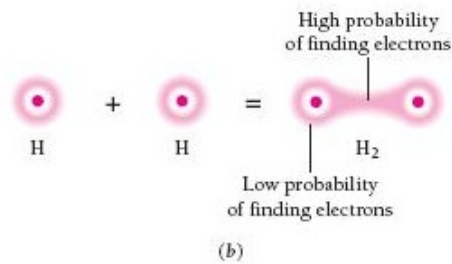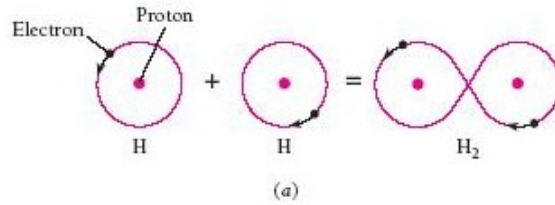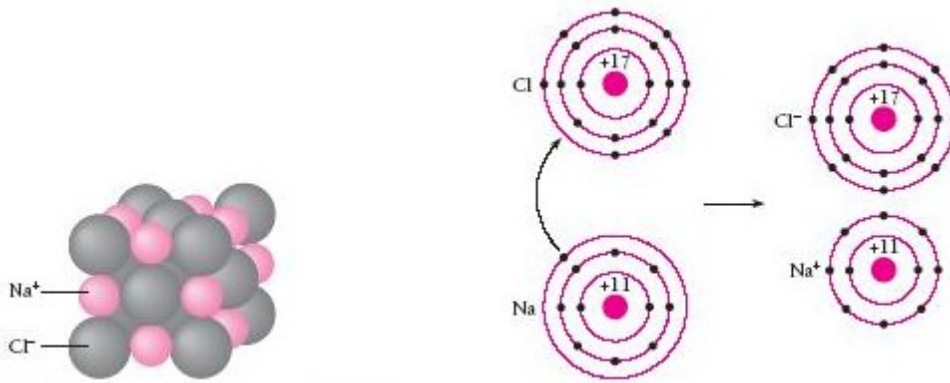# Chapter 6 Molecules

6-1 Molecular Bonds
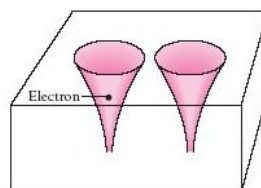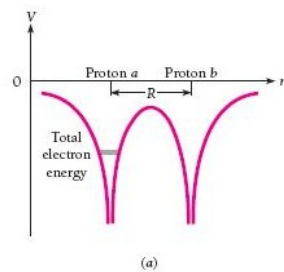
Covalent bond: One or more electrons are shared by the two atoms.
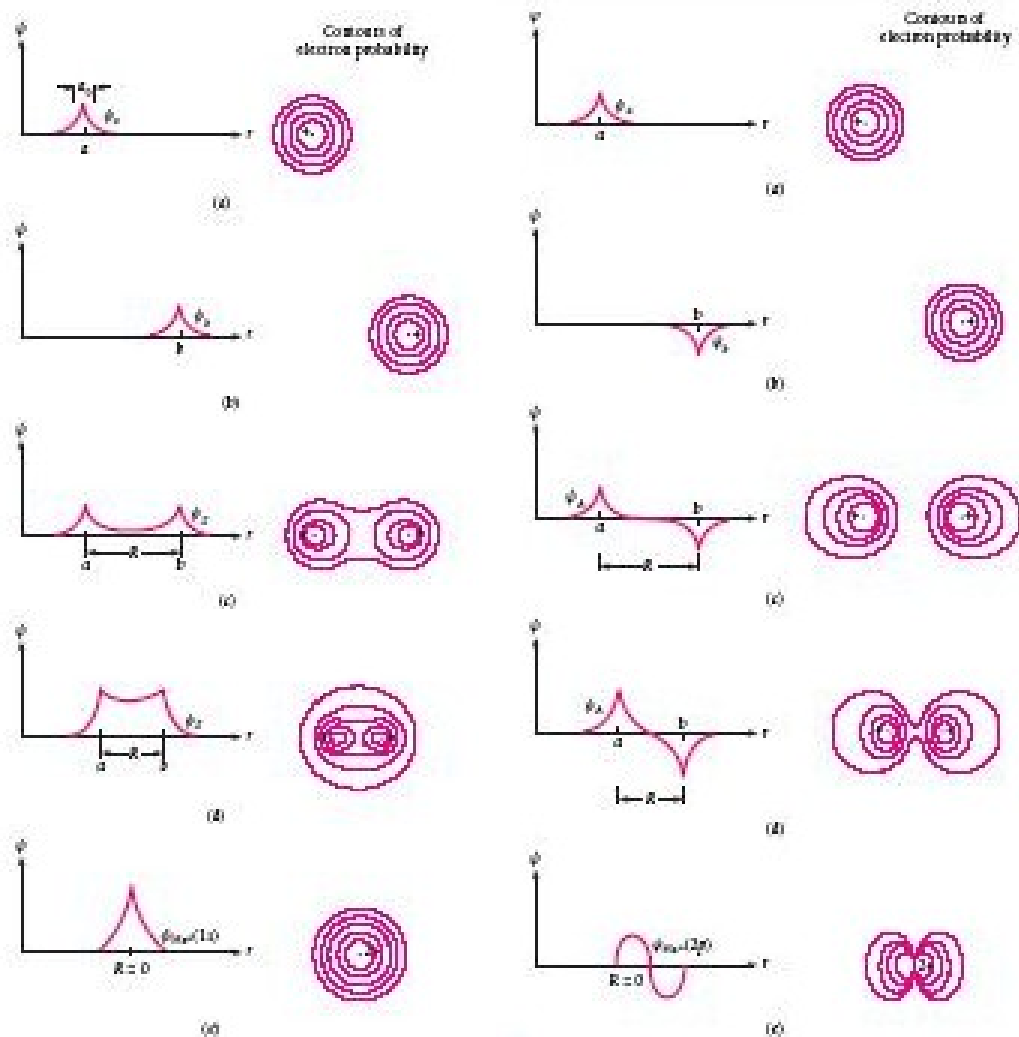

(a)

(b)

Ionic bond: One or more electrons from one atom may transfer to the other, resulting positive and negative ions attract each other.

Electron sharing:

H_2^+ molecular ion: Bonding requires **two symmetric spatial wavefunctions**: **ψ(1,2)=ψ(2,1)**. Antisymmetric spatial wavefunctions can not form chemical bonds. The reason is shown in the following diagrams.

But we must obey Pauli's exclusion principle, the two complete wavefunctions should be antisymmetric. Therefore the two electrons have antiparallel spins.

(Proof) The complete wavefunction is $\Psi(1,2)=\psi(1,2)s(1,2)$, where $\psi(2,1)=\psi(1,2)$ but $s(2,1)=-s(1,2) \Rightarrow \Psi(2,1)=\psi(2,1)s(2,1)=-\psi(1,2)s(1,2)=-\Psi(1,2)$
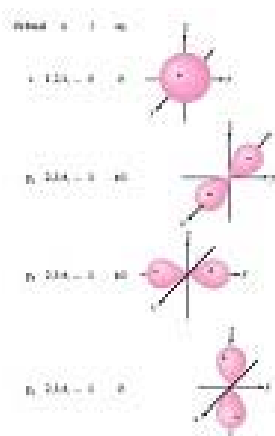
Boundary surface diagram for *s* and *p* atomic orbitals: Each orbital contains two electrons. There is a high density of finding atoms in the shaded region.

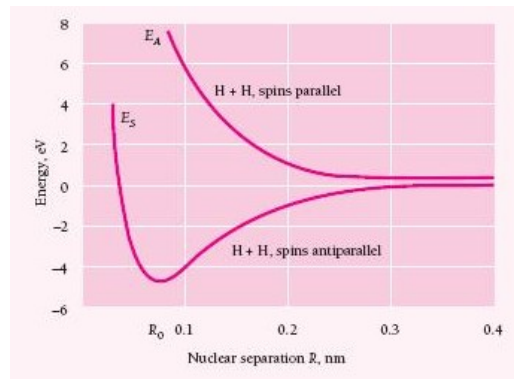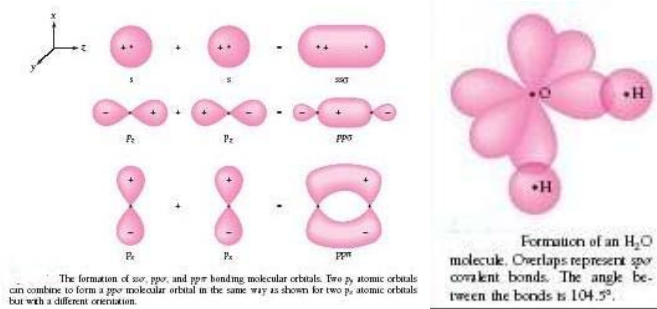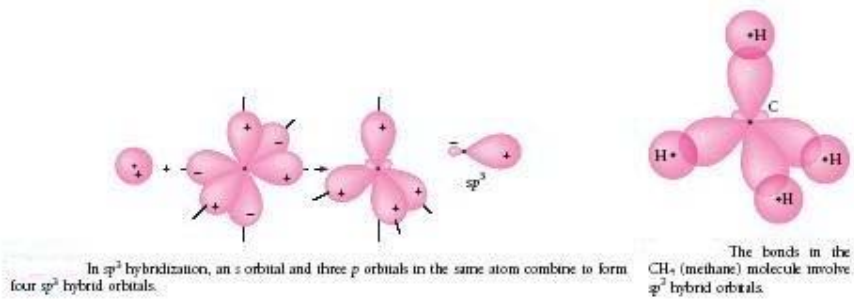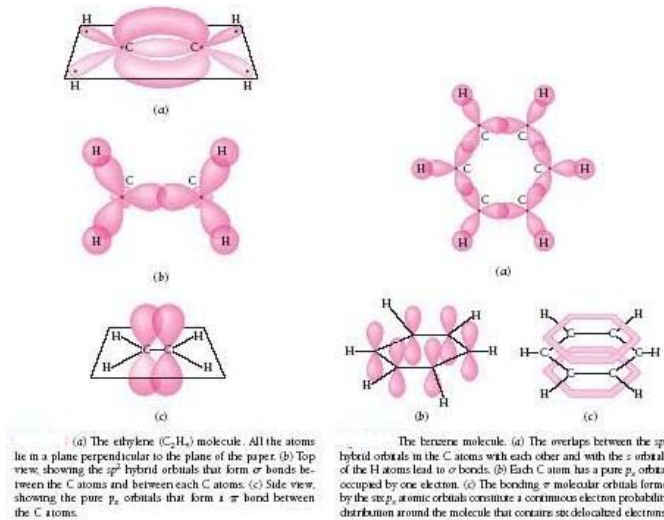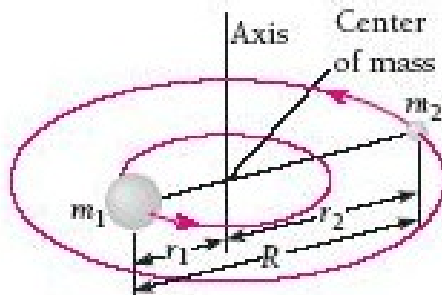**H₂ molecule:** Two H's with antiparallel form a H₂ molecule.

H₂O molecule:

The formation of $ss\sigma$, $pp\sigma$, and $pp\pi$ bonding molecular orbitals. Two p_y atomic orbitals can combine to form a $pp\sigma$ molecular orbital in the same way as shown for two p_z atomic orbitals but with a different orientation.

Formation of an H₂O molecule. Overlaps represent $sp\sigma$ covalent bonds. The angle between the bonds is 104.5°.

CH₄ molecule:

In sp^3 hybridization, an s orbital and three p orbitals in the same atom combine to form four sp^3 hybrid orbitals.

The bonds in the CH₄ (methane) molecule involve sp^3 hybrid orbitals.

Ethylene (C₂H₄) and benzene (C₆H₆) molecules:

(a) The ethylene (C₂H₄) molecule. All the atoms lie in a plane perpendicular to the plane of the paper. (b) Top view, showing the sp^2 hybrid orbitals that form σ bonds between the C atoms and between each C atoms. (c) Side view, showing the pure p_z orbitals that form a π bond between the C atoms.

The benzene molecule. (a) The overlaps between the sp^2 hybrid orbitals in the C atoms with each other and with the s orbitals of the H atoms lead to σ bonds. (b) Each C atom has a pure p_z orbital occupied by one electron. (c) The bonding π molecular orbitals formed by the six p_z atomic orbitals constitute a continuous electron probability distribution around the molecule that contains six delocalized electrons.

6-2 Molecular Spectrum

Major motions within molecules are rotation and vibration.

Molecular rotation: Consider a diatomic molecule that rotates about its center of mass.

Moment of inertia:

$$I=\frac{m_1 m_2}{m_1 + m_2}(r_1 + r_2)^2 = m'R^2$$

Rotational energy level:

$E_J = I\omega^2/2 = L^2/2I = [J(J+1)]\hbar^2/2I.$

Angular momentum: $L=\sqrt{J(J+1)}\hbar$, J=0, 1, 2, …

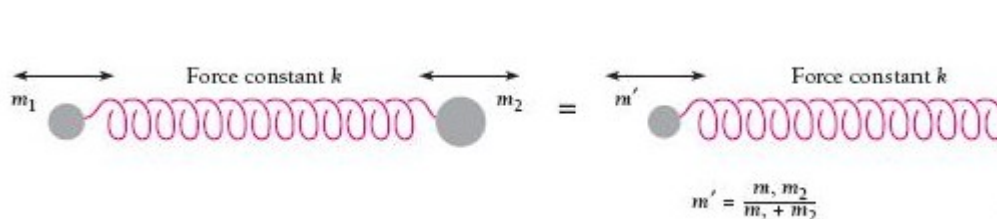**Selection rule of rotational state:** $\triangle J=\pm 1$

Rotational spectra: $v_{J\to J+1}=v_{J+1\to J}=|E_{J+1}-E_J|/h=\dfrac{(J+1)\hbar}{2\pi I}$

Eg. A ^{200}Hg^{35}Cl molecule emits a 4.4-cm-wavelength photon when it rotate from J=1 to J=0. Find its interatomic distance.

(Sol.) J=0, $v=c/\lambda=\dfrac{(0+1)\hbar}{2\pi I}\Rightarrow I$=2.46×10^{-45}

The mass of Hg atom=200×1.66×10^{-27}Kg and the mass of Cl atom=35×1.66×10^{-27}Kg

$m'=\dfrac{m_1 m_2}{m_1 + m_2}$=4.94468×10^{-26}Kg, $R=\sqrt{\dfrac{I}{m'}}$=2.23×10^{-9}m=2.23nm

$m' = \dfrac{m_1 m_2}{m_1 + m_2}$

Molecular vibration: Consider a diatomic molecule that oscillates harmonically.

Frequency of SHM: $v_0=\dfrac{1}{2\pi}\sqrt{\dfrac{k}{m'}}$, where $m'=\dfrac{m_1 m_2}{m_1 + m_2}$

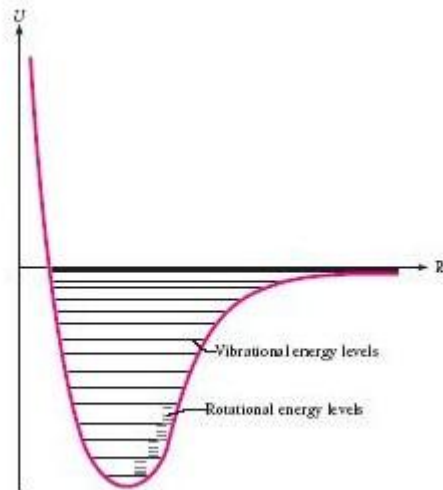**Vibrational energy level:** $E_i=(i+\dfrac{1}{2})hv_0=(i+\dfrac{1}{2})\hbar\sqrt{\dfrac{k}{m'}}$, i=0, 1, 2, …

Selection rule of vibrational state: $\triangle i=\pm 1$

Vibrational spectra: $v_{i\to i+1}=v_{i+1\to i}=|E_{i+1}-E_i|/h=\dfrac{1}{2\pi}\sqrt{\dfrac{k}{m'}}=v_0$
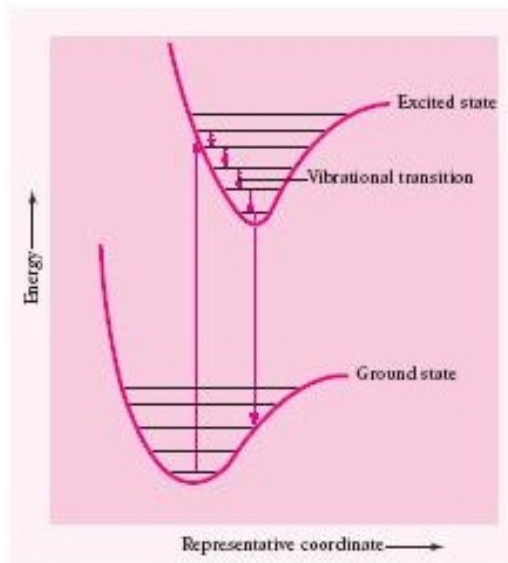
Eg. The force constant k of CO bond is 187N/m. Find the frequency of vibration of the CO molecule and the spacing between its vibrational energy levels.

(Sol.) CO: $m' = 1.14 \times 10^{-26}$Kg, $v_0 = \dfrac{1}{2\pi}\sqrt{\dfrac{k}{m'}} = 2.04 \times 10^{13}$Hz

$\triangle E = |E_{i+1} - E_i| = hv_0 = 1.35 \times 10^{-20}(J) = 8.44 \times 10^{-2}eV$


The potential energy of a diatomic molecule as a function of interatomic distance, showing vibrational and rotational energy levels.

Fluorescence (螢光): Molecules in the ground state absorb short-wavelength photons and enter the excited state. These excited molecules by vibration transitions into the lower energy levels and then drop to the ground state. Therefore they emit long-wavelength photons. It is real-time interaction.

Eg. $H_g + A_r + UV$ light→H_g*+A_r*+visible light
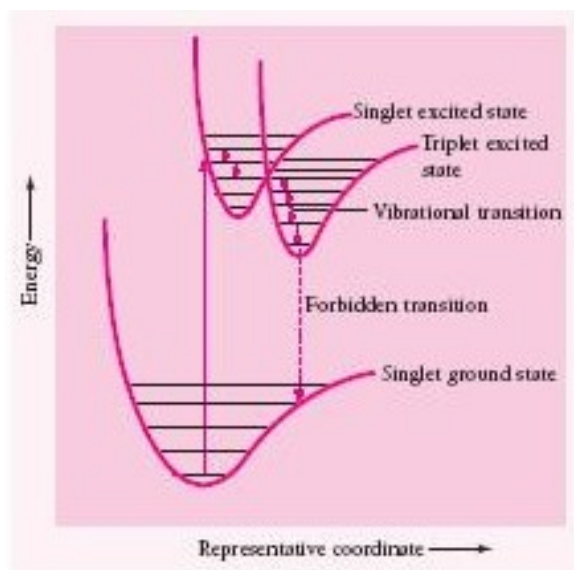
Phosphorescence (磷光): Molecules in the **singlet** ground state absorb short-wavelength photons and enter the **singlet** excited state ($S=0$). In collision, these excited molecules by vibration transitions into the same energy levels of the **triplet** excited level ($S=1$) and then drop to the **singlet** ground state. Therefore they emit long-wavelength photons. A radiative transition from a **triplet** state to a **singlet** state is forbidden by the selection rules, which really mean not that it is impossible but that it has only a small likelihood of occurring. Such transitions accordingly have long half-lives. Phosphorescence radiation may be emitted minutes or even hours after the initial absorption.