P. G. Sem III[rd] core course X

unit II

Transitions →

At room temp. nearly all the molecules in a sample exist in $v=0$, state and transitions that takes place are —

$v=1 \leftarrow v=0$ called fundamental

$v=2 \leftarrow v=0$ called first overtone

$v=3 \leftarrow v=0$ called second overtone

These are the observable intensities

Energy and frequencies of different transitions →

For the transitions

$v=n \leftarrow v=0$

$$E_n = hc\bar{\nu}_e(n+1/2) - ahc\bar{\nu}_e(n+1/2)^2$$

$$E_0 = \frac{1}{2}hc\bar{\nu}_e - \frac{1}{4}hc\bar{\nu}_e a$$

$$\Delta E = nhc\bar{\nu}_e - ahc\bar{\nu}_e\left(n^2+n+\tfrac{1}{4}-\tfrac{1}{4}\right)$$

$$= nhc\bar{\nu}_e - nahc\bar{\nu}_e(n+1)$$

$$= nhc\bar{\nu}_e\{1-a(n+1)\}$$

$$\Delta E = nhc\bar{\nu}_e\{1-a(n+1)\}.$$

Frequency

$$\nu = \nu_e(n+1/2) - a\nu_e(n+1/2)^2$$

$$\nu_n = \nu_e(n+1/2) - a\nu_e(n+1/2)^2$$

$$\nu_0 = \tfrac{1}{2}\nu_e - \tfrac{1}{4}a\nu_e$$

$$\Delta\nu = n\nu_e - a\nu_e\left(n^2+n+\tfrac{1}{4}-\tfrac{1}{4}\right)$$

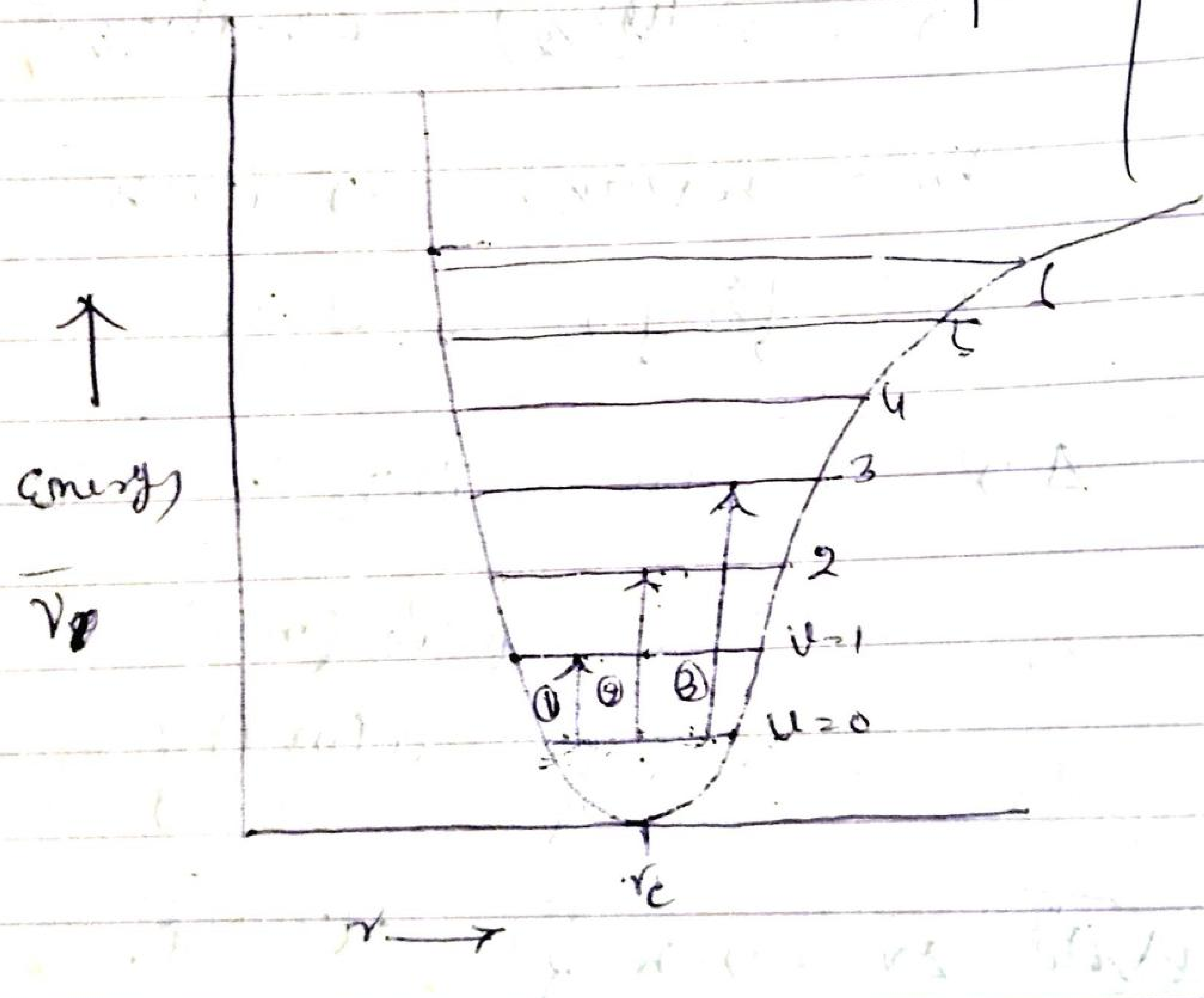
$$= n\nu_e - na\nu_e(n+1)$$

$$= n\nu_e\{1-a(n+1)\}$$

$$\Delta\bar{\nu} = n\bar{\nu}_e\{1-a(n+1)\}.$$

Thus, for —

Transition	Name	Intensity	ΔE	$\Delta \nu$	$\Delta \bar{\nu}$
$v=1 \leftarrow v=0$	Fundamental	High	$h\nu_e(1-2a) \approx h\nu_e$	ν_e	$\bar{\nu}_e$
$v=2 \leftarrow v=0$	First overtone	Low	$2h\nu_e(1-3a) \approx 2h\nu_e$	$2\nu_e$	$2\bar{\nu}_e$
$v=3 \leftarrow v=0$	second overtone	poor	$3h\nu_e(1-4a) \approx 3h\nu_e$	$3\nu_e$	$3\bar{\nu}$



Fundamental ⟶ transition

$v=1 \leftarrow v=0$

$$\Delta E = nh\nu_e \{1 - a(n+1)\}$$

$$= nhc\bar{\nu}_e \{1 - a(n+1)\}$$

$$= h\nu_e \{1 - a(1+1)\}$$

$$= h\nu_e (1 - 2a)$$

$$= hc\bar{\nu}_e (1 - 2a)$$

$$\approx hc\bar{\nu}_e$$

$$\Delta \bar{\nu} = n\bar{\nu}_e \{1 - a(n+1)\}$$

$$= \bar{\nu}_e (1 - 2a)$$

$$\approx \bar{\nu}_e \quad (cm^{-1})$$

i.e. $\bar{\nu} \approx \bar{\nu}_e$

High intensity.

(2) First overtone transition

$v = 2 \leftarrow v = 0$

$$\Delta E = 2h\nu_e \{1 - a(2+1)\}$$

$$= 2h\nu_e (1 - 3a)$$

$$= 2hc\bar{\nu}_e (1 - 3a)$$

$$\sim 2hc\bar{\nu}_e$$

$\Delta \bar{\nu} = 2\bar{\nu}_e \{1 - a(\ldots)\}$

$= 2\bar{\nu}_e \{1 - 3a)$

$\simeq 2\bar{\nu}_e$

i.e. $\bar{\nu} \simeq 2\bar{\nu}_e$ cm^{-1}

Low intensity

(3) Second overtone transition →

$v = 3 \leftarrow v = 0$

$\Delta E = 3h\nu_e(1 - 4a)$

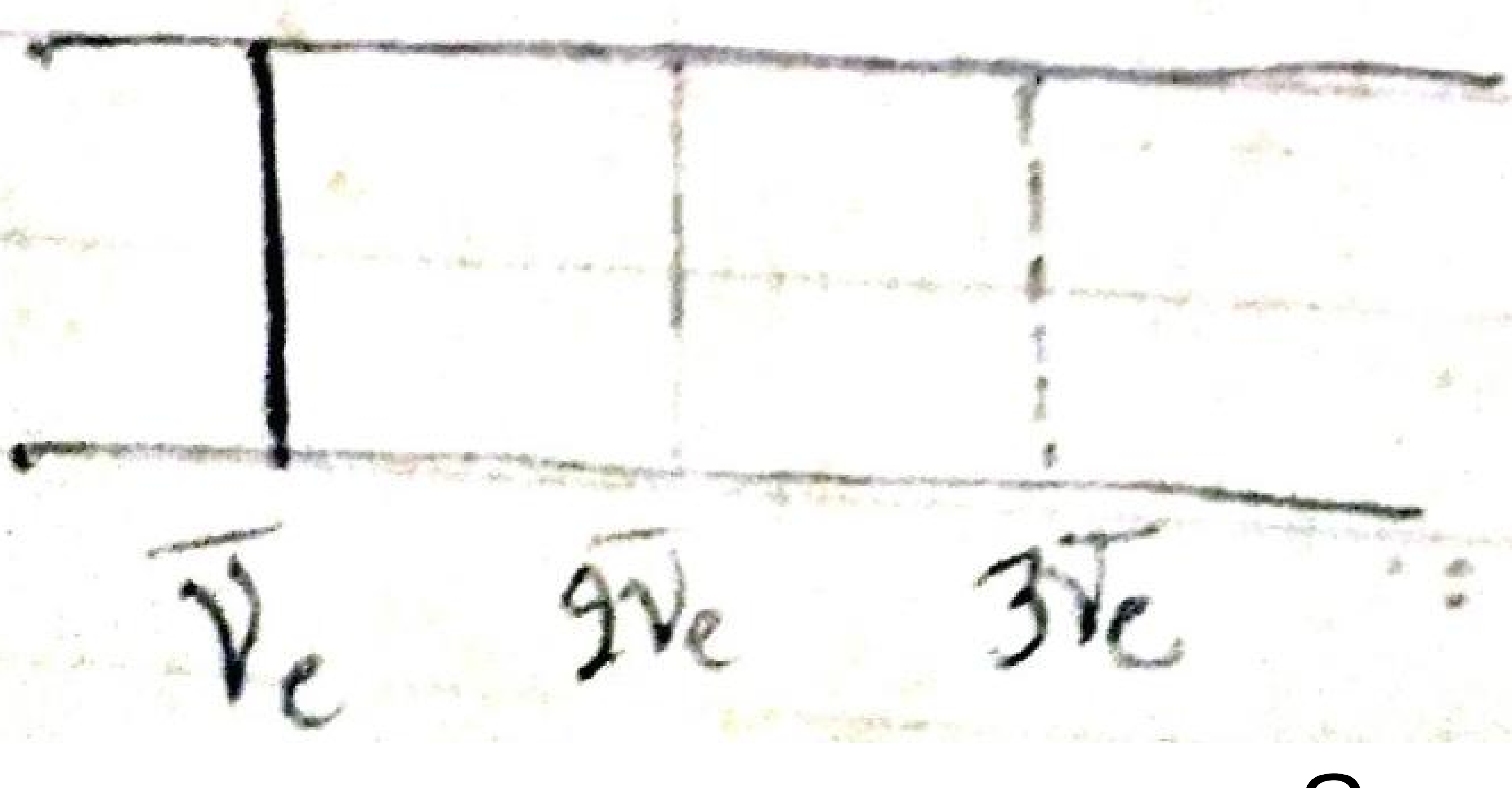
$= 3hc\bar{\nu}_e(1 - 4a)$

$\simeq 3hc\bar{\nu}_e$

$\bar{\nu} = 3\bar{\nu}_e(1 - 4a)$

$\simeq 3\bar{\nu}_e$ cm^{-1} poor intensity

Spectral band —



The first overtone occur at a frequency almost twice that of fundamental absorption and the second overtone occur at approximately thrice of the fundamental absorption.

Hot Band :→

If the temperature is high i.e, greater than 200°C or if the molecule is highly anharmonic a small fraction of molecules may existing in $v=1$ state and give rise to the following weak transition

$v=2 \leftarrow v=1$, Hot band fundamental
$v=3 \leftarrow v=1$, Hot band first overtone
$v=4 \leftarrow v=1$, Hot band 2nd overtone
etc.

(1) Hot band Fundamental —
For the transition

$v=2 \leftarrow v=1$

$$E_2 = hc\bar{\nu}_e(2+1/2) - ahc\bar{\nu}_e(2+1/2)^2$$

$$E_1 = hc\bar{\nu}_e(1+1/2) - ahc\bar{\nu}_e(1+1/2)^2$$

$$\Delta E = hc\bar{\nu}_e - ahc\bar{\nu}_e\left(\frac{25}{4} - \frac{9}{4}\right)$$

$$= hc\bar{\nu}_e - ahc\bar{\nu}_e \cdot 4$$

$$= hc\bar{\nu}_e(1 - 4a)$$

$$\approx hc\bar{\nu}_e$$

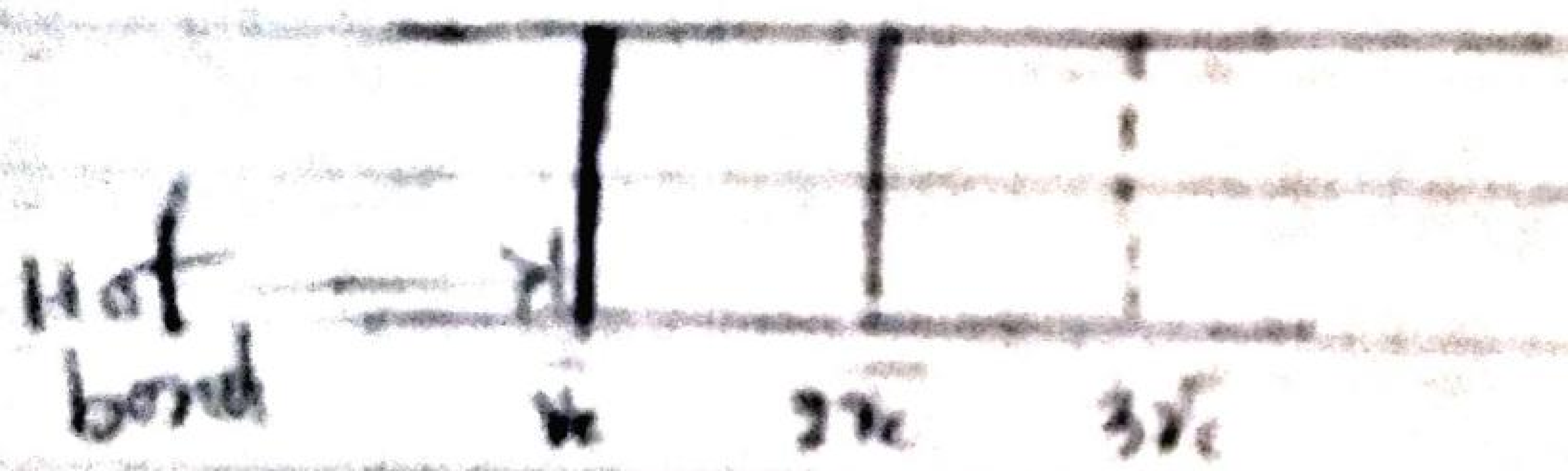
$$\Delta\nu = \nu_e(1 - 4a)\ \text{sec}^{-1}$$

$$\approx \nu_e\ \text{sec}^{-1}$$

$$\Delta\bar{\nu} = \bar{\nu}_e(1 - 4a)\ \text{cm}^{-1}$$

$$\approx \bar{\nu}_e\ \text{cm}^{-1}$$

Spectrum :—



This weak absorption is found to occur close to and at a slightly lower frequency than the fundamental.