The two expressions may be combined into
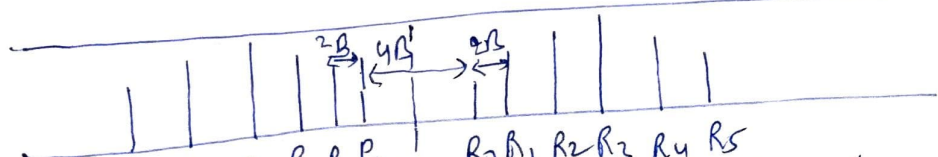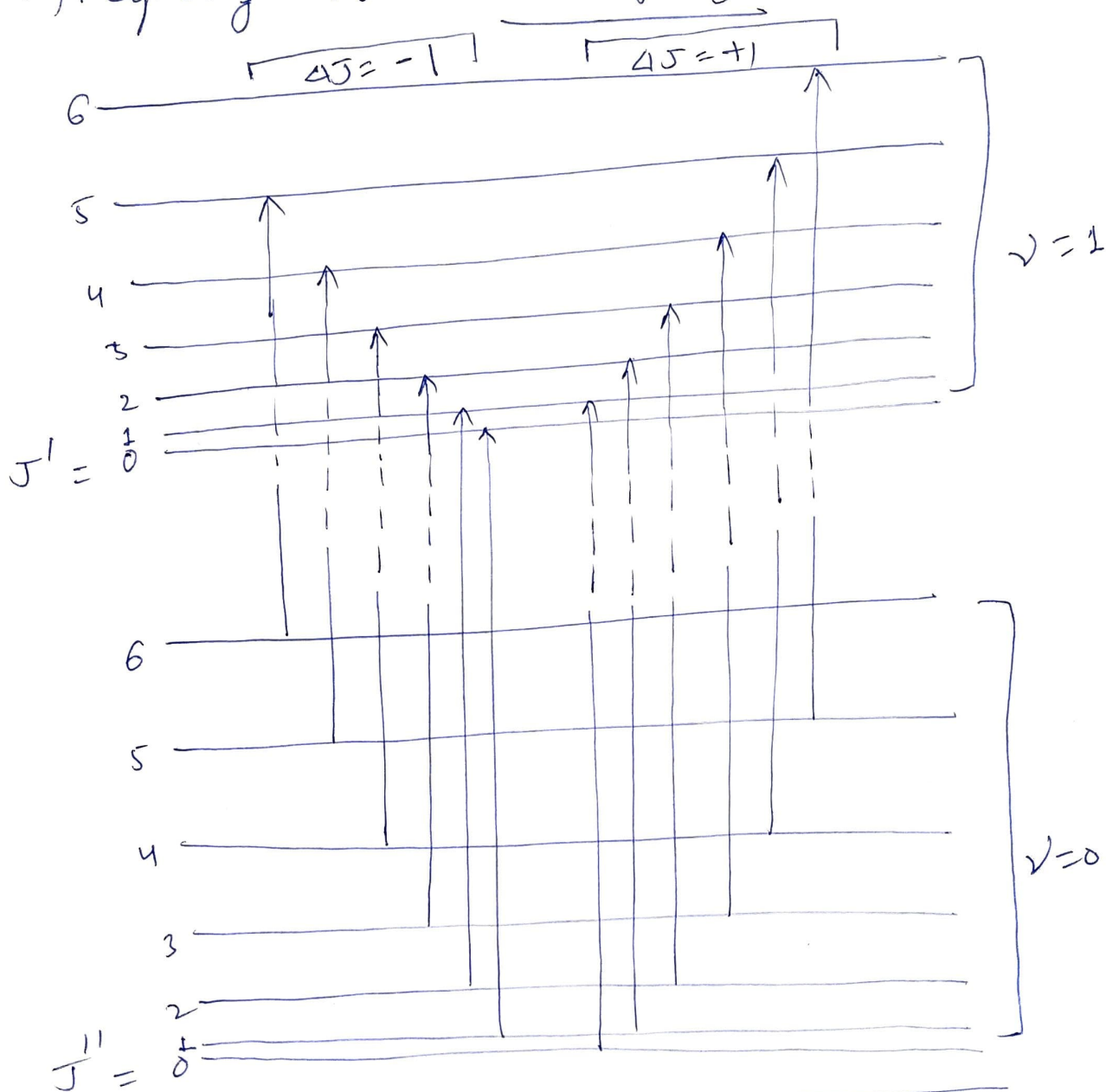
$$\Delta \varepsilon_{J,v} = \bar{\nu}_{spect} = \bar{\omega}_0 + 2Bm \quad cm^{-1} \qquad \text{---} \quad 20(c)$$

$$m = \pm 1, \pm 2 \dots$$

$m \rightarrow$ can not be zero, because that implies J' or J'' to be -1.

$m \rightarrow$ replacing $J''+1$ in eq^n 20(a) and $J'+1$ in 20(b) has positive values for $\Delta J = +1$ and is negative for $\Delta J = -1$.

The frequency $\bar{\omega}_0 \rightarrow$ band origin and **band centre**.

Transitions between $\wedge$ Rotational - Vibrational energy levels of a diatomic molecule together with spectrum arising

Eq^n 20(c) → represents combined vibration-rotation spectrum.

Consists of equally spaced lines (spacing = 2B) on each side of the band origin $\bar{\omega}_0$, since $m \neq 0$, the line $\bar{\omega}_0$ itself will not appear.

Lines to the low frequency side of $\bar{\omega}_0$ → negative m (i.e. $\Delta J = -1$) → **P Branch**

High - frequency side (m positive, $\Delta J = +1$)

→ **R Branch**

Lines arising from $\Delta J =$ -2   -1   0   +1   +2

called: O   P   Q   R   S
                                    branch

The inclusion of the centrifugal distortion constant D leads to the following expression for the spectrum

$$\Delta \varepsilon = \bar{\nu}_{spect} = \bar{\omega}_0 + 2Bm - 4Dm^3 \ cm^{-1} \quad --(21)$$
$$(m = \pm 1, \pm 2, \pm 3, ---)$$

$B \sim B$ of the order $10 \, cm^{-1}$ or less

$D \sim$ only some $0.01 \, \text{to} \, \text{of} \, B$

Good infra-red spectrometer has a resolving power $\sim 0.5 \, cm^{-1}$, $D \rightarrow$ negligible to a very high degree of accuracy.

Anharmonicity factor → not negligible it affects the position of the band origin $(\bar{\omega}_0 = \bar{\omega}_e'(1-2x_e))$ and the selection rules to include $\Delta \nu = \pm 2, \pm 3$ etc. Also allows the appearance of overtone bands having identical rotational structure.

Breakdown of Born-Oppenheimer Approximation:
The Interaction of Rotations and Vibrations

So far we have assumed → Vibrations and rotation can proceed quite Independently of each other.

A molecule vibrates some 10^3 times during the course of a single rotation → the bond length and hence the moment of Inertia and B constant also Changes continually during the rotation.

If vibration is simple harmonic → mean bond length will be same as equilibrium bond length and will not vary with vibrational energy.

The rotational constant B → depend on $\frac{1}{r^2}$, the average value of $\frac{1}{r^2}$ is not same as $\frac{1}{r_{eq}^2}$.

Increase in vibrational energy → Increase in the vibrational amplitude → hence value of B will depend on the V quantum number.

Case of anharmonic vibrations → more complex.

Increase in vibrational energy → increase in the average bond length. The rotational constant thus varies even more with vibrational energy.

In general Since r_{av} increases with vibrational energy → B is smaller in upper ~~vibration~~ vibrational state than in the lower.

In eq^n form

$$B_V = B_e - \alpha \left(V + \tfrac{1}{2} \right) - - (22)$$

$B_v \to$ rotational constant in vibrational level v.

$\alpha \to$ small positive constant for each molecule

fundamental vibrational change, i.e. change

$v=0$ to $v=1$ $v=0 \longrightarrow v=1$

$$B_0 > B_1$$

$$\Delta \varepsilon = \varepsilon_{J', v=1} - \varepsilon_{J'', v=0}$$

$$= \bar{\omega}_0 + B_1 J' (J'+1) - B_0 J'' (J''+1)_{\ \mathrm{cm}^{-1}}$$

where $\bar{\omega}_0 = \bar{\omega}_e (1 - 2 x_e)$.

1. $\Delta J = +1$ $J' = J'' + 1$

$$\Delta \varepsilon = \bar{v}_R = \bar{\omega}_0 + (B_1 + B_0)(J'' + 1) + (B_1 - B_0)(J'' + 1)^2 \ \mathrm{cm}^{-1} \qquad \text{— 23(a)}$$

$$(J'' = 0, 1, 2, \cdots)$$

and

2. $\Delta J = -1$ $J'' = J' + 1$

$$\Delta \varepsilon = \bar{v}_P = \bar{\omega}_0 - (B_1 + B_0)(J' + 1) + (B_1 - B_0)(J' + 1)^2 \ \mathrm{cm}^{-1}$$

$$(J' = 0, 1, 2, \cdots) \qquad \text{— 23(b)}$$

$\bar{v}_P$ and $\bar{v}_R \longrightarrow$ wavenumbers of P and R branch

lines respectively.

So

$$\bar{v}_{P,R} = \bar{\omega}_0 + (B_1 + B_0) m + (B_1 - B_0) m^2 \ \mathrm{cm}^{-1}$$

$$(m = \pm 1, \pm 2, \cdots)$$

Positive m value $\longrightarrow$ R branch   23(c)

negative m value $\longrightarrow$ P branch

Ignoring vibration-rotation interaction, $B_1 = B_0$,

eq^n 23(c) simplifies to 20(c).

Since $B_1 < B_0$ the last term in eq^n 23 (c) is always negative. $\longrightarrow$ irrespective of the sign of m, $\longrightarrow$ the effect on the spectrum of a diatomic molecule $\longrightarrow$ crowd the rotational lines more closely together with increasing m on the R branch side and the P branch side lines become more widely spaces as (negative) m increases.

Normally B_1 and B_0 differ slightly $\longrightarrow$ effect is marked only for high m values.

The Vibrations of Polyatomic Molecules

* The number of fundamental vibrations and their Symmetry

* The Possibility of overtone and combination bands

* The influence of rotation on the Spectra

Fundamental Vibrations and their Symmetry

Consider a molecule containing N atoms:

We can refer to the positions of each atom by specifying three coordinates (i.e, x, y and z Cartesian coordinates). Total no. of coordinate values is $3N$ $\longrightarrow$ molecule has $3N$ degree of freedom $\longrightarrow$ since each coordinate value may be specified quite independently of the others. Once all $3N$ coordinates have been fixed $\longrightarrow$ the bond distances and bond angles of the molecule are also fixed $\longrightarrow$ no further arbitrary specifications.