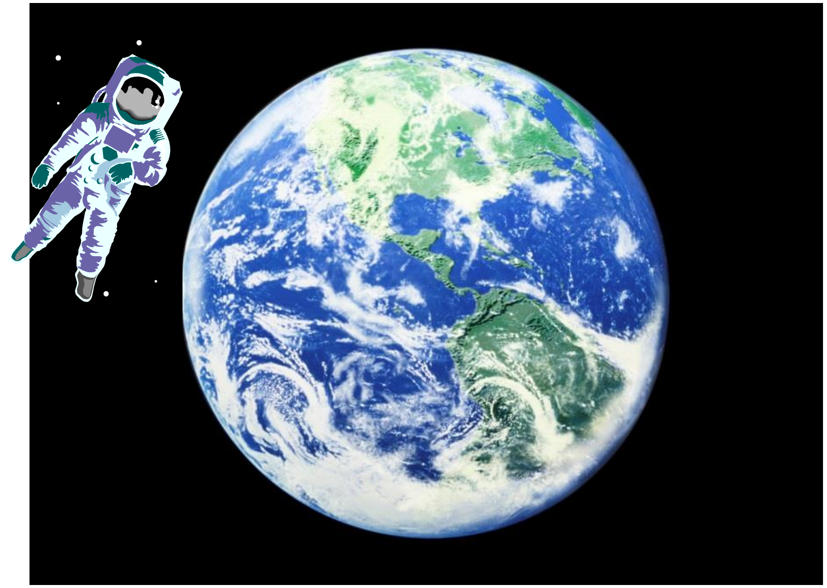
CHEMICAL BONDS

Bonds between Atoms



Each atoms is unique due to their differing;

- **Sizes;**
- **Electron Affinities;**
- **Ionization Energies.**

As the gravitational force varies with size and distance, atoms, like planets, have similar unique and variable inherent strengths and forces that influence other atoms.

Atoms minimize these **imbalances** by forming bonds.

Bonds between Atoms

Atoms strive to **fill** their outer shells with electrons just like a noble gas does.

In a generalized-way atoms can achieve satisfaction by forming two types of bonds: ionic and covalent

Ionic is **gaining** & **losing** electrons
Covalent is **sharing** electrons

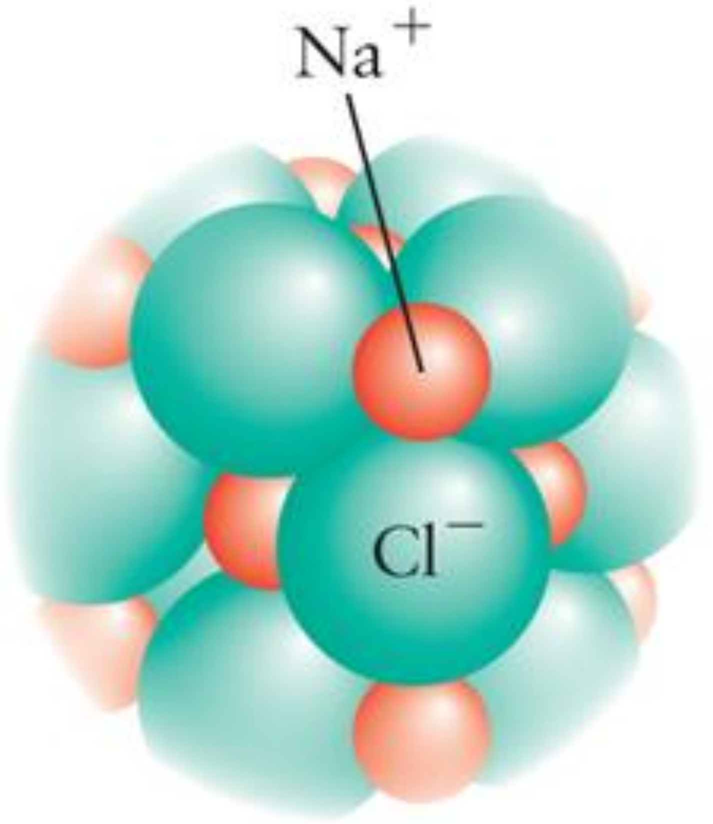
The resulting bond is **lower** in energy than the separate atoms.

If electrons transfer from one or more atoms, the entire compound is held together by **electrostatic attractions** between all the ions.

This attraction is called an **ionic bon** '

Note: the energy is lower when Na^+ and Cl^- ions bind than separated sodium and chlorine atoms.

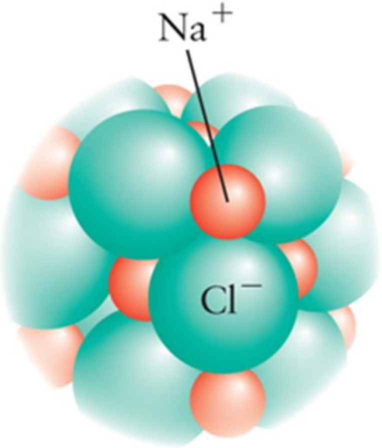
The new partnership is lower in energy than the separate Atoms.

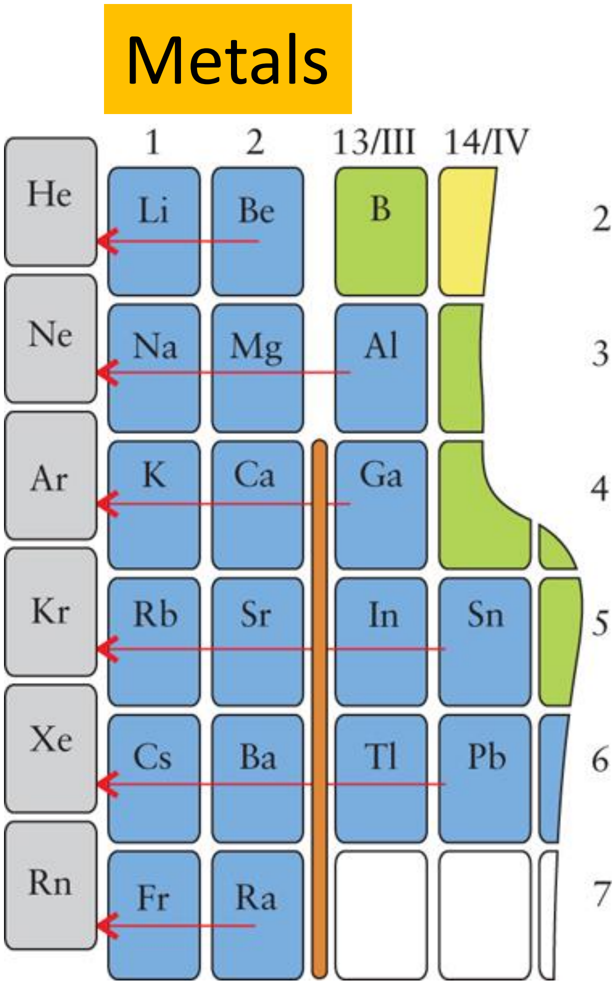


Binary ionic compound form between s-block **metal**, and a **nonmetallic** element.

Cation and anions stack themselves into alternating sodium ions with chloride ions, oppositely charged ions are lined up in all three dimensions.

An example of an ionic **crystalline solid.**





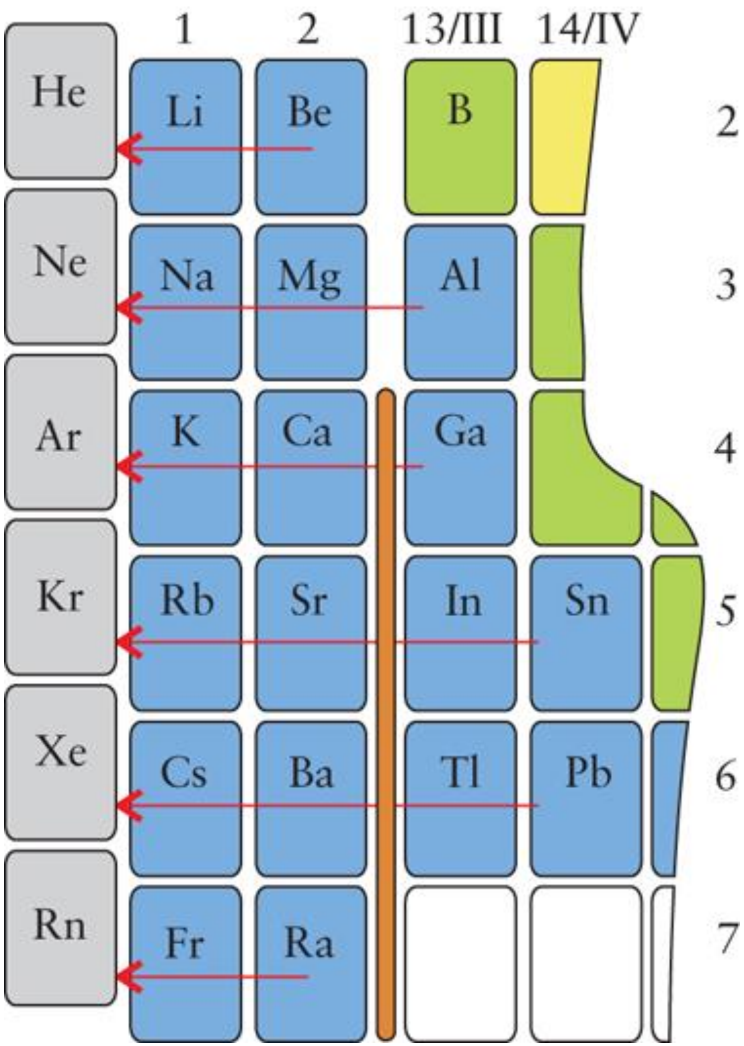
S-block metals form cations, by <u>losing electrons</u> to their **noble-gas core** or octet of electrons.

Al forms the Al^{3+} ending with [Ne] electron configuration by the loss of it's *s* and *p* electrons

noble-gas core

Ion	Configuration
Li^+	[He] ($1s^2$)
Be^{2+}	[He]
Na^+	[Ne] ([He]$2s^22p^6$)
Mg^{2+}	[Ne]
Al^{3+}	[Ne]

Ga^{3+} 4p block **d electrons** remain



Metallic elements, in Period 4 and later, **lose** their s- and p-electrons.

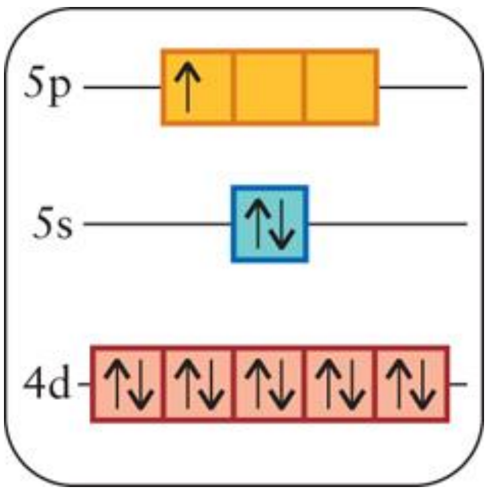
Ga^{3+}, [Ar]$3d^{10}$

The **d electrons** of the p-block atoms **are gripped tightly** by the nucleus and **cannot be lost.**

Write the electron configurations of In^{+} and In^{3+}

Remove electrons from the valence-shell *p*-orbitals **first**, then from the *s*-orbitals

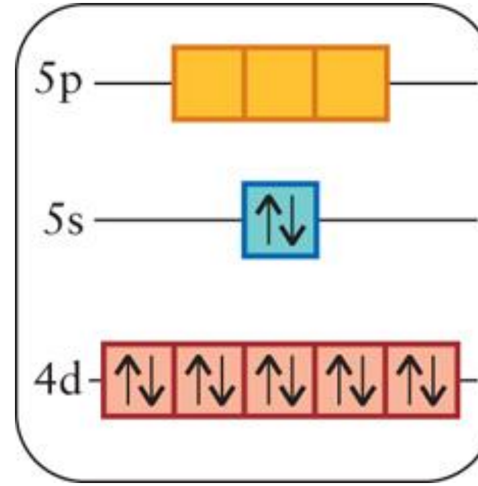
Determine the configuration of the neutral atom.



[Kr]$4d^{10}5s^{2}5p^{1}$

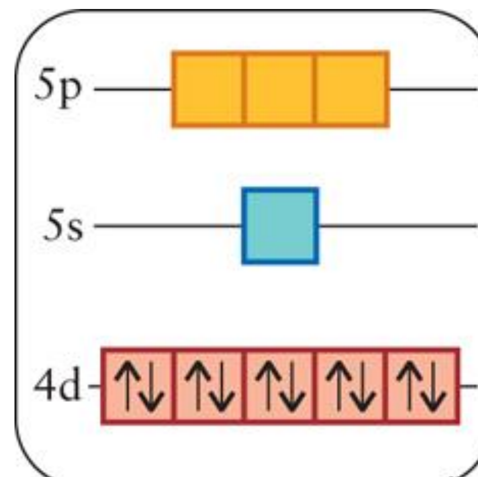
Remove the outermost electron. In^{+}

[Kr]$4d^{10}5s^{2}$



Remove the next two outermost electron. In^{3+}

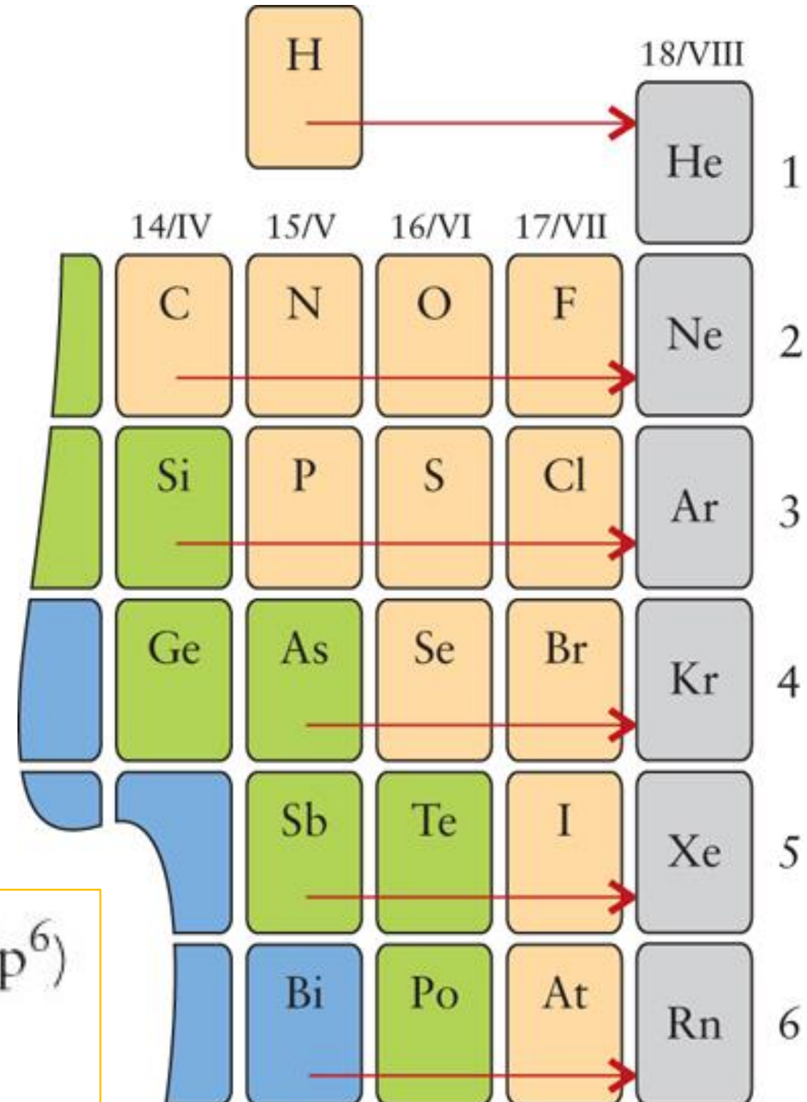
[Kr]$4d^{10}$



Nonmetals **rarely lose electrons** because their **ionization** and **electron affinity** energies are too high.

Instead, nonmetal atom **acquire electrons** to fill their outer shell

N [He]$2s^2 2p^3$ plus 3 e^- to N^{3-}[Ne]

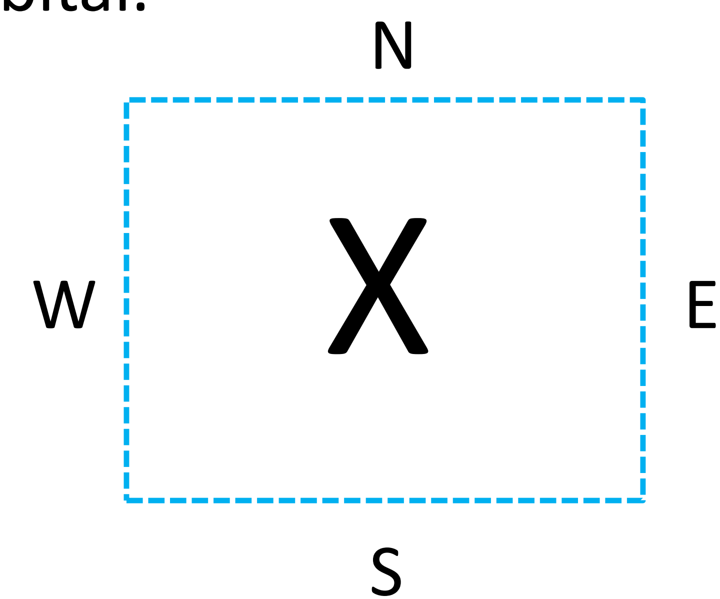


N^{3-}	[Ne] ([He]$2s^2 2p^6$)
O^{2-}	[Ne]
F^-	[Ne]
S^{2-}	[Ar] ([Ne]$3s^2 3p^6$)
Cl^-	[Ar]

G. N. Lewis

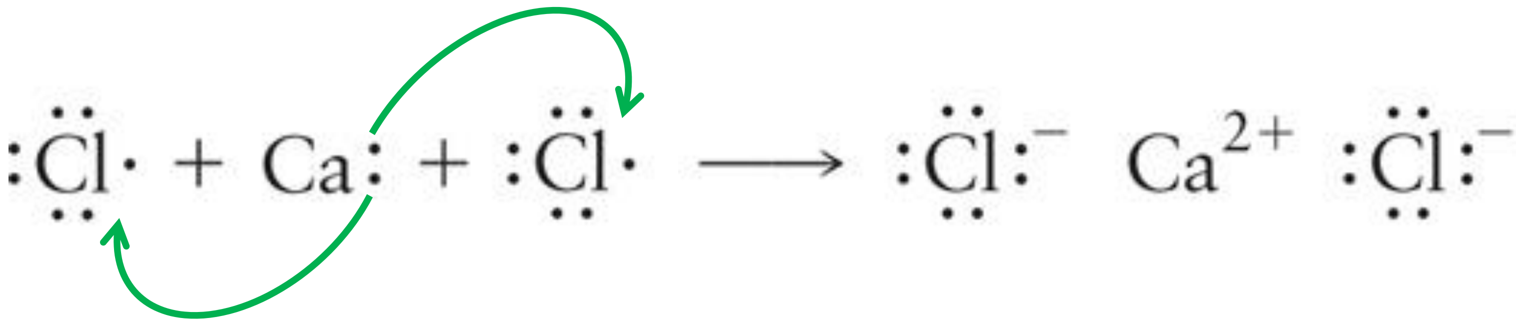
A **single dot** represents a **valence electron** (*outer most electrons in the last shell*) in the atom.

A **pair of dots** represents two paired electrons sharing an orbital.



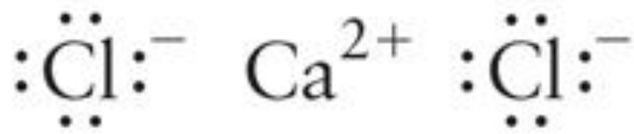
Each symbol is thought of as having four sides, a north, south, east, and west position, where valance electrons are shown as dots

An ionic formula starts by **removing** valance electrons from the metal and **transferring** them to the **nonmetal atom** to complete its valence shell.



The **calcium** atom loses its two valence electrons.

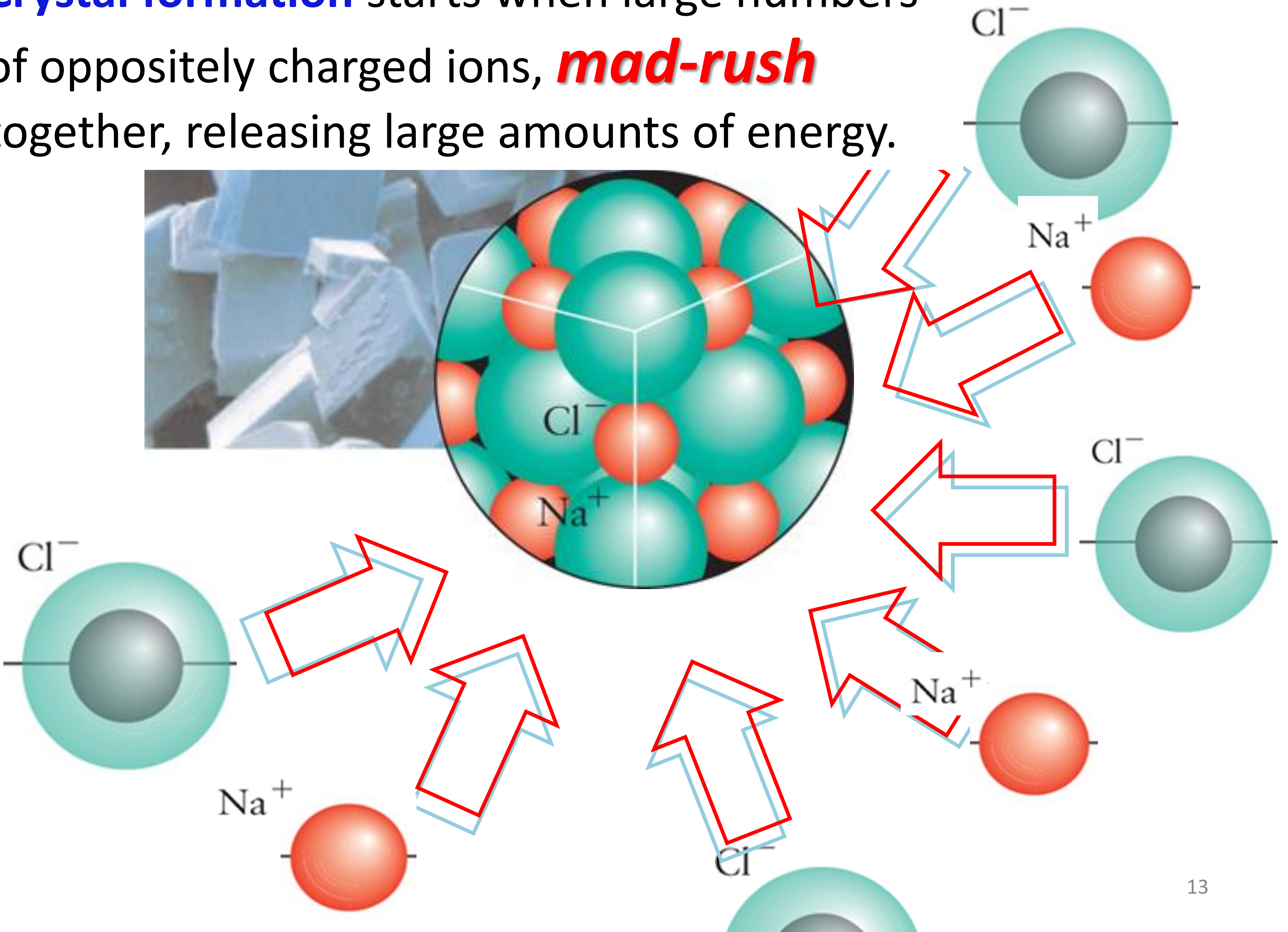
Each **chlorine** atom has one vacancy electron so it forms one bond.

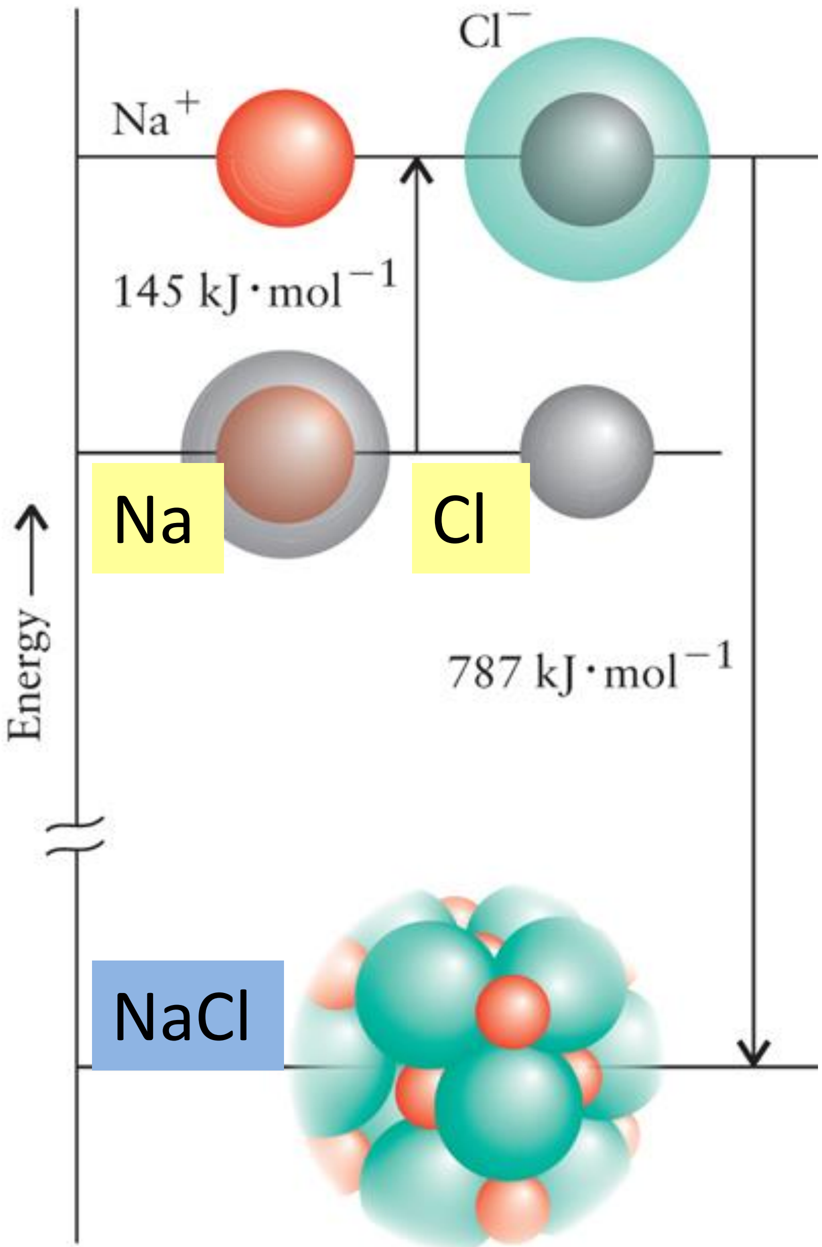


Two chloride ions (Cl^-) ***balances the charge*** for **each** calcium ion (Ca^{2+}) resulting in the formula $CaCl_2$; the overall charges is zero.

There are **no** $CaCl_2$ molecules, only **crystals** of three-dimensional arrays of $CaCl_2$ ions held by the vast array of opposite charges spread throughout the crystal-hence $CaCl_2$ is called a formal unit.

Crystal formation starts when large numbers of oppositely charged ions, ***mad-rush*** together, releasing large amounts of energy.





A **crystal** of sodium chloride has lower energy than separated sodium and chlorine atoms.

Formation of the solid takes place in three steps:

1. Sodium atoms release electrons;

2. These electrons attach to chlorine atoms;

3. Newly formed cations and anions clump together as a crystal.

Crystal Lattice is stability gained when ions form ionic solid

+494 -349 -787 = -642 kJ

2 Cl (g)

Bond disassociation of $Cl_2(g)$ to 2 Cl(g) = +122 kJ

Electron affinity Cl (g) to Cl^- (g) = -349 kJ

Na^+ (g)

Na^+ (g) + Cl^- (g)

Ionization of Na (g) to $Na^+(g)$ = +494 kJ

Na (g)

Sublimation of Na (s) to Na (g) = +108 kJ

$Na(s) + Cl_2(g)$

A **solid** composing of Na^+ and Cl^- ions has a **lower energy** than neutral Na and Cl atoms by -642 kJ

Crystal Lattice energy for Na^+ + Cl^- (g) to the ionic solid Na^+Cl^- (s) = -787 kJ

Heat of Formation of ionic solid from its elements = -411 kJ

Na^+Cl^- (s)

See also Example 7.13

Lattice energy is a "**global**" characteristic of the **entire** crystal, a <u>net lowering</u> of energy in the entire crystal (once the cations and anions clump together as a crystal).

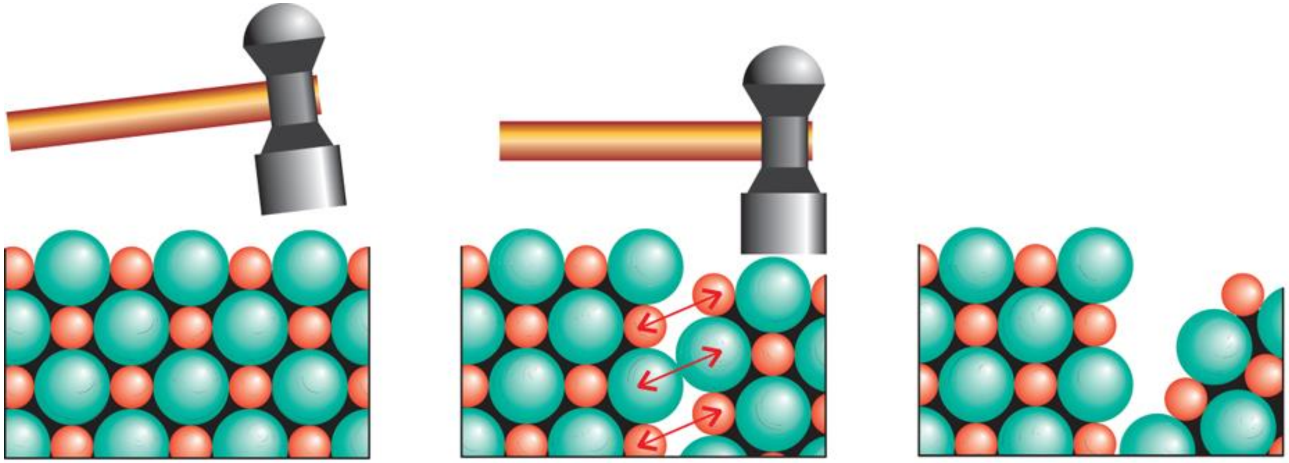
Alkali metal iodide	Lattice energy (kJ·mol^{-1})
LiI	759
NaI	700
KI	645
RbI	632
CsI	601

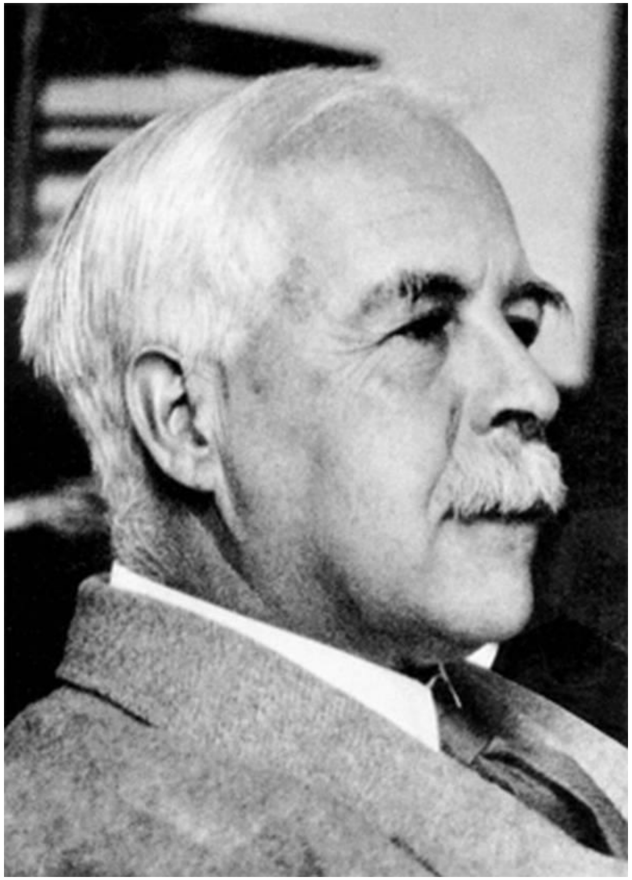
A **high lattice energy** value indicates **a stronger ion pair** which produces a more tightly bonded solid.

Coulomb's Potential Energy measure the strength between individual ion pairs

The **strong attraction** (Coulomb's Potential Energy) between oppositely charged ions accounts for the typical properties of ionic solids:

- **high melting points** and
- **brittleness**.

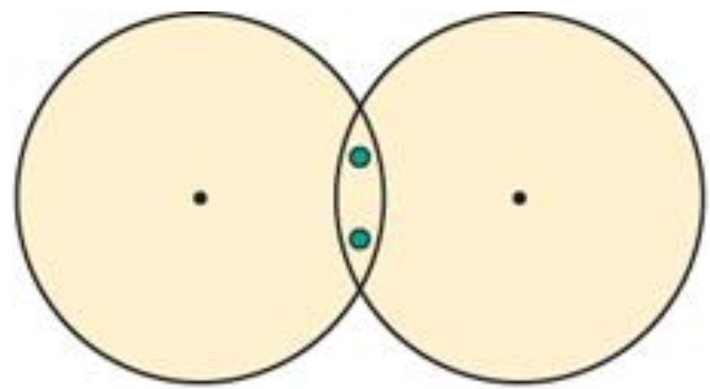




Covalent Bonds form between **two nonmetals** that **do not form into ions**.

The nature of nonmetal bonds *puzzled* scientists until 1916, when **G.N. Lewis** published his explanation.

A brilliant insight, before anyone knew anything about quantum mechanics.

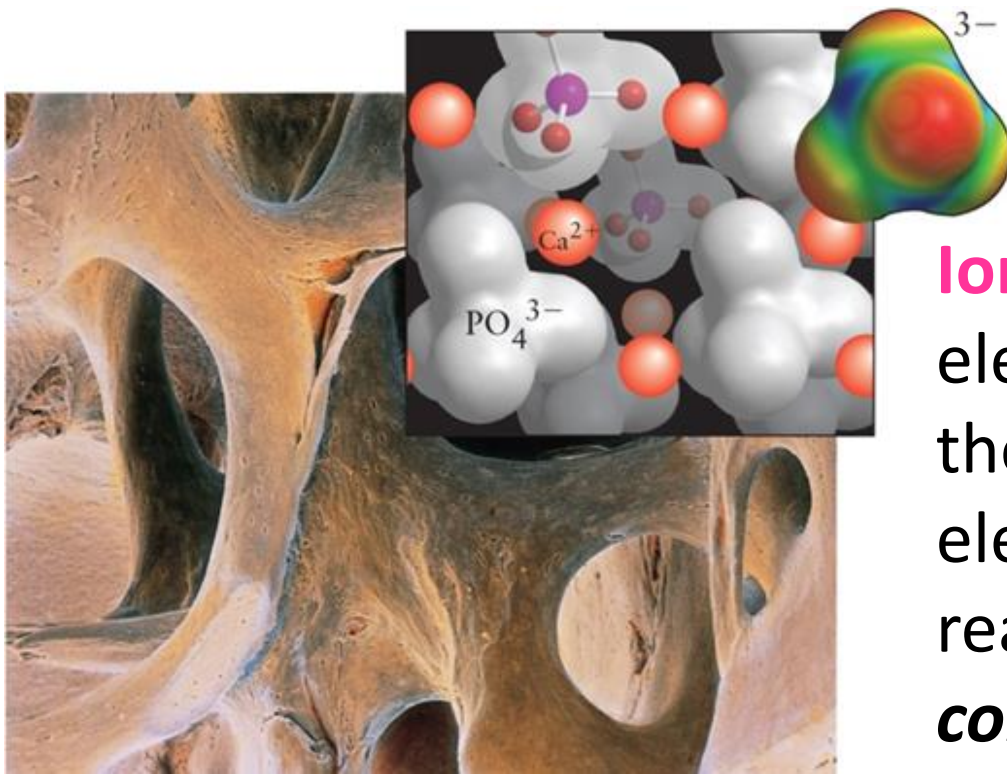


Shared electron pair

No Columbic interactions

Covalent bonds form by atoms **sharing** electrons until they reach a ***noble-gas configuration***.

Lewis called this principle the **octet rule**, reaching a ***noble-gas configuration***

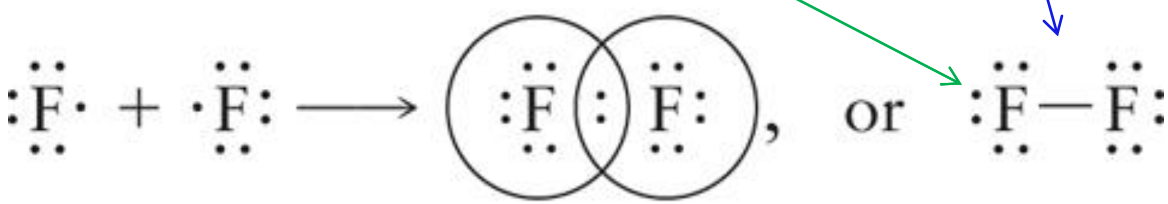


Ionic bonds form when one element **loses** electrons and the other atom **gains** electrons, until both atoms reach a ***noble-gas configuration***.

Lewis: Share to an Octet

A fluorine atom can achieve an octet by accepting a share in an electron from another fluorine atom.

The **octet** (or duplet) shows **lines** (bonding pairs) and **dots** (lone pairs).



Rules to Write Dot Structures

1. Write a skeleton molecule with the lone atom in the middle (Hydrogen can never be in the middle).

2. Find the number of electrons needed (N)

   (8 x number of atoms, 2 x number of H atoms)

1. Find the number of electrons you have (valence e^-'s) (H)

2. Subtract to find the number of bonding electrons (N-H=B)

3. Subtract again to find the number of non-bonding electrons (H-B=NB)

4. Insert minimum number of bonding electrons in the skeleton between atoms only. Add more bonding if needed until you have B bonding electrons.

5. Insert needed non-bonding electrons around (not between) atoms so that all atoms have 8 electrons around them. The total should be the same as NB in 5 above.

Water H_2O

1. S — H O H

2. N — $2 \times 2 = 4$ for Hydrogen
$1 \times 8 = 8$ for Oxygen
$4+8 = 12$ needed electrons

12 N

3. H — $2 \times 1 = 2$ for Hydrogen
$1 \times 6 = 6$ for Oxygen
You have 8 available electrons

- 8 H

4. B — $12 - 8 = 4$ bonding electrons

5. NB — $8 - 4 = 4$ non-bonding electrons

- 4 B

4 NB

6.

H:O:H

$\mathrm{H{:}\ddot{\underset{\cdot\cdot}{O}}{:}H}$ $\mathrm{H - \ddot{\underset{\cdot\cdot}{O}} - H}$

Single bond

Carbon dioxide CO_2

1. S　　O C O

2. N
1 x 8 = 8 for Carbon
2 x 8 = 16 for Oxygen
8+16=24 needed electrons

24 N

3. H
1 x 4 = 4 for Carbon
2 x 6 = 12 for Oxygen
You have 16 available electrons

- 16 H

4. B　24 - 16 = 8 bonding electrons

5. NB　16 – 8 = 8 non-bonding electrons

- 8 B

8 NB

6.

O::C::O

O = C = O

O::C::O

Double bond

Acetylene C_2H_2

1. S H C C H

2. N $2 \times 8 = 16$ for Carbon
$2 \times 2 = 4$ for Hydrogen
$16+4 = 20$ needed electrons

20 N

3. H $2 \times 4 = 8$ for Carbon
$2 \times 1 = 2$ for Hydrogen
You have 10 available electrons

- 10 H

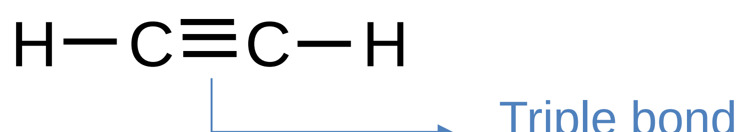
4. B $20 - 10 = 10$ bonding electrons

5. NB $10 - 10 = 0$ non-bonding electrons

- 10 B

0 NB

6.



Practice

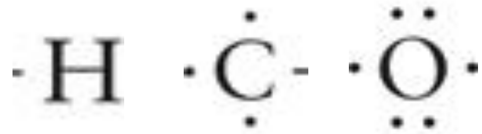
Write the Lewis structure for the:

NH_4^+

CN^-

Helpful reminders (3)

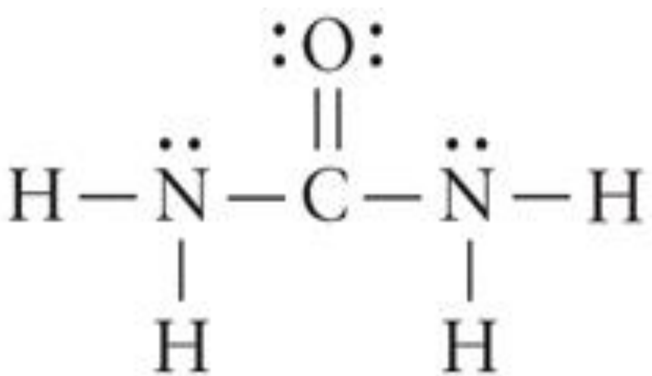
Remember **simple** Lewis Dot diagrams



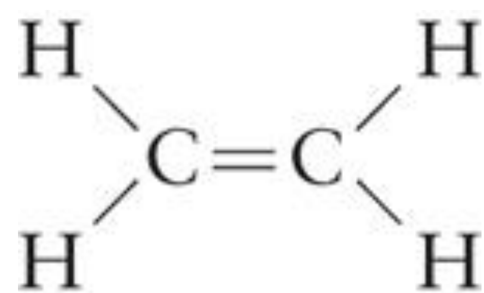
1 bond, 4 bonds, 2 bonds to complete their octet

Molecules have **symmetry**

Urea, $(NH_2)_2CO$



C_2H_4

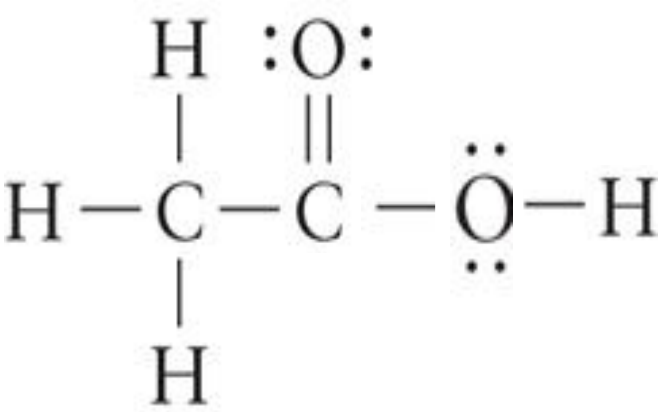


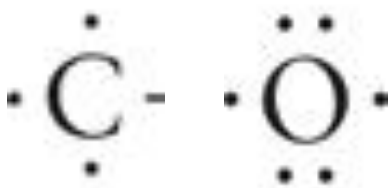
Helpful reminders

Read the formula for order of atom attachment

CH_3COOH

acetic acid



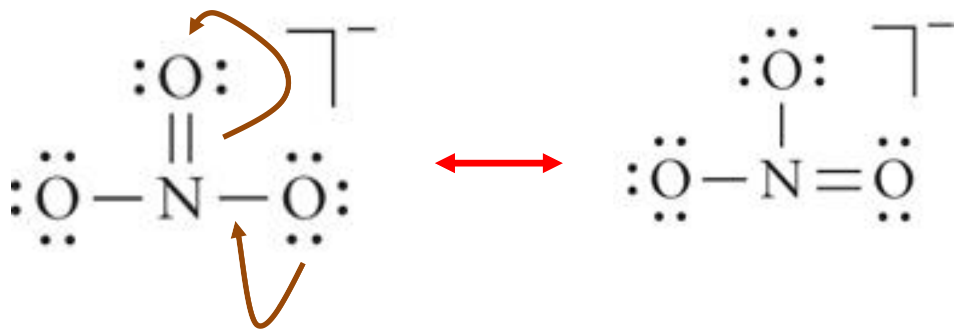


Carbons makes 4 bonds and oxygen makes 2 bonds to complete the octet.

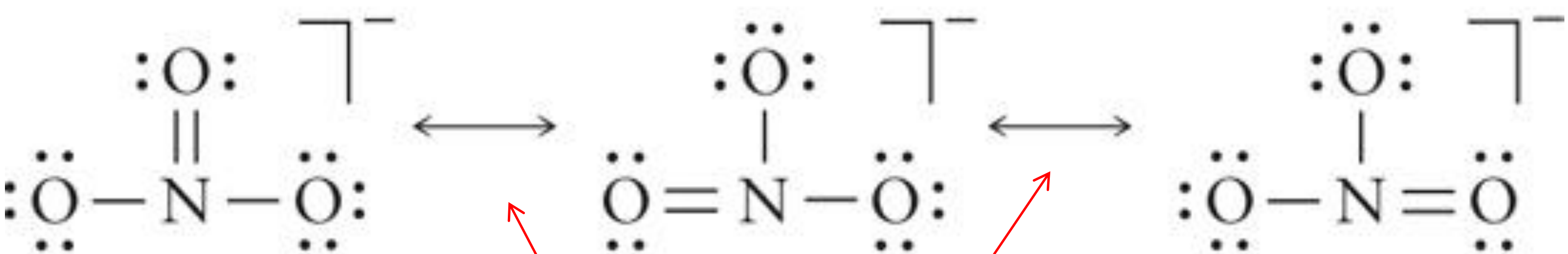
Resonance Structures

Delocalized electrons **hop** from one atom to another; no discretion as long as it's the *same atom pair*.

Nitrate ion, NO_3^-

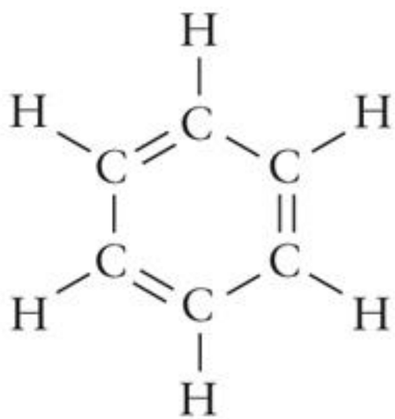


Resonance Structures



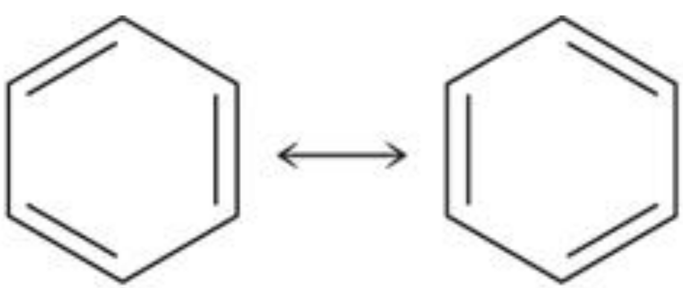
Resonance arrows

Kekulé aromatic structures



Kekulé structure

Kekulé structure, stick form

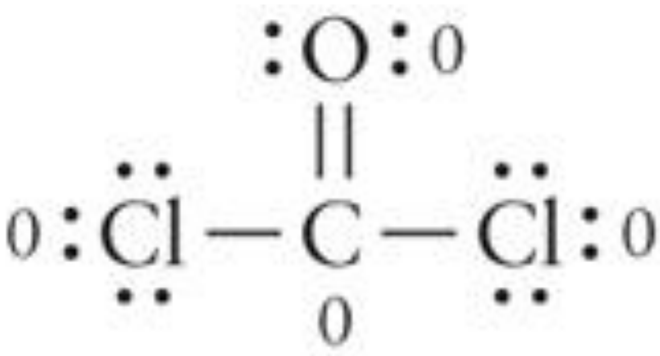


Benzene resonance structure

Final, “**blended**” structure for Benzene

Formal Charge

$$Formal\ Charge = V - \left(L + \frac{1}{2}B\right)$$



O 6 - (4 + ½ 4) = 0

Cl 7 - (6 + ½ 2) = 0

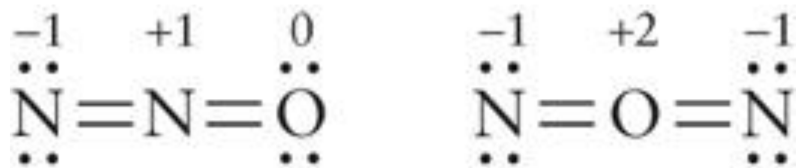
C 4 - (0 + ½ 8) = 0

The sum of formal charges is equal to the overall charge of the molecule or ion; electrically neutral molecule, have a formal charge of zero.

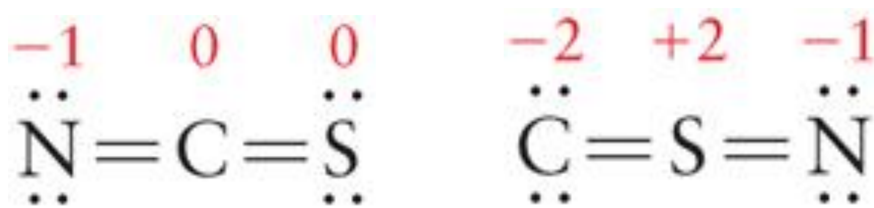
$$Formal\ Charge = V - \left(L + \frac{1}{2}B\right)$$

Formal charges can predict the most *favorable* Lewis structure:

NNO



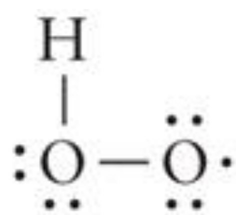
CNS⁻



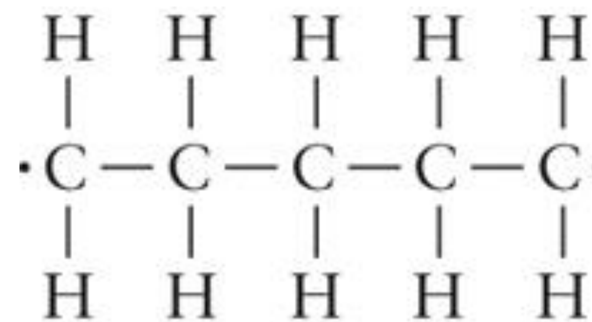
The structure with the lowest formal charges on each atom is the most plausible (lowest energy) structure.

Exceptions to the Octet Rule

Radicals are something you cannot isolate, are very unstable and are highly reactive.

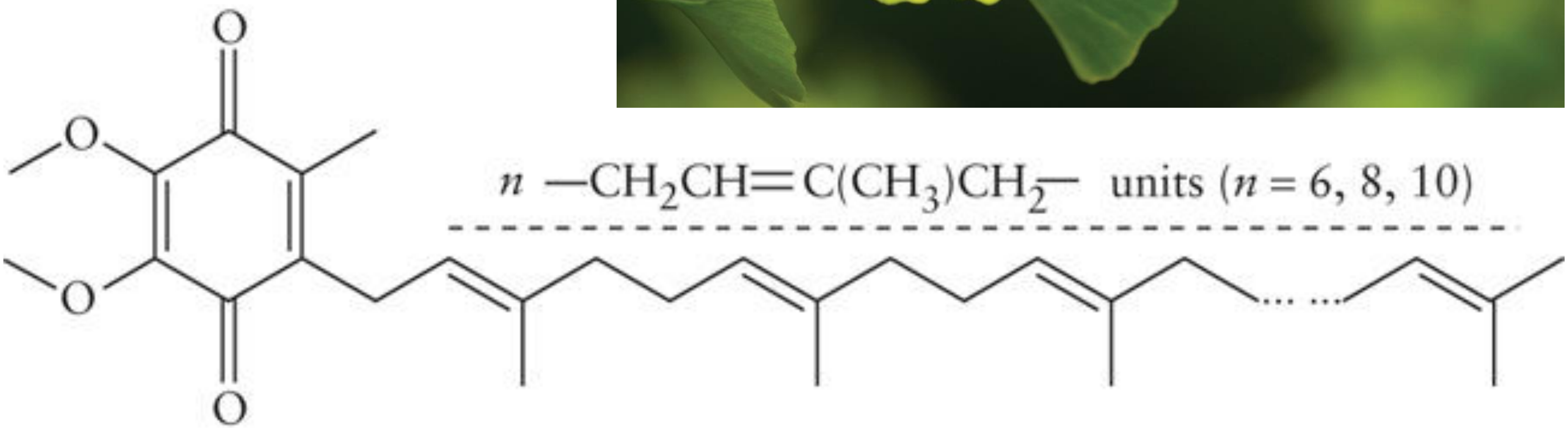


Hydrogenperoxyl, $HO_2\cdot$



A biradical

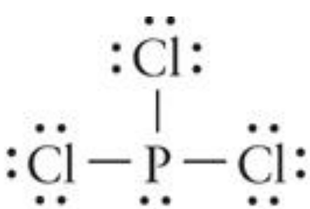
Gingko biloba like other green leafy eatable plants.



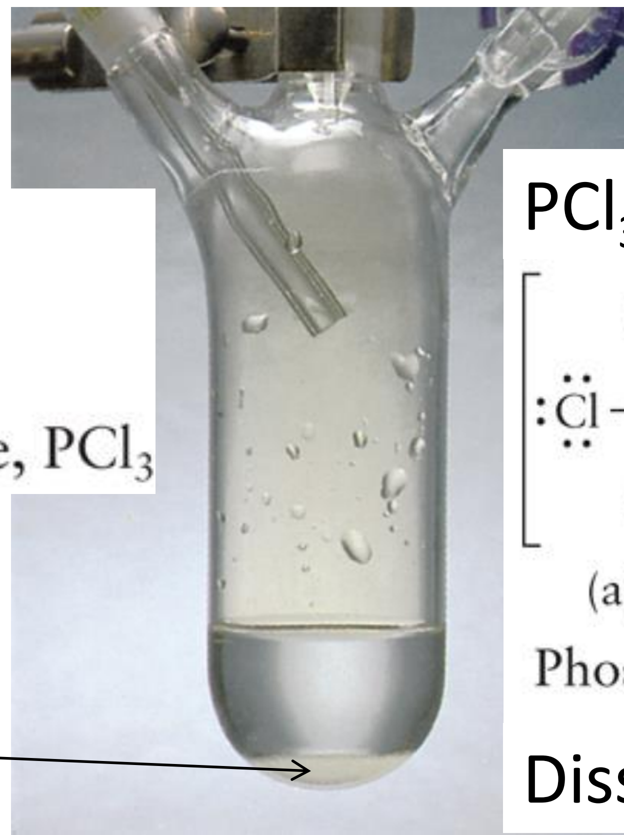
Vitamins A, C and E are antioxidant enzymes, a group of compounds called coenzyme Q. Antioxidants are **free-radical traps**.

Exceptions to the Octet Rule

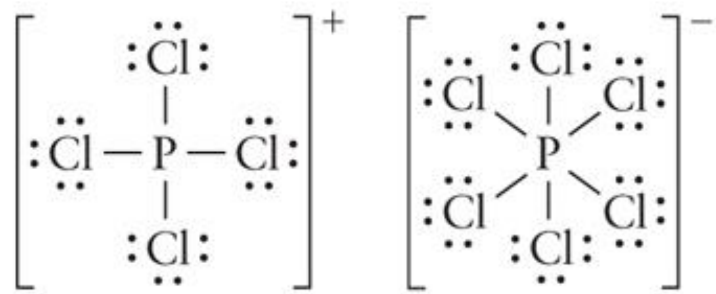
Carbon, **nitrogen**, **oxygen**, and **fluorine obey the octet rule rigorously**. *Period 3* and subsequent periods can accommodate *more than eight electrons* in its valence shell, up to **12 electrons**.



Phosphorus trichloride, PCl_3



$$PCl_3(l) + Cl_2(g) \rightarrow PCl_5(s)$$



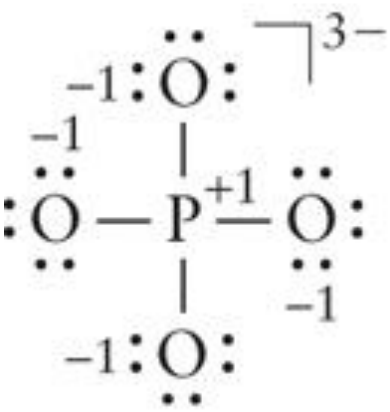
(a) PCl_4^+ (b) PCl_6^-

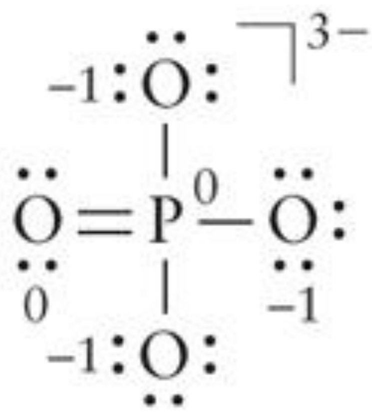
Phosphorus pentachloride, $PCl_5(s)$

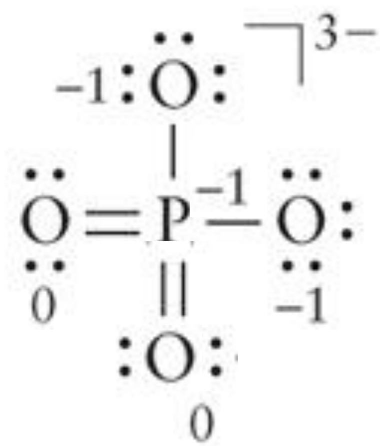
Dissociation of PCl_5

Exceptions to the Octet Rule

Determine the most stable resonance structure







P $5-(0+\frac{1}{2}10)= 0$

O $6-(4+\frac{1}{2}4)= 0$

O $6-(6+\frac{1}{2}1)= -1$

P $5-(0+\frac{1}{2}8)= +1$

O $6-(6+\frac{1}{2}1)= -1$

P $5-(0+\frac{1}{2}12)= -1$

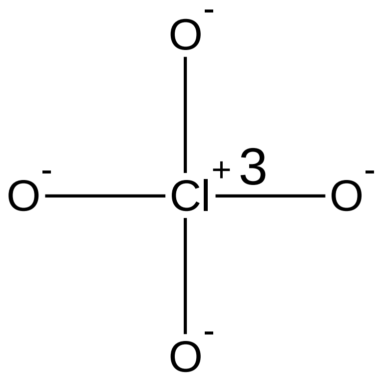
O $6-(4+\frac{1}{2}4)= 0$

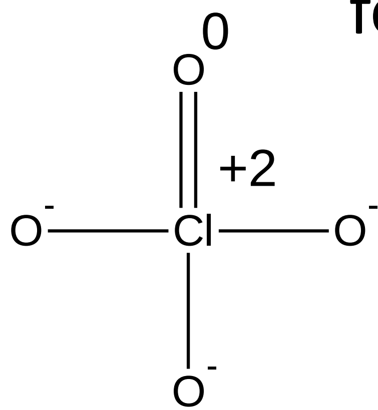
O $6-(6+\frac{1}{2}1)= -1$

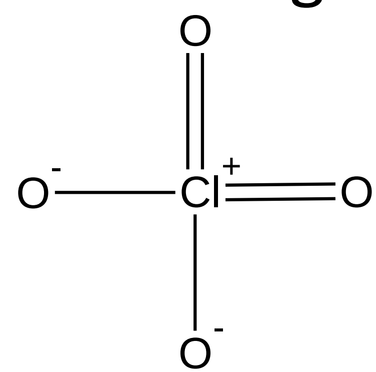
Exceptions to the Octet Rule

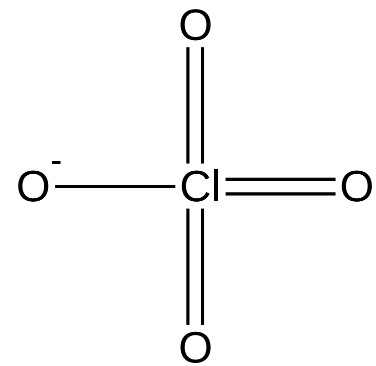
ClO_4^- (VE 7+24+1=32)

12 electrons on the central atom,
fewest charges









Cl: 7-4=+3

O: 6-7= (-1)4

net -1

Cl: 7-5=+2

O: 6-6=0

O: 6-7= (-1)3

net: -1

Cl: 7-6=+1

O: 6-6=0

O: 6-7= (-1)2

net -1

Cl: 7-7=0

O:6-6=0

O: 6-7= -1

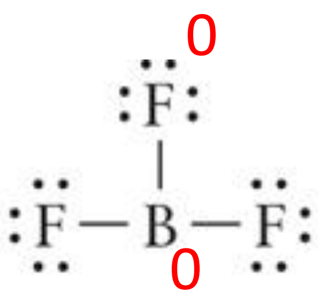
net -1

All atoms have a charge

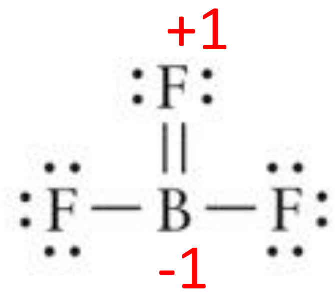
High charge for Cl

Central atom has to many electrons

Self Test
Which is the more stable?



Boron trifluoride, BF_3



Boron trifluoride, BF_3

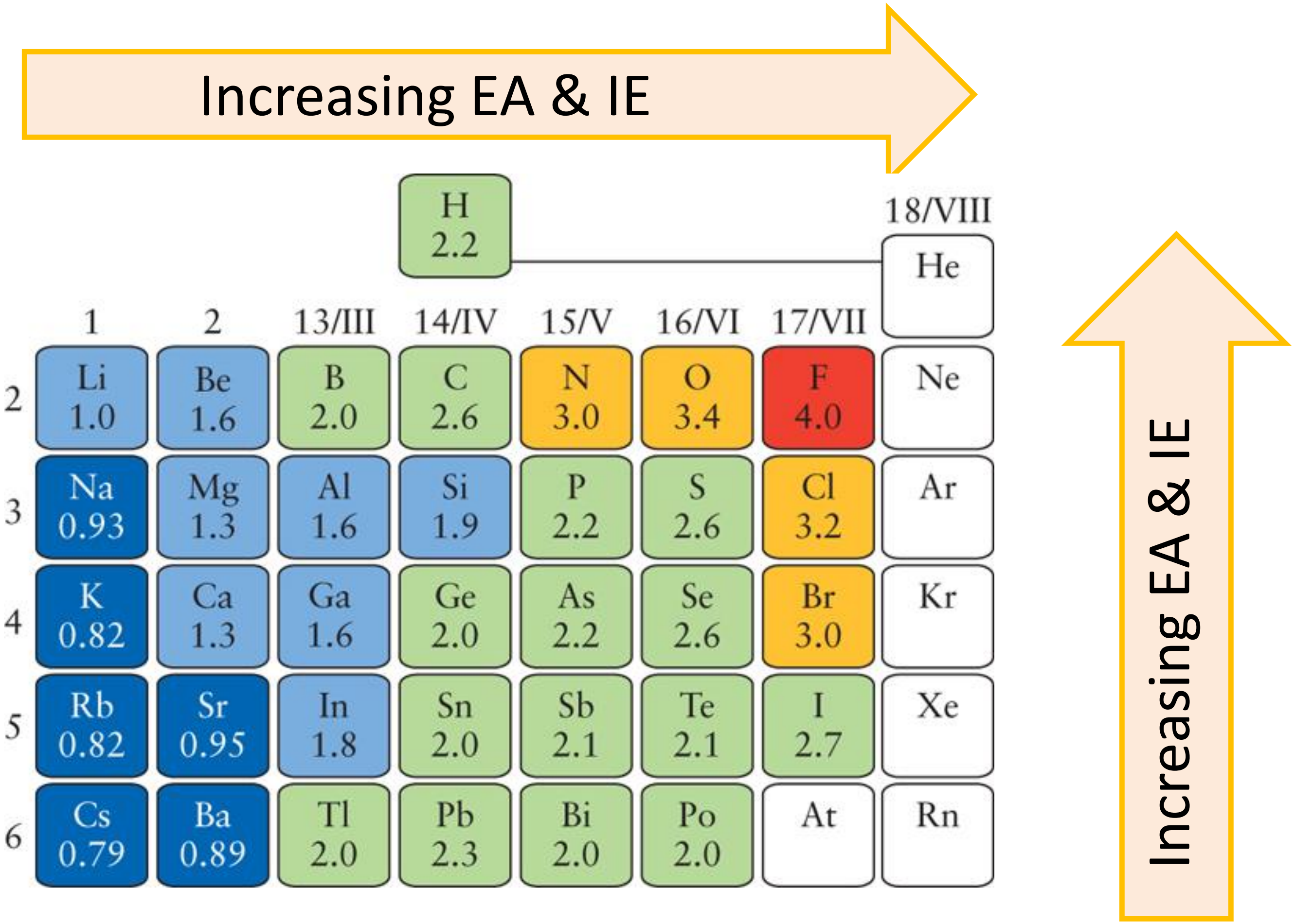
F $7-(6+\frac{1}{2}2)=$ 0

B $3-(0+\frac{1}{2}6)=$ 0

F $7-(4+\frac{1}{2}4)=$ +1

B $3-(0+\frac{1}{2}8)=$ -1

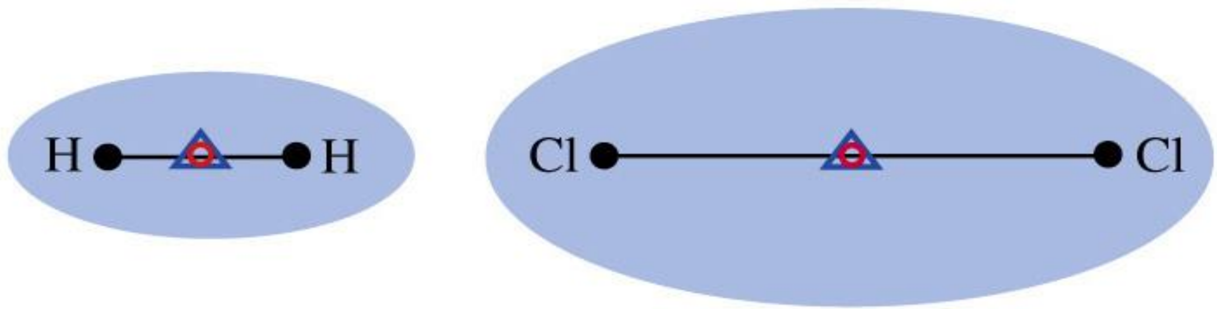
Electronegativity values by Linus Pauling.



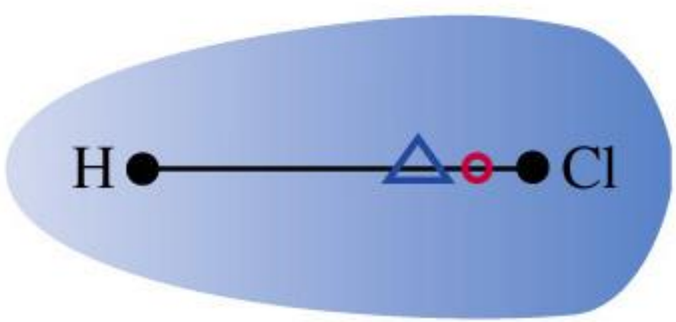
If an atom gives up an electron reluctantly it has **high** **ionization energy** and if the electrons attaches favorable it has **high** **electron affinity**.

Covalent bonds

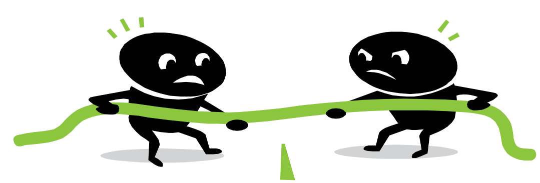
Nonpolar covalent bond: electrons are shared equally.



Polar covalent bond: electrons are shared unequally.



$\overset{\delta+}{H} - \overset{\delta-}{Cl}$ Dipole



Electronegativity & bonds

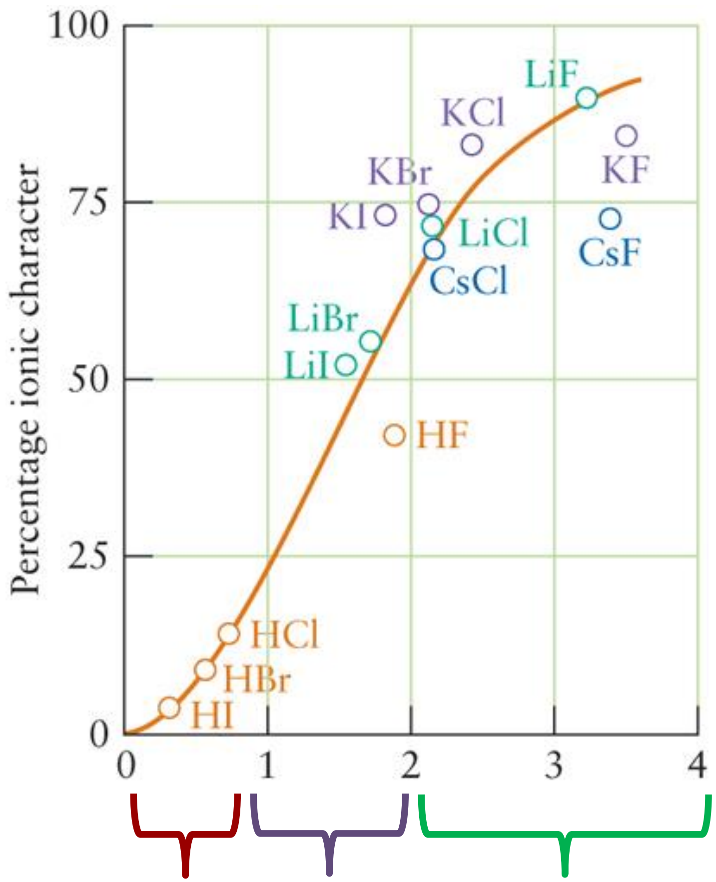
Electronegativity Difference Between Bonded Atoms	Type of Bond
Less than 0.5	Nonpolar Covalent
0.5 to 1.9	Polar Covalent
Greater than 1.9	Ionic

H — H   2.1 – 2.1 = 0   Nonpolar covalent

N — H   3.0 – 2.1 = 0.9   polar covalent

Na — F   4.0 – 0.9 = 3.1   Ionic

Electronegativity difference



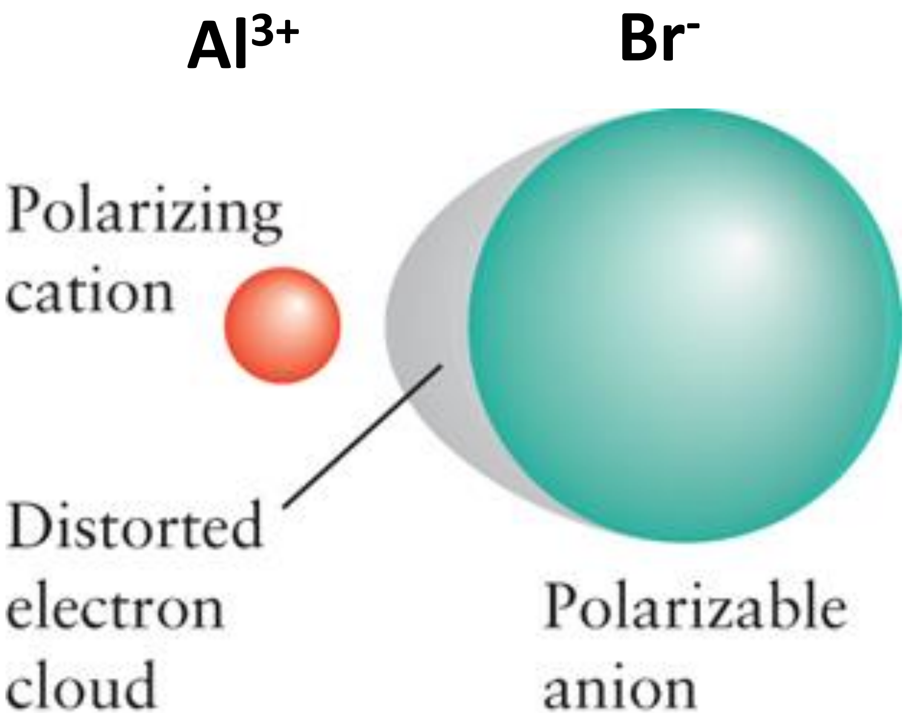
Non-polar Covalent **Polar Covalent** **Ionic**

Li-F

$|1.0 - 4.0| = 3.0$

H-Cl

$|2.2 - 3.2| = 1.0$



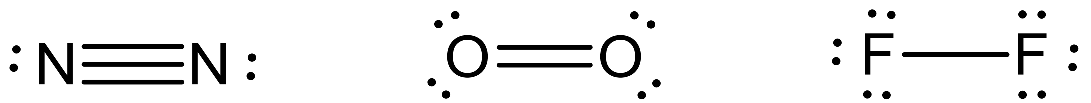
Increasing polarizing power

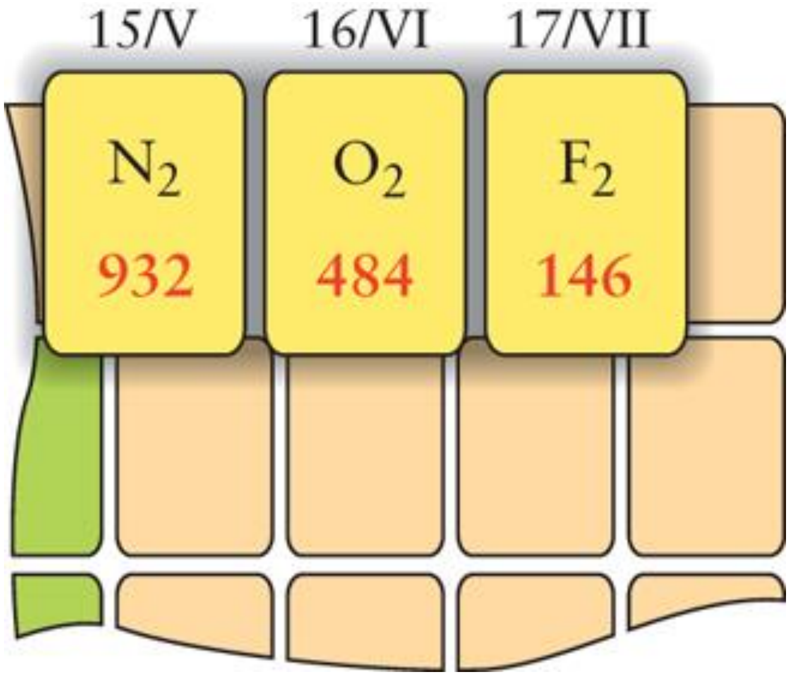
Li^+ Be^{2+}

Na^+ Mg^{2+}

Charge ↑ & Size ↓

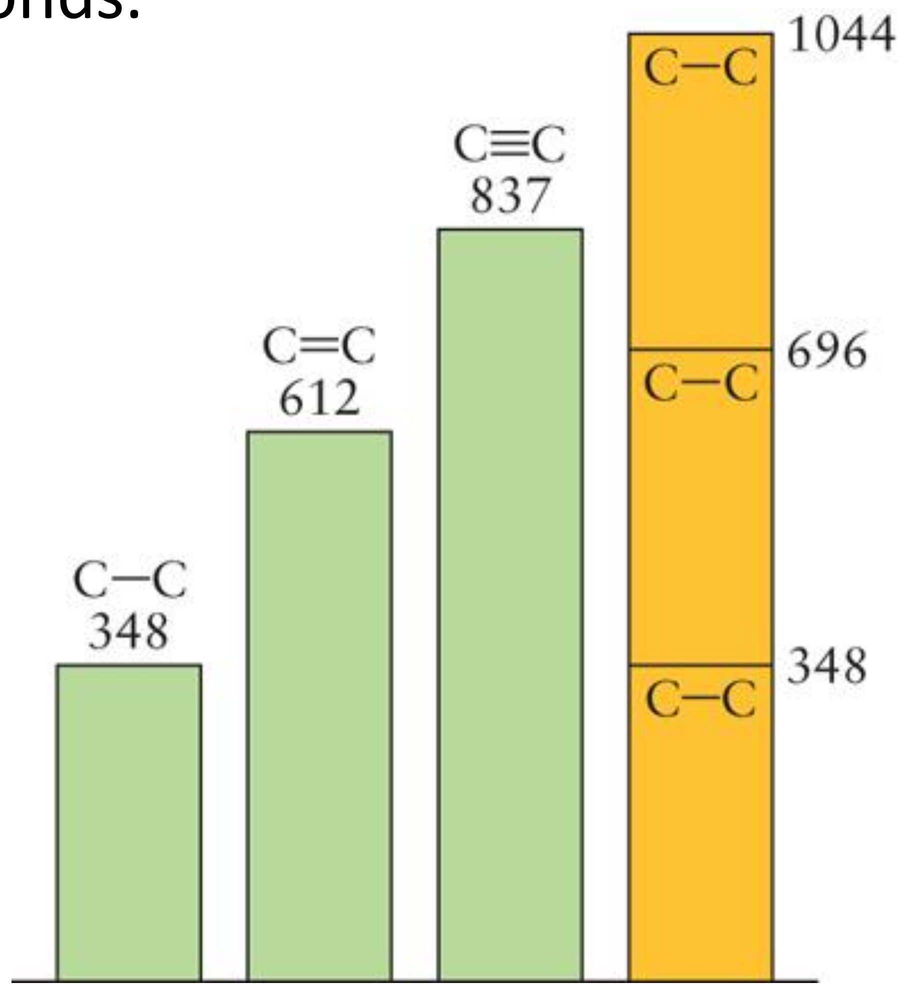
Polarization by small, highly charged cations of larger, nearby anions.





Notice that a single bond is **weaker** than a triple bond.

Electrons in **double** and **triple bonds** are **not as concentrated** between two atoms as they are in a single bonds.



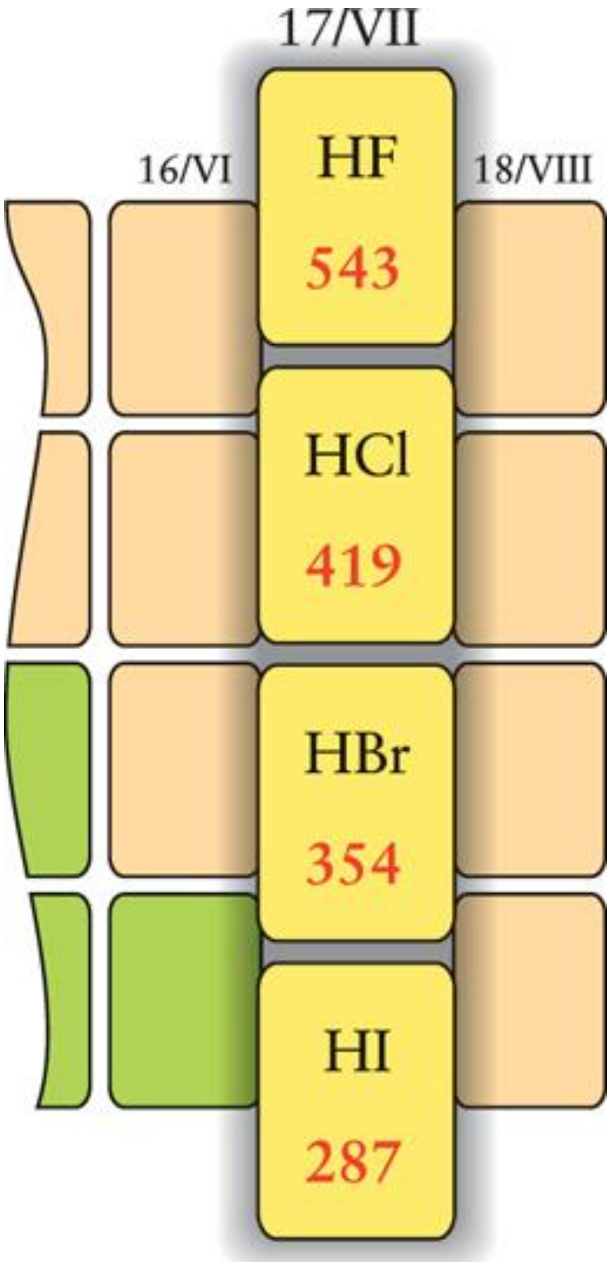
Value if each successive bond were another C-C bond

3× C-C

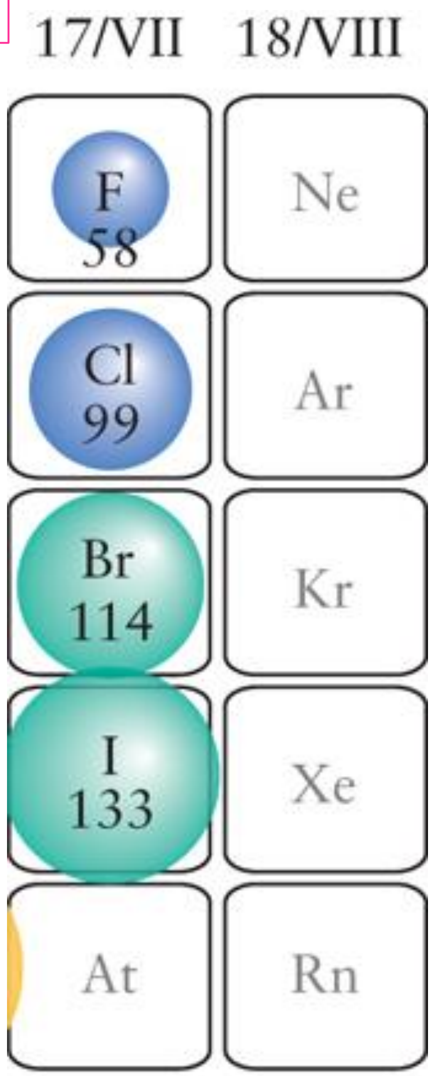
2× C-C

C-C

Strength ↓ as Size ↑

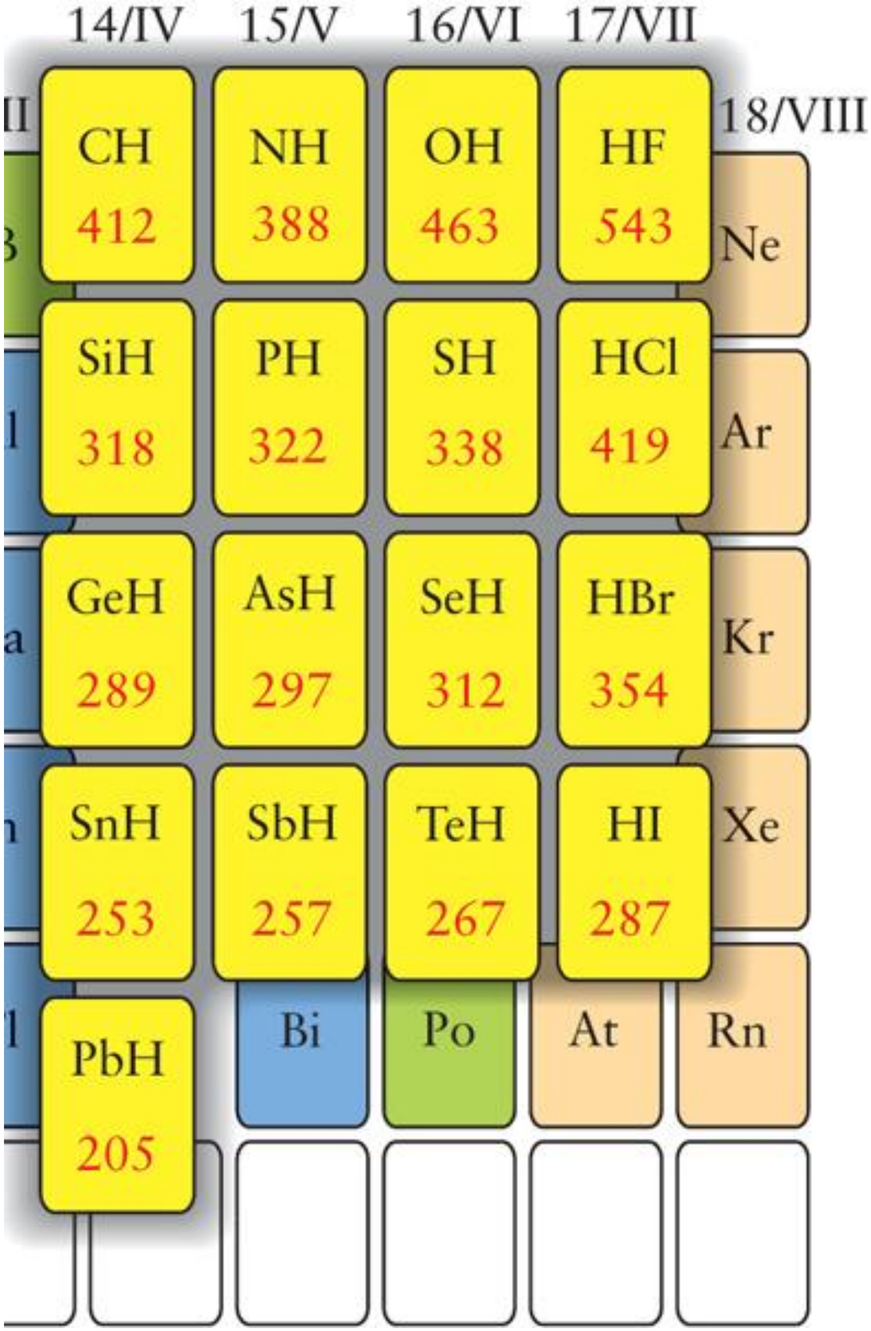


Bond Strength kJ

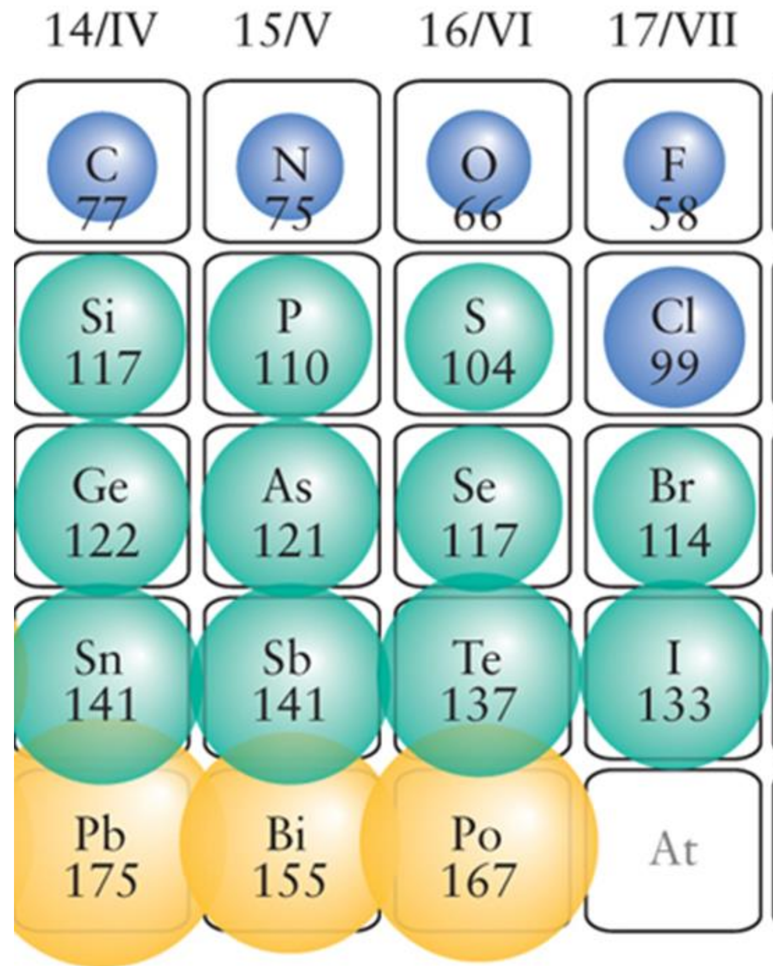


Atomic Radii

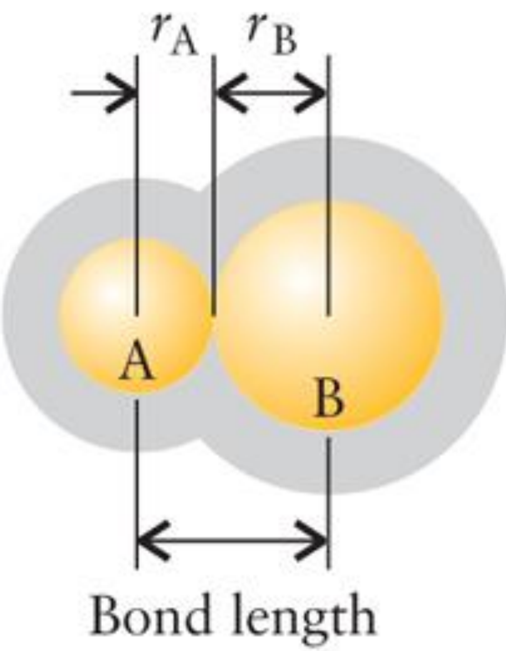
Strength↓ as Size ↑

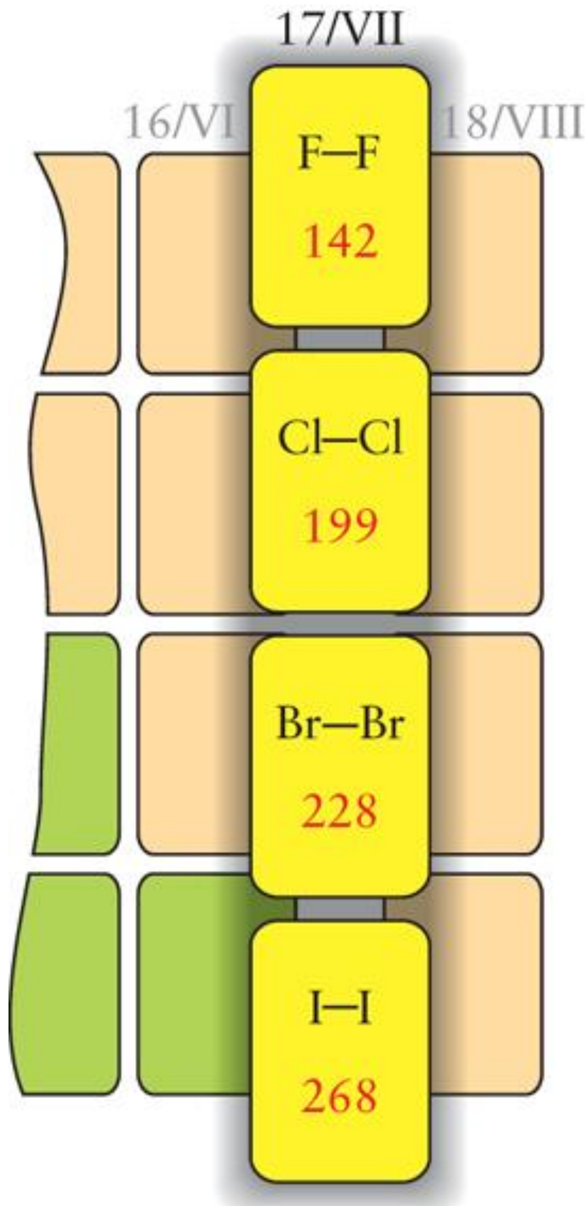


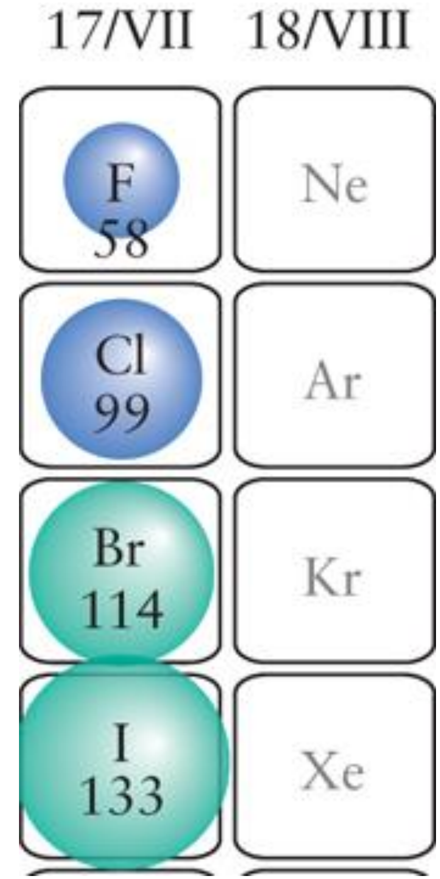
Atomic Radii



Bond Lengths $\uparrow$ as size $\uparrow$





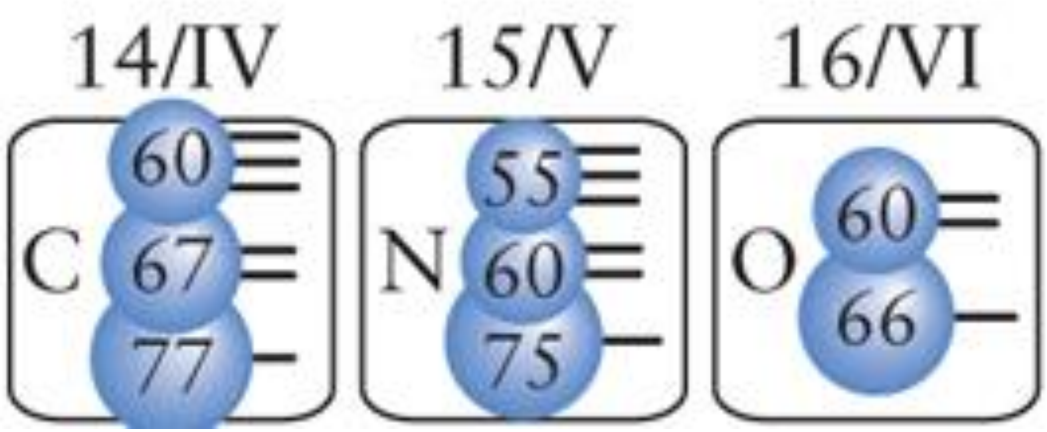


Atomic Radii

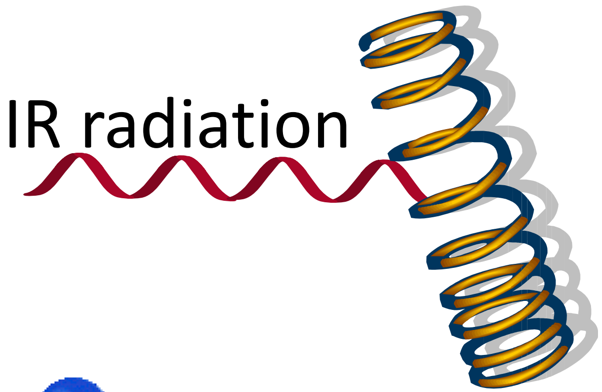
Strong bonds typically are stiffer than weak bonds.

Bond	Average bond dissociation energy
C—H	412
C—C	348
C=C	612
C⋯C*	518
C≡C	837

Triple bonds shorter and stronger

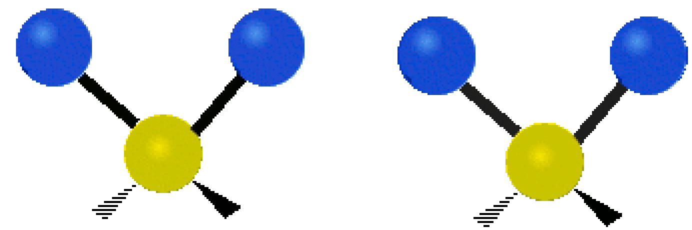


Molecules absorb infrared radiation (1000 nm or about 3×10^{14} Hz) and become vibrationally excited. We treat the bonds like springs.



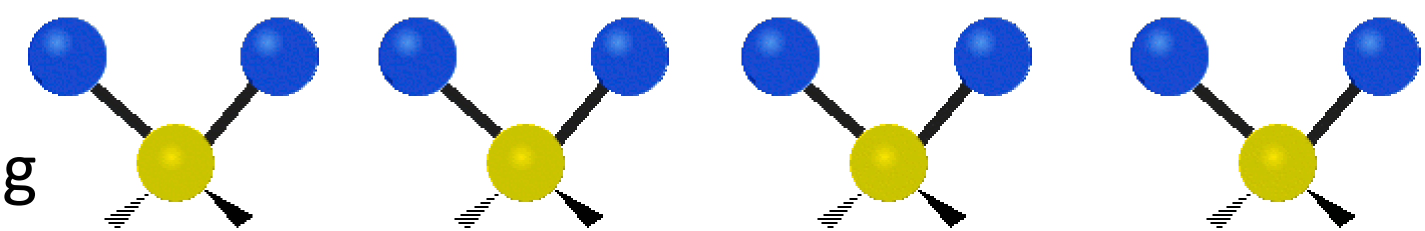
2 basic ways atoms move: stretching and bending

Stretching



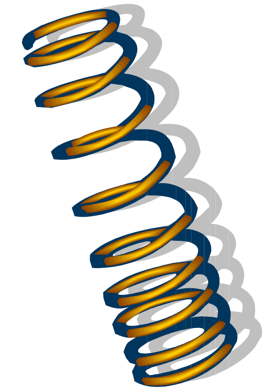
symmetric　　asymmetric

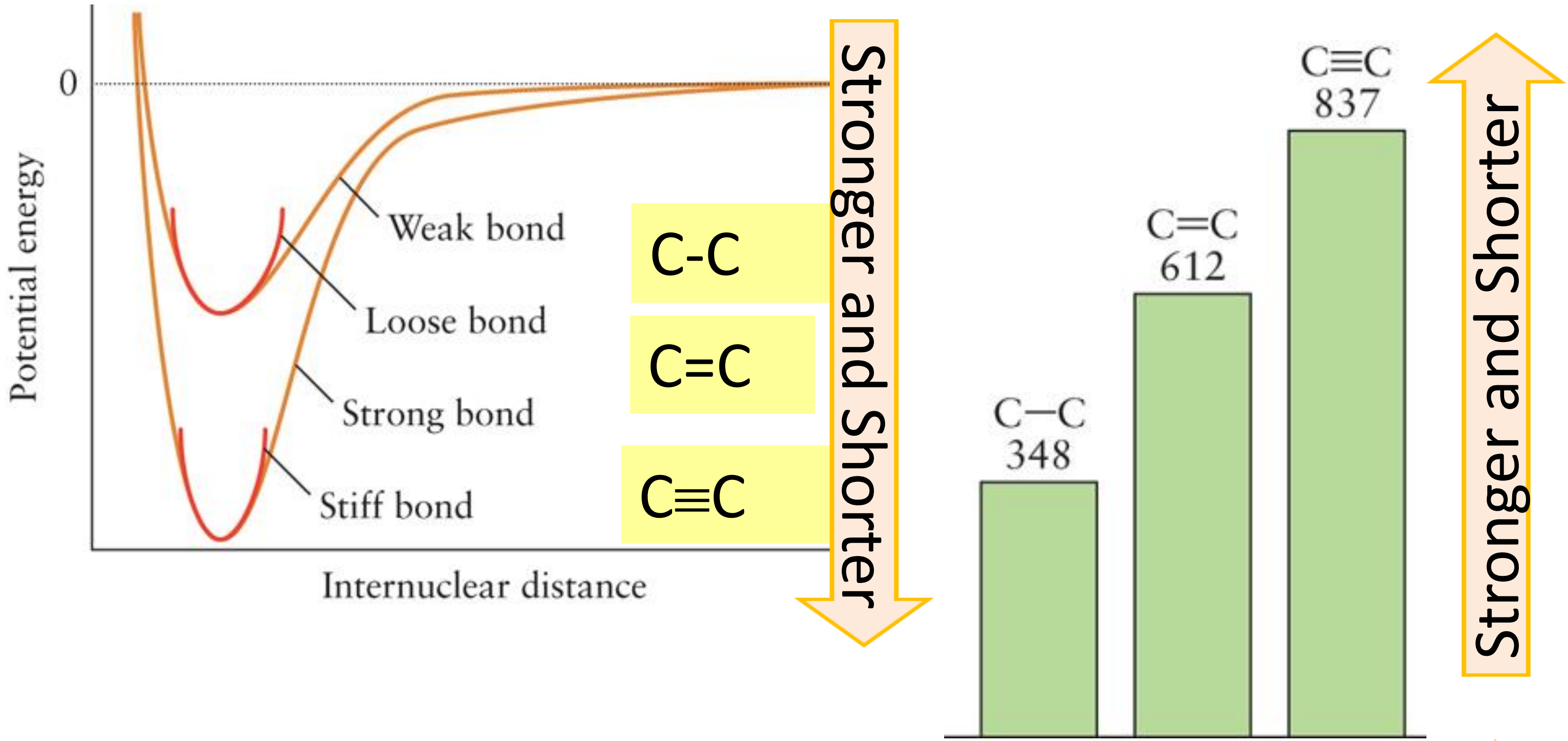
Bending



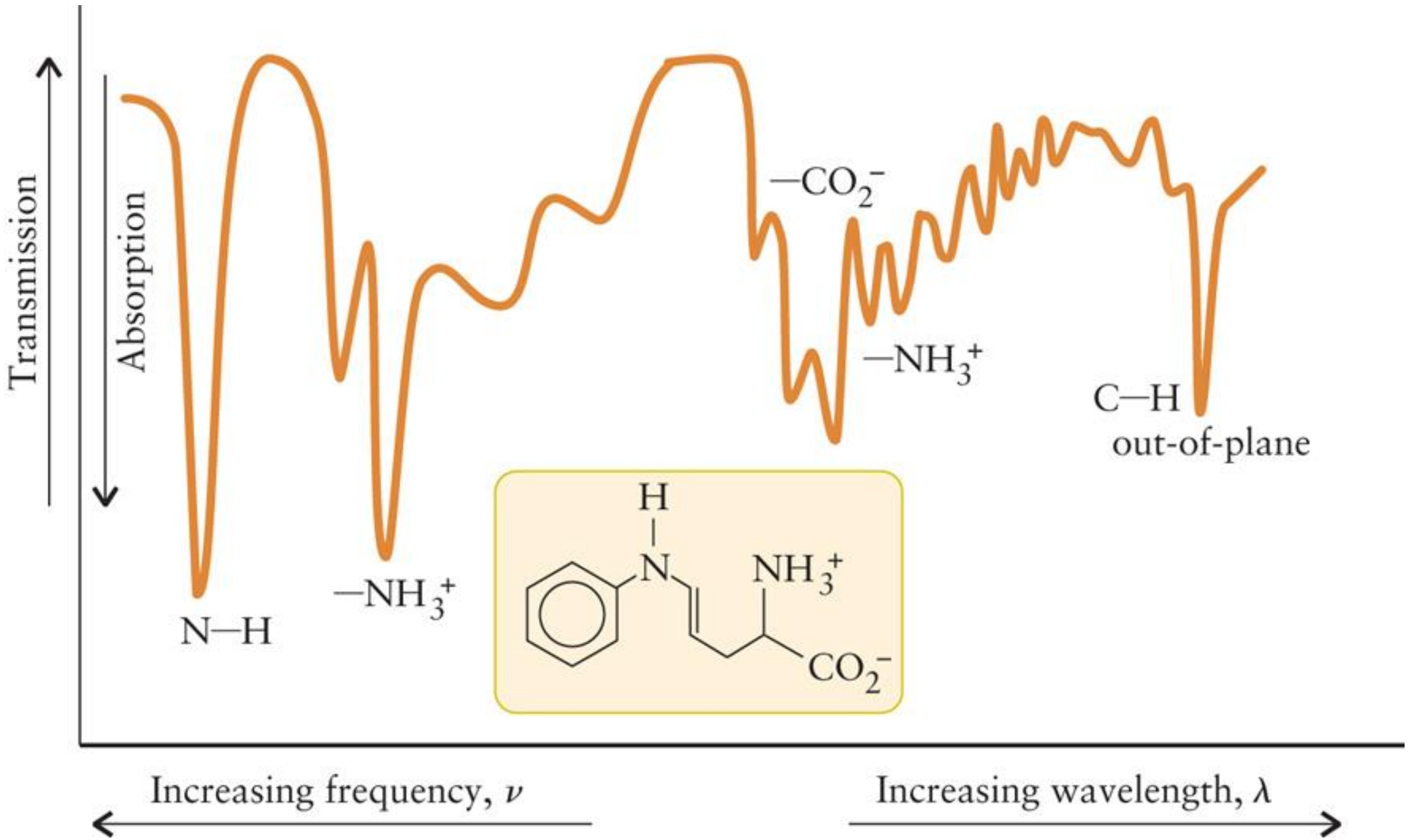
scissoring　　rocking　　wagging　　twisting

Bond strength determines the amount of IR needed to move the bonds.





Infrared spectroscopy of an amino acid



Stronger and Shorter