

Homonuclear diatomic molecules ( $O_2, N_2, \dots$ ) <sup>(6)</sup>

give no infra-red or microwave spectra as they possess no dipole moment, whereas they give a rotational Raman spectra.

Symmetric Top Molecules :- Planar rotator

about the top axis produces no change in the polarizability of a typical symmetric top molecule such as  $CHCl_3$  but end-over-end rotators will produce such a change.

The energy levels are

$$E_{J,k} = BJ(J+1) + (A-B)k^2 \text{ cm}^{-1}$$

$$(J=0, 1, 2, \dots; k = \pm J, \pm(J-1), \dots)$$

The selection rules for Raman spectra <sup>(3)</sup> are

$$\Delta k = 0$$

$$\Delta J = 0, \pm 1, \pm 2 \quad \text{--- (4)}$$

(except for  $k=0$  states  
when  $\Delta J = \pm 2$  only)

$k \rightarrow B$  the rotational quantum number for axial rotation

$\Delta k = 0$  implies that changes in the

angular momentum ~~about the top~~ about the top

axis ~~will~~ will not give rise to a Raman spectrum  
such rotators are Raman inactive

The restriction  $\Delta J = \pm 2$  for  $k=0$  states (7)  
 mean effectively that  $\Delta J \neq \pm 1$  for  
 transitions involving the ground state ( $J=0$ ) since  
 $k = \pm J, \pm(J-1)$ . Thus for all  $J$  values  
 other than zero,  $k$  also may be different  
 from zero and  $\Delta J = \pm 1$  transitions  
 are allowed.

Restricting to positive  $\Delta J$

1.  $\Delta J = +1$  (R branch lines)

$$\begin{aligned} \Delta E_R &= E_{J'=J+1} - E_{J''=J} \\ &= 2B(J+1) \text{ cm}^{-1} \\ &\quad (J=1, 2, 3, \dots \text{ (but } J \neq 0)) \end{aligned} \quad \text{--- (5)}$$

2.  $\Delta J = +2$  (S branch lines)

$$\begin{aligned} \Delta E_S &= E_{J'=J+2} - E_{J''=J} \\ &= B(4J+6) \text{ cm}^{-1} \quad (J=0, 1, 2, \dots) \end{aligned} \quad \text{--- (6)}$$

We shall have two series of lines in  
 the Raman spectrum

$$\left. \begin{aligned} \bar{\nu}_R &= \bar{\nu}_{\text{ex}} \pm \Delta E_R = \bar{\nu}_{\text{ex}} \pm 2B(J+1) \text{ cm}^{-1} \\ &\quad (J=1, 2, \dots) \\ \bar{\nu}_S &= \bar{\nu}_{\text{ex}} \pm \Delta E_S = \bar{\nu}_{\text{ex}} \pm B(4J+6) \text{ cm}^{-1} \\ &\quad (J=0, 1, 2, \dots) \end{aligned} \right\} \quad \text{--- (7)}$$

Spherical Top Molecules → Ex.  $\text{CH}_4$ ,  $\text{SiH}_4$  ⑧  
having tetrahedral symmetry.

The polarizability ellipsoid for such molecules is a spherical surface and rotation of this ellipsoid will produce no change in polarizability. → The pure rotations of spherical top molecules are completely inactive in the Raman.

Asymmetric Top Molecules → All rotations

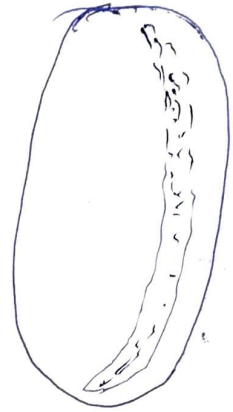
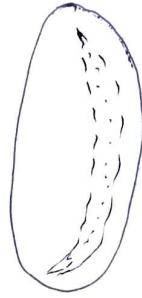
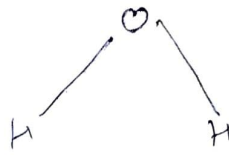
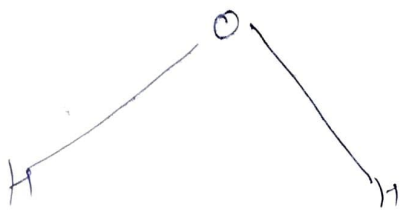
of asymmetric top molecules → Raman active (normally)

Raman spectra → complicated.

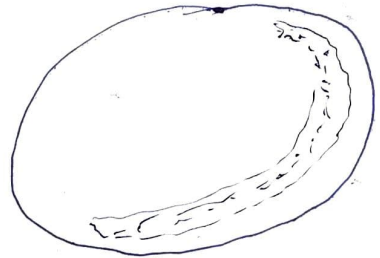
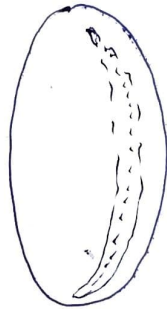
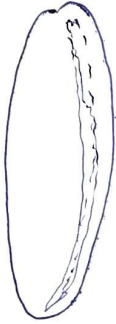
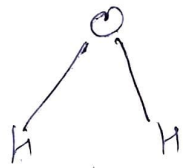
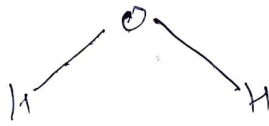
Vibrational Raman Spectra: Raman activity  
of vibrations

If a molecule has a little or no symmetry → it is ~~is~~ easy to decide whether its vibrational modes will be Raman active or inactive: → usually all its modes are Raman active. But when the molecule has considerable symmetry it is not easy to make the decision — whether or not the polarizability changes during the vibrations.

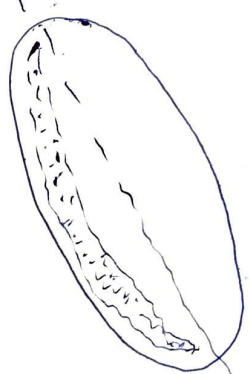
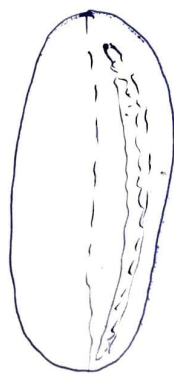
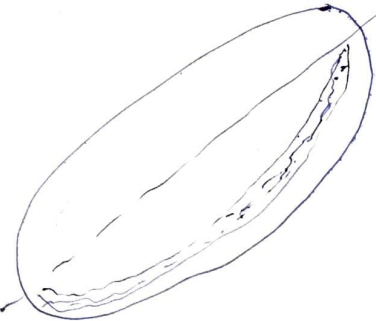
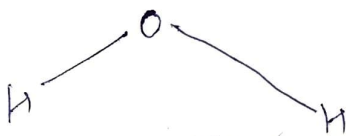
We consider the simple asymmetric top molecule  $\text{H}_2\text{O}$ . The approximate shapes of the polarizability ellipsoid are as follows



$\nu_1$ , symmetric stretching mode



$\nu_2$ , bending mode



$\nu_3$ , asymmetric stretching mode

The change in size, shape, or direction of the polarizability ellipsoid of the water molecule during each of its three vibrational modes. The center column shows the equilibrium position of the molecule, right and left are the extremes of each vibration.

(a) During the symmetric stretch → The molecule as a whole increases and decreases in size; when a bond is stretched, the electrons forming it are less firmly held by the nuclei and so the bond becomes more polarizable. The polarizability ellipsoid of  $H_2O$  may be expected to decrease in size while the bonds stretch and to increase while they compress, but to maintain an approximately constant shape.

(b) bending motion:- Shape of the ellipsoid changes most. Thus if we imagine vibrations of very large amplitude, at one extreme (on the left) the molecule approaches the linear configuration with a horizontal axis, while at the other extreme (on the right) it approximates to a diatomic molecule with a vertical axis.

(c) Asymmetric stretching = both the size and shape remain approximately constant, but the direction of major axis changes markedly.

Thus, all the three vibrations involve changes in at least one aspect of the polarizability ellipsoid → and all are Raman active

