Interpretative Spectroscopy
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Lecture 28

Racah Parameters and Tanabe-Sugano Diagrams

Hello everyone, I welcome you all to MSB lecture series on Interpretative Spectroscopy. I discussed about UV visible spectroscopy in my last couple of lectures, I was discussing about Orgel diagrams, combined Orgel diagrams for two sets of d electronic configuration. The first one was about d^1, d^4, d^6, d^9 for both octahedral and tetrahedral complexes, with one Orgel diagram for high spin complexes, we should be able to interpret data obtained from spectroscopy. And in the same way, another Orgel diagram I showed you that is for d^2, d^3 and d^7, d^8 system for both octahedral and tetrahedral complexes combined together. Also, we saw some anomalies. Energy of some transitions are decreasing and energy of some transitions are increasing, how you can correct that one using Racah parameters considering the nephelauxetic effects. And now we will consider another unique electronic configuration d^5.

So, spectra of d^5 ions, high spin one; we have quite a few examples. Manganese-2 (Mn^{+2}) complexes and iron-3 (Fe^{+3}) complexes are d^5 system. For example, if you say hexafluoromanganate 4 minus $[MnF_6]^{4-}$ or hexaaquamanganate 2 plus $[Mn(H_2O)_6]^{2+}$ or hexafluoroferrate 3 minus $[MnF_6]^{3-}$, all are having d^5 electronic configuration and high spin complexes. If you consider electronic rearrangement in these high spin complexes, and if you recall spin selection rule of delta-S equal to 0 ($\Delta S=0$), these transitions are forbidden, because if you promote an electron that will be going with upward spin, then you will be having 2 spins with the same spin value of plus half. In that case, it is not allowed. That is the reason, they are all spin forbidden transitions. The ground term is ^6S with 11 excited states here.

So, that means transition probabilities are extremely low and here in order to see transition from d^5 system that is from ^6S to ^4G, ^4F, ^4D and ^4P that involves the reversal of one spin. That means, if I promote one of the electrons, it should go this way, that means, basically reversal

of one spin is essential to see the transition from this one to these 4 levels. On the other hand, in order to see transition to these 7 levels, we need to reverse the spin of both the electrons that is doubly spin forbidden. So, in this case what happens, it is very weak. If you look into the spectrum, this how the spectrum looks like for hexaquamanganese 2 plus $[Mn(H_2O)_6]^{2+}$.

So, manganese-2+ (Mn^{+2}) has d^5 high spin electronic configuration all d-orbitals are occupied with one electron each. So, none of the possible d-d transition is spin allowed, since for any transition the spin of the electron must be reversed both higher energy e_g orbitals contain already one electron each. According to Pauli's principle, the spin of the second electron must be reversed. So, therefore, all possible transitions are very weak and hence hexaqua manganese 2 plus $[Mn(H_2O)_6]^{2+}$, is very pale in color. The bands are extremely weak that is reflected in its epsilon value of 0.2 to 0.03 liter per mole per centimeter ($mol^{-1}cm^{-1}$). So, allowed transitions are spin allowed bands are invariably broad. So, you can see here, these are the transitions observed for hexaquamanganese-2 plus $[Mn(H_2O)_6]^{2+}$, these arrows indicate the position of the predicted band positions here. So, now the Orgel diagram, if you write for this unique d^5 electronic configuration for both tetrahedral and octahedral of course, in case of tetrahedral ignore g. Now one can write all possible with ground state being $^6A_{1g}$ and ^6S is $^6A_{1g}$ and now from $^6A_{1g}$ you can see about 6 transitions, the corresponding lambda maximum (λ_{max}) values are shown here.

That is what I showed you in the spectrum here, this spectrum you can identify, those transitions shown here. So, now let us come back to Racah parameters. So, Racah parameters were generated as a means to describe the effect of electron-electron repulsion within the metal complexes and the Racah parameters are A, B and C in the case of Tanube-Sugano diagrams. I will tell you, what is Tanube-Sugano diagrams, we learn about Orgel diagrams, we have another set of diagrams, which are called Tanube-Sugano diagrams. In the case of Tanube-Sugano diagrams, each electron configuration split has an energy that can be related by B, value A is ignored because, it is roughly the same for any metal center and C generally approximately as being 1/4B.

What B represents is an approximation of the bond strength between the ligand and metal. So, comparisons between tabulated free ion B and B of a coordinated complex is called the

nephelauxetic ratio the effect of reducing electron-electron repulsion via ligands that is beta equal to beta-complex over beta-free ion. Now, let us come back to Tanube-Sugano diagrams. So, Tanube-Sugano diagrams are used in coordination chemistry to predict electromagnetic absorption of metal coordination compounds of both tetrahedral and octahedral complexes and ground state is always taken as abscissa x-axis or horizontal axis and provides a constant reference point other energy levels are plotted relative to this ground state which is as same as x-axis. The low spin terms that is states where the spin multiplicities to a spin is lower than the ground states are also included in this Tanube-Sugano diagram, whereas those things are not considered in case of Orgel diagrams.

In order to make the diagram general for different metal ions with the same electronic configuration and to allow for different ligands of different ligand field strength both of which affect Dq that is B and B′, the axis are plotted in units of energy by B and Dq by B by doing this one in one Tanube-Sugano diagram. We can consider the entire band of ligands we come across in the spectrochemical series. What is the difference between Tanube-Sugano diagram and Orgel diagram. Different diagram is required for different electronic arrangement that means every electronic arrangement, you need a separate Tanube-Sugano diagram you need d^1 a separate, d^2 a separate, d^9. All d^1 to d^9 except d^5 you need a separate Tanube-Sugano diagram, but it includes all ligands having different ligand field strength. The axis in a Tanube-Sugano diagram is in terms of crystal field splitting parameter 10Dq or delta octahedral (Δ_{oct}) scaled by the B-Racah parameter. The y-axis is in terms of energy of an electronic transition, E scaled by B. So, diagrams for d^4, d^5, d^6 and d^7 metal ions have a discontinuity in energies as the ligand field is varied. The discontinuity, shown with the vertical line, represents complexes changing from high-spin to low-spin complexes. To the left of the line metal complexes are high-spin as the spin pairing energy is greater than that of the ligand field splitting. To the right of the line metal complexes are low-spin as the spin pairing energy is less than that of the ligand field energy. So, what you can do is take Tanube-Sugano diagrams for each electronic configuration and then read this paragraph here and then observe you can make out the differences how it looks like.

So, you can understand in a better way. So, for example, here I have given for d^6 system. Here d^2 V^{3+}: No fundamental difference between strong and weak field ligands and d^6 cobalt 3 plus (Co^{3+}). You can see, there is discontinuity at 10Dq/B = 20. At this point pairing of

electrons occurs. That means, basically we are moving from weak field to the strong field. As a result, what happens, pairing starts to the left. We have high spin complexes weak field to the right.We have low spin complexes, strong field ligands. That means, free ion ground state is ^5D in the octahedral field. Singlet ^1I of high energy, will be consists of these levels. So, here $^1A_{1g}$ is very important. This state is greatly stabilized by the ligands and drops rapidly in energy as ligand field strength increases.

So, a $^1A_{1g}$ is here. You can see $^1A_{1g}$ and it drops here as we move from left to the right because they become low spin complex. Here it is a high spin complex. It crosses the ground state $^5T_{2g}$ state and becomes the ground state here. $^5T_{2g}$ was here and then it goes up and then $^1A_{1g}$ what happens that becomes ground state here. For example, if you look into $[CoF_6]^{3-}$ high-spin blue in color one peak at 13000 centimeter minus 1(cm^{-1}) and then if you look into this one we have two transitions, that is $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$. So, these two transitions are there, whereas here we will see only one transition in case of $[CoF_6]^{3-}$. So, you can very nicely identify from this d^6 Tanabe-Sugano diagram for d^6 complexes such as $[CoF_6]^{3-}$ and trisethylenediaminecobalt-3plus $[Co(en)_3]^{3+}$ low-spin complex, which shows two transitions.

Now let us look into ligand to metal charge transfer transitions. For example, I have shown here, in case of a tetrahedral complex, low energy filled sigma orbitals and low energy field pi orbital is there and then they cause this kind of low crystal free stability energy because both the electrons when they are donated to the metal what happens the HOMO-LUMO gap shrinks and then this is more destabilized that is the reason most of the halide complexes are very reactive and we use them very conveniently for doing substitution reactions to replace with better ligands.

For example, if you take chloro compounds and if you add water, it immediately forms hexaaqua compound or if you add ammonia you can form hexaammine compound or we can use any other ligand to replace very quickly because reactivity is more in these cases and they are all labile complexes. Then this is about metal to ligand charge transfer transition. You can see here, they have low energy filled sigma orbitals and high energy empty pi orbitals. Examples I had mentioned, they can be CO, PR_3, aromatic groups, alkenes, alkynes, pyridines etcetera. So, here because of the t_{2g} electrons. Non-bonding orbitals are t_{2g}, they combine with pi star (*Π) to generate bonding and anti-bonding orbitals, where

these electrons will occupy and here due to this one, the CFSC the HOMO-LUMO gap increases and they are more stabilized. So, ligand to metal charge transfer transitions are allowed and have very large extinction coefficients.

So, you can see here how this metal and ligand presence would have an impact on ligand to metal charge transfer transition. For example, first row, second row and third row how. It varies, it increases steadily and you go from 3d to 4d to 5d, the gap increases and the energy required is very high or it falls into lower wavelength. So, now symmetry distortion one can see here. Trans-diethylenedifluorochromium [trans-$Cr(en)_2F_2$] compound, d^3 ion distorted from octahedral to D_{4h}-symmetery or tetragonal elongation. In tetragonal elongation, what would happen is energy level of d^3 ion alters, as the symmetry of its environment changes from octahedral to tetragonal, and you can see these different transitions because of the change in the point group from O_h to D_{4h} here.

Now, let us look into couple of problems here. Very simple problems.

Explain why an electronic transition for high-spin $[Mn(OH_2)_6]^{2+}$ is spin-forbidden, but for $[Co(OH_2)_6]^{2+}$ is spin-allowed?

So, in case of hexaaquamanganese 2 plus $[Mn(OH_2)_6]^{2+}$, it is a d^5 system and immediately after knowing, you just write the electronic configuration and crystal field splitting diagram and put the electrons, all 5 electrons, something like this; results in a high spin complex. So, it is spin forbidden, it is very easy and then, but for cobalt it is a d^7 system, again a high spin complex. So, here it is allowed because these 2 electrons can easily go to e_g level. So, this is spin allowed transition. it is very easy here.

Now let us look into another problem: What is the d^n configuration spin-multiplicity and term symbol of the ground state of titanium 3 plus (Ti^{3+}) and vanadium 3 plus (V^{3+}) ions.

So, this titanium 3 plus (Ti^{3+}) is a d^1 system and vanadium is d^2, vanadium 3 plus (V^{3+}) means $3d^34s^2$ becomes a d^2 system.

L value is 2, spin multiplicity will be s equal to half, 2S plus 1 will be 2 (2S+1=2) into half plus 1 it is 2. So, term symbol will be ^2D shown here and similarly if you go for vanadium d^2 system, 2 electrons here. So, L equal to 3. That means F and then S equal to 1, therefore, 2S plus 1 equal to 3. So, this is how the ground state term symbol is ^3F.

I can spin multiplicity is 3 and 2 in this case and you can identify this how. So, all these things can be done easily provided you identify the oxidation state of the metal in the complex and then find out what electronic configuration. Then find out L value, S value and then J value, if needed and then you should be able to write the ground state term symbol.

The electronic spectrum of an aqueous solution of tris-ethylenediamine nickel 2 plus $[Ni(en)_3]2+$ exhibits broad absorptions with lambda maximum 325, 550 and 900 nanometers. First question is: suggest assignments for the electronic transitions, the second one is, which bands are in the visible region. So, for this one you can see here.

Recollect the Orgel diagram for d^2 system or d^8 system: they are essentially same and then if you recall where exactly it comes, you can see here 3 transitions will be there and these 3 transitions you can always write here and of course, here what happens? the energy of this one drops here and then it increases here, you consider like this. So, that does not matter here, that question is not asked only, you should be able to assign once you identify first the ground state term and then 3 other states 1 due to P and 2 due to F excluding the ground state of F system.

So, you should be able to do that which bands are in the visible region. So, 900 nanometer assigned to $^3A_{2g} \rightarrow {}^3T_{2g}$ and 550 is assigned to $^3A_{2g} \rightarrow {}^3T_{1g}$ and then 325 is assigned to $^3A_{2g} \rightarrow {}^3T_{1g}$. So, this how you can identify and assign the values. Among 3 absorptions in this one which is closest to the UV end of the spectrum? does the notation $^3A_{2g} \rightarrow {}^3T_{2g}$ indicate an absorption or emission band why are the 3 transitions, spin allowed and upward arrow. These are the 3 questions you should work out. These questions I am posing to you people. Look into the spectrum and then try to work out for these 3 questions.

So, now one more problem is here:

Aqueous solution of hexaaquavanadium 3 plus $[V(OH_2)]^{3+}$, shows absorptions at 17,200 and 25,600 centimeters assigned to 2 transitions that is already given: $^3T_{1g}(F) \rightarrow {}^3T_{2g}$, $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ transitions. Estimate the values of B and Δo for $[V(OH_2)_6]^{3+}$ compound. This is the compound given and then if you just look into here, the plot E/B versus Δ/B.

So, here B is unknown, but if you take the ratio what we get is E_2/B over E1/B, but if you consider E_2/E_1 the ratio will be 1.49 in order to get that 1.49 you have to do trial points

here. What you should do is, you have to consider at different points for Δ value with respect to this one considering the ground state as well as the excited state between which electronic transition happening, that means $^3T_{1g}(F) \rightarrow {}^3T_{2g}$, $^3T_{1g}$ $(F) \rightarrow {}^3T_{1g}$ you have to consider this. Keep on doing by trial, for example, when this value is 20, what would happen. So, then at this value, what is the E_2/B over E1/B for these two levels between which electronic transition is taking place. You can find out from the plot approximately and get the value here and similarly you make another trial considering delta-o (Δ_o) over B equal to 30 ($\Delta_o/B = 30$) and then again at that value you find out E_2/B over E1/B from y axis and calculate these two values and get 1.46 and then one more trial you do it and you arrive at the one we found from the data.

So, that means there is an approximate answer, but we are now able to estimate B and Δ_{oct} as follows.

You can take here 29 we have in this one what we are getting is 40 and then E_2 is equal to 25600 and B is equal to 640 and then when you take 29 here again E1/B you can take it at ~26.9. Since E_1 equal to 17200 B equal to 640 centimeter inverse (cm^{-1}). So, substitution of the value of B into this one would give an estimate of Δ this is approximately 18600 centimeter minus 1 (cm^{-1}). This how you should be able to do taking simply from Tanube-Suguno diagram. This shows how useful Tanube-Sugano diagram is. By simply looking into the transition and comparing the value of E/B versus Δo/B you can calculate Δo very easily for a given complex. So, let me stop here and come with more examples, maybe at the end.

In my next lecture I shall focus your attention on IR spectroscopy. After that one, I will go to mass spectrometry and then EPR and if time permits Mossbauer and then I would come back to solve problems from all these spectroscopic methods to make you very expert in elucidation of structures. See you all in my next lecture. Thank you.