Representations of Molecular Properties

☞ We will routinely use sets of vectors located on each atom of a molecule to represent certain molecular properties of interest (e.g., orbitals, vibrations).

- ✓ The set of vectors for a property form the **basis for a representation** (or **basis set**).

- ✓ The mathematical description of the behavior of the vectors under the symmetry operations of the group forms a **representation of the group**.

- ✓ In most cases the representation for the property will be the sum of certain fundamental representations of the group, called **irreducible representations**.

☞ A **representation** is a set of symbols (called **characters**) that have the same combinational results as the elements of the group, as given in the group's multiplication table.

- ✓ Typical characters in representations of point groups include the following:

$$0, \pm 1, \pm 2, \pm 3, \pm i = \pm\sqrt{-1}, \pm\epsilon = \pm\exp(2\pi i/n)$$

Irreducible Representations of C_{2v}

Given the multiplication table:

C_{2v}	E	C_2	σ_v	σ_v'
E	E	C_2	σ_v	σ_v'
C_2	C_2	E	σ_v'	σ_v
σ_v	σ_v	σ_v'	E	C_2
σ_v'	σ_v'	σ_v	C_2	E

The following set of substitutions has the same combinational relationships:

C_{2v}	E	C_2	σ_v	σ_v'
Γ_1	1	1	1	1

C_{2v}	$E = 1$	$C_2 = 1$	$\sigma_v = 1$	$\sigma_v' = 1$
$E = 1$	1	1	1	1
$C_2 = 1$	1	1	1	1
$\sigma_v = 1$	1	1	1	1
$\sigma_v' = 1$	1	1	1	1

☞ The substitution of all 1's, which can be made for any point group, forms the **totally symmetric representation**, labeled A_1 in C_{2v}.

C_{2v}	E	C_2	σ_v	σ_v'
A_1	1	1	1	1

Irreducible Representations of C_{2v}

The following set of substitutions also satisfies the multiplication table:

C_{2v}	E	C_2	σ_v	σ_v'
Γ_2	1	1	-1	-1

C_{2v}	$E = 1$	$C_2 = 1$	$\sigma_v = -1$	$\sigma_v' = -1$
$E = 1$	1	1	-1	-1
$C_2 = 1$	1	1	-1	-1
$\sigma_v = -1$	-1	-1	1	1
$\sigma_v' = -1$	-1	-1	1	1

These characters form the A_2 irreducible representation of C_{2v}:

C_{2v}	E	C_2	σ_v	σ_v'
A_2	1	1	-1	-1

Irreducible Representations of C_{2v}

Two other sets of substitutions also satisfy the multiplication table, forming the B_1 and B_2 irreducible representations of C_{2v}:

C_{2v}	E	C_2	σ_v	σ_v'
B_1	1	-1	1	-1
B_2	1	-1	-1	1

Any other set of substitutions will not work: e.g.

C_{2v}	E	C_2	σ_v	σ_v'
	-1	-1	1	1

C_{2v}	$E = -1$	$C_2 = -1$	$\sigma_v = 1$	$\sigma_v' = 1$
$E = -1$	1	1	-1	-1
$C_2 = -1$	1	1	-1	-1
$\sigma_v = 1$	-1	-1	1	1
$\sigma_v' = 1$	-1	-1	1	1

All results are wrong!

Basic Character Table

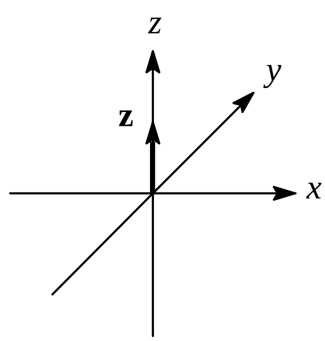
The collection of irreducible representations for a group is listed in a **character table**, with the totally symmetric representation listed first:

C_{2v}	E	C_2	σ_v	σ_v'
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

☞ The characters of the irreducible representations can describe the ways in which certain vector properties are transformed by the operations of the group.

Unit Vector Transformations

✓ Consider the effects of applying the operations of C_{2v} on a unit vector **z**. [Assume $\sigma_v = \sigma_{xz}$ and $\sigma_v' = \sigma_{yz}$.]



Operation	**z** becomes	In matrix notation
E	**z**	[+1]**z**
C_2	**z**	[+1]**z**
σ_v	**z**	[+1]**z**
σ_v'	**z**	[+1]**z**

✓ The four 1 x 1 **transformation matrices**, taken as a set, are identical to the A_1 irreducible representation of C_{2v}.

C_{2v}	E	C_2	σ_v	σ_v'	
A_1	1	1	1	1	z

Unit Vector Transformations

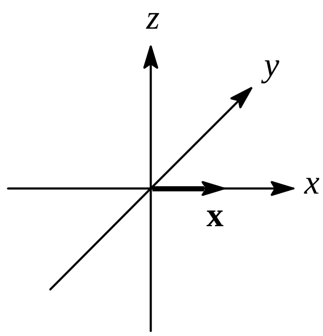
- ☞ "In C_{2v} the vector **z** transforms as A_1 representation (the totally symmetric representation).

OR

- ☞ "In C_{2v} the vector **z** belongs to the A_1 **species** (the totally symmetric species)."

Unit Vector Transformations

✓ Consider the effects of applying the operations of C_{2v} on a unit vector **x**.



Operation	**x** becomes	In matrix notation
E	**x**	[+1]**x**
C_2	**-x**	[-1]**x**
σ_v	**x**	[+1]**x**
σ_v'	**-x**	[-1]**x**

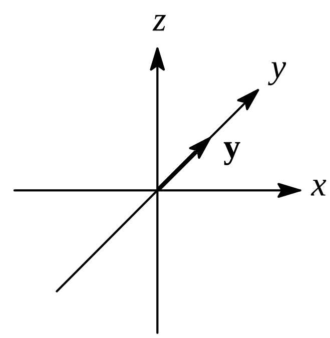
✓ The four 1 x 1 **transformation matrices**, taken as a set, are identical to the B_1 irreducible representation of C_{2v}.

C_{2v}	E	C_2	σ_v	σ_v'	
B_1	1	-1	1	-1	x

☞ "In C_{2v} the vector **x** transforms as B_1."

Unit Vector Transformations

✓ Consider the effects of applying the operations of C_{2v} on a unit vector **y**.



Operation	**y** becomes	In matrix notation
E	**y**	[+1]**y**
C_2	**-y**	[-1]**y**
σ_v	**-y**	[-1]**y**
σ_v'	**y**	[+1]**y**

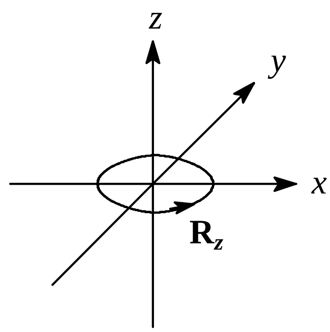
✓ The four 1 x 1 **transformation matrices**, taken as a set, are identical to the B_2 irreducible representation of C_{2v}.

C_{2v}	E	C_2	σ_v	σ_v'	
B_2	1	-1	-1	1	y

☞ "In C_{2v} the vector **y** transforms as B_2."

Rotational Vector Transformations

✓ Consider the symmetry of a rotation about the *z* axis.



Operation	$\mathbf{R_z}$ becomes	In matrix notation
E	$\mathbf{R_z}$	$[+1]\mathbf{R_z}$
C_2	$\mathbf{R_z}$	$[+1]\mathbf{R_z}$
σ_v	$-\mathbf{R_z}$	$[-1]\mathbf{R_z}$
σ_v'	$-\mathbf{R_z}$	$[-1]\mathbf{R_z}$

✓ The four 1 x 1 **transformation matrices**, taken as a set, are identical to the A_2 irreducible representation of C_{2v}.

☞ "In C_{2v} the vector $\mathbf{R_z}$ transforms as A_2."

Character Table with Vector Transformations

C_{2v}	E	C_2	σ_v	σ_v'	
A_1	1	1	1	1	z
A_2	1	1	-1	-1	$\mathbf{R}_z$
B_1	1	-1	1	-1	x, $\mathbf{R}_y$
B_2	1	-1	-1	1	y, $\mathbf{R}_x$