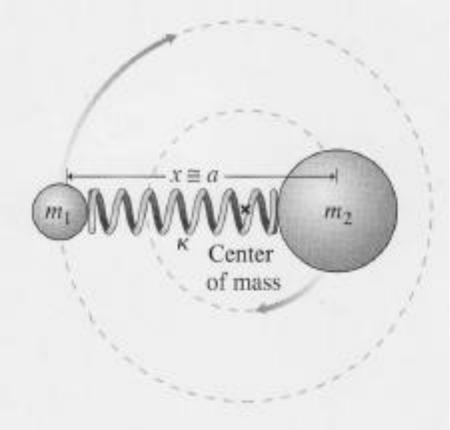
PH102, 2012W, Lecture Notes: February 15, Wed, Class 15

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

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

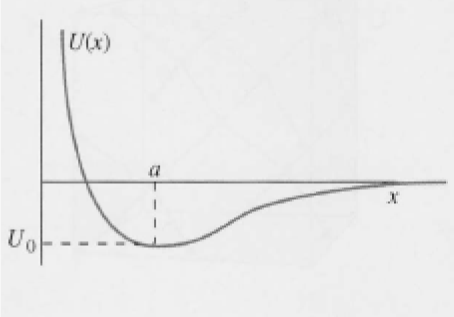
We can rewrite

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

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.

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

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

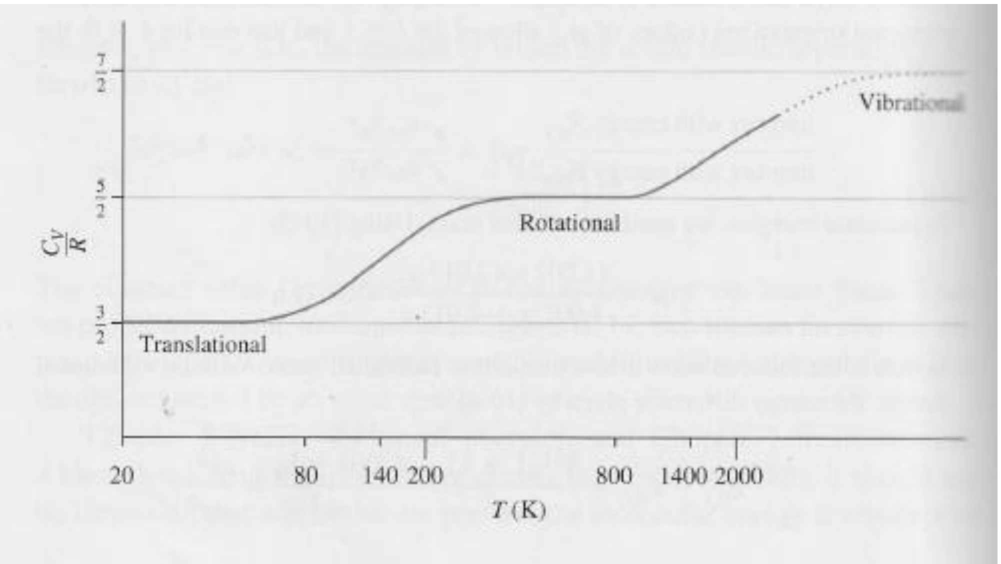
Since

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

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

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

$$E_{higher} - E_{lower} = E_{n,l} - E_{n-1,l\pm 1} = \hbar\sqrt{\frac{k}{\mu}} \pm \frac{\hbar^2}{\mu a^2} I$$

Where $i = 1,2,3 \ldots$

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.

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

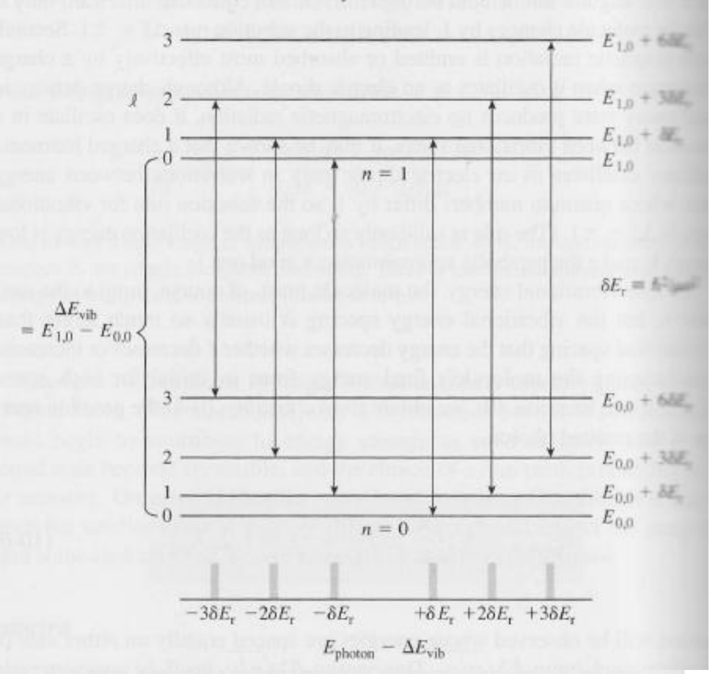
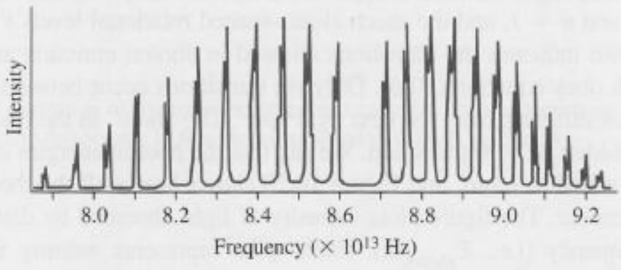
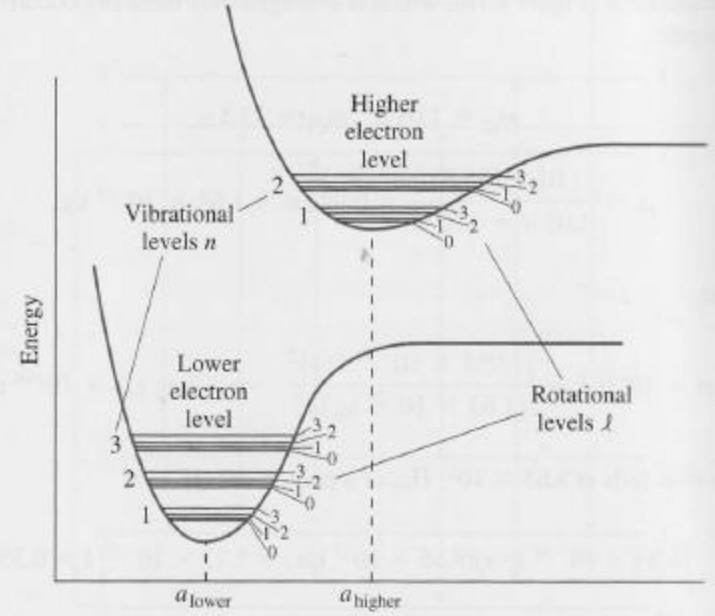


Figure 10.20 Vibration/rotation absorption spectrum of HCl. The "hole" in the middle is due to the forbidden $\Delta \ell = 0$ transition.



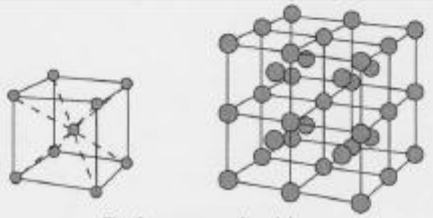
The molecular energy levels due to rotation and vibration can be drawn in the diagram on the right. The potential changes as a diatomic molecule becomes more energetic (excited) due to increase in vibrational motions. Note that when the equilibrium separation (*a*) increases, the potential is situated 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*.

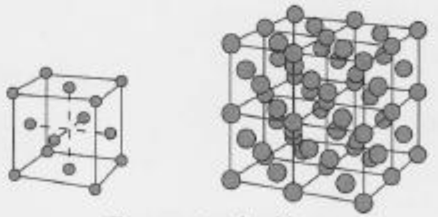
Figure 10.21 Molecular vibrational and rotational levels for two different electron levels.

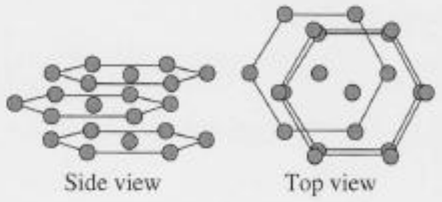


Crystalline Solids

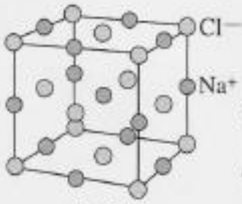
- A large number of atoms are bonded together to create structures of macroscopic scale.
- Crystal lattice is defined as "a structural unit that repeats to fill space without gap and without overlap."
- To fill three dimensional space, there are only 14 possible lattice types, some of which are shown below.


Body-centered cubic
(bcc)

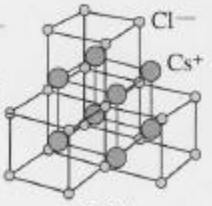

Face-centered cubic
(fcc)


Side view Top view

Hexagonal closest packed
(hcp)



NaCl
(fcc)



CsCl
Simple cubic
(sc)

Another way of categorizing solids is to use what type of bonding is involved in solids:

- **Molecular solid** is formed by the Van der Waals force between molecules due to fluctuations that create instantaneous dipole moments for molecules to form weak bonds. Molecules with permanent dipole moments such as water can form a stronger bond among molecules than those with no permanent dipole moments.
- **Ionic solid** is formed by the Coulomb force between positively and negatively charged ions. Ionic solid is relatively hard with high melting points. It is a poor conductor because electrons are not free. Ionic bond lacks directionality. Ionic solid does not form among elements.
- **Covalent solid** is formed by sharing electrons through covalent bonds. The crystalline lattice is strong, has high melting points, and assumes a geometry determined by the directionality of the covalent bonds. It is a poor conductor because all electrons are locked into the covalent bonds. It is not malleable.
- **Metallic solid** forms through sharing electrons by all ions and electrons are free to move around within the solid. Therefore, metallic solid is a good conductor and it is malleable. Metallic solid forms a lattice structure, but not as strong as a lattice structure formed by covalent bonds.