule is more polar in the excired state.



Ground state
(non-polar)



Excited state
(more polar)

Consequently, in a polar solvent, π^* orbitals will be stabilised relative to π orbitals and hence absorption shifts to longer wavelength.

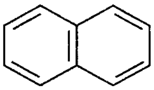
It has been found that an increase in solvent polarity usually shifts $n \rightarrow \pi^*$ *and* $n \rightarrow \sigma^*$ *bands to shorter wavelengths, and* $\pi \rightarrow \pi^*$ *bands of polar compounds to longer wavelengths.*

1.15 Electronic Spectra: Structure Relationships

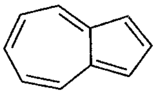
The following structural effects have remarkable influence on the electronic spectra:

(1) Resonance effect
(2) Hyperconjugative effect
(3) Hydrogen bonding effect
(4) Steric effect

1.15.1 Resonance effect on electronic spectra: Resonance stabilises both the ground state and the excited state of a species; the stabilisation effect may be greater in one than in the other. If resonance stabilises the excited state more in comparison to the ground state, the electronic excitation energy (ΔE) will be lower than what it would have been if the resonance had stabilised the ground state more relative to the excited state; and consequently, the λ_{max} value in the former case will be greater than that of the later case. Thus, it is not the magnitude of the resonance energy but whether resonance stabilises primarily the excited state or the ground state that decides the effect of resonance on UV spectra. For example, naphthalene and azulene are two isomeric aromatic compounds.



Naphthalene



Azulene

Resonance stabilises the ground state of napththalene more relative to its excited state, while it stabilises the excited state of azulene less in comparison to its ground state. As a consequence the ΔE of azulene is less than the ΔE of naphthalene. Since the wavelength of absorption depends on the ΔE value, azulene absorbs light at a longer wavelength than naphthalene does. Accordingly, azulene is deep blue in colour while naphthalene is colourless.

Conjugated systems have increased resonance stabilisation in the excited states. Greater number of charge separated structures that can be written for the excited state perhaps brings about the resonance stabilisation of the state. Thus a conjugated system has lower ΔE value and hence longer λ_{max} value than a similar non-conjugated system. In fact, as the conjugation of the chromophores increases, usually deepening of colour also increases. Thus, *the longer the length of the conjugation in system, the longer is the wavelength of absorption and larger is the molar absorptivity.*

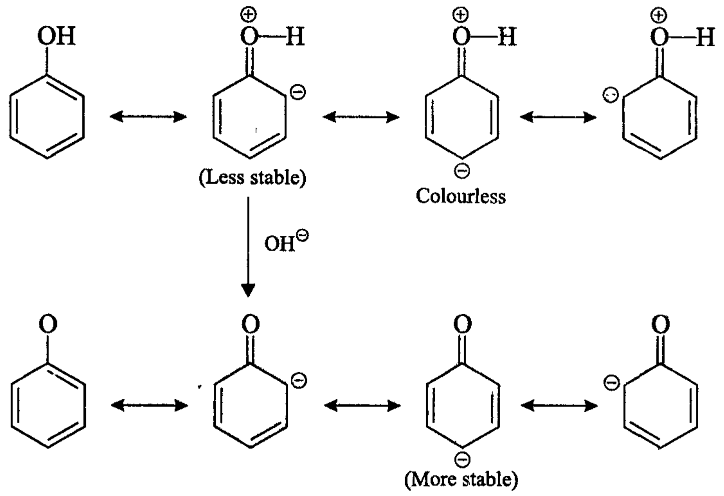
For example :

$C_6H_5—CH{=}CH—C_6H_5$
$\lambda_{max} = 319$ nm
colourless

$C_6H_5—(CH{=}CH)_3—C_6H_5$
$\lambda_{max} = 377$ nm
pale yellow

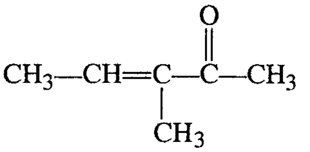
$C_6H_5—(CH{=}CH)_5—C_6H_5$
$\lambda_{max} = 425$ nm
orange

Equivalent resonance, amongst polar structures, stabilises the excited state relative to the ground state, as a result of which absorption occurs at a longer wavelength in the case of a polar species with respect to its non-polar counterpart. For this reason phenol is colourless in the solid state while it is yellow in alkaline medium.

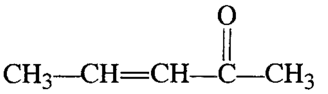


Thus, more resonance stabilisation of the excited state leads to the bathochromic shift, and the hypsochromic shift occurs if the ground state is more resonance stabilised.

1.15.2 Hyperconjugative Effect: Since hyperconjugation too brings stability to the excited as well as to the ground state, it has the same effects on λ_{max} and ε_{max} as resonance shows. Alkyl group present on the conjugated carbon stabilises its excited state than its ground state through hyperconjugation. Thus bathochromic shift occurs if the hydrogen atoms on a chromophoric system are substituted by alkyl group (1° or 2°). Thus 3-methyl-3-penten-2-one absorbs at 236 nm but 3-penten-2-one absorbs at 224 nm for $\pi \rightarrow \pi^*$ transition.


$$CH_3-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$$

3-Methyl-3-penten-2-one
λ_{max} 236 nm

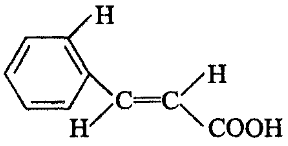

$$CH_3-CH=CH-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$$

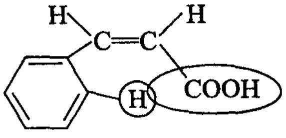
3-Penten-2-one
λ_{max} 224 nm

1.15.3 Hydrogen bonding effect: Owing to greater polarity, the strength of an intramolecular hydrogen bonding increases in the excited state relative to the ground state. Therefore, intramolecular hydrogen bonding stabilises the excited state than its ground state and thus decreases the energy content of the excited state. Hence the ΔE value of the electronic transition of a molecule having intramolecular hydrogen bonding will be lower than what would have been if there were no intramolecular hydrogen bonding. For example, *o*-nitrophenol is yellow in colour while its isomer *p*-nitrophenol is a pale yellow coloured substance.

1.15.4 Steric Effect on UV spectra: We know that the position and intensity of absorption depend on the length of the conjugation; the longer the length of the conjugation, the longer is the wavelength of absorption and the larger is the ε_{max}. If the steric effect hinders the coplanarity of a system, delocalisation of *pi* electrons will be hindered; and as a consequence, the length of conjugation will decrease.

For example, *trans*-cinnamic acid absorbs at a longer wavelength (λ_{max} = 272 nm, ε_{max} = 15,900) than *cis*-cinnamic acid (λ_{max} = 268 nm, ε_{max} = 10,700). This is because the former has a coplanar structure and delocalisation of *pi* electrons occurs completely across the molecule while in *cis* isomer the delocalisation is hindered because it loses coplanarity owing to the overlap of *ortho* hydrogen of the phenyl group and the carboxylic group as shown below:


Trans-cinnamic acid


Cis-cinnamic acid

1.16 Important Chromophores

Conjugated Systems: If two or more similar chromophores are present in a molecule and they are not in conjugation with each other, the effect on the spectrum is usually not additive. There is little electronic interaction between isolated chromophoric groups. However, if two chromophoric groups are in conjugation with each other, a large effect on the spectrum results because the π electron system is spread over atleast four atomic centres. When two chromophoric groups are conjugated, the high intensity (π → π* transition) absorption band is generally shifted 15-45 nm to longer wavelength with respect to the simple unconjugated chromophore. Examples of various conjugated chromophoric groups are given in Table 1.6.

TABLE 1.6 ***λ_{max} of simple conjugated chromophoric groups***

Chromophore	Example	λ_{max} (nm)	Transition	ε_{max}	Solvent
$>C=\overset{\vert}{C}-\overset{\vert}{C}=C<$	Butadiene	217	$\pi \rightarrow \pi^*$	21,000	Hexane
$>C=\overset{\vert}{C}-\overset{\vert}{C}=\overset{\vert}{C}-\overset{\vert}{C}=C<$	1, 3, 5-Hexatriene	258	$\pi \rightarrow \pi^*$	35,000	Hexane
$>C=\overset{\vert}{C}-C\equiv C-$	Vinylacetylene	219	$\pi \rightarrow \pi^*$	7,600	Hexane
		228	$\pi \rightarrow \pi^*$	7,800	Hexane
$>C=\overset{\vert}{C}-\overset{\vert}{C}=O$	Acrolein	210	$\pi \rightarrow \pi^*$	11,500	Ethanol
		315	$n \rightarrow \pi^*$	14	Ethanol
$>C=\overset{\vert}{C}-\overset{\vert}{C}=O$	Crotonaldehyde	218	$\pi \rightarrow \pi^*$	18,000	Ethanol
		320	$n \rightarrow \pi^*$	30	Ethanol
$O=\overset{\vert}{C}-\overset{\vert}{C}=O$	Glyoxal	195	$\pi \rightarrow \pi^*$	35	Hexane
		280	$n \rightarrow \pi^*$	3	Hexane

The UV spectra of α, β unsaturated aldehydes, ketones and conjugated dienes lend themselves to an excellent numerical correlation depending on the number of alkyl, alkyoxyl, acetoxy, etc. substituent groups attached to the ethylenic linkages present. The rules have been formulated by L. Fieser and R.B. Woodward.

1.17 Woodward-Fieser rules For calculating λ_{max} of Conjugated Dienes and polyenes

Base value for *transoid* dienes and heteroannular dienes 214 nm
Base value for *cisoid* dines and homoannular dienes 253 nm

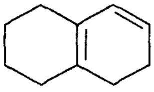
Add for each substitutent attached to the conjugated system

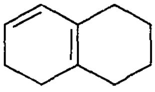
(i)	Double bond extending conjugation	30 nm
(ii)	Alkyl substitutents or ring residues on double bond	5 nm
(iii)	OR (alkoxy)	6 nm
(iv)	Cl, Br	5 nm
(v)	Exocyclic conjugated double bond	5 nm
	Calculated λ_{max} of the compound	= Total nm

It must be noted that acyclic dienes exist in the preferred (strainless) transoid conformation. In compounds containing both homoannular and heteroannular diene systems, the calculations are based on the longer wavelength (253 nm), *i.e.*, the homoannular diene system. The calculated and observed values of λ_{max} usually match within ± 5 nm. Let us clear the terms which are used in Woodward-Fieser rules for conjugated dienes.

1.17.1 Homoannular Dienes: In homoannular dienes, conjugated double bonds are present in the same ring and there have *s-cis* (*cisoid*) configuration (*s* = single bond joining two double bonded carbon atoms) as illustrated below:

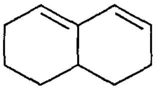

(I)

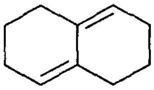

(II)

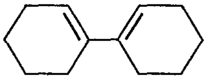

(III)

The *s-cis*-configuation causes strain which raises the ground state energy level of the molecule leaving the higher energy excited state relatively unchanged. Thus the transition energy is lowered resulting in the shift of absorption to a longer wavelength.

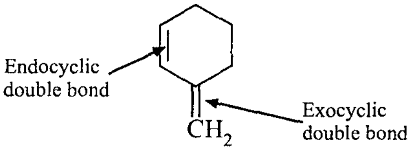
1.17.2 Heteroannular Dienes: In heteroannular dienes, conjugated double bonds are not present in the same ring and these have *s-trans* (transoid) configuration as shown below:


(IV)


(V)


(VI)

1.17.3 Exocyclic Conjugated double bonds: The carbon-carbon double bonds projecting outside a ring are called exocyclic double bonds, *e.g.*,

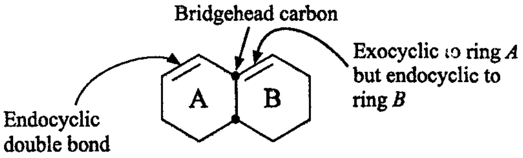


(VII)

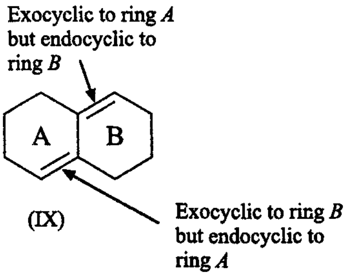
In bicyclic and polycyclic polyenes exocyclic double bonds are always present on the bridgehead carbons.

Note that the same double bond may be exocyclic to one ring, while endocyclic to the other (structures VIII and IX) and sometimes the same double bond may be exocyclic to two rings simultaneously (structure X).

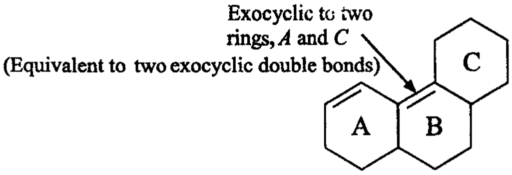
1.17.4 Double Bonds extending conjugation: The parent compound for Woodward-Fieser rule is 1, 3-butadiene which contains only two conjugated double bonds. Total number of conjugated double bonds in a given polyene minus two is the number of double bonds extending conjugation.



(VIII)
(one exocyclic double bond)



(IX)
(Two exocyclic double bonds)



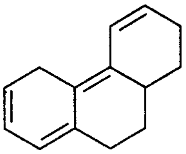
(X)

For example: $CH_2{=}CH{-}CH{=}CH{-}CH{=}CH_2$

3 − 2 = 1; One double bond extending conjugation

$CH_2{=}CH{-}CH{=}CH{-}CH{=}CH{-}CH{=}CH_2$

4 − 2 = 2; Two double bonds extending conjugation

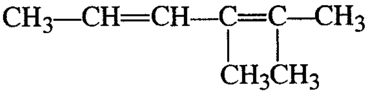


4 − 2 = 2; Two double bonds extending conjugation.

1.17.5 Alkyl Substituents and Ring residues: Only the alkyl substituents and ring residues attached to the carbon atoms constituting the conjugated system of the compound are taken into account.

Number of alkyl substituents or ring residues of the given compound can be known by comparing it with parent compound (having no alkyl substitutents).

Suppose we want to know the alkyl substituents in compound (XI):



$$CH_3{-}CH{=}CH{-}\underset{CH_3}{C}{=}\underset{CH_3}{C}{-}CH_3$$

(XI)

Parent diene of the compound (XI) is 1, 3-betadiene, *i.e.*, (XII):

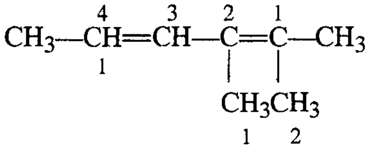
$$CH_2{=}CH{-}CH{=}CH_2$$

(XII)

Let us compare (XII) with (XI):

$$\underset{4}{CH_2}{=}\underset{3}{CH}{-}\underset{2}{CH}{=}\underset{1}{CH_2}$$

(XII)



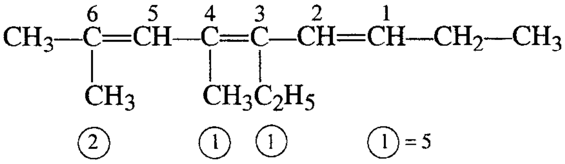
$$\mathrm{CH_3{-}\overset{4}{\underset{1}{C}}H{=}\overset{3}{C}H{-}\overset{2}{\underset{\underset{1}{CH_3}}{C}}{=}\overset{1}{\underset{\underset{2}{CH_3}}{C}}{-}CH_3}$$

(XI)

Match carbon-1, 2, 3 and 4 of parent compound (XII) with carbon-1, 2, 3 and 4 respectively of the compound (XI). Number of substituents on carbon-1, 2, 3 and 4 are indicated by numbers in circle. Thus carbon-1 has two alkyl substituents carbon-2 has one alkyl substituent, carbon-3 has no alkyl substituents and carbon-4 has one alkyl substituent. Thus total number of alkyl substituents is four.

Number of alkyl substituents and ring residues in some conjugated polyenes

Example 1.

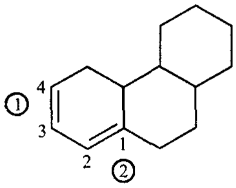


$$\mathrm{CH_3{-}\overset{6}{\underset{\underset{\text{②}}{CH_3}}{C}}{=}\overset{5}{C}H{-}\overset{4}{\underset{\underset{\text{①}}{CH_3}}{C}}{=}\overset{3}{\underset{\underset{\text{①}}{C_2H_5}}{C}}{-}\overset{2}{C}H{=}\overset{1}{\underset{\text{①}=5}{C}}H{-}CH_2{-}CH_3}$$

Parent triene is:

$$\mathrm{\overset{6}{C}H_2{=}\overset{5}{C}H{-}\overset{4}{C}H{=}\overset{3}{C}H{-}\overset{2}{C}H{=}\overset{1}{C}H_2}$$

Example 2.

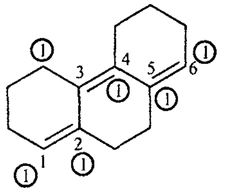


Total number of ring residues = 3

Parent compound is diene

$$\mathrm{\underset{4}{C}H_2{=}\underset{3}{C}H{-}\underset{2}{C}H{=}\underset{4}{C}H_2}$$

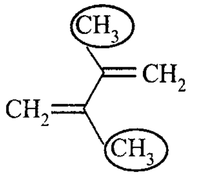
Example 3.



Total number of ring residues = 6

The following examples illustrate how these general rules may be applied.

Example 4.



2,3-Dimethyl-1,3-butadiene

Base value for acyclic diene	214 nm
Two alkyl substitutents (2 × 5)	10 nm
Calculate λ_{max}	224 nm

Observed λ_{max} = 223 nm

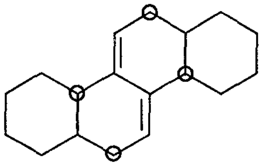
Example 5. $\text{CH}_3\text{—CH=CH—CH=CH}_2$

1, 3-Pentadiene

Base value for acyclic diene	214 nm
One alkyl substituent	5 nm
Calculated λ_{max}	219 nm

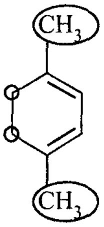
Observed λ_{max} = 220 nm

Example 6.



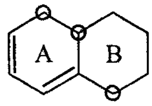
Since the two double bonds occur in two different rings, the diene is heteroannular, and the base value is 214 nm. There are four ring residues attached to the double bonds, increasing the λ_{max} by 4 × 5 or 20 nm. Finally, each double bond is exo to the other ring, adding 2 × 5 or 10 nm. Thus the predicted λ_{max} is 214 + 20 + 10 = 244 nm. The observed value is 245 nm.

Example 7.



Since the double bonds occur in the same ring, the base value of 253 nm (homoannular diene) is used. There are two alkyl substituents and two ring residues attached to the double bonds, increasing the λ_{max} 5 × 4 or 20 nm. Thus the predicted λ_{max} = 253 + 20 = 273 nm; the observed value is 262 nm.

Example 8.



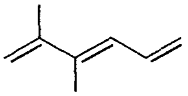
Base value = 253 nm
Three ring residues = 3 × 5 = 15 nm
One exocyclic double bond to ring *B* = 5 nm
Predicted λ_{max} = 273 nm
Observed λ_{max} = 275 nm

Example 9.

$\text{CH}_2\text{=CH—CH=CH—CH=CH—CH=CH}_2$

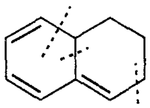
Base value = 214 nm
Two double bonds extending conjugation = 60 nm
λ_{max} = 274 nm

Example 10.



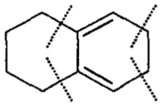
Base value = 214 nm
Two alkyl substituents = 10 nm
One double bond extending conjugation = 30 nm
λ_{max} = 254 nm

Example 11.



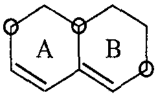
Base value = 253 nm (for homoannular and not for hetero because base value of homo is greater)
Three ring residues = 15 nm
One double bond extending conjugation = 30 nm
One exocyclic double bond = 5 nm
λ_{max} = 303 nm

Example 12.



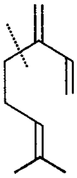
Base value = 253 nm
Four ring residues = 20 nm
Two exocyclic double bonds = 10 nm
λ_{max} = 283 nm

Example 13.



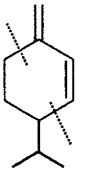
Base value = 214 nm
Three ring residues = 15 nm
One exocyclic double bond to ring *A* = 5 nm
Predicted λ_{max} = 234 nm
Observed λ_{max} = 235 nm

Example 14.



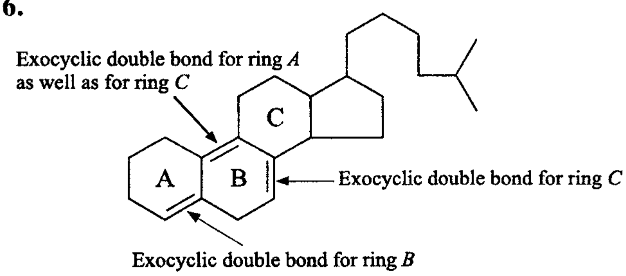
Base value = 214 nm
One alkyl substituent = 5 nm
Calculated λ_{max} = 219 nm
Observed λ_{max} = 224 nm

Example 15.



Base value for heteroannular diene = 214 nm
Two ring residues = 10 nm
One exocyclic double bond = 5 nm
λ_{max} (calculated) = 229 nm
λ_{max} (observed) = 232 nm

Example 16.

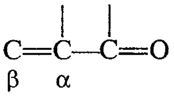


(i) Base value for homoannular deiene = 253 nm
(ii) Six ring residues = 30 nm
(iii) One double bond extending conjugation = 30 nm
(iv) Two exocyclic double bonds = 10 nm
(v) One double bond exocyclic to two rings simultaneously = 10 nm
Calculated λ_{max} = 333 nm

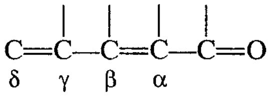
1.18 Woodward-Fieser Rules for calculating λ_{max} of α, β unsaturated carbonyl compounds (enones)

Compounds containing a carbonyl group in conjugation with a double bond are called enones. Spectra of enones are characterised by an intense absorption band in the 215-250 nm region (ε_{max} usually 10,000-20,000) and a weak $n \rightarrow \pi^*$ band at 310-330 nm.

Woodward and Fieser have derived the following empirical rules for calculating the position of λ_{max} of α, β-unsaturated carbonyl compounds (enones).


$$\underset{\beta}{C}=\underset{\alpha}{\overset{|}{C}}-\overset{|}{C}=O$$

Enone


$$\underset{\delta}{C}=\underset{\gamma}{\overset{|}{C}}-\underset{\beta}{\overset{|}{C}}=\underset{\alpha}{\overset{|}{C}}-\overset{|}{C}=O$$

Dienone

Base values :

Acyclic α, β-unsaturated ketones	215 nm
Six-membered cyclic α, β-unsaturated ketones	215 nm
Five-membered cyclic α, β-unsaturated ketones	202 nm
α, β-unsaturated aldehydes	207 nm

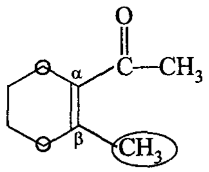
Add for each :

(i) Double bond extending conjugation		30 nm
(ii) Alkyl group, ring residue on:		
α-carbon		10 nm
β-carbon		12 nm
γ and higher carbon		18 nm
(iii) Polar substituents	Position in conjugated system	
—OH	α	35 nm
	β	30 nm
	γ	50 nm
—OAc	α, β, δ	6 nm
—OMe	α	35 nm
	β	30 nm
	γ	17 nm
	δ	31 nm
—Cl	α	15 nm
	β	12 nm
—Br	α	25 nm
	β	30 nm
Exocyclic carbon-carbon double bond		5 nm
Homoannular diene component*		39 nm
Calculated λ_{max} for ethanolic solution		= Total nm

---

*Two conjugated double bonds in the same ring.

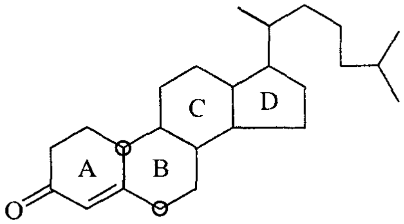
Example 1.



The following examples illustrate how these rules may be applied.

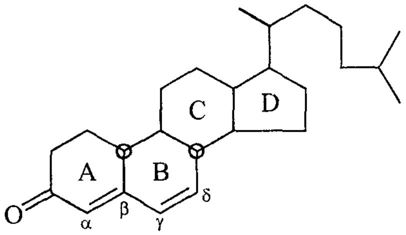
Base Value	215 nm
One α-ring residue	10 nm
One β-ring residue	12 nm
One β-alkyl group	12 nm
Calculated λ_{max}	= 249 nm
Observed λ_{max}	= 245 nm

Example 2.



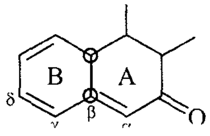
Six-membered ketone, base value = 215 nm
Two β-ring residues = 24 nm
One exocyclic double bond to ring *B* = 5 nm
Calculated λ_{max} = 244 nm
Observed λ_{max} = 241 nm

Example 3.



Six-membered enone, base value = 215 nm
One β-ring residue = 12 nm
One δ-ring residue = 18 nm
One exocyclic double bond to ring *B* = 5 nm
One double bond extending conjugation = 30 nm
Calculated λ_{max} = 280 nm
Observed λ_{max} = 281 nm

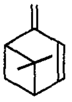
Example 4.

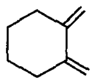


Six-membered enone, base value = 215 nm
One β-ring, residue = 12 nm
One ring residue on higher than γ carbon = 18 nm
Two double bonds extending conjugation = 60 nm
Homoannular diene component = 39 nm
Exocyclic double bond to ring *B* = 5 nm
Calculated λ_{max} = 349 nm
Observed λ_{max} = 348 nm

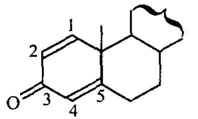
1.19 Angular Distortion and Cross-Conjugation: Steric Inhibition of Resonance

The Woodward-Fieser rules for conjugated dienes and carbonyl compounds give reliable results only where there is absence of strain around the chromophore. Thus the rules are successful for acyclic and most six-membered ring systems. Well authenticated violations of these rules are abundant in compounds in which the chromophore distortion is due to either the ring strain or due to the cross conjugation.* Examples of systems whose UV spectra could not satisfactorily be predicted by Woodward-Fieser rules are shown below:


(1)


(2)

The strained molecule (1) has a λ_{max} at 246 nm whereas the usual calculation gives a value of 229 nm. The diene (2) might be expected to have λ_{max} at 234 nm but the distortion of the chromophore resulting in the loss of coplanarity of the double bonds with consequent loss of conjugation causes the λ_{max} to be as low as 220 nm.



(3)

λ_{max} (Calc.) 244 nm
(Obs.) 244 nm

Since (3) is a cross conjugated dienone, the calculation is based on the enone system giving the higher λ_{max} value, namely, that extending to C_5 and having two β-ring residues and one exocyclic double bond. The Δ^1 bond is ignored in calculating the maximum. The calclated value and observed value in this case are identical. In compound (4) the Δ^1 bond is similarly ignored in calculating the absorption maximum, but the calculated value in this case is not very close to the observed value.

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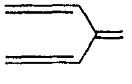
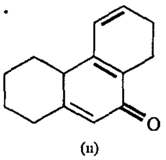
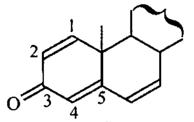
*Cross conjugated systems have the structures (i) and (ii). In (ii) the main chromophore is dienone which is part of the longest conjugated system.


(i)



(ii)



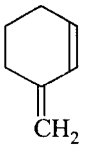
(4)

λ_{max} (Calc.) 280 nm
(Obs.) 298 nm

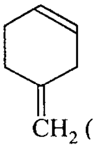
1.20 UV Spectroscopy in Structure Identification

One principal use of UV spectroscopy is to identify structure when the position of a double bond is uncertain on the basis of either IR or other spectroscopic methods. There are many examples where the structure of an organic compound can be determined only by UV spectroscopy.

For example, the following two isomeric compounds can be distinguished on the basis of their UV spectra:



(I)



(II)

Compound I contains a conjugated diene system, which shows an absorption maxima at 232 nm; the calculated value is also 232 nm. Compound II absorbs near 175 nm, the value for a single double bond, because its two double bonds are not conjugated.

Sometimes all possible compounds contain conjugated system (diene, enone, etc.) but in different positions. By knowing the possible structures and using Woodward-Fieser rules, the structure of unknown compound may be determined on the basis of its UV spectra.

1.21 Infrared Spectroscopy

Infrared spectrum gives information about the structural details of organic compounds. It allows the detection and identification of a large number of organic functional groups because they show specific and characteristic absorption in the ifrared region. Infrared spectroscopy observes the vibrations of molecular bonds. This information is used to infer the nature of the bonding and the functional groups present. Of the spectral methods, IR is the only one that allows for direct indentification of the functional groups.

Spectral Region: The infrared region of the spectrum extends from 4000 cm^{-1} to 625 cm^{-1}. The infrared region is split up into three parts:

(i) the near infrared	12,820 cm^{-1} – 3333 cm^{-1}
(ii) the middle infrared	3333 cm^{-1} – 333 cm^{-1}
(iii) the far infrared	333 cm^{-1} – 33 cm^{-1}

The near infrared region corresponds to energies in the range 37 – 10 kcal/mole. Since very few organic molecules absorb radiation in this range, it is seldom used for spectroscopic purposes. Radiation in the middle infrared region has energies ranging from 10 to 1 kcal/mole. This energy is associated with molecular vibrations. Spectroscopy in this region is extremely useful to the organic chemists. The far infrared region has energy 1.0 to 0.1 kcal/mole. This region has been little used for organic spectroscopy, again because few useful absorptions occur here.

The position of an infrared absorption band is specified by its wavelength (λ) measured in **microns** (μm). A micron (or **micrometer**) corresponds to 10^{-6} of a meter or 10^{-4} cm, *i.e.*,

$$1\ \mu m = 10^{-6}\ m \quad \text{or} \quad 1\ \mu m = 10^{-4}\ cm$$

A more common unit, however, is the wavenumber scale. The wavenumber is simply the reciprocal of the wavelength (in cm). Since 1 cm = 10,000 μm, the wavenumber can be calculated by dividing 10,000 by the wavelength in microns. The unit of the wavenumber is cm^{-1}. For example, an absorption at a wavelength 4 μm corresponds to a wavenumber of 2500 cm^{-1}.

$$\bar{\nu}\,(\text{cm}^{-1}) = \frac{1}{\lambda\,(\text{cm})}$$

$$= \frac{10{,}000\ \mu\text{m/cm}}{\lambda\,(\mu\text{m})}$$

$$\lambda\,(\mu\text{m}) = \frac{10{,}000\ \mu\text{m/cm}}{\bar{\nu}\,(\text{cm}^{-1})}$$

$$\bar{\nu} = \frac{10{,}000\ \mu\text{m/cm}}{4\ \mu\text{m}}$$

$$= 2500\ \text{cm}^{-1}.$$

1.22 Measurement of IR spectrum

The instrument used for measuring the absorption of infrared radiation by a molecule is called an infrared spectrophotometer. A diagram of a typical instrument is shown in Fig. 1.15. The instrument is a typical double-beam IR spectrophotometer. It is called a double beam instrument because two beams of radiation are generated, one of which passes through a cell containing the sample dissolved in a solvent and the other passes through a cell containing only the solvent. The sample cells and various optical parts such as prism of the IR spectrophotometer are made of fused rock salt (NaCl) because NaCl is completely transparent to IR radiations. As a result, great care must be taken in handling the cells and contact with moisture must be avoided at all times.

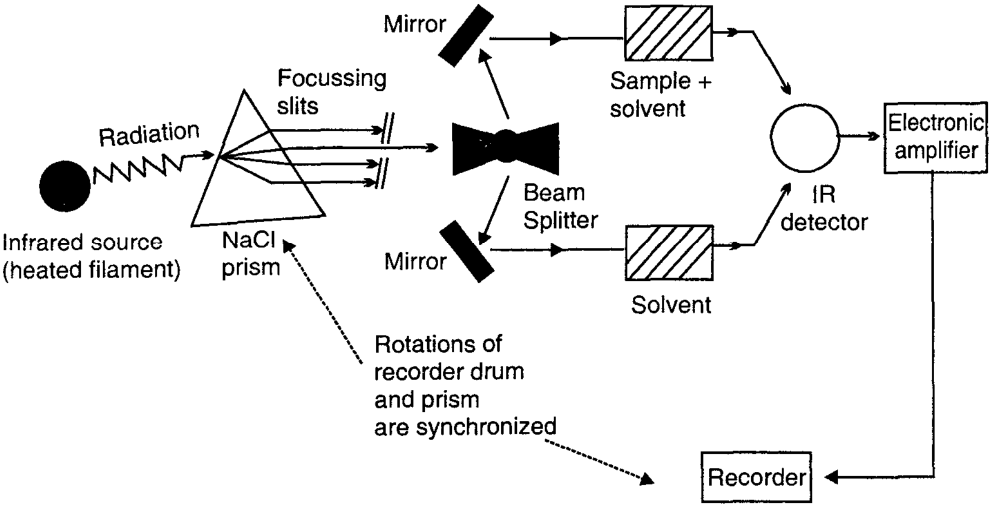


Fig. 1.15 Schematic diagram of a double-beam infrared spectrophotometer

At one end of the instrument is the IR source which emits all wavelengths of infrared radiation. The light from this source is split by NaCl prism. The prism is then rotated to let radiation of increasing wavelength pass through the slits. This gives a single wavelength (monochromatic light) beam that is then split into two beams and focussed by the mirrors. One beam passes through the compound being studied (often dissolved in a solvent) and the other beam passes through solvent alone. The intensities of the two beams are determined by the IR detector which combines them to produce net transmittance. This transmittance signal is recorded on a graph paper as a function of wavelength. The rotations of the prism and recording drum are synchronised so that wavelength (or frequency) and transmittance are correlated on the graph paper. Although absorbance could be plotted, most infrared instruments plot the percent transmittance (% T) which is the ratio of the intensity of the light passing through the sample (I) to the intensity of light striking the sample (I_0) times 100. The % T is plotted versus the wavelength (or frequency) of radiation. The relationship is:

$$\% \, T = \frac{I}{I_0} \times 100$$

IR spectra are obtained by irradiation of the sample with light from IR region ($5000 \, cm^{-1}$ to $500 \, cm^{-1}$) of the electromagnetic spectrum. The units most commonly used are wavenumbers. The wavenumber associated with a given wavelength is obtained by taking reciprocal of the wavelength in centimeter.

1.23 Requirement for the Absorption of Infrared Radiation (Physical Basis of IR Spectroscopy)

For a molecule to absorb IR radiation, it has to fulfil the following two requirements:

1.23.1 Correct wavelength of Radiation: The absorptions that are observed in an IR spectrum are the result of vibrations within a molecule. Atoms within a molecule are not stationary, but are constantly in motion. Consider, for example, the C—H bonds in a typical organic compound. These bonds undergo various stretching and bending motions. A useful analogy to the C—H stretching motion is the stretching and compression of a spring (Fig. 1.16). This vibration takes place with a certain frequency ν.

It is clear from Fig. 1.16 that the stretching of the C—H bond describes a wave motion. A wave of electromagnetic radiation can transfer its energy to the vibrational wave motion of the C—H bond only if the following very important condition is fulfilled: There must be an exact match between the frequency of radiation and the frequency of vibration. This is due to the wave character of atoms

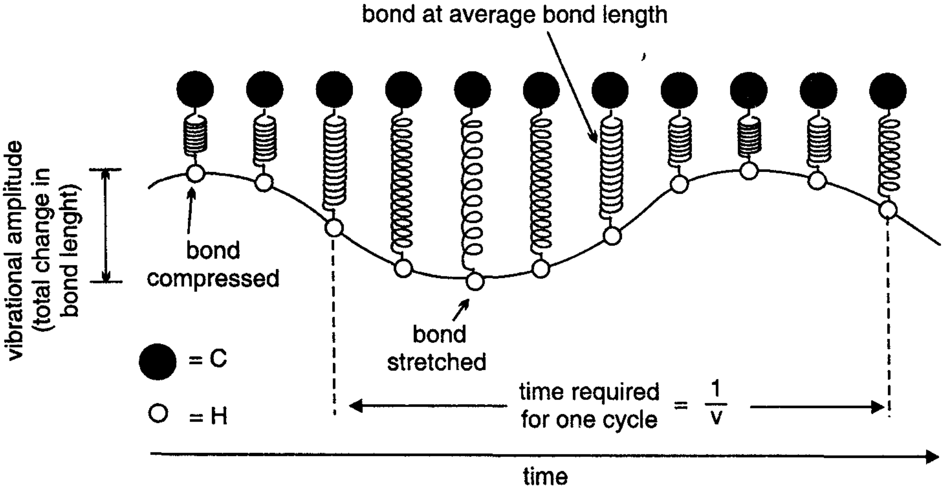


Fig. 1.16 Chemical bonds undergo a variety of vibrations. The one illustrated here is a stretching vibration. The bond, represented as a spring, is shown at various times. The bond stretches and compresses about its average length over time. The time required for one complete cycle of vibration is the reciprocal of the vibrational frequency

that requires equality between wavelength of the radiation and wavelength of the bond vibration in order for energy absorption to occur. Each functional group has its own wavelength. Due to this reason each functional group absorbs different wavelength and thus functional groups are characterised by IR spectroscopy. On the basis of the above discussion, we can conclude two important points:

(i) Bonds vibrate with characteristic frequencies, and

(ii) Absorption of energy from infrared radiation can occur only when there is match between the wavelength of the radiation and the wavelength of the bond vibration.

Thus if C—H vibration has a frequency of 9×10^{13} sec, then it will absorb energy from radiation with the same frequency. Wavelength and wavenumber of this absorbed frequency can be calculated as follows:

$$\begin{aligned}\lambda = \frac{c}{\nu} &= \frac{3 \times 10^{10}}{9 \times 10^{13}} \\ &= 3.33 \times 10^{-4}\ \text{cm} \\ &= 3.33 \times 10^{-6}\ \text{m} \\ &= 3.33\ \mu\end{aligned}$$

The corresponding wavenumber

$$\begin{aligned}\bar{\nu} = \frac{\nu}{c} &= \frac{9 \times 10^{13}}{3 \times 10^{10}} \\ &= 3000\ \text{cm}^{-1}\end{aligned}$$

When radiation of this wavelength (*i.e.*, 3.33 μ) interacts with vibrating C—H bond, radiant energy is absorbed and the bond vibration excited. After energy absorption, bond vibrates with the same wavelength but with a larger amplitude (a large stretch and tighter compression) (Fig. 1.17). This absorption gives rise to the peak in the IR spectrum.

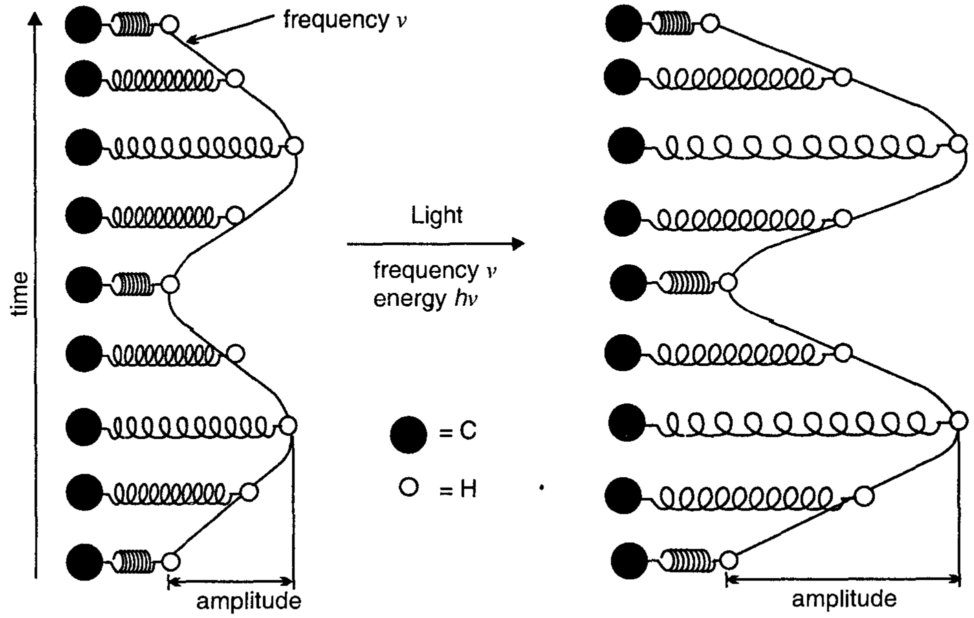


Fig. 1.17 Light absorption by a bond vibration causes the bond (spring) to vibrate at the same wavelength but with a larger amplitude. The frequency of the light must exactly match the frequency of the bond vibration

1.23.2 Electric Dipole: A molecule can absorb IR radiation when its absorption causes a change in its electric dipole (dipole moment).

A bond with a dipole moment can be visualised as a positive charge and a negative charge separated by a spring. If this bond is placed in an electric field (Fig. 1.18), it is either stretched or compressed depending on the direction of the field.

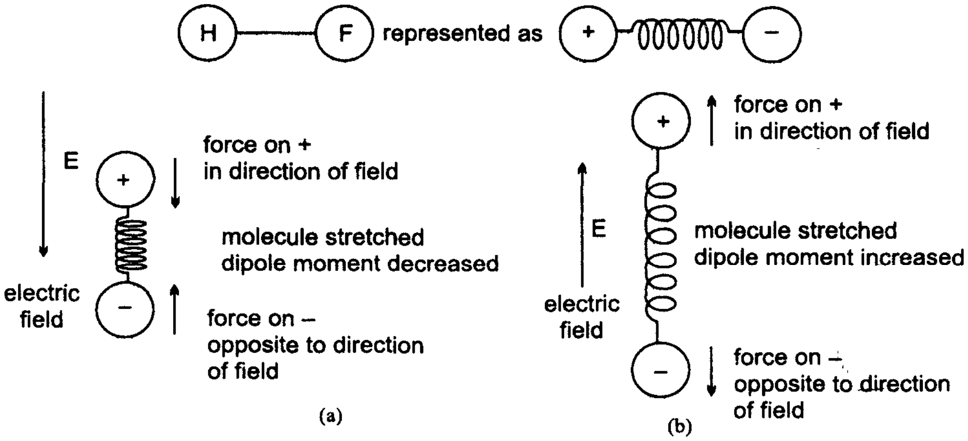


Fig. 1.18 A bond with a dipole moment (as in HF, for instance) is either stretched or compressed by an electric field, depending on the direction of the field. Notice that the force on the positive charge is in the direction of the electric field (E) and the force on the negative charge is in the opposite direction

All electromagnetic radiations are associated with oscillating electric and magnetic vectors at right angles to the direction of propagation. The electric field of the electromagnetic radiation alternately stretches and compresses a polar bond as shown in Fig. 1.18. When the electric field is in the same direction as the dipole moment, the bond is compressed and its dipole moment decreases (Fig. 1.18a)

When the field is opposite to the dipolemoment, the bond stretches and its dipole moment increases (Fig. 1.18b). If this alternate stretching and compressng of the bond (and the periodic change in its dipole moment) occurs at the frequency of the molecules' natural rate of vibration, energy may be absorbed. Vibrations of bonds with non-zero dipole moments generally result in IR absorptions and are said to be **IR active.**

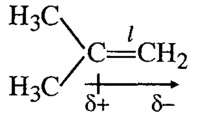
If bond is symmetrical and has zero dipole moment, the electric field of electromagnetic radiation does not interact with the bond. For example, the triple bond of acetylene has zero dipole moment, and the dipolemoment resmains zero if the bond is stretched or compressed. Since the vibration produces no change in the dipole moment, there can be no absorption of energy. This vibration is said to be **IR inactive** and its characteristic frequency is not seen in the IR spectrum. Thus the key to an IR active vibration is that the *vibration must change the dipole moment of the molecule.*

1.24 Selection Rules

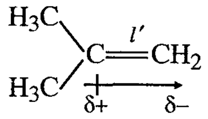
Infrared light is absorbed when the oscillating dipole moment (due to molecular vibration) interacts with the oscillating electric vector of the infrared radiation. For this absorption to occur it is necessary that the dipole moment at one extreme (say stretch position) of a vibration must be different from the dipole moment at the other extreme (compress position) of the position.

This point can be illustrated by comparing the C=C stretching vibrations of two alkenes isobutene and 2, 3-dimethyl-2-butene.

Because of the electron donating characteristics of the methyl group, isobutene has a dipole moment along the C = C double.



C=C bond in
compressed position
$\mu = e \times l$

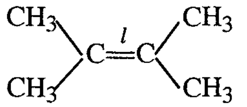


C=C bond in
stretched position
$\mu' = e \times l'$
when double bond
stretched the dipole
moment increases, because
dipole moment is the
product of both charge and distance

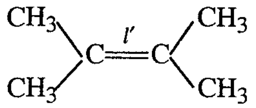
$$(\mu \neq \mu' \Rightarrow \mu' > \mu) \cdot$$

Because isobutene is associated with a change in dipole moment, the C=C stretching vibration occurs at 1640 cm^{-1}.

The alkene 2, 2-dimethyl-2-butene, however, has no dipole moment hence double bond of 2, 2-dimethyl-2-butene does not show IR peak in IR spectrum.



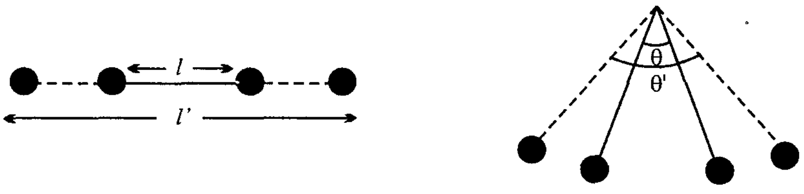
double bond is not polar, *i.e.*, $e = 0$
$\mu = e \times l = 0$
(compressed position)



double bond is not polar, $\mu = e \times l' = 0$
(stretched positions)

1.25 Molecular Vibrations

Infrared spectroscopy measures the changes in the stretching and bending vibrations of covalent bonds, which occur when a molecule absorbs electromagnetic energy in the IR region of the electromagnetic spectrum. The specific bond being stretched or the specific angle being bent depends upon the frequency of radiation being absorbed. A stretching vibrational mode corresponds to change (positive or negative) in bond distance between bonded atoms along the intermolecular axis. (Fig. 1.19a).



Bond stretching
(a)

Bond angle bending
(b)

Fig. 1.19

A bending vibration may consist of a change in bond angle between bonds with a common atom or the movement of a group of atoms with respect to the remainder of the molecules without movement of the atoms in the group with respect to one another (Fig. 1.19b).

Stretching a bond increases the distance between the two nuclei in the bond. If the energy of the system as a function of the distance between the nuclei is plotted, following plot is obtained (Fig. 1.20).

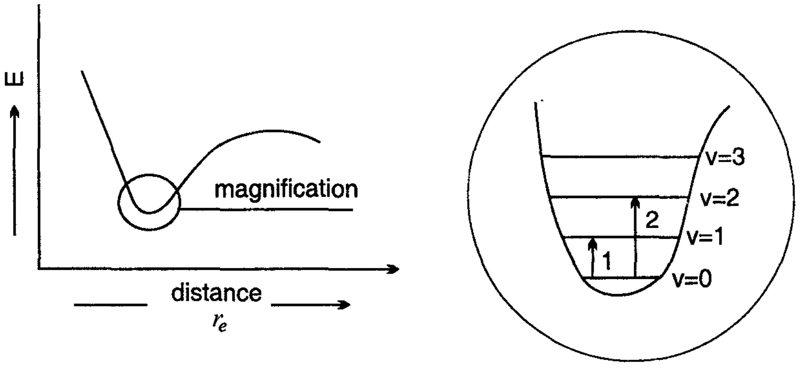


Fig 1.20

In Fig. 1.20 r_e is the equilibrium distance between the nuclei. As the energy of the system increases, the bond can exist in various vibrational excited states V_1, V_2, V_3, etc. The vibrational ground state is V_0. Most molecules exist in the V_0 level at room temperature. Since the absorption of energy is supposed to excite a bond to the next higher energy level, most excitations are from V_0 to V_1. In this level the amplitude of the molecular vibration is greater. In general, such absorption of an infrared light quantum can occur only if the dipole moment of the molecule is different in two vibrational levels.

The vibrational energy of a chemical bond is quantised and can have the value,

$$E_{vib} = \left[V + \frac{1}{2}\right] h\nu$$

where V is the vibrational level ($V = 0, 1, 2$) and ν is the vibrational frequency of the bond. Absorption of radiation with energy equal to the difference between two vibrational energy levels (ΔE_{vib}) will cause a vibrational transition to occur. Transition from the ground state ($V = 0$) to the first excited state ($V = 1$) absorbs light strongly and gives rise to intense bands called the **fundamental bands.** The energy difference (ΔE_{vib}) between the lowest possible energy level of a bond and the next higher energy level is given as :

$$\begin{aligned}\Delta E_{vib} &= E_{vib}(V=1) - E_{vib}(V=0)\\ &= \left[1 + \frac{1}{2}\right] h\nu - \left[0 + \frac{1}{2}\right] h\nu\\ &= \frac{3}{2} h\nu - \frac{1}{2} h\nu\\ &= h\nu\end{aligned}$$

This gives the frequency of a fundamental band. Transitions from the ground state ($V = 0$) to the second excited state ($V = 2$) with the absorption of infrared radiation gives rise to weak bands, called **overtones.** Overtones are always weaker absorptions than corresponding fundamental vibration. An overtone occurs at a frequency that is multiple of the fundamental.

$$\begin{aligned}\Delta E_{vib} &= E_{vib}(V=2) - E_{vib}(V=0)\\ &= \left[2 + \frac{1}{2}\right] h\nu - \left[0 + \frac{1}{2}\right] h\nu\\ &= 2h\nu\end{aligned}$$

Polyatomic molecules may exibit more than one fundamental vibrational absorption bands. The number of these fundamental bands is related to the degree of freedom in the molecule. The number of degree of freedom is equal to the sum of the co-ordinates necessary to locate all the atoms of a molecule in space. Each atom has three degrees of freedom corresponding to the three cartesian co-ordinates (x, y, z) necessary to describe its position relative to other atoms in a molecule. Thus, the total number of degrees of freedom in a molecule will be equal to $3n$, where n is the number of atoms in a molecule. A molecule which is of finite dimensions will, thus, be made up of rotational, vibrational and translational degree of freedom.

$3n$ Degree of freedom = Translational + Rotational + Vibrational

Fundamental bands for the linear molecules

Total degree of freedom for linear molecule $= 3n$
Translational degree of freedom $= 3$
Rotational degree of freedom $= 2$
Vibrational degree of freedom $= 3n - (3 + 2)$
$= 3n - 5$

Each vibrational degree of freedom corresponds to the fundamental mode of vibration and each fundamental mode corresponds to a band. Hence, there will be $3n - 5$ possible fundamental bands for linear molecules.

Fundamental bands for non-linear molecules

Total degree of freedom $= 3n$
Translational degree of freedom $= 3$
Rotational degree of freedom $= 3$
Vibrational degree of freedom $= 3n - (3 + 3)$
$= 3n - 6$

$(3n - 5)$ and $(3n - 6)$ vibrations are called a normal mode. Out of these vibrations ($3n - 5$ or $3n - 6$), $(n - 1)$ vibrations are stretching vibrations and remaining vibrations are bending vibrations.

Bending vibrations for linear molecule $= 3n - 5 - (n - 1)$
$= 3n - n - (5 - 1)$
$= (2n - 4)$
Bending vibrations for non-linear molecule $= 3n - 6 - (n - 1)$
$= 2n - 5.$

The stretching and bending vibrations in a methylene group are given in Fig. 1.21.

Many of these vibrations occur at the same frequency (*i.e.*, same vibrations are degenarated) and not all of the possibile bands are generally seen as independent absorptions. However, additional bands, usually of low intensity, may occur as overtones.

As a result, the IR spectrum of organic compound is usually complex.

1.26 Calculation of Fundamental Stretching Frequencies

The bond between two atoms is like a vibrating spring. The vibrations of the bond are governed by the laws of physics which govern the motion of a spring.

This approximation, called the "Hooke's Law" permits the calculation of fundamental stretching frequency of a bond between two atoms A and B, using the following equation:

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{K(m_1 + m_2)}{m_1 m_2}}$$

where ν = vibrational frequency in cm^{-1} (wavenumber)

c = Velocity of light in cm/sec

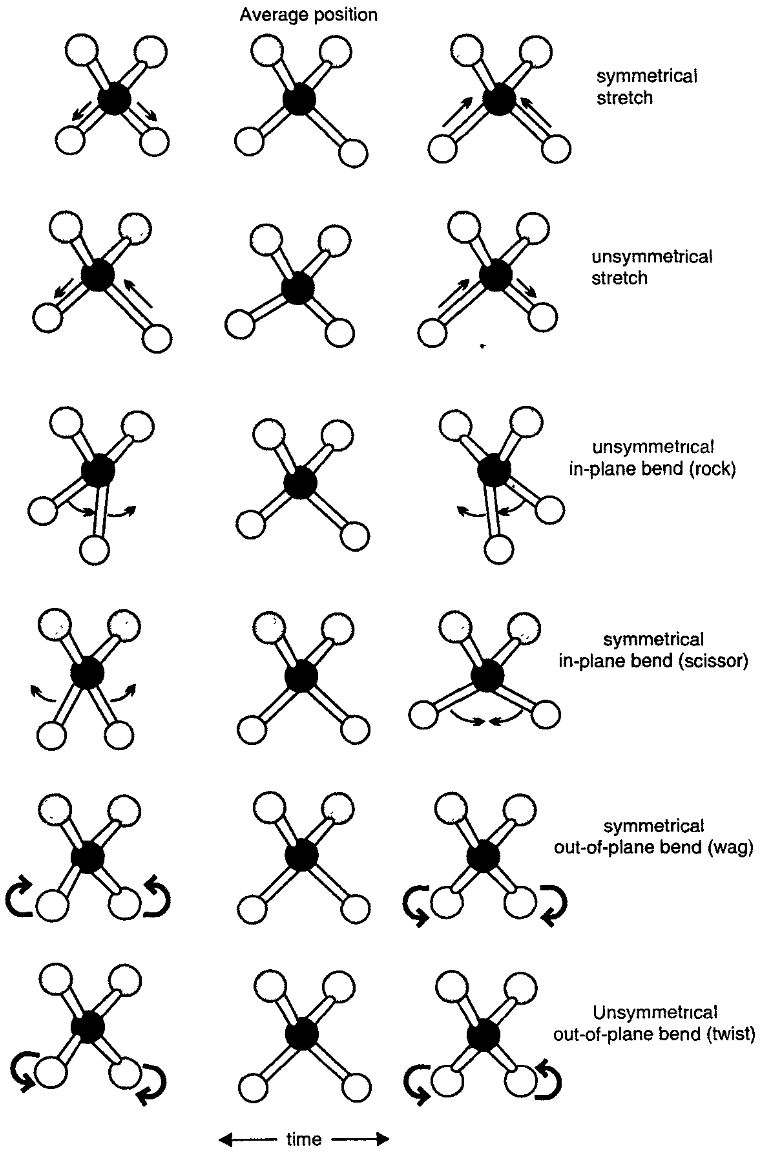


Fig. 1.21 Typical vibrations of a —CH_2— group in an organic compound. Start at the centre figure in each case and move left and right to see how the bonds change with time. The white atoms are hydrogen, the black atoms are carbon and the grey groups are the other groups attached to carbon

m_1 = mass of atom A in g

m_2 = mass of atom B is g

K = force constant in dyne cm^{-1}

$$\frac{m_1 m_2}{m_1 + m_2} = m^0 (\mu) = \text{Reduced mass of the atoms}$$

The force constants for some bonds are given below:

Bond	K in dyne/cm	bond length
$C—C$	5×10^5	1.56
$C=C$	10×10^5	1.33
$C\equiv C$	15×10^5	1.21
$C=O$	12.3×10^5	1.20

Hence K gives useful information regarding the type of bond present in a compound.

From the relationship it is apparent that the **frequency of vibration is directly proportional to the square root of the force constant of the bond.** We also know that the force constant is also related to the bond length. The longer the bond, the smaller the force constant. Thus

$$\nu \propto \sqrt{k}$$

or

$$\nu \propto \frac{1}{\text{Bond length}}$$

Thus there is direct correlation between the nature of a covalent bond and the IR absorption frequency associated with it. For example, the decreasing force constant (*i.e.*, increasing bond length) of carbon-carbon bond is: triple > double > single. Accordingly the stretching frequency of $—C\equiv C—$ is greater than that of $-\underset{|}{C}=\underset{|}{C}-$ which, in turn, is greater than $C—C$ as shown:

$\bar{\nu}$ =	2200 cm^{-1}	1650 cm^{-1}	1200 cm^{-1}
	$C\equiv C$	$C=C$	$C—C$

$$\xrightarrow{\hspace{10cm}}$$

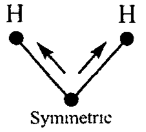
decreasing bond strength
increasing bond length
decreasing wavenumber,
i.e., absorption frequency.

From the above relationship it is also clear that the frequency of vibration is inversely proportional to the square root of the reduced mass. Larger m^0 (μ) implies a smaller wavenumber. For example, bond dissociation energies indicate that a C—H bond (104 kcal/mole) is not much stronger than a C—C bond (88 kcal/mole). Yet the stretching frequencies for these two bonds are 3000 cm^{-1} and 1200 cm^{-1}, respectively. This can be explained by the fact that the reduced mass of the C—H bond is much less than the reduced mass of the C—C bond. Thus, vibrations of higher heavier atoms occur at lower frequency or wavenumber than vibrations, of lighter atoms. The C—H and C—D bonds have essentially the same force constant. Thus the difference in the IR absorption frequencies of these two bonds is due to the mass difference between H and D.

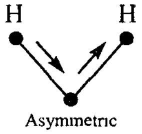
1.27 Factors Affecting Vibrational Frequencies

The vibrational Frequency or wavenumber of absorption can be calculated by Hooke's law. It has been found that the calculated value of frequency of absorption for a particular bond is never exactly equal to its experimental value. The difference is due to the fact that vibration of each group is influenced by the structure of the molecule in the immediate neighbourhood of the bond. The value of absorption frequency is also shifted since the force constant of a bond changes with its electronic state. Following are some of the factors responsible for the shifting of vibrational frequencies from their normal values.

1.27.1 Vibrational coupling (or coupled vibrations): An isolated C—H bond exibits only one stretching frequency but in case of methylene group (—CH_2—) two absorptions occur which correspond to symmetric and asymmetric vibrations as shown below :



Symmetric



Asymmetric

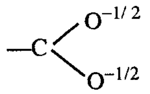
In such cases, asymmetric vibrations always occur at higher wavenumber than symmetric vibrations. These vibrations are known as coupled vibrations since these vibrations occur at different frequencies than that required for an isolated C—H stretching. Similarly, coupled vibrations of methyl group occur at different frequencies compared to —CH_2— group.

Vibrational coupling takes place between two bonds vibrating with similar frequency provided the bonds are reasonably close in the molecule. **Vibrational coupling is a feature of AX_2 groups.** The coupling vibrations may both be fundamentals or a fundamental vibration may couple with the overtone of some other vibrations. The latter coupling is frequently called **Fermi resonance,** after Enrico Fermi who first described it.

Carboxylic acid anhydrides show two C=O stretching absorptions between 1850 – 1800 cm^{-1} and 1790 – 1740 cm^{-1} with a difference of about 50 cm^{-1}. This can be explained due to symmetric and asymmetric stretching. Coupling occurs between two CO groups which are linked through —O—.

Vibration coupling of some AX_2 groups are given in Table 1.7.

TABLE 1.7 ***Typical asymmetric and symmetric strectching frequencies for some common AX_2 groups***

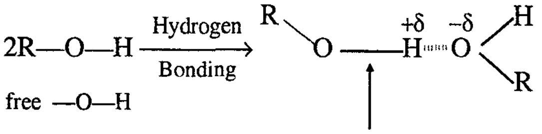
Group	V_{anti}/cm^{-1}	V_{sym}/cm^{-1}
—CH_2—	3000	2900
—NH_2	3400	3300
—NO_2	1550	1400
—SO_2	1350	1150
	1600	1400

1.27.2 Hydrogen Bonding: Hydrogen bonding brings about remarkable downward frequency shifts of the groups involved in it. Stronger the hydrogen bonding, greater is the absorption shift towards lower wavenumber than the normal value. Generally, bands due to intramolecular hydrogen bonds are sharp whereas intermolecular hydrogen bonds give rise to broad bands and these depend on concentration.

Free O—H group of alcohols and phenols show sharp and strong absorption bands in the region 3590 – 3650 cm^{-1}. Sharp, non-hydrogen bonded O—H bands are observed only in the vapour phase, in very dilute solution, in non-polar solvents or when hydrogen bonding is prevented by steric hindrance. Pure sample and concentrated solutions of alcohols and phenols show broad O—H stretching bands in the region about 3200 – 3600 cm^{-1} due to intermolecular hydrogen bonding. The N—H stretching frequencies of amines are also affected by hydrogen bonding in the same way as those of the hydroxyl group but frequency shifts for amines are lesser than those for hydoxyl compounds. This is because nitrogen is less electronegative than oxygen and so the hydrogen bonding in amines is weaker than that in hydroxyl compounds. For example, non-hydrogen bonded primary amines exhibit two bands one near 3400 cm^{-1} and the other near 3500 cm^{-1} due to symmetrical and asymmetrical N—H stretching modes respectively. In pure amines these bands respectively appear in the range 3250 – 3330 cm^{-1} and 3330 – 3400 cm^{-1} due to intermolecular hydrogen bonding.

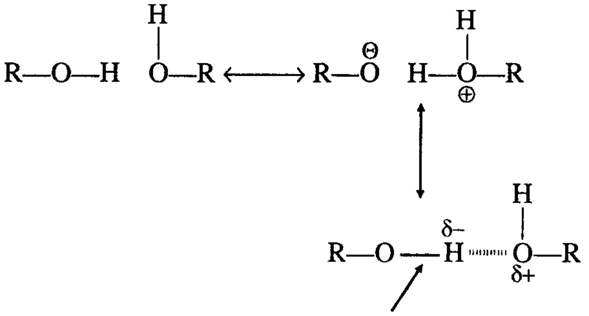
Why does hydrogen bonding lower the absorption frequency?

Let us take the example of hydroxy compounds. On hydrogen bonding the original O—H bond is lengthened (weakened) due to electrostatic attraction between the hydrogen atoms of one molecule and oxygen atoms of the other, and thus the force constant of the O—H bond is reduced resulting in a decrease in its stretching frequency.



(i) increase in bond length
(ii) decrease in force constant
(iii) decrease in $\bar{v}$

Further, the hydrogen bond can be regarded as a resonance hybrid of the following resonating structures, so that hydrogen bonding involves a lengthening of the original O—H bond. This bond is consequently weakened, so the stretching frequency is lowered.



Increase in O—H bond length

Distinction between Inter- and Intramolecular Hydrogen Bondings

In very dilute solution (in non-polar solvents) intermolecular distances are too large to form intermolecular hydrogen bonds. On the otherhand, in pure liquids, solids and concentrated solutions, the molecules are closer to form intermolecular hydrogen bonds. Thus intermolecular hydrogen bonding is concentration dependent. On dilution with non-polar solvents, intermolecular hydrogen bonds are broken, hence there is decrease in intensity or disappearance of the hydrogen bonded O—H band and increase in intensity or appearance of free O—H stretching absorption. The effect of concentration on intermolecular hydrogen bonding is illustrated in Fig. 1.23 (Section 1.29) in which the absorption bands in the O—H stretching region are shown for two different concentratins of cyclohexylcarbinol in CCl_4. The band at 3623 cm^{-1} results from the monomer, whereas broad absorption near 3333 cm^{-1} arises from the polymeric structures due to the intermolecular hydrogen bonding.

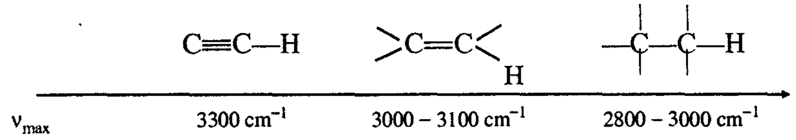
Intramolecular hydrogen bonding is within the same molecule, hence it is not affected by dilution, and so the absorption band is also unaffected.

Thus a compound with intramolecular hydrogen bonding shows almost the same O—H stretching in the concentrated solution as in the very delute solution, this means O—H stretching value does not change with dilution in the cases of intramolecular hydrogen bonding while the same changes with dilution in the case of intermolecular hydrogen bonding. Thus dilution can be used to distinguish between inter- and intramolecular hydrogen bondings.

1.27.3 Electronegativity: As the electronegativity of a bonded atom increases, the shortening of bond length occurs and the large force constant leads to increased vibrational frequency. Again, as the electronegativity of a bonded atom changes, the dipole moment of the bond changes. The absorption intensity being proportional to the square of the change in dipole moment as the dipole moment changes, absorption intensity changes. For example, the decreasing order of electronegativity of carbon in alkane, alkene and alkyne is :

alkyne > alkene > alkane

the C—H stretching frequencies of these compounds are also in the same order:



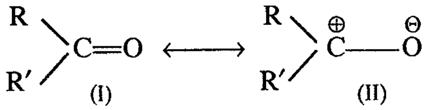
(i) Electronegativity of carbon of the C—H bonds in increasing order.

(ii) Force constant is in decreasing order.

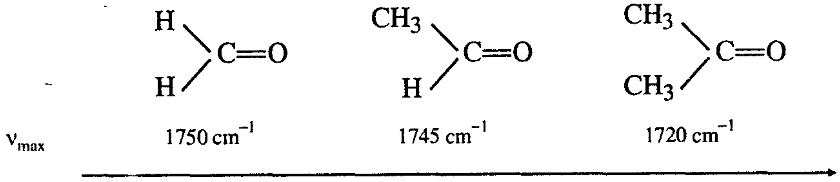
(iii) ν_{max} is also in decreasing order.

1.27.4 Inductive Effect: Inductive effect has profound influence on vibrational frequencies of groups with multiple bonds.

For example, a carbonyl compound may be considered as a resonance hybrid of the following structures :



The stretching frequency of a carbonyl group decreases with increasing number of alkyl groups attached to carbonyl carbon. This is due to +I effect of alkyl groups which favours the structure (II) and lengthens (weakens) the carbon-oxygen double bond, and hence its force constant is decreased resulting in the lowering of the C=O stretching frequency. Let us take the following examples :



(i) carbon-oxygen bond lengths in increasing order (structure II)

(ii) Force constant in decreasing order

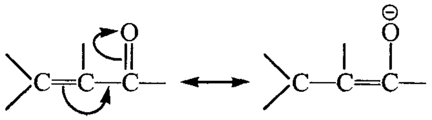
(iii) ν_{max} is in decreasing order

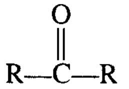
It should be noted why aldehydes absorb at higher frequency than ketones. Similarly, when a group with —I effect is attached to a C=O group, it favours the structure (I) and its stretching frequency is increased due to decrease in bond length or increase in the force constant of the carbon-oxygen double bond. For example, CH_3COCH_3, CH_3COCF_3 and CF_3COCF_3 show $\nu_{C=O}$ bands at 1720, 1769 and 1810 cm^{-1}, respectively.

1.27.5 Resonance Effect: We know that owing to $p-\pi$ and $\pi-\pi$ conjugation single bonds get partial double bond character and double bonds get partial single bond character. It is also known to us that single bonds are weaker than the corresponding double bonds. So, when a single bond acquires a partial double bond character through resonance, the vibrational frequency of the bond is expected to be greater than the normal value because of the shortening of bond length. On the other hand, when a double bond possesses a partial single bond character, the vibrational frequency is expected to be lower than the normal value because of the weakening of the bond strength through resonance. Consider the following examples:

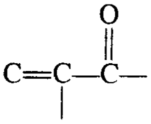
(i) **C=O stretching frequency of saturated and α, β-unsaturated carbonyl compounds.**

In an α, β-unsaturated carbonyl compound π – π conjugation takes place. Due to this conjugation C=O group has a partial single bond character. Thus the C=O bond becomes longer than that in a saturated carbonyl compound; as a result the C=O bond strength decreases and its vibrational frequency becomes less than that of the C=O group in the saturated carbonyl compound.





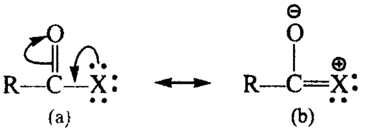
$\bar{\nu}_{max}$ 1725 - 1705 cm^{-1}



$\bar{\nu}_{max}$ 1685 - 1665 cm^{-1}

(ii) **C=O stretching frequency of acid derivations.**

The absorption frequency of saturated aliphatic keto group of a neat sample is 1715 cm^{-1}. Replacement of an alkyl group of a saturated aliphatic ketone by a heteroatom (X) shifts the carbonyl absorption. The direction of the shift depends on whether the inductive effect (a) or resonance effect (b) predominates.



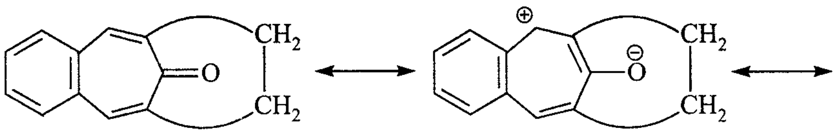
The inductive effect reduces the length of C=O bond and thus increases its force constant and the frequency of the absorption. The resonance effect increases the C=O bond length and reduces its force constant and the frequency of absorption (Table 1.8).

TABLE 1.8 ***The carbonyl absorption of*** $\mathrm{R{-}\overset{X}{\overset{|}{C}}{=}O}$ ***compounds***

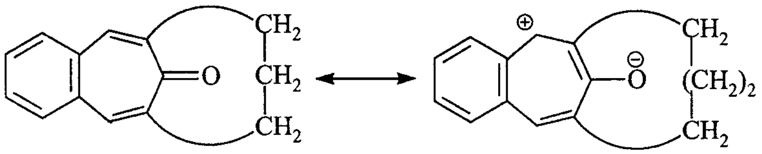
X	ν_{max} C=O	
Cl	1815 - 1785 cm^{-1}	Inductive effect predominates
Br	1812 cm^{-1}	
OH	1760 cm^{-1}	
OR	1750 - 1735 cm^{-1}	
NH$_2$	1695 - 1650 cm^{-1}	Resonance effect predominates
SR	1620 - 1690 cm^{-1}	

An NH_2 group has —I effect as well as +R effect but the latter predominates. Due to the +R effect, the C═O group in an amide gets a partial single bond character and possesses lower vibrational frequency ($\bar{\nu}_{max}$ C═O, 1650 cm^{-1}) than that in the corresponding ester (C═O, 1750 – 1735 cms^{-1}). In the case of an ester the –I effect of the alkoxy group predominates over its +R effect.

1.27.6 Steric effect: Steric effects such as steric inhibition of resonance, transannular effect, etc. influence stretching frequencies of bonds. For example, the —OH stretching ($\nu_{O—H}$) frequency of phenol is 3330 cm^{-1}. This frequency is due to the intermolecular hydrogen bonding. In contrast to phenol 2, 6-di-*tert*-butylphenol, in which steric hindrance prevents intermolecular hydrogen bonding absorption band is obtained at 3600 cm^{-1}. Similarly the C═O stretching frequency of 2,7-dimethylene-4,5-benzo tropone is 1596 cm^{-1}, whereas tetramethylene-4,5-benzo-tropone has a C═O stretching $\nu_{C=O}$ at 1724 cm^{-1}.



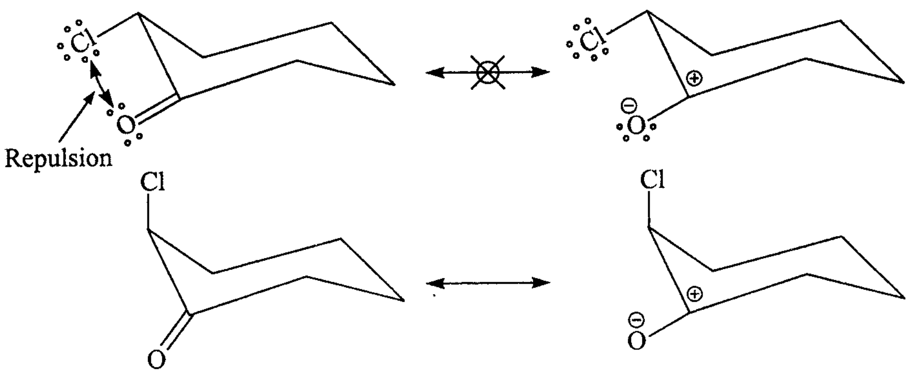
2,7-Dimethylene-4,5-benzotropone



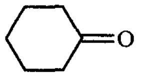
2,7-Tetramethylene-4,5-benzotropone

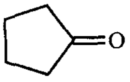
In the later compound, the C═O group is forced out of the plane of the molecule and being non-planar, steric inhibition of resonance occurs and the compound shows normal value for $\nu_{C=O}$. Whereas in the former case C—O double bond lengthens owing to conjugation of the C═O π bond with the rest of the molecule and as a consequence $\nu_{C=O}$ comes down.

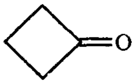
1.27.7 Field effects: Electrostatic or steric through space interaction between two groups within a molecule is called field effect. This field effect often influences the vibrational frequencies of both the groups. It has been observed that the $\nu_{C=O}$ is higher when the Cl atom of α-chlorocyclohexanone occupies the equatorial position than when it is in the axial position. In the equatorial position, the electron cloud of the Cl atom and that of the oxygen atom experience electrostatic repulsion and as a result of which carbon-oxygen bond does not acquire a partial single bond character, if it does so, it will have to face a greater repulsion.



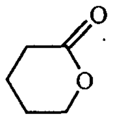
1.27.8 Ring Size: ν_{max} also depends on the size of the ring. For example, carbonyl stretching frequency in cyclic ketones having ring strain is shifted to higher value. The C—CO—C bond angle in strained rings is reduced below the normal value of 120°C (acyclic and six membered cyclic ketones have the normal C—CO—C) angle of 120°C). This leads to an increase in *s*-character in the sp^2 orbital of carbon involved in the C═O bond. Hence, the C═O bond is shortened (strengthened) resulting in an increase in the $\nu_{C=O}$ frequency. This increase in the *s*-character of the outside sp^2 orbital is there because it gives more *p* character to the sp^2 orbitals of the ring bonds which relieves some of the strain, as the preferred bond angle of *p* orbitals is 90°.

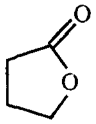

No strain
$\nu_{C=O}$ 1715 cm^{-1}

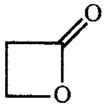

Moderate strain
1745 cm^{-1}


Highly strained
1780 cm^{-1}

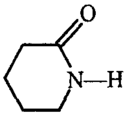
Similar to the ketones, as ring strain in lactones increases, the carbonyl stretching frequency also, increases.

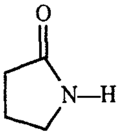

No strain
δ-valerolactone
$\nu_{C=O}$ 1735 cm^{-1}

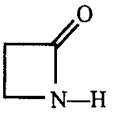

Moderate strain
γ-butyrolactone
1770 cm^{-1}


Highly strained
β-Propiolactone
1800 cm^{-1}

The C═O frequency in lactams too depends on the ring size. Similar to that of ketones and lactones, as the ring strain in lactams increases, the *s*–character of sp^2 carbon of C═O also increases and thus the carbonyl stretching frequency also increases.


δ-valerolactam
No strain
$\nu_{C=O}$ 1670 cm^{-1}


γ-butyrolactam
Moderate strain
1700 cm^{-1}


β-propiolactam
Highly strained
1745 cm^{-1}

1.28. Examination of an Infrared Spectrum

An infrared spectrum consists of :

(1) The functional group region (4000 – 1500 cm^{-1}) and

(2) The fingerprint region (1500 – 667 cm^{-1})

1.28.1 Examination of the functional group region

(A) 3600 – 3200 cm^{-1}: The appearance of bands in this region shows the presence of —OH, —NH_2 and —NH group in the compound. The ≡C—H stretching also shows a medium band near 3300 cm^{-1}.

(B) 3200 – 3000 cm^{-1}: Absorption due to ═C—H stretching and Ar—H stretching occurs in this region.

(C) 3000 – 2500 cm^{-1}: The absorption due to C—H stretching of CH_2 and CH_3 groups occurs in this region. A broad, moderately intense band between 3000 – 2500 cm^{-1} shows the presence of carboxylic acid dimers. Two weak bands at 2720 cm^{-1} and near 2820 cm^{-1} are most characteristic of C—H stretching in aldehydes.

(D) 2300 – 2100 cm^{-1}: In this region alkynes, cyanides, cyanates and isocyanates give absorption. The $-C\equiv C-$ stretching occurs between 2140 – 2100 cm^{-1}, $-C\equiv N$ stretching shows a variable band between 2260 – 2200 cm^{-1}. Isocyanates exhibit strong band near 2280 – 2250 cm^{-1}.

(E) **1900 – 1750 cm^{-1}:** Strong bands due to $C=O$ stretching in aldehydes, ketones, carboxylic acid, amides, esters and lactones occur in this region. Anhydrides show two strong bands in the region 1850 – 1740 cm^{-1}. Amides exibit doublet around 1700 cm^{-1}. It is important to note that the α, β-unsaturation in there compounds lowers the frequency of absorption by 15 – 40 cm^{-1}.

(F) **1750 – 1600 cm^{-1}:** Monosubstituted olefins absorb near 1640 cm^{-1}. Disubstituted trans olefins, tri and tetrasubstituted olefins absorb near 1670 cm^{-1}. Disubstituted *cis* olefins and vinylidenne olefins absorb near 1650 cm^{-1}. Saturated aliphatic ketones show a band at 1700-1720 cm^{-1}.

(G) **1650 – 1515 cm^{-1}:** Primary and secondary amides and a few lactams display bands in the region 1650 – 1515 cm^{-1}.

1.28.2 Fingerprint region: It is not possible for any two different compounds (except enantiomers) to have exactly the same IR spectrum. Therefore, the IR spectrum of a compound is called its **Fingerprint.** The region between 1500 – 667 cm^{-1} is called fingerpoint region because every compound has unique absorption pattern in this region, just as every person has unique fingerprints. The fingerprint region contains many absorption bands caused by bending vibrations as well as absorption bands caused by $C-C$, $C-O$ and $C-N$ stretching vibrations. Since the number of bending vibrations [$(2n-5$ or $(2n-4)$] in a molecule is much greater than its stretching vibrations $(n-1)$, the fingerprint region is rich in absorption bands and shoulders. Thus the superimposability of IR band of the spectra of any two different compounds becomes impossible in this region. However, similar compounds may show very similar spectra above 1500 cm^{-1}.

Fingerprint region is subdivided into following regions :

(A) **1500 – 1350 cm^{-1}:** The appearance of a doublet near 1380 (m) and 1365 (c) cm^{-1} shows the presence of tertiary butyl group in the compound. *Gem* dimethyl shows a medium band at 1380 cm^{-1}.

(B) **1300 – 1000 cm^{-1}:** All classes of compounds, *viz*., alcohols, ethers, esters, lactones, acid anhydrides show strong bands in this region due to $C-O$ stretching. Esters exibit two strong bands between 1380 – 1050 cm^{-1}. Primary alcohols absorb near 1350 – 1260 cm^{-1}. Appearance of bands between 1150 – 1070 cm^{-1} due to $C-O$ stretching in $C-O-C$ group is characteristic of ethers. Phenols absorb at 1200 cm^{-1}.

(C) **Below 1000 cm^{-1}:** This region is very useful in identifying the type of subtitution on the aromatic ring (i). A strong band 770 – 730 cm^{-1} shows monosubstitution.

(ii) *Ortho* and *para* disubstituted compounds show one band each. (735-700 cm^{-1} for *ortho* and 800-860 cm^{-1} for *para*)

(iii) *Meta* disubstituted compounds are recognised by two medium bands in the region 850 – 710 cm^{-1}.

1.29. Characteristic Group Frequencies of Some Organic Molecules

A common feature of infrared spectra of many organic compounds is that certain groups like CH_3, CH_2, CH, CHO, CO, etc. have, more or less, the same frequencies irrespective of molecular environment. This shows that these groups must vibrate independently from the rest of the molecules. On comparing the spectra of related series of compounds one may associate certain vibrational bands with particular group in the molecule. The presence or absence of certain bands in the spectrum may be used to indicate whether a particular functional group is present or absent in the molecule. These frequencies are known as group frequencies and have proved to be very useful for structural identification.

Chemists have studied thousands of IR spectra and have correlated the absorption frequencies to the functional groups. Correlation given in Table 1.9 provides summaries of this information.

TABLE 1.9 ***IR Absorption Frequencies of Functional Groups***

Compound type	Bond Type	Wavenumber (intensity*)
Alkanes	$-\overset{\vert}{\underset{\vert}{C}}-H$	2850-2970 (*s*) 1340-1470 (*s*)
	$-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-$	1100-1300 (*w*)
	$-\overset{\vert}{\underset{\vert}{C}}-D$	2200 (*s*)
	$=\overset{\vert}{C}-H$	3010-3095 (*m*) 675-995 (*s*)
Alkanes		
	$C=C$	1610-1680 (*v*)
Alkynes	$\equiv C-H$	3200-3300 (*s*)
	$-C\equiv C-$	2100-2260 (*v*)
Aromatic	Ar—H	3010-3100 (*m*) 690-900 (*s*)
Aromatic ring	$C=C$	1500-1600 (*v*)
Monohydric alcohols and phenols	—O—H	3590-3650 (*v*)
Hydrogen bonded alcohols and phenols	—O—H	3200-3600 (*v*)
Monomeric carboxylic acids	—O—H	3500-3650 (*m*)
Hydrogen bonded carboxylic acids	—O—H	2500-3000 (*v*, broad)
Amines and amides	$-\underset{\vert}{N}-H$	3300-3500 (*m*)
	—N	1180-1360 (*s*)
Nitriles	$-C\equiv N$	2210-2280 (*s*)
Alcohols, esters and carboxylic acids	$-\overset{\vert}{\underset{\vert}{C}}-O-$	1050-1300 (*s*)
Aldehydes, ketones carboxylic acids and esters	$C=O$	1690-1760 (*s*)
Nitro compounds	$-NO_2$	1500-1570 (*s*) 1300-1370 (*s*)

*Abbreviations: *s* = strong, *m* = medium, *w* = weak, *v* = variable

The region from $1400-4000\ \text{cm}^{-1}$ is specially useful for identification of various functional groups. This region shows absorption arising from streething modes.

The region from $1400\ \text{cm}^{-1}$ to $600\ \text{cm}^{-1}$ is often quite complex because both streething and bending modes give rise to absorption in this region. In this region correlation of an individual band with a specific functional group usually cannot be made with accuracy. However, each organic compound has its own unique absorption in this region. This part of the spectrum is, therefore, called the fingerprint region. Although $1500-4000\ \text{cm}^{-1}$ region may appear same for the similar compounds, the fingerprint region must be different for them.

In the following sections, we will discuss the characteristic IR absorption of compounds containing C—C and C—H bonds and a few functional groups.

1.29.1 Carbon-carbon and carbon-hydrogen bonds: Bonds between sp^3 carbon atoms give rise to weak absorption bands in the IR spectrum. These absorption bands are not very useful for structure identification. Bonds between sp^2 carbons (C═C) often exibit characteristic absorption around 1600–1700 cm^{-1}. Aromatic C═C bands show absorption at slightly lower frequencies (1450–1600 cm^{-1}). Bonds between sp carbon atoms (C≡C) show weak but extremely characteristic absorption at 2100 – 2250 cm^{-1}, a region of the spectrum where most other groups show no absorption.

Almost all organic compounds contain CH bonds. Absorption due to this bond is seen at about 2800 – 3300 cm^{-1}. The CH stretching peaks are often useful in determining the hybridisation of the carbon atom.

sp^3	C—H	2800 – 3000 cm^{-1}
sp^2	C—H	3000 – 3100 cm^{-1}
sp	C—H	≈ 3300 cm^{-1}

1.29.2 *Gem*-Dimethyl Groups: The *gem*-dimethyl grouping often exhibits distinctive absorption in the C—H bending region. This group shows a strong doublet, with peaks of almost equal intensity at 1385 – 1380 cm^{-1} and at 1370 – 1365 cm^{-1}. (Fig. 1.22). Doublets are observed for *gem*-dimethyl groups because of interaction between the in-phase and out-of-phase symmetrical CH_3 bending of the two methyl groups attached to a common carbon atom. This absorption is quite characteristic of compounds containing gem-dimethyl group.

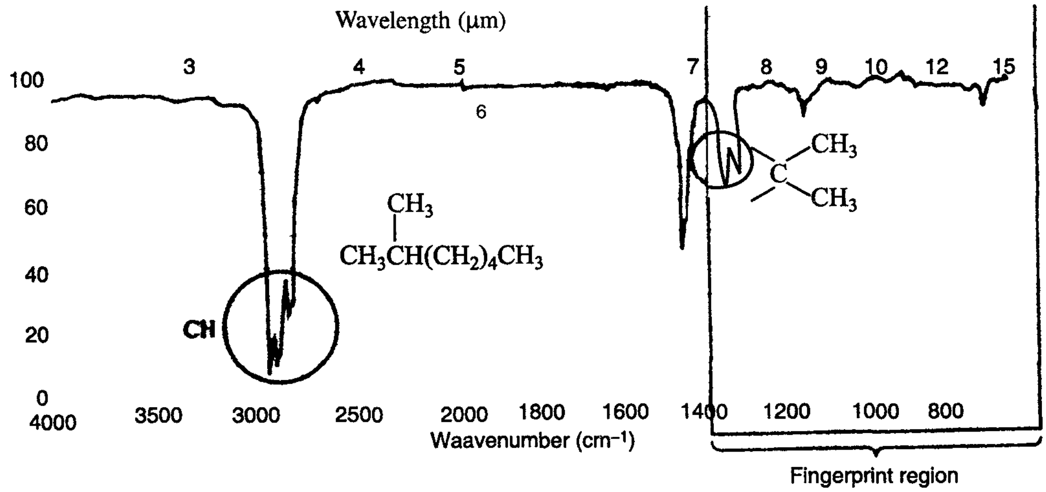
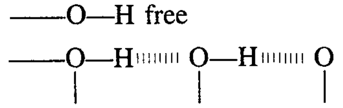


Fig. 1.22

1.29.3 Alcohols and Phenols: The characteristic bands observed in the spectra of alcohols and phenols result from O—H stretching and C—O stretching.



——O—H free

——O—H⋯⋯O—H⋯⋯O

Hydrogen bonding increases bond distance of O—H and thus decreases bond strength. Decrease in bond strength means decrease in ν_{max}.

1.29.4 O—H Stretching vibrations: The free hydroxyl group of alcohols and phenols absorbs strongly in the 3650 – 3584 cm^{-1} region. Sharp free hydroxyl bands are observed only in the vapour phase or in very dilute solution in non-polar solvents. Intermolecular hydrogen bonding increases as the concentration of the solution increases, and additional bands start to appear at lower frequencies 3550 – 3200 cm^{-1}, at the expense of the free hydroxyl group (Fig. 1.23a and 1.23b). The effect of concentration on intermolecular hydrogen bonding is illustrated in Fig. 1.23 in which the absorption bands in the O—H stretching region are shown for two different concentrations of cyclohexylcarbinol in CCl_4. The band at 3623 cm^{-1} (Fig. 1.23a) results from the monomer, whereas broad absorption near 3333 cm^{-1} (Fig. 1.23b) arises from polymeric structures.

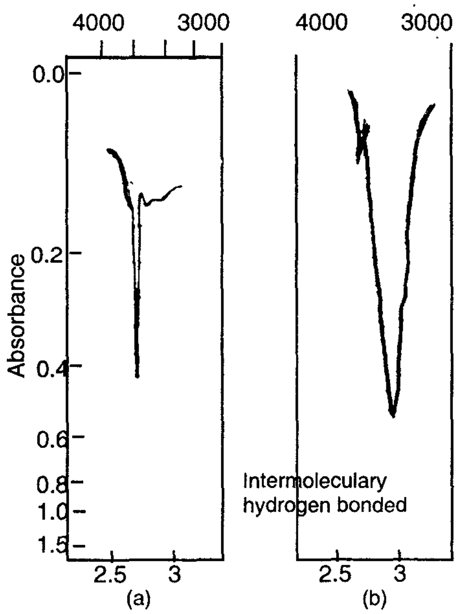


Fig. 1.23 Infrared spectrum of the O—H stretching region of cyclohexylcarbinol in CCl_4, (a) 0.03 *M* (0.406 mm cell). (b) 1.00 *M* (0.014 mm cell)

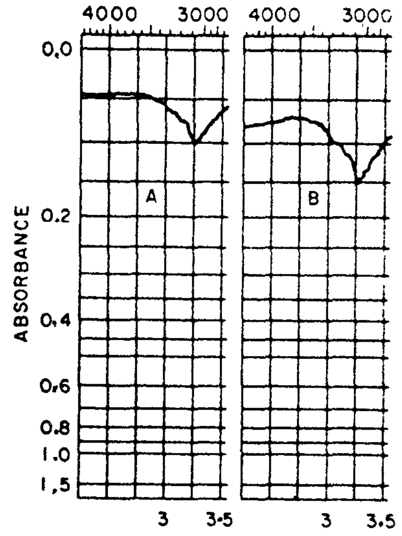
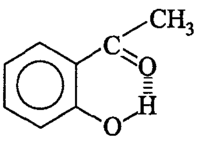


Fig. 1.24 A portion of the infrared spectra of *o*-hydroxyacetophenone. A. 0.03 *M*, cell thickness: 0.41 mm. B. 1.0 *M*, cell thickness: 0.015 mm

In the case of *o*-hydroxyacetophenone, due to intramolecular hydrogen bonding O—H frequency appears at 3077 cm^{-1} as broad, shallow peak and this value is independent of concentration (Fig. 1.24). In contrast, *p*-hydroxyacetophenone shows a sharp free hydroxyl peak at 3600 cm^{-1} in dilute CCl_4, but a neat sample of the compound shows a broad band at 3100 cm^{-1} due to intermolecular hydrogen bonding involving the —OH group.

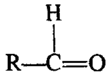
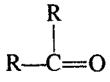
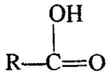
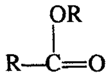


In structures such as 2, 6-di-*t*-butylphenol, in which steric hindrance prevents intermolecular hydrogen bonding absorption band at 3600 cm^{-1} is obtained in IR. The C—O stretching vibrations in alcohols and phenols produce a strong band in the 1200 – 1000 cm^{-1}. These bands are of little diagnostic value.

1.29.5 Ethers: Ethers have a C—O—C stretching band that falls in the fingerprint region at 1050 – 1260 cm^{-1}. Because oxygen is electronegative, the stretching causes a large change in bond moment, therefore C—O absorption is usually strong.

1.29.6 Carbonyl compounds: One of the most distinctive bands in an IR spectrum is the one arising from the carbonyl strecthing mode. This is a strong peak observed in the region between 1640 and 1820 cm^{-1}. The carbonyl group is a part of many functional groups. The exact position of the carbonyl absorption, the positions of other absorption bands in the IR spectrum, and other spectral techniques may be needed to identify the functional group. The positions of carbonyl group absorption for different compounds are given in Table 1.10.

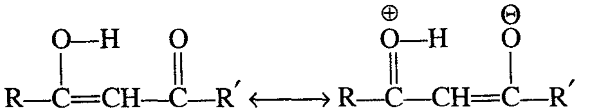
TABLE 1.10 **Stretching vibrations for some C═O group**

Compound		ν_{max} in cm^{-1}
 $\mathrm{R{-}\overset{H}{\overset{\mid}{C}}{=}O}$	Aldehydes	1720-1740
 $\mathrm{R{-}\overset{R}{\overset{\mid}{C}}{=}O}$	Ketones	1705-1750
 $\mathrm{R{-}\overset{OH}{\overset{\mid}{C}}{=}O}$	Acids	1700-1725
 $\mathrm{R{-}\overset{OR}{\overset{\mid}{C}}{=}O}$	Esters	1735-1750
	Amides	1630-1700
	Acid halides	1750-1815

Within the range, the (1640 – 1820 cm^{-1}) exact position of the C═O stretching band is dependent on the following factors : (i) the physical state, (ii) electronic and mass effects of the neighbouring substitutents, (iii) conjugation, and (iv) hydrogen bonding.

Conjugation of C═C bond results in delocalisation of the π electrons of both groups (C═C and C═O). Delocalisation of the electrons of the C═O group reduces its double bond character thereby causing absorption at lower wavenumbers. Conjugation with an olefinic or phenyl group causes absorption in the 1685 – 1666 cm^{-1} region. Additional conjugation may cause a slight further reduction in frequency.

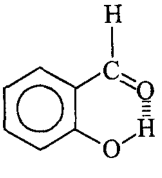
β-Diketones usually exist as mixtures of tautomeric keto and enol forms. The enolic form does not show the normal absorption of conjugated ketones. Instead, a broad band appears in the 1640 – 1580 cm^{-1} region, many times more intense than normal carbonyl absorption. The intense and displaced absorption results from the intramolecular hydrogen bonding, the bonded structure is stablised by resonance.



$$\mathrm{R{-}\overset{O{-}H}{\overset{\mid}{C}}{=}CH{-}\overset{O}{\overset{\|}{C}}{-}R'} \longleftrightarrow \mathrm{R{-}\overset{\oplus}{\overset{O{-}H}{\overset{\|}{C}}}{-}CH{=}\overset{\ominus}{\overset{O}{\overset{\mid}{C}}}{-}R'}$$

Aldehydes C═O stretching vibrations

The carbonyl groups of aldehydes absorb at slighty higher frequencies than those of the corresponding methyl ketones. Aliphatic aldehydes absorb near 1740 – 1720 cm^{-1}. Aldehydic carbonyl absorption responds to structural changes in the same manner as ketones. Electronegative substitution on α-carbon atom increases the frequency of carbonyl absorption. Acetaldehyde absorbs at 1730 cm^{-1} trichloroacetaldehyde absorbs at 1768 cm^{-1}. Conjugation reduces the frequency of carbonyl absorption. α, β-unsaturated acetaldehyde and benzaldehydes absorb in the region 1710 – 1685 cm^{-1}. Intramolecular hydrogen bonding, as in salicylaldehyde, shifts the absorption (1666 cm^{-1} in salicylaldehyde) to lower wavenumbers.



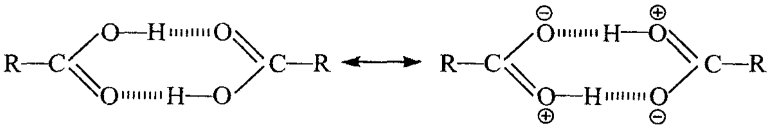
C—H stretching vibrations

Aldehydes show aldehydic C—H stretching absorption in the 2830 – 2695 cm^{-1} region. Some aromatic aldehydes with strong electronegative groups in the *ortho* position may give aldehydic C—H streching band as high as 2900 cm^{-1}. This absorption is not present in ketones.

(vii) Carboxylic Acids: Carboxylic acids exhibit typical C=O absorption and also show a very distinctive O—H band.

O—H stretching vibrations

In liquid and solid phase, carboxylic acids exist as a dimer due to strong intermolecular hydrogen bonding.



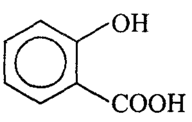
Carboxylic acid dimer display very broad intense O—H stretching absorption in the region 3300 - 2500 cm^{-1}.

Other structures with strong hydrogen bonding such as β-diketones (enol form) also absorb in the region 3300 – 2500 cm^{-1}, but the absorption is usually less intense.

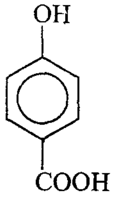
C=O stretching vibrations

Carboxylic acid dimers display C=O streching absorption in the region 1720 – 1705 cm^{-1}.

Intramolecular hydrogen bonding reduces the frequency of the carbonyl stretching absorption to a greater degree than does intermolecular hydrogen bonding. For example:



ν_{max} C=O 1665 cm^{-1}



ν_{max} C=O 1680 cm^{-1}

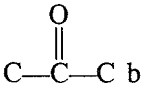
α, β-Unsaturated and aryl conjugated acids show absorption for the dimer in the 1710 – 1680 cm^{-1} region. Extension of conjugation beyond the α, β position results in very little change.

Substitution in α-position with electronegative groups, such as the halogens, brings about a slight increase in the C=O absorption frequency (10 to 20 cm^{-1}).

As mentioned earlier, carbonyl groups of ketones generally absorb in the region 1640 - 1820 cm^{-1}. The position of absorption is also senstitive to ring size. The carbonyl groups of cyclohexanones generally absorb at the same position as the carbonyl groups of saturated aliphatic ketones (hexanone ν_{max} 1715 cm^{-1})

TABLE 1.11

Compound	ν_{max} in cm^{-1}
Cyclohexanone	1700 cm^{-1}
Cyclopentanone	1740 cm^{-1}
Cyclobutanone	1800 cm^{-1}

Table 1.11 shows that highest $C{=}O$ frequencies arise in the strained cylobutanone and this can be explained in terms of bond angle strain; the  $C-\overset{\overset{O}{\|}}{C}-C$ bond angle is reduced below the normal 120° leading to increased *s* character in the $C{=}O$ bond. The $C{=}O$ bond is shortened and therefore strengthened and so $\nu_{C=O}$ is increased. If the bond is pushed forward above 120°, the opposite effect operates, and for this reason di-*tert*-butyl ketone has very low $\nu_{C=O}$ (1697 cm^{-1}). Thus ring strain in cyclic compound causes a relatively large shift to higher frequency. This phenomenon provides a remarkably reliable test of ring size, distinguising clearly between four, five and larger membered ring ketones lactones and lactams.

When the carbonyl group of an ester is present in a five membered ring, absorption owing to stretching vibration occurs at about 30 cm^{-1} higher wavenumber. Thus saturated γ-lactones absorb higher wavenumber than δ lactones.

VERY SHORT ANSWER QUESTIONS

1. Arrange the folowing electromagnetic radiations in order of their decreasing frequencies: Radio waves, UV, visible, IR, X-rays, γ-rays, microwaves.
2. Arrange the following electronic transitions in order of their decreasing energy:

$$\pi \longrightarrow \pi^*,\ n \longrightarrow \pi^*,\ \sigma \longrightarrow \sigma^*,\ n \longrightarrow \sigma^*$$

3. What happens when an organic compound is subjected to UV irradiation ?
4. Can a molecule undergo more than one electronic excitation ?
5. The UV spectrum of acetone shows absorption maxima at 166, 189 and 279 nm. What type of electronic transition is responsible for each of these ?
6. What type of electronic transitions are possible for each of the following compounds:
   (a) Cyclopentene (b) Cyclohexane (c) Dimethyl ether (d) CH_3OH (e) CH_3CHO. List then in order of increasing energy (Δ*E*).
7. Are all the molecules of a substance that are exposed to a specific radiation excited ?
8. Arrange the following compounds in order of their increasing λ_{max} in the UV region:

$$\underset{(A)}{C_6H_5-CH{=}CH-C_6H_5} \quad \underset{(B)}{CH_2{=}CH-CH{=}CH_2} \quad \underset{(C)}{CH_2{=}CH-CH_2-CH{=}CH_2}$$

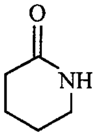
9. Can ionisation of a molecule or breaking of a σ bond occur in the UV region ?
10. Which of the following compounds would be suitable as a solvent for recording UV spectra of organic compounds ?
    (a) Ethanol (b) Cyclohexane (c) Benzene (d) Diethyl ether (e) Acetone
11. What happens to the excited molecules when radiation is cut off ?
12. There are antibonding orbitals σ^* and π^* but not n^*. Explain why ?
13. What is essential condition for a molecule to be IR active, *i.e.*, to absorb IR radiation ?
14. What is main difference between UV and IR spectroscopy ?
15. Why ethanol is a good solvent for UV but not for IR spectroscopy ?
16. Give the wavelength, frequencey and energy changes involved in the normal IR region of the spectrum.
17. Which of the following molecules are IR active and which are IR inactive ?

$$O_2, H_2, HCl, Cl_2, H_2O, CH_2{=}CH_2, N_2$$

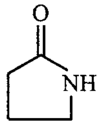
18. What is effect of hybridisation of carbon on the stretching frequency of C—H bonds ?
19. Arrange the following bonds in order of their decreasing vibrational frequencies:

C—Cl, C—C, C—Br, C—H, C—I, C—O

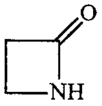
20. Which of the following has the highest $\nu_{C=O}$ frequency ?



(I)



(II)



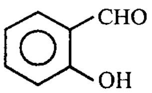
(III)

21. Which of the following has the highest carbonyl stretching frequency:

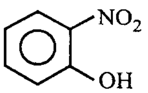
CH_3COOH, CH_3COCH_3, CH_3CHO, CH_3COCl, CH_3CONH_2

22. In which of the following the O—H absorption band will be shifted to a higher frequency on dilution with CCl_4 ?

CH_3OH,



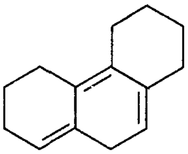
,



23. Arrange the following in order of their decreasing stretching frequencies: O—H, C—C, O—D.

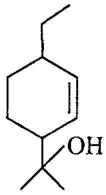
PROBLEMS WITH SOLUTIONS

1. Determine the concentration of a solution of the compound which is kept in 1.00 cm cell having absorbance 1.18, absorption maximum 235 nm and ε_{max} is 1.26×10^4 L mole^{-1} cm^{-1}.
2. Determine the molar absorptivity of the solution which is kept in 1.00 cm cell having concentration 7.6×10^{-5} mole/litre and absorption coefficient is 0.96.
3. Why is absorbance the function of the concentration of the solution and length of the cell ?
4. Hydrogenation of the triene, (*X*) with one equivalent of hydrogen gives three isomeric dienes (A), (B) and (C). What will be the structures of (A), (B) and (C) and how could the expected λ_{max} values distinguish among these isomers ?



(X)

5. Dehydration of compound (A), can give three isomeric conjugated dienes. What will be structures of these dienes? Give a mechanism to account for the formation of these dienes. Can these isomers be distinguished by UV?

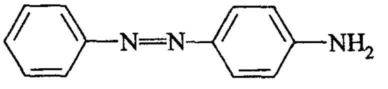


(A)

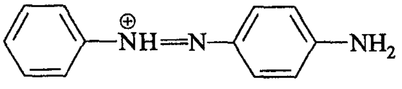
6. The UV spectrum of acetone in hexane shows two absorption maxima ($\lambda_{max} = 279$ nm, $\varepsilon_{max} = 15$ and

$\lambda_{max} = 189$ nm $\varepsilon_{max} = 900$). Identify the electronic transitions associated with each λ_{max} and identify the more intense band. Name the bands of the transitions.

7. The IR spectrum of ethyl benzoate differs from that of methyl phenylacetate in many ways. Guess at least one point of difference and give reason for the same.
8. The O—H stretching value does not change with dilution in the case of 1, 2-ethanediol in carbon tetrachloride but that increases in the case of ethanol on dilution. Explain.
9. Which of the following has a higher UV absorption maximum (λ_{max}) and why?

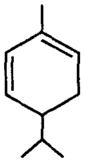


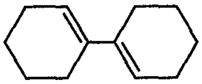
(I)

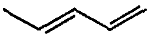


(II)

10. Arrange the following compounds in order of their increasing wavelength of UV absorption maxima (λ_{max})
    (a) Ethylene (b) Naphthalene (c) Anthracene (d) 1, 3-Butadiene
11. How will you distingnish between each of the following pairs of compounds by UV spectroscopy:
    (a) 1, 3-pentadiene and 1, 4-pentadiene
    (b) benzene and anthracene
    (c) 1, 3-hexadiene and 1, 3-cyclohexadiene.
12. Write down the electronic transitions reponsible for the following bands in the UV spectrum of acrolein:
    (i) λ_{max} 210 nm (ε_{max} 11,500)
    (ii) λ_{max} 315 nm (ε_{max} 14)
13. An organic compound can have one of the following structures:

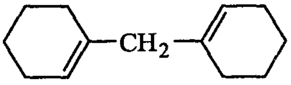

(a)


(b)

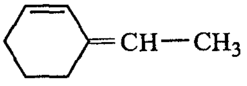

(c)

The λ_{max} of the compound is 236 nm. Which is the most likely structure of the compound? Explain your choice.

14. Which of the following compounds is expected to have higher value of λ_{max} and why?

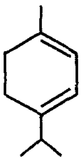


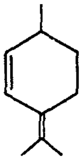
(a)



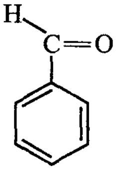
(b)

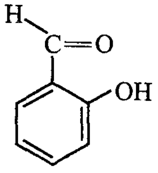
15. The following dienes have the experimental λ_{max} 243 and 265 nm in ethanol. Giving reasons, correlate the λ_{max} values of the structures (a) and (b):

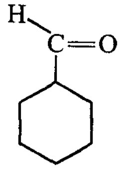

(a)


(b)

16. Giving reasons arrange the following compounds in order of decreasing frequency of carbonyl absorption in their IR spectra:


(a)


(b)


(c)

17. How will you distingnish *o*-hydroxybenzaldehyde (salicylaldehyde) and *m*-hydroxybenzaldehyde with the help of IR spectroscopy?
18. How will you distingnish maleic acid and fumaric acid by their IR spectra?
19. Deduce the structures of isomeric compounds (A) and (B) having molecular formula C_3H_6O and the following IR spectral data:

(A) 1710 cm^{-1} (B) ~ 3300 cm^{-1} and 1640 cm^{-1}

20. Giving reasons arrange the following in increasing order of their ν_{O-H} frequency:

Ethanol, trichloroacetic acid, acetic acid and chloroacetic acid.

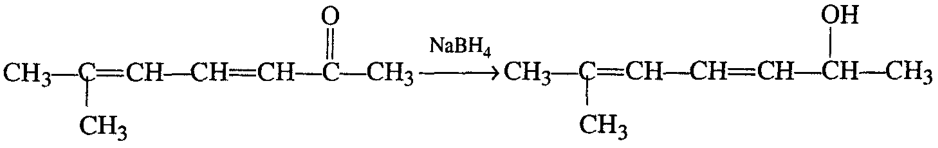
21. Indicate which of the following vibrations will be IR active or inactive?

Molecule		Mode of vibration
(i)	$CH_2=CH_2$	C=C stretching
(ii)	$CH_2=CH_2$	C—H stretching
(iii)	N_2	N≡N strectching
(iv)	SO_2	Symmetrical stretcling
(v)	CO_2	Symmetrical stretching
(vi)	$CH_3—CH_3$	C—C stretching

22. Explain why $\nu_{C=O}$ frequency for *m*-chlorobenzoic acid is higher than that for *p*-chlorobenzoic acid?
23. Draw conclusions about the relationship of λ_{max} to the structure of the absorbing molecule from the following λ_{max} values (in nm):

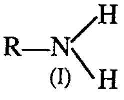
Ethylene (170); 1, 3-butadine (217); 2, 3-dimethyl-1, 3-butadiene (226); 1,3-cyclohexadiene (256); 1, 3, 5-hexatriene (274).

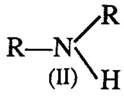
24. How will you distinguish the following pairs of compounds with the help of their IR spectra:
   (i) *o*-Hydroxybenzoic acid and *p*-hydroxybenzoic acid.
   (ii) Acetone and propionaldehyde.
25. How can UV and IR spectroscopy be used to determine the completion of the following reaction:



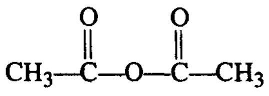
$$CH_3-\underset{CH_3}{\underset{|}{C}}=CH-CH=CH-\overset{O}{\overset{||}{C}}-CH_3 \xrightarrow{NaBH_4} CH_3-\underset{CH_3}{\underset{|}{C}}=CH-CH=CH-\overset{OH}{\overset{|}{C}}H-CH_3$$

26. How would you distingnish between the N—H stretching absorption of a primary amine (I) and a secondary amine (II).


(I)

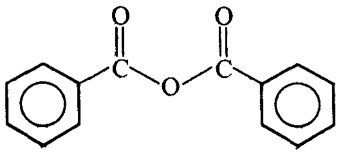

(II)

27. Assign each of the following pairs of absorptions to one of the given compounds:
1865, 1780; 1815, 1750; 1775, 1720 cm^{-1}

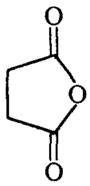


$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3$

(I)

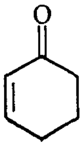


II

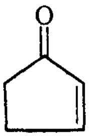


III

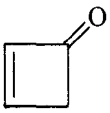
28. Which of the following compounds would give the lowest value of $\nu_{C=O}$ absorption frequency:



I

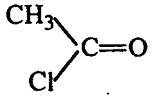


II

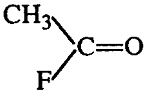


III

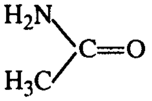
29. Arrange the following compounds in decreasing order of $\nu_{C=O}$ frequency:



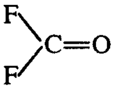
(a)



(b)

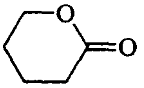


(c)

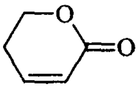


(d)

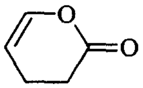
30. The carbonyl stretching absorptions for the following lactones are 1720, 1745 and 1760 cm^{-1}. Match the absorption with the appropriate structure and give reason for your choice.



I



II



III

31. Give suitable explanation for the observation that the ν_{O-H} band appears near 3570 cm^{-1} whereas the ν_{O-D} band near 2630 cm^{-1}.

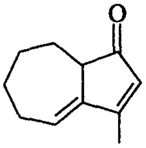
32. Using IR spectroscopy, how will you distingnish the following isomeric compounds:
(a) $CH_3-CH_2-C\equiv CH$ and $CH_3C\equiv CCH_3$
(b) CH_3CH_2OH and CH_3OCH_3
(c) $(CH_3)_3N$ and $CH_3CH_2NHCH_3$

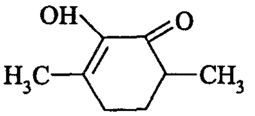
PROBLEMS FOR SELF ASSESSMENT

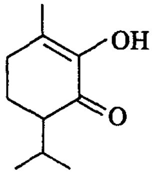
1. Most primary amides show two absorptions in the N—H stretching region (about 3300 cm^{-1}). Consider the resonance structures of amide and suggest a reason for this double peak.
2. Describe the characteristic IR absorption frequencies that would allow you to distinguish between the following pairs of compounds.
   (a) Cyclohexanol and cyclohexanone
   (b) Pentanol and 2-pentanone
   (c) Benzaldehyde and 1-cyclohexene carboaldehyde
   (d) 2, 3-Dimethyl-2-butene and 2, 3-dimethyl-1-butene

(e) Butanoic acid and 3-hydroxybutanal
(f) Butanamide and 3-pentanone

3. Calculate absorption maxima (λ_{max}) for the following compounds:

(a)


(b)


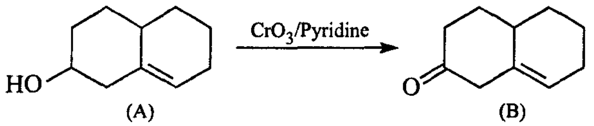
(c)


4. The absorption maximum of methyl chloride (λ_{max} = 173 nm) is less than that of methyl iodide (λ_{max} = 259 nm). Explain why?

5. The position of absorption of acetone in different solvents (279 nm in hexane, 272 nm in ethanol and 265 nm in water) is different. Explain why?

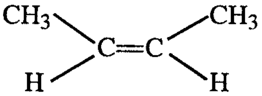
6. The band due to $n \longrightarrow \pi^*$ transition in amine disappears in acid solution. Explain why?

7. How would you use IR spectroscopy to tell if preparation of (B) from (A) by oxidation method is complete?



(A) (B)

8. Distinguish the following pairs of compounds by IR :
(a) $CH_3—CH_2—C{\equiv}CH$ and $CH_3—C{\equiv}C—CH_3$
(b) $CH_2{=}CH—OCH_3$ and $CH_3—CH_2—CHO$

(c)

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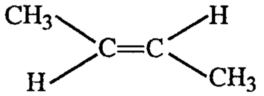
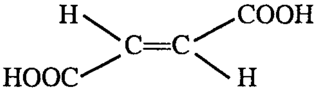


(d)

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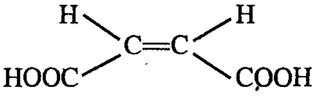
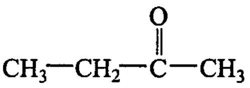
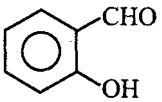


9. How will you distinguish each of the following pairs of compounds by their infrared spectra :

(a) $CH_3CH_2CH_2COOH$ and $CH_3CH_2COOCH_3$ (b)

$CH_3—CH_2—\overset{O}{\overset{\|}{C}}—CH_3$ and $CH_3—CH_2COOCH_3$

(c)

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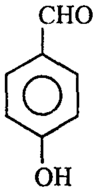
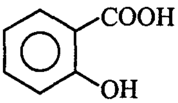


(d)

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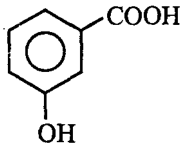
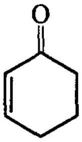


(e)

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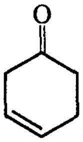
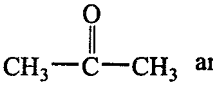
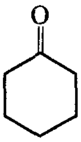
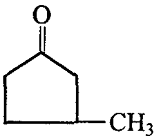


(f)

$CH_3—\overset{O}{\overset{\|}{C}}—CH_3$ and CH_3CH_2CHO

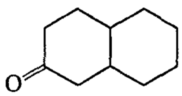
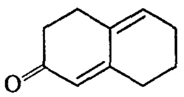
(g)

and


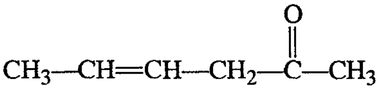
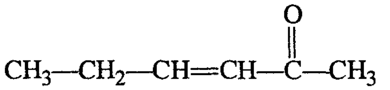
10. Using the Hooke's law, calculate $\bar{\nu}$ for each of the following stretching vibrations. As force constants use 5×10^5, 10×10^5, 15×10^5 dynes cm^{-1} for single, double and triple bonds, respectively.

(a) O—H (b) O—D (c) C=O (d) C≡C (e) C—O

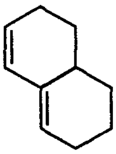
11. Indicate how UV spectroscopy can be used to distinguish between the members of each of the following pairs of compounds?

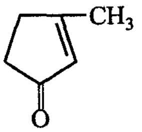
(a) $CH_2{=}CH{-}CH_2{-}CH{=}CH_2$ and $CH_3{-}CH{=}CH{-}CH{=}CH_2$

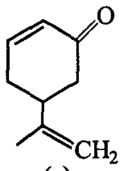
(b)  and 

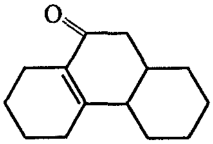
(c)  $CH_3{-}CH{=}CH{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}CH_3$ and  $CH_3{-}CH_2{-}CH{=}CH{-}\overset{O}{\overset{\|}{C}}{-}CH_3$

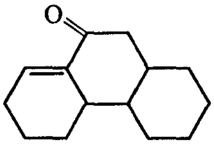
12. Using Woodward-Fieser rules, predict the λ_{max} of each of the following chromophores:


(a)

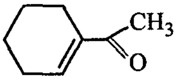

(b)

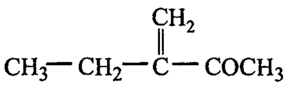

(c)

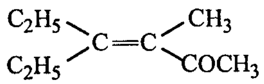

(d)

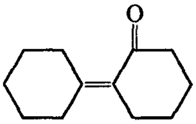

(e)

13. The labels fell off of four flasks of ketones known to have the structures given below. Measurement of the UV spectra of the contents of the four flasks gave λ_{max} at 221, 233, 249 and 258 nm. Assign the λ_{max} values to the appropriate structures.

(a) 

(b)  $CH_3{-}CH_2{-}\overset{CH_2}{\overset{\|}{C}}{-}COCH_3$

(c) 

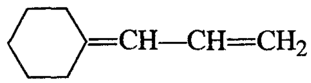
(d) 

14. Compounds (A) to (D) have λ_{max} values of 177, 217, 232 and 277 nm. Match the λ_{max} with the appropriate structure.

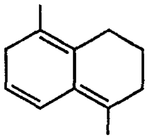
(a) $CH_2{=}CH{-}CH{=}CH{-}CH{=}CH{-}CH{=}CH_2$

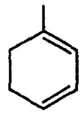
(b) $CH_3{-}CH_2{-}CH{=}CH_2$

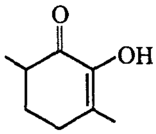
(c) $CH_2{=}CH{-}CH{=}CH_2$

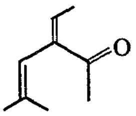
(d) 

15. Using Woodward-Fieser rules, calculate the λ_{max} of ethanolic solution of each of the following:

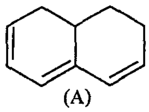

I


II


III

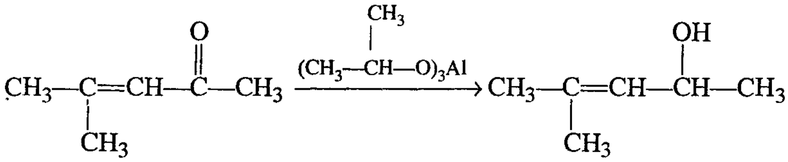

IV

16. Hydrogenation of one mole of the triene (A) with one mole of H_2 gives three isomeric dienes having molecular formula $C_{10}H_{14}$. Show how the expected λ_{max} values could distinguish these isomers :



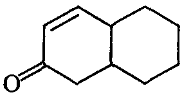
(A)

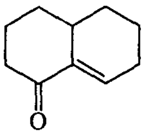
17. How can IR and UV spectroscopy be used to determine when the following reaction is completed?

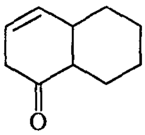


$$CH_3-\underset{CH_3}{\underset{|}{C}}=CH-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{(CH_3-\overset{CH_3}{\overset{|}{C}H}-O)_3Al} CH_3-\underset{CH_3}{\underset{|}{C}}=CH-\overset{OH}{\overset{|}{C}H}-CH_3$$

18. An organic compound can have one of the following structures :



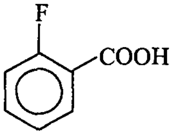
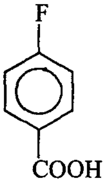




The λ_{max} of the compound is 242 nm. Which is the most likely structure of the compound. Give reason for your choice.

19. Using IR spectroscopy, how will you distinguish between the members of each of the following pairs of compounds?

(a) RNH_2 and $RCONH_2$

(b)  and 

(c) CH_3CH_2CHO and $CH_2{=}CH{-}CH_2OH$

20. Identify the geometrical isomers of stilbene from their UV absorption λ_{max} 294 and 274 nm.

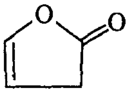
21. Explain why 1, 3-butadiene exhibits a higher value of λ_{max} for $\pi \rightarrow \pi^*$ transition than that of ethylene.

22. Give the equation for calculating stretching frequency a diatomic molecule.

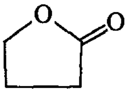
23. Concentrated solutions of ethanol and 1, 2-glycol in CCl_4 exhibit broad ν_{O-H} band near 3350 cm^{-1} in their IR spectra. On dilution with CCl_4, the spectrum of 1, 2-glycol does not change but that of ethanol exhibits a sharp band at 3600 cm^{-1} in addition to the broad band at 3350 cm^{-1}. Explain the observation.

[**Hint:** Intermolecular hydrogen bonding is concentration dependent whereas intramolecular hydrogen bonding is not affected on dilution].

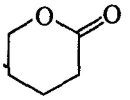
24. Giving suitable reason, arrange the following lactones in order of their decreasing $\nu_{C=O}$ frequency:



(a)

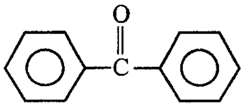


(b)

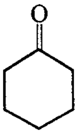


(c)

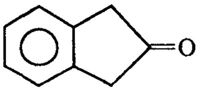
25. Giving suitable reason, arrange the following ketones in decreasing order of their $\nu_{C=O}$ frequency:



(a)

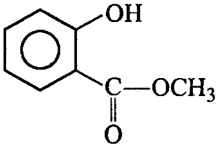


(b)



(c)

26. Write notes on :
    (a) Fingerprint region (b) Fermi resonance (c) Stretching and bending vibrations
27. Calculate the fundamental vibrations of the following molecules:
    (a) Methane (b) Ethanol (c) Acetylene (d) Benzene (e) Carbon dioxide
28. Giving reasons arrange the following compounds in order of increasing wavenumber of carbonyl absorption in their IR spectra :
    (a) Acetophenone, *p*-nitroacetophenone and *p*-aminoacetophenone
    (b) Cyclobutanone, cyclopentanone and cyclohexanone
29. Deduce the structure of isomeric compounds (A) and (B) having molecular formula C_3H_6O and the following IR spectral data :
    (A) 1710 cm^{-1}
    (B) ~ 3300cm^{-1} and 1640 cm^{-1}
30. Ethyl acetate shows $\nu_{C=O}$ absorption at 1735 cm^{-1} whereas phenyl acetate at 1770 cm^{-1}. Explain.
31. Arrange the following compounds in order of increasing absorption frequency of their carbonyl groups. Give reason for your answer.
    C_6H_5CHO, CH_3CHO, CH_3COCl and CH_3COCH_3
32. Explain how conjugation increases λ_{max} of UV absorption.
33. The IR spectrum of methyl salicylate (I) gives the following peaks at :
    3460, 3010, 1710, 1595 and 1450 cm^{-1}



(I)

Attribute these peaks to the following groups :
(i) —O—H (ii) $>C=O$ (iii) C—H benzene ring

34. Assign the following IR absorption bands to a particular carboxylic acid derivative in each case :
    (i) 1715–1750 cm^{-1} (ii) 1750–1815 cm^{-1}
    (iii) 1630–1690 cm^{-1} (iv) 1740–1790 and 1800–1850 (two bands)
35. Match the following IR absorption bands with the appropriate given compounds :
    IR absorption bands :
    (i) 1715 cm^{-1} (ii) 1730 cm^{-1} (iii) 1740 cm^{-1} (iv) 1680 cm^{-1}
    Given compounds :
    (a) $CH_3COOC_2H_5$ (b) CH_3CHO (c) CH_3CONH_2 (d) CH_3COCH_3

ANSWERS TO VERY SHORT ANSWER QUESTIONS

1. γ-rays > X-rays > UV > visible > IR > microwaves > radiowaves
2. $\sigma \longrightarrow \sigma^* > n \longrightarrow \sigma^* > \pi \longrightarrow \pi^* > n \longrightarrow \pi^*$

3. Electrons are excited from bonding molecular orbitals (σ or π) or non-bonding molecular (n) to uncoupied antibonding molecular orbital (σ^* or π^*).
4. Yes, Depending on the wavelength of light used, a molecule can undergo all the possible electronic excitations. For example, formaldehyde ($H_2C{=}O$) can undergo $n \longrightarrow \pi^*$, $\pi \longrightarrow \pi^*$, $\sigma \longrightarrow \pi^*$, $n \longrightarrow \sigma^*$, $\pi \longrightarrow \sigma^*$ and $\sigma \longrightarrow \sigma^*$.
5. 166 nm: $n \longrightarrow \sigma^*$; 189 nm : $\pi \longrightarrow \pi^*$; 729 nm : $n \longrightarrow \pi^*$.
6. (a) $\pi \longrightarrow \pi^*$; $\sigma \longrightarrow \pi^*$, $\pi \longrightarrow \sigma^*$, $\sigma \longrightarrow \sigma^*$ (b) $\sigma \longrightarrow \sigma^*$,
   (c) $n \longrightarrow \sigma^*$, $\sigma \longrightarrow \sigma^*$ (d) $n \longrightarrow \sigma^*$, $\sigma \longrightarrow \sigma^*$
   (e) $n \longrightarrow \pi^*$, $\pi \longrightarrow \pi^*$; $\sigma \longrightarrow \pi^*$, $n \longrightarrow \sigma^*$, $\sigma \longrightarrow \sigma^*$
7. No. absorption of radiation is a random event. Relatively few molecules may be excited.
8. (C) < (B) < (A)
9. The energy required for ionisation is provided by only in the high frequency X-ray and γ-ray regions of the electromagnetic spectrum. However, bonds with low bond dissociation energies, *i.e.*, bonds between atoms which contain at least one lone pair of electrons such as $-\ddot{\underset{\cdot\cdot}{O}}-\ddot{\underset{\cdot\cdot}{O}}-$, $:\ddot{\underset{\cdot\cdot}{X}}-\ddot{\underset{\cdot\cdot}{X}}:$, $-\ddot{\underset{\cdot\cdot}{O}}-\ddot{\underset{\cdot\cdot}{X}}$, $-\ddot{\underset{|}{N}}-\ddot{\underset{\cdot\cdot}{X}}$: may break.
10. Ethanol, cyclohexane and diethyl ether do not absorb above 200 nm, hence can be use as solvents. In contrast, benzene and acetone absorb above 200 nm, hence cannot be used as solvents.
11. The excited molecules give off energy and return to the ground state and the process is called deactivation. Alternatively, the excited molecules may undergo a chemical change depending on their nature. For example, alkenes may undergo *cis-trans* isomerisation.
12. Since n (non-bonding) electrons are not engaged in bonding, there are no corresponding antibonding (n^*) orbitals.
13. In order to be IR active, *i.e.*, to absorb IR radiation, the vibrational mode of the molecule must be accompained by a dipole moment change.
14. Absorption of UV and visible light involves electronic transitions while absorption of IR radiations involves vibrational transition, *i.e.*, the molecule to excited from lower vibrational level to higher vibrational level.
15. Ethanol does not absorb in the UV region but absorbs strongly in the IR region (3200–3600 cm^{-1}).
16. Wavelength range: 2·5–15·0 μm; frequency range: 4000–667 cm^{-1}; the corresponding energy range : 2–10 Kcal/mole.
17. Molecular vibrations of homoatomic molecules O_2, H_2, Cl_2 and N_2 are not accompained by any dipole moment change, hence are IR inactive, *i.e.*, they do not absorb in the IR region whereas the molecular vibrations of HCl, H_2O and $CH_2{=}CH_2$ are accompained by a dipole moment change, hence they are IR active, *i.e.*, they absorb in the IR region.
18. As the hybridisation changes from $sp^3 \longrightarrow sp^2 \longrightarrow sp$, force constant of the bond increases, hence the stretching frequency of the C—H bond increases.

$$\begin{array}{ccc} sp^3 & sp^2 & sp \\ \mathrm{C{-}H} & \mathrm{{=}C{-}H} & \mathrm{{\equiv}C{-}H} \\ 2840\text{–}3000\ cm^{-1} & 3000\text{–}3100\ cm^{-1} & 3300\text{–}3310\ cm^{-1} \end{array}$$

19. C—H > C—C > C—O > C—Cl > C—Br > C—I
20. (III)

21. CH_3COCl

22. CH_3OH

23. O—H > O—D > C—C

SOLUTIONS OF PROBLEMS

1.

$$\varepsilon_{max} = \frac{A}{Cl}$$

$$\therefore \quad C = \frac{A}{\varepsilon_{max}\, l}$$

$$A = 1.18$$

$$\varepsilon_{max} = 1.26 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$$

$$C = \frac{1.18}{1.26 \times 10^4 \times 1.0}$$

$$= 9.37 \times 10^{-5} \text{ M}$$

2.

$$\varepsilon_{max} = \frac{A}{Cl}$$

where

$$A = 0.96$$

$$C = 7.6 \times 10^{-5} \text{ mole/litre}$$

$$l = 1.00 \text{ cm}$$

Therefore,

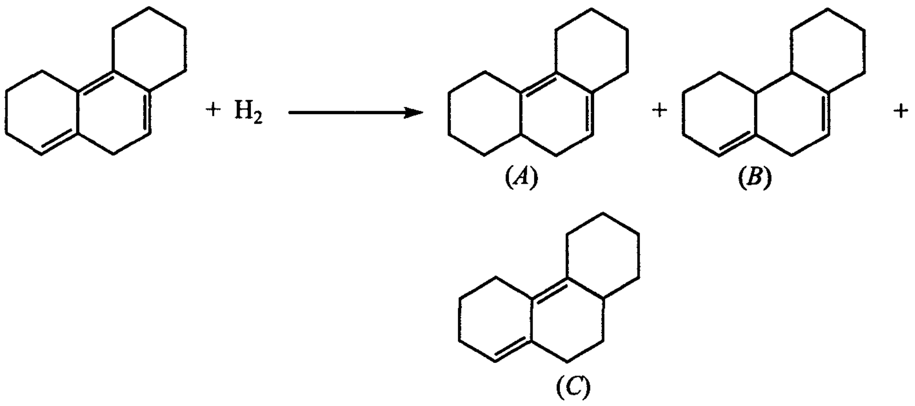
$$\varepsilon_{max} = \frac{0.96}{7.6 \times 10^{-5} \times 1}$$

$$= 1.26 \times 10^4$$

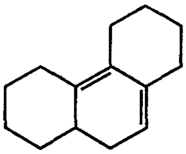
$$= 1.26 \times 10^4 \text{ litre/mol cm}^{-1}$$

3. Absorption in fact is the function of the number of excited molecules. Thus greater the number of excited molecules, the larger is A. The higher the concentration of the solution, the more molecules are exposed to and excited by the radiation. Similarly, the longer the path, the greater is the chance for the radiation to impact and excite molecules.

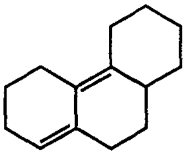
4. (X) on partial hydrogenation will give three isomers whose structures are as follows :



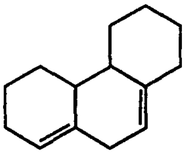
Expected λ_{max} of these three isomers can be calculated from Woodward-Feiser rules as follows:



(A)



(C)

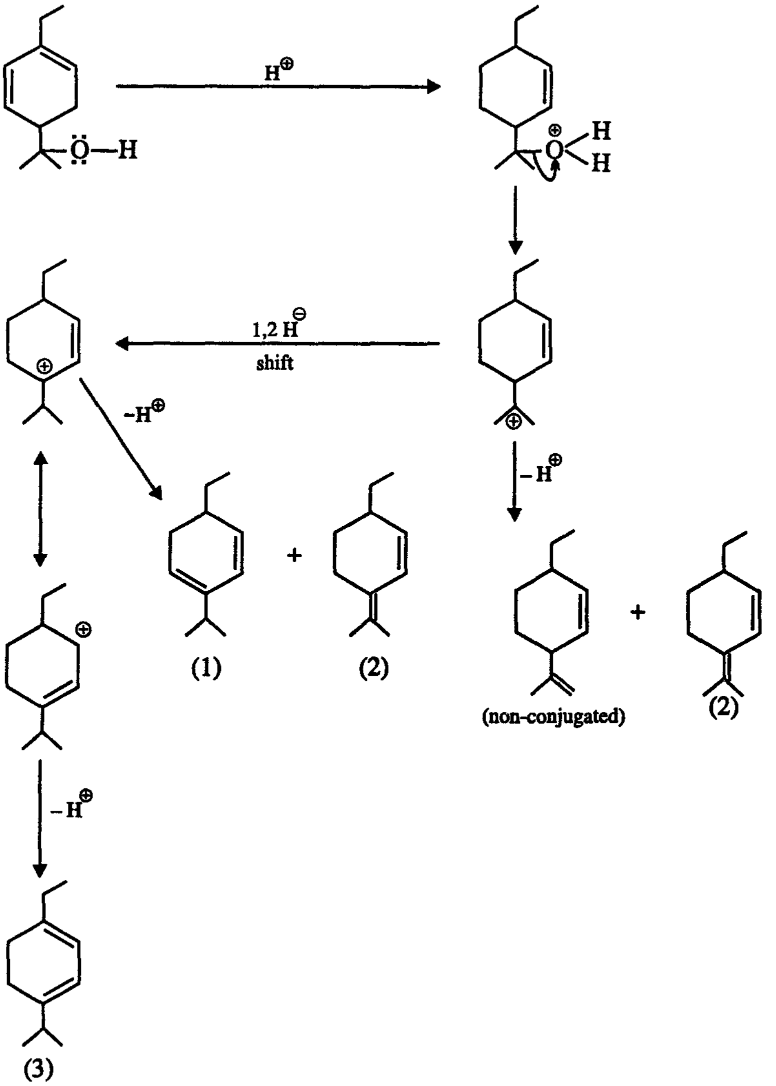


(B)

	(A)	(C)	(B)
Base value	253	214	< 200 (non-conjugated)
Ring residues (five)	= 25	five = 25	—
Exocyclic bonds (three)	= 15	two = 10	—
	λ_{max} = 293 nm	249 nm	< 200 nm

Thus the compound having λ_{max} (< 200 nm) will be (B), the compound having λ_{max} 240 nm will be (C) and the compound having λ_{max} 293 nm will be (A). Therefore, these three isomers can be distingenished by their UV spectra.

5. Dehydration of (A) takes place as shown on page 70:



Expected absorption maxima of these three isomers, namely (1), (2) and (3) can be calculated by using Wood ward-Feiser rule as follows:

Compound	1	2	3
Base value	253	214	253
Ring residues	15 (5 × 3)	20 (5 × 4)	20 (5 × 4)
Exocyclic bonds	—	5 (one)	—
λ_{max}	268 nm	239 nm	273 nm

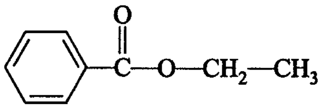
Difference in values of 5 nm or more makes the isomers distinguishable experimentally. Thus the three conjugated dienes can be distinguished by UV.

6. Usual electronic transitions that occur in ketones are $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$. $n \rightarrow \pi^*$ transition requires less energy than $\pi - \pi^*$ transition. We know that smaller energy is associated with longer wavelength of absorption. Hence $\lambda_{max} = 279$ nm, $\epsilon_{max} = 15$ is due to $n \rightarrow \pi^*$ transition and $\lambda_{max} = 170$ nm, $\epsilon_{max} = 900$ is for $\pi \rightarrow \pi^*$ transition.

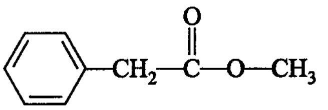
   ϵ_{max} determines the intensity of absorption. Higher ϵ_{max} means more intense is the absorption. Therefore, the $\pi \rightarrow \pi^*$ transition ($\epsilon_{max} = 900$) is more intense than the $n \rightarrow \pi^*$ transition ($\epsilon_{max} = 15$).

   $\pi \rightarrow \pi^*$ transitions give rise to K-bands where there is conjugation in the system. Acetone does not possess conjugated structure. So the peaks that arise from the $\pi \rightarrow \pi^*$ transition should not be designated as K-band. $n \rightarrow \pi^*$ transition produces R-band. Hence $\lambda_{max} = 229$ nm is for the R-band.

7.



Ethyl benzoate



Methyl phenylacetate

In ethyl benzoate C═O group is in conjugation to benzene ring but in methyl phenylacetate this group is not in conjugation to benzene ring. As a consequence the C═O group of ethyl benzoate acquires a single bond character and thus the C═O stretching frequency will occur at a wavenumber lower than that in methyl phenylacetate though they are isomeric compounds.

8. Ethane-1, 2-diol has intramolecular hydrogen bond but ethanol forms intermolecular hydrogen bonds. When a solution of ethane-1, 2-diol is diluted with carbon terachloride, intramolecular hydrogen bonds do not break and so the O—H stretching does not change with delution. In the case of ethanol, the intermolecular hydrogen bonds of the associated complex break with dilution. So in the dilute solution of ethanol in carbon tetrachloride, the O—H stretching occurs for the free —OH group. Thus O—H stretching frequency changes from hydrogen bonded to free —O—H on dilution.

9. We know that the longer the conjugated system, the higher is the value of λ_{max}. The compound I has a longer conjugated system than the II because in the II the protonation of nitrogen has removed one benzene ring from the conjugation with the ring containing the NH_2 group. Thus the compound I has a higher λ_{max} than compound II.

10. (a) < (d) < (b) < (c)

11. (a) 1, 4-Pentadiene is an unconjugated diene whereas 1, 3-pentadiene is a conjugated diene, thus the latter will have a higher λ_{max} than the former.

    (b) Anthracene has a longer conjugated system than benzene, thus anthracene will have a higher λ_{max} than benzene.

    (c) We know that cisoid dienes have a higher λ_{max} than transioid dienes. Acyclic dienes exist in more stable transoid form. Thus 1, 3-cyclohexadiene which can exist only in cisoid form will have a higher λ_{max} than 1, 3-hexadiene.

12. (i) The band at λ_{max} 210 nm (ϵ_{max} 11,500) is a band due to a higher energy allowed transition, and in acrolein it must be due to $\pi \rightarrow \pi^*$ transition.
(ii) The band at λ_{max} 315 nm is a band due to a lower energy transition. The ϵ_{max} 14 indicates that it is a forbidden transition.
Thus this band is due to $n \rightarrow \pi^*$ transition.

13. First of all calculate λ_{max} for each given compound.
The structure (a) is a homoannular diene with two ring residues and one alkyl substituent, hence its calculated $\lambda_{max} = 253 + 3 \times 5 = 268$ nm.
The structure (b) represents a heteroannular diene with four ring residues, hence its calculated $\lambda_{max} = 214 + 4 \times 5 = 234$ nm.
Since the given λ_{max} of the compounds is 236 nm, its most likely structure is (b) because the calculated λ_{max} (234 nm) for this structure is very close to the given value (236 nm).

14. The compound (a) is an unconjugated diene, hence it will have $\lambda_{max} < 200$ nm. The compound (b) is a heteroannular conjugated diene with two ring residues, one alkyl substituent and one exocyclic double bond, hence it is expected to have λ_{max} $(214 + 2 \times 5 + 5 + 5) = 234$ nm, *i.e.*, higher than that of compound (a).

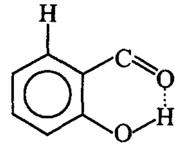
15. The calculated λ_{max} for :

	(a)	(b)
Base value	253 nm	214 nm
Ring residues	$(2 \times 5) = 10$ nm	$(2 \times 5) = 10$ nm
Alkyl substituent	$(2 \times 5) = 10$ nm	$(2 \times 5) = 10$ nm
Exocyclic double bond	—	one 5 nm
Total =	273 nm	239 nm

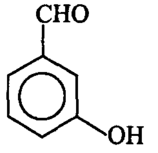
Thus the structure (b) is the diene having the experimental λ_{max} 243 nm because this value is in agreement with the calculated λ_{max} for (b). Similarly, the structure (a) is the diene having the experimental λ_{max} 265 nm.

16. The following is decreasing order of frequency of carbonyl absorption
(c) > (a) > (b)
Cyclohexane carboxaldehyde (a) is an unconjugated aldehyde and will absorb around 1730 cm^{-1}. Due to conjugation of C=O group with the double bonds of the benzene ring, the $\nu_{C=O}$ absorption of benzaldehyde (a) will be shifted to lower frequency ($\approx$ 1700 cm^{-1}). In salicylaldehyde the lowering is due to conjugation as well as intramolecular hydrogen bonding (chelation), thus the $\nu_{C=O}$ absorption frequency is further lowered ($\approx$ 1665 cm^{-1}).

17. In salicylaldehyde due to intramolecular hydrogen bonding, ν_{O-H} and $\nu_{C=O}$ bands are shifted to lower wavenumbers. Since it is intramolecular, change in concentration does not cause any shift in ν_{O-H} and $\nu_{C=O}$ bands. In the case of *m*-hydroxybenzallehyde also ν_{O-H} and $\nu_{C=O}$ bands occur at a lower wavenumber due to intermolecular hydrogen bonding. In this case ν_{O-H} and $\nu_{C=O}$ bands shift to higher wavenumbers on dilution with a nonpolar solvent.

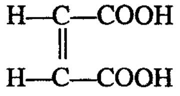


o-hydroxybenzaldehyde



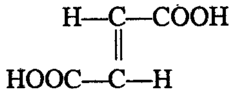
m-hydroxybenzaldehyde

18.



maleic acid

$\nu_{C=O}$ 1720 cm^{-1} (*s*)

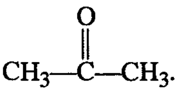


fumaric acid

$\nu_{C=O}$ 1680 cm^{-1} (*s*)

In maleic acid the bulky COOH groups are on the same side of double bond. Hence due to repulsive interaction the C=O group is forced out of the plane of C=C bond. Thus the conjugation is diminished resulting in the appearance of $\nu_{C=O}$ band at a higher frequency as compared to that in fumaric acid where the C=O group is in conjugation with the C=C bond.

19. The IR band at 1710 cm^{-1} is indicative of a C=O (ketonic) group. Thus the compound (*A*) is



$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$.

The band at ~ 3300 cm^{-1} is indicative of an —OH group, and a band at 1640 cm^{-1} shows the presence of a C=C. Thus the compound (*B*) is $CH_2{=}CH{-}CH_2OH$.

20. Due to strong —I effect of CCl_3 group, the ν_{O-H} frequency of Cl_3CCOOH will be lowest. Due to +I effect of ethyl group the ν_{O-H} frequency of ethanol will be highest. $ClCH_2$ group in chloroacetic acid has –I effect and CH_3 group in acetic acid has +I effect, hence ν_{O-H} of chloroacetic acid will be lower than that of acetic acid. Thus the increasing order of ν_{O-H} frequency is:
trichloroacetic acid < chloroacetic acid < acetic acid < ethanol

21. (i) Inactive (ii) Active (iii) Inactive (iv) Active (v) Inactive (vi) Inactive

22. Due to +M effect, Cl decreases the force constant of C=O bond from the *para* position but not from the *meta* position.

23. From the given λ_{max} values of various alkenes the following conclusions can be drawn:

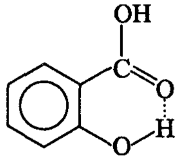
(i) Conjugated alkenes have higher λ_{max} than the unconjugated alkenes, thus ethylene has lower λ_{max} 170 nm than the other given alkenes which are conjugated.

(ii) Longer the conjugated system, the higher is the value of λ_{max}. For example, 1, 3, 5-hexatriene has λ_{max} 274 nm and the given conjugated dienes have λ_{max} 217-256 nm.

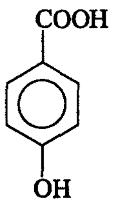
(iii) The presence of an alkyl substituent on a conjugated system increases the λ_{max} *e.g.*, 2, 3-dimethyl-1, 3-butadiene having two methyl substituents has a higher λ_{max} (226 nm) than 1, 3-butadiene λ_{max} 217 nm,

(iv) *cis* conjugated dienes (*e.g.*, 1, 3-cyclohexadiene (λ_{max} 256 nm) have a higher λ_{max} than the *trans* dienes (*e.g.*, 1, 3-butadiene, λ_{max} 217 nm and 2, 3-dimethyl-1, 3-butadiene, λ_{max} 226 nm). It should be noted that acyclic conjugated dienes exist in *transoid* form because it is less strained (more stable) than the cisoid form.

24. In *o*-hydroxybenzoic acid (salicylic acid), due to intramolecular hydrogen bonding ν_{O-H} and $\nu_{C=O}$ bands are shifted to lower wavenumbers. Since it is intramolecular, change in concentration does not cause any shift in ν_{O-H} and $\nu_{C=O}$ absorption bands. On the other hand, in the case of *p*-hydroxybenzoic acid ν_{O-H} and $\nu_{C=O}$ bands also occur at lower wavenumber due to



o-hydroxybenzoic acid



intermolecular hydrogen bondng, but in this case ν_{O-H} and $\nu_{C=O}$ bands shift to higher wavenumbers on dilution of the sample with a nonpolar solvent.

(ii) Acetone will show a strong $\nu_{C=O}$ band at ~ 1715 cm^{-1} whereas this band appears at ~ 1730 nm in propionaldehyde. In addition, propionaldehyde will show a doublet in the range 2700-2900 cm^{-1} due to aldehydic C—H stretching. This doublet generally appears in the case of aldehydes due to Fermi resonance.

25. After completion of the reaction λ_{max} of UV absorption will shift to a considerably lower value because the length of conjugation is decreased in the product as compared to the starting ketone. In the IR spectrum, the band due to $\nu_{C=O}$ will disappear and a new band due to ν_{O-H} will appear (in the region 3200-3600 cm^{-1}) after the completion of the reaction.

26. N—H stretching absorption of a primary amine would appear as a doublet, the two components corresponding to asymmetric and symmetric, modes. The separation is usually 100 cm^{-1}. N—H stretching absorption of a secondary amine would generally have a single absorption maximum.

27. I, 1815, 1750; II, 1775, 1720; III, 1865, 1780 cm^{-1}.

28. Due to decrease in strain, the $\nu_{C=O}$ frequency decreases as the size of the ring increases, hence the compound I would give the lowest value of $\nu_{C=O}$ frequency.

29. (d) > (b) > (a) > (c)

30. I, 1745; II, 1720 and III, 1760 cm^{-1}. The highest $\nu_{C=O}$ frequency of III is due to conjugation of the carbon-carbon double bond with the oxygen *p*-orbital which gives partial positive charge on the oxygen resulting in an increase in the double bond character of the carbonyl group and consequently an increase in $\nu_{C=O}$ frequency as compared to lactones I and II. The I is a saturated lactone whereas in II the C=O group is in conjugation with the carbon-carbon double bond which reduces the double bond character of C=O group in II and consequently its $\nu_{C=O}$ frequency is lowered as compared to that of the I.

31. According to Hooke's law (Section 1.26), the stretcing frequency of a bond increases as the reduced mass of the bonded atoms decreases. Since hydrogen has lesser atomic mass than deuterium, the ν_{O-H} frequency (near 3570 cm^{-1}) is higher than the ν_{O-D} frequency (near 2630 cm^{-1}).

32. (a) $CH_3CH_2C\equiv CH$ will show strong absorption bands at ~ 3300, 2100 and 625 cm^{-1} due to $\equiv$C—H stretching, C$\equiv$C stretching and $\equiv$C—H bending vibrations, respectively. All these bands will be absent in the IR spectrum of $CH_3C\equiv CCH_3$ because the symmetrical substitution makes the C$\equiv$C stretching IR inactive.

(b) CH_3CH_2OH will show absorption bands in the region 3200-3600 cm^{-1} due to ν_{O-H} of intermolecularly hydrogen bonded O—H group and at ~ 1050 cm^{-1} due to ν_{C-O}. These bands will be absent in the IR spectrum of CH_3OCH_3. It will show an absorption band around 1100 cm^{-1} due to C—O—C stretching.

(c) $CH_3CH_2NHCH_3$ will show a medium band in the region 3310-3550 cm^{-1} due to N—H stretching. This band will be absent in the IR spectum of $(CH_3)_3N$.

33. (i) —O—H, 3460 cm^{-1} (ii) $>$C=O, 1710 cm^{-1}
(iii) C—H benzene ring, 3010 cm^{-1}

34. (i) Esters (ii) Acid halides (iii) Amides (iv) Anhydrides

35. (i) (d); (ii) (b); (iii) (a); (iv) (c)

❑❑❑