Vibrations of polyatomic molecules overtone and combination bands (H_2O, CO_2)

Modes of vibration

Consider a molecule containing N atoms. In order to describe their positions it is necessary to specify 3N Co-ordinates or degrees of freedom. In this case, 3N coordinates have been fixed, the bond distances and bond angles of the molecules are also fixed and no further arbitrary specification can be made.

(i) The number of vibrational degrees of freedom for a non linear molecule = $3N-6$ N no of atoms

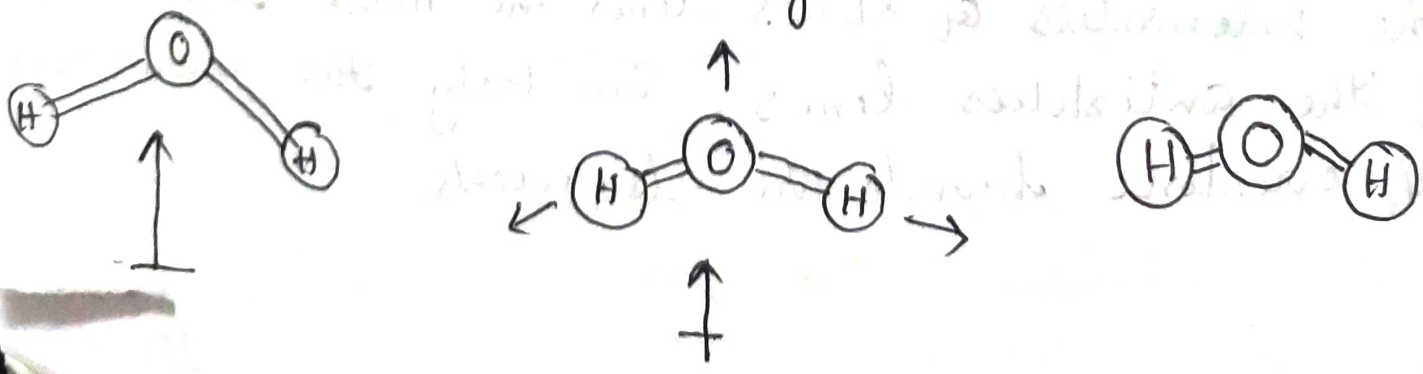
(ii) The number of vibrational degrees of freedom for linear molecule = $3N-5$, N no of atoms

H_2O molecules

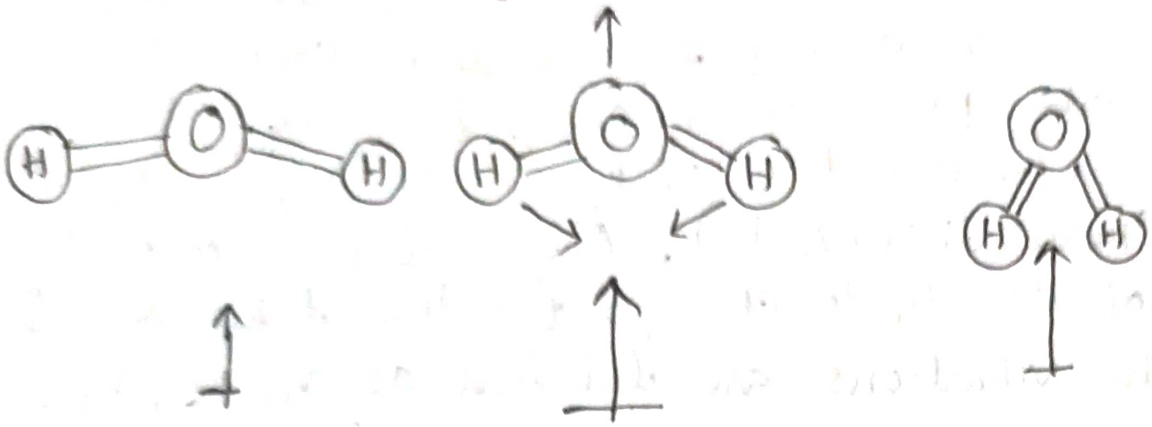
non linear ⟶ triatomic molecule

$3N-6=3$ allowed vibrational modes.

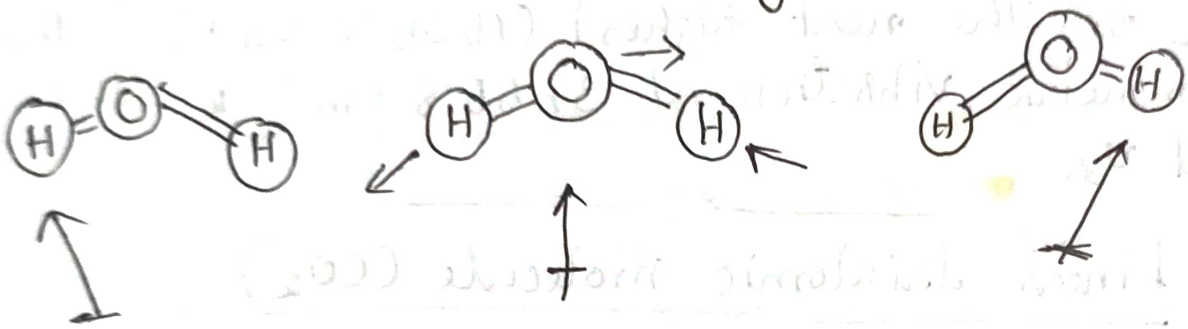
(a) ν_1, symmetric stretching mode



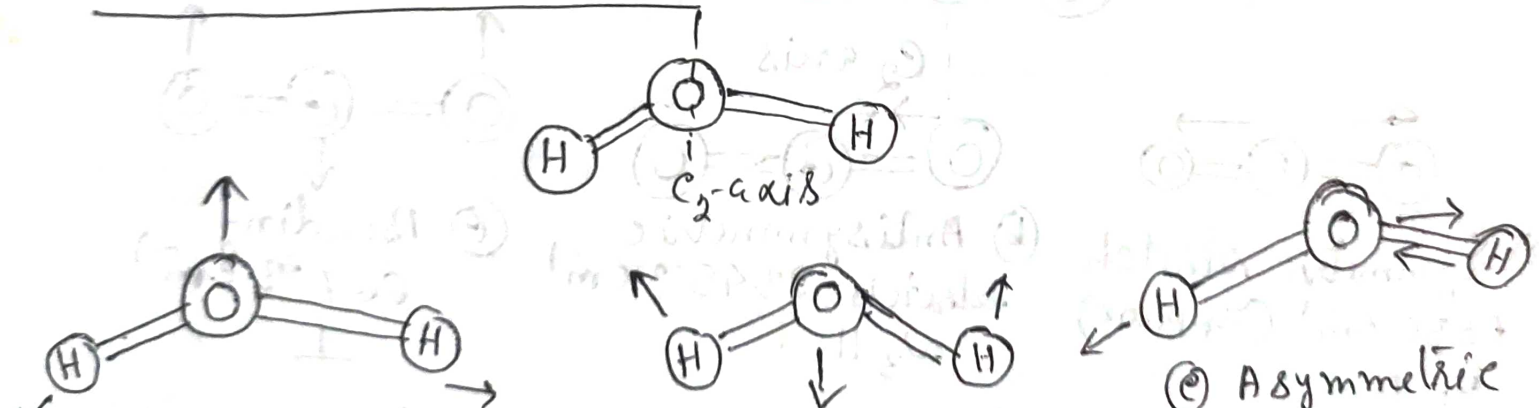
(b) ν_2 - bending mode



(c) ν_3, asymmetric stretching mode



The symmetry of the water molecule and its three fundamental vibrations



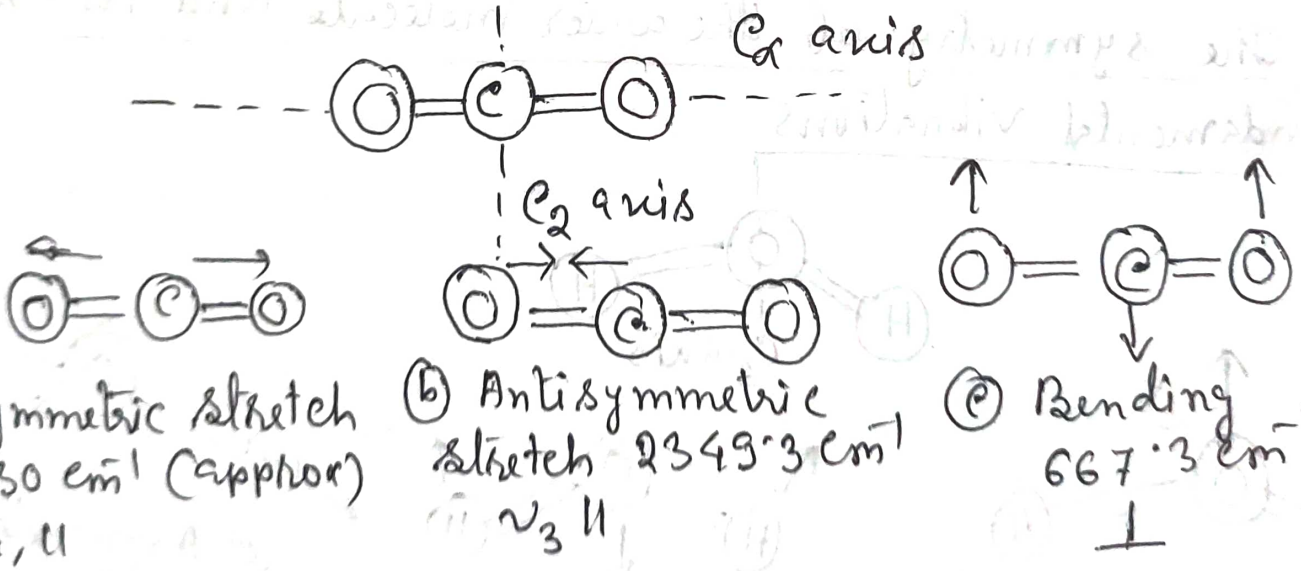
(a) Symmetric stretching
3651.7 cm^{-1}
ν_1, parallel (∥)

(b) Symmetric bend
1595.0 cm^{-1}
ν_2, parallel (∥)

(c) Asymmetric stretch
3755.8 cm^{-1}
ν_3, perpendicular (⊥)

For a molecule to be infra-red active, there must be a dipole change during the vibration and this change may take place either along the line of the symmetry axis (parallel to it or ∥) or at right angles to the line (perpendicular, ⊥). Above figure shows the nature of the dipole changes for the three vibration of water. The vibrations are labelled as ν_1, ν_2, ν_3. Thus the symmetry vibrations of H_2O are labelled ν_1 for the highest fully symmetric frequency (3651.7 cm^{-1}) and ν_2 for the next highest (1595.0 cm^{-1}), the antisymmetric vibration at 3755.8 cm^{-1} is then labelled ν_3.

Linear triatomic molecule (CO_2)



(a) Symmetric Stretch 1330 cm^{-1} (approx) ν_1, ∥

(b) Antisymmetric Stretch 2349.3 cm^{-1} ν_3 ∥

(c) Bending 667.3 cm^{-1} ⊥

Fig. The symmetry and fundamental vibrations of the carbon dioxide molecule.

For the linear triatomic molecule CO_2, for which the normal vibrations are shown in fig.

For this molecule there are two different sets of symmetry axes. There is an infinite number of two fold axes (C_2) passing through the carbon atom at right angles to the bond direction, and there is an ∞-fold axis (C_∞) passing through the bond axis itself.

For linear triatomic molecules, $3N-5=4$ and we could expect four vibrational modes instead of the three. However, consideration shows that ν_2 in fact consists of two vibrations — one in the plane of the paper as drawn and the other in which the oxygen atoms move simultaneously into and out of the plane. The two sorts of motion are, of course, identical in all respect except direction and are termed degenerate; they must, nevertheless, be considered as separate motions and it is always in the degeneracy of a bending mode that the extra vibration of a linear molecule over a non-linear one is to be found.

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