Chemical Applications of Symmetry and Group Theory
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Lecture – 36

Hello and welcome. So this is the last week of this course, today is the first class of this last week. So, in the last class we were learning about different molecules and their normal modes and their symmetries. So using group theory, how we can find out about the characteristics of the normal modes and there we found a very interesting thing. So we discussed about 3 different molecules, belonging 3 different point group symmetries. So, we had planner CO32 minus which was planner having D 3h point group we had trans planner N2F2 belonging to C 2h point group and we also looked at a pyramidal NH 3 belonging to C 3V point groups.

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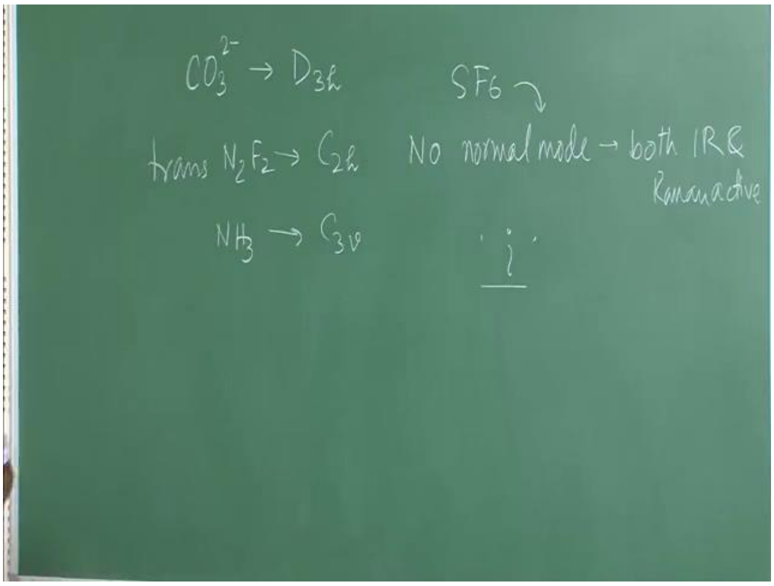

Now when we were discussing about the normal modes and particularly on the context of Vibrational spectroscopy, 2 spectroscopy, we were discussing which gives us information about Vibrational transitions they are infrared spectroscopy and Raman spectroscopy. So in these 3 molecules we figured out; that which of the normal modes are Raman active and which are IR active. So, we figured out that, for this first case, we have normal modes which are both IR active and Raman active.

In the last case that is for C 3V group, we figured out that there are modes normal modes, which are both IR active and Raman active. Now in this particular case we found that no normal modes that is both IR active and Raman active.

So, if we look at some other molecules for example, SF6 we will also see the same behavior as we see in case of trans N2F2 which is a trans planner configuration. Now the common between this particular molecule of this point group or the point group to which SF6 belongs to or say for example, benzyl belongs to all of them are Centrosymmetric. So, Centrosymmetric means, all of them has inversion center, while all the other type of molecule that we discussed they do not have center of inversion. So, from experience so far in last 2 classes we see the molecules which has the center of inversion behave completely differently compared to any other molecules, which are divide up center of inversion.

So, is it a general rule, that for Centrosymmetric molecule no Raman active mode will be in productive and vice versa. While for other type of molecules having no inversion center, no such rule will be applicable. So, is it a general rule or not let us figure that out.

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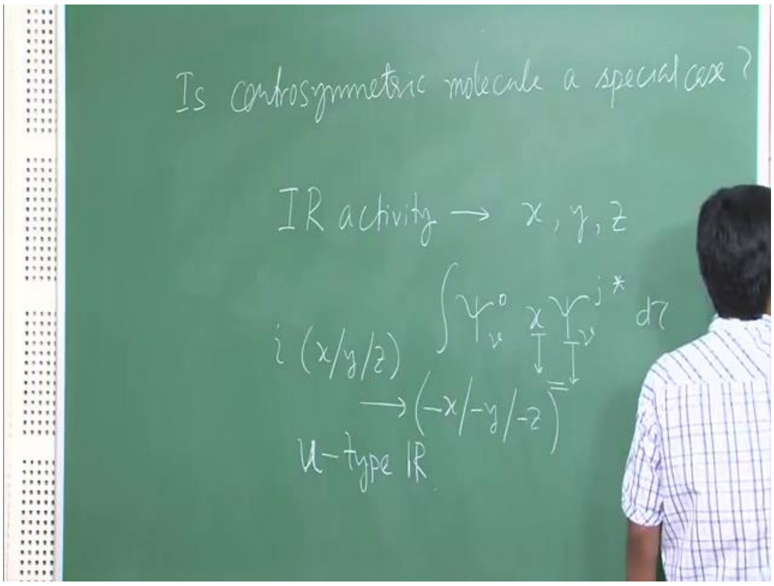

So, let us take in general. So, is centrosymmetric special case here and in this context so, let us figure out. So, for showing IR in spectra for any normal mode, the normal mode should transform as an elusive representations, for which anyone of the Chartism coordinate forms the basis.

So, for any mode to show infrared activity; the normal mode should transform as the elusive representation that has either x or y or z as basis it, it may be more than one also. So, this is the condition because we have seen that transition moment integral is like psi say v i which corresponds to the 0 vibration level, instead of i, I can also write 0 no problem in that, and then you have either x or y or z and you have this.

So In this case since this is this form the basis for totally symmetric IR or this transform as the totally symmetric IR of the particular point rule, then this particular normal mode must transform as the in for the elusive representation to which x form the basis of. So, therefore, the elusive representation or if I say the symmetry of this and this must be the same. So for a molecule which has center of inversion; meaning I have an operation i, what we will the fate of this x y and z.

So, when I operate on either x or y or z we get either minus x or minus y or minus z. So that means this x, y, z they are anti symmetric with respect to inversion. So, when I say anti symmetric with inversion; that means, this must have as u type of symmetry. So, u type symmetry or u type elusive representations I can say. So, it will belong to something like Au or Bu or Eu that kind of symmetry. Therefore, in order to show IR activity, this normal mode also belongs to U type of elusive representations.

So, in general for a molecule having center of symmetry if one particular normal mode has to be observed not transition for a normal mode has to be observed using infrared spectroscopy, then that particular normal mode must be of use symmetry perfect.

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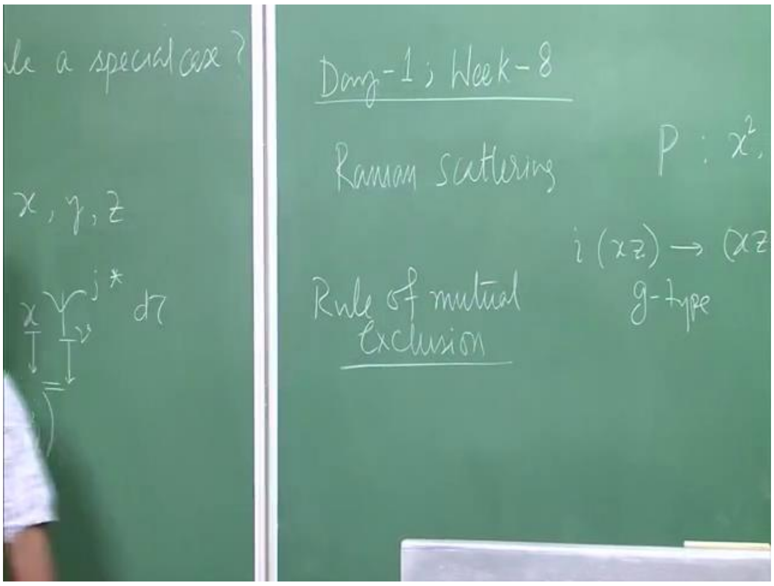

Now, let us look at what happens in case of Raman spectroscopy. So, showing Raman scattering; I have to have the normal mode, which is being excited to level V equals to 1 from V equals to 0 from that must have the same symmetry as that of that any of this polarizibility tenses component, which is something like x square, y square, z square, or x y or x z and so on. Now if I consider n a centrosymmetric molecule.

So, if I operate i on any of this binary functions. So, say xz. So, both x and z they will be inverted, overall it will give me back the same thing. So that means, this is true for any of these functions which form the components of the polarizibility tenses. So therefore, this functions are of g type, meaning that in order to in order to show Raman spectra for any particular vibration transition, the involved normal mode must belong to g type of symmetry.

Now in case of Raman, I need mode which has g type of symmetry, while for showing IR spectra, the normal mode must have the u type of symmetry. Now for a centrosymmetric molecule one IR one info elusive representation cannot have both u and g type of symmetrical; similarly I can say for the particular wave function that we are talking about, a particular normal mode we are talking about.

So, one normal mode cannot have both u and g type of symmetry that is clear. Therefore, those particular normal modes having u type of symmetry we will show only infrared spectra, while those which those normal modes having g type of symmetry or which transform as the infrared the elusive representation belonging to g type they will show only Raman spectra when they are excited to level 1.

So, I can easily see, for a centrosymmetric molecule no to normal mode can have a transition, which is possible to be seen both in IR spectroscopy, as well as Raman spectroscopy and this is kind of exclusion. So, this particular thing is called Mutual Exclusion.

So, rule of mutual exclusion so many of you must have heard of this rule of mutual exclusion, but here is actually the real logic behind this particular rule of mutual exclusion, now you just think about any other molecule where you do not have the inversion symmetry; what happens in that case? In that case you do not have this u type or g type elusive representation present. So, they are this situation does not arise at all because you do not have inversion symmetry in this cases. So, this formation of this x, y, z coordinates as anti symmetric with to respect inversion, this at all does not occur. So, therefore, I do not have to think about having such exclusion.

So, this kind of mutual exclusion is possible only in case of centrosymmetric molecule. So, this is indeed a special case. So, in Vibrational spectroscopy part, we will limit our self up to this point; one can try to look at some more advanced topics like we have been restricting ourselves to the study of fundamental transitions, but one can look at various other things like overtone transitions that was in selection rules or combination bands and one particular interesting things that is extremely important in case of Vibrational spectroscopy, which is known as formulizing news. But we will not go through these topics in this particular electrical service, but if anyone is interested in those topics in advanced level. So, a standard text book like what we suggested at the beginning of this course, they have this topic discussed very well. So, one can go through this one.

So, we will move on to the application of procuring in other types of spectroscopies. So mostly we will deal with the electronic spectroscopy. So, while discussing about vibration level, what we were discussing? We were discussing about the particular one type of particular type of motion, like known as normal mode of vibration and each normal modes for any given molecule, they will constitute a particular state and these states are the Vibrational states. So, if I talk about molecule oscillation. So, this v equal to 0, v is equal to 1, v is equal to 2 and so on, they will be contained in so called potential wave.

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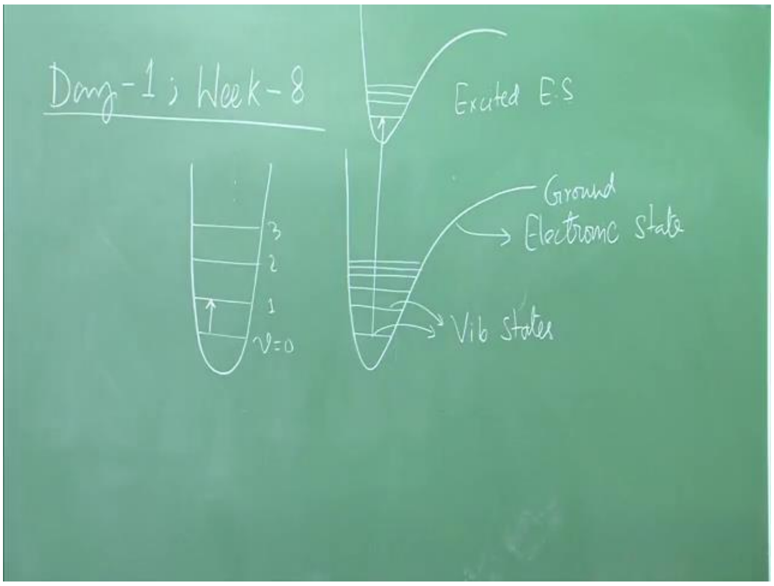

So, if we restrict ourselves to simple harmonic oscillator, then these are different Vibrational level. So, you can keep on going up and we were discussing about how will be the nature of this particular type of motion for one particular normal mode and what will be the symmetry and then finding how I can talk about the allowedness or dis-allowedness of one transition between this levels.

So, we were dealing with this Vibrational translations and we dealt with 2 spectroscopic technique; one is by using the infrared light assets and another one was to excite the molecule to some place, which we call generally a virtual state where there is no real estate and which comes back to one of these Vibrational level. So, we have a proof for the gap between 2 Vibrational levels. So, that was a Vibrational spectroscopy.

Now, this about the simple harmonic oscillator, but in real life you have a potential wave which is depicted by something like most potential and you have the Vibrational levels here also and so on. Now this each will it constitutes the electronic state of molecule. So, these individual things are Vibrational states and this will give you the electronic state. So, you can easily figure out that, one electronics state contains both Vibrational and obviously, the rotational levels.

So, rotational levels will be inputting. So, if we have a situation when this is my ground electronic state and there are some other electronic state at high energy, which also has their own Vibrational levels, that I can think about taking a molecule here, from here to this upper electronic state by giving some form of energy preferably liked and this transition is called electronics transition. So, suppose this is my Ground electronic state and this is my excited electronic state.

So, a transition from here to here will definitely involve the transition of transition between different rotational and Vibrational states within the electronic states. Now in general when we look at ensemble level spectra involving the transition between 2 electronic states, this rotational find rotational transitions are blurred, even in most of the cases Vibrational lines also will be blurred, but within limit of temperature that is if you cool down the system quite a bit, then I can see the vibration lines and even some cases rotational lines as well. Now in our discussion, we will not worry about the rotational level here or rotational transitions, and Vibrational transitions we have looked at already, the selection rules also we have looked at, but only in the context of electronic transition by the Vibrational transition is also involved, we will look at the vibrations in a picked different way.

So, what are the things that we should look at, when I try to deal with an electronic transition? So, here we will try to see how the knowledge of symmetry and group theory can help us getting an idea about the selection rules of the electronic transition, the transition moments the band intensities; all these things how can we get from our knowledge of group theory and symmetry. So, that is what we will look at. So, let us start from the very basic things which will lead us to the selection rules.

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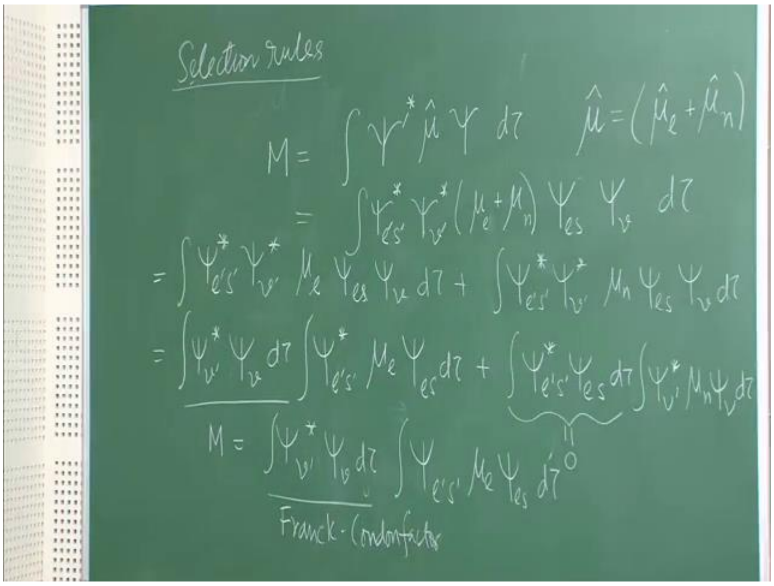

Selection rules

$$M = \int \Psi'^{*} \hat{\mu} \Psi \, d\tau \qquad \hat{\mu} = (\hat{\mu}_e + \hat{\mu}_n)$$

$$= \int \Psi^{*}_{e's'} \Psi^{*}_{v'} (\mu_e + \mu_n) \Psi_{es} \Psi_{v} \, d\tau$$

$$= \int \Psi^{*}_{e's'} \Psi^{*}_{v'} \mu_e \Psi_{es} \Psi_{v} \, d\tau + \int \Psi^{*}_{e's'} \Psi^{*}_{v'} \mu_n \Psi_{es} \Psi_{v} \, d\tau$$

$$= \underline{\int \Psi^{*}_{v'} \Psi_{v} \, d\tau} \int \Psi^{*}_{e's'} \mu_e \Psi_{es} \, d\tau + \underbrace{\int \Psi^{*}_{e's'} \Psi_{es} \, d\tau}_{= 0} \int \Psi^{*}_{v'} \mu_n \Psi_{v} \, d\tau$$

$$M = \underbrace{\int \Psi^{*}_{v'} \Psi_{v} \, d\tau}_{\text{Franck-Condon factor}} \int \Psi_{e's'} \mu_e \Psi_{es} \, d\tau$$

Finally, our aim is to get the selection rule for transition moment for band intensities. And also we will learn about something called Franck-Condon principle. So, like here I showed one arrow from one Vibrational state, in the lower ground electronic state to the upper one of the Vibrational states to the upper electronic state. Now can I draw the arrow just like that or getting certain rules; so those things we will learn and we will also see how we can use this group theory to get information about those aspects. So, in general the probability of any electronic transition is proportional to the square of the transition moment integral.

So, if I say the transition moment integral as any electronic state overall if I am thinking about, and say I write psi prime for the excited state and psi as the ground electronic state, then this is my transitional moment and the transitional moment integral if it is 0 then there is no transition allowed, if this is non 0 then transition is allowed that much we have learned so far. And it is true for anything and everything any transition that we are discussing with. So, depending on the situation my operator may be different.

In case of like Raman, we have seen that; this is a polorizibility case of component. Now when you talk about the electronics transition, there I have the Vibrational states also involved. In case of in a pure Vibrational spectroscopy when we were looking at last week, we looked at very similar kind of thing and there we did not explicitly differentiate with anything else, because we knew that we are talking about vibration; all we are trying to do is looking at how to nuclear that was, to nuclear at bond it and how this bond is executing emotion keeping the center of mass fixed and then we were probing all these motions, there is no transition probabilities and all these things. So, the coordinate that we looked at, that was the nuclear coordinates correct; and that is still there here. So, here we have electronic state, also vibrational state. So, we will explicitly look at either is electronic coordinate or is a Vibrational coordinate.

Now I can write this operator mu overall type of moment operator as sum of nuclear and electronic component and I can separate them. Because this nuclear motion and the electronic motion, there speed is quite different. So, I can easily separate them out. So, if I do that, then I can rewrite this M as and also if I can do this, then I can do the same thing for the overall wave function. So, this wave function is essentially the product of the individual wave functions for electronic, spin and nuclear motion. So, I am talking about the electronic spin here.

So, therefore, I can write this psi prime or in general psi as, psi e s, e stands for electronic and s stands for spin. And psi n or I can also write psi v. So, that you can easily see that this transfers the Vibrational wave functions. So, essentially they stand for one particular normal mode. So once I explicitly write like this I am using this in operator form; I can rewrite this as, so here we have to remember that this should be complex conjuric. So instead of writing the prime on this psi I will write it on this e and s and then, you have psi v and v also here is an excited state. So, I will have the v prime; having the complex conjuric and then you have mu e and mu n and then you have the ground state part. So, you have psi es multiplied by psi v integration over all those space. So, this we can prove.

Now if we can separate this integrals. So, let us start from here. So, I can have psi es prime, psi v prime and I can have it over mu e and you have the left over parts the mu es mu v d ton plus the other integral using this mu in coordinate. So, I have the same thing psi e prime, s prime, psi v prime and then I have this mu n and the ground state part.

So, here this electron and spin; this electronic motion and Vibrational motion I can decouple them, because one depends on the electronic coordinate and the other one the vibration which depends on nuclear coordinate has nothing to do with this mu operator. So, I can have this integral that is mu v prime, mu i v d tau multiplied by the rest of the part that is e prime, s prime over mu e psi e s d tau, plus here also similarly I have this psi e prime, s prime, psi es d tau multiplied by psi of v prime, mu in psi v d ton. So, I have total 4 integrals here right.

So, here if I look at this part, is equal to 0. Why is it so? Because this psi e s or psi e prime is prime, they are the wave function for the electronic states right and this wave functions should be orthogonal future. So, they are normalized as well as orthogonal. So, this particular integral of 2 orthogonal functions; will give me 0. So, therefore, this part is completely 0. So, I am left with only this part. So, here you look at this particular quantity; which gives me there is an overlap integral of 2 wave functions to Vibrational wave functions.

So now, one can ask that, I have this particular integral having a value 0 because of the orthogonality then why not this case, this also should be 0, but actually that and if it need not be 0; why because I am having a transition between 2 Vibrational levels; from here to somewhere, but this Vibrational levels they belong to 2 different electronic state. Therefore it is not necessary that, these psi v and psi v prime will be orthogonal right therefore, that not necessarily 0. So, this time survives. So, therefore, I have my overall aim equals to this part, that is psi v prime psi v d tau multiplied by psi e prime s prime mu electronic psi es d tau and this particular part, that we were just talking about this is known as Frank condo factor.

So, I can take this product of integral which is now my transition moment integral and we can split them even further. So, this electronic part and the spin part that I can speak further. So therefore, what I can write as a 2 different integral. So, maybe I will write here. So, at last when I consider electronic motion and the spin part separately, then I have psi v prime at some places we miss this contribute conjuric part, but you should correct it, d7 multiplied by d7, so multiplied by psi s prime and psi s d7.

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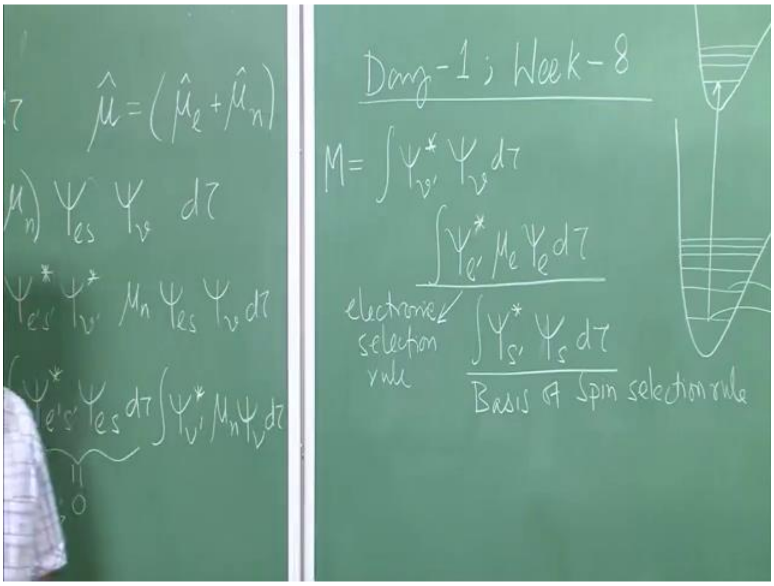

So, we ultimately got 3 integrals; the product of 3 integrals as my transition moment integral. Now if any of this integral is 0, then overall the transition is forbidden, that I can say at this moment, now this is a (Refer Time: 32:40) factor that decides, that from which Vibrational state of the ground electronic state to which Vibrational level of the excited state the electron will make the transition. This part is the electronic transition purely and this is the spin transition. So, this particular part is the basis of spin selection rule and this integral is the basis for electronic selection rule or selection rule for electronic transition.

So, this is the most similar form, but specific selection rules which will born out of this general form when we use the good theoretical knowledge and expand this a little far. So for that we will do in the following classes.

Thank you very much for your attention.