Application of Spectroscopic Methods in Molecular Structure Determination

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Lecture - 33
Ultraviolet Spectroscopy or Electronic Spectroscopy

Hello, welcome to the course on Application of Spectroscopic Methods in Molecular Structure Determination. This is module 33 and we are approaching almost the end of the course with this module. We still have the ultraviolet spectroscopy to cover, which we will deal with in this module and the next module.

Ultraviolet spectroscopy by itself is not an extremely useful tool for structural elucidation of organic compounds, but in combination with infrared spectroscopy and NMR spectroscopy, it serves as additional information for confirming certain functional groups like carbonyl, aromatic and so on. The power of ultraviolet spectroscopy lies in the fact that it can be used in a quantitative fashion. So, estimation purposes the spectrophotometry is widely used technique rather than a spectroscopic method in modern times.

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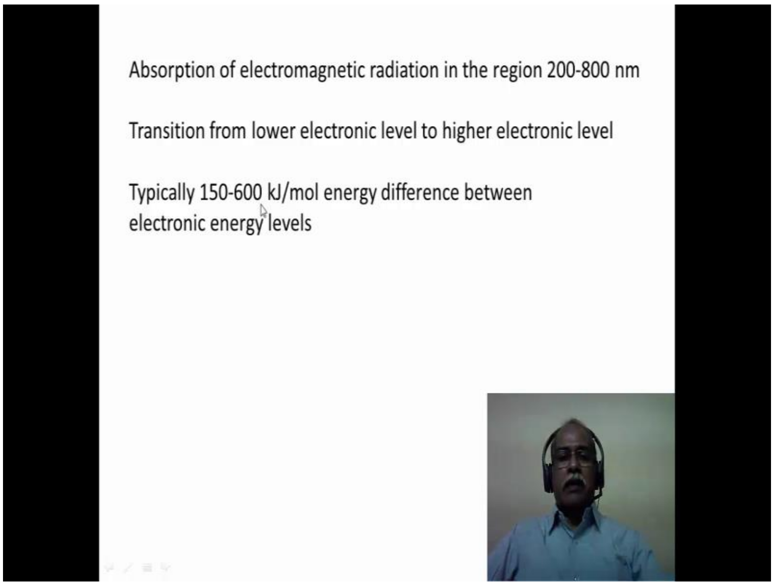

Absorption of electromagnetic radiation in the region 200-800 nm

Transition from lower electronic level to higher electronic level

Typically 150-600 kJ/mol energy difference between electronic energy levels

The ultraviolet region is the region between 200 nanometers to roughly 380 nanometers, above 380 nanometers up to 800 nanometers is the visible region. So, the region between 200 to 800 nanometer is what is used for the ultraviolet visible spectroscopy. The ultraviolet visible spectroscopy is also known as the electronic spectroscopy because we are dealing with transitions from lower electronic level through higher electronic level in the molecule. This region of electromagnetic radiation namely 200 to 800 nanometer roughly corresponds to 152, 600 kilo joules per mole of energy and this essentially is the energy difference between the various electronic levels in a molecule. We will discuss the transition among the various electronic levels in a molecule in the ultraviolet spectroscopy.

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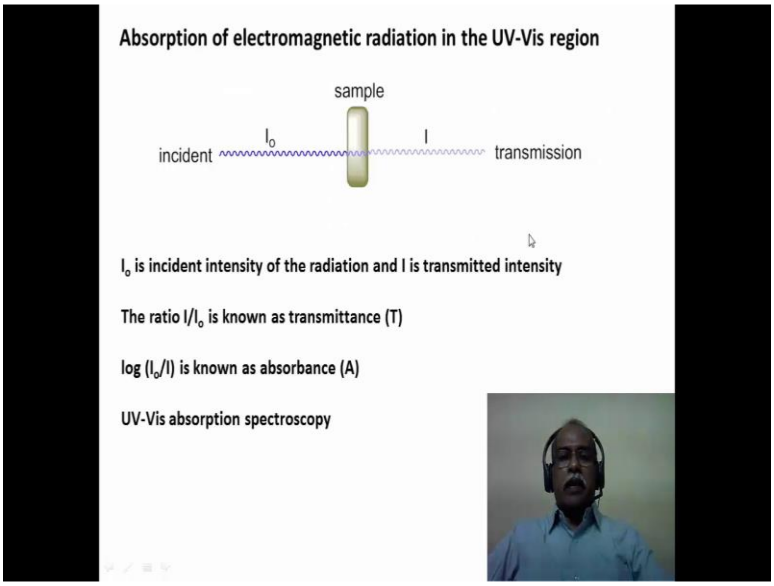

Absorption of electromagnetic radiation in the UV-Vis region

I_o is incident intensity of the radiation and I is transmitted intensity

The ratio I/I_o is known as transmittance (T)

log (I_o/I) is known as absorbance (A)

UV-Vis absorption spectroscopy

Now, this is a diagram that is familiar to you, this has already been dealt with earlier let me recap the facts about this particular diagram. The absorption of electromagnetic radiation in the UV visible region, when you have an electromagnetic radiation of the type ultraviolet and visible, then the incident radiation intensity is I0, it passes through the sample and the sample absorbs certain amount of energy and the residual intensity is transmitted. So, I is the transmitted in (Refer Time: 02:29) which is detected by some kind of a photo multiplier detector in this case.

Now I0 is the incident intensity of the radiation and I is the transmitted intensity of the radiation and the ratio I by I0 is known as the transmittance which represented by the symbol T. Now the logarithmic ratio of the I0 by I is known as the absorbance, indicated by the symbol A, now UV visible spectroscopy is an absorption spectroscopy so one who has to deal with the absorbance in this type of spectroscopic technique.

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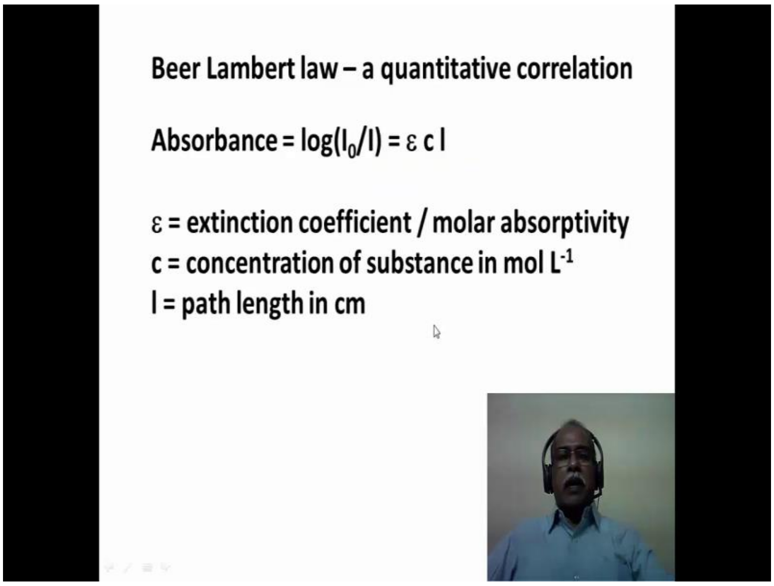

Beer Lambert law – a quantitative correlation

Absorbance = $\log(I_0/I) = \varepsilon c l$

ε = extinction coefficient / molar absorptivity
c = concentration of substance in mol L^{-1}
l = path length in cm

Now, the Beer Lambert law is essentially correlates the absorbance in quantitative terms to the concentration of the substrate that is present in the sample. In other words when the light is passing through the sample, the amount of absorption that takes place of the incident light would depend upon how many molecules it encounters during the path length let us say l in the case. So, the absorbance is directly proportional to the concentration times the path length, longer the path length the more number of molecule the beam of light will encounter and more absorbance will take place.

Now the proportionality constant epsilon is known as the extinction coefficient or the molar absorptivity, c is the concentration of the substance expressed in moles per liter and l is the path length of the cell or the path length of the sample expressed in centimeters. This is an expression that is used for quantification purposes because absorbance is a measurable quantity from the spectroscopy, concentration can be either known or unknown, path length is known. For a pure sample it is fairly easy to determine the epsilon values so if you have a epsilon value and absorbance and the path length, concentration can be determined quite quantitatively using the ultraviolet visible spectroscopy.

In fact, the ultraviolet visible spectroscopy is highly sensitive; sensitive enough to afford detection to the parts per billion kinds of a concentration levels. So, one can see the application of this kind of a spectroscopic method in quantification of organic substances.

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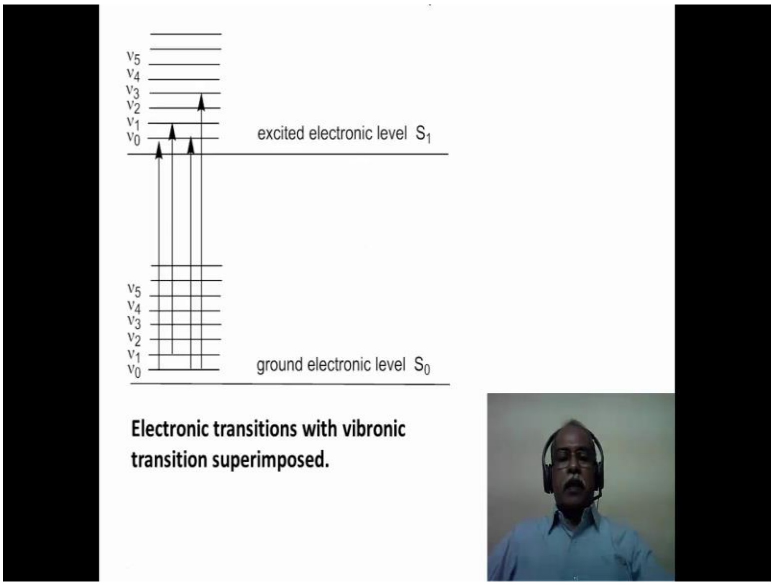

Electronic transitions with vibronic transition superimposed.

Now, the electronic excitation takes place from the ground electronic level to the excited state electronic level both the states are mentioned a singlet state. This would be a 0 level and this is a S1 level, within the electronic level you have various vibrational level starting from vibrational level 0, 1, 2, 3, 4, 5 and so on. So, the electronic transition can be accompanied by superimposition of the vibronic transition as well, in other words if you consider the transition between the 0 vibrational level of the ground state to the 0 vibrational level of the excited state, this would correspond to the S0 transition. On the other hand, if you consider the one arrow that is shown here on the right hand side, this would correspond to the 0 vibrational level of the ground state to the third vibrational level of the excited state so it would correspond to a 0 3 kind of a vibration in the vibronic state of the molecule. So, this is a kind of transitions that occurs in the UV region and one would be dealing with the electronic transition from the ground state electronic levels to the electric excited state electronic level with the accompaniment of the superimposition of the various vibrational levels that are present in each of the electronic levels in a molecule.

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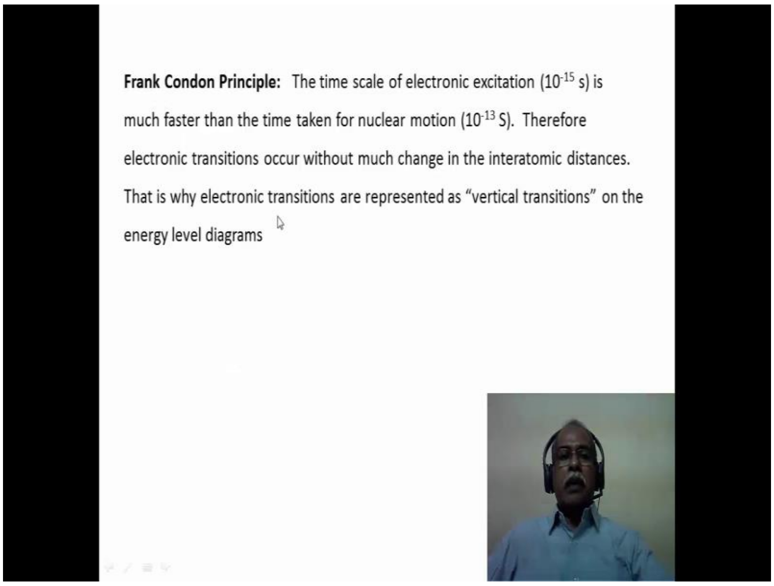

Frank Condon Principle: The time scale of electronic excitation (10^{-15} s) is much faster than the time taken for nuclear motion (10^{-13} S). Therefore electronic transitions occur without much change in the interatomic distances. That is why electronic transitions are represented as "vertical transitions" on the energy level diagrams

Please remember the excitation is the vertical excitation, what is meant by vertical excitation? This is expressed by the Frank Condon Principle, the time scale of electronic excitation is typically of the order of 10 to the power minus 15 seconds, it is a ultra fast process and it is much faster than the time taken for the nuclear motion. In other words for the nuclei to move away from it is equilibrium distance for example, it takes about 10 to the power minus 13 seconds or so. This is about two orders of magnitude faster, the electronic excitation is two orders of magnitude faster than the 100 times faster than the nuclear motion therefore, during an electronic transition there is not much change in the relative positions of the inter atomic distances. That is why electronic transitions are often represented as vertical transitions on the energy level diagram, in other words while going from this state to this particular state, the nucleus essentially states put in the same position there is no vibration that is taking place or there is no motion of the nucleus that is taking place from it is equilibrium position and this is what is known as the Frank Condon Principle.

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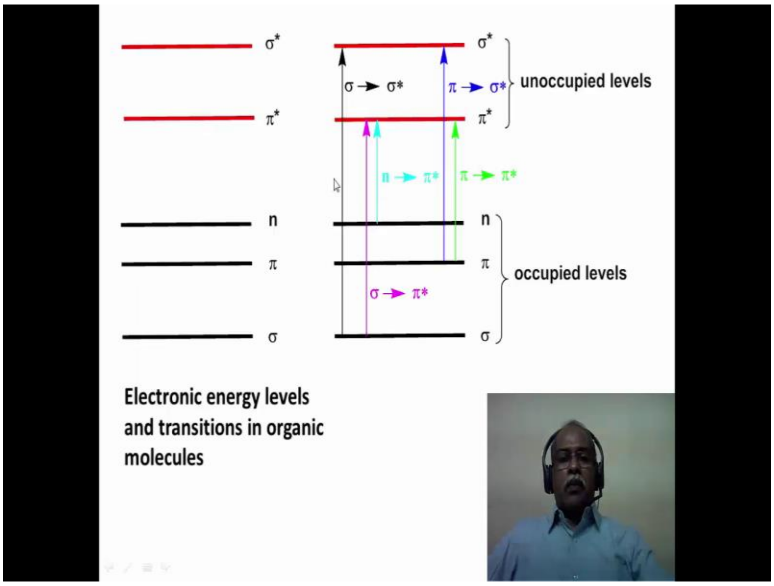

Electronic energy levels and transitions in organic molecules

Now, these are the common energy levels associated with organic molecule. Organic molecules invariably have sigma bonds so we will have sigma electrons, unsaturated compounds will have pi electrons also and compounds with heteroatoms like nitrogen, oxygen, sulphur and so on. In addition to pi electrons and sigma electron, they can also have the non bonded electron then you will have the corresponding pi star molecular orbital and the sigma star molecular orbital.

The possible transitions states are shown here, one can have the highest energy transition which will be from the sigma till sigma star transition this will be of course, a dissociated process because when the electron is pushed from the sigma orbital to a sigma star orbital, the bond order of the sigma bond essentially becomes 0; that would correspond to a dissociation state of the molecule.

Alternatively, the sigma electron can be excited to the pi star level and the pi to pi star level excitation is possible and finally, the n to pi star level excitation is also possible. The sigma, pi and the n are the occupied molecular orbitals, where as the pi start and the sigma stars are unoccupied molecular orbital in the ground state electronic configuration of the molecule. So, in the excited state electronic configuration, when the excitation takes place the molecule attains a different electronic configuration, if there are two sigma electrons present originally here, the sigma to sigma star will essentially put one electron in the sigma star level so that will be a electronic isomer of the ground state molecule, the excited state molecules are generally electronic isomers of the ground state molecule.

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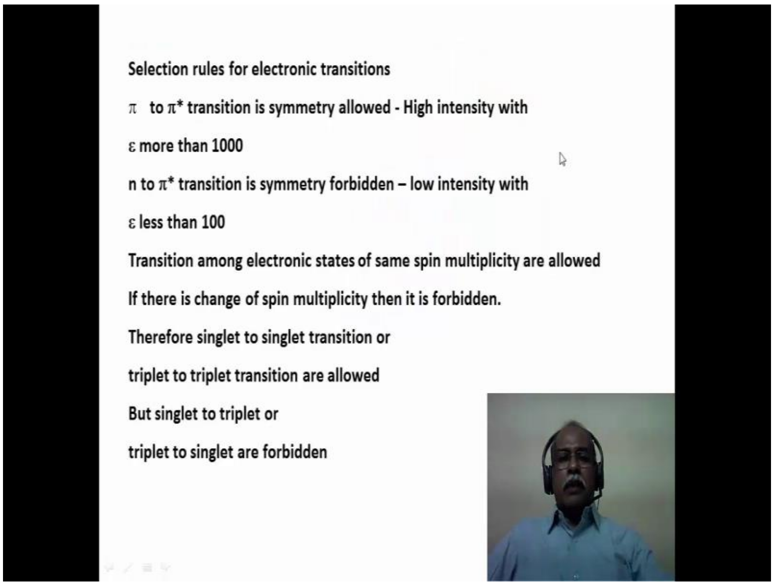

Selection rules for electronic transitions

π to π^* transition is symmetry allowed - High intensity with

ε more than 1000

n to π^* transition is symmetry forbidden – low intensity with

ε less than 100

Transition among electronic states of same spin multiplicity are allowed

If there is change of spin multiplicity then it is forbidden.

Therefore singlet to singlet transition or

triplet to triplet transition are allowed

But singlet to triplet or

triplet to singlet are forbidden

There are selection rules that needs to be followed for the electronic transition for example, the pi to pi star transition is a symmetry allowed process. What is meant by symmetry allowed? Is that it as very high intensity of the order of epsilon more than 1000, 1000 is the bear minimum it can go upto 10 to the power 4 or 10 to the power 5 epsilon depending upon the transition coefficient of that particular electronic transition. On the other hand, the n to pi star transition is a symmetry forbidden transition therefore it is of usually low intensity with epsilon value less than 100 or so. Transition among the electronic states of the same spin multiplicity are allowed, whereas if the spin multiplicity changes during the transition then it is forbidden this is exemplified by the fact that this singlet to singlet, in other words the singlet ground state to a singlet excited state translation or a triplet ground state to the triplet excited state transition are allowed.

Most organic molecules are singlet state in the ground state so singlet transition is possible or allowed whereas the singlet to triplet transition is a forbidden process. So, these are the selection rules that one is to keep in mind while dealing with electronic transition in the eve visible spectroscopy.

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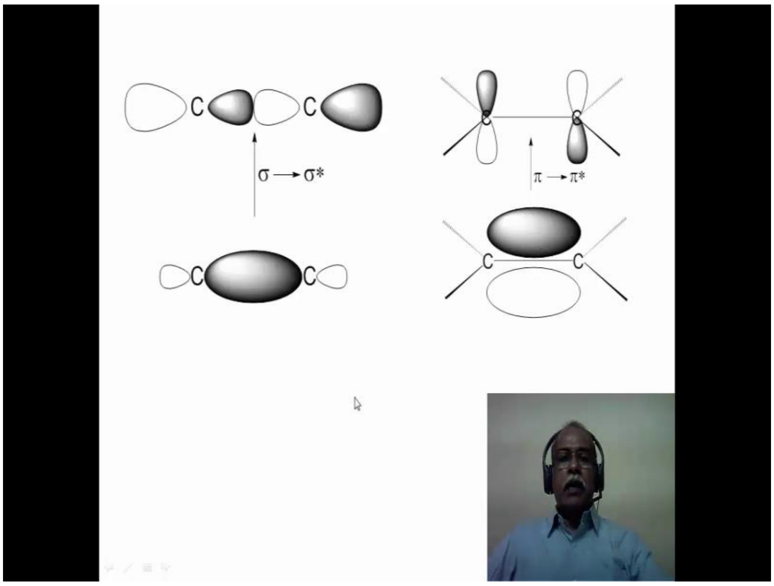

Diagrammatically or pictorially one can represent the sigma to sigma star transition by taking the picture of the sigma orbital and then doing an electronic excitation which corresponds to the sigma to sigma star. Let us take the example of methane as a molecule, methane has carbon hydrogen bond and all of them are sigma electrons only there are pi electrons or lone pair of electrons in methane. So, if one excites the methane in the appropriate wavelength, it will correspond to the sigma to sigma star excitation of the c h bond or if you take ethane for example, one can do the c c sigma bond excitation also.

Now this excitation typically take place in the vacuum ultraviolet region, in the range of about 150 to 160 nanometers range which is not easily accessible because air absorbs in this region, that is why one needs to do the sigma to sigma star transitions which are typically very high energy transitions in the vacuum ultraviolet region. Now, the pi to pi star transitions are relatively speaking lesser in energy as you can see from the diagram.

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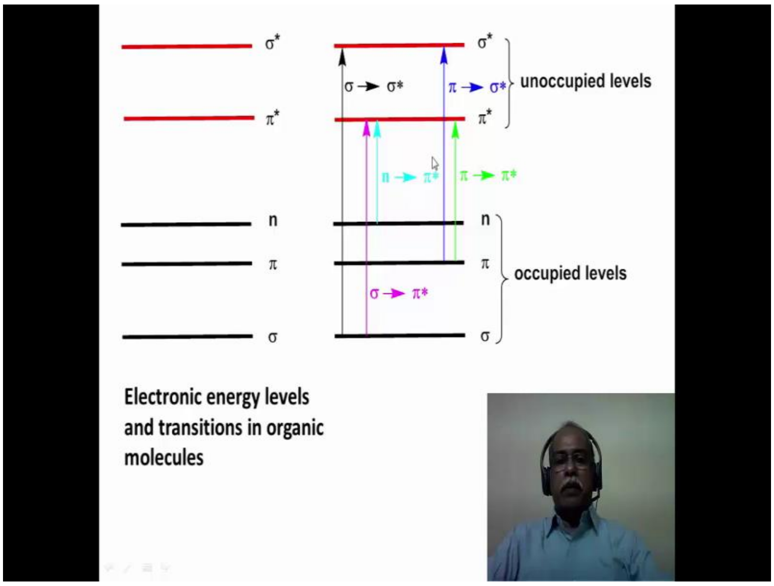

Electronic energy levels and transitions in organic molecules

This is the sigma to sigma star is the highest energy transition, then comes the sigma to pi star transition, then come to pi to pi star transition and n to pi star transition. In other words the order of energy is sigma to sigma star, sigma to pi star and then to pi to sigma star, pi to pi star and n to pi star is the order of decreasing order of the energy of this transition. So, the pi to pi star transition typically occurs in a non conjugated olefins like ethylene for example, somewhere around 180 or 190 nanometers, whereas with conjugation this can get to longer wavelength region which we will say at a later stage. So, this is the pi molecular orbital with no notes present in the system and when it undergoes excitation from pi to pi star, the pi star molecular orbital is represented like this with a single node which will be at the center of the carbon carbon bond. In other words node is point where there is change in the algebraic sign of the molecular orbital going from the slope to the slope for example, if this is a positive loop and this would be a negative loop in terms of the algebraic sign of the coefficient of the molecular orbital in these cases.

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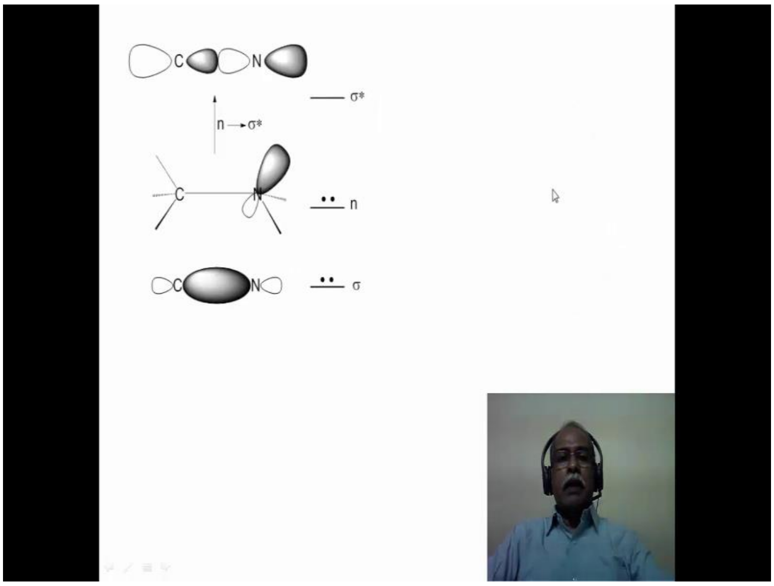

This is a diagrammatic representation of the n to sigma star transition, this is the c n bond which is a sigma bond with 2 electron, the nitrogen also has a lone pair of electron which is represented by that level which is the non bonded level. In other words, the lone pair of electron, the non bonded electrons and this can be excited to the sigma star level. Typically, in the case of primary amiens, which are saturated amiens or ethers, which are saturated ethers, the lone pair of electrons from the heteroatom can be pushed into the sigma star orbital and this would correspond to the n to sigma star transition of the electronic transition of the molecule.

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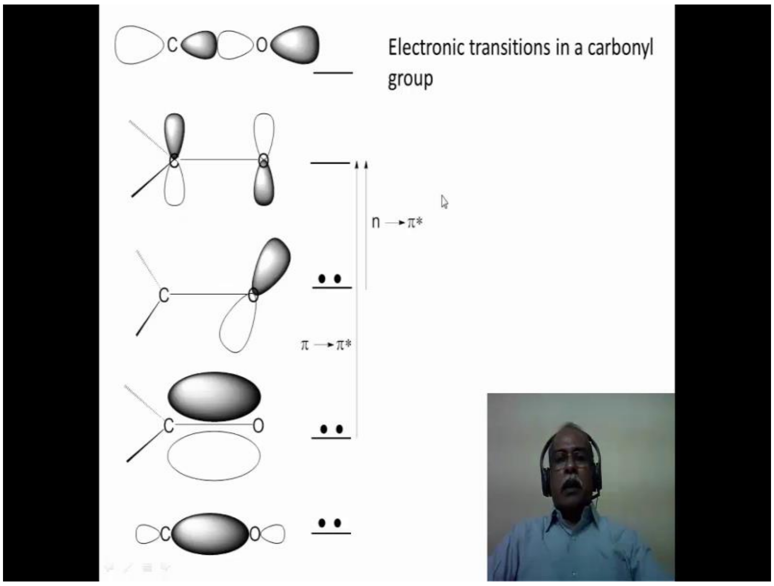
Electronic transitions in a carbonyl group

Now, the electronic transition of a carbonyl group is represented here there are two types of electronic transition that are possible in a carbonyl functional group. We have a c double bond o and the c double bond o has a pi electrons and the oxygen also has lone pair of electron. So, it is possible to have a pi to pi star transition as well as n to pi star transition in the case of carbonyl functional group. The pi to pi star transition is an allowed transition whereas the n to pi star transition is a disallowed or a forbidden transition for example. This is diagrammatically represented the transitions are diagrammatically represented here this would be the sigma of the carbon oxygen bond, single bond and this would be the pi molecular orbital of the carbon oxygen bond and this would be the lone pair of electron on the oxygen one of the lone pairs of electrons on the oxygen which corresponds to p y in this particular case and this will be the pi star molecular orbital of the carbonyl functional group and finally, the sigma star molecular orbital of the carbon oxygen single bond in this particular case.

Now, the transition is from this level which is the pi level to the pi star level which is denoted by the arrow which is shown here the pi to pi star level compared to the n to pi star level is a higher energy transition and hence it occurs at lower wavelength. The n to pi star occurs usually at a longer wavelength, the pi to pi star typically comes in the region of about 200 nanometers or so, whereas the n to pi star appears around 300 nanometers or so in the electronic absorption spectrum or the U V visible spectrum of a carbonyl compound.

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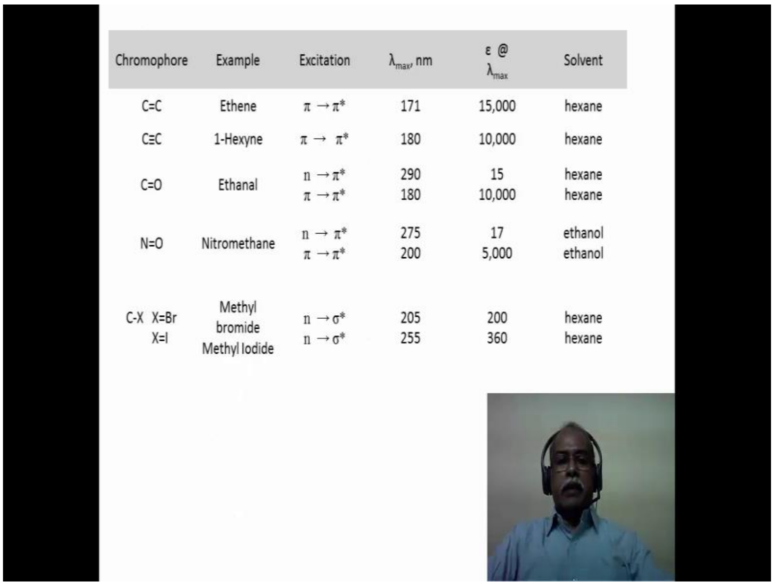

Chromophore	Example	Excitation	λ_{max}, nm	ε @ λ_{max}	Solvent
C=C	Ethene	$\pi \rightarrow \pi^*$	171	15,000	hexane
C≡C	1-Hexyne	$\pi \rightarrow \pi^*$	180	10,000	hexane
C=O	Ethanal	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	290 180	15 10,000	hexane hexane
N=O	Nitromethane	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	275 200	17 5,000	ethanol ethanol
C-X X=Br X=I	Methyl bromide Methyl Iodide	$n \rightarrow \sigma^*$ $n \rightarrow \sigma^*$	205 255	200 360	hexane hexane

Conjugation has it is own effect in this kind of transitions which will see little later. Now, this table essentially lists some of the chromophores. We will see, what is the definition of chromophore in a while. The carbon carbon double bond essentially has a pi to pi star transition which occurs around 171 nanometer, it is an allowed transition that is why the epsilon at the lambda max is very high it is about 10 to the power 15 times, 10 to the power 3 or so measured in hexane as a solvent. Similarly one hexane as an example as a c, triple bond c which also is possible to have the pi pi star transition corresponding to 180 nanometers of 10000 intensity in terms of the epsilon value.

The carbonyl of acetaldehyde which is ethanol for example, has the pi to pi star transition as well as the n to pi star transition. The pi to pi star transition occurs at a higher energy 180 nanometers, whereas the n to pi star transition occurs at a lower energy around 290 nanometers or so. The n to pi star being a forbidden transition has a very low extinction coefficient, the pi to pi star being an allowed transition has 10 to the power 4 extinction coefficient. All the spectra up to now is measured in hexane, nitromethane for example, has n double bond o. So, it is a pi to pi star transition possible for the n double bond o, it also has a lone pair of electron on the oxygen. So, it is possible to excite the lone pair of electrons from the oxygen to the pi star level. The pi to pi star transition occurs at 200 nanometers, whereas the n to pi star transition occurs at 275 nanometers.

In the case of methyl bromide and methyl iodide, you have only lone pair of electrons on the heteroatom namely the bromine and iodine. So, it is possible to have only a n to sigma star which are dissociative state because when the nitrogen lone pair sorry when the lone pair from the bromide or the iodide reaches the sigma star molecular orbital, the bond order of the sigma 1 decreases and their corresponds to a dissociative state. You can see here the effect of halogen from going from bromine to iodine, there is an increase in the wavelength of the system indicating that the methyl iodide is much more easy to excite to the dissociative state compared to the methyl bromide in this particular case.

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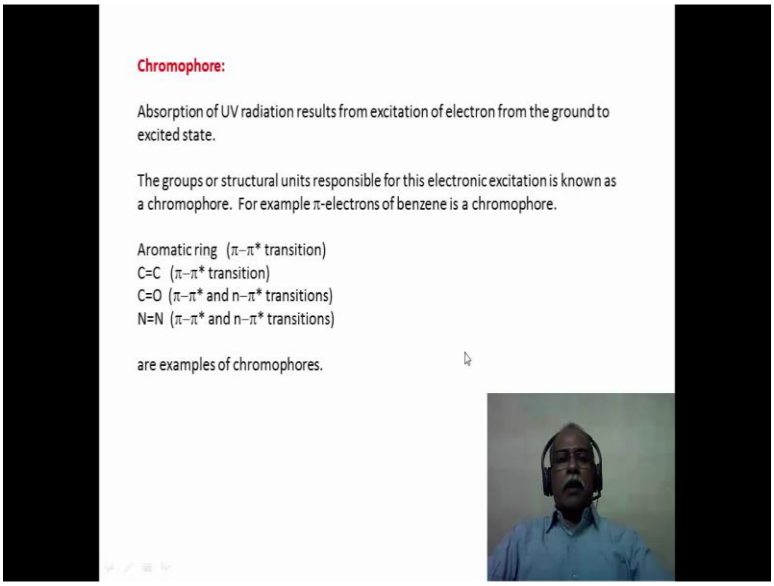

Chromophore:

Absorption of UV radiation results from excitation of electron from the ground to excited state.

The groups or structural units responsible for this electronic excitation is known as a chromophore. For example π-electrons of benzene is a chromophore.

Aromatic ring (π–π* transition)
C=C (π–π* transition)
C=O (π–π* and n–π* transitions)
N=N (π–π* and n–π* transitions)

are examples of chromophores.

Now, let us go into certain definitions that are used in the ultraviolet visible spectroscopy. Absorption results from the excitation from the ground state to the excited state, there are certain groups and structural units which are responsible for the electronic excitation. For example, all these groups which are responsible for the electronic excitation are called the chromophore. If you take benzene, benzene has a lot of pi electrons and this pi electrons are the one that is responsible for the electronic transition. The pi electrons are benzene is a chromophore by themselves, so the aromatic ring has pi to pi star transition, we will see details of this little later, c double bond c c double bond o n double bond n so on. They all have certain electronic transition so they are called the chromophores of that particular molecule.

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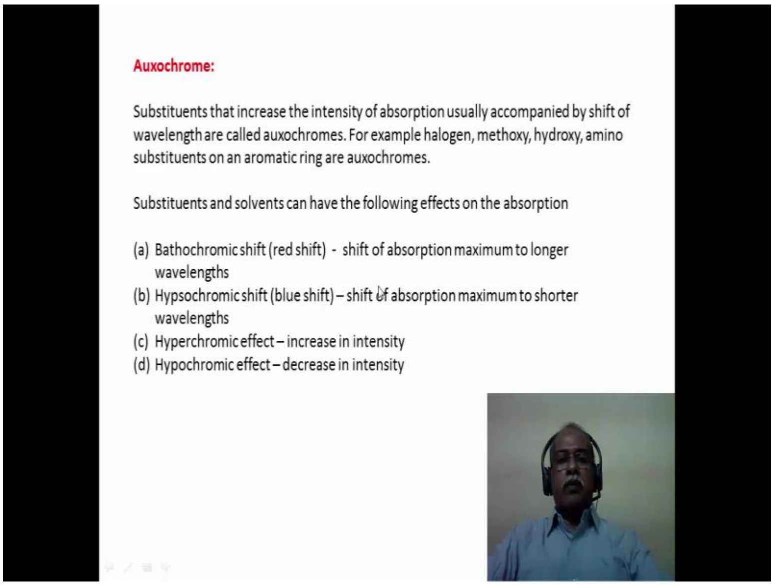

Auxochrome:

Substituents that increase the intensity of absorption usually accompanied by shift of wavelength are called auxochromes. For example halogen, methoxy, hydroxy, amino substituents on an aromatic ring are auxochromes.

Substituents and solvents can have the following effects on the absorption

(a) Bathochromic shift (red shift) - shift of absorption maximum to longer wavelengths
(b) Hypsochromic shift (blue shift) – shift of absorption maximum to shorter wavelengths
(c) Hyperchromic effect – increase in intensity
(d) Hypochromic effect – decrease in intensity

In addition to chromophores there are substituents which enhance or shift the wavelength which are called auxochrome. For example, halogen substitution, methoxy substitution or hydroxy substitution, amino substitution, nitro functional group substitution can be present in aromatic ring and these are all called auxochromes of the chromophore. In other words chromophore undergoes the transition from one state to another electronic state, the auxochrome essentially shifts the wavelength of the transitions by altering the energy levels thereby increasing or decreasing the wavelength of transition of the electronic transition that we deal with.

Substituents and solvents can also have the following effect on the absorption. So, in addition to auxochrome one can have for example, substituents which are present in the molecule which are the auxochromes can have the effect of shifting the wavelength to higher or lower wavelength. Similarly the solvents can also play a role because solvation essentially increases or decreases the energy levels and there by alters the wavelength of radiation by shifting the wavelength to higher or lower wavelength, these are some definitions that one has to bear in mind.

Bathochromic shift means shift of absorption maximum from two longer wavelength, from lower wavelength to higher wavelength is what is known has the bathochromic shift. In other words this is known as red shift because we are going from the blue region to the red region when you shift from two smaller wavelength to longer wavelength. Hypsochromic shift is also known as blue shift, this is absorption maximum shift at to shorter wavelength exactly opposite of the bathochromic shift.

Hyperchromic shift and hypochromic shift has something to do with the intensity and if the intensity increases because of the presence of an auxochrome then the auxochrome is upto have a hyperchromic shift with the increase in the intensity. If the auxochrome causes a diminishing of the intensity then it is called the hypochromic effect, which is the decrease in the intensity. So, in other words here we are dealing with epsilon values whereas the bathochromic shift and the hypsochromic shift we are dealing with lamda max of the transition of the particular transition.

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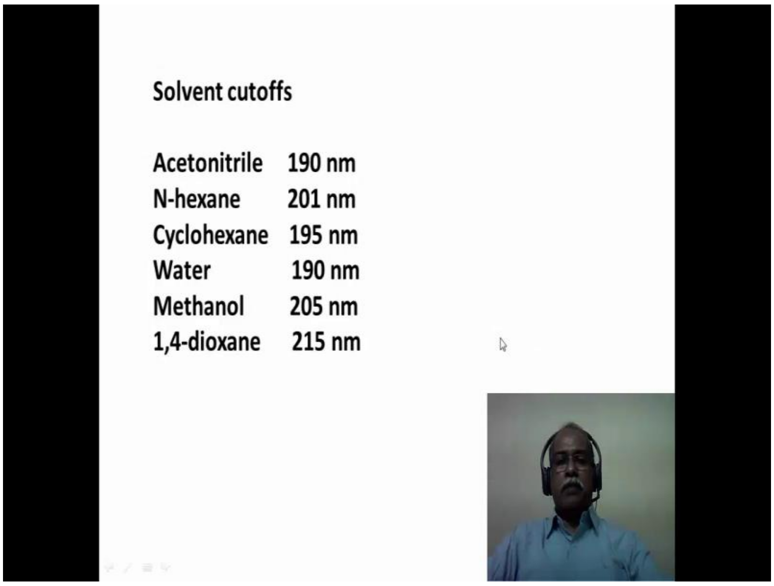

Solvent cutoffs

Acetonitrile	**190 nm**
N-hexane	**201 nm**
Cyclohexane	**195 nm**
Water	**190 nm**
Methanol	**205 nm**
1,4-dioxane	**215 nm**

Ultraviolet spectroscopy can be measured either in the gas phase, in liquid phase or in solution phase. In order to measure this in solution phase, one has to identify suitable solvents making sure the solvent itself does not absorb in the region of interest for the spectroscopy. There are certain solvents which do not have absorption above 200 nanometer or so. For example, acetonitrile is a good solvent; it has a cut off value of 190 nanometers. All the pi pi star and the n pi star excitation of acetonitrile comes much lower than the 190 nanometer.

Water is a good solvent for example, water has the cutoff value of 190 nanometer. Methanol has a cut off of about 205 nanometers so these are supposed to be good solvent, n hexane for example, does not have any pi electrons so it does not undergo any pi pi star transition and that can be used as a solvent in most instances n hexane is or cyclohexane can be used as a solvent because it has only an n pi star at a sorry it has only a sigma to sigma star kind of a transition which occurs in the ultraviolet region of electromagnetic radiation.

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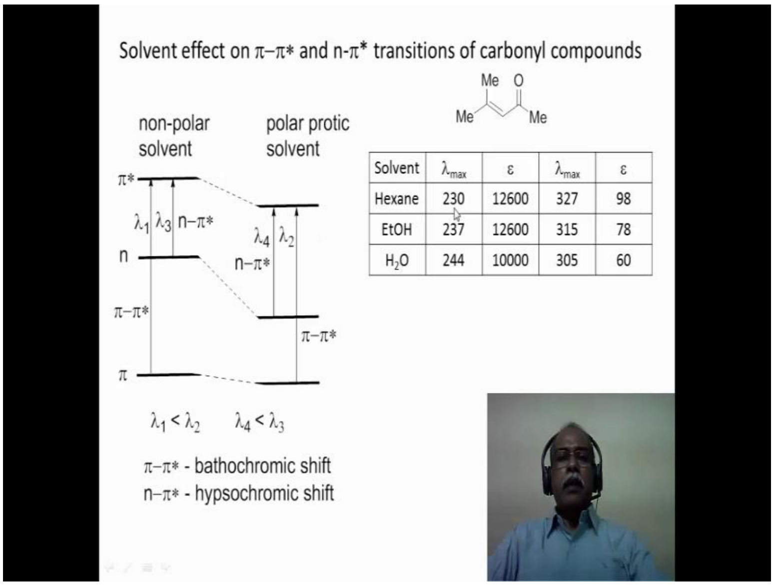

Solvent effect on $\pi-\pi^*$ and n-π^* transitions of carbonyl compounds

Solvent	λ_{max}	ε	λ_{max}	ε
Hexane	230	12600	327	98
EtOH	237	12600	315	78
H_2O	244	10000	305	60

$\lambda_1 < \lambda_2$ $\lambda_4 < \lambda_3$

$\pi-\pi^*$ - bathochromic shift
n–π^* - hypsochromic shift

Let us have a look at the solvent effect on the pi pi star and n pi star transition of a carbonyl compound. The pi pi star is an allowed transition and the n pi star is a forbidden transition and they have their own solvent effects, if these are the energy levels of the carbonyl functional group in a non polar solvent let us say for example, hexane then this would be a transition correspond to the pi pi star transition which is having a higher energy so lower wavelength and this would this is let us say call it as a lambda which is a wavelength of that particular absorption of this particular transition corresponding to that particular transition.

Then you have the n pi star transition which is a lower energy transition. So, this lambda 3 will be much higher than the lambda 1 in terms of the values of the lambda 1 and lambda 3. Now when you measure the same compound in a polar protic solvent like a ethyl alcohol or water what happens is the lone pair of electrons on the heteroatom, let us say on nitrogen or carbonyl functional group we are talking about carbonyl compounds, so we are talking about the lone pair of electron and the oxygen of this it can undergo hydrogen bonding interaction with ethyl alcohol or water they are by stabilizing it by solvation. So, they non bonded level gets stabilized considerable in comparison to a non polar solvent.

The pi star molecular orbital is a more polar state compared to a pi molecular orbital. So, that also gets solvated and it gets stabilized in a protic polar solvent like water or ethyl alcohol. In comparison to that, the pi electron level is relatively non polar so solvent does not have a significant effect in terms of stabilizing that particular state. It is the n level as well the pi star level which undergo a considerable stabilization, as a result of that you can see the pi pi star transition now is of a lower energy. In other words the lambda 2 which corresponds to the pi pi star transition in the polar solvent, in comparison to the lambda 1 which correspond to the pi pi star transition in a non polar solvent.

The lambda 2 is much higher than the lambda 1, in other words the lambda 1 is the higher energy compared to the lambda 2. In other words, from the energy wise this is higher; that means, wavelength wise it will be lower. So, the wavelength lambda 1 is lower than the wavelength lambda 2 higher the energy please remember there is a inverse proportionality between the energy and the wavelength scale and ultraviolet spectroscopy we normally refer everything in the wavelength in nanometers rather than frequency or wave numbers which are directly proportional to the energy. So, higher the energy, lower the number for the lambda and lower the energy here that is higher the number for the lambda. So, lambda 1 is less than lambda 2.

If you look at the n pi star level; it has exactly the opposite kind of an effect. The n pi star state in the polar solvent is much higher energy compared to the n pi star state in the non polar solvent. So, the lambda 4 which is corresponding to the non polar sorry polar solvent transition n to pi star has much lower energy compared this n lambda 3. Now this is illustrated using an example the carbonyl compound which is an alpha beta unsaturated carbonyl compound which is known as mesityl oxide. Mesityl oxide is a colloquial name for this molecule and this molecule the UV visible spectrum has been measured in three different solvent namely hexane, ethyl alcohol and water.

In hexane, the pi to pi star transition occurs for this carbonyl functional group at 230 nanometer, in ethyl alcohol it goes to higher wavelength 237, in a more polar solvent like water it goes even higher than the 237 namely 244 nanometer wavelength and you can see from the epsilon that this is an allowed transition. If you take the n pi star transition which is the at a longer wavelength 327 in hexane for example, when you measure it in a ethyl alcoholic it goes to lower wavelength. In other words the lambda 4 is less than lambda 3, so lambda 3 is more than lambda 4 for example so they decrease in the wavelength is essentially what is explained by means of the solvation of the n level in comparison to the n level in the non polar solvent for example.

As you increase the polarity of the solvent, the pi to pi star goes to a lower energy whereas the n to pi star goes to a higher energy, not much of an effect in terms of the epsilon values are nearly the same in all the polar as well as the non polar solvents.

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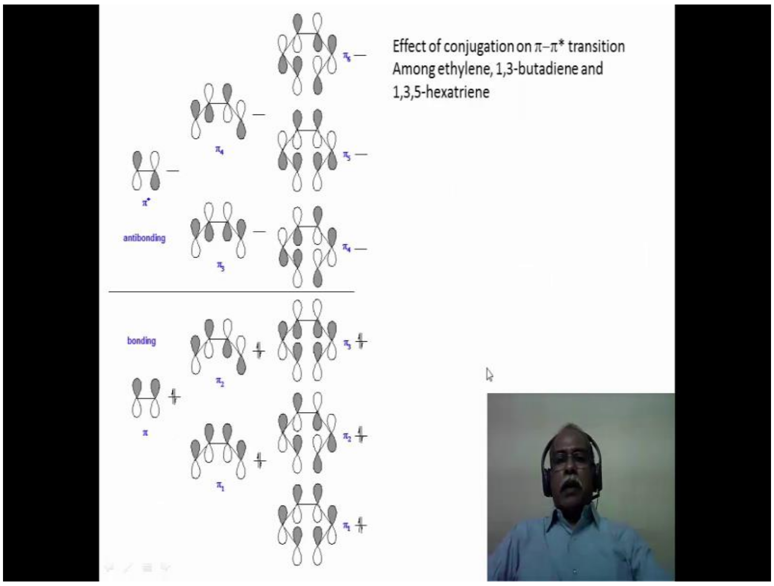

Effect of conjugation on $\pi-\pi^*$ transition
Among ethylene, 1,3-butadiene and
1,3,5-hexatriene

In addition to solvent effect conjugation has a very high effect on the transition of the pi to pi star level. Now, here is a molecular orbital picture for ethylene, butadiene and hexatriene, you can go on in the homologous series; what is important is that this is the pi molecular orbital of ethylene and this is a pi star molecular orbital of ethylene. Similarly, this is pi molecular orbitals of ethylene which are bonded filled molecular orbitals, these are the pi star molecular orbital which are unfilled molecular orbital.

Similarly, hexatriene has 6 pi electrons. So, 3 molecular orbitals occupying 2 each correspond to 6 bonding electrons and then you have the 3 non bonding levels also which are unoccupied or empty molecular orbitals. What is important is the transition pi to pi star, in this particular case correspond to this particular energy gap, which is the very high energy gap. As you go up in the series of the homologous of butadiene to hexatriene, you can see that the pi to pi start level now the energy level is much lower and it gets even further reduced with the increasing conjugation.

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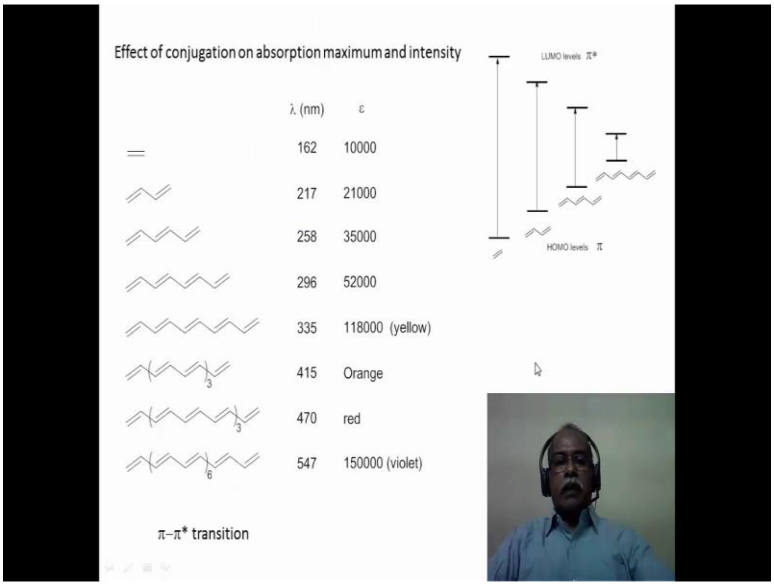

Effect of conjugation on absorption maximum and intensity

λ (nm)	ε
162	10000
217	21000
258	35000
296	52000
335	118000 (yellow)
415	Orange
470	red
547	150000 (violet)

π–π* transition

And this effect is what is felt in the conjugated dienes, trienes, tetraene and so on and at the data illustrates essentially as you increase the conjugation by increasing the number of double bonds, their transition energy decreases in other words the wavelength increases quite considerably. So, ethylene as an absorption around 162 nanometers, butadiene already shifted to 217 nanometer, all of them are measured essentially non polar solvents and in the case of octatriene for example, this is to 296 nanometer. You can also see with the increasing wavelength, there is also a concomitant increase in the transition probability. In other words, the epsilon which is a measure of the molar absorptivity that also considerably increases with increasing conjugation.

Now, if you come to an 8 double bond conjugated double bond, already the substance becomes colored these are observing in the ultraviolet region and it starts to absorb in the visible region at this particular wavelength which gives the yellow color. In other words, it absorbs the violet color that is why it looks yellow and similarly here it absorbs the violet and the indigo and the blue color and that is why it appears as an orange color for example. In this particular case it absorbs the green light that is why it looks like a violet compound. So, when you have 15 double bonds in conjugation with each other, the pi to pi star transition essentially absorbed in the visible region of the electronic spectrum. The effect of conjugation on the homo to lumo level or the pi to pi star level is essentially decreasing the gap of the homo lumo or the pi to pi star level, there by increasing the lamda values of the transition corresponding to that.

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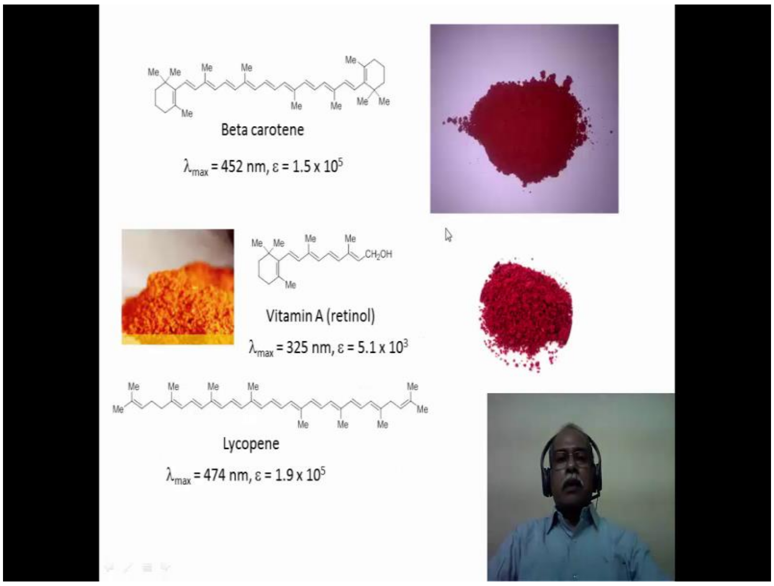

Beta carotene

λ_{max} = 452 nm, $\varepsilon = 1.5 \times 10^5$

Vitamin A (retinol)

λ_{max} = 325 nm, $\varepsilon = 5.1 \times 10^3$

Lycopene

λ_{max} = 474 nm, $\varepsilon = 1.9 \times 10^5$

The effect is so much so that one can actually see in dyes like beta carotene which has 11 conjugated double bonds all of them are transoid with respect to each other for example, and this is available in as a coloring substance in carrots for example, as an absorption maximum was 452 with an epsilon as highest 1.5, 10 to the power 5, in other words it is a highly intense color is what is represented by the epsilon of a 10 to the power 5 extinction coefficient.

Lycopene is another dye which is available in fruits like tomato for example, the skin of tomato the red color is due to the presence of lycopene which is again a conjugated (Refer Time: 29:18) system with 11 conjugated double bonds in conjugation with each other and that as an absorption around 474 nanometer. This is a sample of lycopene which is dark red in color, this is a sample of beta carotene which is also strongly red in color. The one that has only 5 double bonds in conjugation appears as yellow this is a molecule which is known as retinol or vitamin A. This has an absorption maximum of 325, although it is in the UV region the absorption end the tail end of the absorption comes in the visible region and that is why the substance appears as bright yellow for example. There are several organic dyes which are highly colored for example, gasoline is the hydrocarbon which is highly colored it is blue colored in nature that is essentially because of the pi to pi star transition in that particular molecule.

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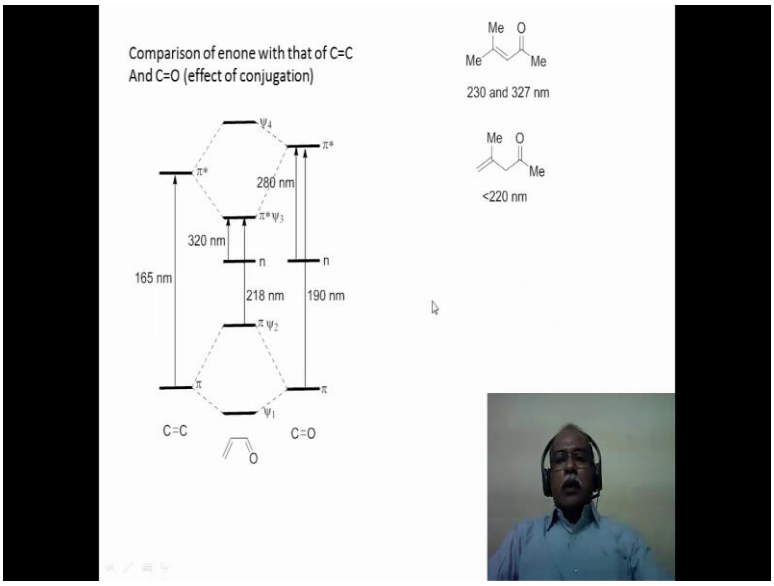

Comparison of enone with that of C=C
And C=O (effect of conjugation)

230 and 327 nm

<220 nm

Now, compared to a conjugated enone, a non conjugated enone has a much lower absorption. This is illustrated by again taking mesityl oxide and the isomer of mesityl oxide, in this molecule the double bond is in conjugation with the carbonyl functional group whereas in this molecule the double bond is not in conjugation with the carbonyl functional group. This molecule does not have any absorption, all the absorption is less than 220 nanometer, there are no absorption bands above 220 nanometers in this particular molecule. So, where as in this molecule if we look at the pi to pi star transition occurs at 230 nanometer, in other words about 10 nanometers at a higher wavelength is where it absorbs, 327 of course correspond to the n to pi star transition which is also absorbed here, but at a lower wavelength because of the conjugation effect is missing here.

This is explained by the effect of conjugation in the diagram shown here, this is an isolated carbon carbon double bond the pi to pi star transition occurs around 165 nanometer like in the case of ethelyne for example, whereas in the case of a carbonyl functional group, the pi to pi star transition occurs around 190 nanometer and the n to pi star transition occurs around 280 nanometers. When these two are in conjugation with each other then a new set of molecular orbitals are formed corresponding to the enone which is a conjugated enone and the effect of conjugation on the carbonyl transition is what is represent at here. The pi to pi star transition becomes lower energy, in other words it is of higher wavelength compared to the 190 or 165 nanometer. The n to pi star also becomes lower energy so 280 nanometers to 320 nanometers it get decreased. So, this essentially explains the effect of conjugation of a carbonyl compound for the n to pi star as well as the pi to pi star transition.

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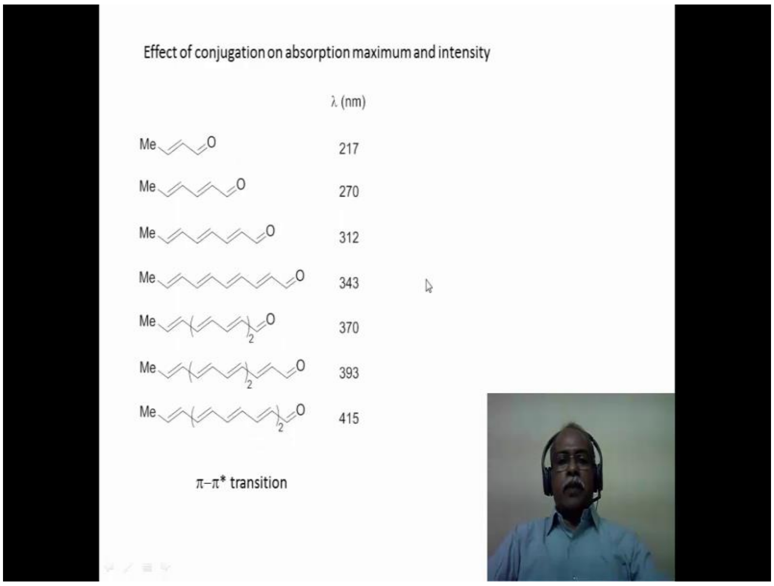

Effect of conjugation on absorption maximum and intensity

λ (nm)

217

270

312

343

370

393

415

π–π* transition

This effect can be clearly seen in the case of conjugated system, this is a single double bond conjugation, this is two double bond conjugation and so on up to for example, 7 double bond conjugation is shown here. As you increase the conjugation progressively, the lambda max also keeps increasing. In other words, it goes from the ultraviolet region to visible region, so this molecule should be either orange or yellow in color in terms of the color of the molecule, which is the absorption in the visible region of 450 nanometer.

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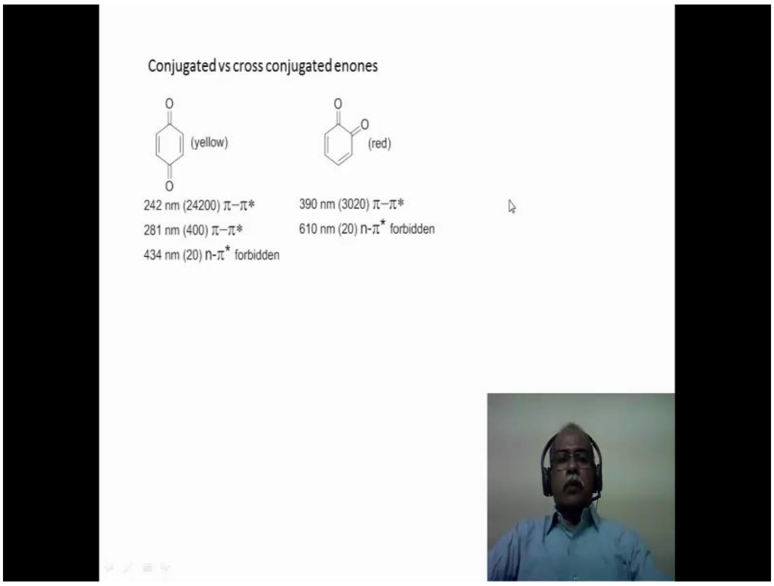

Conjugated vs cross conjugated enones

242 nm (24200) $\pi-\pi^*$
281 nm (400) $\pi-\pi^*$
434 nm (20) $n-\pi^*$ forbidden

390 nm (3020) $\pi-\pi^*$
610 nm (20) $n-\pi^*$ forbidden

Now quinones are, there are two types of quinones available this is a ortho benzoquinone and this is para benzoquinone. Fundamentally they are different in their conjugation properties, if you look at the ortho benzoquinone the two carbonyl functionals groups are conjugated to each other and so the carbonyl functional group conjugate. In other words, there is a through conjugation of the system in this particular case, whereas if you look at the para benzoquinone, the carbonyl functional group is conjugated to this double bond as well as this double bond; however, the carbon carbon double bond of this side is not directly conjugated to the carbon carbon double bond on this side, it has to go through the carbonyl carbon for the conjugation to complete and such systems are considered to be cross conjugated whereas these are linearly conjugated.

You can see here if you start from the oxygen and follow the double bond path way, you will essentially have the entire system conjugated to each other. So, this is a much better conjugation compared to the cross conjugation that is why this substance absorbs at a longer lower wavelength, in other words higher energy absorption is what is taking place, whereas this is red in color which appears because it is absorbing around 610 nanometers or so. So, you can see here the pi to pi star transition correspond to 242 and 281, there are two types of pi to pi star transition in this quinine compound. Whereas, in the case of ortho benzoquinone, the pi to pi star transition occurs at 390 nanometer. In the case of the cross conjugated benzoquinone, para benzoquinone the n to pi star appears at 434, where as in the case of the ortho benzoquinone the n to pi star appears around 610 nanometer. Such a profound effect is because of the conjugation which is either a straight conjugation like here for example, or the cross conjugation in this particular case of the para benzoquinone.

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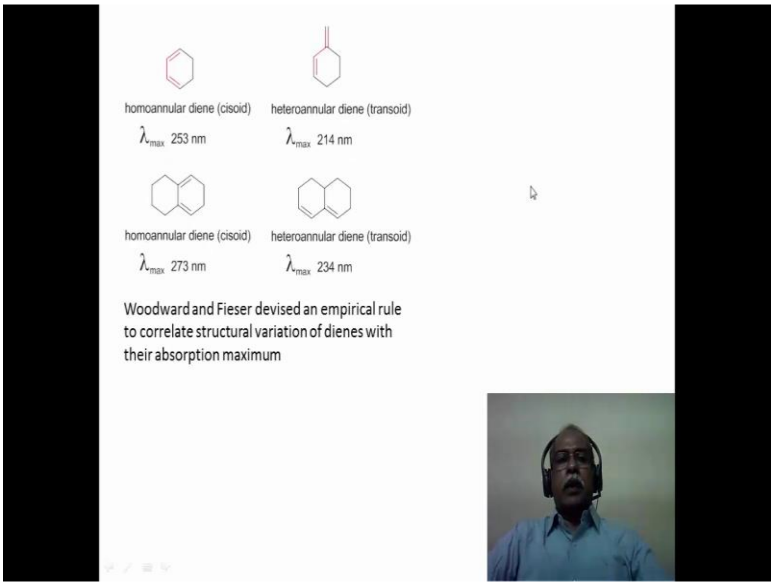

homoannular diene (cisoid) λ_{max} 253 nm

heteroannular diene (transoid) λ_{max} 214 nm

homoannular diene (cisoid) λ_{max} 273 nm

heteroannular diene (transoid) λ_{max} 234 nm

Woodward and Fieser devised an empirical rule to correlate structural variation of dienes with their absorption maximum

Now Woodward and Fieser have worked on a large number of steroid molecules and based on their study, they have arrived at an empirical rule to correlate the structural variation of dienes with the absorption maximum. If we consider this particular diene this is a homoannular diene because the two double bonds are part of one cycle or one cyclic ring system in this particular case and there are also cisoid with respect to each other. Now, if we consider this particular diene, one of the double bond of the diene is part of the cyclic system, the other double bond is essentially in exocyclic kind of a double bond and the two double bonds are transiod with respect to each other with respect to the single bond this is transoid in geometry.

So one would call this as a homoannular diene and this is a heteroannular diene because this double bond is not part of this ring, it is only an exocyclic part of that particular ring. In the Woodward-Fieser rule, one sets a basic value for the conjugated diene which is the homoannular diene or the heteroannular diene as the case may be. The homoannular diene because it is fully conjugated absorbs at a longer wavelength compared to a heteroannular diene, which is the transoid diene which absorbs at a lower wavelength.

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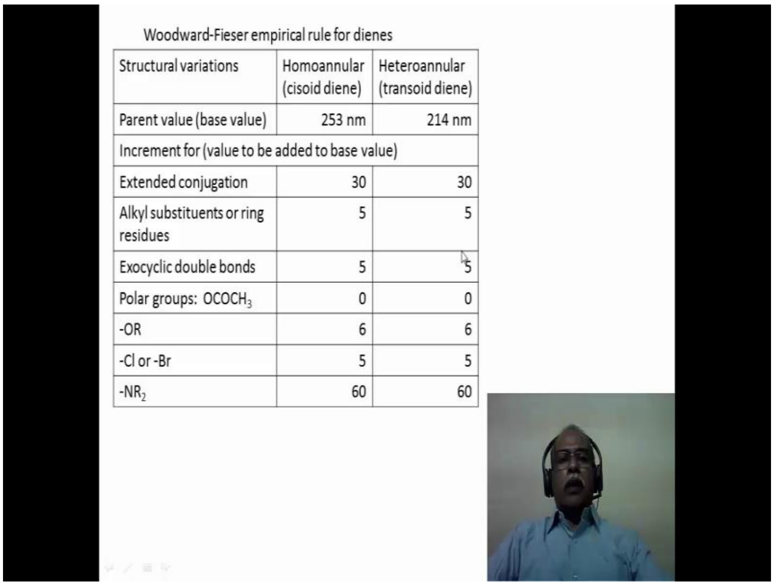

Woodward-Fieser empirical rule for dienes

Structural variations	Homoannular (cisoid diene)	Heteroannular (transoid diene)
Parent value (base value)	253 nm	214 nm
Increment for (value to be added to base value)		
Extended conjugation	30	30
Alkyl substituents or ring residues	5	5
Exocyclic double bonds	5	5
Polar groups: $OCOCH_3$	0	0
-OR	6	6
-Cl or -Br	5	5
$-NR_2$	60	60

Now, what is done is an empirical rule is additive rule is what is being devised, this is called Woodward Fieser empirical rule for dienes. This is a structural variation that can take place and for a homoannular cisoid diene, the base value is taken as 253 nanometer. For a heteroannular transoid diene, the base value is taken as 214 nanometer, this kind of a additivity principle is extremely useful, if there is an unknown structure and you want to find out whether it is a conjugated diene of the homoannular type or the heteroannular type particularly in the steroid molecule. In those days, during the 1960s and 70s, people have extensively used this methodology to find out the structure of organic compounds in terms of the conjugation and so on.

Now, there is an incremental value that is given, we have an extended one additional double bond conjugating, it 30 nanometer has to be added to the base value of 253, so that will become 283, if it is a conjugated triene system. Alkyl substituent or ring residues you will define, what is alkyl substituent ring residue in a minute. So, essentially the substituent that are present in the double bonds for each substituent you add a value of 5 nanometer, if there is an exocyclic double bond, you add a value of 5 nanometer. Polar functional group acetate does not make any difference; however, methoxy or bromochloro or diamino they all contributes significantly, particularly the dye alkylamino contributes quite significantly by shifting the value by 60 nanometers more than the base value for example. Let us have some examples of calculation of this type of additivity rule.

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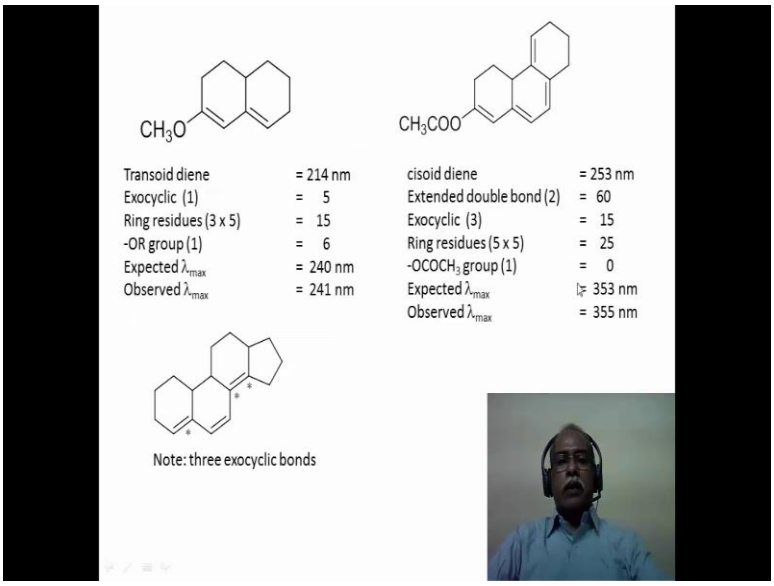

Transoid diene = 214 nm
Exocyclic (1) = 5
Ring residues (3 x 5) = 15
-OR group (1) = 6
Expected λ_{max} = 240 nm
Observed λ_{max} = 241 nm

cisoid diene = 253 nm
Extended double bond (2) = 60
Exocyclic (3) = 15
Ring residues (5 x 5) = 25
-$OCOCH_3$ group (1) = 0
Expected λ_{max} = 353 nm
Observed λ_{max} = 355 nm

Note: three exocyclic bonds

If we consider this molecule here, this is a heteroannular transoid diene. So, the heteroannular transoid diene, the base value is 214 nanometer. So, the 214 nanometer is taken. There is an exocyclic double bond, if you look at this double bond it is a exocyclic to this ring so one exocyclic double bond will add about 5 nanometers and then you have the ring residue, which are these residuals this is one ring residue and this is another ring residue and this is a third ring residue. So, there are 1, 2, 3, 4, 5 ring residuals are there so totally three times sorry there are three ring residuals corresponding to this carbon substituent here, this carbon substituent here and this carbon substituent here.

For each ring residues it is 5 nanometer increments so three times 5 is 15 nanometer increment, there is a methoxy substituent on the double bond that is contributing about 6 nanometer so over all if you had up these numbers it comes to 240 nanometers. Based on the empirical editivity rule the absorbed lambda max is pretty close to the expected value of 240 nanometers. If you take this cisoid diene between a transoid diene and cisoid diene, cisoid diene has a higher base value so you take the base value of the cisoid diene, then add extra conjugation this is an additional conjugation, this is also an additional conjugation. Each extended conjugation corresponds to 30 increment which corresponds to for example, 30 increment for each conjugation value so that will two extra conjugation will correspond to 60 nanometer. This is an exocyclic double bond for this ring, so this is exocyclic double bond to the other ring. There are three exocyclic bonds this is 1 exocyclic bond to this ring and this is another exocyclic bond to this particular ring, this is an exocyclic double bond for this particular ring so the three exocyclic ring each will contribute 5. So, three times 5 is 15, the ring residues there are 5 ring residues, 1, 2, 3, 4 and 5.

In other words you have to take this entire skeleton and look at the number of substituents that are present in the double bonds. This is one substituent in the double bond, this is another substituent in the double bond, this is a third substituent in a double bond this is a forth substituent in the double bond. So, five substituents are present in the double bond 5 times 5 is 26, acetate group of course does not contribute anything. The expected value if you add up all the numbers 353 and the actual experimental value is 355 so very, very close numbers is what you get in this particular case.

If there is a exocyclic double bond common to this ring as well as to this ring, you have to take twice of the values for the exocyclic double bond. In other words this is one exocyclic double bond, this is 1 exocyclic double bond as per as this ring is concerned and this is again another exocyclic double bond as per as this ring is concerned. So, the number of exocyclic double bonds in this particular molecule is 3, so that has to be kept in mind. So, what we have seen in this particular module is the fundamental nature of the electronic transition in an organic molecule, the type of transitions that has present in an organic molecule, particularly olefins and carbonyl compounds is what we have seen. We still have to see the electronic transitions of aromatic molecule which we will consider in the next module.

Thank you very much for your attention.