Course on Analytical chemistry
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Lecture 28
Module 6
Spectrochemical Methods - 3 (Continued)

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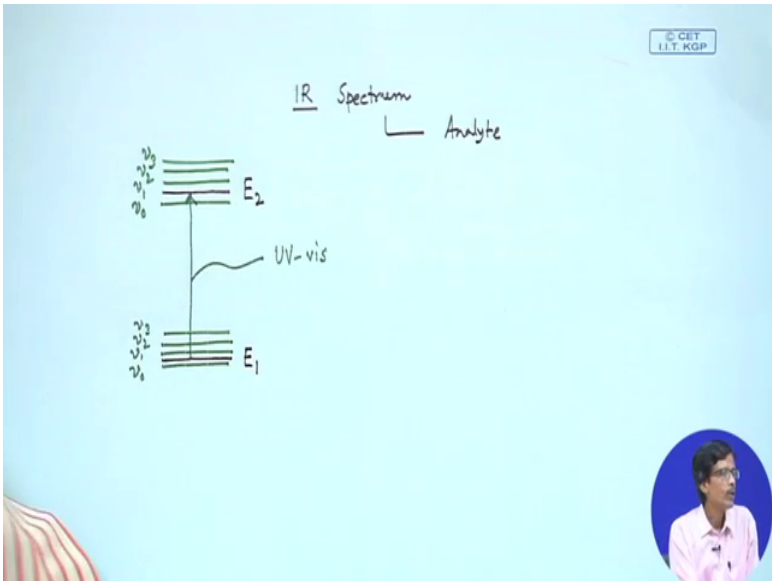

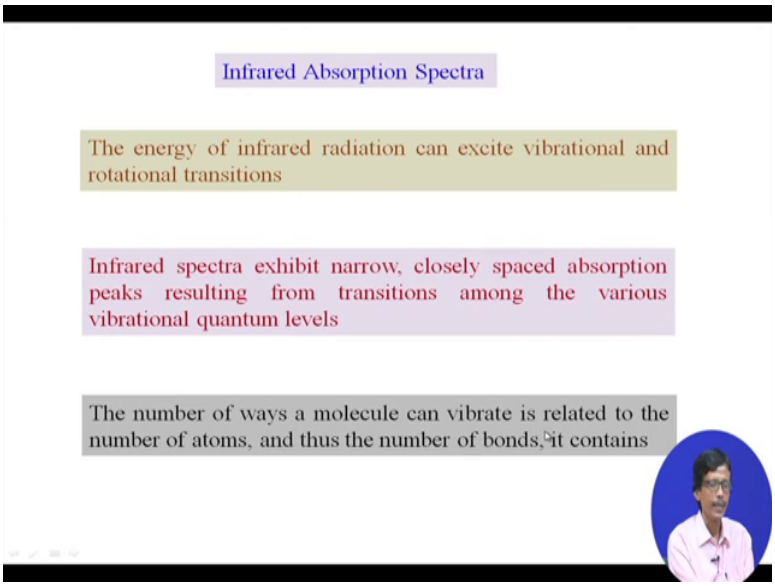

Hello and welcome back to this class where we have started discussing about the IR spectroscopy and we want to record the IR spectrum of any particular analyte which like that of our invisible spectroscopy can show the corresponding absorption in the IR region but why these species are absorbing that we have seen that we can have the corresponding energy

levels what we have seen in case of invisible spectroscopy that it can absorb and from the excitation of this level of E1 to E2 and that you give rise to the corresponding absorption in the UV visible range, now if we have small other levels involved over there the vibrational levels the vibrational quantum levels if they are available.

So we can have the V0, V1, V2, V3 etcetera. Similarly here also V0, V1, V2 and V3 so these are the first vibrational levels of the ground electronics state similarly the second, third, fourth etcetera. And this V0 is also the corresponding first vibrational energy levels of the vibrational quantum level for the first exited electronic state which is E2. So this will basically give rise to the corresponding absorption so what we do basically the energy, the available HU in the infrared region can excite the vibrational as well as the rotational transition because the rotational energy levels are more less and their energy levels are lot that much separated compared to your vibrational and the electronic level.

So what do you find that they can exhibit some narrow and closely space absorption peaks because the energy difference is not much and unlike your electronic spectra which is very broad one and which is well defined in some cases they are closely spaced, so side by side we can have large number of peaks that we will see that for a particular small molecule like that of the thing what we just discussing about the acetone molecule.

Acetone is a solvent molecule and that acetone can also give rise to so many closely spaced IR absorption peaks because we can have CC bond we can have CH bonds and we can have CO bonds and all these bonds can have the stretching, bending, twisting and all the different sorts of vibrations vibrational levels and the vibrational mode available because all these different modes are to be there and which are IR active so the different number of types of these absorptions is related to the number of ways the molecule can vibrate is related to the number of atoms and thus the number of bonds it contains.

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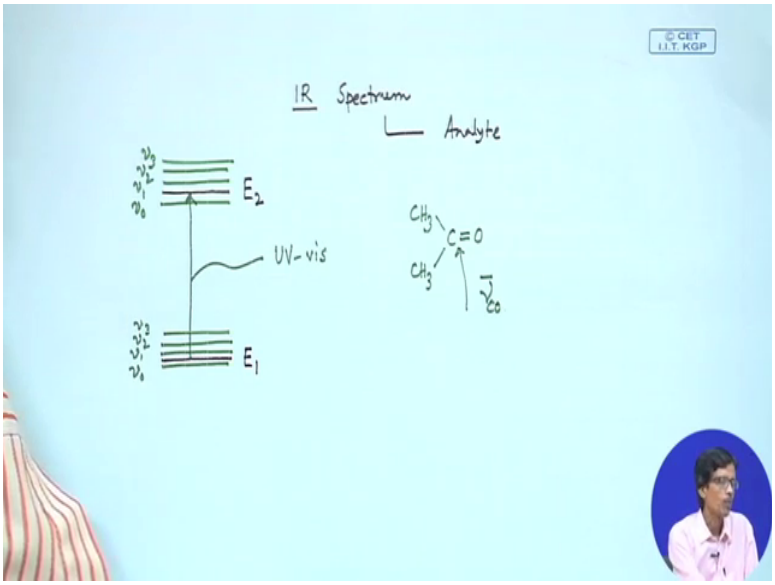

So that means the overall whole structure we can have some idea if it is the corresponding acetone CH3 COCH3 so we can have CC bond CH bonds CO bonds and all these things so we are basically looking for this particular stretching frequency say Nu CO or Nu bar CO this is will be the number unit. So Nu bar CO will characteristically identify the presence of this CO bonds as it is present in case of acetone.

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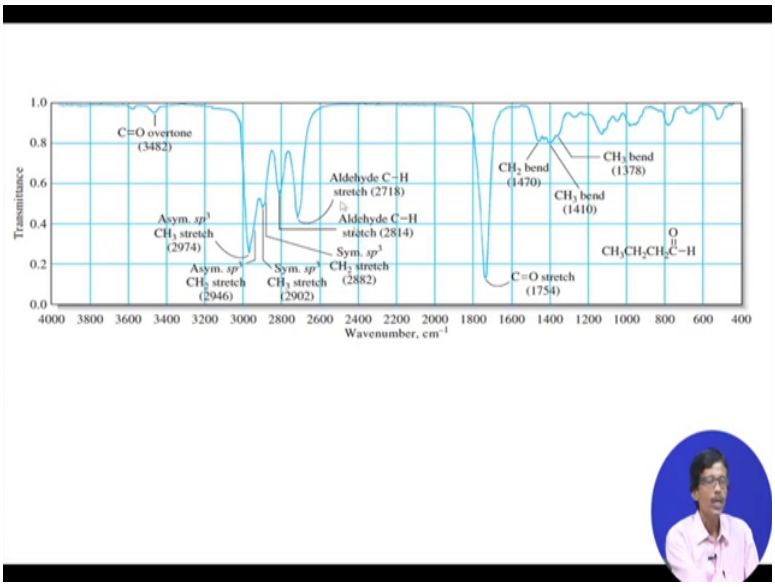

So for much more other types of molecules such as the corresponding one this is one such example is for your butanol molecule which is nothing but CH3 CH2 CH2 COH.

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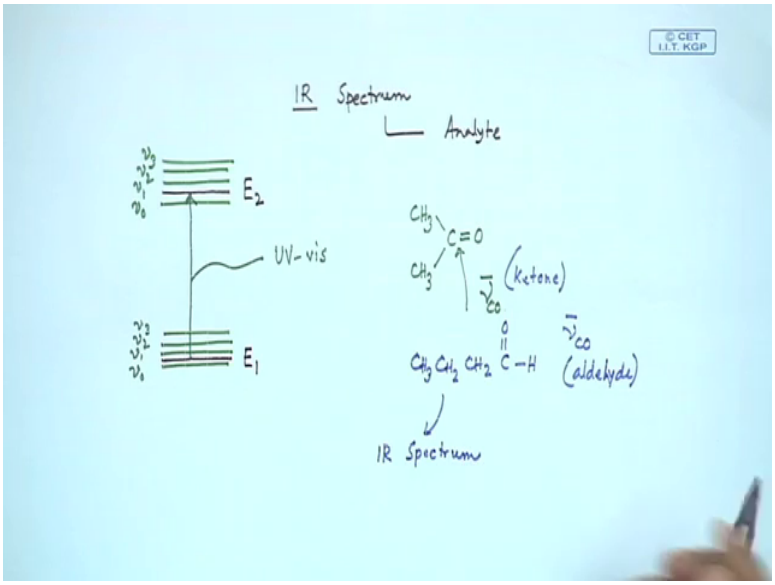

So having this one that means instead of this CO we can have the aldehyde function that means the same CO but this carbon is not attached to two carbon centre over here but can be attach to H. So it can have a difference stretching frequency of Nu bar CO which is for the aldehyde function, aldehyde function and this is for your ketone function.

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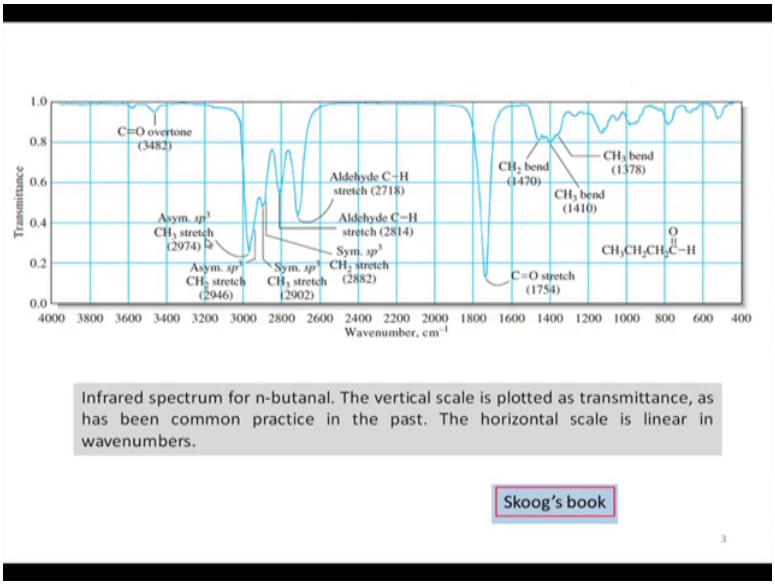

So this butanol that means you can have four carbon centres CH3 CH2 CH2 and COH and if we look at the corresponding IR spectrum of that molecule we see which is a very complex one you see so many bands from there and it is again taken from the Skoog's book.

So any textbook will cover all these bands and the characteristics one but you just look at the corresponding range of the corresponding access that means the x axis we are plotting some wave number unit. So wave number is centimetre inverse is we are plotting from 4000 to 400 it is the standard range of IR spectra and where we can get in the other axis that means the transmittance axis.

This is the a transmittance mode, so what we record over here unlike your invisible spectra where we are plotting the absorbances but in this case we will be plotting the transmittance. So this transmittance only plot from 4000 to 400 so we get the different peaks basically the CO overtone so one such band we call it as overtone band which is at 3482 centimetre inverse then you see these are very closely spaced one so this asymmetric sp3 bound carbon.

So if we have the carbon which is also present in your acetone so in case of your acetone as well as in all these cases we have a corresponding CH3 so that means the carbon hydrogen stretching frequency and when this carbon is sp2 hybridized we get the corresponding stretching frequency at 2974 and the stretching mode is asymmetric one.

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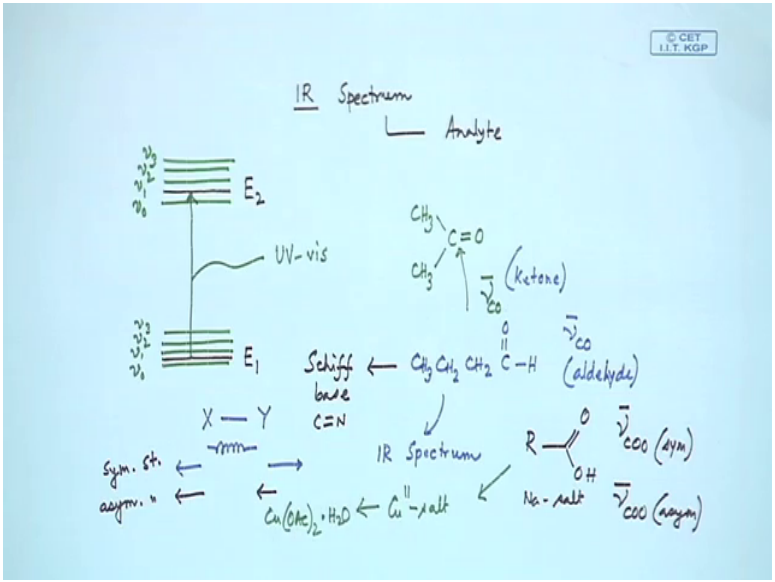

That means just now what we have seen in case of the corresponding connectivity for x and y and if we consider that this is like a spring like arrangement so if we stretch these two atoms through that bond in these two opposite direction, we get a symmetric stretching, but if we get something where this is being moved in this side and this is also moving in side so we get a asymmetric stretching. So where symmetry is not present we get something which is asymmetric stretching frequency and the symmetric stretching frequency which in the most

of the cases which is also characteristics like that of our CO function CHO function and as well as your carboxylate function also that means if we have some acid group RCOOH so there also we have the characteristic carboxy is stretching frequency COO Nu bar is due to symmetric one and COO asymmetric one.

So this particular stretching frequency is also very much characteristics because we can identify these things also, was whenever we have these carbonyl function or this aldehyde function we know that we can modify them for these other reactions like that of our corresponding condensation which we can consider as the schiff based condensation where this COO bond that means C double bond O bond is converted to immune function.

So you see that there is a change that means CO function is going to CN function, so aldehyde is going to immene and therefore the corresponding stretching frequency that means the amount of energy which will be absorbed by these moles will be different. Similarly when this carboxyl function you have so when the free carboxyl function that means the bond this particular corresponding free acid or its corresponding sodium salt if we consider that we can find out the corresponding magnitude or the corresponding values of these stretching frequency for COO and their symmetric stretching frequency for CO but this can give rise to corresponding other metal salts also like your copper 2 salt.

We know that a typical structure we have for copper acetate which is Cu(OAc) whole 2 we write this molecular formulae as Cu(OAc) whole 2 H2O so this acetate is bound to the copper centre. So comparing the free acid comparing the sodium salt, we can have a different type of this corresponding stretching frequency for the carboxyl function and that also not only telling us that what sort of bonding is present between carbon and oxygen and carbon and carbon towards this alkyl function.

But if the new bonds are forming the coordinate bond so the nature of this coordinate bond is also can be found out by looking at the corresponding IS stretching frequency for this CO and this CO and this CC because this will all be changing because this vibrational mode of activation will be different if it is free as acid, if it is as sodium salt or if it is bound to the corresponding copper ion or the copper centre as is corresponding metal ion complex.

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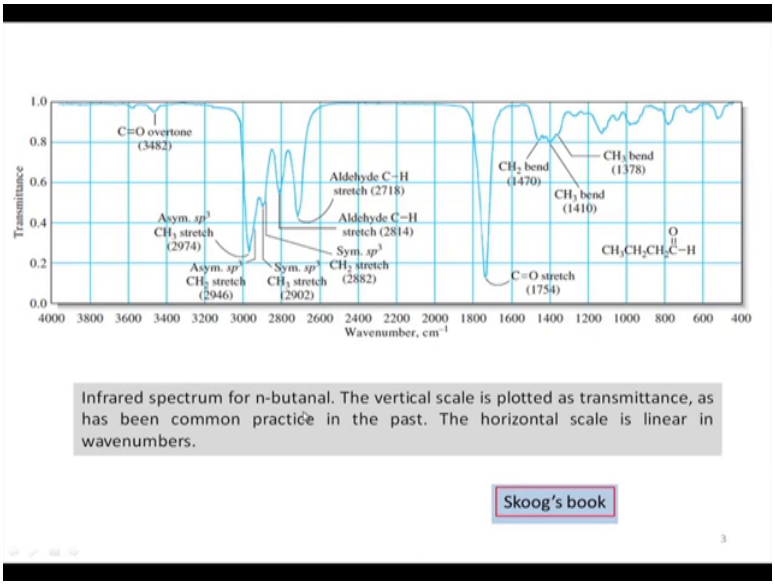

So if we just simply consider, the butanol also there so where we get that the plot of this vertical and the horizontal one is also in the wave number unit. So next we get that the asymmetric sp3, the asymmetric sp3 stretching for the CH2 function that means two we have two CH2 one is adjacent to your aldehyde function and other is attached to your CH3 function then we have the corresponding symmetric sp3 stretching which is you see there is less than 2974 so asymmetric stretching is little bit higher wave number unit compared to your symmetric stretching one, then we are symmetric for the CH2 one.

So all these things are coming due to the presence of this CH3 and CH2 units. And then what we have one more is very much characteristic at 2814 stretching frequency which is this CH is not of the CH of the CH of this CH3 or CH2 or any other CH2 but it is characteristic for the corresponding aldehyde function so you have a 2814 at aldehyde CH and the other one is also the corresponding stretch was aldehyde CH so other one is also be available over here and which one is more characteristic for this function is that as I told you that if you have corresponding carbonyl function for acetone then the corresponding CO function for acid or any other case we have a very characteristic one at 1754 centimetre inverse.

Then we see that at these values which are not strong enough that means that your transmittance is of this particular magnitude that means your corresponding absorbance is also not very high, so these are all bending modes. So bending modes all appear in this particular range of 1400 plus one is at 1470 another is 1410 another is 1378 so they are for mostly for the CH3 and CH2 for not for stretching mode but for the corresponding bending mode of activation.

So you see that all these values of this particular molecule is characteristic one for your very small organic molecule which is your n-butanal.

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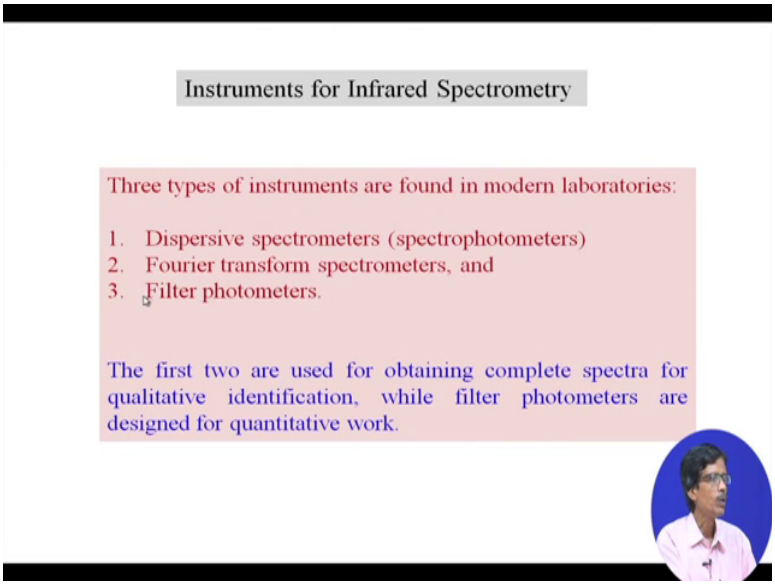

So next what we will see that how we can measure or how we can monitor utilising the corresponding basic instruments that means the instruments what we can have for infrared spectrometry. So this particular one can have three different types of these instruments because is a development from one step to the other where in the different modern laboratories the synthetic laboratories to any other analytical laboratories we find that one type is dispersive spectrometer or we consider as spectrophotometers.

Then we can have Fourier transform spectrometers we call FTIR spectrometers and another one is simple filter photometers utilising IR radiation. So this first two are very useful one in these two cases we have in the use of this for complete spectra for qualitative identification while the filter photometers are designed for quantitative work because we know that invisible spectroscopy utilizing Lambert Beer's law we know that the unknown concentration we can figure out.

Similarly by looking at the corresponding stretching frequency that means the if we monitor the corresponding amount of transmittance or absorbance because these two are related absorbance as well as transmittance. So what we find that the quantitatively we can also monitor the corresponding concentration in case of this filter photometers.

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So the basic instruments what is available in all these laboratories are like this so this is the company the Thermo Fisher company as given us this particular type of instrument.

So this modal is very small one now a days when its bench stop also we consider it and we can use in the different types of laboratory analysis.

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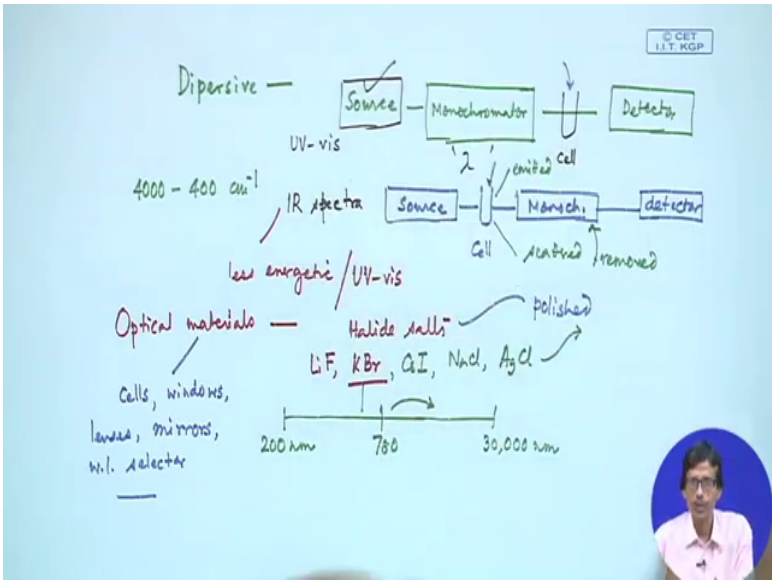

So what we have then all these cases the basic thing that in all cases the instruments what we have the first one is the dispersive one where like that of our invisible spectroscopy we have the corresponding source and we get this particular source through monochromator and we

all know that this particular one where we get this monochromator and then finally we go for the detection.

So is the corresponding configuration that means how where we put this one, so if we have this the combination of this source monochromator and detector what we find that in the case of invisible spectroscopy where this energy this particular available energy of radiation is very high. So we put after we get the radiation monochromatized that means the single wave length so with single wave length radiation we get from the source so monochromator is selecting that particular radiation and we put the sample inside the cell or cuvette then the amount of absorption we monitor through your detection.

But in case of your IR IR study that means IR spectroscopic studies so IR we monitor the IR spectrum or IR spectra what we have we have same source and we have the monochromator and the detector, okay. Now we will bring this cell basically over here because energy is less in case of IR radiation. So now we have the cell which can be placed in between your source and monochromator and then we can have the detector.

So once we put this L and we have the monochromator so this particular one that means the cell when the source is directly falling on the cell sample we can have the emit emitted radiation also and scattered scattered radiation so this emitted fraction of radiation and the scattered fraction of radiation can be eliminated by your monochromator, so will be removed or eliminated by the use of this particular monochromator.

So this is the corresponding advantage we can say for the use of the corresponding cell you can place in between source and the monochromator because this radiation what we use for the measurement is less energetic compare to our invisible spectra that means the energy available in this particular range. So this particular thing and also the corresponding optical materials what we can use these are made up of different halide salts like anyone it can be made up of lithium fluoride, it can be made up of potassium bromide which is most commonly used because we call these as the KBr optics what we can use.

Then cesium iodide we can use, sodium chloride or silver chloride. So this particular range that means the range which is available for the identification because the instrument what we are operating we have seen just now that is operating between 4000 to 400 centimetre inverse so it should be transparent so this KBr basically giving us a window of this IR radiation starting from a nanometre scale of 200 nanometre what we use in spectra to 30,000

nanometre wave length so long our wave length region which we all know that beyond 750 or 780 nanometre.

So it is if it is 780 nanometre we are entering into the IR range. So this optical instruments what we can use the material is our of this salts because all these things that means all the different optical materials will be utilising for the cells making this cell where we can put the sample here, here also and here also we have the samples so making the cells and then windows of the spectrometer then lenses, mirrors and the wave length selector because this particular one should not absorb this radiation and when we see that when we use this KBr samples and these optical components and the optical materials are nothing but the this salts but they are definitely polished.

So the polished salts of this will be utilised for our measurement and that will help us to pass the corresponding IR radiation to be absorbed by the sample taken within this particular cell. Then what we find that we can have the corresponding one is your source, so what are the sources we can use.

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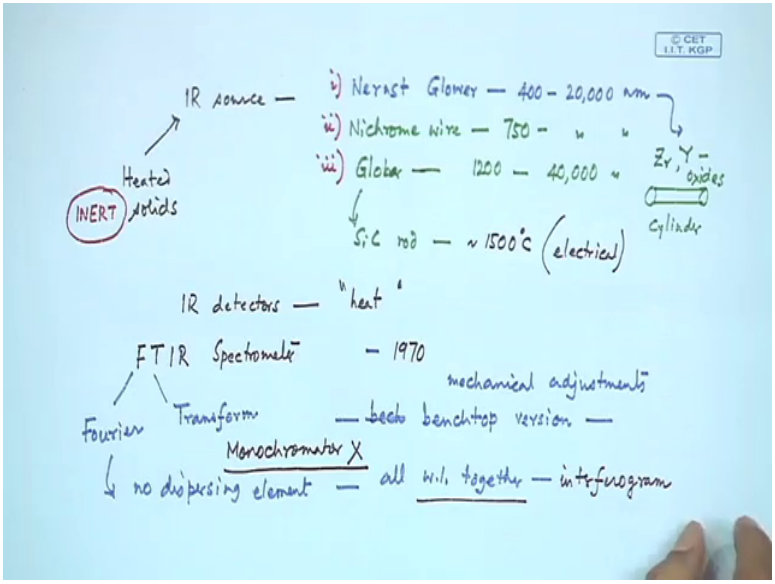

So this give rise to different sources so IR sources so if we heat we all know that heated solids like our body human body which is having at a temperature of 37 degree centigrade we also radiate we also give rise to the IR radiation so the corresponding thermal energy what we release basically that is in the range of IR. So heated solid basically and heated which what particular type of solid it should be INERT, it should not decompose, it should not convert, it

should not react with air or nitrogen. So heated INERT solids will be very much useful and three such sources are in common use.

Mostly all these instruments used throughout their development from normal dispersive IR spectrophotometer to now-a-days available Fourier transform IR spectrometers. So first one is your Nerast Glomer we call it is the Nerast Glomer which can have a range of 400 to 20,000 nanometre in terms of nanometre we are saying because as we move from the invisible range how far we can go towards the longer range that is known.

So Nerast Glomer are nothing but what we know these things again some very INERT material and that INERT material is made up of zirconium and yttrium oxides and we consider or we make it as a cylinder. So cylinder of zirconium and yttrium oxides can give rise to that particular Glomer and when we heat it up it can give rise to the corresponding radiation in this particular range. Then simple Nichrome wire we know can also be useful in the range of 752 to 20,000 nanometre then another well-known source for IR radiation is the Glober call it as a Glober which is only available from 1200 to 40,000.

The other range is higher that is why most of the time we get this one like that of our invisible spectroscopy we have seen that we can use tungsten for the visible range and H2 and the D2 lamp that means the deuterium lamp for the UV range. Similarly if we want to go beyond this particular 20,000 nanometre range we have the use the Glober source. The Glober source is nothing but this particular Glober, Glober source is nothing but a material of silicon carbide rod. So if we see that is a silicon carbide rod so how it will work is the idea is that there is a simple one is the heated solid we have to use and that heated solid so at what particular temperature we should heat it we should heat it at 1500 degree centigrade.

So it is nothing but by presage of electrical energy so electrically if we heat it up to 1500 degree centigrade it will glow. So that particular glowing material solid silicon carbide rod can give rise to the radiation in this particular range. Then comes the corresponding IR detectors what we can use this detectors is as which can respond to the thermal energy or heat. So this particular one should have a corresponding detection mechanism which can be very useful to detect the corresponding energy which is coming out from the corresponding sample for analysis.

So is basically we can go for a corresponding spectral technique which will be considering as the Fourier transform IR spectrometer, it is there for some time in the market from say 1970

so in this years basically it was first appeared in this particular time but at that time it was very bulky, expensive and required mechanical adjustments that is why they were not so handy and we require some handy one we require some of the small one so that is why currently these are available as a bench top version bench top version is now-a-days available and is a mathematical technique named after Fourier, Fourier transform.

So is a Fourier transform technique and it is not a dispersive spectrometer. So no dispersive element is present so no dispersing element so we measure all wave lengths together which gives rise to something which we call it as interferometer through interferometer we get something which is interferogram, so what we see that all the wave lengths will be measuring together and this has no monochromator also so there is advantage.

No monochromator for these sorts of instruments and we can basically use the corresponding same source for monitor all these things and that is why we just see that how we can use the corresponding interferometer.

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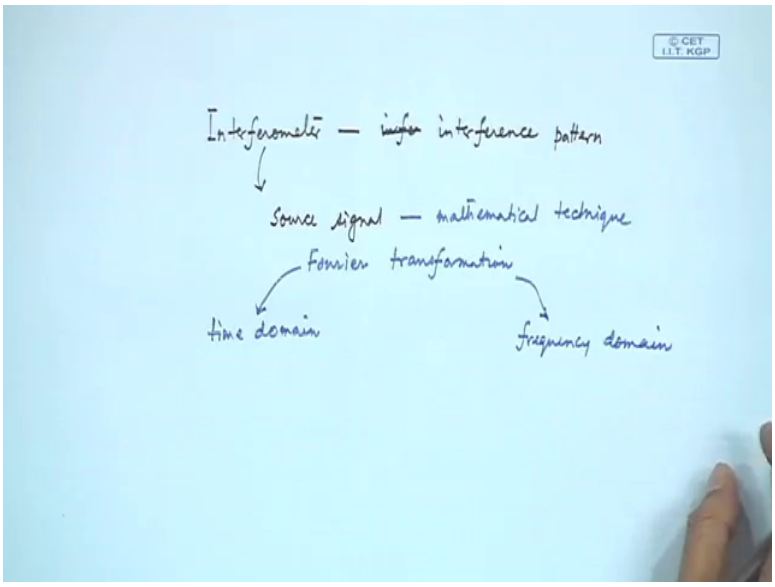

The function and the use of the interferometer which is giving the interferogram and one such known example of that interferometer is Michaelson interferometer, so interferometer which basically give the interference pattern interference pattern and this interference pattern is nothing but your interferrogram, and what this interferometer is doing? It is modulating the source signal.

So you have the source signal and that source signal is modulated and we use some mathematical technique so this mathematical technique is basically known as the

corresponding Fourier transformation. So this Fourier transformation is the important thing that we can measure everything that means all wave lengths together and we basically get the corresponding spectrum as a time domain spectrum and with time basically what we get the signal amplitude with time we plot that will see the next day that how we can plot the corresponding time domain spectrum.

And finally the interferometer will give you the corresponding one with that of our frequency domain spectrum. So that particular change from getting the thing that means from time domain spectrum to a frequency domain spectrum how will you get that and that we will see ultimately in the corresponding spectrum of your FTIR.

So thank you very much.