Molecular Structure
Chapter 08

Ozone, O₃

Overview

VSEPR

- Valence Shell Electron Pair Repulsion theory.
  - Most important factor in determining geometry is relative repulsion between electron pairs.
VSEPR

• Build a picture of the shape of the molecule or ion by counting regions of high electron density.
  • Each bonded atom counts as one region.
  • Each unshared electron pair counts as one region.

VSEPR Theory

• Frequently, we will describe two geometries for each molecule.
  • Electronic geometry is determined by the locations of regions of high electron density around the central atom(s).
  • Molecular geometry is determined by the arrangement of atoms around the central atom(s).
  • Electron pairs are not used in the molecular geometry determination just the positions of the atoms in the molecule are used.

Electron-Pair Geometries

<table>
<thead>
<tr>
<th>Electron Group on Central Atom</th>
<th>Electron Geometry*</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Linear 180°</td>
</tr>
<tr>
<td>3</td>
<td>Trigonal planar</td>
</tr>
<tr>
<td>4</td>
<td>Tetrahedral 109°</td>
</tr>
</tbody>
</table>

*Note: Electron geometry is the arrangement of regions of high electron density around the central atom(s).
**Structure Determination by VSEPR**

- Ammonia, NH₃
- Draw electron dot structure
- Count BP's (bonding pair) and LP's (lone pair) = 4
- The 4 electron pairs are at the corners of a tetrahedron.

```
H—N—H
H
```

- The electron pair geometry is tetrahedral.

**Structure Determination by VSEPR**

- Ammonia, NH₃
- There are 4 electron pairs at the corners of a tetrahedron.

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H—N—H
H
```

- The electron pair geometry is tetrahedral.

**Structure Determination by VSEPR**

- Ammonia, NH₃
- The electron pair geometry is tetrahedral.
- The molecular geometry — the positions of the atoms — is pyramidal.

**Structure Determination by VSEPR**

**Predicting Molecular Geometries**

- To determine the electron pair geometry:
  - draw the Lewis structure
  - count the total number of electron pairs around the central atom
  - arrange the electron pairs in one of the above geometries to minimize e⁻-e⁻ repulsion
  - multiple bounds count as one bonding pair
Structure Determination by VSEPR

- Water, H₂O
- Draw electron dot structure
- Count BP’s and LP’s = 4
- The 4 electron pairs are at the corners of a tetrahedron.

H—O—H

The electron pair geometry is tetrahedral.

Structure Determination by VSEPR

- Water, H₂O

H—O—H

The molecular geometry is bent.

Structure Determination by VSEPR

- Formaldehyde, CH₂O
- Draw electron dot structure
- Count BP’s and LP’s = 3
- There are 3 electron pairs are at the corners of a planar triangle.

The electron pair geometry is PLANAR TRIGONAL with 120° bond angles.

Structure Determination by VSEPR

- Formaldehyde, CH₂O

The electron pair geometry is PLANAR TRIGONAL

The molecular geometry is also planar trigonal.
Methanol, CH₃OH

- Draw electron dot structure

- Define bond angles 1 and 2

\[ \text{H} - \text{C} - \text{O} - \text{H} \]

\[ \text{H} \]

Angle 1 = 109.5°
Angle 2 = 109.5°
In both cases the atom is surrounded by 4 electron pairs.

Phenylalanine, an amino acid

Violations of the Octet Rule

Consider boron trifluoride, BF₃
- The B atom is surrounded by only 3 electron pairs.
- Bond angles are 120°

Geometry described as planar trigonal
Compounds with 5 or 6 Pairs Around the Central Atom

Octahedron

90°

6 electron pairs

5 electron pairs

F

F

F

F

F

F

Trigonal bipyramid

90°

120°

S

F

F

F

F

F

Sulfur Tetrafluoride, SF₄

• Number of valence electrons = 34
• Central atom = S
• Dot structure
• Electron pair geometry - trigonal bipyramid (because there are 5 pairs around the S)

Number of valence electrons = 2
Central atom = Cl

Chlorine Trifluoride, ClF₃
Triiodide Ion, $I_3^-$

Number of valence electrons = 22  
Central atom = I

Linear

$\begin{array}{c}
\text{i} \\
\text{i} \\
\text{i} \\
\text{i}
\end{array}$

IF$_4^-$

Number of valence electrons = 36  
Central atom = I

Square

$\begin{array}{c}
\text{i} \\
\text{i} \\
\text{i} \\
\text{i}
\end{array}$

Molecular Polarity

- Molecules—such as HCl and H$_2$O— can be POLAR (or dipolar).
- They have a DIPOLE MOMENT. The polar HCl molecule will turn to align with an electric field.

Polarity of Molecules

- If two charges, equal in magnitude and opposite in sign, are separated by a distance, then a dipole is established.

Dipole Moments of Polyatomic Molecules

- In a polyatomic molecule, each bond can be a dipole. The orientation of these individual dipole moments determines whether the molecule has an overall dipole moment.
Molecular Polarity

- The magnitude of the dipole is given in Debye units. Named for Peter Debye (1884 - 1966). Received 1936 Nobel prize for work on x-ray diffraction and dipole moments.

Molecules will be polar if
- bonds are polar AND
- the molecule is NOT "symmetric"

Symmetric molecules

Molecular Polarity, H₂O

Band dipoles

Overall dipole moment

Dipole = 2.64 D

0.69

+0.35 -0.35

+0.58 -0.58
Molecular Dipole Moments

- For polyatomic molecules, the dipole moment is the geometric sum of all bond dipole moments.

\[
\text{CO}_2 - \text{Nonpolar} \quad \text{H}_2\text{O} - \text{Polar}
\]

Molecular Polarity

- B—F bonds in BF\(_3\) are polar, but the molecule is symmetrical and NOT polar.

\[
\begin{align*}
\text{B} & \quad \text{F} \\
\text{F} & \quad \text{B} \\
\text{F} &
\end{align*}
\]

B atom is positive and F atoms are negative.

Polarity of Methane, CH\(_4\)

- Methane is symmetrical and is NOT polar.

\[
\text{H}_4\text{C}
\]

Polarity of CH\(_3\)F

- C—F bond is very polar. Molecule is not symmetrical and so is polar.

\[
\begin{align*}
\text{F} & \quad \text{H} \\
\text{C} & \quad \text{H} \\
\text{H} &
\end{align*}
\]
Hybridization

• The combination of atomic orbitals to form a new set of orbitals with the same total electron capacity and with properties and energies intermediate between the original unhybridized orbitals.

Hybridization

\[
\begin{align*}
\text{C} & : 1s^2 2s^2 2p^2 \\
\text{H} & : 1s^1
\end{align*}
\]

Hybridization

\[
\begin{align*}
\text{C} & : 1s^2 2s^2 2p^2 \\
\text{H} & : 1s^1
\end{align*}
\]

Compounds Containing Double Bonds

• An sp\(^2\) hybridized C atom has this shape.
• Remember there will be one electron in each of the three sp\(^2\) lobes and one in the p orbital.
• Two sp\(^2\) hybridized C atoms plus p orbitals in proper orientation to form C=C double bond.

• The portion of the double bond formed from the head-on overlap of the sp\(^2\) hybrids is designated as a σ bond.

• The other portion of the double bond, resulting from the side-on overlap of the p orbitals, is designated as a π bond.

• Thus a C=C bond looks like this and is made of two parts, one σ and one π bond.
Hybridization

<table>
<thead>
<tr>
<th>Hybridization</th>
<th>Electronic Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>sp</td>
<td>linear</td>
</tr>
<tr>
<td>sp(^2)</td>
<td>trigonal planar</td>
</tr>
<tr>
<td>sp(^3)</td>
<td>tetrahedral</td>
</tr>
<tr>
<td>sp(^3)(^d)</td>
<td>trigonal bipyramidal</td>
</tr>
<tr>
<td>sp(^3)(^d)^(^2)</td>
<td>octahedral</td>
</tr>
</tbody>
</table>

Test Your Skills

• Draw the Lewis structure, identify the electronic and molecular geometry, provide the bond angle, type of hybridization, and polarity.

Answers

\[ \text{O} \equiv \text{S} \equiv \text{O} \]

• electronic geometry: trigonal planar
• molecular geometry: bent
• bond angle: 120°
• hybridization: sp\(^2\)
• polarity: polar

\[ \equiv \text{O} \equiv \text{S} \equiv \]

• electronic geometry: trigonal bipyramidal
• molecular geometry: linear
• bond angle: 180°
• hybridization: sp\(^3\)\(^d\)
• polarity: nonpolar
Answers

Electronic geometry: octahedral
Molecular geometry: square pyramidal
Bond angle: 90°
Hybridization: sp^3d^2
Polarity: polar

Answers

Electronic geometry: octahedral
Molecular geometry: square planar
Bond angle: 90°
Hybridization: sp^3d^2
Polarity: nonpolar

Answers

Electronic geometry: tetrahedral
Molecular geometry: tetrahedral
Bond angle: 109°
Hybridization: sp^3
Polarity: nonpolar

Answers

Electronic geometry: trigonal planar
Molecular geometry: trigonal planar
Bond angle: 120°
Hybridization: sp^2
Polarity: nonpolar
Valence Bond Theory
• describes how bonding takes place in terms of overlapping atomic orbitals

VSEPR Theory
• allows the prediction of spatial arrangements of atoms

Used together VB Theory and VSEPR Theory enables us to understand the bonding, molecular shape and properties of many compounds.
<table>
<thead>
<tr>
<th>Molecular Symmetry</th>
<th>Charge</th>
<th>Resonance</th>
<th>Molecular Geometry</th>
<th>Symmetry</th>
<th>Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{A}_1$</td>
<td>1</td>
<td>normal</td>
<td>$sp^3$</td>
<td>$T_{d}$</td>
<td>$\text{Xa}, \text{Xb}$</td>
</tr>
<tr>
<td>$\text{A}_2$</td>
<td>2</td>
<td>skeletal</td>
<td>$sp^3$</td>
<td>$T_{d}$</td>
<td>$\text{Xa}, \text{Xb}$</td>
</tr>
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<td>4</td>
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