

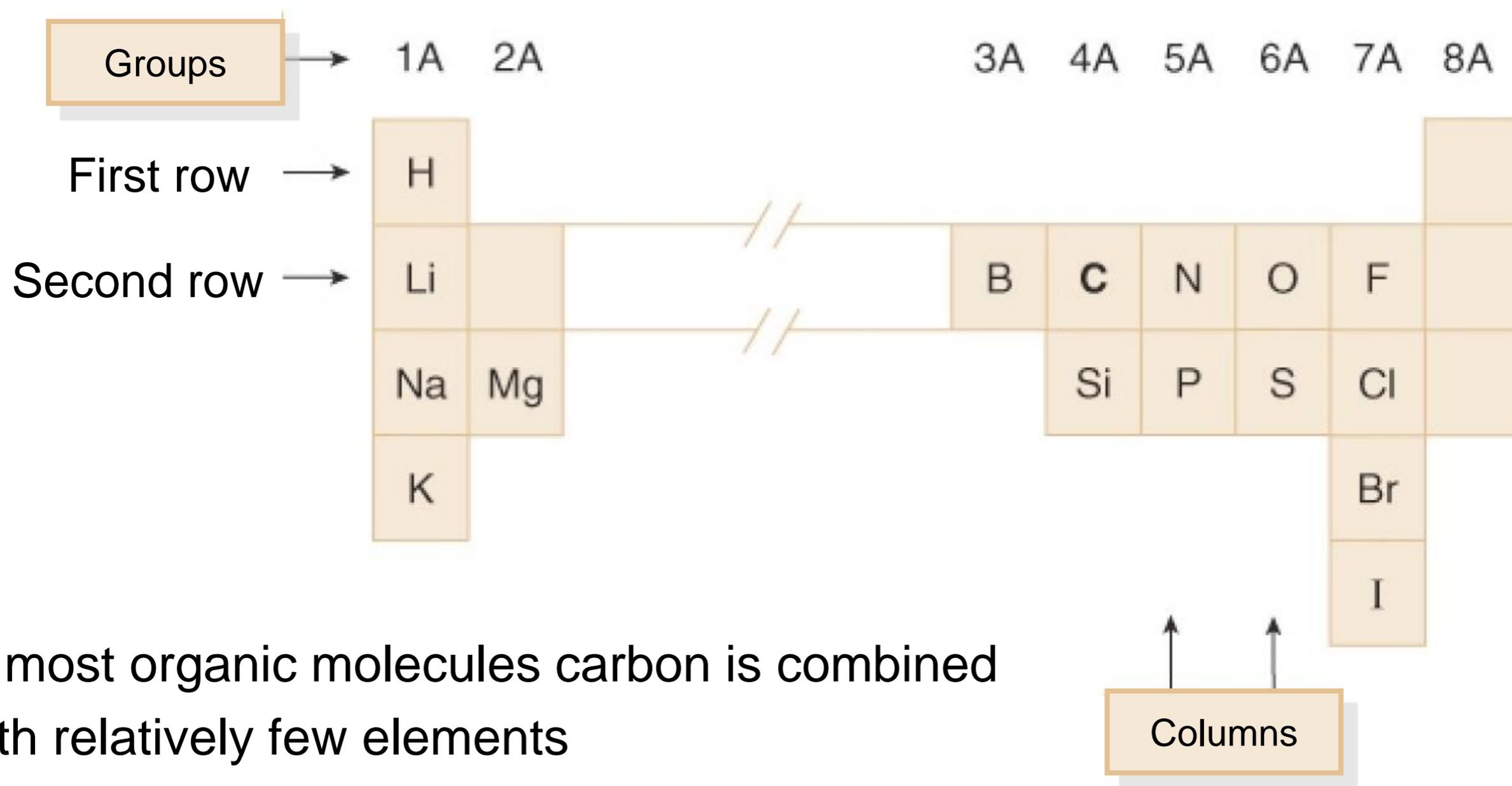
Atomic Structure and Bonding

Chapter 1

Organic Chemistry, *8th Edition*

John McMurry

Common Elements



Lewis' Model

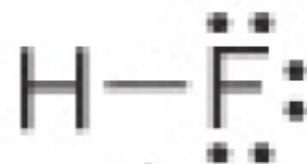
- In Lewis structures electrons are represented as dots.
- Three general rules.
 - Include only valence electrons.
 - If possible, every 2nd row element should have 8 electrons.
 - Every H atom has 2 electrons.

2 electrons (He)

8 electrons (Ne)



Lewis structure

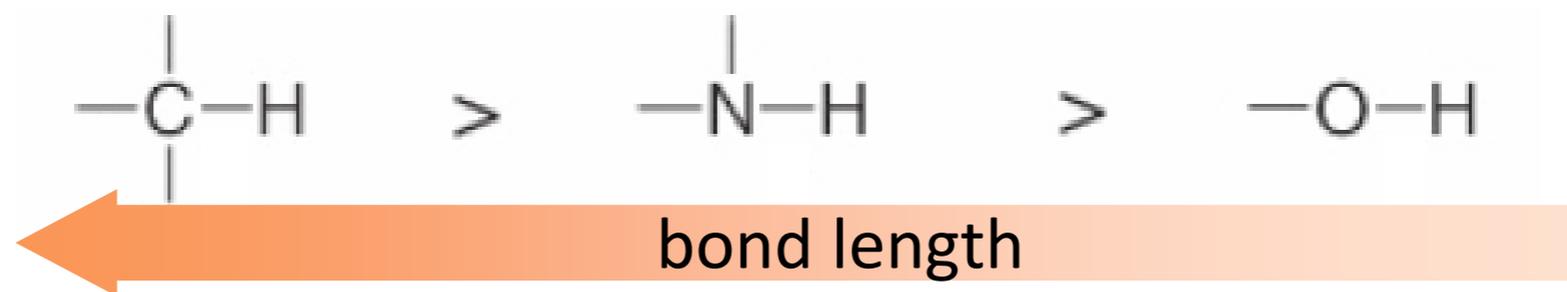


Kekulé structure

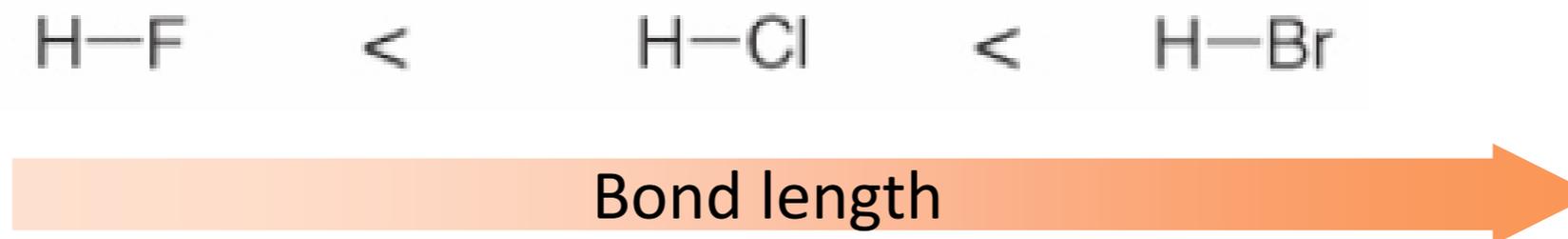
Molecular Shape

- The molecular structure is defined by:
 - bond lengths
 - bond angles

Bond lengths *decrease* along a period.



Bond lengths *increase* along a group



Bond Lengths

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
H-H	0.74	H-F	0.92	C-F	1.33
C-H	1.09	H-Cl	1.27	C-Cl	1.77
N-H	1.01	H-Br	1.41	C-Br	1.94
O-H	0.96	H-I	1.61	C-I	2.13

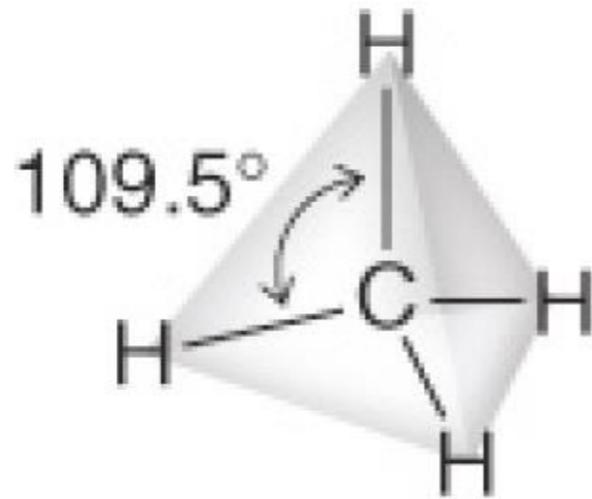
Geometry – VSEPR Theory

- The number of *Valence Shell Electron Pairs* (groups) around an atom defines the geometry of that atom.
- A group is an atom or a non bonding pair of electrons.
- Groups will tend to be as far apart as possible.

Number of groups	Geometry	Angle
2	linear	180°
3	trigonal planar	120°
4	tetrahedral	109.5°

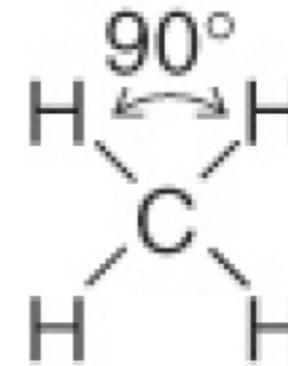
4 groups: CH₄

Tetrahedral



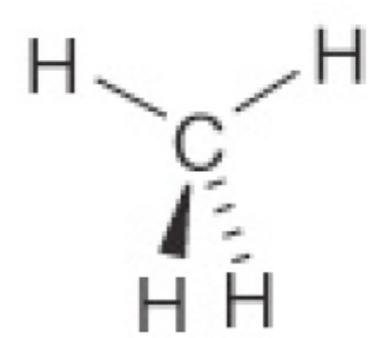
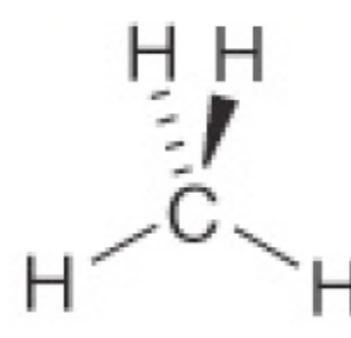
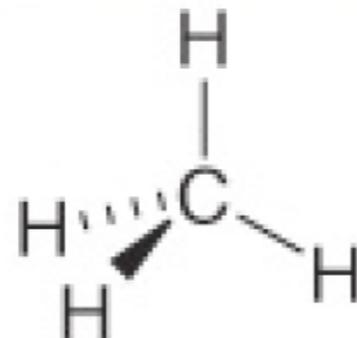
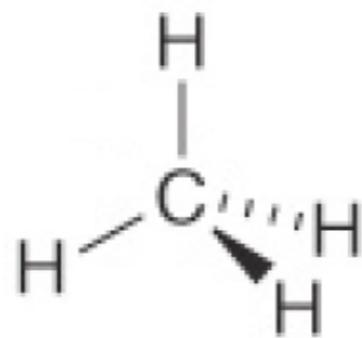
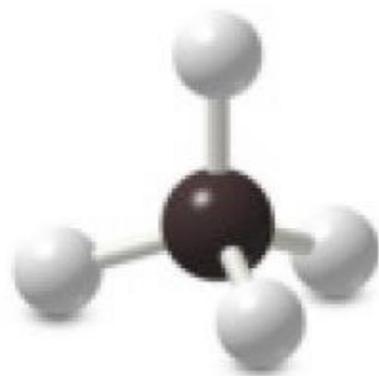
Preferred

Square planar



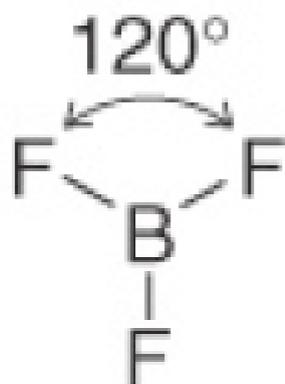
Not observed

Tridimensional representations of methane



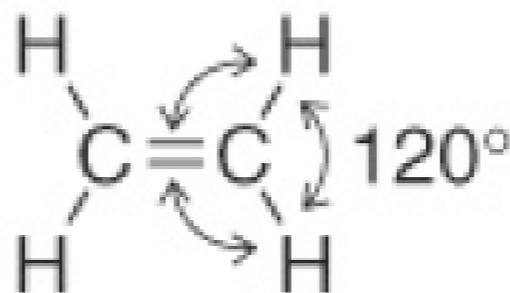
3 groups: BF_3 and C_2H_4

2 trigonal molecules



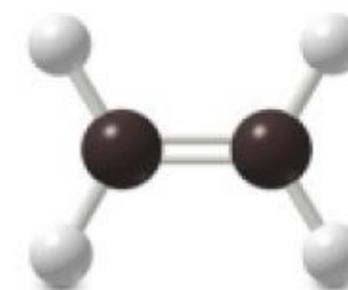
3 atoms around B

All 3 atoms are in the plane

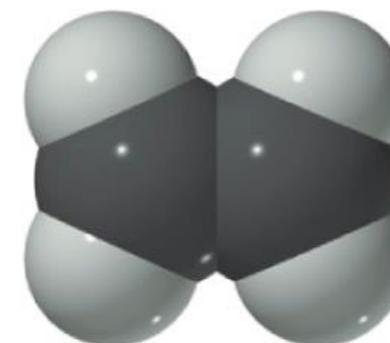


3 atoms around each C

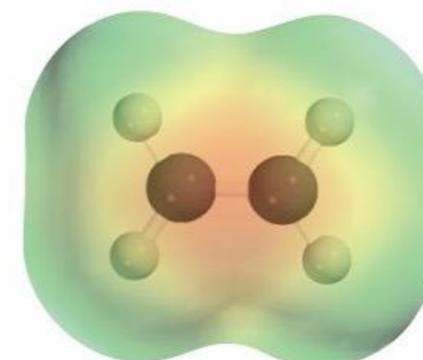
All 6 atoms are in the plane



ball-and-stick model

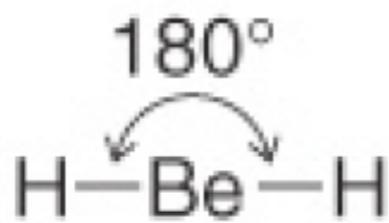


space-filling model

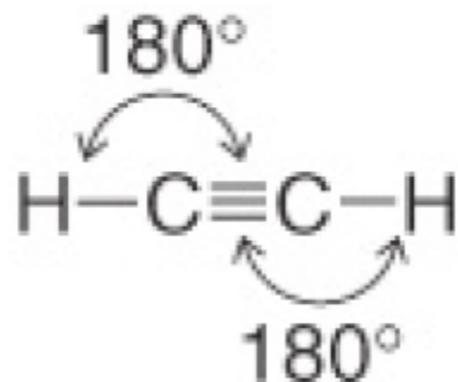


2 groups: BeH_2 and C_2H_2

2 linear molecules



2 atoms around Be



2 atoms around each C

\equiv



Energies of Multiple Bonds

Bond	Bond Dissociation Energy (kJ/M)
$\text{C}-\text{C}$	360
$\text{C}=\text{C}$	700
$\text{C}\equiv\text{C}$	950
$\text{C}-\text{O}$	400
$\text{C}=\text{O}$	750
$\text{C}-\text{N}$	360
$\text{C}=\text{N}$	700
$\text{C}\equiv\text{N}$	950

The Lewis model is not adequate!

Models for the Chemical Bond

- **Valence Orbital** theory.
 - Covalent bonds are formed by the overlap of two atomic orbitals and the electron pair is shared by both atoms.
 - A valence bond is localized between two atoms.
- **Molecular Orbital** theory.
 - n atomic orbitals are combined to give a new set of n molecular orbitals (bonding and antibonding).
 - Molecular orbitals are delocalized on the whole molecule.

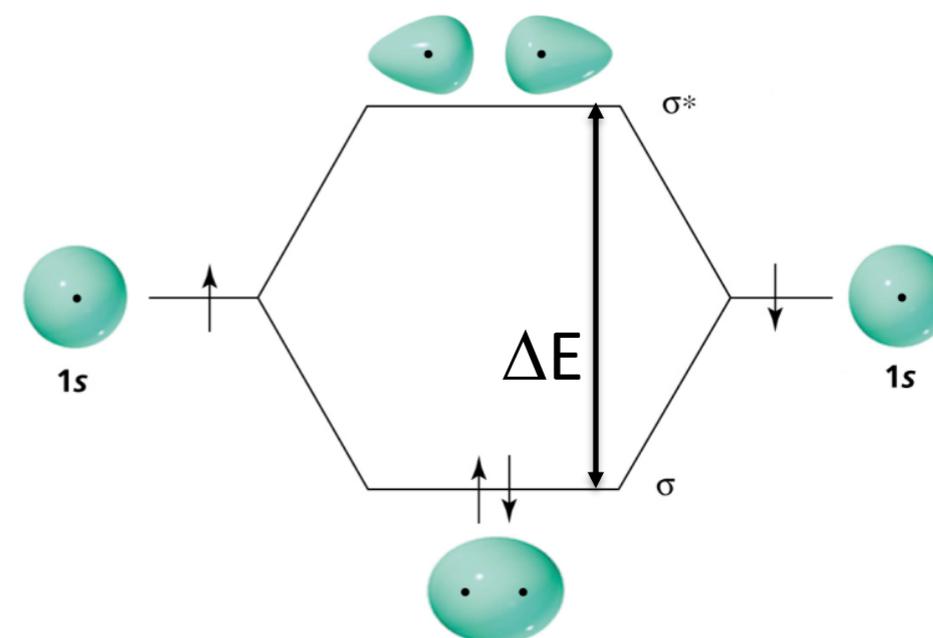
Molecular Orbitals

- Valence electrons occupy molecular orbitals delocalized on the whole molecule.
- The combination of n atomic orbitals gives n new molecular orbitals.
- Bonding orbitals have lower energies and antibonding orbitals have higher energies than the starting atomic orbitals



Robert Mulliken
(1896-1986)

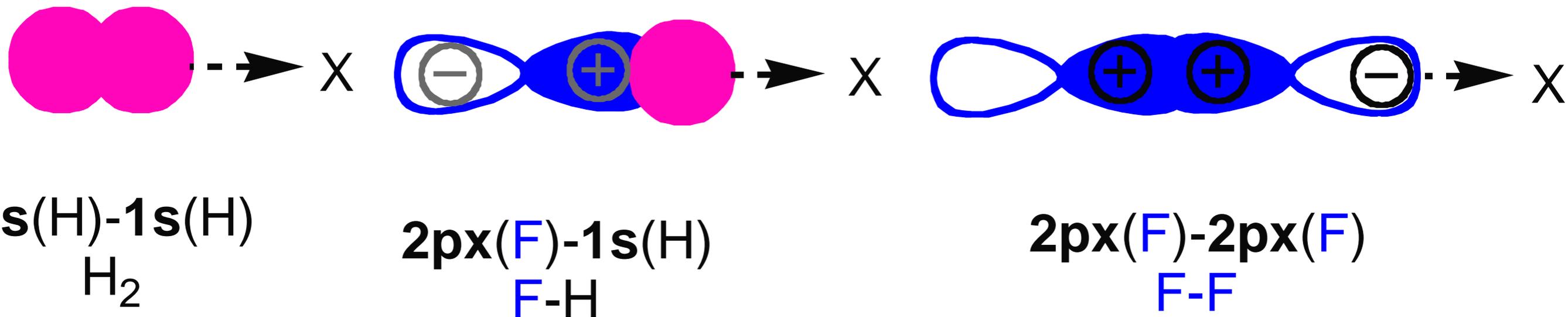
The H₂ molecule:



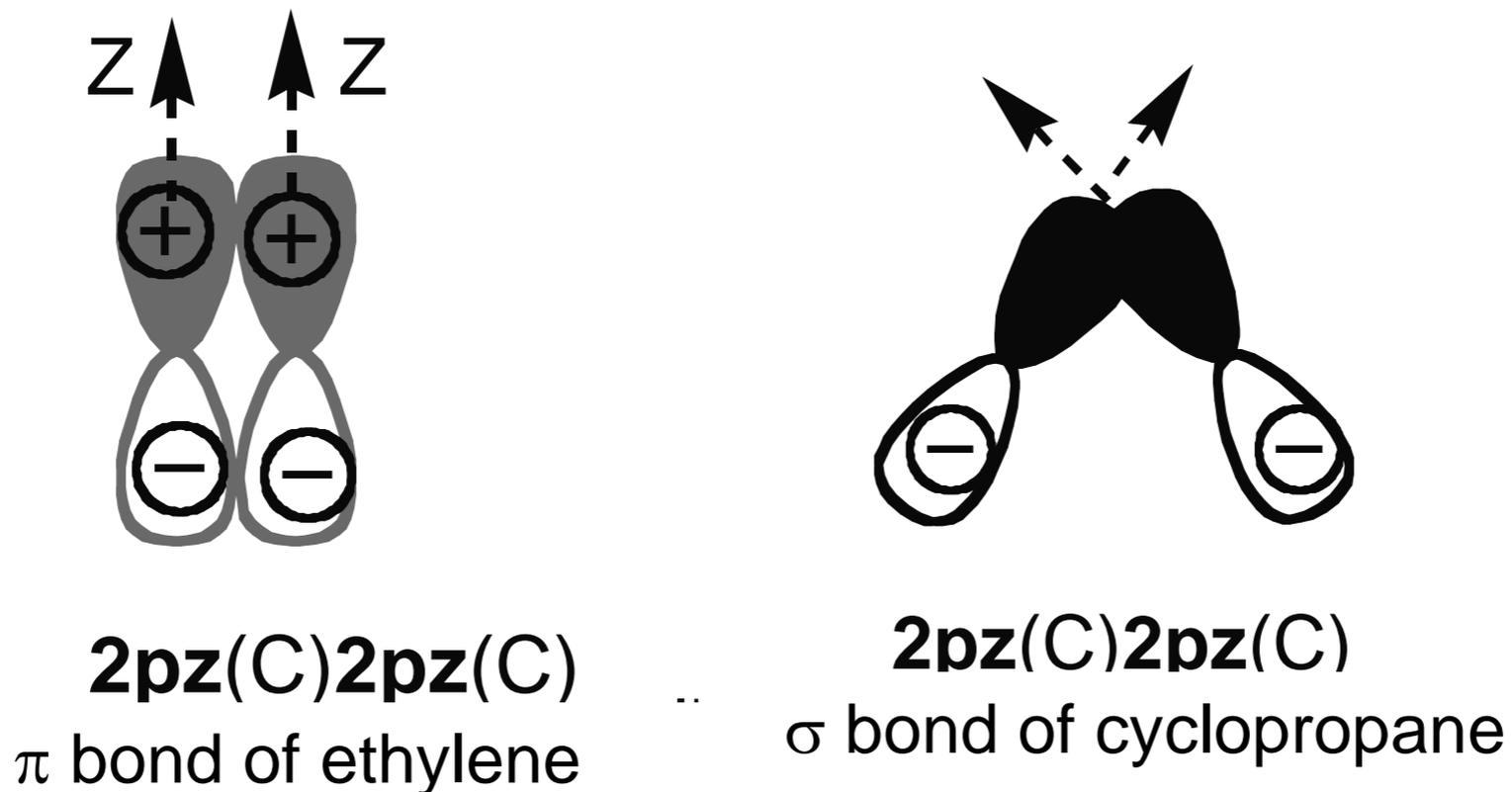
Valence Orbitals

- Bonds are formed by the in-phase overlap of two atomic orbitals each contributing one electron.
- The electron pair is localized between two atoms and is shared by both atoms.
- Hydrogen uses the 1s orbital to form σ bonds.
- 2nd row atoms use hybrid orbitals (sp^3 , sp^2 , sp) to form σ bonds.
- 2nd row atoms use p orbitals to form π bonds that have a nodal plane.
- Atomic orbitals overlap better in σ bonds (co-linear) than in π bonds (parallel).

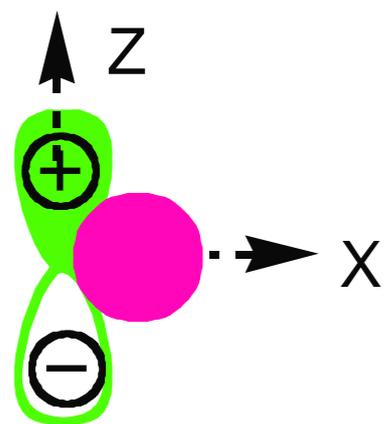
Strong Bonding Interactions: Axial Overlap



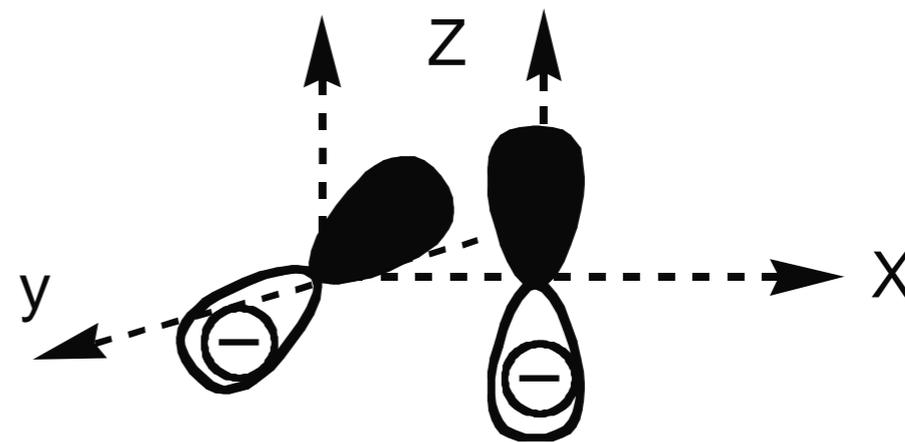
Weak Bonding Interactions: Lateral Overlap



Inexistent Bonding Interactions (0 Overlap)



$2p_x(\text{F})-1s(\text{H})$
F-H



$2p_z(\text{C})2p_z(\text{C})$
Bond in tetra-*t*Bu-ethylene

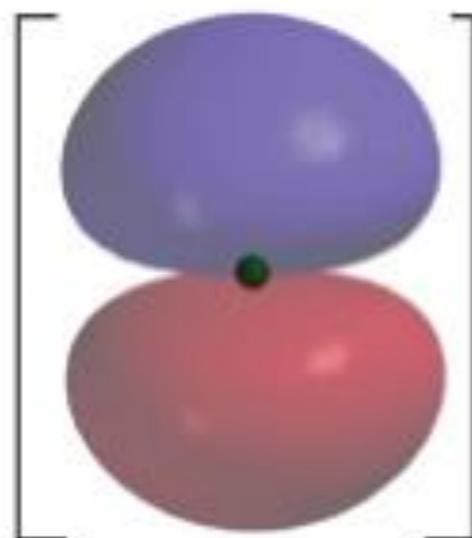
Atomic Orbitals of Carbon



s



p



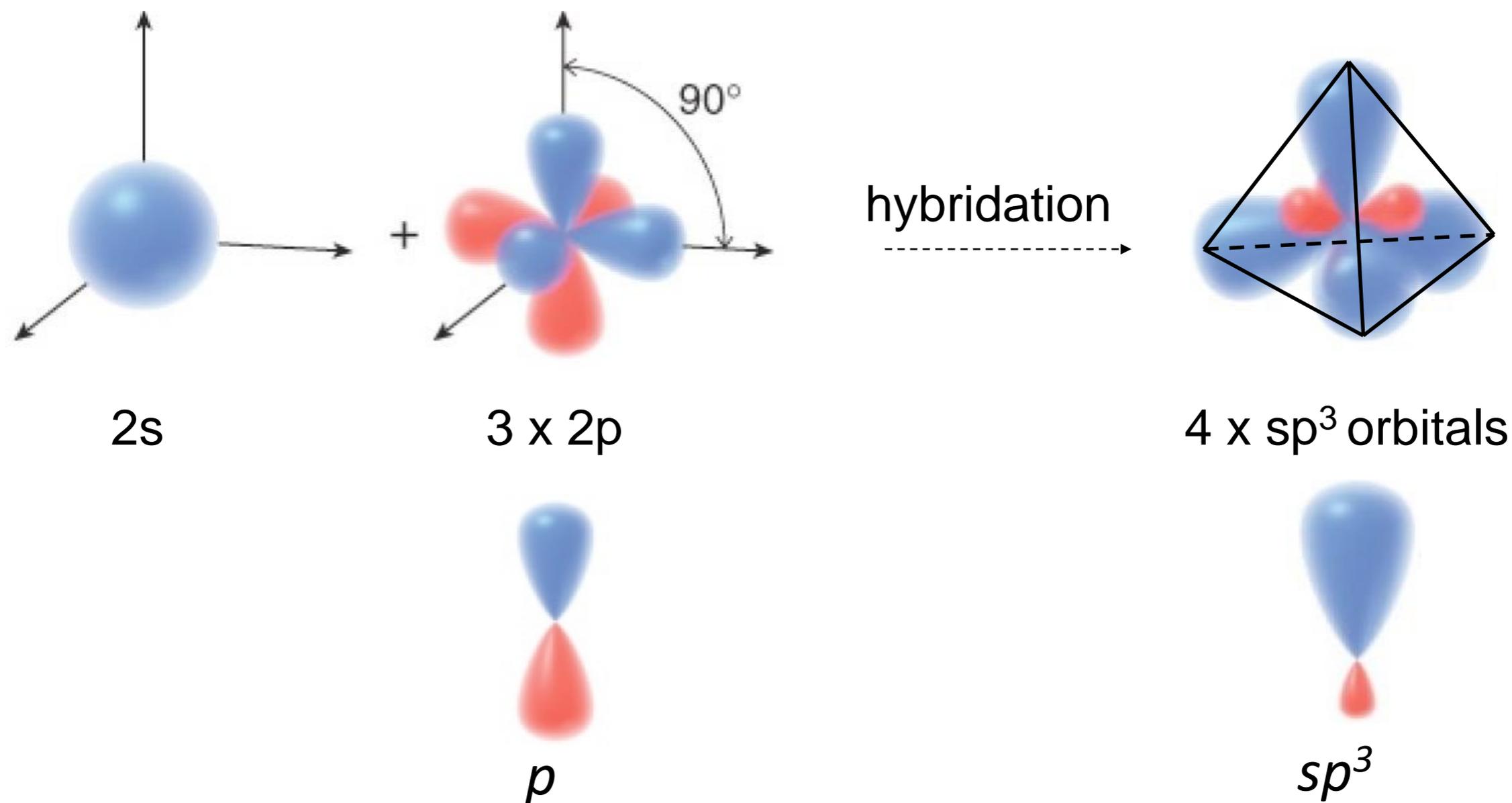
2p



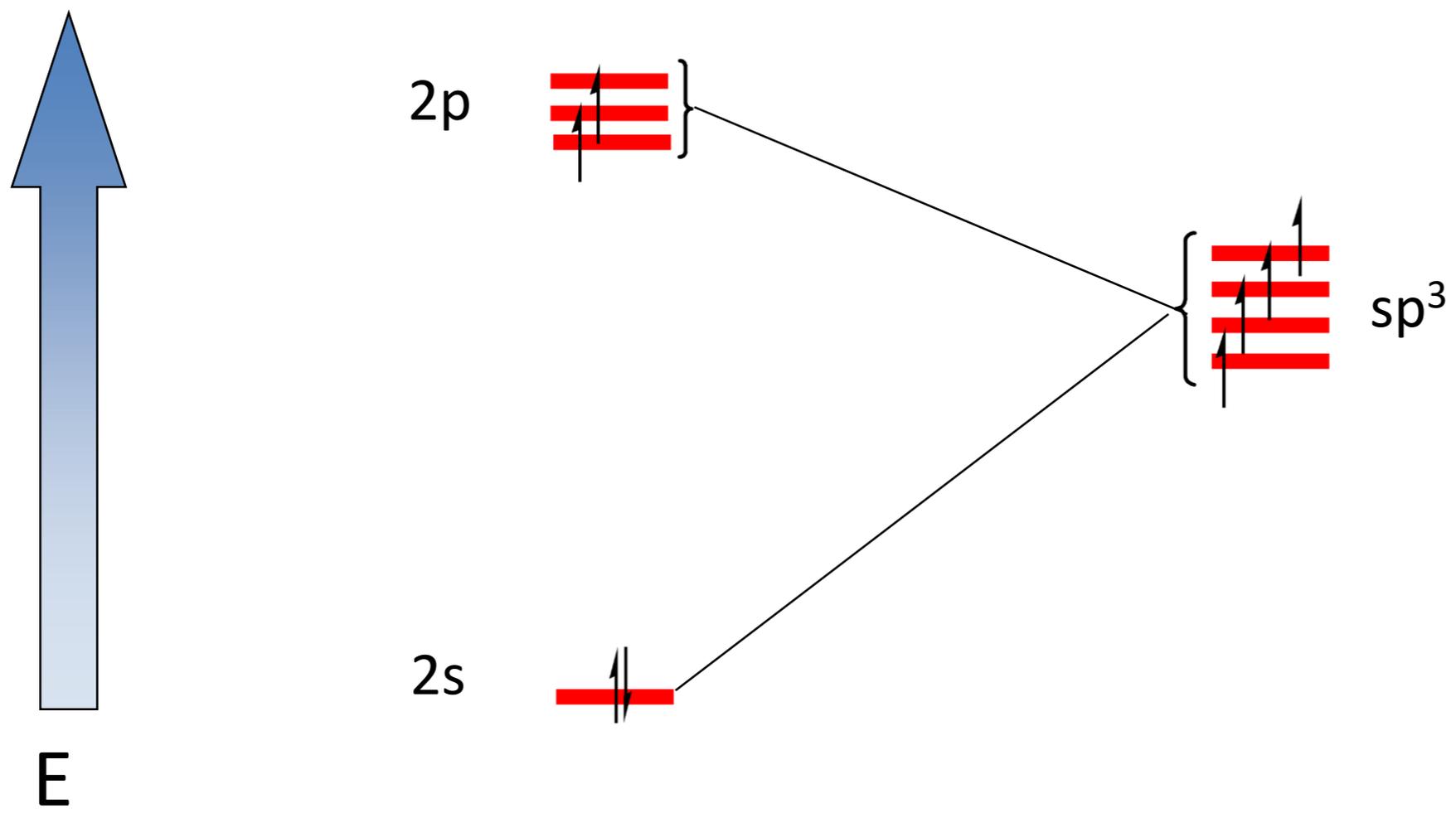
3 x 2p orbitals

sp^3 Hybrids

- The mixing of a spherical $2s$ orbital and three $2p$ orbitals generates four sp^3 orbitals, each with a small and a large lobe.

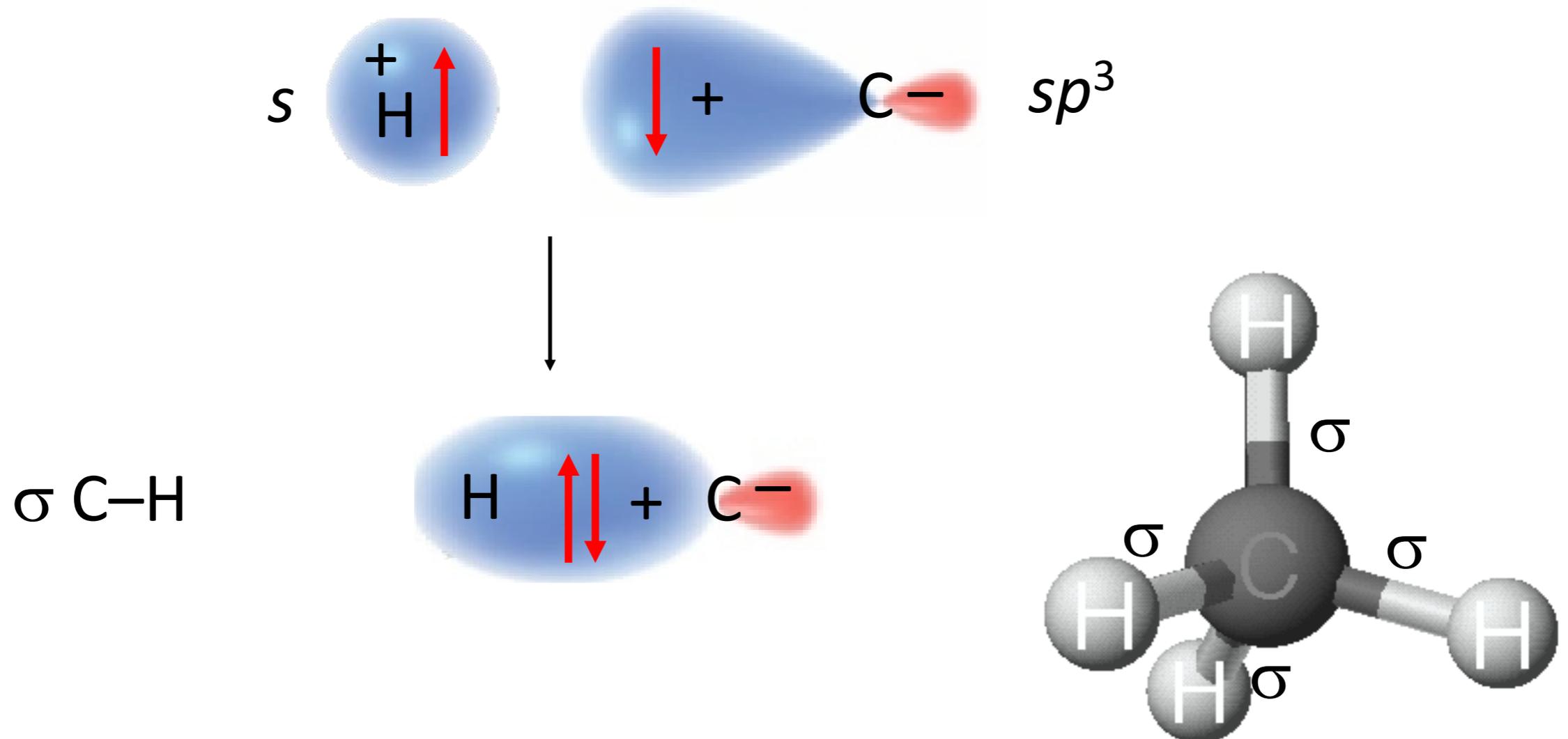


sp^3 Hybrids

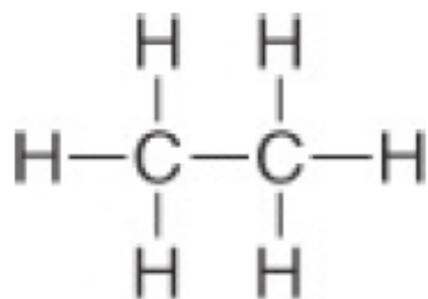


Methane

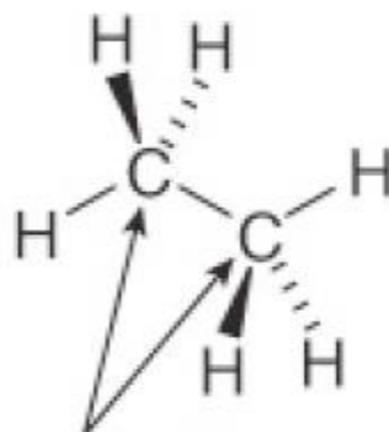
The overlap of a half-full $1s$ orbital of hydrogen with a half-full sp^3 orbital of carbon bond gives a σ orbital.



Ethane

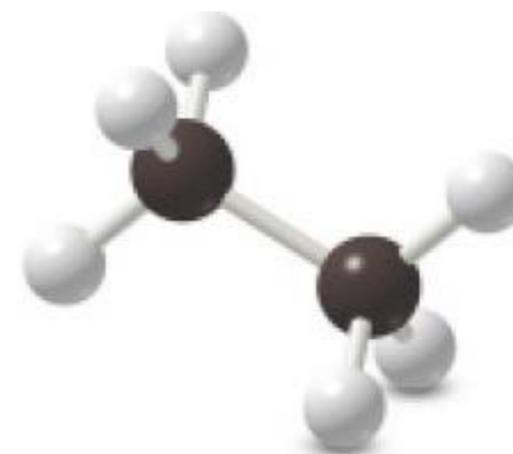


ethane

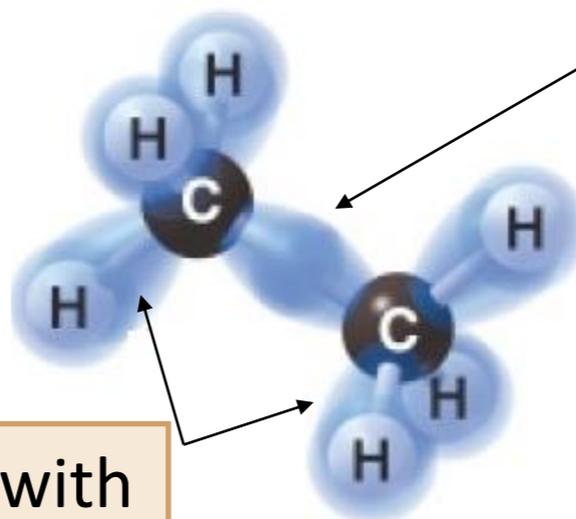


tetrahedral sp^3 C

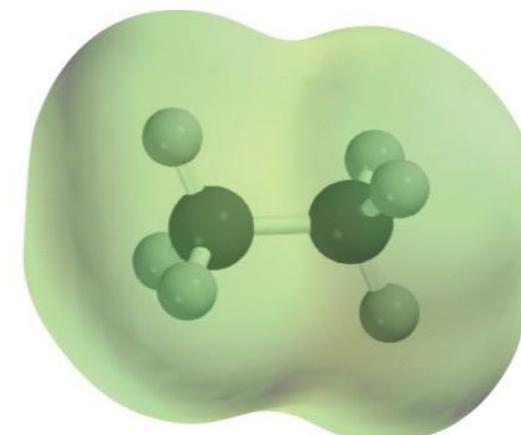
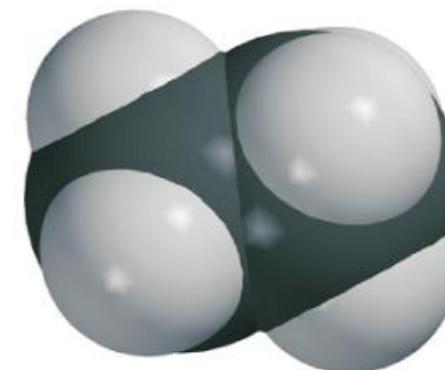
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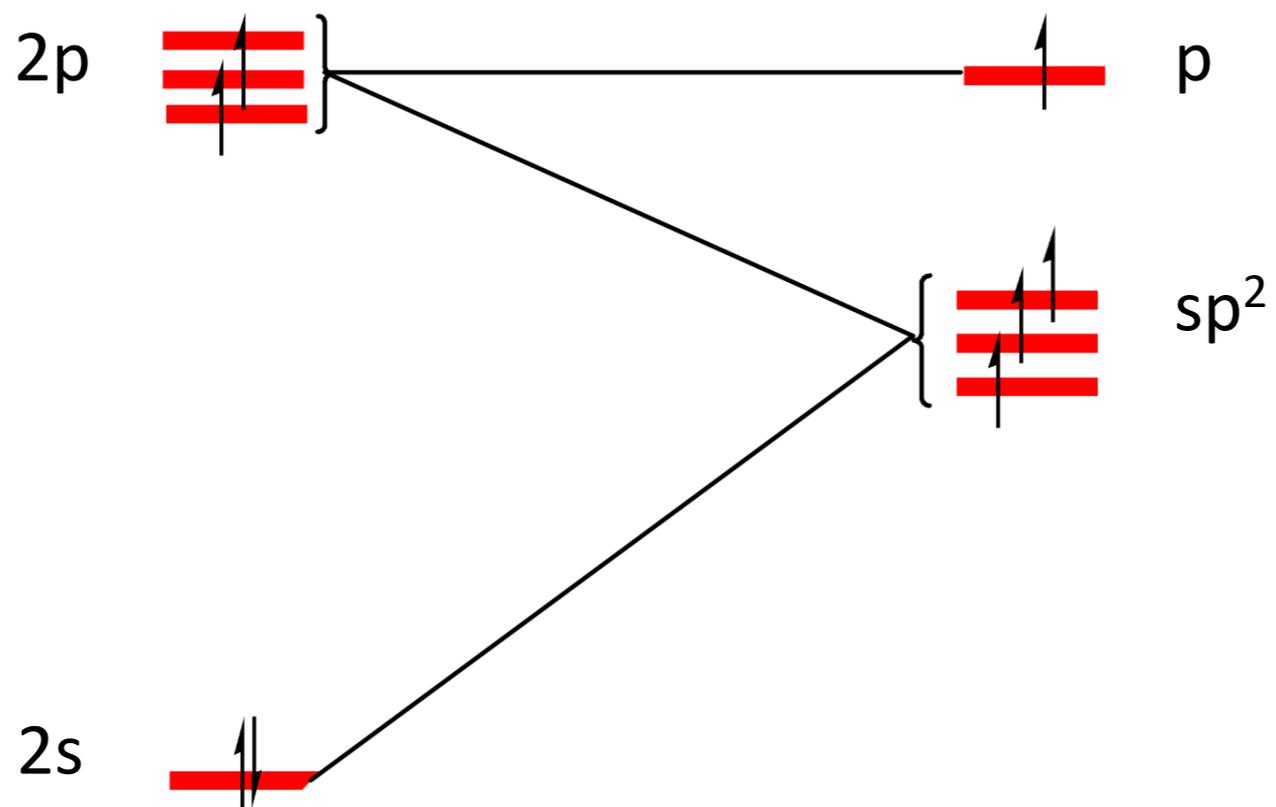
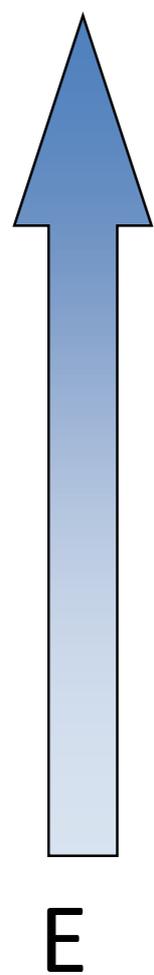
Two sp^3 hybrids overlap giving the C–C σ bond



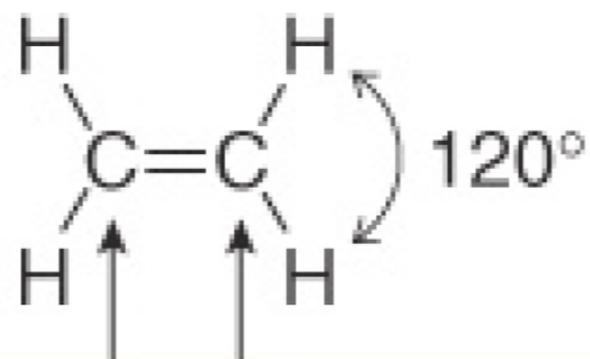
sp^3 hybrids on C overlap with $1s$ orbitals on H giving the C–H σ bonds.



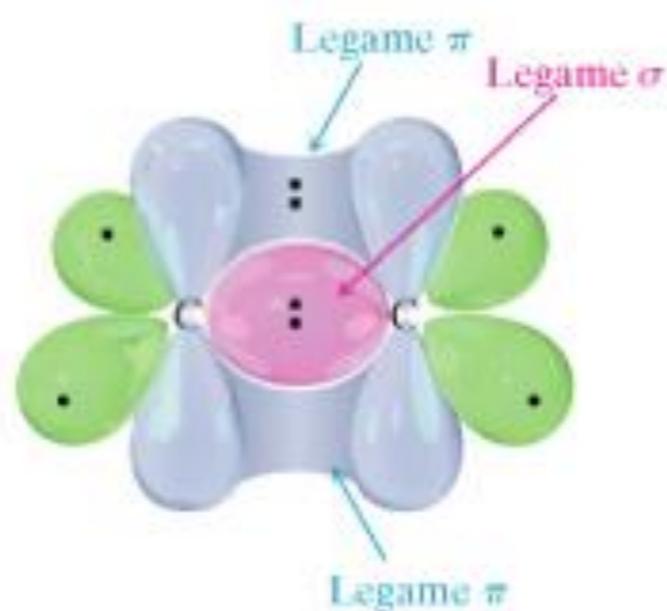
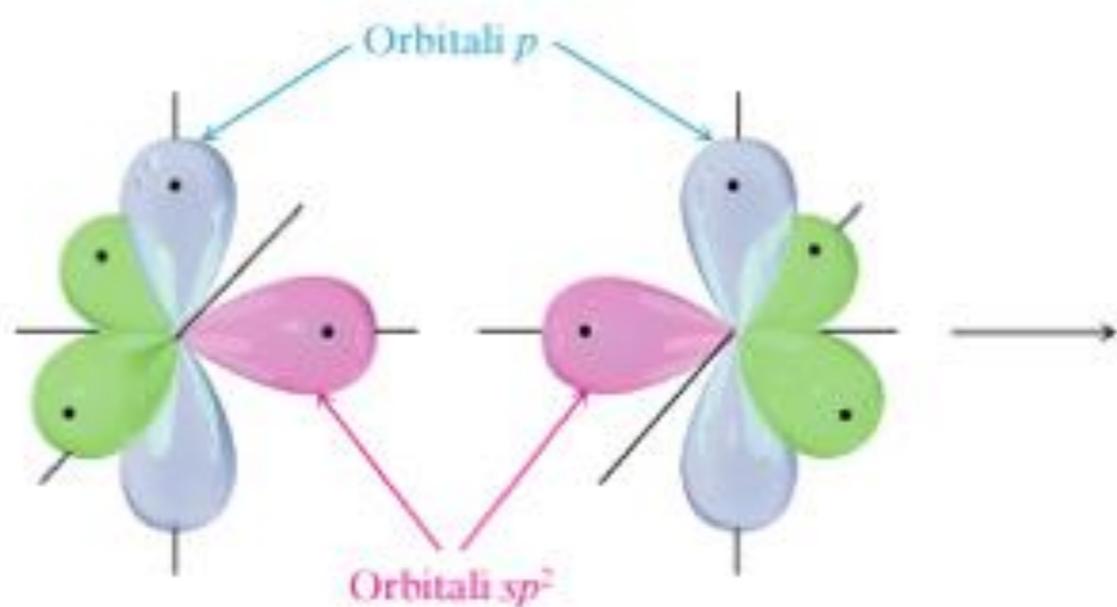
Sp² Hybrids



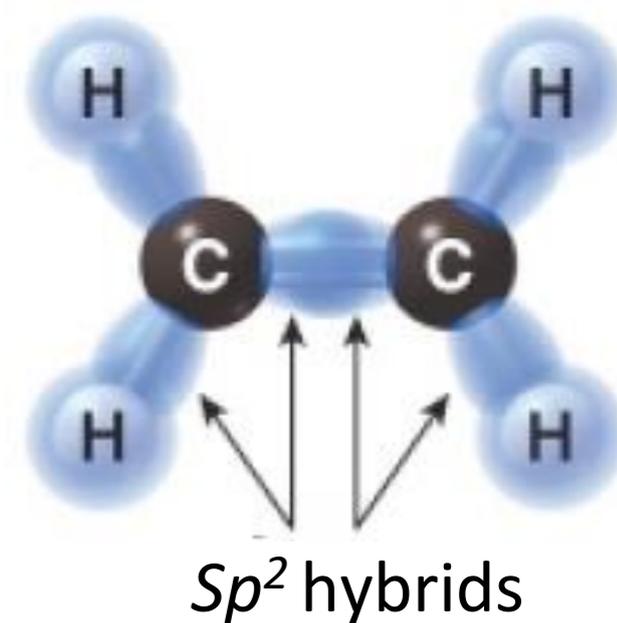
Ethylene C₂H₄



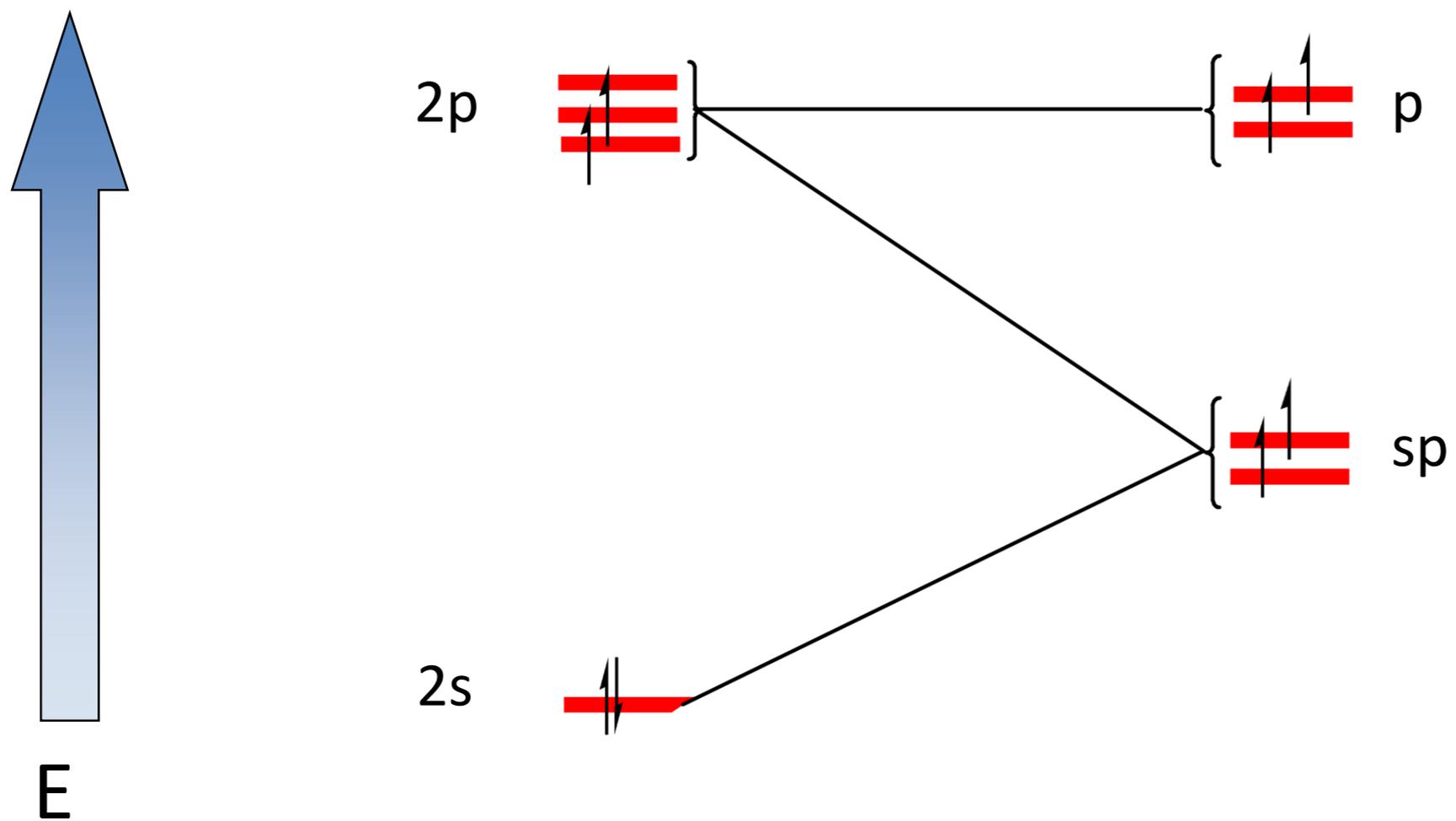
3 groups around C
C atoms are sp^2



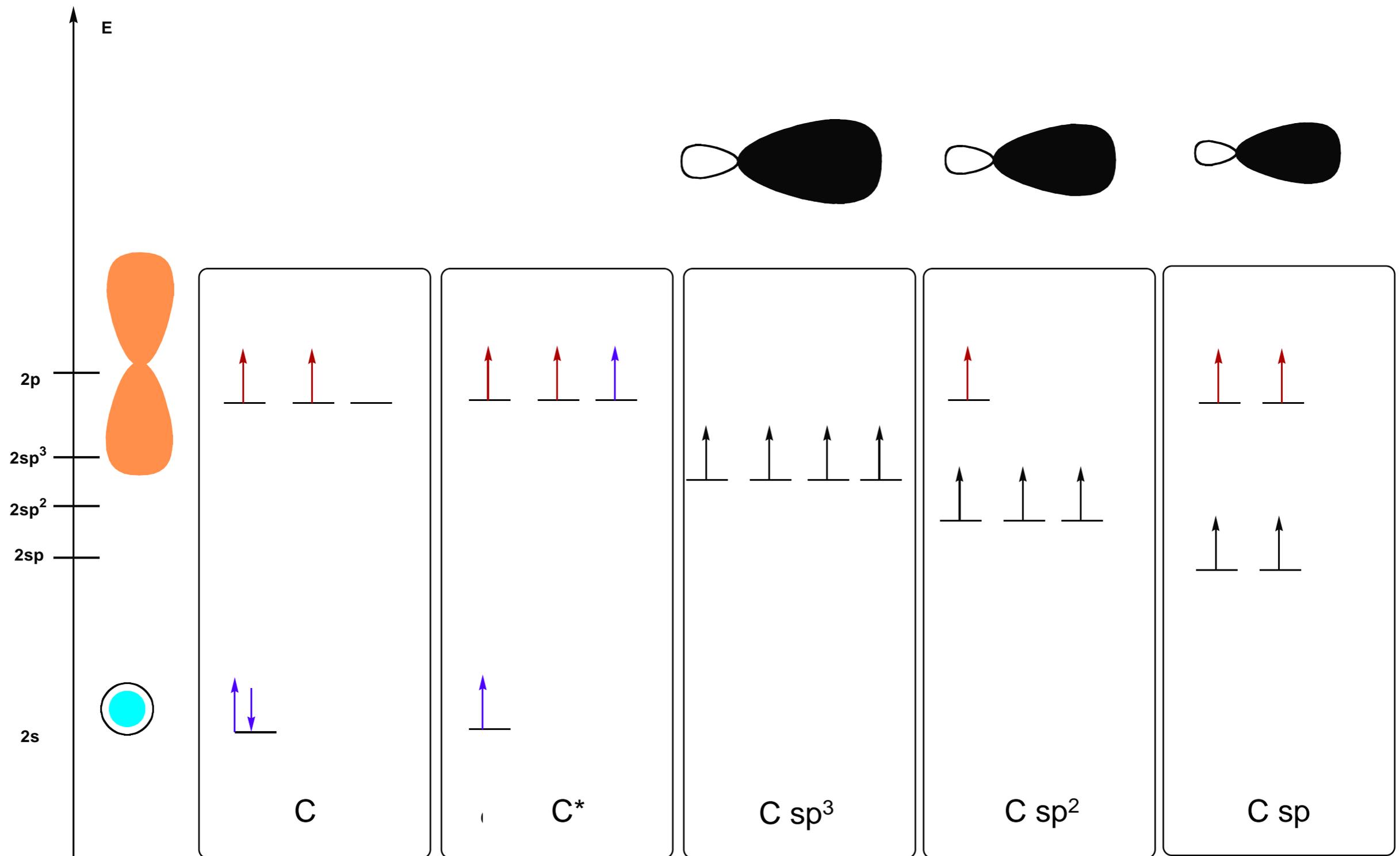
C-C double bond



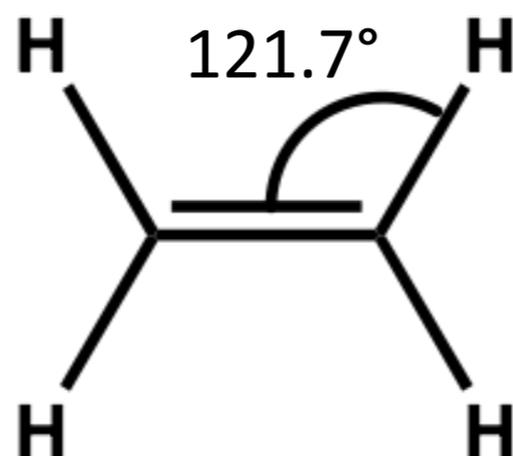
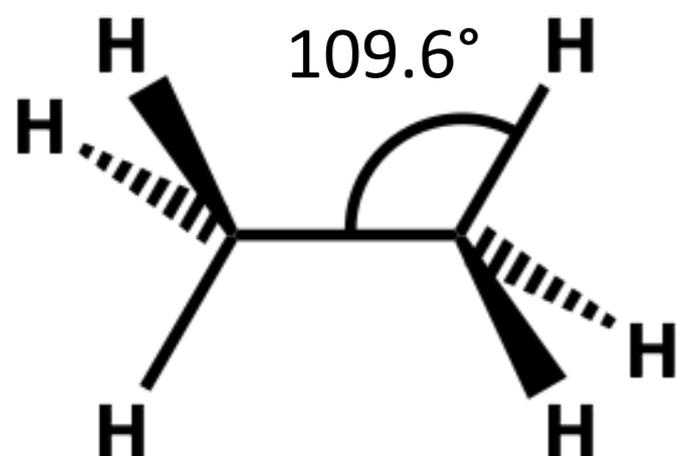
Sp Hybrids



Energy Levels and Orbital Size



Structures of C_2H_6 , C_2H_4 , C_2H_2



d_{C-C} (pm): 154

d_{C-H} (pm): 110

E_{C-C} (kJ/M): 376

133

107.6

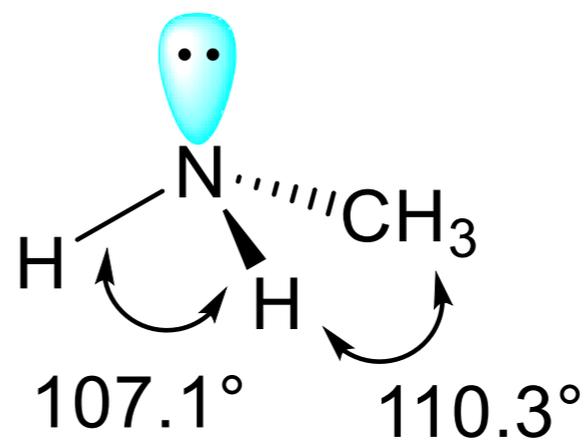
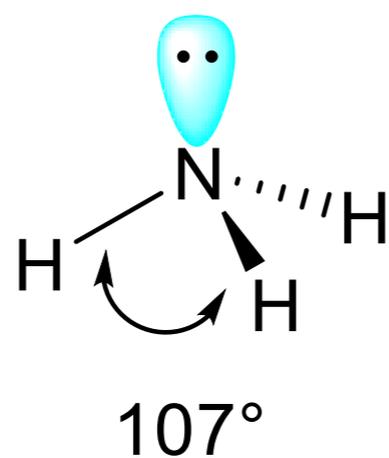
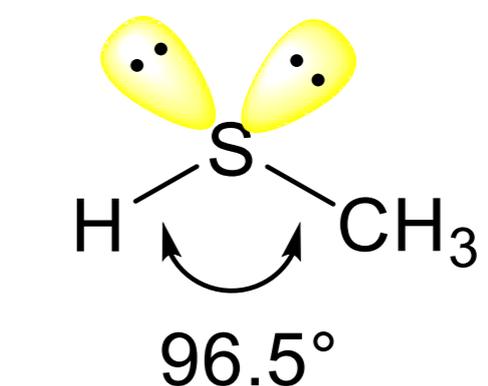
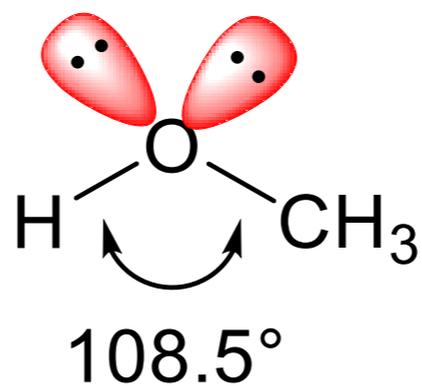
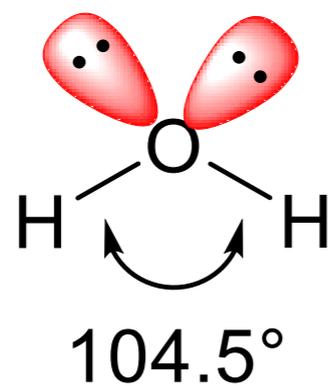
611

120

106

835

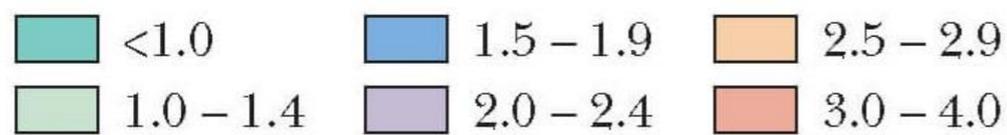
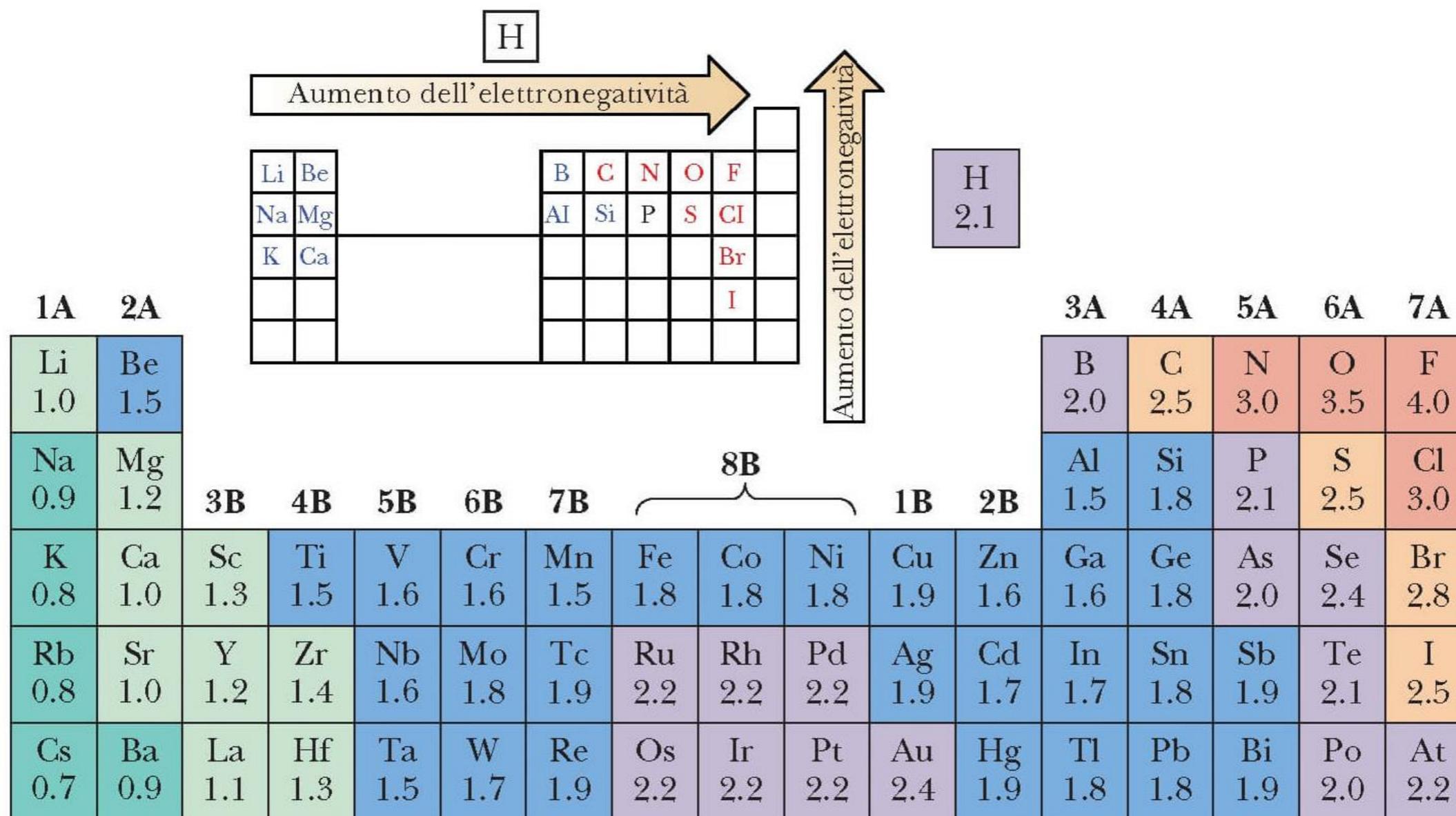
Ibridization of O, S, N



Polar Bonds
Intermolecular Interactions
Delocalised Bonds

Chapter 2
Organic Chemistry, 8th *Edition*
John E. McMurry

Legami covalenti e ionici



Legami covalenti e ionici

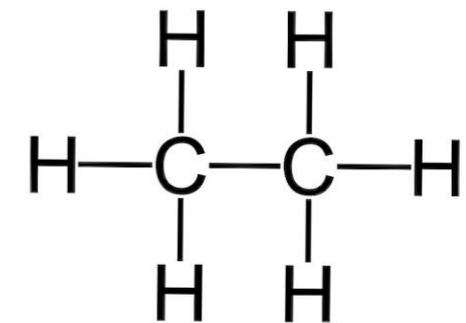
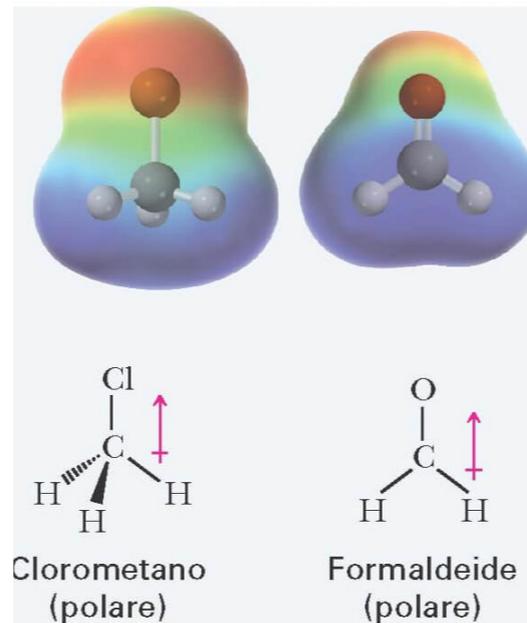
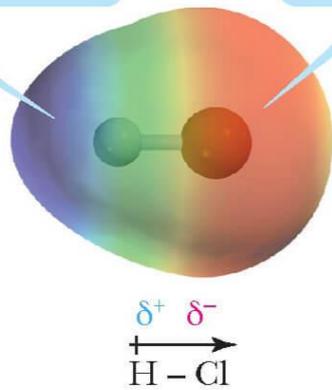
ΔX = differenza di elettronegatività

- $\Delta X > 1.9$ legame ionico
- $\Delta X < 0.5$ legame covalente
- $\Delta X = 0.5 - 1.9$ legame covalente polare

Legame	Differenza di elettronegatività	Tipo di legame
(a) O – H	$3.5 - 2.1 = 1.4$	Covalente polare
(b) N – H	$3.0 - 2.1 = 0.9$	Covalente polare
(c) Na – F	$4.0 - 0.9 = 3.1$	Ionico
(d) C – Mg	$2.5 - 1.2 = 1.3$	Covalente polare

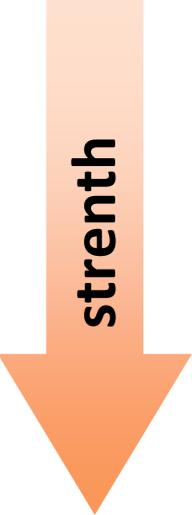
il blu indica una regione a bassa densità elettronica

il rosso indica una regione ad alta densità elettronica



Intermolecular Interactions

- Intermolecular interactions are also called non-covalent and non-bonded interactions.
- Intermolecular interactions depend on the type and number of functional groups.
- In neutral molecules there are three main types of intermolecular interactions.
 - Van der Waals interactions (London dispersion forces) – VDW
 - Dipole-dipole interactions – DD
 - Hydrogen bonds– HB

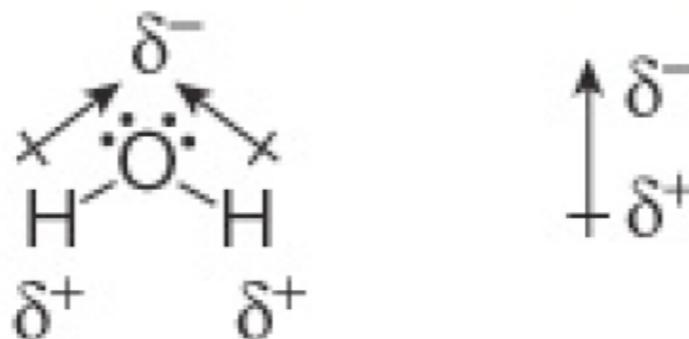


strength

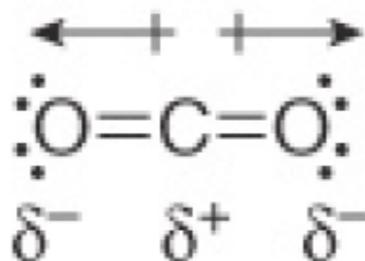
Dipole Moments

- Polar molecules have one or more polar bonds.

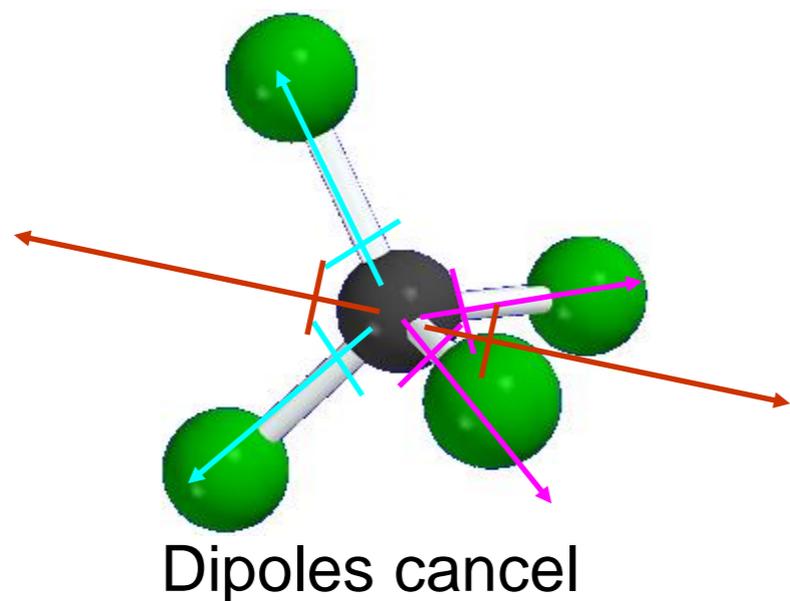
Es. H₂O



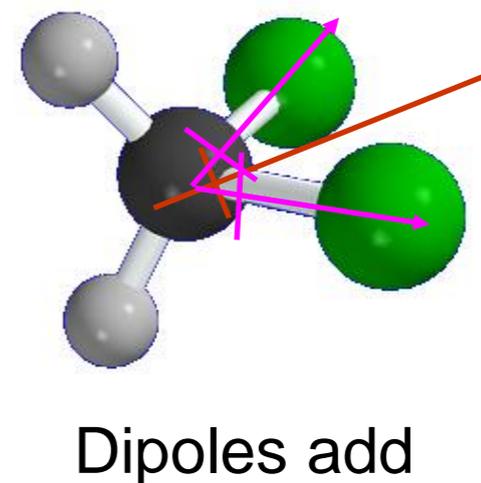
- Apolar molecules either do not have polar bonds or have polar bonds whose dipoles cancel each other. E.g. CO₂



CCl₄ $\delta = 0$ D

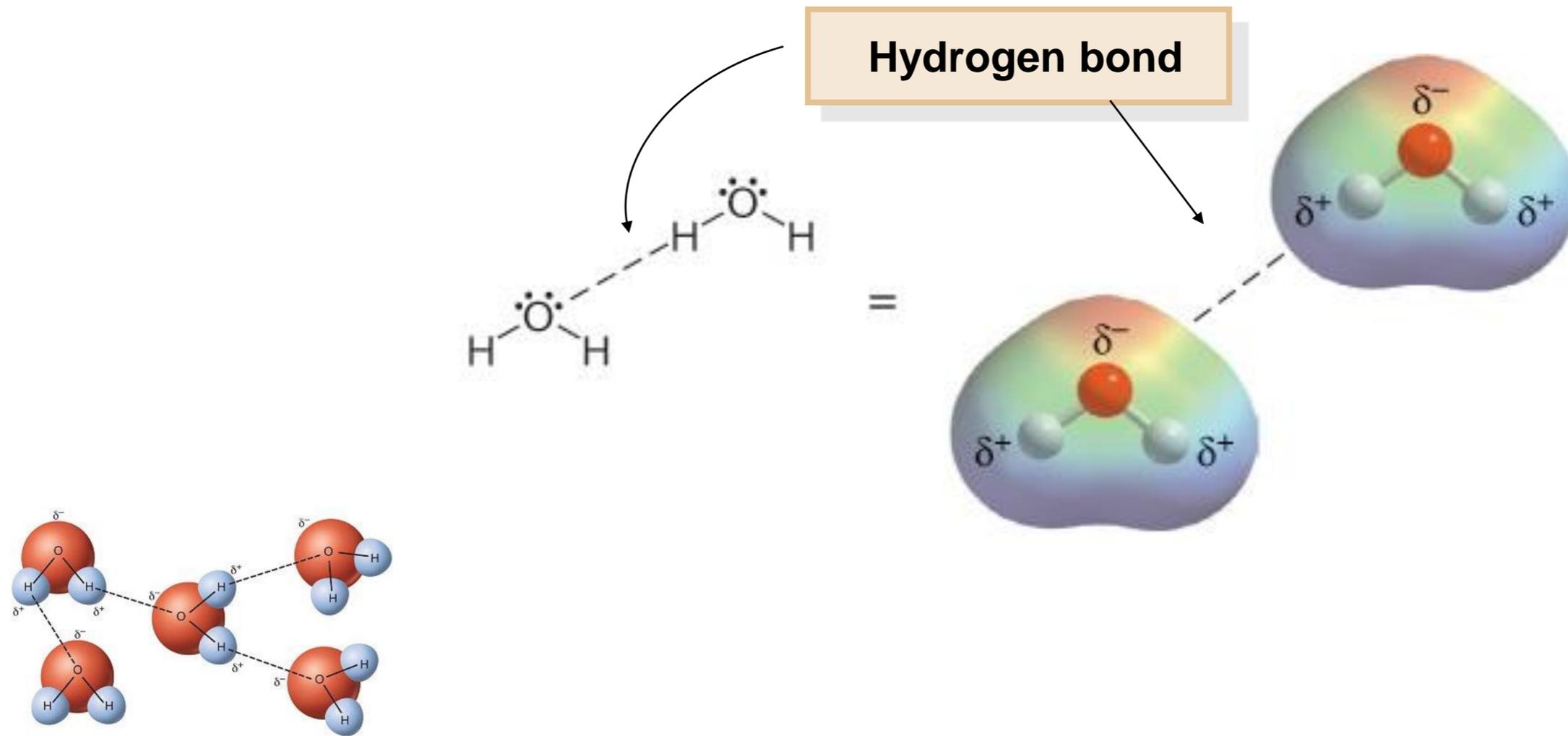


CH₂Cl₂ $\delta = 1.62$ D



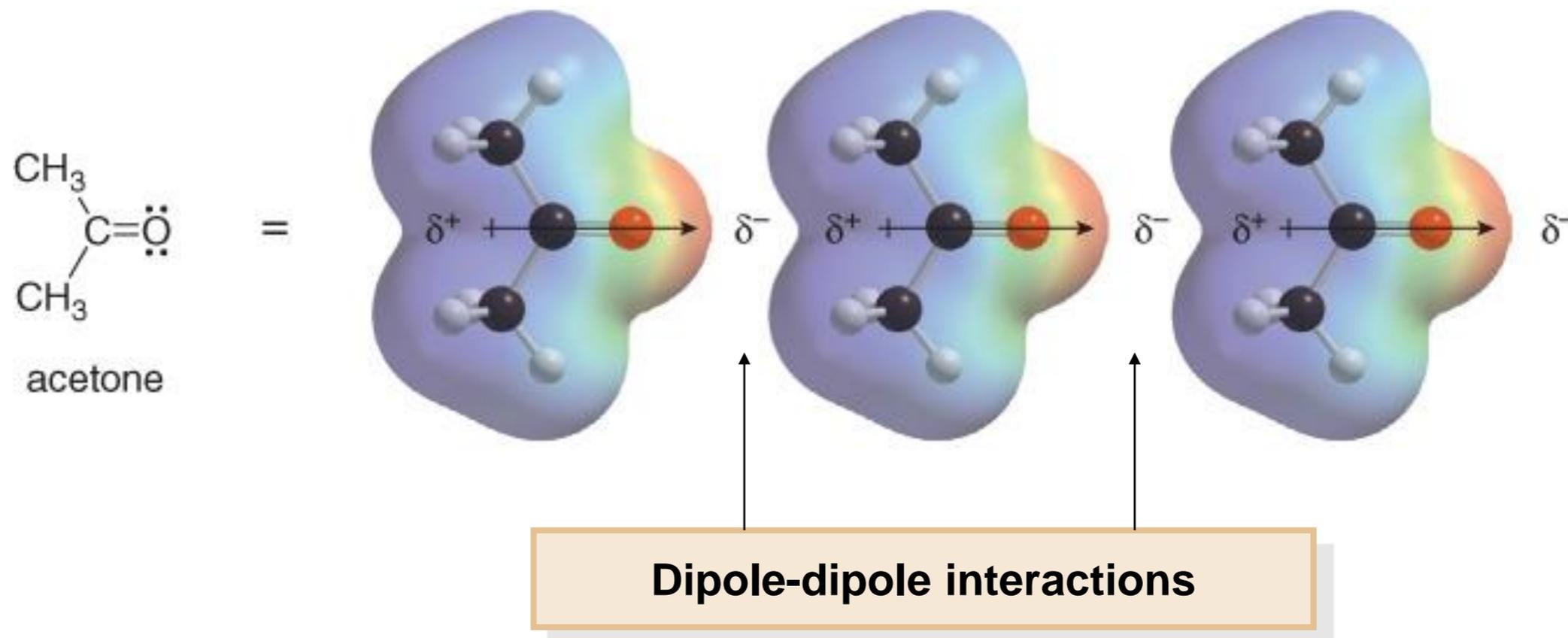
The Hydrogen Bond

The hydrogen bond is an electrostatic interaction between a O-H or N-H group and a lone pair on O or N.



Dipole-Dipole Interactions

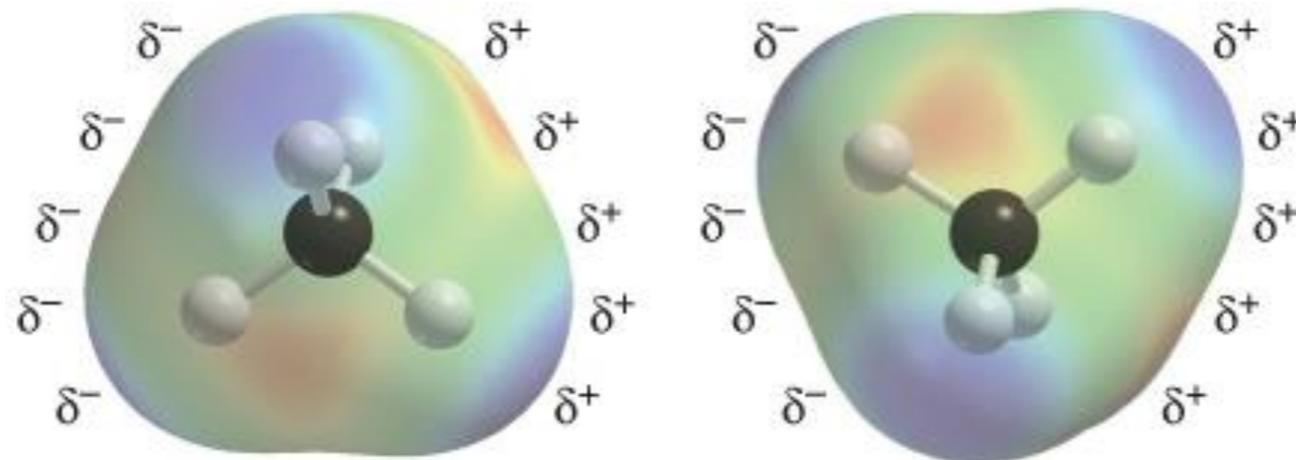
Dipole-dipole interactions are attraction forces between the permanent dipoles of two molecules.



Van der Waals (London) Forces

- VdW forces are weak interactions originating from temporary variations of the molecule's electron density distribution.
- They are the only attractive forces in apolar molecules.

Van der Waals interactions between two CH₄ molecules

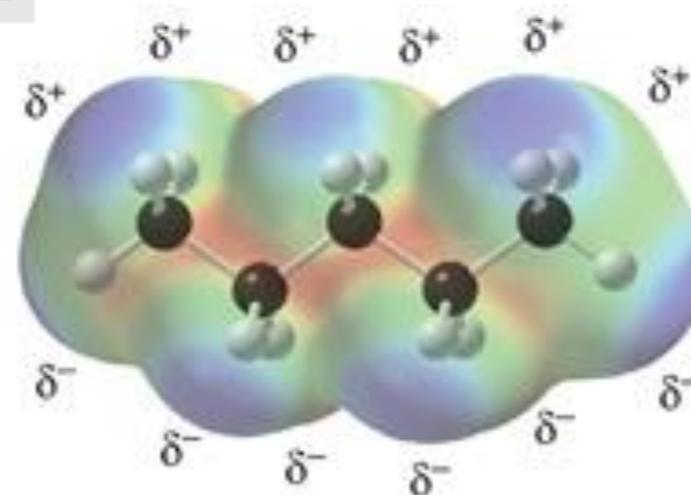
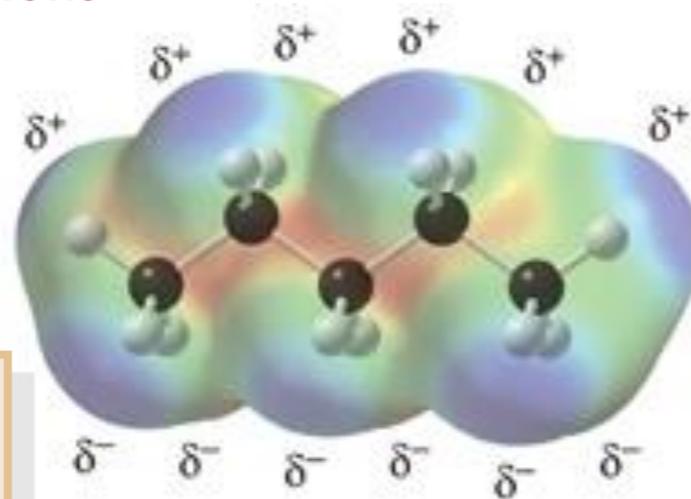


Dipoles generated by a temporary asymmetry in the electron density

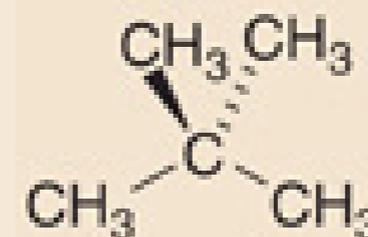
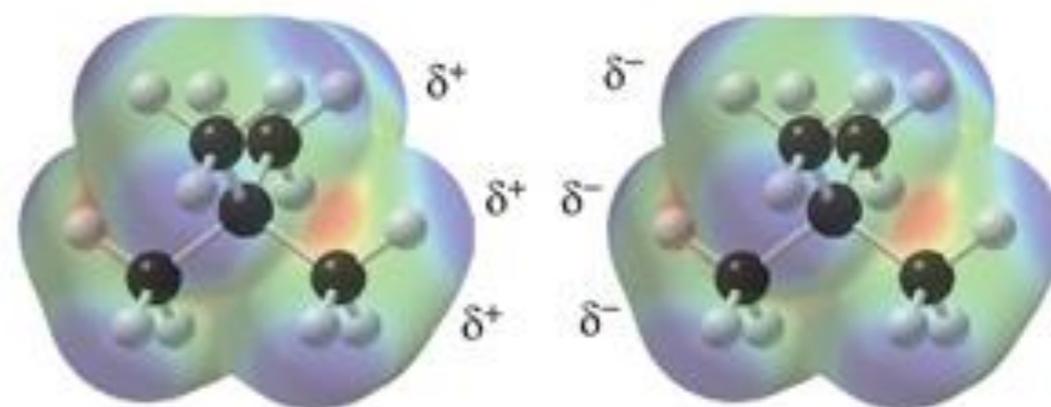
Van der Waals (London) Forces

- Van der Waals interactions are present in all molecules.
- The larger the surface area, the larger the attractive force between two molecules, and the stronger the intermolecular forces.

Long, cylindrical molecules:
stronger interactions



Compact, spherical molecules:
weaker interactions



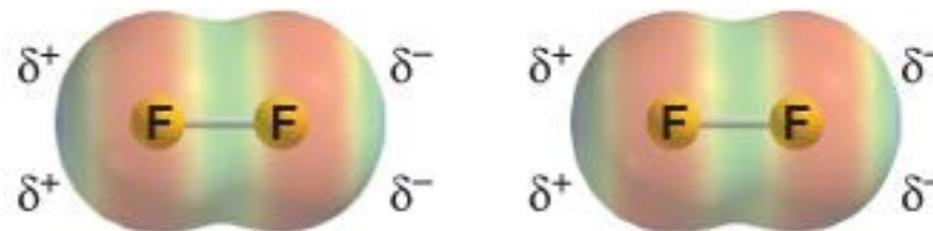
neopentane

Van der Waals (London) Forces

- VdW forces depend on polarizability.
- Larger atoms, like iodine, which have more loosely held valence electrons, are more polarizable than smaller atoms like fluorine, which have more tightly held electrons

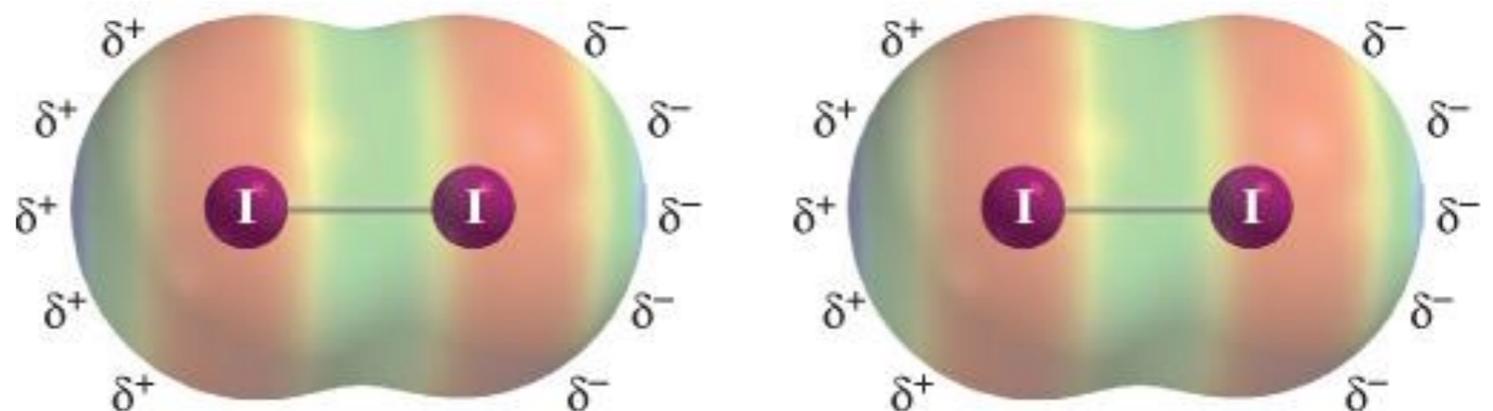
Weak interaction

Small atoms: lower polarizability



Stronger interaction

Large atoms: higher polarizability



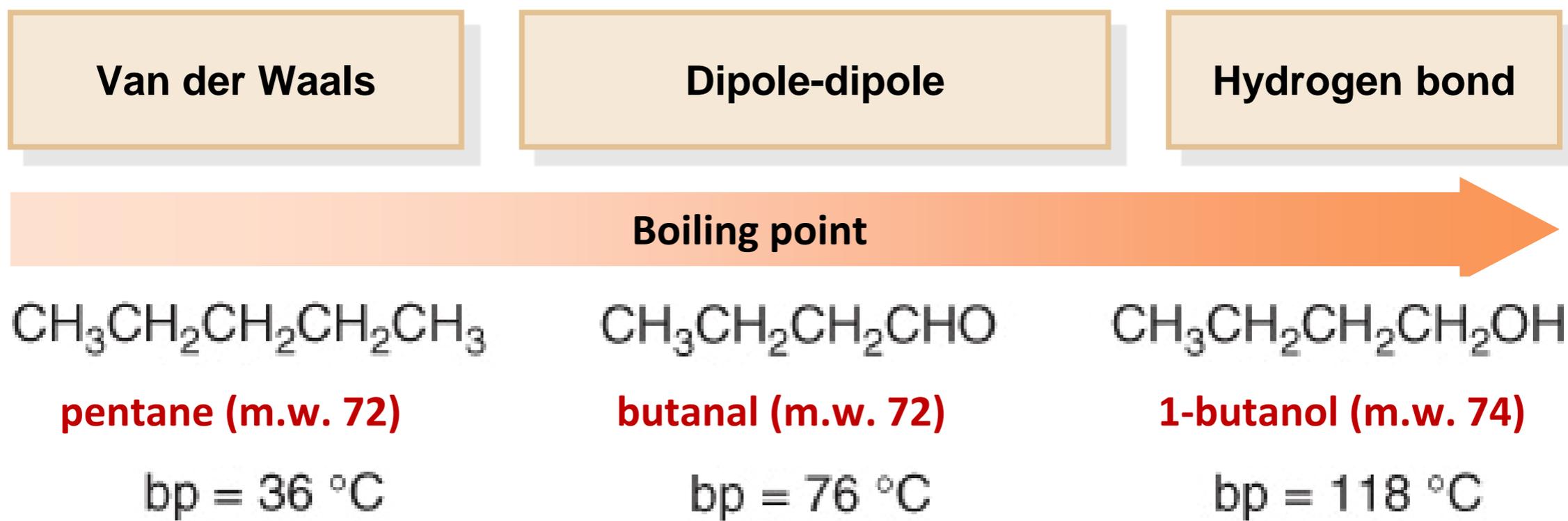
Summary

Interaction	Relative strength	Present in	Examples
Van der Waals VDW	Very weak	All molecules	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$
Dipole-dipole DD	weak	Permanent dipoles	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$
Hydrogen bond HB	strong	Molecules with OH, NH, FH funct. groups	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$
ionic	Very strong	Ionic compounds	NaCl, LiF

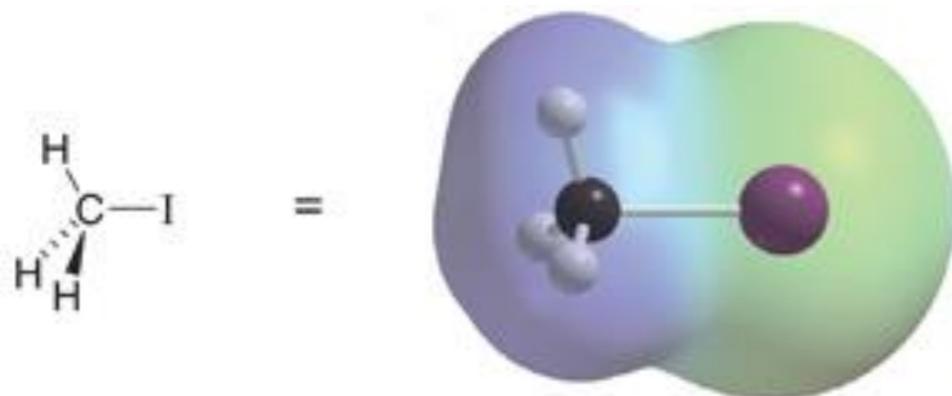
Polar molecules interact strongly than apolar ones.

Boiling Point

- The boiling point is the temperature at which the vapor pressure of a liquid is equal to the external pressure.
- Energy is required to break intermolecular interactions.
- The higher the intermolecular interactions, the higher the b.p..
- Compounds with similar M.W.:

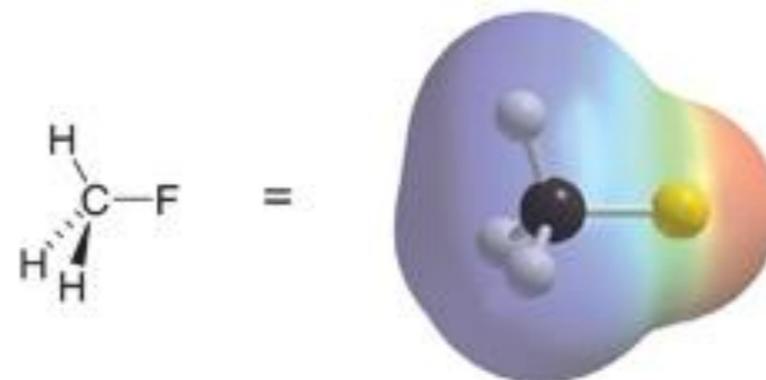


Boiling Point



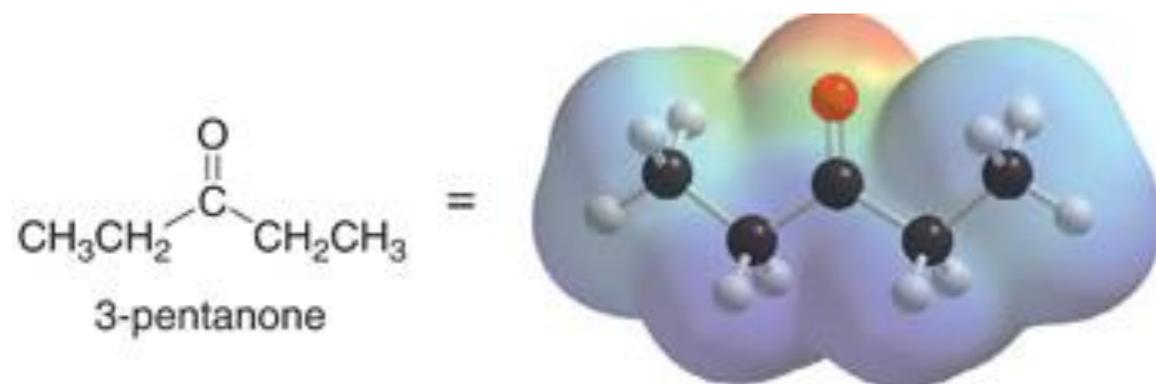
b.p. = 42 °C

I is more polarizable



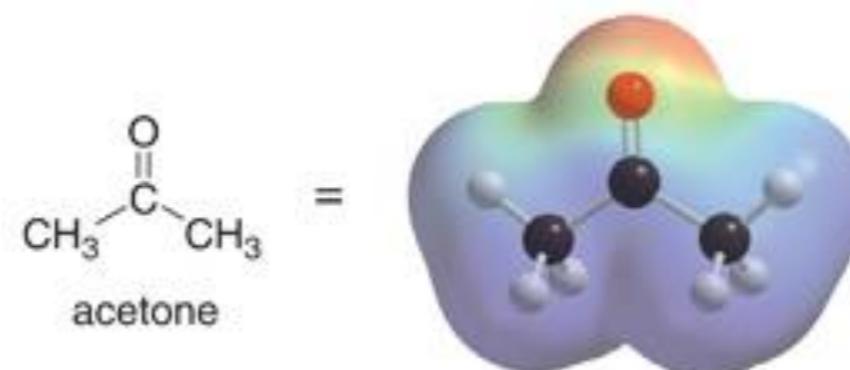
b.p. = -78 °C

Smaller F has a low polarizability



b.p. = 102 °C

Larger surface area



b.p. = 56 °C

Smaller surface area

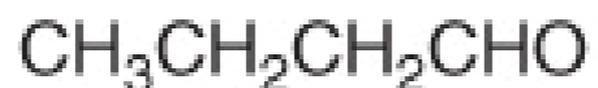
Melting Point

- M.p. and b.p. follow the same trend.



pentane

mp = $-130\text{ }^\circ\text{C}$



butanal

mp = $-96\text{ }^\circ\text{C}$



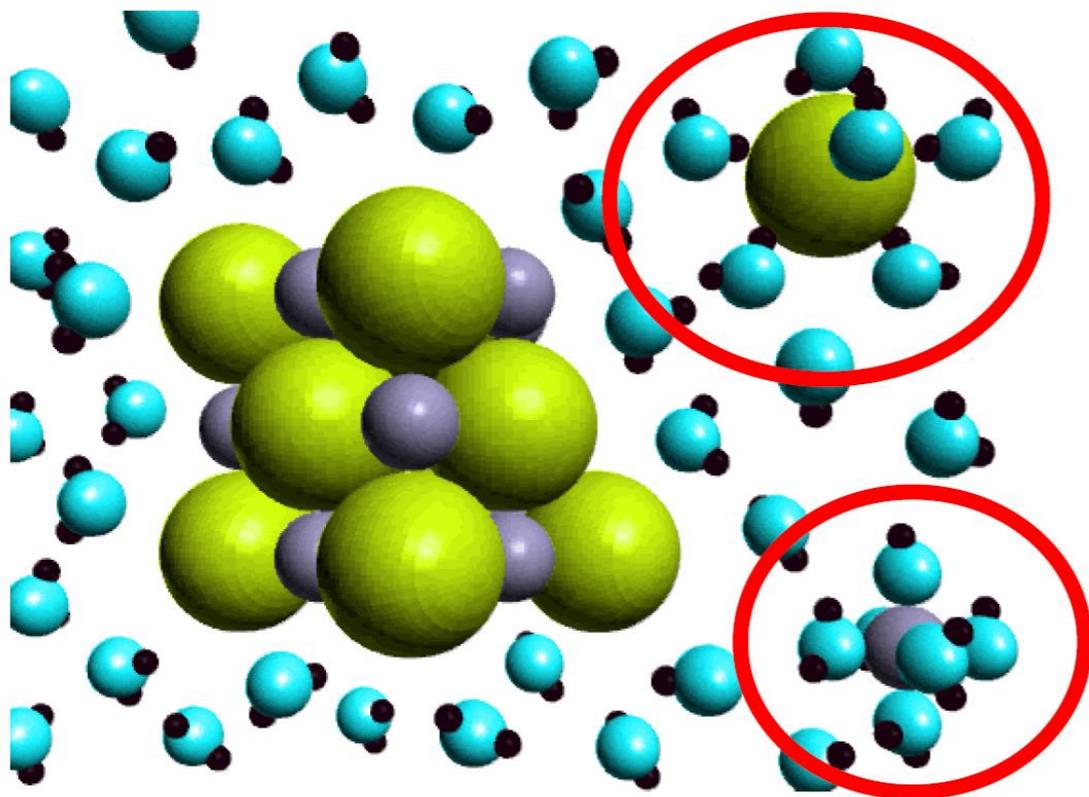
1-butanol

mp = $-90\text{ }^\circ\text{C}$

Melting point

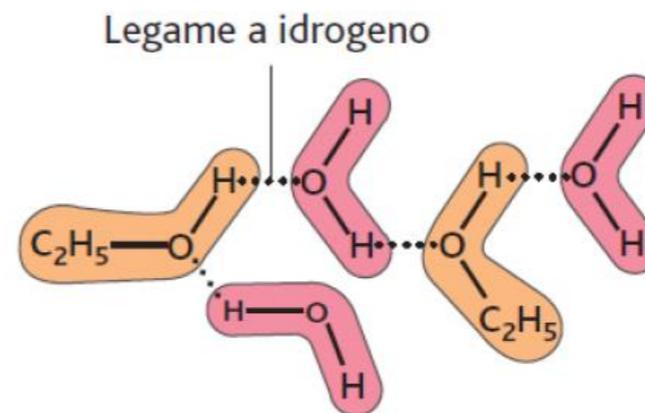


Solubilità



L'immagine mostra un cristallo di Cloruro di sodio che viene dissolto da molecole d'acqua. Il polo negativo delle molecole d'acqua circonda gli ioni Na^+ , mentre il polo positivo gli ioni Cl^- .

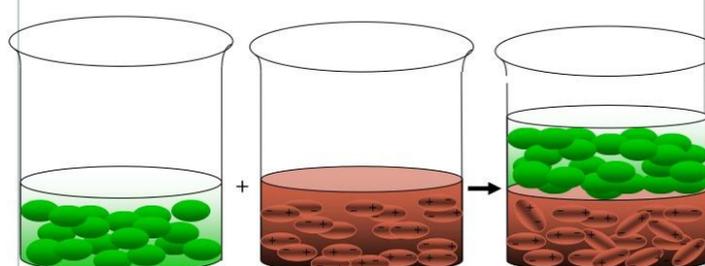
Per solubilizzare un composto il solvente deve interagire mediante interazioni non covalenti con il soluto compensando le interazioni tra molecole di soluto che sono presenti allo stato solido (**solvatazione**).



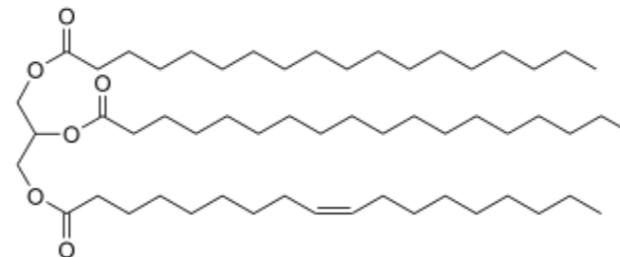
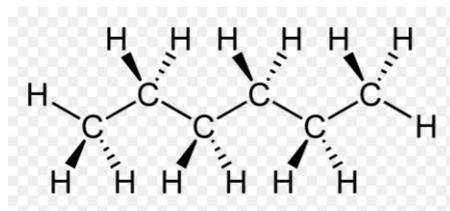
Solubilità

Liquidi polari e apolari

Esano acqua miscela

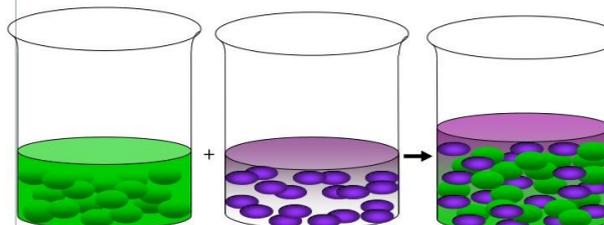


Un liquido apolare non potrà miscelarsi con uno polare, perché **le forze intermolecolari sono diverse**



Liquidi apolari

Esano olio miscela

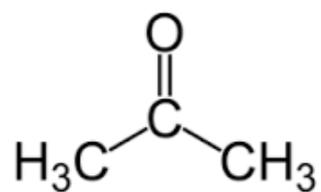


Due o più liquidi apolari si miscelano tra loro perché tra essi si instaurano le forze di Van der Waals.

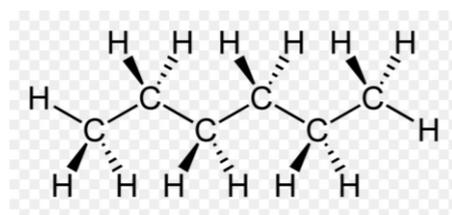


Solubilità: il simile scioglie il simile

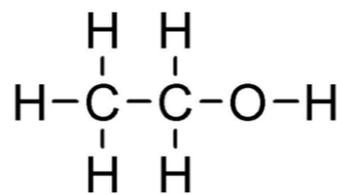
	NaCl (ionico)	Alcol etilico (HB)	Etere etilico (dipolo)	Benzene (apolare)
Acqua (HB)	SI	SI	poco	NO
Acetone (dipolo)	NO	SI	SI	SI
Esano (apolare)	NO	NO	SI	SI



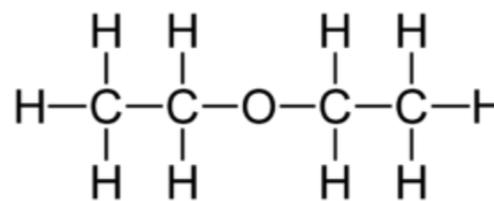
acetone



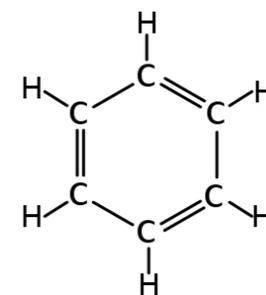
esano



etanolo



dietilere



benzene

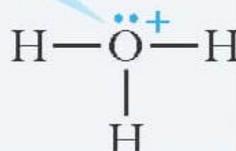
Lewis structures

TABELLA 1.6 Strutture di Lewis di diverse molecole. Il numero degli elettroni di valenza in ciascuna molecola è indicato in parentesi dopo la formula molecolare

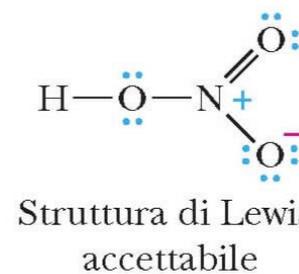
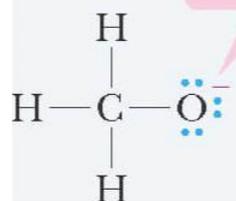
$\text{H}-\ddot{\text{O}}-\text{H}$ <p>H₂O (8) Acqua</p>	$\begin{array}{c} \text{H}-\ddot{\text{N}}-\text{H} \\ \\ \text{H} \end{array}$ <p>NH₃ (8) Ammoniaca</p>	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \end{array}$ <p>CH₄ (8) Metano</p>	$\text{H}-\ddot{\text{Cl}}$ <p>HCl (8) Acido cloridrico</p>
$\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} & \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$ <p>C₂H₄ (12) Etilene</p>	$\text{H}-\text{C}\equiv\text{C}-\text{H}$ <p>C₂H₂ (10) Acetilene</p>	$\begin{array}{c} \text{H} \\ \diagdown \\ \text{C}=\ddot{\text{O}} \\ / \\ \text{H} \end{array}$ <p>CH₂O (12) Formaldeide</p>	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}-\ddot{\text{O}}-\text{C}-\ddot{\text{O}}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$ <p>H₂CO₃ (24) Acido carbonico</p>

$$\text{Carica formale} = \text{Numero di elettroni di valenza nell'atomo neutro non legato} - \left(\begin{array}{l} \text{Tutti gli} \\ \text{elettroni non} \\ \text{condivisi} \end{array} + \begin{array}{l} \text{Metà degli} \\ \text{elettroni} \\ \text{condivisi} \end{array} \right)$$

5 elettroni di valenza:
carica formale +1



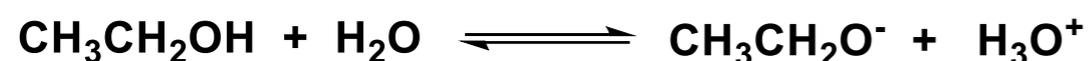
7 elettroni di valenza:
carica formale -1



HNO₃

Delocalizzazione di legami ed elettroni: Risonanza

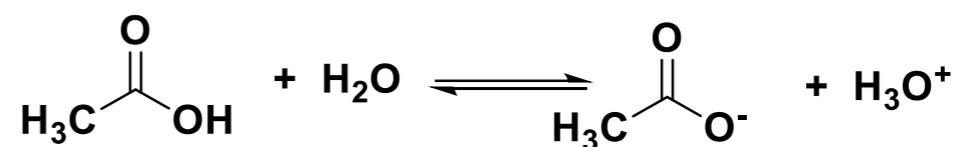
- La struttura e le proprietà di alcune molecole non possono essere spiegate dal semplice modello dell'orbitale di valenza con gli elettroni localizzati.
- In questo caso, una singola struttura di Lewis viene sostituita da un insieme di strutture di Lewis: **si dice che la molecola risuoni tra queste strutture e questo fenomeno è chiamato risonanza.**



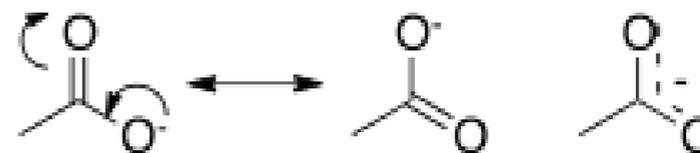
$\text{CH}_3\text{CH}_2\text{OH}$: pK_a 16



Carica localizzata
meno stabile



CH_3COOH : pK_a 4.75



Strutture di risonanza

Ibrido di risonanza

Carica delocalizzata
più stabile

RISONANZA

- Le strutture di risonanza hanno la stessa disposizione degli atomi ma una diversa disposizione degli elettroni (elettroni π e coppie solitarie).
- Le lunghezze e gli angoli dei legami non cambiano nelle strutture di risonanza.
- Le strutture di risonanza devono rispettare le regole di Lewis (ottetto)
- La risonanza è una semplice teoria per adattare le strutture convenzionali di Lewis alla rappresentazione di molecole con elettroni e legami delocalizzati.
- **Le strutture di risonanza non sono reali.** Nessuna singola struttura di risonanza può rappresentare adeguatamente la struttura reale di una specie con elettroni delocalizzati.
- Le strutture di risonanza **non sono isomeri.** Esse differiscono solo nella distribuzione degli elettroni e non nella disposizione dei nuclei.
- Le strutture di risonanza **non sono in equilibrio.**

Risonanza

le frecce curve partono sempre dagli elettroni, che siano quelli che formano legami...

...o quelli che costituiscono coppie elettroniche non condivise

