Advance Analytical Course

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Lecture No # 32

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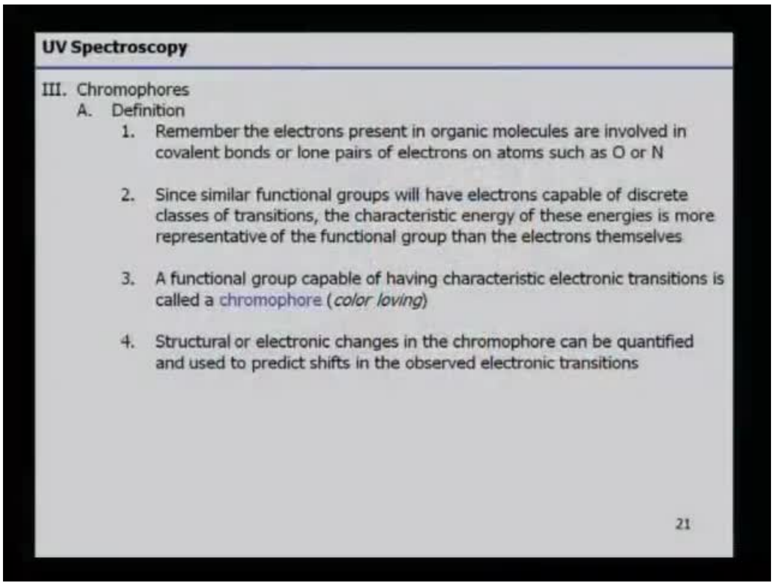

Trying to look at what are the definitions of chromophore. We just talked about chromophore, analyte, molecule, absorption, but what exactly is the part of the molecule, which plays a role in this UV absorption. Remember, the electrons present in organic molecules are involved in covalent bonds or lone pairs of electrons on atoms, such as oxygen and nitrogen. Since similar functional groups will have electrons capable of discrete classes of transition, the characteristic energy of these energies is more representative of the functional group than the electrons themselves.

A functional group capable of having characteristic electronic transition is called chromophore or color loving. Structural or electronic changes in the chromophore can be quantified and used to predict shifts in the observed electronic transitions. That means, whether or not, there is any double bond or there is a double bond with a heteroatom, can be analyzed or can be determined with the help of this because it will allow the pi to pi star transition, then n to pi star transitions to take place and these are only possible in these 2 cases.

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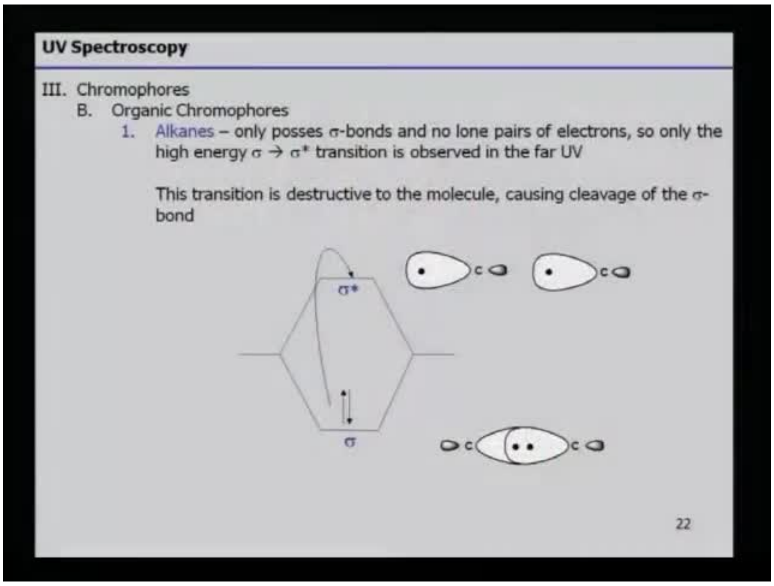

Now, an organic chromophore, if it is an alkane it does not contain any chromophoric group and therefore, it is not analyzed by the UV spectrum, why? Because alkanes only possess sigma bond and no lone pair of electrons, so only the high transition, that is, the pi to the, sorry, sigma to sigma star transition is observed in far UV, and far UV is not our study, is not the routine study in material. This transition is destructive to molecule, causing cleavage of the sigma bond, which is not possible. Only cleavage can take place at a very, very high temperature and that is not the region of the UV energy system.

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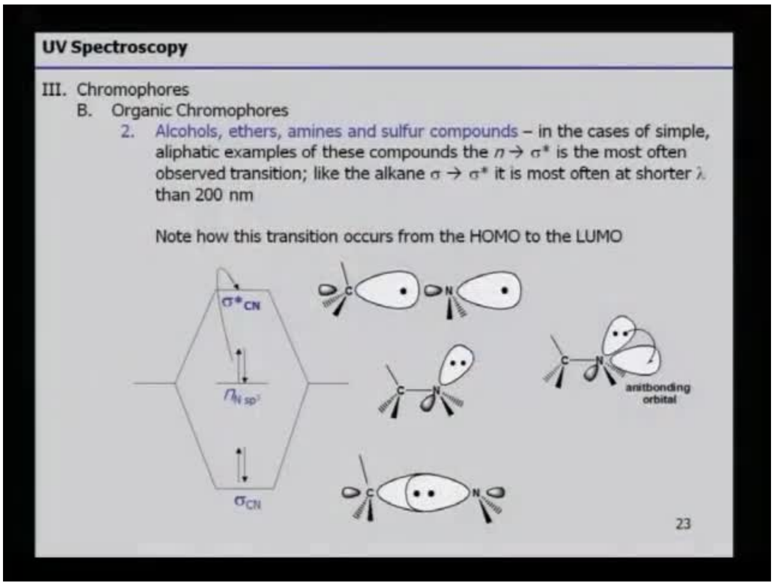

Organic chromophores - such as alcohols, ethers, amines, sulfur compounds - in the cases of simple, aliphatic examples of these compounds, the n to sigma star is most often observed transition; like the alkane sigma to sigma star is most often at shorter wavelength than 200 nanometer, but the limitation of the UV machine is that it can detect only from 200 to 700. So, anything, which is below 200, it cannot analyze.

Note, how this transition occurs in, from the HOMO LUMO point of view? Now, only transitions, which are allowed are from the n to sigma star and from sigma to n. so, that is how, the pictorial molecular determination can be done and the anti-bonding orbitals are also described. How, whether at all it can go or not, whether this transition will fall above 200 nanometer or not, can be understood easily.

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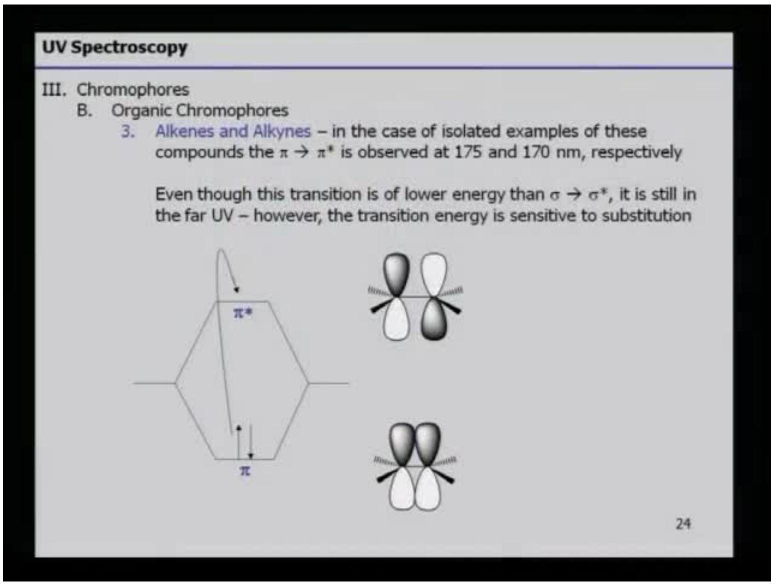

But if there is an organic, organic chromophore, which has alkenes or alkynes, one can expect, that the pi to pi star transition, which we have been talking all along this lecture is possible. And if there is a simple alkene, the, if there is one isolated double bond, it will range from 175 to 170 nanometer in the case of alkene and in the case of alkyne it is 170 nanometer, respectively.

Now, even though the transition is of a lower energy than sigma to sigma star, it is still in far UV region. However, the transition in energy is sensitive to substitution, so this is possible, but it will not be diagnosed very easily because it is still lower in the region of 200 nanometers.

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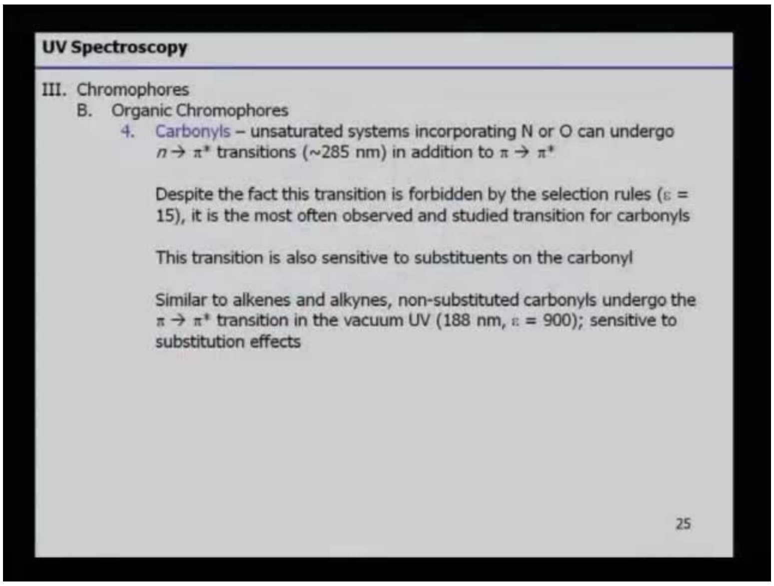

But if the organic chromophore is having a carbonyl - unsaturated system incorporating nitrogen or oxygen, can undergo n to pi star transition, which is fairly above 285 nanometer and, any, in addition, it will also have pi to pi star. So, there will be 2 transitions that will be actually taking place. Despite the fact this transition is forbidden by the selection rule, it is the most often observed and studied transition of carbonyls. This transition is also sensitive to substituents on the carbonyl.

Similar to alkenes and alkynes, non-substituted carbonyls undergo pi to pi star transition in the vacuum region, that is, in the range of 188 nanometer and they are sensitive to substitution effects. So, if there are substitution on either side of the double bond, it will have it is own electronic role to play. Therefore, carbonyls and the, you know, the atmosphere around that double bond is what matters and gives the molar absorptivity, as well as the lambda max.

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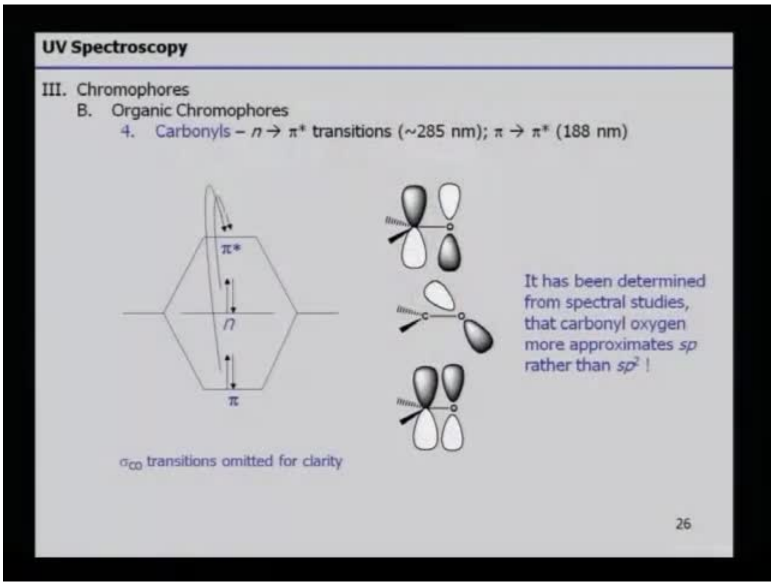

Now, looking at, furthermore, some other organic chromophores carbonyls, which show n to pi star transition and pi to pi star transition, it has been determined from spectral studies, that carbonyl oxygen more approximate than sp, rather than sp 2. So, this is how the transition actually takes place. And in a carbonyl, it is possible to either have 2 jumps, one is from pi to pi star or n to pi star. So, that, these are various options that take place in an organic carbonyl chromophore.

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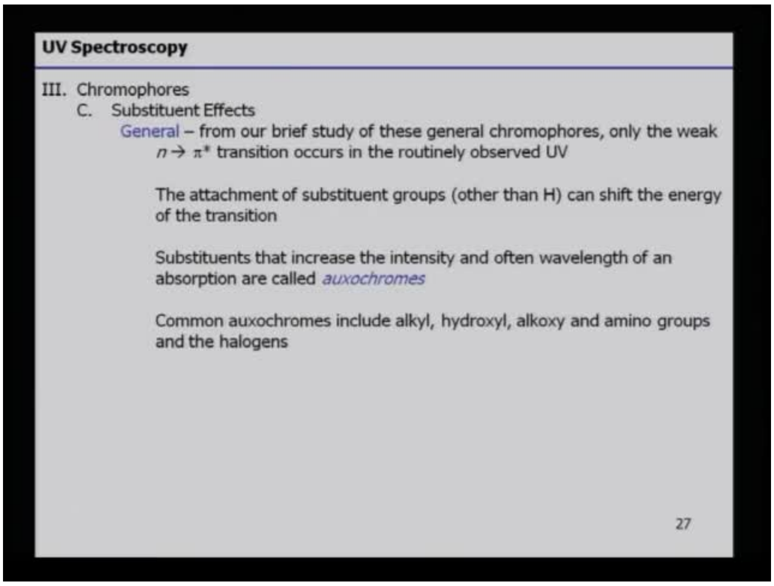

In general, if we have to look at the substituent effects, now as I told you, that the immediate neighbor of this double bond, whether it is a carbonyl double bond or an alkene or alkyne, how does they make an effect on the transition? A general rule says, that from the brief study of general chromophores, only the weak n to pi star transition occurs in the routinely observed UV. The attachment of substituent groups, other than hydrogen, can shift the energy of the transition. Substituents that increase the intensity and often wavelengths of an absorption are called auxochromes.

Sometime, now we understand, that the immediate group, that is attached to the double bond, does play a role in exciting the transition furthermore and therefore, they themselves do not absorb, but they help the chromophore to further enhance the absorptivity, such groups are called auxochromes. Common auxochromes are alkyl, hydroxyl, alkoxy, amino groups and halogens.

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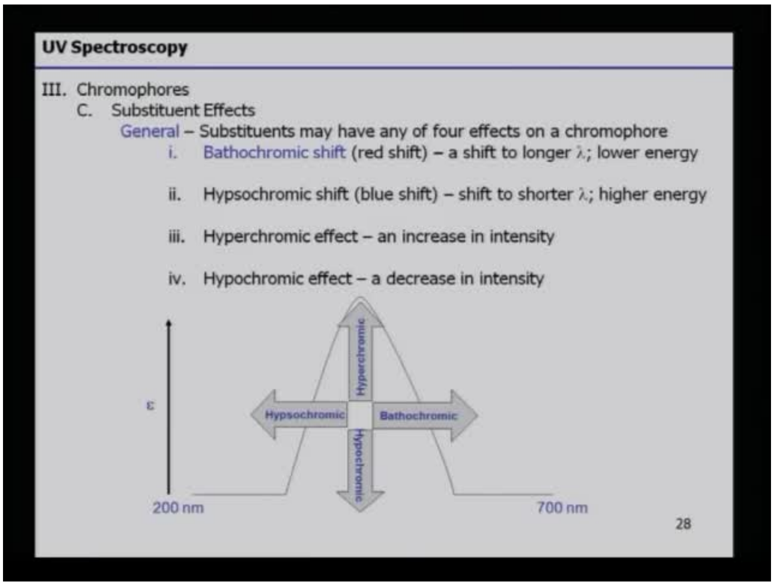

So, you see, that the substituent may have both kinds of effect - it may increase the absorptivity or it may withdraw the electrons towards the cell, causing the, kind of, decrease in absorptivity. Now, substituents may have any of the 4 effects on the chromophore - bathochromic shift, which we say, that increase towards the redness or the red shift, a shift to longer lambda, which is representing lower energy; or it may have a hypsochromic shift, which is moving towards the blue shift or shifting towards shorter wave length, which means higher energy will be required. It may have hyperchromic effect, which means an increase in intensity or it may have hypochromic effect, which means it decreases in intensity. So, all kinds of things can, 4 things can happen because of the substituents, which can affect the chromophore and its absorptivity.

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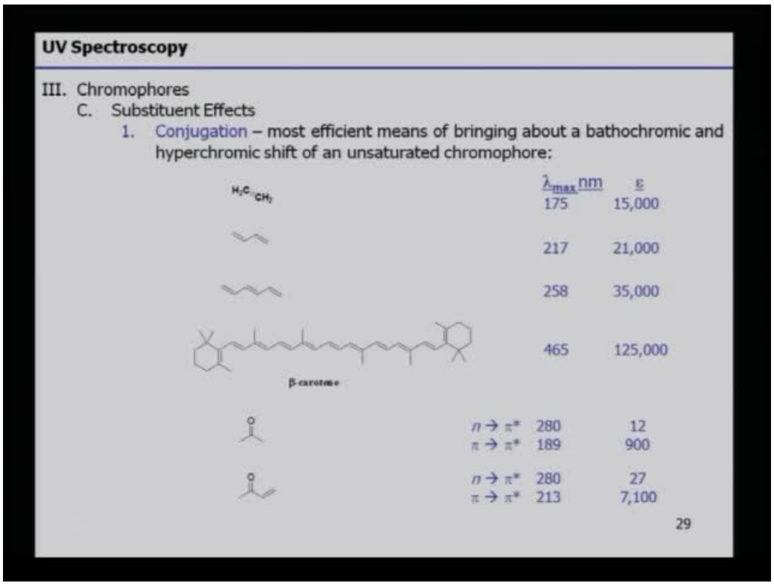

If we try to look at, take simple examples and try to explain to you conjugation - most efficient means of bringing about a bathochromic change or a hyperchromic shift to an unsaturated chromophore. Suppose, if you take a simple ethane, it absorbs, it shows a lambda max, such 175 and it has a molar absorptivity of 15000, but if you take a butadiene, 1 4, 1 3 butadiene, it has a lambda max at 217 and its molar absorptivity is 21000. Furthermore, if there is triene, aliphatic triene, you will see that the molar absorptive, the lambda max is 258.

So, from, so from 175 it became 217 and then 258 and the absorptivity is also going up by, which is now 35000. But if you try to look at a very, very conjugated system like beta carotene, it is 465 showing the lambda max and the molar absorptivity is 125000 as the, so you see, how much the hyperchromic effect has been brought about.

In a simple acetone, you see, there, the n to pi star is 280 and pi to pi star is 180 and their molar absorptivity are very low. Whereas, if there is alkene conjugated to the carbonyl, suddenly you find, that the values have changed quite a large amount and that is, the n to pi star remains the same, but pi to pi star has increased from 189 to 213, and the molar absorptivity has gone up tremendously. So, that is the beauty of conjugation, the more the conjugated system, the higher will be the lambda max and low energy will be required. So, conjugations in an alkene, the absorption from conjugation implies, that an increase in conjugation increases the energy required for electronic transition or excitation.

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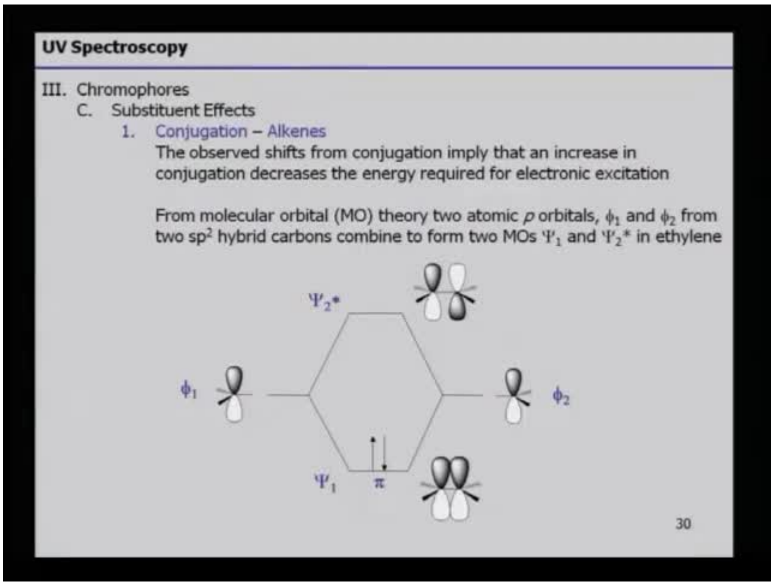

From molucular orbital theory, 2 atomic p-orbitals - the p 1 and the p 2 from 2 sp 2 hybrid carbons combined to form 2 molecular orbitals in ethane. This of course, you know very well, but still I am showing you a pictorial description.

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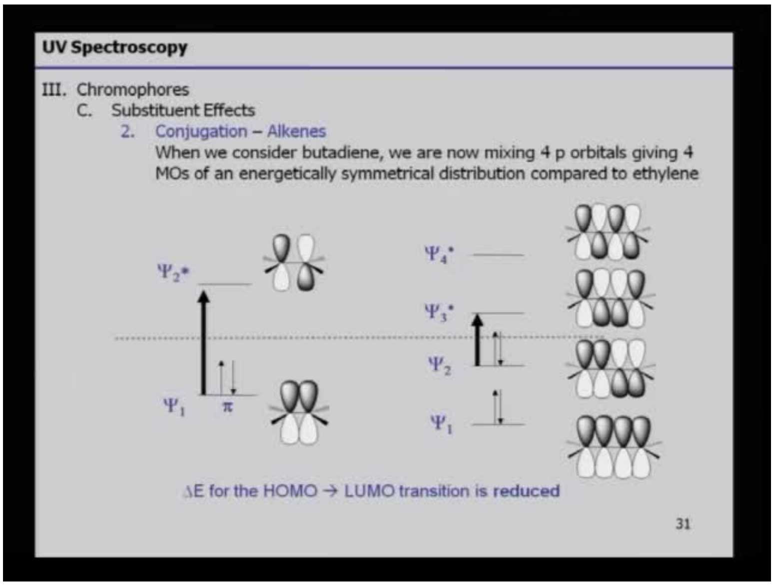

Now, when there is a substituent, what happens, when we consider butadiene? We are now mixing 4 p-orbitals, giving 4 molecular orbitals of an energetically symmetrical distribution to ethane. So, we took the example, why was the lambda max going up from 175 to 217?

The reason is that the delta e of the HOMO to LUMO transition is actually reduced, so lower energy is required to excite and the lambda max becomes higher. So, that is the kind of transitions and this is a more pictorial description of an alkene and a conjugated system.

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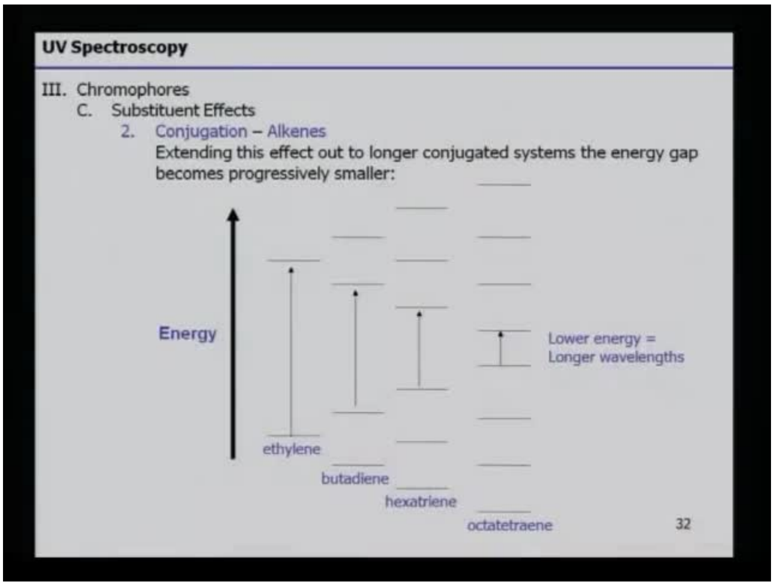

Extending this effect out to longer conjugated system, the energy gap progressively becomes smaller and smaller. So, you see, ethene has a bigger energy gap than butadiene, than hexatriene, and so on and so forth. So, it makes things more clear to you. These pictorial descriptions and these numerical values give you an idea, that the more conjugated the system, the higher will be the wavelength and lesser energy will be required, because the gap is becoming smaller and smaller than looking at more conjugations in alkene.

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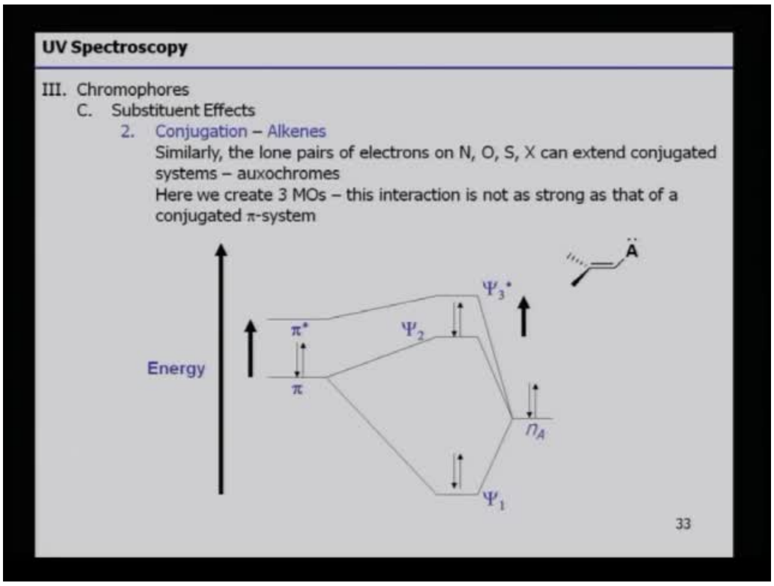

Similarly, the lone pairs of electron on the nitrogen, oxygen, sulfur or halogen can extend conjugated system and act as auxochrome. We, just a while ago, we were talking about auxochromes and you can understand, that now, what is the role of this auxochrome? Why does the lone pair of the nitrogen or the oxygen or the sulfur or the halogen? How do they play a role in these transitions?

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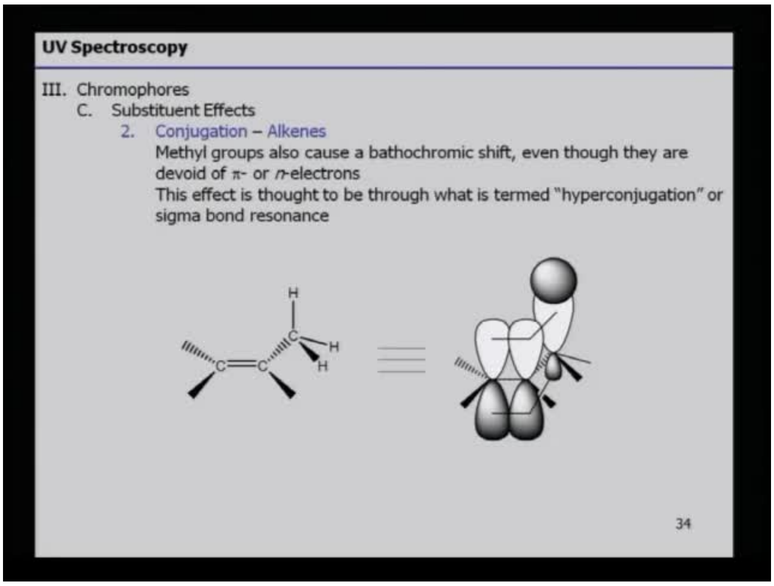

Here, we create 3 molecular orbitals; this interaction is not as strong as that of a conjugated pi system. Nevertheless, the auxochrome definitely contributes. Methyl groups can cause bathochromic shift, even though they are the divide of pi electrons or n electrons. This effect is thought to be, though through the hyperconjugation of the sigma bond resonance.

So, we all know about the hyperconjugation effect and the role of methyl groups. And so, that is what plays a role in that when it is attached to the double bond. The electrons start, the sigma electrons also have a kind of a bond resonance and that causes hyperconjugation, and that contributes to the, you know, electronic effect of the double bond.

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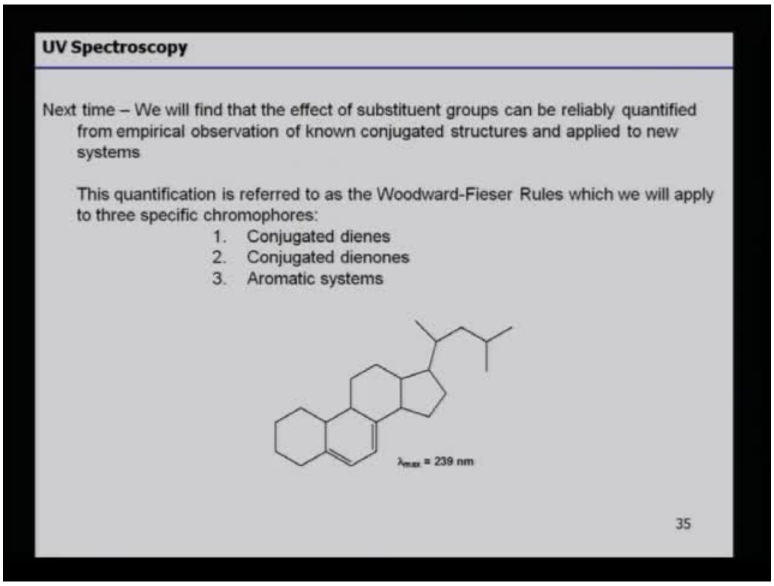

We will find that the effect of substituent group can be reliably quantified from empirical observations of known conjugated structure and applied to new systems. So, there is something called Woodward-Fieser rule. You know, it goes in a very systematic manner, that every bond has one kind of an addition to be made and this quantification is referred or was first, you know, brought into practice by Woodword and Fieser and therefore, the rule's name is named after their names, Woodward-Fieser rule. We, which we can apply to 3 specific chromophores, that is, conjugated dienes, conjugated dienones and aromatic system. It applies very well, because it adds on very systematically, just the way we add, you know, when we take a homologous series, we say methane, ethane, propane, butane and every time we go on adding the molecular weight by CH 2 or 14 units.

Similarly, when we are quantifying the conjugation in the system, then it is applicable, the Woodward-Fieser rule is applicable to conjugated dienes, conjugated dienones and aromatic system, and it works very well and very accurately. You see, that there is this big structure, but it has a diene and so the lambda max is 239 nanometers, as what has been found out.

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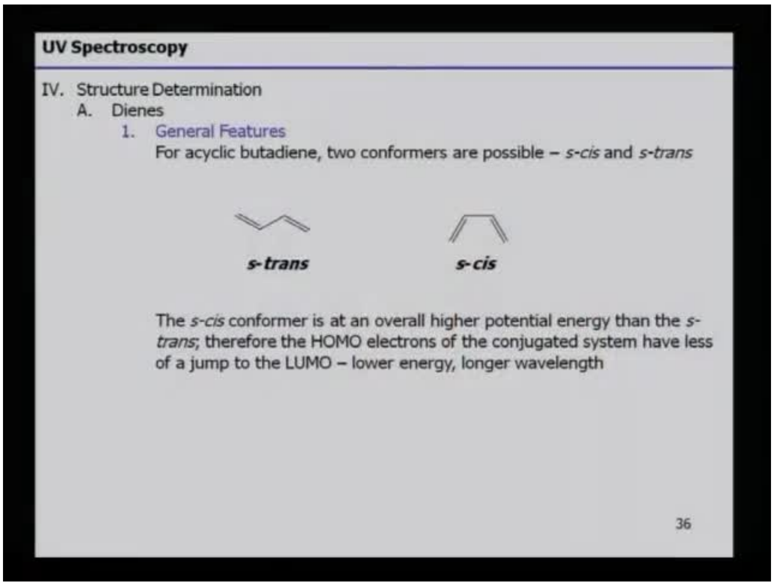

Now, certain dienes, you know, they can be cis diene, they can be trans diene; so, an acyclic butadiene, 2 conformers are possible - the cis and the trans. The cis conformer is at all, by overall higher potential energy than the trans isomer. Therefore, the HOMO electrons of the conjugated system have less to jump to the LUMO - lower energy, longer wavelength. So, there are little things, that need to be understood because the (( )) ease of jump for a trans is much easier than the cis because it is potentially at a higher potential energy state. And therefore, it is the facility, for the electrons to transit from one orbital to another, is more in the trans.

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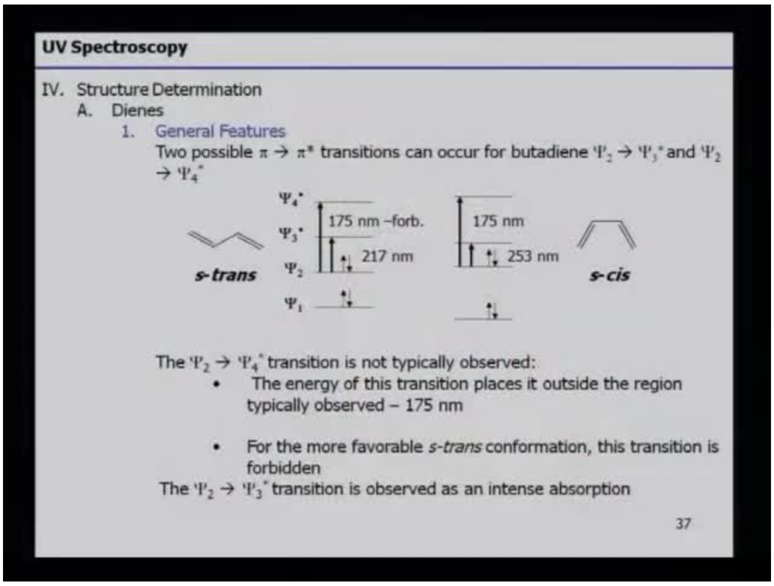

Now, 2 possibilities are there. If we take a diene, pi to pi star transition can occur from butadiene and the, if it is a trans, what are the energy gaps you will see in trans? It is 175 nanometers, which is forbidden and it is 217 nanometers, which is allowed, whereas in cis, the energies are 175 and 253.

So, therefore, the transition is typically, that is allowed the energy of transition, place, places an outside region typically at 175 nanometer and for more favorable trans confirmation, this transition is forbidden. So, therefore, what is absorbed or what is intensified is the one, which is allowed and which can, which the molecule can undergo.

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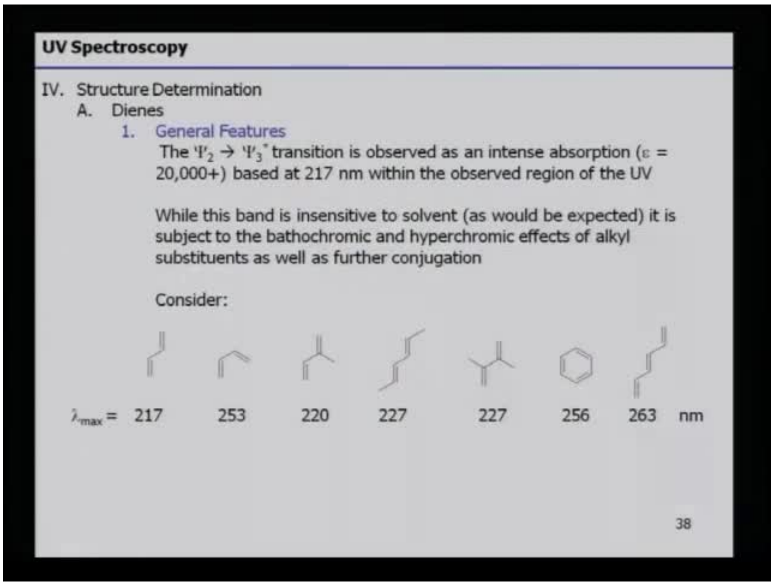

If we tried to look at different types of dienes, you will see, that, you know, the dienes, which are cis will be at a higher lambda max; dienes, which are having an alkyl or more conjugation, will gradually show a change. Therefore, transitions, that are observed in intense absorption, that is, above 20000 based are at 217 nanometers, while, the, this band is insensitive to solvents. It is subject to bathochromic and hyperchromic effect by alkyl substituents and for the conjugation, as can be seen here. The values are increasing gradually from 217 to 253 to 220 to 227, and so on and so forth.

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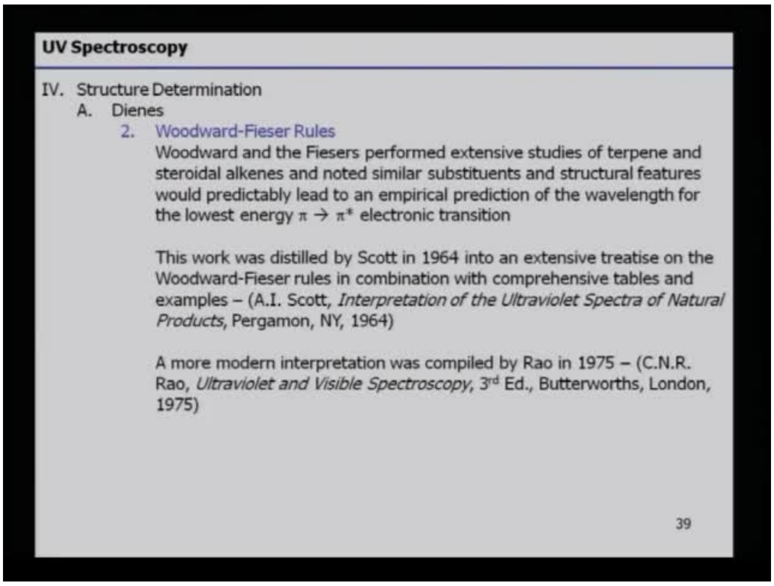

Woodward-Fieser rule - the Woodward and Fieser performed extensive studies of terpene and steroidal alkenes and noted, similar substituents and structural features would predictably lead to an empirical prediction of wavelength for the lowest energy pi to pi star electronic transition.

This work was distilled by Scott in 1964 into an extensive treatise on the Woodward-Fieser rule in combination with comprehensive tables and examples. So, what was done? Professor Scott, in 1964, he tried to put all this information together in a book called, Interpretation of UVs, Ultraviolet Spectra of Natural Products and he came up with this.

A more modern interpretation was compiled by Rao that, the, C N R Rao who has written another book called, Ultraviolet and visible spectroscopy. Now, a huge database is available and Woodword-Fieser rule, application to understand various conjugations in different types of chromophores of a molecule can be understood in a more systematic and more accurate manner.

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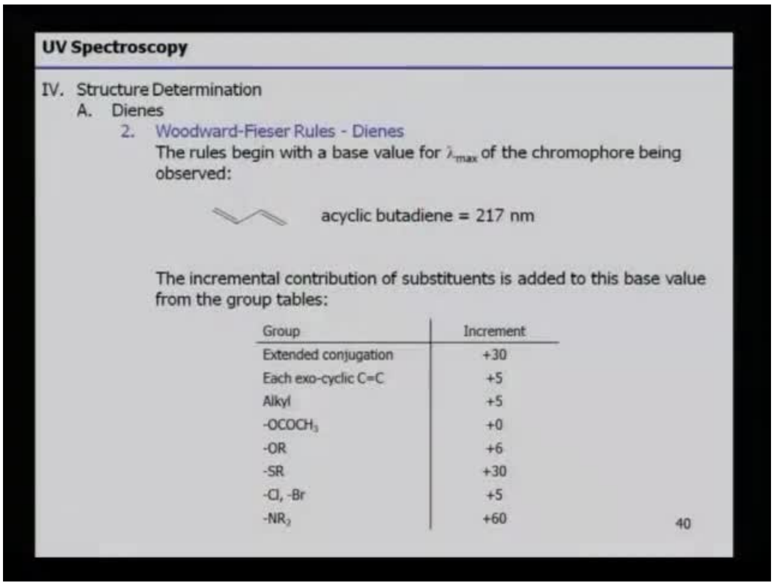

Now, if we tried to look at the rules by, for structural determination, what are the increments that we need to keep in mind? How will it increase? If we increase a degree of conjugation, what is the magnitude by which it will add?

The rule begins with the base value of lambda max of the chromophore being observed. If we take an acyclic butadiene, the base value is 217 nanometer, the incremental contribution of substituents is added to the base value from the group table. If extended conjugation is there, plus 30 each; exocyclic carbon-carbon double bond, plus 5; if an alkyl group is added, plus 5; if an ether group is added, then there is no contribution; if OR is added, that is, alkoxy group is added, then it is plus 6; if SR group is added, it is plus 30; if halogen like chloride or bromide are added, it is plus 5; if amine group is added, it is plus 60.

So, this is the kind of increment you have, one more, one more, one more and you keep on adding plus 5, plus 30, whichever group you are adding.

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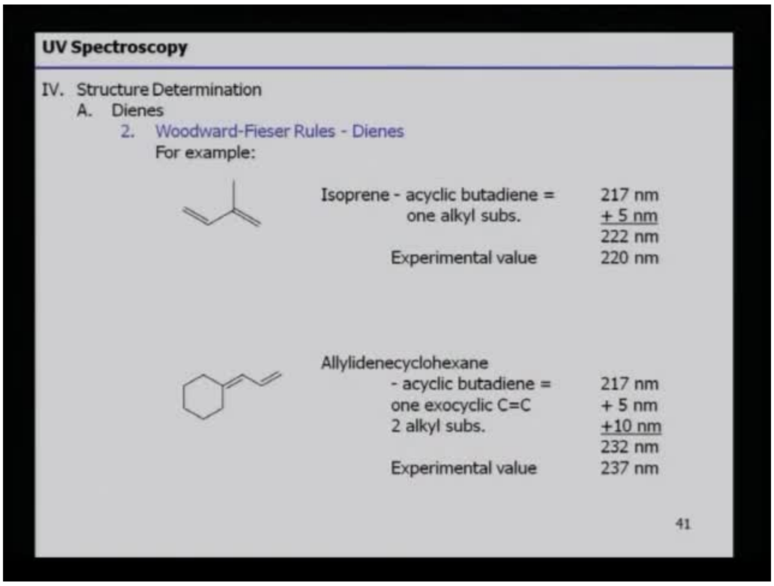

Woodward-Fieser's rule for dienes is, shows, that if there is a substitution, like for isoprene, an acyclic butadiene with 1 alkyl substituent, so base value is 217 plus 5. So, it was observed, that the value worked out to be 222 and the experimental lambda max also shows close to that and which is 220 nanometer.

Similarly, if there is acyclic, if there is a cyclic compound and to that, there is exocyclic diene, that is, allylidienecyclohexane. It has an acyclic butadiene, which is, base number is 217 plus; it has 1 exocyclic C double bond, C plus 5 and 2 alkyl substituents, so plus 10, and it was calculated to be 232 nanometer. And rightly so, the experimental value was very close and it was found to be 237 nanometer. So, you see, that simple, you have to remember the basic values, one addition, how much to be added, it is a simple arithmetic.

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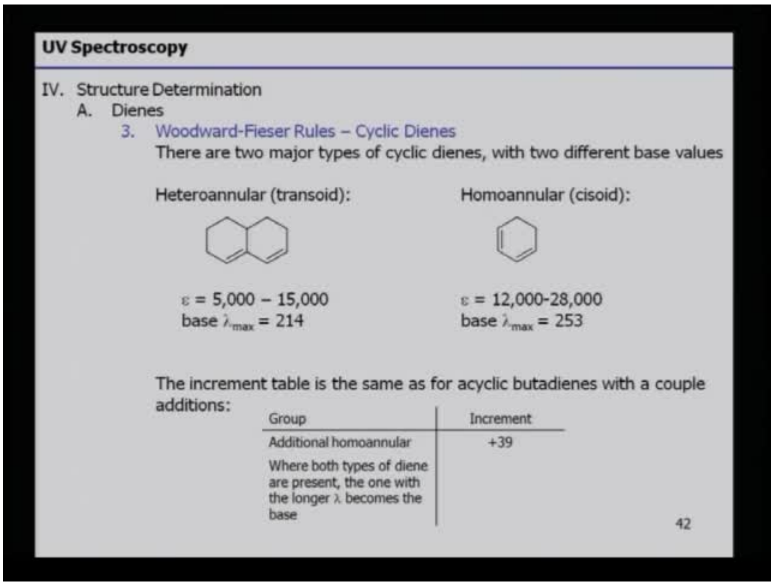

Woodward-Fieser rule cyclic dienes - for even cyclic dienes it holds good. There are 2 major types of cyclic dienes, the 2 different base types are heteroannular, that is, the transoid and the cisoid. That means, the, in 2 rings, the bonds are trans to each other or they are cis to each other in 1 ring. And that will show, that it has a basic value of 214 as lambda max nanometer or 253 because the cis bond and the trans bond.

We have already discussed, the increment table is the same as the acyclic butadiene with a couple of addition, additional homonuclear will add plus 39 and therefore, one has to just keep on adding.

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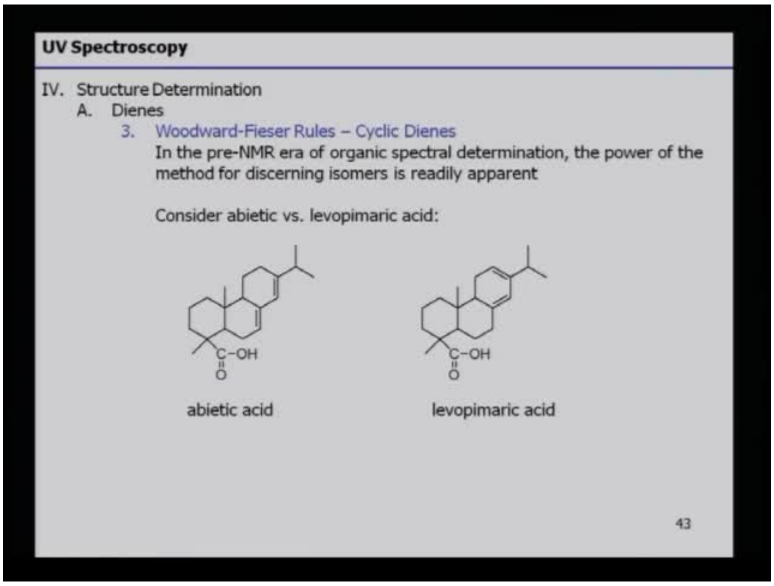

In the pre NMR era of organic spectral determination, the power of the method for discerning isomers is readily apparent. Consider abietic versus levopimaric acid. So, abietic acid and levopimaric acid, they are structurally quite similar, except for the cisoid and the transoid kind of double bonds and they were identified on the basis of UV spectrum for a system of cyclic dienes.

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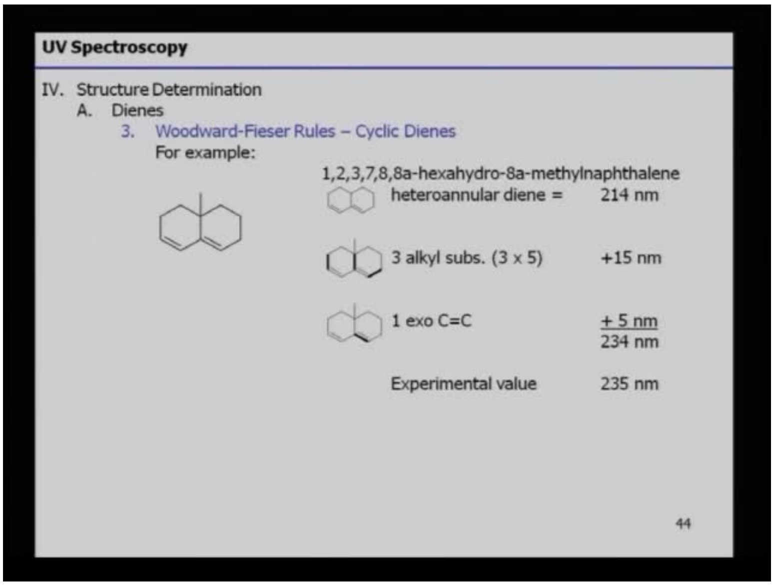

Furthermore, you take an example of 1, 2, 3, 7, 8, 8a-hexahydro-8a-methylnaphthalene, the compound, that is, the nomenclature, IUPAC nomenclature. The basic heteroannular diene will have adsorbance at 214 and every time there is alkyl substitution, so there are 3 alkyl substitutions, so 15 nanometers; 1 exocyclic double bond, so there is another edition of 5. So, the value, that was calculated, turned out to be 234 nanometers and experimental UV spectra showed a lambda max at 235. So, 234 and 235 are quite close to each other.

Therefore, this rule truly holds good. We saw so many examples, except that one should remember the basic incremental rule; if one functional group is added, if one double bond is added, what is to be added and that way, one can calculate.

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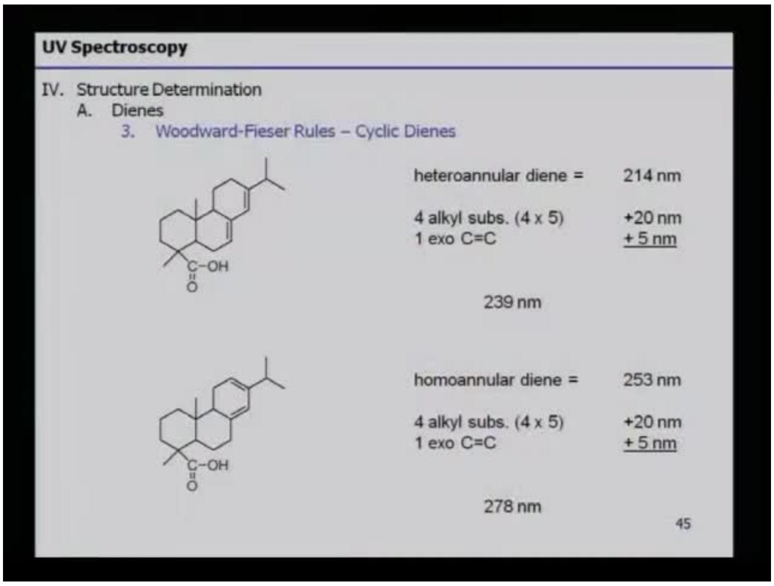

Similarly, for these two acids, abietic acid and levopimaric acid, the calculations could be made. The heteroannular diene was 214 as the basic structure and then 4 alkyl substitution, which means, that 20 nanometer should be added and 1 exocyclic C double bond C, so the total was 239. And it was observed, that the value for the other acid turned out to be 278 because the other component remains the same, the 20 and the 5 addition remains the same, but the basic herteroannular diene and homoannular diene itself at different values, one was one 214 and the other one was 253. Therefore, their calculation turned out to be 239 nanometers and 278 nanometers respectively.

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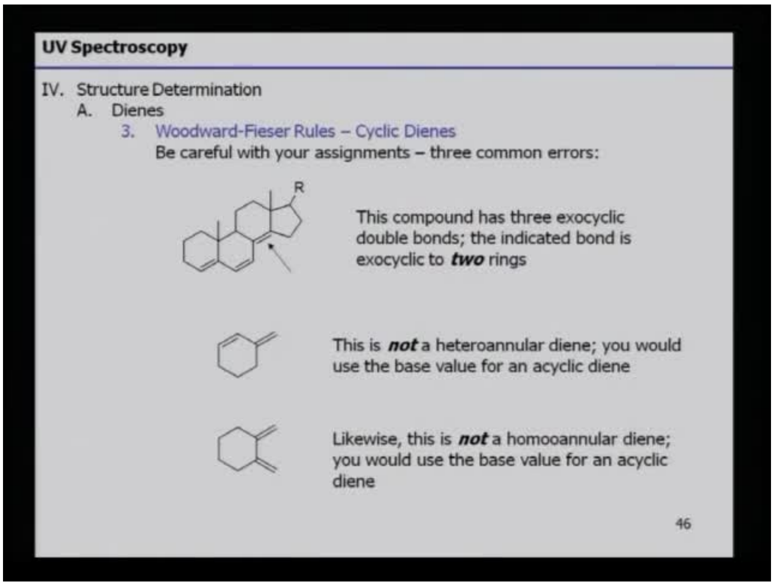

Woodward-Hoffmann rule, be careful when you are assigning because there is a possibility of making certain errors. This compound, there are 3 exocyclic double bonds; the indicated bond is exocyclic to 2 rings, so this is not a heteroannular diene. You would use the base value of an acyclic diene in this case and likewise, this is not a homonuclear diene, but, or homoannular diene, you would use the base value of cyclic diene. So, one has to remember while considering the double bond, whether it is truly an exocyclic double bond? Whether, what to use, whether it is a heteroannular diene or a homoannular diene? That recognition, the analyst must be able to make, otherwise the entire calculation will go haywire.

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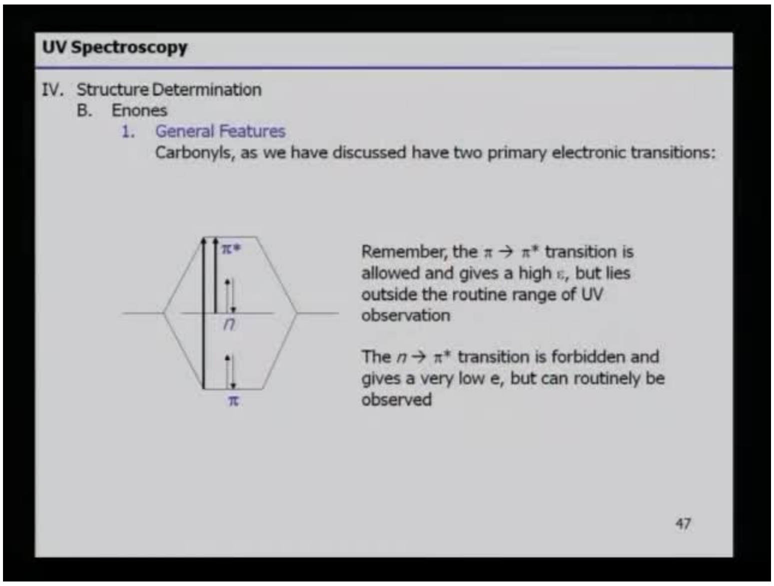

Now, carbonyls have certain, enones have some more contributions to make. Carbon, as we have discussed, have two primary electronic transitions, we have been talking about it time and again, pi to pi star and n to pi star. But n to pi star transition is forbidden and gives a very low e value, but cannot be routinely absorbed. Also, sometimes, it is, one has to keep in mind, that the molar absorptivity by n to pi star is fairly low.

So, does it really, it contributes to the transition? Because that is how it has been actually categorized as forbidden and remember that pi to pi star transition is allowed and gives the high molar absorptivity, but lies outside the routine range of the UV observations. So, there are various kinds of considerations that one must make.

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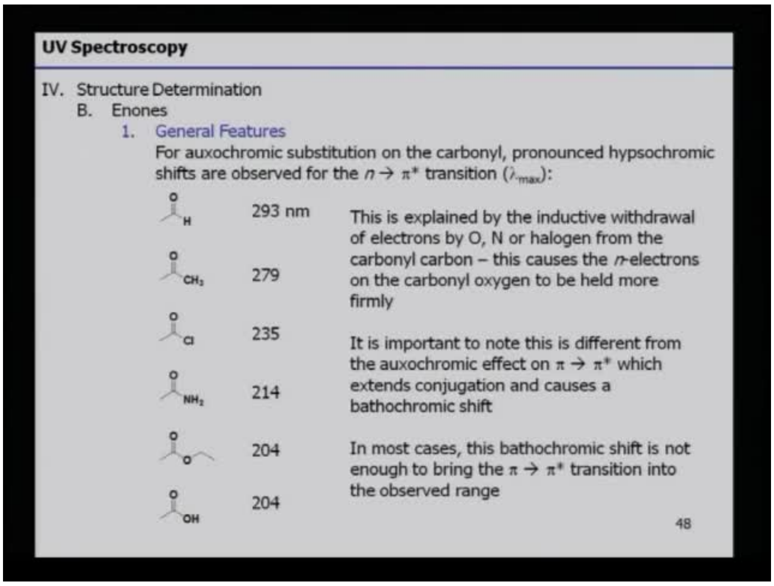

General enones, the values added on because of the auxochromic substitution, should also be understood. For auxochromic substitution on the carbonyl, pronounced hypsochromic shifts are observed for the n to pi star transition.

If you look at an aldehyde, it is 293 nanometers. If the same hydrogen is replaced by an alkyl, the value goes down and it becomes 273; if it is substituted by a halogen, it further goes down by 235. Then, if it is substituted by NH 2, amino group, it goes further down, which is 214. And if it is substituted by oxygen, then in most of the cases, this bathochromic shift is not enough to bring about the pi to pi star’s transition.

So, you see, that how the values are actually becoming less and less and less if we go from hydrogen to methyl and to halogen, to halogen and amino and oxygen and so on and so on, so forth.

So, the electronegativities are changing, the auxochromes activity are changing and therefore, it is not truly contributing to the transitions.

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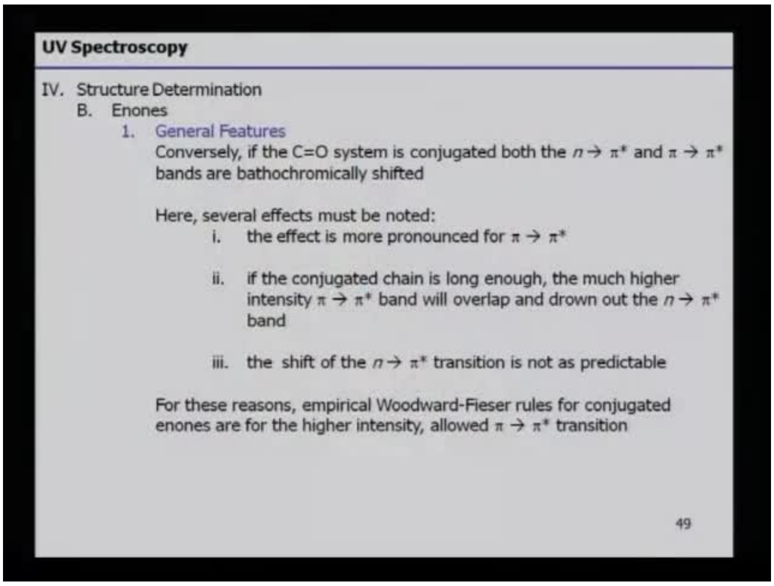

So, conversely, we can say that if C-O system is conjugated, both the n to pi star and pi to pi star bands are bathochromically shifted.

Here, several effects must be noted: the effect is more pronounced for pi to pi star; if the conjugated chain is long enough, the much higher intensity pi to pi star band will overlap and drown out the n to pi star band; the shift of the n to pi star transition is not as predictable.

So, one, we try to calculate the empirical rule or when we try to make use of Woodword-Fieser rule for conjugated enones, which are of very high intensity, we only consider the pi to pi star because there we say, that it is completely overshadowing the n to pi star. And therefore, it is important to understand these intricacies when one is making use of the Woodward-Fieser rules.

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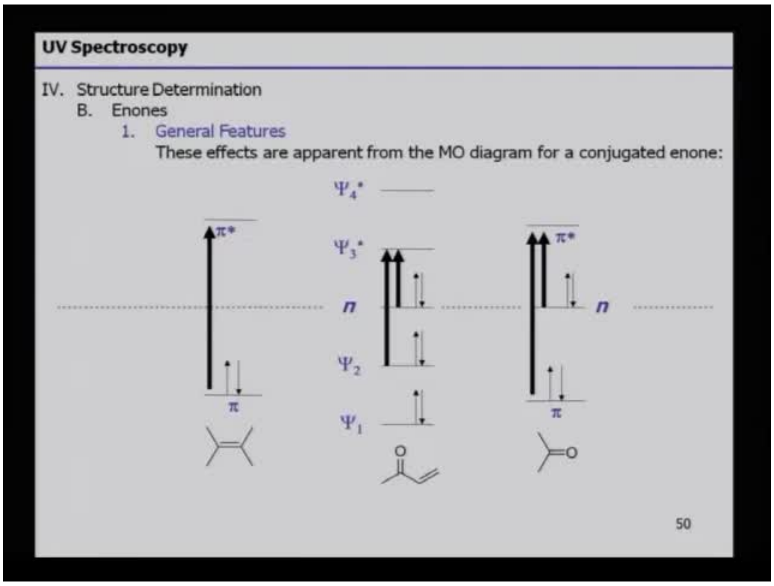

These effects are apparent from the molecular orbital diagram for a conjugated enone. So, you see, there is a simple double bond with alkyl groups. So, if there is only pi to pi star, in the case of enone, there is pi to pi star and n to pi star, whereas if there are alkyl group is attached to the carbonyl, then there is pi to pi star and n to pi star as well, but the gap is bit longer.

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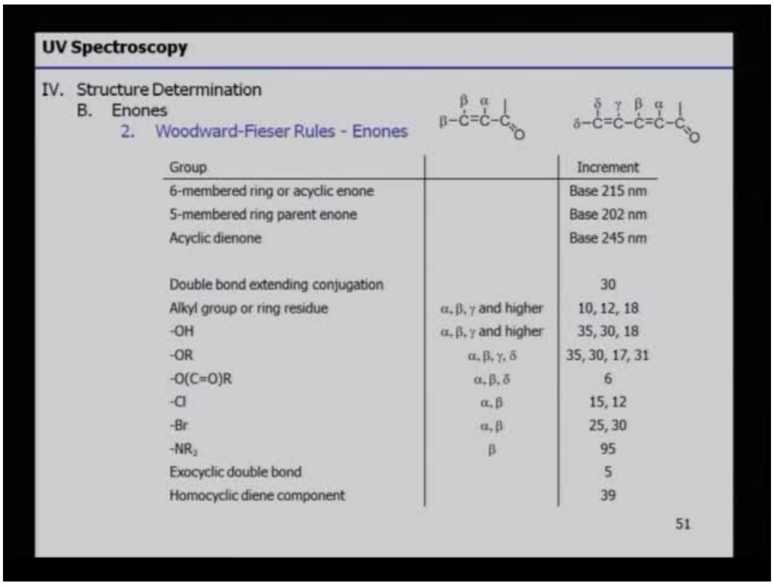

So, if one has to calculate the values for enones, then the alpha and the beta carbonyl next to the carbonyl group, that is, the alpha-carbon and the beta-carbon next to the carbonyl group, will have their own incremental values. 6-membered ring are acyclic enones, the base values is 215; 5-membered ring parent enone, 202 nanometer is the base value; acyclic dienone, the base value is 245 nanometer, over and above if there is a double bond extended, causing extended conjugation, it will have an addition of 30. If there is an alkyl group or ring residue on the alpha, beta or gamma, then it will add to 10 or 12 or 18; if there is an alkyl group or ring residue, then again it will add on to the same 10, 12 and 18. Similarly, if there is an OH group, then it will add; if it is coming on the alpha-carbon or the beta-carbon or the gamma-carbon, then it will have an additional increment of 35, 30 and 18 respectively; if alkoxy group is present on any of the alpha, beta, gamma, delta-carbon, then 35, 17, 31 respectively will be added on as incremental value and so on.

So, one can see, that even here, the Woodward-Fieser rule holds good and the incremental value when added to the base value, give more or less the same as the experimental value and therefore, these rules hold good even for enones.

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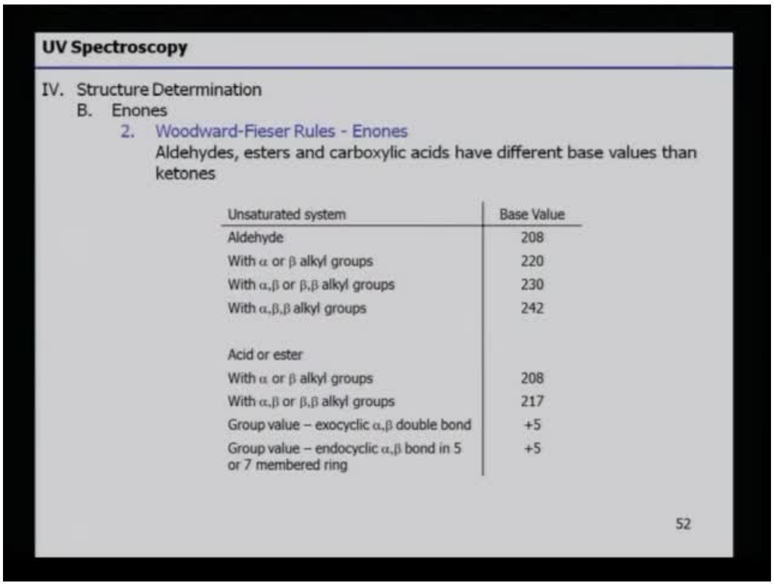

The Woodward-Hoffmann rule, we have discussed just now, is of great importance. And incremental value also, is absorbed when certain solvents are added or when certain solvents are used for analysis. Unlike conjugated alkene, solvent does have an effect on the lambda max, these effects are also described by Woodward-Hoffmann and Woodward-Fieser rule. So, even solvents can make an increment and therefore, they have kept a provision for solvents, and the addition of those solvents increment must be taken into consideration, or they can also call, cause a hypsochromic effect or a hyperchromic effect.

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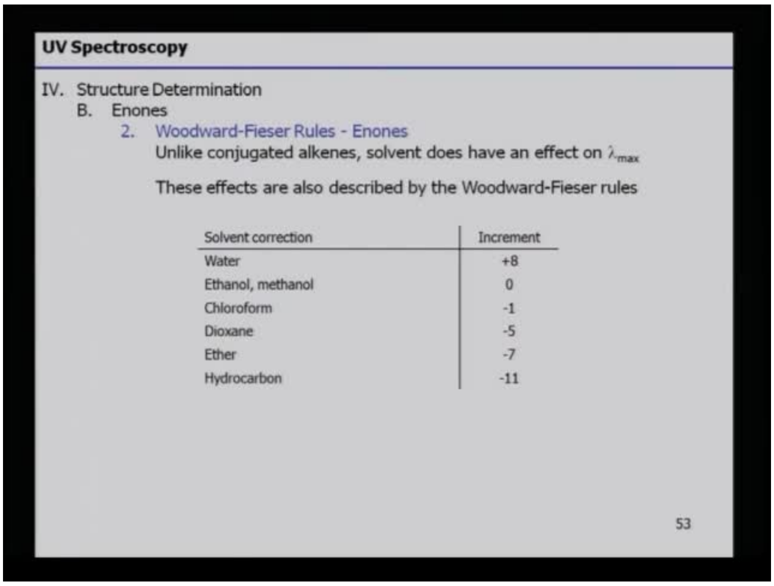

So, if one is using hydrocarbon as solvent, then this should be subtracted minus 11 or ether is used then, minus 7, but if water is added, it is plus 8 and so these things have to be kept in mind.

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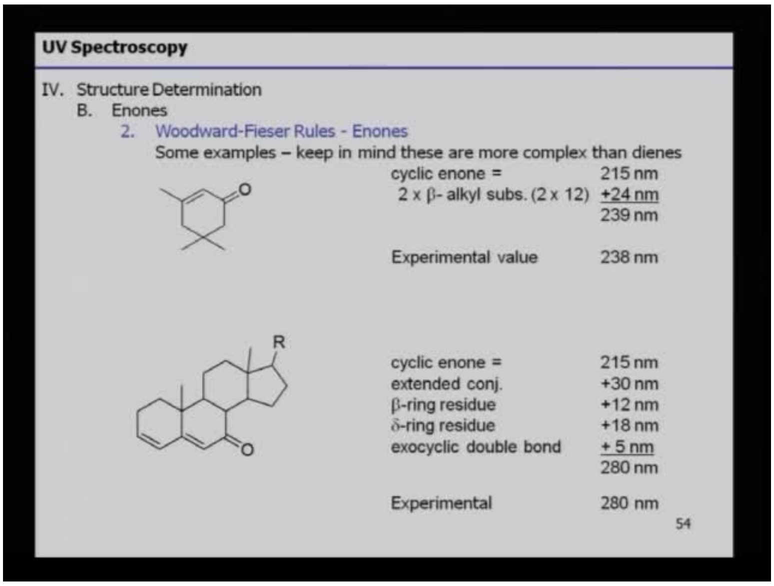

So, we have seen, that in many, many examples, these enones or dienes or conjugated systems have shown very accurate results. Therefore, the Woodward-Fieser rules for calculating and an, experiment, an observed value and matching it with observed value has shown for a large number of compounds, that it is possible to use these rules in order to predict the lambda max.