Raman Spectroscopy

Part III: Vibrational Raman spectroscopy

B.Sc. (H) Chemistry

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Vibrational Raman spectroscopy

- In vibrational Raman spectroscopy we should consider all the fundamental vibrational mode.
- For example, let us consider all the vibrational modes of water molecule.
- As we know that, no. of vibrational modes in a non-linear molecule like water,

the no. of vibrational mode = 3N-6, where N is the no. of atoms.
So, in water molecules no. of vibrational modes are 3.

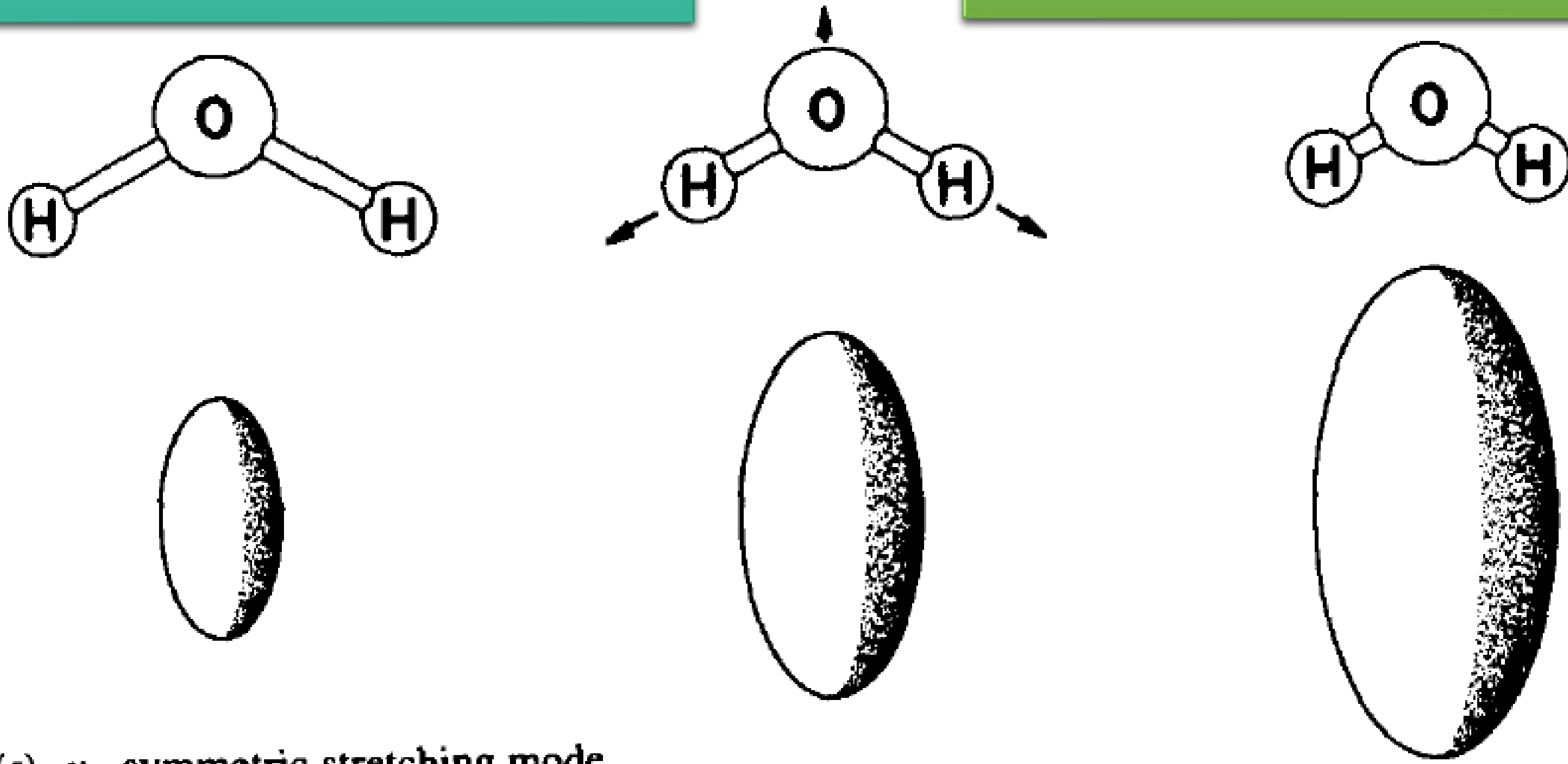
1) ν_1 = Symmetric stretching mode,
2) ν_2 = Bending mode
3) ν_3 = Asymmetric stretching mode,

We will now consider the change in polarizability,
As we know for Raman activity, there must be either ***change in amplitude*** or ***change in direction*** of molecular polarizability.

Vibrational Raman spectroscopy: Sym. Stretching Mode

Bond is stretched
Electrons are less firmly attached to nucleus, High polarization, smaller ellipsoid

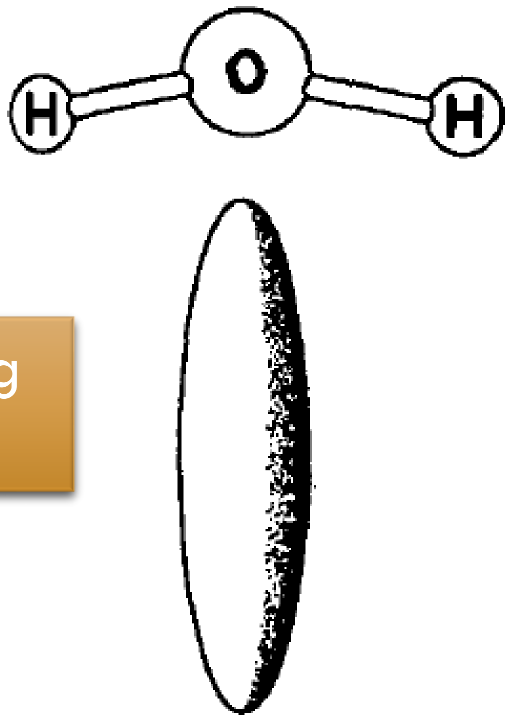
Bond is Compressed
Electrons are firmly attached to nucleus, low polarization, Larger ellipsoid



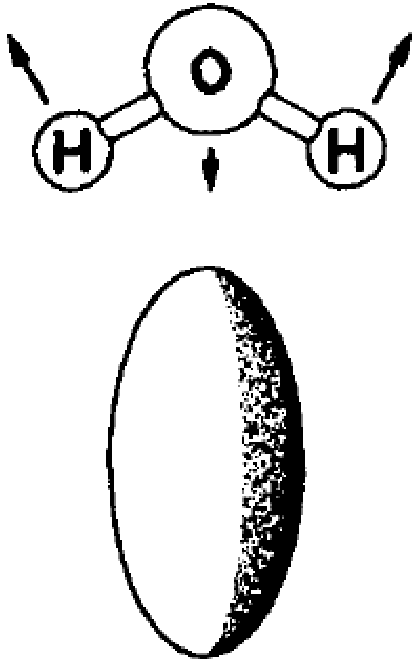
(a) ν_1, symmetric stretching mode

Vibrational Raman spectroscopy: Bending Mode

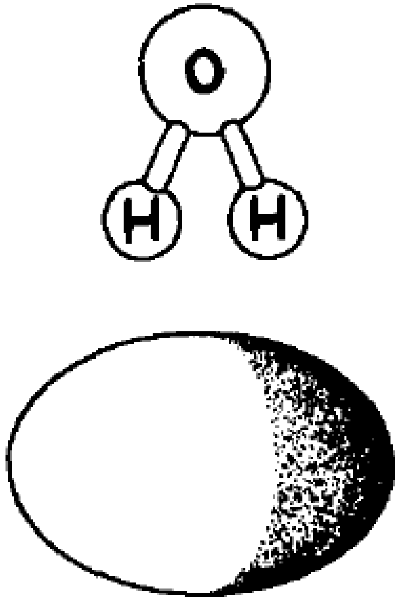
(b) ν_2 Bending mode



Here bond is fully opened i.e, almost like a triatomic linear molecule. So the electron can move a longer way. The polarization in that direction is greater, a minor axis. Major axis is very large.



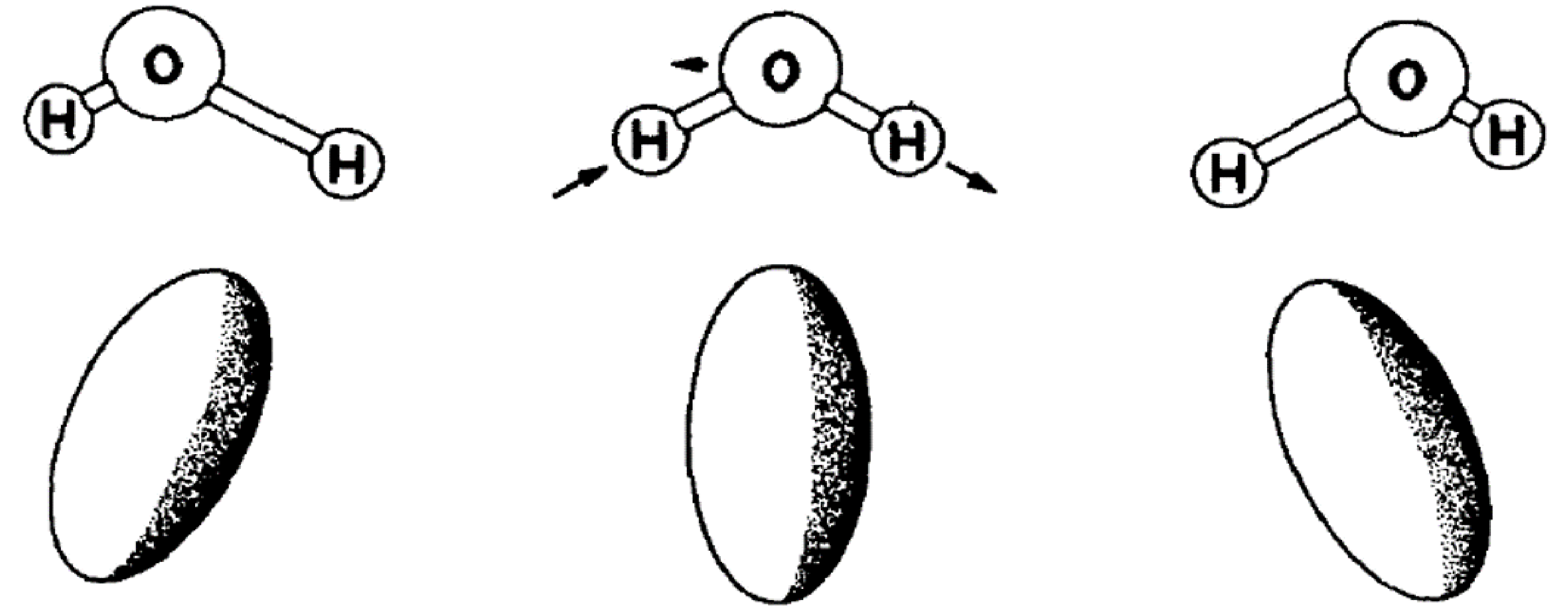
Bend shaped water molecule, so the ellipsoid is smaller and thicker.



Both the bond become co-incidental, H_2O behave like a diatomic molecule, so the direction changes

Vibrational Raman Spectroscopy: Asym. Stretching Mode

In the asymmetric stretching motion, ν_3, where both the size and shape remain approximately constant, but the direction of the major axis changes markedly.



(c) ν_3, asymmetric stretching mode

Vibrational Raman spectroscopy: H_2O

All three vibrations involve obvious changes in at least one aspect of the polarizability ellipsoid, i.e, magnitude or direction. So, all are Raman active.

Vibrational Raman spectroscopy: CO_2

Another but important way to analyse whether the particular vibration is Raman active or not we should consider the *change of polarizability with some displacement* coordinate, normally indicated by the symbol ξ.

For a stretching motion

- Stretching mode-positive ξ
- Compression mode-Negative ξ

For a Bending motion

- ξ measures the displacement of the bond angle from its equilibrium value, positive and negative ξ referring to opposite displacement directions.

Vibrational Raman spectroscopy: CO_2

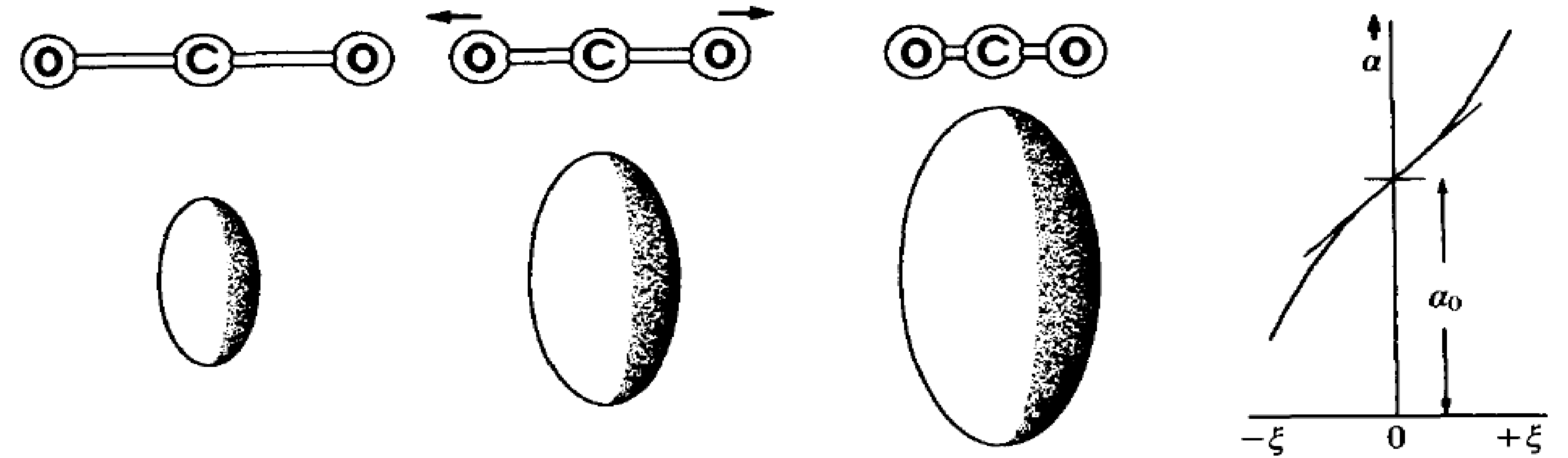
- We can plot the variation of *polarizability* (α) and *displacement* (ξ) via a graph.

- If, $\frac{d\alpha}{d\xi} = 0, \boldsymbol{Raman\ inactive}$

- And if, $\frac{d\alpha}{d\xi} \neq 0, i.e, slope\ is\ non$-zero, then motion is ***Raman Active.***

- The details of the curve are not important since we are concerned only with small displacements; it is *plain* near the equilibrium position (ξ = 0) the curve has a distinct slope, that is $\frac{d\alpha}{d\xi} = 0$ at ξ = 0.

- Thus for small displacements the motion produces a change in polarizability and is therefore ***Raman active.***



(a) ν_1, symmetric stretching mode

Most stretched situation, High polarization, small ellipsoid size

Equilibrium condition, low polarization, little bigger ellipsoid size

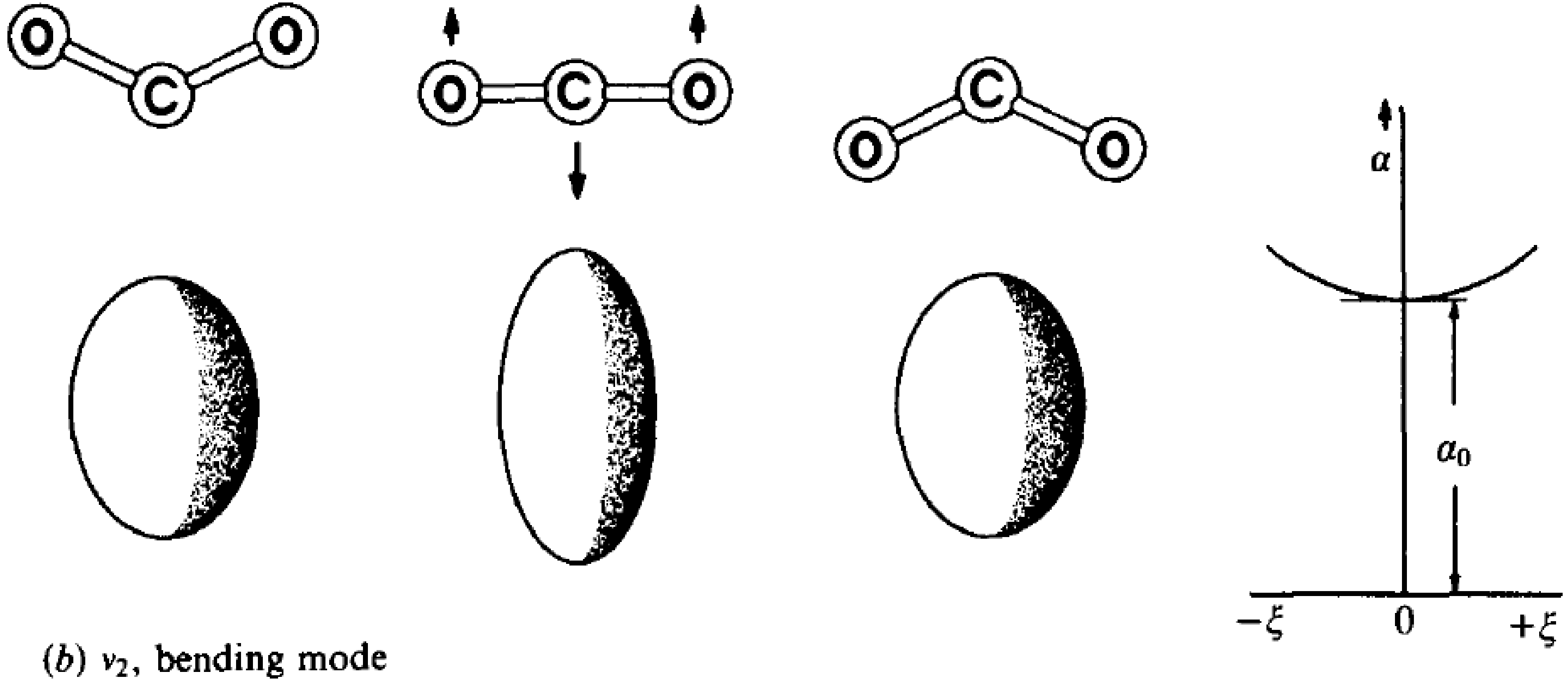
Compressed condition, least polarization, largest ellipsoid size

Graph of polarizability vs displacement

Here, $\frac{d\alpha}{d\xi} \neq 0$ i.e,

Slope is not equal to Zero, ***So Raman active***

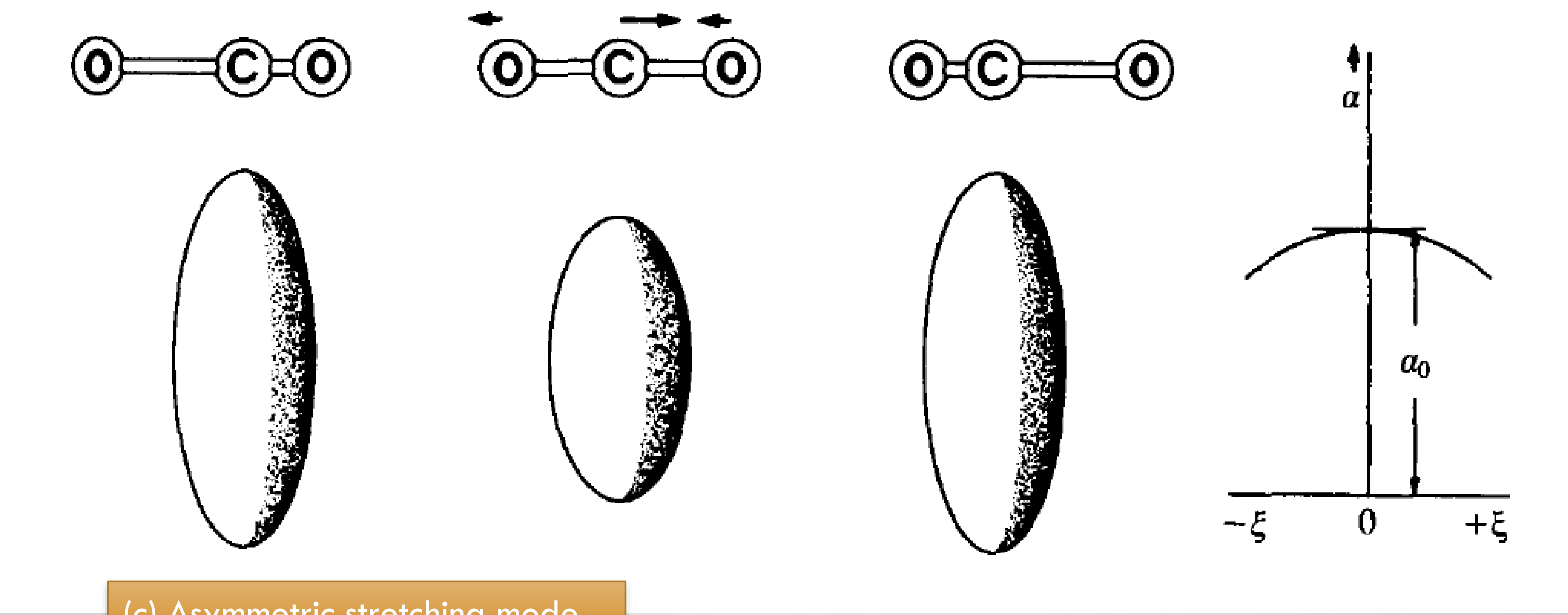
Vibrational Raman spectroscopy: CO_2 Bending Mode



(b) ν_2, bending mode

The Slope at the equilibrium position, ξ = 0, is zero. So this bending vibrational mode is ***Raman Inactive***

Vibrational Raman spectroscopy: CO_2 Asymmetric stretching



(c) Asymmetric stretching mode

The Slope at the equilibrium position, ξ = 0, is zero. So this bending vibrational mode is ***Raman Inactive***

Vibrational Raman spectroscopy: Points to ponder

- The Raman spectrum is forbidden for $d\alpha/d\xi = 0$ but allowed for $d\alpha/d\xi \neq 0$, we can imagine that the 'degree of allowedness' varies with $d\alpha/d\xi$.

- Thus if the polarizability curve has a large slope at $\xi = 0$ the Raman line will be strong; if the slope is small it will be weak; and if zero, not allowed at all.

- From this stems the following very useful general rule:

  Symmetric vibrations give rise to intense Raman lines; non-symmetric ones are usually weak and sometimes unobservable.

- For water molecule, in particular, a bending motion usually yields only a very weak Raman line; e.g. the $\boldsymbol{v_2}$ motion of $\mathbf{H_2O}$, although it is Raman allowed.

- $\boldsymbol{v_3}$ is also not observable in Raman spectra due to $d\alpha/d\xi$ is so small.

Raman and infra-red activities of carbon dioxide

Mode of vibration of CO_2	**Raman**	**Infra-red**
ν_1 : Symmetric stretch	Active	Inactive
ν_2 : Bending	Inactive	Active
ν_3 : Asymmetric stretch	Inactive	Active

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.

Reference

Fundamentals of Molecular Spectroscopy, 4th Ed.

By Colin N. Banwell and Elaine M. McCash

THANK YOU