Concepts of Chemistry for Engineering
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Lecture No. 33
Application of CFSE: Spinel and J-T Distortion

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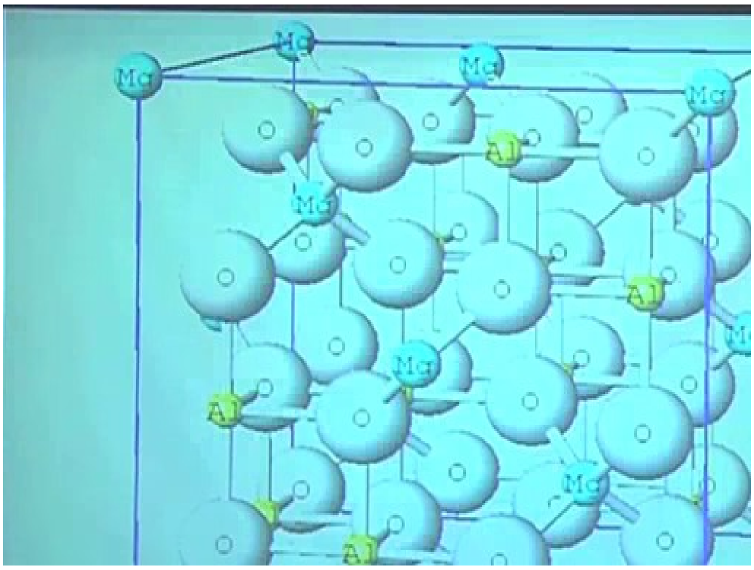

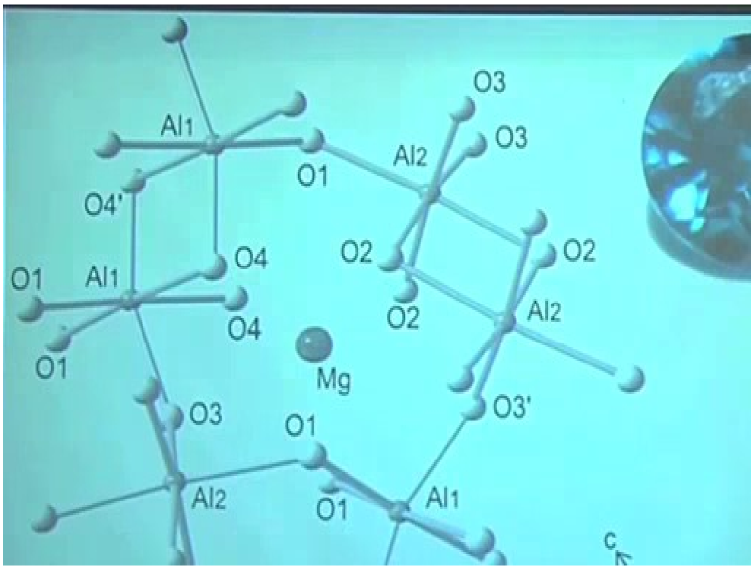

Now, this is the topic today we are going to discuss spinel. Spinel are the ones which is let us say this nice looking, gem looking thing or gem basically magnesium, aluminum oxide. It is beautiful in color. Of course color comes from, you know where the color is coming from those transition.

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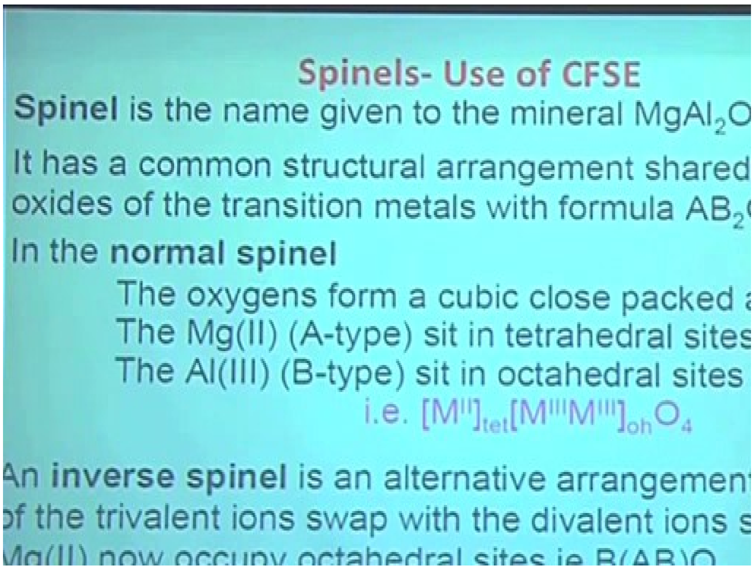

Spinels- Use of CFSE

Spinel is the name given to the mineral $MgAl_2O$

It has a common structural arrangement shared

oxides of the transition metals with formula AB_2

In the **normal spinel**

The oxygens form a cubic close packed

The Mg(II) (A-type) sit in tetrahedral sites

The Al(III) (B-type) sit in octahedral sites

i.e. $[M^{II}]_{tet}[M^{III}M^{III}]_{oh}O_4$

An **inverse spinel** is an alternative arrangemen

of the trivalent ions swap with the divalent ions

Mg(II) now occupy octahedral sites ie B(AB)O

Now, definition of spinel is very simple. You can have either same metal or different metal. It could be, let us say, Fe_3O_4, CO_3O_4 or it could be $MgAl_2O_4$, three metals should be there. Two of them should be the same, as you see. At least two of them has to be, will be the same, usually speaking again or one is different $MgAl_2O_4$ something like that. Now, AB_2O_4 is the general formula for spinel. The normal spinel are the one, there are two types of spinel, as I said, normal there would be abnormal, two spinel, or inverse spinel. Now, we do not say abnormal, inverse spinel.

Normal spinel are the one where you have this electronic configuration. It is always going to be O4, 4 oxides are there that means minus 8, each oxide minus 8, 4 of the oxide will be minus 8. Now, minus 8 means you have almost one possibility, realistic possibility 3 plus 3 plus 2. Of course, other possibilities are there. Those are less likely. Never happens for spinel. So, 3 plus 3 plus 2. Since it is 3 plus in the normal behavior or normal spinel cases, you would expect the octahedral geometry or octahedral geometry will be preferred by 3 plus and tetrahedral geometry will be preferred by 2 plus.

Let us look at the over here magnesium, aluminum. This is octahedral. You can see 1, 2, 3, 4, 5, 6, each aluminum octahedral. You look at magnesium, it is having four ligands. It is in tetrahedral. I think most likely 1, 2, maybe 3 and 4. Magnesium is in tetrahedral geometry, aluminium is in octahedral geometry. So, over here this is further showing you that 1, 2, 3, 4. So, one of them, so it is a little bit complicated looking thing, but if you go by unit sale, if you break down the complex structure and look at the core of it, each of the metal ions AB_2O_4 both the B will be in octahedral geometry.

Sometimes it is just not clear by looking one glance at it. You have to just look it little bit carefully you will be able to understand where it is. And these are the usually the crystal structures. So, there should not be any ambiguity. You just have to look it carefully. So, both the octahedral will be in plus, both the plus 3 oxidized metal will be in octahedral state and the one which is 2 plus will be in tetrahedral geometry and four oxides are there. If this is the case, this is normal spinel.

If other way around, if one of these octahedral M 3 plus has to be pushed out from this octahedral side to tetrahedral side that will be called inverse spinel. So, all it depends on whether one of these M 3 plus will be in octahedral site or tetrahedral site. That is it. Of course, always there will be one metal 3 plus which is in octahedral site. This is common. The second metal 3 plus whether it is exchanging with this other metal. That is what you need to see. Is it clear? Normal spinel normal behavior, 3 plus should be octahedral. It is a privileged class. 3 plus higher oxidation state octahedral should be right. It is a high charge, everything should be, ligand should be interacting more and so on. That is like normal behavior.

If it is other way around octahedral site is coming out and tetrahedral is going into the octahedral one or 2 plus is going into the octahedral one, this is when it is called inverse spinel, normal spinner. Now, when, what is the criteria? Simply you have to see metal, this metal in 3 plus whether it prefers octahedral or metal 2 plus what it prefers, let me show you.

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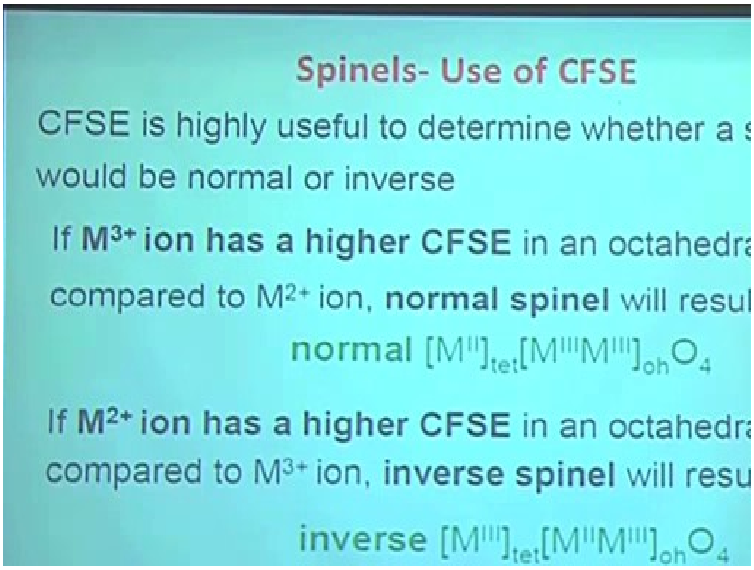


Spinels- Use of CFSE

CFSE is highly useful to determine whether a s

would be normal or inverse

If **M^{3+} ion has a higher CFSE** in an octahedra

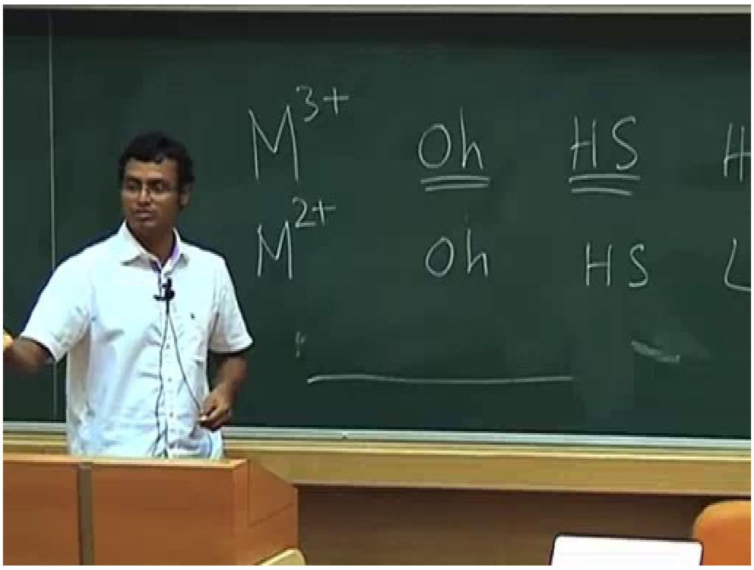
compared to M^{2+} ion, **normal spinel** will resul

normal $[M^{II}]_{tet}[M^{III}M^{III}]_{oh}O_4$

If **M^{2+} ion has a higher CFSE** in an octahedra

compared to M^{3+} ion, **inverse spinel** will resu

inverse $[M^{III}]_{tet}[M^{II}M^{III}]_{oh}O_4$



So, M3 plus ion has, when M3 plus ion has a higher crystal field stabilization energy compared to M2 plus ion then this is a normal spinel. If M2 plus ion has a higher CFSE then it is inverse spinel. So, you do not have to really look at the tetrahedral. You do not have to look at the tetrahedral. You take the metal ion M3 plus, M2 plus for a given metal ion, you find out M3 plus and M2 plus their CFSE, separate CFSE. If M3 plus is more, then normal. If M3 plus is less, having less CFSE compared to M2 plus, then it is inverse. Just read these two lines.

So, expectation is M3 plus in octahedral and this is usually going to be high spin should have high CFSE. Of course, opposite is true. M2 plus octahedral high spin should have low CFSE. CFSE calculation we have learned how to do. If this is done, normal, opposite, inverse, normal spinel, inverse spinel. Do not mix up with calculation of octahedral versus tetrahedral.

Sometimes people end up doing that. They go into wrong direction. So, you have to just calculate octahedral site stabilization energy, like how much stabilization is there. So, that is what it is written. M3 plus ion has a higher CFSE in an octahedral field compared to M2 plus ion in normal spinel and so on. Do not calculate for the M3 plus in tetrahedral.

So, this is where, I mean, yes, then how will you conclude. So, you have to figure out the stability of M3 plus versus M2 plus. This, otherwise it will get confused. What will we be comparing with? CFSE for tetrahedral is usually low, four nines of delta 0, what to calculate.

So, let me give you an example. It will be clearer. More negatives. See any, in terms of energy in chemistry, physics, everywhere, energy means the one which is having low anything, low repulsion is stable, low energy, I mean, it is stable. Anything low would be stabilize. It is like, as I was, I think I was trying to say it is like home feeling. You want to feel home. Everybody wants to belong somewhere. And that is where they want to go. So, always low. Stability should be maximum.

No, no, that is the splitting, delta. So, that is the splitting we are comparing. When we are not changing anything, ligand keeping constant, metal oxidation state varying, metal with a higher oxidation state will have higher splitting. That is somewhat true here. But, I mean, we are not saying that extent to which. We are trying to tell here is M3 plus, M2 plus, yes, you are partially right, M3 plus, M2 plus you just calculate the CFSE. Let me give you this example. Hopefully things will be clear.

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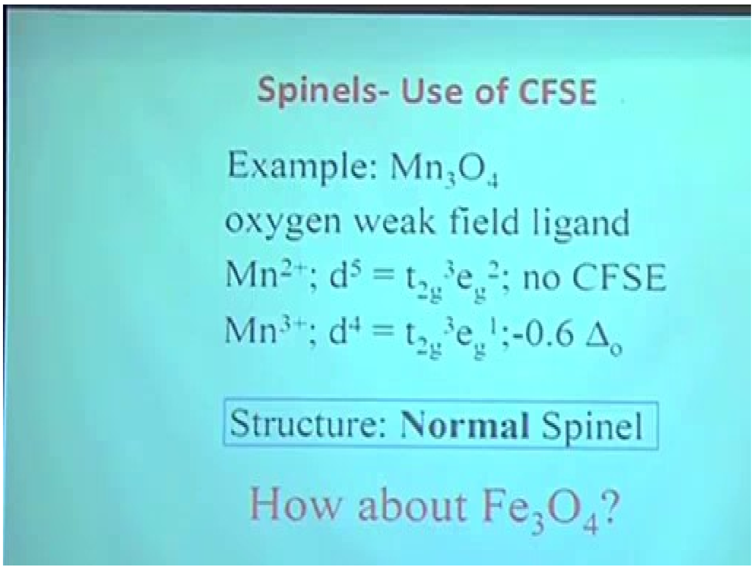

Spinels- Use of CFSE

Example: Mn_3O_4

oxygen weak field ligand

Mn^{2+}; $d^5 = t_{2g}{}^3e_g{}^2$; no CFSE

Mn^{3+}; $d^4 = t_{2g}{}^3e_g{}^1$;$-0.6\ \Delta_o$

Structure: **Normal** Spinel

How about Fe_3O_4?

Mn3O4, of course, here oxygen usually always, I mean, not always again there will be one example which is other way, usually oxides for these cases are going to be the weak field ligand. It is a weak field ligand. Now, unless the metal is very high oxidation state or so oxide will be the weak field ligand. You do not have to worry about the oxide too much, except in one question which will come.

Manganese 2 plus d5 since it is weak field ligand, it is a high spin. That is what I was saying, high spin. Now, high spin is 0 CFSE, manganese 3 plus d4 is t2g3eg1 so you are going to get net minus 0.6 delta 0. That is what do you have calculated, minus 12, minus 6, plus 6, minus 12, plus 6, is minus 6Dq. Now, this is the normal spinel.

How about Fe3O4? Can you calculate Fe3O4? Whoever is trying to calculate? Try give yourself 1 minute. Fe3O4, Fe3 plus and Fe2 plus, try. Whoever got it, hold on for a minute. Inverse spinel, yes, that is the correct answer. Just in a minute I am looking for something.

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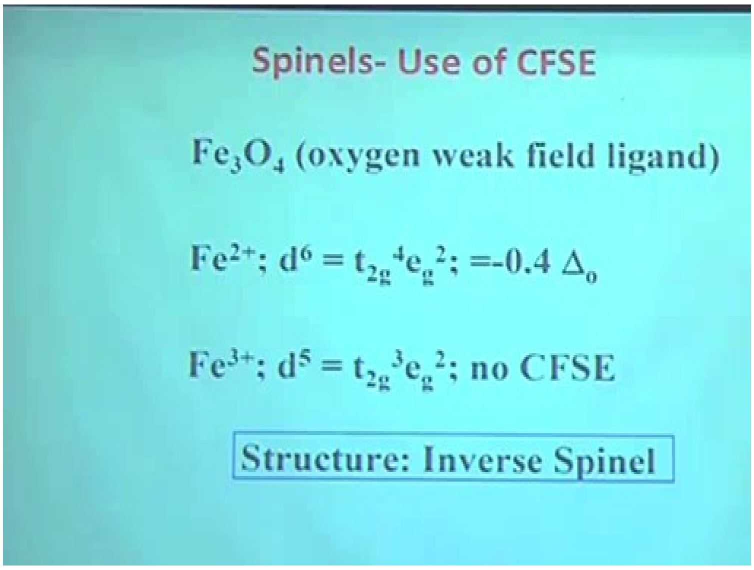

Spinels- Use of CFSE

Fe_3O_4 (oxygen weak field ligand)

Fe^{2+}; $d^6 = t_{2g}^4 e_g^2$; $= -0.4\ \Delta_o$

Fe^{3+}; $d^5 = t_{2g}^3 e_g^2$; no CFSE

Structure: Inverse Spinel

So, I hope you have got this. Fe2 plus, d6 t2g4eg2 high spin, 3 and 2 cancels out, 3 over here and 2 over here cancels out, so minus 4. It is easy. Over here 3 and 2, 0 CFSE. Now, Fe3 as you can see is having less CFSE compared to Fe2. So, that is it, so inverse spinel. Do not, only request is do not complicate too much. You think, but for calculation do this, because if you end up calculating tetrahedral Fe3 plus case tetrahedral, Fe2 plus case tetrahedral, it is going nowhere. It is a simple thing. Higher oxidation state should try to stay in the octahedral site.

The moment higher oxidation state becomes less favorable compared to the lower oxidation state, switch of the power happens. It is just the BJP and Congress. You have to pick up one of them in the center, not the local or Democratic or Republican, you do not have any choice.

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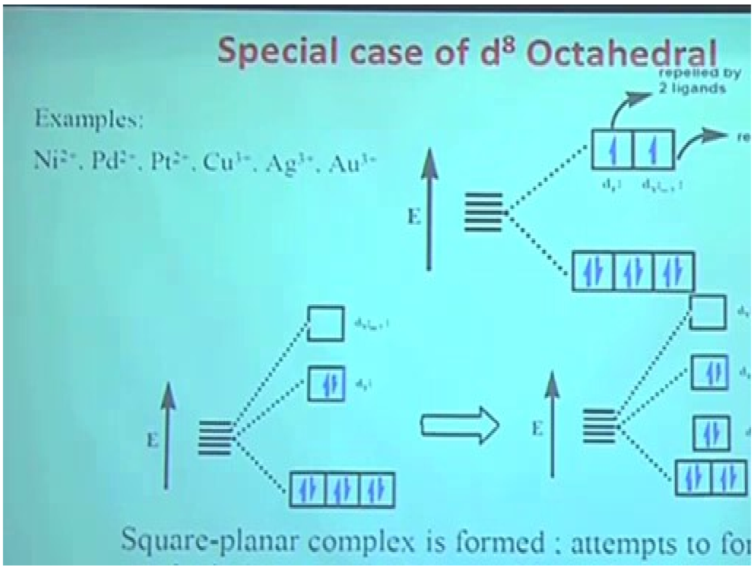

Special case of d^8 Octahedral

Examples:

Ni^{2+}, Pd^{2+}, Pt^{2+}, Cu^{3+}, Ag^{3+}, Au^{3+}

Square-planar complex is formed : attempts to fo

Now, so this is a special case, special case of d8 octahedral. So, what is the special case? We are eluding before that these dz2 orbitals are the one getting repeated by two electrons. This is a d8 electronic configuration as you can see, t2g6eg2 and this is the one repealed by four ligands. That is unfair. That is where what happens is z orbital try to stabilize to minimize the energy to gain more energy.

So, you start with an octahedral situation. But you see d8, you go blank. D8 octahedral will tend to form square planar geometry, because the z you will see square planar complex is formed because z will get destabilized, stabilized. Z is getting stabilized as you can see, Z orbital will get destabilized. This is an unfavorable situation. This is a situation which cannot be tolerated. This is 2 ligands refilling, 4 ligands refilling.

This is the unique situation one, one unique situation. Same electron repelled by, one electron repeated by 2, one electron repelled by 4. In order to bring some sort of calmness to the system z orbital will stabilize. If you want to stabilize x2y2 orbital then the problem becomes, stabilization means repulsion is less, that is the stabilization, repulsion less is the stabilization. If you want to stabilize dx2y2 orbital, then you have to elongate four of the ligands. Stabilization means reducing the repulsion.

If you are stabilizing z square, then you just need to take out those axial ligands. Take, it was here, two axial ligands were here you pull it out, so z will be stabilize, dz square will be stabilized. Of course, further it will be stabilized. Any z component there will get stabilized. So, dxz will be stabilized, dyz will be stabilized. This is the scenario where square planar complex goes. D8 octahedral usually will be, I mean, if it is possible always it will go to the square planar situation. That is also true.

D8 tetrahedral or d8 four ligands are not tetrahedral, d8 configuration four ligands are going to be square planar. This is where you see iron, cobalt, nickel, nickel is nickel 2 plus d8 is square planar. Now, this is one scenario.

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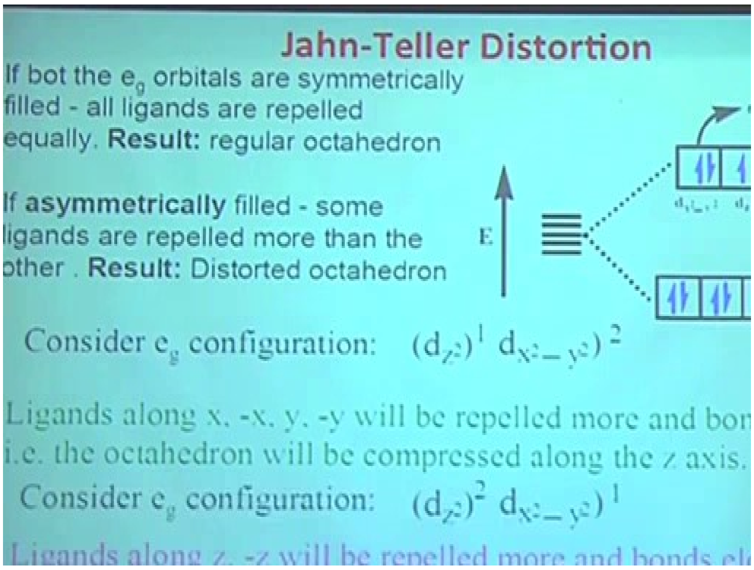

Jahn-Teller Distortion

If bot the e_g orbitals are symmetrically filled - all ligands are repelled equally. **Result:** regular octahedron

If **asymmetrically** filled - some ligands are repelled more than the other . **Result:** Distorted octahedron

Consider e_g configuration: $(d_{z^2})^1 d_{x^2-y^2})^2$

Ligands along x, -x, y, -y will be repelled more and bon

i.e. the octahedron will be compressed along the z axis.

Consider e_g configuration: $(d_{z^2})^2 d_{x^2-y^2})^1$

Ligands along z, -z will be repelled more and bonds el

Other scenario is that eg orbital is unsymmetrically filled. So, you can see that majority of the syllabus is biased towards octahedral, tetrahedral not too much, but that is because octahedral is favored, octahedral is historically more important and that is what most of the study has been done and it is a common geometry, more common geometry I would say. Now, this is the Jahn-Teller distortion. Of course you can, some people pronounce that differently in British, in England you will go pronounced differently, U.S. it will pronounce differently.

Jahn-Teller some people tell, some people tell Jahn-Teller. Whatever it is, it is the same thing JT distortion. So, what we see, if this one is unsymmetrically filled, what are the situation when it is eg3 or eg1. That is the only two possibility. Eg2 will be symmetrically filled, eg4 will be symmetrically filled, eg1 or eg3. If it is filled, then again you are having some sort of a problem. What is the problem? That is what we are coming to. Let me go to the picture.

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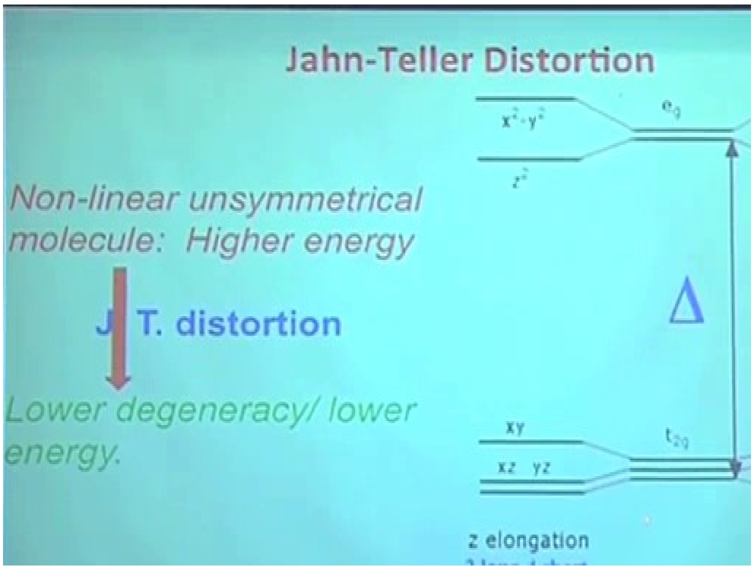
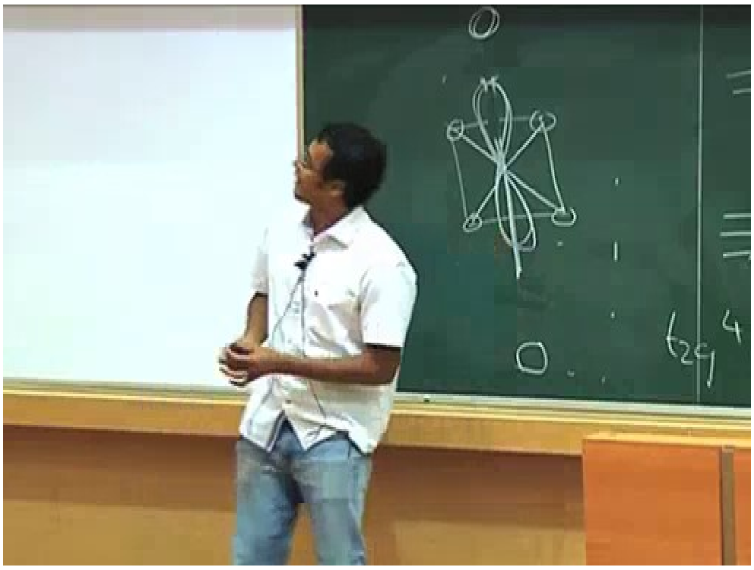


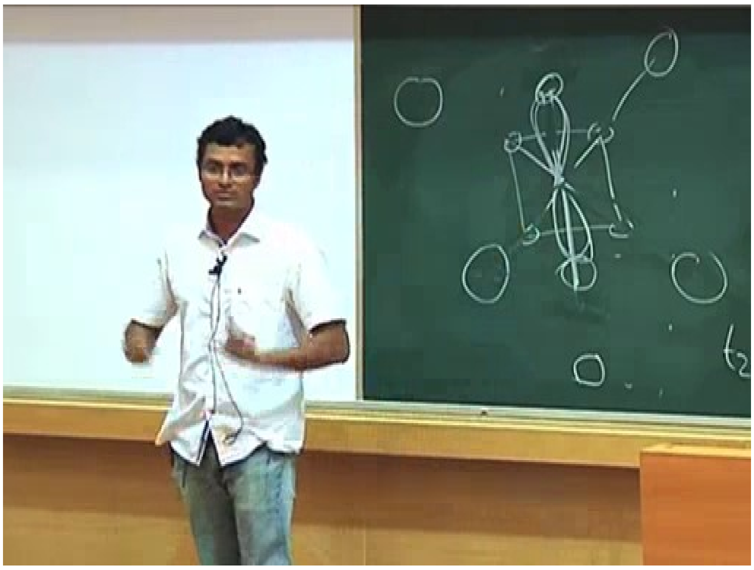
Jahn-Teller Distortion

Non-linear unsymmetrical molecule: Higher energy

J. T. distortion

Lower degeneracy/ lower energy.





This is what is Jahn-Teller distortion. If, of course, t2g is completely filled or symmetrically filled. Either t2g is t2g3eg1 or t2g6eg3, all these configuration. So, what are the configuration t2g3eg1, t2g6eg1, t2g6eg3. So, wherever unsymmetrical situations are possible, of course, t2g3eg3 is not possible, because it would be t2g4, t2g3eg4 is not possible. So, this sort of thing you should be able to recognize very quickly. T2g3eg4 actually should be t2g4eg2. Why means it is a stabilization, you look at. Very good question.

So, t2g3eg, sorry, did I say 3, everything I said is correct, 3 plus 3, 6, 4 plus 2, 6. Now, t2g3eg2, this is the t2g3eg2, high spin if you are even say it. Now, how it can be going over there, because it is giving more energy or destabilizing the system. This sixth electron should come here. So, the always filling anywhere, I mean, you read Hund's principle, you read whatever other principle, system has to be stabilize. When two scenarios are there system goes for stabilization. But when high spin, low spin situation is there, because high spin is accessible, it goes for high spin or it can go to low spin.

Here, after filling out 1, 2, 3, if it is high spin 4, 5, 6th electron will come back from here. It is home, it is stable. So, t2g3eg3 is not a valid configuration, it is t2g4eg2. It is invalid. I mean, literally it is possible for an excited state. If you excite t2g4eg2, then it can come to t2g3eg3. This is usually all we are talking about is ground state electronic configuration. Any confusion on that? No, hopefully not.

Now, JT, Jahn-Teller distortion t2g either fully filled or half filled, t2g6 or t2g3, here it has to be unsymmetrically filled, means eg2 and 4 is out of question, eg1 or eg3, two orbitals are there. What can happen? Two scenarios out there, either dg2 or dx2y2 can be stabilized. Now, stabilization again stabilization means what? Stabilization means repulsion is less. Stabilization means less repulsion. Less repulsion when it can happen, when ligand is not coming. If z square is stabilizing that means along that direction ligands are far. So, this will be too long, that will be.

So, the left hand scenario, this is a base, for octahedral scenario we are drawing, this is the equatorial plane, axial was here. Now, this is let us say normal scenario. If I want to say that dz square orbital is stabilized that means this ligand is not, this is the dz square orbital direction. So, that means ligand is not coming close to this dz square orbital.

This is where the dz square orbital is. So, it is not coming close that means it is going far and that is how dz square can be stabilized. That means two of them, two of the ligands should be at a longer distance and four of them at a shorter distance or relatively shorter distance. The opposite is here.

When, relatively speaking, dx2y2 is getting stabilized that means these are going out. Stabilize means repulsion is less. Ligands, in the second scenario, ligands will be farther, further away and z was over here. So, z-in, this is called z-in, z direction getting in. This is called z-out. It is a very, very simple thing. If you just try to understand very simply, do not complicate things. It is that very simple.

Now, as you can see, z-out, this is the z-out, if you keep on moving more and more z-out becomes your square planar. So, here previous case what we were discussing. If z becomes stabilized more, more, more and so that it is you are taking too far from the metal center octahedral is no longer octahedral, it is becoming square planar, so z-in and z-out.

No, these are having same energy. No, these are degenerate. You cannot dictate the term, you cannot tell who is, where you want. It is just for nomenclature sake. I have written just to tell you or just to write you something I have written, which one is dz2, which one is dx2 you do not know. It same energy, degenerate means same energy. 5d orbitals before crystal field theory we used to think that same energy. We do not discriminate. So, this is just a representation sake.

Not all the cases, but when it is unsymmetrically filled then it is becoming a problem. See three, four scenarios are there eg orbital. Why is eg orbital is getting part of, why t2g not, because those are the one you can see these are the outside. If you see the splitting-wise, those are the one facing the maximum of the ligand repulsion. In eg, four configurations are there, eg1, eg2, eg3, eg4.

Eg2 scenario we have already discussed. Eg2 scenario is the one where we are getting, most often we are getting that d8, t2g6eg2 that is a d8 electronic configuration. It tends to go for a square planar one. You remained with eg1 or eg3. Eg1 and eg3 scenario we are trying to discuss here. So, when it is symmetrically fulfilled, then usually we do not get bothered. It is one way or the other it is just the same. I mean, it is completely full, so nothing to really compare it.

But in this scenario, when you have unsymmetrical filling, then you have the chance of splitting. See similar split, the extent of splitting you can see is not the same here again. Of course, usually speaking, these are the one, eg are the one which are going to face the ligand directly and thereby splitting starts over there. And then of course sometime it also get affected, t2g gets affected. That is where we were showing.

Initially we did not split it. Initially we, when we were discussing t2g6eg2 we were showing that dz2 is getting stabilized. When it is getting further stabilize and this, then it is going to get split further. So, look at the slide almost in every book it has been written really well. If you have any confusion, please come back or discuss with your friends. So, z-in and z-out, this is z-out. Z-out means you are pulling out, stabilization happening.

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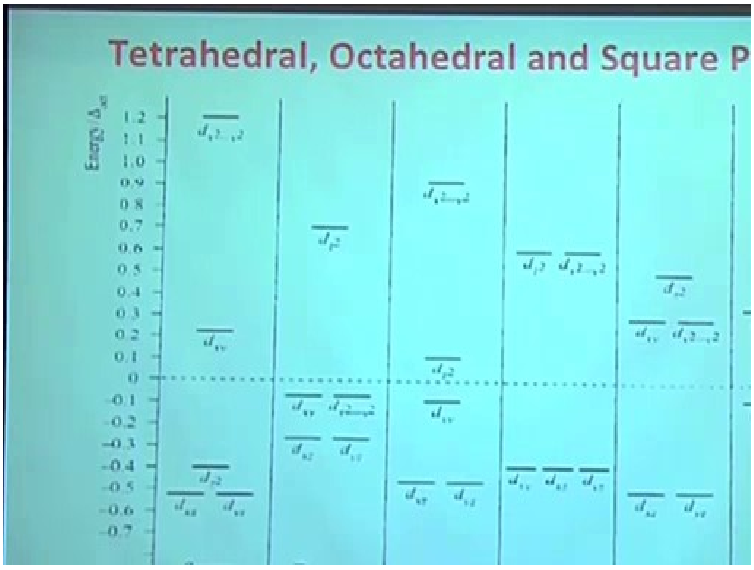

Tetrahedral, Octahedral and Square P

Now, this is a slide which is mostly left for you to digest little bit square planar geometry. So, if you want to memorize sometimes things can be problematic. We want to read you mainly let us say octahedral 3, 2 octahedral. Where is tetrahedral? Tetrahedral is not given here anyway. The geometry and thereby their splitting, how they are going to split. This is not all of them is part of the syllabus again, this is just an overview, giving an idea how ligands are coming, how d orbitals are getting perturbed, which direction d orbitals are located and then from which direction ligands are coming.

Of course, that is what is going to determine what is their geometry. If it is a square planar where it is coming you know. If it is a trigonal bipyramidal or TBP, 3 of them in the equatorial plane, triangle, one from the top, one from the below, so which are the orbitals going to get affected and to what extent and so on. So, these are in the book or may not necessarily you have to read it. You are, but you are supposed to read octahedral, tetrahedral, square planner. I think for fun you can look at that, try to justify a little bit. So, that is it for this chapter.