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Review Article

Forensic Applications of IR/FTIR

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Abstract

Infra-Red spectroscopy plays important role for analysis of several compounds, metals etc. Its use is readily understood from breadth of its applications. The range of material that can be analyzed by IR/FTIR is essentially unlimited. Applications are found in diverse fields such as forensic science, pharmaceuticals, food and agriculture, biological and clinical chemistry, environmental chemistry and many others.

Keywords: IR; FTIR; Dipole; Instrument etc.

Introduction

- Absorption of IR radiation by a molecule is the basis of this kind of spectroscopy
- It is also called absorption spectroscopy
- The extent of this absorption depends on the wavelength/frequency of the IR radiation passing through molecule and structure of the molecule.
- Absorption of radiation leads to a gain in the energy of the molecule.
- This gain in energy leads to a variety of vibrations (bond stretching, bending etc).
- In order to absorb IR radiation a molecule must go a net change in dipole moment because of its vibrational or rotational motion [1].
- No net change in dipole moment occurs during the vibration of homonuclear species such as O_2, N_2, H_2, and Cl_2 and hence these compounds do not absorb in the IR region.
- In recent years it has been proved that even the species such as O_2, N_2, H_2, and Cl_2 show slight IR absorption at high pressure, as a result of distortion during the collisions.
- IR spectroscopy has also been employed for quantitative analysis. However quantitative applications are of less significance than the qualitative applications.

Regions of the IR Spectrum

Different regions of the electromagnetic radiations are given in Table 1.

Table 1: Different regions of the electromagnetic radiations

Types of radiations	Limits (Wave length)	Wave number	Effect on the molecule}
1. Cosmic ray	0.0001 – 0.001 A^o	10^{12} cm^{-1}	Mossbauer (Change in nuclear transitions)
2. γ - rays	0.001 – 1 A^o	10^{10} cm^{-1}	
3. X-rays	1 – 10^2 A^0		Change in core orbitals
4. UV i) for UV	100 – 200nm		
ii) Near UV	200 – 400nm		Change in electronic energy levels
iii) Visible	400 – 800nm	25000 – 12500 cm^{-1}	
5. IR i) Near IR	0.80μm - 2.5μm	12500 - 4000 cm^{-1}	Change in vibrational and rotational movement
ii) Mid IR	2.5μm - 15μm	4000 - 667 cm^{-1}	
iii) Far IR	15μm - 200μm	667 - 50 cm^{-1}	
6. Microwave	0.02 – 100cm		Change in rotational movement
7. Radio waves	1m – 100 m		Change in nuclear spin

1μm =1μ = 10^3 nm = 10^{-4}cm
1 micrometer = 1 micron

IR Spectrum (Absorption Curve)

If a graph is plotted showing the variation of absorption of radiation (or % Transmission) by compound with wavelength or frequency or wave number, we get the absorption curve better known as IR Spectrum of the compound.

Principle

Since absorption of IR radiation by a molecule is the basis of this kind of spectroscopy. It is also called absorption spectroscopy. The extent of this absorption depends on the wavelength/frequency of IR radiation passing through the molecule and the structure of molecule. Absorption of radiation leads to a gain in the energy of the molecule. The gain in energy leads to a variety of vibrations (bond stretching etc) in the molecule.

Theory (Molecular Vibrations)

Absorption in the Infra-red region is due to the changes in the Vibrational and Rotational levels. When radiations with frequency range less than 100 cm^{-1} are absorbed, molecular rotation takes place in the substance. As this absorption is quantised, descrete lines are formed in the spectrum due to molecular rotation. Molecular radiations are set in, when more energetic radiation in the region 10^4 to 10^2 cm^{-1} are passed through the sample of the substance. The absorption causing molecular vibration is also quantised. Clearly, a single vibrational energy change is accompanied by a large number of rotational energy changes. Thus, the vibrational spectra appears as vibrational – rotational bands [2-6].

The vibrational – rotational bands, particularly those occurring between 4000 cm^{-1} and 666 cm^{-1} (2.5 – 15 μ) is of great importance in analytical chemistry. The frequency of wavelength of absorption depends upon:

a. The relative masses of the atoms
b. The force constants or bond strength and
c. The geometry of the molecule

Fundamental Vibrations: There are two fundamental vibrations

i) Stretching vibration
ii) Bending vibration

Stretching Vibration: In this type of vibrations, the distance between two atoms increases or decreases, but the atom remains in the same bond axis. There are two types of stretching vibrations.

a. Symmetric Stretching: in this type of stretching, the movement of atoms with respect to a particular atom in a molecule is in same direction (Figure 1).

Fig. 1: Symmetric stretching

b. Asymmetric Stretching: In these vibrations one atom approaches the central atom while the other departs from it (Figure 2).

Fig. 2: Asymmetric Stretching

Bending Vibration: In this type of vibrations, the position of atom changes with respect to the original bond axis. Bending vibrations are of four types (Figure 4)-

(i) Scissoring: In this type, two atoms approach each other.

(ii) Rocking: In this type, the movement of the atoms takes place in the same directions.

(iii) Wagging: Two atoms move up and below the plane with respect to the central atom.

(iv) Twisting: In this type, one of the atoms moves up the plane while the other moves down the plane with respect to the central atom.

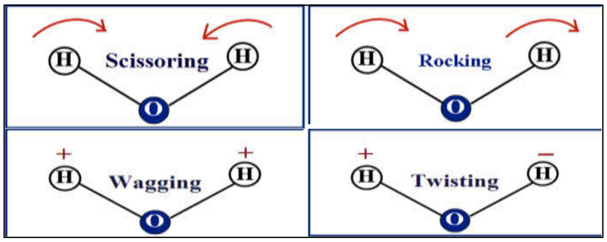


Fig. 3: Scissoring, Rocking, Wagging and Twisting

Number of Fundamental Vibrations: Poly-atomic molecules may exhibit more than one fundamental vibrational absorption bands. The number of these fundamental bands is related to the degree of freedom in a molecule. The number of degree of freedom is equal to the sum of the co-ordinates necessary to locate all the atoms of a molecule in space. Each atom has three degree of freedom corresponding to the three cartesian co-ordiantes (x, y, z) necessary to describe its position relative to other atoms in a molecules.

An isolated atom which is considered as a point mass has only translational degree of freedom. It can not have vibrational and rotational degree of freedoms.

When atoms combine to form molecule, no degree of freedom are lost. Hence total number of degree of freedom = 3n, where n= number of atoms in a molecule. A molecule which is of finite dimensions will thus be made up of rotational, vibrational and translational degree of freedom. So, 3n degree of freedom = Translational + Rotational + Vibrational

Rotational degree of freedom result from the rotation of a molecule about an axis through the centre of gravity. Since we are concerned only with the number of fundamental vibrational modes of a molecule, so we calculate only the number of vibrational degree of freedom of a molecule. Since only three co-ordinates are necessary to locate a molecule in space, we say that a molecule has always three translational degree of freedom (Table 2).

Table 2: Vibrations of Linear Molecule

For A Linear Molecule of N Atoms:	
Total degree of freedom	3n
Translational degree of freedom	3
Rotational degree of freedom	2
Vibrational degree of freedom	(3n – 3 – 2)= (3n–5)

Hence theoretically there will be (3n–5) possible fundamental bands for the linear molecules.

For Example CO_2 (Linear Shaped Molecule)

Number of atoms (n) = 3

Total degree of freedom = 3n = 3×3 = 9

Translational degree of freedom = 3

Rotational degree of freedom = 2

Vibrational degrees of freedom = 9 – 3 – 2 = 4

Hence, for carbon dioxide molecule, the theoretical number of fundamental bands should be equal to four.

For Non-Linear Molecule of N Atoms:

Total degree of freedom = 3n

Translational degree of freedom = 3

Rotational degree of freedom = 3

Vibrational degree of freedom = (3n–3–3)=(3n–6)

For example benzene, C_6H_6

Number of atoms (n) = 12

Total degree of freedom = 3n = 3×12 = 36

Translational degree of freedom = 3

Rotational degree of freedom = 3

Vibrational degrees of freedom = (36 – 3 – 3) = 30

So theoretically there should be 30 fundamental bands in the infra-red spectrum of benzene. It has been observed that the theoretical numbers of fundamental vibrations are seldom obtained. It is because of following reasons:

i. Fundamental vibrations that fall outside the region under investigation, i.e. 2.5 to 15 μ.

ii. Fundamental vibrations are too weak to be observed as bands.

iii. Fundamental vibrations are so close that they overlap i.e. exists as degenerate vibrations.

iv. Certain vibrational bands do not appear for the required change in the dipole-moment in a molecule.

Various Types of Spectra Given by Molecular Species

1. *Nuclear magnetic resonance (NMR) spectra*, which arise from transitions between the nuclear spin energy levels of a molecule in the applied magnetic field.
2. *Nuclear quadrupole resonance (NQR) spectra*, which result from the transitions between the nuclear spin energy level of a molecule arising from the interaction of the unsymmetrical charge distribution in nuclei with the magnetic field.
3. *Electron spin resonance (ESR) spectra*, which arise from transition induced between the electron spin energy levels of a molecule in an applied magnetic field. It is also called electron paramagnetic resonance spectra (EPR).
4. *Rotational or microwave spectra*, which result from transitions between the rotational energy levels of a gaseous molecule on the absorption of radiation falling in the microwave region. The microwave spectra occur in the range 1-100cm^{-1}:
5. *Vibrational and vibrational rotational spectra* originate from transitions induced between the vibrational energy levels of a molecule on the absorption of radiation belonging to infra-red region and generally occur in the range 200-4000 cm^{-1}
6. *Raman spectra* are also related to vibrational and /or rotational transitions in a molecule but in a different manner. In this case, scattering and not the absorption of radiation is measured.
7. *Electronic spectra* arise from electronic transition in a molecule by the absorption of radiation in the visible and ultra violet regions.
8. *Mossbaur spectra* result from absorption of very high energy γ- photons of frequency about 10^{13}MHZ by the nuclei. These spectra are therefore also known as γ- ray spectra.
9. *Photo electron spectra (PES)* arise when a beam of photons of known energy is allowed to fall on the sample and the K.E. of the ejected electron is measured.

Force Constant: In a harmonic oscillator, the resonating force per unit displacement is called force constant F and is given by the equation:

$$F = 4\Pi^2 \nu^2 c^2 \left(\frac{m_1 m_2}{m_1 + m_2} \right)$$

where ν is vibrational frequency, m_1 and m_2 are masses of oscillating atoms, and c is velocity of light.

The force constant for diatomic molecule can be obtained by using above equation provided the value of w is known.

Force constants of some bonds in dynes cm^{-1} are as follows:

Table 3: Vibrational frequencies of different functional groups.

Bonds	C-O	C=O	C-N	C=N	C≡N	C-C	C=C	C≡C
Force Constant $\times 10^5$	4.9	12.3	4.8	12.1	17.5	4.6	9.5	15.8

Calculation of Vibrational Frequencies

One may calculate the region of vibration for a diatomic molecule by applying Hookes' law; the frequency of vibration is directly proportional to the square root of theforce constant of the bond (Table 3). This implies that stronger is bond greater will be frequency of absorption. Further wave number (λ^{-1}), frequency (ν) and energy (E) are directly proportional to each other however; wave length (λ) is inversely proportional to energy. Mathematically Hookes' law is expressed as:

$$\bar{\nu} = \frac{1}{2\Pi C}\sqrt{\frac{F\,(m_1 + m_2)}{m_1 m_2}}$$

where $\bar{\nu}$ is wave number (cm^{-1}), c = velocity of light ($cm\ sec^{-1}$), F = Force constant ($dyne\ cm^{-1}$ or $g\ sec^{-2}$), m_1, m_2 are masses of atoms.

For example, the region of ^{12}C—^{1}H stretching frequency may be calculated as:

$$\bar{\nu} = \frac{1}{2 \times 3.142 \times 2.998 \times 10^{10}} \left[5 \times 10^{5} \times \frac{\dfrac{12}{6.023 \times 10^{23}} + \dfrac{1}{6.023 \times 10^{23}}}{\dfrac{12}{6.023 \times 10^{23}} \times \dfrac{1}{6.023 \times 10^{23}}} \right]^{1/2}$$

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

actual range for C-H stretching is 2850-3000 cm^{-1}

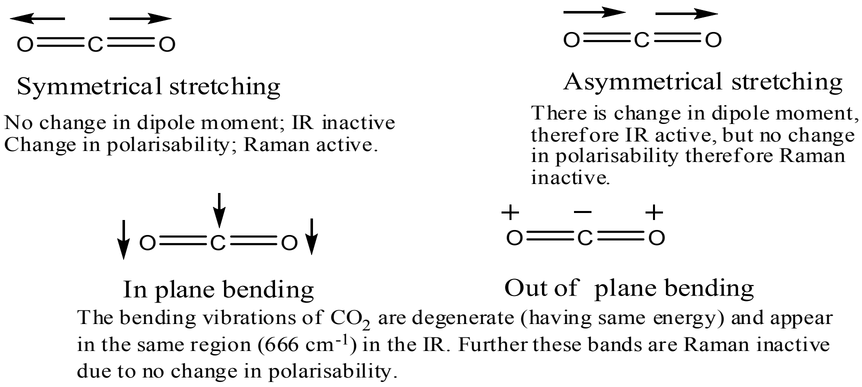
Differences between IR and Raman Spectroscopies

There are several Differences between IR and Raman IR and Raman. Major are enclosed in Table 4.

Table 4: Differences between IR and Raman

Raman	IR
It is due to scattering of light by the vibrating molecule.	It is due to absorption of light by the vibrating molecule.
It is not necessary for a molecule to possess a permanent dipole moment.	In this case molecule must possess a permanent dipole moment.
In this case water can be used as solvent. intense absorption peak in IR.	Water can't be used as solvent due to its
The vibration in Raman is active if it causes change in polarisability.	Vibration in IR is active, which causes change in dipole moment.
Sample can be in any physical state.	Gaseous samples can rarely be used.
It gives an indication of covalent character in molecules.	It gives an indication of ionic character in molecules.
The cost of instrumentation is high.	The cost of instrumentation is comparative ely low

Mutual Exclusion Principle: It states that in a molecule with centre of symmetry, vibrations that are Raman active are IR inactive and vice-versa. In molecules with different elements of symmetry, certain bands may be active in IR, Raman, both or neither. For a complex molecule with no symmetry, all of the normal modes are active in both IR and Raman, but their observance may or may not exist [7-8]. A simple molecule which obeys this principle is $CO_{2.}$ Carbondioxide has an inversion centre or centre of symmetry. Its different active modes in IR and Raman spectroscopy are indicated below in scheme 1.



Symmetrical stretching

No change in dipole moment; IR inactive
Change in polarisability; Raman active.

Asymmetrical stretching

There is change in dipole moment, therefore IR active, but no change in polarisability therefore Raman inactive.

In plane bending

Out of plane bending

The bending vibrations of CO_2 are degenerate (having same energy) and appear in the same region (666 cm^{-1}) in the IR. Further these bands are Raman inactive due to no change in polarisability.

Scheme 1: Different vibrational modes in symmetrical CO_2 molecule

Instrumentation

The FTIR consists of following major parts:

1. Source of IR Radiation
2. Cell compartment
3. Grating
4. Detector

Systematic representation of parts of FTIR are given in Figure 4.

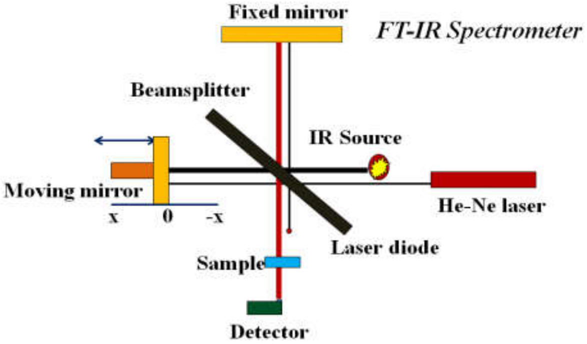


Fig. 4: Systematic representation of parts of FTIR instrument

Source of IR Radiation

Common source in the IR is the Nernst Glower consisting of a mixture of zirconium oxide, ytterbium oxide and erbium oxide heated electrically to about 1500 °C. More intense source consisting of a silicon carbide source (Globar) has also been introduced in modern IR Spectrometers.

Cell Compartment

It houses cells in which the sample under examination is placed. These cells are usually made of rock salt (NaCl), but materials like KBr, CaF_2, CsBr, AgBr etc are also used occasionally. The glass cells being opaque to IR radiation cannot be used [9]. These cells are normally stored in a desicator when they are not in use. Cells are usually cleaned in carbon tetrachloride. Water must be avoided since it can dissolve out the cell windows made of rock salt.

Grating

While NaCl prisms served as monochromators (which convert a broad spectrum of light into monochromatic components) in older spectrometers, diffraction grating is used in modern spectrometers to serve the same function. Lights of different wavelengths can be obtained by rotating the grating relative to the light source.

Detector

A variety of detectors are in use. They may simply be thermocouples whose e.m.f. changes with the radiation falling on them. A Golay detector consists of a sealed cell of xenon gas, a blackened metal plate for the radiation to fall on and a silvered diaphragm. The detector responds to the difference in intensity between the light beams coming from reference and the sample cells.

Some Important Points for Proper Maintenance of IR Spectrophotometer

1. IR cells are normally stored in desiccators when they are not in use.
2. Cells are usually cleaned by carbon tetrachloride, water must be avoided since it can dissolve out the cell windows of rock salt.
3. Hydroxylic solvents like water and alcohol should be avoided as they would not only dissolve out the cell made of rock salt but would also give overlapping bands in certain cases.

Sampling

Gaseous Substance: Gaseous substances are examined as such in specially designed gas cells.

Liquid Substances: Liquid substances are examined in the form of a thin film placed between the rock salt plates of a liquid cell. A drop of the liquid substance is placed on a rock salt plate of the liquid cell and then the other plate of the cell is placed on it so that liquid forms a thin film between two plates

Solid Substances: Solid substances are examined in the form of a pellet or a mull or a solution in a suitable solvent (Figure 5).

Fig. 5: Preparation of sample

a. As pellets: The solid substance (few mg) is mixed thoroughly with carefully dried spectroscopic grade KBr (~ 0.5g) in a gate pestle mortar. The mixed powder or a minipress to get a pallet that is sufficiently transparent. The pellet is then placed in IR sample holder for examination (Figure 6).

Fig. 6: Part of FTIR for preparation of sample

b. As Mulls: The mulling liquid commonly employed is nujol (a highly purified mineral oil). Nujol can sometimes be replaced by liquids such as fluorolube (a chlorofluoro hydrocarbon), hexachlorobutadiene etc. The substance, mixed with nujol, is thoroughly mulled in an agate pestle mortar. A drop or two of the resulting mull is then examined as described earlier under liquid substances. It may be noted that nujol itself has IR bands around 2900 and 1400 cm^{-1} (Figure 7).

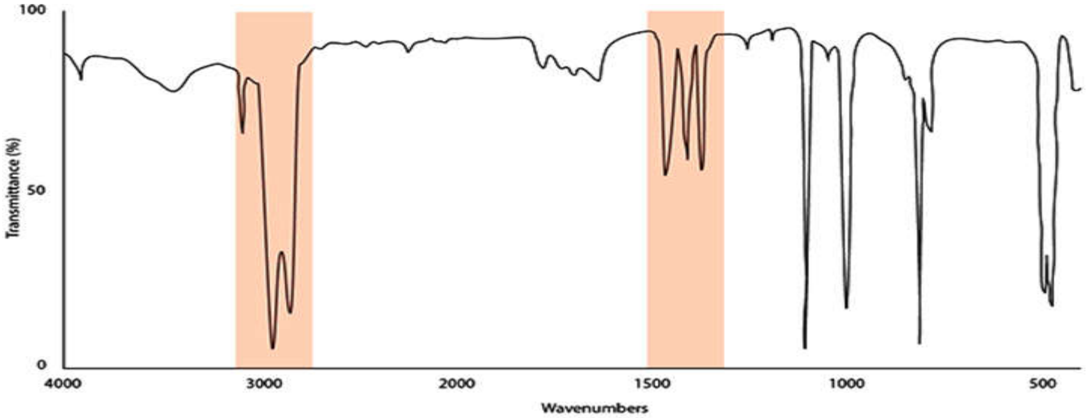
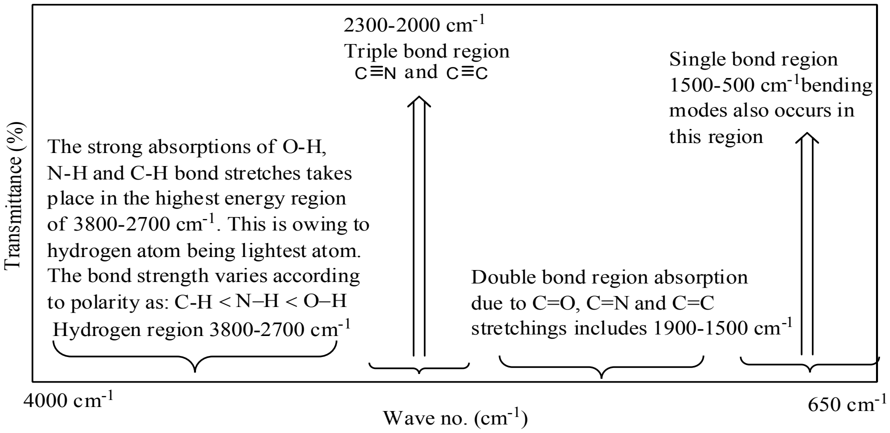


Fig. 7: The IR bands of nujol

c) As solutions: IR spectra of solid can be obtained by dissolving solid into suitable liquid. The solvent to be used must be of spectroscopy grade, must dissolve the solid and must be transparent in most of the mid-IR region. No one solvent is transparent in the entire region and the solvent has to be selected with regard to the region where the compound under study is expected to have IR bands. The most popular solvent for IR spectroscopy are CCl_4, CS_2 and $CHCl_3$. CCl_4 has band only at 700-850 cm^{-1}, CS_2 has bands at 1400-1600 cm^{-1} and 2100-2200 cm^{-1} only and $CHCl_3$ has bands at 600-806 cm^{-1} and 1175-1200 cm^{-1}. Hydroxylic solvents like water and alcohol should be avoided as they could not only dissolve out the cell made of rock salt but would also give overlapping bands in certain cases.

Important Regions of IR Spectrum

There are three important region of I. R. spectrum. 1. Functional group region (4000-1300 cm^{-1}) 2. Fingerprint region (1300-900 cm^{-1}) and 3. Aromatic region (900-650 cm^{-1}), Scheme 2.



The strong absorptions of O-H, N-H and C-H bond stretches takes place in the highest energy region of 3800-2700 cm^{-1}. This is owing to hydrogen atom being lightest atom. The bond strength varies according to polarity as: C-H < N–H < O–H

Hydrogen region 3800-2700 cm^{-1}

2300-2000 cm^{-1}
Triple bond region
C≡N and C≡C

Double bond region absorption due to C=O, C=N and C=C stretchings includes 1900-1500 cm^{-1}

Single bond region 1500-500 cm^{-1}bending modes also occurs in this region

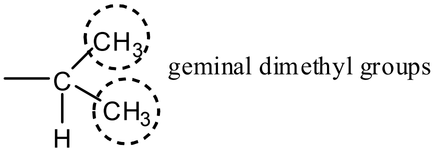
Scheme 2: Representation of different regions of IR spectra.

Functional Group Region

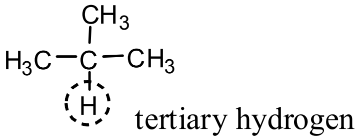
The region of 4000-1300 cm^{-1} is called functional group region. It consists of several functional groups like unsaturation, alcohols, aldehydes, ketones, esters, acids, amides, amines etc. which are discussed as follows.

Alkanes

1. C–H stretching bands = 2900 cm^{-1} (Figure 8).
2. C–C stretching bands = 1400 cm^{-1}
3. A doublet (two bands of approximately equal intensity) between 1370-1380 cm^{-1} for gem-dimethyl group.



4. Tertiary hydrogens in alkanes show a number of bands in fingerprint region (1300-900 cm^{-1})



5. Functional groups with chain shorter than four carbons show bands which may be diagnostic. For example:

Propyl chain CH$_3$-CH$_2$-CH$_2$- (745–735 cm^{-1})

Ethyl chain CH$_3$–CH$_2$- (790–770 cm^{-1})

6. The strong band at 725 cm^{-1} indicates the rocking Vibrational mode of a chain of methylenes longer than four carbon atoms.

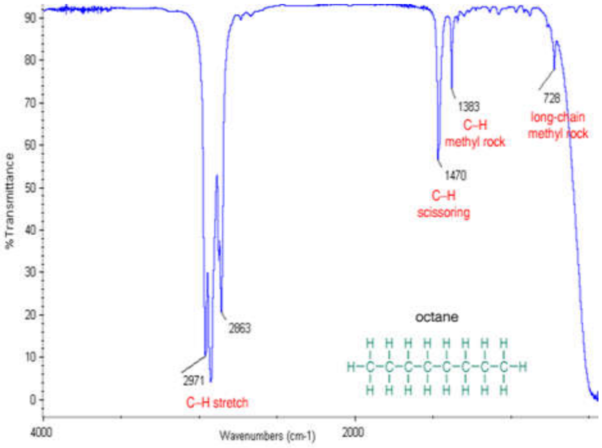


Fig. 8: IR spectra of normal octane.

Alkenes

1. The C-H stretching bands in alkenes appear at a slightly higher frequency (around 3000 cm^{-1}) than alkanes.
2. C-H stretching band at 3000 cm^{-1} or slightly above this frequency is characteristic of unsaturation.
3. C=C stretching band in alkenes is also at a higher frequency (1600-1700 cm^{-1}) than in alkanes and this band is weak to medium (Figure 9, 10).

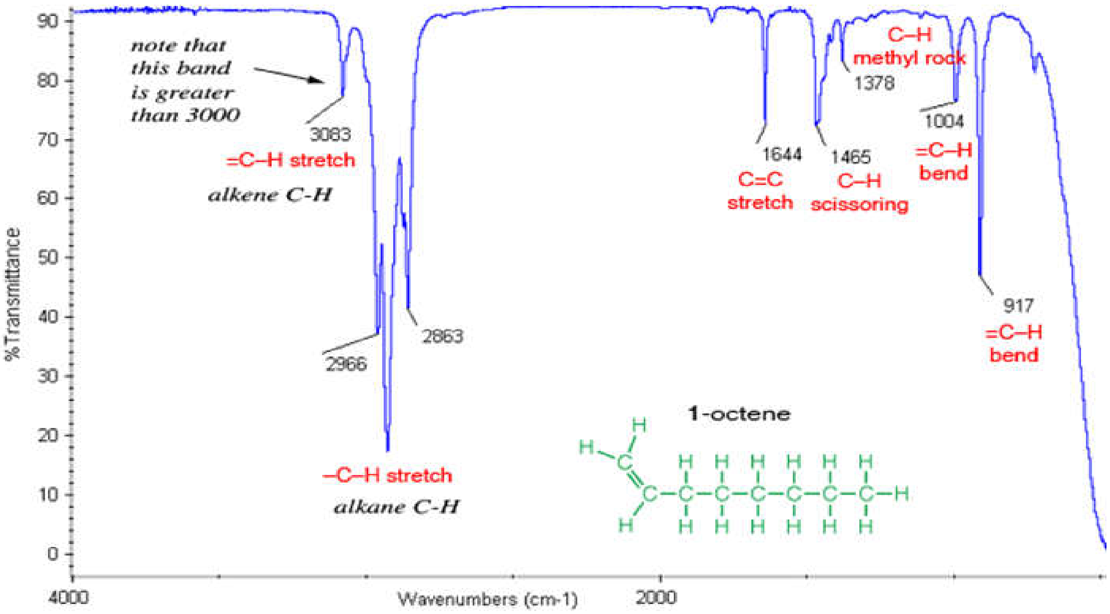


Fig. 9: IR spectra of 1-octene.

4. Extent of substitution of the double bonds are:

RCH=CH_2	1645 cm^{-1}
$R_2C=CH_2$	1655 cm^{-1}
RCH=CH R (cis)	1660 cm^{-1}
R CH=CH R (trans)	1675 cm^{-1}
Tri & Tetra substituted	1670 cm^{-1}

The intensity of this band decreases gradually from medium to weak with increasing substitution of the double bond.

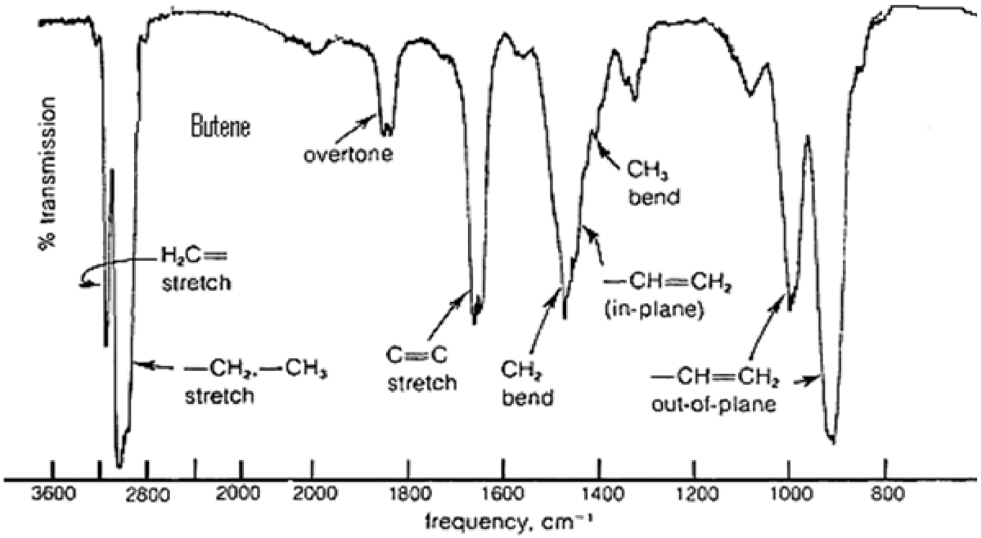


Fig. 10: IR spectra of Butene

Alkynes

1. C–H stretching band in alkynes is at still higher frequency (3310-3270 cm^{-1}) than in alkens and alkanes
2. The Ca"C stretching band in alkynes is fairly weak and appears at 2300-2100 cm^{-1} depending on the location of triple bond (Figure 11). For example

External C≡C	2150-2100 cm^{-1}
Internal C≡C	2250-2200 cm^{-1}

3. It may be noted that symmetrically substituted alkynes say CH_3–C≡C–CH_3 shows no stretching band at all.

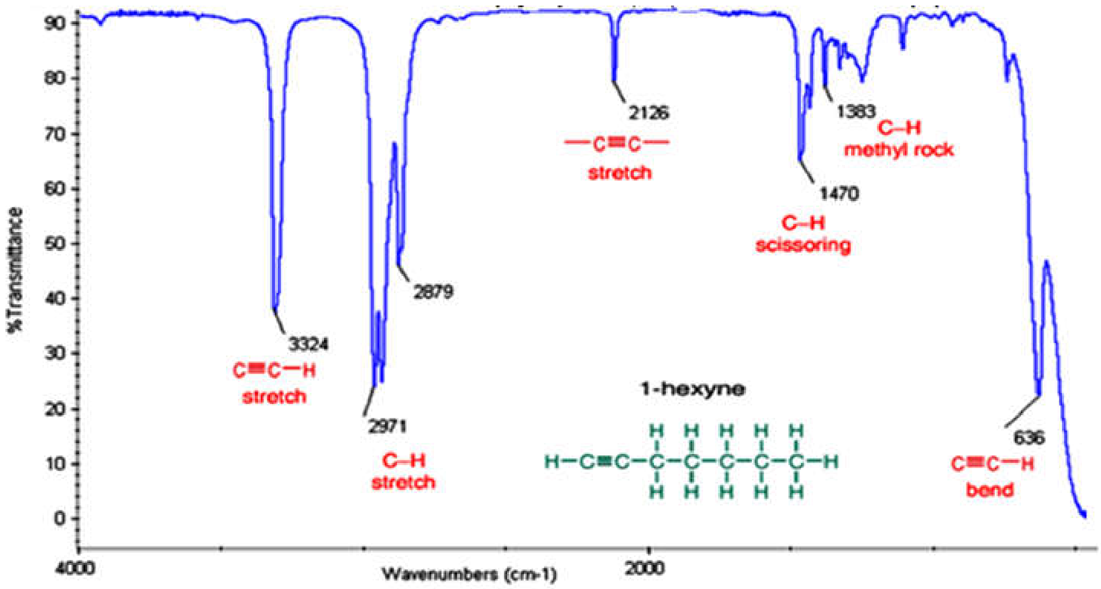


Fig. 11: IR spectra of 1-hexyne

Alicyclic Hydrocarbons

1. Cycloalkanes and cycloalkenes do not show any unique band compared to alkanes/alkenes. Cyclopentane and cyclohexane for example show C–H stretching bands around 2900 cm^{-1}
2. The cyclopropane ring, however, is so strained that it shows a C–H stretching band charactaristic of unsaturated bands around 3100-3000 cm^{-1}

Alcohols

1. Alcohols show a broad intense band at 3650-3500 cm^{-1}. The narrow range in which this band appears gives idea about the class to which an alcohol belongs.

   3640-3630 cm^{-1} Primary alcohol (Figure 12), 3625-3620 cm^{-1} Secondary alcohol (Figure 13) and 3620-3610 cm^{-1} Tertiary alcohol (Figure 14).
2. When IR spectra of alcohols are taken in gaseous form or in very dilute solutions (alcohols mostly exist in the free form) the above bands are observed.
3. When IR spectra of alcohols are taken in liquid films or pallets or concentrated solutions, the precise position depending on relative proportion of the hydrogen bonded form sometimes both peaks at about 3650 cm^{-1} and 3350 cm^{-1} corresponding to 'free' and hydrogen bonded forms respectively appear. That is due to hydrogen bonding the IR band broadens and reduces to its lower value.
4. Alcohols also show strong C–O stretching bands at 1000-1150 cm^{-1}. The precise position of this band varies with the class of the alcohol.

   1150-1100 cm^{-1}, Secondary (2^{o}) & Tertiary (3^{o}) alcohols, 1060-1020 cm^{-1}, Primary (1^{o}) alcohols 1066-1010 cm^{-1} cyclic alcohols.
5. *Distinction between intermolecular and intramolecular hydrogen bondings:* The dilution effect may distinguish the intermolecular and intra molecular hydrogen bondings; while testing solution is successively diluted the intramolecular hydrogen bonding remains unaffected however intermolecular hydrogen bonding weakens. Thus concentrated solution of alcohol or phenol causes the sharp band around 3600 cm^{-1} to be replaced by a broad and less intense frequency band due to intermolecular hydrogen bonding. Thus in a nut shell non hydrogen bonded (free) hydroxyl group yields a sharp band at higher frequency and hydrogen bonded hydroxyl group results abroad band at lower frequency (3360 cm^{-1}) region.

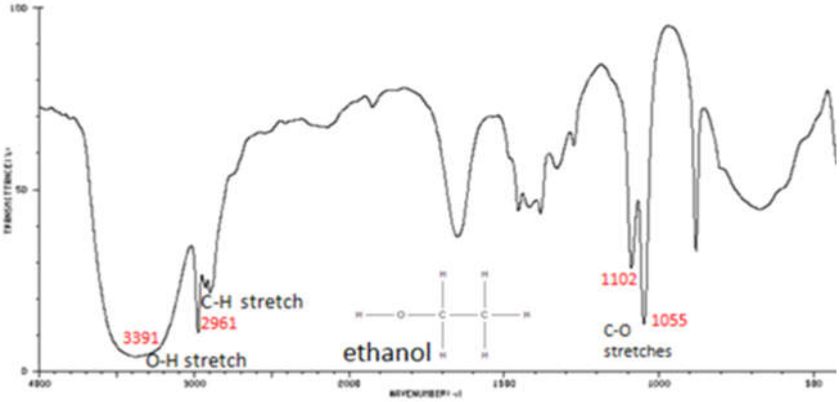


Fig. 12: IR spectra of ethanol

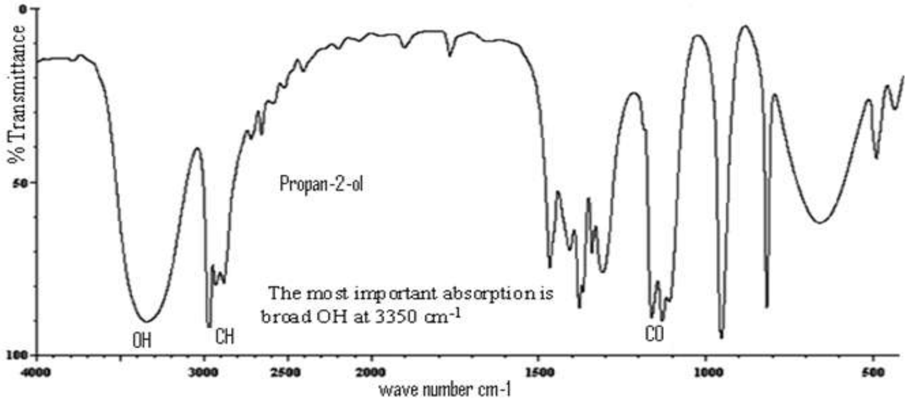


Fig. 13: IR spectra of Propan-2-ol

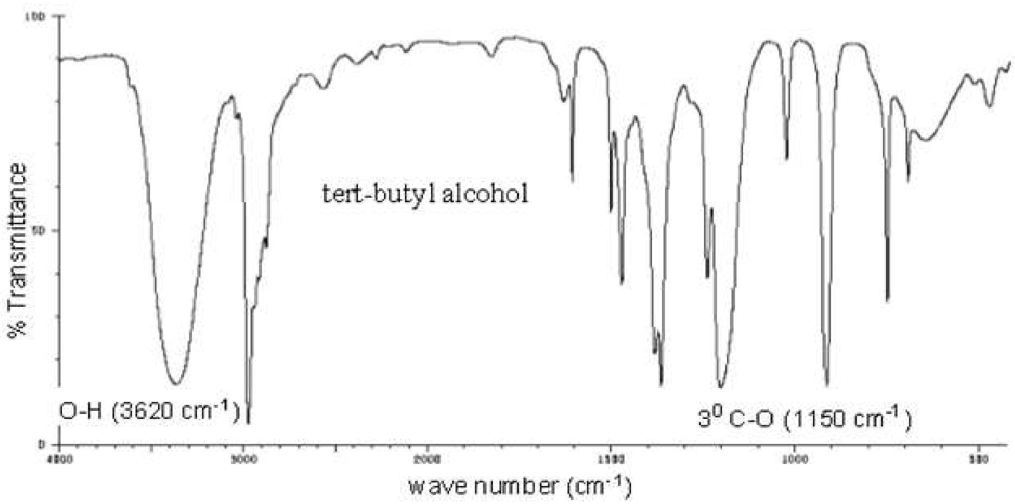


Fig. 14: IR spectra of 2-methylpropan-2-ol.

Ethers

1. They show characteristic C-O stretching bands for various alkoxy groups (Figures 15, 16). For example

-OCH_3 (1190 cm^{-1}), -OCH_2CH_3 (1150, 1100 cm^{-1}), -O- iPr (1175, 1135, 1110 cm^{-1}), -O-n-Bu (1150, 1125, 1075 cm^{-1}), -O-t-Bu (1200, 1150, 1050–1000, 920–820, 770–720 cm^{-1}).

2. In addition, methyl ethers show a strong characteristic methyl stretching band at 2830–2810 cm^{-1}

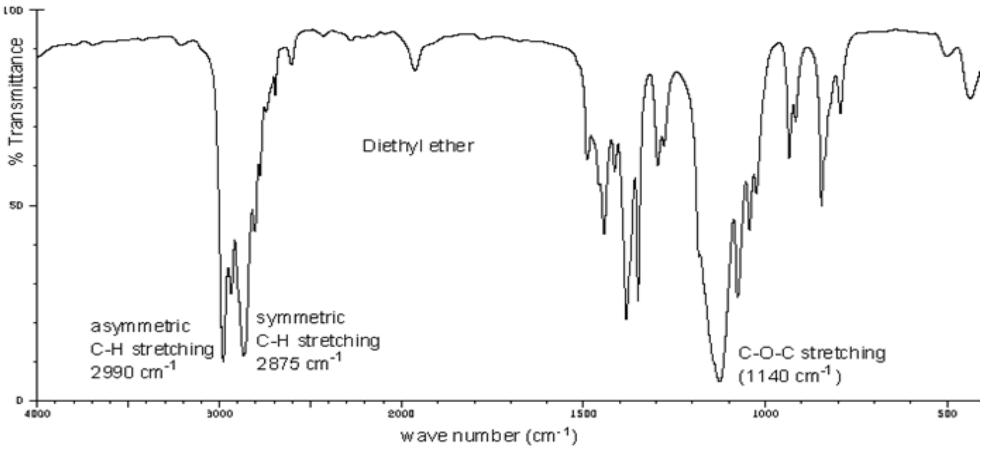


Fig. 15: IR spectra of diethyl ether

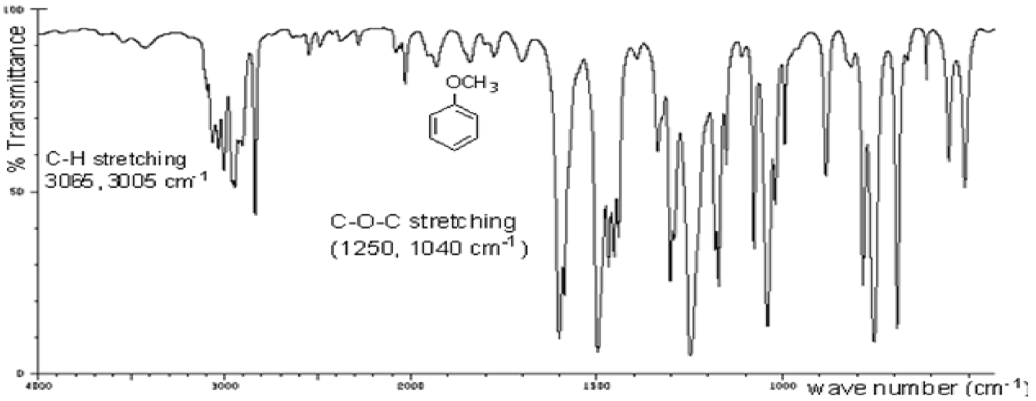


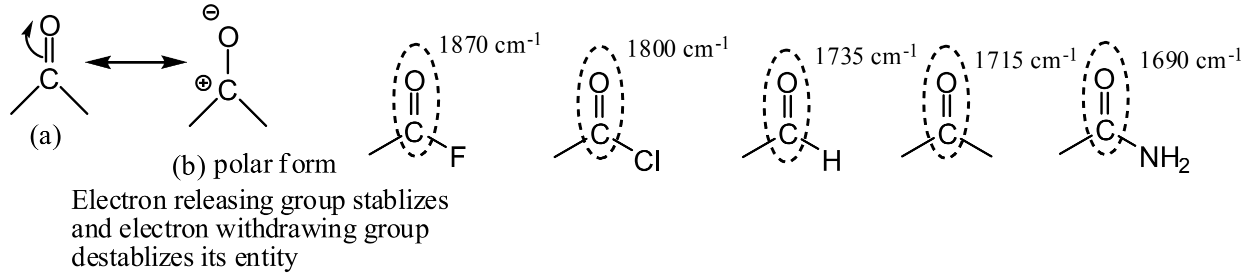
Fig. 16: IR spectra of methoxybenzene

Carbonyl Compounds

Carbonyl compound show a strong sharp band around at 1900-1580 cm^{-1} (Figure 17-20). However, the precise position depending on the nature of parent compound as below:

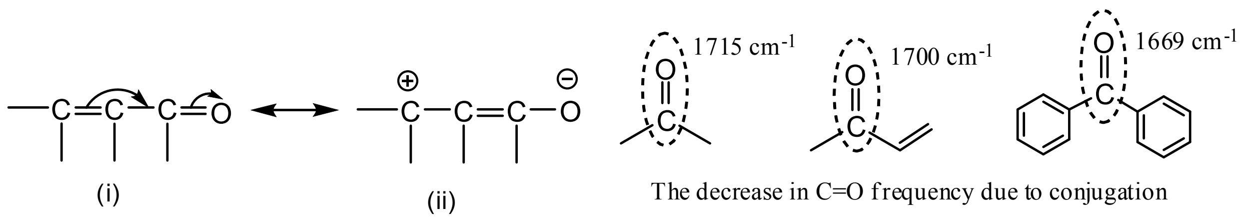
Ketones: Ketones show a strong sharp carbonyl band around 1700 cm^{-1}. There are, however, characteristic shifts in the position of this band depending on the structural environmental as given below (Figures 17-20):

(i) Inductive and Mesomeric Effects: Electron pulling groups decreases the stability of polar contributing form of carbonyl group (b) with an effective increase in double bond character. This causes increase in frequency of absorption for C=O. Conversely an electron pushing group stabilizes the polar form of carbonyl group by mesomeric effect and hence reduces its value (Scheme 3).



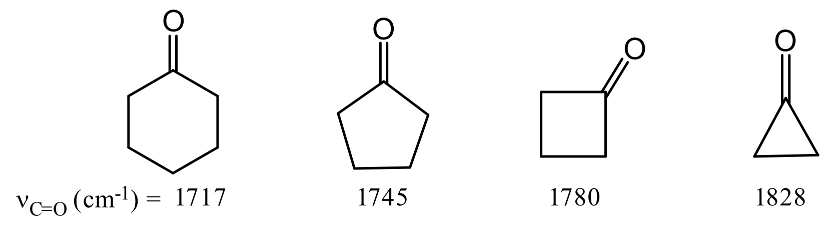
Scheme 3: C=O stretching values for different substituents.

(ii) Conjugation Effect: Conjugation of carbonyl group with double bond (olefinic or aromatic ring) causes delocalization of ð electrons of both C=C bond and C=O bond. This results dwindling of carbonyl stretching frequency from 1717 cm^{-1} to 1690 cm^{-1} and C=C stretching from 1645 cm^{-1} to 1620 cm^{-1}. This lowering is attributed to resonance as represented below (Scheme 4):



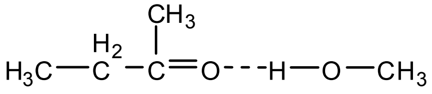
Scheme 4: Resonance and C=O stretching values for á, â-unsaturated ketones.

(iii) Ring Strain Effect: As the ring size decreases angle strain increases and these results increase in the C=O stretching frequency (Scheme 5). The normal value of cyclic carbonyl system is for cyclohexanone (í$_{C=O}$ = 1717 cm^{-1}). This effect is due to the increased interaction between the carbonyl double bond and the associated neighbouring single bonds. This increased interaction, as the ring size reduces causes resistance to the motion of the carbon of carbonyl group during stretching vibrations and thus increases force constant.



Scheme 5: The effect of angle strain on carbonyl stretching vibration.

(iv) Effect of Solvent: Intermolecular hydrogen bonding between a ketone and an alcohol (solvent) causes a slight decrease in the frequency of carbonyl group (Scheme 6). For example a neat sample of 2-butanone absorbs at 1715 cm^{-1} whereas its 10% solution in methanol absorbs at 1706 cm^{-1}.



$H_3C-\overset{H_2}{C}-\overset{CH_3}{C}=O\cdots H-O-CH_3$

Intermolecular hydrogen bonding
between solvent (alcohol) and
compound (ketone)

Scheme 6: Hydrogen bonding between methyl ethyl ketone (sample) and alcohol (solvent)

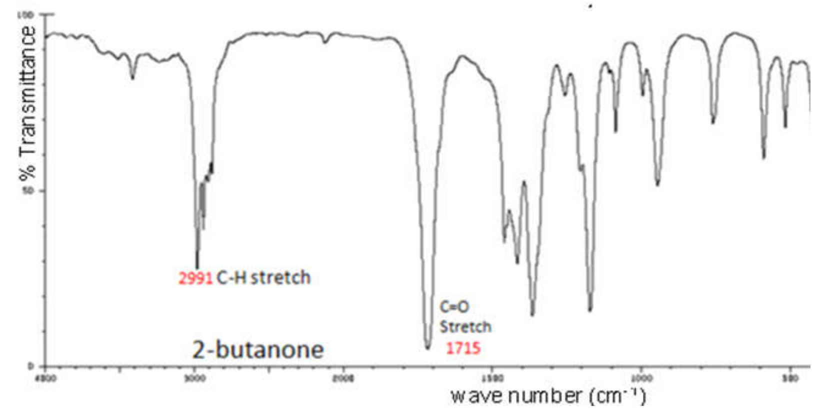


Fig. 17: IR spectra of Butan-2-one

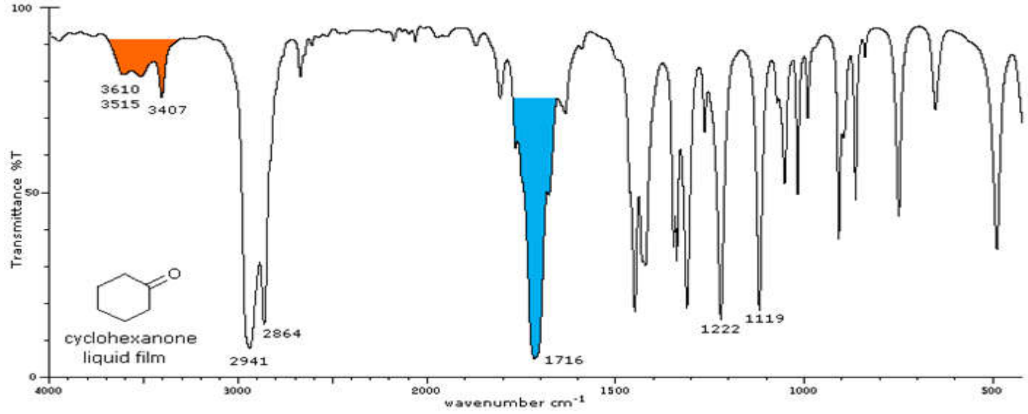


Fig. 18: IR spectra of cyclohexanone

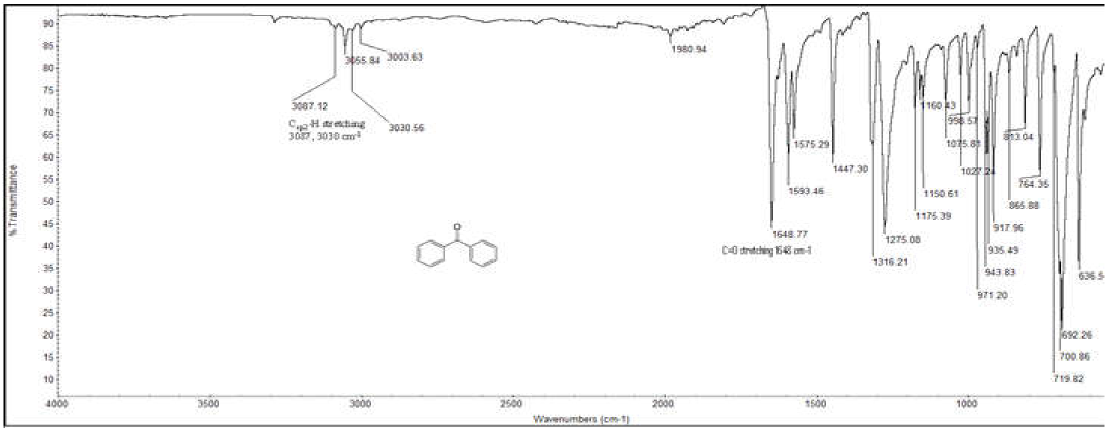


Fig. 19: IR spectra of Benzoquinone

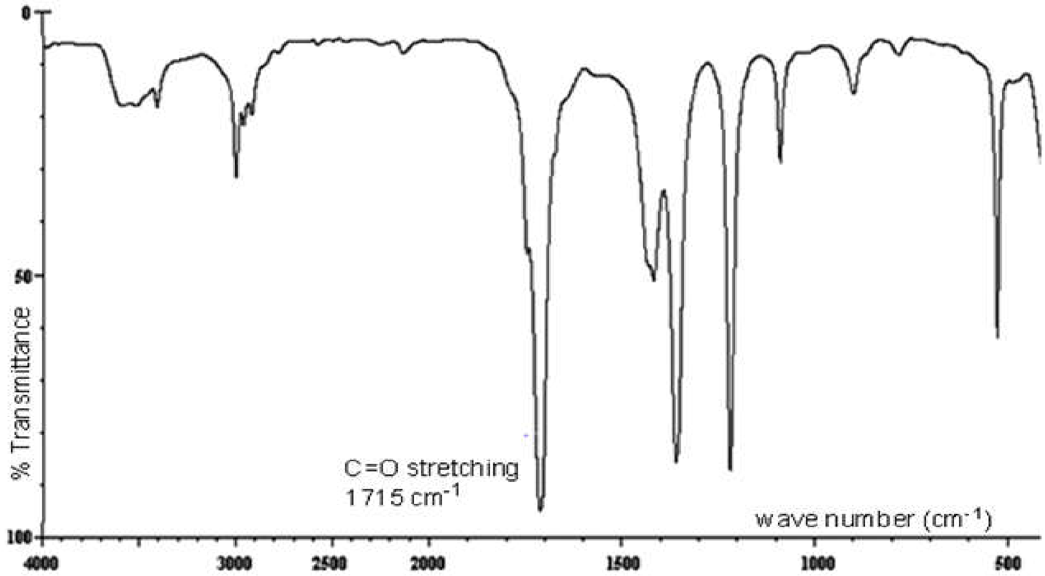


Fig. 20: IR spectra of acetone

$CH_3COCH_2CH_3$ (1715 cm^{-1}), $CH_3COCH{=}CH_2$ (1680 cm^{-1}).

From the above it is clear that:

1. The more is electron withdrawing group, the higher is the frequency of carbonyl band.
2. The more is electron releasing group, the lower is the frequency.
3. Conjugation decreases the frequency of carbonyl band.
4. The more strained is the cyclic ring then higher is the frequency of carbonyl band.

Quinones

1. Quinones are specific examples of á, â-unsaturated carbonyl compounds exhibit characteristic band due to C=O stretching in the range of 1690-1635 cm^{-1} (Figure 21).
2. If carbonyl group is in the other aromatic ring (pyren quinone), C=O stretching further reduces in the range of 1655-1635 cm^{-1} due to extended conjugation.

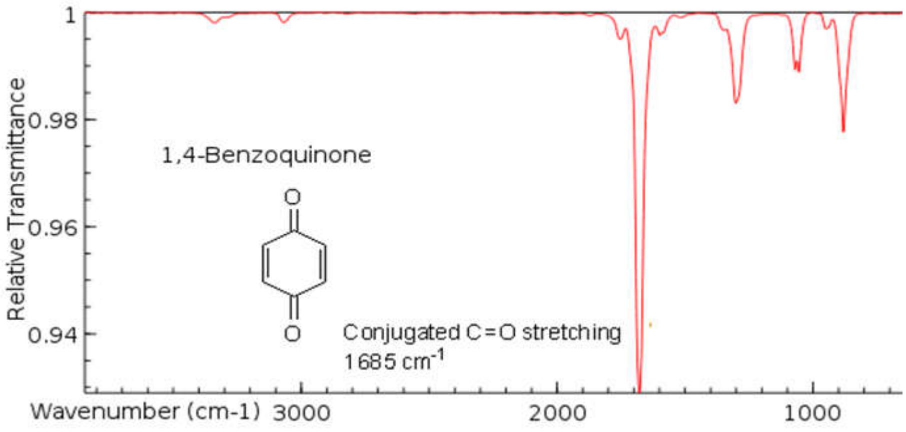


Fig. 21: IR spectra of 1,4-Benzoquinone

b. Aldehydes

1. Aldehydes show the carbonyl band at about 10-15 cm^{-1}; high value to the corresponding ketones. This is due to large +I effect operating in ketones as compared to aldehydes.
2. Conjugative effects on the position of the carbonyl

band in aldehydes are similar to those observed in ketones.

3. Aldehydes show a characteristic C–H stretching band around 2730 cm^{-1} and 2740 cm^{-1} (Figure 22).

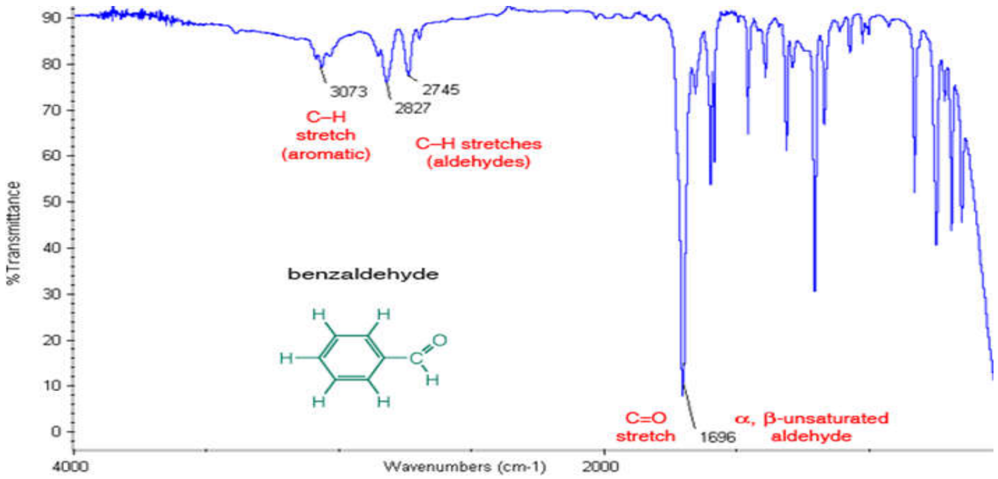
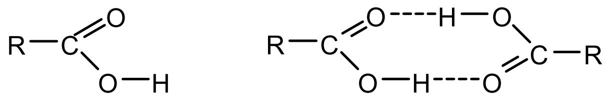


Fig. 22: IR spectra of Benzaldehyde.

c. The C=O bands in Carboxylic Acids:

1. Carboxylic acids generally exist as dimers in the solid state, but in dilute solution they exist mostly in monomeric state (Scheme 7).



(monomer: in dilute solution) (dimer: in solid state or conc. solution)

ν =1750 cm^{-1} ν =1700 cm^{-1}

Scheme 7: Presentation of monomeric and dimeric carboxylic acids.

2. The monomeric acid shows the carbonyl abnd at 1750 cm^{-1} and dimeric acid at 1700 cm^{-1} [10-13].

3. Since dimeric form has strong hydrogen bonding, the O–H stretching band shifts to lower frequency at 2700-2500 cm^{-1}. In the less common monomeric form, however, the O–H stretching band appears around 3500 cm^{-1} (Figure 23).

4. In addition, carboxylic acids show coupled C–O & O–H stretching at 1420 & 1300 cm^{-1}.

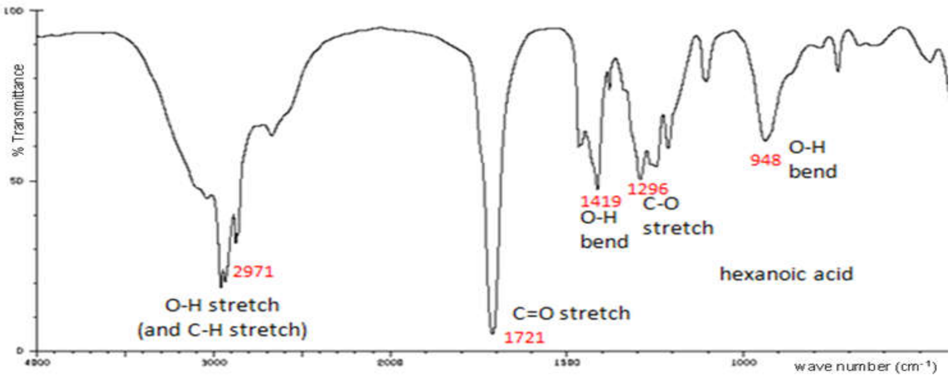


Fig. 23: IR spectra of Hexanoic acid.

d. **Esters**

1. The carbonyl band in esters appears at frequency higher than that observed in ketones (Figure 24). For example,

CH_3 COO C_2H_5	CH_3 CO CH_3
Ethyl acetate	Acetone
Carbonyl band appears between 1755-1740 cm^{-1}	Carbonyl band appears at 1715 cm^{-1}

2. In addition, C–O stretching band appears in 1280–1000 cm^{-1}.

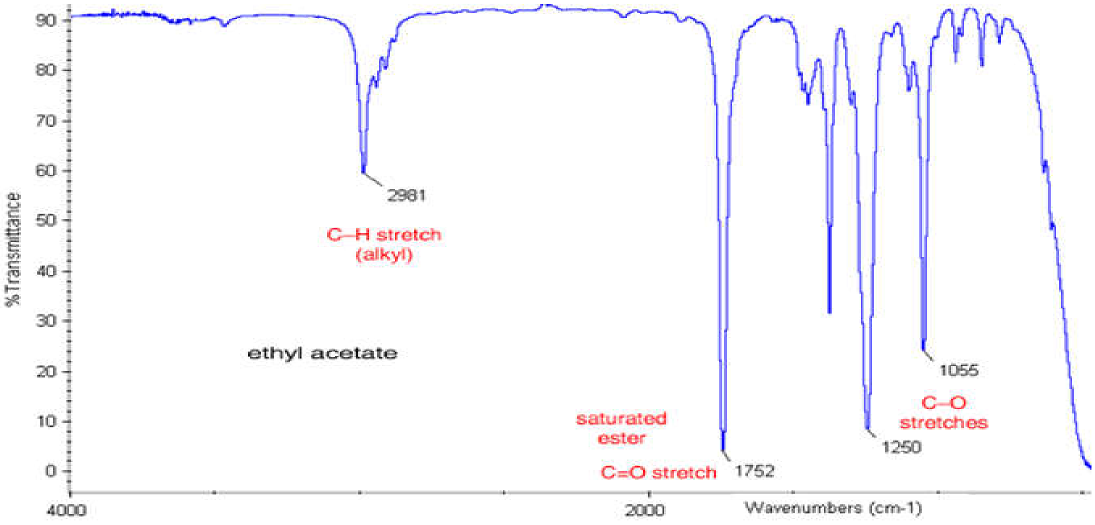


Fig. 24: IR spectra of Ethyl acetate

3. In aromatic ester viz, ethylbenzoate C-H stretch (aromatic) appears at 3078 cm^{-1} and C-H stretch (alkyl) at 2986 cm^{-1}, carbonyl stretch at 1726 cm^{-1} and C-O stretch at 1117 cm^{-1} (Figure 25).

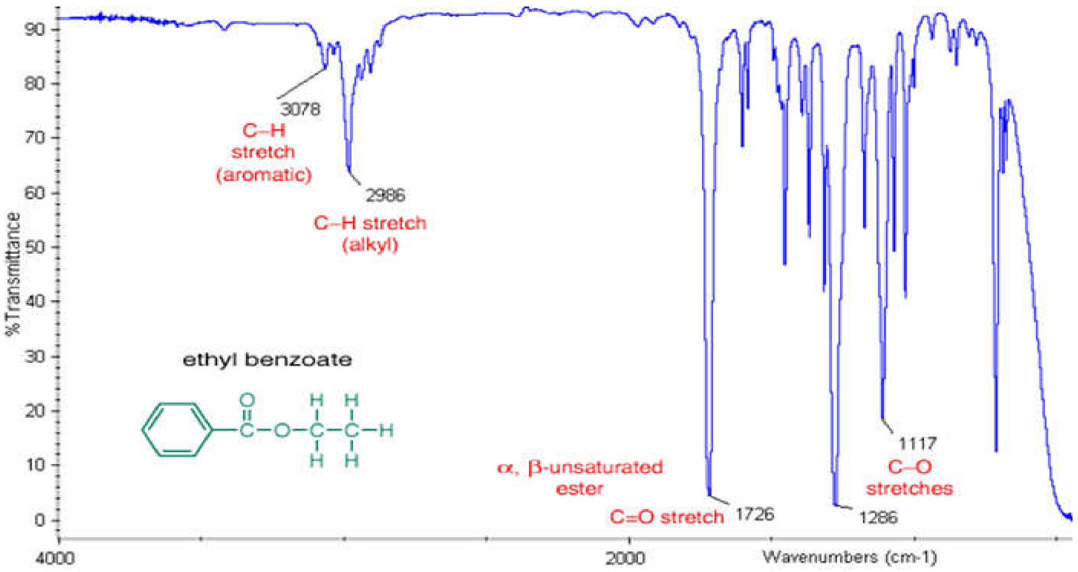


Fig. 25: IR spectra of Ethylbenzoate

Amides

1. Amides show the bands similar to those of amines.
2. In addition, they show a carbonyl band at 1710–1610 cm^{-1}(called amide I-band, Figure 26) and another (called amide II-band) at frequency slightly lower (1670-1640 cm^{-1}) than the carbonyl band for example Acetamide CH_3CONH_2 has amide I-band at 1650 cm^{-1} and amide II band at 1635 cm^{-1} [14-19].
3. The N – H stretching band at 3350, 3175 & 2970 cm^{-1}.

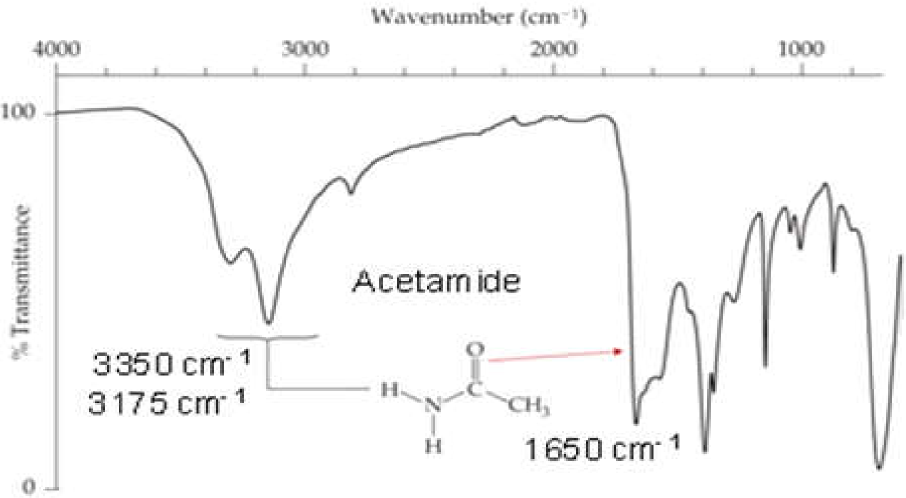


Fig. 26: IR spectra of Acetamide

Acid Anhydrides

1. They are distinguished from other acid derivatives by the appearance of two C=O bands. The two C=O stretching frequencies (asymmetric and symmetric) occurring near 1825, 1760 cm^{-1} respectively with a separation of about 60 cm^{-1}.
2. The higher frequency band in general is more intense in open chain anhydride while the lower band is more intense in case of strained cyclic (three, four and five member) anhydrides.
3. Strong bands appear in the spectrum of anhydrides near 1300-900 cm^{-1}due to C-O stretching vibrations. Non conjugated open chain anhydrides (except acetic anhydride 1125 cm^{-1}) exhibit strong band near 1050-1030 cm^{-1} whereas cyclic anhydrides display bands near 950-900 and 1300-1150 cm^{-1} (Figure 27).

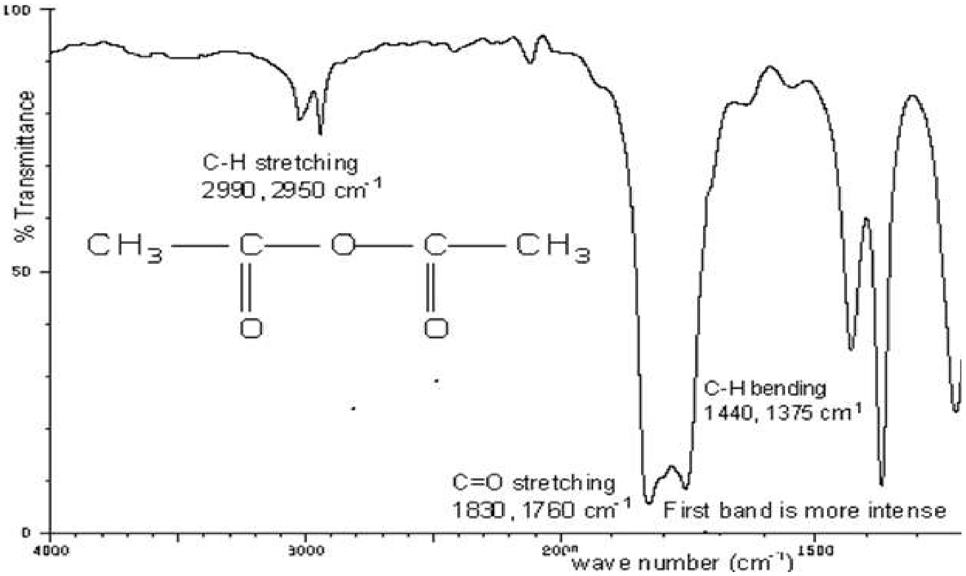
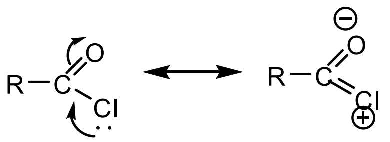


Fig. 27: IR spectra of acetic anhydride.

Acid Halides

1. The appearance of strong C=O stretching absorption in the range of 1870-1770 cm^{-1} is main characteristic of acid halides.
2. Acid chlorides, the most common acid halides exhibits bands for C=O around 1800 cm^{-1} (Figure 28). The high absorption band for C=O in acid chlorides is attributed to electronegativity of chlorine which makes it hard for oxygen to withdraw electrons from carbonyl carbon and hence weakens resonance (Scheme 8).



Scheme 8: Resonance in acidchloride.

3. Conjugated acid halides absorbs at slightly lower frequency band for C=O.
4. In aromatic acid chlorides a strong shoulder usually appears lower side of the C=O band. This occurs due to Fermi resonance between the C=O stretching band and first overtone of the band near 875 cm^{-1} (Figure 29).

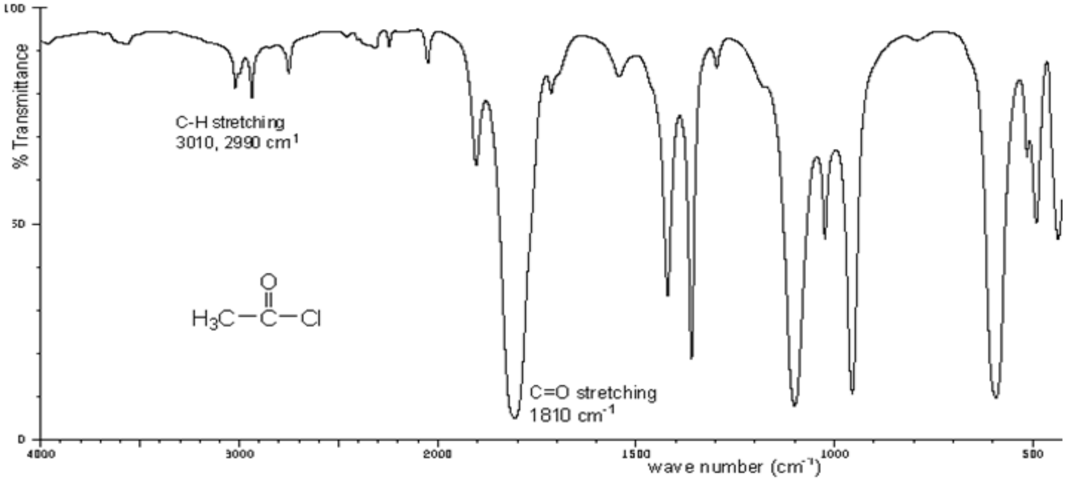


Fig. 28: IR spectra of Acetylchloride.

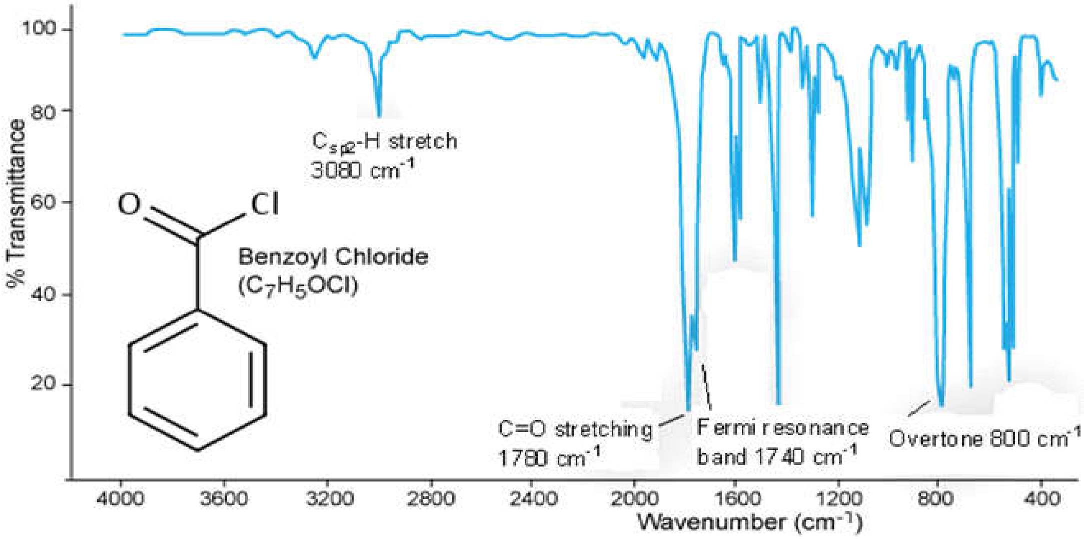


Fig. 29: IR spectra of Benzoylchloride

Amines

1. Primary and secondary amines show the N–H stretching bands at 3500-3300 cm^{-1} and N–H deformation bands at 1650–1500 cm^{-1} (Figures 30, 31).
2. Tertiary amines have no N-H stretching vibrations (Figure 32), however detected indirectly. The tertiary amine is converted into the amine salt (say $R_3N^+HCl^-$) and this salt shows a strong ammonium band in the range 3000–2200 cm^{-1}.
3. Aromatic amines (aniline) are further characterized by bands at 1350–1250 cm^{-1} and 1280-1180 cm^{-1}.
4. N-CH_3 stretching bands at 2850–2750 cm^{-1} sometimes characterize methylamines (N-methyl aniline and N, N-dimethyl aniline).

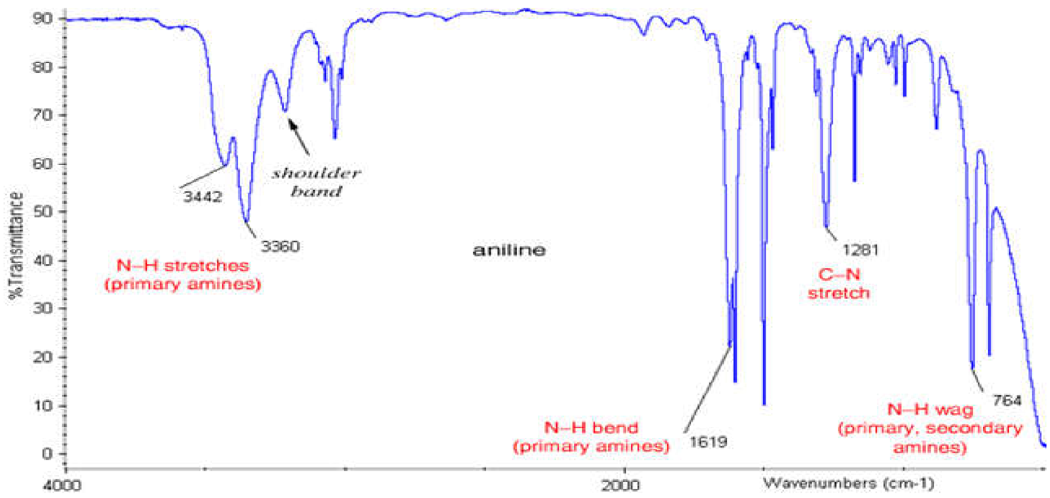


Fig. 30: IR spectra of Aniline

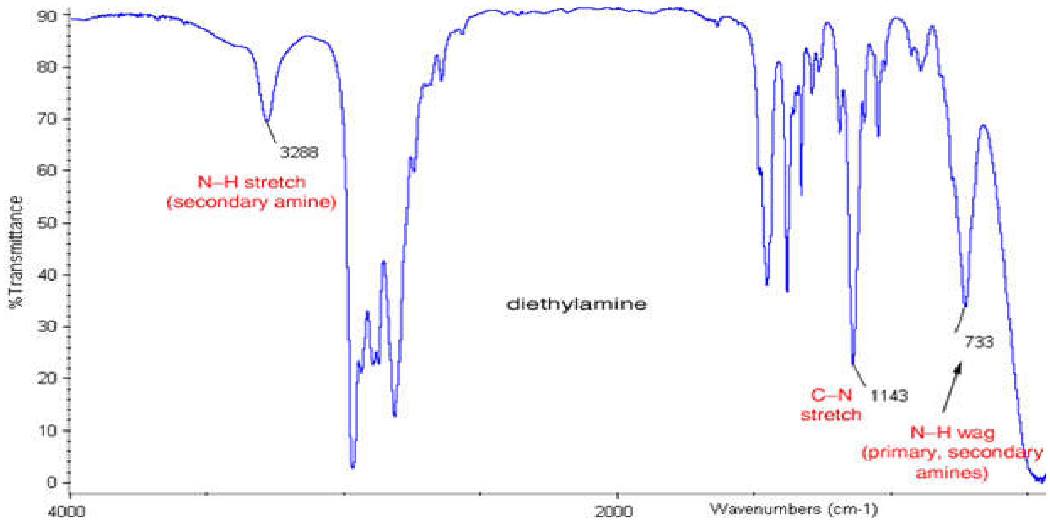


Fig. 31: IR spectra of Diethylamine

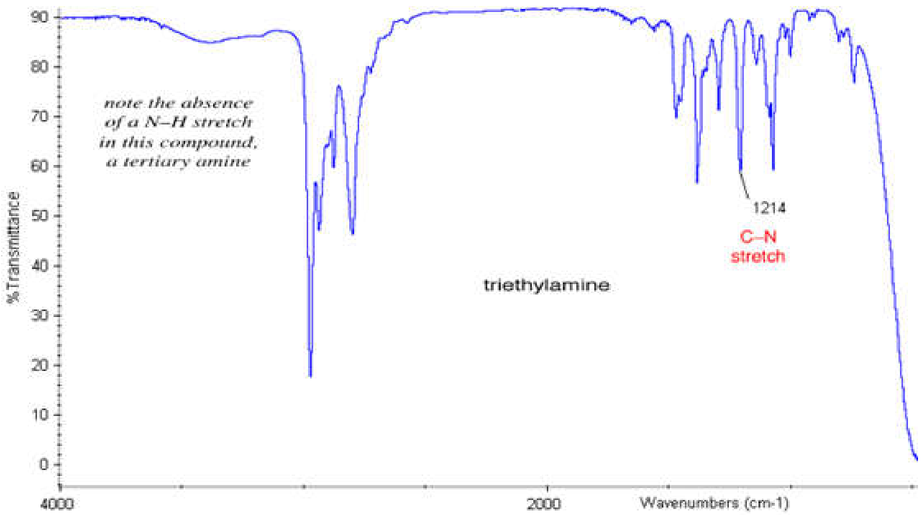
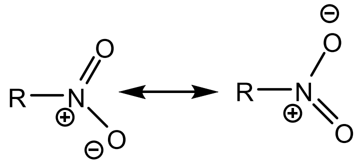


Fig. 32: IR spectra of N,N,N-Triethylamine

Nitro Compounds

1. The nitro group has two similar N-O bonds which yield asymmetrical stretching band in 1565-1515 cm^{-1} and symmetrical stretching band in 1385-1335 cm^{-1}. This is due to highly polar nitrogen –oxygen bond, Scheme 9.



Scheme 9: Resonance in alkylnitrate

2. In aliphatic compounds bands appear slightly at higher frequency (1550-1380 cm^{-1}) than in aromatic compounds (1530-1350 cm^{-1}) (Figure 33). This is due to conjugation of nitro group with aromatic ring.
3. In aromatic nitro compounds, if there is electron releasing group at ortho or para-position with respect to nitro group NO_2 stretching frequency considerably decreases, because of resonance which weakens N-O bond. Conversely electron pulling group enhances the frequency band.

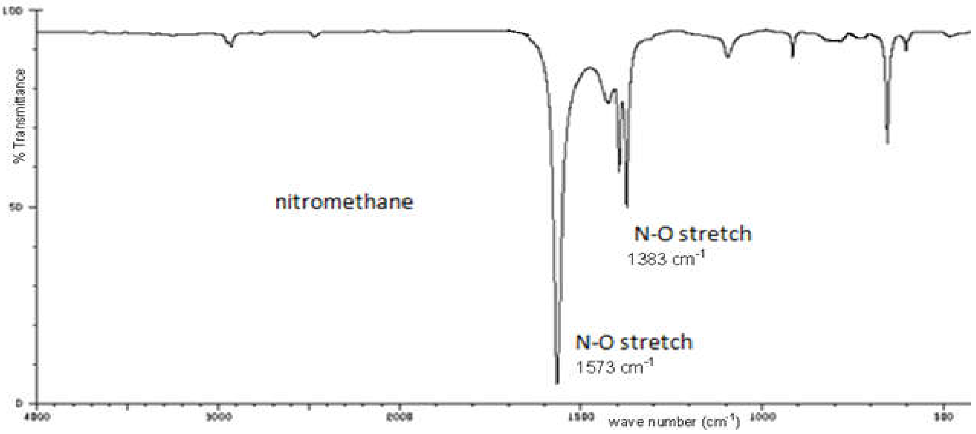


Fig. 33: IR spectra of Nitromethane.

2. Fingerprint Regions in an IR Spectrum

The region 1300-900 cm^{-1}, known as the fingerprint region, of an IR spectrum is characteristic of a molecule as a whole (Figure 34). No two compounds, howsoever closely related, can have identical or super imposable bands in this region. The finger print region of an IR spectrum is thus very useful for establishing the identity of two compounds. In fact, the superimposability of the IR spectra of two compounds is taken as an unimpeachable evidence for the identity of the two compounds.

If the identify of two solid, crystalline compounds is to be established, they must be crystalline under exactly identical conditions before their IR spectra are taken for the purpose.

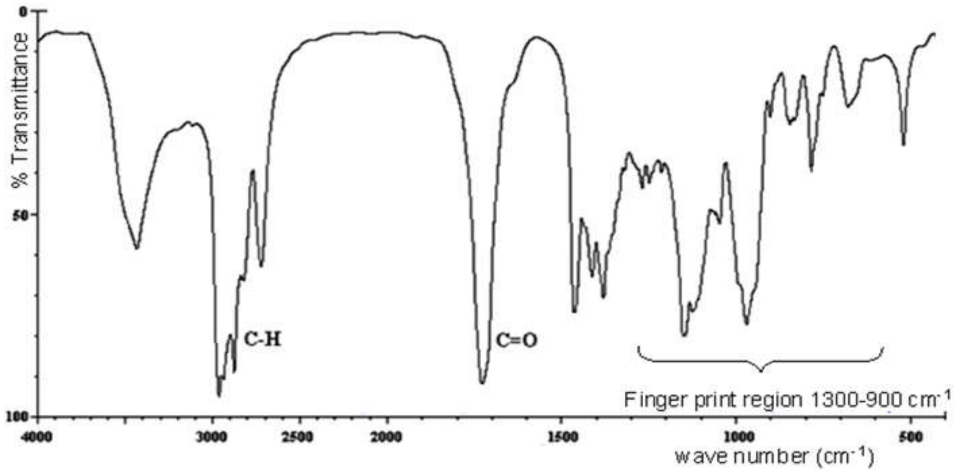


Fig. 34: Fingerprint region of IR spectra.

3. *Aromatic Region (Aromatic hydrocarbons)*

1. At least one strong band between 900 and 650 cm^{-1} is the typical aromatic band.
2. In addition the C = C stretching band at 1600 – 1575 cm^{-1} usually appears as a duplet.
3. The C–H stretching band corresponding to unsaturated hydrocarbons appears at 3100-3000 cm^{-1}
4. There are diagnostic pattern of weak bands between 2000-1650 cm^{-1} for substituted benzene ring. For example.

Mono substituted	Distinct 'fingers', the strongest at 2000 cm^{-1} (Figure 35).
Ortho Substituted	Two triplet bands
Meta Substituted	Two bands and a triplet around 1650 cm^{-1}
Para Substituted	Two bands, the stronger one around 2000 cm^{-1}

5. There are additional characteristic band between 700-850 cm^{-1} for substituted benzene rings. For example.

Mono substituted	770-700 cm^{-1} and 700-680 cm^{-1}
Ortho Substituted	770-735 cm^{-1} (Figure 36).
Meta Substituted	800-750 cm^{-1} and 700-680 cm^{-1} (Figure 37).
Para Substituted	800-850 cm^{-1} (Figure 38).

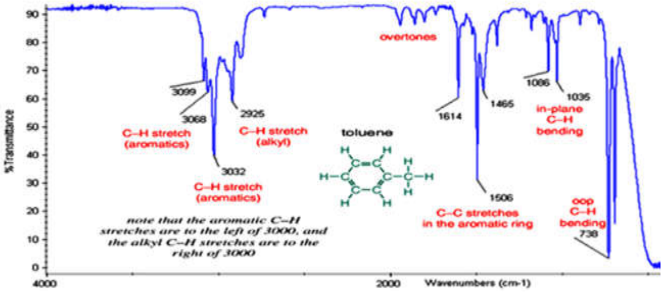


Fig. 35: IR spectra of Toluene

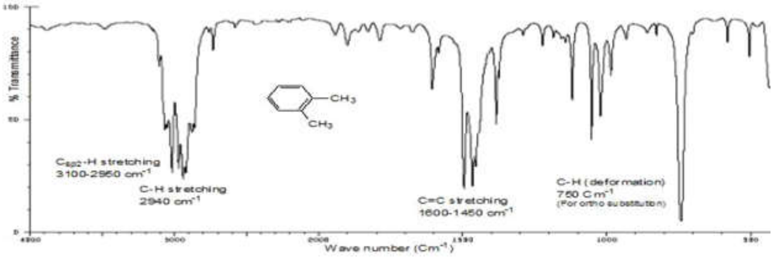


Fig. 36: IR spectra of ortho- xylene

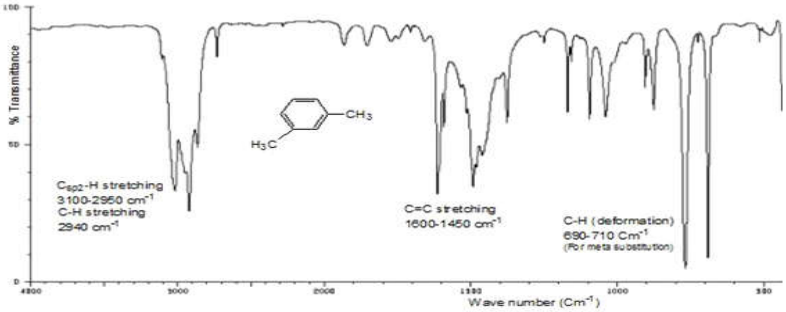


Fig. 37: IR spectra of meta- xylene

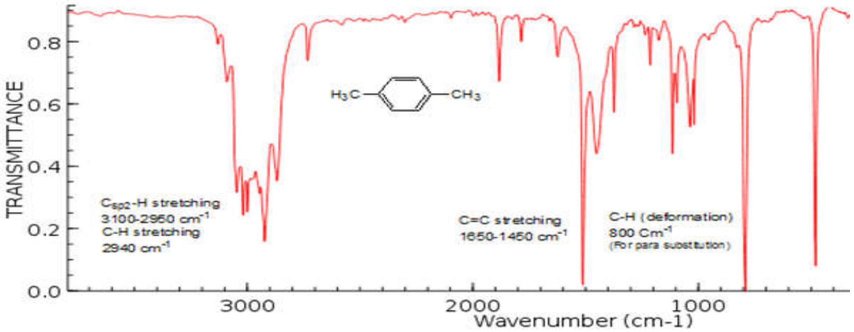


Fig. 38: IR spectra of para- xylene

Simplest Approach for interpreting IR spectrum

1. Is a carbonyl group present?

   The C=O group gives rise to a strong absorption in the region 1820-1660 cm $^{-1}$. The peak is often the strongest in the spectrum and of medium width. You can't miss it.

2. If C=O is present, check the following types (if absent, go to 3).

ACIDS	Is OH also present? Broad absorption near 3400-2400 cm -1 (usually overlapped C-H stretching) is obtained
AMIDES	Is NH also present? Medium absorption near 3500 cm-1 sometimes a double peak, with equivalent halves is observed.
ESTERS	Is C-O also present? Strong intensity absorptions near 1300-1000 cm-1 is apparent.
ANHYDRIDES	have two C=O absorptions near 1810 and 1760 cm-1
ALDEHYDES	Two weak absorptions near 2850 and 2750 cm-1 on the right hand side of CH absorption appears.
KETONES	The above 5 choices have been eliminated

3. If C=O is absent

ALCOHOLS	Check for OH (broad absorption near 3600-3300 cm-1) Confirm this by finding C-O near 1300-1000 cm-1
AMINES	Check for NH (medium absorption (s) near 3500 cm-1)
ETHERS	Check for C-O near 1300-1000 cm-1 and absence of O-H

4. *Double Bonds and / or Aromatic Rings*

   C=C is a weak absorption near 1650cm^{-1} medium to strong absorptions in the region 1650-1450 cm^{-1} often imply

   For an aromatic ring, confirm the above by consulting the CH region; aromatic and vinyl CH occurs to the left of 3000 cm^{-1} (aliphatic CH occurs to the right of this value)

5. *Triple Bonds*

   Ca”N is a medium, sharp absorption near 2250 cm^{-1}

   Ca”C is a weak but sharp absorption near 2150 cm^{-1}

   Also check for acetylenic CH near 3300 cm^{-1}

6. *Nitro groups*

   Two strong absorptions in 1600-1500 cm^{-1} and 1390-1300 cm^{-1} region.

7. *Hydrocarbons*

   None of the above is found, major absorptions are in CH region near 3000 cm^{-1}. Simple spectrum, other absorptions are only near 1450 cm^{-1} and 1375 cm^{-1}.

Fourier Transform Infra red Spectroscopy (FTIR)

- In Conventional or dispersive IR polychromatic or grating will be employed for dispersing the polychromatic radiation.
- The energy of individual frequent is scanned sequentially.
- For good quality spectra (resolution) narrow shuts are required.
- In FTIR an interferometer is employed instead of a grating or prism.
- The spectral information for all the frequencies is obtained at the same time.
- The most common interferometer used is Michelson interferometer (1891).
- of functional groups
- Striation elucidate Identification of compounds
- Analysis on
- Retention of intra – and intermolecular interaction convent technique
- Non – destructive
- Rapid and simple
- Gases, liquids and solids can be examined
- Various sampling Techniques

Main Features of Dispersive and FTIR

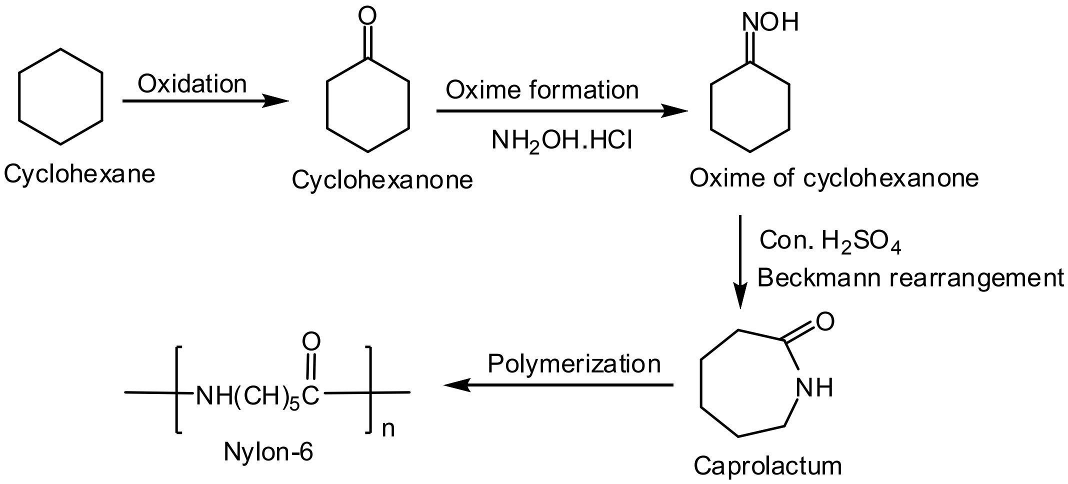
- In Conventional or dispersive IR polychromatic or grating will be employed for dispersing the polychromatic radiation.
- The energy of individual frequent is scanned sequentially.
- For good quality spectra (resolution) narrow shuts are required.

- In FTIR an interferometer is employed instead of a grating or prism.
- The spectral information for all the frequencies is obtained at the same time.
- The most common interferometer used is Michelson interferometer (1891).

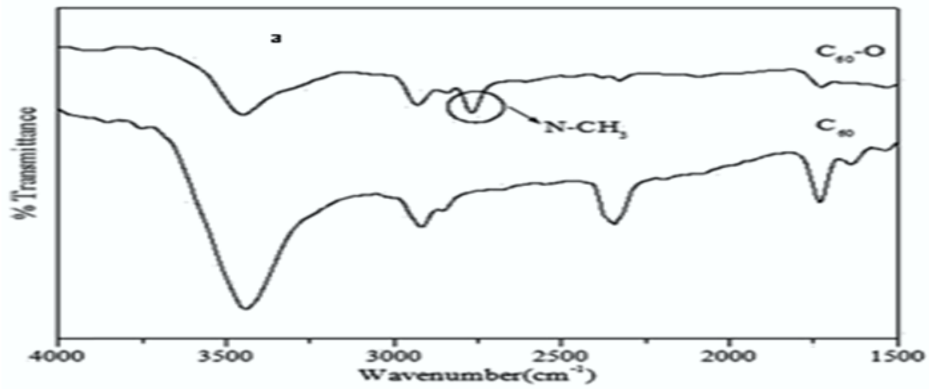
Applications of FTIR

The FTIR microscopes makes almost any type of sample that would be analyzed by FTIR more easily examined on a micro scale. The different applications are described below:

Polymers are ubiquitous in our society, and their prevalence at crime scene causes them to be commonly encountered as forensic evidence. The large variety of polymer types makes it necessary to categorize them by application in order to gain a general understanding of variations within each group. Thus classified, the evidence may often be individualized to a greater extent, its significance more clearly understood, and its evidentiary value enhanced. The forensic examination of fibers by visual light microscopy is complemented by FTIR microscopy. FTIR plays an important role in the systematic approach to the complete characterization of fibers. FTIR data will provide an unequivocal of the generic class, as well as the subclass created by chemical variations within the generic class. In addition, the American society of testing and Materials (ASTM) now lists FTIR spectroscopy as the preferred method of analysis for identifying man-made fibers, stating, " where the data are consistent and the spectra obtained and interpreted by an experienced spectroscopist, the FTIR procedure has no known bias". The IR spectra of nylon-6 fibers (method of synthesis given in scheme 10, below) obtained by different methods are given in figure 39 a-d, below:



Scheme 10: Synthetic route of nylon-6



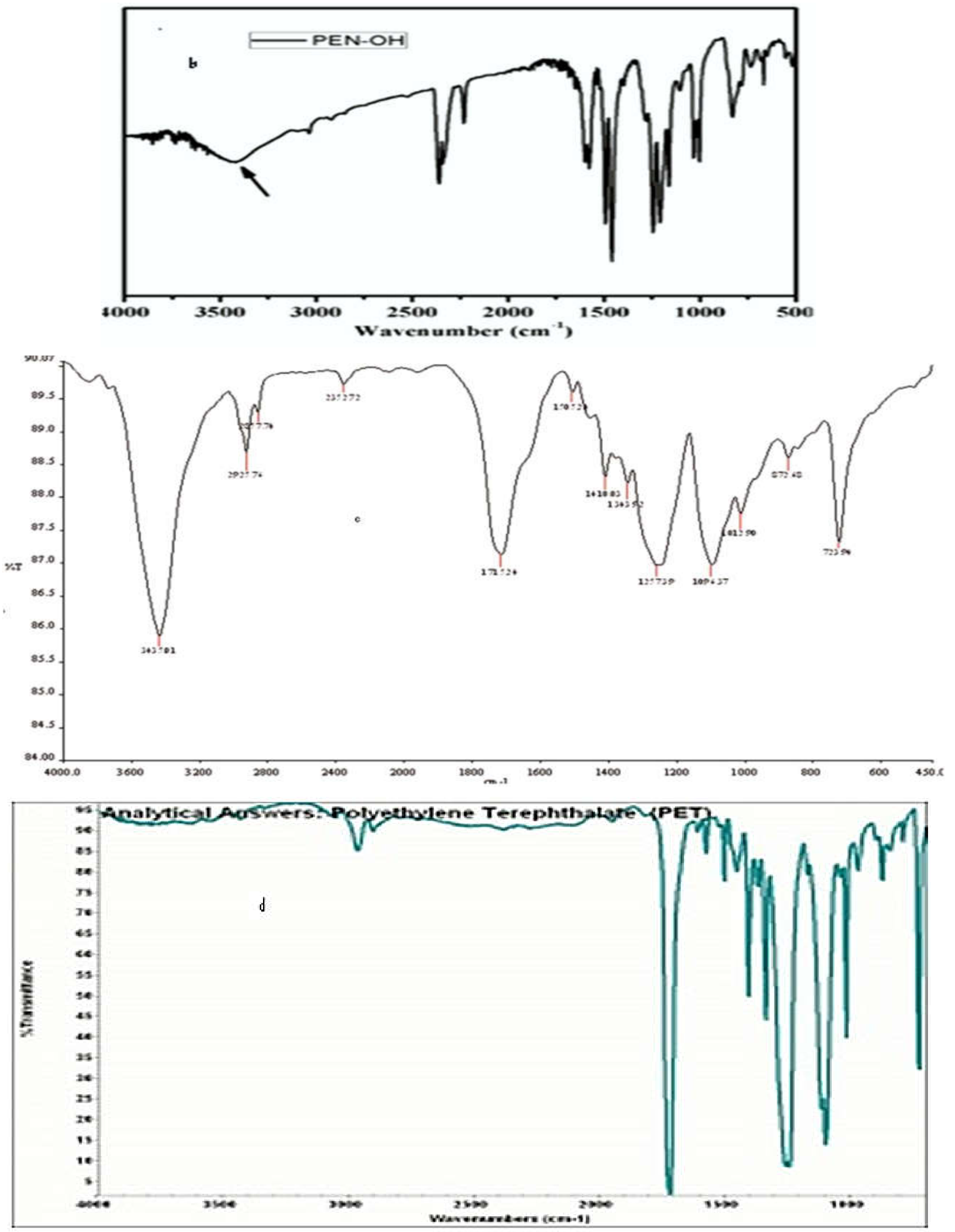


Fig. 39: (a) Spectrum of nylon-6 obtained by lead foil technique on a dispersive instrument, **(b)** Spectrum of nylon-6 fibers obtained by diamond cell on a dispersive instrument, **(c)** spectrum of nylon-6 fibers obtained by diamond cell on FTIR, **(d)** spectrum of fortrel fibers obtained by diamond cell on FTIR. A comparison of spectras a-c explains the effect of different sampling techniques and different instrument types

The ingredients and residues associated with various explosive devices are comprised of a wide variety of different substances, including organic compounds, inorganic salts, and polymers. The wide variety makes FTIR an ideal tool, not for screening such substances, but also for identification in most systematic approach. The two strong absorption bands of symmetric and asymmetric stretching vibrations of the NO_2 group in nitro explosives depend on the type of atoms with which it is directly attached. These vibrations have an important investigative value and their presence and absence in the sample should be the first thing to be noticed. In the spectrum of 2,4,6-trinitrotoluene (Figure 40) the two C-NO_2 asymmetric and symmetric stretching bands appear at 1534 cm^{-1} and 1354 cm^{-1}.

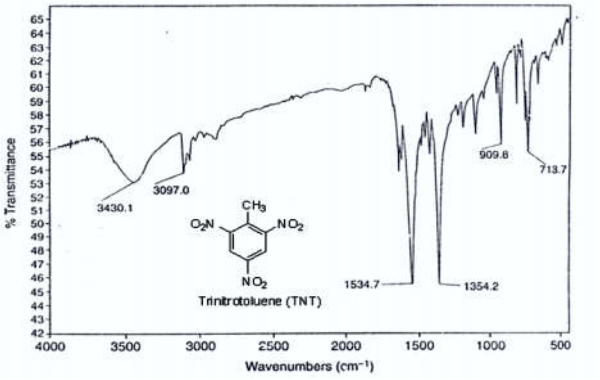


Fig. 40: IR spectrum of Trinitrotoluene (TNT)

The nitrate esters, C-O-NO_2 have two strong asymmetric and symmetric stretching vibrations in the range 1660-1640 cm^{-1} and 1285-1270 cm^{-1} respectively.

It is found that these bands in polynitrate ester explosives split into two or more peaks which is attributed to the existence of rotational isomers, due to hindered rotation around C-C bond. Figures 41-45; spectra of pentaerythritol tetranitrate, ethylene glycol dinitrate, nitroglycerine, nitrocellulose and metriol trinitrate respectively prove this finding.

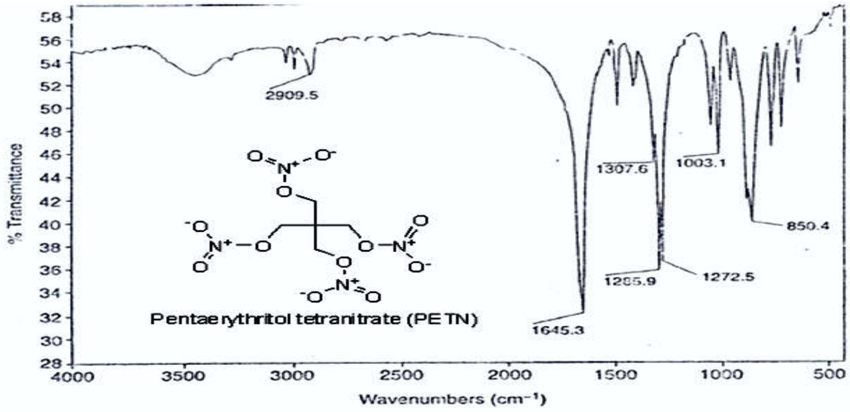


Fig. 41: IR spectrum of pentaerythritol tetranitrate

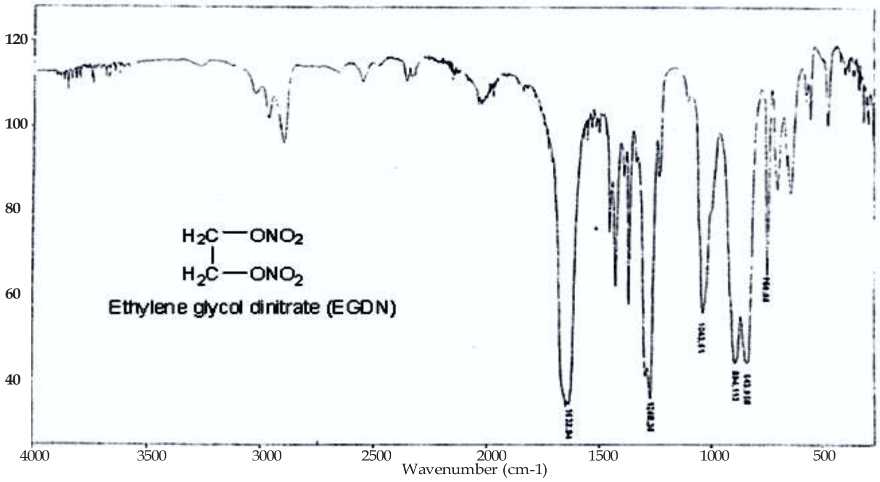


Fig. 42: IR spectra of ethyleneglycol dinitrate

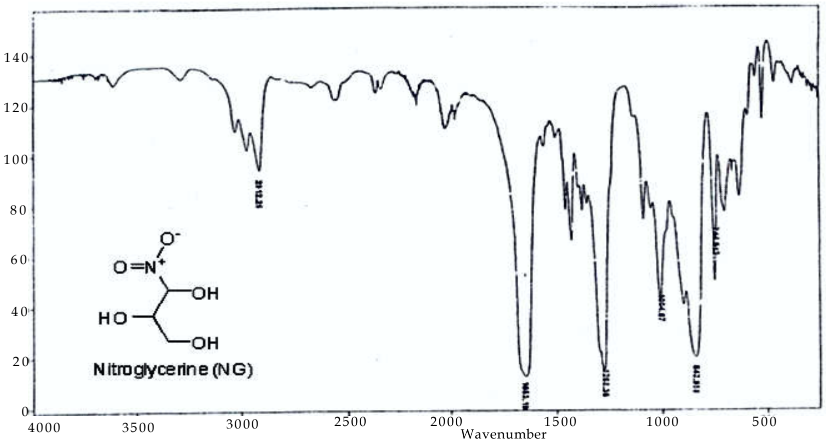


Fig. 43: IR spectra of nitroglycerine

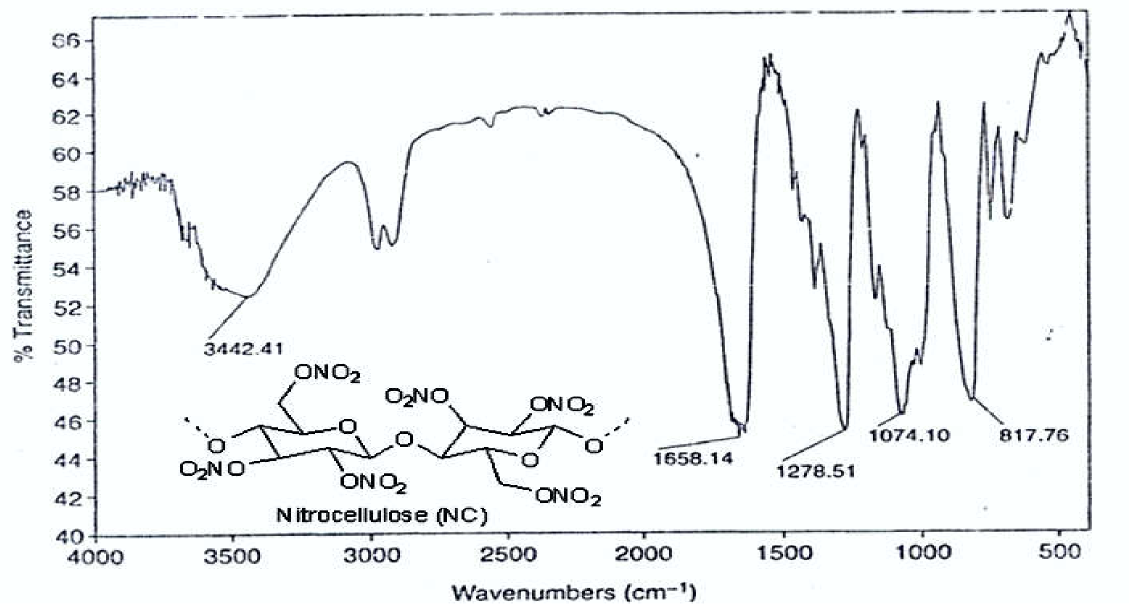


Fig. 44: IR spectra of nitrocellulose

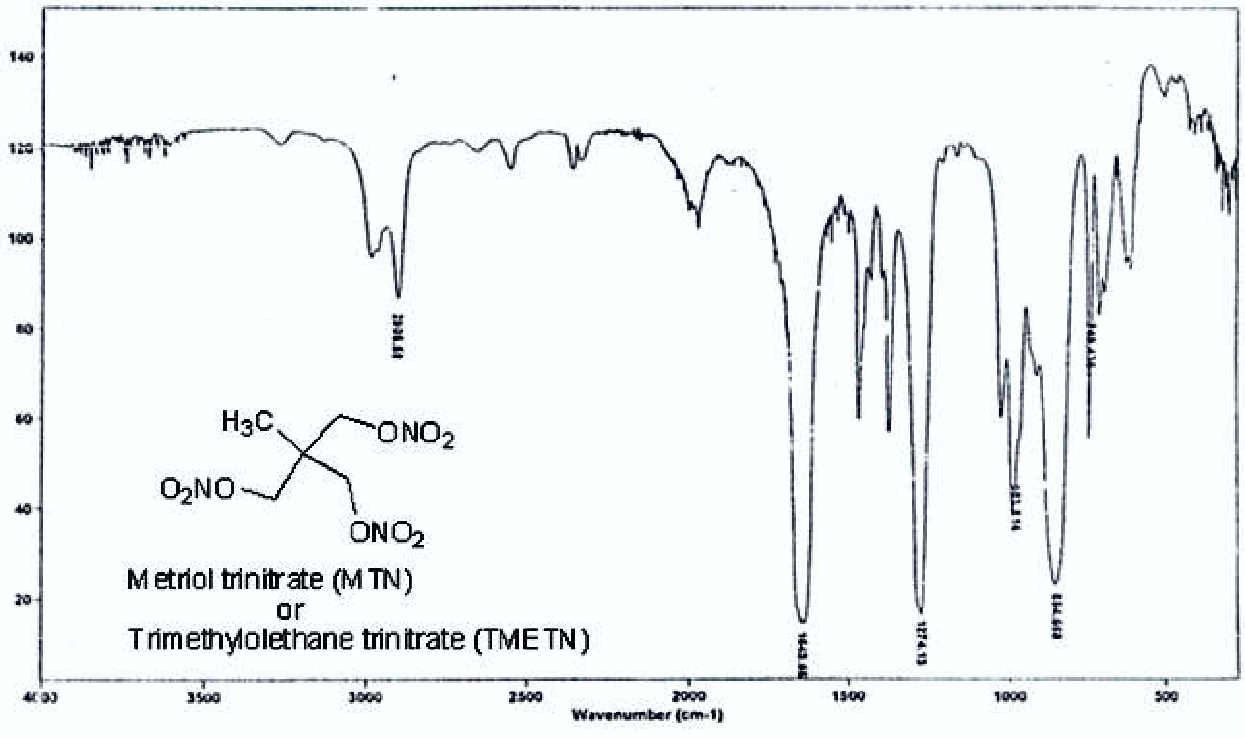


Fig. 45: IR spectra of metriol trinitrate

In nitramine explosives two NO stretching vibrations of the N-NO_2 bond were reported in the range 1590-1530 cm^{-1} and 1310-1270 cm^{-1} for asymmetric and symmetric stretching vibrations respectively. Figures 46 and 47 show the IR spectra of heterocyclic nitramines RDX (tricyclomethylene trinitramine) and HMX (tetracyclomethylene tetranitramine) in which various peaks appear listed in the above region.

The powerful organic peroxide explosives are usually unstable and sensitive to heat, friction and shock, hence they are not considered as primary standard explosives. The band at 872 cm^{-1} was attributed to O-O stretching vibrations in peroxides. The IR spectra of hexamethylene triperoxide diamine is given in Figure 48 [20].

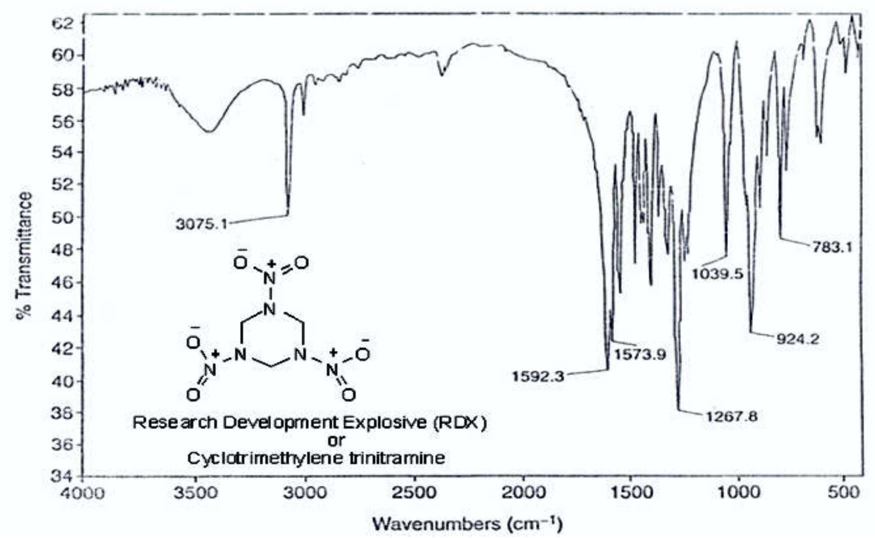


Fig. 46: IR spectrum of RDX

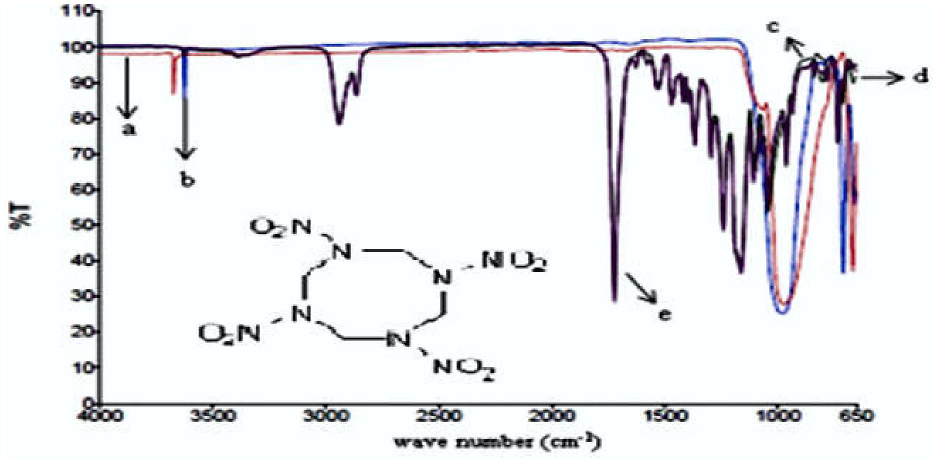


Fig. 47: IR spectrum of HMX

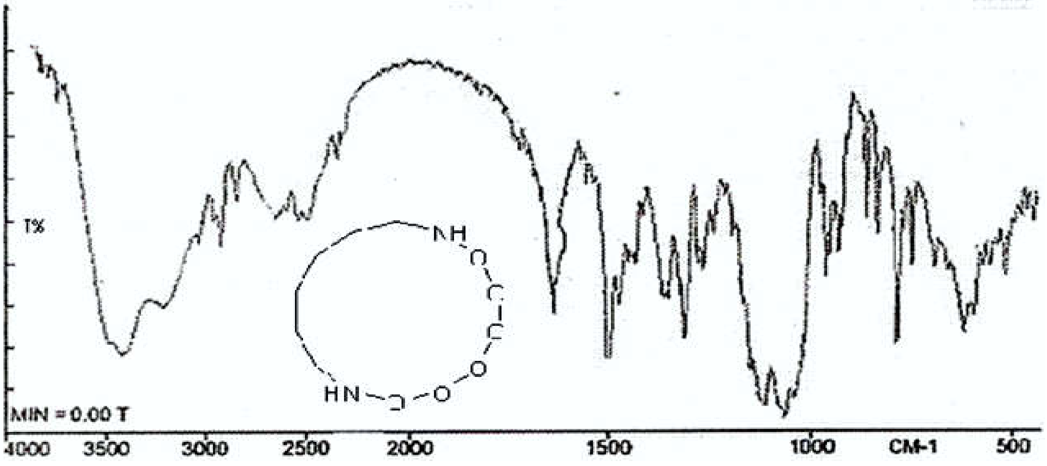


Fig. 48: IR spectrum of hexamethylene triperoxide diamine

Inorganic anions emerge as oxidants in explosive mixtures. Nitrates are important commercial explosives and mixed in black powders namely, dynamite slurries, emulsions and ammonium nitrate-fuel oil (ANFO). The common nitrates salts used in explosives are ammonium (NH_4NO_3) (Figure 50), sodium ($NaNO_3$) and potassium (KNO_3) (Figure 49). Ammonium nitrate is most common and has been identified in many terrorist bombings. Chlorates (ClO$_3^-$) (Figure 51) have usually been avoided in commercial explosives, being very unpredictably dangerous. The appearance of these anions is characterized by IR bands in respective regions viz; nitrates (1380-1350 cm^{-1}; very strong, 840-815 cm^{-1}; medium), chlorates (98-940 cm^{-1}; very strong), sulphates (1130-1080 cm^{-1}; very strong, 680-610 cm^{-1} medium weak), carbonates (1450-1410 cm^{-1}; very strong, 880-810 cm^{-1}; medium). The IR spectra of potassium nitrate, ammonium nitrate, sodium chlorate, potassium chlorate, potassium perchlorate and potassium sulphate are depicted below (Figure 52-54):

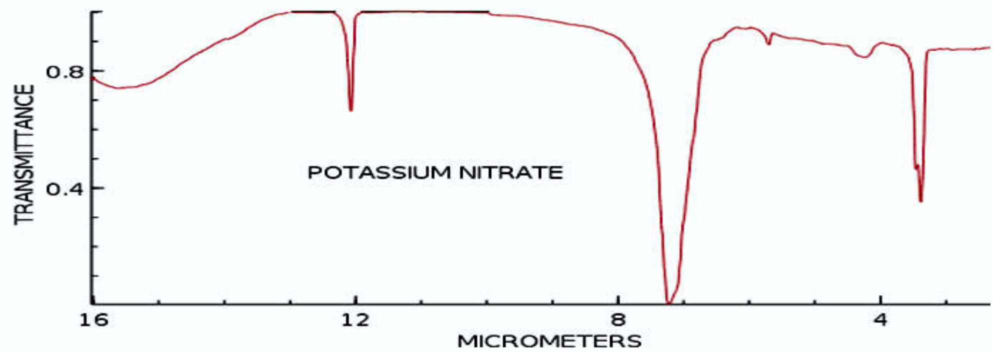


Fig. 49: IR spectrum of potassium nitrate (KNO$_3$)

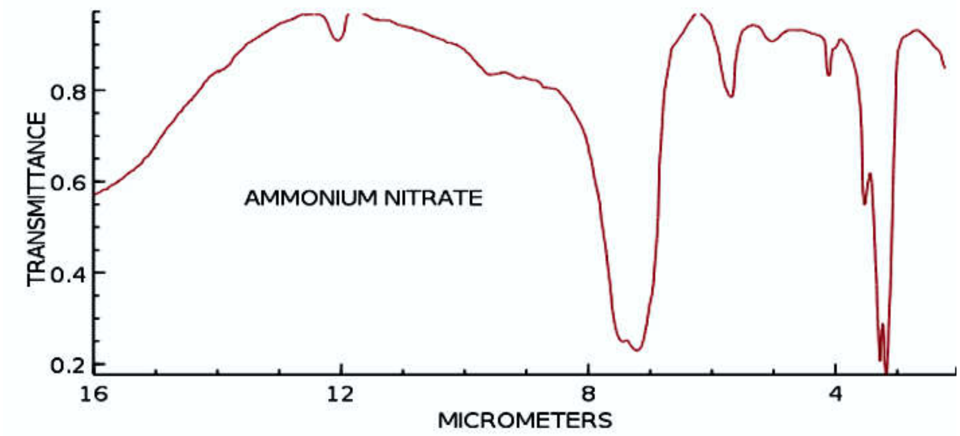


Fig. 50: IR spectrum of ammonium nitrate (NH$_4$NO$_3$)

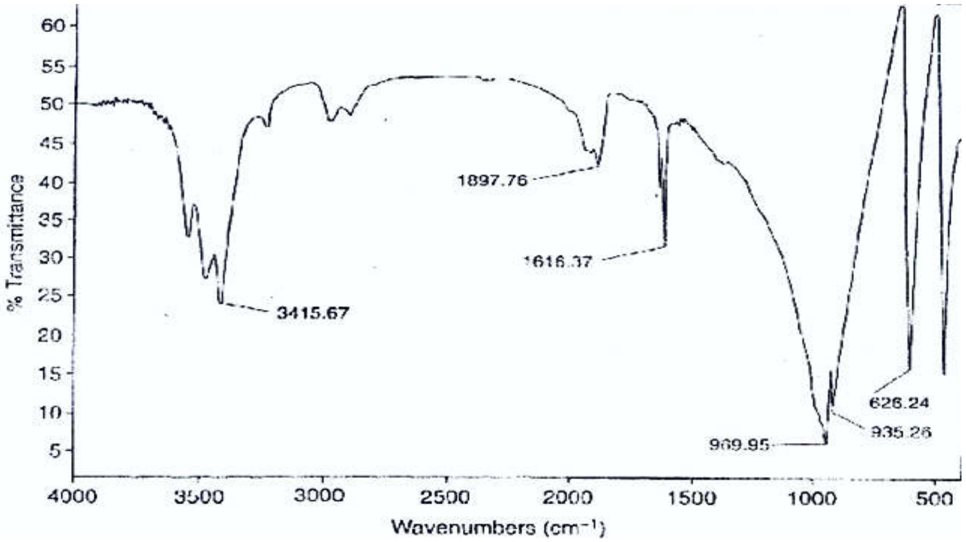


Fig. 51: IR spectrum of sodium chlorate

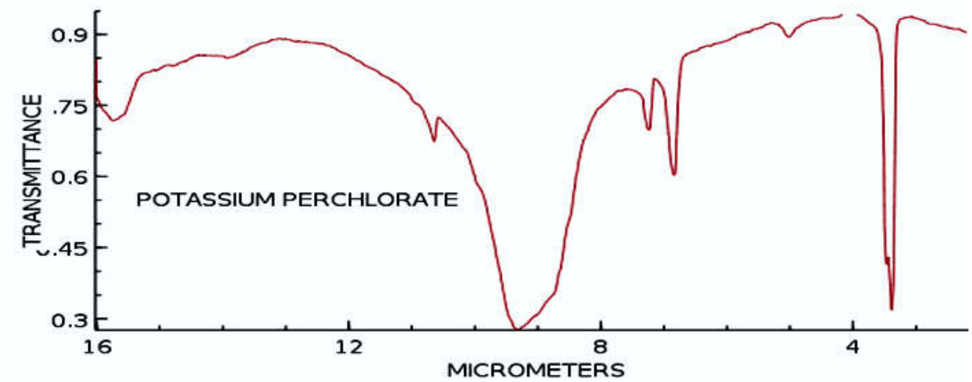


Fig. 52: IR spectrum of potassium chlorate ($KClO_3$)

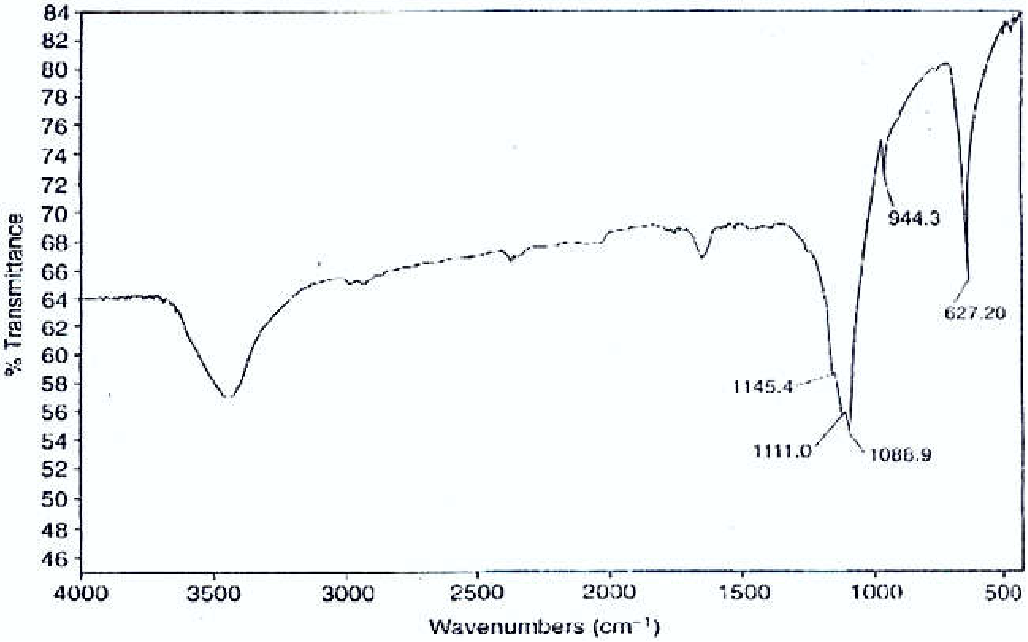


Fig. 53: IR spectrum of potassium perchlorate ($KClO_4$)

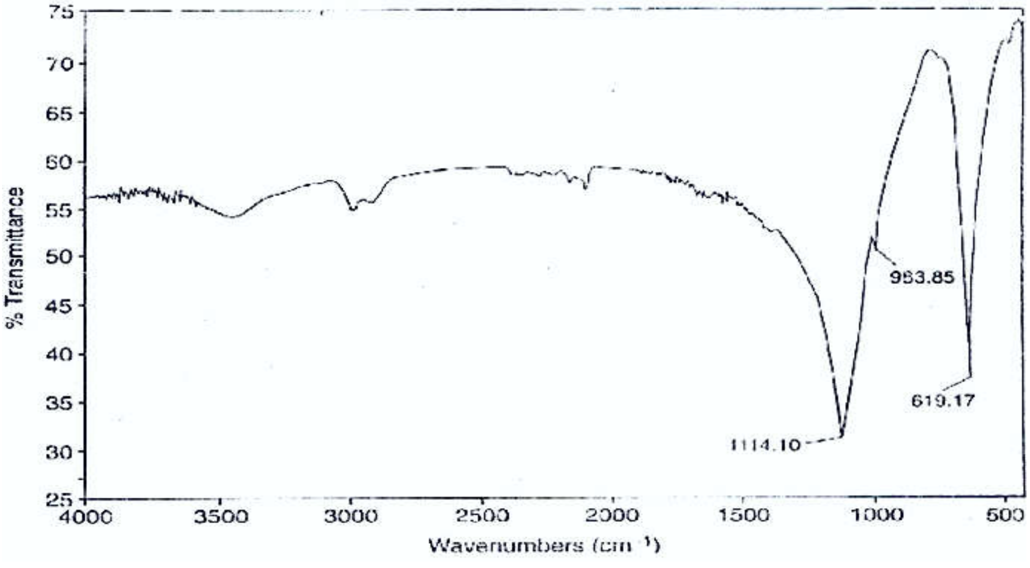


Fig. 54: IR spectrum of potassium sulphate (K_2SO_4)

Automobile producers currently place a great deal of emphasis on polymeric components. The need for lightweight, non-corrosive part has become important. Plastic parts are found throughout automobiles in including the outer bodies. Although there has not been extensive reporting of the analysis of these components using FTIR microscopes, a few papers have appeared.

Adhesives and tapes are frequently removed at crime scenes from explosive devices, bound victims, etc. Bartick and Merrill have reported the application of FTIR for the analysis of black plastic tapes. Both the adhesive and backing were sampled with a standard-size FTIR accessory. This approach works well unless the tape is contaminated and it is difficult to find a clean portion. Contamination of the adhesive poses the most concern because it is more difficult to clean. One advantage of FTIR is that small areas may be isolated within a particular specimen, thus eliminating tedious separation procedures. Additional polymers are frequently found at crime scenes and can often be useful as physical evidence. These are frequently analyzed by FTIR. The ease of preparing samples and recording spectra with FTIR has resulted in the method becoming widespread, not only for micro samples but also for samples that would normally be considered on a microscopic scale. Several methods of sampling inks have been reported which vary for the type of ink and the substrate. FTIR spectra of inks removed from printed paper by scraping inks from graph paper have been reported. The ability to directly obtain FTIR spectra of writing inks on documents with a microscope is difficult because of the absorption of the substrate, typically paper. FTIR is very useful tool for the analysis of many inorganic substances. The acquisition of mineral spectra by both transmission and reflection spectroscopy have been developed. Dentine and enamel from human teeth, calcium phosphates, were compared by reflectance with an FTIR microscope. Another example of mineral analysis was the comparison of several metamorphic phases of single rock.

These can contribute to FTIR spectra and interfere with the interpretation of the data. One must be particularly careful with micro sampling, because the relative contaminants contributions can be significantly greater then routine size samples. For example the presence of a contaminant can also, however, increase the evidential value of a fiber match when the contaminant is shown to be present on both the questioned and known samples. Common binders for water base architectural coatings (house paints) include poly (vinyl acetate) acrylic, PVA acrylic, styrene acrylic, and styrene-butadiene are often used in oil base paints. Like automotive undercoats, house paints may contain a variety of different pigments and extenders. As in the case of automotive undercoats, differences in the types and relative amounts of these pigments serve to differentiate among house paints, and their spectra likewise exhibit considerable diversity.

References

1. Clark, R. J. H. and Hester, R. E., Biomedical Applications of Spectroscopy, Wiley, Chichester, UK, 1996.
2. Gremlich, H.-U. and Yan, B., Infrared and Raman Spectroscopy of Biological Materials, Marcel Dekker, New York, 2000.
3. Jackson, M., Moore, D. J., Mantsch, H. H. and Mendelsohn, R., 'Vibrational Spectroscopy of Membranes', in Handbook of Vibrational Spectroscopy, Vol. 5, Chalmers, J. M. and Griffiths, P. R. (Eds), Wiley, Chichester, UK, 2002.p.3508–3518.
4. Kalasinsky, V. F., Appl. Spectrosc. Rev., 1996; 31: 193–249.
5. Mantsch, H. H. and Chapman, D. (Eds), Infrared Spectroscopy of Biomolecules, Wiley, New York, 1996.
6. Naumann, D., Appl. Spectrosc. Rev., 2001; 36:239–298.
7. Bernath, Peter F. Spectra of atoms and molecules (2nd ed.), 2005.p.304, Oxford University Press.
8. Hollas, John Michael (2004), Modern Spectroscopy (4th ed.), John Wiley & Sons.
9. Petrich, W., Appl. Spectrosc. Rev., 2001; 36:181–237.
10. Goodwin AP, Mynar JL, Ma Y, Fleming GR, Fréchet JM. J Am Chem Soc, 2005; 127:9952.
11. Briandet, R., Kemsley, E. K., & Wilson, R. H. 1996; 71:359-366.
12. Lyman, D. J., Benck, R., Dell, S., Merle, S., & Murray-Wijelath, J. Journal of Agricultural and Food Chemistry, 2003; 51:3268–3272.
13. Kemsley, E. K., Ruault, S., & Wilson, R. H. Food Chemistry, 1995; 54:21–326.
14. Koca, N., Rodriguez-Saona, L. E., Harper, W. J., & Alvarez, V. B. Journal of Dairy Science, 2007; 90:3596–3603.
15. S. Wi,P.Pancoka,T.A.Keiderling, Biospectroscopy 1998; 5:93–106.
16. R. Rahmelow,W.Hubner, Anal.Biochem. 1996; 241: 5–13.
17. S.Y. Lin, Y.S. Wei, M.J. Li, et al. Eur. J. Pharm. Biopharm. 2004; 57:457–464.
18. J.W. Brauner,C.R.Flach,R.Mendeisohn, J.Am. Chem. Soc. 2005; 127:100–109.
19. P.M. Bummer, Int.J.Pharm.132, (1996), 143–151.
20. IR Spectra are taken from http://www.infrared-spectra.com/