

Interpretative Spectroscopy
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Lecture 23
Spin-Orbit Coupling and Term Symbols

Hello everyone, I once again welcome you all to MSB lecture series on interpretative spectroscopy. In my last couple of lectures, I did discussion on UV visible spectroscopy and also, I started discussion on $d-d$ transitions. In case of organic molecules, invariably we come across n to π star ($n \rightarrow \pi^*$), n to σ ($n \rightarrow \sigma^*$) star and π to π star ($\pi \rightarrow \pi^*$) transitions and also rarely σ to σ star high energy transitions. But along with these transitions, we can see one more transition, that is called $d-d$ transition because of the arrival of d -orbitals in compounds, they are called transition elements, 3d, 4d, 5d, where we start with d^1 whether it is $3d^1$, $4d^1$ or $5d^1$, we start with d^1 to d^{10} . So, this about 10 different type of electronic configuration we come across among 3d, 4d, 5d of 30 elements. So, they show this $d-d$ transition and mainly the color of these complexes are due to the $d-d$ transitions and sometime there may be some other transitions. Let us look into all those things in detail.

Now let us look into the $d-d$ transition, I had mentioned $d-d$ transition arises because of filling of electrons to the d orbital and then if you consider octahedral complex, in an octahedral crystal field, the d orbitals lose their degeneracy and split into t_{2g} and e_g levels. t_{2g} is lower in energy, e_g is in higher energy. t_{2g} consists of d_{xy} , d_{xz} and d_{yz} , whereas e_g consists of $d_{x^2-y^2}$ and d_{z^2} , in a typical octahedral field. In case of tetrahedral, opposite of that happens t_2 will be higher in energy and e will be lower in energy, enough information is given in my advanced transition metal chemistry for these geometries by considering the orientation of the orbitals and also approach of the ligands towards the metal. So, based on that the crystal field splitting will occur and the degeneracy of d

orbitals is destroyed and then they will be aligned into different energy levels. So, in case of tetrahedral, we have $d_{x^2-y^2}$ and d_{z^2} , will be lower in energy, whereas d_{xz} , d_{yz} and d_{xy} will be higher in energy that also takes place between them.

A typical example is shown here: If you look into hexaaquatitanium $3+$ $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, a d^1 system here, initially it is $3d^24s^2$. We have removed the 3 electrons so titanium is in $3+$ plus and $3d^1$ system. In this one, one electron is placed in t_{2g} so this electron would be promoted here, this we call it as electronic transition and you should remember, it is going like this here. And then if you consider tetrachlorocobaltate $[\text{CoCl}_4]^{2-}$, a 4 coordinated tetrahedral high spin complex. In high spin complex we have 4 electrons in the ground state, e-state and 3 electrons in the t_2 state and now either this electron or this electron can be promoted. Here you can see, this electron is sitting here in this fashion. So, these two are typical examples of $d-d$ transitions.

Now, we come across another interesting transition called charge transfer transition. Charge transfer transitions are of two types charge can be transferred from the metal to the ligand or ligand to the metal. For example, if you consider potassium permanganate or potassium dichromate they are intensely colored and if you look into the manganese oxidation state, it is plus 7. Now it has no electrons in the valence shell because it had $3d^5 4s^2$; all the 7 electrons have been removed to generate Mn^{7+} . So, $3d^04s^0$. That means, if this compound is intensely colored that is this not due to $d-d$ transition because we do not have any electrons in the $d-d$ transition.

That means, intense violet color may be due to something some electronic transition how electronic transition can happen probably oxygen lone pairs are there. So, it will give electrons to the metal empty orbitals. That means, you can say here due to the charge transfer and without any hesitation you can tell that this is ligand to metal charge transfer transition. For example, if we have oxygen, on subjecting to UV light or visible light, electron is promoted from $2p$ to $3d$. This is a typical ligand to metal charge transfer

transition. In cluster compounds, they have one or more metal-metal bonds, color is due to either sigma sigma star ($\sigma \rightarrow \sigma^*$), pi to pi star ($\Pi \rightarrow \Pi^*$) or delta to delta star ($\delta \rightarrow \delta^*$).

You recall the bonding concepts I explained. For metal-metal bonds where we came across one bond, two bonds, three bonds or four bonds. When you have four bonds we call it as delta bond and we can also have five bonds that is called quintuple bond. If you just recollect your understanding, d_{z^2} , for example, we have a situation like this. So, here d_{z^2} , d_{xy} , d_{xz} and d_{yz} , same thing is here d_{yz} , d_{xz} , d_{xy} and $d_{x^2-y^2}$ and d_{z^2} . It happens when two square planar complexes are interacting with respect to the principal axis and aligned in an eclipsed manner, something like this. So, typically this is the interaction.

Now, if you consider the d orbitals like this, basically, there is head on interaction between two d_{z^2} - d_{z^2} , resulting in a sigma and sigma* MOs, d_{xz} and d_{yz} accounting for 2 pi and pi* MOs and overlapping of d_{xy} - d_{xy} sideways giving delta and delta* MOs. Sigma-star is very high energy and pi-star is little lower in energy and the least energy one is delta -delta*. This is responsible for the charge transfer between metal to metal or in general, all these transitions, if you come across, they are called metal to metal charge transfer transitions. And then in diatomic molecules of non-metals such as F_2 , Cl_2 , Br_2 and I_2 color is due to pi-Sigma* transition ($\sigma \rightarrow \sigma^*$). In O_2 color is due to pi-pi* transition ($\Pi \rightarrow \Pi^*$). In ionic crystals, if we see color in NaCl, LiCl and KCl color is due to F centers, i.e. solid-state defects. Often, rock salt is slightly pink in color. It is due to some solid-state effect or some voids they are occupied by other different hetero anions or cations, mostly here it is cations or it can be anions as well. These are called ionic crystals and the color is due to solid defects.

And of course, always the energy difference (ΔE) can be represented as hc/λ or ΔE is directly proportional to wave number or you can write in this fashion, $\Delta E \propto 1/\lambda \propto (\nu_{\text{bar}})$. So, now, it is very easy to understand and what kind of color a substance shows and then that is due to what by just looking into artist wheel here, each color has a complementary color, the one opposite to it, on the artist wheel on opposite side. So, color an object

exhibits depends on the wavelength of the light that it absorbs. For example, if a substance is absorbing red color that means, it emits a green color and appears as green if the substance is absorbing red color it appears as green and if it is appearing as orange means it is absorbing blue color or if it is absorbing blue color it appears as orange or if it is absorbing violet color it appears as yellow or if it is absorbing yellow color it appears as violet this one should remember. So, complementary color is shown by the substance when it absorbs the other color for electronic transition. So, now, I have given here the wavelength range absorbed by the substance and also the color and also color seen by us.

For example, if a substance absorbs in the range of 380-430, that is violet, the color appears is yellow to green. On the other hand, if the absorbed is in the region of 430-480 that means, color absorbed is in the blue region, and compound or substance appears yellow in color and then again if it is absorbing between 480-490, color absorbed is green to blue and color appears is orange, complementary color, and if it is absorbing in the range of 490-500 nanometer, it is essentially absorbing blue-green color and it appears red here and then between 500-560, green is absorbed and it appears purple. and then 560-580, color absorbed is yellow to green of the light and then we see violet, and 580-590, yellow color is absorbed and it appears blue, and 590-610 orange is absorbed, we see it has green to blue in color, but if it is absorbing between 610-750, red color is absorbed and the substance appears blue to green in color. So, this gives some idea about the wavelength range absorbed and the color corresponding to that one and as a result the complementary color it displays. Now, let us go to some technical things. Here little bit of theory, not worrying too much about complicated theoretical equations or anything, we should try to understand that this all due to the electrons, then how the electrons are there in the orbitals and what they do.

So, little bit of information is needed and in this context this slide is prepared. So, angular momenta for single electron and atom when we consider, we have to consider two things i) one is orbital motion of the electron and also it has a spin. So, that means,

orbital motion is movement of an electron in orbit around the nucleus and then the spin is movement of an electron about its own axis. You can simply correlate this one with the sun and the earth moving in the orbits. So, earth rotating about its own axis and also it is coming around sun.

One is orbital motion and the other one is spin motion, rotating about its own axis (like taking 24 hours by earth) is spin. You can consider a typical electron and orbital motion is like surrounding the sun by earth. So, it is something like that. So, Momentum $\mathbf{m} \times \mathbf{v}$, we know from physics angular momentum is mass x angular velocity, $\mathbf{m} \times \boldsymbol{\omega}$. So, now, orbital angular momentum l is nothing, but it arises due to the orbital motion of electron around the nucleus. So, l equals square root of $l(l+1)$ into $\frac{h}{2\pi}$ [$L = \sqrt{l(l+1)} \frac{h}{2\pi}$] or it can be l equals square root of $l(l+1)$ x \hbar ($L = \sqrt{l(l+1)}\hbar$). We all know that \hbar is equal to $h/2\pi$, where L is total orbital angular momentum. It can be 0 or positive and l is orbital angular quantum number or it is also called as azimuthal quantum number.

So, typically you can show like this, electron revolving around the nucleus. Now, spin angular momentum: it arises due to spin motion of electron about its own axis. So, this is given by term s equals square root of $s(s+1)$ into $\frac{h}{2\pi}$ [$S = \sqrt{s(s+1)} \frac{h}{2\pi}$], the way we gave for orbital angular momentum. So, s equal to spin angular momentum, that means, m_s equals plus or minus half and s equals spin angular quantum number that is half ($1/2$). So, that means, s can be plus half ($+\frac{1}{2}$) or s can be minus half ($-\frac{1}{2}$).

So, plus half is shown in a clockwise and this is shown in anticlockwise. Now, let us look into the total angular momentum quantum number J , J is a combination of both spin and spin motion and orbital motion. So, the total orbital angular moment of an atom, capital L is Σl , azimuthal quantum number and the total spin angular momentum of an atom S equal to $2s$ plus 1 [$S = 2s + 1$], combine to form total angular momentum. A

number that is quantized by the term called J ; l and s do not necessarily have to be pointing in the same direction. Therefore, J can range from $|L+S|$ to $|L-S|$ values.

So, J can have L plus or minus S values [$J = L \pm S$]. It is interaction between orbital and spin angular momentum quantum numbers, how they interact? whether they couple (L plus S), or they interact (L minus S), this how we term this. So, small j equals modulus $|l$ plus s [$j = |l + s|$] or l minus s [$j = |l - s|$]. So, that means, capital J equal to square root of j into j plus 1 into h over 2π [$J = \sqrt{j(j+1)} \frac{h}{2\pi}$], or it can be simplified as j into j plus 1 \hbar [$\sqrt{j(j+1)} \hbar$]. So, where small j is angular momentum quantum number and capital J is total angular momentum. So, this L and S coupling is represented nicely in this figure here, and if you just look into this violet or purple conic that shows total angular momentum J that is purple, orbital L is given in blue here and then spin is given in green, with respect its own axis is given and with respect to the nucleus is given in blue and together L - S coupling is shown in this purple cone.

So, this is how you can represent or illustrate L and S coupling, spin orbital coupling or orbit spin coupling. So, now, let us look into the angular momentum for multi electron atoms or ions. For two electrons atoms or ions, we should consider is total orbital angular momentum which is nothing but the orbital angular momentum for two electrons. So, let us say l_1 and l_2 and then L equal to $|l_1 + l_2|$ until it goes to $|l_1 - l_2|$. This is called Clebsch Gordon series. So, where l is total orbital angular momentum quantum number, it can be again 0 or positive (+ve). It was defined earlier and then L also we know that square root of l into l plus 1 into h over 2π [$L = \sqrt{l(l+1)} \frac{h}{2\pi}$], where L is total orbital angular momentum. Now, for example, let us say l_1 equal to 1 ($l_1 = 1$), and l_2 equal to 2 ($l_2 = 2$), we can calculate and when you have this one, if you start following this rule, what we end up is we get 2 and 1 and 0 values. If you go for l_1 equal to 2 ($l_1 = 2$) and l_2 equal to 2 ($l_2 = 2$), we can get values $4, 3, 2, 1, 0$, like this.

So, now, let us look into spin angular momentum in the same way we looked into orbital

angular momentum. So, the spin angular momentum quantum number for two electrons, say s_1 and s_2 and again we have s_1 plus s_2 , $|s_1+s_2|$ and s_1 minus s_2 , $|s_1-s_2|$. This is again Clebsch Gordon series and where S equal to total spin angular momentum quantum number that can have plus or minus half and then s is we know that square root of s into s plus 1 into h over 2π [$S = \sqrt{s(s+1)} \frac{h}{2\pi}$]. So, for example, s_1 equal to half ($s_1=1/2$) and s_2 equal to half ($s_2=1/2$), what we get is at the end using Clebsch series, we get 1 and 0 values for l . So, now, let us look into together spin orbit coupling. So, L-S coupling also is called Russle-Sanders coupling and here if you consider orbital angular quantum number for two electrons say l_1 and l_2 . From again Clebsch Gordon series will be having $L = |l_1 + l_2|, |l_1 + l_2 - 1|, \dots, |l_1 - l_2|$ and same way if you consider spin also $S = |s_1 + s_2|, |s_1 + s_2 - 1|, \dots, |s_1 - s_2|$ and for lighter elements what we have is $J = |L + S|, |L + S - 1|, \dots, |L - S|$. Here J equal to total angular momentum quantum number J into j plus 1 h over 2π this is square root [$J = \sqrt{j(j+1)} \frac{h}{2\pi}$].

So, J is total angular momentum, see this is how you can use it, but when we should use the l plus s ($l+s$) and when we use l minus s ($l-s$), we can see for $j-j$ coupling for heavier elements. If you consider, we can see l_1 plus or minus s_1 [$j_1 = l_1 \pm s_1$] and j_2 is l_2 plus or minus s_2 [$j_2 = l_2 \pm s_2$]. if you consider J equal to sigma j_i [$\sum j_i$]. So, then it will be j_1 plus j_2 (j_1+j_2), j_1 minus j_2 (j_1-j_2) it comes and this is how we also get square root of j into j plus 1 into h over 2π [$J = \sqrt{j(j+1)} \frac{h}{2\pi}$] and we define J as total angular momentum. So, now let us come to the term symbols. A term symbol or a spectroscopic term represents the energy level of microstates with the same energy of a given electronic configuration. So, here J is the total angular momentum quantum number and $2s$ plus 1 ($2S+1$) is spin multiplicity. So, then we have symbol like this $^{2S+1}J_{L\pm S}$ and J can have L plus or minus S ($L\pm S$). Term symbols we can write for either ground state or excited state for s orbital, p orbital, d orbital or f orbital. For all the four orbitals, we should be able to write.

For example, depending upon L values, we have to give these symbols for terms. When L equal to 0 ($L=0$), S ; when L equal to 1 ($L=1$), P ; L equal to 2 ($L=2$), D ; L equal to 3

(L=3), F; and L equal to 4 (L=4), G; and L equal to 5 (L=5), H; L equal 6 (L=6), it is I and goes on. So, J is excluded in term symbols, because we are using J for total angular quantum number. For an unpaired electron, for example, if there is one unpaired electron, $2s + 1$ will be 1, and if there is half it becomes 2. Similarly, if we have unpaired electrons 2, then $2S+1$ value will be 3, and if you have 3 unpaired electrons, $2S+1$ will be 4 and in the same way if you have 4 unpaired electrons the spin will be 2 this is sigma s (Σ_s) and then $2S+1$ will be 5. When we have 1 electron, $2S+1=1$, we call it as singlet state. When we have $2S+1=2$, it is called doublet state. When we have $2S+1=3$ we call it as a triplet state. When we have $2S+1=4$ is called quadruplet and then when you have 5 it is called quintet. We should remember these things; $2S+1$ value determines the name of the state, it is a singlet, doublet, triplet, quartet or quintet, depending upon the $2S+1$ value of 1, 2, 3, 4, or 5. Then how to find out these term symbols? Let us take a simple example of d^1 . It comes later, so let me take it later. How, one can find out term symbols for various electronic configurations. Before that, let us look into, how to determine the ground state term? There are certain rules, we should follow, while determining the ground state term. The terms are placed in order depending on their multiplicity values that means $2S+1$ value is given at most importance while determining the ground state terms. Highest value of $2S+1$ will be the least energetic one, that means most stable one. The most stable state has highest S value and stability decreases as S value decreases. The ground state possesses the most unpaired electrons that gives minimum repulsion, that means in order to have a larger $2S+1$ value, large number of unpaired electrons should be there. When large number of unpaired electrons are there, it has to be essentially ground state. The minimum repulsion as a result of maximum stability and less energy or lowest energy. For a given value of s, the state with highest l is the most stable. Let us say, we have two systems: both have the same multiplicity $2S+1$. In that case, we have to give priority to highest L value, which is the most stable and then if there is ambiguity for given value of S and L, then the J value has to be considered. The smallest J value is the most stable, if the subshell is less than half filled. For example: for d^1 , d^2 , d^3 and d^4 , L-S is the most stable ground state or if it is for d^6 , d^7 , d^8 and d^9 , L+S value will be most stable one. That means if there is ambiguity for given value of S and L the smallest J value is the most stable, if the subshell is less than half filled, L-S value has to be considered for J. For

example, let us consider carbon here. We have p^2 is the ground state term we have 1D , 3P and 1S and if you consider 3P has a triplet state; maximum S ($2S+1$ value) and ground state term among 1D and 1S . The term 1D is the most stable because $L=2$ as S is same. Between them if you consider, highest L value have to be considered. Highest L value is there among this one is for D and now 3P has 3 terms 3P_0 , 3P_1 and 3P_2 . The smallest value of J is the most stable, as p^2 is less than half filled. So $^3P_0 < ^3P_1 < ^3P_2$ in terms of energy, so that means 3P_0 is the least energetic one and it is the ground term. So, this is how you can write and how to represent through vectors. I will show you in my next lecture.

So, now I have given some ground state terms for different electronic configurations p^n and p^{6-n} , that means whether we have p^1 or p^5 and same thing d^1 , d^9 is something like that they have similar or identical terms. I will calculate those things and show you to make yourself familiar with identifying ground term or calculating the ground term from electronic configuration, that I would do in my next lecture. Then p^1 and p^5 have the same ground state term called 2P and p^2 and p^4 have the same ground term 3P and p^3 has unique 4S and p^6 has 1S and d^1 and d^9 have 2D , d^2 and d^8 have 3F , d^3 and d^7 have 4F , d^4 and d^6 have 5D , d^5 has 6S , d^{10} has 1S . If some of them have very similar terms, you can bring some correlation here for example. if you look into d^1 and d^9 system it is d^1 , 1 electron is there and d^9 is 1 less than completely filled electronic configuration, we have 2D term. If you look into d^2 and d^8 they have identical ground state term that means 2 electrons are there in the d^2 orbital and d^8 two less than completely filled electronic configuration. That means it is very easy to remember and then there is some correlation. Some logic is there; look into d^3 and d^7 , 2 electrons less than half filled electronic configuration, 2 electrons more than half-filled electronic configuration. We have here, that means 2 electrons less than half-filled 2 electrons more than half filled. We have 4F , and then if you look into d^4 and d^6 again 1 less than half filled, 1 more than half filled, we have 5D ground term, and then in case of d^5 , it is unique, 6S is there, and in case of d^{10} , we have 1S . How we arrive at these things?

I will show you, for several electronic configuration how to calculate, how to determine the ground term, in my next lecture. Until then have an excellent time reading about UV spectroscopy and enjoy the course thank you.