Course on Analytical chemistry
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Lecture 29
Module 6
Spectrochemical Methods - 3 (Continued)

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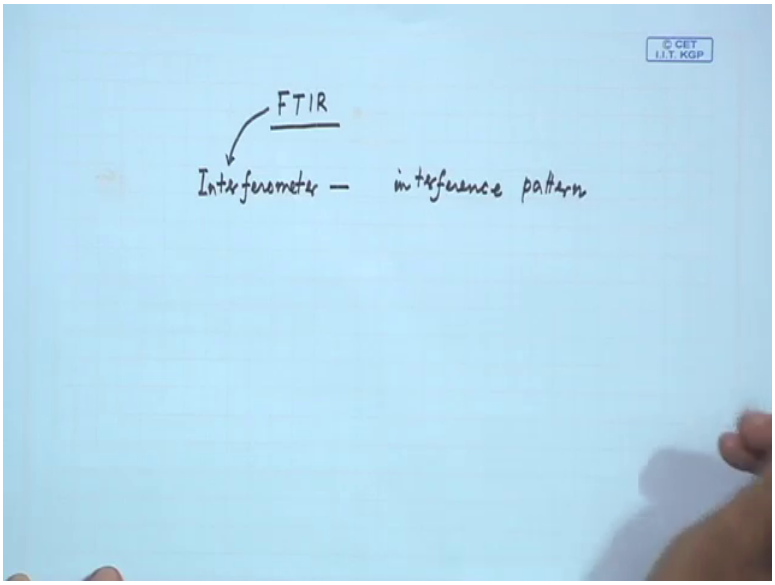

Hello, welcome back to this class of analytical chemistry where we are talking about FTIR spectrometer and one of the basic and the most important part of this instrument what we have seen yesterday or in our previous class is the corresponding interferometer which is needed to get some interference pattern.

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So all these things are there within the very basic component of a FTIR spectrometer what we have seen so is a very compact one and where all the individual parts are present and one such part is there is your interferometer.

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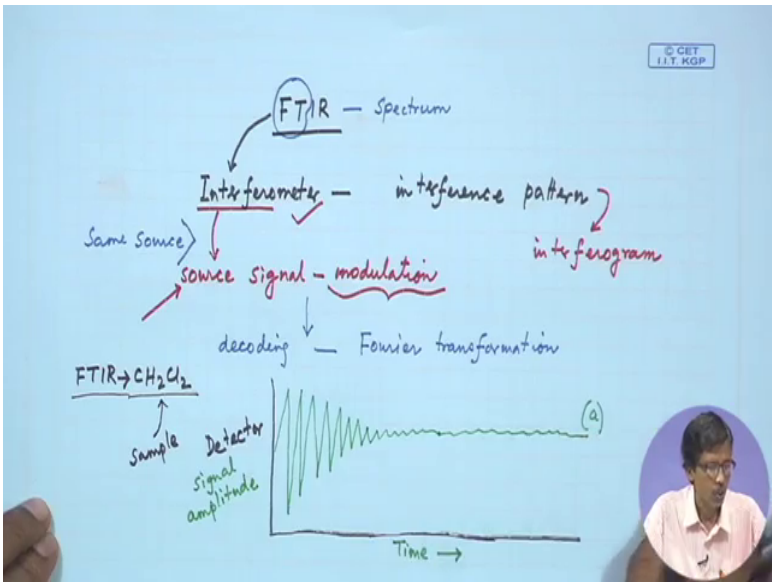

So if that particular interferometer is used for getting the interference pattern and the particular type of interference pattern is known as the corresponding interferogram which is produced from the interferometer. So interferogram is produced what is being done over here that means what interferometer is doing for us is it modulates the source signal. So we have the IR source that we have also discussed that what are the different types of sources we can use.

So by simple thermal activation of some solid material can give rise to the corresponding range of IR frequency and that particular source signal when we get it can be modulated. So the modulation of that particular source signal is important and we can monitor or we can measure this particular modulation for any such source which is also used for, so same source we can use for other type of spectrometer that means the dispersive spectrometer. So for FTIR also the same source we can use but we can have also at the same time the laser housing and that laser housing also can give you for this particular type of modulation.

And once we have these modulation for this particular signal so we have to go for the corresponding decoding by the corresponding mathematical form which is your Fourier transformation. So we can go for Fourier transformation such that we can have the corresponding FTIR spectrum in that we have we will be able to get the corresponding FTIR spectrum and what do you find over there that in this particular case if we take a very simple sample like that of our dichloromethane.

So if we want to have the corresponding FTIR spectrum of dichloromethane, what will happen and what detector will see and very soon will also see the block diagram of the whole instrument where we see that you have source, you have the modulator and all these and these particular things when we have the interferometer what detector is sensing so detector is sensing something which we can consider it as its signal amplitude. So the detector signal amplitude can be measured and that we just simply plot against time.

So this is one form of the spectrum we call it the spectrum A for that particular process, so what we get that particular signal amplitude so it will be modulating like this. So this total outcome of this thing that means this particular signal amplitude against time we can obtain this through this interferometer. So that interferometer is basically giving us these things that means what we get we can consider or we can tell this as the corresponding time domain FTIR spectrum.

So this time domain spectrum can be now decoded for its corresponding Fourier transformation for this signal what we get for your corresponding FTIR spectrum for the sample which is your dichloromethane, so how it will look like?

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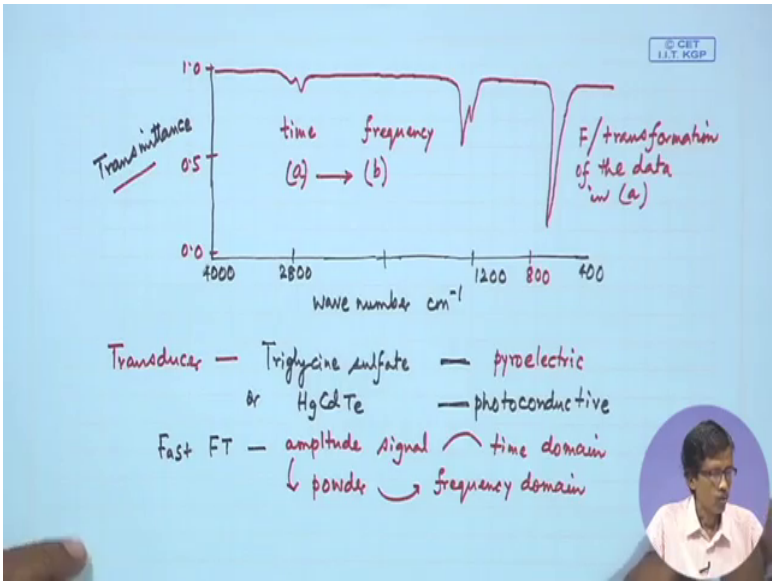

So if we go for this thing that means this will be simply converted to the corresponding frequency as based spectrum where we get the same thing that means the same plot only difference is that how it looks like only that Fourier transformation will give us, that is change in the axis which was originally timed so now it is in the wave numbers centimetre inverse and we can have a centimetre inverse of say 2800 because we start from 4000 to 400 this is the normal range and we can have adjacent point over here and we can also this 1200 one.

And this is now your transmittance, so we will get that as your transmittance and we will be having this particular one for the signal is this that when this is close to 1 and this 0.5, so in this particular range what we get so some small peaks at 2800 then this can up to 1200 so at this point we will have peak like this and then beyond 800 so this it should know this beyond 800 will have this very sharp deep over here and this is the thing.

So very simple one also so we get the corresponding spectrum so whatever data we obtained in the previous plot that means time versus the detector response or the detector signal amplitude, so that can be converted so earlier we have that a so a was there so how we can convert a to b. So earlier one we talk it as the interferogram now it is the corresponding Fourier transformation of the data which data, the data we receive from the interferometer that means the data in a.

So when a we just go to b so this was your time domain one to the corresponding frequency domain. So this is one such important thing that we can have, this particular one for this plot

so what we get over here is that this is part from the interferometer then another most important or the basic component is your transducer. So the signal transducing capability what we can have so what are the very basic or the most commonly used transducer for these sort of instruments are one is the pyroelectric one so is known as pyroelectric transducer and other one is photoconductive so these are the two different or the most commonly used transducers what we can use for this measurement that means the signal what is getting absorbed by the sample.

So this particular pyroelectric transducer so pyroelectric transducer is made of triglycine sulphate so is a sulphate salt of the corresponding organic amino acid triglycine. So three of these glycine units will be there so triglycine sulphate is a solid one so that solid can be behaved as a transducer or which is of pyroelectric type or the photoconductive one is nothing but which is mercury cadmium telluride is a mercury cadmium telluride so these transducer and all these things can give rise to in some cases a first FT that means the first Fourier transformation.

Where we get the corresponding amplitude signals so we have the amplitude signals in time domain, so amplitude signal in time domain which we just can be convert to power this amplitude we basically convert it to power as well as the transmittance and power in the corresponding frequency domain.

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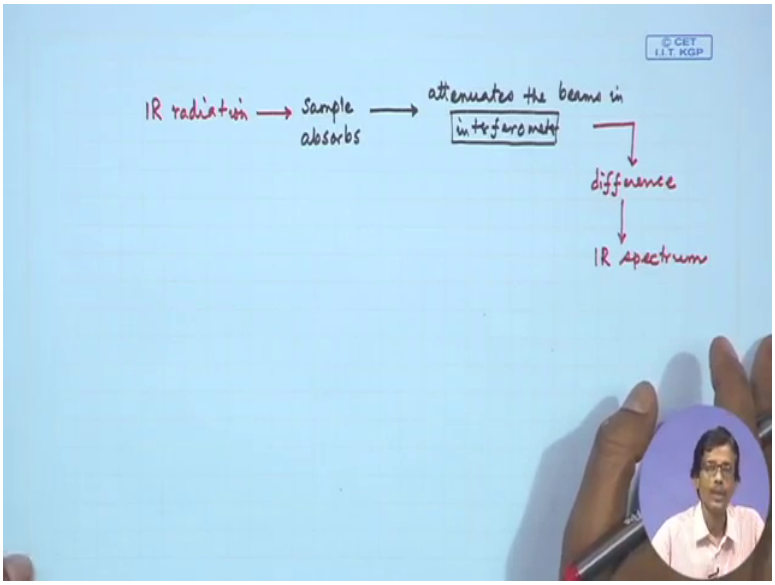

So that is why we see that how the different IR radiation when it falls on the sample so we have the typical IR source or the IR radiation and which is falling on our sample. So what

will happen due to that particular molecular vibration that means the bond stretching and bond bending and bond rocking all these, this sample which is being exposed to the IR radiation will absorb so the absorption will take place then basically we will have the beam. So these beams are there so the IR beams basically can be attenuated or attenuates that means chopping off, the radiation is getting chopped off so attenuates the beam in by the which particular part is being done by your interferometer.

So that is all that means very basic or the heart of the instrument is your interferometer and this particular change basically give you some difference due to this attenuation and ultimately that difference is measured or counted in the corresponding IR spectrum. So finally we get that particular IR spectrum.

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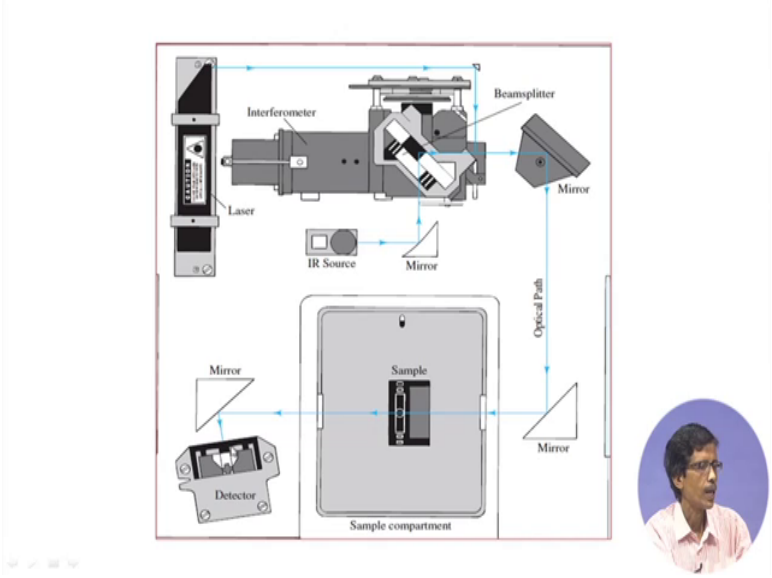

So whole instrument how we use in a stepwise manner and all these things can be seen through this particular block diagram of the instrument where this particular block diagram can be seen so what we see here is that of your IR source so this IR source when it you have, so this IR source is passing this corresponding IR radiation to that particular mirror.

So mirror is basically projecting that particular radiation to this particular beam splitter and this beam splitter is very important because this beam splitter is giving you the corresponding attenuation with regard to that particular another laser source for this particular IR radiation and that is going like this, so this is coming from here with another triangular mirror and then it is guided through this and then again to this particular thing that means you have the corresponding beam splitter.

So the beam is getting splitted and the whole thing within this particular interferometer so when it goes basically so this interferometer is basically responsible for the corresponding signal amplitude recording the corresponding signal amplitude when we have the corresponding chopping off and on of the radiation which is forwarded to the sample. So this again goes via the mirror and then this particular optical path is again guided by the mirror so that is why we talked about so many optical materials which are IR sensitive, so there should not be any IR absorption like the different salts like the potassium bromide or any other salt, inorganic salt.

So when it is finally guided to this sample compartment so this is our basic sample compartment so you have this transparent window and here also the exit window so this is your entry window, which is guiding yours radiation to fall on the sample and after absorption the radiation is coming out of this particular window and again guiding through this mirror and is falling on the detector. So detector is measuring the corresponding intensity so when it is guided by the interferometers so we get the corresponding time domain spectrum which can ultimately be converted to the corresponding frequency domain spectrum.

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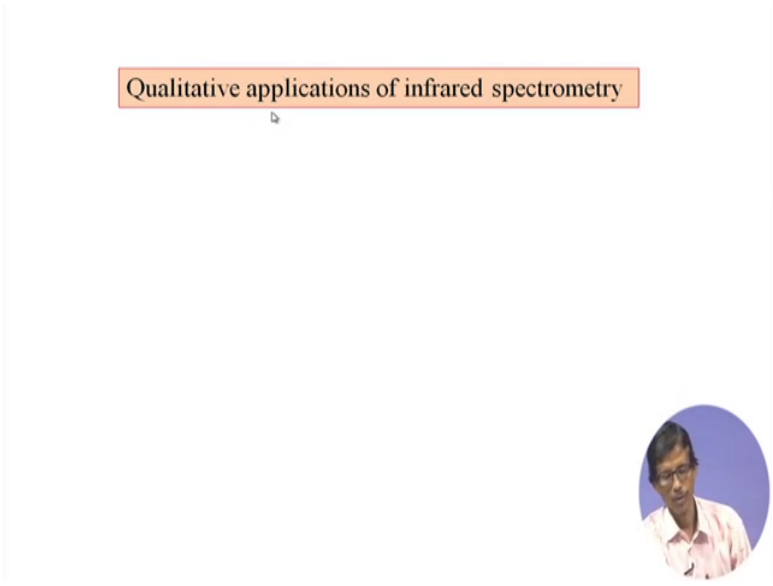

So this particular technique the IR technique what we get from here is that we can apply this particular one for qualitative as well as quantitative analysis.

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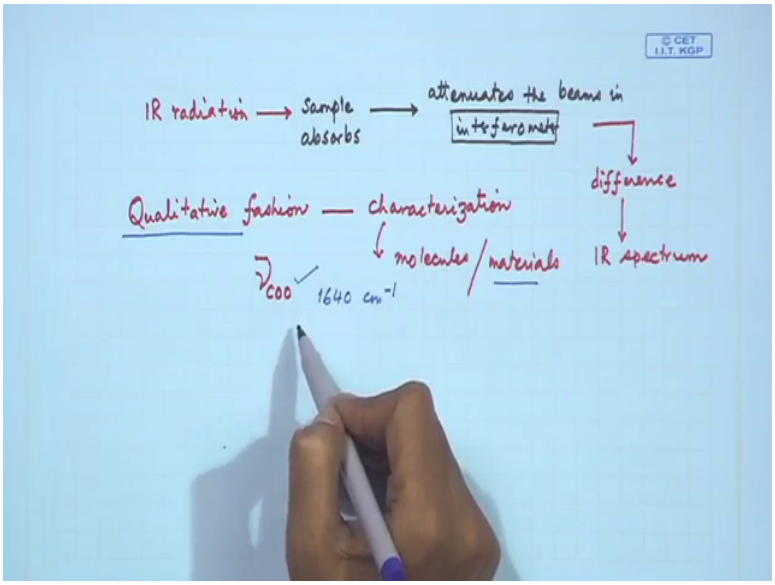

So in a qualitative fashion, in this qualitative fashion what we get that we use this for typical characterization of some molecules or materials having very characteristics stretching frequencies as I told every time that suppose you have the carboxylate function it can be your sodium carboxylate sodium acetate or it can be typically bound to the copper salt. Similarly if the material also has some carboxyl base material sometime it can be also carbonate based material so this carboxylate or the carbonyl based material can be very nicely characterised and the identification or the indication of this band where it is coming whether it is coming at 1640 centimetre inverse or not that gives us some very good idea that qualitatively we can characterise the material by this particular spectroscopy.

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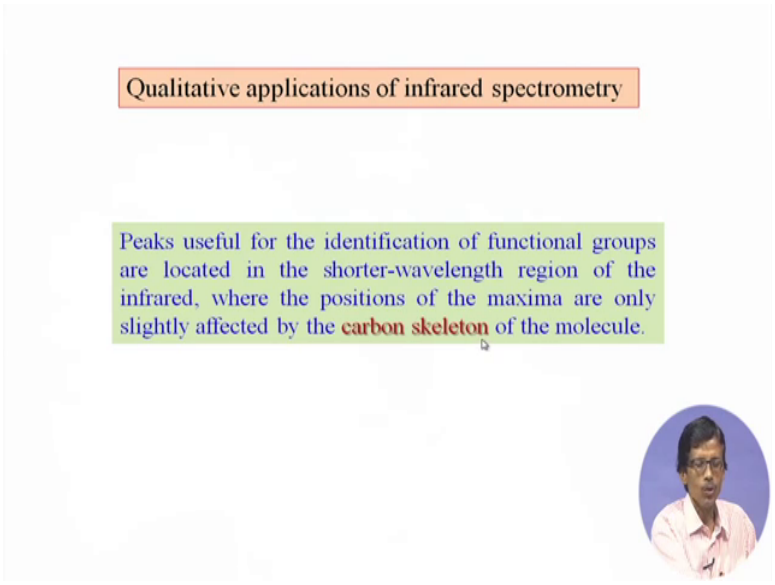

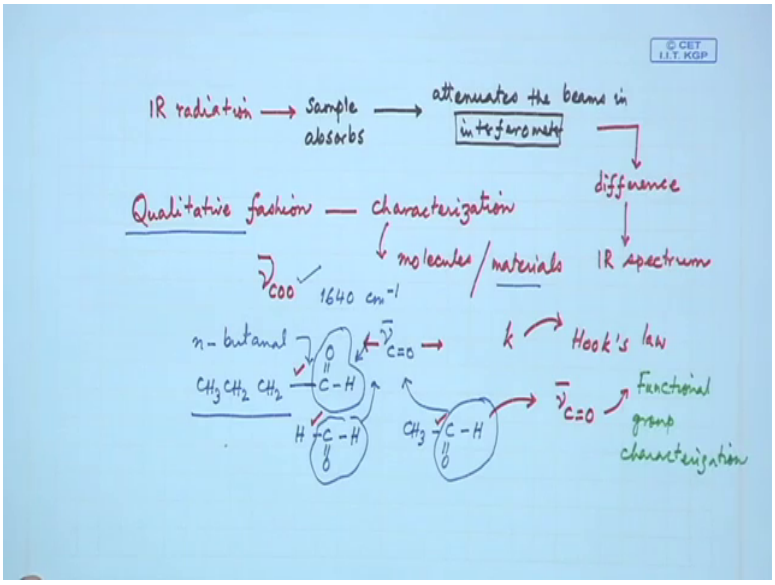

So we should know all the very important peaks positions so in this case the peaks are useful for the identification of the different functional groups. So this when you talk about the different functional group it means that this particular functional group can be present in many biochemical sample any organic sample or any inorganic and iron ore cation which are very much characteristic like that of your agiled ion, thiocyanate ion, cyanide ion all these and when they are located in the short wavelength region of the infrared where the position of the maxima only slightly affected by the carbon skeleton of the molecule.

So as we have seen that n-butanal we are talking about in one of our previous class that n-butnal so which particular one we consider at as the l function that means the aldehyde function. So this aldehyde function will be responsible for giving you the corresponding characteristic function of C double bond O and which is also characteristics for the aldehyde function and this particular one when it is attached to say several others groups like CH3 CH CH2 CH2 and CHO. So if this is there that means is a bear one which is also present in your formaldehyde HCHO or some CH3 function which is your acid aldehyde.

So where this particular CHO function will go so if it is attached to different types of groups like H like CH3 or some long chain aliphatic group. So those will not be changed very much about this particular stretching frequency for this because this particular determination that means the stretching frequency is known as the corresponding one there is a marsh of this carbon and oxygen and the corresponding force constant this small k value is the corresponding force constant which is attaching this carbon to this oxygen and which is governed by the corresponding Hook’s law.

So the presence of the other part that means what is there that means this carbon is attached to whether a beak or long chain whether it is attached to H only or whether it is attached to only CH3 that does not matter much, so we can have this particular functional group stretch frequency with only slight variation. So 10 to 20 centimetres inverse variation you can see for this particular one. So when we tabulate this thing that means this particular stretching frequency will be very much characteristics one for your carbonyl function.

So the tabulation of this group will be definitely be attached to the corresponding functional group characterisation so this is also helpful to give us the corresponding functional group characterization. So IR, therefore very much useful for functional group characterization also.

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Some Characteristic Infrared Absorption Peaks

		Absorption Peaks	
	Functional Group	Wavenumber, cm^{-1}	Wavelength, μm
O—H	Aliphatic and aromatic	3600–3000	2.8–3.3
NH_2	Also secondary and tertiary	3600–3100	2.8–3.2
C—H	Aromatic	3150–3000	3.2–3.3
C—H	Aliphatic	3000–2850	3.3–3.5
C≡N	Nitrile	2400–2200	4.2–4.6
C≡C—	Alkyne	2260–2100	4.4–4.8
COOR	Ester	1750–1700	5.7–5.9
COOH	Carboxylic acid	1740–1670	5.7–6.0
C=O	Aldehydes and ketones	1740–1660	5.7–6.0
$CONH_2$	Amides	1720–1640	5.8–6.1
C=C—	Alkene	1670–1610	6.0–6.2
ϕ—O—R	Aromatic	1300–1180	7.7–8.5
R—O—R	Aliphatic	1160–1060	8.6–9.4

So if we get this and if we see how the difference and all these things that means what are the different groups we can have so this was we are talking about, this aldehyde and the ketone function that means CO, we can have some characteristic infrared absorption peaks from all these levels. So all these levels what we get is that that you have the aldehyde or the ketones which will appear within 1740 to 1660 and if we consider this in terms of the wavelength in micrometre it is in this particular range of 5.7 to 6.0. So what we see that we just go from a corresponding one that means the highest frequency number that means the highest centimetre inverse number to a lower frequency number.

So this wave number is ranging from 1740 to 1660, so that basically gives us the corresponding characteristic value for the carbon atom which is attached to a oxygen through a double bound. So you see what are the other groups available in this particular fashion, so

we can have this particular group for carboxylic as well as amide but there is the change you see now not the corresponding one that means the group attached to that particular one making it to carbonyl or aldehyde but you can consider this for a change where you have the CO function with the attachment of the OH because if you have the CO function and that CO function what we are talking about this you can have H or this CO function can have CH3 or any other.

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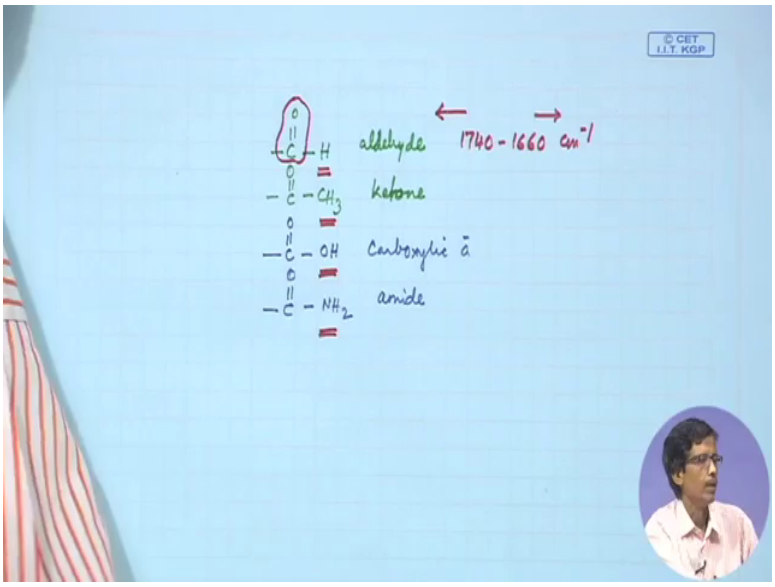

Or giving rise to aldehyde or ketone so how nicely we can identify the presence of aldehyde or ketone in any unknown organic molecule or we can have some other groups also that means when you have OH which is for carboxylic acid or CONH2 the corresponding amide one. So we just try to see the main function that means the CO function and its attachment of this carbon with either carbon or with oxygen or with nitrogen that will slightly modify the basic value of this carbonyl function which is 1740 to 1660 centimetre inverse.

So in which direction it will go either in direction or that direction due to the substitution of either carbon in place of hydrogen so hydrogen is replaced by carbon of the methyl function or some longer chain or the OH function or NH2 function that we will see from this particular table.

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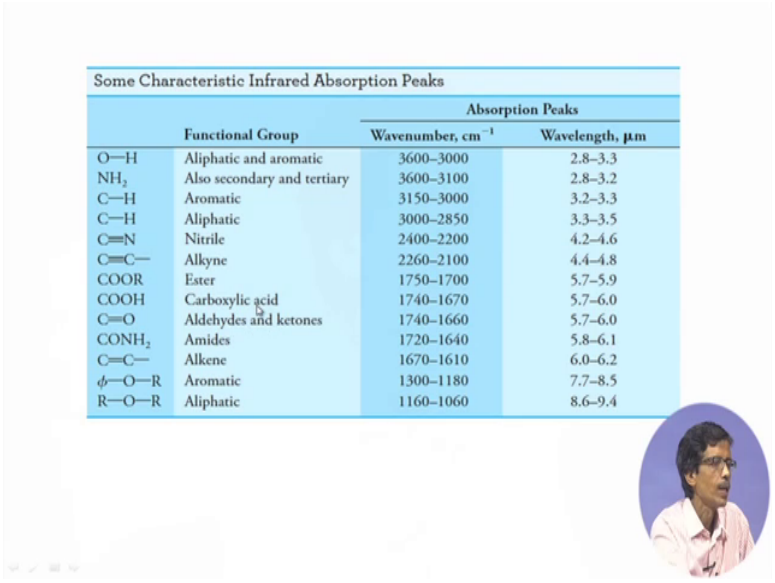

So when we have the carboxylic acid function that means the OH is attached to this particular CO function it is in the same range still this will be in the 1740 to 11670 centimetre inverse only slight change for the corresponding lower lower range of 1670 but when it is amide there is again change from 1740 to 1720 and we see that the limit is also changing from 1660 to 1640.

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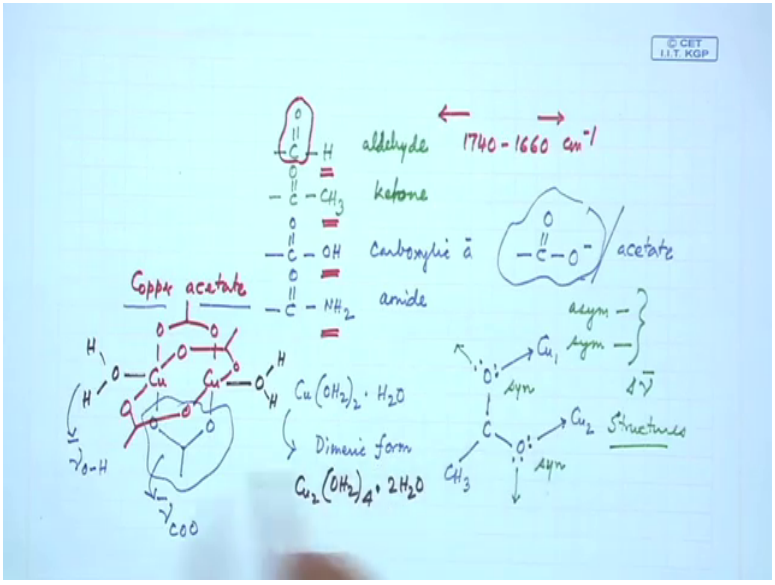

So this basically so these three together we can remember very nicely because we want to identify the presence of the carboxylic also it can be your simple different metal salts that means the metal acetate like copper acetate or iron acetate and all these things and sometime we find that this particular carboxylic acid function can be little bit complex also because we

all know that when we talk about the corresponding binding to a copper centre and the copper acetate what we know is not a very simple acetate as it is supposed to be but this particular carboxylate function which is C double bound O O minus so which is your acetate and ion.

So this acetate anion is basically taking out this particular coordination so this oxygen that means this one of this oxygen will bind to this copper and the other end of oxygen will not come to coordinate to this particular copper centre but it will come to the second copper and this is your acetate function, so one such acetate function is like this so this particular copper acetate the formulae of the copper acetate the exact formulae what we write is one H2O but it is in the dimeric form, and what we are trying to look at it because if we see that if we write this acetate function in this particular fashion what we see that we have the corresponding carbon and you have the corresponding oxygen and you have the oxygen and you have the CH3.

So if the available lone pairs are over here it can also have another lone pairs over here. So when this is binding to one copper so this is copper 1 and when this is binding to copper 2 so this sort of binding we take it or consider it as the syn, syn binding but there will be possibility that it can utilize this particular one that means this one can also bind to some other metal ion or the same metal ion so this will give you syn anti or anti anti type of binding to these two copper centre.

So if there is something that means this not only this particular mode of activation what we get in this particular range but some asymmetric and symmetric stretching of this bonds and one bond is getting longer another bond is getting shorter which is our asymmetric stretching when both of them are longer a symmetry both of them are shorter is also symmetry, so that thing and the change that means the delta Nu bar is also very much characteristic for the type of bonding. So these little bit of this that means the IR spectrum can give rise to the corresponding identification in terms of the corresponding structures of this very simple molecules which are nothing but the typical metal salts.

So in this particular metal salt what we have that this is there so the second one is also like this then the third one and the fourth one so we get when we get this as your dimeric form and in this dimeric form what will be the formulae therefore. Formulae will be CO2 (OH2) whole 4 and 2 water and these two water is when the molecular formulae we write in the centre dot 2 H2O but it is basically bound to these two copper centres.

So this will be your O H H, O H H because the presence of these water molecules also is giving rise to the corresponding stretching frequency for as this this will be for COO. Similarly we get this for your Nu bar OH function. So all these things so if we think that this is a particular structure of copper acetate and we get the characteristic stretching frequencies for this and which also identify that you have a syn syn type of binding for these identification of these copper, salt typical copper salt.

So we get these for not only this copper but all other very characteristic functional groups of the organic molecules and some of them can be bound to the metal ion centre and we get this as their corresponding one for simple change just if we go for a double bonded structure to a triple bonded one but where you happen you see the movement basically movement towards the upper range that means towards 2068 to 2100 centimetre inverse when you go for the triple bonded one.

Similarly for the nitride function organic nitride so immediately when you know that a triple bonded structure is present and the organic nitride is available so that organic nitride can be correlated also for the presence of the cyanide function that means CN minus and that CN minus function can be useful to identify in this particular range of 2400 centimetre inverse to 2200 centimetre inverse and also sometime will find that if you have this five as the phenol function that means the aromatic ether that means PHO CH3 or CH3 OCH3.

So if we have a aromatic ether function that means ROR function and that ROR function will give rise to a corresponding frequency in the range of 1300 to 1180.

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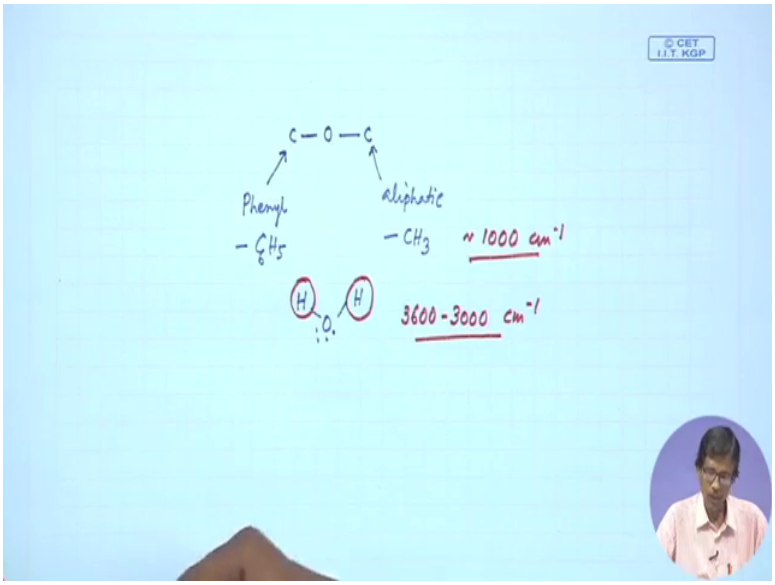

So this identification of these ether so what you find is which is very much characteristic for some function where we have these carbon attached to this oxygen from these two sides. So this carbon can be from your phenyl group that means the aromatic function or this can be from aliphatic one that means this can be your CH3 this can be your phenyl function.

So if we just simply compare this with that of our water molecule so in water molecule what we see that we know that the characteristic OH stretching frequency comes around 3600 to 3000 centimetre inverse. So the change in basic skeleton is not that it is linear it is also like this angular form but the change what we get is there from the corresponding replacement of this hydrogen by this carbon centre will move this particular stretching from in the range of say 1000 centimetre inverse.

So we should always keep in mind that what structural change is taking place and the replacement of the very small atom like hydrogen by the carbon will dramatically change the corresponding stretching frequency from 3600 to 3000 to 1100 centimetre inverse, okay.

Thank you very much.