CHEM103
General Chemistry

Chapter 8: Basic Concepts of Chemical Bonding

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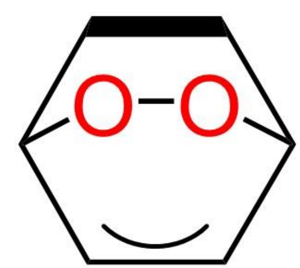


Assignment 7 & Mid-term EXAM

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

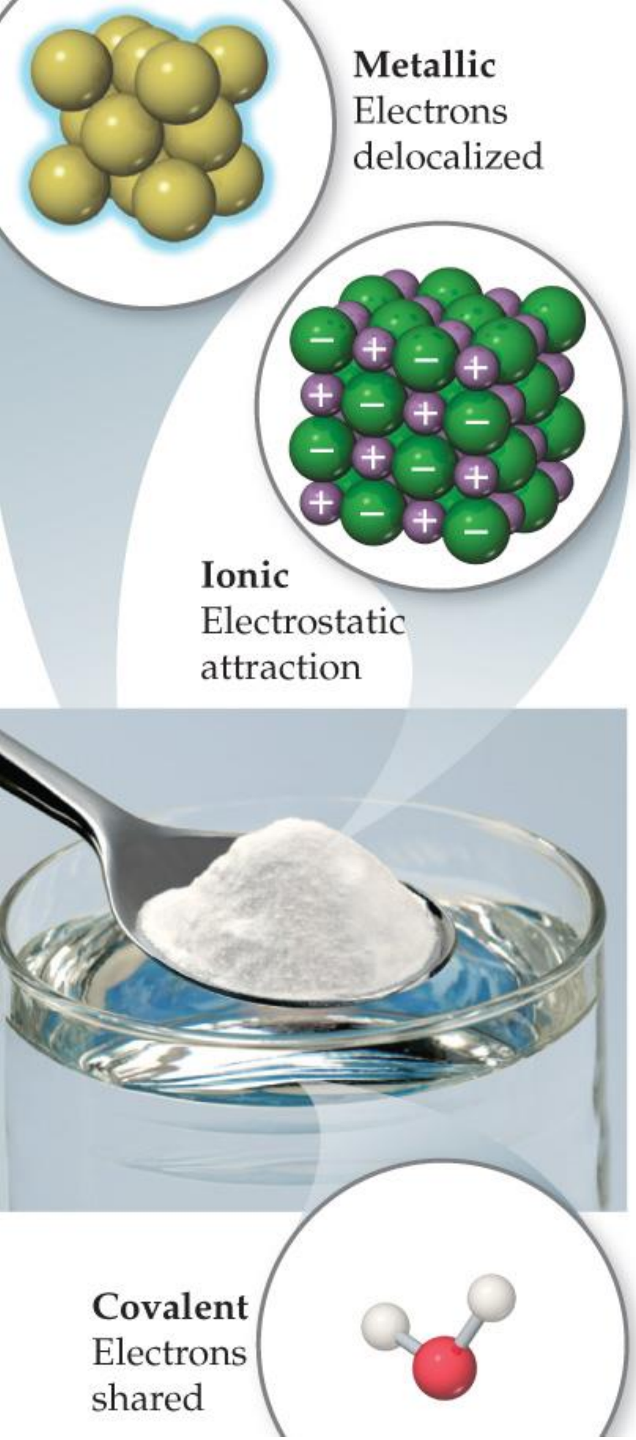
Properties of Metal, Nonmetals, and Metalloids

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.

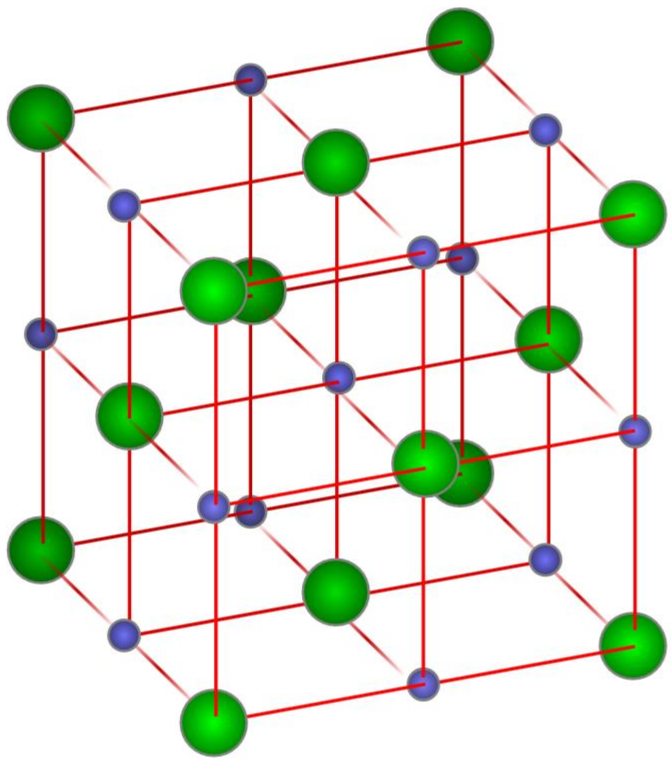
Lewis Symbols & Octet Rule

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	$[He]2s^22p^1$	·Ḃ·	Al	$[Ne]3s^23p^1$	·Ȧl·
4A	C	$[He]2s^22p^2$	·Ċ̣·	Si	$[Ne]3s^23p^2$	·Ṩi·
5A	N	$[He]2s^22p^3$	·Ṇ̇:	P	$[Ne]3s^23p^3$	·Ṗ̣:
6A	O	$[He]2s^22p^4$	:Ọ̇:	S	$[Ne]3s^23p^4$	:Ṩ:
7A	F	$[He]2s^22p^5$	·F̤̈:	Cl	$[Ne]3s^23p^5$	·C̤̈l:
8A	Ne	$[He]2s^22p^6$	:N̤̈e:	Ar	$[Ne]3s^23p^6$	:Ä̤r:

- 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

$$Na(g) \longrightarrow Na^{+}(g) + e^{-}$$

$[Ne]3s^1$ $\quad$ $[He]2s^22p^6$

Ionization energy (I_1): 496

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

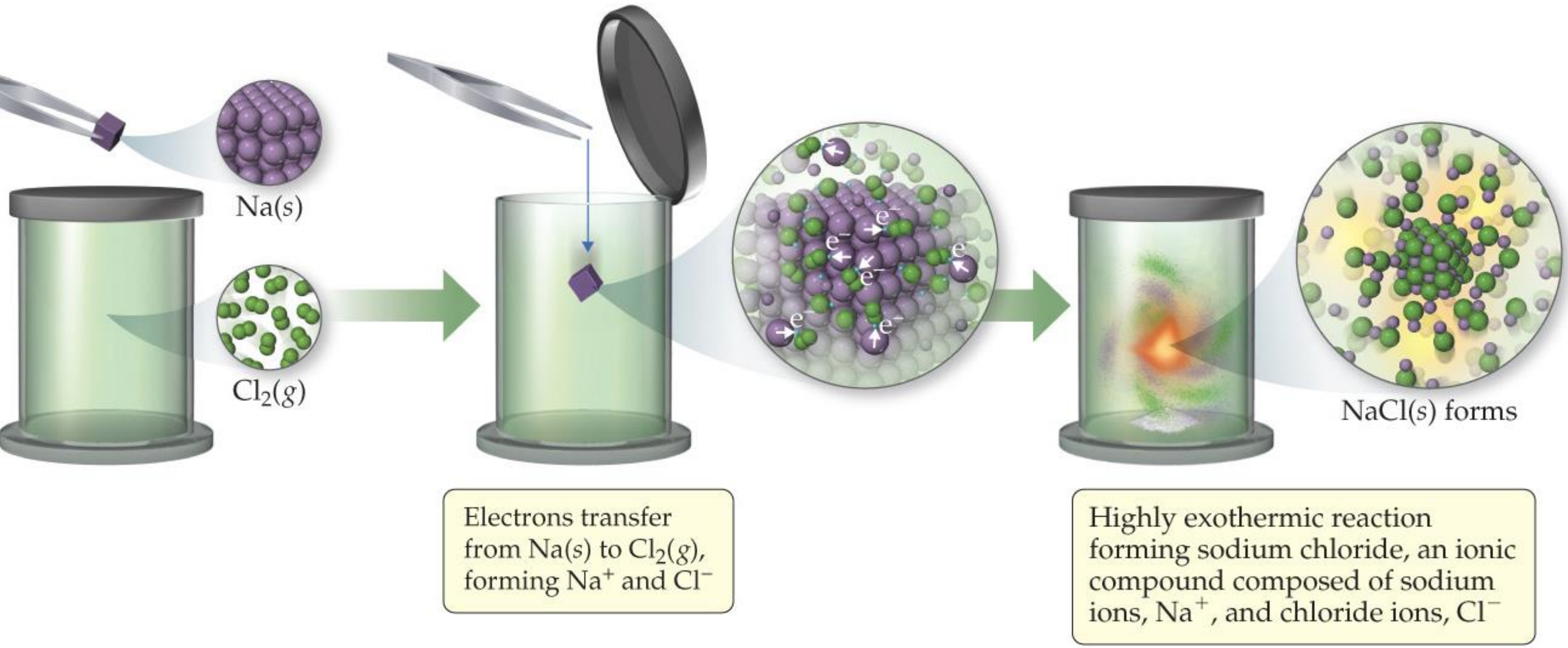
$$Cl(g) + e^{-} \longrightarrow Cl^{-}(g)$$

$[Ne]3s^23p^5$ $\quad$ $[Ne]3s^23p^6$

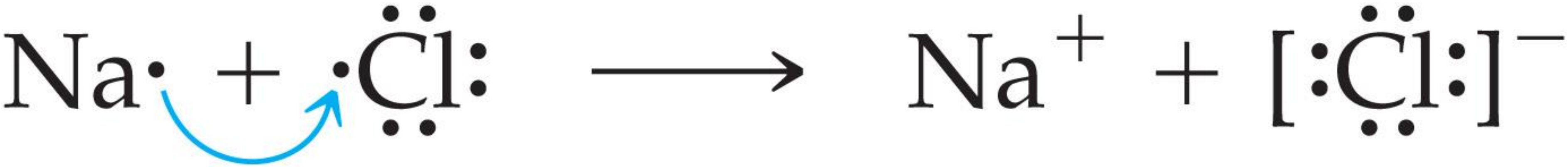
Cl
−349

Electron affinity

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



These two numbers (496 – 349 kJ = 147 kJ) don't explain why the reaction of sodium metal and chlorine gas to form sodium chloride is **so exothermic** (ΔH_f^0 = -410.9 kJ)!



$[Ne]3s^1$ $[Ne]3s^2 3p^5$ $[He]2s^2 2p^6$ $[Ne]3s^2 3p^6$

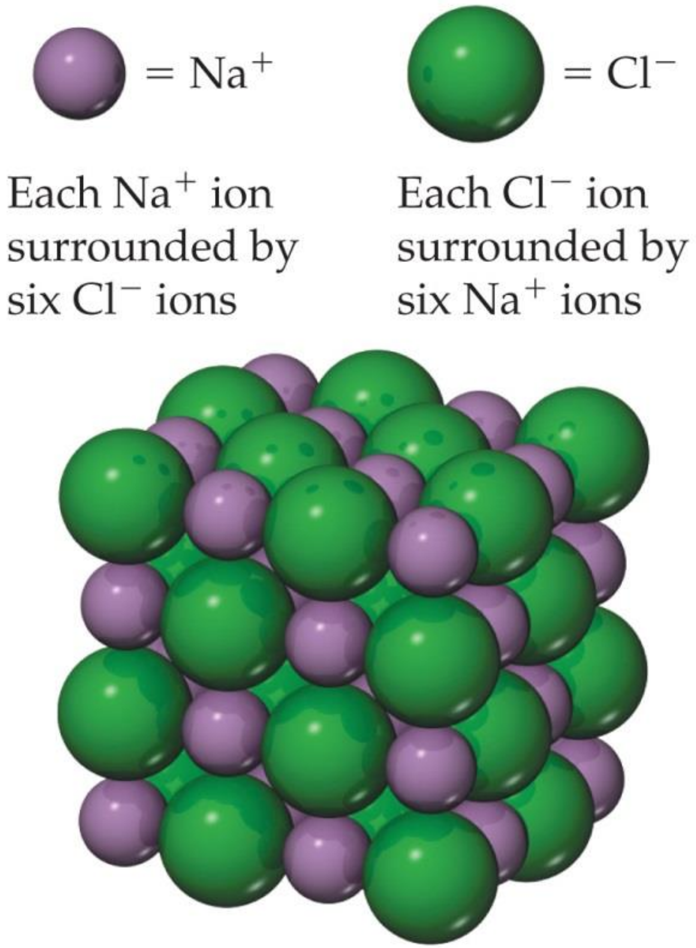
- There must be a third piece to the puzzle.

- 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**.*

$$NaCl(s) \longrightarrow Na^+(g) + Cl^-(g)$$



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

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

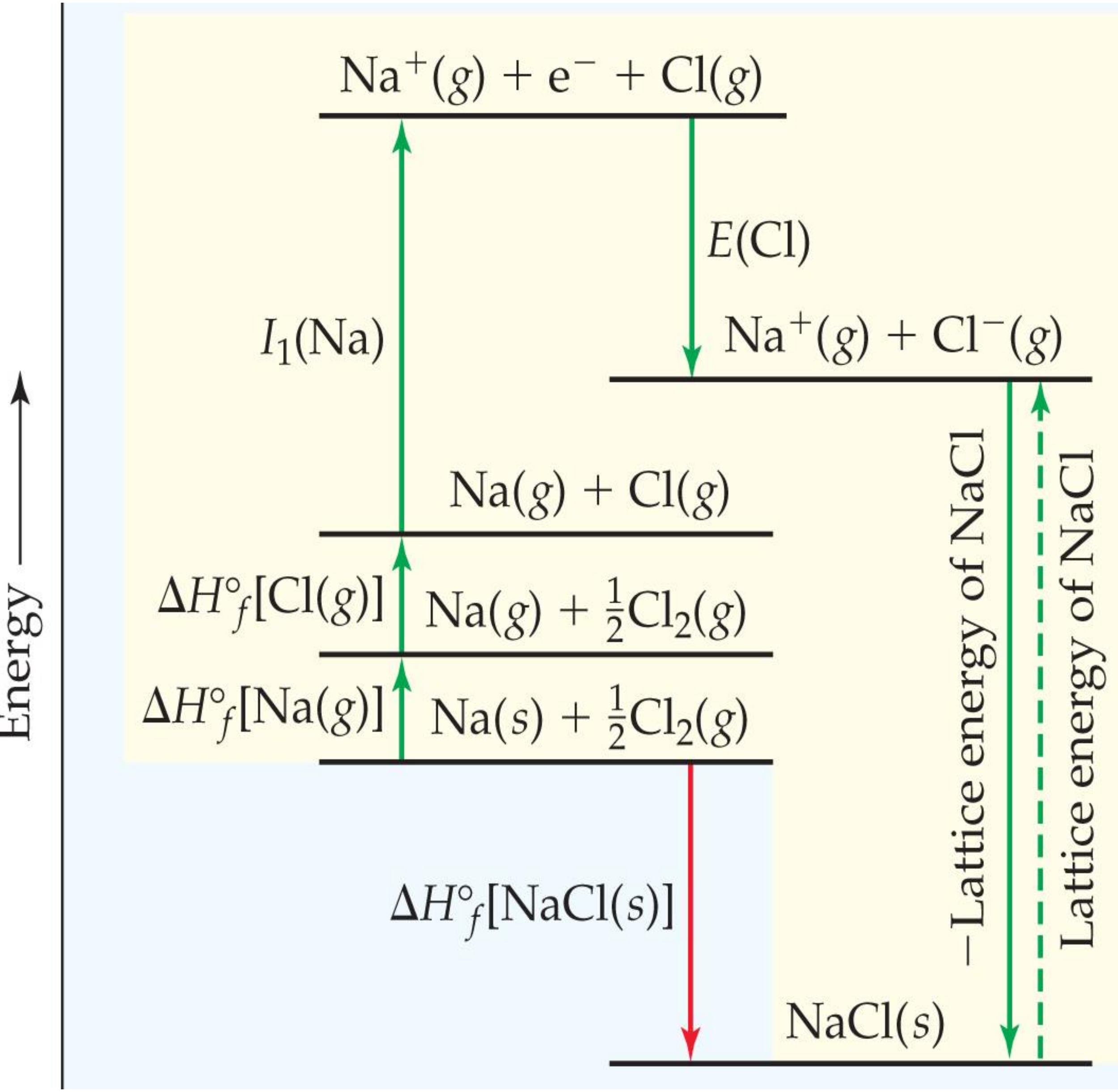
Q: charges
d: distance

Compound	Lattice Energy (kJ/mol)		Compound	Lattice Energy (kJ/mol)	
LiF	1030		$MgCl_2$	2326	M^{2+}
LiCl	834	size	$SrCl_2$	2127	
LiI	730				
NaF	910		MgO	3795	
NaCl	788	size	CaO	3414	M^{2+}
NaBr	732		SrO	3217	
NaI	682				
KF	808		ScN	7547	M^{3+}
KCl	701				
KBr	671				
CsCl	657				
CsI	600				

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

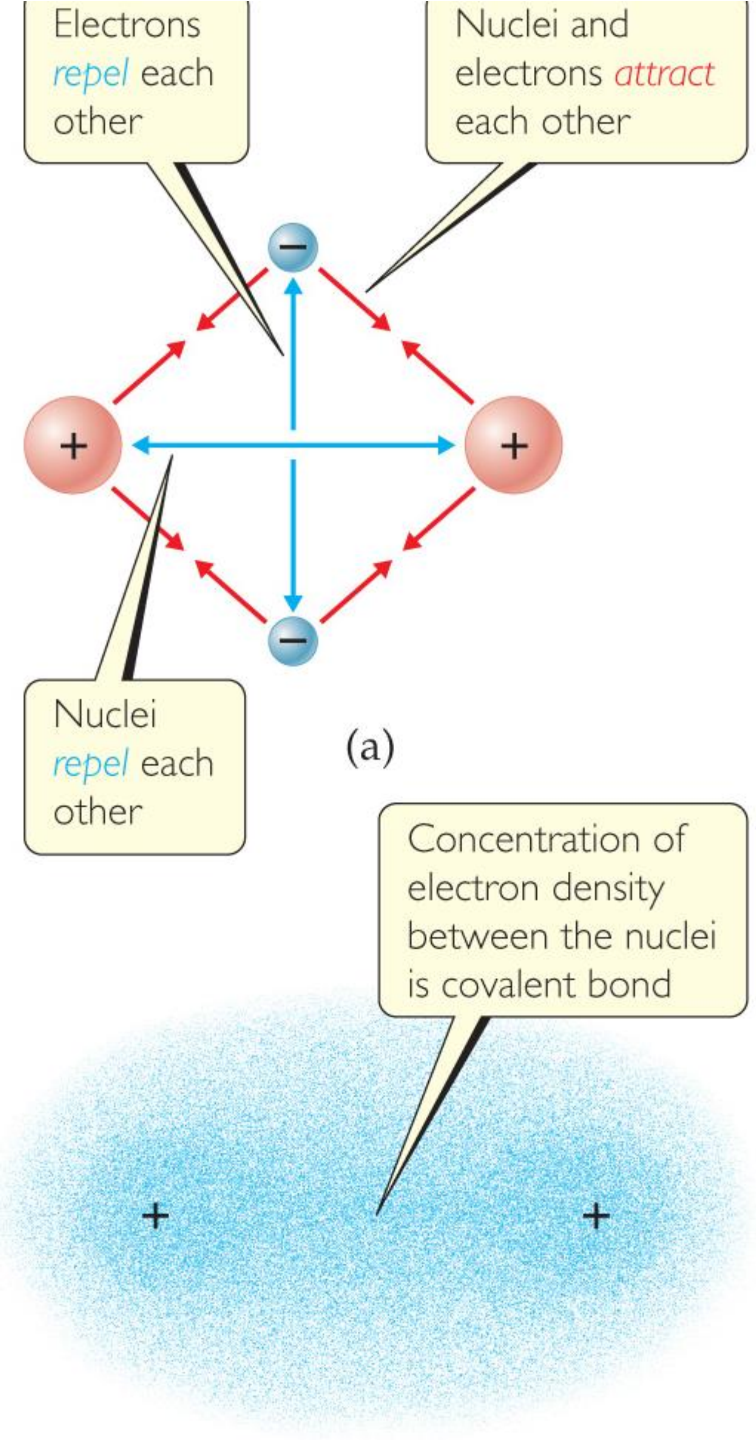
- Ionic compounds: high melting points & usually crystalline（结晶）.

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



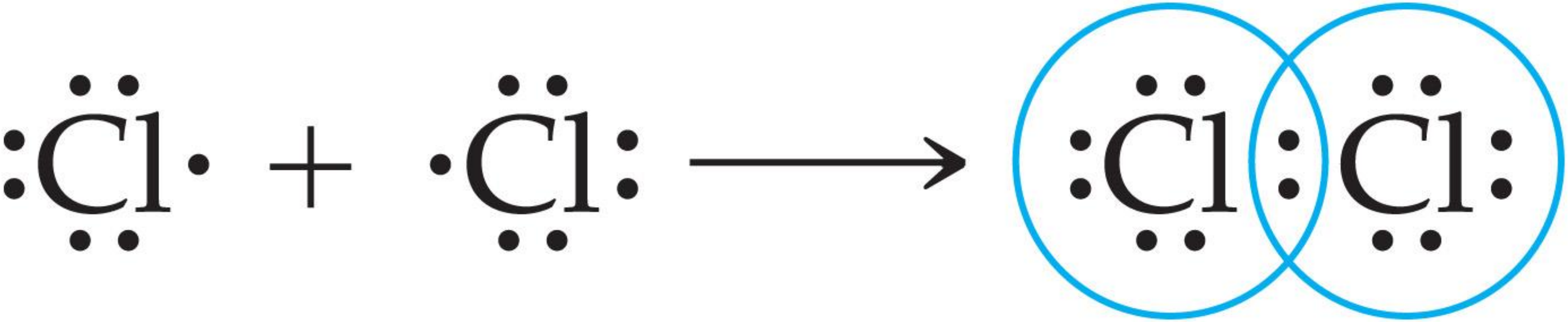
- Lewis proposed that atoms **share electrons** (**1 single covalent bond with 2 electrons**) in covalent bonds (e.g. in H_2), in order to fulfill octet rule (or noble gas configuration).

- There are several electrostatic interactions:

1. Attractions between electrons & nuclei (**major**),

2. Repulsions between electrons,

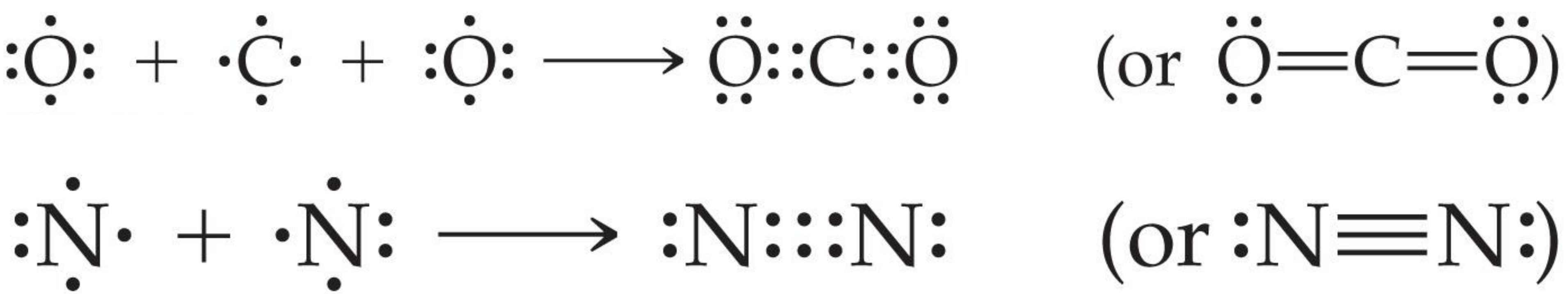
3. Repulsions between nuclei.



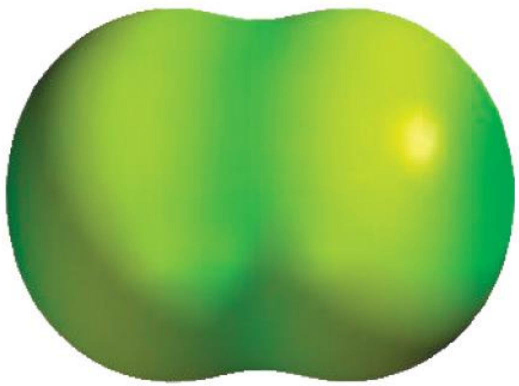
Cl atoms share electrons until they are surrounded by **8 valence electrons** (octet rule, or stable noble-gas configuration).

Multiple Bonds

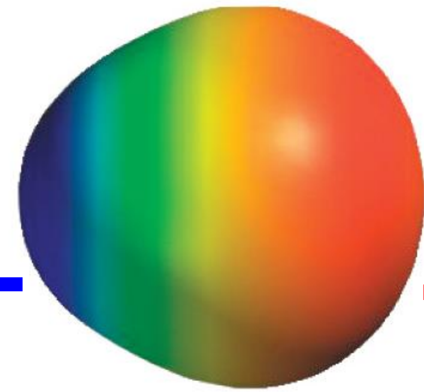
- Two atoms share only **one pair** of electrons: **single bond**.
- Sometimes, **two pairs** of electrons need to be shared between two atoms: **double bonds**.
- **Three pairs** of electrons are shared between two atoms: **triple bonds**.



Non-Polar & Polar Covalent Bonds



Non-polar F_2

+  -

HF Polar极性

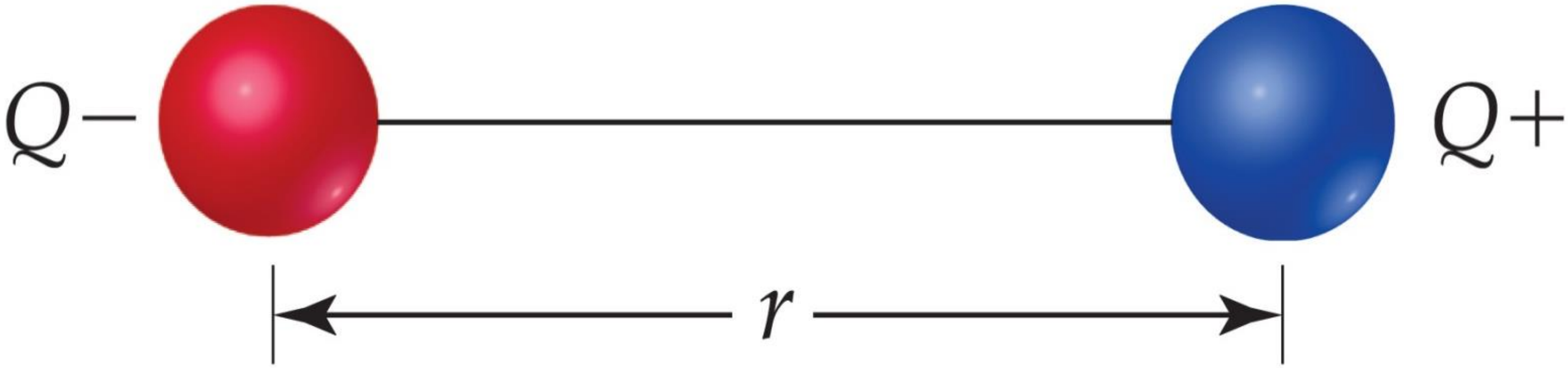
δ+ δ–
H–F

δ: partial charges

• 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.

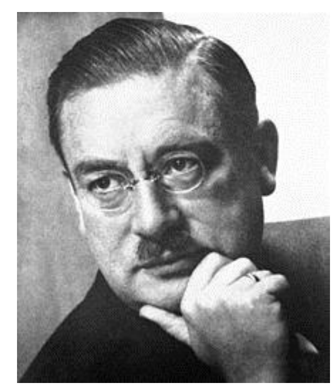


Dipole moment $\mu = Qr$

$\overset{+\!\!\longrightarrow}{\text{H–F}}$

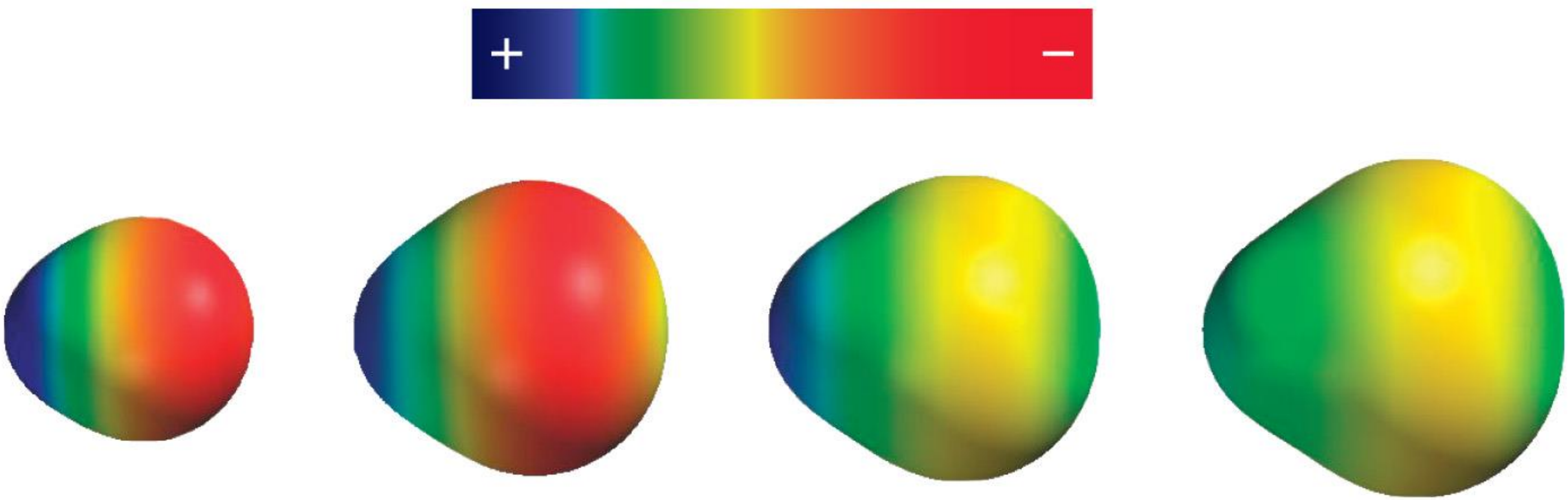
- When two atoms **share electrons unequally**, a **bond dipole**（偶极） results.
- The **dipole moment**, μ, (unit: debyes, D; 1 D = 3.335641×10^{-30} C*m or 0.208194 e*Å) produced by two equal but opposite charges separated by a distance, *r*, is calculated:

$$\mu = Qr$$



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



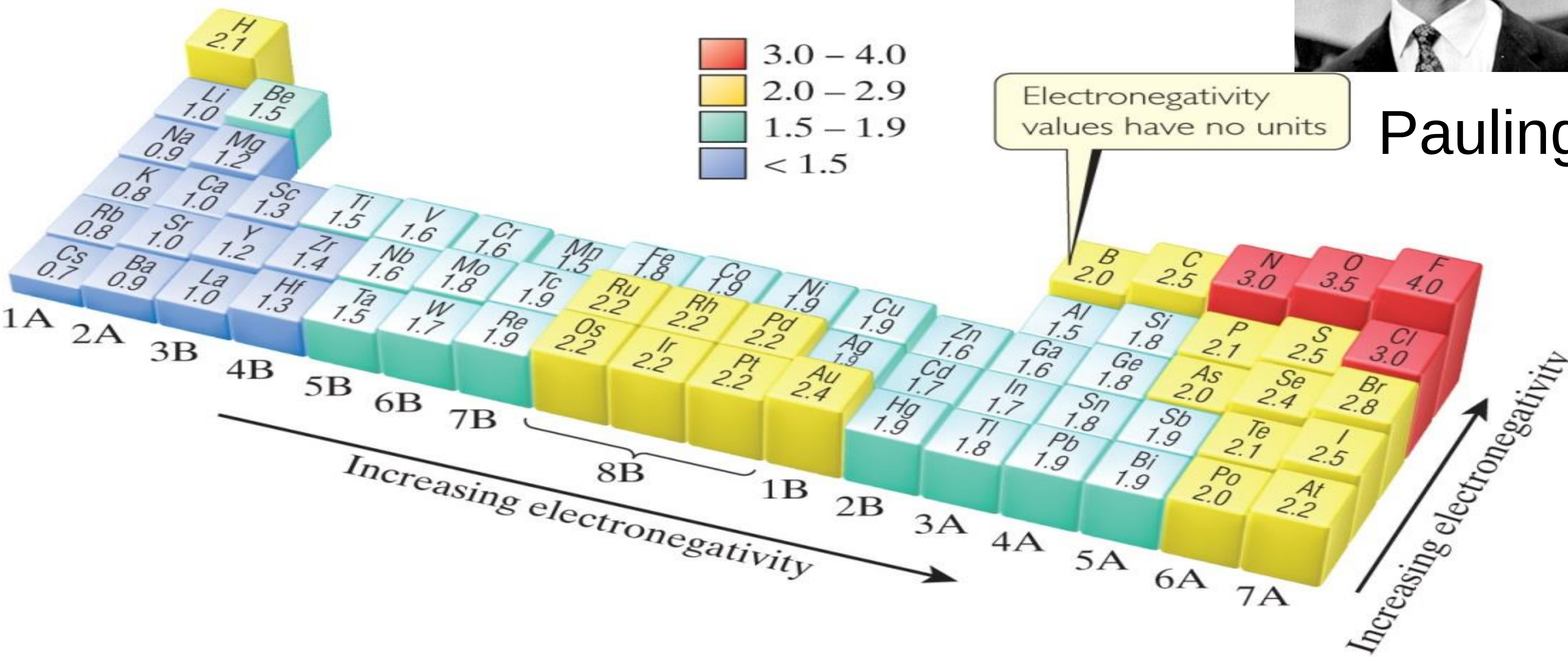
HF HCl HBr HI

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

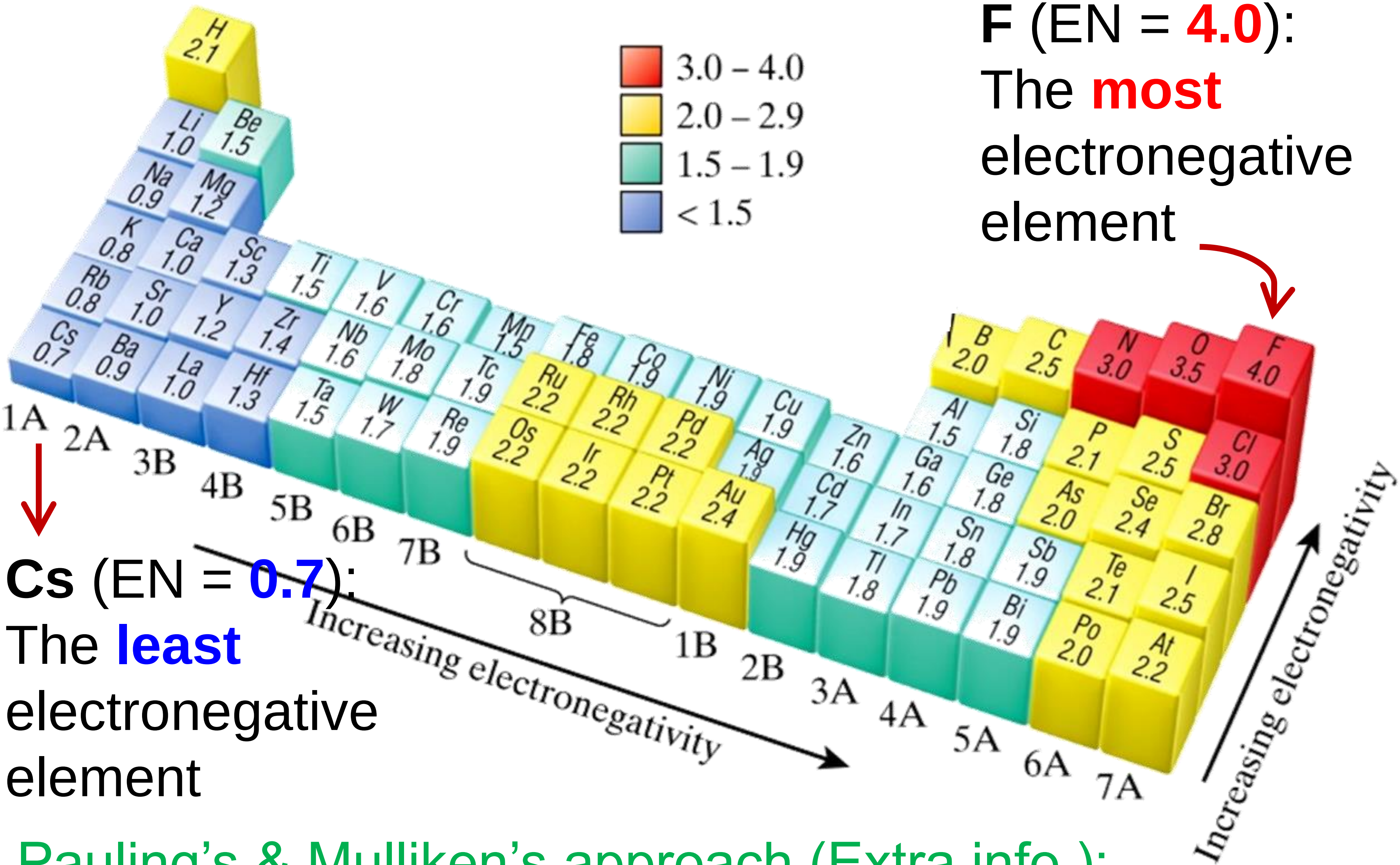
Electronegativity (EN, 电负性)

- ***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



Cs (EN = **0.7**):
The **least** electronegative element

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

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

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

Electronegativity and Bonding

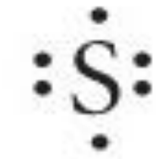
Electronegativity (EN) difference tells us approximated **bonding types**: **ionic or** (polar or non-polar) **covalent**. The **greater the difference in EN** between the two elements forming the bond, the **more ionic** the bond. Typical ranges:

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	**covalent**	F–F	4.0-4.0 = 0.0
	covalent	C–H	2.5-2.1 = 0.4
(Li_2 molecule)	**covalent**	Li –Li	1.0-1.0 = 0.0
	covalent	Au–C	2.5-2.4 = 0.1

Some chemical bonds could contains 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 $\rightarrow$ 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.

$\boxed{\text{B.}}$ 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.

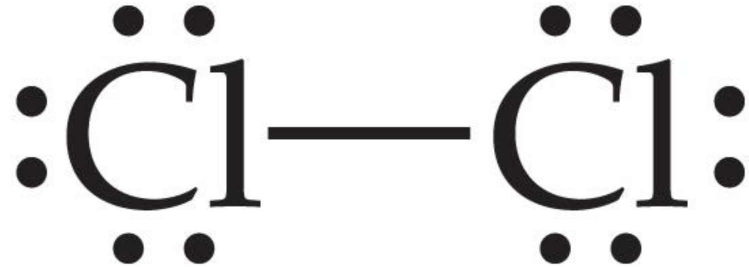
If the charged particles are moved closer together, does μ increase, decrease, or stay the same?

A. Increase, because r increases.

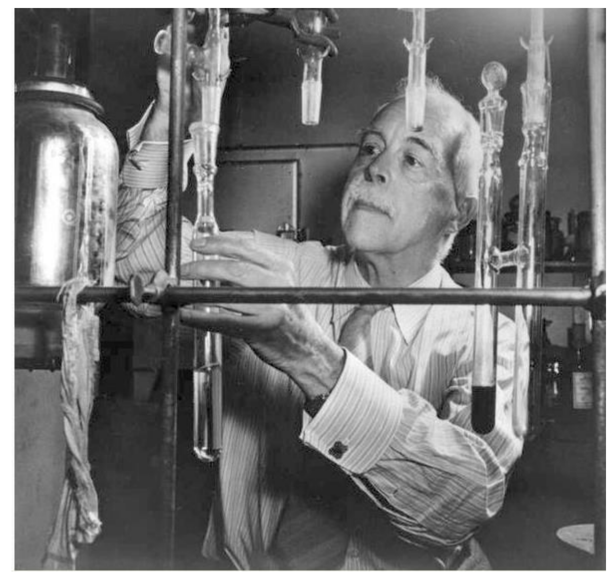
$\boxed{\text{B.}}$ Decrease, because r decreases.

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

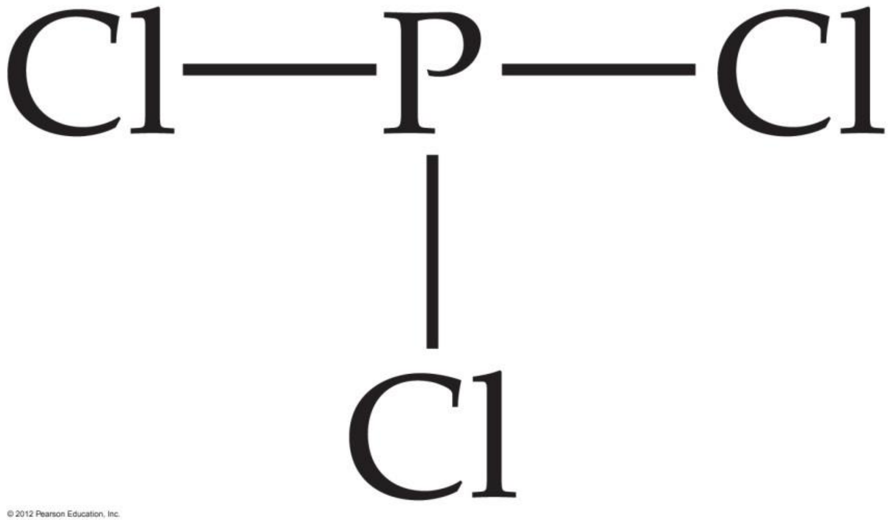
PCl_3

<u>Keep track of the total valence electrons</u>:

5 + 3*7 = **26**

P **Cl**

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.



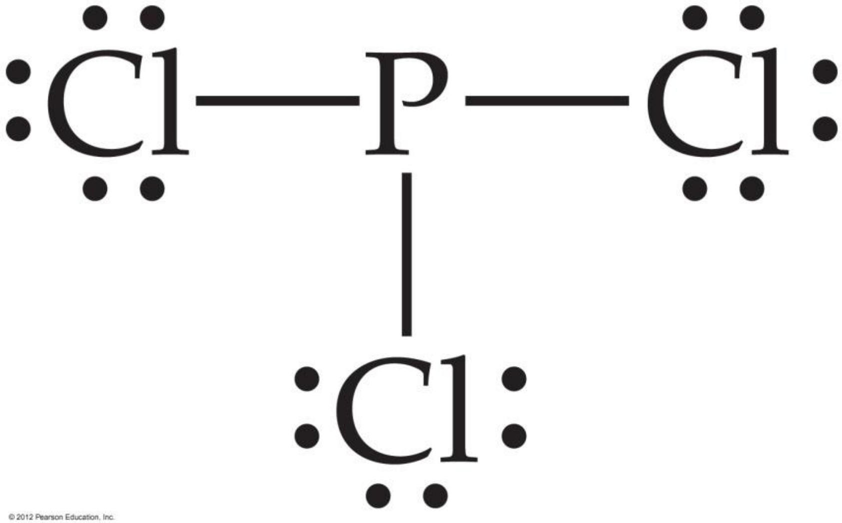
2. The **central atom** is the ***least* electronegative element** (➔ less valance electrons & need more bonds) except hydrogen.

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

<u>Keep track of the electrons:</u>

26 − **6** = 20

(3 covalent bonds with 6 e^-)



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

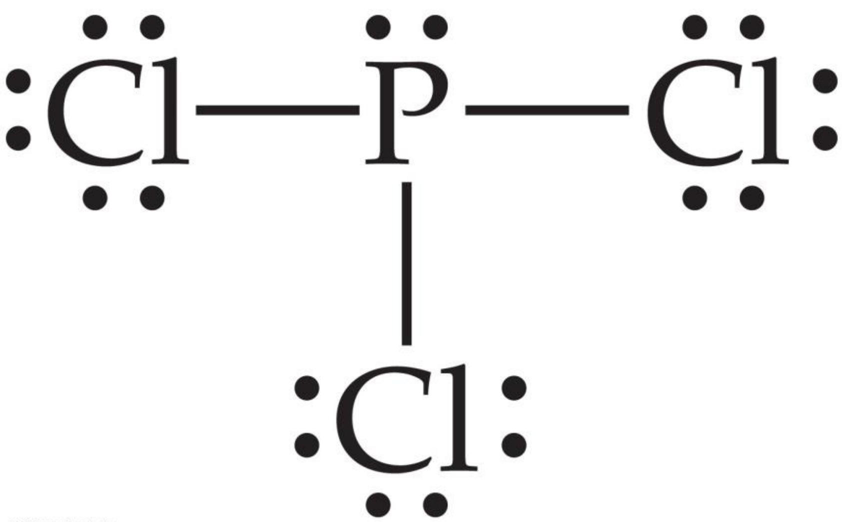
Keep track of the electrons:

*[26 − **6** = 20;*

(3 covalent bonds with 6 e^-)]

20 − **18** = 2

(3*3 lone-pair e^-, 9*2 e^-)



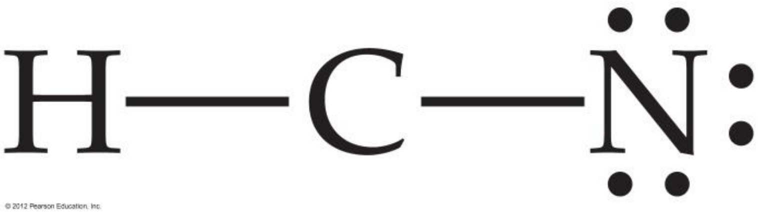
4. Fill the octet of the **central atom** (lower EN).

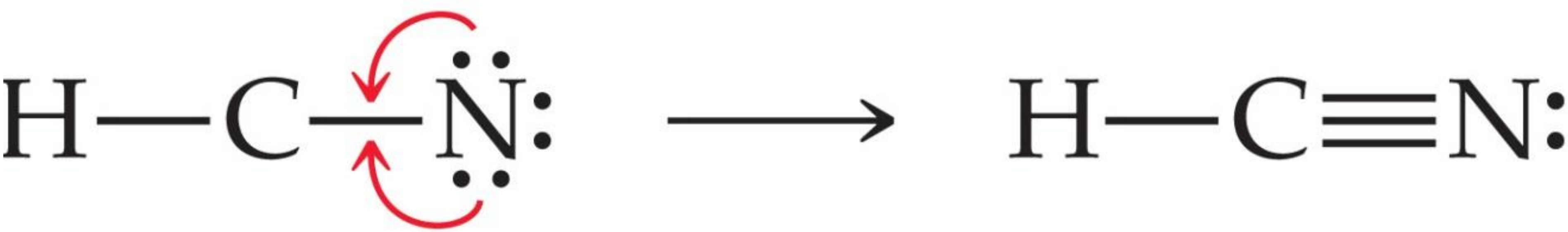
Keep track of the electrons:

2 − **2** = 0

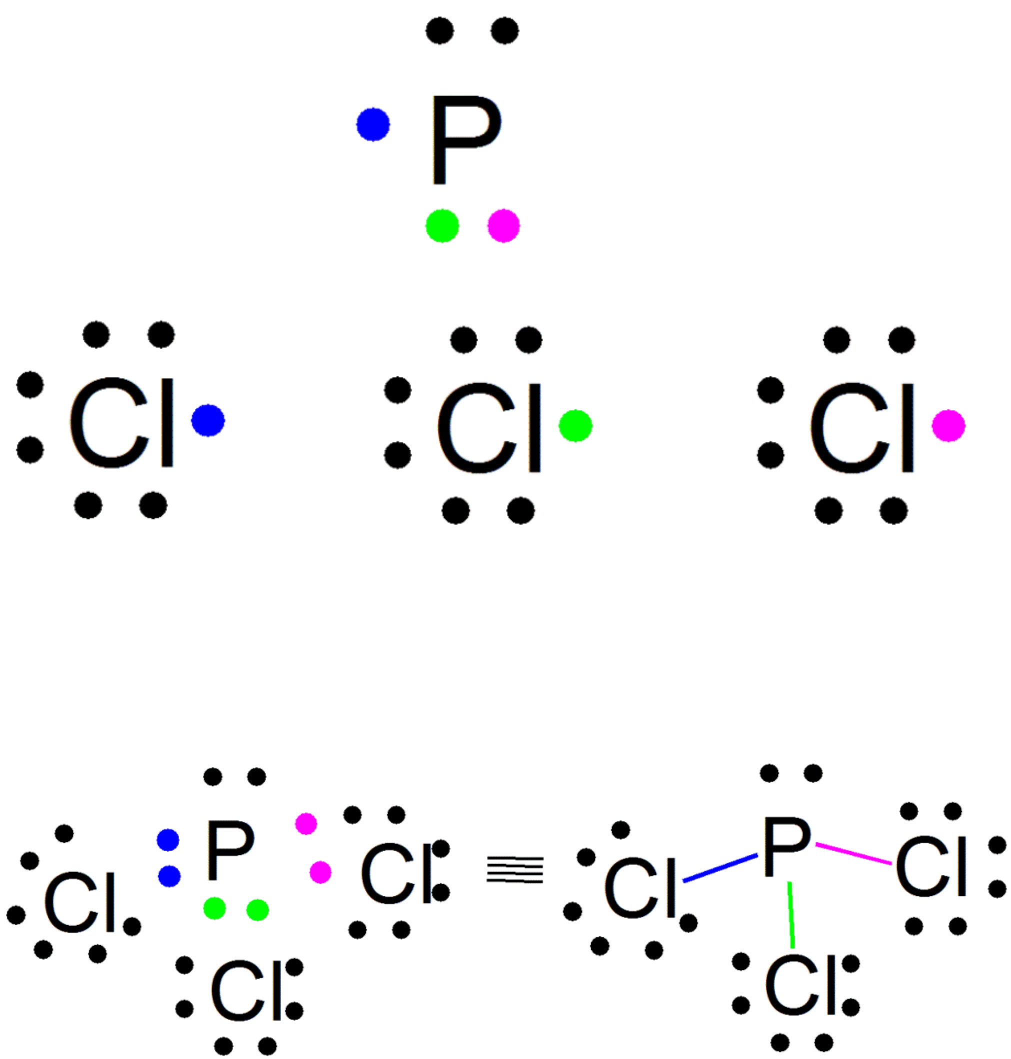
(1 lone-pair e^- on P)

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)



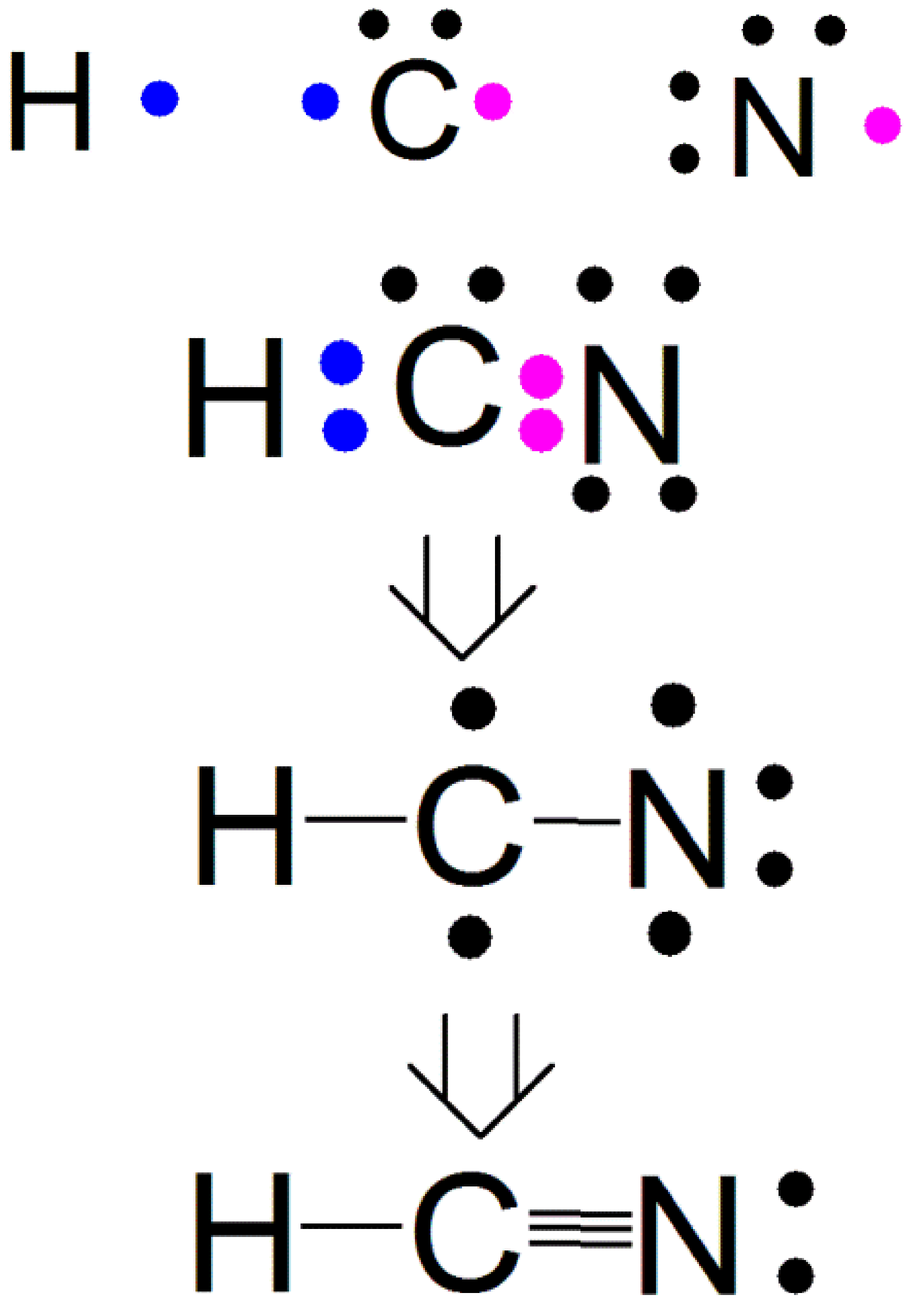
1. Write all atoms and their valence electrons.

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"**:

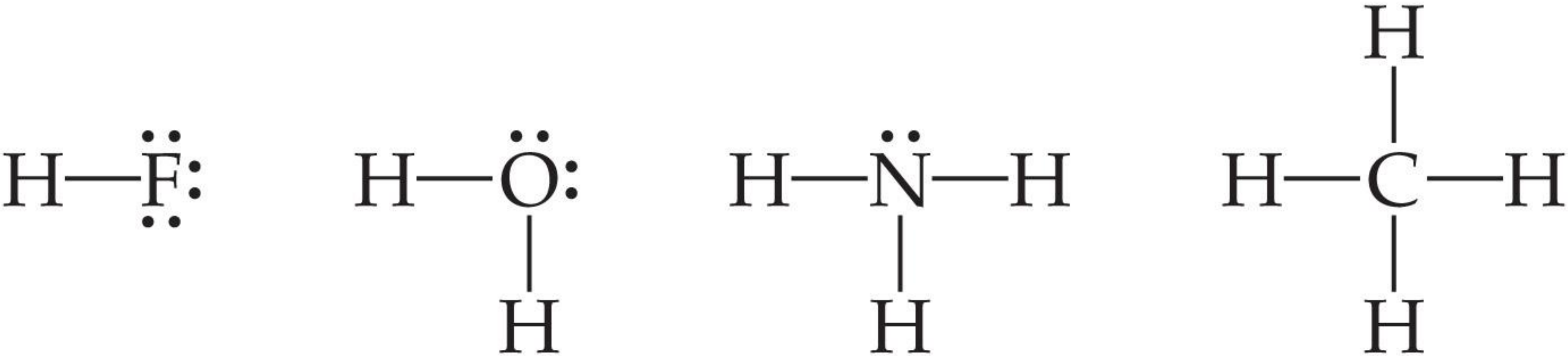
P needs 3 bonds; Cl needs 1 bond.

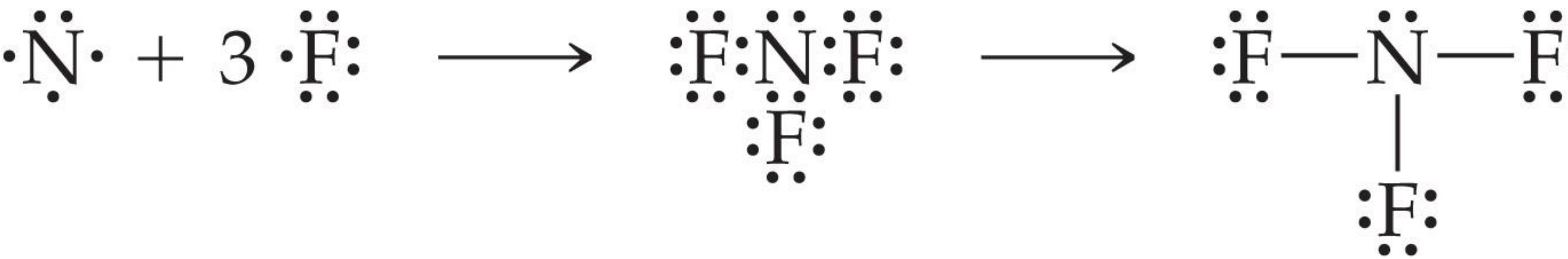


H misses **1**e^-, C misses **4**e^- & N misses **3**e^-.

➔ H needs **1** bonds; C needs **4** bond; N needs **3** bond.

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



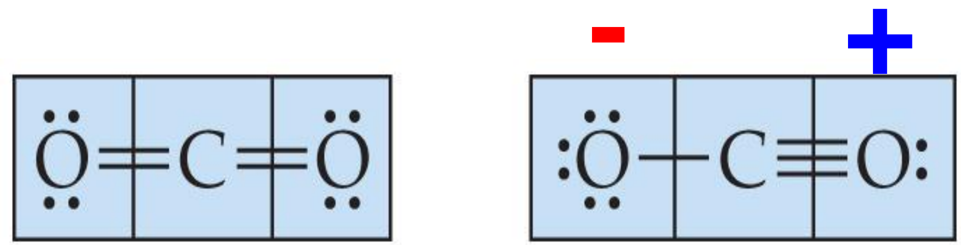


Formal Charge

- **Assign formal charges of each atom in all Lewis structures.**

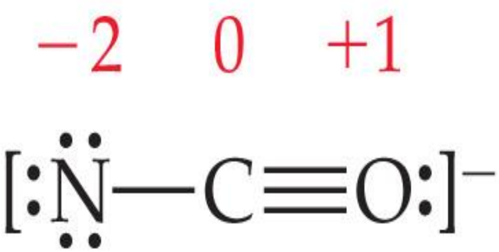
  - Count the electrons in (non-bonding) **lone pairs** (**2e$^-$** each **pair**) and **half the bonding electrons** (**1e$^-$** each **bond**) it shares with other atoms (**N**).

  - 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**).



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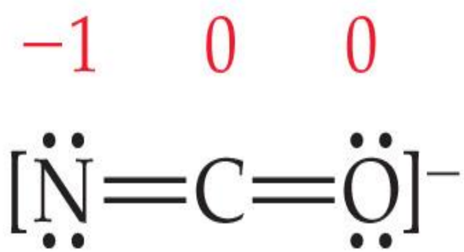
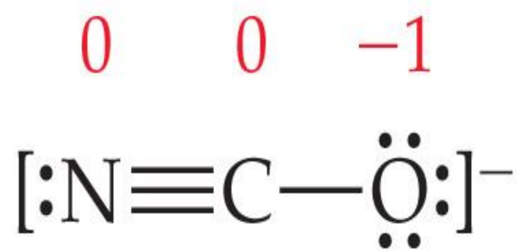
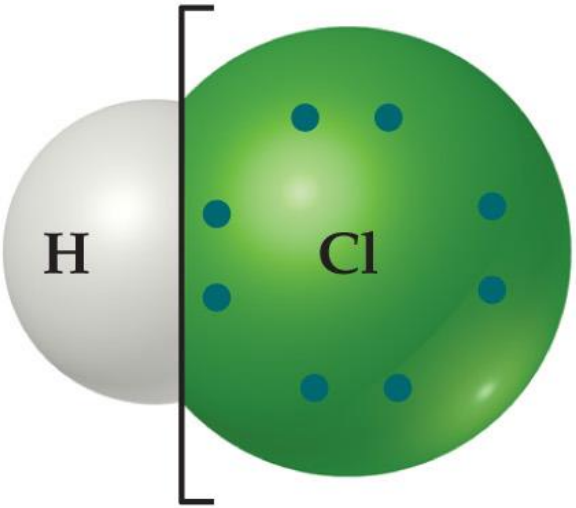


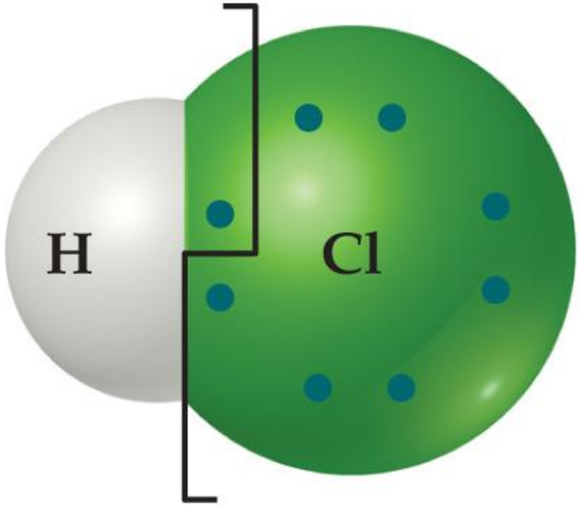
(ii)

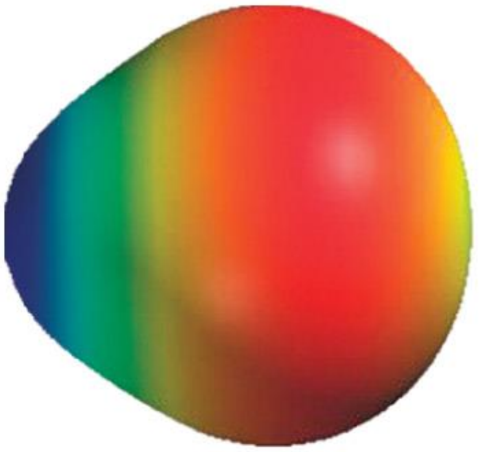


(iii)

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)

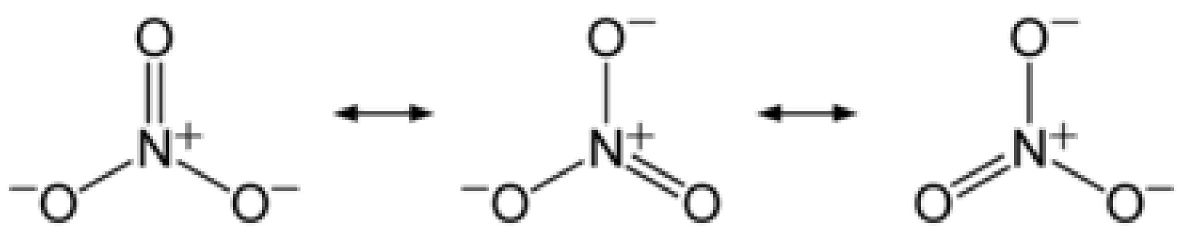
Realistic electron distribution

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.

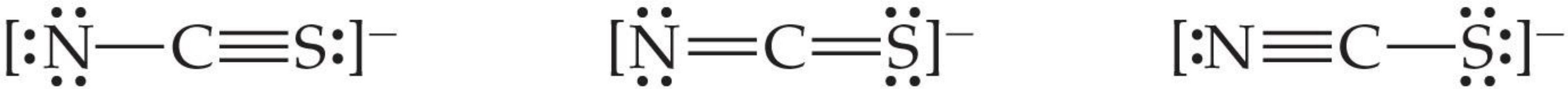
The formal charge on the nitrogen atom in the nitrate ion (NO_3^{1-}) is

a. +2
b. +1
c. 0
d. –1

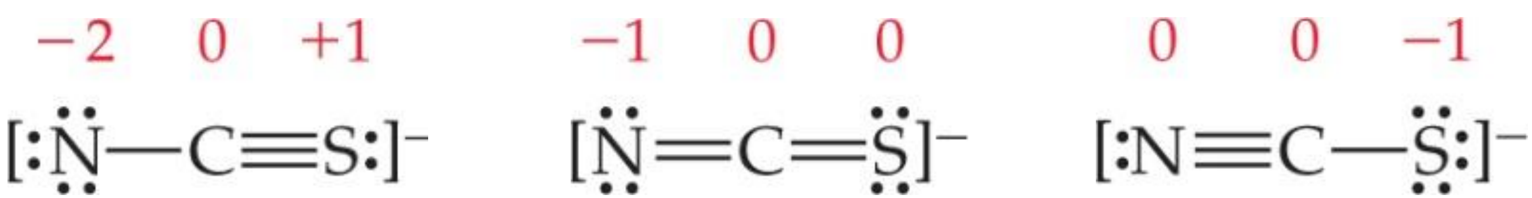


N: 5 – (0 + 8/2) = +1

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?

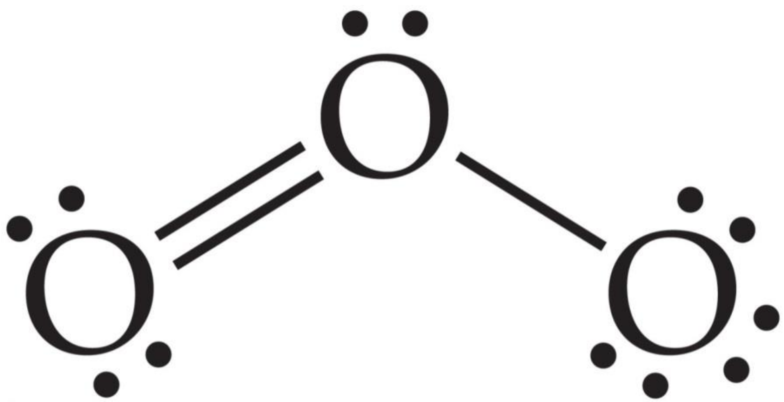


N: 5 – (6 + 2/2) = -2	5 – (4 + 4/2) = -1	5 – (2 + 6/2) = 0
C: 4 – (0 + 8/2) = -0	4 – (0 + 8/2) = 0	4 – (0 + 8/2) = 0
S: 6 – (2 + 6/2) = +1	6 – (4 + 4/2) = 0	6 – (6 + 2/2) = -1

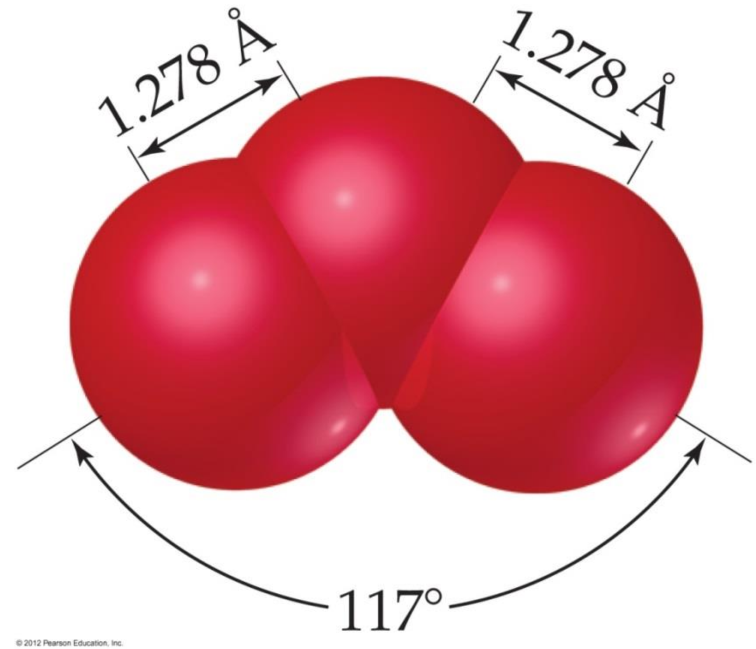
Suppose a Lewis structure for a neutral fluorine-containing molecule results in a formal charge on the fluorine atom of +1. What conclusion would you draw?

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.

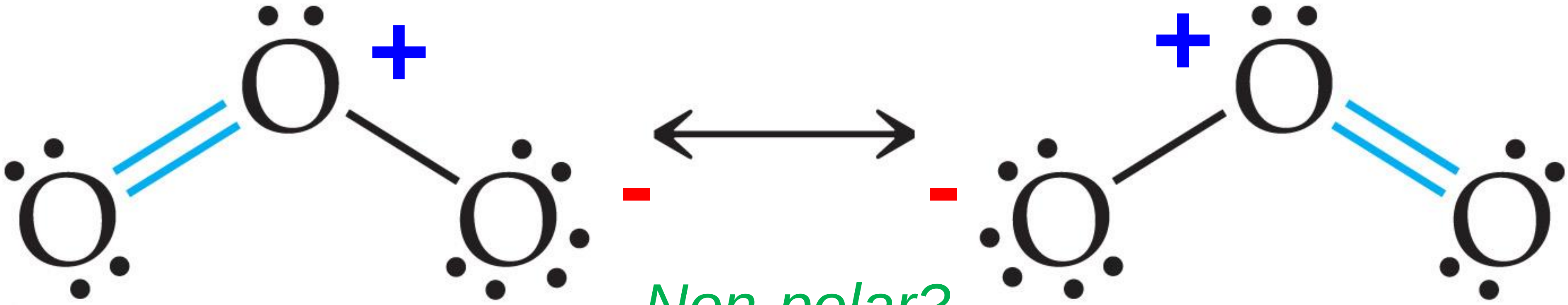
Resonance（共振） Structures



Lewis structure for ozone（臭氧）, O_3.



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

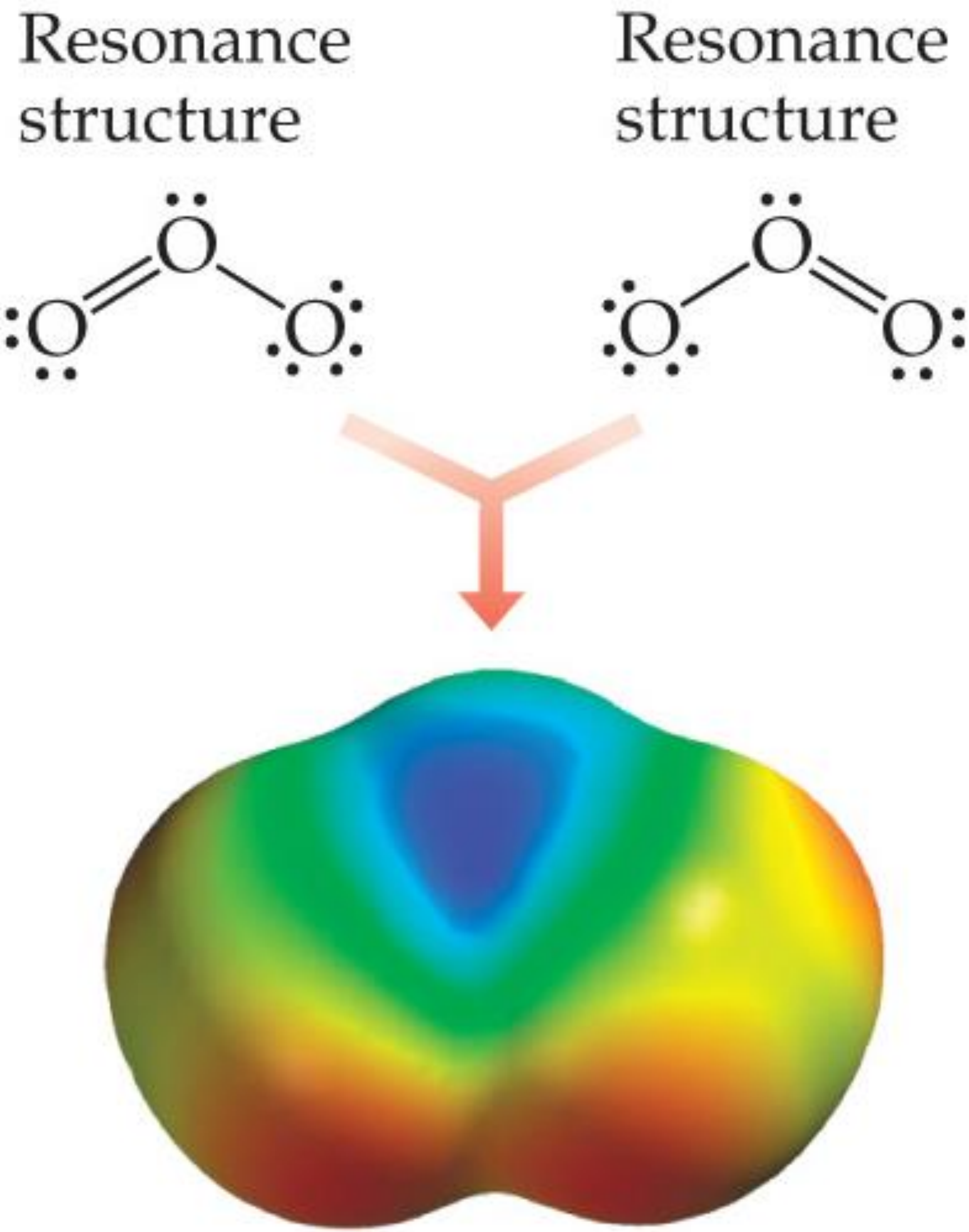


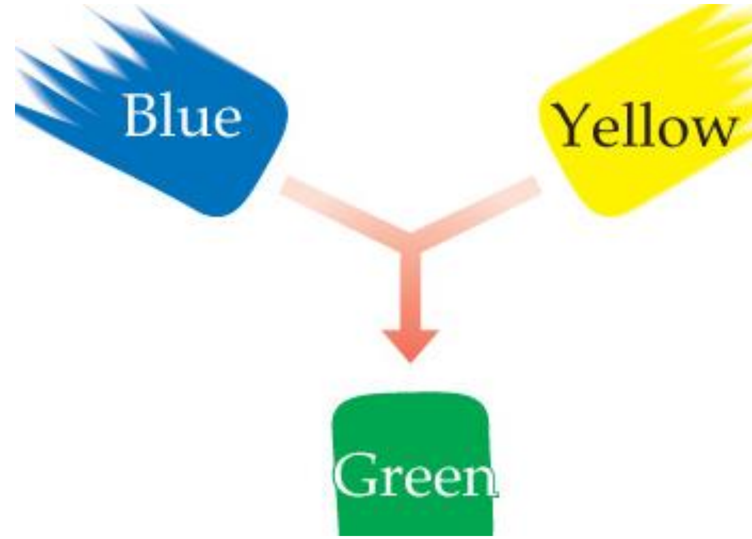
Non-polar?
Dipole?

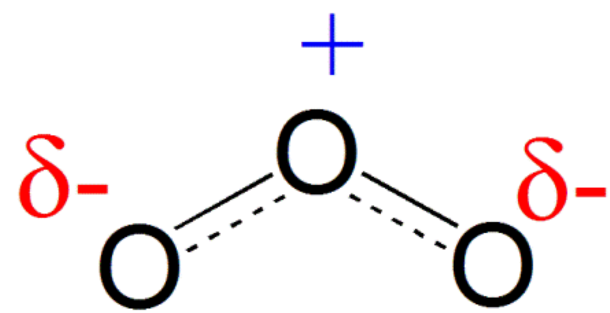
- **One Lewis structure** can**not accurately** depict a molecule like ozone.

- We use **multiple structures**, **resonance structures**, to describe the molecule.

- **Extra info.:** The **more** the **resonance structures**, the **more stabilization** the molecule.

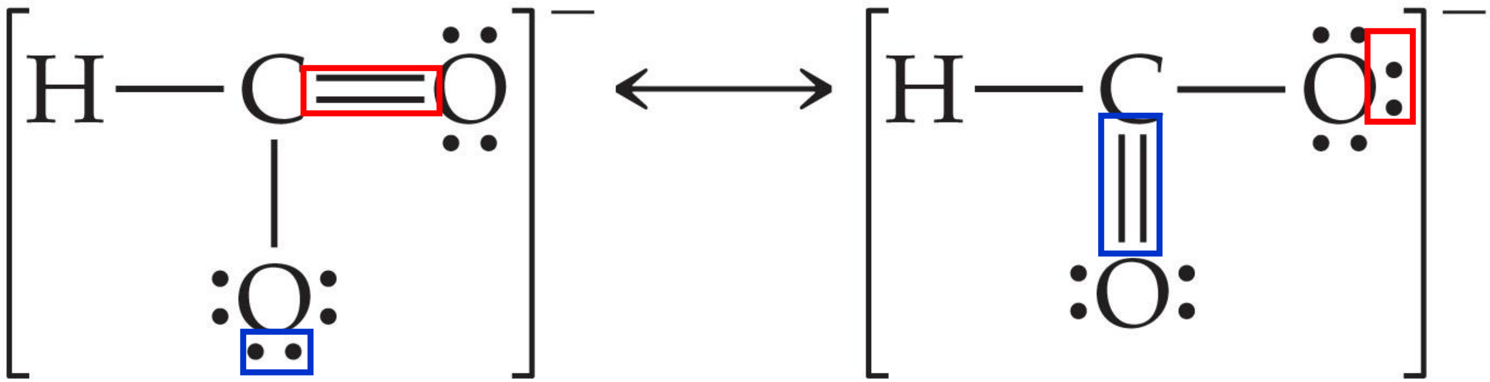


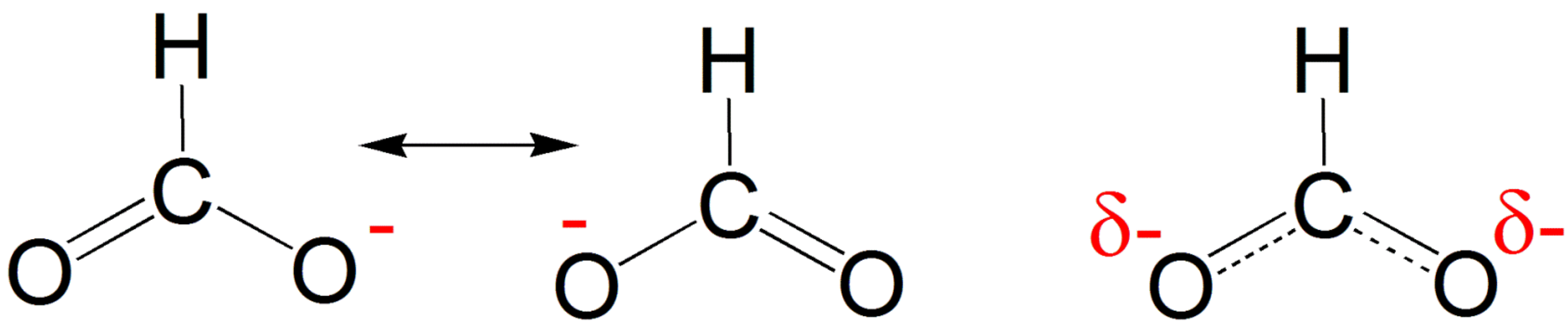




A mixture of two resonance structures: **1.5 O-O bond** & **-0.5 charge** on the outer oxygen atoms.

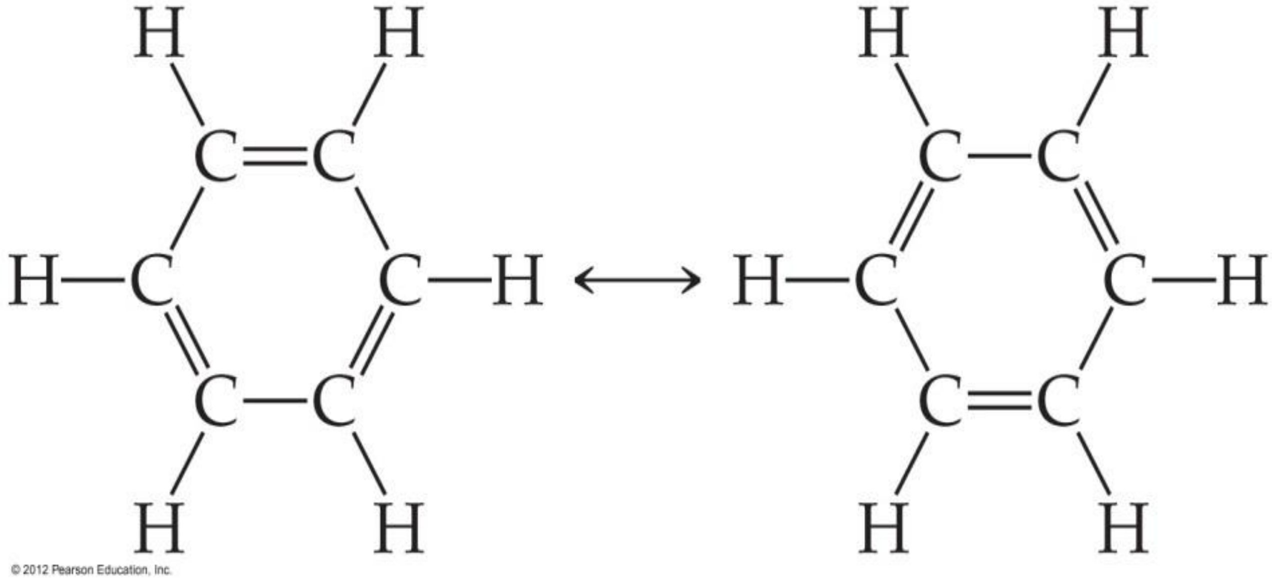
Formate (from formic acid)





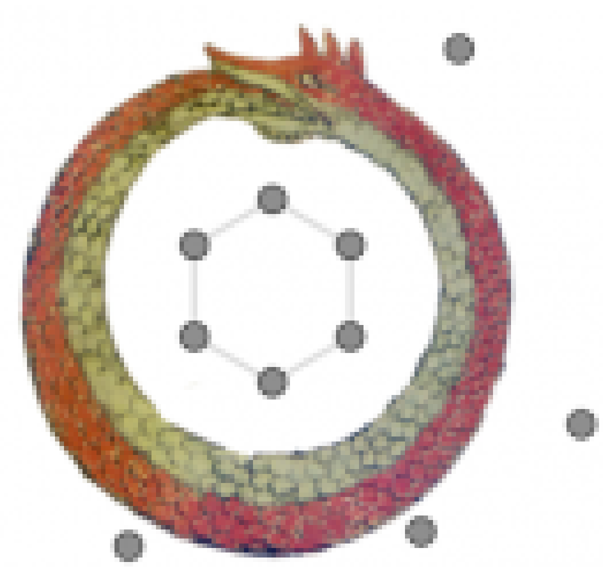
• The **electrons** that form the second C-O bond in the double bonds do **not always stay** between that C & that O, but can move among the two oxygens & the carbon.

• The **electrons** are not **localized**（局域）; they are **delocalized**（离域）for **resonance structures**.



- 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.

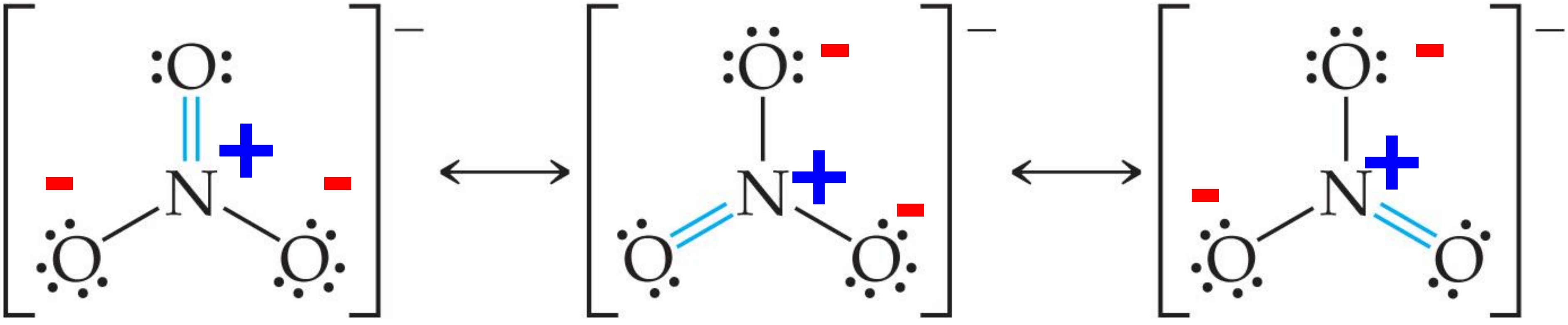
Kekule's dream



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.

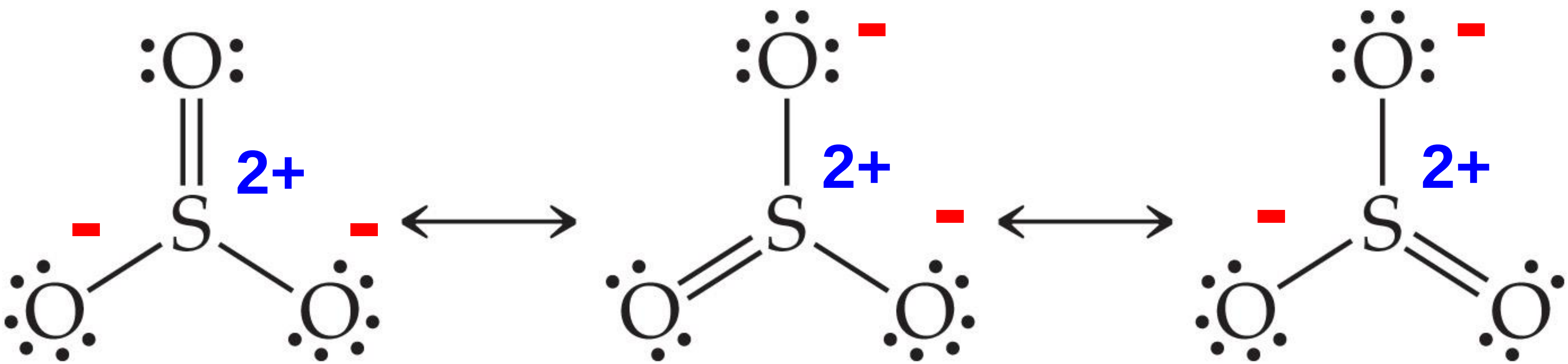
Later, Kekulé had another dream, in which he **saw atoms dance around**, then form themselves into strings, **moving about in a snake-like fashion**. This vision continued until the snake of atoms formed itself into an image **of a snake eating its own tail**. This dream gave Kekulé the idea of the cyclic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

Nitrate



1⅓ bond/atom

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



1⅓ bond/atom

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**;

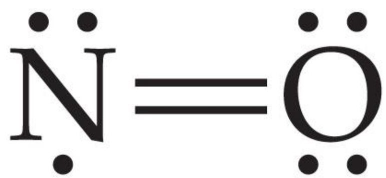
(II) ions or molecules with **less than** an octet;

(III) ions or molecules with **more than eight valence electrons** (an expanded octet): **hypervalence**.

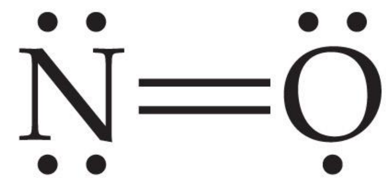
(I) Odd Number of Electrons

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

Nitric oxide



and



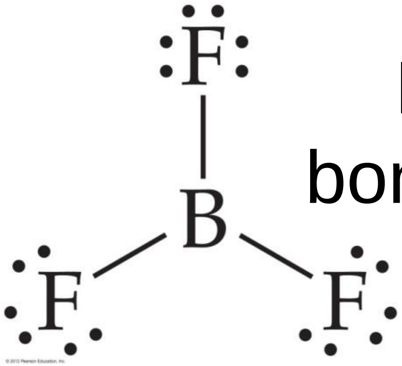
Which one is the dominant Lewis structure?

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

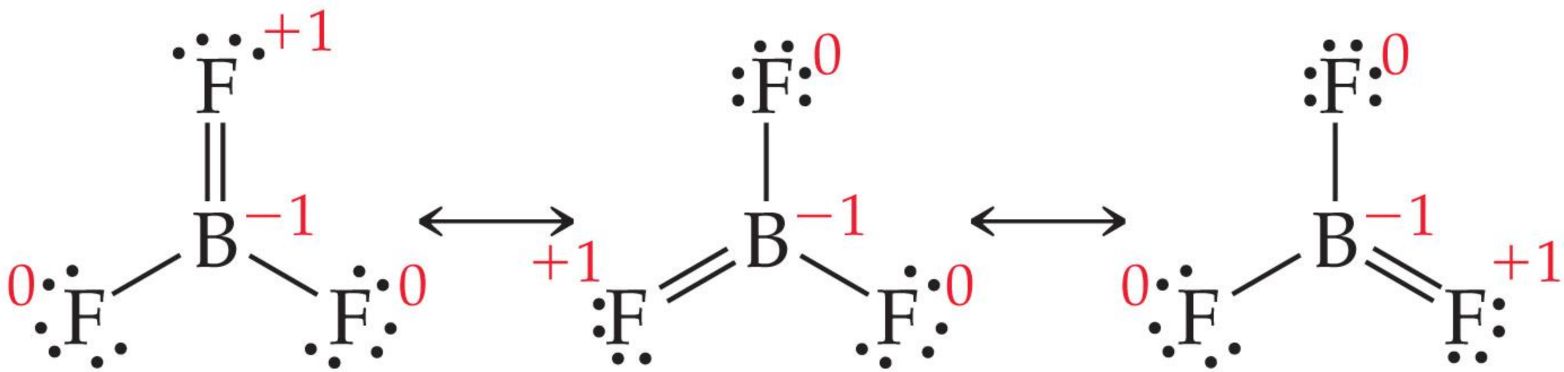
The Nobel Prize in Physiology or Medicine 1998

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

(II) Fewer Than Eight Electrons

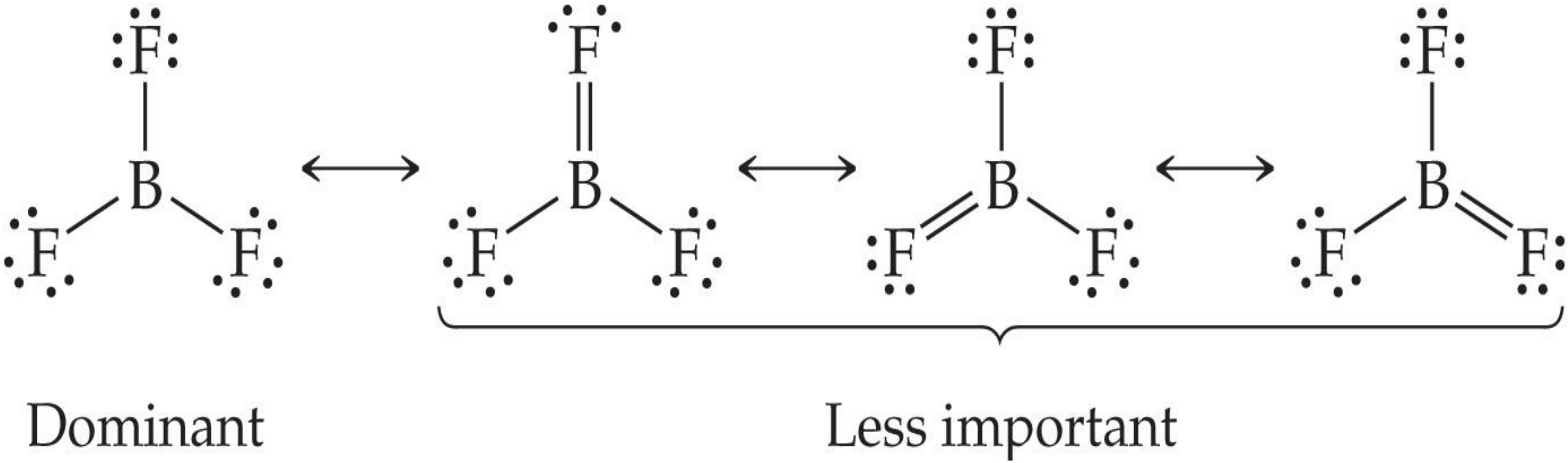


B has only 6 bonding electrons



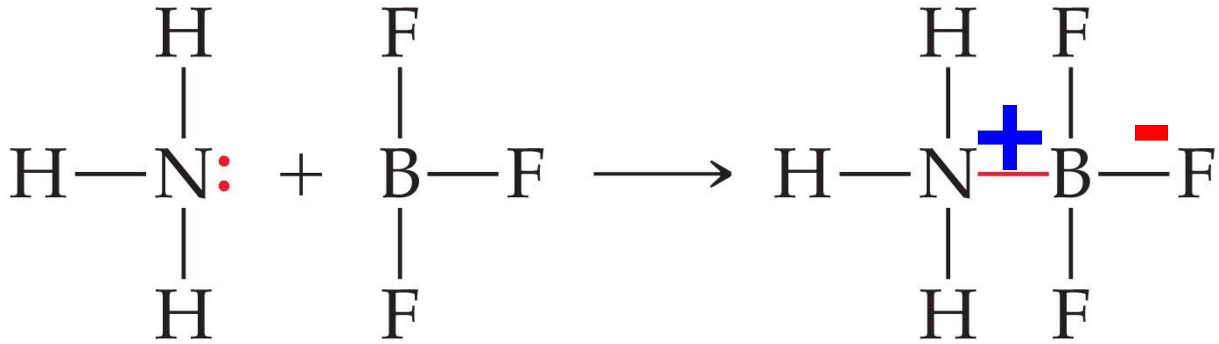
To fulfill octet rule, boron accepts two electrons from fluorine: a *negative* charge on the boron and a *positive* charge on fluorine.

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



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.

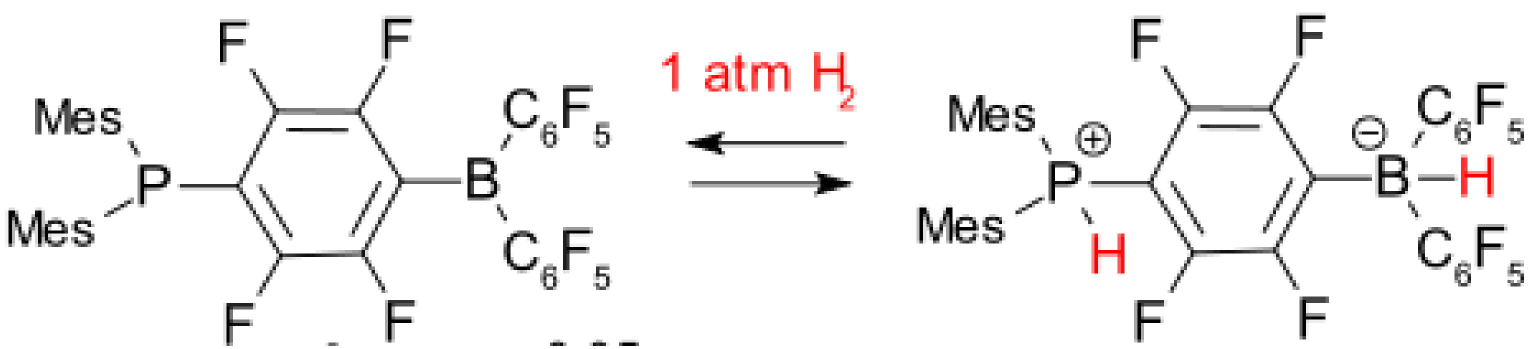
N:
1 lone-pair electrons to donate:
Lewis Base



B:
6 bonding electrons:
Lewis Acid

Adduct (加合物)
B:
8 bonding electrons

Extra info. Frustrated Lewis Pairs (FLP)

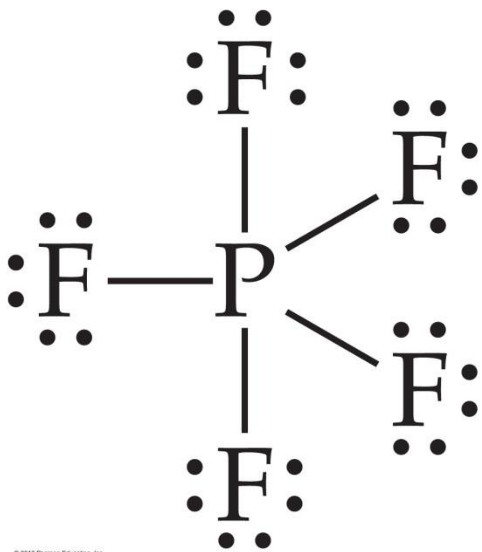


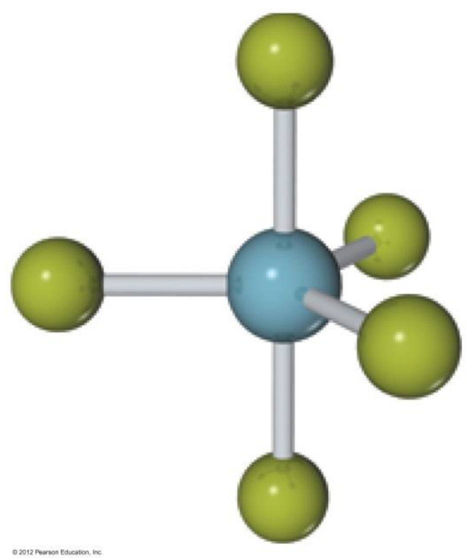
(Science 2006, 314, 1124)

(III) More Than Eight Electrons

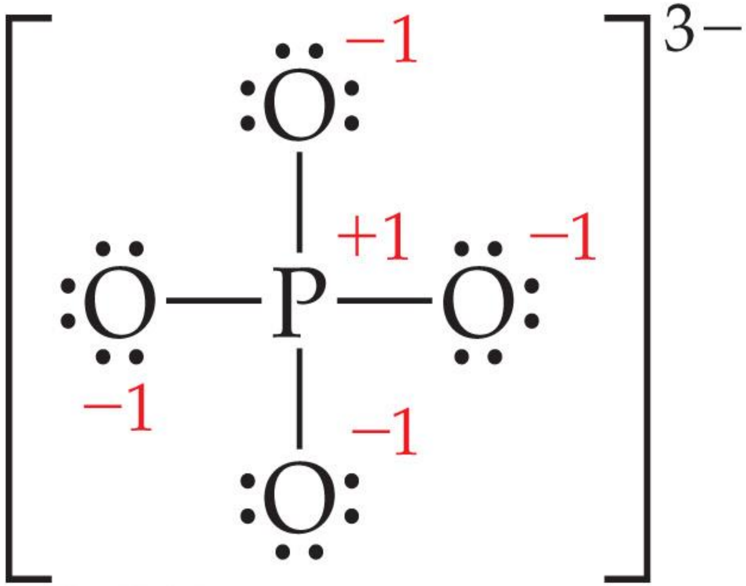
- In PF_5, phosphorus has 10 electrons (**No NF_5**).

- 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**.

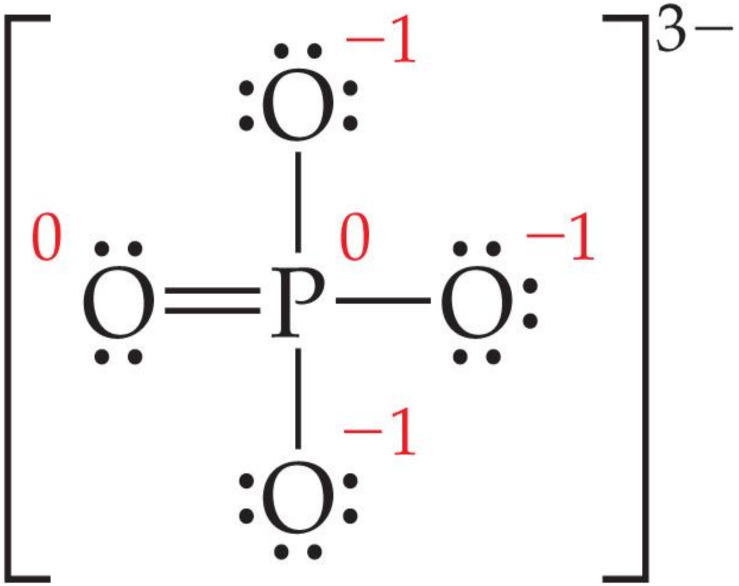




Phosphate



P: **Octet** rule



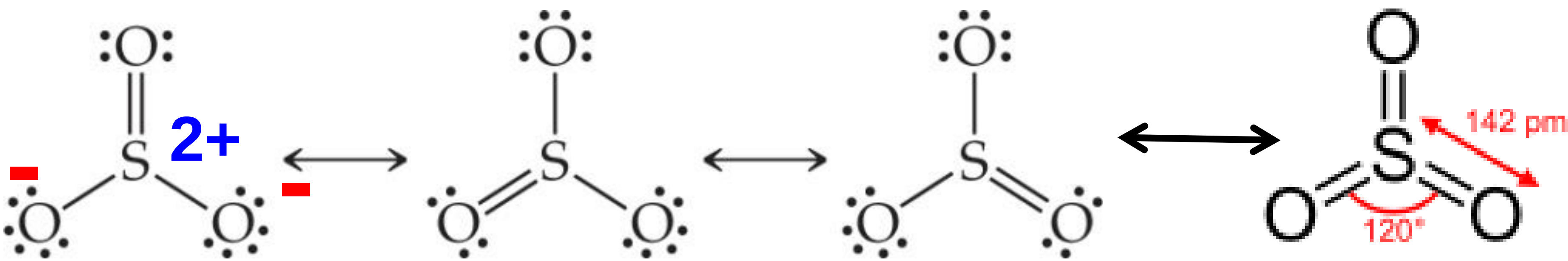
The **best** structure

- The best (hypervalent) structure ***avoids charge separation***.

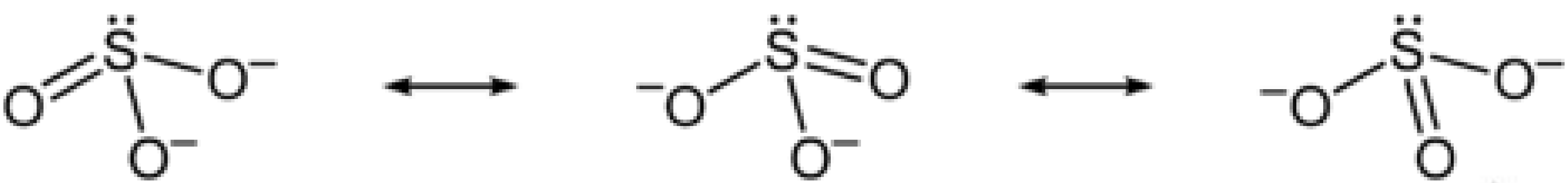
- When the central atom is on the third row or below, it can **expand its octet** in order to **eliminate** some formal **charges**.

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

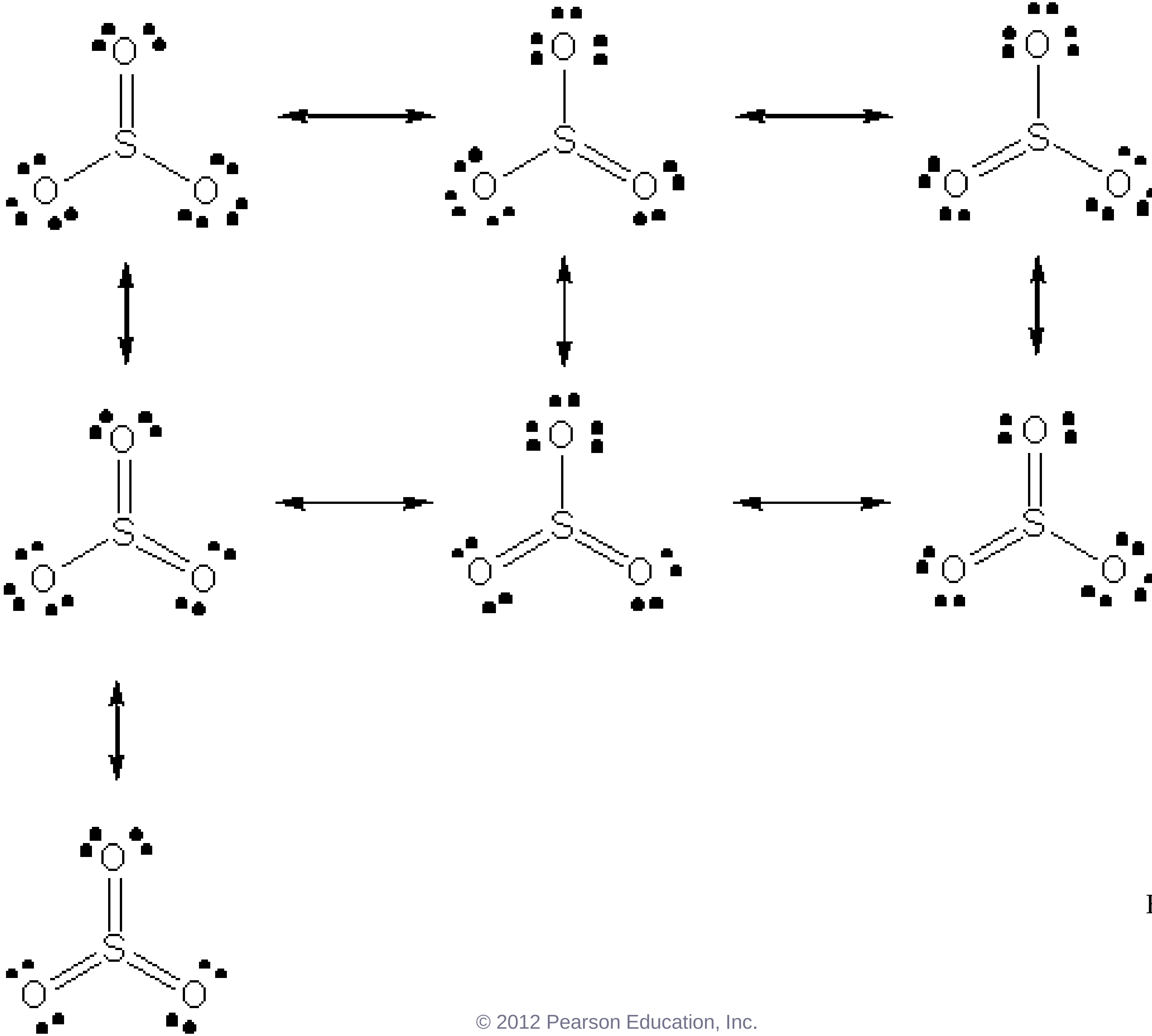
Solution: SO_3 contains 24 valence electrons. Three equivalent resonance structures can be drawn:



SO_3^{2-} ion has 26 electrons, with the below dominant Lewis structure:



SO_3 should have the shorter S-O bonds & SO_3^{2-}(measured S-O bond lengths are 1.42 Å in SO_3 and 1.51 Å in 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. NH_3
c. BF_3
d. PF_5

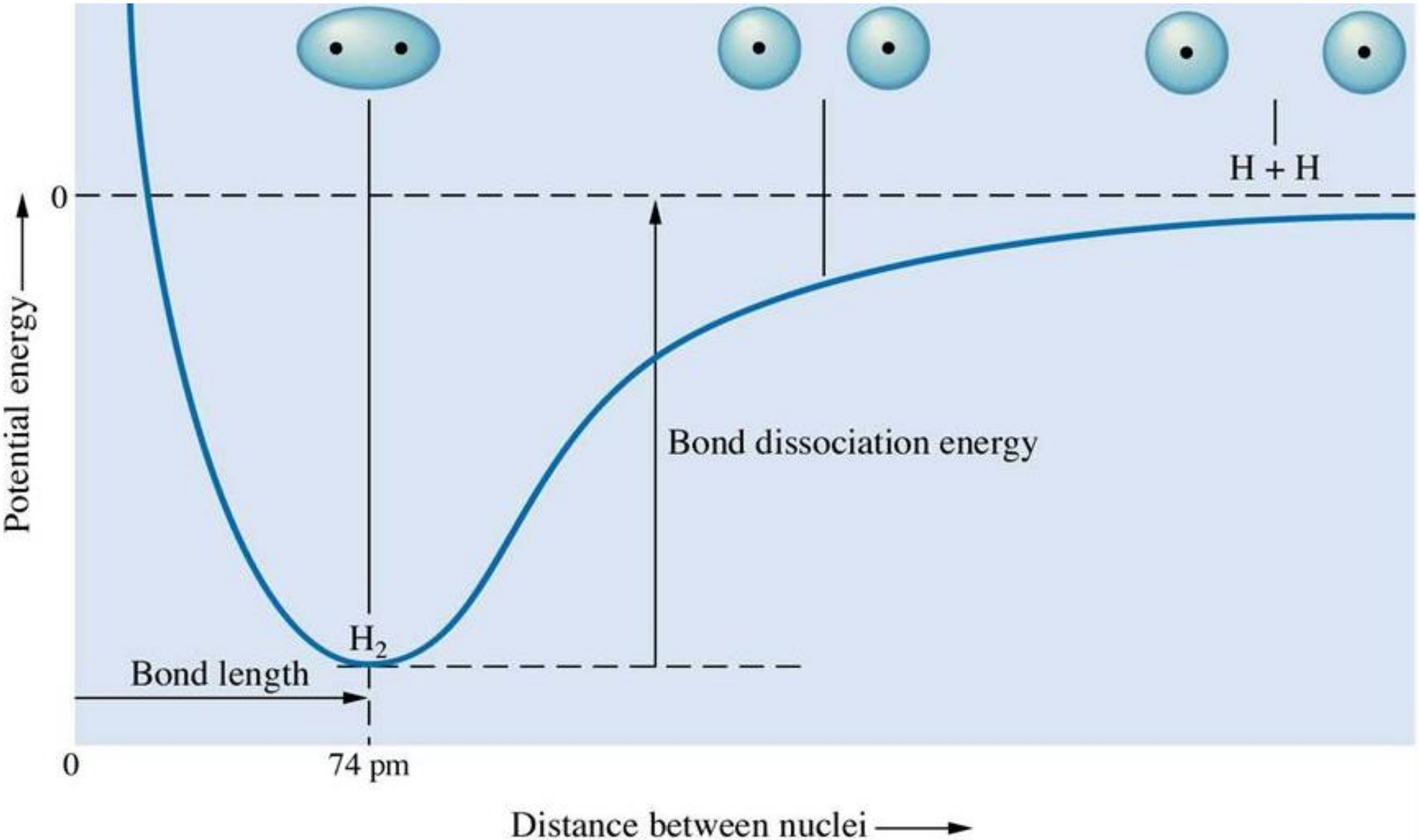
Covalent Bond Strength

- 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^O) with a positive, zero or negative value).

- The bond enthalpy for a Cl-Cl bond, *D*(Cl-Cl), is measured to be 242 kJ/mol.

Potential Energy for H_2



Average Bond Enthalpies

$$\mathrm{H{-}\underset{\displaystyle H}{\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}}{-}H}(g) \longrightarrow \cdot\ddot{\mathrm{C}}\cdot(g) + 4\,\mathrm{H}\cdot(g) \qquad \Delta H = 1660\ \mathrm{kJ}$$

Enthalpies to break 4 C-H bonds of methane: 1660 kJ
➔ **Average** bond enthalpies: ~1660/4 kJ = ~415 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 Enthalpies (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				

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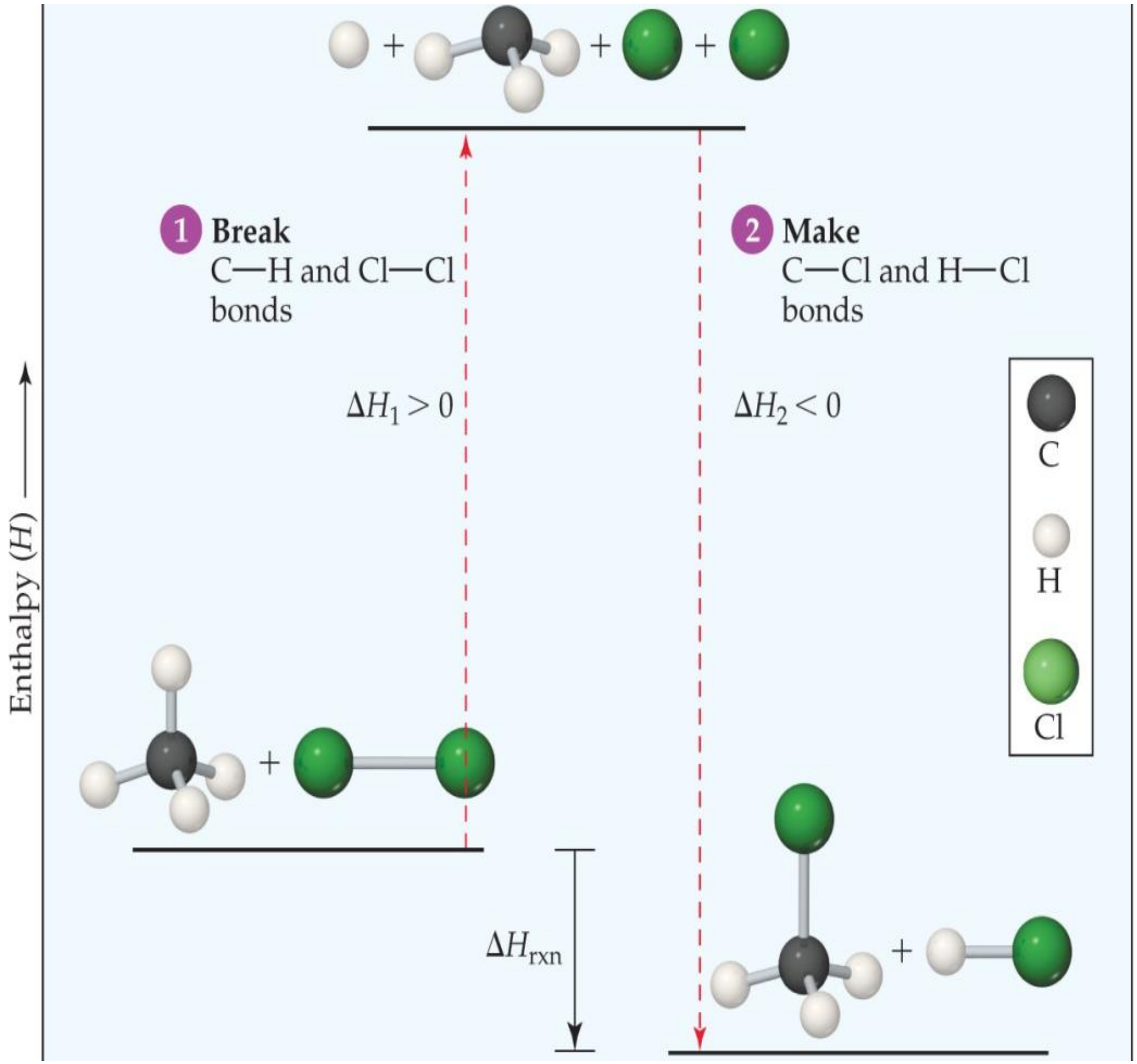
Enthalpies of Reaction



- 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**.

ΔH_{rxn} = Σ(m* bond enthalpies of bonds **broken**) − Σ(n* bond enthalpies of bonds **formed**)

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

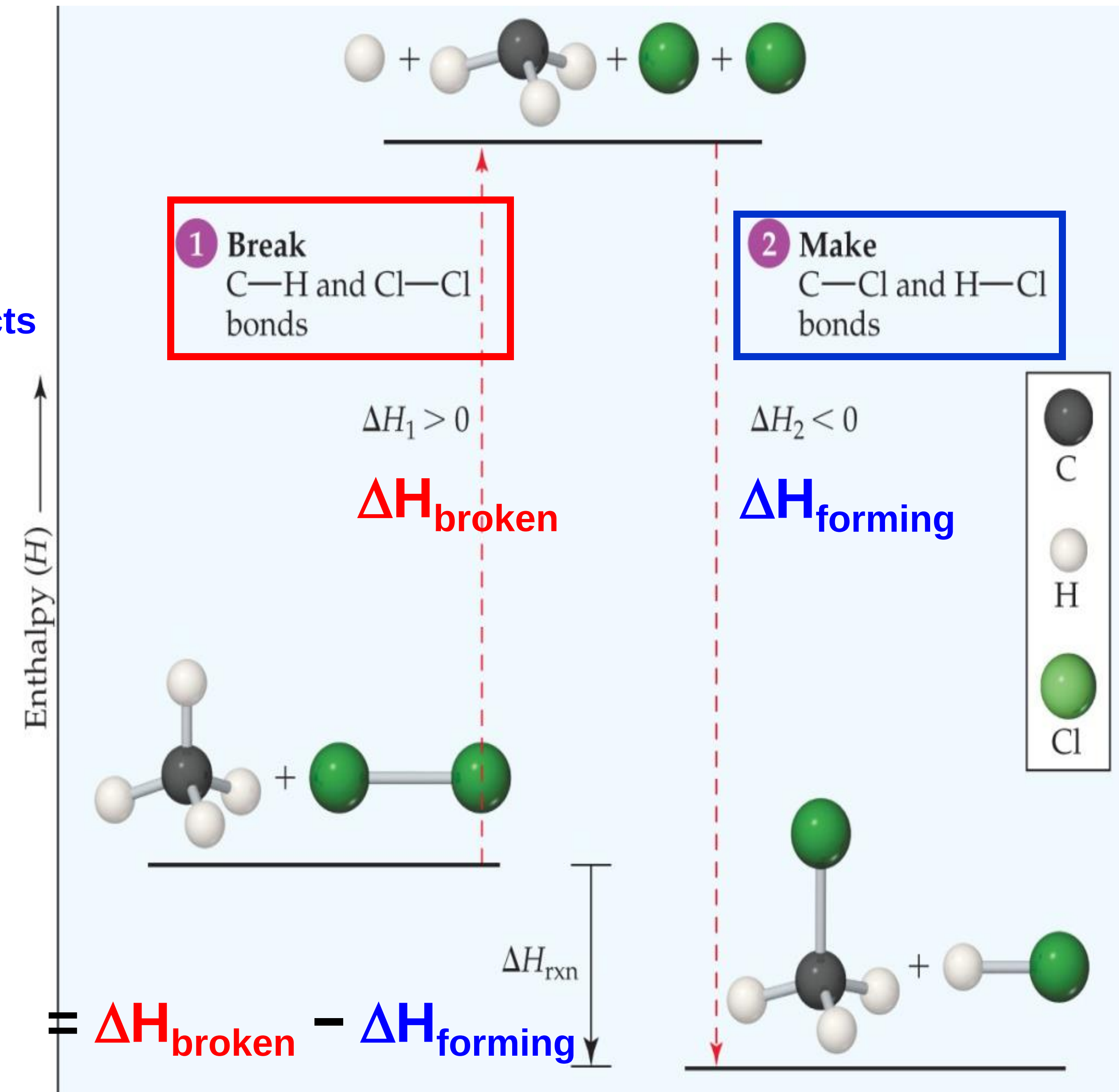
$$CH_4(g) + Cl_2(g) \longrightarrow CH_3Cl(g) + HCl(g)$$

$C + 2H_2(g) + Cl_2(g)$

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

$CH_4(g) + Cl_2(g)$

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



$= \Delta H_{broken} - \Delta H_{forming}$

$$\Delta H_{rxn} = [D(\text{C-H}) + D(\text{Cl-Cl})] - [D(\text{C-Cl}) + D(\text{H-Cl})]$$

$$= [(413\text{ kJ}) + (242\text{ kJ})] - [(328\text{ kJ}) + (431\text{ kJ})]$$

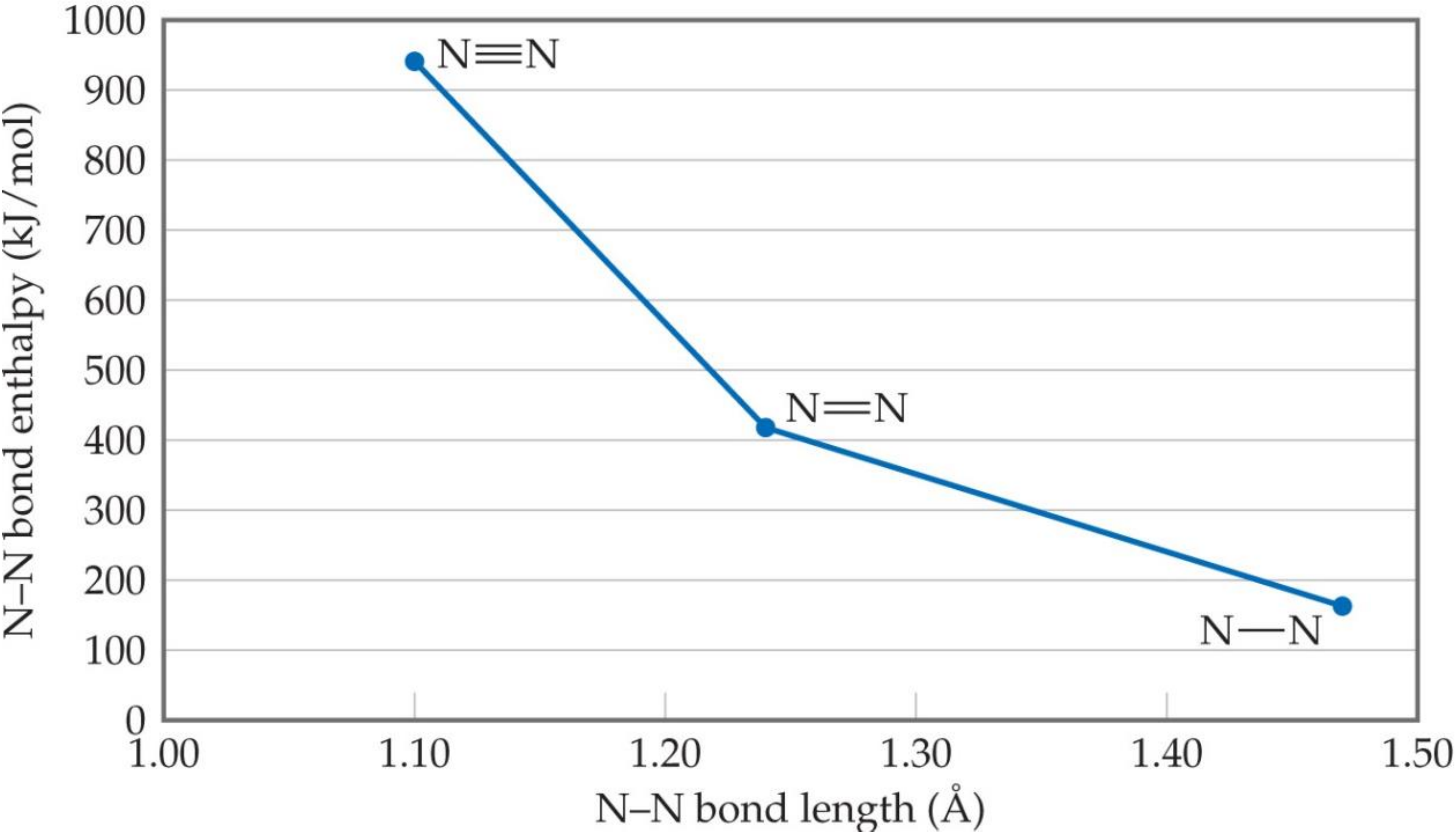
$$= (655\text{ kJ}) - (759\text{ kJ})$$

$$= -104\text{ kJ}$$

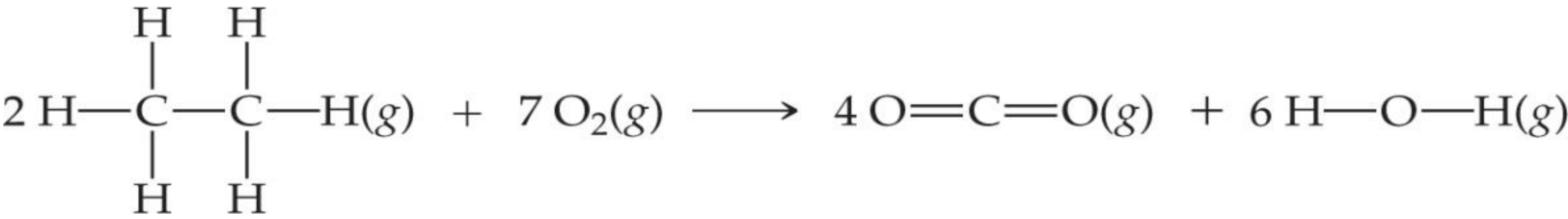
Bond Enthalpy and Bond Length

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**.


N≡N
N=N
N—N
N–N bond enthalpy (kJ/mol)
N–N bond length (Å)
0
100
200
300
400
500
600
700
800
900
1000
1.00
1.10
1.20
1.30
1.40
1.50

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 O_2 molecules.

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

$\Delta H = [12*D(\text{C-H}) + 2*D(\text{C-C}) + 7*D(O_2)] - [8*D(\text{C=O}) + 12*D(\text{O-H})]$

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

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

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 CO_2 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, $C_2H_6(g)$, along with the value $D(C—H) = 413$ kJ/mol to estimate the value for $D(C—C)$?

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

Based on bond enthalpies, which do you expect to be more reactive, oxygen, O_2, or hydrogen peroxide, H_2O_2?

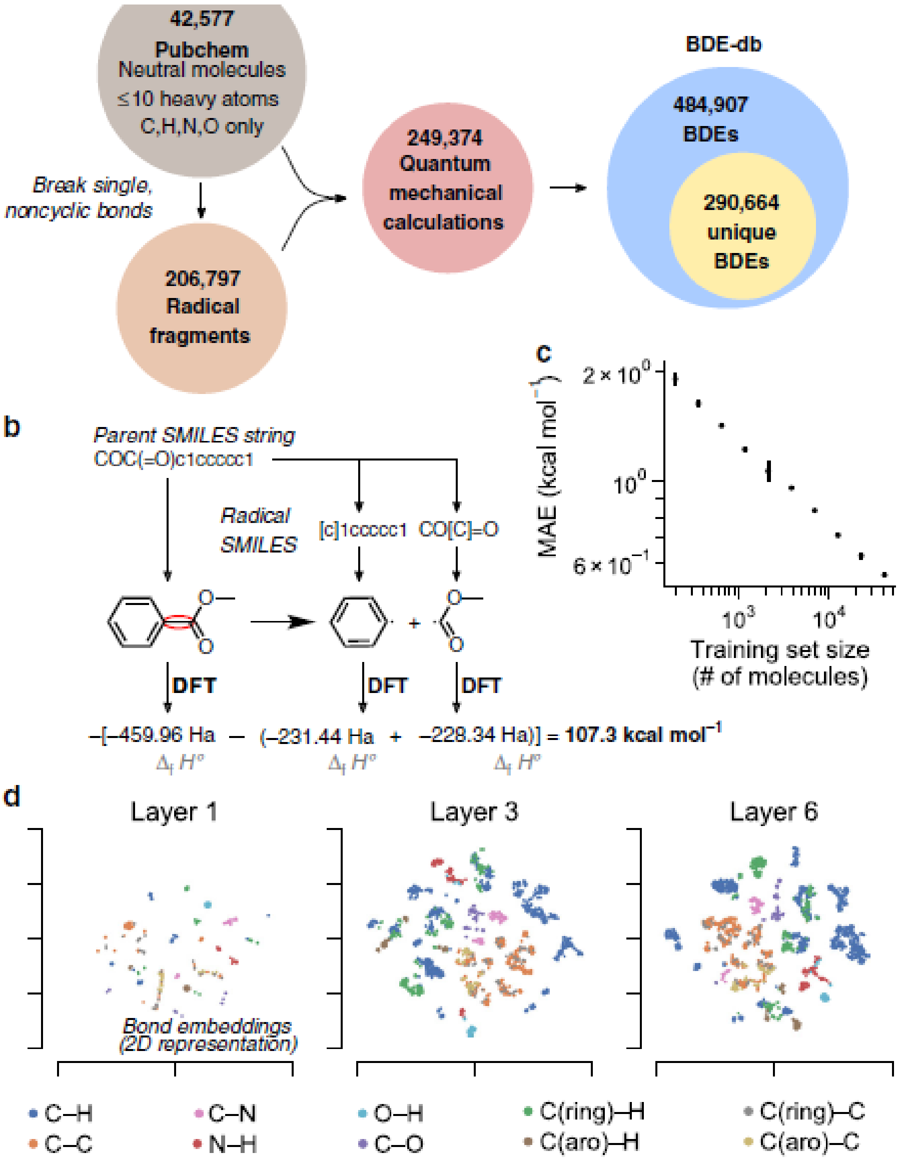
A. O_2 is more reactive, because the O=O bond enthalpy is less than that of the O-O bond enthalpy in hydrogen peroxide.

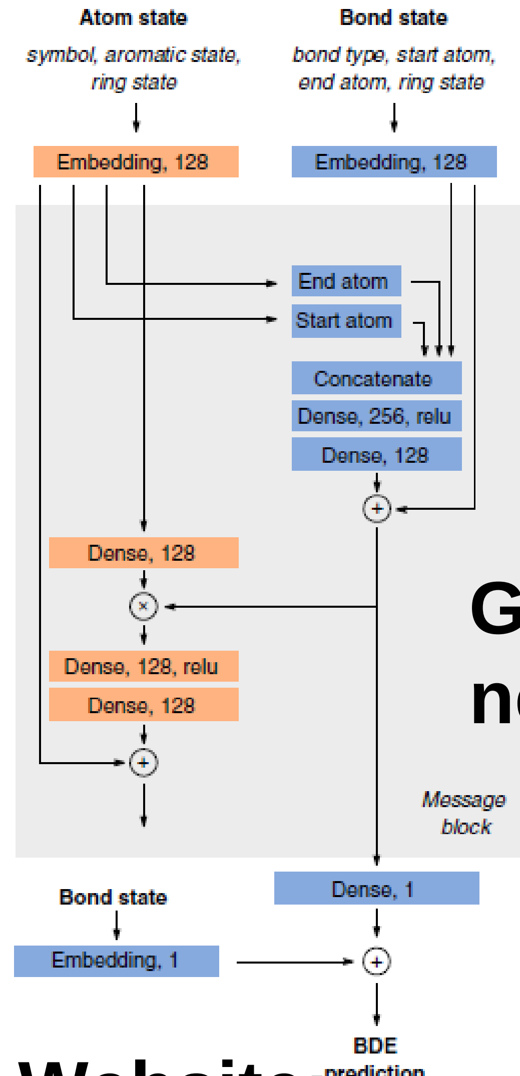
B. O_2 is more reactive, because the O=O bond enthalpy is greater than that of the O-O bond enthalpy in hydrogen peroxide.

C. H_2O_2 is more reactive, because the O-O bond enthalpy is less than that of the O=O bond enthalpy in O_2.

D. H_2O_2 is more reactive, because the O-O bond enthalpy is greater than that of the O=O bond enthalpy in O_2.

Extra info. Machine-learning predictions of Bond Dissociation Energy



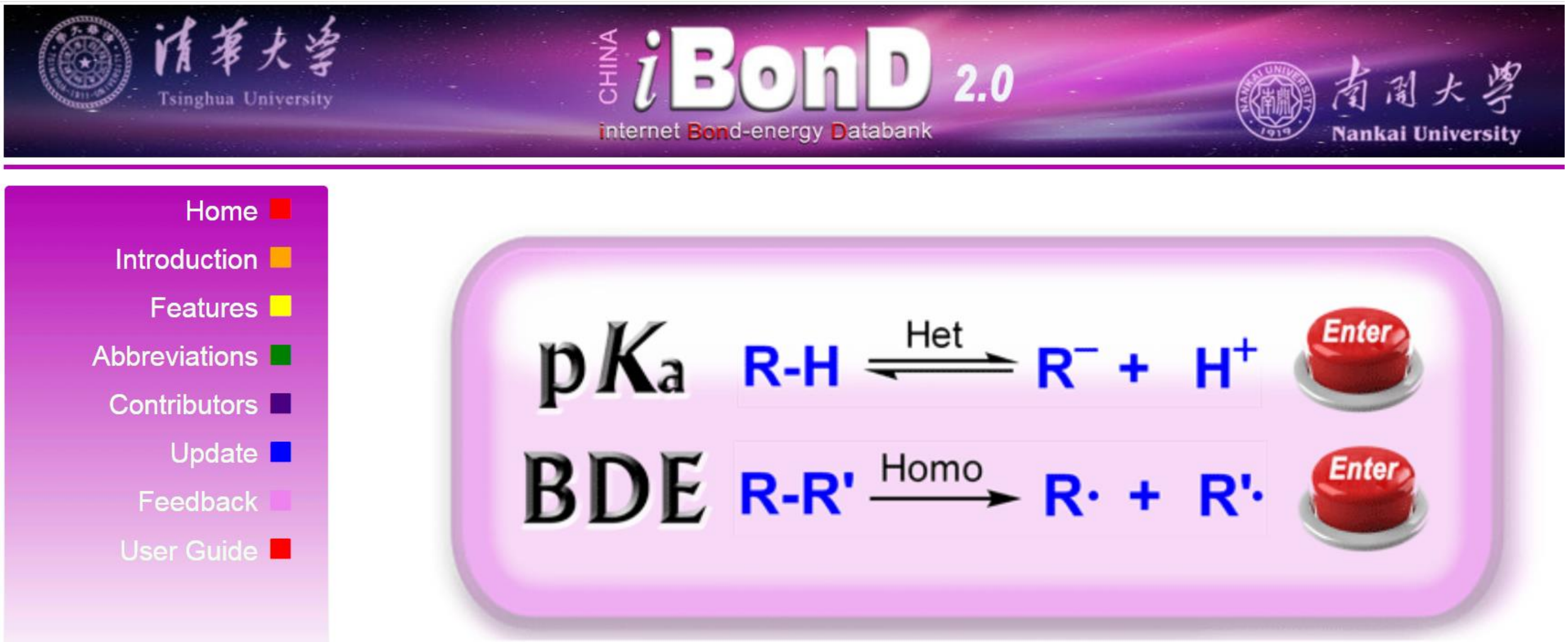


Graph neural network (GNN)

Website: https://bde.ml.nrel.gov/

(Nat. Commun. 2020, 2328)

Extra info. iBonD (Internet Bond-energy Databank)



Website:

http://ibond.nankai.edu.cn/

http://pka.luoszgroup.com/bde_prediction

Extra info. N_2 bond Activation & Functionalization

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

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

$$N_2 + 8H^+ + 8e^- + 16MgATP \xrightarrow{\text{nitrogenase}} 2NH_3 + H_2$$

$$+ 16MgADP + 16PO_4^{3-}$$

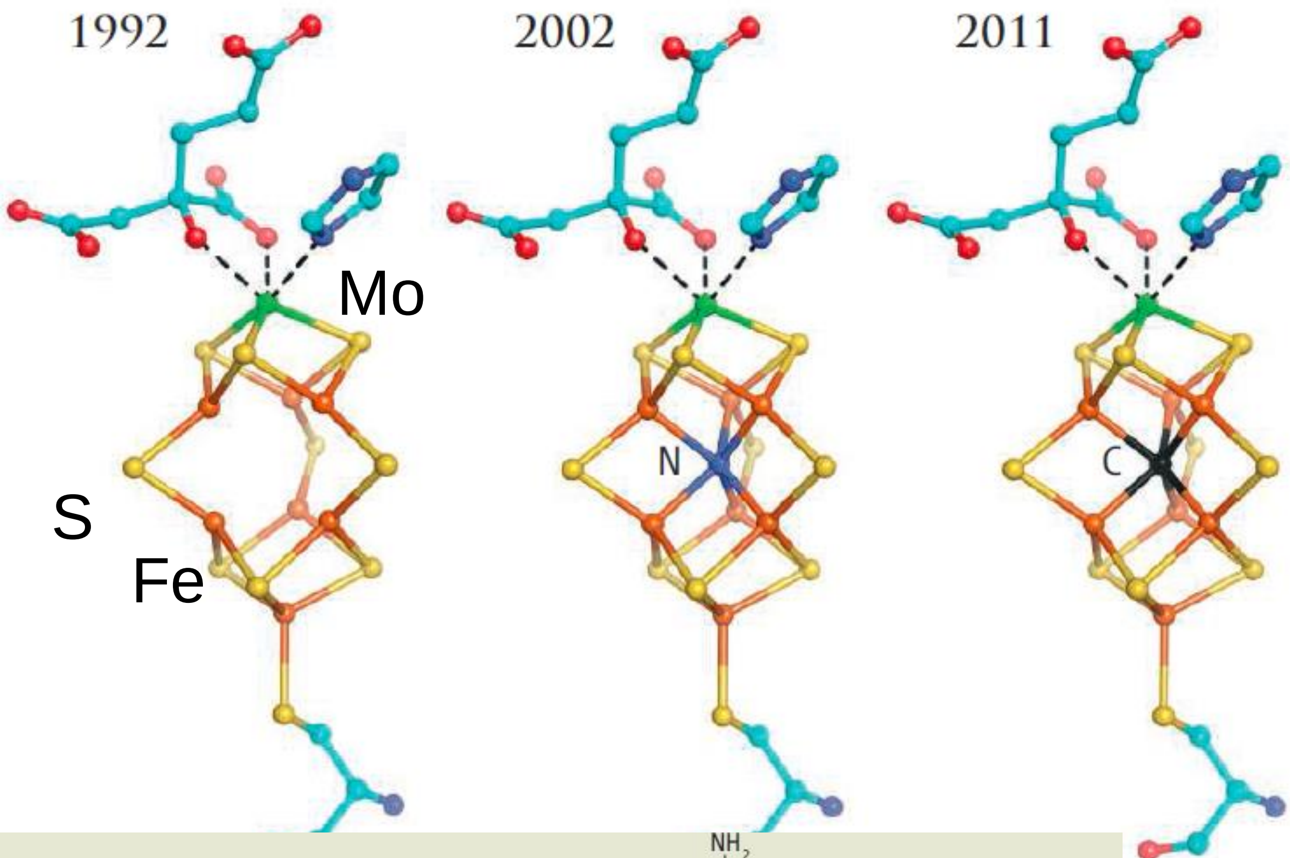
$D(N_2)$: 941 kJ

$$N_2(g) + 3H_2(g) \xrightarrow[\text{300–550}^\circ\text{C, 100–300 atm}]{\text{Haber Bosch catalyst}} 2NH_3(g)$$

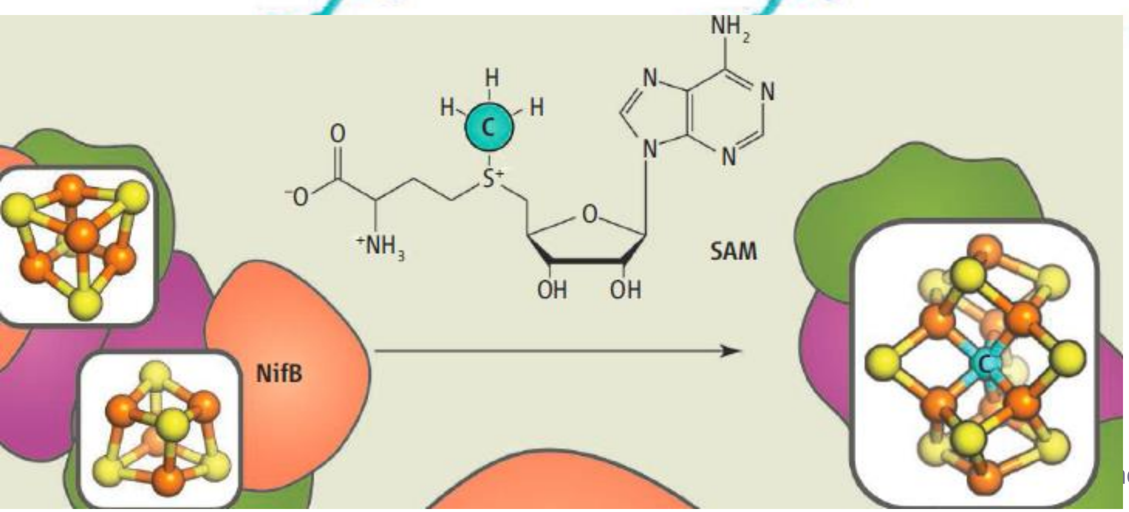
Basic Concepts of Chemical Bonding

(Chem. Soc. Rev. 2014, 547)

Extra info. Nitrogenase

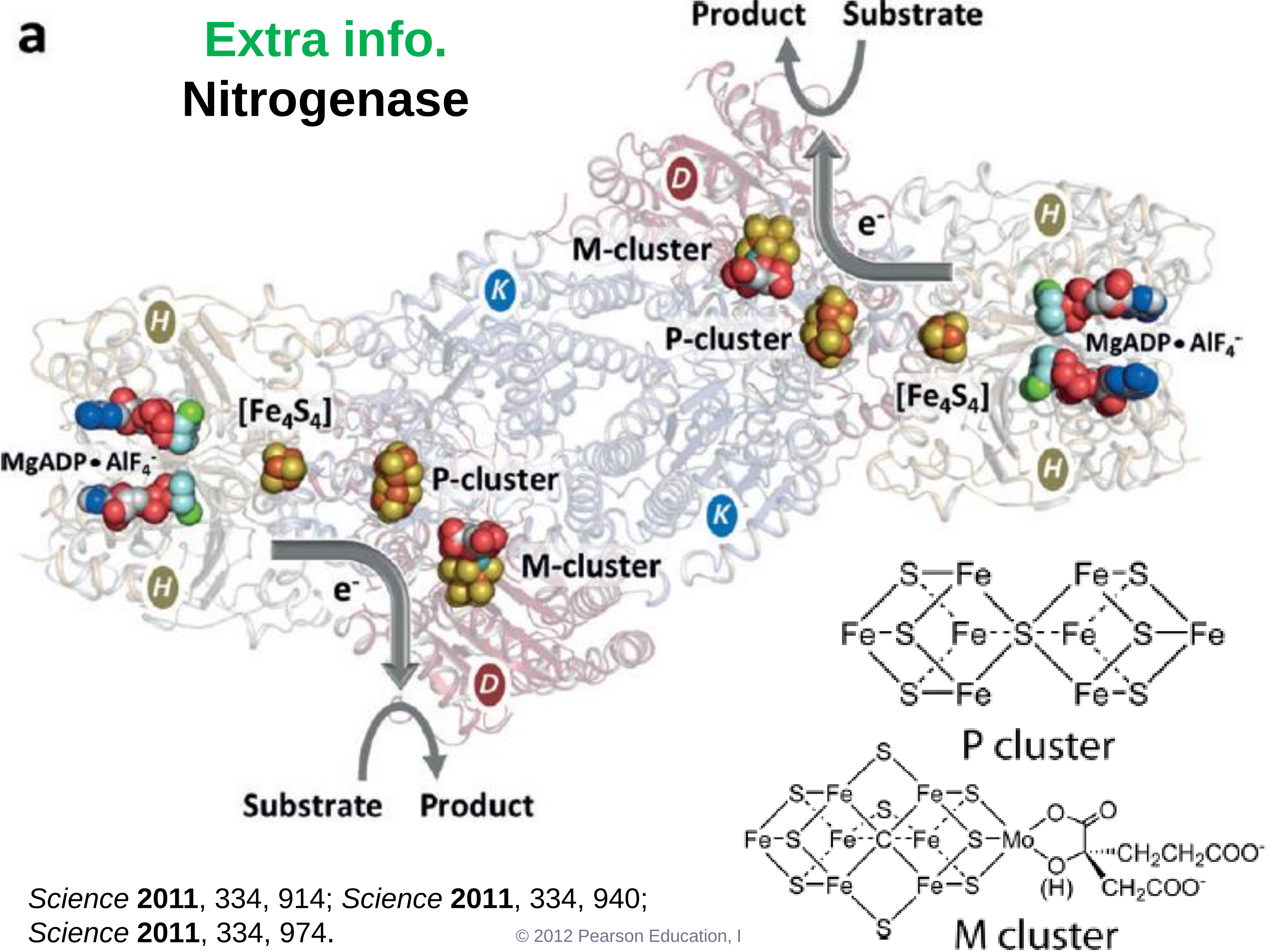


- The **largest & complicated** metal-organic cluster in biology so far;
- The identity of the central atom: **C, not N or O** (spectroscopies)
- C from SAM (methyl donor)



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

Extra info.
Nitrogenase



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

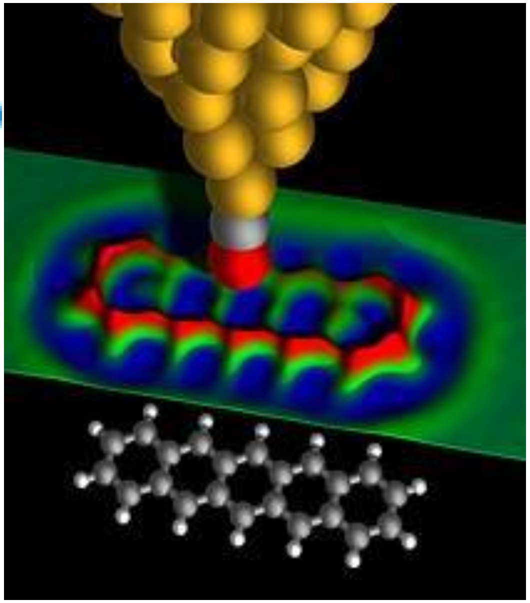
Extra info.

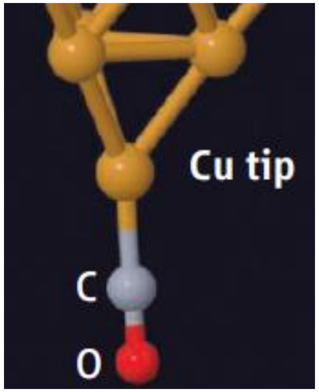
The Chemical Structure of a Molecule Resolved by Atomic Force Microscopy

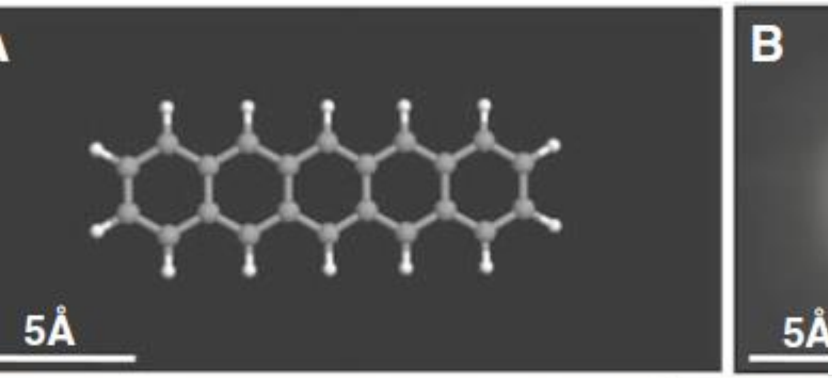
Leo Gross *et al.*

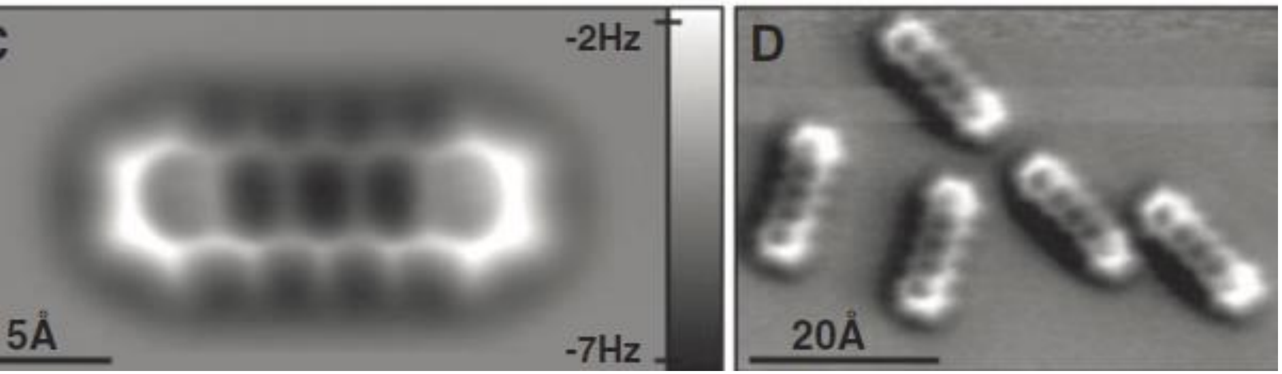
Science **325**, 1110 (2009);
DOI: 10.1126/science.1176210

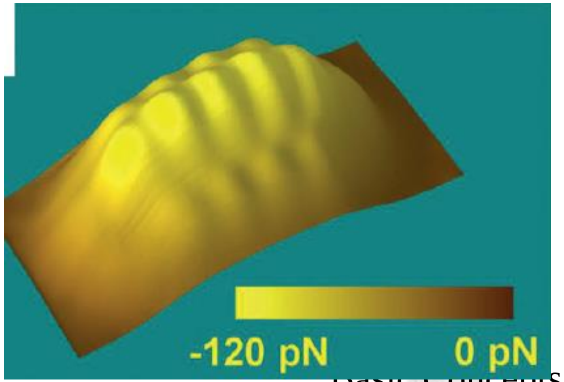
IBM Research











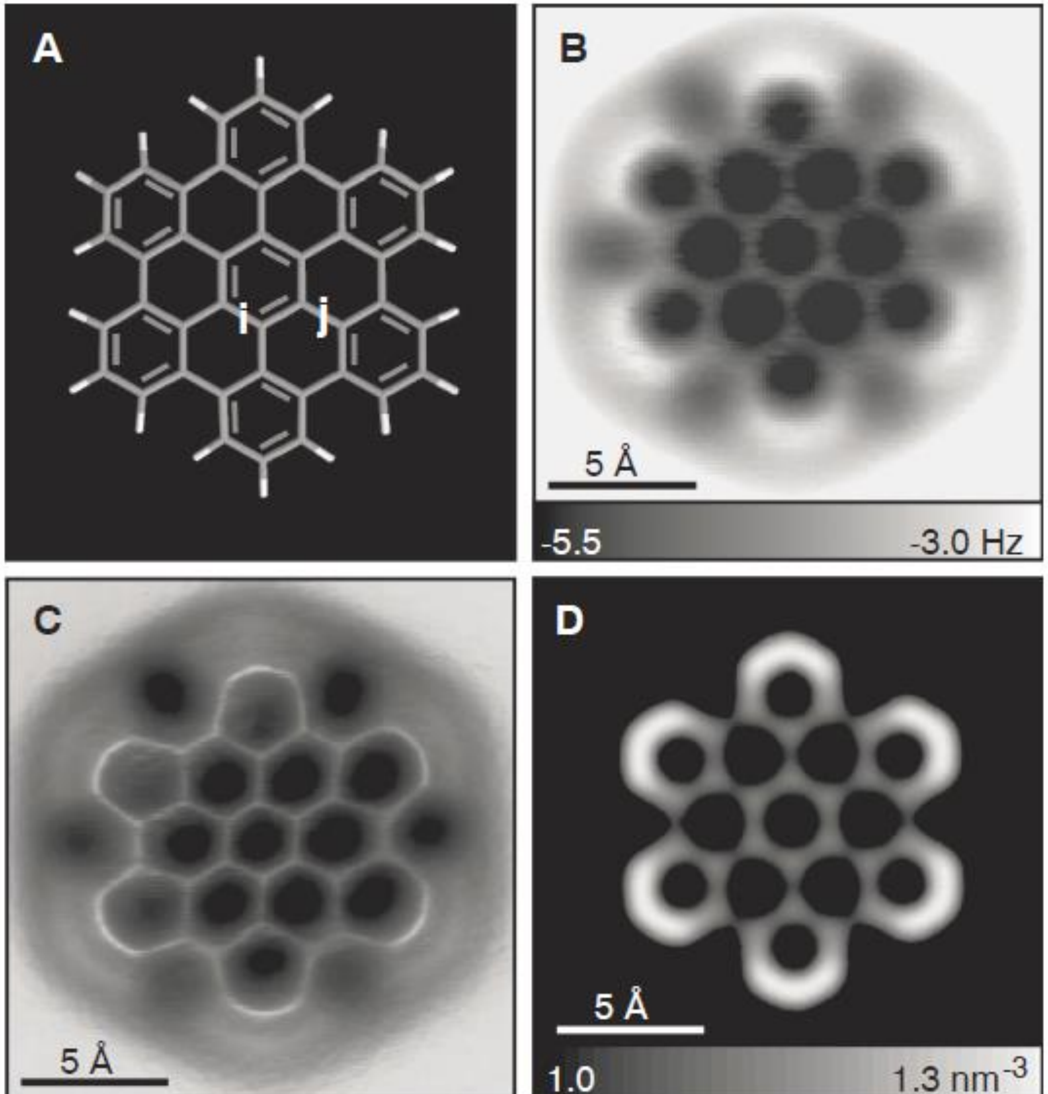
Pentacene on Cu(111) surface

Scanning tunneling microscope (STM) + CO as a tip

Bond-Order Discrimination by Atomic Force Microscopy

Leo Gross *et al.*

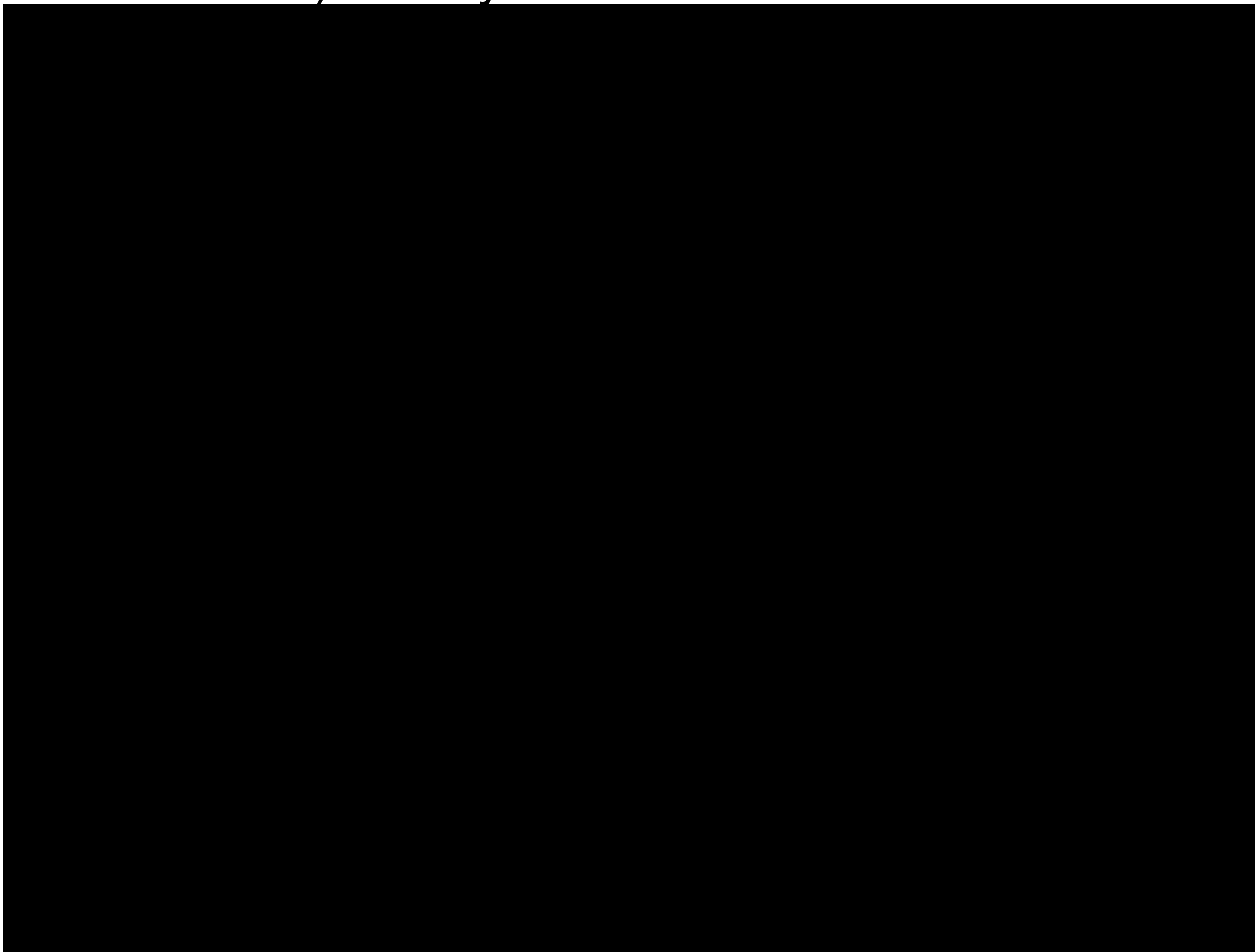
Science **337**, 1326 (2012);
DOI: 10.1126/science.1225621



IBM Research

Extra info.

Making The Worlds Smallest Movie by IBM Research (STM + CO molecules): "A boy and his atom"



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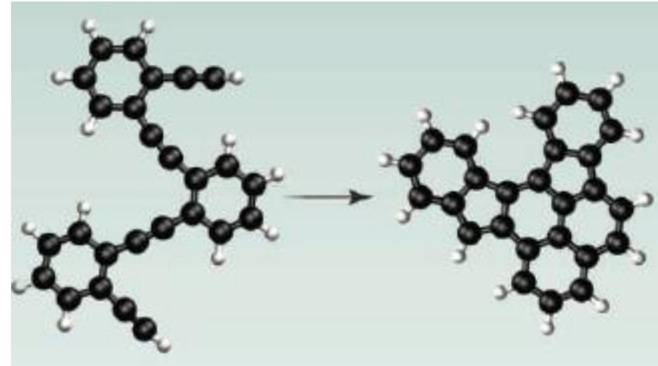
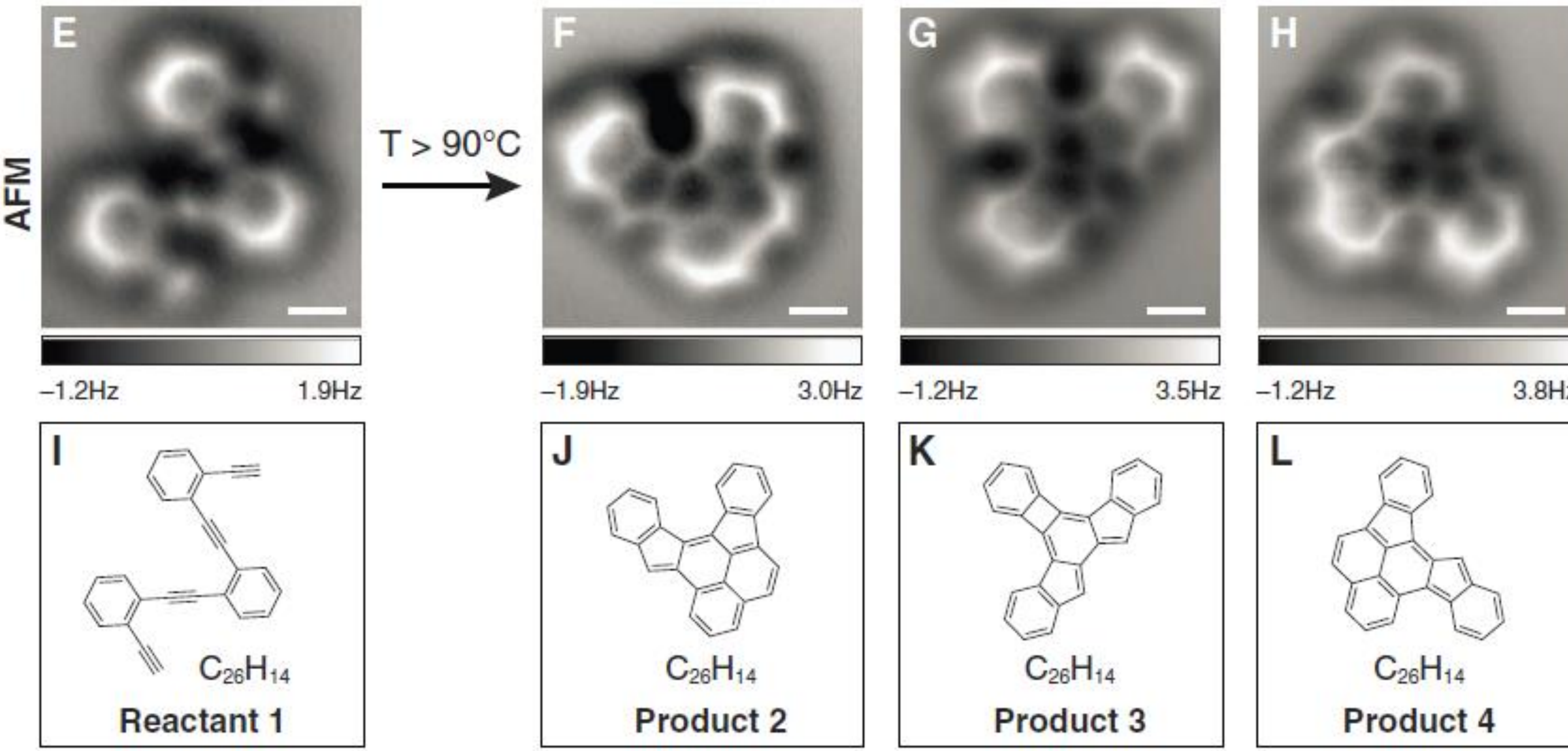
Direct Imaging of Covalent Bond Structure in Single-Molecule Chemical Reactions

Dimas G. de Oteyza *et al.*

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



Extra info.



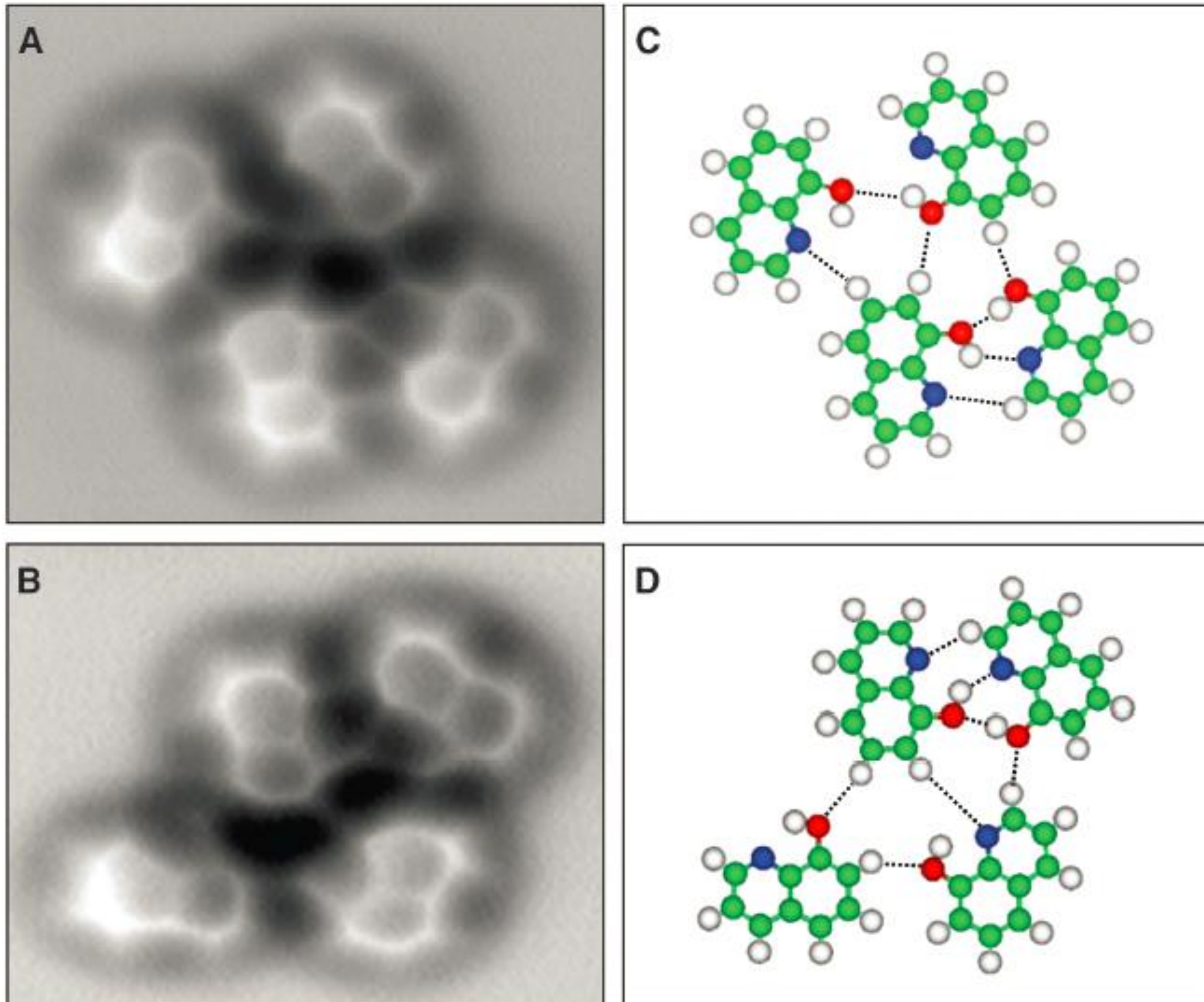
Real-Space Identification of Intermolecular Bonding with Atomic Force Microscopy

Jun Zhang *et al.*

Science **342**, 611 (2013);
DOI: 10.1126/science.1242603

国家纳米科学中心

Extra info.

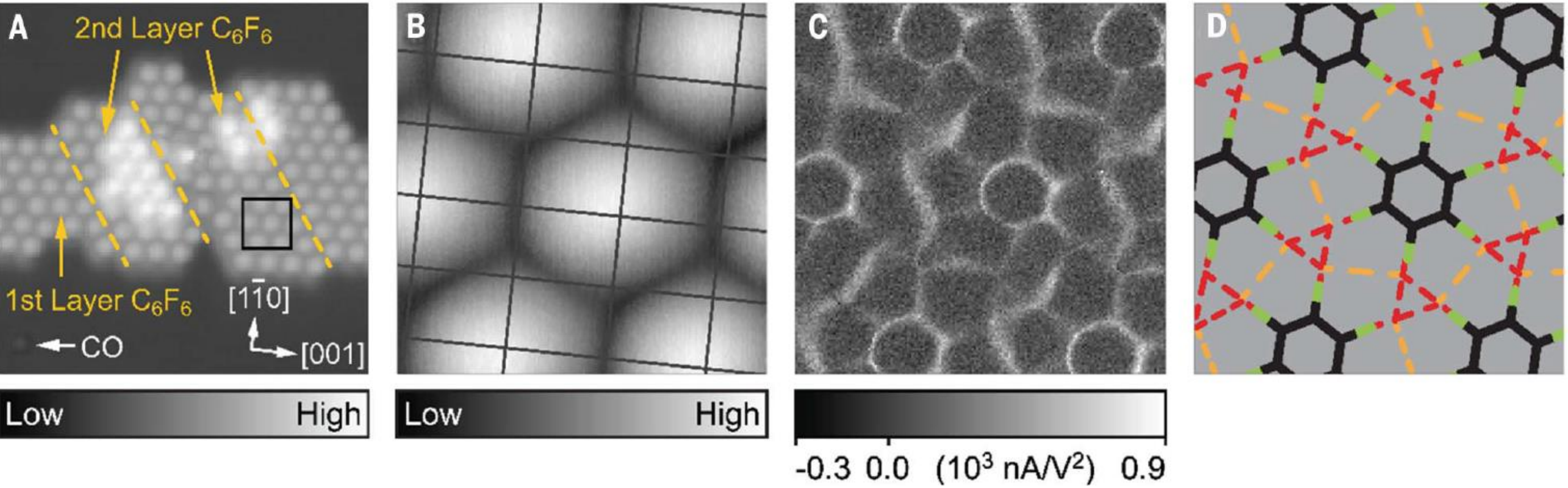


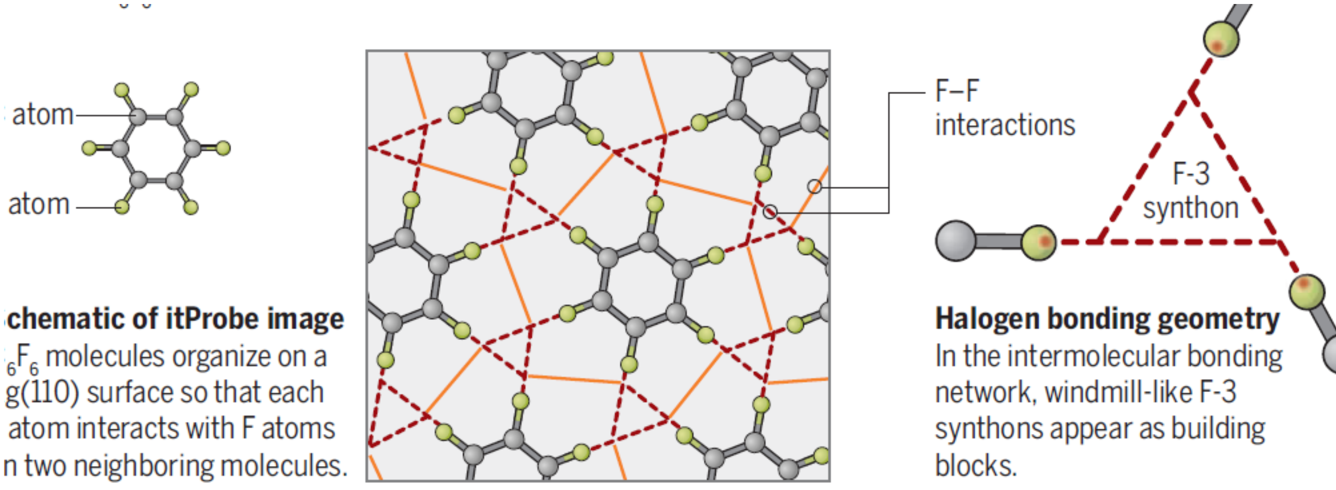
Imaging the halogen bond in self-assembled halogenbenzenes on silver

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.aai8625originally published online September 14, 2017





Basic Concepts of Chemical Bonding

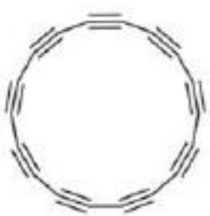
SURFACE CHEMISTRY

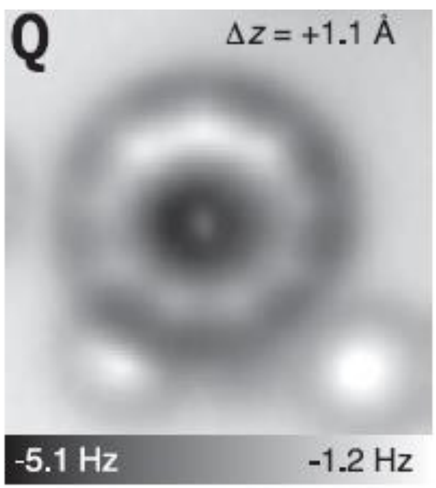
An sp-hybridized molecular carbon allotrope, cyclo[18]carbon

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

Extra info.

Katharina Kaiser[1*], Lorel M. Scriven[2*], Fabian Schulz[1], Przemyslaw Gawel[2†],
Leo Gross[1†], Harry L. Anderson[2†]





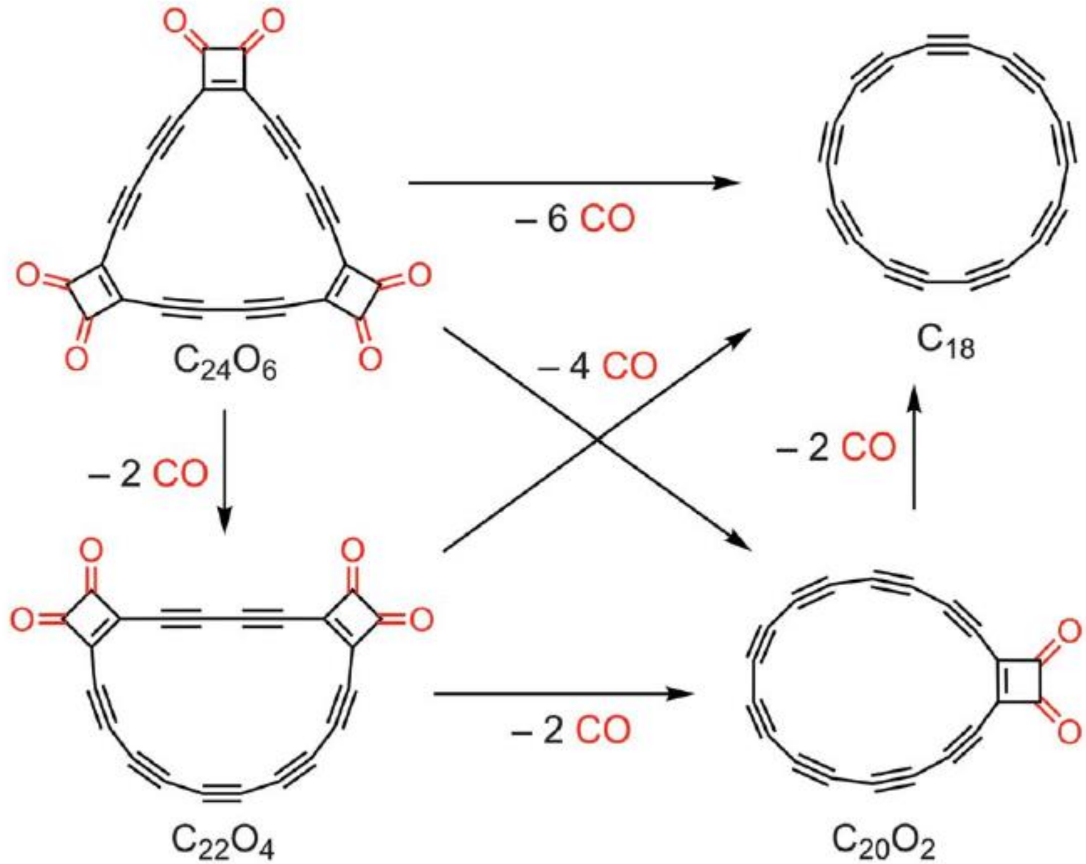


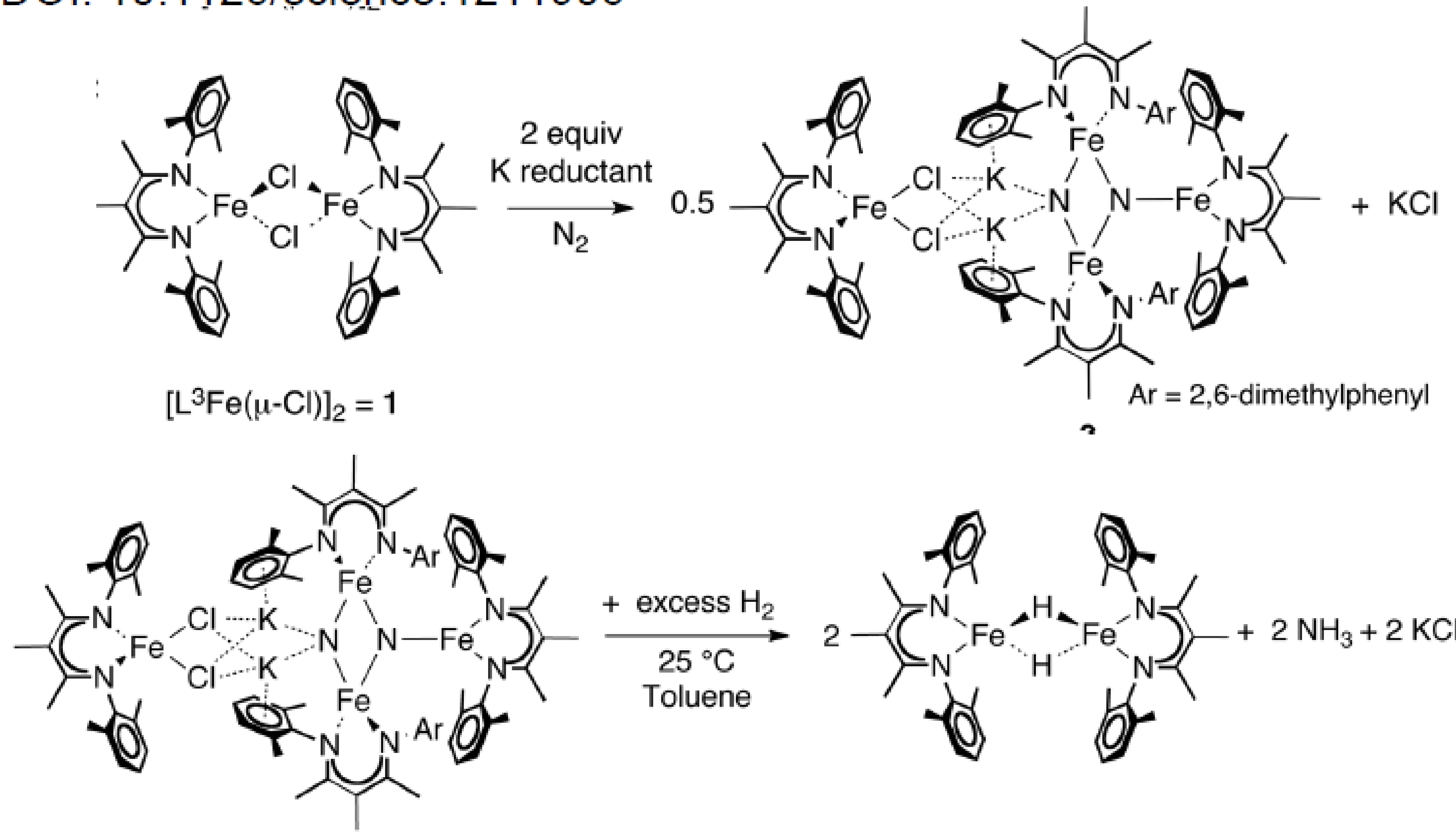
Fig. 2. Reaction scheme for the on-surface formation of C_{18}. Decarbonylation was achieved via voltage pulses that resulted in the loss of two, four, or six CO moieties.

Extra info. Catalysts (recent and selected)

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

Meghan M. Rodriguez, *et al.*

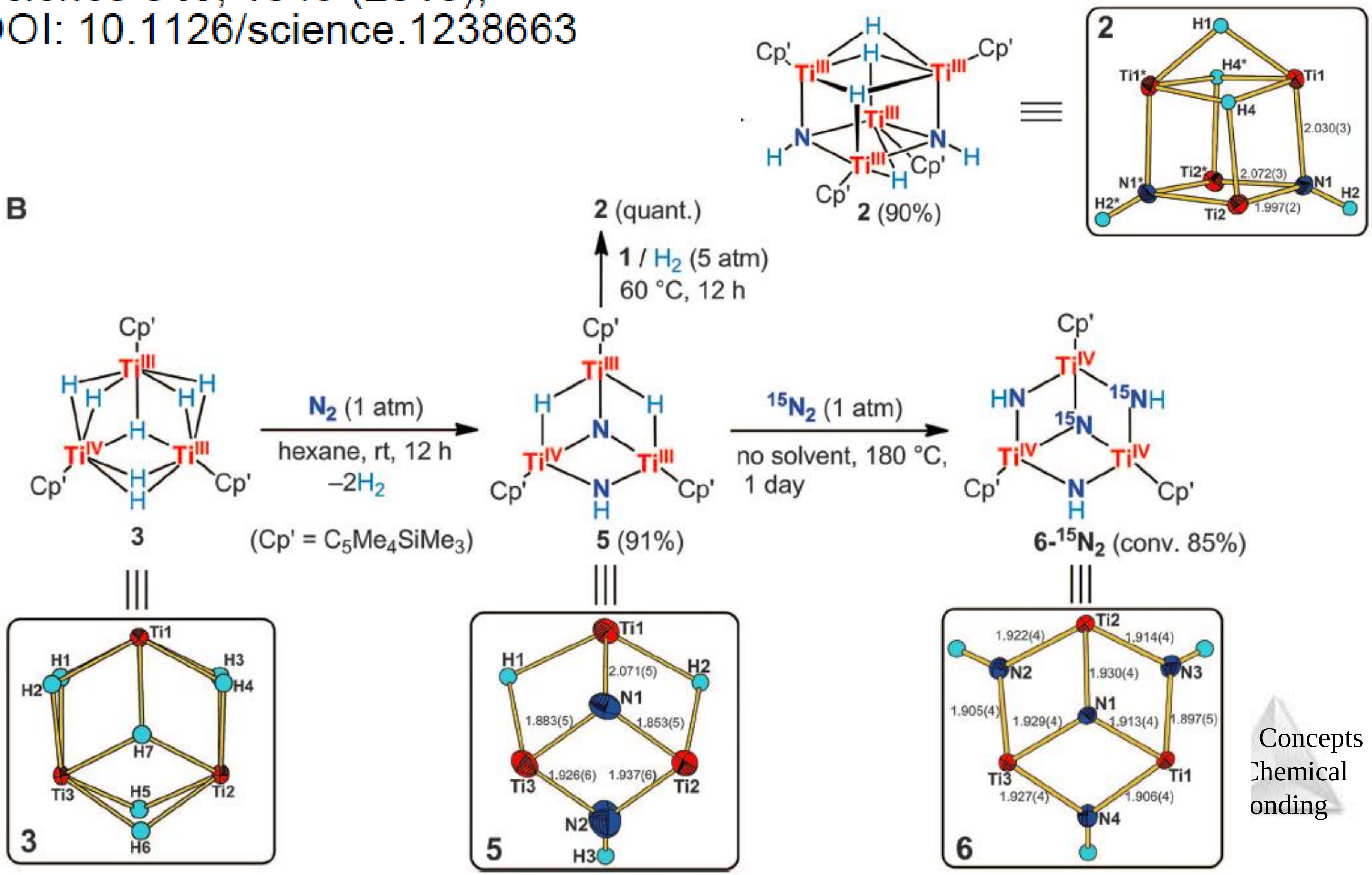
Science **334**, 780 (2011);
DOI: 10.1126/science.1211906



Dinitrogen Cleavage and Hydrogenation by a Trinuclear Titanium Polyhydride Complex

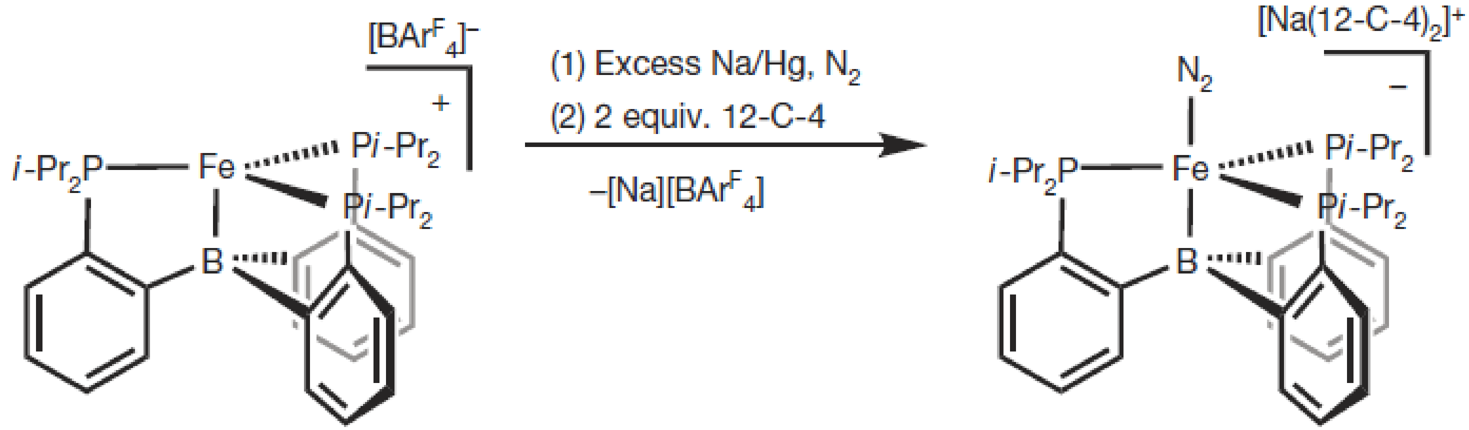
Takanori Shima *et al.*

Science **340**, 1549 (2013);
DOI: 10.1126/science.1238663



Catalytic conversion of nitrogen to ammonia by an iron model complex

John S. Anderson[1], Jonathan Rittle[1] & Jonas C. Peters[1]



[(TPB)Fe][BAr$^F_4$]

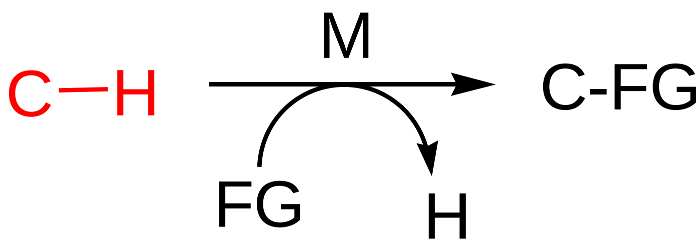
[(TPB)Fe(N_2)]$^-$
[Na(12-C-4)$_2$]$^+$

$$\begin{matrix}[(\mathrm{TPB})\mathrm{Fe}(\mathrm{N_2})]^- \\ [\mathrm{Na(12\text{-}C\text{-}4)_2}]^+\end{matrix} \xrightarrow[\text{(2) 6 equiv. proton sponge}]{\text{(1) 6 equiv. HBAr}^F_4\bullet 2\mathrm{Et_2O},\ -78\ ^\circ\mathrm{C}} \begin{matrix}[(\mathrm{TPB})\mathrm{Fe}(\mathrm{NH_3})]^+ \\ [\mathrm{BAr^F_4}]^- \\ + \\ \text{unidentified} \\ (\mathrm{TPB})\mathrm{Fe}\text{ species}\end{matrix}$$

Extra info.

(Nature 2013, 501, 84)

Extra info. C-H bond Activation & Functionalization



D: 413 kJ

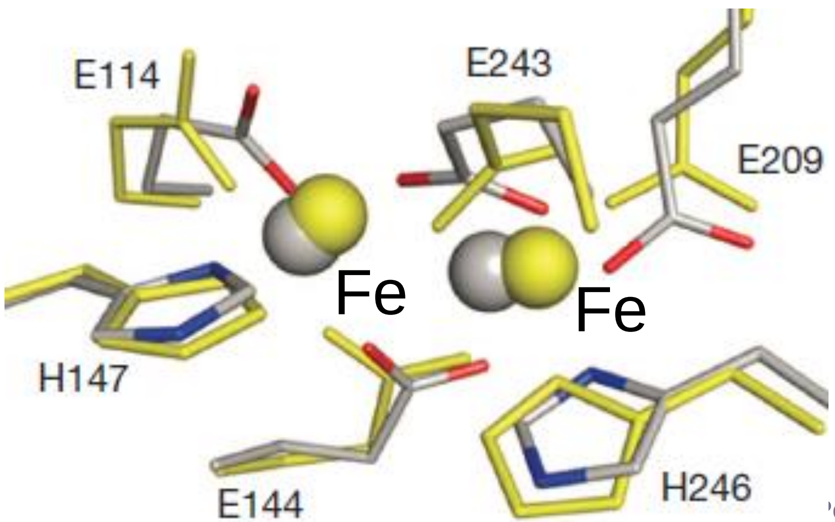
Difficulties

- **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)

$$CH_4 + O_2 + 2H^+ + 2e^- \rightarrow CH_3OH + H_2O$$



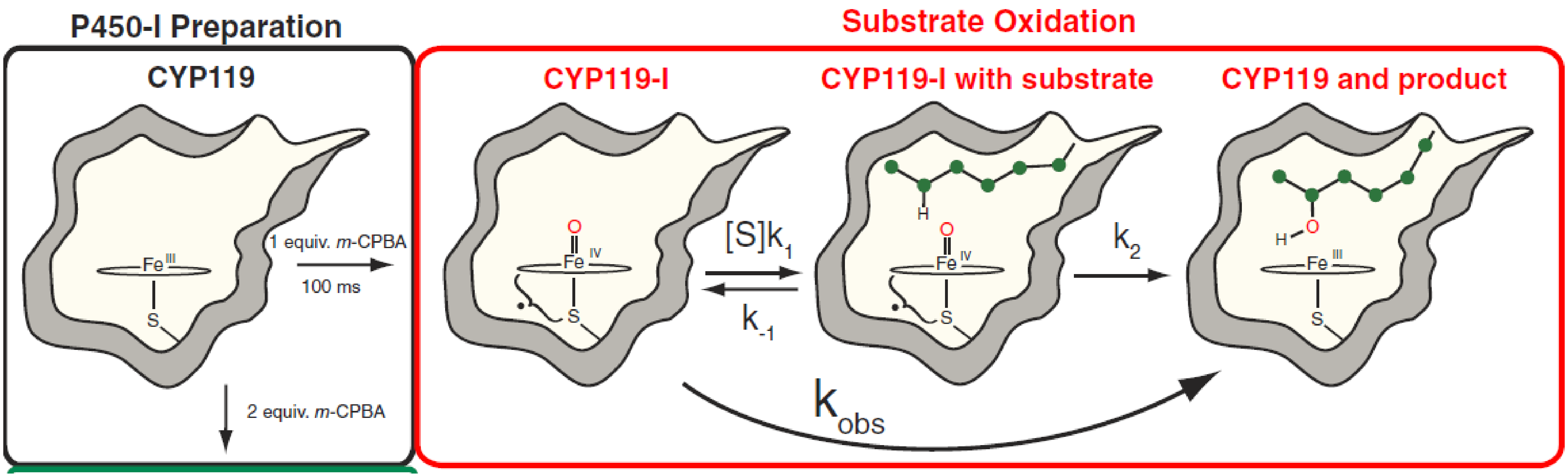
particulate methane monooxygenases (pMMO): Diiron cluster

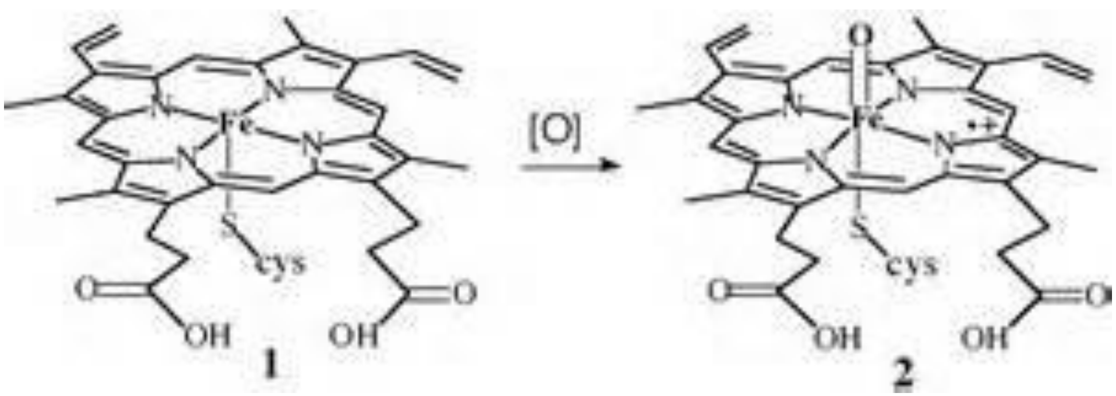
soluble methane monooxygenases (sMMO): Mono-? or Di-copper cluster

(Nature 2013 494 380)

Biology: Cytochrome P450

Extra info.





Reactive high-valent iron-oxo porphyrin

$$O_2 + 2H^+ + 2e^-$$

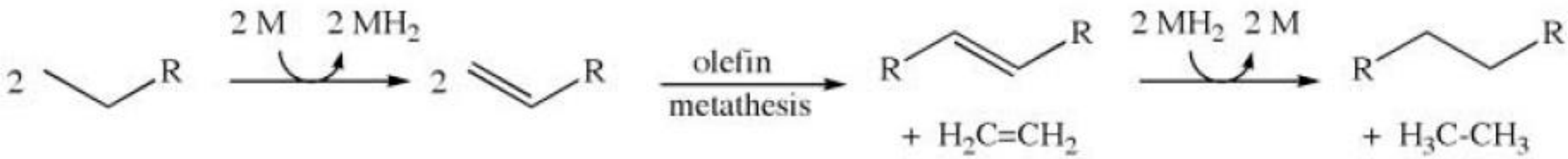
Basic Concepts of Chemical Bonding

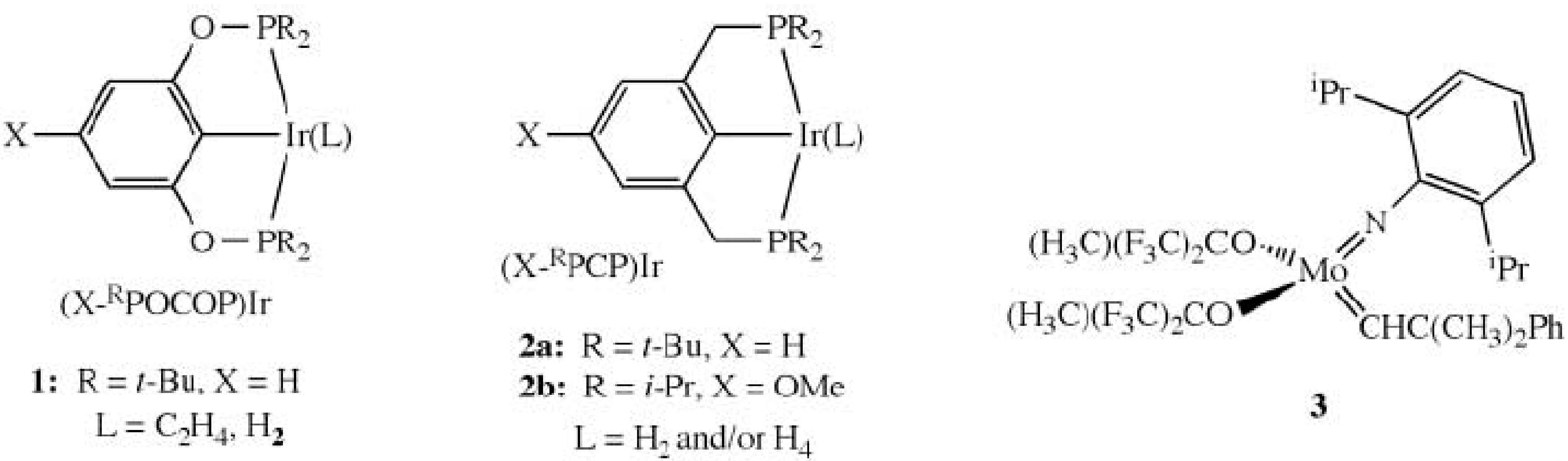
(Science 2010 330 933)

Extra info. Catalysts

$$H_3C\text{-}(CH_2)_n\text{-}CH_3 + H_3C\text{-}(CH_2)_m\text{-}CH_3 \rightarrow$$

$$H_3C\text{-}(CH_2)_{m+n-x}\text{-}CH_3 + H_3C\text{-}(CH_2)_x\text{-}CH_3$$



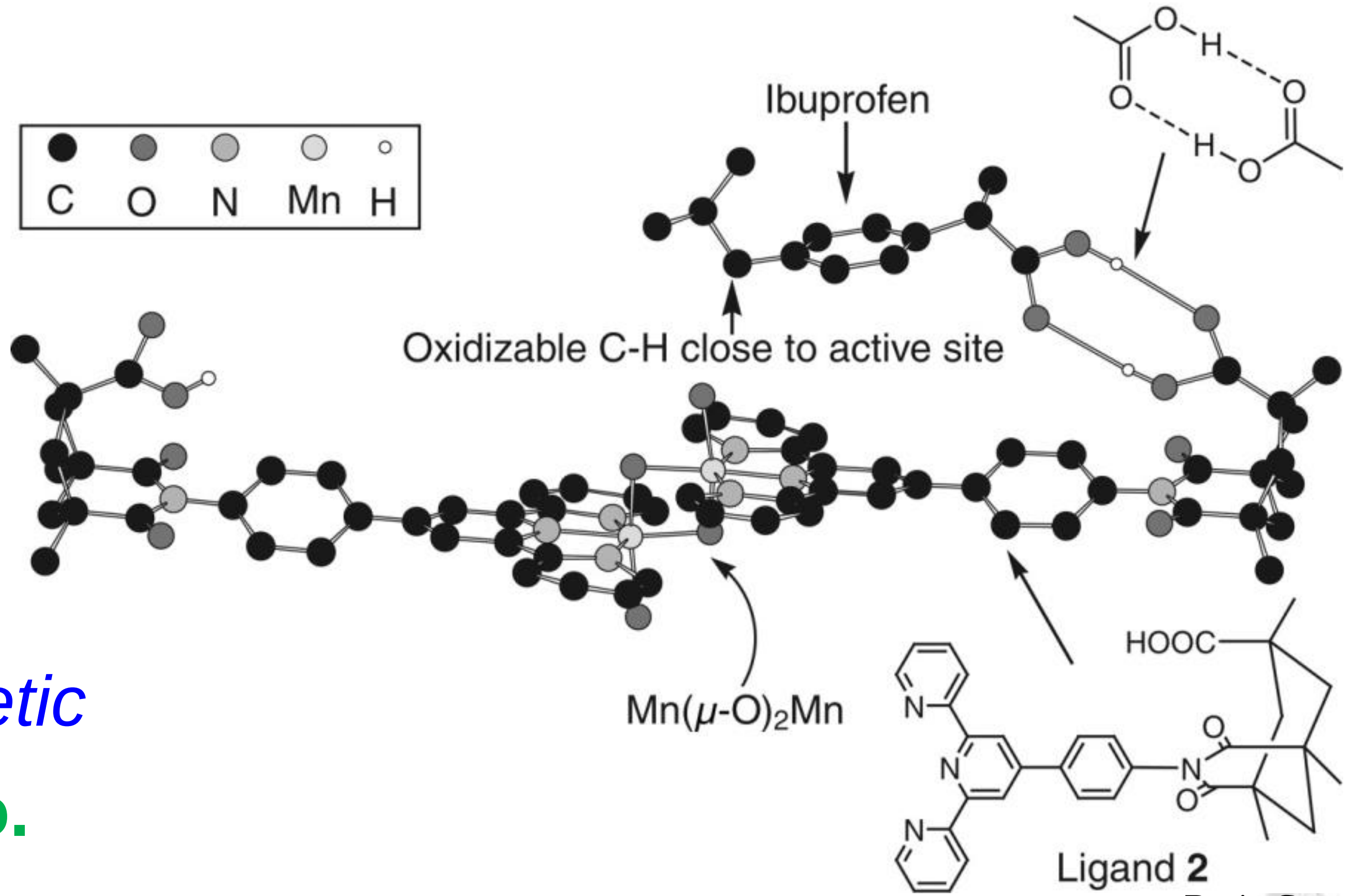


Basic Concepts of Chemical Bonding

(Science 2006, 312, 257)

$$Mn(\mu\text{-}O)_2Mn \quad + \quad \text{ligands} + R\text{-}H \xrightarrow[20\ ^oC]{n\text{-}Bu_4NHSO_5^-} R\text{-}OH$$

0.001 %



Biomimetic

Extra info.

(Science, 2006, 312, 1941)

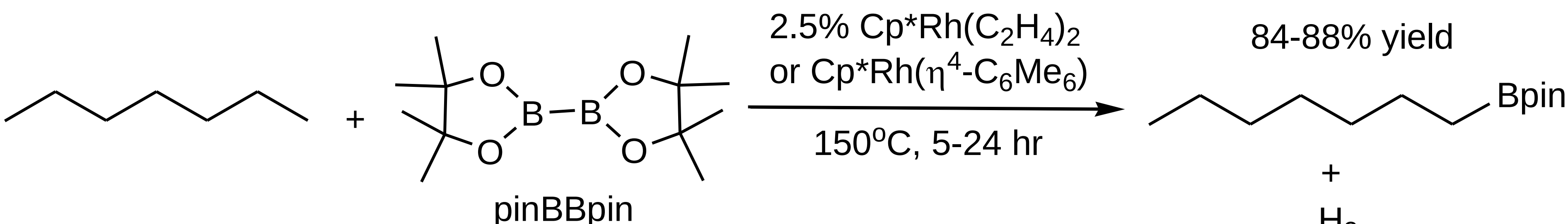
$$CH_4 \longrightarrow CO/H_2 \longrightarrow CH_3OH \xrightarrow{CO} CH_3CO_2H$$

Existing Multi-step Process

$$2CH_4 + 4H_2SO_4 \xrightarrow{Pd(II)} CH_3CO_2H + 6H_2O + 4SO_2$$

(Science, 2003, 301, 814.) 10% yield; ~90% selectivity

Extra info.

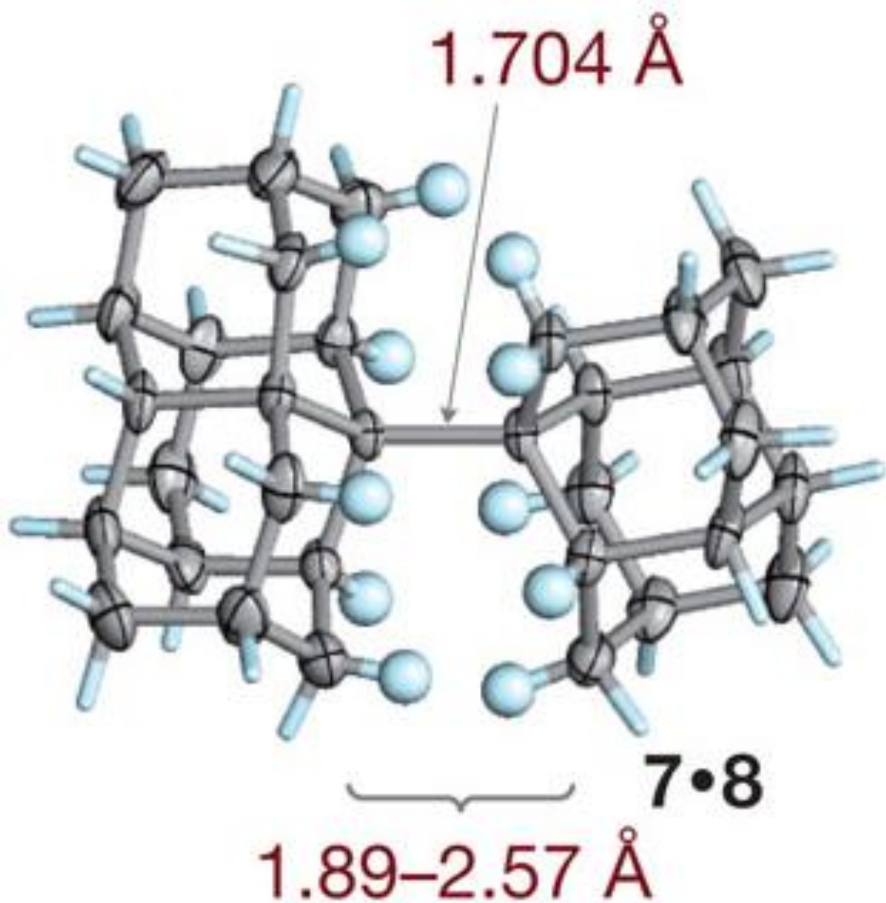


(Science, 2000, 287, 1995)

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



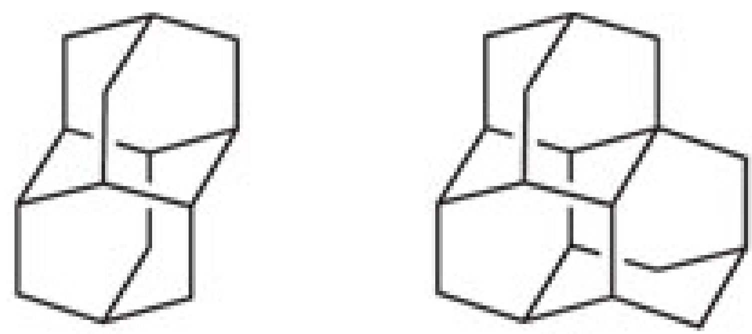
(Nature 2011, 477, 308)

Normal C(sp3)-C(sp3): 1.54

Nano-diamond: 1.704

Stable, decompose > 200^{o}C

Stabilized by attractive dispersion interactions



7 8

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

Thank You for Your Attention!
Any Questions?