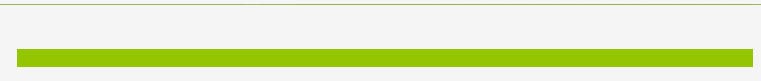
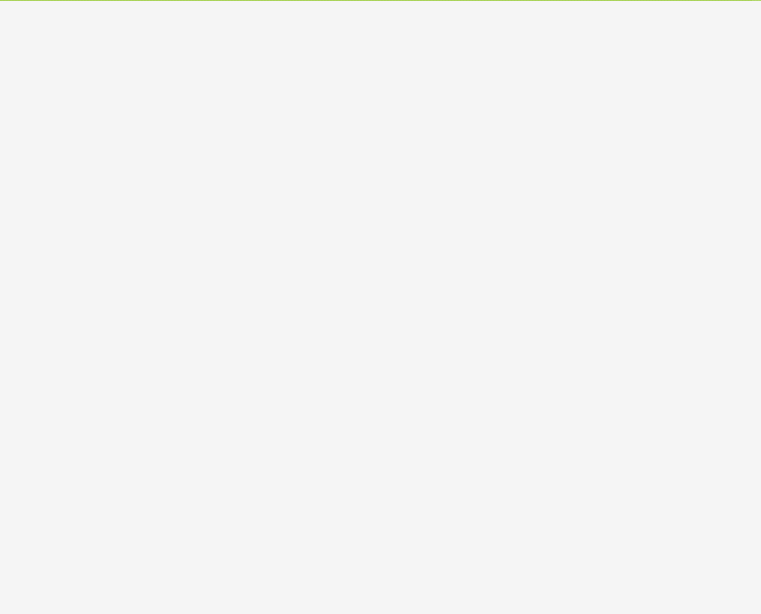
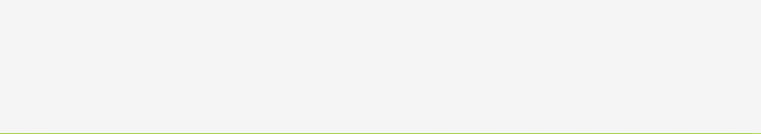


**ROTATIONAL
FINE
STRUCTURE OF
ELECTRONIC-
VIBRATION
SPECTRA**



ROTATIONAL FINE STRUCTURE:

- Under high resolution, each line in a spectrum has a set of closely spaced lines
- Total energy of electronic vibrational spectra is

$$E_t' = E_{el}' + E_v' + B'J'(J'+1) \text{ cm}^{-1}$$

$$E_t'' = E_{el}'' + E_v'' + B''J''(J''+1) \text{ cm}^{-1}$$

- The frequency of the transitions are,
$$\bar{\nu} = (E_{el}' - E_{el}'') + (E_v' - E_v'') + B'J'(J'+1) - B''J''(J''+1)$$

- Transition for which both upper and lower states have no electronic angular momentum about the inter nuclear axis the selection rule is

$$\Delta J = \pm 1$$

For all other transitions

$$\Delta J = 0, \pm 1$$

The restriction is $J=0 \leftrightarrow J=0$

- Consider rotational contribution, for P, Q and R branches, J'' cannot be 0
- The frequency $\bar{\nu}_{v',v''}$ is referred as **band origin**.
- The equilibrium inter nuclear distance of the upper electronic state will be larger than that of the lower.

- The rotational constant B' will be less than B''
- P branch lines- low wavenumber side of the band origin.
- The spacing increases when quantum number increases.
- R branch – high wavenumber side of the band origin.
- The line spacing decreases as increasing quantum number.

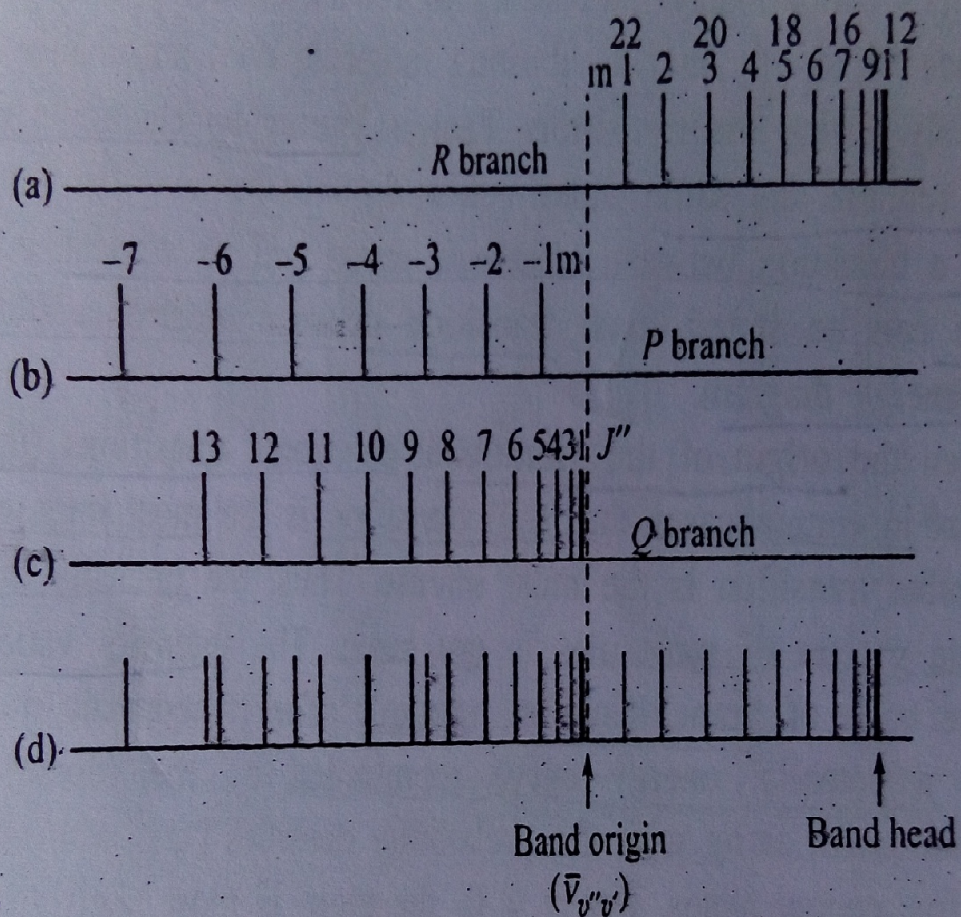


Figure 9.6 The rotational fine structure of an electronic-vibration transition for a diatomic molecule ($B' < B''$). (a) R-branch, (b) P-branch, (c) Q-branch, (d) Complete spectrum.

- Q branch lines lie on the low wavenumber side of the band origin with an increase in spacing with increasing quantum number.
- Complete spectrum – superposition of all the three branches.
- $B' < B''$ band head on high wavenumber side (violet), the band shaded or degraded towards the red.

- When $B' > B''$
- P branch will converge to band head on low wavenumber side of band origin.
- Band head is at red end of spectrum.
- Band is shaded or degraded to the violet end of the spectrum.
- R branch – high wave number side with line spacing increasing with increasing m .
- Q branch – high wave number side of band origin with line spacing increasing with J'' .

- When $B' = B''$ spectrum resembles that of a pure vibration rotation spectrum with no band head.
- The rotational fine structure can be resolved only in simple molecules in gaseous phase.
- In the liquid phase the rotational fine structure is lost, even the vibrational coarse structure disappears.