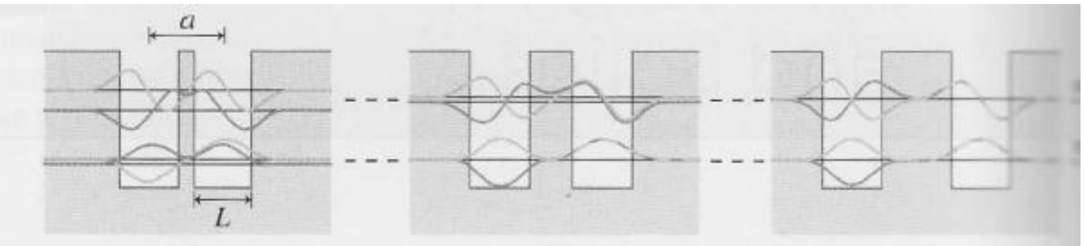
PH102, 2014W, Lecture Notes: February 11, Tues, Class 11
Molecules, Rotation, and Vibration

Molecular Bonding

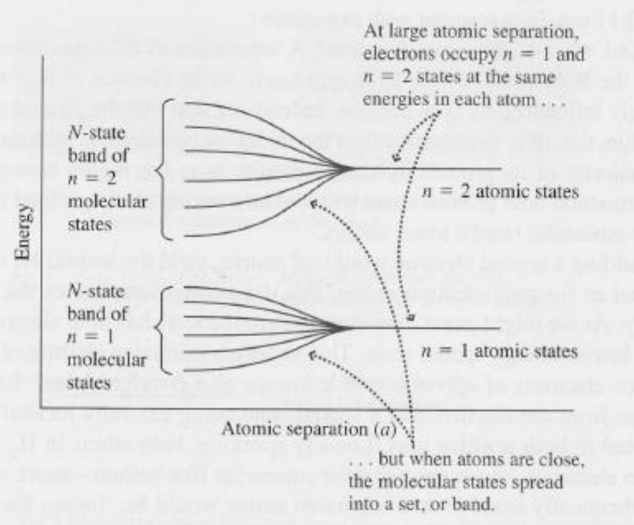
- It is impossible to solve the Schrodinger equation for multi-atom bonding cases. Approximations and qualitative judgments that agree with experimental results are needed to approach the multi-atom bonding situations.
- Two approaches
  - Valence-bond approach: Each shared pair of electrons is represented either by two dots or by a dash between the atoms bonded by them. A molecule consists of individual atoms held together by covalent bonds. Each covalent bond consists of two electrons of opposite spins, each electron is provided by an atom in the molecule. Electrons from each atom in the molecule can be available according to the Hund's rule where electrons in an atom have parallel spin arrangements which are more stable. E.g. H-H, O=O, N≡N
  - Molecular orbital approach: A molecule is regarded as a single entity and outmost electrons of the molecule participate in bonding atoms together. Orbitals belong to the entire molecule rather than individual atoms. Atoms are held together in a molecule because electrons' charge distribution is concentrated between the atomic nuclei. Such bond is called covalent bond where electrons have opposite spins allowing spatial part of the wave functions of electrons to be centrally located so that they can be attracted by positive charges of both nuclei.
  - In both approaches, only the valence electrons are considered to participate in bonding because (1) inner electrons are more tightly bound to the nuclei and thus less responsive and (2) repulsive force between atoms becomes predominant at the region where inner electrons mostly reside.

Atoms Come Close to One Another

- A model using two finite potential wells, each of which approximately represents a potential of an atom that an electron experiences



- When N atoms get close enough, each atomic energy level will split into multiple (N) molecular energy levels for an electron to occupy.

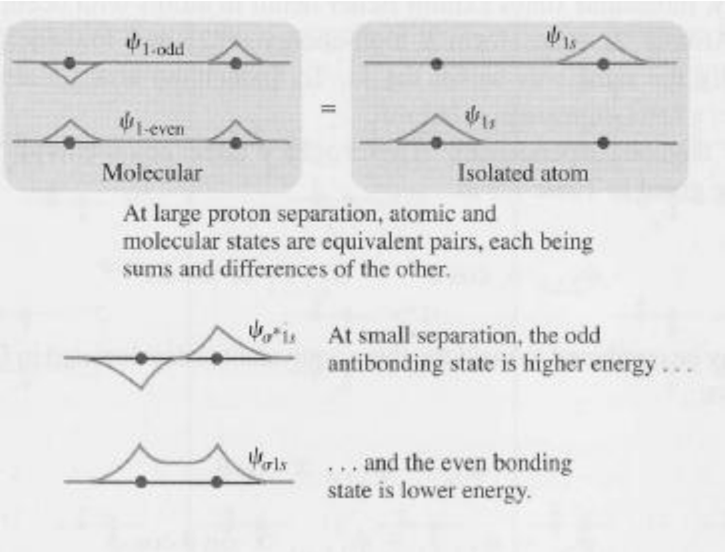


At large atomic separation, electrons occupy $n = 1$ and $n = 2$ states at the same energies in each atom . . .

. . . but when atoms are close, the molecular states spread into a set, or band.

Molecules

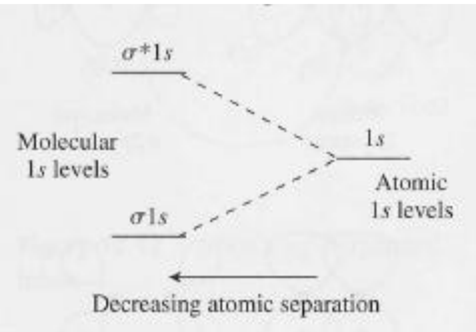
- Atoms form molecules when the molecular state is of lower energy than the separated atoms.
- Electrons can be shared by both atoms in two ways:
  - Bonding state: this lowers energy from the individual atomic energy state
  - Antibonding state: this increases energy from the individual atomic energy state



At large proton separation, atomic and molecular states are equivalent pairs, each being sums and differences of the other.

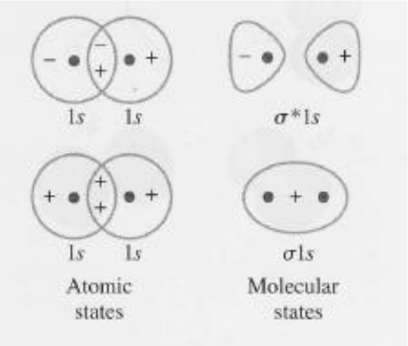
At small separation, the odd antibonding state is higher energy . . .

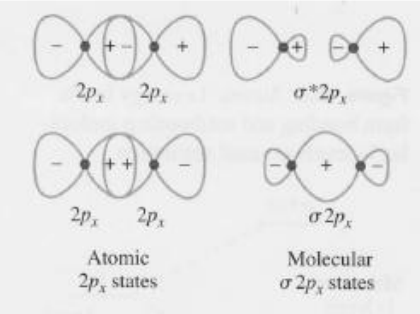
. . . and the even bonding state is lower energy.

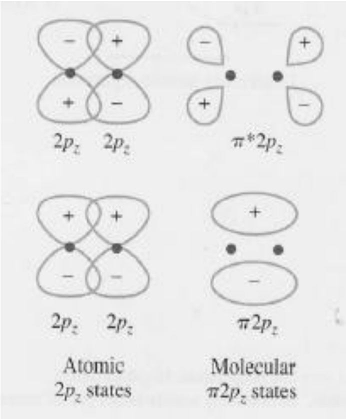


- There are different types of molecular orbitals:
  - Sigma orbital (σ): charge density is largest along the molecular axis
    - two 1s orbitals bonding/antibonding → $\sigma 1s$ / $\sigma^* 1s$
    - Two $p_x$orbitals bonding/antibonding (when x is the molecular axis) → $\sigma 2p_x / \sigma^* 2p_x$
  - Pi orbital (π): charge density is largest off the molecular axis
    - off axis p_y orbitals bond/antibond →$\pi 2p_y$/ $\pi^* 2p_y$

- When bonding/anti-bonding states are created for molecular orbitals, atomic orbitals that are orthogonal to each other do not form bonding/anti-bonding molecular orbitals. That is no bonding/antibonding between $p_x$and p_y; $p_y$and p_z; $p_x$and p_z.







- In the molecular orbital approach, we use orbitals created by bonding and antibonding states of atomic orbitals to arrange electrons.

Figure 10.7 Filling of the 1*s* levels in molecular hydrogen and helium.

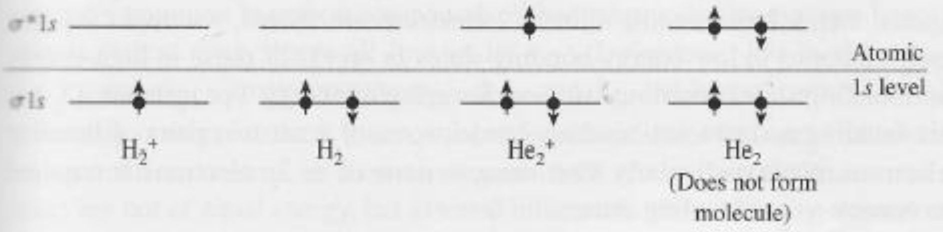
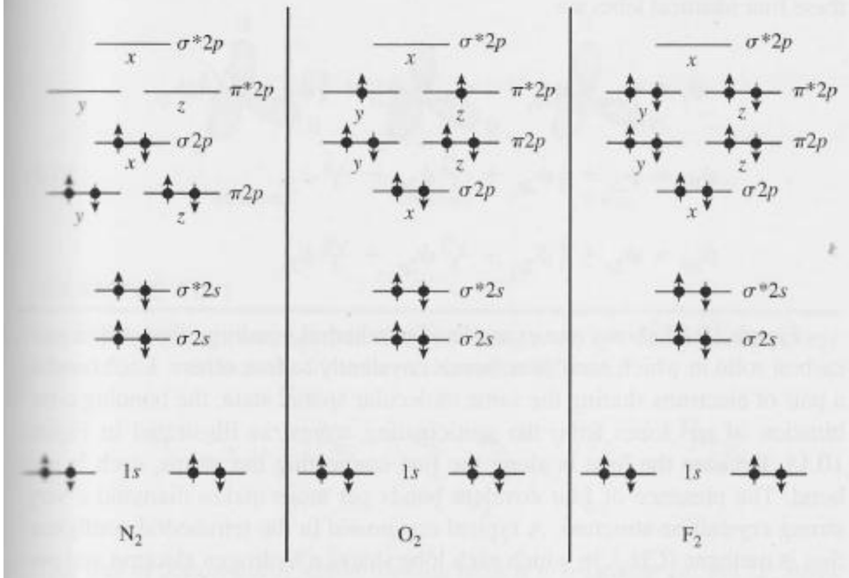
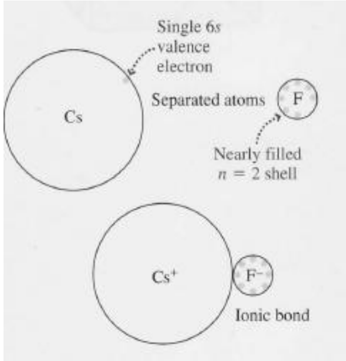


Figure 10.10 Molecular energy levels in nitrogen, oxygen, and fluorine.



  - Inner electrons (1s electrons) are confined to atomic orbitals.
  - The ordering of molecular orbitals varies from element to element.
  - Electrons spread over the degenerate molecular orbitals when possible.
  - Net bonds = ½ (the number of electrons in bonding states – that of electrons in anti-bonding states).
  - The net lowering of energy is contributed by the electrons in the bonding states in excess of those in the antibonding states. Therefore, N_2 is stable than O_2 or F_2.
- Diatomic molecules do not have electric dipole moment because they are symmetric. However, molecules consisting of two different elements can create asymmetric distribution of electric charges, creating polar covalent bonds.

- Ionic Bond occurs when an atom grabs an electron from the other atom and the bond between the two atoms is due to Coulomb interactions.



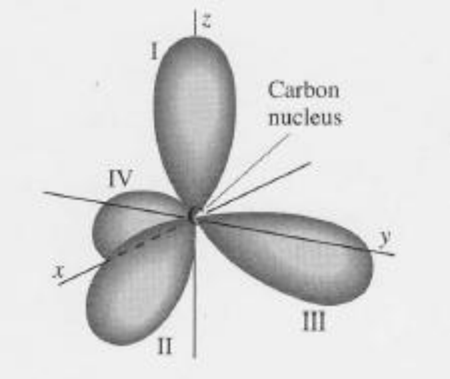
- Hybridized orbital-sp^3: Carbon sometimes share all four n=2 electrons with other atoms creating sp^3 hybridized orbital with the following geometry:

$$\psi_I = \psi_{2s} - \psi_{2p_z}$$

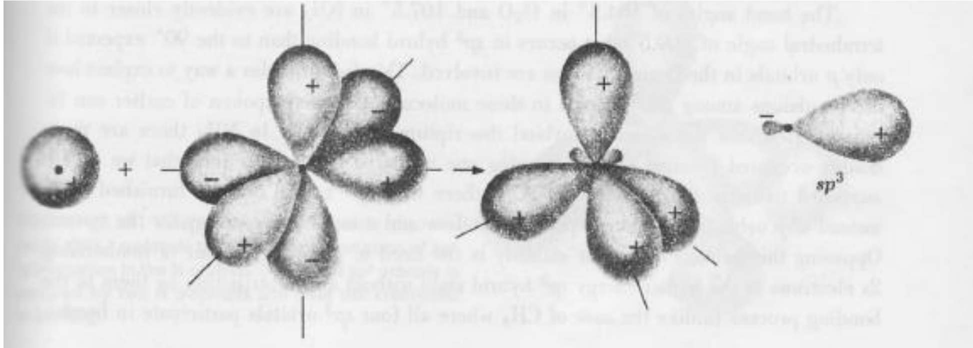
$$\psi_{II} = \psi_{2s} + \frac{1}{3}\psi_{2p_z} - \frac{\sqrt{8}}{3}\psi_{2p_z}$$

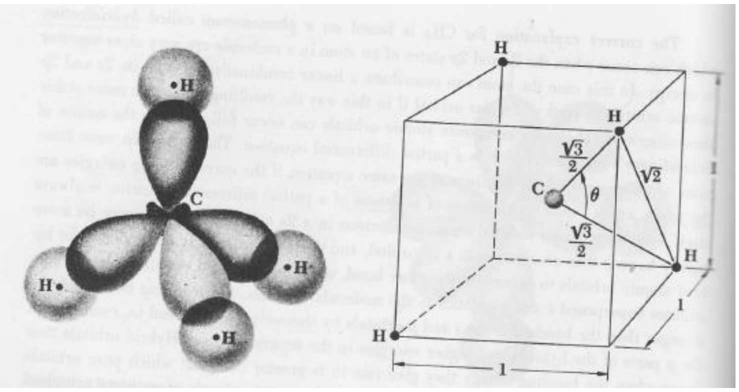
$$\psi_{III} = \psi_{2s} + \frac{1}{3}\psi_{2p_z} + \frac{\sqrt{2}}{3}\psi_{2p_x} - \frac{\sqrt{6}}{3}\psi_{2p_y}$$

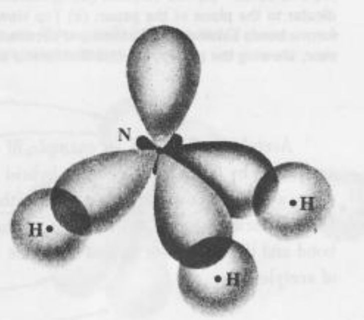
$$\psi_{IV} = \psi_{2s} + \frac{1}{3}\psi_{2p_z} + \frac{\sqrt{2}}{3}\psi_{2p_x} + \frac{\sqrt{6}}{3}\psi_{2p_y}$$



These four lobes are available for σ bonding between electrons. Diamond has this structure, resulting in a very strong structure.

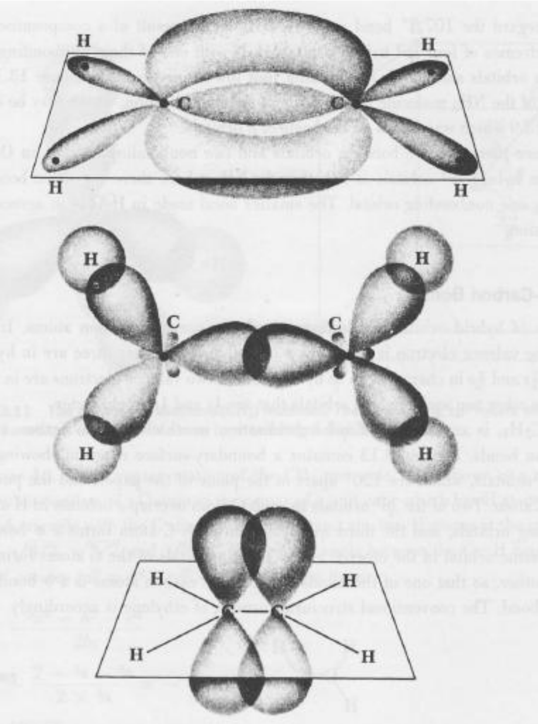






$$\theta = 109.5\,°$$

- Hybridized orbital-sp^2 can be seen in C_2H_4. The sp2 orbital is placed on a plane and have 120 degrees between two lobes. p_z orbital is perpendicular to the plane.



$$\psi_I = \psi_{2s} + \sqrt{2}\psi_{2p_x}$$

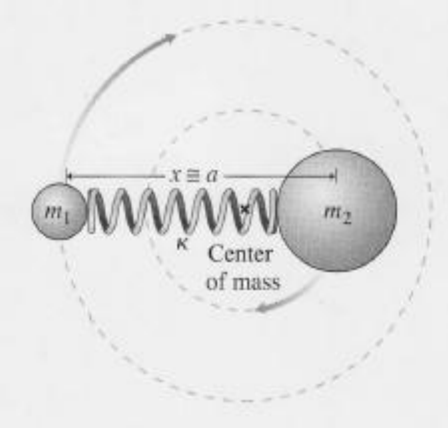
$$\psi_{II} = \psi_{2s} - \sqrt{\frac{1}{2}}\psi_{2p_x} + \sqrt{\frac{3}{2}}\psi_{2p_y}$$

$$\psi_{II} = \psi_{2s} - \sqrt{\frac{1}{2}}\psi_{2p_x} - \sqrt{\frac{3}{2}}\psi_{2p_y}$$

Diatomic Molecules

Molecules have three different energy sources:

- Energy levels electrons occupy in their molecular orbitals
- Rotations at the order of 0.001 eV
- Vibrations at the order of 0.1 eV



Consider a diatomic molecule such as HF as shown in the diagram on the right. Two atoms with mass $m_1 and\ m_2$ are connected through a bond. The distance between the two masses is a. Two atoms rotate around their center of mass. Consider $r_1$as the distance between the center of mass and m_1 and $r_2$as the distance between the center of mass and m_2, so that $a = r_1 + r_2$. The moment of inertia of this molecule along the axis through its center of mass can be written as

$$I = m_1 r_1^2 + m_2 r_2^2 \text{ and } m_1 r_1 = m_2 r_2$$

We can rewrite

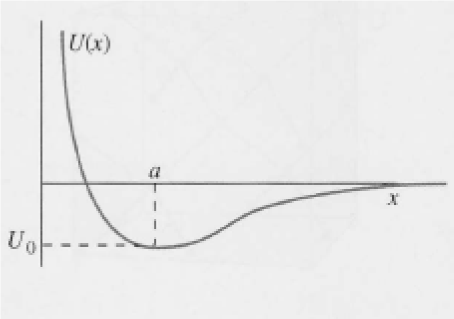
$$I = \left(\frac{m_1 m_2}{m_1 + m_2}\right)(r_1 + r_2)^2 = \mu a^2$$

We call

$$\left(\frac{m_1 m_2}{m_1 + m_2}\right) \equiv \mu \text{ (Reduced mass)}$$

If $m_2 \gg m_1$, μ becomes simply m_1.

The potential energy in a diatomic molecule looks like the figure on the right. The equilibrium separation is represented as a and when the two atoms are separated by larger than a, the potential energy increases. At a very large separation, the two atoms become individual atoms thus no potential exists between the two. When the two atoms are brought together closer than a then the potential energy will increase steeply because of (1) the increase in repulsive energy between the two nuclei and (2) the increase in molecular orbital energy levels as non-valence electrons get closer to occupy the molecular orbital energy levels.



A diatomic molecule will have two energy parts = energy due to vibration from the equilibrium separation + energy due to rotation of the whole molecule

Since the vibration energy term can be approximated to a harmonic oscillator and the rotation energy term can be approximated to energy due to an angular momentum along its rotational axis, we can write

$$E_{n(vib),l(rot)} = E_{vib} + E_{rot} = \hbar\left(n + \frac{1}{2}\right)\sqrt{\frac{k}{\mu}} + \frac{\hbar^2 l(l+1)}{2\mu a^2}$$

$$\text{where} \begin{cases} n = 0, 1, 2 \ldots \\ l = 0, 1, 2 \ldots \\ m_l = 0, \pm 1, \ldots \pm l \end{cases}$$

Estimate the temperature where the rotational energy is 1/10 of the vibration energy of the HD molecule.

$$\frac{1}{10} = \frac{No.\ of\ molecules\ with\ energy\ E_{01}}{No. of\ molecules\ with\ energy\ E_{00}} = \frac{3e^{-E_{01}/k_BT}}{e^{-E_{00}/k_BT}} = 3e^{-(E_{01}-E_{00})/k_BT}$$

$$E_{01} - E_{00} = \frac{\hbar^2}{2\mu a^2}(1\text{x}2 - 0\text{x}1) = \frac{\hbar^2}{\mu a^2}$$

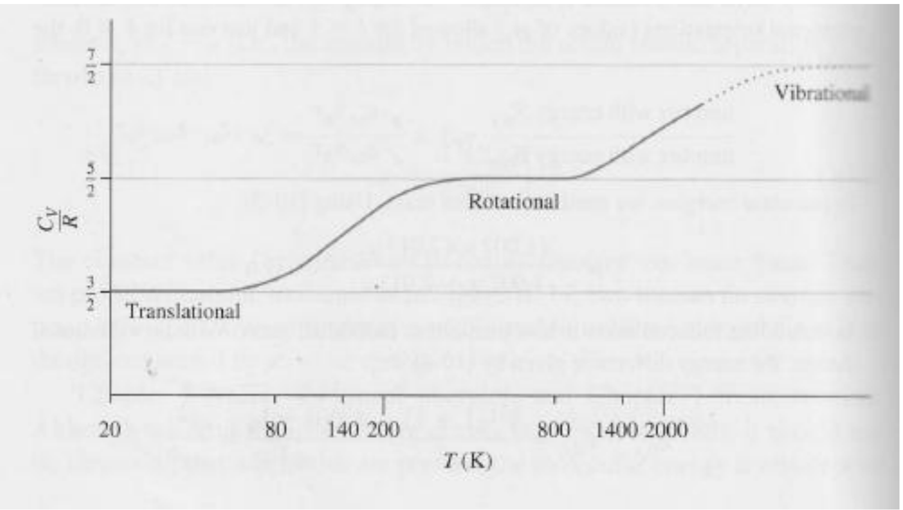
Since

$$\left(\frac{m_1 m_2}{m_1 + m_2}\right) \equiv \mu = \frac{(1.007u)(2.013u)}{1.007u + 2.013u} = 0.671u$$

$$E_{01} - E_{00} = 0.011eV$$

This gives $T = 40K$

This means that rotation does not occur to molecules until the temperature reaches at least 40 degrees K for the HD molecule. This can be seen in the graph below that shows the heat capacity of the hydrogen molecule over temperature. Note that rotational energy begins to contribute to heat capacity around 70 degrees K.



So far we assumed that the rotation and vibration energies are quantized based on our prior results on the atomic spectra. If this is the case, the evidence of quantization can be seen in molecular spectra. Photons released from diatomic molecules should carry the difference between the higher and the lower energy levels. The selection rule for molecular spectra:

- Vibration: $\Delta n = \pm 1$ electromagnetic radiation can be more effectively emitted from electric dipoles. Though stationary molecules may not emit electromagnetic radiation, when vibrating molecules change oscillating states, they can temporarily become dipoles.

- Rotation: $\Delta l = \pm 1$ since photons spin number is 1.

Therefore, photons can carry the following energy

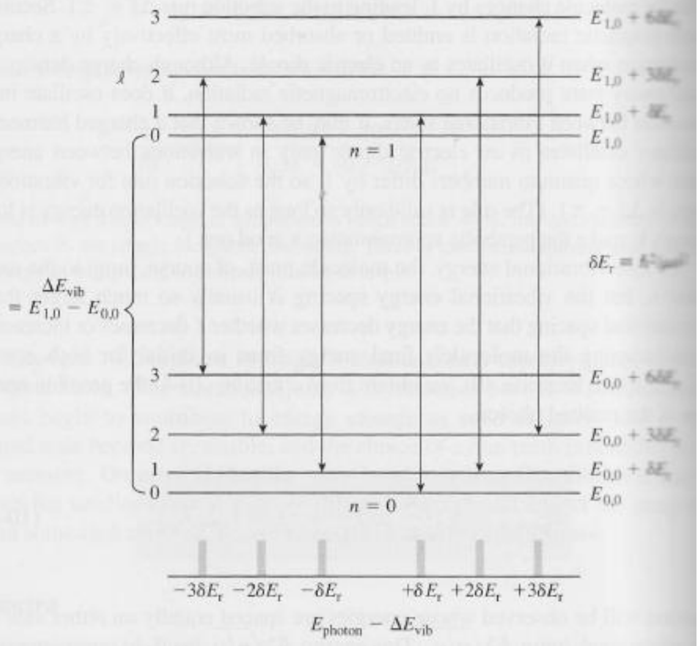
$$E_{higher} - E_{lower} = E_{n,l} - E_{n-1,l\pm1}$$

$$= \hbar\sqrt{\frac{k}{\mu}} \pm \frac{\hbar^2}{\mu a^2} I$$

Where $I = 1,2,3\ ...$

The diagram shows vibrational and rotational energy levels and how photons can be produced when molecules transition from a higher energy state to a lower energy state.

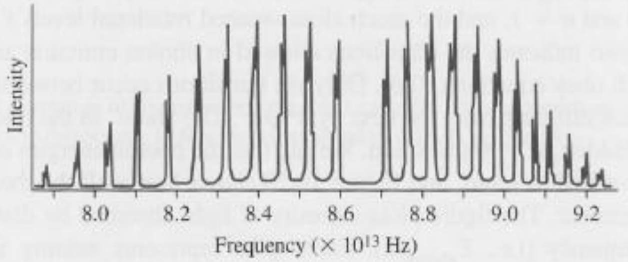
Figure 10.19 Vibrational and rotational energy levels, and photon-producing transitions between them, restricted by selection rules, $\Delta n = \pm 1$ and $\Delta \ell = \pm$



Photons associated with $\hbar\sqrt{\frac{k}{\mu}}$ do not exist in the molecular spectra because the transition between $E_{n,l=0}$and $E_{n,l=0}$ is not allowed.

The absorption spectral of the HCL molecule shows the spikes associated with transitions allowed within rotation+ vibration molecular energy levels.

Figure 10.20 Vibration/rotation absorption spectrum of HCl. The "hole" in the middle is due to the forbidden $\Delta \ell = 0$ transition.



The molecular energy levels due to rotation and vibration can be drawn in the diagram on the right. The potential changes as a diatomic molecule becomes more energetic (excited) due to increase in vibrational motions. Note that when the equilibrium separation (*a*) increases, the potential is situated at a higher energy level. At the same time, the potential becomes wider and shallower. In each potential, vibrational energy levels, *n*, can be drawn, In each vibrational energy level, rotational energy will further increase the energy levels depending upon *l*.

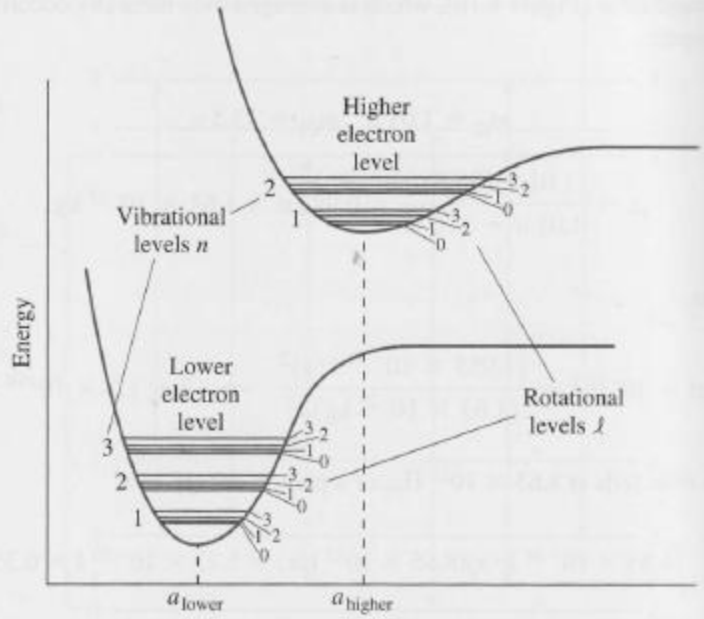


Figure 10.21 Molecular vibrational and rotational levels for two different electron levels.