Main Group Chemistry
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Lecture – 06

Structure and Bonding aspects: VSEPR Theory

Welcome to my lecture series on Main Group Chemistry. In my last lecture I was discussing about the structure and bonding concepts used in main group chemistry. While discuss in structure and bonding aspects I had mentioned about VSEPR theory and also I introduced the terms theoric number and also I discussed the molecules having steric number 2 to 6 and 2 to 7 and now let me discuss on molecules having both bonded page and lone page.

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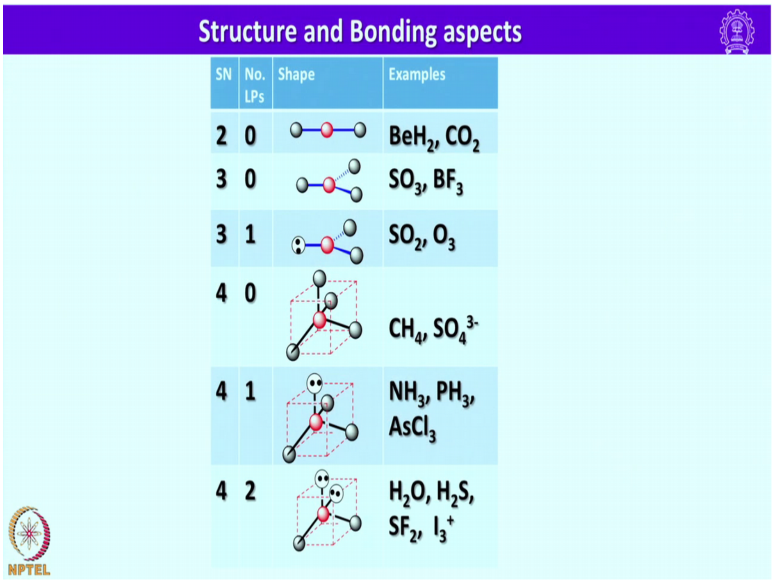

Structure and Bonding aspects

SN	No. LPs	Shape	Examples
2	0		BeH_2, CO_2
3	0		SO_3, BF_3
3	1		SO_2, O_3
4	0		CH_4, SO_4^{3-}
4	1		NH_3, PH_3, $AsCl_3$
4	2		H_2O, H_2S, SF_2, I_3^+

So, in case of steric number 2 there are no lone pairs only bonded pairs are there. So, we can for example, beryllium hydride or CO 2 one can write the structure conveniently. In case of beryllium we have 2 electrons here coming from 1 electron each so that means, essentially 1 electron from hydrogen will combine with 1 electron from beryllium to form a covalent bond similarly another electron from beryllium will combine with hydrogen to form Be H bond. So, it is a linear geometry is there.

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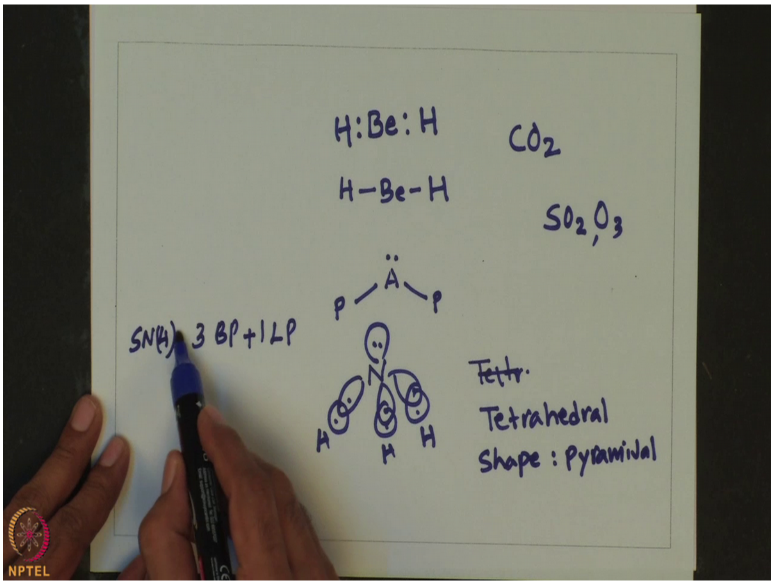

And another example is CO 2 one can also write using this method. So, linear geometry will be there or one can also write something like this. In case of steric number 3 we come across 2 types of molecules having no lone pairs that is BF 3 or SO 3 we can have 2 bond pair and lone pair in that case examples are SO 2 and O 3. So, in this case what happens essentially we have the central atom and we have peripheral atoms, peripheral atoms I have denoted by P central atom A and we have a lone pair. So, this kind of molecules will be there. So, they have bent shape. And here angles may not be not necessarily 120 here it may be little less accommodate to this lone pair this essentially less than 120 where as this angle will be little more.

And in case of steric number 4 we come across 3 kinds of molecules one is 0 lone pairs or having 1 pair or having 2 lone pairs let us look into the molecules having 3 bonded pairs and 1 lone pair. The example is NH 3 are all tertiary amines and also the trivalent compounds of all group 50 elements such as nagsium phosphorus arsenic automany (Refer Time: 03:19) PH 3, tertiary phosmine, PCl 3, PF 3, AsCl 3 all are example of having 3 bond pair and lone pair and have a pyramidal structure. So, in this case N so that means, here essentially N has 3 covalent bonds with 3 hydrogen and this unutilized lone pair will be occupying one of the positions. Here geometry is tetrahedral shape is pyramidal. So, this is how one can write having 3 bonded pairs plus 1 lone pair whereas, steric number 4.

Let us look into the steric number 4 having 2 bonded pairs and 2 lone pairs. Examples are plenty water H 2 S, SF 2, I 3 plus etcetera.

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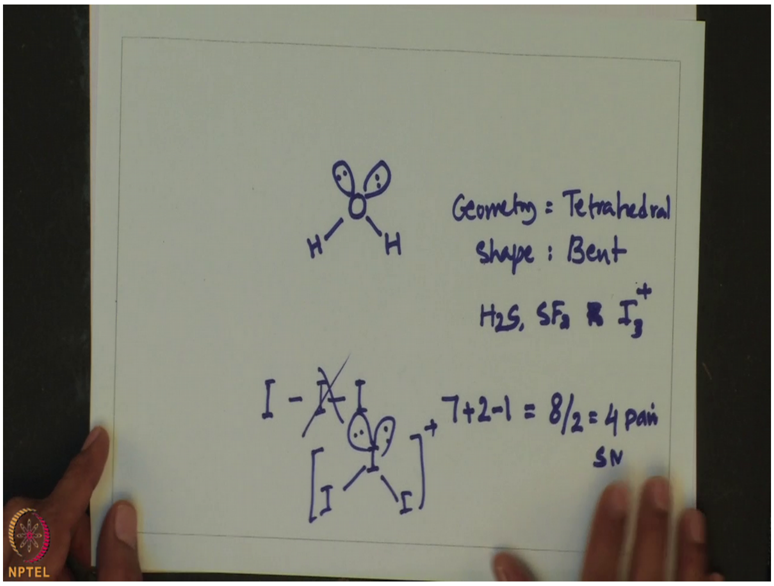

So, let us look into the case of water. So, this is how one can write the geometry for oxygen in water showing the tetrahedral geometry and here while considering the shape while deciding the shape of the molecule one can ignore the lone pairs. So, it has a v shape or bent shape the geometry is again tetrahedral and shape is bent shape besides other examples are H 2 S, SF 2, I 3, I 3 plus. Let us look into I 3 plus in I 3 plus is interesting one of the iodine will be central atom here.

So, first let us count the number of electrons using Lewis method. So, here counting either we can count the all the valence electrons of the central atom and just 1 electrons from the peripheral atoms or we can count everything and try to satisfy the octate either way one can write it. Now I will show you just omitting all the electrons of the peripheral atoms, but considering only 1 electron that makes a covalent bond through sharing with the central atom. So, now, we have I has 7 electrons and these two will be giving 2 electrons, so 9 electrons. Since it has a positive charge 1 electron has to be deducted so we have 8 electrons; that means, we have 4 pairs of electrons are there. So, this is our steric number in this one, in this one essentially it cannot have now this kind of linear geometry it not possible, so this is wrong, this how immediately will come to know that this is not the right way of writing.

So, now first write the central atom and put the lone pair here and put this peripheral atoms. So, this is I 3 plus, I 3 plus the central iodine has the tetrahedral geometry and it has 2 bond pairs and 2 lone pairs. So, if you do any mistake here we should be able to correct it simply by looking into the steric number. Steric number will guide you in writing the precise geometry and also knowing the correct shape of the molecule or ion ok.

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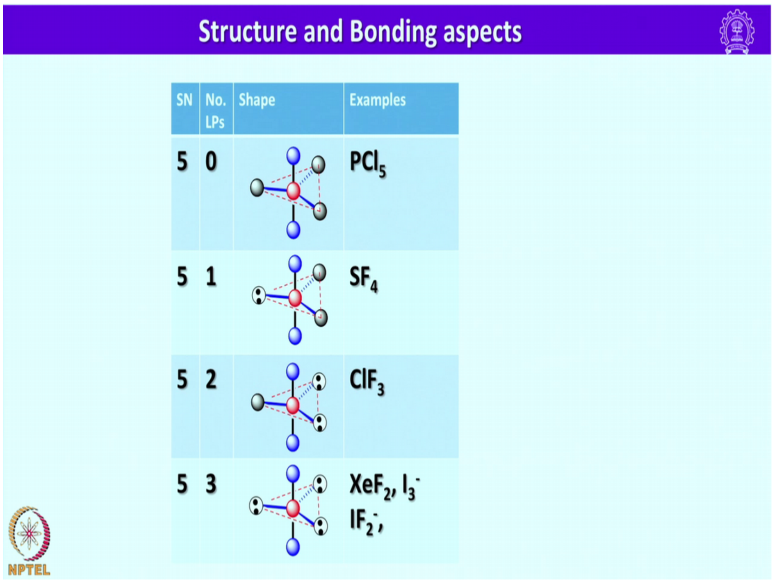

Structure and Bonding aspects

SN	No. LPs	Shape	Examples
5	0		PCl_5
5	1		SF_4
5	2		ClF_3
5	3		XeF_2, I_3^- IF_2^-,

Let us look into PCl 5, PCl 5 as a trigonal bipyramidal geometry PF 5 can also be considered.

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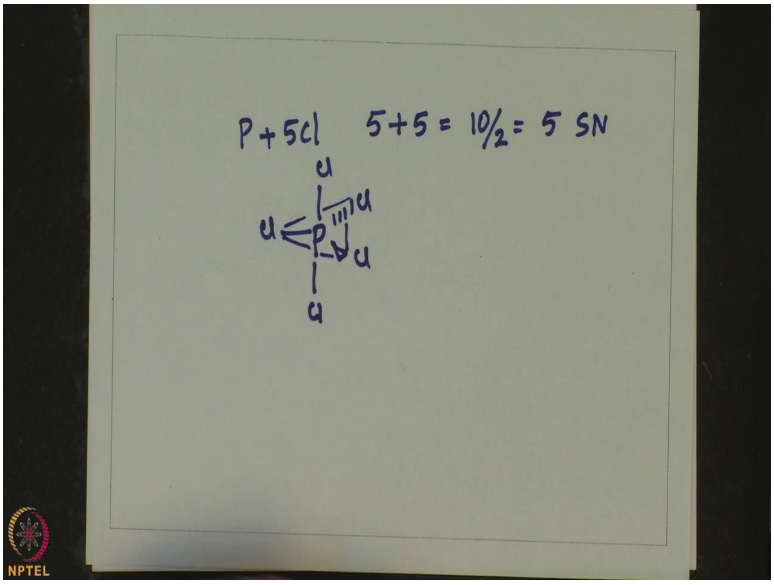

So, here P plus 5 Cl, P has a total of S 2 P 3. So, we have 5 electrons are there with has S 2 P 3 electronic configuration plus each chlorine is giving 1 electron, so we have a total of 5 coming from 5 chlorines. So, we have a 10 electrons, we have a total of 10 electrons divided by 2, 5 is the steric number.

Now, we know the steric number is 5. Now with steric number 5 the geometry that supposed to be considered is trigonal bipyramidal and now place, so this is how we can write the structure of PCl 5 molecule which has trigonal bipyramidal geometry. Let us look into another case of steric number 5, but having 1 lone pair and 4 bonded pair. The example that I have given is SF 4.

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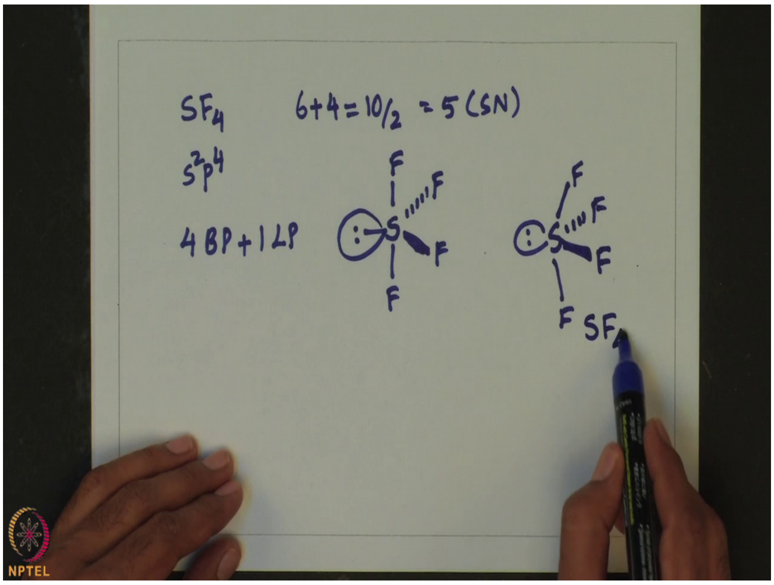

Let us look into the SF 4 molecule here how it will have that kind of structure and shape. So, in case of SF 4 we know that steric number is 5. So, let us determine that one, we have 6 electrons are there from sulphur because this is S 2 P 4 similar to oxygen and 4 electrons are coming one each from chlorine atoms. So, this 6 plus 4 equals 10 by 2 equals 5 is the steric number. In this one what we have is 4 SF bonds are there, so 4 bonded pairs are there plus 1 lone pair is there.

So, first let us write the geometry and then we should consider where this lone pair should be positioned. Now, we have 2 options one is we can place lone pair here or we can keep in axial position. If you keep the lone pair in axial position it makes an angle of 90 with all the equatorial atoms whereas if you place here it makes 120 angle with 2 and 90 degree with 2. So, by placing this one here the molecule can gain extra stability and also lone pairs can get more space to be positioned here, as a result SF 4 has this kind of structure. So, this one it appears like seesaw that is the reason always the shape of SF 4 is recognized as having seesaw structure. Of course, it is not exactly having a seesaw structure essential they are little bit bent to give more space for this lone pairs this are little bit bent towards away from the main position this is the actual structure of SF 4 molecule.

So, in case of Cl F 3 we have a different situation. We have steric number is 5, but we have 2 lone pairs and 3 bonded pairs let us try to calculate and see whether its correct or not; Cl F 3 the central atom is chlorine.

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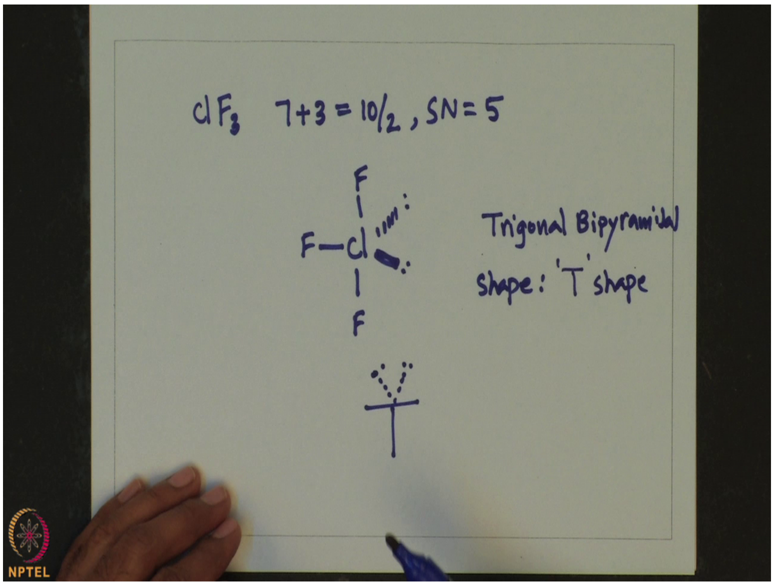

So, chlorine is contributing 7 electrons and chlorine atoms are giving 1 electron each. So, we have again 10 electrons total and steric number is 5. So, now, again the geometry is trigonal bipyramidal. So, now, we have 2 lone pairs taking the hint from SF 4 it is convenient to place them in equatorial position so that the repulsion can be minimum. So, we shell place here lone pairs and remaining fluorine atoms can be placed to axial position one in equatorial position. And here the geometry is trigonal bipyramidal, shape is if we ignore this it appears like T molecule, the shape is T shape. So, this is how it called as having T shape, essentially so these are not considered. So, it appears like having T shape. So, this how one can also write correct structure for Cl F 3 showing 3 bonded pairs and 2 lone pairs.

Another case is in case of steric number 5 is having 3 lone pairs and 2 bonded pairs. Example, I am going to consider here of course, I have examples of XeF 2 xenon difluoride and IF 2 minus and I 3 minus. Let us look into I 3 minus we discussed I 3 plus let us look into I 3 minus now.

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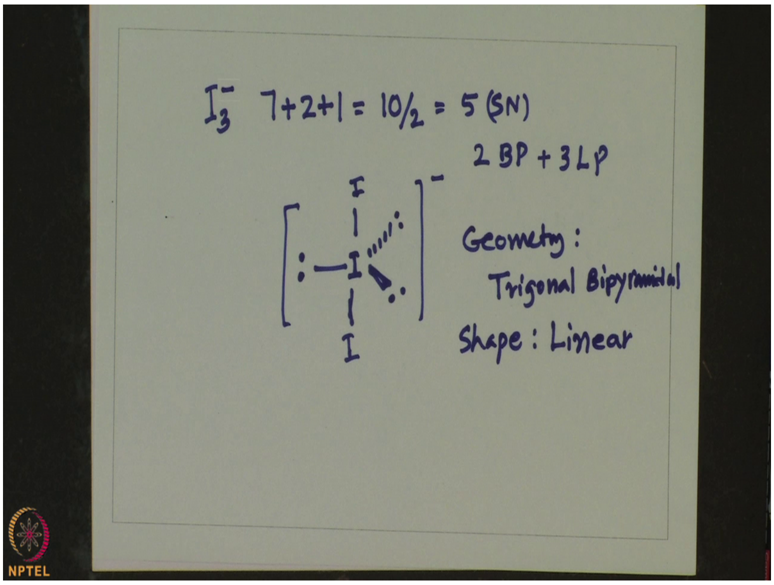

I_3^- 7+2+1 = 10/2 = 5 (SN)

2 BP + 3 LP

Geometry: Trigonal Bipyramidal

Shape: Linear

So, in I 3 minus let us count electrons we have 3 and the central one will be one of the iodine. So, that will give 7 electrons and remaining 12 iodine will give 1 electronic each and plus we have a negative charge. So, total again 10 electrons are there 10 by 2 equals 5 is the steric number.

So, here what we have is 3 2 bonded pairs are there because we have 2 I I bonds plus we have 3 lone pairs. First let us write trigonal bipyramidal geometry as we wrote before. So, this how we can write and now to minimize the repulsion between the lone pairs what we should do is we should place all the lone pairs in the equatorial position like this and remaining 2 iodine atoms can be placed here and this is the structure of I 3 minus. So, here again it is geometries, geometry trigonal bipyramidal shape linear.

And similarly one can write IF 2 minus and also in case XeF 2, let me consider XeF 2 as well because here we have more lone pairs and XeF 2 this has 8 electron S 2 P 6 electronic configuration, so we have 8 electrons and 1 electron each is coming from fluorine.

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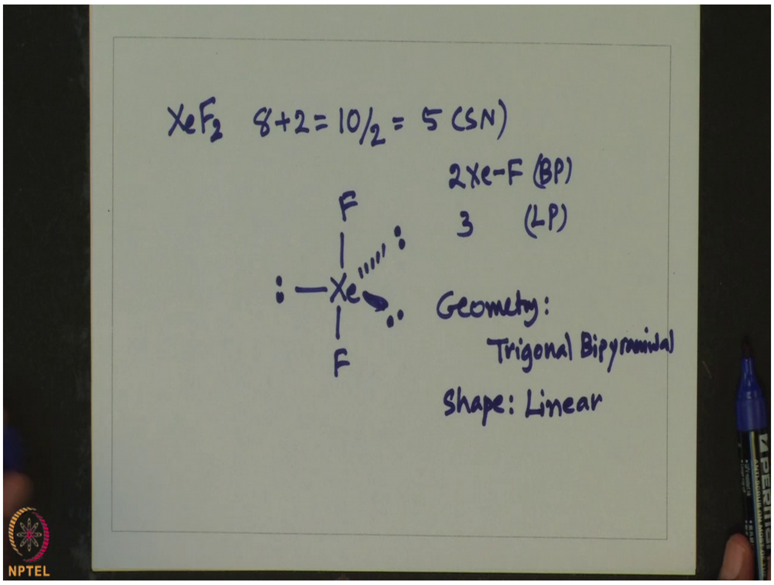

XeF_2 $8+2=10/2=5$ (SN)

2 Xe-F (BP)

3 (LP)

Geometry:

Trigonal Bipyramidal

Shape: Linear

So, we have a again 10 electrons 10 divided by 2 equals 5 is the steric number and in this case we have 2 XeF bonds are there, 2 XeF bonds are there and we have this is bonded pair and 3 lone pairs are there.

So, geometry is again trigonal bipyramidal Xe are the center. So, XeF 2 is geometry is trigonal bipyramidal shape. So, one can write by using this VSEPR theory for any given molecule correct structure and understand the geometry as well as the shapes.

So, let us look into the steric number 6. In this one we have 3 cases having any no lone pair when we have no lone pair, example I am going to consider is sulphur hexafluoride.

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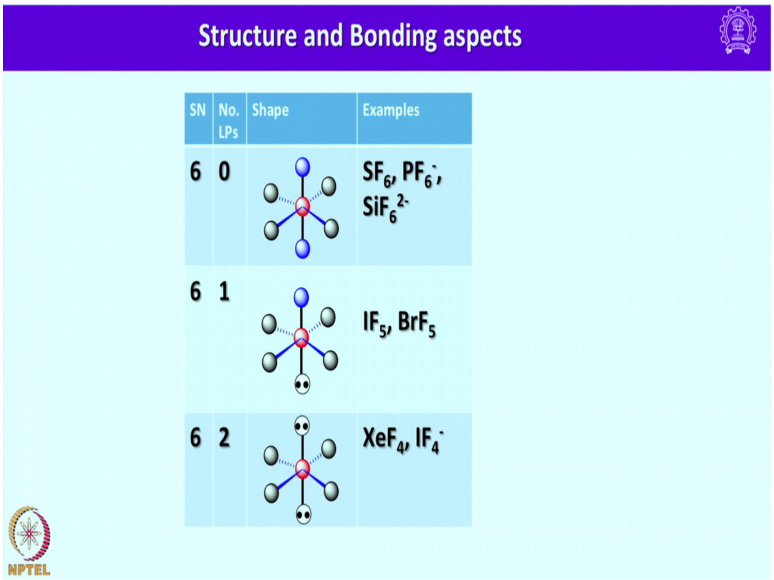

Structure and Bonding aspects

SN	No. LPs	Shape	Examples
6	0		SF_6, PF_6^-, SiF_6^{2-}
6	1		IF_5, BrF_5
6	2		XeF_4, IF_4^-

So, sulphur has 6, S 2 P 4 electronic configuration. So, it is contributing 6 electrons and 6 fluorine atoms are contributing 1 electron each.

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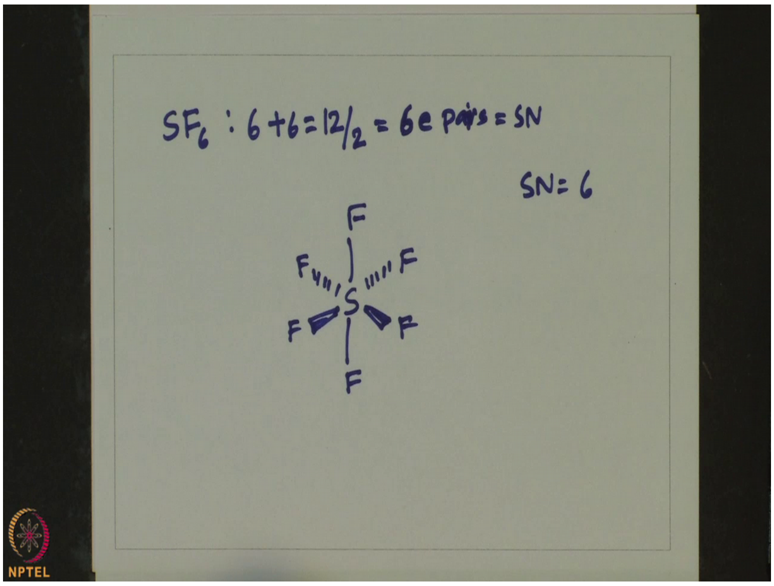

$SF_6 : 6+6 = 12/2 = 6e$ pairs = SN

SN = 6

So, we have a total of 12 electrons divided by 2 equals 6 pairs of electrons. So, 6 electron pairs this is our steric number. So, steric number is 6. So, in this one all are bonded pairs. So, the standard geometry is octahedral. So, the geometry is octahedral here.

Now let us consider another case where we have 1 lone pair and 5 bonded pair example is IF 5. So, let us look into IF 5 here, the steric number is 6, IF 5.

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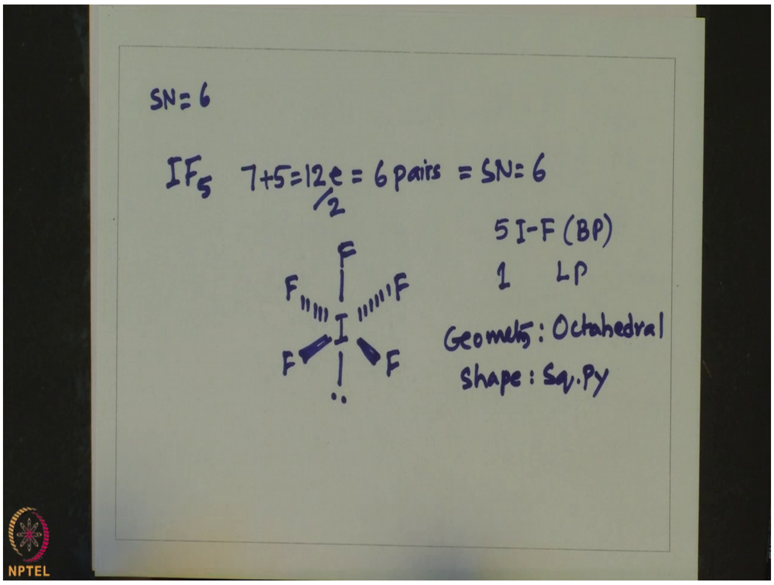

SN: 6

IF_5 $7+5=12e/2 = 6$ pairs $=$ SN: 6

5 I-F (BP)

1 LP

Geometry: Octahedral

Shape: Sq.Py

So, they are called inter hygiene compounds there are plenty of inter hygiene compounds are there neutral ionic as well as cationic. I will be explaining more details about the preparation all those things when I discuss the group 17 elements. Now let us look into IF 5. In case of IF 5 the central atom is I giving 7 electrons and then each F is giving electron, it becomes 5. So, totally we have a 12 electrons that is equal to 6 pairs that is steric number is 6.

So, now out of this one we have 5 if bonds are there, that is bonded pair and then 1 lone pair will be there then. So, geometry is octahedral as usual because the steric number is 6. So, first let us make 5 IF bonds one here, one here, one here, one here, one here, now the lone pair will come and sit in one of the axial position. Now, if you just look into it the geometry is octahedral shape square based pyramid. So, these are the examples where we have a lone pair and as a result we are seeing the square shape for some of the smallest number having steric number 6 with 1 lone pair and 5 bonded pairs.

Another example is brf 5. Let us look into this last one in the series octahedral molecules with steric number 6 having 2 lone pairs and 4 bonded pairs. Example consider here is XeF 4.

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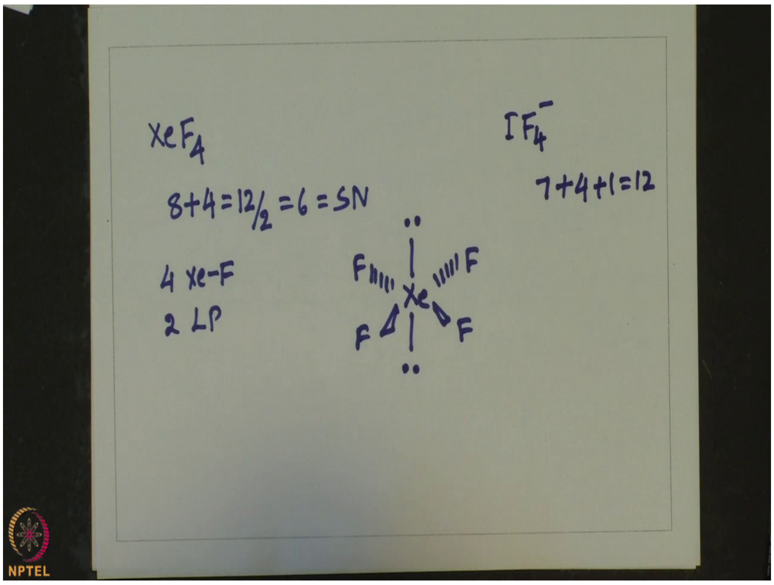

XeF_4

$8+4=12/2=6=SN$

4 Xe-F

2 LP

IF_4^-

$7+4+1=12$

So, in case of XeF 4 again S 2 P 6 electronic configuration is xenon. So, we have 8 electrons and plus 4 fluorine atoms are giving 4 electrons. So, we have a total of 12 electrons that is equal to 6 will be its steric number. In this one we have 2 lone pairs and 4 bonded pairs because we have XeF bonds and 2 lone pairs will be there. The geometry is again octahedral, xenon will be at the centre this are placed here and in axial position 2 lone pairs will occupy.

So, now, the geometry of XeF 4 is octahedral where as the shape is square planar. Except those cases where we come across 2 lone pairs in the axial position we do not have any examples among main group elements that show square planar geometry, square planar geometry is seldom show when we have 4 bonded pairs. The preferred geometry is tetrahedral similarly one can also look into IF 4 minus in case of IF 4 minus again I is giving IF 4 minus I is giving 7 plus 4 in atoms are giving 4 and plus 1 electron is there, so 12 electrons are there. Again the steric number is 6 again the geometry is octahedral and all the IF bonds will be in the plane giving a square planar shape, the geometry still octahedral.

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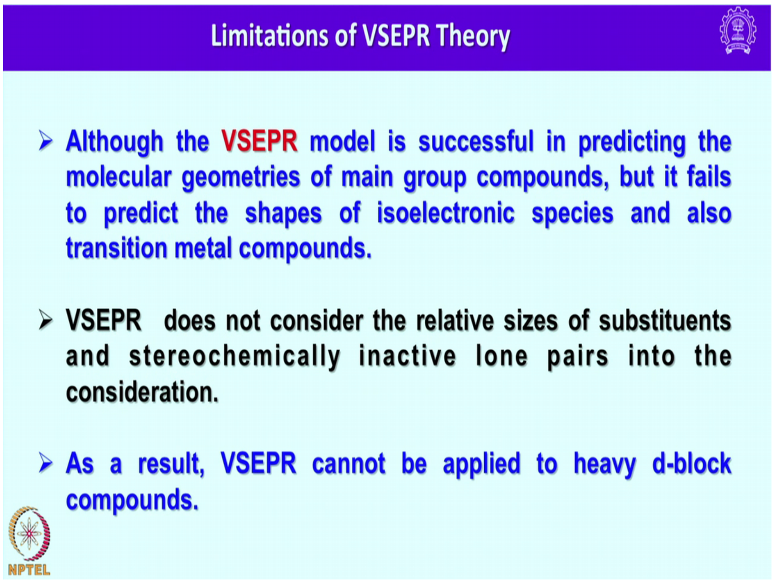

Limitations of VSEPR Theory

- Although the VSEPR model is successful in predicting the molecular geometries of main group compounds, but it fails to predict the shapes of isoelectronic species and also transition metal compounds.
- VSEPR does not consider the relative sizes of substituents and stereochemically inactive lone pairs into the consideration.
- As a result, VSEPR cannot be applied to heavy d-block compounds.

I think this all about valence shell electron pair repulsion theory. It is quite successful in predicting the molecular geometries of main group compounds, but only in few cases it fails to print the shapes of isoelectronic species and also transfer metal compound; that means, when we have isoelectronic species and also when we are considering transfer metals where we have in active lone pairs VSEPR theory does not give a right geometry and shape for those molecules. And another limitation of valence electron pair repulsion theory is it does not considered the relative sizes of substance and as I said stereo chemically inactive lone pairs into the consideration. As a result what happens one needs to look for a different bonding concept for especially explaining the bonding in transition metal complexes.

So, of course, in case of transfer metal complexes 3 theories have been successfully used one is valence bond theory and another one is crystal field theory and another one is molecular orbital theory. And in case of crystal field theory we always talk about the ligands and metal ions as point charges and the interaction between the metal and elegant is purely electrostatic in nature and if the metal is cation and the legend is anion it is ion ion interaction. If the metal is cation and ligand is neutral it is called ion dipolar interaction, but we come across the situation where the metal is neutral and ligand is also a neutral. For example, if you consider nickel, tetracarbonyl, chromium, hexacarbonyl, iron, pentacarbonylw where metal is neutral and ligand is neutral in that case what happens we have to consider the electrostatic interaction of dipolar dipolar in nature.

However, crystal field theory does not explain their electrostatic interaction that exists between dipolar and dipolar species as a result crystal field theory to explain bonding in metal compounds having metal in the 0 valence state. In those cases in order to explain dipolar dipolar interaction some (Refer Time: 25:23) made and that is called ligand field theory. So, ligand field theory explains all 3 kinds of electrostatic interactions and of course, once when we go to more refined method or theory molecular orbital theory that can explain almost all aspects of all compounds without any controversy or without any problems.

In my next lecture I will be focusing your attention on another important theory valence bond theory. Valence bond theory is essentially refined from the valence shell electron pair repulsion theory, introducing the concept of hybridization proposed by Linus Pauling. In my next lecture I will be discussing about the valence bond theory and its application to the compounds of main group elements. Have a pleasant reading.

Thank you very much.