Tetrahedral Electronic Geometry: AB₃U Species (One Lone Pair of Electrons on A)

- Some examples of molecules with this geometry are: NH₃, NF₃, PH₃, PCl₃, AsH₃
- These molecules are our first examples of central atoms with lone pairs of electrons.
  Thus, the electronic and molecular geometries are different.
  All three substituents are the same but molecule is polar.
- NH₃ and NF₃ are trigonal pyramidal, polar molecules.
Tetrahedral Electronic Geometry: AB₃U Species (One Lone Pair of Electrons on A)

Valence Bond Theory

\[ \text{N} \quad [\text{He}] \quad \frac{\uparrow \downarrow}{2s} \quad \frac{\uparrow \uparrow \uparrow}{2p} \quad \text{hybridize} \quad \text{N} \quad [\text{He}] \quad \frac{\uparrow \downarrow \uparrow \uparrow \uparrow}{sp^3} \]

\[ \text{H} - \text{N} - \text{H} \quad 107.3^\circ \]
Molecular and Electronic Geometry

In \( \text{NH}_3 \), H–N–H angle = 107.3°

Tetrahedral electronic geometry

Trigonal pyramidal molecular geometry

In \( \text{NF}_3 \), F–N–F angle = 102.1°
Lone pair/bonded pair repulsions are stronger than bonded pair/bonded pair repulsions.

Bonded pair/bonded pair repulsions are weaker in NF₃ than in NH₃ due to the longer N—F bond.
Tetrahedral Electronic Geometry: 
$AB_3U$ Species (One Lone Pair of Electrons on A)

**Polarity**

**net molecular dipole $> 0$ (large)**

**net molecular dipole $> 0$ (small)**
Tetrahedral Electronic Geometry: \( \text{AB}_2\text{U}_2 \) Species (Two Lone Pairs of Electrons on A)

- Some examples of molecules with this geometry are:
  - \( \text{H}_2\text{O}, \text{OF}_2, \text{OCl}_2, \text{H}_2\text{S} \)
- These molecules are our first examples of central atoms with two lone pairs of electrons.
  - Thus, the electronic and molecular geometries are different.
  - Both substituents are the same but molecule is polar.
- Molecules are angular, bent, or V-shaped and polar.
Tetrahedral Electronic Geometry: AB$_2$U$_2$ Species (Two Lone Pairs of Electrons on A)

Valence Bond Theory (Hybridization)

O [He] | 2s | 2p | four sp$^3$ hybrids

$\begin{array}{c}
\uparrow \downarrow \\
\uparrow \uparrow \uparrow \uparrow
\end{array}$

$sp^3$ Hybridization

2 unshared pairs

Angular (V-shaped or bent)
There are now *two* lone pairs that repel the bonded pairs

*lp–lp* repulsion is strongest
**Polarity**

\[
\text{EN} = \begin{array}{c} 3.5 \\ 2.1 \end{array}
\]

\[\Delta(\text{EN}) = 1.4\]

Molecular dipole; includes effect of two unshared electron pairs
Tetrahedral Electronic Geometry: 
ABU₃ Species (Three Lone Pairs of Electrons on A)

- Some examples of molecules with this geometry are: 
  HF, HCl, HBr, HI, FCl, IBr

- These molecules are examples of central atoms with three lone pairs of electrons. 
  Again, the electronic and molecular geometries are different.

- Molecules are linear and polar when the two atoms are different. 
  Cl₂, Br₂, I₂ are nonpolar.
Tetrahedral Electronic Geometry: ABU$_3$ Species (Three Lone Pairs of Electrons on A)

Dot Formula (HF)

Electronic Geometry (HF)
Tetrahedral Electronic Geometry: ABU₃ Species (Three Lone Pairs of Electrons on A)

Molecular Geometry (HF)

Polarity (HF)
Tetrahedral Electronic Geometry: ABU₃ Species (Three Lone Pairs of Electrons on A)

Valence Bond Theory (Hybridization)

F [He]  2s  \(\uparrow\downarrow\)  2p  \(\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\)  \(\Rightarrow\)  four \(sp^3\) hybrids  \(\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\)
Some examples of molecules with this geometry are:

PF$_5$, AsF$_5$, PCl$_5$, etc.

These molecules are examples of central atoms with five bonding pairs of electrons. The electronic and molecular geometries are the same.

Molecules are trigonal bipyramidal and nonpolar when all five substituents are the same.

If the five substituents are not the same, polar molecules can result, AsF$_4$Cl is an example.
Trigonal Bipyramidal Electronic Geometry: $AB_5$, $AB_4U$, $AB_3U_2$, and $AB_2U_3$

Valence Bond Theory
Trigonal Bipyramidal Electronic Geometry: $AB_5$, $AB_4U$, $AB_3U2$, and $AB_2U_3$
$sp^3d$ hybrid orbitals on P
$p$ orbitals on F
Molecular Geometry

Trigonal Bipyramidal
Polarity

\[ \text{EN} = \begin{cases} 2.1 & \text{P} - \text{F} \\ 4.0 & \end{cases} \]

\[ \Delta(\text{EN}) = 1.9 \]

axial bonds

\[ \begin{array}{c}
\text{F} \\
\text{P} \\
\text{F}
\end{array} \]

180°

equatorial bonds

\[ \begin{array}{c}
\text{F} \\
\text{P} \\
\text{F} \\
\text{F}
\end{array} \]

120°

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Chemistry is fun!