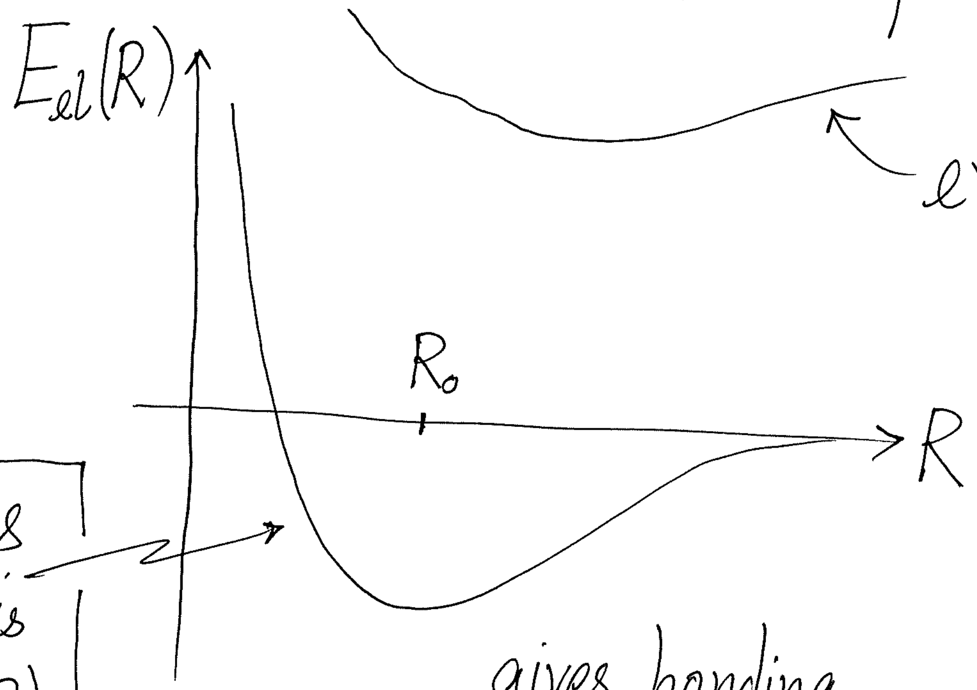
J. Including Nuclei Motions: Full Description of Molecular states

- So far, treated electronic part assuming Nuclei are fixed

$$\hat{H}_{electronic}\,\psi_R(\vec{r}) = E_{el}(R)\,\psi_R(\vec{r}) \qquad [\text{e.g. } H_2^+]$$

where $R = |\vec{R}_A - \vec{R}_B|$ is a parameter



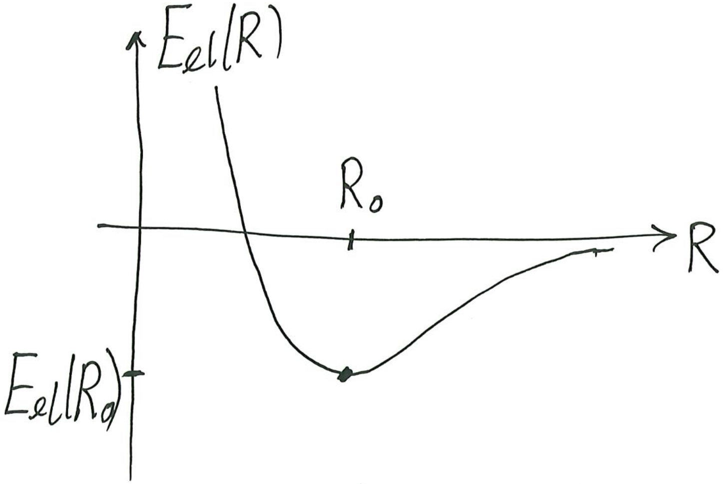
even there may be higher electronic states, they are usually not important in our discussion

∵ many eV's above bonding electronic state

($kT \sim \frac{1}{40}$ eV for 300K)

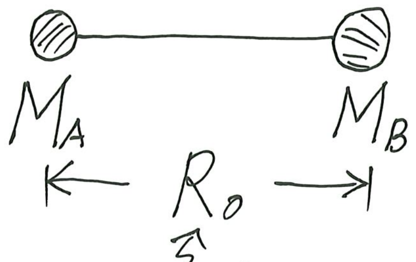
focus on this $E_{el}(R)$

gives bonding



[Lowest electronic state]

If this is all the physics, the molecule will be



(two balls and a stick)

equilibrium separation [rigid]

and energy is $E_{el}(R_0)$

- But we ignored the kinetic energy terms of nuclei

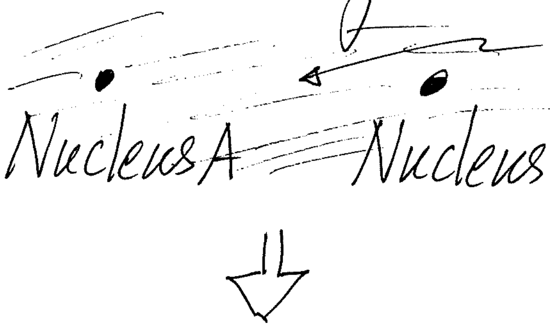
$$\text{ignored so far} \rightarrow \left(-\frac{\hbar^2}{2\mu}\nabla_{\vec{R}}^2\right) + \underbrace{\circ\circ\circ}_{\hat{H}_{el}}$$

[recall: Center of Mass free motion has been separated]

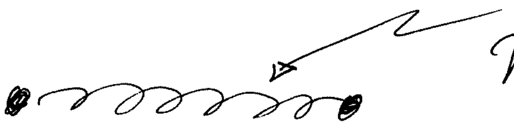
in Step 1 of the Born-Oppenheimer Approximation.

- It is time to put them back!

As we advertized, Step 1 ⇒ electrons give bonding (LCAO-MO)

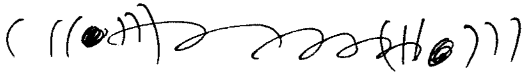


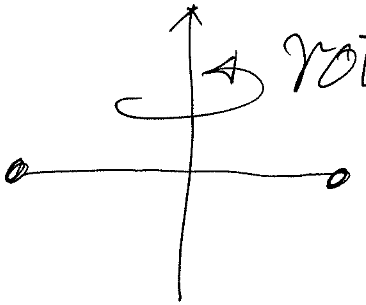
Then Step 2:

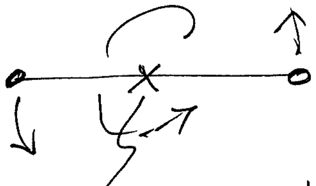


Nuclei Motion

due to
Internal Structure
of molecule
[no such phenomena
in atoms]





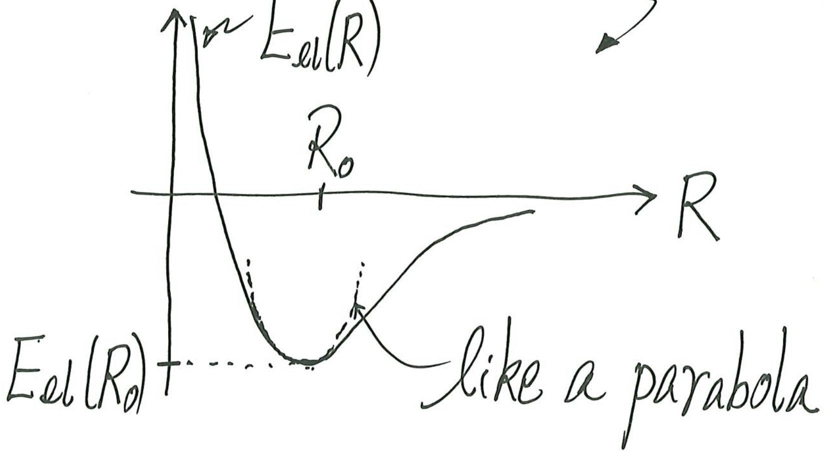


Putting back k.e. term of nuclei relative motion

$$\Big[\underbrace{-\frac{\hbar^2}{2\mu}\nabla^2_{\vec{R}}}_{\text{ignored in Step 1}} + \underbrace{\hat{H}_{el}(R)}\Big]\underbrace{\psi^{el}_R}(\vec{r})\,\psi_N(\vec{R}) = E^{(molecule)}_{total}\,\psi^{el}_R(\vec{r})\,\overbrace{\psi_N(\vec{R})}^{\text{Wavefunction of Nuclei motion}}$$

LCAO (electronic part) gives $E_{el}(R)\,\psi^{el}_R(\vec{r})$

$$\Big[-\frac{\hbar^2}{2\mu}\nabla^2_{\vec{R}} + E_{el}(R)\Big]\psi_N(\vec{R})\,\psi^{el}_R(\vec{r}) = E^{(molecule)}_{total}\,\psi_N(\vec{R})\,\psi^{el}_R(\vec{r})$$

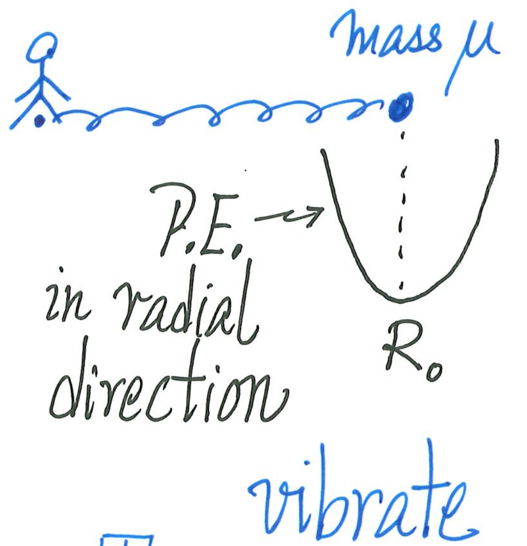


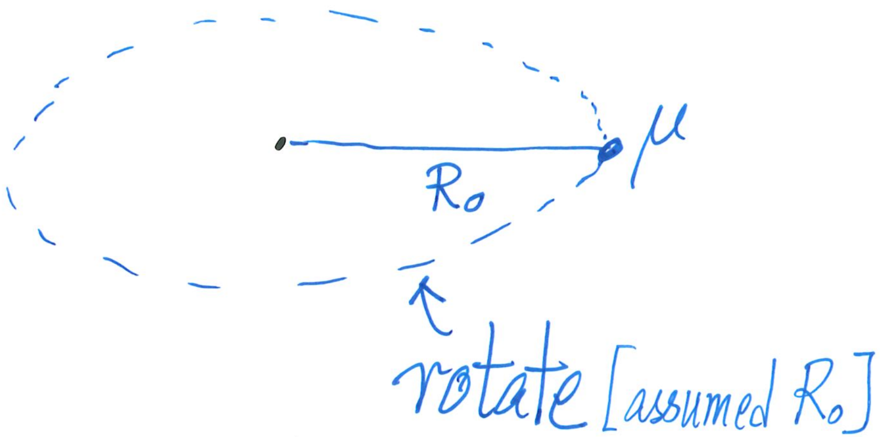
$$E_{el}(R) \approx \underbrace{E_{el}(R_0)}_{\text{a constant}} + \frac{1}{2}\underbrace{\frac{d^2E_{el}(R)}{dR^2}\Big|_{R=R_0}}_{\text{spring constant}}\cdot(R-R_0)^2$$

for $R \approx R_0$

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2_{\vec{R}} + \frac{1}{2}k(R-R_0)^2\right]\psi_N^{\nu}(\vec{R}) = \left(E^{(\text{molecule})}_{\text{total}} - E_{el}(R_0)\right)\psi_N^{\nu}(\vec{R}) \quad (29)$$

- TISE for nuclei relative motion (3D problem)
- $U(R)$ only [not (R_x, R_y, R_z) or (R, Θ, Φ), just R; spherically symmetric]
- $\hat{\vec{P}}$, $\hat{\vec{R}}$ restored their operator roles (ignored in Step 1)
- Pictorially





$\omega = \sqrt{\frac{k}{\mu}}$ is normal mode frequency

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

$$\psi_N(\vec{R}) = \underbrace{\phi_n(R-R_0)}_{\text{(known)}\left\{\begin{array}{l}\text{harmonic oscillator}\\ \text{wavefunction centered at } R_0\end{array}\right.} \cdot \underbrace{Y_{\ell m}(\Theta,\Phi)}_{\begin{array}{c}\text{rotation (rigid rotor problem)}\\ \text{"partice-on-a-sphere"}\end{array}} \qquad (31)$$

$$\left[\frac{-\hbar^2}{2\mu}\nabla_{\vec{R}}^2 + \frac{1}{2}k(R-R_0)^2\right]\psi_N(\vec{R}) = \left[\left(n+\frac{1}{2}\right)\hbar\underbrace{\sqrt{\frac{k}{\mu}}}_{\omega} + \frac{\ell(\ell+1)\hbar^2}{2\mu R_0^2}\right]\psi_N(\vec{R}) \qquad (32)$$

(Done!)

- Made use of solutions to standard QM problems
- Need Eq. (31) to understand transitions between a molecular state (e.g. n, ℓ) to another molecular state (e.g. n', ℓ')
  (c.f. selection rules)

$$\boxed{E^{(molecule)}_{total} = E_{el}(R_0) + \left(n+\frac{1}{2}\right)\hbar\omega + \frac{l(l+1)\hbar^2}{2I}} \qquad (33) \text{ (see Eq. (29))}$$

$$= E_{el}(R_0) + \underbrace{E^{vib}_{n} + E^{rot}_{l}}_{E^N} \qquad (34)$$

Key Result
[allowed energies for a molecule]

$E_{el}(R_0)$: which electronic state (lowest here)

E^{vib}_n: which vibrational level

E^{rot}_l: which rotational level (degeneracy behind m)

E^N ← due to nuclei motion [new! no such terms for atoms]

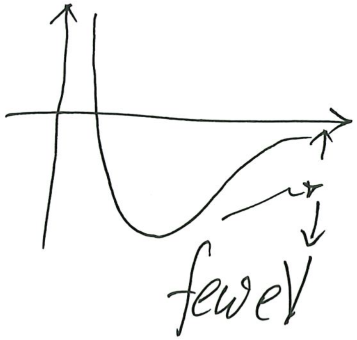
- A full specification of a molecular energy level requires:
  - which electronic state [c.f. HK or Kowloon or NT in mailing]
  - which vibrational level n [c.f. District]
  - which rotational level l [c.f. Street]

Relative strength of terms: Rough Estimates

(i) Electronic

electron confined to $\sim R_0$ (1–3 Å)
[~ atomic]

$$E_{el} \sim \frac{\hbar^2}{mR_0^2} \quad (m = \text{electron mass}) \sim \underbrace{\text{few to tens eV}}_{\text{UV or beyond}}$$



(ii) Vibrational

energy $\sim kx^2$ (SHO) $\quad [k = \mu\omega^2]$

Roughly, $\mu\omega^2 R_0^2 \sim \frac{\hbar^2}{mR_0^2} \Rightarrow \omega \sim \sqrt{\frac{\hbar^2}{\mu m R_0^4}}$

$$\therefore \underset{\sim E^{vib}}{\hbar\omega} \sim \frac{\hbar^2}{\sqrt{\mu m}\,R_0^2} \sim \frac{\hbar^2}{mR_0^2}\cdot\sqrt{\frac{m}{\mu}} \sim \underset{[\text{few eV}]}{E_{el}}\cdot\underset{(\sim 10^{-2})}{\left(\frac{m}{\mu}\right)^{1/2}} \sim 0.01-0.1\,\text{eV}$$

(iii) Rotational

$$E^{rot} \sim \frac{L^2}{2I} \sim \frac{\hbar^2}{\mu R_0^2}$$

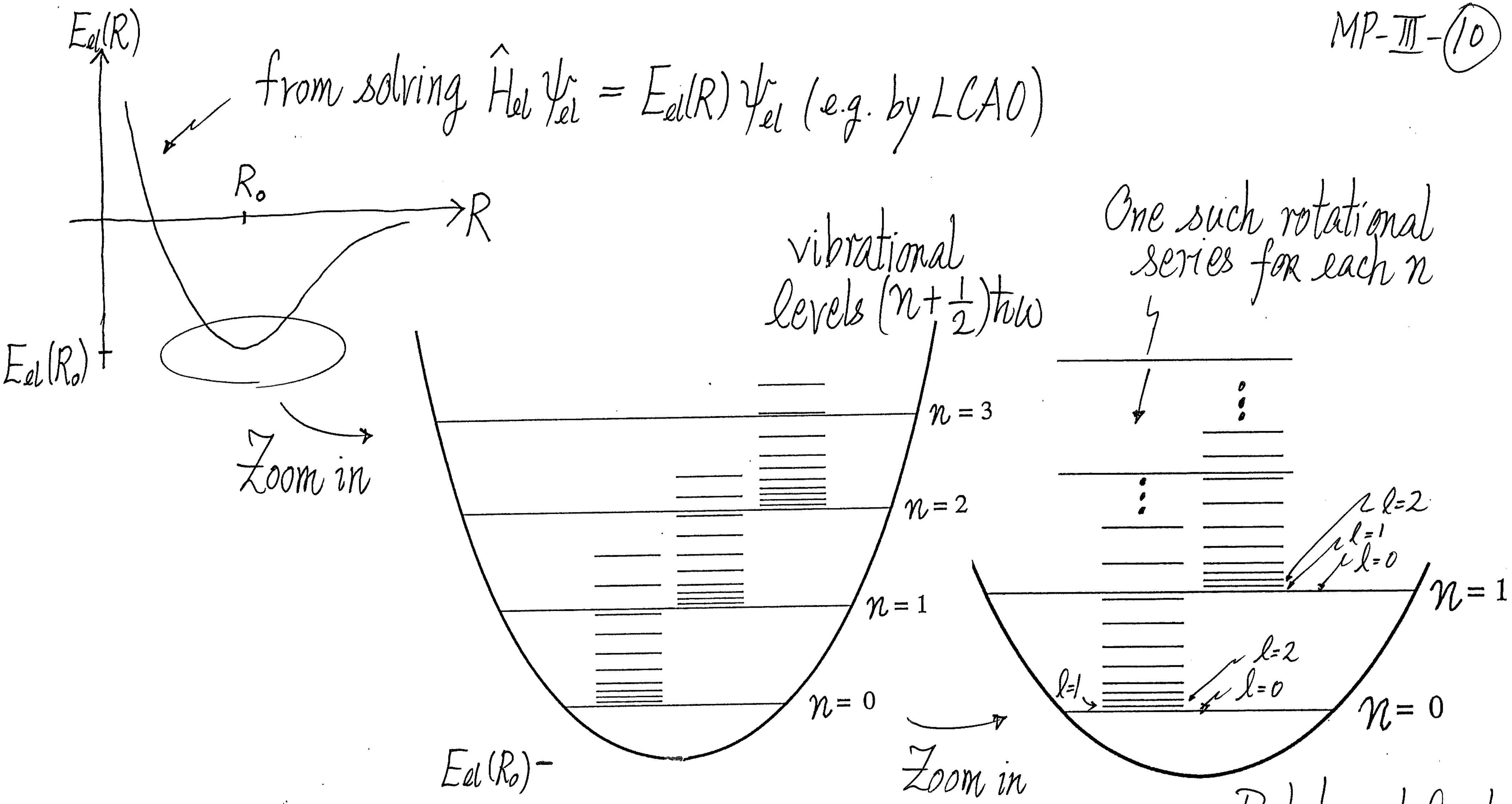
[angular momentum $\sim \hbar$]

$$\sim \frac{\hbar^2}{m R_0^2}\cdot\left(\frac{m}{\mu}\right) \sim E_{el}\cdot\left(\frac{m}{\mu}\right) \sim \underbrace{E_{el}\cdot(\sim 10^{-4})}_{10^{-3}-10^{-4}\,eV}$$

$$\therefore \boxed{\begin{aligned} &E_{el} \sim \text{few to tens eV} \\ &E^{vib} \sim 10^{-2}\cdot E_{el} \sim 0.01-0.1\ eV \\ &E^{rot} \sim 10^{-4}\cdot E_{el} \sim 10^{-2}\cdot E^{vib} \sim 10^{-4}-10^{-3}\,eV \end{aligned}} \tag{35}$$

They are of very different energy scales

[Key Concept]



from solving $\hat{H}_{el}\psi_{el} = E_{el}(R)\,\psi_{el}$ (e.g. by LCAO)

An energy diagram showing the rotational levels associated with each vibrational state in diatomic molecule.

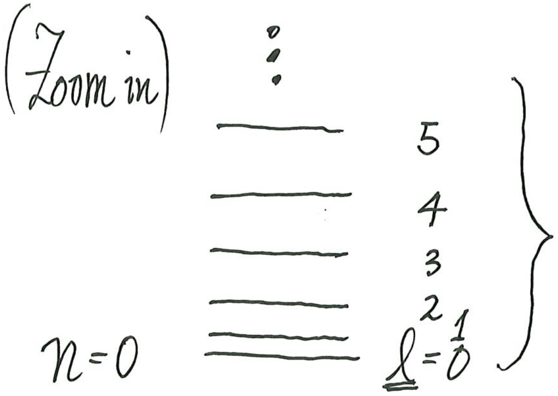
Picture of Key Result Eq. (33)

Rotational levels

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

[each ℓ, $\underbrace{(2\ell+1)}_{\text{degeneracy}}$ values of m]

- A gas of molecules at room temperature ($T \sim 300K$) [$kT \sim \frac{1}{40}$ eV]
  - Almost all of them in $n=0$ vibrational state
    [compare $\hbar\omega$ with kT, and thermal physics]
  - Molecules are thermally excited to occupy rotational levels (spread in different values of ℓ, but $n=0$) belonging to $n=0$ vibrational state



molecules occupy different values of ℓ according to thermal physics

This is the physical picture behind Eq. (33)

$$\boxed{E^{(molecule)}_{total} = E_{el}(R_0) + \left(n+\frac{1}{2}\right)\hbar\omega + \frac{l(l+1)\hbar^2}{2I}} \qquad (35)$$

These are the <u>allowed energies</u> that a diatomic molecule can take on

For allowed energy, there is (are) wavefunction(s). ← [degeneracy]

- Transition from one state to another ⇒ <u>Molecular Spectrum</u>
- $\int \underbrace{\psi^{*}_{final}}_{\text{molecular state}} \hat{H}' \underbrace{\psi_{initial}}_{\text{molecular state}} \underbrace{d\tau}_{\uparrow}$ governs how likely a transition takes place

  all coordinates including nuclei separation

  $(-\vec{\mu}\cdot\vec{\mathcal{E}})$

  ↑ electric dipole

Key Points:

- Rotational, Vibrational, and electronic transitions have very different characteristic energies
- Spectroscopy in different parts of EM spectrum

Regions of the Electromagnetic Spectrum and the Corresponding Molecular Processes [in units other than eV]

Region	*Frequency/Hz*	*Wavelength/m*	*Wave number/cm^{-1}*	*Energy/J·molecule^{-1}*	*Molecular process*
Microwave	10^{9}–10^{11}	3×10^{-1}–3×10^{-3}	0.033–3.3	6.6×10^{-25}–6.6×10^{-23}	Rotation of polyatomic molecules
Far infrared	10^{11}–10^{13}	3×10^{-3}–3×10^{-5}	3.3–330	6.6×10^{-23}–6.6×10^{-21}	Rotation of small molecules
Infrared	10^{13}–10^{14}	3×10^{-5}–3×10^{-6}	330–3300	6.6×10^{-21}–6.6×10^{-20}	Vibration of flexible bonds
Visible and ultraviolet	10^{14}–10^{16}	3×10^{-6}–3×10^{-8}	3300–3.3×10^{5}	6.6×10^{-20}–6.6×10^{-18}	Electronic transitions

physical sense

physical sense

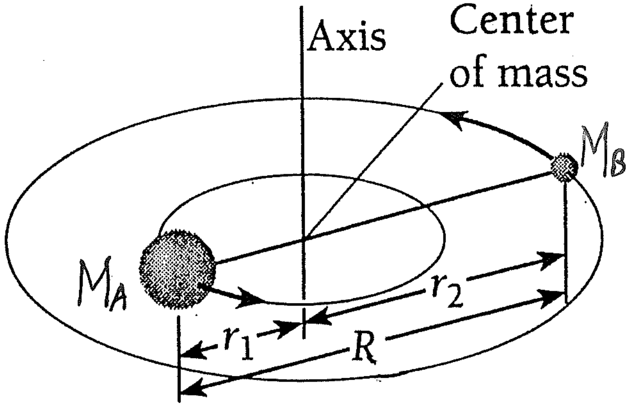
K. Rotational Spectrum

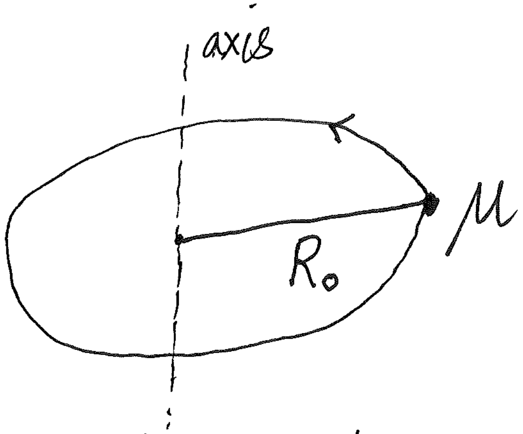
- involve photon energy $\sim \underbrace{\overbrace{10^{-3}\text{ eV}}^{\text{small molecules}}}_{\text{(Far IR)}}$ (OR $\overbrace{\text{smaller}}^{\text{bigger polyatomic molecules}}$)
  (microwave)

  [Freq $\sim 10^{11}$ Hz, Wavelength $\sim$ 1 mm]
- Room temperature (300K, $kT \sim 1/40$ eV ~ 0.024 eV)

  $\Rightarrow$ Gas of molecules usually in lowest electronic and vibrational levels, but distribute in different rotational levels (Boltzmann factor)
- Energy different between neighboring rotational levels $\Delta E^{rot} \sim 10^{-3}$ eV
- Absorption of microwave/far infrared radiation $\Rightarrow$ rotational spectrum

Recall: Rotational Energy Levels





Moment of Inertia

$$I = \mu R_0^2$$

Reduced mass μ

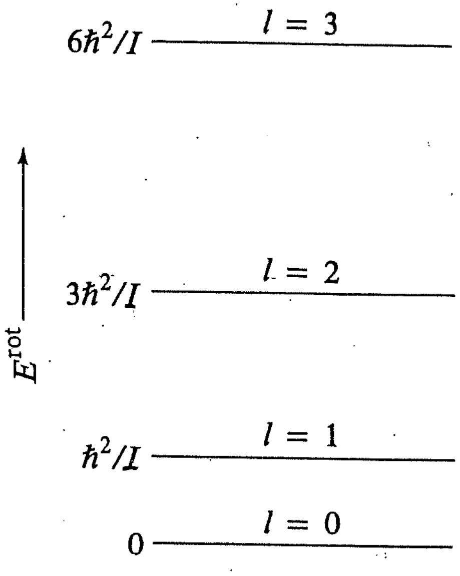
$$\frac{1}{\mu} = \frac{1}{M_A} + \frac{1}{M_B}$$

If $M_A \ll M_B$,

$$\mu \approx M_A$$

[Smaller mass dominates μ]

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



Example: HCl

($R_0 \sim 0.13$ nm)

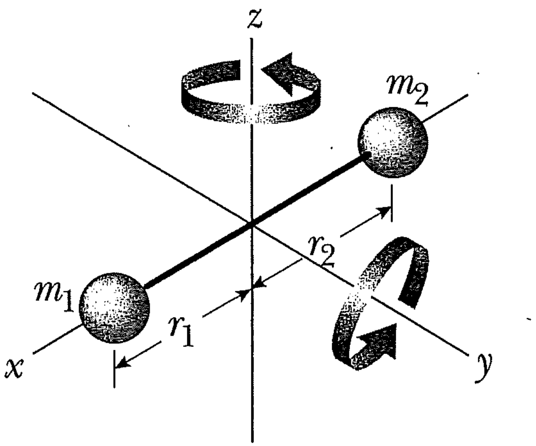
$$\mu \approx m_H$$

$$I = \mu R_0^2 \approx m_H R_0^2$$

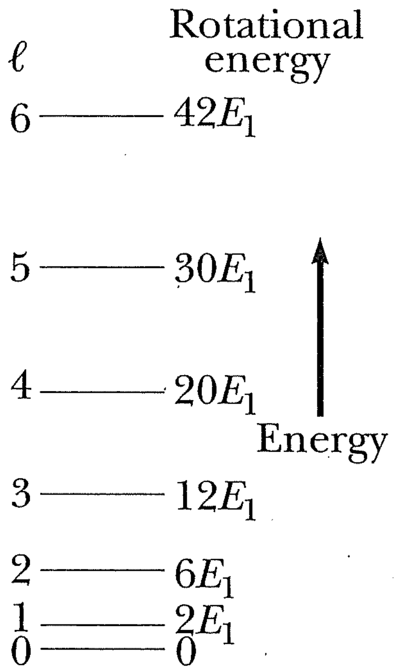
$$\ell = 1 \text{ level}: \quad \frac{\hbar^2}{I} \sim 2\times\underbrace{10^{-3}\,\text{eV}}_{\text{typical of small molecules}}$$

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

$$\boxed{E_1 = \frac{\hbar^2}{2I}}$$



(a)



(b)

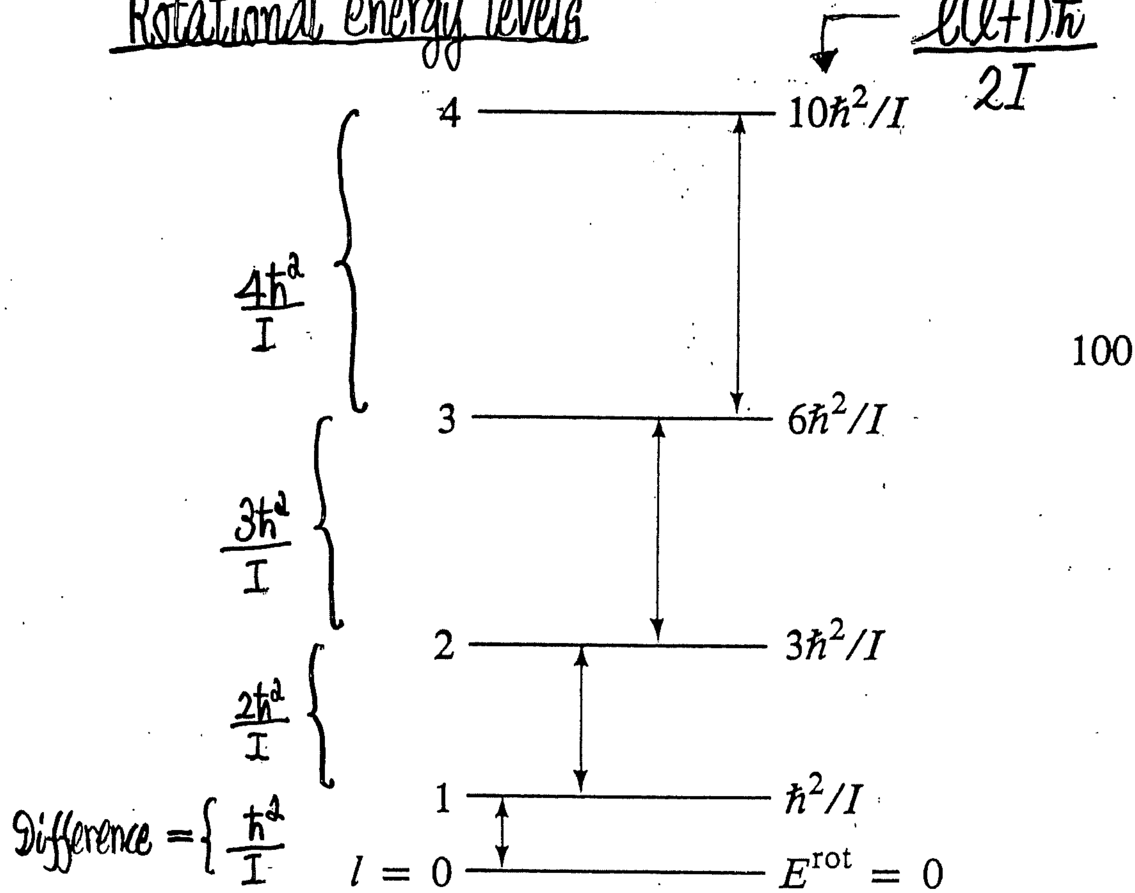
- Note how $\ell(\ell+1)\frac{\hbar^2}{2I}$ behaves

Selection Rule

(36)

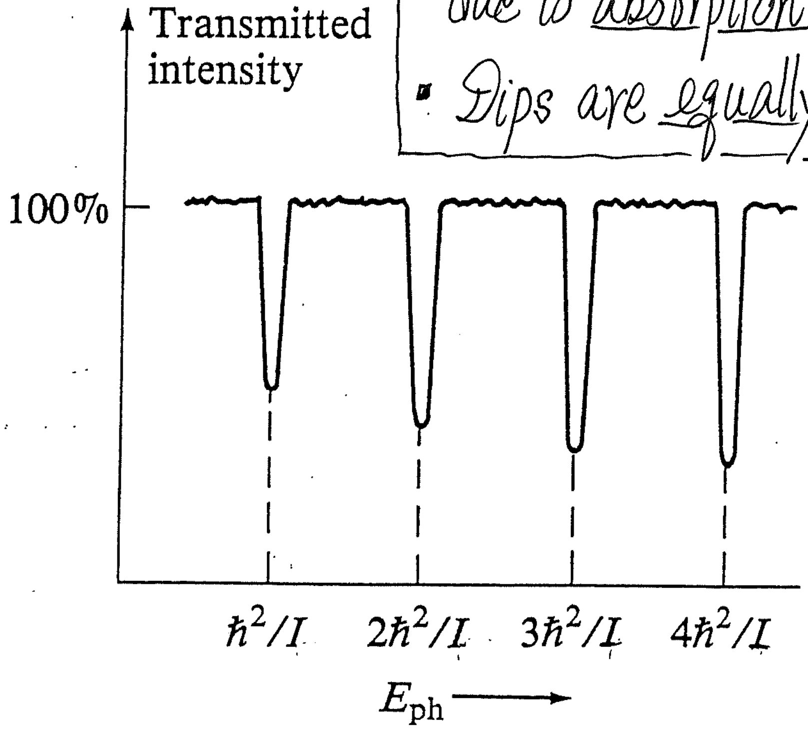
- $\Delta l = \pm 1$ (and molecule has a permanent electric dipole moment)

Rotational energy levels



Rotational Spectrum

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



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

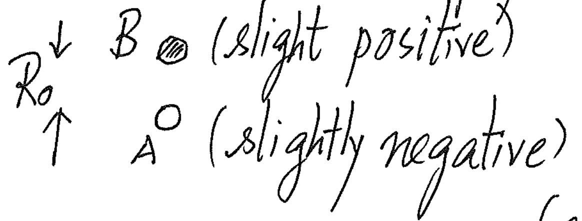
- Read out differences $\Rightarrow \dfrac{\hbar^2}{I} \Rightarrow \underbrace{I}_{\mu R_0^2} \Rightarrow R_0$ (bond length)!
  (if μ is known)

$$\therefore \boxed{\text{Can extract } R_0 \text{ from separation between adjacent lines}} \quad (37)$$

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

Aside: About Eq. (36)

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



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

- $$\int Y^*_{l'm'}(\Theta,\Phi)\ \underbrace{\hat{z}}_{\uparrow\ \text{a direction (OR } \hat{x}\text{, OR } \hat{y})}\ Y_{lm}(\Theta,\Phi)\ \underbrace{\sin\Theta\, d\Theta\, d\Phi}_{d\Omega}$$

[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.

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

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

$$\equiv h\cdot\underbrace{B\cdot\ell(\ell+1)}_{\boxed{\text{frequency}}} \qquad \text{defines } B$$

$$\underset{\text{rotational constant}}{B} = \frac{h}{8\pi^2 I} = \frac{h}{8\pi^2\mu R_0^2} \qquad (\text{Units: } \underline{\underline{\text{Hz}}}) \qquad (38) \quad (\text{given in data book})$$

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

$\Rightarrow$ Difference $= 2B$

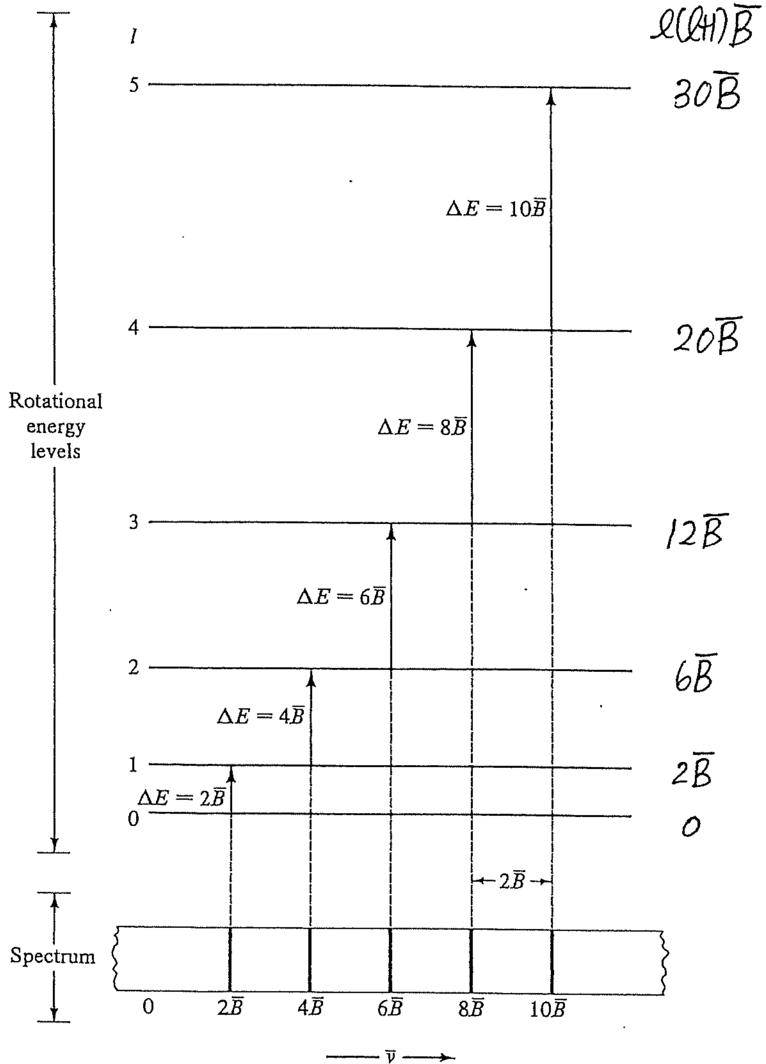
From B, get I, then R_0

- More often, see wavenumber (units: cm^{-1}) instead of Hz

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

$$\underset{[cm^{-1}]}{\overline{B}} = \frac{B}{c} = \frac{h}{8\pi^2 c I} = \frac{h}{8\pi^2 c \mu R_0^2} \quad (39)$$

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



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

Rotational Spectrum

Typical values of $\overline{B}$

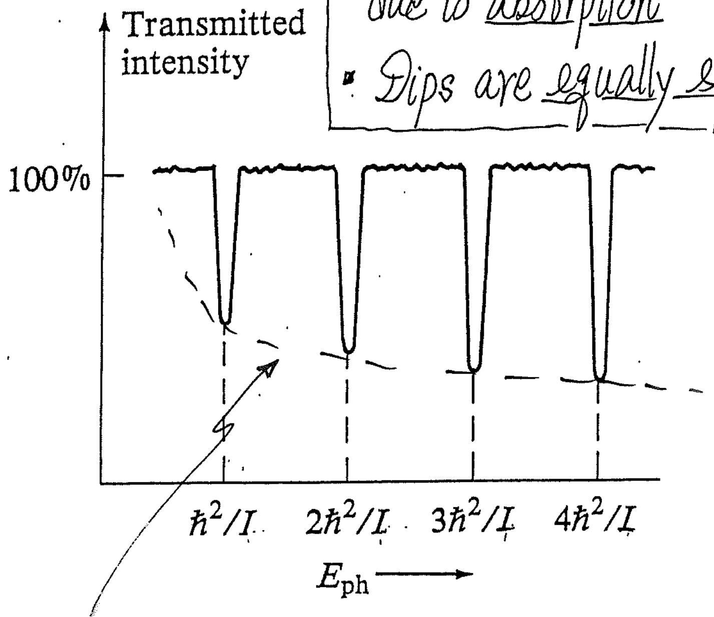
H_2: $\overline{B} = 60.853\ cm^{-1}$

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

(used in data book)

Rotational Spectrum

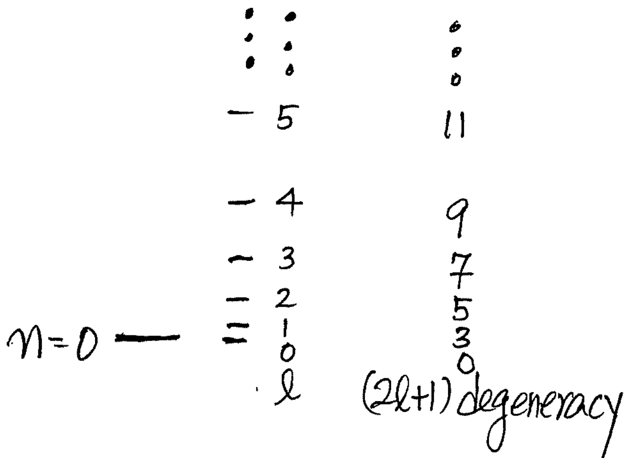
- Dips in Transmission due to absorption
- Dips are equally spaced

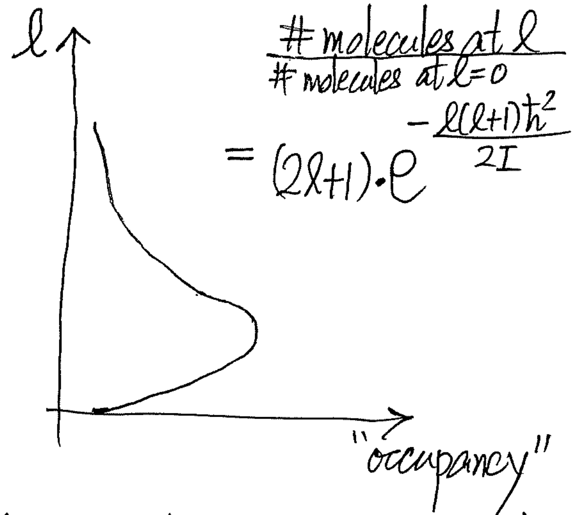


- Why do the dips have different magnitudes?
- Due to different #'s of molecules in rotational levels

Rotational states [Thermal Physics]

(microwave frequencies)($\sim 10^{-3}$ eV)



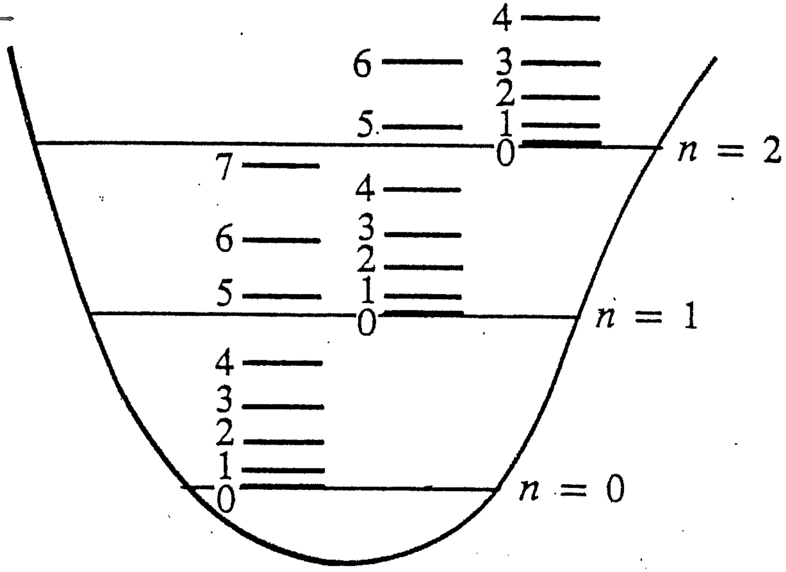


$$\frac{\#\text{ molecules at } l}{\#\text{ molecules at } l=0} = (2l+1)\cdot e^{-\frac{l(l+1)\hbar^2}{2I}}$$

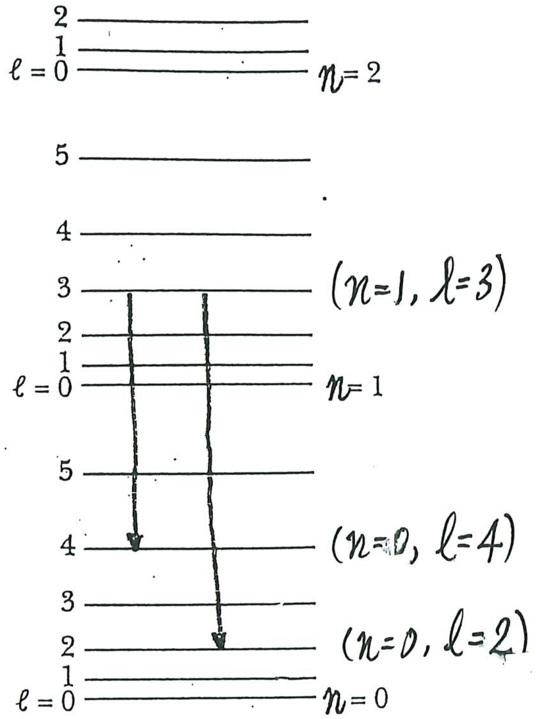
- For rotational states (belonging to vibrational ground state), molecules occupy a few rotational states at room temp.

L. Vibrational- Rotational Spectrum

- Experiments in frequency range involving transitions between vibrational levels (e.g. $n=0 \leftrightarrow n=1$) [and rotational levels are also involved]



Comes from transitions between rotational levels (recall $\Delta l = \pm 1$) belonging to different vibrational levels (recall $\Delta n = \pm 1$) in the same electronic level.



The rotation–vibration levels for a typical molecule. Note that the vibrational levels are separated by much larger energies so that a complete rotational spectrum can be associated with each vibrational level.

[From Serway et.al., "Modern Physics"]

Selection Rules

$\Delta n = \pm 1$ (for vibrational levels)

[molecule's dipole moment must vary as nuclei vibrate]

physics here!

$\Delta \ell = \pm 1$ (for rotational levels)

- From $(n, \ell) \rightarrow (n-1, \ell+1)$ [allowed]

$$E_{photon} = \hbar\omega - (\ell+1)\frac{\hbar^2}{I} \quad (\ell = 0, 1, 2, \ldots)$$

- From $(n, \ell) \rightarrow (n-1, \ell-1)$ [allowed]

$$E_{photon} = \hbar\omega + (\ell+1)\frac{\hbar^2}{I} \quad (\ell = 0, 1, 2, \ldots)$$

(40)

Aside: Transitions involving $n' \leftrightarrow n$ involve

$$\int \underbrace{\phi_{n'}^{*}(r-R_0)}_{\text{oscillator state } n'} \left[-\vec{\mu}\cdot\vec{\mathcal{E}}_0\right] \underbrace{\phi_n(r-R_0)}_{\text{oscillator state } n}\, dr \cdot \left[\text{integral for } \Theta, \Phi\right]$$

if $\vec{\mu}$ = constant (permanent dipole), $\int \phi_{n'}^{*}\, \phi_n \, dr = \underline{\underline{0}} \quad (n \neq n')$ oscillator physics

Need $$\vec{\mu} \approx \underbrace{\vec{\mu}(R=R_0)}_{\text{constant}} + \underbrace{\left.\frac{d\vec{\mu}}{dR}\right|_{R=R_0}}_{\text{electric dipole changes as } R \text{ vibrates about } R_0 \neq 0} \cdot (R-R_0)$$

then

$$\left.\frac{d\vec{\mu}}{dR}\right|_{R=R_0} \int \phi_{n'}^{*}(r-R_0)\,(R-R_0)\,\phi_n(r-R_0)\,dr$$

$$\propto \int \phi_{n'}^{*}(x)\cdot x \cdot \phi_n(x)\,dx \neq 0 \text{ only for } \Delta n = \pm 1$$

Also Needs molecule to have <u>varying $\vec{\mu}$ as it vibrates</u>

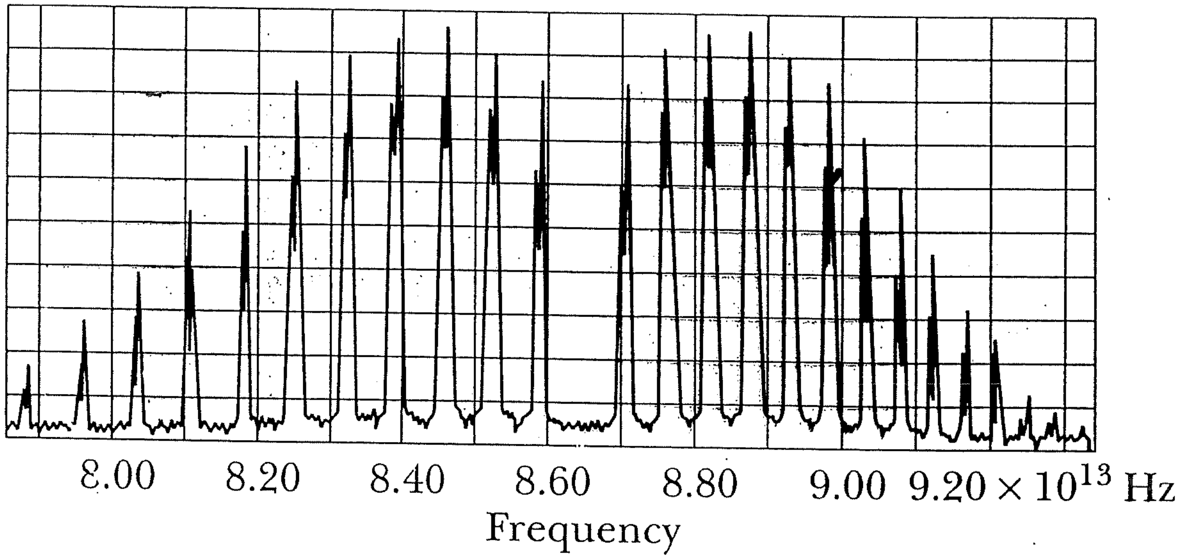
∴ Transitions involving $n \rightarrow n-1$ vibrational levels, E_{photon} are:

$$\boxed{E_{photon} = \hbar\omega \mp \frac{(l+1)\hbar^2}{I} \quad , \; l = 0, 1, 2, \dots} \tag{41}$$

- Vibrational-Rotational Spectrum (of diatomic molecules)
  - Many lines equally spaced on either side of $\hbar\omega$ of spacing $\frac{\hbar^2}{I}$
  - No line at $\hbar\omega$

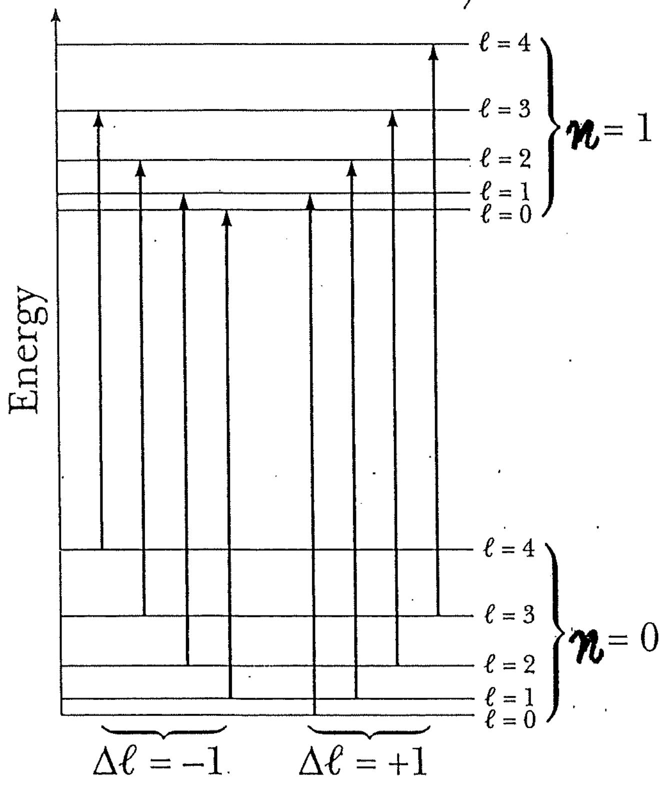
[HCl molecule]

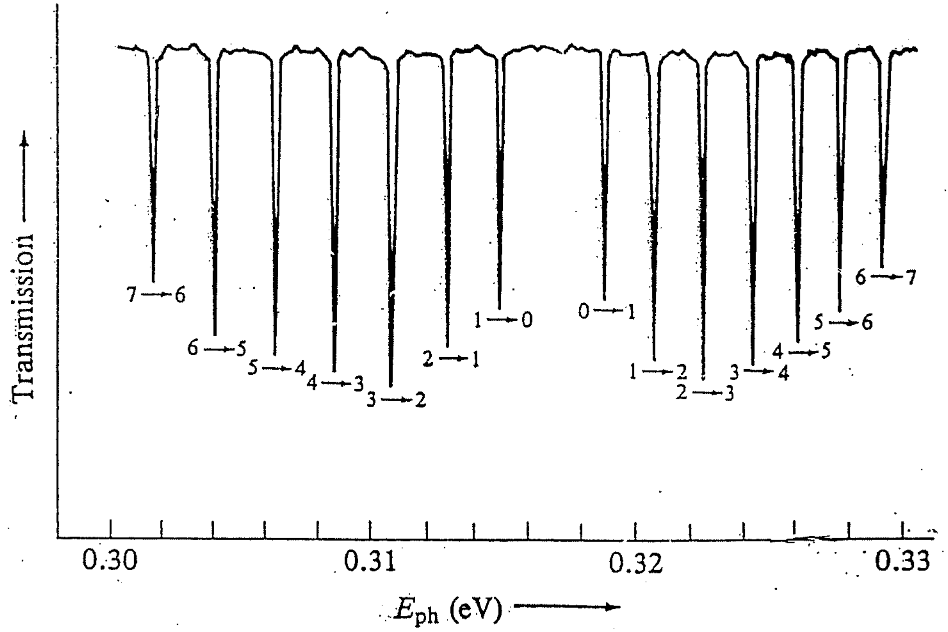
[Absorption spectrum of HCl]



Note: freq. ~ 10^{13}–10^{14} Hz [IR]

Schematically

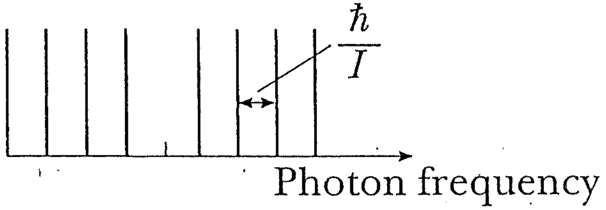




HBr

Note energy scale

Vibrational–rotational absorption spectrum of HBr. All lines correspond to the vibrational transition $n = 0 \Rightarrow 1$, with various different rotational transitions $l \leftrightarrow l + 1$, as indicated.



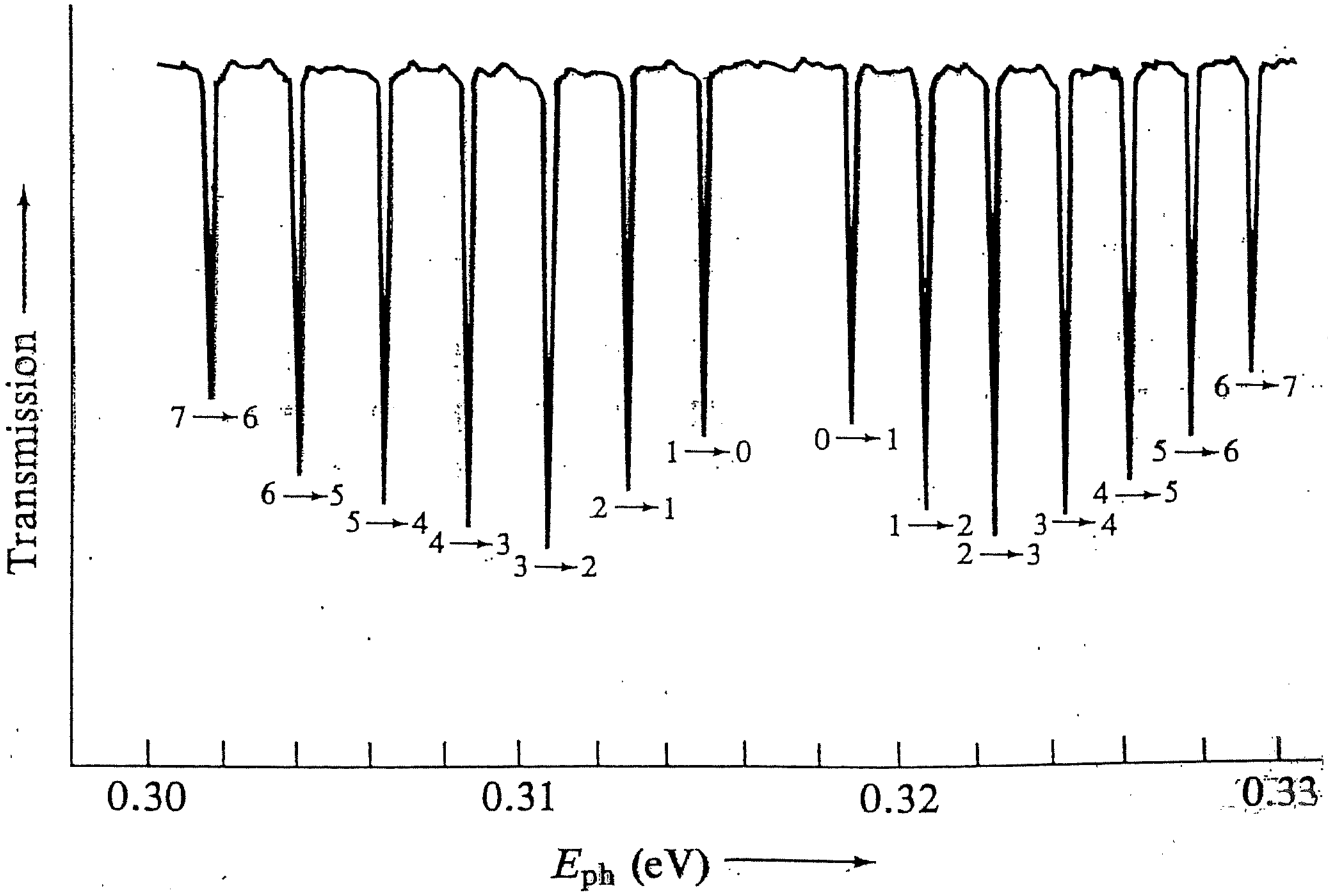
"gap" = $\hbar\omega$

P branch ← → R branch

(a) Read out mid-gap $\Rightarrow \hbar\omega \Rightarrow \omega = \sqrt{\frac{k}{\mu}} \Rightarrow$ Spring constant k
[k reflects bond strength]

(b) Read out equal spacing $\Rightarrow \frac{\hbar}{I} \Rightarrow I \Rightarrow R_0$
[R_0 gives bond length]

An Example: HBr Vibrational-Rotational Spectrum



Extract information

- Identify Mid-gap energy

  ~ 0.317 eV

- What does it mean?

  $\hbar\omega$ with $\omega = \sqrt{\frac{k}{\mu}}$

- What is μ?

$$\frac{1}{\mu} = \frac{1}{M_H} + \frac{1}{M_{Br}} \approx \frac{1}{M_H}$$

[can do it accurately]

- Obtain ω and "spring constant" k (stiffness of bond)

$$k = \mu\omega^2 \sim 2.4 \times 10^3 \frac{\text{eV}}{(\text{nm})^2}$$

(Ex: Be careful of units)

- Identify spacing between equally spaced lines/dips in spectrum

~ 0.002 eV (Ex: Can read out energy over several lines)

- What does spacing mean?

$$\text{spacing} = \frac{\hbar^2}{I} \Rightarrow I = \frac{\hbar^2}{\text{spacing}} \quad ; \quad I = \mu R_0^2$$

- Estimate Bond length R_0?

$$R_0 = \sqrt{\frac{I}{\mu}} \approx \sqrt{\frac{I}{m_H}} = \sqrt{\frac{\hbar^2}{m_H \cdot (\text{spacing})}} \approx \underbrace{0.14\,\text{nm}}_{\text{typical bond length}}$$

(Ex: Be careful of units)

M. Characteristic Vibrational Frequencies of Molecules

- Only with good resolution can we see the details in Vibrational-rotational spectrum
- Lower resolution: see some structure at $h\nu$ [rotational details are $\sim 10^{-2}$ times smaller]

Fundamental Vibrational Frequencies and Effective Force Constants for Some Diatomic Molecules

diatomic molecules

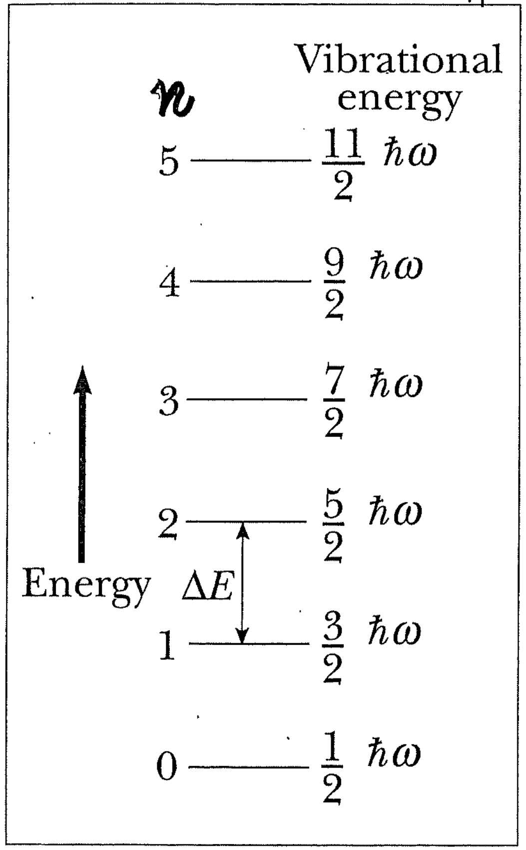
Molecule	Frequency (Hz), $n = 0$ to $n = 1$	Force Constant (N/m)
HF	8.72×10^{13}	970
HCl	8.66×10^{13}	480
HBr	7.68×10^{13}	410
HI	6.69×10^{13}	320
CO	6.42×10^{13}	1860
NO	5.63×10^{13}	1530

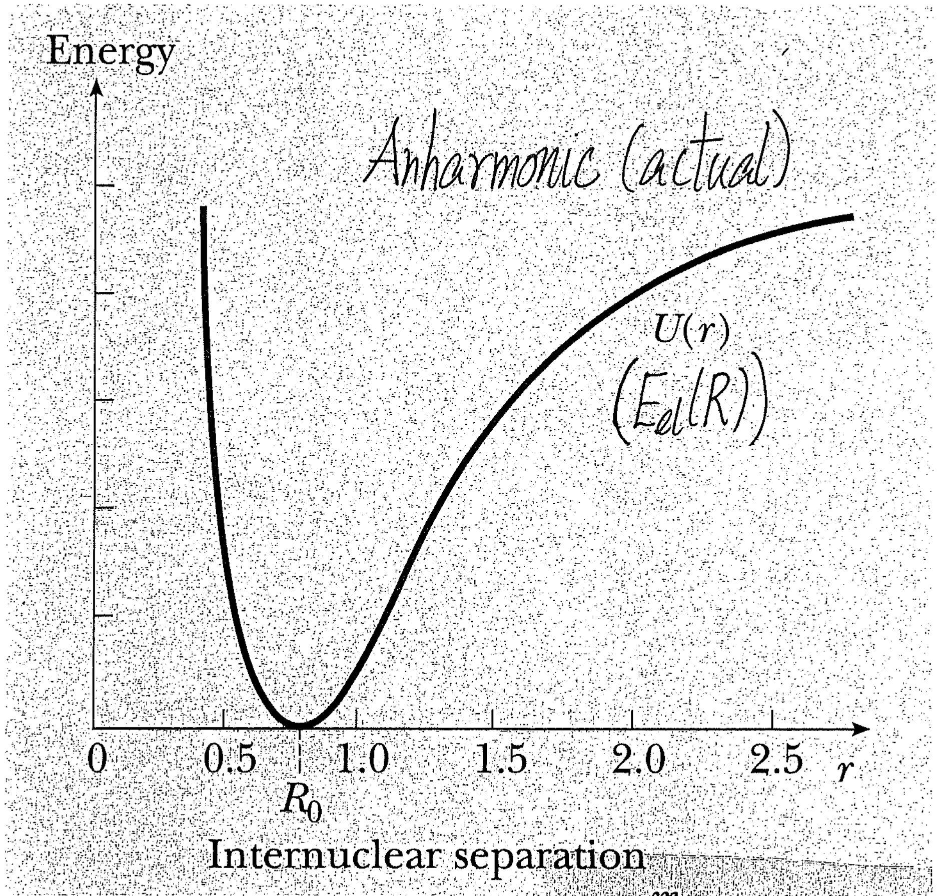
From G. M. Barrows, *The Structure of Molecules*, New York, W. A. Benjamin, 1963.

all of the order of 0.3eV

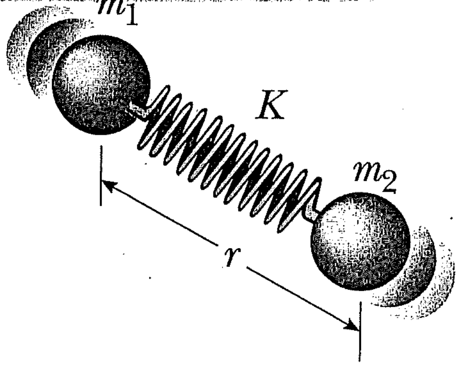
Anharmonic Effect (Optional)

Strictly Parabolic (an approximation)

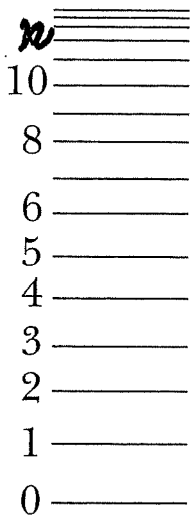




(a)



Actual



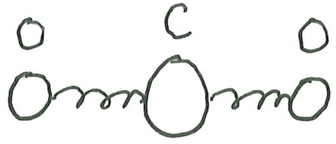
(b)

N. Why CO_2 and H_2O are greenhouse gases but O_2, N_2 are not?

- O_2 , N_2 : No change in electric dipole moment as nuclei vibrate
- How about CO_2 and H_2O?

polyatomic molecules

CO_2 : linear molecule



[3D system]

Find normal modes and normal mode frequencies

different vibrational modes,

some modes have varying dipole moment

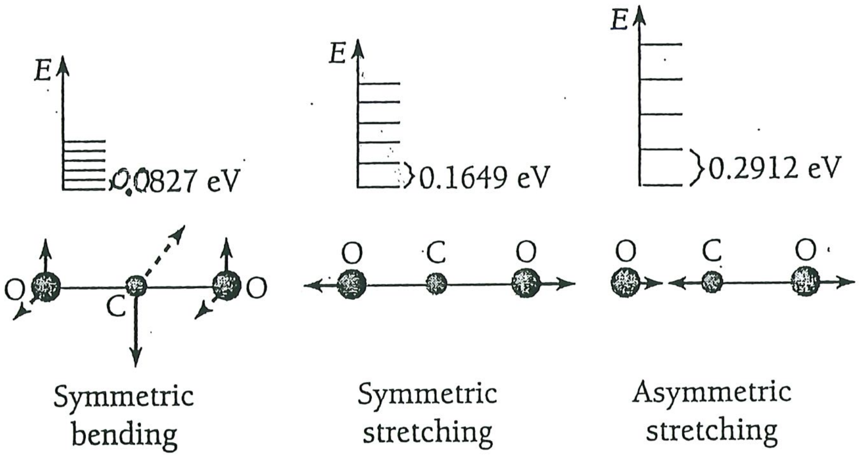
[IR active modes]

[absorb/emit IR]

CO_2 : Normal Modes

0.0827 eV ↕ 667 cm^{-1} ⇝

2 degenerate modes ⇝



Symmetric bending

Symmetric stretching

Asymmetric stretching

The normal modes of vibration of the CO_2 molecule and the energy levels of each mode. The symmetric bending mode can occur in two perpendicular planes.

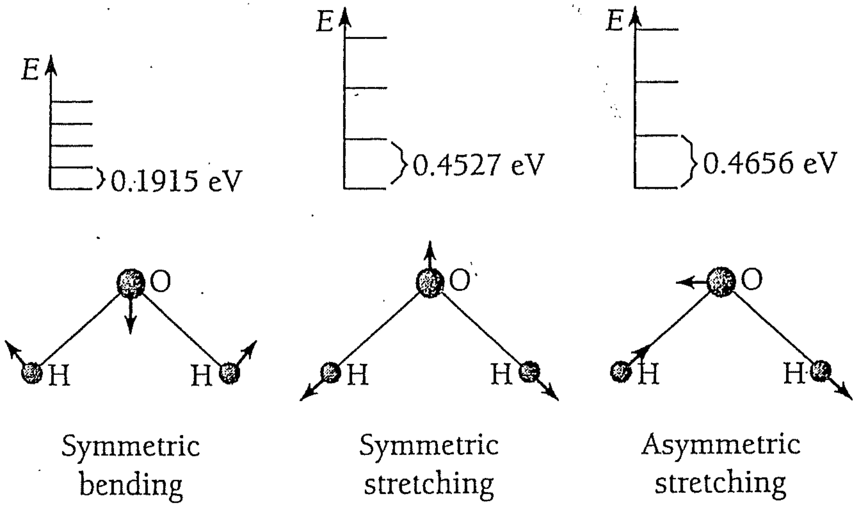
(different normal mode frequencies)
(4 vibrational modes)

- Symmetric Bending Modes of CO_2 are IR active
- This is why CO_2 in atmosphere can keep us warm! (QM keeps us warm)
- But $\underbrace{\text{too much } CO_2}_{\text{(human activities)}}$ in atmosphere will be bad

  [don't blame QM]

H_2O : Normal Modes (H_2O is not[+] a linear molecule)

0.1915 eV
⇕
~1540 cm^{-1}



The normal modes of vibration of the H_2O molecule and the energy levels of each mode.

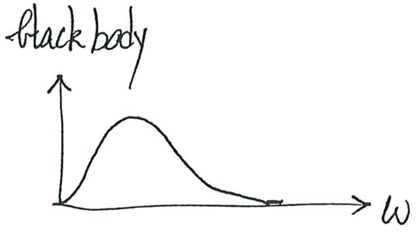
∴ 3 normal modes

[+] Why does it matter? Your classical mechanics in work!

CO_2, H_2O : Greenhouse Gases

- ▨ "$\underbrace{\text{Short}}_{\text{wavelengths}}$ Waves in, $\underbrace{\text{Long}}_{\text{wavelengths}}$ Waves out"
  - ▨ Sun : $T \sim 5800\,K$

    $\Rightarrow$ Black body radiation

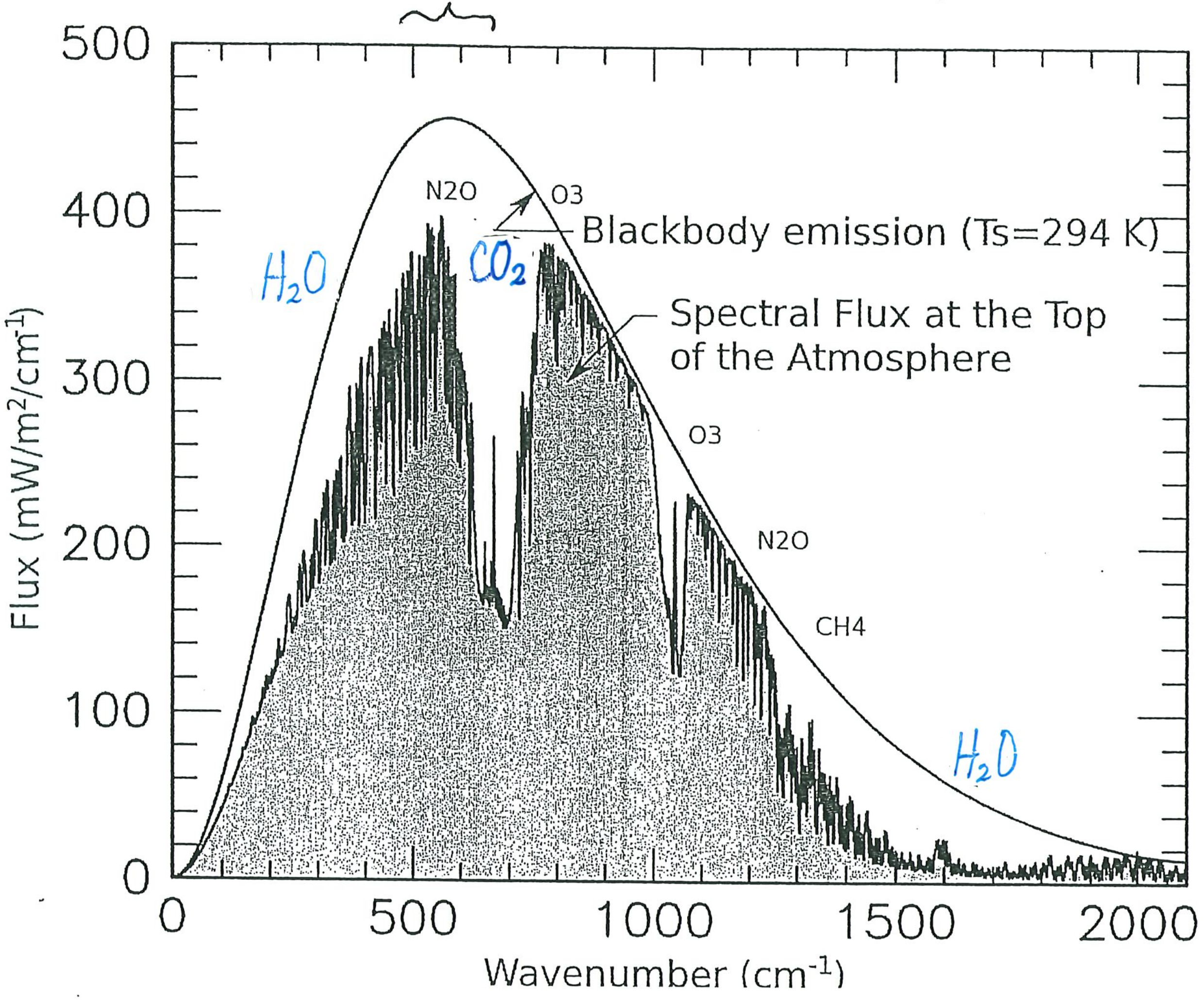
    (peaks at ~ visible range) [our eyes evolve to fit to the Sun's spectrum!]
  - ▨ Radiation comes in, warms the Earth

    $[\sim 1360\ \text{kW}/\text{m}^2]$ (Solar constant)
  - ▨ Earth : $T \sim 300\,K$

    $\Rightarrow$ Black body radiation

    (peaks at ~ IR (wavenumber $\sim 600\ \text{cm}^{-1}$))

peak (~600 cm^{-1}) of Earth's radiations



"Greenhouse Effect"

- CO_2 suppresses heat (IR) loss (keeps us warm)
- But we don't want to be too warm

$$\overset{\uparrow}{O} = \underset{\downarrow}{C} = \overset{\uparrow}{O}$$

CO_2: bending vibrational modes† $\left\{ \begin{array}{l} \text{—— } n=1 \\ \quad \updownarrow \sim 670\ cm^{-1} \text{ (Symmetric Bending)} \\ \text{—— } n=0 \end{array} \right.$

H_2O: absorbs $\lesssim 400\ cm^{-1}$ (rotational modes)

- Earth's atmosphere:

~78% nitrogen⁺, ~20% oxygen⁺, ~0.9% argon

$\boxed{\sim 0.038\%\ CO_2}$ (~2010)

Records: ~1832: 0.028%
~1960: 0.032%
~1970: 0.033%
~1980: 0.034%
~1990: 0.035%
~2000: 0.037%

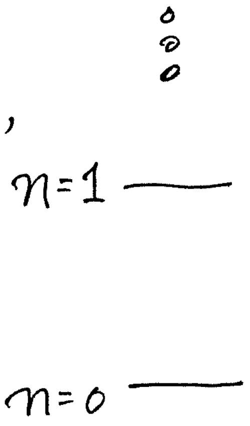
[Do human activities matter?]

[From Fayer, "Absolutely Small"]

⁺ How lucky we are that O_2 and N_2 are not IR active!

0. Summary on Molecular Spectrum

1/. Typically,



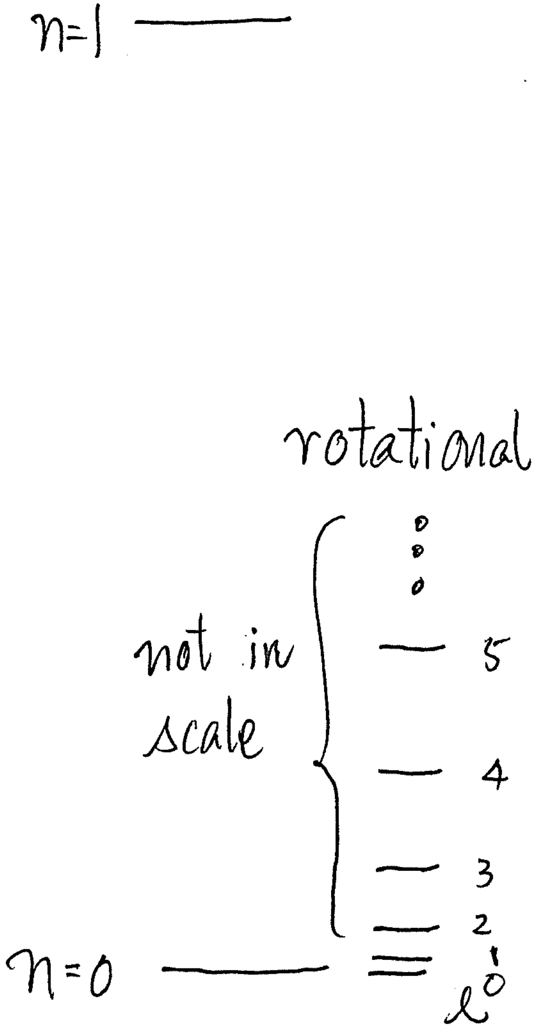
- Molecules at room temperature are in the lowest ($n=0$) vibrational state.

Reason: $\hbar\omega_c \sim 0.1$ eV (could be higher)

$kT \sim 0.024$ eV

- kT is insufficient to excite molecules to $n>0$.

2/. Typically,



kT can excite molecules to <u>different rotational levels</u> belonging to n=0 vibrational state

3/. Transitions: Molecule-Light Interaction

Selection Rules: $\Delta n = \pm 1$ (molecule has varying dipole moment as nuclei vibrate)

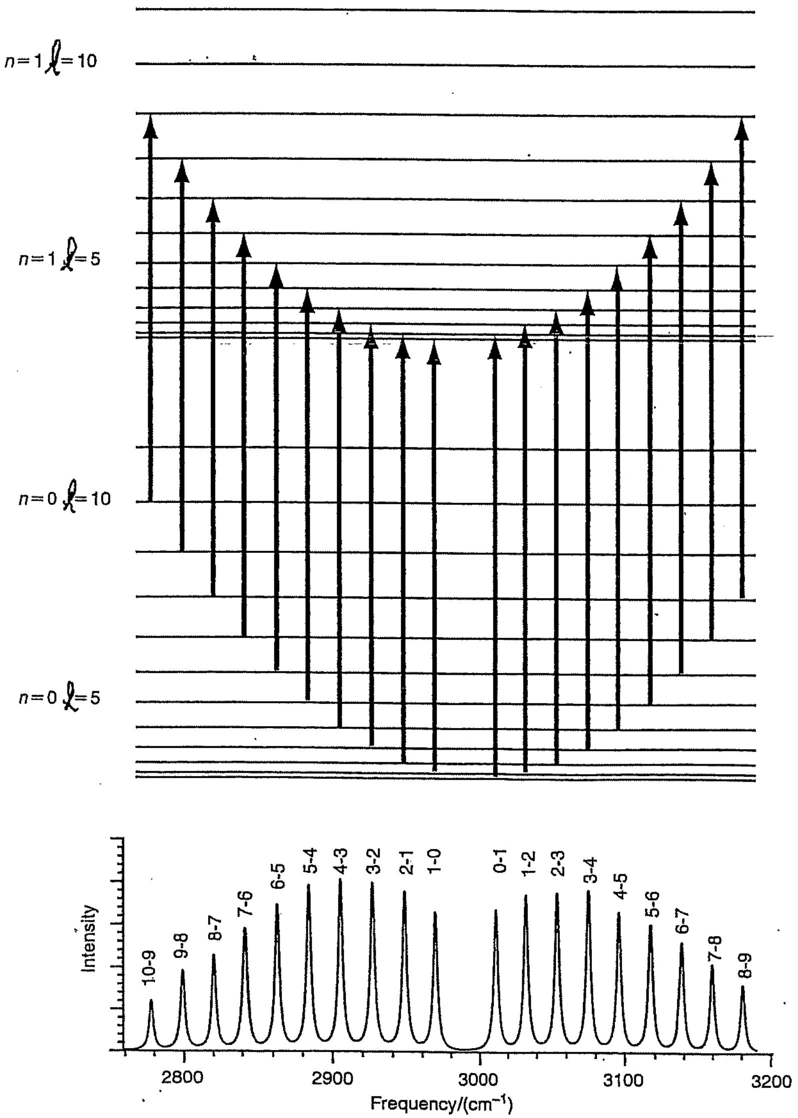
$\Delta l = \pm 1$ (molecule has permanent dipole moment)

4/. Rotational Spectrum

- microwave to far IR
- Does not involve change in n
- $\Delta l = \pm 1 \Rightarrow$ equally spaced spectral lines, with spacing being $\frac{\hbar^2}{I}$ OR $\frac{\hbar^2}{\mu R_0^2}$

$\Rightarrow$ can extract R_0 (bond length)

5/. Vibrational-Rotational Spectrum



- ☒ Gap in middle of spectrum
- ☒ Center of Gap gives $\hbar\omega$ (thus spring constant k and hence bond strength)
- ☒ spacing between lines gives $\frac{\hbar^2}{I}$ (thus bond strength)
- ☒ envelope : thermal occupation of rotational levels

6/. Applications

- Extract $\underbrace{R_0}$ and $\underbrace{k}$ from spectrum (see HBr example)

  bond length from $I = \mu R_0^2$

  bond strength from $\underbrace{\text{mid-gap}}_{\hbar\omega = \hbar\sqrt{\frac{k}{\mu}}}$ in Vibrational-Rotational spectrum

- Identify molecules out there

- Greenhouse gases

7/. Nobel Prizes award to Molecular Spectroscopy

1971 Nobel Chemistry Prize : G. Herzberg [author of textbooks]
1981 Nobel Physics Prize : A. L. Schawlow [laser spectroscopy]
1930 Nobel Physics Prize : C. V. Raman [Raman Spectroscopy]

Final Remarks

- What will happen in Visible/UV range?

Electronic Transitions

- When E_i^{el} changes, no selection rule applies on n anymore

- $E_0^{el}(n=0) \rightarrow E_1^{el}(n=0)$

  $E_0^{el}(n=0) \rightarrow E_1^{el}(n=1)$

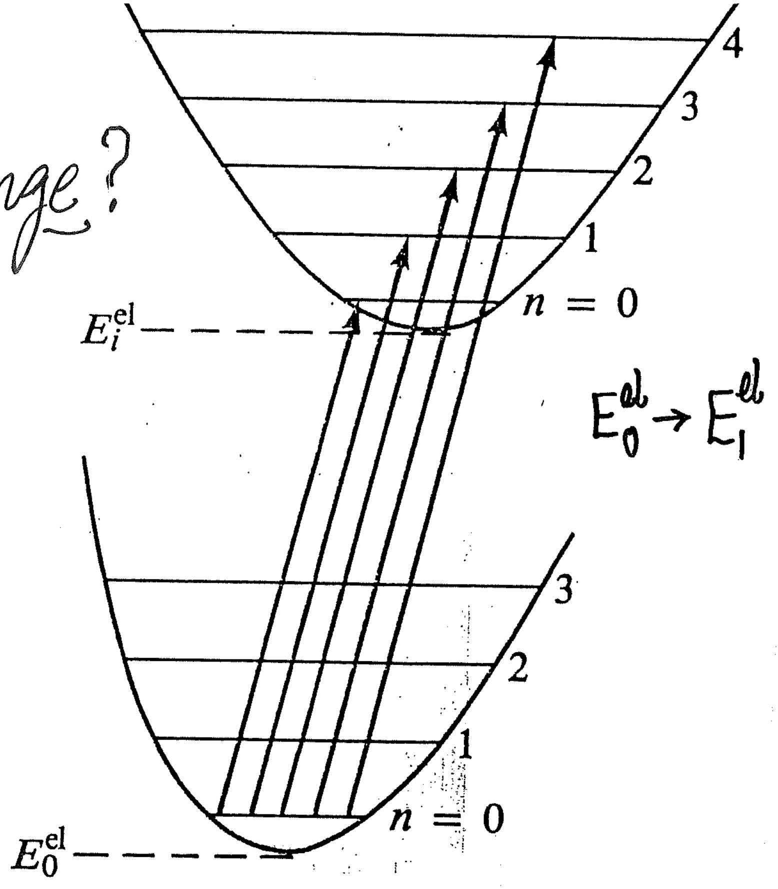
  $E_0^{el}(n=0) \rightarrow E_1^{el}(n=2)$

  ⋮

  Give bands in spectrum

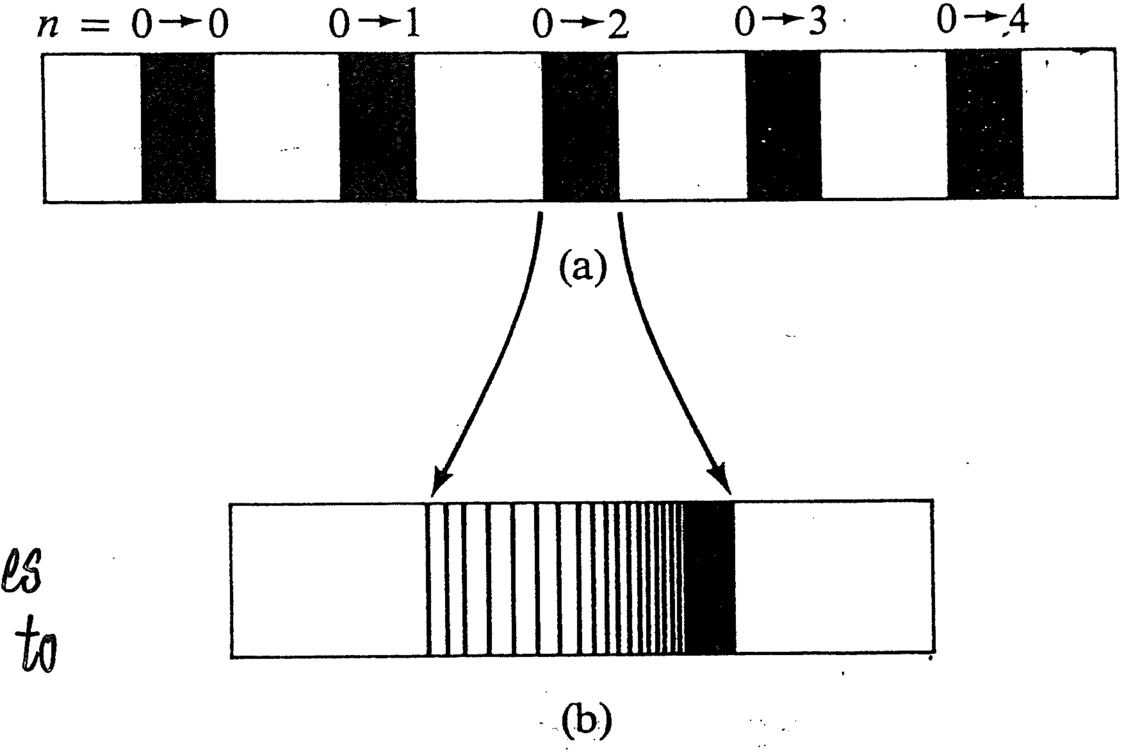
  ⇓

  Actually many lines in higher resolution due to rotational levels



Typical electronic transitions starting from the lowest electronic and vibrational levels. Since there is no selection rule on n in electronic transitions, many different transitions, $0 \rightarrow n$, ($n = 0, 1, 2, 3, \ldots$), are possible for any one final electronic level E_i^{el}.

Electronic Absorption spectrum



- n indicates vibrational levels
- Series of lines corresponding to changes of rotational levels

In UV/visible range