Interpretative Spectroscopy
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Lecture 29

Introduction to IR Spectroscopy-1

Hello everyone, I once again welcome you all to MSB lecture series on interpretative spectroscopy. In my previous lectures, about 8 lectures I focused on UV visible spectroscopy and of course I am giving more emphasis for inorganic molecules in particular d-d transitions, that means 3d, 4d, 5d. Metals having d^1 to d^{10} electronic configuration show different types of absorption depending upon the nature of the ligands and also the nature of the metals and their oxidation states and also under which ligand field they are situated. So, based on all those things, lambda-maximum varies and also, I showed you how we can simplify all electronic configurations, all metal complex having different electronic configuration into simply 3 or 4 categories. One is d^0 and d^{10}, d^0 do not have any electrons and d^{10} is completely filled. Unique cases, for example, you can consider potassium permanganate, potassium dichromate. In case of d^{10} you can consider mercury iodide and then the remaining ones d^5 is a unique one. Then the remaining 8 electronic configurations are d^1, d^4, d^6 and d^9 and then d^2, d^3, d^7 and d^8 and there is some similarities I showed you. For example, if you take d^1, d^4, d^6 and d^9; one electron is there and one less than half field electronic configuration, one more than half field electronic configuration and then d^9 is one less than completely field electronic configuration. So, these four electronic configurations invariably show one d-d transitions and then the second type is d^2, d^3, d^7 and d^8. The similarities you can conclude in this manner. Two electrons, two less than half field, two more than half field and two less than completely field. So, these show three bands in their d-d spectra and then of course, d^5 what happens when you look into selection rule, d^5 high spin complexes have five electrons in t_{2g} and e_g in case of octahedral complexes and in case of tetrahedral complexes we have here two in e and then three in t_2 system.

So, in these cases, what happens since the selection rule says delta-S equal to 0 ($\Delta S = 0$) and delta-L equals plus or minus 1 ($\Delta L = \pm 1$). Strictly speaking none of these d-d transitions should occur as they are all prohibited from Laporte rule, but what happens when you look into metal complexes metal ions under the influence of ligand field, they lose the degeneracy of d orbitals and some of the orbitals will be lower in energy some of the orbitals in higher energy because of extensive mixing of d orbitals with s and p characters. As a result, what happens, they are no longer pure d in nature. As a result, Laporte allowed transition could be seen and hence we will see d-d transitions and selection rule as I mentioned delta S equal to 0 ($\Delta S=0$) and this is quite opposite to what we see in case of nuclear transitions. Nuclear transition, if you recall, it is delta-S equal to plus or minus 1 ($\Delta S = \pm 1$). So, that means a nucleus having spin half will go to spin minus half downward spin, whereas here electron with a upward spin should go like this as upward spin only.

So, delta S equals 0 ($\Delta S=0$) here when you look into d^5 they are spin forbidden and especially when they have center of symmetry, the colors are very weak, but when we look into tetrahedral complexes, they do not have center of symmetry. As a result some mixing is there and hence we see some of these compounds having d^5 electronic configuration with weak field ligands would be little colored, but why d^5 octahedral complexes having high spin still show color. What happens, if you look into the ligands, ligand to metal bonds are not rigid, but they will be vibrating with respect to the mean position. So, because of these vibrations, what happens, often some of these ligands come out of the equilibrium position. As a result, these complexes lose center of symmetry and hence mixing would take place and hence they show color. So, this is all about UV visible spectroscopy and again for d^1, d^4, d^6 and d^9 we can have conveniently one diagram that is called Orgel diagram to explain electronic spectra for both octahedral and tetrahedral complexes. Similarly we can have another Orgel diagram to explain spectra of octahedral and tetrahedral complexes having d^2, d^3, d^7 and d^8 electronic configuration, but when you go to Tanabe-Sugano diagram, every electronic configuration we should have a separate Tanabe-Sugano diagram, but that includes the entire band of ligands that means whether it is a weak field ligand or it is a high field ligand, everything is included and, but we should have one Tanabe-Sugano diagram per one electronic configuration

and also we saw in case of d^2, d^3, d^7 and d^8 there is a drop in the observed frequency of one of the bands or increase. This is due to nephelauxetic effect and that can be corrected using Racah parameters. Another important thing one should remember about UV visible spectroscopy is how to write term symbols, ok, term symbols you should be able to write by simply knowing L azimuthal quantum number, Σl that gives capital L and L can have anywhere between 0 to 1, 2, 3, 4, 5 and then corresponding terms we have S, P, D, F, G, H, I etc. and then 2S+1 is called spin multiplicity and then we have J, it can take values anywhere between L plus or minus S (L ± S) and here what we should remember is when we identify the ground term that should have highest multiplicity. When you look into highest multiplicity maximum number of unpaired electrons will be there. One state which is having highest 2S+1 value will be the least energetic and ground state and then due to some reason if we have two terms both having the same multiplicity value, 2S+1, then we have to consider the L value. Highest value will be the least energetic and then let us say we have multiplicity is same and then L value is same in that case we have to consider the J value. When you consider J value we have to consider L minus S (L-S) for subshells having less than half electronic configuration and then L plus S (L+S) for those which are having more than half electronic configuration. Other one is microstate, microstate will give you ground state along with several possible excited states and formula is very simple: n factorial over r factorial into n minus r factorial. So, n! will tell you the total capacity of the sub shell which we are considering for example if we consider d orbital total capacity is 10 electrons so n! means 10!. If we consider f orbitals, we have 14 electron capacity so it is 14! and then r is the total number of electrons we are considering so d^2 system n! is 10! and r is 2 so this is how you should be able to calculate the microstates. All possible microstates are actually do not show transitions and it is much simplified because we are bringing Leporte selection rule again, and hence it makes understanding and observed spectrum much simpler compared to what we could think of considering all possible microstates. So, this is all about UV visible spectroscopy and I would come back again at the end with more interesting problems to make you familiar with solving problems as far as UV visible spectroscopy is concerned.

Now let us move on to IR spectroscopy. I am sure you are all familiar with infrared spectroscopy. Infrared spectroscopy is a very important tool to chemists to identify what

functional groups exist in unknown samples or samples we have made in the laboratory. The light our eyes see is but a small part of a broad spectrum of electromagnetic radiation in the visible region. I would say on the immediate high energy side of the visible spectrum lies the ultraviolet and on the lower energy side is the infrared. You can see here, we have visible spectrum here and infrared is here and microwave radiation comes here. This is the region we are going to focus as far as infrared spectroscopy is concerned. Having a wavelength range of about 2500 to 16,000 nanometer, the infrared region is capable of revealing information not easily uncovered through basic means so that gives vital information about different types of functional groups present and also the characteristic bands due to the different bonds present in the molecule. The preferred method of infrared spectroscopy is FT-IR that means Fourier transform infrared spectroscopy, commonly used nowadays. IR can aid in the identification of unknown compounds and also it can determine the quality or consistency of a sample. If it is in the large industrial scale production, then how it happens? when infrared radiation is passed through the sample some of the radiation is absorbed by the sample and some of the radiation is passed through are transmitted. The resultant spectrum is nothing but the plot of percentage transmission versus frequency in centimeter inverse (cm^{-1}) of the radiation that is passed through in the infrared region. The energies of photons associated with the infrared region are not large enough to excite electrons, but they are still strong enough to induce vibrational excitation of coherently bonded atoms and groups. That means energy of photons associated with infrared radiation is so small, it cannot really excite an electron from E_1 level to E_2, higher energy level, but on the other hand they can induce vibration of the bonds. That means when we consider a molecule, we have covalent bonds these covalent bonds are not rigid sticks or rods, but are more like stiff springs that can be rotated provided there is a single bond, they can be stretched or they can be bent so these different types of vibrational motions are characteristic to a molecule's component atoms. This information comes directly from infrared spectroscopy. All organic inorganic compounds will absorb infrared radiation that corresponds in energy to these vibrations and infrared spectrometers allow chemists to obtain absorption spectra of compounds that are a unique reflection of their molecular structure. That means an IR spectrum can be considered as a molecular fingerprint of the sample as no two unique

molecular structures produce the same IR spectrum. This is very very important, it may not be possible to understand all the peaks present and one need not have to worry about interpreting all the absorption peaks that are seen in that region, but what one should remember is, this fingerprint region is characteristic of molecules. So, what is the theory involved behind this infrared spectroscopy. IR can provide information about the presence of particular functional groups say whether OH group is there, whether CO group is there, whether amine group is there or there is a C—C double bond, whether P double bond O, or C triple bond N, C double bond N, all this vital information one can extract from simply by looking into IR spectrum of a given molecule. IR data along with NMR and mass spectrometric data can provide the structural features of a compound without any ambiguity. So minimum information about the theoretical aspects of IR is sufficient to use in structural analysis. I am not going into the details of theoretical aspects as I had mentioned. My attention is to focus on interpretation with minimum theoretical background. I try to make you familiar with interpretation of data from various spectroscopic methods that we use routinely while characterizing organic or inorganic molecules. IR absorption band of a compound indicate the presence of functional groups. this is the most important point one should remember. IR absorption bands of a compound indicate the different types of functional groups present in that molecule. So narrow and sharp bonds seen in the spectrum are called peaks. So peak or band positions are given in wave numbers as unit of reciprocal centimeter that you know in the IR spectrum. IR region between 400 to 4000 cm^{-1} is very important. Most of the functional groups have absorptions in this region of 400 to 4000 cm^{-1}. The frequency divided by C, the speed of light, provides the wave number. This one should remember. This indicates, for example, vibrational of frequency 6 x 10^{13} Hz has a corresponding wave number of 2000 centimeter minus 1 (cm^{-1}), that is equal to 6 x 10^{13} Hz over velocity of light 3 into 10 raised to 10 centimeter per second (3 x 10^{10} cm^{-1}). This will give you about 2,000 wave numbers. This is how you can simply calculate the frequency to wave numbers. Band intensities are reported as follows, by looking into the spectrum, we have to identify and we have to give a term depending upon the type of intensity we come across. For example, if it is strong, we have to denote it by S, and if it is medium, we have to say M, and if it is weak, we should say W, and if it is sharp we have to say sharp

Sh. A fundamental vibration is one in which an atom sets a simple harmonic oscillation about its equilibrium position. Each atom, if you consider has three degrees of motional freedom along three axes, such as X, Y and Z directions. That means n atoms have 3n independent motions but in a molecule, the motions are not independent and motions within the molecule are not independent of each other due to having the bonds with the other atoms present in the molecule. As a result, three motions becomes translations of the molecule, where all atoms move simultaneously in the X, Y and Z direction. Another three are rotations where all atoms rotate in the same phase about the X, Y and Z axes. So this is very important, so all atoms move simultaneously in the X, Y and Z direction and all atoms rotate in the same phase about X Y and Z axis so these points are very very important. One should remember, so this leaves now 3n minus 6 (3n-6) motions, in which bond angles and bond distances without altering the center of gravity. That means, it is 3n minus 5 (3n-5) motions for linear molecules. These are referred to as fundamental vibrations of the molecule and are of two types: one is stretching and one is bending. Imagine two a diatomic molecule or three, triatomic molecule, balls connected by springs.

If you consider a diatomic molecule, imagine two balls connected with a spring or diatomic molecule, you know three atoms are connected with two springs, so something like this.

Let us consider a triatomic molecule such as water which contain 3×3-6 = 3 fundamental vibrations. What are those three fundamental vibrations. One is this one symmetrical stretching, and then of course here the stretching frequency nu (ν_s) comes around 3652 centimeter minus 1 (cm^{-1}), and then the second one is asymmetrical stretching and here we refer this one as nu-as (ν_{as}). The other one is scissoring so focus towards scissoring so here this is again represented delta (δ_s) here so (δ_sOH) means it indicates the scissoring frequency corresponds to the OH group in water. This comes around 1596 centimeter minus 1 (cm^{-1}). So, this is a typical example where you can see how 3n minus 6 (3n-6) equal to 3 fundamental vibrations are seen. Now let us consider a triatomic molecule, which is linear We consider triatomic molecules such as water bent of course the shape is bent still oxygen geometry is tetrahedral.

Let us consider a triatomic molecule having linear geometry such as CO_2. So here if you use the same analogy 3×3-5=4 fundamental vibrations are possible. So what are those: symmetrical stretching comes around 1340 centimeter minus 1 (cm^{-1}), that is designated as $\nu_s(co_2)$ and then asymmetrical stretching again very similar to what we saw in case of water. You can see symmetric stretching, the directions given here and in asymmetric stretching this is the direction. Asymmetrical stretching is there not uniform this is also designated at $\nu_{as}(co_2)$. This comes around 2350 centimeter minus 1 (cm^{-1}), and then we have scissoring, that is, bending. We have here, it comes around 666 centimeter inverse (cm^{-1}), and designated as $\delta s(CO_2)$ and then we have scissoring bending. You should know the difference, scissoring bending, this one scissoring bending and here this comes around. Both are identical, so they come around 666 centimeter minus 1 (cm^{-1}). This is how you can identify four fundamental vibrational modes in case of triatomic linear molecules such as CO_2. Now let us consider a CH_2 which is part of a molecule. For example, if you consider ethanol propanol or any aliphatic molecules, where we have CH_2. In this case, 3n plus 6 root does not apply. We have to see what are the possible vibrational modes for -CH_2-, so one is symmetrical stretching, that you can see in most of the molecules around 2850 cm^{-1} and designated as $\nu_s(CH_2)$. Similarly, we have a symmetrical stretching, when I say symmetrical stretching, how these atoms are stretched, in what direction and then asymmetrical stretching. One is in this direction, one is in this direction, one is in this direction, so this is called asymmetrical stretching and here it comes around 2926 centimeter minus 1 (cm^{-1}), and then scissoring, we have δ_s equal to 1465 centimeter minus 1 (cm^{-1}). Apart from these, three fundamental vibrational modes, also we come across: wagging so here wagging is referred to as gamma-s (γ_s) this comes in the range of 1350 to 1150 centimeter minus 1 (cm^{-1}), and then another one is twisting. In twisting, it is tow_{as} (τ_{as}) as it is called as then this comes around 1350 to 1150 centimeter minus 1 (cm^{-1}). And then the other one is rocking both in the same direction this is row-s (ρ_s CH_2) comes around 720 centimeter minus 1 (cm^{-1}). Often the theoretical number of vibrations are not observed and this may be due to symmetric reasons or due to degenerate vibrations. What is degenerate vibrations? Means vibrations of the same frequency. That means although we have clearly seen six possible vibrational modes for CH_2 groups present in a molecule, sometimes we may see only three of them and this is

the theoretically predicted ones, but on the other hand due to some reason, the theoretical number of vibrations are not observed and this may be due to symmetry reasons or due to degenerate vibrations that means vibrations having the same frequency, in that case we might miss one or two and then that might result in the increase in the intensity of few bands.

Let me stop here and come back to you again in my next lecture with more details about infrared spectroscopy. Thank you so much.