Course on Analytical chemistry
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Lecture 27
Module 6
Spectrochemical Methods - 3 (Continued)

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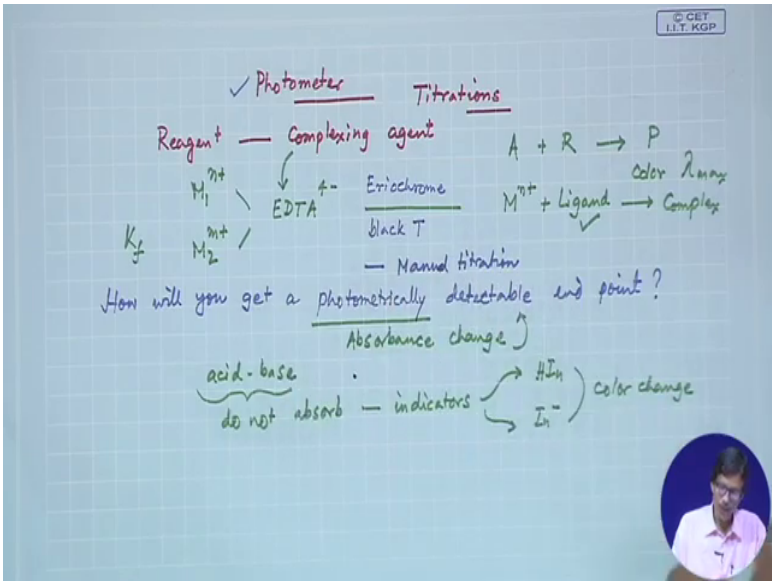

Hello welcome to this class of titrations where we are talking about the photometric titrations because we are using a photometer to identify the N point of some titrations so now we will introduce something where we can see that a particular reagent which can be a complexing agent, so what is that? That means like that of our chromophoric agent what we are talking about so far in our some previous classes where we have seen that the chromophoric agent which can react to some analyte with that reagent giving you some product and product have some specific colour which can absorb at a particular specific wave length of lambda max.

Now when we talk about the complexing agent definitely it is a corresponding complexation reaction we are trying to study so A (())(01:40) analyte which several times I already told you that it can be the corresponding metal iron and this can be your ligand as we all know the metal iron when react with the ligand and ion or the neutral ligand give you the corresponding complex. So we call these ligands as a complexing agent and that complexing agent as we discussed earlier also that one such very good complexing agent is EDTA ethylene Ethylenediaminetetraacetic acid and in the tetra ananic form.

So this EDTA can be used nicely to detect the end point where the EDTA can bind to the metal iron and where we have seen that we can use some metal iron indicators also like Eriochrome black T was used for a direct or manual titration manual titration. So this we all know like our manual titration for acid based reactions so here all these cases when you introduce some photometer or a spectrophotometer our basic intention or basic idea is that we have to have some coloured product or the coloured metal iron or the coloured ligands such that we can monitor the corresponding absorbance during the titration process.

So if we ask our self some very basic question that how will you get a photometrically detectable end point that means we are looking for something where the corresponding change in absorbances will show or detect the end point of any analysis it can be your analyte it can be your metal iron or it can be anything else where there is a sudden change that means it can show the end point very nicely where you have two linear part one is going before the end point and another is going off different slope after the end point.

So in case of simple acid based titration if the reaction that means the reaction of analyte and the reagent we are consuming the analyte which is suppose your base by the acid we use some indicators that means for simple acid bases reaction what do we do they do not absorb in the corresponding wave length range, so we introduce indicators, so indicators of two forms say HIn as we know and In minus and there will be a sudden colour change, we can monitor that also by doing the corresponding photometric titrations so we can detect the end point which can be your photometric end point.

So for these titrations also if we now know that this thing that means your reagent is same and we are looking for the analysis of say two metal irons which is M1 and M2 this two can be of different charges also so both of them can bind to this EDTA and that binding constant or the formation constant if they are different so the species that means the metal iron which is having the higher magnitude of the corresponding stability constant or the formation constant what do we call or what we indicate in terms of the Kf value. So if the Kf value for this particular metal iron say M1, M plus is more so this metal iron can bind EDTA nicely and we get if this is a coloured one we get a change of the corresponding absorbance but if it is not what happens that when all the M1 is exhausted during that time the M2 will not bind to your EDTA.

So when all the M1 will be exhausting so at the end point of that particular case your absorbance will change or increase going from this titration where the M2 is being consumed by your tetra ionic EDTA.

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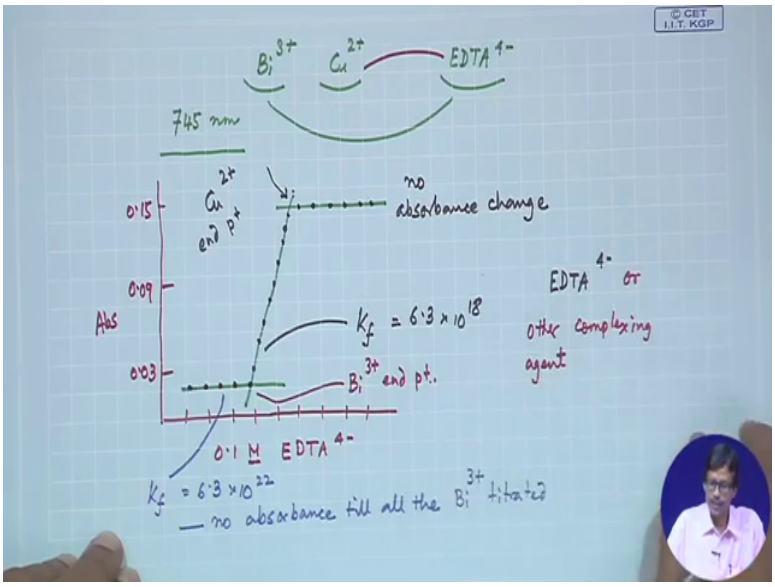

So this is one such example we can see now by saying in the form that if we had two species and two are completely different one is Bismuth 3 plus another is copper 2 plus and we use EDTA 4 minus for its neutralization reaction or the complexation reaction.

So we choose a wave length 745 nanometre where both the cations that means these two as well as the reagent and the corresponding bismuth complex, so remember these three things that this cation, this cation and this cation is silent or it is not absorbing at this particular wave length of 745 nanometre as well as the bismuth EDTA complex. So what we are looking for? We are looking for the corresponding complexes in a copper 2 plus and EDTA we all know very nicely that 1 is to 1 complex is an reaction goes very well so we will detect that particular one so when this bismuth is getting exhausted like your metal iron M1 we get something some slope of the correspond absorbance plot then when all the bismuth has been consumed we get the corresponding complexation reaction between copper 2 plus and EDTA.

So if we try to have the corresponding plot what we see that we will be adding millilitre of your EDTA solution which is point 1 molar EDTA solution I showed you (())(9:00) most of the time we use and it is the absorbance axis this staring from here it is 0.03, 0.09 and say 0.15 only up to 0.15. So what happens that this this particular case you have a straight line part in this particular point up to this particular point then there is a increase in the

absorbance which is cutting over here and then after this point we have again almost again horizontal line.

So this basically gives us something and after this incremental addition of this volume of EDTA these are the corresponding points so we get these points also for the titration so when we plot this we get this so how can we explain this particular plot that means in this particular range when this point 1 molar EDTA has been added up to this much volume so what we get is that in this particular case your bismuth is complexing with your EDTA with a formation constant value of say 6.3 into 10 to power 22 which will be higher than the corresponding Kf value for copper EDTA.

So at this value we do not have any change in absorbances, so no absorbance change or no absorbance till all the this bismuth 3 plus is consumed or titrated so this is therefore shows you that the corresponding end point of your bismuth, then your copper started consuming so this particular point is our bismuth 3 plus end point. So after that what we get is get the corresponding complexation reaction between copper and EDTA which has a corresponding Kf value of 6.3 into 10 to the power 18 it was 10 to power 22 now it is 10 to power 18. So when all of them has been consumed that means EDTA has been consumed by this bismuth so then EDTA will try to react with your copper 2 plus so this will go on increasing till this this particular point which is nothing but your copper 2 plus like that of your bismuth 3 plus copper 2 plus end point and after that if we add more and more of these reagents that means the tetrasodium salt or the disodium salt of EDTA when we add further addition of this particular reagent will not cause any absorbance change.

So no absorbance change beyond this point, so as a result what we get we get this end point that means this much volume of EDTA is equivalent to that of your bismuth present in the solution and from here to here that means this volume to this volume if we subtract this volume this will also give to the corresponding end point for the copper for this complexation reaction beyond that we have consumed all the bismuth well as all the copper so is basically not there is no change of this corresponding absorbance because copper has also been exhausted.

So this way we get the information that a typical reagent such as EDTA 4 minus or other complexing agent can be used for this photometric titration reactions and in one of the case that means the metal iron with the EDTA complextion should absorb, so we can handle aluminium with any of transition metal iron because most of the time we see that the

transition metal iron are giving some coloured species for absorptions in this photometric titrations.

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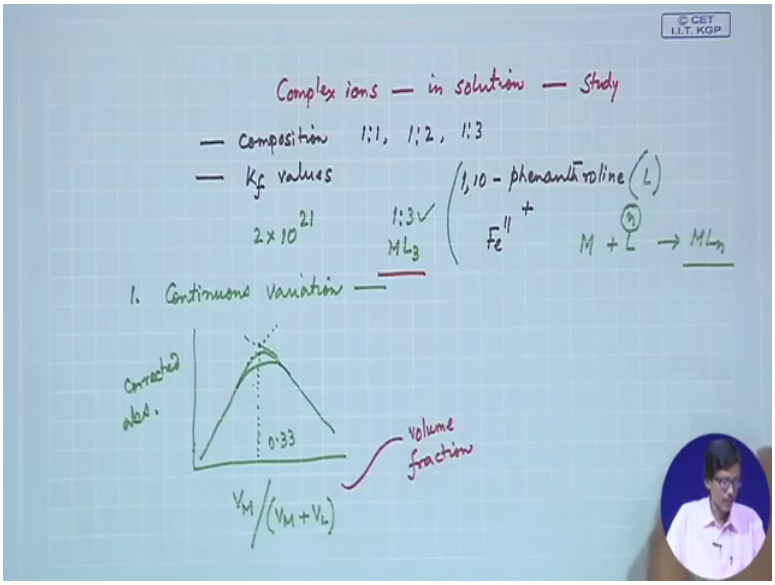

So this can give rise to some important information that if we can have some complex ions in solution which we can study nicely by this sort of complexation reaction. So what we can find? We can find the composition of that complex ion and also the corresponding Kf values because just now we have seen that the different between corresponding Kf values for bismuth and copper with regard to your EDTA can be found out. So with the Kf value is high it will go for corresponding complexation smoothly with the EDTA first then the second species will go and bind.

So composition means what you can have whether you are getting 1 is to 1 complex, 1 is to 2 complex, 1 is to 3 type of complex such as one example of that ligand we all know that 1,10 phenanthroline which can bind very nicely with ferrous ions. So we get this particular complexation reaction and we can study these (())(15:46) its composition and we find the corresponding stoichiometry or the composition of the complex that means this iron 2 can bind with your ligand L as ML3 and this Kf value can also found out for this is in the range about 10 to the power 20 so it is 2 into 10 to the power 21. So we can follow three different techniques basically where we can monitor this absorbances and the copmposition how its changing that means when we go for the thing what we have just seen the titrations with M plus L forming some species MLn

So what is the value of this n? This is your value 1 is to 3, so this is giving rise to some complex and when only one of such ligand if these are all difference n value if it is 6 as we have seen in the case of iron thiocyanate we see that when one of the thiocyane is bound to the ferric ion your colour is changing. So we can monitor that colouration for stoichiometry of 1 is to 1 only but in some other case until and unless you reach the corresponding stoichiometry of 1 is to 6 is hexa coordinated one, n is a monodentate one we can find out the corresponding stoichiometric composition of the metal iron.

So first particular technique is method of continuous variation as the name implies that we will vary the corresponding concentration and if we just try to measure the absorbances and in this case what we plot is corrected absorbances with that of the corresponding volume of M and the volume of L that means the volume fraction we can plot so it is the volume of the metal ion divided by the total volume of the metal ion plus the ligand.

So that change how the corresponding volume of this metal ion can go for the corresponding change in the absorbances so this will go like this and then this just basically will decrease, so this decrease is due to the corresponding dilution of the corresponding form metal iron complex because with addition of more and more of the volume of the species such as the your metal ion it will decrease in that particular point.

So if we just extend the corresponding straight line part, so there is a cross section over here so what you find that the deviation that how much it is deviated from that particular part so that will also indicate about the corresponding stability of the metal ion complex species. So when this particular one is 1 is to 3 your Vm by Vm plus VL value will be 0.33. So at this point when we plot this as the volume fraction we can find out out of that that what is the magnitude of volume fraction where we get this change over or the intersection between these two straight line parts we can find out from there that your stoichiometry for the complexation is 1 is to 3.

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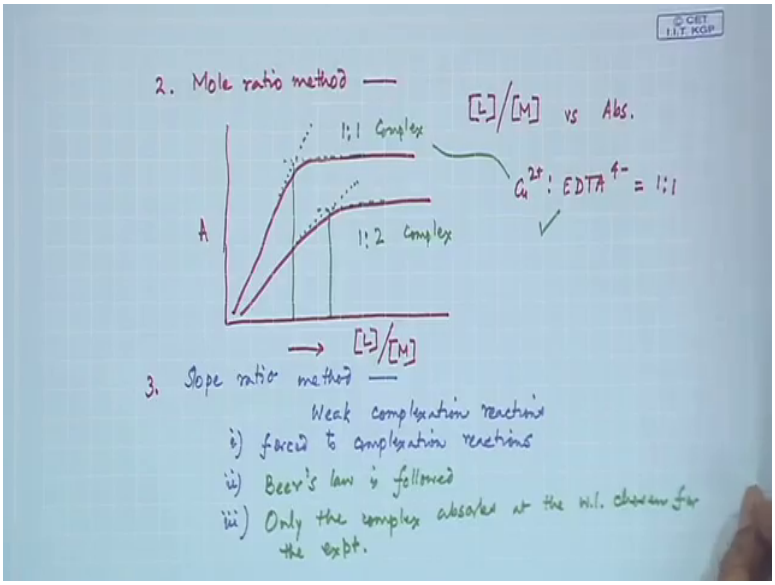

And the similar fashion the second technique what we can use is your mole ratio method. In that particular mole ratio method what we see that we have this M and L so the corresponding ratio of the ligand to that of the metal iron if we plot these versus absorbances. So this is the corresponding mole ratio that means either the ligand versus metal ion or the metal ion versus the ligand we can plot and that mole ratio method can also be useful to determine the corresponding composition and the corresponding formation constant for this species.

So these absorbances again we can plot with that moles of L by moles of M and when we get this one particular case we get the plot like this and in another case it is something like this so these are the two cases of specific example where you see there if we just extend these two parts so there is the thing so this is one such magnitude and if we go for the second one this is also one. So this is for the first one is for 1 is to 1 complex that means this is equivalent the mole ratio is equivalent when 1 is to 1 of this is mixed you have the maximum absorbances for this particular case and when it is less than that so we have to have the corresponding complexation reaction is 1 is to 2 complex we get a different plot.

So in all these cases what you see that the corresponding complexes and reaction which way it is giving you so in some case this particular one that the method of continuous variation is useful, just now what we have seen and we can determine that for a 1 is to 3 types of complexation 1 is to 3 the mole ratio is 1 is to 3 but in two other cases where the complexation is 1 is to 1 like that of what EDTA because this is we have seen just now that for your copper or bismuth so copper 2 plus is to EDTA 4 minus will be 1 is to 1. So that 1 is to 1 ratio is useful there and can be found out through this particular technique and the last

one the third one is basically the one where we can see a slope ratio method is a slope ratio method where we can handle them as for weak complexation reaction weak complexation reactions where you see that in all these cases unlike the other cases where you see that the complexation is very strong and we have a very high magnitude of Kf values but this particular case the weak complexation reaction where the Kf values are small and we go for this and obviously it has some important things to remember there that is being forced that means when you add ligand its forced to complexation reaction and that we want to monitor.

And this particular case also that we should have the corresponding follow up of the Beer's law so the Beer's law is followed otherwise we cannot use this particular process and only the complex like that of our copper EDTA complex only the complex species absorbs at the wave length chosen for the experiment. So these are the things that how we can monitor and how we can use all these complexes and reactions staring from the different method we can utilise that and the photometric titrations or the photometric identifications as well as the determination of the corresponding Kf values are also useful in all these cases.

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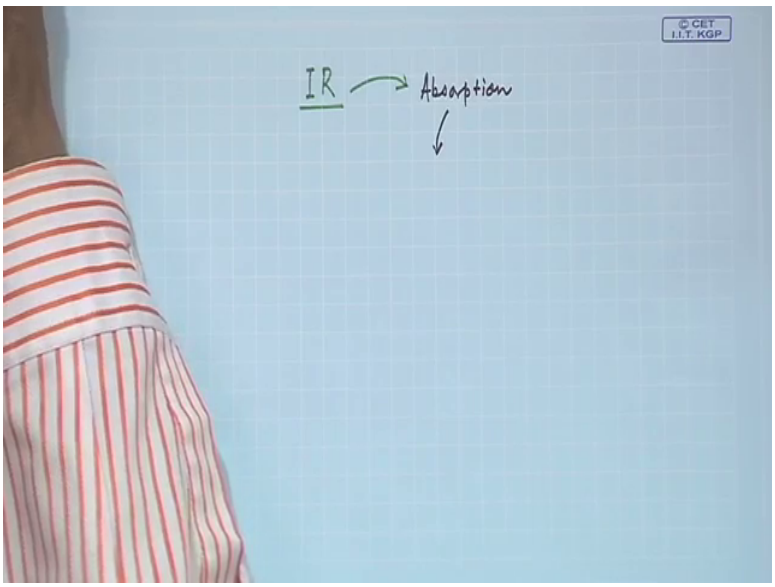

So in the next case where we can move basically another important technique of spectroscopy which is unlike your invisible spectroscopy we will be utilizing the radiation in the infrared range which has a very tremendous scope where the infrared radiation which are weaker in nature and that infrared radiation we will be utilizing for identification of some of the molecules and some of the other species very nicely. So what we get over there that infrared absorption so when we use these like that of all invisible radiation that IR radiation should be

there and some species should be available that like of our molecules, atoms or ions whatever disease is present over there can go for absorption.

So that absorption magnitude of absorption and the characteristic magnitude where it is absorbing is also interesting to know to identify the nature of the corresponding species.

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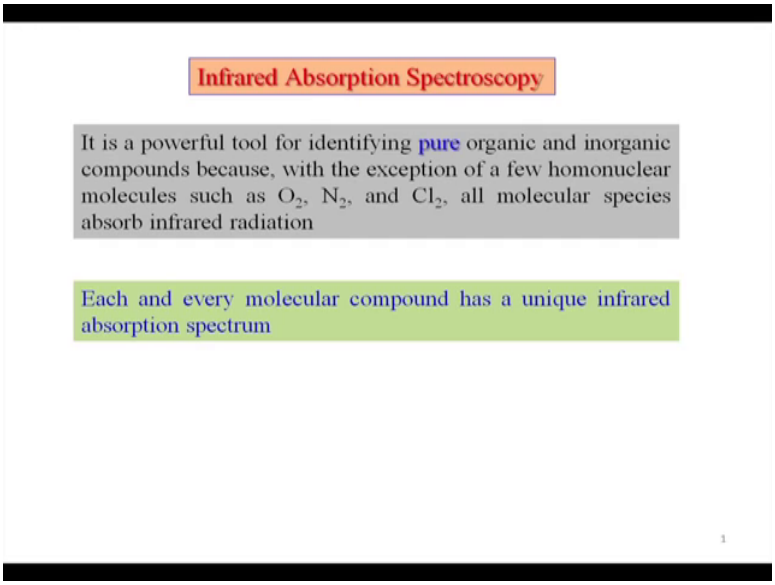

So what we see that is a definitely a very useful or a powerful tool to identify the pure organic and inorganic compound because with the exception of few homonuclear molecules such as your O2, N2 and Cl2 where we do not have any permanent dipole moment will not be able to detect these gases, these gases like oxygen like nitrogen and chlorine but all other molecular species will absorb infrared radiation.

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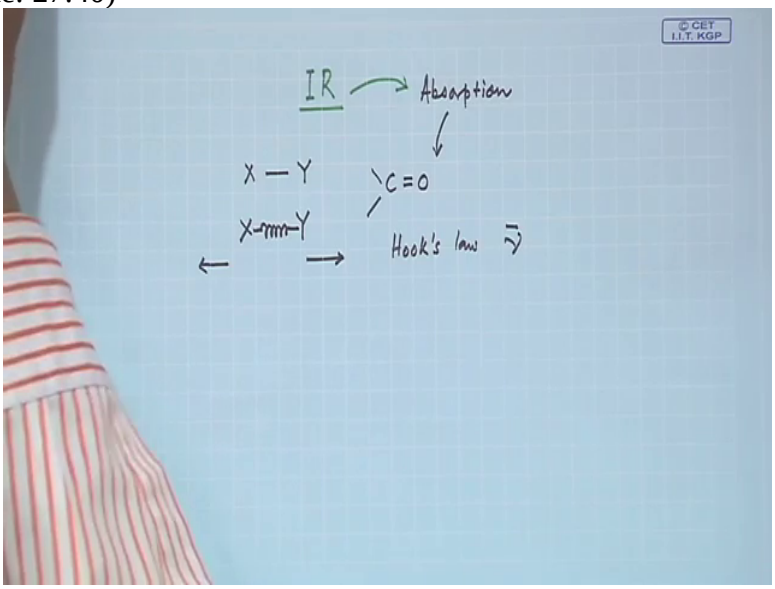

So why do they absorb infrared radiation because each of these compounds or the molecules of the gases as a unique infrared absorption spectrum because in all these cases whatever you see if we consider that 1 is x another is y, so x is attached to y and that attachment is for a particular type of bond it can be say simple CO bond C double bound O also and is (()) (27:47) species also if one is x another is y.

So this particular radiation so this particular molecular species can show the corresponding absorption of this radiation due to this particular bond stretching so they are attached to this bond so bond stretching and bending and twisting all the different modes of vibrations we call them as the molecular vibrations.

So how it looks like that x is attached to y and if that is attached to say some spring type of thing and if we try to elongate this bond we know that it some this this because this is corresponding equilibrium in the nuclear distance and if we try to stretch them we get some frequency for that and that particular one by Hook's law we can find out something which we call as new bar of the wave number with it.

So this it has a particular type of wave number in it which we can co-relate with that of the IR radiation and it is the corresponding match radiation which can be absorbed by this particular molecular species xy such that there will a typical IR absorption and what we want to monitor is that the corresponding absorption of that particular radiation.

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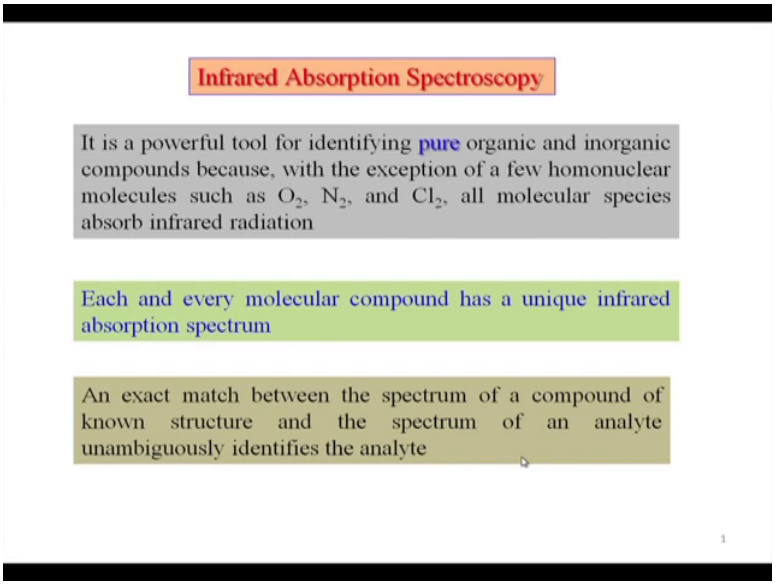

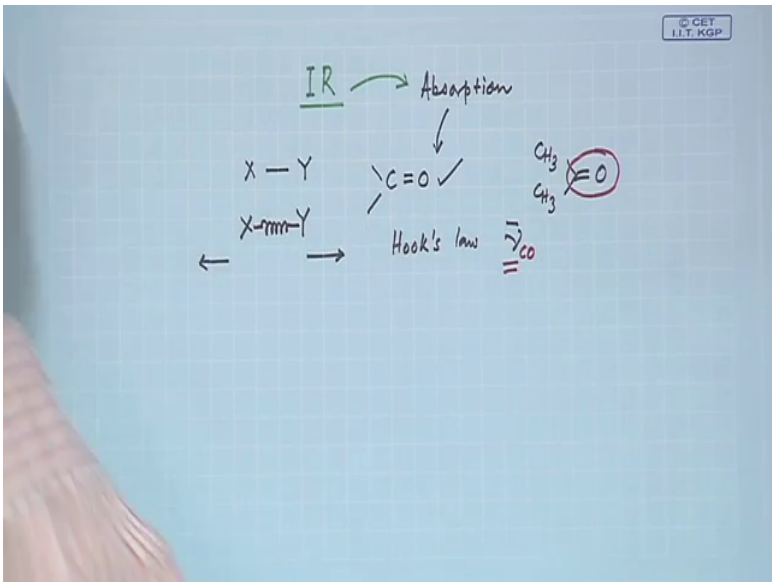

So any of these molecular compounds can show the corresponding absorption and if there is a re-corresponding match so the exact match between the spectrum of a compound of known structure and the spectrum of an analyte which can be identifies the corresponding analyte.

So we know the corresponding known structure and its IR spectrum and if that is present in that particular unknown species we can detect that particular presence of these molecular species, suppose acetone is there in any other liquid or any other solvent we can run the corresponding IR spectra and when you record the corresponding IR spectrum we find that the characteristics spectrum for the acetone is present and we can find out by looking at the corresponding stretching frequency for CO because we all know that acetone is nothing but your CH3, CO CH3 and this particular part that means the CO part is present in the acetone.

So this acetone solvent can give you the corresponding characteristics stating frequency in terms of the corresponding absorbance values of these and we call it a corresponding stretching frequency for the carbonyl function because we all know that the carbonyl is a very unique one for all the different molecular species like that of your different organic molecules where this particular stretching is present.

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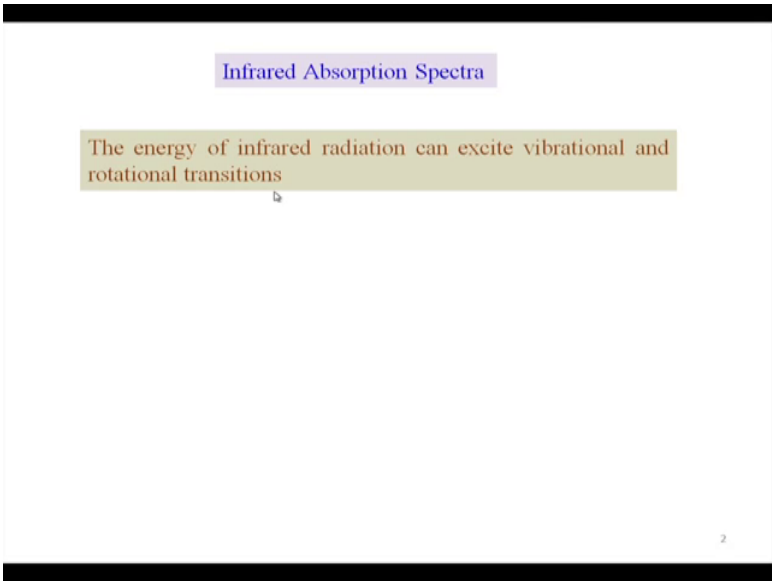

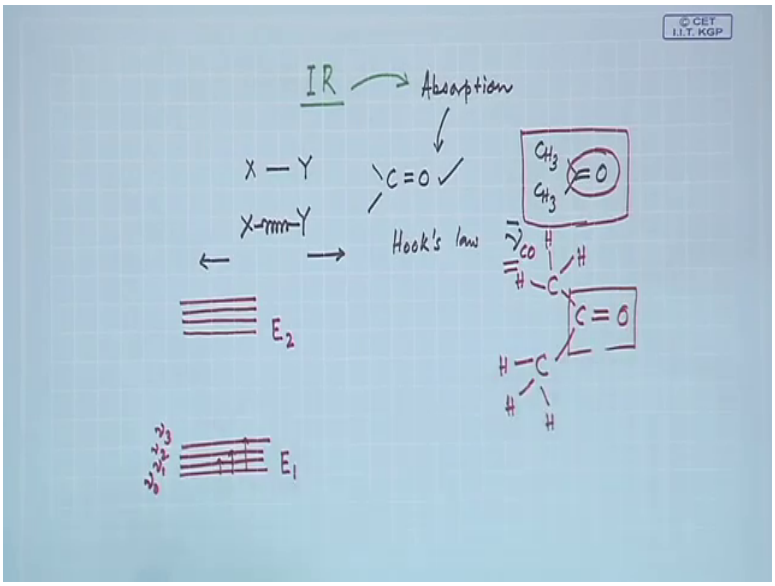

So we also see that when we get the spectrum, so when the IR absorption is taking place so the corresponding spectrum what we will see that this particular spectrum has a corresponding energy in the infrared region and which can excite the different vibrational and rotational transitions. So that we will see that what are those vibration, rotational transition because so far we have seen the two electronic energy levels the E1 and E2 and we are

talking about for the electronic absorption the invisible absorption which is in the in the high energy region.

So these two levels are involved over there now we will be talking about something where within the one particular electronic level we can have several other vibrational levels so we can have the different vibrational levels and the change in energy because it is in the low energy region so that vibrational energy change we will see and that particular energy change will be responsible for its absorption so within one electronic level we have the corresponding V0 is not new its V0, V1, V2 and V3 so these are the corresponding vibration energy levels and we can have the absorption from V0 to V1 and V0 to V2 and V0 to V3 and all these of different energy values can be absorbed by a typical molecular species.

So if we look at these particular things that means the acetone molecule what we have seen that we can have CC bound and C bond and the C double bound and this can also attach to this hydrogen, so you see before this most simple one that means the acetone molecule itself we have so many bonds which are connected by xy combination, so these are the different xy combination and they will have the corresponding absorption and all these different levels.

So in this spectroscopy what will see that which one will be characteristic and which we can detect very nicely to determine the corresponding identity of this particular solvent molecule having this particular functional group, ok? Thank you very much.