Interpretative Spectroscopy

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Lecture 22

Types of Electronic Transitions and Woodward-Fieser Rules

Hello everyone, with great pleasure I shall welcome you all once again to MSB lecture series on interpretative spectroscopy. In my last lecture, I started talking about UV visible spectroscopy. So, let me continue from where I had stopped in my previous lecture. We started talking about electronic transitions, of course, electronic transitions can be broadly classified into four types sigma-sigma* (σ→σ*), n -sigma* (n→σ*), n-pi* (n→Π*) and pi-pi* (Π→Π*). Sigma-sigma* (σ→σ*) are shown by saturated hydrocarbons in which all valence shell electrons are involved in the formation of sigma bond. That means, no electrons are left unutilized for bond formation in the valence shell. So, these transitions require very high energy and occur at lesser wavelengths less than 200 nanometer and fall in vacuum UV region.

If we consider n to sigma* transition (n→σ*), compounds having nonbonding electrons and hetero atoms such as oxygen, nitrogen, sulfur or halogens can show such type of transitions. The energy required for these transitions decrease with the decrease in electro negativity of hetero atom and therefore, the wavelength of absorption increases. And then the third type is n to pi* (n→Π*). Compounds having double bond between hetero atoms, for example, C double bond O, C double bond S, N double bond O, etcetera, show these kinds of n to pi* transitions (n→Π*). These transitions require only small amount of energy and takes place within the range of ordinary ultraviolet region.

However, the intensity of absorption is generally very low and these transitions have an epsilon value of less than 10 raise to 4 (10^4). Of course, here the when you look into overall the energy difference between these levels n to pi* (n→Π*) is the least energetic

that is the reason it requires very low energy for the promotion of the electrons. Pi pi star (Π→Π*) compounds having double bonds show these transitions. The intensity of transition is very high for these transitions. These transitions have epsilon value in the range of 10 to the power of 4 (10^4) or more and they are also allowed transitions.

In electronic spectroscopy, if you look into it, all these compounds have in different region of usable range. That means definitely we have substituent effects. So, what are those? A functional group capable of having a characteristic electron transition is called a chromophore. We should remember the chromophore is responsible for electronic transition. The attachment of a substituent group other than hydrogen can shift the energy of the transition.

That means substituents that increase the intensity and often wavelength of an absorption are called auxochromes. Substituents may have any one of the four effects on chromophore. What are those? We call it as i) bathochromic shift that is also known as red shift. What happens in this one? Shift to longer wavelength, when it goes to longer wavelength means probably we are thinking of decreasing the gap between HOMO and LOMO. So, then it requires low energy, that is the reason it is called bathochromic shift or red shift or shifting to longer wavelength or it is a low energy transition. Then the second one is ii) hypsochromic shift, that is also called blue shift. That means shifting to shorter wavelength and higher energy.

That means, when the gap (HOMO-LUMO) increases, we need to give more energy, that is the reason it is called blue shift and also shift to shorter wavelength and also high energy transition. What is iii) hyperchromic effect? An increase in the intensity of the transition, then iv) hypochromic effect is a decrease in intensity. So, these four terms we come across and these four comes as a consequence of the influence of substituent on chromophore. You can see here in this plot you can see if you say here it is a 200 nanometer and here 700 nanometer and this is epsilon value (ε) you can see hypochromic and hypochromic this is hyperchromic and this is hypochromic and this is bathochromic

and hypsochromic. The moment you see the shift from left to right, it has to be hypsochromic blue shift and right to left means it is bathochromic red shift and as the intensity is going high it is called hyperchromic and intensity is dropping it is called hypochromic.

So, these are the influence of substituents on chromophore which is responsible for electronic transitions. I have given a list of chromophores with the specific example in each case and also the solvent in which we have looked into the transition and the lambda maximum and epsilon (ε), also the type of transition. Very useful table this is, for example, if you look into alkene, we know that we have a double bond. So, immediately we can say it should be a pi-pi transition (Π→Π*) and once it is a pi-pi transition (Π→Π*) you can anticipate little higher epsilon value (ε). This is in the range of 13000 and lambda maximum is 177 nanometer. The solvent considered is n-heptane. Then if you take alkene, we have a triple bond and again solvent user is n heptane it can show lambda maximum in the range of 178 to 125 and then here epsilon value (ε) varies 10000, 2000 or 160 and here it is pi-pi star transition other transitions can also be seen. And then if you consider carbonyl groups make aldehyde acid or a ketone.

So, in this case for example if you consider aldehyde in n-hexane, here you can anticipate 186 as well as 280 and for 186. Epsilon value (ε) is little higher, compared to 280 it is low and then for this acetone in n-hexane 180 and 293 and in case of 180 large epsilon value (ε) will be there. For 293, it is low and here in the large one is due to n – sigma* (n→σ*) and the lower one is due to n-pi* (n→Π*). We know that n to pi* (n→Π*) is of weak intensity and same thing true here. Whenever weak intensity is there, you can conclude that it is not n to sigma star (n→σ*), it is not even pi to pi star (Π→Π*); it is n to pi star (n→Π*). And then carboxylic group if you consider acetic acid as an example, recorded in ethanol, it shows 204 and then 41. So, when you look into the epsilon value, one can conclude that certainly it is due to n to pi* transition (n→Π*). And in case of amido group, for example, if you take acetyl amide, water is taken as a solvent because soluble in water this is 214 and then 60 again same thing it is n to pi star (n→Π*).

With azo compounds, there is N=N. In ethanol 339 and then 5, very low. Again, you can conclude that it is n to pi* (n→Π*). In case of nitro in isooctane as a solvent the value is 280 and epsilon value is again low 22. So, this also again due to n to pi star transition (n→Π*). If you take nitroso group recorded in ethyl ether 300, whereas at 100. In case of 665 20 it is again n to pi star (n→Π*).

In case of nitrate, dioxane is the solvent chosen and then lambda maximum is 270 and then epsilon is very low again. So, what we can see clearly: pi to pi* ((Π→Π*) has higher epsilon value and n to sigma* (n→Π*) also has reasonably higher epsilon value. But, wherever epsilon the absorptive coefficient is very low without any hesitation we can tell this is due to n to pi star transition (n→Π*). This gives some idea about the different type of chromophores and their characteristic lambda maximum (λ_{max}) and epsilon maximum (ε_{max}) and also the type of transition we come across. Then after look into substituent effect let us look into solvent effect.

Solvent effect: when we talk about it, the polarity comes into the picture. Increase in the polarity of the solvents shift n to pi* transition (n→Π*) to shorter wavelength. That means, addition of polar solvent results in blue shift, n to pi* (n→Π*) goes to shorter wavelength or higher energy, that means, gap is increasing. So, this blue shift is mainly due to the greater stabilization of the ground state than the excited state through dipole-dipole interaction. Polar solvent induces dipole-dipole interaction. As a result, what happens the ground state will be dropped in energy than the excited state and hence the energy gap increases and the wavelength decreases and energy required increases in frequency. So, this is a typical polar solvent for example, when you take nonpolar solvent this is the situation when you had a polar solvent, the ground state is more stabilized, means it drops in energy, as a result n-pi star gap (HOMO-LUMO gap) increases and hence it shifts to blue region, it is called blue shift.

That means, if a group is more polar in the ground state than in the excited state,

increasing the polarity of the solvent, shifts the absorption to shorter wavelength. So, this we should remember, come across in hypsochromic shift and this is blue shift. On the other hand, increase in polarity of the solvent shifts the pi to pi star transition (Π→Π*) to longer wavelength, then it is called red shift. So, the red shift is mainly due to the greater stabilization of excited state than the ground state through. Dipole dipole interaction, formation of hydrogen bonds or solvent effect with the polar solvent is responsible for this kind of rearrangement. That means, increase in the polarity of the solvent brings down the pi-pi* gap (Π→Π*) to the lower level, as a result, what happens longer wavelength radiation is required for electronic transition, this is called red shift.

Red shift is mainly due to the greater stabilization of the excited state than the ground state. In case of earlier one, we saw the blue shift is mainly due to the greater stabilization of ground state than the excited state. Opposite is true here; the red shift is mainly due to the greater stabilization of the excited state than the ground state through dipole-dipole interaction. This is probably due to hydrogen bonding or solvation with the polar solvent. So, you can see the situation in non-polar solvent this is the one and in the polar solvent this gap decreases and it goes to red shift that means longer wavelength. That means, if a group is more polar in the excited state then in the ground state the increasing the polarity of the solvent shifts the absorption to longer wavelength. This is again type of solvent effect on pi pi* transition (Π→Π*), previous one was n to pi star transition.

If there is an extended conjugation, an increase in conjugation decreases the energy required for electronic excitation. That means, extensive conjugation brings the gap between pi-pi star (Π→Π*), if the pi is HOMO and pi star is LUMO. This gap is considerably brought down, if you have extended conjugation. From molecular orbital diagram shown here two atomic p orbitals form two sets of sp^2 hybrid carbons combine to form Ψ and Ψ* in ethylene. So, here you can see this is simple ethylene, but if you compare this one to butadiene here mixing of 4p orbitals results in energetically symmetrical distribution of 4 MOS compared to ethylene due to which HOMO-LUMO gap is reduced and hence transition energy goes to longer wavelength.

So, that means, you can compare here, this is for typical ethylene and this first butadiene. Here the gap is considerably lower here, compared to what we see in case of ethylene. That means, ΔE or energy required for HOMO-LUMO transition is reduced here. That means, the conjugation decreases the HOMO-LUMO gap and hence it will be a red shift. So, conjugation effect can be seen for different transitions here with different systems. The longer conjugated systems decrease the energy gap between HOMO and LUMO and it progressively becomes smaller and absorption shifts to longer wavelengths. So, you can see here ethylene to butadiene to hexatriene to octa tetraene.

So, that means, you start from one double bond, two double bonds conjugated, three double bonds conjugated, and four double bonds conjugated, you can see very nicely the energy gap is diminishing and shifting towards the longer wavelength. So, this is called conjugation effect. So, now, let us look into important rules such as Woodward-Fieser rules for calculating lambda maximum for a given compound by considering all functional groups present in it. If you consider HOMO annular diene, a cyclic diene with conjugated double bonds in the same ring, they are called HOMO annular diene. If you have conjugation or conjugated double bonds in the same ring this called cyclic diene, and then we look into hetero annular diene; a cyclic diene with conjugated double bonds present in different rings it can be something like this or it can be something like this.

So, hetero annular diene is one in which we have a typical cyclic diene with conjugation or two double bonds present in different rings and endocyclic double bond, a double bond present in a ring is called endocyclic double bond. Exocyclic double bond, a double bond outside the ring with one of the doubly bonded atoms is a part of a ring. So, this is something like this and here we have both endocyclic double bond and exocyclic double bond, this is a typical example here where you have both. So, this is how some of these unsaturated compounds are defined with terms Homoannular diene, heteroannular diene, endocyclic double bond and exocyclic double bond with example in each case is given here. What is the Woodward-Fieser rules for conjugated dienes, trienes, polyenes etcetera? Let us look into it. Let us consider a parent value.

So, by identifying the type of cyclic system we have to give a parent value. What are those parent value? A cyclic conjugated diene the value is 270 nanometer for HOMO annular conjugated diene it is 253 nanometer in case of hetero annular conjugated diene it is 214 nanometer, we should remember. Now, we should look into the increment provided, we add something else to it. For example, each alkyl substituent or a ring residue add 5 nanometer and for each exocyclic double bond we should add another 5 nanometer and then double bond extending conjugation 30 nanometer. If you have oxochrome such as -OR 6 nanometer, and SR 30 nanometer and if you have O-$COCH_3$ carboxyl group then there is no need to add anything and if you have chlorine or bromine add 5 nanometer, and if have amide group NR_2, add 60 nanometer.

So, one typical example is given here and calculated value here comes 234 nanometers by considering the hetero annular diene here and then the three-ring residue is there. So, add one ring is 5. So, 3 are there 15 and 1 exocyclic double bond is there another 5 increment. So, calculated lambda maximum comes around 234 and if you actually measure it would come very close to this value, given here. Then if you see homoannular diene conjugation within the ring the value designated is 253 and 2 ring residue.

So, 10 nanometer 2 alkyl substituents 10 nanometer, it comes around 273 nanometer. So, this is how one can effectively use Woodward-Fieser rules for conjugated dienes to predict the lambda maximum value (λ_{max}). Now, further continue, if you have alpha,beta-unsaturated compounds, Woodward Fieser rules are available. Parent values are given here: alpha (α), beta (β) unsaturated acyclic or 6-membered ring ketone, the value is 250 nanometer and alpha beta unsaturated 5 membered ring ketone is 202 and alpha beta unsaturated aldehyde is 207 nanometer is the parent value and then increments follow this order. At alpha position, if you have alkyl substituent or ring residue then add 10 nanometer at alpha position, at beta position add 12 nanometer, and at gamma bond higher position add 18 nanometer and for every exocyclic double bond add 5 nanometer and double bond exocyclic to 2 rings simultaneously, that is a 10 nanometer. That means

we have to watch carefully the structure before we give this increment for the parent value, and then double bond extended conjugation give 30 nanometer and homo annular conjugated dienes at 39 nanometer.

So, one such example is considered here: parent value is 215 here because this is alpha beta unsaturated 6-membered ring here, and then one alpha ring is there 10 nanometer and one delta ring is there 18 nanometer one exocyclic double bond is there 5 nanometer one double bond extended conjugation 30 nanometer one homoannular conjugated dienes is there 39 nanometer. So, calculated lambda maximum value for this compound considering the increments added to the parent value it comes around 317 nanometer. So, one can conveniently use this method to predict the lambda maximum (λ_{max}) value and then that can always be compared with the experimental value. So, here some axochromes values are given if alpha (α) position for hydroxy group 35, beta (β) 30 and gamma (γ) 50 and similarly for OR group alkoxy aryl oxy group 35, 30, 37, respectively, for alpha beta and gamma positions and if we have SR functional group. So, in this case, what happens alpha nil, beta 85 and gamma nil, and if you have carboxylic group, alpha position 6 beta also 6 gamma (γ), whether it is in alpha beta or gamma 6 increment has to be given nanometer and for chlorine alpha position 15 beta position 12 and nothing need to be added. If it is in gamma position and then similarly for bromine we add 25 and 30.

So, this is how we can carefully look into the increments by identifying the groups and their position and adding the increments for various auxochromes or other fragments to the parent value, very conveniently, very nicely, very precisely, we can calculate the lambda maximum value (λ_{max}). Now, let us look into the type of electronic transitions responsible for color of compounds. especially coordination compounds. In complexes, instead of looking into the several transitions I showed you, sigma to sigma star, pi to pi star ($\Pi \rightarrow \Pi^*$), n to pi star ($n \rightarrow \Pi^*$), n to sigma star ($n \rightarrow \sigma^*$), these are all mostly confined to organic moieties, nevertheless, we can also see in the metal complexes originating from ligands or metals to an extent and we get one more extra transition that is called d-d transition in metal complexes. For example, if you consider 3*d,* 4*d*, or 5*d* series, they have anywhere from d^1 to d^{10} electrons in their valence shell and then in case of

octahedral compounds, we know from crystal field theory that they are split into t_{2g} and e_g and in case of tetrahedral complexes, e and t_2. Opposite of that one and in case of square planar complexes, we have d_{xy} as HOMO and $d_x2\text{-}_y2$ as LUMO and between them electronic transition takes place that we call it as d-d transitions. So, what are the conditions for d-d transitions. Do really d-d transitions are allowed or not all those things, we shall look into in detail in my next lecture.

Now, I have given one example here: hexa aqua titanium 3+ $[Ti(OH_2)_6]^{3+}$, a d^1 system, and here you can see when the electron is there and this electron after giving the energy, it is promoted here. This is called d-d transition. Similarly, if you take tetrachlorocobaltate 2 minus $[CoCl_4]^{2-}$, it is tetrahedral compound, we have 4 electrons, is a high spin complex we have 4 electrons in e and 3 electrons in t_2. So, here which electron is responsible. So, either e this electron can go or this electron can go that is what we have seen.

Here we can see the transition. So, let us look into more details of d-d transitions in my next lecture. Until then see you, all have a nice time. Thank you.