Chemical Applications of Symmetry and Group Theory

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Lecture – 37

Hello and welcome. So, we were discussing about the application of symmetry rules in case of electronic spectroscopy. So similar to our approach in case of Vibrational spectroscopy, we started looking at the wave functions for the electronic transitions and the corresponding a transition moment integrals, that we are looking at. So the transition moment integral involving all the different components for example, Vibrational and electronic as well as spin. So, whether I should say is you know orbital and spin.

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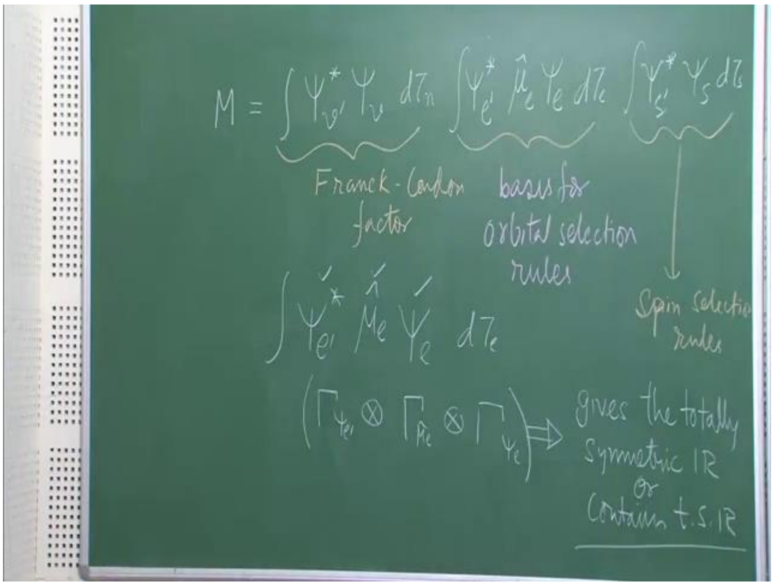

$$M = \underbrace{\int \Psi_{v'}^{*} \Psi_{v}\, d\tau_n}_{\text{Franck-Condon factor}} \underbrace{\int \Psi_{e'}^{*} \hat{\mu}_e \Psi_e\, d\tau_e}_{\text{basis for orbital selection rules}} \underbrace{\int \Psi_{s'}^{*} \Psi_s\, d\tau_s}_{\downarrow\ \text{Spin selectio rules}}$$

$$\int \overset{\checkmark}{\Psi_{e'}^{*}}\, \overset{\checkmark}{\hat{\mu}_e}\, \overset{\checkmark}{\Psi_e}\, d\tau_e$$

$$\left(\Gamma_{\Psi_{e'}} \otimes \Gamma_{\mu_e} \otimes \Gamma_{\Psi_e}\right) \Rightarrow$$ gives the totally Symmetric IR or Contains t.s. IR

So, ultimately what we got my transition movement integral as the product of 3 integrals. So, the first one we got as multiplied by and so these were the 3 integrals that we got ultimately for an electronic over the electronic transition and we came to this by using the condition of orthogonality of 2 electronic labels. So we also mentioned that, this particular integral is called Franck Condon factor. So, the Franck Condon factor gives me the overlap between the wave functions of the Vibrational levels at the lowest electronic state and that in this upper electronic state. So, what it gives me the overall modulation in the electronic spectrum. So, the second part this forms the basis for orbital selection rules and the third one it forms the basis for spin selection.

So, let us start with the spin selection rule part. So, this is probably the first thing that one should look at, whether this particular integral is vanishing or none vanishing, so before going even into the detail discussion about these individual 3 integrals. So, since this is my overall transition moment integral, the alertness of an electronic transition, will be you know affirmative; if the overall integral is none vanishing, otherwise if anyone of this integral is 0 then the corresponding our transition will be forbidden.

Now when we talk about this particular part, so what we look at. So, this is a transition between 2 states having 2 spin states, but, suppose I have a ground state, suppose this and if I want to make a transition to say or maybe say 1, 2 to say, So, in this kind of transition, if I have to look for the loudness of a this particular transition; that is whether it is spin allowed or not, in only thing I have to look for the spin multiplicity of this 2 states, but between which the transition is taken place or one is thinking about having a transition between this 2 states. So, if these 2 states have different spin multiplicities, they are going to be orthogonal. Because this wave Franck is being wave functions, you know having 2 different multiplicities, they are completely orthogonal. So therefore, until and unless the spin multiplicities of the 2 states involved here, the transition is forbidden. So therefore, a case where like you know spin multiplicity 1 to 1 is allowed So that means, if I have a say singlet state, I can have a transition to a singular state, having spin equals to 0. So, spin multiplicity is 1.

Similarly, I can have as a Triplet to Triplet is allowed, but a Singlet to Triplet is forbidden or a Singlet to a quartet is forbidden, while quartet to quartet or singlet to singlet is allowed. So just one has to look at that spin multiplicity and you know one can easily figure out whether the transition is being allowed or not.

So, next have a look at the orbital selection rule right. So that is our particular integral. So, if I just take out this integral, what I have? I have 2 electronic states and the transition involving in between those 2 states. Now just like what we got in case of Vibrational transitions, here also it has to be handled in the very same way. So, at a in this particular case one has to look at this symmetries of each of this functions. So, this situation is very similar to condition when I have 3 different functions and I trying to find out the value of the integral.

So, here I know that this particular these 2 wave functions and operator all of them individually transform according to that, one of the IR of the point group for the molecule. So therefore, the aloofness of this particular condition, we will depend on the direct products of that irreducible presentation to which this belongs. Therefore, my situation is now is such that if I have gamma of psi prime, gamma of mu e and gamma of psi e this direct product. So where these individual gammas are the irreducible representation to according to which these individual functions transformers. So, this is a triple type direct product, we have 3 different individual presentations and having a direct product of among them. So this triple direct product if it gives the totally symmetric illusion presentation as a result or it contains the totally symmetric IR as one of the component then this transition will be allowed. So as usual this is a dipole moment operator. So, it depends on x y and z Curtis and coordinate systems.

Now, for an electronic transition, where the ground state is totally symmetric, suppose I have an electronic state which is totally symmetry, when it is in the ground state then simply my solution becomes such that I will look for whether this IR corresponding to the excited electronic state contains, at least one of the Cartesian coordinates x, y or z as its basis, then only I will have the total integral as non 0. So therefore, an electronic transition for a totally symmetric ground state will be allowed only when the excited state has either x or y or z or maybe you know x y or x, y, z all as its basics or otherwise in general this is the thing one has to look at the triple direct product of this functions and you see whether the transition is allowed or lot. So for example, we will take the case of a of benzene molecule.

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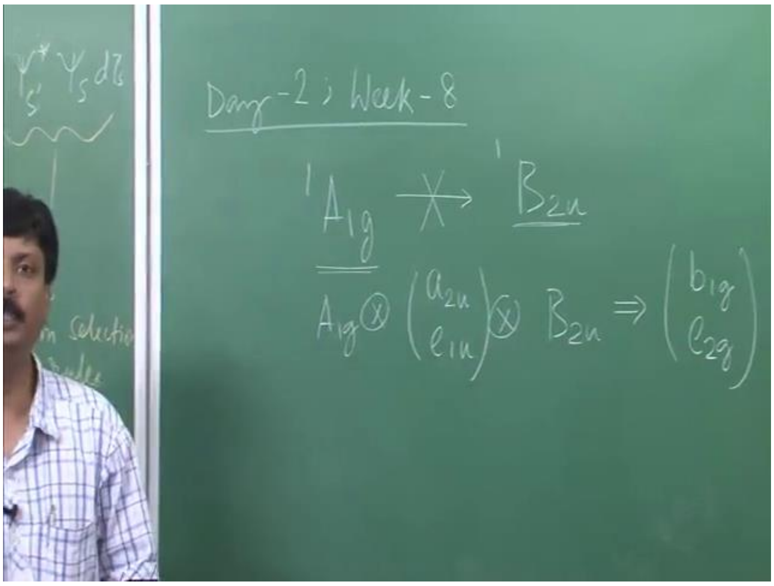

So, if I take for benzene, 2 states 1 A1g then I has a transition to 1 B2u. So, if I try to make a transition like this, then 1st place the spin is (Refer Time: 12:56). So, it is being allowed, no problem about that, but whether it is or vitally allowed or not that one has to figure out. So, what I have to do, I have to see A1g it corresponds to totally symmetric isolate presentation, for d6h point group. Therefore, I have to see whether this one contains in either x or y or z as its basis function or not.

So therefore, I will again look at my character table. So, character table for the 6h point group, if I look at then I see that, this B2u does not transform either according to x or y or z. So, I can immediately say this, this transition is orbital in forbidden. So, if I want to look at this problem even more explicitly, then what I have to do? I have to take a direct product of A1g and initial presentation according to which this dipole moment operator transform, at that is I have to look for the universal presentation for which x, y and z from the basis for. So if I look at that then, I see that z from the basis for A2u. So x and y from the basis of e1u, so then I have to explicitly do the direct products.

So, I wrote it in a particular way that you will be you know seeing in most of the books related to this electronic spectroscopy. So here A2u forms a basis for z axis, while x and y transform as e1u, now for the operator I use the small latter. So, that you know in many cases is used. So, this in the 2 terms within the parentheses means that actually we are doing 2 separate direct products.

So, 1st with A1g, a2u, B2u, one direct product and also A1g, e1u and between 2 different direct products, so after doing that what I get, I get I get, b1g and e2g, so this is for the first one, this is for the second one. So, this 2 are not the total symmetric hear, so clearly this transition is orbitally as in an orbital in forbidden. So, that is one we have already seen. So, in either way you can go, if you are not comfortable in a doing this short way, you can do it explicitly in this format and get the result; if the results does not contain in a totally symmetric, irresolute representation the transition is orbitally disallowed.

So, we will look at this overall electronic transitions in one particular molecule in greater detail, that we said you know maybe a week ago when we were dealing with the symmetry adapted linear combination of phenolphthalein molecules, there we form the state by solving the circular equations; in circular of determinants and using Google approximation and then ultimately using the Hund's rule and Pauli's exclusion principle we filled up, orbital were formed by the linear combination of p pipe orbital of the carbon atoms. So, that will come shortly.

So, at this point I would like to mention one particular thing, that many of you in inorganic books you have, or in a course we have hired about the forbidden of certain transitions; particularly in case of say metal complexes, and have heard about Laporte selection rules.

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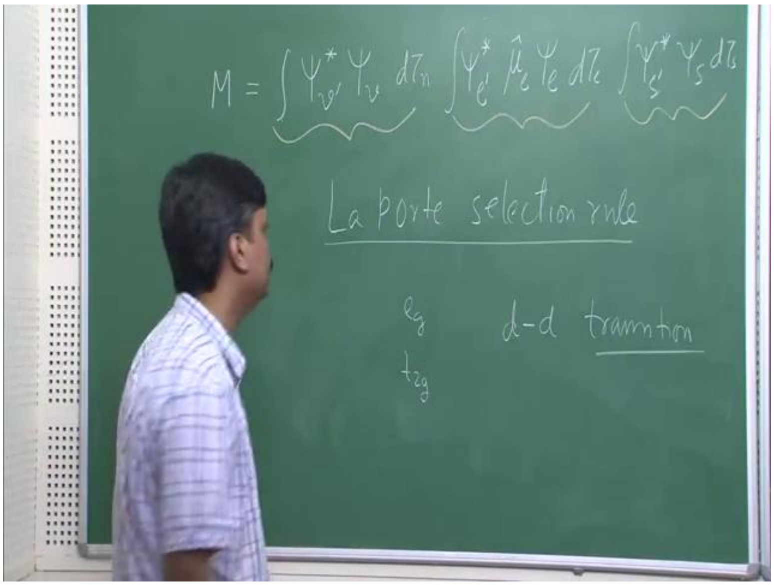

So, what is this Laporte selection rule; in this context I will mention that, so the Laporte selection rule is particularly important in case of synthetic molecule. So, in case of metal complexes what you have legend form, that mainly the sigma bond and the middle are vital basis from the nonbonding electrons or nonbonding vital. So, metal d electrons you have states having t2g and eg symmetry.

So, any transition from t2g to eg, which is nothing but a transition between 2 type of d orbitals, so these types of transitions are known as d d transition and for symmetric molecules such d d transition is forbidden. So, this is what Laporte selection rules testing. Now why is it so? If you look at the transition moment integral here, what do you find that this d orbitals in case of single symmetric molecules, they are of heated. Because if you do an inversion operation, So nothing happens to this d orbitals, if you look at the component functions like either it will be x y or x z or x square, minus y square, or j square like. So, all these functions are invariant to inversion.

So therefore, you have a dipole transition, where operator is of u type. Transitions are taking place between g type orbitals. So therefore, the overall transition moment integral becomes u type and therefore, the values 0. So this type of transition, in middle complexes for Centro symmetric middle complex is this disallowed or forbidden and this is what we have as Laporte selection rules.

Now, let us move on it in attention to the other part, that is particularly this part related the Franck Condon factor. Now we have looked at the Vibrational transitions and the corresponding selection rule how to get those things, now here when we were discussing about the loudness of a transition involving to electronic all vitals, then we assume that that transition was taking place from v equals to 0 of the lower electronic state, to v equals to 0 of the upper electronic statements. So, the situation was something like.

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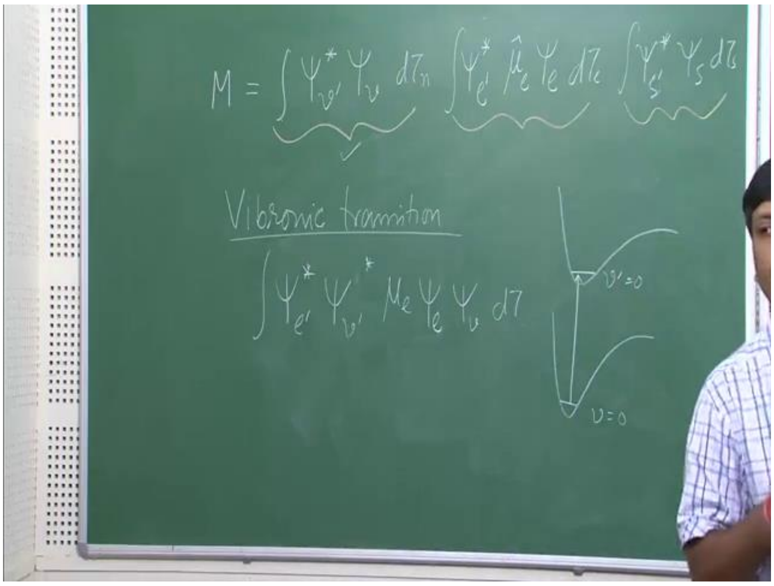

So, this is d prime equals to 0 and here it was v equals to. So, we had a transition like this. So, that both of being both of the volitional states are at their ground states and therefore, belong to the total symmetric IR and I did not have to think about the symmetries of this too because automatically it is taken care of. Now what will happen if there are Vibrational states involved which are not totally symmetric.. So, what will happen if I excite from v is equal to 0 to, v is equal to one v prime equals to one here. So, I should think about a transition which will have both Vibrational transition as well as electronic transitions. So, all together this is known as vibronic transition.

Now, of course, my Vibrational, it is situated on one by this one state to another I have another Vibrational state, but since both of them are the ground that state ground down pipes state. So, we call this as if it is a pure electronic transition there is no contribution coming from the Vibrational state. Now if I think about a situation where I have and then this now you remember that we have earlier decoupled this and you have data. So this is my transition moment integral for a vibronic transition.

So, here you can see that, I have to consider the symmetries for both electronic space as well as the Vibrational state. So, if I have a situation where the symmetry of this Vibrational state, is different from this one, then the whole scenario changes. So one particular example I will give you say for example, we were talking about this in a d d transition in case of Centro symmetric molecule.

Now, if I have instead of say you know at that ground level or the Vibrational states, I give at a time, if you look at the corresponding wave function for Vibrational state. So, if I find an ingrates state here, at that point what happens your overall Centro symmetry of the problem is broken, now the pure Vibrational transition, which where I mean the pure electronic transition, which was not allowed here because of this vibronic coupling, I can have a transition which was earlier forbidden, now can be partially allowed.

So, rest of the things are exactly similar to what we dig in this particular case of electronic just orbital transition state. So, all I have to do, I have to now worry about the isolate presentation, according to which each of this function transform as and have the direct product and try to find out whether or not the totally symmetric presentation is contained in the result or not.

So we will stop here today. And in the following class we will come back with a particular example of the that phenolphthalein molecule for which we formulated the state their energies, and we will try to see how first place we have to find the symmetries of the states, find the symmetry of the orbital in the states, and then we can we comment on the loudness of certain transitions or not.

Thank you very much.