Modern Instrumental Methods of Analysis
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Module No. # 02
Lecture No. # 05
Ultraviolet and Visible Spectrophotometry – 1
Theoretical Aspects

You are welcome to the lecture number 5.

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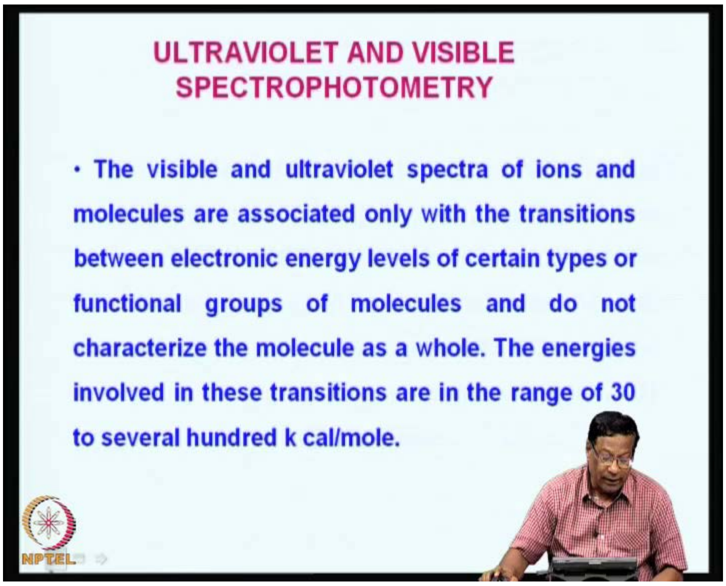

ULTRAVIOLET AND VISIBLE SPECTROPHOTOMETRY

- The visible and ultraviolet spectra of ions and molecules are associated only with the transitions between electronic energy levels of certain types or functional groups of molecules and do not characterize the molecule as a whole. The energies involved in these transitions are in the range of 30 to several hundred k cal/mole.

With this lecture onwards, we will be studying the ultraviolet and visible spectrophotometry followed by fluorescence followed by atomic absorption and several other instrumental techniques.

Now, let us concentrate on the ultraviolet and visible spectrophotometry. Basically, this requires the visible and ultraviolet spectra of the ions and molecules associated only with the transitions between electronic energy levels of certain types of functional groups of molecules and do not characterize a molecule as a whole. That means the information about a molecule what you get is only basically a small part of about the molecule. You cannot characterize the molecule as a whole. It gives you choices regarding the type of the molecule.

So, the electronic transitions that are taking place in a molecule when it is exposed to ultra violet and visible radiation gives rise to certain spectrum and this spectrum can be interpreted in terms of different kinds of transitions that are taking place in the molecule. So, the energies involved in these transitions are in the range of 30 to several 100 kilo calories per mole. So, this is very important.

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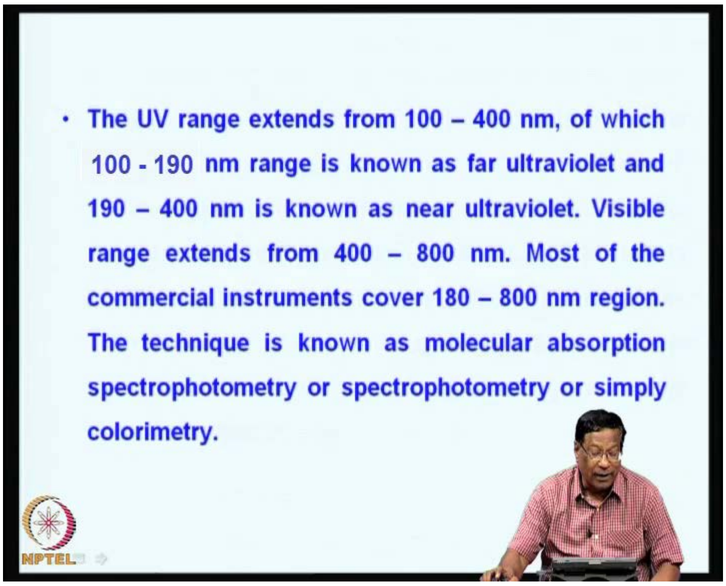

- The UV range extends from 100 – 400 nm, of which 100 - 190 nm range is known as far ultraviolet and 190 – 400 nm is known as near ultraviolet. Visible range extends from 400 – 800 nm. Most of the commercial instruments cover 180 – 800 nm region. The technique is known as molecular absorption spectrophotometry or spectrophotometry or simply colorimetry.

So, basically UV range extends from 100 to 400 nanometer of which 100 to 900 range is known as far ultraviolet and 190 to 400 nanometer is known as near ultraviolet. Visible range extends from 400 to 800 nanometers. Most of the commercial instruments cover 180 to 800 nanometer. Then, there are certain instruments which refer to, which are referred to as calorimeters. These refer to visible range that is from 350 to 700 or 750 nanometers. So, the technique is known as molecular absorption spectrophotometry or spectrophotometry or it is simply known as colorimetry depending upon the type of work what you do or depending upon the instrument.

So, this is the electromagnetic spectrum what we have seen it earlier in our discussion. It starts from the other end that is strongest rays. Most energetic rays are gamma rays and they are followed by X-rays. Then, they are followed by ultraviolet rays and visible light which is followed by near infrared and far infrared followed by microwaves and followed by radio waves. Subsequently, we also have audio waves.

Now, you can see that the frequency range is decreasing from top to the bottom and wavelength keeps on increasing from top to the bottom. For example, gamma rays and cosmic rays. You can see that the maximum absorption, maximum wavelength is up to 1 angstroms. Here the interaction of the matter with the molecules that of the matter in sense gamma rays. These gamma rays react with the nucleus generating nuclear reactions and if you use X-rays, the wavelength changes from 1 angstrom to 10 angstrom units and may be sometimes up to 100. These can be further sub divided as soft X-rays and hard X-rays. So, in the X-rays, we have seen earlier inner electrons from inner shells will be dislocated and the X-ray what you see in our hospitals etcetera corresponds to soft X-ray.

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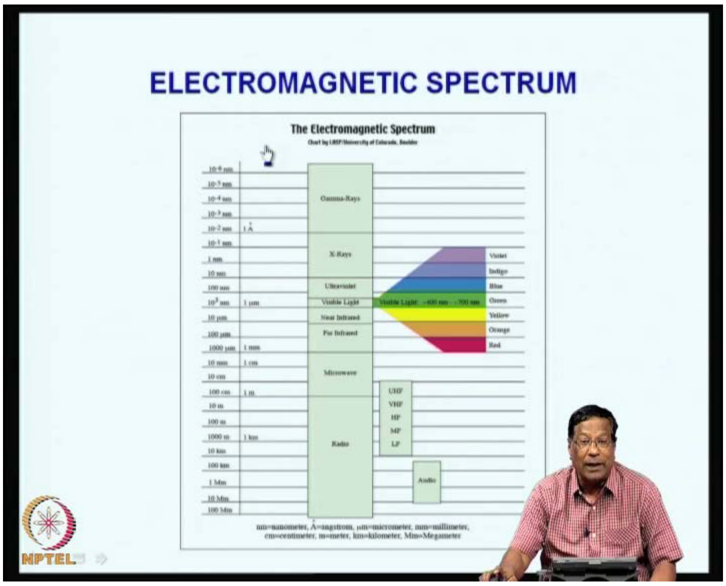

ELECTROMAGNETIC SPECTRUM

Then comes the ultraviolet ray. Ultraviolet rays can be divided into approximately 3 ranges 1 is vacuum ultraviolet. Another is far ultraviolet and another is near ultraviolet. Vacuum ultraviolet rays are usually not easily accessible as part of the electromagnetic radiation for studying the spectrophotometry or molecular changes. Whereas, near ultraviolet range is very suitable for the change for detecting the changes at molecular level, that is molecular excitation levels. Visible light is of course very useful for the spectrophotometry and anything that is colored, you can see all these violet, indigo, blue, green, yellow, orange and red, these are the ranges, different ranges of substances for which our human eye is susceptible. It can recognize these colors and any substance containing having one of these colors can be followed by visible light radiation.

Then, near infrared immediately follows the visible range. Sometimes, this area is also incorporated in some of the modern spectrophotometric instruments and the far infrared of course and infrared, near infrared are the ranges. They all correspond to the infrared spectroscopy. That we will be studying it later.

Now, let us look at what is this range. You can see from the previous spectrum that visible light represents only a small path of the electromagnetic spectrum. The following table shows the transmitted colors and complementary hues. Actually what happens is when you have a substance which is colored and you pass radiation through that, it absorbs part of the radiation and emits what is not absorbed. So, what you see here is what is transmitted or what is absorbed. The complimentary view hue, it is so if you take a look at the wavelength on the left column, you can see that it starts from 380 to 780 nanometers.

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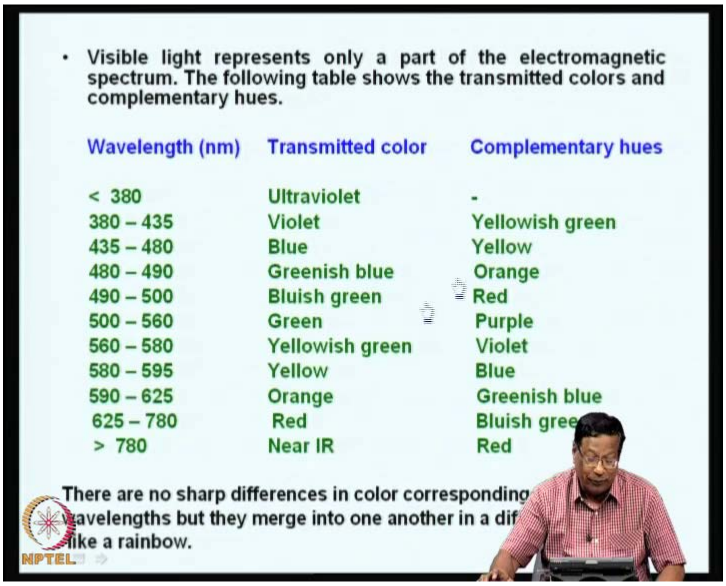

- Visible light represents only a part of the electromagnetic spectrum. The following table shows the transmitted colors and complementary hues.

Wavelength (nm)	Transmitted color	Complementary hues
< 380	Ultraviolet	-
380 – 435	Violet	Yellowish green
435 – 480	Blue	Yellow
480 – 490	Greenish blue	Orange
490 – 500	Bluish green	Red
500 – 560	Green	Purple
560 – 580	Yellowish green	Violet
580 – 595	Yellow	Blue
590 – 625	Orange	Greenish blue
625 – 780	Red	Bluish gree
> 780	Near IR	Red

There are no sharp differences in color corresponding wavelengths but they merge into one another in a dif like a rainbow.

Now, this represents these ranges of wavelengths, represent all the colors that human eye is sensitive to less than 380 human eyes are not sensitive. So, you will be seeing, you will be only feeling the ultraviolet ray, especially people in the morning go out into the sun to get ultraviolet radiation, that is Vitamin D where you are all quite familiar with that. Then, between 380 to 435 nanometers, we have what is transmitted is violet and the complementary hue is yellowish green and then, this merges into blue color between 485 and 480. That means only blue color is transmitted and yellow color is absorbed and 480 to 490 nanometers. Then comes greenish blue followed by 490 to 500 comes bluish green and then, 500 to 560 is green whereas, what you will be pursuing that color is purple.

So, subsequently you will see down the wavelength range 560 to 580, you will be seeing a violet color and then, 580 to 595 appears to you as blue and then, if the substance is greenish blue in color, you would see that it is absorbing between 590 to 625 range and if it is bluish green 625 to 780 and above 780, the material will look red.

You can see that there are no sharp differences in the color corresponding to specific wavelengths, but they merge into one another in a diffused manner like a rainbow. This is very important for us because the absorption spectrum when we plot, it gives you something like a diffused broad peak.

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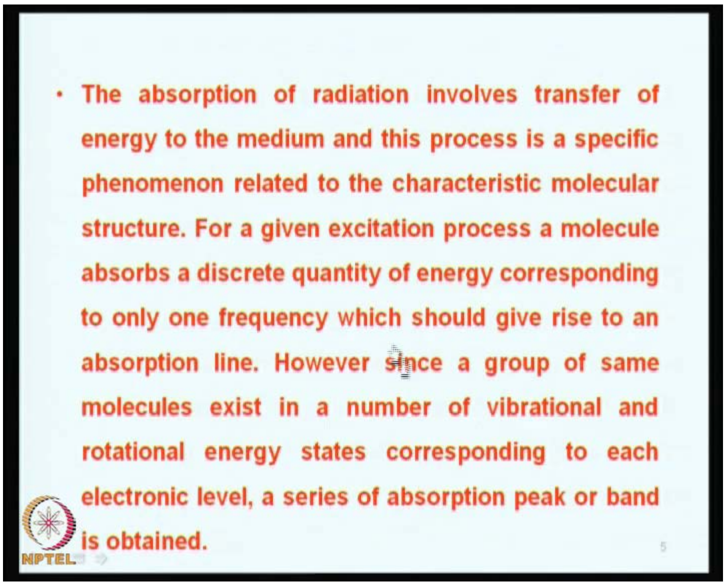

- The absorption of radiation involves transfer of energy to the medium and this process is a specific phenomenon related to the characteristic molecular structure. For a given excitation process a molecule absorbs a discrete quantity of energy corresponding to only one frequency which should give rise to an absorption line. However since a group of same molecules exist in a number of vibrational and rotational energy states corresponding to each electronic level, a series of absorption peak or band is obtained.

So, the absorption of radiation involves basically transfer of energy to the medium and this medium is a, this process is a specific phenomenon related to the characteristic molecular structure. So, for a given excitation process, a molecule absorbs a discrete quantity of energy corresponding to only one frequency which should give rise to one absorption line.

However, since a group of same molecules exist in a number of vibration and rotational energy levels, what you would see is a broad spectrum corresponding to different energy levels in which the electrons are populated, but you can see that here what we were talking is about the molecular structure and the changes that takes place are in the electronic level. So, you can see that the molecules must also have some sort of electronic waves that is electronic energy levels corresponding to different absorption spectrum.

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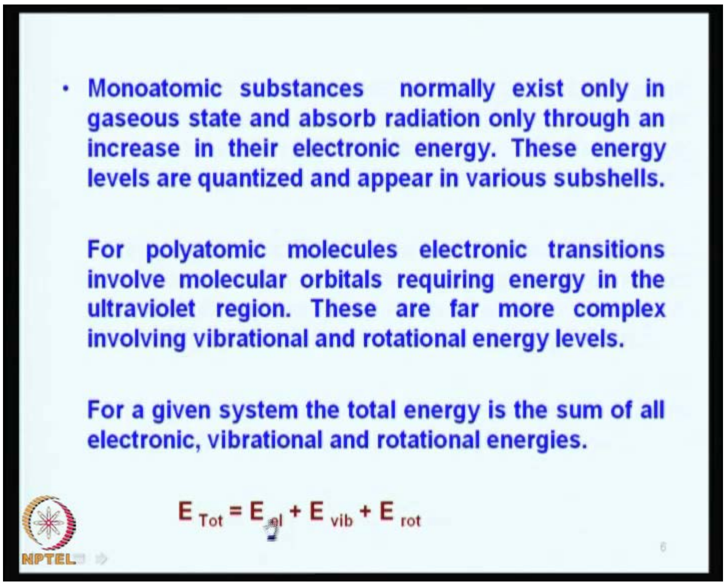

- Monoatomic substances normally exist only in gaseous state and absorb radiation only through an increase in their electronic energy. These energy levels are quantized and appear in various subshells.

  For polyatomic molecules electronic transitions involve molecular orbitals requiring energy in the ultraviolet region. These are far more complex involving vibrational and rotational energy levels.

  For a given system the total energy is the sum of all electronic, vibrational and rotational energies.

$$E_{Tot} = E_{el} + E_{vib} + E_{rot}$$

For example, monoatomic substances normally exist only in gaseous state and absorb radiation only through an increase in the electronic energy. That means a substance which is at vapour stage does not have vibrational and rotational energy level. That means the electrons can go from ground state to higher electronic excited state.

Now, for polyatomic molecules, electronic transitions generally involve molecular orbital’s requiring energy in the ultraviolet region. So, if there are number of atoms in a molecule, the energy required to excite a molecular electron to next higher energy level, that is the electronic level is in the ultraviolet region. So, these transitions are much more complex involving vibrational and rotational energy levels. So, if you take a spectrum of a substance in vapour, you would see very sharp peaks, but if you take it in a solvent, you will not see such sharp peaks. You will see broader peaks.

So, for a given system, the total energy is the sum of all electronic vibrational and rotational energy level which we represent as E total is equal to E electronic, E vibrational plus E rotational. Of course, there could be some amount of reflection taking place, but that we neglect for the time being because with the use of proper equipments, it is possible to reduce the reflection losses.

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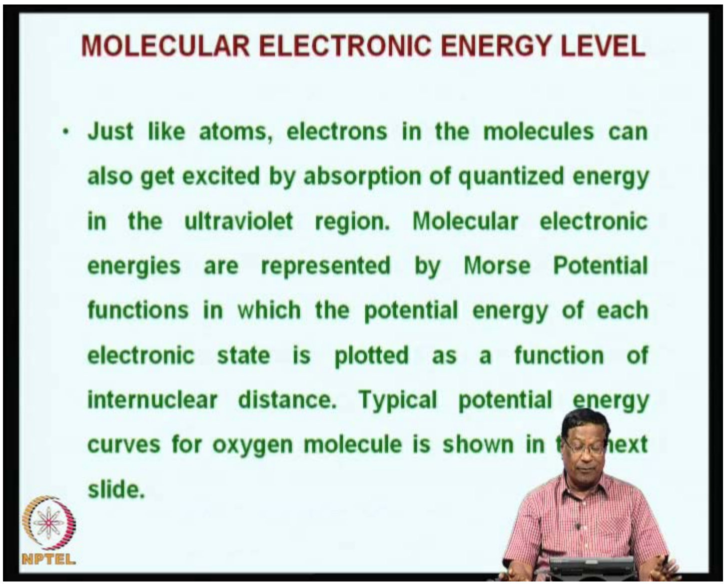

MOLECULAR ELECTRONIC ENERGY LEVEL

- Just like atoms, electrons in the molecules can also get excited by absorption of quantized energy in the ultraviolet region. Molecular electronic energies are represented by Morse Potential functions in which the potential energy of each electronic state is plotted as a function of internuclear distance. Typical potential energy curves for oxygen molecule is shown in t next slide.

So, now what we are looking at just like the atoms, electrons in the molecules can also get excited by absorption of quantized energy in the ultraviolet region atoms. Molecules get excited, but in the molecules electrons get excited, molecular electronic energies are represented by a Morse Potential function in which the potential energy of each electronic state is plotted as a function of inter nuclear distance, that is you plot a inter nuclear distance versus potential energy.

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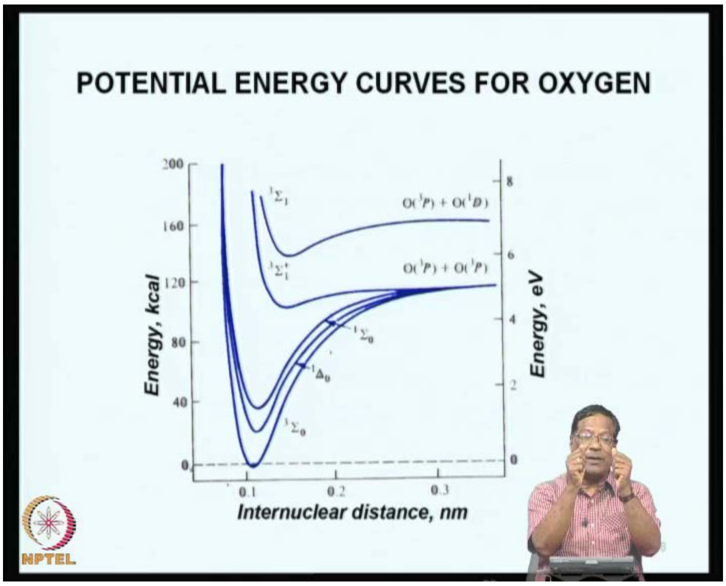

POTENTIAL ENERGY CURVES FOR OXYGEN

Typical potential energy curves for oxygen molecules I am showing you in the next slide that is something like this. This is inter-nuclear distance. When the atoms of the oxygen molecule are far away, the energy is less and as you bring them nearer, some sort of a chemical bonding takes place in between the two atoms.

So, as the atoms come nearer and nearer, the energy of the system reduces and then, comes down and then, stabilizes at the bond level and you try to bring the atom still nearer. Then, the repulsion processes will take precedence and the electrons will repel nucleus repel etcetera. With the result that the energy keeps on increasing. So, that is what you are seeing here. As we bring the atoms nearer and nearer, the energy keeps on decreasing and then, it keeps on increasing as you bring the nucleus nearer and nearer.

So, the optimum distance is obtained somewhere in this range nanometers and what you see here in this figure are the electronic excited states of the oxygen molecule. This is known as ground state. That is first one. Next one is the higher excited state and then, you see the third excited state, fourth excited state and fifth excited state etcetera. Even though, I have drawn this figure only for oxygen, you can see that similar would be the situation, whether you draw a hydrogen molecule or any other molecule or a polyatomic molecule also will essentially show you the same thing.

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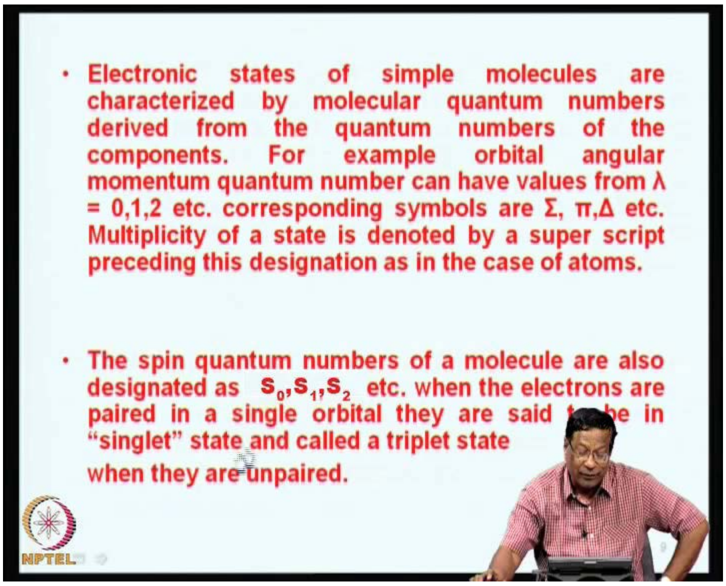

- Electronic states of simple molecules are characterized by molecular quantum numbers derived from the quantum numbers of the components. For example orbital angular momentum quantum number can have values from λ = 0,1,2 etc. corresponding symbols are Σ, π,Δ etc. Multiplicity of a state is denoted by a super script preceding this designation as in the case of atoms.

- The spin quantum numbers of a molecule are also designated as S_0, S_1, S_2 etc. when the electrons are paired in a single orbital they are said t be in "singlet" state and called a triplet state when they are unpaired.

So, the electronic energy states of simple molecules are characterized by molecular quantum number. We do not use the molecular quantum numbers and these molecular quantum numbers are derived from the quantum numbers of the individual atomic components. For example, orbital angular momentum quantum number can have values from 0 1 2 etcetera. Corresponding symbols are sigma, pi, delta etcetera. So, the multiplicity of a state is denoted by a superscript preceding this designation as in the case of atoms. So, there is not much difference except that we call them sigma pi and delta. Essentially, they represent the excitation energy levels of the substance.

So, the spin quantum numbers of the molecules are also designated S0, S1, S2 etcetera. So, when the electrons are paired in a single orbital, they are paired, they are called singlet state. When they are not paired, it is called a triplet state. So, this is a very important concept because most of the time excitation takes place when the from the ground state in which the electrons are paired and when they go to the higher energy state quite often the electrons come off unpaired and that is called as a triplet state.

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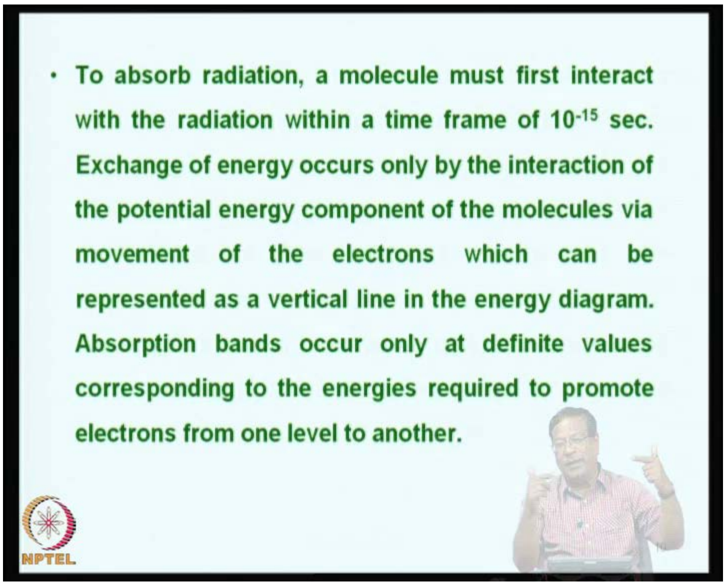

- To absorb radiation, a molecule must first interact with the radiation within a time frame of 10^{-15} sec. Exchange of energy occurs only by the interaction of the potential energy component of the molecules via movement of the electrons which can be represented as a vertical line in the energy diagram. Absorption bands occur only at definite values corresponding to the energies required to promote electrons from one level to another.

Now, let us go to the next slide that is to absorb the radiation, a molecule must first interact with the radiation so within a time frame. For example, first you have to take a sample and take the radiation coming from one end and passing it through the material and then, this has to happen in real time that is radiation has to come through one end and pass through the material and then, go to the detector.

So, to absorb the radiation what a molecule must do is it must first interact with the radiation within a time frame of about 10 raise to minus 15 seconds. Now, this is the time frame in which the material can react with the radiation. Now, exchange of energy must occur only by the interaction of the potential energy component of the molecule via the movement of the electrons which can be represented as a vertical line in the energy diagram. So, absorption bands occur at only at definite values because corresponding to the energy, there has to be a band and the energy required must be exactly equal to promote the electron from one level to the next excited energy level.

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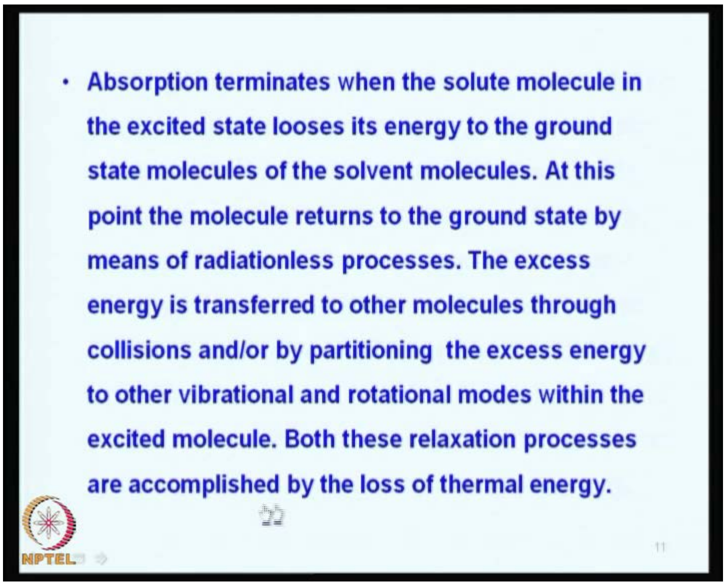

- Absorption terminates when the solute molecule in the excited state looses its energy to the ground state molecules of the solvent molecules. At this point the molecule returns to the ground state by means of radiationless processes. The excess energy is transferred to other molecules through collisions and/or by partitioning the excess energy to other vibrational and rotational modes within the excited molecule. Both these relaxation processes are accomplished by the loss of thermal energy.

So, absorption terminates when the molecule, solute molecule in the excited state loses its energy. Subsequently, the electron has to come down from the excited state to the ground state. Now, this energy must be lost. How will it loose the energy? In spectrophotometry, the excess energy is lost as heat and this heat is dissipated to the solvent molecules. So, the solvent molecules which do not absorb ultraviolet radiation, we take away the absorption energy and return the molecules to the ground state.

At this point the molecule returns to the ground state by means of, we call it as a radiationless process. So, the excess energy is transferred to other molecules through collisions basically and/or by partitioning the excess energy to other vibrational and rotational modes energy changes also may takes place and there also it is possible to lose its extra energy. So, both these relaxation processes are accomplished by the loss of thermal energy. Basically, that is how the energy is lost.

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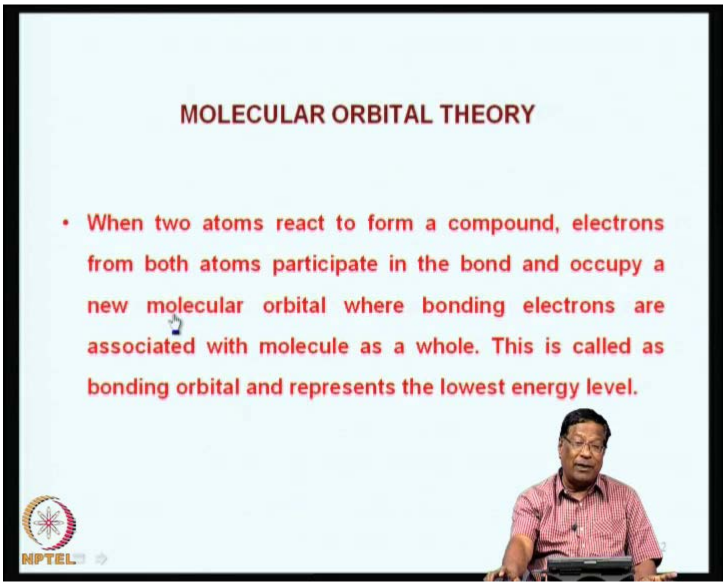

MOLECULAR ORBITAL THEORY

- When two atoms react to form a compound, electrons from both atoms participate in the bond and occupy a new molecular orbital where bonding electrons are associated with molecule as a whole. This is called as bonding orbital and represents the lowest energy level.

So, let us look at what is molecular orbital theory. When two atoms react to form a compound, electrons from both atoms must come together forming a bond and occupy a new molecular orbital, where bonding electrons are associated with the molecule as whole. This is called as bonding orbital because both the electrons in the bond belong to both the atoms and this represents the lowest energy level as we have seen earlier.

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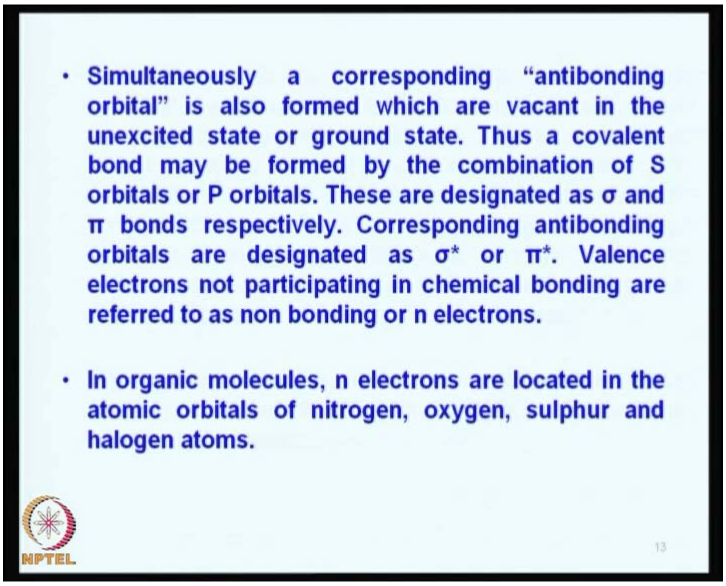

- Simultaneously a corresponding "antibonding orbital" is also formed which are vacant in the unexcited state or ground state. Thus a covalent bond may be formed by the combination of S orbitals or P orbitals. These are designated as σ and π bonds respectively. Corresponding antibonding orbitals are designated as σ^* or π^*. Valence electrons not participating in chemical bonding are referred to as non bonding or n electrons.
- In organic molecules, n electrons are located in the atomic orbitals of nitrogen, oxygen, sulphur and halogen atoms.

Now, simultaneously when a bonding orbital is formed, there will be another orbital at higher excited state which may be empty, but it is of the form all the same. So, a corresponding empty bond antibonding orbital are also formed whenever there is a bonding orbital formation. It may be having electrons, it may not be having electrons, but in the unexcited state basically, we do not have the electrons or in the ground state, the excited orbitals are vacant. Thus, a covalent bond may be formed by the combination of S orbitals or P orbitals.

Now, you will remember that the S orbitals are spherical orbitals and P orbitals are dumbbell shaped orbital and these are designated. So, if the electrons are forming, coming together to form a chemical bond, a single bond, then these are designated as sigma bond, that is a single bond is designated as sigma. If there is a double bond, the second bond must correspond to the pi orbitals and these bonds are known as pi bonds. Corresponding antibonding orbitals are designated as sigma star or pi star.

Valence electrons are not participating in chemical bonding. They are referred to as non-bonding or N electrons. That means some of the electrons do not participate in the bonding. At the same time, they have number of electrons associated with each atom. For example, if you have nitrogen, you will know that there are two unpaired electrons on nitrogen. Similarly, there are two pairs of unpaired electrons on oxygen and sulphur halogen atoms etcetera. So, in organic molecules, these are referred to as N electrons that do not participate in the bonding. So, let us take a look at what happens to these electrons which are not involved in bonding.

Now, you can see here that I have shown you a sigma bond and this is a sigma bond and this is a sigma star. That is excited. You can see that the space region in between is empty here whereas, here the electrons are concentrated in this shape and they could also be down step and then, pi orbital would also be like this and then, pi star orbitals would be like this.

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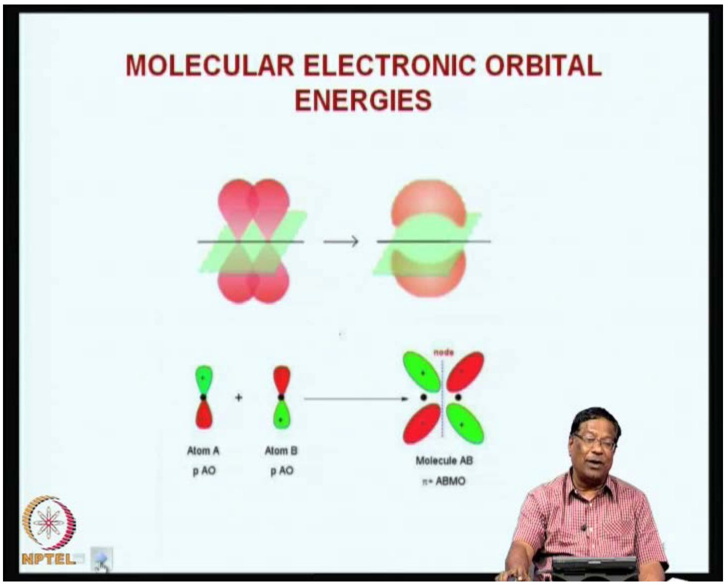

MOLECULAR ELECTRONIC ORBITAL ENERGIES

These are the typical shapes. They are not the actual representations mind you, but only at approximate pictorial representation of the distribution of the electrons around the nucleus. So, you can see that the bonding orbitals and empty bonding orbitals keep on varying depending upon their energy. Now, we have a sigma bond and above that we have a pi bond. That means a ground state of pi bond is at a higher energy level than the sigma bond by this much amount. So, here is the energy bond and non-bonding electrons which are not involved in bonding also remain at higher energy than pi bonding.

Then, we have a pi star bonding corresponding to the pi bonding, that is pi to pi star transitions and sigma bonding corresponding sigma bonding would be having a sigma star antibonding, the antibonding orbital. Now, you can see that if the sigma bond is at a very low energy, sigma star would be having a very high energy. That means it requires lot of energy to promote an electron from sigma bond to sigma star bond.

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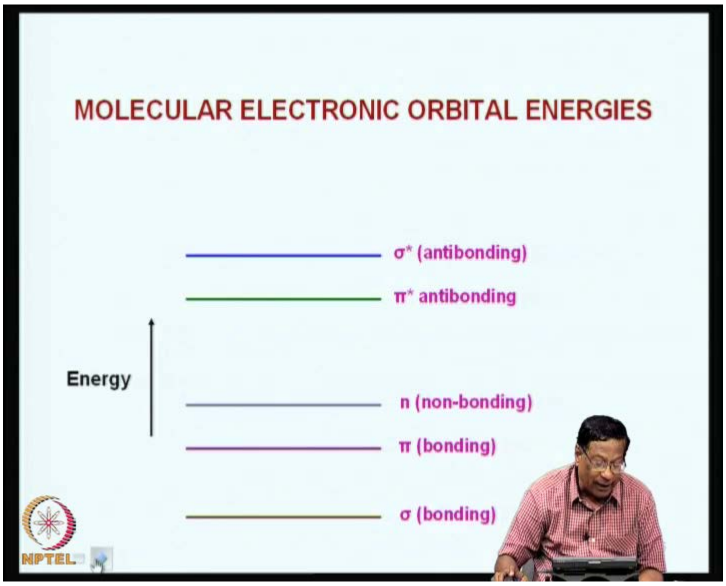

MOLECULAR ELECTRONIC ORBITAL ENERGIES

Sometimes, what happens is it is possible to promote a sigma bond to pi star provided there is a double bond. So, it is possible to promote non-bonding electrons also to pi star or sigma star and these are the different combinations that can happen for an electron getting excited whenever there is ultraviolet radiation.

Now, you I have simply put it like this. The electronic transitions involved in the transition in ultraviolet and visible regions include basically sigma to sigma star and n to sigma star, n to pi star and pi to pi star. Obviously, their relative energies, transitional energies, sigma to sigma star will be having maximum energy and n to sigma star is having slightly lower energy than that pi to pi star transitions are having still lower energy and n to pi energy will be the easiest to excite the electrons, that is non-bonding electrons to higher energy level that is pi star.

Subsequently, several compounds do not show sigma to sigma star transition because such compound should be saturated organic compounds like hydro carbons, where there are only single bonds like methane, ethane and propane and things like that. They can exhibit only sigma to sigma star because there is no pi bond available in the compound and if it contains an element like nitrogen, oxygen, etcetera, non-bonding electrons would be present and n to sigma star transitions would be approximately visible provided their energy falls in the UV range. As you remember below 180 is known as far ultraviolet range which is not accessible to commercial spectrophotometers.

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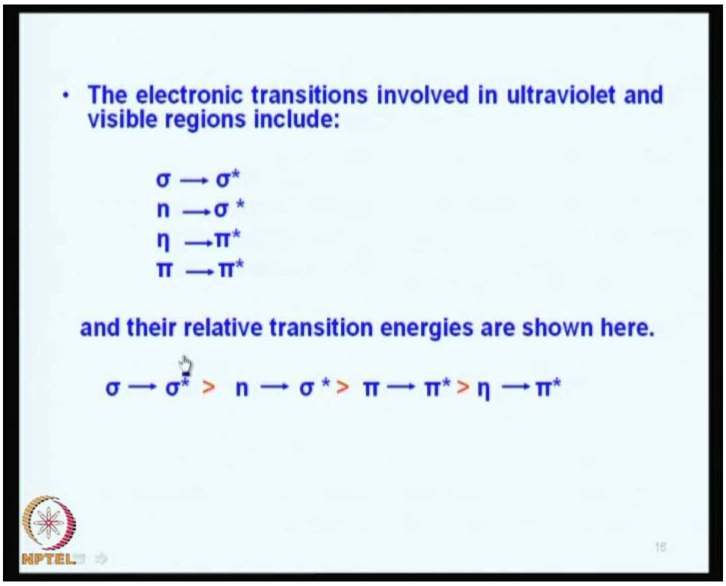

- The electronic transitions involved in ultraviolet and visible regions include:

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

and their relative transition energies are shown here.

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

So, in the end, whatever you see in general if you plot a visible spectrophotometer, so the transitions expected are sigma to sigma star into sigma star pi to pi star and n to pi star. So, let us look at the absorption. That is how we characterize these absorbance.

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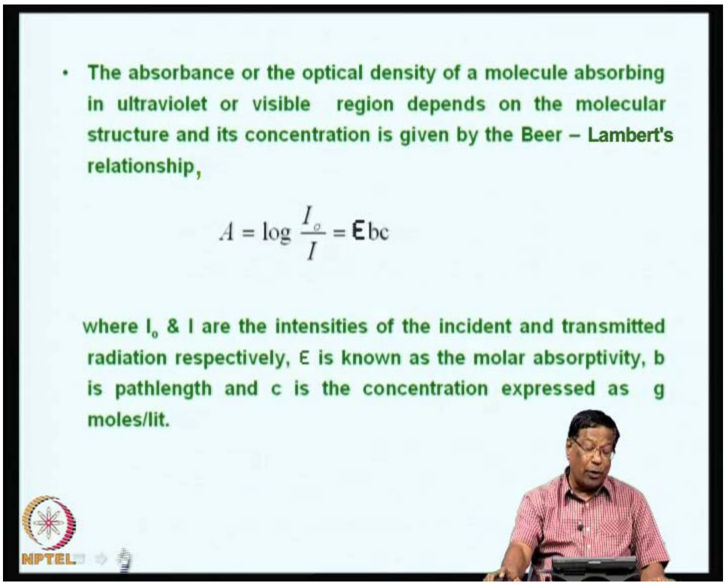

- The absorbance or the optical density of a molecule absorbing in ultraviolet or visible region depends on the molecular structure and its concentration is given by the Beer – Lambert's relationship,

$$A = \log \frac{I_o}{I} = \varepsilon bc$$

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

For example, the absorbance or the optical density of a molecule absorbing in ultraviolet or invisible region depends on the molecular structure and its concentration is given by Beer Lamberts' law, that is a is equal to log of I 0 by I up is equal to epsilon b and c, where I 0 and I are the intensities of incident and transmitted radiation, e is known as the molar absorptive, b is the path length and c is the concentration expressed as gram moles per liter.

Now, we will come back to this, but what I want you to concentrate on this term epsilon e, that is molar absorptive. Now, each molecular orbital involves as you know that when transition, electronic transition takes place, the electron gets excited to next higher energy level and then, the transition probability is given by this molar absorptive. The molar absorptive is very high. Then, the transition will be occurring predominantly. If it is very less, you may not see any absorption peak at all.

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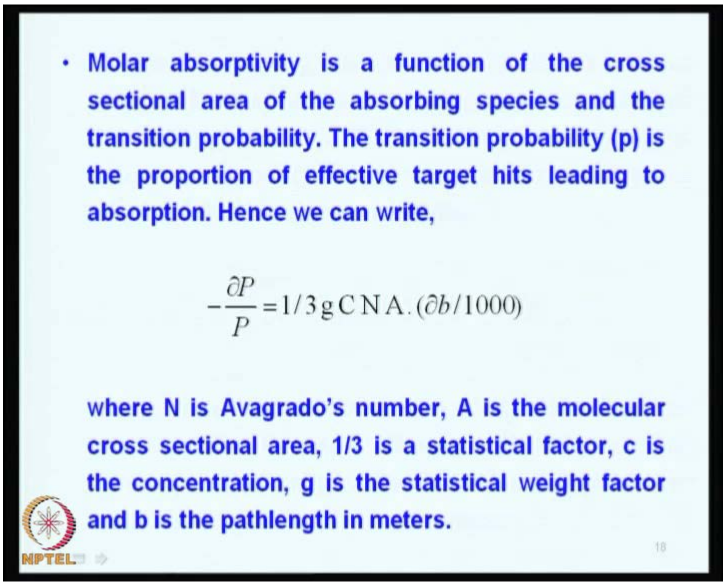

- Molar absorptivity is a function of the cross sectional area of the absorbing species and the transition probability. The transition probability (p) is the proportion of effective target hits leading to absorption. Hence we can write,

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

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, the molar absorptive is basically a function of the cross sectional area of the absorbing species and the transition probability. So, the transition probability is the proportion of effective target hits leading to absorption, that is you are taking a substance material and then, you are passing the radiation and then, the radiation has to go and hit a molecule. The more number of molecules it hits, the more is the transition probability.

That transition probability can be written as there minus delta p by p is equal to one-third, c is concentration, N is Avogadro's number, A is the molecular cross sectional area and b is the path length and 1000 comes from the conversion into moles per liter. So, here you can see that N is Avogadro's number, A is the molecular cross sectional area, one-third is the statistical factor because they are all spread in three-dimensional area and c is the concentration.

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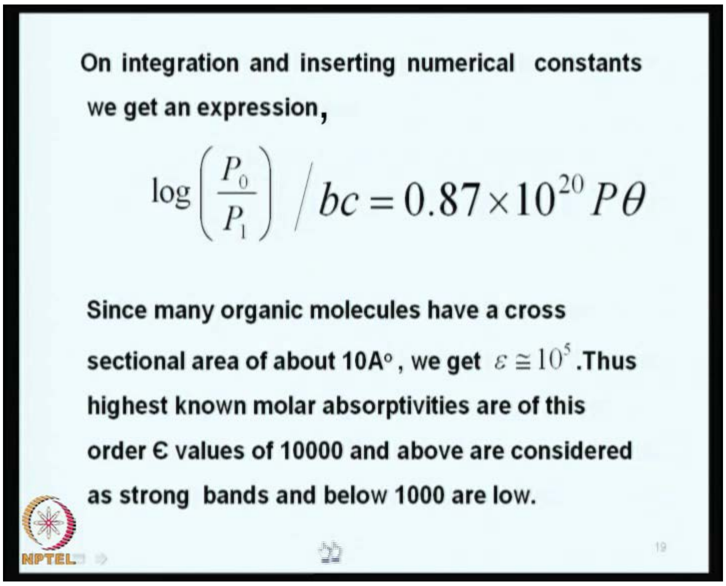

On integration and inserting numerical constants we get an expression,

$$\log\left(\frac{P_0}{P_1}\right) / bc = 0.87\times10^{20} P\theta$$

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.

Now, on integration and inserting numerical constant, we normally get A. Do this kind of integration and then, what do we see here is approximately a value of about 0.87 into 10 raised to 20 into p into theta. Since, many organic molecules have a cross sectional area of about 10 angstroms, the highest value you will end up with for epsilon is about 10 raised to 5 and thus, highest known molar absorptivity’s are also of this order. In general, 10,000 values, epsilon values we consider it as high absorbents, that is strong bands and below 1000 are usually considered as low band, lowest bands.

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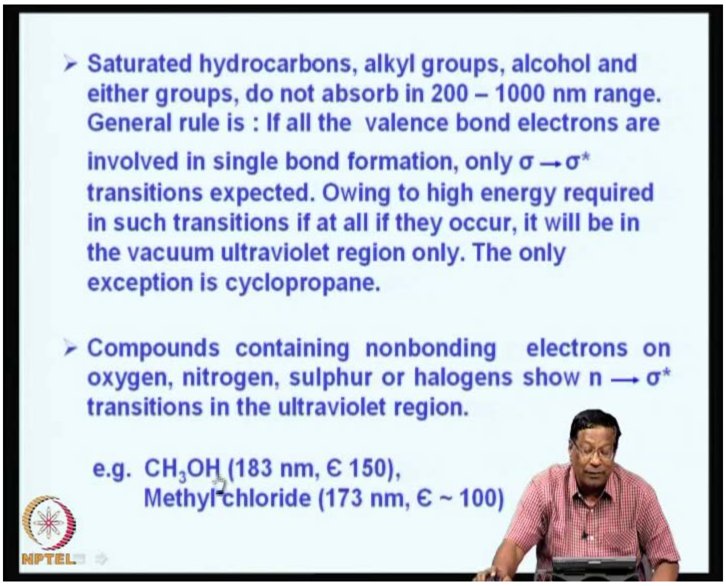

- Saturated hydrocarbons, alkyl groups, alcohol and either groups, do not absorb in 200 – 1000 nm range. General rule is : If all the valence bond electrons are involved in single bond formation, only $\sigma \rightarrow \sigma^*$ transitions expected. Owing to high energy required in such transitions 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 $n \rightarrow \sigma^*$ transitions in the ultraviolet region.

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

Now, saturated hydrocarbons, alkyl groups, alcohol and either groups, etcetera do not absorb in 200 to 2000 range that is 200 to, sorry 200 to 1000 nanometer range. The general rule is if all the valence bonds electrons are involved in a single bond formation only, this sigma to sigma star transition are expected as I have told you earlier. Now, going to high energy required in such transition if at all if they occur, it will be only in vacuum ultraviolet region, the only exception is cyclopropane which shows a lambda max around 177 nanometers.

Compounds, other compounds containing non-bonding electrons on oxygen, hydrogen, nitrogen, halogens etcetera, they also show n to sigma star transitions in the ultraviolet region. For example, you can see here I have written methyl alcohol. It shows a lambda max of about 183 nanometer epsilon is only 150. That means it is not. You can conclude that it is not a very strong bond. That means the absorption peak may not be visible in the ultraviolet range around 183 nanometer, even though oxygen has got non-bonding electrons. Similarly, methyl chloride, this also shows a peak around 173 nanometers, but epsilon value is 100.

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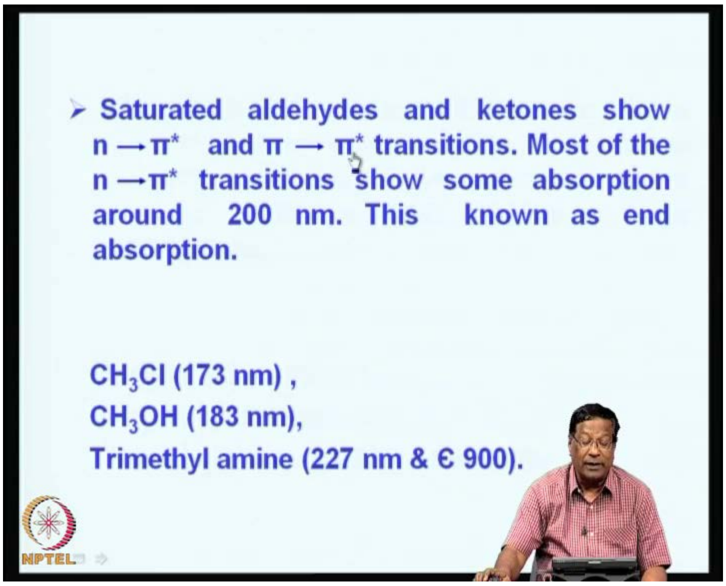

- Saturated aldehydes and ketones show $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. Most of the $n \rightarrow \pi^*$ transitions show some absorption around 200 nm. This known as end absorption.

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

Saturated aldehydes and ketones usually show n to pi star and pi to pi star transitions. Isn’t it? This is how we represent two electrons. Generally, nitrogen we represent as two non-bonding electrons and such compounds will show n to pi star transitions.

Now, if a compound contains only the sigma bonds, for example CH4. You draw it like there are four hydrogen nuclear atoms reacting with carbon. They form four single bonds, that is all are sigma. So, here you can expect only sigma to sigma star transitions. Suppose a compound is having a double bond like in an ethylene group. There is one sigma bond that is sigma. It can show sigma to sigma star and then, there is one pi bond which can show pi to pi star transitions. This is easy to understand.

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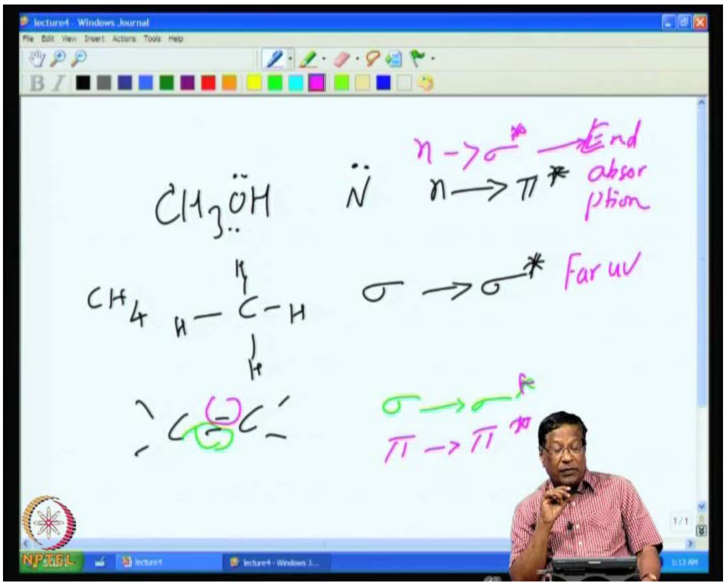

So, what do we expect is in compounds like this hydro carbons, no transitions, only sigma to sigma star. They are all in the far UV range and in some compounds here, n to sigma star, this also could show n to sigma star transition, but this also requires very high energy. Therefore, it will show only in the end as end absorption. What do we want to say is basically all compounds whether they contain sigma to sigma star or n to pi star transition, they show some absorbance in the UV range, especially where 180 to 200 range. This is known as end absorption.

Now, you can see here that we are seeing this CH3, CL173 nanometers. CH3OH will show 183 nanometers and Trimethyl amine will show 227 nanometer peak whereas, its absorption, molar absorptivity is about 900. Now, you can see that this is a slightly stronger band because it is around 1000, but it is still not very strong band.

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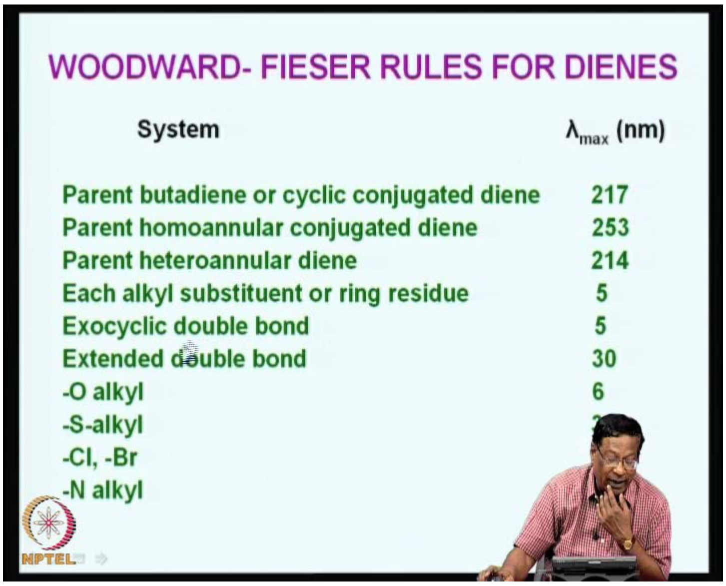

WOODWARD- FIESER RULES FOR DIENES

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	3
-Cl, -Br	
-N alkyl	

Now, we can consider Woodward and Fieser have observed ultraviolet spectrum for number of compounds, more than 1000 compounds and they have formulated a small set of rules in which you can compute at what level, you can expect that peak. For example, these substances will show lambda max at 217.

For example, this is diene. What is a diene? A diene is a substance here. There is one double bond and another double bond separated by a single bond and this is known as a diene. So, such compounds there is a possibility that the electron can get labialized somewhere here and the energy of absorption would come down.

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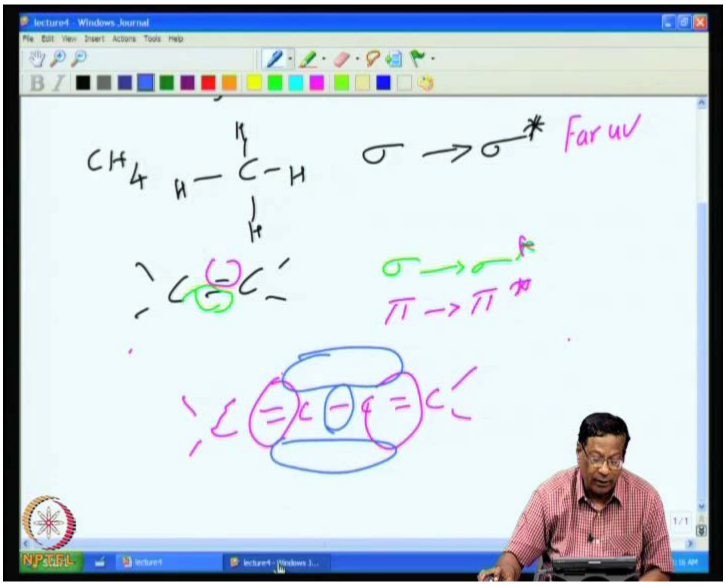

So, what we are looking at is a set of rules which can tell us where the bond can be expected. For example, if you have 13 butadiene, the parent butadiene is cyclic. Conjugated diene will show an absorption peak of about 217 nanometers. You can see that we have 217 nanometers as the basic peak.

Now, you can have homoannular conjugated diene. I will explain to you what it is. If a substance is having double bonds in the same ring like this, then it is known as homoannular diene and if a substance is having double bonds outside the rings, then it is known as hetroannular diene. So, homoannular diene conjugated diene would show a peak at 253 nanometer and then, a parent hetroannular diene would show at 214. Each alkyl substituent or a ring residue would add another 5 nanometers to the peak. That means the peak will be shifted by 5 nanometer if it has got an alkyl substituent and exocyclic double bond also will shift the lambda max to by another 5 units. Then, if there are extended double bond, it will immediately shift to 30 nanometers immediately.

So, there are extended double bonds will give 30 nanometers. Suppose, there is alkyl substituent, then it shifts lambda max to 6 nanometer sulphur or s alkyl groups, that is containing sulphur it will shift to 30 nanometers and chloride bromide substituents. If they are there, again you can expect another 5 nanometers and n alkyl substituents will shift it by 60 nanometers.

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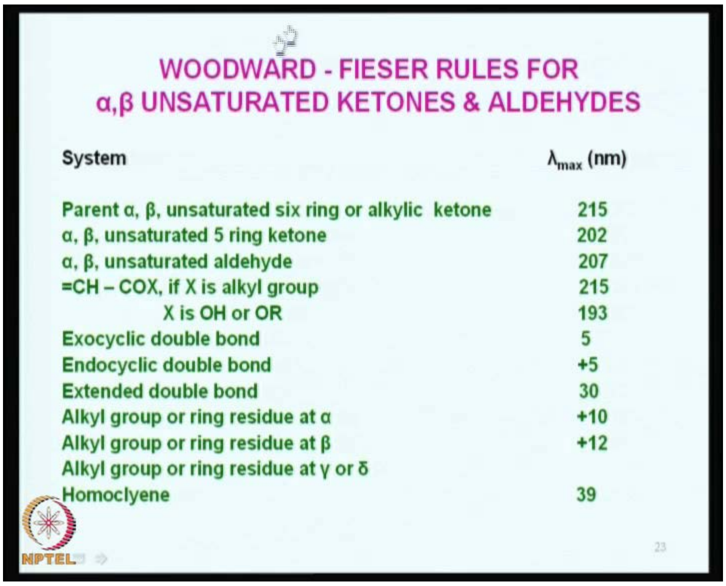

WOODWARD - FIESER RULES FOR α,β UNSATURATED KETONES & ALDEHYDES

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, let us look at aldehydes and ketones. What happens if the compound is aldehyde or a ketone? Now, the parent compound will have 215 nanometers. Suppose, the alpha-beta unsaturated ketone is in five rings, five membered rings, then the base b could appear at 202 nanometers. Suppose, if it is an alpha beta unsaturated aldehydes instead of a ketone, then you can expect the peak to be at 2 naught 7 nanometers. Then, if it is a compound like this substitution COX and X is an alkyl group base peak is at 215 and its X is OH, that is hydroxyl group or group that is something like an ester group here, then it is 193 nanometers.

Exocyclic double bonds as I have mentioned earlier that is double bonds conjugated, but not in the same ring. That will give you peak 5 nanometers away from the expected value and endocyclic double bond also will shift it to another 5 nanometers whereas, an extended double bond will shift it to 30 nanometers.

Suppose an alkyl ring or ring residue at alpha position is there, then it shifts the lambda max by 10 nanometers. Suppose, I mean if it is at beta, then it is 12. Suppose, it is gamma or delta, then it is 18 nanometers and then, if it is homocylene, then it is homodyene, it is 39 nanometers.

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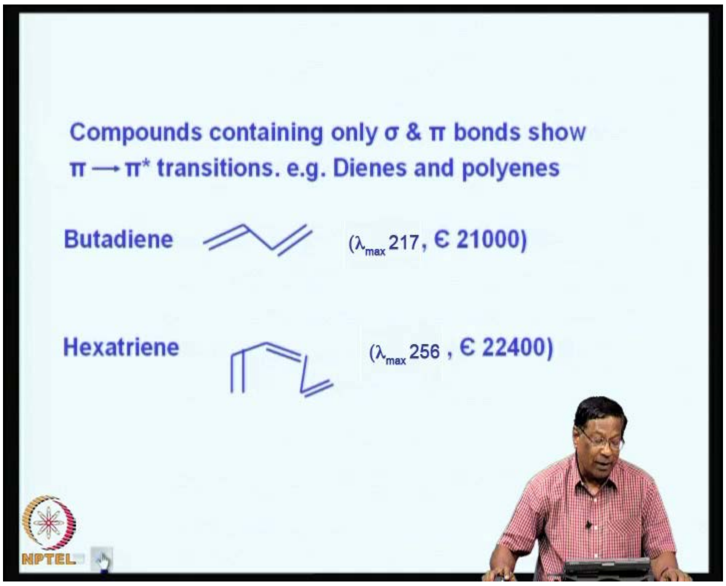

Compounds containing only σ & π bonds show $\pi \longrightarrow \pi^*$ transitions. e.g. Dienes and polyenes

Butadiene (λ_{max} 217, ϵ 21000)

Hexatriene (λ_{max} 256 , ϵ 22400)

Now, these are different areas where you can expect compounds containing only sigma and pi, bonds show pi to pi star transitions because as I have already told, it is the end absorption and another is end to pi star. Only two bonds you can expect. These are in dienes and polyenes. For example, butadiene which this I have here and butadiene will show 217 nanometer, but epsilon is 2000, that is it means it is a very strong band.

Suppose, it is hexatriene 123 double bonds, that is triene and 1 2 3 4 5 6 bonds are there 6 carbon atoms and it shows a lambda max at 256 as expected because more number of double bonds, more would be shifted towards the lambda range and epsilon would be still higher because the transition between the labialized electron among the pi orbitals would be higher in this case. So, the lambda epsilon also value would be very high.

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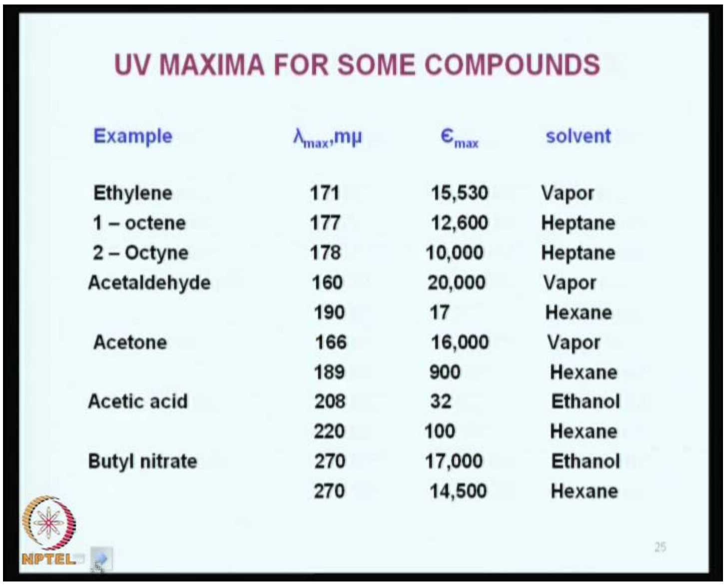

UV MAXIMA FOR SOME COMPOUNDS

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

Now, you can see that for ethylene, the lambda max is at 171 nanometers whereas, epsilon is of the order of about 15530 nanometers, but it is a pure ethylene, that is vapour. It shows at 1 octene. Suppose, it is 1 octene, you would know, you would appreciate that 1 octene is where ethylene is a vapour. 1 octene is a liquid. So, 2 octyne is another liquid. So, its molecular weight is high, but here molecular weight is very less. So, the lambda max would appear at 171. If the molecule is larger, it would shift to slightly longer wavelength.

Similarly, 2 octyne and the epsilon values will also shift to higher values and I have listed some of the substances, vapours etcetera in which solvent, the substance, the spectra has been taken. For example, for acetone, you can see 166 and 16000 in the vapour form whereas, if you take the same spectrum in hexane, you will see the peak at 189. Almost 23 nanometer shifted and the e value, that is epsilon molar absorptivity is also very less.

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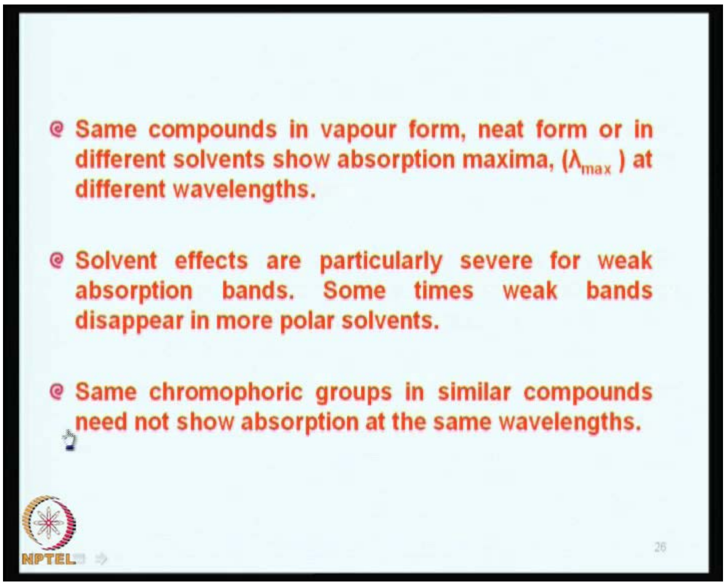

- Same compounds in vapour form, neat form or in different solvents show absorption maxima, (λ_{max}) at different wavelengths.
- Solvent effects are particularly severe for weak absorption bands. Some times weak bands disappear in more polar solvents.
- Same chromophoric groups in similar compounds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

Similarly, other compounds whether in ethanol, hexane and vapour or some other solvent, they would always show some amount of shift in the lambda max depending upon the solvent. So, we can generalize our observations like this that same compounds in vapour form, neat form or in different solvents show absorption maxima at different wavelengths, that is you take the same substance in gaseous form and it will show some lambda max in solvent form. It will be shifted slightly towards the end, that is at longer wavelengths and less sharp peak and if you take still thicker viscosity solvent, then again it will shift to still longer wavelength, but the peaks will lose its, all peaks will lose their sharpness.

Now, solvent effects are particularly severe for weak absorption bands, especially if the band is very small. It is very difficult to detect the small changes and sometimes weak bands disappear in more polar solvents also. This effect is also known and observed.

So, the same chromophoric groups in similar compounds, they need not show absorption at the same wavelength. This is the point we have to remember because assuming this functional group is same, but they are in different compound. For example, take a chromophoric group as chloride, methyl chloride, ethyl chloride, propyl chloride, butyl chloride and then pethyl chloride, hexyl chloride. So, the peak sigma to sigma star peak would keep on shifting to a state longer wavelength region whereas, you expect all chlorine should give you the spectrum at the same point. No, it does not happen. It always shifts depending upon the molecular way. Therefore, we always say that the same chromophoric groups in similar compounds, they need not show absorption at the same wavelength. It is very important for us to understand this concept.

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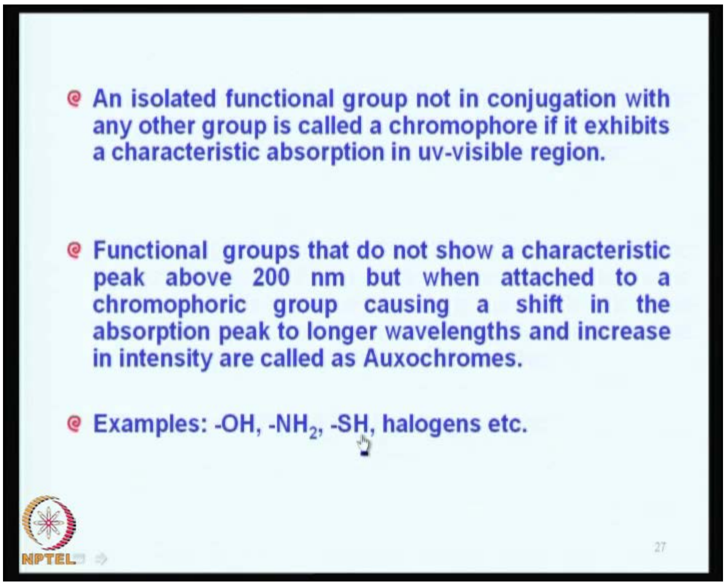

- An isolated functional group not in conjugation with any other group is called a chromophore if it exhibits a characteristic absorption in uv-visible region.
- Functional groups that do not show a characteristic peak above 200 nm but when attached to a chromophoric group causing a shift in the absorption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

So, suppose an isolated functional group not in conjugation with any another group we have, then it is called chromospheres. Just now I referred to that whereas, where we say chlorine in a compound is called chromospheres if it exhibits a characteristic absorption in the visible region.

Suppose, the functional group does not give you an absorption peak, but it helps if there is some other functional group that is like another chromophore is there which can show absorption, that is a chromophore on its own will give you absorption peak whereas, an auxochrome is one which helps the chromophore, but auxochrome does not give the peak on its own. So, you will see that it helps to shift the peak to longer wavelength and increase in intensity. This is another aspect of the action of auxochromes.

So, for example, you can see that hydroxyl groups NH2 groups, that is amine and SH groups (( )) halogens etcetera, all these things are, they do not represent a peak on their own. That means they do not generate a peak on their own because they are not chromophores, but if there is another chromophore, they will shift it to these functions. Groups will help it to shift it to the longer wavelengths.

Now, again I am coming back to this. You can look at alpha beta unsaturated acids and esters, that is suppose if you have a beta mono substituted base value would be 2 naught 8. Suppose, this is alpha beta or beta beta disubstituted, the shift would be the lambda max would be occurring at 253 nanometer and alpha beta disubstituted. It shows a peak at 214, extended double bond as usual. It shows a peak at 30 nanometer exocyclic double bond always 5 and end cyclic double bond in 5 or 7 member ring always 5. So, gamma or delta substituted alkyl group is 18.

You would appreciate that all these numbers have been arrived at, they have been looking at thousands of organic compounds whose spectra have been taken and the average values have been put up for this work. The author, the Woodward Fieser, they were awarded the Nobel Prize and you can see that this is another alpha beta unsaturated ketone compounds containing carboxyl group in conjugation with ethylene group. This is the double bond, this is the carboxyl group and here you can see aldehyde 210, ketonic 210, alpha substituent is 10, beta substituent is 5, exocyclic ring is 5, c double bond o and c double bond c is minus 10, that is if it is there in the 5 membered ring, if it is only in c double bond c is in 5 membered ring, you can add 5 nanometers and Enolic OH you can see the effect auxochrome, that is 35 nanometers in alpha or beta substituent's. Then, suppose if it is alpha chloro, you would get 15 nanometers extra and if it is beta bromo, the lambda max will shift to 23 nanometers.

Now, you see that in aromatic substances, you would get there are only pi to pi star and sigma to sigma star bonds, but you would not see very specific peaks, but you will see the strong absorption bands at 184 nanometer with 47000 molar extinction, molar coefficient. Another at 2 naught 2 and a series of weak bands between 230 and 270. These are associated with the vibrational effects on pi to pi star transitions. These fine structure bands are susceptible to solvent effect, especially alcohols.

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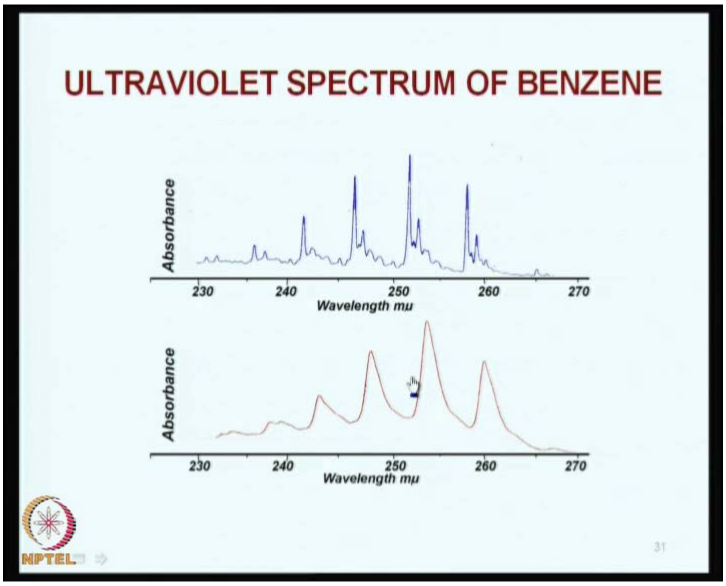

ULTRAVIOLET SPECTRUM OF BENZENE

Now, I will show you the spectrum like this, benzene is like this. You will see such sharp lines whereas, if you take this in vapour form this is in solvent form, that is liquid, you can see the peaks are not so sharp here, but peaks are rather wide and peaks are sharp here and peaks are not so sharp here.

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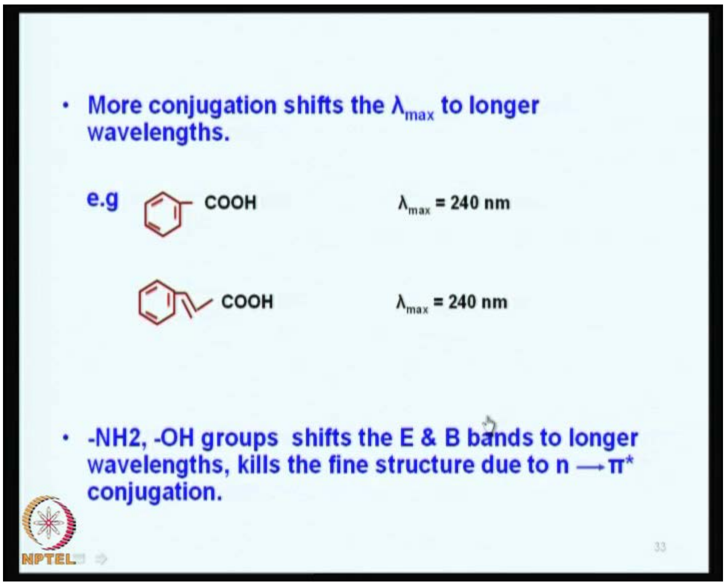

- More conjugation shifts the λ_{max} to longer wavelengths.

e.g COOH λ_{max} = 240 nm

COOH λ_{max} = 240 nm

- -NH2, -OH groups shifts the E & B bands to longer wavelengths, kills the fine structure due to n $\longrightarrow \pi^*$ conjugation.

What we will do is we will take a look at other absorption spectrums in the next class that is where we can really calculate the absorption peak where we can expect it and we will compare then with the actual peak, where it is obtained in comparison with the calculated value. It is very exciting very interesting.

We will meet again. Thank you very much.