INFRARED SPECTROSCOPY

Abstract

Infrared spectroscopy is a very important tool to identify the functional groups present in the organic molecules. It is a non-destructive method. The IR spectroscopy measures the absorption of electromagnetic radiation in infrared region by a sample placed in the path of light. The frequency at which absorption takes place will depends on the nature of the sample and thus it can be used to identify the nature of the sample. Unlike UV spectrum which consists of very few peaks this technique provides a spectrum containing large number of absorption bands from which more information can be derived about the structure of organic compounds. The IR spectroscopy covers the range 10cm^{-1} to 13,000cm^{-1}.

Keywords: Infrared spectroscopy, UV spectrum, vibrational frequency, Molecular vibrations

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I. PRINCIPLE AND THEORY

When a molecule is exposed to IR radiation then the atoms present in that molecule will undergo vibrational motions due to these vibrational motions, the molecule generate some frequency. This frequency is called vibrational frequency, when this freqency is equal to the frequency of the electrical component present in the electromagnetic radiation, then the molecules excites from ground state to higher vibrational energy states by absorbing electromagnetic radiation. Hence a peak is observed as spectrum. Since every vibrational state contains a no. Of rotational energy levels, the vibrational spectrum appears as bands instead of discrete lines. This is the principle of IR spectroscopy.

For a molecule to exhibit IR spectrum it should possess a finite dipole moment. The molecule with zero dipole moment is IR inactive. The range of IR radiation is classified into three different areas.

1. **Near IR:** The far IR region covers the radiation in the frequency range 10-200cm^{-1}. This region is useful for the analysis of molecules containing elements heavier than Fluorine.

2. **Far IR:** The mid IR region covers the radiation from 667-4000cm^{-1}. It is most frequently used IR spectral region i.e, most of the organic functional groups shows absorption in this region.

3. **Mid IR:** Therefore this mid IR region plays a very important role in IR spectroscopy.

The near IR region covers the radiation from 4000-13000cm^{-1}. This region is useful for quantitative analysis of materials.

The value of stretching vibrational frequency of a bond can be calculated by Hook's law, which is represented as

$$\upsilon = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$\bar{\upsilon} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \qquad \mu = \frac{M_1 M_2}{M_1 + M_2}$$

Where K is the force constant of the bond and μ is the reduced mass of the system.

From the eq. it is clear that as the force constant of the bond increases the frequency required for the vibration also increases i.e, for example among C-C, C=C, C=C the stretching frequency for C=C is very high when compared to other bonds. It is due to the fact that the strength of triple bond is very high when compared to double bond and single bond, hence C=C absorbs the radiation at higher frequency.

Similarly as the reduced mass increases the frequency of the absorption decreases. For example the –O-H stretching absorbs the radiation at high frequency when compared to C-C bond. It can be explained on the basis of smaller value of reduced mass for the –O-H when compared to C-C bond.

II. TYPES OF MOLECULAR VIBRATIONS

Generally the molecules undergo two types of vibrations. They are Bending vibrations and Stretching vibrations.

1. **Stretching Vibrations:** A stretching vibration is a rhythmical movement along the bond axis such that the interatomic distance is increasing or decreasing. These vibrations are further classified into two types,

    - **Symmetrical Stretching:** When the stretching and compression occur in a symmetrical fashion, it is called symmetric stretching vibration.
    - **Asymmetric Stretching:** When one bond is compressing while the other is stretching.

2. **Bending Vibrations:** A bending vibration involves the change in bond angles between bonds with a common atom, or the movement of a group of atoms with respect to the remainder of the molecule without movement of atoms in the group. These are further classified into four types,

    - **Scissoring:** Here two atoms joined to a central atom move toward and away from each other with the bending of the bond angle (In plane bending).
    - **Rocking:** Here the structural unit swings back and forth in the plane of the molecule (In plane bending).
    - **Wagging:** The structural unit swings back and forth out of the plane of the molecule (Out of plane bending).
    - **Twisting:** Here the structural units rotate about the bond which joints to the rest of the molecule (Out of plane bending).

III. THEORY OF IR

The infrared spectrum of a molecule results due to transition between two different vibrational energy levels. The vibrational motion of the molecule is similar to that of a simple harmonic oscillator. In such an oscillator the force tending to restore an atom to its original state is proportional to the displacement of the atoms from their original position. It is called Hook’s law ($F = -Kx$).

A chemical bond is considered as two balls attached to a spring. In the case of poly atomic molecules atoms having different masses are connected with a mechanical spring whose frequencies are proportional to the bonding forces of the chemical bonds. The vibrational energy of a chemical bond can be calculated by using the equation $E_{vib} = [V+1/2]h\upsilon$. Absorption of radiation with energy equal to the difference between two vibrational energy levels will cause a vibrational transition to occur. If a transition takes place from $\upsilon=0 \rightarrow 1$ state by absorption of radiation gives an intense band called fundamental band. If transition takes place from $\upsilon=0 \rightarrow 2$ then a weak bands called as overtones are observed.

Polyatomic molecules exhibit more than one fundamental vibrational absorption bands. The number of these fundamental bands are related to the degrees of freedom in a molecule, each atom has three degrees of freedom corresponding to three Cartesian coordinates[x,y,z] necessary to describe its position relative to other atoms in a molecule. A molecule having **N** no. of atoms will have **3N** degrees of freedom where N is no. of atoms present in the molecule.

3N degrees of freedom = Translational motion + Rotational motion + Vibrational motion.

i.e, a molecule having finite dimensions is made up of rotational, vibrational, and translational degrees of freedom. If we take a linear molecule it has three translational motions, two rotational motions and **3N-5** vibrational degrees of freedom. Out of these **N-1** stretching vibrations are possible (no. of bonds equal to N-1) and **2N-4** bending vibrations are possible.

In a nonlinear molecule system there are three translational motions, three rotational motions and **3N-6** vibrational degrees of freedom. Out of these vibrational motions there are **N-1** stretching vibrations are possible and **2N-5** bending vibrations are possible.

Ex:

1. **CO_2** here N=3
   Total degrees of freedom = 3N
   = 3x3 = 9
   Translational degrees of freedom = 3
   Rotational degrees of freedom = 2
   Vibrational degrees of freedom = 3N-5
   = 9-5 = 4
   Stretching vibrational modes = N-1
   = 3-1 = 2
   Bending vibrational modes = 2N-4
   = 2x3-4 = 2

2. **SO_2** here N=3
   Total degrees of freedom = 3N
   = 3x3 = 9
   Translational degrees of freedom = 3
   Rotational degrees of freedom = 3
   Vibrational degrees of freedom = 3N-6
   = 9-6 = 3
   Stretching vibrational modes = N-1
   = 3-1 = 2
   Bending vibrational modes = 2N-5
   = 2x3-5 = 1

IV. FACTORS AFFECTING VIBRATIONAL FREQUENCIES

The vibrational frequency of absorption can be calculated from Hook's law. It was found that the calculated value of frequency for a particular bond is different from the experimental value. It is due to the effect of neighbouring groups or neighbouring bonds present in the molecule. Due to the effect of neighbouring groups the frequency of absorption changes i.e, it is shifted either to high frequency side or to low frequency side. The shift in the frequency also occurs when the same compound is analysed in different states.

Generally there are four important factors that affect the vibrational frequencies in the IR spectroscopy. They are

- Coupled vibrations.
- Electronic effects.
- Bond angle.
- Hydrogen bonding.

1. **Coupled vibrations:** An isolated **C-H** bond exhibit only one stretching vibrational frequency but if we take **CH_2** group two absorptions are observed due to symmetric and asymmetric vibrations, in such cases the asymmetric vibrations influence the symmetric vibrations hence two bands are observed, one at high frequency side (asymmetric stretching) and other at low frequency side (symmetric stretching) i.e, the influence of the stretching frequency of one bond on the other are called “coupled vibrations”.

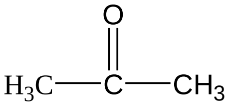
   Acid anhydrides shows two **C=O** stretching absorptions between 1850-1800 and 1790-1740cm^{-1}. These stretching absorptions are due to symmetric and asymmetric vibrational modes. In some cases the fundamental overlaps with overtone to give a new phenomenon called Fermi resonance. i.e, in such cases the transfer of energy takes place from fundamental to overtone and vice versa. In such cases two energy levels are produced which exhibit mixed characteristics in such a way that each level has partial fundamental and partial overtone characteristics. Hence this type of resonance will give a pair of transitions with equal intensities.

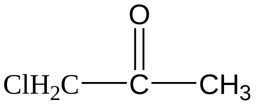
   This phenomenon was first observed by Fermi in **CO_2**. The **CO_2** molecule is linear and exhibit four fundamental vibrations. Out of these vibrations symmetric stretching vibrations are IR inactive. Since the change in dipole moment is zero. The asymmetric stretching mode produces a change in the dipole moment hence it is IR active. The absorption frequency of this molecule is observed at 2350cm^{-1}, which is greater than normal carbonyl stretching frequency. This difference in carbonyl absorption frequency is due to strong mechanical coupling. The two bending vibrations in **CO_2** are equivalent and absorbs at the same frequency 667.3cm^{-1}. The overtone is observed at 1334cm^{-1} i.e, due to Fermi resonance there is a shift in frequency of absorption towards high frequency side.

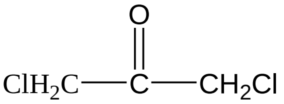
2. **Electronic effects:** The change in absorption frequencies for a particular group takes place when the substituents in the neighbourhood of that group changes. The shift in frequencies is due to same electronic effects which includes…

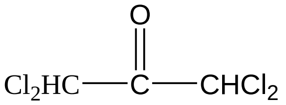
   - Inductive effect
   - Mesomeric effect
   - Space effect

     - **Inductive effect:** When an electronegative atom or group which causes **–I** effect is introduced into the molecule then the bond strength of the molecule increases i.e, the force constant increases, hence the frequency of absorption also increases. There fore a system with electronegative group shows absorption at high frequency side. For example let us consider the absorption frequencies of the following compounds.

Acetone(

$H_3C-\overset{\overset{O}{||}}{C}-CH_3$
) ------1715cm-1

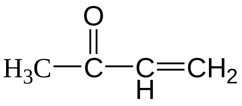
Chloro acetone(

$ClH_2C-\overset{\overset{O}{||}}{C}-CH_3$
) ------1725cm-1

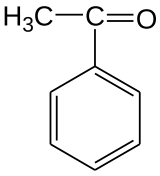
Dichloro acetone(

$ClH_2C-\overset{\overset{O}{||}}{C}-CH_2Cl$
) ------1740cm-1

Tetraichloro acetone(

$Cl_2HC-\overset{\overset{O}{||}}{C}-CHCl_2$
) ------1750cm-1

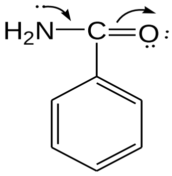
When a group exhibiting **+I** effect is introduced into the molecule then the weakening of bond takes place. Hence force constant is lowered and the wave number of absorption decreases. For example Formaldehyde and Acetaldehyde exhibit wave numbers at 1750cm^{-1} and 1745 cm^{-1}.

- **Mesomeric Effect:** This effect causes lengthening or weakening of bond leading to the lowering of absorption frequency. In most of the cases the mesomeric effect works along with inductive effect. In some cases inductive effect dominates the mesomeric effect. Consider the following compound

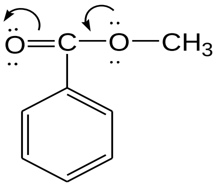
Methyl vinyl ketone----

$H_3C-\overset{\overset{O}{||}}{C}-\underset{H}{C}=CH_2$
------ν = 1706cm^{-1}

Acetophenone----

------ν = 1693cm-1

In both cases **–I** effect is dominated by the mesomeric effect and hence the absorption frequency decreases. In case, where the lone pair of electrons present on an atom is in conjugation with the double bond of a group then the availability of lone pair of electrons plays a very important role. Now let us consider the stretching frequencies of amides and esters,

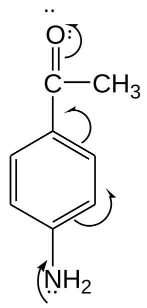


Benzamide
υ(C=O)=1693cm^{-1}

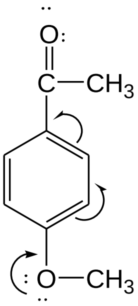


Phenyl Acetate
υ(C=O)=1730cm^{-1}

Since the nitrogen atom is less electronegative than oxygen atom the electron pair on nitrogen atom in amides is more labile (very reactive) and participate in conjugation. Due to greater extent of conjugation, the **C=O** absorption frequency is less in amides when compared to esters. Some of the examples are,



P-amino acetophenone
υ=1677cm-1

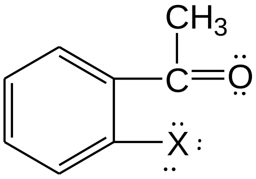


P-methoxy acetophenone
υ=1684cm-1

In **Para** substitution both mesomeric and inductive effects becomes very important and domination of one over the other will decide the frequency of absorption, but in **meta** substitution the inductive effect is taken into consideration

- **Space effect:** In **ortho** substituted compounds, the lone pair of electrons on two atoms influences each other through space, and changes the vibrational frequencies of both the groups. This effect is called Field or Space effect.

Let us take an example



The non bonding electrons present on oxygen atom and halogen atoms causes electrostatic repulsions. This results in a change in hybridisation of **C=O** and makes that group to go out of the plane of double bond, hence conjugation is diminished. Hence absorption occurs at high frequency side. Therefore substituted compounds **cis** isomer absorbs at high frequency than **trans** isomer.

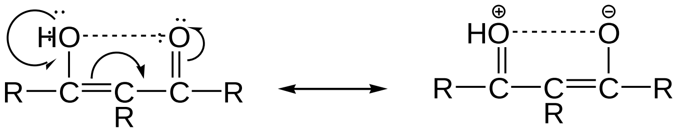
3. **Bond Angle:** It has been observed that the highest **C=O** stretching frequency is observed in strained cyclobutanone. This can be explained in terms of bond angle strain. The bond angle is less than 120^0 it leads to increase the S-character in **C=O** bond. Greater the S-character shortened the bond length between carbon and oxygen. Therefore the **C=O** bond stretching will appear at high frequency side. The bond angle is greater than 120^0, bond length between and oxygen increases, there by the frequency of absorption decreases.

4. **Hydrogen Bonding:** Hydrogen bonding will affect the stretching frequencies to a greater extent. Stronger the hydrogen bonding greater will be the shift in absorption towards high

frequency side. Generally bands due to intramolecular hydrogen bonds are sharp where as intermolecular hydrogen bonds gives rise to broad bands and depends on concentration, i.e, on dilution the intensity of intermolecular hydrogen bonds becomes independent of concentration.

The absorption frequency difference between free and a molecule exhibiting intra molecular hydrogen bonding is very small when compared to intermolecular hydrogen bonded molecules. For preparing the solution we have to use the solvents like **$CHCl_3$**, **CCl_4** and **CS_2** because solvents like acetone and benzene will influence the hydrogen bonding. Since nitrogen atom is less electronegative than oxygen atom, the hydrogen bonding in amines is excess than that of alcohols. There fore amines show N-H stretching at 3500cm^{-1} in solution phase while it shows the spectra at 3300cm^{-1}.

In enols and chelates, strong O-H stretching is observed due to resonance. Let us consider acetyl acetone.



The **OH** group involved in chelation gives raise a broad absorption between 3000cm^{-1}-2500cm^{-1}. The absorption frequency for **C=O** in enolic form occurs at 1630cm-1 and in keto form at 1725cm-1. Therefore due to the existence of hydrogen bonding in the molecule there is a change in absorption frequencies is observed.

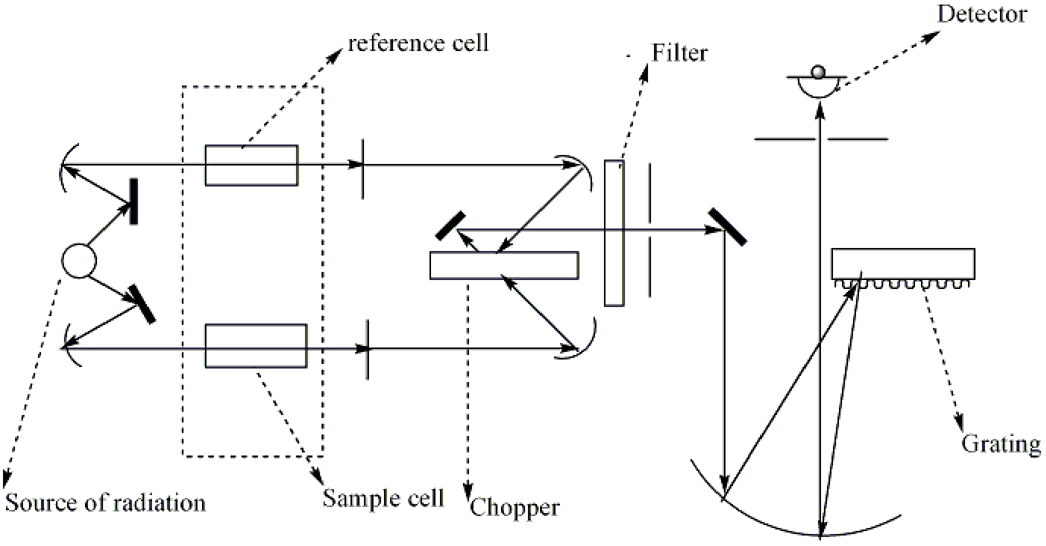
V. INSTRUMENTATION OF IR:

For measuring the IR radiation transmitted by a compound is measured with the help of an instrument called as spectrophotometer. The IR spectrophotometers are classified into two types,

1. Single beam IR spectrophotometer.
2. Double beam IR spectrophotometer.

Among these two spectrophotometers double beam spectrophotometers are most widely used for IR spectroscopy. The difference between UV-Visible spectrophotometer and IR spectrophotometer is the location of chemical sample. In IR spectrophotometer the sample is placed before the monochromator. This arrangement minimises the effect of stray and background radiation and protect the detector from any radiation not selected by the monochromator.

The schematic diagram of double beam IR spectrophotometer is shown as follows,



A double beam spectrophotometer is used to minimise the effect of absorption by atmospheric carbon dioxide and moisture, and to reduce the scattered radiation in this reference cell usually contains the solvent. The important parts in IR spectrophotometer are,

1. Source of radiation.
2. Monochromators.
3. Sample holder and sample preparation.
4. Detectors.

1. **Source of radiation:** IR radiation is produced by electrically heating a source, usually a Nernst glower which is heated to 1000-1800^{0}c are used as source of radiation. Nernst glowers are manufactured from a fused mixture of oxides of zirconium, yttrium and thorium moulded in the form of hollow rods 1-5mm in diameter and 2-5cm long. The ends of the rods are attached to short platinum leads to provide electrical connections. Another source is Globar source, which is the rod of silicon carbide with 0.5cm in diameter and 5cm in length. When it is heated to near 1300^{o}c temperature it emits IR radiation. The maximum frequency of radiation generated by Globar source is in the range 5000-5500cm^{-1}. In comparison with the Nernst glower, the Globar source is less intense source below 10µm, and the Globar source is superior beyond 15µm.

   Some times sources like Nichrome wire, carbon arc, Rhodium wire and Tungsten filaments are also used to produce IR radiation. The Nichrome coil requires no water cooling and little maintenance and gives long service. This source is used where reliability is essential, such as nondispersive instruments and inexpensive spectrophotometers.

2. **Monochromators:** Spectral dispersing devices in IR spectrophotometers are similar to those used in UV-Visible spectrophotometers. The separation of desired frequency can be achieved by means of a monochromator. Prisms and gratings are made with IR transmitting materials such as rock salt, caesium bromide, AgCl, BaF_2 and KBr. However in recent spectrophotometers gratings are used as monochromatoes. The sodium chloride

crystal is used in the range from 4000-650cm^{-1}. Crystalline KBr and CsBr used in far IR region. Prisms with LiF are used in near IR region. The reflecting gratings have several advantages as dispersing devices such as,

- They provide linear dispersion.
- They resist the attack of water.
- The scattered radiation is almost eliminated.

3. **Detectors:** A detector is a device that usually changes the thermal radiation into electrical energy. The detectors in IR spectroscopy are of two types.

- Selective detectors.
- Non selective detectors.

A selective detector is the one, whose response depends upon the wavelength of incident radiation. Eg, photo cells, photographic plates, photoconductive cells, phospors.

A non selective detector is the one whose response is directly proportional to the energy of incident radiation, but independent of wavelength. Eg, thermocouple, bolometer and pneumatic cells.

VI. THERMOCOUPLE

Thermocouple is a best detector used for measuring IR radiation. Thermocouples are usually made by two dissimilar metals such as Bi, Sb or semi conducting alloys in a thin film of cellulose nitrate or other supporting base. It is present placed in evacuated chamber with KBr window to prevent the loss of energy. The radiant energy transmitted from the sample made to incident on the bimetallic junction gets heated and an emf is developed between the two junctions proportional to degree of heating.

The thermocouple depends on Peltier effect in which a potential is developed between two junctions are at different temperatures.

VII. PNEUMATIC DETECTORS

These detectors are developed by Golay. These detectors are suitable in the wavelength region of 15µm. This detector consists of two cells, first cell is filled with an inert gas (Xe) and connected to a small cell through a tube. One end of the small tube is closed by a curved diaphragm which is blackened in one side and coated with silver on the other side, which acts as mirror. When the radiation falls on the first cell heat is conducted to the gas, causing it to expand. Due to the expansion of this gas there is a small movement in the mirror on the second cell. A steady beam of light from the lamp inside the detector is focussed onto the mirror and reflects the light onto a photo cell connected to an amplifier and recorder.

Recent detectors are made from crystals such as Lithium Niobate, Barium Titanate and Triglycine Sulphate. These crystals are known as pyro electrics. These crystals take less time for detection when compared to other detectors.

VIII. BOLOMETERS

Bolometer is an excellent detector introduced by the Langley. It gives electrical signal as a result of change in resistance of metallic conductor with temperature.the main advantage of metal bolometers is fast response time. Recently introduced thermistor bolometer has high sensitivity. These thermistors are made of fused mixture of metal oxides (Mn,Ni,Co) in which the resistance decreases exponentially with increase in temperature.

IX. SAMPLE PREPARATION

The IR spectroscopy can analyse the sample indifferent forms such as solids, liquids and gases.

Liquids are usually analysed as neat or in solution form. Neat liquids are normally placed between two plates of NaCl and pressed together. This provides a film of thickness less than or equal to 0.01mm and the plates are held by capillary action. NaCl is most commonly used salt for making cell windows, because it is quite in expensive. But it was observed that some of the samples dissolve NaCl or react with it. In such cases CaF_2, BaF_2 and AgCl plates are used. If the film thickness is large then the absorption is more and the spectrums are not satisfactory. Usually for neat liquids 1-10mg of sample is required.

X. SOLUTIONS

Solutions are normally handled in the cells having the thickness in the range of 0.1-1mm. the sample volumes are in the range of 0.1-1mL. Generally the sample concentrations are used in the range of 0.05-10%. A reference cell containing only the solvent, in order to minimise the absorption peaks due to the solvent it is placed in the path of reference beam. No solvent is fully satisfactory in mid IR region because the solvent it self absorbs IR radiation. There fore two or more solvents have to be used. A common pair of solvents is CCl_4 & $CS_{2.}$ In restricted wavelength regions acetone, alcohol, water, chloroform and dimethyl formamide are used in limited IR regions. The cap of the cell made with Teflon. Usually for frequencies greater than $1333cm^{-1}$ CCl_4 is used as solvent and frequencies less than $1333cm^{-1}$ CS_2 is used as solvent.

XI. SOLID SAMPLES

Pellets are used for solids that are difficult to dissolve in a suitable IR transmitting solvent. The sample (0.5-1.0mg) is finely powered and grinded with about 100mg of KBr , so as to make a uniform mixture. The mixture is then made into a transparent disc by pressing at high pressure. This pellet is used for the analysis of IR spectrum. It is important to grind the mixture to a fine powder (≤0.2μm) in order to minimise the bonds appears due to scattering.

Mulling is an alternative to make pellets. To about 1-5mg of sample about 2-3 drops of mulling agent is added and ground to a fine paste and this paste is placed between the plates of NaCl to form a thin film. This film is used for obtaining the IR spectra. Commonly used mulling agents are mineral oil or Nujol (hi boiling point hydrocarbon), Fluorolube (a chlorofluoro carbon polymer) and hexa chloro butadiene. All the mulling agents have characteristic IR bands at a specific region of IR spectral range. There fore it is necessary to record the spectrum using two different mulling agents that absorb in different spectral zone in order to get a complete IR spectrum. In the spectral range of 4000-250cm^{-1} Nujol and Fluorolube are used as mulling agents.

XII. GASEOUS SAMPLES:

The vapour is introduced into a special cell usually about 10cm long and it is placed directly in the path of IR beam. The walls of the cell are usually made with NaCl which is transparent to IR radiation. Most of the organic compounds having low vapour pressures are analysed in this phase. Compounds like metal carbonyls, cyclo pentadiethyl compounds and some acetyl acetone complexes are examined in gas phase.