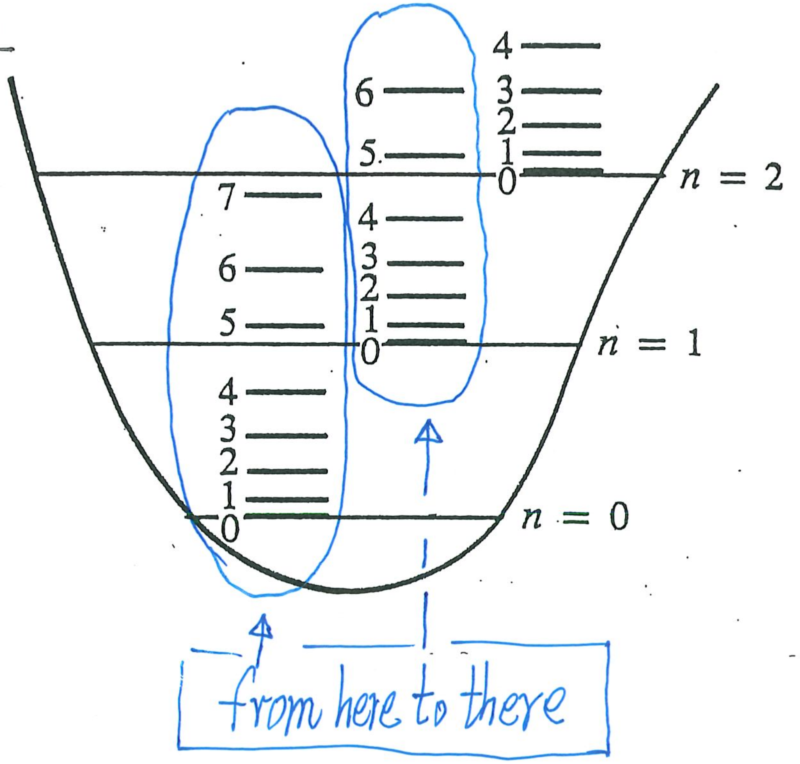
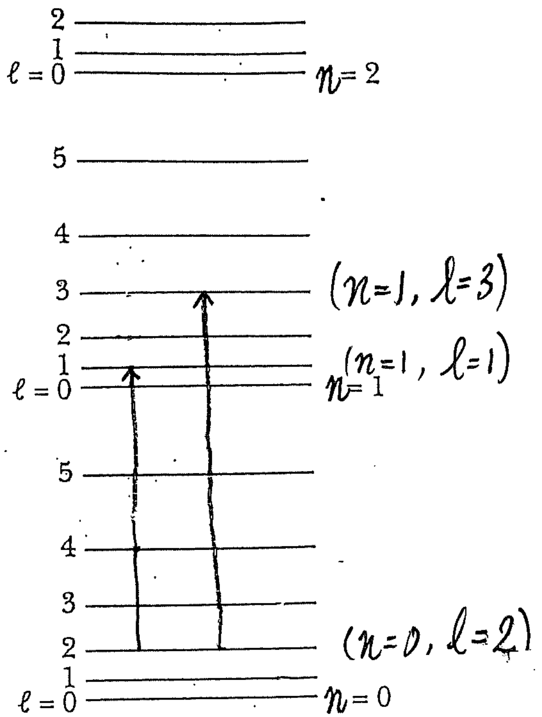
J. Vibrational-Rotational Spectrum

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

Higherresolution seeing structures of 10^{-3}-10^{-4} eV in 0.1 eV



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)

physics here!

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

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

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

$$E_{\substack{\text{photon}\\(\text{absorbed})}} = \hbar\omega + (l+1)\frac{\hbar^2}{I} \qquad (l = 0, 1, 2, \ldots) \quad (45)$$

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

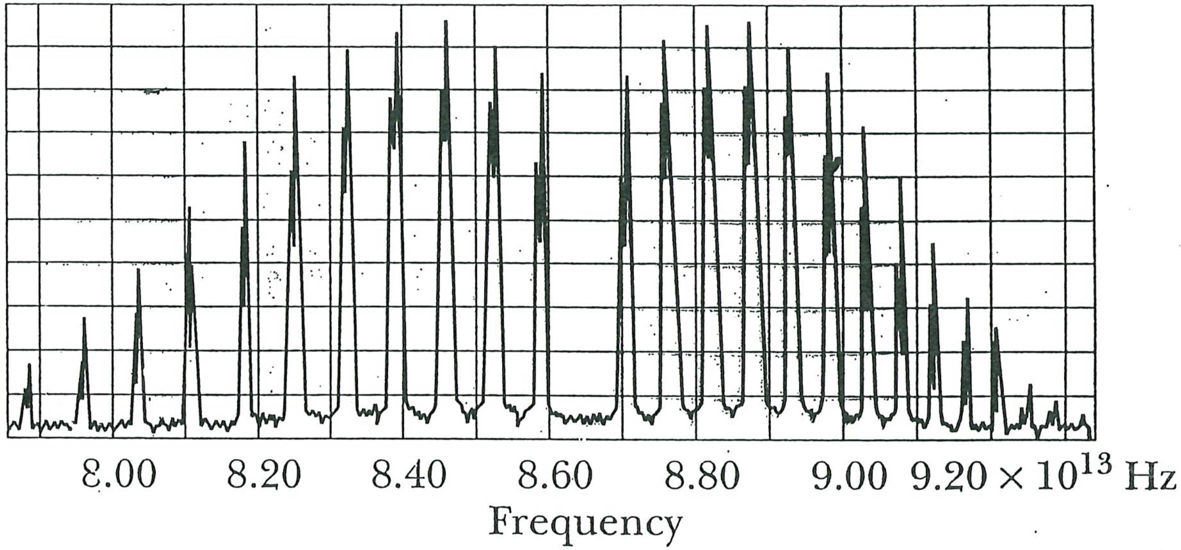
$$E_{\substack{\text{photon}\\(\text{absorbed})}} = \hbar\omega - l\frac{\hbar^2}{I} \qquad (l = 1, 2, \ldots)$$

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

$$\boxed{E_{photon} = \hbar\omega \mp \frac{(\ell+1)\hbar^2}{I}, \quad \ell = 0, 1, 2, \cdots} \tag{46}$$

- 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 $\hbar\omega$

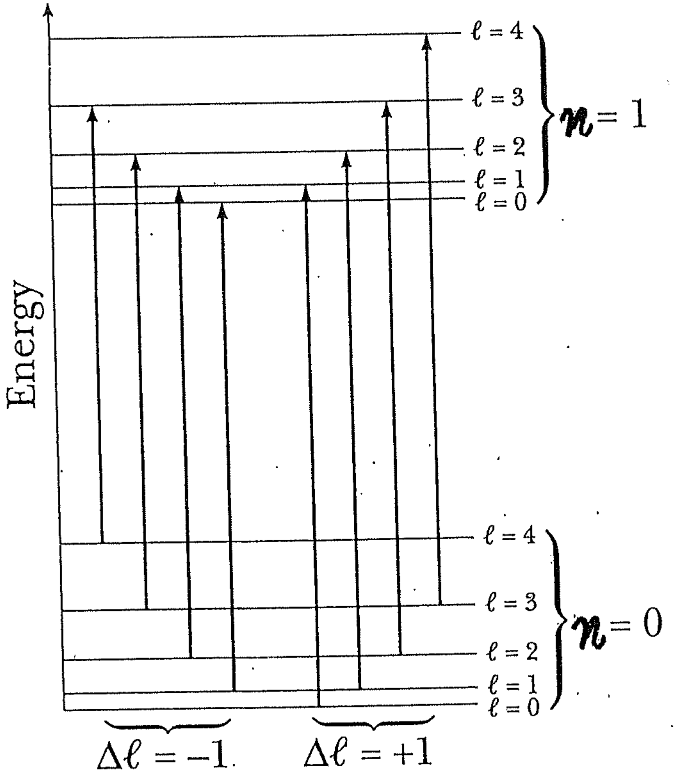
[HCl molecule]

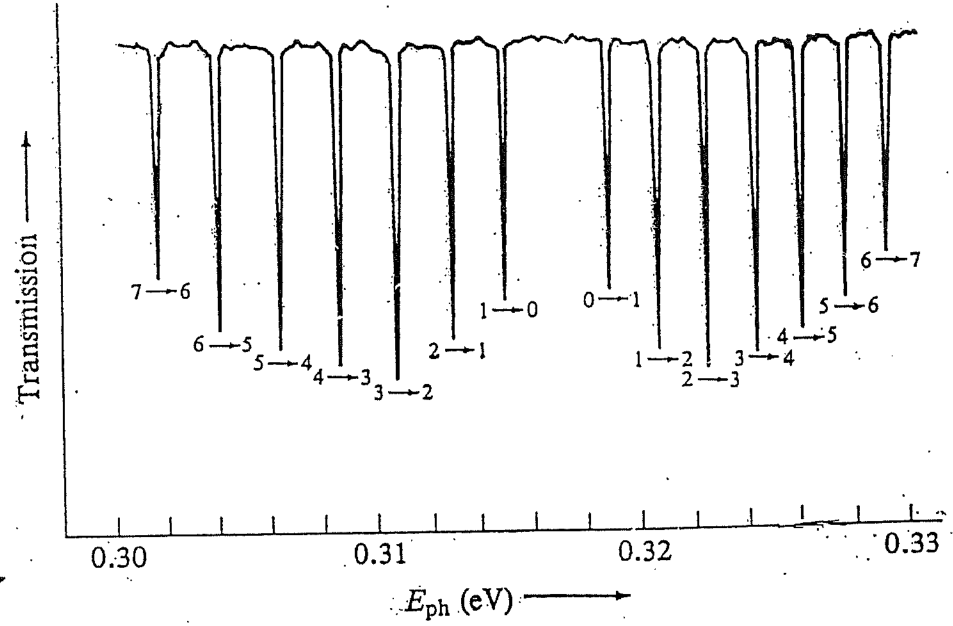


[Absorption spectrum of HCl]

Note: freq. ~ 10^{13} - 10^{14} Hz [IR]

Schematically

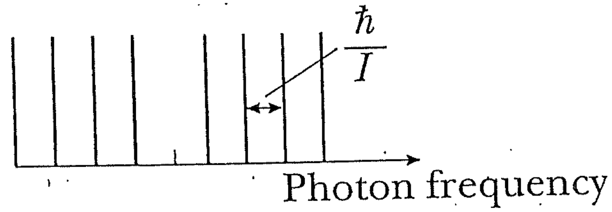




Vibrational–rotational absorption spectrum of HBr. All lines correspond to the vibrational transition $n = 0 \Rightarrow 1$, with various different rotational transitions $l \leftrightarrow l + 1$, as indicated.

Note energy scale

HBr



"gap" = ħω

P branch ← → R branch

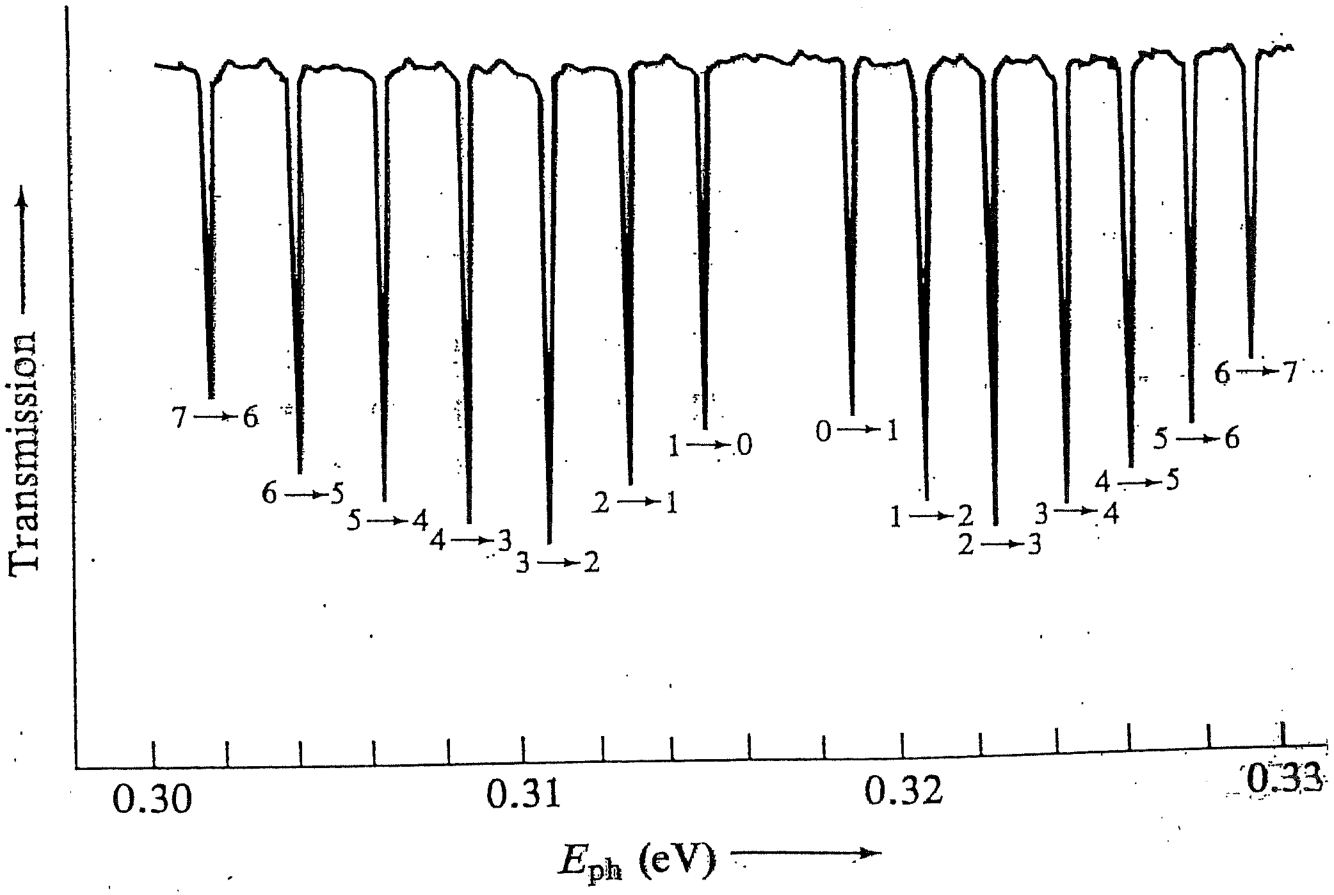
(a) Read out mid-gap ⇒ ħω ⇒ $\omega = \sqrt{\frac{k}{\mu}}$ ⇒ Spring constant k

[k reflects bond strength]

(b) Read out equal spacing ⇒ $\frac{\hbar}{I}$ ⇒ I ⇒ R_0

[R_0 gives bond length]

An Example: HBr Vibrational-Rotational Spectrum



↑ Read out mid-gap energy

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)

$$k = \mu\omega^2 \sim 2.4 \times 10^3 \, \frac{\text{eV}}{(\text{nm})^2} \quad \text{(Ex: Be careful of units)}$$

- Identify spacing between equally spaced lines/dips in spectrum

$$\sim 0.002 \, \text{eV} \qquad \text{(Ex: Can read out energy over several lines)}$$

- What does spacing mean?

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

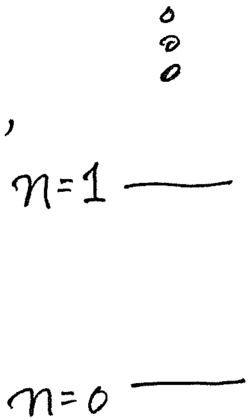
- Estimate Bond length R_0?

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

(1.4 Å)

K. Summary on Molecular Spectrum

1/. Typically,

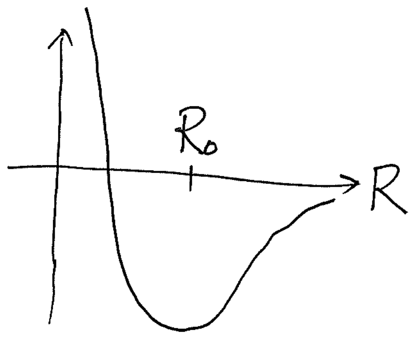


- Molecules at room temperature are in the <u>lowest (n=0) vibrational state</u>.

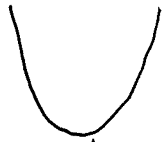
Reason: $\hbar\omega_c \sim 0.1$ eV (could be higher)

$kT \sim 0.024$ eV

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



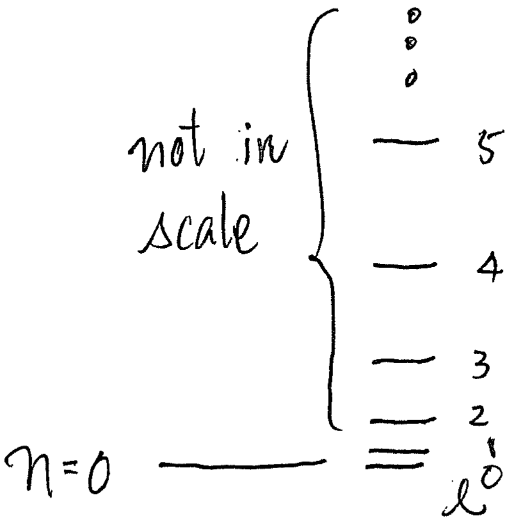
[illegible]



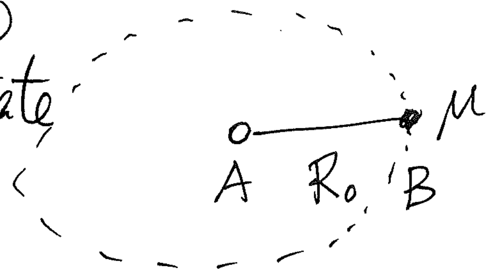
oscillator physics

2/. Typically, $n=1$ ———

rotational levels (10^{-4}-10^{-3} eV)



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



rotor physics

3/. Transitions: Molecule-Light Interaction

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

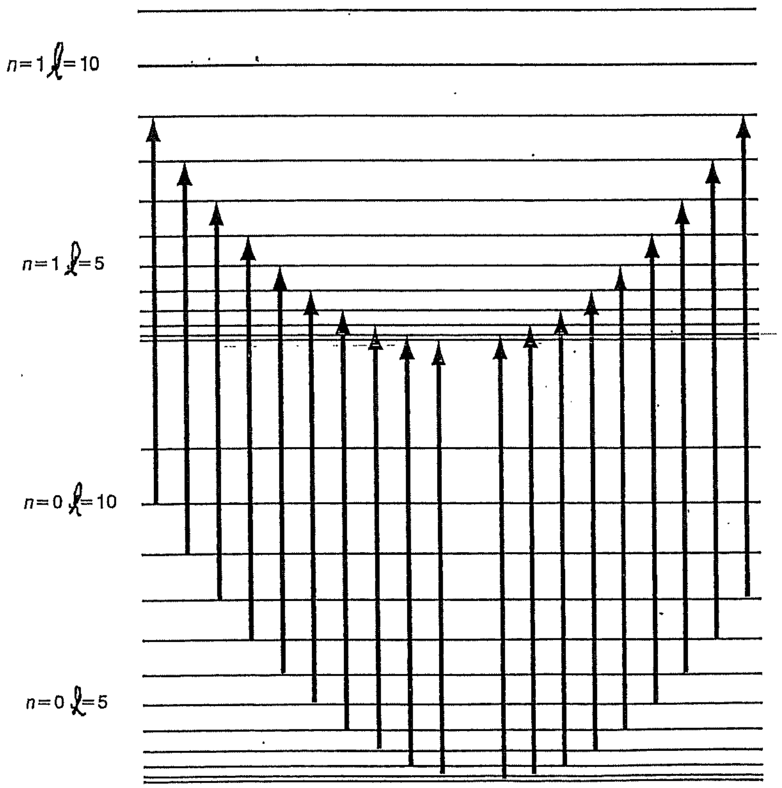
$\Delta l = \pm 1$ (molecule has permanent dipole moment)

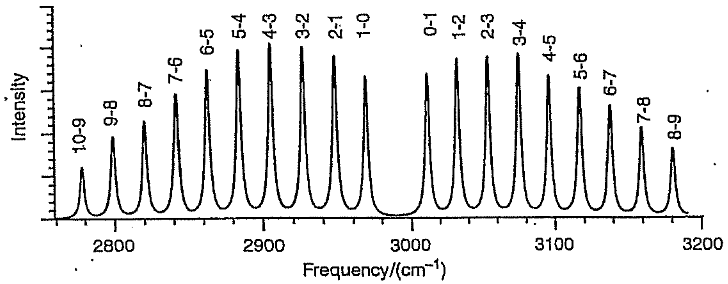
4/. Rotational Spectrum

- 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 $\underbrace{R_0}_{\text{bond length from } I=\mu R_0^2}$ and $\underbrace{k}_{\text{bond strength}}$ 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]

8/. Spectroscopy is an important technique for studying atoms, molecules, solids, materials science, ... It is applied to different areas including physics, chemistry, biology, medicine, astronomy, art, remote sensing ...

Further Reading

R. Kakkar, Atomic and Molecular Spectroscopy: Basic Concepts and Applications
[you know ~60% of the 9-chapter book]

S. Svanberg, Atomic and Molecular Spectroscopy: Basic aspects and practical applications
[you know ~30% of the 500-page book]

OR go ask Prof. WANG Dajun in the Department

Final Remarks (Optional)

- What will happen in $\underbrace{\text{Visible/UV range}}_{\text{Electronic Transitions}}$?
  - When E_i^{el} changes, no selection rule applies on n anymore
  - $E_0^{el}(n=0) \to E_1^{el}(n=0)$

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

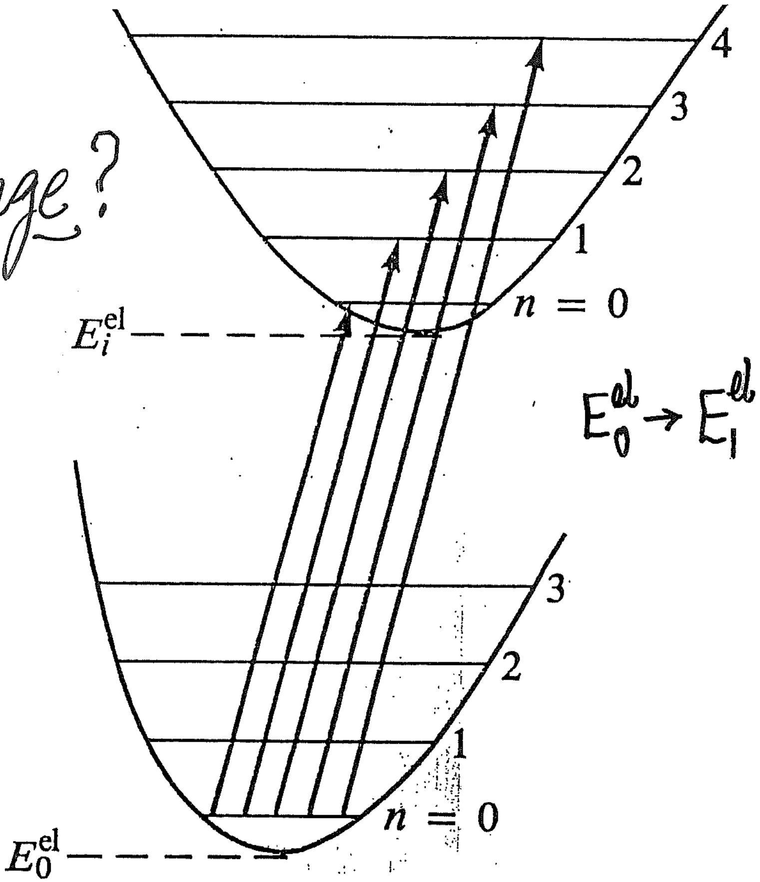
    $E_0^{el}(n=0) \to E_1^{el}(n=2)$

    $\vdots$

    Give bands in spectrum

    $\Downarrow$

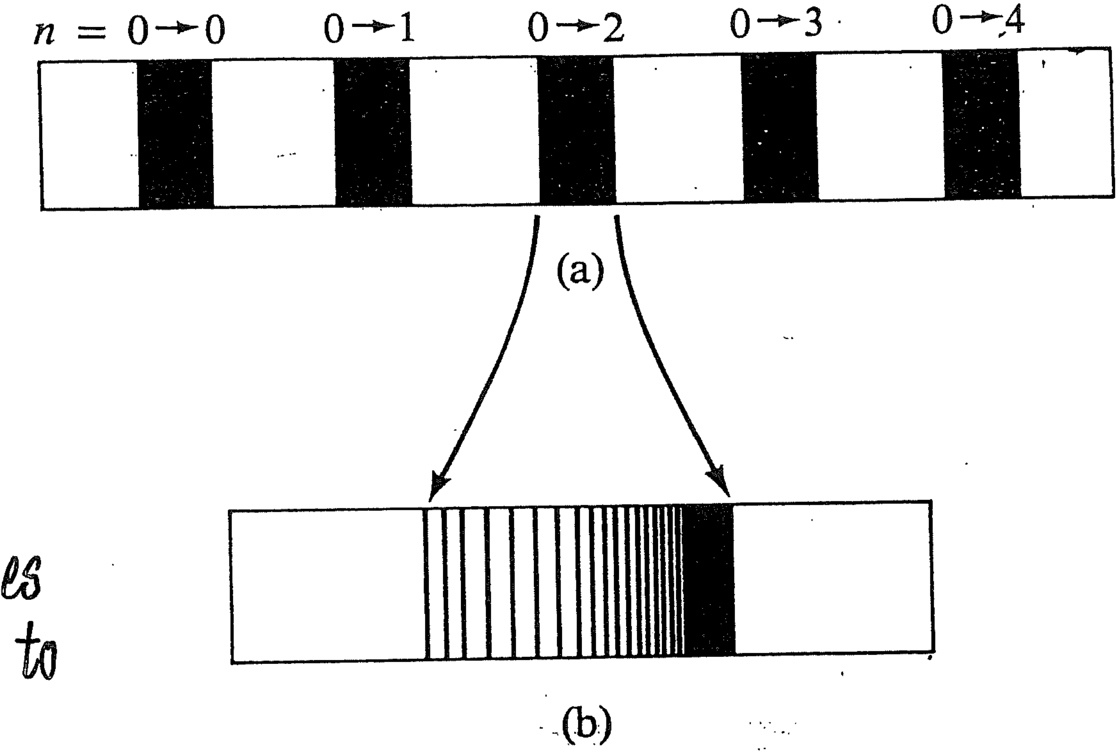
    Actually many lines in higher resolution due to rotational levels



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, $0 \to n$, ($n = 0, 1, 2, 3, \ldots$), 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