Concepts of Chemistry for Engineering
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Lecture 44
Electronic Spectroscopy -I

We have studied quantum mechanics a little bit and we have studied how quantum mechanics can give us a very intricate view of atoms and molecules. Now, the question that one could think of at this point is, is all this true, because we have done some calculation, we have done some mathematics, we have formulated some very nice theory.

But how do we know that all this is true. I do not remember whether I have said this already. But Max Planck, one of the founding fathers of quantum mechanics had said that experimental results are the only truth, everything else is poetry and imagination. So, no matter how elegant the theory is, until and unless it is backed up by experimental observations, we are never sure that all the discussion is correct.

And the experimental manifestation of quantum mechanics is really very elegant. In fact, quantum mechanics, if you remember, started off from some experiments. And all those experiments involve interaction of light with matter, radiation with matter, blackbody emission, photoelectric effect, line spectra of hydrogen all these were experiments that led to quantum mechanics.

And this interaction of radiation with matter goes by the name of spectroscopy. What we will do in this course, very briefly is that we are going to talk a little bit about electronic spectroscopy, which has got to do with transitions involving the electronic energy levels that we studied in atoms and molecules. Outside the lab, in day-to-day life, these electronic levels or you can say electronic spectroscopy is manifested in all these colors that we see.

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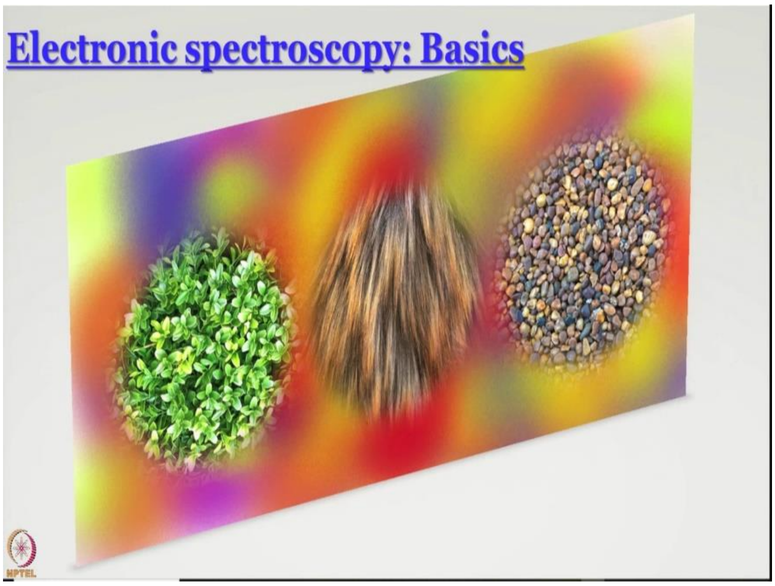

Electronic spectroscopy: Basics

We live in a colorful world and all that colour arises out of transitions involving electronic levels. So, electronic spectroscopy is essentially a study of colors. And not completely because it also involves ultraviolet colors that we cannot see, but colors nevertheless. So, today, we are going to develop the very basics of electronic spectroscopy that gives rise to this colorful world that we all live in. And at the very beginning, let us set something straight.

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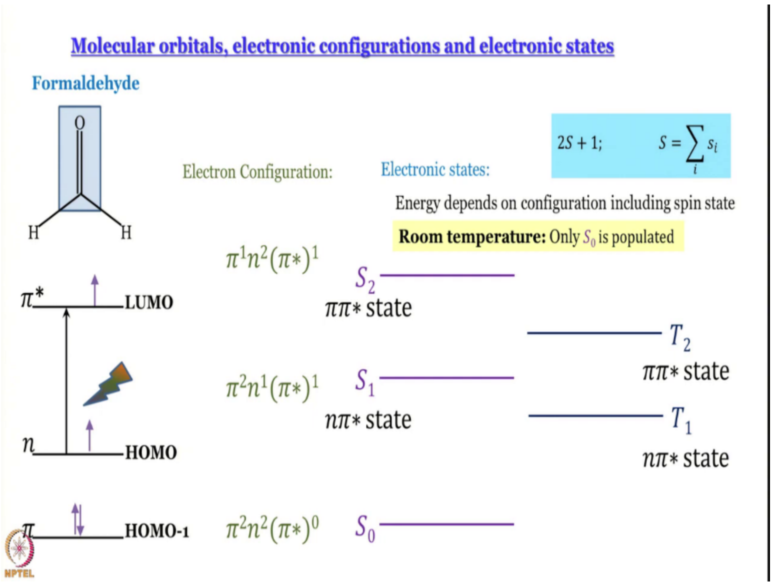

Molecular orbitals, electronic configurations and electronic states

Formaldehyde

Electron Configuration:

Electronic states:

$2S+1; \quad S=\sum_i s_i$

Energy depends on configuration including spin state

Room temperature: Only S_0 is populated

Let us say, let us remind ourselves what are molecular orbitals, we know what electronic configurations are, but we will revisit that in the light of molecular orbitals. And we want to state very clearly what electronic states are because as we are going to say again, there seems to be some confusion about these many times. And we are going to do this using an example, a very simple elegant example of formaldehyde. When we talk about formaldehyde, we are not going to talk about the sigma electrons.

See, all these molecular orbitals that we studied about, we know that there can be sigma molecular orbitals, they can be pi molecular orbitals, they can be nonbonding orbitals also, orbitals that are localized on one of the participating atoms. We are not going to talk about transitions involving sigma orbitals, because if you remove electrons from sigma orbital, that essentially means fragmentation that is also within the realm of electronic spectroscopy.

We are not going to go there, we are going to only talk about the spectroscopy that does not breaks up the molecule into its fragments, we are going to focus in our discussion of formaldehyde on this pi($\boldsymbol{\pi}$) and nonbonding orbitals (**n**) on carbon and oxygen centers. As we know the lowest energy out of them is the bonding pi molecular orbital.

And let us forget, let us remind ourselves because this definition is written wrongly in many of the good books that we study a molecular orbital is an acceptable one electron wave function for a molecule, so wave function. So, lowest energy bonding pi molecular orbital. Then, we are going to have the corresponding antibonding pi star ($\boldsymbol{\pi^*}$) molecular orbital and then we are going to add the non-bonding orbitals on oxygen that energetically lie between pi and pi star, so pi and pi star that is the order.

Now, how many electrons do we talk about, when we talk about n, we are going to talk about only one n because it is the same thing. So, two electrons in pi, two electrons in one of the nonbonding orbitals of oxygen and pi star is empty. What would the electron configuration be? Before that, let us remind ourselves that then the highest energy molecular orbital that is occupied is the non-bonding orbitals.

So, that is the HOMO and pi-MO is the HOMO – 1 molecular orbital. What is pi star? That is a lowest unoccupied molecular orbital LUMO. Our transitions are going to involve these occupied and unoccupied molecular orbitals, they can involve other orbitals also. So, what is the electron configuration for this ground state that we have written already, there are two electrons in pi orbital and two electrons in **n** orbital.

So, the electron configuration is going to be $\pi^2 n^2$, and we will be explicit and write $(\pi^*)^0$ also. So, this is the electron configuration for the ground state and this ground state, ground electronic state is called the S_0 state. Why zero? Because it is the ground state. Why S? Because it is a singlet state. Now, one can develop a more correct and more sophisticated treatment of the singlet triplet business by talking about the spin wave functions, but for the purpose of this course, we are not going to go there, let us just look at the simple picture that we have drawn here.

Here the four electrons that we have drawn, they are all paired up. So, since all electrons are paired, that is called a singlet state. For now, we will use this simple example. Now, let us come to this transition, let us say I give light of sufficient energy, energy that matches the energy gap of the nonbonding and the pi star orbitals.

Remember, Bohr resonance condition is $h\nu = \Delta E$, where ν is the frequency of light, h is Planck's constant, ΔE is the difference in energies of the two energy levels concerned. So, when we give light of the correct frequency that matches Bohr resonance condition one can expect that there is going to be a transition from n to pi star, whether the transition takes place or not, to what extent it takes place, we are going to come to that slowly.

For now, let us just assume that it does happen, what will happen then, an electron will get promoted from n to pi star. Remember something, there is something called one photon rule which says that one photon can only cause the transition of one electron, one photon cannot split up and cause transition of many electrons. So, let us say one electron is now promoted from HOMO to LUMO.

And let us also say that the spins remained paired. So, if the electron in HOMO has up spin the electron in LUMO has down spin, we will come to the other possibility as well shortly, but for now, let us work with this. Now, I hope you agree with me that the energy of the system is going to be more, energy of the molecule is going to be more, when electron is promoted from HOMO to LUMO, energy is different, configuration is also different. What is configuration here?

Now, there are two electrons in pi, one in n and one in pi star. So, this electron configuration is $\pi^2 n^1 \pi^{*1}$, and the way I have drawn it the electrons are paired. So, I get another singlet state and since the energy of the singlet state we agreed is higher than the ground S_0 state, we call it S_1. So, what is S_1, it is a singlet higher energy state or singlet excited state of the molecule.

It is also called the $n\pi^*$ state, because it has reason out of a transition from an n to pi star molecular orbital or you can think that in this state it is the n and pi star molecular orbitals that are singly occupied. So, now see, we can think of this transition the one that we have drawn here $n^2 \pi^*$ as S_0 to S_1 transition also, is the same thing just drawn in different ways. But this is where I get annoyed when people say this, this is where we need to remember that S_0, S1 these are molecular electronic and energy states.

So, molecule goes from S_0 to S_1, when the electron goes from n to pi star with the spin paired. Please remember electron does not go from S_0 to S_1, I keep hearing people saying electron goes from S_0 to S_1, that is, that makes no sense. Electron you can think it goes from the nonbonding orbital to the antibonding pi star orbital which causes the state of the molecule to change from S_0 to S_1 with n pi star state.

There are other ways of designating this transition using the symmetry or what are called term symbols, in this course, we are not going to get into that. But please remember S_0, S_1 these are molecular state. So, molecule goes from S_0 to S_1 when the electron promotion takes place from n to pi star MO, with the electron pair.

There is no reason why electron can go only from n to pi star, it can also go from pi to pi star, let us say we consider that transition and we consider that the electrons are still paired, electron in pi MO, post excitation has let us say off spin and then electron in the pi star MO has down spin.

Now, this can be up, that can be down does not really make a difference. The energy gap is more, so naturally the molecule is going to be promoted to higher singlet state. So, this singlet state is called an S_2 state with electron configuration $\pi^1 n^2 \pi^{*1}$. What would be another name of the S_2 state? This has arisen out of pi to pi star transition. So, it is also called the pi-pi star state, pi-pi star singlet state.

So, these are the singlet states that we talked about, there can be many more singlet states you can have transition from a lower orbital, sigma orbital. The only problem with that is that then the sigma bond will break, you can have in principle pi to sigma star(σ^*), n to sigma star transitions also, but that those will lead to higher energy S_3, S_4 so on and so forth states.

We will, but just looking at these states can something else happen? Can we have transitions involving the same molecular orbitals, but different molecular states? Actually, we can. Let us say, we have this same n pi star transition. But remember what happened last time, last time the electrons remained paired, the electron in HOMO had the opposite spin as the electron in LUMO. This time, let us say they have the same spin, there is been a spin flipping, this kind of a state is called a triplet state. Why singlet? Why triplet?

We will come to that shortly, perhaps I should have said it earlier, so this is a triplet state and it turns out that this state has a little lower energy state. So, it is still n pi star state like S_1, but it has a lower energy than the S_1 state. There are many different ways of explaining this. But I do not want to get into hand waving argument, just believe me when I say that, when we express this problem in terms of the spatial and spin wave functions, this spatial wave functions involved in the S_1 state and the T_1 state are different.

And so, the energies that the expectation value of energy that we get using those different spatial wave functions of the molecule using the molecular Hamiltonian, they are also different. And that is what I want to say at the moment, instead of going into things like Hund's rule and all. What would happen if there is a pi-pi star transition, but the spins would remain parallel? Then I would get T_2 state.

A pi-pi star state which would be lower in energy than the pi-pi star singlet S_2 state. So, what we learned from here is that for electronic states, the energy depends on configuration including spin state, it is not enough to say $\pi^1 n^2 \pi^{*1}$. You have to say, what is the spin wave function.

We have not really discussed spin wave functions here. So, we have to say whether spins are paired or not, then only can you talk about, then only do you have a complete description of the electronic state, then only can you talk about what kind of energy it is associated with. So, not only the spatial part but also the spin part plays an important role in determining the energy of the electronic states.

And finally, we have come to what we have said earlier, what is the meaning of singlet and triplet. Well, capital S is just the sum of all the electron spins. So, if you just look at this diagram here, this is + 1/2 , this is - 1/2, so 1/2 and - 1/2 is 0, this is + 1/2, this is + 1/2, so that gives me 1. So, capital S is 1, 2S +1 is 3, that is why it is a triplet state.

Of course, you can think that what would happen is - 1/2 and this is - 1/2, well it is conventional to take them as + 1/2 and I define like this. What it actually means, triplet state is that, there are three different spin wave functions associated with that spatial part. If you are interested in this, please see the lectures of my course on atoms and molecules, quantum chemistry of atoms and molecules, we have discussed this in more detail in that course.

So, capital S is simply the sum of all these spins, well m_s values and 2S+1 comes from here. So, when you have unpaired electrons, your 2S+1 turns out to be 3, we call it a triplet state.

When we have paired electrons + 1/2 - 1/2 that gives me capital S = 0. So, 2S + 1 is going to be 1, that is called a singlet state. For now, let us be happy with this simple definition.

Another very important thing before we move on to something else is to realize that the energy gap between S_0 and S_1 state are quite large, is in the order of electron volts. So, if you use Boltzmann distribution you will find that S_1, S_2 these are not going to be populated in the ground state only S0 will be populated in room temperature. So, S1, S2, T1, T2 can only hope to get populated if you shine them with light or if you use some other sophisticated technique to populate the higher excited state.

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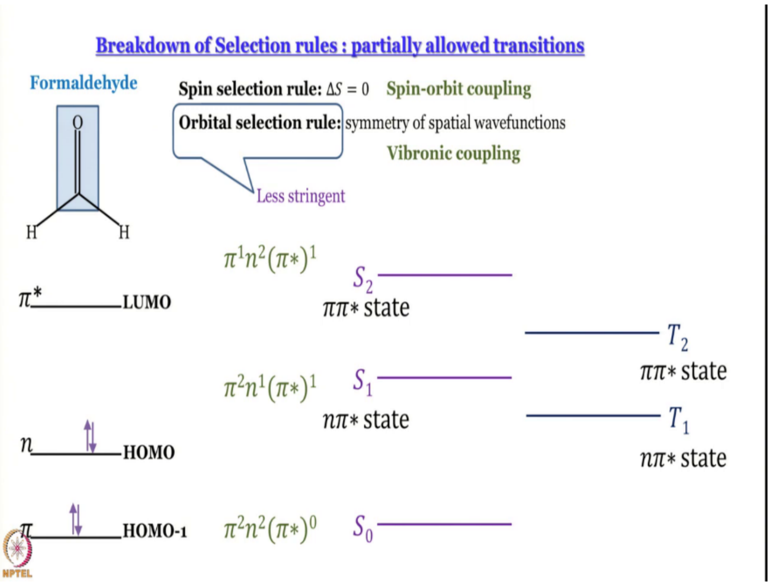

Breakdown of Selection rules : partially allowed transitions

Formaldehyde

Spin selection rule: $\Delta S = 0$ Spin-orbit coupling

Orbital selection rule: symmetry of spatial wavefunctions

Vibronic coupling

Less stringent

$\pi^1 n^2 (\pi*)^1$ S_2 $\pi\pi*$ state

T_2 $\pi\pi*$ state

$\pi^2 n^1 (\pi*)^1$ S_1 $n\pi*$ state

T_1 $n\pi*$ state

$\pi^2 n^2 (\pi*)^0$ S_0

Now, let us come to this question. Just because states are there, energy gap is there, if I supply photons of the correct energy, is the transition going to take place? I told you the answer is no. Let us do a little bit upon that. Some transitions are allowed and some are forbidden. They are forbidden, even if Bohr resonance conditions are met. And that comes from, well that is understood by a little more sophisticated quantum mechanical treatment using something called time dependent perturbation theory.

Once again, I have a course in NPTEL on molecular spectroscopy there we have discussed this in much more detail. Whoever is interested is welcome to see those lectures. But from there we get something called transition moment integral and whether transition moment integral is 0 not, determines whether a transition is forbidden or not. If you have not followed anything that has said in the last couple of minutes, just delete it from your memories, it is okay. We will just take it axiomatically that not all transitions are allowed, there are allowed transitions and there are forbidden transitions.

And in case of electronic states, since the energies are determined by not only the spatial part of the wave functions, but also the spins, both parts of the wave functions have a role to play. So, some transitions are forbidden by spin. So, selection rule, a selection rule tells us which transitions are allowed, a selection rule arises from spins and the spin selection rule is ΔS is equal to 0, which means that you cannot have this transition. Even if you give light that matches the energy gap between S_0 and T_1.

That transition is forbidden by spin selection rule because there ΔS would be equal to + 1, not allowed. Another selection rule that is there for your electronic spectroscopy is orbital selection rule, sometimes called symmetry selection rule, it arises out of symmetry of the spatial wave functions or the molecular orbitals that essentially says that transition can only take place between orbitals of compatible symmetries.

What I mean by compatible symmetry that will require further discussion. We have discussed it in the molecular spectroscopy course, and also in another, yet another NPTEL course, on symmetry in chemistry. For now, we will just go back to our example of formaldehyde. And we will say that this orbital selection rule actually forbids this n pi star transition. And an easy way even though come not completely satisfactory way of thinking of the situation is that see, where is this n orbital? It is in the plane of the molecule, is not it? A formaldehyde.

Where are the pi-pi star orbitals? They are above and below. So, spatial overlap between the n and the pi star orbitals is very small. So electronic coupling is poor, so it is not so easy to perform a transition from n to pi star. For now, let us be happy with this. If you are not happy, you are welcome to see those lectures in little more advanced courses. So, n pi state transition is forbidden by orbital selection rule S0 to T1 or Sn to Tn or Sm to Tm rather, they are forbidden by spin selection rule.

And actually, spin selection rule is much more rigid, but we will come back to that. So, what we have just said is that this S0 to S1 transition is forbidden by orbital selection. But does it not take place? Actually, it does take place to some extent, because selection rules can be made to breakdown, breakdown of selection rules can lead to what are called partially allowed transitions. How does it take place?

Well, again, this is a scope for a wider discussion. For now, let us just say that spin selection rule can break down by what is called spin orbit coupling. Spin as we know is associated with an angular momentum. And there is something called an orbital angular momentum for the electron as well, these two angular momenta are vectors and you can have vector sum, this vector sum is not easy to do, because spin is in some other space not really in physical space, but one can do it and this leads to spin orbit coupling.

And it will be sufficient if you understand for now, that when spin orbit coupling happens, what happens is what was a singlet state, after spin orbit coupling does not remain a pure singlet state, it mixes with triplet state. So, it is partially singlet partially triplet. Not so easy to understand, if we just draw these pictures, but if you think of wave functions, both singlet and triplet states have their own characteristic wave functions in the molecule.

What we are saying is that by spin orbit coupling, this singlet and triplet wave functions can mix with each other and form sort of mixed kind of wave functions and that is what provides a conduit for crossover from singlet to triplet or triplet to singlet, in some cases. So, spin orbit coupling can cause a partial breakdown of spin selection rule and orbital selection rule can break down to some extent by what is called vibronic coupling.

Coupling means interaction, well but vibronic means coupling between vibrational and electronic wave functions. What are we saying? See, this orbital selection rule, as we have said, they arise from symmetry of spatial wave functions. Now, when a vibration takes place then the molecule gets distorted. And this distortion causes symmetry breaking of the wave functions along with the molecule.

And because of this symmetry breaking, something, some transition that are orbitally forbidden, can become partially forbidden, they become what are called vibronically allowed, partially forbidden partially allowed. So, electronically forbidden transitions can become vibronically allowed because of symmetry breaking. And as it turns out, it is easier to cause a breakdown of orbital selection rule, that is less stringent than the spin selection rule. So, you often get what are called vibronic structure in the spectrum as we are going to discuss in the next module.

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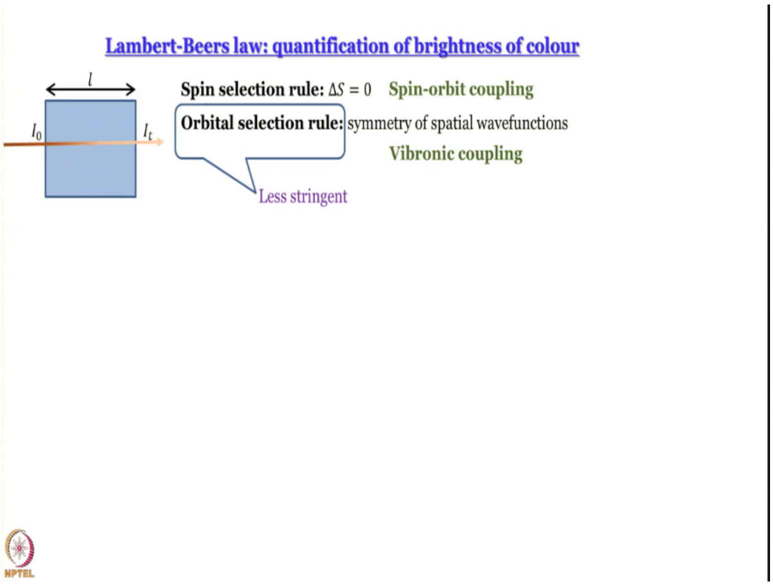

Lambert-Beers law: quantification of brightness of colour

Spin selection rule: $\Delta S = 0$ **Spin-orbit coupling**

Orbital selection rule: symmetry of spatial wavefunctions

Vibronic coupling

Less stringent

So, in the next module, we are going to start from here. We said that these transitions being allowed or forbidden, this is not a one zero situation. So, you can have colour that is, it is not as if something is bright or dark. You can have different shades of colors. Well different intensities of colors, different shades may have got to do with different wavelengths.

So, this is quantified by something called Lambert Beer's law. And from Lambert Beer's law, we will get an idea of exactly what is the extent of allowedness of a transition. We will start from here in the next module and go on to different kinds of transitions and what absorption spectrum look like.