

The selection rule for $J \rightarrow$ depends upon the type of electronic transition undergone by the molecule.

If both the upper and lower electronic state are $^1\Sigma$ state (i.e. states in which there is no electronic angular momentum about the internuclear axis), this selection rule is

$$\Delta J = \pm 1 \text{ only for } ^1\Sigma \rightarrow ^1\Sigma \text{ transitions} \quad \text{--- (5)}$$

for all other transitions the selection rule becomes $\Delta J = 0 \text{ or } \pm 1$ --- (6)

for this later case \rightarrow there is further restriction that a state with $J=0$ cannot undergo a transition to another $J=0$ state

$$J=0 \not\leftrightarrow J=0 \quad \text{--- (7)}$$

\Rightarrow for transitions between $^1\Sigma$ states, P and R branches will only occur, while for other transitions Q branches will appear in addition.

We can expand eqn (4) as follows;

$$\bar{\nu}_{\text{spec}} = \bar{\nu}_{(v', v'')} + B'J'(J'+1) - B''J''(J''+1) \text{ cm}^{-1} \quad \text{--- (8)}$$

B', J' \rightarrow upper electronic state

B'', J'' \rightarrow lower electronic state

Kaution \rightarrow difference between B values in different vibrational levels was very small and could be ignored.

In case of electronic spectroscopy \rightarrow according to the Franck-Condon principle \rightarrow equilibrium ~~distance~~ internuclear distances in the lower and upper electronic states may differ considerably \rightarrow moment of inertia and hence B values \rightarrow in two states will also differ.

Often \rightarrow the electron excited is one of those forming the bond between the nuclei; the bond in the upper state will be weaker and probably longer so that the equilibrium moment of inertia increases during the transition and B decreases. Thus $B' < B''$.

The reverse is sometimes true, however, e.g. when the electron is excited from an antibonding orbital.

Re rotational fine structure could be discussed by applying selection rules (5), (6), (7) to expression (8) for spectral lines.

Taking P, R and Q branches ~~in~~ turn:

1. P branch: $\Delta S = -1$, $J'' = J' + 1$

$$\Delta \varepsilon = \bar{\nu}_p = \bar{\nu}_{(v', v'')} - (\beta' + \beta'')(J'+1) + (\beta' - \beta'')(J'+1)^2 \text{ cm}^{-1} \quad (13)$$

where $J' = 0, 1, 2, \dots$

2. R branch: $\Delta J = +1, J' = J'' + 1$

$$\Delta \varepsilon = \bar{\nu}_R = \bar{\nu}_{(v', v'')} + (\beta' + \beta'')(J''+1) + (\beta' - \beta'')(J''+1)^2 \text{ cm}^{-1}$$

$J'' = 0, 1, 2, \dots$ (9(6))

These two eqs can be combined into

$$\bar{\nu}_{p,R} = \bar{\nu}_{(v', v'')} + (\beta' + \beta'')m + (\beta' - \beta'')m^2 \text{ cm}^{-1}$$

where $m = \pm 1, \pm 2, \dots$ (9(6))

$+$ m values \rightarrow R branch, corresponding to $\Delta J = +1$

$-$ m values \rightarrow P branch, $\Delta J = -1$

m cannot be zero, so that no line from the P and R branch appears at the band origin $\bar{\nu}_{(v', v'')}$.

~~2~~ We draw the appearance of R and P

branches separately in fig (a) and (b), choosing $\beta' < \beta''$ with 10% difference.

With this choice, P branch lines occur on the low wavenumber side of the band origin and spacing between the lines increases with m .

R branch lines appears on the high wavenumber (14) of the origin and line spacing decreases with increasing 'm' → so rapidly that the lines reach a maximum wavenumber and then begin to return to low wavenumbers with increasing spacing.

The point at which the R branch separation decreases to zero is termed the "band head"

3. Q branch: $\Delta J = 0, J' = J''$

$$\Delta \epsilon = \bar{\nu}_Q = \bar{\nu}(v', v'') + (B' - B'')J'' + (B' - B'')J''^2 \text{ cm}^{-1}$$

where $J'' = 1, 2, 3, \dots$ (16)

Here $J'' = J' \neq 0$, due to eq (6)

No line will appear at the origin. Q branch in figure (c). The lines lie to low wavenumber of the origin and their spacing increases. The first few lines of this branch are not usually resolved.

