

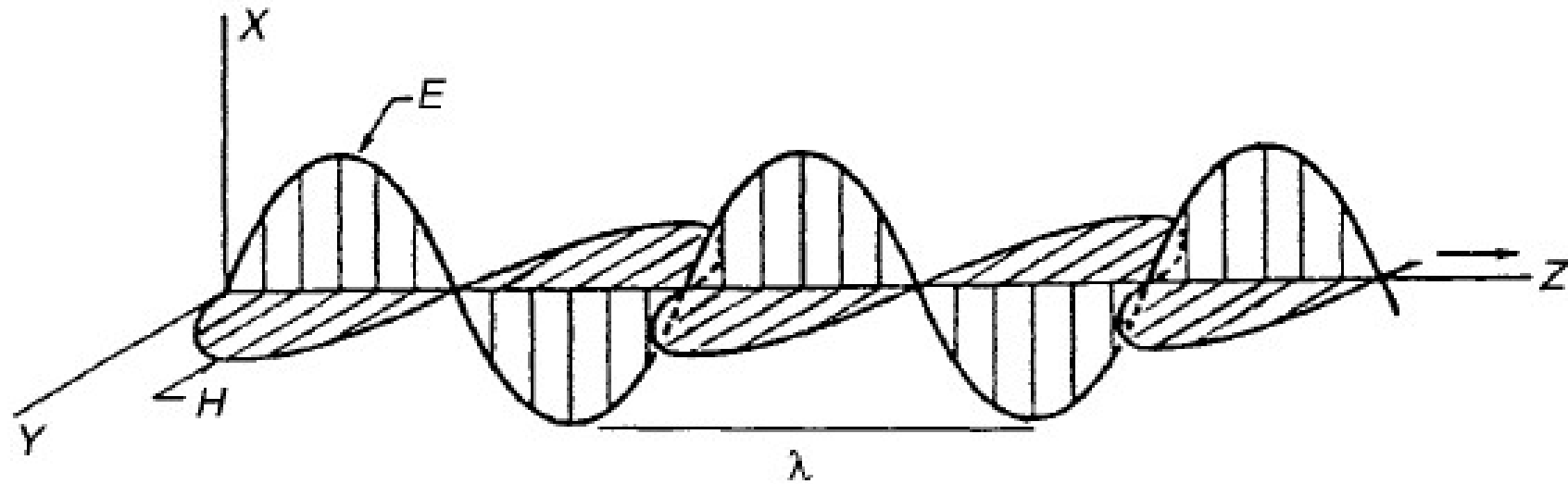


University of Lucknow | Centenary Year
लखनऊ विश्वविद्यालय | शताब्दी वर्ष

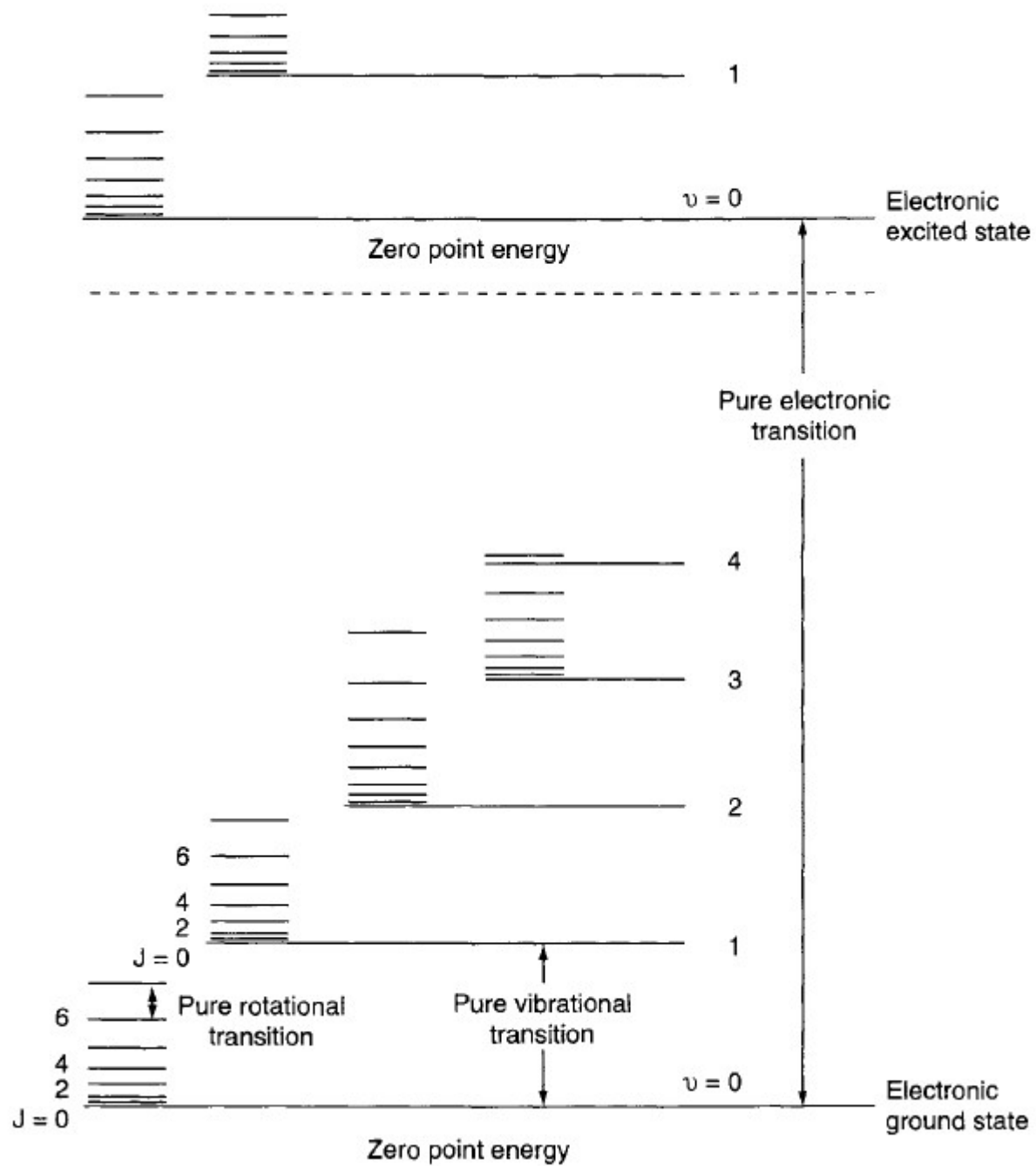


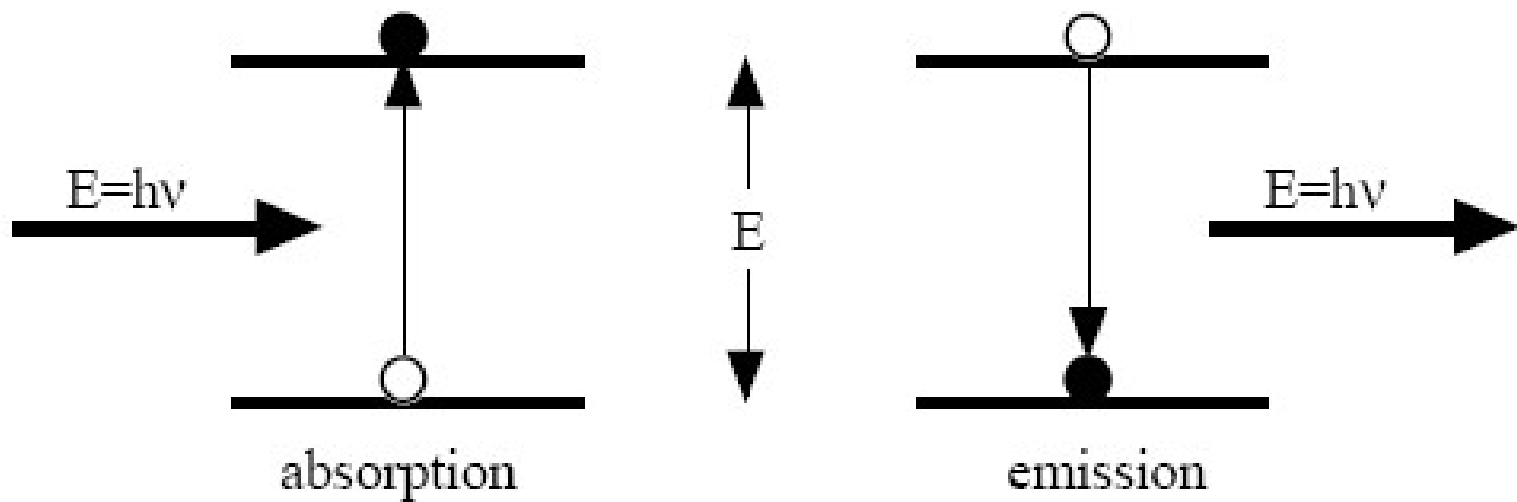
Raman Spectroscopy-I

डा. अभिनव कुमार
सहायक प्राध्यापक
रसायनशास्त्र विभाग
लखनऊ विश्वविद्यालय
लखनऊ

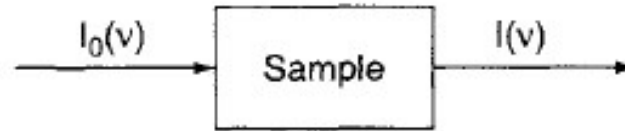


Plane polarized electromagnetic radiation

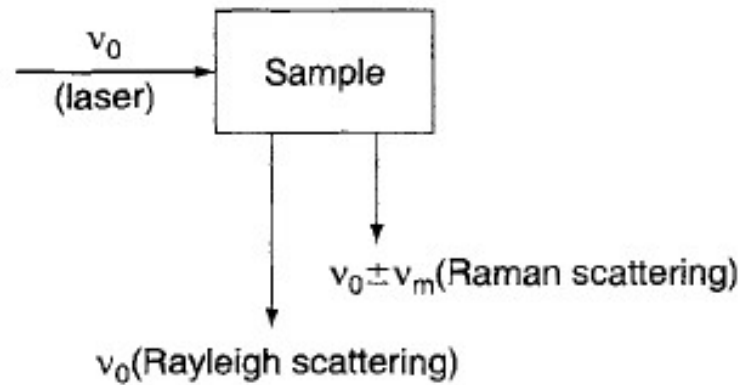




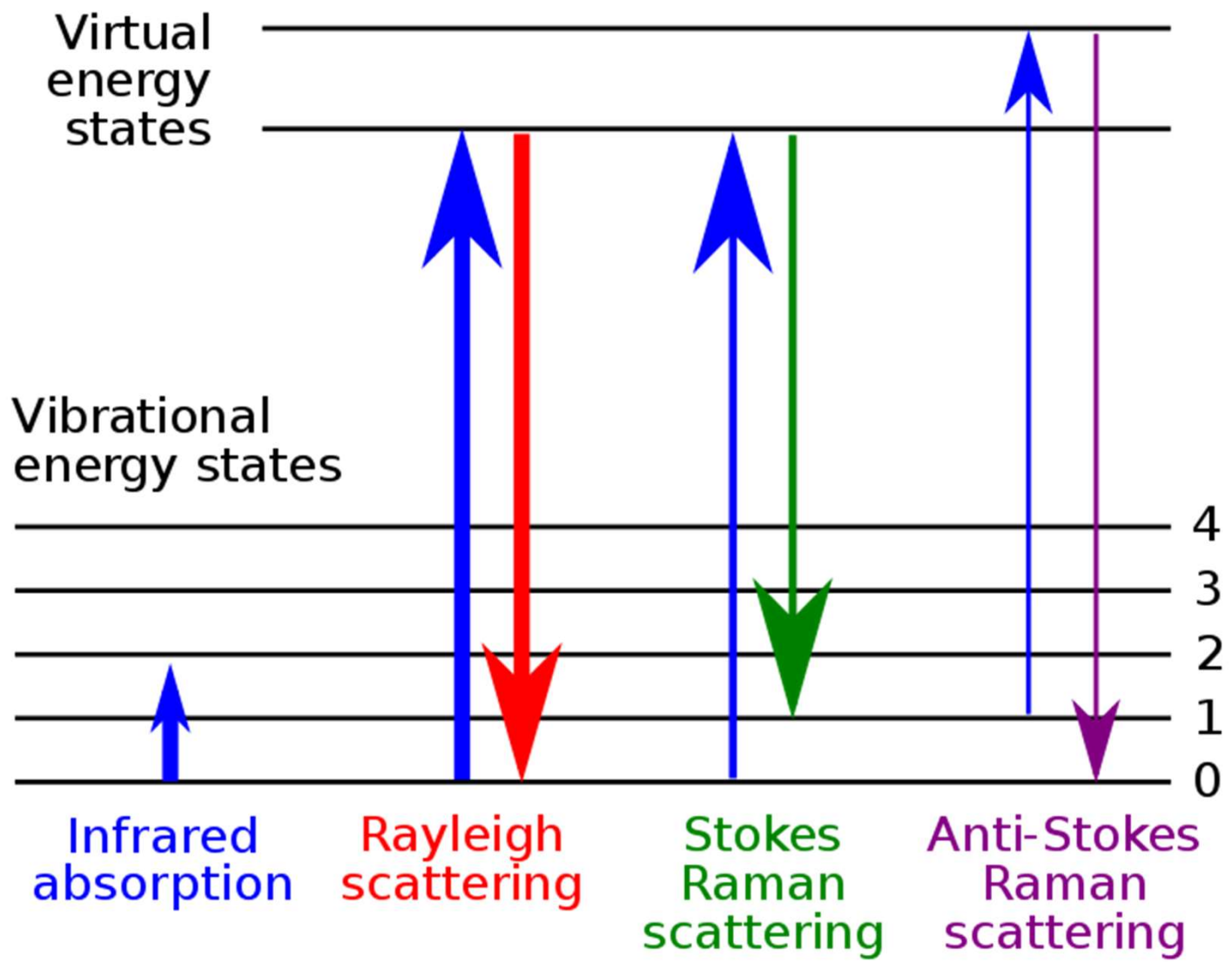
IR



Raman



Differences in mechanism of Raman vs. IR



Classical theory of Raman Scattering

Electric field \Rightarrow Separation of charge centers



Causes an induced electric dipole moment
The molecule is polarized

$$\mu = \alpha E$$

Where α is *polarizability* of the molecule

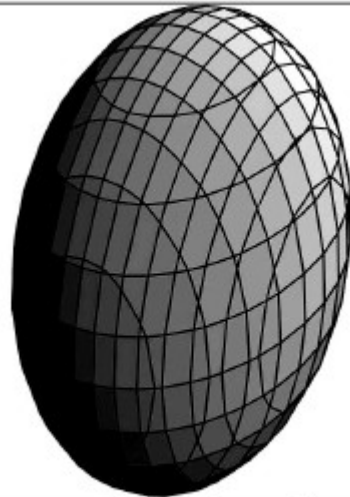
- The polarizability of many molecules depends upon the orientation of the molecule relative to the applied field (rotation) or to separation of the atoms in the molecule (vibration).
- The polarizability is then anisotropic, i.e. depends upon direction.
- The polarizability of the molecule in various directions is conveniently represented by its *polarizability ellipsoid*.
- This is a three-dimensional surface whose distance from the electric centre of the molecule is proportional to $1/\sqrt{\alpha_i}$, where α_i is the polarizability along the line joining a point i on the ellipsoid with the electric centre.

The Ellipsoid

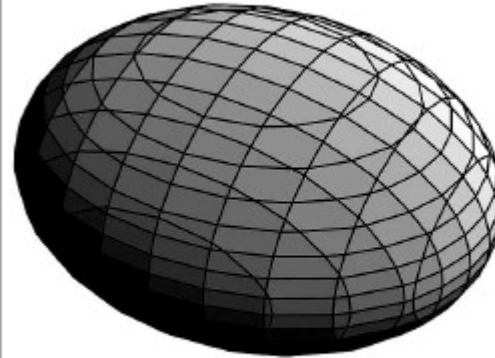
The Ellipsoid is a three-dimensional “quadratic” surface, the points on which satisfy the equation

$$\frac{x^2}{a} + \frac{y^2}{b} + \frac{z^2}{c} = 1$$

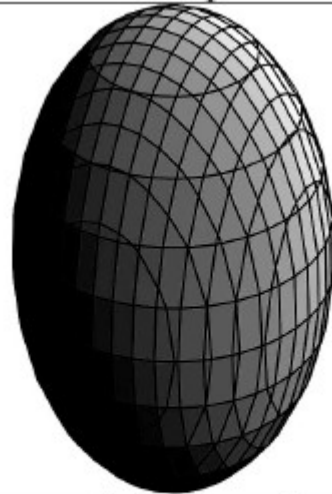
where a , b and c are the lengths of the three semi-axes. There are the following possibilities:



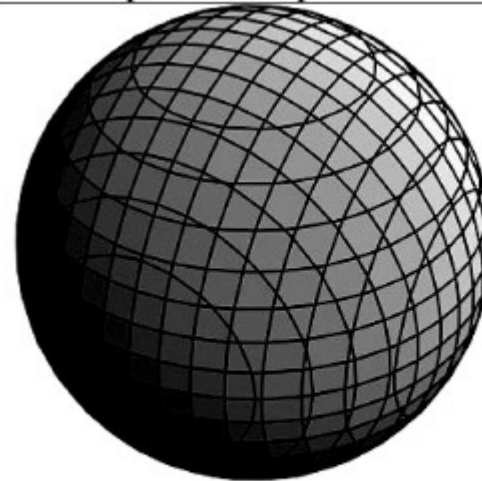
$a = 1, b = 2, c = 3$
oblate ellipsoid



$a = 3, b = 2, c = 1$
prolate ellipsoid

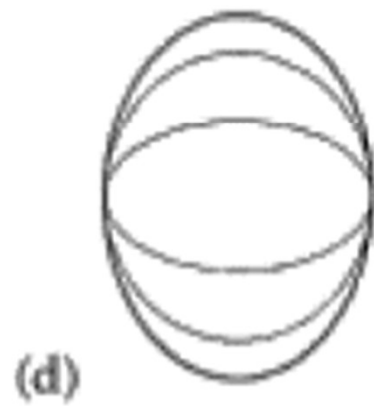
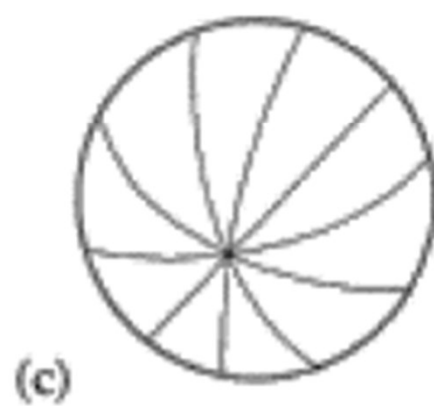
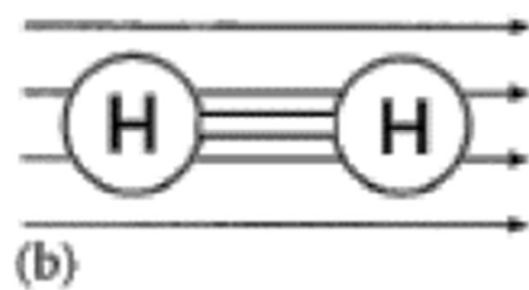
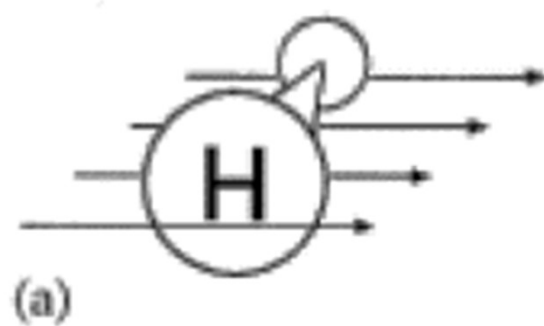


$a = 1, b = 2, c = 3$
oblate spheroid

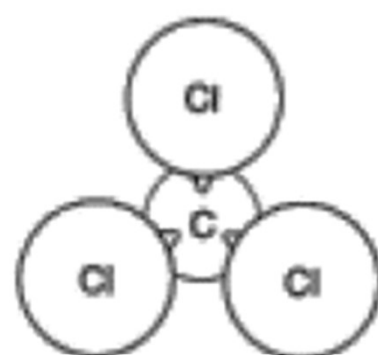
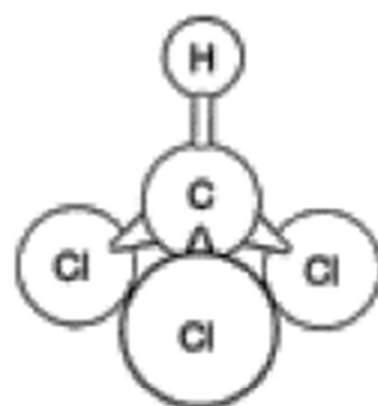


$a = b = c = 3$
sphere

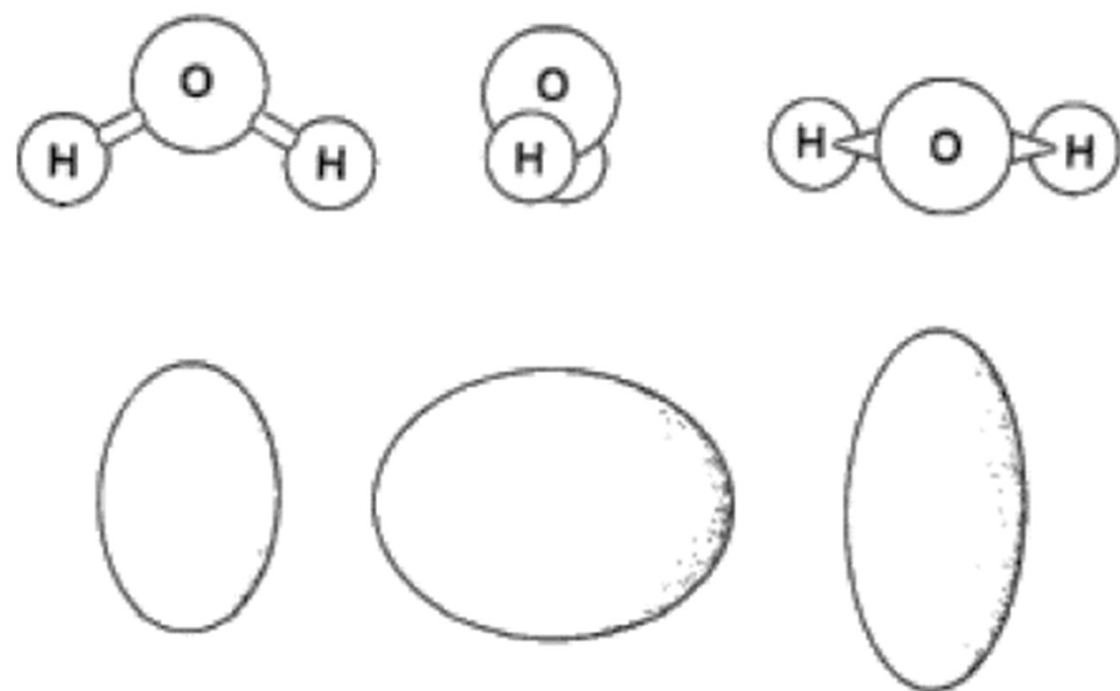
Polarizability ellipsoid for H_2



Polarizability ellipsoid for chloroform



Polarizability ellipsoid for water



Selection Rules for Raman Spectroscopy

- Rotational Raman

Polarizability of the molecule must be anisotropic – it must depend upon the orientation of the molecule.

Linear symmetric molecules such as CO_2 , O_2 , N_2 do have rotational Raman spectra.

Spherical top molecules such as CH_4 , SF_6 do not have rotational Raman spectra.

Rotational Raman Spectra of linear molecules

$$\nu_J = BJ(J + 1) - DJ^2(J + 1)^2 \quad \text{cm}^{-1} \quad (J = 0, 1, 2, \dots)$$

In Raman spectroscopy, the precision of the measurements does not justify the retention of the term involving D , the centrifugal distortion constant, so that the above expression simplifies to:

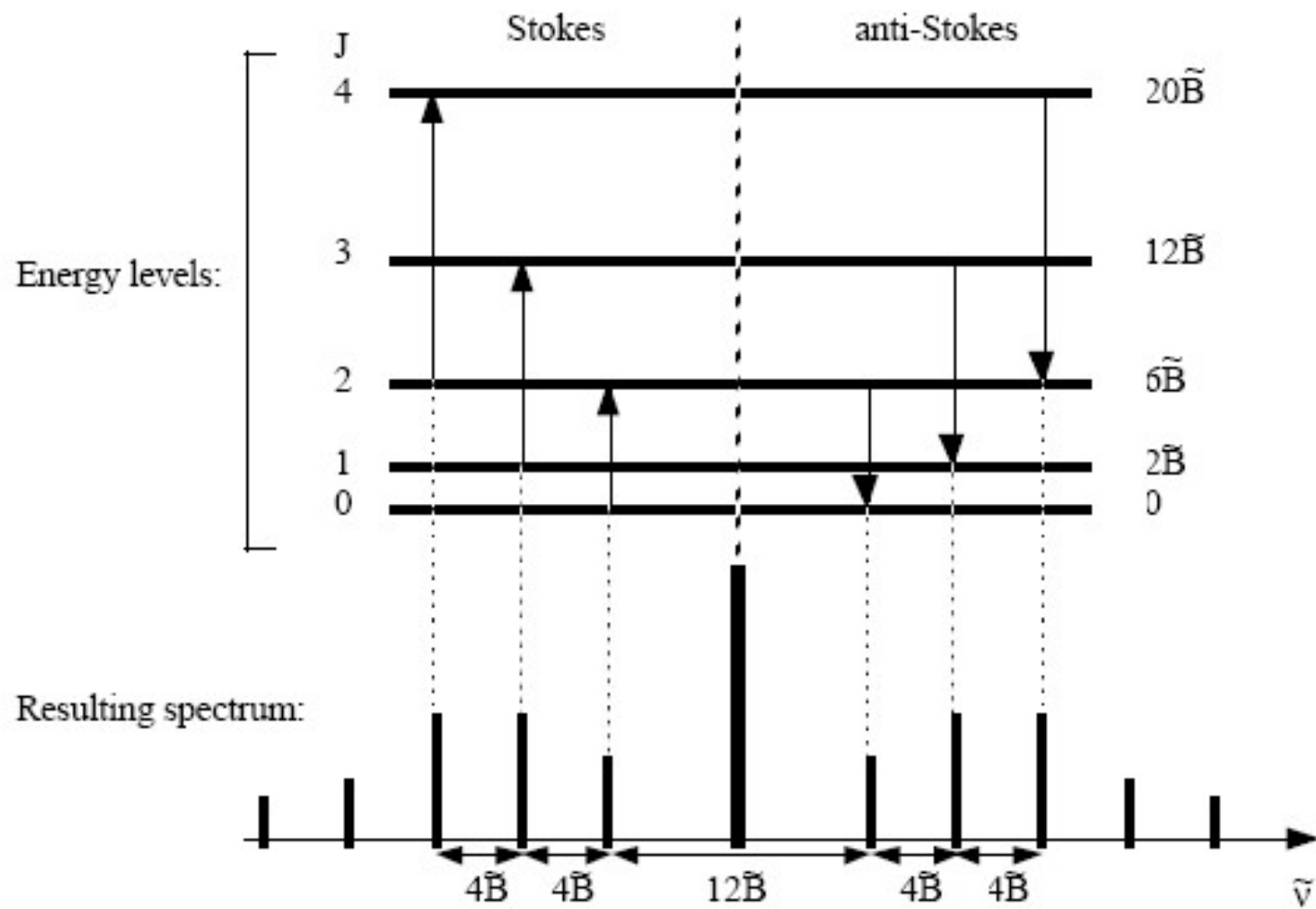
$$\nu_J = BJ(J + 1) \quad \text{cm}^{-1}$$

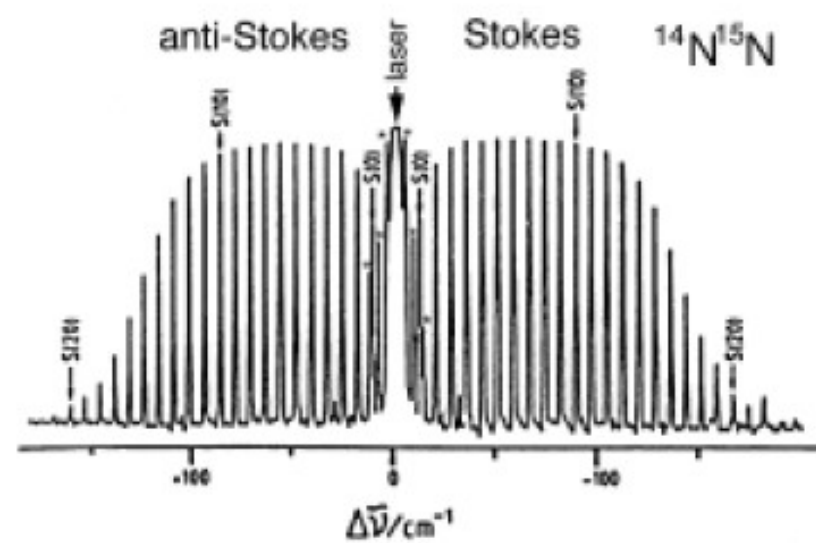
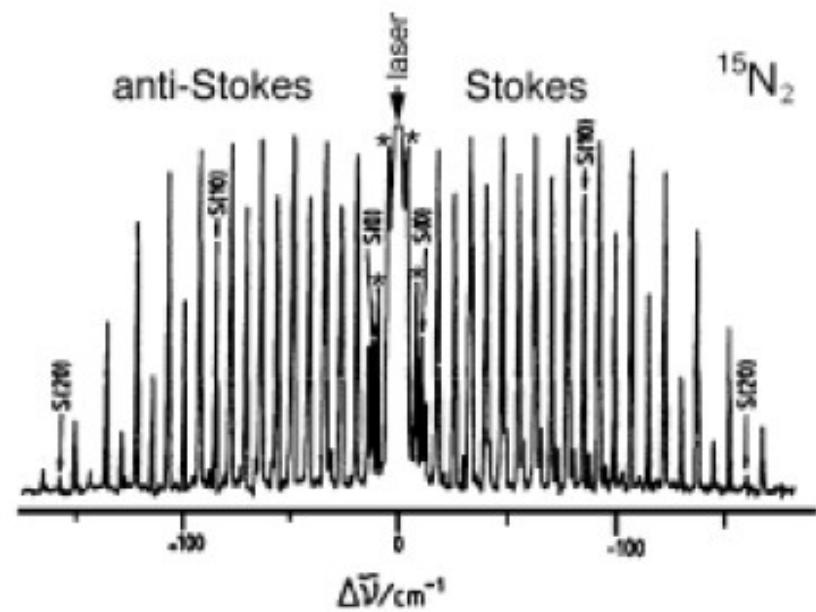
$\Delta J = 0$ or ± 2 (as opposed to $\Delta J = \pm 1$ in pure rotational spectroscopy)

$$\begin{aligned} \Delta \nu &= \nu_{J+2} - \nu_J = B[(J + 2)(J + 2 + 1) - J(J + 1)] = B(J^2 + 3J + 2J + 6 - J^2 - J) \\ &= B(4J + 6) \quad (\text{rigid rotor}) \end{aligned}$$

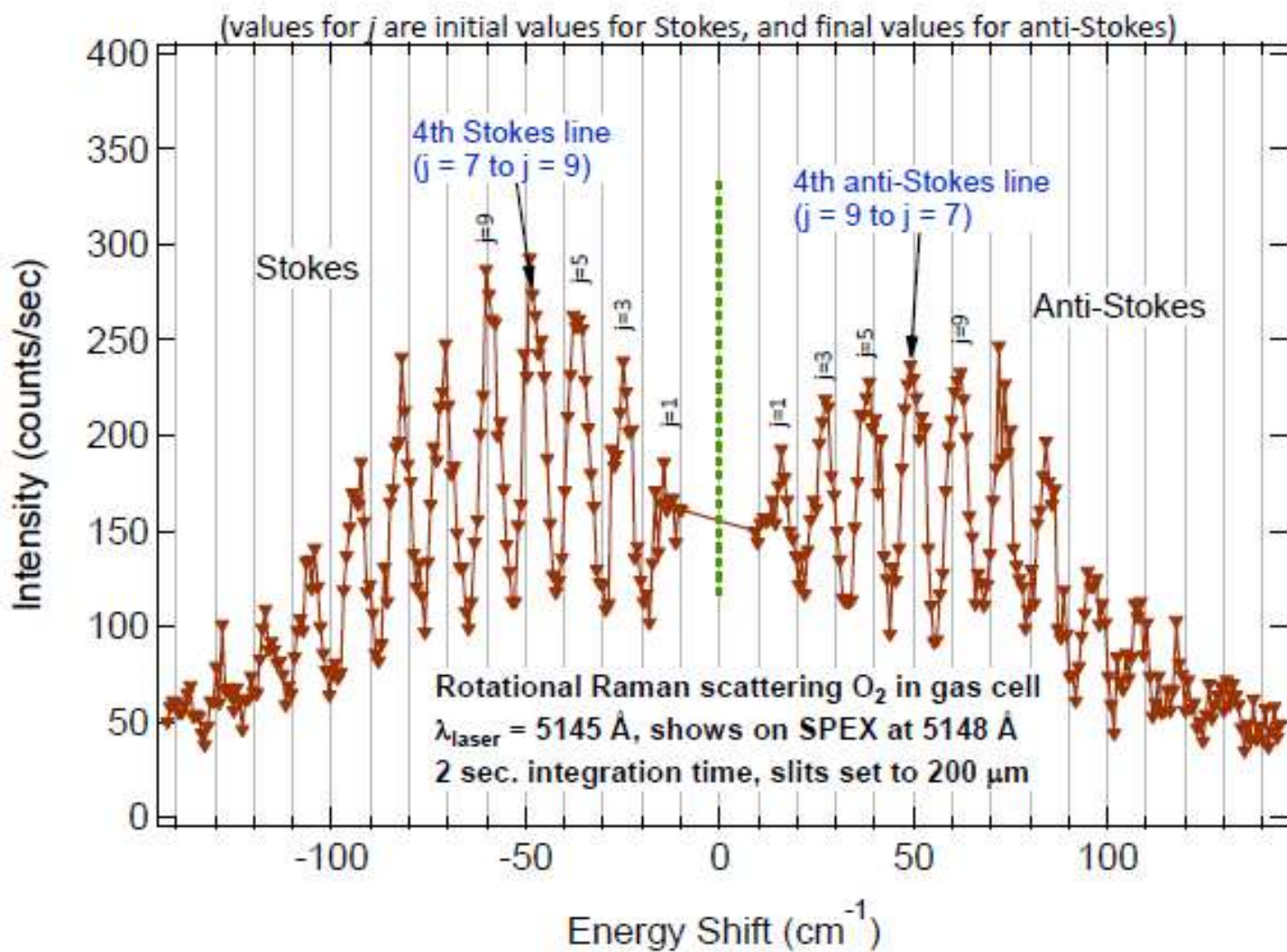
The frequency of the spectral lines is thus

$$\nu_{Raman} = \nu_{excitation} \pm B(4J + 6)$$





Rotational Raman scattering data for O₂ molecules (wavenumber shift)



Symmetric top molecules

Consider the polarizability ellipsoid for CHCl_3 , a spherical top. Only end-over-end rotations produce a change in the polarizability. The energy levels:

$$\epsilon_{j,k} = BJ(J + 1) - (A - B)K^2 \quad (J = 0, 1, 2, \dots; K = \pm J, \pm(J - 1), \dots)$$

The Raman selection rules for a symmetric top molecule are:

$$\Delta K = 0 \quad (\text{isotropic polarizability about the } a \text{ axis})$$

$$\Delta J = 0, \pm 1, \pm 2 \quad (\text{except for } K = 0 \text{ states, when } \Delta J = \pm 2 \text{ only})$$

giving rise to an S branch. A symmetric top molecule has anisotropic polarizability. This selection rule holds for any K.

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

Lines at $\Delta\varepsilon_{\text{R}} = 2B(J + 1)$

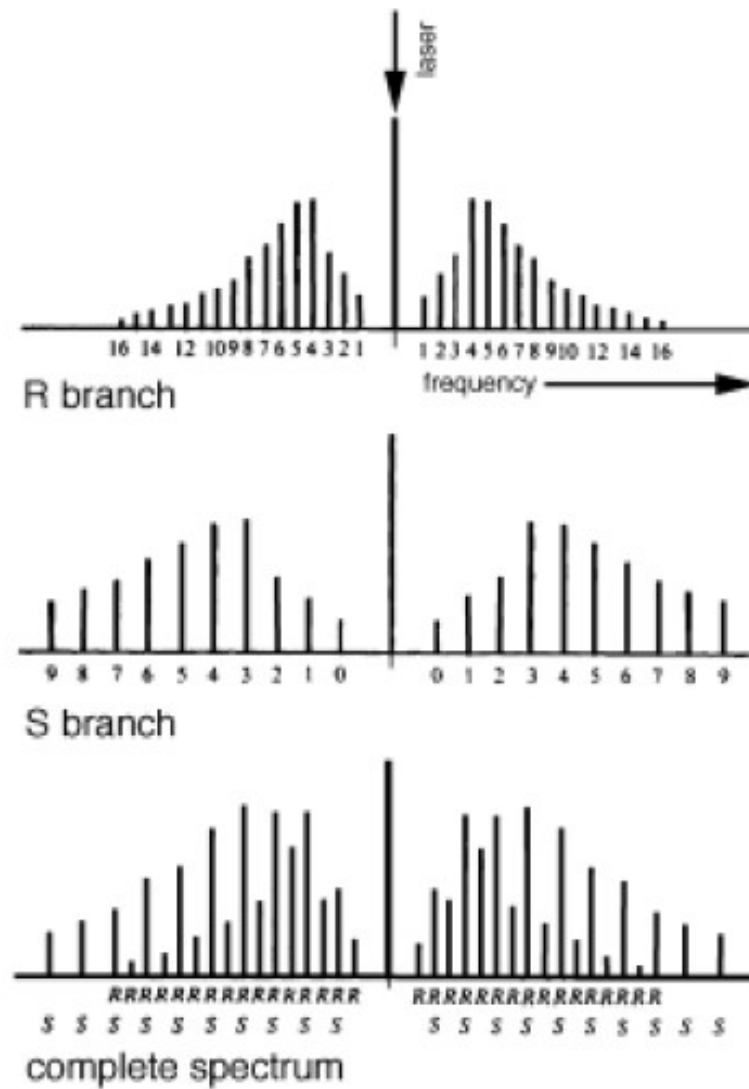
($J = 1, 2, \dots$, but $J \neq 0$)

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

Lines at $\Delta\varepsilon_{\text{S}} = B(4J + 6)$

($J = 0, 1, 2, \dots$)

Raman spectrum of a symmetric top



Vibrational Raman Spectroscopy

There should be change in polarizability of the molecule.

$$\left(\frac{d\alpha}{dq} \right)_e \neq 0$$

The vibrational term values are given by

$$G(\nu) = \frac{E_\nu}{hc} = \bar{\nu}_0 \left(\nu + \frac{1}{2} \right)$$

where, $\bar{\nu}_0 (= \frac{\nu_0}{c})$ is the vibration wavenumber.

The vibrational term values $G(\nu)$ are modified in case of anharmonic oscillator and are given by

$$G(\nu) = \bar{\nu}_e \left(\nu + \frac{1}{2} \right) - \bar{\nu}_e x_e \left(\nu + \frac{1}{2} \right)^2 + \bar{\nu}_e y_e \left(\nu + \frac{1}{2} \right)^3 + \dots$$

Where $\bar{\nu}_e$ is the vibration wavenumber, which a classical oscillator would have for an infinitesimal displacement from equilibrium. The terms x_e, y_e, \dots are anharmonic constants.

When the molecule has both vibrational and rotational energy the total term values S are given by the sum of the rotational term values $F(J)$ and the vibrational term values $G(v)$.

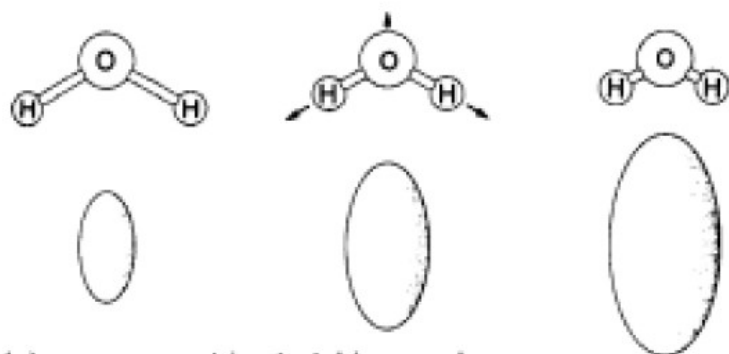
$$S(v, J) = G(v) + F(J)$$

$$= \bar{\nu}_e \left(v + \frac{1}{2}\right) - \bar{\nu}_e x_e \left(v + \frac{1}{2}\right)^2 + \dots + \bar{B}J(J+1) - \bar{D}J^2(J+1)^2$$

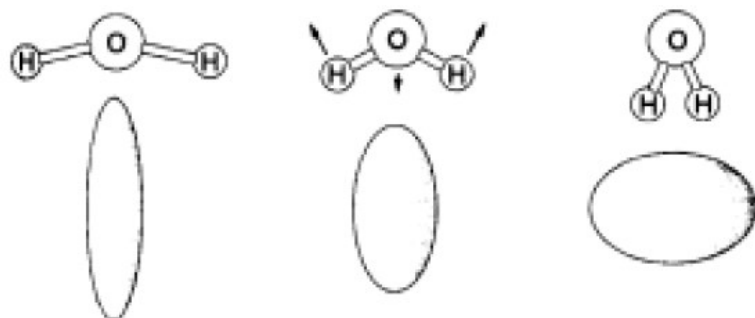
Neglecting the small centrifugal distortion constant

$$S(v, J) = \bar{\nu}_e \left(v + \frac{1}{2}\right) - \bar{\nu}_e x_e \left(v + \frac{1}{2}\right)^2 + \dots + \bar{B}J(J+1)$$

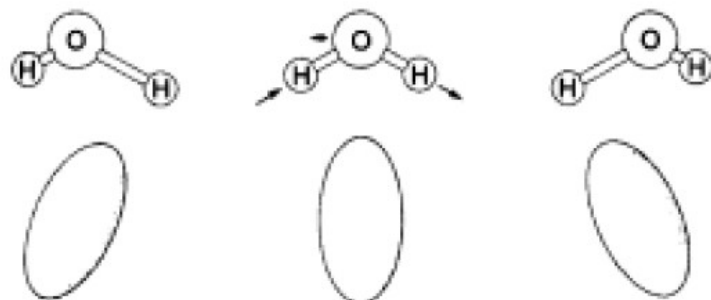
vibrational modes of water



(a) ν_1 , symmetric stretching mode

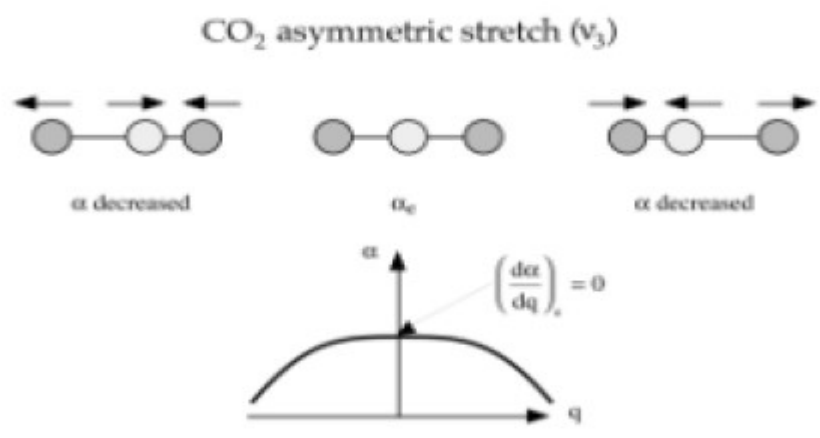
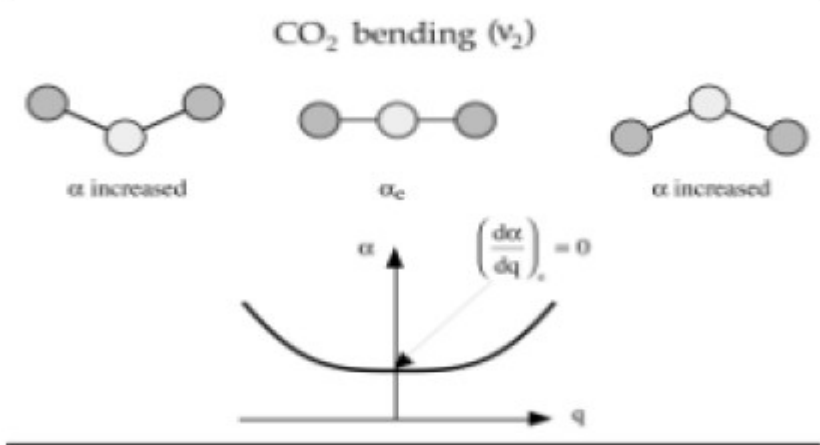
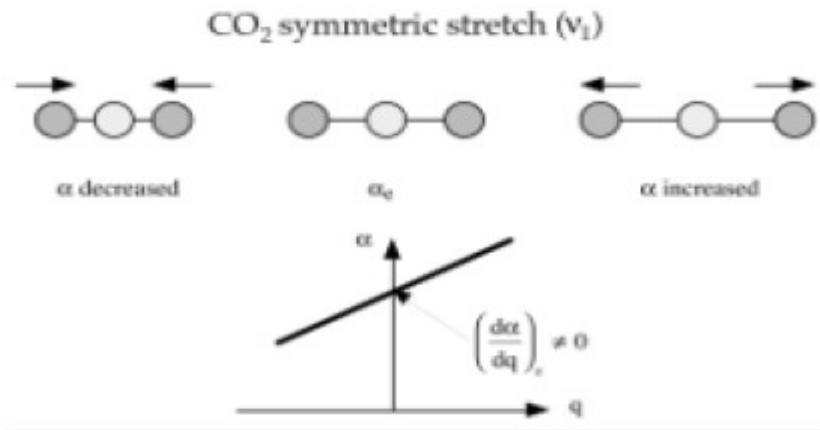


(b) ν_2 , bending mode



(c) ν_3 , asymmetric stretching mode

Band	Infrared	Raman
ν_1	strong	strong
ν_2	very strong	weak
ν_3	very strong	weak



Rule of mutual exclusion

Band	Infrared	Raman
ν_1	inactive	active
ν_2	active	inactive
ν_3	active	inactive

Infrared and Raman bands of HCN

Band	Infrared	Raman
ν_1	weak	very strong
ν_2	very strong	weak
ν_3	strong	weak

Examples of spectral assignments

N₂O

$\tilde{\nu}$ (cm ⁻¹)	Infrared	Raman	band assignment
580	PQR m. (+ T dept.)	m.	2ν ₂ ← ν ₂ hot band
589	PQR s.	v.w.	ν ₂ bend
1167	PR m.	v.w.	2ν ₂ overtone
1285	PR v.s.	v.s.	ν ₁ symmetric stretch
2223	PR v.s.	s.	ν ₃ asymmetric stretch

(m. = medium, w. = weak, s = strong, v.s. = very strong etc.)

(1) $3N - 5$ or $3N - 6$ gives 4 or 3 fundamental vibrational modes. If 4 modes (linear molecule), two are degenerate:

\Rightarrow 3 distinguishable fundamental modes \therefore not all the bands are fundamentals

(2) Look for strong bands in IR or Raman:

589 cm^{-1} low frequency \therefore bending mode (note PQR also)

2223 cm^{-1} highest frequency \therefore asymmetric stretch

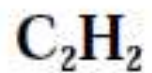
1285 cm^{-1} intermediate frequency \therefore symmetric stretch

(3) Q branches (fundamentals only):

PQR branches in ν_2 , but absent in ν_1 and ν_3 \therefore molecule is linear

(4) Mutual exclusion?

No \therefore molecule is not centrosymmetric \therefore N_2O is N-N-O



$\tilde{\nu}$ (cm ⁻¹)	Infrared	Raman	band assignment
612	–	v. weak	bend
729	PQR	–	bend
1974	–	v. strong	symmetric stretch
3287	PR	–	asymmetric stretch
3374	–	strong	symmetric stretch

(1) Q branches

There is a missing Q branch at 3287 cm^{-1} \therefore molecule is linear

$\Rightarrow 729\text{ cm}^{-1}$ band is bending mode

(2) Mutual exclusion?

Yes \therefore molecule is centrosymmetric

$\therefore \text{C}_2\text{H}_2$ is H-C=C-H

(3) Strong bands in IR or Raman

1974 cm^{-1} very strong Raman \therefore symmetric stretch

3287 and 3374 cm^{-1} high frequency \therefore C-H stretch

3287 cm^{-1} IR active \therefore asymmetric stretch

3374 cm^{-1} Raman active \therefore symmetric stretch

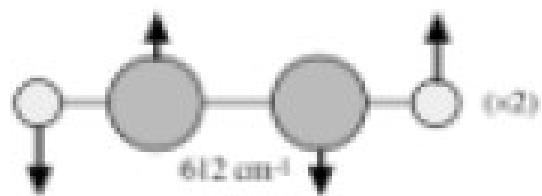
(4) A linear molecule has $3N - 5 = 7$ fundamental vibrational modes.

Two doubly degenerate bending modes \therefore 5 distinguishable vibrational modes

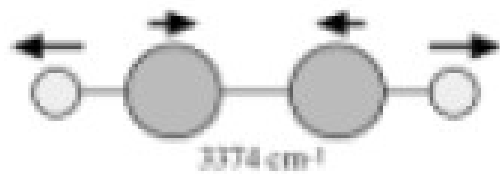
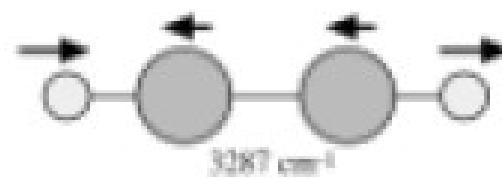
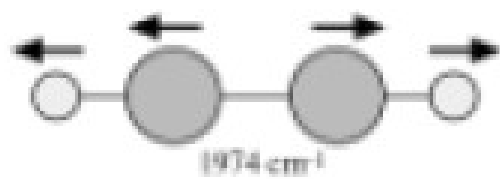
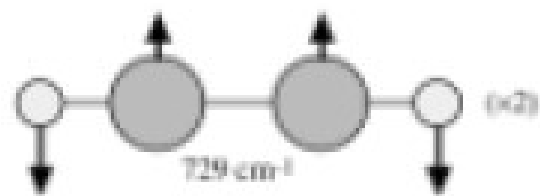
\Rightarrow remaining 612 cm^{-1} band is bending mode

vibrational modes of C_2H_2

Raman active

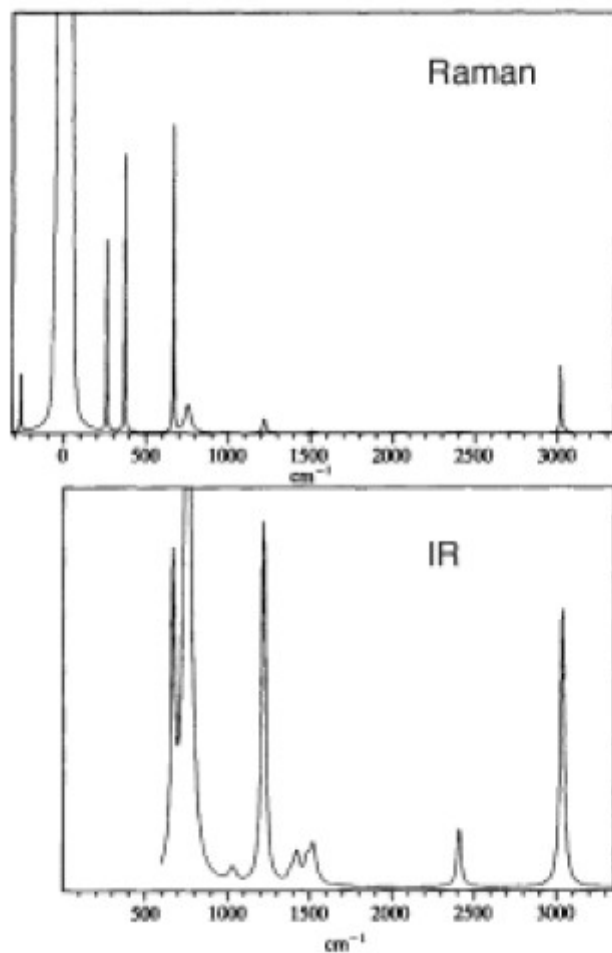


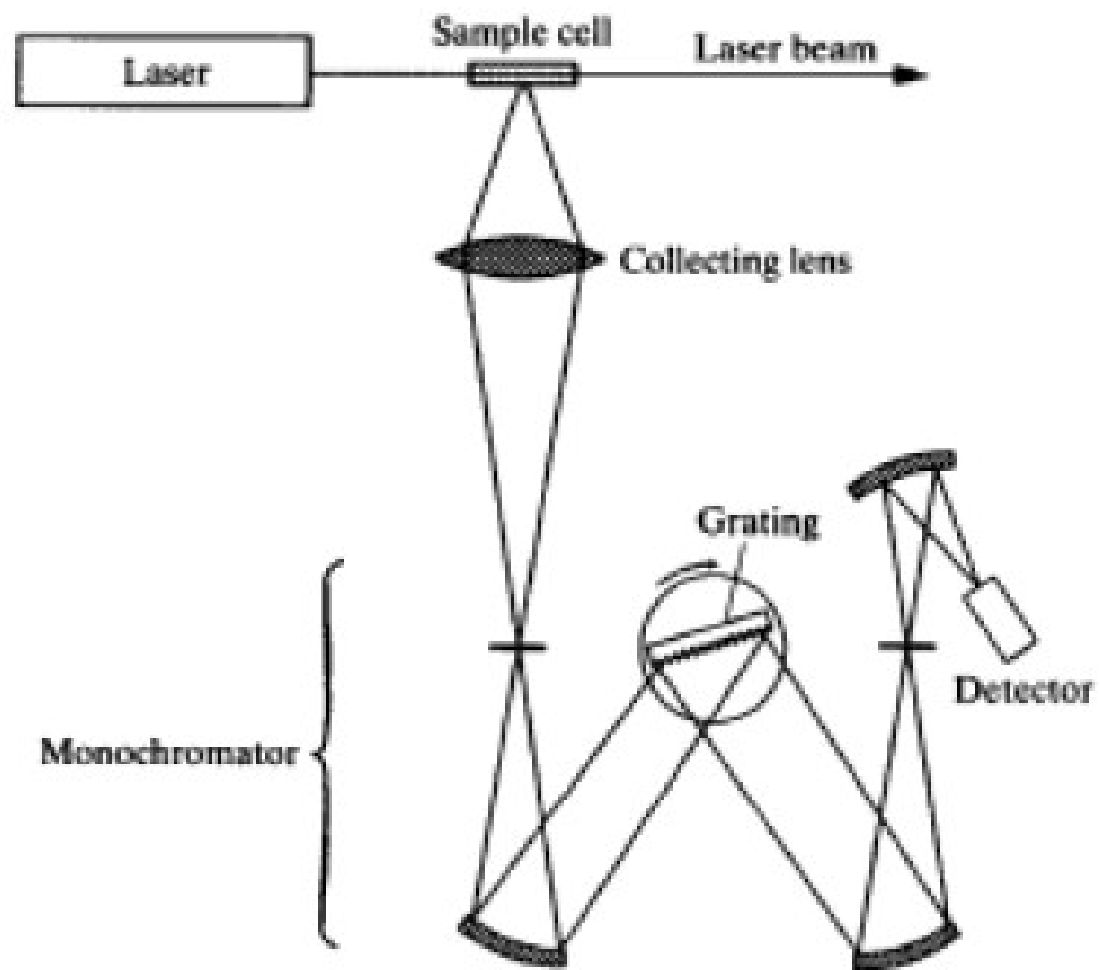
IR active



Combined infrared and Raman: structure determination and band assignment

Raman and infrared spectra of chloroform





Rayleigh Scattering (elastic)



Rayleigh scattering is more dramatic after sunset. This picture was taken about one hour after sunset at 500 m altitude, looking at the horizon where the sun had set.



**Chandrasekhra
Venkata Raman
1888-1970**