

Interaction between rotation and vibrations

In IR spectroscopy the P and R branches appear at equidistance from the band origin. The spacing between P and R branches are equal. P branch lines occur on the low wavenumber side of the band origin. The R branch lines appear on the high wavenumber side of the band origin.

The line spacing in P branch increases ~~from~~ ~~as the involved quantum number increases~~

The line spacing in R branch decreases ~~as the involved quantum number increases~~

This is because of the interaction between rotation and vibration.

For each rotation the molecule vibrates 1000 times. So bond length increases continuously. As bond length changes the rotational constant B and moment of inertia of the molecule changes. Consequently interaction between two energy levels takes place.

As the vibrational energy increases, the vibrational ~~amplitude~~ amplitude of vibration increases. So the value of B depends on the vibrational quantum number. When vibrational energy increases, the average bond length ~~also~~ increases. The B value of higher energy level is ~~less~~ than the lower energy level.

Hence

$$B_v = B_e - \alpha \left(v + \frac{1}{2} \right) \quad \text{--- (1)}$$

B_v - ~~energy~~ vibrational rotational constant

B_e - equilibrium B value

α - constant for a particular molecule

Consider the transition $v=0 \rightarrow v=1$

Consider the B values as B_0 for lower energy level and B_1 for higher energy level

If $B_0 > B_1$

$$\Delta E = E_{J', v=1} - E_{J'', v=0}$$

$$= w_0 + B_1 J'(J'+1) - B_0 J''(J''+1) \text{ cm}^{-1}$$

$$\text{where } w_0 = w_e (1 - 2x_e) \quad \text{--- (2)}$$

R-branch

$$\Delta J = +1 \quad \text{i.e. } J' - J'' = 1$$

$$J' = J'' + 1$$

$${}^R R = w_0 + (B_1 + B_0)(J''+1) + (B_1 - B_0)(J''+1)^2 \text{ cm}^{-1}$$

$$\text{where } J'' = 0, 1, 2 \quad \text{--- (3)}$$

i) For P branch

$$\Delta J = -1 \quad J' - J'' = -1$$

$$J'' = J' + 1$$

$$2^2P = \omega_0 - (B_1 + B_0)(J' + 1) + (B_1 - B_0)(J' + 1)^2 \text{ cm}^{-1}$$

when $J' = 0, 1, 2$ — (4)

Combining eqn (3) and (4)

$$\bar{\omega}_{P2} = \omega_0 + (B_1 + B_0)m + (B_1 - B_0)m^2 \text{ cm}^{-1}$$

— (5)

where $m = \pm 1$

$B_1 < B_0$ so in eqn (5) $(B_1 - B_0)m^2$

is always negative

For R branch $m = +1, +2, +3 \dots$

For P branch $m = -1, -2, -3 \dots$

$$B_1 < B_0$$

Hence in the spectrum of a diatomic molecule as the m value increases the spacing between R branches decreases i.e. closely spaced. But in P branch spacing increases.

