Atomic and Molecular Physics

Course Code: PHYS4009

Lecture Topic

Electronic Spectroscopy – II(a)

By

Prof. Sunil Kumar Srivastava

**Department of Physics
Mahatma Gandhi Central University
Motihari, Bihar-845401**

Outline

- *What are Molecular Orbitals?*

- *Types of Molecular Orbitals*

- *Electronic Configuration of the Molecule*

- *Molecular Electronic States*

- *Electronic Transitions*

- *Rotational Fine Structure*

- *Fortrat Diagram*

- *Franck Condon Principle*

- *Application of Electronic Absorption Spectroscopy*

Part - I

Part – II(a)
Current

Part – II(b)

Formation of Electronic Spectra

When molecule forms, several molecular electronic states forms. Each electronic state has different dependence of molecular energy as function of inter-nuclear separation. i.e. different potential energy curve characterized by a minimum at equilibrium inter-nuclear separation r_e, a dissociation limit D_e, a sets of discrete vibrational energy levels and a sets of rotational energy levels.

The potential energy curve of electronic ground state and electronic excited state differ in shape as well as the position of minimum. Because in excited state electrons are loosely bound the potential energy curve becomes shallower and broader. The excited state and ground state electronic energies are represented as T_e' and T_e'' (in wavenumber) and their difference ν_e is the difference between the minima of the two curves.
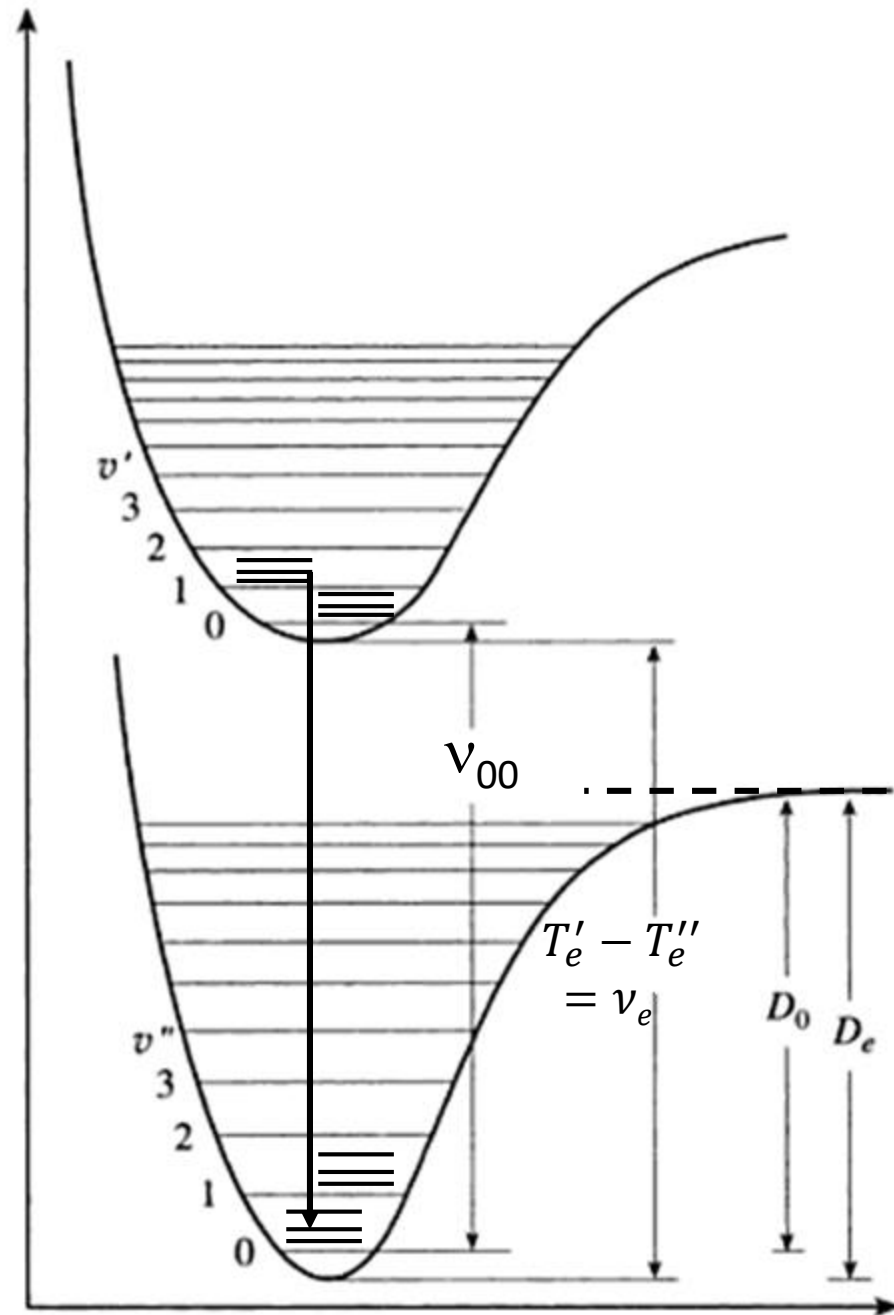
When a transition takes place in a molecule from one electronic state to the other electronic state, the radiation lies in the Ultra-violet or Visible region. The electronic transition is accompanied by a number of transition involving several vibrational levels and rotational level of the ground and excited state.

For electronic transition, there is no restriction on the change in the vibrational quantum number v, that is

$$\Delta v = \text{unrestricted}$$

The transition give rise to a group of fine lines which constitute a band and band-systems. The band system which corresponds to the same upper level (v') but different lower levels (v") are said to form a **v"-progression**; and similarly, if the band system which corresponds to the same lower level (v") but different upper levels (v') are said to form a **v'-progression.**

Vibrational Structure of Electronic Bands

An electronic transition involves a change in all three electronic, vibrational and rotational energies of the molecule. Therefore, the wave numbers arising from an electronic transition are given by

$$\nu = (T_e' - T_e'') + (G' - G'') + (F' - F'')$$

$$\nu_0 = \nu_e + G'(v') - G''(v'') + (F' - F'')$$

Ignoring the rotational structure of the individual bands $(F' = F'' = 0)$

$$= \nu_e + \left\{ \omega_e' \left(v' + \frac{1}{2} \right) - \omega_e' x_e' \left(v' + \frac{1}{2} \right)^2 \right\}$$

$$- \left\{ \omega_e'' \left(v'' + \frac{1}{2} \right) - \omega_e'' x_e'' \left(v'' + \frac{1}{2} \right)^2 \right\}$$

$$\Delta G'_{1/2} = G'(1) - G'(0) = \omega'_e - 2\omega'_e \, x'_e$$

$$\Delta G'_{3/2} = G'(2) - G'(1) = \omega'_e - 4\omega'_e \, x'_e$$

$$\Delta G'_{5/2} = G'(3) - G'(2) = \omega'_e - 6\omega'_e \, x'_e$$

....

similarly,

$$\Delta G''_{1/2} = G''(1) - G''(0) = \omega''_e - 2\omega''_e \, x''_e$$

$$\Delta G''_{3/2} = G''(2) - G''(1) = \omega''_e - 4\omega''_e \, x''_e$$

$$\Delta G''_{5/2} = G''(3) - G''(2) = \omega''_e - 6\omega''_e \, x''_e$$

.........

similarly,

$$\Delta^2 G' = 2\omega'_e x'_e$$

$$\Delta^2 G'' = 2\omega''_e x''_e$$

$$\omega'_e = \Delta G'_{1/2} + 2\omega'_e x'_e$$

$$\omega''_e = \Delta G''_{1/2} + 2\omega''_e x''_e$$

where, ω'_e and ω''_e is the wavenumber spacing of the vibrational energy levels of excited and ground electronic state, respectively, that would occur if the potential energy curve were parabola. The $\omega'_e x'_e$ and $\omega''_e x''_e$ is the vibrational anharmonicity constants of excited and ground electronic state, respectively.

Vibrational progressions and sequences in the electronic spectrum of a diatomic molecule
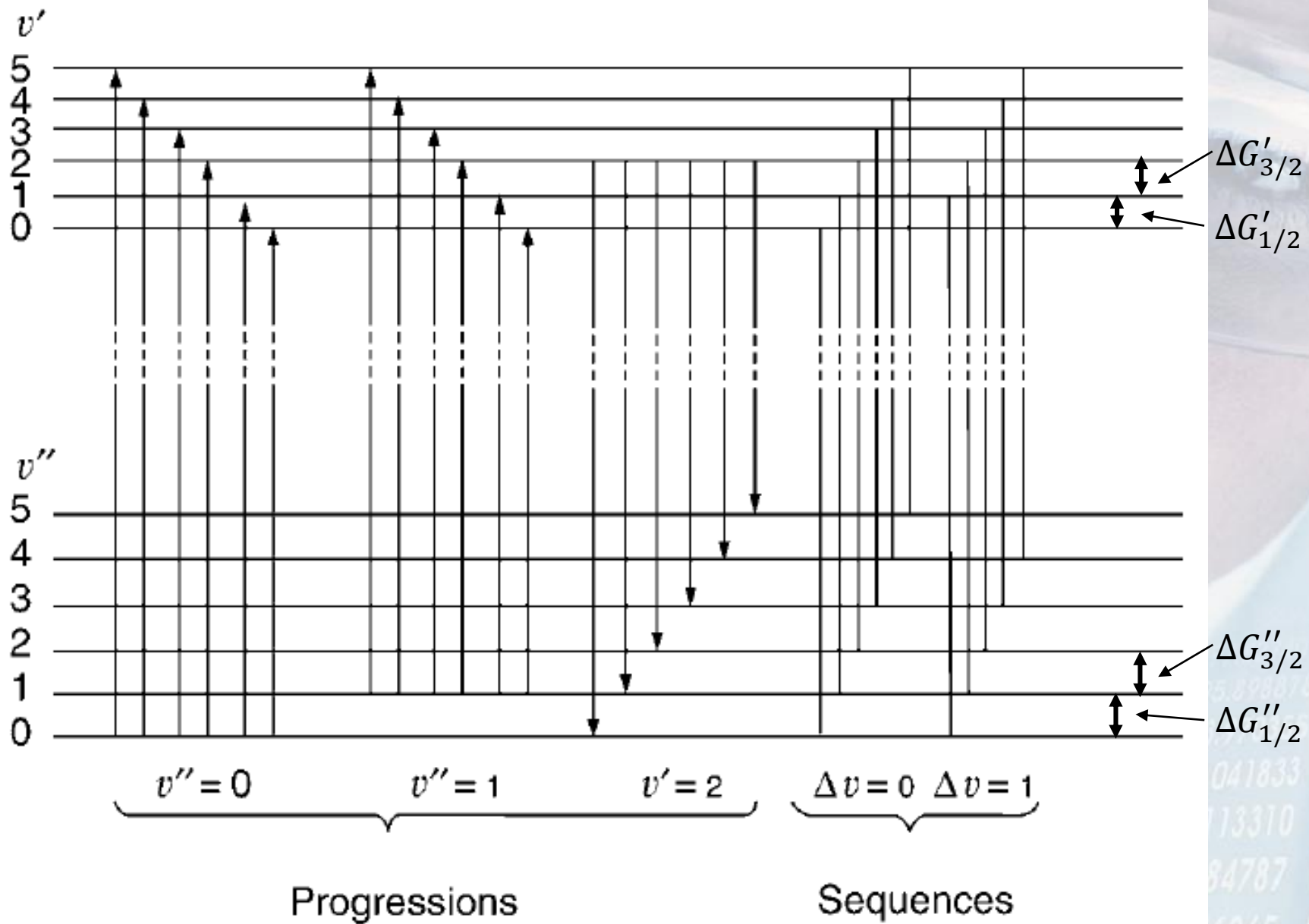
It is seen from the energy level diagram that the entire band system can be divided into a number of easily recognized group, each group consisting of a few close bands. These are called 'sequences' (Δv = constant for each sequence), the corresponds to the same upper level (v') but different lower levels (v") are said to form a v"-progression; and similarly, if the band system which corresponds to the same lower level (v") but different upper levels (v') are said to form a v'-progression.

For the vibronic transitions intensities to be appreciable, it is essential that the initial state of a transition is sufficiently populated for a transition to be observed. Under equilibrium conditions the population $N_{v''}$ of any v" level is related to that of the v" = 0 level by

$$\frac{N_{v''}}{N_0} = exp - \left\{ [G(v'') - G(0)] \frac{hc}{kT} \right\}$$

Vibrational transitions in BiF
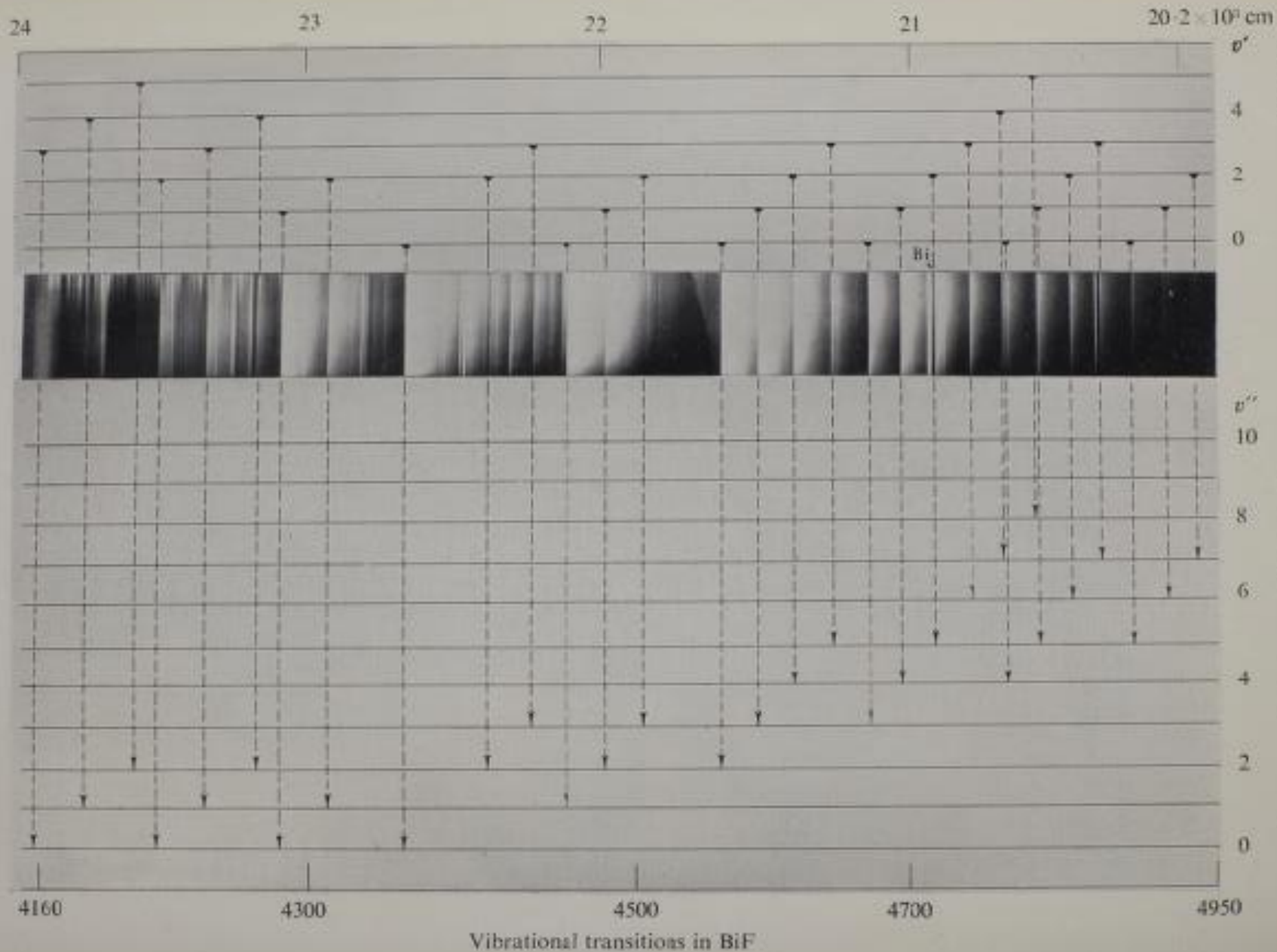
Rotational Fine Structure of Electronic Bands

Considering the rotational structure of the individual bands, the wavenumber of the electronic bands is given by:

$$\nu = \nu_e + (G' - G'') + (F' - F'')$$

$$= \nu_0 + F'(v', J') - F''(v'', J'')$$

$$\nu = \nu_e + B_{v'}J'(J' + 1) - B_{v''}J''(J'' + 1)$$

The selection rule for the transition considering rotational structure between simplest electronic states whose electronic states are cylindrically symmetric is:

$$\Delta J = \pm 1$$

The transition corresponding to $\Delta J = J' - J'' = +1$, give set of lines called **'R-Branch'**; while those corresponding to $\Delta J = J' - J'' = -1$, give set of lines called **'P-Branch'**.

R-Branch: Substituting the value of J' = J'' + 1, we obtain the lines of the R-branch with wavenumbers given by:

$$\nu_R = \nu_0 + 2B_{v'} + (3B_{v'} - B_{v''})J'' + (B_{v'} - B_{v''})J''^2$$

where, the (lower) rotational quantum number J'' = 0, 1, 2, 3, ...
Thus, the R-branch is a series of lines R(0), R(1), R(2), ...
corresponding to J'' = 0, 1, 2, 3, ...

P-Branch: Substituting the value of J' = J'' − 1, we obtain the lines of the P-branch with wavenumbers given by:
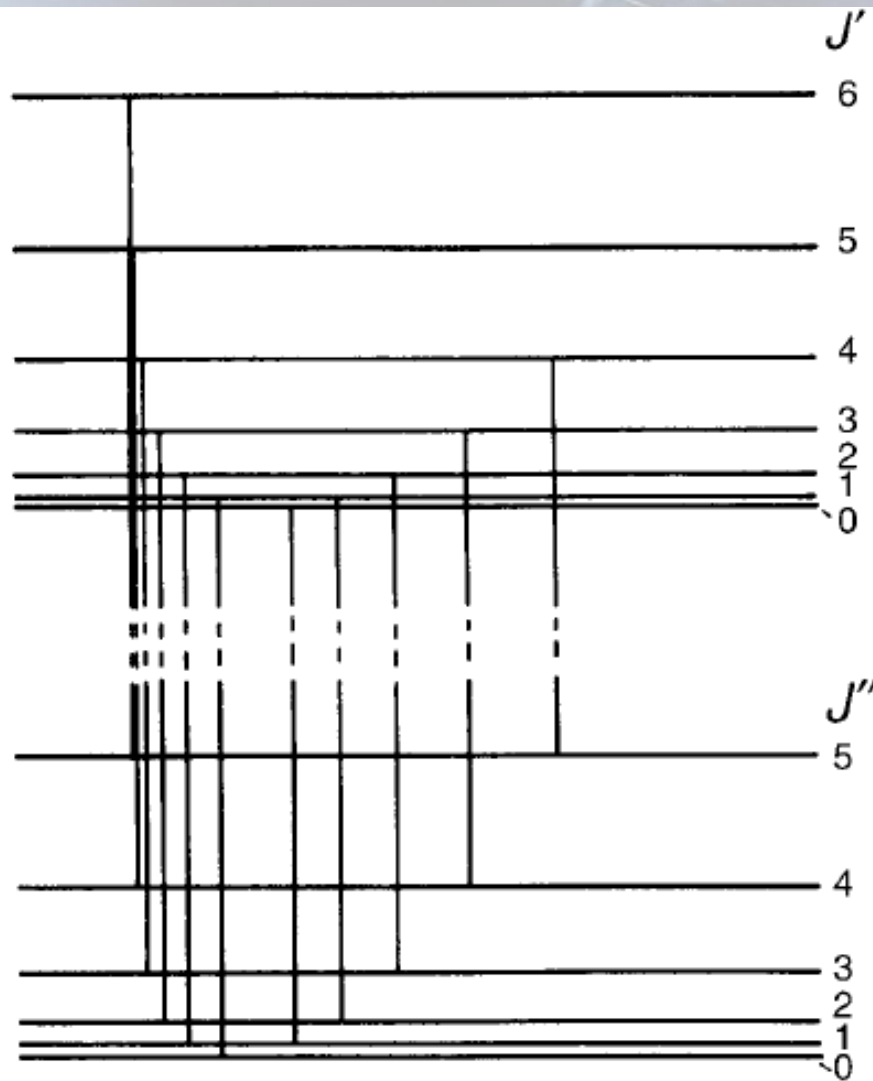
$$\nu_P = \nu_0 - (B_{v'} + B_{v''})J'' + (B_{v'} - B_{v''})J''^2$$

where, the (lower) rotational quantum number J'' = 1, 2, 3, ...
Thus, the R-branch is a series of lines P(1), P(2), P(3), ...
corresponding to J'' = 1, 2, 3, ...

Difference between the Electronic Bands & Vibrational-Rotational Bands

1. In an electronic transition, the rotational constants $B_{v'}$ and $B_{v''}$ belong to different electronic states and so they are widely different. That is, $B_{v'} - B_{v''}$ has a much larger value than that in case of an infrared transition in which $B_{v'}$ and $B_{v''}$ belong the vibrational levels of same electronic state. In electronic bands there is a strong tendency of head formation. On contrary, in vibrational-rotational band the head formation is not at all pronounced.

2. The term $(B_{v'} - B_{v''})$ may be positive or negative; whereas, in case of infrared transition it is necessarily negative. Thus, both, red-degraded and violet-degraded bands are observed in electronic band systems; whereas, only red-degraded bands are observed in vibrational-rotational spectra.

Both the R- and P-branches can be represented by a single parabolic equation:

$$\nu = \nu_0 + (B_{v'} + B_{v''})m + (B_{v'} - B_{v''})m^2$$

where, m = J''+ 1 = 1, 2, 3, ... for lines R(0), R(1), R(2), ...

m = − J'' = -1, -2, -3, ... for lines P(1), P(2), P(3), ...

and   m = 0 for all band origin.

The plot of the above equation when $(B_{v'} - B_{v''})$ is positive (violet-degraded) and when $(B_{v'} - B_{v''})$ is negative (red-degraded), which is a parabolic shape is known as **"Fortrat Parabola"**.

The value of m at which the vertex of the Fortrat parabola (band head) lies is obtained by differentiating above equation and equating $\frac{dv}{dm}$ to zero. This gives:

$$m_{vertex} = -\frac{(B_{v'} + B_{v''})}{2(B_{v'} - B_{v''})}$$

The wavenumber separation between band-head and band-origin is given by:

$$\nu_{head} - \nu_0 = -(B_{v'} + B_{v''}) \frac{B_{v'} + B_{v''}}{2(B_{v'} - B_{v''})} + (B_{v'} - B_{v''}) \frac{(B_{v'} + B_{v''})^2}{4(B_{v'} - B_{v''})^2}$$

$$= \frac{(B_{v'} + B_{v''})^2}{4(B_{v'} - B_{v''})}$$

$\nu_{head} - \nu_0$ is positive for a band degraded to the red, negative for the band degraded to the violet.

All the bands of a band-system are usually shaded in the same direction.

Fortrat Parabola

RED-DEGRADED BAND

VIOLET-DEGRADED BAND
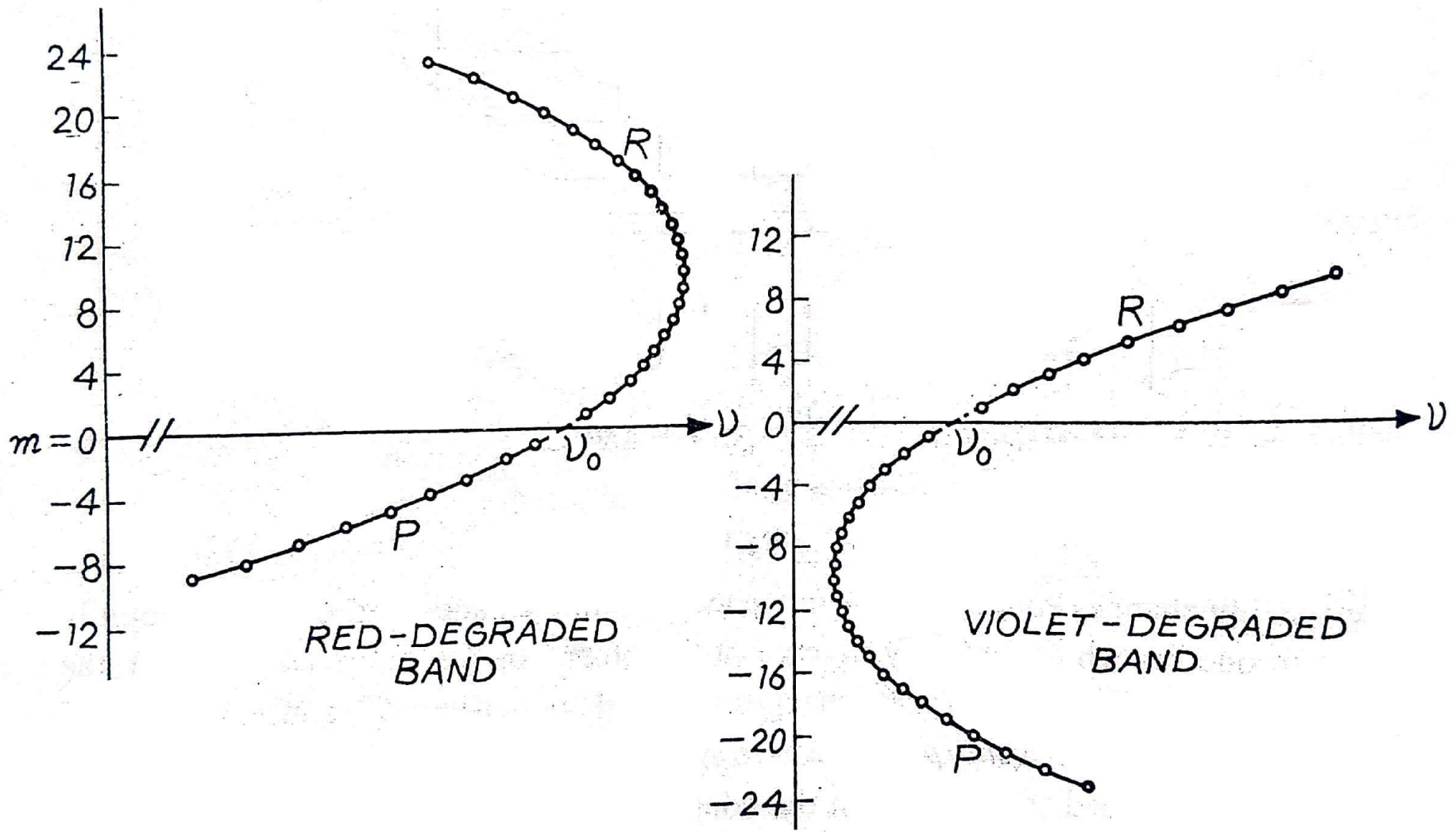
Rotational Structure of Three Branch Bands

There are certain electronic states whose electronic states are not cylindrically symmetrical and has a component of angular momentum along internuclear axis. In this case the resulting band found to have an addition branch known as Q-branch.
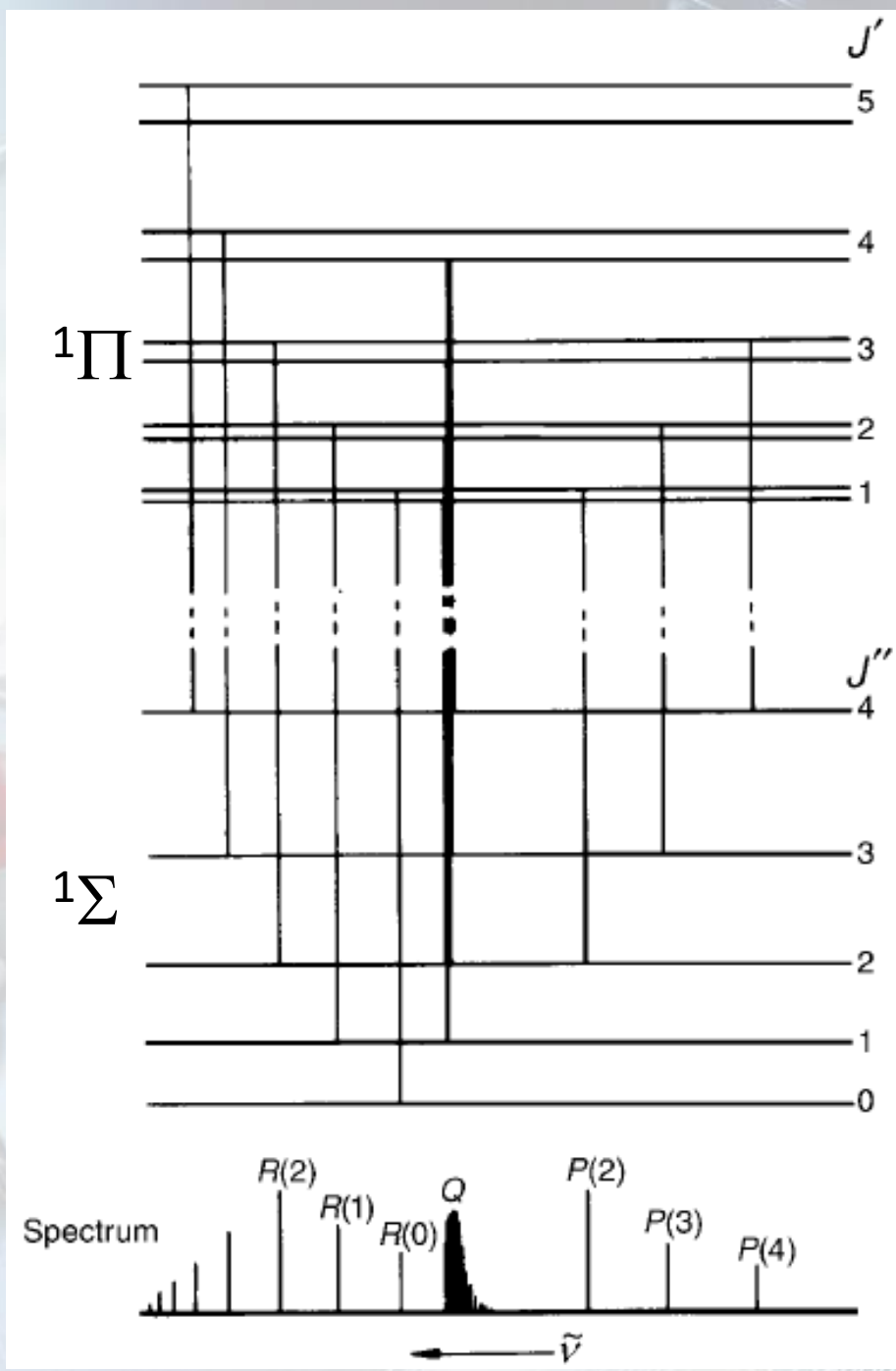
The general expression for the wavenumber of a rotational line of a electronic band is

$$\nu = \nu_e + B_{v'}J'(J' + 1) - B_{v''}J''(J'' + 1)$$

The selection rule for the transition (e.g. $^1\Pi \rightarrow {}^1\Sigma$) in this case is:

$$\Delta J = 0, \pm 1; \qquad but\ J = 0 \leftrightarrow J = 0$$

The transition corresponding to $\Delta J = J' - J'' = \pm 1$, give **'R-Branch' and 'P-Branch'**; while additional transition corresponding to $\Delta J = 0$, give **'Q-Branch'**.

R-Branch: Substituting the value of J' = J" + 1, we obtain the lines of the R-branch with wavenumbers given by:

$$\nu_R = \nu_0 + 2B_{v'} + (3B_{v'} - B_{v''})J'' + (B_{v'} - B_{v''})J''^2$$

where, J" = 0, 1, 2, 3, …… Thus, the R-branch is a series of lines R(0), R(1), R(2), ……… corresponding to J" = 0, 1, 2, ……

P-Branch: Substituting the value of J' = J" − 1, we obtain the lines of the P-branch with wavenumbers given by:

$$\nu_P = \nu_0 - (B_{v'} + B_{v''})J'' + (B_{v'} - B_{v''})J''^2$$

where, J" = 1, 2, 3, …… Thus, the R-branch is a series of lines P(2), P(3), P(4), ……… corresponding to J" = 2, 3, 4, …… , J" cannot be 1 because the level J' = 0 is missing. Hence, P(0) and P(1) is missing in this case.

Q-Branch: Substituting the value of J' = J" − 1, we obtain the lines of the P-branch with wavenumbers given by:

$$\nu_Q = \nu_0 + (B_{v'} - B_{v''})J'' + (B_{v'} - B_{v''})J''^2$$

where, J" = 1, 2, 3, …… Thus, the R-branch is a series of lines Q(1), Q(2), Q(3), ……… corresponding to J" = 1, 2, 3, ……

Fortrat Parabola of Three Branch Bands
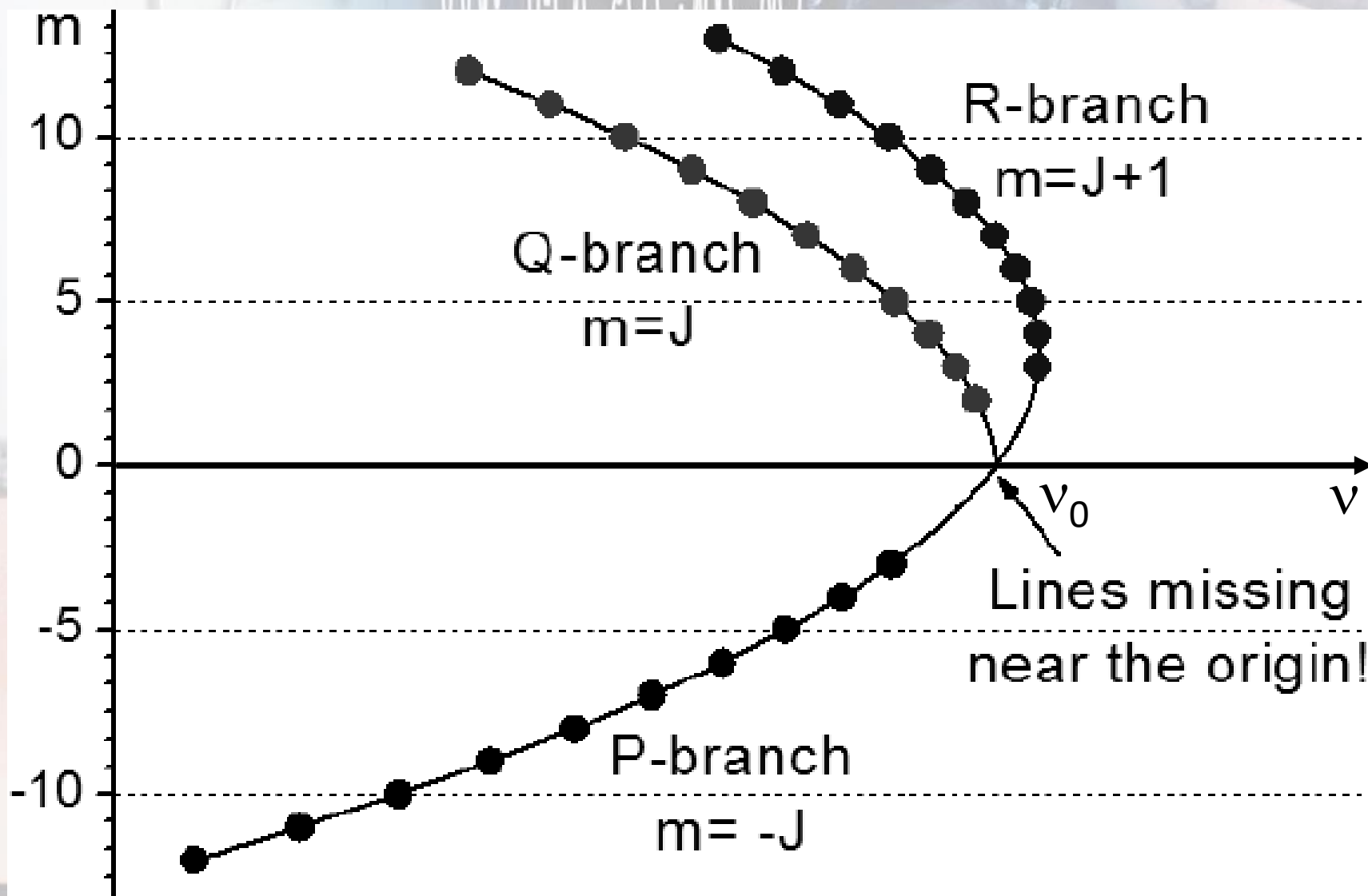
Books for Further Reading

1. Fundamentals of Molecular Spectroscopy by C. N. Banwell (McGraw Hill)

2. Modern Spectroscopy by J. M. Hollas (Wiley)