# Modern Instrumental Methods of Analysis

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## Lecture No. # 32

## Infrared Spectroscopy-2

## Practical Aspects

We were discussing the sample holders, how we can take the sample in different containers and I had told you in the last class, that IR cells are constructed with sealed windows, which are separated by thin gaskets of copper and lead which are weighted with mercury; so, the whole assembly is securely clamped in a stainless still holder. As the mercury penetrates, a gasket it expands producing a tight seal.

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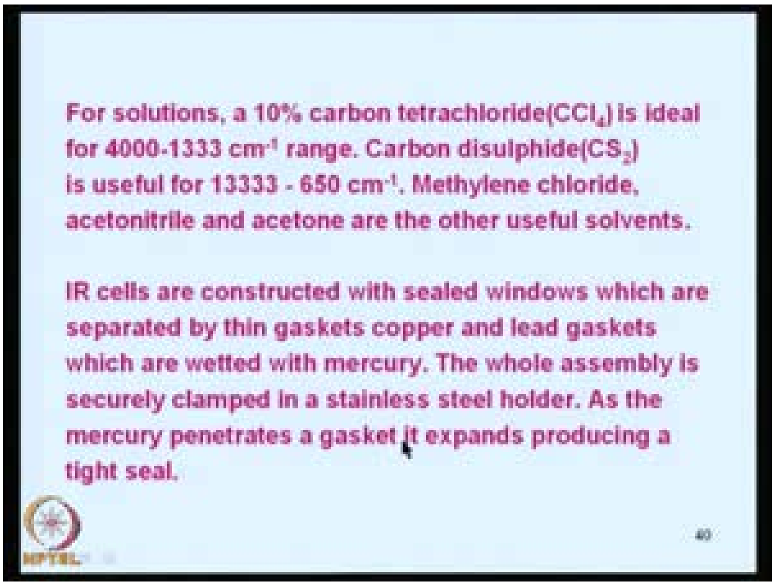

For solutions, a 10% carbon tetrachloride($CCl_4$) is ideal for 4000-1333 $cm^{-1}$ range. Carbon disulphide($CS_2$) is useful for 13333 - 650 $cm^{-1}$. Methylene chloride, acetonitrile and acetone are the other useful solvents.

IR cells are constructed with sealed windows which are separated by thin gaskets copper and lead gaskets which are wetted with mercury. The whole assembly is securely clamped in a stainless steel holder. As the mercury penetrates a gasket it expands producing a tight seal.

So, this is how we hold the sample. for films how do you take the infrared spectrum. So, for polymers, raisins and amorphous solids, the sample is usually dissolved in a volatile solvent and you evaporate the solvent, you will get a thin film of the material. So, a drop of the solution you can place it on the window and then seal the four edges as the solvent, evaporates a thin film of a homogeneous material is deposited which can be scan directly.

For liquids and polymers, a drop of the solution may be placed and squeezed, you can just squeeze them, in case, it is not volatile, you can just squeeze them and then you will get a small a film like material which can be scanned for IR.

Now, what about mulls, I want you to understand that the powders are more difficult to take the IR spectrum. So, powders can be examined, as a thin paste or a mull, you can take about five milligram of the sample, very small quantities, mix it with nujol; nujol is a high molecular weight liquid paraffin just like castor oil. So, you can take nujol, mix it with in a in a small cup, mix with your powder and it will wet the whole thing and you can take the nujol and put it on a finger and put it on IR window and then smear it and then take the spectrum. Now, you can imagine that nujol being a, paraffin, it will have carbon hydrogen bonds, mostly saturated carbon hydrogen bonds.

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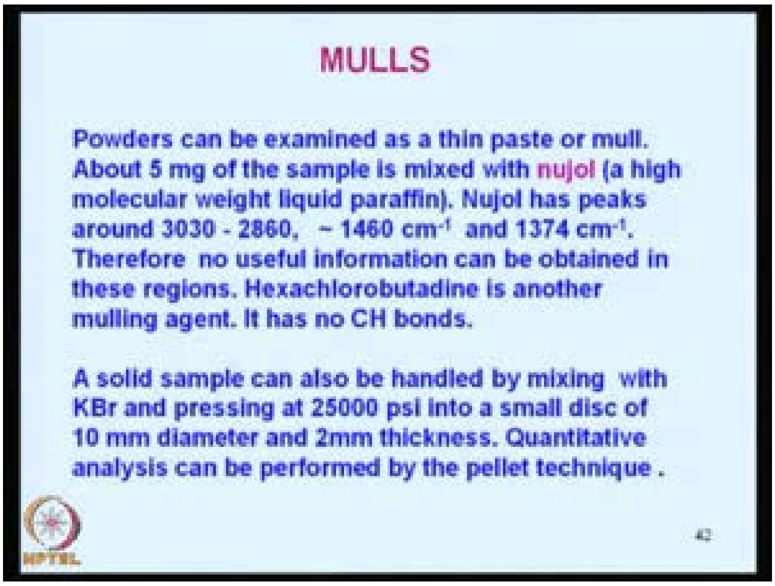

## MULLS

Powders can be examined as a thin paste or mull. About 5 mg of the sample is mixed with nujol (a high molecular weight liquid paraffin). Nujol has peaks around 3030 - 2860, ~ 1460 $cm^{-1}$ and 1374 $cm^{-1}$. Therefore no useful information can be obtained in these regions. Hexachlorobutadine is another mulling agent. It has no CH bonds.

A solid sample can also be handled by mixing with KBr and pressing at 25000 psi into a small disc of 10 mm diameter and 2mm thickness. Quantitative analysis can be performed by the pellet technique .

So, when you take a powder you have to subtract the peaks from nujol. So, nujol has peaks around 3030, around 2860, 1460 and 1374 centimeters inverse. So, these are the nujol peaks, which we will have to discount when you are taking IR spectrum of the samples. Therefore, basically you cannot get any useful information about a compound which contains nujol, in these regions, that is 3030 to 2860, 14- around 1460 and 1374.

In other regions, it is useful. You can also use Hexachlorobutadine as another mulling agent and this is better than nujol, because it has no carbon hydrogen bonds Hexachlorobutadine. So, we can also take a solid sample by mixing it with potassium bromide, just take about 0.5 gram of potassium bromide and your sample and then mix it intimately and then take a small cup into the cup, you put the mixture and then press it.

You will get a very small disc; the disc you can put it and take the spectrum, you will have to press it around 2500 psi, then only you will get a small disc of about 10 mm diameter and 2 mm thickness. Such small handling instruments are available in the market and when you buy an infrared, you can also buy a pellet maker. So, when you make this pellet, it gives you a 10 mm diapellet which about 2 mm thickness; so, quantitative analysis can be performed by using the pellet technique.

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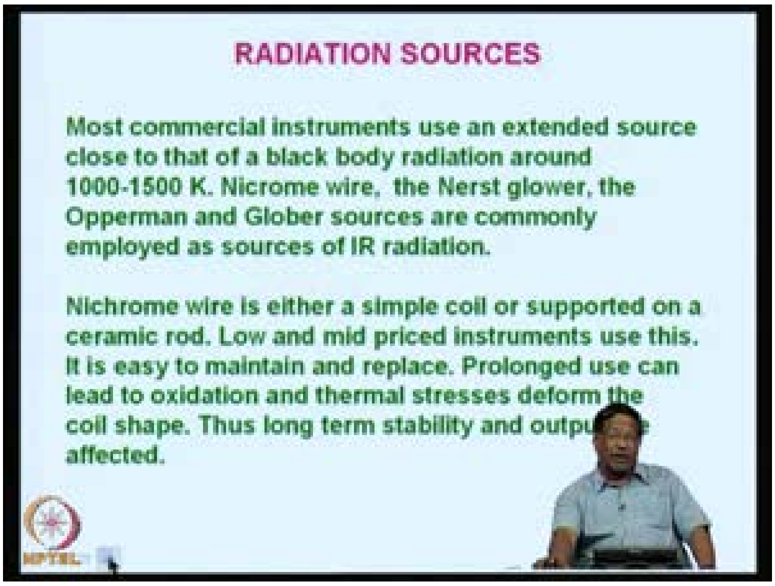

RADIATION SOURCES

Most commercial instruments use an extended source close to that of a black body radiation around 1000-1500 K. Nicrome wire, the Nerst glower, the Opperman and Glober sources are commonly employed as sources of IR radiation.

Nichrome wire is either a simple coil or supported on a ceramic rod. Low and mid priced instruments use this. It is easy to maintain and replace. Prolonged use can lead to oxidation and thermal stresses deform the coil shape. Thus long term stability and outpu[illegible]e affected.

Now, the let us discuss about the instrumentation radiation sources. So, the most commercial instruments use an extended source close to that of a black body radiation, that is what you need basically, it must generate infrared radiation and the any black body radiation if you heat, it will give you around, if you heat it between 1000 and 1500 Kelvin, you will get black body radiation containing infrared. Usually Nicrome wire Nerst glower the Opperman and the Glober sources are commonly employed as sources of infrared radiation. There are four different sources, one is Nicrome wire you can use it, Nerst glower, yes another source, Opperman is another source and Glober source is the another source.

So, Nicrome wire is a simple coil supported on a ceramic rod, you could, you would have seen in even in your houses, if you, if you take the earlier people use to heat in the kitchens using an electric stove, in which a coiled wire use to be put in the electric heater. So, the material is Nicrome wire and it is put round and round and round in a, in the kitchen; now, you can use a similar wire and rotate a fixed on a coil.

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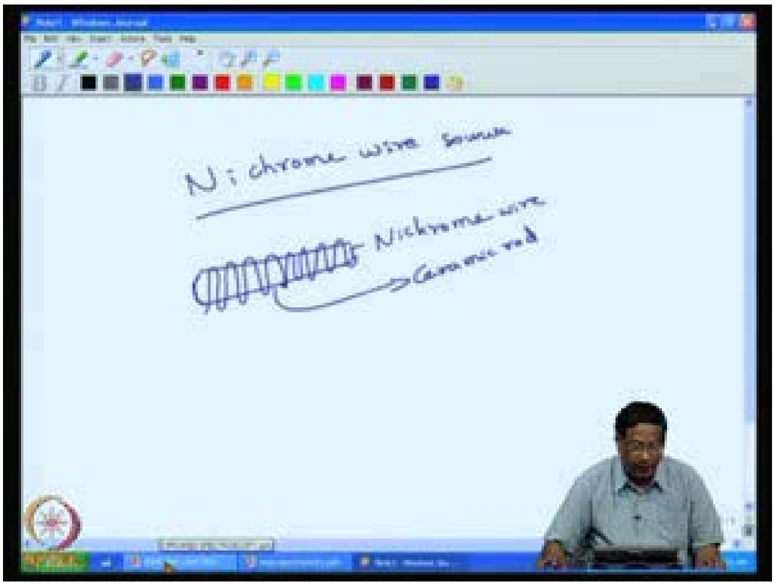

You can use it like this; this is your ceramic a rod and Nicrome wire will go like this. This is Nicrome wire and this is the ceramic rod ceramic; the job of ceramic rod is only to support, support the ceramic wire and it is wound around this and the, it can be used straight away. Nichrome wire is either a simple coil or supported on a ceramic rod and usually low and mid priced instruments use this. It is easy to maintain and replace. So, whenever the wire gets overheated and then gets cut, you can simply take another wire and wind it and put it in the source; so, it is easy to a replace. Prolonged use definitely can lead to oxidation and thermal stresses and that deform the coil shape; thus long term stability and output are affected; therefore, you have to keep on changing the Nicrome wire on and off.

So, this is one source most commonly employed source, I can say, then another is Nernst glower. Nernst glower is composed of a mixture of rare thoxides that are heated by electric current. So, you have to make the rare thoxides and then mix them and then press them into a rod and then use it as a heater and it is heated by electric current. This has a negative coefficient of electrical resistance; that means, most of the oxides are not good conductors; so, to make them conducting you have to supply energy. So, its electrical conductivity increases with increasing temperature, this is what we called a negative temperature coefficient of electrical resistance.

Therefore, external heating, additional external heating is required to start the flow of electricity and it must be fully to control a runaway situation; that means, you keep on heating a externally also and the rod also will generate start a correct conducting the electricity, there will be resistance, it will get hot and you should not you should the temperature.

So, Nernst glower was also commonly used in most of the infrared spectrometers. So, the Opperman, I am coming to the third source, the Opperman, it consists of a ceramic rod again filled with rare thoxides with a coaxial metal wire located inside the centre; that means, you take a small cylinder and then fill the powder and put a wire inside that metal wire at the centre; the wire is heated first, which in turn heats the oxide mixture; this is self regulating and this does not require external heating, in that way it is better than the Nernst glower.

So, the Glober, the, another source is basically an electrically heated silicon carbide rod, it is a black silicon carbide rod, capable of being operated at very high temperatures. In most of the cases external water cooling is essential to help stabilize the source and to reduce the heat dissipation to other components of the infrared instrument.

Typical life spans of all the sources are about two to five years; the most common failure are the fractures in the ceramic rods or rare metal oxide rods or in the Nicrome wire, it may get cut or hotspot may generate or loss of power by oxidation of electrical connections. So, these are the common problems, but they are by regular routine maintenance most of these problems are overcome.

Now, let us talk about the detectors; the detectors are basically thermal detectors or photon sensitive detectors, these two are useful in infrared spectrometry thermal detector there are two types that is one is thermal another is photon sensitive. So, thermal detectors sense the temperature changes, by change in the physical property such as generation of voltage, it may generate voltage or it may change, there may be a change, in the resistance etcetera.

The speed of thermal detectors are influence by thermal or heat capacity of the detector element, which is somewhat lower than the photon counting, because thermal heat sensors there, there has to be some flow of the heat and it takes time, but it more than the photon counting units, but the response of thermal detector is independent of the wavelength of the incident radiations, that is important, because it is not IR wavelength dependent, it is a dependent property of the substance which you are measuring.

So, thermo couple for example, the pneumatic or Golay detector and bolometer are some of the detectors which belong to this class, that is thermal detectors; one is thermo couple another is pneumatic or Golay detector, another is a bolometer and IR response temperatures are of the order of about 10 raise to minus 3 to 10 raise to minus 2 Kelvin only in that range it is not very high. So, these are used extensively in dispersive type instruments and bolo meters are used in FTIR instruments.

We will see what are these things in a short while, the thermocouple is basically two wires, dissimilar wires fabricated in such a way, that they produce a, they are, they are jointed such as antimony and bismuth. So, they produce a small voltage proportional to the temperature of the junction. So, several thermocouples are available in a market, they are connected in series for additional input; that means, you can make the changes slightly higher by using two or three thermocouples. Half of the junctions are hot, the other containing the active element; alternate junctions are cold, that is they are thermally bonded and bonded to the substrate and remain at a relatively lower temperature. So, you have two junctions - one is hot another is cold; thin film technique have also been used to miniaturize these thermocouples.

So, you can have very small miniaturized thermocouples and the entire assembly can be mounted on an evacuated enclosure with IR transmitting windows, because you need the infrared radiation to fall on the detector. So, the detector thermocouple must be housed in an evacuate container, which is fixed with a window which is IR transmitting. So, the conductive heat losses are minimized and the response time in such cases is about 80 micro seconds. So, it should be very fast, otherwise you will not be able to scan the infrared spectrum.

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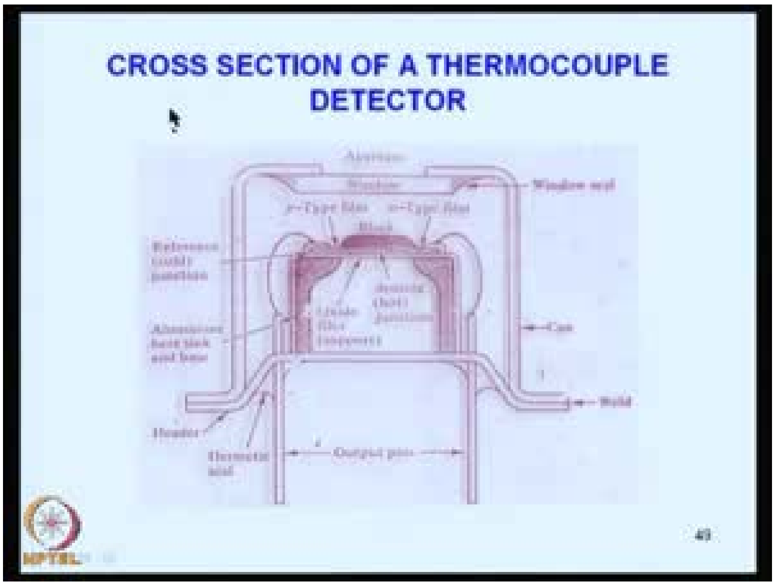

CROSS SECTION OF A THERMOCOUPLE DETECTOR

So, you can see in this film, in this slide, that this is the optical window in the IR; this is a p type, n type junction and this is coated black and oxide film is here, sensing junction is here somewhere in the middle. So, these two junctions are connected and this is a reference junction, cold junction and this is the hot junctions. So, they are adjacent to each other and then aluminum heat sink is there, because any excess heat must be dissipated quickly and then all other things are fairly in place, that is, a we need a window seal here and then we need some welding here, output signs hermitically seal etcetera, these things are more in technical nature. So, this is how a thermocouple works.

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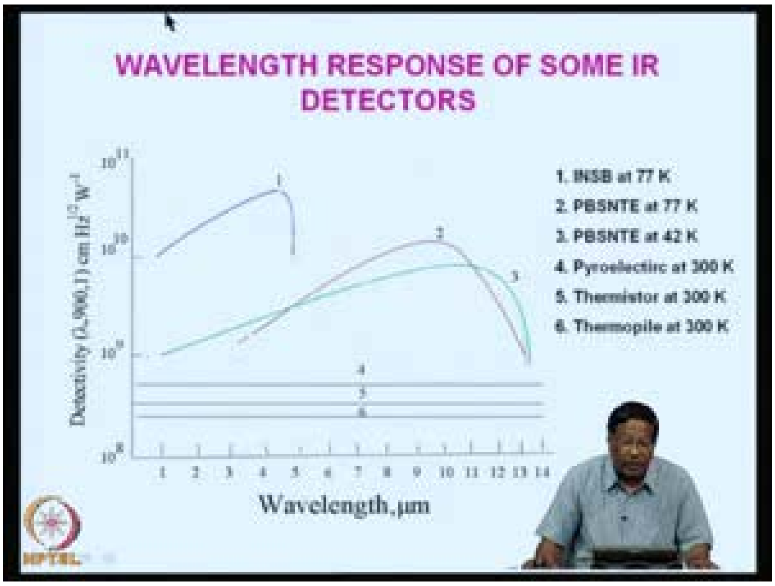

WAVELENGTH RESPONSE OF SOME IR DETECTORS

1. INSB at 77 K
2. PBSNTE at 77 K
3. PBSNTE at 42 K
4. Pyroelectirc at 300 K
5. Thermistor at 300 K
6. Thermopile at 300 K

Now, the wavelength response you can make thermocouples of different materials, for example, you can make this one figure, the first one is indium antimony, this is the response at 77 Kelvin. So, this scale is detectivity is 10 raised to 8 to 10 raised to 11; this starts somewhere around 10 raised to 10 then falls off around 5 micro meters.

Similarly, I have plotted here, lead, tin and tellurium; this is another thermocouple. The third one is lead, tin and tellurium at 42 Kelvin and thermistor is number five, you can see that, it is response is very constant all the time, that is, number five middle one at the bottom and fourth one is pyroelectric material and sixth one is thermopile at 300 Kelvin. So, the pyroelectric, thermistor and thermopile, they are all slightly their response is slightly lower, but they are very constant, over a, over the entire infrared region.

Whereas the indium antimony and then the lead, tin and tellurium etcetera, they are their response are not constant, but they could be the, but they are more sensitive.

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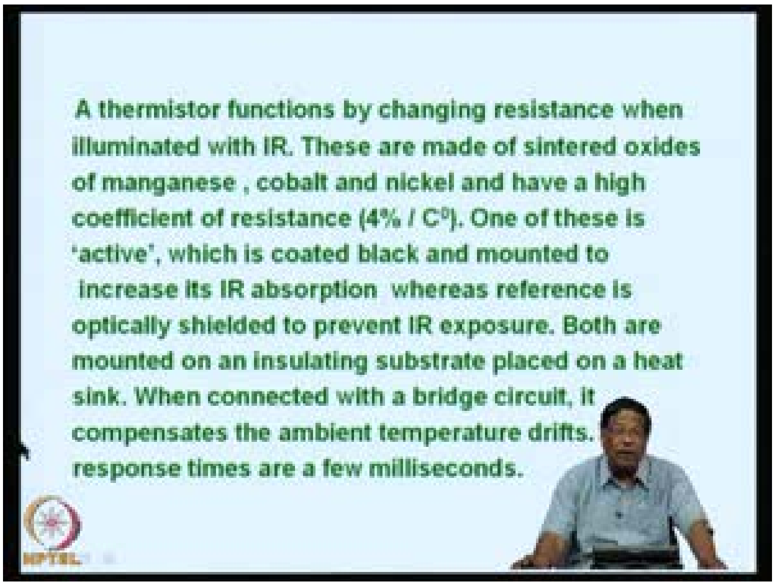

A thermistor functions by changing resistance when illuminated with IR. These are made of sintered oxides of manganese , cobalt and nickel and have a high coefficient of resistance (4% / $C^0$). One of these is 'active', which is coated black and mounted to increase its IR absorption whereas reference is optically shielded to prevent IR exposure. Both are mounted on an insulating substrate placed on a heat sink. When connected with a bridge circuit, it compensates the ambient temperature drifts. response times are a few milliseconds.

So, a thermistor basically functions by changing resistance when illuminated with IR. So, you have to take the infrared radiation fall on a thermistor, then what happens there is a change in the resistance when illuminated with infrared. So, a thermistor is also made of sintered oxides of manganese, cobalt and nickel and has a high coefficient of resistance; one of this is active, the other is coated black and mounted to increase its IR absorption. So, the reference is optically shielded, the other one is not shielded. So, one of them there is always a temperature difference, between the, between the IR exposure both are mounted on an insulating substrate placed on a heat sink, you have to dissipate the extra heat all the time.

So, when connected with a bridging circuit, it compensates the ambient temperature out drifts that is important. So, the response time in this case is also of the order of a few milliseconds, you can note down that most of the responses are in millisecond only that is the requirement of infrared. So, a Golay, let us discuss about the Golay pneumatic detector.

So, the Golay pneumatic detector uses the expansion of a gas as the measuring device. The unit consists of small metallic boxes like this and inside that there is a gas fixed and two boxes you can connect and then as the infrared rays fall, the gas will get heated up and expand. So, the expansion is arranged in such a way that infrared radiation is cut off depending proportionally to the amount of the expanding gas. So, this is the principle.

So, the unit consists of a small metallic cylinder closed by a rigid blackened metal plate of about 2 mm square at one end and a flexible silver diaphragm at the other end. The chamber is filled with xenon; you need a xenon gas for that. The radiation absorbed by the black plate, black and plate causes the gas to expand and deforms the diaphragm which in turn obstructs the light path, this I have already told you.

The response time in this case is about 20 milliseconds, that is, almost similar to t c detectors that is thermal conductivity detectors. The Golay pneumatic detector is a sort of is the best among the lot.

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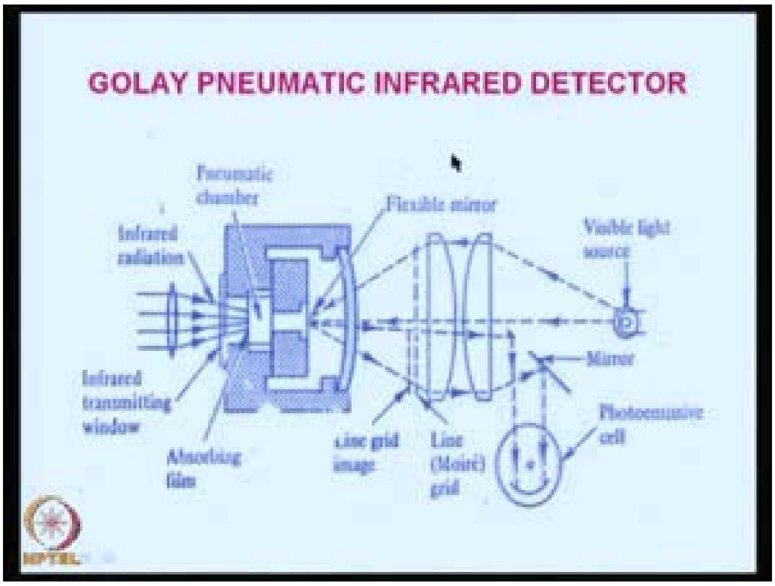

GOLAY PNEUMATIC INFRARED DETECTOR

So, this is the figure schematic figure of a Golay pneumatic infrared detector; you can see the pneumatic chamber is here, infrared radiation is coming from the backside, from this region and there is an infrared transmitting window, an essential part of all IR detectors and there is an absorbing film and this is a flexible mirror and this one is the line grid image, line grid and then you have a photo emissive cell, through which the sample radiation is collected and the infrared radiation is monitored.

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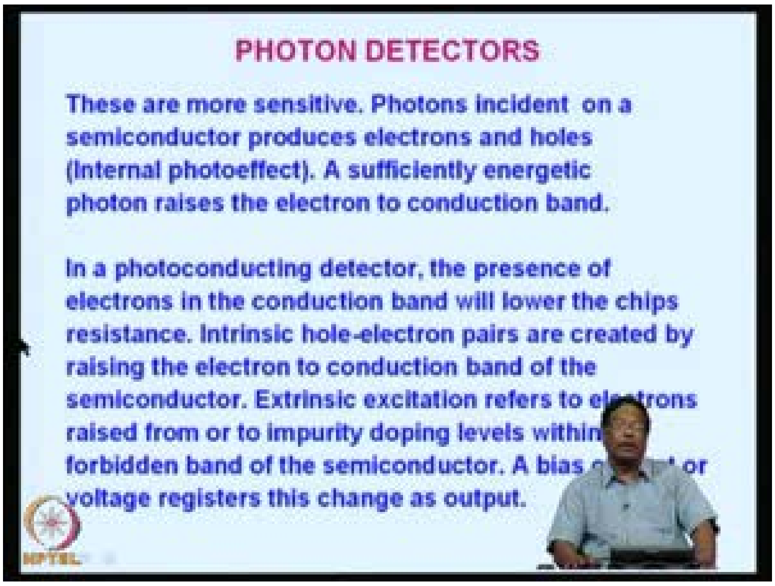

PHOTON DETECTORS

These are more sensitive. Photons incident on a semiconductor produces electrons and holes (Internal photoeffect). A sufficiently energetic photon raises the electron to conduction band.

In a photoconducting detector, the presence of electrons in the conduction band will lower the chips resistance. Intrinsic hole-electron pairs are created by raising the electron to conduction band of the semiconductor. Extrinsic excitation refers to el[illegible]trons raised from or to impurity doping levels within [illegible] forbidden band of the semiconductor. A bias [illegible] or voltage registers this change as output.

So, you can study this in detail and I can only say that Golay cell is the best, as far as my experience also goes. Now, let us discuss about the photon detectors; photon detectors we have discussed already quite a few times and photons incident on a semi conductor produces electrons and holes also.

So, a sufficiently energetic photon raises the electrons to the conduction band. So, in a photo conducting detector, the presence of electrons in the conduction band will lower the chips resistance and intrinsic whole reaction pair wholes and reaction electrons, you know, they are, they always occur in a pair in pairs. They are created intrinsically by raising the electron to the conduction band of the semi conductor material extrinsic. Excitation occurs refers to the electrons raised from or impurity doped levels impurity.

We have to dope the impurities within the forbidden band of the semiconductor. So, a bias current always is generated and the voltage registers this change as the output. So, very interesting and tricky procedure and photo voltaic cells are also approximately similar type, that is, indium and antimony metal p and n type junctions in single crystals; the p type is laid as a thin layer over the n type, the band gap is about 0.23 volts at liquid nitrogen temperature; that means, you have to maintain the detector at liquid nitrogen temperature.

Then you can use other types of detectors based on lead tin detector, telluride detectors etcetera. They extend spectral sensitivity to considerably larger wavelengths than indium antimony, that we have seen the figure earlier and that is, 5-13 micrometers are normal and 6-18 micrometers, you can extend them with lead tin and telluride.

When used with a current mode amplifier, response time is of the order of about 20 nanoseconds not microseconds, twenty nanoseconds is the response time; to that extent these things are better. So, we will not discuss more about the detectors, because our infrared application, infrared spectrometry is more application oriented and rather than instrumentation oriented, there is not much you can do when you are taking the spectrum and the expertise required is in the form of interpretation of the infrared spectrometers .

So, the person who is using infrared continuously will keep on becoming an expert in the infrared interpretation. It is not possible for us to go into too much details about the applications, because as I was telling you the more experience, you get in using these things, the more expert you will be at this stage, even if I explain to you the infrared applications, it will be, it will not be useful to you unless you personally start using the infrared spectrometer, but still it is better to know a little about infrared applications.

In general, infrared peaks occur at the same frequencies for specific groups. If you have an OH group that is an alcoholic group, it will show you the peaks of the OH groups irrespective of the compound which you are measuring; if there is OH group, it is there, if it is not there, that means, OH groups is not there. So, to that extent, you can use them as pass fail test, if you see a particular frequency for a non compound functional group, then the functional group exist otherwise it does not.

For example, you can take carbon oxygen stretching vibration, that is CO group carbonyl group like in acetone, it is, it is a stretching vibration is the same for acetone or di n hexyl ketone any other ketone all of them should show you a carbon oxygen double bond peak and it is different for acetic acid, though because acetic acid will have COOH group; one is CO group, another is OH group.

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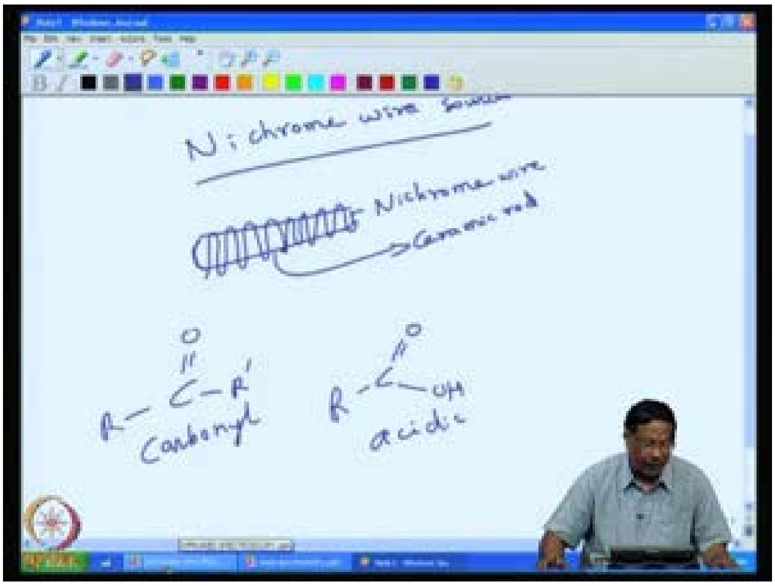

Like what we have seen here; this is a CO group, this is acetylenic group, that is carbonyl and this would be acidic group. So, the CO group in this case, in the carbonyl is slightly different from CO group in the, CO group in the acid. So, the irrespective of that you would see different kinds of peaks and they will give you similar peaks, but slightly different range, where the CO group will appear, it could be due to acetic acid there in, acetic acid there is a an electrical effect which is predominant.

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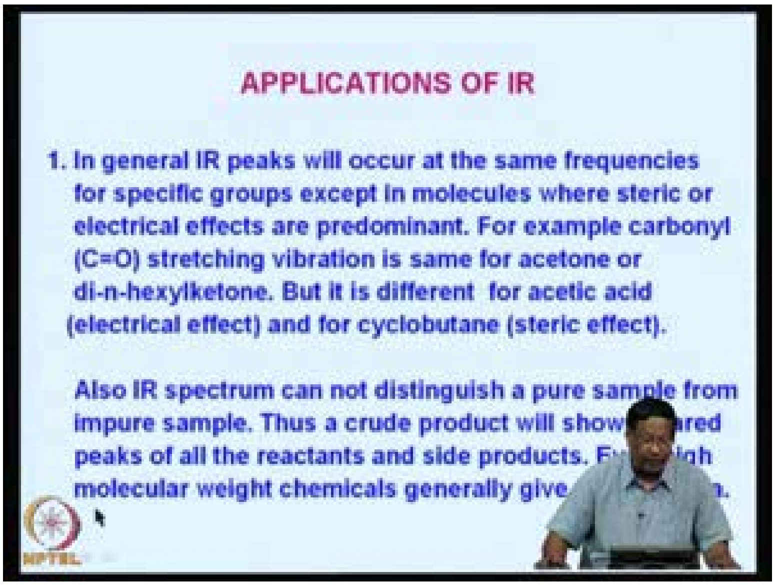

## APPLICATIONS OF IR

1. In general IR peaks will occur at the same frequencies for specific groups except in molecules where steric or electrical effects are predominant. For example carbonyl (C=O) stretching vibration is same for acetone or di-n-hexylketone. But it is different for acetic acid (electrical effect) and for cyclobutane (steric effect).

   Also IR spectrum can not distinguish a pure sample from impure sample. Thus a crude product will show ared peaks of all the reactants and side products. E igh molecular weight chemicals generally give a.

And in cyclobutane, there is a steric effect that is predominant. So, an IR spectrum cannot actually distinguish a pure sample from the impure sample, because if you a sample is very pure other substances are not there; that means, the impure sample may have different functional groups; suppose, you have a mixture of pure sample along with some other substances, then you cannot really identify a substance as pure substance at all. You could say only these functional groups are there and it could be a mixture it could be a pure compound or it could be a mixture. So, a crude product will show infrared peaks of all the reactants and side products; even high molecular weight chemicals generally give very poor spectra; so, the progress how you can use infrared spectrum, to monitor reaction like this.

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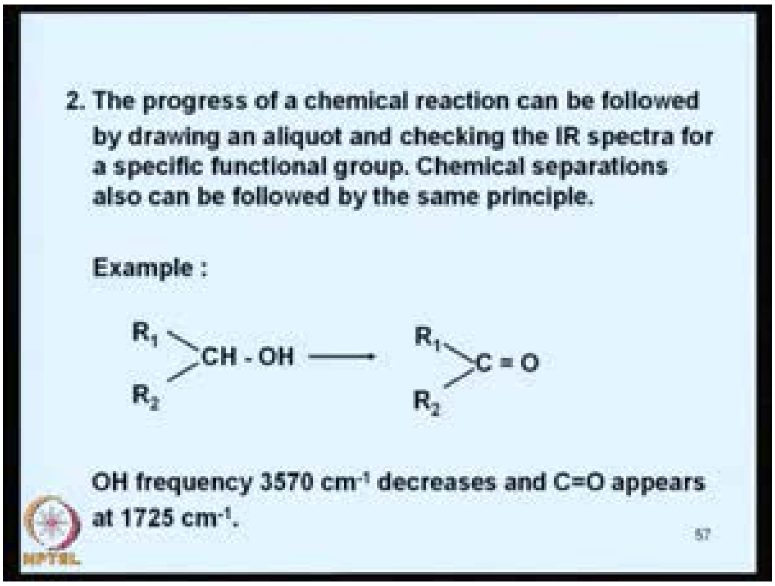

2. The progress of a chemical reaction can be followed by drawing an aliquot and checking the IR spectra for a specific functional group. Chemical separations also can be followed by the same principle.

Example :

$$\begin{matrix} R_1 \\ R_2 \end{matrix} \!\!> CH - OH \longrightarrow \begin{matrix} R_1 \\ R_2 \end{matrix} \!\!> C = O$$

OH frequency 3570 $cm^{-1}$ decreases and C=O appears at 1725 $cm^{-1}$.

Now, for example, you can take a look at the slide the progress of a chemical reaction can be followed by drawing an aliquot and then checking the infrared spectra from time to time, for a specific functional group. The chemical separations can also be followed by the same principle, for example, here this is R 1 R 2 CH OH, that is, secondary alcoholic group, this reaction, this compound is made to undergo reaction to a produce a ketone.

So, the OH frequency is 3570 centimeters inverse for this compound and there is no OH frequency for the ketone group. So, the CO group frequency is at 1725 centimeters inverse. So, as you precede this, 1725 centimeters inverse, appears, should appear as the reaction goes to completion and this OH frequency at 3570 centimeters inverse should be vanishing.

So, this is how you can use infrared spectrum to monitor the reaction. So, you can say that, the, as you take the sample every one hour keep on taking the IR spectrum 3570 should decrease and CO group frequency should increase. So, the most powerful function of an infrared spectrum is in establishing the identity of a sample by comparison using the same medium.

So, an unknown compound what you can do, in, in addition to following a reaction, suppose you want to know, whether a particular compound is there or not, what you do is, you have a data base and compare the peaks in the same medium.

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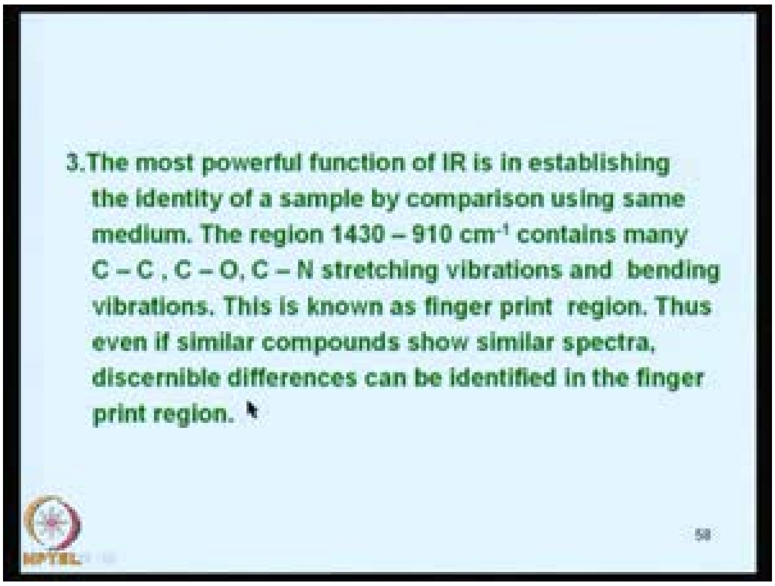

3. The most powerful function of IR is in establishing the identity of a sample by comparison using same medium. The region 1430 – 910 cm$^{-1}$ contains many C – C , C – O, C – N stretching vibrations and bending vibrations. This is known as finger print region. Thus even if similar compounds show similar spectra, discernible differences can be identified in the finger print region.

So, the region of 1430 to 910 centimeter inverse, it contains lot of information corresponding to carbon-carbon stretching, carbon-oxygen stretching and carbon-nitrogen stretching, vibrations and bending vibrations also.

So, this region 1430 to 910 centimeters inverse is known as finger print region. So, even if similar compounds show similar spectra, the finger print region can be a, can be a definite identifying tool for organic compounds, in the same media that you should not forget; suppose, you change the solvent or something like that then you will not be able to do this.

So, another several compilations are actually available listing the characteristic group absorptions, that is, functional group peaks which can be used to characterize an unknown material. So, if a compound shows a peak around 1780 centimeters inverse; let us say, you can infer straight away that, it contains a CO group that is carbonyl group. But it could be an aldelhyde such as CHO or it could be a ketone like C double bond O or it could be an amide that is NHCO or it could be an ester or it could be an acid COOH group, but CO group is always indicated, if you get a peak somewhere around 1718 centimeters inverse for. So, you need further analysis IR spectra or other classical techniques required to identify the compounds absolutely, but if the IR spectrum does not contain that CO group, you can straight away say that, it is not an aldehyde, it is not a ketone, it is not an amide, it is not an ester, it is not a an acid. So, this kind of information is very easily obtainable using IR spectrum.

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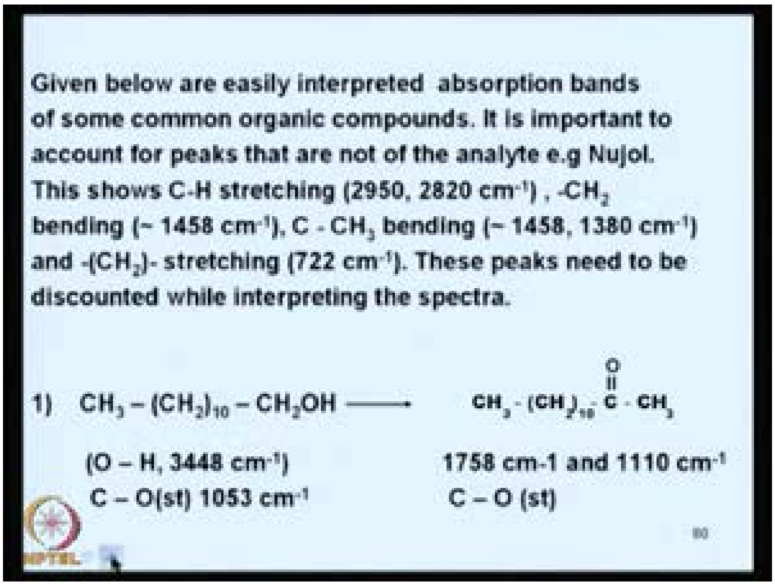

Given below are easily interpreted absorption bands of some common organic compounds. It is important to account for peaks that are not of the analyte e.g Nujol. This shows C-H stretching (2950, 2820 $cm^{-1}$), $-CH_2$ bending (~ 1458 $cm^{-1}$), $C-CH_3$ bending (~ 1458, 1380 $cm^{-1}$) and $-(CH_2)-$ stretching (722 $cm^{-1}$). These peaks need to be discounted while interpreting the spectra.

1) $CH_3-(CH_2)_{10}-CH_2OH \longrightarrow CH_3-(CH_2)_{10}-\overset{O}{\overset{\|}{C}}-CH_3$

(O – H, 3448 $cm^{-1}$)

C – O(st) 1053 $cm^{-1}$

1758 cm-1 and 1110 $cm^{-1}$

C – O (st)

So, I have given here below certain into easily interpreted absorption bands of some organic compounds, it is important to account for the peaks that are not of the analyte. For example, I have told you about nujol. So, we had to disqualify, we have to disqualify or not take into account the peak corresponding to nujol, if you are taking spectrum in nujol. So, nujol shows that 2950 and 2820 centimeters inverse CH stretching and CH 2 bending is appears around 1458 and CCH 3 we will see some of the IR spectrum containing these things and these peaks need not need to be discounted while interpreting the spectra. So, this is the similar example of secondary alcohol going to a ketonic group. And you can see that OH stretching frequency, I will state and these frequencies must vanished and these frequencies corresponding to CO in carbonyl group and CO stretching group at 1758 centimeters inverse should appear.

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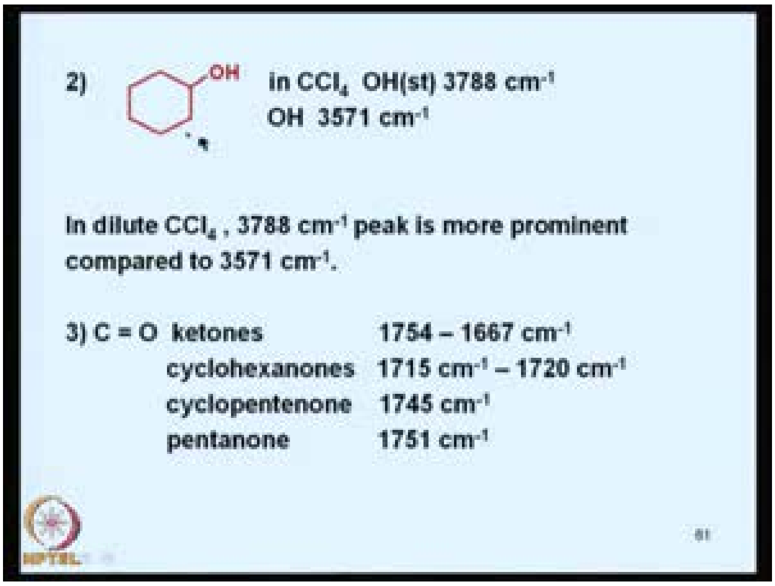

2) in $CCl_4$ OH(st) 3788 $cm^{-1}$
OH 3571 $cm^{-1}$

In dilute $CCl_4$, 3788 $cm^{-1}$ peak is more prominent compared to 3571 $cm^{-1}$.

| | | |
|---|---|---|
| 3) C = O | ketones | 1754 – 1667 $cm^{-1}$ |
| | cyclohexanones | 1715 $cm^{-1}$ – 1720 $cm^{-1}$ |
| | cyclopentenone | 1745 $cm^{-1}$ |
| | pentanone | 1751 $cm^{-1}$ |

So, similarly you can see that in the second example, it is cyclohexanol in CCl 4 OH stretching frequency appears at 3788 centimeters inverse and OH frequency is 3571 centimeters inverse. So, if you get these two peaks you could infer that, it is, it could be an alcohol and saturated alcohol for that matter. In dilute carbon tetrachloride, this 3788 centimeters inverse peak is more prominent compared to 3571 centimeters inverse.

So, similarly, you can see that for ketones, it is the CO group appears at 1754 to 1667 centimeters inverse and for cyclohexanones, it is 1715 to 1720 slight differences and 1745 another is in pentanones, it is 1751, but you can see that most them are between 1715 and 1750 range.

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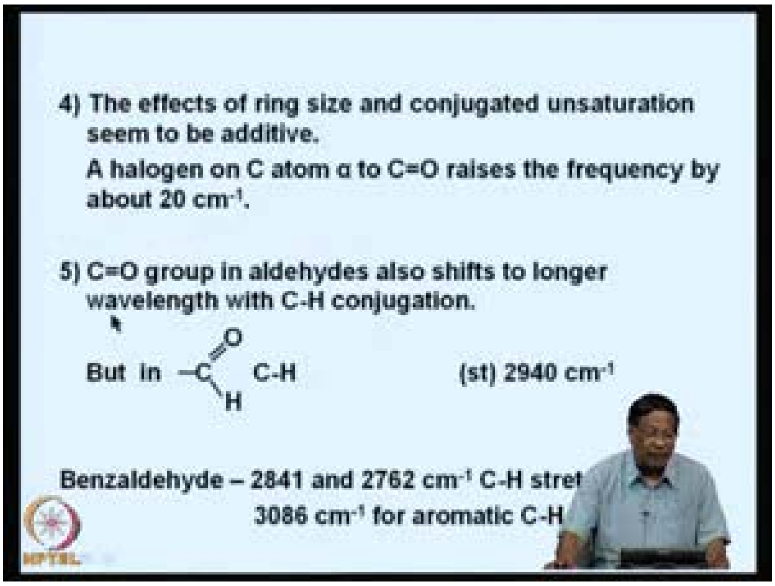

4) The effects of ring size and conjugated unsaturation seem to be additive.

A halogen on C atom α to C=O raises the frequency by about 20 $cm^{-1}$.

5) C=O group in aldehydes also shifts to longer wavelength with C-H conjugation.

But in $-C(=O)H$ C-H (st) 2940 $cm^{-1}$

Benzaldehyde – 2841 and 2762 $cm^{-1}$ C-H stret

3086 $cm^{-1}$ for aromatic C-H

So, like this one can look for different kinds of information using infrared spectrum. You can see here that the effects of the ring size and conjugated un-saturation also you can slightly discern, for example, a halogen on a carbon atom alpha to CO raises the frequency by about 20 centimeters inverse, what do we mean by this, is that, in general whenever we have discussed, the, the shift of wavelength due to liability of the electrons, just like in ultraviolet spectroscopy, here also conjugation shifts the peaks to slightly lower longer wavelengths that is reduces the energy.

But it is not, so prominent like in and quantifiable like in ultraviolet spectroscopy, where we have solved several examples which can be used for calculating precisely the wavelength at which the peak should appear lambda max; now, it is not possible to do it here, but similar effects are seen here, for example, this alpha halogen and carbon atom it shifts the peak to by about 20 centimeters inverse. So, carbon carbonyl group in aldehydes also shifts to longer wavelength with CH conjugation itself like, like this and this stretching frequency appears at 2940 centimeters inverse, whereas, for benzaldehyde it appears at 2841 and 2762 centimeters inverse.

Then the peaks are under strain the compound the bonds are under slight strain. So, they appear at shorter wavelengths 2841 compared to 2940; similarly, 3086 centimeter inverse you would see an aromatic CH stretching frequency. So, like this, it is possible to generate information using infrared spectrum.

For this, you will have to be more familiar with the type of compound you are handling. So, carboxylic acids anhydrides generally show two absorption banks. So, a good organic chemist will, will be able to distinguish between a carboxylic acid anhydride and acids.

So, because it shows two absorption peaks between 1870 and 1740; so, shorter wavelength would be more intense, the moment you show him a spectrum he will say this contains carboxylic acid anhydride, because it is showing two peaks, one of them is more intense; like that, they will be able to get information.

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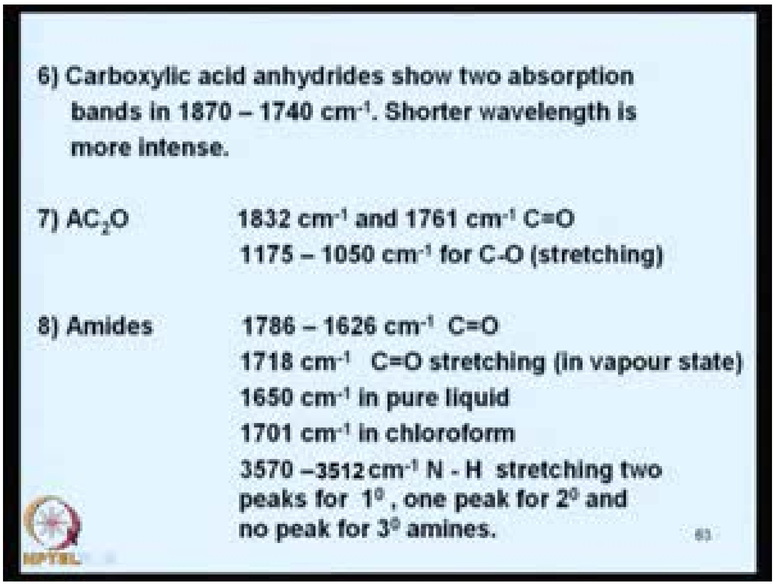

6) Carboxylic acid anhydrides show two absorption bands in 1870 – 1740 cm$^{-1}$. Shorter wavelength is more intense.

7) AC$_2$O 1832 cm$^{-1}$ and 1761 cm$^{-1}$ C=O
1175 – 1050 cm$^{-1}$ for C-O (stretching)

8) Amides 1786 – 1626 cm$^{-1}$ C=O
1718 cm$^{-1}$ C=O stretching (in vapour state)
1650 cm$^{-1}$ in pure liquid
1701 cm$^{-1}$ in chloroform
3570 –3512 cm$^{-1}$ N - H stretching two peaks for 1$^0$ , one peak for 2$^0$ and no peak for 3$^0$ amines.

Similarly, you can see in this slide that AC2O that is anhydride shows 1832 and 1761 centimeter, you do not have to remember these numbers, but as you keep on working in these area, you will be able to familiarize with the numbers much more easily, then trying to remember and try to apply as and when you need for examples in amides you can see that 1876 and 1626 centimeters inverse range is for CO, but 1718 it appears in the vapor state; so, longer wavelength.

So, in pure liquid, suppose the amides itself is a liquid then 1650 centimeters inverse you would get a peak like that there are different information, but what is interesting in this case is the last three lines, that is, 3570 to 3512 centimeters inverse showing N H stretching, it shows two peaks for primary and one peak for secondary and no peak for tertiary amines. That means, if you suspected it to be an amide by looking at the number of peaks in this range, you will be able to decide, whether it is primary amine or secondary amine or tertiary amine.

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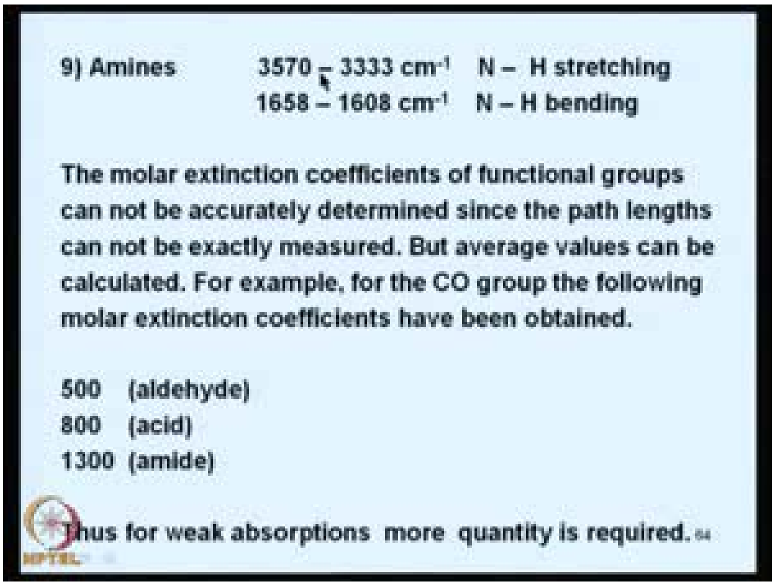

9) Amines 3570 – 3333 $cm^{-1}$ N – H stretching
1658 – 1608 $cm^{-1}$ N – H bending

The molar extinction coefficients of functional groups can not be accurately determined since the path lengths can not be exactly measured. But average values can be calculated. For example, for the CO group the following molar extinction coefficients have been obtained.

| | |
|---|---|
| 500 | (aldehyde) |
| 800 | (acid) |
| 1300 | (amide) |

Thus for weak absorptions more quantity is required.

So, that is very interesting, for example, amines also show, if the it is primary or secondary amine, you would see that 3570 to 3333 centimeters inverse, where N H frequency occurs and N H bending frequency been lower in intensity, they would appear 1658 to 1608 centimeters inverse, because they require less energy.

So, the molar extinction coefficients of functional groups cannot be accurately determined, since the path lengths cannot be measured in a infrared spectrometers, just like in a ultraviolet and visible spectroscopy, if you know the concentration and path length, you can determine the molar extinction coefficient a is equal to epsilon b c, where a is the absorbance epsilon is the molar extinction, coefficient b is the path length and c is the concentration.

Similarly, in infrared, you will not be able to calculate an exactly the molar extinction coefficient, because the path length in between the cells cannot be exactly determined. So, but some average values you can calculate, for example, the CO group, for the CO group you can, you can see in this slide that for aldehyde, it is 500, for acids it is 800 for amides, it is 1300; so, these are these epsilon values.

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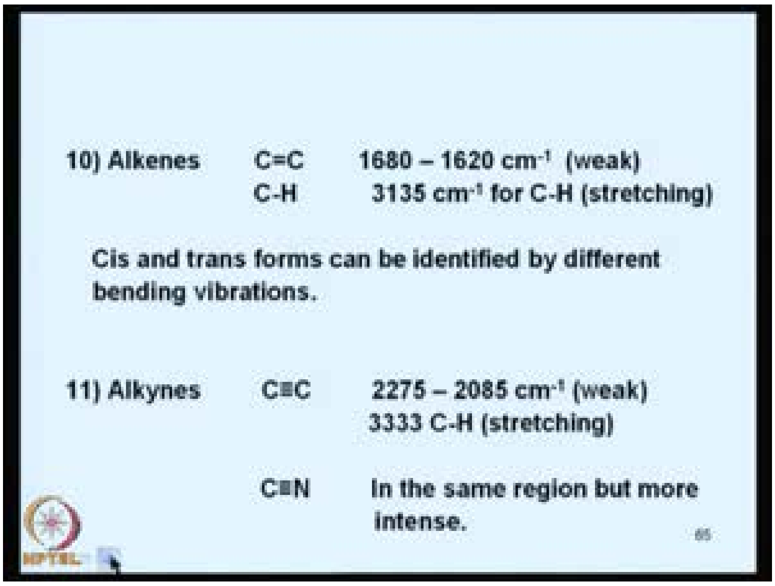

**10) Alkenes** C=C 1680 – 1620 $cm^{-1}$ (weak)
C-H 3135 $cm^{-1}$ for C-H (stretching)

**Cis and trans forms can be identified by different bending vibrations.**

**11) Alkynes** $C\equiv C$ 2275 – 2085 $cm^{-1}$ (weak)
3333 C-H (stretching)

$C\equiv N$ In the same region but more intense.

So, for weak absorptions, more quantity is definitely required, if you want to determine the substances, then you can look at alkenes and alkaline earth materials where alkenes would show two peaks; one is carbon carbon double bond, that is between the range 1680 to 1620 centimeters inverse and they should also show you a CH bond, because all the alkenes will contain C H bonds anyway that will be appearing in the 3135 range centimeters inverse, that is for stretching. So, Cis and Trans forms can be identified by different a bending vibration that is these ranges, 1680 to 1620 ranges.

So, suppose you go for alkyne that is acetylenic type compounds CH 2 CH 2 CH CH 2 CH C 2 H 2. So, here also you would expect a carbon hydrogen stretching bond, because it is C 2 H 2 H 2 and the CH stretching frequency should appear between 33 around 3333 centimeters inverse, whereas a weak band will appear between 2275 to 2085 centimeters inverse. Similarly, another another acetylenic type bond occurs in cyanides in the… So, so, therefore, here also the stretching region is same IR region is same, but they are more intense.

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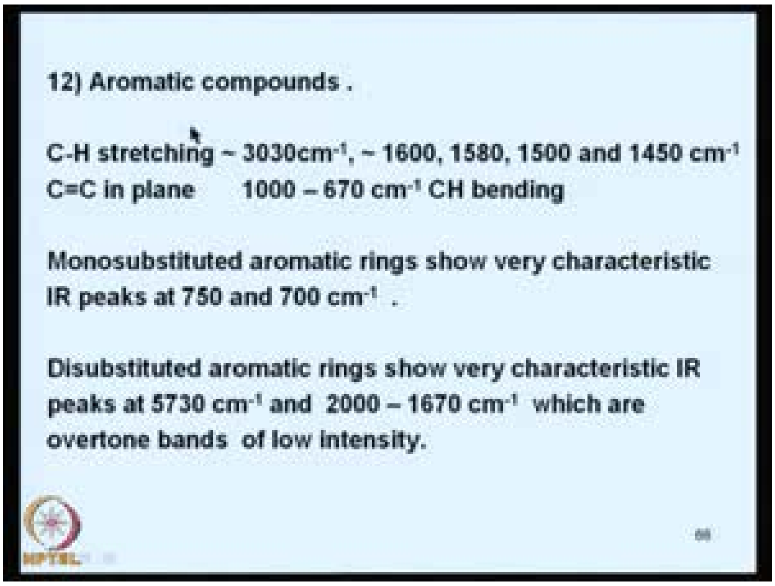

12) Aromatic compounds .

C-H stretching ~ 3030cm$^{-1}$, ~ 1600, 1580, 1500 and 1450 cm$^{-1}$
C=C in plane 1000 – 670 cm$^{-1}$ CH bending

Monosubstituted aromatic rings show very characteristic IR peaks at 750 and 700 cm$^{-1}$ .

Disubstituted aromatic rings show very characteristic IR peaks at 5730 cm$^{-1}$ and 2000 – 1670 cm$^{-1}$ which are overtone bands of low intensity.

So, we can continue discussing like this several compounds, for example, in aromatic compounds, you can say that carbon hydrogen stretching appears a number of gives you a number of peaks starting from 3030 to 1600, 1580, 1500 and 1450 and carbon-carbon in plane bending, you can, you can remember that somewhere around 130, 1000 to 670 centimeters inverse, that is near the end of the IR spectrum, you would see some CH bending frequencies for aromatic compounds; you can a mono substituted aromatic com rings, show very characteristic IR peaks between 750 and 700 centimeters inverse.

So, this is a very important aspect; suppose, you are handling organic compounds with a single substituent, you must see a peak between 750 to 700 centimeters inverse. Di-substituted rings show very characteristic peaks at 5730 centimeter inverse and 2000 to 1670 centimeters inverse; these are actually overtone bands of low intensity. So, Di-substituted aromatic rings also are very easy to determine in a normal IR spectrum.

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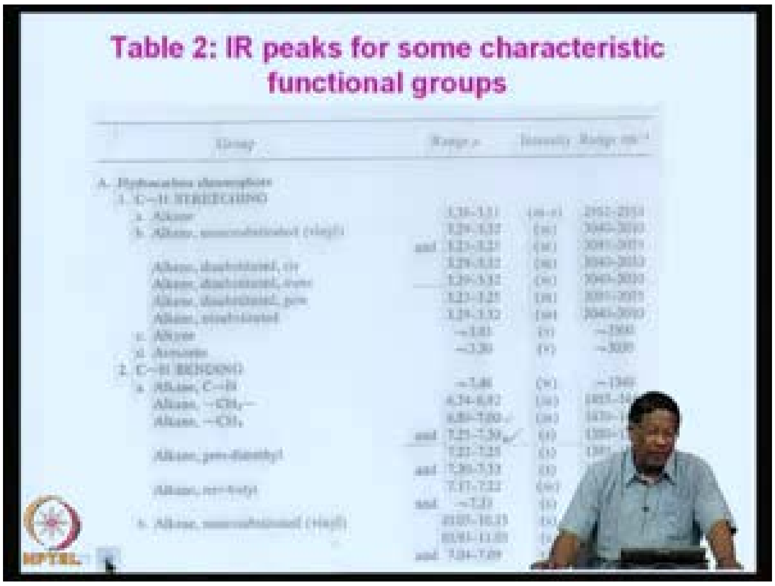

Table 2: IR peaks for some characteristic functional groups

Now, I want to for the sake of brevity, I want to put some of the spectrums, some of the IR frequencies in the, in this lecture and here I have listed the hydrocarbon chromophore CH bending and carbon-carbon multiple bond stretching etcetera and ketone stretching vibration, all, all the things that we have discussed, I have put them in this, these are mostly available in the data base.

For example, aldehydes, where you can ge[t]- expect the peaks of 1740, 1720 and 1705 to 1780 like that the peaks are available; this will serve you, this table will serves you to quickly identify the different kinds of IR infrared peaks corresponding to specific functional groups. These are the functional groups on the left side and these are the micrometers, that is a wavelength range in microns and this is the centimeters inverse.

So, I have put some of them for your benefit and alcohols and phenols etcetera, also are there, you should be able to differentiate between primary alcohol, secondary alcohol and tertiary alcohol; similarly, just like what I had explained to you regarding amines primary amines, secondary amines and tertiary amines, you should be able to distinguish using this data.

So, unsaturated nitrogen compounds also I have put, that is c triple nitrogen, that is a triple bond just like a aetylenic groups, aryl isocyanates etcetera, they all show you stretching frequency betwee2002 to 2070 between 2260 to 2070 range.

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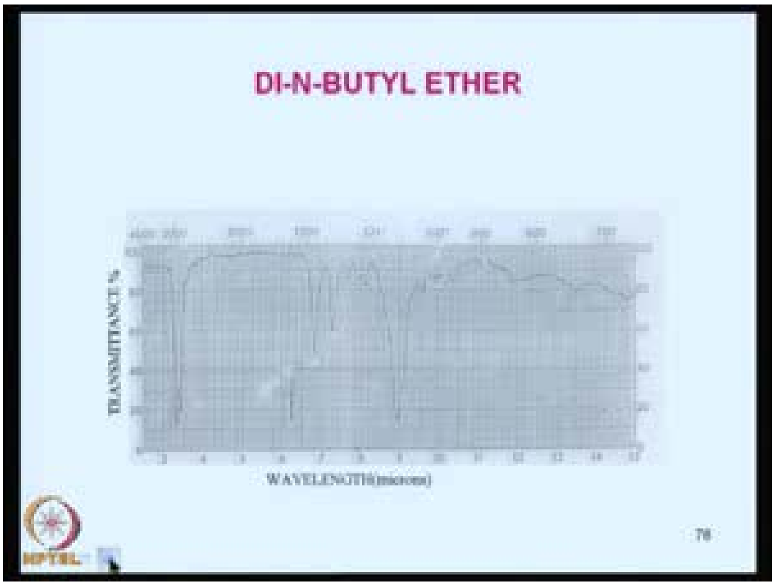

DI-N-BUTYL ETHER

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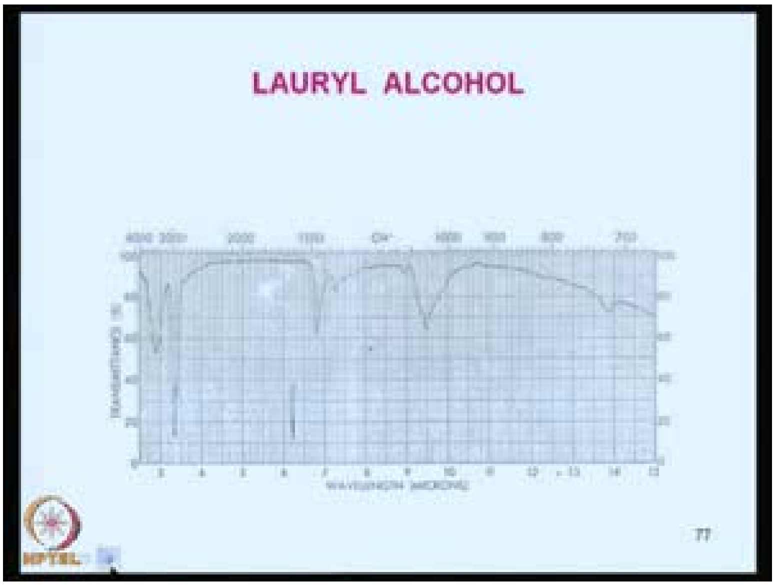

LAURYL ALCOHOL

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**So**, I think you should be able to get a quick spectrum identification using this table. Now, let us look at some of the spectra and this is for di n butyl ether, here you could see that the peaks are CH stretching frequencies are here and bending frequencies are here and because it is an ether it is an, this thing, this is the CO bending frequency. So, lauryl alcohol, it has got only one OH group and long chain molecule molecular compound. So, OH stretching frequency, you should be able to find in this region.

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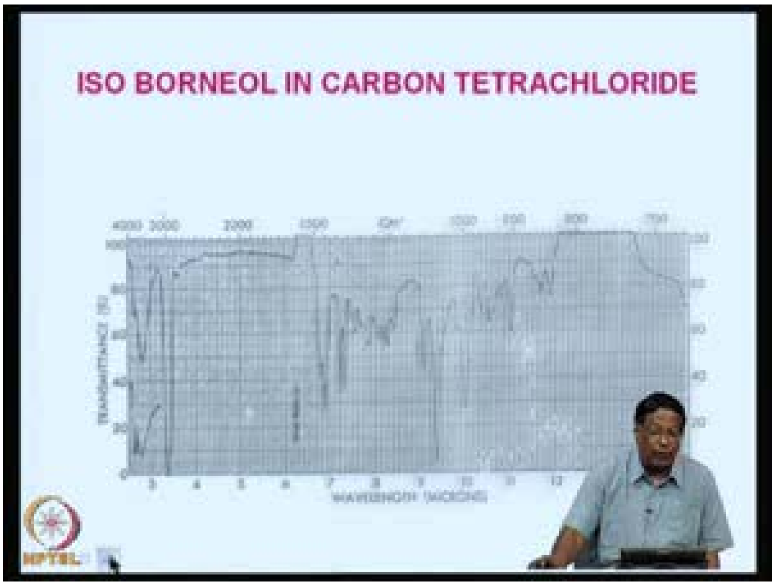
ISO BORNEOL IN CARBON TETRACHLORIDE

So, I have collected some more Iso Borneol and in carbon tetrachloride, you can see that the range is from 4000 to 700 here and the same thing is in microns plotted here and what is plotted is transmittance, in this case. So, cyclohexanone, I have put and cyclopentanone, you should be able to quickly see the differences between cyclohexanone and cyclopentanone.

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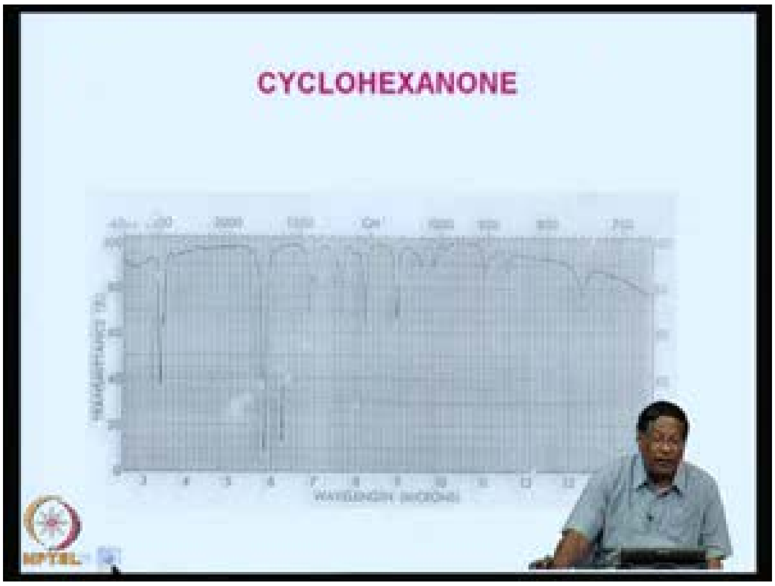
CYCLOHEXANONE

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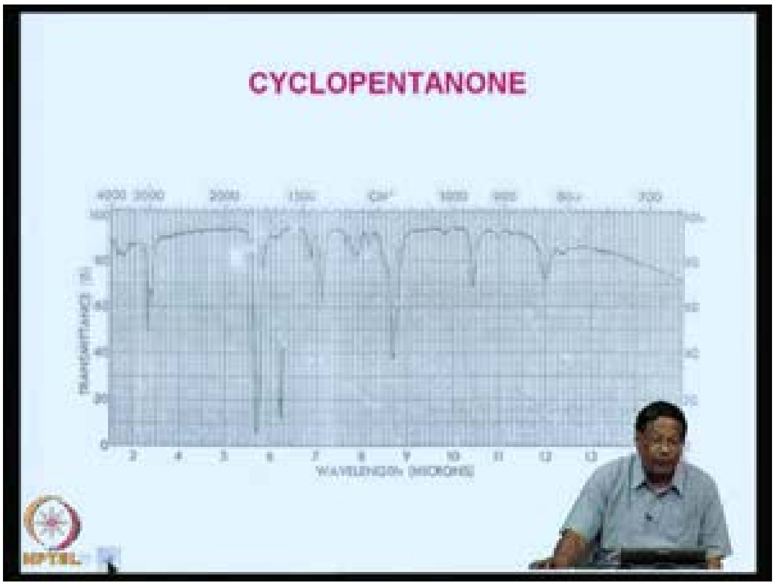

## CYCLOPENTANONE

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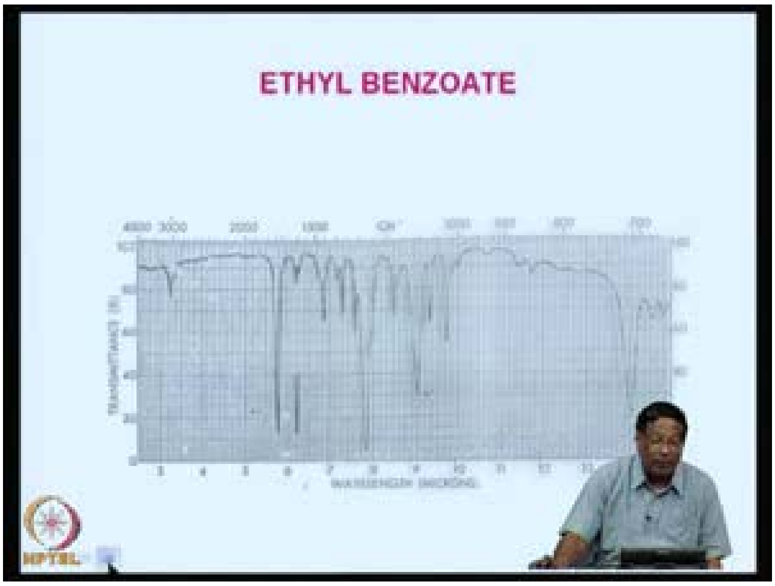

## ETHYL BENZOATE

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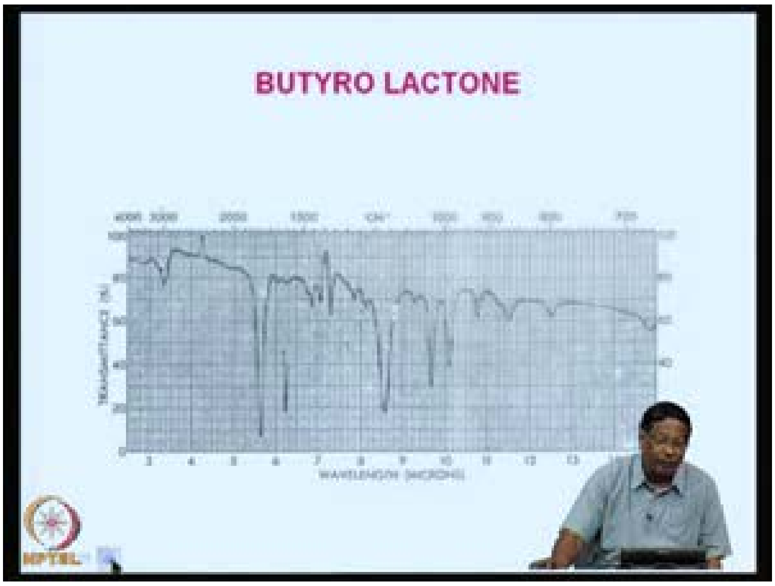

BUTYRO LACTONE

So, ethyl benzoate again you would see number of bending vibrations occurring in the finger print region, that is between 400 to 900 range and this is a very characteristic of the substances and this is for butyro lactone and ethyl acetoacetate is another one I have put and nonanoic acid benzoic acid, I have put and these things, I have put. So that, you can correlate the spectrums what I have put on the slides, you can correlate the spectrums what I have put on the slides as well as from the table. So that, with a little bit of exercise, you should be able to identify each peak comfortably, that is the whole idea of putting the tables as well as some graphs; it is only for your experience and to get a feel of how the organic compound spectra can be correlated to different substances.

So, you can now, I will not do not want to dwell more at this stage, on the IR identification and IR application, because it is a, an entirely different matter altogether to use the spectrum and use the IR spectrum, our focus in this course is on the instrumentation and the applications. So, what are, we have seen different kinds of applications with respect to spectra.

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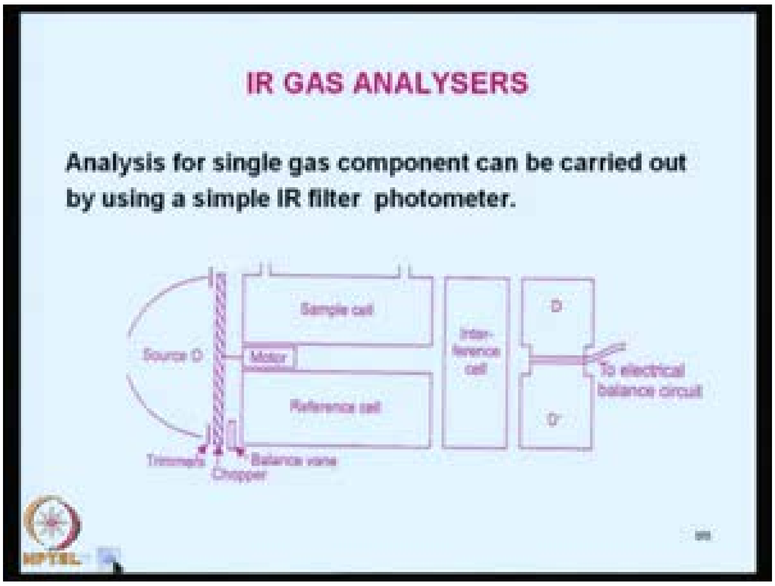

## IR GAS ANALYSERS

**Analysis for single gas component can be carried out by using a simple IR filter photometer.**

Now, let us discuss a little bit about infrared gas analyzers what is happening here an infrared gas analyzer is basically a filter infrared spectrometer which can be used for the analysis of single components or specific components in a mixture; suppose, you have petrochemical industry producing a polymer, then you would have spectrum of monomer as well as polymer and side products etcetera. So, most of them would be in the form of gases, because of their low molecular weights and such substances in a gas mixture can, they be identified quantitatively using infrared spectrum; so, spectrometry.

So, for this we use different kinds of instrument that is known as non dispersive infrared analyzers. So, basically they are all infrared, just like filter spectrophotometers these are also, we do not have a substance monochromator which can add a separate the wavelengths, we are taking the all the radiations generated from a single source.

So, what we have here is the energy of the infrared is split into two beams, you can see in the previous slide, in this slide that what I have here is a source infrared source, here is a mirror, which reflects all the infrared radiation and here I have a sample cell, here I have a reference cell. So, the sample and reference cells are different and there is an interference cell which contains substances, which are interfering in the determination and I have two detectors here D and D dash.

So, the sample cell will give you radiation and connect it to D with respect to D. So, the detector D will show you the response with respect to sample and detector D dash will show you response with respect to reference cell. So, both D and D dash are connected to an electrical balance circuit, but they are separated by a small diaphragm and which can show if D is more, it will press it down and D dash will be less; if D dash is more, it will press it up and it will both are in a way connected. So, How we can use this kind of information for the analysis of infrared responsive compounds in a process flow cell. The energy is actually split into two beams directed towards the bolometer wired in a balanced circuit that is what I was trying to show you in the previous figure. The sample gas flows through a cell on the top, that is, it extends across the both to one beam passes through a filter cell and the other one through a compensating cell. So, a filter cell contains pure gas being analyzed and compensating cell contains a gas similar to that being analyze. So, for example, in the analysis of ethylene, ethane and methane, let us take the example ethylene, ethane and methane three wavelengths, we need to select three wavelengths corresponding to each one of them in the IR region.

So, if a filter cell is filled with ethylene, all IR absorbed by ethylene will be completely eliminated from D 1, that is from the detector and also from the sample. So, this is the function of the cell interference cell, filter cell, in the previous figure I had shown you. So, How we can use this kind of information, we can, we will take a look in the next class, that is, we will talk about interference cells, non dispersive IR with respect to different compounds, quantitative analysis that is. So, thank you very much, we will continue our discussion on non dispersive IR and quantitative analysis in the next class.