Chemical Applications of Symmetry and Group Theory

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Lecture – 34

Welcome back. We were discussing about the possibility of finding out which particular modes of a given modes of vibration for a given molecule will be infrared active Raman active; and if one is in productive, then in which polarization, which direction it will be the transition will be taking place. So, we need to know about the selection rules.

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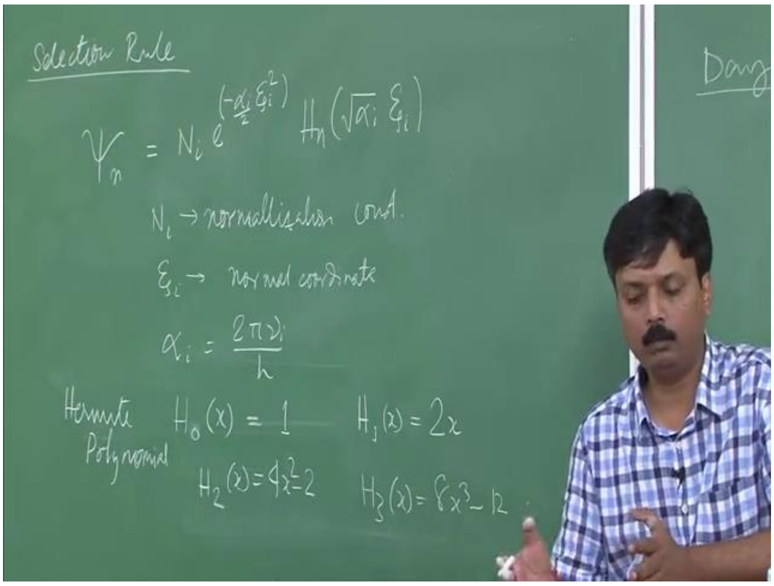

So, basically we want to find out which one of them is infrared active and which one is Raman active or which one are Raman active.

So, let us start with formulating, how we can find out about the about the possibility of 1 particular type of activity; that is infrared active or Raman active. So, what are the selection rules associated with that? Now, we will talk about selection rules of molecular vibration. So, we know that any normal mode which can be expressed as the wave function and we can write this wave function as a function of the normal coordinate. So, normal coordinate is the coordinate about which the vibration takes place.

So, this molecular vibration, the wave function for this normal modes I can write as, psi n, which I can write as N i and x i. So, you can find this in any textbook of quantum mechanics. So, here in this expression what we have, we have normalization constant. So, N i’s are normalization constant, and this xi i is i th normal coordinate. And this alpha it is a function of the frequency of the normal mode. So, alpha i I can write as by this. So, now this is a wave function for any particular normal mode. Therefore, as we have discussed earlier this wave function should form the basis for an irreducible representations of the particular point to you molecule belongs to.

Here one thing I forgot to mention, this is a polynomial, this is called hermite polynomial, which is a function of this coordinate, so here root over alpha i, xi i. Now, this 1 is such that, for n equals to 0, n equals to 1, 2 and 3, the values are different. So, this in here represents the provisional quantum number right. So, if it is in N is equal to 0; that means, we are in the ground vibrational level, and 1 more thing, like I expressed this in a normal mode in terms of this equation, this is valid for, you know a particular model, which is the harmonic oscillator model. So, most of you are probably aware of this.

So, now this hermite polynomial, if I have n equals to 0, then I have a value of 1. So, if I have if I considered h 1, in general I have a value of 2 x, so then h 2. So, so similarly I can write for h 2 and h 3 and so on. So, this gives me a value of 4 x square minus 2, while this gives me 8 x cube minus 12 and so on.

So, now when I, when I operate any symmetry operation, on this wave functions, what should I get? I should get as a plus 1 or minus 1, and multiplied by the same, same function back. That is what it should be because these wave functions from the basis for the irreducible representation of this particular molecule that we are considering, and if we are considering one dimensional irreducible representations then obviously I should have you know this plus or minus 1 its character.

Now, if I considered, if I considered you know, n equals 0, and if I have many normal mode of, normal modes, having many that many number of normal coordinates then all of them, if they are at the lowest modes energy state, that is the lowest Vibrational quantum number 0, then I have my molecule in the ground vibrational level.

So, I need to know what is the frequent, what is the symmetry property of this ground vibrational level. Now this ground Vibrational level what is the form of the wave function at the ground state? So, at ground vibrational level, I have h 0, which is giving 1.

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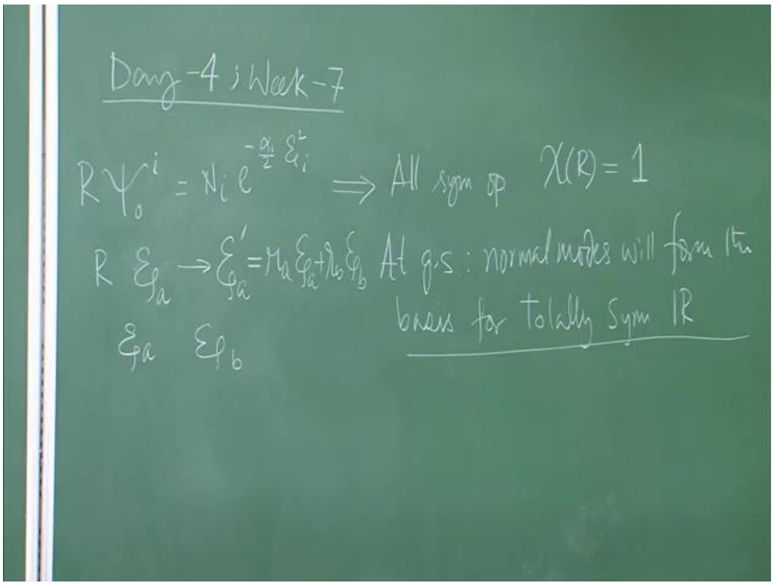

Day-4 ; Week-7

$R\psi_0^i = N_i e^{-\frac{\alpha_i}{2}\xi_i^2} \Rightarrow$ All sym op $\chi(R) = 1$

$R\ \xi_{q_a} \rightarrow \xi'_{q_a} = r_a \xi_{q_a} + r_b \xi_{q_b}$ At g.s : normal modes will form the basis for totally Sym IR

ξ_{q_a} ξ_{q_b}

So, therefore, what I have is psi 0, for any ith normal mode, as N i, e to the power minus alpha i, by 2, and xi square, because other part is 1. Now at this condition what is the symmetry of this particular function? Or in other word if I ask, that which i r of the point group this particular function, which is a ground state will transform as.

So, let us find out. So, here you know if I offer it r on psi, I will get something out of this right? So, here for psi 0, I have a function, but you know, suppose this is a function of this coordinate. So, the symmetry of this function is governed by this normal coordinate right? Now how to I get this normal coordinate? I get this normal coordinate by the symmetry adopted linear combination of these atomic motions. So, if this xi transforms as one particular irreducible representation, then that will be the irreducible representations that might you know this function will also transform as.

So, if I apply and r on this xi. So, this is a coordinate system. So, r we either change it to plus 1 or minus 1. So, this will give me plus or minus xi i. So, in whatever case, either his plus or minus, if I apply r on this function, this is going to give me back always plus 1, as plus 1 times this function. Therefore, if I operate all the symmetry operation, if I perform all the symmetry operation, the characters irrespective of the operation, is always going to be plus 1, what does that mean; that means, this is, this particular function, which is the grounds state, ground vibrational state wave function, it will form the basis of total these symmetry irreducible representations. So, so at ground state, normal modes, that ground state normal mode will form the basis for totally symmetric individual representation.

Now, here obviously I assume something, I assume that this you know, energy levels that I am talking about, is non degenerate. There is only one particular energy state is there, one particular state is there for that particular energy value. Now if I have a situation if I would have a situation, where I have more than one state, having the same energy. So, I have a case of degenerated. So, there also I can very easily show that this particular property of the normal modes and the ground provisional level remains intact. So, how can I do that? Suppose I have, here I considered that 1 particular normal coordinate.

So, suppose I have say xi a, and xi b, they form my set of 2 degenerate vibrational, 2 degenerate normal coordinates for 2 normal modes of vibration, at the ground state, then I can express this, I can express this, the transformation of xi a, such that xi a will form something like xi a is prime, and if this 2 a degenerate as assumed, then what will happened I can write this 1 as something like say, r a times xi a, plus r b times xi b. Now if my xi a, is normalized, then this coefficient r a and r b, also will be taken in such a way that this guy is normalized. So, if I take this xi a, square is equal to 1, in a normalized condition, then that will imply that xi a prime is also equal to 1. So, both of them are normalized.

Therefore I have no problem, because I can express xi b, is xi b, also in the same way. So, therefore, the matter again become like the same case as we discussed earlier. So, therefore, irrespective of the fact, whether this normal mode is, normal mode of vibration we are considering when it is ground state, is degenerate or non degenerate, it will always form the basis for the totally symmetric irreducible representations, of the particular point group that we are considering. So, this is true always.

Now, what will be the case of excited state? So, we have talked about the ground state that is if I call psi 0.

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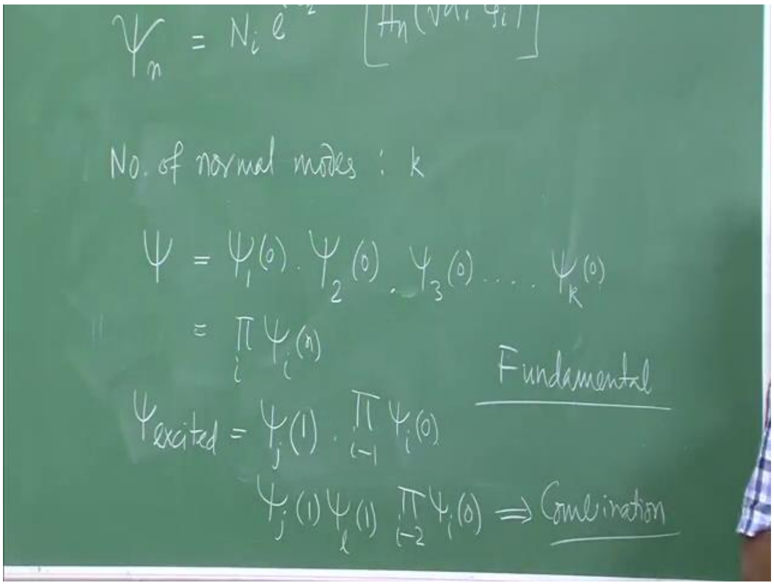

$$\Psi_n = N_i e \left[H_n(\sqrt{\alpha_i}\, q_i)\right]$$

No. of normal modes : k

$$\Psi = \Psi_1(0) . \Psi_2(0) . \Psi_3(0) \ldots \Psi_k(0)$$

$$= \prod_i \Psi_i(0)$$

Fundamental

$$\Psi_{excited} = \Psi_j(1) . \prod_{i-1} \Psi_i(0)$$

$$\Psi_j(1) \Psi_l(1) \prod_{i-2} \Psi_i(0) \Rightarrow \text{Combination}$$

Now, I am talking about excited state. So, the symmetry of the excited state will be governed by this part right? Why because we have just seen that this part, no matter what always will be transforming as the totally symmetry individual representation. So, I am not bothered about this part anymore. So, I have to take into care of this particular symmetry. So, as we said earlier, the first excited state are you know, n equals to 1, h is, h 1 is equal to 2 x, when I am talking about each of x, correct? So, so if I am talking about psi 1, I will have its symmetry governed by this. So, here I have say x. So, if I like in terms of this normal coordinate, I can replace it here.

So, I will have, some sort of symmetry right, so here to be an odd symmetry. Now similarly I can find out about psi 2. So, psi 2 to again it will have a continuation coming from h 2, which is. So, this is an even function. So, the nature of the wave function at the excited state will be governed by the symmetry of this normal coordinate correct. So, either I will find an odd function, or an even function.

Now, in case of Vibrational transitions, so what are the different kinds of transition from which state to which state we can write. So, suppose I have a molecule which has total overall k number of normal modes. So, let us consider a molecule, with the number of normal modes, equals to say k, associate with k different normal coordinates. So, I can write down the total wave function, of this, by taking a product of each and individual wave functions. Suppose I have say psi 1 at particular energy state, and let me call it as a

0. Then make a product with next one, sorry psi 3 so on up to psi k. Now this 0, within the parenthesis, it, gives me the particular quantum number, where this particular wave function is residing, that is a particular normal mode is residing. So, here in this particular case, I am considering that all my normal modes, the first, second, third or the kth one, all of them are residing in their 0th level. That means all of them are in ground 0. So, therefore, this is the total wave function of this molecule is in ground state.

Now, suppose one of these, suppose the jth one, is residing on the n equals to 1, that is the first excited state, then how can I write? So, this 1 overall I can in general write the psi as, and I can write this 1 as n. Now suppose I have a situation, where my psi is say psi j, is residing on state 1, and rest of them, that is I minus 1, is still residing on till the (Refer Time: 20:32) level. So, this configuration is the, you know, first excited state configuration, and at this, this means that one of the normal mode must have, like what was the situation here from here, one of this jth normal mode has made a transition from step n equals to 0, to n equals to 1, and this type of transition is known as fundamental transition, fundamental vibrational transition.

There are other type of transitions, suppose I would have this particular jth normal mode, would have made a transition into this step 2, supposed to be psi of j 2, mean that mean that it has undergone 2 successive transition, from 0 to 1, and 0 to 2. That would give you the first overtone, if you could have gone to third level, it will give me a second overtone, and also it could be that instead of only 1 normal mode, it could be 2 normal modes.

Say for example, if I would write psi j, and the psi L, have gone to state 1, and the rest of that wave functions that is normal modes, they asked residing at level 0 still, then this would be called a combination transition. So, we can have this combination transitions, we can have this overtone transition, all these things, apart from this fundamental. Now the matter of fact, is the fundamental transition probability, are where much higher than the overtone, or on the other sense we can say, this overtone transition and combination transitions, they are much less probable compared to the fundamental. So, we will stick to the fundamental transition only alright. So, if I write down the excited state wave function, for particular fundamental transition, as by a different symbol.

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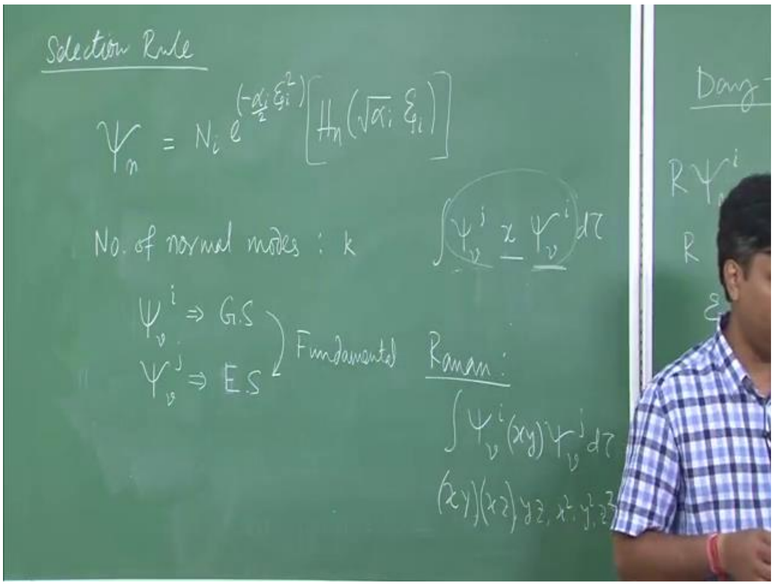

Selection Rule

$$\psi_n = N_i e^{\left(-\frac{\alpha_i}{2}\xi_i^2\right)}\left[H_n\left(\sqrt{\alpha_i}\,\xi_i\right)\right]$$

No. of normal modes : k

$$\int \psi_v^j \, \underline{z} \, \underline{\psi_v^i} \, d\tau$$

$\psi_v^i \Rightarrow$ G.S

$\psi_v^j \Rightarrow$ E.S

Fundamental

Raman:

$$\int \psi_v^i (xy) \psi_v^j \, d\tau$$

$(xy), (xz), yz, x^2, y^2, z^2$

Say I write down as, a say, I will write that this is psi v, say I, as my ground state wave function, where all of the normal modes are residing on the zeroth level, while see psi v j, is the case where one of the normal modes is residing the first vibrational level. I mean v equals to 1 so that a transition from here to here, will give me the fundamental transition, so I am writing this particular notation now.

Now, we have to find out that, how to we know about the transition probabilities. So, if I want to consider this fundamental transition, I can write the transition moment integral, as psi v j, over all space, this is my transition probability. Now in this transition moment, integral that I have, this mu is a dipole operator, so, which can be broken in terms of, you know, the charge and the distances, and this r associated with this, can be explicitly in terms of x y and z. This, we discussed some time back very briefly. So, this one I can rewrite in 3 separate integrals. In terms of x y and z, charge has nothing to do with this integral. So, we do not consider about that. And I can have the same thing say state of x, another case I will have y, in another case I will have z. So, I will have total 3 integral which are possible.

Now, I need to talk about the, you know, the result of this integration. So, this particular transition (Refer Time: 25:29) integral, will survive only when the direct product of this. So, what is that? With each of this wave function we will transform as the one of the irs, it will form the basis for when one of the irs of the particular point that we are concerned.

So, if I replace these wave functions, by their symmetry property, meaning, irreducible representations to which the form the basis for, then the direct product of those irreducible representations, either should be equal to the total symmetry irreducible representations, or should contain totally symmetry irreducible representations. So, then only I will have nonzero value for this integral, otherwise this integral vanish, so that is true for each one of them, either x or y or z integral. Now I have just seen that this psi I, which I took as my ground state. In case of psi I, it forms the basis for the totally symmetry irreducible representations. Fine, that is true for any ground state my mission level.

Now, we are left with this two, because I dont have to worry about this one, whatever will be the symmetry of this, will be the symmetry irreducible representations. So, now, what that does this mean? That this particular wave function, that is the wave function of the excited state, must have the must belong to the ir to which x belongs to, right? Because only when the irreducible representations corresponding to this wave function and this function are same the direct product is going to contain the totally symmetry ir, correct? And in this direct product must yield totally irreducible representations, or the product of this must contain the totally symmetric irreducible representations. In order to have a direct product with this one which is only totally symmetry in nature will give the non vanishing value for the integral.

In other words, if I say what do I have it here, it says, and this we are talking about the infrared, you know, transition right? So, the transition, infrared transition, is possible only when the excited state contains, or the irreducible representations corresponding to the excited state wave function must be the irreducible representations to which either x or y or z belongs to. Then only I can have the transition. So, that is my selection rule. So, this one I need not worry about. So, I only need to look at the excited state wave function, and it is corresponding irreducible representations, and then find the irreducible representations to which x transformed as if this 2 are not the same, their direct product is not going to give me the totally symmetric irreducible representations. So, I will find out which of this or which of these integrals will survive, and I will get the infrared activity. So, this is about the infrared activity.

Now, what about the Raman activity, so in case of infrared spectroscopy, I deal with this integral, where the operator is nothing, but the x y z (Refer Time: 29:54) and coordinate.

What happens in case of Raman? I have a similar type of transition moment integral, involving psi, of, why this p is nothing, but the polarizability. So, I will have many transitions moment integral possible, based on that what component of the polarizability intension we are you know talking about. So, the polarizability has you know component like say x y, x z, y z, or x square, y square, z square, or their combinations for example, x square minus y square, x squared plus y squared, and all those things. So, this, this individual, you know, functions, they formed that component for this polarization attention. So, I can have, the transition moment integral, for Raman transition, Raman vibrational transition, by taking this you know functions x y, x z and so on.

Now, rest of the things will follow as such. So, I need to find out. So, instead of this particular one, I can have an integration integrals which looks like, say x y. So, the case becomes same again, this I am not worried about, because this already belongs to totally symmetry irreducible representations. Now this normal mode, excited you know state wave function, and this particular function, x y, they must form the basis of the same irreducible representations, and then only this transition moment integral will survive.

So, thereby, all I have to do, I have to look at the character table, and particularly the area 4 of the character table, where you find this particular functions, and that will tell you exactly that, this x y, this function it forms the basis of this particular irreducible representations, or x z forms and that particular irreducible representations. So, you exactly know, what is the, you know, irreducible representations, according to which this wave function with transform. Once you know that, you look for that you know is irreducible representations, to which the operator that is x y or x z will transform, and then if they are not same you got your answer, its not, this direct product is not going to contain that totally symmetric ir. Therefore, this particular integral will vanished. If it contains the total symmetric ir, the integral will survive.

So, there will be a definite probability of transition, and one thing here, like for this kind of transition, you will be able to say, that if this x integral survives, then not only the transition is allowed, because if I am talking about the allowedness of infrared transition, then I will see either 1 of them that is x integral or y integral or z integral survives, or more than one survives, it can happen that if it survives in each case or it can happen, but it survives only in one case, that is in case of x or y.

So, if it survives in one particular integral, then I call this transition is allowed and allowed in that particular direction. So, for example, this is allowed allowed x direction, then I say this transition is allowed and this is polarized in x direction, or it is x polarized. Similarly, if I have both x and y is having both x and y integrals having nonzero value and then I will say the transition is allowed, and the transition is polarized in x y (Refer Time: 34:10). In the same way I can talk about a, for Raman transitions also.

After knowing this, I am ready to go back and talk about the, like we will found out certain state of irreducible representation which represents the normal mode genuine normal vibrational modes for (Refer Time: 34:38) molecule rate in the previous class. So, out of those normal modes which are Raman active, which are infrared active that we can state clearly; we will do that in the following class, till then have a good day.

Thank you very much.