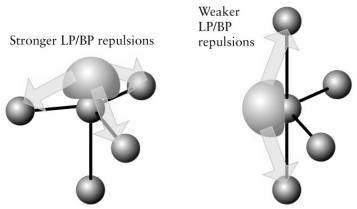
9.3 Molecules with Lone Pairs at the Central Atom (continued)

- Strengths of electron pair repulsions

  lone pair-lone pair > lone pair-bonding pair > bonding pair-bonding pair
- In the electron arrangement, lone pairs occupy positions as far from one another and from bonding pairs as possible
- **AX_2E** (O_3), **AX_3E** (NH_3) and **AX_2E_2** (H_2O) molecules
  - **observed bond angles are smaller** than the predicted from the electron arrangement

- **AX_4E** (SF_4), **AX_3E_2** (ClF_3) and **AX_2E_3** (XeF_2) molecules
  - trigonal bipyramidal electron arrangement (**5 pairs**)
  - the **lone pairs occupy equatorial positions** (provides the lowest repulsion)



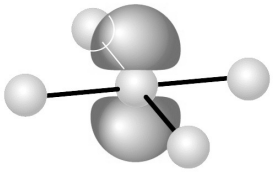
AX_4E molecule

⇒ arrangement **(b)** is preferred

⇒ the molecular shape is "**seesaw**"

Fig. 9.8

- **AX_4E_2** (XeF_4) molecules
  - octahedral electron arrangement (**6 pairs**)
  - the **lone pairs occupy positions** on the opposite sides of the central atom (provides the lowest repulsion)



AX_4E_2 molecule

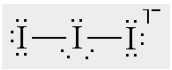
⇒ lone pairs across the central atom

⇒ the molecular shape is "**square planar**"

Fig. 9.9

Example: Determine the electron arrangement and molecular shape of I_3^-.

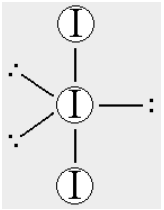
1. Lewis structure:



2. Electron Arrangement: **trigonal bipyramidal** (**3** lone pairs + **2** bonded atoms = **5**)

3. Lone pairs go in equatorial positions

4. Molecular shape: **linear** (atoms in axial positions)



Charge Distribution in Molecules

9.4 Polar Bonds

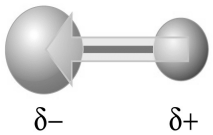
- Unequal sharing of the bonding electrons – ***EN*** difference between the bonded atoms
  - the more electronegative atoms acquire **partial negative charges** (have greater share of the bonding electrons)
  - the less electronegative atoms acquire **partial positive charges**
- **Polar covalent bond** – partial ionic character
  - partial atomic charges increase with increasing ***DEN***

$\delta^+H–F^{\delta-}$

- Partial atomic charges create **electric dipoles**
- **Dipole moment** (***m***) – a measure of the magnitude and direction of an electric dipole
- All polar bonds have **bond dipoles**

– ***m*** increases with increasing the partial charges (***Q***) and the bond distance (***r***) → ***m*** = ***Qr***
– the direction of ***m*** is from plus to minus
– units → **C·m**
→ **debye** (**D**)

1 D = 3.336×10^{-30} C.m

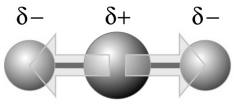


22 Dipole moment

9.5 Polar Molecules

- **Molecular dipole moment** (associated with the molecule as a whole) – can be represented as a sum of the bond dipoles of all bonds
- **Nonpolar** molecules – zero dipole moment

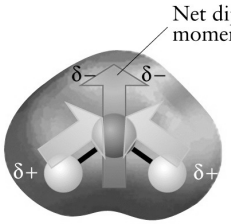
– homonuclear diatomic molecules (**H_2**, **O_2**, **F_2**, ...)
– polyatomic molecules where the bond dipoles cancel each other



23 Carbon dioxide, CO_2

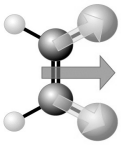
CO_2 is nonpolar – the bond dipoles of the **C–O** bonds cancel

- **Polar** molecules – nonzero dipole moment
  - heteronuclear diatomic molecules (**HF**, **CO**, ...)
  - polyatomic molecules where the bond dipoles do not cancel each other

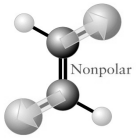


H_2O is a polar molecule because the bond dipoles of the O-H bonds do not cancel (bent shape)

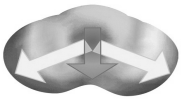
- The polarity of molecules depends on the polarity of the bonds and the molecular geometry (must be known)



24 *cis*-Dichloroethene, CHCl=CHCl



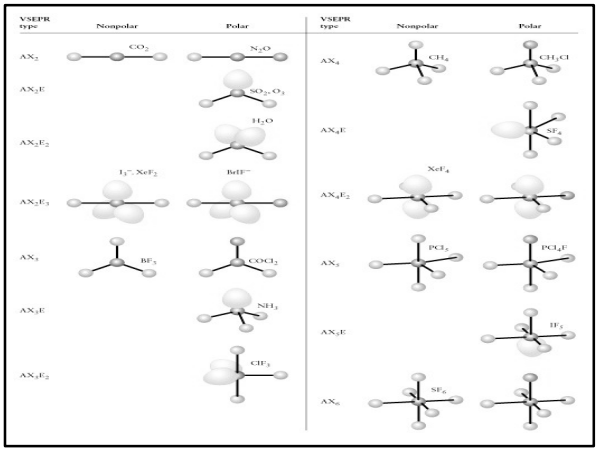
25 *trans*-Dichloroethene, CHCl=CHCl



29 Ozone, O_3

– ozone (**O_3**) is bent (lone pair at the central atom, trigonal planar arrangement)
– the **O–O** bonds are slightly polar (see the formal charges in the Lewis structure)
– polar molecule – bond dipoles don't cancel

- Highly symmetric molecules are normally nonpolar
  - **AX_n** molecules (n=2, 3, 4, 5, 6) where **X** are atoms of the same element
  - molecules with symmetrically positioned lone pairs (**AX_2E_3**, **AX_4E_2**)
- Molecules with asymmetrically positioned lone pairs or different atoms attached to the central atom are normally polar
  - **AX_2E**, **AX_2E_2**, **AX_3E**, **AX_3E_2**, **AX_4E**, **AX_5E**, …
  - **CF_3H**, **CF_2H_2**, **SO_2**(bent), ...

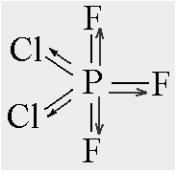


Example: Is **PCl_2F_3** a polar molecule?

1. The Lewis structure is similar to **PCl_5** (five atoms bonded to the **P** atom, no lone pairs)

⇒ **trigonal bipyramidal shape**

2. The **Cl** atoms are larger and take two of the equatorial positions; the **F** atoms are smaller and take the two axial and one of the equatorial positions



The **P–F** dipoles are larger than the **P–Cl** dipoles (***DEN*** is larger for **P** and **F**)

The molecule is **polar** – the bond dipoles don't cancel (asymmetric arrangement)