Electronic spectra

Electronic spectra of diatomic molecule:

According to Born – Oppenheimer approximation Electronic, vibrational and rotational energies are independent of each other.

i.e., $\boxed{\boldsymbol{E_{total} = E_{elec} + E_{vib} + E_{rot}}}$

Change in the total energy is $\Delta E_{total} = \Delta E_{elec} + \Delta E_{vib} + \Delta E_{rot}\ Joules$

$$\Delta\varepsilon_{total} = \Delta\varepsilon_{elec} + \Delta\varepsilon_{vib} + \Delta\varepsilon_{rot}\ cm^{-1}$$

$$\boxed{\Delta\varepsilon_{elec} \approx 10^3 \times \Delta\varepsilon_{vib} \approx 10^3 \times \Delta\varepsilon_{rot}}$$

Thus, vibrational changes will produce a **coarse structure** and rotational changes will produce a "**fine structure**" on the electronic spectra.

Pure rotation is shown only by molecules possessing a **permanent dipole moment**. Vibrational spectra require a **change of dipole moment** during vibration.

However **electronic spectra are given by all molecules**, since changes in the electronic distribution are always accompanied by a dipole change.

Thus, homonuclear molecules ($H_2, N_2, \ldots$) gives electronic spectra and show vibration and rotation.

Thus, Structure of homonuclear molecular may be derived from electronic spectra.

Vibrational course structure: Progressions

Ignoring rotational changes, we get

$E_{tot} = E_{elec} + E_{vib}\ J$

$\varepsilon_{tot} = \varepsilon_{elec} + \varepsilon_{vib} \quad cm^{-1}$

$$\boxed{\varepsilon_{tot} = \varepsilon_{elec} + \left(v + \tfrac{1}{2}\right)\bar{\omega}_e - x_e\left(v + \tfrac{1}{2}\right)^2 \bar{\omega}_e} \; cm^{-1} \qquad v = 0,1,2, \dots$$

Energy levels of this equation are shown in **fig 4.1**

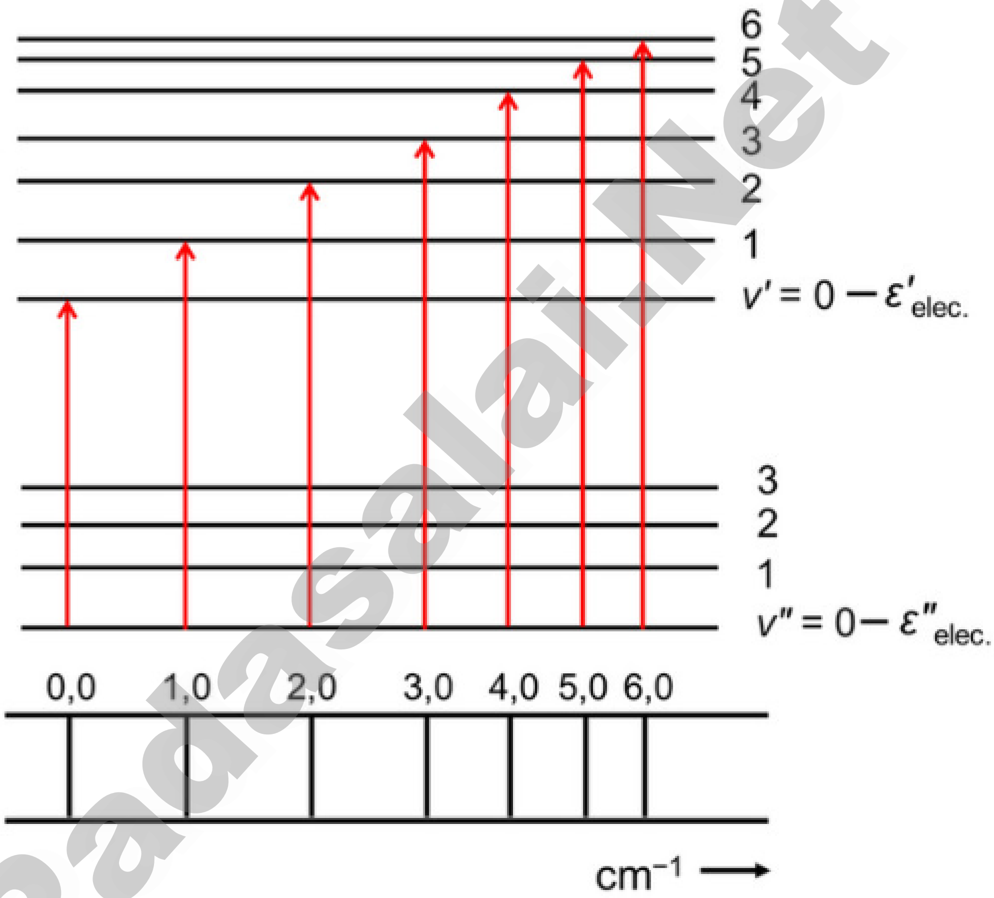


Figure 4.1. Schematic illustration of the vibrational "coarse structure" of a band during electronic transition (due to absorption) from the ground ($v'' = 0$) state to a higher state

- The spectral lines are called "**band**" because they appear broad and diffuse at low resolution and are labelled conventionally (v', v'').
- **There is no selection rule for v when a molecule undergoes electronic transition,** i.e. every transition $v'' \rightarrow v'$ has some probability of occurring.

- Because all molecules exist in the lowest vibrational state ($v = 0$), only transitions originating from this state $\{(0,0),(1,0),(2,0) etc.\}$ ($Figure$ 4.1) will have appreciable intensities.
- These lines are called v' **progression** because the value of v increases by 1 for each line in the set.

The diagram **fig 4.1** shows that the lines in a band crowd together more closely at high frequencies due to anharmonicity.

The wave number of spectral lines can be written as

$$\bar{\nu}_{spec} = (\varepsilon' - \varepsilon'') + \left\{\left(v' + \frac{1}{2}\right)\bar{\omega}_e' - x_e'\left(v' + \frac{1}{2}\right)^2 \bar{\omega}_e'\right\} - \left\{\left(v'' + \frac{1}{2}\right)\bar{\omega}_e'' - x_e''\left(v'' + \frac{1}{2}\right)^2 \bar{\omega}_e''\right\}$$

For* (0, 0) *transition

$$\bar{\nu}_{spec} = (\varepsilon' - \varepsilon'') + \left\{\left(\frac{1}{2}\right)\bar{\omega}_e' - x_e'\left(\frac{1}{2}\right)^2 \bar{\omega}_e'\right\} - \left\{\left(\frac{1}{2}\right)\bar{\omega}_e'' - x_e''\left(\frac{1}{2}\right)^2 \bar{\omega}_e''\right\}$$

And provided some half dozen lines can be observed in the band, values for $\omega_e', x_e', \varpi_e''$ and x_e'' and $(\varepsilon' - \varepsilon'')$ can be calculated.

- $\boldsymbol{\varepsilon' - \varepsilon''} \rightarrow$ separations between electronic states.

From the band spectrum, the vibrational frequency and anharmonicity constant in the ground state **(ϖ_e'' and x_e'')**, and excited electronic state **(ω_e' *and* x_e')** are calculated.

The information about excited states is valuable since excited states are unstable and the molecule exist in them for very short time.

Rotational Fine structure of Electronic – Vibration spectra:

Under high resolution each line in the electronic spectrum consists of a set of closely spaced lines. These lines caused by the rotational fine structure.

Taking the rotational energy into account,

$\varepsilon'_t = \varepsilon'_{el} + \varepsilon'_v + B'J'(J'+1)\ cm^{-1}$; $J' = 0,1,2,..$

$\varepsilon''_t = \varepsilon''_{el} + \varepsilon''_v + B''J''(J''+1)\ cm^{-1}$; $J'' = 0,1,2,..$

Then the frequency:

$$\bar{\nu} = \varepsilon'_t - \varepsilon''_t = (\varepsilon'_{el} - \varepsilon''_{el}) + (\varepsilon'_v - \varepsilon''_v) + B'J'(J'+1) - B''J''(J''+1)$$

Take $(\varepsilon'_{el} - \varepsilon''_{el}) + (\varepsilon'_v - \varepsilon''_v) = \bar{\nu}_{v',v''}$

$\boldsymbol{\bar{\nu} = \bar{\nu}_{v',v''} + B'J'(J'+1) - B''J''(J''+1)}$ **--- (1)**

Selection Rule for J:

$\Delta J = \pm 1$ (For upper and lower states have no electronic angular momentum)

$\Delta J = 0, \pm 1; but\ J = 0 \nLeftrightarrow J = 0$ (For all other transitions)

For P Branch: $\boldsymbol{\Delta J = -1\ ;\ \Rightarrow J' - J'' = -1}$

$\boldsymbol{\bar{\nu}_P = \bar{\nu}_{v',v''} - (B'+B'')(J'+1) + (B'-B'')(J'+1)^2}$ $\boldsymbol{;If\ J' = 0, 1, 2 \ldots}$ **-- (2)**

For R Branch: $\boldsymbol{\Delta J = +1\ ;\ \Rightarrow J' - J'' = +1}$

$\boldsymbol{\bar{\nu}_R = \bar{\nu}_{v',v''} + (B'+B'')(J''+1) + (B'-B'')(J''+1)^2}$ $\boldsymbol{;If\ J'' = 0, 1, 2 \ldots}$ **-- (3)**

For Q Branch: $\boldsymbol{\Delta J = 0\ ;\ \Rightarrow J' = J''}$

$\boldsymbol{\bar{\nu}_Q = \bar{\nu}_{v',v''} + (B'+B'')J''^2 + (B'-B'')J''}$ $\boldsymbol{;If\ J'' = 1, 2 \ldots}$ **--- (4)**

$\boldsymbol{\bar{\nu}_{v',v''}} \rightarrow$ **Called as Band origin.**

Equations (2), (3), can be combined into a single equation as

$\boldsymbol{\bar{\nu}_{P,R} = \bar{\nu}_{v',v''} + (B'+B'')m + (B'-B'')m^2}$ $\boldsymbol{;If\ m = \pm 1, \pm 2, \ldots}$ **-- (5)**

For R branch $\boldsymbol{m = +1, +2, \ldots}$

For P branch $\boldsymbol{m = -1, -2, \ldots}$

For the band origin $m = 0$

If $B' < B''$,

The band head is formed in the R- branch and the band is degraded towards the red.

If $B' > B''$,

The band head is formed in the P- branch and the band is degraded towards the violet.

If $B' = B''$, both P & R branches will have equally spaced and the band would be headless.

Fortrat parabola:

The plot of equation (5) for both red degraded band and violet degraded band called Fortrat parabola.

The value of m at which the vertex of Fortrat parabola lies is at

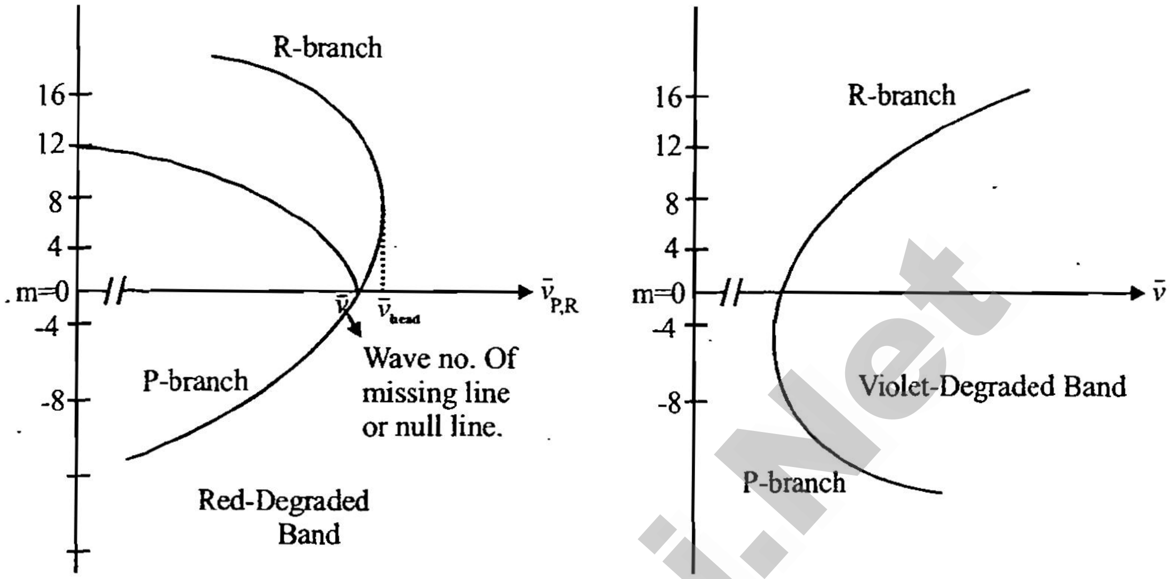
$$\frac{d\bar{\nu}_{P,R}}{dm} = 0$$

From equation (5), $m_{vertex} = -\frac{(B'+B'')}{2(B'-B'')}$

Substituting this m value in equation (5),

$$\bar{\nu}_{P,R} - \bar{\nu}_{v',v''} = -\frac{(B'+B'')}{4\,(B'-B'')}$$

If $\bar{\nu}_{P,R} - \bar{\nu}_{v',v''} = +ve \rightarrow$ degraded to the red and $\bar{\nu}_{P,R} - \bar{\nu}_{v',v''} = -ve \rightarrow$ degraded to the violet .


R-branch
16
12
8
4
m=0
-4
-8
P-branch
Wave no. Of
missing line
or null line.
Red-Degraded
Band
R-branch
Violet-Degraded Band
P-branch