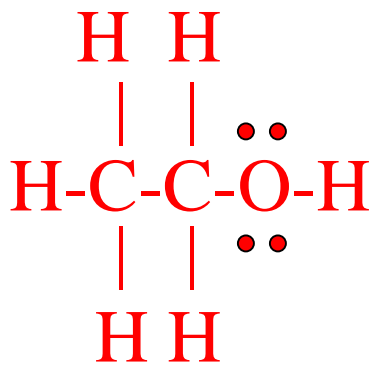
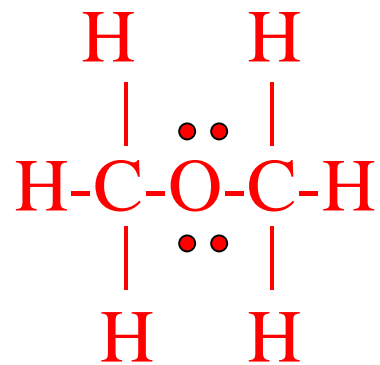


Chapter 9

Molecular Structures



ethanol

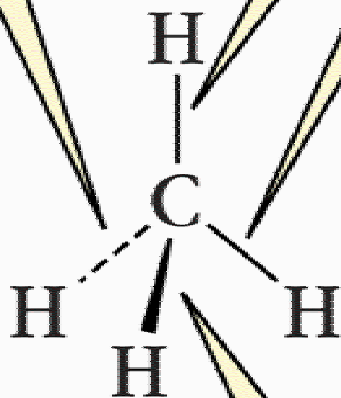


dimethyl ether

Perspective Structure

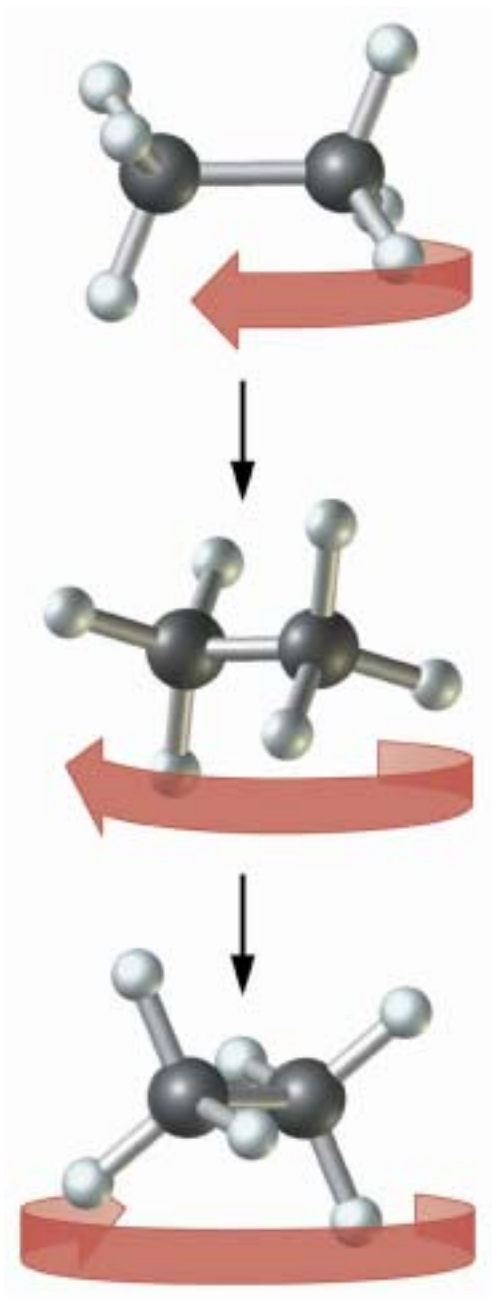
This bond is behind the page.

These bonds are in the plane of the page.



This bond is extending in front of the page.

Rotation of Ethane Molecule



Balloon VSEPR Models



Linear



Triangular planar



Tetrahedral



Triangular bipyramidal



Octahedral

What is the “shape” of the molecule?

- How are valence electrons in a molecule distributed among the orbitals?
- What are the shapes of these orbitals?
- What order are they occupied?

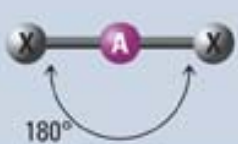

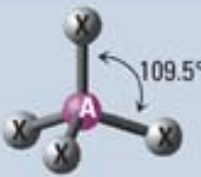
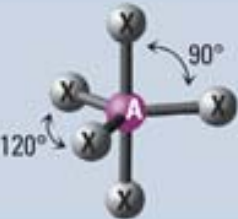

Molecular Geometry

VSEPR Theory

Valence Shell Electron Pair Repulsion Theory

- draw Lewis electron dot structure
- count the number of bonding electron pairs about central atom (double and triple bonds count as one pair for shape prediction)
- count the number of lone pairs of electrons
- match electron pair information to shapes

Idealized VSEPR Geometries

Molecular model					
Type	AX_2E_0	AX_3E_0	AX_4E_0	AX_5E_0	AX_6E_0
Electron-pair geometry	Linear	Triangular planar	Tetrahedral	Triangular bipyramidal	Octahedral
Molecular geometry	Linear	Triangular planar	Tetrahedral	Triangular bipyramidal	Octahedral
Example	BeF_2	BF_3	CH_4	PCl_5	SF_6

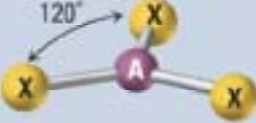

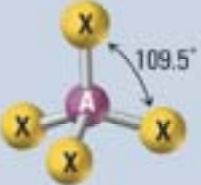


Electron Pair & Molecular Geometries

TABLE 9.1 Examples of Electron Pair Geometries and Molecular Geometries Predicted by VSEPR Model

Type (X = atoms bonded to central atom A; E = lone pair on central atom)	Number of lone pairs on central atom	Electron-pair geometry	Molecular geometry	Example
AX_2E_0	None	Linear	Linear	CO_2 , $BeCl_2$
AX_2E_1	One	Triangular planar	Angular	$SnCl_2$
AX_2E_2	Two	Tetrahedral	Angular	H_2O , OCl_2
AX_2E_3	Three	Triangular bipyramidal	Linear	XeF_2
AX_3E_0 CO_3^{2-}	None	Triangular planar	Triangular planar	BCl_3 ,
AX_3E_1	One	Tetrahedral	Triangular pyramidal	NCl_3
AX_3E_2	Two	Triangular bipyramidal	T-shaped	ClF_3
AX_4E_0	None	Tetrahedral	Tetrahedral	CH_4 , $SiCl_4$
AX_4E_1	One	Triangular bipyramidal	Seesaw	SF_4
AX_4E_2	Two	Octahedral	Square planar	XeF_4
AX_5E_0	Five	Triangular bipyramidal	Triangular bipyramidal	PF_5
AX_5E_1	One	Octahedral	Square pyramidal	BrF_5
AX_6E_0	None	Octahedral	Octahedral	SF_6

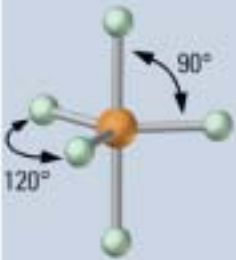



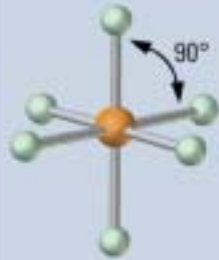
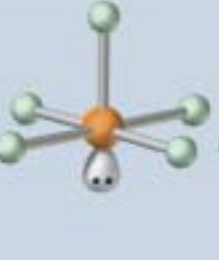
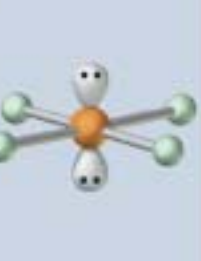


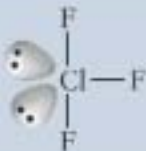
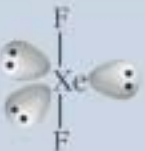


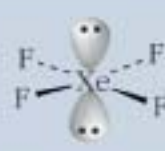
VSEPR Theory

Three and Four Electron Pairs

Molecular model	Three electron pairs		Four electron pairs		
					
	No lone pairs	One lone pair	No lone pairs	One lone pair	Two lone pairs
Type	AX_3E_0	AX_2E_1	AX_4E_0	AX_3E_1	AX_2E_2
Electron-pair geometry	Triangular planar	Triangular planar	Tetrahedral	Tetrahedral	Tetrahedral
Molecular geometry	Triangular planar	Angular	Tetrahedral	Triangular pyramidal	Angular
Example	BCl_3	$GeCl_2$	CCl_4	NCl_3	OF_2

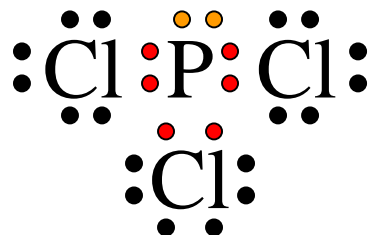
VSEPR Theory

Five and Six Electron Pairs

Molecular model	Five electron pairs				Six electron pairs		
							
Type	AX_5E_0	AX_4E_1	AX_3E_2	AX_2E_3	AX_6E_0	AX_5E_1	AX_4E_2
Example							
Electron-pair geometry	Triangular bipyramidal	Triangular bipyramidal	Triangular bipyramidal	Triangular bipyramidal	Octahedral	Octahedral	Octahedral
Molecular geometry	Triangular bipyramidal	Seesaw	T shaped	Linear	Octahedral	Square pyramidal	Square planar

Shape: PCl_3

Lewis Electron Dot Structure



on P atom

••3 bond pairs

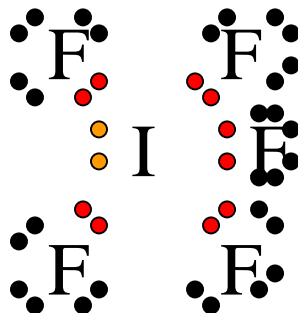
••1 lone pair

→ AB_3E

trigonal pyramidal shape

Shape: IF₅

Lewis Electron Dot Structure



on I atom

•• 5 bonds pairs

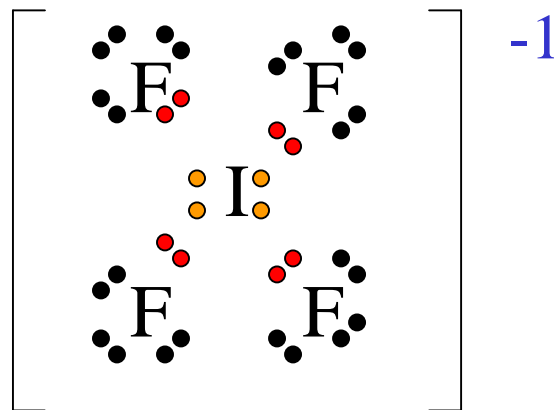
•• 1 lone pair

→ AB₅E

Square pyramidal shaped

Shape: IF_4^{-1}

Lewis Electron Dot Structure



on I atom

• 4 bonds pairs

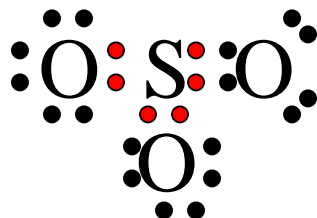
• 2 lone pair

→ AB_4E_2

Square planar shaped

Shape: SO_3

Lewis Electron Dot Structure



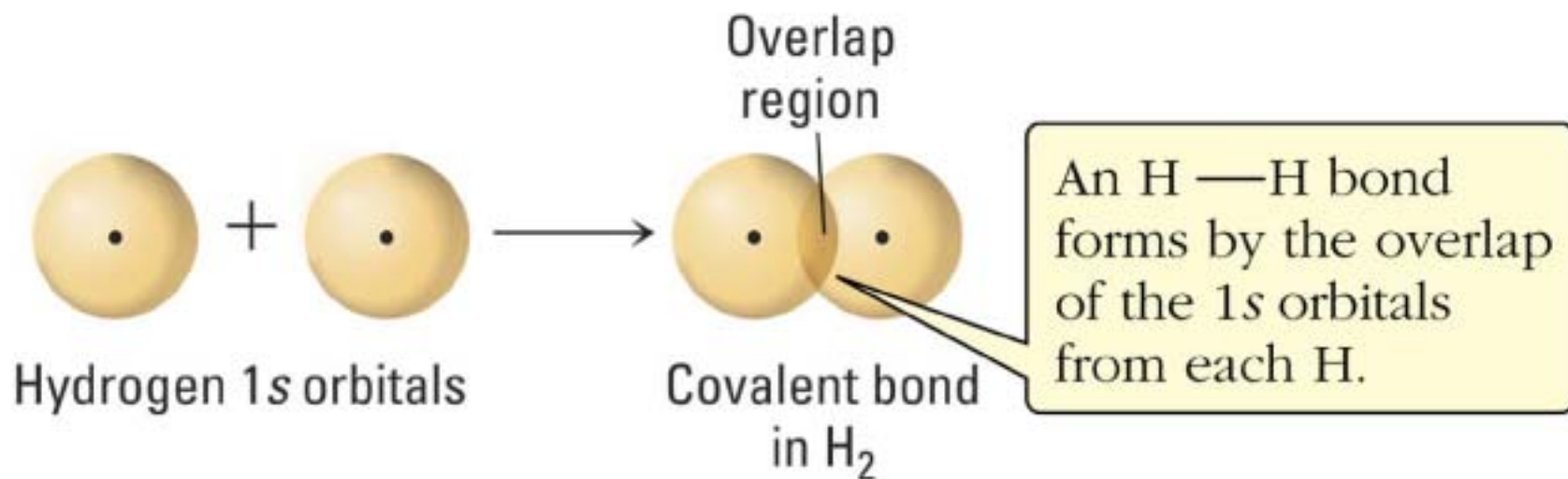
on S atom

• 3 bond pairs

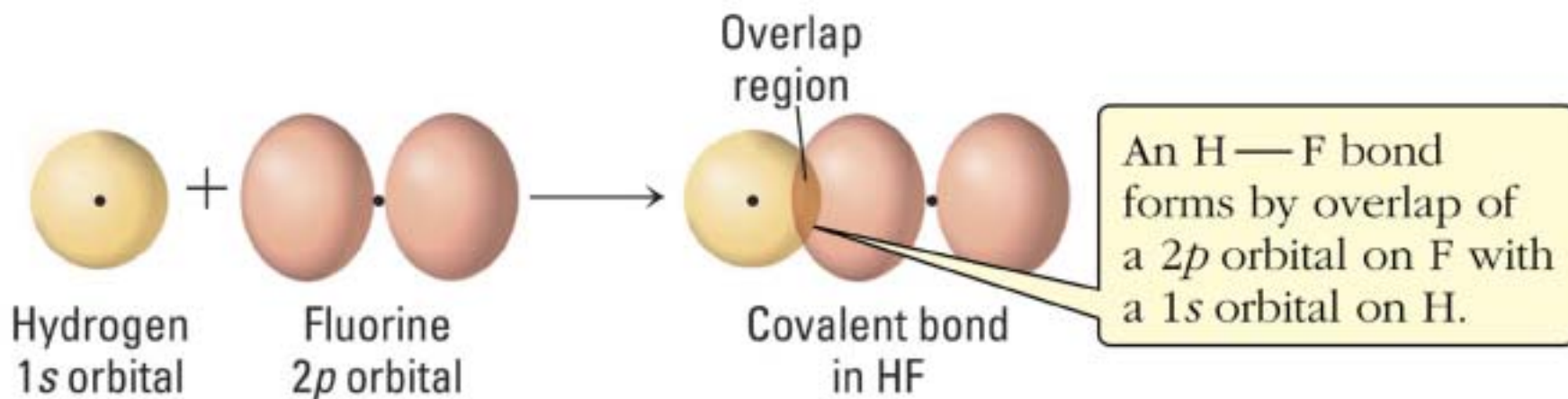
0 lone pairs \rightarrow AB_3

trigonal planar shape

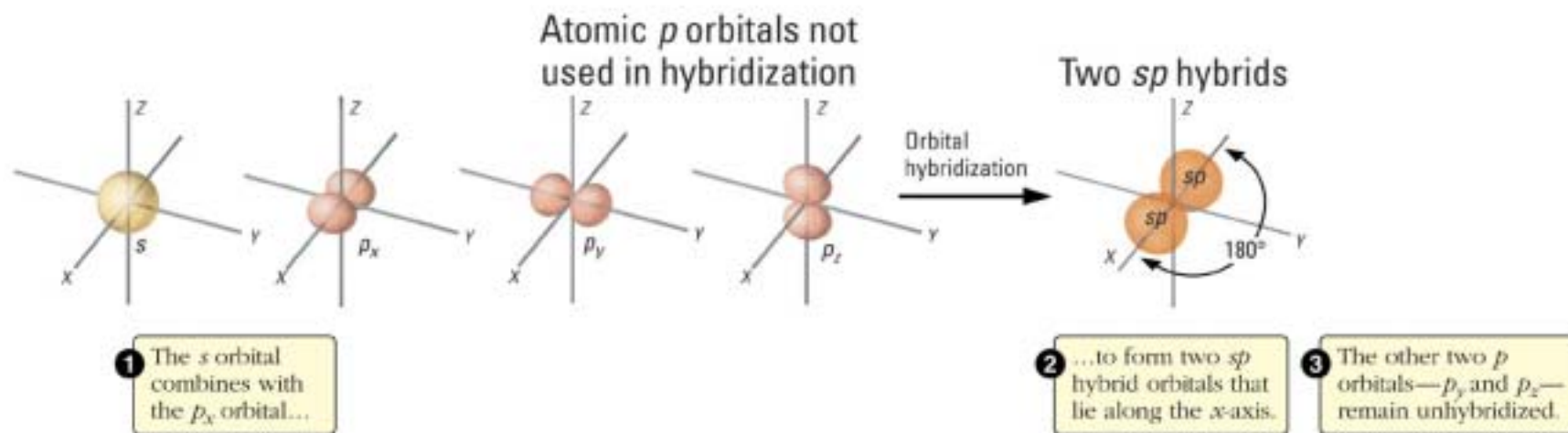
Hydrogen Molecule



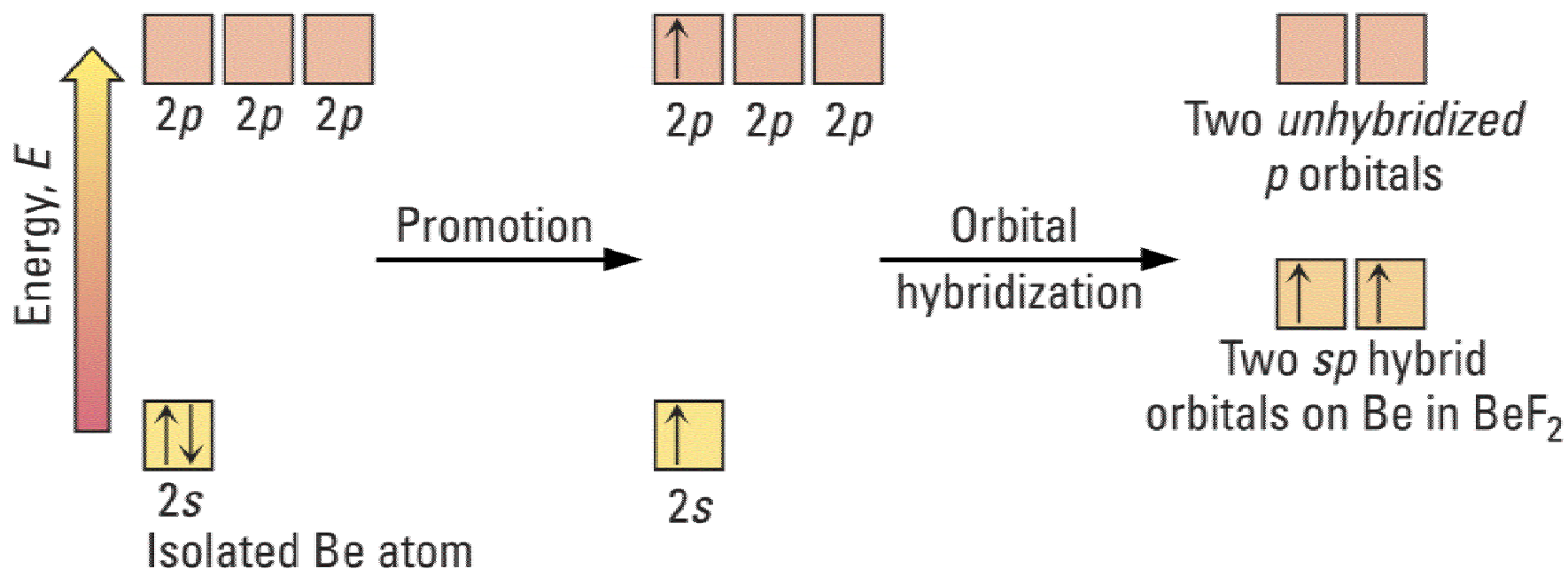
Hydrogen Fluoride Molecule



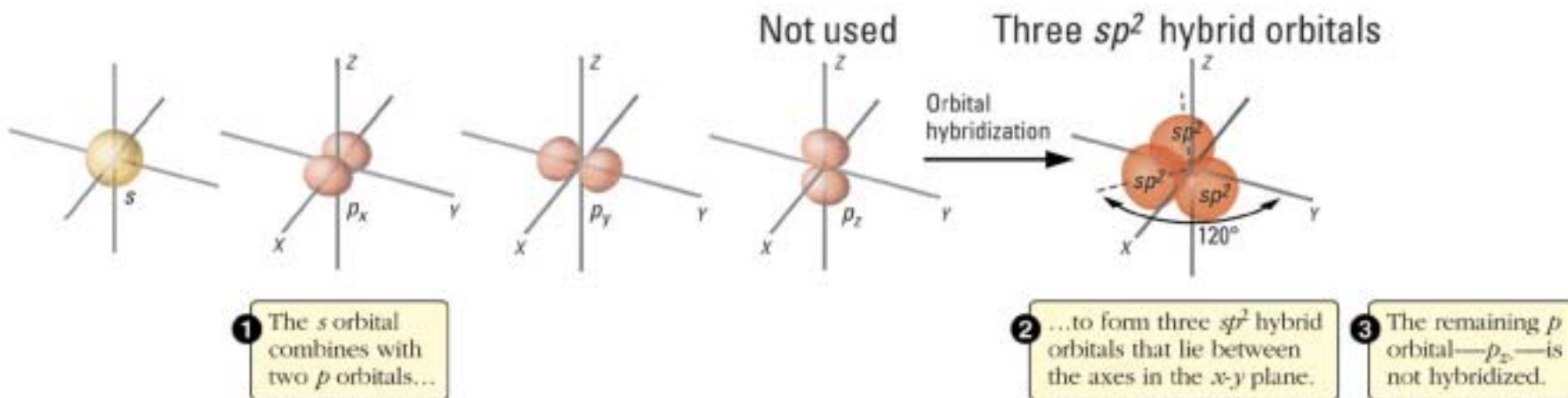
sp Hybrid Orbitals



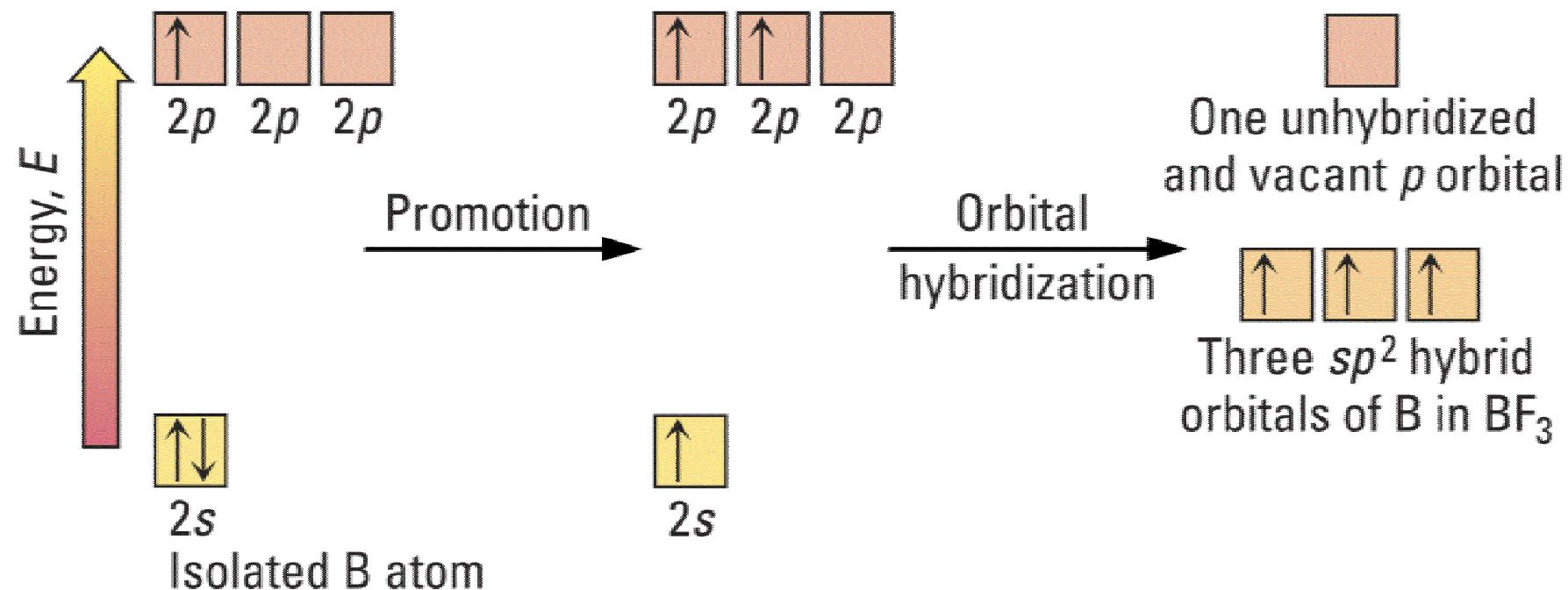
Hybridization in BeF₂



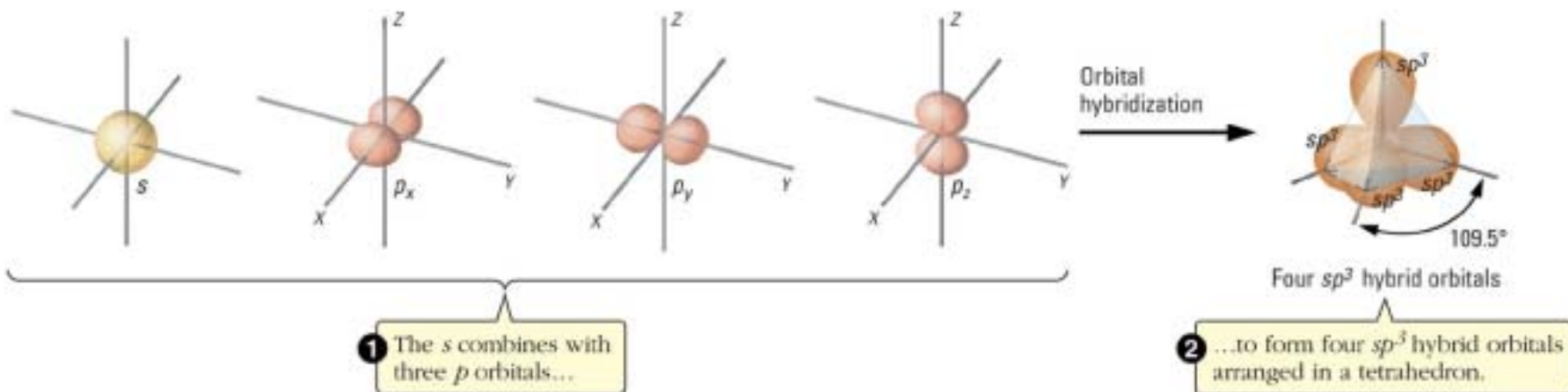
sp^2 Hybrid Orbitals



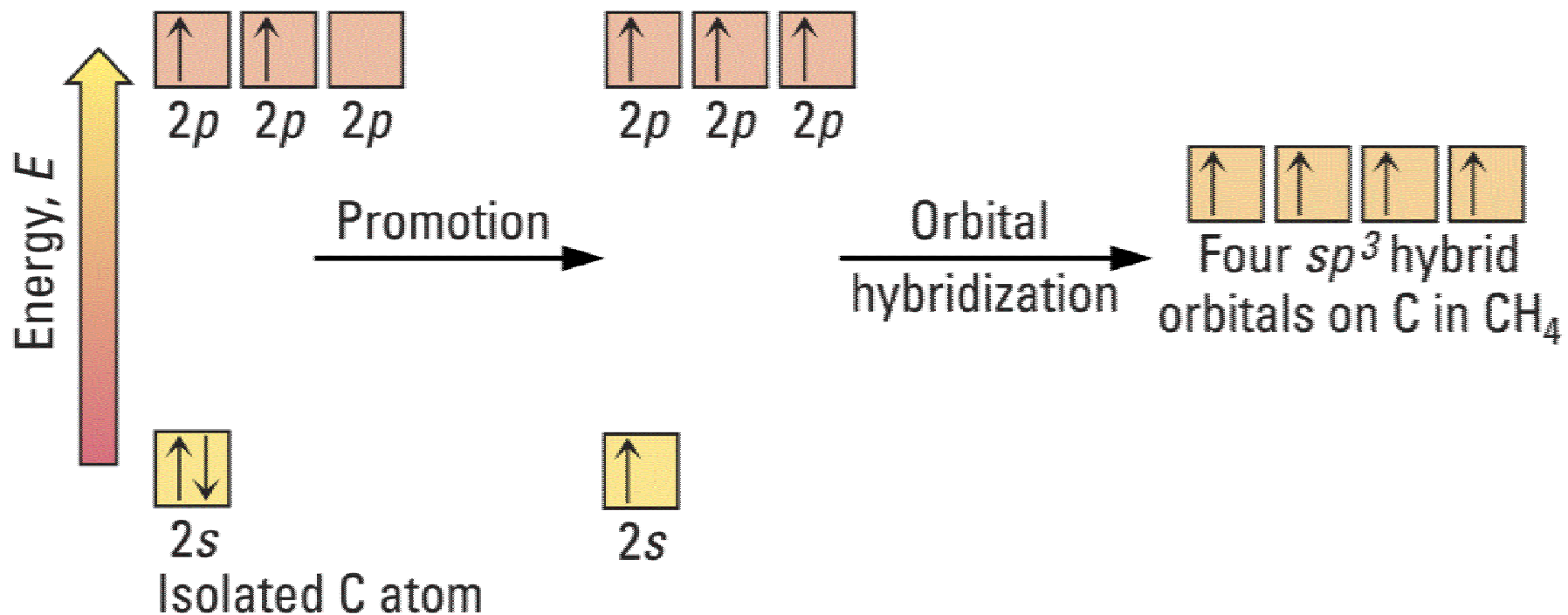
Hybridization in BF_3



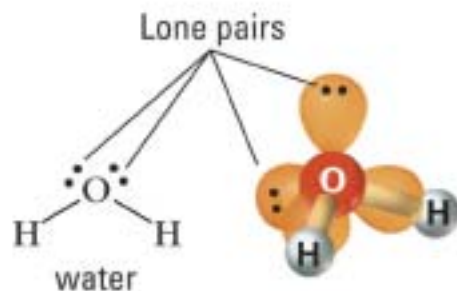
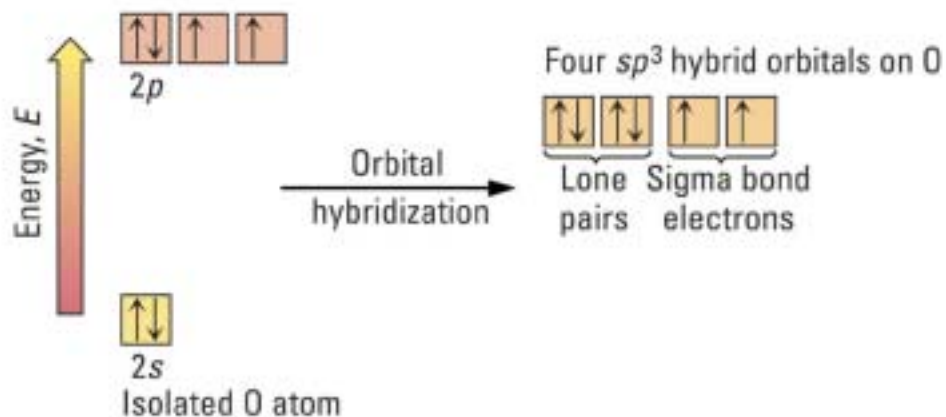
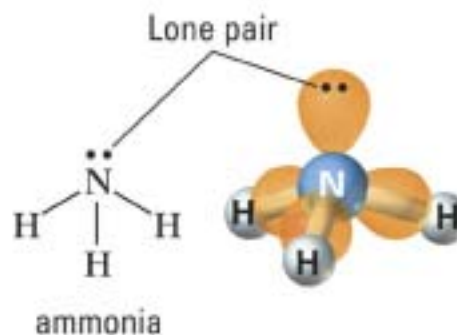
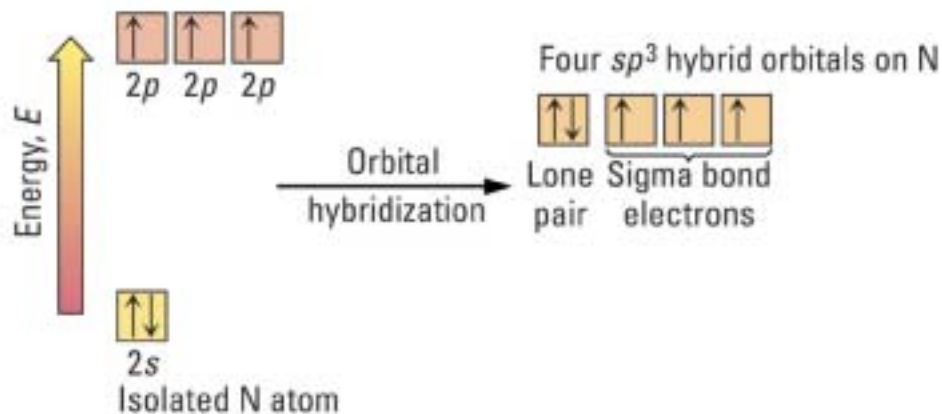
sp^3 Hybrid Orbitals



Hybridization in CH₄



Hybridization in NH_3 & H_2O

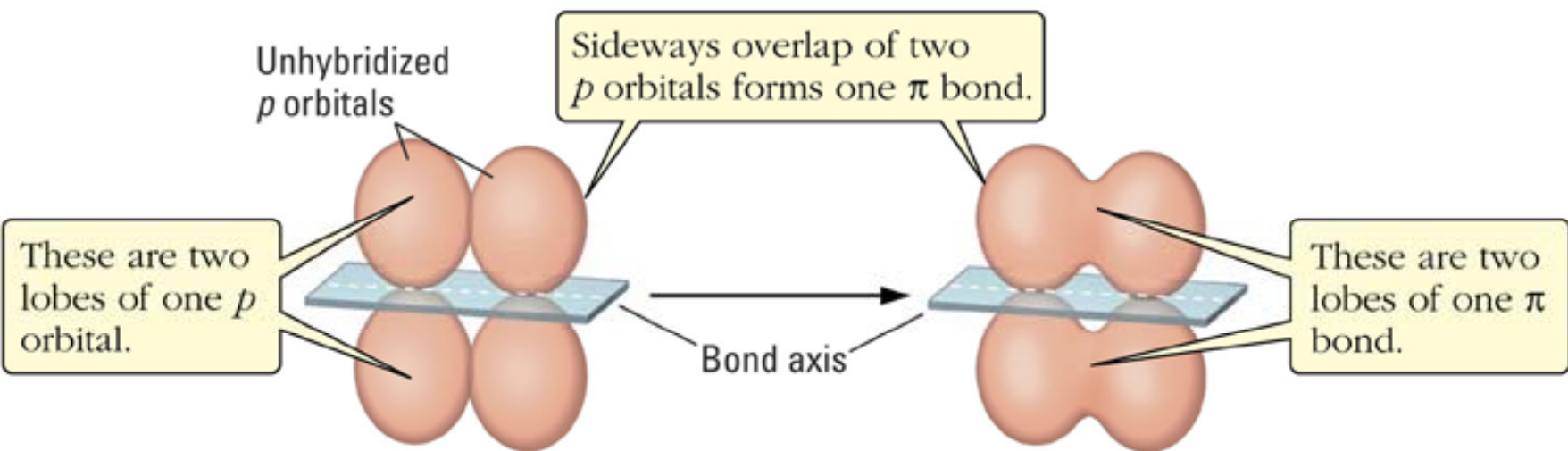


Hybrid Orbital Geometries

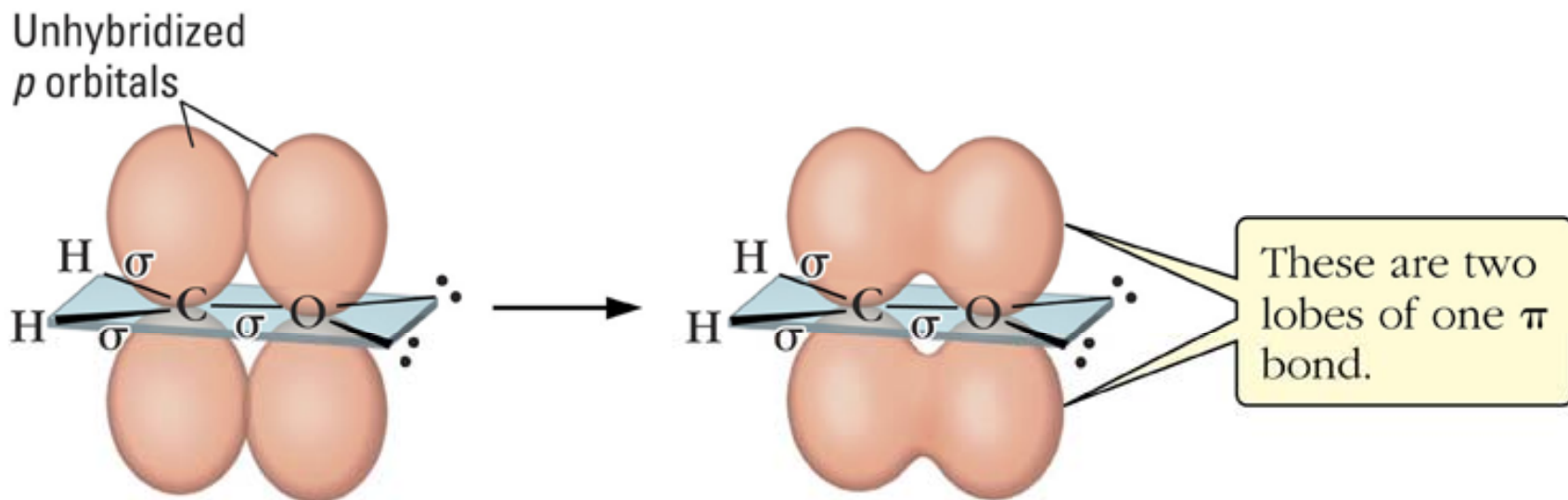
TABLE 9.2 Hybrid Orbitals and Their Geometries

	Linear	Trigonal planar	Tetrahedral
Atomic orbitals mixed	One s and one p	One s and two p	One s and three p
Hybrid orbitals formed	Two sp	Three sp^2	Four sp^3
Unhybridized orbitals remaining	Two p	One p	None

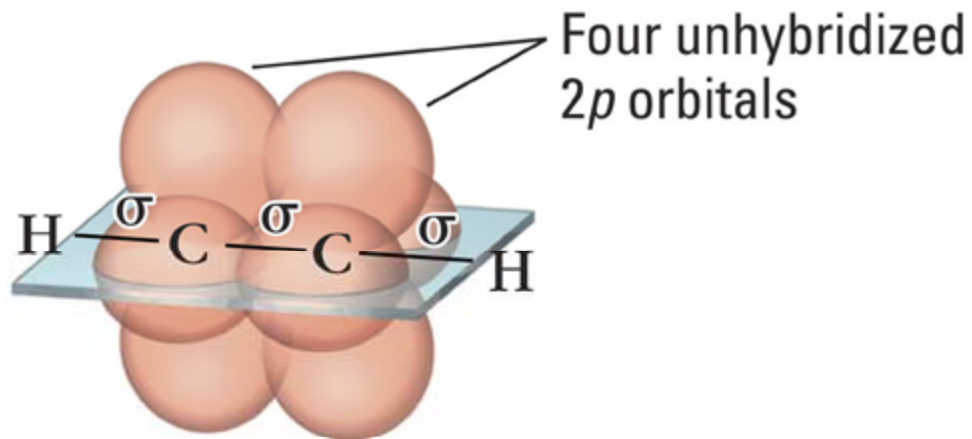
Pi Bond



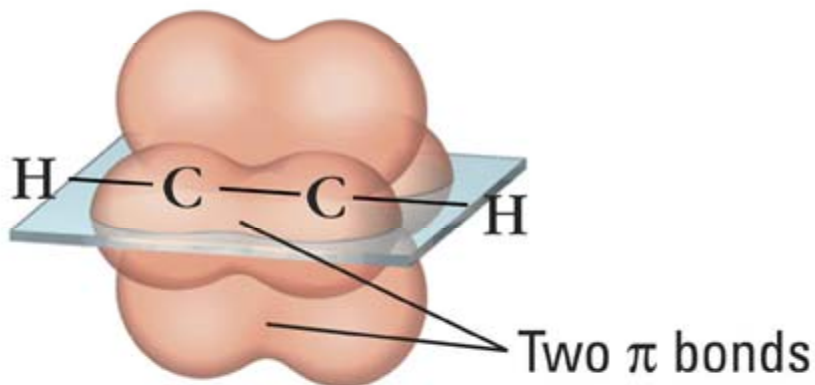
Bonding in Formaldehyde



Bonding in Acetylene

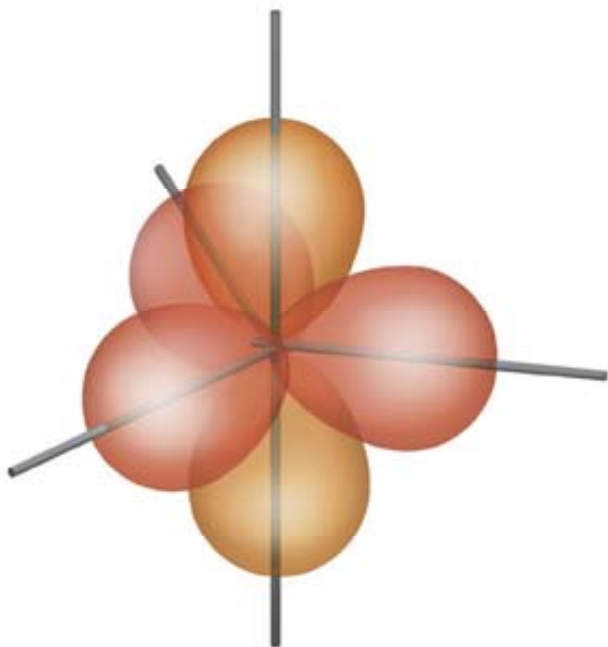


(a) Sigma bonds in acetylene

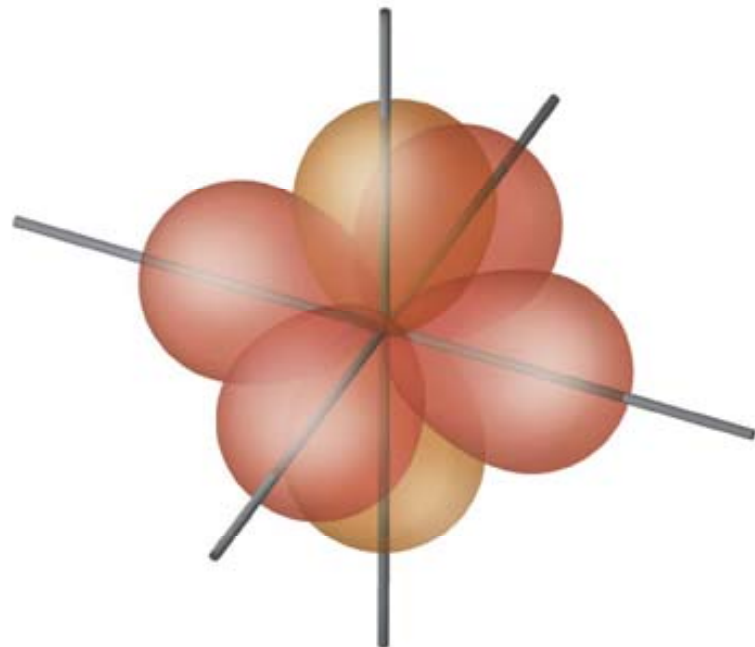


(b) Pi bonds in acetylene

Hybridization in Expanded Octet



(a) Trigonal bipyramidal
 sp^3d hybridization



(b) Octahedral
 sp^3d^2 hybridization

Sigma Bond σ

Bond with the greatest electron density on a line connecting the atomic nuclei

s-s type

p-p type

s-p type

s-sp³ type

s-sp² type

s-sp type

p-sp³ type

p-sp² type

p-sp type

sp³ - sp³ type

sp²-sp² type

sp - sp type

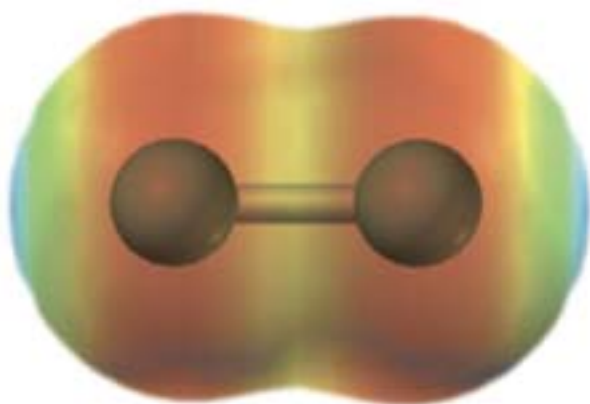
etc., including all combinations of s, p, d, and hybrid orbitals

Pi Bond π

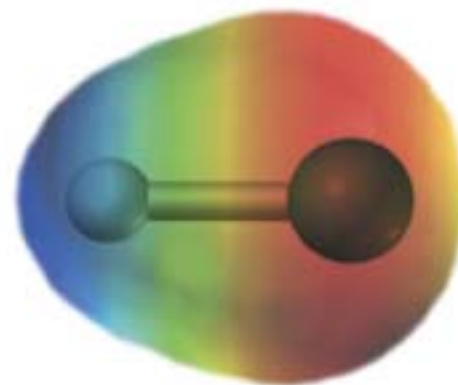
Bond with the greatest electron density above and below a line connecting the atomic nuclei

p–p type

Molecular Polarity

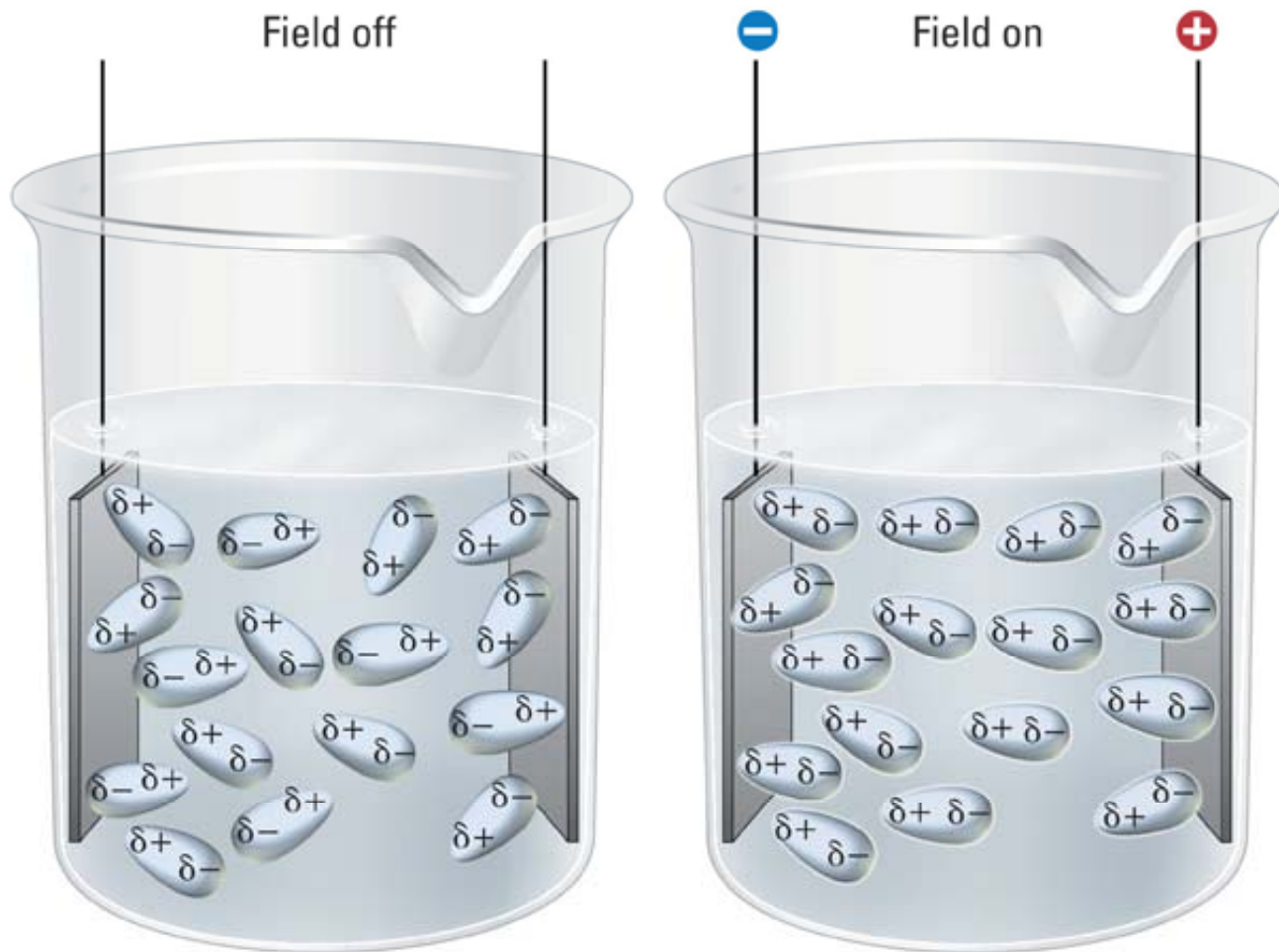


Nonpolar
molecule, Cl₂



Polar molecule,
HCl

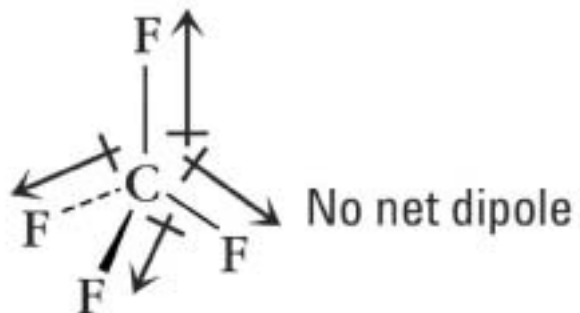
Polar Molecules



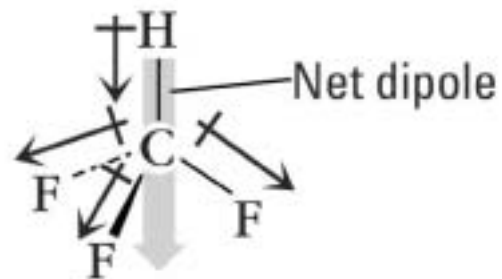
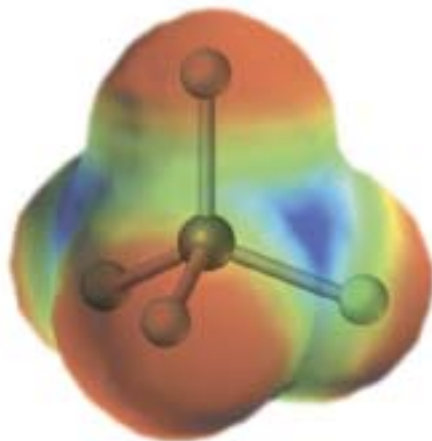
Dipole Moments of Select Compounds

Molecule	Moment	Molecule	Moment
H ₂	0	CO ₂	0
HF	1.78	NH ₃	1.47
HBr	0.79	NCl ₃	0.39
BrF	1.29	CH ₄	0
BrCl	0.52	CH ₃ Cl	1.92
H ₂ O	1.85	CHCl ₃	1.04

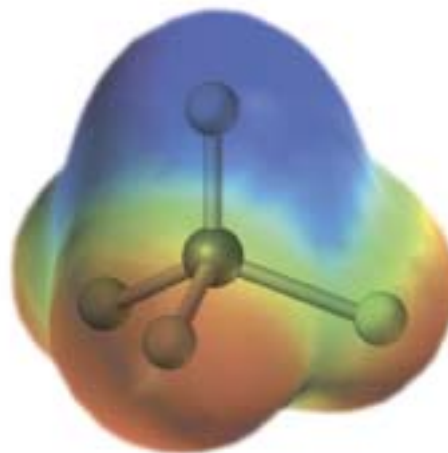
Molecular Polarity



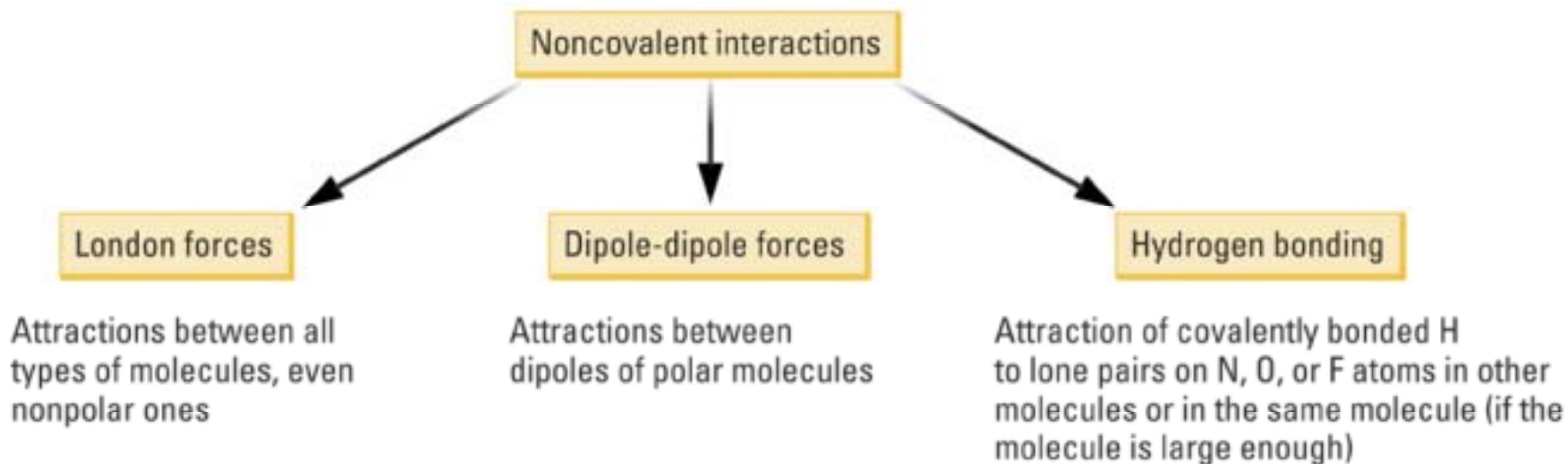
CF_4 is nonpolar



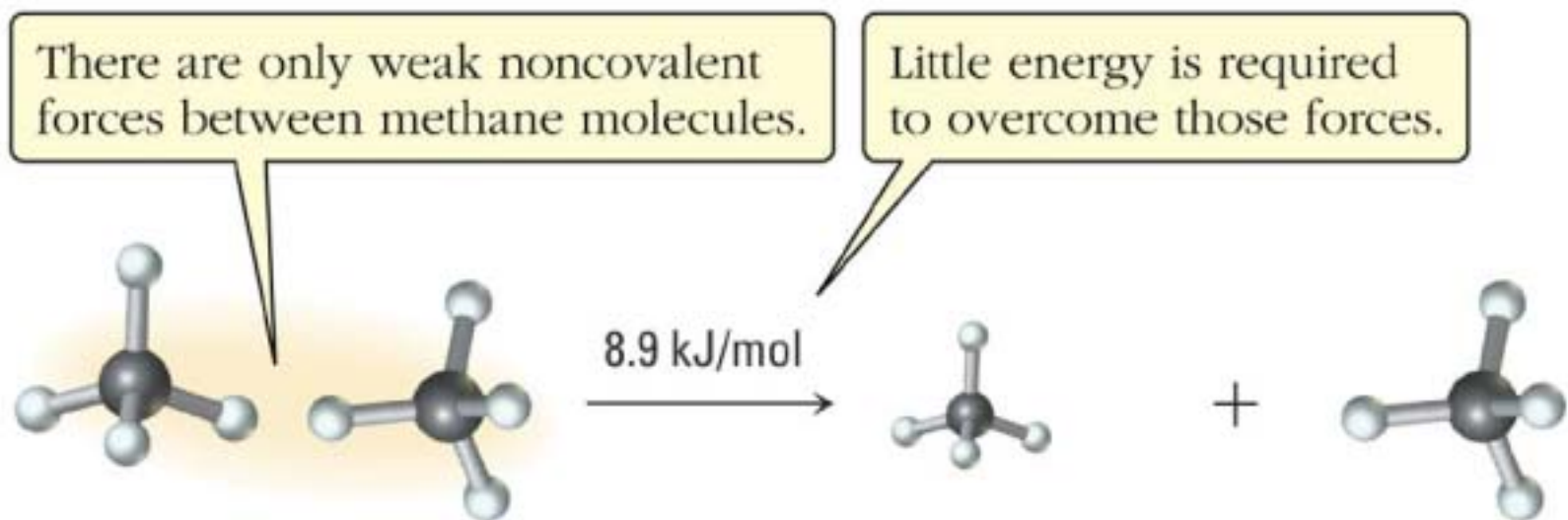
CHF_3 is polar



Types of Intermolecular Forces

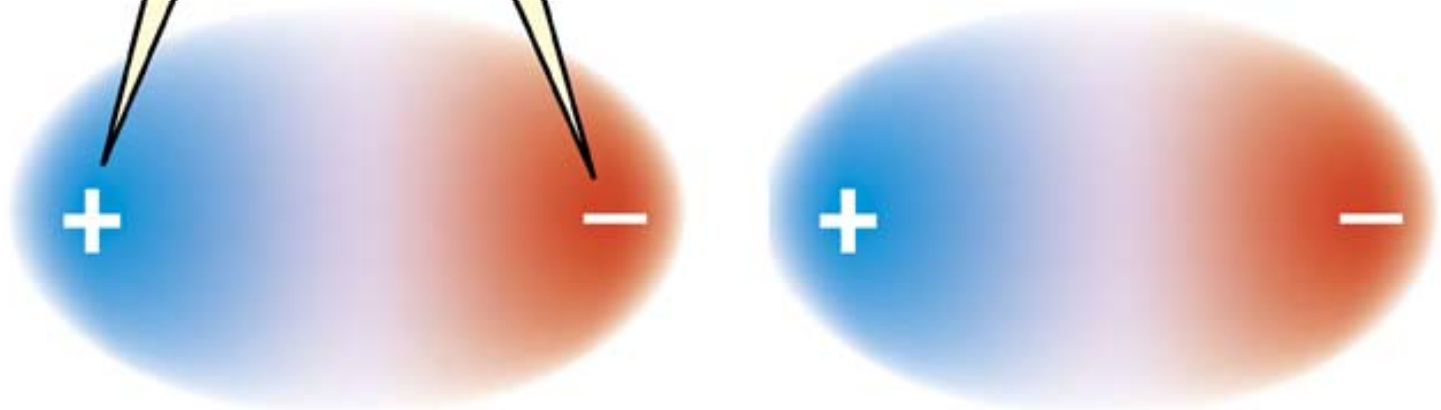


Intermolecular Forces in Methane



London Forces

These are temporary partial charges.



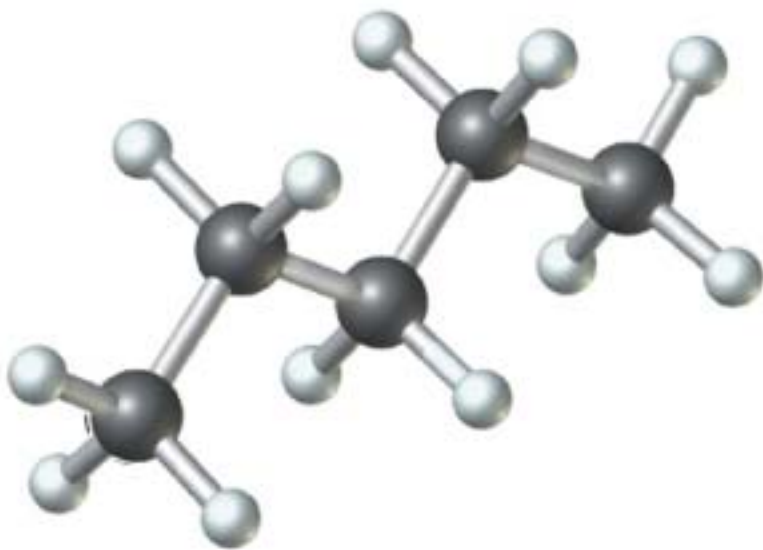
Boiling Points of Nonpolar Substances

TABLE 9.5 Effect of Numbers of Electrons on Boiling Points of Nonpolar Molecular Substances

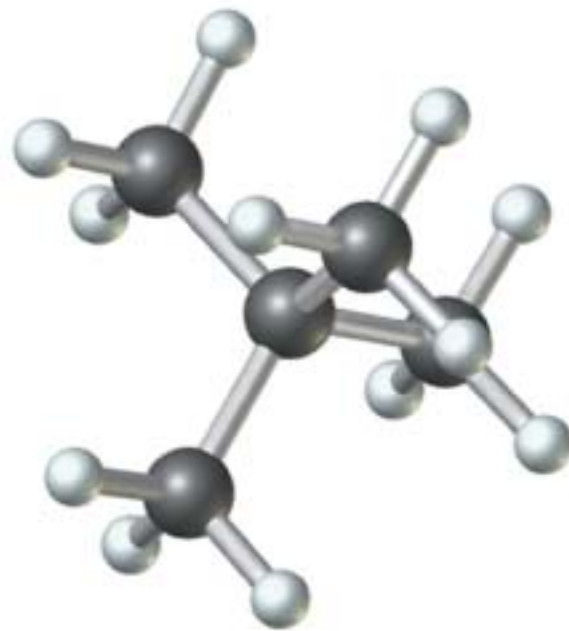
Noble gases			Halogens			Hydrocarbons		
	No. e's	bp (°C)		No. e's	bp (°C)		No. e's	bp (°C)
He	2	-269	F ₂	18	-188	CH ₄	10	-161
Ne	10	-246	Cl ₂	34	-34	C ₂ H ₆	18	-88
Ar	18	-186	Br ₂	70	59	C ₃ H ₈	26	-42
Kr	36	-152	I ₂	106	184	C ₄ H ₁₀ *	34	0

* Butane.

Structures & Boiling Points

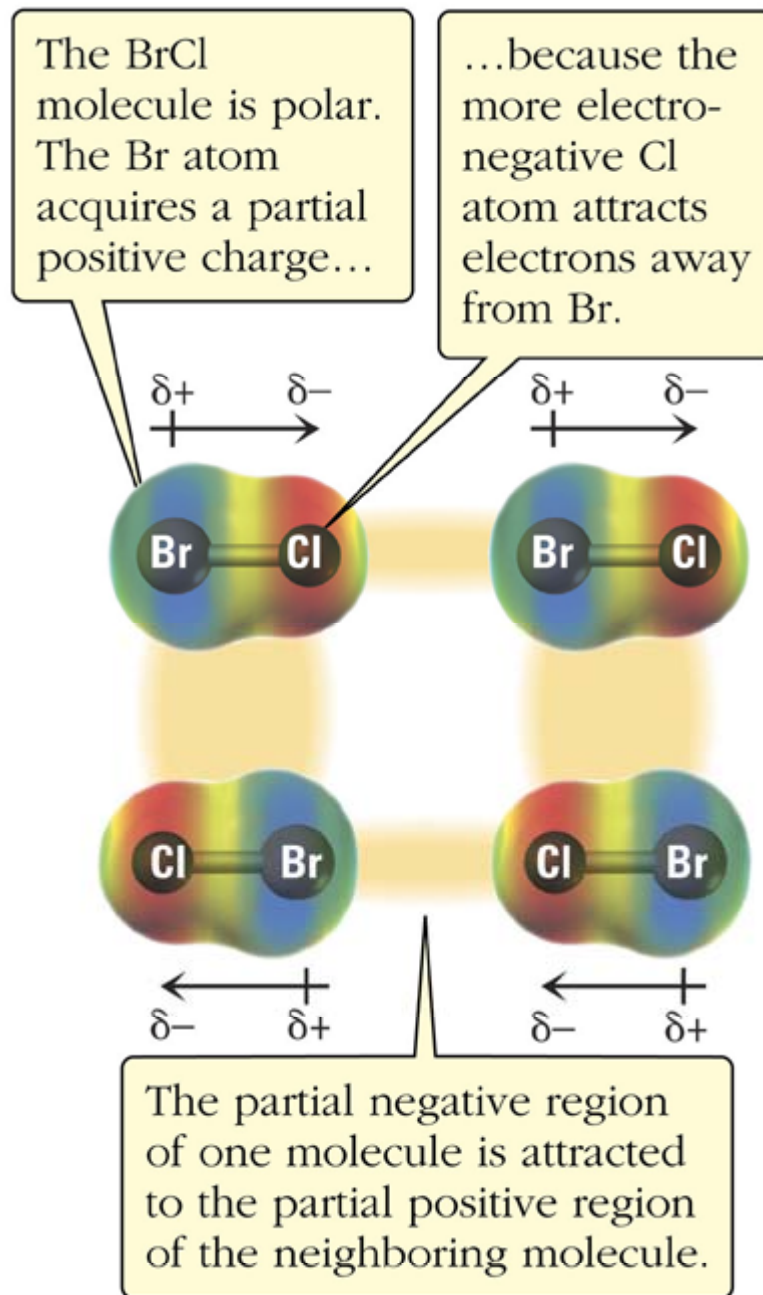


pentane, bp = 36.0 °C



2,2-dimethylpropane, bp = 9.5 °C

Dipole-Dipole Attractions



Boiling Points of Nonpolar and Polar Substances

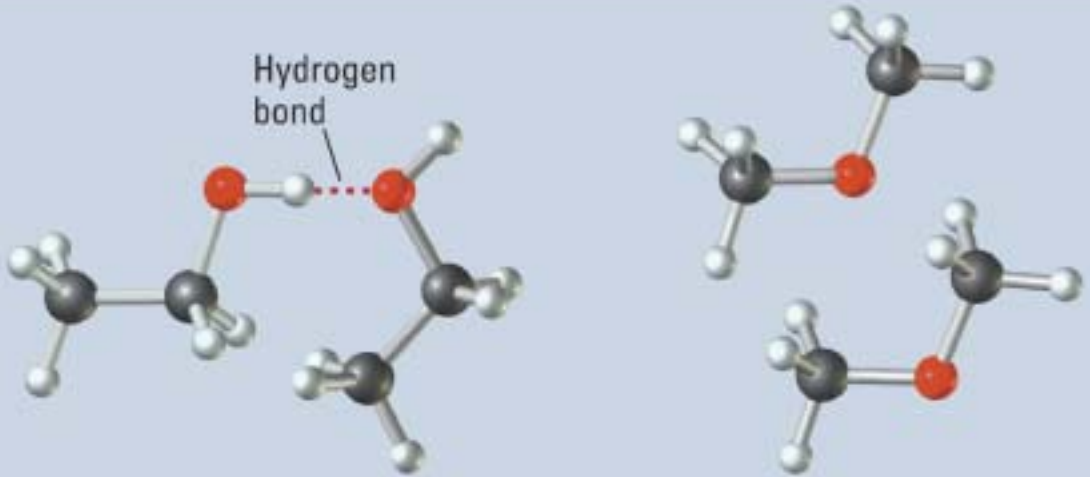
TABLE 9.6 Numbers of Electrons and Boiling Points of Nonpolar and Polar Substances

Nonpolar molecules			Polar molecules		
	No. e's	bp (°C)		No. e's	bp (°C)
N ₂	14	-196	CO	14	-192
SiH ₄	18	-112	PH ₃	18	-88
GeH ₄	36	-90	AsH ₃	36	-62
Br ₂	70	59	ICl	70	97

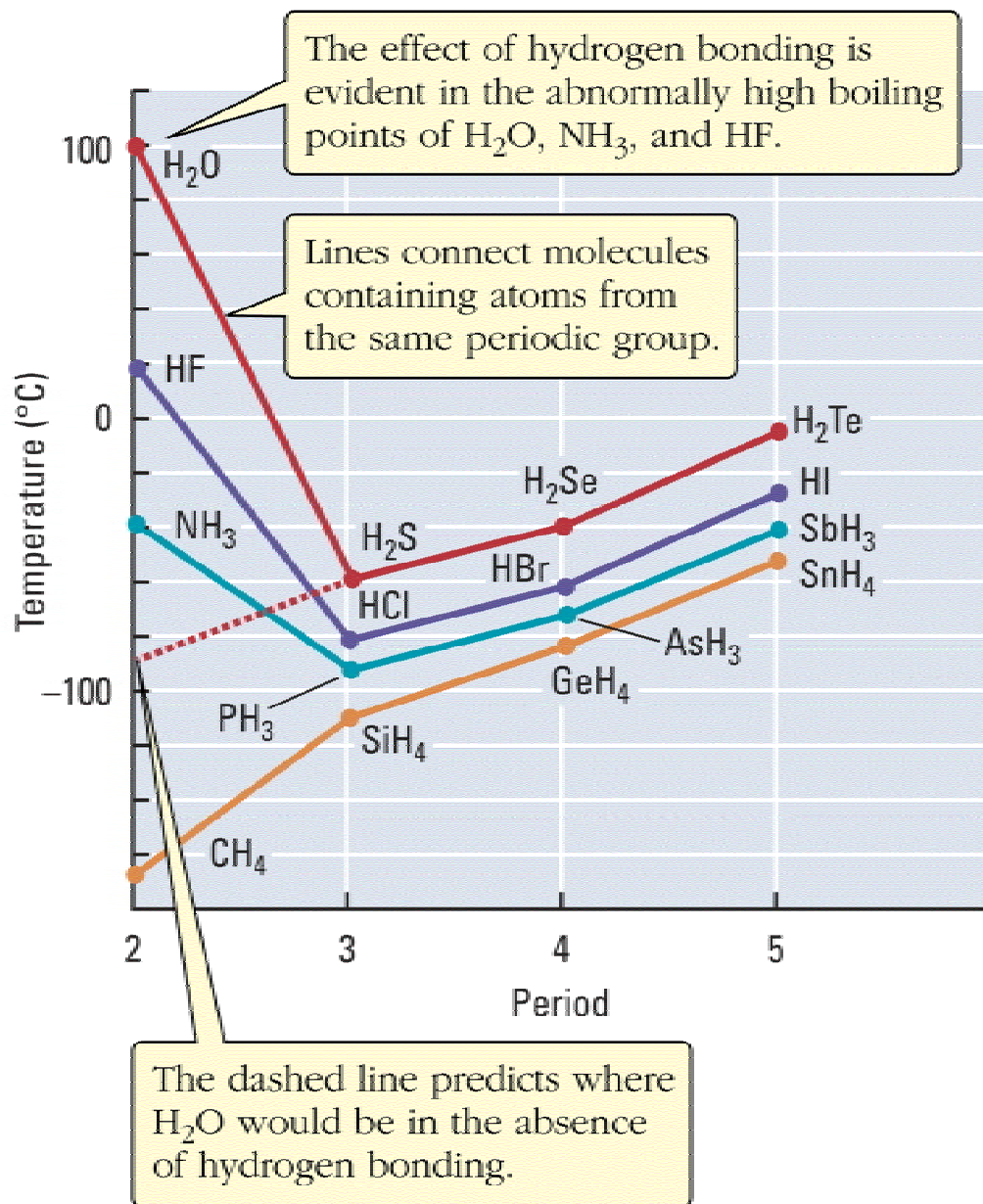
Hydrogen Bonds

- Attraction of hydrogen atom for an electron pair on a small, very electronegative atom

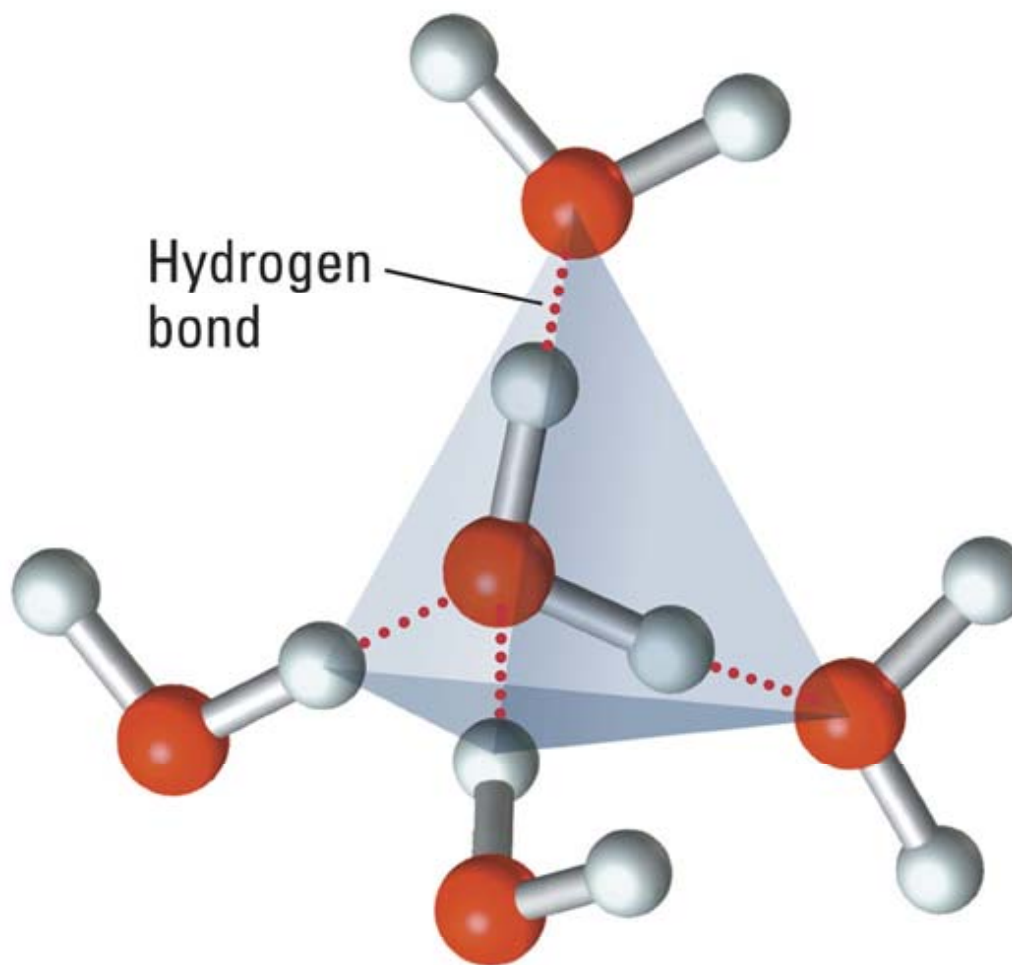
Hydrogen Bonding in Ethanol

Molecular model	 <p>ethanol $\text{CH}_3\text{CH}_2\text{OH}$</p> <p>dimethyl ether CH_3OCH_3</p>
Dipole moment, D	1.69 1.30
Melting point, °C	-114.1 -141.5
Boiling point, °C	78.29 -24.8

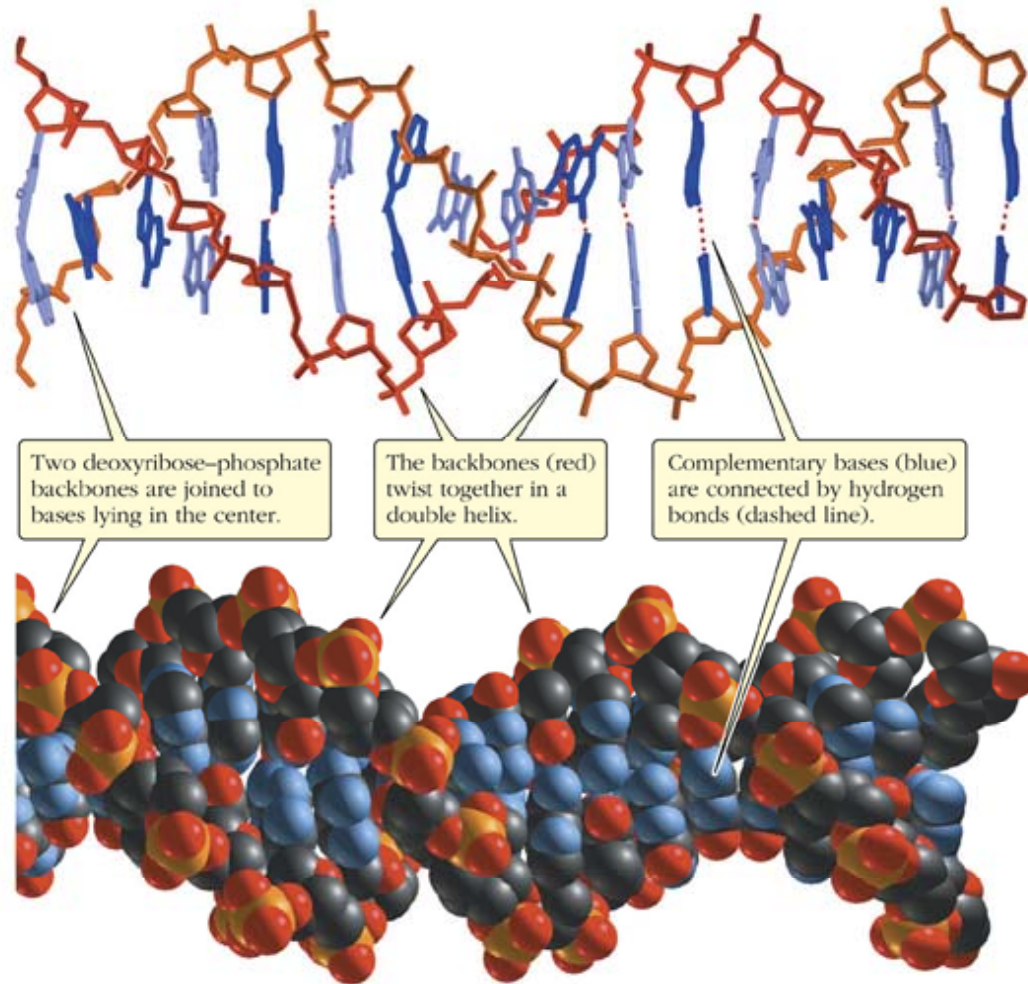
Hydrogen-Containing Binary Compound Boiling Points



Hydrogen Bonding in Water



Double Stranded DNA



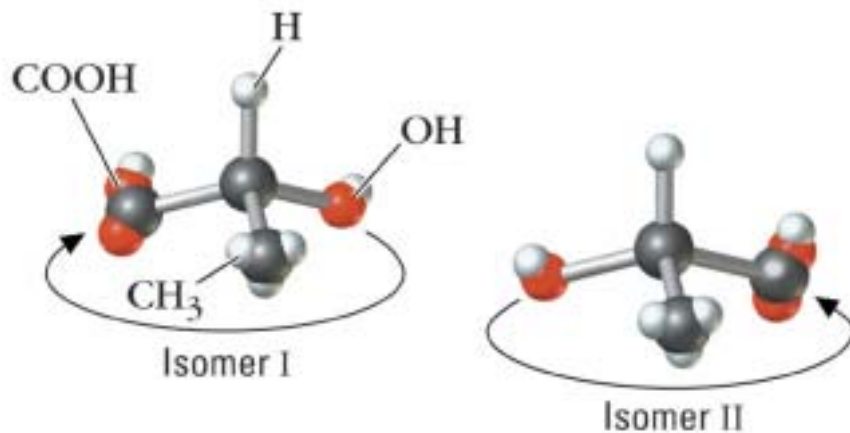
Comparison of alkanes with no dipole, a dipole and H-Bonding

Molecule		Molecular weight	Dipole moment (D)	Boiling point (°C)
Ethane	CH ₃ CH ₃	30	0	-89
Formaldehyde	HCHO	30	2.3	-21
Methanol	CH ₃ OH	32	1.7	64
<i>n</i> -Butane	CH ₃ CH ₂ CH ₂ CH ₃	58	0	-0.5
Acetone	CH ₃ COCH ₃	58	3.0	56.5
Acetic acid	CH ₃ COOH	60	1.5	118
<i>n</i> -Hexane	CH ₃ (CH ₂) ₄ CH ₃	86	0	69
Ethyl propyl ether	C ₅ H ₁₂ O	88	1.2	64
1-Pentanol	C ₅ H ₁₁ OH	88	1.7	137

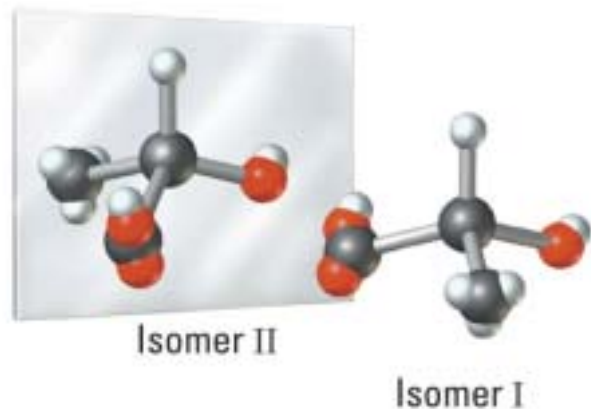
^a In order to make comparisons meaningful, molecules have been put into three groups of similar molecular weights and size. Within each group the first molecule is non-polar and interacts purely via dispersion forces, the second is polar and the third also interacts via H-bonds.

In large molecules, the van der Waal's interactions add up and become significant.

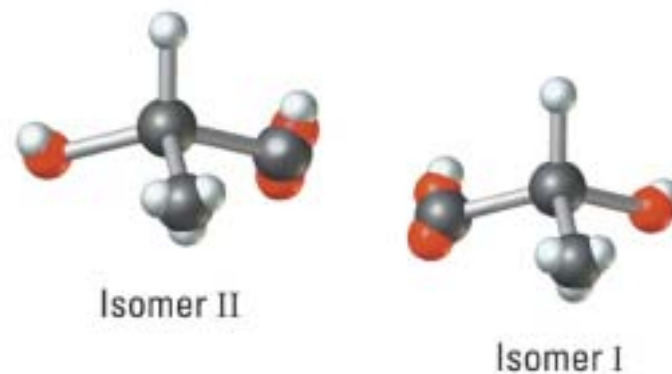
Chiral Molecules



(a)



(b)



(c)