Modern Instrumental Methods of Analysis

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Module No. #02

Lecture No.# 06

Ultra Violet and Visible Spectrophotometry-2

Theoretical Aspects

Welcome to the next section of our discussion on the ultra violet and visible spectrophotometry. In the last class, we have decided, we have discussed about the molecular orbital theory, and we have shown that the bourns expected in organic compounds are of the type: sigma to sigma star, that is the single bond, and pi to pi star that is a double bond, and then there would be non-bonding electrons, which also can get excited to n to sigma star and n to pi star.

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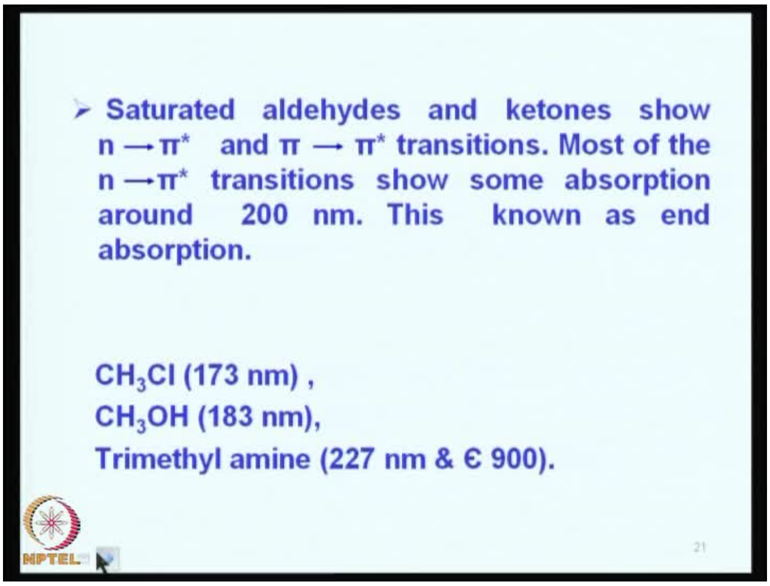

- Saturated aldehydes and ketones show $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. Most of the $n \rightarrow \pi^*$ transitions show some absorption around 200 nm. This known as end absorption.

CH_3Cl (173 nm) ,
CH_3OH (183 nm),
Trimethyl amine (227 nm & ϵ 900).

So, these are the type of, types of transition expected in the organic compounds. And in general, I have already told you that n to pi star transition are of least energy, and pi to pi star transition are of slightly higher energy, and n to sigma star are still higher, and sigma to sigma star would be occurring in the vacuum ultra violet regions. Now, the question is, is it possible to correlate the structure of the organic compounds by relating to the peaks that are observed in ultra violet and visible region. Mostly, we will be discussing about the organic compounds in the ultra violet region.

So, this is what, slide I had shown you in the last class, that is, if we have CHCL3 CH3 CL, the lambda max expected is at 173 nanometers, for methanol the lambda max is 183 nanometers; this would be because, this is occurring in the ultra violet range very near the end e, this would be n to sigma star transition.

Similarly, in trimethyl amine there are only n h two groups, there is only 1 n h 2 group, and then all other bonds are sigma bonds, that means there are no double bonds or triple bonds in this case.

So, the only peak that is expected is n to sigma star, because sigma to sigma star transition are not expected in u v region, and n to sigma star transition would be occurring at 227 nanometers, and epsilon would be 900- that is the molar extinction coefficient.

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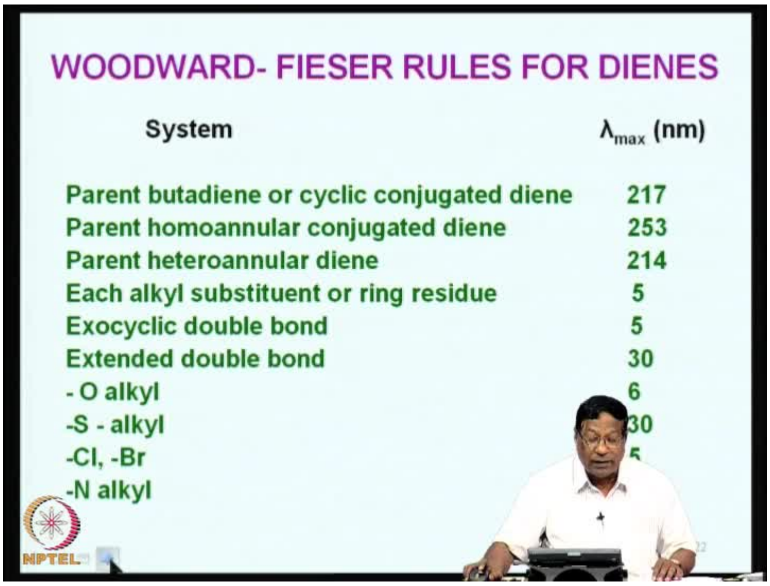

WOODWARD- FIESER RULES FOR DIENES

System	λ_{max} (nm)
Parent butadiene or cyclic conjugated diene	217
Parent homoannular conjugated diene	253
Parent heteroannular diene	214
Each alkyl substituent or ring residue	5
Exocyclic double bond	5
Extended double bond	30
- O alkyl	6
-S - alkyl	30
-Cl, -Br	5
-N alkyl	

Now, is it possible to correlate larger molecules, if they could contribute to the lambda max. Now, I have given you in the last class, this slide that is known as Woodward-Fieser rules for dienes; so, dienes means alternate double bonds separated by a single bond. So, if we have a butadiene or parent butadiene, say or a cyclic conjugated diene, the peak expected is at 217, if both the double bonds are in the same ring, then we can expect the peak at 253, that is the basic thing.

Suppose there are substituents, these substituents will act to labialize the electrons, and then the lambda max is, the energy of the system would be still ahead, and then would be shifted to the, longer, on a longer wavelength, that means the lambda max would be shifted to longer wavelength. So, what would be the contribution? For each alkyl substituent or ring residue, we add 5 nanometers, that means, instead of 217, if there is an alkyl substituent, it will go up to 222 nanometers. Suppose there is an exocyclic double bond, then that also will contribute to the shifting of the lambda max by another 5 units.

What is an exocyclic double bond? It is a double bond attached to a ring out side; and extended double bond is again the same diene system in which one more double bond is there separated by a single bond, that we call it extend double bond.

Now, there are some specific group, for example, if it is O alkyl group, that is for example, OCH 3 OC 2 H5, something like that, then that group will contribute to shift the lambda max by another 6 units.

Then, S alkyl groups like SCH 3 etcetera., they would contribute to shifting to the right side, that is wavelength side by 30 nanometers; chloride bromide etcetera., they would shift it to the another 5 nanometers; N alkyl groups would of course do it for up to 60 nanometers.

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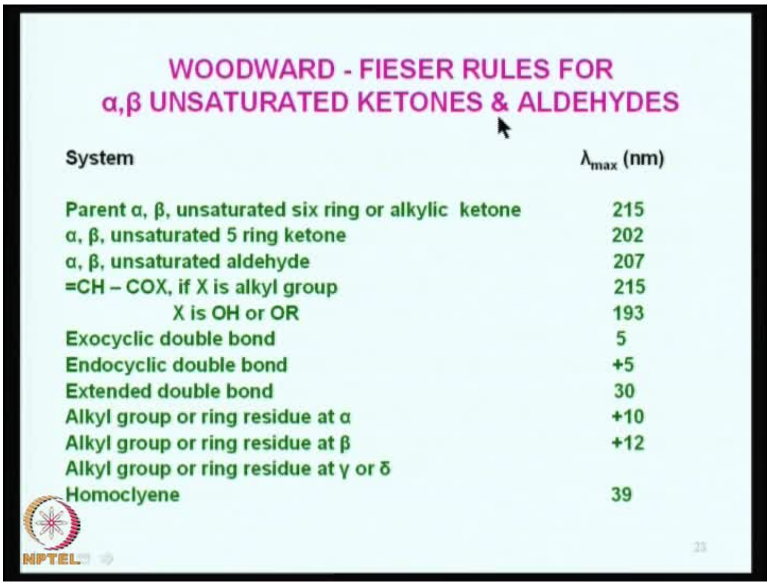

WOODWARD - FIESER RULES FOR α,β UNSATURATED KETONES & ALDEHYDES

System	λ_{max} (nm)
Parent α, β, unsaturated six ring or alkylic ketone	215
α, β, unsaturated 5 ring ketone	202
α, β, unsaturated aldehyde	207
=CH – COX, if X is alkyl group	215
X is OH or OR	193
Exocyclic double bond	5
Endocyclic double bond	+5
Extended double bond	30
Alkyl group or ring residue at α	+10
Alkyl group or ring residue at β	+12
Alkyl group or ring residue at γ or δ	
Homoclyene	39

Now, we will see another, says, we have another system, that is, alpha beta unsaturated ketones and aldehyde, do also show some sort of structural relationship to the ultra violet lambda max position. Now, without any substituents if we have an alpha beta unsaturated ketonethen, the base value would be 215, and if it is, see a, located in a 5 member ring, then it is 202 nanometers.

Now, if it is an alpha beta unsaturated aldehyde, then you would expect the lambda max to be around 207 nanometers. Now, again substituents, if they are like this CH COX where X is an alkyl group, the base value itself would be 215, and if it x is a hydroxyl group or in ester group, you would see that the base value would be somewhere around 193 nanometers.

Now, if there is an exocyclic double bond, another 5 nanometers need to be added to locate the lambda max; and if there is an Endocyclic double bond, another 5 nanometers to be added; and extend double bond as usual adds another 30 nanometers.

Suppose, there is an alkyl group or ring residue at the alpha position, then we have to add 10 nanometers; suppose there is an alkyl group or ring residue at gamma or delta position, then it should be added group another 18 nanometer here; now, if it is a homodyne, you have to added a component of 39 nanometers.

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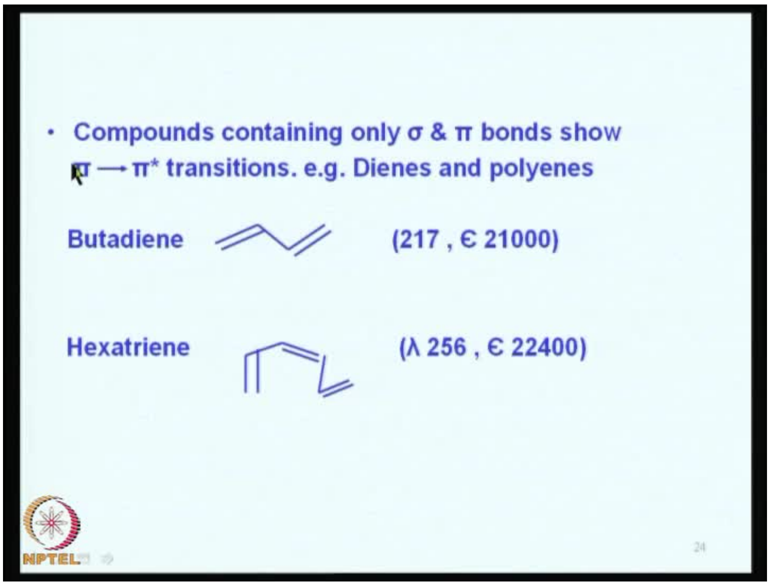

- Compounds containing only σ & π bonds show $\pi \rightarrow \pi^*$ transitions. e.g. Dienes and polyenes

Butadiene (217 , Є 21000)

Hexatriene (Λ 256 , Є 22400)

So, these are some of the systems. Now, I just want, like to show you, that pi to pi transitions occurring in these situations, because this is butadiene there is a double bond, single bond and double bond. So, for this lambda max would be 217 and epsilon would be 21000, which means we will be having very strong bind.

Suppose it is hexatriene, that is 3 double bonds separated by this single bond and another single bond, that is an addition to this double lambda max by this third double bond, and it will be shifted to, it is shifted to 256 nanometers, and molar absorptivity is around 22400.

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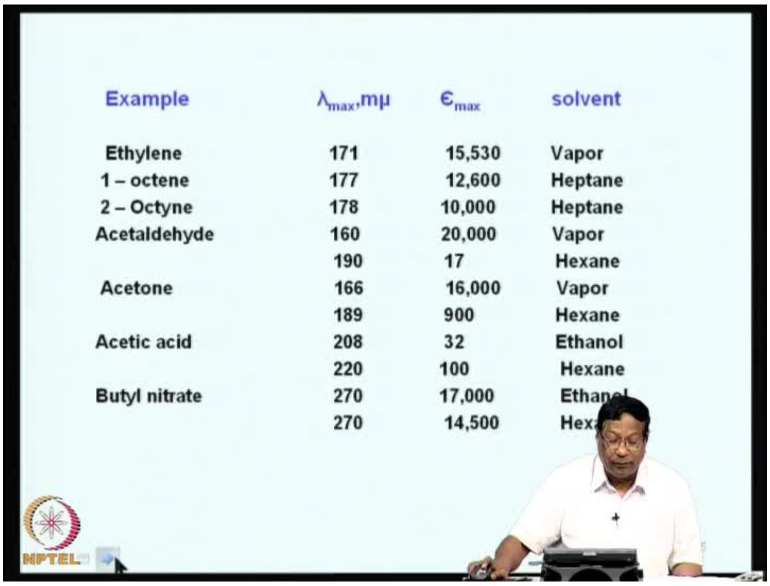

Example	λ_{max}, mμ	ϵ_{max}	solvent
Ethylene	171	15,530	Vapor
1 – octene	177	12,600	Heptane
2 – Octyne	178	10,000	Heptane
Acetaldehyde	160	20,000	Vapor
	190	17	Hexane
Acetone	166	16,000	Vapor
	189	900	Hexane
Acetic acid	208	32	Ethanol
	220	100	Hexane
Butyl nitrate	270	17,000	Ethan
	270	14,500	Hex

I have given your this table where the different lambda max have been recorded.

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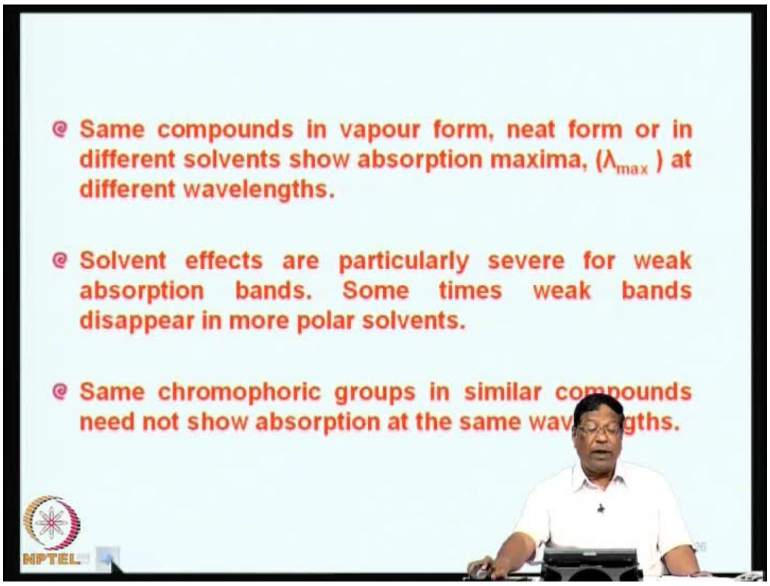

- Same compounds in vapour form, neat form or in different solvents show absorption maxima, (λ_{max}) at different wavelengths.
- Solvent effects are particularly severe for weak absorption bands. Some times weak bands disappear in more polar solvents.
- Same chromophoric groups in similar compounds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

More data can be had, some from the data bases. If you look at any text book for organic chemistry or spectrophotometry, you would see some more data, which we can correlate to the transitions that are occurring in the ultra violet region, corresponding to sigma sigma star, n to sigma star, pi to pi star etcetera.

Now, if you have understand some of the important things, for example, the same compound, suppose you take in, one compound in the vapour form, one compound as liquid, that is neat for, or dissolve the compound in some other solvent, what type of lambda max you would be expecting? What type of ultra violet spectrum? Now, in the, you can easily expect that there would be molecular-molecular interactions; therefore, they show lambda max at slightly differing wavelengths.

This is very important, because one should not confuse that the peak corresponding to the lambda max could belong to some other compound; that is not correct.

So, solvent effects are particularly severe for weak absorption bands, sometimes weak bands disappear in more polar solvents; especially weak bands if they are not easily visible, you change the solvent to more polar, they will completely disappear, and less polar, they could be still visible.

Now, suppose you have similar compounds, same chromophoric group, then the lambda max need not show at the same wavelengths, it could be shifted because the compound is similar but not exactly same. Basically, what to expect is, a chromophoric group like NH2 or OH group excreta in C2 system, C3 system or C5 system, all of them need not show exactly the lambda max at the same wavelength. This point you have to remember when ever we are doing some problems.

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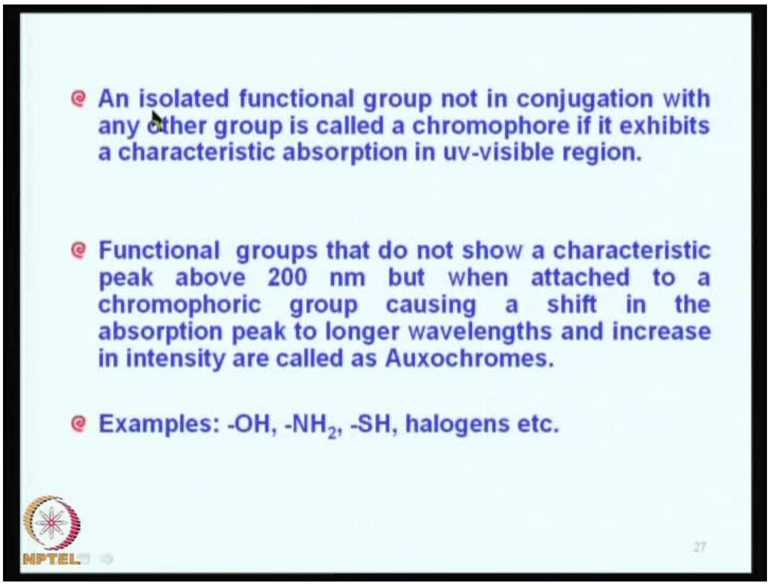

- An isolated functional group not in conjugation with any other group is called a chromophore if it exhibits a characteristic absorption in uv-visible region.
- Functional groups that do not show a characteristic peak above 200 nm but when attached to a chromophoric group causing a shift in the absorption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

And what is the chromophore? I have already defined it earlier for you- and it means 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 nanometer, but when attached to a chromophoric group in the compound they do cause a shift in the absorption peak, that is lambda max to longer wavelength and increase its intensity, such groups by themselves do not show a peak, but they will increase the lambda max, they are known as Auxochromes; and examples are OH, NH2, SH, halogens etcetera.

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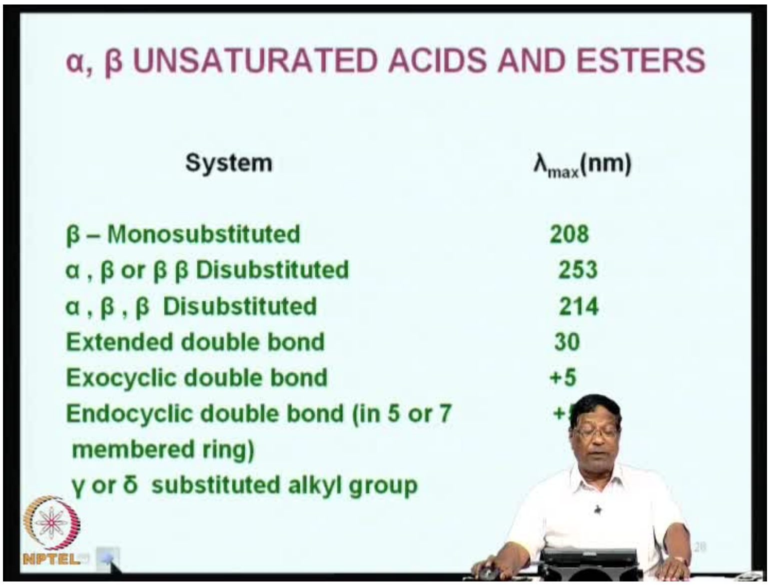

α, β UNSATURATED ACIDS AND ESTERS

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)	+
γ or δ substituted alkyl group	

So, this is what we have to been discussing, because of the presence of OH groups, NH2 groups etcetera, that is these Auxochromes would like to, would rather tend to increase the lambda max to the longer wavelengths.

Now, this is another system; alpha beta unsaturated acids, and this things, here we have monosubstituted, disubstituted, and alpha beta, and beta beta, that is, on the beta compound we have two substitutions, and then some times alpha beta and beta beta distributed extended double bond is 30, exocyclic double bond is 5, endocyclic is 5, gamma or delta substituted alkyl group is 18.

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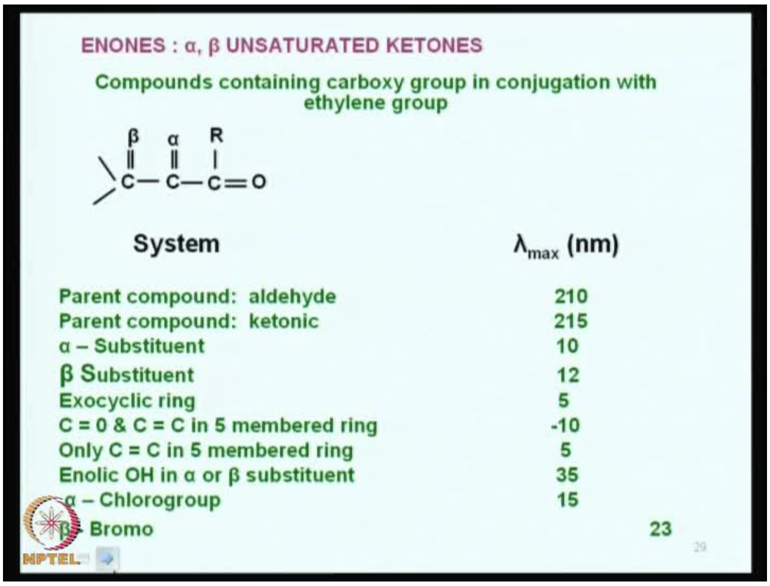

ENONES : α, β UNSATURATED KETONES

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

Now, right now, it may look slightly confusing to you, but when we solve some problems, we will be able to sort out very easily where the lambda max can occur.

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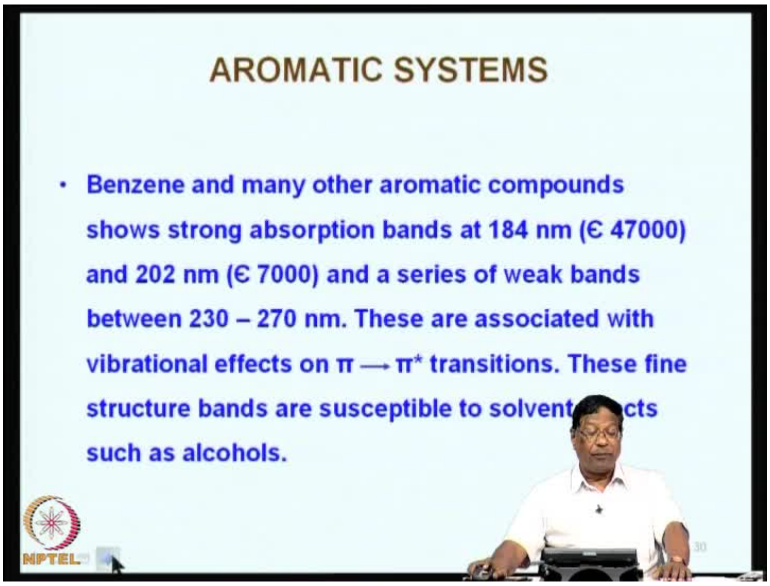

AROMATIC SYSTEMS

- 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.

Now, the, we can see that here, it is a system of double bond, that is alpha beta unsaturated ketone, we have already discussed, and aromatic systems, we have benzene and several other systems. Aromatic system, they show a strong absorption bands at 184 nanometer with a molar absorptivity of 47000 and 202 of 7000, and a series of weak band, these are associated with vibration effects on the pi to pi star transitions.

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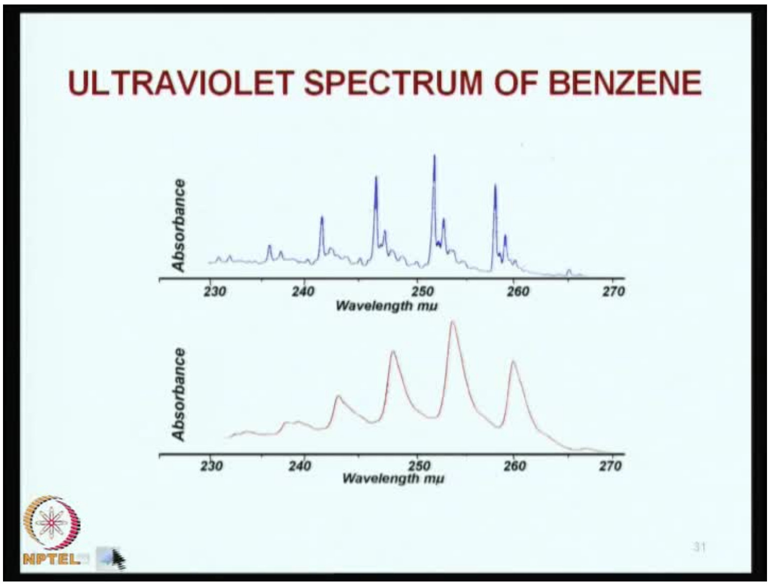

ULTRAVIOLET SPECTRUM OF BENZENE

Now, this is a figure which I wanted to show you- the top one is vapour form, the bottom one is in the liquid form, through the of benzene aromatic system.

So, you can see that peaks are sharper here, number of peaks are there 1, 2, here there is a 230, there is one 232, there is one 240, like that about seven to eight peaks are there; but if you take a look at this spectrum in a solvent, as a liquid, we can see that all this fine structures are missing, and what you would be seeing is basically a simple broad peak that is there.

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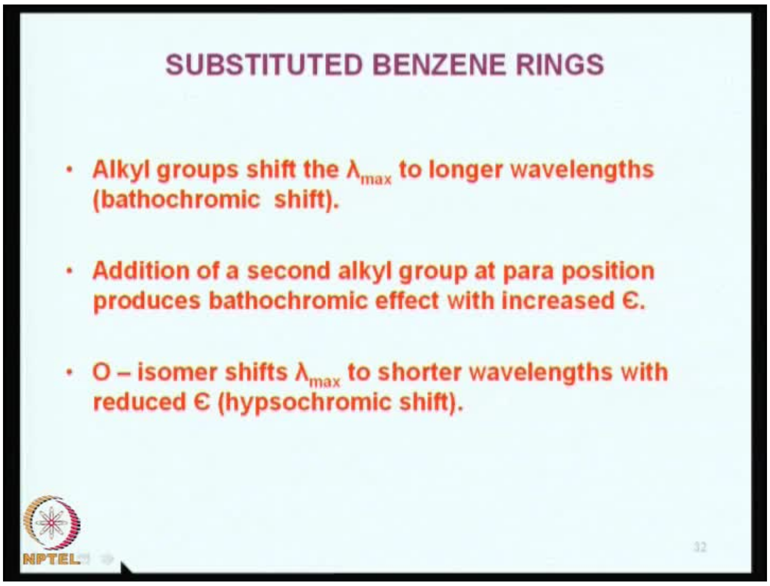

SUBSTITUTED BENZENE RINGS

- 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 Є.
- O – isomer shifts λ_{max} to shorter wavelengths with reduced Є (hypsochromic shift).

So, substituted benzene rings also contribute to some extent; the shift towards the longer wave lengths, for example, alkyl groups shift the lambda max to longer wavelength, known as bathochromic shift; and addition of a second alkyl group at para position produces bathochromic effect, with increased epsilon; ortho isomer shifts the lambda max to shorter wavelength with reduced epsilon.

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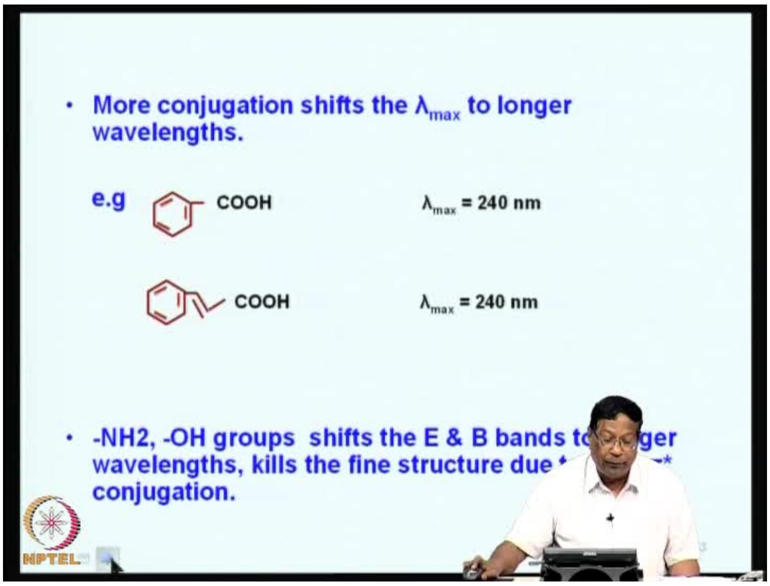

- More conjugation shifts the λ_{max} to longer wavelengths.

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

COOH $\lambda_{max} = 240$ nm

- -NH2, -OH groups shifts the E & B bands t ger wavelengths, kills the fine structure due * conjugation.

Now, this is the benzene ring with COOH group we can see that the lambda max is at 240 nanometers, and for the COOH also there is lambda max 240. Similarly, NH2 groups, OH groups, etcetera, shift the bands- these are different bands designated in the aromatic position in the spectrum- bands to longer wavelength, and kills the fine structure due to n to pi star conjugation.

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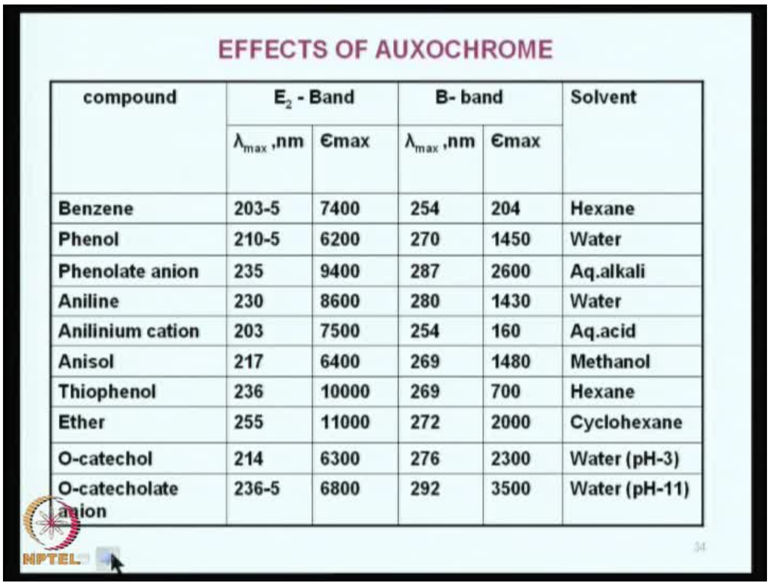

EFFECTS OF AUXOCHROME

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)

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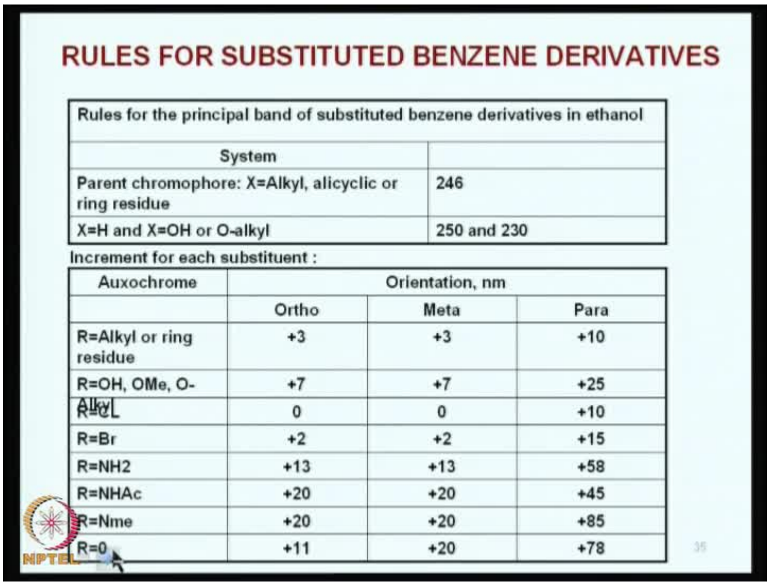

RULES FOR SUBSTITUTED BENZENE DERIVATIVES

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

Now this is effects of Auxochrome, I have listed here for you to appreciate the effects of the substituents and change in the lambda max. Since we have already covered this, we will not go ahead and discuss this further, and these also we have seen it.

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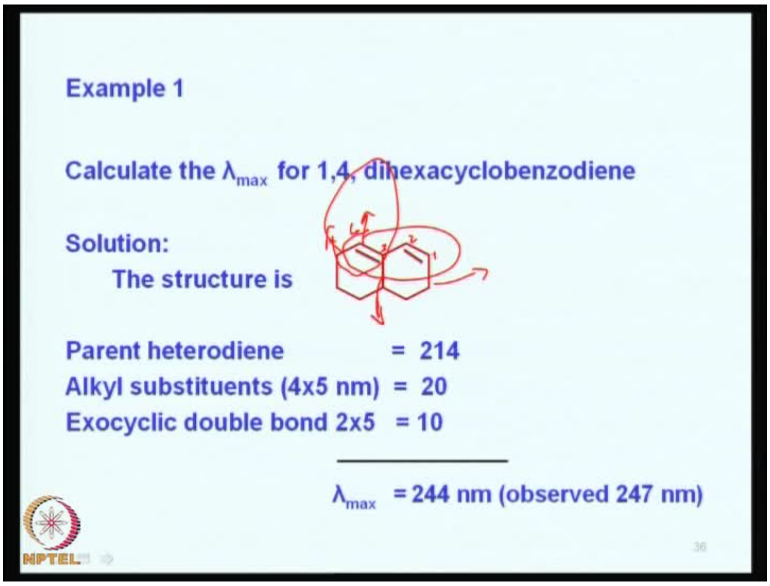

Example 1

Calculate the λ_{max} for 1,4, dihexacyclobenzodiene

Solution:

The structure is

Parent heterodiene = 214

Alkyl substituents (4x5 nm) = 20

Exocyclic double bond 2x5 = 10

λ_{max} = 244 nm (observed 247 nm)

Now, let us try to solve some examples. Now, first example I have chosen is, calculate the lambda max for 1, 4, dihexacyclobenzodiene; so, the structure is like this... and parent, here we can see that a diene system is like this, and here we can see the double bonds are separated here, there is 123 and 4, it is extended over 4 carbon items separated by a single bond between 2 and 3.

So, the parent heterodyne lambda max would be, is at 2 and 4, and then you can see that there are one substituent here, there is another substituent here and then there is one more substituent here, and there is one more substituent here; so, there are 4 substituents, and unlike, if there are CH 3 groups or C2 H5 groups etcetera, it is alkyl substituent, but even it is not an alkyl substituents just as shown here, we need to take this part of the thing as a substituent and we have to calculate.

So, that gives us alkyl substituents, 4 are there, 1234, I have a marked, and with the arrows, and that adds 20 nanometers, and there is one exocyclic double bond, that is this double bond, to the right side ring, that is a double bond attached outside the ring to be outside the ring, but still in to the diene system. So, that is known as exocyclic double bond. So, this double bond adds another 5, another 5, so, there are two exocyclic double bonds that makes it, so, that makes it 244 nanometers.

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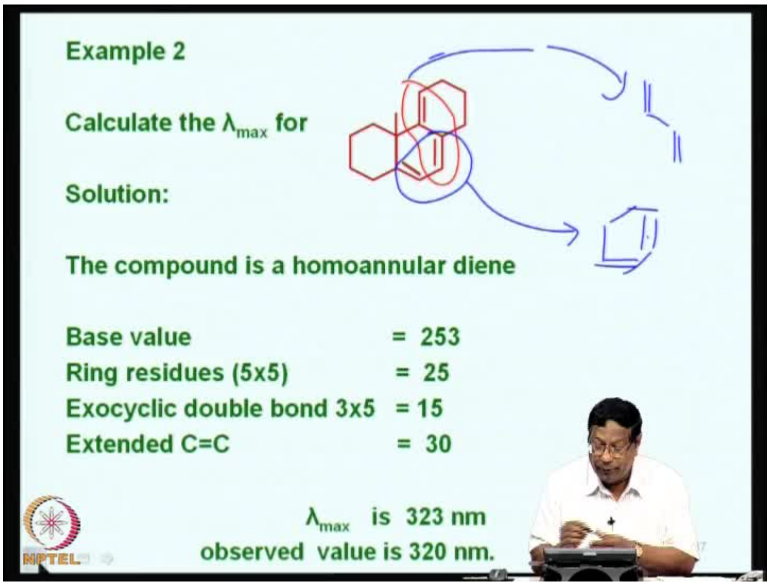

Example 2

Calculate the λ_{max} for

Solution:

The compound is a homoannular diene

Base value = 253
Ring residues (5x5) = 25
Exocyclic double bond 3x5 = 15
Extended C=C = 30

λ_{max} is 323 nm
observed value is 320 nm.

So, let us take another compound like this. There are a 3 cyclohexane rings, and there is a double bond system, here, here and here. And now, the basic, base value is 253 nanometers because there is a double bond in the same ring, and this is known as homoannular diene; and now you may say that there is a double bond system that is not in the ring.

Suppose we take this range, then we have, it is a heteroannular diene, this could be a confusion for you, because whether to, whether to choose that color, that heteroannular diene or this diene, this part or this part, this is the heteroannular diene, this is homo, this is homoannular diene and this is the heteroannular diene; now, which one you take is the question, the question is whichever is higher value, you take that. So, basically what you choose is a heteroannular diene, and its base value is 253 nanometers.

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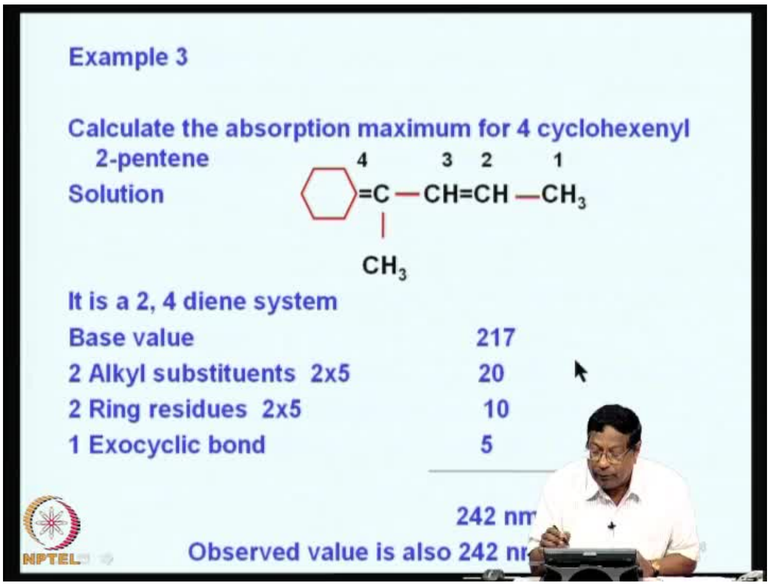

Example 3

Calculate the absorption maximum for 4 cyclohexenyl 2-pentene

Solution

It is a 2, 4 diene system

Base value	217
2 Alkyl substituents 2x5	20
2 Ring residues 2x5	10
1 Exocyclic bond	5
	242 nm

Observed value is also 242 n

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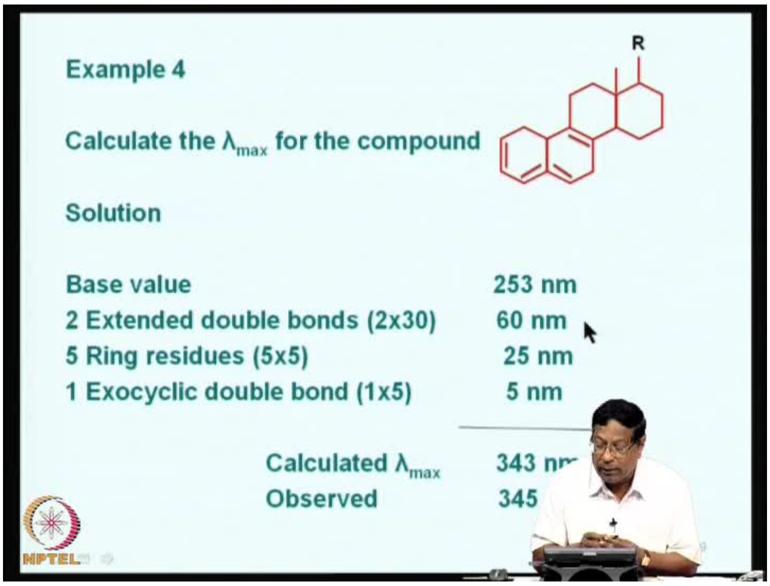

Example 4

Calculate the λ_{max} for the compound

Solution

Base value	253 nm
2 Extended double bonds (2x30)	60 nm
5 Ring residues (5x5)	25 nm
1 Exocyclic double bond (1x5)	5 nm
Calculated λ_{max}	343 nm
Observed	345

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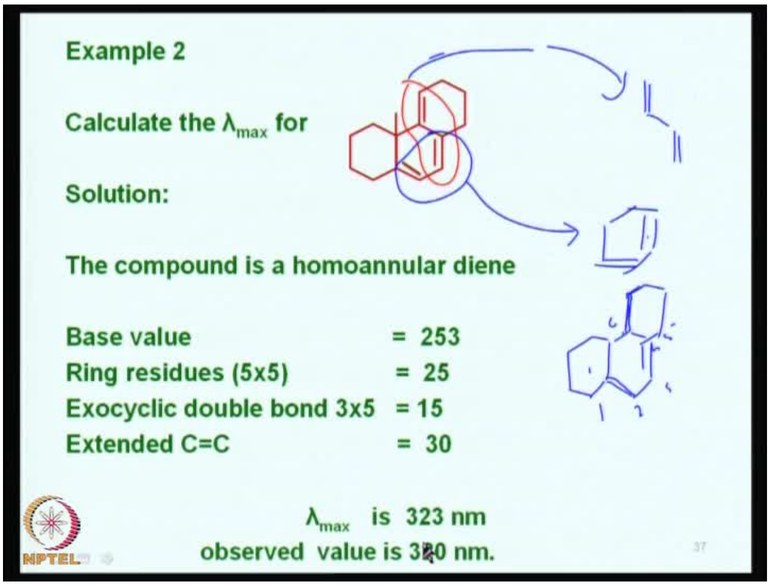

Example 2

Calculate the λ_{max} for

Solution:

The compound is a homoannular diene

Base value = 253
Ring residues (5x5) = 25
Exocyclic double bond 3x5 = 15
Extended C=C = 30

λ_{max} is 323 nm
observed value is 320 nm.

Now, there are ring residues, for example, here how many substituents are there? This is 1, this is 2, this is 3, this is 4, that is we have a figure like this, and one more is here, double bond, so, this is a homoannular diene; this is carbon number123456 like that, there is 2 substituents here on carbon number 1, and then there is 1 substituent on carbon number 4, and a 1 substituent on carbon number, here, and another substituents here.

So, how many substituents are there? Five substituents, five substituents are there; one is here, two then three, and then four, this is fifth one. So, if you take 5 into 5 that would be, that will add to the lambda max of 25 nanometers.

And there is one exocyclic double bond, because this double bond is outside the ring, but attached directly to the double bond- so this one- so, that will add up to 5, and then you can see this double bond is exocyclic to this ring, so, one more, and this double bond is the exocyclic to the middle ring; so there are 3 exocyclic double bonds, that is, will add 15 nanometers. Now, there is one extended double bond, if you take this homoannular diene, it is separated by one single bond and again another double bond, that is the liability this increased, so, this will add to the shifting of the lambda max by adding another 30 nanometers; so, if we add up all this, it is a, lambda max works out to 323 nanometers. Now what is the observed value? You can see here, it is 320; so you can see how closely there is a match between the calculated and observed values.

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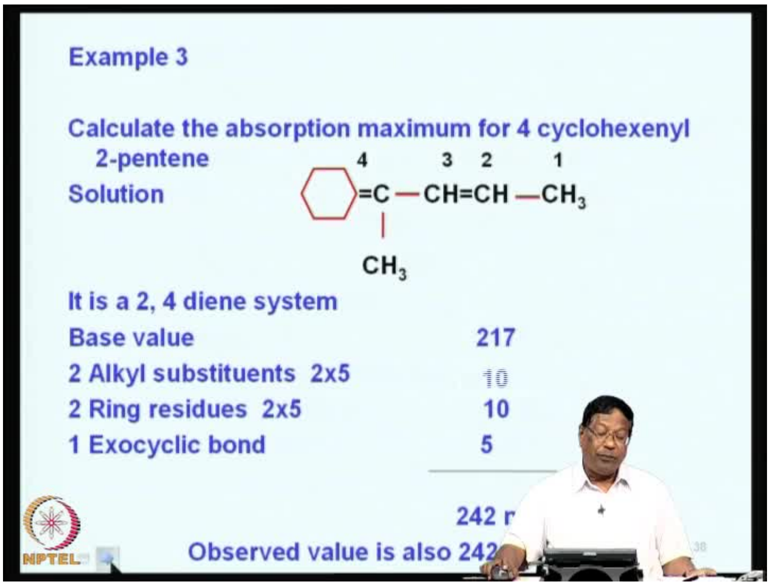

Example 3

Calculate the absorption maximum for 4 cyclohexenyl 2-pentene

Solution

It is a 2, 4 diene system

Base value	217
2 Alkyl substituents 2x5	10
2 Ring residues 2x5	10
1 Exocyclic bond	5
	242 r

Observed value is also 242

Now, let us take another example. Let us calculate the absorption of maximum for 4 cyclohexenyl 2 pentene. This is cyclohexenylgroup- and then there is a double bond, this is the one substituents, and then a double bond between carbon number 3 and 2, and there 1CH group at the end, and this double bond is separated by this double bond by a single bond, that means it is a diene systems; because they are basically no other functional groups, so you call it a diene system, and it is a 2 4 diene system, because I have put numbers here 1234, so, two it start, double bond starts from here, four double bond starts from here -so it is a 24 diene system. So, the base value for a diene system is 217 nanometers.

Now, how many substituents are there, alkyl substituents? There is one here, alkyl, that is methene group on carbon item number four, there is another substituent; so, two alkyl substituents are there, that adds to20; and then on this carbon items there are 2 bonds, one here and one here, so these 2 will add another 5 5 nanometers, so, that will, that we call it as a ring residue, and that will add another 10 nanometers; and then this double bond is a attached to this ring outside, from outside, so, it is an exocyclic double bond. If you add up all these things, so, there are no other contributions, so, if you add up all these things, it works out to 242 nanometers.

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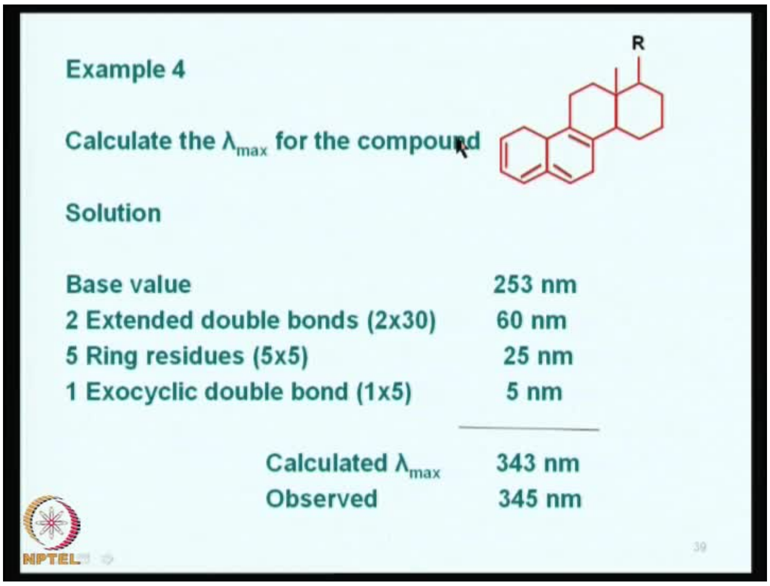

Example 4

Calculate the λ_{max} for the compound

Solution

Base value	253 nm
2 Extended double bonds (2x30)	60 nm
5 Ring residues (5x5)	25 nm
1 Exocyclic double bond (1x5)	5 nm
Calculated λ_{max}	343 nm
Observed	345 nm

If you take the spectrum, once again, in solution, what is observed value? It is 242 nanometers. See how closely these things show the labiality, which can be attributed directly to the observed and calculated value; it is a beautiful system basically, you would really enjoy working with the some more examples, and see the correlation between the structure and the lambda max.

Now, take this example, lambda max for the, for this compound. Now, we can see that there are 4 compounds, 4 rings, 1234, and there are 4 double bonds in this compound, and 2 of them are in the same ring- this one and this one- so, it is a homoannular diene; and this ring and this ring is extended the double bond; and then there is another extended double bonds here. So let us calculate; base values is 253; 2 extended double bonds- 60 nanometers; 3 ring residues, 5 ring residue is 25 nanometers; 1 exocyclic double bond is 5 nanometers; and calculated value is343 and observed value is 345. Again a very close matching has been observed in this system.

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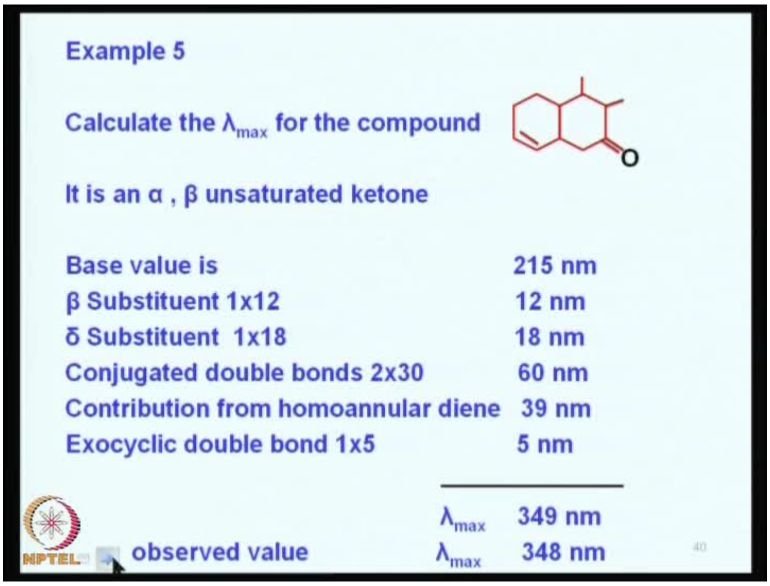

Example 5

Calculate the λ_{max} for the compound

It is an α , β unsaturated ketone

Base value is	215 nm
β Substituent 1x12	12 nm
δ Substituent 1x18	18 nm
Conjugated double bonds 2x30	60 nm
Contribution from homoannular diene	39 nm
Exocyclic double bond 1x5	5 nm
λ_{max}	349 nm
observed value λ_{max}	348 nm

So, let us take one more example. This is a Ketonic system, and there is one double bond- it is an alpha beta saturated ketone. Base value is 215; beta substituent is 12; there is 1 delta substituent, that is 18; conjugated double bonds, there are 2, so, it is 60 nanometers; contribution from homoannular diene is 39; exocyclic double bond is 1 is to 5, one into 5, so, 349, and the observed value is 348 nanometers.

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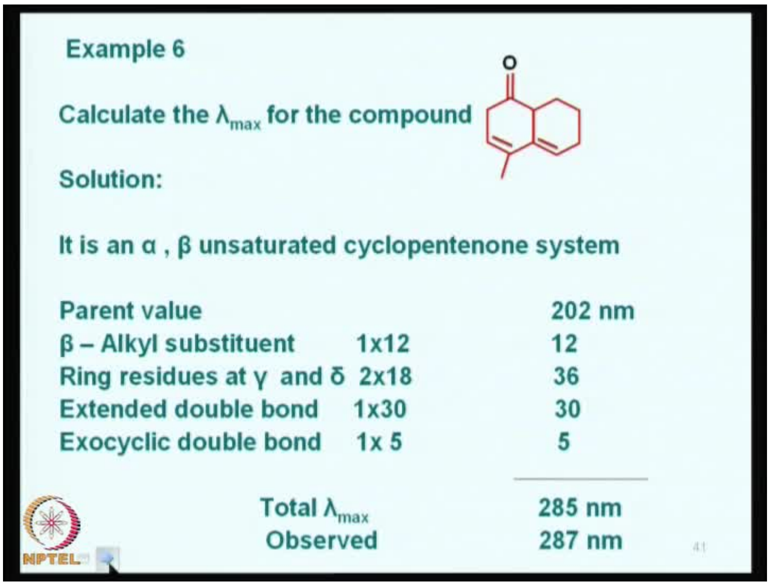

Example 6

Calculate the λ_{max} for the compound

Solution:

It is an α , β unsaturated cyclopentenone system

Parent value		202 nm
β – Alkyl substituent	1x12	12
Ring residues at γ and δ	2x18	36
Extended double bond	1x30	30
Exocyclic double bond	1x 5	5
Total λ_{max}		285 nm
Observed		287 nm

Now, you calculate the lambda max for this compound- it is cyclopentenone system, alpha beta unsaturated cyclopentenone. And here the parent value is 202; and beta substituent- these things you can work out yourself- ring residues at gamma and delta there are 36; extended double bond is 30; 1 exocyclic double bond is 5; so 285 is total value whereas observed value is 287.

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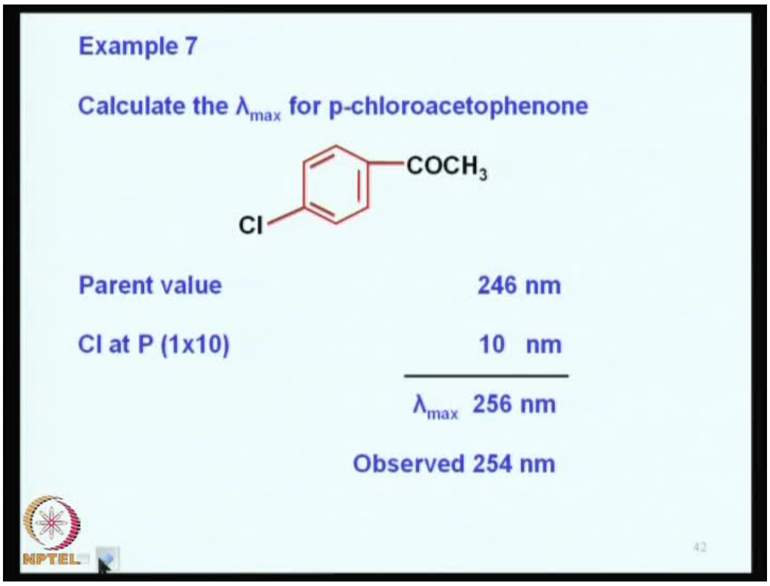

Example 7

Calculate the λ_{max} for p-chloroacetophenone

Parent value	246 nm
Cl at P (1x10)	10 nm
λ_{max}	256 nm

Observed 254 nm

This para chloroacetophenone is my next example, which I have chosen for you. And here you can see this is an aromatic ring now, it is not a diene system or triene system; because it is an aromatic ring, there is acetophenone group here and there is one chloro group here.

Now the parent value for an aromatic system is 246; there is one chlorine atom at the para position, that is 123, it is a six member ring, opposite side is para, and next 2 adjacent sides are ortho, and these two sides, other 2 are meta; ortho ortho meta para, again meta ortho and para, like this. So, the expected value is 256 and observed value is 254 nanometers; very good correlation.

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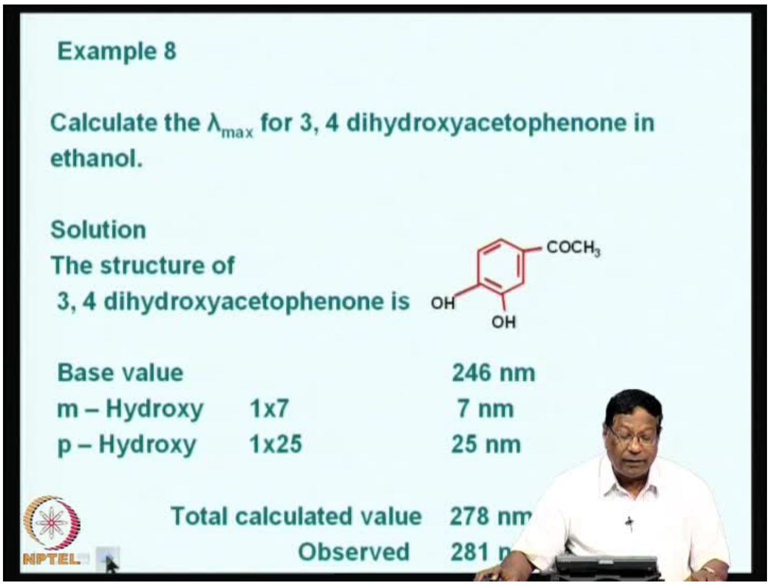

Example 8

Calculate the λ_{max} for 3, 4 dihydroxyacetophenone in ethanol.

Solution

The structure of 3, 4 dihydroxyacetophenone is

Base value		246 nm
m – Hydroxy	1x7	7 nm
p – Hydroxy	1x25	25 nm
	Total calculated value	278 nm
	Observed	281 n

Now, we will take another example, that is- 3, 4 dihydroxyacetophenone; benzene ring, this is actopheone group, 3, 4, dihydroxyl; there are two hydroxyl groups, one two three and four, so, it is a 3, 4 dihydroxyl, 2 hydroxyl groups attached to that. The base value is 246, there 2 4 means 1 2 the meta value; a hydroxyl group at the meta position, this adds only 7 nanometers, because it does not to exactly get involved into the labialization of the electron, non-bondingelectrons present on oxygen to shift it to longer value because of this (( )) hindrance; but para hydroxyl adds quite a lot, that is, 1 into 25 nanometers, so, that is 25; so, total calculated value is 278 and observed value is 281. Again, that is a very close matching between these things.

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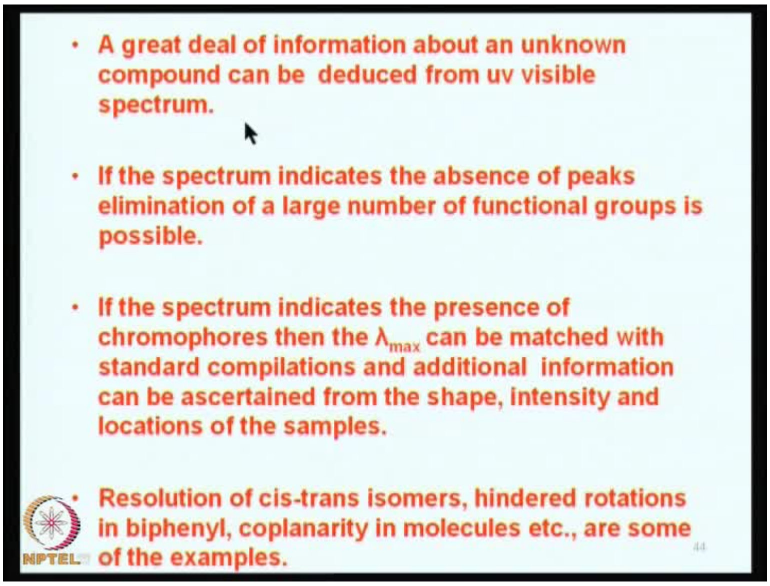

- A great deal of information about an unknown compound can be deduced from uv visible spectrum.
- If the spectrum indicates the absence of peaks elimination of a large number of functional groups is possible.
- If the spectrum indicates the presence of chromophores then the λ_{max} can be matched with standard compilations and additional information can be ascertained from the shape, intensity and locations of the samples.
- Resolution of cis-trans isomers, hindered rotations in biphenyl, coplanarity in molecules etc., are some of the examples.

So, like this a great number of information, a great deal of information about an unknown compound can be deduced from UV visible spectrum. For example, you can see that, if you do not get any spectrum, any peaks in the ultra violet region, then you can safely conclude, that it could be a hydrocarbon, and then it does not have any functional groups such as, methyl group, alcoholic group, hydroxyl group, NH2 groups, and several other functional groups, you can straight away eliminate.

And if this spectrum actually indicates the absence of peaks, elimination of a large number of functional groups is possible. This is very simple to understand- if there is a peak, there is a chromophore; and then if there is a chromophore, then there has to be a peak. If the compound is saturated without any substituent, basically, it means that there are no substituents, and no substituent means no peaks; if there is a substituent you will get a peak.

If the substituent, to get a peak the substituent should be a chromophore, and suppose the chromophore alone is not there, for example, no chromophore that means no UV spectrum, it could be a transparent solution or substance, which can be used as a solvent for other substances, because this does not so any peak; so, whatever peaks you can determine for a unknown compound would correspondent only to that.

So, a substance which does not so any peak in UV region or visible region, again, it means that they can be used as solvents; now, if the substance, indicates the presence of the chromophore, then we can match the lambda max with the standard compilations, and additional information can be ascertained from the shape, of the above, shape of the peaks, intensity and location. For example, I have showed you the peak of benzene; if it is in vapour form, you would see, you remember that you have seen it as sharp peaks.

So, any substance which shows very sharp peak could be in the form of a vapour. Suppose it show very broad peaks, then it is a solvent, the spectrum has been taken from the solvent; so, the intensity.

Suppose the substance, it gives a, molar absorptivity is very high, you will get a very sharp peak and very tall peak with large, with large peak area; that means there is a good chromophore, which can be a characteristic of the substance, and then location of the peaks, that is also very important. Suppose we have a cis-and-trans isomer, then it is possible to determine which is cis and which is trans only by the use of ultra violet and visible spectrophotometry.

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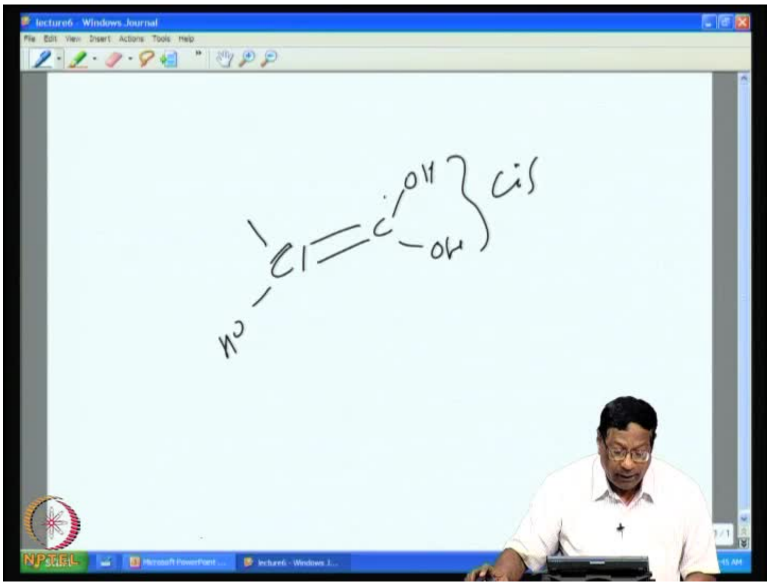

Now, the hindered rotations in by phenyl group… Now, this figure, suppose there is a group here and another group here- it is known as trans; and a group on the same side, these two are cis. So, the substituents, you can always check whether it is cis are trans by the positions of the peaks; hindered rotation, coplanarity in molecules etcetera, all this things carry information about such things, can be obtained by some of the techniques using UV spectrum. Now, it is time for us to look at inorganic compounds. Now, we know that all organic compounds show some absorbance or the other in the UV region, it may be near the end point or it may not be near the end point, near the end exception.

Now, what about inorganic compounds? The inorganic compounds by themselves are not really colored, so, you would know several organic inorganic compounds which are colored, for example, potassium permanganate, it is violet in color; if you take a small quantity of potassium permanganate, when you buy from a shop, and just put it in water it will show violet colored solution, and it is a permanganate ion that is responsible for the color. Similarly, you have dichromate- potassium dichromate- that is a yellow colored solution.

Copper salts, in generals they are all blue colored, and if you dissolve it in water, it will give a blue colored solution. Cobalt, nickel, some of these things are colored solution, but several elements and metals salts are all color less. Now, what happens to the determination of such compound? Do they show an ultra violet and visible spectrum or not, is the question. The answer is, they do show, provided you convert them into a colored substance by a chemical reaction.

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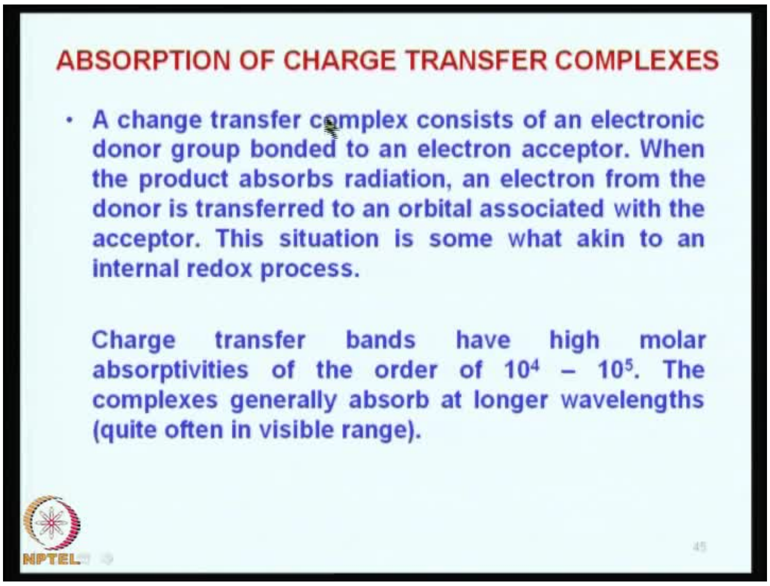

ABSORPTION OF CHARGE TRANSFER COMPLEXES

- A change transfer complex consists of an electronic donor group bonded to an electron acceptor. When the product absorbs radiation, an electron from the donor is transferred to an orbital associated with the acceptor. This situation is some what akin to an internal redox process.

  Charge transfer bands have high molar absorptivities of the order of $10^4 - 10^5$. The complexes generally absorb at longer wavelengths (quite often in visible range).

So, the colored compounds, in general, of the inorganic substances consist of a charge transfer complex of an electronic donor group bonded to an electron acceptor, that is one has to be a donor and one has to be an elector, an acceptor.

Now, when the product absorbs radiation, an electron from the donor is transferred to the orbital of the acceptor. Now, that is a, this is somewhat akin to charge transfer, so, this situation is somewhat akin to an internal redox process.

So, charge transfer bands have high molar absorptivity of the order of 10 raised to 4 to 10 raised to 5.

Now, you would remember that molar absorptivity is of 10 raised to 4 to 10 raised to 5 range are basically very strong absorption bands; so, it is possible to determine the substances in very lower and small quantities. The complexes generally absorb at longer wavelengths, that means they are all in the visible range

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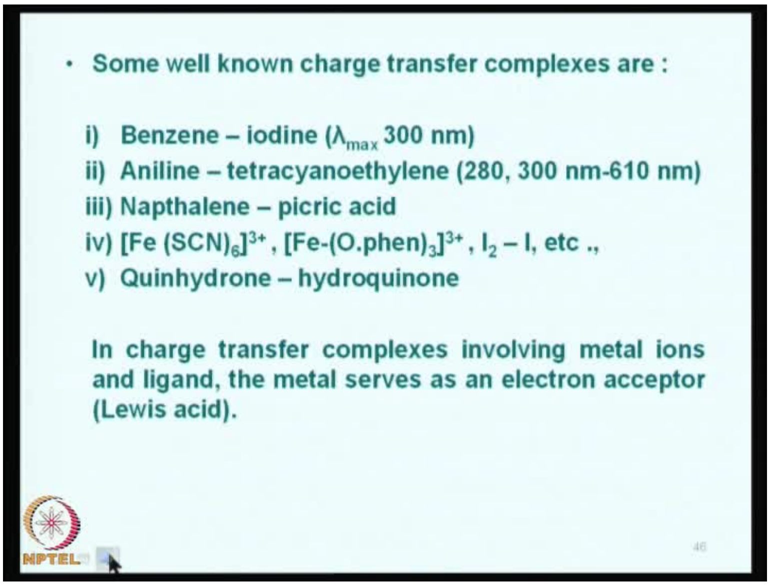

- Some well known charge transfer complexes are :

i) Benzene – iodine (λ_{max} 300 nm)
ii) Aniline – tetracyanoethylene (280, 300 nm-610 nm)
iii) Napthalene – picric acid
iv) [Fe (SCN)$_6$]$^{3+}$, [Fe-(O.phen)$_3$]$^{3+}$, $I_2 - I$, etc .,
v) Quinhydrone – hydroquinone

In charge transfer complexes involving metal ions and ligand, the metal serves as an electron acceptor (Lewis acid).

Now, some of well known charge transfer complexes are like: benzene and iodine, just take little quantity of iodine into, put it into benzene, it will be brown colored; so this brown colored solution is basically a charge transfer complexes, and it shows the lambda max of the part 300 nanometers.

And aniline tetracyanoethylene is another charge transfer complex which shows lambda max at 280,300,610 nanometers

Naphthalene picric acid is another one. Ferric thiocyanate and ferrous ortho phenanthroline system; -and iodine two iodide- iodine iodide system; quinhydrone hydroquinone system- these are all basically charge transfer complexes.

The first two examples, the first three example are organic charge transfer complexes that means, there is no reaction as such in between, between these two substances, that is benzene iodine, there is no reaction, but it does show a color compound because of the charge transfer effects; and whenever charge transfer effects involve metal ions, like this ion, and then a dichromate, permanganate etcetera (( )) containing thiocyanate, ortho phenanthroline, iodine etcetera., iodide, these things will show in general lambda max in the visible region, and some of them do serves as an electron acceptor, that means it is a lewis acid- That lewis acid in one which accepts electrons.

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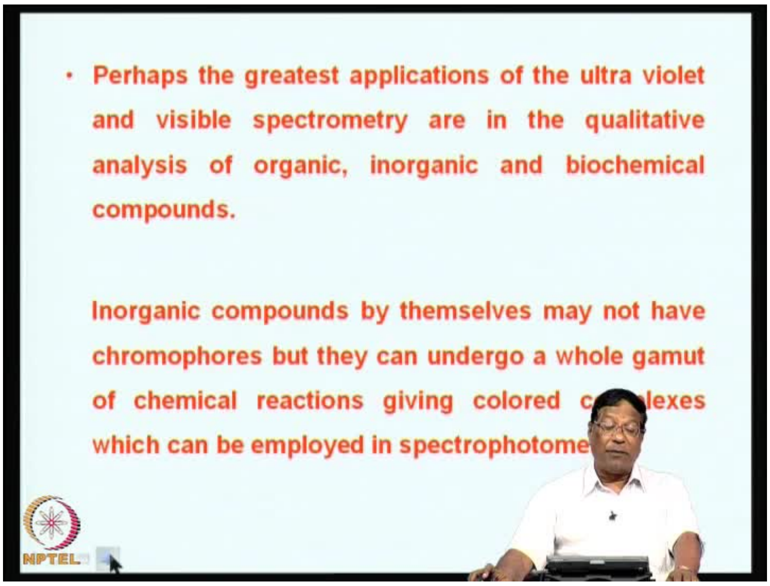

- Perhaps the greatest applications of the ultra violet and visible spectrometry are in the qualitative analysis of organic, inorganic and biochemical compounds.

Inorganic compounds by themselves may not have chromophores but they can undergo a whole gamut of chemical reactions giving colored c lexes which can be employed in spectrophotome

Perhaps, the greatest applications of the ultra violet and visible spectrometry are in the qualitative analysis, quantitative analysis of organic, inorganic and biochemical compounds. You would appreciate that actually there are, more than 30 million spectrophotometric analysis are being performed every day, all over the world, for the determination of organic compounds, inorganic compounds and bio chemical compounds.

Organic compound, you can understand that the most of them are in the, are containing only carbon, hydrogen and some functional groups. Inorganic compounds- they represent all most all the elements of the periodic table, what we come across in our day today application except radioactive elements. And biochemical- blood, urine, plasma and semen, hair and body parts, and such biochemical compounds are also amenable to spectrophotometry by ultra violet and visible spectrophotometry.

But as I told you, inorganic compounds by themselves may not have chromophore, but they can undergo a whole gamut of chemical reactions- hundreds of thousands chemical reactions- which they, by which they end up giving colored complexes; and once you get a colored complex, you can be sure that an ultra violet and visible spectrophotometric procedure is possible for the determination of the colored compound, whether it is, whether you relate it to the colored compound as such or species, original species, it is up to you.

And in general, the determinations do not, do not specify which one is which, but you can always correlate it to the original parent compound, in which you are, compound or an element in which you are interested

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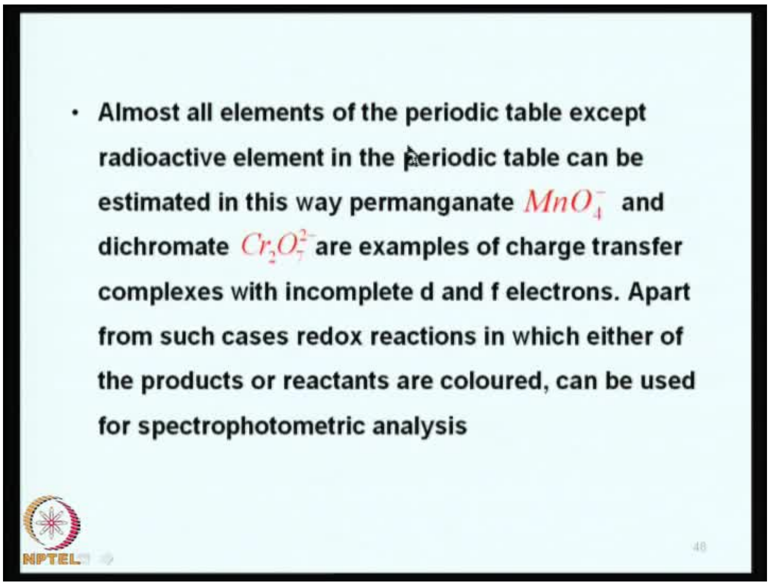

- **Almost all elements of the periodic table except radioactive element in the periodic table can be estimated in this way permanganate MnO_4^- and dichromate $Cr_2O_7^{2-}$ are examples of charge transfer complexes with incomplete d and f electrons. Apart from such cases redox reactions in which either of the products or reactants are coloured, can be used for spectrophotometric analysis**

So, almost all elements… so, what is our conclusion? Almost all elements of the periodic table except radioactive elements in the periodic table can be estimated in this way; permanganate and dichromate are the examples of charge transfer complexes with incomplete d and f orbit, so, the charge transfer can take place between the incomplete d and f orbitals and deligants.

Apart from such cases, redox reactions in which either of the products… redox reaction means, one is the oxidation another is reduction; so, if the compound could be, if a compound is oxidizing, it may be colored, and the oxidizing compound reduces the color in another substance, because these redox reaction do not occur singly, if one compound has to be oxidized, a reducing compound has to be there, so, they are always in pairs. That is why we call them redox reactions.

So, in redox reaction in which the product could be colored or the reactants are colored. Suppose the products are colored and reactants are not colored, then products can be estimated and reactants can be estimated; or reactants are colored and products are not colored, that is also another possibility; so such reaction can also be used for spectrophotometric analysis.

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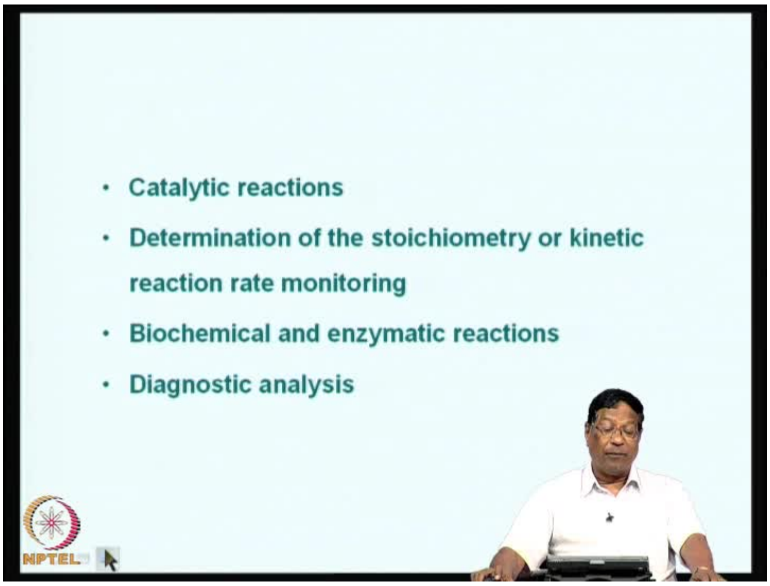

- Catalytic reactions
- Determination of the stoichiometry or kinetic reaction rate monitoring
- Biochemical and enzymatic reactions
- Diagnostic analysis

Now, what are the types of reaction that, things we can do, reactions? One is catalytic reactions; you need a very small quantity of catalysis to continue the reaction. So, what happens, catalytic reactions can be monitored by ultra violet and the visible spectrophotometry.

And then you can do the determination of the stoichiometry; suppose you want to know what is the ratio of the metal to the legend in a came compound, so, that you can do, determine by the spectrophotometric; or we can do the kinetic reaction rate monitoring, this is also very nice, easy to determine, because as, if the product are colored, as the reaction rate increases, the product color will increase, and you can monitor the color of the substance.

Similarly, biochemical and enzymatic reactions, these can be monitored, provided one of the reactants or product has to be colored, that we should not forget, that is basically, fundamental requirement; especially in visible region it has to be colored, one of the seven colors of the rainbow, yellow, red or green, blue, and orange, purple, and all those things.

Then we can do the diagnostic analysis such as, blood analysis, urine analysis, and etcetera.

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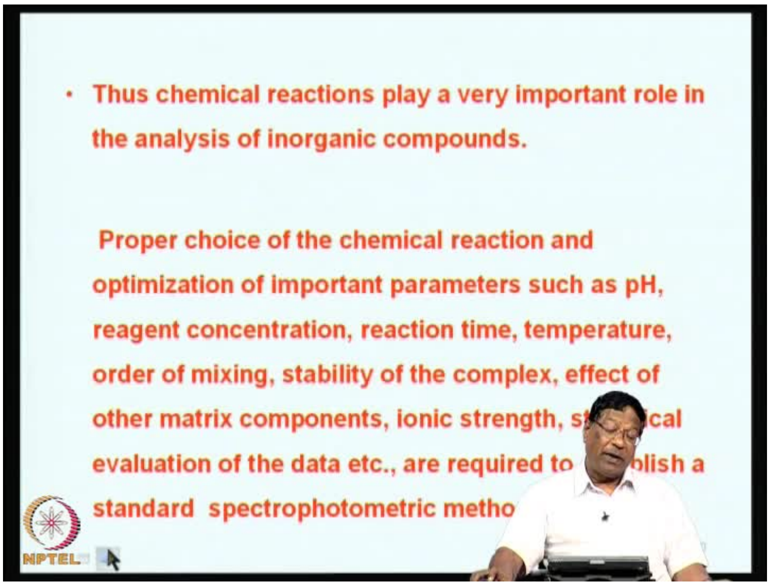

- Thus chemical reactions play a very important role in the analysis of inorganic compounds.

Proper choice of the chemical reaction and optimization of important parameters such as pH, reagent concentration, reaction time, temperature, order of mixing, stability of the complex, effect of other matrix components, ionic strength, st cal evaluation of the data etc., are required to blish a standard spectrophotometric metho

That also…all in all we can determine the compounds, inorganic, organic compounds in several systems, and the chemical reactions play a very important role in the analysis of inorganic compounds.

What you should be doing basically is, you have to have a proper choice of the chemical reaction, and optimization of the important parameters to carry out the chemical reaction. What are the parameters? One is pH another is reagent concentration, reaction time, temperatures, order of mixing, stability of the complex, effect of other matrix components, ionic strength, statistical evaluation of the data etcetera., you have to look at all this things if you want do standardize a spectrophotometric method; that is you as well spectrophotometric method.

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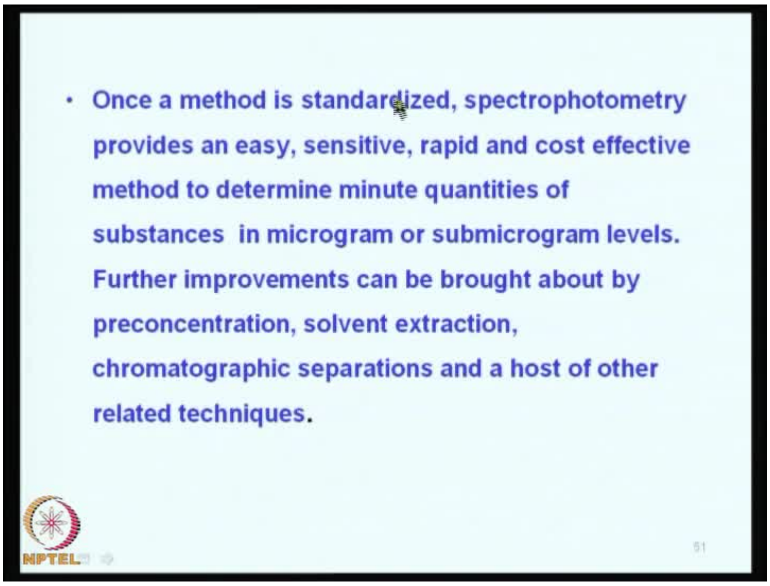

- Once a method is standardized, spectrophotometry provides an easy, sensitive, rapid and cost effective method to determine minute quantities of substances in microgram or submicrogram levels. Further improvements can be brought about by preconcentration, solvent extraction, chromatographic separations and a host of other related techniques.

So, once a method is standardized, spectrophotometry provides an easy, sensitive, rapid and cost effective method to determine minute quantities of substances in either in microgram level or in submicrogram level, and sometimes nanogram levels also- it very important. And then you can, some of the compounds which are not so colored, for example, copper salts, naturally colored, but their concentrations you can determine nearly in the milligram quantities; they are also important in the day to day chemical analysis, but they provide a very easy method.

So, the further improvements and sensitivity also can be brought about, that is, molar extension coefficient can be further improved by preconcentration techniques, solvent extraction, chromatographic separations and a host of other related techniques.

Why do you need to do preconcentration? Very important; but the requirement would there, if you were to determine gold in an ore for the example, the presence of gold would be of the order of about 1 or 2 micrograms per gram; so, if you want do determine gold, it is essential to separate all other compounds except gold and try to concentrate gold in a small solution or in a button, (( )) button, and that is where the preconcentration techniques comes.

Sometimes you may not, there may be too many other things in a given system, for example, if you want to determine gold again, in sea water, so, you would appreciate the sea water composition is a very complex one, and it contains 3.5 percent of sodium chloride; now, gold would be in nanograms or picogram level, and if you want to determine picogram level in presence of percentage levels, you can image how much effect they could have, and solvent extraction of gold would help in separating it from all other substances.

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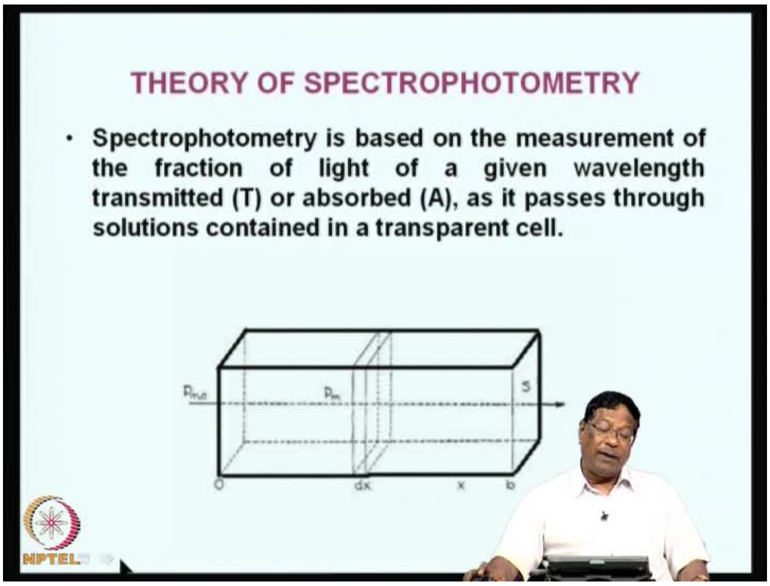

THEORY OF SPECTROPHOTOMETRY

- Spectrophotometry is based on the measurement of the fraction of light of a given wavelength transmitted (T) or absorbed (A), as it passes through solutions contained in a transparent cell.

Similarly, separations can be achieved from chromatographic separations, and a host of other related techniques would help in sorting out the chemical analysis. Now this brings us to the end of the discussion, that is, the theoretical discussions about the spectrophotometry, but now let us looks at the practice of spectrophotometry and the theory of spectrophotometry.

What you, what we are trying to do is, to arrive at a relationship between the absorbance, that is, transmittance of a given sample, and how it is related to the radiation. Now, that is what we are to essentially discussing now. For example, spectrophotometry is based on the measurement of the fraction of light of a given wavelength transmitted or absorbed, as it passes through solutions contained in a transparent cell. Imagine this is a transparent cell, radiation is coming through this, and then this will contain your solution, and then it passes out; so, in the process, this solution would absorb parts of the radiation, and then it will, what is not absorbed is sent out.

So, your initial radiation, that is p 0, and transmitted radiation, p, can be correlated by the quantity of this substance that is present in this box, and since the box is having exact dimensions, the path length can be very accurately measured and the concentration can be determined; and the determination can be quantified using all these techniques, and there could be, they can be correlated using the, by using simple mathematical operations which is a known as beer lumbert’s law, and that derivation and other related aspects we will see in the next class.