Atomic and Molecular Absorption Spectrometry for Pollution Monitoring

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Lecture – 10

Structure property relationship of organic compounds

A many of these organic compounds are present in the air, present in water, present in solid ways. So, if you want to determine these compounds in the environment this is how we go about doing it. If there is methanol or something like that you must get a peak corresponding to sigma to sigma star and n to sigma star, because there are no double bonds. So, like that if it is an ethylene structure, in a gaseous environment then what do you do?

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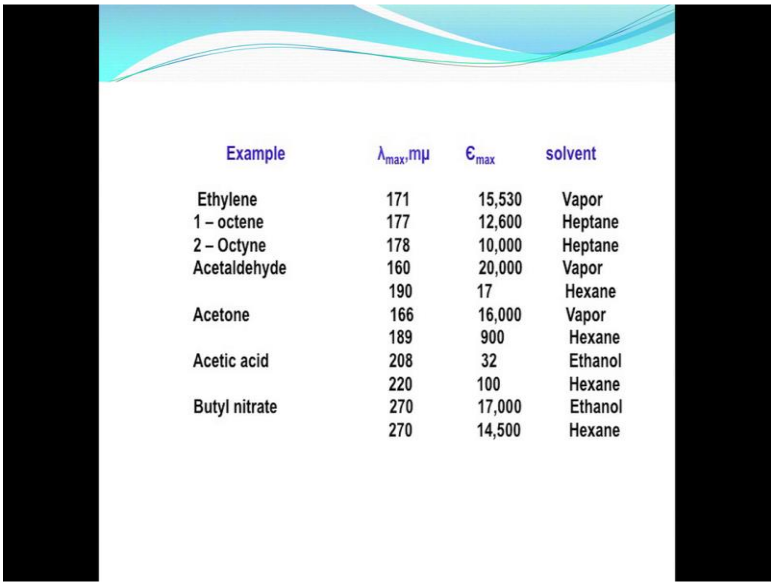

Example	λ_{max},mμ	ϵ_{max}	solvent
Ethylene	171	15,530	Vapor
1 – octene	177	12,600	Heptane
2 – Octyne	178	10,000	Heptane
Acetaldehyde	160	20,000	Vapor
	190	17	Hexane
Acetone	166	16,000	Vapor
	189	900	Hexane
Acetic acid	208	32	Ethanol
	220	100	Hexane
Butyl nitrate	270	17,000	Ethanol
	270	14,500	Hexane

Then I will show you this table- the first one is ethylene: it shows a peak at 171 nanometers, and epsilon value is 15530, and solvent is vapour; if it is there in the air it has to be in the vapour form. So, similarly 1 octene, it has got a very high molecular weight, but it has got a 1 octene mean 1 double bond; 1 double bond between first and second carbon atom and eight total octane means 8 carbon atom. So, it shows a peak at 177. And lot of the single bonds, but only one double bond. So, it has peak has shifted from 171 to 177. And epsilon value is 12600. For typical this thing, for typical value it is a fairly strong band, that means it shows a discernible peak if it is there in the air or in the liquid.

Similarly acetaldehyde, not so good, because this corresponds to sigma to sigma star transition; so 20000 is a strong one, but it is not in the preview of normal spectrophotometer, because the normal spectrophotometers operate between 180 to 1100 nanometers. So this one, it also shows a peak at 190 and as I told you 180 is the minimum 190 it should show a peak, but it has got a very low molar absorptivity only 17, so it will not be visible. Same thing is true with acetone 166 not good, but it is in vacuum region, not seen in the spectrophotometer. 189, yes it is around 900 fairly very near the limit. So, you will definitely see a small peak or a hump. If it is acetic acid: you know that acetic acid is soluble in water and it shows a peak at 208 nanometers and this has got 32 only.

So, this corresponds to sigma to sigma star or n to sigma star, because acetic acid sigma to sigma star are normally not shown 208 if it shows a peak and if it is a very weak peak it has with 32 molar absorptivity; what you will conclude is it has to be n or n to pi star, that electrons on the oxygen should get excited to sigma star; n to sigma star is only 32. But, another shows another peak 220 and 100 epsilon not a very good peak, but butyl nitrate it shows 270 and 17000; excellent one; 270 another peak around almost at the same level with 14000 first, so it is some sort of double act in butyl acetate.

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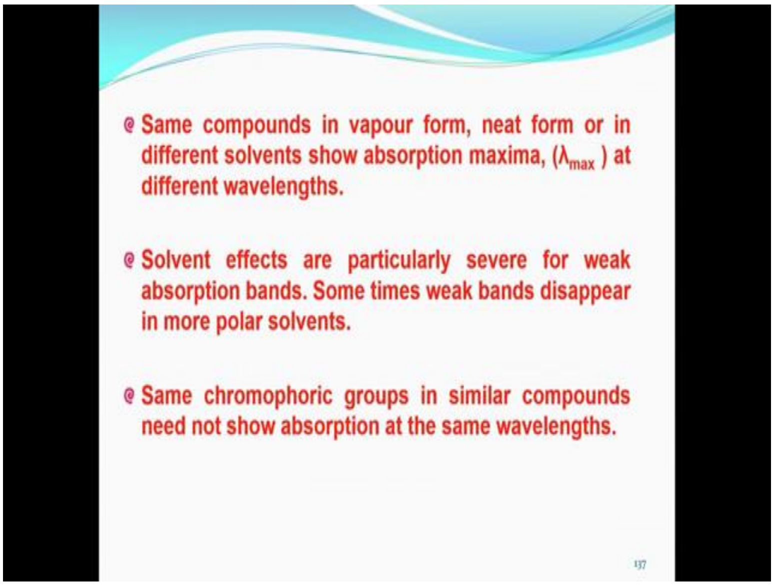

- Same compounds in vapour form, neat form or in different solvents show absorption maxima, (λ_{max}) at different wavelengths.
- Solvent effects are particularly severe for weak absorption bands. Some times weak bands disappear in more polar solvents.
- Same chromophoric groups in similar compounds need not show absorption at the same wavelengths.

So, what we conclude from this table? That is same compounds in vapour form neat form; neat form means in the without any solvent; vapour form means the substance in a vapour or in different solvents- I can dissolve substance in different solvents and find out the absorption spectrum. So, the same compound in each form there will be a slight difference in vapour form or neat form or different solvents. I have shown you here in the previous slide this is the 270- 17000 ethanol and 270 and 14500 in hexane; here the difference is between the molar absorptivity. Solvents are different, same substance and wavelength is same. In acetic acid: it is 208 and 220 ethanol and hexanes are the solvents, sometime vapour, sometime heptane like that is the conclusion. From the same compounds in the vapour form neat form or in different solvents show absorption maximum at different wavelengths.

And then solvent effects are particularly severe for weak absorption bands; that means, if as far as possible you should take a spectrum with neat form, without any diluent. Sometimes weak band disappear if you do it in solvents, more polar solvents. And same chromophoric group, same substance with a functional group can show different wavelength but the same peak; that is n to pi star or pi to pi star in same chromophoric group in similar compounds. That is in aldehydes it shows different peaks, depending upon the molecular weight and molecular cross section that we have already discussed in the previous slides that is minus dp by dt is equal to one-third of g into n is that number avogadro's number etcetera where maximum is 10 raised to 5. So, for all compounds the lambda max will be different.

And in molar absorptivity also will be different, but the chromophoric group may be same. What is a chromophoric group? A chromophoric group is a functional group like alcohol, aldehyde, ketone, amine and then many other compounds like that or acids they are known as chromophoric groups. And these compounds can be present in different compounds with different molecular weights, but the absorption peak what they show should only correspond to n to pi star and sigma n to sigma star.

So, if the molecular weight differs the same chromophoric group will show you different peak. So, your possibility of finding different organic compounds in a given matrix always increases. That is the beauty of spectrophotometry especially in the environmental monitoring with respect to pollutants. So, these conclusions are very important, I expect you to remember all this and it will be useful for your test also.

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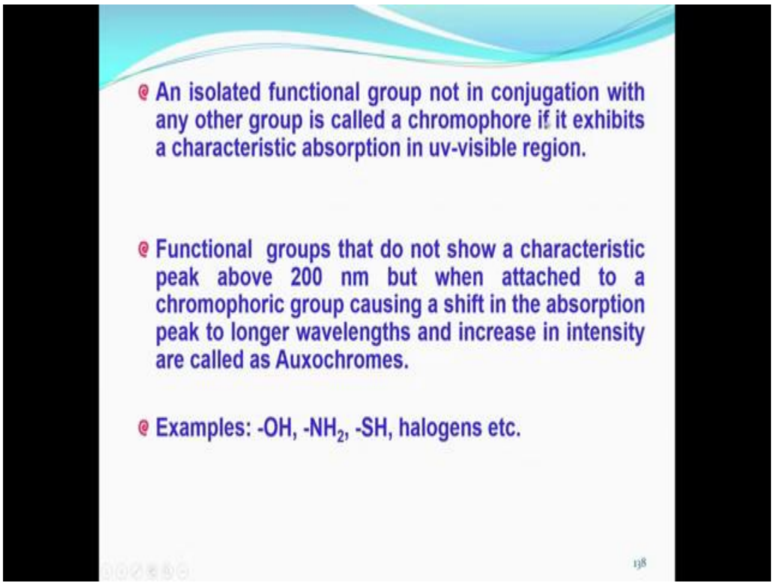

- An isolated functional group not in conjugation with any other group is called a chromophore if it exhibits a characteristic absorption in uv-visible region.
- Functional groups that do not show a characteristic peak above 200 nm but when attached to a chromophoric group causing a shift in the absorption peak to longer wavelengths and increase in intensity are called as Auxochromes.
- Examples: -OH, $-NH_2$, -SH, halogens etc.

Now, another lesson we learn is an isolated functional group not in conjugation with any other group is called a Chromophore this is the definition. So, I have already explained to you aldehydes, ketones, acids these are all functional groups. But this functional group should not be in conjugation with any other group; that means not separated by a single bond and another functional group. So, functional groups that do not show a character- I come to middle point now I am talking about it; functional group that do not show a characteristic peak above 200 nanometer.

But when attached to a chromophoric group it can cause a shift to longer wavelengths and increase in intensity also; that means, if there are two functional groups then they may add a little bit to the peak and push it to the right. Instead of 200 it may show you a peak around 210 may be 205 may be 220. But it is a characteristic peak corresponding to particular transition, but influenced by another functional group. So, such functional groups are called as Auxochromes. These for example, these OH, NH 2, SH, mercaptans halogens all these things will show you a peak which should appear at longer wavelengths, but on their own these things should do not show a peak. If there is CH 3 OH for example, you would not get peak for OH, but if it is there in diene or something like that it can push the peak towards the right. That is the beauty of these auxochromes.

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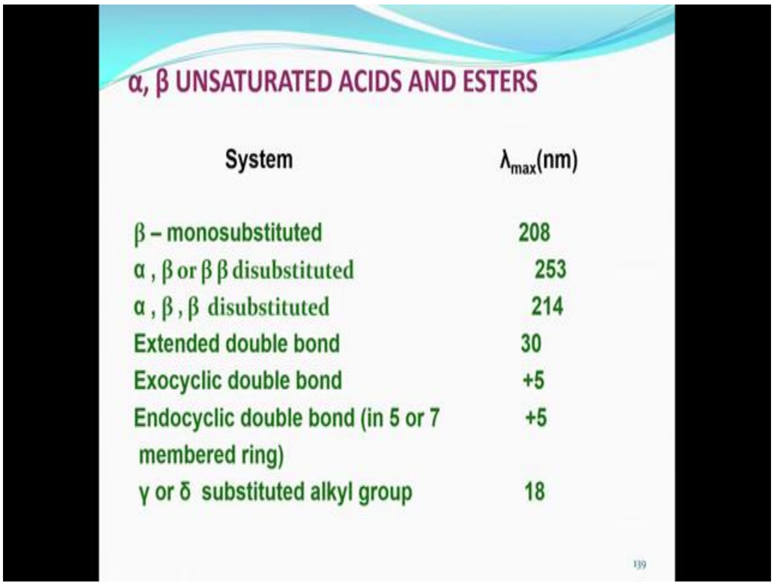

α, β UNSATURATED ACIDS AND ESTERS

System	λ_{max}(nm)
β – monosubstituted	208
α , β or β β disubstituted	253
α , β , β disubstituted	214
Extended double bond	30
Exocyclic double bond	+5
Endocyclic double bond (in 5 or 7 membered ring)	+5
γ or δ substituted alkyl group	18

Now, coming back to the Woodward-Fieser rules; for acids and esters there is a possibility that again these things can be empirically correlated. How do we do that? These when we have beta mono substituted substances; that means, from the second carbon atom from the functional group that is alpha beta unsaturated now CH 2 double bond C double bond CH single double bond CH like that. If there is a substituent on beta carbon atom then the base value is 208. And alpha beta or beta beta disubstituted substances the peak will be like 253 nanometer base peak.

Always remember the numbers what I am giving you are base peaks and remaining are the addendums something like addendums. An alpha beta or beta beta disubstituted will give you a peak at 253 and alpha beta and beta disubstituted 214. Extended double bond all as usual it gives you 30 nanometers, straight away it pushes the lambda max by 30 nanometers. Exocyclic as usual that is a double bond attached to ring from outside; double bond is attached to a ring outside that is 5 nanometers it will push endocyclic double bond is also going to give you another 5 nanometers, but it has to be in 5 or 7 membered ring. Gamma or delta substituted alkyl groups can push the lambda max by about 18 nanometers.

That means, a carbon atom from the double bond you start counting alpha beta gamma delta like that as you go away it can say push the lambda max by 18 units, but remember all these things need to be connected by a single bond double bond structure; that is conjugation, if there is no conjugation the effect could be nil- you have to remember that.

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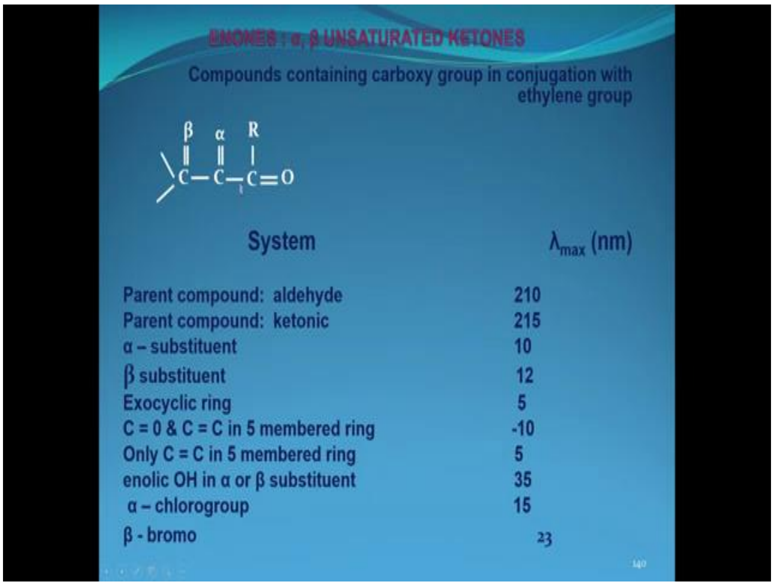

ENONES : α, β UNSATURATED KETONES

Compounds containing carboxy group in conjugation with ethylene group

System	λ_{max} (nm)
Parent compound: aldehyde	210
Parent compound: ketonic	215
α – substituent	10
β substituent	12
Exocyclic ring	5
C = 0 & C = C in 5 membered ring	-10
Only C = C in 5 membered ring	5
enolic OH in α or β substituent	35
α – chlorogroup	15
β - bromo	23

So here is another example: I have shown you tried to show you here. This is the double bond, double bond, single bond, double bond, single bond, double bond. This is CRO: R may be far is hydrogen, then its CHO Aldehyde. So, parent compound is aldehyde in this case and lambda max is 210 nanometers. If the parent compound is a ketone; that means if this double bond is somewhere on alpha position with oxygen where alpha is written and all others alkyl groups the base value would be 215 nanometers. And if it is alpha substituent for assuming CHO is the functional group, next carbon atom is alpha, next is beta, then next here is gamma, one more carbon atom delta, and this carbon atom is also gamma with respect to this carbon atom; so alpha beta gamma.

Now, if it is functional group: this is the functional group alpha, this is alpha, this is beta, this is gamma, this is gamma, if the line extents it is delta. So, every alpha substituent as you can see here it adds by 10 nanometer, it pushed the peak by 10 nanometers, beta substituent by 12, exocyclic as usual its 5, entire carbon oxygen in carbon carbon double bond in five membered ring it will increase the required energy so the peak will be pushed on the left side by 10 nanometers. And only carbon carbon in 5 membered ring is 5. Enolic OH or alpha substituent here wherever if there is an OH group here in alpha and beta positions, this is beta and if there is an OH group you can see the jump is maximum 35 nanometers, because all the hydrogen can be in conjugation again. So, it effectively increases the conjugation thereby reducing the energy required for transition from n to sigma star or pi to pi star. So, alpha chlorogroup it gives you 15, beta chromo group gives you about 23 nanometers, it pushes the lambda max.

So, so far we had discussed about the aliphatic carbon atom not one of them is aromatic. Now, aromatic substance do they confirm to this kind of rule that is the question. Quite often we see that there are number of peaks even in aromatic compounds in ultraviolet region. And we are not discussing about in infrared or far in ir etcetera NMR in this thing because for normal pollution control course we come across these compounds in the environment. So, there is no question of determining the structure or something like that. Our aim is to identify different organic compound present in the air or water or in solid based.

So, if there are aromatic compounds in the environment, as there are whichever environment you take nowadays we see lot of aromatic compounds including the camphor what you burn in your this thing etcetera, many of them are aromatic compounds they will all be in the air. So, in your day to day requirement of your organic compounds you will come across many times. Phenyls, you know floor cleaning chemicals, water cleaning chemicals, paints and sprays, you know room spray, and many of these things, attars, and room freshener, body freshener, you know they give an advertisement that India [FL] India [FL]- all those things contain organic compounds which are aromatic in nature. And many of the food materials, they contain benzene, benzoic acid, and many of them are used as food preservatives.

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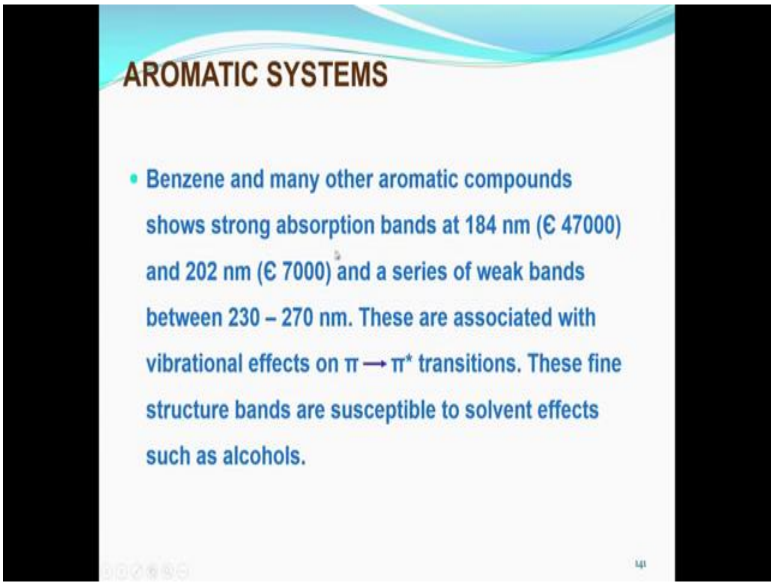

AROMATIC SYSTEMS

- Benzene and many other aromatic compounds shows strong absorption bands at 184 nm (Є 47000) and 202 nm (Є 7000) and a series of weak bands between 230 – 270 nm. These are associated with vibrational effects on π → π* transitions. These fine structure bands are susceptible to solvent effects such as alcohols.

So, all of them if they are represent in the environment do they show some sort of peaks in the UV visible range that is the question. The answer is yes, they do show certain peaks. For example, benzene and many other organic compounds show strong absorption bands at 184, 202 and a series of weak bands between 230 and 270 nanometers. These are associated obviously in benzene and aromatic structures you will see only single bond double bond structures. So, single bond can give only rise to say sigma to sigma star, there all in vacuum ultraviolet range. So, all these peaks are attributed to pi to pi star transitions.

These fine structure bands are susceptible to solvents also. So, if it is a pure compound you will get very sharp peak, if it is present in some solvent it will show you a broad peak. That is another identification of whether a substance is pure or not pure. I will show you some of these figures later.

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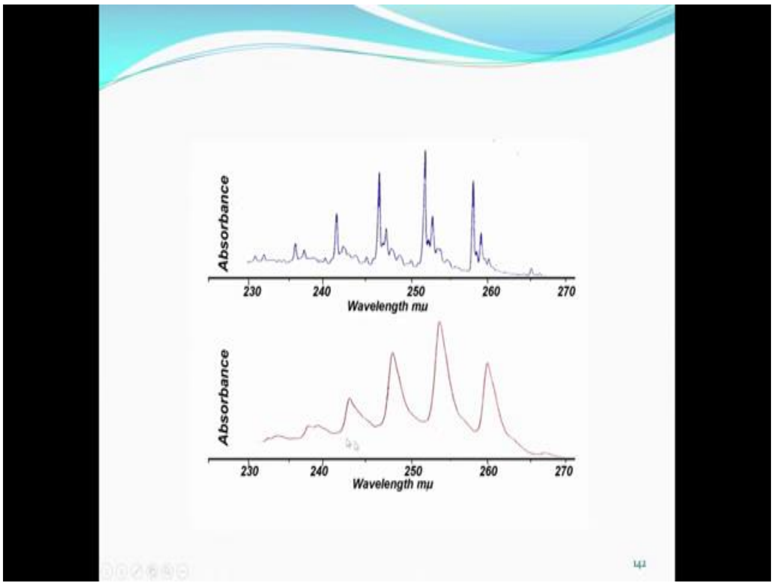

See here the bottom figure is in a solvent. See here in the top you see a peak around 230 and then 240, somewhere around 242 to here it is 250 there is one peak, here there is one more peak and between 255, 258, 259 there is one big peak with a shoulder, and one more peak at around 259; like that it shows a peak. This is all we UV range, ultraviolet range from 180 to 350 it goes, but all aromatic compounds as I was telling you will show you a number of peaks this is characteristics of aromatic compound; any aromatic compound should show you these peaks. So, it is like a pass fail test.

So, if you see a structure something like this we immediately say- yes it contain some sort of organic compound. Now the same peak if it is there present in a solvent you see the structure of the peak how it is coming. The peaks are almost same, but small disturbances they are all leveled out here, and corresponding to this peak there is this peak, and these peaks are all wiped out, and corresponding to this there is one more peak pushed to the right the something like an auxochrome, and this peak is merged into one peak pushed slightly around here and somewhere around 260, again that is also pushed. So, the top one is in the vapour form, the bottom one is in the solvent.

So, in a solvent peaks look smarter, beautiful, but it does not actually represent the basic structure of the chemical. So, if you want to take a real look whether the substance is pure or not you should always take it in the neat form without any solvents, and this is a perfect case to show. And this is for aromatic substances.

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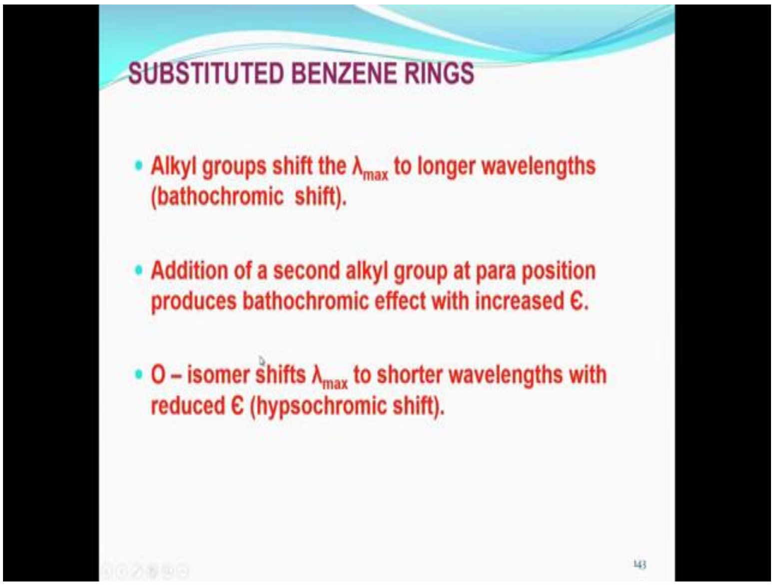

SUBSTITUTED BENZENE RINGS

- Alkyl groups shift the λ_{max} to longer wavelengths (bathochromic shift).
- Addition of a second alkyl group at para position produces bathochromic effect with increased ϵ.
- O – isomer shifts λ_{max} to shorter wavelengths with reduced ϵ (hypsochromic shift).

Again substitution helps a little bit. So, how does it help? An alkyl group shifts the lambda max to longer wavelengths. If there is any alkyl group in benzene ring we will see the same structure, but all peak shifted to longer wavelength; this is known as bathochromic shifts. Very important shift observed in many aromatic compounds, because 99 percent of the time we do not deal with benzene alone as a component or a constituent, it will always be substituted with some groups, even the Dettol and other things what we have seen, what we use in day to day medical of a hospitals etcetera they all show you a peak shifted to longer wavelength, because it contains some alkyl groups present on the benzene ring- toluene xylene all those compounds.

So, if second alkyl group xylenes it has got two alkyl groups one may be at ortho one may be at para one may at meta that is adjacent second adjacent third adjacent; third adjacent would be opposite, exactly opposite to the first one. So, again it produces a bathochromic effect with increased molar absorptivity.

Similarly, an isomer if it is the groups are attached to carbon atom then they shift is to shorter wavelengths.

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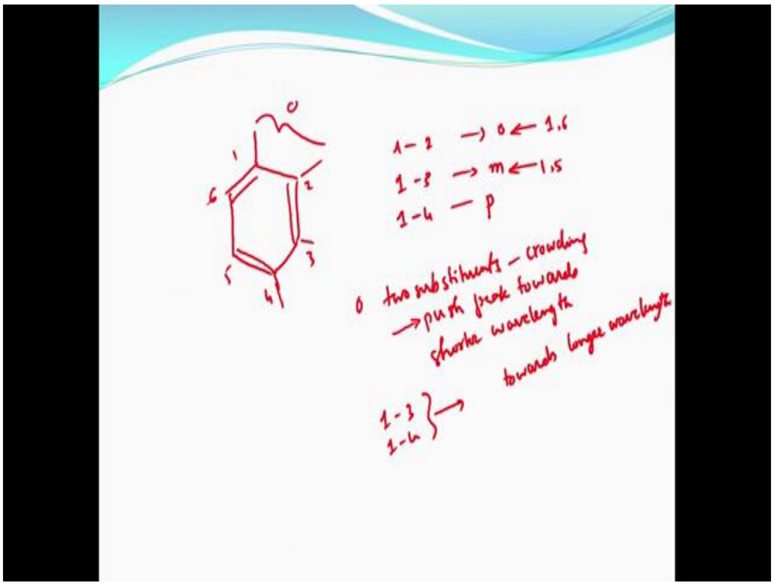

1-2 → o ← 1,6
1-3 → m ← 1,5
1-4 — p

o two substituents – crowding
→ push peak towards
shorter wavelength

1-3 }
1-4 } → towards longer wavelength

What I will do is I want to show you this kind of thing. So if I have a benzene ring like this, this a position second position, third position, fourth position. So, a substituent this is ortho, and this is 1, 2, 3, 4, 5, 6 numbered ring. And 1 and 2 is ortho, 1 and 3 is meta, and 1 and 4 if there is a substituent then it is para. So, the 1 and 5 would be again meta only. And 1 and 6 is ortho again.

So, if there are two groups on 1 and 2 positions in ortho position two substituents, these represent crowding; crowding of the electronic structure between 1 and 2. So, this should increase repulsion between the electrons, so it is not favored, so it requires more energy to excite the electrons, so it will push the peak towards shorter wavelengths. Compared to this 1 and 3, and 1 and 4 these push the electrons push the peak towards longer wavelengths.

So, alkyl group shifts the lambda max to longer wavelengths, that is number one bathochromic shift. Addition of second alkyl group par para produces bathochromic shift, increased epsilon ortho isomer shifts to shorter wavelengths. This is understood now I hope.

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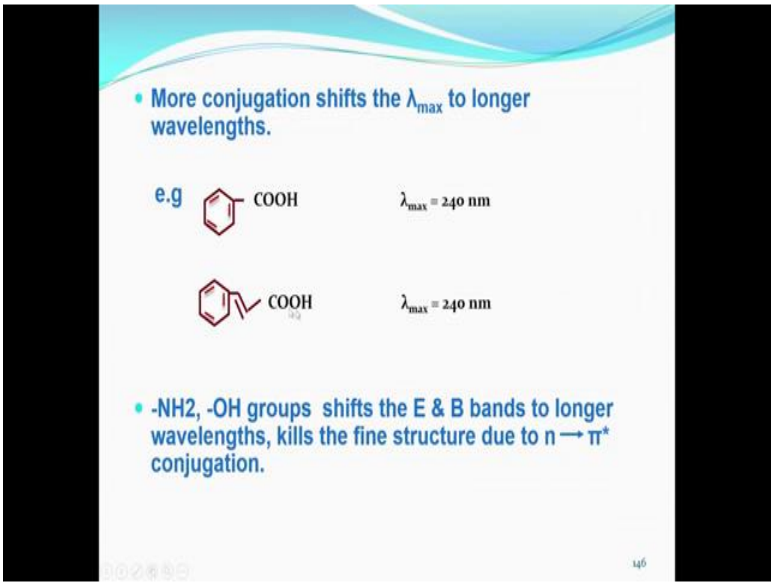

- More conjugation shifts the λ_{max} to longer wavelengths.

e.g COOH $\lambda_{max} = 240$ nm

COOH $\lambda_{max} = 240$ nm

- -NH2, -OH groups shifts the E & B bands to longer wavelengths, kills the fine structure due to n → π* conjugation.

So, more conjugation should shift it to longer wavelength expected. Suppose I have a group like this COOH and here I have a single bond double bond and single bond and again COOH group. So, this should shift the lambda max to longer wavelength. Similarly NH 2 OH 2 groups shifts the epsilon and E and B bands, these are designated as E band and B band, R band like that, and they shift to longer wavelengths.

But they kill the fine structures which I had shown you earlier for benzene ring, because all of it would be n to pi star transitions fine structure will go away.

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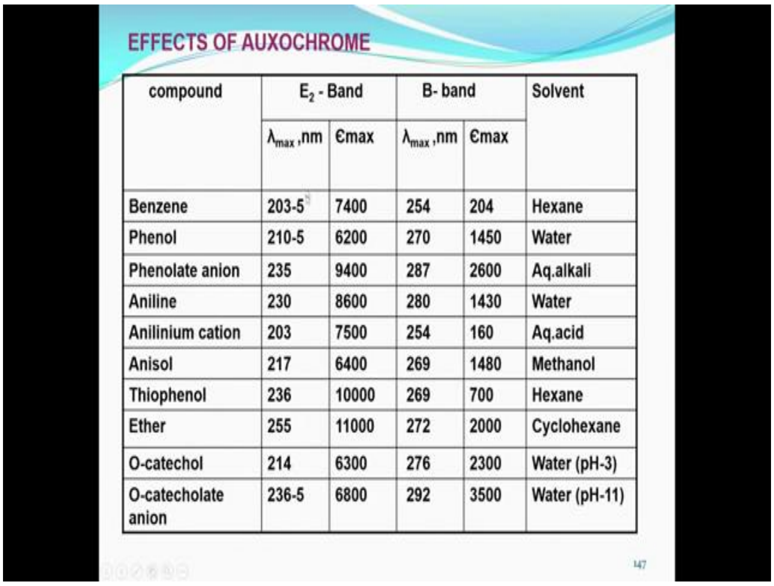

EFFECTS OF AUXOCHROME

compound	E_2 - Band		B- band		Solvent
	λ_{max} ,nm	Єmax	λ_{max} ,nm	Єmax	
Benzene	203-5	7400	254	204	Hexane
Phenol	210-5	6200	270	1450	Water
Phenolate anion	235	9400	287	2600	Aq.alkali
Aniline	230	8600	280	1430	Water
Anilinium cation	203	7500	254	160	Aq.acid
Anisol	217	6400	269	1480	Methanol
Thiophenol	236	10000	269	700	Hexane
Ether	255	11000	272	2000	Cyclohexane
O-catechol	214	6300	276	2300	Water (pH-3)
O-catecholate anion	236-5	6800	292	3500	Water (pH-11)

So, some effect of auxochromes I have listed here. For example, benzene E 2 they are designated as E band and B band and 203, 210 these are all sigma to sigma star something like that these are all pi star bands. So, you can see that the peaks are shifted and the lambda max keep on increasing with different functional group- phenol, phenolate, aniline, anilinium cation, anisole, thiophenyl, etcetera different compounds.

Remember all these compounds can be present in the environment, in the water, in the river, in the air, in the solid substances like that. So, we can see that many of them are water soluble in the last table now- aqueous alkali water, aqueous acid, methanol, methanol is again miscible with water; like that many of them are present in the environment.

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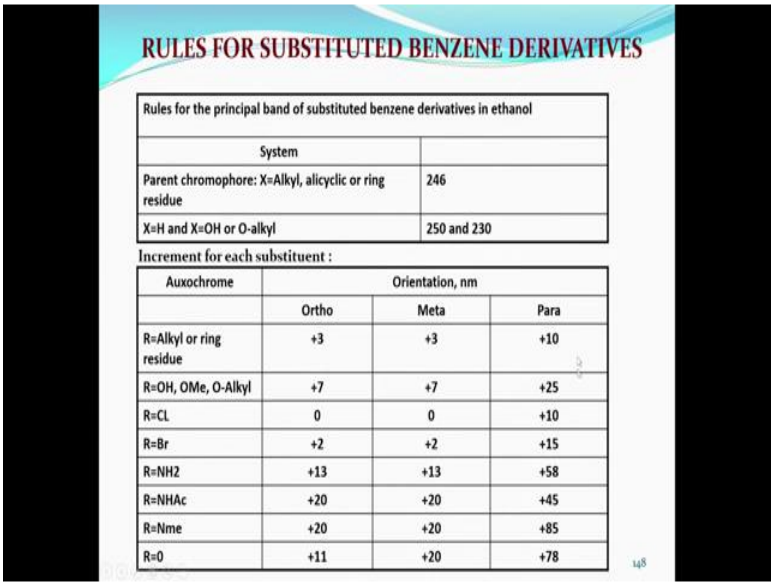

RULES FOR SUBSTITUTED BENZENE DERIVATIVES

Rules for the principal band of substituted benzene derivatives in ethanol	
System	
Parent chromophore: X=Alkyl, alicyclic or ring residue	246
X=H and X=OH or O-alkyl	250 and 230

Increment for each substituent :

Auxochrome	Orientation, nm		
	Ortho	Meta	Para
R=Alkyl or ring residue	+3	+3	+10
R=OH, OMe, O-Alkyl	+7	+7	+25
R=CL	0	0	+10
R=Br	+2	+2	+15
R=NH2	+13	+13	+58
R=NHAc	+20	+20	+45
R=Nme	+20	+20	+85
R=0	+11	+20	+78

Similarly, but this is the typical rule, again this is not empiric this is again empirical. In the empiricals this thing what we say is x is equal to hydrogen x is equal to OH or O-Alkyl. So, parent chromophore is x alkyl alicyclic or ring residue, so to that what I want to tell you is these are the substances if there is r alkyl group it will add 3 at ortho, 3 at meta, and 10 at para. Again it gives you a feel, whether the substance is in the required group or not, whether it is shifting just by knowing the actual and pushed wavelength lambda max we can say without doing any chemical analysis whether it is ortho meta or para a unknown compound. Same thing, if it R is equal to OH, Ome that is oxygen containing compound OH, OMe and O-Alkyl. This may be OCH 3, this may be over OC 5 H 5 or something like that, ortho meta is 7, but para is 25.

Similarly, I suppose the substituent is chloride it does not shift if it is there in ortho position, but at para if the substituent is chloride is at para then you can see that 10. Same thing is true with bromide 2 and 2 and 15; amine is 58, compared to this thing because amine is an electron releasing agent because it has got 2 electrons- lone pair of electrons on NH 2 group which can participate in the conjugation of the benzene ring. Similarly NHAc is 20, 20 and 45. And then Nme is 20 20 and 85; n methyl groups. R-O is gain 11 and 20 that leads to approximately 78 nanometer pushing wavelength to the right; that is towards longer wavelength.

So, like that there are several things. For more details you should look into the text books and to gain an insight. I have tried to give you as much insight as possible with respect to the organic compounds in UV and visible region. What I would like you to do is in the next class is we look at the structures and solve some problems, where the peak is expected and where it is actually. So, that is in a way like testing the Woodward-Fieser rules that we will do. And then we will move on to instrumentation and as per Beer-Lamberts law etcetera.

Thank you very much. Have a nice day.