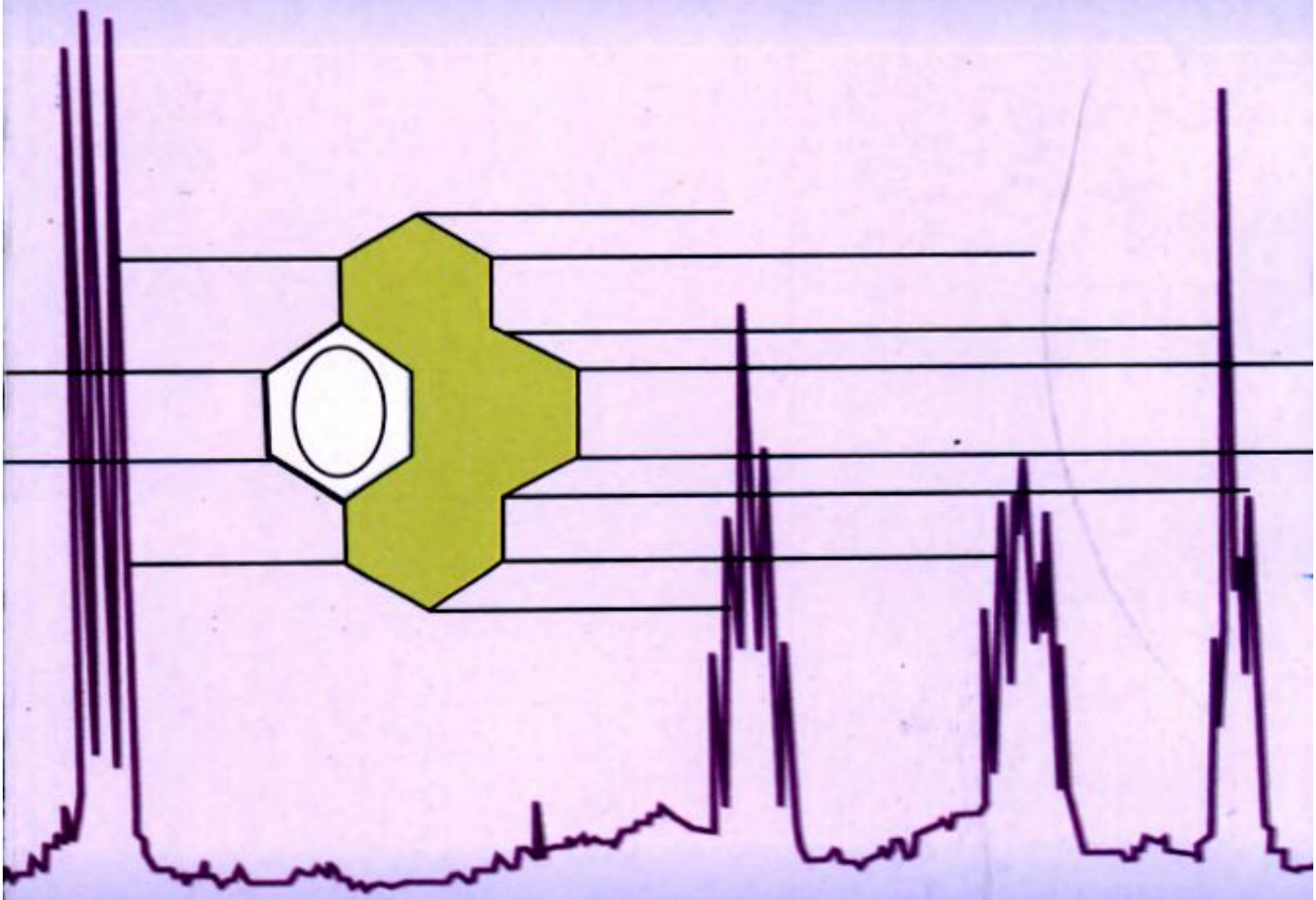
6th Edition

Spectroscopy of Organic Compounds



P. S. KALSI

NEW AGE INTERNATIONAL PUBLISHERS

Sixth Edition

Spectroscopy of Organic Compounds

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The outer cover diagram shows the alkane region of 220 MHz PMR spectrum of [10] paracyclophane where the methylene signals are shifted to higher field, the closer these are to the middle of the chain. The induced field is diamagnetic in the centre of the ring.
(*Courtesy* Professor Michael J. McGlinchey,
McMaster University, Hamilton)

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CHAPTER 1 ENERGY — THE ELECTROMAGNETIC SPECTRUM AND THE ABSORPTION SPECTRUM

THE NAMES of various forms of electromagnetic energy have now become familiar terms. The X-rays are used in medicine, the ultraviolet rays lead to sunburns and the radio and radar waves used in communication and visible light are all different forms of the same phenomenon, *i.e.*, electromagnetic radiation.

1.1 WAVE-LIKE PROPAGATION OF LIGHT

Each type of electromagnetic radiation, *i.e.*, radio waves, ultraviolet, infrared, visible, etc., has both the properties of a wave as well as a particle. Electromagnetic radiation can be described as a wave occurring simultaneously in electrical and magnetic fields and it can also be described as if it consisted of particles called quanta or photons. Wavelength (λ) or frequency (ν) are used to describe a wave. The distance between consecutive crests (or troughs) is the wavelength (Fig. 1.1). The wavelengths of electromagnetic radiation are expressed in either meters (m), millimeters, (1 mm = 10^{-3} m), micrometers (1 μm = 10^{-6} m) or nanometers (1 nm = 10^{-9} m).

In addition to its wavelength, the radiation may also be characterised by its frequency (ν), which is defined as the number of complete cycles per second (cps), also called Hertz (Hz after the German physicist H.R. Hertz,

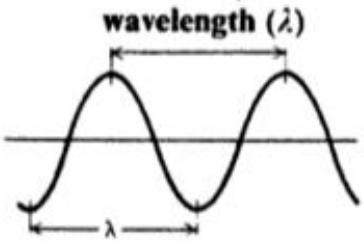
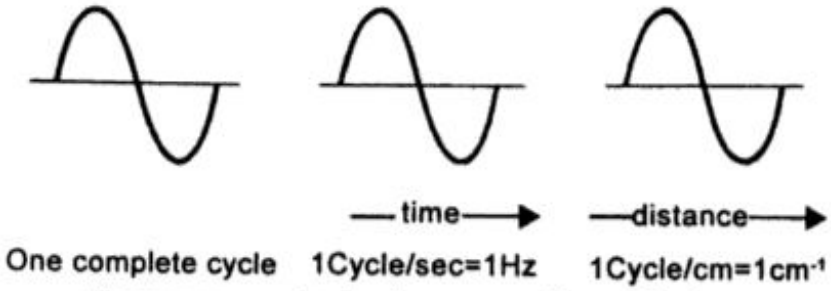


Fig. 1.1 : Wavelength of electromagnetic radiation



Frequency of electromagnetic radiation

Fig. 1.2

Fig. 1.2). By their definitions, wavelength and frequency are inversely proportional (eq. 1, Scheme 1.1).

Moreover, the energy of a quantum (a photon) of electromagnetic energy has direct relation with its frequency (eq. II), and conversely the energy of a photon is inversely proportional to the wavelength (eq. III, Scheme 1.1).

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

where ν = frequency in Hz.,
$c = 3 \times 10^{10}$ cm/sec (the speed of light), and
λ = wavelength in cm.

$$E = h\nu \qquad \text{(II)}$$

where h = Planck's constant
ν = the frequency, Hz.

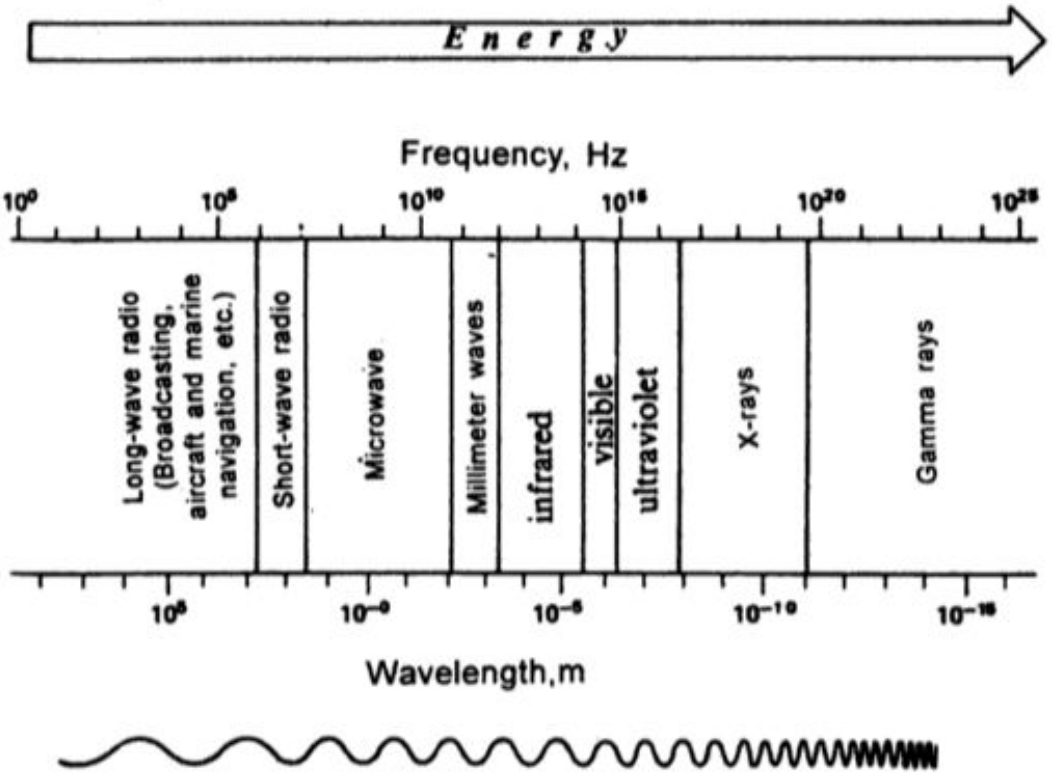
$$E = \frac{hc}{\lambda} \qquad \text{(III)}$$

Scheme 1.1

Thus, the higher the frequency of radiation the greater will be its energy (X-rays are more energetic than rays of visible light). The radiation of long wavelength has low energy and that of short wavelength has high energy, *i.e.*, a photon of ultraviolet light has more energy than a photon of visible light.

1.2 ELECTROMAGNETIC SPECTRUM

The spectrum of electromagnetic radiation is shown (Fig. 1.3 and Table 1.1). The wavelengths of visible light range from 400 nm (violet) to 750 nm (red) (1 nm = 10^{-9} m or 10^{-7} cm). The visible region however, is a very small part of the entire electromagnetic spectrum. Wavelengths



THE ELECTROMAGNETIC SPECTRUM
(The various categories overlap except in the case of visible light)

Fig. 1.3

Table 1.1 : *Regions of Electromagnetic Spectrum*

Region	Wavelength, λ	Frequency, ν, in Wave Numbers, cm^{-1}	Energy, kcal/mole (kJ/mole)
Cosmic rays	5×10^{-5} nm		
Gamma (γ) rays	10^{-3} — 0.14 nm		
X-rays	0.01 — 15 nm		
Far ultraviolet	15 — 200 nm	666,667 — 50,000	1,907 — 143 (7979.8 — 598.3)
Near ultraviolet	200 — 400 nm	50,000 — 20,000	143 — 71.5 (598.3 — 299.2)
Visible	400 — 800 nm	25,000 — 12,500	71.5 — 35.7 (299.2 — 149.4)
Near infrared	0.8 — 2.5 μ	12,500 — 400	35.7 — 11.4 (149.4 — 47.7)
Vibrational infrared	2.5 — 25 μ	4,000 — 400	11.4 — 1.14 (47.7 — 4.8)
Far infrared	0.025 — 0.5 mm	400 — 200	1.14 — 0.57 (4.8 — 2.4)
Microwave radar	0.5 — 300 mm	200 — 0.033	0.57 — 9.4×10^{-5} ($2.4 - 2.2 \times 10^{-4}$)
Various radio frequencies	0.3 — 10^{9} m		

slightly shorter than those of the visible region fall into the ultraviolet region, while slightly longer wavelengths fall into the infrared region. Radio waves on the other hand, with wavelengths measured in meters, are far removed from the visible portion of the spectrum.

1.3 SYMBOLS

Some of the common symbols used in spectroscopy are given in Table 1.2.

Table 1.2 : *Symbols Used in Spectroscopy*

Symbol	Definition
ν	frequency in Hz (cycles per second)
λ	wavelength
μm	micrometer, same as micron (μ), 10^{-6} m
nm	nanometer, same as millimicron (mμ), 10^{-9} m
Å	Angstrom, 10^{-10} m or 10^{-1} nm
cm^{-1}	wave number: frequency in reciprocal cm, or $1/\lambda$

The different regions of the electromagnetic spectrum from the region X-rays to those of micro and radio waves have been used to determine structures of atoms and molecules (Table 1.3).

Table 1.3 : *Summary of Spectroscopic Techniques in Organic Chemistry*

SPECTROSCOPY	Radiation absorbed	Effect on the molecule
Ultraviolet (uv)-visible	Uv-visible (λ = 200 — 750 nm)	changes in electronic energy levels within the molecule
Infrared (ir)	Infrared (λ = 2.5 — 16 μm)	changes in the vibrational and rotational movements of the molecule
Nuclear magnetic resonance (nmr)	Radio ν, 60 — 500 MHz	induces changes in the magnetic properties of certain atomic nuclei

1.4 ABSORPTION OF ELECTROMAGNETIC RADIATION BY ORGANIC MOLECULES

Quanta of defined energy bring about specific excitations

Molecules absorb electromagnetic radiation in discrete "packets", of energy or quanta, which are measurable by spectroscopy. Absorption occurs only when the radiation supplying exactly the right packet interacts with the compound ($\Delta E = h\nu$). In UV/vis spectroscopy, *e.g.*, absorption of light results in the promotion of an electron from the HOMO to the LUMO.

Organic molecules absorb radiation, in discrete "packets" of $\Delta E = h\nu$, which are also called quanta of energy (Fig. 1.4).

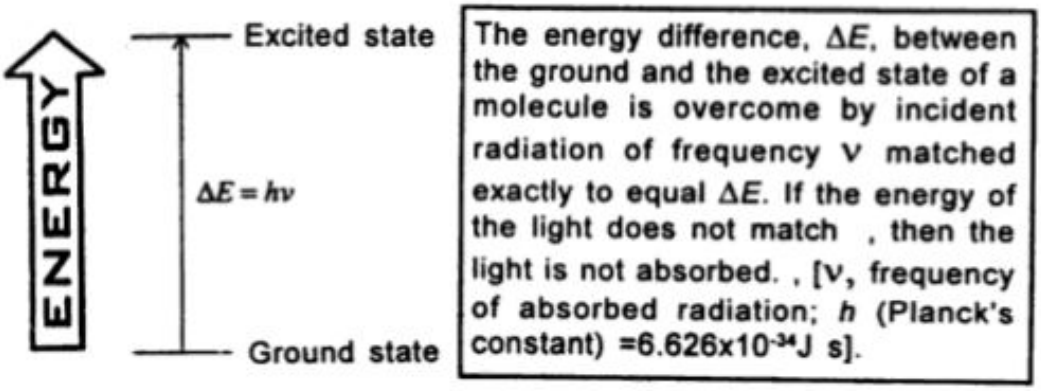


Fig. 1.4

The spectra of a compound, *i.e.*, the response of a substance subjected to radiation of various wavelengths, are among the most important physical properties of an organic compound. Spectroscopy, therefore, is a powerful tool in the hands of an organic chemist for structure determination. When, one considers a molecule, it is found that it is associated with several different types of motion. .The molecule as a whole rotates, the bonds undergo vibrations and even the electrons move. Each of these kinds of motion is quantised, *i.e.*, the molecule can exist only in distinct states which correspond to discrete energy contents. Thus absorption occurs only when radiation supplying exactly the right "packet" of energy impinges on the compounds under study. Each state is characterised by one or more quantum numbers and the energy difference between two such states, ΔE, is related to a light frequency ν by Planck's constant h (Fig. 1.4).

Spectroscopy is essentially a technical procedure by which the energy differences between the allowed states of a system are measured (mapped and recorded) by determining the frequencies of the corresponding light absorbed.

In short, the absorbed quanta of energy brings about different kinds of excitations in a molecule, and each requires its own distinctive energy, ΔE. That is, each type of excitation (motion) corresponds to the absorption of light in a different region of the electromagnetic spectrum. Ultraviolet and visible light brings about movement of valence shell electrons, typically from a filled bonding molecular orbital to an unfilled antibonding orbital. The energy needed for this transfer lies in the range 40-300 kcal mole^{-1}. Infrared radiation causes vibrational excitation of the molecular framework of a compound (ΔE is 2-10 kcal mole^{-1}); quanta of microwave radiation effect rotation around bonds ($\Delta E \sim 10^{-4}$ kcal mole^{-1}) and radio waves reorient nuclear spins ($\Delta E \sim 10^{-6}$ kcal mole^{-1}), a phenomenon which forms the basis of nuclear magnetic resonance spectroscopy.

1.5 A SPECTROPHOTOMETER — AN ABSORPTION SPECTRUM AND UNITS

An infrared or ultraviolet spectrophotometer, for example, allows light of a given frequency to pass through a sample and detects the amount of transmitted light (*i.e.*, not absorbed). The instrument compares the intensity of the transmitted light with that of the incident light. Automatic instruments gradually and continuously change the frequency, and an automatic recorder plots a graph of absorption versus frequency or wavelength, *i.e.*, a spectrum.

The spectrum of a compound thus represents a graph of either wavelength or frequency, continuously changing over a small portion of the electromagnetic spectrum versus either per cent transmission (%*T*) or absorbance (*A*). The per cent transmission is the per cent of the intensity of the original radiation which passes through the sample.

$$\%T = \frac{\text{Intensity}}{\text{Original intensity}} \times 100$$

When a compound does not absorb any radiation at a particular wavelength, the per cent transmission is 100 at that wavelength. Absorption of radiation at a particular wavelength leads to a decrease in the per cent transmission to appear in the spectrum as a dip, called a peak, or absorption band. Absorbance is a measure of the absorption of radiation by a sample:

$$A = \log\left(\frac{\text{Original intensity}}{\text{Intensity}}\right)$$

In this case, an increase in absorption appears as an increase (not a decrease) of the signal.

Because of the great difference in the wavelength of different regions it is not convenient to use the same units throughout to specify a particular position in the spectrum. In the uv (200-400 nm) and visible (400-800 nm) regions, the wavelengths are expressed as nanometers (nm, 1 nm = 10^{-9} m), in the infrared region (4000-600 cm^{-1}), the wavelengths are expressed in micrometers (μm, 1 μm = 10^{-6} m) or as the reciprocal wavelength in centimeters, $1/\lambda$ termed the wave number $\bar{\nu}$. In the radio frequency region (NMR) absolute frequencies are used rather than the wavenumbers. Thus a wavelength of 5 meters corresponds to a frequency of c/λ or 6×10^7 Hz (Hz = Hertz, defined as cycles per second) and can be written as 60 MHz.

1.6 ENERGY LEVELS AND ABSORPTION BANDS/ ABSORPTION LINES

A **spectrum** is simply a plot of the amount of light which is absorbed versus the frequency (or wavelength) of the light. The spectrum yields

information about the spacing of the energy levels of the molecule. Since these energy levels depend on the structure of the molecule, this information therefore, (with practice) is used to determine the structure of the compound.

In some types of spectroscopy there are only a few, well-separated energy levels. In these cases, only a very narrow range of wavelengths is absorbed each time the molecule is excited from its lowest-energy state to some higher-energy state, to give an absorption line for each of these transitions. The spectrum consists of a number of these absorption lines. In many cases, however, there are a number of energy sublevels in each energy state. In these cases a number of closely spaced wavelengths are ab-

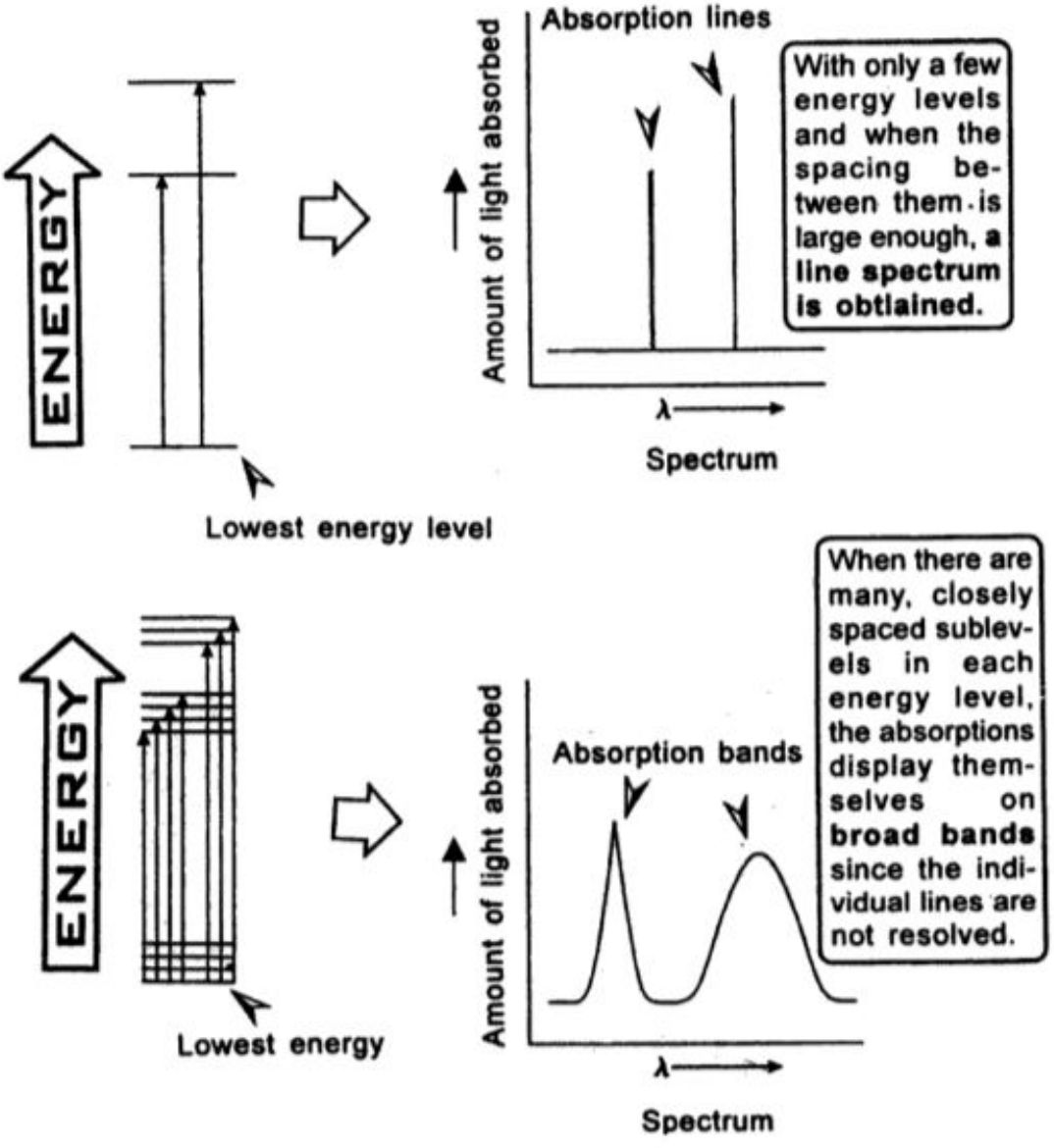


Fig. 1.5

sorbed. The lines are often so close together that they cannot be resolved and the absorption appears as a broad peak or band (Fig. 1.5).

FURTHER READING

E.F.H. Britlain, W.O. George and C.H.J. Wells, *Introduction to Molecular Spectroscopy*, Academic Press, London, 1970.

CHAPTER 2 ULTRAVIOLET (UV) AND VISIBLE SPECTROSCOPY

ULTRAVIOLET AND visible spectroscopy (electronic spectroscopy) is primarily used to measure the multiple bond or aromatic conjugation within molecules.

Electronic Spectroscopy

- Electronic spectroscopy involves the measurement of absorption of energy when electromagnetic radiation of the proper energy is provided. An electron is promoted from the HOMO to the LUMO
- As conjugation increases, the HOMO-LUMO gap decreases and the position of the $\pi \rightarrow \pi^*$ absorption shifts to longer wavelengths (lower energy)
- Simple aldehydes and ketones like simple alkenes do not have a $\pi \rightarrow \pi^*$ absorption in the region of uv spectrum readily accessible to most spectrometers.

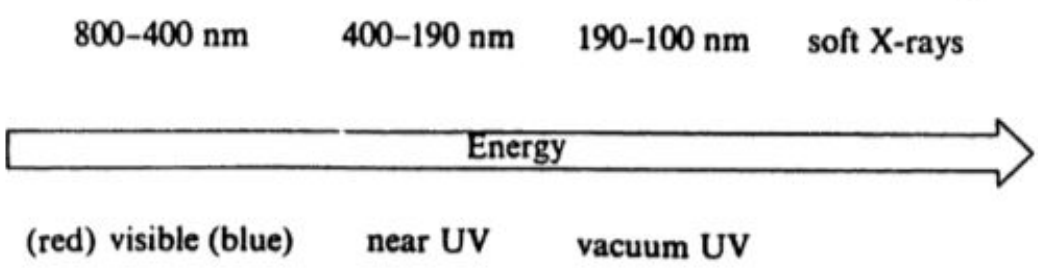
2.1 INTRODUCTION

Ultraviolet and Visible Spectroscopy

- UV/vis spectroscopy requires electromagnetic radiation of high energy.
- The visible region corresponds to 800-400 nm and ultraviolet region to 400-200 nm.

The uv region extends from 1000-4000 Å or 100-400 nanometers (nm). It should be noted that uv measurements are reported directly in nm, and the corresponding range in cm^{-1} is given in Table 1.1. The further subdivision of the uv into near uv and the far or vacuum uv is given in Scheme 2.1. The vacuum uv (below 200 nm) is so named because the molecules of air absorb radiation in this region, and thus this region is accessible only with special vacuum equipment.

On passing electromagnetic radiation in the ultraviolet and visible regions through a compound with multiple bonds, a portion of the radiation is normally absorbed by the compound. The amount of absorption depends on the wavelength of the radiation and the structure of the



Scheme 2.1

compound. The absorption of radiation is due to the subtraction of energy from the radiation beam when electrons in orbitals of lower energy are excited into orbitals of higher energy. Since this is an electron excitation phenomenon, uv is sometimes called electronic spectroscopy. Ultraviolet spectrum records the wavelength of an absorption maximum, *i.e.*, λ_{max} and the strength of the absorption, *i.e.*, molar absorptivity (extinction coefficient ε_{max}) as defined by the combined Beer-Lambert law:

$$\log (I_0/I) = \varepsilon.l.c \text{ or } \varepsilon = A/cl$$
(the combined Beer-Lambert law)

where:

I_0 is the intensity of the incident light (or the light intensity passing through a reference cell)

I is the light transmitted through the sample solution

$\log (I_0/I)$ is the absorbance (A) of the solution (optical density, OD)

c is the concentration of solute (in mol dm^{-3})

l is the path length of the sample (in cm)

ε is the molar absorptivity (extinction coefficient).

$E^{1\%}_{1\,cm}$ Absorption $[\log_{10} (I_0/I)]$ of a 1 per cent solution in a cell with a 1 cm path length. This is used in place of ε when the molecular weight of a compound is not known, or when a mixture is being examined.

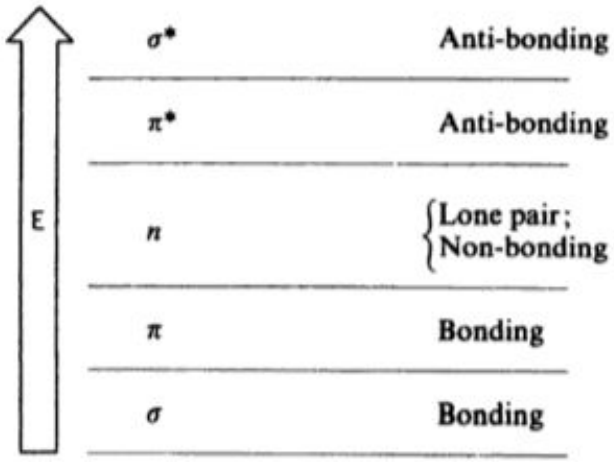
The molar absorptivity ε is constant for an organic compound at a given wavelength, and is reported as ε_{max} — the molar absorptivity at an absorption maximum. It may be mentioned that ε is not dimensionless, but is correctly expressed in units of 10^{-2} m^2 mol^{-1} but the units are, by convention, never expressed. Since values for ε_{max} can be very large, an alternative convention is to report its logarithm (to the base 10), $\log_{10} \varepsilon_{max}$.

In an infrared spectrum, one uses labels like strong (*s*) medium (*m*) and weak (*w*) to define the intensity of different bands, however, in discussing uv absorptions the value of ε is reported (to know, how intense the absorp-

tion is). Its value varies from 10^0–10^4 and one, considers the absorptions of the order of 10^4 very strong and those less than 10^3 as weak. The intensity of the peak is a measure of transition probability, and the peaks with low ε values often arise from transitions which are formally "forbidden".

2.2 ELECTRONIC TRANSITIONS DEFINITION OF SOME TERMS AND DESIGNATION OF UV ABSORPTION BANDS

On absorption of energy by a molecule in the ultraviolet region, changes are produced in the electronic energy of the molecule due to transitions of valence electrons in the molecule. These transitions consist of the excitation of an electron from an occupied molecular orbital, *e.g.*, a non-bonding *p* or bonding π-orbital to the next higher energy orbital, *i.e.*, an anti-bonding, π* or σ*, orbital. The anti-bonding orbital is designated by an asterisk. Thus, the promotion of an electron, *e.g.*, from a π-bonding orbital to an anti-bonding (π*) orbital is designated: $\pi \rightarrow \pi^*$ (pi to pi star). As shown, (Scheme 2.2), it is clear that $n \rightarrow \pi^*$ transition requires less energy compared to $\pi \rightarrow \pi^*$ or a $\sigma \rightarrow \sigma^*$ transition.

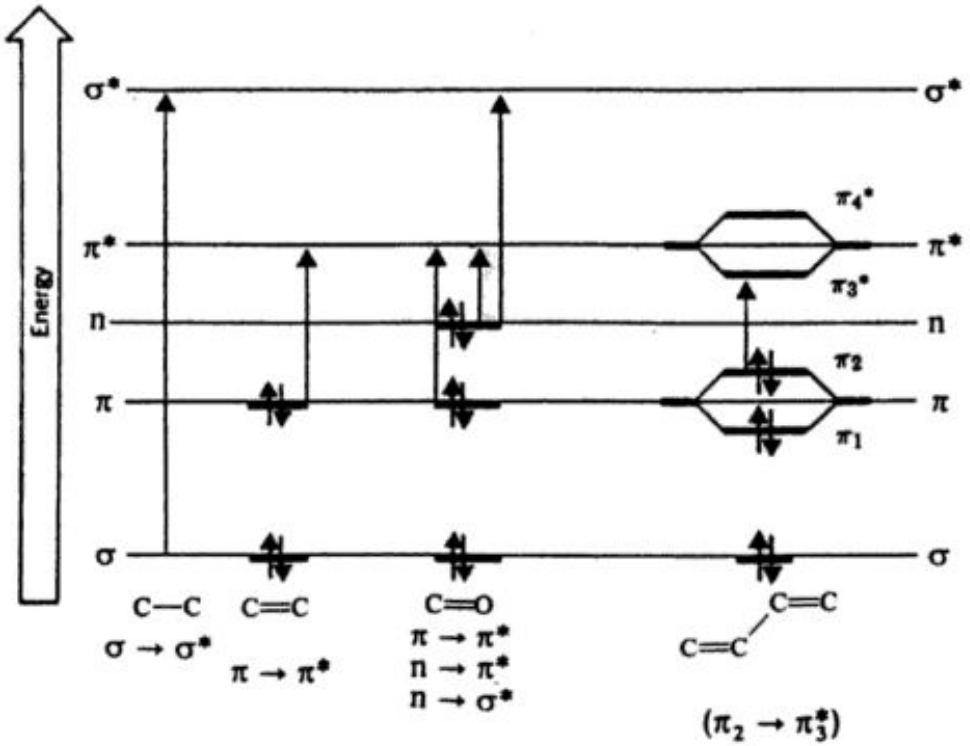


Electronic Energy Levels

Scheme 2.2

(a) The Designation of Various Transitions. In Scheme (2.2a), the relative energies of the more important orbitals are illustrated.

(i) $\sigma \rightarrow \sigma^*$ ***Transition.*** A transition of a electron from a bonding sigma orbital to the higher energy antibonding sigma orbital is designated $\sigma \rightarrow \sigma^*$ ('sigma to sigma star'). In alkanes, *e.g.*, this is the only transition available. Sigma bonds are, in general, very strong, this therefore, is a high energy process (Scheme 2.2a) and these transitions require very short



Scheme 2.2a

wavelengths, *i.e.,* high energy ultraviolet light ~ 150 nm. A study of such transition is done in vacuum ultraviolet region since below 200 nm oxygen present in air begins to absorb.

(ii) n → σ* Transition. This transition involves saturated compounds with one hetero atom with unshared pair of electrons (*n* electrons), *i.e.,* saturated halides, alcohols, ethers, aldehydes, ketones, amines, etc. These transitions require comparatively less energy than $\sigma \rightarrow \sigma^*$ transitions. Water absorbs at 167; methyl alcohol at 174; methyl chloride at 169 and methyl iodide at 258 nm. In saturated alkyl halides, the energy required for this transition decreases with the increase in the size of the halogen atom (or decrease in the electronegativity of the atom). Due to the greater electronegativity of chlorine (than iodine) the *n* electrons on chlorine atom are comparatively difficult to excite. The *n* electrons on iodine atom are loosely bound. Since this transition is more probable in case of methyl iodide, its molar extinction coefficient is also higher than methyl chloride. $n \rightarrow \sigma^*$ Transitions are sensitive to hydrogen bonding. Alcohols, *e.g.,* form hydrogen bonds with the solvent molecules. Such association occurs due to the presence of non-bonding electrons on the hetero atom and thus, this transition requires greater energy.

(iii) $\pi \rightarrow \pi^*$ ***Transition (K-band).*** This transition is available in compounds with unsaturated centres, *e.g.*, simple alkenes, aromatics, carbonyl compounds, etc. This transition requires lesser energy then $n \rightarrow \sigma^*$ transition. In a simple alkene, although several transitions are available (Scheme 2.2a), the lowest energy transition is the $\pi \rightarrow \pi^*$ transition and a absorption band around 170-190 nm in unconjugated alkenes (Table 2.3) is due to this transition. In the case of, *e.g.*, saturated ketones, the most intense band around 150 nm is due to $\pi \rightarrow \pi^*$ transition.

(iv) $n \rightarrow \pi^*$ ***Transition (R- band).*** In this transition, an electron of unshared electron pair on a hetero atom is excited to π^* anti-bonding orbital. This transition involves least amount of energy than all the transitions and therefore, this transition gives rise to an absorption band at longer wavelengths. In saturated aliphatic ketones, *e.g.*, the $n \rightarrow \pi^*$ transition around 280 nm is the lowest energy transition (Scheme 2.2a). This $n \rightarrow \pi^*$ transition is 'forbidden' by symmetry consideration, thus the intensity of the band due to this transition is low, although the wavelength is long (lower energy).

(v) Conjugated Systems and Transition Energies. In conjugated dienes, the π orbitals of the separate alkene groups combine to give new orbitals, *i.e.*, the two new bonding orbitals which are designated π_1 and π_2 and two anti-bonding orbitals which are designated π^*_3 and π^*_4. One can easily see (Scheme 2.2a) the relative energies of these new orbitals, and it is apparent that now the $\pi_2 \rightarrow \pi_3^*$ transition of a conjugated diene is of very low energy than $\pi \rightarrow \pi^*$ transition on an unconjugated alkene. Consequently the $\pi_2 \rightarrow \pi_3^*$ transition of, *e.g.*, butadiene (λ_{max}, 217 nm) is bathochromically shifted relative to the $\pi \rightarrow \pi^*$ transition of ethylene λ_{max} 171 nm, Table 2.4. Conjugated ketones, *i.e.*, α, β-unsaturated ketones as well, show both an $n \rightarrow \pi^*$ and a $\pi \rightarrow \pi^*$ transition both of lower energy, *i.e.*, at higher wavelength than those of isolated systems.

(b) Designation of Bands. One may designate the uv absorption bands by using electronic transitions or the letter designation. The band due to $\pi \rightarrow \pi^*$ transition in a compound with conjugated π system is usually intense ($\varepsilon_{max} > 10{,}000$) and is frequently referred to as the *K*-band (German *Konjugierte*). The examples of the compounds in which *K*-band appears are butadiene, mesityl oxide. Benzene itself displays three absorption bands at 184, 204 and 256 nm and of these the band at 204 nm is often designated as *K*-band, and this designation is used in other benzenes as well (Table 2.7).

The $n \rightarrow \pi^*$ transition (*R*-band German, *Radikal*) in compounds with single chromophoric groups *i.e.*, carbonyl or nitro are forbidden with ε value less than 100.

In conjugated systems the energy separation between the ground and excited states is reduced and the system then absorbs at longer wavelengths and with a greatly increased intensity (*i.e.*, *K*-band is intense and at longer wavelength). Moreover, due to the lessening of the energy gap, the $n \rightarrow \pi^*$ transition due to the presence of the heteroatom, *i.e.*, the *R*-band also undergoes a red shift with little change in intensity.

The ***B*-bands,** *i.e.*, benzenoid bands are characteristic of aromatic and heteroaromatic compounds. In benzene the *B*-band is at 256 nm which displays a fine structure, *i.e.*, the band contains multiple peaks. Significantly the *K*-band and *B*-band of benzenes have low intensities.

The ***E*-band**, *i.e.*, ethylenic bands are characteristic of aromatic systems like *B*-bands.

(c) Chromophores and Auxochromes. A chromophore is a covalently unsaturated group responsible for electronic absorption, *e.g.*, C=C, C=O and NO_2. Examples of simple compounds containing chromophoric groups are ethene (Table 2.3), benzene (Table 2.7) and acetone (Sec. 2.9). An auxochrome represents a saturated group containing unshared electrons which when attached to a chromophore changes both the intensity as well as the wavelength of the absorption maximum, *e.g.*, OH, NH_2, Cl. The effect of NH_2 group on λ_{max} and ε_{max} can be seen by, *e.g.*, comparing the position of *B*-band in benzene and aniline (Table 2.7); in aniline the *B*-band becomes more intense and displays itself at longer wavelength. Combining chromophores (as in 1, 3-butadiene) or extending conjugation can also significantly affect position and intensity of absorption bands (Table 2.4, also see sample problem 59, Chapter 7).

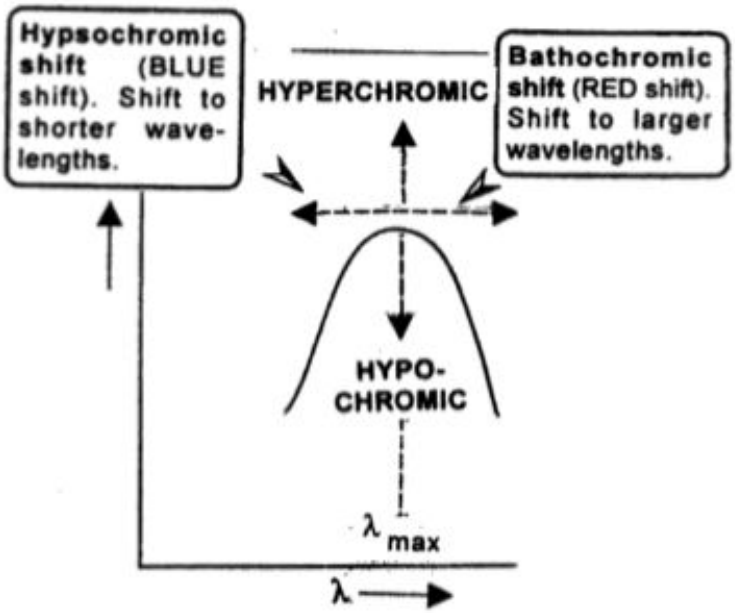
(d) Red and Blue Shifts. Groups which give rise to electronic absorption are termed *chromophores*. The term *auxochrome* is used for substituents containing unshared electrons (OH, NH, SH, halogens, etc.). When attached to π electron chromophores, auxochromes generally move the absorption maximum to longer wavelengths (lower energies). Such a movement is called a *bathochromic* or *red shift*. The term *hypsochromic* denotes a shift to shorter wavelength (*blue shift*). Increased conjugation usually results in increased intensity, termed *hyperchromism*. A decrease in intensity of an absorption band is termed *hypochromism* (Scheme 2.2b).

(e) Transition Probability—Allowed and Forbidden Transitions.

The excitation of an electron may not always take place from a bonding orbital or lone pair to an anti-bonding of non-bonding orbital, when a compound absorbs ultraviolet/visible light. The extinction coefficient, $\varepsilon_{max} = 0.87 \times 10^{20}$ P.a.

where P = transition probability with values from 0 to 1.

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



Scheme 2.2b

The value of ε_{max} is found to be around 10^5 when the chromophore has a length of the order of 10 Å or 10^{-7} cm. A chromophore with low transition probability will have $\varepsilon_{max} < 1000$. Thus there is a direct relationship between the area of the chromophore and the absorption intensity (ε_{max}). There are some other factors as well which govern the transition probability. Depending upon the symmetry and the value of ε_{max}, the transitions may either be allowed or forbidden. The transitions with the values of (extinction coefficient) ε_{max}, more than 10^4 are usually called allowed transitions. They generally arise due to $\pi \rightarrow \pi^*$ transitions. In butadiene the absorption at 217 nm, ε_{max} 21000 is the allowed transition. There are however, other $\pi \rightarrow \pi^*$ transitions in the conjugated system and their intensities depend on the "allowedness" of the transitions.

The forbidden transition is a result of the excitation of one electron from the lone pair present on the hetero-atom to an anti-bonding π^* orbital. The $n \rightarrow \pi^*$ transition near 300 nm in case of carbonyl compounds with ε_{max} value between 10-100, is the result of forbidden transition. The values of ε_{max} for forbidden transitions are generally below 10^4.

The allowedness of electronic transitions is related not only with the geometries of the lower and higher energy molecular orbitals but also with the symmetry of the molecule as a whole. Symmetrical molecules, (*e.g.*, benzene is highly symmetrical), have more restrictions on their transitions than comparatively less symmetrical molecules. Because of this reason the electronic absorption spectrum of benzene molecule is simple.

2.3 GENERAL APPLICATIONS OF ULTRAVIOLET SPECTROSCOPY — A SUMMARY

In practice, ultraviolet spectroscopy is largely limited to conjugated systems for the most part. For practical purposes the limits of visual perception may be taken as 750 nm (red) and 400 nm (violet) and therefore, ultraviolet commences around 400 nm. Organic applications of ultraviolet spectroscopy are mainly concerned in the region above 200 nm (near uv region) and hardly at all in the region below 200 nm (far uv region). Some of the most significant applications of uv spectroscopy to organic chemistry are as under.

(a) Extent of Conjugation. The longer the conjugation, the longer the maximum wavelength of the absorption spectrum as shown in the case of isomeric conjugated dienes, trienes and tetraenes (Fig. 2.1).

Sufficient conjugation shifts the absorption to wavelengths which reach the visible region of the spectrum, *i.e.,* a compound with sufficient conjugation becomes coloured. Thus lycopene, a compound which gives red colour to tomatoes has eleven conjugated double bonds (Fig. 2.1).

(b) Distinction Between Conjugated and Non-Conjugated Compounds. Generally electronic spectroscopy can differentiate conjugated

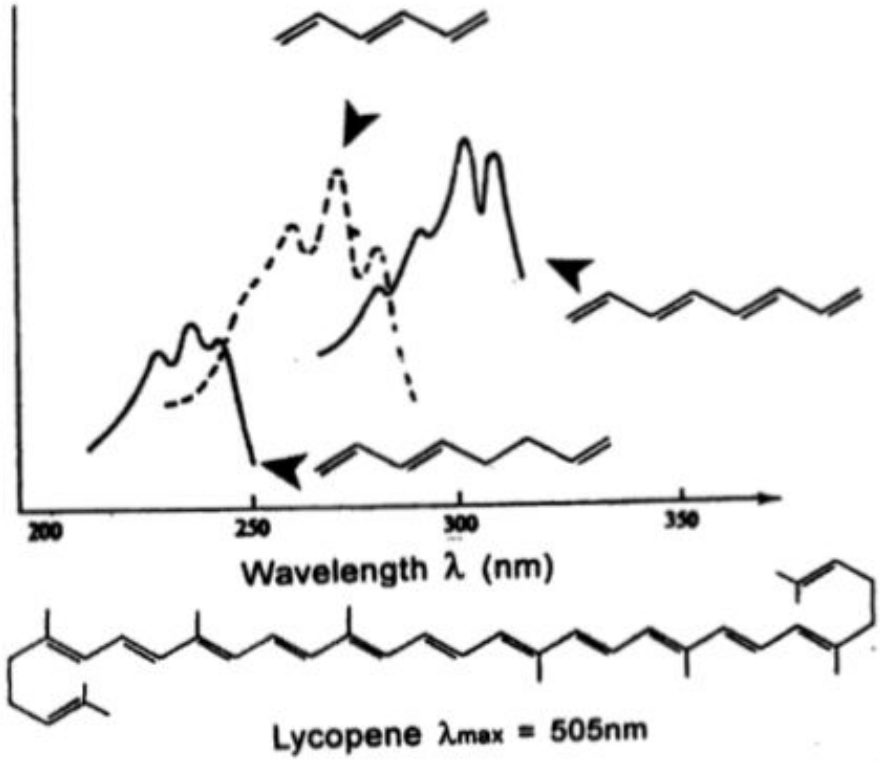


Fig. 2.1

dienes from non-conjugated dienes, conjugated dienes from conjugated trienes, α, β-unsaturated ketones from their β, γ-analogues.

(c) Detection of a Chromophore in an Unknown Compound by Comparison of its Spectrum with that of a Known Compound. Absorption in the near ultraviolet, *i.e.,* above 200 nm is invariably associated with the presence of unsaturated groups or of atoms with unshared pairs of electrons. The saturated hydrocarbons which do not have these structural elements absorbs below 200 nm, a region not of much significance for structural study of organic compounds. Thus, interestingly, a complex steroidal molecule, cholest-4-en-3 one is easily recognised to have an α, β-unsaturated ketone moiety similar to that in mesityl oxide by their spectral resemblance (Fig. 2.2).

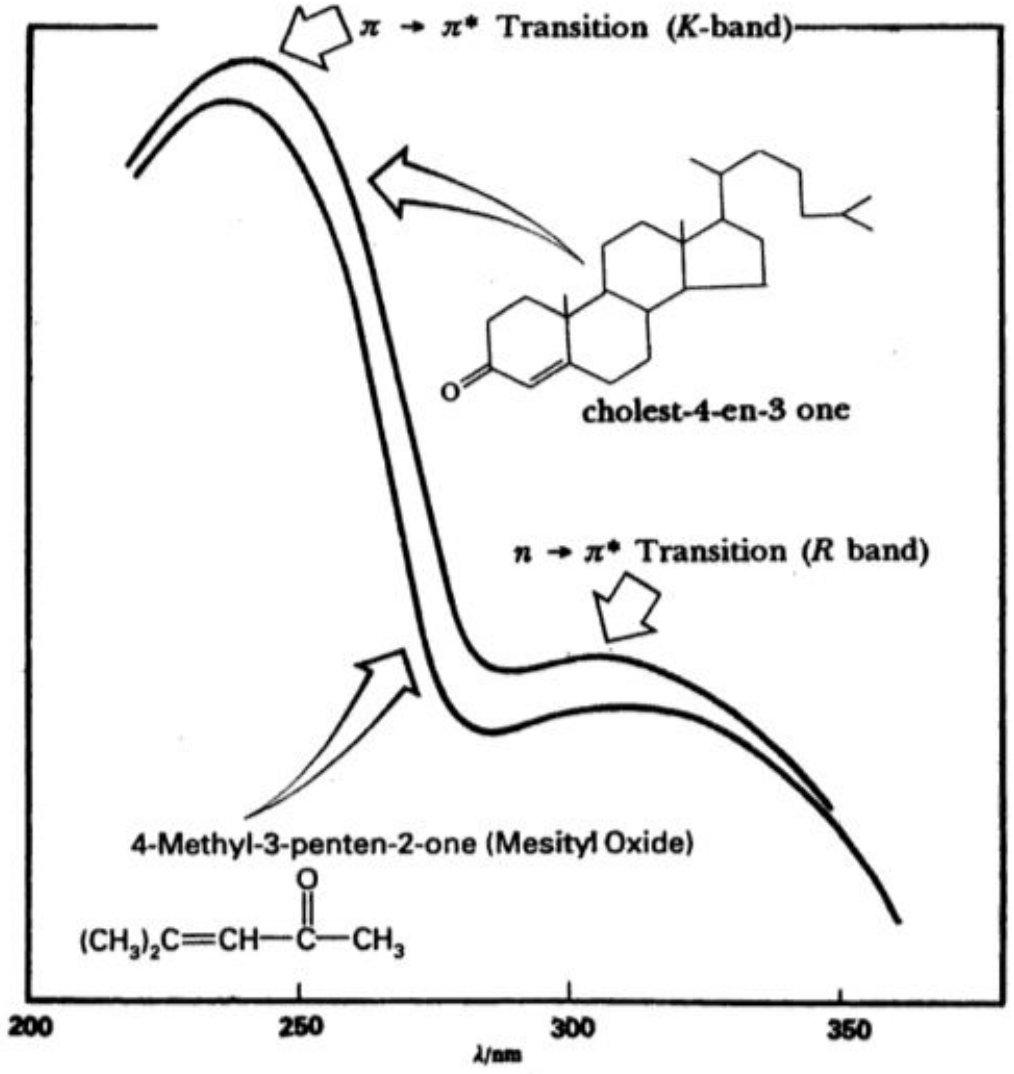
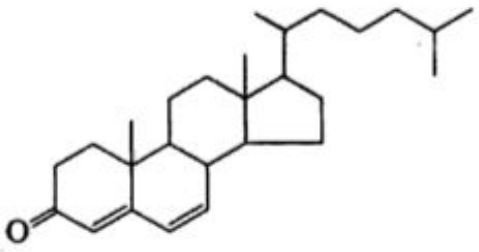


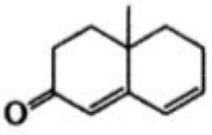
Fig. 2.2

Thus, if the UV spectrum of a known small molecule is comparable with an unknown larger molecule, the two may have the same chromophore (Scheme 2.2c).

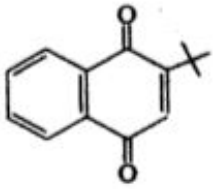
The presence of a 1,4-naphthoquinone system was suspected (and then confirmed by other studies) to be present in vitamin K_1 since a model 1,4-naphthoquinone derivative was found to have UV spectrum similar to this vitamin (Scheme 2.2c).



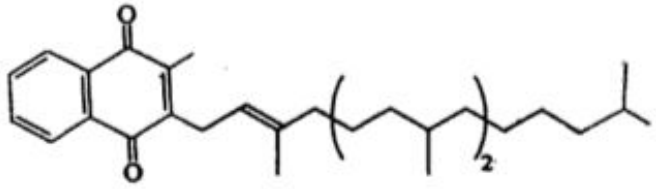
λ_{max} = 284nm



λ_{max} = 283nm



2-*tert*-Butyl-1,4-naphthoquinone



Vitamin K_1

λ_{max} (nm)	ε
249	19,600
260	18,000
325	2,400

λ_{max} (nm)	ε
248	18,600
264	14,200
331	2,730

Scheme 2.2c

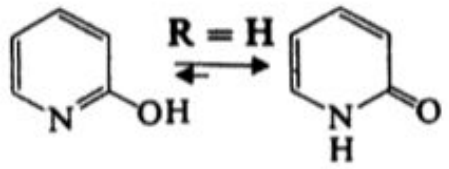
(d) Identification of a Chromophore (Functional Group). Simple conjugated chromophores, *i.e.,* dienes and α, β-unsaturated ketones have ε values of 10000-20000. The longer simple conjugated systems have principle maxima (usually also the longest wavelength maxima) with correspondingly higher ε values. Low intensity absorption bands around 270-350 nm with ε values of 10-100, are the result of the $n \rightarrow \pi^*$ transition of ketones (Fig. 2.2). In between these extremes, the presence of absorption bands with ε values of 1000-10000 almost always indicate the presence of an aromatic system. Several unsubstituted aromatic systems display bands with these intensities (absorption is the result of a transition with a low transition probability, low because of the symmetry of the ground and excited state). When the aromatic nucleus is substituted with groups which can extend the chromophore, strong bands appear with ε

values above 10000, however, bands with ε values below 10000 are generally still present.

(e) Study of Strain. The degree of conjugation may suffer in strained molecules, *i.e.*, loss of π-orbital overlap in 2-substituted diphenyls or acetophenones. Electronic spectroscopy can therefore, be used to know the extent of such strain by correlating the change in spectrum with angular distortion. The position of absorption is also influenced in a systematic way by substituents.

(f) Study of Geometric Isomerism. The *trans* isomer absorbs at a longer wavelength and with a larger molar extinction coefficient than *cis* isomer.

(g) Study of Tautomerism. Ultraviolet spectroscopy can be used to identify stable tautomeric species (Scheme 2.3). 2-Hydroxypyridine (I, R = H); pyrid-2-one (II, R = H) equilibrium has been shown to lie far to the right, *i.e.*, the ultraviolet spectrum of the solution resembles that of a solution of *N*-methylpyrid-2-one (II, R = Me) and is different from that of 2-methoxypyridine (I, R = Me). In this equilibrium (II with an α, β-unsaturated ketone system) predominates. The uv spectrum of the solution is comparable with that of solution of *N*-methyl-pyrid-2-one (II, R = CH_3) and differs from that of 2-methoxypridine (I, R = CH_3).



2-methoxypyridine

R = Me	R = Me	R = H
λ_{max} < 205 nm (ε > 5300) 269 nm (ε 3230)	λ_{max} 226 nm (ε 6100) 297 nm (ε 5700)	λ_{max} 224 nm (ε 7230) 293 nm (ε 5900)

Scheme 2.3

(h) Study of Strutural Features in Different Solvents. The absorption maximum (λ_{max} 290 nm), *i.e.*, the *R*-band shown by chloral hydrate in hexane is not seen in spectrum of the compound measured in aqueous solution to show that structure of the compound $CCl_3.CHO.H_2O$ in hexane changes to $CCl_3CH(OH)_2$ in aqueous medium.

(i) As an Analytical Tool. In suitable cases, the reaction rates and the p*Ka* values can be determined to make UV/Vis spectroscopy a powerful analytical tool.

2.4 SPECTROPHOTOMETER AND SPECTRUM RECORDING

In modern recording spectrophotometers the intensities transmitted by solvent and solution (of the compound in the same solvent) are continuously monitored. The instrument is designed to make a comparison of the intensities of the two beams at each wavelength of the region. If the compound absorbs light at a particular wavelength, the intensity of the sample beam (I_s) will be less than the reference beam (I_R). The instrument thus records a plot of the wavelength of the entire region versus the absorbance (A) of light at each wavelength. The absorbance at a particular wavelength is defined by the equation: $\mathbf{A}\lambda = \log (I_R/I_s)$ and such a graph is called an absorption spectrum.

For the visible and near ultraviolet region (750-350 nm). A tungsten filament lamp is used, while below 350 nm the hydrogen gas discharge lamp is a preferred source.

The spectrum below 200 nm is called the vacuum ultraviolet since the molecules of air absorb radiation in this region, air must be absent from the sample and spectrometer to record spectra in this region. Vacuum ultraviolet is, therefore, accessible only with specially, designed instruments. Ultraviolet spectrum is normally recorded with samples dissolved in solvents like water ethanol or hexane which are transparent within the wavelength range used in the study of organic compounds. Cells are normally made of quartz, since glass does not transmit ultraviolet radiation well. The solution cells can have path lengths from 1-10 cm, with 1 cm the most common.

2.5 SPECTRUM, SHIFTS OF BANDS WITH SOLVENTS

(a) The Absorption Band. Absorption bands in an ultraviolet spectrum are typically very broad when compared to an infrared or NMR spectrum. This is because, the energy put into the sample is sufficient to allow a large number of different electronic transitions to occur between the several different allowed vibrational and rotational energy levels of the molecule (Fig. 2.3). No doubt, each transition is quantized, however, the ΔE values are very close, so that complete resolution in the solution phase is not possible. Thus a broad band is displayed which consists of all these overlapped transitions. In the case of simple organic molecules, it is possible to resolve these bands in the gas phase. In other words, if only transitions in electron energy levels were involved the uv/visible spectra for all compounds would consist of fairly sharp lines, *i.e.,* very narrow absorption bands. The absorption of energy leads to electrons, initially in the ground state, moving to an excited state (an energy level of greater energy than ground state). A change in the electronic energy is accompanied by a

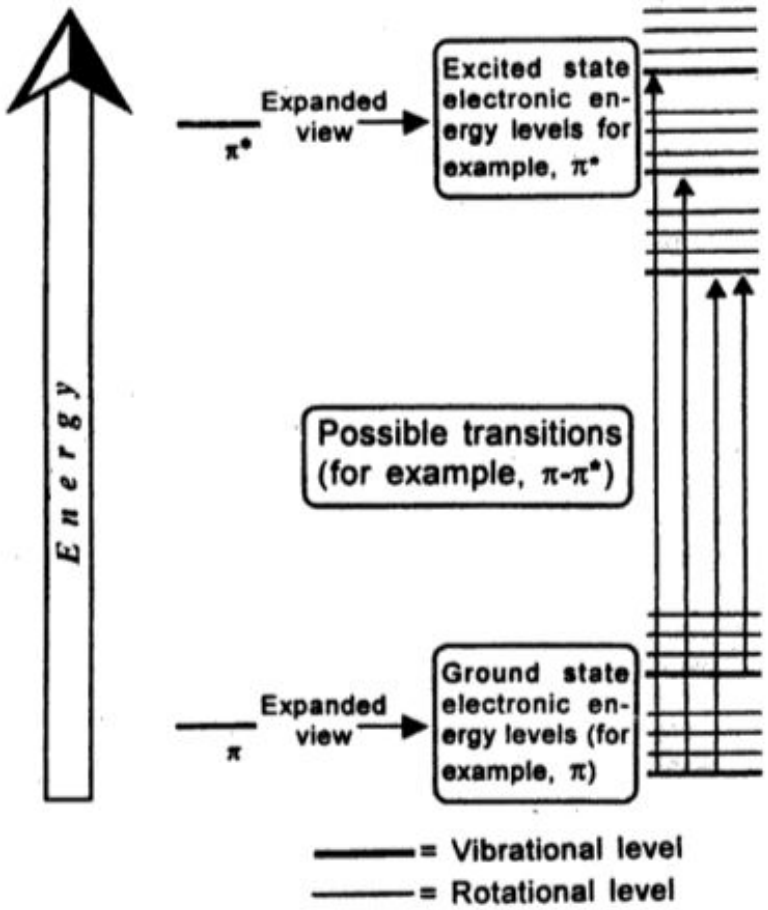


Fig. 2.3

corresponding change in the vibrational and rotational energy levels. The vibrational and rotational energy changes by themselves give rise to infrared absorption spectra. However, when they accompany ultraviolet/visible absorptions a large number of possibilities exist within each electronic state and the individual absorption bands normally become very broad. The energy transition is a change that will actually be from a vibrational energy level in the electronic ground state to one of several vibrational levels within the excited state.

The ultraviolet spectrum of an organic compound is measured from its very dilute solution, *e.g.*, 1 mg of the compound with a molecular weight of 100-200 dissolved in a solvent (which must be transparent within the wavelength range being examined) and made up to say 100 ml. A part of this solution is transferred to a cell which is placed in the spectro-photometer along with a matched cell with pure solvent. Two equal beams of ultraviolet light are passed, one through the solution of the compound and the other through the solvent. The intensities of the transmitted beams are now compared over the entire wavelength range of the instrument.

The ultraviolet spectrum of isoprene (Fig. 2.4) shows a broad absorption band in the region 210-240 nm. The absorption is at its maximum at 222.5 nm, a wavelength which is usually reported; *i.e.*, λ_{max} 222.5 nm, along with the solvent. In addition to this wavelength of maximum absorption (λ_{max}), the strength of the absorption (molar absorptivity), ε_{max} is also reported. The molar absorptivity is the proportionality constant which relates the observed absorbance (A) at a particular wavelength, λ, to the molar concentration, C of the sample and the length, l (in centimeters) of the path of the light beam through the sample cell and this quantitative relation is expressed by the Beer-Lambert equation (Sec. 2.1) which for isoprene comes out to be 10,800. The uv data for isoprene is thus recorded as λ_{max} 222.5 nm (ε = 10,800). Thus, the value of ε is an important information whose value may be worked from the Beer-Lambert law (Sec. 2.1). This equation may be gainfully rewritten as in Scheme 2.3a.

$$\varepsilon = \frac{\text{Absorbance} \times \text{Molecular weight} \times 100}{\text{Weight (mg) of the compound in 100 ml} \times \text{Path length in cm}}$$

Scheme 2.3a

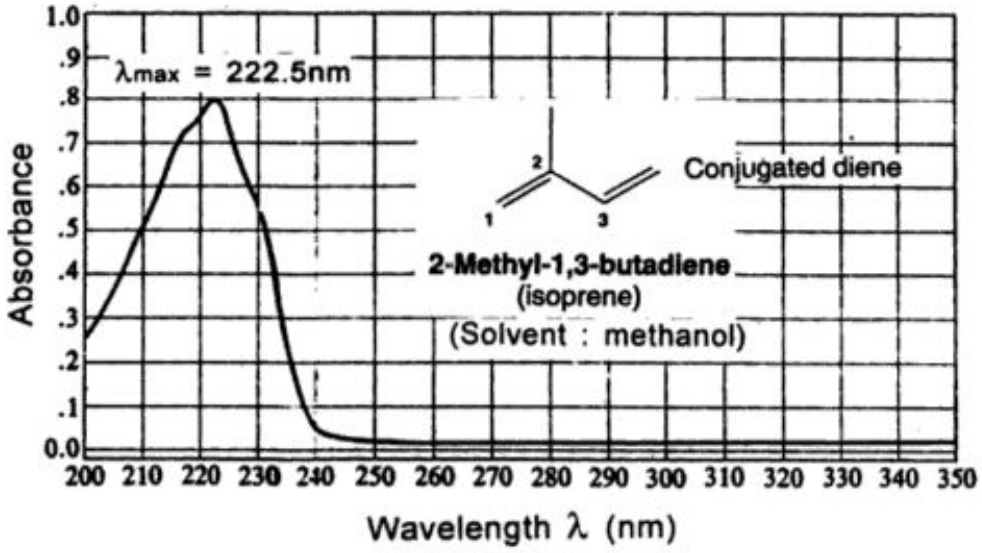


Fig. 2.4

Thus, if the solution of the compound, *e.g.*, (C_4H_8O, 106 mg) in ethanol (100 ml) in a 1 cm long cell has a λ_{max} 295 nm and corresponding absorbance 0.28, the value of ε comes out to be:

$$\varepsilon = \frac{0.28 \times 72 \times 100}{106 \times 1} = 19$$

(b) Solvents Used in Ultraviolet Spectroscopy. All molecules have absorption bands (CH_4 125 nm, far uv). Therefore, the solvent must be transparent within the wavelength range being examined. Table 2.1 gives a list of some commonly used solvents, and the minimum wavelength from which they may be used in 1 cm cells.

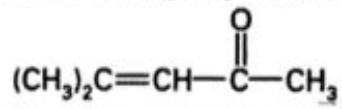
Table 2.1 : *Common Solvents Used in Ultraviolet Spectroscopy*

Solvent	Minimum wavelength for 1 cm cell, nm
Water	190
Cyclohexane	195
Hexane	200
Methanol	200
Ethanol	200
Ether	215
Methylene dichloride	220
Chloroform	240

(c) Shifts of Bands with Solvents. The transitions of polar bonds, like C=O but not ethylene, are affected by solvent polarity. As solvent polarity is increased, $\pi \rightarrow \pi^*$ bands undergo red shifts. This is so since excited state is more polar than the ground state and hence stabilisation is greater relative to the ground state in polar solvents. The $n \rightarrow \pi^*$ bands undergo blue shifts, since ground state with two n electrons receives greater stabilisation than the excited state with only one n electron. These opposite trends are clear by examining the data of mesityl oxide (Table 2.2). There is more on shift of bands with solvents under Section 2.9a.

Table 2.2 : *Effect of Solvent Polarity on the Spectrum of Mesityl Oxide*

Influence of Solvent on the UV λ_{max} and ε_{max} of the $n \longrightarrow \pi^*$ and $\pi \longrightarrow \pi^*$ Excitations of 4-Methyl-3-penten-2-one (Mesityl Oxide)



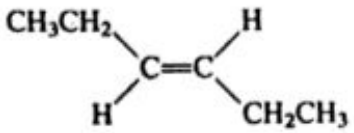
Solvent	$\pi \rightarrow \pi^*$ (ε)	$n \rightarrow \pi^*$ (ε)
n-hexane	230 (12,600)	327 (98)
Ether	230 (12,600)	326 (96)
Ethanol	237 (12,600)	315 (78)
Water	245 (10,000)	305 (60)

2.6 THE ISOLATED DOUBLE BOND

A $\pi \rightarrow \pi^*$ transition can occur in a simple unconjugated alkene like ethene, and other alkenes with isolated double bonds below 200 nm and thus is not readily measured. The alkyl substituents or the ring residues when present on the olefinic carbon atoms shift the absorption band toward, longer

waves. A comparison of ethene (no alkyl substituent), 1-octene (one alkyl substitution) and *trans*-2-hexene (two alkyl substituents shows that with increasing alkyl substitution, the wavelength of absorption increase from 171 to 177 to 184 nm (Table 2.3). As might be expected cyclohexene (two ring residues on the olefinic carbons) closely resembles *trans*-2-hexene.

Table 2.3 : *Long Wavelength Absorption Maximum of Unsaturated Hydrocarbons*

STRUCTURE	λ_{max} (*nm*)	ϵ_{max}
$CH_2{=}CH_2$ Ethene	171	15,530
$CH_3(CH_2)_5CH{=}CH_2$ 1-Octene	177	12,600
 *trans*-2-Hexene	184	10,000
 Cyclohexene	182	7,600

Thus, from the wavelength of absorption, one may distinguish between di-, tri- and tetra-substituted double bonds in acyclic and alicyclic systems.

2.7 THE CONJUGATED DOUBLE BOND

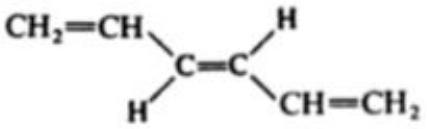
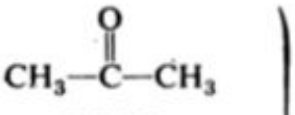
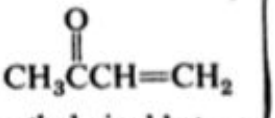
Conjugation and UV/vis light absorption

Conjugation leads to lower energy (longer wavelength) $\pi \rightarrow \pi^*$ absorptions which are observable by UV/vis spectrometers. Conjugation is a mechanism to delocalize electrons—***[a way one end of the molecule may "communicate" with the other chemically]***. Electronic spectra give information on the extent of conjugation. Substituents especially those which extend conjugation decrease the HOMO-LUMO energy difference. Most organic compounds which are coloured is due to their small HOMO-LUMO gap so that absorption occurs in visible region.

Conjugation of a double bond with another double bond or a C=O group causes the absorption bands to shift to longer wavelengths with greater

intensity (ε_{max}). Thus compared with the parent acyclic diene, 1,3-butadiene which has its principal maximum at 217 nm, the simple triene, *trans*-1,3,5-hexatriene absorbs at 256 nm. Thus each double bond extending the conjugation causes the absorption to occur at longer wavelength by about 40 nm in the lower polyenes (Table 2.4).

Table 2.4 : *Effect of Conjugation on uv Spectra*

STRUCTURE	λ_{max} (nm)	ϵ_{max}
$CH_2=CH_2$ Ethene	171	15,530
$CH_2=CH-CH=CH_2$ 1,3-Butadiene	217	21,000
 *trans*-1,3,5-Hexatriene	256	50,000
 acetone	187	$\pi \longrightarrow \pi^*$ excitations
 methyl vinyl ketone	219	

When a molecule absorbs light at its longest wavelength, an electron is excited from its highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). In alkenes and alkadienes the highest occupied molecular orbital is a bonding π orbital and the lowest unoccupied molecular orbital is an anti-bonding π^* orbital. The wavelength of the absorption maximum depends on the energy difference between these two levels. The energy gap between highest occupied molecular orbital and lowest unoccupied molecular orbital of ethene is greater than that between the corresponding orbitals of 1,3-butadiene. Less energy is therefore, required for $\pi \rightarrow \pi^*$ transition of 1,3-butadiene than similar transition in ethene (Fig. 2.5).

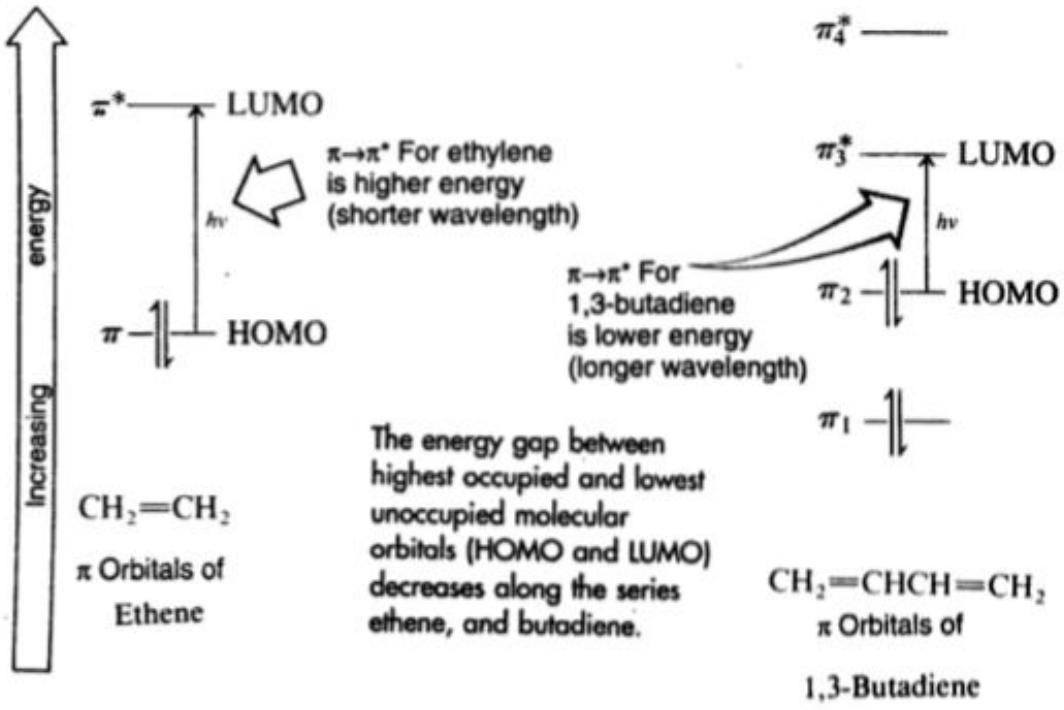
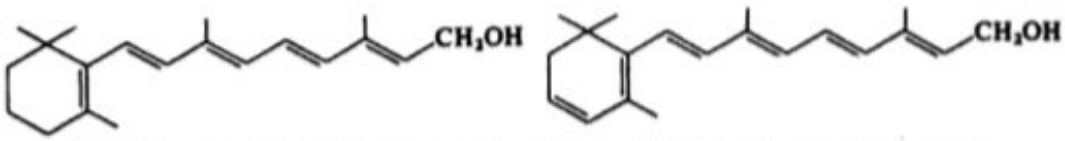


Fig. 2.5

Thus 1,3-butadiene absorbs uv radiation of longer wavelengths (less energy) while ethene requires absorption of light of greater energy (shorter wavelength). On adding more conjugated double bonds to a molecule, the energy required to reach the first excited state even decreases further. Thus, more the number of conjugated double bonds in a compound the longer will be the wavelength at which the compound will absorb light. This is seen by comparing the uv absorption data of vitamins A_1 and A_2, in latter which has an additional double bond in conjugation the position of absorption is at longer wavelength (Scheme 2.4).



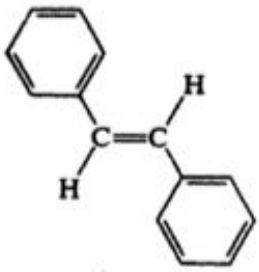
Vitamin A_1	Vitamin A_2
λ_{max} =325nm(ε= 51,000)	(has two absorption maxima) λ_{max} =287nm(ε= 22,000) and 351nm (ε=41,000).

Scheme 2.4

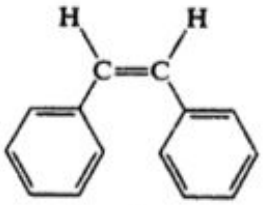
Sufficient conjugation shifts the absorption to wavelengths that reach the visible region of the spectrum, *i.e.*, a compound with sufficient conju-

gation becomes coloured. Lycopene, the compound responsible for the red colour of tomatoes, has eleven conjugated double bonds (Sec. 2.2). Various structural and stereostructural features may effect the absorption of a conjugated diene and some of these factors are presented.

(a) Effect of Geometrical Isomerism and Steric Effects. In compounds where geometrical isomerism is possible *e.g.,* in stilbene, the *E*-isomer (*trans*-stilbene) absorbs at a longer wavelength with greater intensity than *Z*-isomer (*cis*-stilbene) due to steric effects (Scheme 2.5). Coplanarity is needed for the most effective overlap of the π-orbitals and increased ease of the $\pi \rightarrow \pi^*$ transition. The *Z*-isomer is forced into a nonplanar conformation due to steric effects.



trans-stilbene
λ_{max} = 295nm, ε = 27,000

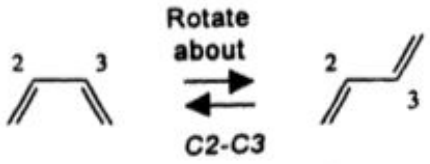


cis-stilbene
λ_{max} = 280nm, ε = 13,500

Scheme 2.5

As a rough rule of thumb, the greater the distance between the ends of a conjugated chromophore the greater is ε_{max}.

(b) Effect of *S-Cis (Cisoid)* and *S-Trans (Transoid)* Conformations. An acyclic diene largely exists in the preferred *S-trans* (*transoid*) conformation as is so in the case of butadiene (Scheme 2.6). This is so, since most acyclic dienes can rotate about their central single bond to give either a *cisoid* or a *transoid* conformation. When a diene forms a part of a ring



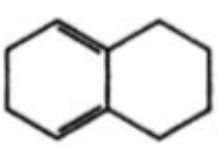
***S-cis* ~ 2.5%** ***S-trans* ~ 97.5%**
1,3-Butadiene
(*S*=single bond)

1,3-Butadiene
S-trans
λmax = 217nm,
ε = 21,000

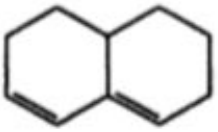
1,3-Cyclohexadiene
S-cis
λmax = 256nm,
ε = 8,000

Scheme 2.6

system as in 1,3-cyclohexadiene, it is forced into a (*S-cis*) *cisoid* configuration with far-reaching effects on absorption (Scheme 2.6). The wavelength of absorption is thus shifted towards the longer wavelength region and intensity is lowered in comparison with acyclic dienes. These effects are apparent from the data for 1,3,-butadiene (*S-trans*) and 1,3-cyclohexadiene (*S-cis*). Mono- and poly-cyclic dienes fall into two classes depending on whether the double bonds are in the same ring or in different rings. Members of the first class are called homoannular dienes and have the *S-cis* arrangement their absorption closely resembles 1,3-cyclohexadiene. The heteroannular dienes, the second category are *S-trans* and are spectrally related to butadiene (Scheme 2.7).



Homoannular diene is bathochromically shifted by 39nm compared to heteroannular diene.

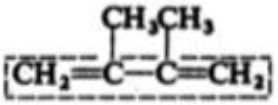


Homoannular diene
(*cisoid* or *s-cis*)
Less intense,
ε = 5,000-15,000
λmax = 273nm

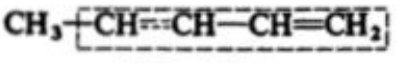
Heteroannular diene
(*transoid or s-trans*)
More intense,
ε = 12,000-28,000
λmax = 234nm

Scheme 2.7

(c) Effect of Alkyl Substitution and Ring Residues. Each alkyl substituent or ring residue attached to the conjugated diene chromophore displaces λ_{max} by about 5 nm toward longer wavelengths. Thus, compared with butadiene (λ_{max}, 217 nm), in 2,3-diemethyl-1, 3-butadiene, the two added methyl groups on C-2 and C-3 of the basic conjugated diene system result in a 5+5 or 10 nm increase in λ_{max} (Scheme 2.7a). In 1,3-pentadiene,



2,3-Dimethyl-1,3-butadiene



1,3-Pentadiene

λ^{calc}_{max}
217 (base value,1,3-butadiene
+ 5 x 2 [two alkyl substituents]
227 nm

λ^{obs}_{max} = 226 nm

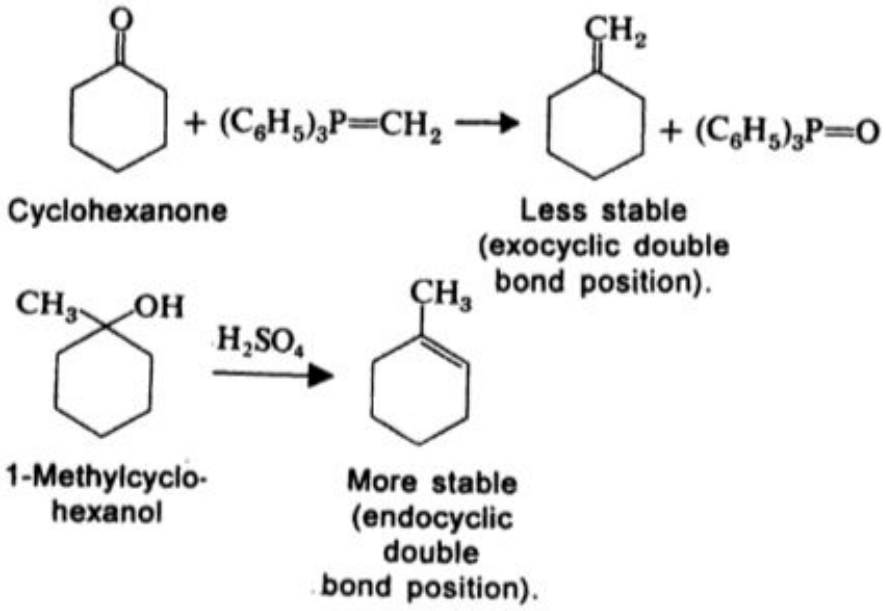
λ^{calc}_{max}
217 (base value,1,3-butadiene
+ 5 (1 alkyl substituent).
222 nm

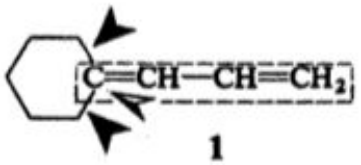
λ^{obs}_{max} = 223 nm

Scheme 2.7a

the observed λ_{max} is close to the calculated value. However, the *trans* isomer absorbs at a longer wavelength and with a larger molar extinction coefficient. This is generally true of *cis* and *trans* isomers, and uv spectroscopy is one of the method, that can be used gainfully to confirm the structure of geometric isomers (also see Scheme 2.5). Coplanarity is needed for the most effective overlap of the π orbitals and lower energy of the $\pi \rightarrow \pi^*$ transition. A *cis, i.e., Z* isomer, (unlike the *trans, i.e., E* isomer) adopts a nonplanar conformation due to steric effects.

(d) Effect of Exocyclic Double Bond. In, for example, 1,methylcyclohexene the double bond is inside the ring and it is recognised as the endocyclic position. This stable isomer (more substitution on the double bond) is prepared by the dehydration of 1-methyclohexanol. The less stable isomer has the double bond projecting outside the ring and is recognised as exocyclic position. This less stable isomer is prepared by the Wittig reaction from cyclohexanone (Scheme 2.8). Each exocyclic





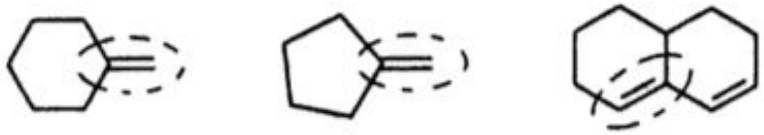
1

λ_{max}^{calc}	
217	(base value) 1,3-butadiene
+5x2	(2 alkyl substituents *i.e.*, 2 ring residues)
+ 5	(1 exocyclic double bond)
232 nm	

λ_{max}^{obs} = 236.5 nm

Scheme 2.8

location of a double bond causes a displacement of the λ_{max} by 5 nm toward longer wavelengths (red shift). The compound 1, may be regarded as 1,3-butadiene derivative in which the two hydrogen atoms of one of the terminal CH_2 group are replaced by two ring residues (these are equal to two alkyl substituents, see fully filled arrows). These ring residues add 2×5 nm to the λ_{max}. Since the double bond attached to the cyclohexane is exocyclic (see the half filled arrow), therefore, additional 5 nm must be added. Thus it is important to locate the exocyclic position of a double bond in a compound (Scheme 2.8a).



The double bonds exocyclic to a ring

Scheme 2.8a

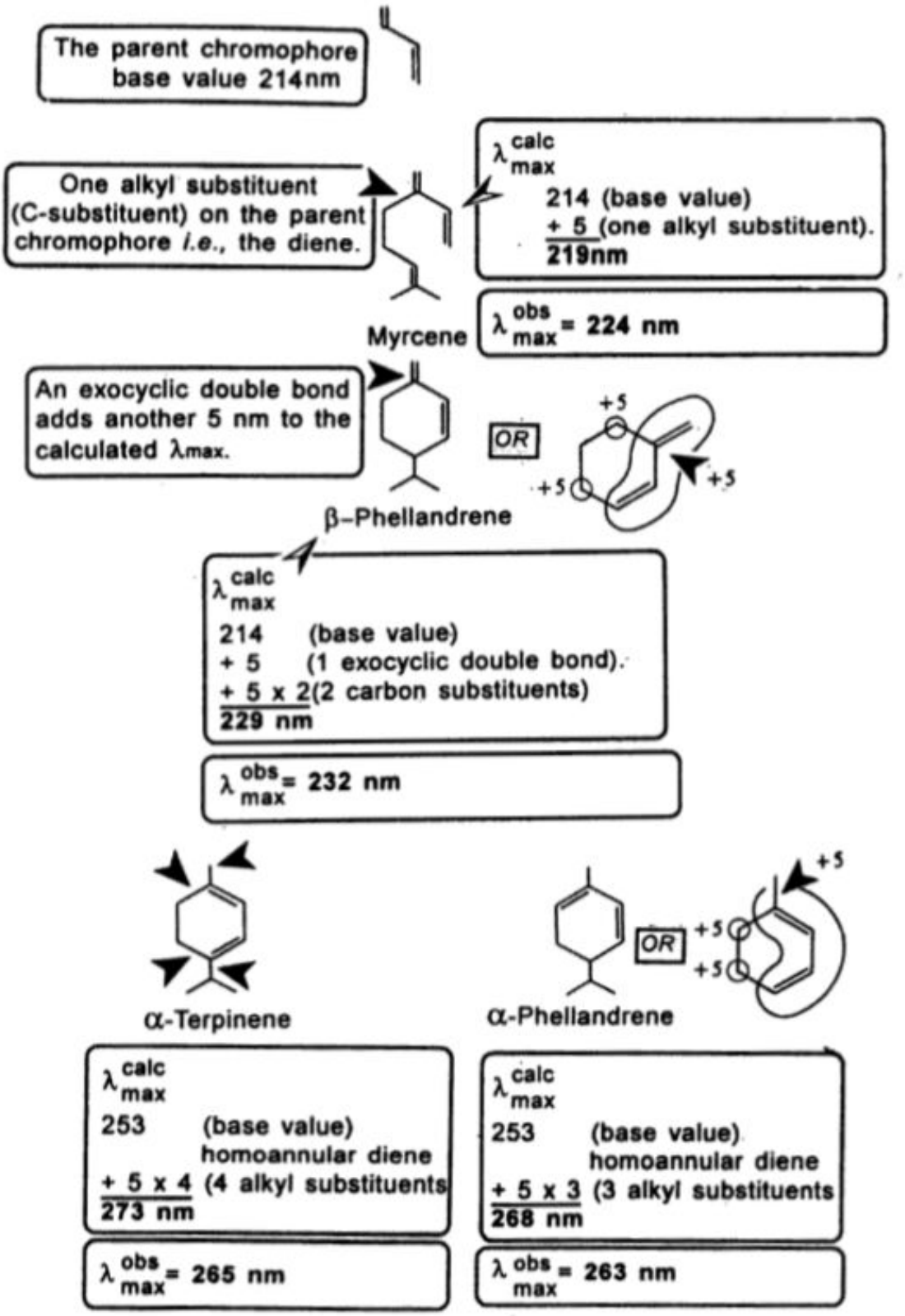
(e) Woodward-Feiser Rules (Calculation of uv Absorption Wavelength in Conjugated Dienes and Trienes). That diene absorption is in fact, influenced by structure in a surprisingly regular way, was appreciated by Woodward. He gave rules for calculating λ_{max}, which in their improved form are due to Feiser and are given in Table 2.5. Note, that unlike the base value of 217 nm used for predicting the λ_{max} values in Schemes (2.7a and 2.8), the Woodward-Fieser rules fix this value (for acyclic and heteroannular dienes) at 214 nm. (Further examples are in Chapter 7).

Table 2.5 : *Woodward and Fieser Rules for Diene and Triene Absorption*

	$\pi \rightarrow \pi^*$ Transition (*K*-band) λ_{max} (nm)
acyclic and heteroannular dienes	214 nm
homoannular dienes	253 nm
Addition for each substituent	
—R alkyl (including part of a carbocyclic ring)	5 nm
—OR alkoxy	6 nm
—Cl,—Br	5 nm
—OCOR acyloxy	0 nm
—CH=CH—additional conjugation	30 nm
if one double bond is exocyclic to one ring	5 nm
if exocyclic to two rings simultaneously	10 nm

Conjugated dienes and trienes (in ethanol) ε_{max} 6000-35000 ($\times 10^{-2}$ m^2 mol^{-1})

The calculated and experimental values of λ_{max} match within $\pm$ 5 nm, as shown by the examples (Scheme 2.9). In the case of acyclic diene,

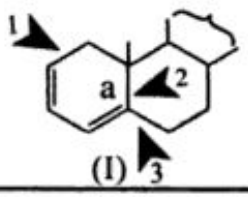


Scheme 2.9

myrcene there is only alkyl *i.e.,* C-substituent on the diene system. On the related monocyclic system β-phellandrene two additional factors need consideration, *i.e.,* now there are two ring residues (carbon substituents) on the diene system and one of the double bond has become exocyclic to the ring. In α-terpinene the diene is homoannular with four carbon substituents on it (shown by arrows) and these are a methyl group, an isopropyl group and two ring residues, while in α-phellandrene there are only three substituents.

Both the dienes (I and II) are homoannular and can be calculated to have a maximum at 273 nm. It may be noted that in (I), Δ^4 bond is exocyclic to ring B while none of the double bonds in (II) has exocyclic position. In (I) one has three ring residues while in (II) there are four ring residues instead, to make the total same in both the cases (Scheme 2.10).

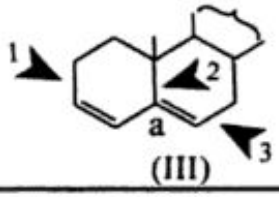
In compounds that contain both homoannular and heteroannular diene systems the calculations are based on the homoannular diene system. When one or two double bonds extend the conjugation, in addition to adding 30 nm for each extension the carbon substituents on the entire conjugated system are taken into account as shown for compounds (IV and IVa, Scheme 2.11):



(I)

λ_{max}^{calc}	
253	(base value) homoannular diene
+15	(3 ring residues,1,2,3, *i.e.*,alkyl substituents).
+ 5	(1 exocyclic double bond,*a*)
273 nm	

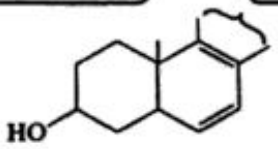
λ_{max}^{obs} = 275 nm



(III)

λ_{max}^{calc}	
214	(base value) heteroannular diene
+15	(3 ring residues,1,2,3, *i.e.*,alkyl substituents).
+ 5	(1 exocyclic double bond,*a*)
234 nm	

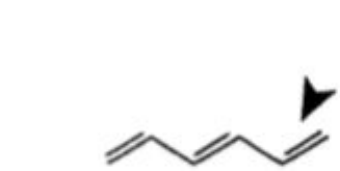
λ_{max}^{obs} = 235 nm



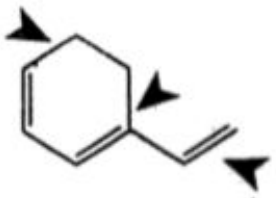
(II)

No exocyclic double bond
(the diene has four alkyl substituents.
λ_{max}^{calc} = 273 nm ; λ_{max}^{obs} = 275 nm;

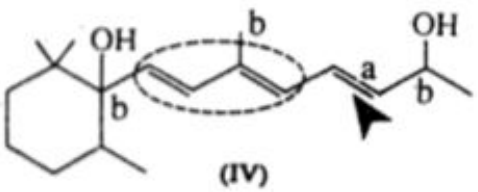
Scheme 2.10



Add 30nm for the additional conjugated double bond to the base value of 214nm of acylic (*s-trans* triene).



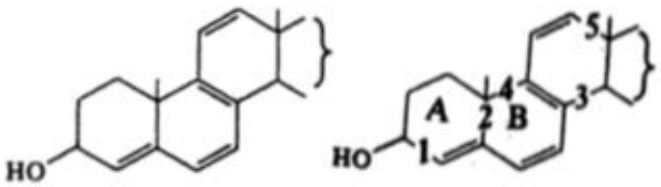
Add 30nm for the additional conjugated double bond to the base value of 253nm of *cisoid* cyclic diene. Add also 5 x 2 for two alkyl groups.



(IV)

λ_{max}^{calc}	
Parent (circled)	214
double bond extending conjugation (a)	30
3 alkyl groups (b)	15
	259 nm

λ_{max}^{obs} = 263 nm



(IVa)

- The homoannular diene system in ring B. (Used as the base value).
- Two double bonds extend this conjugation.
- The double bond in ring A is exocyclic to ring B.

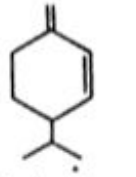
λ_{max}^{calc}	
Parent chromophore (*cisoid* diene)	253
Alkyl substituents	5x5
Exocyclic double bond	5
Extended conjugation	2x30
	343nm

λ_{max}^{obs} = 355nm

Scheme 2.11

(f) Effect of Strain Around the Diene Chromophore-Exceptions to Woodward Rules. The Woodward rules for conjugated dienes do not give

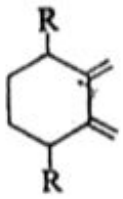
reliable results if strain is present around the chromophore. Thus compared to β-phellandrene (V) (Sec. 2.7e), the strained molecule verbenene (VI, Scheme 2.12) has an absorption maximum at 245.5 nm, while the calculated value for both is 229 nm. In diene (VII) the distortion of the chromophore, presumably out of planarity with consequent loss of conjugation, causes the maximum to be as low as 220 nm, (ε 10,050). Calculated absorption maximum is, 214 + 2 × 5 (exo) + 2 × 5 (alkyl) = 234. In diene (VIII, Scheme 2.12) however, the coplanarity of the diene is more likely and it gives a maximum at 243 nm (ε15800) to show that this is so, however, it still does not agree with the expected value, *i.e.*, 234 nm (Scheme 2.12).



β-phellandrene

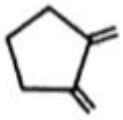
(V)

(VI)



(VII)

R = H
220 (10,050)
R = Me, <220
calcd. 234



(VIII)

Scheme 2.12

Electronic spectra

Ultraviolet and visible spectroscopy allows to estimate the extent of conjugation in a molecule. Peaks in electronic spectra are usually broad and reported as λ_{max} (nm). The relative intensities are given by the molar absorptivity (extinction coefficient ε).

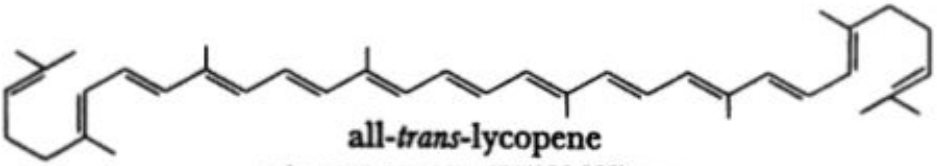
2.8 POLYENES

Among this class mention may be made of plant pigments known as carotenoids which are extended polyenes containing up to eleven conjugated double bonds. The Woodward's rules (Table 2.5) work well only for conjugated systems of 4 double bonds or less. For conjugated polyenes having more than 4, double bonds the Fieser-Kuhn rules (eq. 1) are used (Scheme 2.13). When applied to all *trans*-lycopene, one gets the results shown in eq. 2. In this compound, of the 13 double bonds only 11 are conjugated (n = 11). There are 8 substituents (methyl groups and chain residues on the polyene system (M = 8). Moreover, since in this conjugated polyene system there are no ring systems or exo- and endo-cyclic double bonds

$$\lambda_{max}\,(\text{hexane}) = 114 + 5M + n(48{\cdot}0 - 1{\cdot}7n) - 16.5\,R_{endo} - 10R_{exo} \quad 1$$

$\epsilon_{max} = (1.74 \times 10^4)n$ where

n = no. of conjugated double bonds
M = no. of alkyl or alkyl-like substituents on the conjugated system
R_{endo} = no. of rings with endocyclic double bonds in the conjugated system
R_{exo} = no. of rings with exocyclic double bonds



all-*trans*-lycopene

λ_{max}^{obs} 504(170,000); 474(186,000) nm

$$\lambda_{max}^{calc} = 114 + 5(8) + 11[48.0 - 1.7(11)] - 0 - 0 = 476\ \text{nm} \quad 2$$

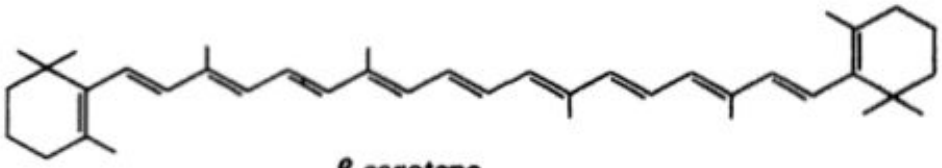
$\lambda_{max}^{obs} = 474$ nm (hexane)

$\epsilon_{max}^{cal.} = 1.74 \times 10^4(11) = 19.1 \times 10^4$

ϵ_{max}^{obs} (hexane) $= 18.6 \times 10^4$

Scheme 2.13

($R_{exo} = R_{endo} = 0$). Similar agreement is found for all *trans* β-carotene (Scheme 2.14).



β-carotene

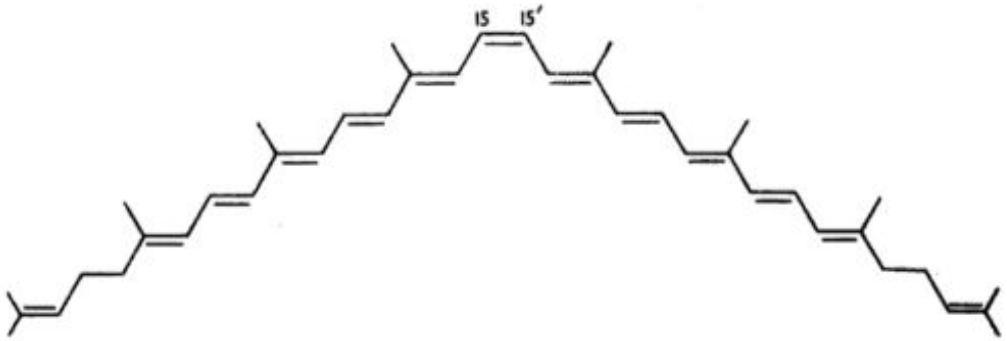
$\lambda_{max}^{calc.} = 453.3$ nm $\quad \epsilon_{max}^{calc.} = 19.1 \times 10^4$

$\lambda_{max}^{obs} = 452$ nm (hexane) $\quad \epsilon_{max}^{obs} = 15.2 \times 10^4$

Scheme 2.14

In a long-chain polyene, change from *trans* to *cis* configuration at one or more double bonds lowers both the wavelength and the intensity of the absorption maximum, as seen in the case of neolycopene A, which is

stereoisomeric with all *trans*-lycopene. For neolycopene A the predicted maximum is unchanged, however, its spectrum shows an additional band at 361 nm with about one-half the intensity of the visible absorption. This band is obviously associated with the *cis* double bond in the polyene chain which is apparently breaking the conjugation at this point (Scheme 2.15).



neolycopene A

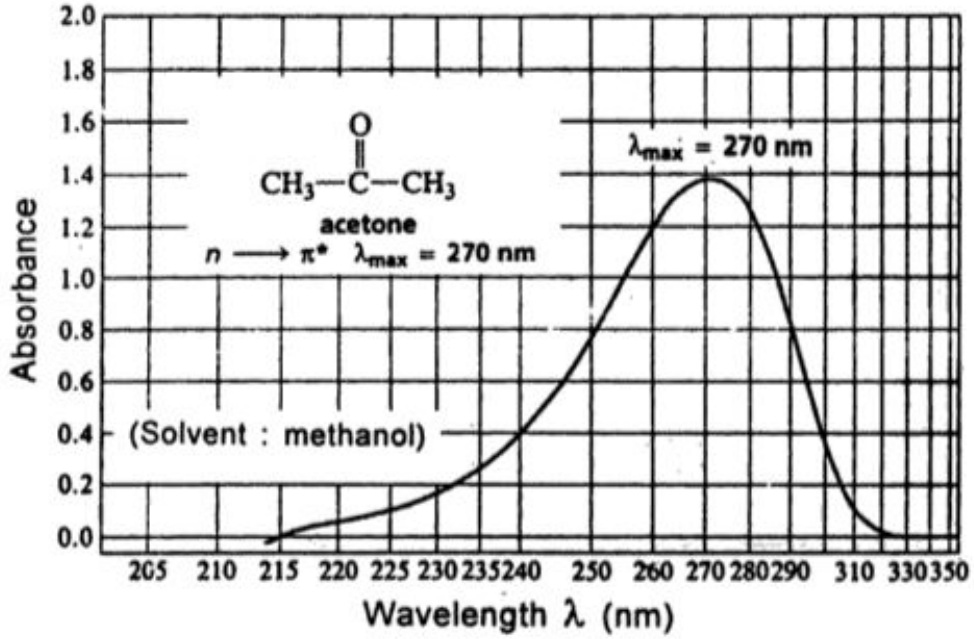
λ_{max}^{nhe} 500(100,000); 470(122,000); 361(68,000) nm

Scheme 2.15

2.9 CARBONYL COMPOUNDS

(a) Saturated Carbonyl Compounds. Carbonyl groups show characteristic absorption due to non-bonding electrons on the oxygen atom. These non-bonding electrons are not tightly held as are *pi* electrons and these are, therefore, excited to anti-bonding orbitals by lower energy uv radiation. Saturated ketones and aldehydes show three absorption bands, two of which are observed in the far ultraviolet region (Scheme 2.2a). *A* $\pi \rightarrow \pi^*$ transition absorbs strongly near 150 nm; and $n \rightarrow \sigma^*$ transition absorbs near 190 nm. The third band (*R*-band, $n \rightarrow \pi^*$) appears in the near ultraviolet in the 270-300 nm region. The *R*-band is a weak symmetry forbidden band ($\varepsilon_{max} < 30$) and is due to excitation of an oxygen lone-pair electron to the anti-bonding π-orbital of the carbonyl group. This band is used for identification work (Fig. 2.6).

The introduction of polar substituents, *e.g.*, a halogen on the α-carbon in the case of an aliphatic ketone has no effect of the $n \rightarrow \pi^*$ transition. In the case of cyclic ketones, however, the presence of such substituents raise by 10-30 nm (when axial) or lower by 4-10 nm (when equatorial), the λ_{max} of the parent compound. Thus compared with parent unsubstituted steroid (I) the 6 α-bromo-derivative (II, equatorial Br) shows a decrease in λ_{max}, while the 6 β-epimer (III, axial Br) displays a wavelength shift of +26 nm with intensification of the absorption. The data may provide useful infor-



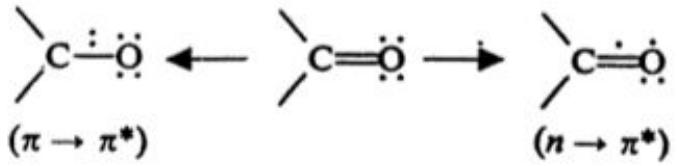


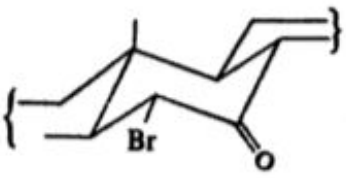
Fig. 2.6

mation to know the preferred conformation in a non-rigid system (Scheme 2.16). Thus 2-chlorocyclohexanone may have either conformation (IV) or (V). Compared with cyclohexanone (λ_{max} 282 nm), 2-chlorocyclo-hexanone absorbs at 293 nm corresponding to a shift of + 11 nm to indicate that the more important conformation is (IV).

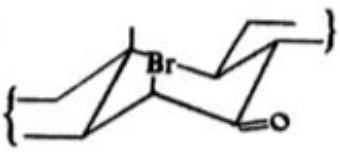
When the carbonyl group is substituted by an auxochrome — as in an ester, an acid, or an amide — the π^* orbital is raised but the *n* level of the lone-pair is left largely unaltered. As a consequence the $n \rightarrow \pi^*$ transition of these compounds is shifted to shorter wavelengths (200-220nm) range. Thus compared to acetaldehyde λ_{max} 293 nm the *R*-bands of ethylacetate, acetic acid and acetamide are shifted to 207, 204 and 220 nm respectively. The presence, therefore, of a weak band in the 275-295 nm region is positive identification of a ketone or aldehyde carbonyl group.

(b) α, β-Unsaturated Aldehydes and Ketones. Compounds in which carbon-oxygen double bond is conjugated with a carbon-carbon double bond (enones) have their absorption at longer wavelengths due to a decrease in the energy difference between ground and excited states. Thus

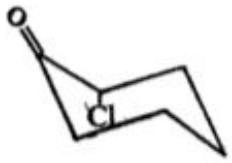
(I)
λ_{max} = 283nm,
ε = 56



(II)
λ_{max} = 279nm,
ε = 72



(III)
λ_{max} = 309nm,
ε = 182

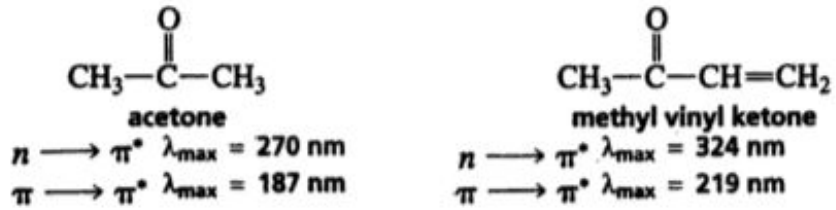


(IV)

(V)

Scheme 2.16

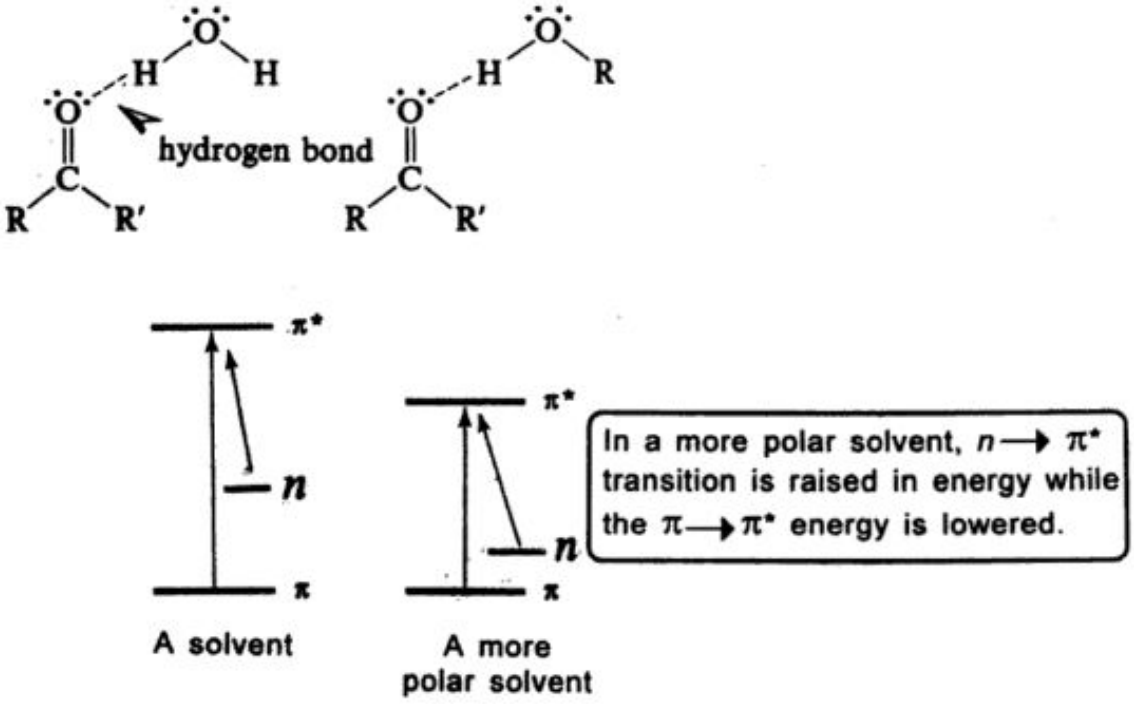
both the $n \rightarrow \pi^*$ (*R*-band) and $\pi \rightarrow \pi^*$ transitions (*K*-band), for example are at longer wavelengths (lower energies) in 3-buten-2-one (methyl vinyl ketone) than in the non-conjugated acetone (Scheme 2.17). The excited state is relatively more stabilised by conjugation than the ground state, as a result, the magnitude of the energy transition is decreased.



Scheme 2.17

The enones can therefore, be easily characterised by an intense absorption band (*K*-band) in the 215-250 nm region (ε_{max} usually 10,000-20,000), and a weak $n \rightarrow \pi^*$ band (*R*-band) at 310-330nm (see Fig. 2.2). The change of solvent polarity effects the wavelength of the transition.

R-bands show a blue shift on increasing the polarity of the solvent (Sec. 2.5 c). Acetone absorbs at 279 nm in *n*-hexane while in water the λ_{max} is at 264.5 nm. One can explain this blue shift on the basis of hydrogen bonding (eq I, Scheme 2.18). When the non-bonded electrons on the oxygen co-ordinate with a hydroxylic solvent, the net energy of the *n*-electrons is lowered. Thus the distance to the π^*-level will be higher and as a result



Scheme 2.18

in a polar solvent the $n \rightarrow \pi^*$ transition (the *R*-band) will be of higher energy or lower wavelength (blue shift). The amount of blue shift has been used as a measure to the strength of the hydrogen bond.

The *K*-band, *i.e.*, the $\pi \rightarrow \pi^*$ transition, on the other hand shifts to longer wavelength (lower energy) in a more polar solvent. The polar excited state of the $\pi \rightarrow \pi^*$ transition is stabilised by hydrogen bonding in more polar solvent. This lowers the distance between π and π^*, with a subsequent lowering in the energy or raising the wavelength of the transition. The data for the α, β-unsaturated ketone, mesityl oxide are given in Table 2.2.

The Woodward rules (Table 2.6) again can be used to calculate the position of intense $\pi \rightarrow \pi^*$ transition (*K*-band) not the weak $n \rightarrow \pi^*$ transition (*R*-band) for α, β-unsaturated carbonyl compounds.

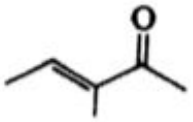
The λ_{max} for a $\pi \rightarrow \pi^*$ absorption band in the UV spectrum of compound (I, Scheme 2.19) is calculated as below. The base value is 215 nm; for one α-alkyl group add 10 nm, for one β-alkyl group add 12 nm; the total is 215 + 10 + 12 = 237 nm. This is within 1 nm of the observed value (for which ε_{max} is 4600). If the spectrum is recorded in water, λ_{max} would move to 245 nm, *i.e.*, $\pi \rightarrow \pi^*$ bands undergo a red shift. A few other examples which serve to illustrate the application of these rules to a variety of α, β-unsaturated carbonyl compounds are presented (Scheme 2.19, also see problems in Chapter 7).

Table 2.6 : *Rules for α, β-Unsaturated Aldehydes and Ketones*

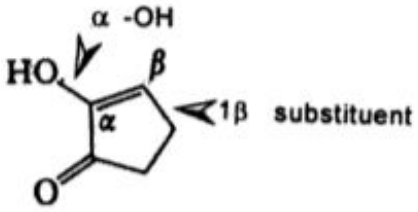
λ_{max} for $\pi \rightarrow \pi^*$ transitions ε_{max} 4500-20,000 ($\times 10^{-2} m^2 mol^{-1}$)
αβ-Unsaturated carbonyl compounds (in ethanol)

Value assigned to				
ketones — C=C—CO —	acyclic or 6-ring cyclic		215 nm	
	5-ring cyclic		202 nm	
aldehydes — C=C—CHO			210 nm	
acids and esters —C=C—CO_2 H(R)			197 nm	
extended conjugation			add 30 nm	
—C= C—C= C —CO - etc.				
homodiene component			add 39 nm	
Increments for				
	α	β	γ	δ
—R alkyl (including part of a carbocylic ring)	10 nm	12 nm	18 nm	18 nm
—OR alkoxy	35 nm	30 nm	17 nm	31 nm
—OH hydroxy	35 nm	30 nm	30 nm	50 nm
—SR thioether	—	80 nm	—	—
—Cl chloro	15 nm	12 nm	12 nm	12 nm
—Br bromo	25 nm	30 nm	25 nm	25 nm
—OCOR acyloxy	6 nm	6 nm	6 nm	6 nm
—NH_2,—NHR, —NR_2 amino	—	95 nm	—	—
if one double bond is exocyclic to one ring		5 nm		
If exocyclic to two rings simultaneously		10 nm		
"Estimated" λ_{max}^{EtOH}	Total	———		
solvent shifts				
methanol	0			
chloroform	– 1 nm			
dioxan	– 5 nm			
diethyl ether	– 7 nm			
hexane	– 11 nm			
cyclohexane	– 11 nm			
water	+8 nm			

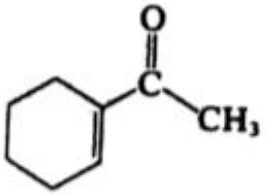
When cross-conjugation (α, β-unsaturation on both sides of carbonyl group) is present in a compound then the value of maximum absorption is calculated by considering the most highly substituted conjugated system,



(I)
3-Methylpent-3-en-2-one



Enol of 1,2-cyclopentanedione



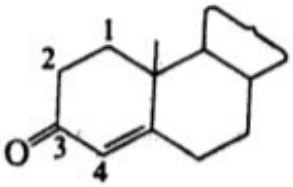
1-Acetylcyclohexene

Calculated λ_{max}^{EtOH}	
202	(base value)
+12	(1β substituent)
+35	(α -OH)
249 nm	

Observed λ_{max}^{EtOH} = 247nm

Calculated λ_{max}^{EtOH}	
215	(base value)
+10	(1α substituent)
+12	(1β substituent)
237 nm	

Observed λ_{max}^{EtOH} = 232nm



Cholest-4-en-3-one

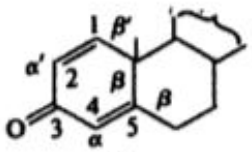
Calculated λ_{max}^{EtOH}	
215	(base, $\Delta^{4,5}$ system)
+24	(2β substituents)
+ 5	(1 exocyclic double bond)
244 nm	

Observed λ_{max}^{EtOH} = 245nm

Scheme 2.19

i.e., the more active monoenone chromophore. Thus, in the case of structure (I, Scheme 2.20) the calculations do not take into account the 1,2-double bond or the β group on it. The uv spectroscopy is, therefore, of value in distinguishing the structure (I) and (II). The extended dienone (II) absorbs fully 30 nm to longer waves. In the case of compound (I) the calculations taking into account the $\Delta^{1,2}$ system on the other hand gives 227 nm as the predicted value (Scheme 2.20).

(c) Effects of Solvent Polarity. Since carbonyl compounds are polar, α, β-unsaturated carbonyl compounds show two different shifts; the $\pi \rightarrow \pi^*$



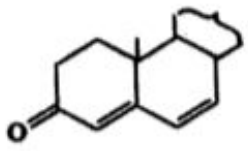
(I)

Cholesta-1,4-dien-3-one

Calculated λ_{max}^{EtOH}

215 (base, Δ^4-system)
+24 (2β substituents)
+ 5 (1 exocyclic double bond)
244 nm

Observed λ_{max}^{EtOH} = 245 nm



(II)

Calculated λ_{max}^{EtOH} = 280 nm

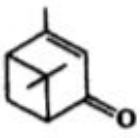
Observed λ_{max}^{EtOH} = 284 nm

Scheme 2.20

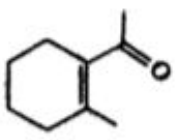
band (*K*-band) moves to longer wavelength (bathochromic, *i.e.*, red shift) while the $n \rightarrow \pi^*$ band (*R*-band) moves to shorter wavelength (hypsochromic, *i.e.*, blue shift).

(d) Effect of Structure-Strain-Steric Effect in Biphenyls and Chromophore Distortion. UV spectroscopy is highly sensitive to distortion of the chromophore whether it is brought about by ring strain or by steric hindrance. This spectroscopic technique can thus be used with advantage to demonstrate that distortion is present in a molecule. This is reflected in a marked decrease in intensity and may also lead to either a blue or a red shift of the absorption maximum.

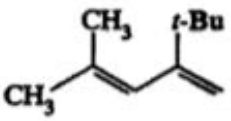
Verbenone III is calculated to have a maximum at 239 nm but actually shows a maximum at 253 nm, *i.e.*, and increment for strain of 14 nm. Compound IV displays its *K*-band at the predicted wavelength but with greatly decreased intensity. The steric hindrance in IV prevents coplanarity (Scheme 2.21).



(III)
Verbenone



(IV)
λ_{max} = 243nm,
ε = 1400



λ_{max}^{EtOH}	225	231
ϵ_{max}^{EtOH}	6400	10,000

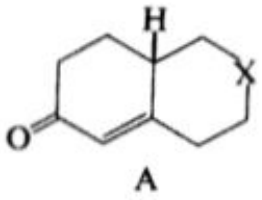
A

Scheme 2.21

Similarly, a nonbonded steric interaction between CH_3 and *tert*-butyl in (A, Scheme 2.21) is more effective than a nonbonded CH_3 and CH_3 interaction in destabilising the s-trans conformation. In the *tert*-butyl analogue, conjugation is inhibited by rotation about the sp^2-sp^2 C—C bond to give a twisted diene.

Another example of steric hindrance to conjugation is found in biphenyls. In biphenyl itself the two aromatic rings are in conjugation, the resonance energy is maximum when the rings are coplanar and will be zero when the rings are held at 90° to each other. When coplanarity and therefore, maximum π overlap of the two rings in biphenyl is severely sterically inhibited, the biphenyl derivative behaves more like the sum of the two independent aromatic chromophores (See problem 17).

(e) Non-Conjugated Interacting Chromophores. Normally the non-conjugated systems do not effect each other, as seen, *e.g.*, in the case of compound (I, Sec. 2.9, b) where cross-conjugation was successfully ignored while calculating the absorption maximum. Interestingly, however, several cases of non-conjugated interactions are known. The unsaturated ketones A display their $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions shifted in opposite directions when X becomes more electronegative. Presumably the π^* orbital is raised by transannular interaction with the $>N^+Me_2$ group, however, as the *n* electron is closer to the $>N^+Me_2$ group in the excited state than in the ground state, the $n \rightarrow \pi^*$ transition is of lower energy (Scheme 2.22).



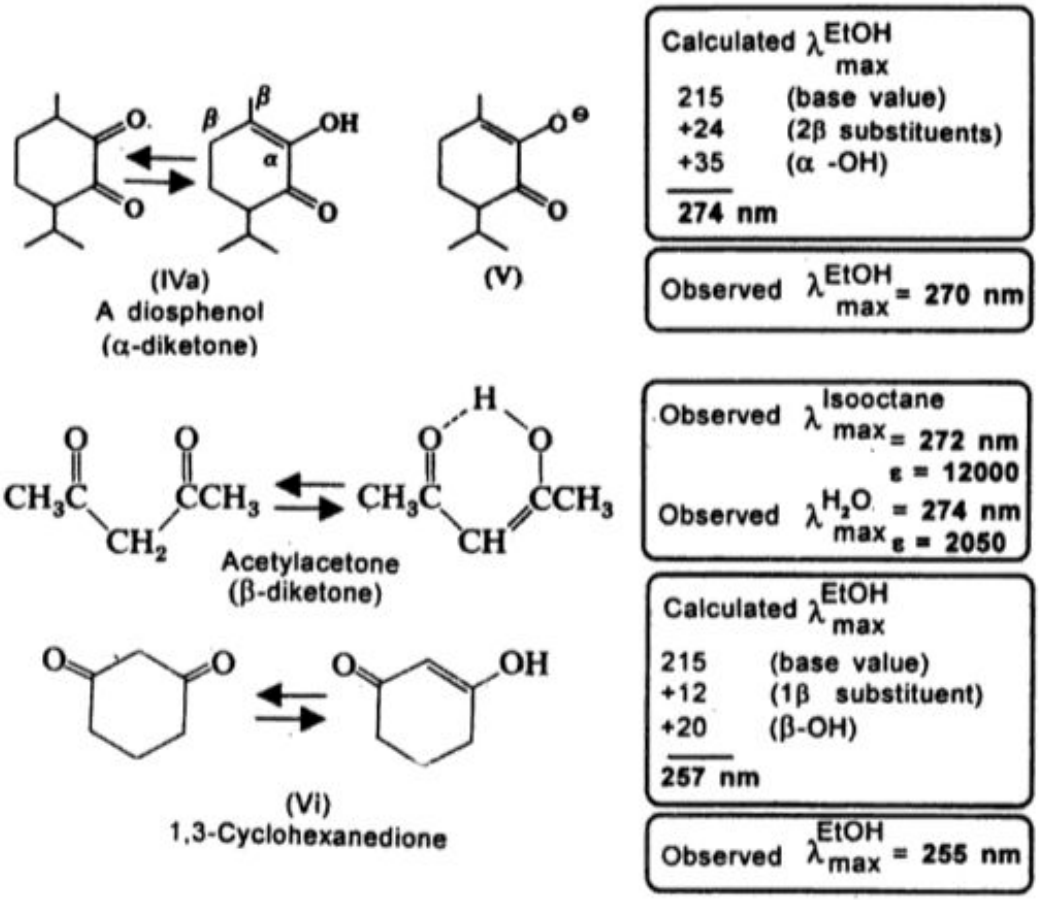
A

X	λ_{max}	
CH_2	238 nm	308.5 nm
NMe_2	229 nm	318.5 nm

Scheme 2.22

(f) Dicarbonyl Compounds. In cyclic α-diketones, the enolic form is generally more stable than the keto form and therefore, the absorption is related to that of an α, β-unsaturated carbonyl system. Six-membered cyclic α-diketones (IV a) known generally as diosphenols, exist in solution largely in the enolised form. In strong alkaline solution the absorption shifts to about 50 nm to longer waves, due to the formation of the enolate ion, *e.g.*, (V) to enable diosphenol structures to be characterised (Scheme 2.23).

Likewise, β-diketones are often encountered in the enolic form as seen in the case of acetylacetone. This compound exists in the enolic form to



Scheme 2.23

the extent of about 90% in solution in non-polar solvents and the absorption directly depends on the concentration of the enol tautomer. However, in the case of acetylacetone agreement with the calculated wavelength (257 nm) is indifferent. This may be due to the fact that the strong internal hydrogen bond forces the carbonyl group and the double bond into a configuration different from that which is present in cyclic structures, *e.g.*, in diosphenol. Cyclohexane-1,3-dione in cyclohexane (a hydrocarbon solvent) displays a weak absorption near 290 nm ($\varepsilon_{max} \sim 50$), but in ethanol it has λ_{max} 280 nm (ε_{max} 20,000). The diketone can show the equilibrium Scheme 2.23). In the hydrocarbon solvent the equilibrium lies towards the diketo form which displays itself by exhibiting the weak $\lambda_{max} = 295$ nm $n \rightarrow \pi^*$ absorption. The β-hydroxyenone tautomer is favoured in the presence of polar protic solvent and this form has the expected λ_{max} as calculated by the Woodward-Fieser rules (Scheme 2.33). Deprotonation of this enol gives the enolate anion which shows more intense absorption and at longer wavelengths than the enolic form. The formation of enolate ion in alkaline solution in these cases also shifts the strong absorption band, *e.g.*, in acetylacetone to 293 nm. Quinones represent α-, or vinylogous

α-diketones. The spectrum of *p*-benzoquinone is thus found to be similar with that of a typical α, β-unsaturated ketone with the strong *K*-band appearing at 242 nm and a weak *R*-band near 434 nm (Scheme 2.24). The colour of the simpler members is due to the weak $n \rightarrow \pi^*$ transition which is also present in α-diketones. The $n \rightarrow \pi^*$ transitions of α-diketones in the diketo form gives rise to two bands one in the usual region near 290 nm ($\varepsilon \sim 30$) and a second (ε 10-30) which stretches into the visible 340-440 nm region to give yellow colour to some of these compounds.

λ_{max}^{hexane} = 242 nm (ε 24 000) ← $\pi \rightarrow \pi^*$ *K*-band
281 nm (ε 400) } ← $n \rightarrow \pi^*$ *R*-band
434 nm (ε 20) }

Scheme 2.24

2.10 AROMATIC SYSTEMS — BENZENE AND ITS SUBSTITUTION DERIVATIVES

Benzene (I) shows three absorption bands (Solid line, Fig. 2.7) at 184 nm (ε_{max} 60,000); 203.5 nm (ε_{max} 7400, often called *K*-band) and at 254 nm (ε_{max} 204, often called *B*-band). The intense band near 180 nm is a result of an allowed transition, while the weaker *K* and *B* bands near 200 and 260 nm respectively result from forbidden transitions in the highly symmetrical benzene molecule.

The *B*-band of benzene and many of its homologues show a great deal of fine structure in the vapour phase or in non-polar solvents. The fine structure originates from sub-levels of vibrational absorption upon which the electronic absorption is superimposed.

When the spectrum is determined in polar solvents, interactions occur between solute and solvent which tend to reduce the fine structure. The presence of fine structure similar to that shown in (Fig. 2.7) is indicative of the simple aromatic molecules. When benzene is substituted by simple alkyl groups the absorptions are shifted slightly to longer wavelength (Scheme 2.25) and the fine structure remains intact.

This small bathochromic shift is ascribed to hyperconjugation between the alkyl group and π system of the ring (Scheme 2.25). The second alkyl group is most effective in producing a red shift if it is in the *para* position. The *para* isomer absorbs at the longest wavelength whereas the *ortho* isomer generally absorbs at the shortest wavelength. This effect is due to steric interaction between the *ortho* substituents, which effectively

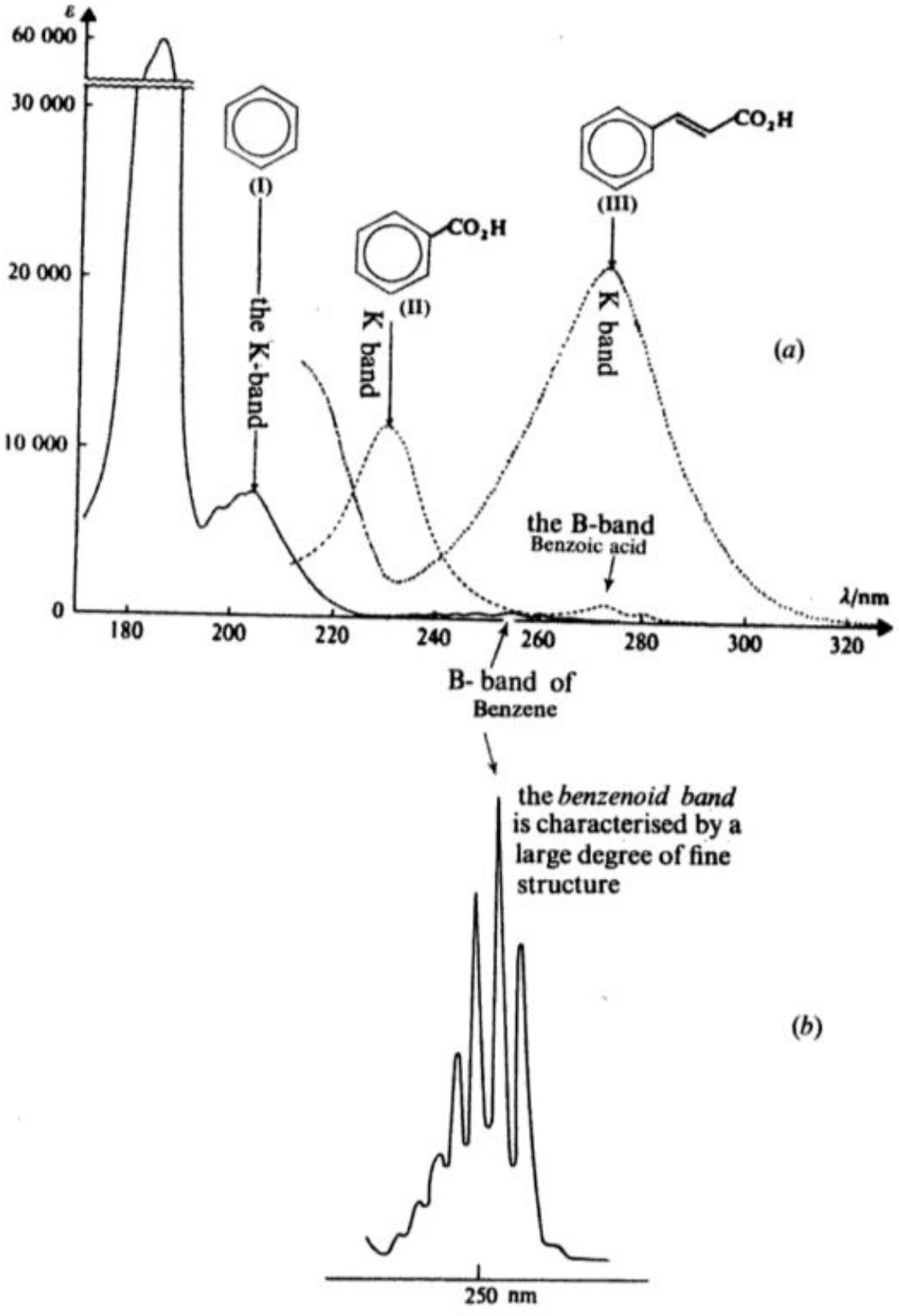
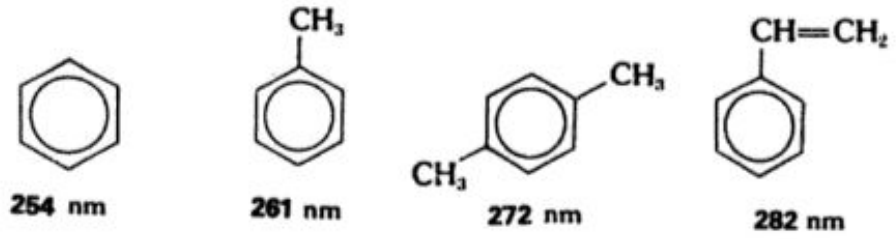
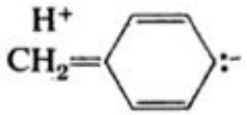


Fig. 2.7
Figure 2.6a, reproduced with permission from D.H. Williams and I. Fleming, *Spectroscopic Methods in Organic Chemistry*, McGraw-Hill 1988.)



***Long-wavelength electronic absorption maxima* the *B*-band for some aromatic hydrocarbons**



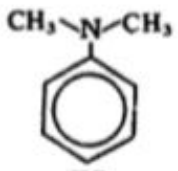
Scheme 2.25

reduce hyperconjugation. When however, non-bonding pair substituents (—OH, —NH_2, —OR, etc.) are present on the benzene ring (Table 2.7) the absorptions are shifted substantially to longer wavelengths and the fine structure of the *B*-band is either seriously diminished or wholly eliminated, because of n - π conjugation. When the heteroatom is attached to the benzene ring, the interaction between the non-bonding electron pair (s) on it and the π electrons of the ring is most effective when the p orbital of the non-bonding electrons lies parallel to the π orbitals of the ring. This arrangement is seriously disturbed due to twisting in sterically crowded molecules, *e.g.*, by the presence of bulky substitution in the *ortho* position of the molecule like dimethylaniline IV (Scheme 2.26). The absorption of dimethylaniline IV above 170 nm shows four distinct bands. Those at 176,200 and 296 nm are essentially transitions of the aromatic electrons while the fourth band, near 250 nm is due to electron transfer. The intensity of the band due to electron transfer (E.T.) is thus reduced to half in V while this band is eliminated altogether in VI. The residual absorption shown by VI constitutes the usual transitions of an aromatic system which closely resembles that of the alkyl benzene VII.

A reference to Fig. 2.7 and Table 2.7 shows how the wavelength and intensity of the absorptions peaks increase with an increase in the extent of the chromophore. On adding more and more conjugation to the benzene ring, the *K*-band (at 203.5 nm in benzene) effectively 'moves' to longer wavelength, faster than the *B*-band. Thus benzoic acid shows the *K*-band at 230 nm the *B*-band being still clearly visible at 273 nm, however, with the longer chromophore of cinnamic acid the *K*-band shifts to 273 nm and the *B*-band is completely enveloped.

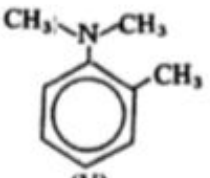
Table 2.7: λ_{max} *of the substituted benzene rings Ph-R*

	λ_{max}^{EtOH}, nm and (ε_{max})					
R	the *K*-band		the *B*-band			
—H	203.5	(7400)	254	(204)		
—Cl	209.5	(7400)	263.5	(190)		
—OH	210.5	(6200)	270	(1450)		
—OMe	217	(6400)	269	(1480)		
—CN	224	(13000)	271	(1000)		
$—CO_2^-$	224	(8700)	268	(560)		
$—CO_2H$	230	(11600)	273	(970)		
$—NH_2$	230	(8600)	280	(1430)		
$—O^-$	235	(9400)	287	(2600)		
—COMe	245.5	(9800)				
$—CH{=}CH_2$	248	(14000)	282	(750)	291	(500)
—CHO	249.5	(11400)				
—Ph	251.5	(18300)				
—OPh	255	(11000)	272	(2000)	278	(1800)
$—NO_2$	268.5	(7800)				
$—CH{=}CHCO_2H$	273	(21000)				
—CH=CHPh	295.5	(29000)				



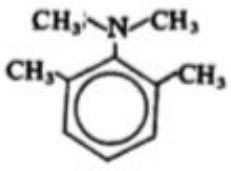
(IV)

λ_{max} (ϵ_{max}) 176(56,800)
200(22,200)
250(13,750) (ET band)
296(2300)



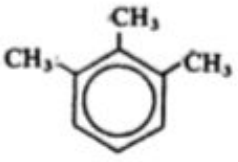
(V)

185(30,800)
207(11,400)
247(6300) (ET band)
288*sh*(1200)



(VI)

λ_{max} (ϵ_{max}) 194(36,100)
211(8600)
259(2200)



(VII)

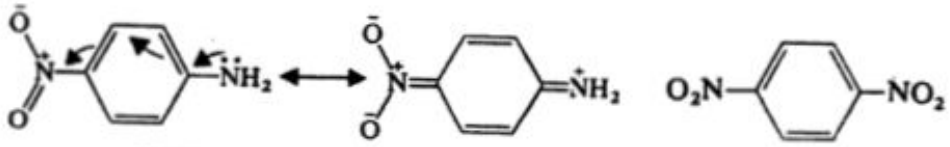
195(55,000)
214(8900)
258(166)

Scheme 2.26

In the case of disubstituted benzenes, when electronically complementary group, *i.e.,* an amino and a nitro are situated *para* to each other as in VIII, a pronounced red shift in the main absorption band, *i.e., K*-band is observed (Table 2.8). This effect of the presence of an electron donating and electron attracting groups *para* to one another leads to the extension of the chromophore through the benzene ring as shown in (VIII Scheme 2.27). This extension of the chromophore is not possible when these groups are located *ortho* or *meta* to each other or if the *para* disposed groups are not complementary as in IX. In these cases the spectrum displays close resemblance with the separate non-interacting chromophores.

Table 2.8 : *Absorption Characteristics of Disubstituted Benzenes*

Compound	$\pi \rightarrow \pi^*$ Transition *K*-band	
	λ_{max}	ε_{max}
o-NO_2 Phenol	279	6,600
m-NO_2 Phenol	274	6,000
p-NO_2 Phenol	318	10,000
o-NO_2 Aniline	283	5,400
m-NO_2 Aniline	280	4,800
p-NO_2 Aniline	381	13,500



VIII
obs. λmax = 381nm

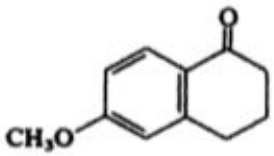
IX
261 nm

Scheme 2.27

Some quantitative assessments have been made (Table 2.9) in the case of substituted benzenes of the type R-C_6H_4-COG when the electron donating group is complemented by an electron withdrawing carbonyl group with regard to the principal band. This is explained by the use of values of table to the compounds X and XI (Scheme 2.28). Often naturally occurring aromatic compounds have a complex substitution pattern and the rules given in Table 2.9 are then of great value to assign structure. The fungal metabolic griseofulvin provides an example of this type, which contains two separate chromophores, *i.e.,* an α, β-unsaturated ketone chromophore and a substituted benzene (aromatic) chromophore. The spectrum of the dihydroderivative displays a strong band at 290 nm (ε_{max} 22,000), a weaker peak at 324 nm (ε_{max} 5300), and a shoulder near 250 nm (ε_{max} 21,000), all of which must be connected with the aromatic chromophore. The absorption of the isolated carbonyl group being negligible. The calculated

Table 2.9 : *Rules For the Principal Band of Substituted Benzene Derivatives*

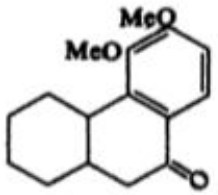
R—C_6H_4—COG		Calc. λ_{max}^{EtOH} *nm*
Parent chromophore:		
G = alkyl or ring residue	and R = H	246
G = H		250
G = OH or O Alkyl		230
Add for R:		
alkyl or ring residue	*o,m*	3
	p	10
-OH, -OMe, -O-alkyl	*o,m*	7
	p	25
O^-	*o*	11
	m	20
	p	78
Cl	*o,m*	0
	p	10
Br	*o,m*	2
	p	15
NH_2	*o,m*	13
	p	58
NHAc	*o,m*	20
	p	45
NHMe	*p*	73
NMe_2	*o,m*	20
	p	85



(X)

Parent value 246 nm
***Ortho* alkyl** 3 nm
***Para* methoxyl** 25 nm

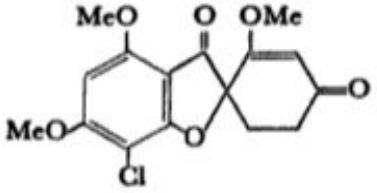
Calc: λ_{max}^{EtOH} = 274 nm Obs: λ_{max}^{EtOH} = 276 nm



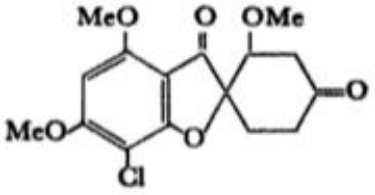
(XI)

Calc.: λ_{max}^{EtOH} = 246 + 25 + 7 + 3 = 281 nm

Obs.: λ_{max}^{EtOH} = 278 nm



griseofulvin



dihydro-derivative

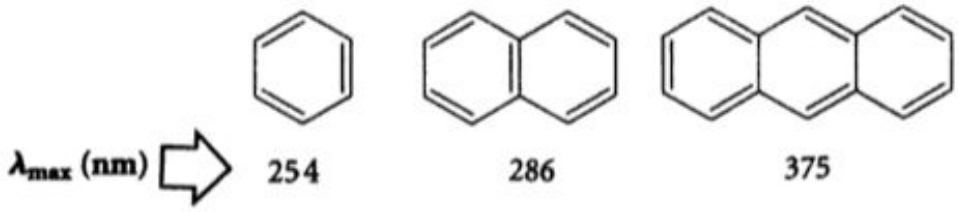
Scheme 2.28

wavelength is 246 (parent chromophore) + 2 × 7 (*o*-O Alkyl) + 0(*m*-Cl)) +25 (*p*-OCH_3) = 285 nm in agreement with the observation of an intense band at 290 nm. In griseofulvin the aromatic bands occur in essentially the same position but as expected there is additional absorption near 252 nm (ε_{max} 13,000) dut to the α, β-unsaturated ketone chromophore. The calculated λ_{max} is 257 nm. Thus the spectrum of griseofulvin is in complete accord with the assigned structure.

The values of Table 2.9 are valid only in the absence of steric hindrance to coplanarity.

2.11 POLYCYCLIC-AROMATIC HYDROCARBONS

The spectra of these compounds are highly complicated, but are uniquely characteristic of each aromatic system and thus provide useful fingerprints for identification purposes (Fig. 2.8). The introduction of relatively non-polar substituents like alkyl or acetoxyl groups have little influence on λ_{max} or ε_{max}. Thus, methylanthracenes are readily recognised to have the anthracene chromophore by a comparison of their uv spectra. As the number of condensed rings increases the absorption moves progressively to longer wavelengths (Scheme 2.29) until it occurs in the visible region, *e.g.*, in the case of pentacene λ_{max} 580 nm (blue) five benzene rings joined in a linear fashion.

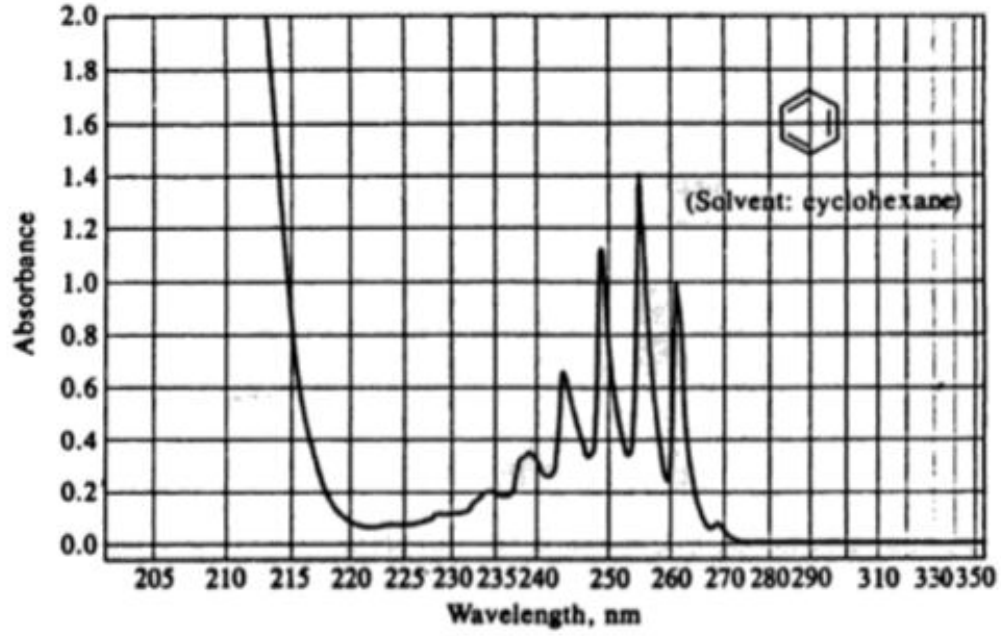


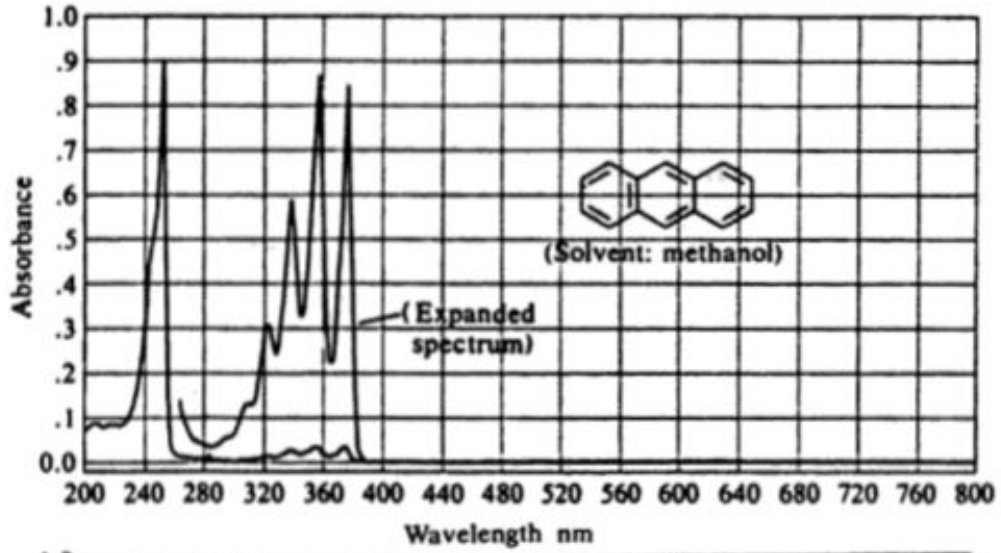
Scheme 2.29

2.12 HETEROAROMATIC COMPOUNDS

Broadly speaking the spectra of heteroaromatic compounds are similar with their corresponding hydrocarbons. The absorptions of 5-membered ring heteroaromatic compounds are thus compared with that of cyclopentadiene (intense absorption near 200 nm and moderately intense absorption near 238 nm), and pyrrole, *e.g.*, displays comparable adsorption data λ_{max} 209 nm, ε_{max} 6,730 and λ_{max} 240 nm, ε_{max} 300.

Similarly the spectrum of pyridine is comparable with that of benzene, the only difference being that the *B*-band of pyridine is more intense with somewhat diminished fine structure. This transition is allowed for pyridine but forbidden for the more symmetrical benzene molecule. An increase in





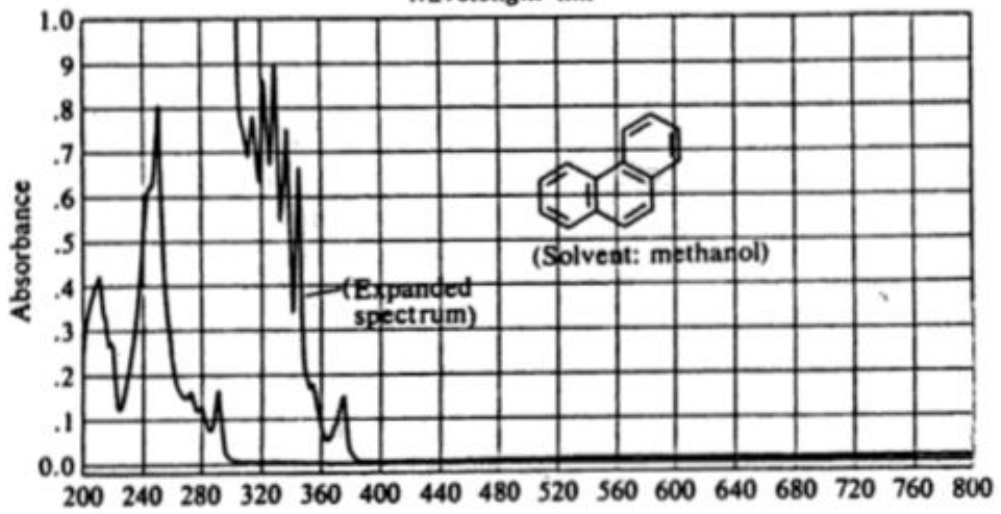


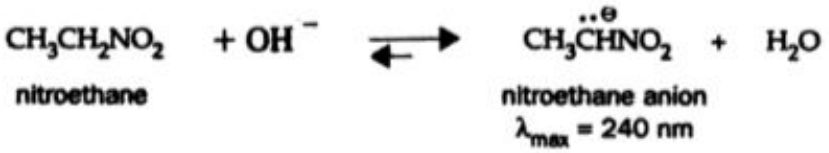
Fig. 2.8

the solvent polarity does not effect either the position or intensity of *B*-band of benzene, but produces a hyperchromic effect on this band of pyridine and its homologues. This effect is assigned to hydrogen bonding through the lone pair of electrons of the nitrogen atom. There is a possibility of the generation of tautomeric systems as seen in 2-hydropyridines. These systems tautomerise almost entirely to 2-pyridones (Sec. 2.3).

2.13 ANALYTICAL USES OF UV SPECTROSCOPY

UV/Vis spectroscopy has other uses that make it a good analytical tool. A reaction rate can be measured using UV/Vis spectroscopy provided one of the reactants or one of products absorbs UV or visible light at a wavelength where the other reactants or products have little or no absorbance. The anion of nitroethane has a λ_{max} at 240 nm, but neither H_2O nor the other reactants show any significant absorbance at this wavelength. To measure the rate at which the hydroxide ion removes a proton from nitroethane (that is, the rate at which the nitroethane anion is formed), the UV spectrophotometer is now adjusted to measure absorbance as a function of time instead of absorbance as a function of wavelength. Nitroethane is added to a quartz cell containing a basic solution, and the rate of the reaction is determined by monitoring the rate of increase in absorbance at 240 nm (Fig. 2.9).

The p*Ka* of a compound can be determined by UV/Vis spectroscopy provided either the acidic form or the basic form of the compound absorbs



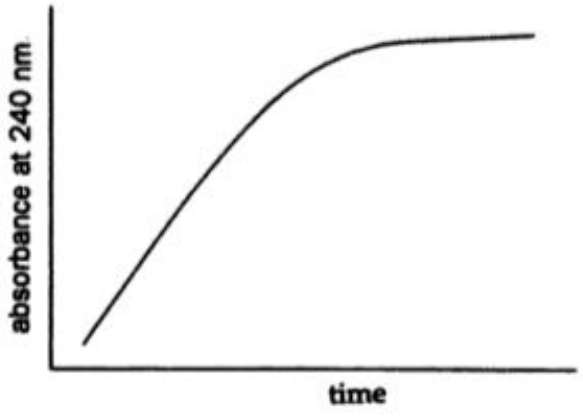


Fig. 2.9

UV or visible light. Consider the phenolate ion, it has a λ_{max} at 287 nm, if the absorbance at 287 nm is measured as a function of pH, the pKa of phenol can be known by determining the pH at which exactly one-half the increase in absorbance takes place (Fig. 2.10). At this pH, half of the phenol is converted into phenolate ion, therefore, this pH represents the p*Ka* of the compound. From the Henderson-Hasselbalch equation, one knows that the p*Ka* of the compound is the pH at which half the compound exists in its acidic form and half exists in its basic form.

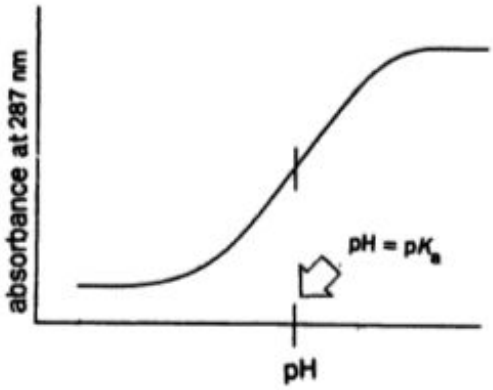
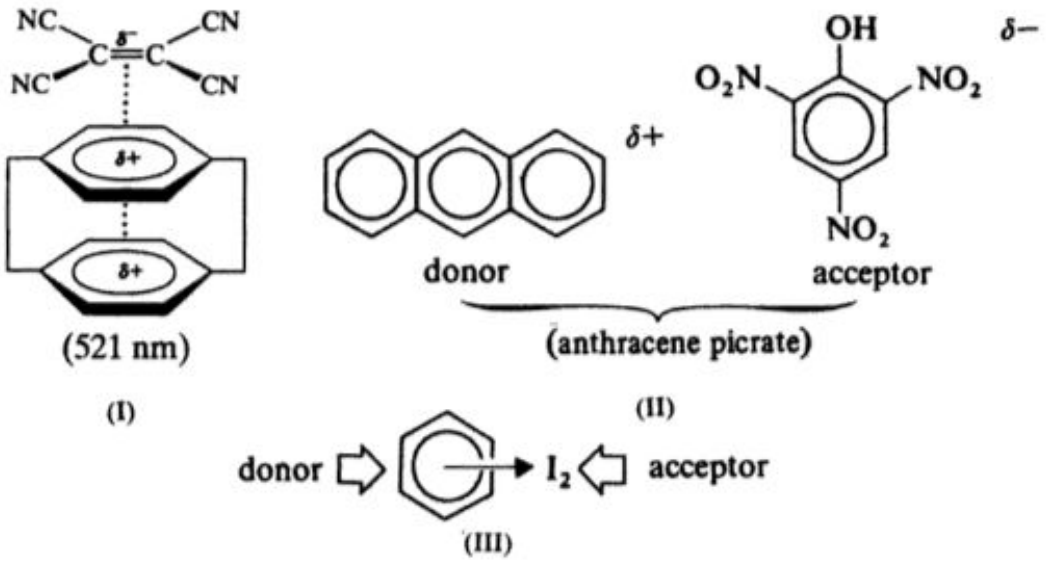


Fig. 2.10

2.14 STUDY OF CHARGE TRANSFER COMPLEXES

In these complexes, better called *EDA* complexes (Electron donor-acceptor complexes) the donor may donate an unshared pair or a pair of electrons in a π orbital of a double bond or an aromatic system. The evidence for the formation of these type of complexes is electronic spectroscopy. Such complexes generally display a spectrum (a charge-transfer spectrum) which is not the sum of the spectra of the parent individual molecules. These complexes are often coloured since the first excited state of the complex is relatively close to the ground state, consequently there is usually a peak in the visible or near UV region. Thus the colourless components TCNE and paracyclophane give a coloured complex λ_{max} 521 in CH_2Cl_2 (*I*, Scheme 2.30). Another example of such a complex is the formation of a picrate between picric acid and, *e.g.*, an aromatic hydrocarbon like anthracene (*II*, Scheme 2.30).

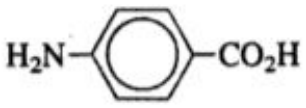
Lastly mention may be made of complexes in which the acceptor is, *e.g.* iodine which accepts electrons from, *e.g.*, benzene, probably via the expansion of the outer shell to hold on to 10 electrons. For the reason of complex formation iodine losses its purple colour in benzene (III, Scheme 2.30).



Scheme 2.30

2.15 USE OF SUNSCREENS

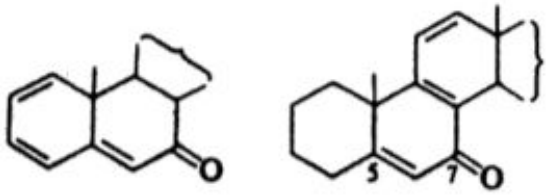
Simple substituted benzenes absorb between 250 and 290 nm (see Table 2.9). The water soluble *p*-aminobenzoic acid (PABA) has a λ_{max} at 289 nm with a high extinction coefficient of around 19,000. Due to this property PABA is used in many sunscreen lotions to protect the skin from potential cancer-causing high energy UV radiation.



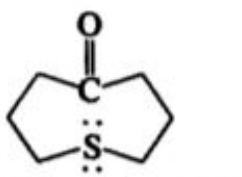
p-aminobenzoic acid
(PABA)
λ_{max} = 289 nm

EXERCISES AND PROBLEMS

1. (a) On the basis of Woodward rules, calculate the expected position of the absorption maximum in the following trienones I and II. How you compare the calculated value with the observed values of λ_{max} 230 nm (ε18,000); 278 nm (ε 3720) and 348 nm (ε 11,000) in the case of I and at λ_{max} 256 nm and 327 nm in the case of II.



(I) (II)

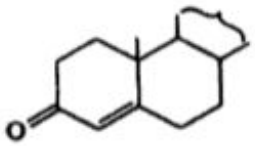


λ_{max} 238 nm, ϵ_{max} 2535

(III)

(b) The medium ring compound III shows λ_{max} 328 nm ε_{max} 2535 explain.

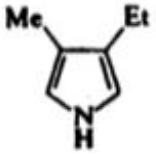
2. Cholest-4-en-3-one gives an enol acetate which has λ_{max} at 238 nm. Suggest the structure for the enol ester.



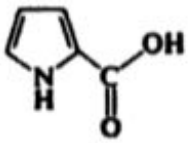
$(CH_3CO)_2O$ → The enol acetate

Cholest-4-en-3-one

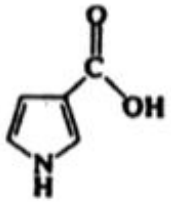
3. The pyrrole derivatives (I-III) show the indicated wavelength of absorption, explain.



(I)
λmax 203nm,
ε = 5670

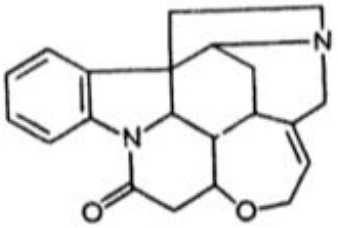


(II)
λmax 262nm,
ε = 12,000

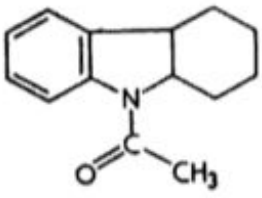


(III)
λmax 245nm,
ε = 4,800

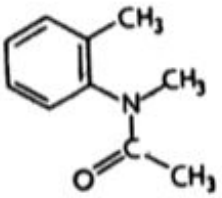
4. The absorptions by the essential chromophoric elements present in strychnine (IV) are compared with those present in two model compounds (V) and (VI). Comment on the structure and absorption.



(IV)
$\lambda_{max}(\varepsilon_{max})$ 257(16,000)
281(4200)
290(3400)

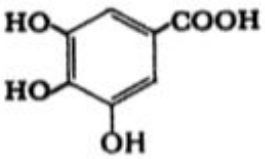


(V)
257(16,000)
281(3700)
290(3400)

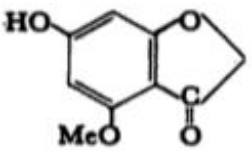


(VI)
270(300)

5. Calculate λ_{max} for the benzene derivatives (VII and VIII).



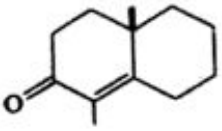
(VII)



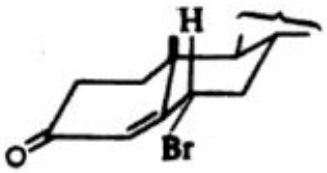
(VIII)

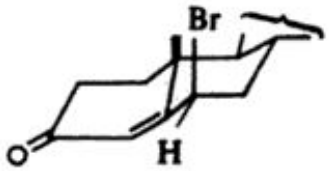
6. Which structure features may produce a bathochromic or a hypsochromic effect in an organic compound.

7. Aniline absorbs at 230 nm (ε 8600), however, in acid solution the main absorption band is seen at 203 nm (ε 7500) and is comparable with benzene. Explain.
8. Explain the substitution pattern on the following enone and calculate the position of *K*-band.

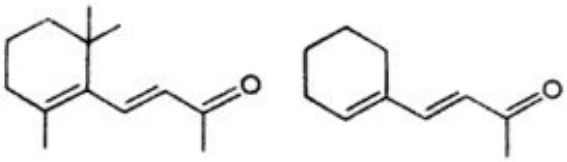


9. How ultraviolet spectroscopy can be used to distinguish between the equatorial and axial conformations shown below.



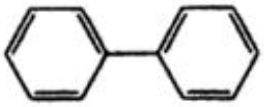


10. The position of absorption of acetone shifts in different solvents: 279 nm (hexane); 272 nm ethanol and 264.5 (water). Explain.
11. How the uv spectral data λ_{max} 296 nm, ε_{max} 10,700 and λ_{max} 281 nm, ε_{max} 20800 help in deciding between structures (IX and X).

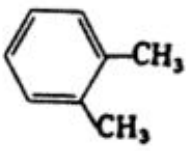


(IX) (X)

12. Which radiation, infrared or ultraviolet has (i) shorter wavelength, and (ii) lower energy?
13. What happens on absorption of infrared and uv radiation by a molecule.
14. What determines the wavelength of uv light absorption by an organic compound.
15. At what wavelength the coloured compounds absorb.
16. Which out of benzene (colourless) or quinone (yellow) has more easily promoted electrons.
17. Biphenyl shows the following uv absorption data. In its 2,2′-dimethyl derivative however, the absorption pattern becomes almost similar to *O*-xylene. Explain.



Biphenyl (planar conformation)
***K*-Band,λ_{max} 252nm,ε = 19,000**

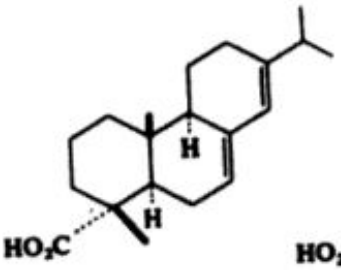


O-Xylene
λ_{max} 262nm,ε = 270

18. In the following compounds both the experimental as well as calculated λ_{max} values are given. Recalculate the expected λ_{max} for each compound and compare with the given values.

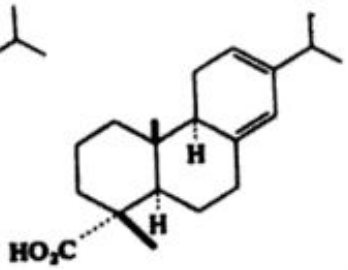
2,4(8)-*p*-Menthadiene

λ^{obs}_{max} = 243nm,
ε =18,000
λ^{calc}_{max} = 239nm



Abietic acid

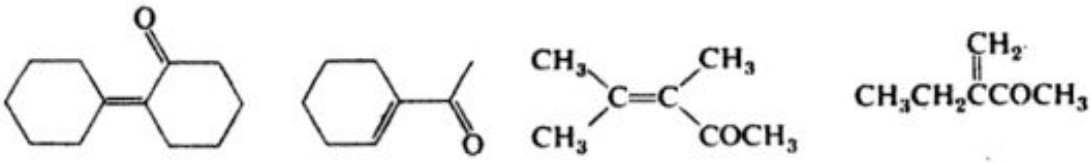
λ^{obs}_{max} = 241nm,
ε =26,200
λ^{calc}_{max} = 239nm



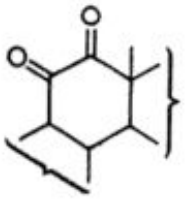
Laevopimaric acid

λ^{obs}_{max} = 272nm,
ε =6,300
λ^{calc}_{max} = 278nm

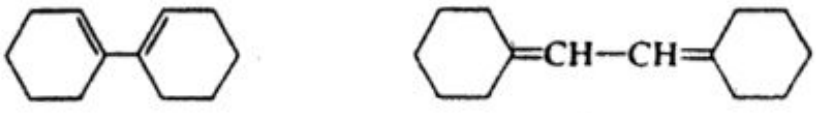
19. The labels fell off from the four bottles of ketones shown to have the structures shown below. Measurement of the ultraviolet spectra of the contents of the four bottles gave λ_{max} at 221, 249, 233 and 258 nm. Assign structures to the appropriate λ_{max}.



20. How will you confirm the presence of α-diketone system in the following steroid?

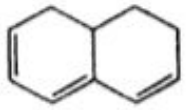


21. Why the λ_{max} for the diene (I) is observed at lower nm than (II).

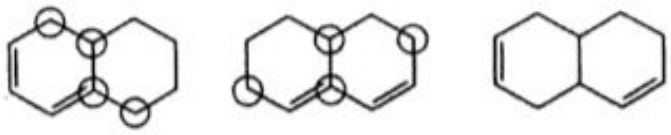


(I) (II)

22. The following triene on partial hydrogenation gives three products, which are separated by glc. How uv spectroscopy and application of Woodward-Fieser rules will help to identify the products.

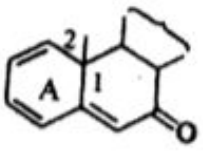


unknown structure $C_{10}H_{14}$



ANSWERS TO THE PROBLEMS

1. (a)



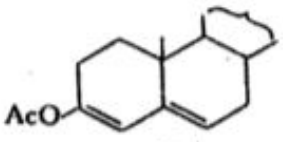
Parent value	215 nm
β-substituent 1	12 nm
ω-substituent 2	18 nm
2 × extended conjugation	60 nm
Homoannular diene component	39 nm
Exocyclic double bond (the αβ-double bond is exocyclic to ring A)	5 nm
Calc. λ_{max}	349 nm

In simple polyenes (Fig. 2.1) the long chromophore gives rise to several peaks. The longest wavelength peak (348 nm) in (I) is in excellent agreement with the predicted value.

Compound (II) is a cross-conjugated trienone, the main chromophore is the linear dieneone portion as the Δ^5-double bond is not in the longest conjugated system. The calculation gives a value of 324 nm. The observed value (256 nm) may be due to the Δ^5-7-one system (λ_{max} 244 nm, *i.e.*, 215 + 2 × 12 + 5).

(b) It is apparently a non-conjugated system, however, an effective overlap of the π orbital for the C=O group and the *p* (*n*)-orbitals of the heteroatom generates transannular conjugation.

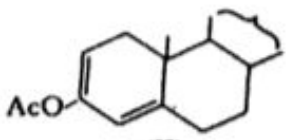
2. Of the two possible enol acetates I or II which can be formed, the structure must represent the heteroannular diene I on the basis of comparison with the position of calculated absorption maximum.



(I)

234 nm

Calc. λ_{max}



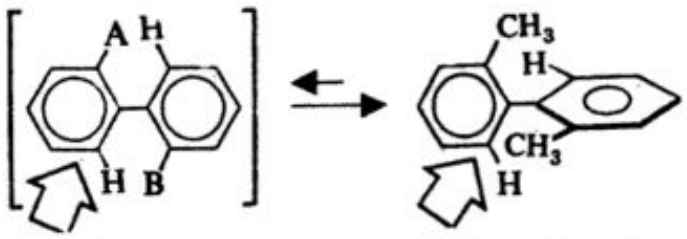
(II)

273 nm

3. A simple pyrrole (I) and a pyrrole with an electron withdrawing substituent (II and III) have strikingly different absorption maxima, since the conjugation present from the nitrogen lone pair through the pyrrole ring to the carbonyl group increases the

length of the chromophore and leads to longer wavelength absorption (compare with disubstituted benzenes, Sec. 2.10).

4. This is a case of twisting in a sterically-crowded molecule. Care must be exercised in the choice of model compounds for structural work. The necessary elements of the chromophoric group in strychnine (IV) are present in *N*-methylaceto-*O*-toluidide (VI). However, this compound is not useful as a model because the *O*-methyl substituent does not allow the acetyl and phenyl groups to adopt the same relative configuration as in (IV). The hexahydrocarbazole (V) has the correct configuration and its absorption is almost indistinguishable from that of (IV).
5. For VII, 285 nm and for VIII 269 nm, the observed values are 284 and 270 nm respectively.
6. A bathochromic shift (red shift) may occur by a change of medium or by the presence of an auxochrome. A hypsochromic shift (blue shift) may be caused by a change of the medium or by such structural changes like removal of conjugation.
7. Due to the removal of conjugation of the lone pair of electrons on the nitrogen atom of aniline with the π-bond system of the benzene ring on protonation.
8. One α-substituent, two β-ring residues and one exocyclic double bond: 215 + 10 + 24 + 5 = 254 nm.
9. The long wavelength band $n \rightarrow \pi^*$ (*i.e.*, *R*-band) of α, β-unsaturated ketones is influenced by the presence of a polar group in the γ-position. The effect of an axial substituent to displace the *R*-band to longer wavelength being greater than equatorial isomer (compare the α-substituted saturated ketones).
10. This is the expected shift of the $n \rightarrow \pi^*$ transition of acetone to shorter wavelength (blue shift) by changing to solvents of increased polarity.
11. The compound with λ_{max} 296 nm has almost one half intensity, *i.e.*, ε_{max} 10,700 of this band than the other compound. This decrease in intensity is the result of steric hindrance by methyl group and its effect on the absorption of conjugated systems. Thus the compound with decreased intensity of the *K*-band is (IX).
12. The wavelengths of uv light are shorter than infrared radiation and the latter is relatively low energy radiation.
13. Absorption of infrared radiation by a molecule results in increased vibrations of covalent bonds (2-12 kcal/mole) while absorption of uv light results in electronic transitions; promotion of electrons from low energy ground state orbitals to higher energy excited state orbitals (40-70 kcal/mole).
14. The case of electron promotion. If a molecule requires more energy for electron promotion light of shorter wavelengths will be absorbed. Molecules which require less energy absorb at longer wavelengths.
15. Longer than 400 nm.
16. Quinone.
17. Although biphenyl is slightly twisted, the angle of twist is small, therefore, conjugation between the rings is not affected. Biphenyl thus shows a very intense absorption band at 252 nm (*K*-Band). Biphenyl derivatives with bulky substituents in the *ortho* positions are more stable in twisted conformations than in the planar conformation, which suffers serious non-bonded compressions from the juxtaposed substituents. The loss of conjugation in the twist conformation of 2,2-dimethylbiphenyl is reflected in its uv spectral data, which now structurally is like two moles of *O*-xylene.



Planar conformation (A=CH_3 and B=CH_3) 2,2'-Demethylbiphenyl

Twist conformation 2,2'-Demethylbiphenyl

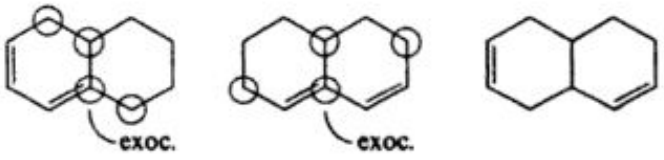
B-Band, λ_{max} 270nm, ε = 800

19. (Hint) The first compound from left hand side is expected to show its λ_{max} at 259 nm. Base value 215; for one α-alkyl substituent add 10 nm for two β-alkyl groups add 2 × 12 nm; for a double bond exocyclic to two rings add 10 nm; (215 + 10 + 24 + 10 = 259 nm).
20. It will largely exist in the enolic form as revealed by the observed λ_{max} 281 nm (ε_{max} 9,700) which matches with the cal. λ_{max} (on enolisation the double bond becomes exocyclic to one ring). On acetylation the spectrum is restored to that calculated for the system now with OAc in the α-position. Further confirmation will come from the measurement of the spectrum of the enolised form in alkaline solution which will show the expected bathochromic shift of some 50 nm, *i.e.*, 281 nm → 330 nm.

λ_{max}^{obs} = 281 nm (ϵ_{max} 9700)

λ_{max}^{calc} = 215 + 2 × 12 + 5 + 35 = 279 nm (215 + 2 × 12 + 5 + 6 (OAc) = 250 nm

21. In both the dienes, there are 4 ring residues as substituents. In diene (II), the two double bonds are exocyclic, thus in it λ_{max} will be higher by 2 × 5 = 10 nm.
22. The markedly differed values are expected from each of the structures.



base value:	253 nm	217 nm	<200 nm
alkyl groups × 5:	15	15	(not conj.)
exocyc. C=C × 5:	5	5	
expected λ_{max}:	273 nm	237 nm	<200 nm

SUMMARY

1. Range of electronic spectroscopy, 200-400 nm; ultraviolet, 400-800 nm, visible.
2. A chromophore is a covalently unsaturated group (*e.g.*, C=C, C=O, NO) responsible for electronic absorption. An auxochrome is a saturated group with nonbonded electrons (*e.g.*, OH, NH_2 and Cl) which, when attached to a chromophore, changes the wavelength as well as the intensity of an absorption.
   A bathochromic shift (red shift) is the shift of absorption to a longer wavelength while a hypsochromic shift is the shift of absorption to a shorter wavelength (a blue shift).
3. Absorption of ultraviolet (200-400 nm) light leads to electronic transitions, *i.e.*, promotion of electrons from the ground-state orbitals to orbitals of higher energy. In the lowest energy transition, an electron is promoted from the highest occupied molecular orbital (HOMO) of a molecule to the lowest unoccupied molecular orbital (LUMO). Extended conjugation decreases the HOMO-LUMO energy difference and consequently λ_{max} is shifted to longer wavelengths. With extensive conjugation (as, *e.g.*, is present in lycopene) the HOMO-LUMO energy gap becomes so small that the compound has its λ_{max} in the visible range of the spectrum. The wavelength λ of absorption is inversely proportional to the energy required.
   The uv spectrum is a plot of absorbance *A* or molar absorptivity ε vs λ, where $\varepsilon = A/cl$. The position of maximum absorption is recorded as λ_{max}.
   The important electronic transitions are $\pi \rightarrow \pi^*$ for conjugated systems and $n \rightarrow \pi^*$. Increasing amount of conjugation results in the shift of λ_{max} toward longer wavelengths. Compounds which absorb at wavelengths longer than 400 nm appear coloured. An $n \rightarrow \pi^*$ transition requires less energy than a $\pi \rightarrow \pi^*$ or a $\sigma \rightarrow \sigma^*$ transition.
4. A low priced and a good solvent for uv spectroscopy is 95 per cent ethyl alcohol, which is transparent down to about 210 nm. Commercial absolute ethanol contains residual benezene which absorbs in the ultraviolet.
5. The transitions of polar bonds like carbonyls, but not ethylenes, are affected by solvent polarity. As solvent polarity is increased $\pi \rightarrow \pi^*$ bands undergo red shifts and $n \rightarrow \pi^*$ bands undergo blue shifts.
6. $n \rightarrow \pi^*$ Band (*R*-Band) of ketones ε 10-100, 270-330 nm, for both saturated and α, β-unsaturated ketones is one of the most important of the weak absorption bands. Its measurement requires concentrated solutions and is difficult due to the presence of nearby bands with large ε values. However, *R*-Bands are frequently important for diagnostic purposes. They are further characterised by hypsochromic or blue shift with an increase in solvent polarity.
7. The organic molecules, *e.g.*, butadiene and mesityl oxide with conjugated π-systems display *K*-bands which are due to $\pi \rightarrow \pi^*$ transitions. The aromatic molecules like, styrene, benzaldehyde or acetophenone with chromophoric substitution also show *K*-bands. These $\pi \rightarrow \pi^*$ transitions have normally high molecular absorptivity, ε_{max} more than 10,000.
   The *K*-bands ($\pi \rightarrow \pi^*$ transitions) of enone systems undergo a bathochromic shift on increasing solvent polarity while these bands of diene systems are not affected by change of solvent polarity.

8. In dienes and trienes the effect of substitution is additive and the position of λ_{max} can be predicted in open chain dienes and dienes in six-membered rings by applying Woodward-Fieser rules. The ε values are dependent on the square of the chromophore length and thus *trans*-diene maxima are more intense than those of *cis*-dienes, *i.e.*, ε for planar *S-trans* dienes: 25,000, ε for *S-cis* or homoannular dienes: 10,000-15,000. When planarity is destroyed by steric hindrance or by ring distortion, the following changes occur. Increase in ε; decrease in ε and blue shift in λ; and disappearance of conjugative effect. Calculations for homoannular dienes are only valid for six-membered rings.
9. In α, β-unsaturated aldehydes and ketones as well, the expected position of the maxima can be calculated from Woodward-Fieser-Scott rules.
10. Unlike dienes, the enone $\pi \rightarrow \pi^*$ maxima are dependent on solvent polarity. The following solvent corrections (nm) convert into value for ethanol; methanol 0; chloroform + 1; ether + 7; hexane + 11; water - 8; and dioxane + 5. For *s-trans* enones ε is usually > 10,000, while ε for *S-cis* enone is usually < 10000.
11. The presence of benzenoid bands (*B*-bands) point to the presence of aromatic or heteroaromatic system in an organic compound. Benzene, for example, shows a broad absorption band with fine structure between 230-270 nm. The *B*-bands shift to longer wavelengths than the more intense $\pi \rightarrow \pi^*$ transitions if a chromophoric group is present on the aromatic system. This is seen in the case of styrene ($\pi \rightarrow \pi^*$ transition, λ_{max} 224 nm, ε_{max} 12,000) and a *B*-band at λ_{max} 282 nm, ε_{max} 450.
12. Sharp peaks are seldom observed in an ultraviolet spectrum and instead, broad absorption bands are observed, because vibrational, and rotational effects are superimposed on the electronic transitions, so that an envelope of transitions arises.
13. Not all transitions from filled to unfilled orbitals are allowed, the symmetry considerations, *i.e.*, symmetry relationship between the two orbitals being important. When a transition is 'forbidden', the probability of that transition occurring is low, and consequently the intensity of the associated absorption band is also low.
14. The $n \rightarrow \pi^*$ transitions of aldehydes and ketones are "forbidden". These are weak UV absorptions with values of λ_{max} between 270-330 nm.

FURTHER READING

H.H. Jaffé and M. Orchin, *Theory and Applications of Ultraviolet Spectroscopy*, John Wiley and Sons, Inc. New York, 1962.

I.B. Lambert, H.F. Shurvell, L. Verbit, R.G. Cooks, and G.H. Stout, *Organic Structural Analysis*, Macmillan Publishing, New York, 1976.

CHAPTER 3 INFRARED SPECTROSCOPY (IR)

THIS IS one of the most widely used tools for the detection of functional groups in pure compounds and mixtures and for compound comparison. The spectrum is obtained in minutes using a few mg of the compound which can also be recovered.

3.1 INTRODUCTION

The advent of the instrumental methods like infrared has now made the task of an organic chemist comparatively simpler. Structural identification can now be achieved in a matter of weeks, or at the most months, of compounds of a complexity greater than those of the compounds which defied the life work of many of the great nineteenth and early twentieth century organic chemists. This becomes readily apparent by considering the examples of structure elucidation of camphor and cholesterol.

The correct empirical formula of camphor, $C_{10}H_{16}O$ (Scheme 3.16) was determined in 1833, but the structure was deduced sixty years later. During the period of this structure determination even the nature of oxygen function which could be now evident at once from the infrared spectrum as a ketone, was not known until 1883 when an oxime derivative was prepared.

The lengthy and laborious task of finding the size of alicyclic rings during the classical studies of structure elucidation in the case of steroids is cited as second example. This method involved the conversion of a steroidal ketone to a dicarboxylic acid with hot chromic acid followed by pyrolysis. The net result of such a reaction sequence was either a ketone or an anhydride. According to Blanc's rule, on pyrolysis, dicarboxylic acids in which the carboxylic groups are separated by one, two or three carbon atoms form anhydrides whereas those with longer intervening carbon chains form ketones. This process for the structure elucidation in case of cholesterol took several years and involved large quantities of cholesterol. Would a modern organic chemist apply these or similar techniques to solve a problem of similar or allied nature? The answer is no. An organic chemist would now determine the size of an alicyclic ring by creating a carbonyl

group on it and by determining the position of dependable and strong carbonyl stretching absorption in the infrared spectrum around 1700 cm^{-1} (Sec. 3.7, h). The same organic group in different compounds absorbs approximately in the same spectral region. As an example, the stretching frequency of a C=O group occurs around 1700 cm^{-1} and is not greatly dependent on the size and shape of the rest of the molecule, as seen in the case of cyclohexanone (Scheme 3.14), which absorbs at 1717 cm^{-1} and a steroidal six-membered ketone also absorbs around the same frequency.

In infrared spectroscopy the main preoccupation of an organic chemist is the region 4000-650 cm^{-1}. This is still the most readily examined region which covers the absorptions due to the fundamental vibrations of almost all the common functional groups of organic compounds. A further very important consequence is the fact that functional groups in organic compounds have absorptions which are characteristic not only in position but also in intensity. Highly polar groups like carbonyl, have stretching fundamentals with intensities of the order of several hundred units while C=C stretching in the case of, *e.g.*, a trisubstituted double bond may be even less than ten units. Therefore, a successful interpretation of an infrared spectrum is largely dependent on an appreciation of the intensities of the observed bands. It would thus be wrong to assign a minor band around 1700 cm^{-1} in the spectrum of a compound to the presence of a carbonyl grouping. Therefore, an intelligent interpretation of the spectrum becomes highly essential, which requires considerable practice derived from experience of interpreting spectra of known compounds. The clues thus obtained from the spectrum when wisely used can shorten dramatically the time required for the elucidation of structure.

3.2 ABSORPTION IN THE INFRARED REGION — THE CHART PAPER — PRESENTATION OF THE IR SPECTRA

In Chapter 2 it was seen that many organic compounds absorb light in the visible and ultraviolet regions of the electromagnetic spectrum when electrons are excited from lower energy molecular orbitals to higher ones. Organic compounds also absorb electromagnetic energy in the infrared region of the spectrum. Infrared radiation does not have sufficient energy to cause the excitation of electrons, however, it causes atoms and groups of atoms of organic compounds to vibrate faster about the covalent bonds which connect them. The vibrations are quantised and as they occur, the compound absorbs infrared energy in particular regions of the spectrum. The position of an infrared absorption band is specified in frequency units by its wavenumber $\bar{\nu}$ measured in reciprocal centimeters (cm^{-1}), or by its wavelength, λ, measured in micrometers (μm; old name micron, μ, eq. I).

$$\bar{\nu} = \frac{1}{\lambda} \text{ (with } \lambda \text{ in cm)} \quad \text{or} \quad \bar{\nu} = \frac{10{,}000}{\lambda} \text{ (with } \lambda \text{ in } \mu\text{m)} \qquad \text{(I)}$$

In an infrared spectrophotometer, infrared radiation of successively increasing wavelength is passed through the sample of the compound and the per cent transmittance measured. The format of the chart paper used in one model of an infrared spectrophotometer is shown (Fig. 3.1). An infrared spectrum is the graph of per cent transmittance versus either increasing wavelength or decreasing frequency. Infrared spectrum shows per cent transmittance versus frequency expressed as wavenumbers, which have the units of reciprocal centimeters (cm^{-1}), as well as may show per cent transmittance versus wavelength in microns (μ) or micrometers (μm).

Each dip in a spectrum called a band or peak, represents absorption of infrared radiation at that frequency by the sample. A 100 per cent transmittance means no absorption and if all the radiation is absorbed the transmittance is 0 per cent.

Many of the vibrational modes in the *finger print region* depend on complex vibrations involving the entire molecule, it is impossible for any two different compounds (except enantiomers) to have precisely the same infrared spectrum. In fact, this region from 1500 to 500 cm^{-1} is called the fingerprint region (which is normally scanned up to around 600 cm^{-1}) because the pattern of absorptions in this region are unique to any particular compound, just as a person's fingerprints are unique.

The scale of the spectrum may not be entirely linear and many modern IR spectrophotometers give plots where at 2000 cm^{-1}, the scale is doubled. Thus the peaks from 2000-4000 cm^{-1} occupy lesser space of the plotted chart than the peaks in the 600-2000 cm^{-1} range. This is done to have greater detail in the fingerprint region.

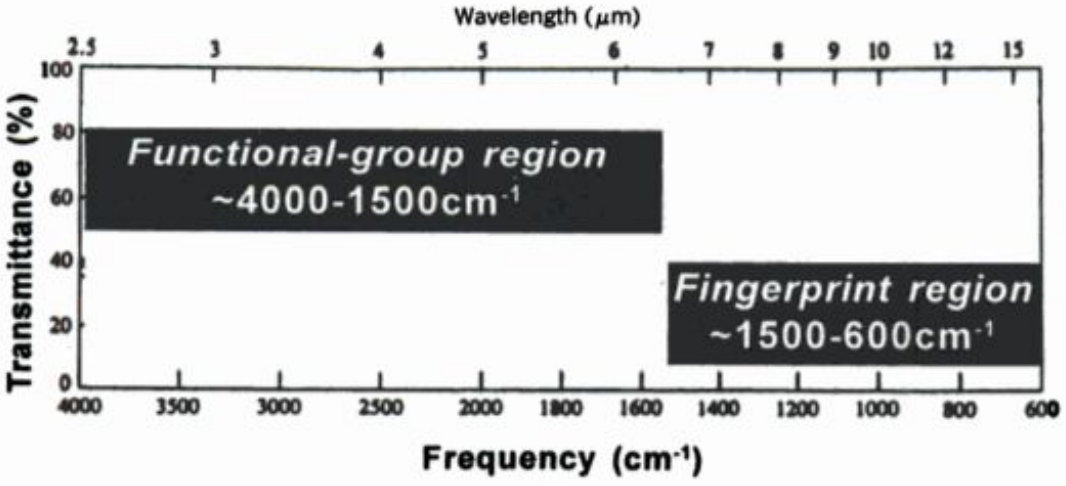


Fig 3.1

The infrared region constitutes three parts (Fig. 3.2); the near infrared, the middle infrared and the far infrared. The near infrared region corresponds to energies in the range 37-10 kcal mole^{-1}. As there are few absorptions of organic molecules in this range, it is of little use for spectroscopic purposes. Radiation in the middle infrared region has E = 10-1 kcal mole^{-1}, which corresponds to the differences commonly observed between vibrational states.

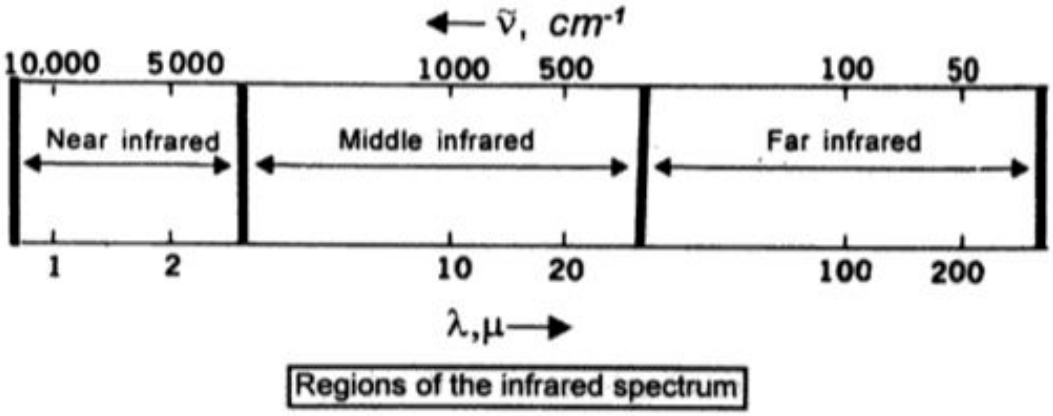
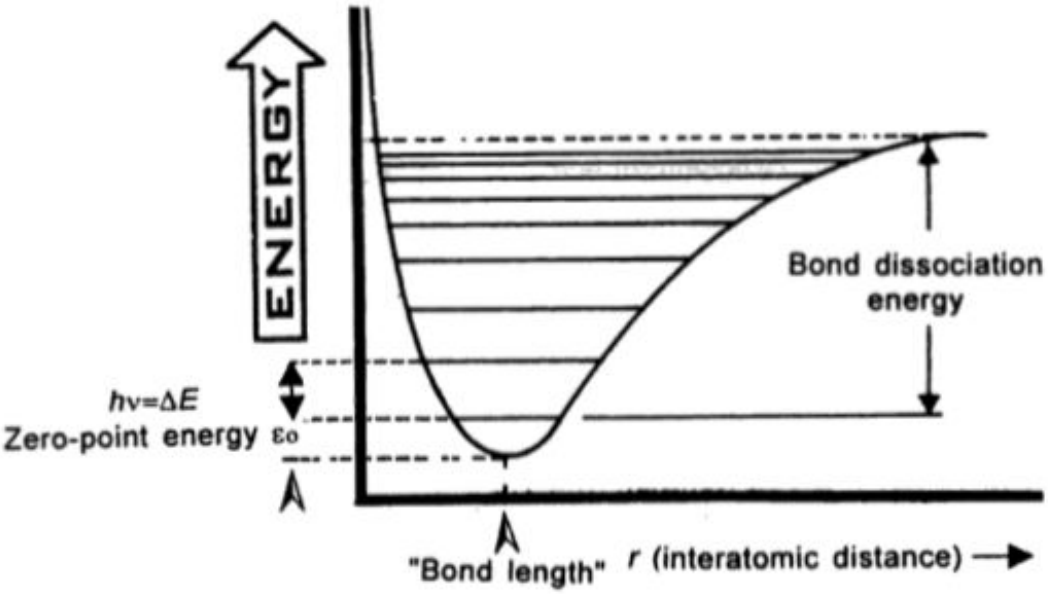


Fig. 3.2

Spectroscopy in this region (usually 4000-650 cm^{-1}) is extremely useful for the study of organic compounds. The far infrared region has E = 1.0 – 0.1 kcal mole^{-1}. This region is also of not much use for organic spectroscopy since only few useful absorptions occur here.

3.3 MOLECULAR VIBRATIONS — COMPLEXITY AND SIMPLICITY OF IR SPECTRA

(i) Vibrational Motion is Quantised. In their vibrations covalent bonds behave as if they were tiny springs connecting the atoms. Atoms in a molecule do not remain at fixed positions with respect to each other, but actually vibrate back and forth about an average value of the interatomic distance (Fig. 3.3a). This vibrational motion is quantised, as shown (Fig. 3.3) for a diatomic molecule. At room temperature most of the molecules in a given sample are in the lowest vibrational state. However, on absorption of light of the appropriate energy the molecule becomes "excited" to the second vibrational level. In this level the amplitude of the molecule vibration is greater. Generally, such absorption of an infrared light quantum can occur only if the dipole moment of the molecule is different in the two vibrational levels. In summary, when the atoms vibrate they can do so only at certain frequencies as if the bonds were "tuned". Consequently covalently bonded atoms have only particular vibrational

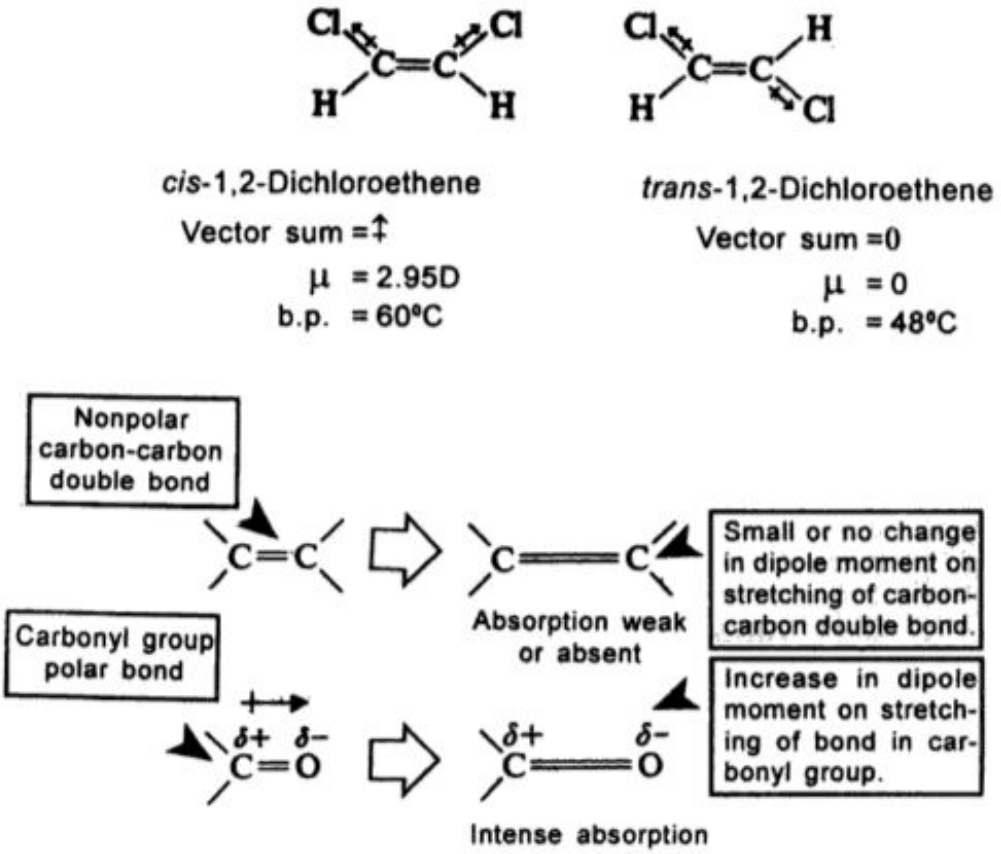


Vibrational levels for vibrating bond.
Horizontal lines represent the various vibrational energy levels

Fig. 3.3

energy levels, *i.e.*, the levels are quantised. For the excitation of a molecule from one vibrational energy level to another, the molecule has to absorb IR radiation of a particular energy (*i.e.*, radiation of particular wavelength or frequency).

(ii) Change in Dipole Moment and Infrared Spectra. In general, molecular vibrations which will lead to a change in the dipole moment of the molecule will give rise to absorption bands in the infrared. Otherwise, they are said to be infrared inactive and will show no absorption. For example, the symmetrical stretching of the C=C bond in ethylene (a molecule with a centre of symmetry) will not produce a change in the dipole moment of the molecule. Therefore this mode of vibration is, infrared inactive. This also explains why *trans* dichloroethylene shows no C=C stretching whereas the *cis* isomer shows this band. It must be emphasised that both isomers show bands for C—H and C—Cl stretchings (Scheme 3.1). Carbon monoxide (C≡O) and iodine chloride (I—Cl) absorb infrared light, but hydrogen (H_2), nitrogen (N_2), chlorine (Cl_2) and other symmetrical diatomics do not. A large change in dipole moment will usually give rise to strong absorption. Accordingly, bands of hydrocarbons which are only composed of carbon and hydrogen atoms are weak, whereas bands associated with bonds connecting atoms differing considerably in electronegativity, *e.g.*, C=O are usually quite strong (Scheme 3.1). Vibrational modes which are IR inactive may give rise to observable bands in the Raman spectra (*i.e.*, they may be Raman active). Laser Raman



Scheme 3.1

spectroscopy is an important tool to supplement the structural information available from IR spectroscopy.

The symmetrical C=O stretching of carbon dioxide is infrared inactive while the bending modes are identical. Their vibrations appear in the same position in the spectrum (degenerate).

Bonds with zero dipole moments sometimes give weak absorptions, since molecular collisions rotations and other vibrations make them unsymmetrical, part of the time.

(iii) Fundamental Vibrations—Water and Carbondioxide—Degenerate Vibrations. The simplest vibration motions in molecules giving rise to absorption of infrared radiation are stretching and bending. A non-linear molecule with n atoms generally has $3n$-6 fundamental vibrational modes. Methane, then, has $3(5) - 6 = 9$ fundamental modes, and ethane has $3(8) - 6 = 18$ fundamental modes. Many of these vibrations occur at the same frequency and are therefore ''degenerate'' so all the possible peaks are not seen as independent absorptions.

Consider the three fundamental vibrational modes of non-linear triatomic water molecule (Fig. 3.3a). The two O—H bonds can stretch in phase with each other (symmetric stretching), or they can stretch out of phase (anti-symmetric stretching). The H—O—H bond angle can also

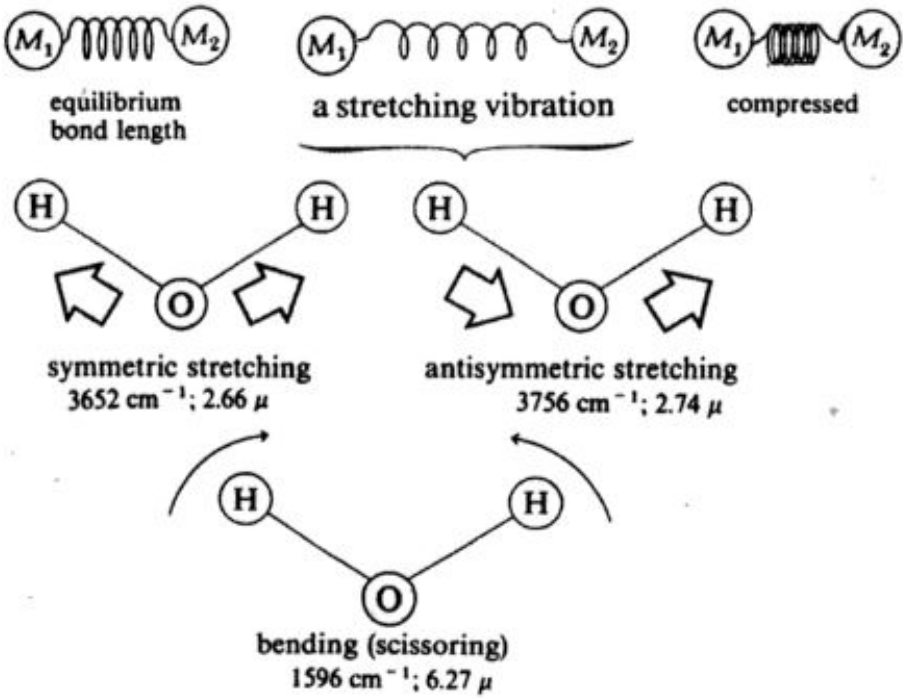


Fig. 3.3a

change in a bending vibration, making, *e.g.*, a scissoring motion. Other bending modes are twisting, rocking, etc. (See Fig. 3.4).

Linear molecules, *e.g.*, CO_2 have $3n$-5 vibrational degrees of freedom and CO_2 with three atoms, thus, has four fundamental vibrations [(Scheme 3.1a, $3 \times 3 - 5 = 4$)]. The stretching and bending vibrations of interest for

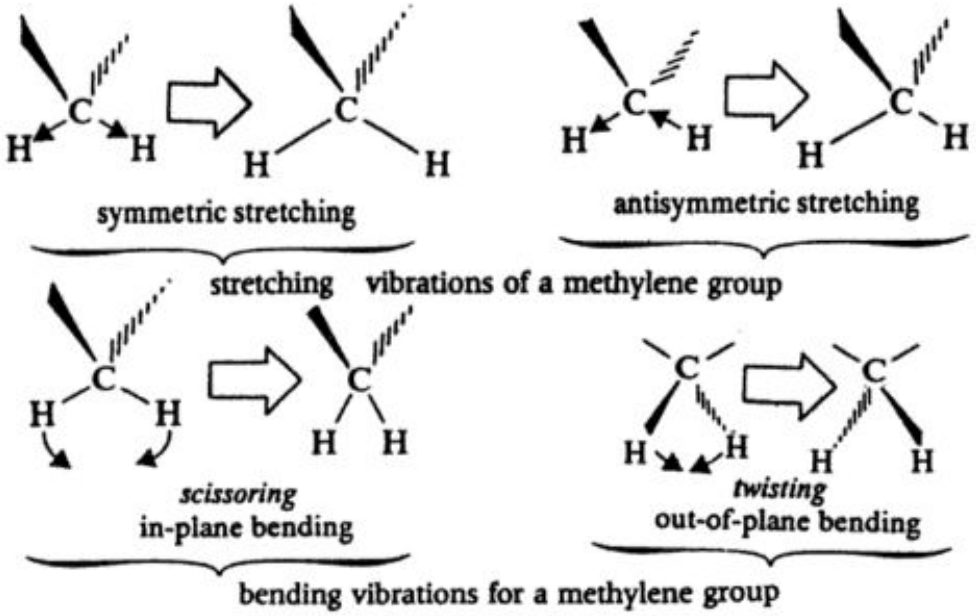
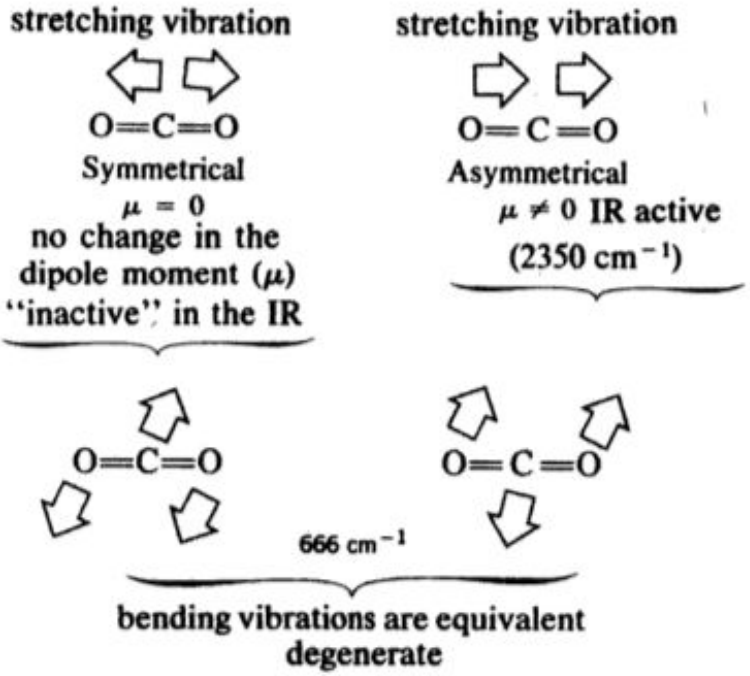


Fig. 3.4



Scheme 3.1a

infrared spectroscopy for two atoms joined by a covalent bond around tetrahedral carbon are shown (Fig. 3.4). In stretching the distance between two atoms increases or decreases, however, the atoms remain in the same bond axis. These vibrations require higher energy and occur at higher frequency. In bending or deformation the distance between two atoms remains constant, but the positions of the atoms may change with respect to the original bond axis. This type of vibration requires lower energy and occurs at lower frequency.

The stretchings of aldehyde carbon hydrogen bond and C=O for a saturated aldehyde are shown (Fig. 3.5) along with their intensity in the infrared spectrum.

When one looks to the entire spectrum of the aldehyde (Fig. 3.5), it is immediately apparent that things are not as simple as expected. Clearly, several bands can be seen distinctly, while some of these appear as poorly resolved shoulders. The primary reason for the complex nature of the infrared spectrum is the possibility of a variety of vibrations in a molecule, many of these vibrations are mechanically coupled. The molecule which absorbs infrared light undergoes not only stretching but also various bending motions and combinations of the two as well.

As the first complication in the IR spectrum of the aldehyde (Fig. 3.5) one considers Fermi resonance (See, Sec. 3.3, vii) which will be discussed in detail *vide infra.*

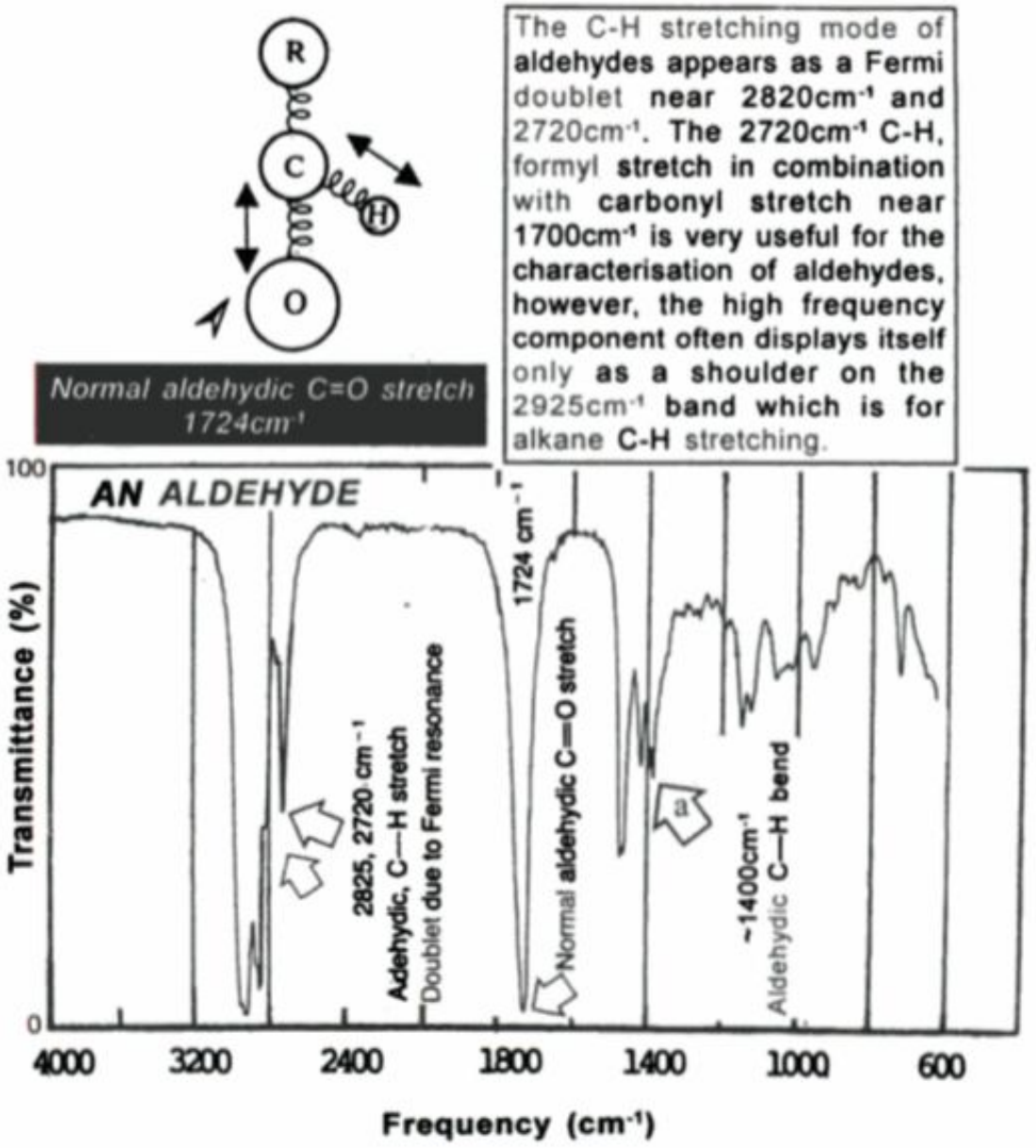


Fig. 3.5

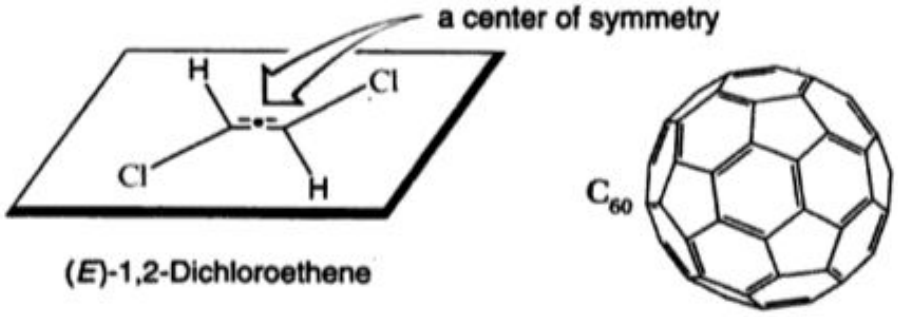
Normally aldehydes show aldehydic C—H stretching absorption in the 2850-2720 cm^{-1} region as medium intensity bands (two). The appearance of two bands is attributed to Fermi resonance between the fundamental aldehydic C—H stretch and the first overtone of the aldehydic C—H bending vibration which appears around 1400 cm^{-1}. Only one C—H stretching band is observed for aldehydes whose C—H bending band is shifted appreciably from 1400 cm^{-1}.

An absorption of medium intensity near 2720 cm^{-1}, accompanied by a carbonyl absorption band is good evidence for the presence of an aldehyde group.

To one skilled in the interpretation of infrared spectra the absorption patterns can yield an enormous amount of information about chemical structure. An organic chemist has neither the time nor the need to develop this level of understanding. The value of IR spectroscopy is generally to determine the presence and absence of characteristic functional groups. Thus, *e.g.*, a carbonyl group shows a strong absorption near 1700 cm^{-1}. Then it is followed to know its exact position so as to assign it to an aldehyde or a ketone; a carboxylic acid; an ester or if a ring then on the size of the ring.

(iv) Symmetry and Infrared Spectra. Majority of organic compounds have little or no symmetry. Molecules with high symmetry have simple infrared spectra. If a molecule has a centre of symmetry, it has no permanent dipole moment and therefore, a vibration that is symmetric does not generate an oscillating dipole. This vibration does not absorb in the infrared (inactive vibration). Thus *trans*-dichloroethylene (with a centre of symmetry does not show a C=C stretch, see Scheme 3.1). In (*E*)—1,2-dichloroethene (Scheme 3.1b) the centre of symmetry is located at the midpoint of the carbon-carbon double bond. A centre of symmetry is a central point within a molecule through which all the atoms or groups of atoms can be interchanged to give the original molecule. Because of its high symmetry Buckminsterfullerene (C_{60}) has only four absorption bands in its IR spectrum. Its ^{13}C NMR spectrum is even simpler, consisting of a single peak at δ 143.2 to show that all 60 carbons are identical.

When all the four hydrogen atoms of methane vibrate symmetrically, methane does not absorb infrared radiation.

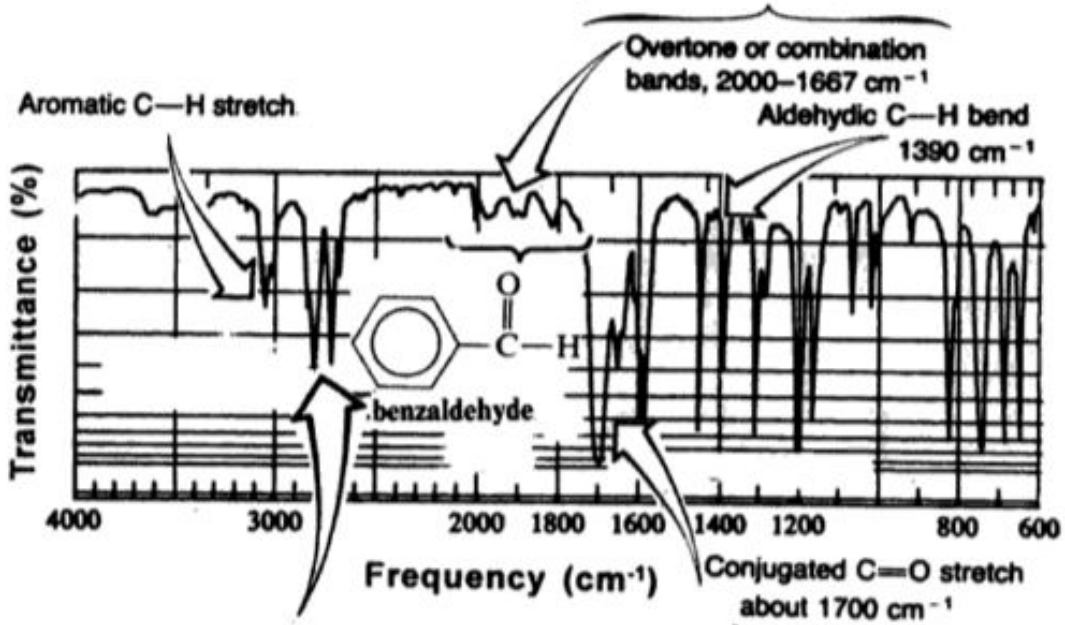


(*E*)-1,2-Dichloroethene

Scheme 3.1b

(v) Overtone Peaks and Combination Bands. Most of the vibrations which are discussed in this book are called fundamental vibrations, which occur when a molecule absorbs IR radiation of appropriate energy needed to promote it from the ground state to its first vibrationally excited state. Other bands also occur, however, corresponding to excitation to the second, third, or even fourth excited states. These bands are called overtones,

which, however, are very weak, but these can be important for characterisation of certain classes of compounds, particularly, benzene derivatives. Thus compared to saturated aldehyde, a comparison of its IR spectrum (Fig. 3.5) with that of an aldehyde (Fig. 3.5a), the presence of weak overtone or combination bands from 2000-1667 cm^{-1} is sufficient to indicate the compound to be a benzene derivative. (The compound is benzaldehyde, other features in agreement with this structure are absorption above 3000 cm^{-1} for unsaturation at 1700 cm^{-1} conjugated C=O stretch and a band at 1390 cm^{-1} for aldehydic C—H bend.)



Aldehydic C—H stretch as a Fermi doublet 2825cm^{-1} and 2720cm^{-1}. In this purely aromatic aldehyde, the 2825cm^{-1} band is clearly seen (and is not as a shoulder see Fig 3.5), since now there is no overlap with other CH strentching band around 2925cm^{-1}). The doublet is due to Fermi resonance between the overtone of the aldehydic C—H bending which would have a frequency near 2x1400cm^{-1} and the aldehydic C—H mode near 2720cm^{-1}.

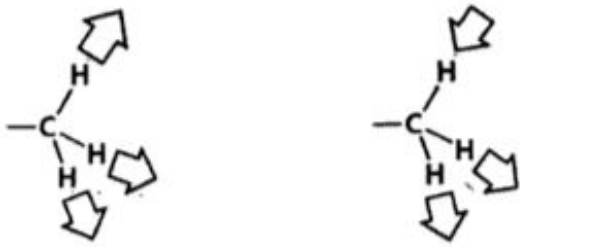
Fig. 3.5a

Thus the theoretical fundamental vibrations (absorption frequencies) are only seldom observed. The complexity of vibrational modes, due to overtone peaks and coupling peaks make the interpretation of most infrared spectra difficult. The overtone peaks are higher frequency harmonics of fundamental vibrations and display themselves at or near integral multiples of the fundamental vibration (*e.g.*, see Fig. 3.10). Thus, *e.g.*, an infrared absorption at 600 cm^{-1} may well have weaker overtone peaks near 1200 cm^{-1}, 1800 cm^{-1}, 2400 cm^{-1} and so on.

[*Overtones may arise in two ways. When a molecule in the lowest or first vibrational state is excited to the third vibrational level, the energy*

needed is almost twice that required for excitation to the second vibrational level. It is not exactly twice as much since the higher levels tend to lie closer together than the lower levels (see Fig. 3.3). Another type of overtone, commonly called a "combination band" occurs when a single photon has precisely the correct energy to excite two vibrations at once. For this to happen, the energy of the combination band must be the exact sum of the two independent absorption].

(vi) Coupled Vibrations. Vibrational coupling takes place between two bonds (through a common atom) vibrating with similar frequency, provided that the bonds are reasonably close in the molecule; the coupling vibrations may both be fundamentals or a fundamental vibration may couple with the overtone of some other vibration. The latter coupling is often called Fermi resonance, after E. Fermi, who discovered it. For a methyl group, the three hydrogen atoms all have the same mass, and the C—H bonds are all of similar strength, so the vibrations will not be independent. Instead, the vibrational modes are coupled and appear as symmetric and anti-symmetric CH_3 stretching vibrations (Scheme 3.1c, also see Sec. 3.7b).



Scheme 3.1c

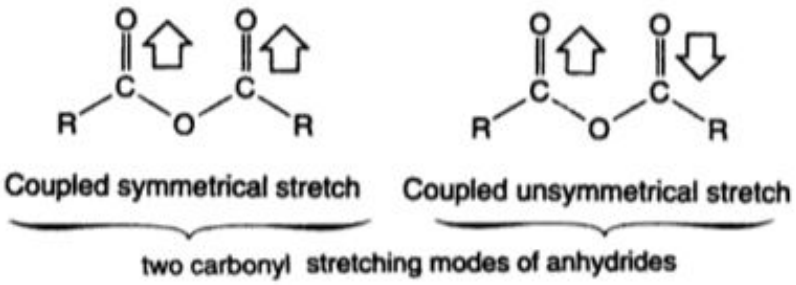
Coupled vibrations within a group of three atoms (rather than four as for methyl group) is even more common and the examples include, the methylene group —CH_2-; nitro —NO_2 and amino groups —NH_2. Each group displays two bands corresponding to symmetric and anti-symmetric stretching modes (anti-symmetric usually being of higher frequency).

Carbon dioxide molecule has two C═O bonds with a common carbon atom (Scheme 3.1a). It has two fundamental stretching vibrations; and absorption (2350 cm^{-1}) occurs at a wavelength longer than that observed for the carbonyl group in an aliphatic ketone (around 1715 cm^{-1}). This difference in carbonyl absorption frequencies displayed by the carbon dioxide molecule results from strong coupling or interaction. In contrast, two ketonic carbonyl groups separated by one or more carbon atoms show normal carbonyl absorption (1715 cm^{-1}) since coupling is now prevented by the intervening carbon atoms.

Coupling is useful for the detection of:

(A) ***Primary amines and primary amides via two coupled N—H stretching bands*** (see Figs. 3.21-3.23 and 3.24).

(B) ***Carboxylic anhydrides via two C═O stretching absorptions*** (see Fig. 3.28). In the anhydrides, there are two carbonyl stretching frequencies and these two bands are not the result of independent stretching of the separate carbonyls since both symmetrical as well as unsymmetrical anhydrides show two C═O stretching bands. These two bands are caused by the coupled symmetrical and unsymmetrical stretching modes in these compounds (Scheme 3.1d).



Scheme 3.1d

(C) ***Nitro compounds, sulfones, carboxylate anions, etc.*** (see Table 3.1).

(D) ***Secondary amides — Amide III Band.*** Coupling also occurs between dissimilar modes such as stretching and bending vibrations when the frequencies of the vibrations are similar and the two groups involved are adjacent in the molecule. In secondary amides, *e.g.*, the C—N stretching vibrations is of a similar frequency to that of the NH bending mode. Interaction of these two vibrations of the C—N—H group gives rise to two bands in the spectrum one at a higher and one at a lower frequency than the uncoupled frequencies. These bands are known as amide II and amide III bands. (The C═O mode known as the *amide I band*). Thus amide II band (N—H bending) of secondary amides in dilute solutions displays in the region 1550-1510 cm^{-1}. The amide III band (C—N stretching) is seen as a weak band near 1250 cm^{-1} and both these bands are a result of coupling between N—H bending and C—N stretching of the C—N—H component.

In summary coupling of peaks results from the coupling of two vibrations by addition ($\bar{\nu}_1 + \bar{\nu}_2$) and by subtraction ($\bar{\nu}_1 - \bar{\nu}_2$) only certain combinations of these coupling vibrations are allowed, *i.e.*, only certain combinations are possible within the constraints of quantum mechanics.

(vii) Fermi Resonance. A special kind of coupling of a fundamental vibration with an overtone or combination, shifts, group frequencies and introduces extra bands. Generally an overtone or combination band is very weak in comparison with a fundamental (*e.g.*, see the weak overtone bands in the IR spectrum of benzaldehyde). However, on Fermi resonance since, there is sharing of intensity, the overtone can come out to be a strong band.

The infrared spectrum of benzoyl chloride shown partly in the C=O region (Fig. 3.5b) displays two bands in the carbonyl region at 1790 cm^{-1} and 1745 cm^{-1}. If this were an unknown compound,one might be misled to conclude that the compound has two non-adjacent carbonyl groups in the molecule. However, the lower frequency band is, in fact, due to the overtone of the CH bending mode at 875 cm^{-1} in Fermi resonance with the C=O stretching fundamental (see Fig. 3.34).

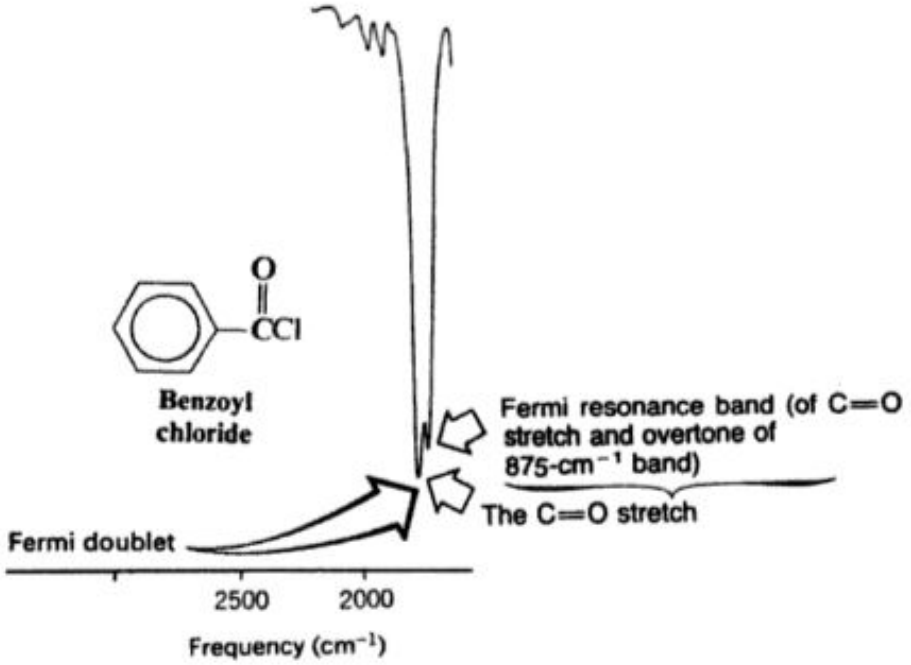


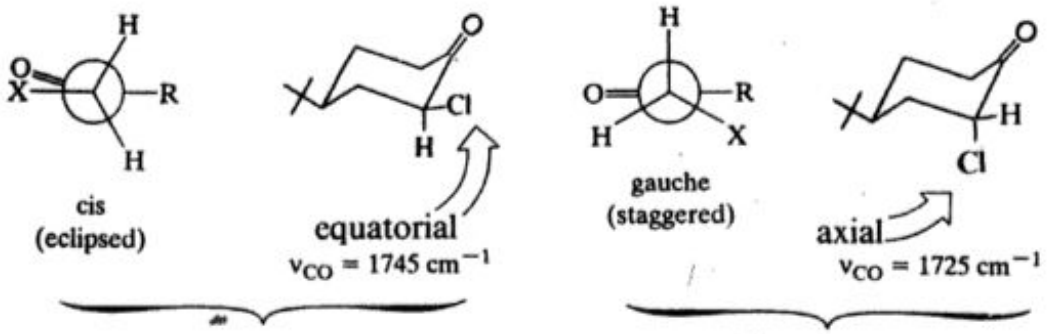
Fig. 3.5b

Another example of Fermi resonance is found in the spectrum of cyclopentanone (see Fig. 3.29).

The C—H stretching region of an aldehydic group provides another example of Fermi resonance (see Figs. 3.5 and 3.5a) by displaying a Fermi doublet.

(viii) Conformational Isomerism

(a) α-Haloketones. Due to rotational isomerism, in some compounds, *e.g.*, α-haloketones (Scheme 3.1e) two C=O stretching bands are observed. One of these bands is around the normal frequency, whereas the other is at

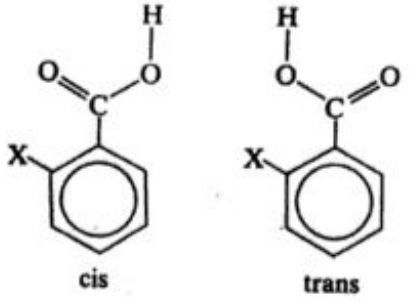


Scheme 3.1e

higher frequencies due to the eclipsed interaction between the halogen atom and the C=O group.

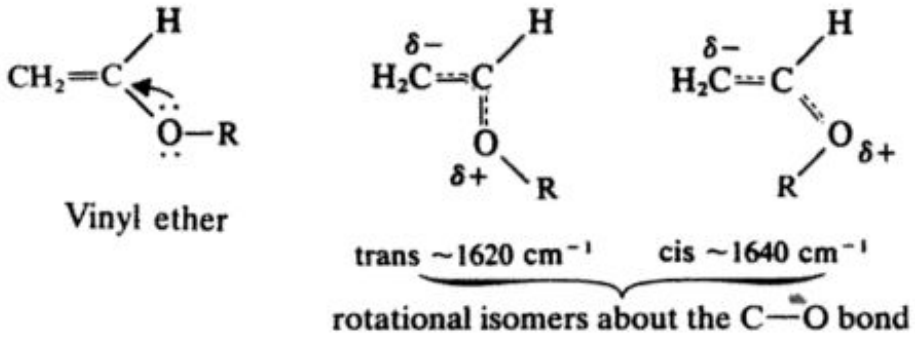
In α-halo-cyclohexanones two distinct carbonyl stretching frequencies can be seen. One band is found near 1745 cm^{-1}, due to the equatorial conformation, and a second band near 1725 cm^{-1} due to the axial isomer. The relative proportions of axial and equatorial forms change with phase, temperature, and solvent, and these changes can be studied in the vibrational spectra. In cyclohexanols, the equatorial C—OH stretching frequency is 1050-1030 cm^{-1}, while in the axial conformation the frequency is lowered by 30-10 cm^{-1}.

(b) O-Halogenated benzoic acids. In *ortho*-halogenated benzoic acids one can see two carbonyl stretching frequencies, due to the two rotational isomers (Scheme 3.1f) and these are named as *cis* and *trans* with respect to the halogen and C=O groups.



Scheme 3.1f

(c) Effect on C=C stretching and =C—H bending vibrations. Vinyl ethers also show two bands for their C=C stretching vibrations which are around 1640 cm^{-1} and around 1620 cm^{-1} and correspond to the presence of two rotational isomers. These bands show expected variations in their intensities with change in temperature. Due to coplanarity in the *trans* isomer (Scheme 3.1g) (maximum resonance) the double bond character of

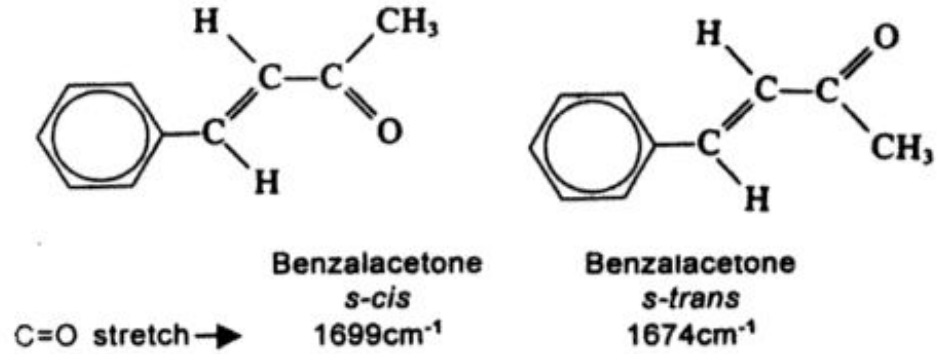


Scheme 3.1g

the alkene linkage is reduced. Steric hindrance reduces resonance in the *cis* isomer.

The two bands arising from =C—H bending vibrations in terminal alkenes occur near 1000 and 900 cm^{-1}. In the spectra of vinyl ethers, these bands are shifted to longer wavelengths due to resonance. In the case of vinyl ethers, the CH_2 bending band also displays itself as a doublet due to the presence of two different rotational isomers.

(d)* α, β-*Unsaturated Ketones. An α, β-unsaturated ketone may exist in s-*cis* or s-*trans* conformation. Steric effects (s-*cis* form) reduce the coplanarity of such systems, thereby reducing the effect of conjugation. Thus in several α, β-unsaturated ketones which exist in two conformations, the s-*cis* form absorbs at a higher frequency than the s-*trans* form. Thus benzalacetone is CS_2 at room temperature shows two bands due to the presence of both conformations (Scheme 3.1h, also see Scheme 3.12).



Scheme 3.1h

3.4 CALCULATION OF VIBRATIONAL FREQUENCIES

One may calculate the general region where a vibration will occur by using Hooke's law derived for the motions of a spring (eq. II, Scheme 3.2).

According to Hookes' law, the frequency of vibration is directly proportional to the square root of the force constant of the bond. The force constant is particular to and characteristic of a given bond. Like other physical constants of a compound, *e.g.*, melting point, it is yet another physical constant. The force constant may be linked to the stiffness, *i.e.*, strength of the spring. Moreover, the frequency is inversely proportional to the square root of the reduced mass, $(m_1 + m_2)/m_1 m_2$ of the system. Thus, greater the mass, the lower the frequency of absorption. Similarly, the stronger the bond, the greater will be the frequency of absorption. In short, one may expect some sort of correlation between infrared absorption frequencies and the nature of the chemical bond, *i.e.*, stronger the bond, more the amount of energy required to stretch it. One knows that wave numbers are proportional to energy, and thus, they provide information on bond strength as shown (Scheme 3.2a).

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{f(m_1 + m_2)}{m_1 m_2}} \qquad \text{II}$$

Hooke's law

$\bar{\nu}$ = vibrational frequency in cm^{-1} (wavenumber), c = velocity of light in cm sec^{-1}, m_1 = mass of atom 1 in g. m_2 = mass of atom 2 in g, and f = force constant in dyne cm^{-1} (g $séc^{-2}$). The equation corresponds to a simple model of two units coupled by a spring in which the force constant is the restoring force provided by the spring.

the general region in which the $^{12}C—^{1}H$ stretching frequency will occur is

$$\bar{\nu} = \frac{1}{2\pi\ 2.998 \times 10^{10}\ \text{cm sec}^{-1}} \times \sqrt{\frac{5.0 \times 10^{5}\ \text{g sec}^{-2}\left(\frac{12}{6.023} + \frac{1}{6.023}\right) \times 10^{-23}\ \text{g}}{\left(\frac{12}{6.023} \times 10^{-23}\ \text{g}\right)\left(\frac{1}{6.023} \times 10^{-23}\ \text{g}\right)}}$$

$$\bar{\nu} = 3032\ \text{cm}^{-1}$$

actual range for *C—H Stretching* is 2850-3000 cm^{-1}

Scheme 3.2

C≡C	C=C	C—C
$\bar{\nu}$ = 2150 cm^{-1}	1650 cm^{-1}	1200 cm^{-1}

C=O vs. C=S		C—H vs. C—D	
$\bar{\nu}$ = 1700 cm^{-1}	1350 cm^{-1}	3000 cm^{-1}	2200 cm^{-1}

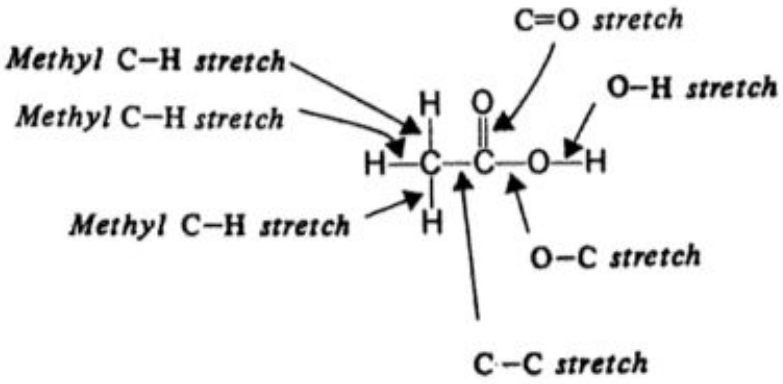
Scheme 3.2a

From a knowledge of bond dissociation energies, one knows that a C—H bond (104 kcal/mole, *i.e.*, 435 kJ/mole in methane) is only slightly stronger than a C—C bond (88 kcal/mole, *i.e.*, 368.2 kJ/mole, in ethane). Even then, the difference is nicely reflected in the stretching frequencies of these two bonds (Scheme 3.2a). From this simple picture using balls and springs two general and useful conclusions are drawn:

1. The frequency of a vibration will be directly proportional to the *strength* of the bond (the force constant). As expected, then, the stretching vibration of a triple bond will appear at a higher frequency than that of either a double or single bond (Scheme 3.2a).
2. The frequency of the vibration will be inversely related to the *masses* of the atoms bonded to one another. Thus, the heavier the atoms, the lower the frequency of the vibration will be (Scheme 3.2a).

In summary, the vibrational frequency of a bond is therefore, expected to increase, when the bond strength increases, and also when the reduced mass of the system decreases. One can thus generally predict that C=C and C=O stretchings will have higher frequencies than C—C and C—O stretchings, respectively. One also expects to find C—H and O—H stretching absorptions at higher frequencies than C—C and C—O stretchings. Similarly one would predict O—H stretching to be of higher frequency than O—D stretching. The stretching frequencies of groups involving hydrogen (a light atom) such as C—H, N—H and O—H all occur at relatively high frequencies.

One may use the equation (Hookes' law) to expect that every individual bond in a molecule may show a specific absorption band in the infrared spectrum. One may also predict the relative positions of these bands. For example, the stretching vibrations of various bonds (ignoring the bending vibrations) in acetic acid are presented (Scheme 3.2b). As the O—H bond strength is higher than C—H; thus, O—H stretching frequency is observed



Possible stretching vibrations in Acetic Acid
Scheme 3.2b

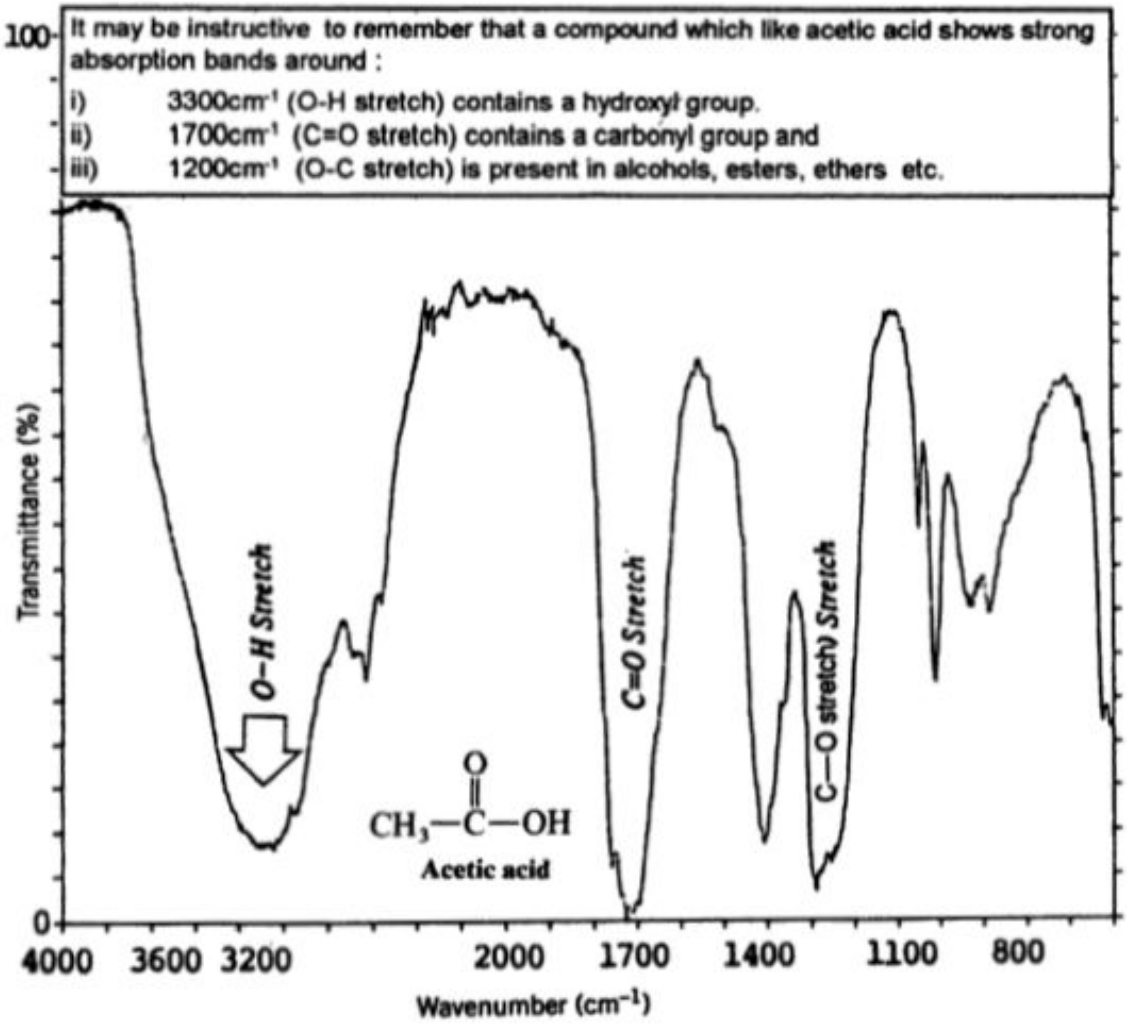
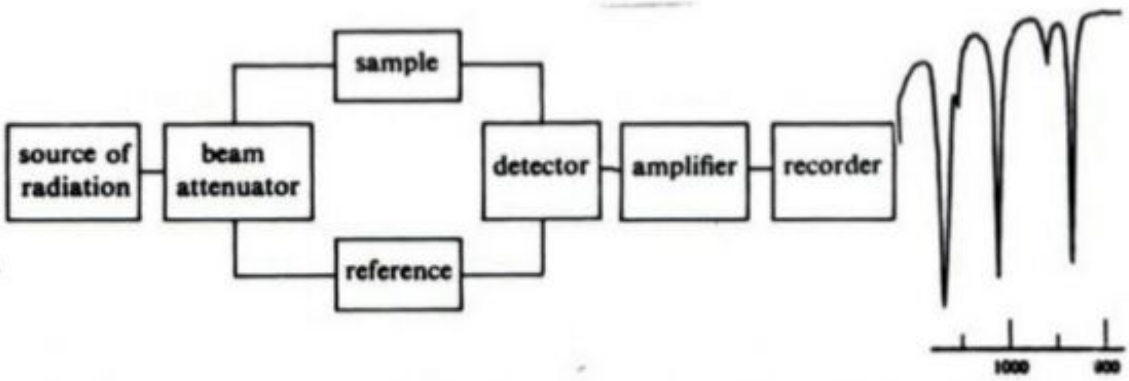


Fig. 3.6

at higher frequency than the C—H stretching frequency. The infrared spectrum of acetic acid is presented in Fig. 3.6.

3.5 INSTRUMENTATION

(a) The Instrument. The IR spectrophotometers operate according to simple principles. The complex mechanical and electrical devices present in the system (not shown here) are necessary to transform very small variation in energy absorbed into an accurately recorded spectrum. A simplified working of the double beam instrument is shown in Fig. 3.7a. One portion of the beam is passed through the sample cell while the other through the reference cell. Thus the solvent in the reference cell and in the sample cell are balanced out and the spectrum contains only the absorption peaks of the sample itself. The Fig. 3.7b displays the modern FT-IR instrument (Fourier transform infrared spectrophotometer). A FT-IR instrument gives the same information as a simple infrared spectrophotometer, however, the



Schematic diagram of a recording spectrophotometer. Strategically placed monochromators are not shown in this diagram because of variations in the design and nature of the spectrophotometer.

Fig. 3.7a

Fig 3.7b

performance of former overweighs with respect to speed, sensitivity and much smaller requirements, of the sample. In FT-IR, infrared radiation is split into two beams. One of these beams is kept static while the other is moving (moving mirror). These are then combined to get a modulated beam. In this modulated beam there will be either more light energy (constructive interference) or less light energy (destructive interference) for a given wavelength. The modulated beam is passed through the sample digitised, and then Fourier-transformed by a computer to give the infrared spectrum.

The New Model 16 PC FT-IR spectrophotometer from the Perkin-Elmer is controlled by Digital Equipment Corporation's 316-SX personal computer running Infrared Data Manager software, offering users

an analytical-grade instrument with a variable resolution to 2 cm^{-1} and a frequency range from 7800 to 350 cm^{-1}.

Infrared radiation is produced by electrically heating to 1000-1800°, a Globar or a Nernst filament. The Globar is a rod of silicon carbide whereas the Nernst filament is a high resistance element composed mainly of the sintered oxides of zirconium, cerium and thorium. The Globar is more effective at lower frequencies. The dispersion of light by any prism material is directly dependent upon its refractive index which changes with light frequency. Due to this, different prism materials are effective over different frequency range. Improvements in spectral resolution may therefore, be obtained by correct selection of the prism. Sodium chloride prisms are chosen as a compromise to cover the entire range to avoid interchange of prisms. The sodium chloride prism gives very good resolution in the 1300-650 cm^{-1} range, and has acceptable resolution in the 1950-1600 cm^{-1} range, however, above 2000 cm^{-1} the dispersion is not satisfactory. With gratings better resolutions are obtained than with prisms. A grating consists of thin lines on a smooth reflecting surface, the spacing between lines is of the order of few angstroms depending upon the desired wavelength range.

(b) Sample Handling. Infrared spectra of both gases and liquids may be obtained by direct study of the undiluted specimen, solids are however, usually dispersed in a number of possible media. The spectra of gases or low boiling liquids can be obtained by expansion of the sample into an evacuated cell. Solids can be examined in crystalline form by dilution in a mull, an alkali halide disc or by spreading as pure solid on cell plate. The most widely used method is that of nujol mull. For a spectrum examined as nujol mull air is the reference material. In this method the sample (2-5 mg) is ground together with the mulling agent (1-2 drops) using a pestle and mortar. Nujol is a high boiling fraction from petroleum (usually medicinal paraffin) and has absorption bands at 2920-2860 (C—H, stretch) and around 1460 and 1380 cm^{-1} (CH bend of CH_2 and CH_3). Obviously, when nujol is used as a mulling agent no information can be obtained in the regions near these bands. The spectrum of a solid sample is often best determined as an alkali halide pellet. About 1-3 mg of substance and 100-200 mg of alkali halide (KBr or KCl) are ground together, dried to remove moisture and pressed at room temperature under high pressure into a small disc. As KBr does not absorb infrared radiation in the region 4000-650 cm^{-1} a complete spectrum of the solid is obtained. The spectrum of a liquid is most often determined as a liquid film. For this a small drop of the liquid is placed on a sodium chloride plate, another sodium chloride plate is placed on top of the drop and the spectrum is then examined. For free flowing liquids, a neat spectrum may be determined using a cell (0.005-0.1 mm thickness). This is particularly useful for compounds which do not contain intense bands in the spectrum (*e.g.*, aliphatic hydrocarbons, Fig. 3.9).

It is frequently desirable to study the spectrum of a substance in solution. In IR all solvents absorb strongly in at least few regions of the spectrum. Because of this, in order to minimise solvent absorption, concentrated solutions and cells with short path lengths are used. Usually cells of a path length of 0.1 mm are preferred. With 0.1 mm cells a 10 per cent solution generally gives a satisfactory spectrum. The most commonly used solvents are CCl_4, CS_2 and $CHCl_3$.

A glossy film can be deposited from the solution or melt in the case of a polymeric material for obtaining infrared spectrum.

(c) Special Cautions During Scanning. Many spectra show a band at 2350 cm^{-1}. This band due to CO_2 is seen in all spectra recorded with single beam instruments. It also appears as small peaks when measured with a double beam instrument in which the light paths due to sample and reference are not correctly compensated. In order to avoid this, the room should be well ventilated or a CO_2 absorbent should be placed within the instrument. Traces of moisture cause absorption around 3700 cm^{-1} which could be mistaken for a hydroxyl band. The presence of water of crystallisation gives rise to a weak band at 3600-3100 cm^{-1} which is usually narrow. In such cases a weak band in the 1640-1615 cm^{-1} due to H—O—H bending is also observed.

A polystyrene film is commonly used for calibration of wave numbers. The calibration is done using the bands at 3026, 3003, 2924, 1601, 1495 and 906 cm^{-1}. It is a common practice to record an infrared spectrum along with the polystyrene band at 1601 cm^{-1} marked on as a check of frequency accuracy.

3.6 APPLICATIONS OF INFRARED SPECTROSCOPY

(a) Compound Comparison — Fingerprint Region. The infrared region (4000-650 cm^{-1}) is of prime importance for the study of an organic compound. Since infrared spectra contain a large number of bands, the possibility that two different compounds will have the same infrared spectrum is exceedingly small. For this reason an infrared spectrum has been called the "fingerprint" of a molecule. Thus, if two pure samples give different infrared spectra, the compounds must be different. If they give the superimposable spectra then they represent the same compound.

The region from 4000-1500 cm^{-1} (high frequency part) to the left in an infrared spectrum is useful for the identification of functional groups. This region shows absorption arising from stretching modes. The region to the right of 1500 cm^{-1} (1500-600 cm^{-1}) is usually complex since both stretching and bending modes give rise to absorption here. In this region correlation of an individual band with a specific functional group is often difficult. However, each organic compound has its own unique absorption

pattern in this region. This part of the spectrum is, therefore, called finger-print region (Fig. 3.1) Although the high frequency part of a spectrum may appear the same for similar compounds, the patterns in the high frequency region must also completely match for two spectra to represent the same compound. One, thus sees a complete superimposability of the infrared spectra (Fig. 3.8) of two samples of the crystalline alcohol menthol

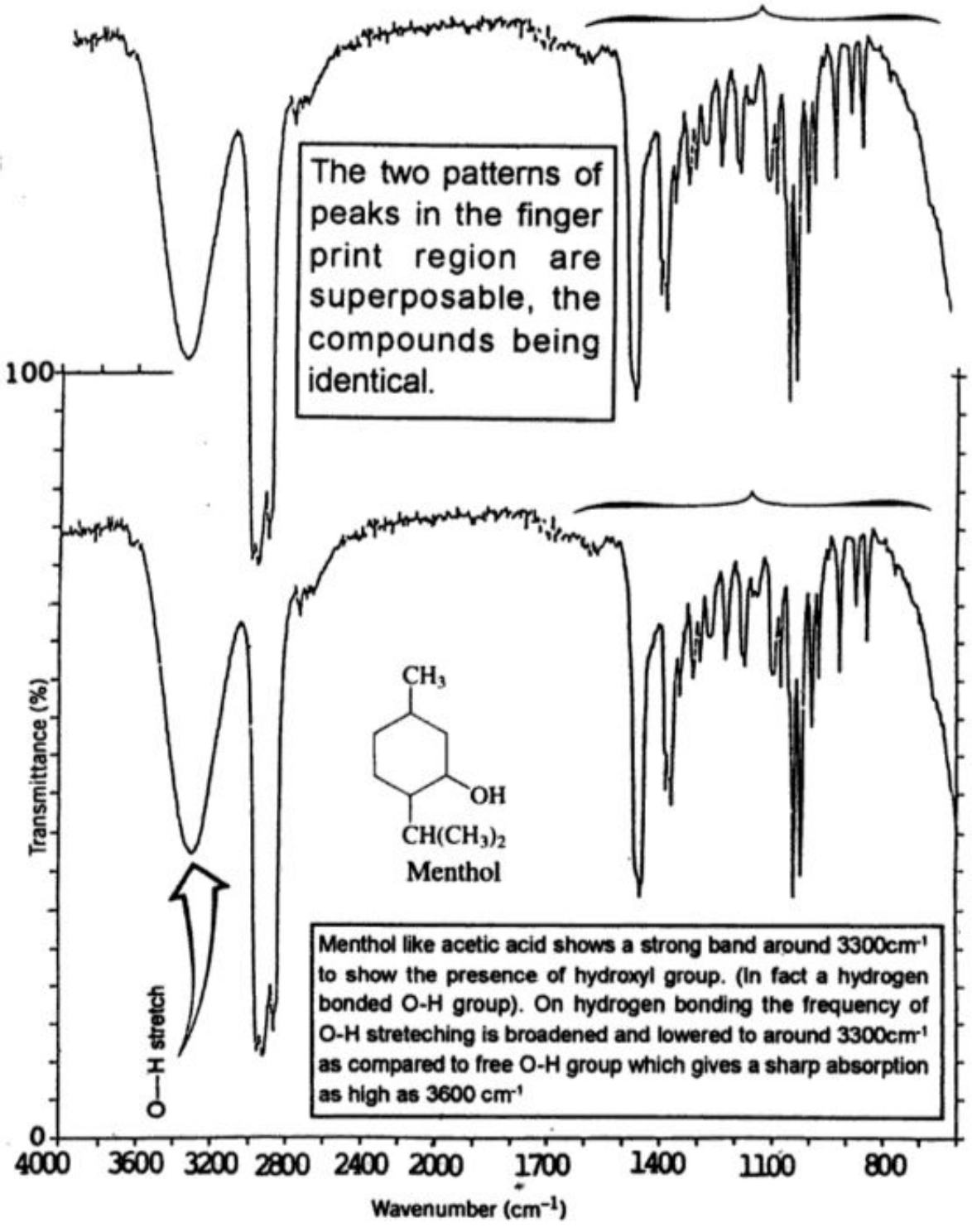


Fig. 3.8

isolated from two different sources. This spectral comparison thus, provides confirmation on their identity. The infrared spectrum of thymol, another crystalline naturally occurring compound (Fig. 3.8a), as expected, shows a completely different pattern in the fingerprint, region when compared to the pattern displayed by menthol. Both the compounds contain the hydroxyl group as their functional group, even then the shape of the patterns in the high frequency part of the spectrum are also different.

Another point which needs mention here, is that, aromatic compounds (Fig. 3.8a) often display numerous bands in the fingerprint region than their aliphatic counterparts (Fig. 3.8).

When, *e.g.*, the infrared spectra of two stereoisomeric steroids androsterone and epiandrosterone are examined three strong bands in the functional group region around 3600, 2950 and 1740 cm^{-1} due of OH, CH and C=O stretching vibrations respectively are seen in both the spectra.

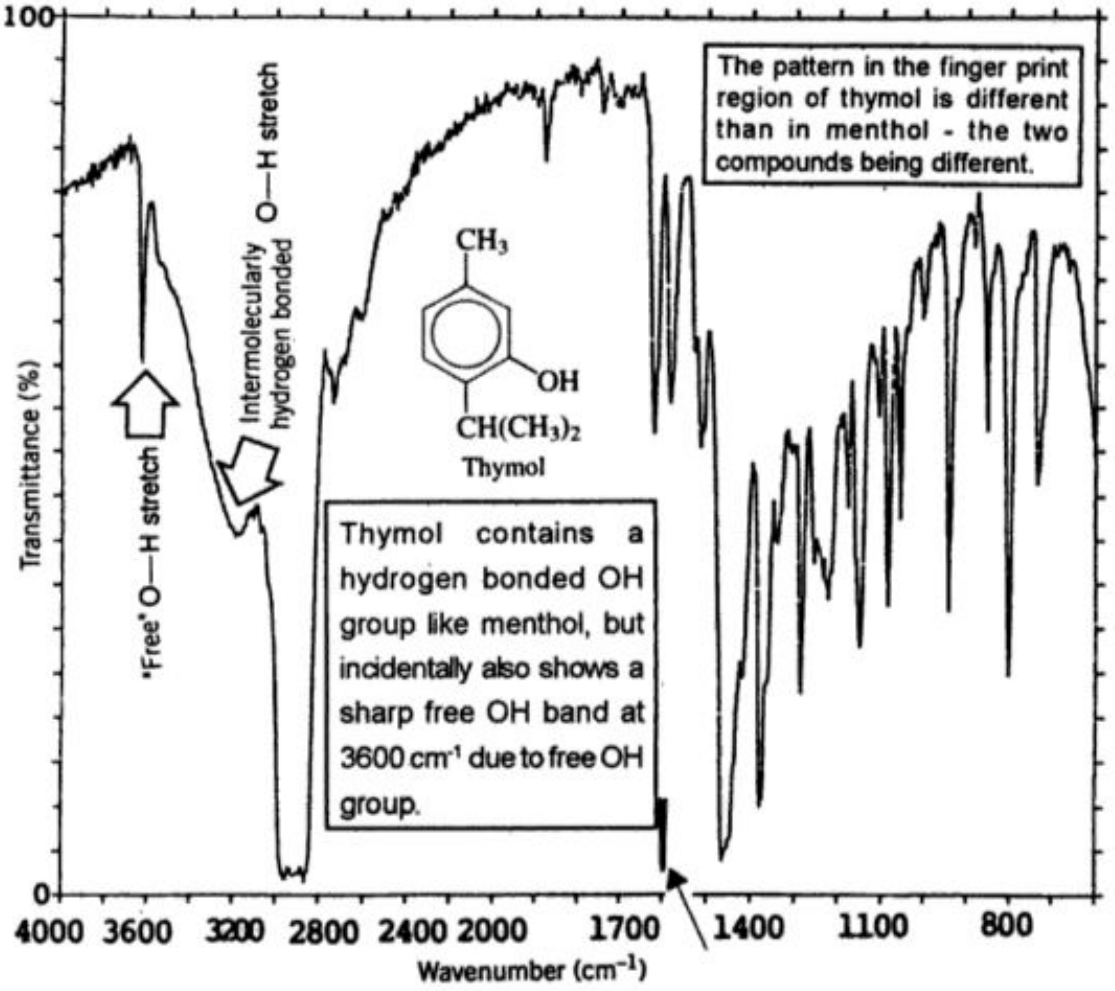
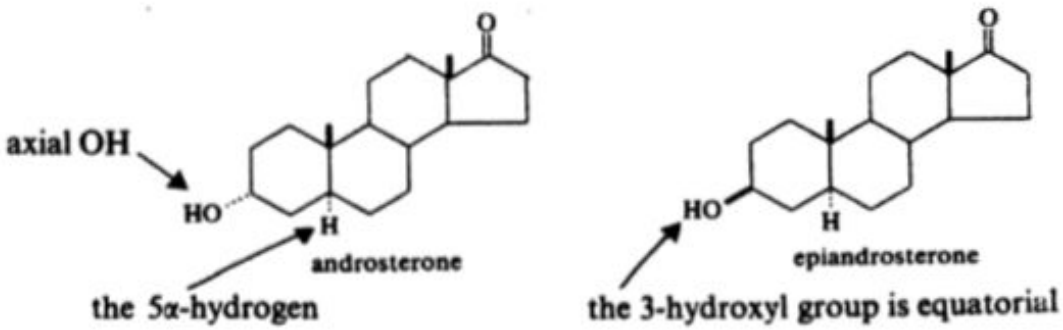


Fig. 3.8a

However, a comparison of their spectra in the fingerprint region shows them to be entirely different. The only difference in their structures is the stereochemistry of the C—3 OH group (Scheme 3.2c).



Scheme 3.2c

Thus, the pattern of the infrared spectrum in the fingerprint region is very sensitive and changes even with minor chemical or stereochemical alternations in a molecule. Significantly the individual *d*- or *l*-optical isomers of an enantiomeric pair always give identical (superimposable) spectra, when studied in solution, since in the solid state these may show differences due to crystal habit. The comparison by infrared method, therefore, excludes the resolution of the racemic mixture say at the end of the synthesis and provides as excellent method of comparison of an optically active natural product with the racemic product. In this situation a comparison by melting point determination will not help since an optical isomer and the racemic mixture may have different melting points. As an added advantage, liquid compounds can be compared directly by comparison with published curves in the fingerprint region. Thus formation of crystalline derivatives for melting point determination can be avoided.

(b) The Intensity of Infrared Bands. The bands in an infrared spectrum are classified by intensity: strong (*s*), medium (*m*), weak (*w*), and variable (*v*) (Fig. 3.12). The position of all bands is given in cm^{-1}. The number of similar groups in a molecule changes the relative strengths of the absorption bands in a spectrum. For example, the stretching band of a single O—H group in a compound displays itself as a relatively strong absorption (Fig. 3.16) whereas a single C—H stretch is comparatively weaker. On the other hand, however, if a molecule has many C—H bonds the collective effect of the C—H absorption gives a band which is strong as in the case of C—H stretching band of octane (band 1, Fig. 3.9).

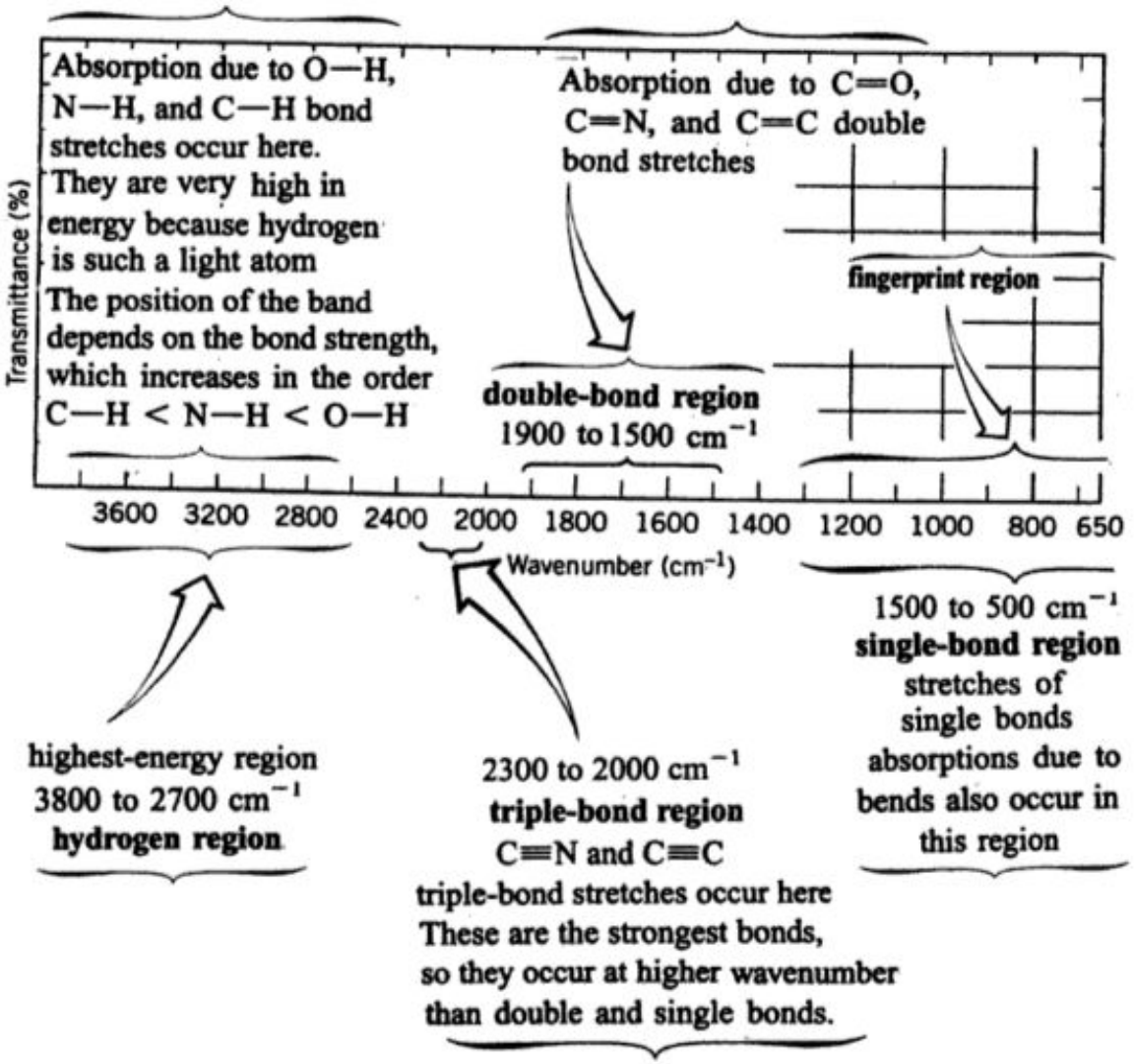
(c) Preparing for the Interpretation of Infrared Spectra

(i) ***A Quick Overall View of the Entire IR Spectrum.*** IR spectroscopy provides a fast and effective way to identify functional groups present in a

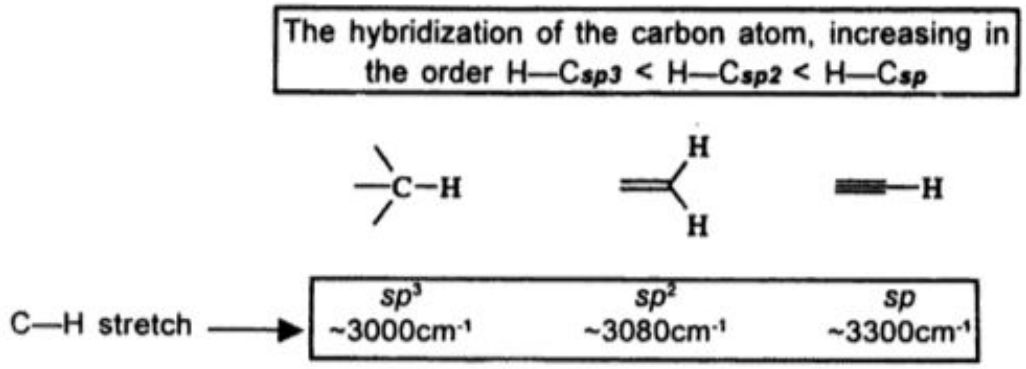
molecule by looking to absorptions (bands) corresponding to the bond types present in these functional groups. It is important to remember that the absorption frequency of a given bond type can vary somewhat depending on the structure. Thus it is convenient, *e.g.*, to know that a C=O group will give its stretching near 1700 cm^{-1} and in the case of an acyclic saturated ketone, the frequency of absorption is close to 1715 cm^{-1}. It is also possible to identify structural features in a molecule which tend to strengthen or weaken a bond and therefore, lead to shift the infrared absorption frequencies.

For a quick overall assessment of the spectrum for the detection of functional groups consider the characteristic regions for different functional groups (Scheme 3.2d).

Considering the highest energy region (3800-2700 cm^{-1}, Scheme 3.2d), it is generally seen that more polar bonds are generally stronger than



Scheme 3.2d



Scheme 3.2e

less polar bonds and thus absorb at higher frequencies [C—H, 3000 cm^{-1}; N—H 3300 cm^{-1} and O—H 3600 cm^{-1} (free not hydrogen bonded), bond strength increases in the order C—H < N—H ≤ O—H]. The C—H bond strength varies slightly because the hybridisation of the carbon atom increasing in the order [Scheme 3.2e, which also depicts the increase in the polarity of C—H bonds, thus C—H stretch of the system C≡C—H occurring at the highest frequency when compared to C-H stretches in C=C—H (3080 cm^{-1} and alkanes (3000 cm^{-1})].

This knowledge, *e.g.*, may be quickly applied to infrared spectra (*A—C*; Fig. 3.8b), for the assignment of characteristic absorptions to different functional groups. All the three spectra have a strong common band 1 and its position near 3000/2950 cm^{-1} shows a C—H stretch and thus an alkane residue.

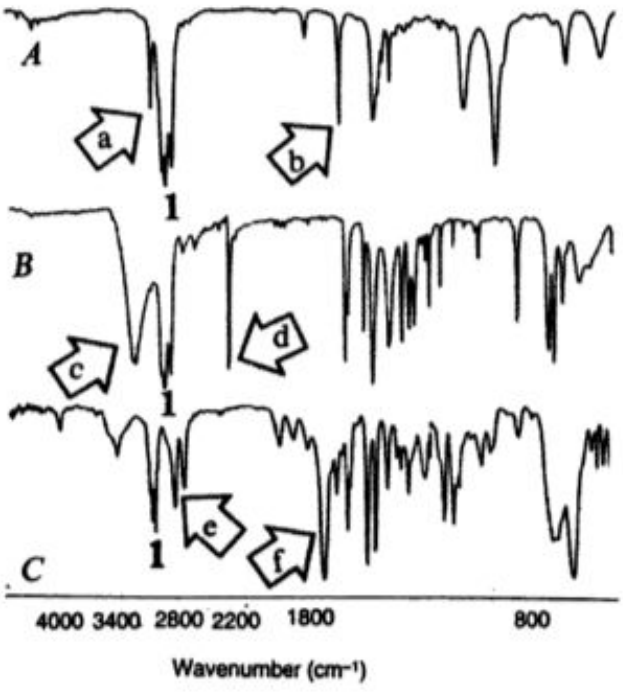


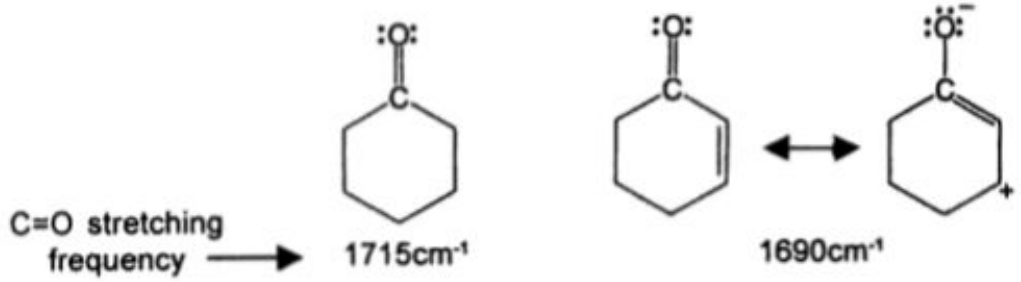
Fig. 3.8b

Spectrum A. The band (a) around 3080 cm^{-1} is the C—H stretch of C≡C—H and this coupled with C≡C stretch near 1650 cm^{-1} (band b) shows the presence of a double band in the compound.

Spectrum B. A strong broad band around 3400 cm^{-1} (band c) shows the presence of a hydroxyl group and the band (d) around 2200 cm^{-1} shows the presence of a triple band C≡C or C≡N.

Spectrum C. The band (f) around 1700 cm^{-1} shows the presence of a carbonyl group. This along with the presence of C-H stretching of aldehydic group around 2720 cm^{-1} as a Fermi doublet (band e) points to the presence of an aldehyde group.

Conjugation lowers the absorption frequencies of each conjugated group (due to a lowering of the bond order) because of the contributions of resonance forms with lower bond orders (Scheme 3.2f).



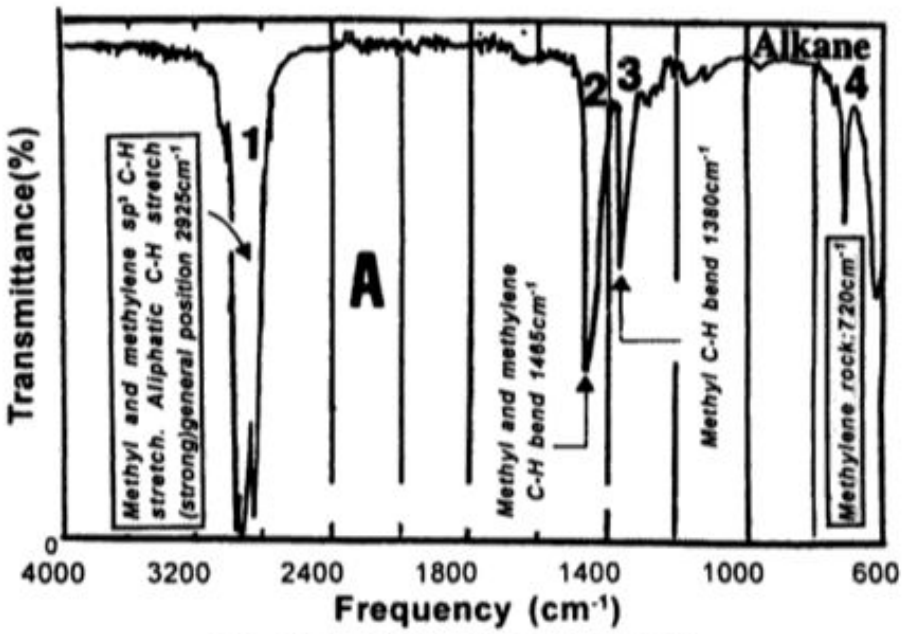
1715cm^{-1} (C=O stretch) 1647cm^{-1} (C=C stretch) C=O stretch 1690cm^{-1} C=C stretch 1623cm^{-1}

With conjugation the double bond character is reduced *e.g.*, one may see in the resonance formulation of 2–cyclohexenone a partial single bond character of the carbonyl group. This shifts the C=O stretching band to lower frequency.

Scheme 3.2f

Hydrogen bonding causes the absorption frequency of acidic protons to vary widely, depending on the solution concentration. In general, the greater the H bonding, the lower is the frequency of absorption. Thus, normal free O—H stretching frequency of a compound in a dilute non-basic solvent is centred around 3600 cm^{-1} on increasing the concentration, the O—H stretching becomes broad and moves to lower frequencies.

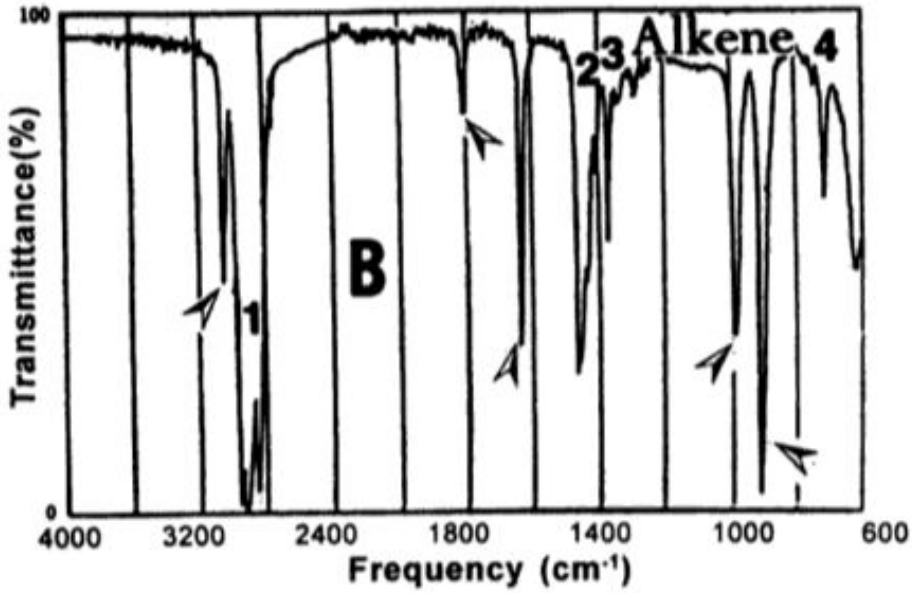
(ii) ***Identification of an Alkane Residue.*** Most organic molecules contain alkane residues and their general appearance may be seen, e.g., in the infrared spectrum of octane (Fig. 3.9A). As a first essential step for the



$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
(Octane)

Characteristic infrared group frequencies alkanes

Four major absorption bands are apparent, ~ 2925, 1465, 1380 and 720cm⁻¹ Band No. → 1 2 3 4
C—H stretch [Band **1**,strong (typical value 2925cm⁻¹)]
CH_2 and CH_3 bend [Bands **2**,strong(~1465cm⁻¹) and **3**,strong(~1380cm⁻¹)] respectively.
CH_2 rocking [Band **4**,medium (~720cm⁻¹)]



$CH_3CH_2CH_2CH_2CH_2CH_2CH=CH_2$
(1-Octene)

Fig. 3.9

interpretation of spectra of organic molecules, it is important to learn and identify the main absorption bands in an alkane. Thus, generally, speaking the strong absorption band (1), centred around 2925 cm^{-1} represents the C—H stretching absorption (also represented as C—H str.). This band is due to the C—H stretching of both methyl and methylene groups (Fig. 3.9A).

Most of the time, it is sufficient to locate the mean position of this aliphatic C—H stretch (centred around 2925 cm^{-1}). In fact, the C—H stretching modes of methyl and methylene groups both have asymmetric and symmetric C—H stretching modes and these give four absorption bands just below 3000 cm^{-1}. In most spectra, all the four bands overlap, but when resolved (particularly with a grating instrument) the four bands may be clearly visible. In Figure 3.9 A, three of these four bands in the C—H stretching band marked (1) are evident.

Three other bands in the spectrum (Fig. 3.9A) marked (2), (3) and (4) are due to C—H bending motions. All saturated hydrocarbons including cycloalkanes show similar absorptions.

The bending vibrations of C—H bonds of methyl and methylene groups occur at different frequencies, *i.e.,* around 1465 cm^{-1} as a band of medium intensity (mainly due to C—H bending of methylene groups and also of methyl groups, band 2) and a medium intensity band around 1380 cm^{-1} (due to C—H bending of methyl groups, band 3). These are called the C—H bend absorptions and these are also alternatively referred to as deformations and a C—H deformation band is also labelled as C—H def. More precisely it may be mentioned that symmetrical C—H bending vibrations of $—CH_3$ groups occur near 1380 cm^{-1} while the asymmetrical bending vibrations near 1465 cm^{-1} which overlap the C—H bending vibrations of methylene groups.

The fourth somewhat weaker band in the spectrum of octane (Fig. 3.9A) is at 720 cm^{-1} and represents the methylene rocking vibration in which all the methylene groups rock in phase. This band generally appears for straight-chain alkanes containing at least four adjacent methylene groups *i.e.,* $—(CH_2)_n—$, $n \geq 4$.

When one looks to the spectrum of 1-octene (Fig. 3.9B), it is immediately clear that its infrared spectrum has similar bands compared with octane, since saturated portions in both the compounds are same. Thus, the typical aliphatic C—H stretching absorption (band 1) appears around the same position as in octane. The other comparable bands due to bending motions (marked 2, 3 and 4), again stand out at about the same positions as in octane. However, several characteristic, additional bands appear in the spectrum of 1-octene (marked by arrows), when compared with octane. The presence of these bands and their position may be used as a diagnostic tool to show both, the presence of unsaturation, as well as the substitution

pattern of the alkene. This example, thus shows the strength of infrared spectroscopy in detecting the presence of functional groups.

The absence, *e.g.*, of saturated C—H absorption (i.e., bands 1, 2 or 3, Fig. 3.9A) in a spectrum provides an evidence for the absence of such a part structure in a compound under study. This is seen in the case of chlorobenzene, which does not have a methyl or a methylene group. When one looks to the spectrum of this compound (Fig. 3.10) in the region marked with a thick line, it is clearly seen that there is no absorption around 1380 cm^{-1} (C—H bending region of methyl groups). The band at 1446 cm^{-1} is one of the typical bands for the C = C ring stretching of benzene. The other bands for this stretching mode are at 1584 and 1478 cm^{-1}. It may be mentioned that in the infrared spectrum of chlorobenzene, one now sees an aromatic C—H stretch which is above 3000 cm^{-1}. Any compound having C—H stretch above 3000 cm^{-1} contains some unsaturation (the aliphatic C—H stretch is below 3000 cm^{-1} with the general position at 2925 cm^{-1} *i.e.*, band 1, Fig. 3.9). As a passing remark it is sufficient to mention, for the time being, that in addition to aromatic C—H stretch, C=C ring stretch, a compound can be considered aromatic only if the

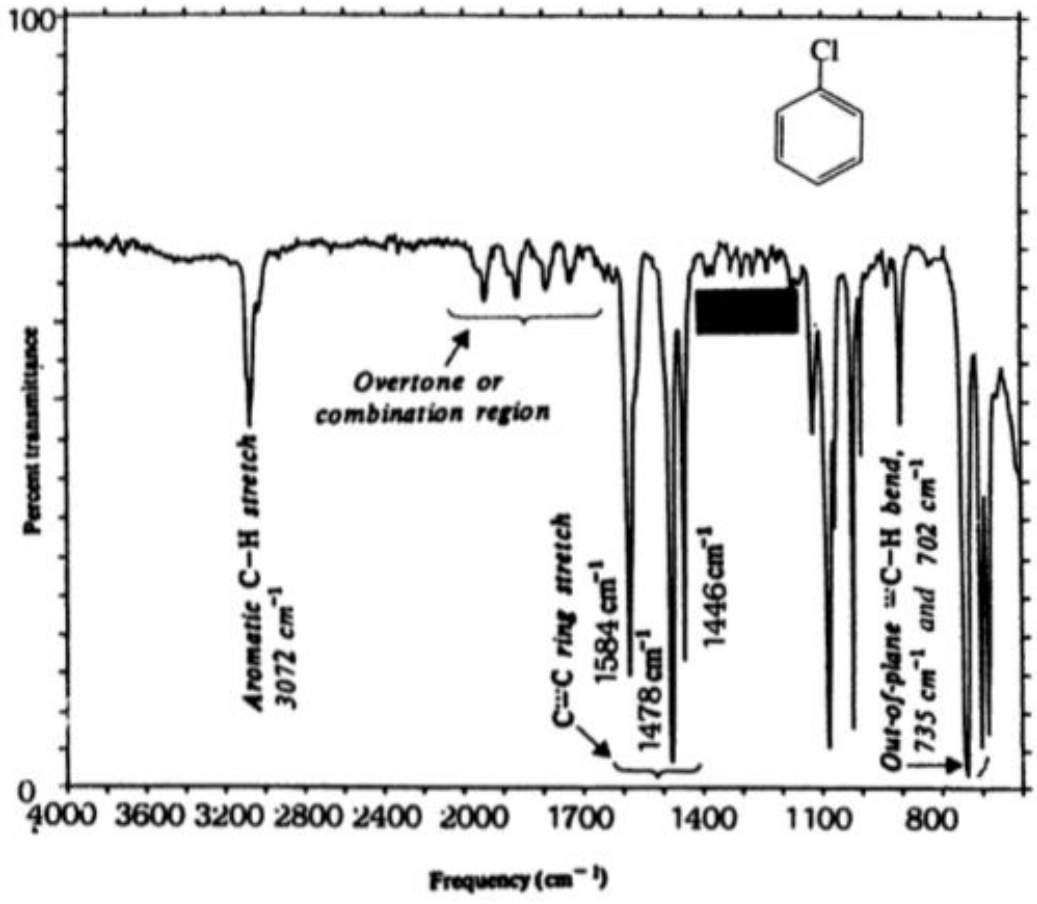


Fig. 3.10

spectrum has at least one strong absorption below 900 cm^{-1} (out of plane C ⋍ C—H bend). Chlorobenzene has strong absorptions at 735 and 702 cm^{-1} which indicate its aromaticity. The weak set of bands between 1650 – 2000 cm^{-1} (overtones) also help in labelling a compound aromatic.

Some special structural features may also be identified. Thus 1380 cm^{-1} band due to C—H bending vibrations of a methyl group is seen as a doublet if more than one methyl group is present on the same carbon. This feature is seen in infrared spectrum of isopropyl bromide (Fig. 3.11, also see problem 1 Chapter 3, spectrum 13, and sample problem 25, Chapter 7).

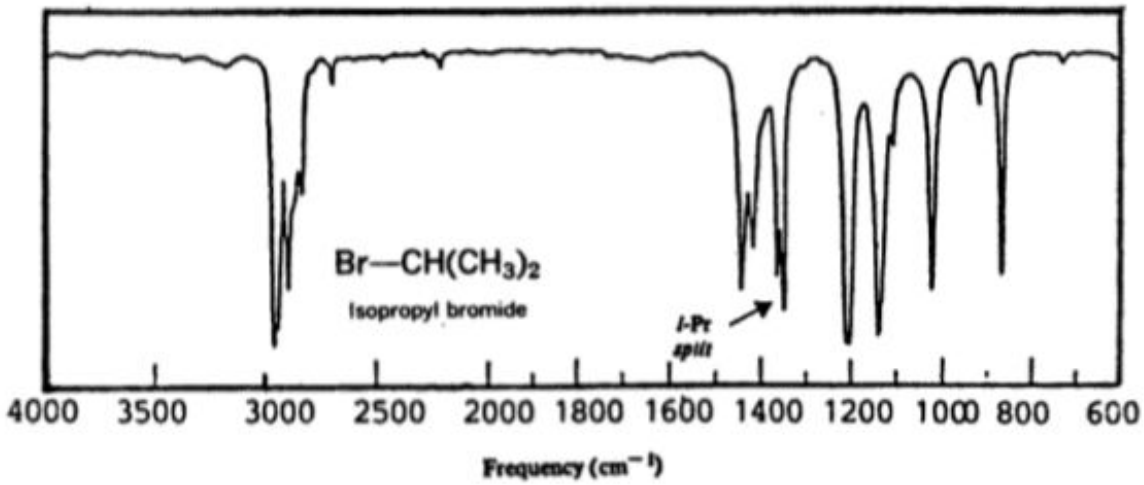
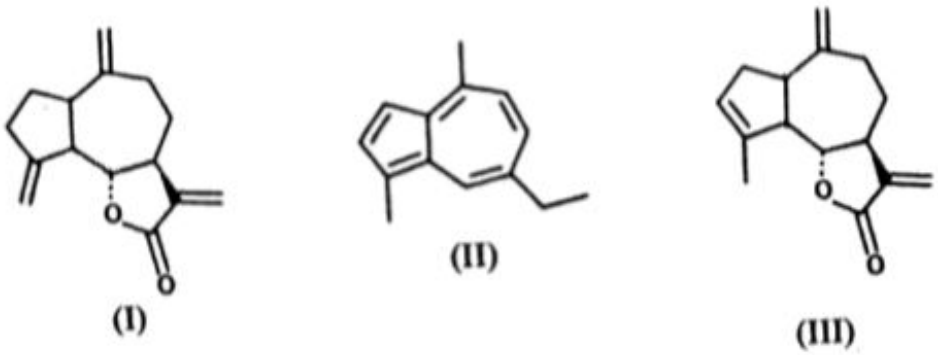


Fig. 3.11

The bending vibrations of C—H bonds of methyl and methylene groups occur at different frequencies, around 1380 cm^{-1} and 1465 cm^{-1} respectively. The naturally occurring sesquiterpenoid lactone dehydrocostuslactone was shown to have a carbon skeleton (II, Scheme 3.2g along with the lactone lock up as shown). All the three double bonds present in the compound were suspected to be of methylenic type (exo-cyclic in this case) since the lactone did not show any absorption in the 1380 cm^{-1} region

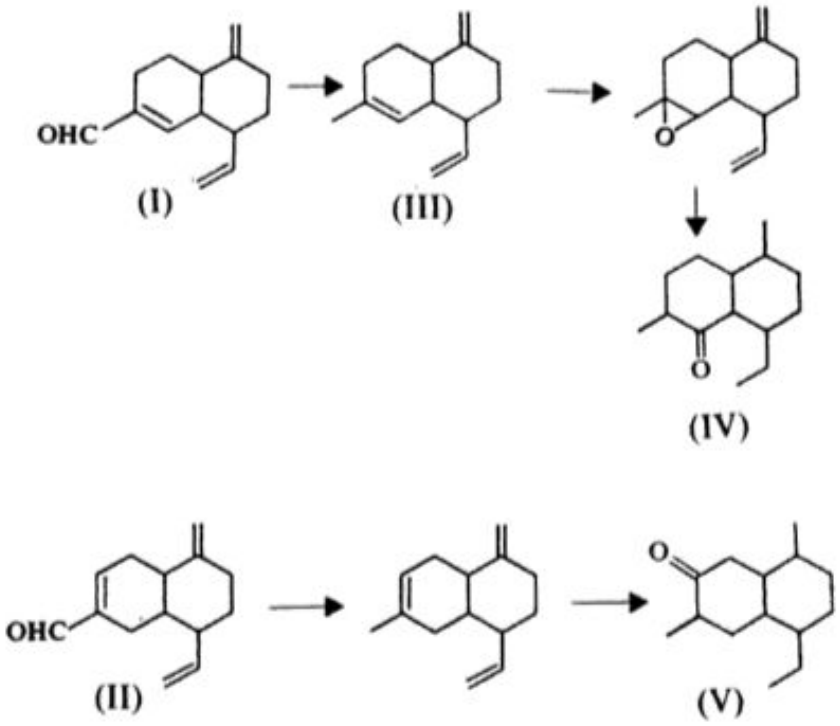


(I) (II) (III)

Scheme 3.2g

(absence of C—H bending bands of the methyl group around 1380 cm^{-1}) to show the absence of a methyl group. This clever infrared observation pointed to gross structure (I, Scheme 3.2g) and excluded several structures, *e.g.*, (III, Scheme 3.2g) which would have a methyl group and would be expected to display an absorption around 1380 cm^{-1}. Further degradative work coupled with other spectral data indeed confirmed structure (I, Scheme 3.2g) for dehydrocostuslactone.

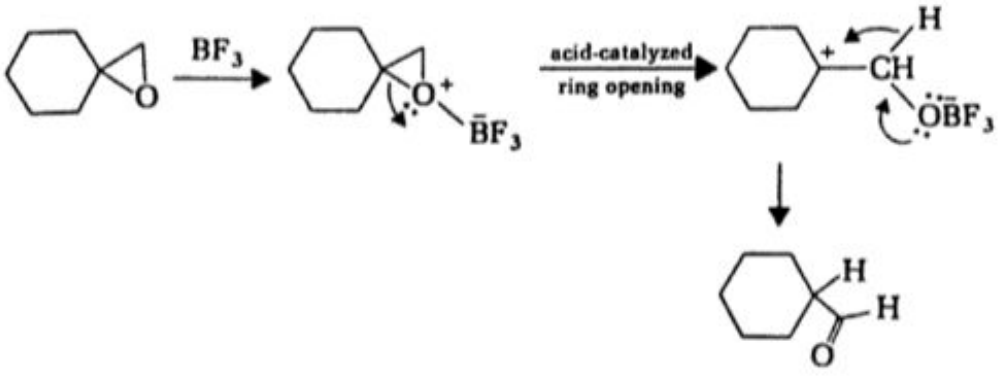
The bending (sometimes called scissoring) motion of saturated —CH_2-groups gives a band of medium to strong intensity around 1465 cm^{-1}. When the —CH_2-group is adjacent to a carbonyl or nitro group, the frequency is lowered to around 1420 cm^{-1}. During the structure determination of a novel naturally occurring C14 aldehyde, at one stage a distinction had to be made between two alternative structures (I and II, Scheme 3.2h).



Scheme 3.2h

The structure was indicated to be (I, Scheme 3.2h) since its parent hydrocarbon III on selective monoepoxidation and the rearrangement of the epoxide with BF_3 gave a ketone (IV) which did not show a shoulder or band around 1420 cm^{-1} due to the absence of a methylene group in the α-position to the C=O group. A similar series of reactions on the alternative structure (II, Scheme 3.2h) would have given a ketone (V) with the expected absorption around 1420 cm^{-1}.

On treatment with acid in the absence of nucleophiles, epoxides usually rearrange into aldehydes or ketones (Scheme 3.2i). Boron trifluoride is

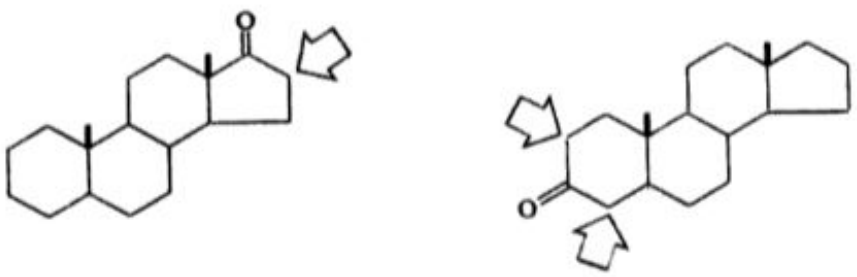


Scheme 3.2i

a non-nucleophilic Lewis acid commonly used to carry out this reaction. The first step is co-ordination of the Lewis acid with the oxygen of the epoxide. If a nucleophile is present, a substitution would be anticipated at the carbon of this activated epoxide. In the absence of nucleophiles, the C—O bond can break, forming the more stable of the two possible carbocations. This ion can now undergo a 1, 2 hydride migration to give a carbonyl compound.

The disappearance of a C—H bending vibration on replacement with deuterium has use in structure elucidation. The selective deuteration at the active α-positions of cyclopentanone can be detected in the infrared spectrum. The spectrum of cyclopentanone shows bands due to CH bending at 1455 and 1406 cm^{-1}. In the cyclopentanone-α,α,α,α-d_4 spectrum, only the 1455 cm^{-1} band is retained. This experiment reveals that the 1406 cm^{-1} band is due to the active α-methylene groups whereas the 1455 cm^{-1} band represents the β-methylene groups.

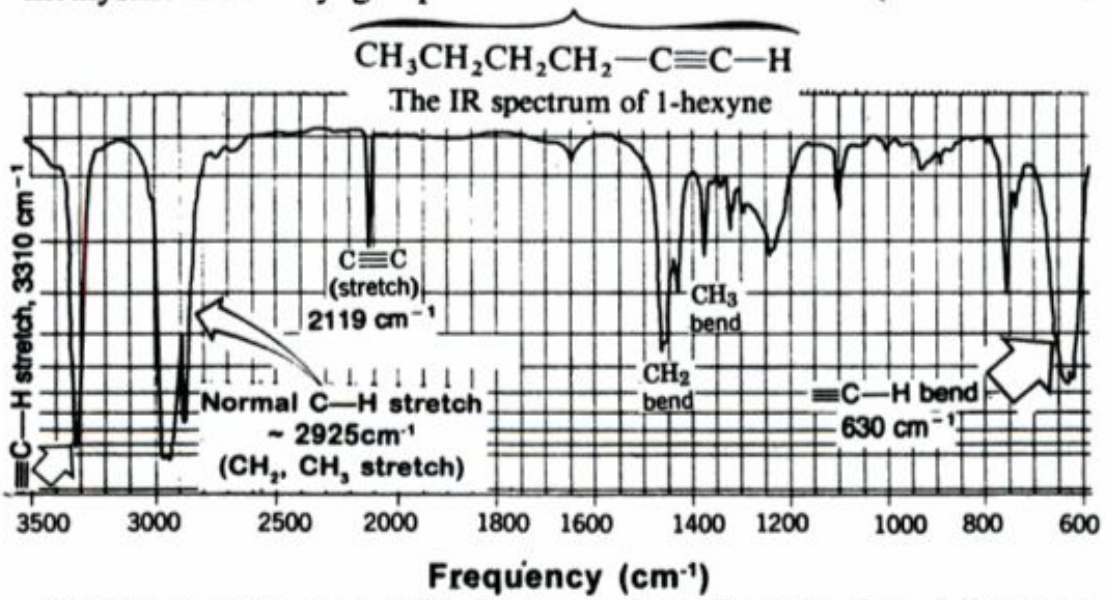
Similarly, deuteration of the α-methylene group in the 17-ketosteroid (I, Scheme 3.2j) results in the disappearance of a band in the infrared spectrum at 1408 cm^{-1}. There are two α-methylene groups in the 3-ketosteroid (II, Scheme 3.2j) and therefore, bands at 1432 and 1422 cm^{-1} which are assigned to these groups disappear on deuteration.



(I) (II)

Scheme 3.2j

(iii) ***Effect of Introduction of Some Structural Residues — Alkene, Alkyne, Nitrile and Aromatic Residues in an Alkane System.*** Firstly, inspect the infrared spectrum of 1-hexyne (Fig. 3.12). Aside from the alkyl C—H stretching (~ 2925 cm^{-1} band 1, Fig. 3.9) and bending vibrations of methylene and methyl groups at about 1465 and 1380 cm^{-1} (bands 2 and 3,



Typical Infrared (IR) Abrosption Bands for Alkynes

RC≡CH	3300cm^{-1}	*Strong*	≡C—H stretch
	2100-2140cm^{-1}	*Medium*	C≡C stretch
	600-700cm^{-1}	*Strong*	≡C—H bend
RC≡CR	2190-2260cm^{-1}	*Very weak*	C≡C stretch

$R—C\overset{\mu}{\equiv}C—H$ ⇦ C≡C stretch observed around 2100 to 2200 cm^{-1}
terminal alkyne

$R—C\equiv C—R'$ ⇦ C≡C stretch may be weak or absent a very small or zero dipole moment.
internal alkyne

C—H ⇦ sp^3 hybridized, $\frac{1}{4}$ *s* character ~2925cm^{-1}

C=C—H ⇦ sp^2 hybridized, $\frac{1}{3}$ *s* character ~3080cm^{-1}

C≡C—H ⇦ *sp* hybridized, $\frac{1}{2}$ *s* character ~3300cm^{-1}

Carbon-hydrogen bond stretching

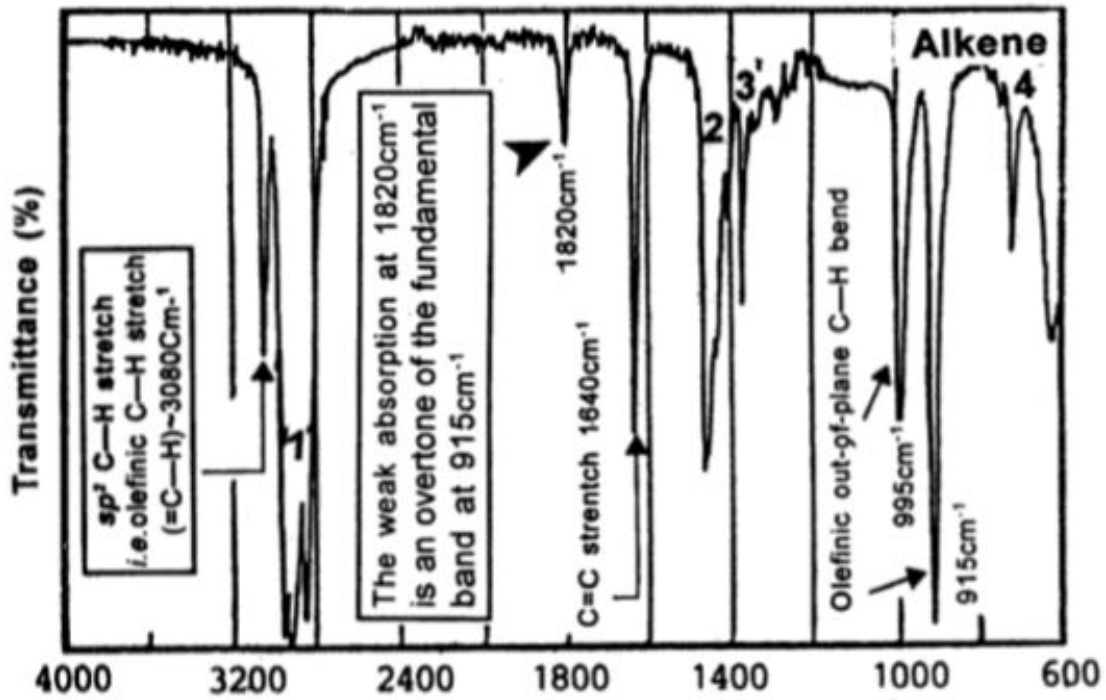
Fig. 3.12

Fig. 3.9) respectively, one sees several distinctive bands that do not appear in the spectrum of corresponding alkane octane (Fig. 3.9). These new bands occur in the general positions: 3310, 2119 and 630 cm^{-1} and represent ≡C—H stretching, C≡C stretching, and ≡C—H bending modes respectively. It is significant to note that the alkyne ≡C—H stretching absorption at 3310 cm^{-1} is distinctly separated and occurs at higher frequency from the alkane C—H stretching (centred around 2925 cm^{-1}) and is a strong band.

The alkyne C—H stretchings, *i.e.*, C—H stretching vibration in terminal alkynes occurs at higher frequencies than that due to an alkane C—H. The C—H bonds involving *sp*-hybridised carbon are strongest and those involving sp^3-hybridised carbon are weakest, the order of bond strength being $sp > sp^2 > sp^3$. Stronger bonds are more difficult to stretch (higher force constant) and require greater energy or higher light frequency. The C—H stretching bands of hydrogens attached to sp^2-hybridised carbon, *i.e.*, =C—H stretching (olefinic C—H stretching) bands occur around 3080 cm^{-1} as in 1-octene (Fig. 3.13) which is also the region for the aromatic C—H stretching as seen in the infrared spectrum of an alkylbenzene, *e.g.*, toluene (Fig. 3.14). In fact, one may detect (when resolved) several sharp bands due to aromatic C—H asymmetric and symmetric stretching vibrations in the 3000-3100 cm^{-1} region (Fig. 3.14). The olefinic and aromatic C—H stretching frequencies can therefore, be distinguished from the saturated C—H absorptions, since the latter occur below 3000 cm^{-1}. Thus, the C—H stretching bands of hydrogens attached to sp^3-hybridised carbon atoms occur at lowest frequencies as expected.

Similar to the observations made in the infrared spectrum of 1-hexyne, the spectrum of alkene, 1-octene shows additional bands (compared with octane) at 3080 (olefinic C—H stretching vibration) 1640 cm^{-1} (carbon-carbon double bond stretching vibration) and at 995 and 915 cm^{-1} (olefinic out of plane C—H bendings typically shown by compounds containing vinyl double bonds (—CH=CH_2). The alkenes with vinylidine double bond (>C=CH_2) show only one olefinic C—H bend around 890 cm^{-1} as seen in the spectrum of 2-methyl-1-heptene (Fig. 3.35). The nature and type of the double bond can be determined from the olefinic C—H bendings (Fig. 3.13, Sec. 3.7 f, iii and Fig. 3.62).

If one, returns to the infrared spectrum of toluene (Fig. 3.14), with the information already gained by interpreting the spectrum of chlorobenzene; it is immediately clear that the infrared spectrum (Fig. 3.14) is of an alkyl benzene. The strong peaks below 900 cm^{-1}, *i.e.*, at 727 and 693 cm^{-1} clearly indicate its aromativity. The peaks at 3090, 3060 and 3040 cm^{-1} also show the presence of unsaturation (*i.e.*, the presence of aromatic C—H stretch). However, the peaks at 2918 and 2875 cm^{-1}, also point to the presence of aliphatic C—H stretch and an alkylbenzene is thus indicated.



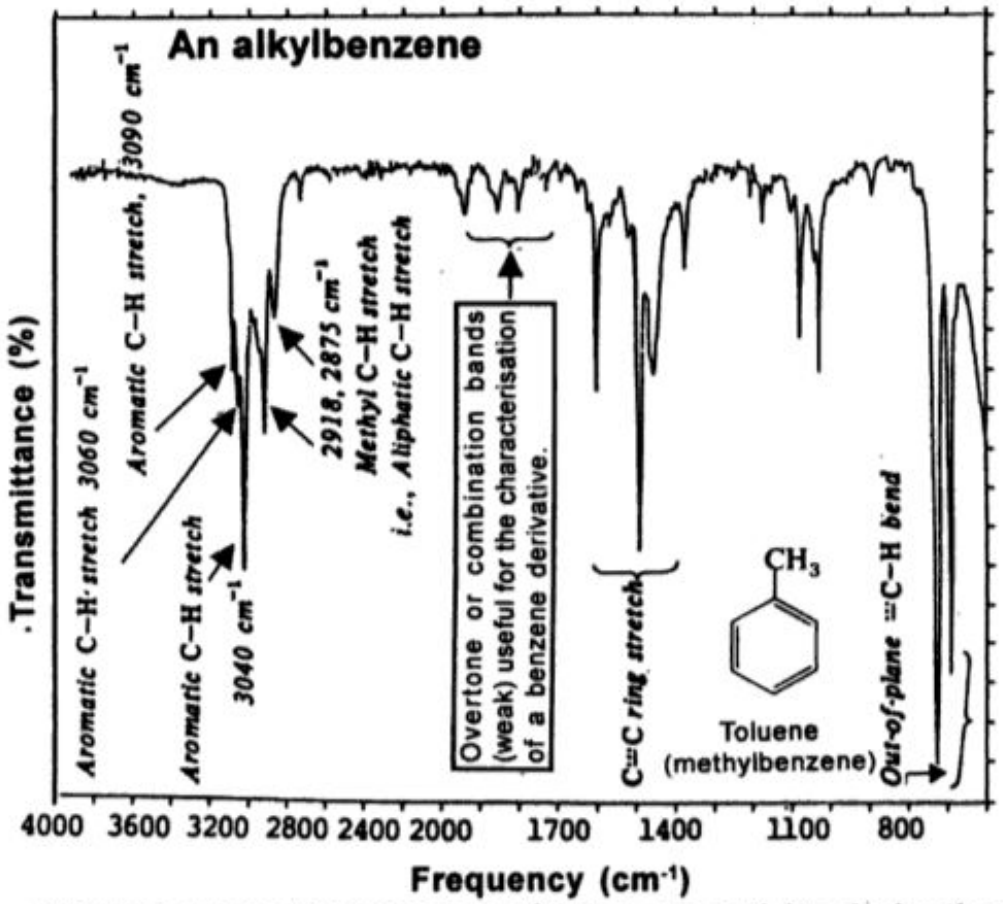
n-$C_6H_{13}CH{=}CH_2$ 1-Octene

Characteristic infrared group frequencies alkenes

	Frequency (cm^{-1})		
$RCH{=}CH_2$	**3080–3140**	m	=C—H stretch
	1800–1860	m	overtone
	1645	m	C=C stretch
	990	s	C—H out-of-plane bend
	910	s	C—H out-of-plane bend
$R_2C{=}CH_2$	**3080–3140**	m	=C—H stretch
	1750–1800	m	overtone
	1650	m	C=C stretch
	890	s	C—H out-of-plane bend
cis-RCH=CHR	3020	w	=C—H stretch
	1660	w	C=C stretch
	675–725	m	C—H out-of-plane bend
trans-RCH=CHR	3020	w	=C—H stretch
	1675	vw	C=C stretch
	970	s	C—H out-of-plane bend
$R_2C{=}CHR$	3020	w	=C—H stretch
	1670	w	C=C stretch
	790–840	s	C—H out-of-plane bend
$R_2C{=}CR_2$	1670	vw	C=C stretch

Fig. 3.13

This coupled with the presence of C = - - - C stretching absorptions at 1606, 1495 and 1460 cm^{-1} confirm the compound to be aromatic in nature and thus an arene. Substitution patterns on the ring can be judged from the out



Infrared group frequencies of benzene and its derivatives.

Aromatic C-H stretch	3040-3010cm⁻¹ (Unsaturation)	Medium	Often obsecured
Overtone or combination bands	2000-1650cm⁻¹	Weak	
C=C C ring stretch	~1600cm⁻¹	Medium	Stronger if the ring is further conjugated. This is usually the strongest of the two or three bands.
	~1580cm⁻¹	Medium	
	~1500cm⁻¹	Medium	
Out-of-plane =C-H bend	below 900cm⁻¹	Strong	

Fig. 3.14

of plane bending of the ring C—H bonds in the region 900-675 cm^{-1} and these bands are highly informative (Sec. 3.7, g and Fig. 3.62).

The infrared spectrum of 2-hexyne $CH_3—C{\equiv}C—(CH_2)_2—CH_3$ (not given) might, however, confuse an inexperienced person. As there is no acetylenic hydrogen, there is no ≡C—H stretching absorption around 3300 cm^{-1}. Moreover, there is no visible C≡C stretching absorption

around 2120 cm^{-1}, either, since the disubstituted triple bond has a very small dipole moment (also see, Fig. 3.36).

The C≡N stretch also displays itself around 2200 cm^{-1} which is of variable intensity. On conjugation as in aryl nitriles the frequency gets lowered and the band becomes stronger (Fig. 3.15). The presence of nitriles can be detected from this band.

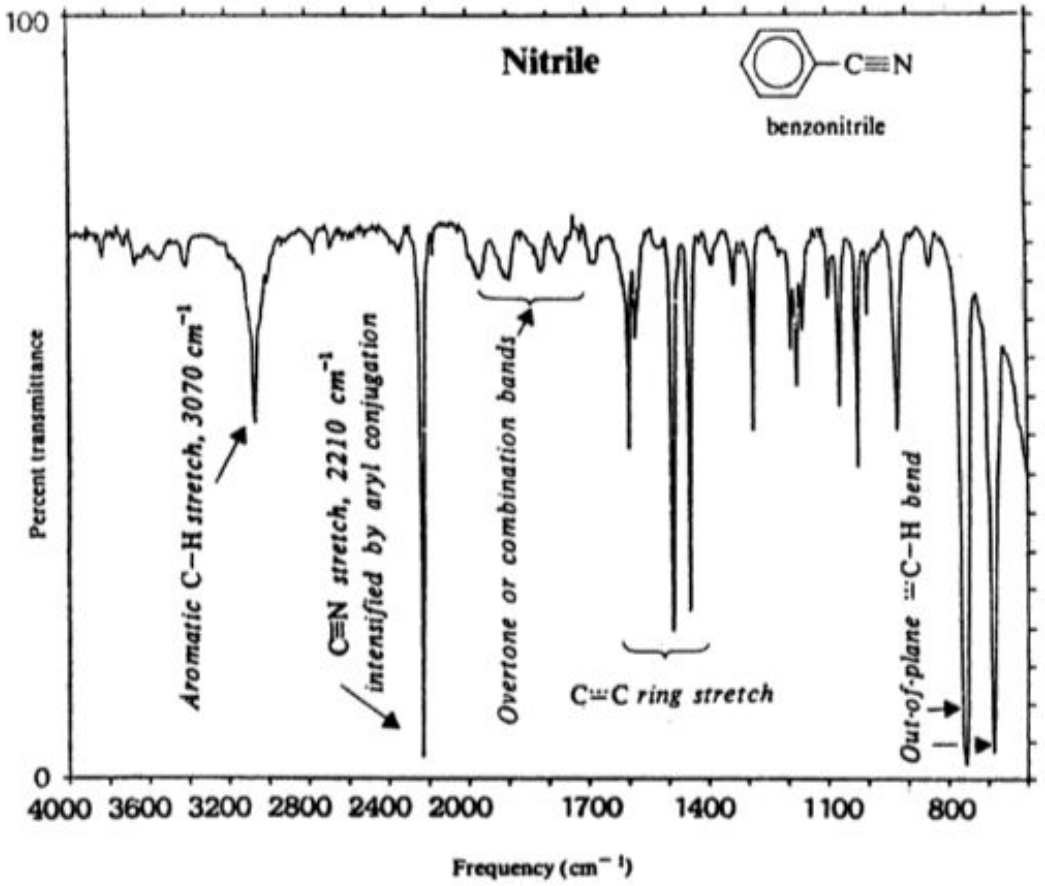


Fig. 3.15

(iv) ***Interpretation of Infrared Spectra —A Step Further* (*Alcohols, Aldehydes, Ketones and Ethers*).** In Section 3.6c, it is made clear as to how an organic chemist can use infrared spectroscopy in a semiempirical way to detect the presence of unsaturation or a benzene ring in an organic compound. The presence or absence of an absorption band, points to the presence or absence of a functional group in a compound. This is so, since most of the common functional groups give rise to characteristic absorption bands in the defined regions of the infrared range. Here more examples are presented to emphasise this point. The infrared spectra of organic compounds are complex and it is neither practical nor useful from the interpretation point of view to assign each absorption band to a

particular vibration. However, it is significant that for each functional group there are characteristic absorptions which are used empirically for the detection of that particular functional group.

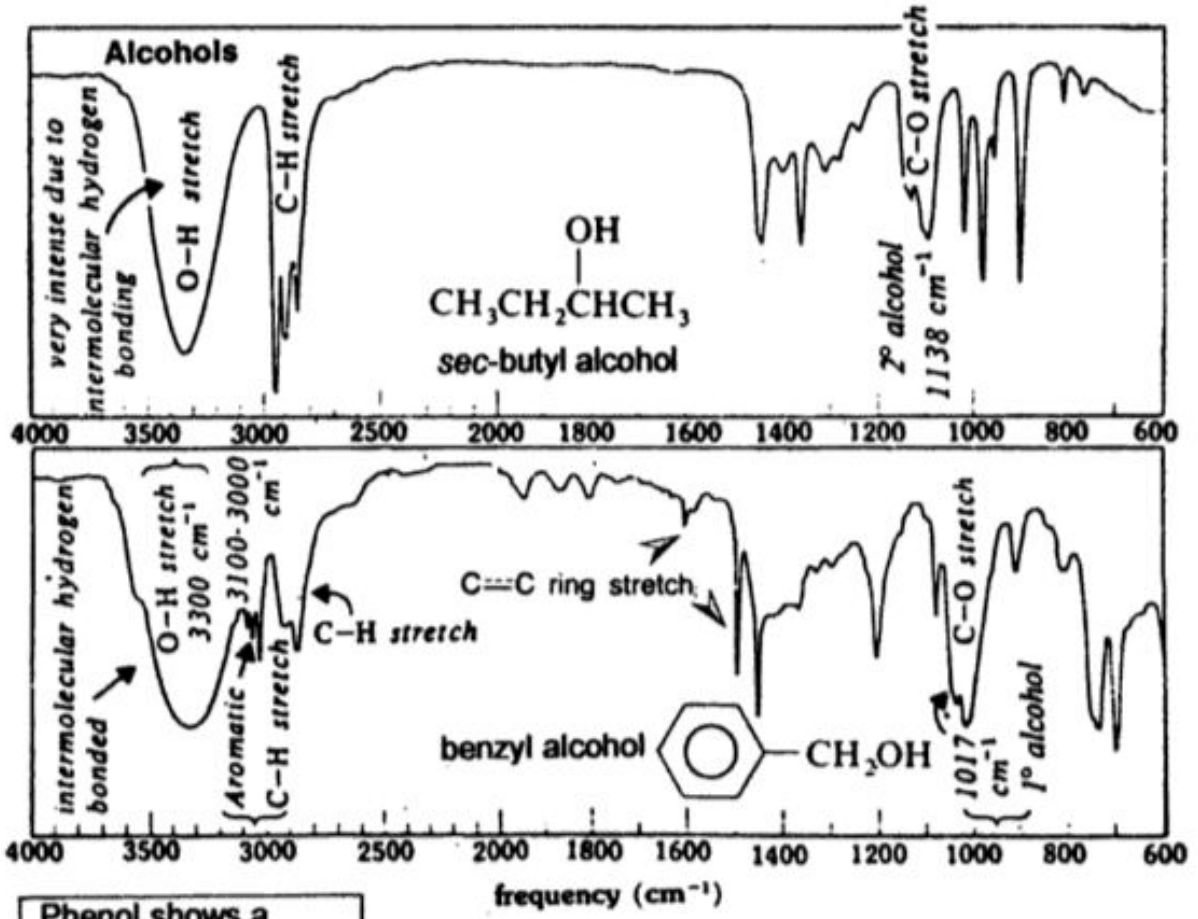
It is indeed not necessary that one should memorise all of the absorption ranges. At the same time it is indeed essential to commit a few members and ranges to memory. As an example, it may be sufficient to remember that an alcohol or a phenol can be recognised from its infrared spectrum from the O—H stretch in the region 3200-3600 cm^{-1} as seen, *e.g.*, in the spectrum of *sec*-butyl alcohol (Fig. 3.16). Alcohols also give a strong and broad band due to C—O stretching in the 1000-1200 cm^{-1} region. The exact frequency of this band is often used to distinguish between primary, secondary and tertiary alcohols. Thus, when one compares the locations of these bands in *sec*-butyl alcohol and benzyl alcohol (Fig. 3.16), it is immediately realised that in the former the C—O stretch is at a higher frequency. Like alcohols phenols (ArOH) also display both O—H and C—O stretchings. The C—O stretchings of phenols appear at higher frequencies as in phenol itself (Fig. 3.16).

A strong absorption band in the region around 1700 cm^{-1} is due to C=O stretching and the presence of this band points that the compound may be a ketone, aldehyde, carboxylic acid, carboxylic ester, lactone, acid halide, anhydride, amide or a lactam (Fig. 3.60). Thus 3-pentanone shows its C=O stretch at 1715 cm^{-1} as an intense absorption (Fig. 3.17). Aldehydes generally absorb 10-15 cm^{-1} above the corresponding ketones. Several factors (Sec. 3.7h) alter the C=O stretching frequency, *e.g.*, conjugation with an olefinic or phenyl group causes a shift of C=O absorption to lower frequencies by about 30 cm^{-1} as can be seen by examining the infrared spectrum of *p*-tolualdehyde (Fig. 3.18, C=O, stretching 1700 cm^{-1}). The important difference between an aldehyde and a ketone is that an aldehyde has a H bonded to the carbonyl carbon. This C—H (aldehydic) bond shows two characteristic stretching bands (doublet due to Fermi resonance) between 2830-2695 cm^{-1}. Thus unlike *p*-tolualdehyde which shows its aldehydic C—H stretch at 2825 and 2717 cm^{-1} (Fig. 3.18) these bands are not detectable in the infrared spectrum of 3-pentanone (Fig. 3.17). For Fermi resonance see Sec. 3.3, (ii) and 3.3, (vii).

When an organic compound contains an oxygen atom and if the O—H and C=O stretchings are absent in its infrared spectrum it may then represent an ether as a possibility. Ethers can be recognised by their strong C—O stretching bands at 1060-1275 cm^{-1} which falls in the fingerprint region. Since oxygen is electronegative, the stretching causes a large change in bond moment and as a result, the C—O stretching absorption is usually strong (Fig. 3.19). In the case of highly unsymmetrical ethers, *e.g.*, alkyl aryl ethers, the two C—O bonds couple and thus show anti-symmetric and symmetric C—O stretchings, *i.e.*, two bands.

O-H stretching, strong, broad

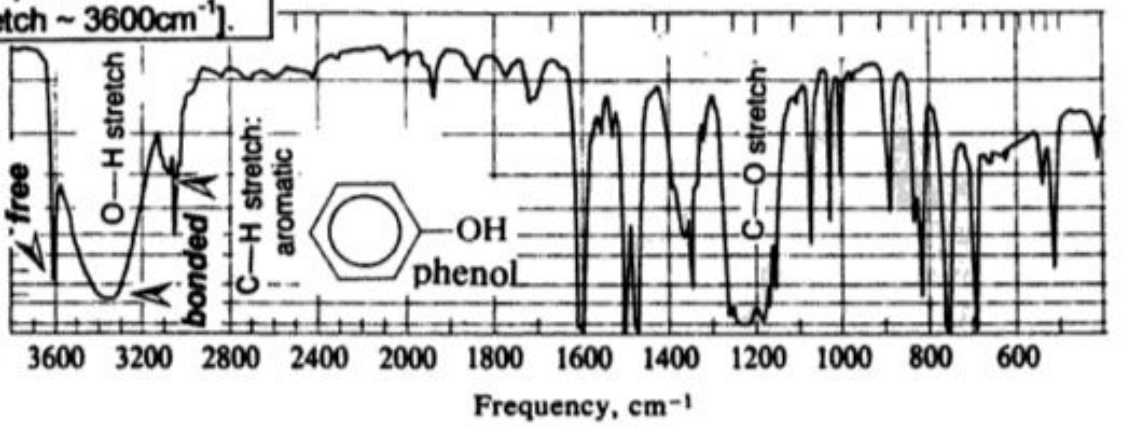
Alcohols, ROH (or phenols, ArOH) 3200–3600 cm^{-1}



Phenol shows a broad O-H stretch [intermolecular hydrogen bonded~ 3400cm^{-1}] and a sharp free O-H stretch ~ 3600cm^{-1}].

C-O stretching, strong, broad

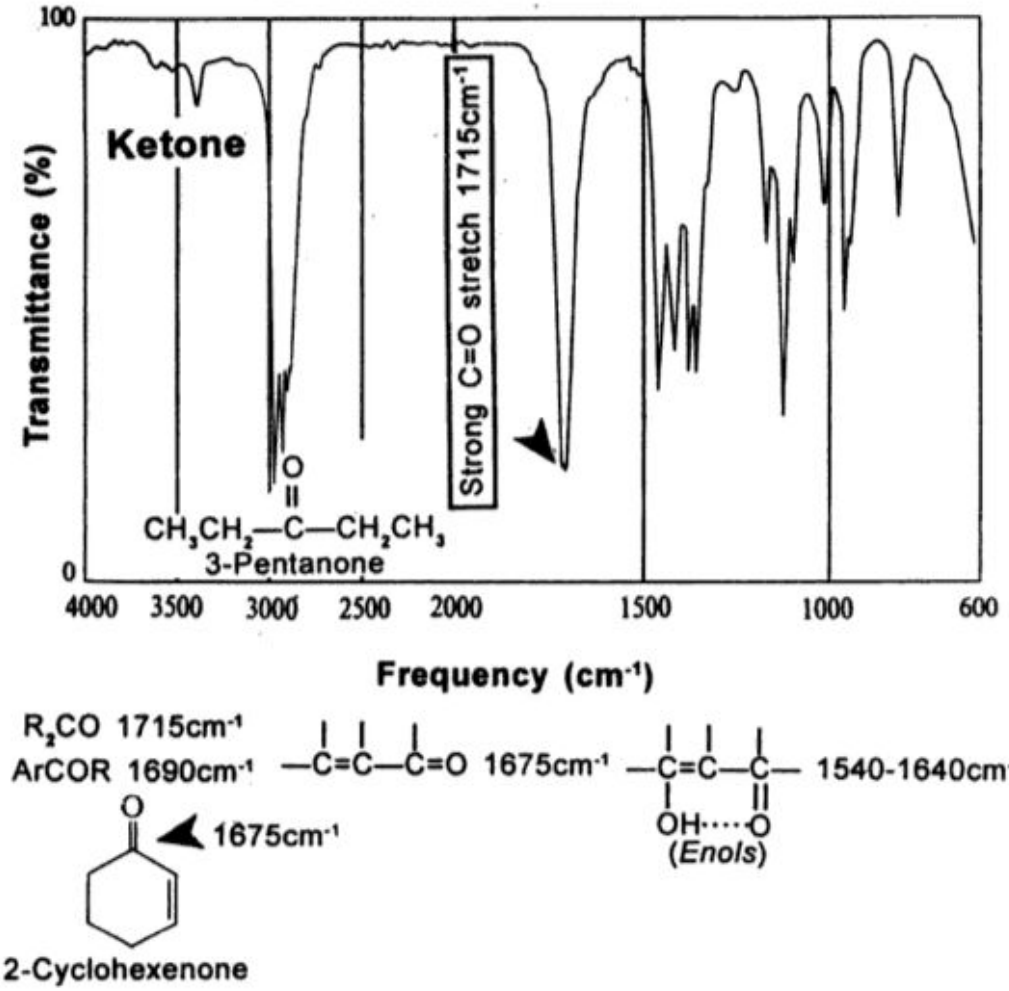
1° ROH	about 1050 cm^{-1}	3° ROH	about 1150 cm^{-1}
2° ROH	about 1100 cm^{-1}	ArOH	about 1230 cm^{-1}



Infrared spectra of *sec*-butyl alcohol and benzyl alcohol.

Fig. 3.16

In the case of dialkyl or diaryl ethers the symmetric C—O stretch is infrared inactive and only the anti-symmetric C—O stretch is observed.

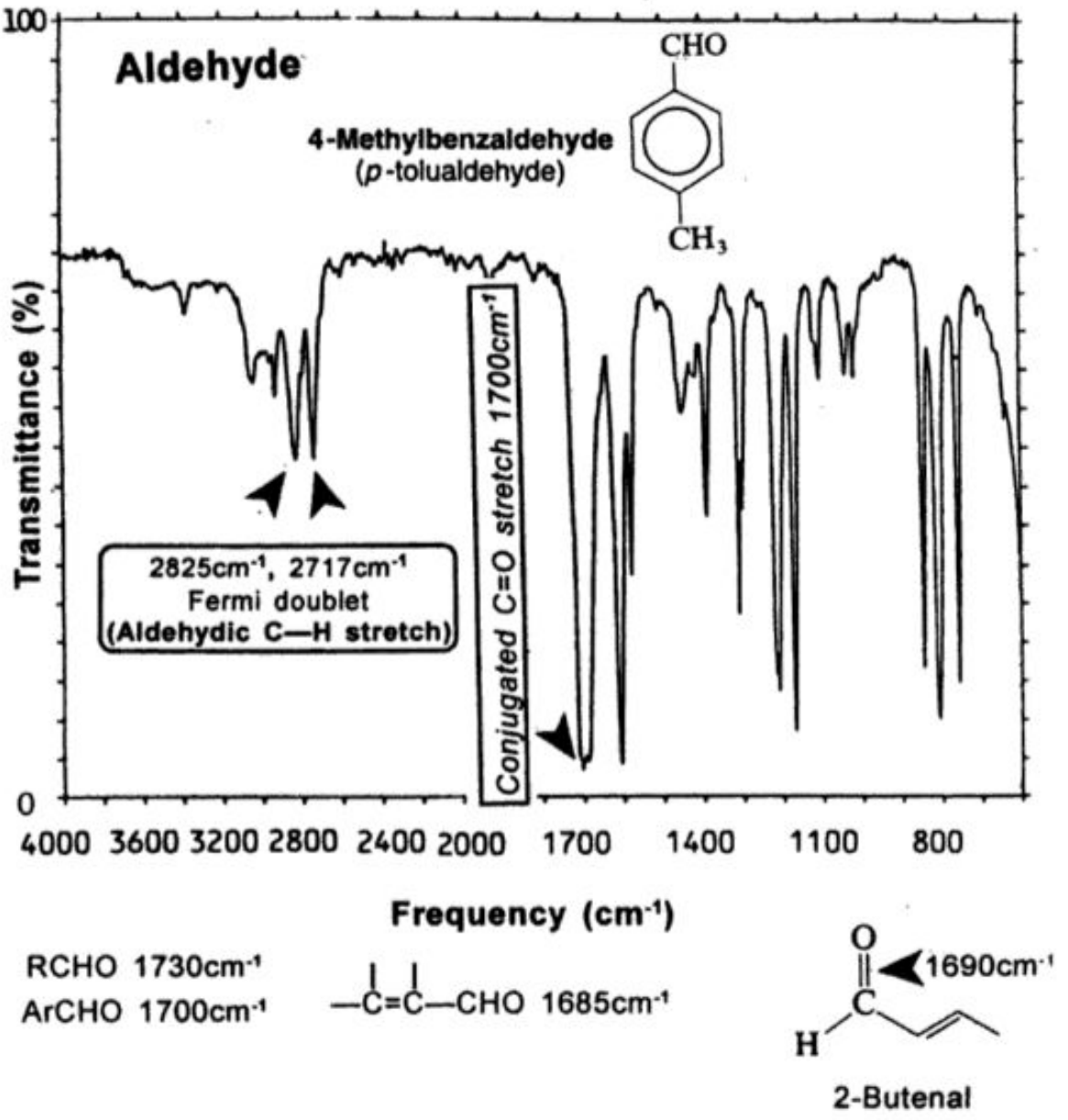


Characteristic C=O stretching frequencies of ketones

Fig. 3.17

When a compound has more than one functional group, then each shows up separately in its infrared spectrum. In the spectrum (Fig. 3.20) of piperonal the bands in the C—H stretching region are assignable to aromatic, aliphatic and aldehydic C—H stretch. The presence of two functional groups, *i.e.,* an α, β-unsaturated aldehydic group and an ether group (methylene ether) is distinctly clear from the strong bands at 1690 and 1230 cm^{-1} respectively. Similarly in the infrared spectrum of *p*-nitrobenzoic acid, the presence of a COOH group (bands 1 and 2) and a nitro group (bands 3 and 4) is clear.

Further values can be checked by reference to tables of data. These are given under figures and are also presented under summary (Figs. 3.58-3.62). In modern practice, however, infrared spectroscopy is used as an adjunct to pmr and cmr spectroscopy. This combination makes the identification of the functional groups and the solution of structural problems



Characteristic C=O stretching frequencies of aldehydes

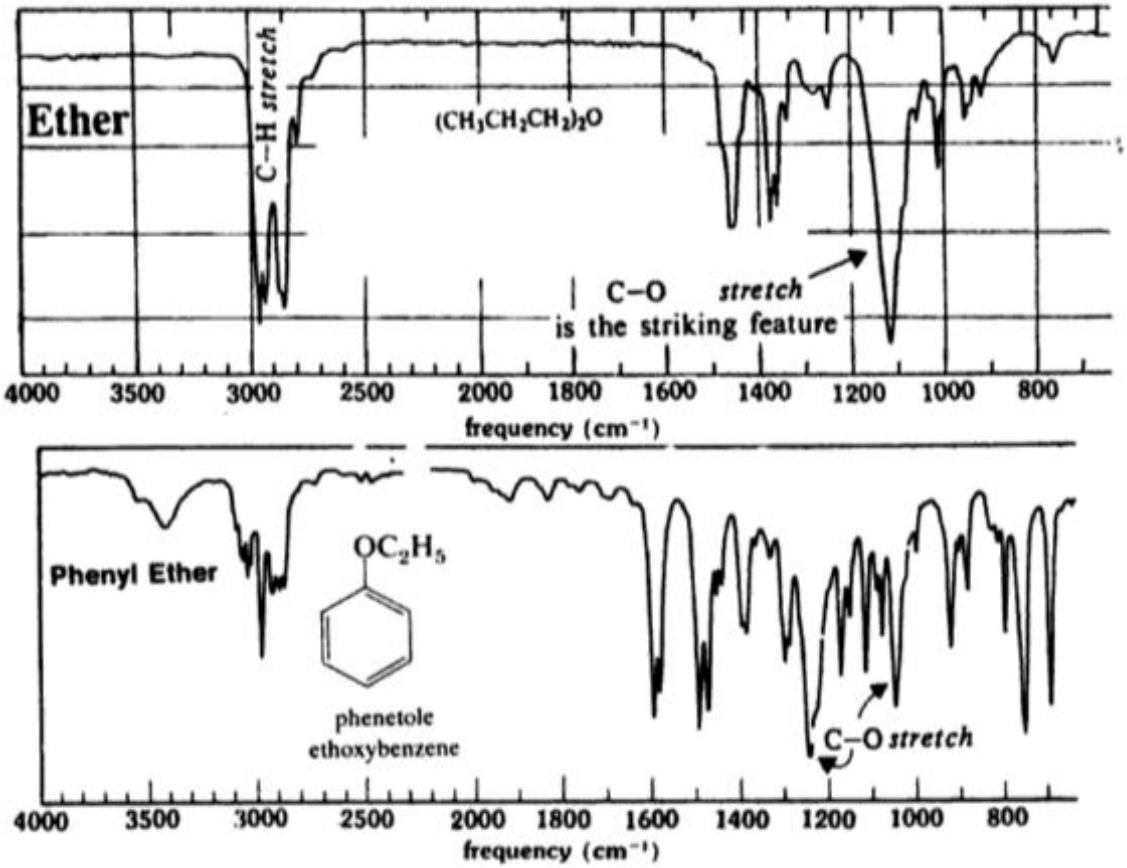
Fig. 3.18

rather easy. If, *e.g.*, the infrared spectrum of a compound suggests that the structure is an aldehyde its pmr must be checked.

3.7 INTERPRETATION OF INFRARED SPECTRA—CHARACTERISATION OF FUNCTIONAL GROUPS AND FREQUENCY SHIFTS ASSOCIATED WITH STRUCTURAL CHANGES

(a) Hydroxy Compounds, Amines, Amides and Carboxylic Acids.

(i) Similarities in O—H and N—H Stretching Bands—Characterisation of Amines. The hydroxyl groups of alcohols and phenols are very easy to recognise from their typical O—H stretching absorptions (Fig. 3.16) in the region around (3650-3200 cm^{-1} which is to the left of aliphatic C—H stretch (around 2925 cm^{-1}). The stretching frequencies of N—H bonds of



C—O stretching, *strong, broad* cm^{-1}

Alkyl ethers 1060–1150

Aryl and vinyl ethers 1200–1275
and, weaker, at 1020–1075

Fig. 3.19

amines and amides give absorption in about the same region where the O—H absorbs and thus can sometimes be confused with those of O—H stretching frequencies. However, since oxygen is more electronegative than nitrogen, O—H stretching results in a greater change in bond moment, than does N—H stretching, therefore, one can see that the O—H stretching band is stronger than the N—H stretching band (Fig. 3.21). In dilute solutions, O—H stretching appears as a sharp band at higher frequency around 3600 cm^{-1} due to free O.H group. In spectra of neat (undiluted) liquids or solids intermolecular hydrogen bonding broadens the band and shifts its position to lower frequency (3200-3500 cm^{-1}). Because of much weaker tendency to form hydrogen bonds the associated N—H stretching absorption is usually sharper. The intensity of N—H stretching absorption is also usually less than O—H absorption. Moreover, in dilute solutions the N—H absorption never goes as high as the free

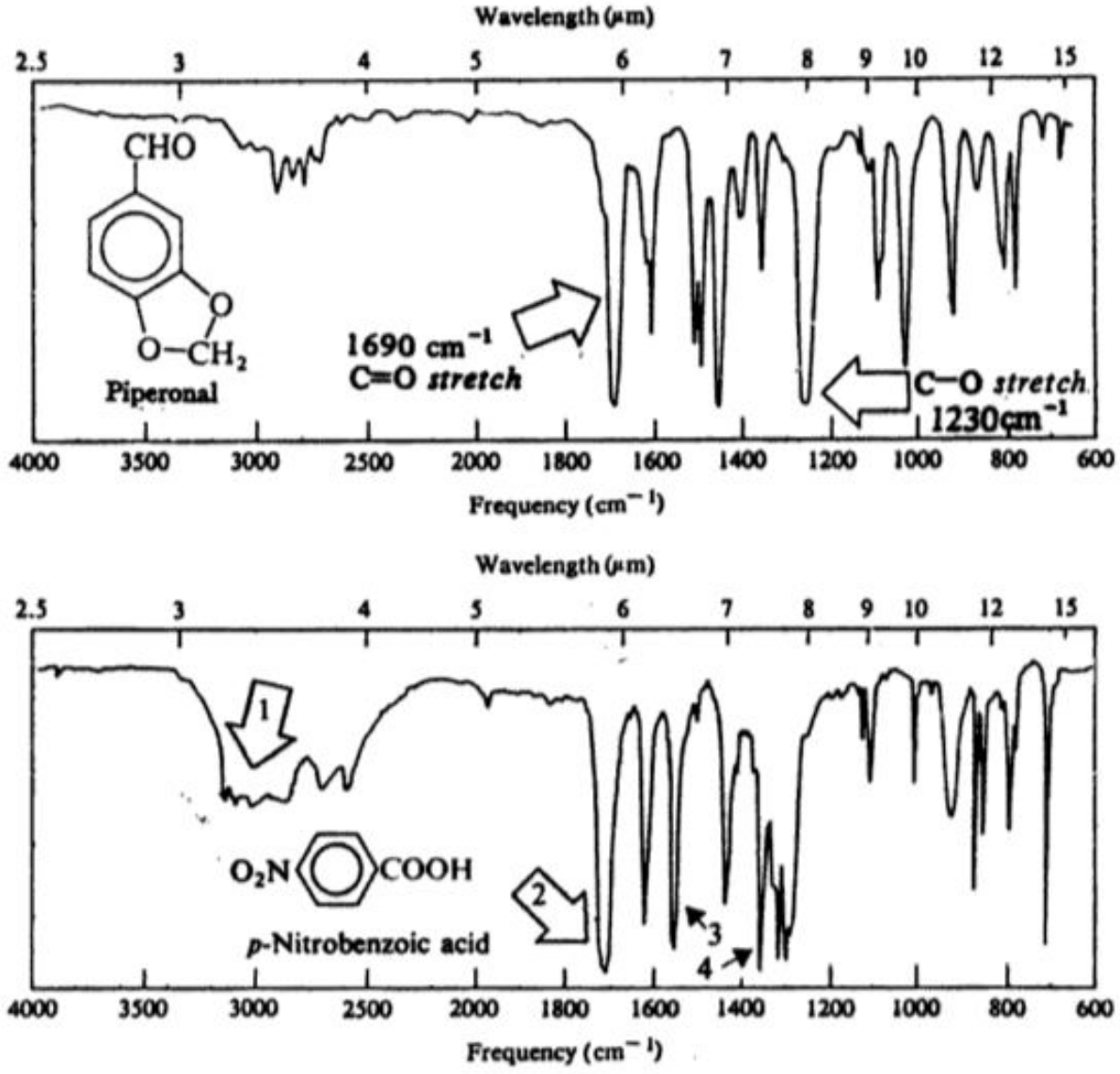


Fig. 3.20

O—H range around 3600 cm^{-1}. The N—H stretching frequency of a secondary amine consists of one band, whereas primary amines display two bands (due to vibrational coupling) around 3200 and 3500 cm^{-1} (an asymmetric stretching band which is stronger of the two and a symmetric stretching band, Fig. 3.21. In the case of a tertiary amine, since there is no N—H, there is no absorption in this region (Fig. 3.22).

As with alcohols in dilute solutions the free N—H stretching vibrations of amines are shifted to higher frequencies. The shifts are not large because of the weaker hydrogen bonding of amines than alcohols, *i.e.*, around 250 cm^{-1} for amines versus 300 cm^{-1} for alcohols. The other bands in the spectrum of amines are N—H bending vibrations (1650-1580 cm^{-1} Fig. 3.21). The N—H bending bands of aliphatic secondary amines are very weak and are therefore, seldom seen in their infrared spectra.

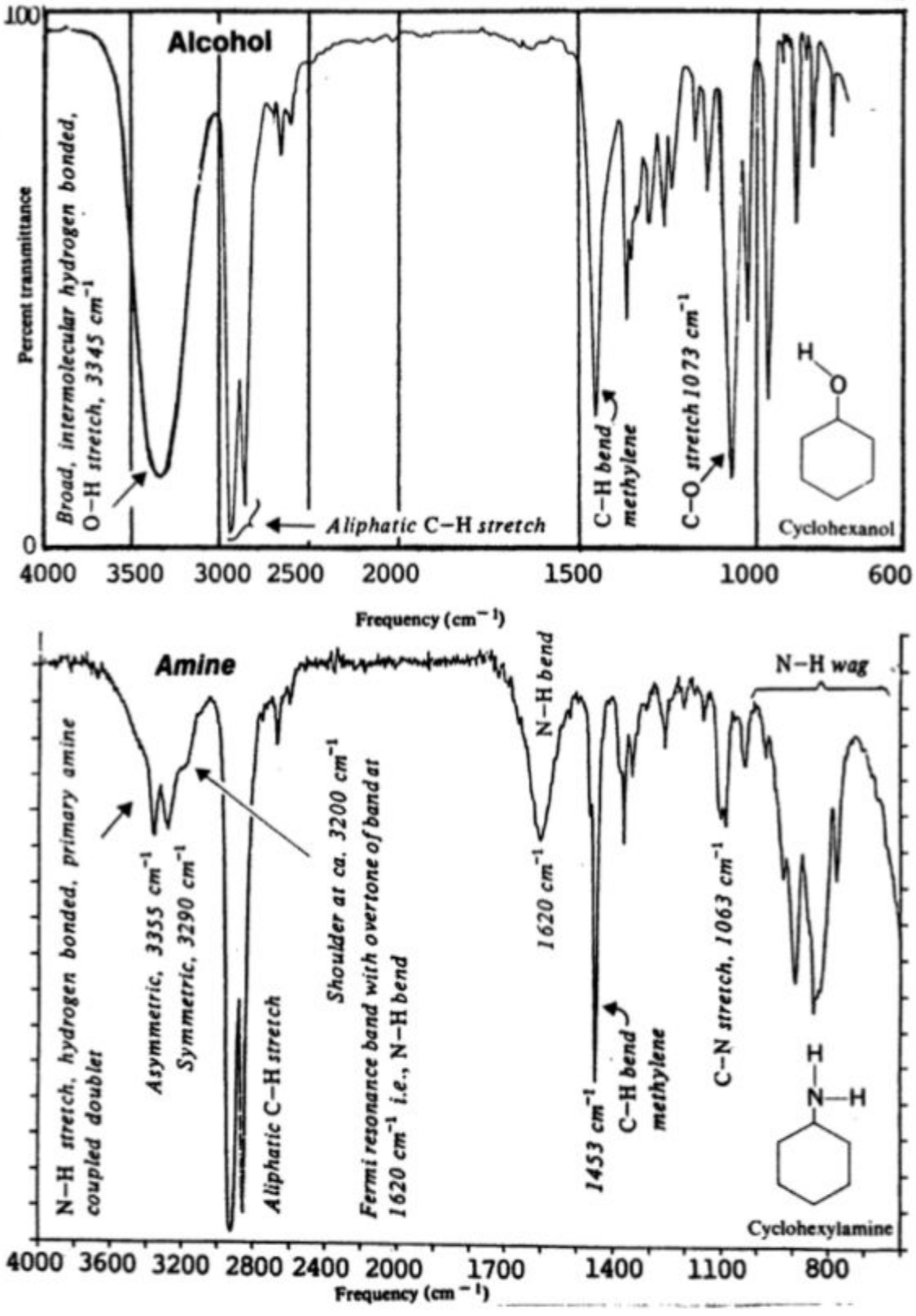


Fig. 3.21

The unconjugated C—N linkages in amines give medium-weak bands (1250-1020 cm^{-1}) due to C—N stretching vibrations. Aromatic amines

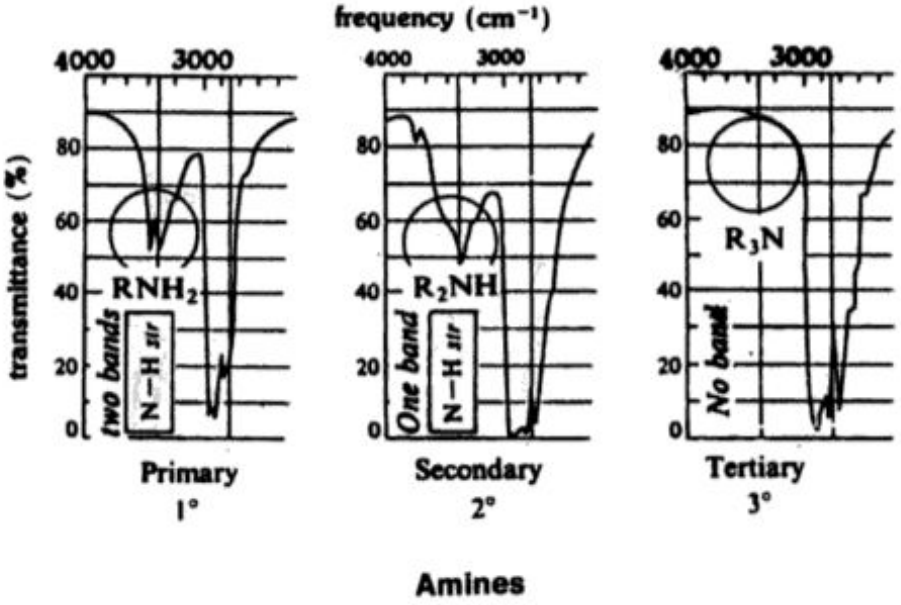
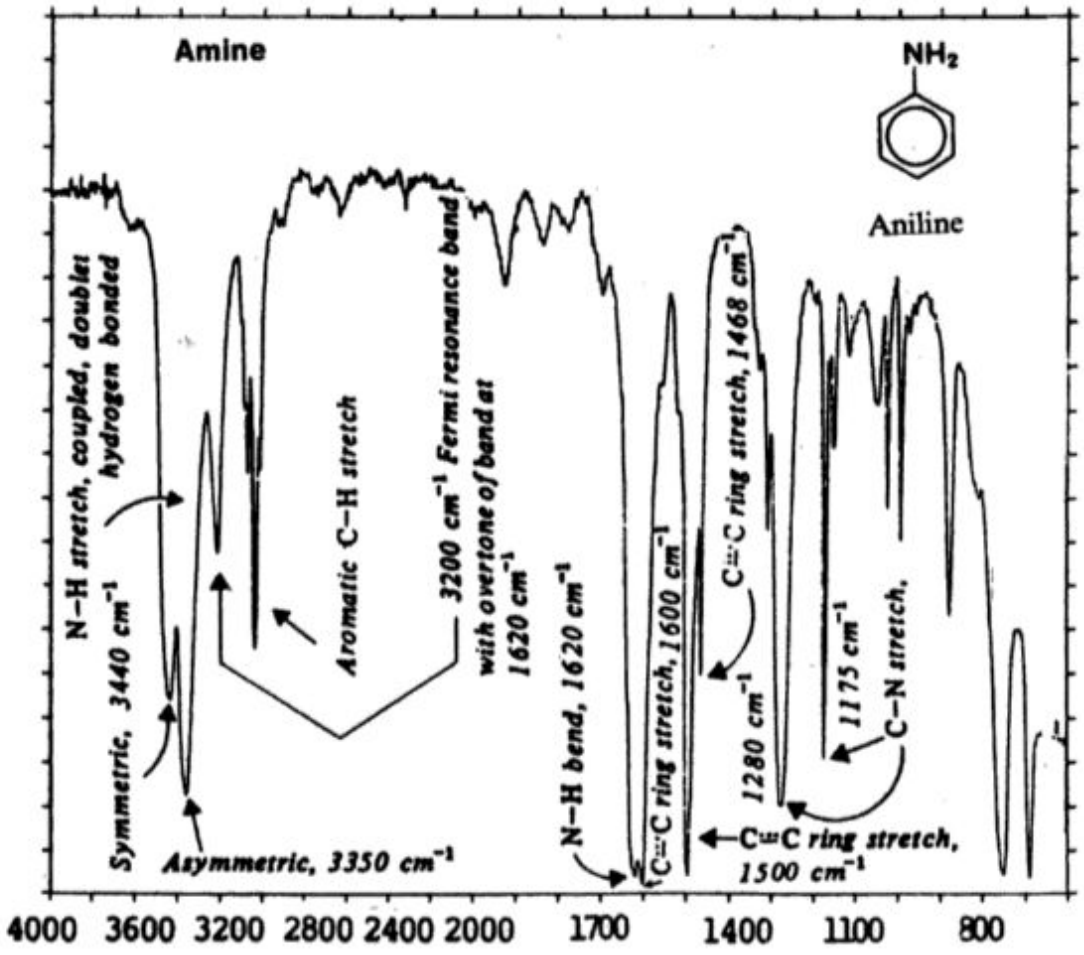


Fig. 3.22

(Fig. 3.23) show strong C—N stretching absorption near 1300 cm^{-1}. The higher frequency is because the force constant of the C—N bond is increased due to resonance with the benzene ring. Still another N—H bending band displayed by primary and secondary amines is the N—H wagging (900-600 cm^{-1}) seen in the spectrum of cyclohexylamine (Fig. 3.21).

(ii) Infrared Spectra of Amides. In amides the N—H stretching vibrations give absorptions (3140-3500 cm^{-1}), to the left of aliphatic C—H stretching absorption. This is about the same region where N—H of amines and O—H absorb. Just as in amines, the primary amides ($RCONH_2$) show a double band in this region (Fig. 3.24) due to vibrational coupling. Secondary amides RCONHR with only one N—H bond show one band, while tertiary amides $RCONR_2$ with no N—H bond show no absorption in this region. The N—H stretching is reduced by hydrogen bonding, though to a lesser degree as compared to O—H stretching.

Simple amides show lower carbonyl stretching frequencies than the other carboxylic acid derivatives, absorbing around 1650 to 1690 cm^{-1}. This low-frequency absorption is due to the resonance in the amide functional group. The resonance picture shows that the C=O bond of the amide carbonyl group is somewhat less than a full double bond (Fig. 3.24). This bond is not as strong or as the C=O bond in a simple ketone or carbocylic acid, thus it has a lower stretching frequency. If the amide is conjugated, the carbonyl stretching frequency is lowered still further. When a carbonyl group of the amide is involved in hydrogen bonding its stretching frequency is again lowered. The carbonyl absorption of amides (known as the



N—H stretching 3200–3500 cm^{-1}

1° Amines	2° Amines	3° Amines
Often two bands	*One band*	*No band*

N—H bending

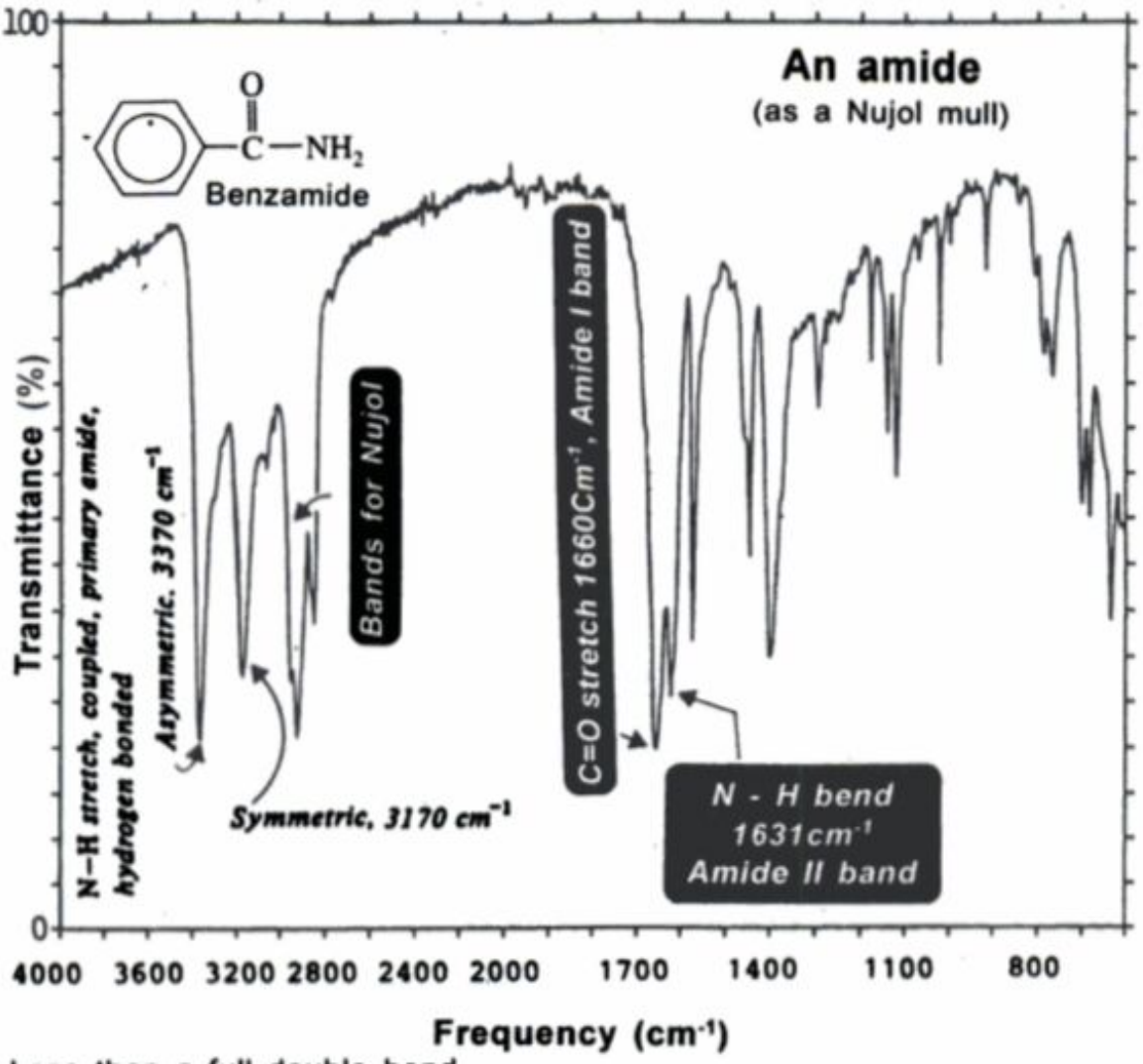
1° Amines Strong bands 650–900 cm^{-1} (*broad*) and 1560–1650 cm^{-1}

C—N stretching

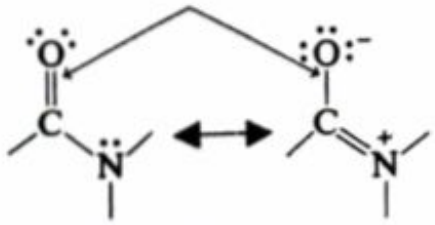
Aliphatic 1030–1230 cm^{-1} (*weak*) (3°: *usually a doublet*) **Aromatic** 1180–1360 cm^{-1} (*strong*) *Two bands*

Fig. 3.23

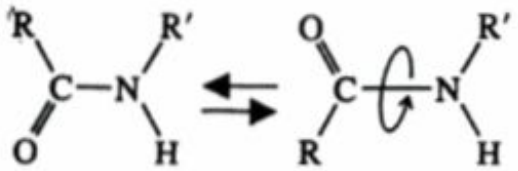
amide I band) of a pure sample, *i.e.*, when hydrogen bonding is maximum shows itself around 1650 cm^{-1}. On dilution of the sample with a non-hydrogen bonding solvent, the extent of hydrogen bonding decreases and



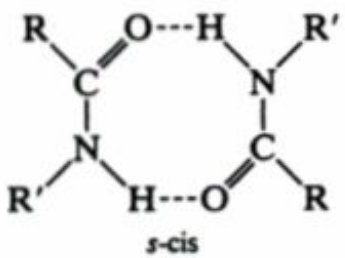
Less than a full double bond



Resonance picture of the amide

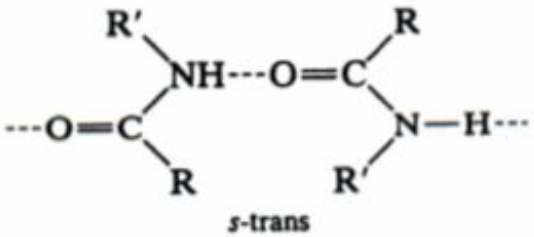


s-cis-monomer *s-trans*-monomer



s-cis

cis-dimer



s-trans

trans-polymeric association

Fig. 3.24

the C=O absorption (amide I band) is shifted to a higher frequency around 1690 cm^{-1}. The carbonyl frequency of tertiary amides is however,

independent of its physical state as hydrogen bonding with another tertiary amide group is not possible.

The amide II band of primary amides appears (1640-1600 cm^{-1}) just to the right of the C=O absorption (amide I band) and it is often enveloped by the amide I band. The amide II band is due to N—H bending and therefore, a tertiary amide does not show this band.

The secondary amides in the solid state show the amide II band in the region 1570-1515 cm^{-1}, *i.e.,* at lower frequencies than their primary counterparts. In non-popular solvents, as dilute solutions, primary amides display two NH stretching frequencies of medium intensity corresponding to the asymmetrical and symmetrical NH stretching vibrations. These bands occur near 3500 cm^{-1} and 3400 cm^{-1} respectively. In the solid state spectra, these bands are observed near 3350 and 3180 cm^{-1} due to hydrogen bonding.

The secondary amides, exist mainly in the *trans* conformation, the free NH stretching vibration in dilute solutions is near 3430 cm^{-1}. In more concentrated solutions and in solid samples, *i.e.,* when hydrogen bonding is operative the free NH band is replaced by multiple bands in 3320-3140 cm^{-1} region. Since the amide group can bond to form dimers, with a *cis*-conformation, and polymers, with a *trans* conformation, the C=O absorption of amides shows itself at lower frequencies than "normal" carbonyl absorption due to resonance effect and hydrogen bonding.

In secondary amides, the C—N stretching vibration is of similar frequency to that of N—H banding mode. Interaction (coupling) of these two vibrations in the component C—N—H gives rise to two bands one N—H bending (amide II band) is as a consequence at a higher frequency (1550-1510 cm^{-1}). The second C—N stretching (amide III band) is at lower frequency near 1750 cm^{-1} [for details see Sec. 3.7a (ii)].

(iii) Infrared Spectra of Carboxylic Acids. Carboxyl groups are the easiest to detect by infrared spectroscopy. This is because of the co-presence of C=O stretching absorption in the correct region (~ 1710 cm^{-1}), with the exceedingly broad O—H stretching absorption. The O—H band, begins at about 3300 cm^{-1} and slopes into the aliphatic C—H absorption band and thus is centred around 3000 cm^{-1}. The infrared spectrum of a long chain acid (Fig. 3.25) is typical. The broad O—H stretching band corresponds to the hydrogen bonded dimers. As a result of strong hydrogen bonding a free O—H stretching around 3530 cm^{-1} can be detected only if the infrared spectrum of a carboxylic acid is scanned in very dilute solutions in non-polar solvents or in vapour phase. Similarly the monomers of, *e.g.,* saturated aliphatic acids show their C=O stretching near 1760 cm^{-1}, as shown in the infrared spectral determination of undecynoic acid (Fig. 3.26). The solid line spectrum (Fig. 3.26) is that of the solution of undecynoic acid and the —COOH group is readily recognised from the

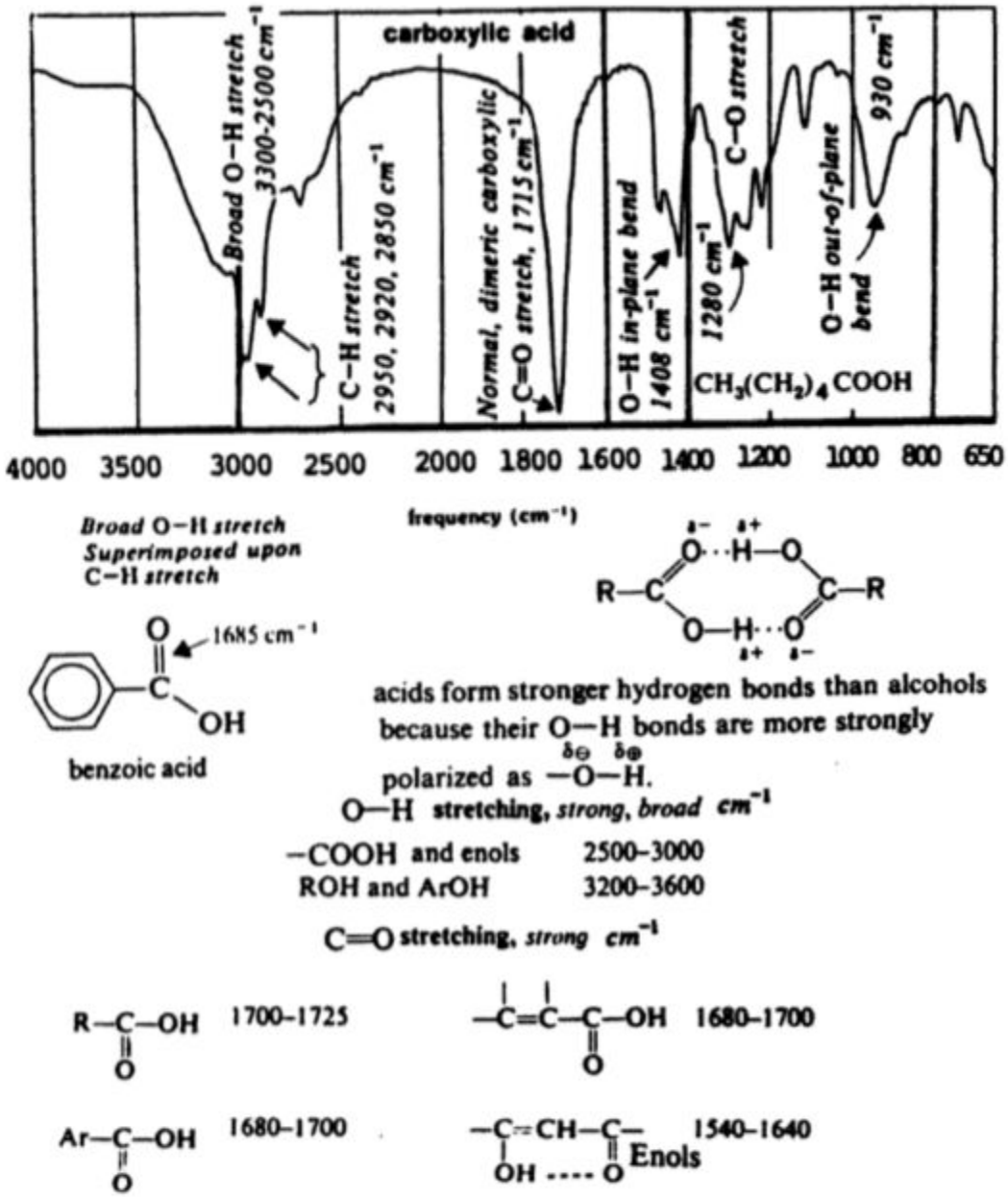


Fig. 3.25

broad bonded O—H stretching of the dimer together with the strong C=O stretching band at 1715 cm^{-1}. This spectrum (solid line) also shows rather weak absorptions at 3530 and 1760 cm^{-1} due to the presence of monomeric acid which is not involved in hydrogen bond formation. On further dilution the spectrum (dotted line) clearly shows the expected enhancement in the bands at 3530 and 1760 cm^{-1}. The dimeric structures, however, persist in solution in hydrocarbon solvents and to a significant extent even in the vapour phase. The presence of a carboxylic acid group (—COOH) can be confirmed by its conversion into a salt and looking for coupled vibrations (see Sec. 3.7c and Table 3.1).

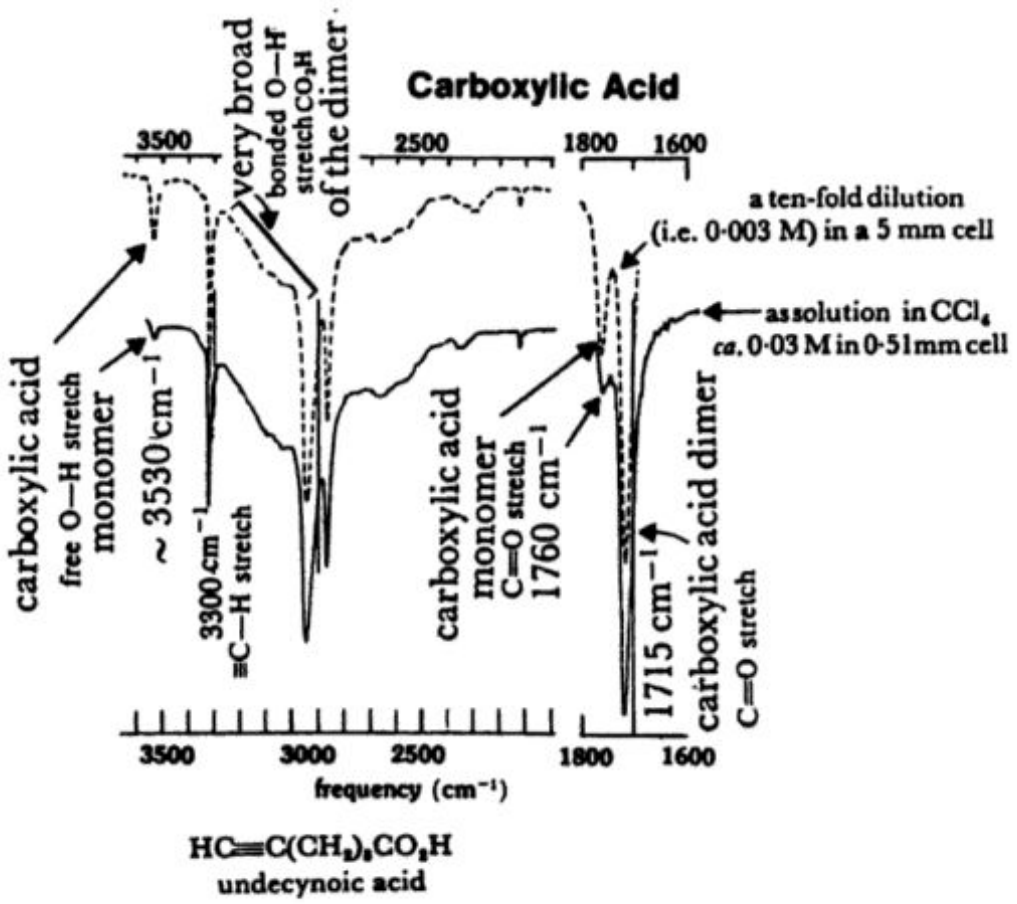
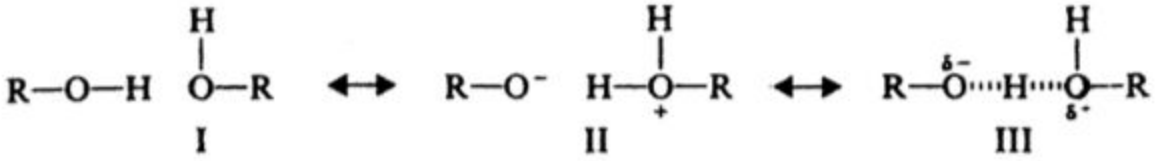


Fig. 3.26

(iv) Effect of Hydrogen Bonding — A Study of Alcohols. Hydrogen bonding changes the position and shape of an infrared absorption band. The spectra (Figs. 3.16 and 3.21) are of pure compounds and as a result the hydrogen bonding is extensive and, therefore, one observes only a wide band for the O—H stretching vibrations, *e.g.*, in the case of cyclohexanol (Fig. 3.21) and that too at lower frequencies, around 3330 cm^{-1}. When hydrogen bonding is less extensive a sharper and less intense band is observed at higher frequencies around 3600 cm^{-1}. In the case of intermolecular hydrogen bonding some OH groups are bonded, some are not and thus both peaks may show (Figs. 3.8a and 3.16). The sharp non-hydrogen bonded O—H absorption band around 3600 cm^{-1} can be observed in the vapour phase, in dilute solution or if steric hindrance prevents hydrogen bonding. Generally, the infrared spectra of pure solids, liquids (*i.e.*, cyclohexanol, Fig. 3.16) and many solutions show only the broad hydrogen bonded band. The reason that bonded O—H stretch appears at lower frequency than free O—H stretch is assigned to lengthening of the original O—H bond on hydrogen bonding as shown (Scheme 3.3). One may regard the hydrogen bond as a resonance hybrid, as a result the bond is weakened, its force constant is reduced and therefore, the stretching frequency gets



lengthening of O—H bond in hydrogen bonding

Scheme 3.3

lowered. In short, the value of the O—H stretching is the measure of the strength of a hydrogen bond. The stronger the hydrogen bond, the longer is the O—H bond, the lower the vibration frequency and broader and more intense will be the absorption band.

(v) Distinction Between Inter- and Intramolecular Hydrogen Bonding. In very dilute solution, formation of intermolecular hydrogen bonds does not take place as the molecules are widely separated. Increasing the concentration of the alcohol or phenol causes the sharp band around 3600 cm^{-1} to be replaced by a broad and lower frequency band which is assigned to OH groups that are associated through intermolecular hydrogen bonding. Consider the plots of spectra (3.27) of *t*-butyl alcohol as the pure liquid and as its solutions in carbon tetrachloride in the high frequency region. In the spectrum of pure liquid (Fig. 3.27, I) one, only observes a strong bonded O—H stretch around 3360 cm^{-1}. In its solution with carbon tetrachloride, the 3360 cm^{-1} O—H absorption is accompanied by a sharp band at 3620 cm^{-1} (Fig. 3.27, II). On further dilution the 3620 cm^{-1} band becomes more intense relative to the 3360 cm^{-1} band (Fig. 3.27, III). These two bands are both due to O—H stretch. The band at higher frequency is due to the stretching mode of "free" hydroxy. The stretching mode of hydrogen-bonded or "associated" O—H occurs at lower frequency (3360 cm^{-1}).

Distinction between inter- and intramolecular hydrogen bonding can thus be made by the effect of dilution. Intramolecular hydrogen bonds remain unaffected and as a result the absorption band also remains unaffected. Intermolecular hydrogen bonds are however, broken on dilution and as a result there is a decrease in the bonded O—H absorption and an increase in or the appearance of free O—H absorption. Hydrogen bonding in chelates and enols is very strong (Scheme 3.4) and as a result the observed O—H stretching frequencies may be as low as 2800 cm^{-1}. Since these bonds are not easily broken on dilution by an inert solvent, free O—H stretching may not be seen at low concentrations.

(b) Coupled Interactions — Fermi Resonance. Reasons for Two N—H Stretching Bands in Primary Amides. Amines and Characterisation of

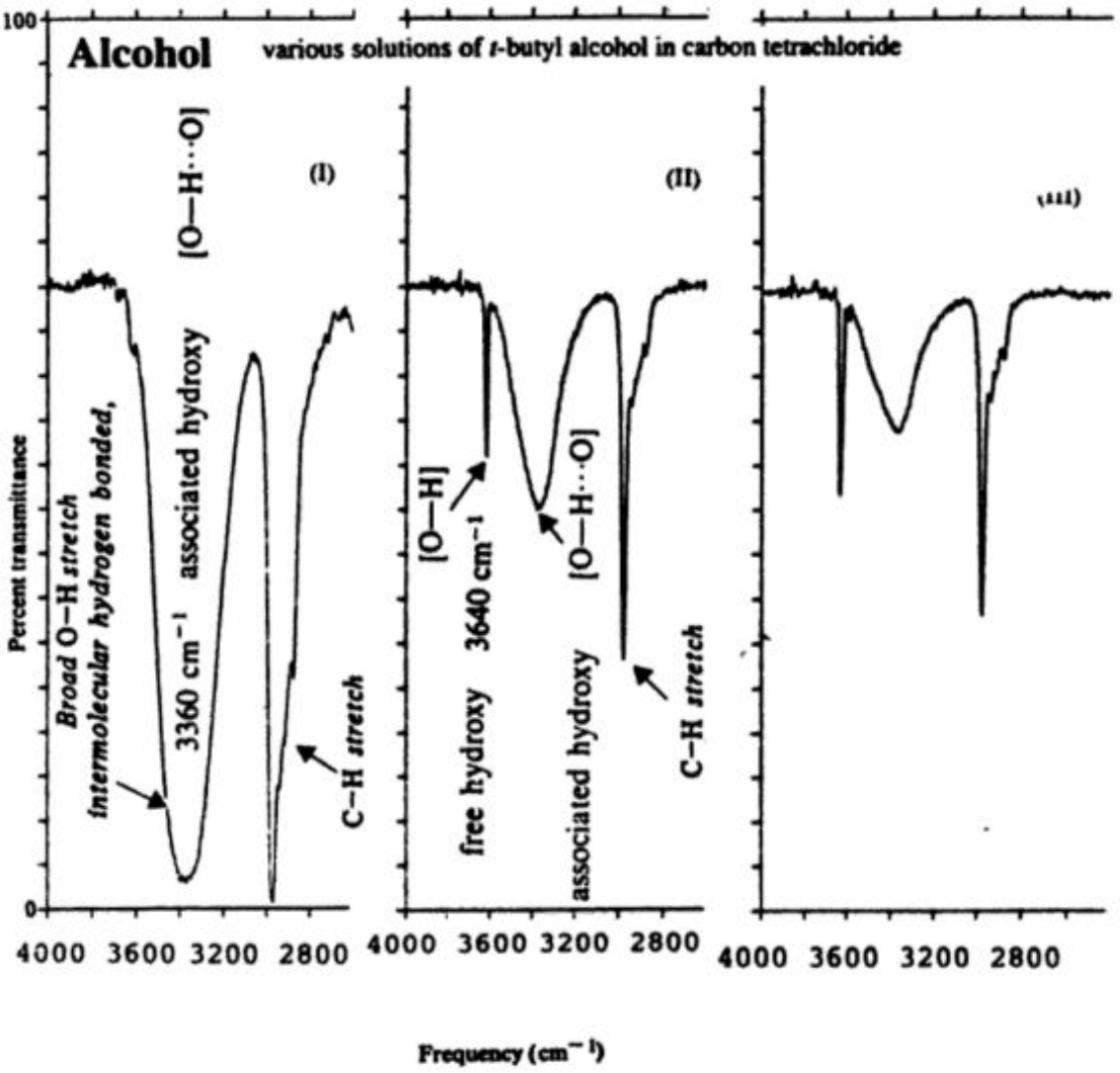


Fig. 3.27

chelate of (methyl salicylate)

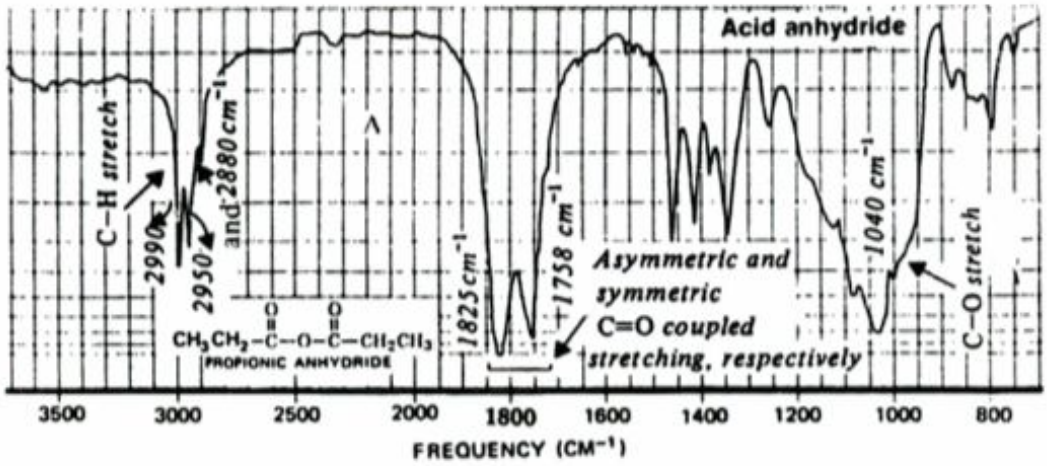
enol of ($CH_3COCH_2COCH_3$)

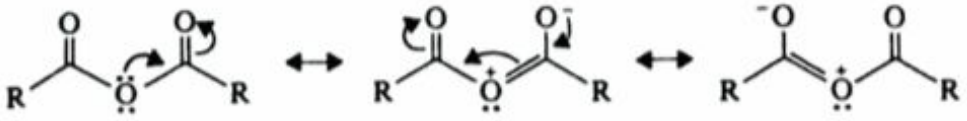
Scheme 3.4

Carboxylic Anhydrides. In case, *e.g.*, a C—H bond is isolated, one will expect only one C—H stretching frequency. The C—H stretching vibrations in CH_2 groups however, combine together to display two coupled vibrations of different frequencies, the asymmetric and symmetric. The C—H coupled vibrations of CH_3 groups are of different frequencies than

CH_2 groups and one can detect all the four C—H stretching vibrations in the high resolution infrared spectra of compounds having CH_2 and CH_3 groups.

Normally it may be sufficient to define the C—H stretch from its general position where it is centred, *i.e.*, around 2925 cm^{-1} as seen in the infrared spectrum of octane (Fig. 3.9). However, one can see clearly at least three of these C—H stretching bands (not marked) in the same figure. As another example, one can see clearly at least the three C—H stretchings of CH_2 and CH_3 groups in the spectrum of propionic anhydride (Fig. 3.28). Vibrational coupling occurs between two bonds vibrating individually near the same frequency and provided that the bonds are reasonably close





anhydrides—resonance forms

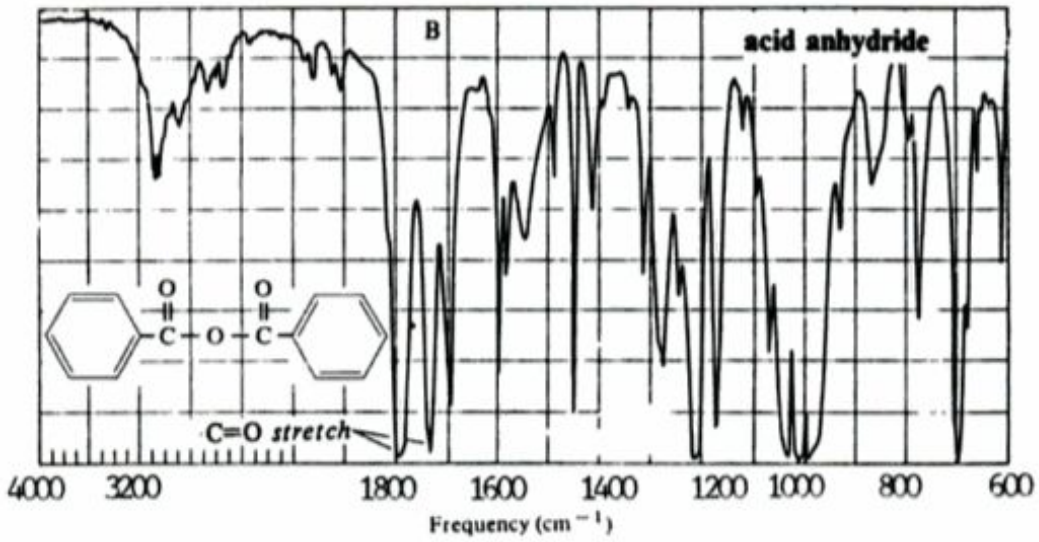


Fig. 3.28

in the molecule. The coupling vibrations may both be fundamentals or a fundamental vibration may couple with the overtone of some other vibration. The later coupling is called Fermi resonance, after Enrico Fermi who first described it. Coupling accounts for the two N—H stretching bands in the spectra of primary amines and amides (Figs. 3.21 and 3.24).

Strong vibrational coupling between stretching vibrations requires a common atom between the groups. An example of this coupling is found in carboxylic acid anhydrides. These show two C=O stretching adsorptions (Fig. 3.28) with a separation of about 60 cm^{-1}. Coupling occurs between the two carbonyl groups, which are indirectly linked via O. The interaction becomes effective probably because of the slight double-bond character in the carbonyl-oxygen bonds due to resonance which also keeps the system coplanar.

The general range for the C=O stretching bands of acyclic saturated acid anhydrides is 1850-1800 and 1790-1740 cm^{-1} which are due to its asymmetrical and symmetrical stretchings. The higher frequency band is more intense in acyclic anhydrides, while the lower frequency band is more intense in cyclic anhydrides. This feature can be gainfully used to distinguish between acylic and cyclic anhydrides. Conjugated anhydrides show a decrease in C=O stretchings due to resonance (Fig. 3.28B). All acid anhydrides display their C—O stretching as one or two strong bands in the region 1300-1050 cm^{-1}.

Fermi resonance, commonly contributes further to the complexity of an infrared spectrum. The effect as explained above is observed as an apparent splitting of a fundamental, such as (C=O) stretching into two bands. It has its origin in the sharing of intensity between the fundamental and an overtone or combination tone of very similar frequency. Under the usual conditions the spectrum of cyclopentanone displays, as expected a single carbonyl stretching absorption. When adequate resolution is employed its spectrum (Fig. 3.29) shows two carbonyl absorptions in the carbonyl stretch region (1745 and 1730 cm^{-1}), due to Fermi resonance with an overtone or combination band of an α-methylene group. The small absorption band around 3450 cm^{-1} in the overtone of C=O stretch. Aroyl chlorides, *e.g.,* can be identified by the Fermi resonance band (Fig. 3.34).

(c) Further Use of Coupled Interactions — Detection of Nitro Compounds, Carboxylic Acid Salts, Sulphones, Amino Acids and Amine Salts. Nitro groups of nitroalkanes can be identified by strong infrared bands around 1550 and 1400 cm^{-1}, whereas the corresponding bands in the spectra of aromatic nitro compounds occur at slightly lower frequencies. These symmetric and asymmetric N=O stretching bands due to the presence of two similar N=O bonds constitute a dependable method to detect nitro groups (Table 3.1). The infrared spectrum (Fig. 3.30) shows the presence of a nitro group by displaying these bands.

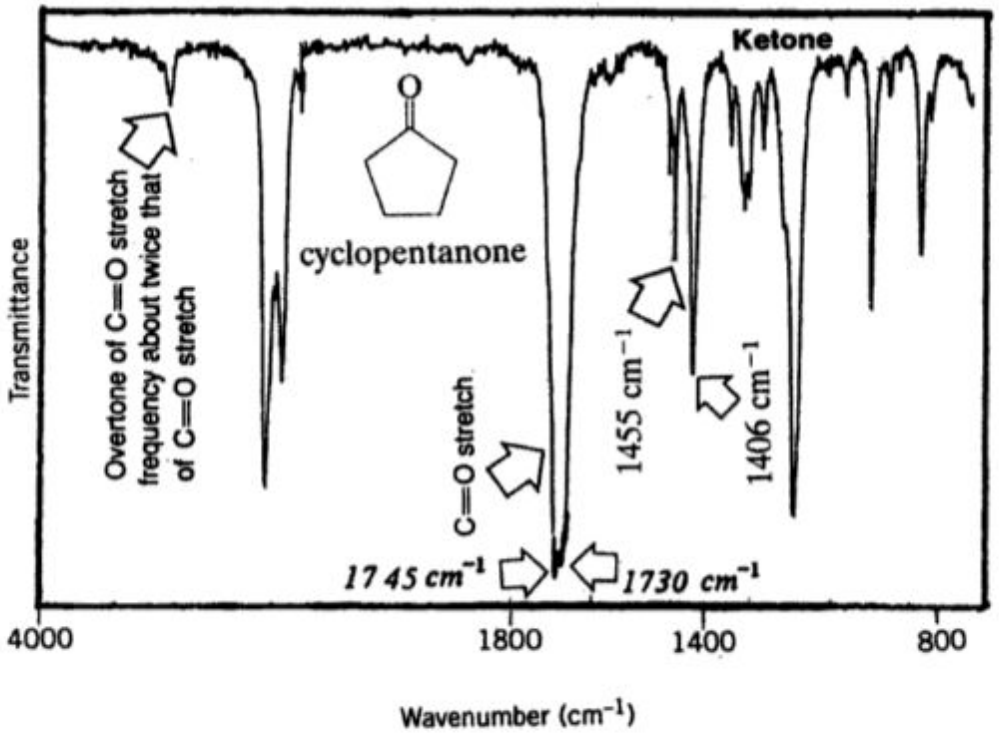
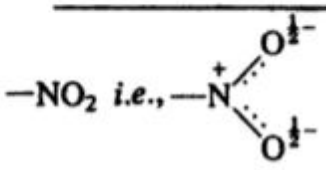
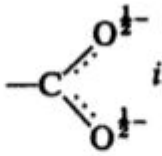
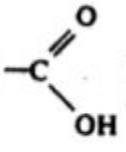
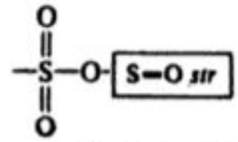
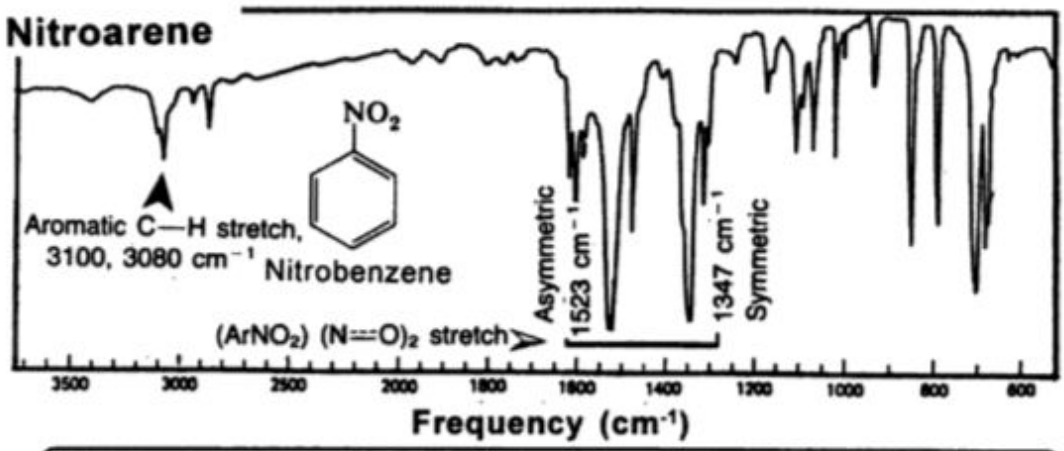


Fig. 3.29

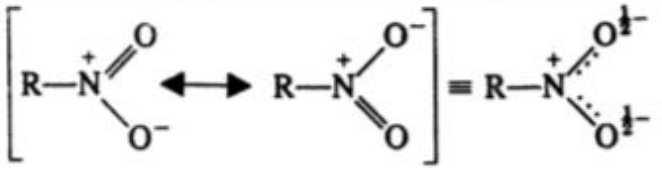
Table 3.1

group	stretch	Asymmetric	Symmetric
	coupled Vibrations	~ cm⁻¹	
$-NO_2$ *i.e.*, 	N=O str	1550	1400
 *i.e.*, salts of 	C=O str	1600	1400
$-SO_2-$ *i.e.*,  or 	S=O str	1350	1150

The S=O stretching bands remain indeed constant in position and the presence of strong asymmetric and symmetric S=O stretching bands again provide a reliable method for the detection of sulphones and sulphonic acid derivatives which contain O=S=O groups.



The nitro group (—NO_2), like the carboxylate anion, is well formulated as a hybrid of two equivalent resonance structures.

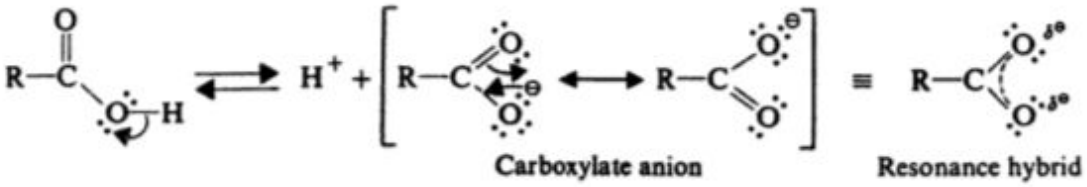


N=O ***Stretching Vibrations***

Group	Intensity	Range cm^{-1}
O—NO_2, Nitrates	(s)	1650–1600
	and (s)	1300–1250
C—NO, Nitroso compounds	(s)	1600–1500
O—NO, Nitrites	(s)	1680–1650
	and (s)	1625–1610

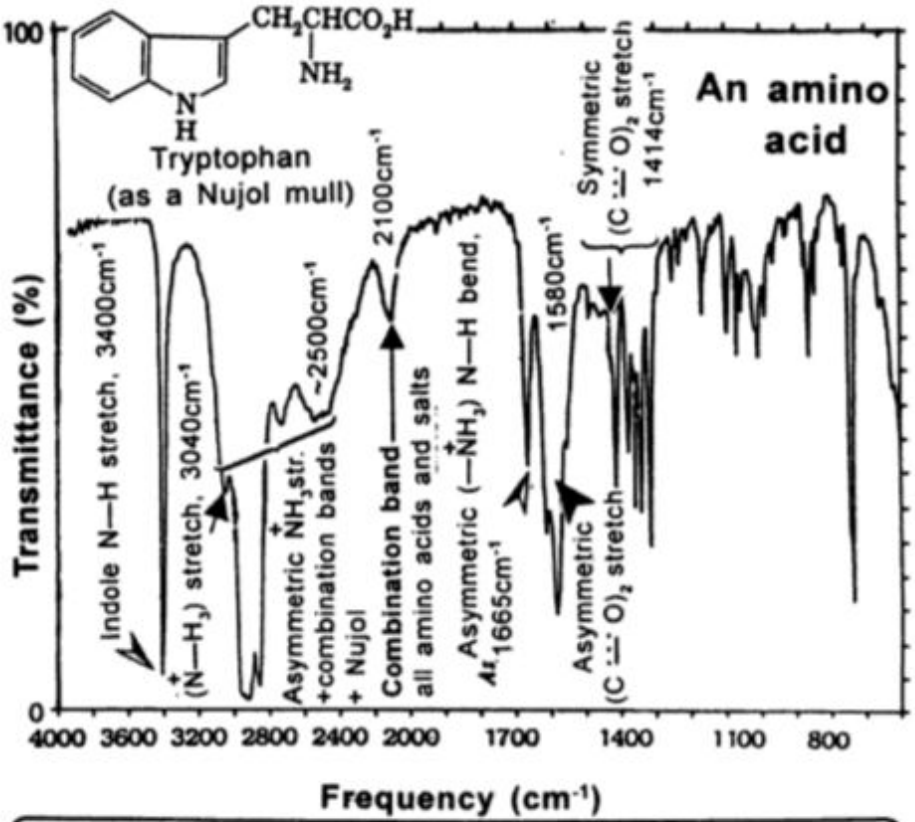
Fig. 3.30

The conversion of a —COOH group of a carboxylic acid to a salt generates a carboxylate anion. The carboxylate anion thus formed (Scheme 3.4a) shows two characteristic coupled crbonyl absorption bands (see Table 3.1) and the O-H stretching band disappears. A carboxylic acid can be converted into its salt by reacting it with a tertiary aliphatic amine in a chloroform solution and can thus be easily recognised.



Scheme 3.4a

The infrared spectra of amino acids show the presence of zwitterionic groups. When one looks to the spectrum of tryptophan (Fig. 3.31), apart

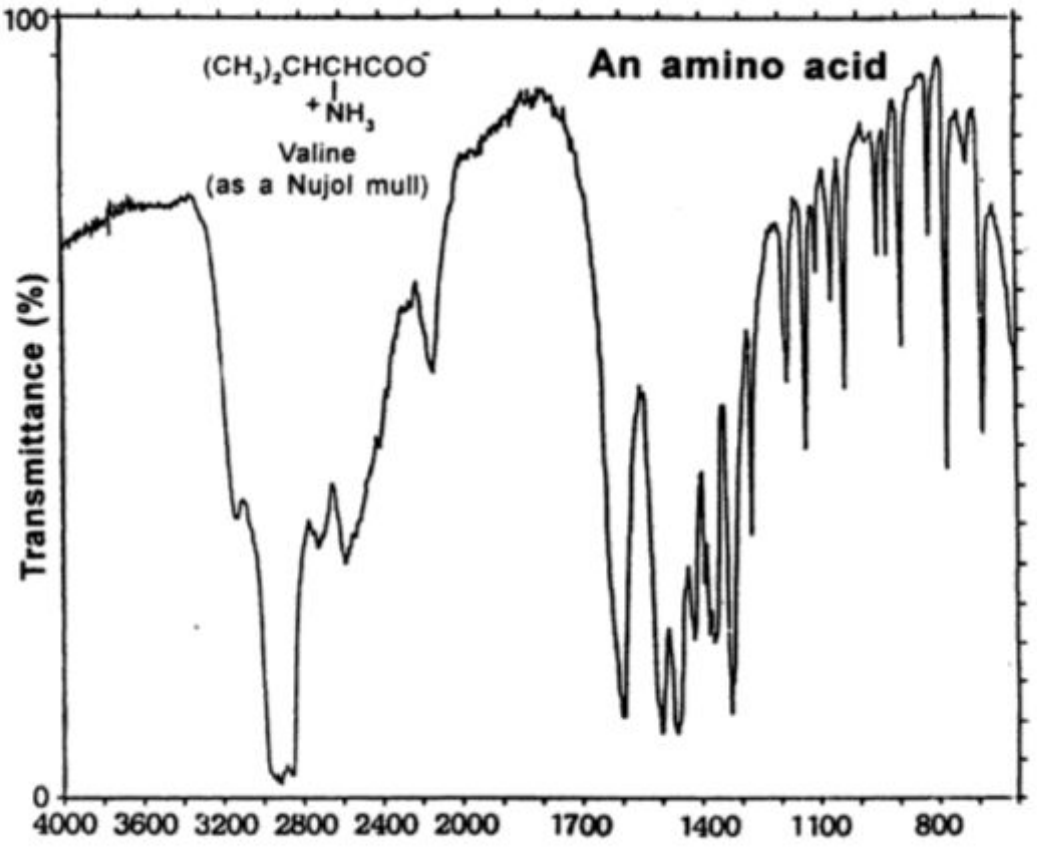


Since amino acids contain both a basic group(—NH_2)and an acidic group (—COOH), they are amphoteric compounds. In the dry solid state,amino acids exist as *dipolar ions*,a form in which the carboxyl group is present as a carboxylate ion.

Fig. 3.31

from the characteristic indole N—H stretch (3400 cm^{-1}) the other typical bands which point to an amino acid are clearly seen. These are the N—H stretching of the primary ammonium group —N^+H_3, which appear as a broad and strong band(s) in the general range 3100-2600 cm^{-1} , under the saturated C—H absorption. Another characteristic band around 2100 cm^{-1} is the combination band shown by all amino acids and their salts. In fact, this band along with the band around 2500 cm^{-1} (overtones) are the two bands which are very common with amino acids and primary amine salts. In addition to N—H bending vibrations 1665 cm^{-1}, the carboxylate ion absorbs strongly near 1600 cm^{-1} and weakly around 1400 cm^{-1}. Another interesting features in the infrared spectrum of tryptophan is the band around 740 cm^{-1}, which is typical C—H out of plane bend of a 1,2-disubstituted benzene ring. One can detect all of these bands in the spectrum of another amino acid valine (Fig. 3.32).

On acidification the protonated amino acid is generated which then shows the true C=O stretching at higher frequency (around 1720 cm^{-1}) than the carboxylate C :-: O stretch.



$$H_2NCHRCOO^- \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} {}^+H_3NCHRCOO^- \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} {}^+H_3NCHRCOOH$$

The dipolar ion

Fig. 3.32

(d) Overtone Bands. Additional bands, may occur as overtones (at approximately $\frac{1}{2}, \frac{1}{3}, \frac{1}{4}$ .... and so on, the wavelength of the fundamental mode). Overtones may arise in two ways. If a molecule in the lowest or first vibrational state is excited to the third vibrational level, the energy required is almost twice that required for excitation to the second vibrational level. It is not exactly twice as much because the higher levels tend to lie closer together than the lower levels. Fortunately, however, the intensities of overtones are 1/10 to 1/100 those of the fundamental. The intensity of the overtone decreases as the order of the overtone increases (*i.e.,* 2nd overtone is less intense than 1st overtone). As a result 2nd and higher overtones are rare while 1st overtones are observed only for strong bands.

An overtone that often may cause a problem in interpretation is that of the carbonyl group, since, carbonyl stretch is a strong absorption around 1700 cm^{-1}. It often gives rise to a noticeable overtone around 3400 cm^{-1} a

region of hydroxyl stretching. This can be seen in the spectrum of ethyl acetate (Fig. 3.33).

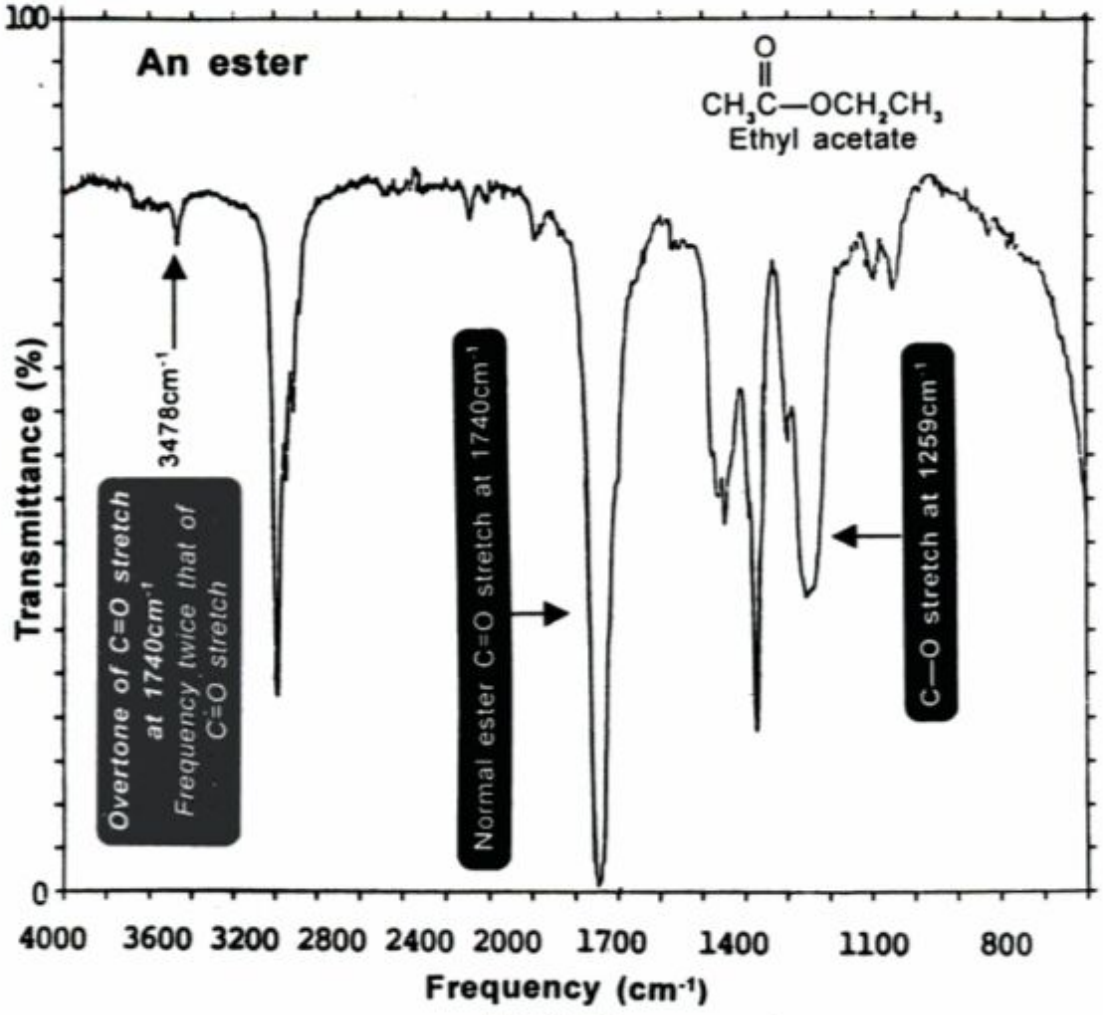
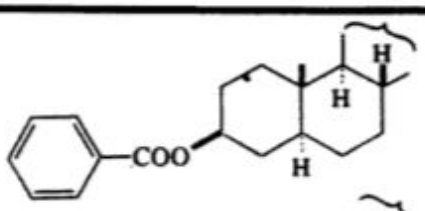
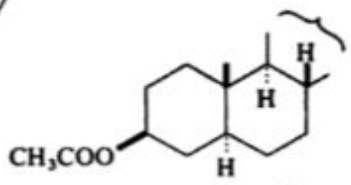
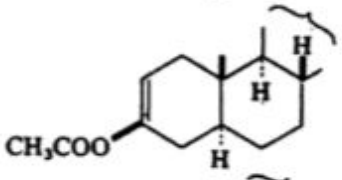
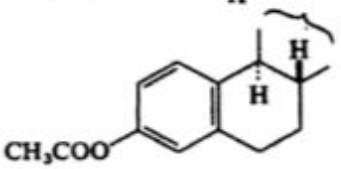
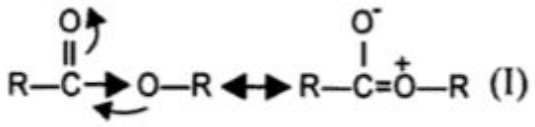


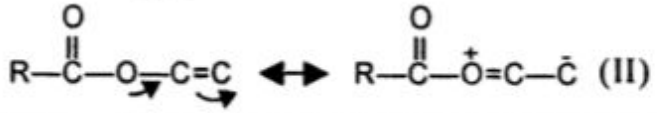
Fig. 3.33

(e) Frequency Shifts Due to Inductive and Mesomeric (Resonance) Effects — Infrared Spectra of Esters and Acyl Halides. One has already been that in amides the $+M$ effect leads to weakening of the C=O bond (Fig. 3.24). This factor leads to lowering of the C=O stretching frequency to around 1650 cm^{-1} compared to that in a ketone, *e.g.,* 3-pentanone (1715 cm^{-1}, Fig. 3.17).

Esters, *e.g.,* ethyl acetate have two characteristic absorptions due to C=O stretching around 1735 cm^{-1} and C—O stretching around 1200 cm^{-1} (Fig. 3.33). The carbonyl frequency of saturated esters is higher than that of corresponding ketones. In the case of esters there seems to be a conflict between inductive and mesomeric effects (eq I, Scheme 3.5). In alkyl esters it seems that the force constant of the carbonyl bond is increased by the electron attracting tendency (inductive effect) of the adjacent oxygen atom. However, by looking only at carbonyl frequency, one cannot distin-

Steroid Ester		C=O stretch	C—O stretch
1		1720cm^{-1}	1270cm^{-1}
2		1735cm^{-1}	1239cm^{-1}
3		1755cm^{-1}	1217cm^{-1}
4		1766cm^{-1}	1204cm^{-1}





In (II) the *-I* effect of oxygen becomes dominant

Scheme 3.5

guish compounds belonging to these two classes. Thus an ester and a cyclopentanone for example, have nearly the same C=O stretch. This differentiation is possible by looking at C—O stretch, which is a strong band and easily distinguishable from C—C stretch. Another point of difference is that the carbonyl of an ester has greater intensity.

If the acetate ester of the saturated steroidal alcohol 2 is taken as a reference, conjugation with the carbonyl group, as in benzoate ester 1, induces a lowering of the C=O stretching frequency in accord with other carbonyl compounds. The introduction of unsaturation into the alcohol moiety of the ester, as in the enol acetate 3 or the phenolic acetate 4 induces a C=O frequency displacement in the opposite direction. Significantly with the increase in the C=O stretching of enolic and phenolic acetates the C—O stretching shows a fall. This can be attributed to suppression of the resonance (eq. I) by competition of the system (eq. II) for the electrons of the ester oxygen atom (Scheme 3.5).

In acid halides, the $-I$ effect of a halogen dominates over $+M$ and as a result, unconjugated acid chlorides show their C= O stretching in 1815-1785 cm^{-1} region. Significantly the C=O stretching position shows only small, if at all dependance on conjugation as seen in the case of benzoyl chloride (Fig. 3.34). Aromatic acid chlorides absorb strongly at 1800-1770 cm^{-1}. A band near 1750-1735 cm^{-1} in the spectrum of benzoyl chloride is due to Fermi resonance between the C=O band and the overtone of the longer wavelength band near 875 cm^{-1}. Aroyl chlorides can be identified by this Fermi resonance band.

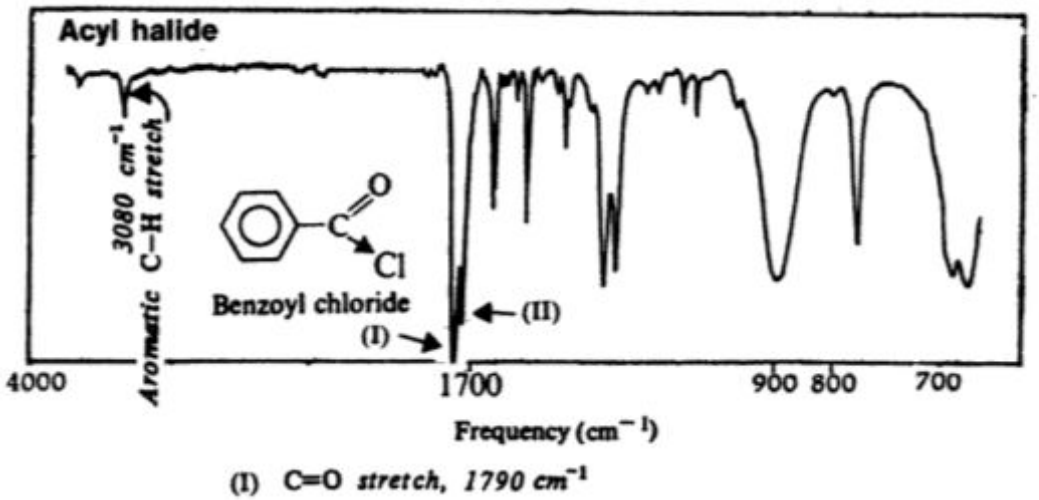
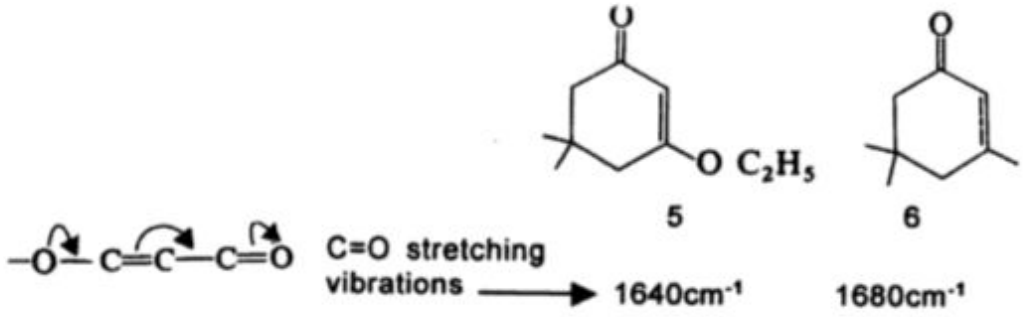


Fig. 3.34

For further details of Fermi resonance (see Sec. 3.3, vii).

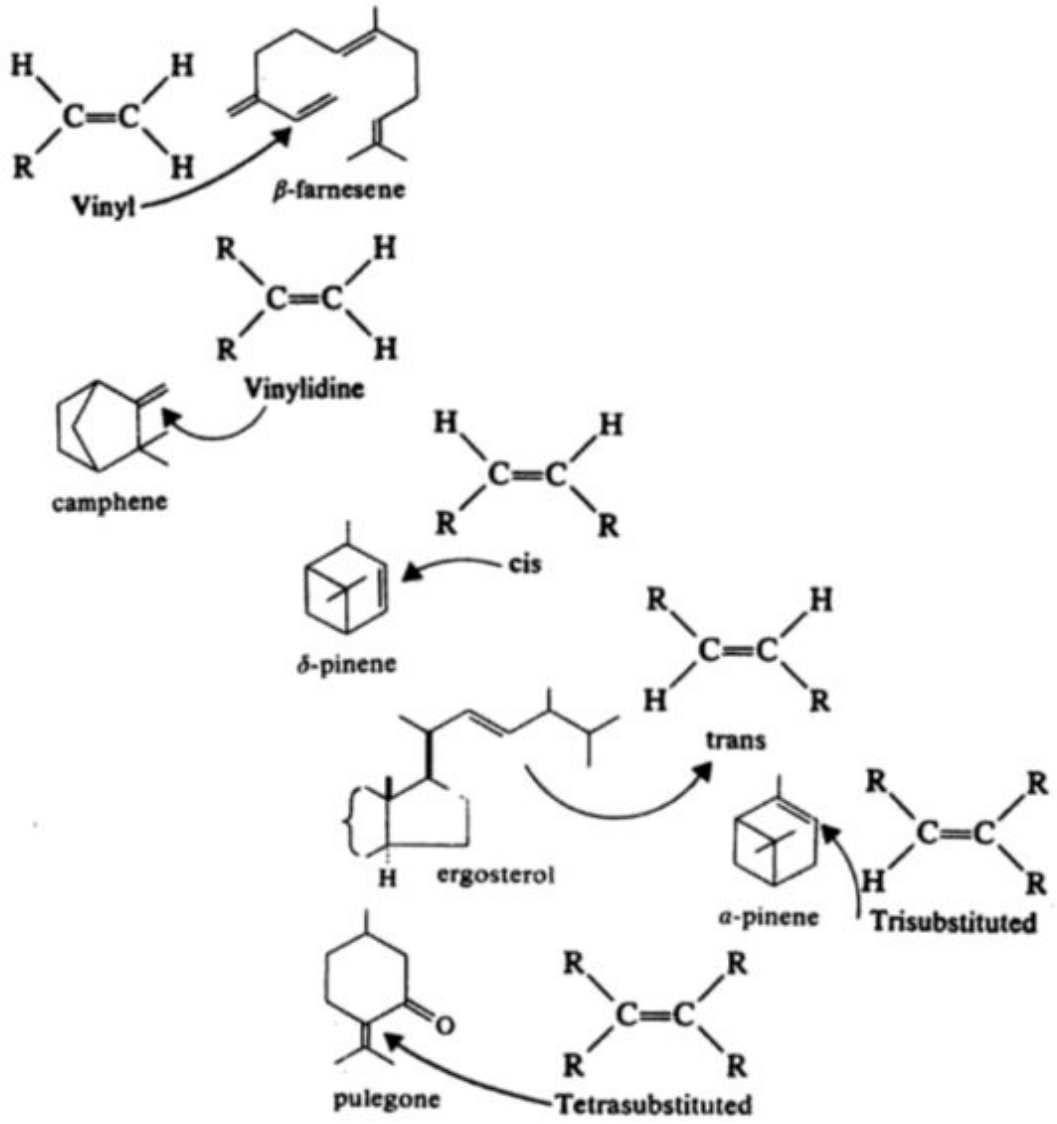
As compared with ordinary esters vinylogous esters show their C=O stretching at considerably low frequencies. The double bond character of the ester carbonyl is greater (C=O, 1735 cm^{-1}) as compared with that of saturated ketones (1715 cm^{-1}). The greater double bond character of ester carbonyl and consequently its higher stretching is obviously due to greater $-I$ effect of the oxygen atom as compared with its mesomeric effect (eq. I, Scheme 3.5). However, this is not the situation in the case of vinylogous esters (α, β-unsaturated ketones with β-alkoxy groups). Dimedone ethyl ether 5, shows two strong bands of almost equal intensity at 1640 cm^{-1} (C=O) and at 1603 cm^{-1} (C=C) This C=O stretch is too low as compared with 1680 cm^{-1} in 6, whose structure is comparable with 5 and is due to special electric effects shown in vinylogous esters (Scheme 3.5a). In these cases $-I$ effect of the oxygen atom is not operative and therefore, the only $+M$ effect leads to considerable weakening of the C=O bond.



Scheme 3.5a

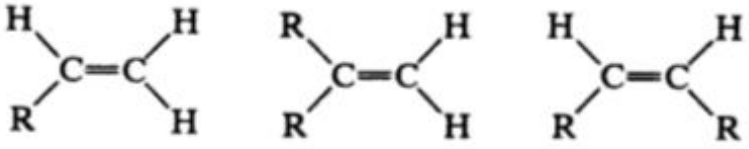
(f) Study of Alkenes-Substitution Pattern. The alkenes are named according to substitution on the two unsaturated carbon atoms as shown in Scheme 3.6. The identification of a particular alkene type can be made

The common names of alkenes

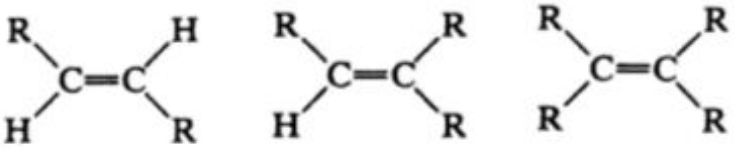


Scheme 3.6

easily by looking to three regions of the infrared spectrum, *i.e.*, the olefinic C—H stretching, C=C stretching and olefinic C—H bending vibrations and are detailed in Fig. 3.13. General values are again presented in Scheme 3.7.



	Vinyl	Vinylidine	*Cis*
C=C stretch	1640cm^{-1} medium	1640cm^{-1} medium	1660cm^{-1} weak
=C—H bend	990cm^{-1} strong 910cm^{-1} strong	900cm^{-1} strong	720cm^{-1} medium



	trans	Trisubstituted	Tetrasubstituted
C=C stretch	1670cm^{-1} absent	1670cm^{-1} weak	absent
=C—H bend	970cm^{-1} strong	830cm^{-1} medium	absent

IR group frequencies of alkenes (general positions)

Scheme 3.7

(i) =C—H Stretchings. In the case of alkenes the olefinic C—H stretching vibration occurs at higher frequencies than an alkane C—H stretchings. This is due to the fact that alkene C—H bonds have greater s-character and are stronger than alkane C—H bonds. It is difficult to stretch stronger bonds (higher force constant) therefore, these require greater energy or higher light frequency. Thus alkenes which have at least one hydrogen attached to the double bond normally absorb in the region around 3080 cm^{-1} (Scheme 3.7). This band which is sharp and of somewhat medium intensity can be easily recognised on the left of main C—H stretching band, *e.g.*, in the spectra (Fig. 3.35A and B). The relative intensity of this band, compared with the band for saturated C—H stretch, is roughly proportional to the relative numbers of the two types of hydrogens in the molecule.

(ii) C=C Stretching. The alkene C=C stretching band occurs in the region around 1640 cm^{-1}. This band is most intense in the case of methylenic (vinylidine) and vinyl double bonds (Fig. 3.35A and B). As more alkyl

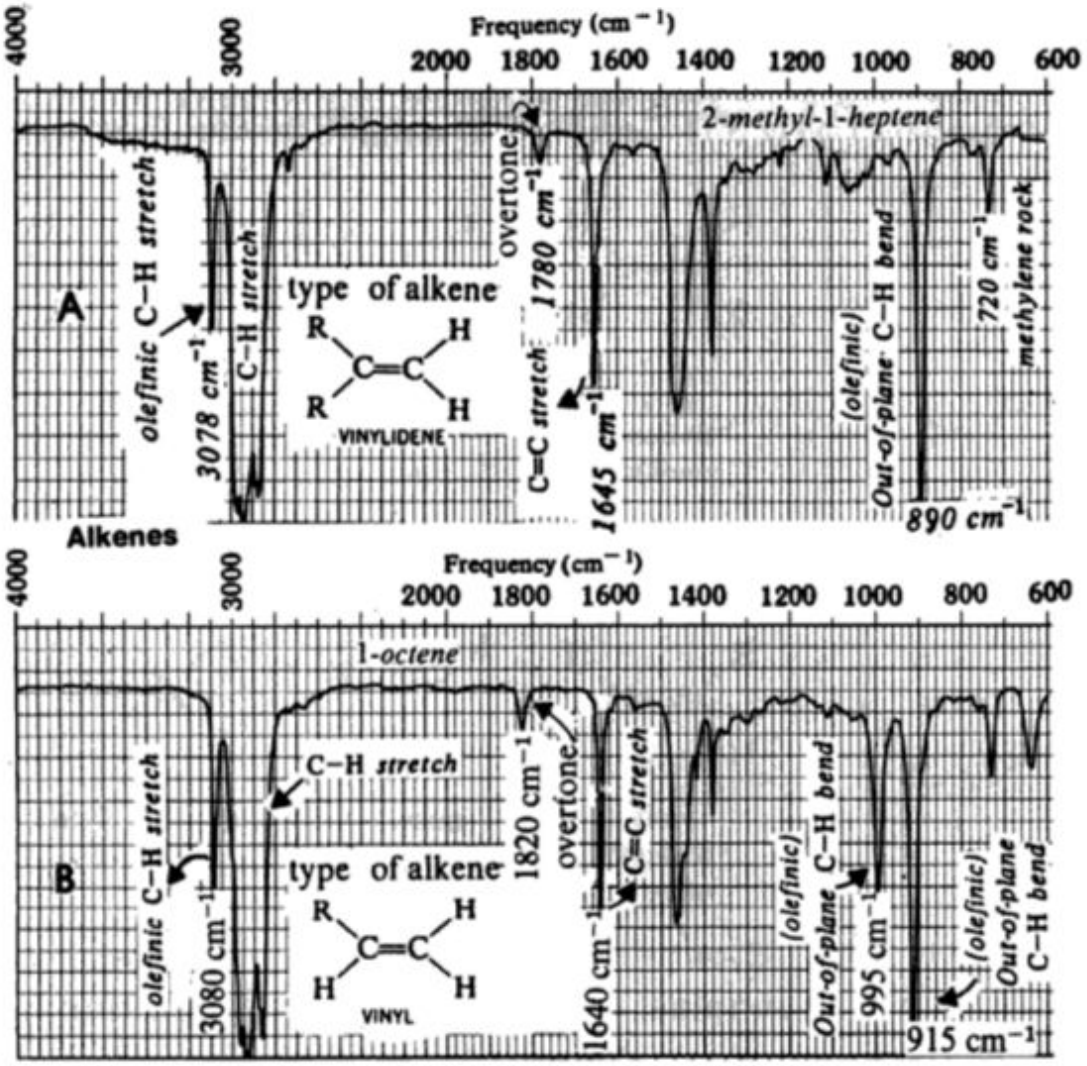
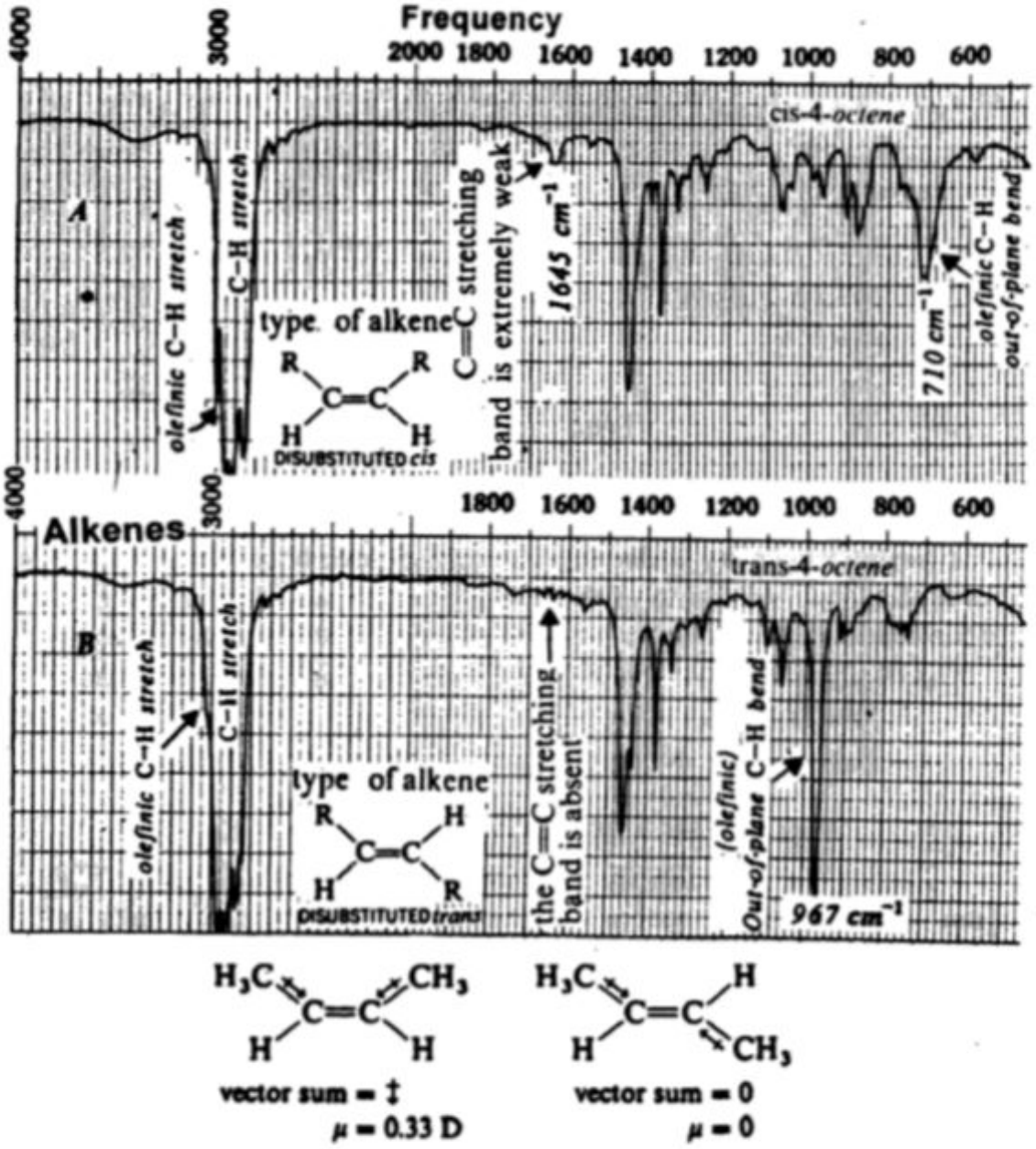


Fig. 3.35

groups are added, the intensity of the absorption decreases since the vibration now results in a smaller change of dipole moment. In the case of trisubstituted, tetrasubstituted and relatively symmetrical di-substituted alkenes this is the case and the C=C stretching band in these cases is at higher frequency ~1660 cm^{-1} and is often of low intensity and thus difficult to detect (Fig. 3.36A). Note that the C=C stretching band is absent in the infrared spectrum (Fig. 3.36B) of *trans*-4-octene, since this vibration in this molecule results in no change in dipole moment. (This molecule has a centre of symmetry, see Scheme 3.1b.)

(iii) =C—H Bending. The olefinic C—H out-of-plane bending modes, give rise to absorption bands in the region 700-1000 cm^{-1}. These are highly useful for establishing the type of double bond in a compound. The characteristic positions of these bands for various types of alkenes are given in Scheme 3.7 and displayed in spectra shown in Figs. 3.35 and 3.36. The C—H out-of-plane bending band gives rise to a characteristic overtone at



In a *cis*-disubstituted alkene, the vector sum of the two dipole moments is directed perpendicular to the double bond. In a *trans*-disubstituted alkene, however, the two dipole moments tend to cancel out. If the alkene is symmetrically *trans*-disubstituted, the dipole moment will be exactly zero. For example, *cis*-2-butene has a nonzero dipole moment, while the *trans*-isomer has no measurable dipole moment.

Fig. 3.36

about 1820 cm^{-1} for alkenes of the type R—CH=CH_2 and at 1780 cm^{-1} for alkenes of the type R_2C=CH_2, but not for other alkenes (Fig. 3.35).

The infrared spectrum of limonene (Fig. 3.37) displays all the expected bands typical of the two double bonds, *i.e.*, vinylidene (methylenic double bond) and trisubstituted double bonds. The C=C stretching which

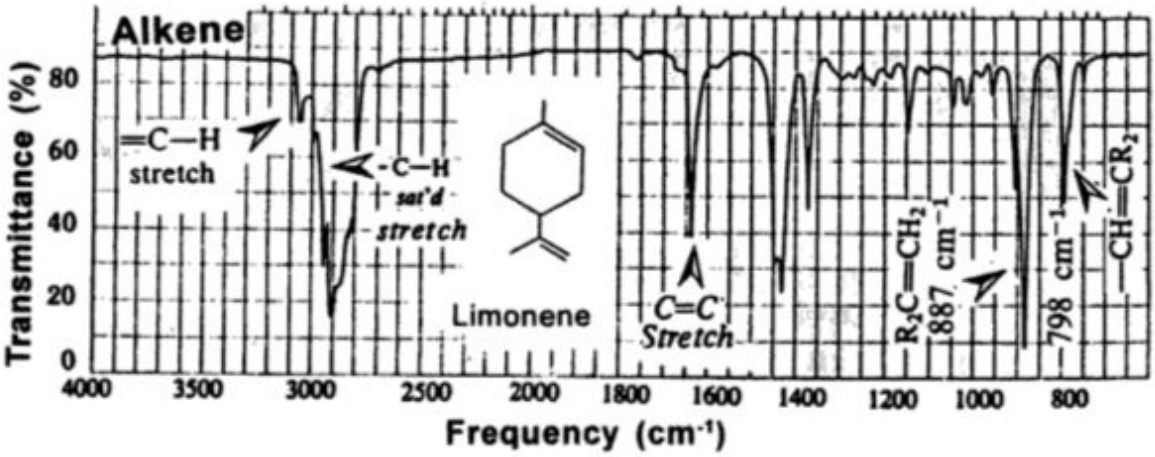
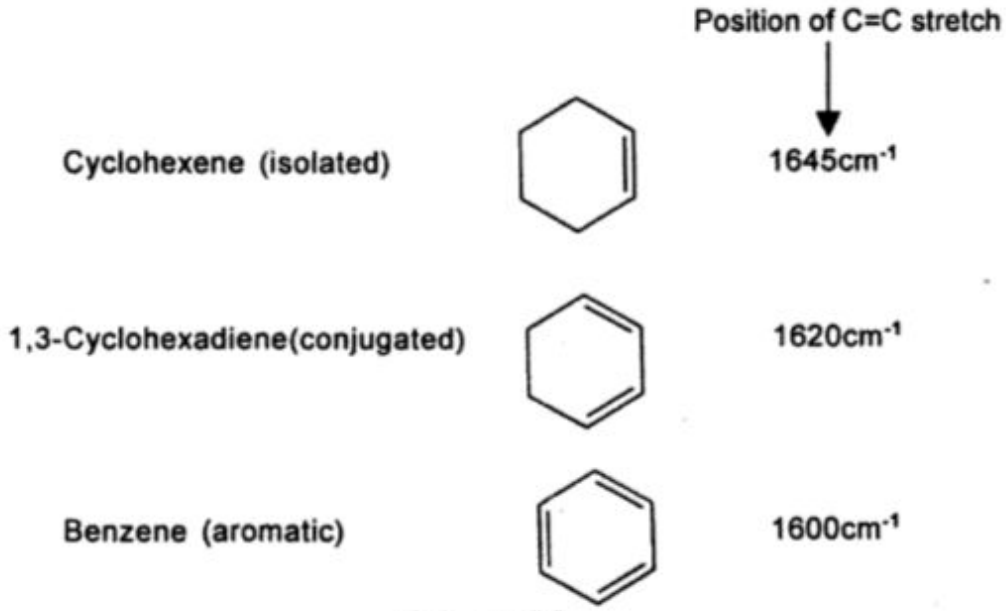


Fig. 3.37

is of medium intensity is due to vinylidene double bond, since in its absence the C=C stretching of the trisubstituted double bond would have been weak as described earlier. The conjugation of an olefinic double bond with α, β-unsaturation, a C=O or an aromatic ring not only lowers the C=C stretching by about 30 cm^{-1} but also enhances the intensity of this

C=C stretch ⟶ ~ 1650Cm^{-1} ~ 1610Cm^{-1}

On conjugation of an olefinic double bond the C=C stretch is lowered and the intensity of absorption is increased. Resonance results in partial *pi*-bond character between the two double bonds, with decreased electron density and decreased stiffness in the double bonds themselves. Conjugated double bonds therefore vibrate at lower frequencies than do similar isolated double bonds.



Scheme 3.8

band (Scheme 3.8). This is seen in the infrared spectrum of progesterone (Fig. 3.38), which has a trisubstituted double bond in conjugation with a carbonyl group. The C=C stretching of a trisubstituted double bond which otherwise is weak, as a result of conjugation becomes enhanced and appears around 1610 cm^{-1}.

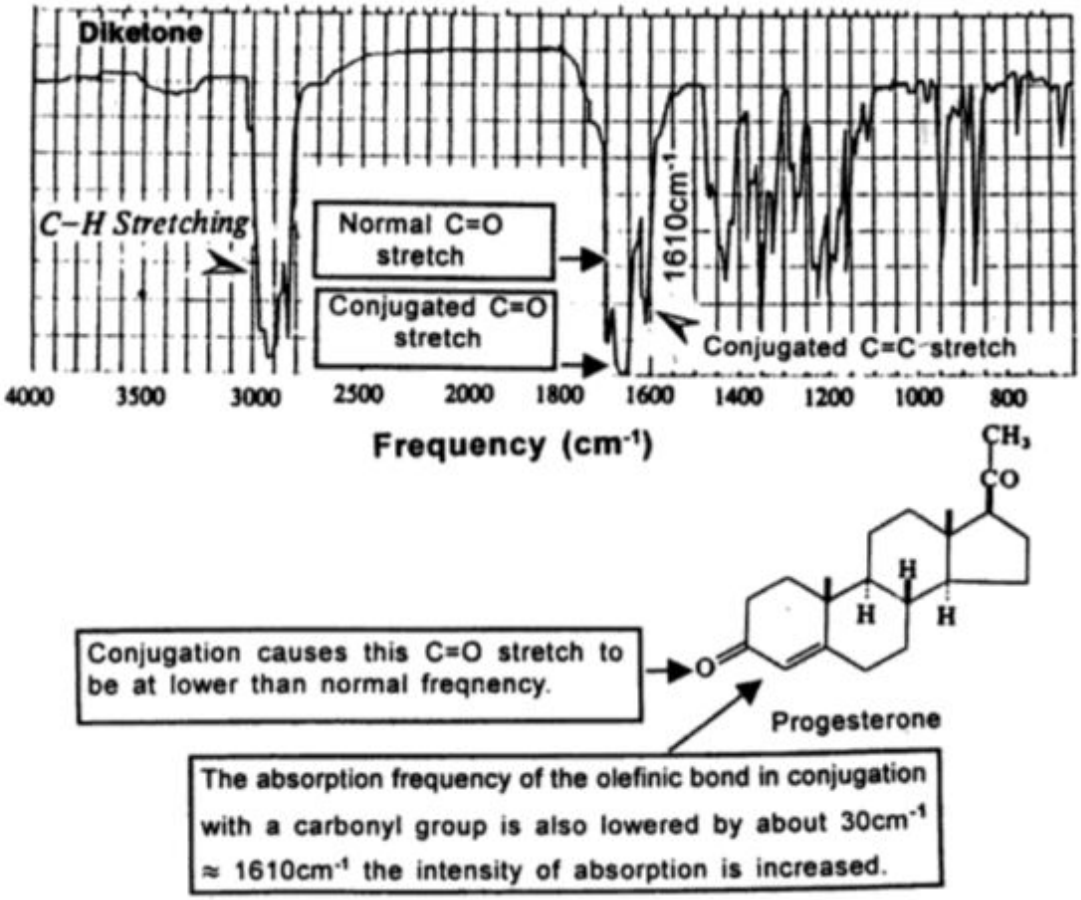
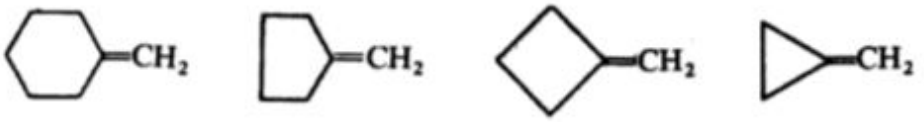


Fig. 3.38

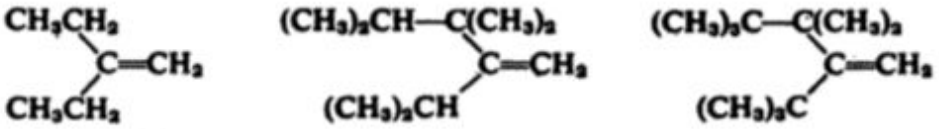
The C=C stretching frequency of exocyclic olefinic double bond (vinylidene double bond) is known to increase with a decrease in the ring size (Scheme 3.9). Thus compared with methylenecyclohexane which absorbs at 1651 cm^{-1}, methylenecyclobutane absorbs at 1690 cm^{-1}. Change in the bond angles also alter C=C stretching, thus spreading of the angle due to the size of R groups lowers the C=C stretching of the vinylidene double bond in the compounds shown (Scheme 3.9).

Significantly, the ring strain has also a marked influence on the olefinic C—H bending vibrations, the frequency of absorption gets lowered. The normal CH bending frequency of a trisubstituted olefin which occurs around 830 cm^{-1} (Scheme 3.7) gets lowered to 788 cm^{-1} in α-pinene and copaene (Scheme 3.10). The normal olefinic C—H bending vibrations, which occur around 890 cm^{-1} (Scheme 3.7) in the case of vinylidene double bond are again lowered to 875 cm^{-1}, *e.g.,* in β-pinene.

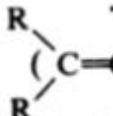


1651cm^{-1} 1657cm^{-1} 1690cm^{-1} 1750cm^{-1}

The C=C stretching frequency of an exocyclic double bond increases with decreasing ring size.

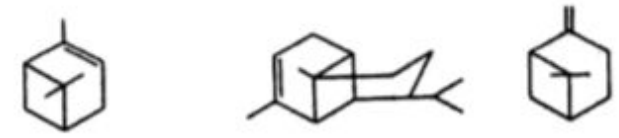


1652cm^{-1} 1639cm^{-1} 1621cm^{-1}

Spreading of the  angle, lowers the C=C stretching of the vinylidene double bond.

Effect of steric strain on C=C stretching of vinylidene double bond.

Scheme 3.9



α-Pinene Copaene β-Pinene

The frequency of =C-H bending vibrations of trisubstituted and vinylidene double bonds, in strained molecules get lowered from their normal positions.

Scheme 3.10

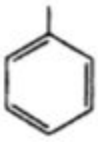
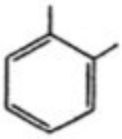
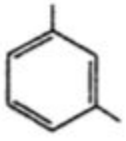
Cumulated double bonds (X=Y=Z) display unusually high double bond frequencies. Thus allenes >C=C=CH$_2$ absorb around 1950 cm^{-1} due to asymmetric C=C=C stretching. A strong band appears in many spectra around 2349 cm^{-1} due to carbon dioxide O=C=O (inequalities in path length).

(g) Aromatic and Heteroaromatic Compounds. The presence of a phenyl group in a compound can be detected with a fair degree of certainty from its infrared spectrum. Moreover, the number and positions of substituent groups on the ring can also be ascertained from the spectrum. For example, in Figure 3.39 one sees the individual infrared spectra of toluene and xylenes. That each spectrum is of a benzene derivative is clear

from several common features, notably the two bands near 1600 and 1500 cm^{-1} which, although of variable intensity, have been assigned to the stretching vibrations of the carbon-carbon bonds of the aromatic ring. In some compounds, there is an additional band around 1580 cm^{-1}. Once these bands are detected the band around 3030 cm^{-1} (aromatic C—H stretch) serves to confirm the presence of this group. The substitution pattern in an aromatic is identified by looking at the C—H out of plane bending bands (Table 3.2) and also from the combination bands (overtones) between 1650-2000 cm^{-1}. The position of absorption of the out-of-plane bending bands depends on the number of adjacent hydrogen atoms on the ring. A monosubstituted benzene displays two very strong bands, between 690 and 710 cm^{-1} and between 730 and 770 cm^{-1} (Fig. 3.39A). Infrared spectra of a variety of other monosubstituted benzenes have been presented earlier and these two strong bands can be easily detected (Figs. 3.15 and 3.16). *Ortho*-substituted benzenes show only a strong band between 735 and 770 cm^{-1} (This band can be clearly identified in the spectrum of *O*-Xylene, Fig. 3.39B.) *Meta*-substituted benzenes (like monosubstituted benzenes) also display two bands, but at different positions and the intensity of one band is stronger than the other, *i.e.,* one band is between 680 and 725 cm^{-1} and one very strong band between 750 and 810 cm^{-1}. *Para*-substituted benzenes (like *ortho*-substituted benzenes) give a single strong band however, this is at higher frequencies (790-850 cm^{-1}) than *ortho*-disubstituted benzenes. Use of this (CH out of plane

Table 3.2

Out-of-Plane C–H Bending Vibrations

Aromatic substitution type		FREQUENCY RANGE, cm^{-1}
Monosubstituted benzene		690–710 and 730–770
Ortho-disubstituted benzene		735–770
Meta-disubstituted benzene		680–725 and 750–810
Para-disubstituted benzene		790–850

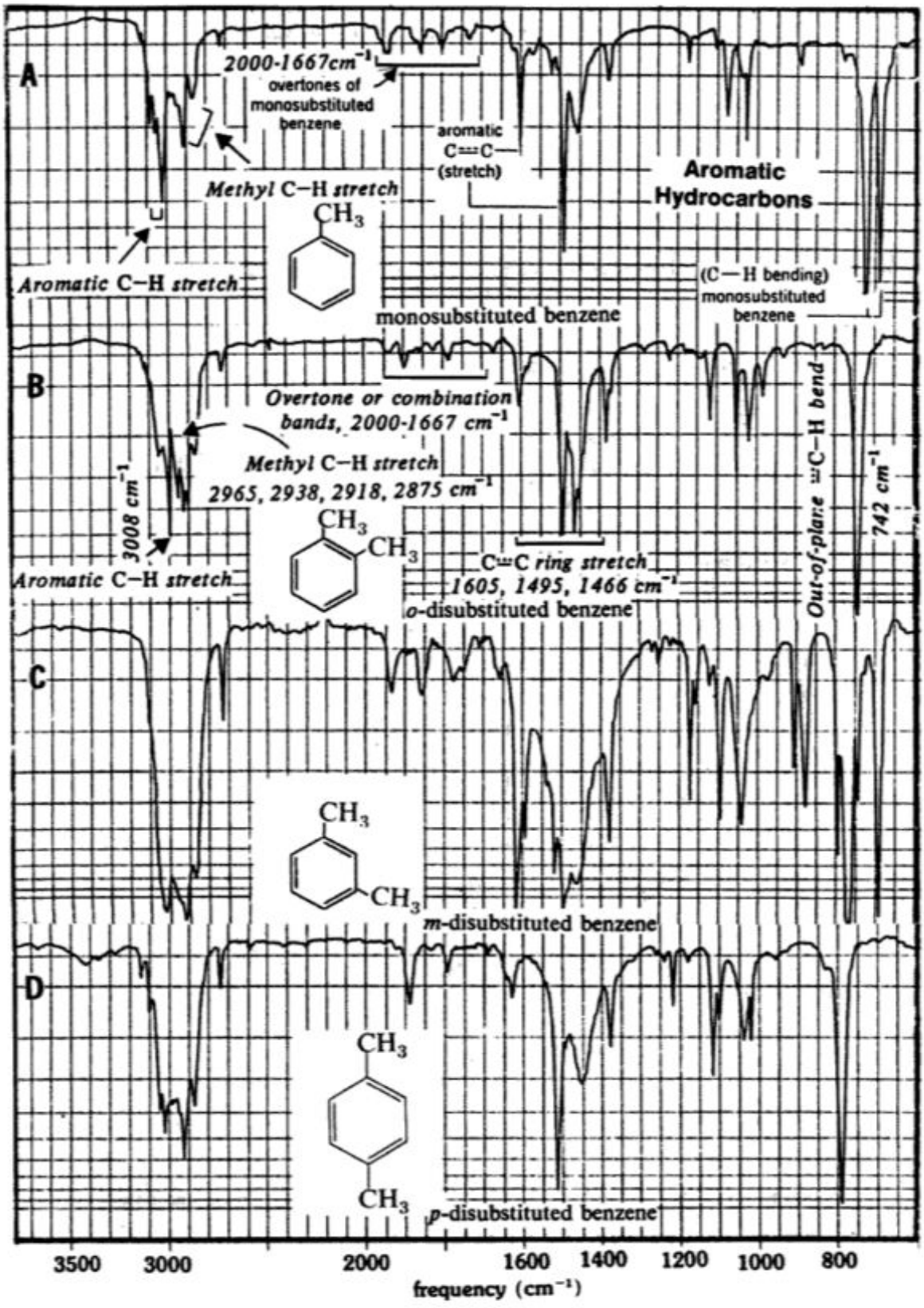
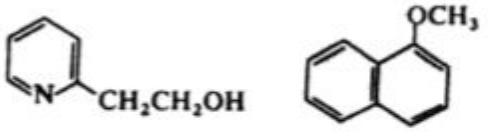


Fig. 3.39

bending) region can also be made to decide the substitution pattern in other 6-membered aromatics such as pyridines, quinoline, isoquinoline and naphthalene, etc. Thus (I) shows a band at 760 (4 free adjacent hydrogens) whereas (II) shows bands at 792 and 760 cm^{-1} (3 and 4 free adjacent hydrogens) respectively (Scheme 3.11).



(I) (II)

Scheme 3.11

In fact, the spectra of heteroaromatic compounds display the vibrational modes similar to that displayed by aromatics. Thus, the infrared spectrum of pyridine (Fig. 3.40) shows identical features of a monosubstituted benzene.

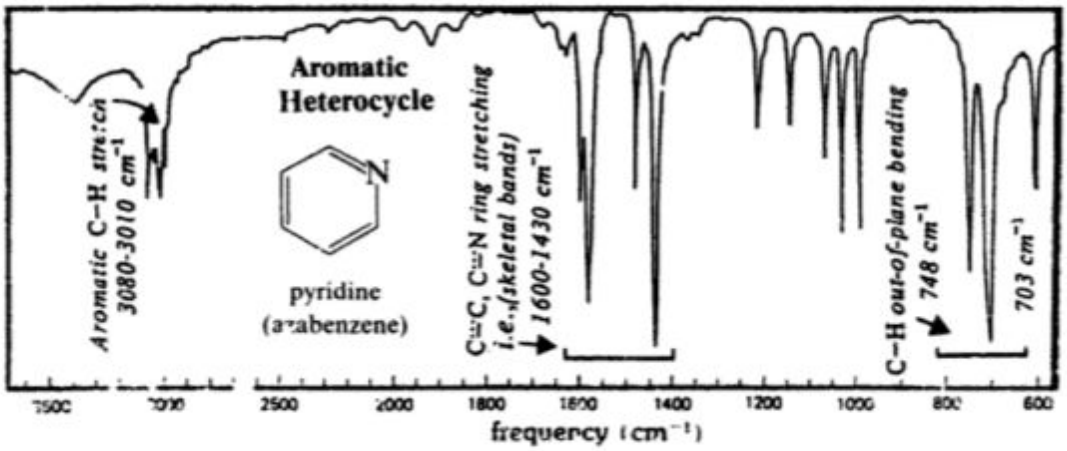


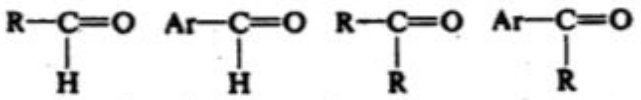
Fig. 3.40

(h) Position of Carbonyl Absorption Effect of Conjugation and Conformational Effects. The 'normal' carbonyl stretching frequency of a neat sample of a saturated aliphatic ketone around 1710 cm^{-1} and an aldehyde 1725 cm^{-1} (Fig. 3.60) is affected by several factors, *e.g.,* conjugation (see Scheme 3.2f), hydrogen bonding (Sec. 3.7a, v), electronic effects and ring strain, etc. A distinction between an aldehyde and a ketone is also possible from a study of their infrared spectra (Sec. 3.6c, iii). Here a brief mention of the factors that influence the C=O stretching frequencies is made again. The example of progesterone (Fig. 3.38) was taken to show that conjugation lowers the frequency of both C=O and C=C stretching vibrations. Conjugation of C=O, *e.g.,* with a C=C or an aryl group leads to

the delocalisation of the π electrons of both the unsaturated groups (see Scheme 3.2f). The double bond character, *e.g.,* in the C=O group is reduced and therefore, the C=O stretching in a conjugated ketone occurs at lower frequencies (~ 30-40 cm^{-1}).

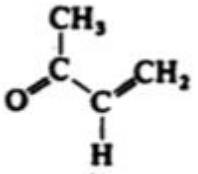
In fact, most of α, β-unsaturated acyclic ketones may exist as two conformations, *i.e., S-cis* and *S-trans* and as a result two carbonyl bands are shown by compounds of this type, a normal band around 1720 cm^{-1} and a lower frequency band around 1690 cm^{-1}. It is assumed that the lower frequency band is due to *S-trans* conformer, where the electron delocalisation is more effective (also see Scheme 3.1h). The dominance of *–I* effect of a halogen over *+M* effect is evident in acid halides (Sec. 3.7e). The general trends of change in structure in relation to the position of C=O stretching are summarised again. Interestingly, a cyclopropyl ring behaves much like a π-system, in conjugation with the carbonyl π bond. The C=O stretching frequency of a ketone which has cyclopropyl conjugation is thus decreased as in, *e.g.,* (II) compared with (I Scheme 3.12).

α,β -Unsaturated ketone α,β -Unsaturated aldehyde

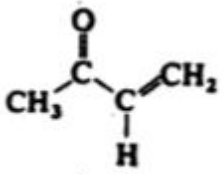


C=O stretch → 1725cm^{-1} 1700cm^{-1} 1710cm^{-1} 1690cm^{-1}

Conjugation lowers the frequency of both C=O stretch and C=C stretch.

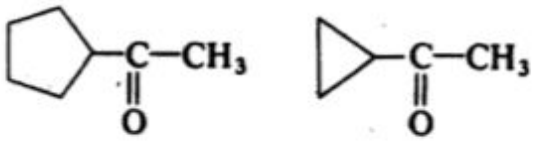


s-trans



s-cis

Steric effects can reduce the coplanarity in α,β-unsaturated ketones (*s-cis* form) to reduce the effect of conjugation, thus *s-cis* form absorbs at higher frequency than *s-trans* form.

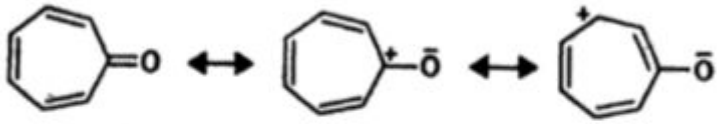


(I) (II)

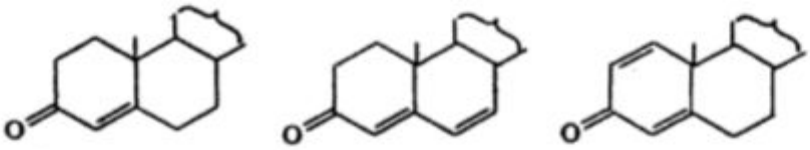
C=O stretch → 1710cm^{-1} 1700cm^{-1}

Scheme 3.12

Extension of a conjugated system by additional double bonds has generally much less effect on the C=O stretching frequencies than the first double bond. Thus, compared with the conjugated C=O stretching at about 1665 cm^{-1} in the case of progesterone (see Fig. 3.38), the steroids (III and IV Scheme 3.12 a), absorb at the same frequency. On the other hand, tropone shows its C=O stretching at 1638 cm^{-1} a value which is very much lower than the steroids (III) and (IV). The lowering of the C=O stretching frequency in the case of tropone is obviously due to considerable weakening of the C=O double bond due to strong resonance — stabilised electron delocalisation (*i.e.,* tropone represents a series of dipolar structures which constitute the aromatic tropylium system).



Tropone has its C=O stretch at 1638cm^{-1}



Progesterone

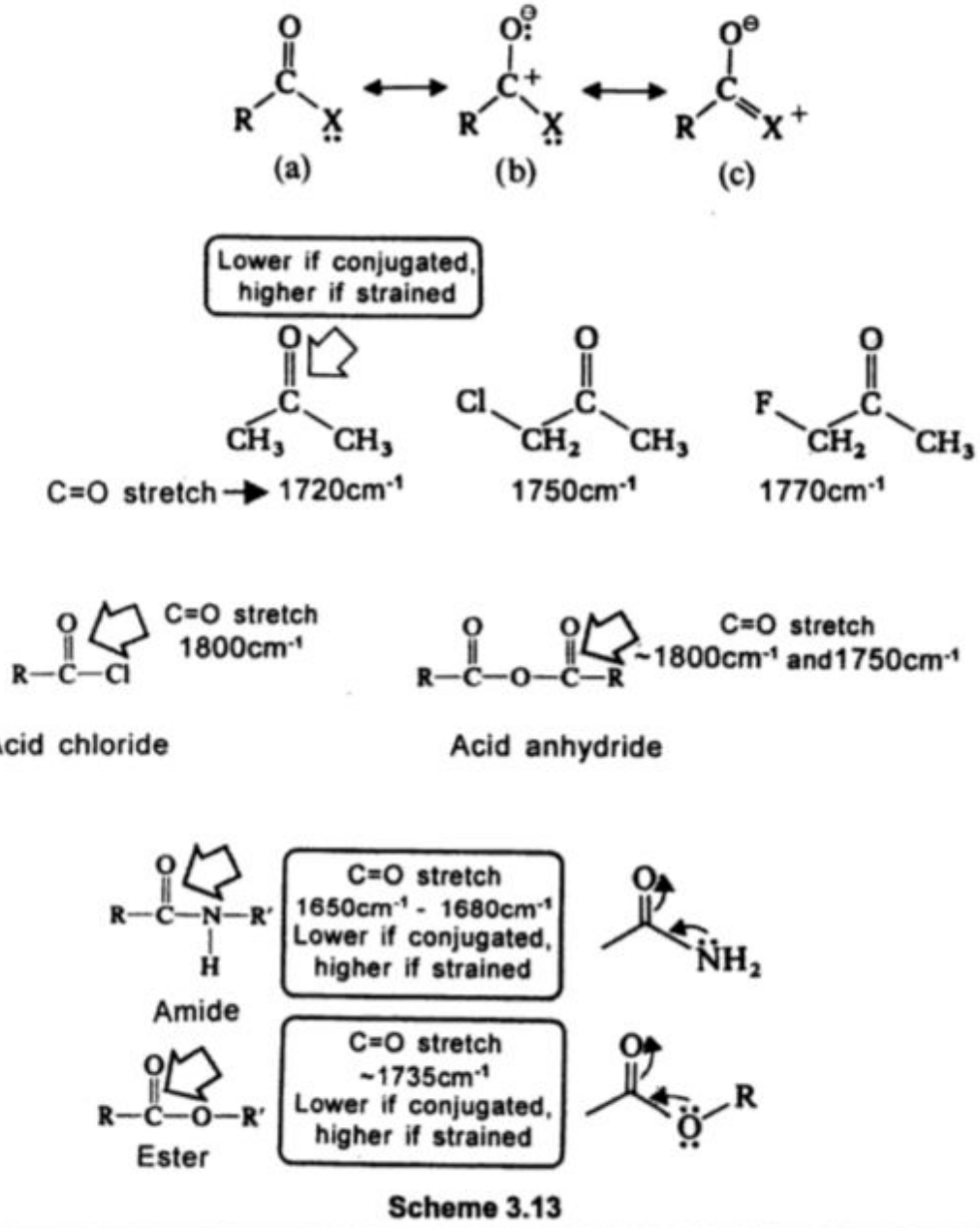
C=O stretch → 1665cm^{-1} 1665cm^{-1} 1666cm^{-1}

Scheme 3.12a

(i) Inductive and Mesomeric Effects — A summary. The position of absorption of the carbonyl group in a saturated acylic ketone which occurs at/near 1720 cm^{-1} is regarded as the 'normal' frequency. Deviation from this absorption position maybe correlated with the influence of electronic and steric effects which arise from the nature of the substituents (R and X) attached to the carbonyl group.

The effects are summarised below and a more detailed consideration of specific cases have been earlier exemplified under each functional group type.

(ii) Inductive Effects. When X is an electron-attracting group (*e.g.*, Cl) the contribution to the resonance hybrid of the polar forms (b and c Scheme 3.13) will be lower, and consequently this will lead to a stronger, shorter carbonyl-oxygen bond due to the increased importance of the form (a). There will thus be a consequent increase in the frequency of absorption. Thus the presence of electron withdrawing substituents near the carbonyl group raise the C=O stretching frequency (Scheme 3.13). This increase is



Scheme 3.13

further enhanced when the electron withdrawing substituent is directly attached to the carbonyl carbon as in an acid chloride (see Fig. 3.34).

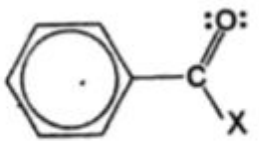
(ii) Mesomeric Effects. When a group X can effectively conjugate with the carbonyl group, either by virtue of lone electron pairs or π-electrons, the direction and magnitude of the frequency shift is related to the balance between such electron delocalisation and any accompanying inductive effects.

When X is a carbon-carbon unsaturated bond then the inductive effects are virtually absent and the contribution of (c) to the mesomeric hybrid is greatly increased resulting in the carbonyl bond having less double bond character, with a consequent decrease in the frequency of absorption (see Scheme 3.12). When X is either —NH_2 or —OR (Scheme 3.13) interesting

comparisons can be reached. In amides the mesomeric effect of the nitrogen lone pair is more important than the inductive effect of the nitrogen, and this leads to a decrease in the frequency of carbonyl absorption.

In esters, however, the inductive effect of the oxygen (which is more electronegative than nitrogen) gains more importance to result in an increase in the frequency of carbonyl absorption. This opposite frequency shift observed with amides and esters, arising from the different balance between the relative importance of mesomeric and inductive effects is in keeping with the relative chemical reactivity which these two groups display (see problem 99 in Chapter 7).

In several molecular groupings, particularly those containing multiple bonds, the simple inductive effects are opposed by mesomeric delocalisation effects. The following carbonyl stretching frequency data measured under standard conditions may be examined (Scheme 3.13a). The double bond character of the C=O group depends on the electronegativity of X (electron withdrawal, $-I$) and on its power to supply

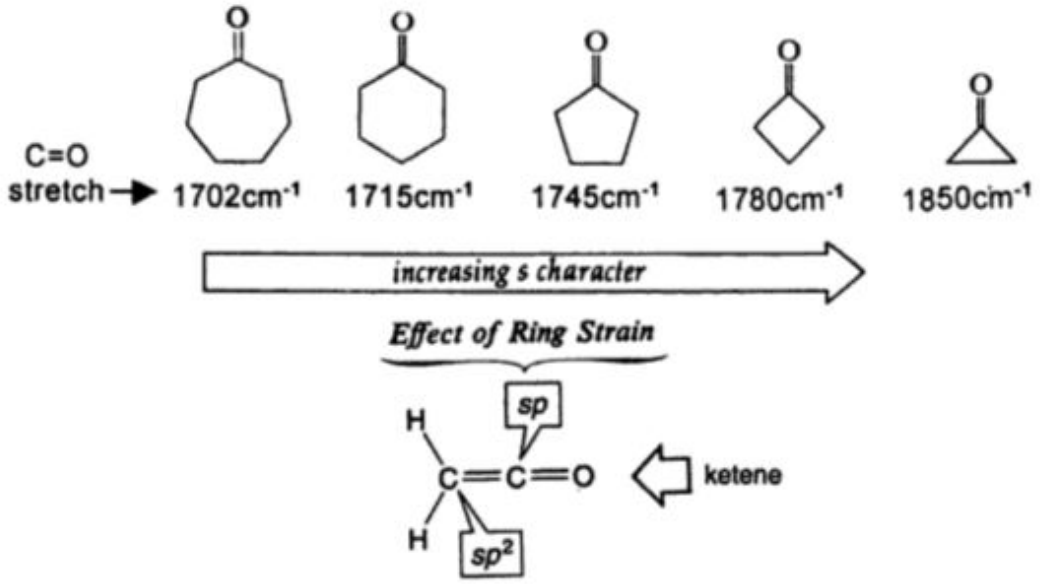


X =	Br	OPh	OMe	H	Me	NMe_2
C=O stretch→ (hexane)	1760cm^{-1}	1750cm^{-1}	1735cm^{-1}	1714cm^{-1}	1697cm^{-1}	1660cm^{-1}
	-I	*-I.(+M)*	*-I.(+M)*			*-I.(+M)*

Scheme 3.13a

electrons by the mesomeric (*i.e.*, resonance) process ($+M$). The double bond character is increased (leading to a rise in C=O stretching) by electron withdrawal. The C=O stretching frequency, however, depends on the overall balance between these two effects. Thus, with X=Br the inductive effect is dominant, but with X=NMe_2 the $+M$ character of the nitrogen atom takes precedence. In the phenyl ester there is some delocalisation of the electrons into the phenyl ring. The increase in carbonyl frequency of an ester as compared to a ketone suggests that $-I$ effect (of OR) is more important than the $+M$ effect.

(iv) Effect of Strain — Ring Strain. Ring strain in cyclic compounds causes a comparatively large shift of the C=O stretching to a higher frequency. This provides a dependable test to distinguish clearly between three, four, five and larger membered ring ketones. Six-ring ketones show the normal frequency found for the open chain compounds (Scheme 3.14). Two explanations have been advanced to explain this influence of strain on C=O stretching frequency. The C—CO—C bond angle is reduced below the normal (~120° in acyclic and six-membered ring ketones) 120° in



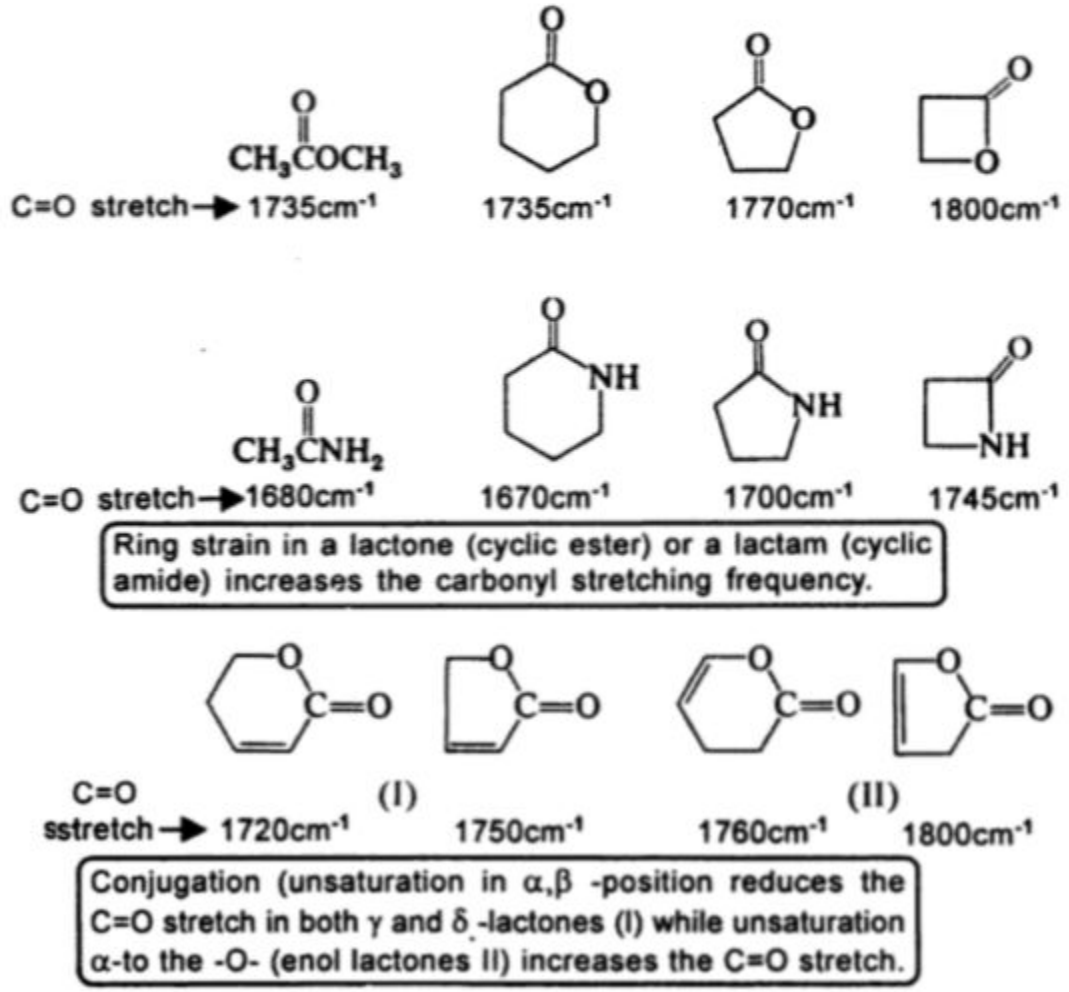
Scheme 3.14

strained rings. This leads to an increase in the *s* character in the C=O bond, which is, therefore, strengthened and consequently C=O stretching frequency is increased. Normal acyclic ketones can be recognised by a strong band at 1720 cm^{-1}. Branching at the α-carbon atoms leads to an increase in the C—$\hat{C}$O—C bond angle leading to a decrease in frequency of absorption from the normal value of 1720 cm^{-1} to, for example 1698 cm^{-1} in di-*t*-butylketone. Conversely as the C—$\hat{C}$O—C bond angle is decreased the absorption frequency rises as seen in the case of cyclopentanone and cyclobutanone in comparison to cyclohexanone.

Ketenes have very strong carbonyl group as the inner carbon is *sp* hybridised and is not the usual sp^2. The more *s* character in a bond, the stronger it is, therefore, ketenes absorb in the IR at very high frequency (~2150 cm^{-1}).

In an alternate explanation it has been suggested that C=O stretching is affected by the adjacent C—C stretching. When the ring is strained the interaction with C—C bond stretching leads to an increase in the energy needed to produce C=O stretching and as a consequence C=O stretching frequency increases.

The same effect is observed with cyclic esters, which are called lactones and with cyclic amides, which are called lactams (Scheme 3.15). In fact carbonyl stretching frequency reaches its maximum in highly stained β-lactones (~ 1800 cm^{-1}). When a lactam ring is fused to another ring, a general increase in the C=O stretching vibrations to the extent of 20-50 cm^{-1} is observed. As is the case with unsaturated acetates in the case of lactones as well, their C=O stretching depends on the location of the double bonds (see Scheme 3.5). Thus unsaturation in the α, β-position reduces the



Scheme 3.15

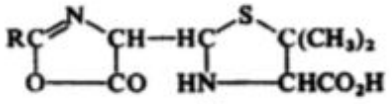
C=O stretch in *e.g.*, both δ and γ-lactones (I, Scheme 3.15). On the other hand unsaturation α to the —O— group (enol δ and γ lactones II, Scheme 3.15) increases the C=O stretch.

(v) Effect of Ring Strain of Bicyclic Systems. The characteristic C=O stretching frequencies of cyclic carbonyl systems apply to polycyclic systems as well. Thus the carbonyl group of camphor which is part of a five-membered ring displays its stretching frequency at 1740 cm^{-1} which is characteristic of a cyclopentanone (Scheme 3.16). The fact that the C=O group in the bicyclic system of camphor is also part of a six-membered ring is to be ignored, since it is the character of ring strain that shows up in the spectrum. The ring-strain effects depend to a great degree on the overall structure, variations of a few cm^{-1} from the expected values may be observed. Thus the bicyclic ketone 2-bicyclo [2.2.2] octanone shows its C=O stretching band at 1731 cm^{-1}, a position which is far higher than expected for a cyclohexanone ring. A careful examination of the structure of this bicyclic ketone shows, however, that its six-membered ring is in a boat conformation rather than a chair.

Scheme 3.16

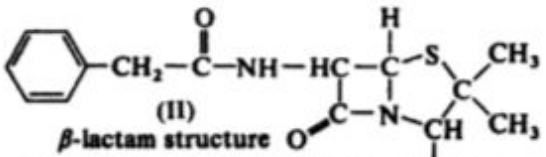
(vi) Carbonyl Stretching Frequency and Structure.

(a) Structure of penicillin. An excellent example involving infrared spectra of acid derivatives and cyclic carbonyls is found in the structure elucidation of penicillin. At one stage, two structures (I and II) looked possible for penicillin. The infrared spectra of several penicillins were examined and a correlation between various bands and functional groups was carried out by examining the spectra of synthetic model compounds. These contained different parts of structures I and II, that had been proposed on chemical evidence. The methyl ester and sodium salt of benzylpenicillin showed the bands as shown under II (Scheme 3.17).



(I)

oxazolone structure



(II)

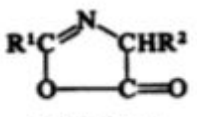
β-lactam structure

a fused thiazolidine-β-lactam

penicillin G (benzylpenicillin)

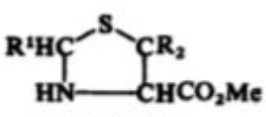
Methyl ester: 3 333, 1 770, 1 748, 1 684, 1 506 cm^{-1}

Sodium salt: 3 333, 1 770, 1 613, 1 681, 1 515 cm^{-1}



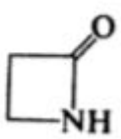
oxazolones

(III)



thiazolidines

(IV)



β-lactam

(V)

C=O *stretch*, 1745 cm^{-1}

Scheme 3.17

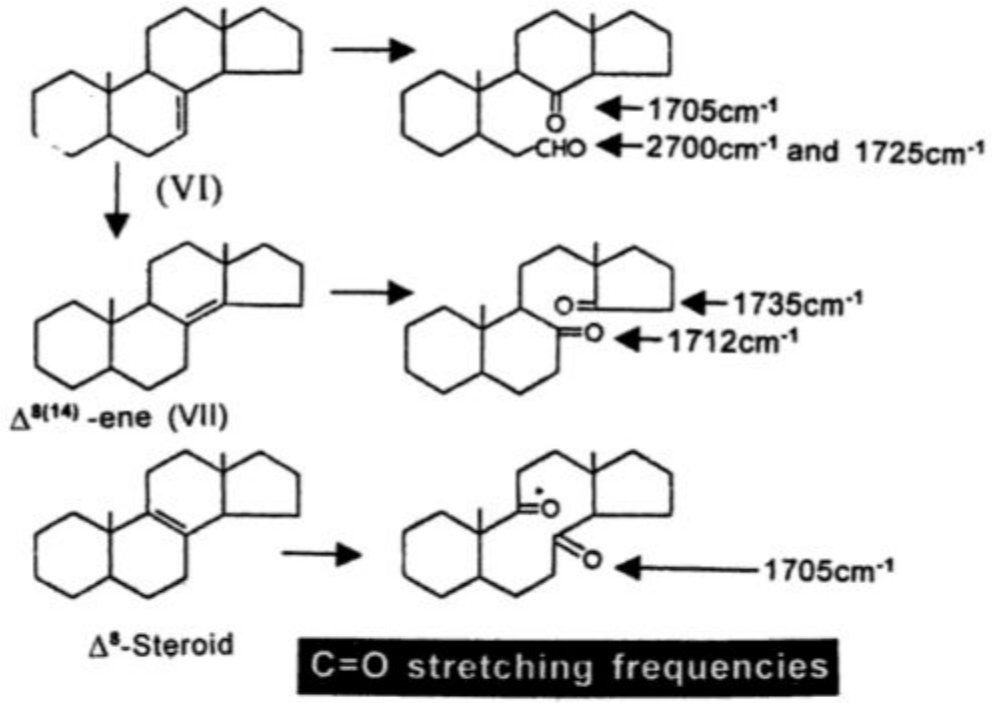
The band at 3333 cm^{-1} in both compounds was assigned to the NH stretching and the 1748 cm^{-1} band of the ester and the 1613 cm^{-1} band of the salt were assigned to the carbonyl stretching in the carboxyl group. The model oxazolones (III) showed two characteristic bands, one at 1825 cm^{-1} for the carbonyl group and one at 1675 cm^{-1} for the C=N group. The thiazolidines (IV) displayed only the carbonyl band (~ 1748 cm^{-1} and another band at 1613 cm^{-1}). The oxazolone, structure was therefore, rejected since it could account only for the 1684 cm^{-1} band of penicillins and not for bands at 1770 and 1506 cm^{-1}. It was soon realised that the bands at 1684 and 1506 cm^{-1} corresponded to the amide I and amide II bands. These results suggested that penicillins have the secondary amide structure, *i.e.*, (II).

In bi- and polycyclic β-lactams where the lactam ring is fused to another ring the C=O frequency gets raised, thus the β-lactam carbonyl group in benzylpenicillin methyl ester (II) absorbs at 1770 cm^{-1}. The recognition of this difference between the β-lactam carbonyl frequency in monocyclic (V, 1745 cm^{-1}) and fused ring systems provided a key step in the interpretation of the infrared spectra of the penicillins and the elucidation of ring structure.

(b) Detection of double bonds via conversion to carbonyl compounds. A quantitative term associated with the intensity of an absorption band in the study of uv spectroscopy is known as absorptivity. The absorptivity varies greatly for the various functional groups. Thus, for instance, the carbonyl group may have an absorptivity of several hundred, while a trisubstituted olefin has absorptivity of only five. It is, therefore, possible that the expected absorption of a double bond may not be detectable whereas the carbonyl group in the same molecule will give a very strong absorption. Occasionally some routine methods like hydrogenation may also fail to detect such double bonds. Compounds with an unhydrogenatable double bonds are rare but some are known. Thus, steroids having a double bond, in 8,14-position are resistant to hydrogenation by all known methods. These, however, can be detected by a positive test with tetranitromethane and they form epoxides. A steroid Δ^7-ene (VI) is similarly unhydrogenetable but when shaken with an active catalyst in the presence of hydrogen it undergoes isomerisation to the $\Delta^{8(14)}$-ene (VII). A trisubstituted double bond (—C=CH—), *e.g.*, in a compound is often difficult to detect from its ir, since its C=C stretching is weak and C—H bending is often difficult to detect because of the same reasons. A tetrasubstituted double bond being relatively symmetrical gives no C=C stretching absorption and also cannot give C—H bending bands. However, unlike for tri- and tetrasubstituted double bonds, infrared is more reliable in

identifying vinylidene >C= CH_2, vinyl —CH= CH_2 *cis* and *trans* disubstituted —CH=CH— double bonds from their C—H bending vibrations at characteristic positions. The PMR is of course the technique of choice for the identification of all types of di and tri- substituted double bonds. PMR method, however, also fails to detect the tetrasubstituted double bond.

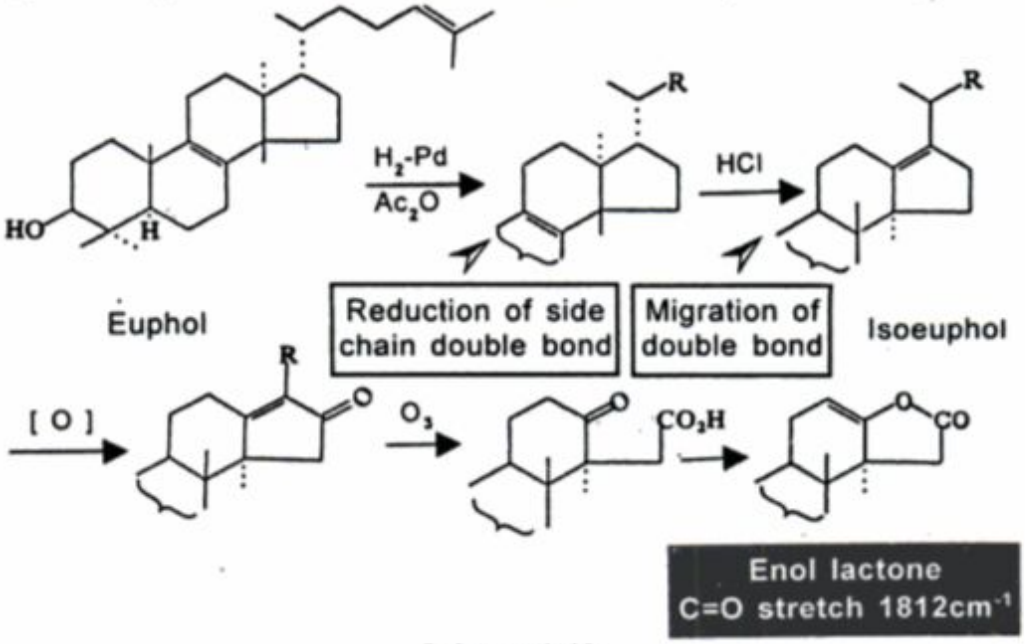
The position of an isolated tri- or tetrasubstituted double bond may be located by refluxing the compound with osmium tetroxide in ether and by subsequent reduction of the osmate ester with lithium aluminium hydride and cleaving the resulting diol with lead tetracetate. The resulting compound is then scanned in the reliable carbonyl region. The characteristic absorptions of the dicarbonyl compounds can then be assigned to either an aldehyde or a cyclopentanone or a cyclohexanone. Significantly the method differentiates between a $\Delta^{8(14)}$-and a Δ^{8}-steroid when both the double bonds are tetrasubstituted (Scheme 3.18).



Scheme 3.18

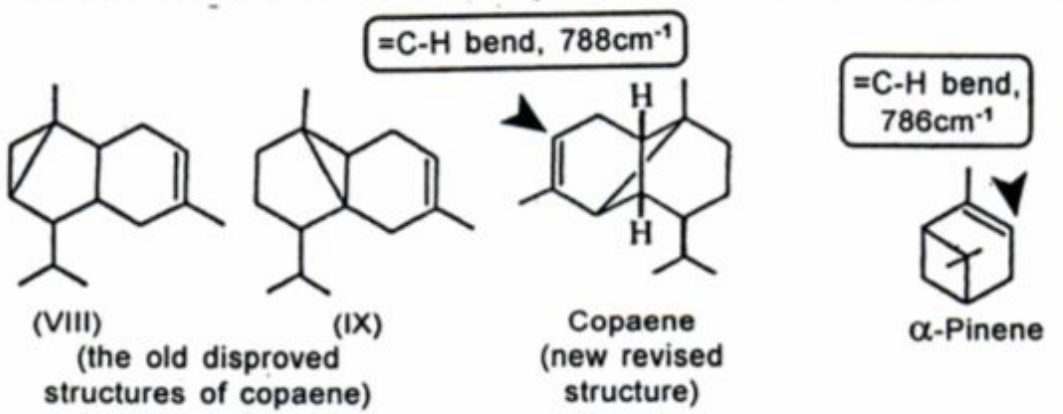
(c) Structure of euphol. The C=O stretching frequency of an enol-γ-lactone gets raised to around 1800 cm^{-1} (see, Scheme 3.15). Degradation of a natural product to an enol-γ-lactone and its identification by infrared spectroscopy plays an important role in its structure determination. Elucidation of structure of euphol presented many puzzling problems. On acid treatment it undergoes isomerisation involving the migration of methyl groups and double bond to give isoeuphenol. Degradation of isoeuphenol

to an enol-γ-lactone and its characterisation by infrared spectroscopy played an important role in its structure elucidation (Scheme 3.19).



Scheme 3.19

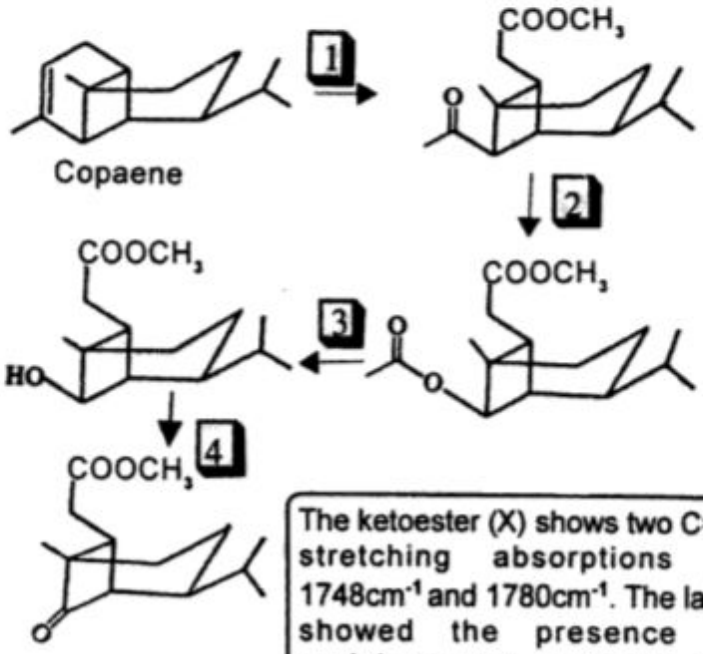
(d) Structure of copaene and β-vetivone. Copaene, a sesquiterpene hydrocarbon was assigned several variant structures containing a cyclopropane ring from time to time, *e.g.,* (VIII and IX, Scheme 3.20). Copaene on dehydrogenation leads only to the formation of cadalene and a structure like (IX) should afford cadalene and an azulene. Based on these data structure VIII had been in vogue for several years. Eventually the correct structure of copaene was independently determined by two groups of



The C-H bending of the trisubstituted double bond at 786cm⁻¹ in α-pinene (strained system) is compareable with that in copaene to show the presence of related structural moiety in copaene.

Scheme 3.20

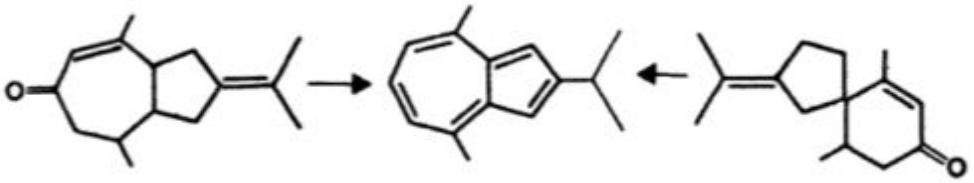
workers led by Sukh Dev and de Mayo. Copaene readily absorbs one mole of hydrogen and the resulting dihydrocopaene behaved unlike a compound containing a cyclopropane ring. These data necessitated a revision of the structure of copaene. Secondly, like α-pinene the bicyclo [3.1.1] heptane system present in copaene shows its C—H bending vibration at a lower frequency of 788 cm^{-1} which disappears on hydrogenation. The degradation of copaene (Scheme 3.21) to a ketoester (X) which showed its C=O



Scheme 3.21

stretching absorptions at 1780 and 1748 cm^{-1} confirmed the presence of cyclobutanone in (X) and therefore, a cyclobutane ring in copaene. First step involved the ozonolysis and oxidative cleavage of ozonide with alkaline hydrogen peroxide followed by esterification with diazomethane. In second step, the methyl ketone was reacted with perbenzoic acid in the presence of an acid catalyst, *p*-toluenesulphonic acid. This reaction converts the methyl ketone group by insertion of oxygen to an ester and the overall product is the diester. This reaction is called Baeyer Villiger rearrangement. Step three involved hydrolysis and re-esterification and in the final fourth step oxidation gave a ketoester (X).

β-Vetivone on dehydrogenation gave 1,5-dimethyl, 7-isopropylazulene (XII), this lead initially to a disproved structure (XI) for the terpenoid (Scheme 3.22). An infrared check showed that its dihydroderivative in which the double bond in conjugation with the carbonyl



(XI)
β-Vetivone
(The old disproved structure)

(XII)
An azulene
(obtained on dehydrogenation)

(XIII)
β-Vetivone
(The new revised structure)

If structure (XI) was correct then its dihydroderivative in which the double bond in conjugation with the carbonyl group was reduced, should have been a cycloheptanone derivative (with C=O stretch ~1702cm^{-1}) which is not the case.

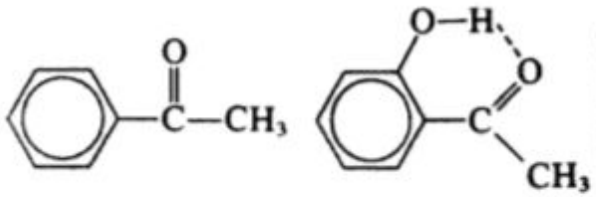
Scheme 3.22

group was reduced, showed its C=O stretching at 1720 cm^{-1} which was typical of a cyclohexanone rather than a cycloheptanone which should have shown its C=O stretch around 1702 cm^{-1}. Indeed further work showed that β-vetivone contained a six-membered ring and represented a spirocyclic system. The formation of the azulene derivative on dehydrogenation was due to a skeletal change.

(vii) Effect of Hydrogen Bonding and Enols. When a carbonyl group is involved in hydrogen bonding its C=O stretching frequency is lowered. As a result of intermolecular hydrogen bonding between a ketone and a hydroxylic solvent, *e.g.,* methyl alcohol a decrease in the absorption frequency of C=O is observed. A neat sample of methyl ethyl ketone absorbs at 1715 cm^{-1} whereas a 10 per cent solution of the ketone in methanol absorbs at slightly lower frequency 1706 cm^{-1}.

Intra-molecular hydrogen bonding is another factor which lowers the carbonyl stretching frequency by about 50 cm^{-1}. This lowering is, however, dependent on the strength of the hydrogen bond. *ortho*-hydroxyacetophenone (XV) shows its C=O stretching at a much lower frequency as compared with acetophenone (XIV, Scheme 3.23, 1685 cm^{-1}).

β-Diketone, *e.g.,* acetylacetone exists as mixture of tautomeric ketone and enol forms. Simple ketones exist largely in the keto form with only a trace of the enol (vinyl alcohol) form present at equilibrium. In contrast β-dicarbonyl compounds (Scheme 3.23a) often contain a considerable amount of enol form in equilibrium with the dicarbonyl form. Keto enol tautomerison is a case of constitutional isomerism where isomers (tautomeric forms) are readily interconvertible and can be detected by infrared spectroscopy. The detection of such tautomers by NMR has been described (see sample problem 22 in Chapter 7).

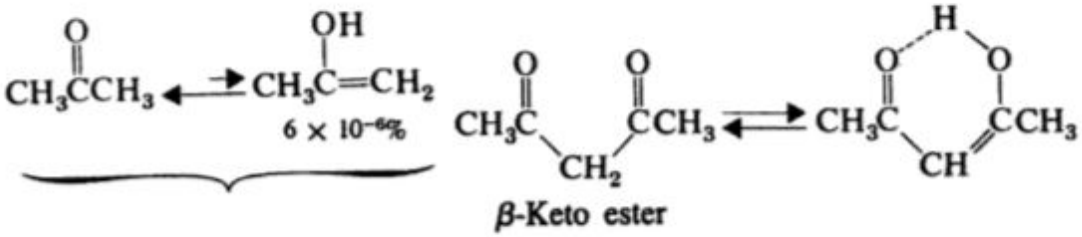


(XIV)
Aceto-
phenone
C=O stretch
1685cm^{-1}

(XV)
O-Hydroxy-
acetophenone
C=O stretch
1634cm^{-1}

The C=O stretch of aceto-phenone 1685cm^{-1} [lower frequency than the normal C=O stretch (1715cm^{-1}) due to conjugation with the phe-nyl group] is further lowered by about 50cm^{-1} to 1634cm^{-1} in (XV) as a result of hydrogen bonding.

Scheme 3.23



Scheme 3.23a

In, *e.g.*, a β-ketoester the keto form has two C=O groups (Fig. 3.40a) which have separate stretching frequencies, thus two peaks (a doublet) is

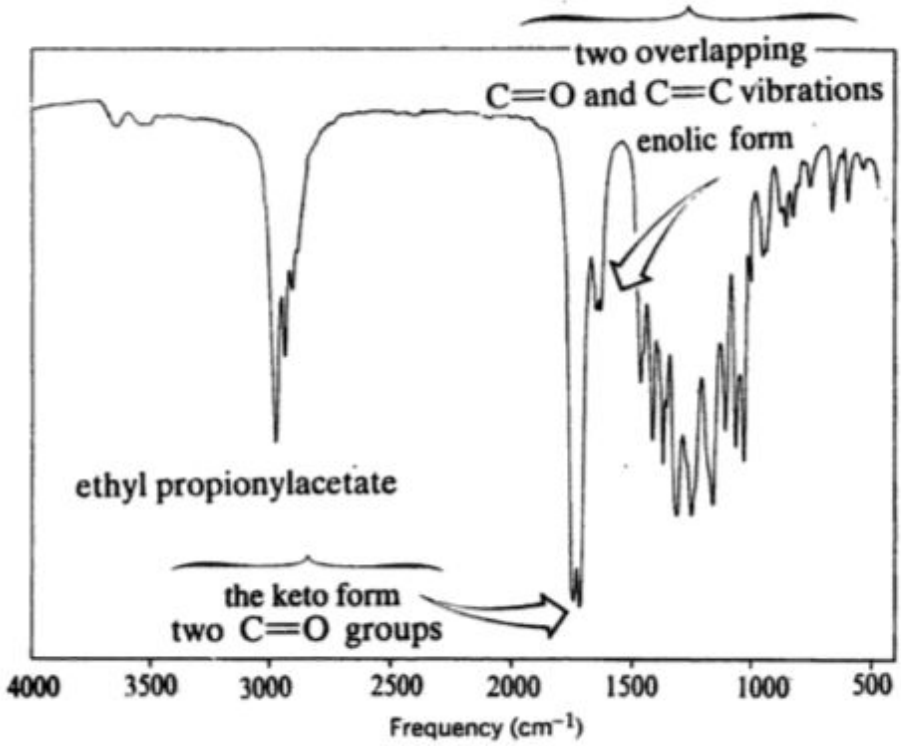
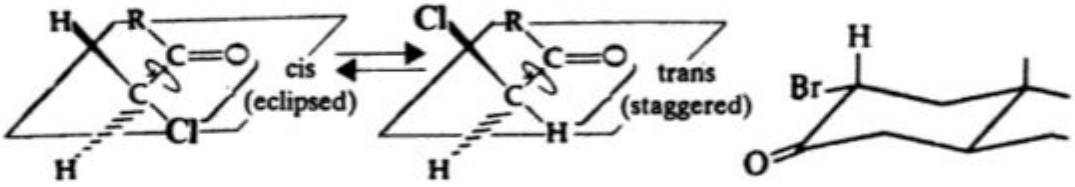


Fig. 3.40a

often seen in the ketone carbonyl stretching region, near 1700 cm^{-1}. The enol form, on the other hand, has only one carbonyl group and its stretching frequency is lowered by 100-80 cm^{-1} due to hydrogen bonding and conjugation.

However, the enol form also has an alkenic double bond which should give a C=C stretching band between 1650-1600 cm^{-1}. The C=O and C=C vibrations may then display themselves as two overlapping bands with closely spaced peaks. An example of such tautomerism is shown (Fig. 3.40a). The compound ethyl propionylacetate clearly shows the presence of both keto and enol forms.

(viii) Field Effects. Two or more polar groupings situated in the same molecule but insulated electronically from each other by single bonds, influence one another if brought close together. These dipolar, non-bonded interactions (field effects) are of electrostatic origin. These display themselves particularly well in α-haloketones (Scheme 3.24) where a strongly electronegative atom can be brought near in space to a carbonyl group. A simple acyclic α-haloketone, $RCOCH_2Cl$ is normally free to adopt several conformations, two of which (I and II) are shown. The coplanar, 'opposed' conformer (I, Scheme 3.24) is found to have a higher carbonyl frequency. However, two carbonyl frequencies are displayed proving that both rotational isomers are present. In rigid systems, like 2-halo-3-keto-steroid (III, Scheme 3.24) only one frequency is recorded. When the bromine atom is near the oxygen, its negative field repels the non-bonding electrons of the oxygen atom, as a consequence the force constant of the C=O bond is increased.



(I) Raised C=O stretch 1740cm^{-1} | (II) 'Normal C=O stretch 1720cm^{-1} | (III) Raised C=O stretch 1733cm^{-1}

Scheme 3.24

(i) Compounds Containing Nitrogen

(a) Nitro Compounds. These compounds show two very intense absorption bands in the 1560-1500 cm^{-1} and 1350-1300 cm^{-1} region of the spectrum due to asymmetric and symmetric stretching vibrations of the highly polar nitrogen-oxygen bonds. Aromatic nitro compounds show

bands at slightly lower frequencies than the aliphatic compounds because of a conjugation of the nitro group with the aromatic ring, which slightly weakens the nitrogen-oxygen bonds. The spectrum of nitrobenzene is typical of this class of compounds (see Fig. 3.30).

(b) Nitroso Compounds. These compounds may represent C—NO or N—NO type. Tertiary C-nitroso compounds tend to dimerise, and secondary and primary C-nitroso compounds readily rearrange to oximes. In the monomeric state they absorb in the 1600-1500 cm^{-1} region, however, in solution they exist preferentially as dimers and then absorb near 1290 cm^{-1} (*cis*) or 1400 cm^{-1} (*trans*). N-Nitroso compounds show a band near 1450 cm^{-1} in solution in carbon tetrachloride.

(c) Nitrites. These compounds display their N=O stretching vibration as two bands near 1660 cm^{-1} and 1620 cm^{-1}; these are attributed to the *trans* and *cis* forms of the nitrite (Scheme 3.24a).

Scheme 3.24a

(d) Unsaturated Nitrogen Compounds. All of these absorb in the 2300-2000 cm^{-1} region of the spectrum. Stretching of the C≡N bond in aliphatic nitriles shows a band at 2260-2240 cm^{-1}, which is shifted to lower frequency by conjugation with a double bond or aromatic ring. Conjugation also tends to increase the intensity of the band which is very strong in, for example, benzonitrile (see Fig. 3.15). The various types of nitriles do, however, show marked variations in the intensity of the bands depending on the electronic effects of substituents attached to the nitrile group. Thus any substituent which tends to decrease the dipole moment of the bond would be expected to produce a decrease in the intensity and vice versa. Isocyanates display a very intense absorption band near 2275-2240 cm^{-1} which is not affected by conjugation. The bands are very much more intense than the bands of nitriles with similar structure and this feature allows a ready distinction.

(e) Oximes and Imines. These compounds show a band of variable intensity due to stretching of the C=N bond in the 1690-1590 cm^{-1} region of the spectrum, and is generally more intense than C=C stretching bands which also appear here. The oximes additionally show a band for the O—H stretching vibration around 3200 cm^{-1}.

(f) Azo Compounds. These compounds show stretching of the —N=N- bond which is only a weak absorption near 1600 cm^{-1}. This absorption is

shifted to lower frequency by conjugation. In aromatic compounds the band is mostly masked by the aromatic ring C=C stretching vibrations.

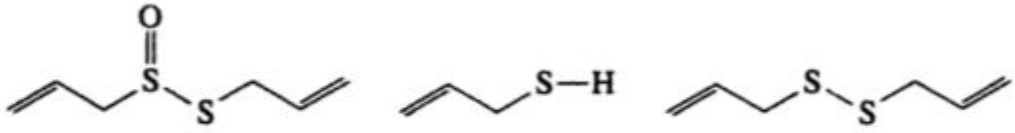
(j) Organo Sulphur Compounds

(a) Thiols. The S—H stretching vibration of thiols gives rise to a weak band at 2590-2550 cm^{-1}. Unlike the O—H stretching band in the alcohols, the position of this band is not much affected by hydrogen-bonding effects, and the absorption exhibited by neat liquid films and by dilute solutions of a thiol are similar. Although the band is weak it has diagnostic value as few other bands appear in this region of the spectrum. This band may however, be masked if a carboxyl group is also present in the molecule.

(b) Thioketones and Dithioesters. These compounds display their C=S stretching bands in the 1270-1190 cm^{-1} region. Since, the C=S bond is not as polar or as strong as the C=O bond the absorption band is not very intense and appears in the low frequency region of the spectrum; coupling with other bands in this region can make identification some what tedious.

(c) Sulphoxides. As the S=O bond is highly polar, it gives rise to a strong absorption near 1050 cm^{-1} which can be readily recognised. The position of the band is not affected by attached double bonds or aromatic rings as conjugation of the S=O bond and an adjacent π-electron system is not extensive. However, electro-negative substituents cause a shift to higher frequency which is due to a reduced contribution by the polar S—O structure to the resonance hybrid with a consequent increase in S=O character to give a stronger bond.

Garlic is a rich source of sulphur containing compounds and some of the sulphur containing functional groups are readily identified by IR (Scheme 3.24b). The S=O bond in allicin, the principal volatile compound obtained from crushed garlic, displays intense band at 1080 cm^{-1}. Allicin is unstable and at room temperature, the 1080 cm^{-1} IR absorption disappears. The major decomposition product which could be either a disulphide or a thiol was assigned a disulphide, structure since it did not show bands typical for a S=O or a thiol group.



Allicin
IR: 1080 cm^{-1}

2-Propene-1-thiol
IR: 2535 cm^{-1}

2-Propenyl disulfide
IR: No S=O or S—H bands

Scheme 3.24b

(d) Compounds Containing Sulphone Group. Sulphones, sulphonamides, sulphonyl chlorides, sulphonic acids, sulphonates and organic sulphates, all contain the SO_2 group which can be readily identified by the presence of two strong bands in the 1415-1300 cm^{-1} and 1200-1120 cm^{-1} regions, due to the asymmetric and symmetric stretching vibrations respectively (see Table 3.1). Often the high frequency sulphone band is split when the spectrum is recorded in carbon tetrachloride solution or the solid state. Sulphonic acids can be further recognised by the broad hydrogen bonded O—H stretching absorption centred at ~3000 cm^{-1}. Primary and secondary sulphonamides will show two or one N—H stretching bands respectively near 3300 cm^{-1}.

(k) Halogen Compounds

Halogenated hydrocarbons display strong absorption due to stretching vibrations of carbon-halogen bond (see, Figs. 3.11 and 3.43). Aliphatic C—Cl absorption is observed in the general range 850-550 cm^{-1} as a medium intensity band and C—Br absorption is in the range 650-550 cm^{-1} while for C—I the range is 600-465 cm^{-1}. Thus the absorption for C—I and most C—Br bonds occurs outside the normal range available on many routine instruments.

The CH_2 wagging mode in compounds with a CH_2X group gives rise to a strong band whose frequency depends on X (X = Cl, Br and I). When X is Cl the range is 1300-1250 cm^{-1}, for Br the band is near 1230 cm^{-1} while for, I the wagging mode is still a lower frequency band around 1170 cm^{-1}.

3.8 STRUCTURAL DIAGNOSIS — THE FINAL STEP — UTILITY OF INFRARED SPECTROSCOPY IN STRUCTURE ELUCIDATION

Some of the ways of the use of infrared spectroscopy to organic chemistry have already been presented. In the present section an overall view is presented since it is not possible to provide a standard interpretational method. The following general lines of approach have proved their value. It is significant to note that it is not possible to identify a given organic compound merely by the interpretation of its infrared spectrum. The identity depends largely on the assessment of all other evidence, *i.e.,* chemical degradation, physical and other spectroscopic data.

(a) Interpretation of the Spectra of an Unknown Compound. Gainfully the initial interpretation of the infrared spectrum of an entirely unknown compound will involve spending some minutes in searching and assigning the particular bands to the corresponding functional groups. This

approach may involve the following points, *e.g.*, as applied to the structure elucidation of a novel C_{14} naturally occurring compound I.

1. The spectrum should be recorded over full range using the proper thickness of the sample of the compound so that at least one band absorbs strongly. This is shown in the infrared spectra recorded in Fig. 3.41 (I as liquid film and II in nujol suspension).

2. Pick out the strong bands, particularly in the functional group region (4000-1500 cm^{-1}) using the correlation charts (Figs 3.58-3.62) to deduce which are the functional groups present. Seek confirmation elsewhere in the spectrum to identify the functional groups correctly. Reference to spectrum of compound I, (Fig. 3.41) shows the presence of C=O stretching (1678 cm^{-1}). When associated with the medium intensity C—H stretching (2703 cm^{-1}) for aldehydes the compound comes out to be an aldehyde. The lower frequency of C=O stretch shows that it has α, β-unsaturation. The presence of olefinic C—H stretch (=C—H, 3060 cm^{-1}), C=C stretch (1634 cm^{-1}) and these coupled with several typical bands in the fingerprint region at 995 and 918 cm^{-1}; 892 cm^{-1} and at 810 cm^{-1} show the presence of all three types of double bonds namely vinyl, vinylidene and trisubstituted respectively. It may be noted that C=C stretch at 1634 cm^{-1} is not only displaced to lower frequency than normal position (1650 cm^{-1}) for these double bonds but the intensity of this absorption is also more than normal (Scheme 3.8). Thus the aldehyde is α, β-unsaturated.

3. All the other available data both, spectroscopic (NMR, UV, etc.) and chemical should accord with any structures postulated. The UV spectrum of (I), λ max 232 nm, ε 12,320 confirms the presence of conjugation. When (I) is reduced with lithium aluminium hydride it gives a compound (II), in whose infrared spectrum (Fig. 3.41), the aldehyde bands (1678 and 2703 cm^{-1}) have completely disappeared and have been replaced by the hydroxyl absorption at 3400 cm^{-1}. In the alcohol (II) the olefinic absorptions are much as in the starting compound (I). The alcohol (II) does not show any characteristic UV absorption of a conjugated system to confirm that (I) indeed is α, β–unsaturated aldehyde and the double bonds in (I), and thus in II are not conjugated among themselves. In the spectrum of (II) since now there is no conjugation, the C=C stretch around 1640 cm^{-1} is of normal intensity.

4. A functional group which displays many characteristic absorptions can usually be identified more definitely than a function that gives rise to only one characteristic adsorption. Thus ketones (C=O stretching) are less easily identified than esters (C=O stretching and C—O stretching); esters are less easily identified than amides C=O stretching, N—H stretching, N—H bending and so on. The presence of a band at the right frequency does not, however, prove the presence of a given functional group.

Compound (I) does not have a *cis*-disubstituted double bond, but it infrared spectrum (Fig. 3.41) has a strong absorption (marked by an arrow) in

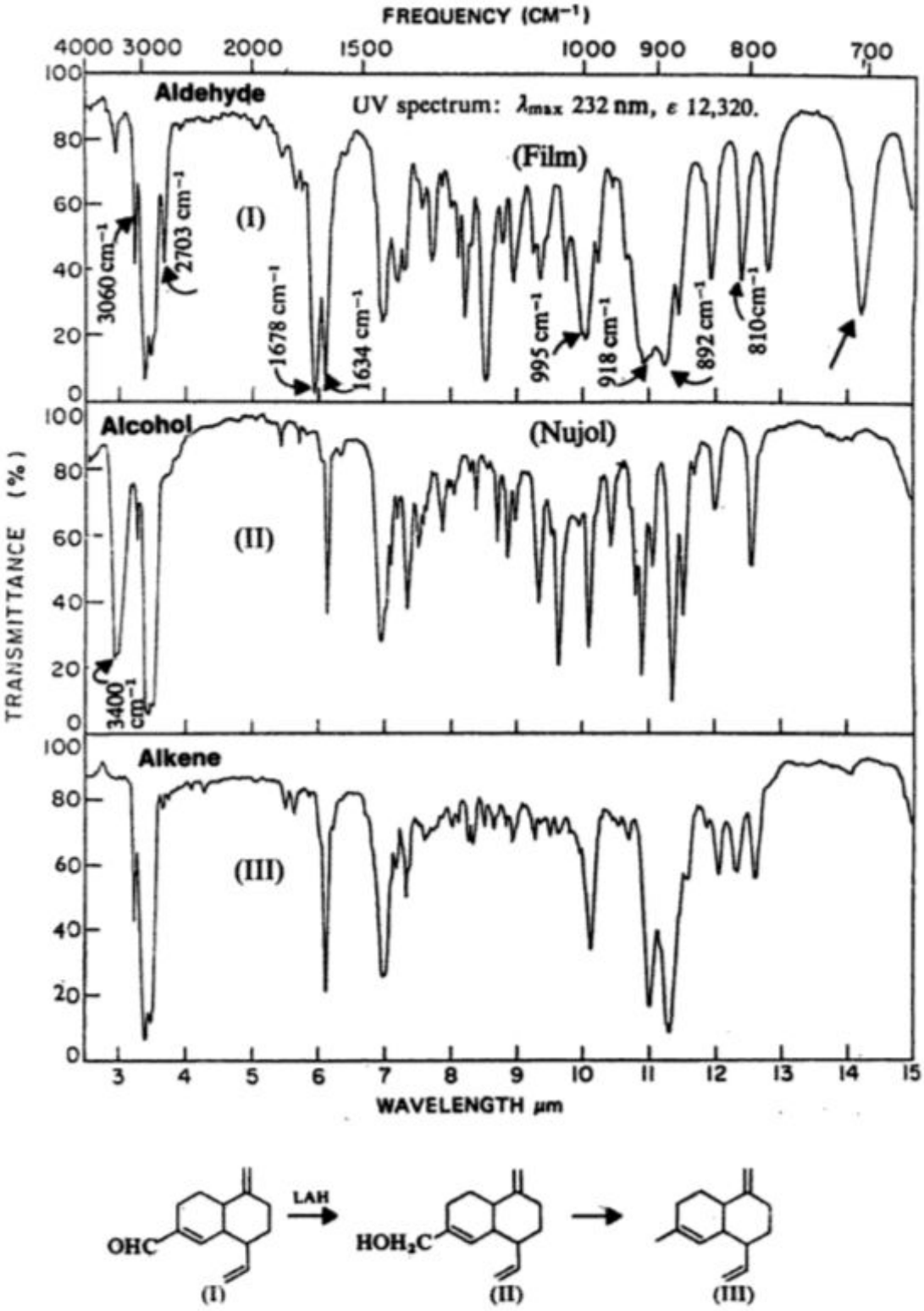
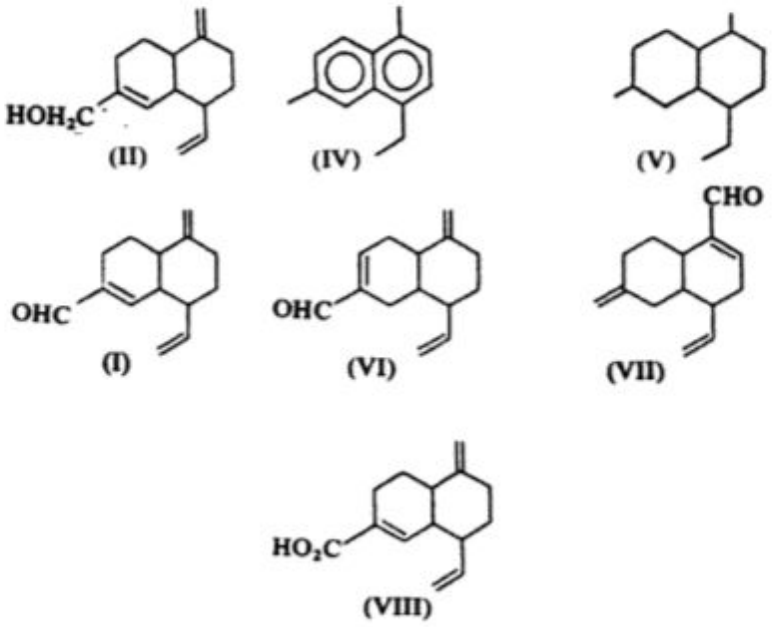


Fig. 3.41

the right region for the C—H olefinic bending vibrations around 710 cm^{-1} (Scheme 3.7). The disappearance of this band in the parent alcohol (II) or the parent hydrocarbon (III) further shows that indeed this band in (I) does not represent any functional group.

5. As pointed out above, both chemical and other spectroscopic data should be in accord with the initial assignment of bands to the presence of functional groups. Carry out further chemical degradation and spectral work to reach the structure. Mass spectra of various derivatives confirmed the molecular weight of the compound. This was confirmed by a simple experiment involving finding out the molecular weight of the corresponding carboxylic acid (VIII) by neutralisation equivalent. On dehydrogenation, II gave a naphthalene identified as 1,6-dimethy-4-ethyl naphthalene (IV, Scheme 3.24c). This pointed to the carbon skeleton V for I and based on these facts three structures (I, VI and VII) could be assigned to the naturally occurring aldehyde (Scheme 3.24c). Out of these (I) was confirmed on the basis of further chemical degradation.



Scheme 3.24c

(b) Identification By Compound Comparison. Most infrared spectra have considerable detail particularly in the 'fingerprint' region, *i.e.*, below 1500 cm^{-1}. The direct comparison of two spectra which have been recorded under the same sampling conditions is still one of the best methods of establishing the identity or non-identity of two compounds. Similar compounds no doubt have similar spectra but exact correspondence is only possible if samples are identical. The individual (+)- or (–)-optical isomers of an enantiomeric pair always give identical spectra. The racemic mixture

however, may show differences in the solid state which, of course, disappear in solution. The comparison by infrared method therefore, excludes the tedious resolution of the racemic mixture, *e.g.,* at the end of a synthesis and provides an excellent method of comparison of an optically active natural product with the racemic product. As an added advantage liquid compounds can be compared directly by comparison with published spectra in the fingerprint region.

The two crystalline isomeric sesquiterpene alcohols khusol and khusinol were isolated from vetiver oil. The infrared spectra of both the alcohols (Fig. 3.42) as expected, are different. The determination of their structures and absolute configurations rests on judicious set of inter-relationships which involved the selective removal of the oxygen function from both the alcohols to define their parent hydrocarbons (Scheme 3.25). Strikingly these hydrocarbons (XI) were found to have superimposable infrared spectra (Fig. 3.42) and were therefore identical. Moreover, it was found that these spectra were further superimposable on (XII) a, hydrocarbon whose structure and absolute configuration was known earlier from rigorous chemical degradation and physical methods. The specific rotation data (Scheme 3.25) showed that (XI) prepared from khusol or khusinol represented the enantiomer of (XII). This infrared identification of (XI) therefore, confirmed the carbon skeleton, the placement of two double bond in it and the stereochemistry of the isopropyl group and at the ring juncture in both the alcohols. The final structures of khusol and khusinol only required the location of hydroxyl groups. In the case of khusol, *e.g.,* it was decided by stepwise oxidation which gave an aldehyde (1724 and 2710 cm^{-1}) and finally an acid and therefore it must be a primary alcohol. Since the above infrared feature (normal C=O stretch) of the aldehyde and also UV spectrum were not characteristic of an α, β-unsaturated aldehyde of the two alternative structures, structure as shown (Scheme 3.25) was accepted.

(c) Assignment of Structures — Matching Spectra with Related Systems — Some Complicating Factors. It is now a normal routine to check each stage of synthesis or structure elucidation with the help of all spectral methods available. Experience is no doubt the best teacher in such practices. To illustrate this method of control a few example are presented.

In order that the bonding of the type depicted in XIII and XIV is possible, it is necessary for the molecular geometry to permit the formation of a —OH- - -O— bond not larger than 3.3 Å. Thus with chair conformation, *cis*-cyclohexane-1,2-diol can exit only in one form, *i.e.,* one of the hydroxy is equatorial while second is in axial conformation and the —OH- - -O— bond distance is computed to be 2.34 Å (based on normal values of bond lengths and valence angles). This compound therefore, shows an associated hydroxyl band with a maximum at 3587 cm^{-1}. On the other hand, a

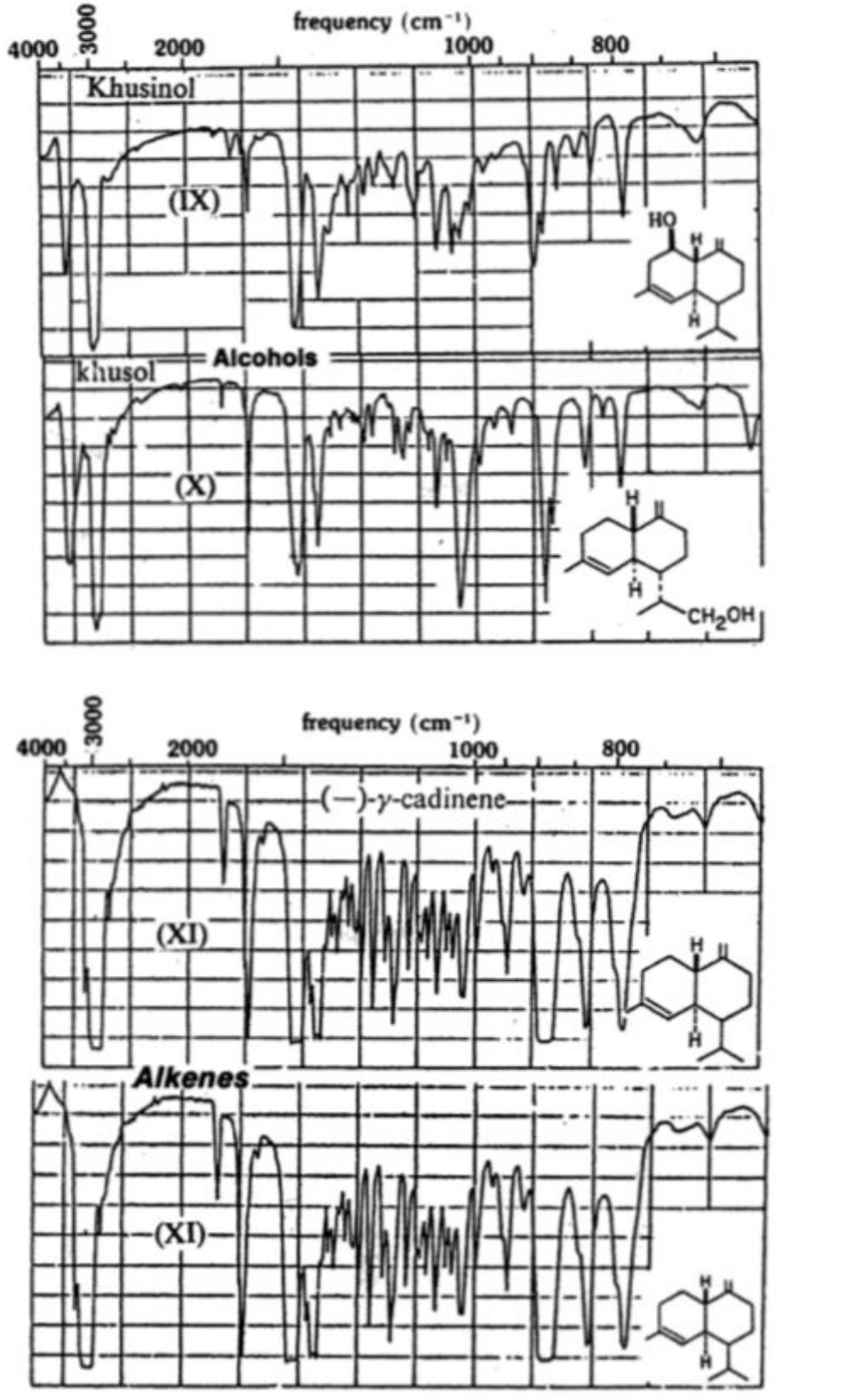
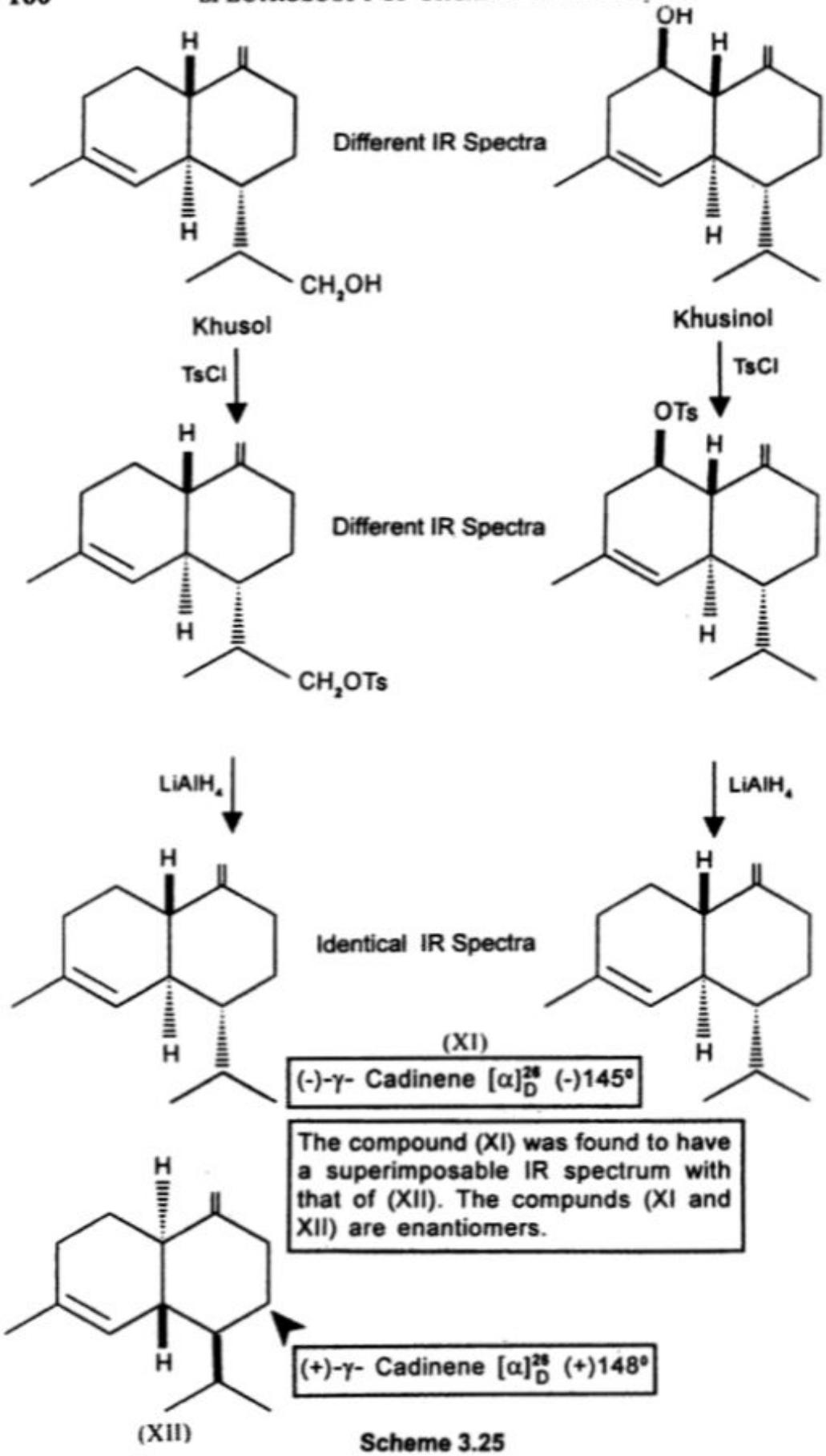
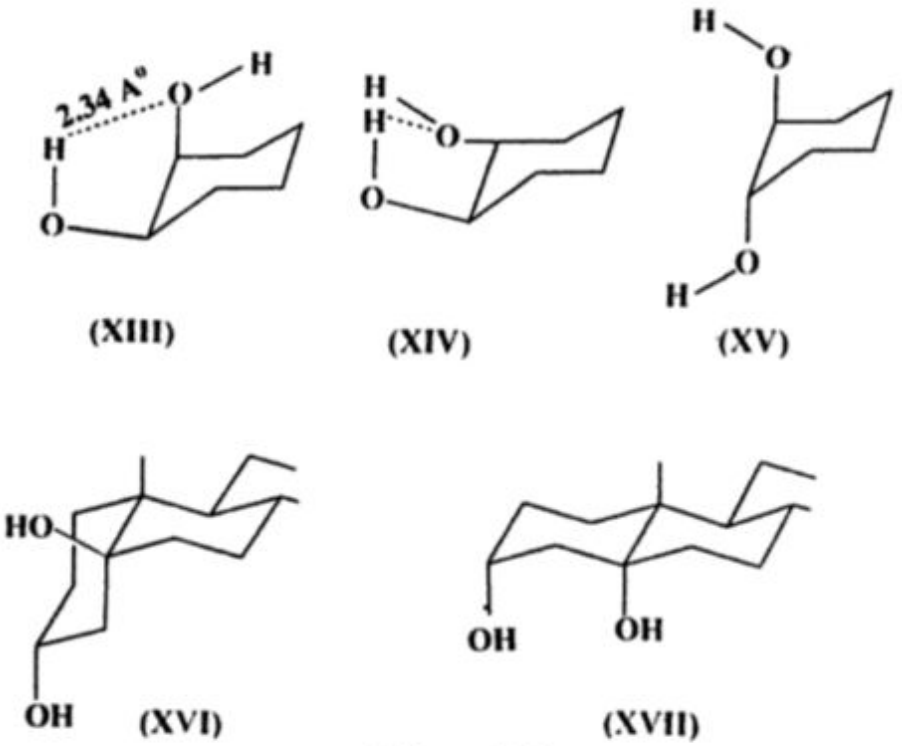


Fig. 3.42



Scheme 3.25

trans-cyclohexane-1,2-diol can have two conformations XIV with both the groups equatorial and XV with both axial. In XIV the —OH- - -O— bond distance is 2.34 Å while in structure XV if the bond is formed it would be longer than 3.3 Å. Actually in the spectrum an associated hydroxyl band is detected and therefore, it may be inferred that the diol has the equatorial conformation (Scheme 3.26). This feature has been utilised in the study of stereochemistry of diols. Transannular hydrogen bonding is frequently encountered in the steroids and revealed by infrared spectroscopy. Thus, cholestan-3α, 5 β-diol (XVI) shows only a band at 3620 cm^{-1} while cholestan-3α, 5 β-diol, (XVII) displays two bands at 3620 and 3521 cm^{-1} (Scheme 3.26).



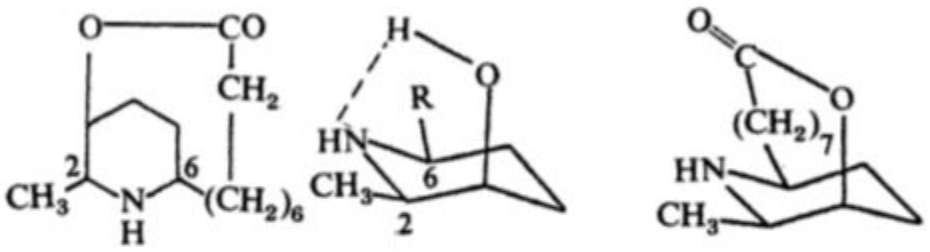
(XIII) (XIV) (XV)

(XVI) (XVII)

Scheme 3.26

Carpine is a crystalline alkaloid and is a piperdine derivative. The product of the opening of its lactone ring, carpamic acid, is cleaved by lead tetracetate and not by periodic acid and thus is a 1,2-amino alcohol (XVIII). The groups at C—2 and C—6 are *cis* and equatorial. The complete configuration of carpine is based on the comparison of the infrared spectrum of methyl carpamate XIX with the model compounds. A strong hydrogen-bonded hydroxyl band showed that the hydroxyl group is axial and (XIX) is the only possible conformation to meet this requirement and, therefore, carpine has the conformation (XX) (Scheme 3.27).

Many cyclohexanones show their C=O stretching frequencies in the range where medium ring size ketones absorb (~1705 cm^{-1}) and in all such

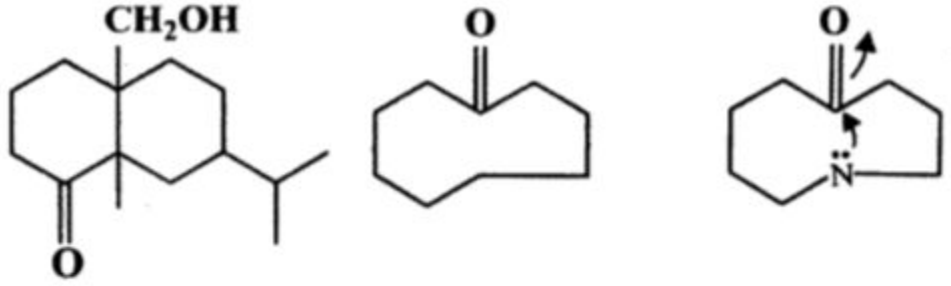


(XVIII) (XIX) (XX)

$R = -(CH_2)_7CO_2CH_3$ Carpine

Scheme 3.27

cases the α-carbons are highly alkylated. Thus, as compared with the value of 1714 cm^{-1} for cyclohexanone, 2,2-dimethyl-cyclohexanone absorbs at a very much lower value of 1702 cm^{-1} while 2-methylcyclohexanone absorbs normally (1715 cm^{-1}). Hydroxy-valeranone (XXI, Scheme 3.28) is a typical 2,2-alkyl substituted cyclohexanone and shows its stretching frequency at 1692 cm^{-1} and this observation was of value in the structure elucidation of this natural product. Abnormal C=O stretching frequencies have been shown by several medium-sized rings which, *e.g.*, contain a nitrogen atom as in (XXIII). This is due to transannular electron donation from the hetero atom to the carbonyl group.



C=O stretch →

(XXI) Hydroxy-valeranone 1692 cm^{-1} (XXII) 1705 cm^{-1} (XXII) 1670 cm^{-1}

Scheme 3.28

3.9 IR RADIATION AND GREENHOUSE EFFECT

The concentration of carbon dioxide in the atmosphere has been increasing due to human activity: industrial revolution and burning of large amounts of organic carbon (natural gas, oil, coal, trees and other biomass). An increase in carbon dioxide "a greenhouse effect" leads to traping of more heat on earth thus preventing it from escaping into space, leading to increase in global temperature.

The ultraviolet and visible radiation from the sun brings energy to earth which is absorbed and converted to vibrational, translational and even chemical energy. A part of the vibrational energy is reemitted as infrared radiation; and carbon dioxide of normal air absorbs strongly from 2300-2400 cm^{-1}. Apart from water (infrared absorption 4000-3400 cm^{-1} O—H stretches, and 1800-1200 cm^{-1} O—H bends), two other major components N_2 and O_2 do not absorb IR radiation since their dipole moments do not change on vibration.

3.10 INFRARED RADIATION AND AUTOMOBILE POLLUTANTS

The exhaust from the poorly maintained automobiles contains carbon monoxide and hydrocarbons as two pollutants. These two pollutants are detected by remote sensing which consists of a source of IR radiation on side of the road for the intensity of absorption of CO (2170 cm^{-1}) and hydrocarbons (3000-2800 cm^{-1}; Fig. 3.42a). Incorporation of a detector, calibrator, video, and a computer records the picture of the number plate along with the per cent of pollutants. On this basis, the owner of the vehicle can be fined.

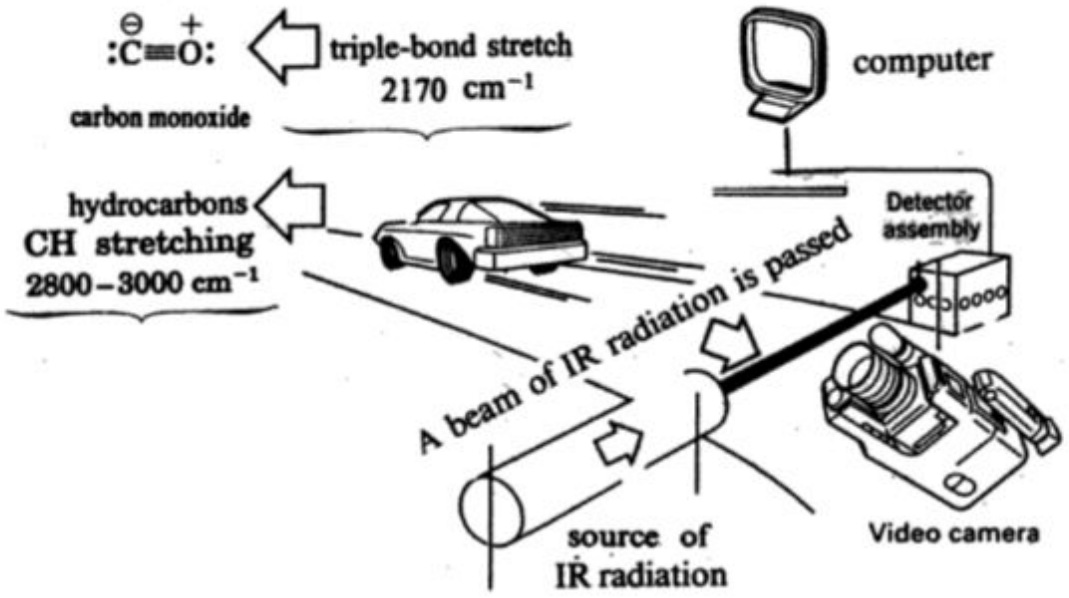


Fig. 3.42a

3.11 THE BREATH ANALYZER TOOL

For determining ethanol level in blood, use of IR spectrophotometers specifically designed for the O-H stretching region (near 3400 cm^{-1}) is made.

The diffusion of blood alcohol through the lung occurs into the blow of breath which is subjected to IR spectroscopy in the O-H stretching region. The test is useful for the determination of the alcohol level in the breath and therefore, in the blood.

EXERCISES AND PROBLEMS

1. Placed below are the infrared spectra of thirteen compounds, (Fig. 3.43-3.49). In some of these spectra, either the main functional group is identified (by marking some of the corresponding bands in the high frequency region), or some significant bands are located. Analyse the other bands to confirm the assignments and comment on the overall structural features.

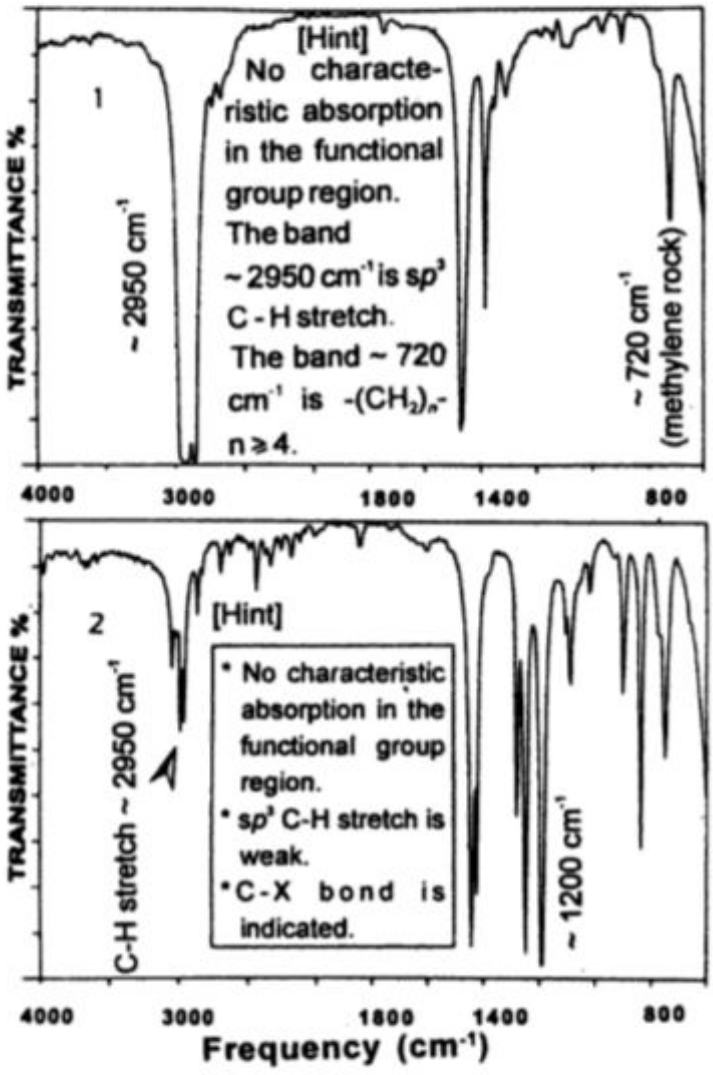


Fig. 3.43

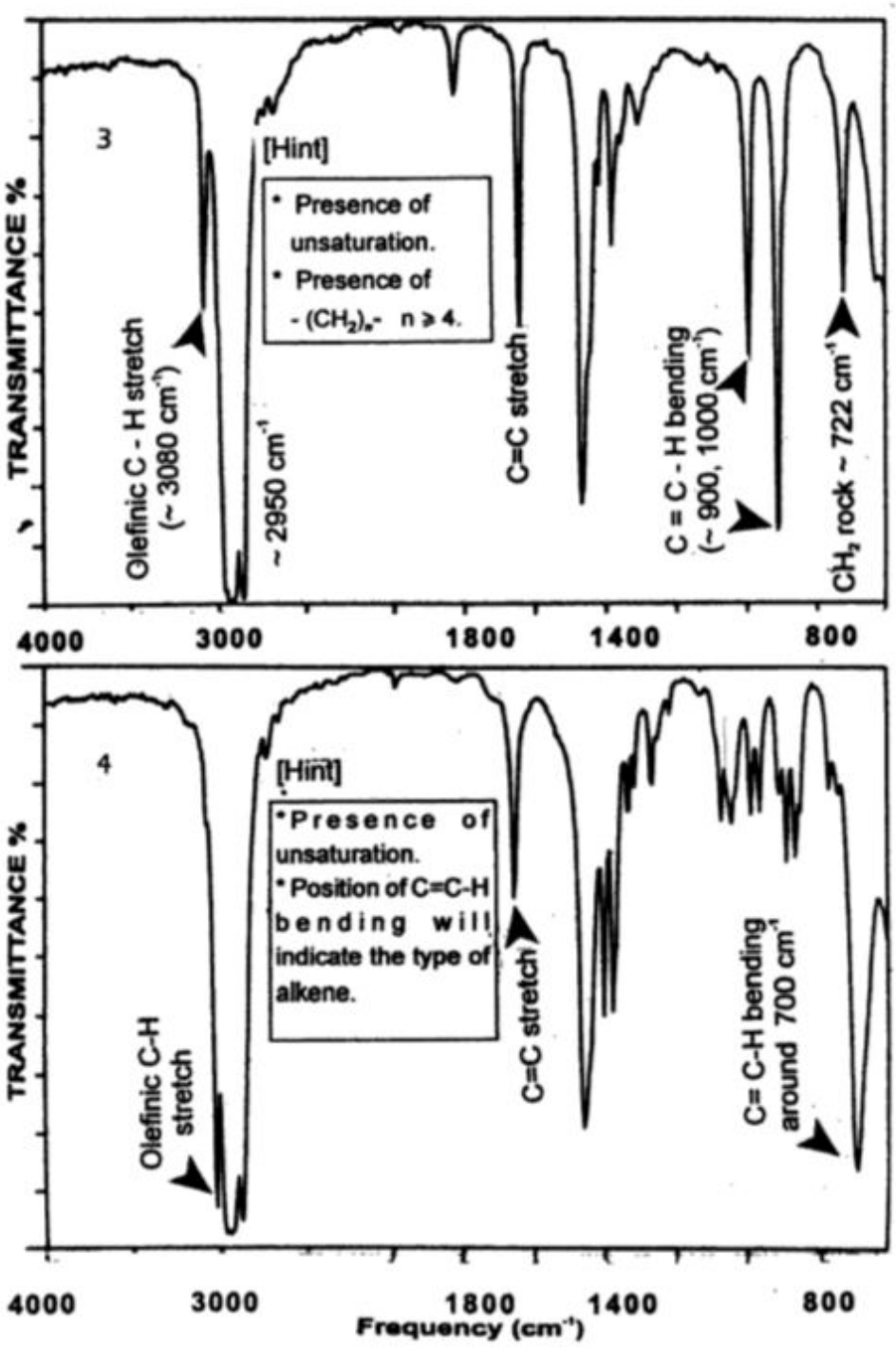


Fig. 3.44

2. An organic compound $C_8C_8O_2$ gives the infrared spectrum shown in Figure 3.50. Comment on the structural features in the compound.
3. Comment briefly on the stretching frequencies of the following bonds:

Bond		Frequency Range, cm^{-1}
Alkyl	C—H	2853-2962
Alcohol	O — H	3590-3650

	Bond	Frequency Range, cm^{-1}
Amine	N — H	3300-3500
	C ≡ C	2100-2260
	C ≡ N	2220-2260
	C = C	1620-1680
	C = O	1690-1750

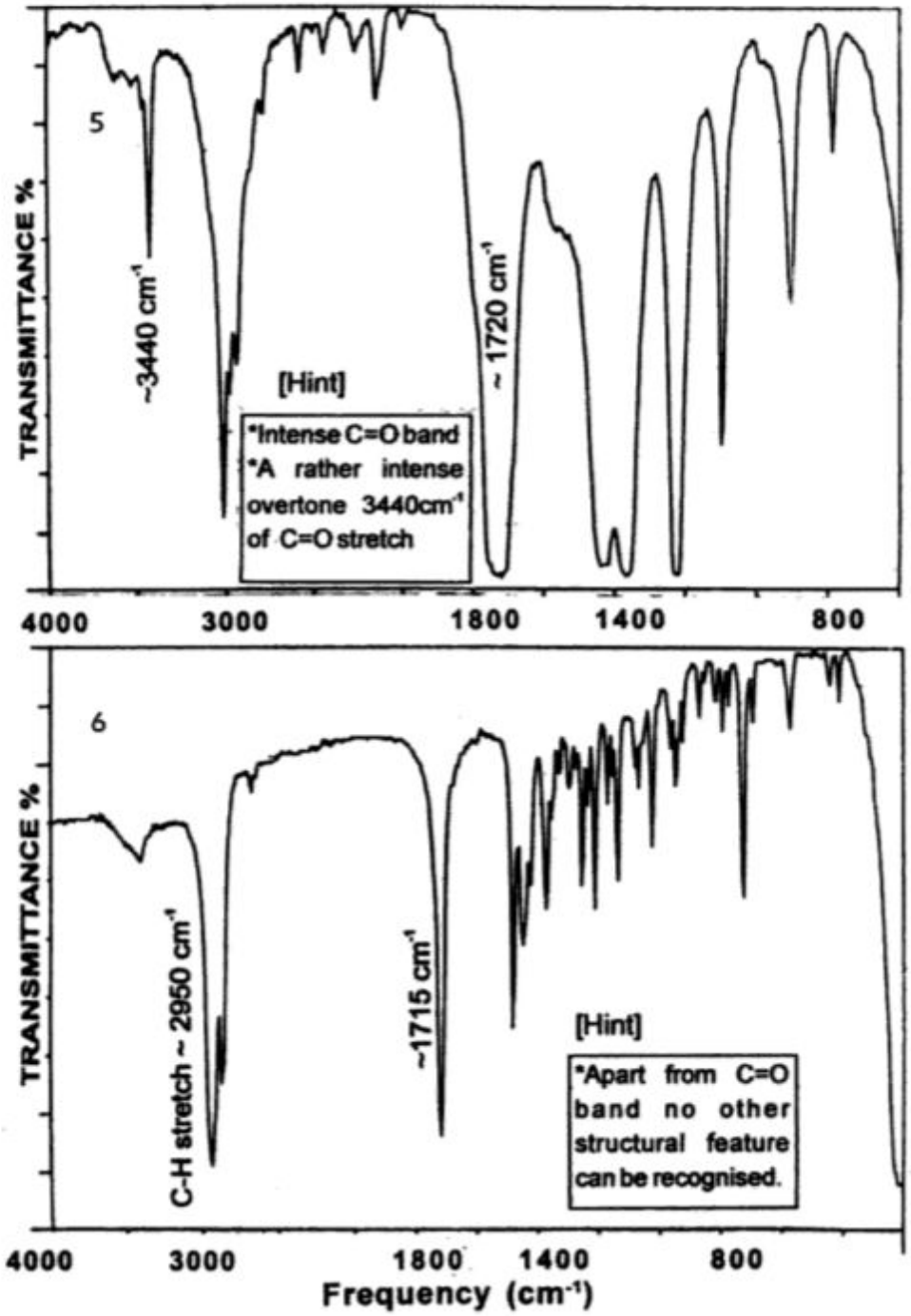


Fig. 3.45

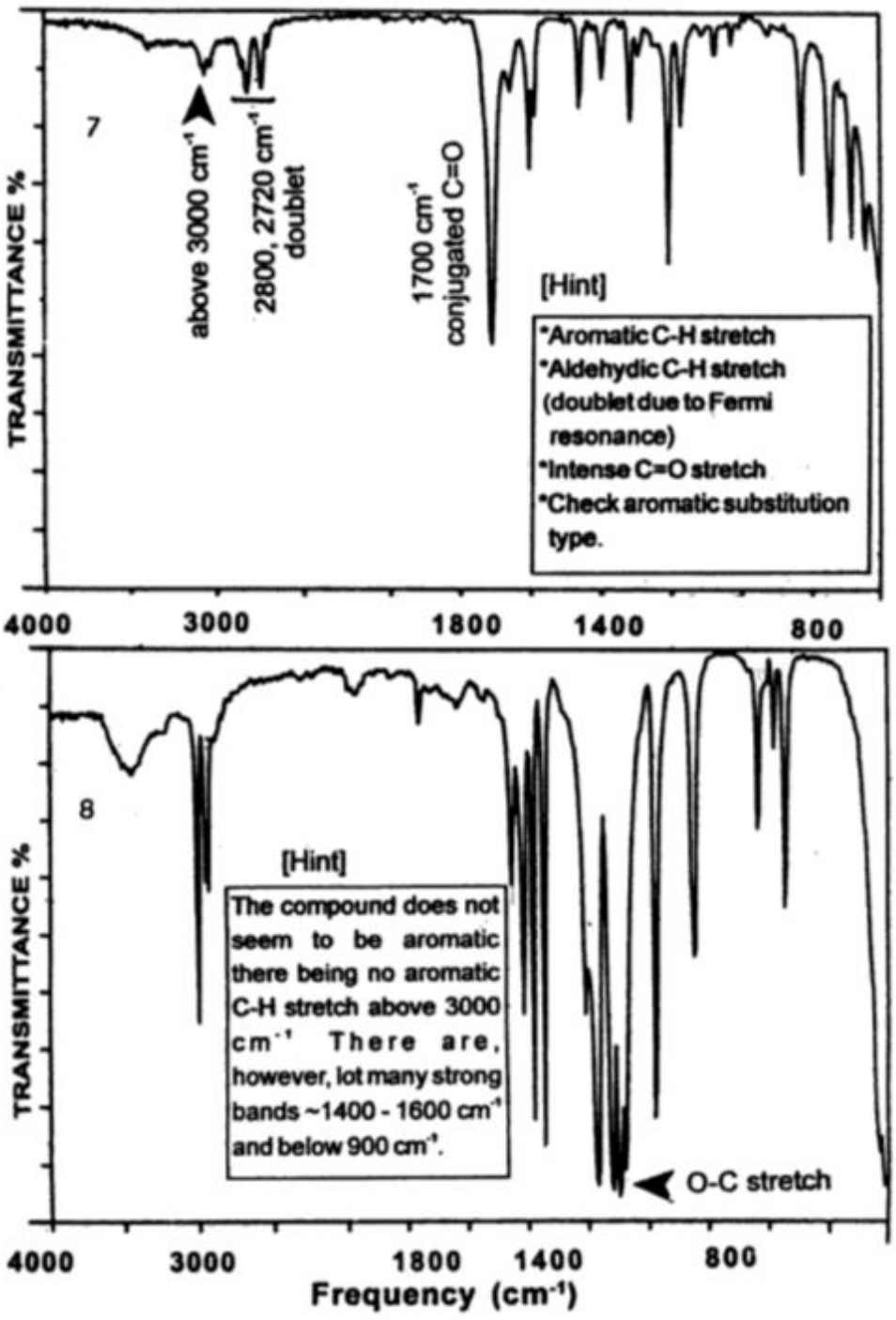
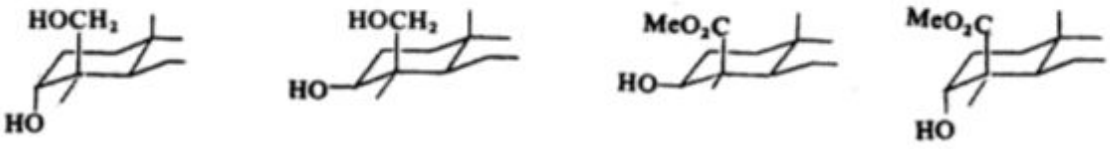


Fig. 3.46

4. Comment on the indicated O—H and C=O stretching vibrations for the stereoisomeric pairs: I, 3641 and II, 3629 and 3550 cm^{-1}; III, 3548 and 1709 cm^{-1} and IV, 3635 and 1723 cm^{-1}.



(I) (II) (III) (IV)

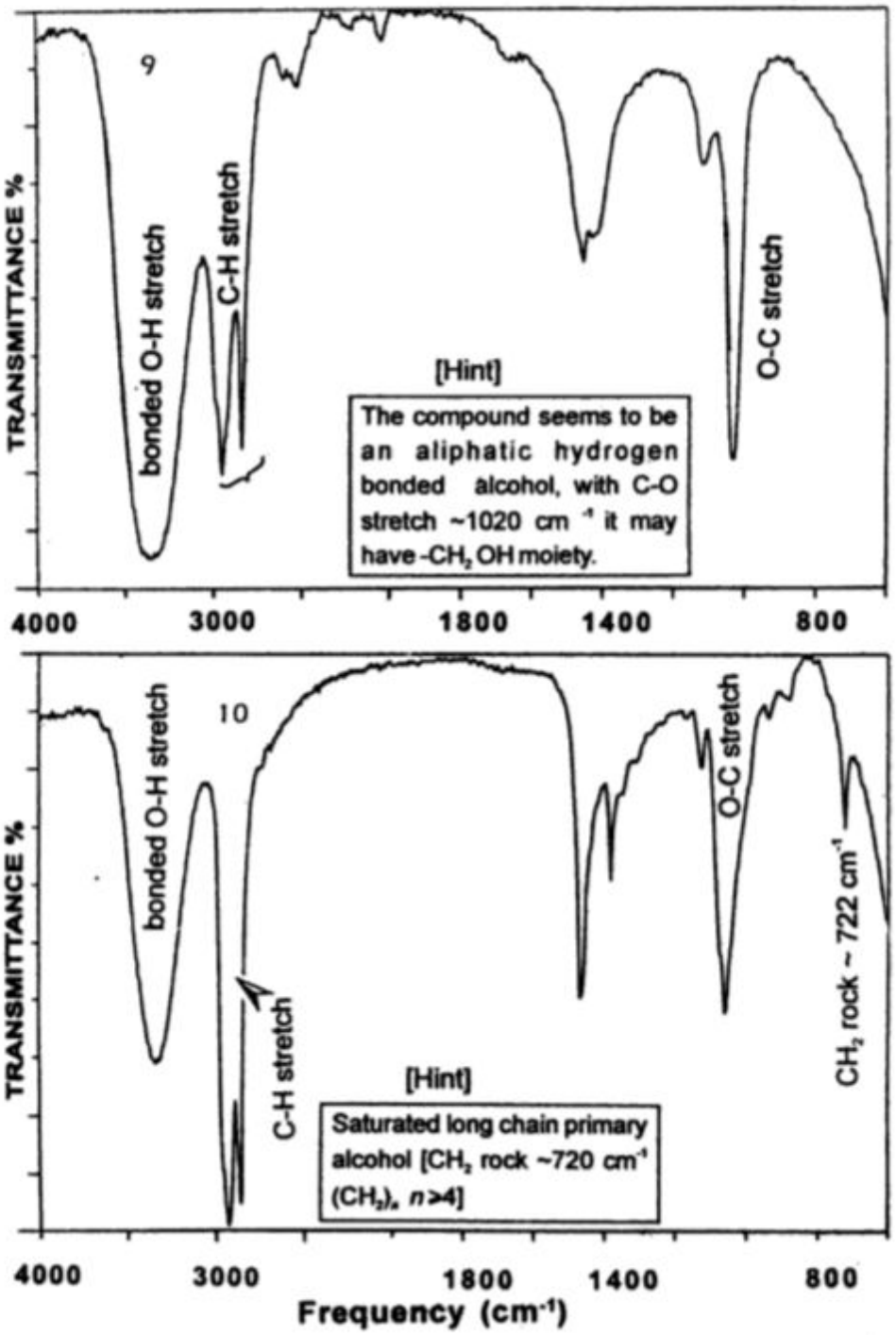
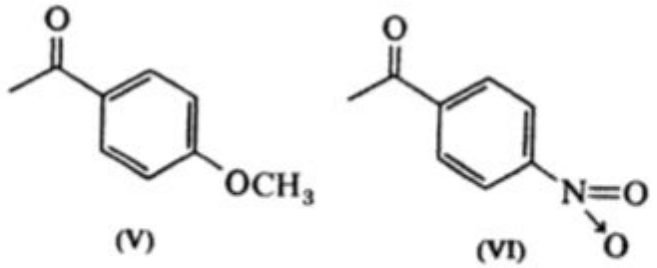


Fig. 3.47

5. Which out of compounds (V and VI) is expected to show a lower C=O stretching frequency?



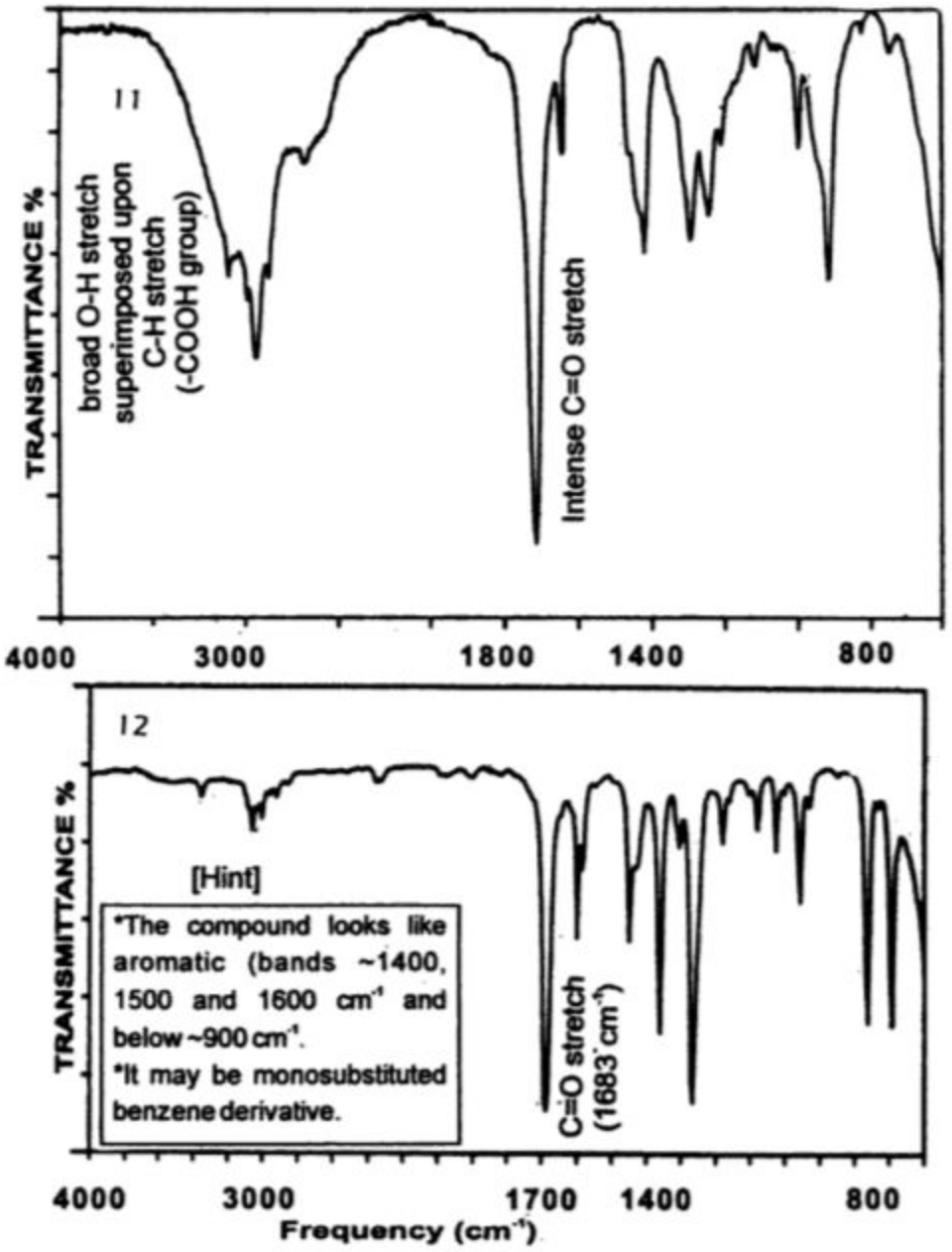
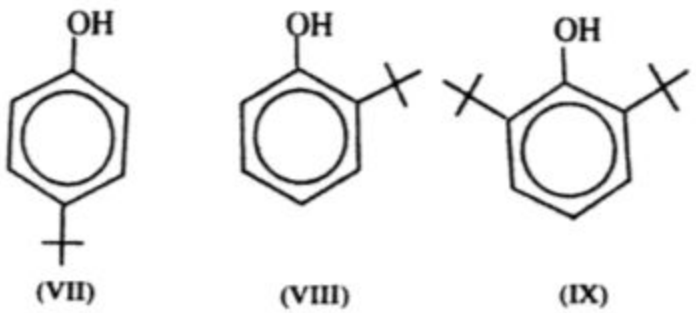


Fig. 3.48

6. Esters of *o*-chlorobenzoic acid show two C=O stretching frequencies. Explain.
7. In the substituted phenols the O—H stretching is at 3608 cm^{-1} in (VII), at 3605 and 3643 cm^{-1} in (VIII) and at 3643 cm^{-1} in (IX). Explain.



(VII) (VIII) (IX)

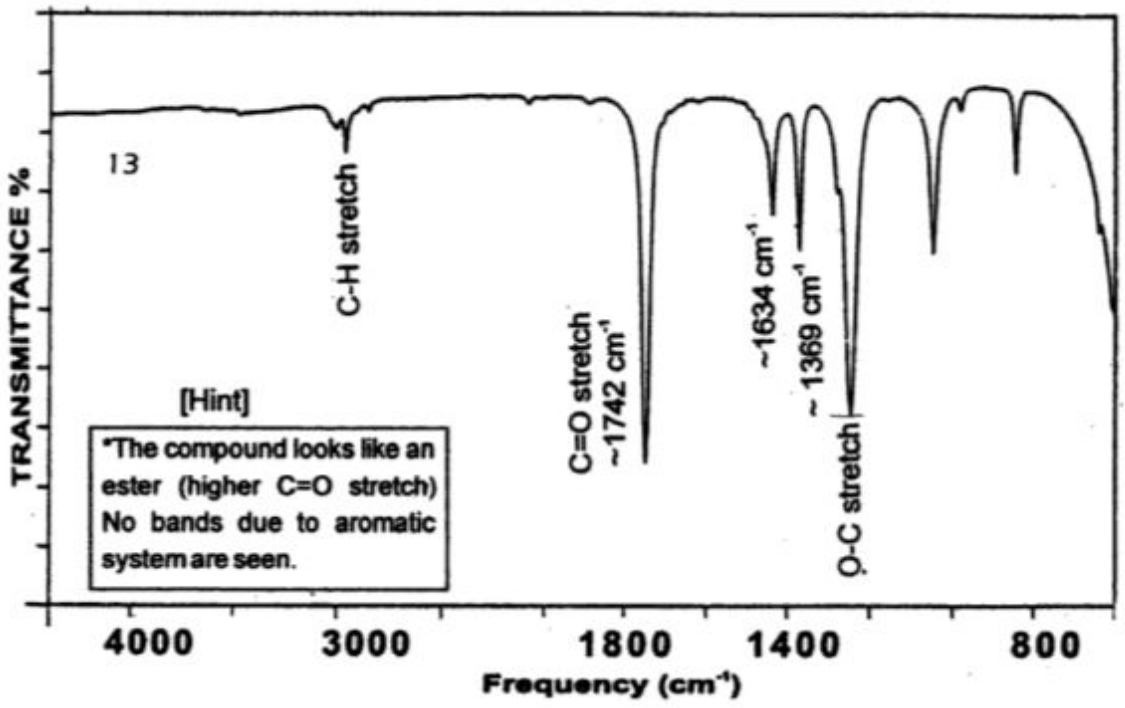


Fig. 3.49

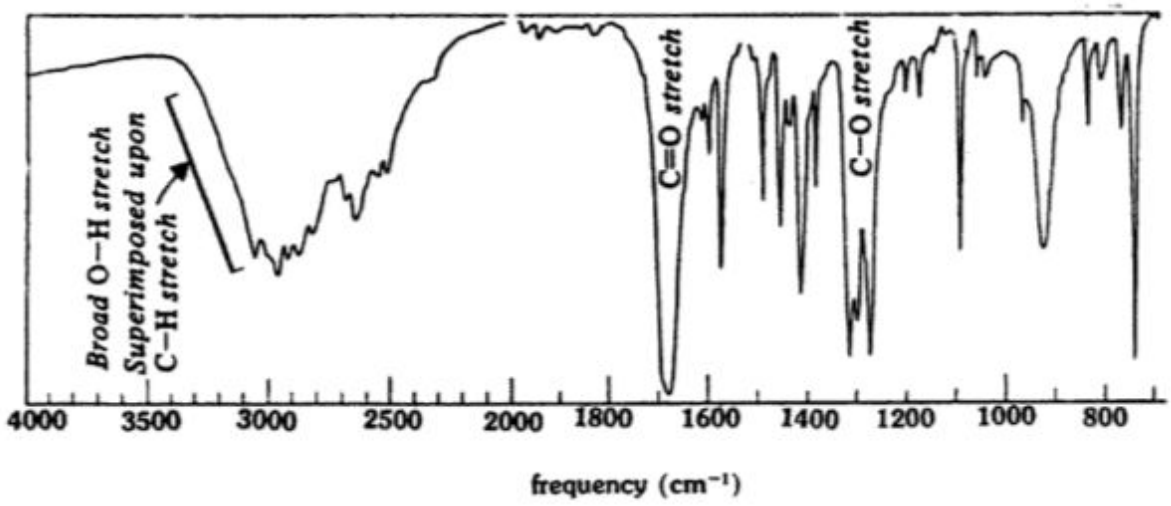
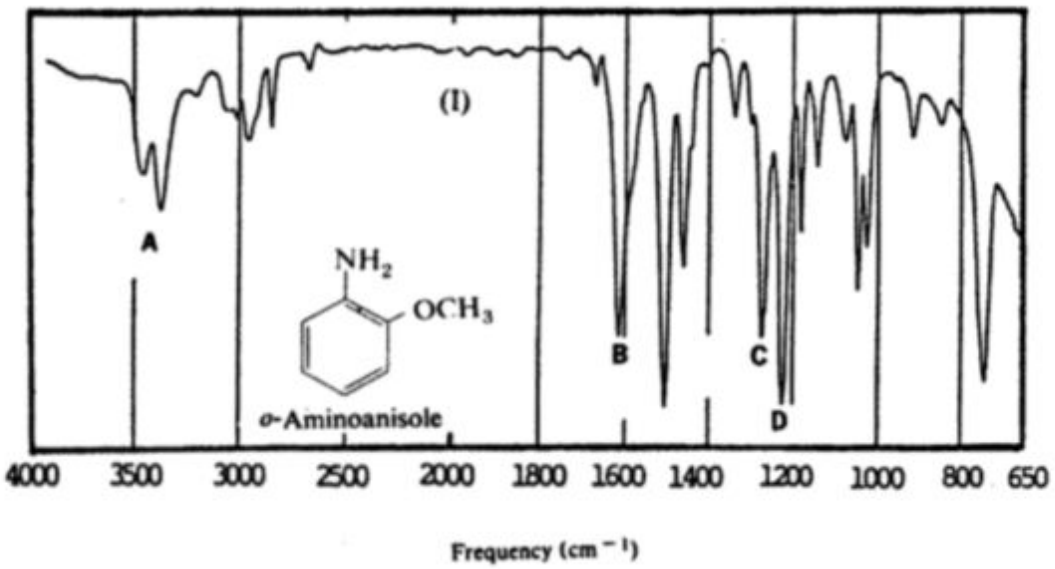


Fig. 3.50

8. 2-Hydroxy-3-nitroacetophenone shows two carbonyl stretching frequencies at 1692 and 1658 cm^{-1}. Explain.
9. *O*-Nitrophenol has an O—H band at 3200 cm^{-1} in KBr pellet as well as in $CHCl_3$ solution, whereas in the *para* isomer the values are different in the two media (pellet 3330; $CHCl_3$ solution 3520 cm^{-1}). Explain by writing structures and their effect on their volatility.
10. In the infrared spectra of two compounds (Fig. 3.51), the bands due to functional groups have been marked, identify these bands.



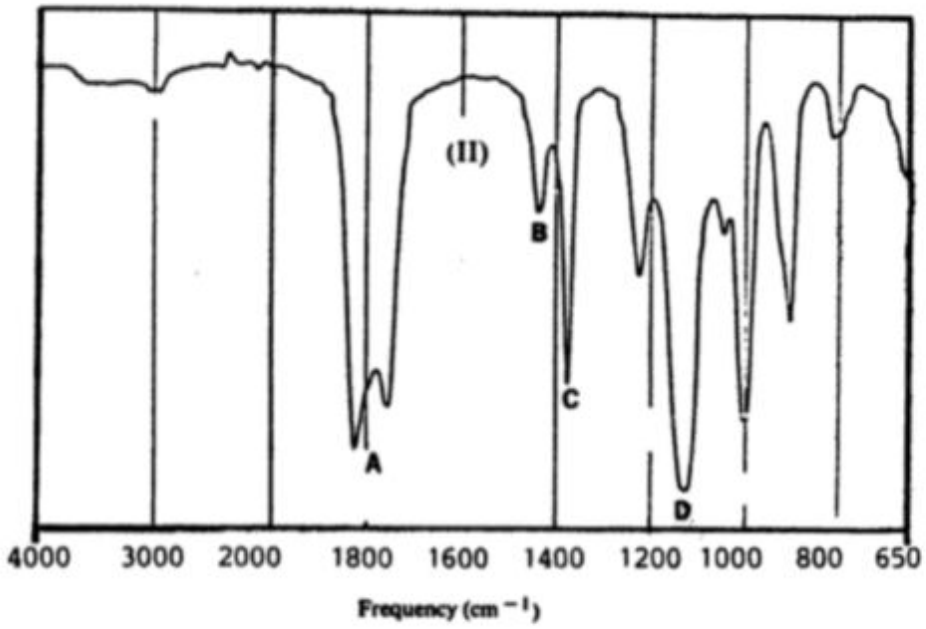
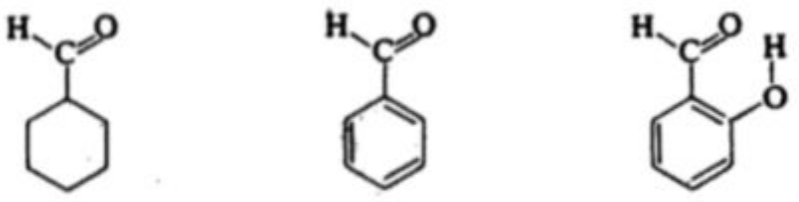


Fig. 3.51

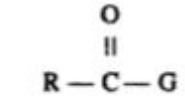
11. Predict the frequency shift of the carbonyl absorption in the aldehydes 1-3.



1 **2** **3**

12. An acyl group is readily detected from the infrared spectroscopy since the C=O stretching frequency varies with the functional group, *i.e.*, with G. From the follow-

ing trends in the strong carbonyl stretching absorption peak in the 1700 cm^{-1} region, identify a particular acid derivative in each case.



(i) 1,700–1,815 cm^{-1} (5.65–5.51 μ)
(ii) 1,740–1,790 cm^{-1} and 1,800–1,850 cm^{-1} [two bands]
(iii) 1,720–1,750 cm^{-1}
(iv) 1,630–1,690 cm^{-1}

13. Certain acyl compounds, *e.g.*, carboxylic acids, aldehydes and amides have further distinctive features other than explained in exercise 15 above. Explain.
14. Infrared absorption due to carbonyl stretching occurs at higher frequencies than stretching of the carbon-carbon double bond. Explain.
15. An unsaturated hydrocarbon containing a vinylidene (>C=CH_2) double bond displays the infrared spectrum shown in Figure 3.52, I. The spectral changes on its dihydroxylation with O_sO_4 and subsequent rupture of σ bond with periodic acid to give a ketone are presented in figures II and III. Assign the bands in each spectrum to respective functional groups.

ANSWERS TO THE PROBLEMS

1. *Spectrum 1.* It displays a strong aliphatic C—H stretch around 2950 cm^{-1} and C—H bending of methyl and methylene groups around 1380 and 1465 cm^{-1}. The methyl C—H band at 1380 cm^{-1} is not split into a doublet, thus isopropyl or tertiary butyl moieties are absent. This together with a strong methylene rock at 720 cm^{-1} shows that the compound is a straight chain saturated hydrocarbon. The compound is dodecane.

Spectrum 2. The spectrum displays bands for aliphatic C—H stretch (rather weak), and C—H bending of methylene group around 1450 cm^{-1}. There is no C—H bending of the methyl group (The region from 1300-1400 cm^{-1} being blank). The compound is 1,2-dibromoethane.

Spectrum 3. The compound typically shows the presence of unsaturation. The nature of double bond can be assessed form the C—H bending vibrations which are located around 1000 and 900 cm^{-1} (vinyl double bond). There is a methylene rocking band around 720 cm^{-1}. The compound is thus a long chain alkene, with terminal unsaturation. The compound is 1-tetradecene. Note the typical overtone band around 1825 cm^{-1}.

Spectrum 4. The compound is unsaturated. The presence of C—H bending at 700 cm^{-1} shows the compound to contain *cis*-disubstituted double bond. The compound is *cis*-2-hexene.

Spectrum 5. It is a carbonyl compound. An inspection of the methyl and methylene C—H bending region shows that the band below 1400 cm^{-1} is more intense than the one above 1400 cm^{-1}. This shows the presence of a methyl group on a carbonyl. The compound is acetone.

Spectrum 6. It represents a saturated ketone, whose C=O stretch at around 1715 cm^{-1} is suggestive of either an acyclic ketone, a six-membered ring ketone or an eleven or

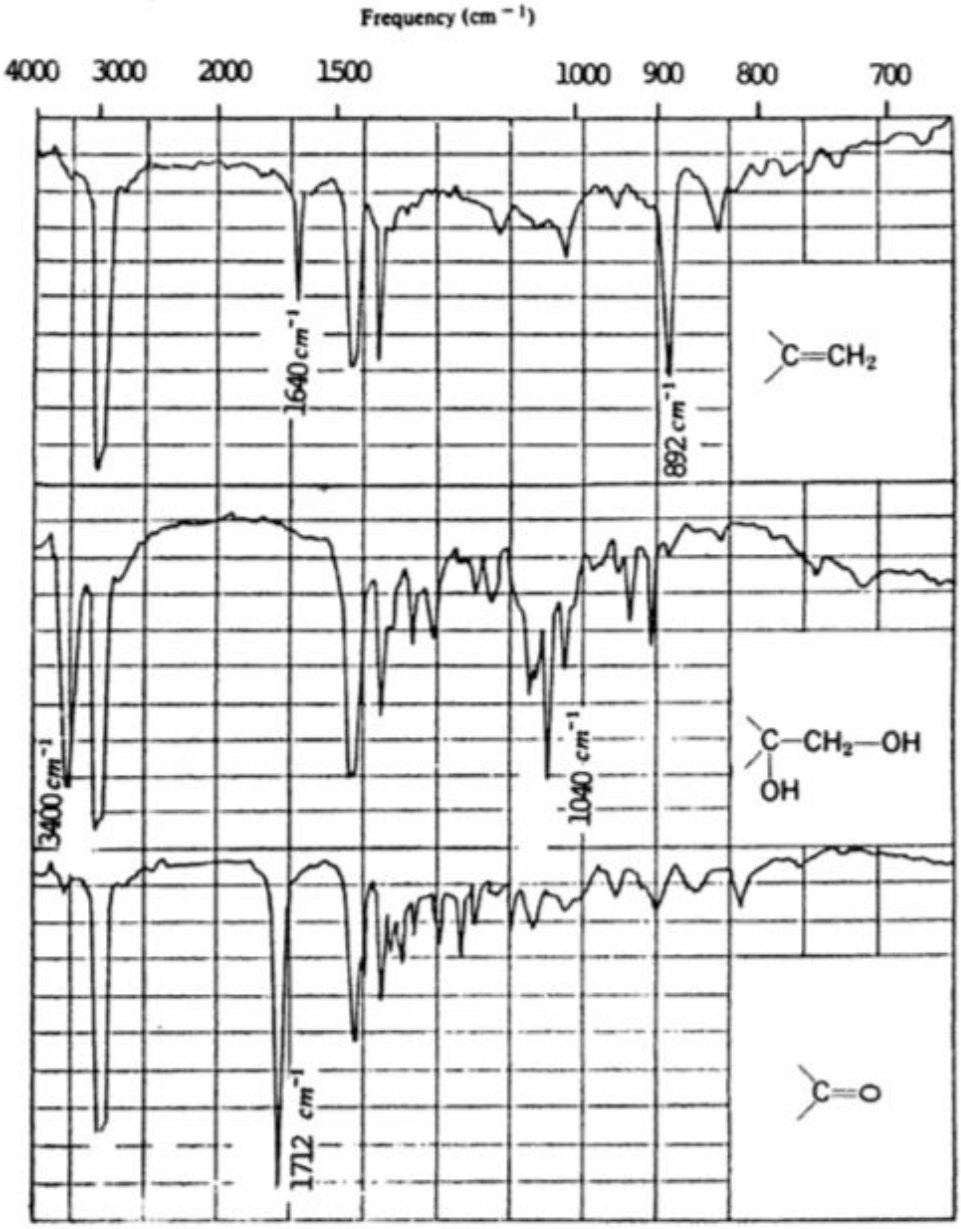
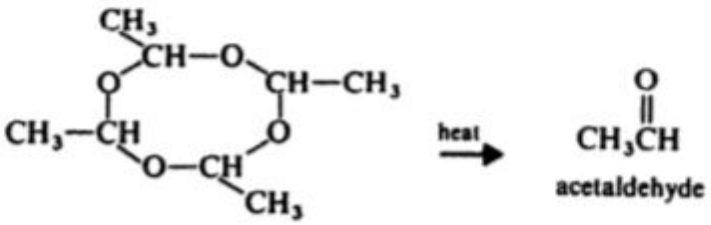


Fig. 3.52

higher membered ring ketone. 7-10-Membered ring ketones show their C=O stretch around 1702 cm^{-1} while 5,4 and 3-membered ring ketones show higher C=O stretchings at 1745, 1780 and 1825 cm^{-1} respectively. The compound is cyclododecanone.

Spectrum 7. The presence of aromatic C—H stretch above 3000 $^{-1}$, aldehydic C—H stretch near 2700 and 2800 cm^{-1} and C=O stretch around 1700 cm^{-1} and typical out of the plane C—H bendings show that the compound is a monosubstituted benzene derivative. The compound is benzaldehyde.

Spectrum 8. The compound represents metaldeyde, *i.e.*, the tetramer of acetaldehyde. The C—O stretching region between 1000-1200 cm^{-1} is indeed full of strong bands.



metaldehyde acetaldehyde

Spectrum 9. The spectrum is of an alcohol as evident from strong O—H and C—O stretchings. The compound is methyl alcohol.

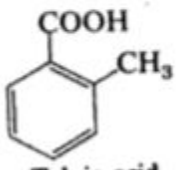
Spectrum 10. There is a strong O—H stretch, and this coupled with C—O stretch at 1025 cm^{-1}, shows it to be a primary alcohol. The compound is l-decanol.

Spectrum 11. The spectrum shows typical and broad O—H stretch which is superimposed upon C—H stretch. This coupled with C=O stretch around 1720 cm^{-1} shows that the compound is a carboxylic acid. There is unsaturation in the compound as shown by the presence of C=C stretch around 1625 cm^{-1}. The C—H bendings around 900 cm^{-1} (s) and 975 cm^{-1} show the presence of vinyl double bond. The compound is 6-heptenoic acid.

Spectrum 12. The spectrum shows aromatic C—H stretch above 3000 cm^{-1} and also aliphatic C—H stretch below 3000 cm^{-1}. The C=O stretch 1683 cm^{-1} is at lower frequency than the normal C=O stretch which is around 1725 cm^{-1}. This is probably due to its conjugation with the phenyl group. The presence of C ⋯ C ring stretchings and out of plane C—H bendings are typical of a monosubstituted benzene. The compound is acetophenone.

Spectrum 13. The C—H stretch is weak, however, it cannot be aromatic since its position is below 3000 cm^{-1}, it is therefore assigned to aliphatic C—H stretch. The presence of C=O stretch (1742 cm^{-1}) along with C—O stretch 1240 cm^{-1} shows the compound to be a saturated ester. A shrewed eye will detect that in the methyl, methylene C—H bending region of the two bands at 1434 and 1369 cm^{-1}, the band at lower frequency is more intense. This shows the presence of CH_3—C=O moiety (Fig. 3.38). The compound is methyl acetate.

2. Strong broad O—H stretch is centred at around 3000 cm^{-1} and superimposed upon the region of C—H stretch. This coupled with the presence of strong C=O stretch around 1690 cm^{-1} confirms the presence of a conjugated —COOH group and accounts for both the oxygen atoms. The presence of combination bands, aromatic C=C stretch around 1400, 1500 and 1600 cm^{-1} and strong C—H bending at 735 cm^{-1} further shows that the aromatic substitution type is *ortho*-disubstituted benzene. The compound is *O*-toluic acid.

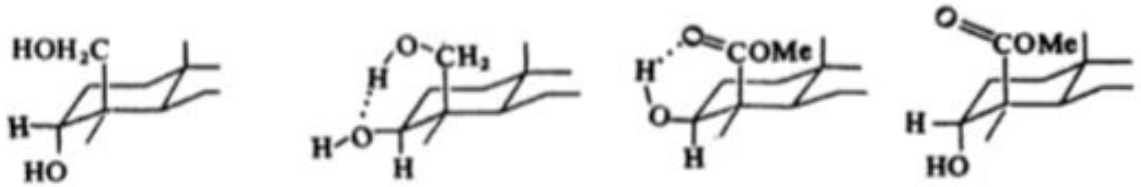


o-Toluic acid

3. The stretching frequency of a bond and therefore, its position in an infrared spectrum is related to two factors; the masses of the bonded atoms — light atoms vibrate at higher frequencies than heavier ones — and the relative stiffness of the bond. Triple

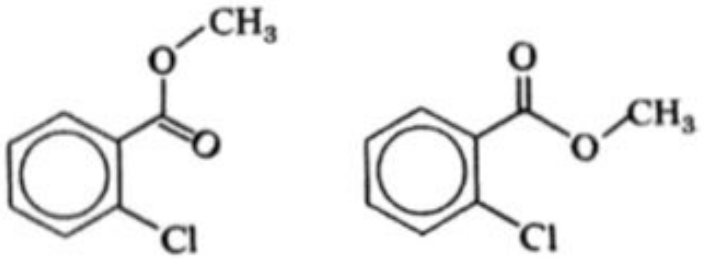
bonds being stiffer, vibrate at higher frequencies than double bonds and double bonds are stiffer and thus vibrate at higher frequencies than single bonds. The stretching frequencies of groups involving hydrogen, *i.e.*, a light atom such as C—H, N—H and O—H all occur at relatively high frequencies. As expected, the triple bonds vibrate at higher frequencies than double bonds.

4. In these stereoisomeric pairs of compounds I and II and III and IV only one member from each pair permits hydrogen bonding leading to lowering in the O—H and C=O stretchings.



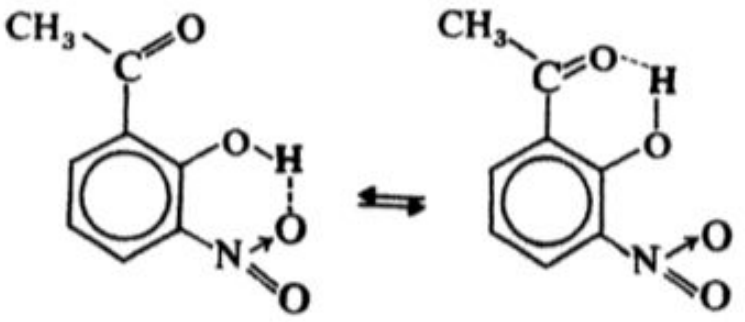
5. The presence of *p*-OMe group (a + *M* group) in V assists the mesomeric shift to decrease the bond order of C=O bond leading to lower C=O stretching frequency. A *p*-NO_2 (—M group) tends to oppose these trends and thus in (VI) the C=O stretching frequency is higher than V.

6. In *O*-chlorobenzoic acid esters the field effect shifts the C=O frequency in the rotational isomer (VII) and not in the isomer (VIII). Normally both the isomers are present, so that two C=O stretching absorptions are observed.

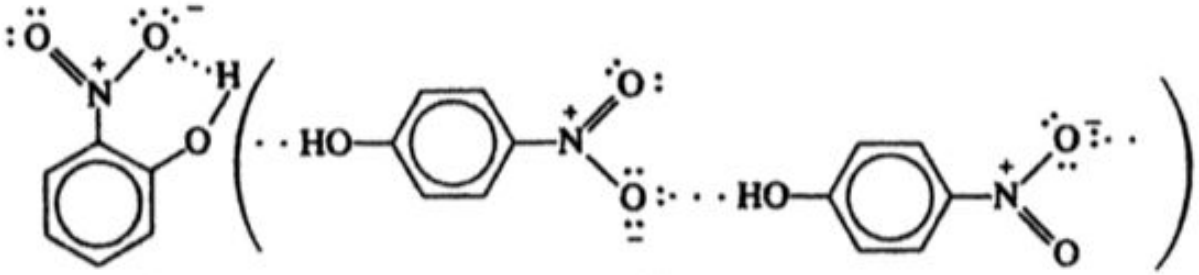


(VII) (VIII)

7. In *p*-*t* butylphenol (VII) only a single hydroxyl frequency is seen at 3608 cm^{-1} due to associated OH group. In the *O*-isomer (VIII), bands are seen at both 3605 and 3643 cm^{-1} showing that in some molecules there is association whereas in others the OH is not hydrogen bonded due to crowding by *t*-butyl group. In 2.6 di-*t*-butyl phenol (IX) only a single hydroxyl frequency is seen at 3643 cm^{-1}, since two different molecules are not able to approach close enough to form an intermolecular hydrogen bond.
8. Due to competing hydrogen bond formation and therefore as a result of the equilibrium shown below. The structure with free carbonyl shows the normal conjugated C=O stretch, however, on association with the OH group the C=O stretch is further shifted to lower frequency.



9. **2-hydroxy-3-nitroacetophenone**



***o*-Nitrophenol**
(more volatile because of intramolecular hydrogen bonding)

***p*-Nitrophenol**
(less volatile because of intermolecular hydrogen bonding)

10. In spectrum (I), Figure 3.51, A is NH stretch (coupled vibrations); B is NH bend, C is C—N stretch and D is O—C stretch. In spectrum (II), A is the coupled C=O stretch and the high frequency points to a carboxylic acid anhydride; B and C is C—H bend of $CH_3-\overset{|}{C}=O$ moiety and D is O—C stretch. The compound is acetic anhydride.
11. Cyclohexane carboxaldehyde 1, being saturated will absorb around 1730 cm^{-1}. In benzaldehyde 2, the absorption will be shifted to lower frequency (1700 cm^{-1}) due to conjugation. In salicylaldehyde 3, the internal (chelated) hydrogen bonding causes a further large frequency shift to around 1666 cm^{-1}.
12. (i) Acid chlorides $R-\overset{O}{\overset{\|}{C}}-Cl$

(ii) Anhydrides $R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R$

(iii) Esters $R-\overset{O}{\overset{\|}{C}}-OR$

(iv) Amides $R-\overset{O}{\overset{\|}{C}}-NH_2$

13. Carboxylic acids show a strong and broad O—H stretching frequency in the region 2,500 to 3,000 cm^{-1}, which is absent in esters. Furthermore, carboxylic acids show a C—O stretching frequency at ~1,250 cm^{-1}, whereas the C—O stretching in esters normally occurs as two relatively strong bands in the region 1,050 to 1,300 cm^{-1}. Aldehydes and ketones show no absorption in this broad region, thus they are readily

distinguishable from carboxylic acids and esters. Amides display N—H stretching in the 3,050 to 3,540 cm^{-1} region and show another strong absorption band in the 1,600 to 1,645 cm^{-1} region due to N—H bending.

14. This is explained in terms of the π bond stretch of the C=O bond, which is considerably stronger than the π bond in C=C.
15. The changes from an alkene (C=C stretch 1640 cm^{-1}, C—H bend 892 cm^{-1}) to a diol (OH stretch 3400 cm^{-1} C—O stretch 1040 cm^{-1}) and finally to a ketone C=O stretch (1712 cm^{-1}) are marked on the spectra.

SUMMARY

1. The infrared region from 4000-650 cm^{-1} is useful or structural information of organic compounds. This region is split into two parts, 4000-1300 cm^{-1}, the high frequency part, *i.e.*, the functional group region and the low frequency part 1300-650 cm^{-1}, the fingerprint region.
2. Most of the functional groups give absorption bands in the high frequency part of the spectrum, which, therefore has a small number of bands The fingerprint region contains a large number of bands and is rich in detail. This part is used for compound comparison.
3. As most organic compounds contain alkane residues, therefore, the strong aliphatic C—H stretch centred around 2925 cm^{-1} and the medium intensity bands for their C—H bendings around 1465 (CH_3, —CH_2) and 1380 cm^{-1} (CH_3) are generally present in an infrared spectrum (Fig. 3.7). Aromatic and olefinic C—H stretch is above 3000 cm^{-1}.

   To assist the student in his understanding, the main regions, where most of the common functional groups absorb are shown in thick lines with respect to three aliphatic bands, *i.e.*, C—H stretch (2925 cm^{-1}) and C—H bend (—CH_3, —CH_2—, 1465 and —CH_3 1380 cm^{-1}). However, the absence of these absorption bands due to the absence of alkyl residues does not offer any difficulty to assign bands to the presence of other functional groups.
4. The absorption of functional groups on the higher (left hand side) and lower (right hand side) frequency side of the main aliphatic C—H stretch are presented in Fig. 3.53. Among the prominent bands on the higher frequency side of this band mention may be made of O—H stretching band which is used to recognise the presence of alcohols and phenols. The value of O—H stretching frequency is used gainfully to detect hydrogen bonded (~ 3400 cm^{-1}) or free hydroxyl groups (~ 3600 cm^{-1}). The N—H stretchings occur around the same region. However, N—H absorptions are much sharper (weak tendency to form hydrogen bonds), weaker in intensity and in dilute solutions never give rise to absorptions as high as the free O—H groups (*i.e.*, 3600 cm^{-1}).

   A carboxylic acid is very easy to recognise because of the special shape of the broad bonded O—H stretch which lies across the aliphatic C—H stretch (Fig. 3.25). Primary amines and amides show two bands (coupled N—H stretchings) and can thus be distinguished from their secondary counterparts which normally show one band; in tertiary systems since there is no H on N, these bands are absent.

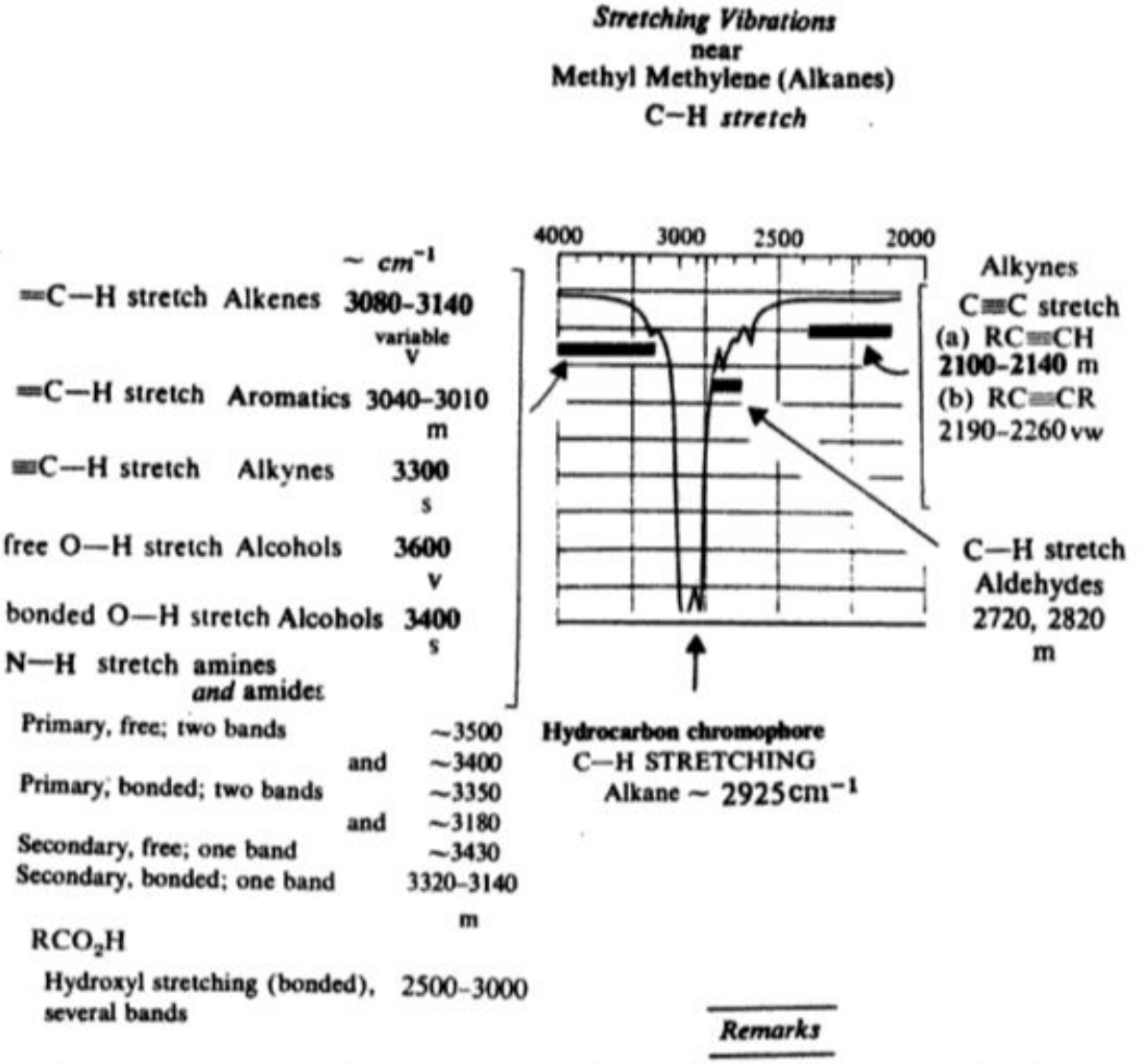


Fig. 3.53

5. On the right hand side of the aliphatic C—H band, one may look for one or a pair of bands around 2720 and 2820 cm^{-1} for the C—H stretch of an aldehyde group and these bands can be assigned to such a group only provided there is strong C=O stretch around 1700 cm^{-1}.
6. The S—H and C≡C stretchings are normally weak absorptions and can be detected in the high frequency region it being less complicated. Though weak, these bands are highly significant in detecting such groups.
7. Overtones and combination tones of lower frequency bands also display themselves in the high frequency part of the infrared spectrum. These are weak bands (except when Fermi resonance occurs). Their appearance and position in a spectrum can be gainfully used for identification of some structural features. Such combination bands in aromatic and heteroaromatic systems show themselves in the 2000-1650 cm^{-1}

region (Fig. 3.10). The C—H out of plane bending bands of alkenes of vinylidene type give typical overtones which are useful for their identification (Fig. 3.35).

8. The C—H bending vibrations of the CH_3 group give a band around 1370 cm^{-1} (Fig. 3.54). This band is split into a doublet when more than one methyl group is present on the same carbon (Fig. 3.11). A comparison of the intensity of the bands in this region can often detect the presence of CH_3—C=O moiety in an organic compound (Spectra 5 and 13, problem 1 Chapter 3).

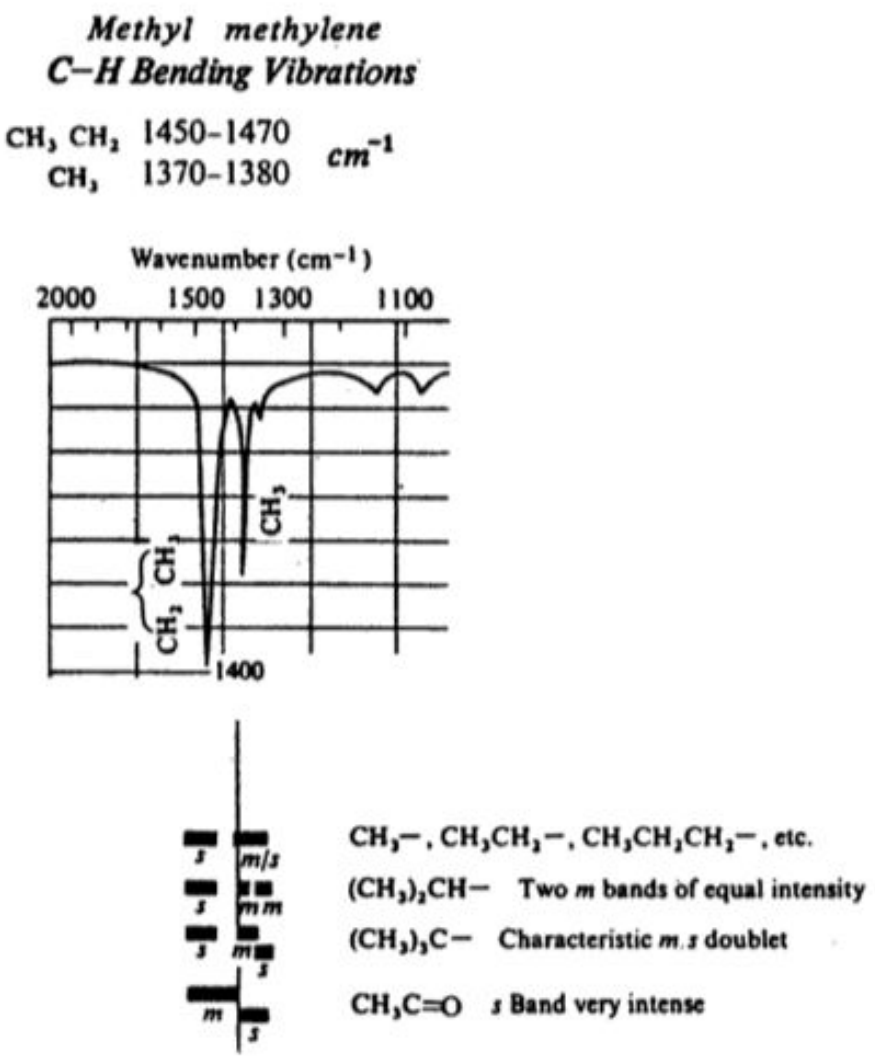


Fig. 3.54

9. The presence of a carbonyl group can be confirmed by a strong C=O stretch around 1700 cm^{-1} (Fig. 3.55) The C=O stretching gets lowered on conjugation or if the carbonyl group is involved in hydrogen bond formation. Ring strain influences the C=O stretch in a systematic way and increases the C=O stretching frequency from, *e.g.*, 1715 cm^{-1} of cyclohexanone to each next lower number by about 30 cm^{-1}.
10. The C=O stretch of an amide is termed amide-I band which is closely followed by amide-II band which represents mostly N—H bending vibrations (Fig. 3.24).
11. Primary amines show their N—H bending vibrations around 1650-1590 cm^{-1} and this band is almost undetectable in the case of secondary amines. The secondary aromatic amines, however, show this band around the same region.

C=O Stretching Vibrations (1650–1800 cm⁻¹)	cm^{-1}	*Remarks*
1. Aldehydes		
RCHO	1725	
C=CCHO	1685	
ArCHO	1700	
2. Ketones		
$R_2C=O$	1715	
C=C—C=O	1675	
Ar—C=O	1690	
four-membered cyclic	1780	
five-membered cyclic	1745	
six-membered cyclic	1715	
3. Carboxylic acids		
RCOOH	1760 (monomer)	
	1710 (dimer)	
C=C—COOH	1720 (monomer)	
	1690 (dimer)	
RCO_2^-	1550–1610, 1400 (two)	
4. Esters		
RCOOR	1735	
C=C—COOR	1720	
ArCOOR	1720	
γ-Lactone	1770	
δ-Lactone	1735	
5. Amides		
$RCONH_2$ (C=O stretching, Amide I)	1690 (free)	Amide II; mostly N—H bending
	1650 (associated)	Primary —$CONH_2$
RCONHR′	1680 (free)	In solution ~1600 cm^{-1}
	1655 (associated)	Solid state ~1640
$RCONR'_2$	1650	Secondary —CONH—
β-lactam	1745	In solution 1550–1510 cm^{-1}
γ-lactam	1700	Solid state 1570–1515
δ-lactam	1640	Amines N—H Bending vibrations
6. Acid anhydrides	1820, 1760 (two)	Primary 1650–1590
7. Acyl halides	1800	Aromatic ~1500 cm^{-1}

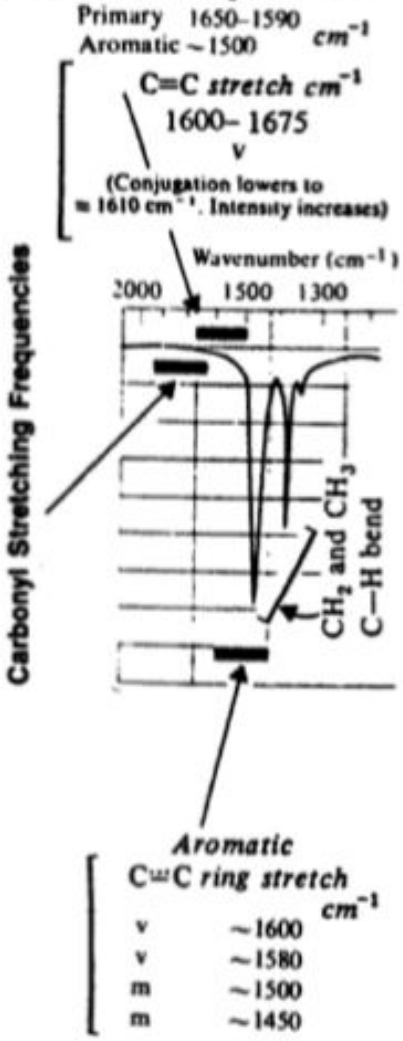
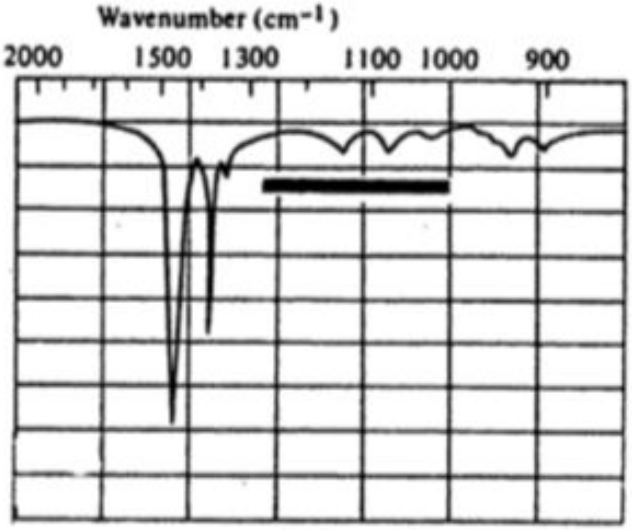


Fig. 3.55

12. The acid anhydrides and carboxylate anions show two bands as their C=O stretch due to coupled vibrations (Fig. 3.55) and are therefore, easily recognised and

C–O Stretching Vibrations
a strong band
1020–1275 cm^{-1}

ETHERS ALCOHOLS PHENOLS ESTERS AND LACTONES
CARBOXYLIC ACIDS CARBOXYLIC ACID ANHYDRIDES



Remarks

AMINES C—N
Stretching vibrations

Aliphatic 1250 – 1020 (cm^{-1})
m

Aromatic 1350–1280
s

Remarks

Classification of an alcohol as primary, secondary or tertiary can frequently be successful using the bands

1° ROH about 1050 cm^{-1} 3° ROH about 1150 cm^{-1}
2° ROH about 1100 cm^{-1} ArOH about 1230 cm^{-1}

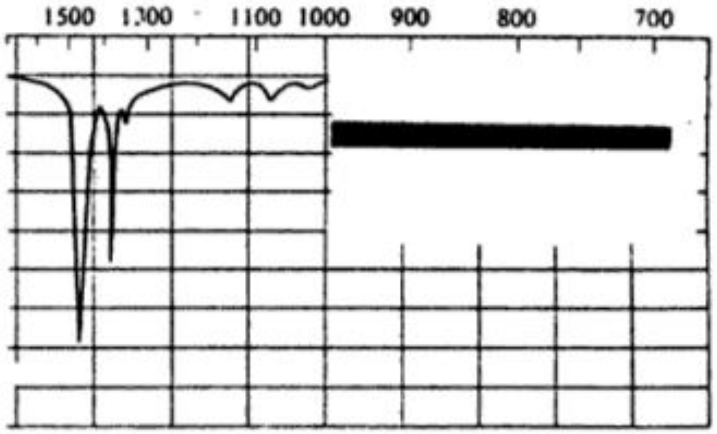
Alkyl ethers 1060–1150 cm^{-1}

Aryl and vinyl ethers 1200–1275 cm^{-1} (and, weaker, at 1020–1075 cm^{-1})

Fig. 3.56

assigned to particular groups from their position. Nitro and sulphone groups are also recognised from their coupled N=O and S=O stretchings (Table 3.1).

C–H Bending Vibrations
olefinic and Aromatic



C—H out-of-plane bend

Alkene Class	Frequency, cm^{-1}	Intensity
$RCH{=}CH_2$ VINYL	**990** **910**	s s
$R_2C{=}CH_2$ VINYLIDENE	**890**	s
cis-RCH=CHR DISUBSTITUTED	675–725	m
trans-RCH=CHR DISUBSTITUTED	**970**	s
$R_2C{=}CHR$ TRISUBSTITUTED	790–840	s
$R_2C{=}CR_2$ TETRASUBSTITUTED	—	

Aromatic, substitution type:

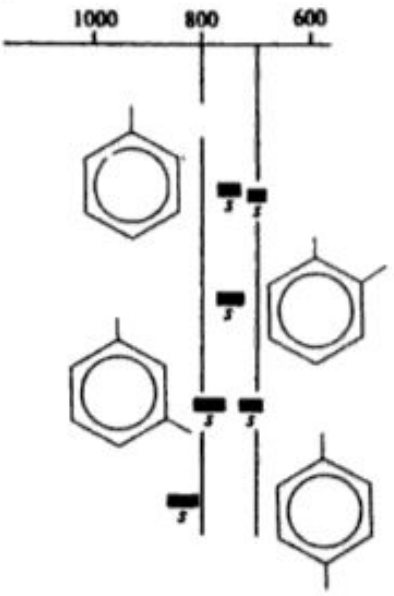


Fig. 3.57

13. As indicated (Fig. 3.55) the C=C stretching region is 1600-1670 cm^{-1}. The C=C stretch is a well formed band of medium intensity in the case of vinyl and vinylidene double bonds (Fig. 3.35) and is weak for trisubstituted and disubstituted double bonds. The presence of olefinic C—H stretch around 3080 cm^{-1} (Fig. 3.53) along with C=C stretch is a positive indication of the presence of a double bond, its substitution pattern can be known from C—H out of the plane bending vibrations (Scheme 3.7, Fig. 3.57). The intensity of the otherwise weak C=C stretch, *e.g.*, of a

trisubstituted double bond gets increased and its position lowered on conjugation (Scheme 3.8, Fig. 3.38).

14. A reference to Fig. 3.39 further shows that aromatic C = C ring stretchings occur between 1450-1600 cm^{-1}, extending to the left of C—H bending band of methyl and methylene group at 1450 cm^{-1}.
15. A variety of compounds show C—O stretching vibrations in the region 1020-1275 cm^{-1} (Fig. 3.56).
    The assignment of a carbonyl C=O stretching band to an ester group is confirmed by locating the strong band in the C—O stretching region.
16. Olefinic and aromatic C—H out-of-plane bending vibrations (Fig. 3.57) not only confirm the presence of such structural units but also throw light on their substitution pattern.

FURTHER READINGS

1. N.P.G. Roeges, *A Guide to the Complete Interpretation of Infrared Spectra of Organic Structures*, John Wiley and Sons Ltd., Chichester, UK 1994.
2. L.J. Bellamy, *The Infrared Spectra of Complex Molecules*, Vols. 1 and 2, Chapman and Hall Ltd., London, 1975/80.