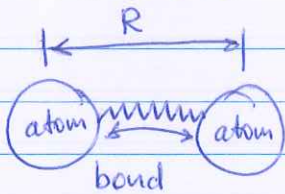


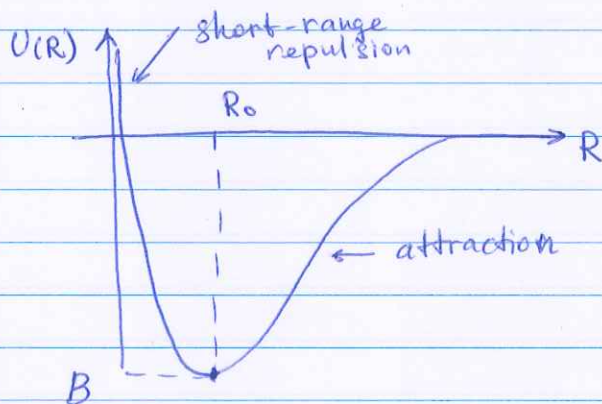
## Molecular spectra

Previously, we concentrated on electron energy states, considering a heavy nucleus stationary (no energy)

While electrons can be excited in molecules, for a ~~moment~~ now we will assume that electrons are in their lowest energy state (ground state), and concentrate on energy associated with the motion of atoms as wholes.



To form a molecule, there must be mutual attraction b/w the atoms (i.e. attractive force, i.e., reduction in potential energy)



$R_0$  - average distance b/w the atoms

$B = U(R_0)$  - minimum energy binding energy

## Molecular degrees of freedom

→ translational motion (kinetic)

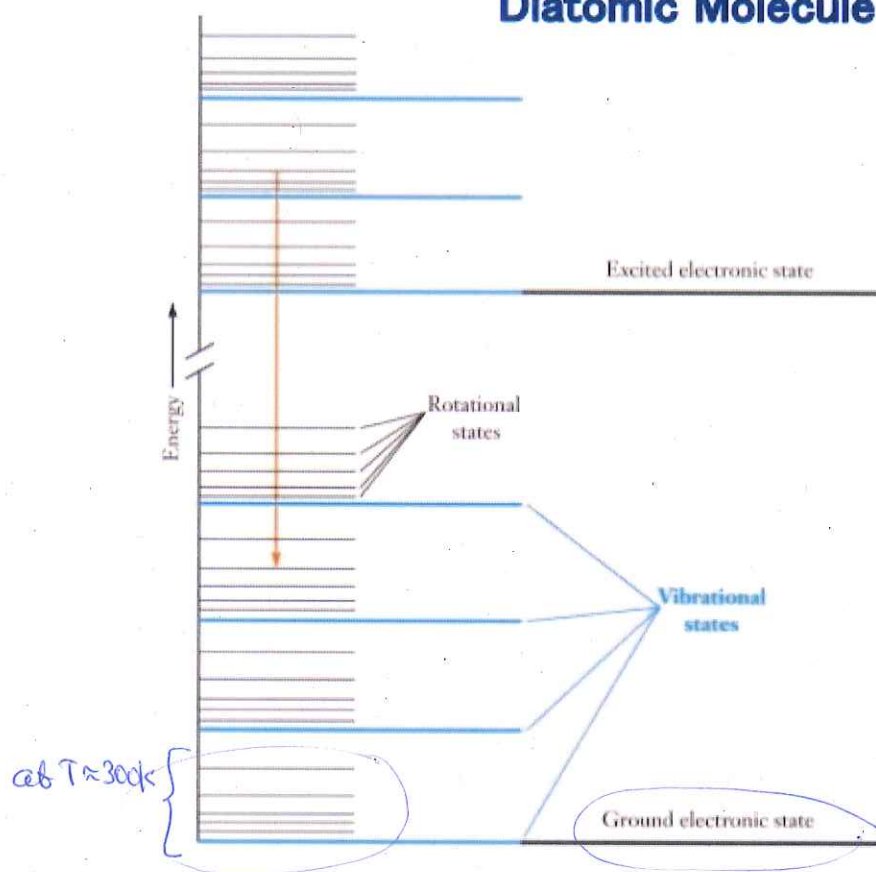
$$E_{\text{trans}} = \frac{1}{2} Mv^2 - \text{not quantum}$$

$$E_{\text{trans}} \sim 0.03 \text{ eV (typically)}$$

→ vibration } quantized

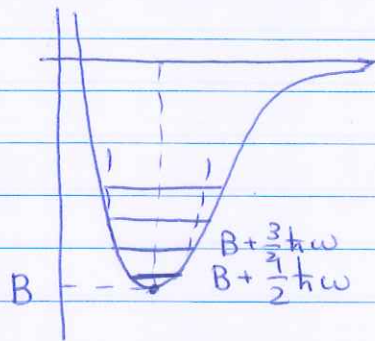
→ rotation } quantized

# Electronic, Vibrational, and Rotational Energy Levels of a Diatomic Molecule



**Exercise:** Indicate the molecular state in which it is electronically in the ground state, vibrationally in the first excited state, and rotationally in the ground state.

Molecular vibrations — relative motion of atoms around equilibrium position ( $R=R_0$ )



We can approximate the potential energy there using a harmonic potential

$$U(R) = U(R_0) + \frac{1}{2} \left. \frac{\partial^2 U}{\partial R^2} \right|_{R=R_0} \cdot (R-R_0)^2$$

Simple harmonic oscillator  $\omega = \sqrt{\left. \frac{\partial^2 U}{\partial R^2} \right|_{R=R_0} \cdot \frac{1}{\mu}}$   
 where  $\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$  reduced mass

$$E_{\text{vib}} = \hbar\omega \left( \nu + \frac{1}{2} \right) \quad \nu - \text{vibrational quantum number}$$

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

Equidistant energy spectrum!

Typical values of  $\hbar\omega \approx 0.1 - 0.3 \text{ eV}$   
 larger than the thermal energy ( $0.03 \text{ eV}$ )  
 At room temperature typically only the ground vibrational state is populated.

More realistic potential  $U(R) = B + D(1 - e^{-a(R-R_0)})^2$   
 Morse potential

if  $|R-R_0| \ll \frac{1}{a} \rightarrow U_{\text{Morse}}(R) \approx Da^2(R-R_0)^2$   
 $\omega = \sqrt{2Da^2/\mu}$

Next correction

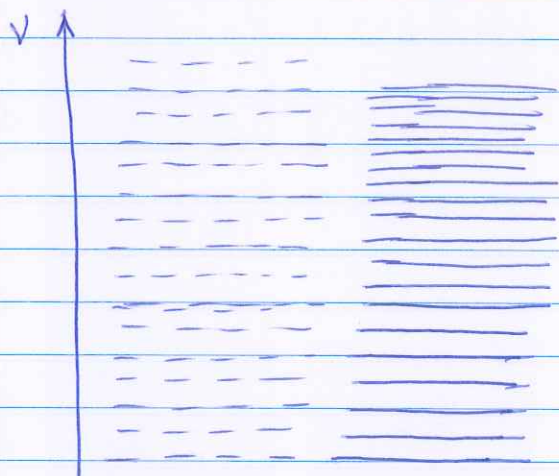
$$U_{\text{Morse}}(R) \approx Da^2(R-R_0)^2 - Da^3(R-R_0)^3$$

we can use the wavefunctions describing a simple harmonic oscillator, and then find a corrections to the energies

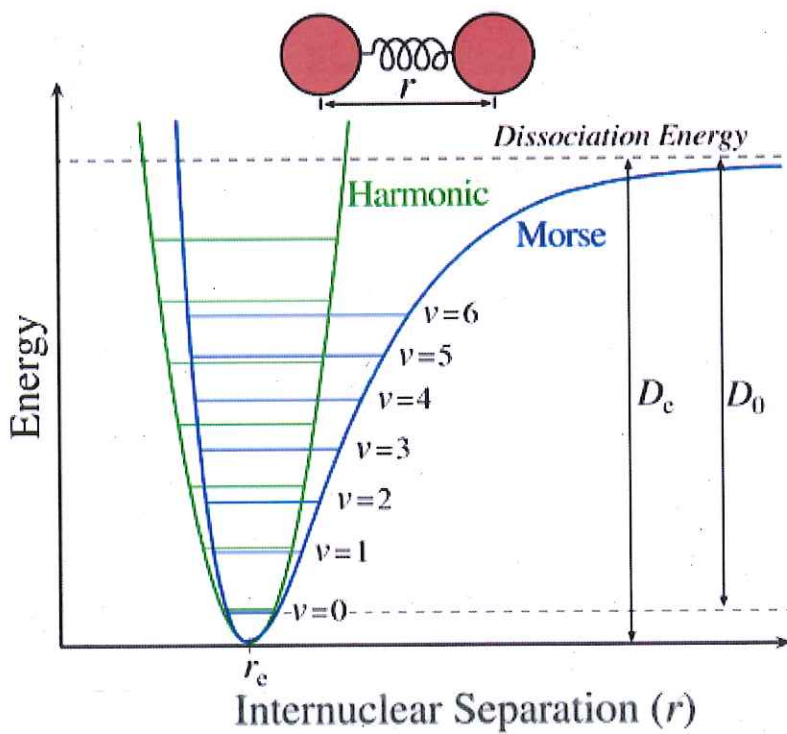
$$E_{\text{vib}} = \hbar\omega \left( \nu + \frac{1}{2} \right) - \frac{\hbar^2\omega^2}{4D} \left( \nu + \frac{1}{2} \right)^2$$



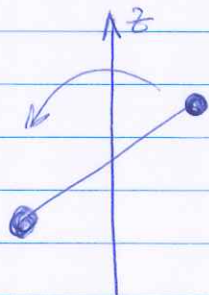
As  $\nu$  increases, the separation b/w the levels decreases



Higher  $\nu$  —  
larger vibration amplitude  
→ atoms move farther  
away and become  
weaker bound, so it  
is easier to move them  
apart



## Rotational energy



Assume a rigid molecule  
(valid approximation)  
Molecules can rotate  
around one, two or three axes

I - moment of inertia

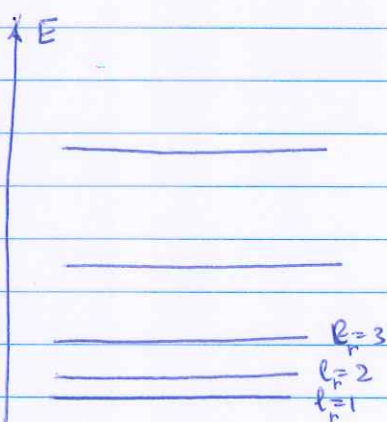
Kinetic energy, associated with rotation

$$K_{\text{rot}} = \frac{1}{2} I \omega^2 = \frac{L^2}{2I}$$

Rotational energy is quantized  $\rightarrow \hat{L}^2$  is quantized

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

$l_r$  - rotational quantum number (different from electron  $l$  orbital #)



$$\begin{aligned} \Delta E_{l_r+1} - \Delta E_{l_r} &= \frac{\hbar^2(l_r+1)(l_r+2)}{2I} - \frac{\hbar^2 l_r(l_r+1)}{2I} = \\ &= \frac{\hbar^2(l_r+1)}{2I} (l_r+2 - l_r) = \frac{\hbar^2}{2I} (l_r+1) \end{aligned}$$

Minimum energy separation

$$\Delta E_2 - \Delta E_1 = \frac{\hbar^2}{2I} \text{ typically } \sim 0.001 - 0.01 \text{ eV}$$

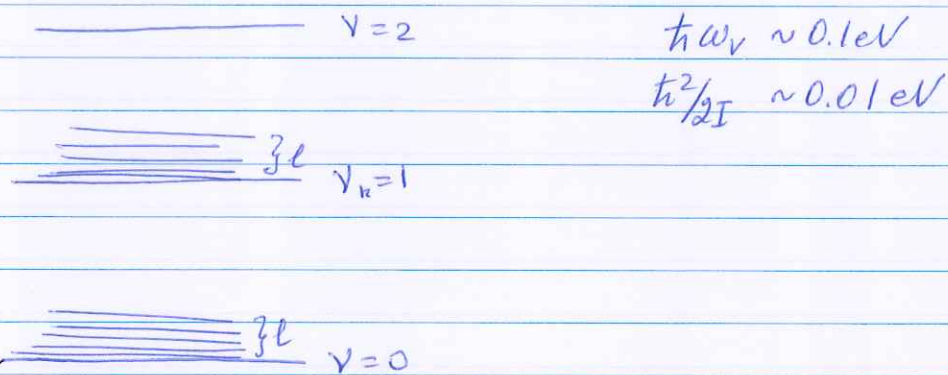
at room temperature many  
rotational levels are populated

## Molecular spectra

Molecules are normally in ground electronic state (requires several eV to excite)

Internal energy - vibrational and rotational

$$E_{\text{int}} = \hbar\omega_v \left(\nu + \frac{1}{2}\right) + \frac{\hbar^2}{2I} l_r(l_r+1)$$



Optical transmission - a molecule changes its states, and a photon ~~is~~ is emitted or absorbed

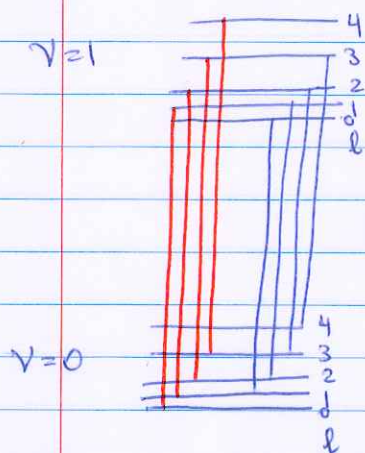
$$E_{\text{photon}} = E_f - E_i$$

Selection rules:  $\Delta l_r = \pm 1$   
(due to ~~momentum~~ angular momentum conservation, photon spin angular momentum ~~is~~  $S=1 \Rightarrow \Delta l_r = \pm 1$ )

Due to the properties of the simple harmonic oscillator functions  $\Delta \nu = \pm 1$



Normally, molecules are in a ground vibrational state ( $v=0$ )



$$\Delta v = 1$$

$$\Delta l_r = \pm 1$$

$$v=0, l_r=0 \rightarrow v=1, l_r=1$$

$$\Delta E_{01} = \hbar\omega_v + \hbar^2/I$$

$$v=0, l_r=1 \rightarrow v=1, l_r=2$$

$$\Delta E_{02} = \hbar\omega_v + 2\hbar^2/I$$

$$\Delta E_{l_r, l_r+1} = \hbar\omega_v + (l_r+1)\hbar^2/I$$

$$\text{or } v=0, l_r=1 \rightarrow v=1, l_r=0$$

$$\Delta E_{10} = \hbar\omega_v - \hbar^2/I$$

$$v=0, l_r=2 \rightarrow v=1, l_r=1$$

$$\Delta E_{21} = \hbar\omega_v - \hbar^2/I$$

$$\Delta E_{l_r+1, l_r} = \hbar\omega_v - (l_r+1)\hbar^2/I$$

No transition with  $\Delta E = \hbar\omega_v$

### Vibration-Rotation Transitions

Transitions from the ground vibrational state to the first excited state of HCl with a change  $\Delta j = \pm 1$  in rotational angular momentum.

