Raman Spectroscopy

RAMAN'S SPECTROGRAPH
THE FIRST RAMAN SPECTRUM WAS
OBTAINED WITH THIS SPECTROGRAPH
IN 1928.

What happens when light falls on a material?

Transmission
Reflection
Absorption
Luminescence

Elastic Scattering
Inelastic Scattering
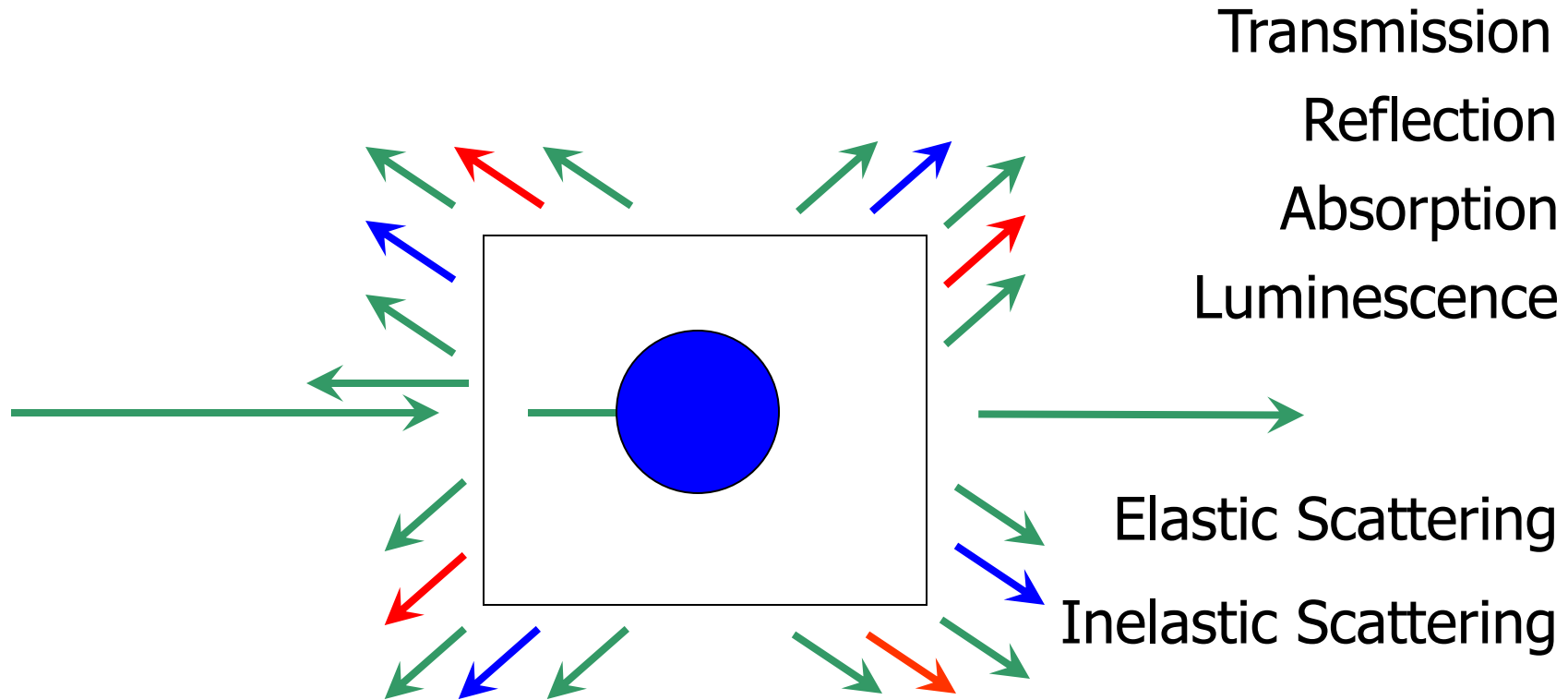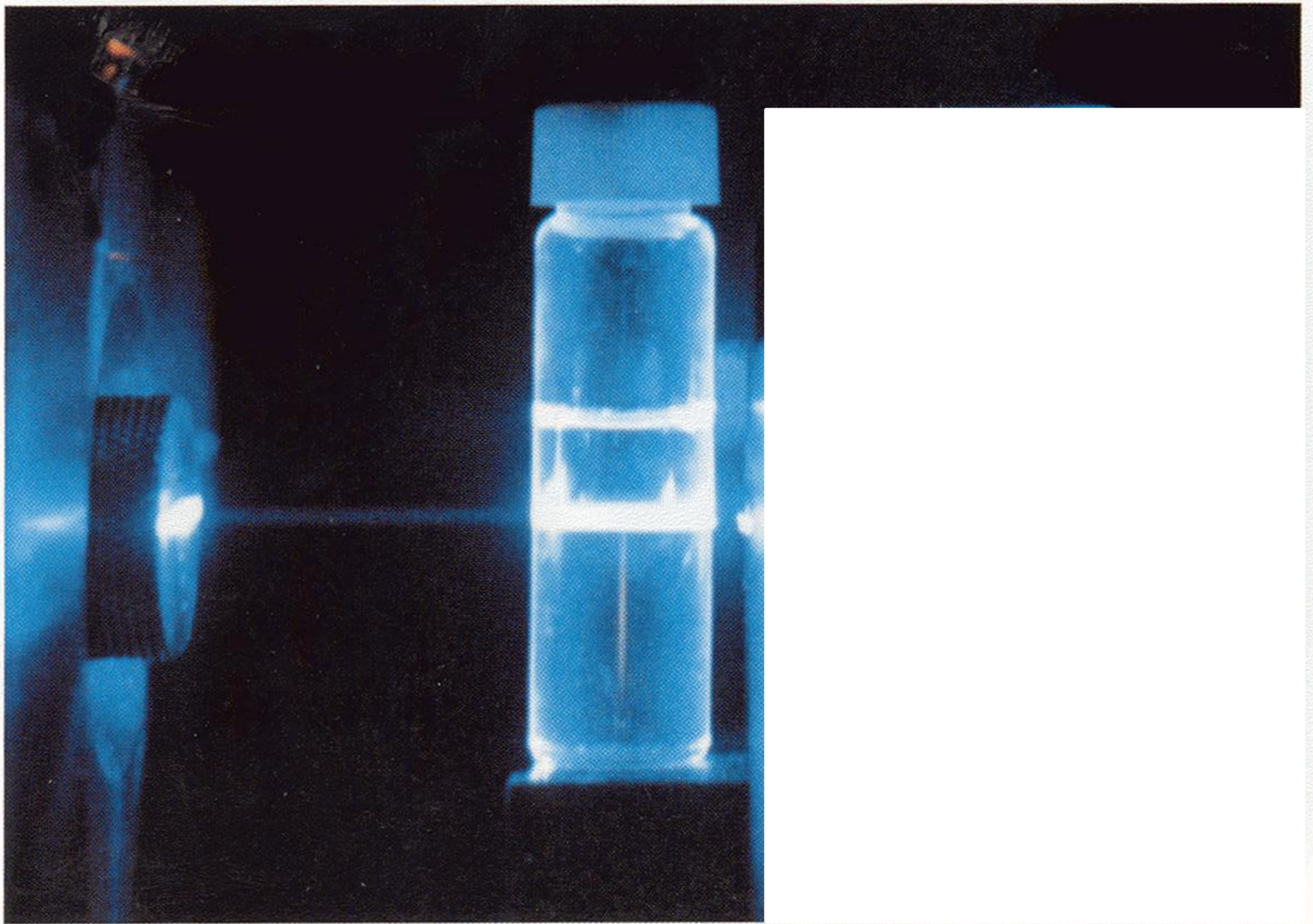
Raman scattering visible to the unaided eye, from a 488 nm laser beam passing through liquid cyclohexane. Left vial exhibits mostly Rayleigh scattering which obscures much weaker Raman scattering. Right vial is viewed through a 488 nm band rejection filter, which permits observation of longer wavelength Raman scattering.

Raman, Fluorescence and IR

Absorption

and emission
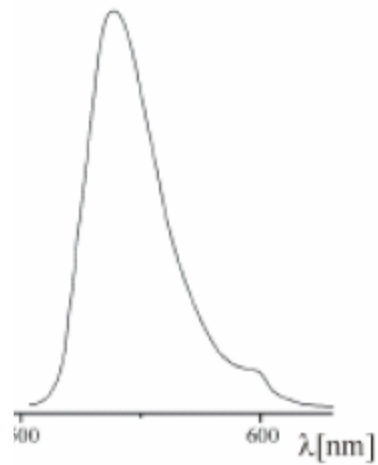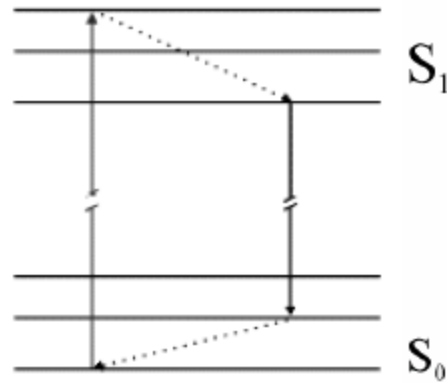
6.1 Scattering

In addition to being absorbed and emitted by atoms and molecules, photons may also be *scattered* (approx. 1 in 10^7 in a transparent medium). This is not due to defects or dust but a molecular effect which provides another way to study energy levels.

This scattering may be:

Elastic and leave the molecule in the same state (Rayleigh Scattering) or

Inelastic and leave the molecule in a *different* quantum state (Raman Scattering)

Nobel Prize 1904
(physics)

Nobel Prize 1930
(physics)

6.2 Rayleigh Scattering

Lord Rayleigh calculated that a dipole scatterer $\ll \lambda$ scatters with an intensity:

no. of scatterers — polarizability

$$I = I_0 \frac{8\pi N \alpha^2}{\lambda^4 R^2}\left(1 + cos^2\theta\right)$$

wavelength — distance scatterer - observer

n.b., $I \propto \dfrac{1}{\lambda^4}$

5 times more effective for 400nm than 600nm
Hence the sky is blue!

Raman Scattering

Scattering is not an oscillating dipole phenomenon!

The presence of an electric field E induces a polarization in an atom/ molecule given by

polarizability

$$\mathbf{P} = \alpha\mathbf{E}$$

If the field is oscillating (e.g., photon) $\quad \mathbf{P} = \alpha\mathbf{E}_0\cos(2\pi\nu_0 t)$

In atoms the polarizability is isotropic, and the atom acts like an antenna and re-radiates at the incident frequency – Rayleigh Scattering only

In molecules the polarizability may be anisotropic, and depends on the rotational and vibrational coordinates. This can also give rise to Raman Scattering.

Gross Selection Rule:

To be Raman active a molecule must have anisotropic polarizability

[Less restrictive than the need for a dipole moment, symmetric molecules can be Raman active]
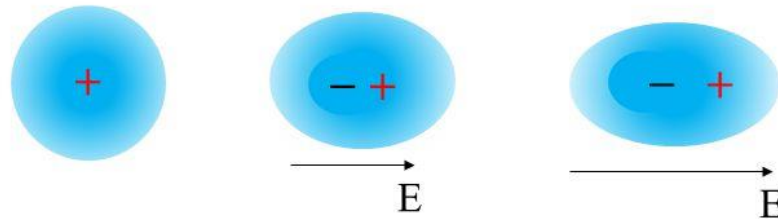
Polarization

Amount of polarization $\vec{p}$ in most materials is *proportional* to the magnitude of the applied electric field:

$$\vec{p} = \alpha \vec{E}$$

α - "*polarizability*" of a material

In an induced dipole, is the distance between the charges fixed? The distance is proportional to the strength of the applied field.


As discussed, when an atom or molecule is brought into an electric field E , an electric dipole moment μ is induced in the system. The magnitude of this induced dipole moment is proportional to the electric field, μ = α E where α is known as the polarizability.

- Except <u>for the case of spherical symmetry</u>, the magnitude of the induced dipole moment depends on the direction of the electric field. For example, in case of a diatomic molecule, <u>the induce dipole moment will be higher in magnitude when the electric field direction is along the inter-nuclear axis than that of the perpendicular to the inter-nuclear axis</u>.

Change in Polarizability
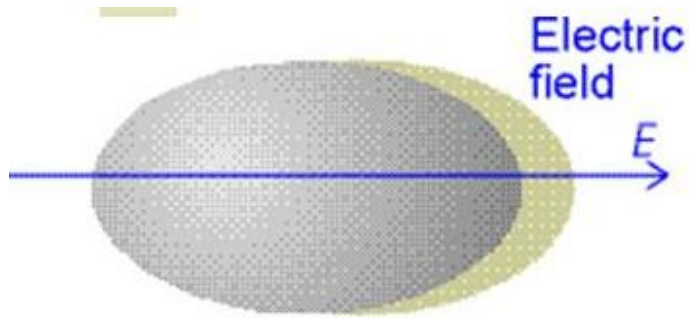
(a)
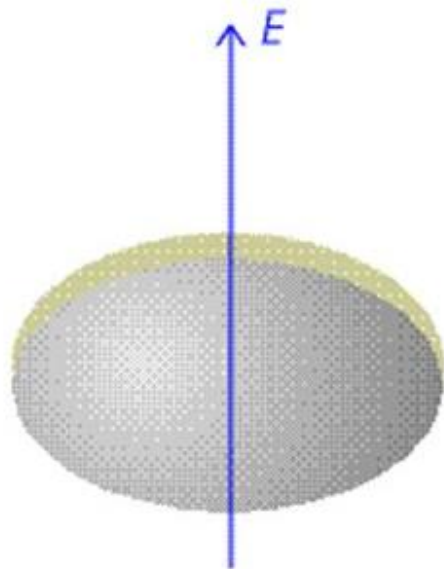
(b)

An electric field applied to a molecule results in its distortion, and the distorted molecule acquires a contribution to its dipole moment (even if it is nonpolar initially). The polarizability may be different when the field is applied (a) parallel or (b) perpendicular to the molecular axis (or, in general, in different directions relative to the molecule); if that is so, then the molecule has an anisotropic polarizability.

Anisotropic Nature of Polarizability

● The polarization of a molecules need not be identical in all directions.
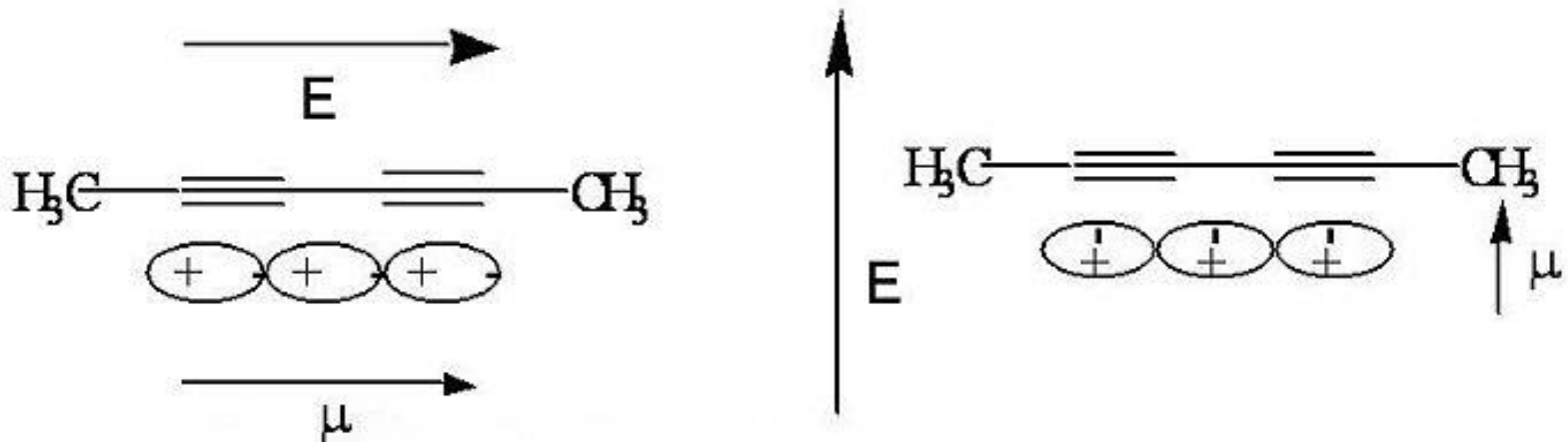
Polarisability Change during Rotation

In case of a diatomic and linear molecule, the ***induce dipole moment*** will be higher in magnitude when the electric field direction is along the inter-nuclear axis than that of the perpendicular to the inter-nuclear axis.
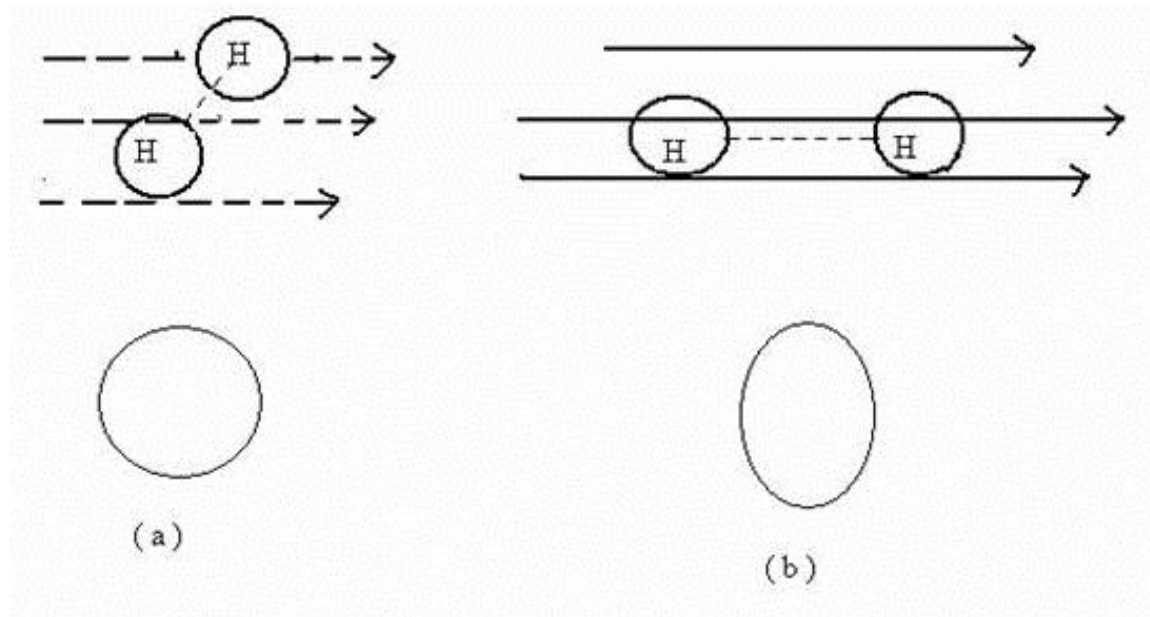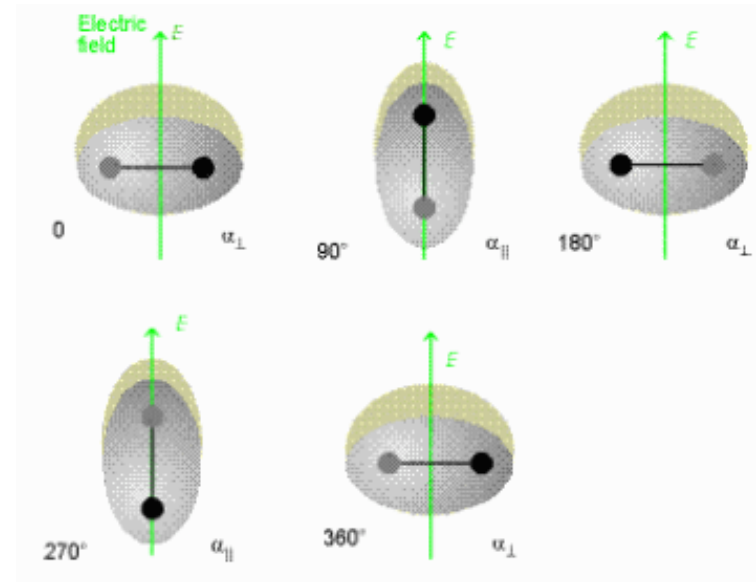

Polarisability Ellipsoid of Hydrogen in two different orientations.

Classical theory Raman scattering: Rotational Raman

$$P_{in} = \alpha\, E$$

$$\alpha = \alpha_0 + \Delta\alpha\, \cos(2\omega t)$$

$$E = E_0 \cos(2\pi v_0 t)$$

$$P_{in} = (\alpha_0 + \Delta\alpha\, \cos(2\omega t)) \times E_0 \cos(2\pi v_0 t)$$

$$= \alpha_0\, E_0 \cos(2\pi v_0 t) + \frac{1}{2} E \Delta\alpha\, \{\cos(2\pi v_0 - 2\omega)t + \cos(2\pi v_0 + 2\omega)t\}$$

Rayleigh   **Stokes**   **Anti-Stokes**

$$\Delta\alpha \neq 0$$

Polarizability should be changed during rotation

Classical theory Raman scattering : Vibrational Raman

- An oscillating electric field (incident photon) causes the molecule to have an **induced** dipole:

$$\mathbf{P} = \alpha \mathbf{E} \qquad \mathbf{E} = \mathbf{E}_0 \cos(2\pi\nu_0 t)$$

$$\mathbf{P} = \alpha \mathbf{E}_0 \cos(2\pi\nu_0 t)$$

$$\alpha = \alpha_0 + \left(\frac{\partial\alpha}{\partial r}\right)_{r_0} (r - r_0) + \dots$$

-
$$\mathbf{P} = \alpha_0 \mathbf{E}_0 \cos(2\pi\nu_o t) + \left(\frac{\partial\alpha}{\partial q_i}\right)_0 \mathbf{E}_0 \cos(2\pi\nu_o t) q_i^0 \cos(2\pi\nu_i t)$$

$$= \alpha_0 \mathbf{E}_0 \cos(2\pi\nu_o t) + \frac{1}{2}\left(\frac{\partial\alpha}{\partial q_i}\right)_0 \mathbf{E}_0 q_i^0 \left[\cos\left(2\pi(\nu_o - \nu_i)t\right) + \left(\cos 2\pi(\nu_o + \nu_i)t\right)\right]$$

Rayleigh   **Stokes**   **Anti-Stokes**

$$\left(\frac{\partial\alpha}{\partial r}\right)_{r_0} \neq 0$$

In order for a vibrational mode to be Raman active, the polarizability must change during the vibration, and for a rotation to be Raman active, the polarizability must change as the molecule rotates in an electric field.

$$I_{\text{scatt}} \propto \left| \mathbf{P} \cdot \mathbf{E}_0 \right|^2 = \left| \left(\partial \alpha / \partial q_i \right)_0 \right|^2 I_0^2$$

Thus, the polarizability must change linearly with vibrational motion for vibrational Raman scattering to occur. The greater the change, the more intense the Raman scattering. If α is unchanged or at a minimum/maximum, there is no Raman scattering.

Quantum Picture of Raman scattering : Vibrational Raman

$$\mu_{fi} = \left\langle v_f \left| \alpha(0) + \left(\frac{d\alpha}{dx}\right)_0 x + \cdots \right| v_i \right\rangle \mathcal{E}$$

$$= \langle v_f | v_i \rangle \alpha(0) \mathcal{E} + \left(\frac{d\alpha}{dx}\right)_0 \langle v_f | x | v_i \rangle \mathcal{E} + \cdots$$

$$\langle v_f | v_i \rangle \quad = 0 \qquad f \neq i$$

Raman active if $(d\alpha/dx)_0 \neq 0$ and $\langle v_f | x | v_i \rangle \neq 0$. Therefore, the polarizability of the molecule must change during the vibration; this is the gross selection rule of Raman spectroscopy. Also, we already know that $\langle v_f | x | v_i \rangle \neq 0$ if $v_f - v_i = \pm 1$; this is the specific selection rule of Raman spectroscopy.

Molecular Picture of Scattering Events
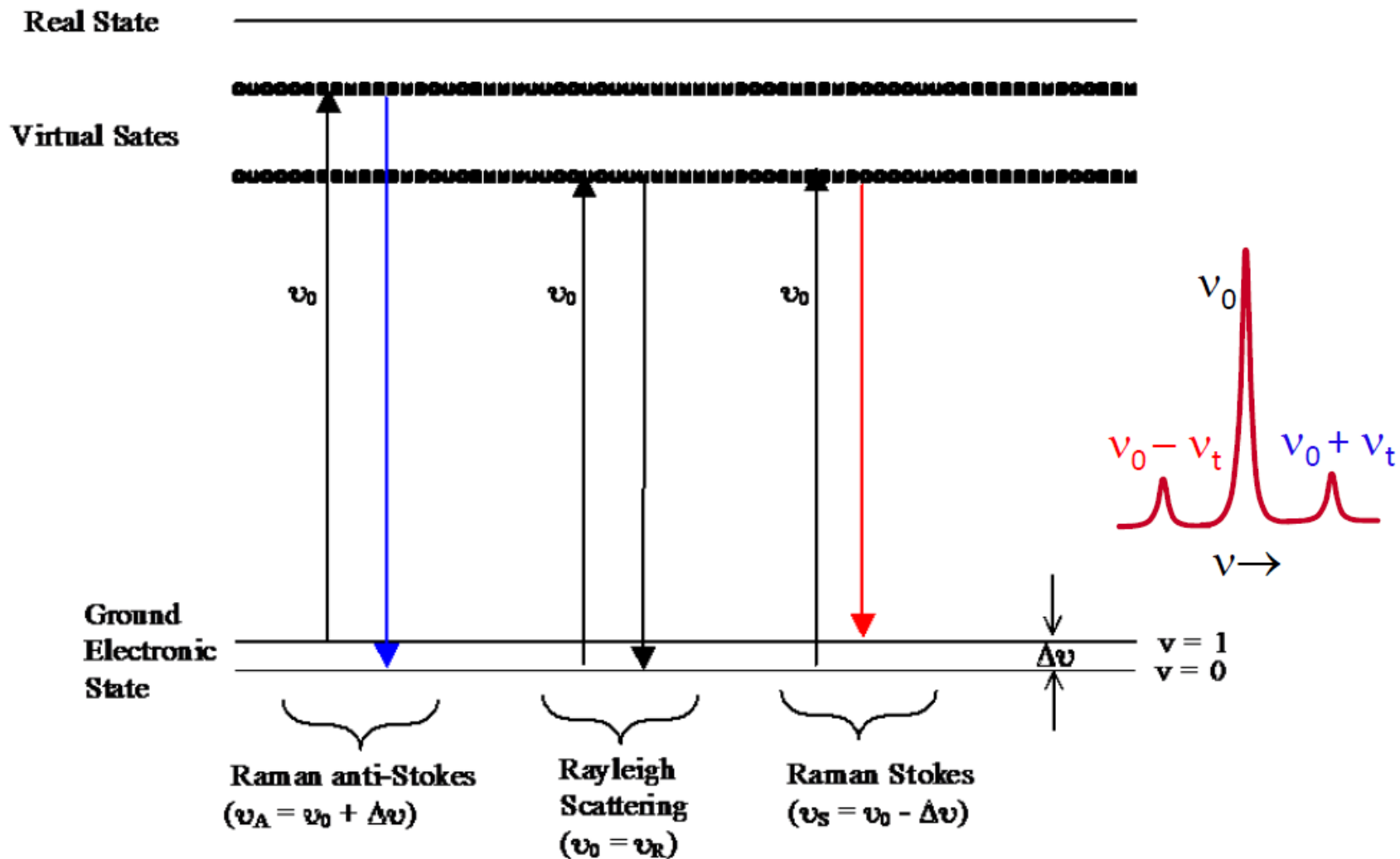
Polarizability Ellipsoids of CO_2
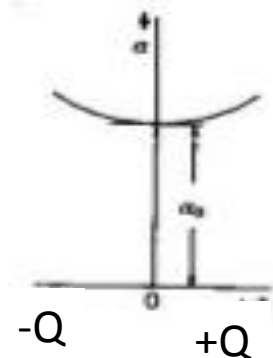## ational Modes and Raman Act

O ——C—— O   O —C— O   O—C—O

α_0 $\dfrac{\partial \alpha}{\partial Q} \neq 0$

-Q   +Q

v_1 Symmetric Stretch

α_0 $\dfrac{\partial \alpha}{\partial Q} = 0$

-Q   +Q

v_2 Bending Mode

O ——C—O   O —C— O   O—C ——O

α_0 $\dfrac{\partial \alpha}{\partial Q} = 0$

-Q   +Q
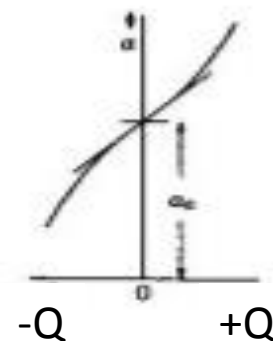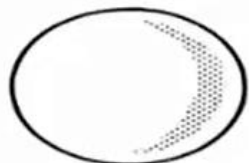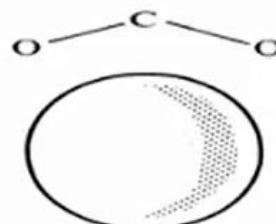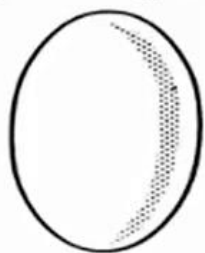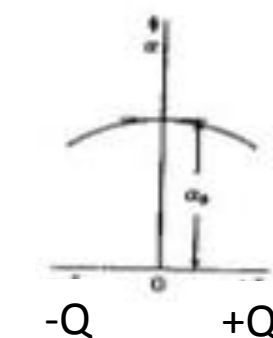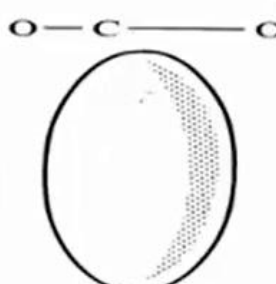
Assymetric stretching mode

Rotational Raman

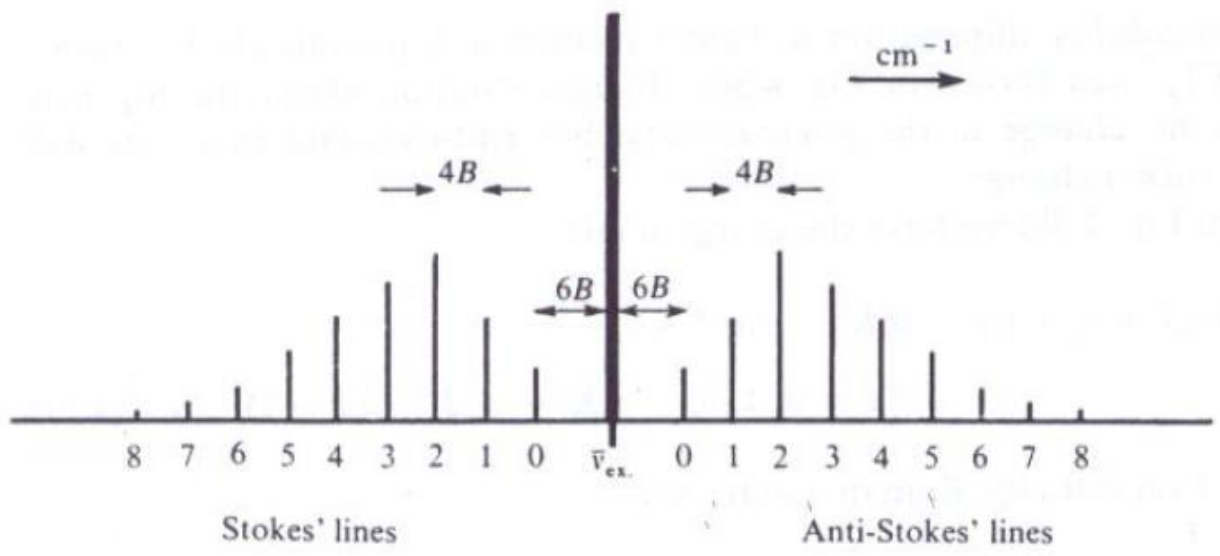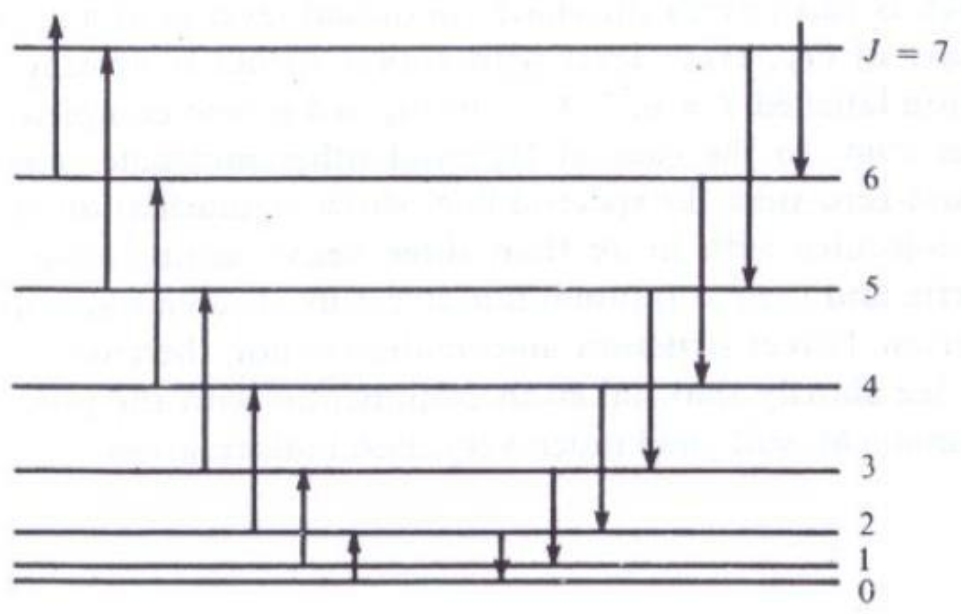Linear molecules $\qquad \Delta J = 0, \pm 2$

For Linear Molecules

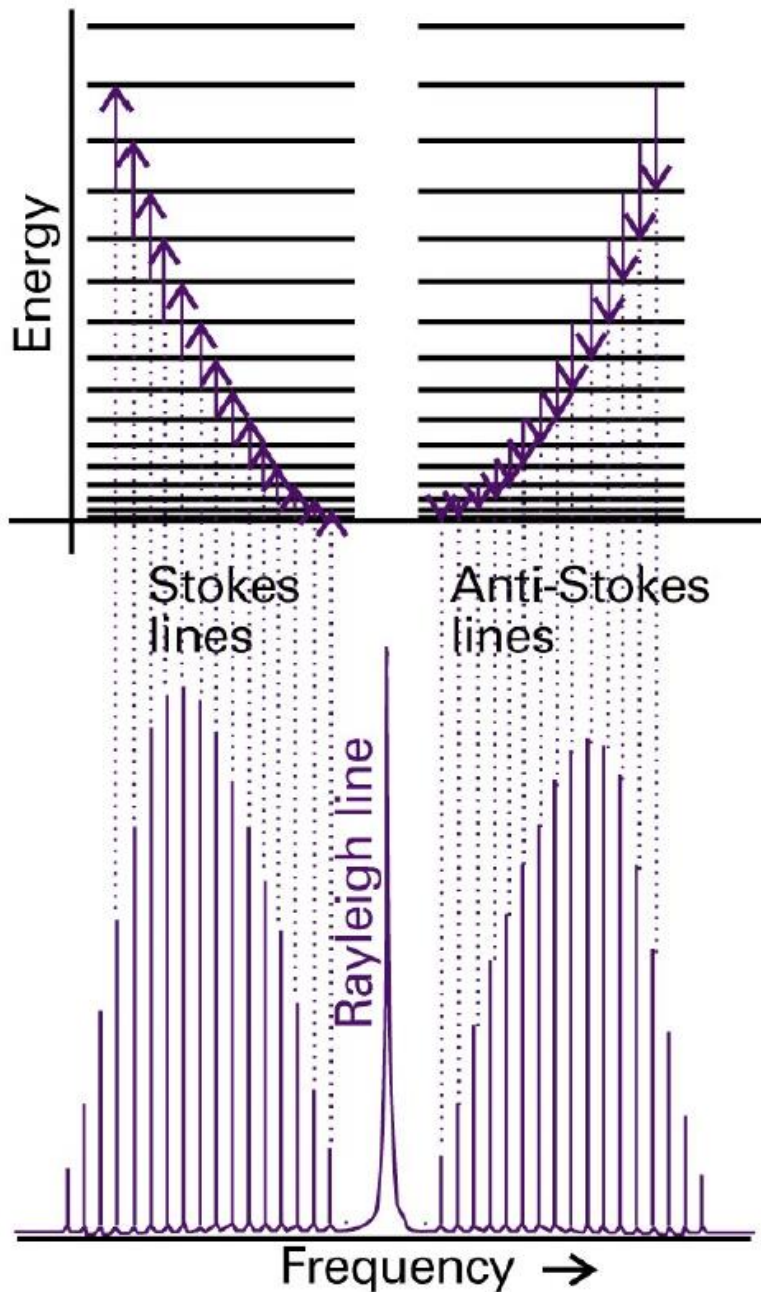$$\Delta \tilde{\nu}_R = \tilde{B}J'(J'+1) - \tilde{B}J''(J''+1)$$

$$\Delta \tilde{\nu}_R = \nu_0 \pm \tilde{B}(4J+6)$$
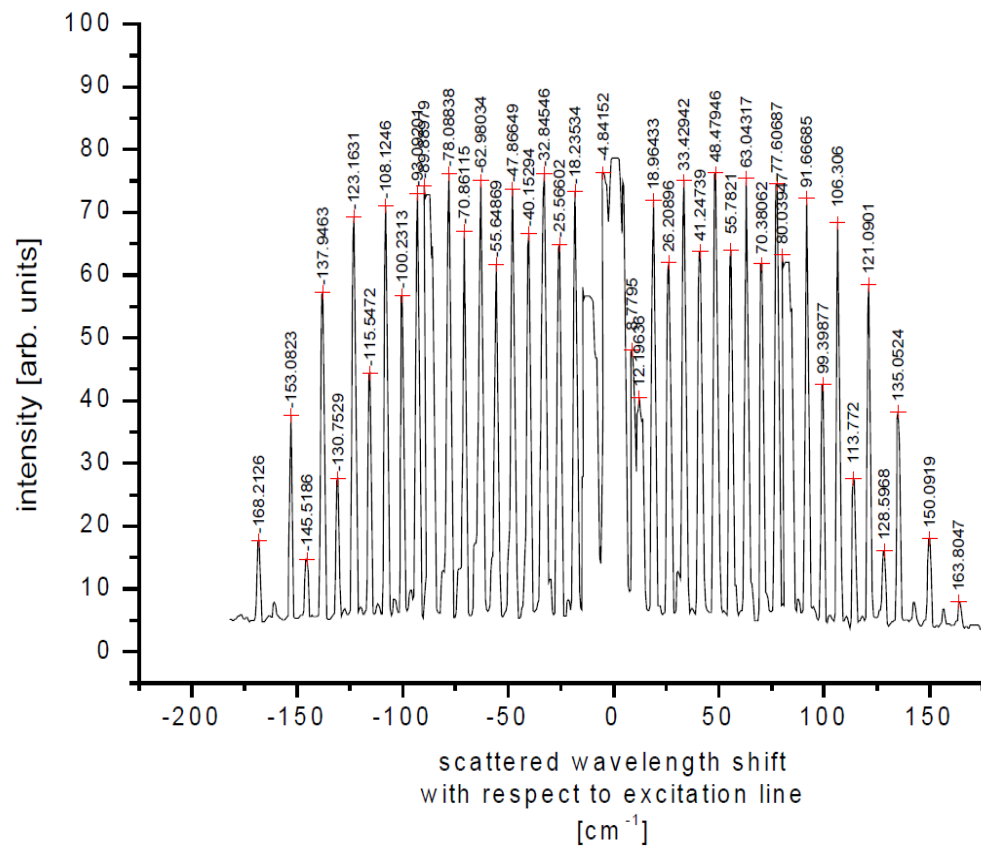
Stokes (-)   **anti-stokes (+)**

- a gap of $6B$ between ν_0 and 1st lines of each branch
- lines in each branch of equal spacing $= 4B$

$J = 7$

6

5

4

3

2
1
0

cm^{-1}

$4B$ $4B$

$6B$ $6B$

8 7 6 5 4 3 2 1 0 $\bar{v}_{ex.}$ 0 1 2 3 4 5 6 7 8

Stokes' lines   Anti-Stokes' lines
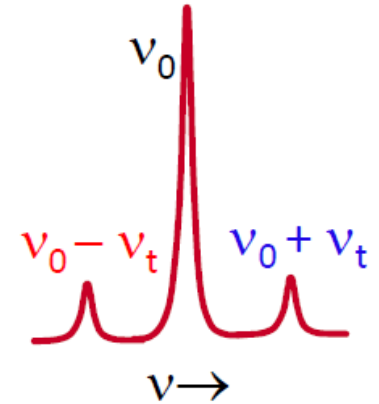
Rotational Raman spectra of Diatomic Molecule

Rotational Raman Spectrum of $^{15}N_2$

Vibrational Raman Spectra

$\Delta\vartheta = \pm1$

Real State

Virtual Sates

υ_0 υ_0 υ_0

Ground
Electronic
State

$\Delta\upsilon$

v = 1
v = 0

Raman anti-Stokes
$(\upsilon_A = \upsilon_0 + \Delta\upsilon)$

Rayleigh
Scattering
$(\upsilon_0 = \upsilon_R)$

Raman Stokes
$(\upsilon_S = \upsilon_0 - \Delta\upsilon)$

ν_0

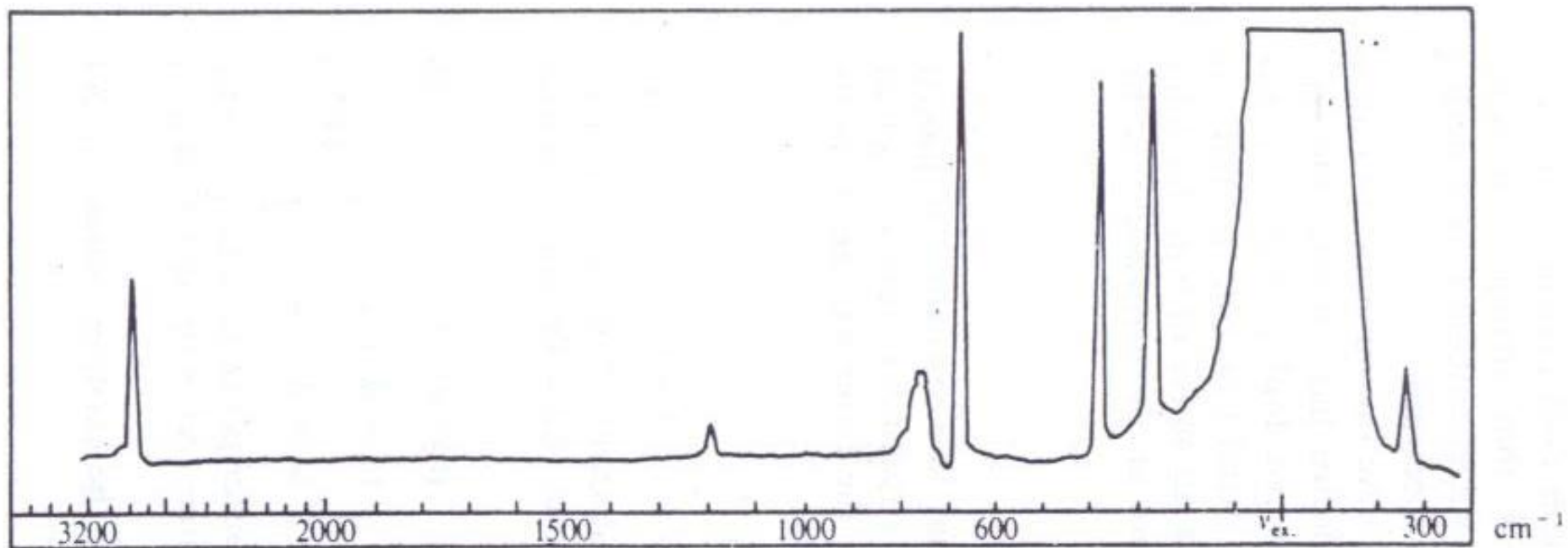$\nu_0 - \nu_t$ $\nu_0 + \nu_t$

$\nu \rightarrow$
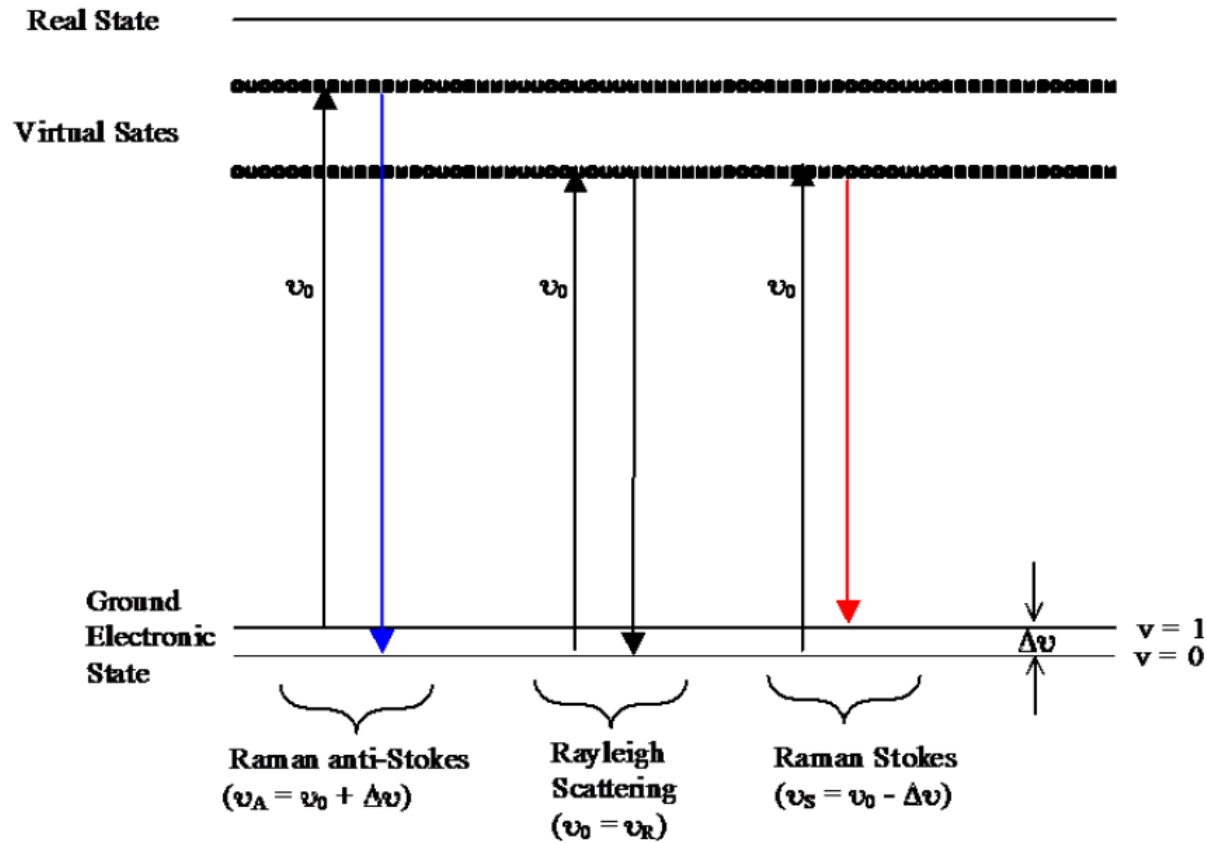
Vibrational Raman Spectroscopy
(with rotational (sub)-structure)

$\vartheta = 0$ to $\vartheta = 1$ transition
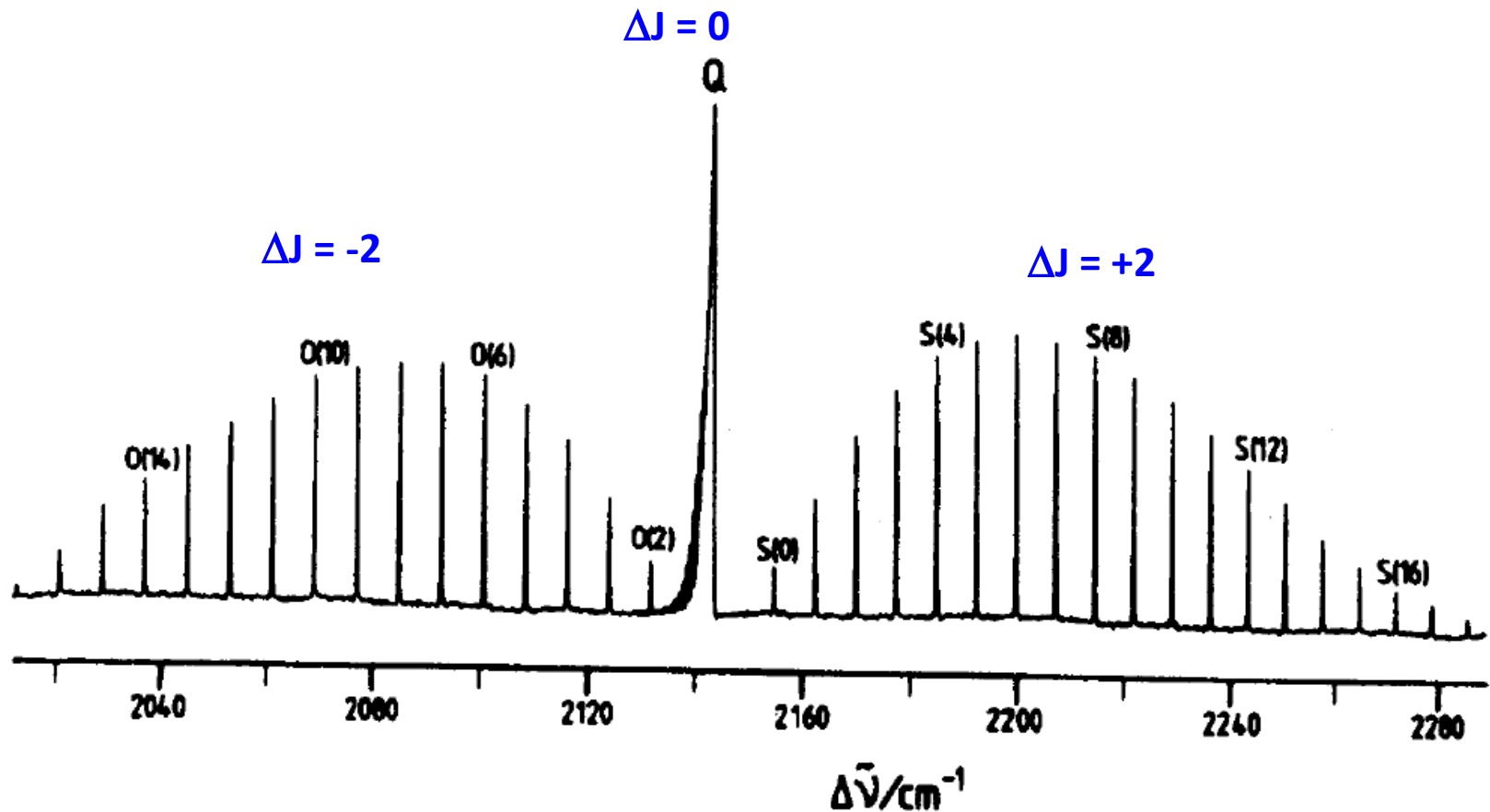
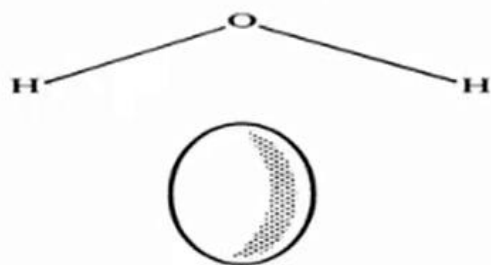The 1–0 Stokes vibrational Raman spectrum of CO showing the O-, Q-, and S-branch rotational structure
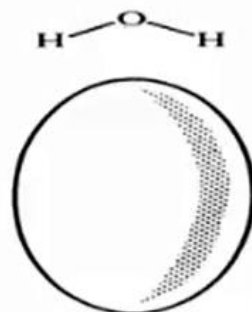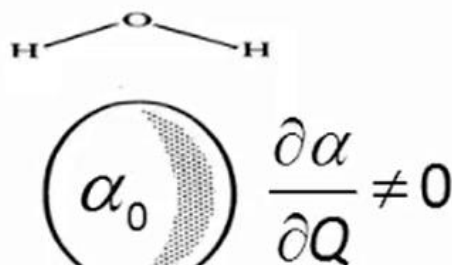
Raman Spectra of CHCl₃

Polarizability Ellipsoids of H_2O Vibrational Modes and Raman Activity

Size

α_0 $\dfrac{\partial \alpha}{\partial Q} \neq 0$ **Raman Active**

(a) v_1, symmetric stretching mode

Shape

α_0 $\dfrac{\partial \alpha}{\partial Q} \neq 0$ **Raman Active**
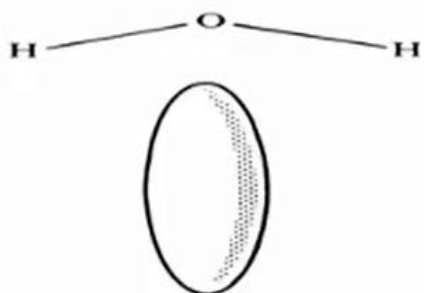
(b) v_2, bending mode
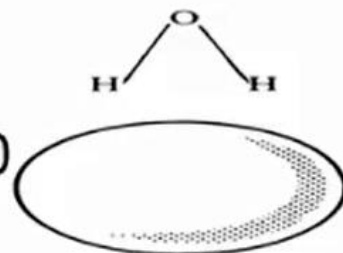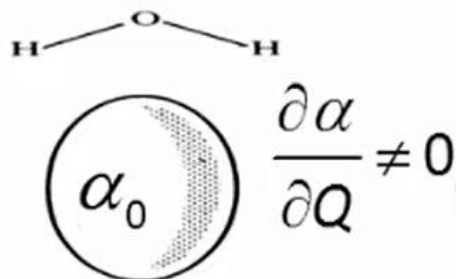
Orientation
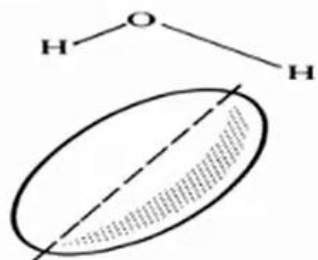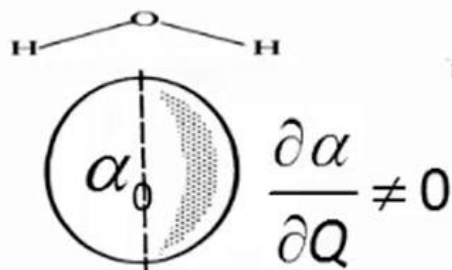
α_0 $\dfrac{\partial \alpha}{\partial Q} \neq 0$ **Raman Active**
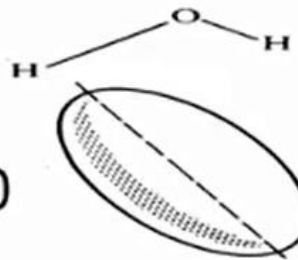
(c) v_3, asymmetric stretching mode

Mutual Exclusion Principle

For molecules with a center of symmetry, no IR active transitions are Raman active and vice versa

v_3 (2349 cm^{-1})

IR

v_1 (1388 cm^{-1})

Raman

v_2 (667 cm^{-1})

(c)

IR

acetylene

$D_{\infty h}$

mode 1 Σ_g^+
Raman

mode 2 Σ_g^+
Raman

mode 3 Σ_u^+
Infrared

mode 4 Π_g
Raman

mode 5 Π_u
Infra Red
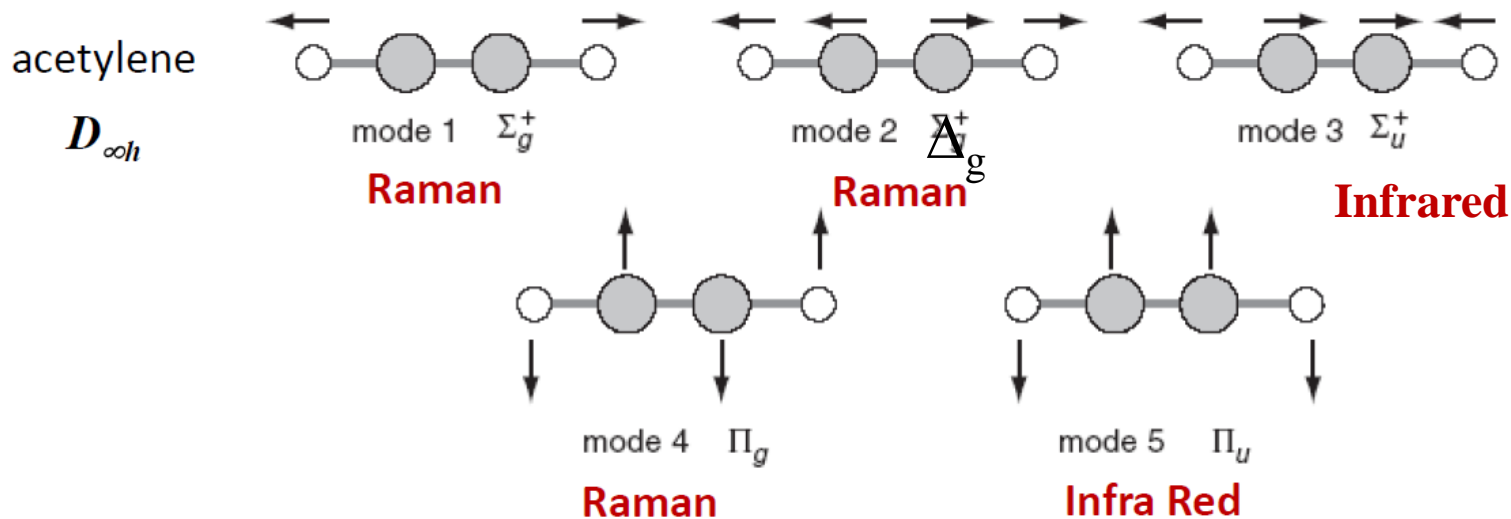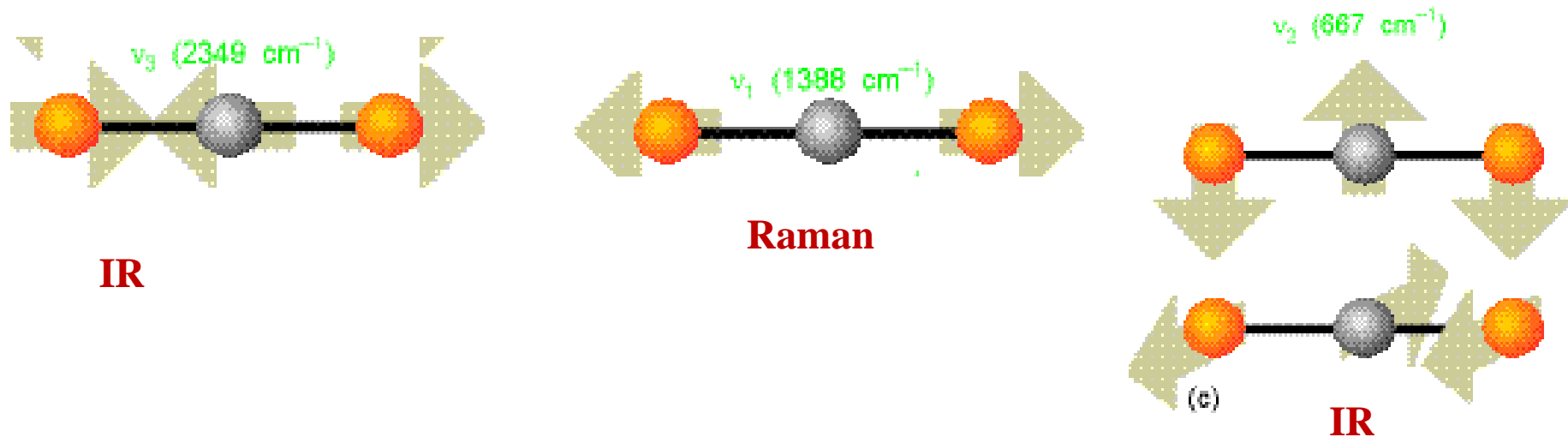
The *Vibrational Raman Spectra of Homonuclear diatomic molecules* are of Special interest because they yield force constants and rotational constants that are not available from microwave and Infrared Absorption spectroscopy.

Advantages of Raman over IR

• Water can be used as solvent.

•Very suitable for biological samples in native state (because water can be used as solvent).

• Although Raman spectra result from molecular vibrations at IR frequencies, spectrum is obtained using visible light or NIR radiation.

 =>Glass and quartz lenses, cells, and optical fibers can be used. Standard detectors can be used.

• Few intense overtones and combination bands => few spectral overlaps.

• Totally symmetric vibrations are observable.

•Raman intensities α to concentration and laser power.

Advantages of IR over Raman

• Simpler and cheaper instrumentation.

• Less instrument dependent than Raman spectra because IR spectra are based on measurement of intensity *ratio*.

• Lower detection limit than (normal) Raman.

• Background fluorescence can overwhelm Raman.

• More suitable for vibrations of bonds with very low polarizability (e.g. C–F).
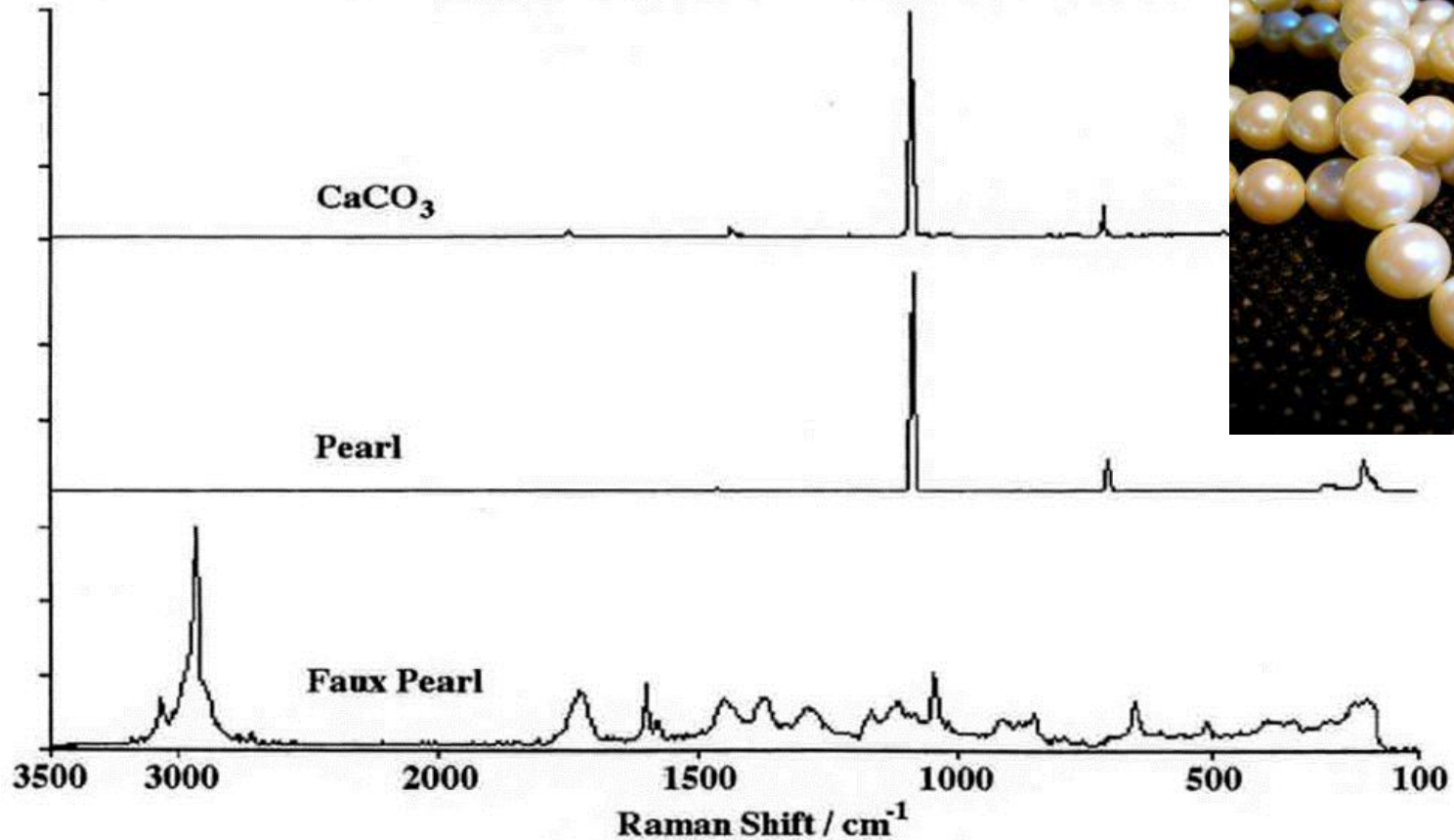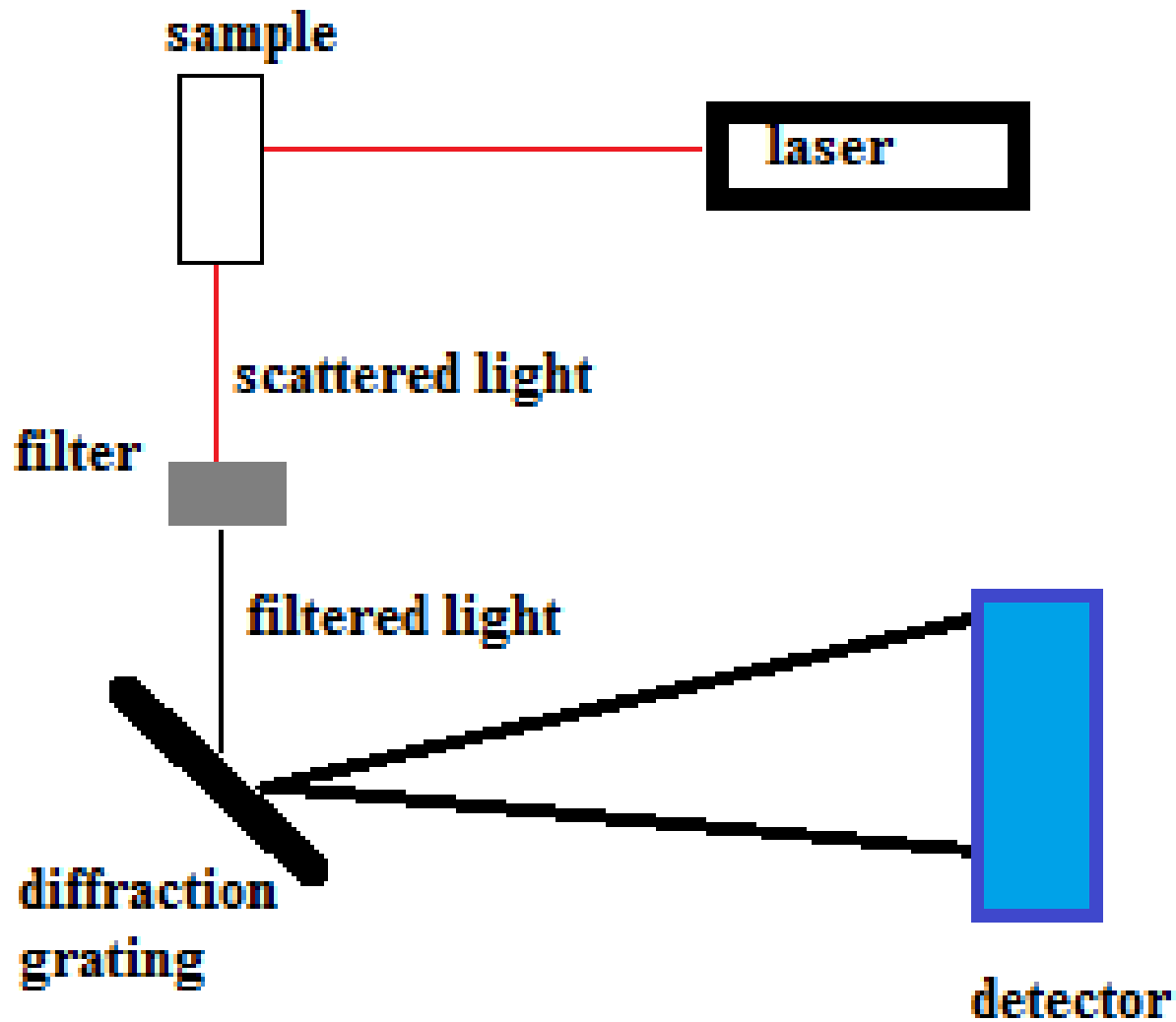
Raman and Fraud

Figure 3 The Raman spectra of calcium carbonate (top), natural pearl (middle), and faux pearl (bottom). (Adapted with permission from Ref. 9.)

Raman Instrumentation

Polarizability Tensor is Symmetric

$\alpha_{xy} = \alpha_{yx}$, $\alpha_{yz} = \alpha_{zy}$, and $\alpha_{xz} = \alpha_{zx}$, which reduces the matrix components from 9 to 6
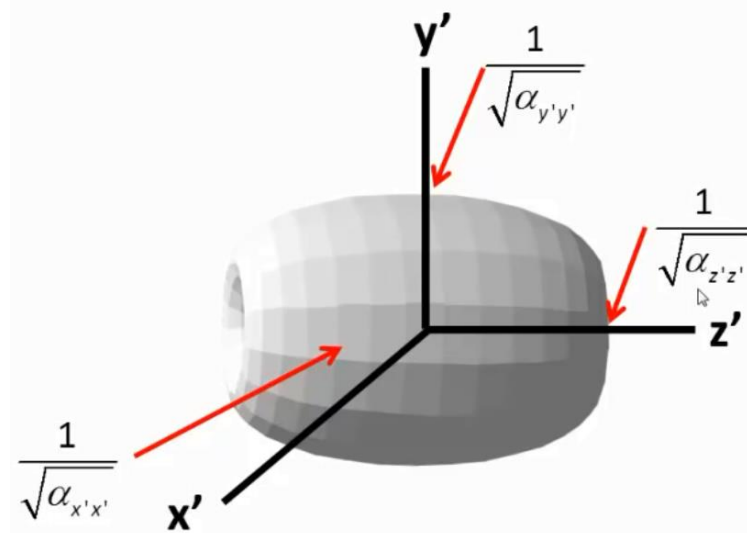
$$\begin{bmatrix} P_x \\ P_y \\ P_z \end{bmatrix} = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix}$$

Symmetric tensors can be transformed to a new coordinate system of x′, y′ and z′ such that only the diagonal elements $\alpha_{x'x'}$, $\alpha_{y'y'}$, and $\alpha_{z'z'}$ are nonzero. It is in this new coordinate system that we graphically represent the polarizability ellipsoid.

Conventional Mathematical Description of the Raman Polarizability Ellipsoid

$$\frac{x'^2}{\left(\dfrac{1}{\sqrt{\alpha_{x'x'}}}\right)^2} + \frac{y'^2}{\left(\dfrac{1}{\sqrt{\alpha_{y'y'}}}\right)^2} + \frac{z'^2}{\left(\dfrac{1}{\sqrt{\alpha_{z'z'}}}\right)^2} = 1$$

constitute the lengths of the polarizability ellipsoid semiaxes

END