

Diatomic Vibrating Rotator

Example - CO, HCl,

Since the difference between energies of rotational and vibrational motion is very large, rotation is unaffected by vibrational change. That is a diatomic molecules can execute (निरीक्षित करता) ~~execute~~ rotation and vibration quite independently. This is known as - Born oppenheimer approximation. This approximation tantamount (equal in meaning or value) to assuming that the combined rotational-vibrational energy is simply the sum of the separate energies. Thus,

$$E_{total} = E_{rot} + E_{vib} \quad \text{joules.}$$

$$\bar{V}_{total} = \bar{V}_{rot} + \bar{V}_{vib} \quad \text{cm}^{-1}$$

$$= B J(J+1) - D J^2(J+1)^2$$

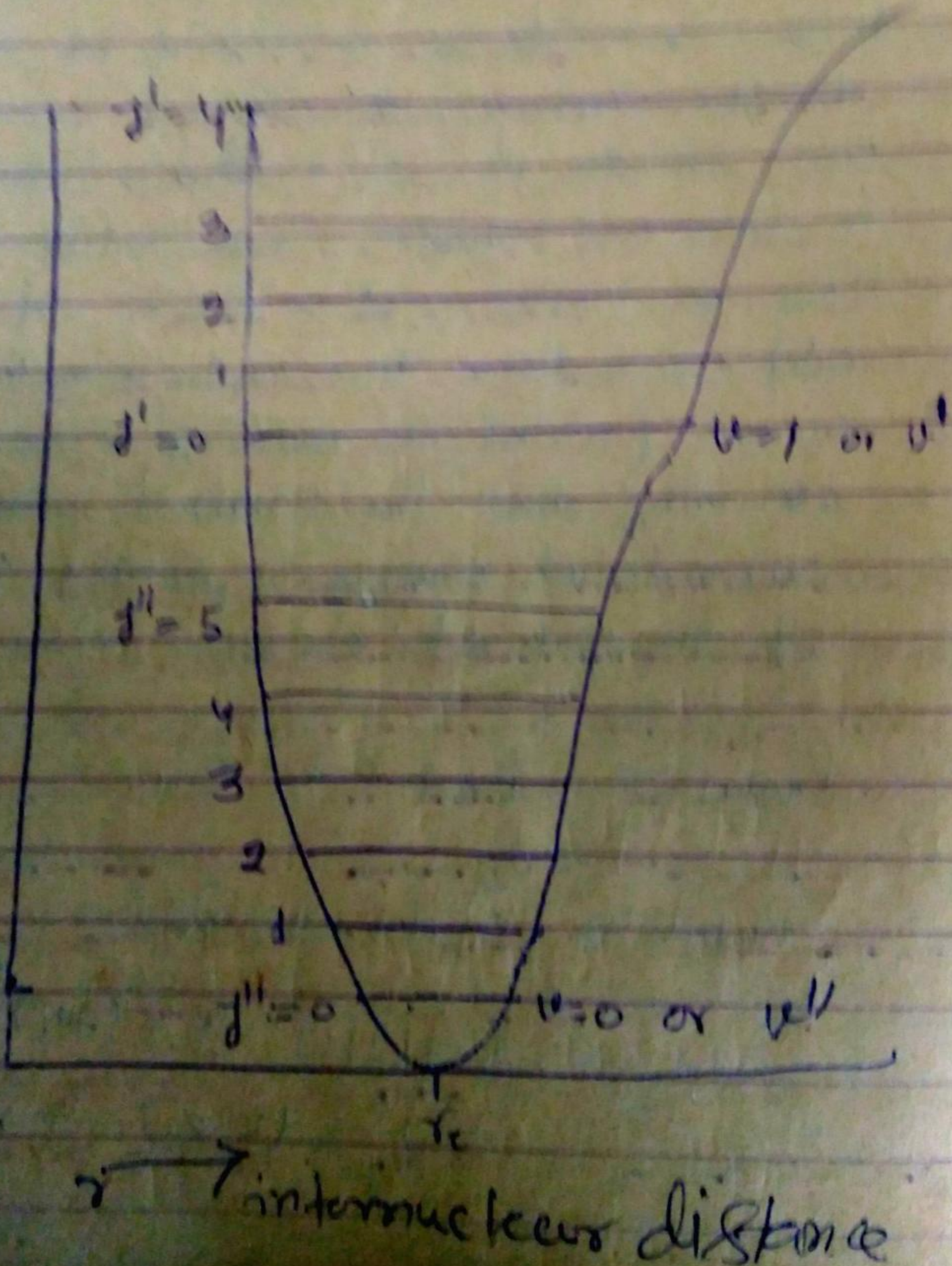
$$+ \left\{ \bar{V}_e (v + \frac{1}{2}) - a \bar{V}_e (v + \frac{1}{2})^2 \right\} \quad \text{cm}^{-1}$$

Distortion constant D has a small
 anharmonicity effect on the spectrum
 and hence can be neglected.

$$E_{\text{total}} = B J(J+1) + \tilde{\nu} (v+1/2) - D(v+1/2)^2$$

Rotational levels, for $v=0$ and $v=1$
 vibrational levels exist at

Rotational energy levels for different
 vib levels states of a diatomic molecule
 (Spring 2)



Rotational constant B is the same for all values of J and V .

Selection Rule

$$\Delta J = \pm 1$$

and

$$\Delta V = \pm 1, \pm 2, \pm 3, \dots$$

$\Delta J \neq 0$ except under rare conditions.

$\Delta V = 0$, corresponding to only rotational transitions.

A vibrational change is always associated with simultaneous rotational transitions.

Energy Separation for

The Transitions

for the transitions

$$v=1 \longleftarrow v=0$$

and

$$j' \longleftarrow j''$$

$$\bar{v}(v=1, j') = \bar{B} j'(j'+1) + \bar{v}_e (1 + v/2) - a \bar{v}_e (1 + j'/2)$$

$$\bar{v}(v=0, j'') = \bar{B} j''(j''+1) + \frac{1}{2} \bar{v}_e - \frac{1}{4} a \bar{v}_e$$

$$\Delta \bar{v} = \bar{B} (j'^2 + j' - j''^2 - j'')$$

$$+ \bar{v}_e - 2a \bar{v}_e$$

$$= \bar{B} \left\{ (j'^2 - j''^2) + (j' - j'') \right\}$$

$$+ \bar{v}_e (1 - 2a)$$

$$= \bar{B} \left\{ (j' + j'')(j' - j'') + (j' - j'') \right\}$$

$$+ \bar{v}_e (1 - 2a)$$

$$= \bar{B} (j' + j'') (j' + j'' + 1)$$

~~$$\Delta \bar{\nu}_{\text{vib. rot}} = \bar{B} (j' - j'') (j' + j'' + 1) + \bar{\nu}_e (1 - 2a)$$~~

$$\Delta \bar{\nu}_{\text{vib. rot}} = \bar{B} (j' - j'') (j' + j'' + 1) + \bar{\nu}_e (1 - 2a)$$

Neglecting the anharmonicity

$$\Delta \bar{\nu} = \bar{B} (j' - j'') (j' + j'' + 1) + \bar{\nu}_e$$

$$= \bar{\nu}_e + \bar{B} (j' + j'' + 1) (j' - j'')$$

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Case I \Rightarrow

For the transitions,

$$v=1 \leftarrow v=0$$

$$j'=1 \leftarrow j''=0$$

$$2 \leftarrow 1$$

$$3 \leftarrow 2$$

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

$$\therefore j' = j'' + 1$$

$$\Delta \bar{\nu} = \bar{\nu}_e + \bar{B} (j' - j'') (j' + j'' + 1)$$

$$= \bar{\nu}_e + \bar{B} (j'' + 1 - j'') (j'' + 1 + j'' + 1)$$

$$A_{11} = \frac{1}{2} + \frac{1}{2} (\delta'' + \delta')$$

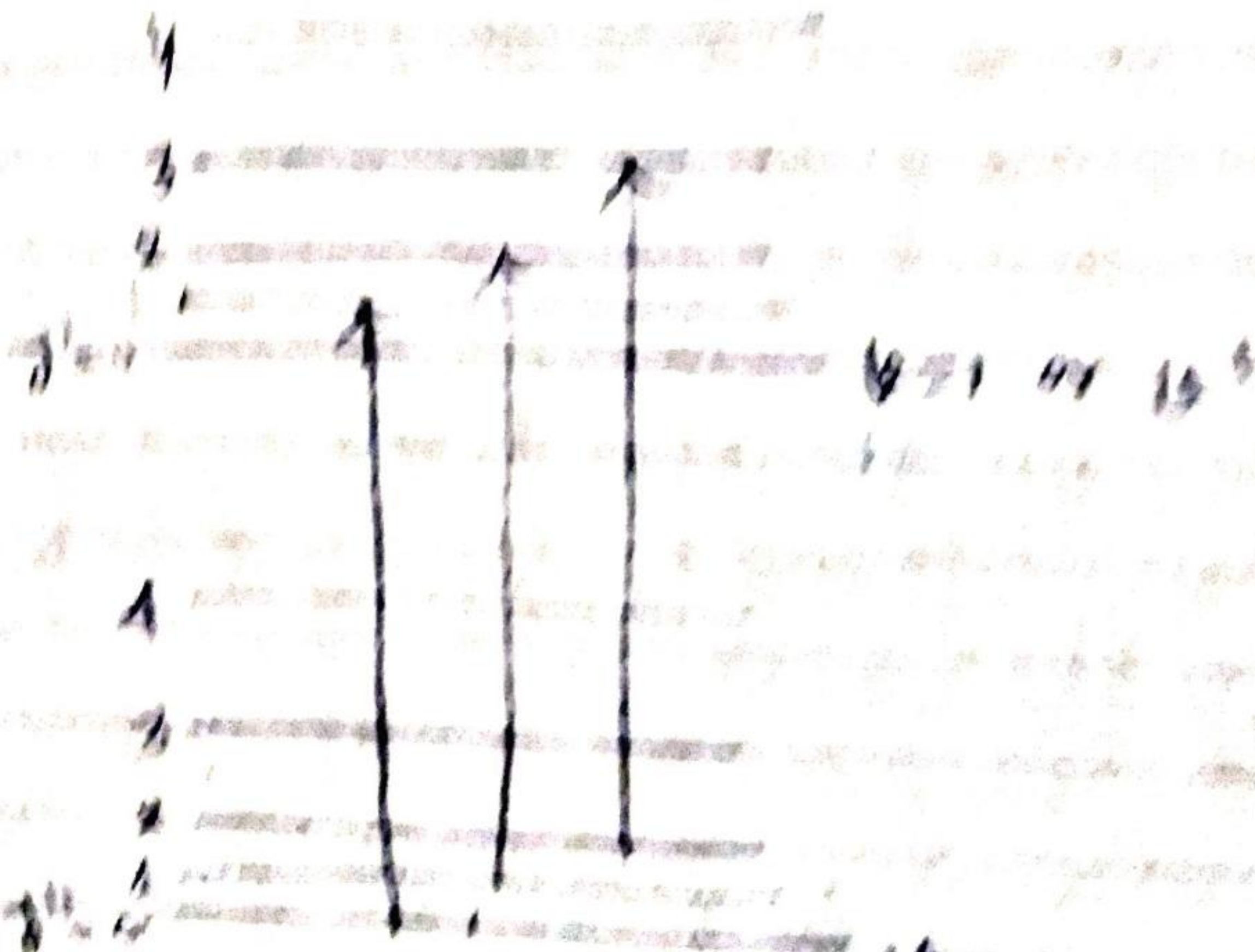
$$= \frac{1}{2} + \frac{1}{2} (\delta'' + \delta') \text{ cm}^2$$

$$= \frac{1}{2} + \frac{1}{2} \cdot 1$$

Let us $m = \delta'' + \delta'$

$$\delta'' = 0, 1, 2, 3$$

$$\delta' = 1, 2, 3, 4$$



$$A_1 = 1$$

$$A_2 = \delta' + \delta'' = 1 + 1$$

$$\delta' = \delta'' = 1$$