M.Sc. Semester-II

Compulsory Paper-7 (CP-7)

Group Theory and Spectroscopy

I. Symmetry and Group Theory in Chemistry

Lecture 3 : Character Table, Character Table for C_{2v} Point Group

Dr. Rajeev Ranjan

University Department of Chemistry

Dr. Shyama Prasad Mukherjee University, Ranchi

Symmetry and Group Theory in Chemistry : 25 Hrs

Symmetry elements and symmetry operation, Group and Subgroup, Point group, Classification and representation of groups, The defining property of a group, Sub group and Class, Group multiplication table for C_{2V}, C_{2h} and C_{3V} point group, Generators and Cyclic groups. Similarity Transformation, Table of conjugates for C_{2V}, C_{2h} and C_{3V} point group, Schonflies symbols.

Matrix notation for symmetry operation, Representations of groups by matrices (representation for the Cn, Cnv, Cnh and Dnh groups to be worked out explicitly). Character of a representation, Mulliken symbols for irreducible representations, Direct product relationship, Applications of group theory to quantum mechanics-identifying non-zero matrix elements.

The great orthogonal theorem (without proof) and rules derived from this theorem. Derivation of the orthonormalization condition. Character table. Construction of character table: C_{2V} and C_{3V} (only). Reducible representations and their reduction. Total character and their calculation. Application of character table in determination of IR and Raman active vibrations: H_2O, BF_3 and N_2F_2

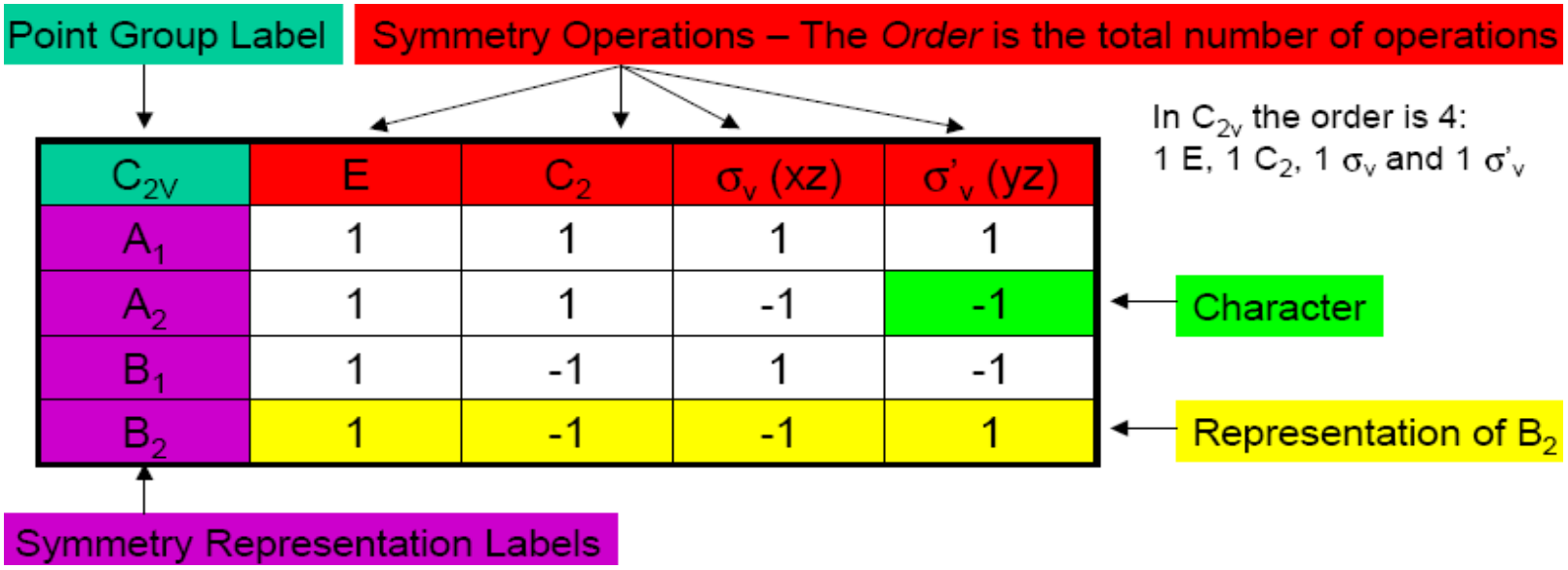
Coverage:

1. Character Table
2. Character Table for C_{2v} point group
3. Representations of Symbols
4. Applications of Group Theory

Character Tables

The symmetry properties of each point group are summarized on a *character table*. The character table lists all of the symmetry elements of the group, along with a complete set of *irreducible representations*.

Character Table (C_{2v})



C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

Character Table (C_{2v})

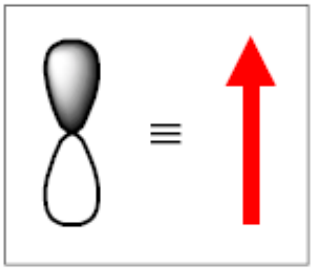
"A" means symmetric with regard to rotation about the principle axis.
"B" means anti-symmetric with regard to rotation about the principle axis.
Subscript numbers are used to differentiate symmetry labels, if necessary.
"1" indicates that the operation leaves the function unchanged: it is called "symmetric".
"-1" indicates that the operation reverses the function: it is called "anti-symmetric".

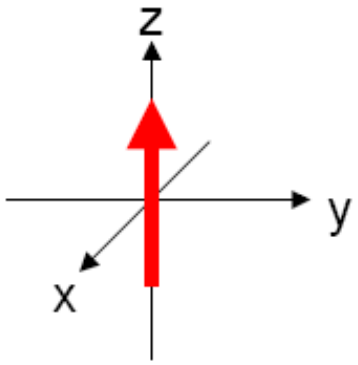
C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)	Symmetry of Functions	
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

The functions to the right are called *basis functions*. They represent mathematical functions such as orbitals, rotations, etc.

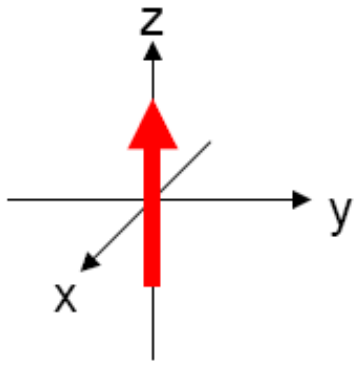
Lecture 3 : Character Table, Character Table for C_{2v} Point Group

A p_z orbital has the same symmetry as an arrow pointing along the z-axis.





E
C_2
σ_v (xz)
σ'_v (yz)

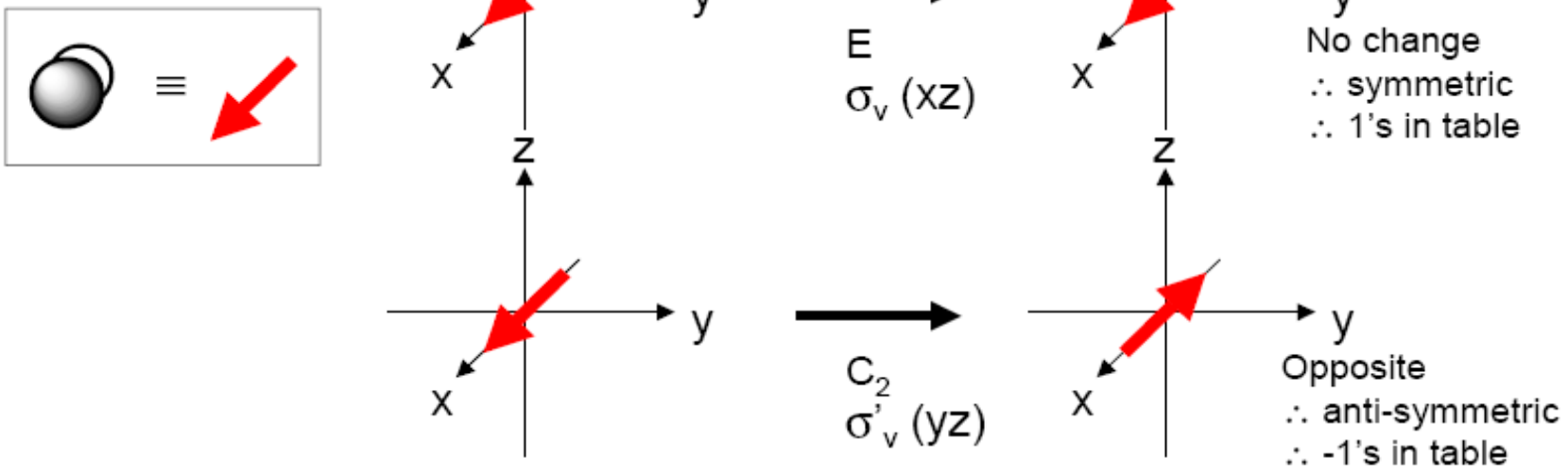


No change
∴ symmetric
∴ 1's in table

C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
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

Lecture 3 : Character Table, Character Table for C_{2v} Point Group

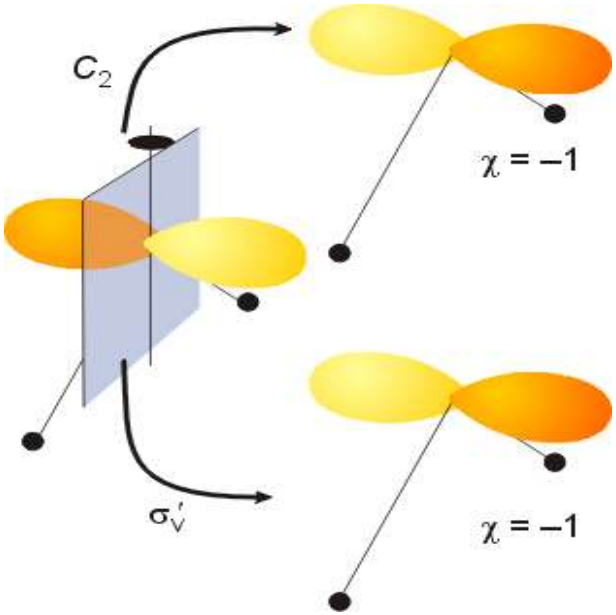
A p_x orbital has the same symmetry as an arrow pointing along the x-axis.



C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
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

Lecture 3 : Character Table, Character Table for C_{2v} Point Group

The p_x orbital



If a p_x orbital on the central atom of a molecule with C_{2v} symmetry is rotated about the C_2 axis, the orbital is reversed, so the character will be -1.

If a p_x orbital on the central atom of a molecule with C_{2v} symmetry is rotated about the C_2 axis, the orbital is reversed, so the character will be -1.

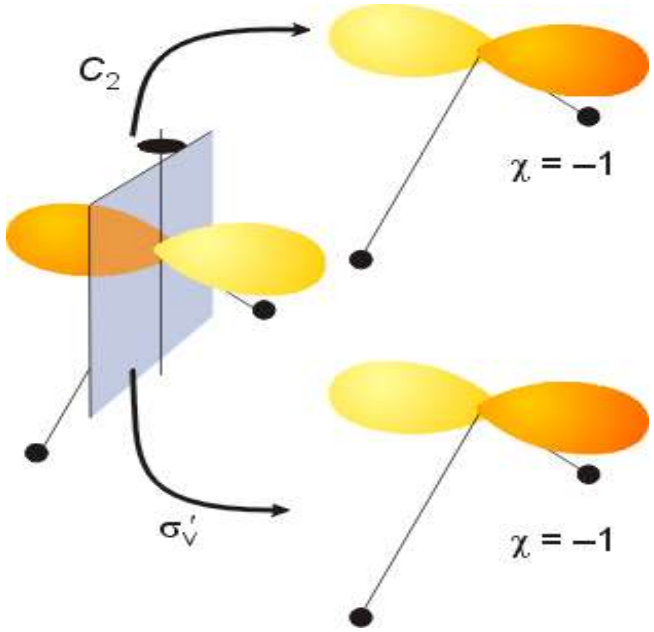
Lecture 3 : Character Table, Character Table for C_{2v} Point Group

The p_x orbital

C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
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

Lecture 3 : Character Table, Character Table for C_{2v} Point Group

The p_x orbital



If a p_x orbital on the central atom of a molecule with C_{2v} symmetry is reflected in the yz plane, the orbital is also reversed, and the character will be -1.

C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
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

Lecture 3 : Character Table, Character Table for C_{2v} Point Group

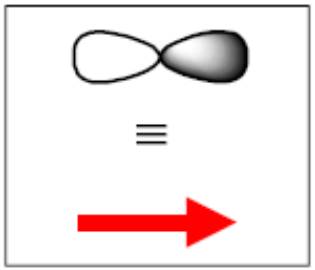
The p_x orbital

If a p_x orbital on the central atom of a molecule with C_{2v} symmetry is reflected in the xz plane, the orbital is unchanged, so the character is +1.

C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
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

Lecture 3 : Character Table, Character Table for C_{2v} Point Group

A p_y orbital has the same symmetry as an arrow pointing along the y-axis.



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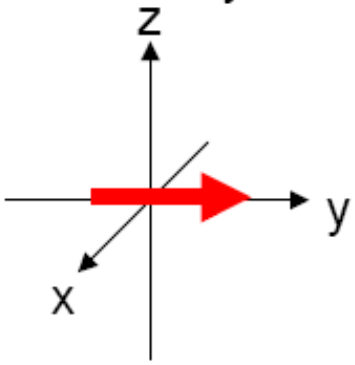
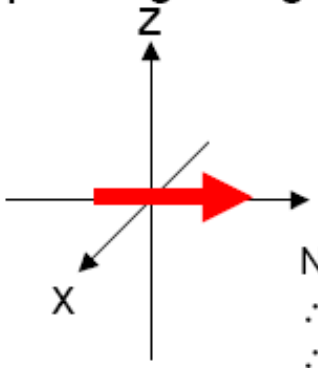
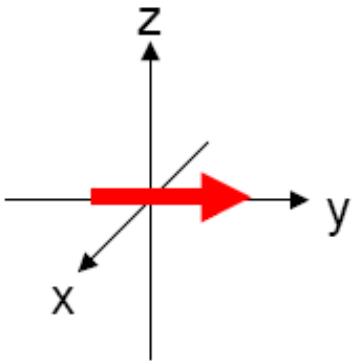


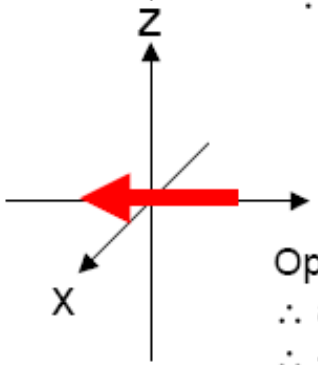
E
σ'_v (yz)



No change
∴ symmetric
∴ 1's in table



C_2
σ_v (xz)



Opposite
∴ anti-symmetric
∴ -1's in table

C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
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

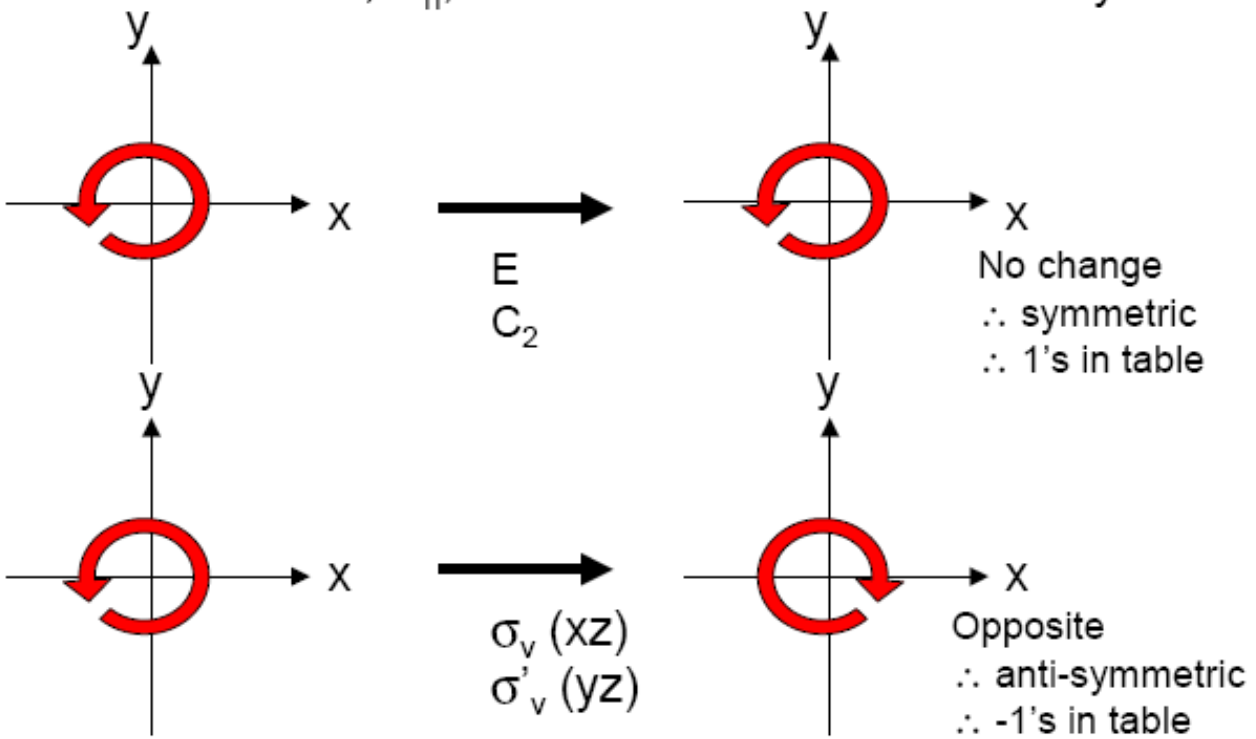
Lecture 3 : Character Table, Character Table for C_{2v} Point Group

Rotation about the n axis, R_n, can be treated in a similar way.

The z axis is pointing out of the screen!

If the rotation is still in the same direction (e.g. counter clock-wise), then the result is considered symmetric.

If the rotation is in the opposite direction (i.e. clock-wise), then the result is considered anti-symmetric.



C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
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

Lecture 3 : Character Table, Character Table for C_{2v} Point Group

d orbital functions can also be treated in a similar way

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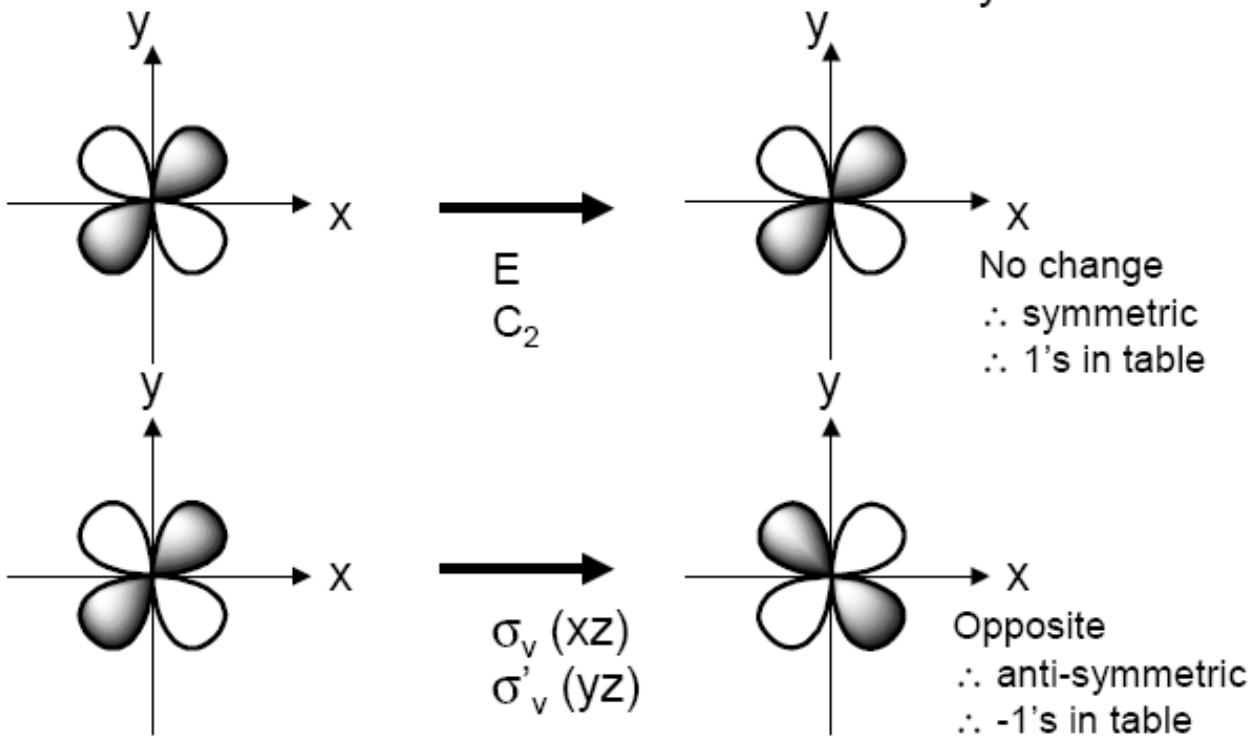


C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Character Table Representations

1. Characters of +1 indicate that the basis function is unchanged by the symmetry operation.
2. Characters of -1 indicate that the basis function is reversed by the symmetry operation.
3. Characters of 0 indicate that the basis function undergoes a more complicated change.

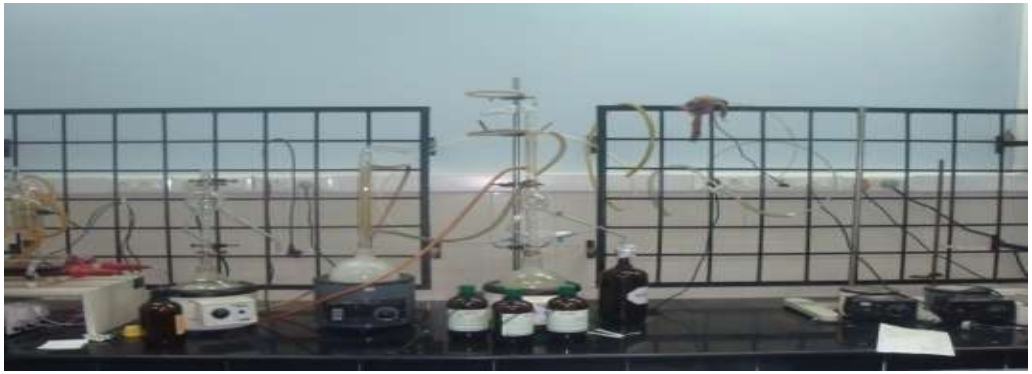
Representations of Symbols

1. An *A* representation indicates that the functions are symmetric with respect to rotation about the principal axis of rotation.
2. *B* representations are asymmetric with respect to rotation about the principal axis.
3. *E* representations are doubly degenerate.
4. *T* representations are triply degenerate.
5. Subscrips *u* and *g* indicate asymmetric (*ungerade*) or symmetric (*gerade*) with respect to a center of inversion.

Applications of Group Theory

1. Predicting polarity of molecules. A molecule cannot have a permanent dipole moment if it
    a) has a center of inversion
    b) belongs to any of the D point groups
    c) belongs to the cubic groups T or O
2. Predicting chirality of molecules. Chiral molecules lack an improper axis of rotation (S_n), a center of symmetry (i) or a mirror plane (σ).
3. Predicting the orbitals used in σ bonds. Group theory can be used to predict which orbitals on a central atom can be mixed to create hybrid orbitals.
4. Determining the symmetry properties of all molecular motion (rotations, translations and vibrations). Group theory can be used to predict which molecular vibrations will be seen in the infrared or Raman spectra.

Thank You



Dr. Rajeev Ranjan
University Department of Chemistry
Dr. Shyama Prasad Mukherjee University, Ranchi