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Review Article

AN OVERVIEW ON INFRARED SPECTROSCOPY

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ABSRACT

This review mainly focuses on the principal, instrumentation, interpretation, application of infrared spectroscopy. Infrared (IR) radiation refers broadly to that part of the electromagnetic spectrum between the visible and microwave region. Of greatest practical use to the organic chemist is the limited portion between 4000 and 400cm -1. Infrared spectroscopy monitors the interaction of functional groups in chemical molecules with infrared light resulting predictable vibrations that provides a "fingerprint" characteristic of chemical or biochemical substances present in the sample. Infrared spectroscopy is a technique that probes the vibrations within a material. Infrared spectroscopy has always been a powerful tool for the identification of organic materials. The development of Fourier transform infrared (FTIR) spectroscopy has introduced a popular method for the quantitative analysis of complex mixtures, as well as for the investigation of surface and interfacial phenomena.

KEY WORDS- IR, FTIR

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INTRODUCTION

Infrared spectroscopy (IR spectroscopy or vibrational spectroscopy) is the measurement of the interaction of infrared radiation with matter by absorption, emission, or reflection. It is used to study and identify chemical substances or functional groups in solid, liquid, or gaseous forms. The method or technique of infrared spectroscopy is conducted with an instrument called an infrared spectrometer (or spectrophotometer) which produces an infrared spectrum. An IR spectrum can be visualized in a graph of infrared light absorbance (or transmittance) on the vertical axis v/s frequency or wavelength on the horizontal axis. Typical units of frequency used in IR spectra are reciprocal centimetres (sometimes called wave numbers), with the symbol cm–1. Units of IR wavelength are commonly given in micrometres (formerly called "microns"), symbol µm, which are related to wave numbers in a reciprocal way. A common laboratory instrument that uses this technique is a Fourier transform infrared (FTIR) spectroscopy.

Infrared (IR) radiation refers broadly to that part of the electromagnetic spectrum between the visible and microwave region. Of greatest practical use to the organic chemist is the limited portion between 4000 and 400cm -1. There has been sum interest in the near-IR (14,290-4000cm-1) and the far-IR region (700-200cm-1)

Although the IR spectrum is characteristics of the entire molecule, it is through that certain groups of atoms give rise to bands at or near the same frequency regard less of the structure of the rest of the molecule. It is the persistence of these characteristics band that permits the chemist to obtain useful structural information by simple inspection and reference to generalized charts of characteristics group frequencies.

HISTORY

Chemical IR spectroscopy was emerged as a science in 1800 by Sir William Herschel.

Michelson invented interferometer in 1881.

Infrared spectrometers have been commercially available since the 1940s.

At that time, the instruments relied on prisms to act as dispersive elements, but by the mid 1950s, diffraction gratings had been introduced into dispersive machines. The most significant advances in infrared spectroscopy, however ,have come about as a result of the introduction of Fourier-transform spectrometers. In 1960 Cooley -Turkey

developed an algorithm which quickly does a Fourier transform .This type of instrument employs an interferometer and exploits the well-established mathematical process of Fourier-transformation.

PRINCIPLE

Infrared radiation of frequencies less than about 100cm-1 is absorbed and converted by an organic molecule into energy monocular rotation. These absorptions is quantized; thus a molecular rotation spectrum consist discrete lines.

IR radiation in the range from about 10000 -100cm-1 is absorbed and converted by an organic molecule into energy of molecular vibration. This absorption is also quantized, but vibration spectra appear as bands rather than as lines because a single vibrational energy change is accompanied by a number of rotational energy changes. It is with these vibrationalrotational band, particularly those occurring between 4000 and 400cm-1. The frequency or wavelength of absorption depends on the relative masses of the atoms, the force constants of the bonds, and the geometry of the atoms.

This technique is based upon the simple fact that a chemical substance show marked selective absorption in the infrared region .after absorption of IR radiation , the molecule of the chemical substance vibrates at many rates of vibration, giving rise to close packed absorption bands ,called an IR absorption spectrum which may extend over a wide wavelength range. Various bands will be present in the IR spectrum which will corresponding to the characteristic functional group and bond present in the chemical substance. Thus, an IR spectrum of a chemical substance is a fingerprint for its identifications.



Frequency, v (nu), is the number of wave cycles that pass through a point in one second. It is measured in Hz, where 1 Hz = 1 cycle/sec. Wavelength, λ (lambda), is the length of one complete wave cycle. It is often measured in cm (centimetres). Wavelength and frequency are inversely related:

 $v = c/\lambda$ and $\lambda = c/v$

where c is the speed of light, 3 x 1010 cm/sec

Energy is related to wavelength and frequency by the following formulas:

 $E = h v = h c/\lambda$

where h = Planck's constant, 6.6 x 10–34 joules-sec

Note that energy is directly proportional to frequency and inversely proportional to wavelength.

The IR region is divided into three regions: the near, mid, and far IR. The mid IR region is of greatest practical use to the organic chemist. This is the region of wavelengths between 3 x10⁻⁴ and 3x 10⁻³ cm. Chemists prefer to work with numbers which are easy to write; therefore, IR spectra are sometimes reported in μ m, although another unit, v (nu bar or wavenumber), is currently preferred.

A wavenumber is the inverse of the wavelength in cm:

$$v^{--} = 1/\lambda$$

where v is in units of cm–1, λ is in units of cm and now;

E = h c v

In wavenumbers, the mid IR range is 4000–400 cm–1. An increase inwavenumber corresponds to an increase in energy.

Infrared radiation is absorbed by organic molecules and converted into energy of molecular vibration. In IR spectroscopy, an organic molecule is exposed to infrared radiation. When the radiant energy matches the energy of a specific molecular vibration, absorption occurs. The wavenumber, plotted on the X-axis, is proportional to energy; therefore, the highest energy vibrations are on the left. The percent transmittance (%T) is plotted on the Y-axis. An absorption of radiant energy is therefore represented by a "trough" in the curve: zero transmittance corresponds to 100% absorption of light at that wavelength.

Band intensities in IR spectrum may be expressed either as transmittance (T), or absorbance (A). transmittance is defined as the ratio of radiant power transmitted by a sample

to the radiant power incident on the sample. On the other hand, absorbance is defined as the logarithm, to the base, 10, of the reciprocal of transmittance, i.e.,

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

RANGE OF INFRARED REGIONS

| Region | wavel | ength (λ), μm | wavenumbers (v^{-}) |
|--------------------------|-------------|---------------|--|
| frequencies | | | |
| | | cm^{-1} | (<i>v</i>), Hz |
| Near 10 ¹⁴ | 0.78 to 2.5 | 12800 to 4000 | 3.8×10^{14} to 1.2×10^{1 |
| Middle 10 ¹² | 2.5 to 50 | 4000 to 200 | $1.2 \text{ x } 10^{14} \text{ to } 6.0 \text{ x}$ |
| Far 10 ¹¹ | 50 to 1000 | 200 to 10 | 6.0×10^{12} to 3.0×10^{1 |
| Most used | 2.5 to 15 | 4000 to 670 | $1.2 \ge 10^{14}$ to $2.0 \ge 10^{13}$ |

Near-Infrared Region

- In the near-infrared (NIR) region, which meets the visible region at about 12,500cm⁻¹ (0.8micrometer) and extend to about 4000cm⁻¹ (2.50micrometer), there are many absorption band that result from harmonic overtones of fundamental and combination band often associated with hydrogen atoms.
- ✤ The first overtones of the O-H and N-H stretching vibration near 7140cm⁻¹ and 6667cm⁻¹ respectively, and combination band that result from the C-H stretching and deformation vibration of alkyl group at 4548cm⁻¹ and 3850cm⁻¹.
- The absorptivity of near infrared bands is from 10-1000 times less than that of mid infrared bands.
- Thicker sample layer (0.5-10mm) compensates for this smaller molar absorptivity. Because the absorptivity is so low, the NIR beam penetrate deeper into a sample in reflectance techniques, giving a more representative analysis.
- Near infrared spectroscopy is valuable tool for the analyzing mixture of the aromatic amines.

- Primary aromatic amines are characterised by two relatively intense absorption band near 1.97 and 1.49μm.
 - The band at 1.97µm is combination of N-H bending and stretching modes.
 - 1.49µm is the first over tone of the symmetric N-H stretching vibrations.
- Secondary amines exhibit an over tone band but do not absorb appreciably in the combination region. These difference in absorption provide the basic for the rapid quantitative analytical methods. The analyses are normally carried out on 1% solutions in CCl₄ using 10-cm cells. Background correction are obtained at 1.575 and 1.915µm.
- Tertiary amine does not exhibit appreciable absorption at either wavelength. The overtone and combination bands of aliphatic amines are shifted to about 1.525and 2.000µm respectively.
- Near infrared reflectance spectra find wide acceptance in the food and grain industry for the determination of protein, fat, moisture, sugar, oils, iodine number etc.
- NIR reflectance spectra have also been used for the determination of the substance in wood, components of polymer, and even geological exploration from aircraft. The intensities are weak but measurable and reproducible.

Mid -infrared region

- This region is divided into,
 - 1. Group frequency region, 4000-1300cm⁻¹(2.50-7.69μm).
 - 2. Fingerprint region, 1300-650cm⁻¹(7.69-15.38µm).
- In the group frequency region the principle absorption bands are assigned to vibration units consisting of only two atoms of a molecule that is, units that are more or less dependent on only the functional group that gives the absorption and not on the complete molecular structure. Structural influence does reveal themselves, however, as significant shift from one compound to another.
- The C-H stretching frequencies are especially helpful in establishing the type of compound present, for example,

 $\# C \equiv C-H$ occur around 3300cm⁻¹(3.03µm)

aromatic and unsaturated compounds around 3000-3100 cm⁻¹(3.33-3.23 µm)

Aliphatic compound at 3000-2800 cm⁻¹(3.33-3.57 µm)

- The intermediate frequency range ,2500-1540cm⁻¹ is often called the unsaturated region. Triple bonds, and very little else, appear from 2500-2000cm⁻¹. Double bond frequencies fall in the region from 2000-1540cm⁻¹.
- ✤ By judicious application of accumulated empirical data, it is possible to distinguish among C=O, C=C, C=N, N=O, and S=O bands.
- The major factors in the spectrum between 1300 and 650cm⁻¹ are single bond stretching frequencies and bending vibration of polyatomic system that involve motions of bonds linking a substituent group to the remainder of the molecule. this is the fingerprint region.

Far infrared region

- The region 667-10cm⁻¹(15.0-1000μm) contains the bending vibration of carbon, nitrogen, oxygen and fluorine with atom heavier than mass 19, and additional bending motions in cyclic or unsaturated systems.
- The low frequency molecular vibration in the far infrared are particularly sensitive to changes in the overall structure of the molecule; thus, the far infrared bands often differ in a predictable manner for different isomeric forms of the same basic compound.
- The infrared frequency of the organometallic compounds is often sensitive to the metal ion or atom.
- ✤ This region mainly used for the study of the organometallic or inorganic compounds.

MOLECULAR VIBRATIONS

The relative position of atoms in a molecule are not fixed but instead fluctuate continuously because of a multitude of different types of vibrations and rotations about the bonds in the molecules. For a simple diatomic or triatomic molecule, it is easy to define the number and nature of such vibrations and relate these to energies of absorption. An analysis of these kind becomes difficult if not impossible for molecule made up of many atoms. Not only do large molecule have a large no. of vibrating centers, but also interactions among several centers can occur and must be considered for a complete analysis.

Vibration falls into two categories,

- Stretching vibration.
- Bending vibration.

Stretching vibration: A stretching vibration involves a continuous change in the interatomic distance along the axis of the bond between two atoms.

a). Symmetric stretching

The atoms of a molecule either move away or towards the central atom, but in the same direction.

b) Asymmetrical stretching

One atom approach towards the central atom which other departs from it..

Bending vibration : They involve the movement of atoms which are attached to a common central atom, such that there is change in the bond axis and bond angle of each individual atom without change in their bond length.

- Bending vibrations generally required less energy and occur at longer wavelength than stretching vibration.
- Bending vibrations are of two types:
 - 1. In plane bending
 - 2. Out plane bending

a) In plane bending vibration

Rocking: in plane bending of an atom occur where in they swing back and forth with respect to central atom.

Scissoring: in the plane bending of atoms occur where in they move back and forth that is, theyapproach to each other.

b) Out plane blending :

Wagging: two atoms oscillate up and below the plane with respect to central atom.

Twisting: one of the atoms moved up the plane while other down the pane with respect to the central atom.

INSTRUMENTATION OF INFRARED (IR) SPECTROSCOPY

The usual optical materials, glass or quarts absorb strongly in the infrared region consequently the apparatus for measuring infrared spectra is appreciably different from that for the visible ultraviolet regions. The main part of an IR spectrometer are as follows

- IR radiation sources
- Monochromators.

- Sample cells and sampling of substances.
- Detectors.

The IR Radiation Sources.

In common with other types of absorption spectrometers, infrared instruments require a source of radiant energy which provides a means for isolation narrow frequency bands. The radiation source must emit IR radiation which must be

- (i) Intensive enough for detection
- (ii) Steady
- (iii) Extend over the desired wavelength

Although these radiations are continuous, only selected frequencies will be absorbed by the sample. The various popular sources of IR radiations are:

(a)Incandescent lamp: In the near infrared instruments an ordinary incandescent lamp is generally used. However, this fails in the far infrared because is it glass enclosed and has low spectral emissivity.

(b)Nernst Glower: It consists of a hollow rod which is about 2mm in diameter and 30mm in length. The glower composed of rare earth oxides as zirconia, yttria and thoria.

•Nernst glower is non- conducting at room temperature and must be heated by external means to bring it to a conducting state. Glower is generally heated temperature between 1000 to 18000C. It provides maximum radiation at about 7100 cm-1 (1.4μ).

•The main disadvantage Nernst glower is that is emit IR radiation over wide wavelength range; the intensity of radiation remains steady and constant over long periods of time.

• One main disadvantage of Nernst is its frequent mechanical failure. Another disadvantage is that its energy also concentrated in the near infrared regions of the spectra.

(c) Globar source: It is a rod of sintered silicon carbide which is about 50mm in the length and 4mm in diameter. When it is heated to a temperature between 1300 and 17000C, it strongly emits radiation in the IR region. It emits maximum radiation at 5200 cm-1.

•Unlike the Nernst glower, it is self-starting. As its temperature coefficient positive, it have been conveniently controlled with variable transformer.

•Unlike the Nernst glower, it is more satisfactory, for it work at wavelengths longer than 650 cm-1 (0.15µ).

•The main disadvantage is that it is a less intense source than the Nernst glower.

(d)Mercury Arc: In the far infrared region (wave number <200 cm-1) the sources described above lose their effectiveness and special high-pressure mercury arc lamp are used. Beckman devised the quartz mercury lamps for the same region in a unique manner. At the shorter wavelengths, the heated quartz envelop emits the radiation whereas at longer wavelengths the mercury plasma provides radiation through the quartz.

Monochromators:

The radiation source emits radiation of various frequencies. As the sample in IR spectroscopy absorbs only at certain frequencies, it therefore becomes necessary to select desired frequencies from the radiation source and reject the radiations of other frequencies. This selection has been achieved by means of monochromators which are mainly of two types:

a.PrismMonochromator: Any prism used as a dispersive element must be constructed of materials (such as various metal halide salts) which transmit in the infrared. While glass and quartz were utilized in the visible and ultraviolet, they absorb and are unsatisfactory in the infrared. Because of its high dispersion in region of 4 to 15μ m, a region which is of special importance for functional group student, sodium chloride is probably the most common prism salt. It is unfortunate that many of these salt materials are subject to mechanical and thermal instability and/or water solubility. Protection against damage must be continuously exercised.

Single Pass Monochromators

The sample is kept at or near the focus of the beam, just before the entrance slit 'A' to the monochromator. The radiation from the source after passing through the sample and entrance slit, strikes the off-axis parabolic Littrow mirror B which render the radiation parallel and sends it to the prism C. The dispersed radiation after reflecting from a plane. Mirror D returns through which it finally passes into the detector section.

Double Pass Monochromators

The double pass monochromator produces more resolution than themonochromator in the radiation, before in finally passes on the detector. In both mono-pass and double-pass monochromators, sodium chloride (rock-salt) prism in employed for the entire region from 4000 to 650cm-2 (2.5 to 15.4 μ) Prism of lithium fluoride or calcium fluoride give more resolution in the region where the significant stretching vibration are located.

b.Grating Monochromator: If a prism in a prism monochromator is replaced by grating higher dispersion can be achieved. Reflection gratings offer linear dispersion and may be constructed from a wide variety of materials. Several getting, each with different ruling (lines/cm) are necessary to cover the wide wavelength (energy) range associated with infrared radiation. Various combinations transmission or interference filter with gratings, or filters without gratings, are utilized.

The grating is essentially a series of parallel straight lines cut into a plane surface. Dispersion by a grating follows the law of diffraction. It follows the following mathematical relation.

$$n \lambda = d (\sin i \pm \sin 0)$$

When n is the order (a whole number), λ the wavelength of the radiation, d the distance between grooves, i the angle of incidence of beam of IR radiation and 0 the angle of dispersion of light of wavelength.

- For radiation of different wavelengths (λ), the angle of dispersion (θ) is different. At a grating separation of light occurs because light of different wavelengths is different angles.
- Grating monochromator possesses the following advantages over prism Monochromator :
- Grating can be made with materials aluminium which are not attacked by moisture. On the other hand, metal salt prisms are subject to etching from atmosphere moisture.
- Grating monochromators can be used over considerable wavelength ranges.
- A getting is generally used in combination with is small prism which acts an order sorter sometimes filter transparent over limited wavelength can be used in combination with gratings.

Sample cells and sampling of substances.

As infrared spectroscopy has been used for the characterization of solid, liquid or gas samples, it is evident that samples of different phases have to be handled. but these sample must be treated differently. However, the only common point to the sampling of different phases is that material containing the sample must be transparent to IR radiation. This condition restricts our selection to only certain salts like NaCI or KBr. However, a final choice of salt will depend on the wavelength range to be studied

a. Sampling of solids

Four techniques are generally employed for preparing solid samples. these are:

Solid Run-in solution

Solid may also be dissolved in an non-aqueous solvent provided there is non chemical interaction with the solvent and also provided the solvent does not absorb in the studied range. A drop of the solution is placed on a alkali metal disk and the the solvent allowed to evaporate, leaving a thin film of the solute, or the entire solution is placed in a liquid sample cell. If the solution of solid can be prepared in a liquid sample cell. If the solution of solid can be prepared in a suitable solvent, then the solution is run in one of the cells for liquids. But this method cannot be used for all solid because suitable solvents are limited in number and there is no single solvent which is transparent throughout the IR region. When the investigating solids are in solutions, the absorption due to solvent has to be compensated by keeping the solvent in a cell of same thickness as that containing the sample, in the path of the reference beam of double -beam spectrometer.

Solid Films:

If a solid is amorphous in nature the sample is deposited on the surface of KBr or NaCI cell by evaporation of a solution of the solid. This technique is useful for rapid qualitative analysis but becomes useless for carrying out quantitative analysis.

Mull technique

In this technique, the finely ground solid sample is mixed with Nujol (mineral oil) to make a thick paste which is then made to spread between IR transmitting windows. This is then mounted in a path of infrared beam and the spectrum is run. Although Nujol is transparent throughout IR region yet it has the disadvantage that it has the absorption maxima at 2915, 1462, 1376 and 719 cm⁻¹. When IR spectrum of solid sample is taken in Nujol mull,

absorption bands of the sample that happen to coincide with the absorption bands of the

Nujol mull will be hidden, but other will be clearly seen in the IR spectrum. The solid sample in the Nujol has to be used in combination with hexachlorobutadiene which absorbs in the regions 1630-1510, 1200-1140 and 1010-760 cm⁻¹. As the absorption bands of Nujol mull and hexachlorobutadiene appear in the different regions, their use in combination permits the recording of IR spectrum.

This method is good for qualitative analysis but not for quantitative analysis.





In this technique a small amount of finely ground solid sample is intimatelymixed with about 100 times its weight of powdered potassium bromide. The finely ground mixture is then passed under very high pressure in a press (at least 25,000 p sig) to form a small pellet (about 1-2 mm thick and 1 cm in diameter). The resulting pellet is transparent to IR radiation and is run as such.A device for pressing the

mixture of KBr and solid sample to form a pellet . The powder (KBr + sample) is introduced as shown, then the upper screw A' is tightened until the powder is compressed into a thin disc. After compressing the sample, one removes the bolts (A and A) and places the steel cylinder with the sample disc inside it in the path of the beam of infrared spectrometer and a "blank' potassium bromide pellet of identical A' thickness is kept in the path of the reference Fig. 3.12: Device for processing potassium bromide discs. beam. An advantage of this method over Nuj Mull method is that the use of KBr eliminates the problem of bands which appear in the IR spectrum due to the mulling agent. In this case, no such bands appear. Other advantages of this method over the Nujol method are :

1. KBr pellets can be stored for long periods of time.

2. As the concentration of sample can be suitably adjusted in the pellets, it can be used for quantitative analysis.

3. The resolution of the spectrum in the KBr is superior to that obtained with mulls. The pellet technique has a number of disadvantages also such as:

- It always has a band at 3450 cm, from the OH group of moisture present (always) in the simple. Thus, care must be observed in investigations concerning the region of the OH band in the sample.
- The high pressure involved during the formation of pellets may bring about polymorphic changes in crystallinity in the samples, (specially inorganic complexes) which may cause complications in IR spectrum. In some cases, even substitution of the legend by bromide may be possible in inorganic complexes.
- This method is not successful for some polymers which are difficult to grind with KBr. From the above discussion, one may draw the important conclusion that one may employ the Nujol method for running crystalline compounds (including complexes) in the solid state and may reserve the KBr pellet method for remaining solid samples.

b. Sampling of Liquids: Samples that are liquids at room temperature are usually put frequently with no preparation, into rectangular cells made of NaCI, KBr or ThBr and their IR spectra are obtained directly. The sample thickness should be so selected that the transmittance lies between 15 and 20 percent. For most liquids introduction this will represent a thin layer of 0.01-0.05 mm in thickness.



If a cell possesses good quality windows, flat and parallel, its thickness, 1. in cm can be calculated from the following equation :

$2t = N/w_1 - w_2$

where N is the number of fringes between wave numbers w, and w_{2} .

For double-beam work, "matched cells" are generally employed. One cell will contain the sample while the other will have a solvent used in the sample. Matched cells must have same thickness. All cells should be protected from moisture because they dissolve in water. For

similar reasons organic liquid samples must be dried before pouring into cells. But one seldom be really sure of the thickness of an infrared cell unless it is new and this is one reason that quantitative analysis in the infrared is less precise than in the visible or ultraviolet region.

c. Sampling of Gases.

The gas sample cell is similar to the cell for liquid samples inasmuch as the surfaces in the light path are made of KBr, NaCI, and so on. To compensate for the small number of molecules of a sample that is contained in a gas, however, the cells are larger; usually they are about 10 cm long, but they may be up to 1 m long. Multiple reflections can be used to make the effective path length as long as 40 m, so that constituents of the gas, can be determined.

The gas must not react with the cell windows or the reflecting surfaces. Gas analyses are performed with IR, but the method is not commonly used because of its lack of sensitivity, Moisture must be avoided. Its strong absorption bands at 3.710 cm and 1625 cm- may interfere in the analysis. In addition, the windows and other instrument components which are constructed of soluble, salts may be damaged.

Detectors.

Bolometer:

A bolometer usually consists of a thin metal conductor. When radiation, such as IR, falls on this conductor, its temperature changes. As the resistance of a metallic conductor changes with temperature, the degree of change in resistance is regarded as measure of the amount of radiation that has fallen on the bolometerA . bolometer is made one arm of the Wheatstone bridge. A similar strip of metal is used the balancing arm of the bridge. This strip is not exposed to IR radiation. When no radiation falls on the bolometer, the bridge remains balanced If IR radiation falls on the bolometer, the bridge becomes unbalanced due to change in the electrical resistance which causes a current to flow through the galvanometer (G). The amount of current flowing through the galvanometer is a measure of the intensity of the



radiation falling on the detector. The response time for a bolometer is 4 m sec.

Thermocouple:

The Thermocouple detector is based upon the fact that an electrical current will flow when two dissimilar metal wires are connected together at both ends and a temperature differential exists between the two ends The end exposed to the infrared radiation is called the "hot junction". To increase the energy gathering efficiency, it is usually a "black body." The other connection, the "cold junction," is thermally insulated and carefully screened from stray light. The electricity which is directly proportional to the energy differential between the two connections.If two welded joints are kept at different temperatures, a small electrical potential is developed between the joints. A thermocouple is closed in an evacuated steel casing With a KBr (or Csl) window to avoid losses of energy by convection. In the IR spectroscopy, one welded joint (called cold junction) is kept at a constant temperature and is not exposed to IR radiation, but the other welded joint called hot junction is exposed to the IR radiation which



temperature of the junction. difference between the two potential difference which IR radiation falls on the hot

junction. The response time of a thermocouple is about 60 m sec.

Thermistors :

A thermistor is made of a fused mixture of metal oxides. As the temperature of the mixture increases, its electrical resistance decreases (as opposed to the bolometer). This relationship between temperature and electrical resistance allows thermistors to be used as IR detectors in the same way as bolometers. The thermistor typically changes resistance by about 5% per "C. Its response time also slow.

Golay Cell : It consists of a small metal cylinder which is closed by a blackened metal plate at one end and by a flexible metalized diaphragm at the other. After filling the cylinder with xenon, it is sealed. When I radiation is allowed to fall on the blackened metal plate, it heats thegas which causes it to expand. The resulting pressure increase in the gas deforms the metallized diaphragm which separates two chambers. Light from a lamp is made to fall on the diaphragm which reflects the light on to a photocell. Motion of the diaphragm changes the output of cell.



Photoconductivity cell:

This is a non-thermal detector of greater sensitivity. It consists of a thin layer of lead sulphide or lead telluride supported on glass and enclosed into an evacuated glass envelope. When IR radiation is focused on lead sulphide or lead telluride, its conductance increases and causes more current to flow, Response time is 0.5 msec.Photoconductivity, cell has high sensitivity and good speed of response in infrared detection, but it suffers from many practical disadvantages. When operated at room temperature, it has a very restricted range, usually limited to the near infrared. The range can be broadened by drastic cooling.

Semiconductor Detectors:

Semiconductors are materials that are insulators when no radiation falls on them, but which become conductors when radiation falls on them. Exposure to radiation causes a very rapid change in their electrical resistance and therefore a very rapid response to the IR signal. The basic concept behind this system is that an IR photon displaces an electron in the detector, changing conductivity greatly.materials, such as each telluride, indium antimonide, and germanium doped with copper or mercury, have been used as semiconductor detectors. In general, a semiconductor detector is fabricated with the semiconductor material deposited on glass in a sealed, evacuated envelope. Exposure to radiation causes a rapid change in the material conductivity. The response time of this detector is the time required to change the semiconductor from an insulator to a conductor, which is frequently as short as 1 sec. Semiconductor detectors are very sensitive, very fast, and are finding wide acceptance in the field of IR spectroscopy.



Pyroelectric Detector:

A dielectric placed in an electrostatic field becomes polarized, depending on the dielectric constant. If the field is removed, the polarization usually disappears, except with ferroelectric compounds, which retain a strong residual polarization. Sometimes their residual polarization is temperature sensitive. Such materials are pyroelectric. pyroelectric detector consists of a thin dielectric flake on the face of which an electrostatic charge A appears when the temperature of the flake changes. This happens upon exposure to infrared dilation Electrodes attached to the flake collect the charge, creating a voltage. A pyroelectric flake is cut from a single crystal and is very small. It varies in size from about 0.25 to 12.0 mm². The radiation from the IR instrument must be focused on this small flake for operation, which is often demanding and never convenient.

The most common pyroelectric is triglyceride sulphate (TGS); however its response rapidly deteriorates above 45° C and is lost above the Curie point (49° C). For this reason, it is usually cooled in liquid N₂ .Recently deuterated TGS detectors have become available which can be used at room temperature. They are the detector of choice with Fourier transform IR, superseding Golay detectors. Their response is fast, so they can be used for multiplex scanning, a process often employed in Fourier transform in IR.



FOURIER TRANSFORM SPECTROMETERS

In a Michelson interferometer adapted for FTIR, light from the polychromatic infrared source, approximately a black-body radiator, is collimated and directed to a beam splitter. Ideally 50% of the light is refracted towards the fixed mirror and 50% is transmitted towards the moving mirror. Light is reflected from the two mirrors back to the beam splitter and some fraction of the original light passes into the sample compartment. There, the light is focused

on the sample. On leaving the sample compartment the light is refocused on to the detector. The difference in optical path length between the two arms to the interferometer is known as the retardation or optical path difference (OPD). An interferogram is obtained by varying the retardation and recording the signal from the detector for various values of the retardation. The form of the interferogram when no sample is present depends on factors such as the variation of source intensity and splitter efficiency with wavelength. This results in a maximum at zero retardation, when there is constructive interference at all wavelengths, followed by series of "wiggles". The position of zero retardation is determined accurately by finding the point of maximum intensity in the interferogram. When a sample is present the background interferogram is modulated by the presence of absorption bands in the sample.

Commercial spectrometers use Michelson interferometers with a variety of scanning mechanisms to generate the path difference. Common to all these arrangements is the need to ensure that the two beams recombine exactly as the system scans. The simplest systems have a plane mirror that moves linearly to vary the path of one beam. In this arrangement the moving mirror must not tilt or wobble as this would affect how the beams overlap as they recombine. Some systems incorporate a compensating mechanism that automatically adjusts the orientation of one mirror to maintain the alignment.

When FTIR spectrometers first appeared in the marketplace, they were bulky, expensive (>\$100,000), and required frequent mechanical adjustments. For these reasons, their use was limited to special applications where their unique characteristics (speed, high resolution, sensitivity, and unparalleled wavelength precision and accuracy) were essential. FT instruments have now been reduced to benchtop size and have become reliable and easy to maintain. Furthermore, the price of simpler models has been reduced to the point where they are competitive with all but the simplest dispersive instruments (--\$15,000 and more). For these reasons, FT instruments have largely displaced dispersive instruments in the laboratory.

Components of FT Instruments

The majority of commercially available FTIR instruments are based on the Michelson interferometer, although other types of optical systems are also encountered. We shall consider the Michelson design only.Components are,

IR sources

FTIR spectrometers are mostly used for measurements in the mid and near IR regions. For the mid-IR region, 2–25 μ m (5,000–400 ^{cm–1)}, the most common source is a silicon carbide element heated to about 1,200 K (Globar). The output is similar to a blackbody. Shorter wavelengths of the near-IR, 1–2.5 μ m (10,000–4,000 ^{cm–1}), require a higher temperature source, typically a tungsten-halogen lamp. The long wavelength output of these is limited to about 5 μ m (2,000 ^{cm–1}) by the absorption of the quartz envelope. For the far-IR, especially at wavelengths beyond 50 μ m (200 ^{cm–1}) a mercury discharge lamp gives higher output than a thermal source.

Detectors

Mid-IR spectrometers commonly use pyroelectric detectors that respond to changes in temperature as the intensity of IR radiation falling on them varies. The sensitive elements in these detectors are either deuterated triglycine sulphate (DTGS) or lithium tantalate (LiTaO3). Cooled photoelectric detectors are employed for situations requiring higher sensitivity or faster response. Liquid nitrogen cooled mercury cadmium telluride (MCT) detectors are the most widely used in the mid-IR.

Beam splitter

An ideal beam-splitter transmits and reflects 50% of the incident radiation. However, as any material has a limited range of optical transmittance, several beam-splitters may be used interchangeably to cover a wide spectral range. For the mid-IR region, the beam splitter is usually made of KBr with a germanium-based coating that makes it semi-reflective. KBr absorbs strongly at wavelengths beyond 25 μ m (400 cm–1) so CsI is sometimes used to extend the range to about 50 μ m (200 cm–1). ZnSe is an alternative where moisture vapor can be a problem but is limited to about 20 μ m (500 cm–1.).CaF2 is the usual material for the near-IR, being both harder and less sensitive to moisture than KBr but cannot be used beyond about 8 μ m (1,200 cm–1). In a simple Michelson interferometer one beam passes twice through the beam splitter but the other passes through only once. To correct for this an additional compensator plate of equal thickness is incorporated. Far-IR beam splitters are mostly based on polymer films and cover a limited wavelength range.

Attenuated total reflection (ATR):

- It is a sampling technique used in conjunction with infrared spectroscopy which enables samples to be examined directly in the solid or liquid state without further preparation.
- Light undergoes multiple internal reflections in the crystal of high refractive index, shown in yellow. The sample is in contact with the crystal.
- ATR uses a property of total internal reflection resulting in an evanescent wave. A beam of infrared light is passed through the ATR crystal in such a way that it reflects at least once off the internal surface in contact with the sample.
- This reflection forms the evanescent wave which extends into the sample. The penetration depth into the sample is typically between 0.5 and 2 micrometres, with the exact value determined by the wavelength of light, the angle of incidence and the indices of refraction for the ATR crystal and the medium being probed.
- The number of reflections may be varied by varying the angle of incidence.
- The beam is then collected by a detector as it exits the crystal. Most modern infrared spectrometers can be converted to characterise samples via ATR by mounting the ATR accessory in the spectrometer's sample compartment.
- The accessibility, rapid sample turnaround and ease of ATR-FTIR has led to substantial use by the scientific community.
- This evanescent effect only works if the crystal is made of an optical material with a higher refractive index than the sample being studied.

Otherwise, light is lost to the sample. In the case of a liquid sample, pouring a shallow amount over the surface of the crystal is sufficient. In the case of a solid sample, samples are firmly clamped to ensure good contact is made and to remove trapped air that would reduce signal intensity.

• The signal to noise ratio obtained depends on the number of reflections but also on the total length of the optical light path which dampens the intensity. Therefore, a general claim that more reflections give better sensitivity cannot be made.

Typical materials for ATR crystals include germanium, KRS-5 and zinc selenide, while silicon is ideal for use in the Far-IR region of the electromagnetic spectrum.

• The excellent mechanical properties of diamond make it an ideal material for ATR, particularly when studying very hard solids, although the broad diamond phonon band between 2600 and 1900 cm-1 significantly decreases signal to noise in this region.

• The shape of the crystal depends on the type of spectrometer and nature of the sample. With dispersive spectrometers, the crystal is a rectangular slab with chamfered edges,

seen in cross-Other geometries thin sheets.





section in the illustrations. use prisms, half-spheres, or

FTIR spectrometers can

be single-beam or double

beam instruments. the optics of a basic single-beam spectrometer, which sells in the range of \$15,000 to \$20,000. A typical procedure for deter mining transmittance or absorbance with this type of instrument is to first obtain a reference interferogram by scanning a reference (usually air) twenty or thirty times, coadding the data, and storing the results in the memory

of the instrument after transforming it sample is then radiation path and repeated. The ratio reference spectral



computer (usually to the spectrum). A inserted in the the process of sample and data is then

computed togive the transmittance at various frequencies. From this ratio the absorbance is calculated as a function of wavenumber. Ordinarily, modern IR sources and detectors are sufficiently stable so that reference spectra need to be obtained only occasionally.

A double-beam spectrometer is a mirrors directing the interferometer beam through the sample and reference cells are oscillated rapidly compared to the movement of the interferometer mirror so that sample and reference information can be obtained at each mirror position. The double-beam design compensates for source and detector drifts.

ADVANTAGES

Over most of the mid-IR spectral range, FT instruments have signal-to-noise ratios that are better than those of a good-quality dispersive instrument, usually by more than an order of magnitude. The enhanced signal-to-noise ratio can, of course, be traded for rapidscanning, with good spectra being attainable in a few seconds in most cases. Interferometric instruments are also characterized by high resolutions (<0.1 cm) and highly accurate and

A theoretical advantage of FT instruments is that their optics provide a much larger energy throughput (one to two orders of magnitude) than do dispersive instruments, which are limited in throughput by the need for narrow slit widths. The potential gain here, however, may be partially offset by the lower sensitivity of the fast-response detector required for the interferometric measurements. Finally, it should be noted that the interferometer is free from the problem ofstray radiation because each IR frequency is, in effect, chopped at a different frequency.

(1) very high-resolution work that is en countered with gaseous mixtures having complex spectra resulting from the superposition of vibrational and rotational bands.

(2) the study of samples with high absorbances.

(3) the study of substances with weak ab sorption bands (for example, the study of compounds that are chemisorbed on catalyst surfaces).

(4) investigations requiring fast scanning such as kinetic studies or detection of chromatographic effluents.

(5) collecting IR data from very small samples.

(6) obtaining re flection spectra.

5.INTERPRETATION OF IR SPECTROSCOPY



6.APPLICATION OF IR SPECTROSCOPY

Inorganic Complexes Introduction It is generally a difficult task to carry out the spectral analysis of complexes even if their structures are known. The main reasons for this are:

1. High Modes of Vibrations:

As complexes usually consist of not less than five atoms, it means that the minimum number of their normal modes of vibrations will be ten. In some cases, this value is even very large. For example, metal hexamine complexes consist of 25 atoms, so that they possess 69 normal modes of vibrations. Out of these, some will be infrared inactive and while some others will appear at an identical wave number, still leaving a large number of modes of vibration which give rise to a large number of bands in the IR spectra. It means that the IR spectra of the complexes are composite.

2.Lower Symmetry of Complexes:

Formation of mixed ligand and polynuclear complexes is generally accompanied by a decrease in their symmetry which still further increases the number of bands in their ir spectra.

3.Formation of Chelates:

When complexes involve chelate formation of relatively large molecules ,in their IR spectra a large number of new bands appear in their IR spectra which further complicates the interpretation of the complexes. From the above discussion it follows that the IR spectra of complexes are very complicated. In order to interpret their IR spectra, certain assumptions (never fully justified) are kept in mind which are as follow

- (i) Complex formation only affects slightly the vibrations of the ligand.
- (ii) The vibrations of a ligand do not undergo coupling (even if coupling is there, extent), with the vibrations of another ligand or with the skeletal vibrations.
- (iii) When a ligand is coordinated to a central atom, this should not change the symmetry of the ligand.

4. Miscellaneous Examples

The following are some important applications which give important clues to the structures of coordination compounds. This also includes an application which is used to detect the presence of an impurity in an organic compound

(a)Determination of Purity:

Infrared spectroscopy has been used for establishing the purity of compound. Whenever a compound is having an impurity, it reduces the sharpness of individual bands, causes the appearances of extra bands and a general blurring of the spectrum. Conditions for detection of impurities are most favourable when the impurity possesses strong bands in that IR region where the main components do

not show strong bands in that region. For example, the small quantities of ketone in a hydrocarbon can be detected because the latter does not have practically any absorption band near 1720 cm-1 which is a characteristic frequency of carbonyl group. In spectroscopy method of detection of impurities has been widely used for production control of many chemicals on an industrial scale.

(b)Shape of Symmetry of a Molecule:

Infrared spectra can be used to deduce the shape or symmetry of a molecule. This can be illustrated by considering the example of nitrogen dioxide. If NO, is linear, only two bands should be active in its IR spectrum (cf Co,) and if bent, three bands should be IR active (of H,O). But the infrared spectrum of NO, gives three peaks at 750, 1323 and 1616 cm which shows that it is a bent and not linear molecule. Arguments such as this can be extended and applied to large molecules which possess various types of symmetry. For example, the IR spectra have been used to elucidate the structures of XeF, XeF, and XeF, which are linear, square planar and octahedral structure respectively

(c) Presence of Water in a Sample:

If a sample contains lattice water, three characteristic bands, one in the 3600 to 3200 cm region, second in the 1650 cm region and theIR spectrum will contain third in the 600-300 cm region. On the other hand, if the water is coordinated to a metal ion, anadditional band in the 880-650 cm region is observed An interesting examples of detection of watermolecule is in the clathrate compound N (CN), NHCH, H,0. Although IR spectrum clearly showed the presence of water, it could not be detected in a single crystal X-ray study of this compound.

(d)Measurement of Paints and Varnishes.

Frequently, paints and varnishes are measured by reflectance analysis, a process where in the sample is irradiated with IR light and the reflected light is introduced into an IR instrument. The paint, or other reflecting surface, absorbs radiation in the same manner as a traversed solution. Its IR spectrum can be obtained from the reflection. This technique can be used to identify the paint on appliances or automobiles without destroying the surface. Scraps of paint from automobiles involved in wrecks can be examined. From the data obtained the make and year of the car can be determined.

(e) Examination of Old Paintings and Artifacts.

Another interesting application is the examination of old paintings and artifacts. It is possible to identify the varnish used on the painting and the textile comprising the canvas, as well as the pigments in the paint. From this information fake "masterpieces" can be detected. Modern paints use materials that were not available when many masterpieces were painted. The presence of new paints confirms that the painting must have been done recently. An expert fake uses "old" paint.

(f)In Industry:

In industry, IR spectroscopy has three important uses. First it Can be used to determine impurities in raw material. This is necessary to ensure good products. Second it can be used for quality control, that is, for continuously checking tie composition and the percent present of the required product. This is the cheapest way to produce satisfactory products. The third use is for the identification of materials made in industrial research laboratories, or of materials made by competitors.

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