Advance Analytical Course

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Lecture No. # 33

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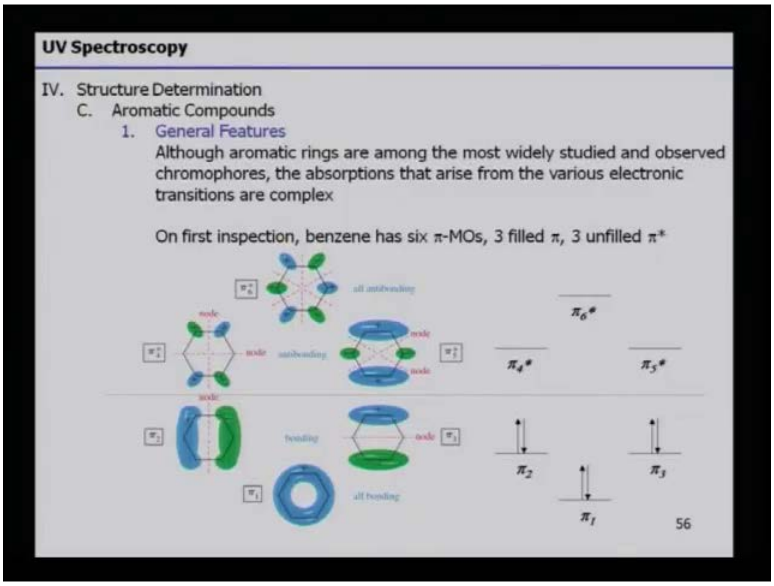

UV Spectroscopy

IV. Structure Determination
  C. Aromatic Compounds
    1. General Features
    Although aromatic rings are among the most widely studied and observed chromophores, the absorptions that arise from the various electronic transitions are complex

    On first inspection, benzene has six π-MOs, 3 filled π, 3 unfilled π^*

Continuing with UV spectroscopy, when we try to look at the structure determination of aromatic compounds, the scenario is a little different. Although, aromatic rings are among the most widely studied chromophoric group, the absorption that arise from various electronic transitions are pretty complex.

On first inspection, benzene has 6 pi molecular orbitals, out of which 3 are filled and 3 are unfilled pi star orbitals. Now, as the picture would depict here, that these pi 1, pi 2, pi 3 are the filled orbitals and pi star 4, 5, and 6 are the anti-bonding molecular orbitals, where the transition of the probable electron is possible.

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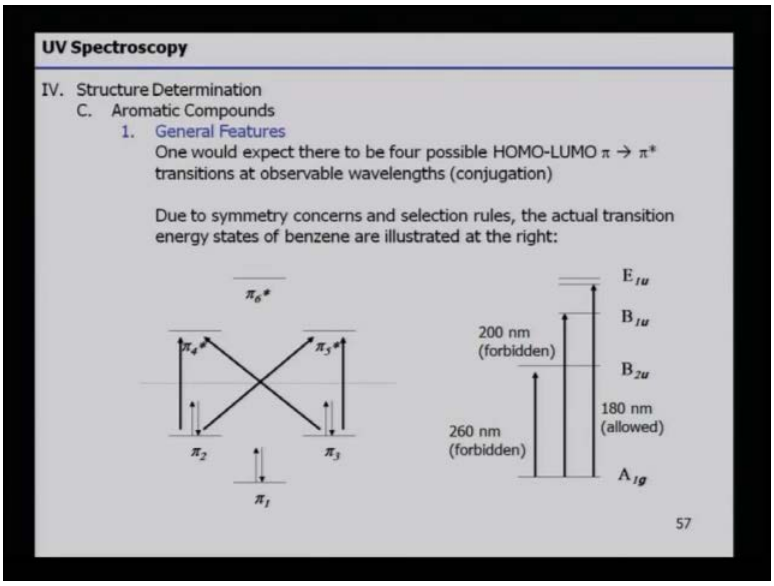

UV Spectroscopy

IV. Structure Determination
    C. Aromatic Compounds
        1. General Features
        One would expect there to be four possible HOMO-LUMO $\pi \rightarrow \pi^*$ transitions at observable wavelengths (conjugation)

        Due to symmetry concerns and selection rules, the actual transition energy states of benzene are illustrated at the right:

In general, the general features of an aromatic compound, one would expect there to be four possible homo-lumo pi to pi star transition at observable wavelengths, that is, because of the conjugation. Due to symmetry concern and selection rules, the actual transition energy states of benzene are slightly different, and therefore, there are some forbidden transitions and there are some allowed transitions.

The allowed transition is at 180 nanometer, whereas the forbidden ones are at 260 and 200 nanometers. So, that shows, that from pi 3 it cannot go to pi 4, from pi 2 it cannot go to pi 5. So, these are the forbidden zones which are not allowed, but from pi 2 it can go to pi 4, from pi 3 it can go to pi 5. So, these are certain allowed transitions and there are some forbidden transitions. Although, the wavelength may be higher, but yet, these symmetry rules, and symmetry concern, and selection rules hold good for aromatic compounds.

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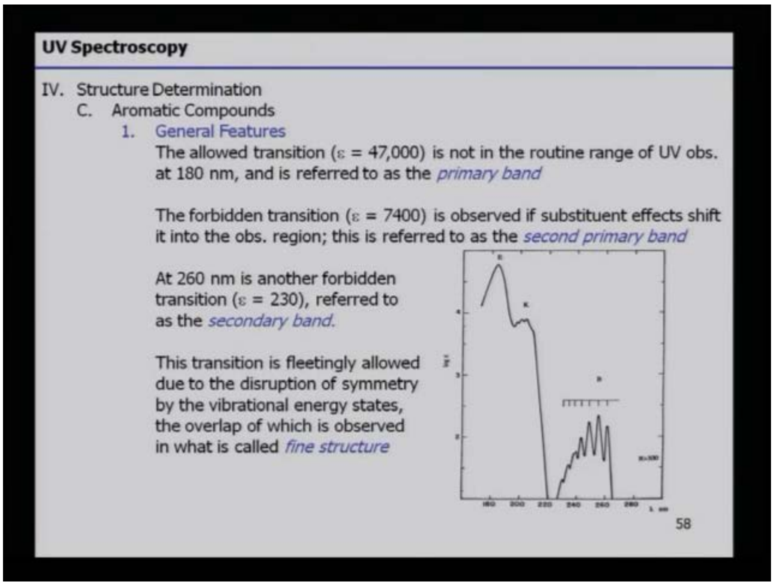

UV Spectroscopy

IV. Structure Determination
  C. Aromatic Compounds
    1. General Features

The allowed transition (ε = 47,000) is not in the routine range of UV obs. at 180 nm, and is referred to as the *primary band*

The forbidden transition (ε = 7400) is observed if substituent effects shift it into the obs. region; this is referred to as the *second primary band*

At 260 nm is another forbidden transition (ε = 230), referred to as the *secondary band.*

This transition is fleetingly allowed due to the disruption of symmetry by the vibrational energy states, the overlap of which is observed in what is called *fine structure*

In general, if we try to look at the molar absorptivity also, it is found that the allowed transition has a molar absorptivity of the order of 47,000 and is not the routine range of the UV at 180 nanometer, as referred to as the primary band. The forbidden transition, which has a molar absorptivity at 7400, is observed if substituent effects shift it into the observable region; this is referred as second primary band. At 260 nanometer, is another forbidden transition which has a molar absorptivity, very low, that is 230 and is referred to as secondary band. This transition is fleetingly allowed due to disruption of symmetry by the vibrational energy states, the overlap of which is observed in what is called the fine structure.

So, you see, there are various types of bands, and sometimes, very fine structures that zig-zag noise type of thing is also seen, which is due to the secondary band. But the main observable, and you know, the graph that is or the spectrum that is seen for aromatic compounds is mainly in the region of 180 nanometers. And it has a very good molar absorptivity; that means the peak will be fairly high.

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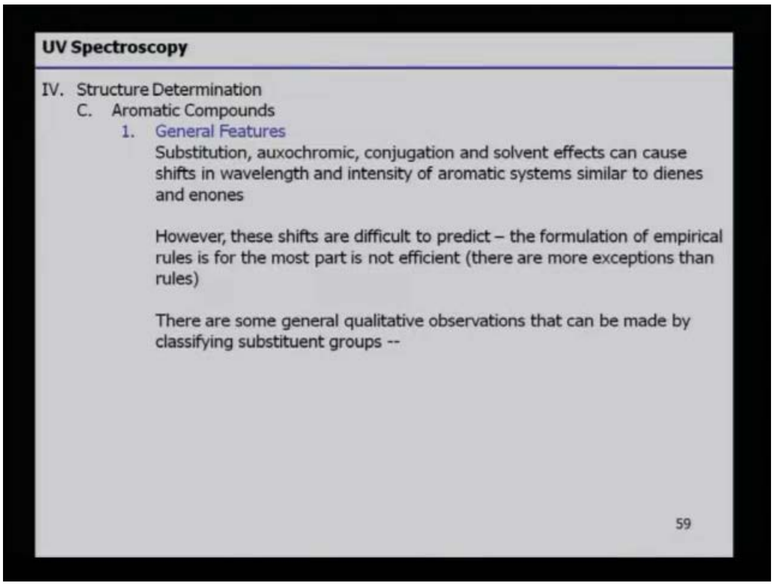

UV Spectroscopy

IV. Structure Determination
    C. Aromatic Compounds
        1. General Features

Substitution, auxochromic, conjugation and solvent effects can cause shifts in wavelength and intensity of aromatic systems similar to dienes and enones

However, these shifts are difficult to predict – the formulation of empirical rules is for the most part is not efficient (there are more exceptions than rules)

There are some general qualitative observations that can be made by classifying substituent groups --

Now, in general substitution, auxochromic group presence, conjugation and solvent effect can cause shifts in wavelength and intensity of aromatic system similar to dienes and enones.

We just saw that because of the presence of a substituent, because of a presence of an auxochromic group, or due to enhanced conjugation, that is, you know, double bond-single bond- double bond, there is a possibility that the wavelength will shift and it will also affect the intensity of the peak.

So, if these rules hold good. However, these shifts are difficult to predict - the formula of empirical rule is for the most part is not efficient, and therefore, there are some exceptional rules also in this case. There are some general qualitative observations that can be made by classifying substituent groups on the benzene ring.

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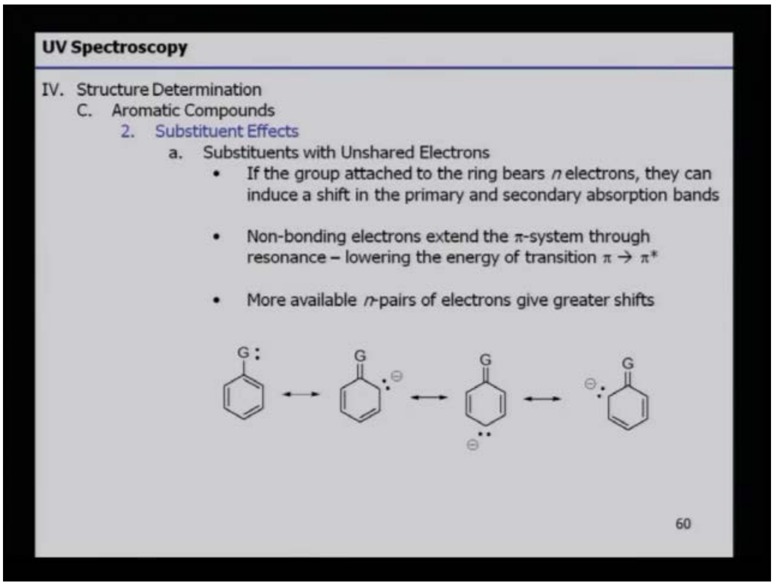

UV Spectroscopy

IV. Structure Determination
- C. Aromatic Compounds
  - 2. Substituent Effects
    - a. Substituents with Unshared Electrons
      - If the group attached to the ring bears *n* electrons, they can induce a shift in the primary and secondary absorption bands
      - Non-bonding electrons extend the π-system through resonance – lowering the energy of transition $\pi \rightarrow \pi^*$
      - More available *n*-pairs of electrons give greater shifts

Now, substituent with unshared electron: if a group attached to the ring bears n electrons, that is the lone pair electrons, they can induce a shift in the primary or secondary absorption bands. Non-bonding electron extends the pi-system through resonance - lowering the energy of transition between pi to pi star.

So, because of their contribution, you see the lone pair on the G actually, that is the group, is actually participating with the ring, and therefore, the electronic densities at the ortho and para positions are enhanced. Therefore, the pi to pi star will also face a lowering of energy. More available lone pairs or n electrons, the greater is the shift. So, more the number, the more will be the contribution and lower will be the energy requirement, because the ring is getting enriched from the outside source or that is the participation of the lone pairs. So, these are certain things which need to be remembered.

Even the substituent’s have an effect on the ring. The presence of n electron, gives the possibility of n to pi star transition also. If this occurs, the electron now remove from G, can becomes an extra electron in the anti-bonding pi orbital of the ring.

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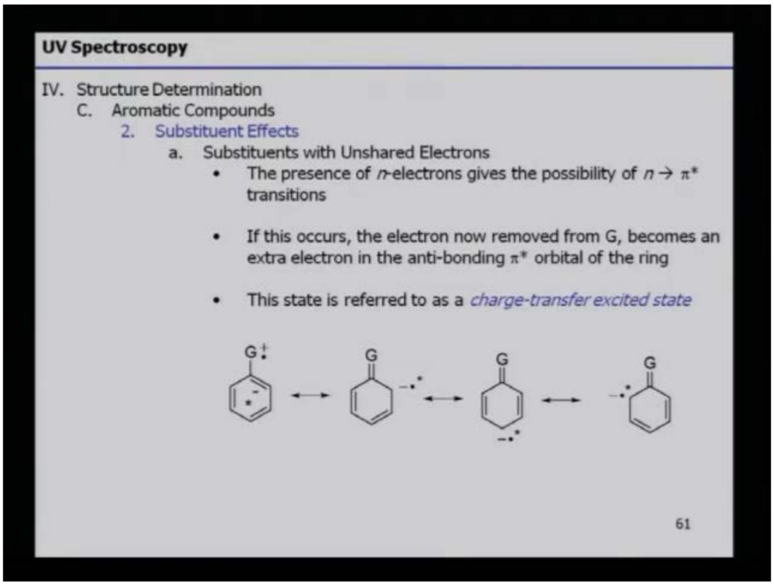

UV Spectroscopy

IV. Structure Determination
  C. Aromatic Compounds
    2. Substituent Effects
      a. Substituents with Unshared Electrons
        - The presence of *n*-electrons gives the possibility of $n \rightarrow \pi^*$ transitions
        - If this occurs, the electron now removed from G, becomes an extra electron in the anti-bonding π^* orbital of the ring
        - This state is referred to as a *charge-transfer excited state*

This state is referred as charge-transfer excited state. Now, what happens? The electron from the lone pair is now coming within the ring. And therefore, the ring is a having an extra electron and the group is devoid of one of the electron which has got excited. And therefore, these also participate in the clouding of the anti-bonding orbitals. So, this is a very typical case, where the substituent plays a participatory role.

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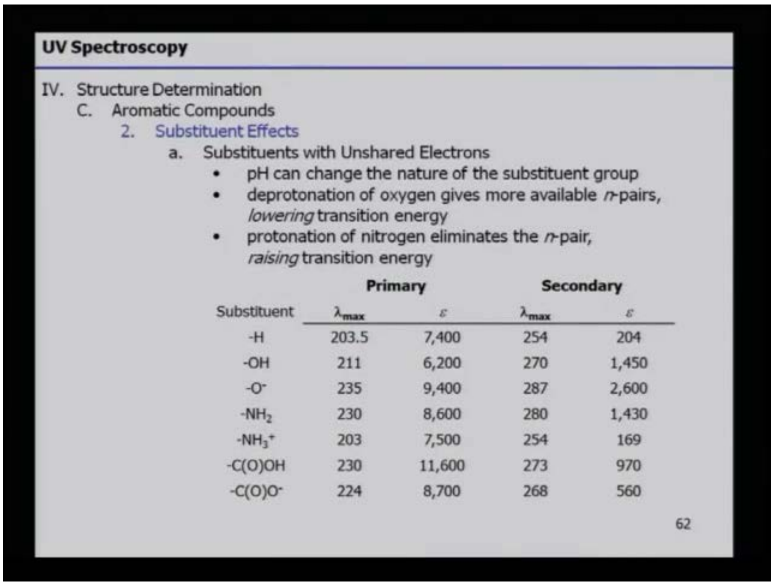

UV Spectroscopy

IV. Structure Determination
  C. Aromatic Compounds
    2. Substituent Effects
      a. Substituents with Unshared Electrons
        - pH can change the nature of the substituent group
        - deprotonation of oxygen gives more available *n*-pairs, *lowering* transition energy
        - protonation of nitrogen eliminates the *n*-pair, *raising* transition energy

	Primary		Secondary	
Substituent	λ_{max}	ε	λ_{max}	ε
-H	203.5	7,400	254	204
-OH	211	6,200	270	1,450
$-O^-$	235	9,400	287	2,600
$-NH_2$	230	8,600	280	1,430
$-NH_3^+$	203	7,500	254	169
-C(O)OH	230	11,600	273	970
$-C(O)O^-$	224	8,700	268	560

The substituent effect: substitutions or substituents with a unshared electron; pH can change the nature of the substituent; deprotonation of oxygen gives more available n-pairs, lowering transition energy. Protonation of nitrogen eliminates the n-pair raising transition energy. So, suppose if pH has to be altered, what all can happen to the substituent? If it is an oxygenated substituent, then deprotonation may take place or if it is a nitrogen substituent, then protonation of nitrogen can also take place, but they will have an opposite effect. By deprotonation of oxygen, it will be more available, the lone pair will now be available into the ring, and therefore, there will be a lowering in the transition energy.

However, if an amine group is protonated, what will happen? The lone pair is already reacted; so, it is not available for the ring participation. Therefore, there will be a rise in the transition energy. So, if we try to look at the primary and the secondary effects of these, if there is a simple substituent H; the lambda max is 203 and the molar absorptivity is 7400; and if it is OH, it is the lambda max is 211 and the molar absorptivity goes down; if it is a O minus, the lambda max goes up and the molar absorptivity also goes up.

If it is a simple amine - NH 2, then the lambda max is 230 and the molar absorptivity is 8600; but if the same amino group is protonated, that is NH 3 plus, then the lambda max reduces to 203 and the molar absorptivity also reduces.

So, it is all related to what is the situation of the substituent, whether it is a hetero atom, and if the substituent is a hetero atom, there is a possibility of the lone pair to participate, but due to pH alteration, it can either get protonated or it can get deprotonated and both will have a reverse action on the transition energy of the transition state. Therefore, substituents play a very major role in the aromatic compounds

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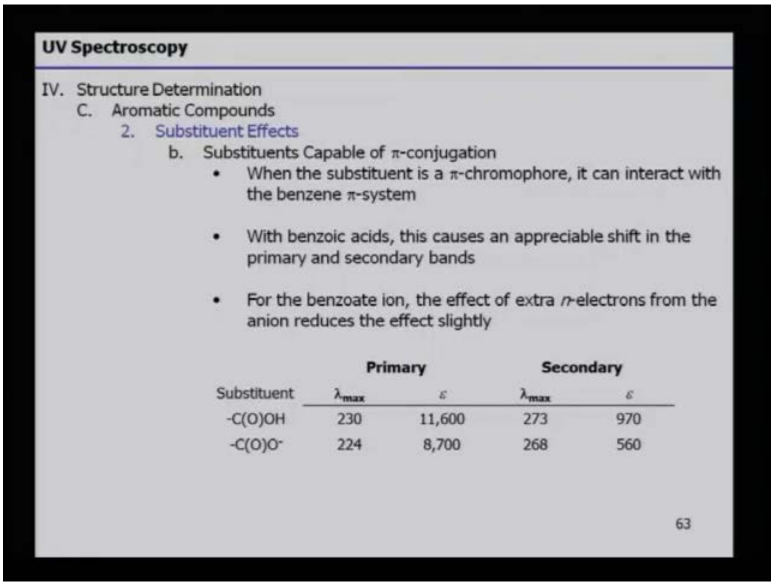

UV Spectroscopy

IV. Structure Determination
  C. Aromatic Compounds
    2. Substituent Effects
      b. Substituents Capable of π-conjugation
        - When the substituent is a π-chromophore, it can interact with the benzene π-system
        - With benzoic acids, this causes an appreciable shift in the primary and secondary bands
        - For the benzoate ion, the effect of extra *n*-electrons from the anion reduces the effect slightly

	Primary		**Secondary**	
Substituent	λ_{max}	ε	λ_{max}	ε
-C(O)OH	230	11,600	273	970
-C(O)O$^-$	224	8,700	268	560

Substituents capable of pi conjugation. Now, if there is a possibility for pi conjugation, even then substituents play a very important role, because they can interact with the pi system of the benzene ring. With benzoic acid, this causes an appreciable shift in the primary and secondary bands.

So, now we have seen that aromatics have two types of bands: one is the primary band and the secondary band. So, it will affect both, in the case of the benzoic acid. For the benzoate ion, the effect of extra n electrons from the anion reduces the effects slightly. So, if we try to look at a simple benzoic acid, the lambda max is 230 and the molar absorptivity is 11600.

If we look at the benzoate ion, it actually goes up, because now O minus is now participating with the ring, and the lambda max goes to 224; but the molar absorptivity goes down and it is now 8700. So, you see the primary bands are rarely affected drastically, looking at the condition of the acid and its salt.

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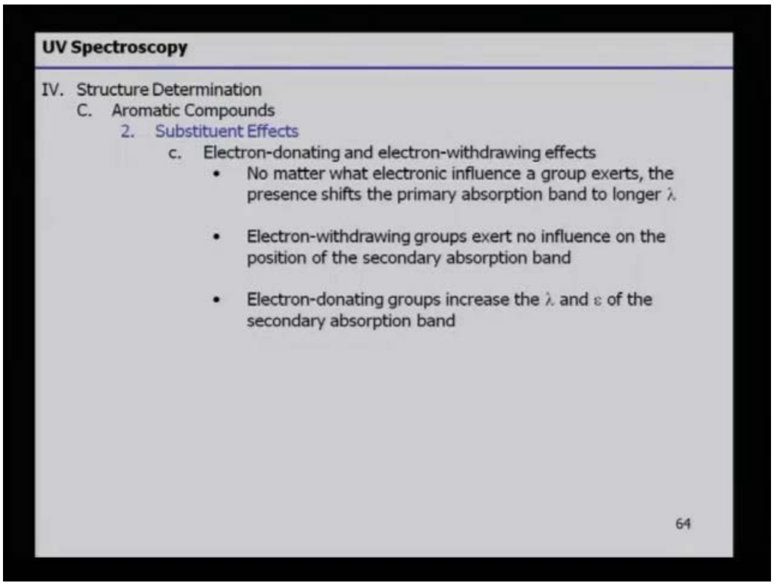

UV Spectroscopy

IV. Structure Determination
  C. Aromatic Compounds
    2. Substituent Effects
      c. Electron-donating and electron-withdrawing effects
        - No matter what electronic influence a group exerts, the presence shifts the primary absorption band to longer λ
        - Electron-withdrawing groups exert no influence on the position of the secondary absorption band
        - Electron-donating groups increase the λ and ε of the secondary absorption band

If the substituent has an electron-donating or an electron-withdrawing effect, then what will happen? No matter what electronic influence a group exerts, the present shifts to the primary absorption band to a longer lambda. Electron-withdrawing group exert no influence on the position of the secondary absorption band; electron-donating group increases the lambda and the molar absorptivity of the secondary absorption band also.

So, you see that both primary and secondary bands are in a way affected, whether there is an electron-withdrawing group or an electron-donating group, because if there is an electron-donating group, it will increase the densities at the ortho and para position. But, if it is an electron-withdrawing group, it will make the meta position slightly higher, in electron density as compared to the ortho and para. And therefore, they will have their own effect on the primary band and the secondary band.

So, these things, these are very, very intricate information, that one should have an understanding, while calculating the UV of a predicted sample. And therefore, it is possible to do that, because structure determination, one can predict what would be the wavelength approximately. And it has been found, that by Woodward-Fieser rule, the calculated value of the lambda max has been found to be for a very, very, very large number of compounds similar, very close to each other and sometimes even the same.

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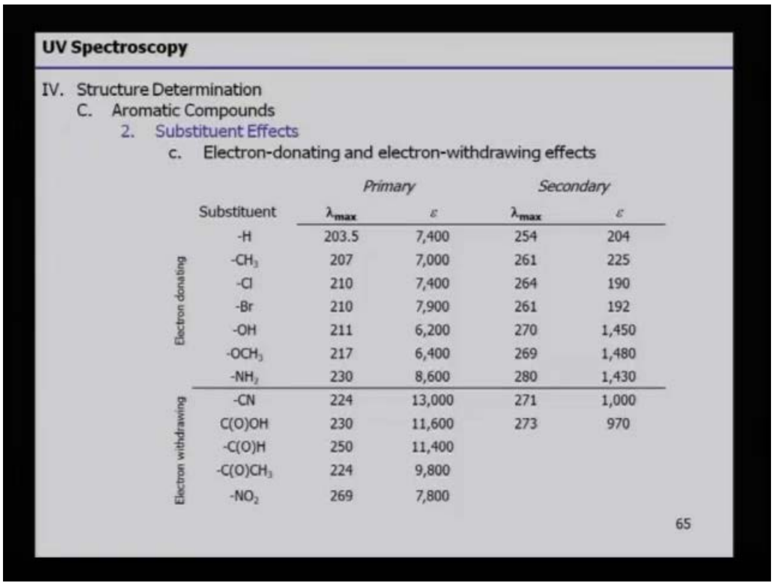

UV Spectroscopy

IV. Structure Determination
  C. Aromatic Compounds
    2. Substituent Effects
      c. Electron-donating and electron-withdrawing effects

		Primary		*Secondary*	
	Substituent	λ_{max}	ε	λ_{max}	ε
	-H	203.5	7,400	254	204
Electron donating	$-CH_3$	207	7,000	261	225
	-Cl	210	7,400	264	190
	-Br	210	7,900	261	192
	-OH	211	6,200	270	1,450
	$-OCH_3$	217	6,400	269	1,480
	$-NH_2$	230	8,600	280	1,430
Electron withdrawing	-CN	224	13,000	271	1,000
	C(O)OH	230	11,600	273	970
	-C(O)H	250	11,400		
	$-C(O)CH_3$	224	9,800		
	$-NO_2$	269	7,800		

Now substituents which are electron-donating and substituents which are electron-withdrawing have certain effects, and you can see, that if you look at the electron-donating substituents, the lambda max goes on increasing, but however, it does not make much of a difference on the molar absorptivity.

However, if we see electron-withdrawing group, again the lambda max may increase or decrease, but molar absorptivity goes down drastically, in the case of electron-withdrawing group, when we consider the primary band. That is not so much of an effective situation in the secondary band, but there are changes, the lambda max does change; it increases as we go down the electronegative series of the electron-donating groups.

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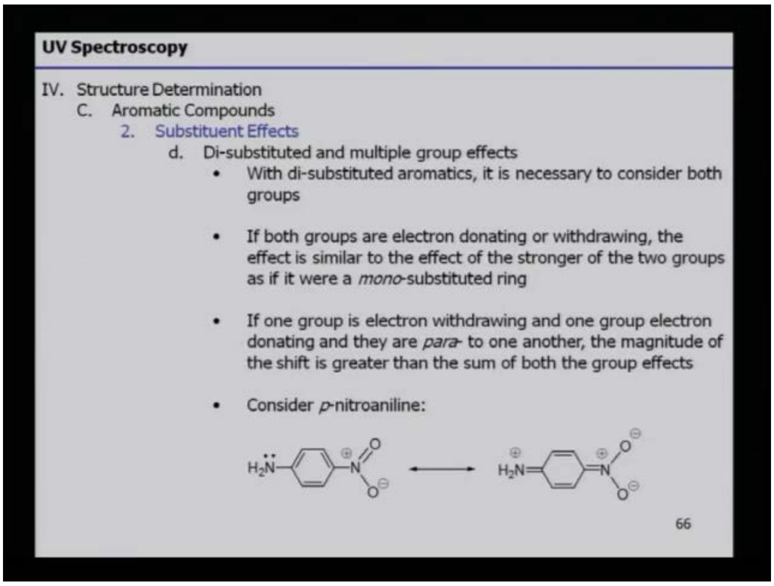

UV Spectroscopy

IV. Structure Determination
  C. Aromatic Compounds
    2. Substituent Effects
      d. Di-substituted and multiple group effects
        - With di-substituted aromatics, it is necessary to consider both groups
        - If both groups are electron donating or withdrawing, the effect is similar to the effect of the stronger of the two groups as if it were a *mono*-substituted ring
        - If one group is electron withdrawing and one group electron donating and they are *para*- to one another, the magnitude of the shift is greater than the sum of both the group effects
        - Consider *p*-nitroaniline:

Similarly, if there are di-substituents or if there is a multi-group effect, everything is going to make a difference in the electronic environment of the molecule. With di-substituted aromatic, it is necessary to consider both the groups. You cannot say that only one group is participating, why? Because, both the groups are in conjugation with the benzene pi rings, so, if they are in conjugation, they will participate with each other and will have a collective effect. If both groups are electron-withdrawing or withdrawing the effect is similar to the effect of stronger of the two groups, it may be said that it is a mono substituted ring. If one group is electron-withdrawing, and one group is electron-donating, and they are para to each other, the magnitude of shift is greater than the sum of both the groups that can effect.

So, if we try to look at an amino group attached to the ring and at the para position, there is an electron-withdrawing group that is the nitro group, what will happen everything will be in conjugation as shown in the slide.

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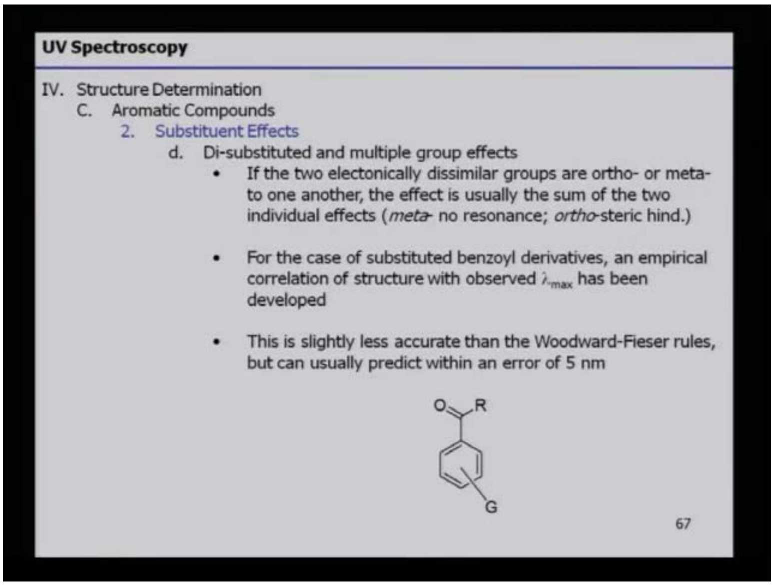

UV Spectroscopy

IV. Structure Determination
  C. Aromatic Compounds
    2. Substituent Effects
      d. Di-substituted and multiple group effects
        - If the two electonically dissimilar groups are ortho- or meta- to one another, the effect is usually the sum of the two individual effects (*meta-* no resonance; *ortho*-steric hind.)
        - For the case of substituted benzoyl derivatives, an empirical correlation of structure with observed λ_{max} has been developed
        - This is slightly less accurate than the Woodward-Fieser rules, but can usually predict within an error of 5 nm

Similarly, there are other effects that can be discussed; di-substitution can also have a lot of effect on the electronic situation of the molecule.

If the two electronically dissimilar groups are ortho- or meta- to each other, the effect is usually the sum of the two individual groups and we call it meta-no resonance or ortho-steric hindrance. So, if they are at a meta position or at ortho position, the two electronically dissimilar groups, then they will have an effect on each other.

For the case of substituted benzoyl derivatives, an empirical correlation of structure with observed lambda max has been developed. This is slightly less accurate than the Woodward-Fieser rule, but can usually predict within an error of 5 nanometers.

So, now there are some assumptions; there are some calculations, which have been tested for such di-substituted effects participation in the structure determination of aromatic compounds. But then, there is a level of error also possible, and the level of error or the difference in the calculated and the experimental value, can be as high as 5 nanometers.

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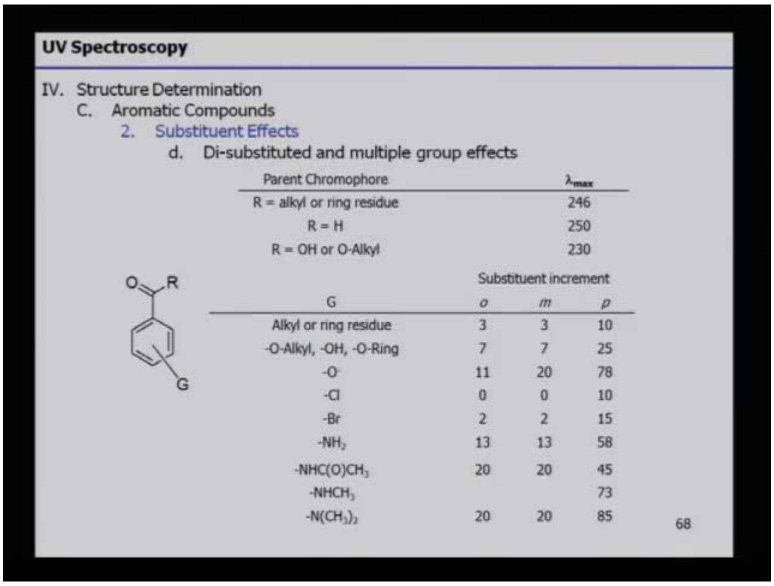

UV Spectroscopy

IV. Structure Determination
    C. Aromatic Compounds
        2. Substituent Effects
            d. Di-substituted and multiple group effects

Parent Chromophore	λ_{max}
R = alkyl or ring residue	246
R = H	250
R = OH or O-Alkyl	230

G	Substituent increment *o*	*m*	*p*
Alkyl or ring residue	3	3	10
-O-Alkyl, -OH, -O-Ring	7	7	25
$-O^-$	11	20	78
-Cl	0	0	10
-Br	2	2	15
$-NH_2$	13	13	58
$-NHC(O)CH_3$	20	20	45
$-NHCH_3$			73
$-N(CH_3)_2$	20	20	85

So, this has to be kept in mind that it is not as accurate as the Woodward-Fieser rule, which we saw for the acyclic compounds or the non-aromatic compounds. So, several examples have been given - what is the parent chromophore, and the parent chromophore will have a basic lambda max, then to that with the group that is attached more and more increment of the substituents can be added and a total of the final substituent and the calculated wavelength can be ascertained.

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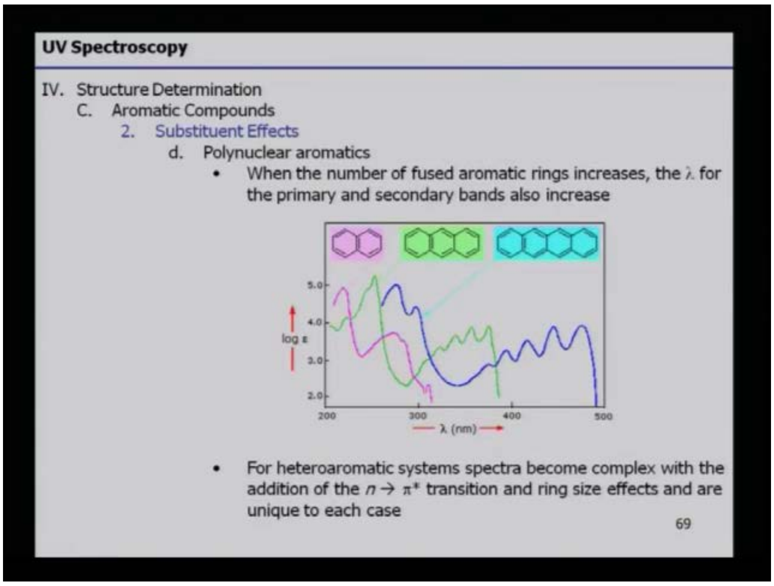

UV Spectroscopy

IV. Structure Determination
    C. Aromatic Compounds
        2. Substituent Effects
            d. Polynuclear aromatics

- When the number of fused aromatic rings increases, the λ for the primary and secondary bands also increase

- For heteroaromatic systems spectra become complex with the addition of the $n \rightarrow \pi^*$ transition and ring size effects and are unique to each case

Now, when we try to look at the aromatic compounds, the poly nuclear aromatics, when many benzene rings or more than 1 is present, and the benzene rings are attached to each other or fused to each other, like in the case of naphthalene, phenanthrene and so on. Then, what happens to the UV spectrum? When the number of fused aromatic rings increases, the primary and the secondary bands also increase. So, you see the primary and the secondary bands are associated with aromatic compounds. When they are associated with aromatic compounds, if the number of rings are increasing, then they will definitely contribute to both the primary bands and the secondary bands.

For heteroaromatic system, spectra become complex with the addition of n pi star transition and ring size effects are unique to each case. So, so you see that when it is a double, just two rings - that is, naphthalene cases - the spectrum looks like the pink one; when it has three rings fused to each other, the spectrum looks like the green one; and when it is a four aromatic rings fused to each other, one after the other, the spectrum moves more towards visible region, leaving the UV region and it is shown in by the blue lines.

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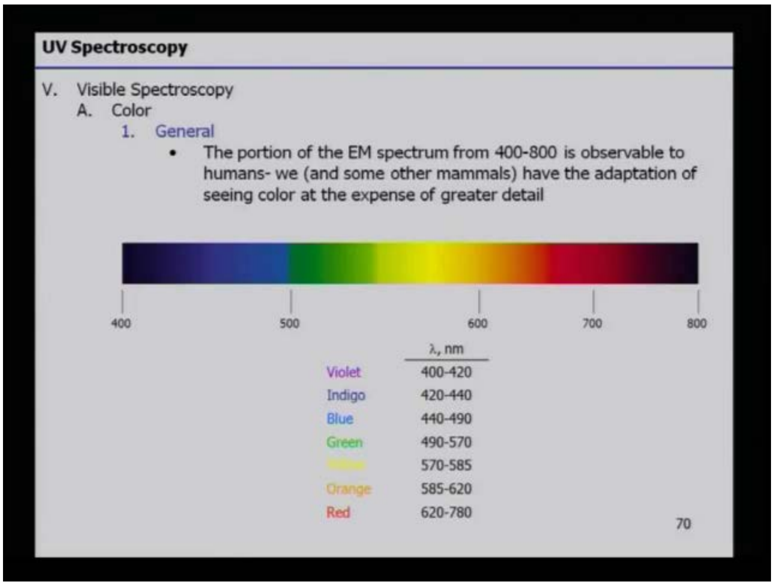

UV Spectroscopy

V. Visible Spectroscopy
  A. Color
    1. General
      - The portion of the EM spectrum from 400-800 is observable to humans- we (and some other mammals) have the adaptation of seeing color at the expense of greater detail

	λ, nm
Violet	400-420
Indigo	420-440
Blue	440-490
Green	490-570
Yellow	570-585
Orange	585-620
Red	620-780

Now, so far, we were trying to understand the UV spectroscopy and how to determine structure with the help of UV spectroscopy. What does a lambda max indicate? How to interpret and calculate lambda max and then compare with the unknown. Now, let us try to apply it to visible spectroscopy also, because UV goes hand in hand with visible;

although, the visible range is very small as compared to the UV range, but still, it is important to understand, the portion of electromagnetic spectrum from 400 to 800 nanometer is observable to the human eye. We and some other mammals, have the adaptation of seeing colors at the expense of greater details.

So, you see that the visible region is extremely small region - just between 400 to 800 nanometers - and this region is perceivable by our eyes and eyes of some of the other mammals. And so, it has been divided into different colors: violet, indigo, blue, green, yellow, orange and red and we call it vibgyor; as you all know that, you know, this is the color range of the visible region.

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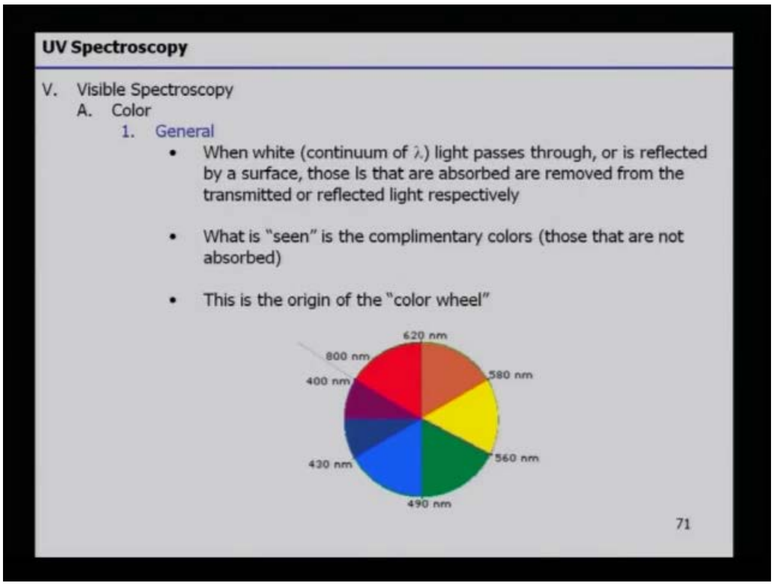

UV Spectroscopy

V. Visible Spectroscopy
  A. Color
    1. General
      - When white (continuum of λ) light passes through, or is reflected by a surface, those ls that are absorbed are removed from the transmitted or reflected light respectively
      - What is "seen" is the complimentary colors (those that are not absorbed)
      - This is the origin of the "color wheel"

Now, when white light, that is, continuum of the lambda max light passes through or is reflected by a surface, those that are absorbed are removed from the transmitted or reflected light respectively. What is "seen" is the complimentary colors, those that are not of absorbed. This is the origin of "color wheel"; so what we see is actually the complimentary color. So, one which is actually being absorbed, is not seen by us. So, that should be very clear, that light when it is passes through on a reflected surface, some of this is actually absorbed, and when it is absorbed, the transmitted light will be devoid of that portion of light, which has been absorbed and what we see is what is reflected. So, it is a complimentary, that substance which was not absorbed or the light part which was not absorbed, was actually seen by us. And that creates a color wheel, which have different wavelength, regions are shown here.

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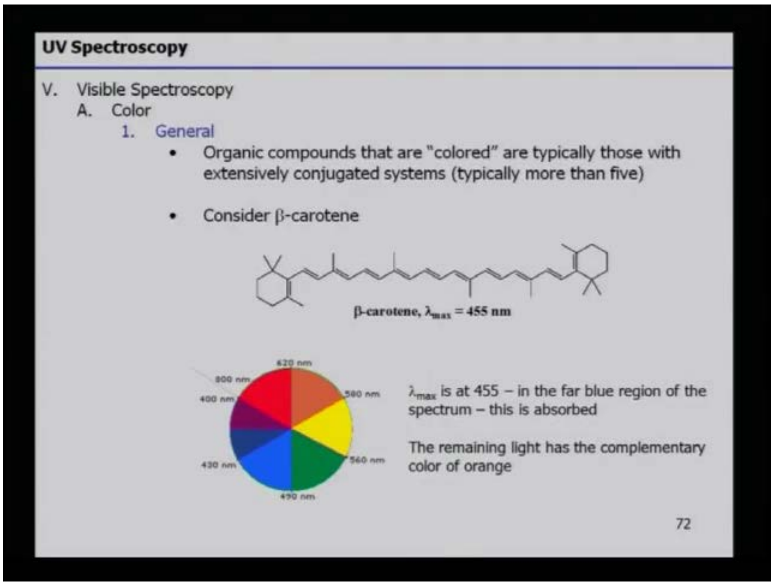

UV Spectroscopy

V. Visible Spectroscopy
  A. Color
    1. General
      - Organic compounds that are "colored" are typically those with extensively conjugated systems (typically more than five)
      - Consider β-carotene

β-carotene, $\lambda_{max} = 455$ nm

λ_{max} is at 455 – in the far blue region of the spectrum – this is absorbed

The remaining light has the complementary color of orange

In general, when we see a colored compound, we try to understand how the structure must be of this, because the moment it comes to the visible region, it must be understood by the analyst, that it has a fairly large number of conjugation, to push it from UV region to visible region. Any colored compound must have a substantially large area of conjugation of double bond and single bond. Only then, it will be pushed to the visible region. If it has only one isolated double bond or just two bonds, it will be colorless and it will remain in the UV region, not in the visible region; first thing that should be made very clear.

Organic compounds are colored, and are typically those with extensively conjugated system, typically more than 5. So, you now understand very clearly, that if there are 5 or more conjugated bonds, then only the substance is likely to be a colored compound. Consider beta-carotene, now you look at this huge structure, which has a lambda max at 455 nanometer. This particular compound - beta-carotene - has a lambda max at 455, is the far blue region of the spectrum that is absorbed. The remaining light has the complimentary color of orange. So, what and actually beta-carotene, which is present in carrots is orange. We know that, carrots are orangish red, and the orangish red color is imparted by the compound beta-carotene; and beta-carotene has huge number of conjugation; and the lambda max is 455 which is in the visible region.

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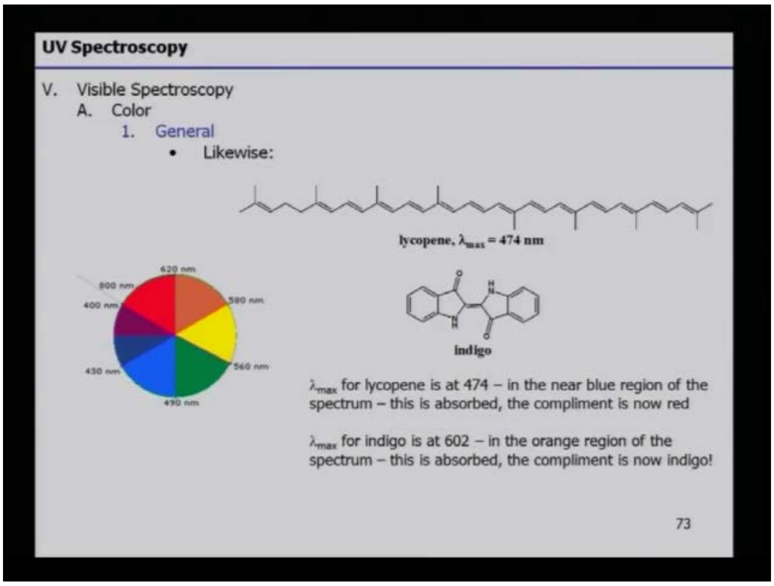

UV Spectroscopy

V. Visible Spectroscopy
  A. Color
    1. General
      - Likewise:

lycopene, $\lambda_{max} = 474$ nm

indigo

λ_{max} for lycopene is at 474 – in the near blue region of the spectrum – this is absorbed, the compliment is now red

λ_{max} for indigo is at 602 – in the orange region of the spectrum – this is absorbed, the compliment is now indigo!

Likewise, if we try to look at lycopene, it too has a very extended conjugation and the lambda max of lycopene is 474. Now, you see that, lambda max for lycopene is 474, is the near blue region of the spectrum that is absorbed and the complimentary red color is what we see. So, lycopene to us appears as a red compound; but it is actually absorbing the blue region of the visible region. So, that is to be understood very clearly, that what is absorbed is just the opposite end of what we perceive. So, if a compound is appearing red, it must be absorbing in the blue region; if the compound is appearing blue, then it must be absorbing the light of the red region.

The second example, that has been taken is an example of indigo; indigo dye which is used for dying jeans and denim, and all kinds of blue fabric. This indigo dye, the lambda max is 602 nanometer. It is in the orange region of the spectrum. This is absorbed and the complimentary color that is unabsorbed is the blue color and that is what we perceive. So, indigo appears to be blue to us, but it has actually absorbed orange color.

So, this is the concept of complimentary color. What we perceive is just the opposite end of what is actually being absorbed from the visible region of the electromagnetic spectrum.

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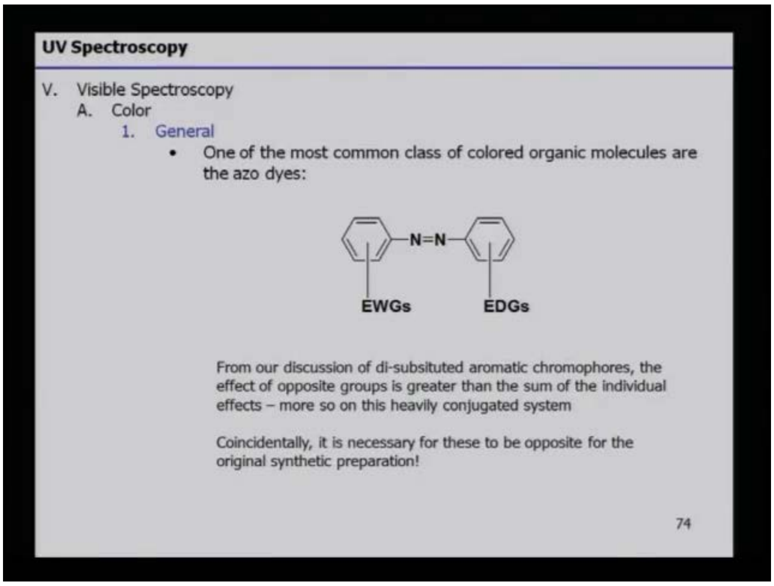

UV Spectroscopy

V. Visible Spectroscopy
  A. Color
    1. General
      - One of the most common class of colored organic molecules are the azo dyes:

From our discussion of di-subsituted aromatic chromophores, the effect of opposite groups is greater than the sum of the individual effects – more so on this heavily conjugated system

Coincidentally, it is necessary for these to be opposite for the original synthetic preparation!

Now, when we try to understand certain rules that are applicable to visible spectroscopy, one of the most common classes of colored organic molecules, are the azo dyes. Azo is a nitrogen-nitrogen double bond with aromatic rings. So, the main part of the molecule is the central nitrogen-nitrogen double bond, then there are two aromatic rings, and then the aromatic rings can have substituents, which are electron-withdrawing group - EWGs.

From our discussion of di-substituted aromatic chromophores, the effect of opposite group is greater than the sum of individual effects. More so, this heavily conjugated system is then… Now you see there is this electron-withdrawing group, benzene ring, then nitrogen-nitrogen double bond, again benzene ring, and then again electron-withdrawing groups. So, the whole system is having a beautiful pi conjugation. Coincidentally, it is necessary for these to be opposite for the original synthetic preparation. So, you see that, these kind of conjugated systems are synthetically prepared.

Although, azo dyes have been banned, but they are of great significance, because they are… at one point of time in the dying industry, azo dyes were the only compounds which could provide very good coloration to all types of fabric, be it synthetic fabric or natural fabric; so you see that, they had a big market, and there the beauty of the colored compound lies in the structure and the structure had extensive pi conjugation. So, that was the beauty of these azo dyes, from the structural point of view; in general, they are now considered to be environmentally unsafe.

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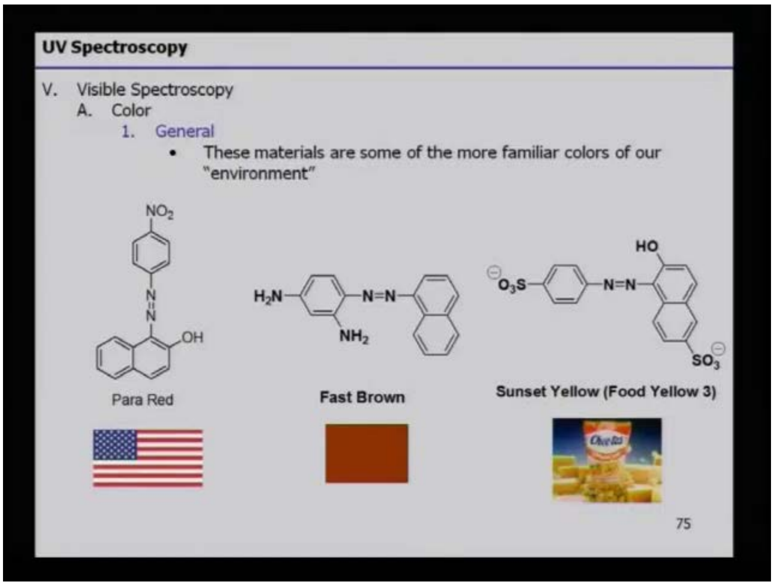

UV Spectroscopy

V. Visible Spectroscopy
  A. Color
    1. General
      - These materials are some of the more familiar colors of our "environment"

Para Red

Fast Brown

Sunset Yellow (Food Yellow 3)

These materials are some of the more familiar colors of our environment: the para red, the fast brown and the sunset yellow which is used in the food. These are the structures, because these are all colored compounds, and they are used for various purposes, and the sunset yellow of course, is a good azo compound, because it is use in food industry. However, the some of the azo dyes, 16 azo dyes have been banned, because they have been found to be carcinogenic and mutagenic.

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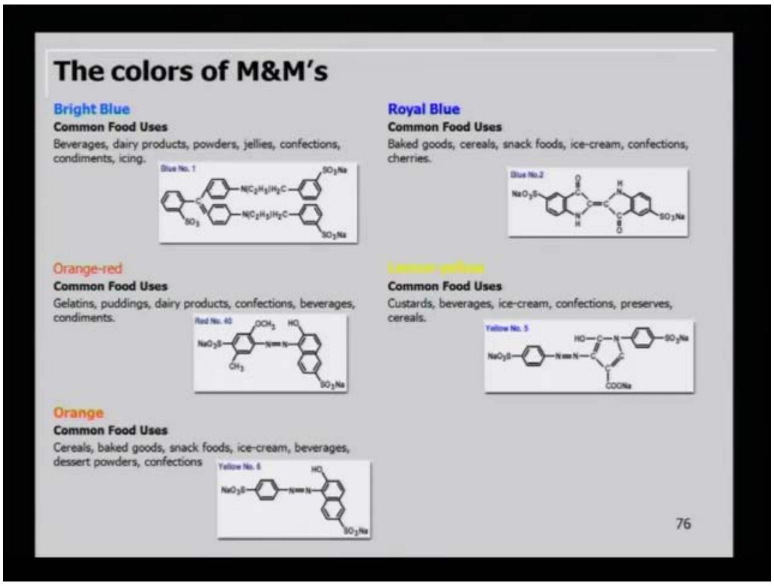

The colors of M&M's

Bright Blue

Common Food Uses

Beverages, dairy products, powders, jellies, confections, condiments, icing.

Royal Blue

Common Food Uses

Baked goods, cereals, snack foods, ice-cream, confections, cherries.

Orange-red

Common Food Uses

Gelatins, puddings, dairy products, confections, beverages, condiments.

Lemon-yellow

Common Food Uses

Custards, beverages, ice-cream, confections, preserves, cereals.

Orange

Common Food Uses

Cereals, baked goods, snack foods, ice-cream, beverages, dessert powders, confections

A huge number of such compounds can be enlisted. There is no end to these list of compounds, because the more the conjugation, the better would be the structure from the point of view of its conjugation.

Some of the common food dyes are, that is the blue-color, which is used in beverages, dairy products, powders, jellies, confectioneries, condiments, icing, etcetera is the blue number 1; and then red,orange which is used in gelatins, puddings, the dairy products, confectioneries, beverages, condiments is red number 40. Similarly, orange common uses - food dye is used in cereals, baked foods, etcetera. You look at the structure of the yellow number 6 and so on. So, you see that the more the conjugated system, the better it is and that imparts color of different types: blue, red, orange, yellow, and so on and so forth.

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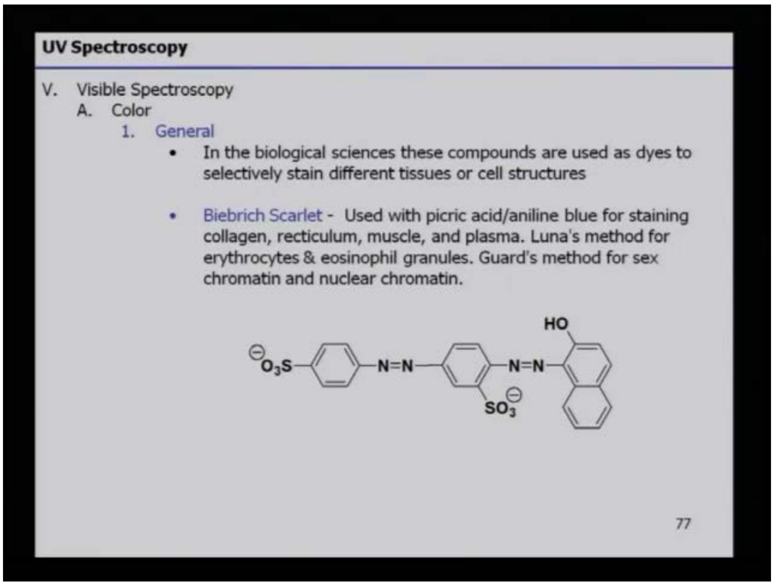

UV Spectroscopy

V. Visible Spectroscopy
  A. Color
    1. General
      - In the biological sciences these compounds are used as dyes to selectively stain different tissues or cell structures
      - Biebrich Scarlet - Used with picric acid/aniline blue for staining collagen, recticulum, muscle, and plasma. Luna's method for erythrocytes & eosinophil granules. Guard's method for sex chromatin and nuclear chromatin.

Therefore, there are certain, you know, parameters that have to be understood carefully. In biological sciences, these compounds are used as dye to selectively stain different tissues or cell structures. Even these dyes are used for staining purposes, particularly in the biological system; the biebrich scarlet is a dye used with picric acid/aniline blue for staining collagen, reticulum, muscle, and plasma. Luna’s method for erythrocytes and eosinophil granules has also been used. And these are very, very important dyes, which are specifically used in biological system.

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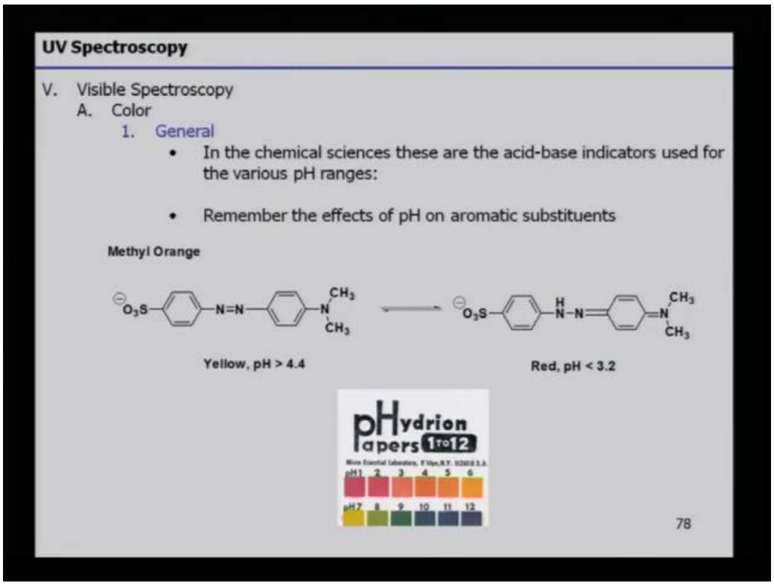

UV Spectroscopy

V. Visible Spectroscopy
  A. Color
    1. General
      - In the chemical sciences these are the acid-base indicators used for the various pH ranges:
      - Remember the effects of pH on aromatic substituents

Methyl Orange

Yellow, pH > 4.4

Red, pH < 3.2

If we then try to understand, that even in the pH range, you know, that pH paper that has been made, there are dyes which are changing color at a particular level of pH. In the chemical sciences, where we look at acid-base indicators used in various pH range, remember, that you have seen the pH paper, and that effect of pH on the aromatic system is what is the science behind the generation of the pH paper or the manufacturing science that we say. Methyl orange, which has yellow color when it is below 4.4, actually changes to red color when the pH goes still for the down to 3.2.

So, just by protonation, we just learnt about protonation, deprotonation, these can change the pH, and therefore, the color also changes. So, that is where it comes to very interesting science and many, many such uses are possible for these compounds, and therefore, it is a very interesting science, when we try to understand the chemistry of UV spectroscopy and visible spectroscopy.

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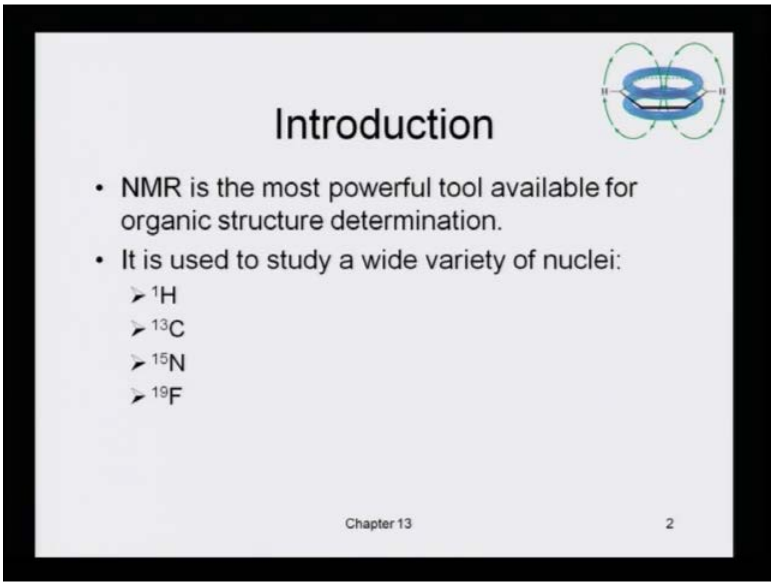

Introduction

- NMR is the most powerful tool available for organic structure determination.
- It is used to study a wide variety of nuclei:
  - ^{1}H
  - ^{13}C
  - ^{15}N
  - ^{19}F

Chapter 13 2

Now, we come to a new chapter which is called NMR spectroscopy. It is an interesting science, because here we learnt about the chemical environment around the carbon chain, how many hydrogen or protons that are present, and to be able to predict that carbon chain also, that is done by C 13 NMR. It deals with the radio frequency and that is why it comes under the category of spectroscopy. Let us try to look at this, NMR is the most powerful tool available for organic structure determination.

So, you see that it is not easy to be able to describe a structure by just one tool. Time and again, I have told, that we need the information from UV, from IR, from mass and NMR, to be able to collectively then decide about the structure. It is used to study a wide variety of nuclei, that is the proton, Carbon 13, Nitrogen 15, Fluoride 19, Phosphorus 31.

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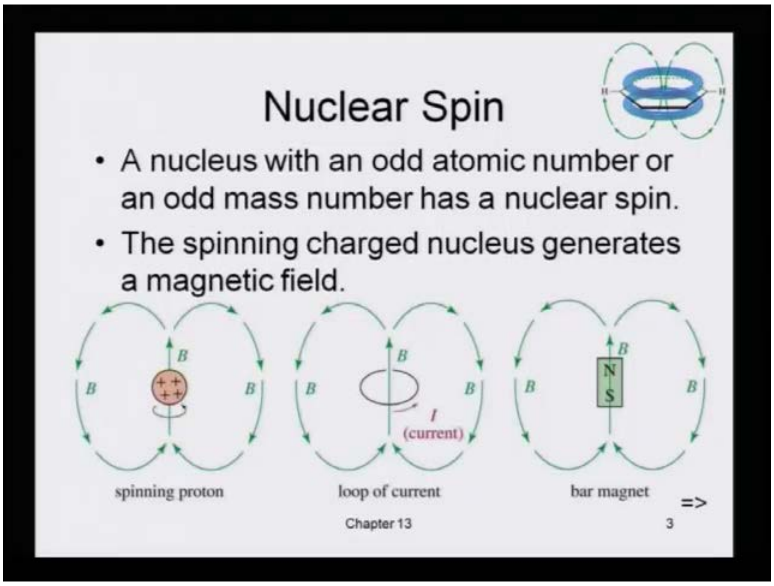

Nuclear Spin

- A nucleus with an odd atomic number or an odd mass number has a nuclear spin.
- The spinning charged nucleus generates a magnetic field.

The nuclear spin; actually, these nuclei are very special. It is not that, any and every isotopic species can be used for NMR analysis. It is precisely, only the proton, and the C 13, and the N 15, and the F 19, and the phosphorus 31 - those, only can be taken for NMR study. A nucleus with an odd atomic number or an odd mass number has a nuclear spin. So, you see that any nuclei, which has an odd number, only that atomic number and odd mass number has a nuclear spin, and if the mandatory fact for this is, that it should have a nuclear spin.

The spinning charge nucleus generates a magnetic field. Any charged body, if it is spinning, it creates a magnetic field; that is how the electromagnetic system arises. And this is how a spinning proton creates a current and it becomes like a small magnetic bar, it is almost equivalent, the magnetic field that is generated, creates that kind of an electromagnetic field.

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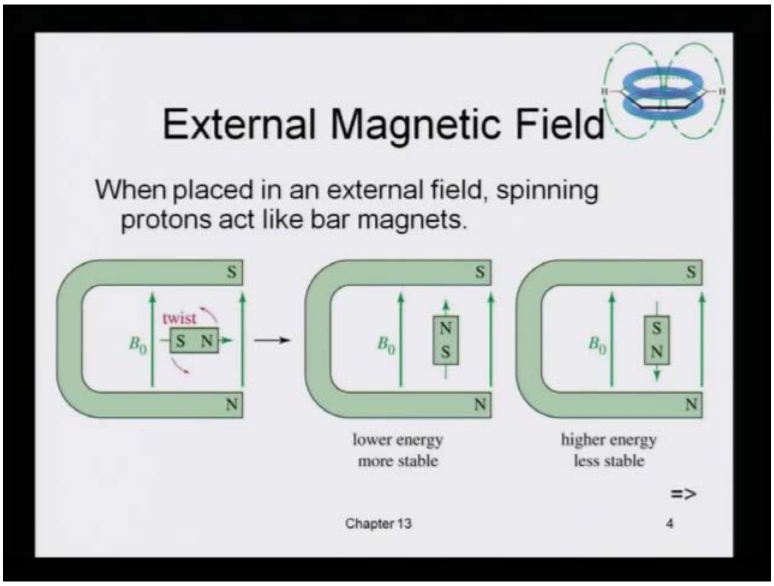

External Magnetic Field

When placed in an external field, spinning protons act like bar magnets.

lower energy
more stable

higher energy
less stable

Chapter 13

4

Now, external magnetic - when this small magnet is placed in an external field, the spinning proton acts like a magnet bar. So what happens, suppose, now, this is a small magnet; now, this magnet is made to sit in another big magnet, they will have different fields; so, it will either align itself or it will twist itself; if it aligns itself, it is more stable and the there is a lowering of energy; if it reverses itself, then it will become less stable and it will become energetically very high.

Now, these are some basics, which we need to understand before entering into the understanding of nuclear magnetic resonance spectroscopy - the NMR spectroscopy. So, with this background, we just start understanding what NMR is all about. There are two energy states for any system: one is the alpha state and the other is the beta state.

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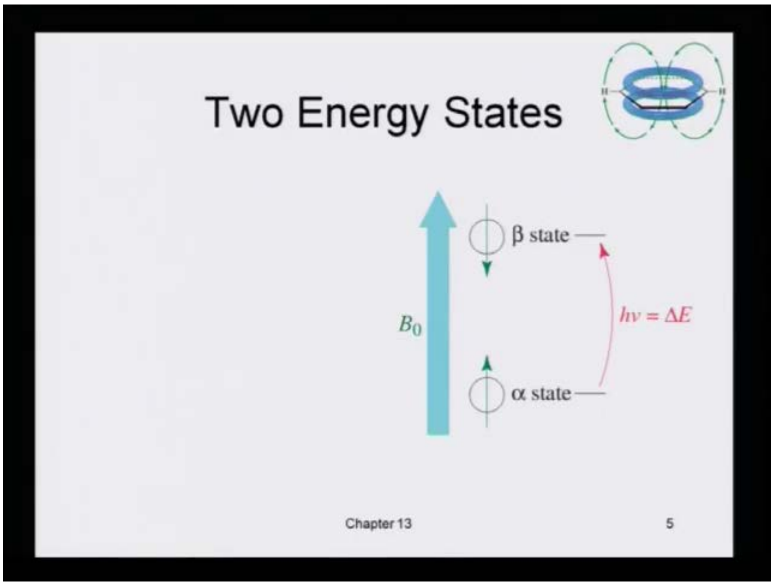

Two Energy States

Now, there is a different of h nu or delta E between these two states, when as what I showed you, it can either align itself or it can reverse itself. So, these are the lower energy state and the higher energy state which we are comparing.