Symmetry and Group Theory
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Lecture - 51
OH Complex and Group-Subgroup Relation

Take an example of 3-dimensional IR and while doing this what we will do is we will take the scenic route and we will learn something that is very useful to us that is how to use the descent of symmetry to make our job a little easier. You understand this is such a small molecule, right. Such a small symmetry point group, even that took us almost 1 hour.

So if you keep on doing this, just imagine what will happen if you want to work out something for say, say even naphthalene. Okay, I am not even talking about bigger molecules. So we need to find shortcuts. That is what we will try to do. So 3D IRs.

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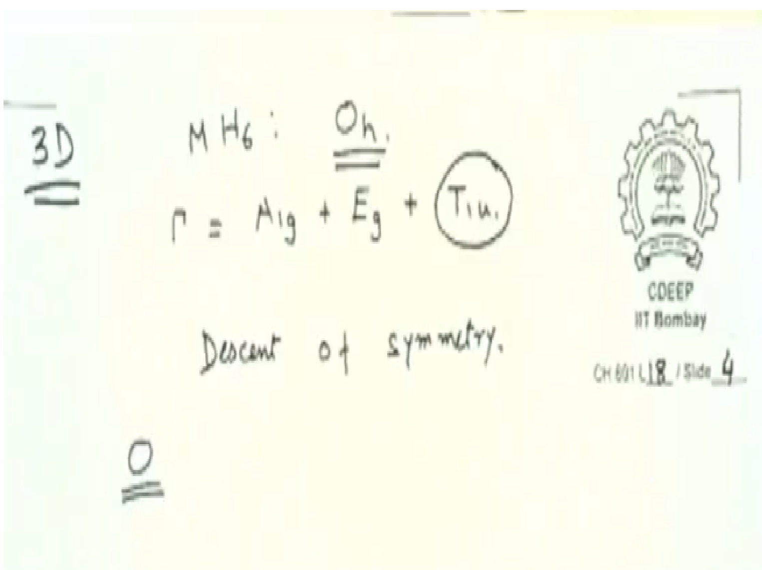

So let us take MH 6. What is the point group of MH 6? Octahedral. How many symmetry operations are there in octahedral? 48. So let us see if we can work with a fewer symmetry operations today. So I will decrease your agony somewhat by giving you the answer. The gamma that you get, okay I am talking about this molecule okay.

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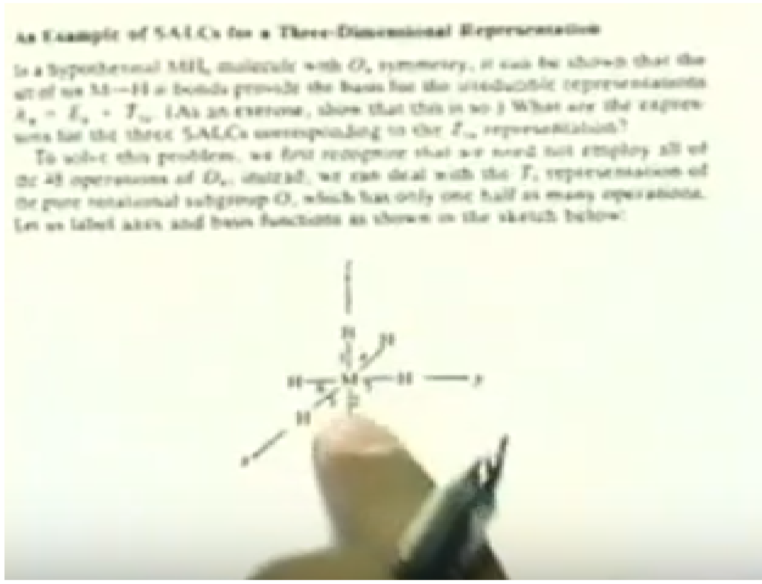

MH 6. Maybe you can copy it so that we are sure about the deductions of x, y, and z. Please copy the structure and write down 1, 2, 3, 4 also. So along z we have 1 and 2. Along x we have 3 and 4, along y we have 5 and 6. You are free to draw x, y, and z in whichever direction you like. But just to be on the same page, make sure that 1 and 2 lie along z direction, 3 and 4 lie along x direction, 5 and 6 lie along y direction, okay.

So how many orbitals are there now? We are still talking about sigma bonding, 6. So 6-dimensional reducible representation right? That breaks down into A 1g + E g + T 1u right. You can work it out yourself and satisfy yourself that this is what indeed happens, okay? And what we will do is we are going to focus on this T 1u. How many symmetry operations are there you said? 48, right. That will be a very tedious work.

So now let us learn how to use the short cut. The short cut is available in the form of descent of symmetry. That is what we are going to do here and we are going to use not the full O h group but rather the subgroup O. And in case you are wondering what I am talking about, this is O h and this is O, okay.

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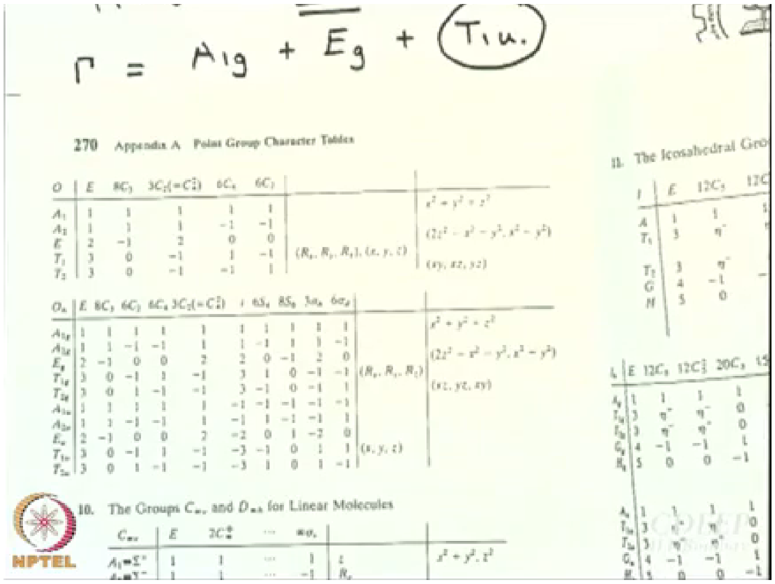

What do we have in O h? We have E, 8C 3, 6C 2, 6C 4, 3C 2, i, 6S 4, 8S 6, 3 sigma h, 6 sigma d, 48. What do you have in O? E, 8C 3, 3C 2 = C 4 square, 6C 4, 6 C2. Do you see that O is actually a subgroup of O h. Whatever is there in O is there in O h, right? But the advantage of working with O and not O h is very clear. How many symmetry operations are there? 1 + 8 9 + 3 12 + 12 24 half. Half the number of symmetry operations.

So for this purpose we are going to work with O and before going there I want to show you, I want to talk a little bit about descent of symmetry. I hope you have not completely forgotten this picture that we had flashed 2, 3 times wrongly and at least once correctly.

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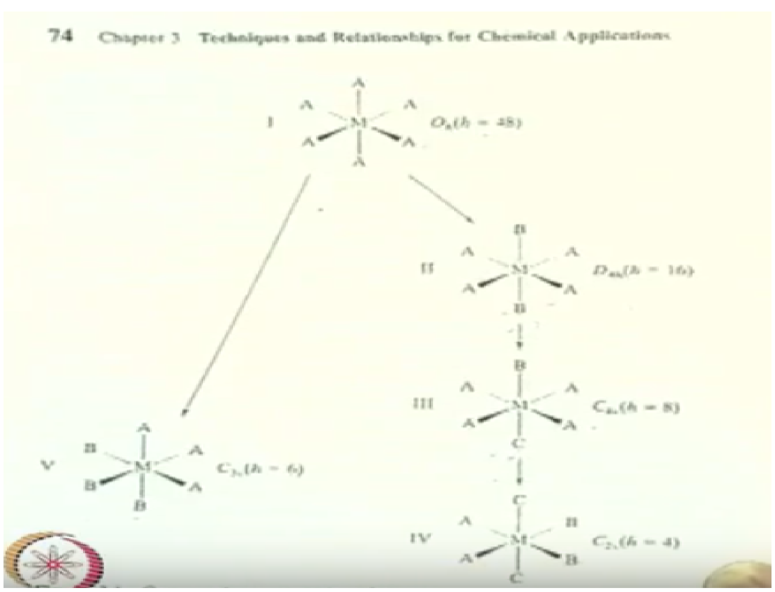

I had goofed up while drawing that diagram that time, but Carter has not goofed up okay. So this is a manifestation of descent of symmetry. You start with MA 6 that is O h and order is 48. Then what you do is you just substitute these 2 A's in axial position by B's. What is the symmetry point group now? It is D 4h, right? And D 4h is a subgroup of O h. h is only 16, actually it is better than O. But here we cannot use that. We still need to use O.

We will come back to why. And then what you do is you substitute this B by C. Then it becomes C 4v because the horizontal plane is lost and from here you can go to C 2v if you substitute this by C and substitute these 2 by B. So this is your group subgroup relationship. By chemical substitution you can go on lowering symmetry and you go from a group of higher symmetry to a group of lower symmetry, okay?

And all these groups of lower symmetry that we can arrive at by simple substitution from here would be subgroups of this bigger group. I think we had discussed this briefly earlier also, okay. And this is one kind of subgroup, this is another kind of subgroup. You cannot come to C 3v from C 4v for example. Because that C 3 axis is not even there in C 4v. Understand what I am saying? C 3v is not a subgroup of your D 4h. Because D 4h does not have a C 3 axis right?

So it depends on which symmetry elements you have sacrificed by substitution. So from O h you come to C 3v directly, no problem. What you have done is you have retained the C 3 axis but once you go from O h to D 4h you have already sacrificed the D 3 axis, C 3 axis, right? It is not there anymore. So from here you cannot go directly to C 3v. So C 3v is not a subgroup of D 4h. It is a subgroup of O h. D 4h is a subgroup of O h.

C 4v is a subgroup of O h as well as a subgroup of D 4h. From D 4h you can go to C 4v and what is the meaning of subgroup? That means some of the symmetry operations of the big group, original group are retained, some are gone, okay. Now, so what effect does this have on the character table? What effect does this have on the character table? Some of the symmetry operations are retained and some are gone. Let us see what effect it has on the character table.

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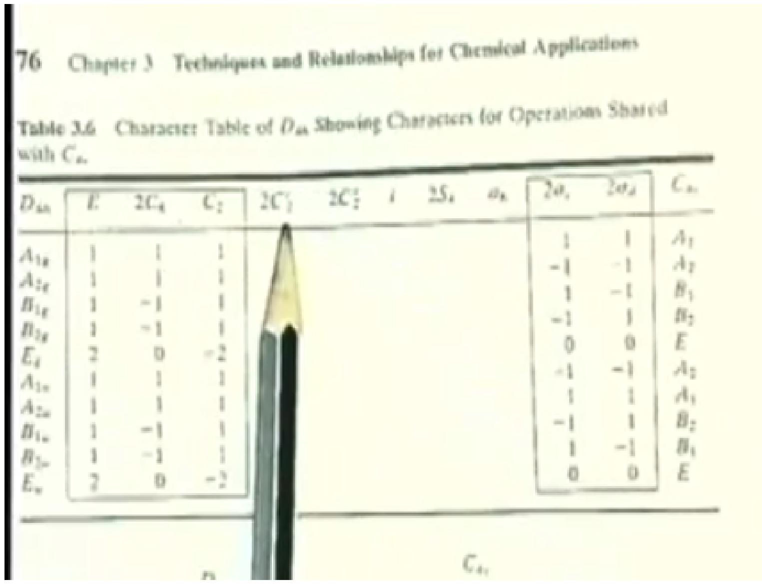

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Table 3.6 Character Table of D_{4h} Showing Characters for Operations Shared with C_{4v}

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	C_{4v}
A_{1g}	1	1	1						1	1	A_1
A_{2g}	1	1	1						−1	−1	A_2
B_{1g}	1	−1	1						1	−1	B_1
B_{2g}	1	−1	1						−1	1	B_2
E_g	2	0	−2						0	0	E
A_{1u}	1	1	1						−1	−1	A_2
A_{2u}	1	1	1						1	1	A_1
B_{1u}	1	−1	1						−1	1	B_2
B_{2u}	1	−1	1						1	−1	B_1
E_u	2	0	−2						0	0	E

So I am talking about D 4h. For now neglect this part. These are all the symmetry operations that are there in D 4h, okay? We just discussed this is it not? Is it big enough? E, 2C 4, C 2, 2C 2 dash, 2C 2 double dash, i, 2S 4, sigma h, 2 sigma v, 2 sigma d okay? Now think of a subgroup C 4v. This is D 4v. C 4v do you remember what would be the symmetry operations, C 4v. If I say C 4v principle axis is C 4. What else will be there? So C 4 square C 2 will always be there.

Sigma v will be there and see you cannot call it sigma d anymore. They also become sigma v's. Anything else that will be there? E, 2C 4 will be there. C 2 = C 4 square will be there. C 2 dash will not be there anymore right? C 2 dash is gone, right? Because you have gone from D 4h to C 4v. That horizontal plane is gone. So it is something like ammonia with another hydrogen, something like that C 4v. Something like this, okay? So there is no horizontal plane, no nothing.

C 2 double dash is gone, i is gone, S 4 is gone, sigma h is gone. 2 sigma v and 2 sigma d now combine to become 4 sigma v's is it not? So I just show you the character table then.

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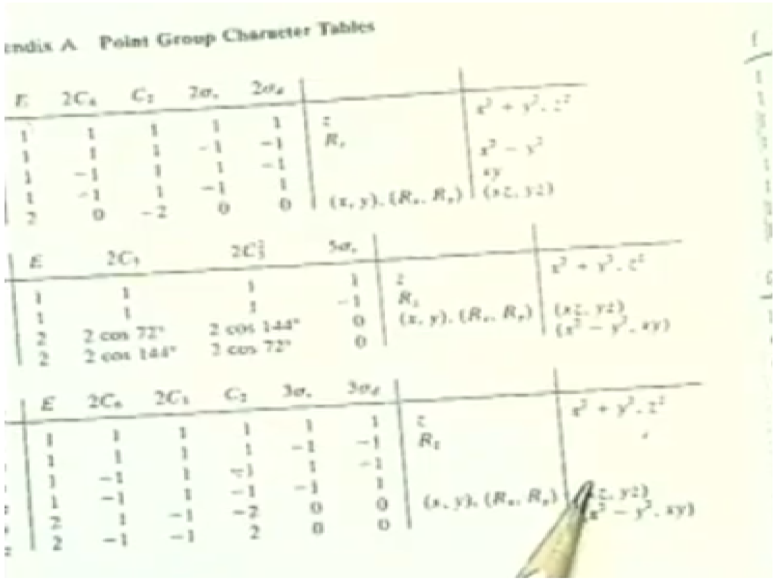

endix A Point Group Character Tables

E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
1	1	1	1	1	z	x^2+y^2, z^2
1	1	1	−1	−1	R_z	
1	−1	1	1	−1		x^2-y^2
1	−1	1	−1	1		xy
2	0	−2	0	0	$(x, y), (R_x, R_y)$	(xz, yz)

E	$2C_5$	$2C_5^2$	$5\sigma_v$		
1	1	1	1	z	x^2+y^2, z^2
1	1	1	−1	R_z	
2	2 cos 72°	2 cos 144°	0	$(x, y), (R_x, R_y)$	(xz, yz)
2	2 cos 144°	2 cos 72°	0		(x^2-y^2, xy)

E	$2C_6$	$2C_3$	C_2	$3\sigma_v$	$3\sigma_d$		
1	1	1	1	1	1	z	x^2+y^2, z^2
1	1	1	1	−1	−1	R_z	
1	−1	1	−1	1	−1		
1	−1	1	−1	−1	1		
2	1	−1	−2	0	0	$(x, y), (R_x, R_y)$	(xz, yz)
2	−1	−1	2	0	0		(x^2-y^2, xy)

C 4v. E, 2C 4, C 2 oh they actually have retained 2 sigma v 2 sigma d fine. So this 2 sigma d is also retained. This is more of a memory of the original group. It does not become sigma v, fine, my mistake, alright.

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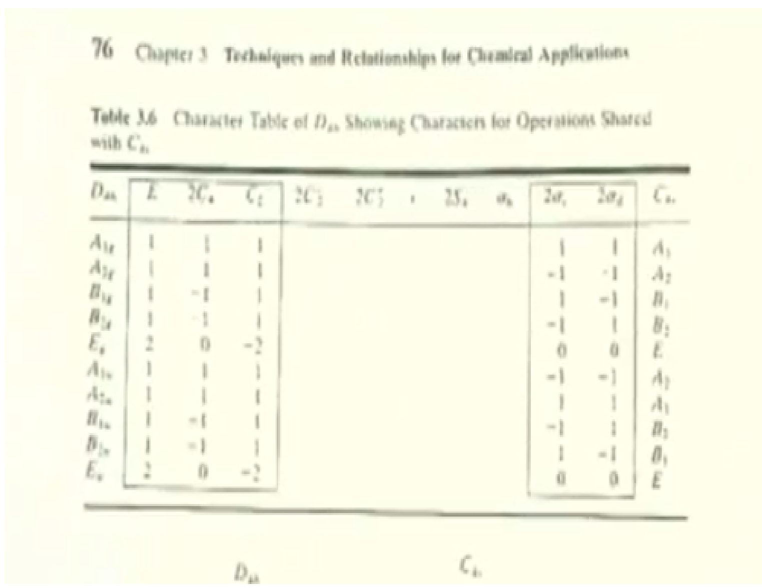

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Table 3.6 Character Table of D_{4h} Showing Characters for Operations Shared with C_{4v}

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	C_{4v}
A_{1g}	1	1	1						1	1	A_1
A_{2g}	1	1	1						−1	−1	A_2
B_{1g}	1	−1	1						1	−1	B_1
B_{2g}	1	−1	1						−1	1	B_2
E_g	2	0	−2						0	0	E
A_{1u}	1	1	1						−1	−1	A_2
A_{2u}	1	1	1						1	1	A_1
B_{1u}	1	−1	1						−1	1	B_2
B_{2u}	1	−1	1						1	−1	B_1
E_u	2	0	−2						0	0	E

D_{4h} C_{4v}

So now what we have now in this figure is that all the symmetry operations, the characters for all the symmetry operations that are not there in C 4v have been removed. Characters for all the symmetry operations that are there in C 4v as well as D 4h are retained, okay. And now what we can do is looking at these characters we can try to see what is the symmetry species with respect to C 4v.

If I do not have this, if I have all the characters then I have the symmetry species A 1g, A 2g, B 1g, B 2g, etc. for D 4h okay. Then I have all the characters in between. Please ask if it is confusing okay. Now what I am saying is now what I have done is I have only kept the characters for the symmetry operations that are retained in C 4v, okay.

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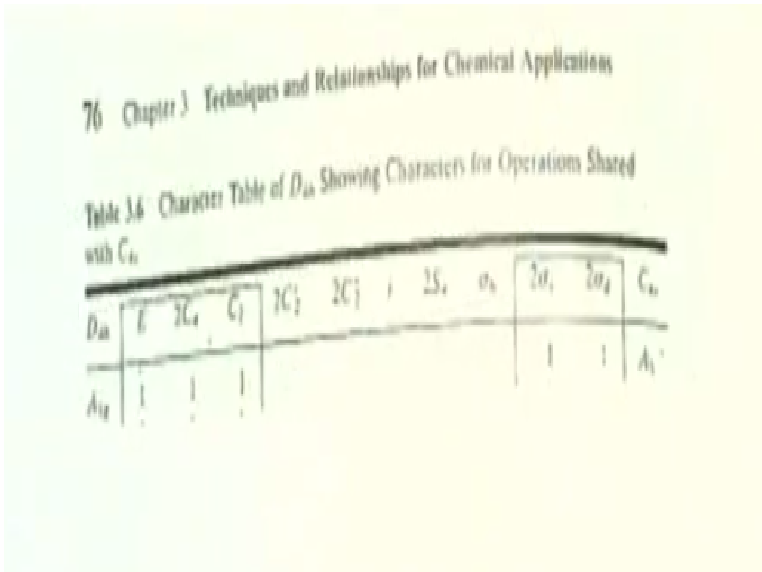

Now if I look at these lines. So what are the characters? 1, 1, 1, 1. It has to be A 1, right. So see what was A 1g in D 4h becomes A 1 in C 4v okay. So I have what is called a correspondence. Remember you studied correspondence in math some time when you were in school. One-one correspondence, one-many correspondence, many-one correspondence, remember? So now we are starting to develop a correspondence between the symmetry species of the parent group and the daughter group, okay? What is the next one? 1, 1, 1, -1, -1. You can work it out or not?

For C 4v what will the symmetry species be? Carefully moving the paper, it is A 2, understand. So similarly you can work it out for everything and this is what transpires. Is it okay now, can you see? So what was A 1g in D 4h is A 1 in C 4v. What was A 2g in B 4h is A 2 in C 4v. What was B 1g in D 4h is B 1 in C 4v. B2 g has become B 2. It has lost the respect that was there because i is gone, okay? It is not B 2g anymore, it is only B 2. E g is E.

A 1u is, A 1u is what? A 2. A 2u is A 1. So do not think that you will just drop that g and u and it will become fine. See what has happened. When you started with g you could just drop that respect thing and you would have got the label. Here for u, not only does it lose the u, but u becomes me also. 1 becomes 2, 2 becomes 1, alright, right? So now see what you could do is you could represent this as a correlation diagram is it not?

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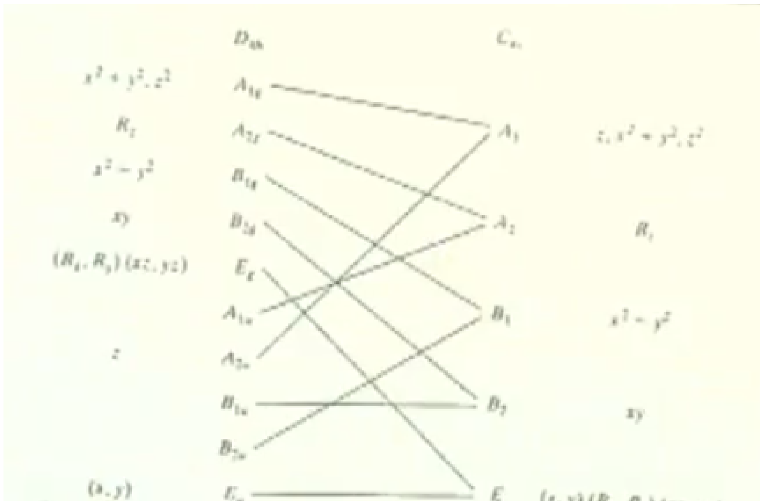

Figure 3.3 Correlation diagram showing relationships between the species of D_{4h} and C_{4v}.

A 1g becomes A 1, A 2u also becomes A 1. So what kind of correspondence is this? Many one. Let us just say many-one, okay. It is not necessarily that, it is not necessary that it is going to be many-one all the time. It can be one-many also. A 2g becomes A 2. A 1u also becomes A 2. Once again many-one. B 1g and B 2u become B u. E g and E u become E. And we have already discussed everything.

So here what happens is that it is always a 2 to 1 correspondence or many-one correspondence. But what is happening essentially is that the number of symmetry species is going down, okay? So you get kind of a merging. So see what happens to the basis. X square + y square and z square were the basis for A 1g and z was the base for A 2u. Since it is a many-one correspondence what has happened is that now z as well as x square + y square as well as z square all form basis for A 1, okay? Alright.

So what we can do is using group subgroup relation we can go down to a group of lower symmetry and consequently a smaller order, smaller number of symmetry operations. So the problem will be smaller, easier to handle and then we can go back also maybe. We can try to go back to the bigger original group, okay. That is going to be the theme of most of our work henceforth wherever we need it, not always. But now before going further on that, let me show you another example.

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hapter 3 **Techniques and Relationships for Chemical Applications**

Table 3.7 Character Table for C_{4v} Showing Characters for Operations Shared with C_{2v}

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$	
	E		C_2	σ_v, σ_v'		C_{2v}
A_1	1		1	1		A_1
A_2	1		1	−1		A_2
B_1	1		1	1		A_1
B_2	1		1	−1		A_2
E	2		−2	0		?

7. Notice that there is no representation in C_{2v} with characters corre-
g to the E representation of C_{4v}. We can determine the two repre-
ns of C_{2v} that correlate to this set of characters by treating them as
ng a reducible representation, Γ_E, in the smaller group. By inspec-
see that $\Gamma_E = B_1 + B_2$.

C 4v and C 2v. C 4v and C 2v are also group subgroups. C 2v is a subgroup of C 4v. For C 4v what do you have you have E, 2C 4, C 2, 2 sigma v, 2 sigma d. And C 2v everywhere he knows by heart you have E, C 2v, 2 sigma v okay. Once again, the character table of C 2v is blocked out here and this is the correlation diagram.

There is something interesting here. Earlier, see what happened, the original group the parent group as well as the subgroup both had 2-dimensional representations right. So the two 2-dimensional representations just became the 2-dimensional representation that was there in the subgroup is it not? Here however we got a problem. Because C 2v famously does not have more than one-dimensional representations, right?

So now what is bound to happen is that this E group is going to split. That is what is shown here. A 1, 1, 1, 1 is of course A 1 in C 2v. A 2, 1, 1, -1 is A 2 in C 2v. B 1 is 1, 1, 1 A 1 in C 2v okay. B 2, 1, 1, -1 is A 2 in C 2v. Problem lies with E because the characters are 2, -2, 0. There is no 2, -2, 0 in C 2v. So as far as C 2v is concerned 2, -2, 0 is bound to be a reducible representation okay which of course is bayen haath ka khel for all of us now. We have a reducible representation, we know how to reduce it, right? Apparently it was not so bayen haath ka khel for the author so he has shown it like a bacha. But you know how to do it right? You can work out the coefficients and you can infer that E becomes B 1 + B 2. So now when we draw the correlation diagram, this is what the correlation diagram looks like.

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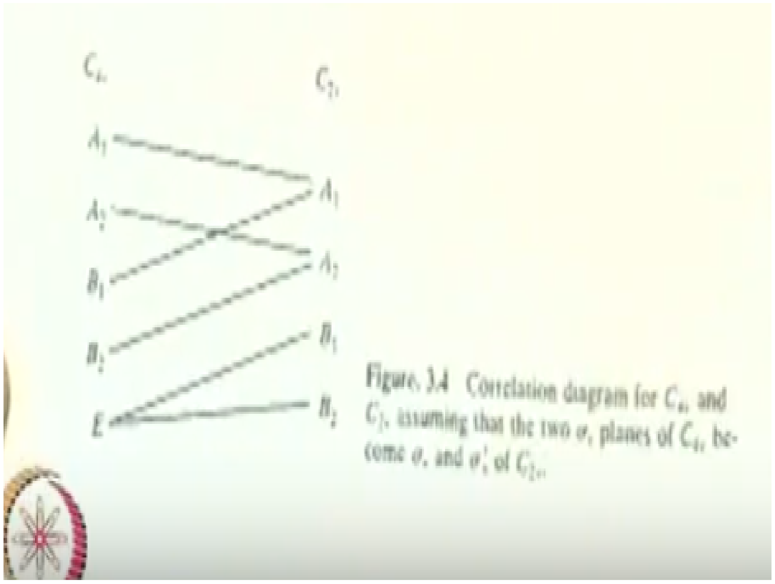

A 1, A 2, B 1, B 2, E and here you have A 1, A 2, B 1, B 2. A 1, B 1 become A 1. A 2 and B 2 become A 2 and E splits into B 1 and B 2. So this is an example where you have many to one as well as one-many correspondence, okay? Now I want to give you a homework problem. Before that I need to discuss a little bit. I am digressing, I am digressing from that O h O problem. We will go there but before that let us discuss something.

See this group subgroup relation is obviously going to be very convenient where we have large groups, right? What are the largest groups that you can think of? The largest groups are for the no, not icosahedron. Icosahedron is complicated. The largest groups are for the simplest molecules. H 2 and H Cl. C infinity H and D infinity, C infinity V and D infinity H, right? So that is where this group subgroup relation is bound to be very useful.

So I just want to introduce that today and give you a problem that I did not get time to discuss in the previous class is there in Carter's book. Right now what I am showing is Carter's book. Please go through the problem.

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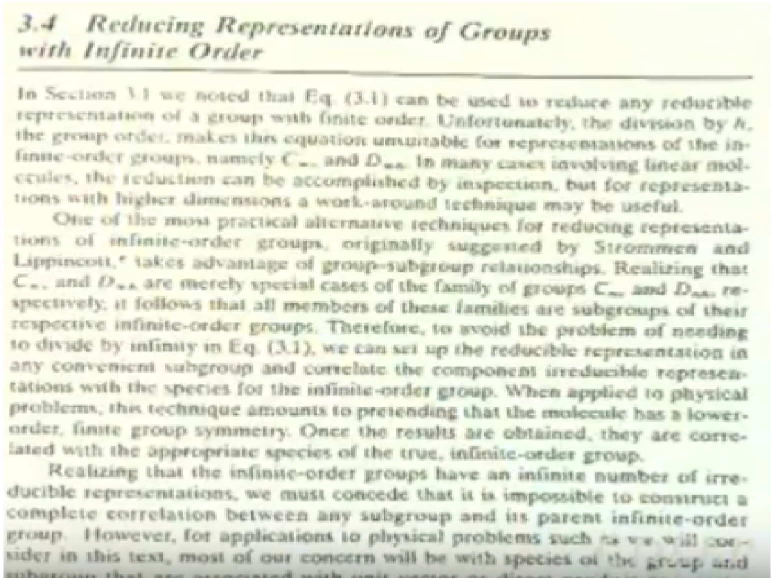
3.4 Reducing Representations of Groups with Infinite Order

In Section 3.1 we noted that Eq. (3.1) can be used to reduce any reducible representation of a group with finite order. Unfortunately, the division by h, the group order, makes this equation unsuitable for representations of the infinite-order groups, namely $C_{\infty v}$ and $D_{\infty h}$. In many cases involving linear molecules, the reduction can be accomplished by inspection, but for representations with higher dimensions a work-around technique may be useful.

One of the most practical alternative techniques for reducing representations of infinite-order groups, originally suggested by Strommen and Lippincott,* takes advantage of group–subgroup relationships. Realizing that $C_{\infty v}$ and $D_{\infty h}$ are merely special cases of the family of groups C_{nv} and D_{nh}, respectively, it follows that all members of these families are subgroups of their respective infinite-order groups. Therefore, to avoid the problem of needing to divide by infinity in Eq. (3.1), we can set up the reducible representation in any convenient subgroup and correlate the component irreducible representations with the species for the infinite-order group. When applied to physical problems, this technique amounts to pretending that the molecule has a lower-order, finite group symmetry. Once the results are obtained, they are correlated with the appropriate species of the true, infinite-order group.

Realizing that the infinite-order groups have an infinite number of irreducible representations, we must concede that it is impossible to construct a complete correlation between any subgroup and its parent infinite-order group. However, for applications to physical problems such as we will consider in this text, most of our concern will be with species of the group and

So how do you reduce representations of groups of infinite order. What would be the first step? I want to bring some sanity into this infinite groups. What will I do? Which symmetry operation will I try to get rid of? Or which symmetry element. Definitely C infinity, right? The moment you change C infinity to a smaller C then what you have is in place of an infinite group I am going to have a finite group, right? So the general practice is this. Go from the most difficult problem to the easiest problem.

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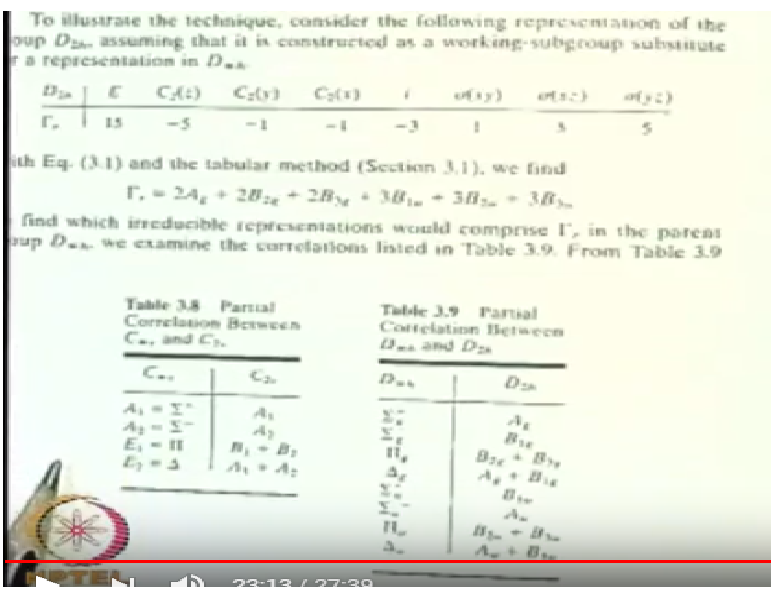
To illustrate the technique, consider the following representation of the group D_{2h}, assuming that it is constructed as a working-subgroup substitute for a representation in $D_{\infty h}$.

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
Γ_r	15	−5	−1	−1	−3	1	5	5

With Eq. (3.1) and the tabular method (Section 3.1), we find

$$\Gamma_r = 2A_g + 2B_{2g} + 2B_{3g} + 3B_{1u} + 3B_{2u} + 3B_{3u}$$

To find which irreducible representations would comprise Γ_r in the parent group $D_{\infty h}$, we examine the correlations listed in Table 3.9. From Table 3.9

Table 3.8 Partial Correlation Between $C_{\infty v}$ and C_{2v}

$C_{\infty v}$	C_{2v}
$A_1 = \Sigma^+$	A_1
$A_2 = \Sigma^-$	A_2
$E_1 = \Pi$	$B_1 + B_2$
$E_2 = \Delta$	$A_1 + A_2$

Table 3.9 Partial Correlation Between $D_{\infty h}$ and D_{2h}

$D_{\infty h}$	D_{2h}
Σ_g^+	A_g
Σ_g^-	B_{1g}
Π_g	$B_{2g} + B_{3g}$
Δ_g	$A_g + B_{1g}$
Σ_u^+	B_{1u}
Σ_u^-	A_u
Π_u	$B_{2u} + B_{3u}$
Δ_u	$A_u + B_{1u}$

So when you are working with D infinity H change that infinity axis to a C 2 axis, okay? So go from C infinity to C 2. Largest to smallest. C 1 axis is of course is just E right. So when you do this these are the partial correlations. It has to be partial correlation, right? It has a infinite number of symmetry species anyway. So this is a partial correlation between C infinity v and C 2v. This is a partial correlation between D infinity h and D 2h, okay.

So what I like you to do is this. Thus shown you this reducible representation, okay? And that they have been kind enough to work it out for you to say that this is 2A g + 2B g + 2B 3g + 3B 1u + 3B 2u + 3B 3u right? Now I want to go back to the D infinity h group. What will be this breakdown? Look at this A g is what, sigma g +, the totally symmetric group. So instead of A g I am going to write sigma g +. Please write down sigma g +.

One sigma g + for every A g. So how many sigma g pluses do we have? How many sigma g + symmetry species do we have? You understand the problem right? For some problem, I have gone from D infinity h to D 2h and I have got this representation. Do not worry about what the basis is and this has broken down into this linear sum okay. Now I want to I am trying to go back to D infinity h okay using this correlation diagram.

Correlation diagram has to be either provided or you have to work it out. Here it is provided, okay? So instead of 2A g I am going to write 2 sigma g +. What will I write in place of 2B 2g? B 2g + B 3g is pi g. Do you have B 2g + B 3g here? We do. 2 multiplied by B 2g + B 3g. So it is 2 B 2g + B 3 g becomes 2 pi g, right? 2 pi g. So, so far we have got 2 sigma g +, plus 2 pi g. What next? 3B 1u. So B 1u can be sigma u plus but it can also be delta u.

What is it going to be? There are 3, so it can be sigma g plus + delta u also. Then there has to be an A u, right? So you do not worry about it. So what will it be? 3 sigma u + right? 3 sigma u +. What is left? 3 multiplied by B 2u + B 3u. What is that? Pi u. So 3 pi u. So this is how we can go from a larger group to a subgroup and back, okay? This is the answer that you must have got.

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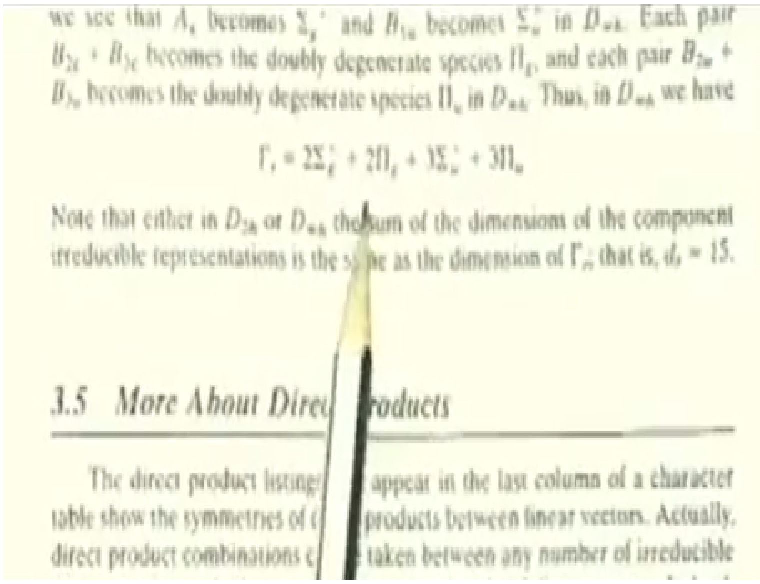

we see that A_g becomes Σ_g^+ and B_{1u} becomes Σ_u^+ in $D_{\infty h}$. Each pair $B_{2g} + B_{3g}$ becomes the doubly degenerate species Π_g, and each pair $B_{2u} + B_{3u}$ becomes the doubly degenerate species Π_u in $D_{\infty h}$. Thus, in $D_{\infty h}$ we have

$$\Gamma_r = 2\Sigma_g^+ + 2\Pi_g + 3\Sigma_u^+ + 3\Pi_u$$

Note that either in D_{2h} or $D_{\infty h}$ the sum of the dimensions of the component irreducible representations is the s ne as the dimension of Γ_r; that is, $d_r = 15$.

3.5 More About Direc roducts

The direct product listing appear in the last column of a character table show the symmetries of c products between linear vectors. Actually, direct product combinations c taken between any number of irreducible

Sigma R = 2 sigma g plus + 2 pi g + 3 sigma u plus + 3 pi u, okay. Now with that background I would like you to do some self-study. Page 117 to 126. It is basically carbon dioxide. Carbon dioxide as sigma as well as pi bonds, right? Please take this as a self-study problem. MH 6 is an octahedral molecule O h point group. I have been kind enough to tell you that the reducible representation in using the 6 1s orbitals on the hydrogen atoms gets broken down into A 1g + E g + T 1u.