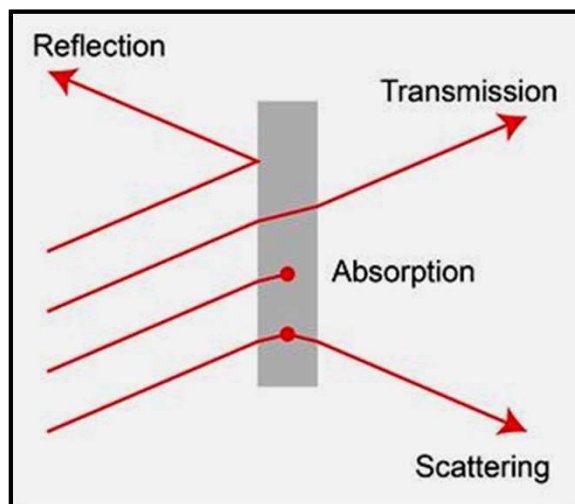




# *Theory of Raman Spectroscopy*

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## ***Fate of the Radiation Falling on a Sample***



## Light and Spectroscopy

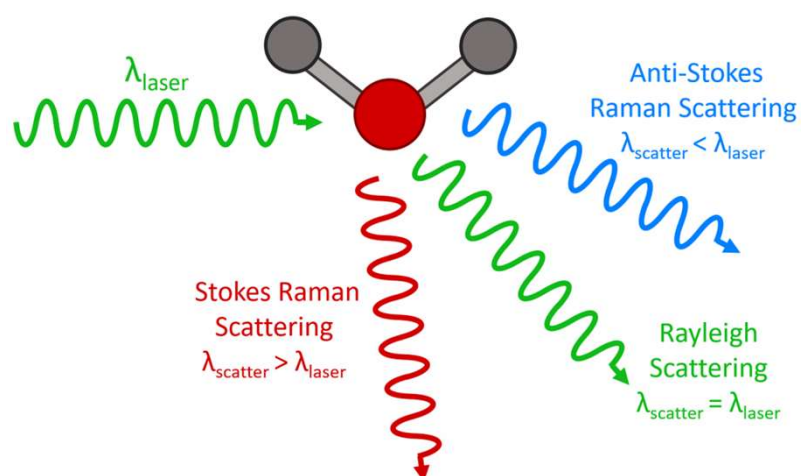
- Light interacts with matter in different ways, **transmitting** through some materials, while **reflecting** or **scattering** off others.
- Both the material and the colour (wavelength) of the light affect this interaction.
- **We call the study of this light 'spectroscopy'**. Which parts of the visible spectrum enter our eyes determines which colours we perceive.

## What is Raman Spectroscopy?

- Raman spectroscopy is an analytical technique where scattered light is used to measure the vibrational energy modes of a sample.
- It is named after the Indian physicist C. V. Raman who, together with his research partner K. S. Krishnan, was the first to observe Raman scattering in 1928.

- Raman spectroscopy can provide both chemical and structural information, as well as the identification of substances through their characteristic Raman 'fingerprint'.
- Raman spectroscopy extracts this information through the detection of Raman scattering from the sample.

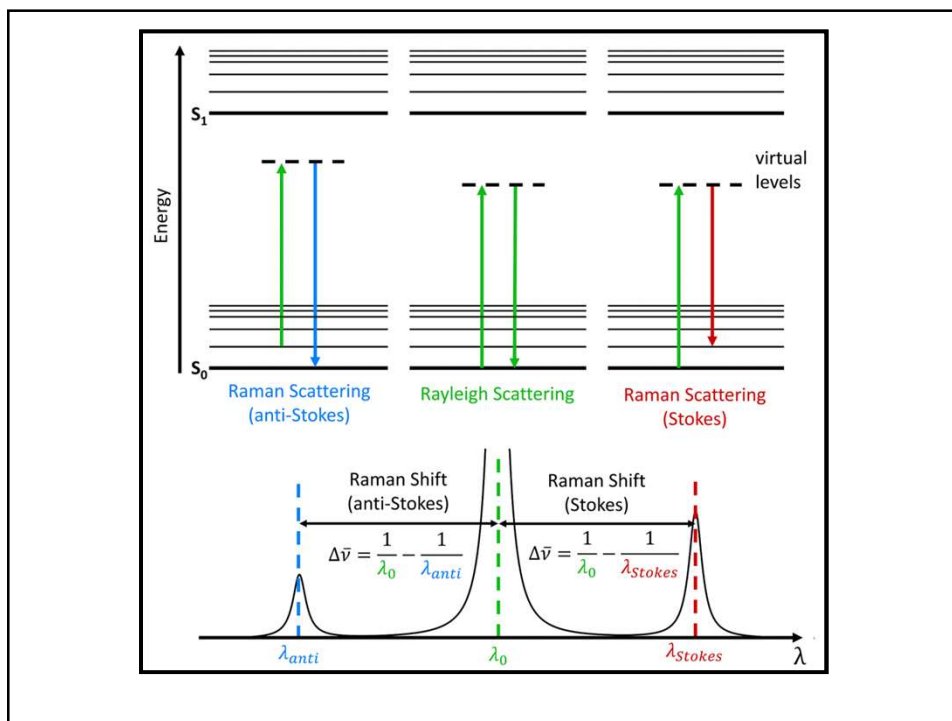
## What is Raman Scattering?



## Raman Scattering

- When light is scattered by molecule, the oscillating electromagnetic field of a photon induces a polarization of the molecular electron cloud.
- This leaves the molecule in a higher energy state with the energy of the photon transferred to the molecule.

- This can be considered as the formation of a very short-lived complex between the photon and molecule which is commonly called the virtual state of the molecule.
- The virtual state is not stable and the photon is re-emitted almost immediately, as scattered light.



## Rayleigh Scattering

- In the vast majority of scattering events, the energy of the molecule is unchanged after its interaction with the photon.
- The energy, and therefore the wavelength, of the scattered photon is equal to that of the incident photon.
- This is called elastic (energy of scattering particle is conserved) or Rayleigh scattering and is the dominant process.

## Raman Scattering

- In a much rarer event (approximately 1 in 10 million photons) Raman scattering occurs, which is an inelastic scattering process with a transfer of energy between the molecule and scattered photon.
- If the molecule gains energy from the photon during the scattering (excited to a higher vibrational level) then the scattered photon loses energy and its wavelength increases which is called Stokes Raman scattering (after G. G. Stokes).

- Inversely, if the molecule loses energy by relaxing to a lower vibrational level the scattered photon gains the corresponding energy and its wavelength decreases; which is called Anti-Stokes Raman scattering.
- Quantum mechanically Stokes and Anti-Stokes are equally likely processes.
- However, with an ensemble of molecules, the majority of molecules will be in the ground vibrational level (Boltzmann distribution) and Stokes scatter is the statistically more probable process.

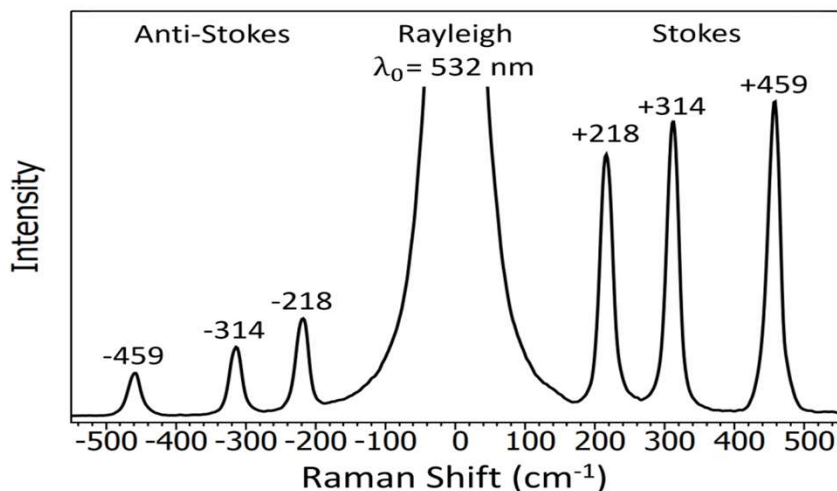
- As a result, the Stokes Raman scatter is always more intense than the anti-Stokes and for this reason, it is nearly always the Stokes Raman scatter that is measured in Raman spectroscopy.
- The wavelength of the Raman scattered light will depend on the wavelength of the excitation light.
- This makes the Raman scatter wavelength an impractical number for comparison between spectra measured using different lasers.

## Raman Shift

- **The Raman scatter position is therefore converted to a Raman shift away from excitation wavelength**

$$\Delta\bar{\nu}(cm^{-1}) = \left( \frac{1}{\lambda_0(nm)} - \frac{1}{\lambda_1(nm)} \right) \times \frac{(10^7 nm)}{(cm)}$$

## Raman Spectrum of $\text{CCl}_4$



## Classical Theory of Raman Effect

- When an electrically neutral molecule is kept in a uniform electrical field, it is polarized.
- The extent of polarization is given by the induced dipole moment

$$\mu = \alpha \cdot E$$

$\alpha$  – Polarizability of the molecule

A second degree tensor



## Classical Theory of R.E

- When a radiation of frequency  $\nu$  is falling on a molecule, the electrical field felt by the molecule is

$$E = E_0 \sin 2\pi\nu t$$

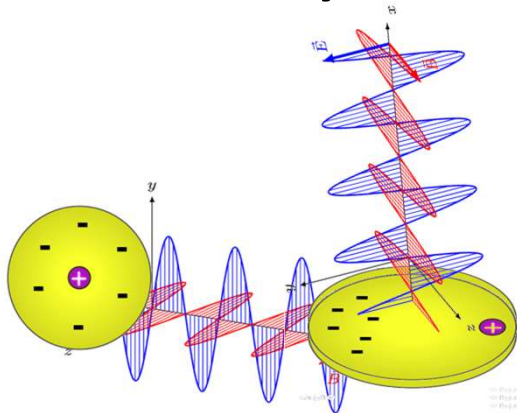
- This electrical field polarizes the molecule and makes it to oscillate with the same frequency.

- The associated induced dipole moment is

$$\mu = \alpha.E = \alpha E_0 \sin 2\pi\nu t$$

- Such an oscillating dipole emits radiation of its own oscillation frequency, which is called **Rayleigh Scattering**

## Classical Theory of Raman Effect



## Raman Scattering

- If the molecule undergoes rotation or vibration also, then the polarizability of it changes, hence the emitted frequencies also - **Raman Scattering.**
- Lets assume that the polarizability of the molecule  $\alpha$  is changed by the vibrational frequency of the molecule  $\nu_{vib}$

$$\alpha = \alpha_0 + \beta \sin 2\pi\nu_{vib}t$$

$$\alpha = \alpha_0 + \beta \sin 2\pi\nu_{vib}t$$

Where,

- $\alpha_0$  is the equilibrium polarizability
- $\beta$  is the rate of change of polarizability with vibration
- $\nu_{vib}$  is the vibrational frequency

$$\mu = \alpha E = (\alpha_0 + \beta \sin 2\pi\nu_{vib}t) E_0 \sin 2\pi\nu t$$

- By expansion and using the relation,

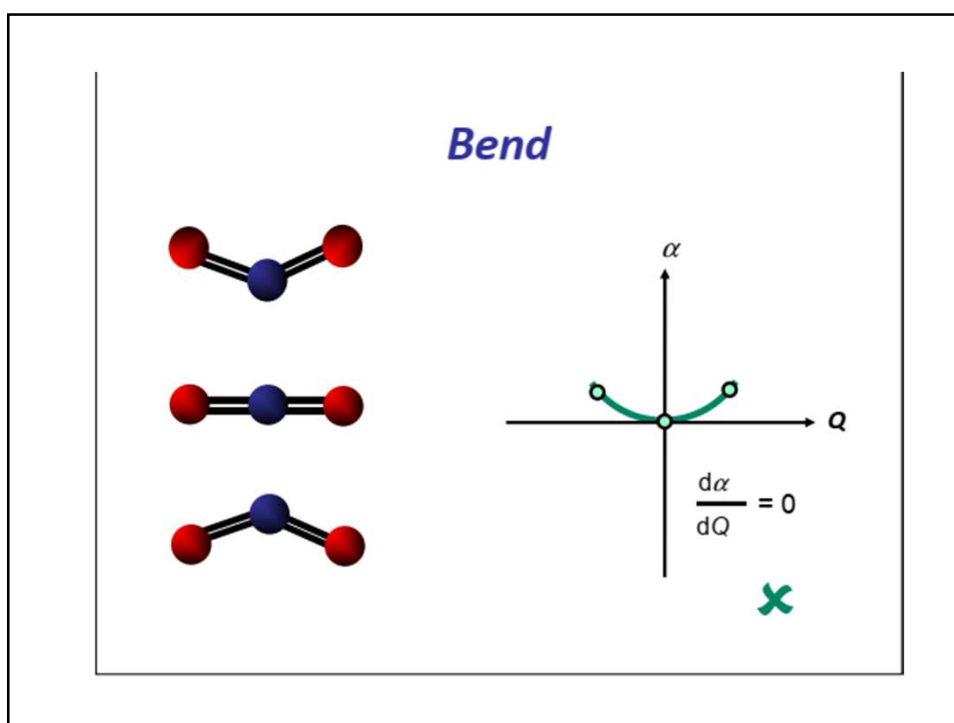
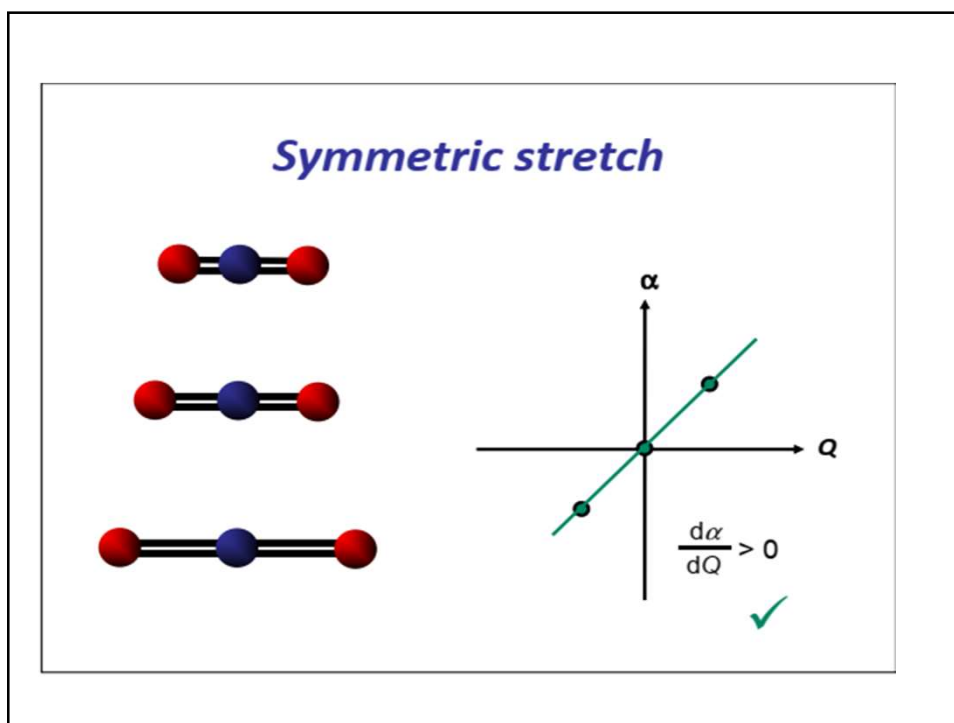
$$\sin A \sin B = \frac{1}{2} [\cos(A - B) - \cos(A + B)]$$

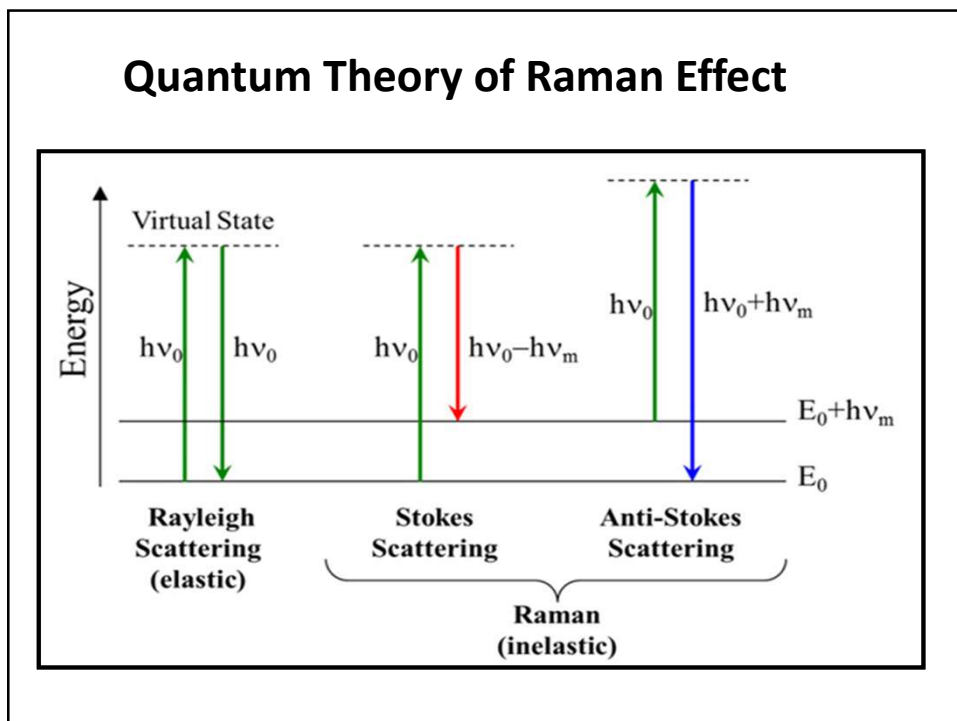
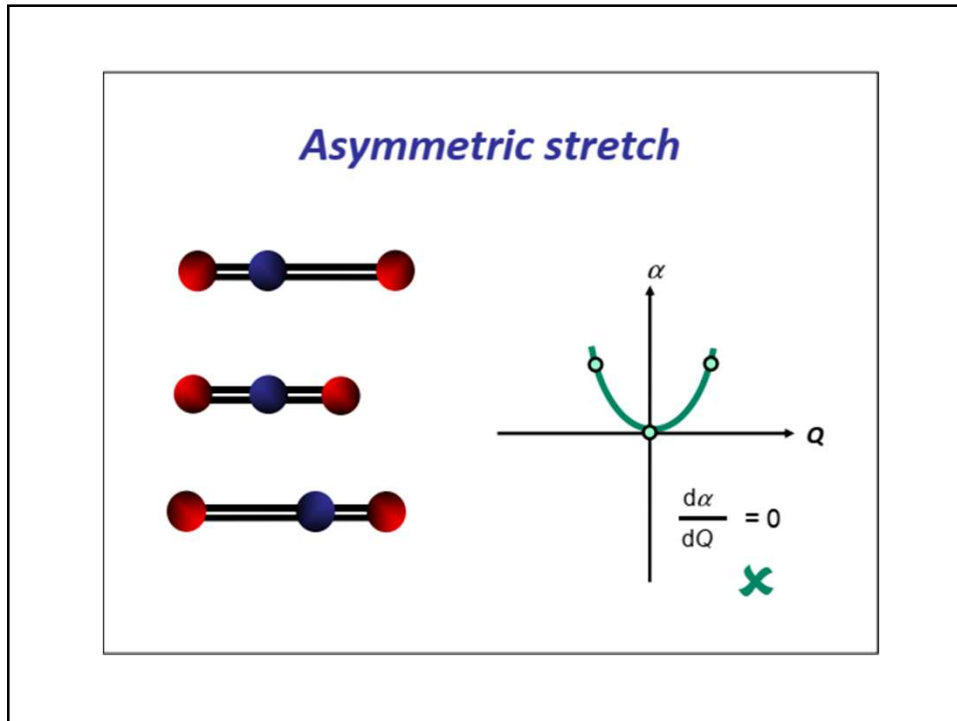
$$\mu = \alpha_0 E_0 \sin 2\pi\nu t + \frac{1}{2} \beta E_0 [\cos 2\pi(\nu - \nu_{vib})t - \cos 2\pi(\nu + \nu_{vib})t]$$

Above equation shows that the oscillating dipole has three frequency components namely,

- $\nu$  **Rayleigh Line**
- $(\nu + \nu_{vib})$  **Raman Line (Anti-Stokes)**
- $(\nu - \nu_{vib})$  **Raman Line (Stokes)**

- The Raman shift is depending on the  $\beta$  value.
- If the polarizability change with vibration is zero then the Raman shift is also zero, i.e. the vibration is not Raman active.



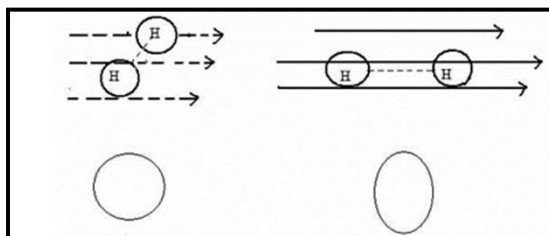


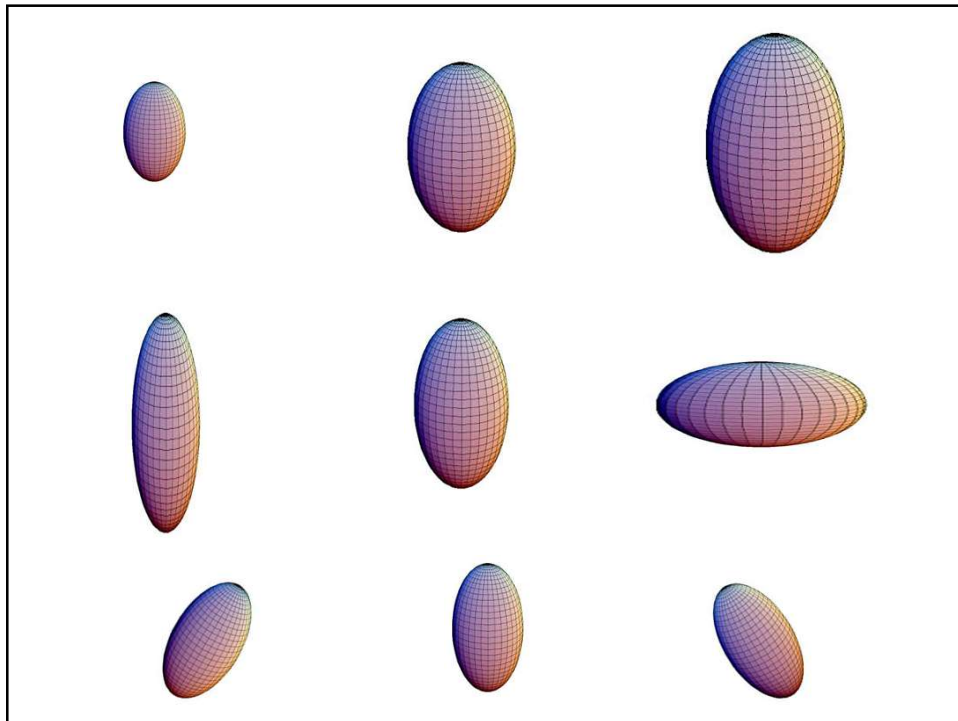
## Raman Activity

- **When a vibration is Raman active?**  
The polarizability ellipsoid should change in
  - Shape
  - Size
  - Orientation

## Polarizability Ellipsoid

- 3D figure created by tracing the values of  $(1/\nu\alpha)$
- For many molecules  $\alpha$  is different in different directions – anisotropic.





Raman  
Activity of  
 $H_2O$   
Vibrations

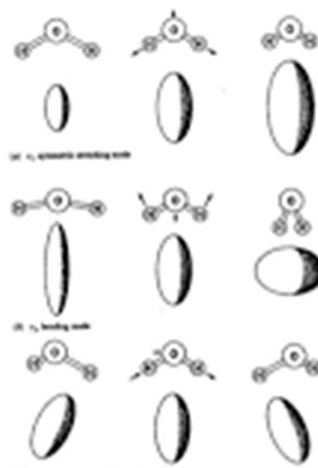
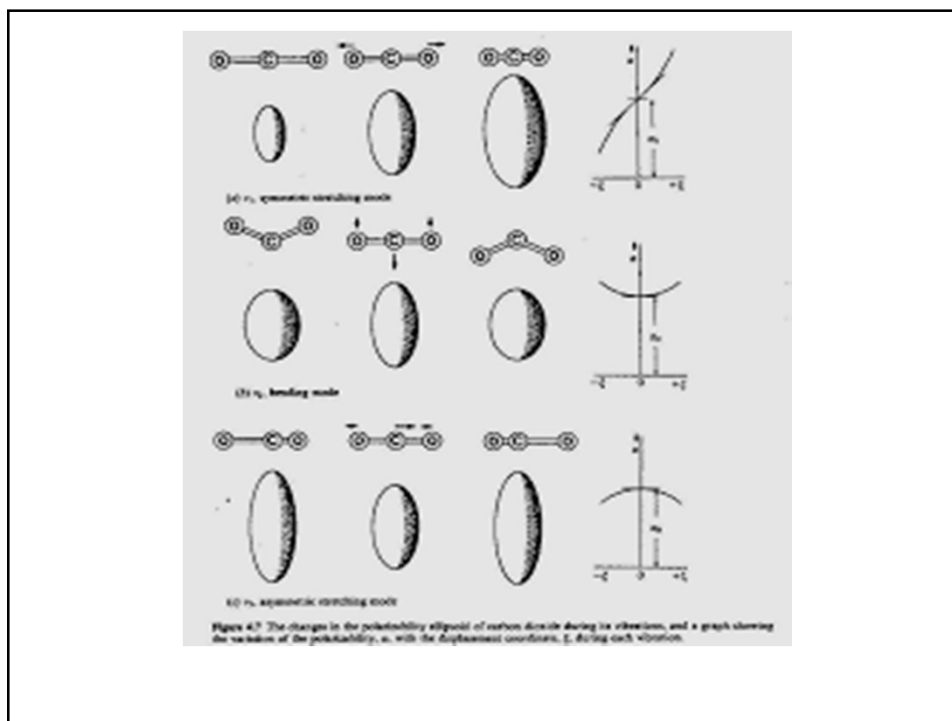


Figure 14. The change in size, shape, or direction of the polarizability ellipsoid of the water molecule during each of its three vibrational modes. The space curves show the equilibrium position of the molecule, while its right and left are the instantaneous positions at each vibration.



## Rotational Raman

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

For Linear Molecules

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

$$\Delta \bar{\nu}_R = \nu_0 \pm \bar{B}(4J + 6)$$

Stokes (-)    anti-stokes (+)

- a gap of  $6B$  between  $\nu_0$  and 1<sup>st</sup> lines of each branch
- lines in each branch of equal spacing =  $4B$

Two photons involved in Raman process, each is a spin-1 particle, so a maximum change in angular momentum quantum number of  $\pm 2$  is possible. This then gives a selection rule for Rotational Raman Transitions

$$\Delta J = \pm 2$$



**Energy levels  $\Delta J = +2$** 

$$\begin{aligned}\Delta\varepsilon &= \varepsilon_{J'=J+2} - \varepsilon_{J''=J} \\ &= B(4J + 6)cm^{-1}\end{aligned}$$

Since:  $\Delta J = +2$ , these lines are called S branch lines .

$$\Delta\varepsilon_s = B(4J + 6)cm^{-1} \quad (J = 0,1,2,\dots)$$

$J \rightarrow$  rotational quantum number in the lower state.

If the molecule gains rotational energy from photons, we have a series of S branch lines to the low wave number side of the exciting line [Stokes].

If the molecule loses energy to the photon, S branch lines appear high wave number side (anti stokes)

The wave numbers of the spectral lines are,  
 $\bar{\nu}_s = \bar{\nu}_{ex} \pm \Delta\varepsilon_s = \bar{\nu}_{ex} \pm B(4J + 6)cm^{-1}$

+ sign - anti stokes ; - sign stokes line

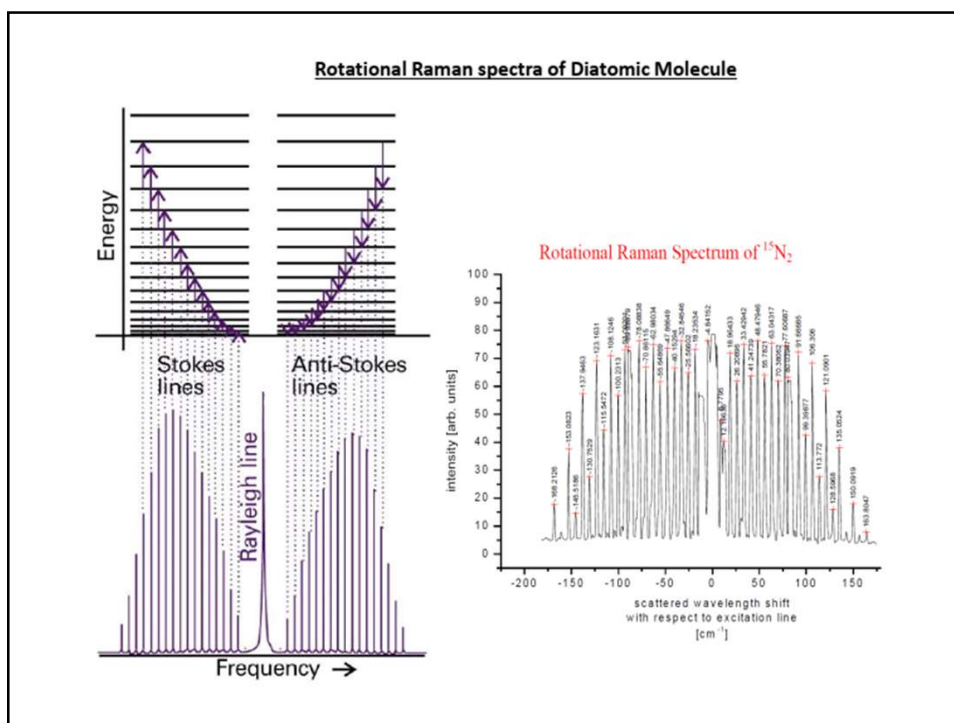
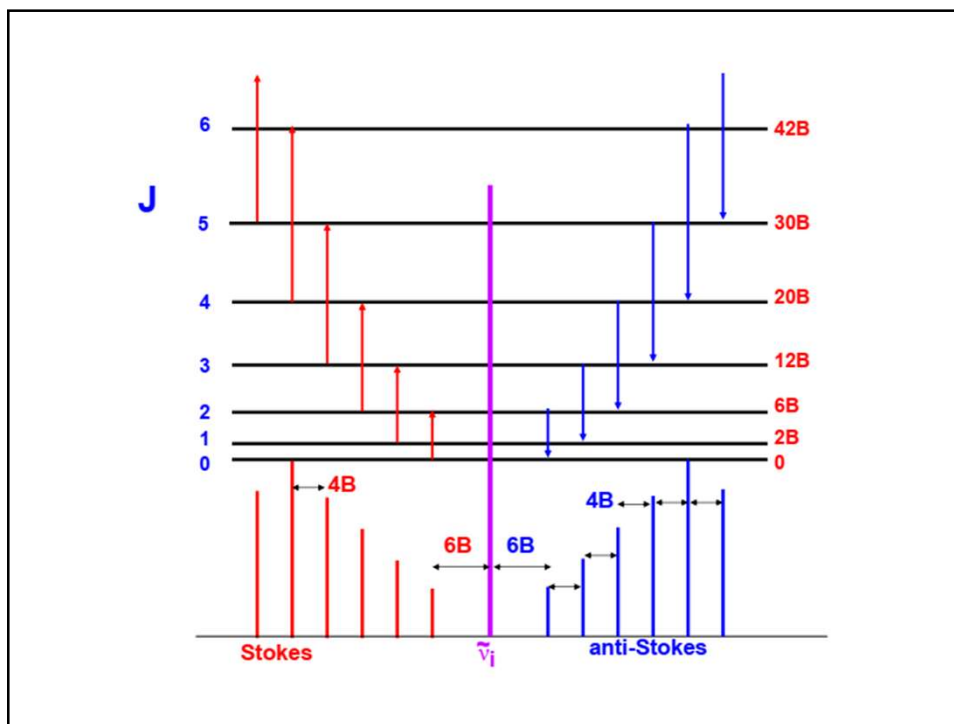
$\bar{\nu}_{ex} \rightarrow$  wave number of the exciting radiation.

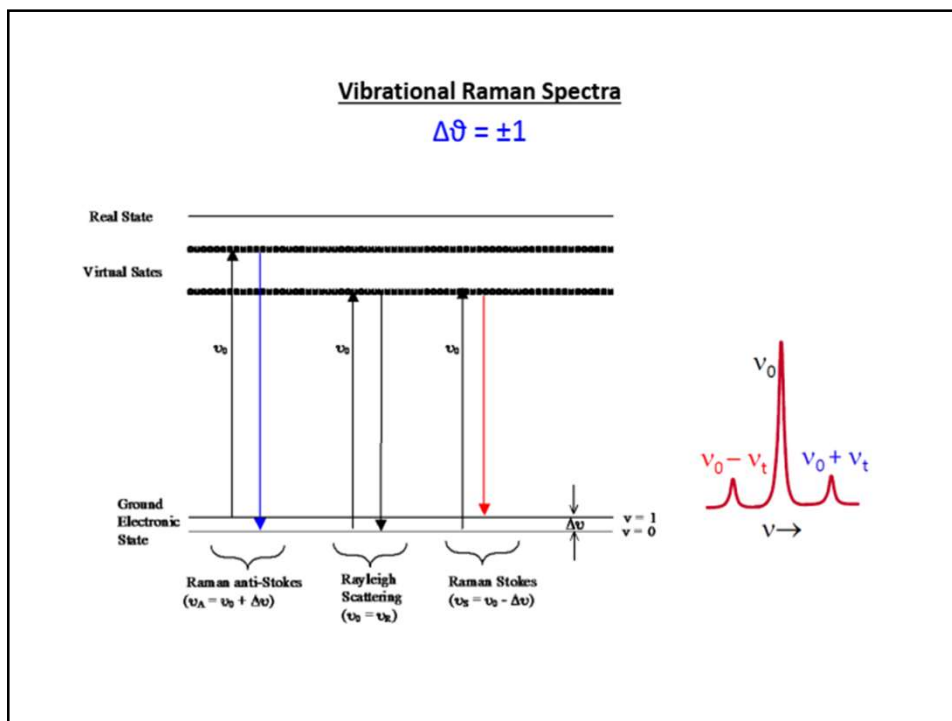
The allowed transitions and the Raman spectrum arising are shown in Fig 4.4

$$\begin{aligned}J = 0 &\Rightarrow \bar{\nu}_s = \bar{\nu}_{ex} + 6B \text{ cm}^{-1} \\ J = 1 &\Rightarrow \bar{\nu}_s = \bar{\nu}_{ex} + 10B \text{ cm}^{-1} \\ J = 2 &\Rightarrow \bar{\nu}_s = \bar{\nu}_{ex} + 14B \text{ cm}^{-1}\end{aligned}$$

Thus the separation of the first line from the exciting line is  $6B \text{ cm}^{-1}$

While the separation b/w the successive line is  $4B \text{ cm}^{-1}$



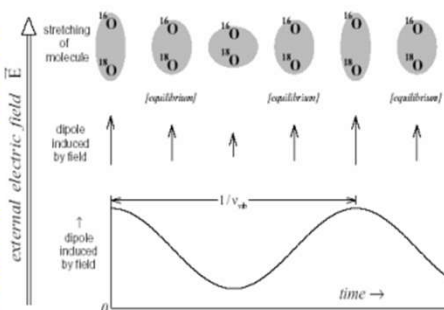


The classical description of vibrational Raman spectroscopy is qualitatively similar to that presented above for rotational Raman spectroscopy. In this case the vibration of the molecular bond is accompanied by a periodic stretching and compression of the electron distribution which gives an oscillation of the component of the molecular polarizability along the direction of the electric field.

Using  $\mu_{\text{induced}} = \alpha E$  shows that this gives rise to an induced dipole which oscillates in phase with the vibrational motion.

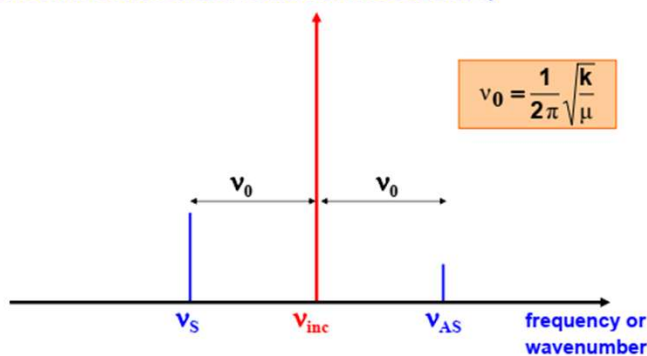
$$\alpha(t) = \alpha_0 + \delta\alpha \cos(2\pi\nu_{\text{vib}}t)$$

Where  $\delta\alpha$  is the amplitude of the change in the polarizability during one vibrational cycle and  $\alpha_0$  is the average value over a cycle.



## Raman Spectrum: Diatomic Molecule

Diatomic molecule has only one vibrational frequency (i.e. only one mode) Therefore the Raman spectrum of a diatomic molecule should consist of a single Stokes and a single antiStokes line (ignoring overtone and hot bands and rotational fine structure)



Relative intensity of antiStokes line to Stokes line gives the temperature of the sample (Boltzman distribution)

## Vibrational Raman spectra

$$\epsilon_v = \omega_e \left( v + \frac{1}{2} \right) - \omega_e x_e \left( v + \frac{1}{2} \right)^2 \text{ cm}^{-1}$$

( $v = 0, 1, 2, \dots$ )  
 $\omega_e$  – equilibrium frequency in  $\text{cm}^{-1}$

### Selection Rule

$$\Delta v = 0, \pm 1, \pm 2, \dots$$

Same for Raman and IR spectroscopy

The probability of  $\Delta v = 0, \pm 1, \pm 2, \dots$   
 Decreasing rapidly

$$v = 0 \rightarrow v = 1 \Rightarrow \Delta \epsilon_{\text{fund}} = \omega_e (1 - 2x_e) \text{ cm}^{-1}$$

$$v = 0 \rightarrow v = 2 \Rightarrow \Delta \epsilon_{\text{overtone}} = 2\omega_e (1 - 3x_e) \text{ cm}^{-1}$$

Since the Raman scattered light is of low intensity we can ignore completely all the weaker effects [*overtones, hotbands*]  
 Raman lines to appear at distances from the exciting line corresponding to each active fundamental vibrations

$$\text{i.e., } \bar{\nu}_{fund} = \bar{\nu}_{ex} \pm \Delta\varepsilon_{fund} \text{ cm}^{-1}$$

### **Rotational fine structure**

We need not consider in detail rotational fine structure of Raman spectra in general  
 Because such fine structure is rarely resolved (except for diatomic molecules)  
 For diatomic molecules the vibration – rotation energy is

$$\Delta\varepsilon_{J,v} = \left(v + \frac{1}{2}\right) \omega_e - \left(v + \frac{1}{2}\right)^2 \omega_e x_e + BJ(J+1) \quad (v = 0,1,2,\dots; J = 0,1,2,\dots)$$

In Raman, we ignore centrifugal distortion for diatomic molecule selection rule  
 $\Delta J = 0, \pm 2$

$$\Delta J = 0 \Rightarrow \Delta\varepsilon_Q = \bar{\nu}_0 \text{ cm}^{-1} \text{ for all } J$$

$$\Delta J = +2 \Rightarrow \Delta\varepsilon_S = \bar{\nu}_0 + B(4J + 6) \text{ cm}^{-1} \text{ for } J = 0,1,2,\dots$$

$$\Delta J = -2 \Rightarrow \Delta\varepsilon_O = \bar{\nu}_0 - B(4J + 6) \text{ cm}^{-1} \text{ for } J = 2,3,4,\dots$$

Where we write  $\bar{\nu}_0 = \omega_e(1 - 2x_e)$

For Stoke's lines (lines to low frequency of the exciting radiation )

$$\bar{\nu}_Q = \bar{\nu}_{ex} - \Delta\varepsilon_Q = \bar{\nu}_{ex} - \bar{\nu}_0 \text{ for all } J$$

$$\begin{aligned} \bar{\nu}_O &= \bar{\nu}_{ex} - \Delta\varepsilon_O \\ &= \bar{\nu}_{ex} - \bar{\nu}_0 + B(4J + 6)cm^{-1} \text{ for } J = 2,3,4, \dots \end{aligned}$$

$$\bar{\nu}_S = \bar{\nu}_{ex} - \Delta\varepsilon_S$$

$$= \bar{\nu}_{ex} - \bar{\nu}_0 - B(4J + 6)cm^{-1} \text{ for } J = 0,1,2,..$$

The strong Q branch line is present in the Raman spectrum but in IR spectrum Q branch is absent .

### *Antistoke's line*

Much weaker anti *Stoke's* lines will occur at the same distance from but high frequency side of exciting line

For larger molecule we can ignore the rotational fine structure since it is not resolved. Even the O and S ( or *O , P, R and S*) bands are rarely observed since they are very weak compared with Q branch

## Vibrational-Rotational Raman spectroscopy

This fine structure is rarely resolved except in the case of diatomics. We can write the vib-rot energy levels as (see vib-rot notes)

$$S(n, J) = \left(n + \frac{1}{2}\right) \tilde{\nu} - \left(n + \frac{1}{2}\right)^2 \chi_e \tilde{\nu} + B J(J+1)$$

where  $n = 0, 1, 2, \dots$ ;  $J = 0, 1, 2, 3 \dots$  and again we have ignored the centrifugal distortion (D term).

For diatomic molecules  $\Delta J = 0, \pm 2$  and combining this with the fundamental transition  $n = 0 \rightarrow n = 1$  gives

**Q-Branch**  $\Delta J = 0: \Delta \varepsilon_Q = \tilde{\nu}(1 - 2\chi_e) \text{ cm}^{-1} \quad J = 0, 1, 2, 3, \dots$

**S-Branch**  $\Delta J = +2: \Delta \varepsilon_S = \tilde{\nu}(1 - 2\chi_e) + B(4J + 6) \text{ cm}^{-1} \quad J = 0, 1, 2, \dots$

**O-Branch**  $\Delta J = -2: \Delta \varepsilon_O = \tilde{\nu}(1 - 2\chi_e) - B(4J + 6) \text{ cm}^{-1} \quad J = 2, 3, 4, \dots$

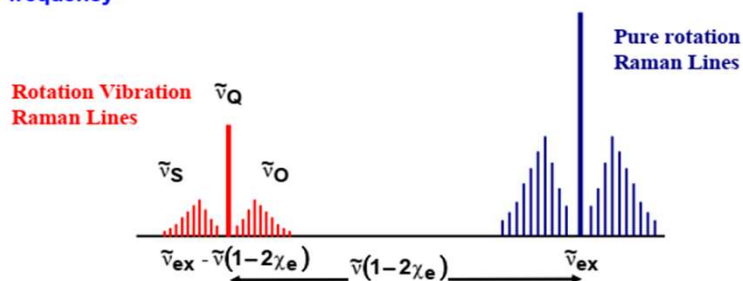
Stokes lines, lying at low frequency (wavenumber) side of exciting radiation will occur at wavenumbers given by.

$$\tilde{\nu}_Q = \tilde{\nu}_{\text{ex}} - \Delta \varepsilon_Q = \tilde{\nu}_{\text{ex}} - \tilde{\nu}(1 - 2\chi_e) \text{ cm}^{-1} \quad J = 0, 1, 2, 3, \dots$$

$$\tilde{\nu}_S = \tilde{\nu}_{\text{ex}} - \Delta \varepsilon_S = \tilde{\nu}_{\text{ex}} - \tilde{\nu}(1 - 2\chi_e) - B(4J + 6) \text{ cm}^{-1} \quad J = 0, 1, 2, \dots$$

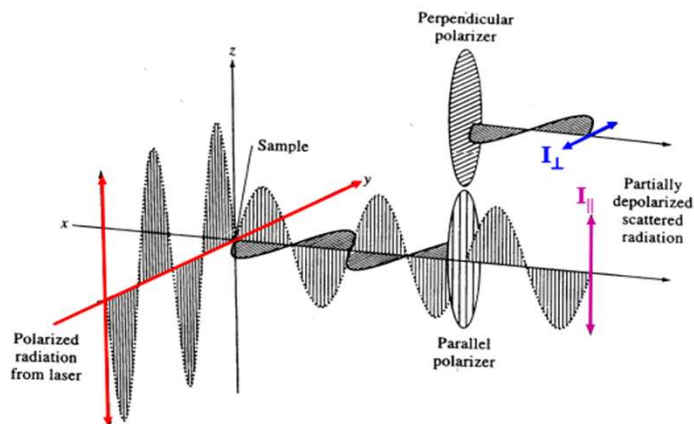
$$\tilde{\nu}_O = \tilde{\nu}_{\text{ex}} - \Delta \varepsilon_O = \tilde{\nu}_{\text{ex}} - \tilde{\nu}(1 - 2\chi_e) + B(4J + 6) \text{ cm}^{-1} \quad J = 2, 3, 4, \dots$$

$\nu_{\text{ex}}$  is the frequency of the incident (exciting) radiation, e.g. laser frequency



## Polarisation Effects in Raman Spectrum

If the incident light is polarised then the Raman process can change the state of polarisation of the scattered radiation, it can become partially depolarised, i.e. the scattered radiation can be elliptically or even circularly polarised.



## Depolarisation Ratio

we can quantify this effect as follows. The intensity of the Raman Scattered radiation measured through a polariser aligned (i) parallel  $I_{\perp}$  and (ii) perpendicular  $I_{\parallel}$  to the plane of polarisation of the incident light.

The **Depolarisation Ratio  $\rho$**  of a particular Raman line is then defined as

$$\rho = \frac{I_{\perp}}{I_{\parallel}}$$

If the scattered light is unpolarised then  $I_{\perp} = I_{\parallel}$  and  $\rho = 1$ .

If the scattered light retains its initial polarisation then  $I_{\perp} = 0$  and  $\rho = 0$ .

A Raman line is classified as **depolarised** if  $\rho \geq 0.75$ .  
and is classified as **polarised** if  $\rho < 0.75$ .

Only totally symmetric vibrations give rise to polarised lines. So by measuring the depolarisation ratio we can distinguish between symmetric vibration modes and other modes (bending, asymmetric ..)



## Instrumentation for Raman Spectroscopy

**Sources:** Lasers are used almost exclusively for Raman Spectroscopy.

High intensity  $\Rightarrow$  **good signal-to-noise ratio.**

**Narrow linewidths of laser good for resolving Raman lines.**

Common laser sources are

|             |                  |        |
|-------------|------------------|--------|
| Argon Ion   | 488 and 514.4 nm | Uv/vis |
| Krypton Ion | 530 and 647 nm   | vis    |
| Helium Neon | 623 nm           | vis    |
| Diode Laser | 782 ad 820 nm    | vis/IR |
| Nd/YAG      | 1064 nm          | IR     |

The intensity of a Raman line is proportional  $\nu^4$ .  $I \propto \nu^4$

$\Rightarrow$  Argon and Krypton Ion lasers have an advantage over other laser sources.

Example: Argon line at 488 nm produces a line 2.7-times more intense as those excited by He/Ne laser for the same input power.

$$\left(\frac{\nu_{\text{Ar}}}{\nu_{\text{HeNe}}}\right)^4 = \left(\frac{c}{\lambda_{\text{Ar}}} \cdot \frac{\lambda_{\text{HeNe}}}{c}\right)^4 = \left(\frac{623}{488}\right)^4 = 2.66$$

However, the diode laser and Nd/YAG also have advantages.

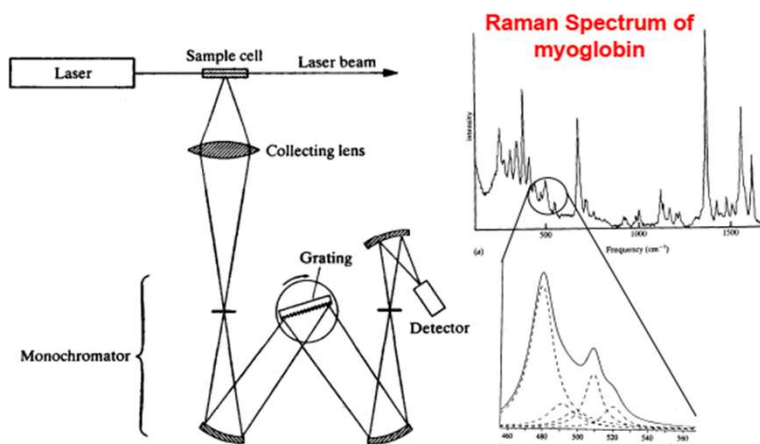
They operate in the near infrared  $\Rightarrow$

- 1) They can be operated at much higher power without causing **photodissociation** of the sample (up to 50 W).
- 2) These photons are not energetic enough to excite electronic states in the molecule so there is little or no fluorescence radiation to swamp the Raman signal. (see figure on next overhead)

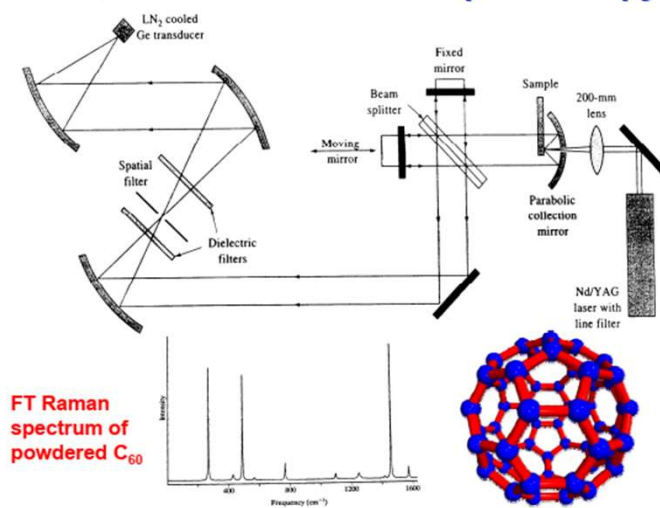
**Sample Illumination:** Much easier than IR spectroscopy, since Raman signal is usually in the visible/ near IR region this means that special windows, mirrors, lenses are not required, ordinary glass may be used.

Easier to focus laser to a small spot size (microRaman)  $\Rightarrow$  small samples may be investigated.

## Conventional Raman Spectrometer



## Fourier Transform Raman Spectroscopy



## Mutual Exclusion Rule

- It states that no normal modes can be both Infrared and Raman active in a molecule that possesses a centre of symmetry
- This is a powerful application of group theory to vibrational spectroscopy, and allows one to easily detect the presence of this symmetry element by comparison of the IR and Raman spectra generated by the same molecule.

## Group Theoretical Explanation

- The rule arises because in a centrosymmetric point group, IR active modes, which must transform according to the same irreducible representation generated by one of the components of the dipole moment vector (x, y or z), must be of *ungerade* (u) symmetry, i.e. their character under inversion is -1,
- while Raman active modes, which transform according to the symmetry of the polarizability tensor (product of two coordinates), must be of *gerade* (g) symmetry since their character under inversion is +1.

- In the character table there is no irreducible representation that spans both IR and Raman active modes, and so there is no overlap between the two spectra.

| $D_{6h}$ | $E$ | $2C_6$ | $2C_3$ | $C_2$ | $3C_2'$ | $3C_2''$ | $i$ | $2S_3$ | $2S_6$ | $\sigma_h$ | $3\sigma_d$ | $3\sigma_v$ |              |                                 |
|----------|-----|--------|--------|-------|---------|----------|-----|--------|--------|------------|-------------|-------------|--------------|---------------------------------|
| $A_{1g}$ | 1   | 1      | 1      | 1     | 1       | 1        | 1   | 1      | 1      | 1          | 1           | 1           | $R_z$        | $x^2 + y^2, z^2$                |
| $A_{2g}$ | 1   | 1      | 1      | 1     | -1      | -1       | 1   | 1      | 1      | 1          | -1          | -1          |              |                                 |
| $B_{1g}$ | 1   | -1     | 1      | -1    | 1       | -1       | 1   | -1     | 1      | -1         | 1           | -1          |              |                                 |
| $B_{2g}$ | 1   | -1     | 1      | -1    | -1      | 1        | 1   | -1     | 1      | -1         | -1          | 1           |              |                                 |
| $E_{1g}$ | 2   | 1      | -1     | -2    | 0       | 0        | 2   | 1      | -1     | -2         | 0           | 0           | $(R_x, R_y)$ | $(xz, yz)$<br>$(x^2 - y^2, xy)$ |
| $E_{2g}$ | 2   | -1     | -1     | 2     | 0       | 0        | 2   | -1     | -1     | 2          | 0           | 0           |              |                                 |
| $A_{1u}$ | 1   | 1      | 1      | 1     | 1       | 1        | -1  | -1     | -1     | -1         | -1          | -1          |              |                                 |
| $A_{2u}$ | 1   | 1      | 1      | 1     | -1      | -1       | -1  | -1     | -1     | -1         | 1           | 1           | $z$          |                                 |
| $B_{1u}$ | 1   | -1     | 1      | -1    | 1       | -1       | -1  | 1      | -1     | 1          | 1           | -1          |              |                                 |
| $B_{2u}$ | 1   | -1     | 1      | -1    | -1      | 1        | -1  | 1      | -1     | 1          | 1           | -1          |              |                                 |
| $E_{1u}$ | 2   | 1      | -1     | -2    | 0       | 0        | -2  | -1     | 1      | 2          | 0           | 0           | $(x, y)$     |                                 |
| $E_{2u}$ | 2   | -1     | -1     | 2     | 0       | 0        | -2  | 1      | 1      | -2         | 0           | 0           |              |                                 |

## Mutual Exclusion Principle - violations

- This does not mean that a vibrational mode which is not Raman active must be IR active.
- In fact, it is still possible that a mode of a particular symmetry is neither Raman nor IR active.
- Such spectroscopically "silent" or "inactive" modes exist in molecules such as ethylene ( $C_2H_4$ ), benzene ( $C_6H_6$ ) and the tetrachloroplatinate ion ( $PtCl_4^{2-}$ ).

Thank You!!!