Symmetry and Group Theory
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Lecture - 43
Symmetry Adapted Linear Combinations (SALC)

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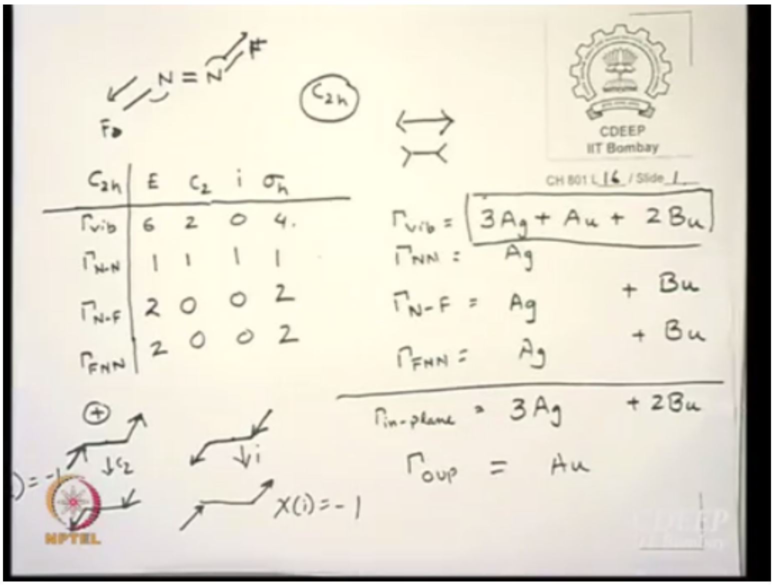

C_{2h}	E	C_2	i	σ_h
Γ_{vib}	6	2	0	4
Γ_{N-N}	1	1	1	1
Γ_{N-F}	2	0	0	2
Γ_{FNN}	2	0	0	2

$\Gamma_{vib} = \boxed{3A_g + A_u + 2B_u}$

$\Gamma_{NN} = A_g$

$\Gamma_{N-F} = A_g + B_u$

$\Gamma_{FNN} = A_g + B_u$

$\Gamma_{in-plane} = 3A_g + 2B_u$

$\Gamma_{oup} = A_u$

E C2, help me, i sigma h, very good, now what we said is that we are already constructed gamma vib, there is no problem with that I believe, right. Tell me what is gamma vib, I wanted the characters, 6 2 0 4 great and then from there we broke it down and we said gamma vib is equal to what? 3 Ag + Au + 2 Bu, 3 + 1 = 4 + 2 = 6 alright. Now next what we wanted to do is we wanted to assign the internal motions, different kinds of internal motions of the molecule to this symmetry species, we want to know which is which, okay.

And the basis that we use for them are gamma NN because NN stretch is unique right. There is no reason why we should take it along with the NFs right, we can take this separately. Gamma NN is 1, second one was gamma NF, NF stretch and the third one was the angles FNN or NNF I do not remember what I wrote that time, alright. Let us try to construct the reducible representation or irreducible representations at least in one case with these, gamma NN.

Let us talk about gamma NN first. What will be the character for the C2 should be 1 or -1, there is a confusion right, because this is a normal mode, I do not have Ni model for the normal mode that is the problem. Assuming you are colour blind, cannot differentiate between blue and black, this is the NN stretch, the whole thing. It does not matter if you turn it around by 180 degrees, it remains the same, is not it.

If this was the blue cap, this was also the blue cap in that situation even if I turn it by 180 degrees does the sign change? If there is a question please ask, Alekhya question? sure about this, this is 1. Please ask if you have a question, 1. Similarly what about i that should also be 1 because this is not a vector it is just a line or maybe it is easier if I draw it like this, a double headed line. Now if you perform C2 nothing changes right arrows remain in the same direction and this is easier to understand.

This is + and this is – okay got it now, C2 or i will not take you from here to here, very good, what about sigma h? of course 1, okay. So where does this belong? gamma NN would be equal to Ag, one of the Ag's is taken, so far so good. What about Nf, how many Nfs are there 1, 2, right. So I can draw them like arrows, one arrow here, one arrow there that is + right and when they come in they are minus two arrows right, two arrows separately, okay.

What will be the character of E, 2 dimensional basis, so character should be 2 alright, C2? What will be the character of C2, 0, why because these are the 2 arrows, this is one, this is one, rolling arrows, these are the 2 arrows right and this is where C2 is, this is C2. If you perform C2 what will happen, the blue arrow will go where black arrow now is, black arrow will come where blue arrow now is, they interchange.

So if you think of the matrix, what will be the matrix be? 0110 off diagonal, nonzero earlier it go off diagonal, right. So rolling stone gathers no marks that principles applies here also. Question? What about this, are you okay so far? So it is going to be -1 in C2 0 what about i the same thing will happen, blue and black arrows will interchange places and they go off diagonal, the 1s will go off diagonal.

So 0 and what about sigma h 2, they are left where they are. So now you can break that down and you can tell me what is gamma NF. You know how to break this down? Ai = 1/h sum over i, chi R, chi iR, using that you work it out, decompose it into consequent IRs and tell me what you get. Do we get Ag + Au or do we get Ag + Bu, Ag + Bu or Ag + Bu or do we get Au + Bu or do we get 2 Bu? Ag + Bu, Do you all agree?

(()) (07:25) too lazy to work it out, so you have to tell me. Ag + Bu is what we are saying so I will go with that, the better we correct, now it is a little better, okay. Ag + Bu. Now what about F NN the angles. This angle and this angle what do you get character of E, character of C2, 0, character of i, 0, character of sigma h, 2. So once again gamma NF NN = Ag + Bu right so this is the total and so far what have we got.

I will call this gamma in plane, for all the in plane motions I have got 3Ag + 2Bu. So this Au is like we have Sourav Ganguly in the last season that he played for IPL is no taker right. So what is this Au going to be? Of course we have accounted for all the in plane motion that we could think of. Now you see for, now we need to see the character table. How did you work all this out without character table, you have the character table with you? very good.

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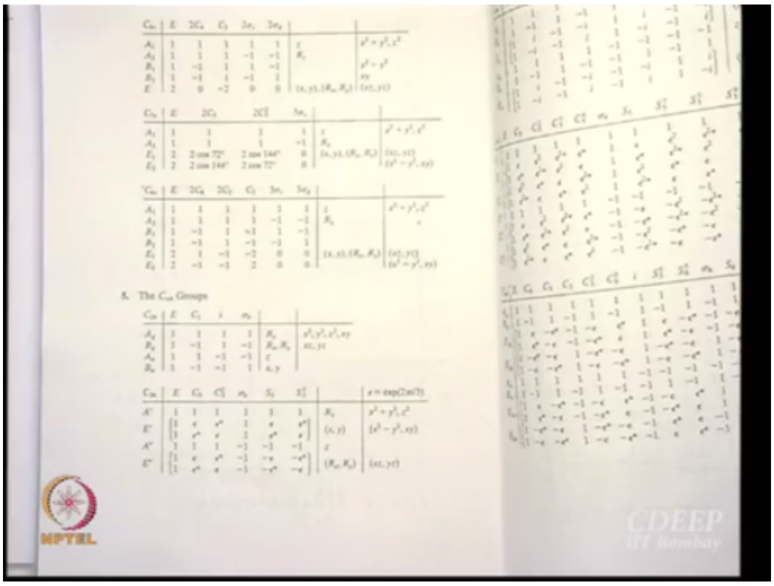

Today I have got this different book partially because we are discussing this and partially because I do not have to zoom to show you the character table. The character table is printed in a little bigger font, you can read, cannot you. So C2h, in C2h look at the characters of sigma h, Bg is -1 Au is -1. We do not have to worry about Bg because we do not have a Bg vibration anyway.

We do have Au vibration and character of that Au vibration, character of sigma i for the Au vibration is -1 that means 1 it has to be out of plane know. Out of plane like this, if this is plus and this is minus so plus to minus can be obtained by sigma h is not it. This is a molecule right. Little more flexible fingers would have been very nice, one more joint, just one more joint in every finger would have done the trick.

So this is plus phase right and this is minus phase. So this plus and minus are they not related by sigma h this is sigma h plus minus, are they not related by sigma h. Now they are related by sigma h. The change sign right, plus becomes minus when you apply sigma h, right or wrong, okay got it, it is our question originally. So if you now workout all the characters think of this, this is plus, this is minus, what will be the character of E? 1.

What will be the character of C2? C2 is also 1 right. This is C2, 1 right. Then what is next i what will i be, i will be -1 and sigma h is -1, 11-1-1 what is that Au. Au 11-1-1 okay, but what I am saying is you do not even have to go that far because you already know that only Au is there, only one out of frame motion is there. So just sigma h is good enough, but if you want you can work out all the characters no problem, alright.

See the thing is first of all what we have done is we have just taken the in plane stretch and bend right. From there we have got it. Let us see what the vibration should look like, but before that let us complete this story. So let me write this gamma out of plane then should be what Au. Now everything is taken care of. Now let us think of individual types of motion. Where did we get Bu from, we got Bu from NF, okay.

So what is NF, NF stretch, so now for Bu the characters are 1 C2 gives you -1 and i also gives you -1 okay and we are talking about NF stretch so maybe we can think of something like this, 1 is going out and the other is coming in okay, this is plus what will be minus then, okay, so now see if I apply C2 what happens, apply C2 to this, do I not get this right. So character is -1 right.

If I invert what do I get? Do I not get this? inversion means start from here go to the center, go to equal distance on the other side, now the beginning of the arrow has to show up there, that is inversion is not it. Start from this arrow head go to the center go here then arrow head should come here. Start from this arrow head go to the center, go there arrow head should come there.

So character of i is also -1 is not it. So 1-1-11 what is that, that is Bu. If there is a question, please ask. **“Professor - student conversation starts”** okay. You are okay up to C2. What is the meaning of inversion? Inversion means you start from a point, you go to the center right and then go to an equal distance on the other side then you should get the same point, that is the meaning of inversion, right.

So if I start from this point, start of an arrow, go to the center and come here as a result of inversion I should get a start of the arrow here.

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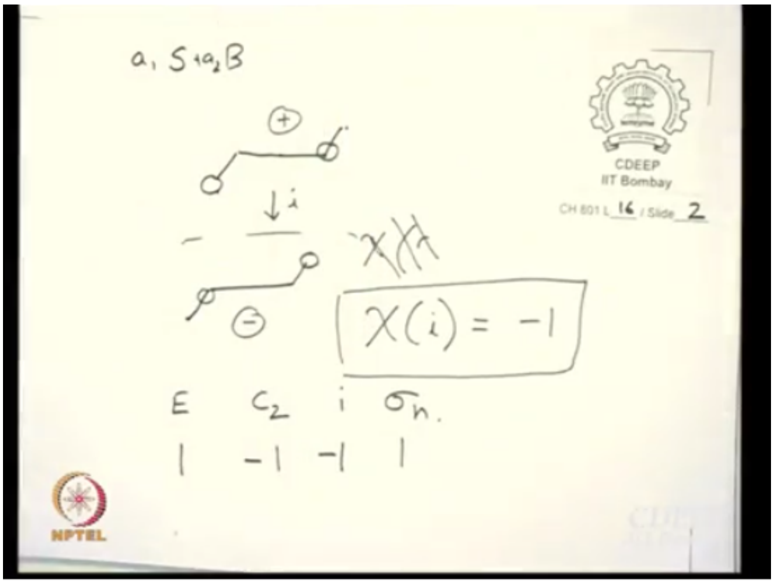

Let me draw on a fresh page. I will now make it even easier. Easier for me to draw, okay. So now if I invert this what should I get, start from her go to the center, go here then I should get the start of an arrow, no circle. Start from here go to the center go here I should get a circle. Start from here go through the center equal distance on the other side, I should get a circle here.

I will start from here to the center to here, no circle right, but then this is plus and this is minus, this is plus phase of vibration, this is minus phase of vibration, therefore I get chi of i to be equal to -1, alright. So what we have got is E C2 i sigma h, this character is +1, this character is -1-1 and then here if you apply sigma h what will happen, circles will remain where there were, dots will remain where they are so +1, 1-1-11.

What is 1 -1-11 Bu, are you answered, any other question **“Professor - student conversation ends”**. And do not forget what we do is for any kind of symmetry we have to take a linear combination. If you have some kind of a stretch and some kind of a bend, we always say of the right symmetry we say it is a1 stretch + a2 bend. What determines a1 and a2, the bond strength then atomic weight et cetera, a lot of things, that is something that we cannot determine using symmetry alone, that becomes a computational chemistry problem.

But then even to start the computational chemistry problem first of all you need to determine the symmetry and you have to do a symmetry classification of the normal modes. Many of you have used Gaussian I think. Again C2 people who have used Gaussian right. So there if you look at the output of Gaussian you will see that the first thing that is done right, after geometry optimization is determination of the point group.

Just go through the readout of Gaussian you will see. Next what they do is they perform a symmetry classification of normal mode right, what right or wrong? What you do not run Gaussian, you run Lorentzian or what, okay. **“Professor - student conversation starts”** point group is always C1, no but then I have also run Gaussian I have got the right point groups. **“Professor - student conversation ends”.**

I have not really used Gaussian so much, what I have used in the past is GAMS. GAMS is another program like Gaussian the difference is like the difference between windows and Linux. GAMS is an open source software so you can change things. So any way so this is how it is done. First of all, you have to do a symmetry consideration right. After that you start your computation otherwise computation becomes very complicated and you can lose your way alright okay.

Are we answered about the vibrations now, now can I go ahead, any other question on vibration normal mode, no. Now we go on to what we intend to discuss today. We intend to discuss today symmetry adapted linear combinations or what are called SALCs, sometimes they are pronounced as SALC. So we are going to talk about SALCs. Okay now the real fun begins to be honest. See I had told you once I think, not once many times that what to do in this course is that we want to play the astrologer.

Right we want to write down the kundli of molecules right and then we want to match kundlies and now we are really in a stage where we have started matching kundlies. We want to see what kind of symmetries different orbitals have and then we see that which orbital can be a good wife for which other orbital that is basically the idea of what we are going to do okay. I am not encouraging matching of kundlies in real life, it is just an example.

So see what we do is now for the rest of the course we discuss bonding and little bit of electronic spectroscopy. Everybody has studied bonding at some level or the other right. So what it is that you do in bonding? What is that you study, what are the different theories of bonding? **“Professor - student conversation starts”** VBT, MOT (()) (22:34) right. So we will start with VBT, what are the advantages of VBT? Simple that is the one answer **“Professor - student conversation ends”**

VBT is very simple easy to conceptualize, easy to understand. What is the problem with VBT? the problem is it is too simple. When you do not write one word 2 then it is the advantage and when you write that word then it becomes a disadvantage right. Main disadvantage is it is too simple VBT can only work properly in the (()) (23:10) of 2 center 2 electron bonds, okay. Anything beyond that is really beyond the scope of VBT.

But then because of it is simplicity many times we try to make up stories like resonance. Resonance is just friction there is no such thing as resonance, okay. So we just try to make up such stories in our attempt to expand (()) (23:35) of this nice simple theory into more complicated situations that it is not really supposed to handle right. It cannot handle anything beyond 2 centered 2 electron bond.

So as long as you talk about the ground state sometimes we even manage to get away with it right. The entire organic chemistry teaching is based on pushing errors and writing resonance structures after all right, but you cannot really go beyond certain level if you want to work with VBT that is why we want to use molecular orbital theory good thing about molecular orbital theory is that it is more general right.

It allows for delocalization, no issue. What is the problem with MOT? Do not forget we are in a symmetry class. So whatever I have said for VBT should more or less apply for MOT. I said that VBT is good because it is simple that because it is simple right. MOT is good because it is general, it is bad because it is general. Sometimes it overdoes things. Remember hydrogen molecule everybody has studied MOT treatment of hydrogen molecule H2.

So there it gives equal weightage to the ionic structure which is obviously wrong. In VBT the good thing is that the coefficient is in your hand. We cannot say that the coefficient is 0.0000001 okay in MOT in it is attempt to be too general it kind of gets over enthusiastic and unnecessarily emphasizes the ionic structure for H2, but there are too many advantages. One advantage is that it allows for delocalization without having to resort to any kind of friction.

Second thing is that it gives you access to the excited states right and also it gives you the concept of anti-bonding orbitals. Very often we think that anti-bonding orbitals are useless right but they are not they are extremely useful anti-bonding orbitals are used everywhere in things that are very well known to us from things that we might not thought about. Can you tell me out some examples of anti-bonding orbitals? where they are useful in chemistry?

It is actually a thin book called the importance of anti-bonding orbitals by Orchin and Jaffe. Very old book must be 1950s or 1960s okay. I do not think if it is there in the library, but can you tell me of any application of anti-bonding orbital that you know in chemistry. In reaction mechanisms of course then you must be an organic chemist who believes in MOT more than VBT then only you can use it.

Something more common? Catalysis, that is the part of reactions anyway, in structure of molecules, so once again you are giving me more difficult answers than what I am expecting what I had in my mind was back bonding in case of carbonyl complexes. In carbonyl complexes why are they so strong because the anti-bonding orbital is used to receive electrons from the metal right.

That is I think the most common example that everybody studies at fairly early stage of the undergraduate study that is one, the other example that I am going to tell you is something that you know what you have never thought about perhaps. So if I am going to ask you the question that I really like to ask everywhere. Why is phenol acidic? Alcohol is not acidic, why is phenol acidic?

Benzyl alcohol, what is the formula of benzyl alcohol CH2H and what is the formula of phenol. So you take away one CH2 it becomes highly acidic, if the CH2 is there it is not acidic at all why. Once again you have studied it right. Everybody knows the answer to it, tell me. I see that I have scared people so much that do not even want to give an easy answer. Why is phenol acid come on people?

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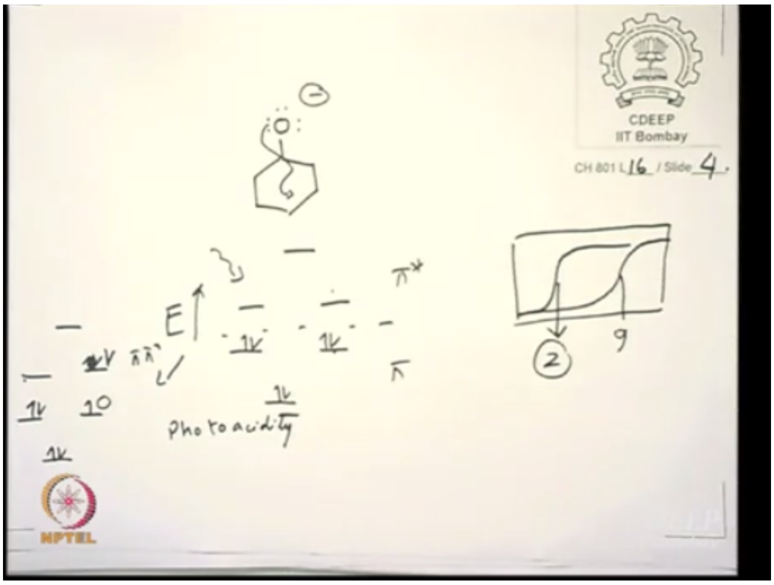

“Professor - student conversation starts” Conjugate base is stable why? So see now guess the answer right. **“Professor - student conversation ends”** What we usually say and I am okay with that is that because this negative charge on oxygen is delocalized over the ring. Generally, we explain it by drawing those resonance structure which are of course all friction, but that is a right answer. The negative charge on O- does get delocalized over the ring right but where will it go.

I think you know this energetics of benzene right, you know that there are 6 MOs right, (()) (29:01) so these are the pi bonding MOs and these are the pi star anti-bonding MOs okay and in this benzene ring these bonding MOs are completely full, okay. Now see if the electron cloud has to come in where can you accommodate this incoming electron cloud? You can accommodate it only in the pi star orbital right.

And that is what is done that is what makes phenol more acidic. **“Professor - student conversation starts”** Very good that takes us directly to the next point that I am trying to make which is actually, which kind of forms the back bone of perhaps 50% of the research done in our group it is an acid fine. Does anybody remember what is the PKA of phenol or naphthol or some such thing typically what it is.

Yes, so (()) (29:57) **“Professor - student conversation ends”** I will take an average right if you perform a pH titration curve you get the inflection point at around 9, 9.5 depending on which phenol you have taken. So it is acidic but it is not all that strongly acidic. What is the meaning of PKA 9 that means the concentration of photons in the medium has to be as low as 10 to power -9 molar for the molecule to be able to give up a proton, is not it?

So you need the alkaline medium. No what I am tell you is this suppose you perform a pi pi star excitation; pi pi start excitation everybody knows or not. Electron goes to some light of suitable wavelength incident on the molecule right and an electron gets promoted from let us say homo to lumo. So pi pi star excitation leads to the formation of what is called the pi pi star excited state. So this then will be the electron configuration.

Let us say like this one electron promotion, now see what I have done I have now created some space in the lower energy molecular orbital where the incoming electron cloud can be accommodated, will that not be a happier situation. So what I am telling you is that an organic molecule which is acidic in ground state becomes a better acid in the excited state this phenomenon goes by the name photo acidity, right.

Maybe you have studied this in molecular photochemistry course, you people took that course last semester right. Molecular photochemistry organic chemistry was it discussed? okay. So but this is actually molecular photochemistry okay. So what I like to say is that excited molecules do, see what happens when we are excited about something, we usually do it better. So molecules similarly when they are excited they do whatever it is that they do in a little more efficient manner and this is the reason.

Similarly, you can show why an organic base, an aromatic base should become a stronger base in the excited state okay. So this is called photo acidity. So if I can now construct the exited state PKA if I can now calculate it, I have calculated from something as simple as fluorescence spectrum, okay. What should it happen, should it be less than 9 or should it be more than 9, less than right, less than 9.

How much less than 9 do you think that we get say for beta naphthol what does it become let us take a guess. So it will be somewhere here right something like this, this value for beta naphthol is 2 you are right, so understand what has happened. This molecule in the ground state can give up a proton only when the external concentration of protons is as low as 10 to the power of -9 molar.

The same molecule when you shine light on it, it can give up a proton when the external concentration of protons is as high as 10 to the power -2 molar we are talking about 7 orders of magnitude difference, no joke. That is how effective photo acidity can be and things like that can only be accessed by molecular orbital theory in case you forgot where this discussion started.

So what we will do is we will mainly talk about molecular orbital theory for the rest of the course. We might talk about ligand field theory or crystal field theory when we talk about the inorganic complexes, okay. So what we want to do is we want to see how a discussion of symmetry, how use a character tables can help us perform molecular orbital theory treatment on molecules. Organic molecules to start with and then inorganic molecules.