

CHEM103

General Chemistry

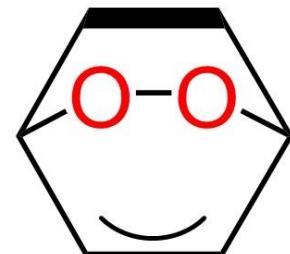
Chapter 8: Basic Concepts of Chemical Bonding



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Education, Inc.

Department of Chemistry
SUSTech



Assignment 7 & Mid-term EXAM

Homework 7

Due date: 31st Oct. (Mon)

Mid-term exam (Chapters 1-9)

Bring your calculator & student ID card

10:00AM-12:00 PM, 13th Nov. (Sun).

Review on Chapter 7

Development/History of Periodic Table

Periodic Trends:

Effective Nuclear Charge: Shielding

Sizes of Atoms & Ions: (non)bonding atomic radius;
Ionization Energy

Electron Affinity

Properties of Metal, Nonmetals, and Metalloids

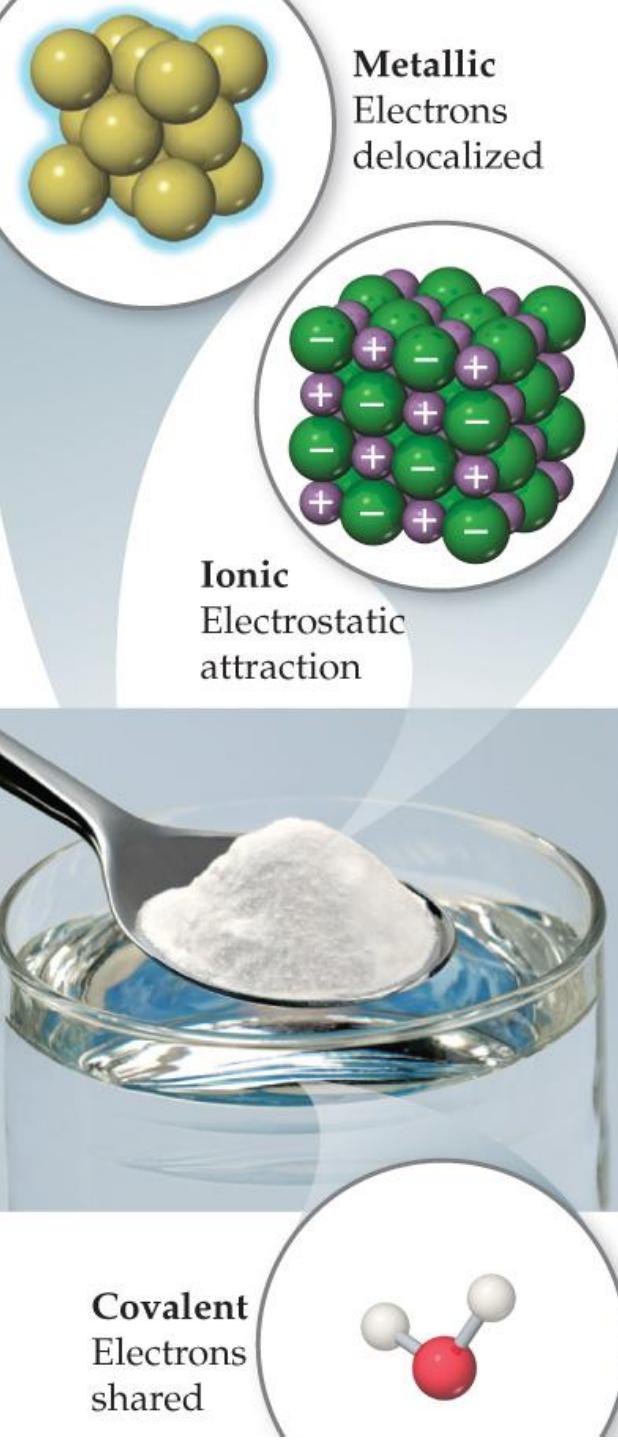
Key Outline of Chapter 8

Lewis Symbol, Octet Rule

1. Ionic Bond: Lattice Energy
2. Covalent Bond: Polar, Dipole Moment, Formal Charge, Bond Strength/Enthalpy
 3. Metallic Bond

Electronegativity, Lewis Structure,
Resonance Structures, Localized and
Delocalized Electrons

Chemical Bonds



- 3 basic types of chemical bonds:
- 1. Ionic bond**
 - *Electrostatic attraction* between oppositely charged ions (i.e. cations and anions).
 - 2. Covalent bond**
 - *Sharing* of electrons.
 - 3. Metallic bond**
 - Metal atoms bonded to several other atoms in a sea of electrons, which are relatively free to move.

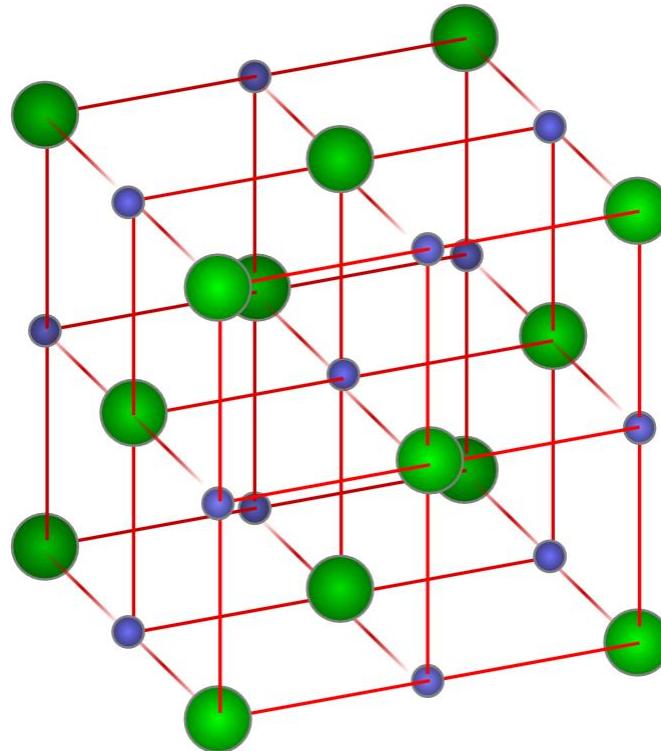
Lewis Symbols & Octet Rule

| Group | Element | Electron Configuration | Lewis Symbol | Element | Electron Configuration | Lewis |
|-------|---------|------------------------|--------------|---------|------------------------|-------|
| 1A | Li | [He] $2s^1$ | Li· | Na | [Ne] $3s^1$ | Na· |
| 2A | Be | [He] $2s^2$ | ·Be· | Mg | [Ne] $3s^2$ | ·Mg· |
| 3A | B | [He] $2s^2 2p^1$ | ·B· | Al | [Ne] $3s^2 3p^1$ | ·Al· |
| 4A | C | [He] $2s^2 2p^2$ | ·C· | Si | [Ne] $3s^2 3p^2$ | ·Si· |
| 5A | N | [He] $2s^2 2p^3$ | ·N: | P | [Ne] $3s^2 3p^3$ | ·P: |
| 6A | O | [He] $2s^2 2p^4$ | :O: | S | [Ne] $3s^2 3p^4$ | :S: |
| 7A | F | [He] $2s^2 2p^5$ | ·F: | Cl | [Ne] $3s^2 3p^5$ | ·Cl: |
| 8A | Ne | [He] $2s^2 2p^6$ | :Ne: | Ar | [Ne] $3s^2 3p^6$ | :Ar: |

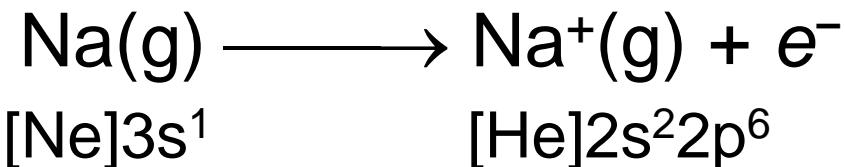
- Lewis proposed to use **chemical symbols plus dots** (●) to represent the valence electrons around an atom: **one dot → one valence electron.**
- Main-group atoms (not transition metal) tend to get, lose or share electrons until they are surrounded by **8 valence electrons (octet rule, stable noble-gas configuration).**

Ionic Bonding

(Ionic Compounds: Metal + Non-Metal mostly)

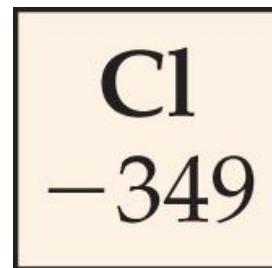
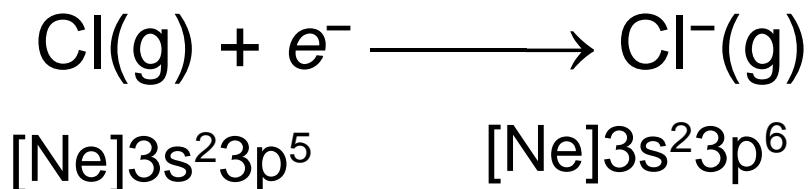


Energetics of Ionic Bonding



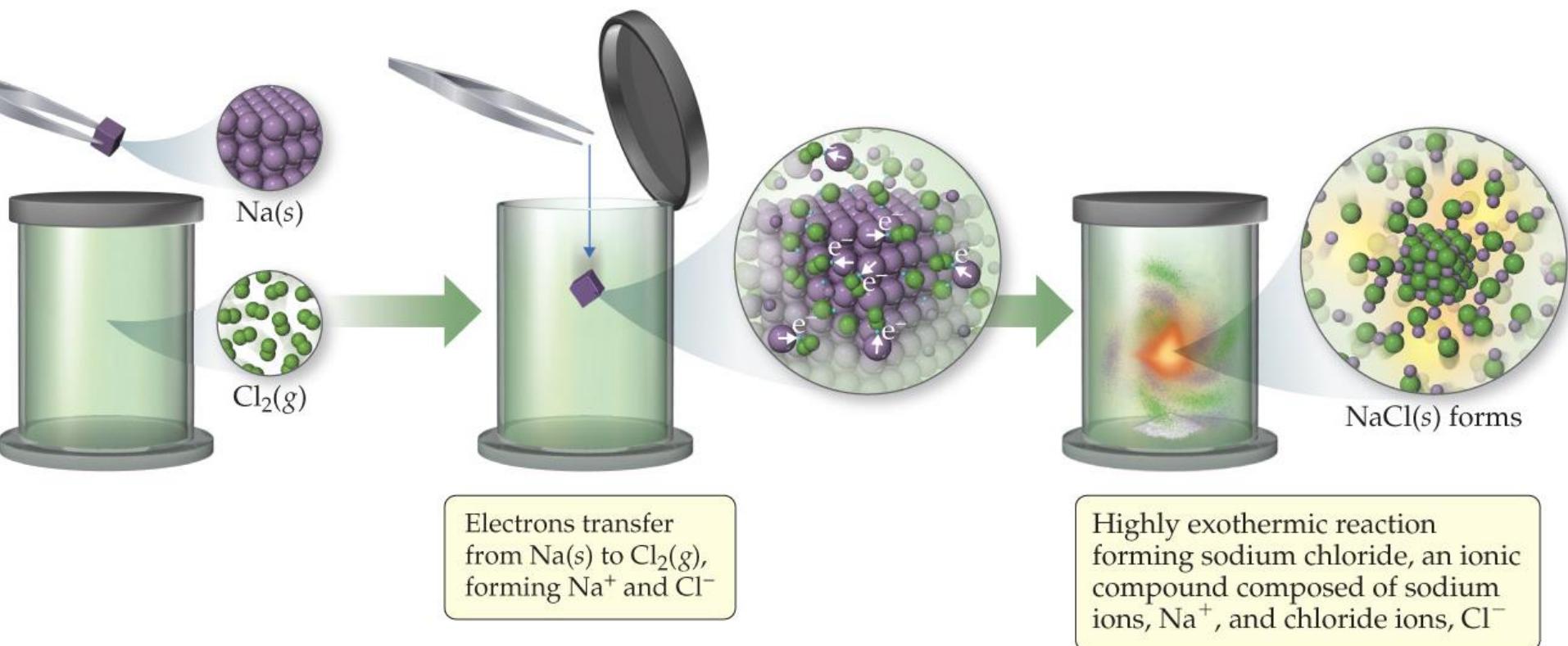
Ionization energy
 (I_1) : 496

It takes 496 kJ/mol to remove the first electron from sodium atoms.

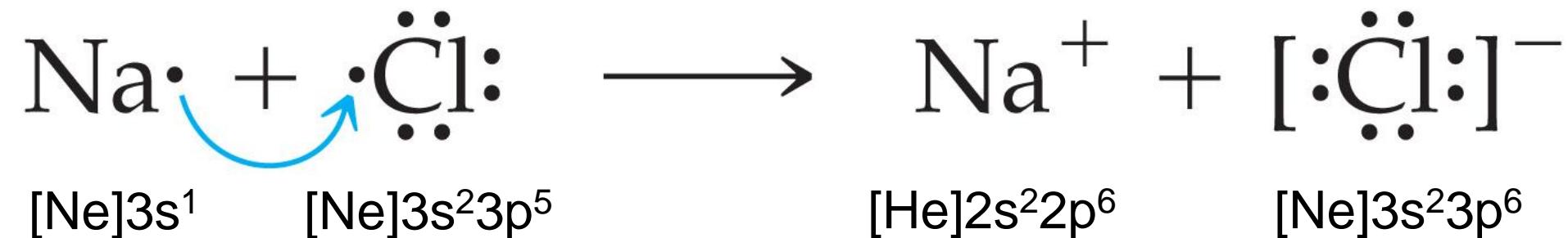


Electron affinity

We **get** 349 kJ/mol **back** by giving electrons to chlorine atoms.



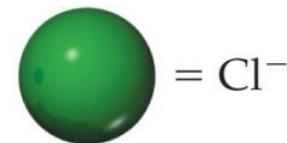
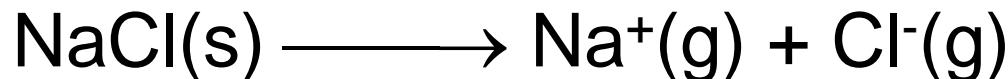
These two numbers ($496 - 349 \text{ kJ} = 147 \text{ kJ}$) don't explain why the reaction of sodium metal and chlorine gas to form sodium chloride is **so exothermic** ($\Delta H_f^0 = -410.9 \text{ kJ}$)!



- There must be a third piece to the puzzle.
- What is as yet unaccounted for is the **electrostatic attraction** between the newly formed **sodium cation & chloride anion**, after one *electron transfer* from Na to Cl.

Lattice (晶格) Energy

- This third piece of the puzzle is the **lattice energy**:
The energy required to completely separate 1 mole of a solid ionic compound into its gaseous ions.



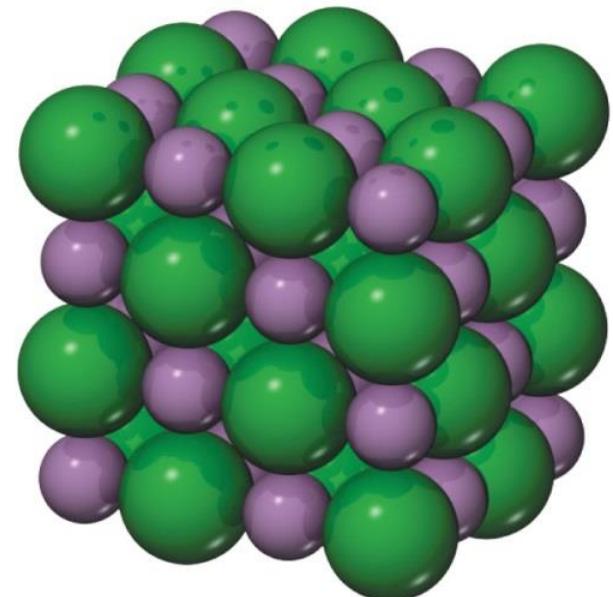
Each Na⁺ ion surrounded by six Cl⁻ ions

Each Cl⁻ ion surrounded by six Na⁺ ions

- The energy associated with electrostatic interactions is governed by Coulomb's law:

$$E_{\text{el}} = \kappa \frac{Q_1 Q_2}{d}$$

Q: charges
d: distance



| Compound | Lattice Energy (kJ/mol) | Compound | Lattice Energy (kJ/mol) |
|----------|----------------------------|-------------------|----------------------------|
| LiF | 1030 | MgCl ₂ | 2326 |
| LiCl | 834 | SrCl ₂ | 2127 |
| LiI | 730 | | |
| NaF | 910 | MgO | 3795 |
| NaCl | 788 | CaO | 3414 |
| NaBr | 732 | SrO | 3217 |
| NaI | 682 | | |
| KF | 808 | ScN | 7547 |
| KCl | 701 | | |
| KBr | 671 | | |
| CsCl | 657 | | |
| CsI | 600 | | |

size

size

M²⁺

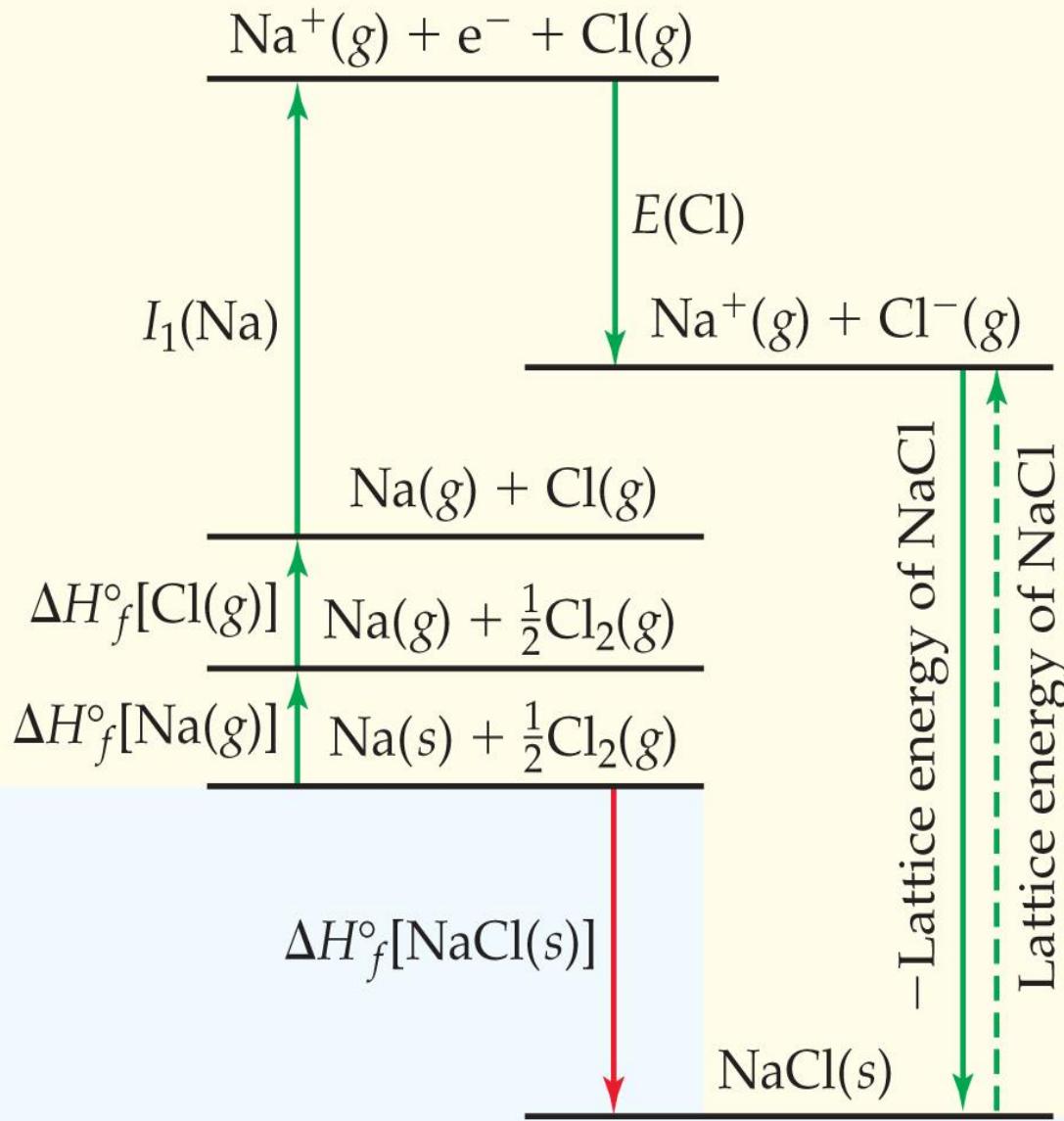
M²⁺

M³⁺

- Lattice energy **increases with the charge & decreasing size** of ions.

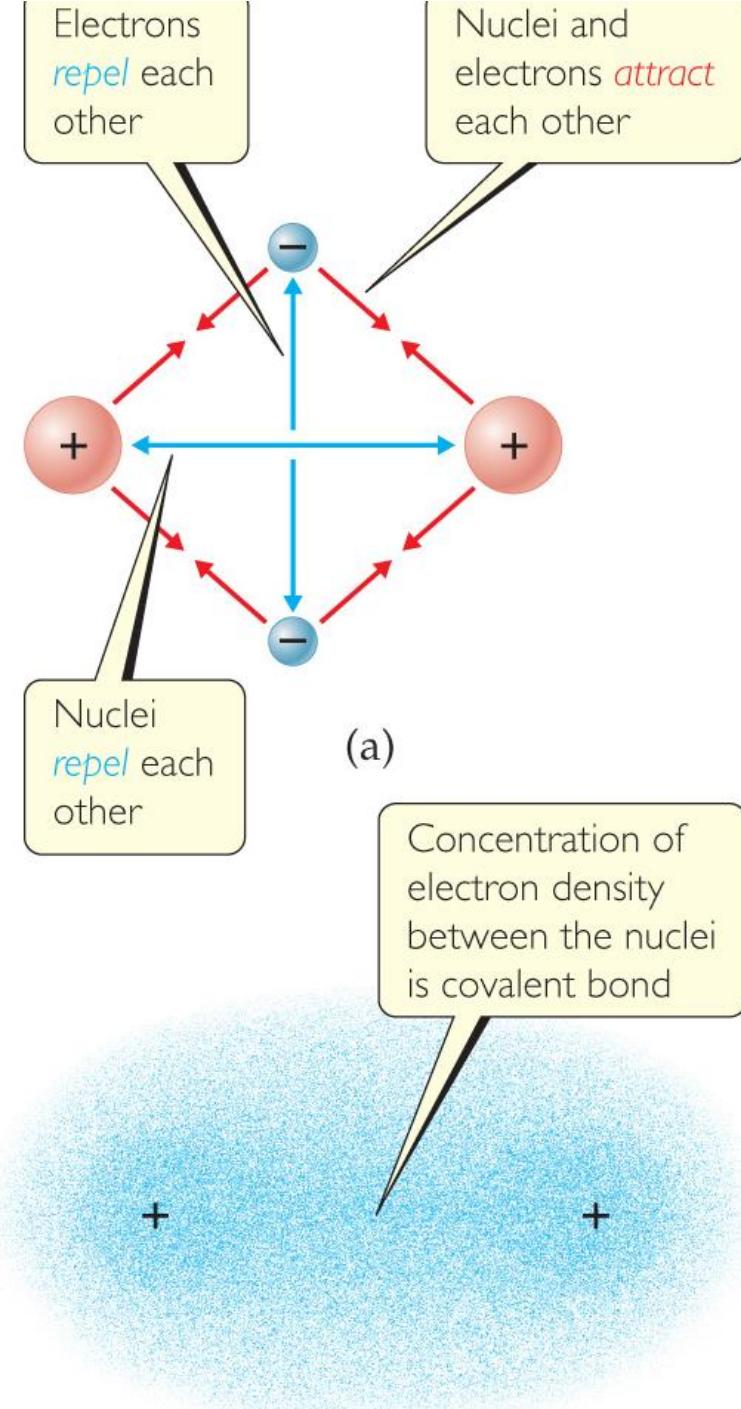
- Ionic compounds: high melting points & usually crystalline (结晶).

Energetics of Ionic Bonding



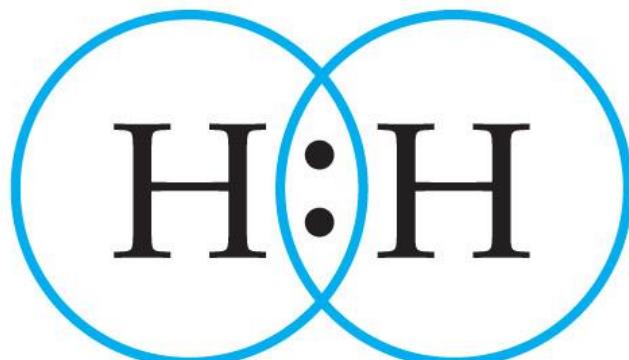
By accounting for all three energies (**ionization energy**, **electron affinity**, & **lattice energy**), we can get a good idea of the energetics involved in such a process: Born-Haber cycle.

Covalent (共价) **Bonding**

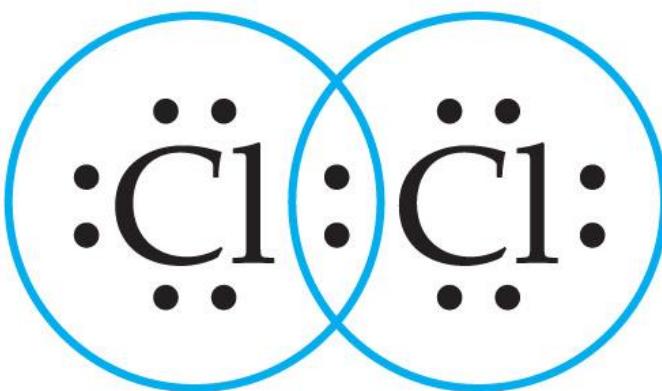
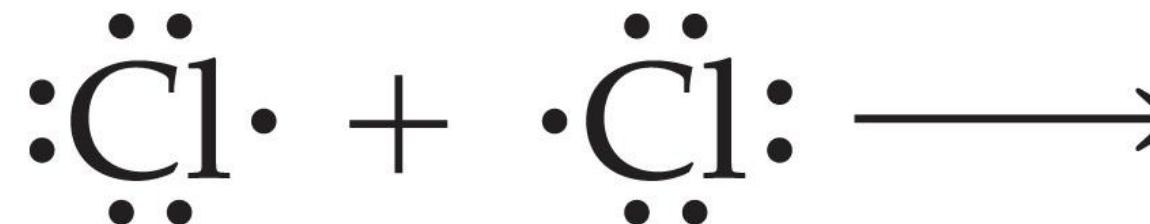


- Lewis proposed that atoms **share electrons** (**1 single covalent bond with 2 electrons**) in covalent bonds (e.g. in H_2), in order to fulfill octet rule (or noble gas configuration).

- There are several **electrostatic interactions**:
 - Attractions** between electrons & nuclei (**major**),
 - Repulsions** between electrons,
 - Repulsions** between nuclei.



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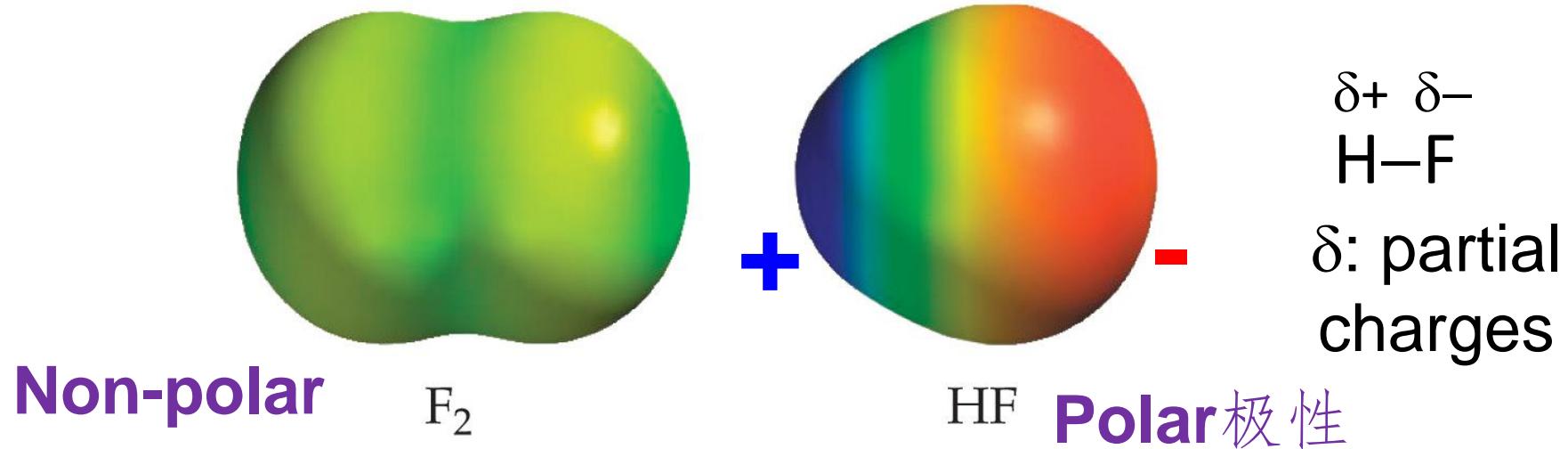
Cl atoms share electrons until they are surrounded by **8 valence electrons** ([octet rule](#), or stable noble-gas configuration).

Multiple Bonds

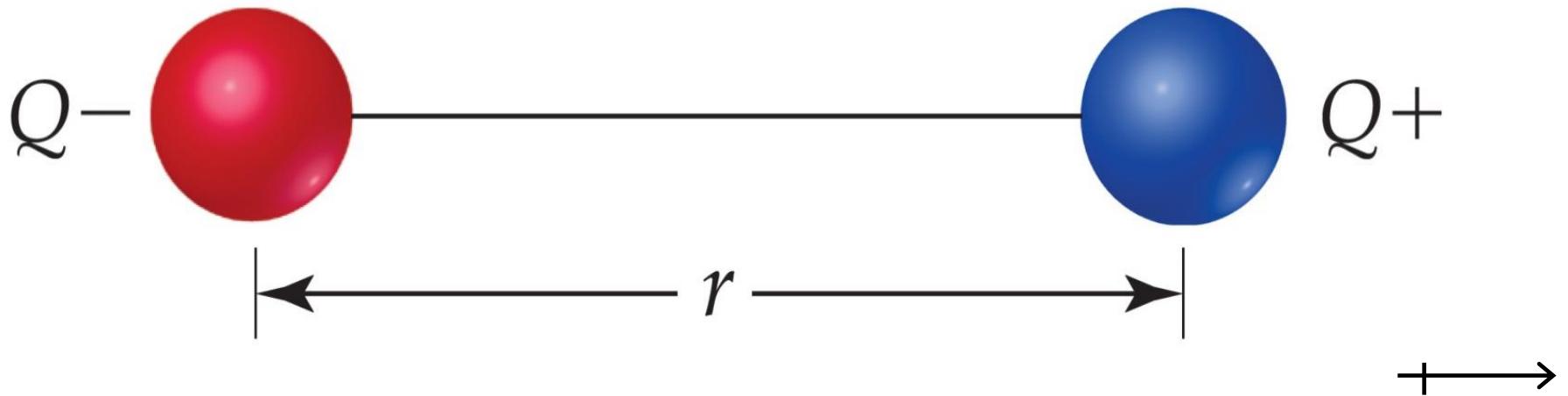
- Two atoms share only **one pair** of electrons: **single bond**.
- Sometimes, **two pairs** of electrons need to be shared between two atoms: **double bonds**.
- **Three pairs** of electrons are shared between two atoms: **triple bonds**.



Non-Polar & Polar Covalent Bonds



- Although atoms often form compounds by sharing electrons, the electrons are **NOT always shared equally** (均等地) between two atoms.
- Fluorine pulls harder/stronger on the electrons it shares with hydrogen than hydrogen does.
- The **fluorine** end of the molecule has **more electron density (negative charge)** than the hydrogen end.

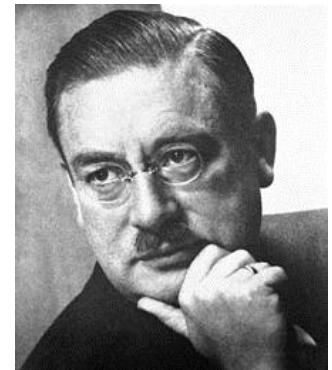


$$\text{Dipole moment } \mu = Qr$$

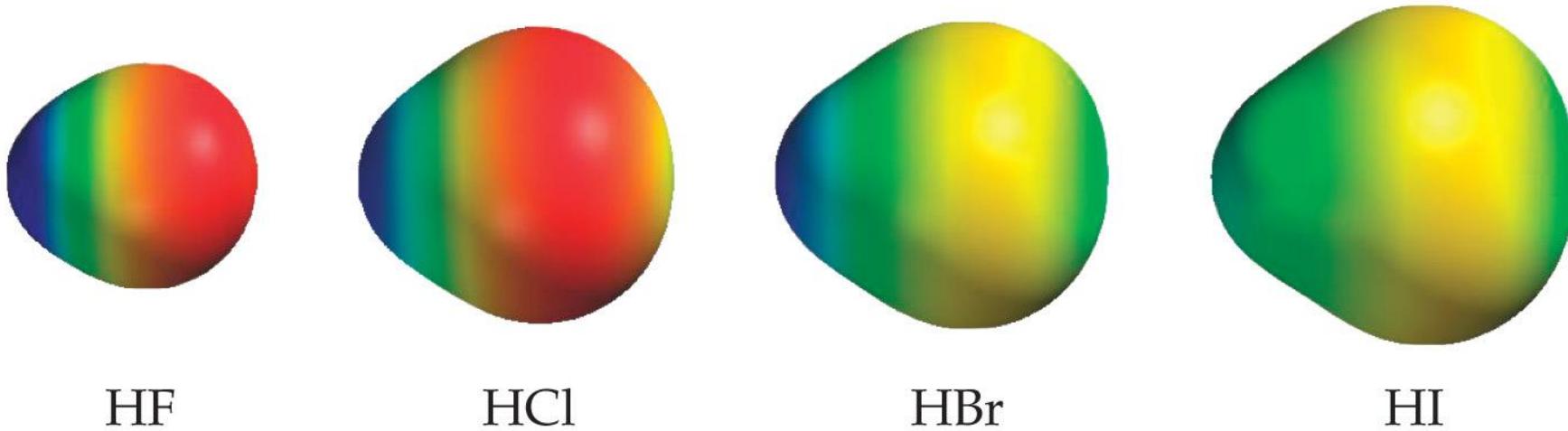
- When two atoms **share electrons unequally**, a **bond dipole** (偶极) results.
- The **dipole moment**, μ , (unit: debyes, D; 1 D = 3.335641×10^{-30} C*m or 0.208194 e*Å) produced by two equal but opposite charges separated by a distance, r , is calculated:

$$\mu = Qr$$

Peter Debye



| Compound | Bond Length (Å) | Electronegativity Difference | Dipole Moment (D) |
|----------|-----------------|------------------------------|-------------------|
| HF | 0.92 | 1.9 | 1.82 |
| HCl | 1.27 | 0.9 | 1.08 |
| HBr | 1.41 | 0.7 | 0.82 |
| HI | 1.61 | 0.4 | 0.44 |



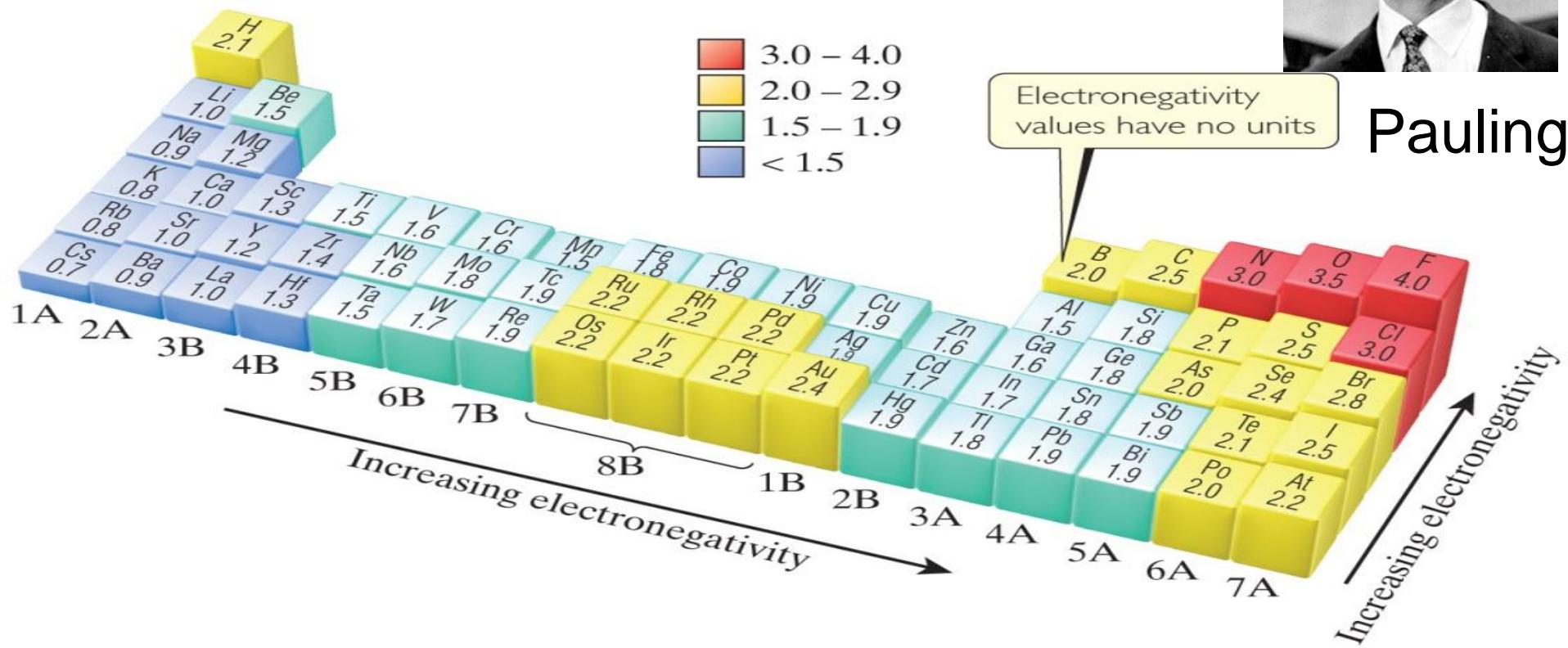
The **greater** the **electronegativity difference** of 2 atoms, the **more polar** the bond (which can influence **solubility & some physical & chemical properties**).

Electronegativity (EN, 电负性)

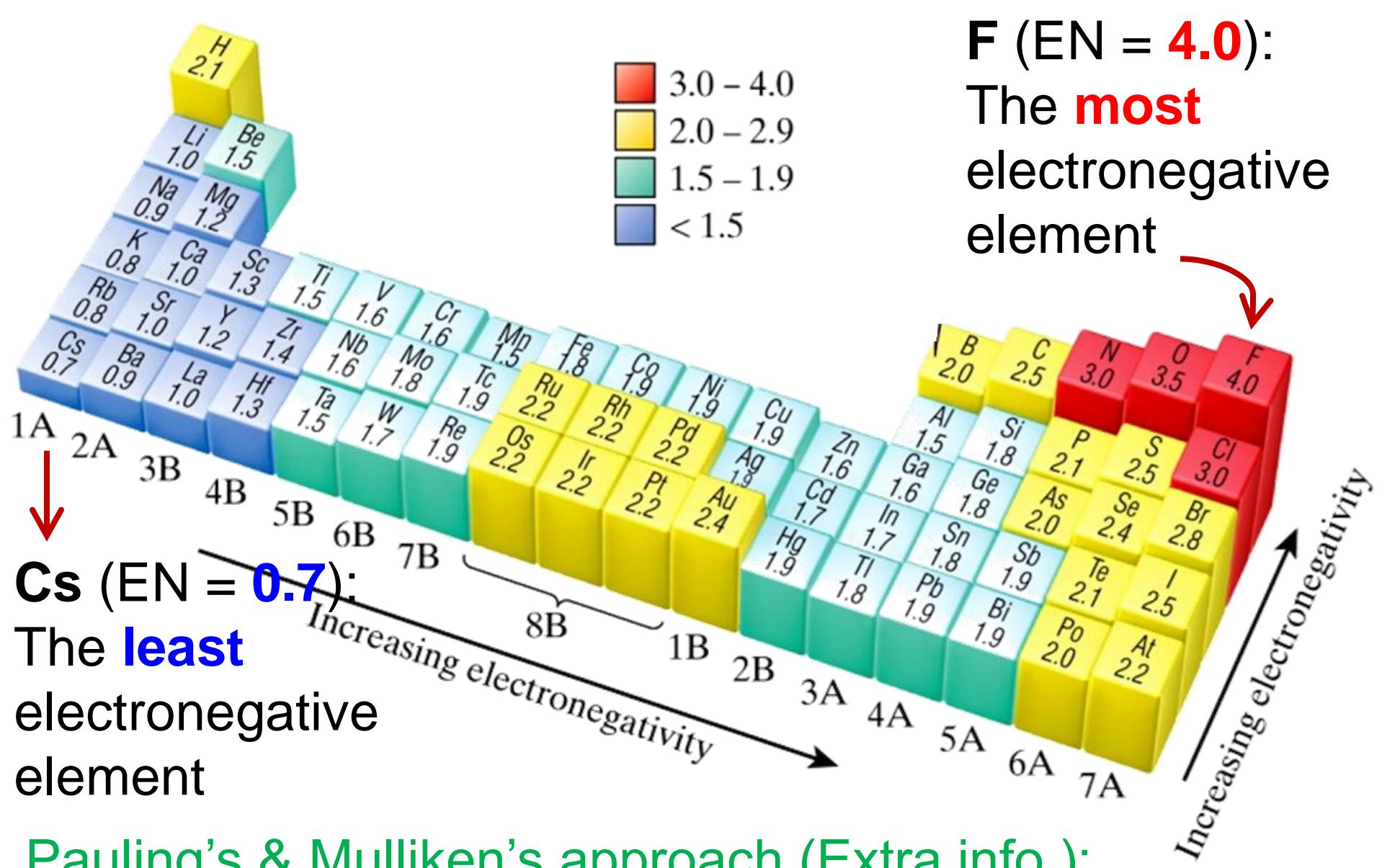
- **Electronegativity:** the ability of atoms in a molecule to **attract electrons** to themselves.
- On the periodic chart, electronegativity **increases**:
 1. from **left to right** across a row.
 2. from the **bottom to the top** of a column.



Pauling



F (EN = 4.0):
The **most**
electronegative
element



Pauling's & Mulliken's approach (Extra info.):

$$\chi_A - \chi_B = (eV)^{-1/2} \sqrt{E_d(AB) - [E_d(AA) + E_d(BB)]/2}$$

$$\chi = (E_i + E_{ea})/2$$

Electronegativity and Bonding

Electronegativity (EN) difference tells us approximated bonding types: **ionic or** (polar or non-polar) **covalent**.

The **greater the difference in EN** between the two elements forming the bond, the **more ionic** the bond.

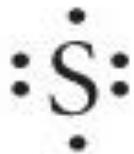
Typical ranges:

| EN difference | Type | Example | EN |
|------------------------------------|-----------------------|---------|---------------|
| > 2.0 | Ionic | LiF | 4.0-1.0 = 3.0 |
| 0.5-2.0 | polar covalent | HF | 4.0-2.1 = 1.9 |
| <0.5 (Li ₂ molecule) | covalent | F–F | 4.0-4.0 = 0.0 |
| | covalent | C–H | 2.5-2.1 = 0.4 |
| | covalent | Li –Li | 1.0-1.0 = 0.0 |
| | covalent | Au–C | 2.5-2.4 = 0.1 |

Some chemical bonds could contain **ionic (complete electron transfer)** & **covalent (complete sharing)** characters.

The Lewis symbol for a sulfur atom includes how many dots?

- a. 5
- b. 6
- c. 7
- d. 8



The octet rule states that atoms tend to gain, lose, or share electrons until they have _____ valence electrons.

- a. 5
- b. 6
- c. 7
- d. 8

Which compound below has the largest lattice energy?

- a. NaCl
- b. KBr
- c. CaO
- d. CsI

Which choice below correctly lists the elements in order of increasing electronegativity (least → most)?

- a. C < N < O < F
- b. N < C < O < F
- c. N < C < F < O
- d. C < N < F < O

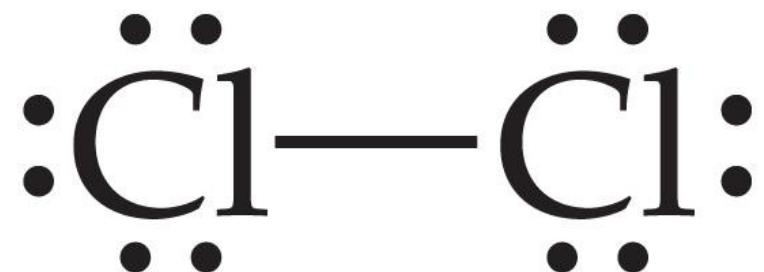
Describe the electron transfers that occur in the formation of calcium fluoride from elemental calcium and elemental fluorine.

- A. Each calcium atom loses one electron and each fluorine atom gains two electrons.
- B. Each calcium atom loses two electrons and each fluorine atom gains one electron.
- C. Each calcium atom gains one electron and each fluorine atom loses two electrons.
- D. Each calcium atom gains two electrons and each fluorine atom loses one electron.

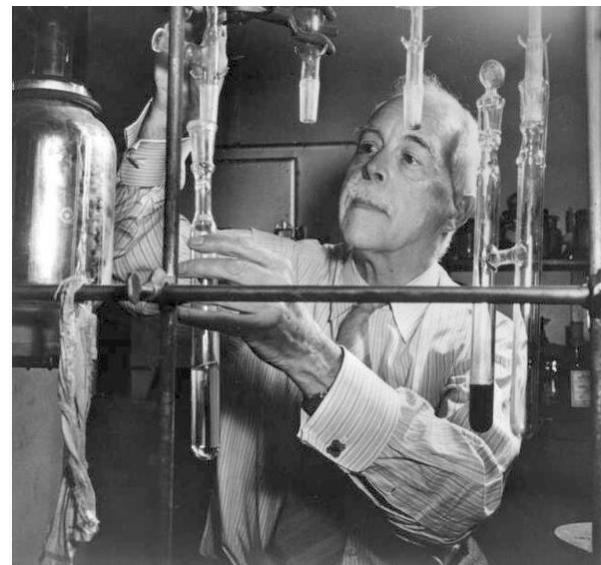
If the charged particles are moved closer together, does μ increase, decrease, or stay the same?

- A. Increase, because r increases.
- B. Decrease, because r decreases.
- C. Stays the same because the values of Q and r change in opposite but equal directions.

Lewis Structures

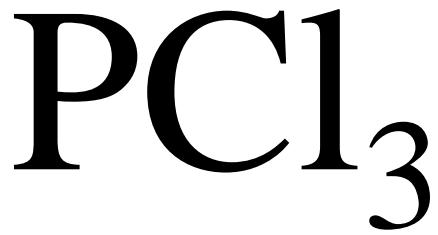


Lewis structures are representations of molecules showing all valence electrons: bonding (by lines) & nonbonding (lone-pair 孤对, by dots) electrons.



Gilbert Newton Lewis

Writing Lewis Structures



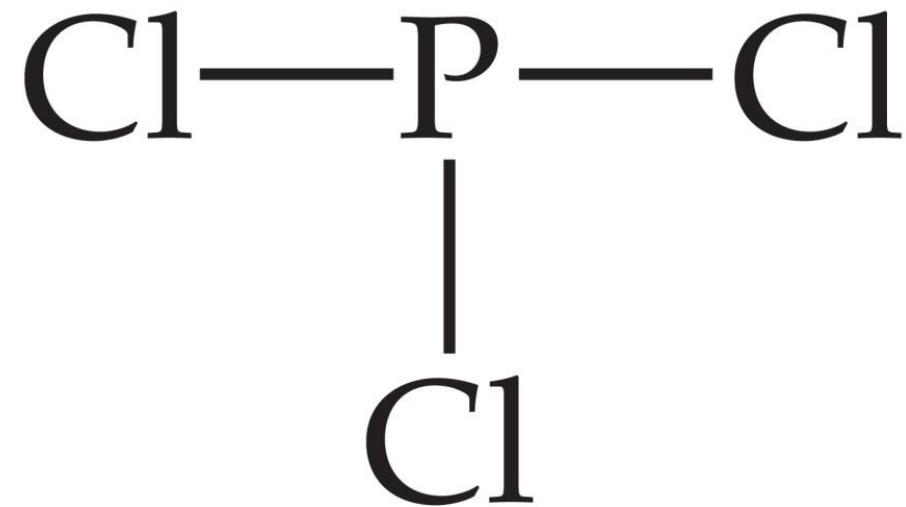
Keep track of the

total valence electrons:

$$5 + 3*7 = \textcolor{red}{26}$$



1. Count the total number of **valence electrons** of all atoms in the polyatomic ion or molecule.
 - If it is **an anion**, **add one electron** for each negative charge.
 - If it is **a cation**, **subtract one electron** for each positive charge.



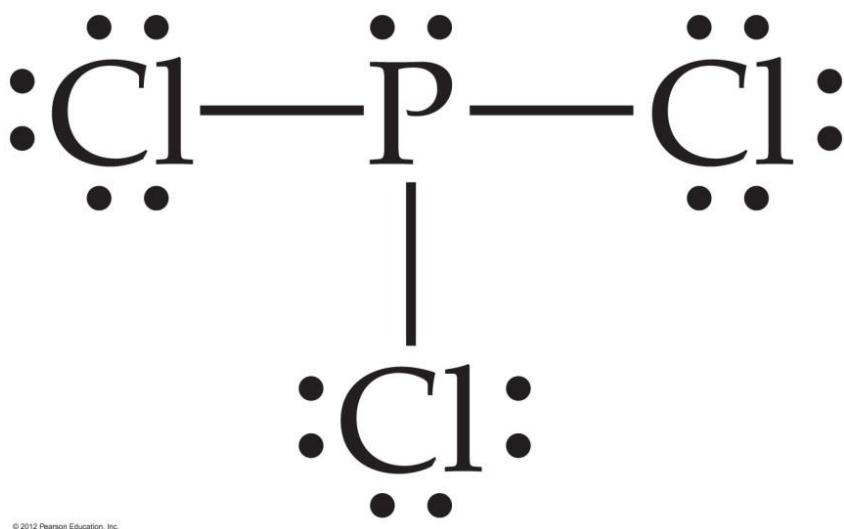
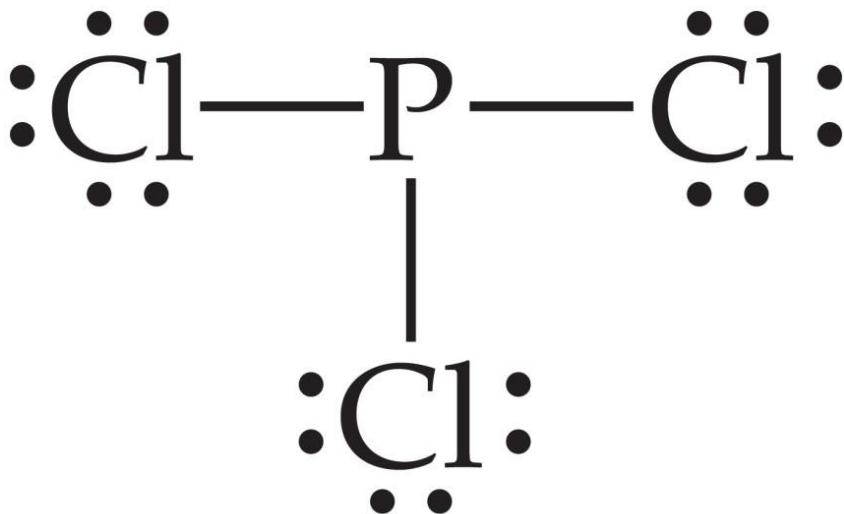
Keep track of the electrons:

$$26 - 6 = 20$$

(3 covalent bonds with 6 e⁻)

2. The **central atom** is the ***least electronegative element*** (→ less valance electrons & need more bonds) except hydrogen.

Generally **connect** the outer atoms to it by **single bonds**.



3. Fill the octets of the outer atoms (higher EN).

Keep track of the electrons:

$$[26 - 6 = 20;$$

(3 covalent bonds with 6 e⁻)

$$20 - 18 = 2$$

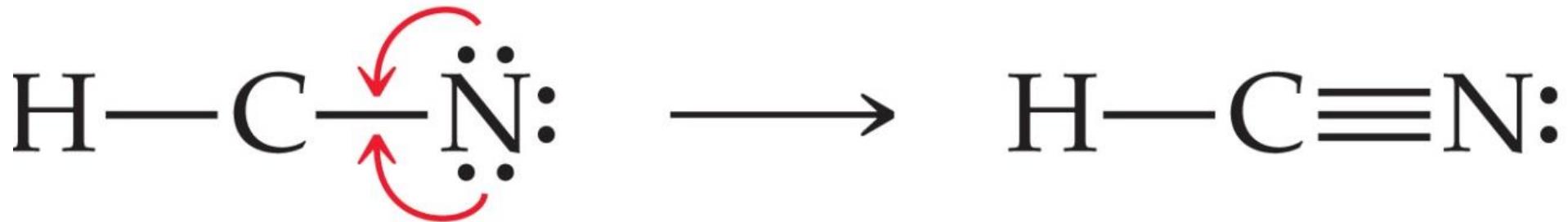
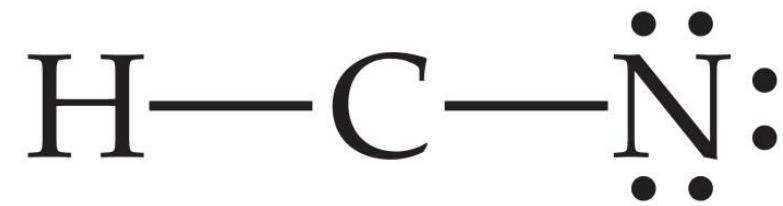
(3*3 lone-pair e⁻, 9*2 e⁻)

4. Fill the octet of the central atom (lower EN).

Keep track of the electrons:

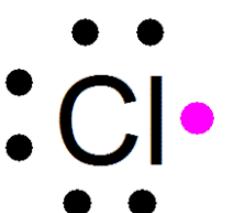
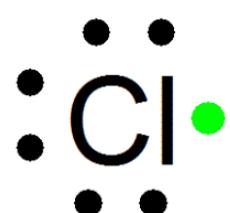
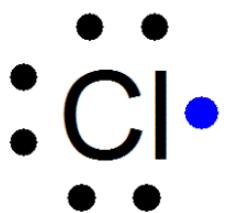
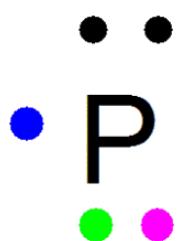
$$2 - 2 = 0$$

(1 lone-pair e⁻ on P)



5. If you run **out of electrons** before the central atom meet an octet rule, you can **form multiple bonds** (double bond or triplet bond) until it meets.

Writing Lewis Structures (My Method)

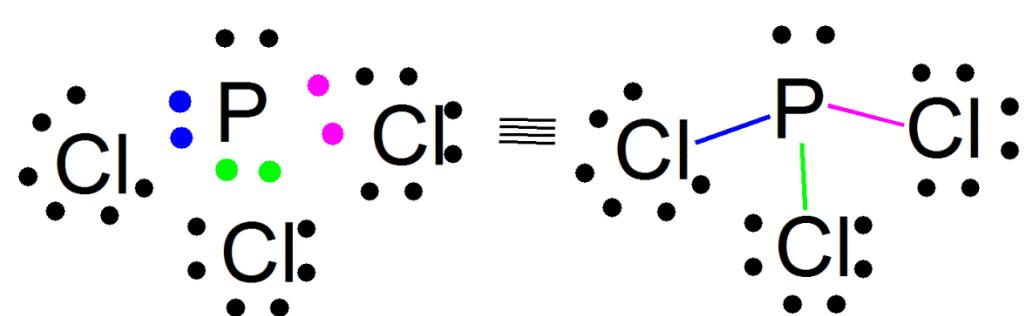


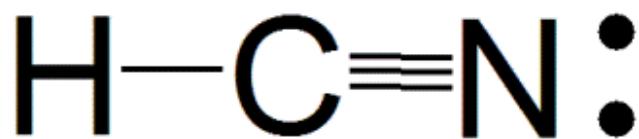
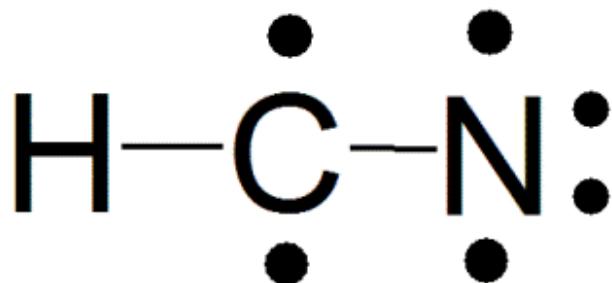
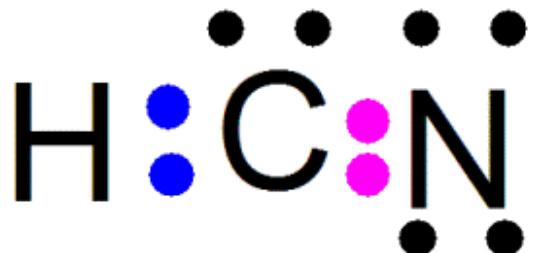
1. Write all atoms and their valence electrons.

2. Count how much **missing electrons** to achieve the **octet rule**: P misses $3e^-$ & Cl miss $1e^-$.

→ To fulfill the octet rule, try to **form number of bonds**, which is **same as** number of the “**missing electron**”:

P needs 3 bonds; Cl needs 1 bond.

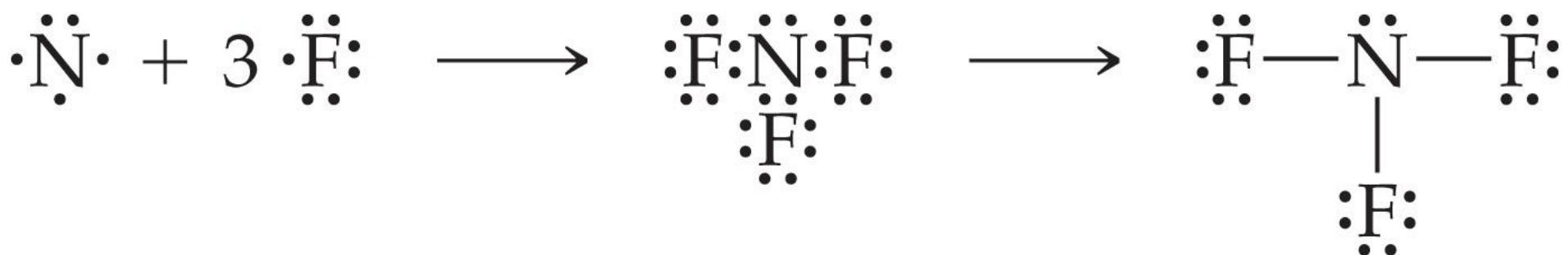
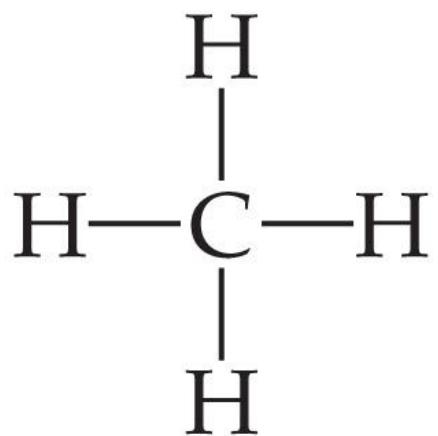
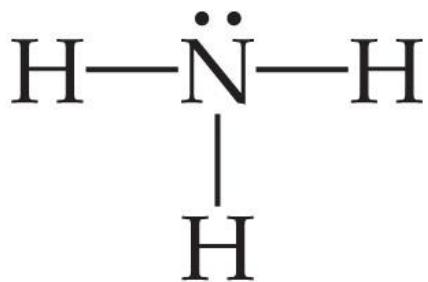
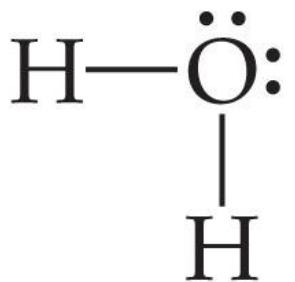




H misses $1e^-$, C misses $4e^-$ & N misses $3e^-$.

→ H needs 1 bonds; C needs 4 bond; N needs 3 bond.

H-C bond is formed and C-N triple bond is needed.



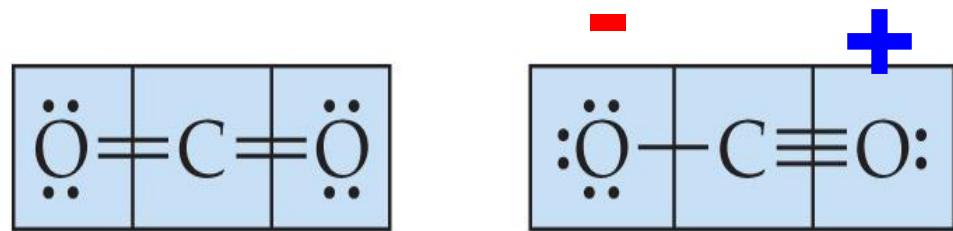
(or $\ddot{\text{O}}=\text{C}=\ddot{\text{O}}$)



(or $:\text{N}\equiv\text{N}:)$

Formal Charge

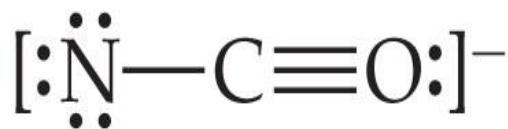
- Assign formal charges of **each atom** in all Lewis structures.
 - Count the electrons in (non-bonding) **lone pairs** ($2e^-$ each **pair**) and **half the bonding electrons** ($1e^-$ each **bond**) it shares with other atoms (**N**).
 - Subtract that (**N**) from the number of **valence electrons** N_{VE} for that atom: the difference is its **formal charge** ($N_{VE} - N$).



| | | | | | | |
|--------------------------------|---|---|---|----|---|----|
| Valence electrons: | 6 | 4 | 6 | 6 | 4 | 6 |
| -(Electrons assigned to atom): | 6 | 4 | 6 | 7 | 4 | 5 |
| Formal charge: | 0 | 0 | 0 | -1 | 0 | +1 |

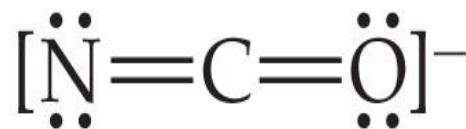
- The **dominant** (likely **most stable**) **Lewis structure**
 - is the one with **the fewest charges** (least unfavorable charge separation).
 - puts a **negative charge** on the **most electronegative atom** (or a **positive charge** on the **least electronegative atom**).

-2 0 +1



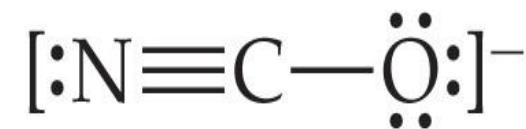
(i)

-1 0 0



(ii)

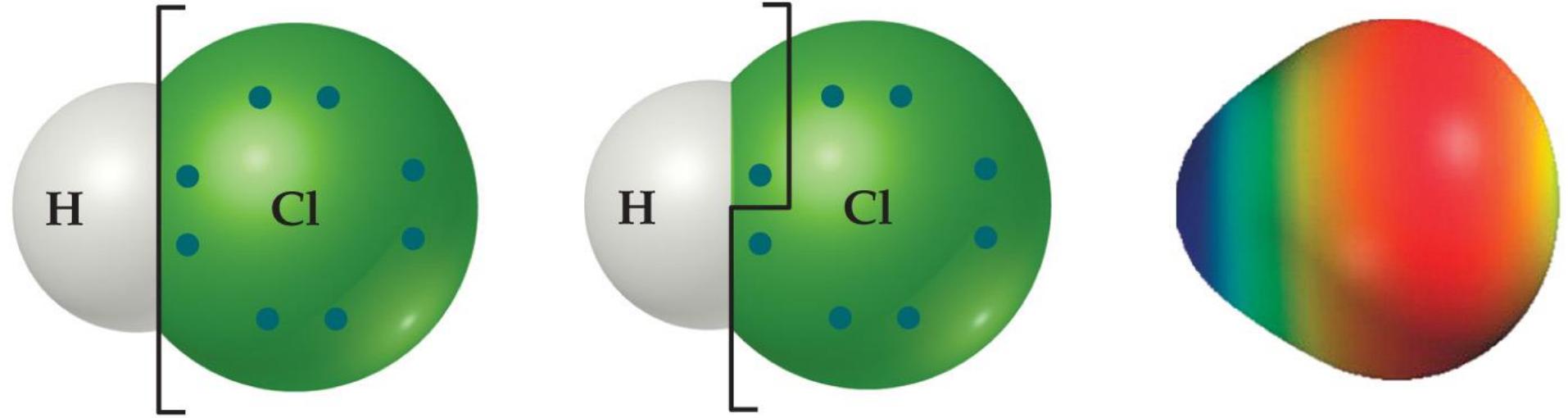
0 0 -1



(iii)



Oxidation Number, Formal Charge & Electron Density Distribution



Oxidation number

H: +1; Cl: -1

(**Ionic**; complete electron transfer)

Formal charge

H: 0; Cl: 0

(**Covalent**; equal sharing of electrons)

Realistic
electron
distribution

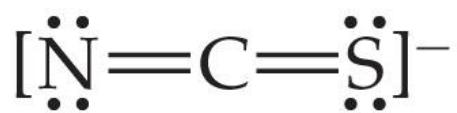
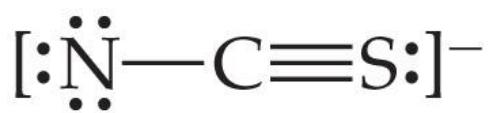
The carbon disulfide (CS_2) molecule has

- a. two single bonds.
- b. two double bonds.
- c. a single bond and a double bond.
- d. a single bond and a triple bond.

The formal charge on the nitrogen atom in the nitrate ion (NO_3^{1-}) is

- a. +2
- b. +1
- c. 0
- d. -1

Three possible Lewis structures for the thiocyanate ion, NCS⁻

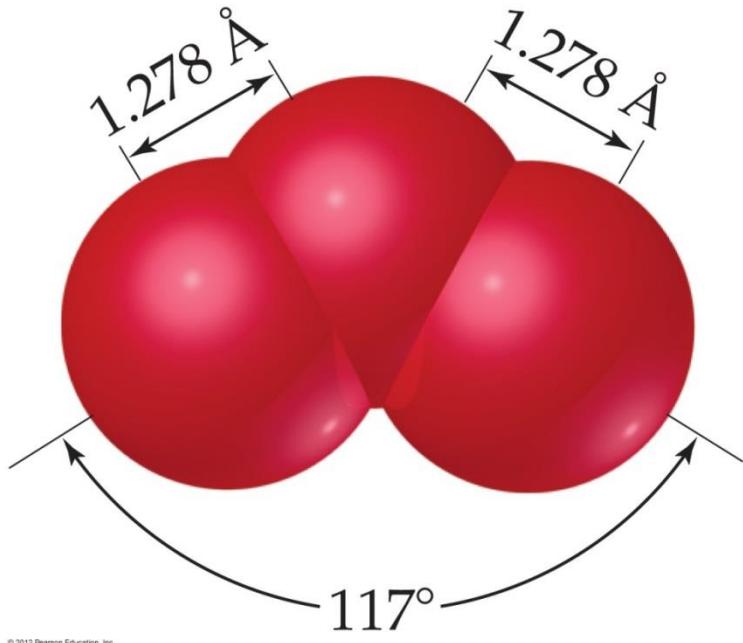
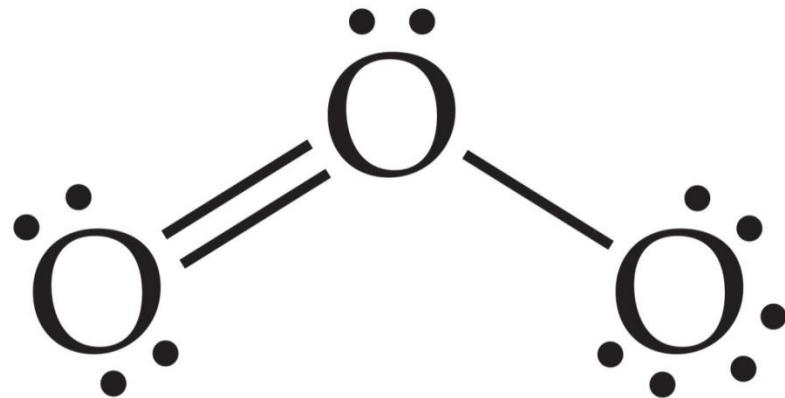


- (a) Determine the formal charges in each structure.
- (b) Based on the formal charges, which Lewis structure is the dominant one?

Suppose a Lewis structure for a neutral fluorine-containing molecule results in a formal charge on the fluorine atom of +1. What conclusion would you draw?

- A. The structure actually represents an ion.
- B. The F atom in the structure must have four covalent bonds attached to it.
- C. There must be another F atom in the structure carrying a –1 formal charge, since F is the most electronegative element and it should carry a negative formal charge.
- D. There must be a better Lewis structure, since F is the most electronegative element and it should carry a negative formal charge.

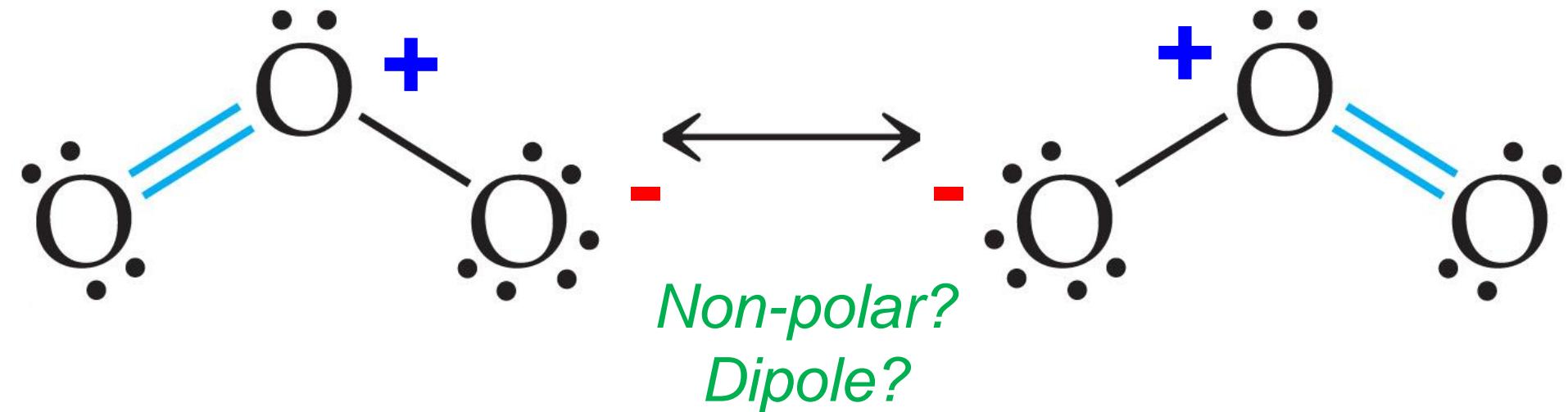
Resonance (共振) Structures



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The true & observed structure of ozone has the same O-O bond lengths and a charge of -1/2 for both outer oxygen atoms.

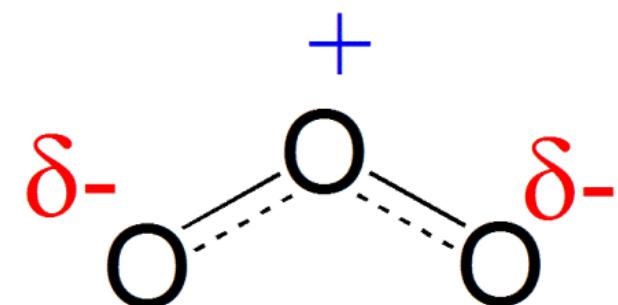
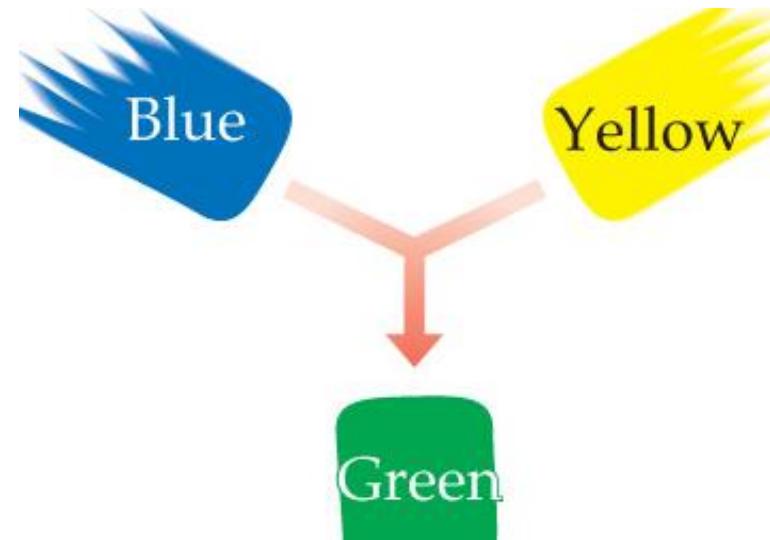
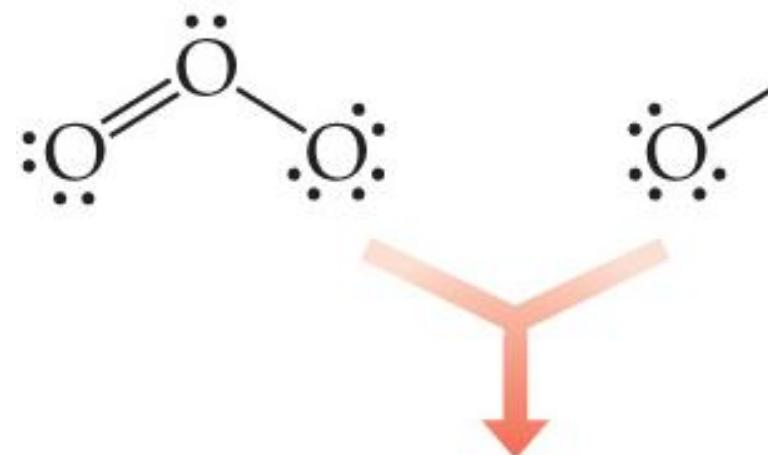
Basic Concepts
of Chemical
Bonding



- **One Lewis structure** cannot accurately depict a molecule like ozone.
- We use **multiple structures**, **resonance structures**, to describe the molecule.
- **Extra info.:** The **more the resonance structures**, the **more stabilization** the molecule.

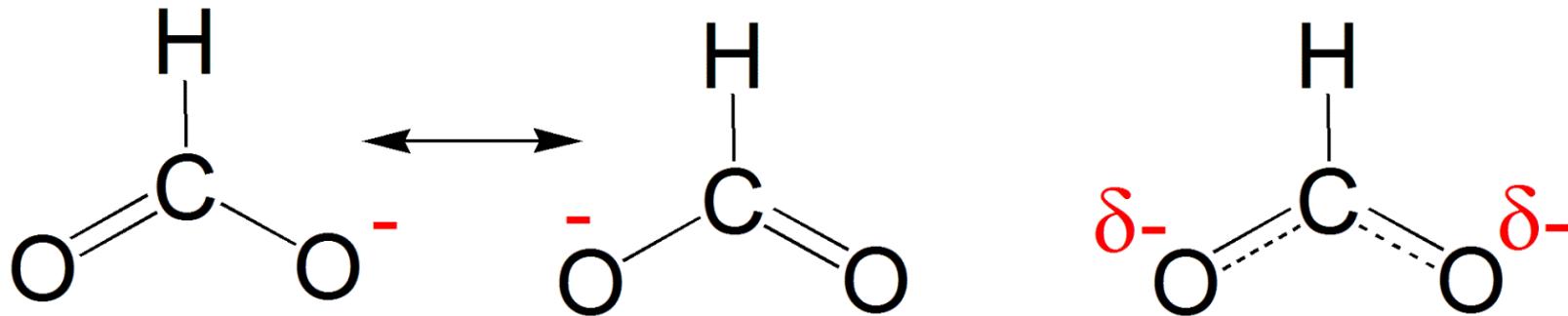
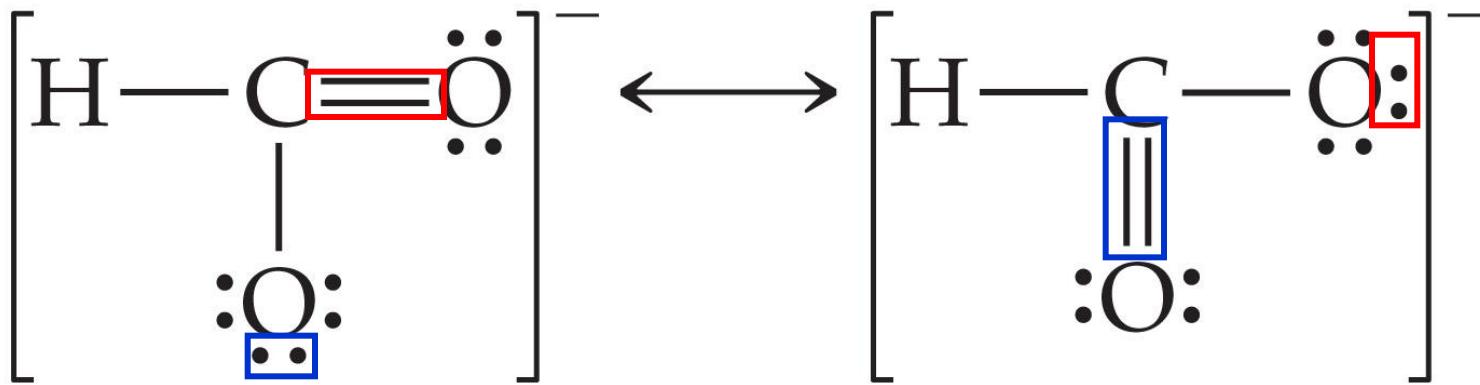
Resonance
structure

Resonance
structure

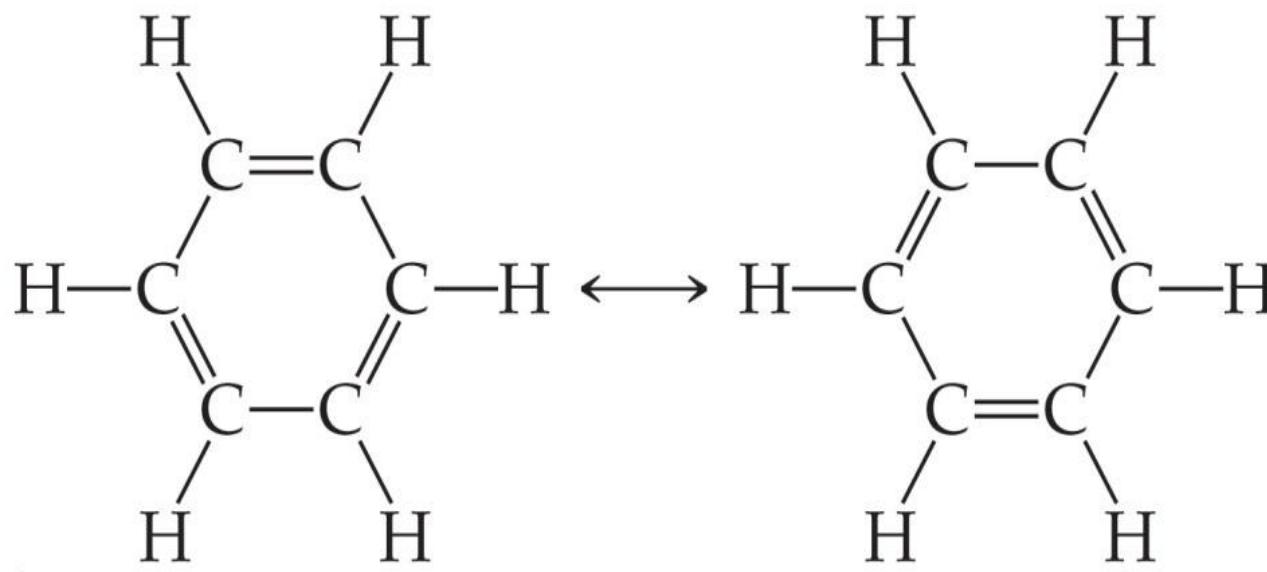


A mixture of two resonance structures: **1.5 O-O bond & -0.5 charge** on the outer oxygen atoms.

Formate (from formic acid)



- The **electrons** that form the second C-O bond in the double bonds do **not always stay** between that C & that O, but can move among the two oxygens & the carbon.
- The **electrons** are not **localized** (局域); they are **delocalized** (离域) for **resonance structures**.



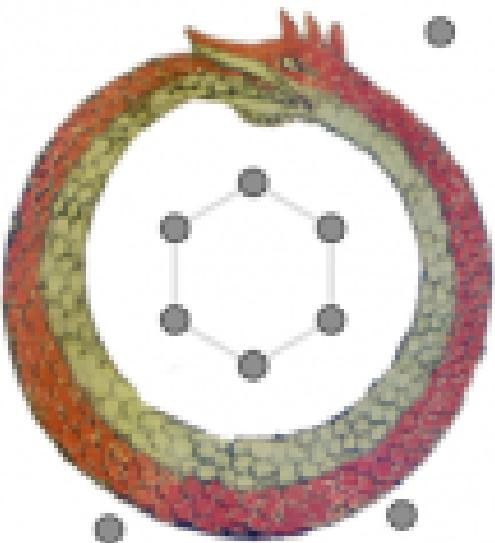
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- The organic compound **benzene**, C_6H_6 , has two resonance structures.
- It is commonly depicted as a hexagon with **a circle** inside to signify **the delocalized electrons** in the ring.

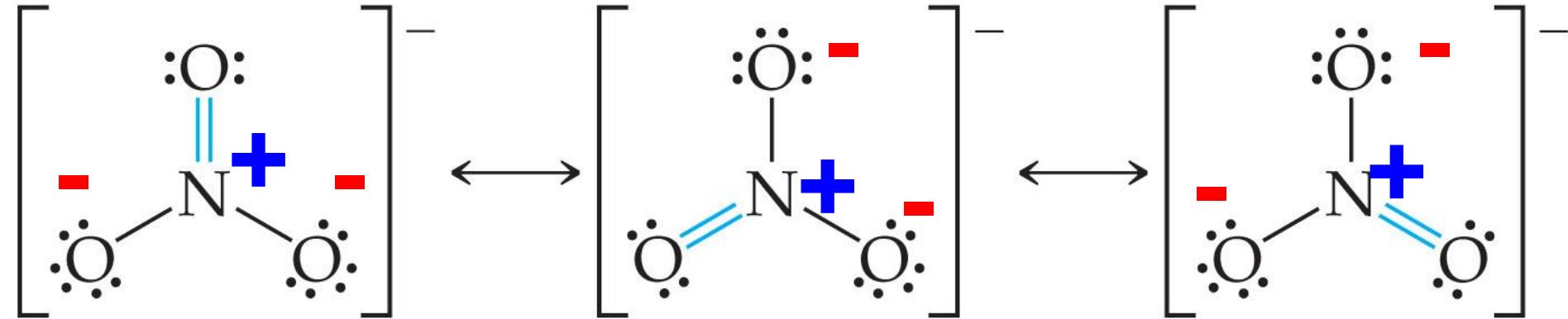
Kekule's dream



In 1890, at the 25th anniversary of the benzene structure discovery, Friedrich August Kekulé, a German chemist, reminisced (追忆说) about his major accomplishments and told of two dreams. In his first dream, in 1865, he saw **atoms dance around and link to one another.** He awakened and immediately began to sketch what he saw in his dream.

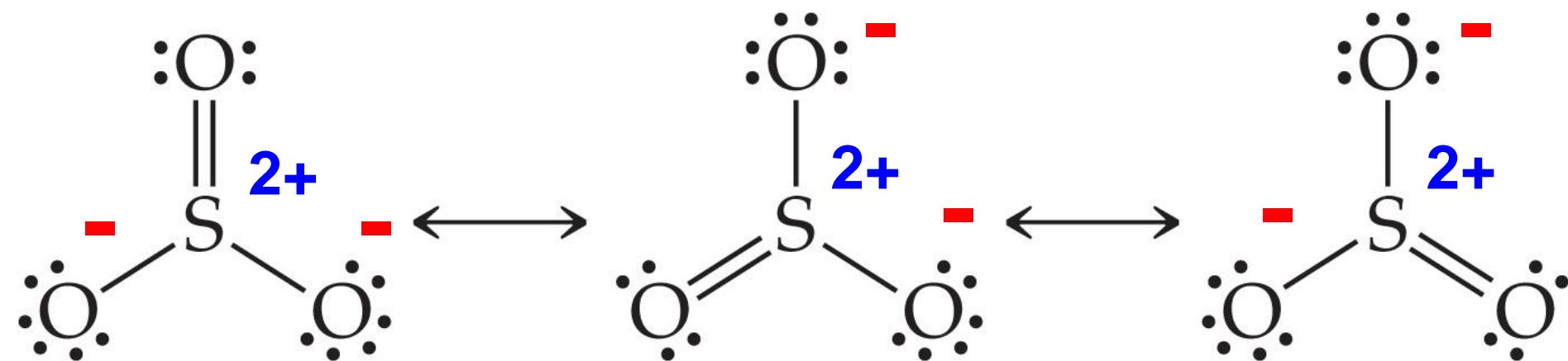
Later, Kekulé had another dream, in which he **saw atoms dance around**, then form themselves into strings, **moving about in a snake-like fashion.** This vision continued until the snake of atoms formed itself into an image **of a snake eating its own tail.** This dream gave Kekulé the idea **of the cyclic structure of benzene.**

Nitrate



1½ bond/atom

Sulfur Trioxide (S follows octet rule & *not all resonance structures shown here* -- not include hypervalence)



1½ bond/atom

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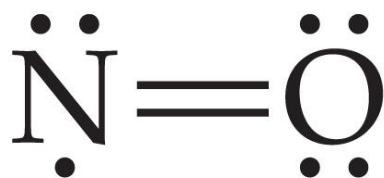
Exceptions to the Octet Rule

- There are three types of ions or molecules that **do not** follow the octet rule:
 - (I) ions or molecules with an **odd** (奇数) **number of electrons**;
 - (II) ions or molecules with **less than** an octet;
 - (III) ions or molecules with **more than eight valence electrons** (an expanded octet): **hypervalence**.

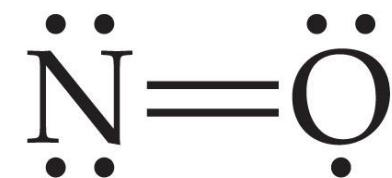
(I) Odd Number of Electrons

Although relatively rare and usually quite **unstable & reactive**, there are some ions and molecules with an odd number of electrons.

Nitric oxide



and



Which one is the dominant Lewis structure?

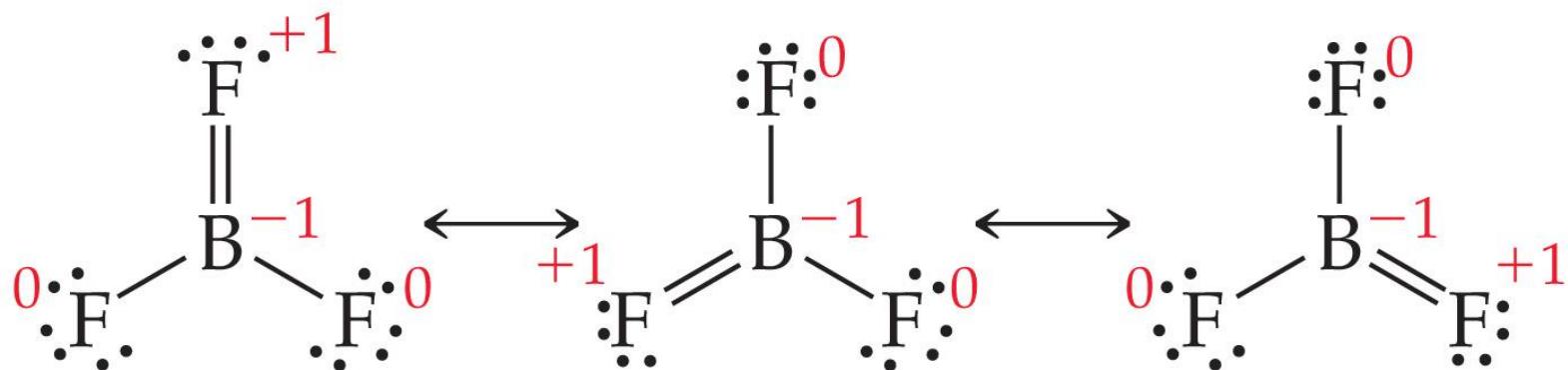
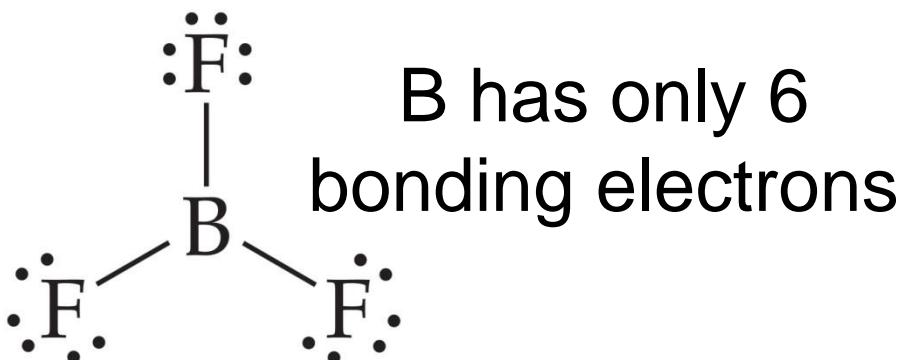
Extra info. Nitric molecule (one unpaired electron: free radical 自由基) is “a signaling molecule in the cardiovascular (心血管) systems.”



The Nobel Prize in Physiology or Medicine 1998

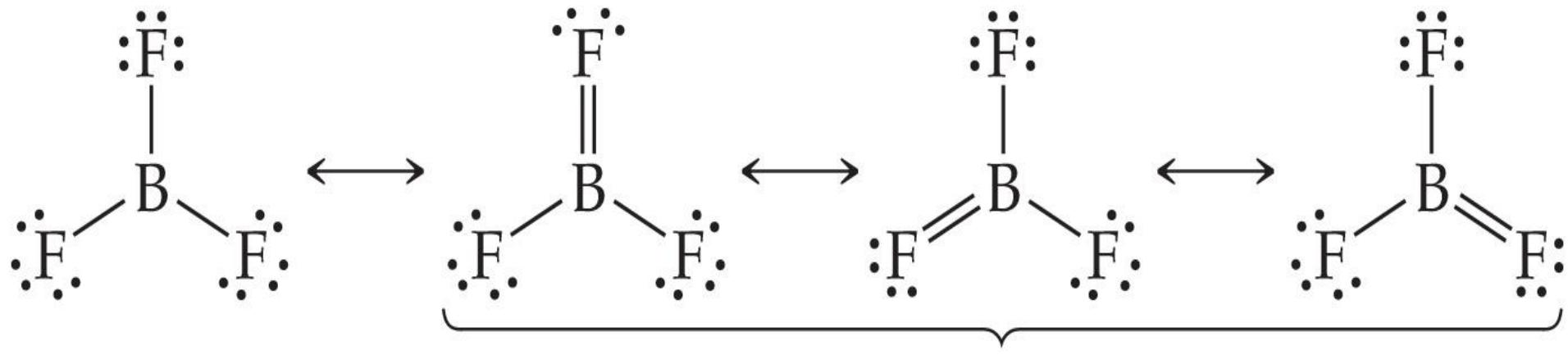
Robert F. Furchtgott, Louis J. Ignarro, Ferid Murad

(II) Fewer Than Eight Electrons



To fulfill octet rule, boron accepts two electrons from fluorine: a *negative* charge on the boron and a *positive* charge on fluorine.

This would not be an accurate picture of the distribution of electrons in BF_3 .



Dominant

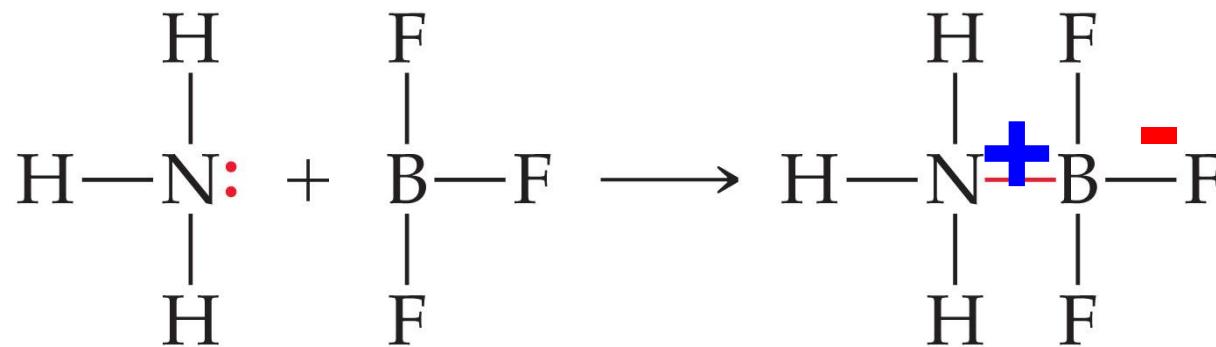
Less important

Therefore, structures that put a double bond between boron and fluorine (**the more electronegative**) are much less important than the one that leaves boron with only 6 valence electrons.

N:

1 lone-pair
electrons to
donate:

Lewis Base



B:

6 bonding
electrons:

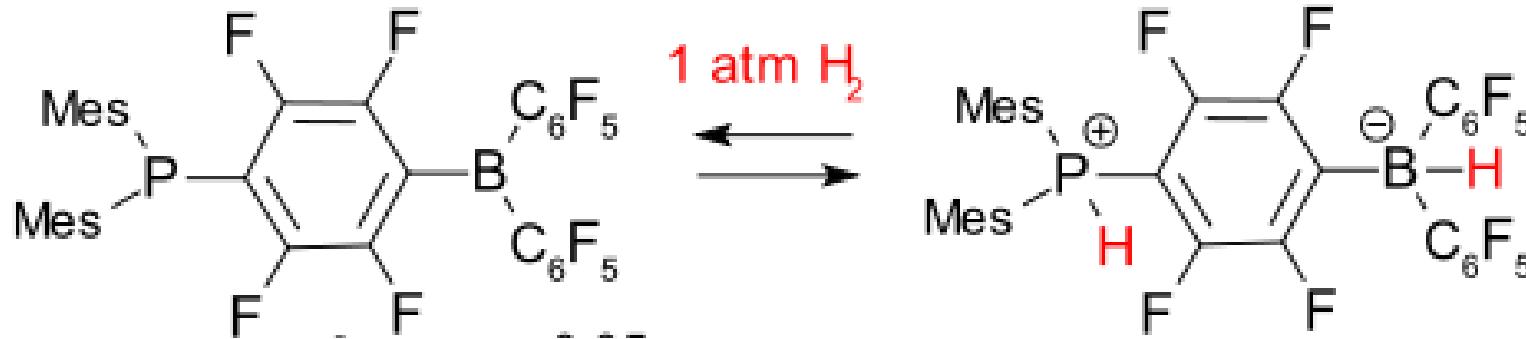
Lewis Acid

Adduct (加合物)

B:

8 bonding
electrons

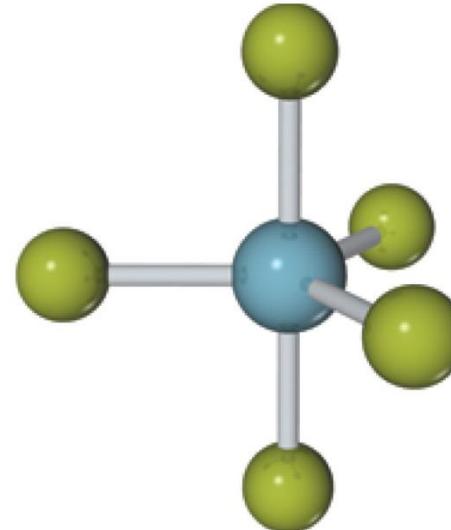
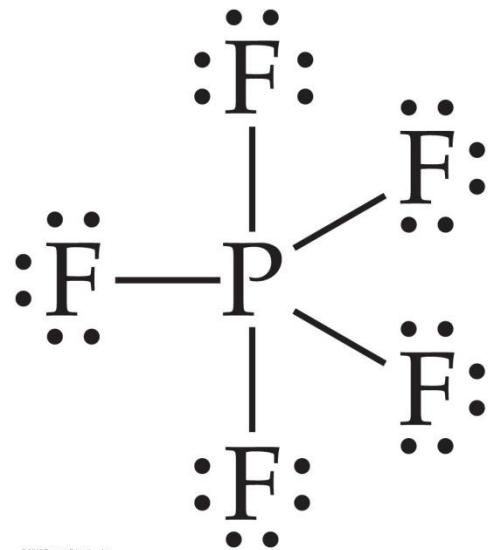
Extra info. Frustrated Lewis Pairs (FLP)



(Science 2006, 314, 1124)

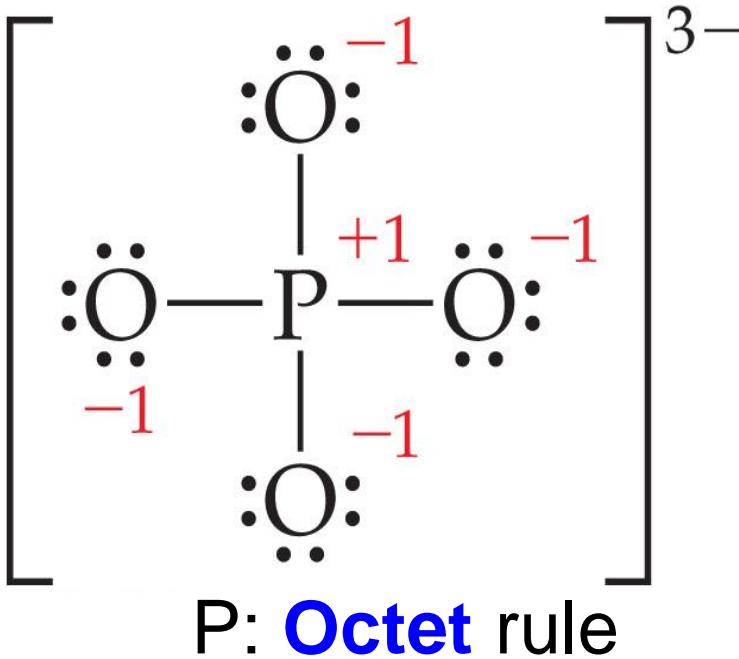
(III) More Than Eight Electrons

- In PF_5 , phosphorus has 10 electrons (**No NF_5**).
- It is allowed to **expand the octet** of atoms on the **third row or below (hypervalent 超价)**: presence of unfilled *d* orbitals and larger size of the atom to have **more bonding**.

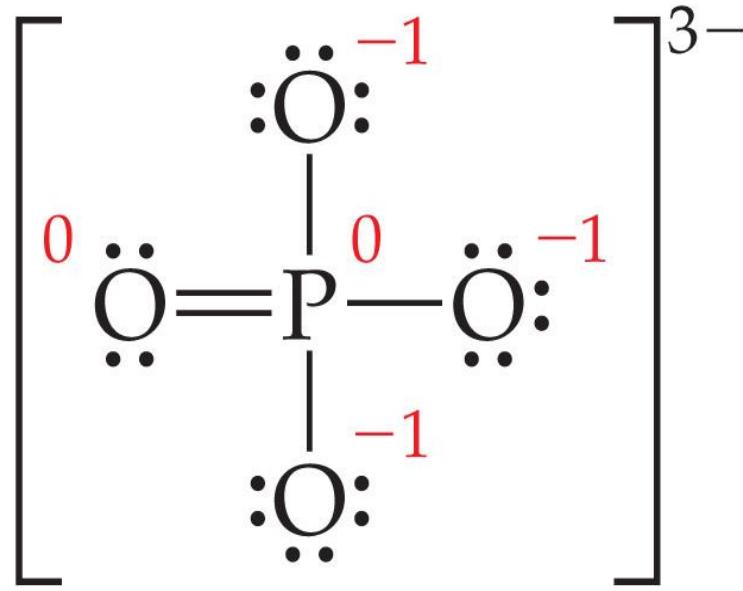


Basic Concepts
of Chemical
Bonding

Phosphate



P: **Octet rule**



The **best** structure

- The best (hypervalent) structure **avoids charge separation**.
- When the central atom is on the **third row or below**, it can **expand its octet** in order to **eliminate** some formal **charges**.

Which is predicted to have the shorter sulfur–oxygen bonds,
 SO_3 or SO_3^{2-} ?

The formate ion (HCO_2^{1-}) is stabilized by resonance, which suggests that the oxygen atoms' formal charges are:

- a. -1 and -1
- b. 0 and 0
- c. -1 and 0
- d. $-1/2$ and $-1/2$

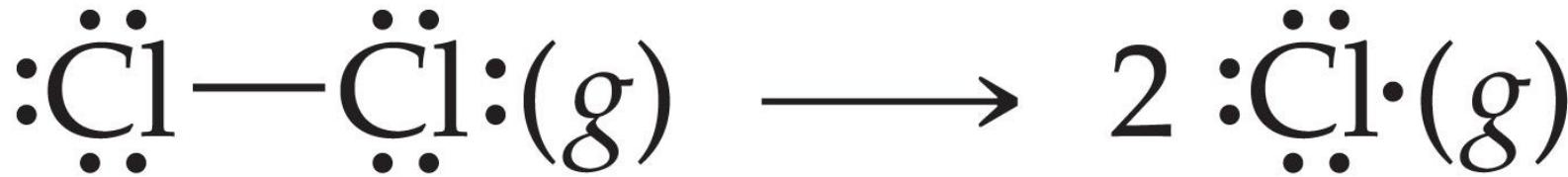
Which molecule below violates the octet rule?

- a. PF_5
- b. CH_4
- c. NBr_3
- d. OF_2

Which molecule below has an unpaired electron?

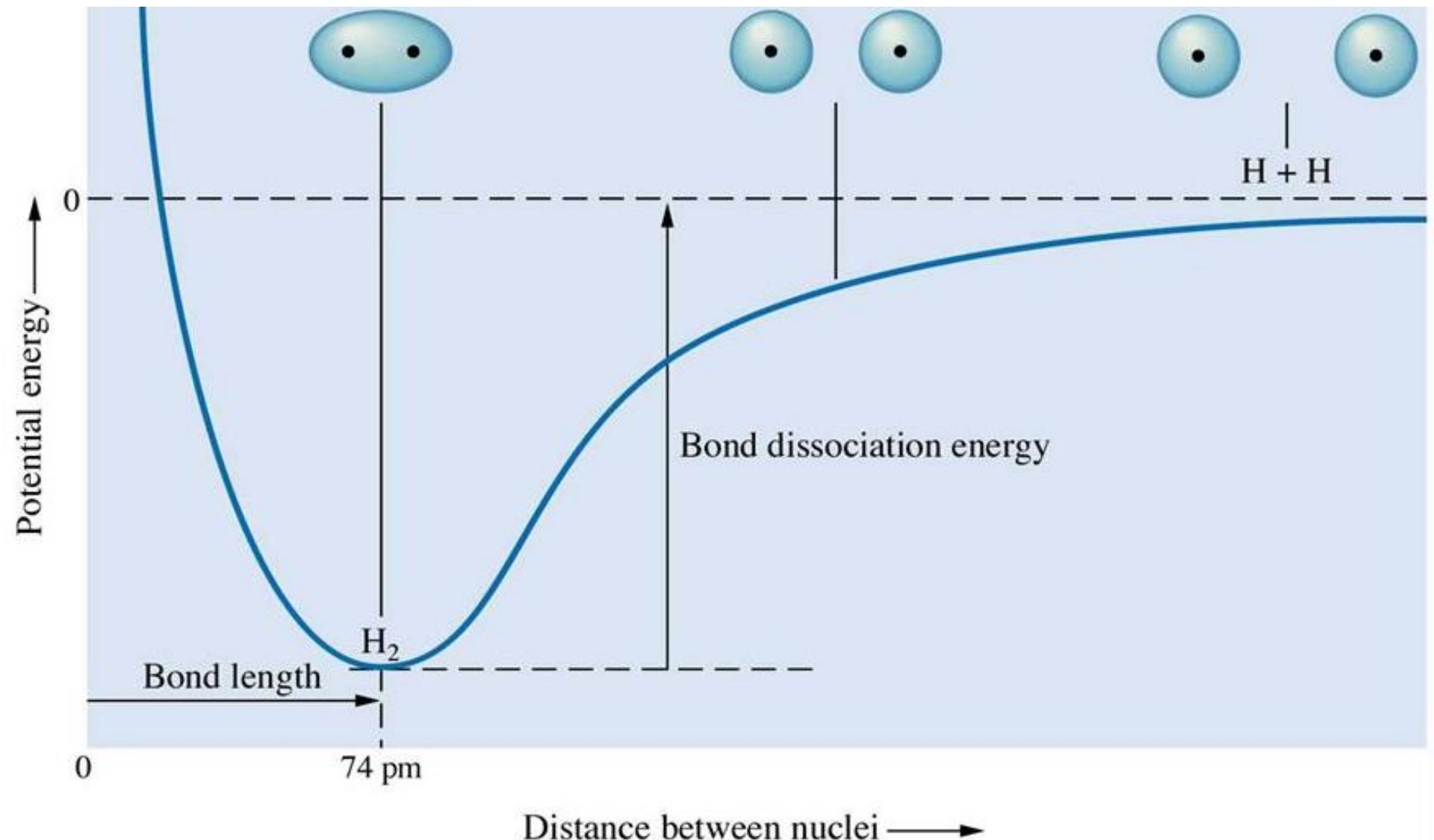
- a. NO
- b. NH₃
- c. BF₃
- d. PF₅

Covalent Bond Strength

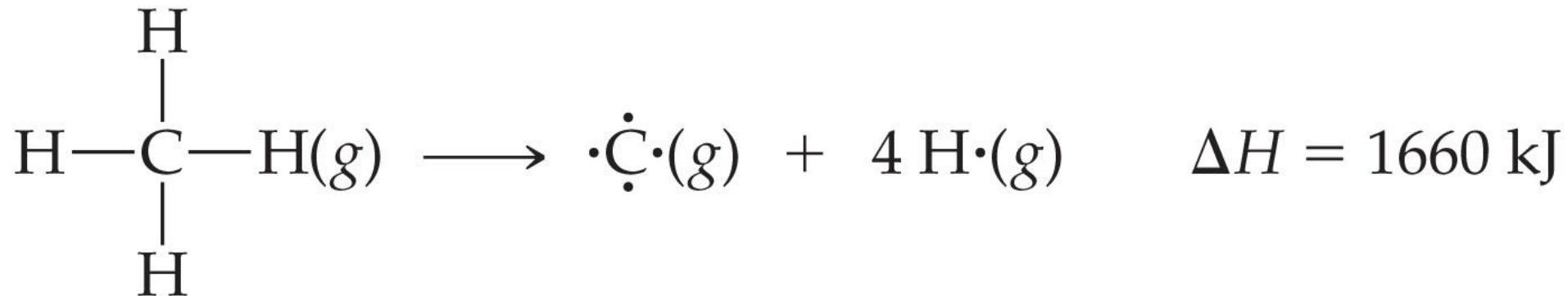


- The **strength** of a **bond** is measured by **energy** required to **break** the bond (bond dissociation energy 键离解能, BDE). The **more energy** required, the **stronger** the covalent **bond**.
- Bond enthalpy:** enthalpy change for the **breaking of a bond** in **one mole** of a **gaseous** substance → **always positive** (endothermic vs. enthalpy of formation (ΔH_f°) with a positive, zero or negative value).
- The bond enthalpy for a Cl-Cl bond, $D(\text{Cl-Cl})$, is measured to be 242 kJ/mol.

Potential Energy for H₂



Average Bond Enthalpies



Enthalpies to break 4 C-H bonds of methane: 1660 kJ
→ **Average** bond enthalpies: $\sim 1660/4 \text{ kJ} = \sim 415 \text{ kJ}$

Not absolute bond enthalpies of C-H bond **for all compounds**; the C-H bonds in methane is a bit different than the C-H bond in chloroform, CHCl_3 .

Average bond enthalpies are **positive**.

Table 8.4 AVERAGE BOND ENERGIES (KJ/MOL)

C vs. Si
(except with O or Cl)
Stronger

Weaker

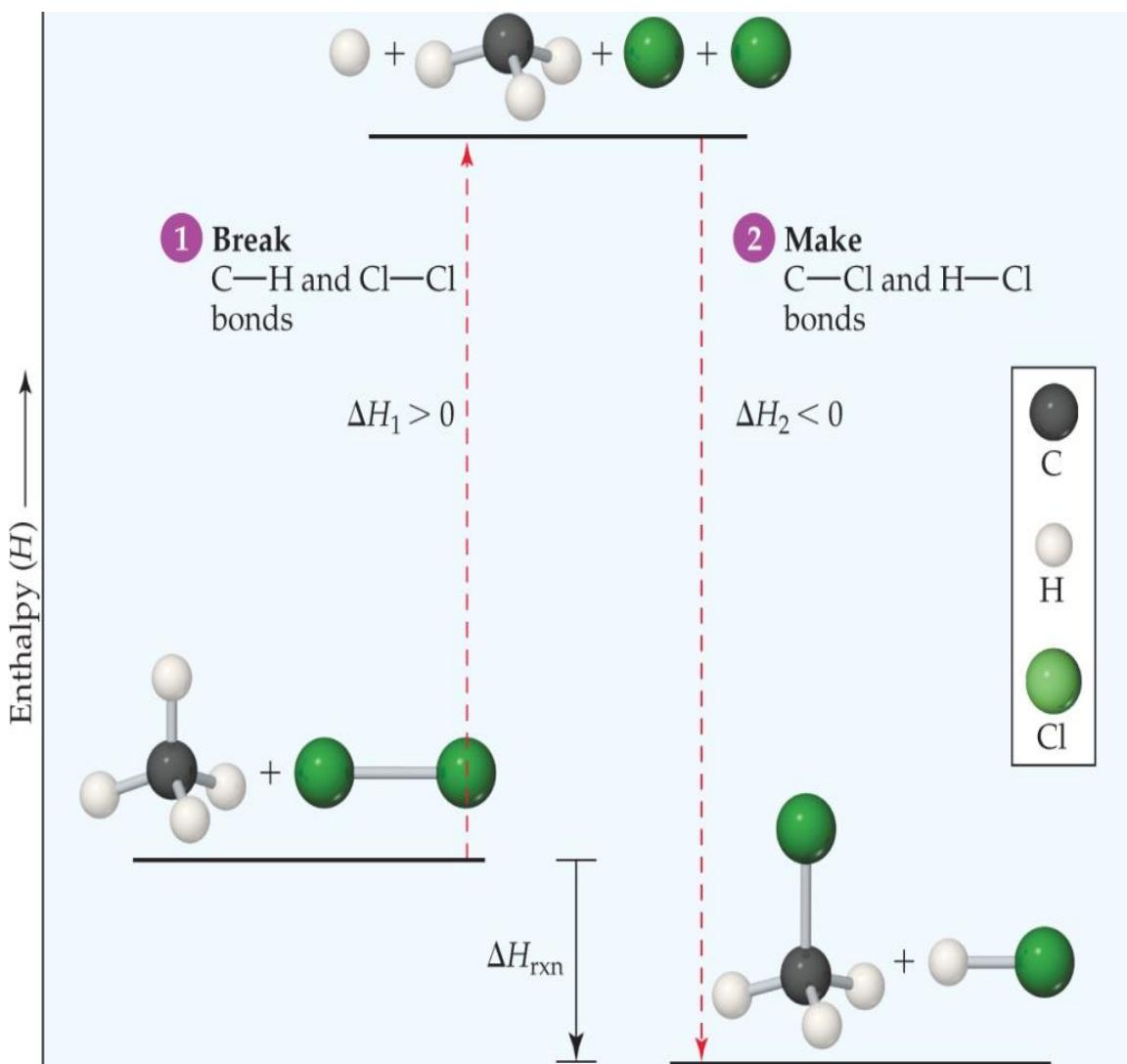
| Single Bonds | | | | | | | |
|--------------|-----|------|-----|------|-----|-------|-----|
| C—H | 413 | N—H | 391 | O—H | 463 | F—F | 155 |
| C—C | 348 | N—N | 163 | O—O | 146 | | |
| C—N | 293 | N—O | 201 | O—F | 190 | Cl—F | 253 |
| C—O | 358 | N—F | 272 | O—Cl | 203 | Cl—Cl | 242 |
| C—F | 485 | N—Cl | 200 | O—I | 234 | | |
| C—Cl | 328 | N—Br | 243 | | | Br—F | 237 |
| C—Br | 276 | | | S—H | 339 | Br—Cl | 218 |
| C—I | 240 | H—H | 436 | S—F | 327 | Br—Br | 193 |
| C—S | 259 | H—F | 567 | S—Cl | 253 | | |
| | | H—Cl | 431 | S—Br | 218 | I—Cl | 208 |
| Si—H | 323 | H—Br | 366 | S—S | 266 | I—Br | 175 |
| Si—Si | 226 | H—I | 299 | | | I—I | 151 |
| Si—C | 301 | | | | | | |
| Si—O | 368 | | | | | | |
| Si—Cl | 464 | | | | | | |

Multiple Bonds

| | | | | | | |
|-----|------|-----|-----|-----|-----|--|
| C=C | 614 | N=N | 418 | O=O | 495 | |
| C≡C | 839 | N≡N | 941 | | | |
| C=N | 615 | N=O | 607 | S=O | 523 | |
| C≡N | 891 | | | S=S | 418 | |
| C=O | 799 | | | | | |
| C≡O | 1072 | | | | | |

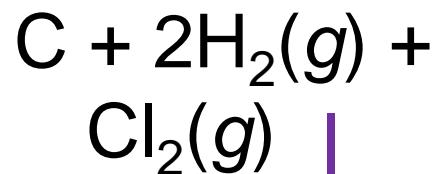
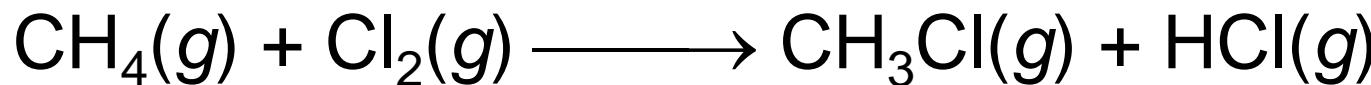
Enthalpies of Reaction

- Another efficient way to estimate ΔH_{rxn} is to compare the bond enthalpies of bonds broken to the bond enthalpies of the new bonds formed.



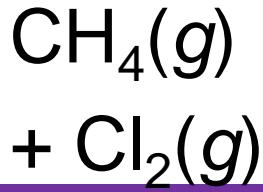
$$\Delta H_{rxn} = \sum(m^* \text{ bond enthalpies of bonds broken}) - \sum(n^* \text{ bond enthalpies of bonds formed})$$

Chapter 5: $\Delta H_{rxn} = \sum n^* \Delta H_{f,\text{products}} - \sum m^* \Delta H_{f,\text{reactants}}$

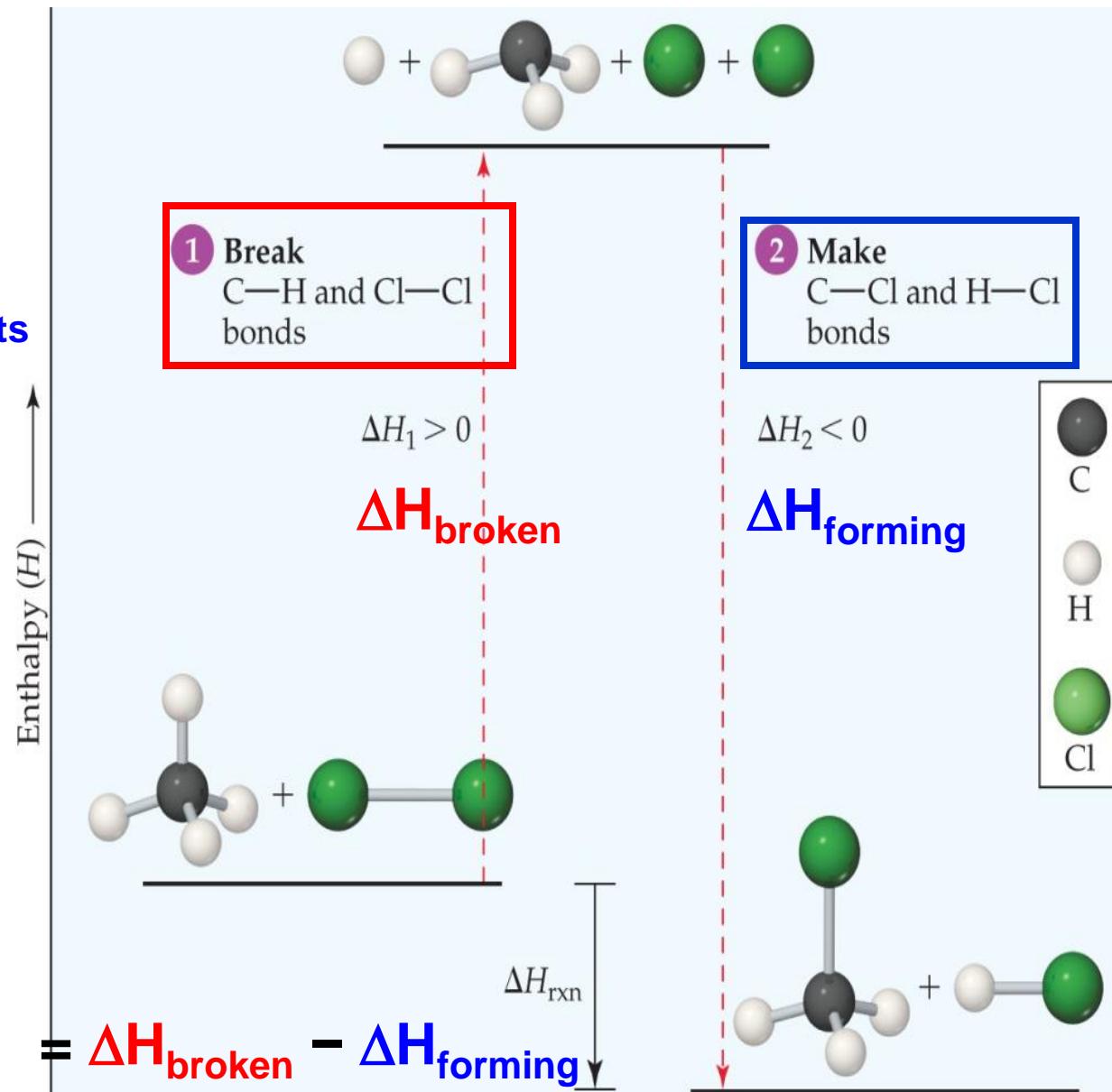


$$-\Delta H_{f,\text{reactants}}$$

$$\Delta H_{f,\text{products}}$$



One C-H bond & one Cl-Cl bond are broken; one C-Cl & one H-Cl bond are formed.

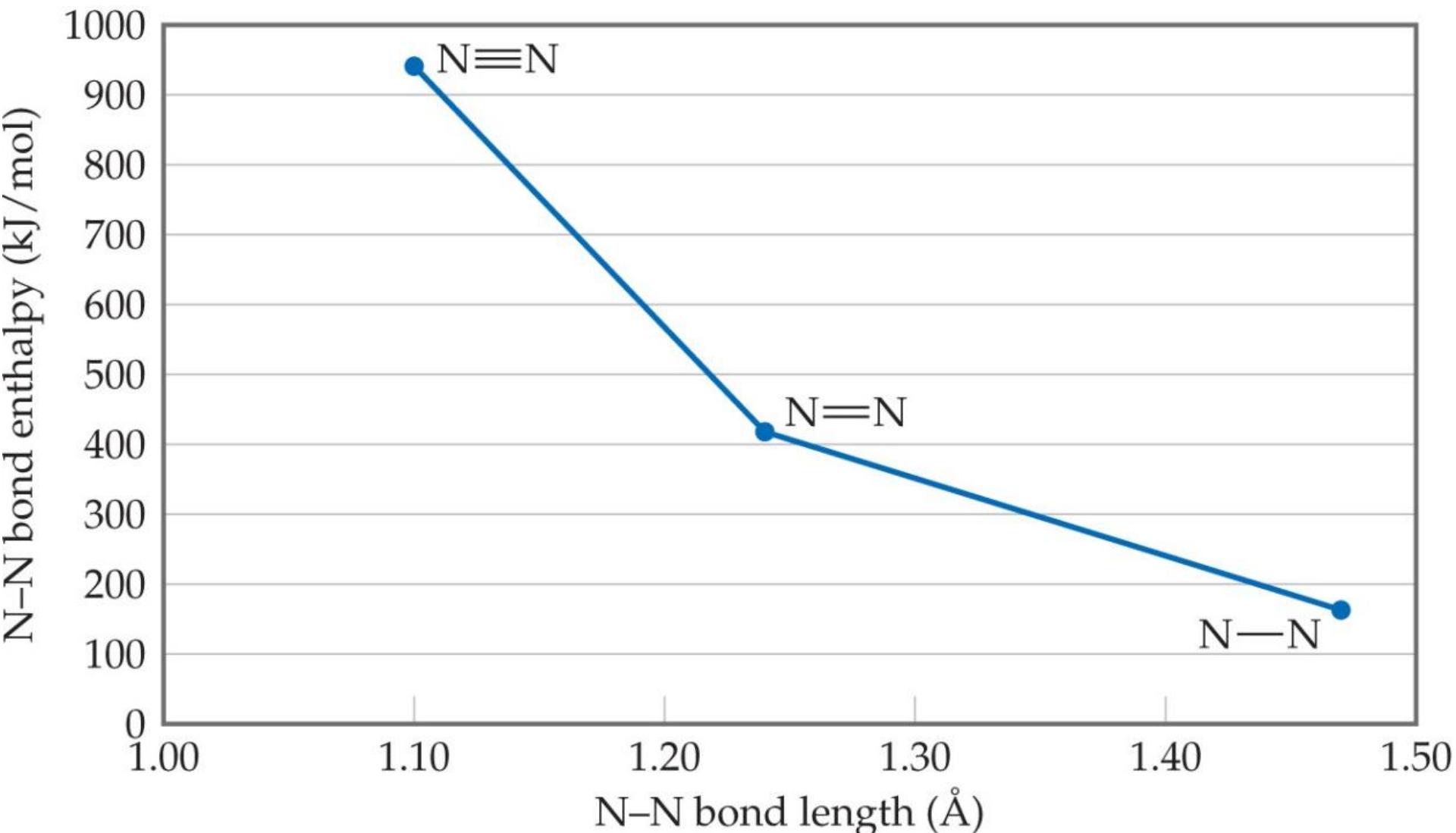


$$\begin{aligned}\Delta H_{rxn} &= [D(\text{C-H}) + D(\text{Cl-Cl})] - [D(\text{C-Cl}) + \\&\quad D(\text{H-Cl})] \\&= [(413 \text{ kJ}) + (242 \text{ kJ})] - [(328 \text{ kJ}) + (431 \text{ kJ})] \\&= (655 \text{ kJ}) - (759 \text{ kJ}) \\&= -104 \text{ kJ}\end{aligned}$$

Bond Enthalpy and Bond Length

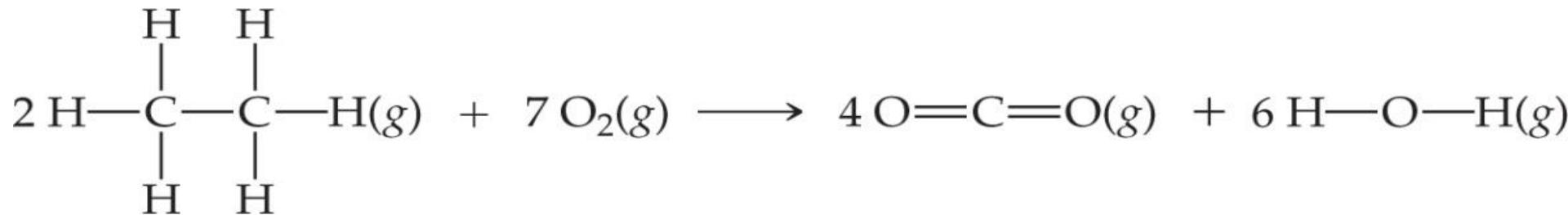
| Bond | Bond Length (Å) | Bond | Bond Length (Å) |
|------|-----------------|------|-----------------|
| C—C | 1.54 | N—N | 1.47 |
| C=C | 1.34 | N=N | 1.24 |
| C≡C | 1.20 | N≡N | 1.10 |
| C—N | 1.43 | N—O | 1.36 |
| C=N | 1.38 | N=O | 1.22 |
| C≡N | 1.16 | O—O | 1.48 |
| C—O | 1.43 | O=O | 1.21 |
| C=O | 1.23 | | |
| C≡O | 1.13 | | |

- We can also measure an average bond length for different bond types.
- The **more the number of bonds** between 2 atoms, the **shorter the bond length & the larger the bond enthalpy**.



Basic Concepts
of Chemical
Bonding

Using data from Table 8.4, estimate ΔH for the reaction



In the **reactants: break** 12 C-H bonds and 2 C-C bonds in the 2 ethane molecules + 7 O=O bonds in the 7 O₂ molecules.

In the **products: form** 8 C=O bonds and 12 O-H bonds.

$$\Delta H = [12*D(\text{C-H}) + 2*D(\text{C-C}) + 7*D(\text{O}_2)] - [8*D(\text{C=O}) + 12*D(\text{O-H})]$$

$$= [12(413 \text{ kJ}) + 2(348 \text{ kJ}) + 7(495 \text{ kJ})] - [8(799 \text{ kJ}) + 12(463 \text{ kJ})]$$

$$= 9117 \text{ kJ} - 11948 \text{ kJ} = -2831 \text{ kJ}$$

For atoms X and Y, the bond enthalpy of an X-Y bond is _____ the bond enthalpy of an X=Y bond.

- a. greater than
- b. less than
- c. equal to
- d. variable, depending on X and Y

For atoms X and Y, the bond length of an X-Y bond is _____ the bond length of an X=Y bond.

- a. greater than
- b. less than
- c. equal to
- d. variable, depending on X and Y

Ionizing an H_2 molecule to H_2^+ changes the strength of the bond. Based on the description of covalent bonding given previously, do you expect the H—H bond in H_2^+ to be weaker or stronger than the H—H bond in H_2 ?

- A. Stronger, because a H-H covalent bond in H_2^+ has one less electron than in H_2 .
- B. Stronger, because a H-H covalent bond in H_2^+ has one more electron than in H_2 .
- C. Weaker, because a H-H covalent bond in H_2^+ has one less electron than in H_2 .
- D. Weaker, because a H-H covalent bond in H_2^+ has one more electron than in H_2 .

The C—O bond length in carbon monoxide, CO, is 1.13 Å, whereas the C—O bond length in CO₂ is 1.24 Å. Without drawing a Lewis structure, do you think that CO contains a single, double, or triple bond?

- A. Single covalent bond
- B. Double covalent bond
- C. Triple covalent bond

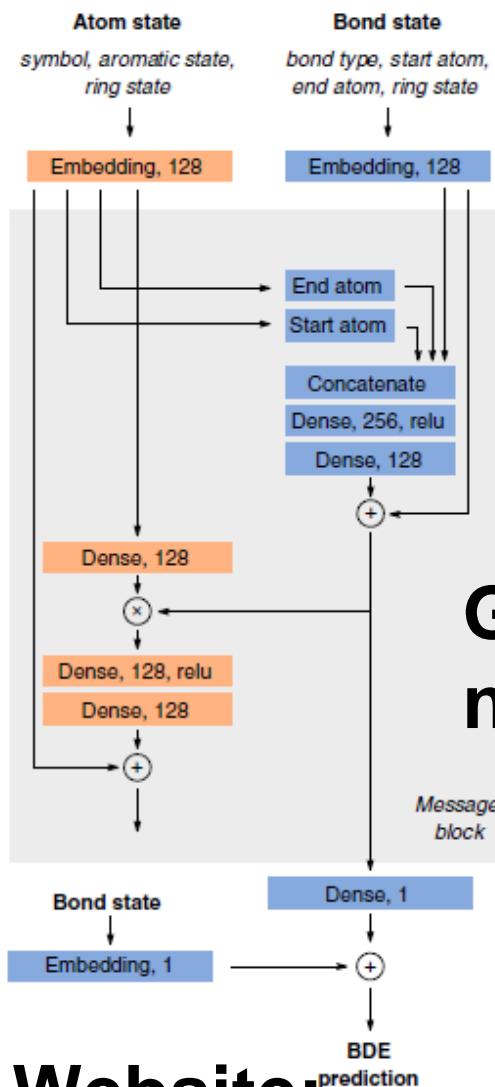
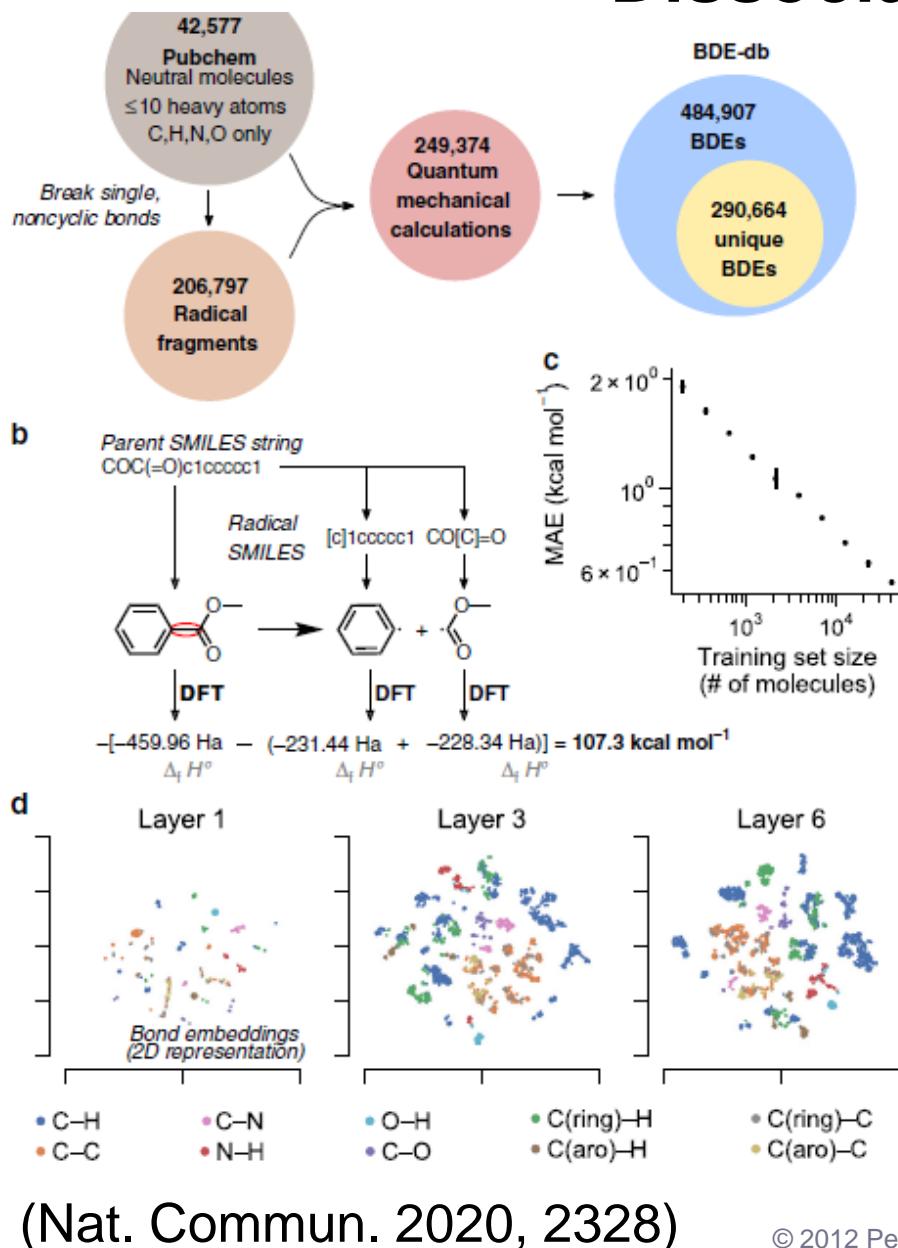
How can you use the enthalpy of atomization of the hydrocarbon ethane, C₂H₆(g), along with the value $D(\text{C}—\text{H}) = 413 \text{ kJ/mol}$ to estimate the value for $D(\text{C}—\text{C})$?

- A. The enthalpy of atomization / 7 bonds broken = a good estimate of $D(\text{C-C})$.
- B. The enthalpy of atomization - 6 [$D(\text{C-H})$] = a good estimate of $D(\text{C-C})$.
- C. The enthalpy of atomization + 6 [$D(\text{C-H})$] = a good estimate of $D(\text{C-C})$.
- D. The enthalpy of atomization / 7 bonds broken - 6[$D(\text{C-H})$] = a good estimate of $D(\text{C-C})$.

Based on bond enthalpies, which do you expect to be more reactive, oxygen, O₂, or hydrogen peroxide, H₂O₂?

- A. O₂ is more reactive, because the O=O bond enthalpy is less than that of the O-O bond enthalpy in hydrogen peroxide.
- B. O₂ is more reactive, because the O=O bond enthalpy is greater than that of the O-O bond enthalpy in hydrogen peroxide.
- C. H₂O₂ is more reactive, because the O-O bond enthalpy is less than that of the O=O bond enthalpy in O₂.
- D. H₂O₂ is more reactive, because the O-O bond enthalpy is greater than that of the O=O bond enthalpy in O₂.

Extra info. Machine-learning predictions of Bond Dissociation Energy



Website:

<https://bde.ml.nrel.gov/>

Graph neural network (GNN)

Basic Concepts
of Chemical
Bonding

Extra info. iBonD (Internet Bond-energy Databank)



清华大学

Tsinghua University

CHINA

iBonD 2.0

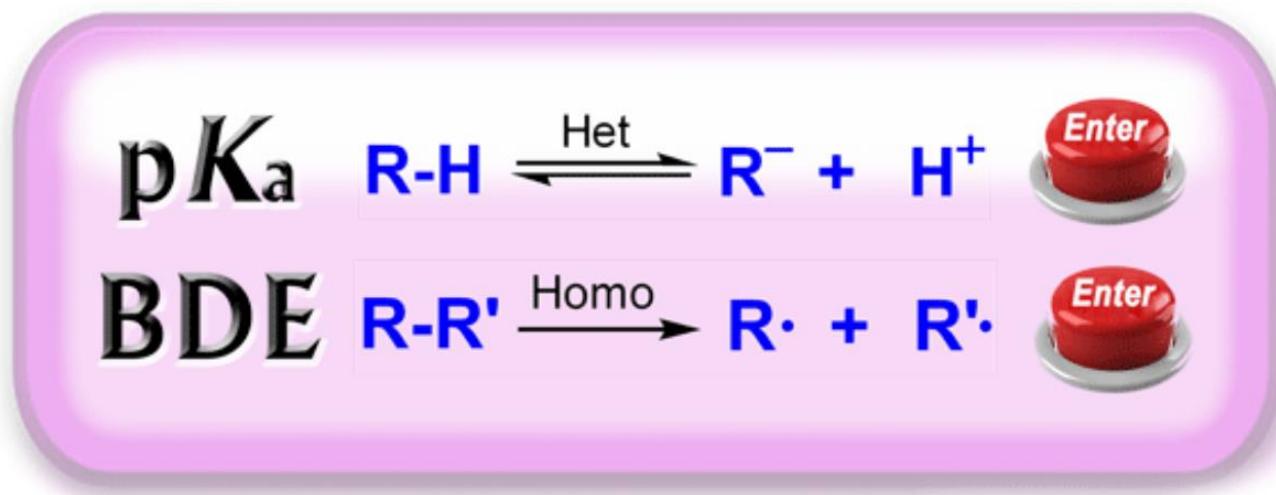
internet BonD-energy Databank



南开大学

Nankai University

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- Feedback ■
- User Guide ■



Website:
<http://ibond.nankai.edu.cn/>

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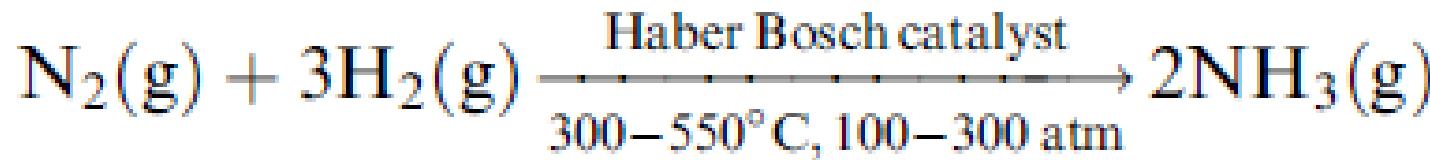
Extra info. N₂ bond Activation & Functionalization



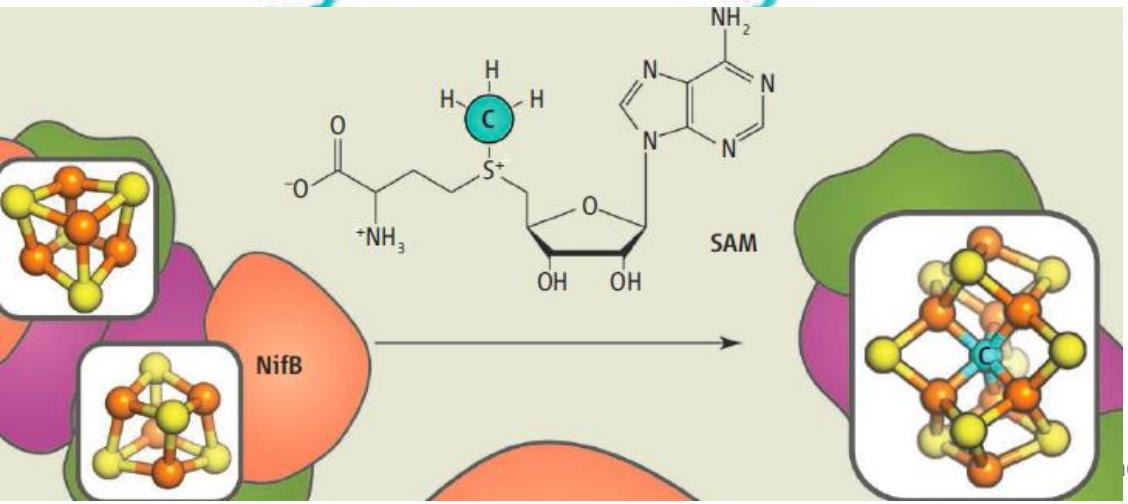
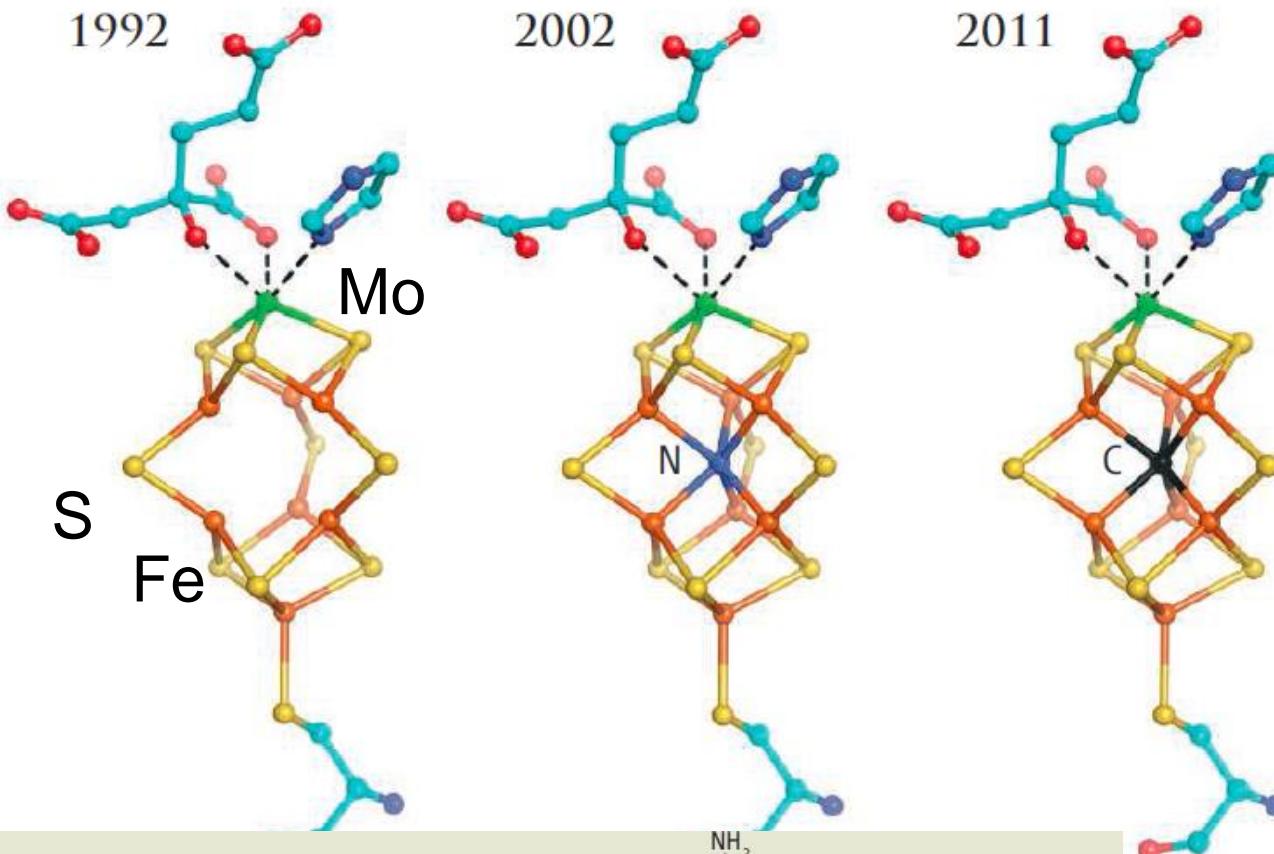
$$\Delta H^\circ = -92.22 \text{ kJ mol}^{-1}, \Delta S^\circ = -99 \text{ J mol K}^{-1}$$



D(N₂): 941 kJ



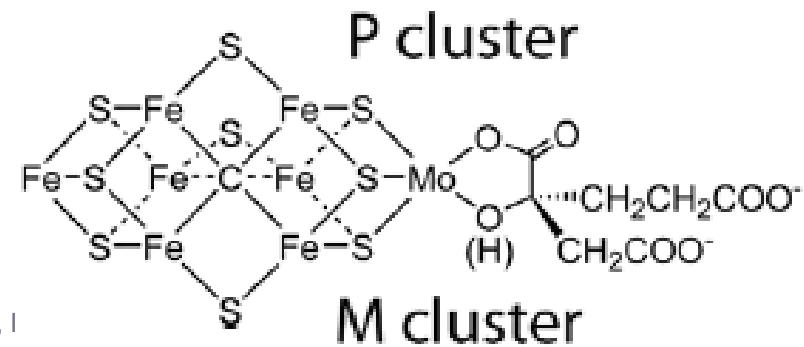
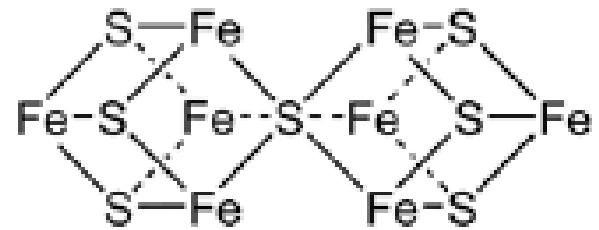
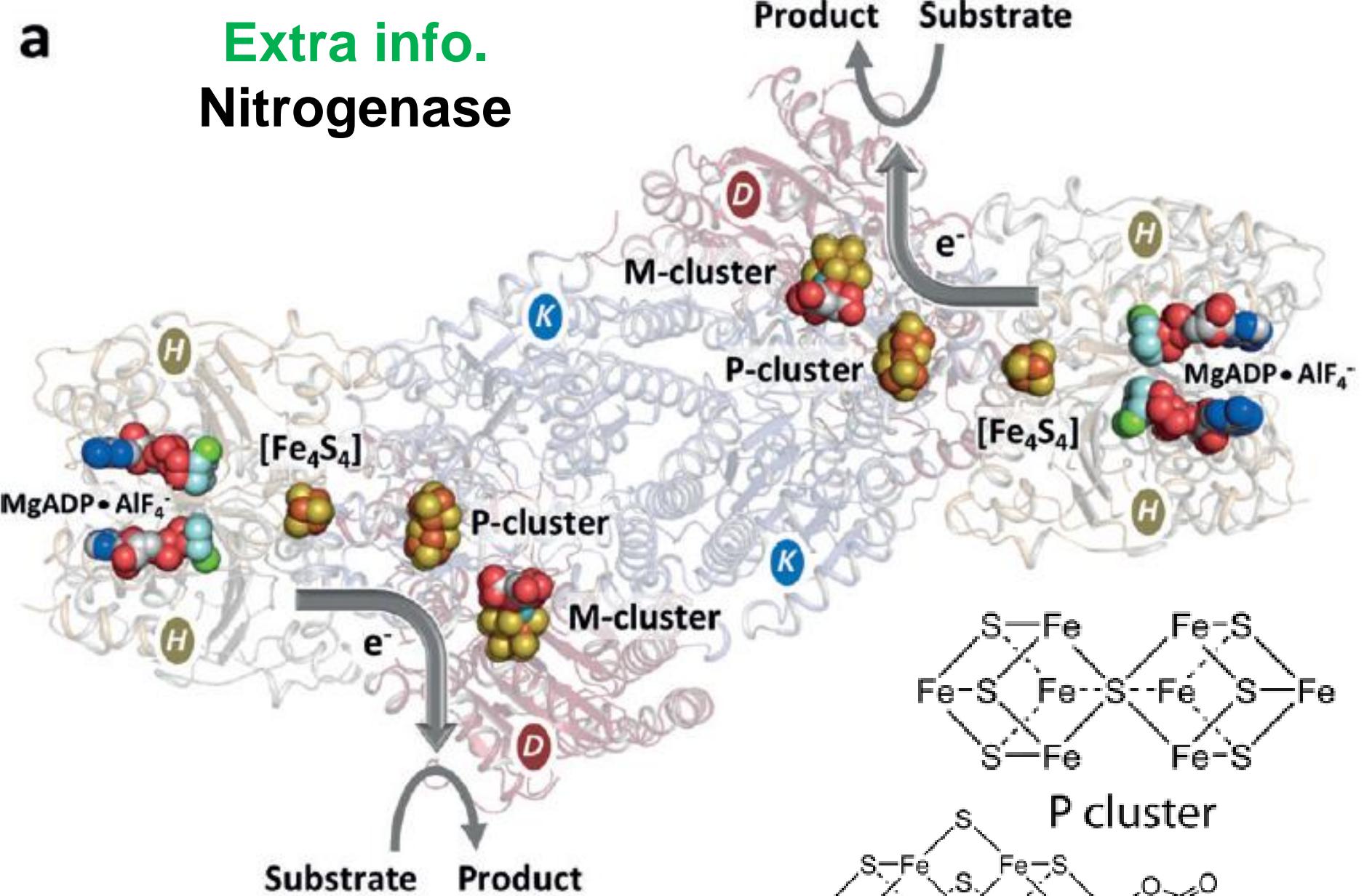
Extra info. Nitrogenase



- The **largest & complicated** metal-organic cluster in biology so far;
- The identity of the central atom:
C, not N or O
(spectroscopies)
- C from SAM
(methyl donor)

(Science 2011, 334, 914;
2011, 334, 940; 2011, 334,
974; Science 2012, 337,
1618; 2012, 337, 1672;)
Basic Concepts
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Bonding

a Extra info.
Nitrogenase



Science 2011, 334, 914; Science 2011, 334, 940;
Science 2011, 334, 974.

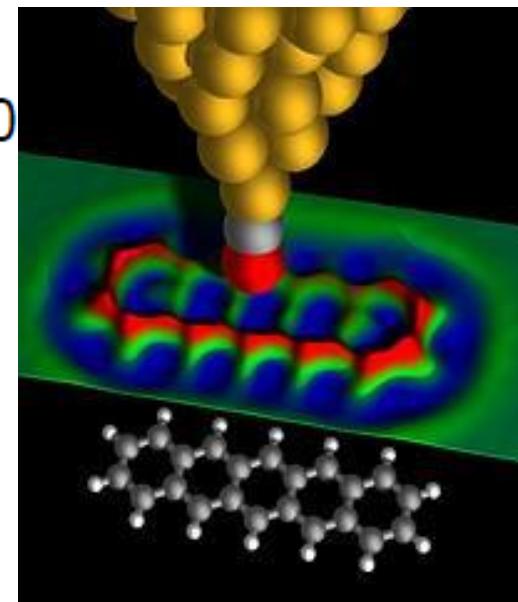
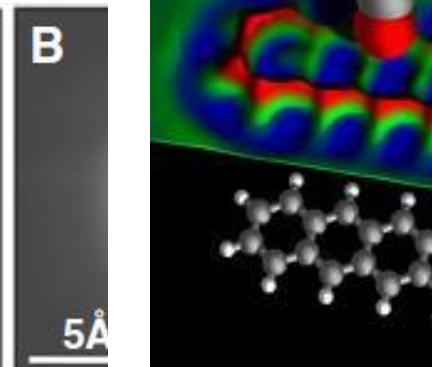
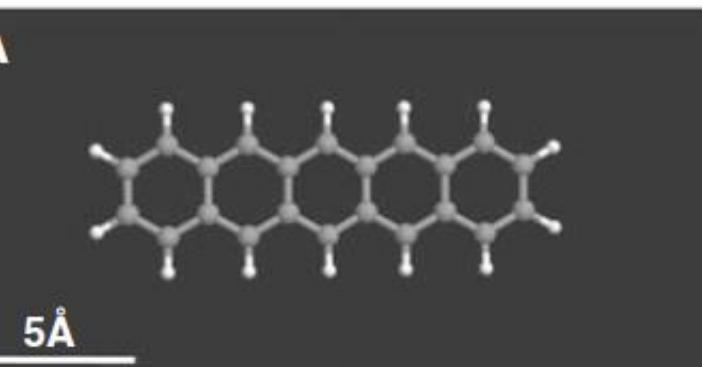
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Extra info.

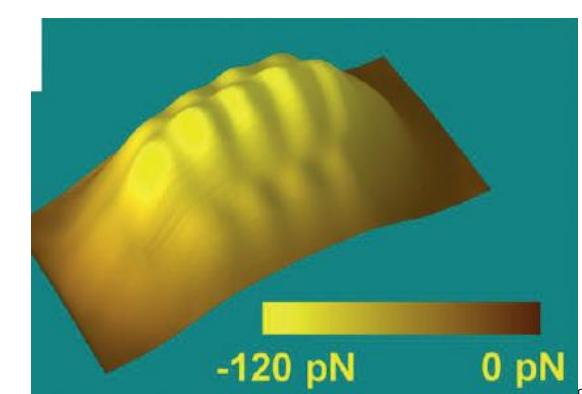
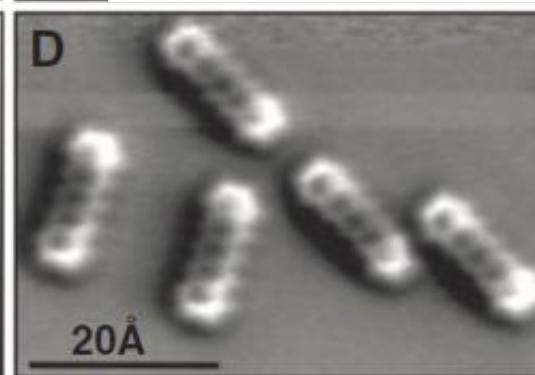
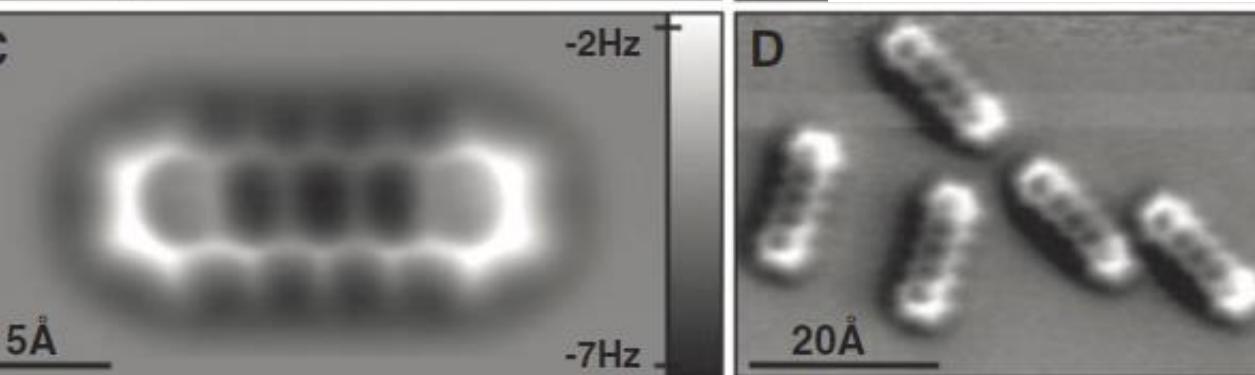
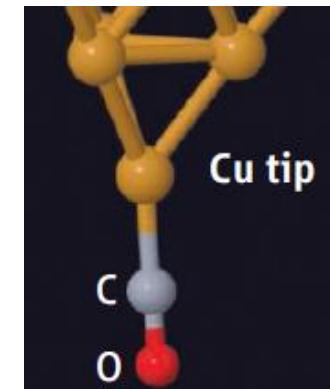
The Chemical Structure of a Molecule Resolved by Atomic Force Microscopy

Leo Gross *et al.*

Science 325, 1110 (2009);
DOI: 10.1126/science.1176210



IBM Research



Pentacene on Cu(111) surface
Scanning tunneling microscope (STM) + CO as a tip

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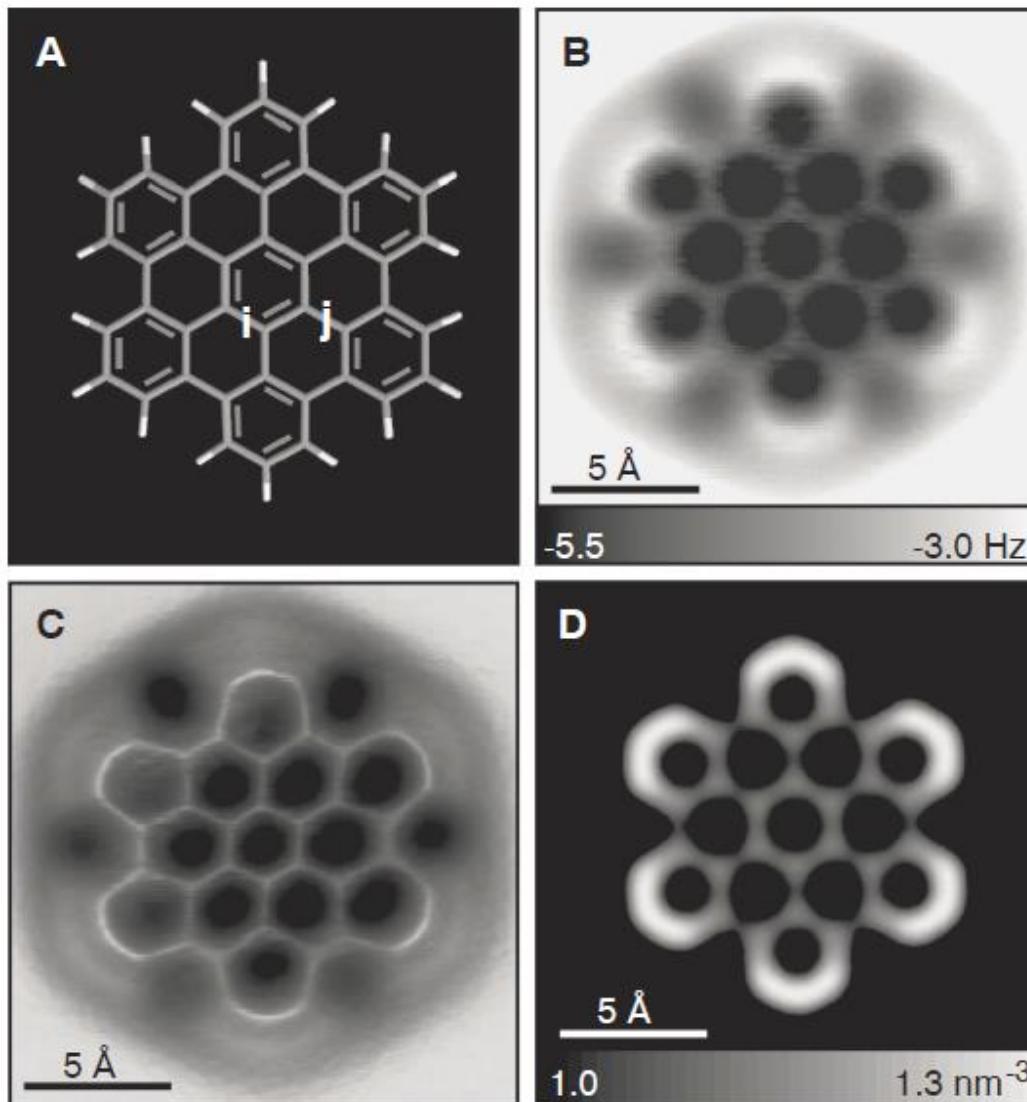
Basic Concepts
of Chemical
Bonding

Bond-Order Discrimination by Atomic Force Microscopy

Leo Gross *et al.*

Science 337, 1326 (2012);

DOI: 10.1126/science.1225621



IBM Research

Extra info.

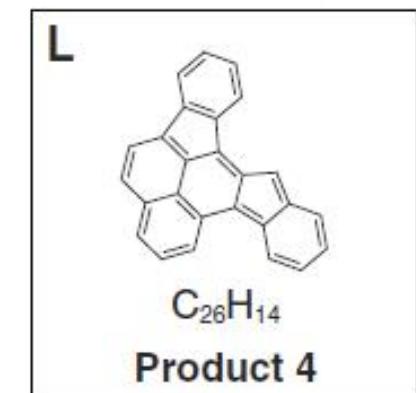
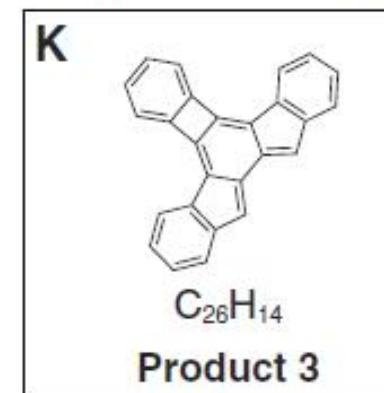
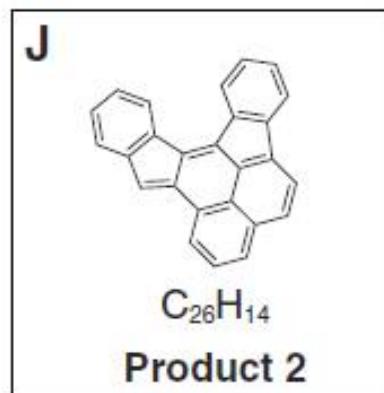
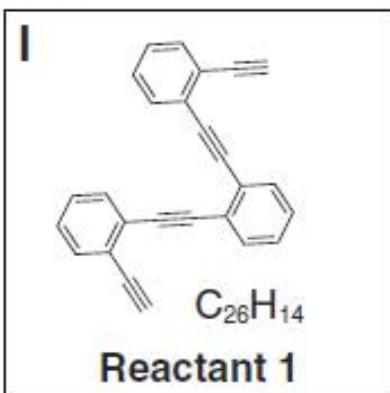
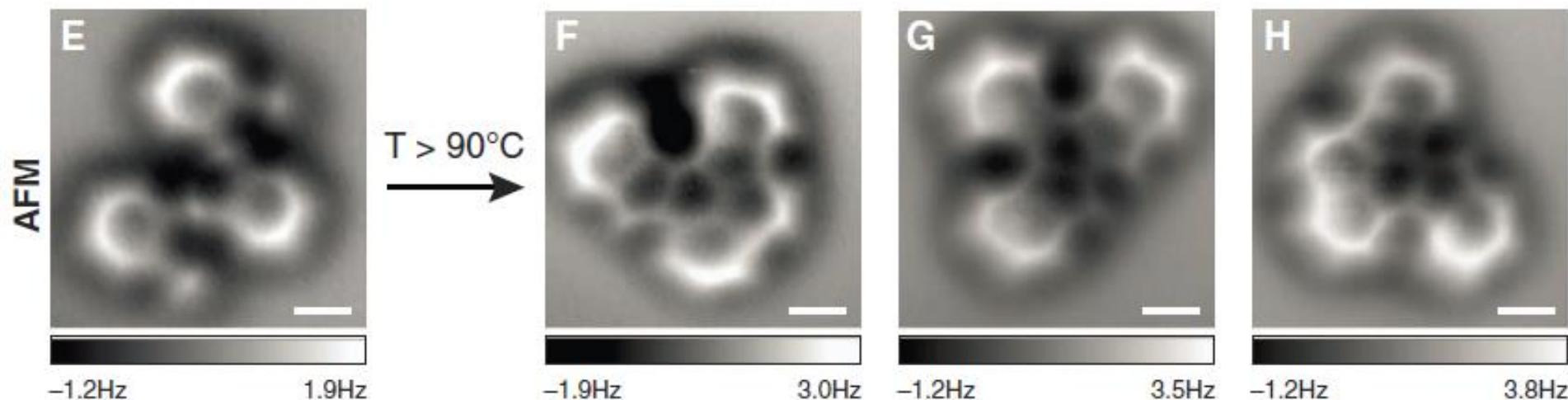
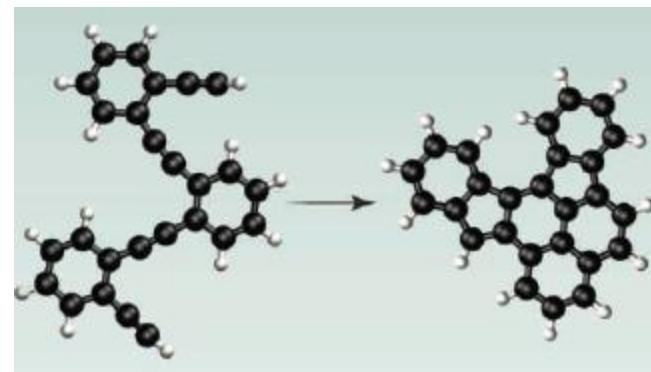
Basic Concepts
of Chemical
Bonding

Direct Imaging of Covalent Bond Structure in Single-Molecule Chemical Reactions

Dimas G. de Oteyza *et al.*

Science **340**, 1434 (2013);
DOI: 10.1126/science.1238187

Extra info.



Real-Space Identification of Intermolecular Bonding with Atomic Force Microscopy

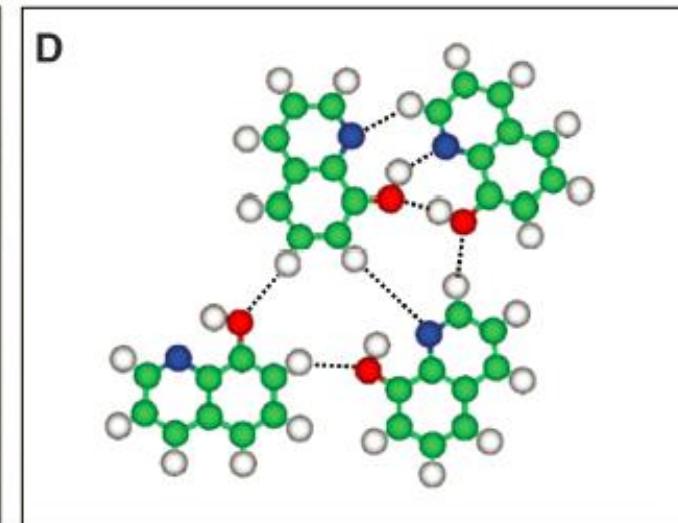
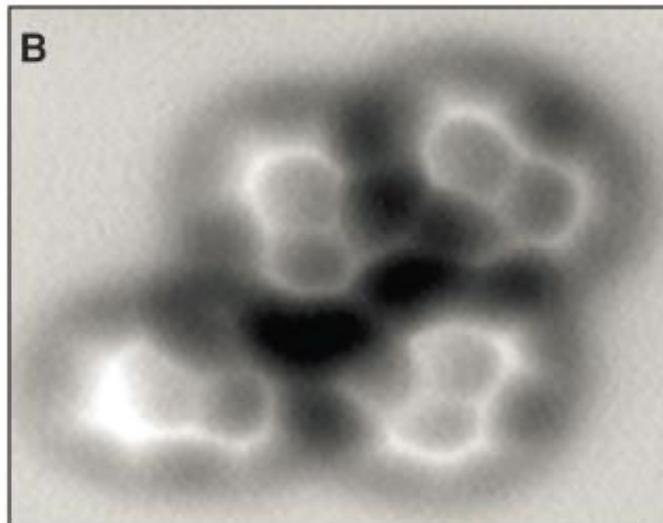
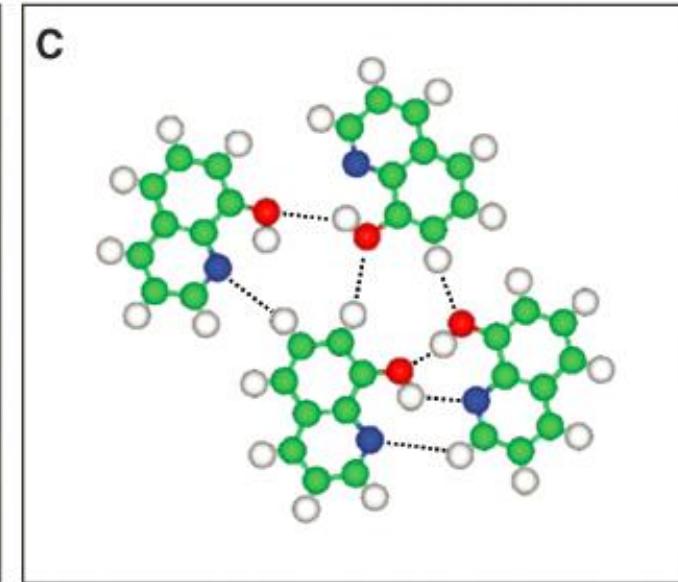
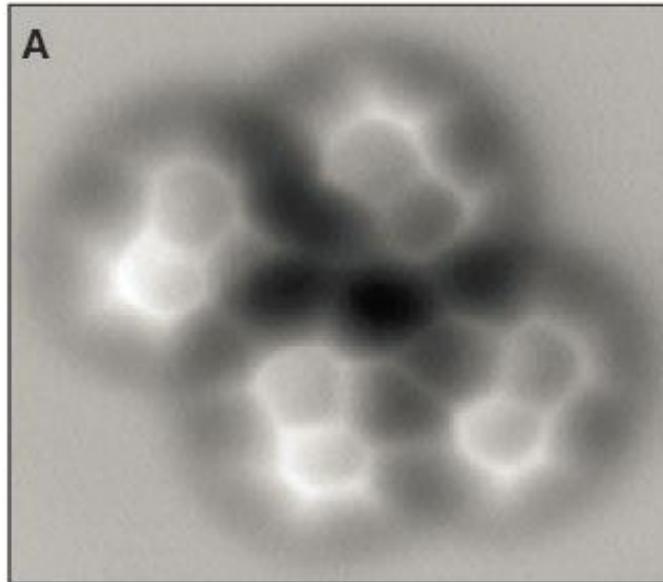
Jun Zhang et al.

Science 342, 611 (2013);

DOI: 10.1126/science.1242603

国家纳米科学中心

Extra info.



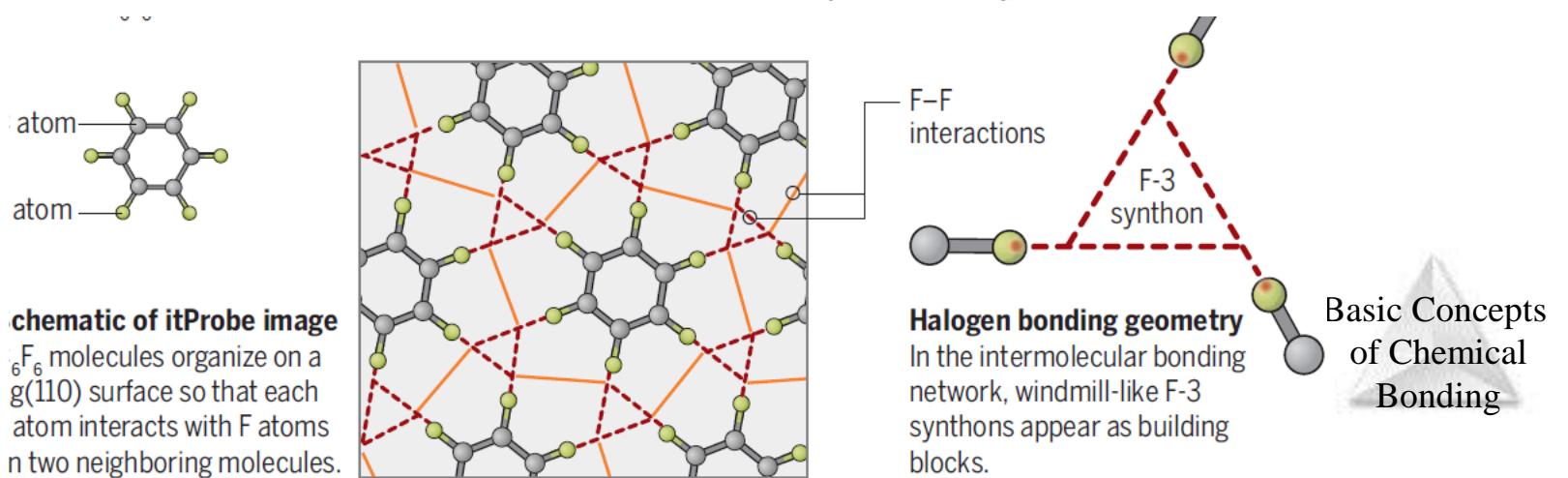
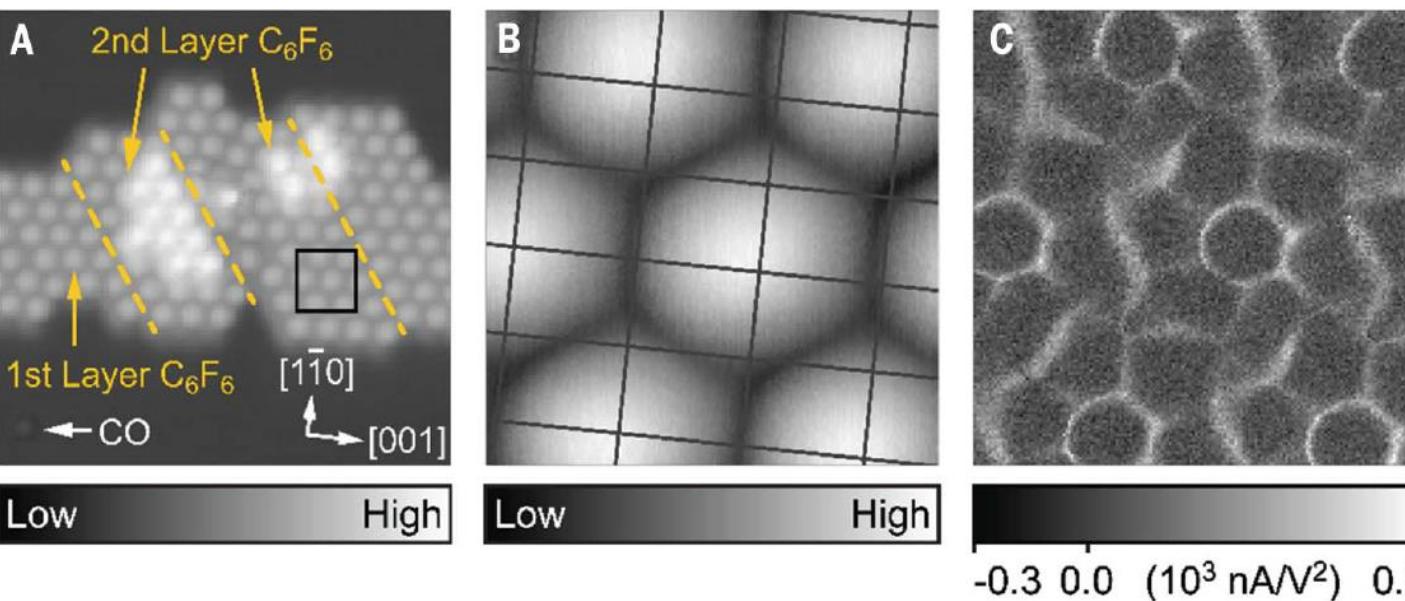
Imaging the halogen bond in self-assembled halogenbenzenes on silver

Zhumin Han, Gregory Czap, Chi-lun Chiang, Chen Xu, Peter J. Wagner, Xinyuan Wei, Yanxing Zhang, Ruqian Wu and W. Ho

Extra info.

Science 358 (6360), 206-210.

DOI: 10.1126/science.aai8625 originally published online September 14, 2017



An sp-hybridized molecular carbon allotrope, cyclo[18]carbon

Kaiser et al., *Science* **365**, 1299–1301 (2019)

Extra info.

Katharina Kaiser^{1*}, Lorel M. Scriven^{2*}, Fabian Schulz¹, Przemyslaw Gawel^{2†},
Leo Gross^{1†}, Harry L. Anderson^{2†}

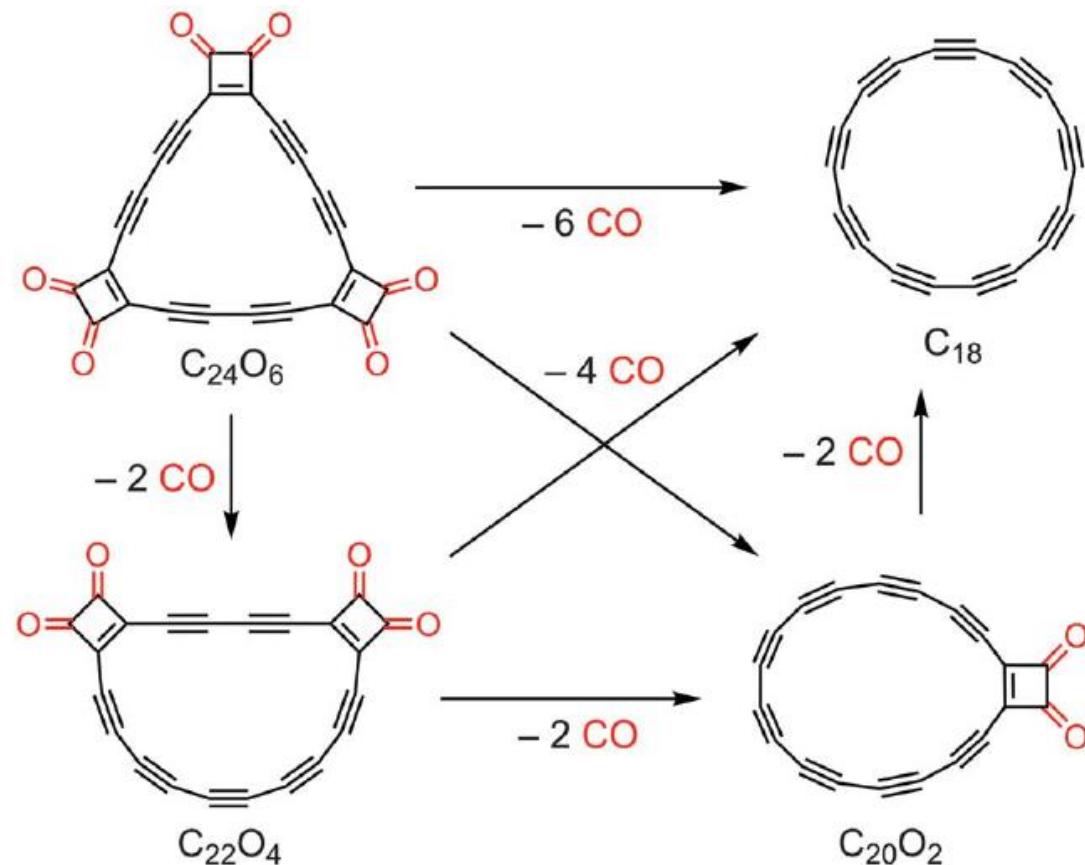
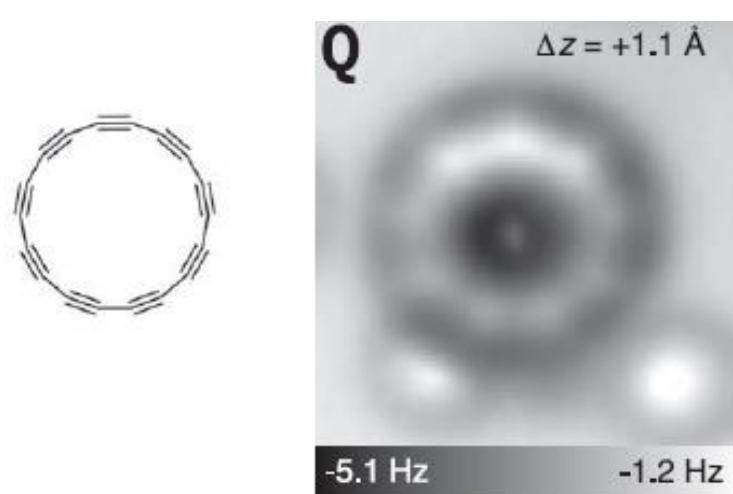


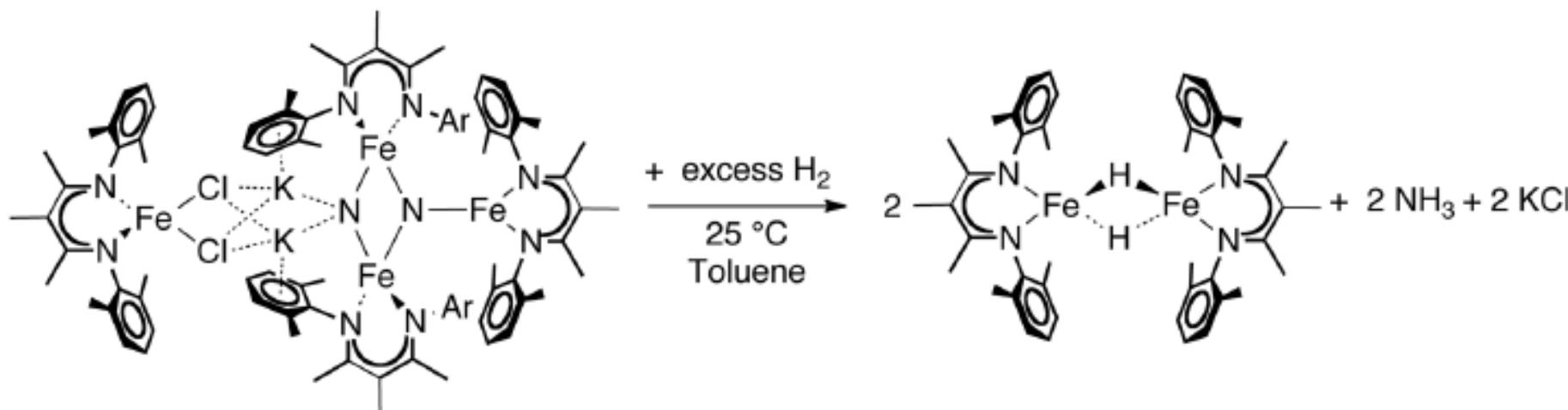
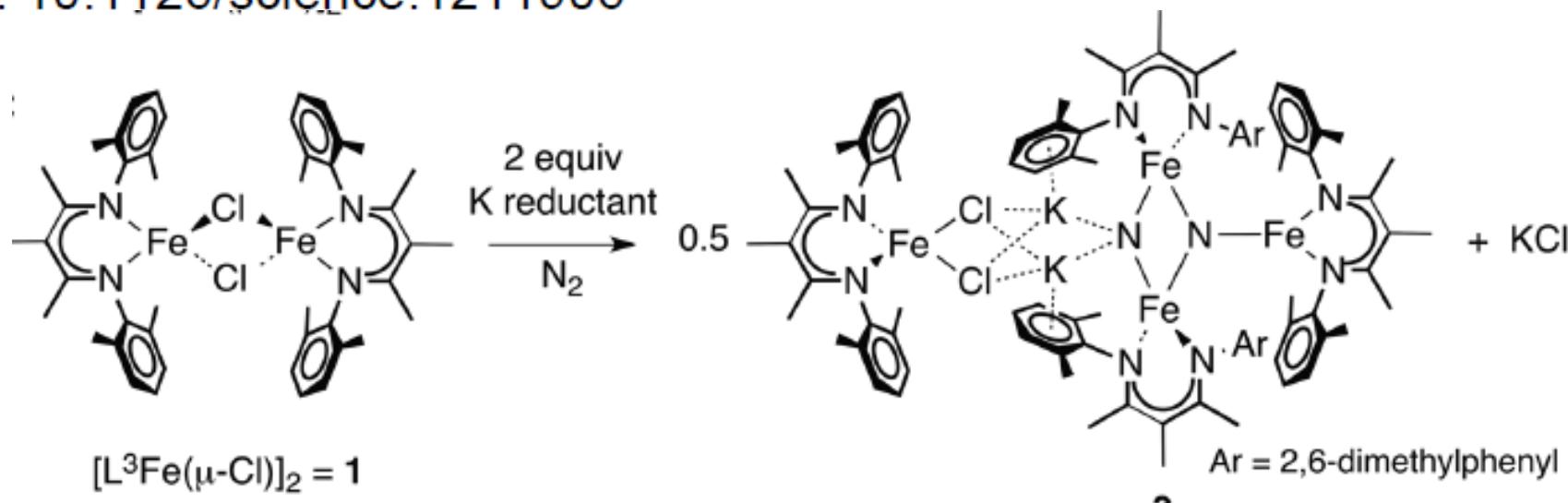
Fig. 2. Reaction scheme for the on-surface formation of C_{18} .

Decarbonylation was achieved via voltage pulses that resulted in the loss of two, four, or six CO moieties.

Extra info. Catalysts (recent and selected)

N_2 Reduction and Hydrogenation to Ammonia by a Molecular Iron-Potassium Complex

Meghan M. Rodriguez, et al.
Science **334**, 780 (2011);
DOI: 10.1126/science.1211906



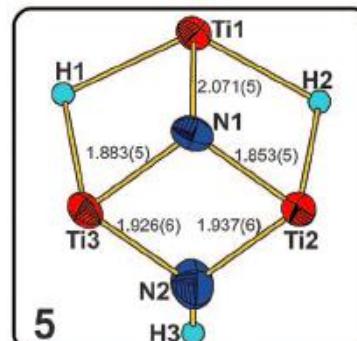
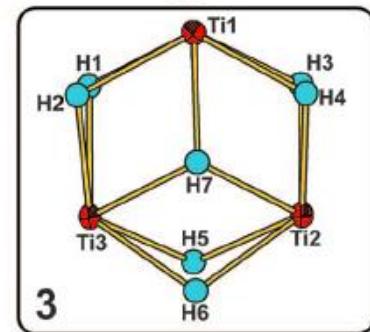
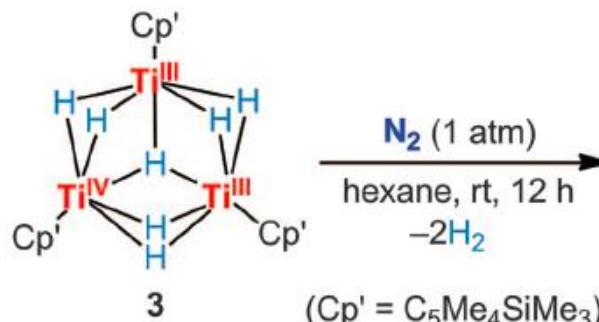
Dinitrogen Cleavage and Hydrogenation by a Trinuclear Titanium Polyhydride Complex

Takanori Shima *et al.*

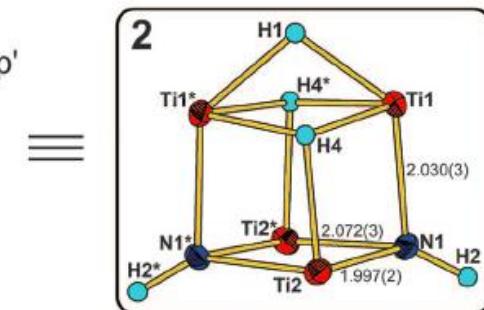
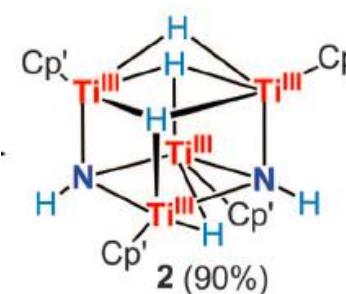
Science 340, 1549 (2013);

DOI: 10.1126/science.1238663

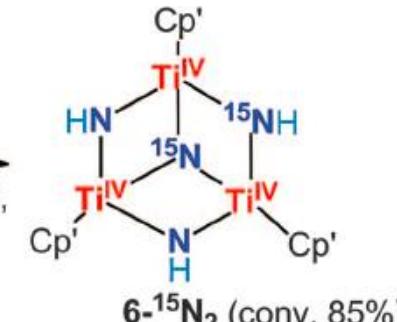
B



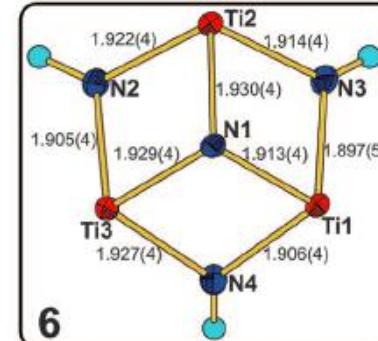
2 (quant.)
1 / H_2 (5 atm)
 60°C , 12 h



$^{15}\text{N}_2$ (1 atm)
no solvent, 180°C ,
1 day

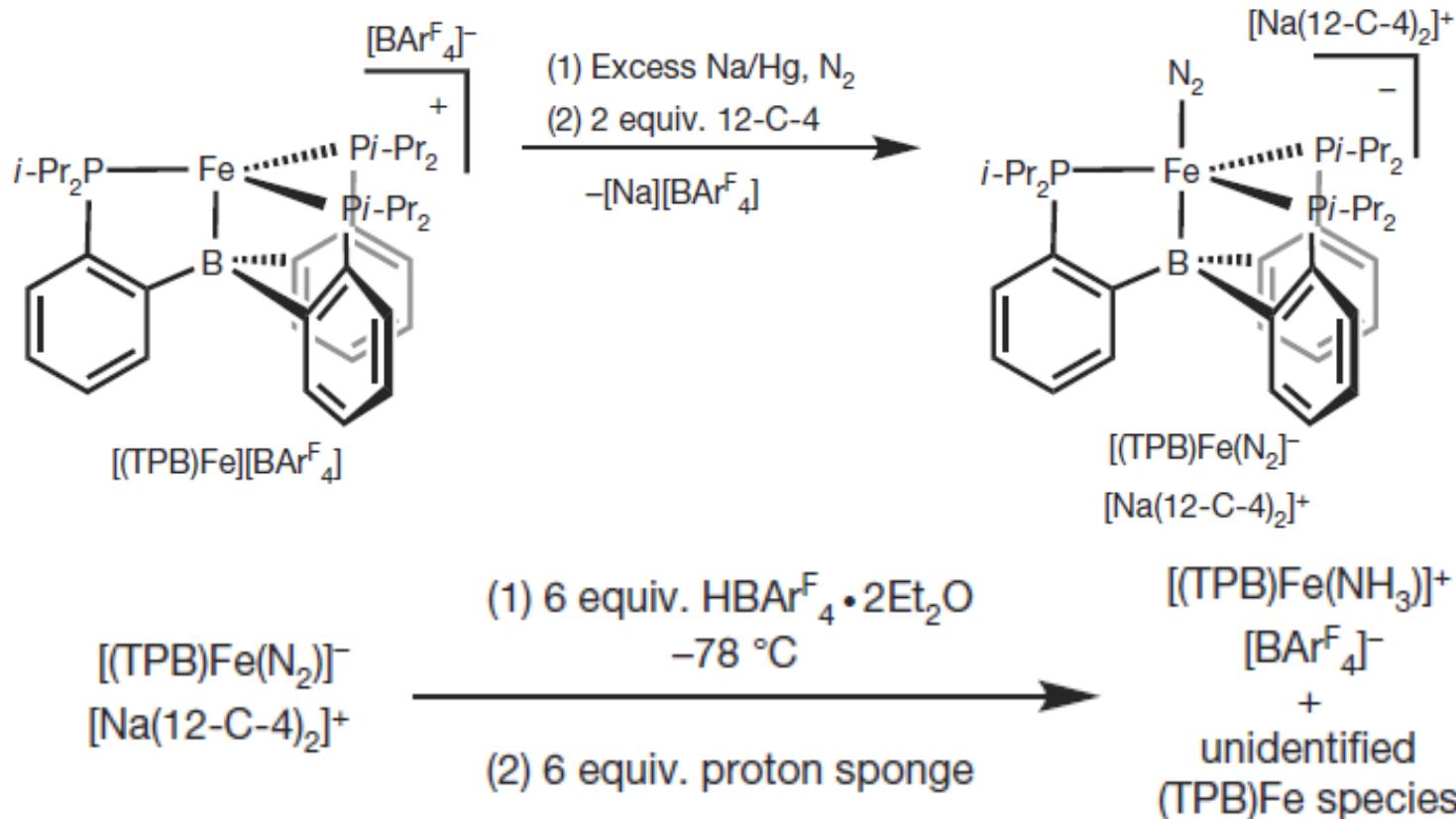


6- $^{15}\text{N}_2$ (conv. 85%)



Catalytic conversion of nitrogen to ammonia by an iron model complex

John S. Anderson¹, Jonathan Rittle¹ & Jonas C. Peters¹

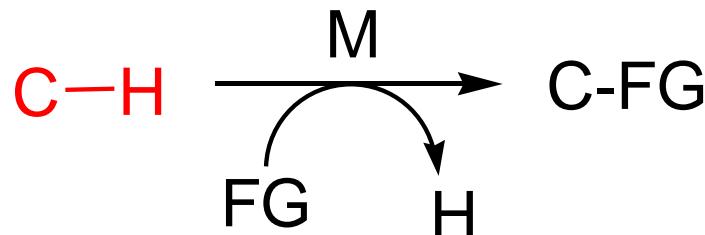


Extra info.

(Nature 2013, 501, 84)

Extra info. C-H bond Activation & Functionalization

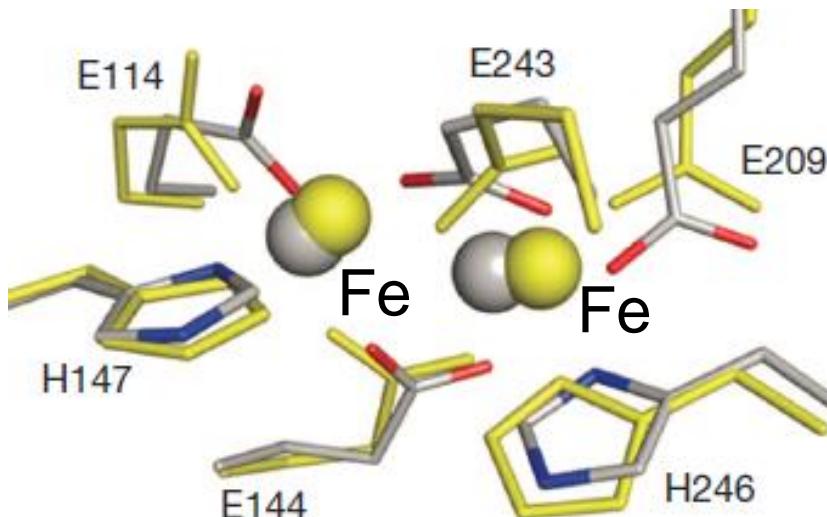
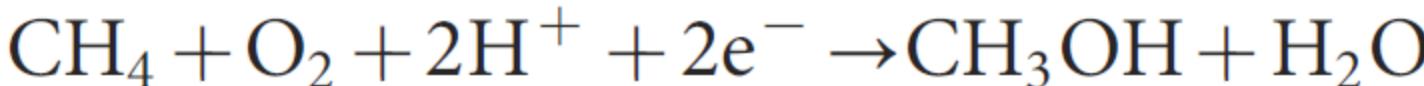
Difficulties



D: 413 kJ

- Very strong, non-polar
- Very high pKa
- Very high ionization energy
- Very low electron affinity
- Selective or Specific activation?
Very active topic (Nobel Prize??)

Biology: methane monooxygenase (CH_4 : the strongest C-H BOND)



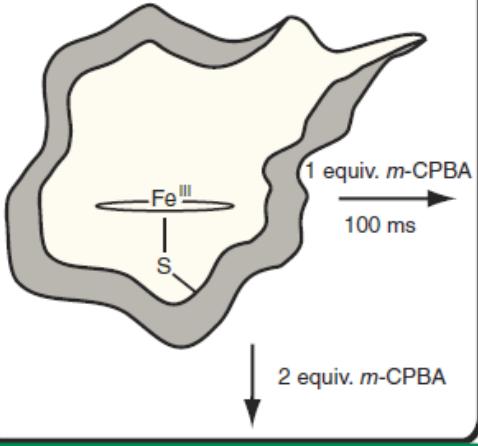
particulate methane monooxygenases (pMMO):
Diiron cluster
soluble methane monooxygenases (sMMO):
Mono-? or Di-copper cluster
(Nature 2013 494 380)

Biology: Cytochrome P450

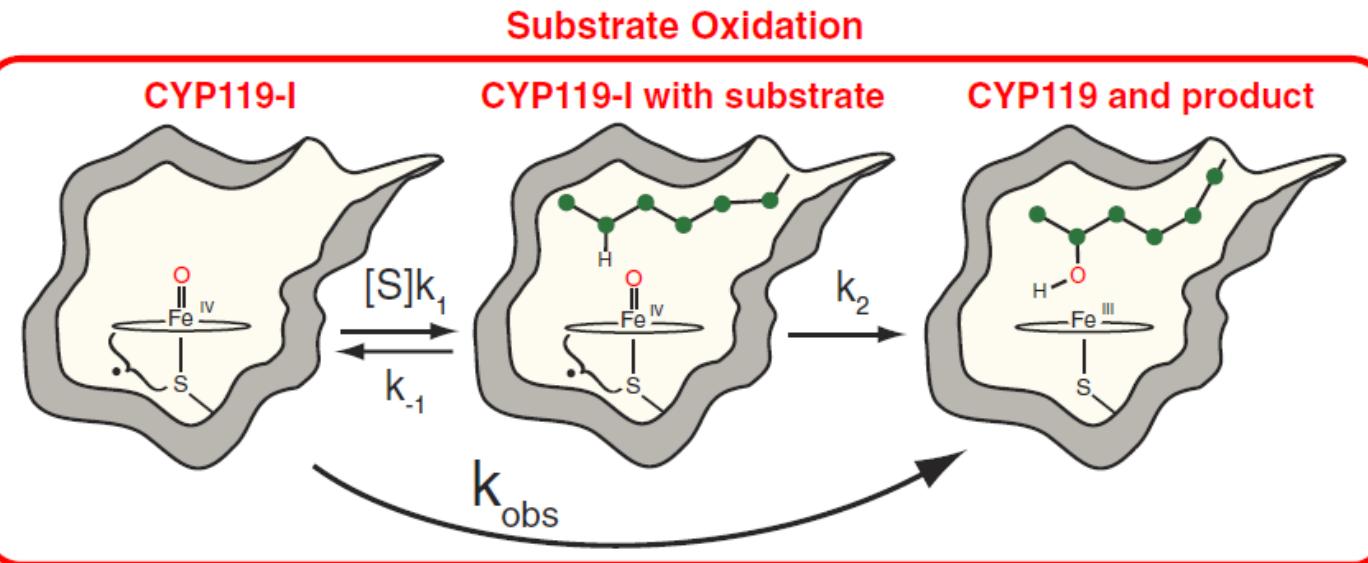
Extra info.

P450-I Preparation

CYP119



CYP119-I

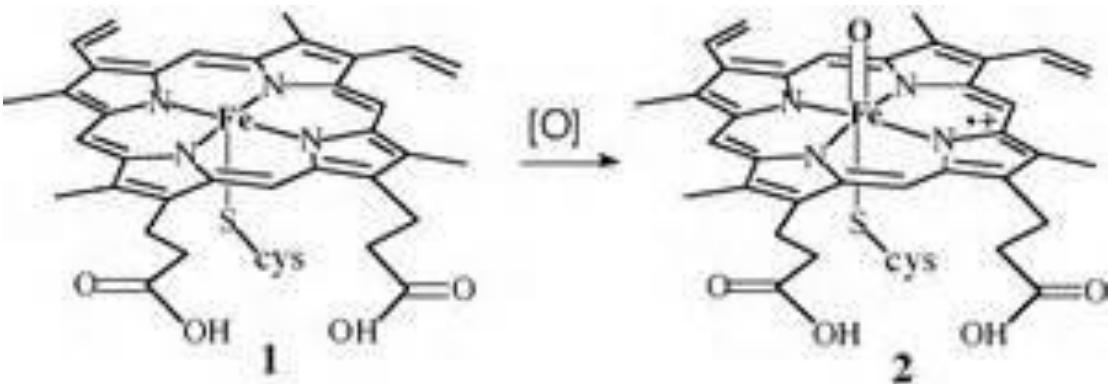


Substrate Oxidation

CYP119-I with substrate

CYP119 and product

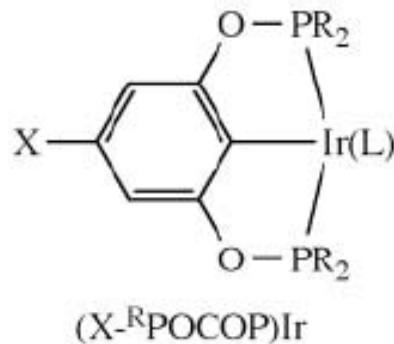
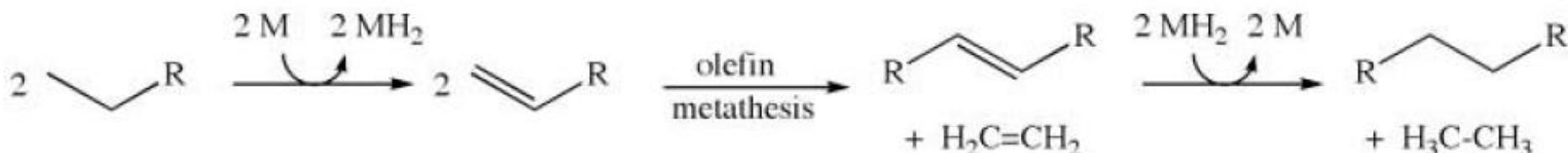
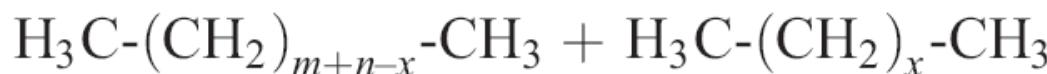
Reactive high-valent iron-oxo porphyrin



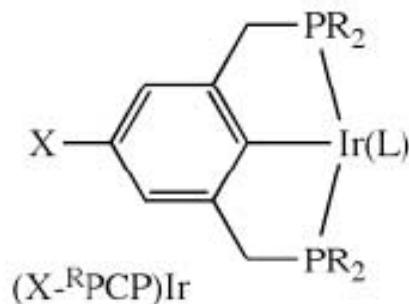
Basic Concepts
of Chemical
Bonding

(Science 2010 330 933)

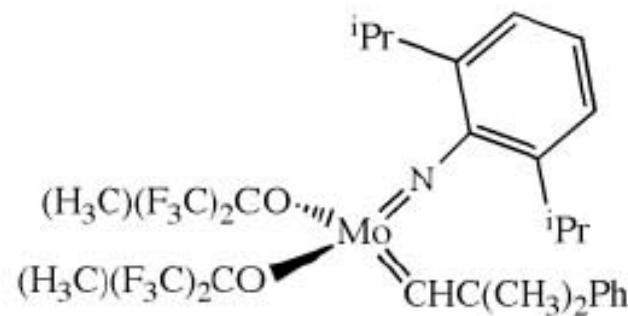
Extra info. Catalysts



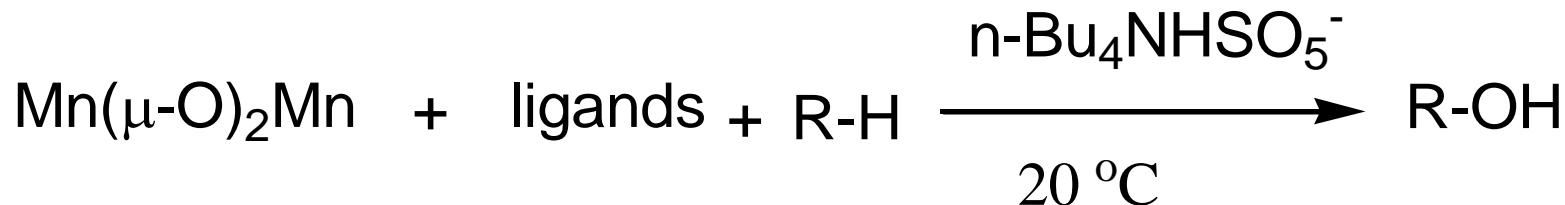
1: $\text{R} = t\text{-Bu}$, $\text{X} = \text{H}$
 $\text{L} = \text{C}_2\text{H}_4, \text{H}_2$



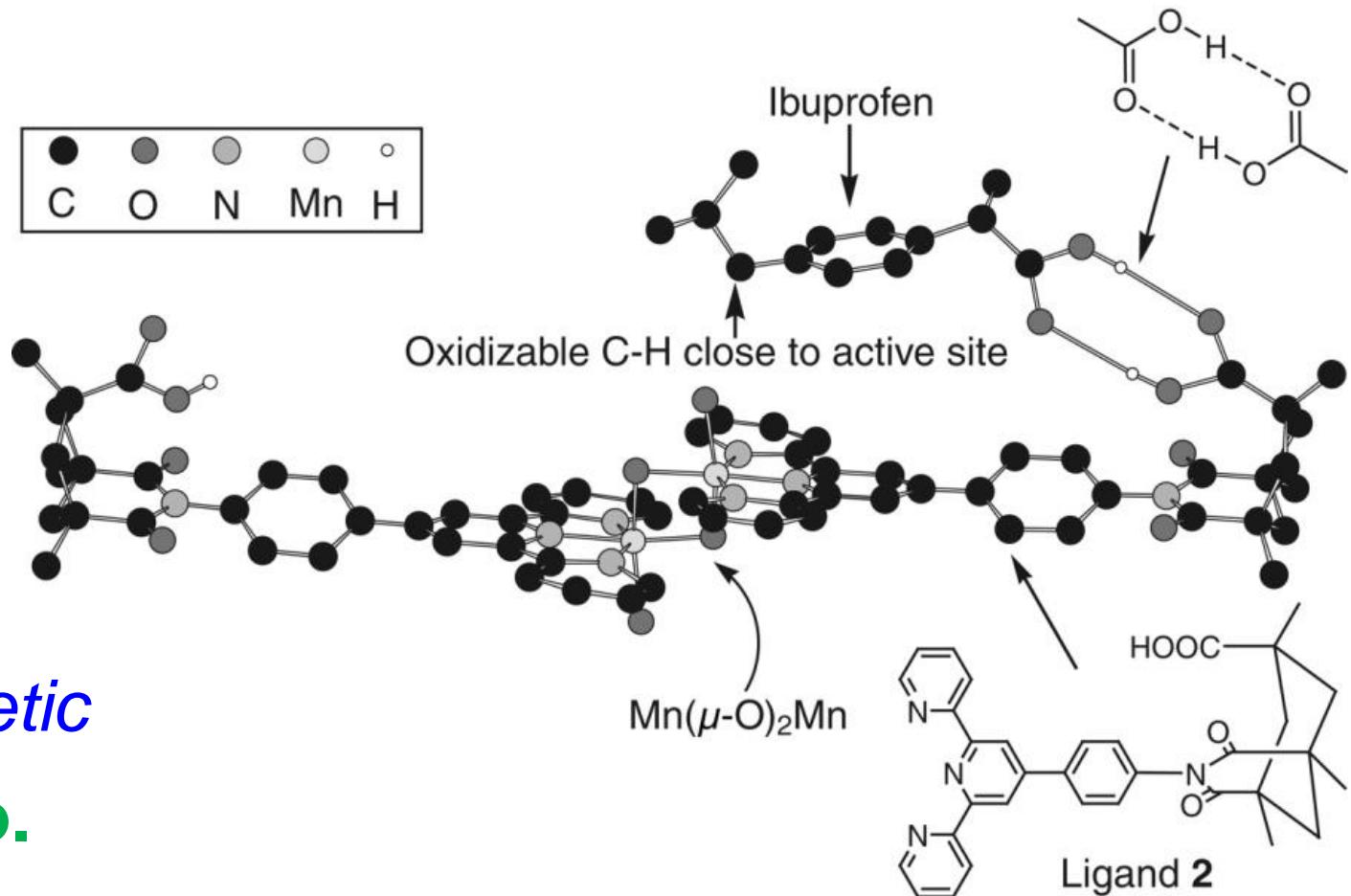
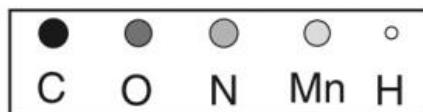
2a: $\text{R} = t\text{-Bu}$, $\text{X} = \text{H}$
2b: $\text{R} = i\text{-Pr}$, $\text{X} = \text{OMe}$
 $\text{L} = \text{H}_2 \text{ and/or H}_4$



(Science 2006, 312, 257)



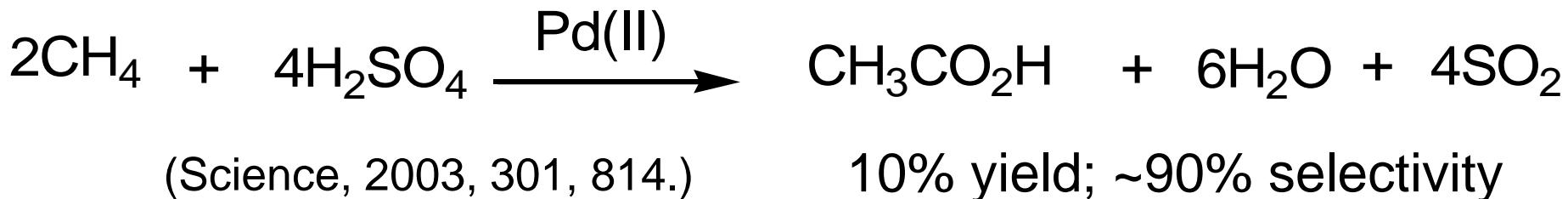
0.001 %



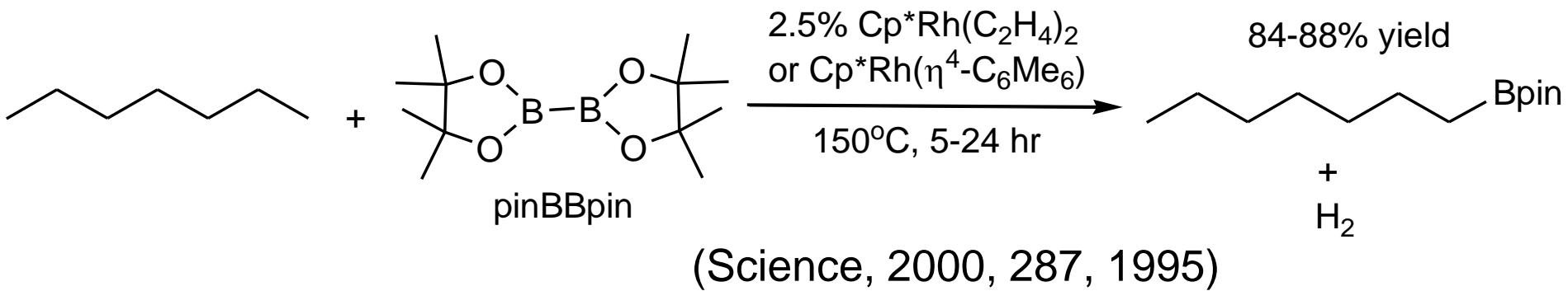
Biomimetic
Extra info.

(Science, 2006, 312, 1941)

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of Chemical
Bonding



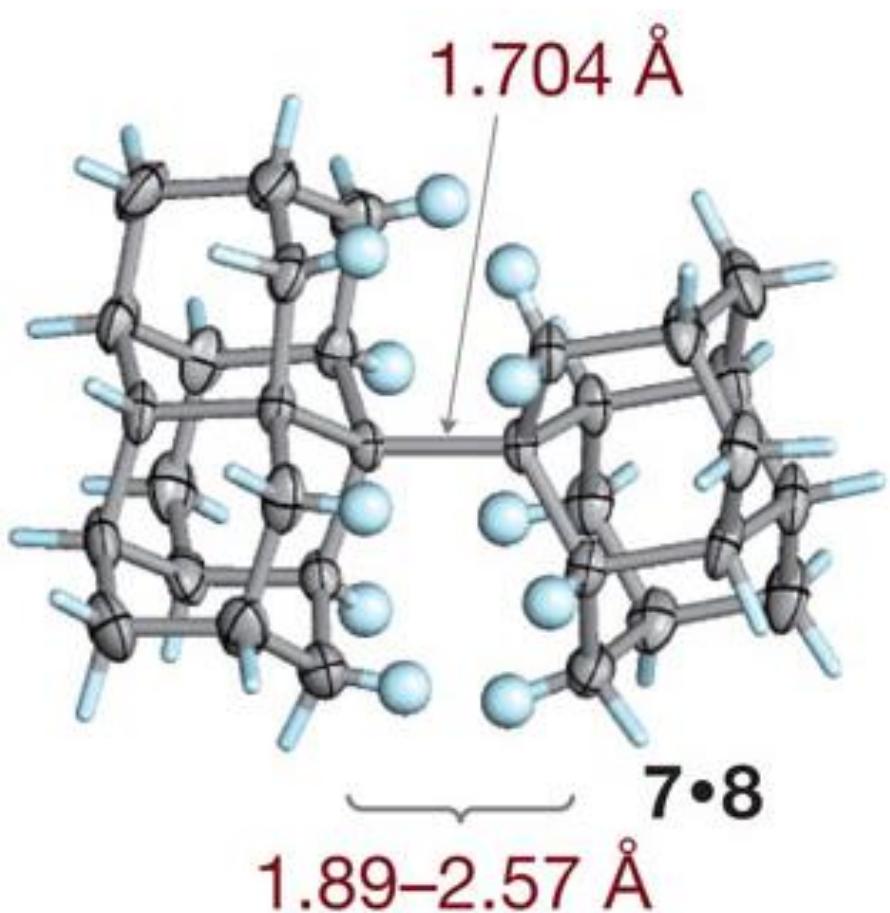
Extra info.



Many C-H activation and functionality works

(Reviews: Nature 2007, 446, 391; Nature 2008 455 314; Chem. Rev. 2010, 624; 2010, 890; 2010; 1147; 2011; 1315; Chem. Soc. Rev. 2009, 38, 3242)

Extra info. Extremely long alkane C–C bonds through dispersion forces



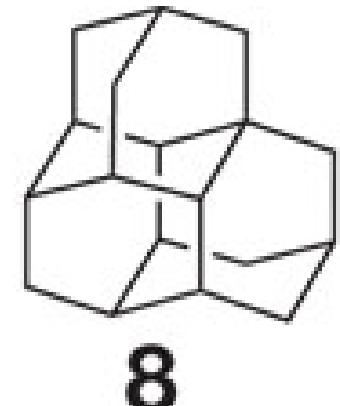
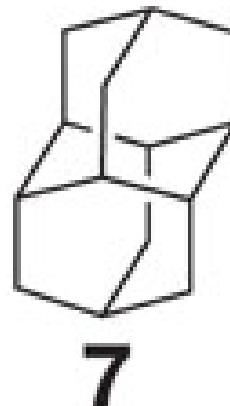
(Nature 2011, 477, 308)

Normal C(sp³)-C(sp³): 1.54

Nano-diamond: 1.704

Stable, decompose > 200°C

Stabilized by attractive dispersion interactions



Key Summary for Chapter 8

Lewis Symbol, Octet Rule

- 1.Ionic Bond: Lattice Energy
- 2.Covalent Bond: Polar, Dipole Moment, Formal Charge, Bond Strength/Enthalpy
- 3.Metallic Bond

Electronegativity, Lewis Structure,
Resonance Structures, Localized and
Delocalized Electrons

Basic Concepts
of Chemical
Bonding

**Thank You for Your
Attention!
Any Questions?**

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