

Translational movement uses three of the  $3N$  degrees of freedom leaving  $3N-3$ . In general, also, the rotation of a non-linear molecule can be resolved into components about three perpendicular axes. Spectra of these axes also require three degrees of freedom. Now molecule is left with  $3N-6$  degrees of freedom.

The only other motion allowed to it is internal vibrations, a non-linear  $N$ -atom molecule can have  $3N-6$  different internal vibrations!

Non-linear:  $3N-6$  fundamental vibrations -- (24)(a)

If, the molecule is linear, there is no rotation about the bond axis  $\rightarrow$  hence only two degrees of rotational freedom required. So  $3N-5$  degrees of vibrational freedom.

Linear:  $3N-5$  fundamental vibrational -- 24(b)

In both cases, since an  $N$  atom molecule has  $N-1$  bonds (for acyclic molecules) between its atoms,  $N-1$  of the vibrations are bond-stretching motions,

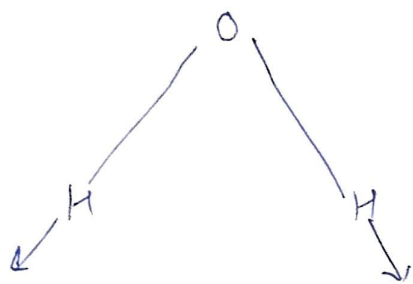
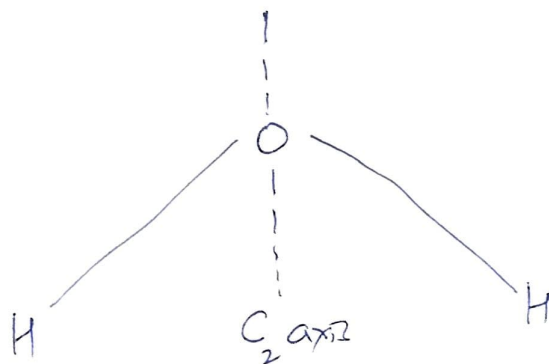
the other  $2N-5$  (non-linear) or  $2N-4$  (linear) (45)  
are bending motions.

For a diatomic molecule (perfectly linear):

$N=2$ ,  $3N-5=1 \rightarrow$  only one fundamental vibration. However,  $3N-5$  rule says nothing about the presence, absence, or intensity of overtone vibrations  $\rightarrow$  these are governed by anharmonicity.

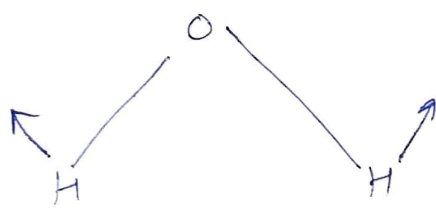
$H_2O \rightarrow$  non-linear triatomic.

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



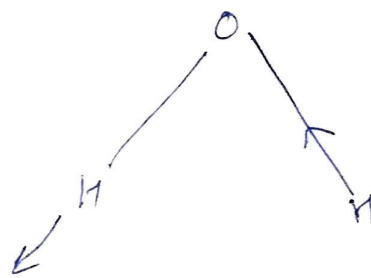
Symmetric stretching  
 $3651.7 \text{ cm}^{-1}$

$\nu_1$ , Parallel ( $\parallel$ )



Symmetric bending  
 $1595.0 \text{ cm}^{-1}$

$\nu_2$ , parallel



antisymmetric stretch  
 $3755.8 \text{ cm}^{-1}$

$\nu_3$ , perpendicular ( $\perp$ )

These three vibrational motions  $\rightarrow$  normal modes of vibration (or normal vibrations)  $\rightarrow$  normal vibration is defined as a molecular motion in which all the atoms move in phase and with the same frequency.

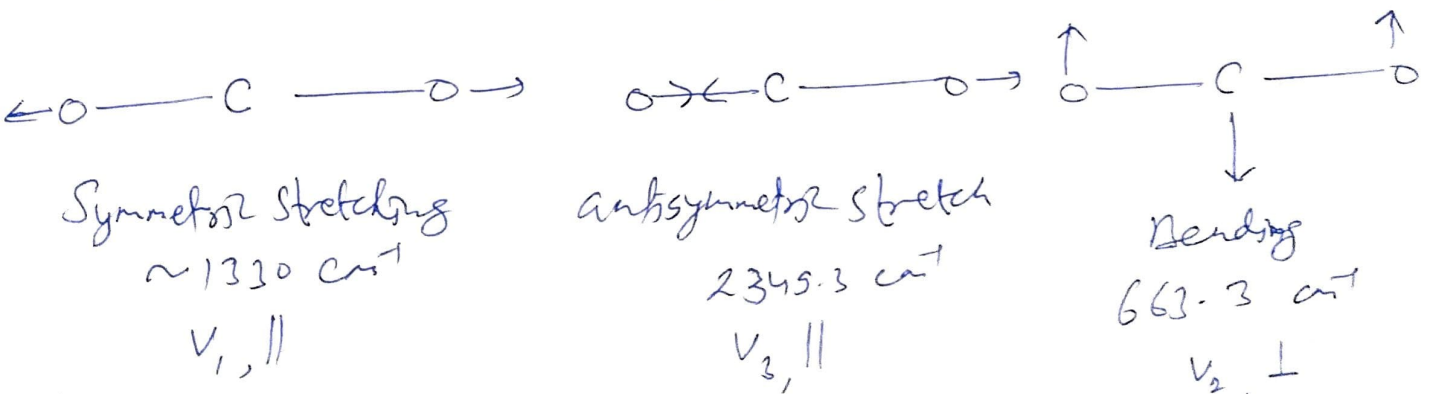
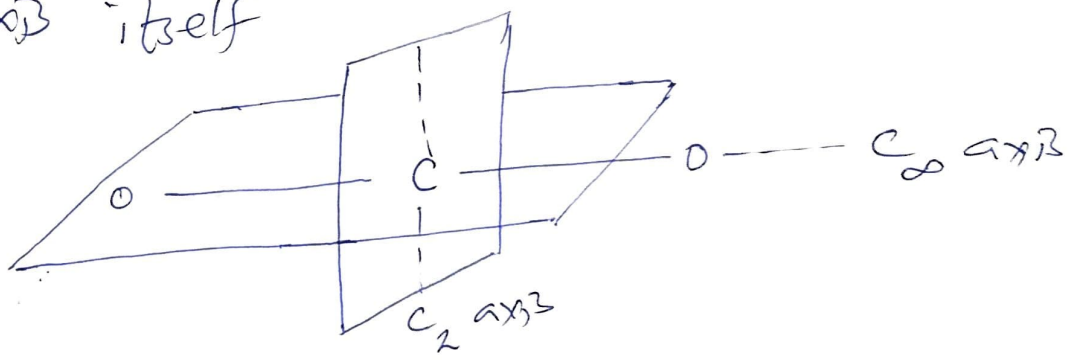
Water molecule contains some elements of symmetry.

$C_2$  axis  $\rightarrow$  shown by dashed line

$\rightarrow$  Twice in every complete revolution the molecule presents an identical aspect to an observer. This molecule has only the one rotational symmetry axis and ~~it~~ it is conventional to refer the molecular vibrations to this axis.

$CO_2 \rightarrow$  linear triatomic molecule. 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  $\infty$ -fold axis ( $C_\infty$ ) passing through the bond axis itself



Symmetrical stretching  
 $\sim 1330 \text{ cm}^{-1}$   
 $\nu_1, \parallel$

antisymmetrical stretch  
 $2345.3 \text{ cm}^{-1}$   
 $\nu_3, \parallel$

Bending  
 $663.3 \text{ cm}^{-1}$   
 $\nu_2, \perp$

For  $CO_2$ ,  $3N-5 = 4 \rightarrow$  we would expect four vibrational modes instead of three.



$\nu_2 \rightarrow$  consists of two vibrations, one in the plane (47)  
of the paper, and other in which the oxygen atoms  
move simultaneously into and out of the plane. The  
two sorts of motion are, of course, are identical  
in all respect except direction and are termed  
"degenerate".

### Overtone and Combination frequencies

When the restriction to simple harmonic motion  
is lifted, we have again as in the case of  
the diatomic molecule  $\rightarrow$  the possibility of first,  
second, etc., overtones occurring at frequencies  
near  $2\nu_1, 3\nu_1, \dots, 2\nu_2, 3\nu_2, \dots, 2\nu_3, \dots$  etc,  
where each  $\nu_i$  is a fundamental mode. The  
intensities fall off rapidly. However, in  
addition, the selection rules now permit "combination  
bands" and "difference bands".

$$\nu_1 + \nu_2, 2\nu_1 + \nu_2, \nu_1 + \nu_2 + \nu_3 \text{ etc.}$$

$$\nu_1 - \nu_2, 2\nu_1 - \nu_2, \nu_1 + \nu_2 - \nu_3$$

### The Influence of Rotation on the Spectra of Polyatomic Molecules

The selection rule for the simultaneous rotation  
and vibrations of a diatomic molecule was

$$\Delta J = \pm 1, \pm 2, \pm 3, \dots \quad \Delta J = \pm 1, \Delta J \neq 0$$

and this gives rise to a spectrum consisting of approximately equally spaced line series on each side of a central minimum ~~is~~ designated as the band centre. (42)

The vibrations of complex molecules could be subdivided into those causing a dipole change either (1) parallel or (2) perpendicular to the major axis of rotational symmetry.

The selection rules for the rotational transitions of complex molecule depend on the type of vibrations,  $\parallel$  or  $\perp$ , which the molecule is undergoing.

The selection rules and the energies depend on the shape of the molecule also.

We deal with linear molecule.

### Linear molecule

Parallel Vibrations: The selection rule for these is identical with that for diatomic molecules, i.e.

$$\Delta J = \pm 1, \quad \Delta v = \pm 1 \quad \text{for simple harmonic motion} \quad \text{--- 25 (a)}$$

$$\Delta J = \pm 1, \quad \Delta v = \pm 1, \pm 2, \pm 3, \text{ ---}$$

for anharmonic

The spectra will be similar in appearance to P and R branches with lines about equally spaced on each side  $\rightarrow$  no line at band centre. --- 25 (b)