H. Rotational Spectrum

- involve microwave or slightly higher (Far IR) [$\nu \sim 10^{11}$ Hz, $\lambda \sim 1$ mm]
- $kT \sim 1/40$ eV $\Rightarrow$ consider only $n=0$ vibrational level

$\therefore$ Only $E_\ell^{rot} = \dfrac{\ell(\ell+1)\hbar^2}{2I} = \ell(\ell+1)\cdot\dfrac{\hbar^2}{2I}$ matters

labelled by ℓ

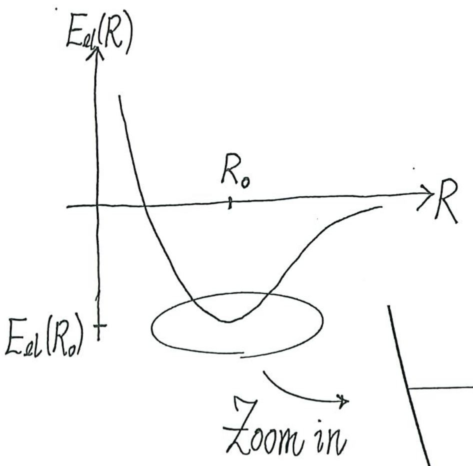
$I = \mu R_0^2$ $\quad\left[\dfrac{1}{\mu} = \dfrac{1}{M_A} + \dfrac{1}{M_B}\right.$ diatomic molecules$\Big]$

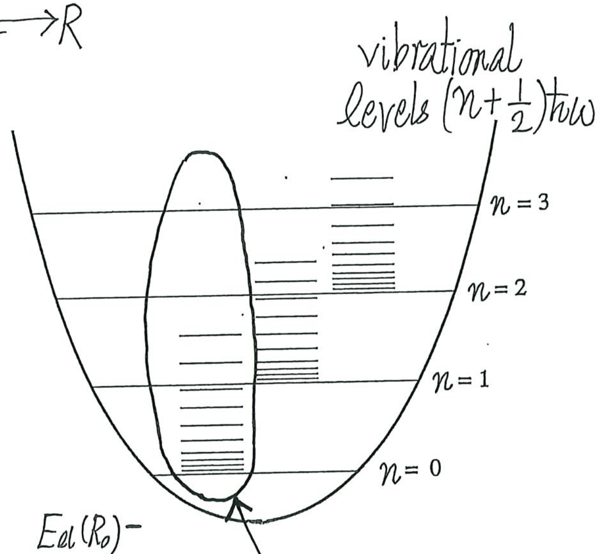
$\boxed{\text{bond length}}$ μ is dominated by the lighter mass

$$M_A \ll M_B$$

$$\frac{1}{\mu} = \frac{1}{M_A} + \frac{1}{M_B} \approx \frac{1}{M_A} \Rightarrow \mu \approx M_A$$

e.g. HCl, $\mu \approx m_H$ (proton mass), $R_0 \sim 0.13$ nm $\Rightarrow \dfrac{\hbar^2}{I} \sim 2\times10^{-3}$ eV



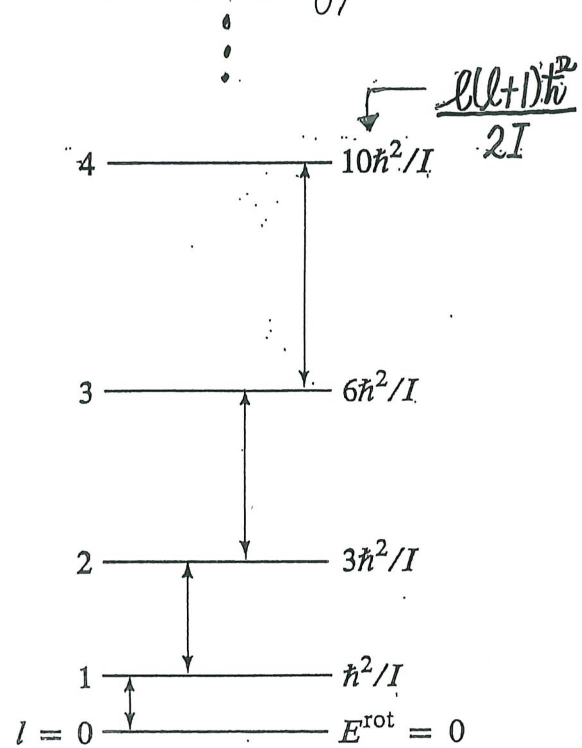


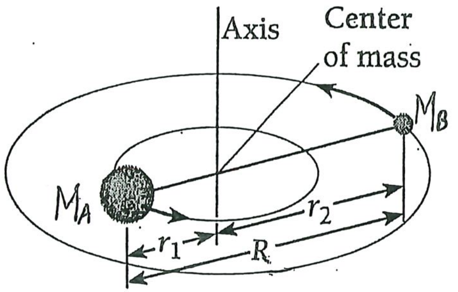
For rotational spectrum look here

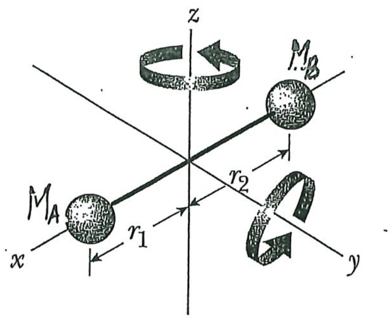
$$E_\ell^{rot} = \ell(\ell+1)\frac{\hbar^2}{2I}$$

ℓ	0	1	2	3	4	5	6	...
E_ℓ^{rot}	0	$\frac{\hbar^2}{I}$	$3\frac{\hbar^2}{I}$	$6\frac{\hbar^2}{I}$	$10\frac{\hbar^2}{I}$	$15\frac{\hbar^2}{I}$	$21\frac{\hbar^2}{I}$	...

Rotational energy levels







$\boxed{\text{Transitions between rotational levels give rotational spectrum}}$

Selection Rule (41)

- $\Delta l = \pm 1$ (and molecule has a permanent electric dipole moment)

Note pattern of differences in energy

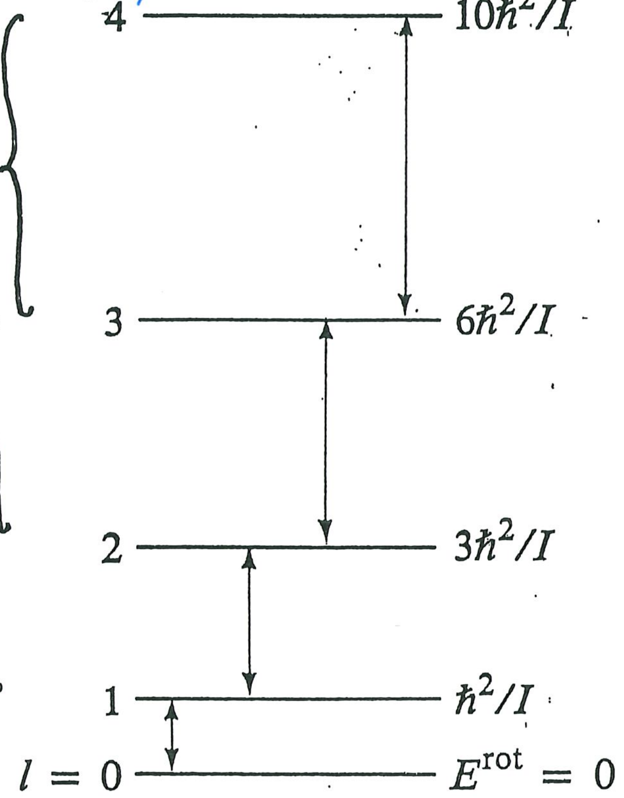
$\frac{l(l+1)\hbar^2}{2I}$

$\frac{4\hbar^2}{I}$

$\frac{3\hbar^2}{I}$

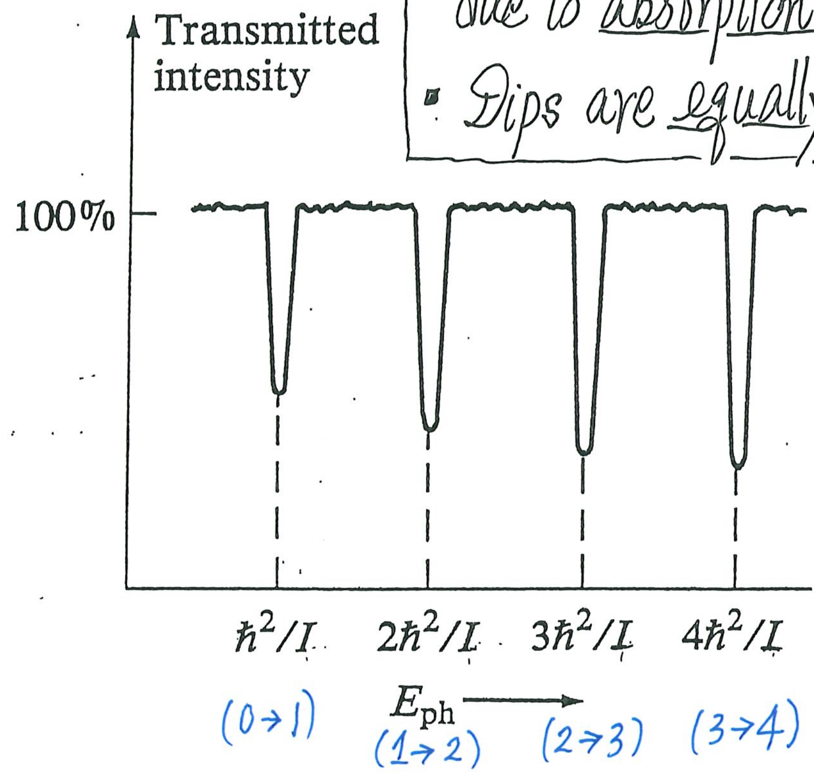
$\frac{2\hbar^2}{I}$

Difference = $\left\{ \frac{\hbar^2}{I} \right.$



Rotational Spectrum

- Dips in Transmission due to absorption
- Dips are equally spaced



$(0 \to 1)$ $(1 \to 2)$ $(2 \to 3)$ $(3 \to 4)$

- If we see structure in spectrum will equally spaced lines in absorption/transmission (in energy/freq.) with spacing $\sim 10^{-3}$ eV, then we know that rotational levels are involved.

- Read out differences $\Rightarrow \dfrac{\hbar^2}{I} \Rightarrow \underbrace{I}_{\mu R_0^2} \Rightarrow R_0$ (bond length)!
  (if μ is known)

  $\therefore$ $\boxed{\text{Can extract } R_0 \text{ from separation between adjacent lines}}$ (42)

- Applied to identify molecules in large molecular clouds in our galaxy (using radio telescopes)

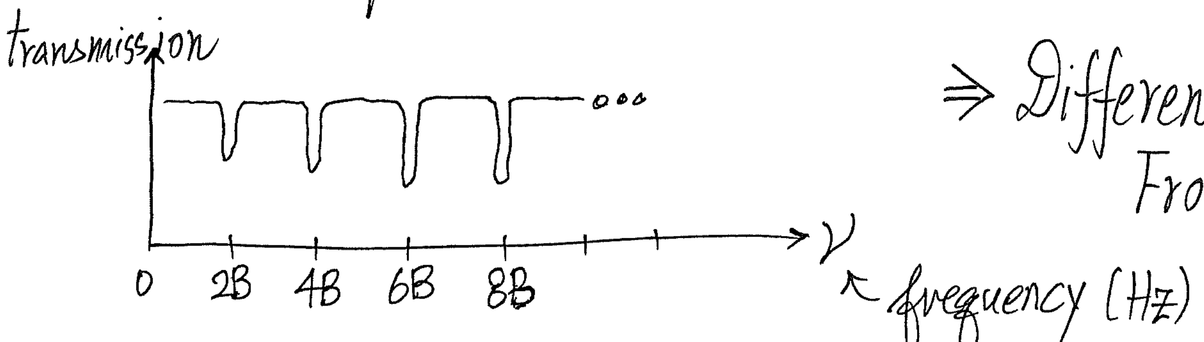
The "Rotational Constant" (Talking to Spectroscopists) [no new physics]

$$\underbrace{E_\ell^{rot.}}_{\boxed{\text{energy}}} = \frac{\hbar^2}{2I}\ell(\ell+1) = \frac{h^2}{8\pi^2 I}\ell(\ell+1) \qquad (I = \mu R_0^2)$$

$$\equiv h\cdot \underbrace{B\cdot \ell(\ell+1)}_{\boxed{\text{frequency}}} \quad \text{defines } B \qquad [\, h\nu \text{ is an energy}]$$

$$\underbrace{B}_{\boxed{\text{rotational constant}}} = \frac{h}{8\pi^2 I} = \frac{h}{8\pi^2 \mu R_0^2} \quad (\text{Units: } \underline{\underline{\text{Hz}}}) \qquad (43) \quad (\underline{\text{given in data book}})$$

- In terms of B and expressing E_{ph} by its frequency ν, the rotational spectrum becomes $(\Delta\ell = \pm 1)$



$\Rightarrow$ Difference $= 2B$

From B, get I, then R_0

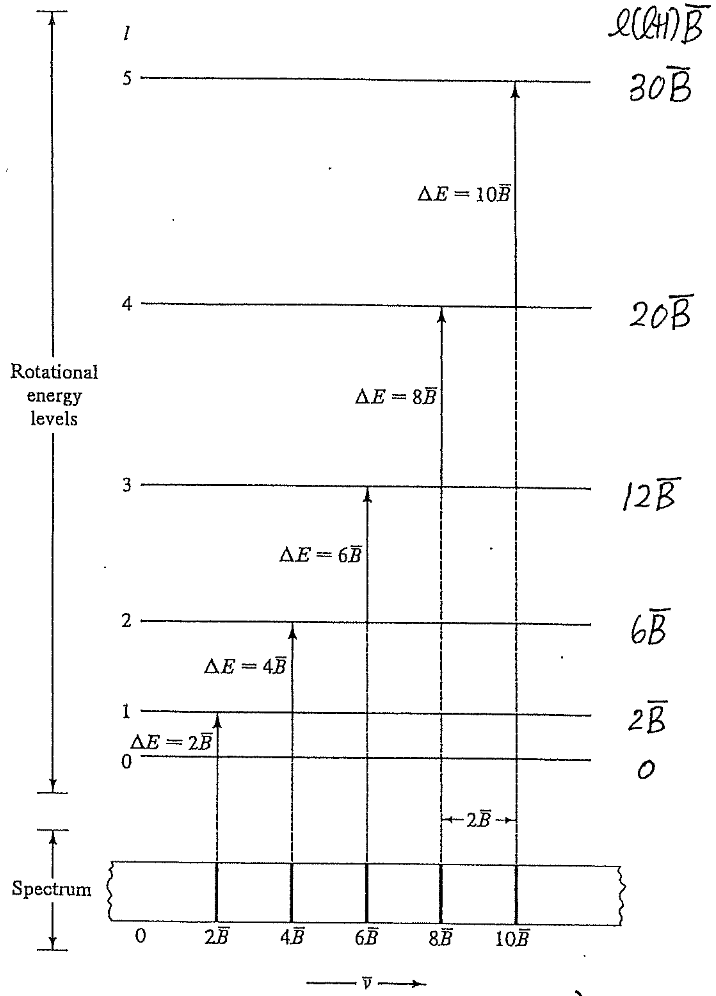
- More often, see wavenumber (units: cm⁻¹) instead of Hz

$$E_l^{rot} = \frac{\hbar^2}{2I} l(l+1) = \frac{h^2}{8\pi^2 I} l(l+1) = h \underbrace{B}_{(Hz)} l(l+1) = hc \cdot \underbrace{\bar{B}}_{(cm^{-1})} \cdot l(l+1)$$

$$\bar{B} = \frac{B}{c} = \frac{h}{8\pi^2 c I}$$

$$[cm^{-1}] = \frac{h}{8\pi^2 c \mu R_0^2} \quad (44)$$

$\bar{B}$ is also called the rotational constant



$\bar{\nu}$ (wave number) (cm^{-1}) ← Note units

Typical values of $\bar{B}$

H_2: $\bar{B} = 60.853\ cm^{-1}$

O_2: $\bar{B} = 1.44563\ cm^{-1}$

(used in data book)

Rotational Spectrum

$\Downarrow$

$\bar{B} \Rightarrow R_0$

Aside: About Eq. (41) selection rule

- Saw $\Delta l = \pm 1$ in atomic transitions
- Same physics here!
- $\hat{H}' = -\vec{\mu} \cdot \vec{\mathcal{E}}$

R_0 ↓ B (slight positive)
↑ A (slightly negative)

$\uparrow \vec{\mu} = q R_0 \hat{z}$
$= \mu \hat{z}$
($q \neq 0$, permanent $\vec{\mu}$)

$$\mu \cdot \int Y^*_{l'm'}(\Theta, \Phi) \; \underbrace{\hat{z}}_{} \; Y_{lm}(\Theta, \Phi) \; \underbrace{\sin\Theta \, d\Theta \, d\Phi}_{d\Omega}$$

↑ a direction (OR $\hat{x}$, OR $\hat{y}$)

[like $Y_{1,\text{something}}$ in the middle]

$\therefore$ l' and l differ by ± 1 for $\int \cdots d\Omega \neq 0$

$\Delta l = \pm 1$

But it needs a $\vec{\mu} \neq 0$ (at equilibrium separation R_0) to start with.