

Greenwood & Earnshaw

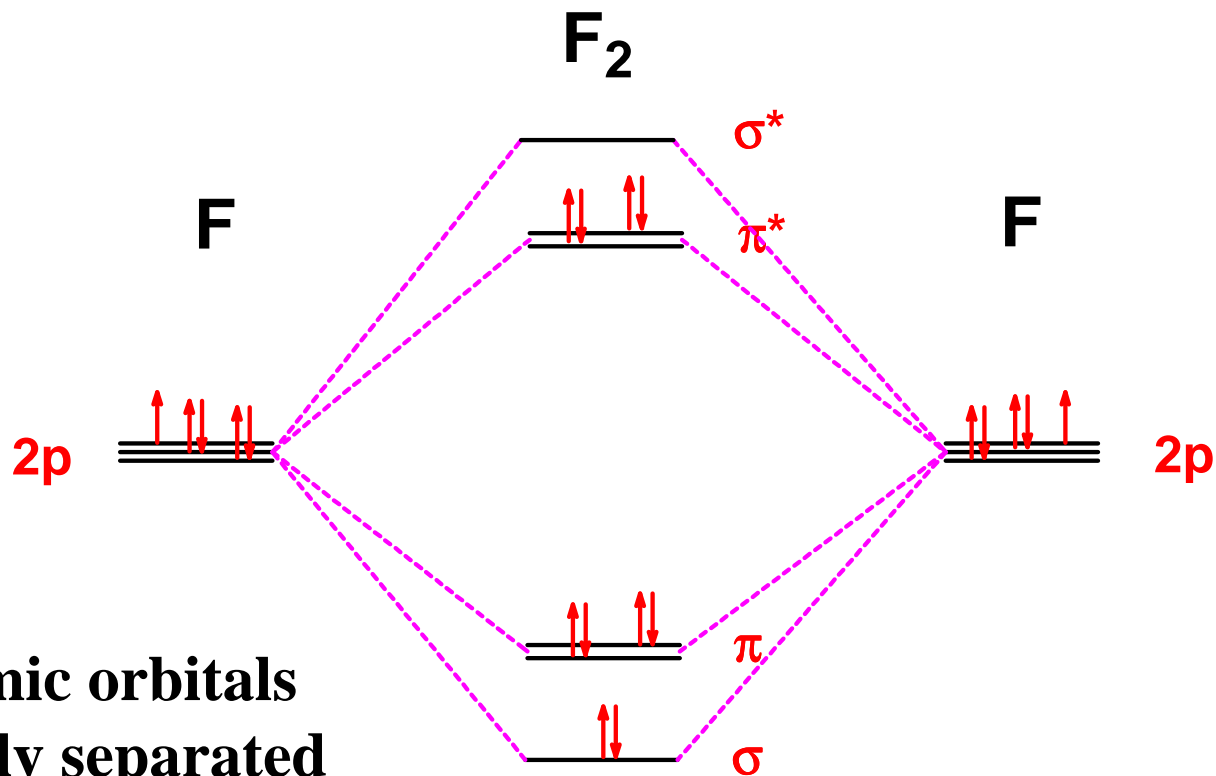
2nd Edition

Chapter 17

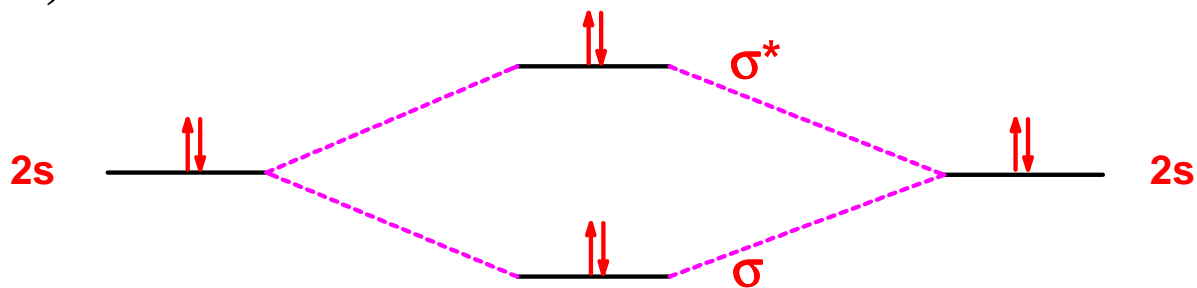
The Halogens

**Fluorine, Chlorine, Bromine, Iodine
and Astatine**

Molecular Orbital Diagram – F₂



**2s & 2p atomic orbitals
are too widely separated
in energy to allow
significant mixing
(hybridization) to occur.**



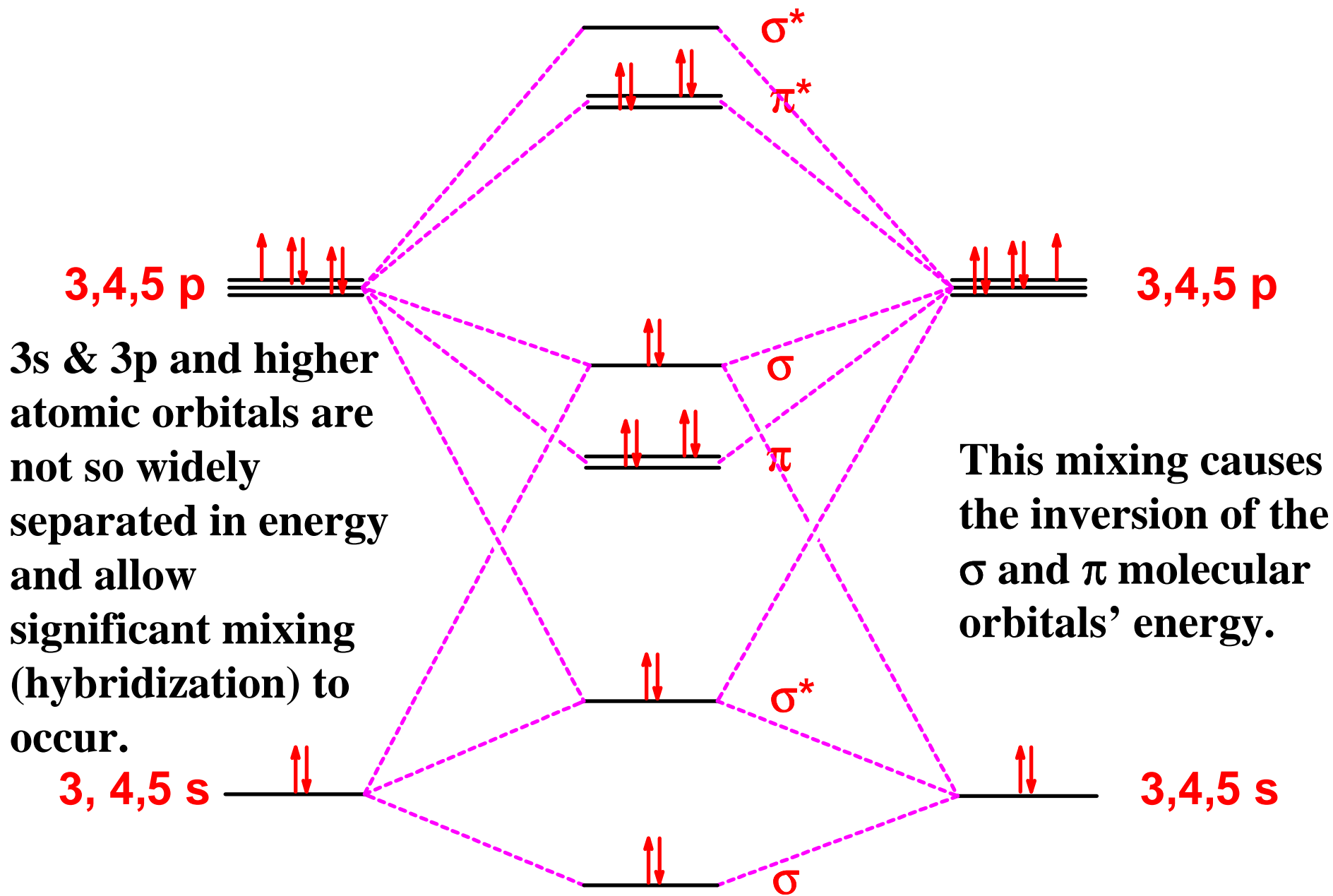
Bond Energies for the Halogens, kJ/mol

X	XX	HX	BX ₃	AlX ₃	CX ₄
F	159	574	645	582	456
Cl	243	428	444	427	327
Br	193	363	368	360	272
I	151	294	272	285	239

Fluorine bond energies are “anomalous”. The F-F bond is very weak due to lone-pair/lone-pair repulsions (cf. O-O, N-N). Fluorine has tightly held, non-polarizable electrons, the atoms are small and no low-lying “d” atomic orbitals exist. The fluorine lone pairs are strong π -donors to atoms having low-lying empty orbitals. Fluorine forms strong, polar bonds to carbon, hydrogen and many other elements. Fluorine is very electrophilic and strongly oxidizing.

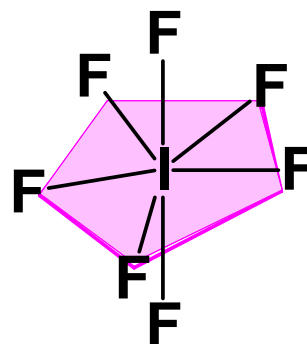
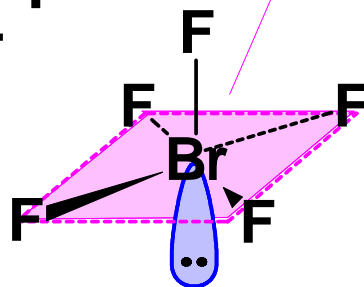
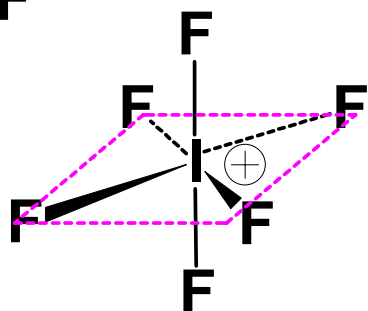
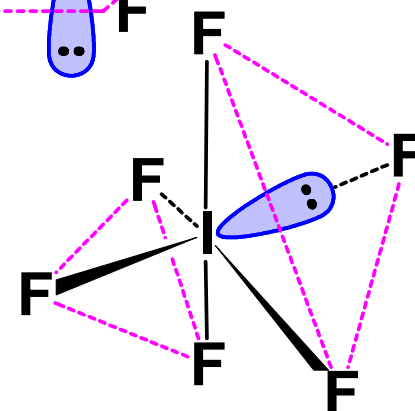
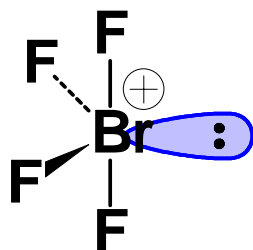
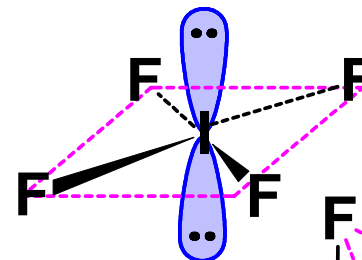
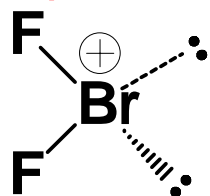
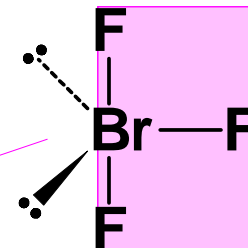
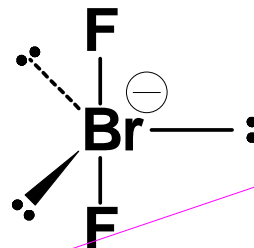
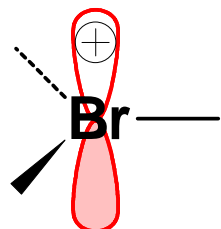
X ₂	F ₂	Cl ₂	Br ₂	I ₂	At ₂
<i>E</i> °/V	2.866	1.395	1.087	0.615	~0.3

Molecular Orbital Diagram – Cl₂, Br₂, I₂



Y is the heavier halogen!

diatomic



$Cs^+IF_8^-$
square antiprismatic?

Interhalogens

Trihalide Anions

- The heavier halogen is invariably in the center position.
- The anion is linear or near linear. One Deviation is for Br_3^- which is 171° most 176° or higher.
- The bonding is almost certainly 3c-4e bonding.
- The two bonds in YX_2 species need not be equivalent and may vary with the cation.
- The bond length is longer than the single bond covalent radii. The formal bond order is 0.5. In BrI_2^- the Br-I bond is longer than the I-I bond.
- Iodine forms an extensive set of polyiodine anions: I_n^- $n = \text{odd}$; I_n^{2-} $n = \text{even}$, I_{16}^{4-} . (see page 837).

Iodine Oxides and Oxoacids of Iodine

