Application of Spectroscopic Methods in Molecular Structure Determination
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Lecture – 34
Ultraviolet Spectroscopy or Electronic Spectroscopy

Hello, welcome to module 34 of the course on Application of Spectroscopic Methods in Molecular Structure Determination. We will continue with the Ultraviolet Spectroscopy in this module. Also in the earlier module, we talked about Ultraviolet Spectroscopy of olefinic compounds and carbonyl compounds, the effect of conjugation, the effect of auxochrome and all those things we discussed.

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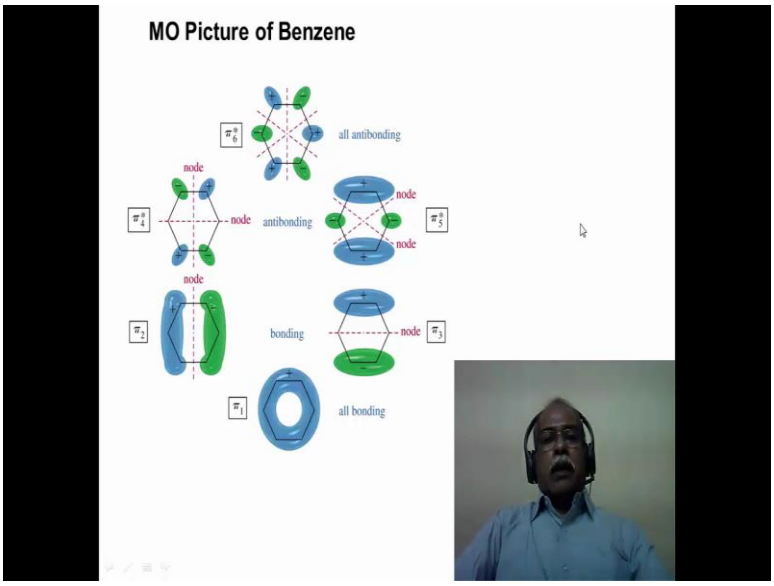

MO Picture of Benzene

We will start with the aromatic system in this particular module. Aromatic Chromophore is an important chromophore, which can be readily identified by Ultraviolet Spectroscopy. This is a pictorial representation of the molecular orbitals of Benzene itself and the first 3 molecular orbitals of the bonding molecular orbitals. The top 3 molecular orbitals are the anti bonding molecular orbitals. The first pi 1 molecular orbital does not possess any node, where as the second and the third molecular orbital possess.

One node which is represented by the red dotted line, it passes through these atoms which are the nodal point, passes through the midpoint of this carbon carbon bond and this carbon carbon bond, which is the nodal point in this particular case. As you go up in the molecular orbital picture, the number of nodes increases, this has 2 nodes each for example, these are degenerate energy levels, in other words pi 2, pi 3 are degenerate and pi 4 and pi 5 all also degenerate and these are antibonding molecular orbital finally, pi 6 is an antibonding molecular orbital of highest energy in this particular case.

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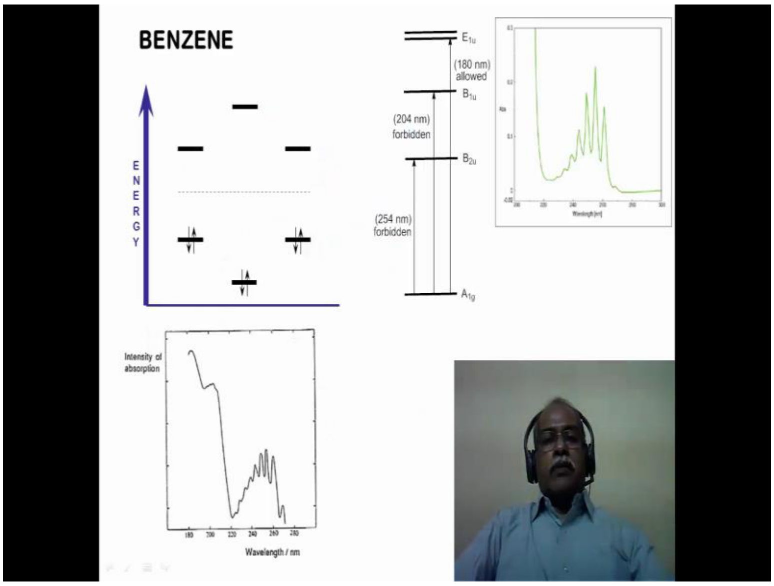

In terms of the electron, filling the degenerate levels gets filled with the first. The lowest electronic state gets filled and then the degenerate level gets filled and if were to talk about the electronic transition of Benzene, you can talk about the pi to pi star transition between these two levels or between these two levels or between these two levels and these two levels.

One can also talk about the pi to pi star level, which is corresponding to this particular level here. In other words, Benzene is expected to show only one line, if all the energy levels are going to be degenerate and the distances are the energy gap between them or equivalent in terms of this energy difference is equivalent this energy difference because of the degeneracy and so on.

However, Benzene gives distinctly three different types of absorption band, as it is shown here. This is corresponding to the Benzene electronic spectrum; there is a band around 184 nano meter or so. There is another band around 200 nanometer, which is this particular band and finally, there is a third band which is a vibrational structure is very clearly seen.

The fine lines that you see in the spectrum are the essentially due to the vibration level of the Benzene electronic transition. So, this is explained by taking this particular energy level diagram. Where you have various electronic levels of the pi system all of them correspond to pi to pi star. Some of them are symmetry forbidden and some of them are allowed. The 180 nanometer is the most intense transition, which is the symmetry allowed transition, whereas the 204 nanometer and 254 nanometer are forbidden in nature. So, the forbiddeness essentially causes the decrease in the intensity of that particular transition in the benzenoid compounds.

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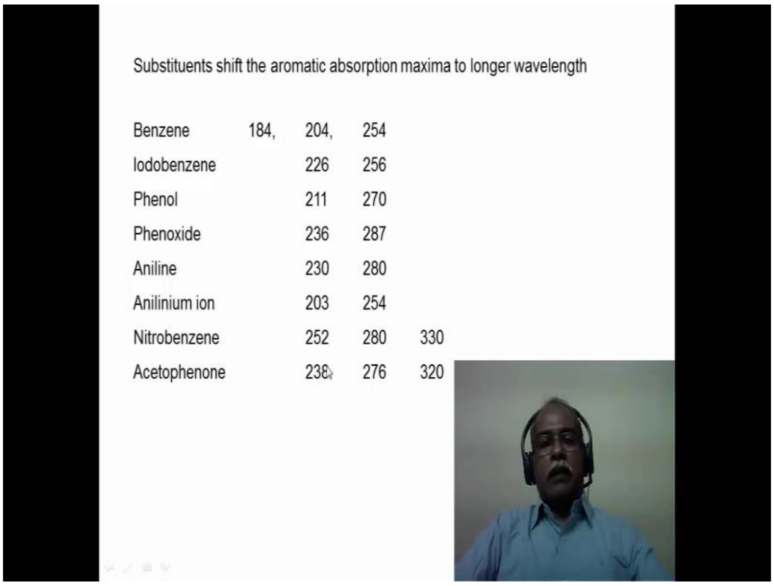

Substituents shift the aromatic absorption maxima to longer wavelength

Benzene	184,	204,	254	
Iodobenzene		226	256	
Phenol		211	270	
Phenoxide		236	287	
Aniline		230	280	
Anilinium ion		203	254	
Nitrobenzene		252	280	330
Acetophenone		238	276	320

Now, when Benzene is substituted with auxochromes like for example, iodobenzene, phenol, phenoxide and so on. The functional groups are essentially auxochrome, there are two effects that it does. One is that, it shifts the aromatic absorption maxima to longer wavelength, as we can see from Benzene. It is going from 204 nanometres to 226 nanometer. By the time, you come to the nitrobenzene, for example, the pi to pi star transition goes to 254 nanometer. It is interesting to see that the aniline essentially shifts the Benzene absorption by auxochromic effect of the ammonium functional group from 204 nanometer to 230 nanometer essentially, because of the participation of lone pair of electron on the nitrogen on to the aromatic ring.

However, if the lone pair protonated the spectrum essentially appears like a Benzene spectrum. This is 204 and 244 where is anilinium ion is essentially like a Benzene kind of a structured 203 and 254. In other words, the auxochrome effect is diminished once the nitrogen lone pair gets protonated in the case of aniline to anilinium ion. So, this is essentially illustrate the auxochrome effect of the various substitutions that are present in the Benzene ring causing the shift of the wavelength to go to higher wavelength region in the case of pi to pi sub transitions of Benzene.

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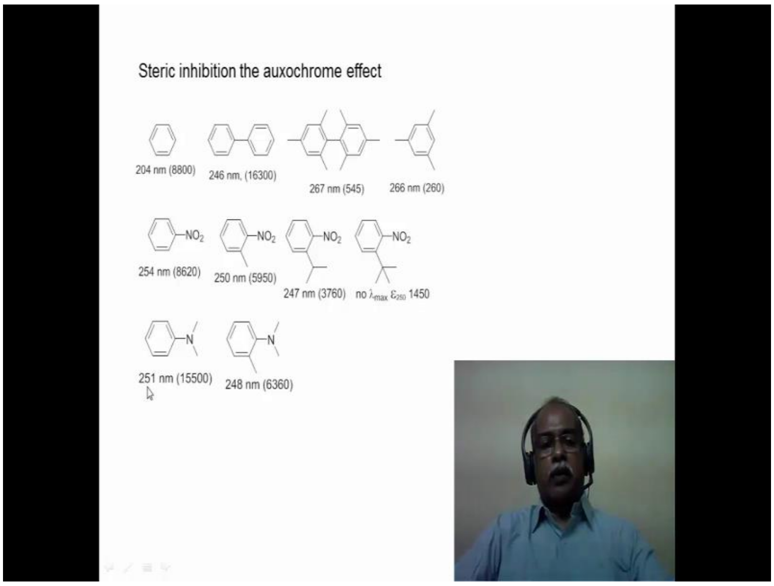

Steric inhibition the auxochrome effect

204 nm (8800)

246 nm, (16300)

267 nm (545)

266 nm (260)

254 nm (8620)

250 nm (5950)

247 nm (3760)

no λ_{max} ε_{250} 1450

251 nm (15500)

248 nm (6360)

However, steric effects can inhibit the auxochrome effect. That is what is shown in this particular system. If we take Benzene, it has absorption of 204 nanometer. On the other hand, if you take biphenyl the corresponding transition aromatic pi to pi star transition is shifted to 246.

In other words, one of the phenyl group acts as an auxochrome group for the other phenyl group causing the transition to go to at longer wavelength of 256. Now, if we have additional methyl groups that also can have the auxochromic effect. So, it is further shifted to 267 nanometer but this is expected to have even much longer wavelength. But that longer wavelength effect is not seen here clearly because this essentially behaves like trimethylbenzene only.

The effect of this particular auxochrome namely the trimethyl substituted phenyl auxochrome is not felt on this particular ring or vice versa. In other words, this is like a simple trimethylbenzene spectrum is what is seen. This is because you have the ortho substituents, which are going to make these to ben phenyl ring out of plane with respect to each other. So, the delocalization of electron, extended delocalization of electron is not going to take place because of the steric inhibition of the methyl groups, which are present in the ortho functional group.

This is better illustrated in the case of nitrobenzene, nitrobenzene has an absorption maxima 254 nanometer, corresponding to the lowest energy pi to pi star transition. For example, when introduce a methyl group, it is shifted to 250 nanometer and the intensity is also reduced to 5950 from 8620, which is the epsilon value. The numbers that are given in the paranthesis are the epsilon value or the extinction coefficient value of this transitions.

Now, when you have an isopropyl group that is even bulkier group, which puts the NO2 out of plane with respect to the aromatic rings, the auxochrome effect will be felt only if the no two is in plane with the aromatic system for the electron withdrawing effect to take place. If the nitro functional group is orthogonal or at a different angle with respect to the dihedral angle of the nitro group and the plane of the Benzene ring is different, then the effect will not be felt. In fact, the effect is diminished from 250 to 257 nanometer, when you have a tertiary butyl group

Finally, it not even seen as the lambda max, it appears as the shoulder in the 200 nanometer band and the epsilon value considerable decreases from 3660 to 1450 or so. At 250 nanometer range of this particular spectrum, if you take n and dimethylaniline, the nn dimethylaniline amino functional group is the auxochrome. When you introduce an ortho methyl substituent, the nitrogen lone pair cannot be in plane with aromatic ring. So, the delocalization disinhibited, steric inhibition of delocalization is what takes place. So, as a result of that the effect is hypsochromic shift is what is being seen to go to a lower wavelength region from 254 to 248 nanometer in this particular case.

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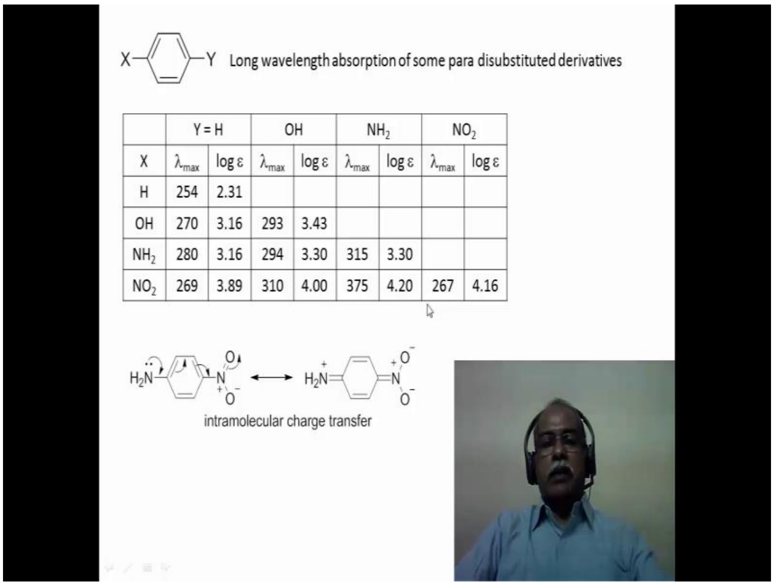

X–C6H4–Y Long wavelength absorption of some para disubstituted derivatives

	Y = H		OH		NH_2		NO_2	
X	λ_{max}	log ε	λ_{max}	log ε	λ_{max}	log ε	λ_{max}	log ε
H	254	2.31						
OH	270	3.16	293	3.43				
NH_2	280	3.16	294	3.30	315	3.30		
NO_2	269	3.89	310	4.00	375	4.20	267	4.16

intramolecular charge transfer

On the other hand, if the two functional groups are not sterically hindered and they are further away as in the case of the para disubstituted derivative and if one of them is an electron donating group and another one is an electron withdrawing group. You can observe, intramolecular charge transfer band in the aromatic system. That is what is illustrated in this particular table. If you look at the table carefully, the auxochrome effect is very clearly seen going from Benzene at 254 to phenol 270, aniline 280 and nitrobenzene 269 measured. In this particular case, I believe in a ethyl alcohol as a solvent and the second substituent not only adds to the bathochromic shift of this system.

On the other hand, it not only adds to the bathochromic shift of the pi pi star transition, when you have an electron donating and electron withdrawing functional group in conjugation with each other, we can write a resonance structure, which corresponds to the charge transfer structure that is one of the reason. When you take for example, either the para nitrophenol, which is this particular molecule or para nitroaniline, which is this particular molecular, here the wavelength of pi pi star transition essentially comes to the visible region.

In other words, para nitrophenol is a yellow colors substance, para nitroaniline is a deeper yellow color substance whereas, phenol aniline and nitrobenzenes are practically colorless. I mean nitrobenzene is sort of pale yellow but phenol and aniline are practically colorless liquids and the color essentially is happening because of the shift of the wavelength, longer wavelength region which is essentially because of the intramolecular charge transfer, which is represented by the canonical structures that are shown here.

In addition to the bathochromic shift, one can also see the hyperchromic shift in terms of the epsilon value increasing considerably as you go from Benzene to para nitro para amino nitrobenzene. For example, as a maximum hypochromic shift in terms of the epsilon value increasing by two orders of magnitude corresponding to the Benzene itself.

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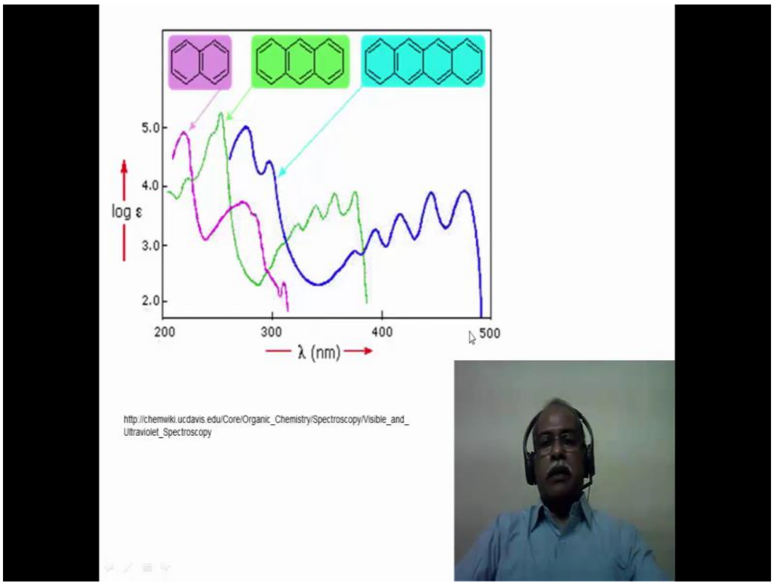

http://chemwiki.ucdavis.edu/Core/Organic_Chemistry/Spectroscopy/Visible_and_Ultraviolet_Spectroscopy

Now, as we go from the Benzene to higher polycyclic aromatic ring system, there is a progressive shift of the pi to pi star transition in the aromatics system because of the extended conjugation that is present here. This spectrum, this spectra is shown here correspond to naphthalene, which is in the violet color. The green color is the Anthracene spectrum and the blue color corresponds to the Tetracene spectrum. You can see here the longest wavelength pi to pi star transition, all of them show vibrational fine structure. In addition to that, you also have the higher energy bands, which are the pi to pi star transition allowed pi to pi star transition of this aromatic system.

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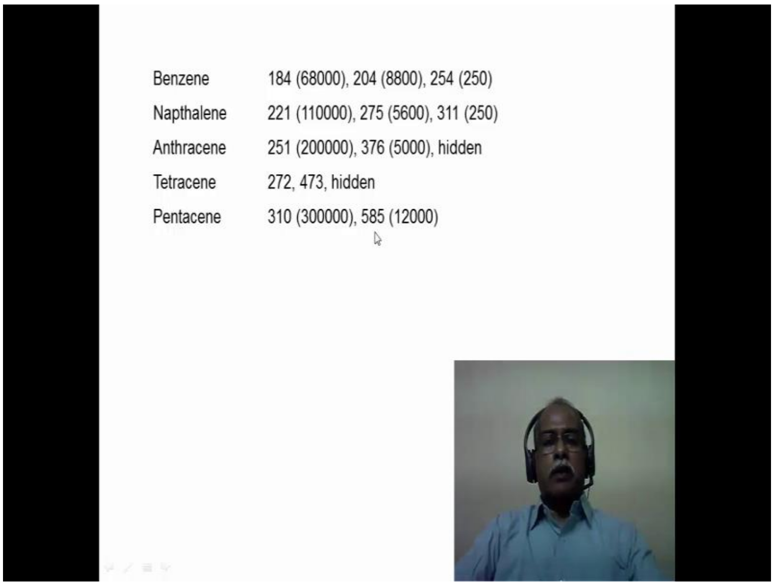

Benzene	184 (68000), 204 (8800), 254 (250)
Napthalene	221 (110000), 275 (5600), 311 (250)
Anthracene	251 (200000), 376 (5000), hidden
Tetracene	272, 473, hidden
Pentacene	310 (300000), 585 (12000)

So, the message here is that as you increase the conjugation and go to linearly fused longer acne systems, the wavelength get shifted from the ultraviolet to near the visible region. So much so that, when you go from the Benzene to Pentacene for example, Benzene is colorless, Napthalene is colorless, Anthracene is also colorless, Tetracene is sort of redish orange in color, Pentacene is also bluish in color. In terms of the color that is appearing, shifting the wavelength of pi pi star transition into the visible region has you progressively increase the conjugation effect of the aromatic system.

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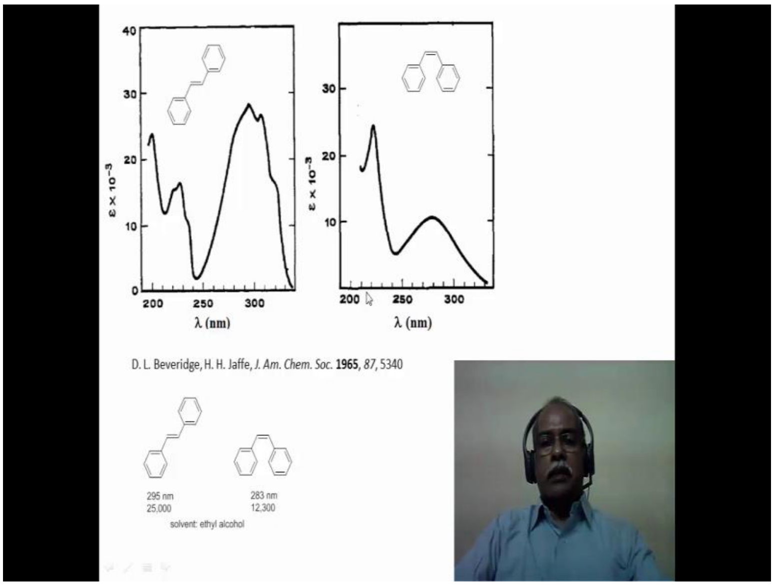

D. L. Beveridge, H. H. Jaffe, *J. Am. Chem. Soc.* **1965**, *87*, 5340

295 nm
25,000

283 nm
12,300

solvent: ethyl alcohol

The conjugation effect is also used for distinguishing the cis and trans isomer. The trans isomer is supposed to have least steric interaction. In other words, this aromatic ring and this aromatic ring can be in conjugation with the pi system. So, through conjugation is possible and that puts the pi to pi star transition at a longer wavelength compared to a cis isomer in the cis isomer because of the steric inrance, both the Benzene rings cannot be in plane with the pi the carbon carbon double bond here. The central carbon carbon double bond because of steric entrance one of the phenyl group will be out of planes. So, the through conjugation is not as effective as in the case of the trans isomer. So, the wavelength of absorption for example, if the trans stilbene is 295 nanometer and also epsilon is almost twice that of the cis isomer. The cis isomer has an absorption around 283 nanometer.

Essentially one can distinguish, if both the isomers are available. Then one can distinguish by comparing the two spectra of this compound. The one that has a longer wavelength region absorbs in the longer wavelength region would be the trans isomer. The one that absorbs at the lower wavelength region will be the cis isomer in this particular case.

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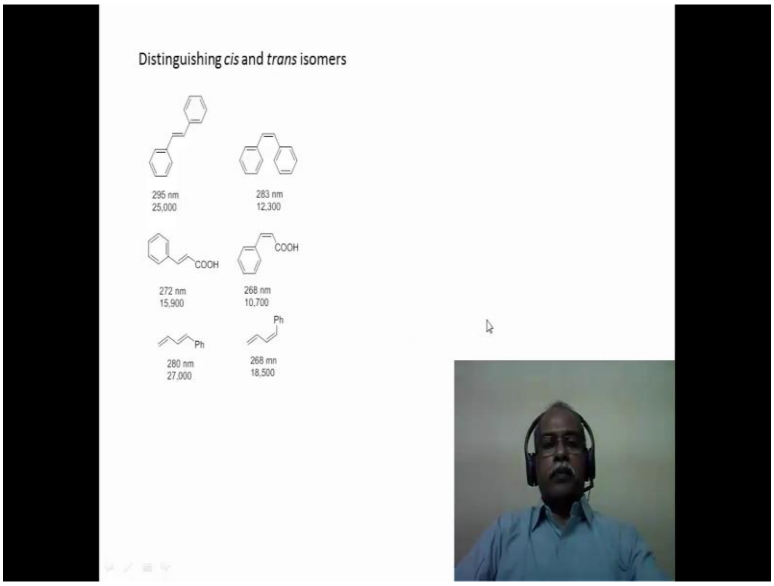

Distinguishing *cis* and *trans* isomers

295 nm
25,000

283 nm
12,300

272 nm
15,900

268 nm
10,700

280 nm
27,000

268 mn
18,500

The cis trans isomer is some distinction is clearly seen in the case of trans stilbene. Cinnamic acid also shows the same effect the trans cinnamic acid is 272 nanometer. Here the extended conjugation is all the way up to the carbonyl functional group of the carboxylic acid. The cis cinnamic acid has an absorption around 285 nanometer. What is even more important is the hypochromic shift of the trans isomer in comparison to the cis cis isomer. In terms of the epsilon value being about 1.5 times more than the epsilon value of the cis isomer. This is the phenyl butadiene. In the case of phenyl butadiene this is the trans isomer and this is a cis isomer. Once again trans isomer has the longer absorption wavelength with the higher extinction coefficient compared to the cis isomer which as a lower wavelength absorption and lower extinction coefficient also.

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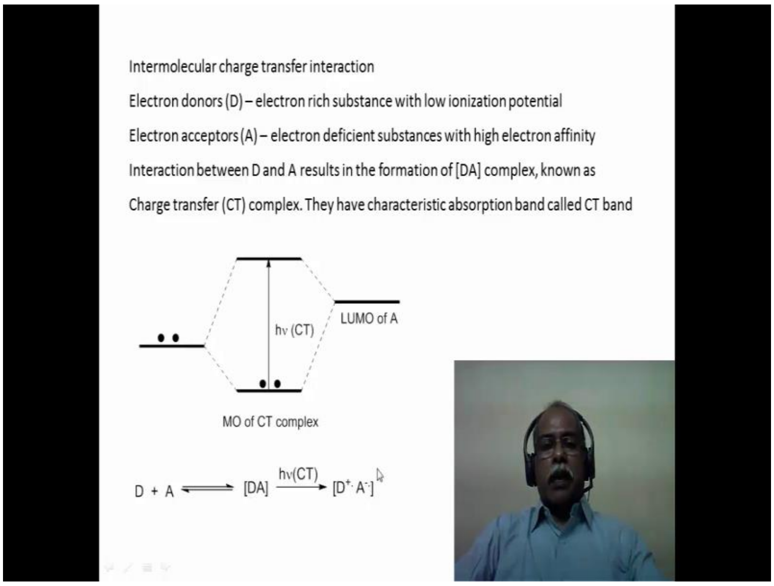

Intermolecular charge transfer interaction

Electron donors (D) – electron rich substance with low ionization potential

Electron acceptors (A) – electron deficient substances with high electron affinity

Interaction between D and A results in the formation of [DA] complex, known as Charge transfer (CT) complex. They have characteristic absorption band called CT band

$$D + A \rightleftharpoons [DA] \xrightarrow{h\nu(CT)} [D^{+\cdot} A^{-\cdot}]$$

Now, apart from the pi to pi star transition, one can also look for inter molecular charge transfer transition. Earlier we saw the example of intramolecular charge transfer, here the charge transfer is essentially the electron hopping from one end of the molecule to the other end of the molecule, that is why it is called by intramolecular charge transfer transition. One can observe the intramolecular charge transfer transition also provided a donar molecule and an acceptor molecule come close to each other. What is an electron donar, electron donar or substances which are electron rich in nature with low ionization potential. Whereas electron acceptors are substances, which are electron deficient in nature with very high electron affinity that is what the characteristic feature of the electron donor and an electron acceptor.

Electron donor should be low ionization potential molecule. Electron acceptor should be high electron affinity molecules, the interaction between a donar and the acceptor can result in the formation of a charged tresser complex. This is a pi complex kind of a system is what we are referring to often. This is essentially known as the charge transfer complex. They have characteristic absorption band called the CT band. Now, if you take the highest occupied molecular orbital of the donor which is this particular, which is a occupied field molecular orbital. So, it is highest occupied molecular after donar the lowest unoccupied molecular orbital of the acceptor which is shown here, which is an empty molecular orbital. When they come in close proximity to each other, there is an energy level which is created, which is characteristic of the molecular orbital of the charge transfer complex itself. So, this will be the homo of the charge transfer complex and this will be the lumo of the charge transfer complex. Essentially, the charge transfer band is the transfer of electrons from the highest occupied molecular orbital of the CT complex to the lowest unoccupied molecular orbital of the CT complex.

So, when the donor and acceptor comes close proximity, there is a charge transfer complex formation, with an accompanying new band corresponding to the CT excitation. When that particular wavelength is used for exciting the molecule, it causes an electron transfer from the donar to the acceptor forming the donar cation radical and an acceptor anion radical. An example of such a process is what is given here.

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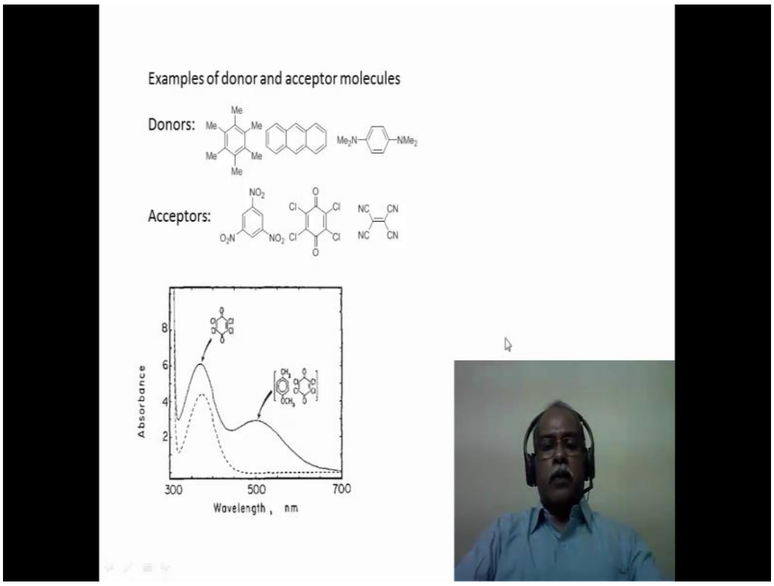

Examples of donor and acceptor molecules

Donors:

Acceptors:

Let us first go with the donors and acceptors. The characteristic molecules, which can act as donor hexamethylbenzene Anthracene, any aromatic system without any electron withdrawing functional group would be a donor. On the other hand, if you have electron donating function of group like the dimethyl amino functional group, that will be a good donor in nature. Electron acceptors will make the molecule electron deficient in nature.

So, quinonoid compound tetracyanoethylene kind of a compound or trinitrobenzene kind of a compound can be acceptors in terms of having high electron affinity in this system.

Now, if you take this spectrum, the first dotted line spectrum corresponds to the chloranil spectrum itself. In other words, chloranil has a absorption around 340 nanometres or so corresponding to the pi to pi star transition of chloranil. When chloranil is mixed with para methoxy toluene, para methoxy toluene is a colorless substance, whereas chloranil is a pale yellow substance. When these two are mixed together, a bright orange color is what is seen in this spectrum and this is because of the formation of a charge transfer complex, the donor, which is a para methoxy toluene and the acceptors, which is tetetrachlorobenzoquinone, which is chlorine for example, this band is a unique band which corresponds to this species that is produced by mixing this with para methoxy toluene. So, this is the charge transfer absorption band corresponding to about 500 nanometer lambda max and this band is not present either in the either of the starting material namely the para methoxy toluene or the para chloranil. For example, this is formed only when these two substances are mixed because of the formation of the charge transfer band corresponding to the formation of the charge transfer complex.

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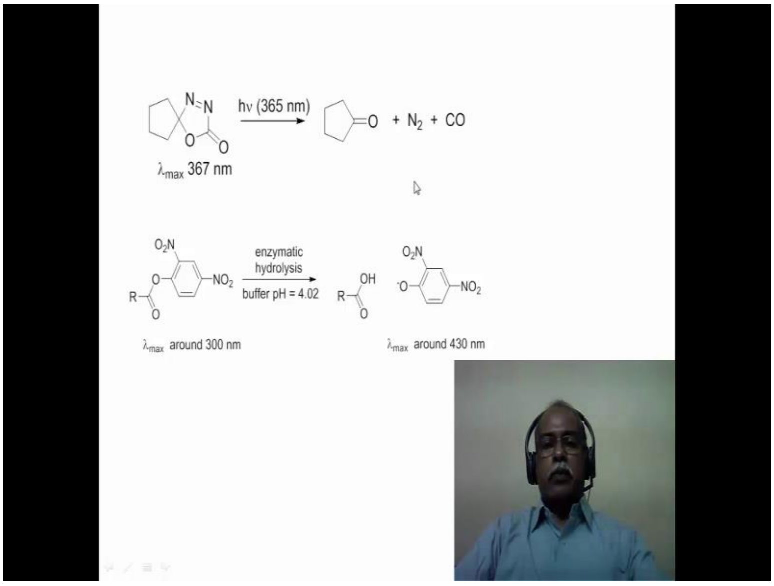

Now, photochemistry is closely associated with electronic absorption spectroscopy for example, electronic absorption spectroscopy and we used very conveniently for following certain photochemical reaction. Let us take the example of this particular photo transformation, this is a spirocyclic compound and the spirocyclic compound has an absorption maxima around 367 nanometer when this molecule is irradiated with the wavelength of radiation 365 it essentially undergoes molecular exclusion of molecule of nitrogen and carbon monoxide to give cyclopentanone. Cyclopentanone does not have any absorption in the region the starting material is absorbing. So, cyclopentanone has an absorption typically in the vacuum ultraviolet region of less than 200 nanometers OR SO.

If one wants to follow the kinetics of this particular reaction, one can take this substance of known concentration, irradiate the substance and follow it by spectrophotometry because the band at 360 nanometer will keep on decreasing in the intensity because of the decomposition of this molecule to cyclopentanone. Cyclopentanone, itself does not absorb in this regions. So, the decrease in the intensity of absorption can be quantified using the Beer Lamberts Law and hence the kinetics of this kind of a photo chemical reaction can be easily studied using ultraviolet visible spectroscopy.

Another application of ultraviolet visible spectroscopy is shown here, enzymatic hydrolysis is often followed or any enzymatic reaction is often followed by spectrophotometry as a technique and illustrative example is shown here the R group may be a large protein or a DNA kind of a molecule to which, a para nitro phenolic 2 4 dinitrophenolic group is at attached for example, if one wants to study the hydrolysis by means of a hydrolytic enzyme this can be done using the spectrophotometry.

The aqueous solution with the buffer of 4.2 is what is taken in this particular case, when the molecule undergoes hydrolysis, this molecule the 2, 4 dinitrophenoxy derivative as an absorption around 300 nanometer not more than 300 nanometer. On the other hand, when it is hydrolysed under the conditions of PH of 4.2 buffer solution of 4.2, this exist has the phenolate anion. The phenolate is a strong auxochrome and it causes the shift to about 100 nanometer shift to (Refer Time: 19:34) the lamda max of this particular species is 430 nanometer. So, as the hydrolysis proceeds the absorption around 430 nanometer will keep on increasing until it reaches the saturation of complete conversion to the phenoxy species here. If you one wants to follow the enzymatic kinetics hydrolysis kinetics, one can just observe this species and quantify the species present in the solution because this species epsilon value can be easily measured by making the pure phenolate from the phenol and the sodium hydroxide solution for example. So, the quantification and kinetic measurements can be easily done using spectrophotometry.

This would be a true application of the quantitative aspect of the spectrophotometry in this particular case.

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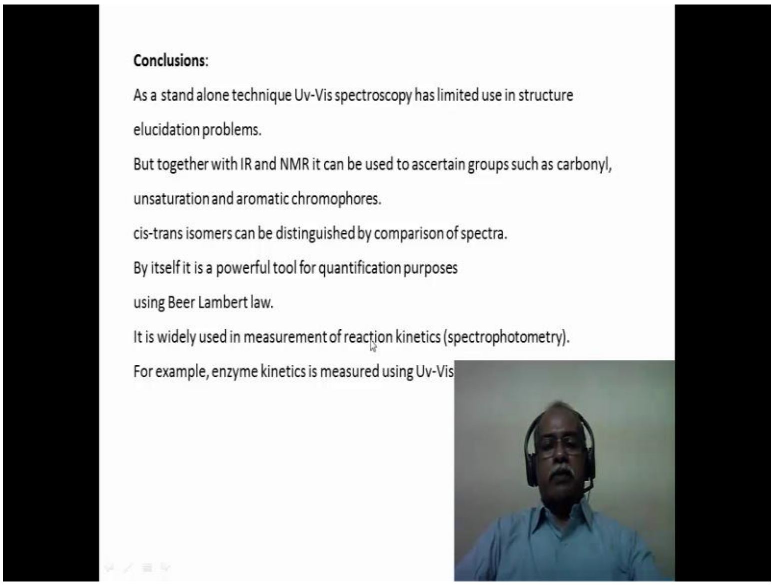

Conclusions:

As a stand alone technique Uv-Vis spectroscopy has limited use in structure elucidation problems.

But together with IR and NMR it can be used to ascertain groups such as carbonyl, unsaturation and aromatic chromophores.

cis-trans isomers can be distinguished by comparison of spectra.

By itself it is a powerful tool for quantification purposes using Beer Lambert law.

It is widely used in measurement of reaction kinetics (spectrophotometry).

For example, enzyme kinetics is measured using Uv-Vis

So, what we have seen in this particular, the last two modules is that, as a standalone technique UV visible spectroscopy has very limited using structural elucidation problem. But, when it is put together along with infrared and NMR spectroscopy, it can be used for ascertaining certain functional group like carbonyl unsaturation and aromatic chromophores. Of course, the IR and NMR can by themselves tell about the presence of carbonyl functional group and aromatic functional group. This will be additional information that one can obtain from the UV visible spectroscopy. You also saw examples of cistrons isomers being distinguished by comparison of the spectra. Unless you have both the samples of the cis isomer as well as the trans isomer the comparison becomes difficult.

We have only one isomer, it is not possible to distinguish based on the spectroscopic data by itself. It is a very powerful tool for quantification purposes using Beer Lamberts Law, in other words using the Beer Lamberts Law, one can quantify the substances that are present in a solution using the spectrophotometric technique. Spectrophotometry is very widely used in the kinetic measurements for example. So, we saw 1 or 2 examples of the application of the quantitative aspects of UV visible spectroscopy in measuring the kinetics of the chemical reaction; either photochemical reaction or a thermal reaction the enzyme kinetic measurement is one application of the UV visible spectroscopy. I hope you enjoyed this particular module.

Thank you very much for your attention.