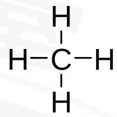
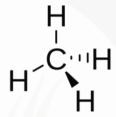
14 Covalent bonding: Orbitals

※ Hybridization and the localized electron model

Ex. CH_4 Lewis structure:



VSEPR:



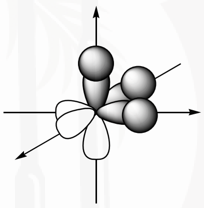
tetrahedral

Valence orbitals involved in C: 2s, 2p_x, 2p_y, 2p_z

An isolated orbital view

one H bonding with 2s of C

three H bonding with 2p of C



Fact: The four bonds are equal length

The bond angles are the same

⇨ The isolated orbital view is not correct

The idea of hybridization

Four identical orbitals are generated from

2s, 2p_x, 2p_y, 2p_z

⇨ Represented as four sp^3 hybridized orbitals

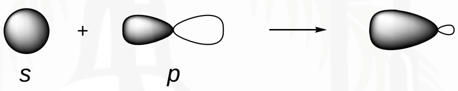
Related math

A linear combination of 2*s* and 2*p*
to give four new wave functions

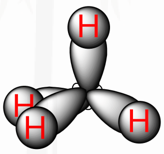
	phase
$\Psi_1 = ½\,[\Phi_s + \Phi_{p_x} + \Phi_{p_y} + \Phi_{p_z}]$	+ + + +
$\Psi_2 = ½\,[\Phi_s + \Phi_{p_x} - \Phi_{p_y} - \Phi_{p_z}]$	+ + – –
$\Psi_3 = ½\,[\Phi_s - \Phi_{p_x} + \Phi_{p_y} - \Phi_{p_z}]$	+ – + –
$\Psi_4 = ½\,[\Phi_s - \Phi_{p_x} - \Phi_{p_y} + \Phi_{p_z}]$	+ – – +

Note: symmetrical or antisymmetrical
(no + + + –)

✓ The shape

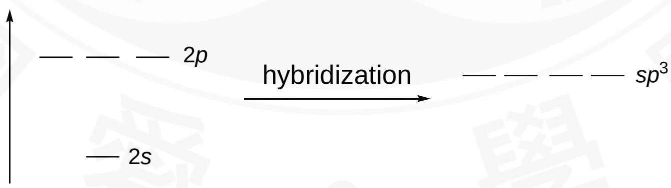


CH_4

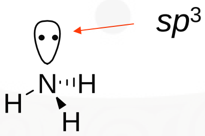


Divide the space equally

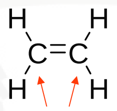
✓ Energy diagram



Ex. NH_3



◎ *sp*^{2} hybridization

Ex. Ethylene 

VSEPR: planar with angle of 120^o

⇨ Can not be *sp*^{3}

sp^2 hybridization

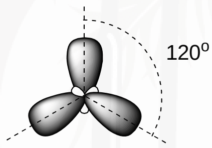
hybridize one *s* with two *p*s and leave one *p* untouched

s: has no directionality

p: has directionality

⇨ The three *sp*^{2} orbitals adopt the directionality of the two *p*s

⇨ Lying on the same plane

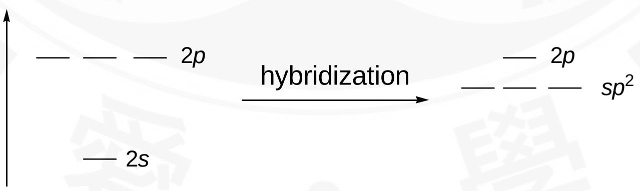


Divide the plane equally

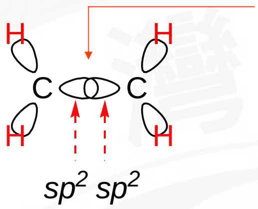
→ Trigonal planar geometry

The untouched *p* orbital is orthogonal to this plane

✓ Energy diagram



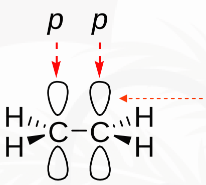
✓ The overall structure



Head-to-head overlap
: σ bond

What about the orthogonal *p* orbitals?

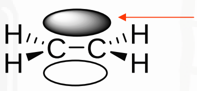
⇨ Form a bond



Overlap sideways: π bond
Has to be on the same plane
for maximum overlap

The σ and π bond constitute the double bond

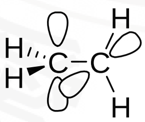
σ bond: e⁻ density is centered between the two nuclei
π bond: e⁻ density is centered on the sideways

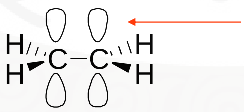


More exposed
→ More reactive

Sideway overlap is not so efficient: usually weaker

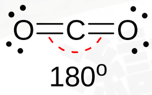
When the two *p* orbitals are orthogonal: no overlap
→ No π bond





On the same plane
⇨ Maximum overlap

◎ *sp* hybridization

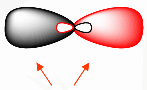
Ex. 

C: hybridization of one *s*

one *p*

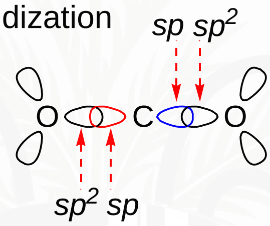
→ Adopt the directionality of the *p*

→ Linear

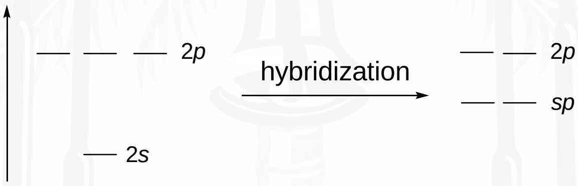


Two *sp* orbitals

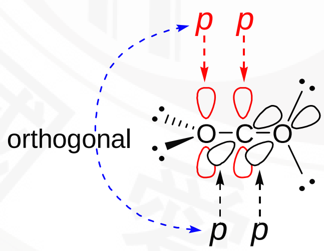
O: uses sp^2 hybridization

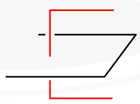


✓ Energy diagram



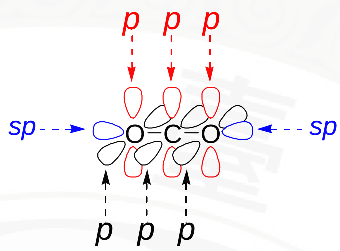
✓ Two orthogonal *p* orbitals of C are used in π bonding





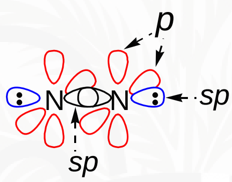
Still an oversimplified view

Another possibility



Fact: electron density is cylindrically symmetrical around the O-C-O axis

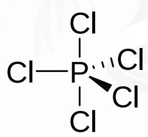
Ex. :N≡N:



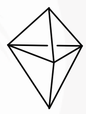
Contains two orthogonal π orbitals

◎ *dsp*^{3}

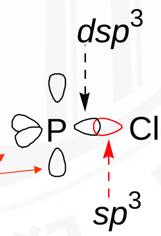
Ex. PCl_5



Trigonal bipyramidal

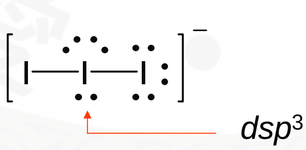


P: hybridization of
one *s*
three *p* ⇨ Five *dsp*^{3}
one d



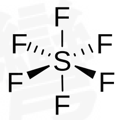
slightly
different shape

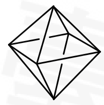
Ex. I_3^-



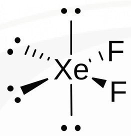
◎ d^2sp^3 → octahedral

Ex. SF_6





XeF_4

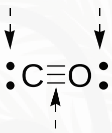


More examples

CO

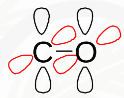
$9 + 6 = 10$

sp *sp*



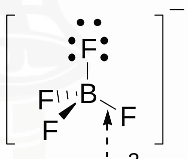
σ: *sp-sp*

π



BF_4^-

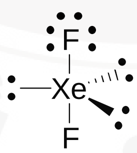
$3 + 4 \times 7 + 1 = 32$



sp^3

XeF_2

$8 + 7 \times 2 = 22$



dsp^3

※ The molecular orbital theory (MO)

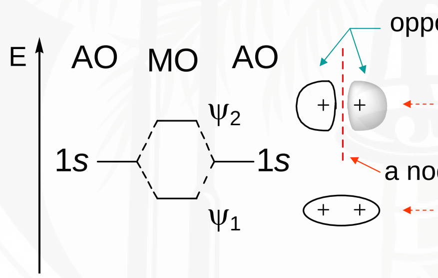
The VB theory can not explain some properties

⇨ MO theory:
consider a new set of molecular orbitals are formed through the linear combination of atomic orbitals (LCAO)

Ex. H_2

Two MOs from two AOs (1*s*)

$$\Psi_1 = \Phi_{1sA} + \Phi_{1sB}$$
$$\Psi_2 = \Phi_{1sA} - \Phi_{1sB}$$



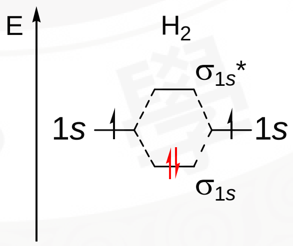
Anti-bonding MO
e^-s are concentrated at the outside → σ_{1s}^*

Bonding MO
e^-s are concentrated between the two nuclei → σ_{1s}

Orbital numbers are conserved:
n AO → n MO

Electrons are filled from the lowest level ⇨

Configuration: σ_{1s}^2 ⇦

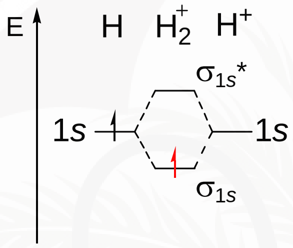


◎ Bond order

$$\text{bond order} = \frac{\#\text{ of bonding e}^- - \#\text{ of anti-bonding e}^-}{2}$$

For H_2: $\quad \text{bond order} = \frac{2-0}{2} = 1$

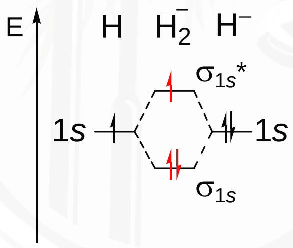
Ex. H_2^+



$$\text{bond order} = \frac{1-0}{2} = \frac{1}{2}$$

Experiment:
Bond E = 255 kJ/mol
(cf. H_2: BE = 458 kJ/mol)

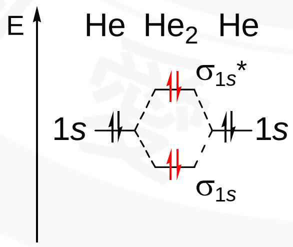
Ex. H_2^-



$$\text{bond order} = \frac{2-1}{2} = \frac{1}{2}$$

Fact: very unstable, does not exist
→ The model is still too simple

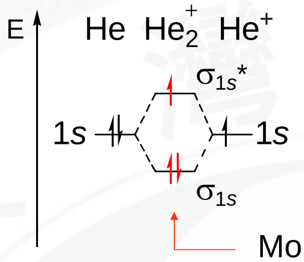
Ex. He_2?



$$\text{bond order} = \frac{2-2}{2} = 0$$

→ He_2 does not exist

What about He_2^+



$$\text{bond order} = \frac{2-1}{2} = \frac{1}{2}$$

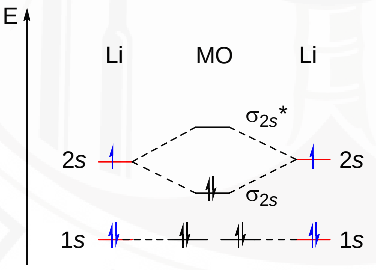
Exp: BE = 250 kJ/mol

More stable than in the atom form

※ Bonding in homonuclear diatomic molecules

The 2nd period

Li_2

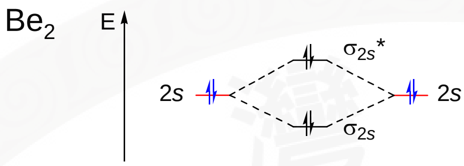


Inner shell orbitals too small to overlap

$$\text{bond order} = \frac{2-0}{2} = 1$$

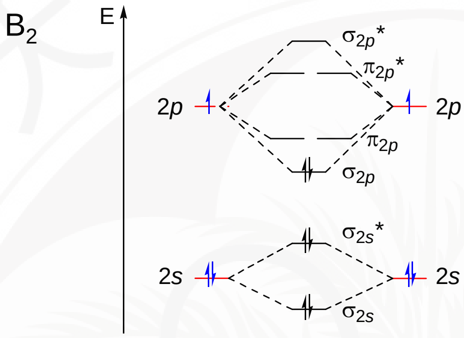
In fact, Li does not exist as Li_2

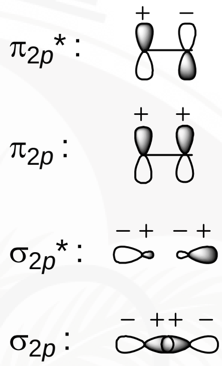
→ Forms metallic bond



$$\text{bond order} = \frac{2-2}{2} = 0$$

In fact: forms metallic bond





Fact: paramagnetic

◎ Magnetism

Two types: paramagnetic
diamagnetic (反磁)

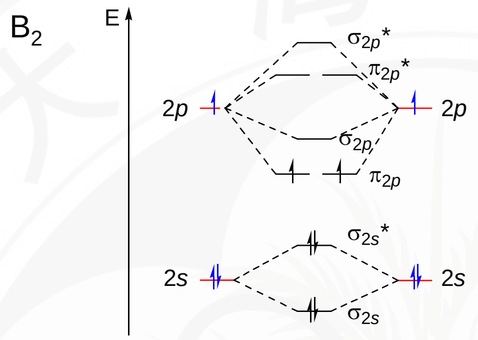
In a magnetic field:

Compound with unpaired electrons
- Has a permanent magnetic moment
- Attracted by a magnetic field
- → Paramagnetic (strong)

Compound with paired electrons
- A magnetic moment will be induced by external magnetic field
- Repelled by the magnetic field
- → Diamagnetic (weak)

The model for B_2 is not correct

Correction: Mixing of 2*s* and 2*p*

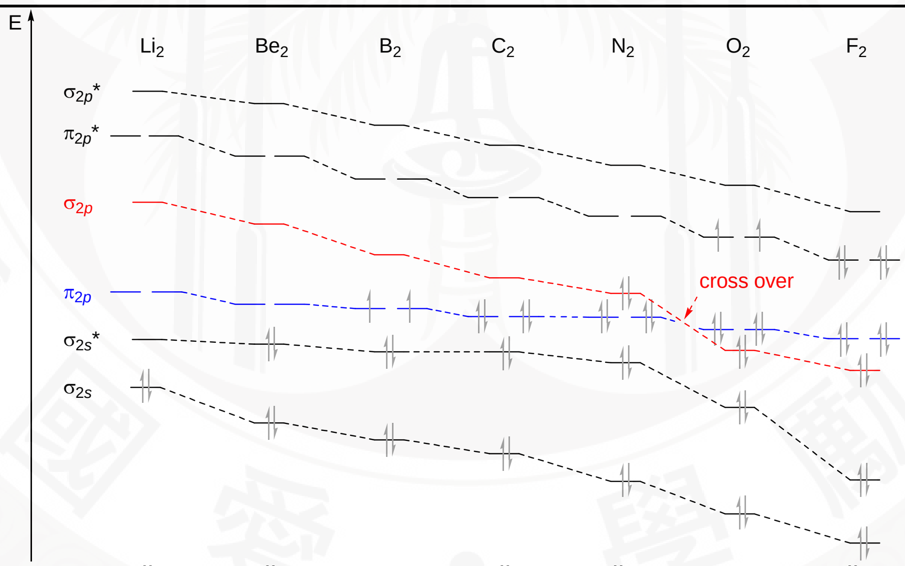


$$\text{bond order} = \frac{4-2}{2} = 1$$

Contains two unpaired e^-s

→ Paramagnetic

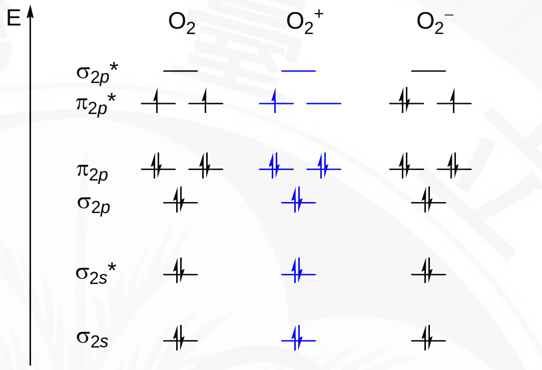
a better model



	Li_2	Be_2	B_2	C_2	N_2	O_2	F_2
	dia-	dia-	para-	dia-	dia-	para-	dia-
BO			1	2	3	2	1
BE (kJ/mol)			290	620	942	495	154
BL (Å)			1.59	1.31	1.10	1.21	1.43

Note: The magnetic property of O_2 can not be predicted by localized electron model
Difficult to draw proper Lewis structure

Ex. O_2, O_2^+, O_2^-



BO $\quad \frac{8-4}{2}=2 \quad \frac{8-3}{2}=2.5 \quad \frac{8-5}{2}=1.5$

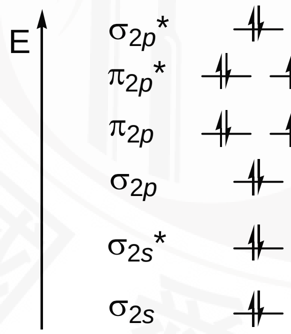
BE $\quad$ 495 $\quad$ 643 $\quad$ 395 kJ/mol

Electronic config:

$(\sigma_{2s})^2\,(\sigma_{2s}^*)^2\,(\sigma_{2p})^2\,(\pi_{2p})^4\,(\pi_{2p}^*)^1$

Ex. Ne_2 and P_4
Bond order and magnetism?

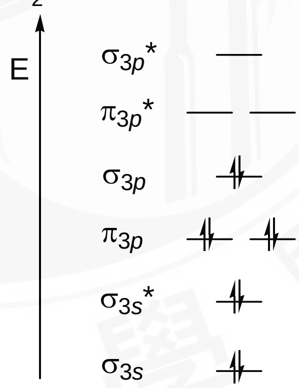
Ne_2



bond order $= \frac{8-8}{2} = 0$

⇨ Ne_2 does not exist

P_2

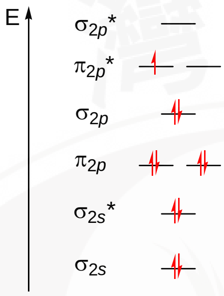


bond order $= \frac{8-2}{2} = 3$

Diamagnetic

※ Heteronuclear diatomic molecules

✓ NO



$$\text{Bond order} = \frac{8-3}{2} = 2.5$$

Paramagnetic

✓ NO^+

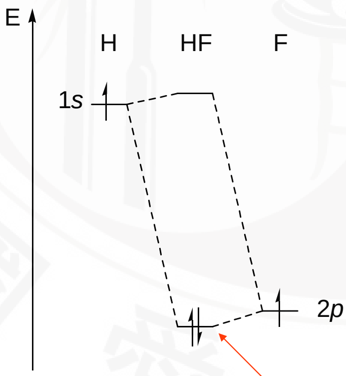
$$BO = \frac{8-2}{2} = 3$$

Diamagnetic

CN^-: similar

✓ HF

Large difference in orbital energies
(cf. IP: H 1311 kcal/mol; 1681 kcal/mol)



Cf. Bond cleavage
Homolytic cleavage:

HF → H• + F• ΔH^1 = BE

Heterolytic cleavage:

HF → $H^+ + F^-$ ΔH^2

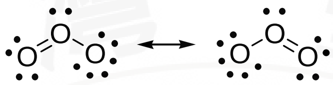
HF → $H^- + F^+$ ΔH^3

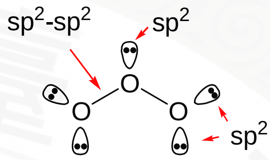
Note: $\Delta H^1 \neq \Delta H^2 \neq \Delta H^3$

More F_{2p} like
→ Highly polarized bond
→ e^- density closer to F

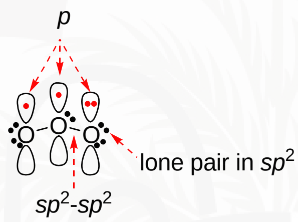
※ Combining the localized electron and MO models

✓ O_3 LE model for resonance





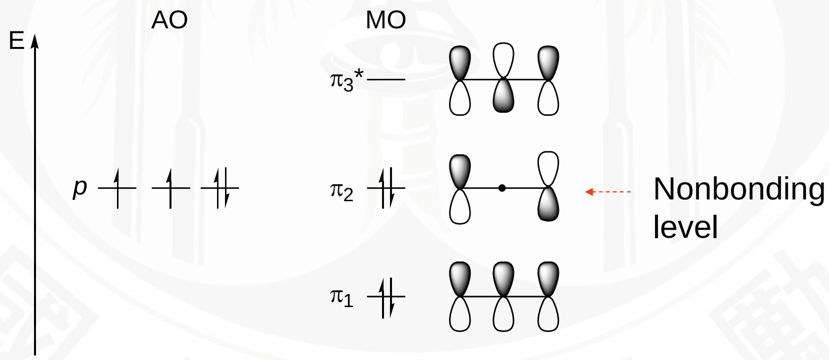
The difference of the two resonance structures
→ Only the π bond
→ Consider σ bonds with LE model
Use MO to treat the π bonding



LE model treats:
5 lone pairs
2 σ bonds
→ A total of 14 electrons

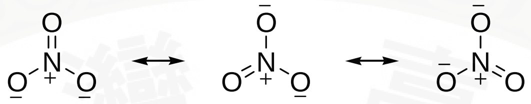
MO treats: 4 π electrons

Energy diagram of the π MOs of O_3

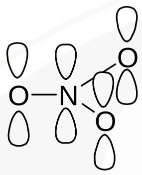


In this MO view:
the four π electrons are delocalized over the three oxygens

✓ NO_3^-

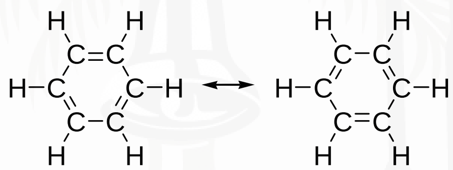


MO:

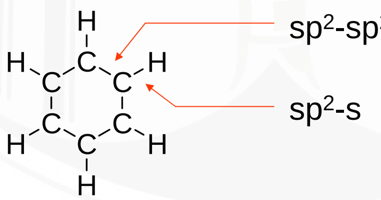


6 π electrons
delocalized over 4 atoms

✓ Benzene



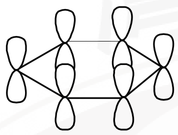
LE (σ)



MO (π)

Composed of 6 p orbitals provided by the 6 Cs

each provides 1 e^- with a total of 6 π e^-s



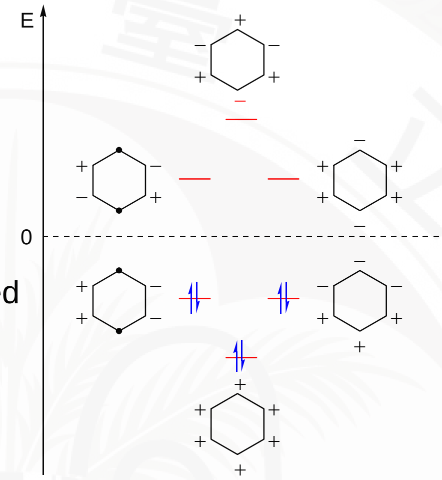
6 π electrons

delocalized over 6 carbons

in a closed cycle

⇨ 6 new π MOs are generated

⇨ In fact, highly stabilized (compared with 3 isolated double bonds)



※ Orbitals: human inventions

Remember

Orbitals are mathematical functions

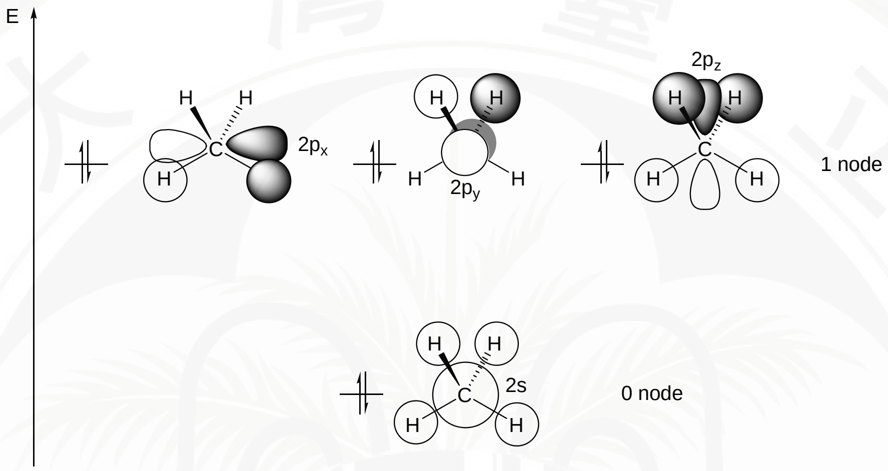
The pictorial orbitals are simplified model but useful to understand

More approximation ⇨ simple model, less accurate

Less approximation ⇨ complicate model, more accurate

Example of a complicate model:

The bonding MO of methane (CH_4)



※ Molecular spectroscopy

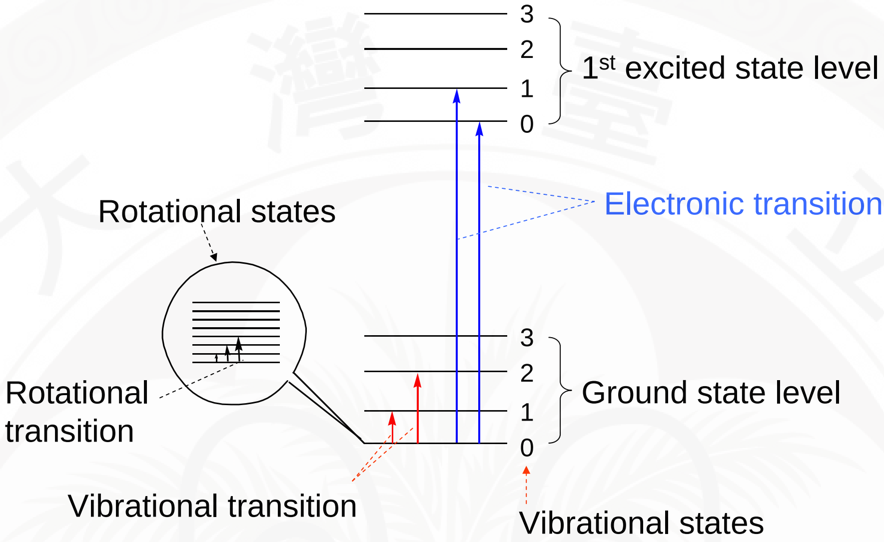
When a molecule changing from one electronic state
to another electronic state

⇨ It absorbs or emits electromagnetic radiation
⇨ called electronic transition
⇨ corresponds to ultraviolet (UV) or visible light

There are different vibrational states
⇨ transitions between these states
correspond to infrared (IR) light

There are rotational states
⇨ microwave

✓ An energy diagram picture



Increasing λ →

γ-rays	x-rays	UV	visible	IR	microwave	radio-wave
0.1 nm		200	400–800	2–50 μm		

$\underbrace{200 \quad 400\text{–}800}_{\text{nm}}$

◎ Rotational spectroscopy

related to the size of the molecule

(bond length information)

Ex. For a linear molecule

$$E_J = \frac{\hbar^2}{2I} J(J+1)$$

J : rotational quantum #

$J = 0, 1, 2, \ldots\ldots$

I : moment of inertia

For diatomic molecule

$I = \mu R_e^2$ $\quad$ μ : reduced mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

R_e = average bond length

When $J = 0$ ⇨ $E_0 = 0$

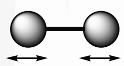
$J = 1$ ⇨ $E_1 = \dfrac{\hbar^2}{I}$

$$\underbrace{E_1 - E_0} = \frac{\hbar^2}{I}$$

Obtained from exp ⇨ get bond length info

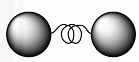
◎ Vibrational spectroscopy

For simple diatomic molecule



Stretching mode

Cf.



m_1 $\quad$ m_2

← This model can be described by Hooke's law

$$\bar{\upsilon} = \frac{1}{\lambda} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

k : force constant

μ : reduced mass

✓ k is related to the bond strength

✓ Masses of the atoms involved are inversely proportional to stretching frequency

For molecules, the vibrational states are quantized

$E_v = h\upsilon_o(v + ½)$ υ_o : a characteristic freq of the vibration

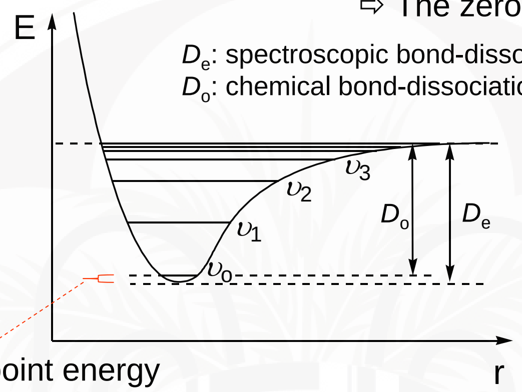
$v = 0, 1, 2, ...$ (for harmonic oscillator)

When v = 0 $E_o = \dfrac{h\upsilon_o}{2}$ ← The lowest state is not zero

⇨ The zero point energy

D_e: spectroscopic bond-dissociation E

D_o: chemical bond-dissociation E



Zero point energy

✓ Unit used by IR spectroscopy

$$\bar{\upsilon} = \frac{1}{\lambda} \quad ⇨ \quad \bar{\upsilon} \propto \upsilon$$

Wave number (波數): cm^{-1}

✓ Stronger bond ⇨ higher $\bar{\upsilon}$

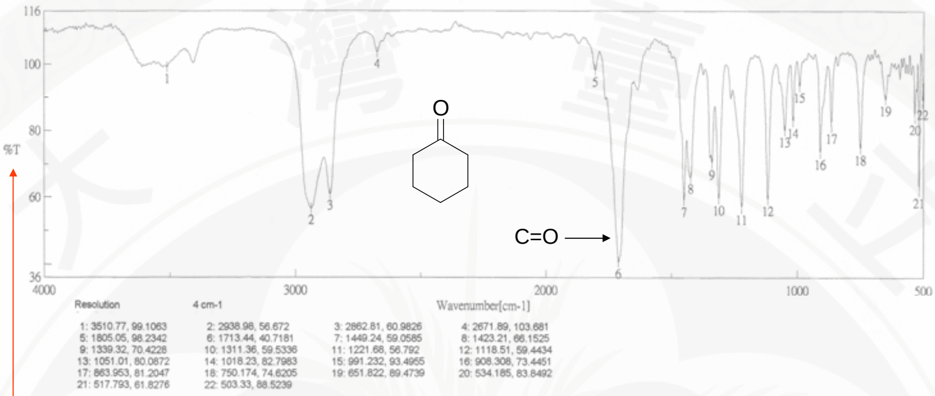
Higher mass ⇨ lower $\bar{\upsilon}$

Ex.	H-C	H-O	(stretching)
	3000	3300	cm^{-1}

Broad: due to hydrogen bonding

C=C	C=O	C≡C	(stretching)
~1650	~1700	~2200 cm^{-1}	

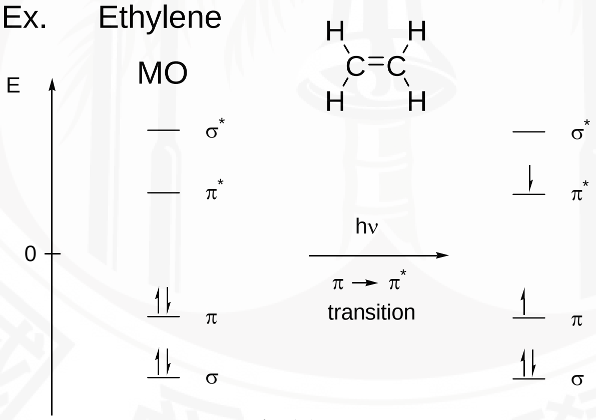
✓ A typical IR spectrum



% transmission

※ Electronic transition: UV-visible spectroscopy

Ex. Ethylene



Note:
Bond order = 1
⇨ The π bond is destroyed

Ground state (基礎態) S_o

Excited state (激發態)
A singlet state (單重態) S_1

λ_{max} = 171 nm

Broad signal due to vibrational and rotational states

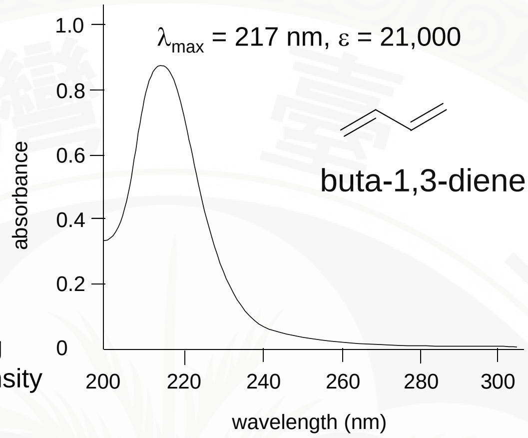
✓ A typical spectrum

Absorbance
$A = -\log T$

T (transmission)
$= \dfrac{I}{I_o}$

Emerging light intensity

Original light intensity



Beer's law: $A = \varepsilon bc$

concentration in M
cell length in cm
extinction coefficient ($cm^{-1}M^{-1}$)

◎ Observing rate processes

Ex. Taking picture of a moving car
The resolution depends on the shutter speed

Recall Heisenberg uncertainty principle:

$$\Delta p \bullet \Delta x \geq \frac{\hbar}{2} \quad \Rightarrow \quad m\Delta u \bullet \Delta x \geq \frac{\hbar}{2}$$

$$\Rightarrow \quad m(\Delta u)^2 \bullet \frac{\Delta x}{\Delta u} \geq \frac{\hbar}{2}$$

$$\Rightarrow \quad m(\Delta u)^2 \bullet \frac{\Delta x}{\Delta x / \Delta t} \geq \frac{\hbar}{2}$$

$$\Rightarrow \quad m(\Delta u)^2 \bullet \Delta t \geq \frac{\hbar}{2}$$

$$m(\Delta u)^2 \bullet \Delta t \geq \frac{\hbar}{2} \qquad \Rightarrow \qquad \frac{1}{2} m(\Delta u)^2 \bullet \Delta t \geq \frac{\hbar}{4}$$

$$\Rightarrow \quad \Delta E \bullet \Delta t \geq \frac{\hbar}{4} \qquad \Rightarrow \qquad h\Delta\upsilon \bullet \Delta t \geq \frac{\hbar}{4}$$

$$\Rightarrow \quad h\Delta\upsilon \bullet \Delta t \geq \frac{h}{2\pi 4} \qquad \Rightarrow \qquad \Delta t \geq \frac{1}{8\pi\Delta\upsilon}$$

Qualitatively: $\upsilon \uparrow$ ⇨ $\Delta t \downarrow$ (faster rate process)

For UV 10 nm apart ⇨ $\Delta t \geqq 1.4 \times 10^{-18}$ s

For IR 6 cm^{-1} apart ⇨ $\Delta t \geqq 2.2 \times 10^{-13}$ s

Lifetime has to be this long to differentiate