

CH6. Symmetry

Symmetry elements and operations

Point groups

Character tables

Some applications

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Symmetry elements

symmetry element: an element such as a rotation axis or mirror plane indicating a set of symmetry operations

symmetry operation: an action that leaves an object in an indistinguishable state. Indicated here by boldface

note: $\mathbf{C}_2 \times \mathbf{C}_2 = \mathbf{C}_2^2 =$ two successive \mathbf{C}_2 rotations

Types of symmetry elements:

1. E = identity element - do nothing
2. C_n = proper rotation axis = rotation by $(360 / n)^\circ$
3. σ = mirror plane = reflect object in plane
4. i = inversion center or center of symmetry
5. S_n = improper rotation axis, a C_n axis combined with reflection through a perpendicular σ

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Elements and operations

Ex: C_3 axis (symmetry element) is associated with 3 operations:

C_3 = rotation about the axis by 120°

$C_3^2 = C_3 \times C_3$ = rotation by 240°

C_3^3 = rotation by $360^\circ = E$

$C_3^4 = C_3$ and etc...

Ex: S_4 axis indicates the following operations:

S_4 = rotation by 90° then σ

$S_4^2 = C_2$

$S_4^3 = C_4^3 \times \sigma$

$S_4^4 = E$

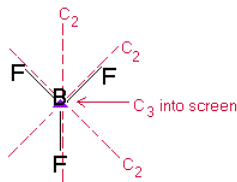
$S_4^5 = S_4$ and etc...

$S_n^n = E$ for n even, and $S_n^n = \sigma$ for n odd

Also $S_2 = i$

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More about symmetry elements



Objects (molecules) may have more than one C_n . The axis with highest n is called the *principal rotation axis*.

σ_h = horizontal mirror plane, perpendicular to principal C_n

σ_v (or σ_d) = vertical (or dihedral) mirror planes, parallel to (containing) the principal C_n

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Point Group Examples

BF_3	SF_6
H_2O	SF_5Cl
NH_3	White cube, opposite faces black
HF	
CO_2	<i>See website and assigned exercises for many more practice examples</i>
CH_4	
CH_3Cl	
CF_2BrCl	

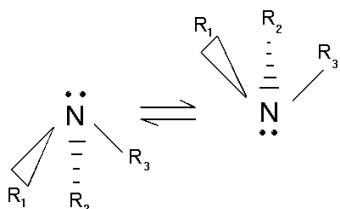
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Symmetry rules

- All molecules in cubic groups, D groups, or with i , are non-polar, all others can be polar.
- Objects with any σ or S_n axis are not chiral, all others are chiral.
- Atoms exchanged by any symmetry operation are chemically identical, otherwise, they are chemically distinct.

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Fluxionality in amines



The inversion rate depends on the activation energy required to form the pseudo-planar intermediate, for this molecule it's less than 20 kJ/mol.

- Consider a tertiary amines with three different substituents on N, ex: ethylmethylamine $\text{NH}(\text{CH}_3)(\text{CH}_2\text{CH}_3)$
- Point group is C_1 , chiral by symmetry rules (has a non-identical mirror image). Experiments, however, show no optical activity, and no resolution of stereoisomers by chiral chromatography.
- Fluxionality occurs more rapidly at RT than the optical measurement or column separation.
- NMR (a probe with a shorter time) confirms that 2 enantiomers do exist.

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Character Tables

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$	basis functions
A_1	1	1	1	1	1	z, z^2
A_2	1	1	1	-1	-1	R_z
B_1	1	-1	1	1	-1	$x^2 - y^2$
B_2	1	-1	1	-1	1	xy
E	2	0	-2	0	0	$(x,y), (xz, yz), (R_x, R_y)$

- Column headings give all symmetry operations (separated into classes). For C_{4v} there are **E**, **$2C_4$** , etc...
- Classes are operations that transform into one another by another group operation. In C_{4v} , $C_4^2 = C_2$ is in a class by itself.
- **$2C_4$** is short notation for the operations C_4 and C_4^3
- The order, h, is the sum of the coefficients of the headings and is total number of operations. For C_{4v} , $h = 8$.

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Conventions

- The z axis contains the principal rotation axis
- The molecule is oriented so that bond axes are along x and y when possible
- a σ_v will contain perpendicular C_2 when present
- a σ_d will bisect perpendicular C_2 or bond axes when possible.

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Irreducible reps and characters

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$	
A_1	1	1	1	1	1	z, z^2
A_2	1	1	1	-1	-1	R_z
B_1	1	-1	1	1	-1	$x^2 - y^2$
B_2	1	-1	1	-1	1	xy
E	2	0	-2	0	0	(x,y) (xz, yz) (R_x, R_y)

Note: The class heading E, for the identity operation, coincidentally has the same symbol as the irreducible rep label E.

- Each row corresponds to an irreducible representation, Γ_{irred} , which are orthogonal vectors in h-space
- The numbers are called characters, χ , and indicate how Γ_{irred} acts under a class of operations. In the simplest case, $\chi = 1$ means that Γ_{irred} is unchanged, and $\chi = -1$ means that it inverts. Ex: in C_{4v} , for $\Gamma(A_2)$, $\chi(C_4) = +1$, i.e. A_2 is unchanged by the operations C_4 and C_4^3

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Symmetry labels

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$	
A_1	1	1	1	1	1	z, z^2
A_2	1	1	1	-1	-1	R_z
B_1	1	-1	1	1	-1	$x^2 - y^2$
B_2	1	-1	1	-1	1	xy
E	2	0	-2	0	0	(x,y) (xz,yz) (R_x,R_y)

- The labels on the Γ_{irred} indicate some of the χ values:

A or B means that $\chi(E) = 1$

A is for $\chi(C_4) = 1$

B is for $\chi(C_4) = -1$

E means $\chi(E) = 2$

T means $\chi(E) = 3$

- The subscript g (gerade) means that $\chi(i)$ is positive, u (ungerade) that $\chi(i)$ is negative.

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Basis functions

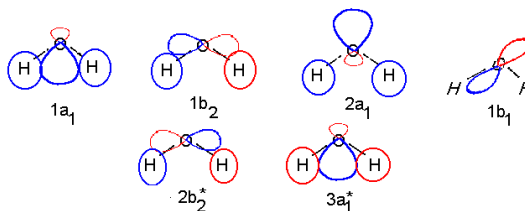
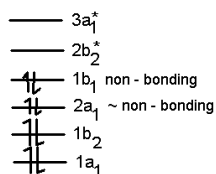
C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$	
A_1	1	1	1	1	1	z, z^2
A_2	1	1	1	-1	-1	R_z
B_1	1	-1	1	1	-1	$x^2 - y^2$
B_2	1	-1	1	-1	1	xy
E	2	0	-2	0	0	(x,y) (xz,yz) (R_x,R_y)

- Basis functions have the same symmetry as atomic orbitals: x for p_x , y for p_y , xz for d_{xz} , etc... or are rotations about x, y, z axes (R_x, R_y, R_z). They also transform as a Γ_{irred} .
- s-orbitals are spherically symmetric and have $\chi = 1$ for any operation, so they always have the symmetry of the first Γ_{irred} listed (A_1 in the C_{4v} point group).
- MO's can also be assigned and labelled with Γ_{irred} .

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Assign labels to MO's in H₂O

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



Molecule is in yz plane

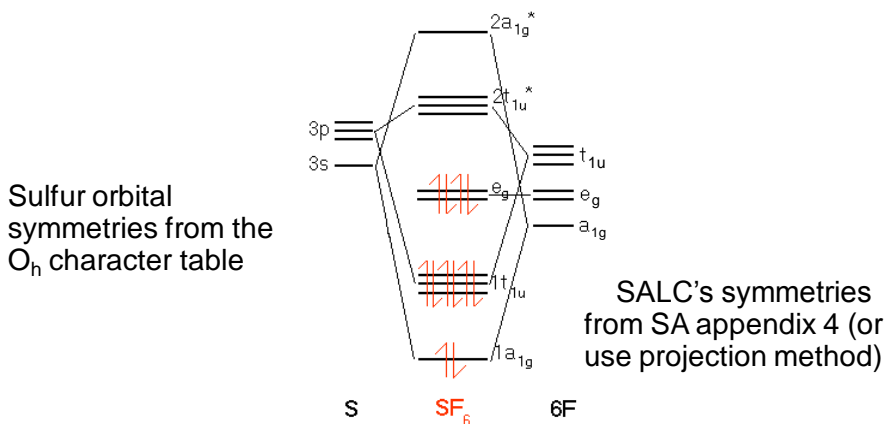
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Orthogonality of Γ_{irred}

- all Γ_{irred} within a point group are **orthogonal, their cross-products are zero.**
- MO's that have different symmetry labels have no net overlap
- For metal-ligand compounds, label symmetries of metal orbitals from basis functions, and interact with same symmetry SALC's only.

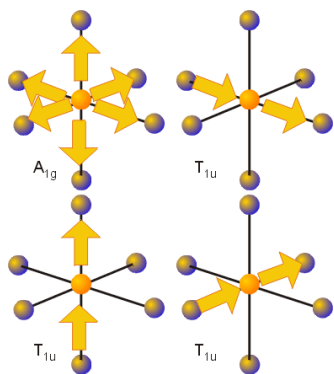
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Symmetry labels and bonding



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IR and Raman selection rules



- In IR absorption, allowed vibrational modes have the same symmetry as the transition moment operator (x , y , or z)

O_h molecules have only T_{1u} vibration modes IR active.

- For Raman absorption, allowed modes have the symmetry of a polarizability operator (x^2 , y^2 , z^2 , xy , xz , yz , or any linear combination)

For O_h molecules, A_{1g} , E_g , and T_{2g} are the allowed symmetries. An A_{1g} Raman stretching mode is pictured to the left.

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O_h character table

O _h	E	8C ₃	6C ₂	6C ₄	3C ₂ '	i	6S ₄	8S ₆	3σ _h	6σ _d	
A _{1g}	1	1	1	1	1	1	1	1	1	1	x ² +y ² +z ²
A _{2g}	1	1	-1	-1	1	1	-1	1	1	-1	
E _g	2	-1	0	0	2	2	0	-1	2	0	(x ² -y ²), z ²
T _{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R _x , R _y , R _z)
T _{2g}	3	0	1	-1	-1	3	-1	0	-1	1	(xy, yz, zx)
A _{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A _{2u}	1	1	-1	-1	1	-1	1	-1	-1	1	
E _u	2	-1	0	0	2	-2	0	1	-2	0	
T _{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)
T _{2u}	3	0	1	-1	-1	-3	1	0	1	-1	