Interpretative Spectroscopy

Prof. Maravanji S. Balakrishna

Department of Chemistry

Indian Institute of Technology Bombay

Lecture 26

Selection Rule of Electronic Transition

Hello everyone, welcome you all to MSB lecture series on Interpretative Spectroscopy. So, we are discussing about UV visible spectroscopy. In my last lecture, I was discussing about the *d-d* transitions and other conditions. Let us continue knowing more about that. Electronic spectra of transition metal complexes: here happens is essentially electrons are excited from the ground state to one of the excited states. Such electronic transitions require high energy compared to other transitions.

So, during electronic transition, we also come across low energy vibrational, rotational transitions, because each electronic level is associated with several vibrations levels, which in turn are associated with or having several rotational levels. So, in electronic spectra such transitions are too close in energy to be resolved into separate absorption bands. The energy required for vibrational excitation is very very minimal compared to the energy required for electronic transition from one level to another one. As a result, they cause broadening of the absorption band in *d-d* spectra and as a result the bandwidth observed in d-d spectra are in the range of 1000 to 3000 centimeter minus 1 (cm^{-1}).

So, in a free gaseous metal ion, if you consider d orbitals are degenerate, no *d-d* transitions are observed, but in a complex, degeneracy is lost because of ligand field splitting. The orbitals split into two or more levels. For example, if you consider octahedral level, we will be having octahedral field, and we will be having t_{2g} composed of d_{xy}, d_{xz} and d_{yz} orbitals, which is lower in energy than higher energy, e_g level composite of d_{x2-y2} and d_{z2} levels. But in the tetrahedral, opposite happens, so e will be the ground state in the HOMO level and t_2 will be the LUMO level. So, the magnitude of

this Δ_o or Δ_t depends on the nature of the ligands and affect the energy of electronic transitions and hence the frequency of absorption maxima. For example, if you are considering weak field ligands of course, you can look into spectrochemical series.

How we arrived at a given position for a ligand in the spectrochemical series is considering the donor and acceptor properties of the ligands. And if you recall what I taught in advanced transition metal chemistry that all ligands whatever you come across can be simply classified into three categories. One is pure sigma donor ligands such as water and ammonia; all neutral oxygen donor ligands and also alkylamines and arylamines. On the other hand, the next one is sigma donor and pi donor ligands such as halogens. Here what we have is low energy filled sigma orbitals and low energy filled pi (Π) orbitals.

When such ligands interact with the metal, both of them will be donating to the metal and hence CFSC, the HOMO-LUMO gap drops relatively compared to what we saw n case of pure sigma donor ligands such as ammonia and water. The third category is sigma (σ) donor and pi (Π) acceptor ligands, example carbon monoxide, phosphines and nitrogen heterocycles. In this case what happens they have low energy field sigma orbitals and high energy empty pi orbitals are there. And in this case because of the sigma donation and then pi donation back from the metal to the ligand what happens the energy gap between HOMO and LUMO increases as a result these complexes are more stabilized and also in case if you want to have a *d-d* transition it requires very high energy. So, that means the magnitude of Δ_O depends on the nature of the ligands and affect the energy of electronic transition and hence the frequency of absorption maxima.

Extent of splitting is related to the ligand position in the spectrochemical series. The ligand position in the spectrochemical series is very very important in electronic spectroscopy. Here just look into all d-orbitals, all are classified into four categories here, there is some reason behind classifying like this. So, first d^0 and d^{10} complexes are usually colorless; not always. Why they are colored for that I will come back soon; with

d^0 and d^{10} you cannot anticipate d-d transition. But on the other hand, if you look into d^1, d^4, d^6, d^9 they have some similarities in the same way if you consider d^2, d^3, d^7 and d^8, they also have some similarities and d^5 is unique.

What are the similarities between d^1, d^4, d^6 and d^9? So, d^1 we have one electron, d^4 one less than half filled electronic configuration, and d^6 one more than half filled electronic configuration, and d^9 one less than completely field electronic configuration. So, that means here they have some similarities and they show very similar electronic or UV visible spectra. On the other, hand if you look into d^2, d^3, d^7, d^8 they have similarities because in d^2, we have two electrons and d^3 we have less than two electrons for half field electronic configuration and d^7, we have two electrons more than half filled electronic configuration and d^8, we have two less than completely field electronic configuration. That means again they have similarities and the spectra look almost identical except for some anomalies here. These compounds are colored and d^5 compounds are little bit pale colored ones, especially when they are tetrahedral compounds. They are almost colorless when they are octahedral homoleptic complexes having centro symmetry. We will learn all those things in detail. But now let us look into HgI_2. It is brick red color and here electronic configuration. If you consider mercury, d^{10} it has electronic configuration, no *d-d* transition is there, but still it is intensely colored. When you consider potassium permanganate or potassium dichromate, metal exists in highest possible oxidation states, that means Mn is in plus seven state (Mn^{+7}). All electrons have been removed and it has a d^0 electronic configuration, but still $KMnO_4$ is intense purple in color. Similarly, if you look into potassium dichromate, chromium is in plus six state and d^0 system and also intense orange red color, and similarly if you look into bismuth triiodide we have $d^{10}s^2$ electronic configuration, it is orange red in color and if you look into prussian blue here we have iron(III) (Fe^{3+}) and iron(II) (Fe^{2+}) are there. This also very intense in color. We will see one by one, why what is the origin of color in these compounds as you cannot anticipate any d-d transition. So, iodide has very high polarizability which results in anionic charge getting easily transferred to the mercury 2 plus (Hg^{2+}) cation. So, this process releases some energy which falls in the visible spectrum hence we can say that compounds like $KMnO_4$, HgI_2 etcetera are colored, that means what we come across a

term called charge transfer transition. When we talk about charge transfer transition, the moment we look into the electronic configuration, we should be able to tell in which direction charge is transferred, for example, if you look into d^{10} it is metal to ligand charge transfer transition, on the other hand if you look into $KMnO_4$ it is d^0, it is ligand to metal charge transfer transition and if you look into prussian blue here we have iron in 3 state (Fe^{3+}) and iron in 2 state (Fe^{2+}). It is metal to metal charge transfer transition. Some of these charge transfer transitions are responsible for the appearance of intense color in these compounds. So, now we should come back to the selection rules of electronic transitions. When we were writing microstates, we saw several possible excited states and then if electrons are promoted to each state from the ground state then the electronic spectra would have been very complicated and elucidation or interpretation would have been very difficult, but however all these transitions are governed by certain rules that we call it as selection rules for electronic transition; what are those? So, electronic transition may be classified as intense or weak according to the magnitude of epsilon-maximum (ε_{max}) that corresponds to allowed or forbidden transitions that means, what are allowed transitions? These transitions have epsilon-maximum value of 10 raise to 4 (10^4) or more and probability of their occurrence is very high. These are generally due to pi-pi* ($\Pi \rightarrow \Pi^*$) transitions and are allowed transitions. Example, pi-pi* transition ($\Pi \rightarrow \Pi^*$) in 1,3-butadiene shows absorption at 270 nanometer and epsilon-maximum has 20900, represents an allowed transition, then if allowed transition term comes, there should be forbidden transitions as well. Here if you look into it, n-pi* transition ($n \rightarrow \Pi^*$) is forbidden. For this transition, e-maximum (ε_{max}) is generally less than 10 raise to 4 (10^4).

For example, if you consider n-pi* transition ($n \rightarrow \Pi^*$) of saturated aldehydes and ketones which exhibit a weak absorption of low intensity near 285 nanometer and having e-maximum value less than 100 because they are forbidden transitions. That means which transitions are forbidden and which transitions are allowed, we can look into it now. Not all theoretically possible electronic transitions are actually observed, that is what I told you because, they are governed by a selection rules selection rules are there to distinguish

between allowed and forbidden transitions and allowed transitions occur forbidden do occur, but much less common and are of low intensity in nature. So, now the first one is Laporte selection rule. What is Laporte selection rule? The transition should have delta L (ΔL) equals plus or minus 1 (± 1). If that is allowed, they are called Laporte allowed and have high absorbance. That means during electronic transition azimuthal quantum number should change. It should not be 0. This is about Laporte selection rule, and then what is spin selection rule? During the electronic transition, electron does not change its spin. The electron is getting excited to the higher level it should stay something like, this is allowed and then if this electron goes like this, is not allowed. That means, what it says is delta S, ($\Delta S=0$) equal to 0 that means during electronic transition electron does not change its spin. It should go to excited level something like this. It is not allowed to go and something like this.

This is exactly opposite to NMR selection rule where in order to see nuclear spin transition, flipping of nucleus, when you are applying radio frequency in a direction perpendicular to the applied magnetic field, the frequency of that matches the precession frequency of the nucleus, then what happens, it will start wobbling and coming out more and more, out of the axis of magnetic field and it flips. If you consider in NMR, delta S (ΔS) equal to plus or minus 1, (± 1). One should remember where as in case of electronic transition it is delta S equals 0 in nuclear transition it is opposite upward spin will become downward spin. So, here the spin state does not change, that means *d-d* transits are strictly speaking Laporte forbidden that means we should not anticipate any *d-d* transition at all because it says delta L (ΔL) equal to 0 ($L=0$) and all *d*-orbitals have the same delta L (ΔL) value and of course since they are Laporte forbidden, that can be seen from the epsilon value, molar absorptivity coefficient will be in the range of 5 to 10 liters per mole per centimeter minus. When transition metal forms a complex then why do we observe d-d transition? When transition metal forms a complex, metal is surrounded by ligands mixing of d and p-orbitals may occur and as a result, transition no longer d-d in nature. Of course, you can also recollect from valence bond theory about hybridization. In case

of a tetrahedral complexes, when a tetrahedral compound is formed, the hybridization we are considering is d^2sp^3 or sp^3d^2.

That means one *s*, three *p* and two *d*-orbitals, d_z2 and d_x2-_y2, will combine to generate a set of 6 hybrid orbitals which are having the properties of all the ligands which are involved in this hybridization. As a result, what would happen, the d-orbitals present in sp^3d^2 are no longer *d*-orbitals we observed in free gaseous metal ion. Mixing of d-p-orbitals may occur, as a result transitions are no longer pure *d-d* in nature. When that is split into t_{2g} and e_g they are no longer d-orbitals of same property that we saw when it is not kept in the ligand field. Now because of the mixing they lose original *d* character. As a result, what happens, it becomes Laporte allowed and hence we see *d-d* transition.

So, because of slight relaxation in Laporte rule d-d transitions are observed. Mixing is common when complexes lack center of symmetry. Mixing is even more pronounced when they lack center of symmetry. So, now let us look into tetrabromomanganese 2 minus, this is tetrahedral. So, manganese in plus 2 state (Mn^{+2}) it is a d^5 system and then if you look into pentaminechlorocobalt 2 plus $[Co(NH_3)_5Cl]^{+2}$ is octahedral with unsymmetrical substitution and both the compounds are colored. In case of $[MnBr_4]^{2-}$, it is a tetrahedral compound, we have something like this. So, in d^5 system, all the electrons have spin like this and here if we promote one of the electrons, it should go here or here or here. If it goes here, both the electrons will be having the upward spin and that is not allowed. That is the reason this is spin forbidden transition, nevertheless in tetrahedral compounds that is allowed and you can see they show color because they lack center of symmetry and same thing is true in case of this one, in d^7 here.

So, here any of these electrons with downward spin can under go and transition. Here also it does not have   center of symmetry, unsymmetrical substitution is there. These compounds are colored. On the other hand, if you look into homoleptic compounds such as hexammine cobalt 3 plus $[Co(NH_3)_6]^{3+}$ or hexammine copper 2 plus $[Cu(NH_3)_6]^{2+}$, they have center of symmetry, no mixing of *p* and *d* orbitals is observed and as a result,

they are not colored or very pale colored in nature. Why this color comes despite they having center of symmetry, that means when the metal to ligand bond vibrates, the ligand spends an appreciable amount of time out of their center of symmetry equilibrium position. As a result, small amount of mixing does occur and low intensity transitions are observed. That means, when they are vibrating with respect to the mean position, it so happens that all the ligands will be at different positions from the central metal atom. As a result, they come out of center of symmetry equilibrium and hence this is essentially due to the mixing of p and d orbitals and that results in low intensity transitions.

Now you can see, spin forbidden transitions will be having very less epsilon value typically less than 1 and the example is hexaaquamanganese 2 plus $[Mn(H_2O)_6]^{2+}$, a homoleptic compound having center of symmetry, and again having d^5 electronic configuration, this spin forbidden and also Laporte forbidden, and if you consider Laporte forbidden and spin allowed, they will be having epsilon value anywhere between 1 to 10 and 10 to 1000, respectively. For example, if you look into hexaaquatitanium 3 plus $[Ti(H_2O)_6]^{3+}$ a d^1 system, here center of symmetry is there, octahedral homoleptic compounds have low epsilon value and then if you look into tetra chloronickelate 2 minus $[NiCl_4]^{2-}$. This is a tetrahedral compound, center of symmetry is not there and it is a spin allowed system, and here the value is about 10 to 1000. So, it is slightly better and in case of charge transfer we can see 1000 to 50000, for example, manganese ion in potassium permanganate $[KMnO_4]$, this is essentially ligand to metal charge transfer transition. Now let us look into the system and type of spectra and see whether they are Lapporte allowed and spin allowed.

So, when a transition is Laporte allowed and spin allowed that has to be charge transfer transition, and they will be having very high epsilon values. Example $[TiCl_6]^{2-}$, partly allowed and some p-d mixing is there, we will see d-d transition, here it is 500. If you take tetrahedral compounds of bromo and chloro. So, tetrabromocobaltate $[CoBr_4]^-$ or tetrachloro cobaltate $[CoCl_4]$- are Laporte forbidden and spin allowed. We have quite a few here it is again termed as d-d transition epsilon values in the 10 to rise to 10 (10^{10})

where we have center of symmetry is there for example, hexaaquatitanium 3 plus $[Ti(H_2O)_6]^{3+}$ or hexaaquavanadium 3 plus $[V(H_2O)_6]^{3+}$ here. Then partly Laporte allowed and spin forbiddeb are those where we have typical d^5 system, epsilon value is very low 4 here and if it is spin forbidden and Laporte forbidden, the value has a very minimum, 0.02 epsilon value (ε). In those *d-d* transitions are very weak and very weak intense in nature. Intensity is very very weak and these are especially having d^5 system having center of symmetry, example is hexaaquamanganese 2 plus $[Mn(H_2O)_6]^{2+}$. Then let us look into what are the factors that affect Christophi's stability energy and absorption wavelength.

So, the absorption wavelength is directly proportional to the CFS energy, that is governed by spectrochemical series. I have given here a very extended spectrochemical series. Here most of the ligands are included, the magnitude of delta (Δ) depends on the charge on metal, metal whether it is measured in +1 state, +2 state or +3 state and also it depends on their position in the periodic table. That means, whether it is 3d series, 4d series or 5d series and also the ligand field strength. All these 3 factors have an influence on the magnitude of CFSE and on increasing the field strength, wavelength decreases so that means as CFS energy increases and HOMO-LUMO gap increases, as a result, what happens? high energy is required, wavelength decreases for those and you can see here in case of octahedral, the energy gap between HOMO-LUMO is very high and that is slightly less in case of tetrahedral and here in case of square planar we are considering this transition here d_z2 to d_{xy} level. So, now let us consider metal to ligand charge transfer transition, if the metal is in a low oxygen state, that means it is electron rich and the ligand possess low lying empty orbitals. They should have pi* (Π^*) in case of aromatic ligands or carbon monoxide or n heterocyclic carbene or sigma star (σ^*) in case of phosphines, then a metal to ligand charge transfer transition occurs. We should remember here, metal is in low oxygen state, when the metal is in low oxygen state, it has more electrons, it is almost vulnerable for oxidation that means it can readily give electrons.

Those metals when they are combined with ligands having low lying empty orbitals like pi star (Π^*) or sigma star (σ^*), then a metal to ligand charge transfer is smooth and you

can see MLCT here. MLCT transitions are common for coordination compounds having pi-acceptor (Π) ligands. Whatever the back donation, we call it metal to ligand back donation. It is nothing but metal to ligand charge transfer. Upon the absorption of light, electrons in the metal orbitals are excited to the ligand pi star orbitals. So, metal pi (Π) orbitals like d_{xy}, d_{yz}, and d_{xz} combine with pi star (Π^*) to generate a set of molecular orbitals: bonding and anti-bonding and this bonding will be occupied by the electrons taken from the metal. This we call it as metal to ligand charge transfer or metal to ligand back bonding. So, metal to ligand charge transfer transitions result in intense bands. Example if you consider tris-2,2'-bipyridyl ruthenium 2 plus, this orange colored complex is being studied as the excited state resulting from this charge transfer which has a lifetime of microseconds and the complex is a versatile photochemical redox reagent. So, other examples are tetracarbonylphenanthroline tungsten [$W(CO)_4(phen)$] and also 2,2'-bipyridyl-tricarbonyl iron [$Fe(CO)_3(bipy)$] compounds. Several examples you can find which exhibit metal to ligand charge transfer transitions.

So, let us learn more about charge transfer transitions in my next lecture until then have an excellent time. Thank you.