

Theory of Group for Physics Applications
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Lecture – 24
Character tables & molecular Applications - II

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C_{3v} Character Table

	E	$2C_3$	$3\sigma_v$	linear	quadratic
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	-1	R_z	$(x^2 - y^2, xy)$
E	2	-1	0	$(x, y), (R_x, R_y)$	(xz, yz)

The third representation can be found from orthogonality and $\chi(E) = 1$.

Note:

- C_3 and C_3^2 are identical after a C_3 rotation and are thus in the same class ($2C_3$)
- The three mirror planes are identical after C_3 rotations \rightarrow same class ($3\sigma_v$)
- The E representation is two dimensional ($\chi(E) = 2$), mixing x, y . This is a result of C_3 .
- x and y considered together have the symmetry of the E representation

Try proving that this character table actually has the properties expected of a character table.

So, that is not altogether clear the way it is introduced here, but we will see little bit later. So, the way at this point I would say is you think of the z rotation and well actually we have not found a geometric way of identifying what this A_2 is, in it. So, for the time being let this being will come back to it. The whole molecule is considered and we consider all the axes anytime, so on, ok. So, let us look at the second part.

So, the application of symmetry and here as he says promises that we will learn something about IR and Raman spectra can be interpreted using symmetry. So, here is a slightly more realistic molecule and we are going to work out its character table and then also work out the spectroscopic content. So, there are 2 nitrogens and 4 oxygens, and 2 O_4 , this is a D_{2h} , D_2 basically meaning it basically because the it does not have 90 degree rotation symmetry only 180, but it has dihedral planes. So, it has the plane which contains the molecule itself is part of the symmetry group.

Now, begins the physical thing where we will come to the rotations the elements of rotation as well. So, for N_2O_4 we may predict that there will be $(3N-6)$ vibrational modes

because for any molecule the 3 degrees of rotation which are just bulk translation of the molecule and the 3 rotations which are just rigid rotation of the molecule as a whole they do not enter spectroscopy. So, they have to be subtracted out.

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Using Symmetry: Vibrational Spectroscopy

IR and Raman spectra can be interpreted using symmetry.

- For nonlinear molecules, the number of vibrational modes is $3N - 6$, where N is the number of atoms and $3N$ the number of degrees of freedom
- Consider N_2O_4 , which is D_{2h}
- Each atom can move in three dimensions
 - If all atoms move the same amount in the same direction the molecule moves, which is a translation, not a vibration (accounts for three degrees of freedom)
 - Molecule can also rotate around the three orthogonal axes (which accounts for three more degrees of freedom)
- So for N_2O_4 we predict that there will be $3N - 6 = 12$ vibrational modes

The slide includes a chemical structure of N_2O_4 (two nitrogen atoms bonded together, each with two oxygen atoms) and a 3D coordinate system with x and y axes.

So, if there are 6 elements then there are totally 18 elements, but out of which 6 have to be always subtracted. So, 3 times the number of atoms in the molecule 3 and minus 6 that many vibrational modes can be there with stress and strain the molecule.

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Using Symmetry: Vibrational Spectroscopy

We can use character tables to determine the symmetry of all 18 motions and then assign them to translation, rotation, or vibration.

We can also tell which vibrations are IR or Raman active.

Procedure:

- Assign x,y,z coordinates to each atom.
- Determine how each axis transforms for every class of symmetry operation in the group.
 - If an atom moves, the character for all of its axes is 0
 - If an atom is stationary and the axis direction is unchanged, its character is 1
 - If an atom is stationary and the axis direction is reversed, its character is -1
- Sum the characters in each class to determine the reducible representation Γ

The slide includes a chemical structure of N_2O_4 with x, y, and z axes assigned to each atom.

Now, says we can find character tables to determine symmetry of all the 18 motions. This is where we will get into motions like R_x , R_y also, which are translations rotations and vibrations. So, first take each of these and assign x, y, z coordinate to them determine how each of the axis transforms for every class of symmetry operation in the group. Now because we are clever we already know what are classes we do not bother writing individual elements in a class. And this is the simple rule.

If an atom moves the character for all its axis is 0, if an atom is stationary and the axis direction is unchanged then the character is +1, if atom direction is reverse and character is -1. And the sum of the characters in each class to determine the irreps of the whole representation. So, for each of the molecules we calculate this and then add to get.

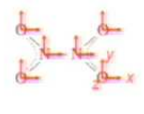
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Using Symmetry: Vibrational Spectroscopy

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
Γ	18	0	0	-2	0	6	2	0

E : all 18 axes unchanged $\rightarrow \chi = 18$
 $C_2(z)$: all atoms move $\rightarrow \chi = 0$
 $C_2(y)$: all atoms move $\rightarrow \chi = 0$
 $C_2(x)$: oxygens move
 N's x unchanged
 N's y,z reversed $\rightarrow \chi = -2$
 i : all atoms move $\rightarrow \chi = 0$
 $\sigma(xy)$: z axes reversed
 x,y axes unchanged $\rightarrow \chi = 6$
 $\sigma(xz)$: oxygens move
 N's x,z unchanged
 N's y reversed $\rightarrow \chi = 2$
 $\sigma(yz)$: all atoms move $\rightarrow \chi = 0$

Γ is the reducible representation for all motions of N_2O_4



So, if we want the bulk representation with identity containing 18 elements as many as there are axis for each of the atoms. And then the characters are computed for each of the class of motions. So, for example, you take C_2 which is the 180 degree rotation around the z axis and ask what happens under that to z.

So, following this rule if an atom moves then the character for all its axis is 0. So, under z rotation which is with this as thus the centre of the molecule has the axis. If you rotate all the atoms are rotating in it.

So, under this z axis rotation the character is just 0, then if you look under the same rotation the fate of y again all the atoms move, so you get 0. So, C_2 of x the oxygen's all move, but the N's of the x are unchanged and N's of the y and z are reversed. So, in this case y is. So, x axis is this way.

So, the after the rotation the x of the two N's are not changed, but the y and z are reversed. So, under 180 degree rotation C_2 which is about the x axis the x axis is pointing this way and if you rotate then the x's are unchanged, but y and z are reversed because you will carry out a rotation like this.

So, for individual atoms its individual coordinate you have to see its fate under this rotation. So, under x rotation this is what happens and so the character of this C_{2x} is -2, because that is the one in which at least two of the coordinates the x components of these are not touched, but the other two everything is everything moves. So, around in the x axis rotation and in the y axis rotation everything moves. So, you get 0s there.

Then the reflection planes. So, σ_{xy} , in the xy plane only the z axis is reversed for all the molecules, for all the atoms in the molecule if you do a xy rotation the z axis is reversed. But x and y axis are unchanged. So, for the reversals you will get minus signs for the things that remain unchanged you will get plus signs. So, totally you will get 6, I am not calculated this, but I think that is what its saying and so on.

The yz reflection if you take, the yz plane and flip all the atoms move, so character is 0. So, there is a shortcut way of calculating the character of this given, this is not an irrep this you are doing the generic 3D rotations and for that particular representation one can just calculate all the characters and under identity nothing moves so we get 18 and so on.

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Using Symmetry: Vibrational Spectroscopy

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	I	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
Γ	18	0	0	-2	0	6	2	0

4. Now reduce Γ to its irreducible components using the character table and the following property of groups:

$$\# \text{ of irreducible representations of a given type} = \frac{1}{\text{order}} \sum_R \left(\# \text{ of operations in the class} \times \text{character of reducible representation} \times \text{character of irreducible representation} \right)$$

$\# A_g = 1/8 [18+0+0+2+0+6+2+0] = 3$
 $\# B_{1g} = 1/8 [18+0+0+2+0+6-2+0] = 3$
 $\# B_{2g} = 1/8 [18+0+0+2+0-6+2+0] = 2$
 $\# B_{3g} = 1/8 [18+0+0-2+0-6-2+0] = 1$
 $\# A_u = 1/8 [18+0+0-2+0-6+2+0] = 1$
 $\# B_{1u} = 1/8 [18+0+0+2+0-6+2+0] = 2$
 $\# B_{2u} = 1/8 [18+0+0+2+0+6-2+0] = 3$
 $\# B_{3u} = 1/8 [18+0+0-2+0+6+2+0] = 3$

So, $\Gamma = 3A_g + 3B_{1g} + 2B_{2g} + B_{3g} + A_u + 2B_{1u} + 3B_{2u} + 3B_{3u}$

Character table for D_{2h} point group

	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	I	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
A_g	1	1	1	1	1	1	1	1
B_{1g}	1	1	1	-1	1	1	-1	-1
B_{2g}	1	1	-1	1	1	-1	1	-1
B_{3g}	1	1	-1	-1	1	1	-1	1
A_u	1	1	1	1	-1	-1	-1	-1
B_{1u}	1	1	1	-1	-1	-1	1	1
B_{2u}	1	1	-1	1	-1	1	-1	1
B_{3u}	1	1	-1	-1	-1	1	1	-1

So, now, the question is how do we split this up into irreducible representations and uses the theorem that we equal quoting today m , the x the weightage of a particular irrupt in a particular irreducible rep is equal to 1 over the size of the group times number of operations in a class, the p_i times the character D times $*$. So, character of reducible representation, times character of the irreducible representation in that class and sum over the class this is our formula right, you remember this formula.

So, now, it begins to look very busy and complicated, but it is not really except that he is filled out here the entire character table which we do not have time to derive right now and he has also borrowed, but let us see all the classes in it. So, if you look at the top row which lists all the classes there is class of the identity, then there is class of C_{2z} , z axis rotation, y axis rotation, and x axis rotation.

So, each one has different effects because the there are 2 nitrogen's lying along one axis. So, if you do x axis rotation versus y axis rotation you get different classes, if they are not equivalence class. And then there is full space inversion I and then there are reflections in the xy plane which flip z axis or xz plane and zx plane, just if you look at the molecule once again it is clear that all of these are possible ok, yeah.

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Using Symmetry: Vibrational Spectroscopy

The reducible representation is the sum of 18 irreducible reps:
 $\Gamma = 3A_g + 3B_{1g} + 2B_{2g} + B_{3g} + A_u + 2B_{1u} + 3B_{2u} + 3B_{3u}$

5. Now use the character table to subtract the translations and rotations, leaving the representations corresponding to the vibrations.

Translations (X, Y, Z) = $B_{1u} + B_{2u} + B_{3u}$
 Rotations (R_x, R_y, R_z) = $B_{1g} + B_{2g} + B_{3g}$
 Vibrational modes (all that remain) = $3A_g + 2B_{1g} + B_{2g} + A_u + B_{1u} + 2B_{2u} + 2B_{3u}$

These are the symmetries of the 12 vibrational modes of N_2O_4

	E	C_2	C_2	C_2	C_2	i	σ	σ	σ	σ
A_g	1	1	1	1	1	1	1	1	1	1
B_{1g}	1	1	1	-1	-1	1	1	1	-1	-1
B_{2g}	1	1	-1	1	-1	1	1	-1	1	-1
B_{3g}	1	1	-1	-1	1	1	-1	1	-1	1
A_u	1	1	1	1	1	-1	-1	-1	-1	-1
B_{1u}	1	1	1	-1	-1	-1	-1	1	1	1
B_{2u}	1	1	-1	1	-1	-1	-1	1	-1	1
B_{3u}	1	1	-1	-1	1	-1	-1	1	1	-1

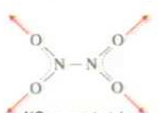
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Using Symmetry: Vibrational Spectroscopy

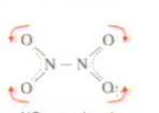
Let's consider the vibrational modes of N_2O_4 in a little more detail.

Vibrations = $3A_g + 2B_{1g} + B_{2g} + A_u + B_{1u} + 2B_{2u} + 2B_{3u}$

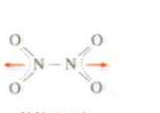
Using the table, we can guess what these modes might look like.
 e.g., the three A_g modes are totally symmetric:



NO₂ sym. stretch

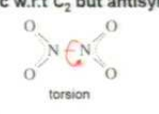


NO₂ sym. bend



N-N stretch

the A_g mode is symmetric w.r.t C_2 but antisymmetric w.r.t σ and i :



torsion

So, now, this table is then filled out, this is the thing we are skipping right now, but in principle you identify this g the g the once that remain symmetric and the once that are not g and so there are a's and b's I do not know this notation or detail very well.

But hopefully since we know there are these many classes we expect that many irrep and since there are that many ones available we have to fill with ones are -1s and then by orthogonality the sum we can guess and the others we can fill up by orthogonality. And we can also classify the properties at least of xy I can argue the R_z , R_y at least in this

particular table. So, at least in this table we can see that that R_z corresponds to has the same properties as xy . So, it is essentially xy rotation and R_y is xz rotation and R_x is yz rotation.

So, the product of the two axis as same property as the proper rotation in that plane ok. And these classes are the irreps are identified by what they do to each of these and then there are the ones that reverse the signs of x , y and z . The point is we can construct this kind of a table for this molecule and once you do it you can now resolve your generic representation which you take to be 18 dimensional where all the x y and z for each of the atoms is used as a carrier space.

The carrier space now which is not written here the carrier space now is all the atom all the coordinates of all the atoms for that representation the identity will contain 18, it will be a size 18 representations. So, I character of identity will be 18 and then these characters were figured out like on the previous page.

So, this particular character table that was worked out it can be resolved into the irreps by using this and one can find out the weightage factors of each of these.

So, that is filled up in the next page. So, this is the statement now the 18 sized reducible representation can be split up into the 8 classes, you can count here. So, there is a mistake here 8 not 18, 8 irreducible representations this can be split like this with the weightage factors as worked out here by doing the full orthogonality thing.

So, what does all this mean? Well, what now we can do is identify the properties of the vibrational modes. So, now, he point out that in this table after all the there are out of the 18th dimensional representation 3 things are just the bulk motion of the whole molecule. So, where x y and z axis moved and those correspond to B_{1u} , B_{2u} and B_{3u} . So, they are identified here B_1 , B_2 , B_3 this is the fate of x , y and z and then there are rotations about the x axis, y axis and z axis and these happened to be B_{1g} , B_{2g} , B_{3g} .

So, as you remember u was, g was symmetric u was unsymmetric and if you have two axis then, the signs of both cancel each other and remain symmetric if you have only one axis then you get a signs. So, it remains unsymmetric.

But these 6 are essentially to be removed ones, the translations will contain each of these ones and rotations of the bulk molecule will contain each of the B_{1g} , B_{2g} , B_{3g} ones. So, we remove 1 1 out of these ok. So, B_{1u} is here it has weightage two here, we knock one of them off and we are left with one B_{1u} . So, let us it 3 A_g because A_g is not to be removed, but B_{1u} should be there is should be only one here, so 1 B_{1u} . So, this 2 B_{1u} becomes 1 B_{1u} . The B_{2u} , from 3 B_{2u} it will become 2 B_{2u} and B_{3u} becomes 2 B_{3u} .

So, we remove the contributions to this character which comes just from bulk motion of the molecule therefore, what remains are all the vibrational degrees of freedom and its size should be 12 now this representation. If this is the formula for vibrations the generic vibration you will have all of these present ok. And in fact, is pointing out what in physics we call normal modes if you actually setup the lagrangian of this system with the symmetry is correctly then you will find that you can diagonalize the. So, you will have let us say interaction between N and O, N and O, but so the coordinates of this and coordinates of this will be coupled coordinates of this and this will be coupled.

So, you will have a term like $\frac{1}{2} kx^2$, the potential energies $\frac{1}{2} kx^2$. So, if the strength of this bond is some spring constant k then you will have $\frac{1}{2} k$ times position of this O minus position of this N the difference squared in the potential energy. So, if you write the potential energy if you now find the equations of motion which are derivatives of this you will get linear terms, but so equation of motion \ddot{x} will contain $x - y - k_x - y$.

So, the right hand side will be a matrix this mixes x and y , y and z and so on. But the theorem you will learning classical mechanics is that you can diagonalize this matrix. So, that you identify vibrational modes that are eigen modes of this matrix of oscillations. And that is what he has essential indicated here just heuristically you can guess what will be eigen modes. So, simplest mode he as shown is where each of the bonds stretches symmetrically by exactly same amount on all sides, ok. This is one mode.

Another mode where that two O's come together or go away from each other; So, instead of focusing on only one of them if you look at the collective thing then it is easier to see what will be the eigen modes, but algebraically you will find them if you carry out that canonical transformation of the coordinates.

A_u mode is symmetric. So, there is a rotation about this which will not mix with anyone, anything else.

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Using Symmetry: Vibrational Spectroscopy

The character table tells us whether the vibrational modes are IR active and/or Raman active.

To be **IR active** (allowed), the vibration must change the dipole moment of the molecule.

- Only irreducible representations with x, y, z symmetry do this

N_2O_4 vibrations = $3A_g + 2B_{1g} + B_{2g} + A_u + B_{1u} + 2B_{2u} + 2B_{3u}$

IR active: $B_{1u} + 2B_{2u} + 2B_{3u}$

Character table for D_{2h} point group

	E	C_2	C_2	C_2	C_2	i	σ	σ	σ	σ	Linear functions	Quadratics
	x, y, z	x, y, z	x, y, z	x, y, z	x, y, z	x, y, z	x, y, z	x, y, z	x, y, z	x, y, z	x, y, z	x, y, z
A_g	1	1	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	1	-1	-1	1	1	1	-1	-1	R_z	xy
B_{2g}	1	1	-1	-1	1	1	-1	-1	1	1	R_y	xz
B_{3g}	1	1	-1	1	-1	1	-1	1	-1	1	R_x	yz
A_u	1	1	1	1	1	-1	-1	-1	-1	-1		
B_{1u}	1	1	1	-1	-1	-1	-1	-1	1	1	x	
B_{2u}	1	1	-1	-1	1	-1	1	1	-1	-1	y	
B_{3u}	1	1	-1	1	-1	-1	1	-1	1	1	z	
A_g	1	1	1	1	1	1	1	1	1	1		

NPTEL

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So, the only the irreducible representations with x, y and z symmetry do this because the dipole moment is proportional to coordinate x, y and z and so only the ones that, so from this list we written only the ones that touch x, y and z you know here bottom as was shown on the previous transparency is red yeah this red box is the x y z box and that is the only one that really matters to IR.

So, drop the A_g , drop the B_g drop all the g's and drop the A_u 's well and you are left with 1 B_u , 2 times 2 B_u and 2 times 3 B_u and so these are the only things you will get in the IR spectrum of the molecule.

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Using Symmetry: Vibrational Spectroscopy

The character table tells us whether the vibrational modes are IR active and/or Raman active.

To be Raman active (allowed), the vibration must change the polarizability of the molecule.

- Only irreducible representations that transform like the binary products of x, y , and z (i.e., $xy, xz, yz, x^2, y^2, z^2$ or their linear combinations) do this

N_2O_4 vibrations = $3A_g + 2B_{1g} + B_{2g} + A_u + B_{1u} + 2B_{2u} + 2B_{3u}$

Raman active: $3A_g + 2B_{1g} + B_{2g}$

*Note that the A_u mode is IR and Raman silent.

	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	σ_{xy}	σ_{xz}	σ_{yz}	Raman	IR
A_g	1	1	1	1	1	1	1	1	g	+
B_{1g}	1	1	1	-1	1	1	1	-1	R_x	+
B_{2g}	1	1	-1	1	1	-1	1	-1	R_y	+
B_{3g}	1	1	1	-1	1	-1	-1	1	R_z	+
A_u	1	1	1	1	-1	-1	-1	1	u	-
B_{1u}	1	1	1	-1	-1	-1	1	1	x	+
B_{2u}	1	1	-1	1	-1	1	1	-1	y	+
B_{3u}	1	1	1	-1	-1	1	-1	1	z	+

And similarly to be Raman active I hope you all know what is Raman effect; it is produces supplementary lines around the main line and that happens due to polarizability. So, for to be Raman active the vibration must change the polarizability of molecule and this happens when the irreducible representations transform like the binary products of x, y and z .

So, it was either x, y 's you know any of these. And that in this table is this set of actions shown here and so only the g's matter. The subscript g elements matter. And you can now imagine why they have device this notation because what the type g will all enter the Raman spectrum. So, the first 3 terms matter and the rest do not matter to it.

And in fact, the A_u does not enter anything, we can check what is A_u . So, A_u is this particular irrep where the 3 kinds of rotations did nothing have character 1. So, if we certainly note that A_u does not has no specific properties under either x or under products of x and y and it does not show up in the IR or Raman spectroscopy.

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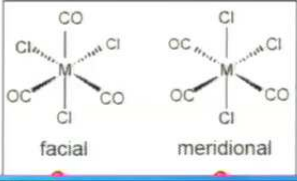
Using Symmetry: Selected Vibrational Modes

We may be interested in the vibrations of specific groups in a molecule rather than all possible motions of the molecule.

e.g., C-O stretching in metal carbonyl complexes

In this case, we can create reducible representations of the bond vectors of interest, determine their irreducible components, and find the active modes.

Example: can we use IR/Raman spectroscopy to distinguish between *fac*- $\text{ML}_3(\text{CO})_3$ and *mer*- $\text{ML}_3(\text{CO})_3$ isomers?



facial meridional

So, that is basically the summary of this and there is an example that has been worked out using this which you can read because I have put up the transparency.

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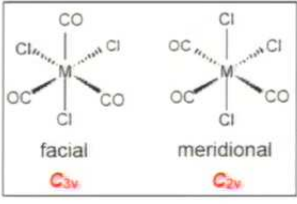
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facial meridional

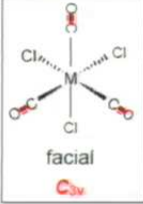
C_{3v} C_{2v}

This particular; just to explain what it is about; He says how will you distinguish the same chemical content molecule $\text{ML}_3(\text{CO})_3$, and so *fac* and *mer* were the chlorine and the CO radicals are exchanged, ok.

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Using Symmetry: Selected Vibrational Modes

Let's create reducible representations of the C-O bonds in each molecule:



$\chi = 1$ if unchanged
 $\chi = 0$ if changed

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ	3	0	1

Character table for C_{3v} point group

	E	$2C_3$ (120°)	$3\sigma_v$	linear, rotations	quadratic
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	(x, y) (R_x, R_y)	x^2-y^2, xy (xz, yz)

Reduce to irreducible representations:

$$\text{\# of irreducible representations of given type} = \frac{1}{\text{order}} \sum \left(\begin{matrix} \text{\# of operations in the class} \\ \times \end{matrix} \begin{matrix} \text{character of reducible representation} \\ \times \end{matrix} \begin{matrix} \text{character of irreducible representation} \end{matrix} \right)$$

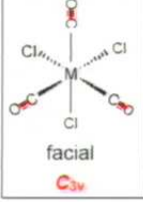
$\# A_1 = 1/6[3+0+3] = 1$
 $\# A_2 = 1/6[3+0-3] = 0$
 $\# E = 1/6[6+0+0] = 1$

So, this chlorine and this CO basically are exchange, but the rest of the stuff does not change its location with respect to some central thing M. And so he points out that this then because of the symmetric placement of the chlorines has a C_{3v} symmetry whereas, this has only C_{2v} symmetry because now there is no rotational symmetry, only a 180 rotation. So, therefore, the weightages of the various symmetry classes will reduce between the two.

(Refer Slide Time: 24:04)

Using Symmetry: Selected Vibrational Modes

Let's create reducible representations of the C-O bonds in each molecule:



$\chi = 1$ if unchanged
 $\chi = 0$ if changed

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ	3	0	1

Character table for C_{3v} point group

	E	$2C_3$ (120°)	$3\sigma_v$	linear, rotations	quadratic
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	(x, y) (R_x, R_y)	x^2-y^2, xy (xz, yz)

Reduce to irreducible representations:

$$\text{\# of irreducible representations of given type} = \frac{1}{\text{order}} \sum \left(\begin{matrix} \text{\# of operations in the class} \\ \times \end{matrix} \begin{matrix} \text{character of reducible representation} \\ \times \end{matrix} \begin{matrix} \text{character of irreducible representation} \end{matrix} \right)$$

$\# A_1 = 1/6[3+0+3] = 1$
 $\# A_2 = 1/6[3+0-3] = 0$
 $\# E = 1/6[6+0+0] = 1$

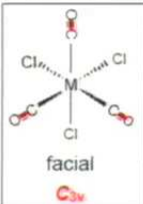
So, $\Gamma = A_1 + E$

And from that you can see that which, so this the fac isomer is expected to have two peaks in both its IR and Raman.

(Refer Slide Time: 24:05)

Using Symmetry: Selected Vibrational Modes

Let's create reducible representations of the C-O bonds in each molecule:



facial
 C_{3v}

Character table for C_{3v} point group

	E	$2C_3$ (α)	$3C_2$	linear, rotations	quadratic
A_1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	(x, y) (R_x, R_y)	$(x^2 - y^2, xy)$ (xz, yz)

$\Gamma = A_1 + E$

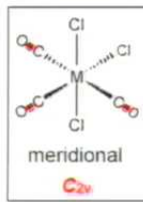
IR active (x,y,z): A_1 and E (2 peaks predicted)

Raman active (quadratic): A_1 and E (2 peaks predicted)

→ The fac isomer is expected to have 2 peaks in both its IR and Raman spectra.

(Refer Slide Time: 24:15)

Let's create reducible representations of the C-O bonds in each molecule:



meridional
 C_{2v}

Character table for C_{2v} point group

	E	C_2 (z)	σ_v (xz)	σ_v (yz)	linear, rotations	quadratic
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

$\chi = 1$ if unchanged
 $\chi = 0$ if changed

C_{2v}	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$
Γ	3	1	3	1

Reduce to irreducible representations:

of irreducible representations of given type = $\frac{1}{\text{order}} \sum \left(\begin{matrix} \text{\# of operations in the class} \\ \times \end{matrix} \begin{matrix} \text{character of reducible representation} \\ \times \end{matrix} \begin{matrix} \text{character of irreducible representation} \end{matrix} \right)$

$A_1 = 1/4[3+1+3+1] = 2$
 # $A_2 = 1/4[3+1-3-1] = 0$
 # $B_1 = 1/4[3-1+3-1] = 1$
 # $B_2 = 1/4[3-1-3+1] = 0$

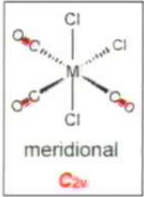
So $\Gamma = 2A_1 + B_1$

Whereas, the other one which is only C_{2v} has 3 peaks and in both it is IR.

(Refer Slide Time: 24:17)

Using Symmetry: Selected Vibrational Modes

Let's create reducible representations of the C-O bonds in each molecule:



Character table for C_{2v} point group

Γ	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$	linear, rotations	quadratic
A_1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1		xy
B_1	1	-1	1	x, R_y	xz
B_2	1	-1	-1	y, R_x	yz

$\Gamma = 2A_1 + B_1$

IR active (x,y,z): A_1 and B_1 (3 peaks predicted)

Raman active (quadratic): A_1 and B_1 (3 peaks predicted)

→ The *mer* isomer is expected to have 3 peaks in both its IR

So, this you can read out of this slide, but this is the practical way that this can be applied. And I will try to find out for example, that we can do reasonably within the portion we have covered, ok.