

Symmetry, Point Groups and Character Tables

Character Table for C_{3v}

	E	$2C_3$	$3\sigma_v$		
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)

The first row lists the symmetry operations of the group

These are:

E (identity)

C_3 (proper rotation by $2\pi/3$)

σ_v (reflection in vertical mirror plane, i.e. one containing the C_3 axis)

Order of group

= number of *non-redundant* symmetry operations (= 6 in this case)

Symmetry operations are collected into classes. Operations belong to the same class if they can be interconverted by another symmetry operation of the group

e.g. the two C_3 operations are C_3^1 and C_3^2 ($C_3^3 = E$)

$$C_3^2 = \sigma_v C_3^1$$

and the three σ_v 's are interconverted by C_3

The **first column block** lists the Mulliken symbols for the irreducible representations of the group, according to whether they are one-dimensional (A or B), two-dimensional (E), or three dimensional (T).

The **second column block** lists the characters of the matrices (of smallest possible dimension) that describe the symmetry operations.

There are five important properties of the irreducible representations (irr's)....

1. The number of irr's equals the number of classes.
2. In any given representation the characters of all matrices belonging to operations in the same class are identical
3. The sum of the squares of the dimensions of the irr's equals the order of the group (h)
for C_{3v} , $1^2 + 1^2 + 2^2 = 6$
4. The sum of the squares of the characters in any irr equals h
e.g. for E in C_{3v} , $2^2 + 2(-1^2) + 3(0^2) = 6$
5. The vectors whose components are the characters of two different irr's are orthogonal, i.e.

$$\sum_R \chi_i(R) \chi_j(R) = 0 \quad \text{when } i \neq j$$

e.g. for A_2 and E in C_{3v} ,

$$(1)(2) + 2(1)(-1) + 3(-1)(0) = 0$$

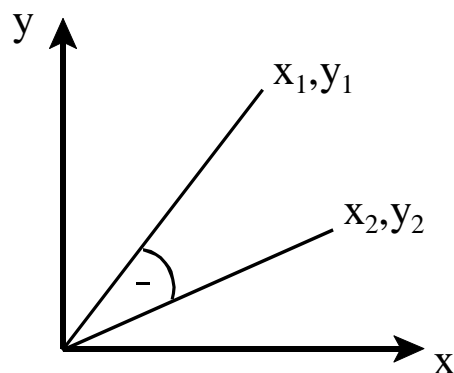
The third column block shows which irr's correspond to *translations* (unit x, y, z vectors) and *rotations*.

The fourth column block gives the corresponding information for quadratic functions

Matrix Representation of Symmetry Operations in C_{3v}

Method 1: effects on point (x,y,z)

Rotation about z-axis



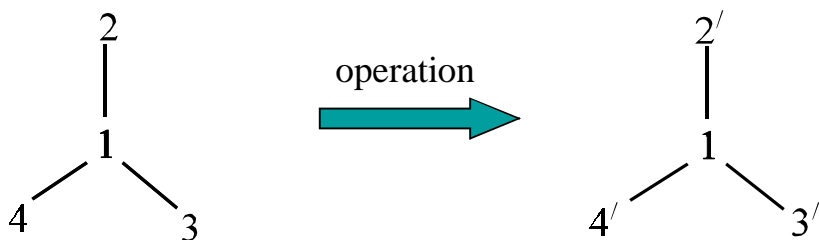
Since $x_2 = x_1 \cos \theta + y_1 \sin \theta$
 $y_2 = -x_1 \sin \theta + y_1 \cos \theta$
and $z_2 = z_1$

The matrix is

$$\begin{bmatrix} \cos \theta & \sin \theta & 0 \\ -\sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \text{ or for the case of } C_3^1 \begin{bmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Note that the trigonometric convention is that a *clockwise* rotation corresponds to *negative* θ .

Method 2. Numbered atoms in a molecule, e.g. NH_3



Thus for clockwise C_3^1

$$\begin{bmatrix} 1' \\ 2' \\ 3' \\ 4' \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} 1 \\ 2 \\ 3 \\ 4 \end{bmatrix}$$

	Γ_{atoms}		Γ_{xyz}	
C_3^1	$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix}$	$\chi = 1$	$\begin{bmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$\chi = 0$
C_3^2	$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \end{bmatrix}$	$\chi = 1$	$\begin{bmatrix} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$\chi = 0$
σ_2	$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix}$	$\chi = 2$	$\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$\chi = 1$
σ_3	$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}$	$\chi = 2$	$\begin{bmatrix} 1/2 & -\sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$\chi = 1$
σ_4	$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$	$\chi = 2$	$\begin{bmatrix} 1/2 & \sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$\chi = 1$
E	$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$	$\chi = 4$	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$\chi = 3$

Reduction of Representations

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

a_i is the number of times the i -th irr appears in the representation

For Γ_{atoms}

$$a(\mathbf{A}_1) = 1/6\{4(1) + 2(1)(1) + 3(1)(2)\} = 2$$

$$a(\mathbf{A}_2) = 1/6\{4(1) + 2(1)(1) + 3(-1)(2)\} = 0$$

$$a(\mathbf{E}) = 1/6\{4(2) + 2(-1)(1) + 3(0)(2)\} = 1$$

$$\text{So } \Gamma_{\text{atoms}} = 2\mathbf{A}_1 + \mathbf{E}$$

Similarly we can show that $\Gamma_{\text{xyz}} = \mathbf{A}_1 + \mathbf{E}$

The wave-functions of a molecule are bases for irreducible representations of the symmetry group to which the molecule belongs.

Examples using atomic orbitals

s-orbitals transform as the totally symmetric representation

(A_1 in C_{3v})

p-orbitals transform as the coordinates x, y, z

(E and A_1 in C_{3v})

d-orbitals transform as the binary and quadratic functions (xz, x^2-y^2, etc)

The **Direct Product** of two degenerate functions X_1, X_2, \dots, X_m and Y_1, Y_2, \dots, Y_n is the set of functions $X_i Y_k$. The direct product is also a representation of the group.

The characters of a direct product representation equal the products of the characters of the original representations...

i.e. $\chi(\mathbf{R}) = \chi_1(\mathbf{R})\chi_2(\mathbf{R})$ for each operation \mathbf{R}

We can demonstrate this with examples from C_{3v}

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

Direct Product	E	$2C_3$	$3\sigma_v$	Result
A_1A_2	1	1	-1	A_2
A_2E	2	-1	0	E
E^2	4	1	0	A_1+A_2+E
A_1A_2E	2	-1	0	E

In spectroscopy we observe transitions between two energy states of molecules, E_i and E_j , that are defined by wave-functions ψ_i and ψ_j .

Radiation of frequency ν is absorbed or emitted when

$$h\nu = E_i - E_j$$

The *intensity* of the absorbed or emitted radiation is determined by the magnitude of the Transition Moment which takes the general form

$$\int \psi_i \hat{O} \psi_j d\tau$$

where \hat{O} is the appropriate transition moment operator – its nature depends upon the type of spectroscopy involved.

A spectroscopic transition will be observed *only* if the transition moment integral is non-zero. [This statement is the basis for all spectroscopic selection rules.]

For an integral to be non-zero, the function must be “even”

$$\int_{-\infty}^{\infty} f(x) dx \neq 0 \quad \text{i.e. } f(x) \neq f(-x)$$

if $f(x) = -f(-x)$ the function is “odd” and

$$\int_{-\infty}^{\infty} f(x) dx = 0$$

Simple examples of odd functions are $y = x$, x^3, \dots

Even functions $y = x^2, x^4, \dots$

An odd function is invariant under all operations of the symmetry group to which the molecule belongs. This means that the function must form a basis for the *totally symmetric irreducible representation* of the group, i.e. the one with all characters = +1.

For an integral involving the product of two wave-functions ψ_A and ψ_B (which are bases for irreducible representations) we can generate a direct product representation Γ_{AB} which can be broken down into a sum of irreducible representations, see Table.

Γ_{AB} will contain the totally symmetric representation *only if* ψ_A and ψ_B transform as the *same* irreducible representation.

This is easily proved from the reduction formula

$$a_{TS} = \frac{1}{h} \sum_R \chi_{AB}(R) \chi_{TS}(R)$$

$$= \frac{1}{h} \sum_R \chi_{AB}(R) \quad \text{since all } \chi_{TS} = 1$$

But since $\chi_{AB}(R) = \chi_A(R) \chi_B(R)$

$$a_{TS} = \frac{1}{h} \sum_R \chi_A(R) \chi_B(R)$$

which from the properties of irr's = 1 only if $\chi_A = \chi_B$ for all R's.

The transition moment integral involves a *triple* product.

This will be non-zero only if the direct product of two of the functions is or contains the same representation as is given by the third function.

Generally, when dealing with the transition moment integral we evaluate the representations spanned by the product of the wave-functions $\psi_i \psi_j$ and compare these with the representation of the operator \hat{O} .

The interaction of electromagnetic radiation with a molecule can occur through coupling of the oscillating electric or magnetic vectors of the radiation with changes in electric or magnetic dipoles in the molecule, with higher multipoles, or with polarizability tensors. The most important type of interaction is through the electric dipole.

Such transitions are said to be “electric dipole allowed” and are considerably more intense than any other.

The relative intensities are

electric dipole	1
magnetic dipole	$\sim 10^{-5}$
electric quadrupole	$\sim 10^{-6}$

An electric dipole allowed transition will be observed if there is a change in the molecule's dipole moment between the states corresponding to ψ_i and ψ_j . This can occur as a result of a molecular vibration (\rightarrow Infrared spectroscopy) or as a result of an intramolecular electron displacement (\rightarrow Electronic spectroscopy). In both cases the transition moment operator \hat{O} is the *electric dipole operator* which has the form

$$\mu = \sum_i e_i x_i + \sum_i e_i y_i + \sum_i e_i z_i$$

where e_i is the charge on the i -th particle, and x_i , y_i and z_i are its coordinates.

We are only interested in the symmetry properties of this operator, and these are determined by the symmetry of the three cartesian coordinates x , y , and z .

Thus μ belongs to the irreducible representation(s) that transform as (the translations) x , y , z , shown in the Character Table for the group.