Course on Analytical Chemistry
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Lecture No 22
Module 5
Spectrochemical Methods – 2 (Continued)

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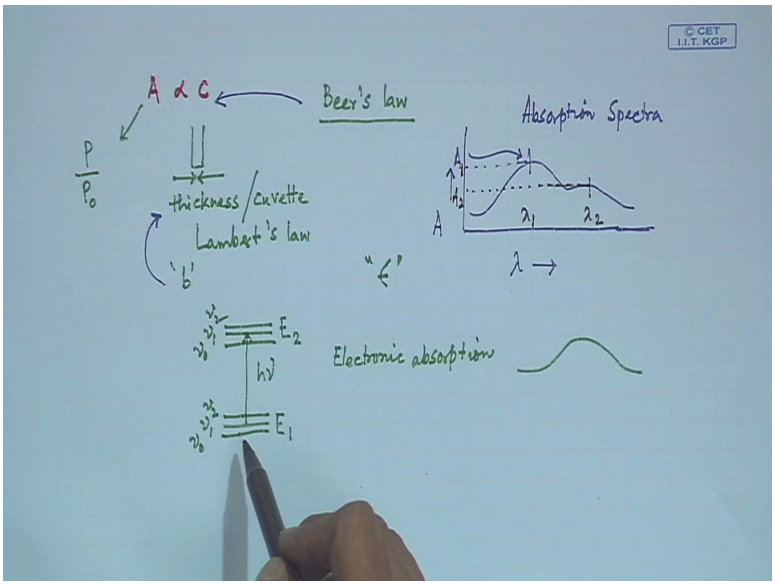

Hello welcome to the class of that electronic spectrum what we were discussing so far and we are utilizing a very simplified diagram where we are utilizing these two levels to see how the tetrazine spectrum we are getting. So for a broad electronic spectrum for this one which is present in aqueous medium. So some interaction with the water molecule can take place such that we only observe the corresponding transition from E1 level to E2 level and which is not giving us any final detail of that particular transition of the tetrazine in water medium.

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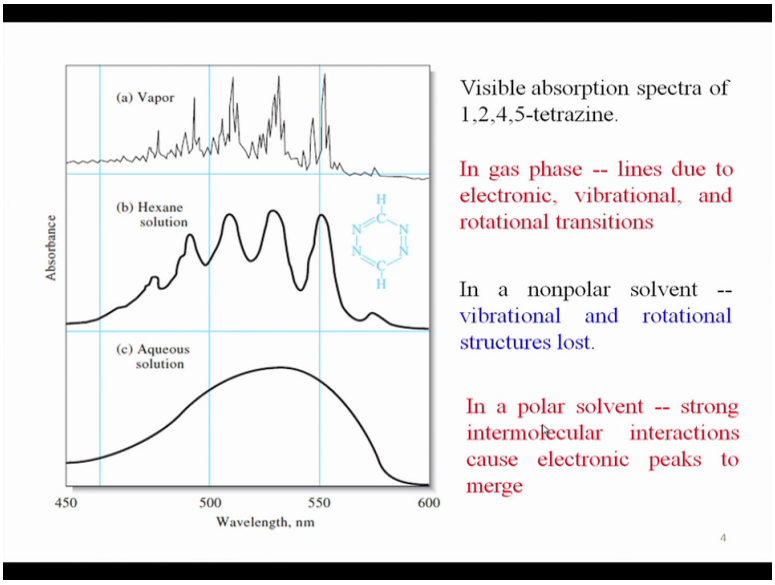

But if we go for that in Hexane solution what we have seen just now that in Hexane solution within the broad electronic absorption spectrum we get the corresponding finis structure so these finis structures somehow trying to explain us about the different vibrational levels associated to E1 as well as associated to E2 for those transitions. So this particular transition though it belongs to the E1 to E2 transition but can be from b0 of the E1 level to b1 of the E2 level.

Similarly the second one also so the minute difference in the corresponding vibrational levels of the molecule is responsible to give us the corresponding changes or the corresponding finite details of the absorption spectrum in Hexane solution. Because the number of molecules in Hexane solution it depends on the corresponding solubility if the Aqueous solution was highly concentrated that means more and more number of the tetrazine molecules are keeping side by side they are very close and they start slowly some interactions.

So the vibrations we are not able to observe in the Aqueous solution but in Hexane solution the number of molecules if it is less we are able to see the corresponding vibrations of these bonds that means the carbon nitrogen double bond, carbon nitrogen single bond and carbon hydrogen single bond also. So that basically is seen very well in the case of its corresponding Vapors state.

So if we take that molecule simply in the vapor state so this particular first band you see that at 550 nanometer for what we get for the Hexane solution is further splitted into 1, 2, 3, 4, 5, 6 bands. So within one vibrational levels we can have several rotational levels also.

So if it is not that all the vibrational levels are involved so all the vibrational levels giving us some averaged one so the vibrational as well as the rotational find structure is possible to get when we have a solution not in solution but only in the vapor state where the number of this tetrazine molecules are less because we all know that in the vapor state when we vaporize that particular thing the molecules available in the particular medium that means the cell which we are utilizing for measuring the corresponding absorption is the corresponding gaseous cell or the cuvette responsible to trap the gas or the vapor is there.

So less number of this molecule so further details related to their vibrational level as well as their rotational level. So what we get that in gas phase basically the lines due to all three levels. So why this levels we get why all these final levels we are getting because of the involvement of electronic vibrational and rotational transitions.

But in this particular class we are not going to discuss about the corresponding feature related to the corresponding vibrational level transitions or the rotational level transitions. So in the next or next to next class when we will be talking about the infrared spectral measurements or infrared spectroscopy or FTIR spectroscopy the most standard nomenclature for this is FTIR spectroscopy. So when we will be utilizing the FTIR spectroscopy there we can find the corresponding signature for the vibrations of the different bonds.

But right now what we are talking about in terms of the only the electronic spectrum and the corresponding energy and it is fine for the Aqueous solution when we get the average transition at 525 nanometer, so gas phase basically giving us the detail feature involving all of them all three of them. And in nonpolar solvent also these vibrational and rotational structures these final details are lost we are getting some average which is also present in the different electronic transitions for involving this E1 and E2 levels.

And when we go for this water medium so if we can get this is Hexane solution this is one lambda, this is another lambda, this is third lambda, this is fourth lambda so all together four and these two small signature which is characteristic because the shape and nature of the spectrum is also very much characteristic for these molecules. So all individual molecule can

have these feature where we see that the molecule can have the individual feature which is very much characteristic and reproducible at the same time.

So most of the time when we find that a particular molecule or a compound is soluble in water, we will be utilizing water as the solvent which is a polar solvent and as we all know and the type of interaction because the solvent water itself is also a molecule. So this molecule can interact with the tetrazine molecule so we get a intermolecular interaction and some of this electronic peaks if we consider this is one electronic peak, and another electronic peak, another electronic peak, another electronic peak they basically merge together and we get a broad peak.

But this broad peak is also a characteristic one for our analysis because we can use this as the corresponding set because you see the average of these all these so you pass if you pass the average line through all these so this will be like this. So this is also the same one but we are looking in terms of the corresponding identification of the unknown compensation. Suppose we are trying to get the corresponding unknown concentration in polar solvent like water solvent.

So this particular one and its corresponding lambda max which is your 525 nanometer and the absorbance value at this point will be characteristic one to tell you the unknown concentration of tetrazine in water medium.

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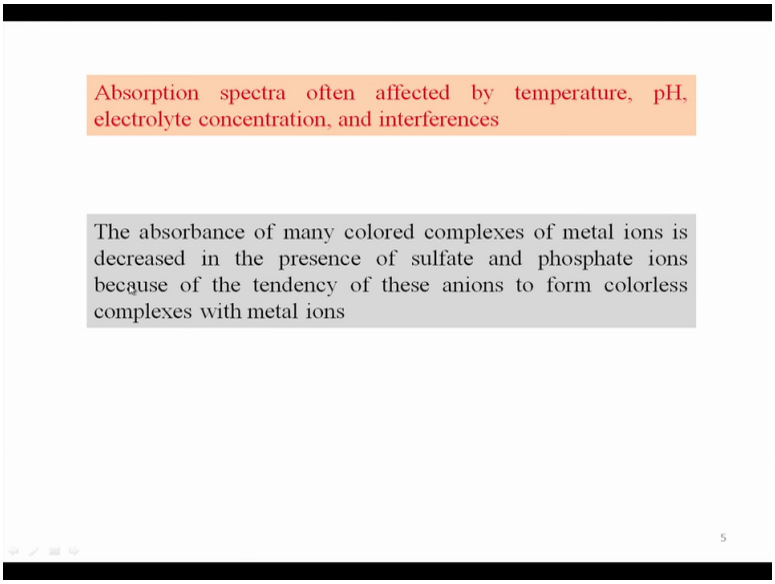

So that is the basic understanding or basic idea of getting a particular electronic spectrum and which can also be effected by temperature so when we can have some mechanism or some

procedure so the procedural thing related to that corresponding cuvette if we can take this particular cuvette in a variable temperature that means it is thermostated cuvette so thermostated cuvette can give rise to the corresponding spectrum in different temperature.

We can have different solutions the solutions can be in different pH values suppose we make a solution in acidic pH say 3 or 4 pH or we make the solution in basic pH of 7 or 8 that has some interesting relationship in terms of some physical quantity to determine. So your absorption spectra will definitely change with pH. Suppose we are recording an absorption spectrum which is colored one in solution for a solution weak acid weak organic acid.

So if we change the pH we know the different proportions of the acid and its corresponding conjugate base will change and depending upon the relative concentration of those things we will see that how pH can change the corresponding absorption spectrum. Then the different electrolyte concentration because these different electrolyte concentrations can interact with the corresponding species which is responsible for this absorption and if there is any interferences such that your water molecule or the solvent can interact with the paired molecule which is responsible for your absorption. As we all know the different absorbances of the different metal ions particular the transition metal ions that 3D, 4D metal ions.

We know from our school days that these transition metal ions can show some color but in this case that means the absorbance of many colored complexes of metal ions is decreased in presence of sulfate and phosphate ions.

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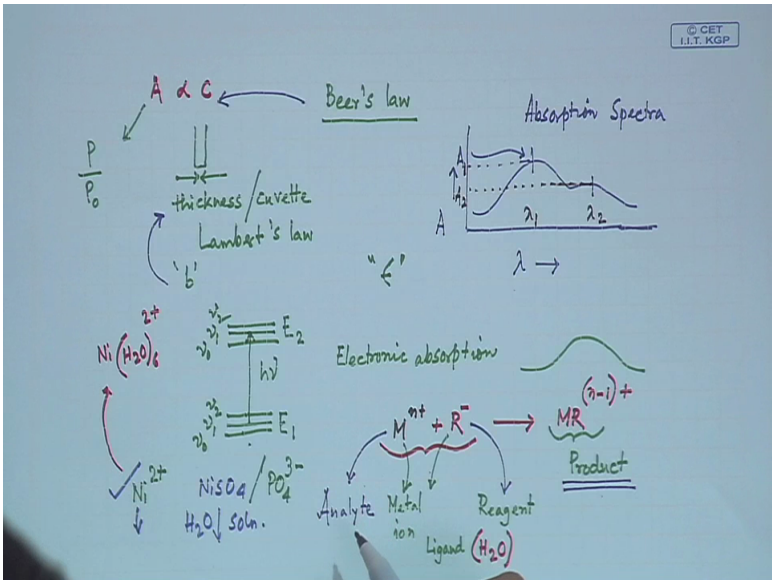

So if we have a metal ions say which we will consider it as Mn plus and this Mn plus is reacting with say reagent reagent can be neutral or reagent can be anionic, so what is forming over there so it will be combining with your reagent metal ion is combining with reagent with the overall charge of n minus 1 because this is one negative charge of that particular reagent such that this interaction is pretty strong between the positively charged cation metal ion cation and the negatively charge anion or the reagent or sometime we call it as a ligand.

So in our terminology what we are talking here in terms of the analytical chemistry is that we will be considering this as your analytes, so when we call it as analytical chemistry we level it as a analyte and we level this one also as a reagent. So R stands for your reagent and when this analyte is reacting with your reagent we get as the product and we will see also that you can have the opportunity of recording something in terms of this corresponding record of electronic spectra or absorption spectra where we are handling these three things. The analyte, the reagent and the product and what we are looking for we are looking for only one particular colored solution.

So it is expected that in this particular case your product is colored such that this is a colorless species, this is also a colorless reagent giving rise to a colored product and we are trying to find out this particular product in terms of measuring the formation of this concentration in solution and in the same time what we are also looking at we are also looking at its corresponding formation if your MR is not formed in solution we will not be able to measure its corresponding concentration in solution.

And if the species is not so stabled because it is forming at one time ok fine but at the same time it is going dissociated or it is associating some other species present in the solution. So that will be the difficulty and those things we should also be take care in our mind such that you have a direct product formation and this reaction goes towards the right hand side and the maximum amount of product formation can lead to the corresponding enrichment for its corresponding concentration responsible for its coloration and responsible for its corresponding color absorption.

So when we consider this in terms of another thing that since we are talking about this M as metal ion because we will see that how we can utilize analytical chemistry to determine the unknown concentration of metal ion or any other analyte based on the metal ion with some reagent so this can be your metal ion is purely metal ion for this reaction and now what will be your reagent then when it is metal ion we all know that this Are minus can be your ligand we all know that the metal ion the transition metal ions the first transition series elements that means the titanium the catanic titanium definitely titanium 3 plus vanadium, chromium, manganese, iron, cobalt, nickel, copper, as well as zinc because zinc is colorless all other will be colored.

So if we find that the metal ion in a environment where this is your ligand but we all know that a typical solution which can give rise to nickel 2 plus into the solution such that it is coming from a salt of nickel which is nickel sulfate. So if we use nickel sulfate for this solution and this Mn plus is your nickel 2 plus and we all know which is in solution which is colored or faintly colored but when it dissolved it in solution that means nickel sulfate is dissolved in water. So we try to make the solution in water we get Ni 2 plus in the solution.

And at the same time what we can see that the corresponding color of this Ni 2 plus will be dependent on something where we can consider this H2O is functioning as a ligand, your H2O is your ligand. So the species out of this is not the Beer Ni 2 plus but it will be the corresponding species which is mostly stabled which is surrounded by 6 water molecules which is hexaaquanickel 2 plus ion.

So this nickel 2 plus ion will be there and if it is colored and depending upon its color intensity we can measure its concentration. So the metal ion can react with your ligand ligand can be H2O such that you get a corresponding product product is nothing but your hexaaqua complex so this hexaaqua complex can be monitored by electronic spectrum such that you can find out the unknown concentration of this.

But it so happens that your corresponding intensity the color intensity is not very high we use some reagent as we all know now that once for our qualitative identification and quantitative estimation we have utilized one reagent for attachment or binding or coordination to the nickel center is your one particular well known reagent is Dimethylglyoxime DmgH2. So dimethylglyoxime we all know that it can bind very strongly to your nickel center and that give rise to a rose red coloration and in water medium it gives rise to the corresponding precipitation.

So now the challenge or the problem or the difficulty is that how we get that particular rose red product or the precipitate out of your reaction of nickel 2 plus with DmgH2 in basic medium the ammonia color medium we consider such that your DmgH2 can be deprotonated and we get some neutral DmgH whole 2 precipitate. If that can be solubilized in some organic solvent and that solution we can use for the corresponding color measurements.

So this is the thing that if you can have this but we have determine this one that means the corresponding nickel sulfate we have dissolved but in the solution that means we know that one nickel it giving you one sulfate concentration the corresponding ions are one is to one but if there are large amount of sulfate such that some industrial solution or industrial effluent or something the industric people where they are making coins we all know the nickel is a very good component for alloy formation.

So this nickel is giving rise to some solution where some other treatment not from the nickel salt but some other treatment like using of sulphuric acid can giving rise to huge amount of sulfate concentration and not only the sulfate concentration we should also be very much careful about the corresponding presence of the phosphate concentration.

So in that particular solution what solution we are handling how to choose or how to find out this particular apply or the application of the reagent which can give rise to the corresponding coloration of the solution such that we should avoid in most of these cases also in the determination of iron that we should have avoid these anions sulfate, phosphate and all sort of these anions because they basically give rise to this particular thing that means when they are forming back the corresponding salt like ferrous sulfate or the ferric sulfate or nickel sulfate or nickel phosphate or ferric phosphate they can reduce the corresponding color and sometime like that of your ferric phosphate the product is colorless.

So we should avoid or we should consider the corresponding anion when we are talking in terms of the corresponding MR formation.

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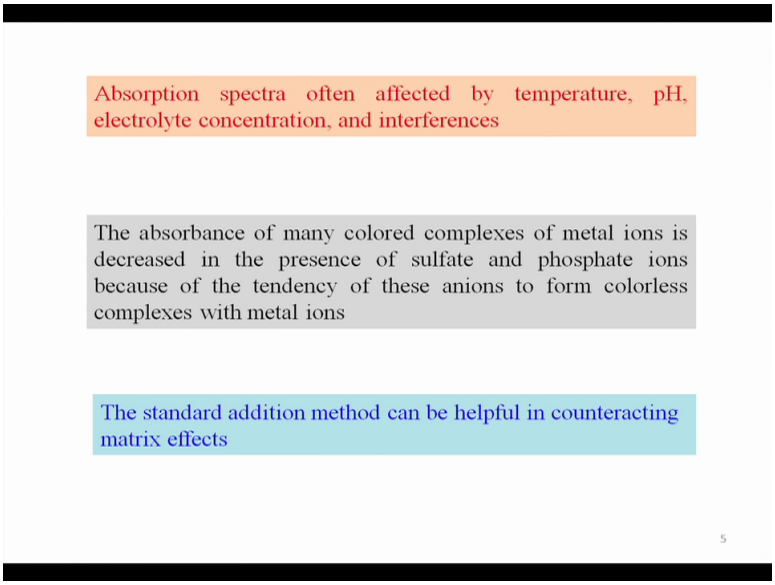

So that is why we are talking here as the (())(19:13) sulfate and phosphate ion should be avoided of the possible interaction with the complexes for their corresponding colorless phosphate or sulfate formation. And we will find that a particular technique basically will be utilized for the standard addition method can be helpful in counteracting matrix effect.

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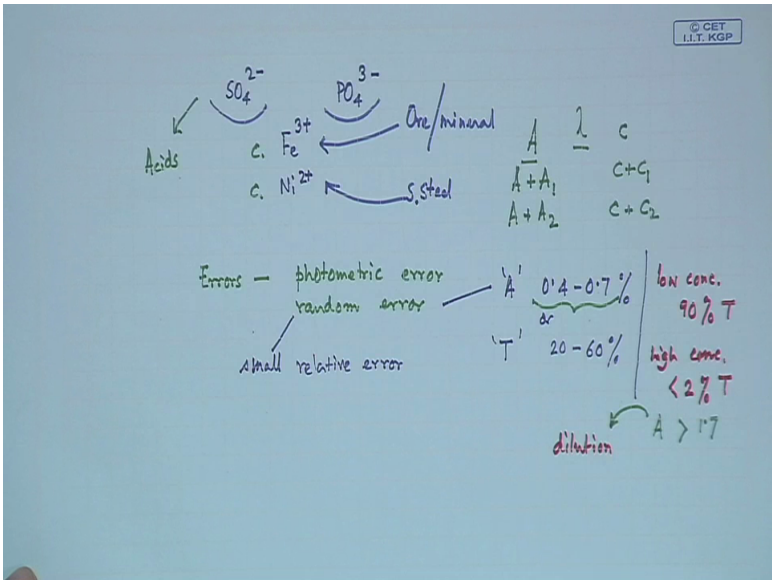

So if we consider this particular one that means the corresponding interference from the sulfate anion and the phosphate anion and we are looking for the determination of say ferric

ion or nickel ion where this concentration will be directly proportional to the corresponding measured absorbance but what we can use that when we can get these as the source from some ore or mineral or this can be in some stainless steel sample.

So steel S Steel stainless steel sample or any other thing industrial important from some battery material are all these so these things in some these acids because sometimes we can use these as acids that means sulphuric acid can be used, phosphoric acid can be used, for the dissolution of this ore or the mineral or the stainless steel.

So for the dissolution purpose most of the time we handle acids so the anions will remain with this particular solution and we are trying to find some concentration of this iron and this nickel with that of your absorbance at a particular lambda value. So what we should do we can have some error that means the corresponding environments what we consider it as a corresponding matrix effect.

So this matrix effect will be there due to the presence of this sulfate and phosphate can be avoided by a technique which is known as the standard addition technique because this absorbance value at a particular lambda is directly proportional to the concentration of the C of this particular unknown analyte to be determined.

Now if we add any know concentration of this particular iron or the nickel and we add so C becomes C plus C1. So we know that the absorbance will be A plus A1. So this particular thing so and again we can add some another incremental amount of the standard solution which has been prepared from a standard metal ion solution like that of your nickel sulfate or ferrous sulfate.

So A plus A2 can also be measured where the C the original one with some added C2. So from these we get something that means we will find that this absorbances are additive in nature, so this can be added up and when we are talking in terms of the same species either nickel or iron we can find out this particular unknown concentration very accurately through this particular technique instead of finding out your unknown concentration directly from the known concentration versus absorbance plot.

Because if your sample is very pure that means the pure nickel and the pure iron we know that the molecular species which will be responsible for your absorbance but if there is any interference in terms of the matrix effect where some phosphate and sulfate can take care or can consume some amount of the analyte or the metal ion that means your actual

concentration will be less. But through this standard addition technique we will be able to find out or we can remove the corresponding error for that particular purpose.

So if we have these measurements so the measurements in this particular term we can have some errors and due to the instrument we can have some photometric errors so some photometric error is there, then some random error. So how we can tackle or how we can take care of these particular errors.

So this random error is very small this is the small relative error so is a small relative error and it has some relationship with a typical procedure. So this random error can tell us that if we can have a corresponding absorbance value that means A value we can measure in the range of 0.4 to 0.7 we should not go below to this value and we should not go above this value which is directly related to the amount for your T value the transmittance for the corresponding transmittance is only 20 to 60 percent.

So if you have a corresponding transmittance of 20 to 60 percent we should be able to get a corresponding absorbance value at 0.7 to down to 0.4 but if we have a very low concentration. So in this particular range if we get a corresponding low concentration so very low concentration such that you can have a 90 percent transmittance and a absorbance value of say 0.045.

So that we should avoid that we should not have anything where the concentration is very less and your transmittance is only 90 percent that means only 10 percent is getting absorbed which we should avoid. Similarly at relatively high concentration when we have a very high concentration where the transmittance is less which is about 2 percent T transmittance.

So if we have a 2 percent transmittance so that will also affect your corresponding value in A and A is then going upto say 1.7, though your instrument can measure a magnitude of 1.7 absorbance but it is better to avoid that particular one such that we can remain in this particular range. Because when we go this particular range it means that you have a very high concentration and that very high concentration means that your molecules which are responsible for your color is staying side by side and they start interacting with each other that is not acceptable or that is not well associated with the measurement.

So we what we do to decrease this particular 1.7 absorbance which is highly concentrated solution to a low concentrated solution is that you proportionately dilute it so the dilution is

the path and this dilution is the process such that you reach this particular absorbance values to this particular values.

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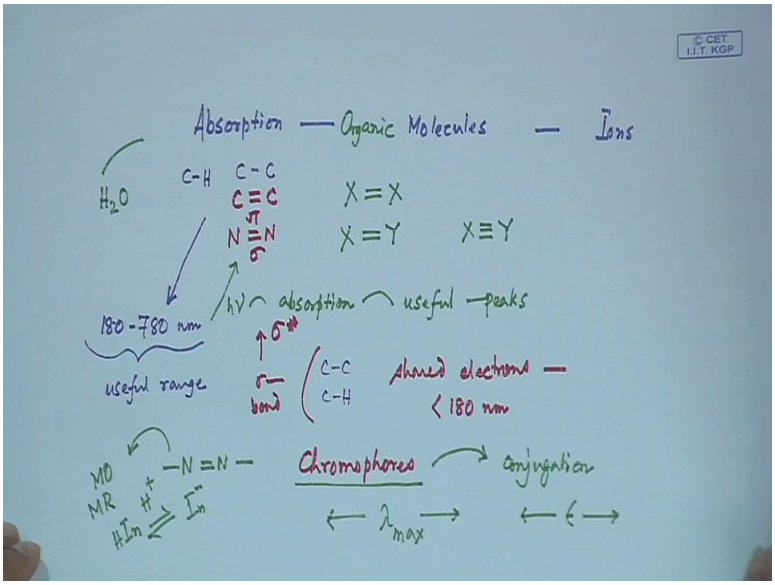

So which are the particular molecules basically now we will see that what type of species we can have which is responsible for your color absorption. So far we are talking about the absorption and some molecules definitely molecules or some ions we have seen the metal ions that ions are responsible for your color and these molecules that we have seen just now that it can be your corresponding analyte reagent combination or analyte reagent product metal ions is reacting with your reagent.

But these molecules can be a typical molecule because we will all be interested to know about if we can have a very simple thing that means the water molecule any solution which is there in your test tube how we can analyze by this particular technique the spectrometric technique to identify the water molecule. So what will be its corresponding electronic absorption?

So the electronic absorption of this water molecule or any other organic molecule so any other organic molecule if we can consider which we all know that a center it can be carbon which is bound to another carbon which is X. Similarly X can also bound to Y or your X can bound to Y with a triple bond and what we see here is that is a very simple thing that when these two are bound we all know that the C-C double bond or a nitrogen nitrogen double bond, one is your sigma bond and another is your pi bond and the sigma bonds are strongly held.

So when we try to excite this particular species that means we put the corresponding radiation in terms of its corresponding h nu. So the electrons which are present in the pi level for making your pi bonds will only be excited. So the more easily excited electrons in the pi level in the double bonded molecule or in the triple bonded molecule will be excited and once it is excited so you get the corresponding absorption.

So what happens due to that absorption absorption should be useful for our measurements that means useful peaks it gives useful peaks in the electronic spectrum. So this particular case that means when we have all these and not only the C-C double bond we can think of C-C single bond also and C-H single bond also.

So C-C single bond and C-H single bond what we can get is that so far we are talking about mostly the visible region because we are talking in terms of metal ions which are colored and we can see through our naked eyes the corresponding colors for these species as the corresponding blue, or green, or red coloration. But here in these cases we may not see this particular colored solution or the colored vapor or the colored gas.

So we can go down to a range of 180 to 780 nanometer the useful range this is our useful range to excite all these. So to excite this double bond to excite this triple bond we can use this particular range which is well below the your corresponding ultraviolet range and in upper level of the corresponding visible range.

So but for these two cases that means for the C-H and C-C case that means C-C and C-H case we are talking in terms of the corresponding only sigma bond. So these the sigma bond we are talking about. So this can be excited that means the sheared electrons in the sigma bond which are firmly bound with a very strongly bound and it needs more energy to be excited into the higher level.

So the electrons present in the sigma level as we all know can be promoted to the sigma star level which is the anti-bonding level and this promotion from the sigma bond to the sigma star level can require some energy which will be in the lower range of the ultraviolet range which is less than 180 nanometer.

So if we can have some mechanism such that we can record this particular range that means less than 180 nanometer, we can find out this particular thing as useful but in most cases this unsaturation that means the unsaturated organic compounds bearing unsaturated functional groups can show absorption can so show absorption in the UV visible range.

So what we see that this particular one that means can be defined as chromophores, so in our next class we will continue from here in such a way that we should be able to identify those chromophores which are responsible for your color absorption such that N double bond N we all know that N double bond N the azo function which can be a very good part of the acid based indicators like Methyl Orange or Methyl Red, they can show two different colors.

So we all consider it as the corresponding HIn that means the weak acids and after dissociation of that particular proton it goes to In minus. So the formation of these two only there will be a color change from one part to the other and this basically going for the corresponding thing that means this particular bond that is double bond and if there is more conjunction how far we can move the corresponding absorption spectrum for this particular chromophoric part which is the (())(33:49) part and it is attached to its conjugation.

That means more number of double bonds C-C double bonds or sometimes can be (())(34:02) N-N double bond also is present. So how this corresponding lambda max value the maximum absorption can go up and go down. As well as we will see that how the corresponding values since we are able to move it from left to right so we can shift it from the red region or the blue region. So it is red shifting or blue shifting linearly the corresponding epsilon values can also be changed depending upon the maximum absorption.

So that we will see in the next class that how the chromophoric thing can be utilized for our all these measurements which can ultimately lead to our measurement for the unknown concentrations, thank you very much.