

T. D. C. Part IIIrd
Chem. paper V^{an} (Physical Chemistry)
Calculation of $\bar{\nu}_e$, a , k and $\bar{\nu}_c$

To calculate 'a'

Let

$$\begin{aligned}\bar{\nu}_f &= \bar{\nu}_e (1 - 2a) && \text{fundamental} && \text{(i)} \\ \bar{\nu}_1 &= 2\bar{\nu}_e (1 - 3a) && \text{1st overtone} && \text{(ii)} \\ \bar{\nu}_2 &= 3\bar{\nu}_e (1 - 4a) && \text{2nd overtone} && \text{(iii)}\end{aligned}$$

Dividing (ii) by (i)

$$\frac{\bar{\nu}_1}{\bar{\nu}_f} = \frac{2(1 - 3a)}{1 - 2a}$$

$$\text{or, } \bar{\nu}_1 (1 - 2a) = 2\bar{\nu}_f (1 - 3a)$$

$$\text{or, } \bar{\nu}_1 - 2a\bar{\nu}_1 = 2\bar{\nu}_f - 6\bar{\nu}_f \cdot a$$

$$\begin{aligned}\text{or, } \bar{\nu}_1 - 2\bar{\nu}_f &= 2a\bar{\nu}_1 - 6a\bar{\nu}_f \\ &= 2a(\bar{\nu}_1 - 3\bar{\nu}_f)\end{aligned}$$

$$\text{or, } 2a = \frac{\bar{\nu}_1 - 2\bar{\nu}_f}{\bar{\nu}_1 - 3\bar{\nu}_f}$$

$$= \frac{2\bar{\nu}_f - \bar{\nu}_1}{3\bar{\nu}_f - \bar{\nu}_1}$$

$$\text{or, } a = \frac{2\bar{\nu}_f - \bar{\nu}_1}{3\bar{\nu}_f - \bar{\nu}_1} \cdot \frac{1}{2}$$

To calculate $\bar{\nu}_e$ \Rightarrow

since,

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

$$\therefore \bar{\nu}_e = \frac{\bar{\nu}_f}{1 - 2a}$$

To calculate force constant "K" \Rightarrow

since,

$$\bar{\nu}_e = \frac{1}{2\pi c} \sqrt{K/\mu}$$

$$\text{or, } \bar{\nu}_e^2 = \frac{1}{4\pi^2 c^2} \frac{K}{\mu}$$

$$\therefore K = 4\pi^2 \mu \bar{\nu}_e^2 c^2$$

$$K = 4\pi^2 c^2 \mu \bar{\nu}_e^2$$

To calculate bond length " r_{eq} " \Rightarrow

$\therefore \Delta\bar{\nu}$ = frequency separation between peaks of P & Q branches of fundamental absorption

$$= \sqrt{\frac{8BKT}{hc}}$$

B is given.

and

$$\bar{B} = \frac{h}{8\pi^2 \mu r^2 c^2}$$

Hence, ' r ' is calculated.

The vibrations of Polyatomic molecules :-

With increase in no. of atoms in the molecule there is increase in the ~~nature~~ of the complex nature of the spectrum. But slight ~~extension~~ extension to the simple theory are sufficient to explain the spectra. The following factors go to the determination of nature of spectra :-

- ① No. of fundamental vibrations
- ② Overtone bands.
- ③ Combination and difference bands
- ④ Rotational fine structure i.e. P & R branches.

I.R Spectrum for H₂O :->

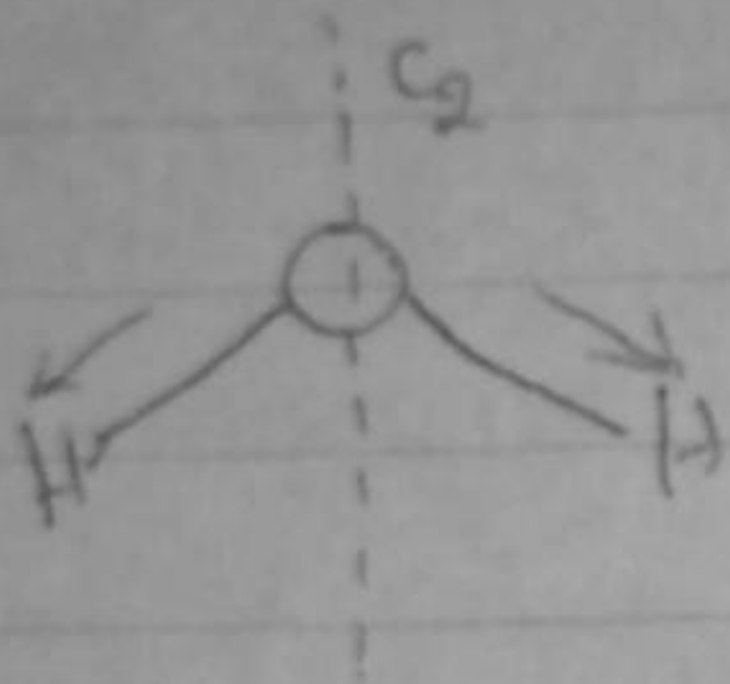
The molecule is triatomic and non-linear therefore,

$$\begin{aligned} \text{No. of vibrational modes} &= 3N - 6 \\ &= 3 \times 3 - 6 = 3. \end{aligned}$$

The vibrational modes are also called 'normal modes' vibration. (same frequency).

The vibration of H₂O molecules are -

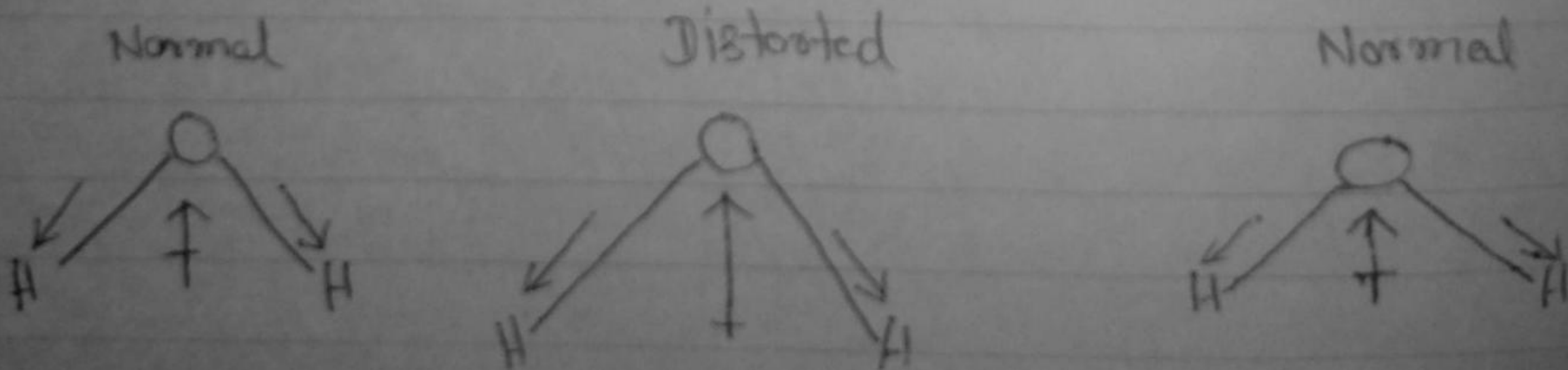
(i) Symmetric Stretching :->



(Symmetric Stretching \rightarrow Sym. stretching means that the vibration is unchanged in phase on rot by 180° about the symmetry axis C₂).

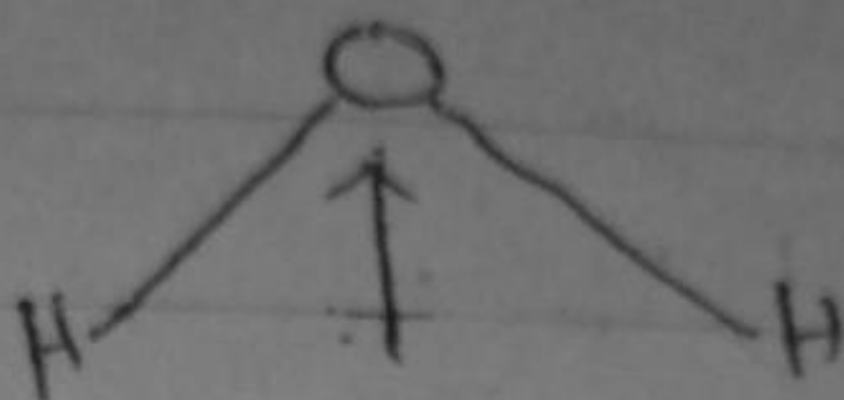
(a) $\bar{\nu} = 3652 \text{ cm}^{-1}$

(b) Dipole fluctuation :->



Distorted

Normal



i.e. Dipole moment (μ) fluctuates

\therefore I.R active.

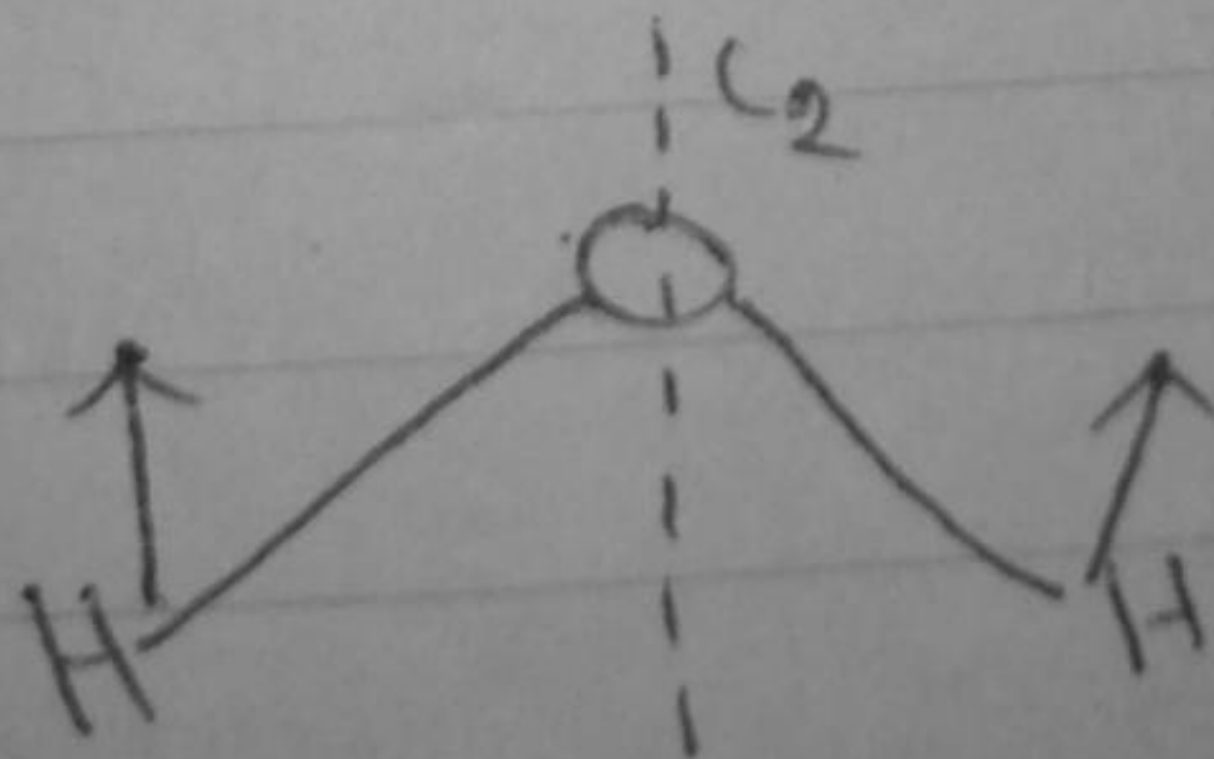
(c) Dipole fluctuation occurs along C_2 axis

\therefore vibration is parallel.

(d) In symmetric vibrations $\bar{\nu}$ of this is maximum.

\therefore vibration is called ν_1 .

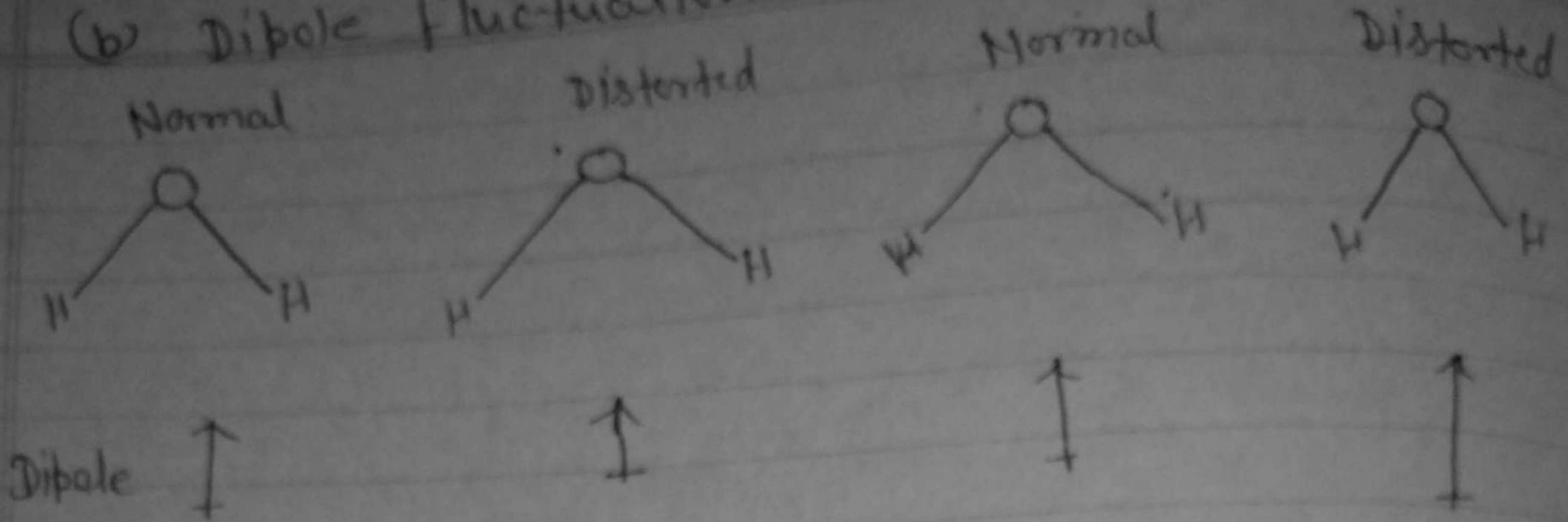
(12) Symmetric Bending \Rightarrow



(a)

$$\bar{\nu} = 1595 \text{ cm}^{-1}$$

(b) Dipole fluctuation: \rightarrow

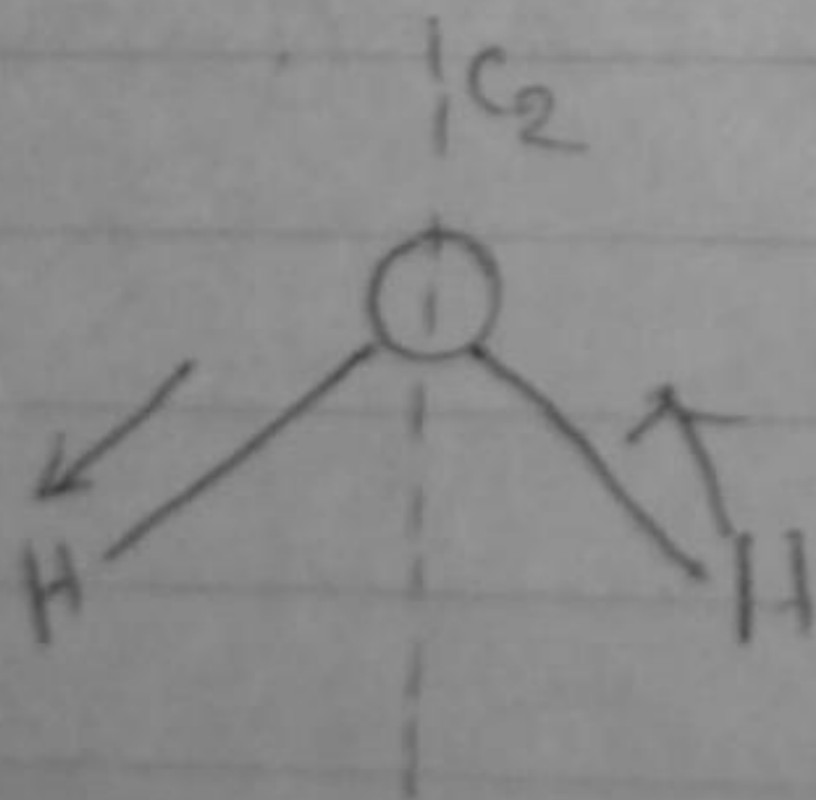


i.e. Dipole moment fluctuates
 \therefore I.R active.

(c) Dipole fluctuation occurs along C_2 axis,
 \therefore vibration is parallel.

(d) ν_2 - vibration.

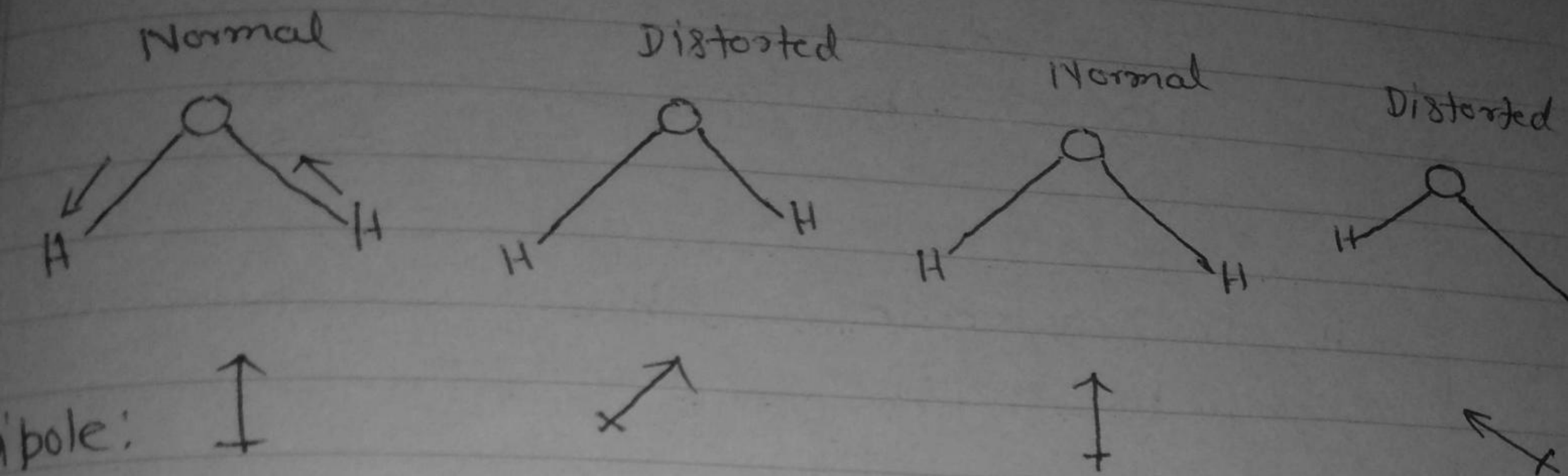
(iii) Antisymmetric stretching: \rightarrow



(Antisymmetric stretching because on vibration rotation by 180° about C_2 axis, vibration is changed in phase.)

(a) $\bar{\nu} = 3756 \text{ cm}^{-1}$.

(b) Dipole fluctuation $\therefore \rightarrow$.



i.e. Dipole moment fluctuates,
~~is~~ & hence I.R. active.

(c) Vibration is perpendicular, as dipole change occurs \perp to C_2 axis.

(d) vibration: ν_3

Thus the molecule has 3 I.R. bands
i.e., if a molecule has 3 I.R. bands, &
is triatomic, it is non-linear (no P.R. bands)