

Rule of Mutual exclusion

If a molecule has a centre of symmetry then Raman active vibrations are infra-red inactive, and vice versa. If there is no centre of symmetry then some (but not necessarily all) vibrations may be both Raman and infra-red active.

Example

O_2 (polarizable ~~not~~ magnitude ~~mode~~ → small ellipse)
 O → magnitude of polarizable is low (side)

H₂O molecule

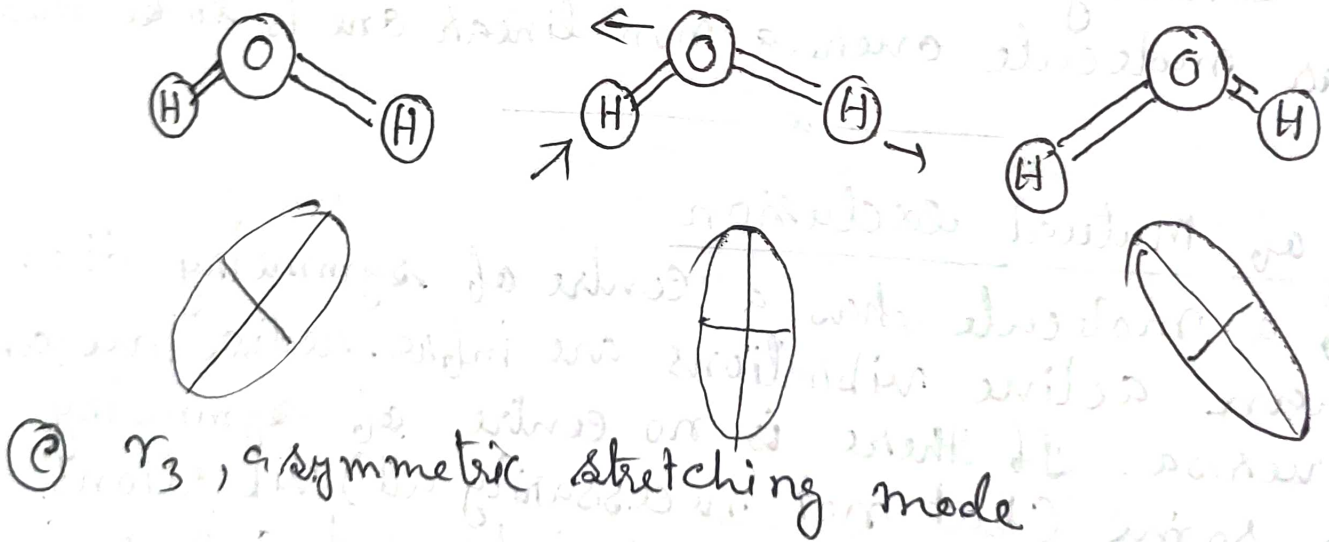
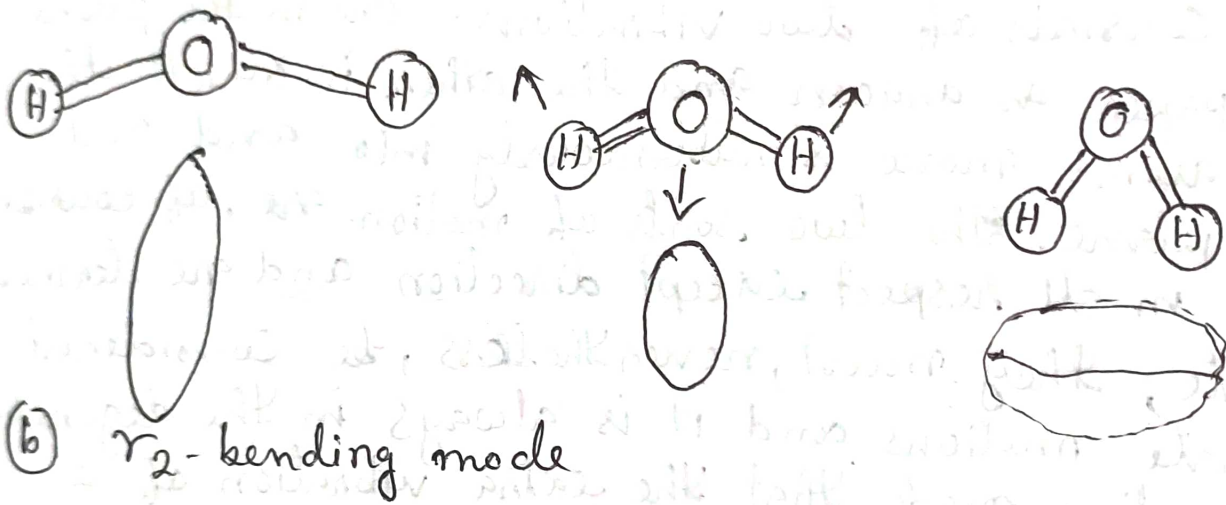
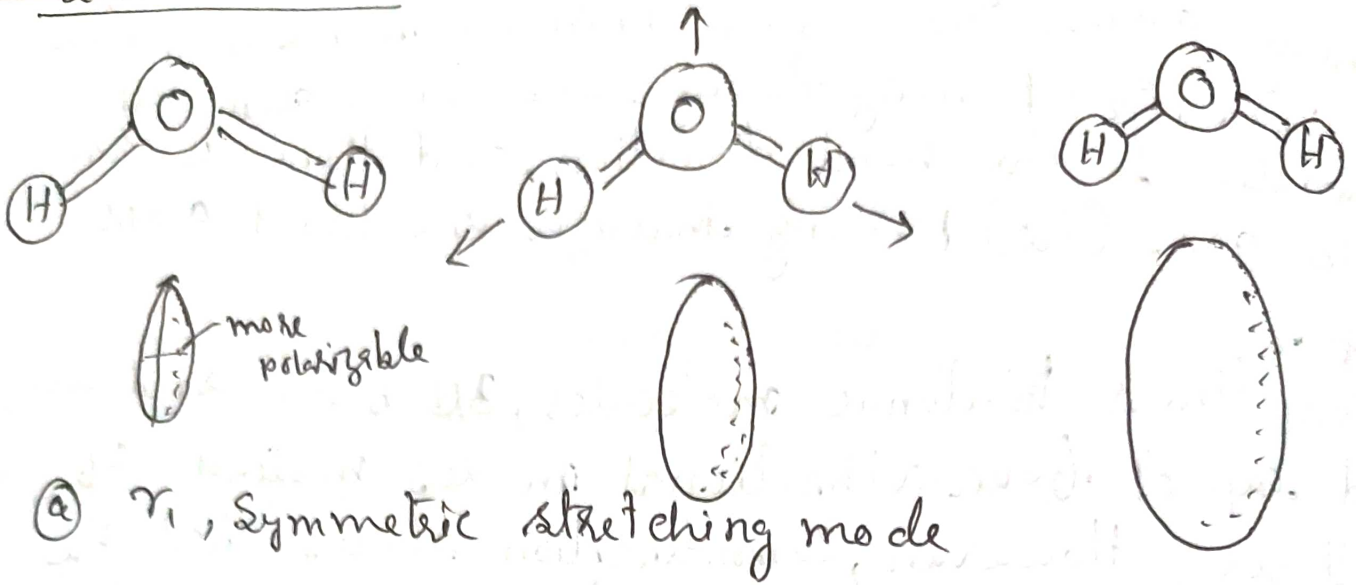


Figure The change in size, shape or direction of the polarizability ellipsoid of the water molecule during each of its three vibrational modes

During the symmetric stretching, the molecules 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 bond becomes more polarizable. Thus, the polarizability ellipsoid of H_2O may be expected to stretch, and to increase while they compress, but to maintain an approximately constant shape. On the other hand, while undergoing the bending motion, it is the shape of ellipsoid which 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. For asymmetric stretching motion, ν_3 where both the size and shape remain approximately constant, but the direction of the major axis changes markedly. Thus all three vibrations involve obvious changes in at least one aspect of the polarizability ellipsoid, and all are Raman active.

CO₂ molecule

- (a) ν_1 , symmetric stretching mode
- (b) ν_2 , bending mode
- (c) ν_3 asymmetric mode

Raman and infrared-activities of carbon dioxide

mode of vibration CO ₂	Raman	infrared
ν_1 : symmetric stretch	→ Active	Inactive
ν_2 : bend	— Inactive	active
ν_3 : asymmetric stretch	— Inactive	active