Infrared Spectroscopy for Pollution Monitoring
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Lecture-19
Fourier Transform Infrared Spectroscopy

Greetings to you, we are coming nearly closer of the course and now we are going to discuss only the detector followed by applications, yesterday we were discussing about the detectors and I have talked to you about the thermocouple detectors. Thermocouple detectors are basically are very very useful in most of the detectors where the temperature difference can be measured up to 0.01 degree centigrade of Kelvin.

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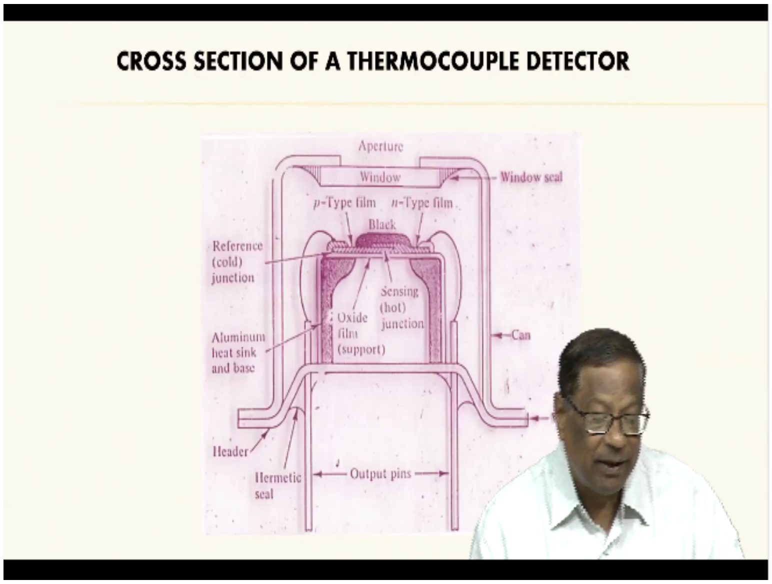

CROSS SECTION OF A THERMOCOUPLE DETECTOR

We can measure that and they are very very useful, so yesterday I have shown you this slide regarding this of the thermocouple detector I am not going into details because yesterday I have already covered ok. So but I had also covered that the about a little bit about the thermocouple characteristics.

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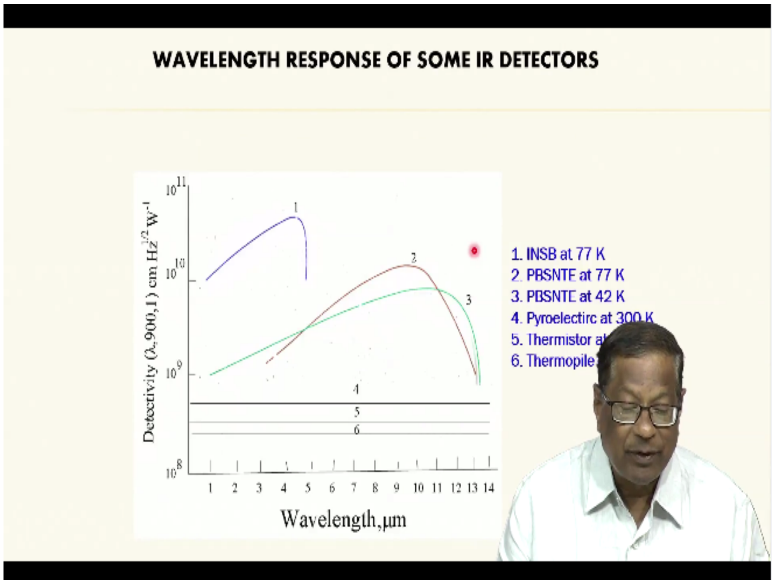
WAVELENGTH RESPONSE OF SOME IR DETECTORS

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

I had shown you this 6 thermocouples one is Indian antimony etc. and this is second is late payment tellurium, letwin and tellurium at different temperature pyroelectric, thermistor, and thermopile etc. and we have to maintain them around room temperature these 3 that is pyroelectric, thermistor, and thermocouple approximately 300 Kelvin but the others you need a coolant, because they work at very low temperature.

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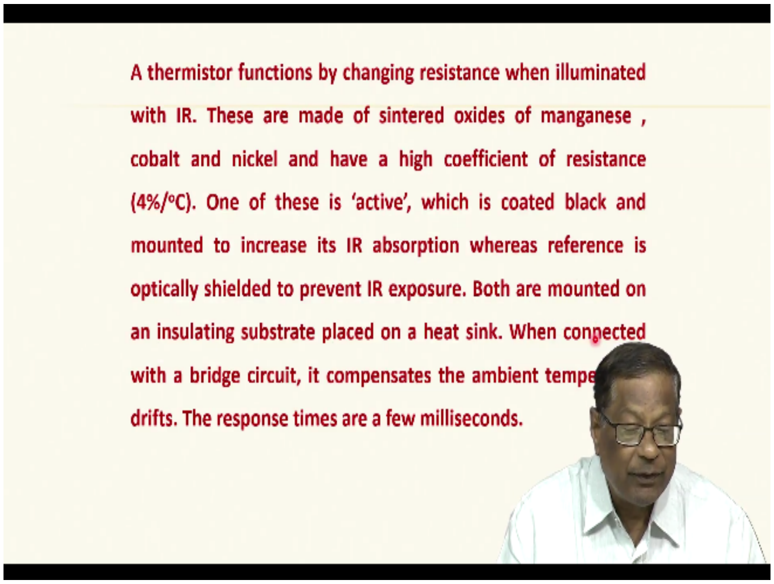
A thermistor functions by changing resistance when illuminated with IR. These are made of sintered oxides of manganese , cobalt and nickel and have a high coefficient of resistance (4%/°C). One of these is 'active', which is coated black and mounted to increase its IR absorption whereas reference is 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 tempe drifts. The response times are a few milliseconds.

So they become costlier and the maximum number of IR nowadays what you see all have thermocouples as the detectors ok. But there are other detectors also. For example this I had shown you thermostat functions by it functions by changing the resistance when illuminated with IR ok. These are all made of sintered oxides of manganese and things like that.

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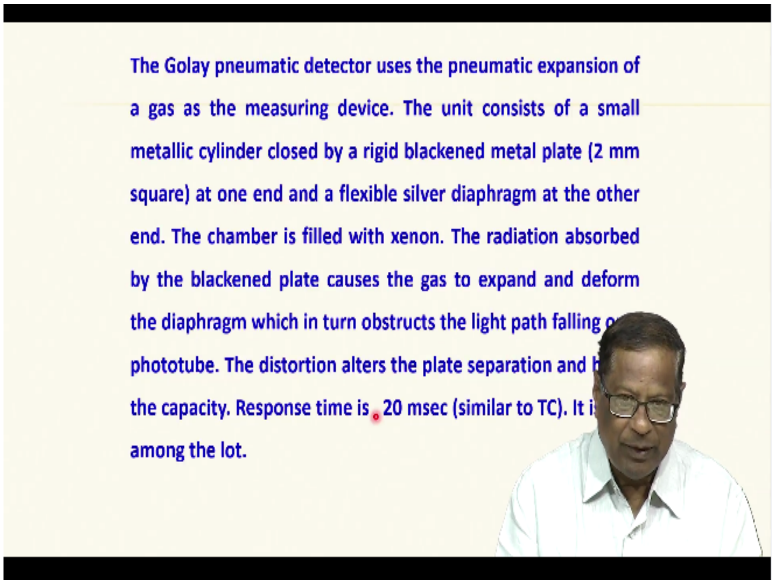

The Golay pneumatic detector uses the pneumatic expansion of a gas as the measuring device. The unit consists of a small metallic cylinder closed by a rigid blackened metal plate (2 mm square) at one end and a flexible silver diaphragm at the other end. The chamber is filled with xenon. The radiation absorbed by the blackened plate causes the gas to expand and deform the diaphragm which in turn obstructs the light path falling o
phototube. The distortion alters the plate separation and
the capacity. Response time is 20 msec (similar to TC). It i
among the lot.

And I was about to teach you about the golay pneumatic detector yesterday. So this uses the pneumatic expansion of a gas as a measuring device ok. So the unit actually consists of a small metallic cylinder on which I put an expandable frame diaphragm. So first I take a cylinder put some gas in that and then put a seal of a gasket which is expandable. So it is closed it normally we do not need any other radiation to fall on that.

So the gasket is closed by a rigid black and metal plate we need a metal plate to keep it a stable and that is about 2 mm square ok at one end and a flexible silver diaphragm at the other end, so very simple I will show you very shortly what is the structure of the how it is made. So the chamber now we are having metallic cylinder with frame and where to fill that we fill it with Argon or xenon go either of it.

We fill it with xenon and the radiation falls on the black and plate ok, when the black and plate is there it will absorb all the radiation that is falling on the black plate. So it gets heated, so the heating causes the gas to expand. So but where it will expand it has to expand one side is the metal plate top side is the flexible diaphragm. So it will expand and just push the diaphragm upward ok.

So what I do is when the diaphragm is push upward it stops a radiation fixed above a particular level that means radiation will be cut off when it expands ok, it is just like entering a lift when you are entering a left until you reach the left it does not show you anything that it may be closing or whatever it is but the moment you put your leg lift will sense that somebody is coming in and it will open again.

So that is how this diaphragm and the IR radiation are positioned, so the moment the diaphragm expands IR radiation gets cut off ok. So this abstract the light path following on a photo tube, once they obstruct it would not reach the detector placed across the cylinder. So this distortion alters the plate separation and therefore the capacity. So the radiation so long as the IR radiation is cut off the absorbance will come down and depending upon how much it is cut off ok by 10%, 20%, 30% transmission anyway.

And the capacity it would be 100% that also can be programmed and the response time of this detector is 20 milliseconds ok, so 20 milliseconds that is quite similar to TC. So if it is quite similar to TC we can use golay pneumatic detector as well as thermal conductivity detector both. So it is best among the lot because once the golay detector pneumatic detector is in place there it has got a long life ok and cost is also not very much.

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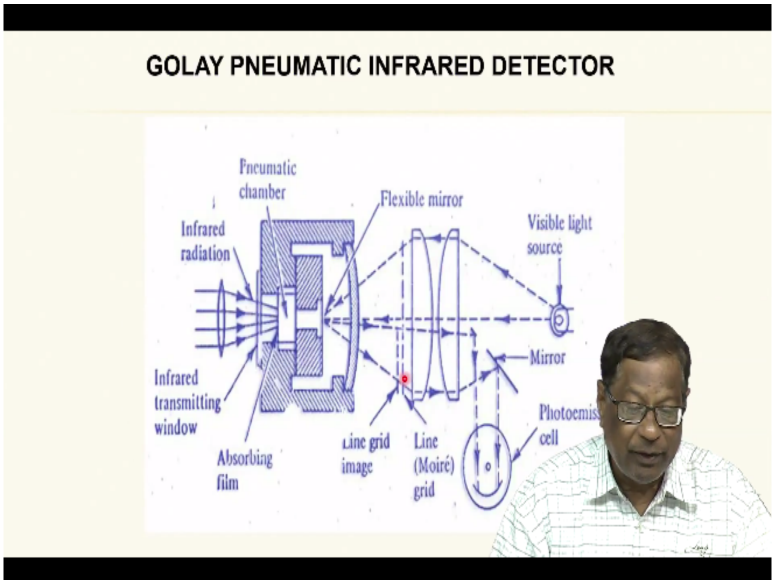

GOLAY PNEUMATIC INFRARED DETECTOR

That is production cost ok, so this is how the golay pneumatic infrared detector looks like, here what I have looked at this slide carefully, I have the radiation coming here infrared radiation all parallelized and then I have a lens here to focus and fall on the blackened metallic this is a metallic plate ok, pneumatic chamber, pneumatic chamber is a metallic plate is outside up to the edge ok. And the whole thing is put it in a each seat, the shaded portion in this figure is the heat sink.

That means as soon as the heat is detected and it is off it means dissipated for that and made ready for the next wavelength for coming, that is why we need a heat sink in most of the thermocouple detectors ok or even Golay detector. This is also based on the heat detection only. So here this is there infrared transmitting window made of KBR sodium chloride and things like that, we have already discussed about it.

And this is the absorbance film IR absorption film and the there is another flexible mirror here and then I have the line grade image coming here and this is the actual line great and this is the diaphragm ok. This is the line grade that means IR radiation can vary only between this and this maxim, this is 100% transmission on the top here this is a double beam type like thing. So it goes here and go there visible light sources there.

And 100% and absorption maxima, so line grade images obtained and then I have another small mirror here and then the it is taken through this and then I have a photo emissive cell because the radiation source IR radiation was finally fall on the photo emissive cell to generate the electricity current. So that current is measured always, see what in general whatever we are going to measure is the heat difference and that heat difference is connected to the thermocouple or whatever it is the heat difference.

And the IR radiation also should be falling on a photo emissive 2 photo emissive cell which will generate the current. So they finally what is recorded is a current only, but the mechanism of IR detection is different that is why we have different detectors. So golay cell is one of them, now you can you can go back and you will understand this slide much better because it is a golay pneumatic detector, it will say expansion of the gas that is xenon or argon.

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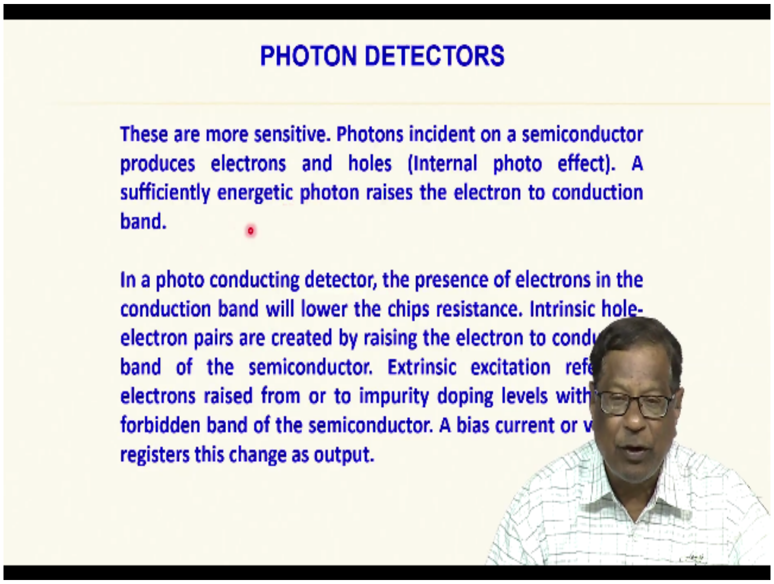

PHOTON DETECTORS

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

In a photo conducting 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 cond
band of the semiconductor. Extrinsic excitation refe
electrons raised from or to impurity doping levels with
forbidden band of the semiconductor. A bias current or v
registers this change as output.

The unit consists of small metallic cylinder closed by right blackened plate etc. etc. so the gas when it expands obviously it will obstruct the IR radiation reaching the detector ok. So that is how the detector works. Then we have other types of detectors they are so it is known as photon detector directly, they are photons incident on a semiconductor. These are all very common nowadays and so the photons will produce the electrons and holes depending upon whether it is an NP type or Pn type.

If it is NP type it will produce the electrons first on the other side by side it will produce holes. So that is the internal photo effect is sufficiently energetic photon raises an electron to conduction band and it is just like a what we have already discussed that is most of the metals have a conduction band and there form band and so the photoelectrons read and then the detection can be carried out.

So in a photo conducting detector the presence of electrons in the conduction band will lower the chips resistance that is the IR. So the intrinsic electron hole pair in both of them you cannot produce an electron without producing a hole. So they are all there in as and when they are produced every electron will produce a whole, electron there removed for the current generation of current detection and whatever it is it produces a hole in the whole also can move.

So the electron is raised to the conduction band of the semiconductor, so extrinsic excitation refers to the electrons rays from or to the impurity doping levels normal most of these NP type detector are made by doping the Silicon or Germanium with different metals that is a different science by itself. But it is already around degree level physics classes so you can look it up and the doping level depend upon the intensity what you need.

So you can operate at 1%, 2% of by 10 PPM and depending upon whatever is the required application. So within the forbidden band of the semiconductor only you have to do that is the limit which the doping element. So a Bias current or a voltage resistance this change as the output, that is all. So photo detectors are also popular nowadays and when you buy an instrument IR instrument you should find out which one is the which are the detectors employed in the infrared spectrum.

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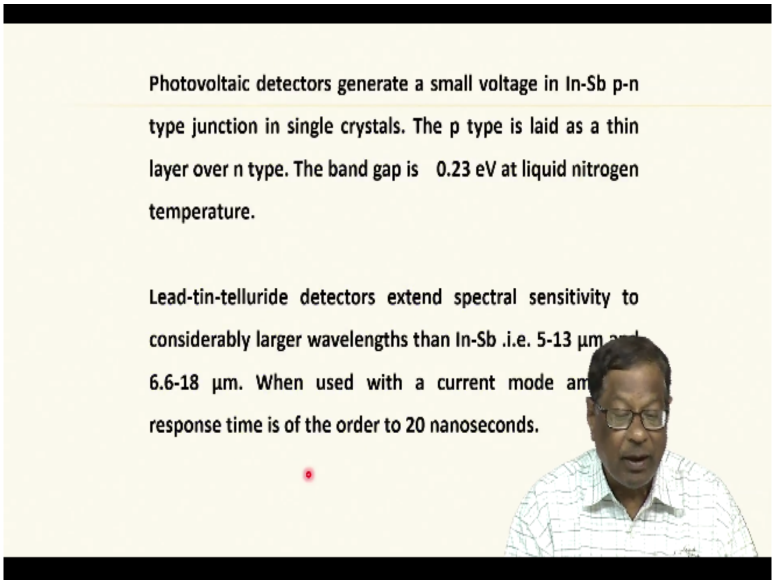

Photovoltaic detectors generate a small voltage in In-Sb p-n type junction in single crystals. The p type is laid as a thin layer over n type. The band gap is 0.23 eV at liquid nitrogen temperature.

Lead-tin-telluride detectors extend spectral sensitivity to considerably larger wavelengths than In-Sb .i.e. 5-13 µm 6.6-18 µm. When used with a current mode am response time is of the order to 20 nanoseconds.

So the cost quite often the cost is also dependent upon what type of detectors they are used, you can also calculate the year law says etc. etc. lifetime and all those things and decide on a proper IR instrument with suitable detector that is why we are learning all these things. So photovoltaic detector generate a small voltage in the INSB that is Indian antimony PN type junction in single crystals the area should there remember the figure what I had shown you earlier.

That I should I show you once again ok let me I just to remind you which figure you should go back this is the figure, ok so go back to this figure and you can correlate what I am going to teach you now with these things. So photovoltaic detector generator small voltage in Indian antimony PN type junction in single crystal. So the p type is layer as a thin layer over the end tag. So both of them are sagged, the band gap is approximately 0.23 electron volts at liquid nitrogen temperature.

Because you remember they were all around 77 degree Kelvin. So lead-tin-telluride are detectors are also there, they extend the spectral sensitivity to larger wavelength that is 5 to 13 micrometer. So if you want to do for IR then you need to go for lead-tin-telluride detector because up to 10 microns and millimicrons now is for IR that is why you should remember the range of infrared near infrared and then infrared and far infrared.

So the lead-tin-telluride can be used from 5 to 30 micrometer there so most of those things are used for infrared work for co-ordinate complexes of the metals ok. So the other range is 6.6 to 18 micrometers when so when we used to take current mode amplifier response time another important factor for you to learn about the response time of all detectors when you buy an instrument. So response time is of the order of about 20 nanoseconds that is fantastic is not it.

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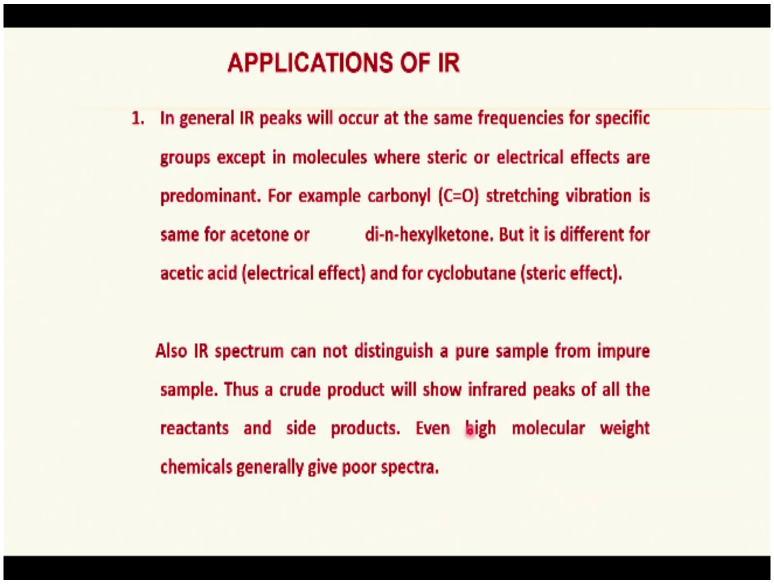

APPLICATIONS OF IR

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 infrared peaks of all the reactants and side products. Even high molecular weight chemicals generally give poor spectra.

So there are different ways of doing it, now I come to the applications of infrared, we have finished our discussion with infrared instrumentation, why I want to spend some time on application says I have want to reassure you about the complexity of the infrared do not be afraid why because the moment one sees an infrared spectrum what you will see actually is nothing but a few peaks on a graph paper and the number of peaks you will see.

So once first reaction is a bafflement what do I do with so many peaks, how do I identify and what is the thing I am looking for like that there are the questions will be arising in your mind. So in general what I want to tell you is the IR peaks appear for the same functional groups in the same area. So if you are looking for a particular functional group that is characterization of a compound in terms of it functional group when I give you a sample whether you do whether it is an aldehyde or amine or something like that you do not have to go to table or working table to for chemical analysis.

You just take the IR spectrum and if it is amine it will show amine functional group with aldehyde, which is aldehyde functional group carbohydrate that will show and then carboxylic acid that also will show like that different functional groups will show peaks exactly at the same position. So without knowing the actual compound you can straight away classify the unknown organic compound that it is an amine it is an aldehyde, it is a Ketone like that one can classify.

So the steric effects and the electrical effects etc. they always there for different compounds having the same functional group, that is propionaldehyde, butyraldehyde, there will be some differences ok but both of them are aldehydes. So they have to show aldehyde peaks at the exact spot where aldehyde peak is expected, other peaks you can one can identify whether it is propionaldehyde or butyraldehyde by depending looking at the propionaldehyde IR spectrum ok or butyraldehyde IR spectrum you can listen.

Like that any compound you want to identify you take the spectrum of a well-known purified compound and see how is the pattern ok. So now take a look at I am going to explain to you what are the different kinds of functional groups that we come across where to expect the peaks, look at this slide now.

I have written here the carbonyl group this is C double bond O carbonyl group aldehydes, ketones, bio gas and then carboxylic acid etc. So CO stretching frequency vibration is the same for acetone or di-n-hexylketone or any ketone for that matter here I have written only di-n-hexylketone but it can be same. So it is but different from carbonyl group that is a group of acetic acid by ketone and acetones ketone is acetone is a ketone.

And hexylketone is a ketone but acetic acid is having the same of part of the functional group, C-O is common remaining is O-H, C-O-O-H if you remember a little bit of chemistry the actual functional groups is C-O-O-H. So all these aldehydes ketones et cetera they all share common C-O bond plus another functional group aldehyde will have H as their another part and ketones will have another functional group.

Acetic acid will have O-H group like that different (()) (21:31) options, so I have the IR spectrum will be different for acetone, di-n-hexylketone but it is different from acetic acid and also it is different from cyclobutane. Now when I say cyclobutane it should compare acetone to hexylketone di-n-hexylketone and Cyclobutane. So none of these would be similar IR spectrum that is acetone di-n-hexylketone because of the steric effects.

So this is what I was trying to tell you the functional group will appear but actual spectrum will be entirely different. Now IR spectrum cannot distinguish a pure sample from an impure sample that you must understand very clearly. The crude product if you are carrying out a particular reaction a crude product will have impurity also. So the impurity is there, pure product is there, reactants are there ok.

I want you to understand whenever we carry out a reaction we take a particular organic compound we add some reagent, let the reaction continue and then at the end of the reaction we expect a product ok to either we had some technical compound and cool it and then distillate whatever it is whatever is the process there are reactants then there are products then there are bi-products, then there are parallel products intermediate like that.

If you take out a reaction mixture you will have all these compounds and infrared spectrum cannot distinguish any of these compounds separately. That is if you take a reaction mixture if where it will show the peaks of all the compounds, it will be much more complex than any pure compound. So one is clearly baffled by the complexity of the spectrum when you are following a particular chemical reaction.

So if I have a pure sample and some impurity is mixed in that it cannot show that the sample is pure or impure, it will just show the functional group and keep quiet, it is up to you to decide that. So how do you decide you take a pure compound spectrum and see whether they were there is any change in the pattern of the pure compound IR and the current sample IR sample what you have taken, so a crude product will show infrared peaks of all the reactants and the side products.

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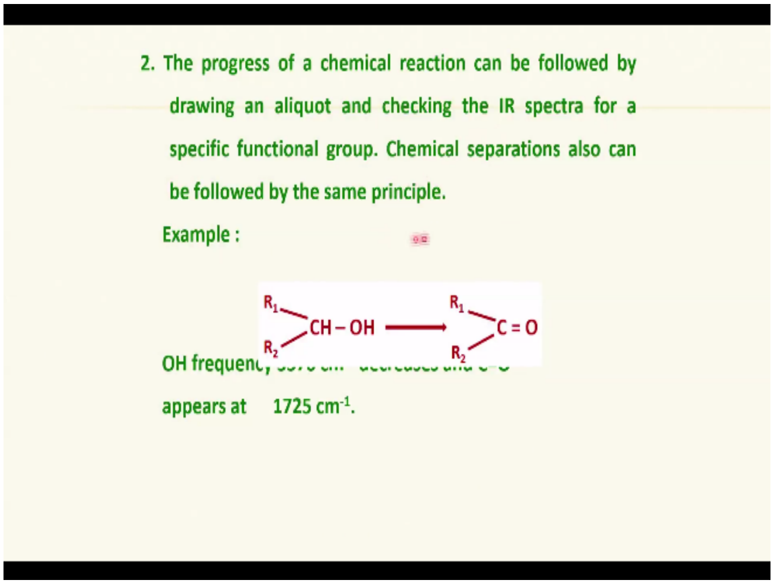

2. The progress of a chemical reaction can be followed by drawing an aliquot and checking the IR spectra for a specific functional group. Chemical separations also can be followed by the same principle.

Example :

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

Even higher molecular weight chemicals generally give very poor spectra this you should understand ok. Now look at this slide down, the progress so what is the use of a IR you may ask, so if I am carrying out a reaction the progress of a chemical reaction can be followed by drawing and aliquot of the reaction mixture and checking the infrared spectra for a specific functional group, that specific functional group should be part of the product or part of the reactant.

If it is a reactant the specific functional group peak IR peak will disappear and if it is a product having a specific functional group you are looking for then it will start appearing ok. So if it is a reaction mixture ok, the reactant is disappearing and product is appearing anytime you take a mixture both of them will appear. So how will you follow a chemical reaction you keep on looking at the both the peaks ok of the reactant as well as product specific peaks.

And when the peak of a reactant completely disappear you say that ok the reactant is no more there, it all of it is reacted, so their product becomes pure, so like that one can follow a chemical reaction using infrared. Now look at this reaction I have given you 1 example what is this compound this is R1, R2 CH-OH, so on the left hand side I have a reactant which is having a functional group OH.

That is it is an alcohol it is a secondary alcohol, so when this alcohol is oxidized this OH group will disappear and then I get a compound like R1 C=O R2 that is a Ketone ok, if R2 R1 is hydrogen then I get an aldehyde, if it is not a hydrogen then it is a ketone. So the OH frequency of the reactant is appears at 3570 cm inverse, this I had explained to you earlier also when I was introducing you to infrared in spectrometry ok.

So OH stretching frequency this is and this stretching frequency decreases as the reaction goes on and this concentration of the secondary alcohol decreases and it when it is totally when all of it is converted to the product. Now how does the product look like, product will have a functional group known as ketonic group or carbonyl group that appears at 1725cm cm inverse. So when you are carrying out this reaction you will be looking at the disappearance of the 3570 cm inverse.

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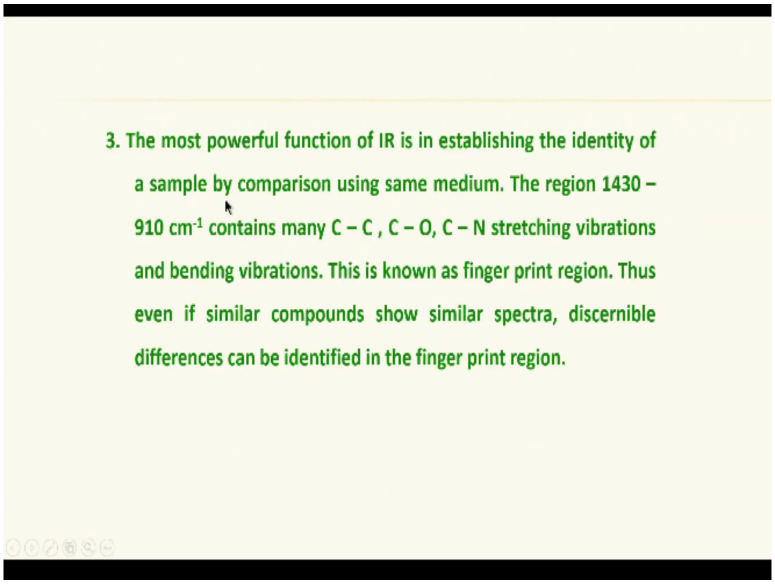

3. The most powerful function of IR is in establishing the identity of a sample by comparison using same medium. The region 1430 – 910 cm^{-1} contains many C – C , C – O, C – N stretching vibrations and bending vibrations. This is known as finger print region. Thus even if similar compounds show similar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

And appearance of 1725 cm inverse peak in the infrared, this is how the application of IR becomes very common. So the most powerful function of infrared is in the in establishing the identity of a sample by comparison using the same medium. Because again the medium assume very important role in comparisons. If I change the solvent IR may appear differently. So the region 1430 to 910 cm inverse.

This is where stretching of frequencies of carbon-carbon, carbon-oxygen, carbon-nitrogen and occur and some bending vibrations also occur. So you will assume you will know that almost all organic compounds will be having carbon-carbon double, single bonds many of them and carbon oxygen bonds will also will be having single bond C-O-H ok, O-H is C-O H. So C-O single bond frequency will be there.

And then CN single bond frequency, so many stretching frequencies and bending frequencies occur between 1430 to 910 cm inverse. This region is known as fingerprint region, that means you take a look at the pure compound you will be able to immediately identify ohh this compound is this, this spectrum belongs to a compound like this if ketone, it is this thing like that, so the fingerprint you will also be able to tell whether there is oxygen or not in the compound.

Whether there is nitrogen or not in the compound you can tell because if the CS these elements are not there the peaks corresponding to CO and CN will not appear, so whatever is you the real expertise of an infrared comes from looking at 1430 to 910 cm inverse range ok. This is known as fingerprint region. So even if speed similar compounds show similar spectra discernible differences do occur only in the fingerprint region ok take a look at this slide very interesting.

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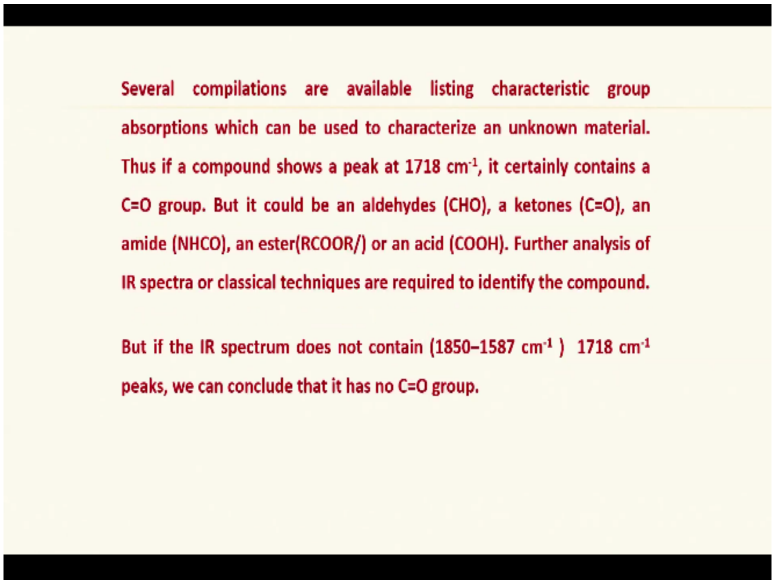

Several compilations are available listing characteristic group absorptions which can be used to characterize an unknown material. Thus if a compound shows a peak at 1718 cm^{-1}, it certainly contains a C=O group. But it could be an aldehydes (CHO), a ketones (C=O), an amide (NHCO), an ester(RCOOR/) or an acid (COOH). Further analysis of IR spectra or classical techniques are required to identify the compound.

But if the IR spectrum does not contain (1850–1587 cm^{-1}) 1718 cm^{-1} peaks, we can conclude that it has no C=O group.

So I want you to record this and give special attention to this ok compilation are available already the how do you compare, there will be I say you compare, but how do you compare, there are several compilation available in the textbooks, in the a database, in the computer problem microprocessor also in the same computer what you are going to buy there will be a database for different IR spectrum stored.

So when you are carrying at a particular reaction all you got to do is simply recall the particular IR spectrum and compare and the comparison also can be done using computers that becomes much more easier than personal visualization of each peak. So it is a little cumbersome, so several compilations are available listing characteristic groups which can be used to characterize an unknown material take a look at this slide now.

This compound as if a compound shows a peak at 1718 cm inverse we can definitely say it contains a C-O group carbonyl group but it could be an aldehyde, it could be a Ketone, it could be an amide, it could be ester, or it could be an acid, further analysis of IR spectra by IR only or some other classical technique are required to identify the compound. But if the IR spectrum does not contain these peaks that is 1850 to 1587 in that range if the IR spectrum does not contain any peak or 1718 cm inverse that is C-O bond**.**

So carbonyl group if it does not contain you can happily conclude that it has no C-O group, no so it is not a ketone, it is not an aldehyde, it is not an ester, it is not an amide, it is not an acid. So elimination becomes very easy ok. So this is another way of putting the infrared spectrum information to use. So given below I give number of examples here these are easily interpreted absorption bands of some common organic compounds.

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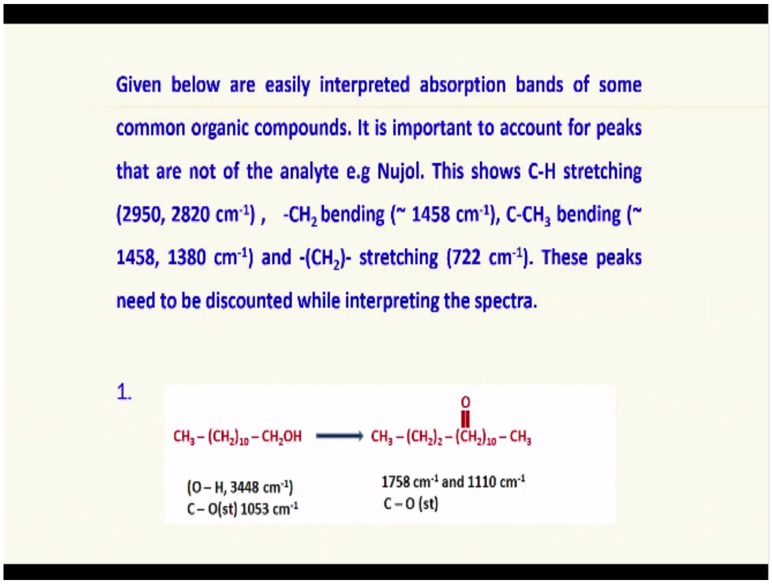

Given below are easily interpreted absorption bands of some common organic compounds. It is important to account for peaks that are not of the analyte e.g Nujol. This shows C-H stretching (2950, 2820 cm^{-1}), $-CH_2$ bending (~ 1458 cm^{-1}), $C-CH_3$ bending (~ 1458, 1380 cm^{-1}) and $-(CH_2)-$ stretching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

1.

$$CH_3-(CH_2)_{10}-CH_2OH \longrightarrow CH_3-(CH_2)_2-\overset{\overset{O}{\|}}{(C}H_2)_{10}-CH_3$$

(O – H, 3448 cm^{-1})
C – O(st) 1053 cm^{-1}

1758 cm^{-1} and 1110 cm^{-1}
C – O (st)

I cannot give you all, there are quite a few organic compounds with specific functional groups it is not possible for us to cover everything. But it is not necessary also, what is important is to account for peaks that are not of the analyte ok. For example if I am using a solvent at a discount the solvent peaks. If I am using a nujol I told you that it shows you table at around 141398 are something you have to discount that.

So like that IR spectrum in the IR spectrum several peaks need to be discounted corresponding to solvent, corresponding to the media, corresponding to impurity like that there will be a lot of variations, but as you continue your work in organic chemistry or infrared spectrometer you will become an expert slowly. So I am going to cover here only typical peaks ok typical functional groups and their IR positions.

So that you can remember a few, but there is no need for you to remember, now a days data bases are quite efficient to remind you and IR peak what you get there also identified by the way of cm way of number that is like you know 171458cm if you look at new an IR spectrum from FT-IR you will not even see a graph, you will just see the peaks but at the bottom of each peak the exact wavelength or centimeters in cm inverse is printed.

So you do not even have to look where is the peak what is the actual position of the peak etc. So nujol shows C-H stretching frequencies around 2950 and 28 cm 28 it shows a CH2 bending 1458 C-CH3 bending at these things and CH2 stretching frequency at 722 cm inverse. So these peaks need to be discounted while you are taking the spectra in nujol ok. So look at the reaction couple of reaction I am showing you here.

This is again a secondary alcohol CH3 (CH2)10 CH2OH here I can expect OH stretching frequency for the reactant at 3448 and carbon oxygen stretching frequency at 1053 and here only the Ketone I get one C-O group that is at 1758 and 1110 is the CO stretching frequency ok, single bond. So quite often you will also see that when you look at the IR peaks you will see that sometimes we write into bracket s into bracket w into bracket m like that.

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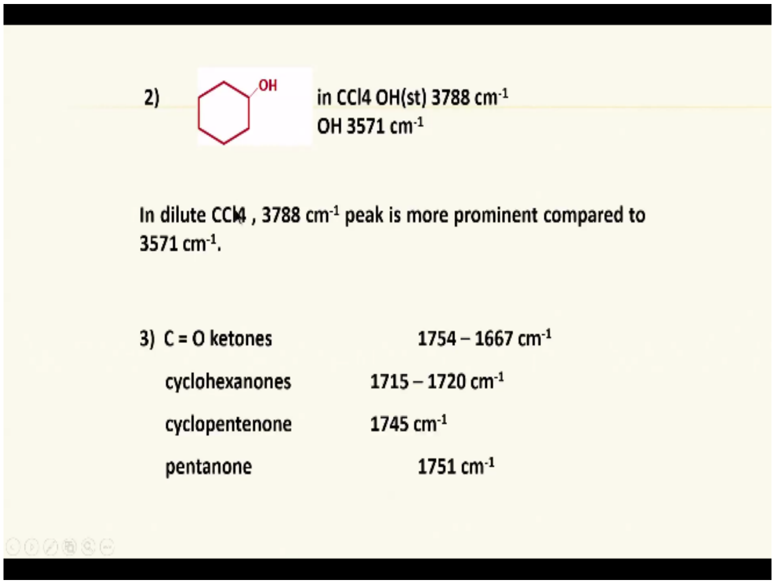

2) in CCl4 OH(st) 3788 cm^{-1}
OH 3571 cm^{-1}

In dilute CCl4 , 3788 cm^{-1} peak is more prominent compared to 3571 cm^{-1}.

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

So those notations correspond to strong, weak and medium ok. So I do not know let us take a second look at the second slide ok this is again a secondary alcohol, this is C6H6 group, so it is C6 H2 H2H2 1, 2, 3, 4, 5 C6 H10 OH ok yeah C6 H10 OH that is cyclohexane and it is taken in carbon tetrachloride solvent, it should show OH stretching at 3788 that we expect now is not because it has got a know it if I know the structure I can expect where is the peak.

And OH stretching frequency also I should expect. So in dilute carbon tetrachloride 3788 cm peak is more prominent compared to 3571 cm inverse, what does it mean if I change the cyclohexanol or add a little bit of carbon tetrachloride this peak is more prominent corresponding to CCl4 than 3571 peak. So one has to be careful regarding how to take the spectrum ok. Similarly if I have a ketone I can expect a peak somewhere here.

A cyclohexanone in the same range approximately 1715 cyclopentanone 1745 and pentanone alone normal pentanone will show you 1715. So anywhere a peak between 1715 to 1754 is the peak for C-O group. We will continue our discussion in the next class ok. So try to mull what I have been teaching you regarding the application. So there is no need to get panic but a cool headed thinking will help u. So it will also as you grow in experience you will be able to identify many peaks yourself, thank you we will continue our discussion.