Chemical Applications of Group Theory

Some Readings

Chemical Application of Group Theory

F. A. Cotton

Symmetry through the Eyes of a Chemist

I. Hargittai and M. Hargittai

The Most Beautiful Molecule - an Adventure in Chemistry

H. Aldersey-Williams

Perfect Symmetry

J. Baggott

- The symmetry of molecules and solids is a very powerful tool for developing an understanding of bonding and physical properties
 - Used to predict the nature of molecular orbitals
 - Used to predict if electronic and vibration spectroscopic transitions can be observed
- We will cover the following material:
 - Identification/classification of symmetry elements and symmetry operations
 - Assignment of point groups
 - » The point group of a molecule uniquely and fully describes the molecules symmetry

- Identifying polarity and chirality using point groups
- Introduction to what a "Character Table" is
- Assigning symmetry labels to "Symmetry adapted linear combination or orbitals"
- Assigning symmetry labels to of vibration modes
- Determining the IR and Raman activity of vibrational modes
- We have learnt the point group theory of molecular symmetry. We shall learn how to use this theory in our chemical research.

Representation of groups Matrix representation and reducible representation

Total Representation for C_{2v}

Individually block diagonalized matrices



Reduced to 1D matricesirreducible representationx [1][-1][1][-1] $\Gamma_x = 1$ -1y [1][-1][-1][1] $\Gamma_y = 1$ -1z [1][1][1][1] $\Gamma_z = 1$ 1 $\Gamma_{Rz} = 1$ 1-1

1.2 Reducing of representations

- Suppose that we have a set of n-dimensional matrices, *A, B, C, ...*, which form a representation of a group. These n-D matrices themselves constitute a matrix group.
- If we make the same similarity transformation on each matrix, we obtain a new set of matrices,

$$A' = \Gamma A \Gamma^{-1}; B' = \Gamma B \Gamma^{-1}; C' = \Gamma C \Gamma^{-1} \dots$$

- This new set of matrices is also a representation of the group.
- If A' is a blocked-factored matrix, then it is easy to prove that B',C'... also are blocked-factored matrices.

$$A' = \begin{bmatrix} [A_1] & & \\ & [A_2] & \\ & & [A_3] & \\ & & & [A_4] \end{bmatrix}, B' = \begin{bmatrix} [B_1] & & \\ & & [B_2] & \\ & & & [B_3] & \\ & & & & [B_4] \end{bmatrix}, \dots$$

$$A_1, A_2, A_3... \text{ are } n_1, n_2, n_3... \text{-D submatrices with } n = n_1 + n_2 + n_3 + \dots$$

 Furthermore, it is also provable that the various sets of submatrices

 $\{A_1,B_1,C_1\dots\},\ \{A_2,B_2,C_2\dots\},\ \{A_3,B_3,C_3\dots\},\ \{A_4,B_4,C_4\dots\},$

are in themselves representations of the group.

- We then call the set of matrices A,B,C, ... a reducible representation of the group.
- If it is not possible to find a similarity transformation to reduce a representation in the above manner, the representation is said to be irreducible.
- The irreducible representations of a group is of fundamental importance.

2. Character Tables of Point Groups



2.1 Construction of Character Table

Total Representation for C_{2v}

Individually block diagonalized matrices



Reduced to 1D matricesirreducible representationx [1][-1][1][-1] $\Gamma_x = 1$ -1y [1][-1][-1][1] $\Gamma_y = 1$ -1z [1][1][1][1] $\Gamma_z = 1$ 1 $\Gamma_{Rz} = 1$ 1-1 $\Gamma_{Rz} = 1$ 1-1

Translations

Movements of whole molecule – represent by vectors

e.g. y vector	E operation	y' (after operation) = y
	C ₂	y' = -y (i.e. y' = -1 x y)
	σ _v (<i>xz</i>)	y' = -y
	σ _v (<i>yz</i>)	y' = y
z vector	all operations	z' = z
x vector	E operation	x' = x
	C ₂	x' = -x
	σ _v (<i>xz</i>)	$\mathbf{x}' = \mathbf{x}$ \mathbf{H}' \mathbf{H}
	σ _v (<i>yz</i>)	x' = -x
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Translations

Consider effect of symmetry operation on the vector Write +1 for no change, -1 for reversal

		Е		C ₂	σ _v (<i>xz</i>)	σ _v (<i>yz</i>)			
z ve	ctor	+1		+1	+1	+1	A ₁		
у		+1		-1	-1	+1	B ₂		
X		+1		-1	+1	-1	B ₁		
						-			
C _{2v}	E	C_2	σ _v (xz	z) σ _v (<i>yz</i>)	Labels A	₁ etc. are			
A ₁	+1	+1	+1	+1	<i>symmetry species</i> ; they summarise the effects of symmetry operations on the				
A ₂	+1	+1	-1	-1					
B ₁	+1	-1	+1	-1					
B ₂	+1	-1	-1	+1	vectors.		H',		

These translation vectors constitute a set of bases of C_{2v} group¹

Rotations

Similarly for rotations of the molecules

	E	C ₂	σ _v (<i>xz</i>)	σ _v (<i>yz</i>)	
z vector	+1	+1	+1	+1	A ₁
У	+1	-1	-1	+1	B ₂
x	+1	-1	+1	-1	B ₁
R _z	+1	+1	-1	-1	A ₂
R _y	+1	-1	+1	-1	B ₁
R _x	+1	-1	-1	+1	B ₂
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Characters

The numbers +1 and -1 are called *characters*.

The *character table* has all possible symmetry species for the *point group*. It is the same for all molecules belonging to the point group – e.g. C_{2v} for H_2O , SiH_2CI_2 , $Fe(CO)_4CI_2$, etc.

Note: the character table lists the symmetry species for translations and rotations.

A,B show symmetry with respect to rotation. 1,2 distinguish symmetry with respect to reflections Character table

C _{2v}	Е	C ₂	σ _v (<i>xz</i>)	<i>h</i> = 4
A ₁	+1	+1	+1	+1	Z
A_2	+1	+1	-1	-1	R _z
\mathbf{B}_1	+1	-1	+1	-1	x, R _y
B_2	+1	-1	-1	+1	y, R _x
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2.2 symmetry species: Mulliken symbols

C_{3v}	Ε	$2C_{3}$	$3\sigma_{\nu}$		
A_1 A_2	1	1 1	1 -1	z R.	$x^2 + y^2, z^2$
<i>E</i>	2	- 1	0	$(x, y)(R_x, R_y)$	$(x^2 - y^2, xy)(xz, yz)$

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- All 1-D irreducible reps. are labeled by either A or B, 2-D irreducible rep. by E, 3-D irreducible rep. by T and so on.
- A: symmetric with respect to C_n rotation, i.e., $\chi(C_n)=1$.
- B: asymmetric with respect to C_n rotation, i.e., $\chi(C_n)=-1$.
- Subscriptions 1 or 2 designates those symmetric or asymmetric with respect to a $C_2 \bot$ or a σ_v .
- Subscripts g or u for universal parity or disparity.
- Superscripts ' or '' designates those symmetric or asymmetric with respect to $\sigma_{\rm h}$

2.3 Symmetry of molecular properties

Translations and rotations can be assigned to symmetry species – and so can other molecular properties



Characters for more than one object or action

We can make representations of several things

e.g. H 1s orbitals in H₂O



orbital 1 orbital 2

E operation

orbital 1' = orbital 1

orbital 2' = orbital 2

Each is unchanged (= 1 x itself), so the character is 2

Strictly speaking the character is the *trace* (sum of diagonal terms) of the *transformation matrix.*

$$\left(\begin{array}{cc}
1 & 0\\
0 & 1
\end{array}\right)$$

Characters for more than one object or action

Representations of several things

e.g. H 1s orbitals in H₂O orbital 1 orbital 2

 C_2 operation

orbital 1' = orbital 2

orbital 2' = orbital 1

There is no contribution from the old orbital 1 to the new one (= 0 x itself), so the character is 0

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The trace of the transformation matrix is zero.
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Characters for more than one object or action

Representations of several things

e.g. H 1s orbitals in H ₂ O	+ O orbital 1 o	+ orbital 2	2			
E operation	character is +	2				
C2	0					
σ _v (<i>xz</i>)	0					
σ _v (<i>yz</i>)	+2	C _{2v}	Е	C ₂	$\sigma_v(xz)$	σ _v (<i>yz</i>)
so overall:			+2	0	0	+2

This the reducible representation of the set of 2 orbitals.

Reducible representations

This set of characters does not appear in the character table

- but it can always be expressed as a sum of lines

Character table

C _{2v}	Е	C ₂	σ _v (<i>xz</i>)) σ _v (<i>yz</i>)	<i>h</i> = 4		
A ₁	+1	+1	+1	+1	Ζ		
\mathbf{A}_2	+1	+1	-1	-1	R _z		
B ₁	+1	-1	+1	-1	x , R _y		
B_2	+1	-1	-1	+1	<i>y, R</i> _x		
+ + +							
A ₁ is the symmetric combination							
$\Lambda \perp R$ is the irreducible representation							

Must be an A and a B to make the second number = 0

Must then be $A_1 + B_2$ to make final number = 2



B₂ is the asymmetric combination

A₁ + B₂ is the *irreducible representation* of the two orbitals

Reducing representations

The hard way – solve a set of simultaneous equations

The easy way – use the formula provided

Formula is
$$a_i = \frac{1}{h} \sum_R g_R \cdot \chi(R) \cdot \chi_I(R)$$

 a_i is the number of 'things' (orbitals etc.) of symmetry species Ihis the order of the group g_R is the order of class R (the number of operations of that type)

 $\chi(R)$ is the character for operation R in the reducible representation

 $\chi_i(R)$ is the character for operation *R* in the character table for symmetry species *i*

• This formula was derived from the "Great orthorgonality theorem".

Reducing representations

e.g. s orbitals on F atoms of XeOF₄



Point group ?



Point group algorithm – XeOF₄ Start here



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Formula is $a_i = \frac{1}{h} \sum_{R} g_R \cdot \chi(R) \cdot \chi_I(R)$ **Reducible representation 4** 0 2 0 0 2**C** Character table C_{4v} $1C_2$ $2\sigma_v$ 1E $2\sigma_{v'}$ *h* = 8 +1 +1 +1 A₁ +1 +1 Ζ A_2 +1 +1 -1 R, +1 -1 B₁ -1 +1 +1 +1 -1 B_2 -1 +1 +1 -1 +1 Ε -2 0 $(x, y) (R_x, R_y)$ +2 0 0 No. of A_1 motions = 1/8 [1.4.1 + 2.0.1 + 1.0.1 + 2.2.1 + 2.0.1] = 1 No. of A_2 motions = 1/8 [1.4.1 + 2.0.1 + 1.0.1 + 2.2.(-1) + 2.0.(-1)] = 0

Formu	la is a	$_{i}=\frac{1}{h}$	$\sum_{R} g_{R}$. X(R	\mathcal{X}_{l}). \mathcal{X}_{l} (R)	
Reducible representa	ation 4	0	0	2	0		
Character table C _{4v}	1E	2C ₄	1C ₂	$2\sigma_v$	$2\sigma_{v'}$	<i>h</i> = 8	
Α	1 +1	+1	+1	+1	+1	Z	
Α	₂ +1	+1	+1	-1	-1	R _z	
В	1 +1	-1	+1	+1	-1		
B	₂ +1	-1	+1	-1	+1		
E	+2	0	-2	0	0	(x, y) (R _x , R	(_y)
No. of A ₁ motions =	No. of A ₁ motions = 1/8 [1.4.1 + 2.0.1 + 1.0.1 + 2.2.1 + 2.0.1] = 1						
No. of A_2 motions = 1/8 [1.4.1 + 2.0.1 + 1.0.1 + 2.2.(-1) + 2.0.(-1)] = 0							= 0
No. of B_1 motions = 1/8 [1.4.1 + 2.0.(-1) + 1.0.1 + 2.2.1 + 2.0.(-1)] = 1							
No. of B_2 motions = 1/8 [1.4.1 + 2.0.(-1) + 1.0.1 + 2.2.(-1) + 2.0.1] = 0							
No. of E motions =	1/8 [1.4.2	+ 2.0.0) + 1.0.((-2) + 2	2.2.0 + 2	2.0.0]	= 1

Character table C _{4v}	1E	2C ₄	1C ₂	$2\sigma_v$	$2\sigma_{v^{\prime}}$
Reducible representation	4	0	0	2	0
Irreducible representation	A ₁ + E	3 ₁ + E			

Note: E is *doubly degenerate* – accounts for two equivalent combinations of orbitals



3. Symmetry adapted Linear Combinations of AOs– A convenient way to construct MOs

Symmetry of wavefunctions of a molecule

Symmetry Operation on Schrödinger Eq.



If eigenvalue *E* is not degenerate, then

$$R\psi = c\psi$$

Which means ψ is a basis for some 1-D I.R..

If eigenstate E is l-fold degenerate, then

 $\mathbf{E} \quad \clubsuit \quad \{ \psi_1, \psi_2, \dots, \psi_l \}$

$$R\psi_{i} = \sum_{j=1}^{l} r_{ij}\psi_{j} = \begin{bmatrix} r_{11} & r_{12} & \cdots & r_{1l} \\ r_{21} & r_{22} & \cdots & r_{2l} \\ \vdots & \vdots & \ddots & \vdots \\ r_{l1} & r_{l2} & \cdots & r_{ll} \end{bmatrix} \begin{bmatrix} \psi_{1} \\ \psi_{2} \\ \vdots \\ \psi_{l} \end{bmatrix}$$

Which means set { $\psi_1, \psi_2, ..., \psi_l$ } is a basis for this *l*-D I.R.

In LCAO approach of MO theory, we have

$$\Psi = \sum_i c_i \phi_i$$

So we need to solve the secular equation

$$\sum_{i=1}^{n} c_i (H_{ir} - ES_{ir}) = 0, \qquad (r = 1, 2, \dots, n)$$

$$\begin{bmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots & H_{1n} - ES_{1n} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \cdots & H_{2n} - ES_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ H_{n1} - ES_{n1} & H_{n2} - ES_{n2} & \cdots & H_{nn} - ES_{nn} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{bmatrix} = 0$$

We can transform the original bases of AO's into Linear Combinations of AO's which have the same properties of some I.R.s (Symmetry Adapted Linear Combination), therefore the Secular Equation is block diagonalized.



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\$tep 1 Reduce the REP spanned by the AO basis.

Obtain the n_i 's for each I.R.

\$tep 2 Construct n_i SALCs for each I.R..

Step 3 Transform the hamiltonian matrix into block diagonalized form, and solve it.

Example 1:

 H_20

LCAO with the following atomic orbitals

O: $2s; 2p_x, 2p_y, 2p_z$

2H: $1s_a, 1s_b$

Symmetry: C_{2v}

• Neglecting the O 1s orbital/electrons.

H_2O



Character Table

C_{2v}	Ι	C_2	$\sigma_{ m v}$	$\sigma_{\rm v}'$		Symm	etry of AOs
A_1	1	1	1	1	Ζ	from (Dxygen
A_2	1	1	-1	-1	xy	A_1 :	$2s$, $2p_z$
B_1	1	-1	1	-1	X,XZ	B_1 :	$2p_x$
<i>B</i> ₂	1	-1	-1	1	y,yz	<i>B</i> ₂ :	$2p_y$

I $C_2 \sigma_v \sigma_v'$ C_{2v} 1 1 1 A_1 1 Ζ 1 1 -1 -1 A_2 XY1 -1 1 -1 B_1 X,XZ B_2 1 -1 -1 1 y,yz $\chi(\mathbf{R})$ 2 0 0 2 $\frac{n_{A_1} = \frac{1}{4}(1 \times 2 + 1 \times 0 + 1 \times 0 + 1 \times 2) = 1}{n_{B_1} = \frac{1}{4}(1 \times 2 - 1 \times 0 + 1 \times 0 - 1 \times 2) = 0}$ $\frac{n_{A_2} = \frac{1}{4}(1 \times 2 + 1 \times 0 - 1 \times 0 - 1 \times 2) = 0}{n_{B_2} = \frac{1}{4}(1 \times 2 - 1 \times 0 - 1 \times 0 + 1 \times 2) = 0}$ $\Gamma = A_1 + B_2 \implies$ Two 1-D REPs

Symmetry Reduction of 2-D Bases Set $\{1s_a, 1s_b\}$

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SALC - *Symmetry Adapted Linear Combination of AOs*

For this trivial problem, it is very simple, we intuitively determined the new basis as

$$A_1: \frac{1}{\sqrt{2}}(1s_A + 1s_B) + +$$

$$B_2: \quad \frac{1}{\sqrt{2}} \left(1 \mathbf{s}_{\mathrm{A}} - 1 \mathbf{s}_{\mathrm{B}}\right)$$

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+
H20

A_1 symmetry AOs or SALCs for LCAO



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Too complicated for analysis!



H2O- Hybridization of Oxygen's 2s and $2p_z$



H20- Hybridization of Oxygen's 2s and $2p_z$





H20- Summary on Chemical Bonding



H20- Summary on Molecular Energy Level Sequences



Use Projection operator to construct SALCs

• Definition:
$$\hat{P}^{j} = \frac{l_{j}}{h} \sum_{R} \chi(R)^{j} \hat{R}$$

- for j-th ir. rep. of the point group. This equation was derived from the "great orthogonality theorem".
- A non-normalized SALC can be constructed from bases set by the formula:

$$\Psi_{SALC}^{j} = \hat{P}^{j}\phi_{i} = \frac{l_{j}}{h}\sum_{R}\chi(R)^{j}\hat{R}\phi_{i}$$

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Example: π -MOs of C₃H₃ (D_{3h})



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Another way to derive the third MO:

1. Find an operation to covert the second wavefunction into an nonequivalent one (not \pm) of the original one). A C₃ operation works well. Then we have

$$C_3^1 \Psi_1^E = \frac{1}{\sqrt{6}} (2\phi_2 - \phi_3 - \phi_1)$$

2. A linear combination of this new one and the original one gives rise to $C^{1}\Psi^{E} + A \Phi \Psi^{E} = (2\phi - \phi - \phi) + (\frac{1}{2})(2\phi - \phi - \phi)$

$$C_{3}^{1}\Psi_{1}^{E} + A \bullet \Psi_{1}^{E} = (2\phi_{2} - \phi_{3} - \phi_{1}) + (\frac{1}{2})(2\phi_{1} - \phi_{2} - \phi_{3})$$
$$= \frac{3}{2}(\phi_{2} - \phi_{3})$$
$$\Psi_{2}^{E} = \frac{1}{\sqrt{2}}(\phi_{2} - \phi_{3})$$

A general simplification

• Reducing the symmetry to C₃ subgroup.

$$\hat{P}^{A} \phi_{1} \approx \sum_{R} \chi(\hat{R})^{A} \hat{R} \phi_{1} = E \phi_{1} + C_{3}^{1} \phi_{1} + C_{3}^{2} \phi_{1} = \phi_{1} + \phi_{2} + \phi_{3}$$

$$\hat{P}^{E(1)}\phi_1 \approx \sum_R \chi(\hat{R})^{E(1)} \hat{R}\phi_1 = \phi_1 + \varepsilon C_3^1 \phi_1 + \varepsilon * C_3^2 \phi_1 = \phi_1 + \varepsilon \phi_2 + \varepsilon * \phi_3$$

 $\hat{P}^{E(2)}\phi_1 \approx \sum_{\bar{x}} \chi(\hat{R})^{E(2)} \hat{R}\phi_1 = \phi_1 + \varepsilon^* \phi_2 + \varepsilon \phi_3$

$$\Psi_1^A = A\hat{P}^A\phi_1$$

= $A(\phi_1 + \phi_2 + \phi_3) = \frac{1}{\sqrt{3}}(\phi_1 + \phi_2 + \phi_3)$

$$\Psi_1^E = A(\hat{P}^{E(1)}\phi_1 + \hat{P}^{E(2)}\phi_1)$$

= $A(2\phi_1 + 2\cos(\frac{2\pi}{3})\phi_2 + 2\cos(\frac{2\pi}{3})\phi_3) = \frac{1}{\sqrt{6}}(2\phi_1 - \phi_2 - \phi_3)$

$$\Psi_{2}^{E} = A(\hat{P}^{E(1)}\phi_{1} - \hat{P}^{E(2)}\phi_{1})$$

= $Ai(2\sin(\frac{2\pi}{3})\phi_{2} - 2\sin(\frac{2\pi}{3})\phi_{3}) = \frac{1}{\sqrt{2}}(\phi_{2} - \phi_{3})$

Example 2:
$$C_{6}H_{6}$$
 $D_{6h} \rightarrow C_{6}$

$$\frac{C_{6}}{A} \begin{bmatrix} E & C_{6} & C_{3} & C_{2} & C_{3}^{2} & C_{6}^{5} \\ 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & -1 & 1 & -1 & 1 & -1 \\ 1 & e^{+} & -e^{+} & -1 & -e^{+} & e^{+} \\ E_{2} & 1 & -e^{+} & -e^{-} & 1 & -e^{+} & -e^{+} \\ 1 & -e^{+} & -e^{-} & 1 & -e^{+} & -e^{-} \\ 1 & -e^{-} & -e^{+} & 1 & -e^{-} & -e^{+} \\ 1 & -e^{-} & -e^{-} & -e^{+} & 1 \\ 1 & -e^{-} & -e^{-} & -e^{+} & 1 \\ 1 & -e^{-} & -e^{-} & 1 \\ 1 & -e^{-} & -e^{-} & -e^{+} \\ 1 & -e^{-} & -e^{-} & 1 \\ 1 & -e^{-} & -e^{-} & -e^{+} \\ 1 & -e^{-} & -e^{-} & -e^{+} \\ 1 & -e^{-} & -e^{-} & -e^{-} \\ 1 & -e^{-} &$$

$$\Psi^{E_1}(1) = A(\hat{P}^{E_1(1)}\phi_1 + \hat{P}^{E_1(2)}\phi_1) = 2A(\phi_1 + \cos(\frac{\pi}{3})\phi_2 - \cos(\frac{\pi}{3})\phi_3 - \phi_4 - \cos(\frac{\pi}{3})\phi_5 + \cos(\frac{\pi}{3})\phi_6)$$
$$= \frac{1}{\sqrt{12}}(2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6)$$

$$\Psi^{E_1}(2) = A(\hat{P}^{E_1(1)}\phi_1 - \hat{P}^{E_1(2)}\phi_1) = 2Ai(-\sin(\frac{\pi}{3})\phi_2 - \sin(\frac{\pi}{3})\phi_3 + \sin(\frac{\pi}{3})\phi_5 + \sin(\frac{\pi}{3})\phi_6)$$
$$= \frac{1}{2}(\phi_2 + \phi_3 - \phi_5 - \phi_6)$$

Similarly, we have

$$\Psi^{E_2}(1) = A(\phi_5 + \phi_6) = \frac{1}{\sqrt{12}} (2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 + \phi_6)$$
$$\Psi^{E_2}(2) = A(\phi_5 - \phi_6) / i = \frac{1}{2} (-\phi_2 + \phi_3 - \phi_5 + \phi_6)$$



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Molecular vibrations - number of modes



4 atoms - can move independently in *x, y,* z directions 3N degrees of freedom for a N-atom molecule. If atoms fixed, there are: 3 translational degrees 3 rotational degrees and the rest (3N-6) are vibrational modes

No. of modes of each symmetry species

Example - SiH_2CI_2 Point group C_{2v}



Perform symmetry operations

Count +1, -1, 0 if vector transforms to itself, minus itself, or moves



Operation E

Si atom	<i>x</i> transforms into Si <i>x</i>	count +1	
	<i>y</i> transforms into Si <i>y</i>	count +1	
	z transforms into Si z	count +1	
		total +3	
Same for other 4 atoms	grand total +15		





Operation $\sigma_v(xz)$ Si atom x transforms into Si x count +1

- y transforms into Si -y count -1
- *z* transforms into Si *z* count +1

total +1

 H_1 and H_2 also lie in xz plane, and behave as Sicount +1 each Cl_1 and Cl_2 swap placescount 0

grand total +3



z transforms into Si *z* count +1

total +1

count 0

 H_1 and H_2 swap places

 CI_1 and CI_2 also lie in *yz* plane, and behave as Si count +1 each grand total +3

No. of modes of each symmetry species

Example - SiH₂Cl₂ Point group C_{2v}

Overall we have:

- E $C_2 \quad \sigma_v(xz) \quad \sigma_v(yz)$
- +15 -1 +3 +3

This is the *reducible representation* of the set of 3N (=15) atomic displacement vectors

We reduce it to the *irreducible representations*, using a formula

Reduce the reducible representation

No. of A₁ motions = 1/4 [1.15.1 + 1.(-1).1 + 1.3.1 + 1.3.1] = 5

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$$a_i = \frac{1}{h} \sum_{R} g_R \cdot \chi(R) \cdot \chi_i(R)$$

Reducible representation 15 -1 3 3

Formula is

Character table

C _{2v}	1E	1C ₂	1σ _v (<i>xz</i>) 1σ _v (<i>yz</i>)		<i>h</i> = 4	
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	у, R _x	уz

No. of A_1 motions = 1/4 [1.15.1 + 1.(-1).1 + 1.3.1 + 1.3.1] = 5 No. of A_2 motions = 1/4 [1.15.1 + 1.(-1).1 + 1.3.(-1) + 1.3.(-1)] = 2 No. of B_1 motions = 1/4 [1.15.1 + 1.(-1).(-1) + 1.3.1 + 1.3.(-1)] = 4 No. of B_2 motions = 1/4 [1.15.1 + 1.(-1).(-1) + 1.3.(-1) + 1.3.1] = 4

Translations, rotations, vibrations

Symmetry species of all motions are:-

 $5A_1 + 2A_2 + 4B_1 + 4B_2$ - the *irreducible representation*

3 of these are *translations* of the whole molecule 3 are *rotations*

Symmetry species of translations are given by vectors (*x*, *y*, *z*) in the character table

Symmetry species of rotations are given by R_x , R_y and R_z in the character table

Translations, rotations, vibrations

Symmetry species of all motions are:-

Symmetry species of vibrations are:- $4A_1 + A_2 + 2B_1 + 2B_2$

What does each of these modes look like?

2 rules

- (i) there is 1 stretching vibration per bond
- (ii) must treat symmetry-related atoms together

2 rules

- (i) there is 1 stretching vibration per bond
- (ii) we must treat symmetry-related atoms together

We therefore have:-

two stretching modes of the $SiCl_2$ group two of the SiH_2 group

The remaining five modes must be deformations (angle bending vibrations)

We therefore have:-

two stretching modes of the SiCl₂ group

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We can stretch the two Si-Cl bonds together *in phase* or together *out of phase* Is vibration symmetrical with respect to each symmetry operation?

- if yes +1, if no -1

From the character table, this belongs to the symmetry species A₁

We call the mode of vibration $\nu_{\text{sym}} \operatorname{SiCl}_2$

Is vibration symmetrical with respect to each symmetry operation?

- if yes +1, if no -1

From the character table, this belongs to the symmetry species B₂

We call the mode of vibration v_{asym} SiCl₂

We therefore have:-

two stretching modes of the $SiCl_2$ group and two stretching modes of the SiH_2 group

We can stretch the two Si-H bonds together *in phase* or together *out of phase*

From the character table, this belongs to the symmetry species A₁

We call the mode of vibration $\nu_{\text{sym}} \, \text{SiH}_2$

From the character table, this belongs to the symmetry species B₁

We call the mode of vibration $\nu_{\text{asym}} \operatorname{SiH}_2$





Vibrational modes of SiH₂Cl₂

We now have:-

two stretching modes of the $SiCl_2$ group two of the SiH_2 group

The remaining five modes must be deformations (angle bending vibrations)

As with stretches, we must treat symmetryrelated atoms together

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From the character table, this belongs to the symmetry species A₁

We call the mode of vibration $\delta_{\text{sym}} \operatorname{SiCl}_2$ (or SiCl_2 scissors)





From the character table, this belongs to the symmetry species A₁

We call the mode of vibration $\delta_{\text{sym}}~\text{SiH}_{2}$ (or SiH_2 scissors)





From the character table, this belongs to the symmetry species B₁

We call the mode of vibration ω SiH₂ (or SiH₂ wag)





From the character table, this belongs to the symmetry species B₂

We call the mode of vibration ρ SiH_2 (or SiH_2 rock)





From the character table, this belongs to the symmetry species A₂

We call the mode of vibration τ SiH₂ (or SiH₂ twist)





Vibrational modes of SiH₂Cl₂

Overall, we now have:-

two stretching modes of the SiCl₂ group $+ B_{2}$ A₁ two of the SiH₂ group + B₁ A₁ five deformation modes $2A_1 + A_2 + B_1 + B_2$ Together, these account for all the modes we expect:

$$4A_1 + A_2 + 2B_1 + 2B_2$$

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Observing vibrations

Infra-red spectroscopy

Consider symmetry properties		C_{2v}	Е	C ₂	σ _v (<i>x</i> ,	z) σ _v (<i>yz</i>)	<i>h</i> = 4
$01 \text{ upoles } \mu_x, \mu_y a$	\mathbf{A}_{1}	A ₁	+1	+1	+1	+1	Ζ
e.g. SiH ₂ Cl ₂	H C	A ₂	+1	+1	-1	-1	R _z
		B ₁	+1	-1	+1	-1	<i>x, R</i> _y
	CI CI	B ₂	+1	-1	-1	+1	y, R _x

Dipoles are vectors, with same symmetry properties as *x*, *y*, *z*

In this case, μ_z has A_1 symmetry

Therefore A_1 vibrations involve dipole changes along the *z* axis, and so all A_1 modes must be *infra-red active*.

Observing vibrations

Infra-red spectroscopy

Consider symmetry properties of dipoles μ_x , μ_y and μ_z		C _{2v}	Е	C ₂	σ _v (<i>x</i>	z) σ _v (<i>yz</i>)	<i>h</i> = 4
		A ₁	+1	+1	+1	+1	Z
e.g. SiH ₂ Cl ₂	H H	A ₂	+1	+1	-1	-1	R _z
	5	B ₁	+1	-1	+1	-1	$\boldsymbol{x}, \boldsymbol{R}_y$
	CI CI	B_2	+1	-1	-1	+1	y , R _x

Similarly B₁ and B₂ modes involve dipole changes along *x* and *y* axes, and so must be *infra-red active*.

A₂ modes cannot involve dipole changes, and are *infra-red inactive*. For any point group, no more than 3 IR-active symmetry species.

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Obs	ervi	ing	vib	rati	ion	S		
Infra-rec	l spe	ectro	scop	у				
Our exam	ples							
SiH ₂ Cl ₂	Γ _{vib} :	= 4A ₁ 4 8 ab	+ A ₂ · sorpt	+ 2B ₁ + 2 ion b	+ 2B ₂ + 2 ands	activ in IR s	e modes spectrum	
XeOF ₄	Γ _{vib} :	= 3A ₁ 3 6 a	+ 2B ₁ bsorp	+ B ₂ tion b	+ 3E + 3 bands	active in IR	e modes spectrum	
	Char C₄v A₁ A₂ B₁ B₂ E	racter E +1 +1 +1 +1 +1 +2	table 2C₄ +1 +1 -1 -1 0	C ₂ +1 +1 +1 +1 -2	2σ _v +1 -1 +1 -1 0	2σ _v , +1 -1 +1 +1 0	h = 8 z R _z (x, y) (R _x , R _y)	x ² + y ² , z ² x ² - y ² xy (xz, yz)
								9 3



Activity – vibrational mode active if and only if it involves a polarisability change

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Observing vibrations

Raman spectroscopy

Dipoles are vectors - μ_x etc. – symmetry properties as *x*, *y*, *z* Polarisabilities are tensors – α_{xx} , α_{xy} etc. – properties as *xx*, *xy*

- listed in final column of character table

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Good Luck In the Final Exam!

Final Exam

- Content: Chapters 5-9
- Time: June 13, 8:00-10:00
- Venue: 群贤二-102
- Tools: 科学计算器、笔等普通文具
- 考前答疑: June 10-12,

嘉锡楼316(圆弧形办公室)

