SPHERICAL HARMONICS

$$Y_l^m(\theta,\phi) = \Theta_l^{|m|}(\theta)\Phi_m(\phi)$$

$$Y_l^m(\theta,\phi) = \left[\left(\frac{2l+1}{4\pi}\right)\frac{(l-|m|)!}{(l+|m|)!}\right]^{\frac{1}{2}} P_l^{|m|}(\cos\theta)e^{im\phi}$$

$$l = 0,\ 1,\ 2,... \qquad m = 0,\ \pm 1,\ \pm 2,\ \pm 3,...\pm l$$

Y_l^m's are the eigenfunctions to $\hat{H}\psi = E\psi$ for the rigid rotor problem.

$$Y_0^0 = \frac{1}{(4\pi)^{1/2}} \qquad Y_2^0 = \left(\frac{5}{16\pi}\right)^{\frac{1}{2}}(3\cos^2\theta - 1)$$

$$Y_1^0 = \left(\frac{3}{4\pi}\right)^{\frac{1}{2}}\cos\theta \qquad Y_2^{\pm 1} = \left(\frac{15}{8\pi}\right)^{\frac{1}{2}}\sin\theta\cos\theta e^{\pm i\phi}$$

$$Y_1^{-1} = \left(\frac{3}{8\pi}\right)^{\frac{1}{2}}\sin\theta e^{i\phi} \qquad Y_2^{\pm 2} = \left(\frac{15}{32\pi}\right)^{\frac{1}{2}}\sin^2\theta e^{\pm 2i\phi}$$

$$Y_1^1 = \left(\frac{3}{8\pi}\right)^{\frac{1}{2}}\sin\theta e^{-i\phi}$$

Y_l^m's are <u>orthonormal</u>: $\iint Y_{l'}^{m'*}(\theta,\phi)Y_l^m(\theta,\phi)\sin\theta d\theta d\phi = \delta_{ll'}\delta_{mm'}$

Krönecker delta $\delta_{ll'} = \begin{cases} 1 & \text{if } l = l' \\ 0 & \text{if } l \neq l' \end{cases}$ $\quad \delta_{mm'} = \begin{cases} 1 & \text{if } m = m' & \text{normalization} \\ 0 & \text{if } m \neq m' & \text{orthogonality} \end{cases}$

Energies: (eigenvalues of $\hat{H}Y_l^m = E_{lm}Y_l^m$)

Switch $l \rightarrow J$ conventional for molecular rotational quantum #

Recall $\quad \beta = \dfrac{2IE}{\hbar^2} = l(l+1) \equiv J(J+1) \qquad J = 0,\ 1,\ 2,...$

$$\therefore \quad \boxed{E_J = \frac{\hbar^2}{2I} J\left(J+1\right)}$$

E

J = 3 ——— $E_3 = \dfrac{6\hbar^2}{I}$ $\quad Y_3^0,\ Y_3^{\pm 1},\ Y_3^{\pm 2},\ Y_3^{\pm 3}\ \left(\text{7x degenerate}\right)$

J = 2 ——— $E_2 = \dfrac{3\hbar^2}{I}$ $\quad Y_2^0,\ Y_2^{\pm 1},\ Y_2^{\pm 2}\ \left(\text{5x degenerate}\right)$

J = 1 ——— $E_1 = \dfrac{\hbar^2}{I}$ $\quad Y_1^0,\ Y_1^0\ \left(\text{2x degenerate}\right)$

J = 0 ——— $E_0 = 0$ $\quad Y_0^0\ \left(\text{nondegenerate}\right)$

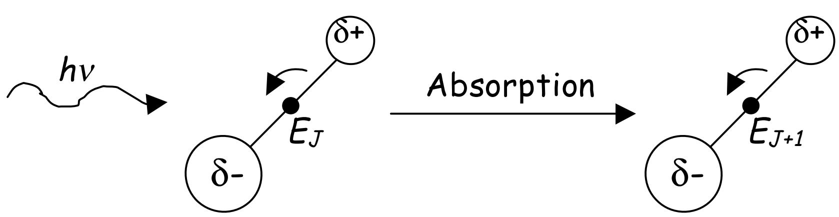
Degeneracy of each state $\qquad g_J = \left(2J+1\right)$

from $m = 0,\ \pm 1,\ \pm 2, ..., \pm J$

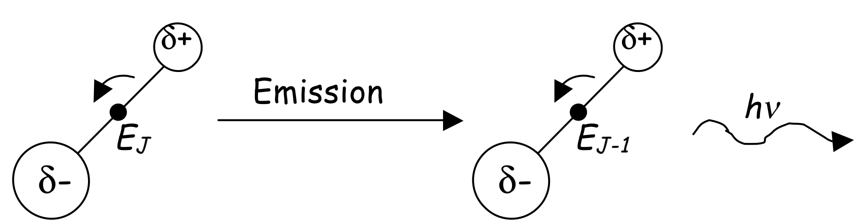
Spacing between states $\uparrow$ as $J \uparrow$

$$E_{J+1} - E_J = \frac{\hbar^2}{2I}\Big[\left(J+1\right)\left(J+2\right) - J\left(J+1\right)\Big] = \frac{\hbar^2}{I}\left(J+1\right)$$

Transitions between rotational states can be observed through spectroscopy, i.e. through absorption or emission of a photon



or



Molecules need a <u>permanent dipole</u> for rotational transitions.
Oscillating electric field grabs charges and torques the molecule.

Strength of transition $$I_{JJ'} \propto \left| \frac{d\mu}{dx} \int_{-\infty}^{\infty} \psi_{J'}^{*} \left(\xi \cdot \mu \right) \psi_J \, dx \right|^2$$

electric field of light

dipole moment of rotor

Leads to selection rule for rotational transitions: $\boxed{\Delta J = \pm 1}$

Recall angular momentum is <u>quantized</u> (in units of $\hbar$).
Photon carries one quantum of angular momentum.
<u>Conservation of angular momentum</u> $\Rightarrow$ $\Delta J = \pm 1$
Angular momentum of molecule changes by 1 quantum upon absorption or emission of a photon.

$$E_{\substack{photon \\ J \to J+1}} = h\nu_{\substack{photon \\ J \to J+1}} = \Delta E_{rot} = E_{J+1} - E_J = \frac{\hbar^2}{I}\left(J+1\right) \qquad \nu_{\substack{photon \\ J \to J+1}} = \frac{h}{4\pi^2 I}\left(J+1\right)$$

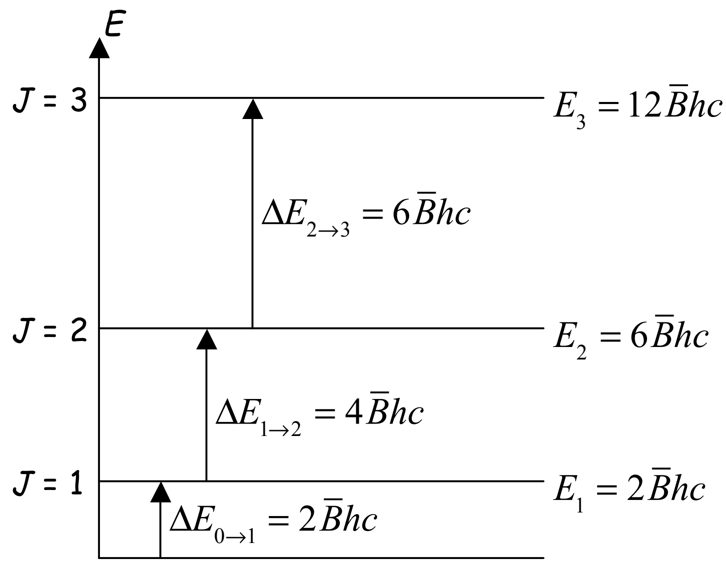
Define

$$B \equiv \frac{h}{8\pi^2 I} \quad \text{rotational constant (Hz)}$$

and

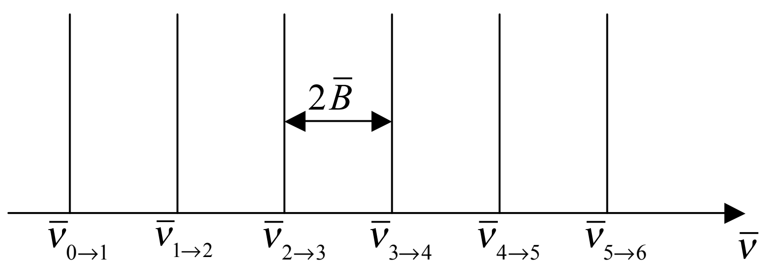
$$\overline{B} \equiv \frac{h}{8\pi^2 c I} \quad \text{rotational constant (cm}^{-1}\text{)}$$

$$\therefore \qquad \nu_{J \to J+1} \ (\text{Hz}) = 2B\left(J+1\right) \qquad \overline{\nu}_{J \to J+1} \ (\text{cm}^{-1}) = 2\overline{B}\left(J+1\right)$$



This gives rise to a rigid rotor absorption spectrum with <u>evenly spaced</u> lines.

J = 0



Spacing between transitions is $\boxed{2B \text{ (Hz) or } 2\bar{B} \text{ (cm}^{-1}\text{)}}$

$$\bar{\nu}_{J+1\to J+2} - \bar{\nu}_{J\to J+1} = 2\bar{B}\left[\left(J+1\right)+1\right] - 2\bar{B}\left(J+1\right) = 2\bar{B}$$

Use this to get microscopic structure of diatomic molecules directly from the absorption spectrum!

Get $\bar{B}$ directly from the separation between lines in the spectrum.

Use its value to determine the bond length r_0!

$$2\bar{B} = \frac{h}{4\pi^2 cI} \qquad I = \mu r_0^2 \qquad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$\therefore \qquad \boxed{r_0 = \left[\frac{h}{8\pi^2 c\bar{B}\mu}\right]^{\frac{1}{2}} \ (\bar{B} \text{ in cm}^{-1}) \quad \text{or} \quad r_0 = \left[\frac{h}{8\pi^2 B\mu}\right]^{\frac{1}{2}} \ (B \text{ in Hz})}$$