Shapes of molecules, hybrid orbitals and symmetry descriptions

Lectures 10/11 2017 362 Spring term

Some of these ppt slides from Dr. Oleg Ozerov's lecture in 2014

Lewis Structures

- **A bond between two atoms is formed by means of sharing of a pair of electrons**
- **Each atom shares electrons with neighbors to achieve a total of eight valence electrons**
- ***Determine connectivity of the atoms in the molecule***
- ***Sum up the total number of valence electrons in the molecule***
- ***Distribute the electrons so that each atom acquires an octet (duet for H!) in either***

  a) bonding pairs (denoted : or –) shared between a pair of atoms, or

  b) lone pairs (denoted :) that belong to a single atom (i.e., "unused" in making bonds and occupy more space than bonded pairs).

Examples: HF, CF_4, NH_3, $COCl_2$, CO, CO_2, N_2O, H_2CN_2, N_3^-, N_5^+

Vocabulary and Concepts

Valence, Oxidation Number, and Formal Charge: Three Related but Fundamentally Different Concepts

Valence: Number of electrons an atom uses in bonding.

Oxidation State or Number: Charge on atoms according to a set of rules That consider the electronegativity of atoms within the molecule or material.

1) In pure element, Oxidation Number = 0
2) F, the most electronegative element, in a molecule is -1
3) O is typically -2; sometimes (in peroxides), -1
4) Alkali metals, +1; Alkaline Earth metals, +2; Gp 3, generally +3; Transition metals variable + charged.
5) H is +1 when combined with more electroneg. element; -1 when combined with more electropositive element. *Therefore, H in compound with any M is a hydride, H^{-1}.*
6) Summation of Ox. States must equal charge on ion; or zero if neutral molecule.

Formal Charges: Charge on atom according to equation:

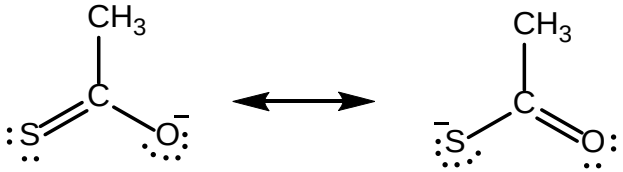
F.C. = # valence electrons - # of electrons in non-bonded pairs – ½ # of electrons in bonds

Coordination number: Number of atoms bonded to the atom in question.

Parkin, G. *J. Chem. Educ*. **2006**, *83*, 791
Jensen, W. B. *J. Chem. Educ.* **2006**, *83*, 1751

Resonance Structures: A Way to Delocalize Electrons in Valence Bond Descriptions

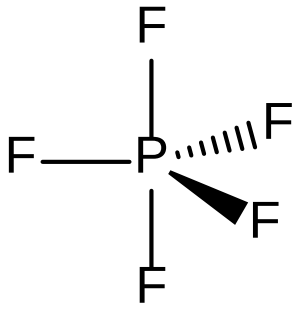
- **Resonance structures represent different Lewis structures for the same molecule**
- Resonance structures must have the same connectivity and the same total no. of electrons
- **Resonance structures are *not isomers*, but are various limiting descriptions of the same molecule.**
- If a molecule can be represented by more than one viable resonance structure, its electronic structure should be thought of as a "blend" of the resonance structures. Such "blending" generally lowers the energy of the system.
- **Resonance structure may be of equal or unequal importance ("weight").**
- Guiding principles: **Favor** octets; **minimize** formal charges*; **disfavor** formal positive charge on more electronegative atoms

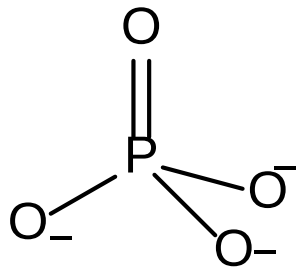


*Pauling's Electroneutrality Principle

Hypervalence

- Hypervalence may be a misnomer by some definitions, but it would probably be the most commonly used misnomer in chemistry
- Aka “octet expansion”
- Can be represented either by an increased number of atoms bound to the “hypervalent” atom or by an increased number of (multiple) bonds to the “hypervalent” atom. Applies to 3rd row and higher non-metals bonds to highly electronegative elements.

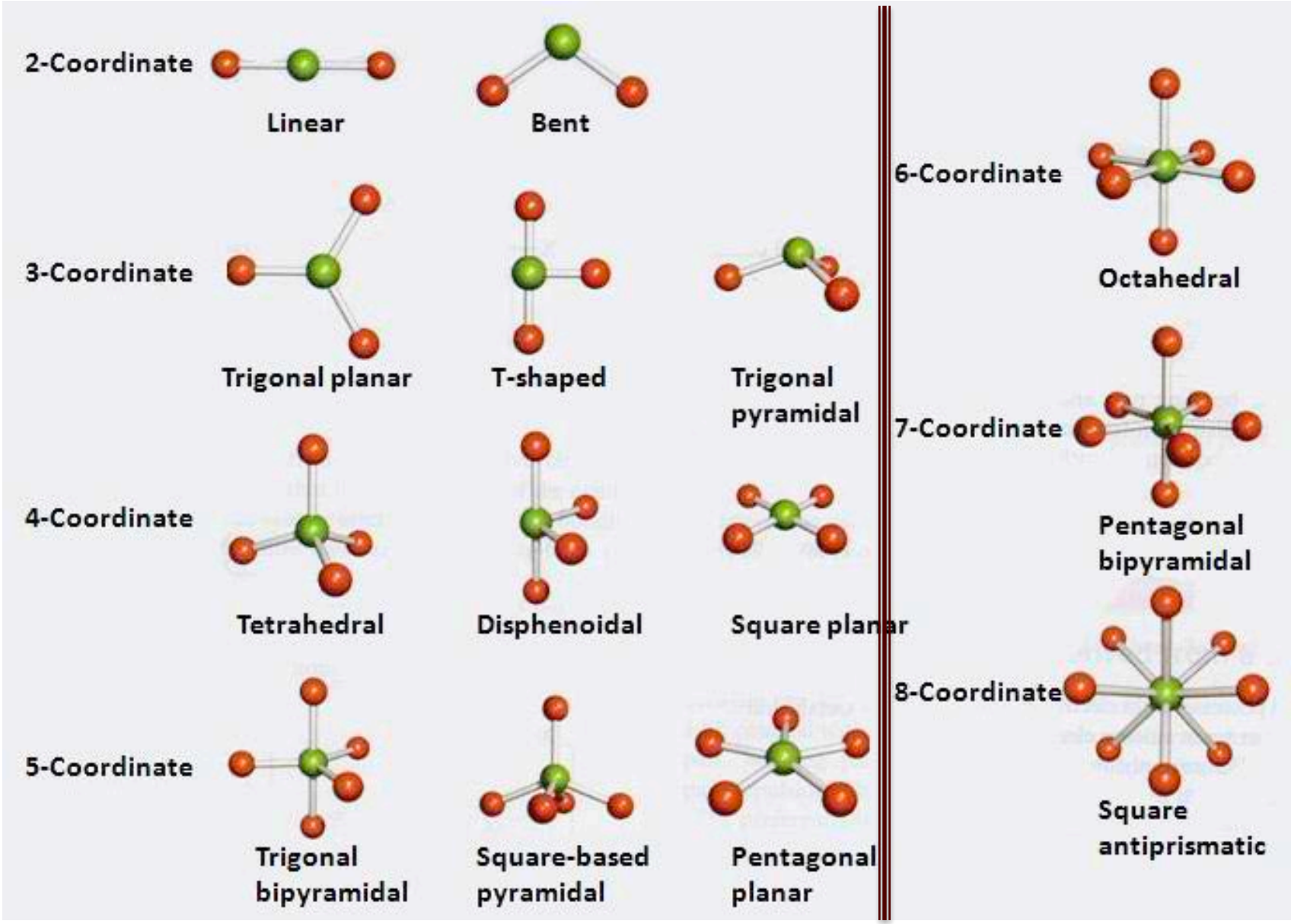


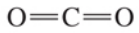
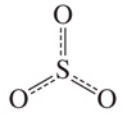
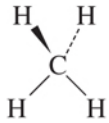
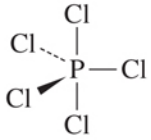
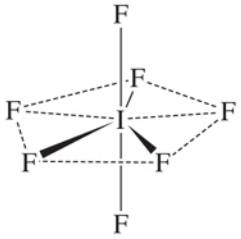
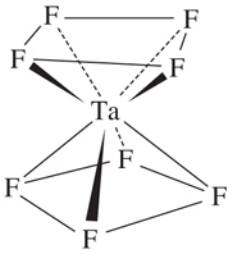


Geometries may be predicted via VSEPR: Valence Shell Electron Pair Repulsion

- **Electron pairs of bonds and lone pairs repel each other**
- **The geometry around any atom is a consequence of minimizing these repulsive interactions**
- Lone pairs are considered to be larger than bonding pairs
- **Multiple bonds are considered to be in the same space as, but larger than, single bonds**
- **Several common geometries depending on the number of "occupants" around the atom in question**
- **The "Steric number" of the molecule determines the hybrid orbitals used to account for sigma bonds and lone pairs**

Descriptions of geometries in mono-centric molecules: It is where The atoms are. . .



Steric Number	Geometry	Examples	Calculated Bond Angles	
2	Linear	CO_2	180°	
3	Trigonal (triangular)	SO_3	120°	
4	Tetrahedral	CH_4	109.5°	
5	Trigonal bipyramidal	PCl_5	120°, 90°	
6	Octahedral	SF_6	90°	
7	Pentagonal bipyramidal	IF_7	72°, 90°	
8	Square antiprismatic	TaF_8^{3-}	70.5°, 99.6°, 109.5°	

Hybrid orbitals

$sp = s + p_z$

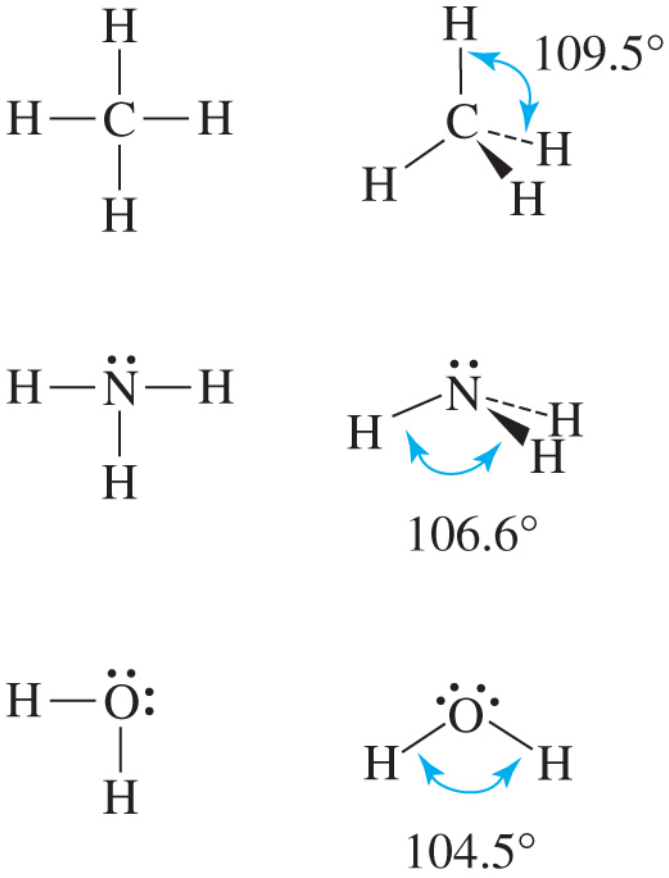
$sp^2 = s + p_x + p_y$

$sp^3 = s + p_x + p_y + p_z$

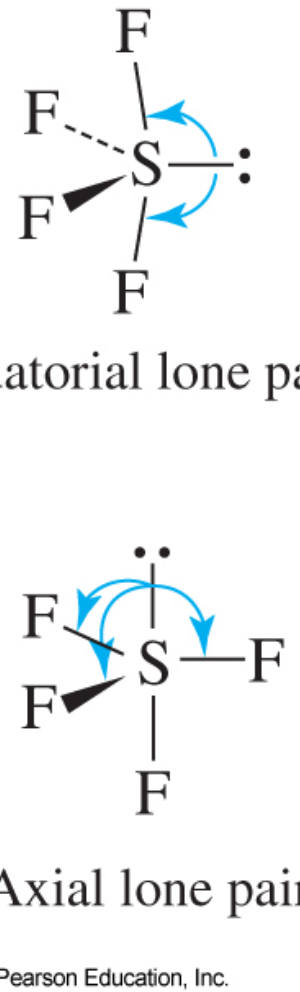
$sp^3d = (s + p_x + p_y) + (p_z + d_{z^2})$

$sp^3d^2 = s + p_x + p_y + p_z + d_{x^2 - y^2} + d_{z^2}$

VSEPR rationalizes bond angles and geometry of molecules



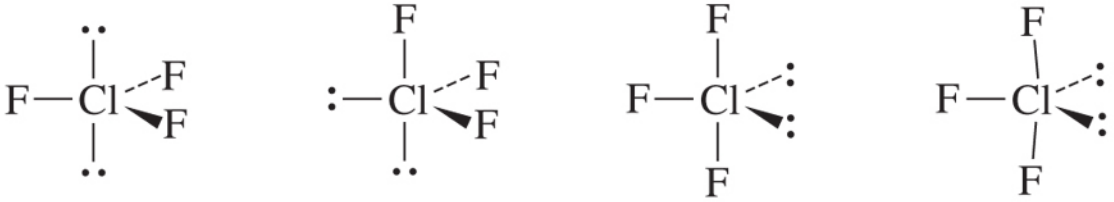
For H_2O and NH_3, lone pairs are in sp^3 hybrid orbitals; for H_2S and PH_3 No hybrid orbitals needed.



For SF_4 the lone pair is more stable in the sp^2 subset of the sp^3d hybrid orbitals

How about the 5 pairs of electrons about Cl in ClF_3?

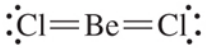
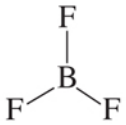
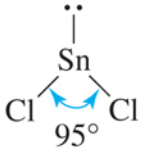
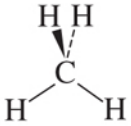
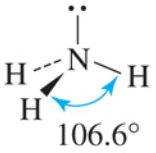
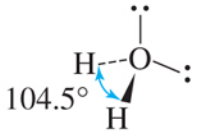
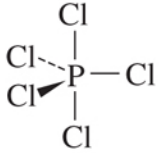
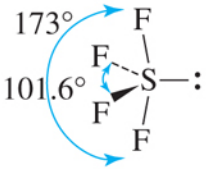
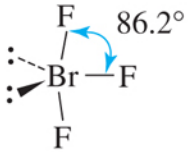
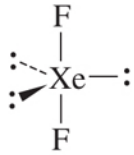
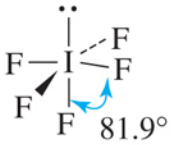
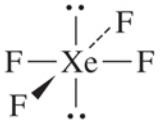
Analysis of lone pair/lone pair vs. lone pair/bonded pair vs. bonded pair/bonded pair repulsions



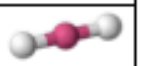
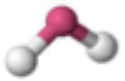
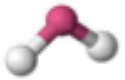
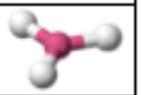
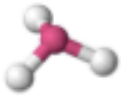
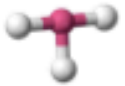
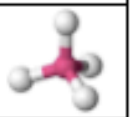
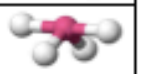
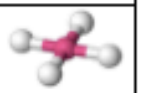
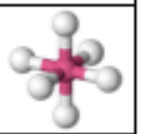
A B C Experimental

Interaction	Calculated			Experimental
	A	B	C	
lp-lp	180°	90°	120°	Cannot be determined
lp-bp	6 at 90°	3 at 90°	4 at 90°	Cannot be determined
		2 at 120°	2 at 120°	
bp-bp	3 at 120°	2 at 90°	2 at 90°	2 at 87.5°
		1 at 120°		Axial Cl—F 169.8 pm
				Equatorial Cl—F 159.8 pm

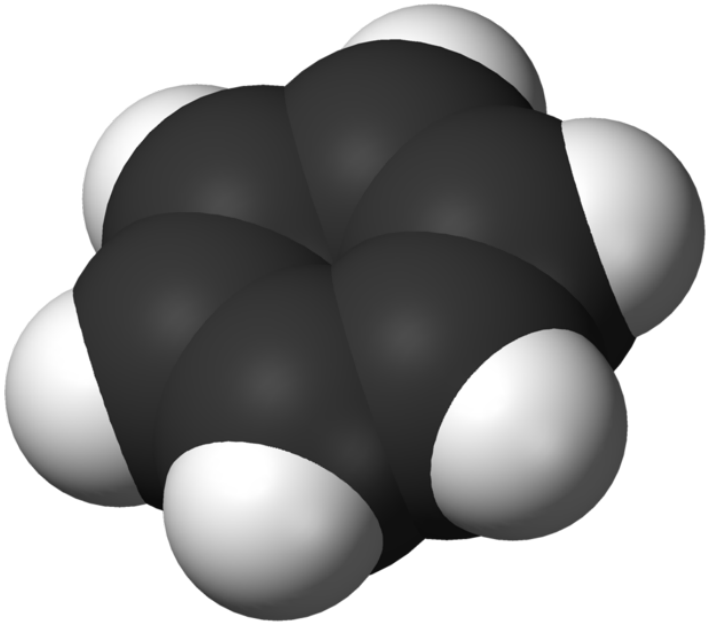
Conclusion: larger pairs of electrons adopt equatorial plane positions, i.e., sp^2 subset

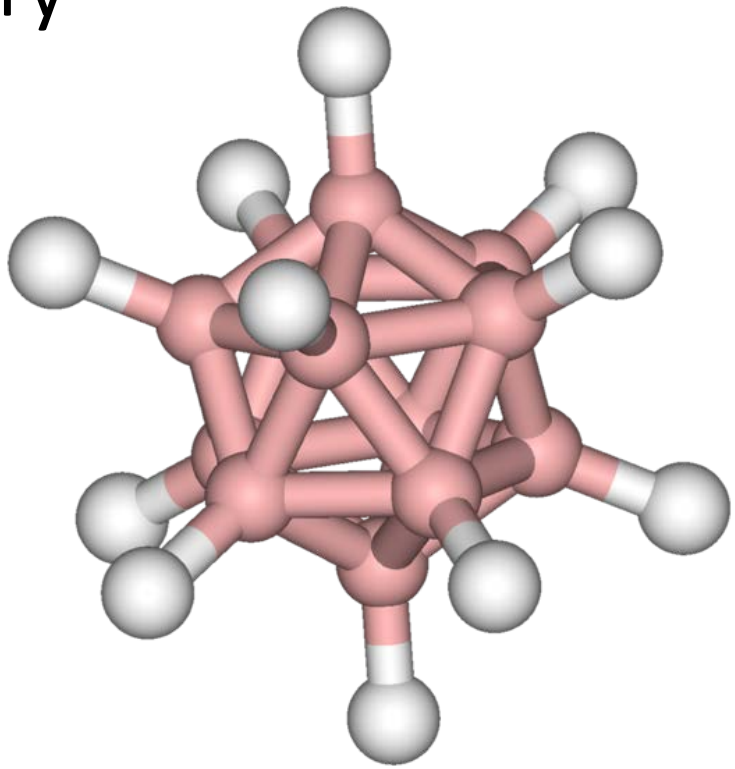
Steric Number	*Number of Lone Pairs on Central Atom*			
	None	*1*	*2*	*3*
2				
3				
4				
5				
6				

VSEPR Theory

# of Atoms	# of electron pairs	Formula Type	Geometry	Bond Angle	Examples	Hybridization	Structure
3	0	AB_2	Linear	180	CO_2, CS_2, BeH_2		
3	1	AB_2	Bent	117.5	$GeCl_2$, SO_2, NO^-_2	sp^2	
3	2	AB_2	Bent	105	H_2O, H_2S	sp^3	
4	0	AB_3	Trigonal planar	120	BCl_3, $AlBr_3$,	sp^2	
4	1	AB_3	Pyramidal	107	NH_3, PCl_3, $AsBr_3$	sp^3	
4	2	AB_3 (Inter halogen)	T-shaped	90, 180	ICl_3, BrF_3,	sp^3d	
5	0	AB_4	Tetrahedron	109.5	CCl_4, CH_4, $SiBr_4$	sp^3	
5	1	AB_4	Distorted tetrahedron (Seesaw)		SF_4, SBr_4, $SeCl_4$	sp^3d	
5	2	AB_4	Square planar	90, 180	XeF_4,	sp^3d^2	
6	0	AB_5	Trigonal bipyramidal	90, 180, 120	PCl_5,	sp^3d	
6	1	AB_5 (Inter halogen)	Square pyramid		ClF_5, ICl_5, IBr_5	sp^3d^2	
7	0	AB_6	Octahedron	90, 180	SF_6	sp^3d^2	

Symmetry



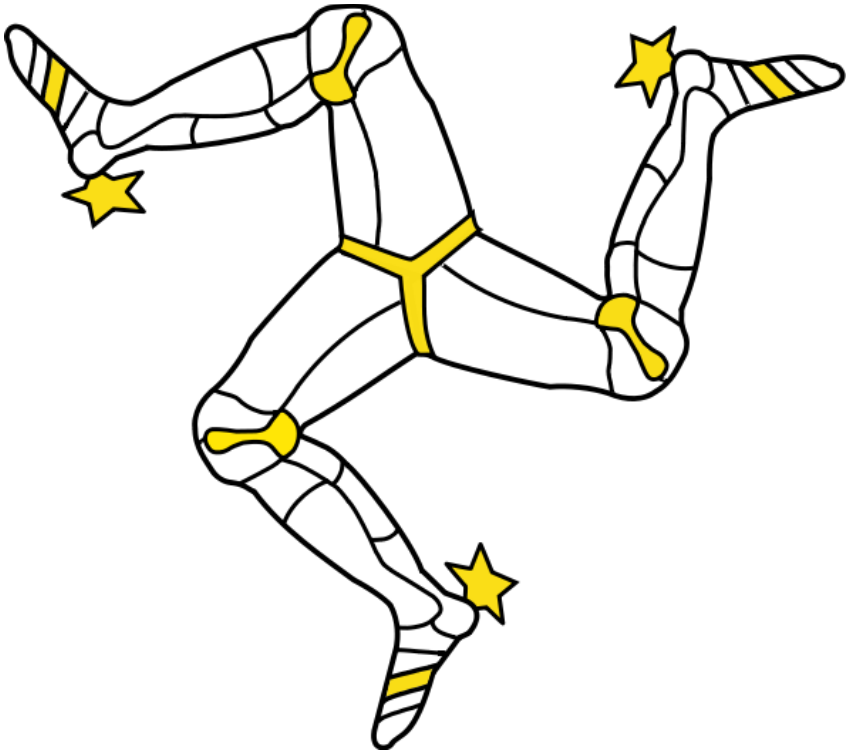


Intuitively, we know symmetry when we see it.

But how do we put in quantitative terms that allows us to compare, assign, classify?

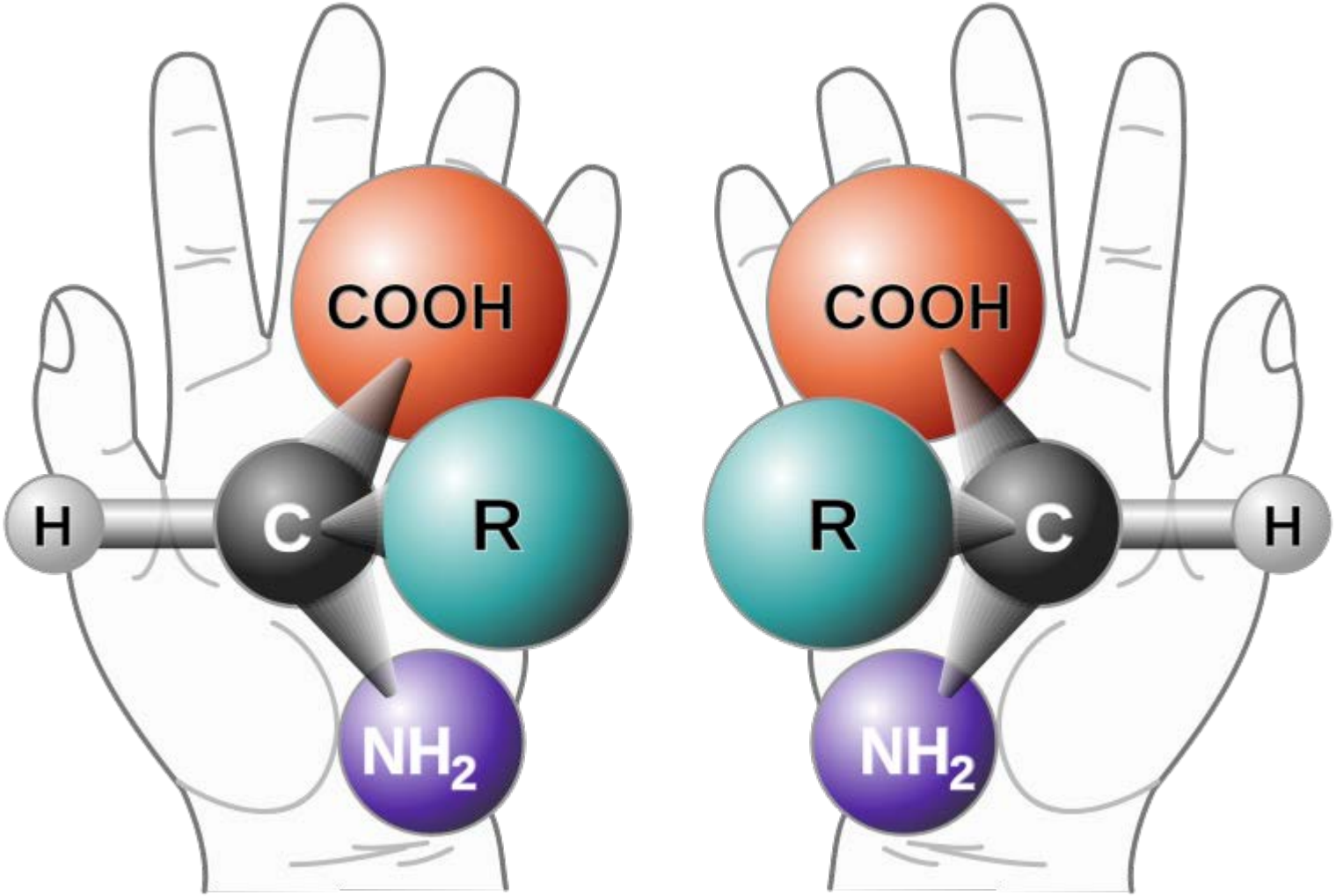
Symmetry: mirror planes

Symmetry



C_3 Rotation Axis

Chirality: Non-superimposable mirror images (aka optical isomers or enantiomers)



Specifically, a chiral compound can contain no improper axis of rotation (S_n), which includes planes of symmetry and inversion center. Asymmetric molecules are always chiral.

Symmetry Operations and Symmetry Elements

Definitions:

- A **symmetry operation** is an operation on a body such that, after the operation has been carried out, the result is indistinguishable from the original body (every point of the body is coincident with an equivalent point or the same point of the body in its original orientation).
- A **symmetry element** is a geometrical entity such as a line, a plane, or a point, with respect to which one or more symmetry operations may be carried out

Symmetry Operation	Symmetry Element	Notation
Identity	-	E
Reflection in a plane	Plane of symmetry	σ
Proper rotation	Rotation axis (line)	C_n
Rotation followed by reflection in the plane perpendicular to the rotation axis	Improper rotation axis (line)	S_n
Inversion	Center of inversion	I

Let’s look for these in molecules

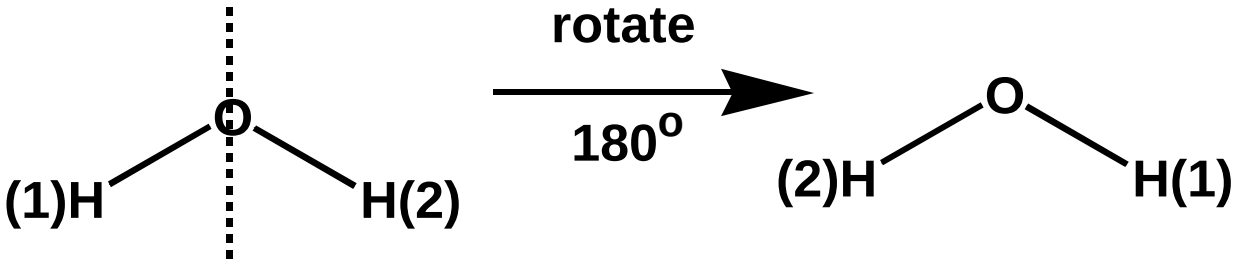
Notes
(i) symmetry operations more fundamental, but elements often easier to spot.

(ii) some symmetry elements give rise to more than one operation - especially rotation - as above.

ROTATIONS - AXES OF SYMMETRY

Some examples for different types of molecule: e.g.

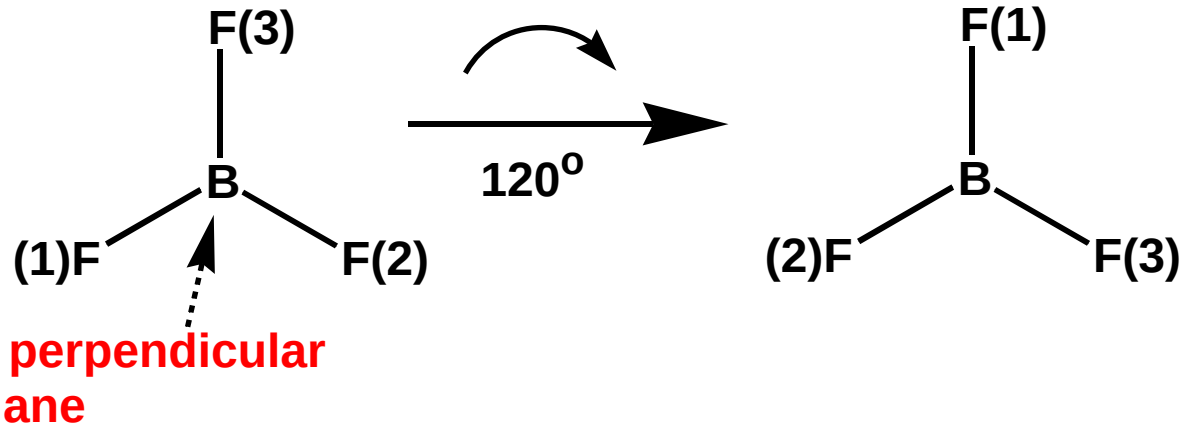
H_2O



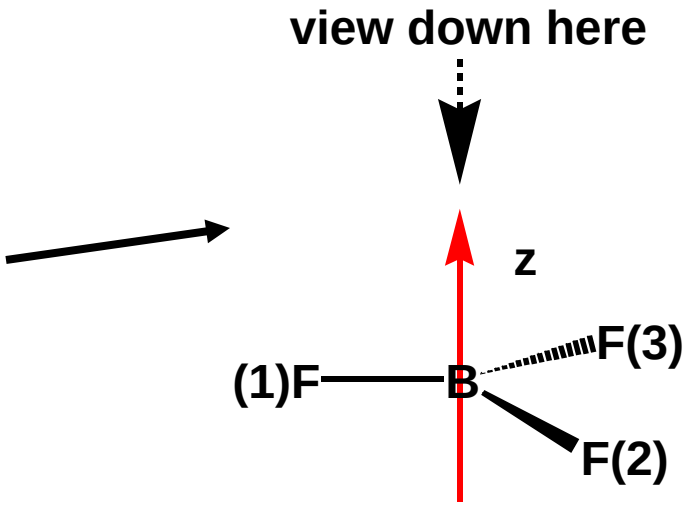
Line in molecular plane, bisecting HOH angle is a rotation axis, giving indistinguishable configuration on rotation by 180^o.

BF_3

By VSEPR - trigonal, planar, all bonds equal, all angles 120^o. Take as axis a line perpendicular to molecular plane, passing through B atom.



N.B. all rotations CLOCKWISE when viewed along -z direction.

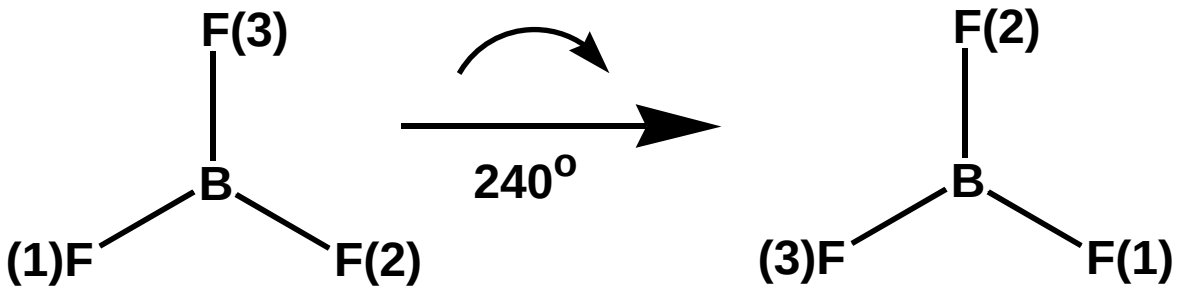


Symbol for axes of symmetry

C_n

where rotation about axis gives indistinguishable configuration every $(360/n)^o$ (i.e. an n-fold axis)

Thus H_2O has a C_2 (two-fold) axis, BF_3 a C_3 (three-fold) axis. One axis can give rise to >1 rotation, e.g. for BF_3, what if we rotate by 240^o?



Must differentiate between two operations.

Rotation by 120^o described as C_3^1,

rotation by 240^o as C_3^2.

In general C_n axis (minimum angle of rotation $(360/n)^o$) gives operations C_n^m, where both m and n are integers.

When m = n we have a special case, which introduces a new type of symmetry operation.....

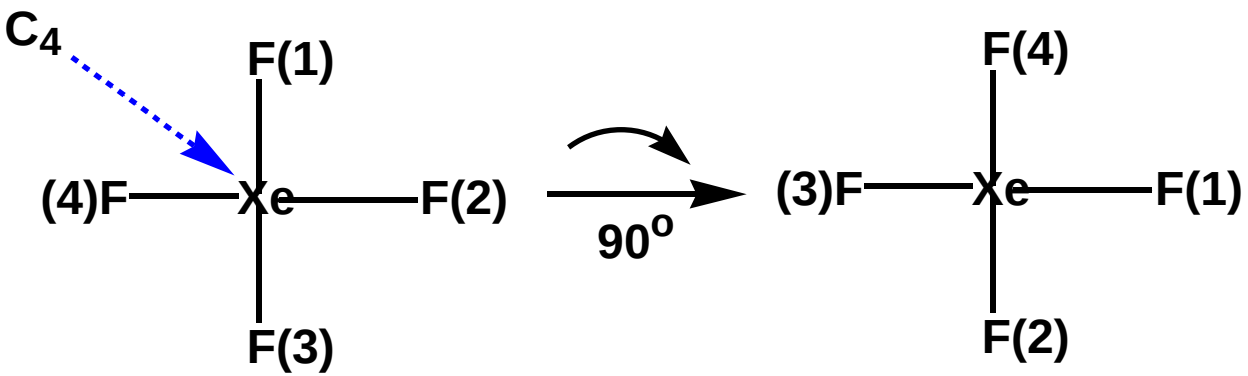
IDENTITY OPERATION

For H_2O, C_2^2 and for BF_3 C_3^3 both bring the molecule to an IDENTICAL arrangement to initial one.

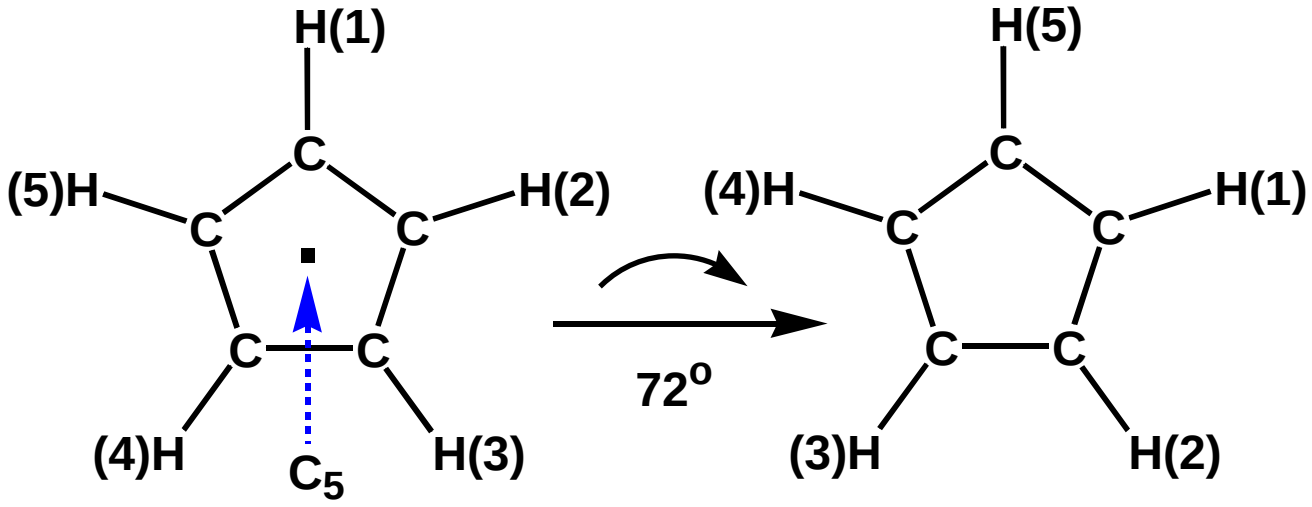
Rotation by 360^o is exactly equivalent to rotation by 0^o, i.e. the operation of doing NOTHING to the molecule.

MORE ROTATION AXES

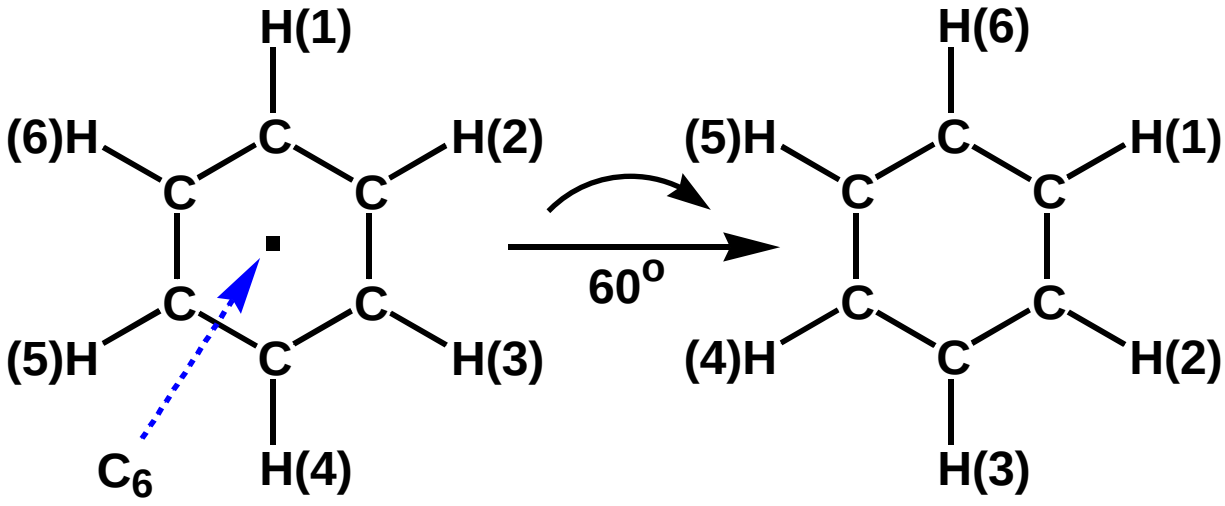
xenon tetrafluoride, XeF_4



cyclopentadienide ion, $C_5H_5^-$

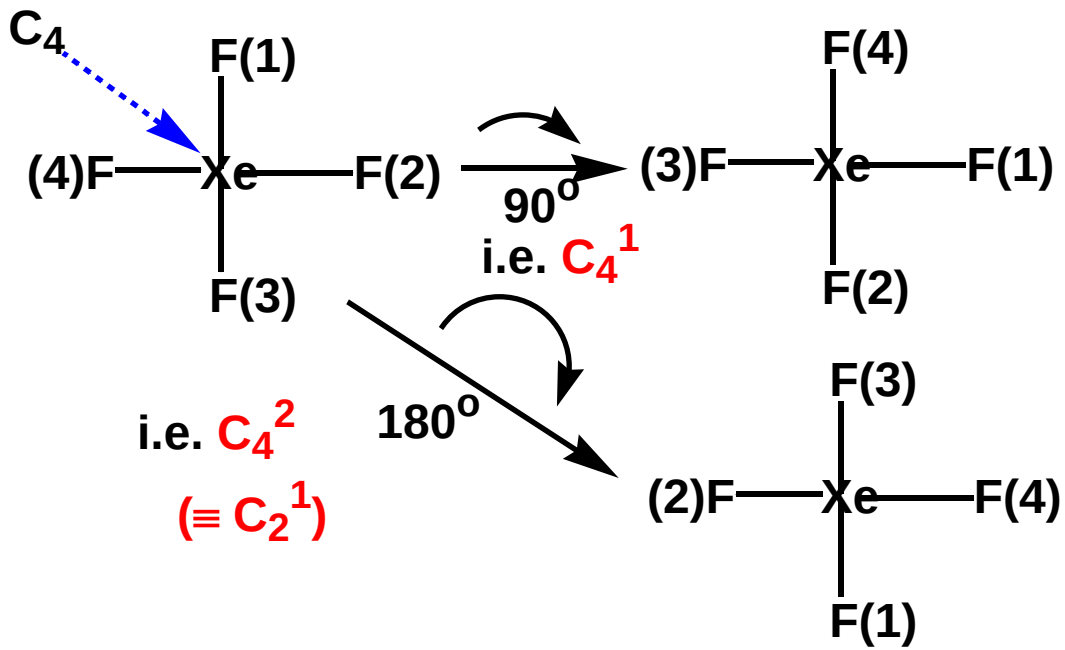


benzene, C_6H_6



Examples also known of C_7 and C_8 axes.

If a C_{2n} axis (i.e. even order) present, then C_n must also be present:



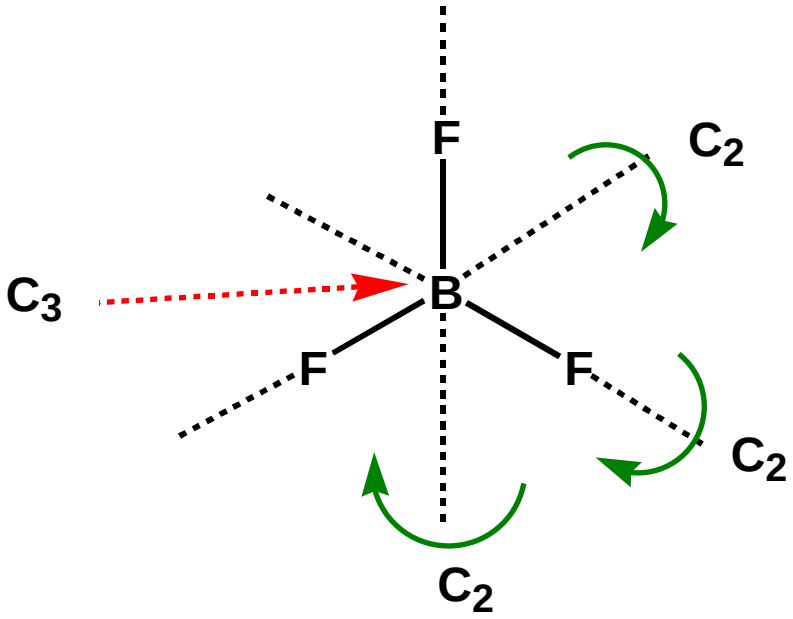
Therefore there must be a C_2 axis coincident with C_4, and the operations generated by C_4 can be written:

$C_4^1, C_4^2 (C_2^1), C_4^3, C_4^4 (E)$

Similarly, a C_6 axis is accompanied by C_3 and C_2, and the operations generated by C_6 are:

$C_6^1, C_6^2 (C_3^1), C_6^3 (C_2^1), C_6^4 (C_3^2), C_6^5, C_6^6 (E)$

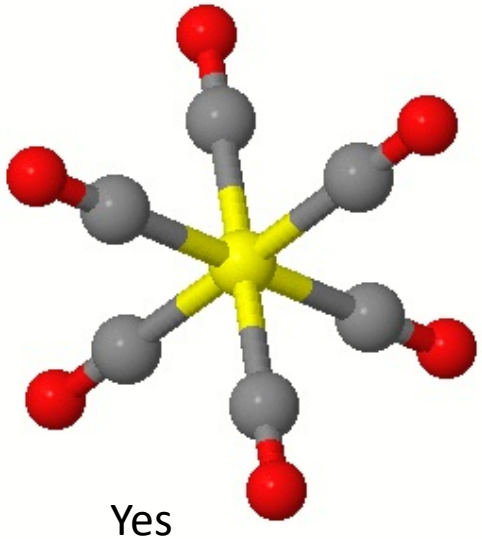
Molecules can possess several distinct axes, e.g. BF_3:



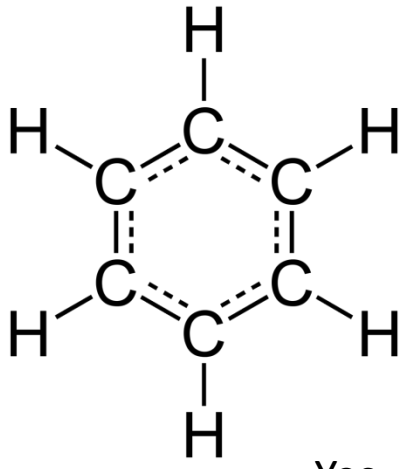
Three C_2 axes, one along each B-F bond, perpendicular to C_3

Mirror Planes within BF_3. Of two types,

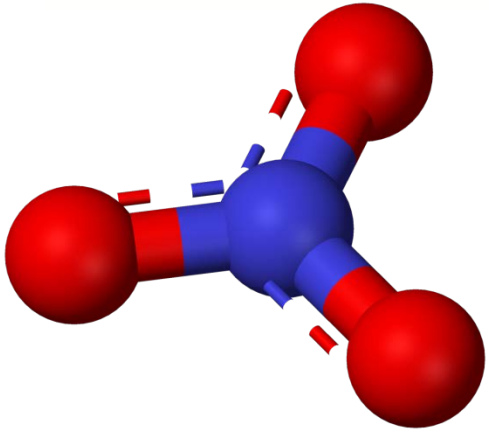
Center of Inversion in Molecules: x,y,z -> -x, -y, -z



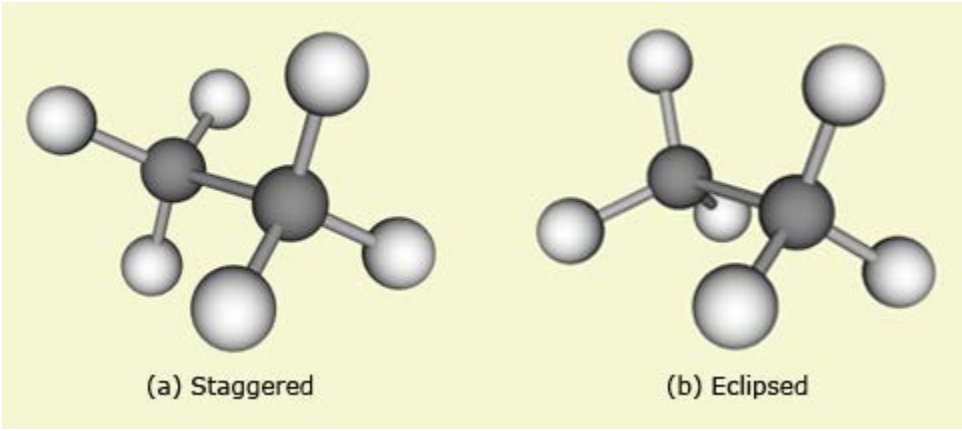
Yes



Yes



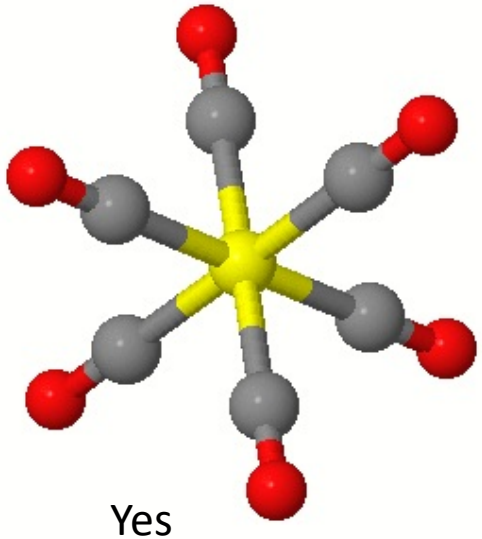
No



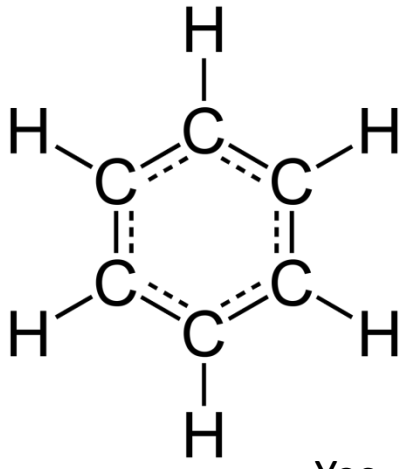
Yes

No

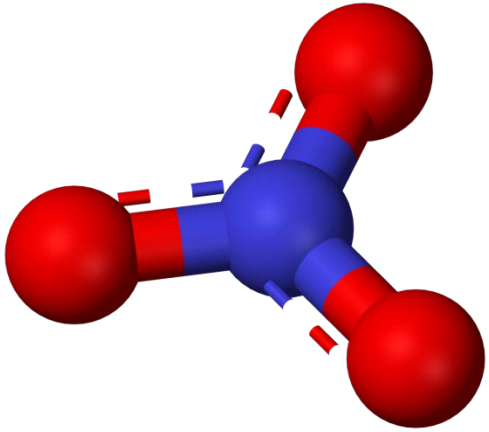
(Proper) Rotation in Chemistry



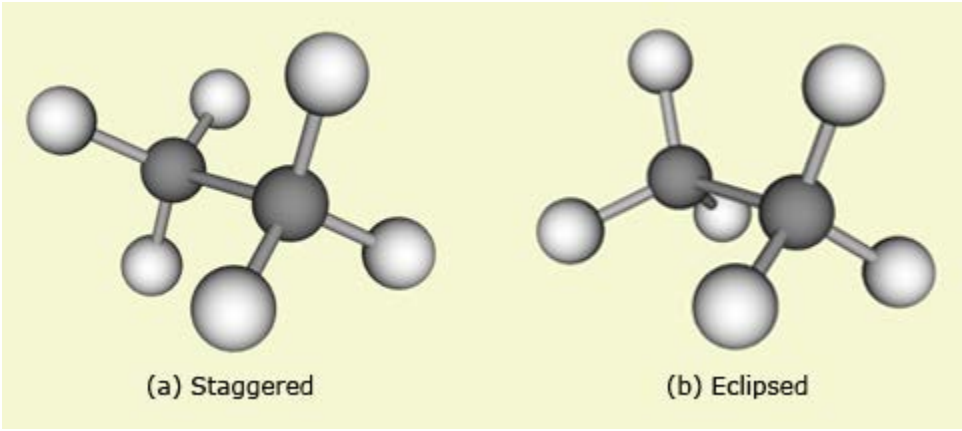
Yes



Yes



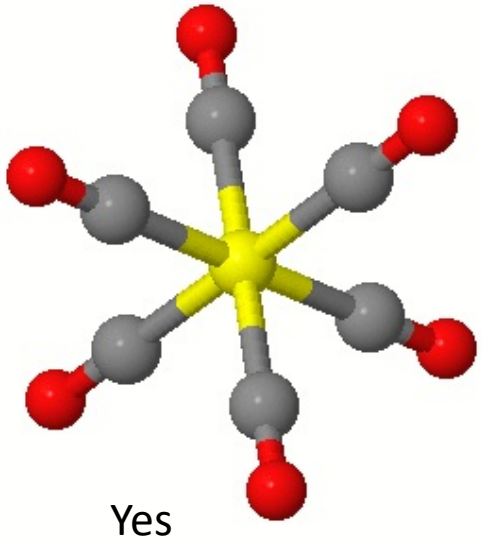
Yes



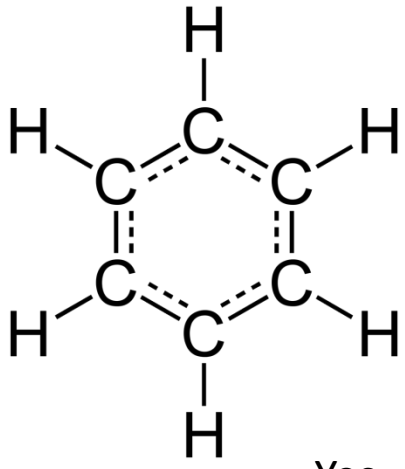
Yes

Yes

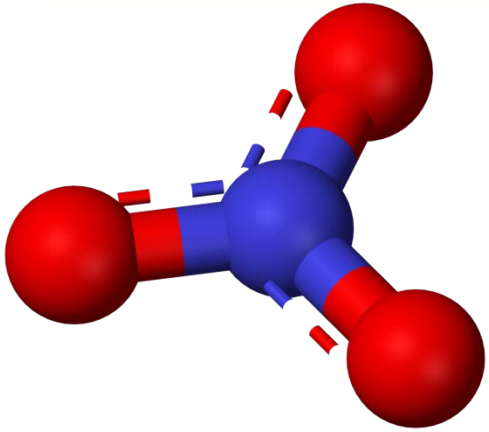
Reflection in a Plane in Chemistry



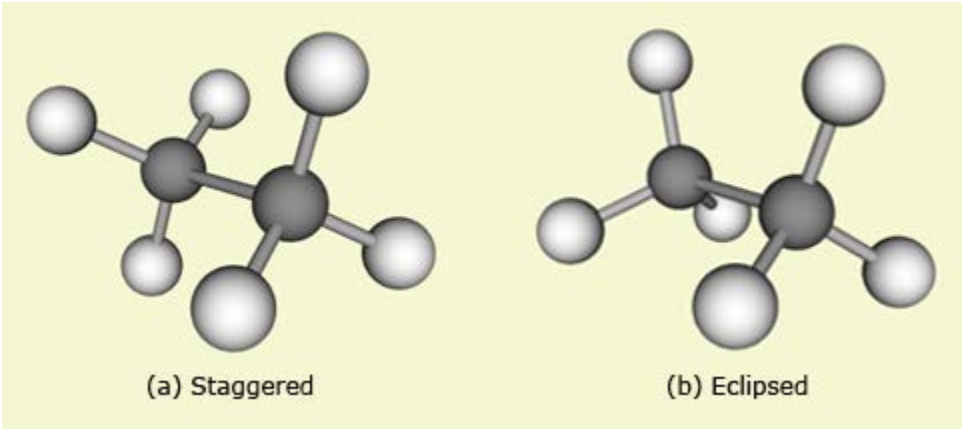
Yes



Yes

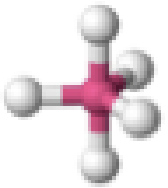
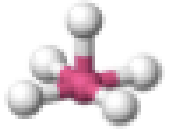
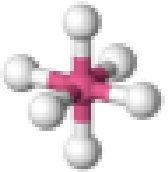


Yes

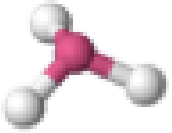


Yes

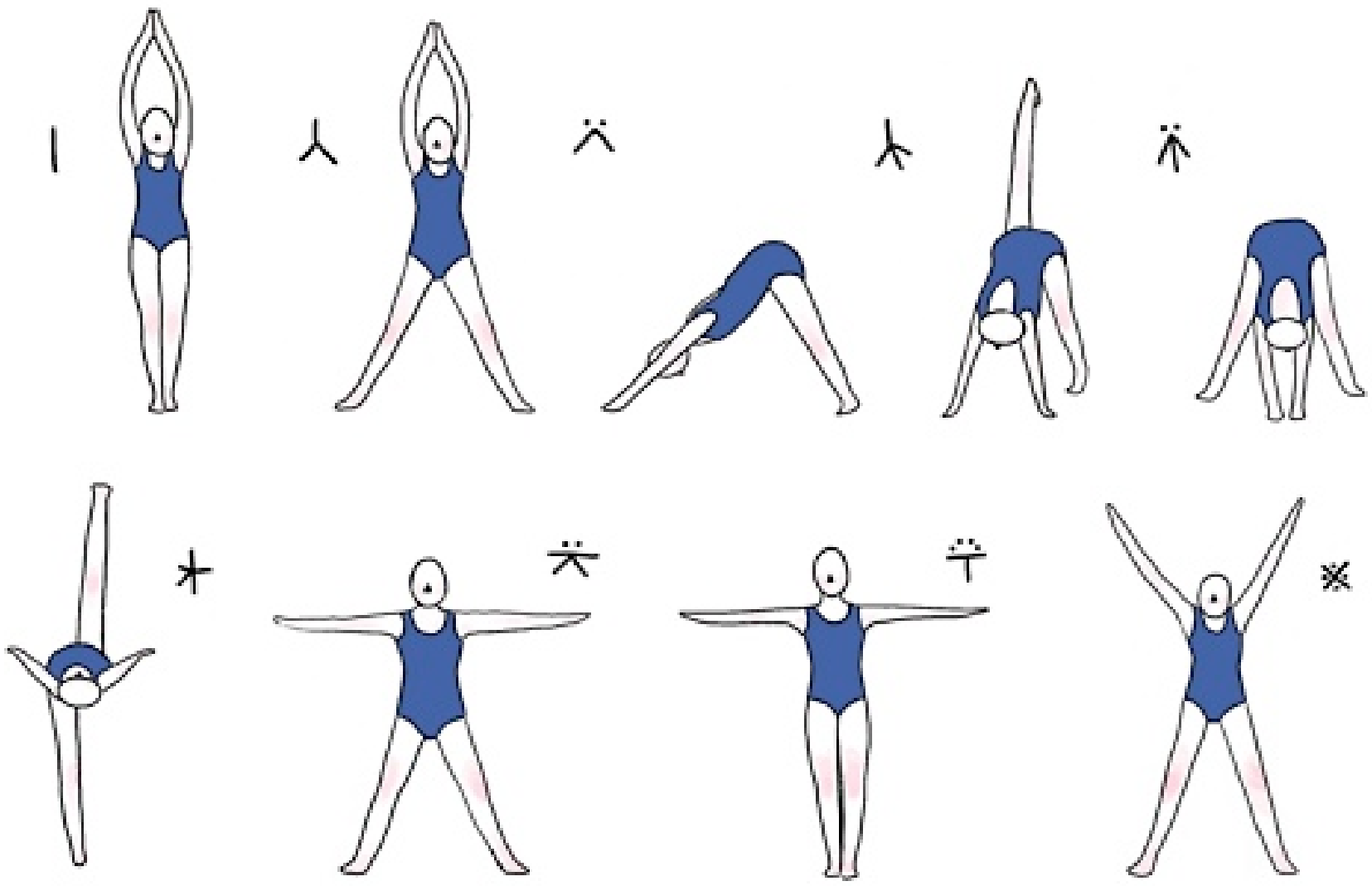
Yes

5	0	AB_4	Tetrahedron	109.5	CCl_4, CH_4, $SiBr_4$	sp^3	
5	1	AB_4	Distorted tetrahedron (Seesaw)		SF_4, SBr_4, $SeCl_4$	sp^3d	
5	2	AB_4	Square planar	90, 180	XeF_4,	sp^3d^2	
6	0	AB_5	Trigonal bipyramidal	90, 180, 120	PCl_5,	sp^3d	
6	1	AB_5 (Inter halogen)	Square pyramid		ClF_5, ICl_5, IBr_5	sp^3d^2	
7	0	AB_6	Octahedron	90, 180	SF_6	sp^3d^2	

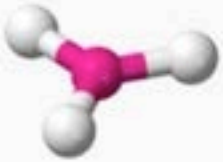
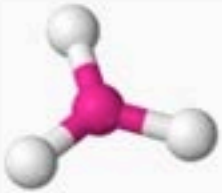
VSEPR Theory

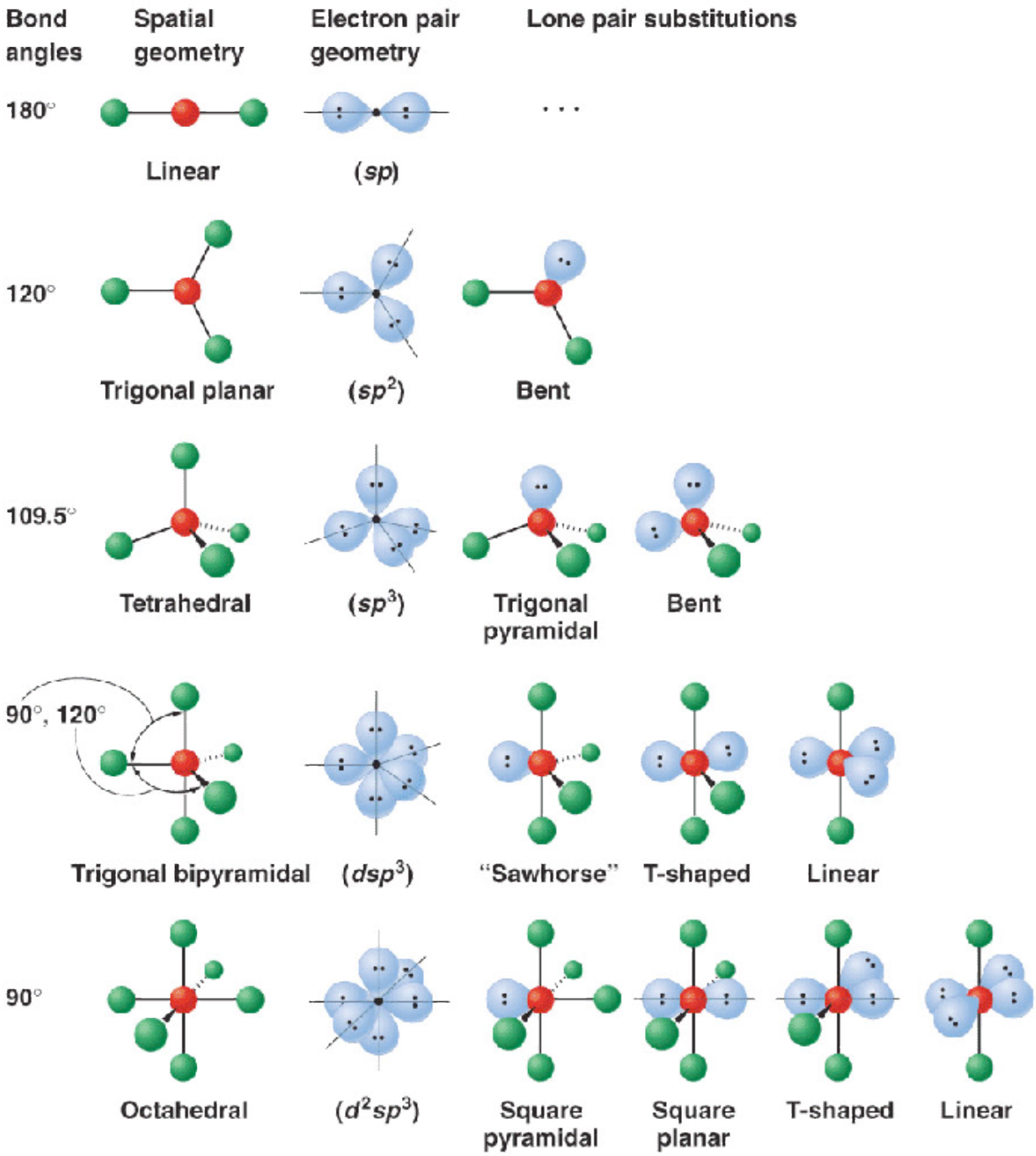
# of Atoms	# of electron pairs	Formula Type	Geometry	Bond Angle	Examples	Hybridization	Structure
3	0	AB_2	Linear	180	CO_2, CS_2, BeH_2		
3	1	AB_2	Bent	117.5	$GeCl_2$, SO_2, NO^-_2	sp^2	
3	2	AB_2	Bent	105	H_2O, H_2S	sp^3	
4	0	AB_3	Trigonal planar	120	BCl_3, $AlBr_3$,	sp^2	
4	1	AB_3	Pyramidal	107	NH_3, PCl_3, $AsBr_3$	sp^3	
4	2	AB_3 (Inter halogen)	T-shaped	90, 180	ICl_3, BrF_3,	sp^3d	

VSEPR YOGA



VSEPR and the AXE Description of Electron Arrangements

Molecule Type	Shape	Electron arrangement†	Geometry‡	Examples
AX_2E_0	Linear			$BeCl_2$, $HgCl_2$, CO_2
AX_3E_0	Trigonal planar			BF_3, CO_3^{2-}, NO_3^-, SO_3
AX_4E_0	Tetrahedral			CH_4, PO_4^{3-}, SO_4^{2-}, ClO_4^-, $TiCl_4$, XeO_4
AX_5E_0	Trigonal bipyramidal			PCl_5
AX_6E_0	Octahedral			SF_6, WCl_6



A Simple Approach to Point Group Assignments