Atomic and Molecular Absorption Spectrometry for Pollution Monitoring

Dr. J R Mudakavi
Department of Chemical Engineering
Indian Institute of Science, Bangalore

Lecture – 09
MO theory

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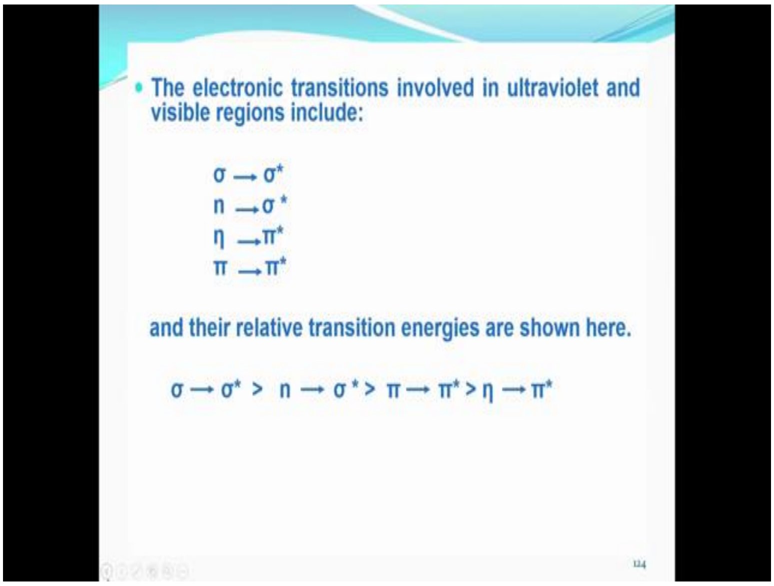

- The electronic transitions involved in ultraviolet and visible regions include:

$\sigma \rightarrow \sigma^*$
$n \rightarrow \sigma^*$
$\eta \rightarrow \pi^*$
$\pi \rightarrow \pi^*$

and their relative transition energies are shown here.

$\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > \eta \rightarrow \pi^*$

Greetings to you, after we have discussed about the various electronic transition, we will continue our discussion on the prediction of the molecular absorption peak. Here we had stopped in the last class that is I had told you that the electronic transitions are of four types and these include sigma to sigma star n to sigma star n to pi star and pi to pi star transitions.

Basically you can imagine this in terms of organic compounds where you have a sigma single bond double bond and elements functional group with nonbonding electrons that is spare electrons and. So, sigma to sigma star transition essentially implies that it is a saturated compound there are no unsaturation no pi bonds and nothing like that and then n to sigma star is a transition of electrons from functional group containing oxygen nitrogen phosphorous etcetera these are nonbonded electrons present on single atoms if you look at electronic structure of ammonia or something like that you will recur immediately recognize that there are 2 nonbonding electrons on nitrogen same thing is with true is with same thing is true with oxygen which has 2 pair of lone pair, 2 pair of lone pair electrons.

Similarly with sulphur etcetera and those are the nonbonding electron and corresponding transition can take place only from n to sigma star. So, the nonbonding electron are designated as n and then their compounds where there are double bonds that is where pi bond is involved we expect pi to pi star and n to pi star transitions. So, transition from pi to pi star would be of higher energy then n to pi star because they are bonded pi to pi star transition the electrons involved are bonded whereas, n to pi star transition are not involved in bonding. So, their relative transition energy also we had discussed in last class that sigma to sigma star should be require very high energy n to sigma star should have slightly lesser energy, but this will have higher energy this requires higher energy in terms of electro calories kilo calories or electron volt from then pi to pi star and pi to pi star transition would be requiring higher energy than n to pi star.

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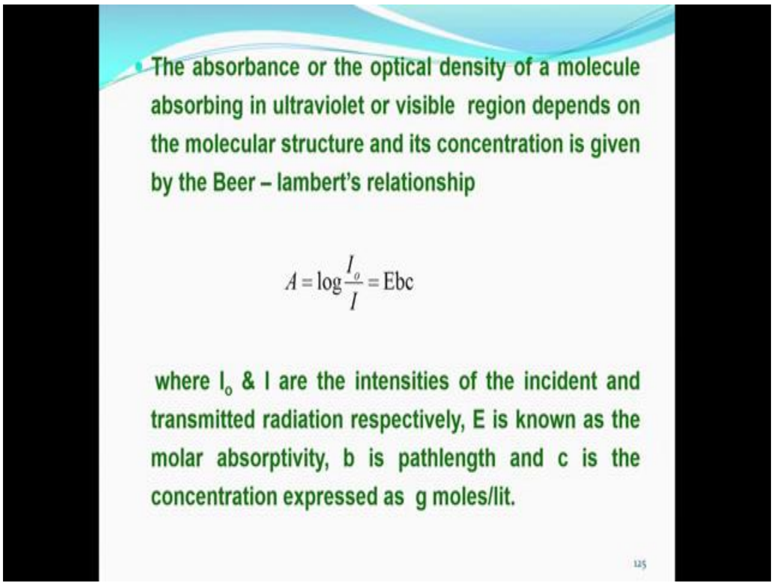

- The absorbance or the optical density of a molecule absorbing in ultraviolet or visible region depends on the molecular structure and its concentration is given by the Beer – lambert's relationship

$$A = \log\frac{I_o}{I} = \text{Ebc}$$

where I_o & I are the intensities of the incident and transmitted radiation respectively, E is known as the molar absorptivity, b is pathlength and c is the concentration expressed as g moles/lit.

So, these are the different kinds of transitions we expect. So, the absorbance or the optical energy optical density of a molecule absorbing in ultraviolet or visible region depends on molecular structure just I was explaining to you sigma to sigma star pi to pi star these are all molecular structures basically representing different bonds sigma bond pi bond nonbonded electrons etcetera. So, it is obvious that absorbance or the optical density of molecule depends on molecular structure for example, a saturated compound cannot show you pi to pi star transition and a compound which do not have lone pair of electrons cannot give you a n to pi star transition or n to sigma star transition it is very simple you understand.

But the whole absorption process depends upon Beer Lambert’s law which states that absorbance A equal to logarithm of I 0 by I that is also represented as epsilon bc Ebc where here you should recognize I 0 and I are the intensities of the incident and transmitted radiation and e is known as molar absorptivity b is the path length and c is the concentration expressed as gram moles per liter we will come back to this again during the during our discussion in this course, but for time being we will do later we will do the derivation of this, but for time being what I want you to understand is the absorbance or the optical density of a molecule depends upon the initial intensity and final intensity that is a substance has to pass through assuming you have a substance captured in space volume like this and then a radiation is coming and passing through the absorbing molecule and what comes out that is represented by I 0 initial and I is the final.

So, part of it is getting absorbed by the molecule and that ratio logarithmic ratio of that of the intensities of the incident and transmitted light is given by epsilon that is molar absorptivity that is dependent on the molecular structure path length that is size of absorbance size of the molecule that is path length and c is the concentration if concentration is more the absorbance will be more.

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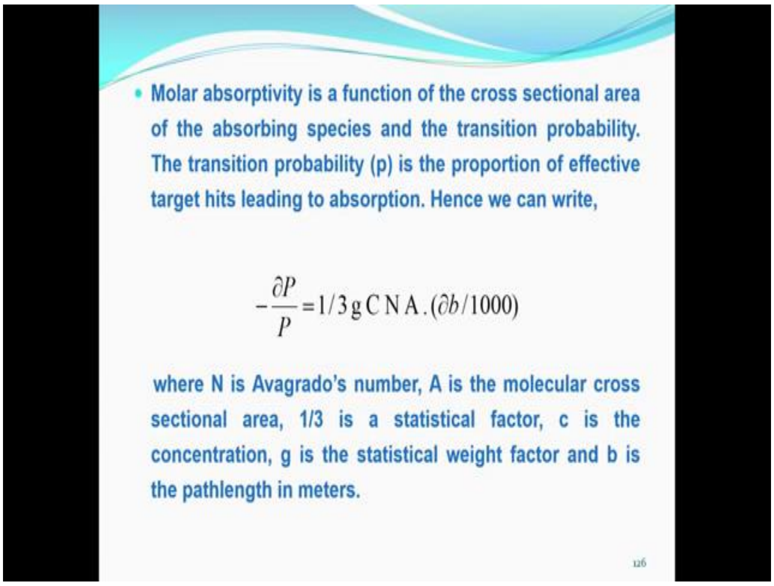

- Molar absorptivity is a function of the cross sectional area of the absorbing species and the transition probability. The transition probability (p) is the proportion of effective target hits leading to absorption. Hence we can write,

$$-\frac{\partial P}{P} = 1/3\, g\, C\, N\, A\, .(\partial b/1000)$$

where N is Avagrado’s number, A is the molecular cross sectional area, 1/3 is a statistical factor, c is the concentration, g is the statistical weight factor and b is the pathlength in meters.

So, we will come back to this derivation of this later, but for time being what I want you to concentrate is how it is related to the structure of a molecule basically molar absorptivity is a functional of the size of the molecule if the size is bigger absorbance will be higher.

So, it depends upon the cross section of the molecule that is number one number 2 again it depends on the transition probability what are possible transitions expected from a given molecule suppose it is a saturated molecule we can easily expect that it will be it will give you only sigma to sigma star suppose it has got pi bond the unsaturated compound ethylene propylene and. So, many other compounds like that then you can expect sigma to sigma star as well as pi to pi star transition then suppose there are it contains nitrogen or something you would expect sigma to sigma star pi to pi star n to pi star transitions as well as n to sigma star transition.

So, the total structure the actual number of transitions depends upon the probability of the transition that is more number of transitions higher would be the intensity for that the energy of the incoming radiation should coincide quantum mechanically with the energy difference between the 2 excited states those 2 excited states transitions energy is defined is determined by the by the difference between the energy level if the incident radiation is matching with that quantum mechanically energy wise then the transitions will take place. So, it is always the question of probability. So, we have a relationship something like this minus delta P by P is given by one third of g concentration and then n is the number of molecules a is the molecular cross section area and b is path length delta b and that is converted into meters or something.

So, here the decrease in the intensity minus delta P by P represents the corresponding decrease in the intensity absorption P here you can here you have to always assume that I am going to use P and I as the incident energy for the throughout our this course and using them interchangeably I 0 I P 0 and P like that. So, here I have written P and it is the probability now. So, minus delta P by P is given by one-third of the one-third of all these expressions one third g C N A delta b by 1,000 where n is Avogadro’s number because we want to express it in terms of molecular weight and is molecular cross section area how big is the molecular size and one third is statistical factor because any molecule if you take it will be having a 3 dimensional structure in space.

So, since our direction of the incident radiation will be only in one direction measurement also will be in one direction we take it as one third probability that is a statistical factor and c is the concentration g is the statistical weight factor which I was explaining to you that it has to match with the probability and b is the path length. So, this expression if you put all these numbers Avogadro’s number you know concentration we can find out for a given molecule g is the probability statistical weight factor b is the path length if we put all this of the at the optimum level.

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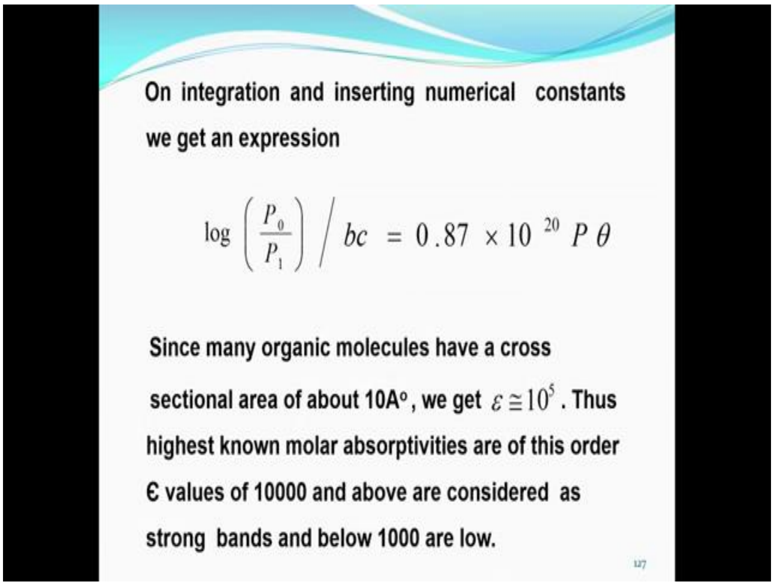

On integration and inserting numerical constants we get an expression

$$\log\left(\frac{P_0}{P_1}\right) \Big/ bc = 0.87 \times 10^{20} P\theta$$

Since many organic molecules have a cross sectional area of about 10A°, we get $\varepsilon \cong 10^5$. Thus highest known molar absorptivities are of this order

Є values of 10000 and above are considered as strong bands and below 1000 are low.

Then what we end up is we then we integrate and insert the numerical constants we will get an expression something like this logarithm of P not by P 1 again these 2 I am interchanging instead of P not by P I have written as P naught by P I have written P naught by P 1 corresponding to a particular output and that I have to after integrating taking out the constants on left side I get bc concerned these 2 are constants which corresponds to 0.87 into 10 raised to 20 and P into theta.

Since many organic molecule have a cross sectional area about 10 angstroms. So, epsilon maximum epsilon that is molar extra absorptivity what we get is approximately 10 raised to 5 this I want you to remember that this is the optimum this maximum concentration which corresponds to the minimum detectable quantity. So, if the absorption coefficient is very high how much you can get maximum 10 raised to 5. So, that determines the minimum detectable quantity in a given spectrophotometer. So, this 10 raised 5 is our limit I have never seen in my career more than 10 raised to 5 at any time it may 5 into 10 raised to 5 10 into 10 raised to 5 like that, but 10 raised to 6, 10 raised to 7 I have not seen, but if it were. So, we would have been able to determine which spectrometry nano gram materials.

Now, this restricts us to parts per million or parts per billion that is microgram and nano gram sub nanogram basically. So, the highest known molar absorptivities are of this order that is 100,000 and above are considered as strong band. So, below 1,000 are low intensity they may either quantum mechanically not observable or it could be very weak band also.

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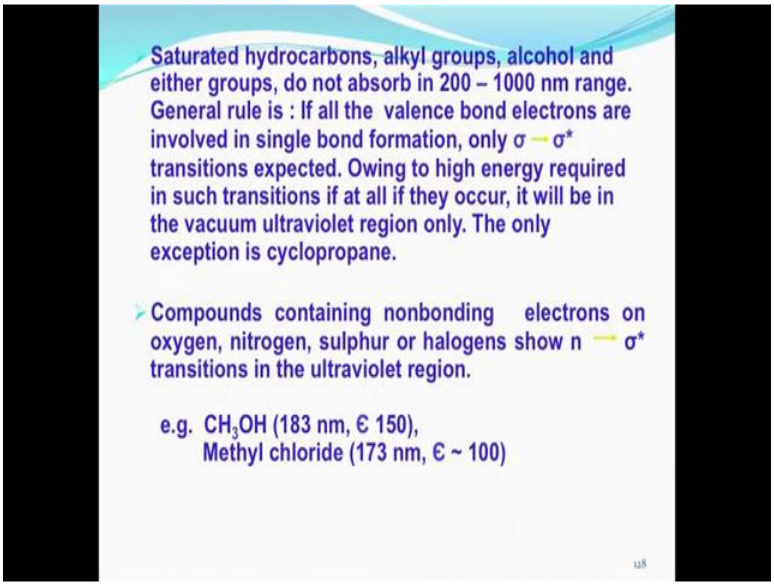

- Saturated hydrocarbons, alkyl groups, alcohol and either groups, do not absorb in 200 – 1000 nm range. General rule is : If all the valence bond electrons are involved in single bond formation, only σ → σ* transitions expected. Owing to high energy required in such transitions if at all if they occur, it will be in the vacuum ultraviolet region only. The only exception is cyclopropane.
- Compounds containing nonbonding electrons on oxygen, nitrogen, sulphur or halogens show n → σ* transitions in the ultraviolet region.

e.g. CH_3OH (183 nm, Є 150),
Methyl chloride (173 nm, Є ~ 100)

So, saturated hydrocarbons alkyl groups alcohols and either groups they do not absorb in 200 to 1000 nanometer range why because there are no pi bonds only sigma bonds. So, all these saturated hydrocarbons alkyl groups alcohols and ether and all these things 200 to 1,000 nanometer range they do not absorb. So, if all the valence bond electrons are involved in single bond transmission transformation single bond formation we have only sigma to sigma star transition expected. So, owing to high energy requirement in such cases if at all if occur it will be in vacuum ultraviolet region only. So, the only exception is cyclopropane which absorbs at 197 nanometer which is in the purview of a spectrophotometer, normal laboratory spectrophotometer, the only thing that can be detected sigma to sigma star transition is cyclopropane.

So, coming to next point the second point on the slide what we see is compounds containing nonbonding electrons on oxygen nitrogen sulphur or halogens show n to sigma star transition in the ultraviolet region why because oxygen nitrogen sulphur and halogen all these have nonbonding electrons now a between n and in this slide you can see between n and sigma star there is arrow at the bottom actually this arrow should be between the 2 due to some technical problem it has moved a little bit same thing has happened between sigma and sigma star also you can see here at the bottom the arrow, but I want you to note it down we will try to correct it if possible, but let me see. So, such compound coming back to this slide such compounds will show CH 3, oh, for example, methyl alcohol it shows a sigma to sigma star transition of one hundred eighty 3 nanometers in a spectrophotometer what is the epsilon value it is 150; that means, you the intensity of the peak is very small. So, when intensity is very small you may see it is a peak or only as small hump in the spectrum.

So, look at the next slide again methyl chloride what is the structure of methyl chloride I can show you this.

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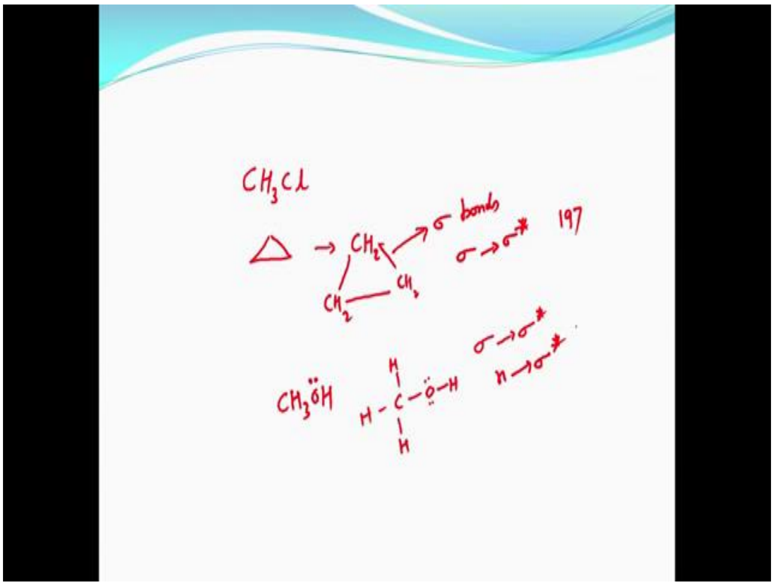

I was the explaining to you the CH 3 CL cyclopropane I had explained to you this is nothing, but CH2, CH2, CH2 and this is CH2 these are the sigma bonds. So, what we expect see only sigma to sigma star transition. So, this is occurs at 197. Similarly in CH3 oh this is what we are discussing now this oxygen has 2 pair of electrons which are not bonded if I had to write the structure of this I would write like this; this is CH3 sorry that is a single bond this H. So, this is CH3 oh there are 2 lone pair electrons here and here I can expect between carbon and hydrogen carbon and hydrogen 3 carbon and hydrogen atoms and between carbon and oxygen, oxygen and hydrogen all these things can give me sigma to sigma star transition that is one set.

Second set is there are 2 lone pair of electrons on oxygen I have written at top and bottom. So, I can write n to sigma star this transition is also expected, but n to pi star no not possible because there is no pi bond in this structure. So, we will go back and then we go back to the slide compound. So, see this is what I was explaining to you methyl chloride and CH3 it will give you 183 nanometer and 173, these are in vacuum ultraviolet region they are not in the normal instruments available in the laboratory and if you look at the epsilon value you will get 150 as one value for CH 3 OH and only 100 as the molar absorptivity I have already explained to you that molar absorptivity of below 1,000 are absolutely useless you may just see a small hump or you may not see anything.

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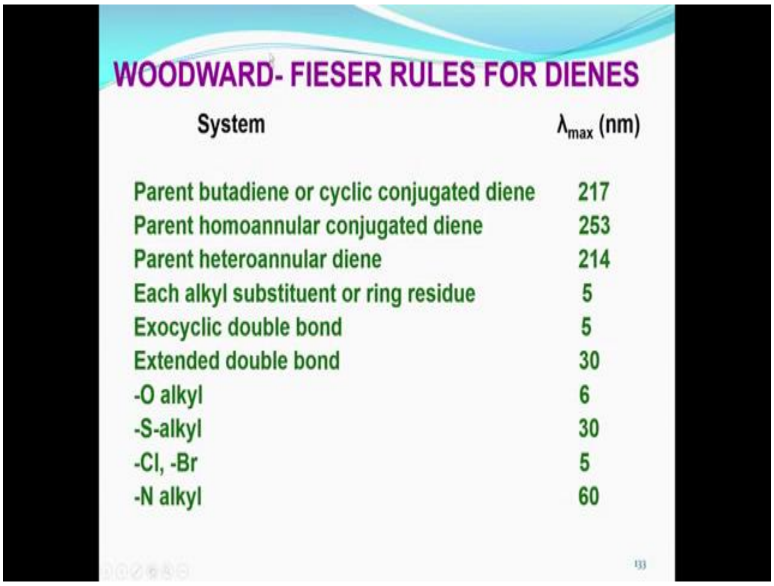

WOODWARD- FIESER RULES FOR DIENES

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	60

Lot of people have studied how to correlate the structure of an organic compound and the expected peak for a given compound UV, visible UV or it may be visible or anything like that and these are available in the form of some empirical rules known as Woodward Fieser rule these rules are mostly applicable for organic compounds, but not please remember because in some of the slides I may show aromatic structure, but aromatic structure is not accounted for in this Woodward Fieser rules. So, they have formulated empirical rules for the substances containing single bond double bond say pi bonds and then nonfunctional functional groups containing oxygen nitrogen etcetera how the actual wavelength where it can be expected.

So, this is for they had examined more than fifty thousand organic compound like this and formulated these rules for this reason they were awarded a noble price. So, in general what it actually represents is a system and you have to determine the structure. So, the if you have a parent butadiene structure that is a CH2 double bond c h c h single bond c h then double bond CH2 something like that will do lot of problem based on this. So, parent butadiene will be have will show a basic peak at 217, now if the diene is a is in a ring separated by a single bond; that means, 2 double bonds separated by a single bond that is known as diene if both such a structure is inside a ring then it known as homoannular diene we will see this structure later, but for the time being I want you to remember these structures So that we can look at it in a different way.

So, parent heteroannular diene one double bond is inside a ring and one double bond is outside a ring and alkyl substitute there are number of organic substance substituents and alkyl substituents are a ring residue will add 5 nanometer to the basic structure and if there is an exocyclic double bond you should remember this and exocyclic double bond is a double bond attached to ring outside; that means, double bond is attached to ring which is double bond should be outside the ring. So, that is one that will that will add any every exocyclic double bond if it there it will add about 5 nanometers to the base value that is 2 1 7 or 2 5 3 or 2 1 4 these are the basic structures.

So, if there is o alkyl substance then it adds 6, every extended double bond that adds 30, nanometers s alkyl is at 30, chloride bromide substituents (Refer Time: 22:26) they will add about 5 and n alkyl will add about 60 slide; 60 nano nanometers to the expected peak position.

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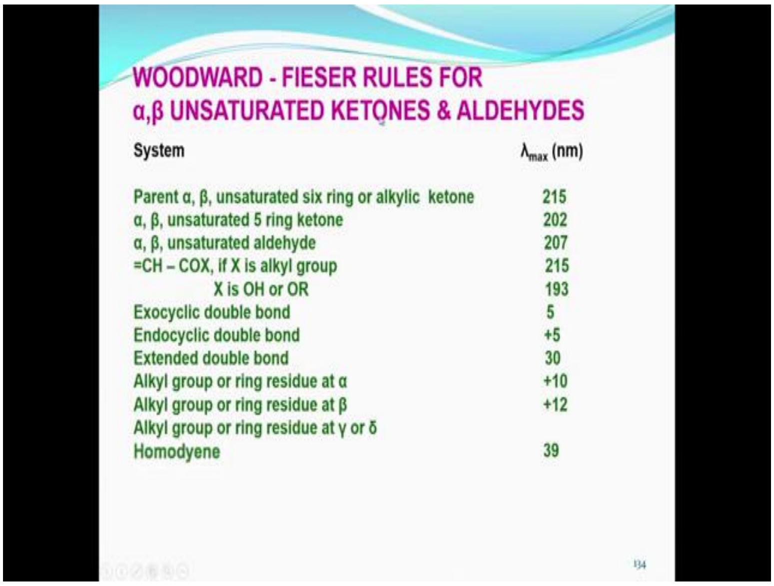

WOODWARD - FIESER RULES FOR α,β UNSATURATED KETONES & ALDEHYDES

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	
Homodyene	39

So, similar structure have been reported for alpha beta unsaturated compounds and which include aldehyde and ketones. So, if you have an alpha beta unsaturated see here six rings or alkylic ketone what do we mean is a double bond separated by as single bond and attached to a double bond. So, double bond single bond double bond single bond like that the structure should be there in that I will try to show you in the next few seconds next few minutes what do structure mean, but the basic structure should have a peak at 215.

Suppose it is a 5 membered ring then the based value will be 202 suppose it is alpha beta unsaturated aldehyde then it is approximately 207 see that how much energy that they have put in the find out the base values that is important. So, if it has got double bond c h and COX where X is an alkyl group or X is oh, group or group then the base values will change accordingly. So, for exocyclic double bond which I have I already explained to you that a double bond attached to a ring is known as exocyclic double bond and that is 5 nanometers it will add endocyclic double bond it will add 5 extended bond is again thirty alkyl group or ring residue at alpha beta positions is the 10 and 12 and if it is a homodyene then it is 39 nanometers homoannular diene; that means, both double bond inside a single ring is known as homodyene.

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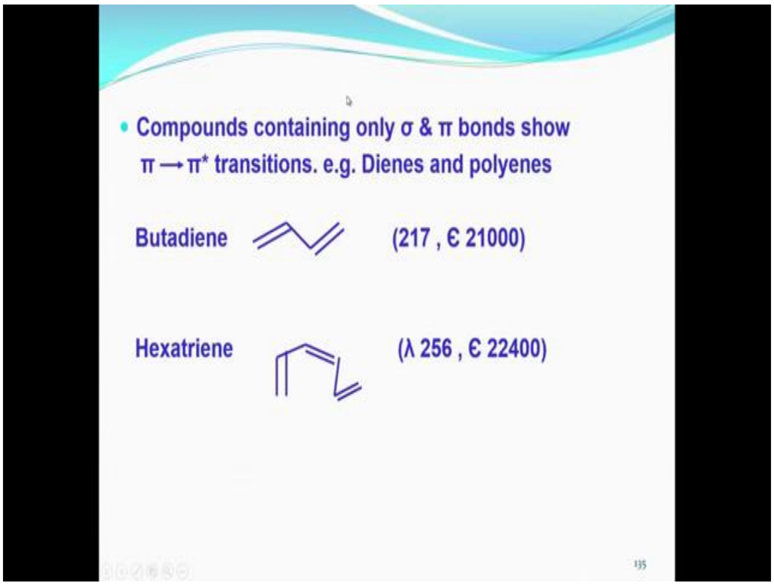

- Compounds containing only σ & π bonds show π → π* transitions. e.g. Dienes and polyenes

Butadiene (217 , Є 21000)

Hexatriene (λ 256 , Є 22400)

So, compounds containing only sigma and pi bonds suppose there are no N electrons no oxygen no sulphur no chlorine no halogens example is butadiene this is conjugated diene which I had explained to you. So, earlier in my previous slide that is butadiene parent butadiene or cyclic conjugated diene. So, this is the structure of the butadiene this represent CH 2 CH, CH 2 CH, CH2, CH 2 CH, CH2, CH2 and this is a hexatriene this is 3 double bond double bond single bond double bond. So, these are examples diene and polyenes they contain only sigma bond and pie bond.

So, the best value base value for this according to Woodward Fieser rule is 217 and epsilon value is 21,000 for the triene, it is 256 nanometers and the epsilon value is 22,400. So, what do we derive what information we derive from this information if we derive that a butadiene will show an absorption peak 217 nanometers and its epsilon value is 21,000; that means, it shows a very sharp peak at 217, similarly hexatriene will show a very sharp peak at the 256 because the molar absorptivity is very high. So, I have put together some more examples for you that we will discuss in next module.

Thank you.