Rotational-Vibrational spectra

Both spectra are found together in diatomic molecule i.e. vibrational & rotational motion occur together.

Then total Energy of such Molecule is given as:

$$E = E_{vib} + E_{rot}$$

$$= \left(n + \frac{1}{2}\right) h\nu_0 + Bj(j+1)$$

Where, n – vib. Q. No.

j – rot. Q. No.

ν_0 – vib. freq of Molec

B – Rot. const of Mole.

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Now;

if the vib states of atom changes from n_1 to n_2 and Rot. State from j_1 to j_2 then change in Energy :-

$$\Delta E = E_1 - E_2 = \left[\left(n_1 + \frac{1}{2}\right) h\nu_0 + B j_1 (j_1+1)\right] - \left[\left(n_2 + \frac{1}{2}\right) h\nu_0 + B j_2 (j_2+1)\right]$$

$$= (n_1 - n_2) h\nu_0 + B(j_1 - j_2)(j_1 + j_2 + 1)$$

freq of line obtained in the transf.

$$\nu = \frac{\Delta E}{h} = (n_1 - n_2)\nu_0 + \frac{B}{h}(j_1 - j_2)(j_1 + j_2 + 1)$$

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Transition Rules for Rot-Vib Spectra

In various states, the allowed transitions are for: $\Delta n = \pm 1$

& $\Delta j = \pm 1$ only

for; $n_1 = 1$ & $n_2 = 0$

& $j_1 = 0, 1, 2 \ldots$ $j_2 = 0, 1, 2 \ldots$

$\Delta j = +1$ & $\Delta j = -1$

$$\nu = \nu_0 + \frac{B}{h}(j_1 - j_2)(j_1 + j_2 + 1)$$

$\Delta j = +1 \rightarrow$ from higher j value to lower j

$\Delta j = -1 \rightarrow$ from lower j to higher j

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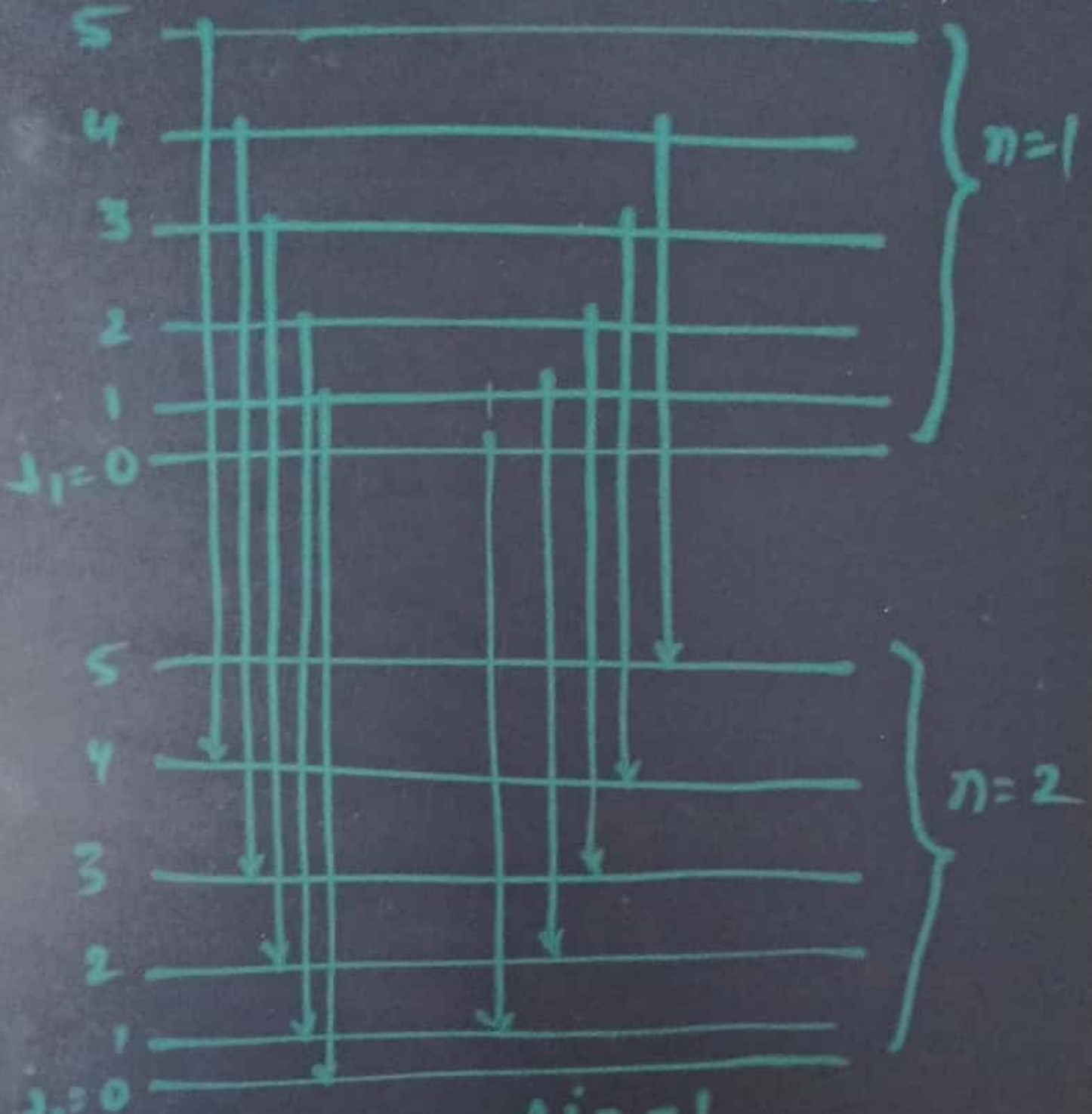
Possible Transitions

from $n_1 = 1$ to $n_2 = 0$



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R - Brach

— Spectrum for which $\Delta J = +1$

→ frequencies are given as:

$$\nu_R = \nu_0 + \frac{2B}{h} J_1$$

$$J_1 = 1, 2, 3, \ldots$$

P Brach

— spectrum for which $\Delta J = -1$

→ frequencies are given as:

$$\nu_P = \nu_0 - \frac{2B}{h} J_2$$

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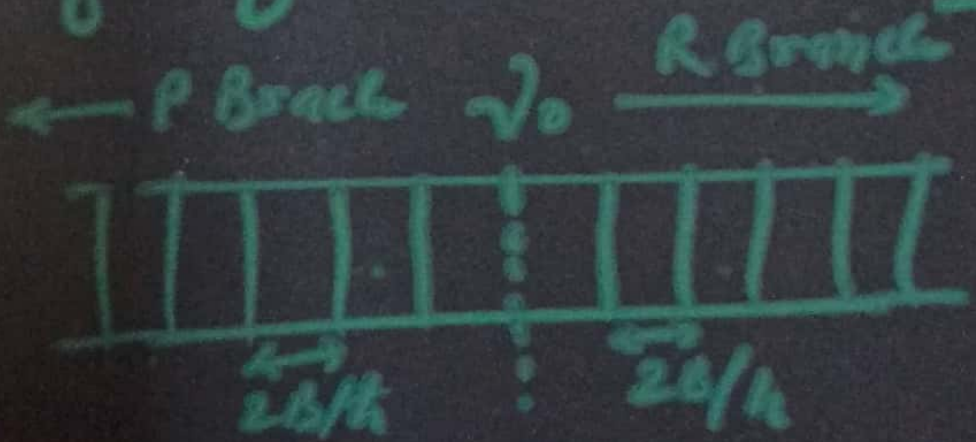
ν_0 — Band origin

Spectrum — has equispaced line of width $\frac{2B}{h}$ about the fundamental freq ν_0; spectra on right of ν_0 or freq greater than ν_0 is called R Branch while spectral Band on Left of ν_0 is called P Branch



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