Molecular geometry: VSEPR

VSEPR: Valence Shell Electron Pair Repulsion.

For main group compounds, the VSEPR method is such a predictive tool and unsurpassed as a handy predictive method.

It is a remarkably simple device that utilizes a simple set of electron accounting rules in order to predict the shape

Application of the VSEPR method requires some simplifying assumptions about the nature of the bonding.

Despite this, the correct geometry is nearly always predicted, and the exceptions are often rather special cases.

Use VSEPR rules to predict the shapes and geometries of the central atoms of the following:

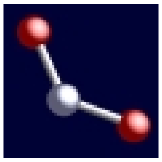
- BeH_2
- $[BeF_4]^{2-}$
- SF_6
- $[IO_3]^-$
- $[IO_4]^-$
- $[IO_6]^{5-}$
- $[GaBr_4]^-$
- $[NCS]^-$
- $[SnPh_3]^-$
- SO_2
- SO_3
- $SOCl_2$
- SO_2Cl_2
- $MeC{\equiv}N$
- $HC{\equiv}CH$
- H_2CCH_2
- CO_2
- $[CO_3]^{2-}$
- $[NO_3]^-$
- NH_2^-
- $XeOF_4$
- $[SbCl_6]^-$
- $[H_3O]^+$
- $[NH_4]^+$
- IF_5
- $[AlCl_6]^{3-}$
- Me^-
- $SbPh_5$
- $[SO_4]^{2-}$
- O_3
- Me_2SO
- PCl_3
- $[SbO_4]^{3-}$

What About NO_2 ???

Another complication crops up when there are *unpaired* electrons. This is well illustrated for nitrogen dioxide.

21/2 electron pairs must be placed into *three* orbitals. Therefore the geometry is based upon a trigonal-planar arrangement of electron pairs. Since the lone-pair orbital is only half filled, it demands less space, and the O-N-O angle opens out a little (to 134.1°) from the ideal trigonal angle of 120°.

Addition of one electron to NO2 gives the nitrite anion NO2-. This last electron completes the half-occupied lone-pair orbital and this filling of the orbital causes it to fill out, and so close the O-N-O bond angle to 115°.



Transition metal systems

The method delineated above works very well for main group compounds but is less useful for transition metal compounds. The problem is that the lone pairs in transition metal complexes do not occupy directional orbitals in the same way as those in main group compounds.

In fact, despite the larger number of electrons involved, the first order prediction of shape for transition metal complexes is *simpler* than for main group compounds.

Simply counting *ligands* and placing the attached ligand groups as far apart from each other as possible.

Six ligands therefore adopt an octahedral configuration, five a trigonal-bipyramidal configuration, and four a tetrahedral configuration.

There are exceptions however. There is an important group of 16-electron compounds with four attached ligands and which are d^8 metals. Many of these are square-planar complexes. There is also an interesting group of complexes which are d^0 ML_6 species. These tend to be trigonal-prismatic rather than octahedral.

History of Noble Gas Compounds

Before 1962:

• all noble gases are inert

• weakly bonded species

• gaseous cationic species: diatomic molecules between noble gas atoms or other atoms (H, O, N, Hg)

• very short lifetimes

History of Noble Gas Compounds

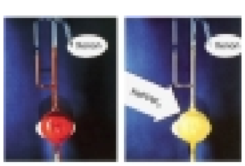
1962, Bartlett and Lohmann:

• demonstrated the great oxidizing strength of PtF_6 in producing $O_2^+PtF_6^-$

• $IP(Xe) \approx IP(O_2)$

$$Xe + PtF_6 \xrightarrow{RT} XePtF_6 + Xe(PtF_6)_2$$

- dependent on reactant ratio
- red-tinged yellow solid



Graham, L.; Graudejus, O.; Jha, N. K.; Bartlett, N. Concerning the nature of $XePtF_6$. *Coord. Chem. Rev.* **2000**, *197*, 321-334.

Compounds of Xenon

Xenon Fluorides

- readily preparable from the elements
- thermodynamically stable

XeF_2

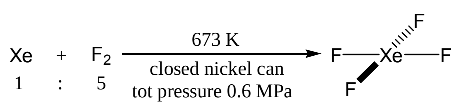
XeF_4

XeF_6

- not known: XeF_8

XeF_4

- first noble gas binary fluoride synthesized



- colorless as crystals, liquid, or vapor
- strong oxidative fluorinator, but has high kinetic inertness like XeF_2

The Amazing $[AuXe_4]^{2+}$

- Seidel and Seppelt: 2000, Goal: AuF
- AuF_3 + HF/SbF_5
  → dark red solution
- -78°C : $AuXe_4^{2+} (Sb_2F_{11}^-)_2$
- Bond = 272.8 – 275.1 pm
- Stable up to -40°C
- Raman: 129 cm^{-1} Au-Xe
- X ligand