

Molecules and Molecular Bonds

- ◆ Two kinds of bond between the atoms in molecule are distinguished.
- ◆ One of them is called *heteropolar* (or **ionic**). Two ions of opposite signs form this bond.
- ◆ The second kind of bond is called *homopolar* (or **covalent**). A pair of electrons having oppositely directed spins forms this bond.

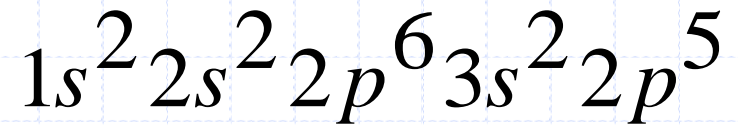
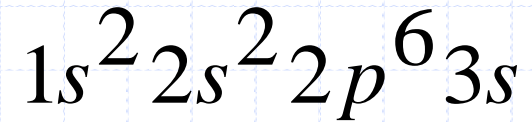
Potential energy

- ◆ The total potential energy of the system can be approximated by the expression
- ◆ r is the internuclear separation, A and B are parameters associated with the attractive and repulsive forces, and n and m are integers.

$$U = -\frac{A}{r^n} + \frac{B}{r^m}$$

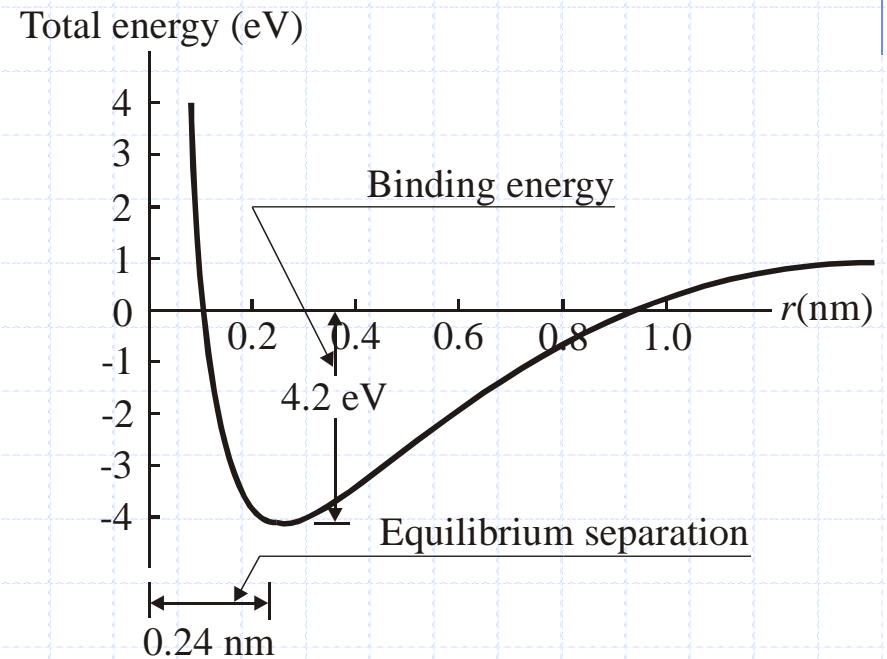
Ionic Bonds

- ◆ Ionic bond is due to the Coulomb attraction between oppositely charged ions. Sodium chloride, NaCl.
- ◆ Sodium has an electronic configuration
The ionization energy to form Na⁺ is 5.1 eV.
- ◆ Chlorine, has an electronic configuration
- ◆ For chlorine, the electron affinity is 3.6 eV.
- ◆ Therefore, an energy equal to $5.1 - 3.6 = 1.5$ eV must be provided to neutral Na and Cl to change them to Na⁺ and Cl⁻ ions at infinite separation.



Total energy versus internuclear separation

- ◆ *The total energy of the molecule has a minimum value of -4.2 eV at the equilibrium separation, which is about 0.24 nm.*
- ◆ *Dissociation energy is 4.2 eV.*



Covalent Bonds

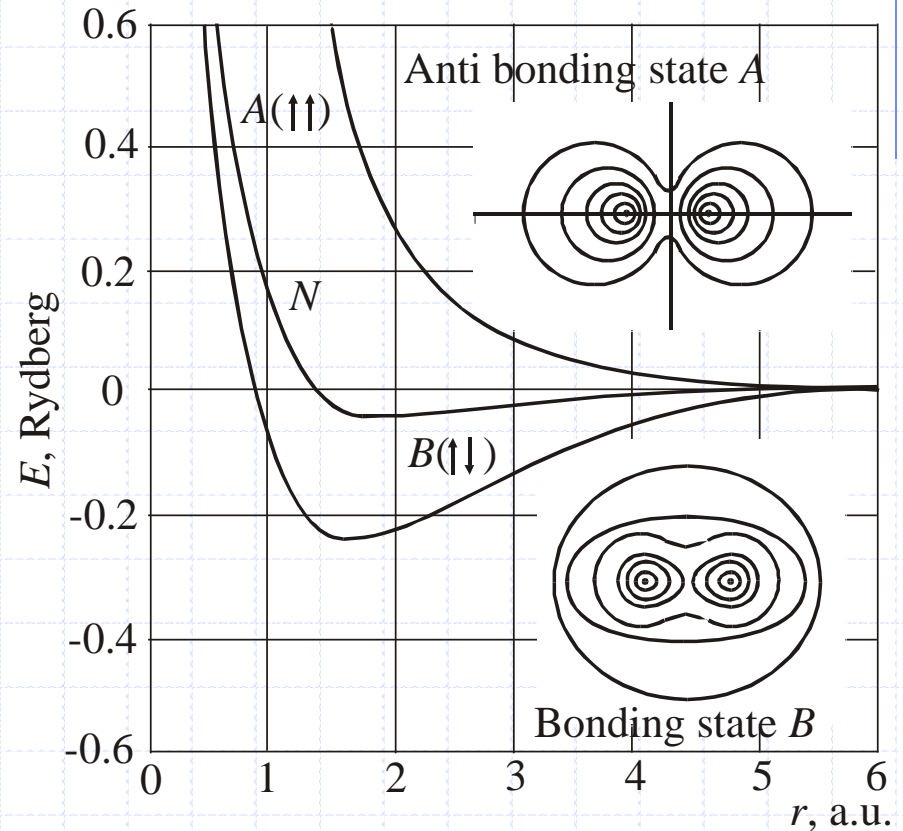
- ◆ A covalent bond between two atoms in a molecule can be visualized as the sharing of electrons supplied by one or both atoms.
- ◆ In the case of the H_2 molecule, the two electrons are equally shared between the nuclei and occupy *molecular orbital*.
- ◆ When the atoms are brought together, the interaction between them splits the $1s$ -state into two states with different energies.
 σ_g (bonding) molecular orbital is build up as the result of summation of $1s$ -orbitals. σ_u (anti-bonding) molecular orbital is build up as the result of subtraction $1s$ -orbitals. In a molecule H_2 , both electrons having the anti-parallel spins are in σ_g -state and build the strong bond.
- ◆ Because of the exclusion principle, the two electrons in the ground state of H_2 must have opposite spins.

Energy of H₂ molecule versus internuclear separation

◆ *Curve N is theoretical calculation. In state A (antibonding) electrons have parallel spins. In state B (bonding) electrons have opposite spins. Distributions of the charge densities are shown by the outlines.*

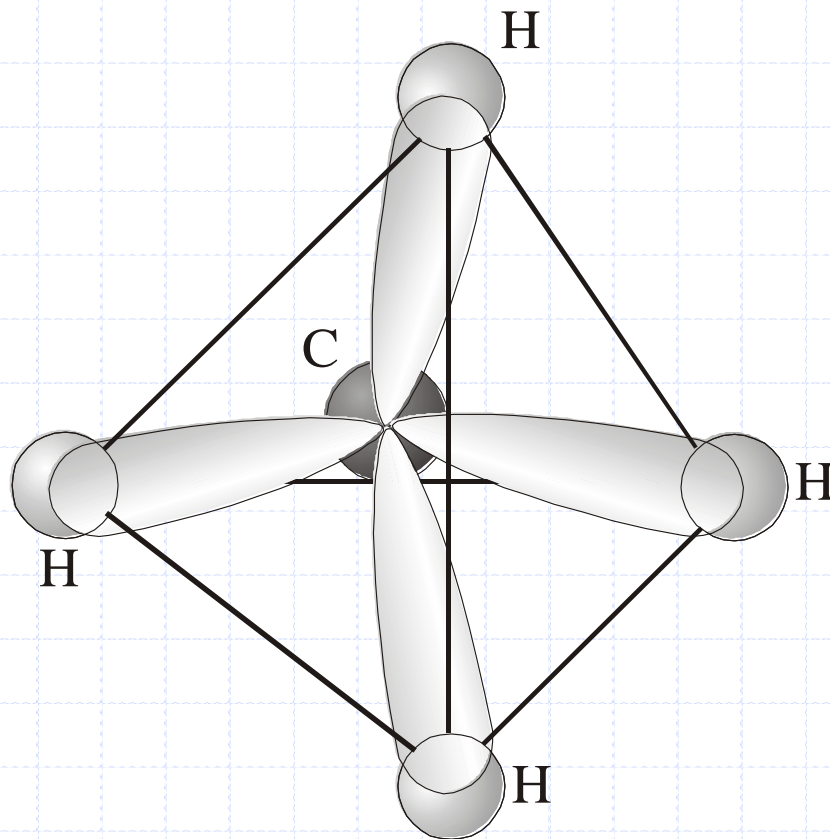
1 a.u. = 0.53 Å.

1 Rydberg = 13.6 eV.



Bonds in the CH₄ molecule

- ◆ *A schematic representation of the angular dependence of four covalent bonds in the CH₄ molecule. The carbon atom is at the center of a tetrahedron having hydrogen atoms at its corners.*



The Energy and Spectra of Molecules

- ◆ The energy of molecule to be divided into four categories:
 - ◆ (1) electronic energy (E_{el});
 - ◆ (2) translational energy (E_{trans});
 - ◆ (3) rotational energy (E_{rot});
 - ◆ (4) vibrational energy (E_{vib}).

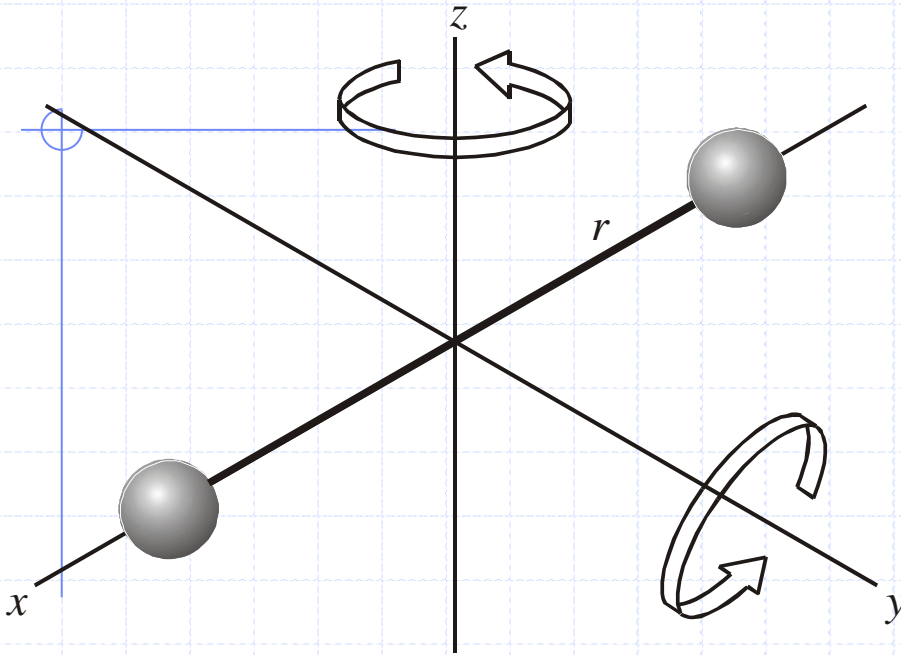
Total energy of the molecule

- ◆ the total energy of the molecule is

$$**E = E_{el} + E_{trans} + E_{rot} + E_{vib}**$$

- ◆ The electronic energy of a molecule is very complex because it involves the interaction of many charged particles.
- ◆ The translational energy is unrelated to internal structure, hence this molecular energy is unimportant in interpreting molecular spectra.

Rotational Motion of a Molecule



(a)

$$E_{rot} = \frac{1}{2} I \omega^2$$

$$I = \left(\frac{m_1 m_2}{m_1 + m_2} \right) r^2 = \mu r^2$$

I is the moment of inertia

r is the atomic separation

μ is the reduced mass of the molecule

- ◆ **A diatomic molecule oriented along the x axis has two rotational degrees of freedom, corresponding to rotation around the y and z axes.**

angular momentum

- ◆ Quantum mechanics restricts angular momentum values to multiples of \hbar :

$$I\omega = \sqrt{J(J+1)}\hbar$$

where J is an integer called the *rotational quantum number*,

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

the allowed values of the rotational kinetic energy

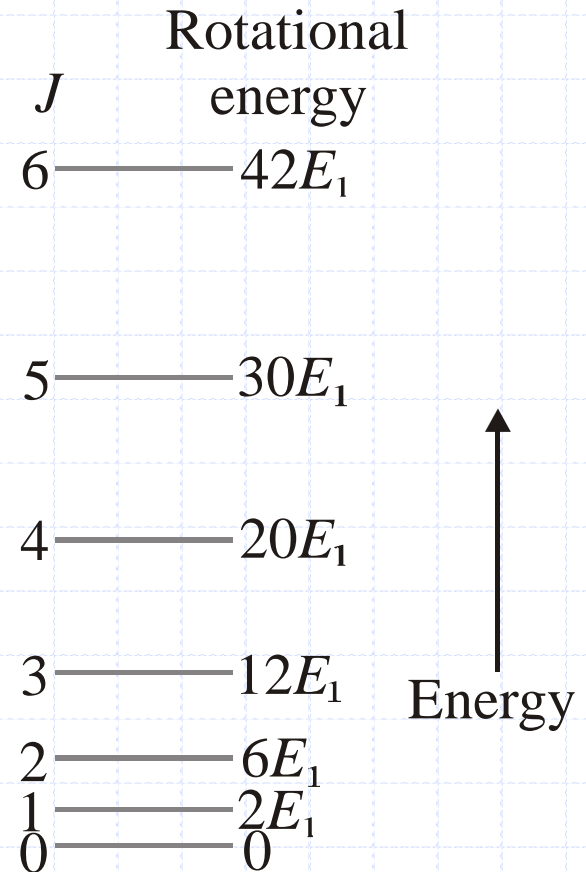
$$E_{rot} = \frac{1}{2} I \omega^2 = \frac{1}{2I} (I\omega)^2 = \frac{(\sqrt{J(J+1)\hbar})^2}{2I}$$

$$E_{rot} = \frac{\hbar^2}{2I} J(J+1) \quad J = 0, 1, 2, \dots$$

- ◆ *the rotational energy of the molecule is quantized and depend on its moment of inertia*

The allowed rotational energies of a diatomic molecule

- ◆ The spacing between adjacent rotational energy levels of most molecules lies in the microwave range of frequencies ($f \approx 10^{11}$ Hz) or far infrared.
- ◆ The allowed rotational transitions of linear molecules are regulated by the selection rule $\Delta J = \pm 1$.



(b)

Energy of transition

◆ the allowed transitions are given by the condition

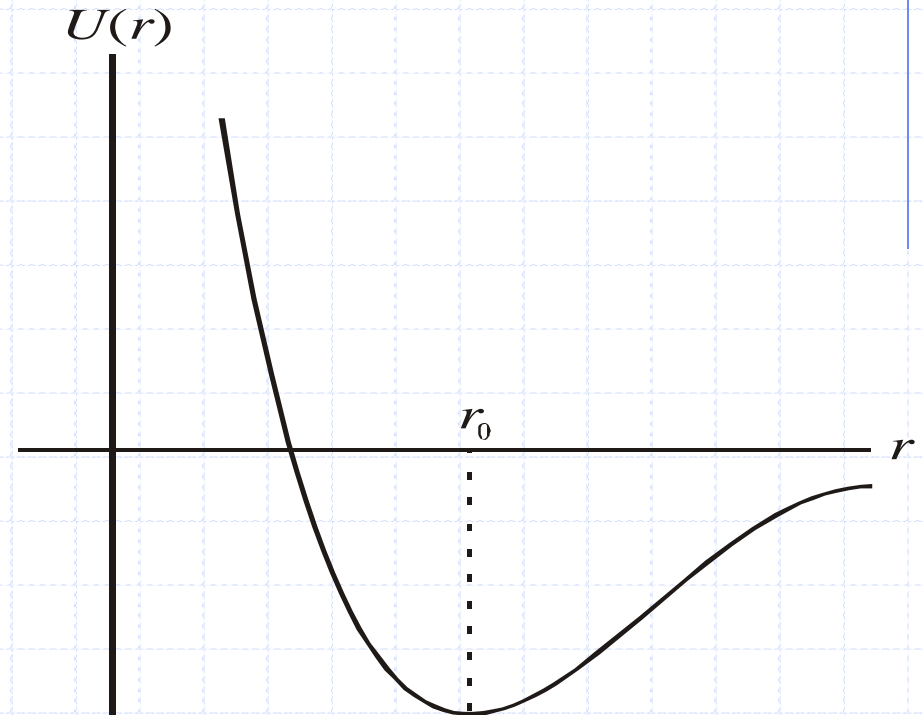
$$\Delta E = E_J - E_{J-1} = \frac{\hbar^2}{2I} [J(J+1) - (J-1)] = \frac{\hbar^2}{I} J = \frac{h^2}{4\pi^2 I} J$$

Because $\Delta E = hf$, where f is the frequency of the absorbed microwave photon, the allowed frequency for the transition $J = 0$ to $J = 1$ is

$$f_1 = \frac{h^2}{4\pi^2 I}$$

Vibrational motion of molecules

- ◆ A molecule is a flexible structure in which the atoms are bonded together. If disturbed, the molecule can vibrate and acquire vibrational energy.



The fundamental vibration is along the molecular axis.

The classical frequency of vibration is

$$f = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

μ is the reduced mass, k is a force constant. *The vibrational energy of the molecule is quantized*

$$E_{vib} = \left(\nu + \frac{1}{2}\right)hf, \quad \nu = 0, 1, 2, \dots$$

• ν is an integer called the *vibrational quantum number*, $\nu = 0, 1, 2, \dots$

If the system is in the lowest vibrational state, for which $\nu = 0$, its zero-point energy is $(1/2)hf$. The accompanying vibration - zero-point motion - is always present, even if a molecule is not excited. In the first excited state, $\nu = 1$ and the vibrational energy is $(3/2)hf$ and so on.

the vibrational energy is

$$E_{\nu ib} = \left(\nu + \frac{1}{2}\right) \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} \quad \nu = 0, 1, 2, \dots$$

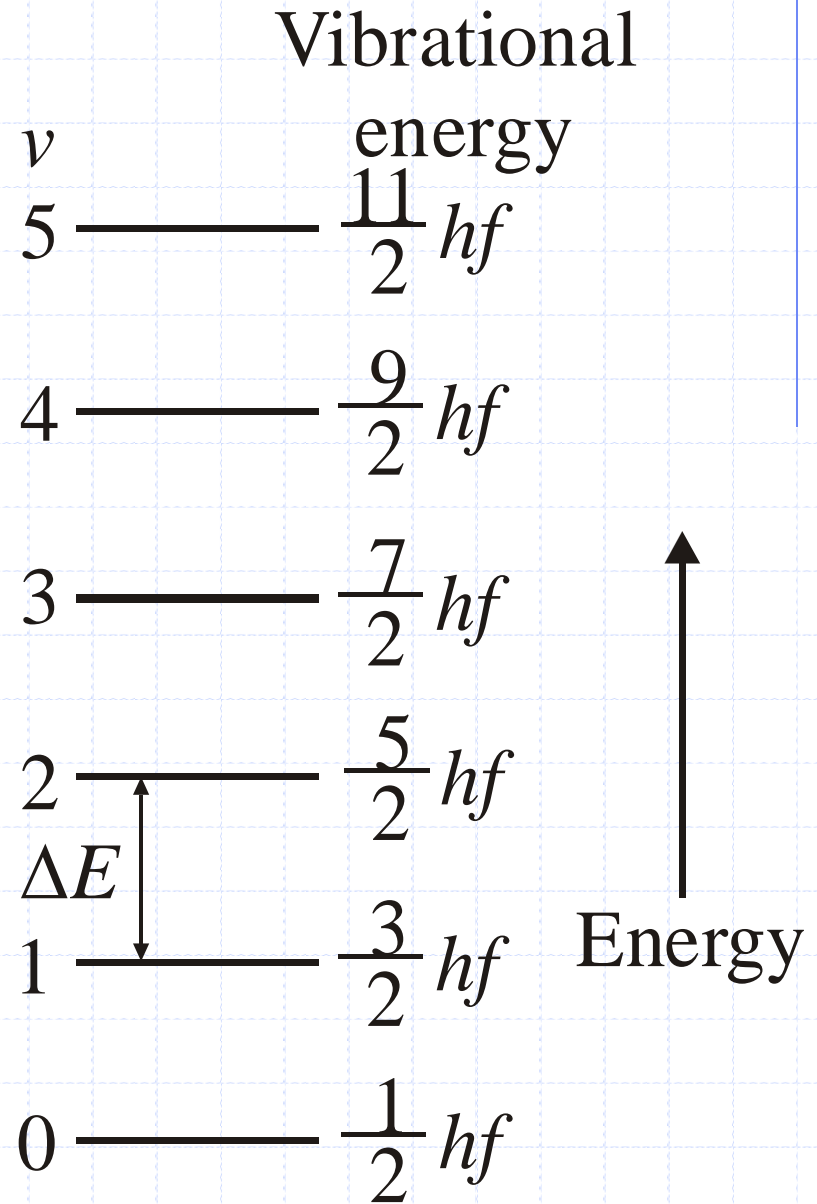
The selection rule for the allowed vibrational transitions is $\Delta v = \pm 1$.

the energy difference between any two successive vibrational levels is

$$\Delta E_{vib} = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} = hf$$

◆ Allowed vibrational energies of a diatomic molecule, where f is the fundamental frequency of vibration

◆ Transitions between vibrational levels lie in the *infrared region* of the spectrum.



Molecular Spectra

An excited molecule rotates and vibrates simultaneously. At the first approximation, these motions are independent, and so the total energy of the molecule is

$$E = \frac{\hbar^2}{2I} [J(J + 1) + (\nu + \frac{1}{2})hf]$$

Energy levels can be calculated from this expression, and each level is indexed by quantum numbers, J and ν .