

# **Raman Spectroscopy**

## **Recommended Reading:**

**Banwell and McCash Chapter 4**

**Skoog, Holler Nieman Chapter 18**

**Atkins, Chapter 16**

**Inelastic scattering of light is sometimes called the Raman effect, named after its discoverer, the Indian scientist**

**C V Raman**

**Raman won the Nobel prize in 1930 for his discovery, accomplished using filtered sunlight as a monochromatic source of photons, a colored filter as a monochromator, and a human eye as detector. The technique became widely used after the invention of the laser.**

[http://www.fact-index.com/r/ra/raman\\_spectroscopy.html](http://www.fact-index.com/r/ra/raman_spectroscopy.html)

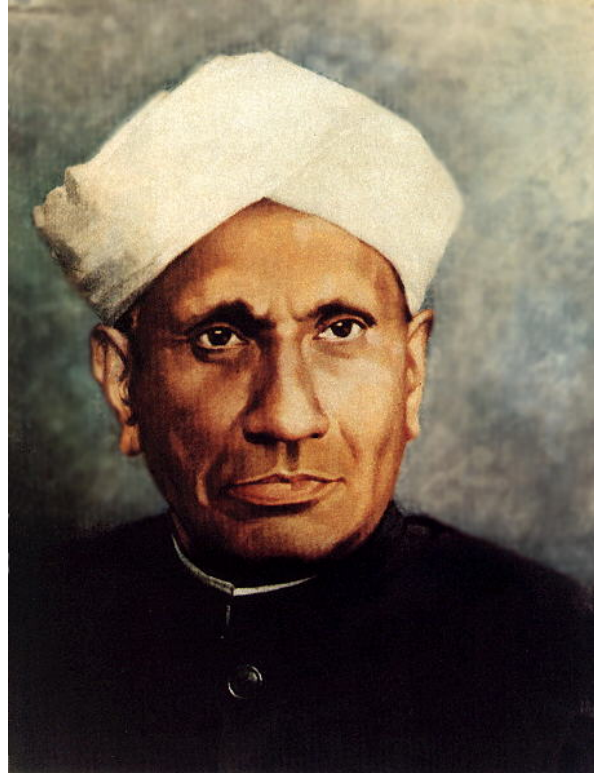
# Raman Spectroscopy

**What is it?** Raman Spectroscopy determines vibrational and rotational level spacings from the energy (wavenumber) shifts of **scattered light**.

**How do we do it it?** Molecular transition energies are observed by measuring the shifts in frequency of light scattered when a molecule is subjected to an intense beam of monochromatic light.

**Why we do it it?** Previously we noted that molecules with no permanent dipole moment would have no pure rotational spectrum, and that molecular vibrational motion for which there was no oscillation dipole would have no IR absorption or emission spectra. Raman spectroscopy allows us to determine rotational and vibrational level spacings for such systems, and hence to determine bond lengths and force constants for such molecules. That is we can use Raman spectroscopy to study  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$  ....

# C.V.Raman

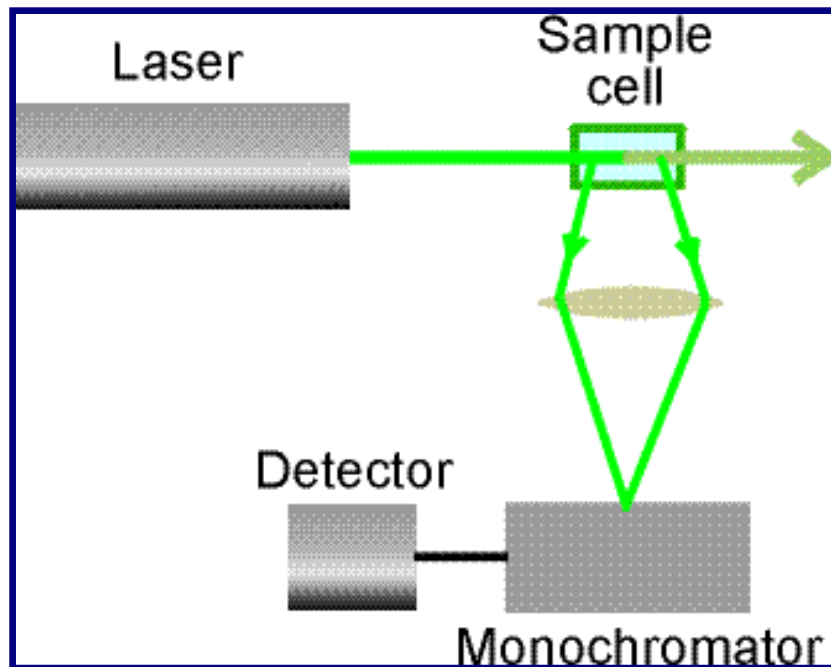


**Sir Chandrasekhara Venkata  
Raman India (1888-1970)**

**Nobel Prize, 1930; for his work on  
the scattering of light and for the  
discovery of the Raman Effect**

# Basic Experiment

In **Raman spectroscopy** the energy levels of the molecules are explored by examining the frequencies present in the radiation **scattered** by the molecules.



The photons can be scattered either

## 1) ELASTICALLY

Scattered photon has the same energy as the incident photon  $\Rightarrow$

## Rayleigh Scattering

or

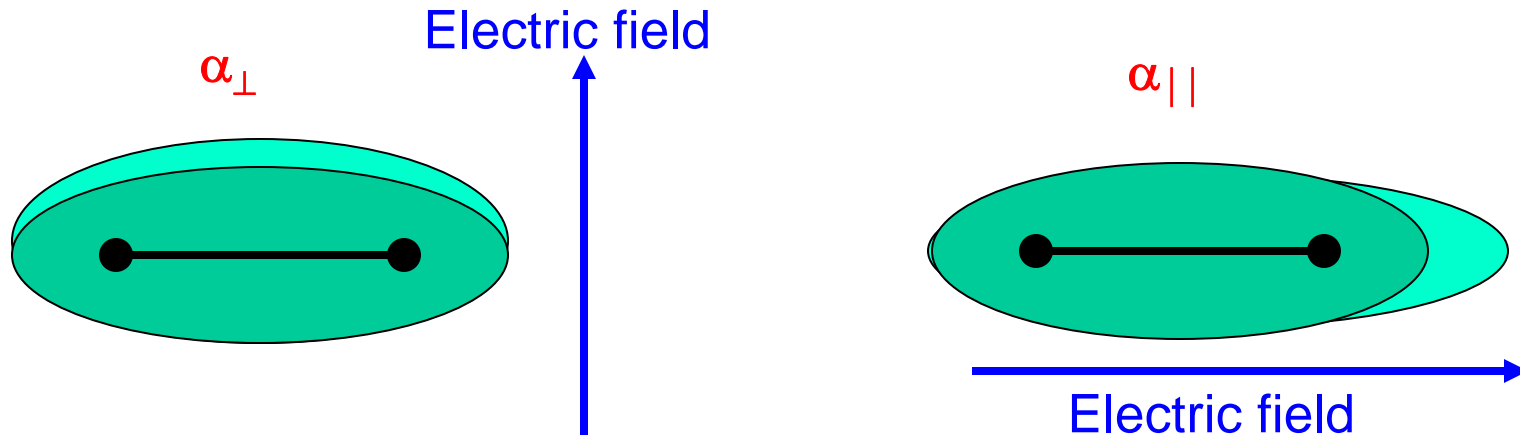
## 2) INELASTICALLY

Scattered photon has an energy that is less than or greater than the incident photon  $\Rightarrow$  **Raman**

## Scattering.

About 1 in  $10^7$  photons are in elastically scattered  $\Rightarrow$  very weak process

# Polarizability $\alpha$



When an **electric field**  $E$  is applied to a molecule, its **charge distribution** is distorted.

This induces a **dipole moment**  $\mu$ , in the molecule.

The magnitude of the induced dipole moment varies linearly with the strength of the electric field  $E$  (for weak fields)

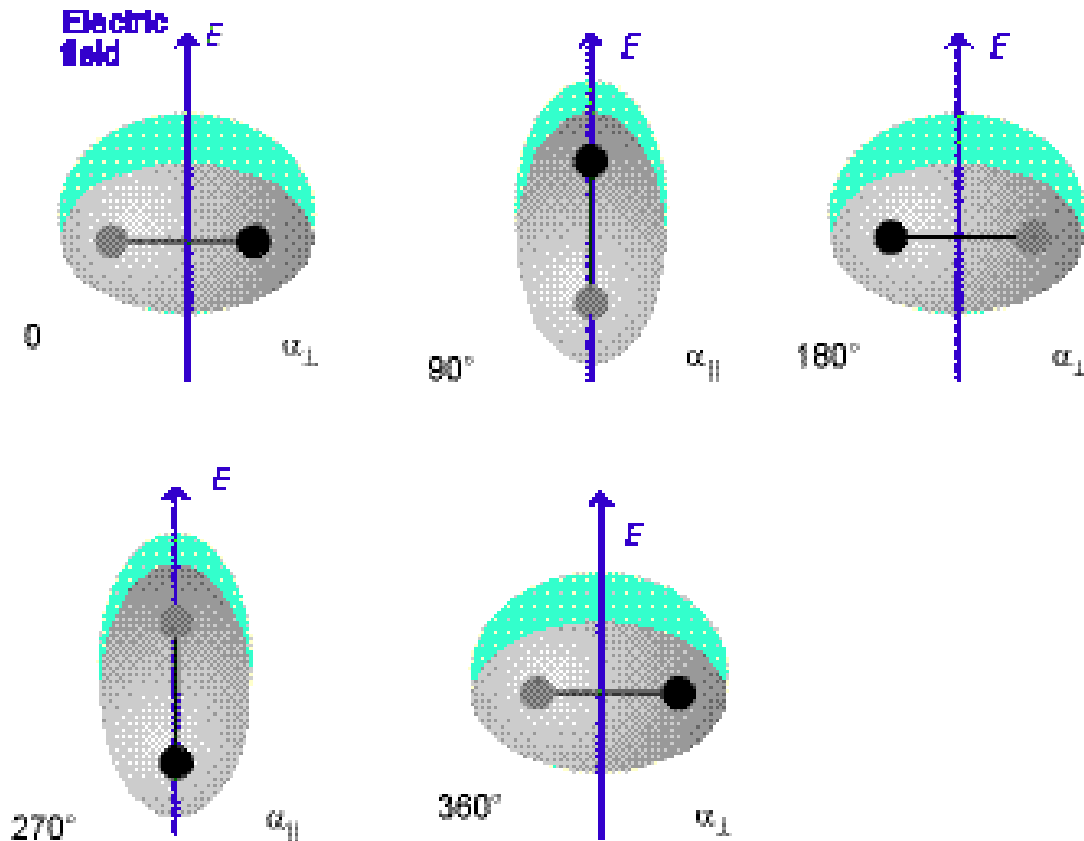
$$\mu = \alpha E$$

The proportionality constant  $\alpha$  is called the **polarizability** of the molecule.

$\alpha$  is a measure of how easy it is to distort the charge distribution of the molecule.

$\alpha$  depends on the direction of the electric vector relative to the axis of the molecule. i.e. it is a **Tensor quantity**

# Rotational Raman Spectroscopy



Gross Selection Rule:  
The molecule must be  
**anisotropically polarizable**

Spherical molecules are isotropically polarizable and therefore do not have a Rotational Raman Spectrum

All linear molecules are **anisotropically polarizable**, and give a Rotational Raman Spectrum, even molecules such as  $O_2$ ,  $N_2$ ,  $H_2$ ... which do not have a Pure Rotational Spectrum!

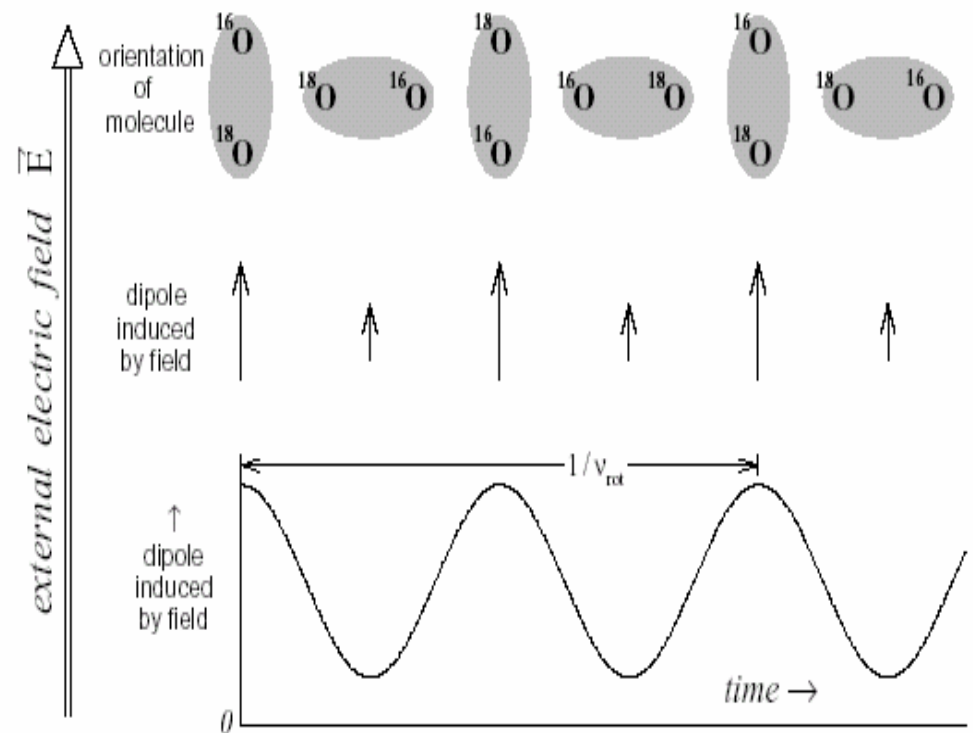
⇒ can study rotational levels of molecules that are inaccessible by Microwave Spectroscopy.

When a molecule is subjected to a strong external electric field  $\underline{E}$  that field will distort the molecules electron charge distribution to induce a small dipole moment which (to first order) is proportional to the electric field:

$$\underline{\mu}_{\text{induced}} = \alpha \underline{E} \quad (\alpha \text{ is a Tensor quantity})$$

where  $\alpha$  is the polarizability of the molecule, a property which indicates how readily its electron distribution can be distorted by the external field.

If  $E$  is a static laboratory field the induced dipole may interact with light in the normal manner and transitions can occur. However, if the external field is due to an intense beam of light, then this is a second order process, since the light first creates the dipole and then interacts with it ! Transitions created in this manner will be very weak but observable.





# Specific Selection Rule

Electric field is due to electromagnetic radiation of frequency  $\omega_i$ .

Induced dipole moment  $\mu$  is then

$$\mu = \alpha \mathbf{E}(t) = \alpha \mathbf{E}_0 \cos \omega_i t$$

$E_0$  = amplitude of electric field. If molecule is rotating at an angular frequency  $\omega_R$ , then its polarizability will be time dependent (if it is anisotropic), and

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

where  $\alpha_0 = (2\alpha_{\perp} + \alpha_{\parallel})/3 =$  *spherical average* of parallel and perpendicular components and  $\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp} =$  *polarizability anisotropy*

$\alpha$  ranges from  $\alpha_0 - \Delta\alpha$  to  $\alpha_0 + \Delta\alpha$  as the molecule rotates through  $2\pi$

**Factor of 2** because polarizability returns to its initial value twice during every revolution of the molecule

Substituting the expression for the polarizability into the expression for the induced dipole moment gives

$$\mu = (\alpha_0 + \Delta\alpha \cos 2\omega_R t) \times (E \cos \omega_i t) = \alpha_0 E \cos \omega_i t + E \Delta\alpha \cos \omega_R t \cos \omega_i t$$

$$\mu = \alpha_0 \mathbf{E}_0 \cos \omega_i t + \frac{1}{2} \mathbf{E}_0 \Delta\alpha \{ \cos(\omega_i + 2\omega_R) t + \cos(\omega_i - 2\omega_R) t \}$$

# Rotational Raman Spectroscopy

$$\mu = \alpha_0 E \cos \omega_i t + \frac{1}{2} E \Delta\alpha \{ \cos(\omega_i + 2\omega_R) t + \cos(\omega_i - 2\omega_R) t \}$$

Component oscillating at the same frequency as incident radiation  $\Rightarrow$   
**Rayleigh Scattering**

Component oscillating at frequency  $\omega_i + 2\omega_R$ ,  $\Rightarrow$   
**Anti-Stokes Scattering**  
 $\Rightarrow$  Higher energy

Component oscillating at frequency  $\omega_i - 2\omega_R$ ,  $\Rightarrow$   
**Stokes Scattering**  
 $\Rightarrow$  Lower energy

Note that Stokes and Anti-Stokes components disappear if  $\Delta\alpha = 0$  so molecule must be anisotropically polarizable.

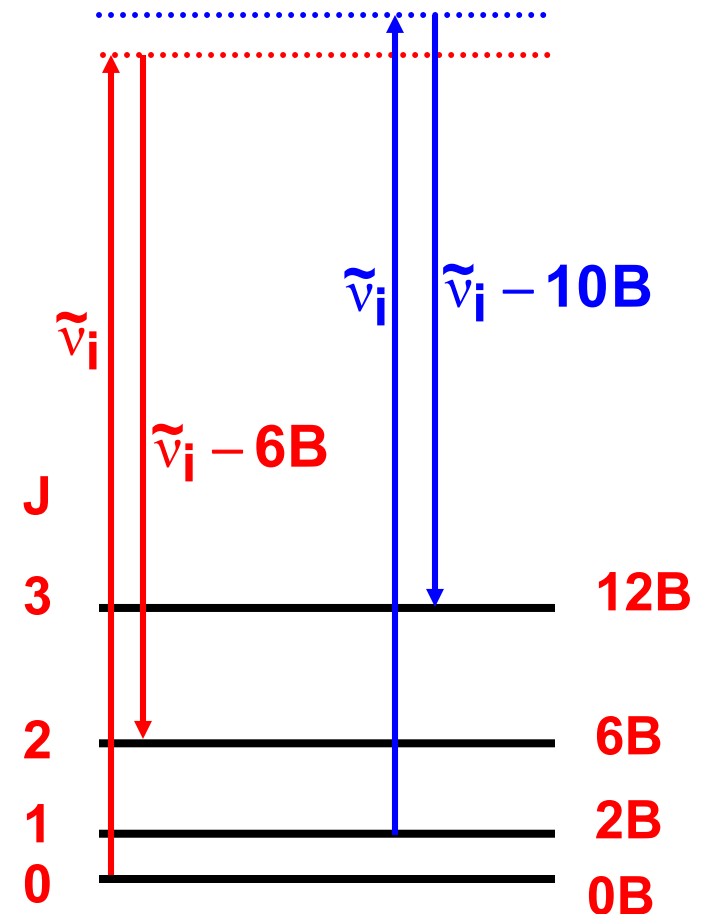
Two photons involved in Raman process, each is a spin-1 particle, so a maximum change in angular momentum quantum number of  $\pm 2$  is possible. This then gives a selection rule for Rotational Raman Transitions

$$\Delta J = \pm 2$$

# Rotational Raman Spectrum: Stokes Lines

We can predict the form of the **rotational Raman spectrum** of a linear rotor by applying the selection rule  $\Delta J = \pm 2$  to the rotational energy levels. When the molecule makes a transition with  $\Delta J = +2$  the scattered radiation leaves the molecule in a higher rotational state, so the wavenumber of the incident radiation, initially  $\tilde{\nu}_i$ , is decreased. These  $\Delta J = +2$  transitions account for the **Stokes lines** in the spectrum.

$$\begin{aligned} \tilde{\nu}(J+2) - \tilde{\nu}(J) &= \tilde{\nu}_i - \{F(J+2) - F(J)\} \\ &= \tilde{\nu}_i - [B(J+2)(J+3) - BJ(J+1)] \\ &= \tilde{\nu}_i - 2B(2J+3) \quad (1) \end{aligned}$$



The Stokes lines appear on the low frequency side of the incident radiation and at displacements of  $6B$ ,  $10B$ ,  $14B$ , .... from  $\tilde{\nu}_i$  for  $J = 0, 1, 2, \dots$

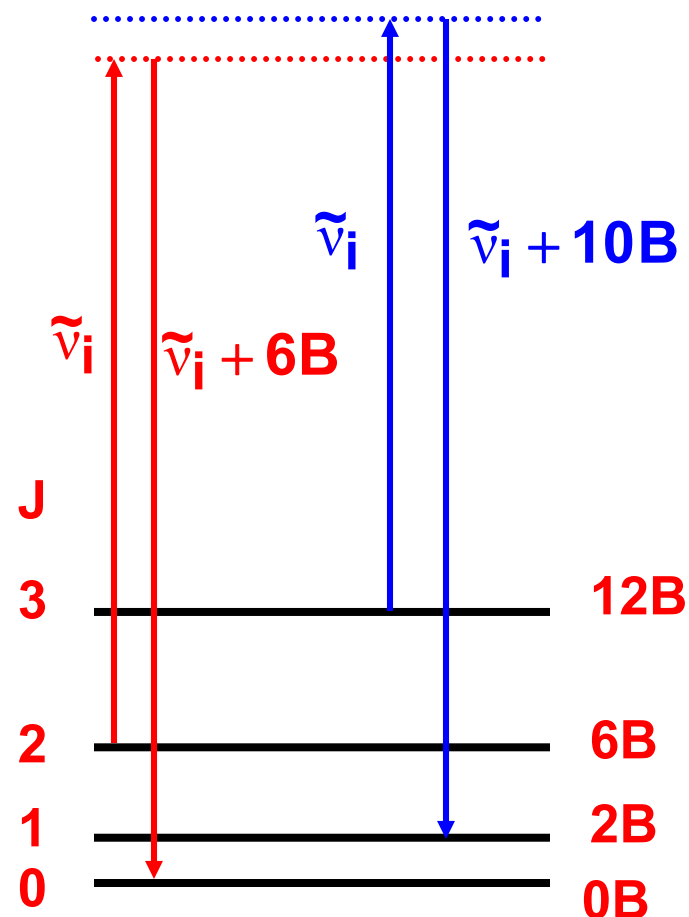
# Rotational Raman Spectrum: Anti-Stokes Lines

When the molecule makes a transition with  $\Delta J = -2$ , the scattered photon emerges with increased energy. These transitions account for the **anti-Stokes lines** of the spectrum.

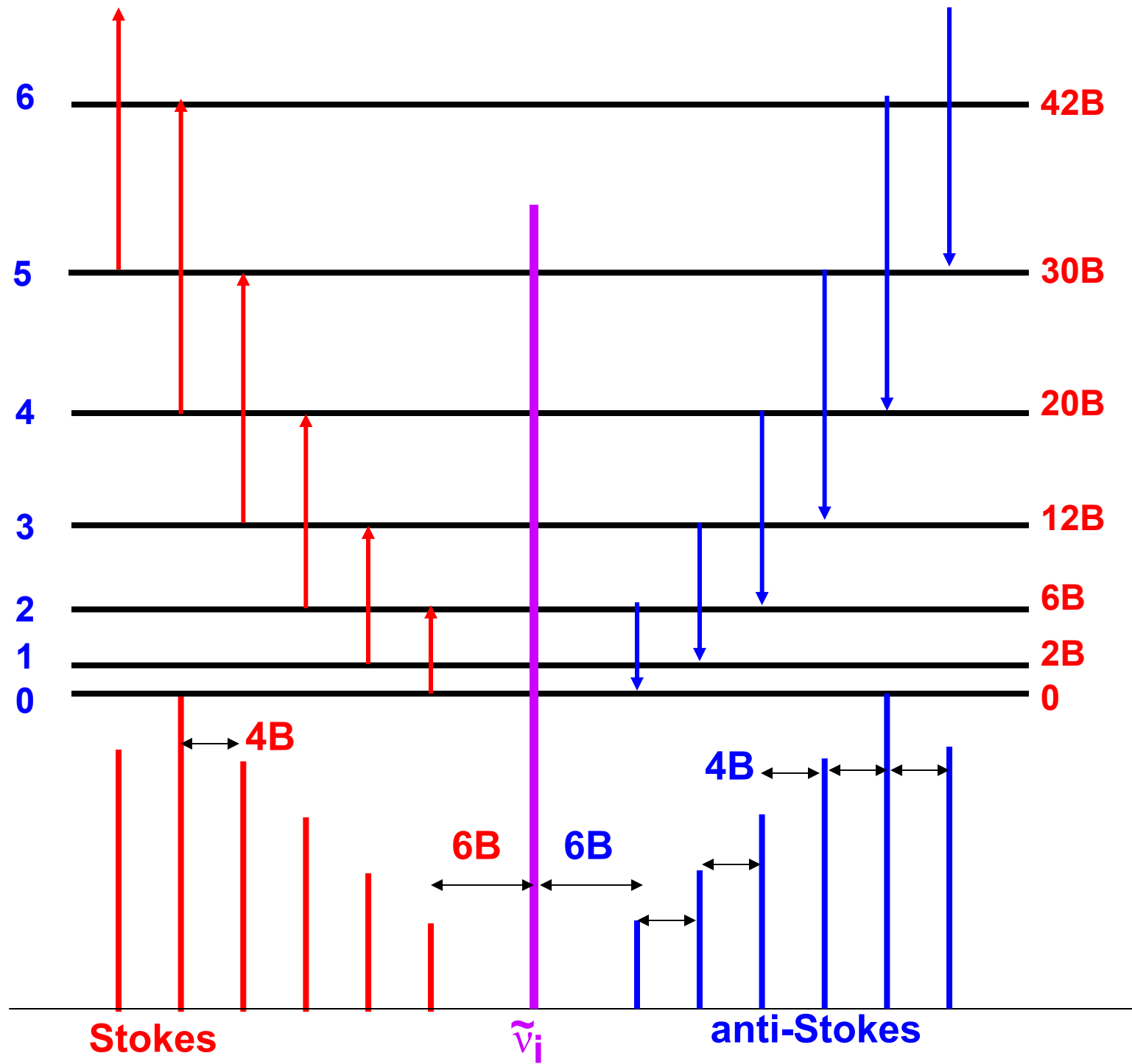
$$\begin{aligned} \tilde{\nu}(J-2) - \tilde{\nu}(J) &= \tilde{\nu}_i + \{F(J-2) - F(J)\} \\ &= \tilde{\nu}_i + [B(J-2)(J-1) - BJ(J+1)] \end{aligned}$$

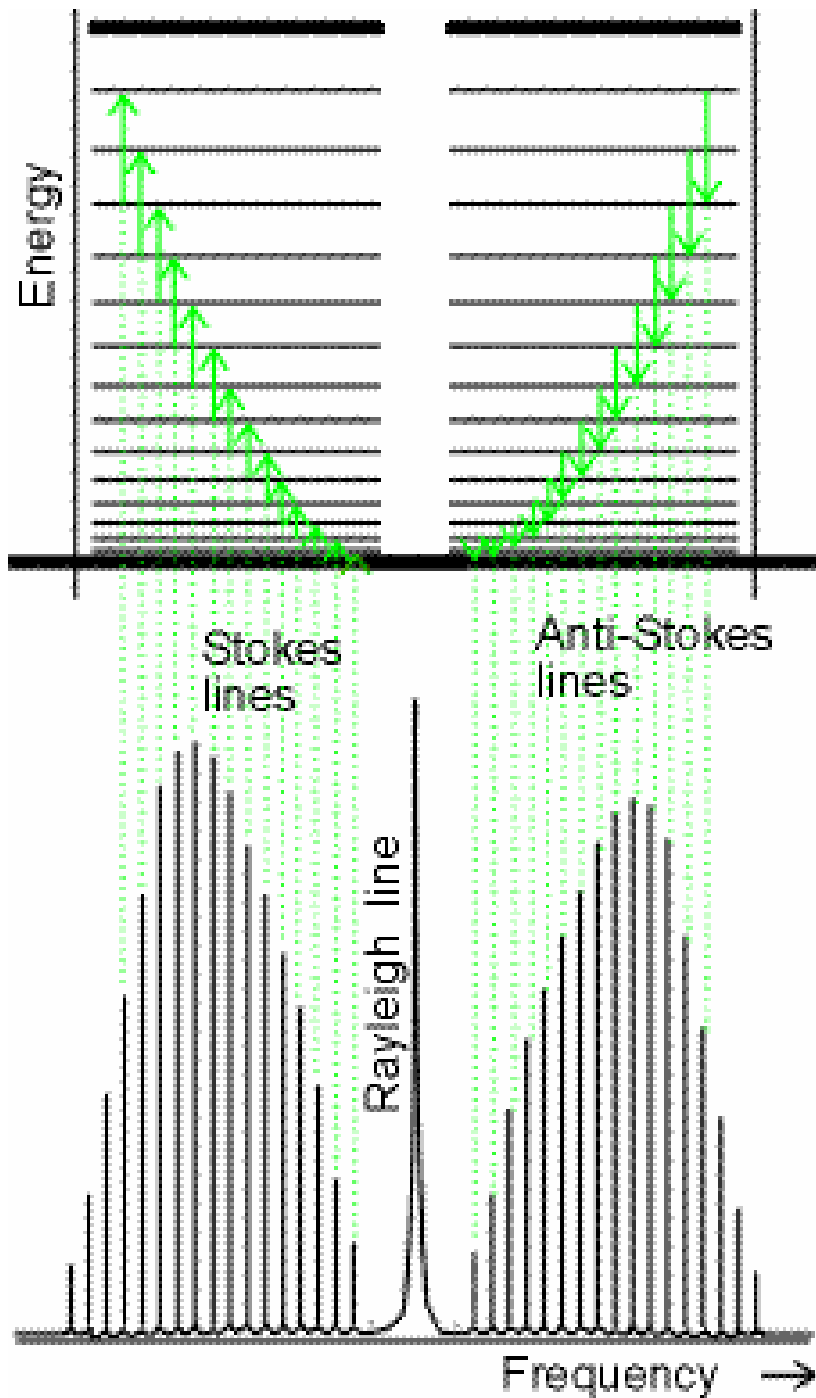
$$= \tilde{\nu}_i + 2B(2J-1) \quad (2)$$

The anti-Stokes lines occur at displacements of  $6B$ ,  $10B$ ,  $14B$ ...for  $J = 2, 3, 4$ ..to the high frequency side of the incident radiation; Note that  $J = 2$  is the lowest state that can contribute to the spectrum under the selection rule  $\Delta J = -2$ .



**J**





The separation of adjacent lines in both the Stokes and anti-Stokes regions is  $4B$ , so from its measurement  $I$  can be determined and then used to find the bond lengths exactly as in the case of microwave spectroscopy.

**Example:** Predict the form of the rotational Raman spectrum of  $^{14}\text{N}_2$  for which  $B = 1.99\text{cm}^{-1}$ , when it is exposed to monochromatic 336.732 nm laser radiation

The molecule is rotationally Raman active because end-over-end rotation modulates its polarizability as viewed by a stationary observer. Because  $\lambda_i = 336.732$  nm corresponds to  $29697.2\text{ cm}^{-1}$  equations (1) and (2) give the following line positions:

<b>J</b>	<b>0</b>	<b>1</b>	<b>2</b>	<b>3</b>
<b>Stokes Lines</b>				
$\nu / \text{cm}^{-1}$	29685.3	29677.3	29669.3	29661.4
$\lambda / \text{nm}$	336.868	336.958	337.048	337.139
<b>Anti-Stokes Lines</b>				
$\nu / \text{cm}^{-1}$			29709.1	29717.1
$\lambda / \text{nm}$			336.597	336.507

There will be a strong central line at 336.732 nm accompanied on either side by lines of increasing and then decreasing intensity (as a result of the transition moment and population effects). The spread of the entire spectrum is very small, so the incident light must be very monochromatic (laser).

# Pure Vibrational Raman Spectroscopy

**Gross Selection Rule:** The polarizability of the molecule must change as the molecule vibrates.

For all diatomic molecules the interaction between the electrons and nuclei changes as the molecule vibrates  $\Rightarrow$  a change in polarizability  $\Rightarrow$  all diatomic molecule (homonuclear and heteronuclear) are **vibrationally Raman active**.

Analysis becomes much more difficult for polyatomic molecules, need to apply group theory to decide if a particular vibrational mode is Raman active.

**Specific Selection Rule:**

- 1) Harmonic Approximation  $\Delta n = \pm 1$ .
- 2) Anharmonic Approximation  $\Delta n = \pm 1, \pm 2, \pm 3, \dots$

**I.e same selection rules as for pure vibrational (IR) spectroscopy**



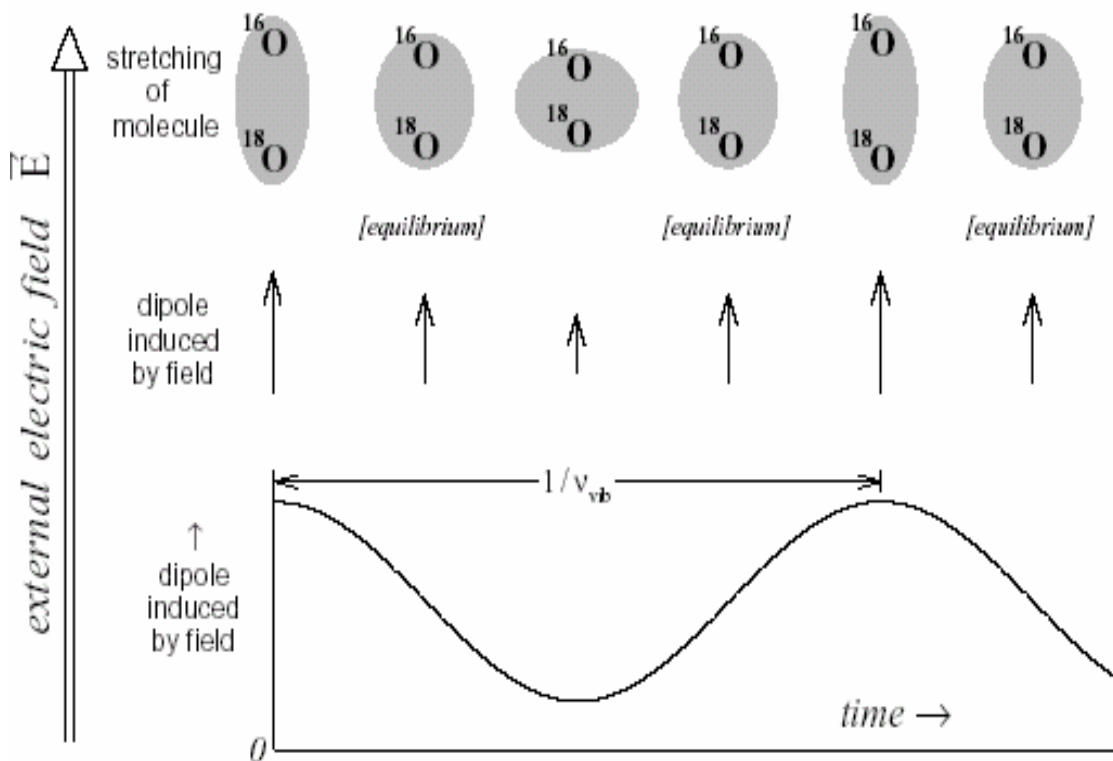
The classical description of vibrational Raman spectroscopy is qualitatively similar to that presented above for rotational Raman spectroscopy.

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  $\underline{\mu}_{\text{induced}} = \alpha \underline{E}$  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/ \_\_\_\_\_



Just as in rotational Raman spectroscopy, if the external field is due to an intense beam of monochromatic light, the substitution of

$$\alpha(\mathbf{t}) = \alpha_0 + \delta\alpha \cos(2\pi\nu_{\text{vib}}\mathbf{t}) \quad \text{into} \quad \underline{\mu}_{\text{induced}} = \alpha \underline{E}$$

gives the following expression for the time dependent induced dipole moment

$$\mu = \alpha_0 \mathbf{E}_0 \cos(2\pi\nu_i \mathbf{t}) + \frac{1}{2} \mathbf{E}_0 \delta\alpha \{ \cos[2\pi(\nu_0 + \nu_{\text{vib}}) \mathbf{t}] + \cos[2\pi(\nu_0 - \nu_{\text{vib}}) \mathbf{t}] \}$$

Just as in rotational Raman spectroscopy, this equation shows Rayleigh scattering at the same frequency as the incident light. Stokes scattering at the frequency  $(\nu_0 - \nu_{\text{vib}})$  and anti-Stokes scattering at the frequency  $(\nu_0 + \nu_{\text{vib}})$

Key difference from rotational case is the fact that here the frequency shift is  $\pm\nu_{\text{vib}}$  (rather than  $\pm 2\nu_{\text{vib}}$ ). As a result the vibrational Raman selection rule is based on the very strong preference for  $\Delta n = \pm 1$  which governs normal infrared spectroscopy.

# Structure of Vibrational Raman Spectra

For every vibrational mode of the molecule, the energy of the mode is given by

$$\begin{aligned} G(n) &= \frac{E_n}{hc} = \left(n + \frac{1}{2}\right) \tilde{\nu}_0 - \left(n + \frac{1}{2}\right)^2 \chi_e \tilde{\nu}_0 \\ &= \tilde{\nu}_0 \left[ 1 - \chi_e \left(n + \frac{1}{2}\right) \right] \left(n + \frac{1}{2}\right) \end{aligned}$$

where

$$\omega_0 = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

exactly the same expression we had for vibrational spectroscopy.

For Raman active modes we can observe the following transitions:

**Fundamental:**  $\Delta n = \pm 1$ .

where  $\Delta n = +1$  corresponds to the **Stokes line**. The molecule starts in the  $n = 0$  state, is excited by the incident radiation and deexcites to the  $n = 1$  state.

Thus the molecule has gained energy and the scattered photon has lower energy than the incident photon. The energy of the scattered photon is

$$\tilde{\nu}_i - (\tilde{\nu}_1 - \tilde{\nu}_0) = \tilde{\nu}_i - G(1) - G(0) = \tilde{\nu}_i - \tilde{\nu}_0 (1 - 2\chi_e)$$

where  $\tilde{\nu}_i$  where is the wavenumber of the incident radiation

$\Delta n = -1$  corresponds to the **Anti-Stokes line**. The molecule starts in the  $n = 1$  vibrational state, is excited by the incident radiation and deexcites to the  $n = 0$  vibrational state.

Thus the molecule has lost energy and the scattered photon has higher energy than the incident photon. The energy of the scattered photon is

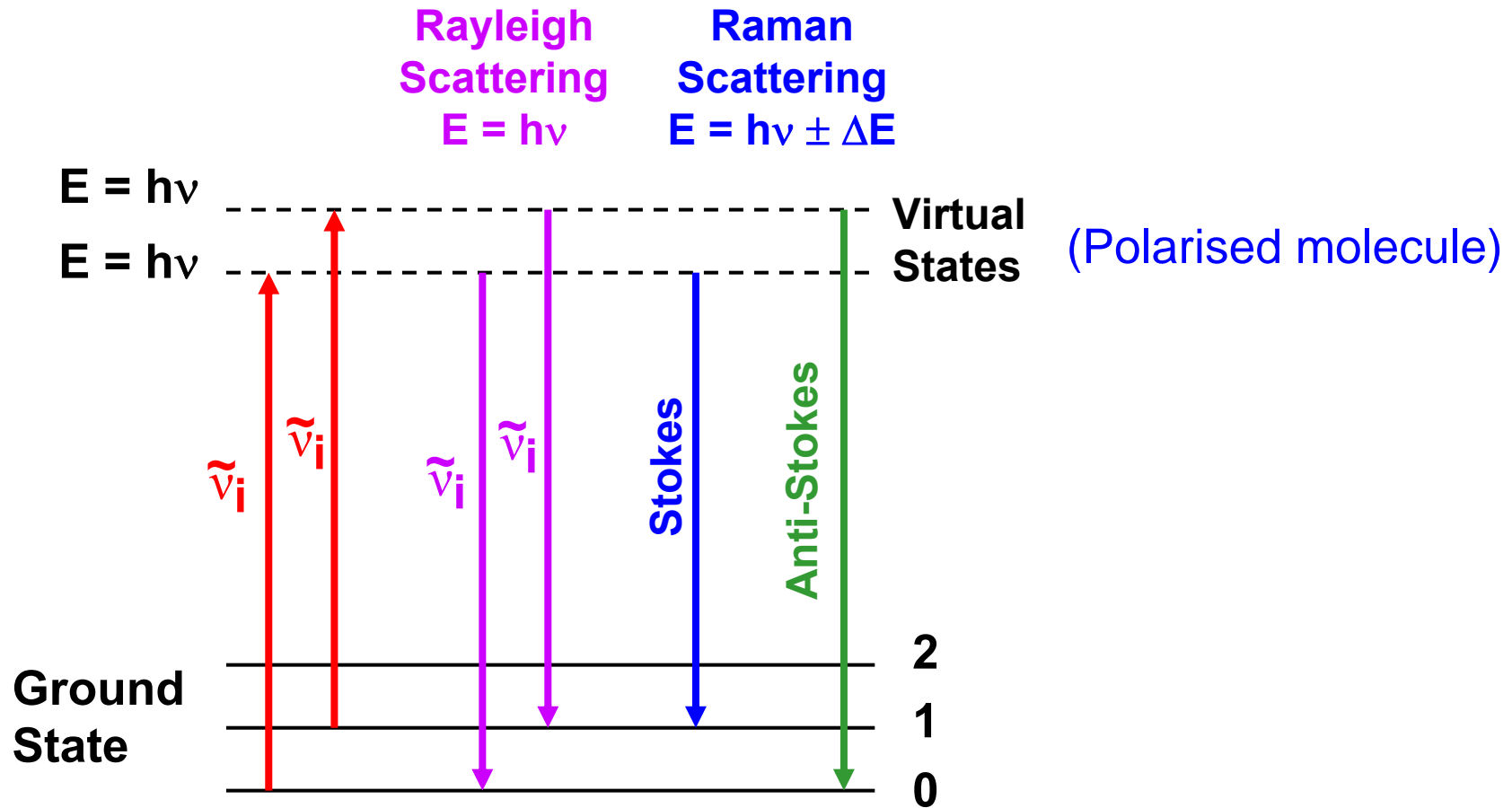
$$\tilde{\nu}_i + (\tilde{\nu}_0 - \tilde{\nu}_1) = \tilde{\nu}_i + G(0) - G(1) = \tilde{\nu}_i + \tilde{\nu}_0(1 - 2\chi_e)$$

However, recall that at room temperature very few molecules are in the  $n = 1$  vibrational state (Boltzmann Distribution). So the Stokes line will be very weak compared to the Anti-Stokes line (often the Stokes line is not observed).

It is possible to determine the temperature of the system from the ratio of the intensity of the Stokes line to the intensity of the AntiStokes line.

Pure Vibrational Raman spectrum is very simple, A series of intense lines to the low wavenumber (frequency, energy) side of the exciting (laser) line with a weaker mirror image series of lines on the high wavenumber side.

# Vibrational Raman Process



# Vibrational Raman Spectrum

It is also possible to observe **Overtone Bands** and **Hot Bands** in Raman spectra.

Overtones:  $\Delta n = 2, 3, \dots$

I.e overtones are produced by the following transitions

**First Overtone**:  $n = 0 \rightarrow n = 2$

$$\tilde{\nu} = \tilde{\nu}_i - (\tilde{\nu}_2 - \tilde{\nu}_0) = \tilde{\nu}_i - \mathbf{G}(2) - \mathbf{G}(0) = \tilde{\nu}_i - 2\tilde{\nu}_0(1 - 3\chi_e) \text{ anti-Stokes}$$

**Second Overtone**:  $n = 0 \rightarrow n = 3$

$$\tilde{\nu} = \tilde{\nu}_i - (\tilde{\nu}_3 - \tilde{\nu}_0) = \tilde{\nu}_i - \mathbf{G}(3) - \mathbf{G}(0) = \tilde{\nu}_i - 3\tilde{\nu}_0(1 - 4\chi_e) \text{ anti-Stokes}$$

Hot Bands: produced by the following transitions

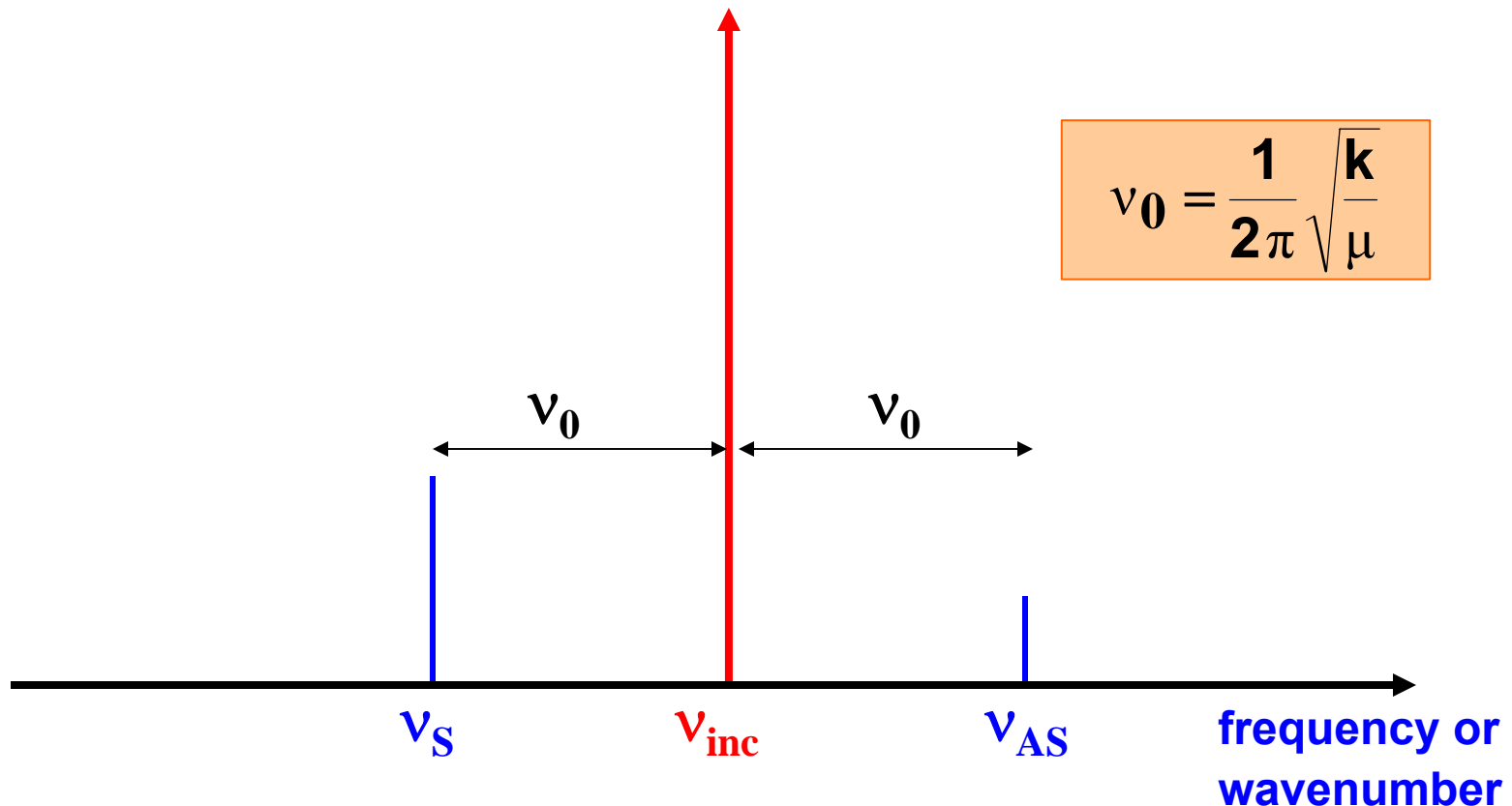
$$n = 1 \rightarrow n = 2 \quad \tilde{\nu} = \tilde{\nu}_i - (\tilde{\nu}_2 - \tilde{\nu}_1) = \tilde{\nu}_i - \mathbf{G}(2) - \mathbf{G}(1) = \tilde{\nu}_i - \tilde{\nu}_0(1 - 4\chi_e)$$

with weaker hot bands for  $n = 1 \rightarrow n = 3, 4, 5\dots$

However, since the Raman Scattering Process is very weak we can ignore all processes such as Overtones and Hot bands since these are weak even in IR spectra. So we only need to consider the fundamental transitions  $n = 0 \rightarrow n = 1$ .

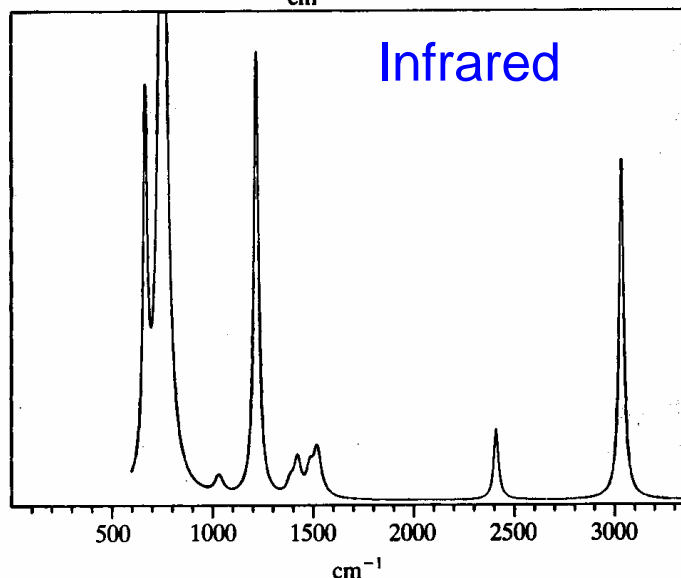
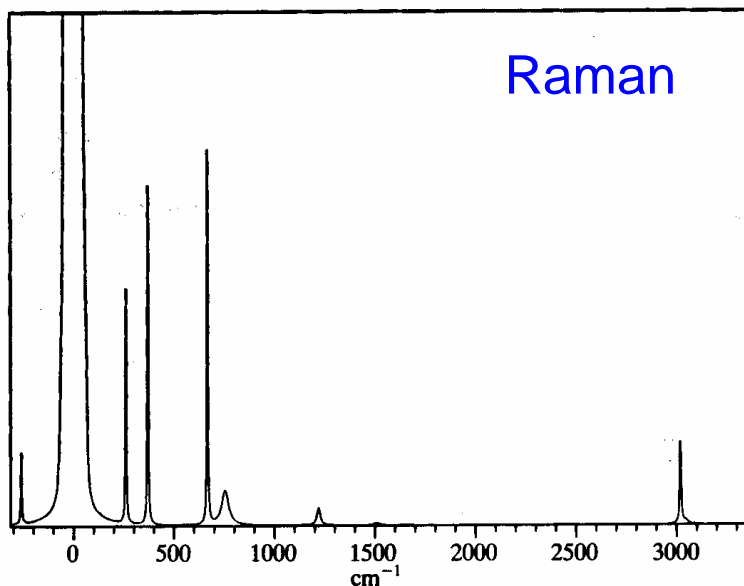
# Raman Spectrum: Diatomic Molecule

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



example: CHCl3 molecule.  
Symmetric top molecule with 5 atoms  $\Rightarrow 3N - 6 = 15 - 6 = 9$  vibrational modes, however, due to symmetry 3 modes are degenerate  $\Rightarrow 6$  vibrational modes.

Modes are seen at 262, 366, 668, 761, 1216 and 3019 cm<sup>-1</sup>. All six modes are both IR and Raman active. Exciting source is Ar 488 nm laser line

In the Raman spectrum on the left the wavenumber of the incident (laser) radiation is set to zero, so x-axis shows wavenumbers of the vibrational modes (and not absolute values)



# Raman Activity in Polyatomics

In general for polyatomic molecules it is usually necessary to apply Group Theory in order to decide whether a particular vibration of the molecule is Raman active or not. But some general rules apply:

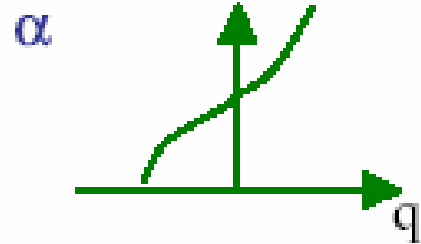
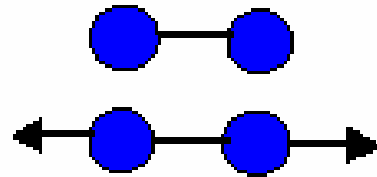
If the molecule has no symmetry (e.g. HCN) then usually all of its vibrational modes are Raman active

In molecules that possess symmetry (e.g. CO<sub>2</sub>, H<sub>2</sub>O) then **Symmetric vibrations give rise to intense Raman lines, non symmetric vibrations are usually weak and sometimes unobservable. In particular bending modes usually yield a very weak Raman line.**

**Rule of Mutual Exclusion:**

**If the molecule has a centre of symmetry, then Raman active vibrations are infrared inactive and vice versa. If there is no centre of symmetry in the molecule then some or all of the vibrations may be both Raman and IR active.**

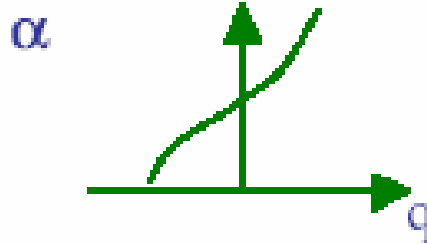
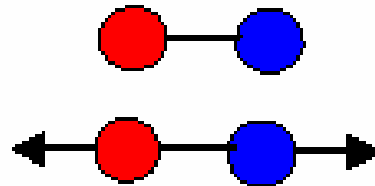
# Raman Activity



$$d\alpha/dq \neq 0$$

Raman ✓

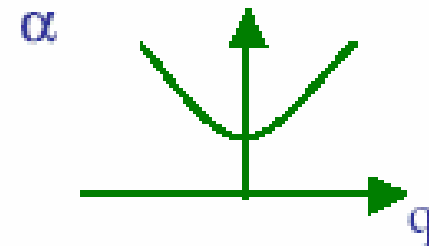
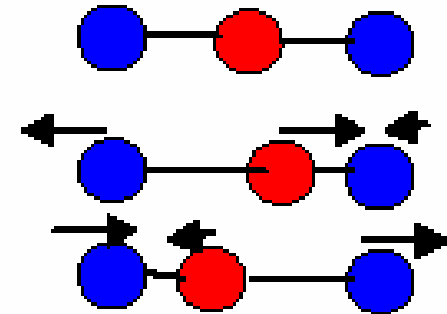
IR ✗



$$\neq 0$$

✓

✓



$$= 0$$

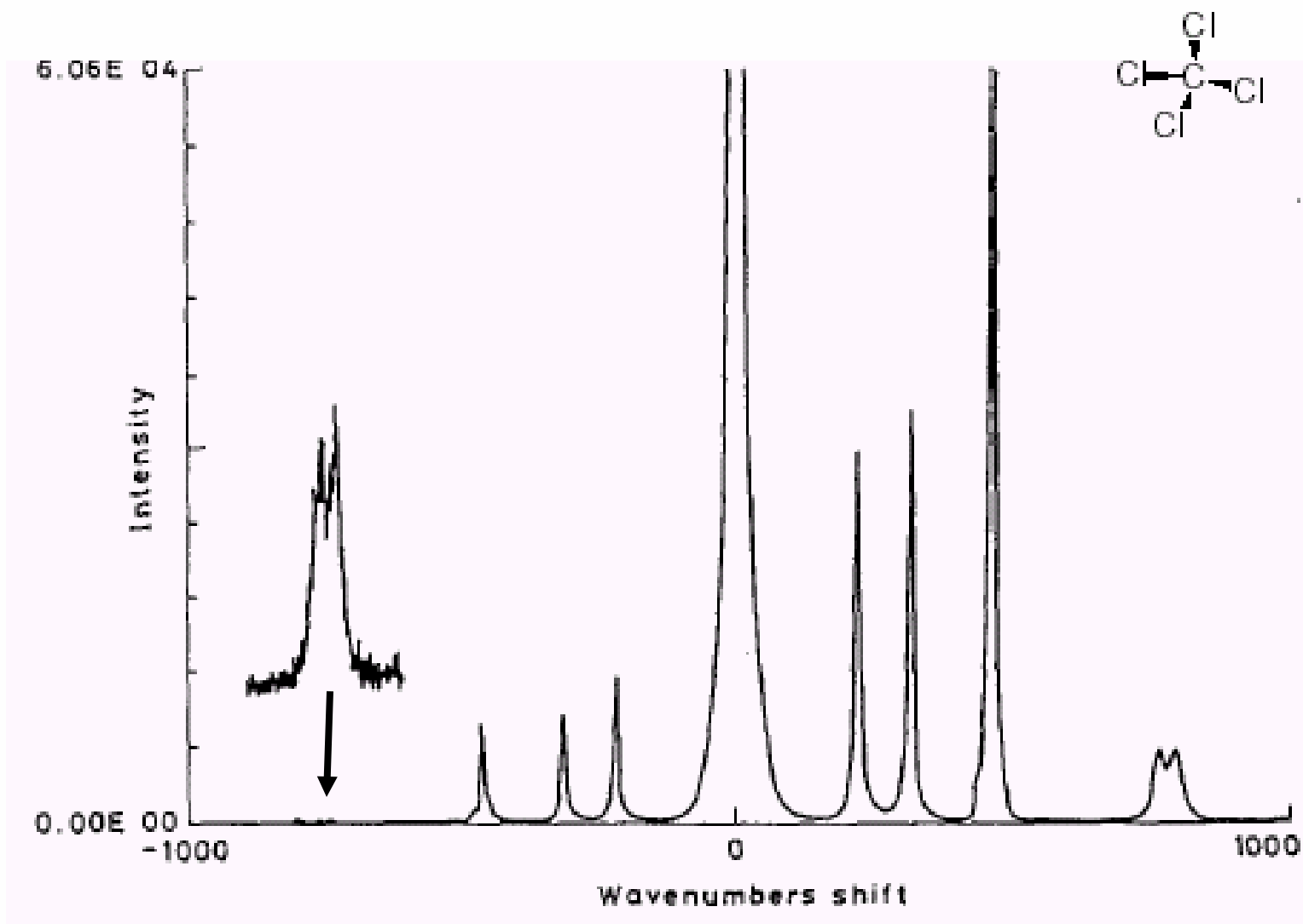
✗

✓

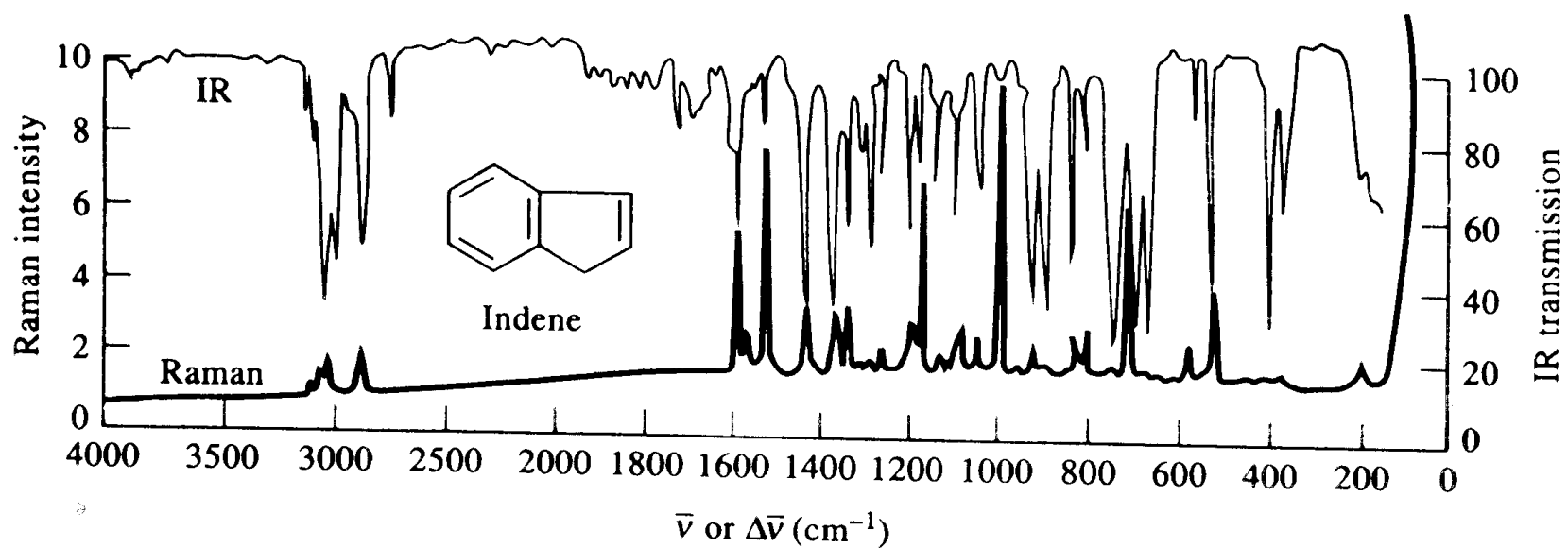
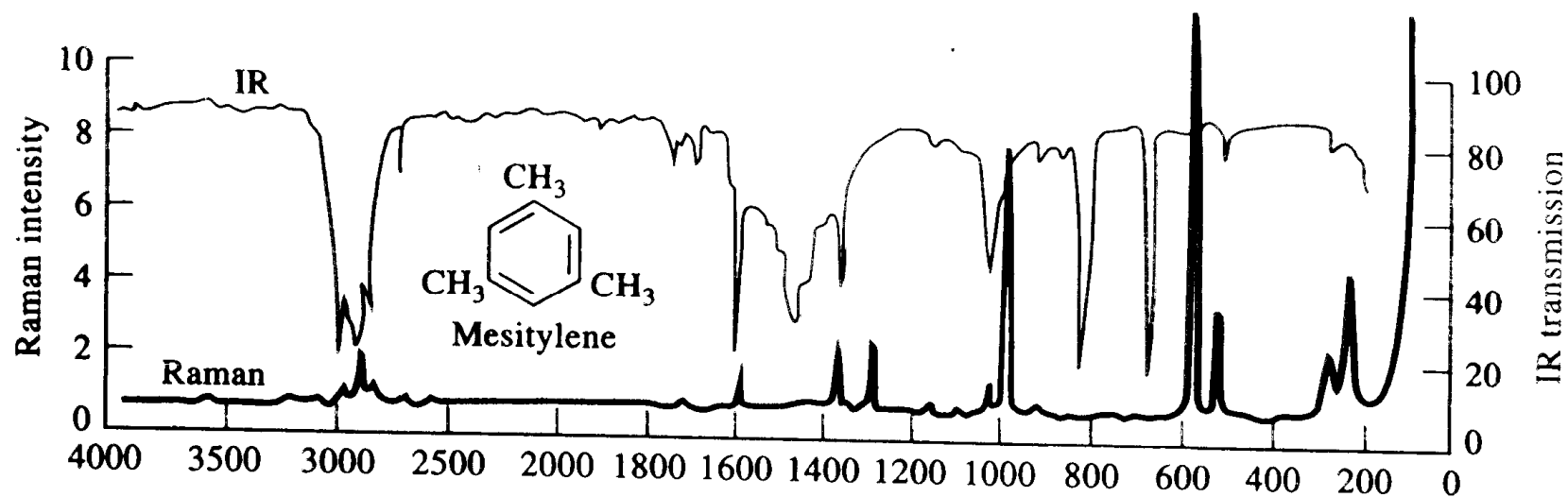
# Vib. Raman Spectra: Example $\text{CCl}_4$

Anti-Stokes

Stokes



# Comparison of Raman and IR Spectra



# 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)

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

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**

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

**S-Branch**

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

**O-Branch**

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

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

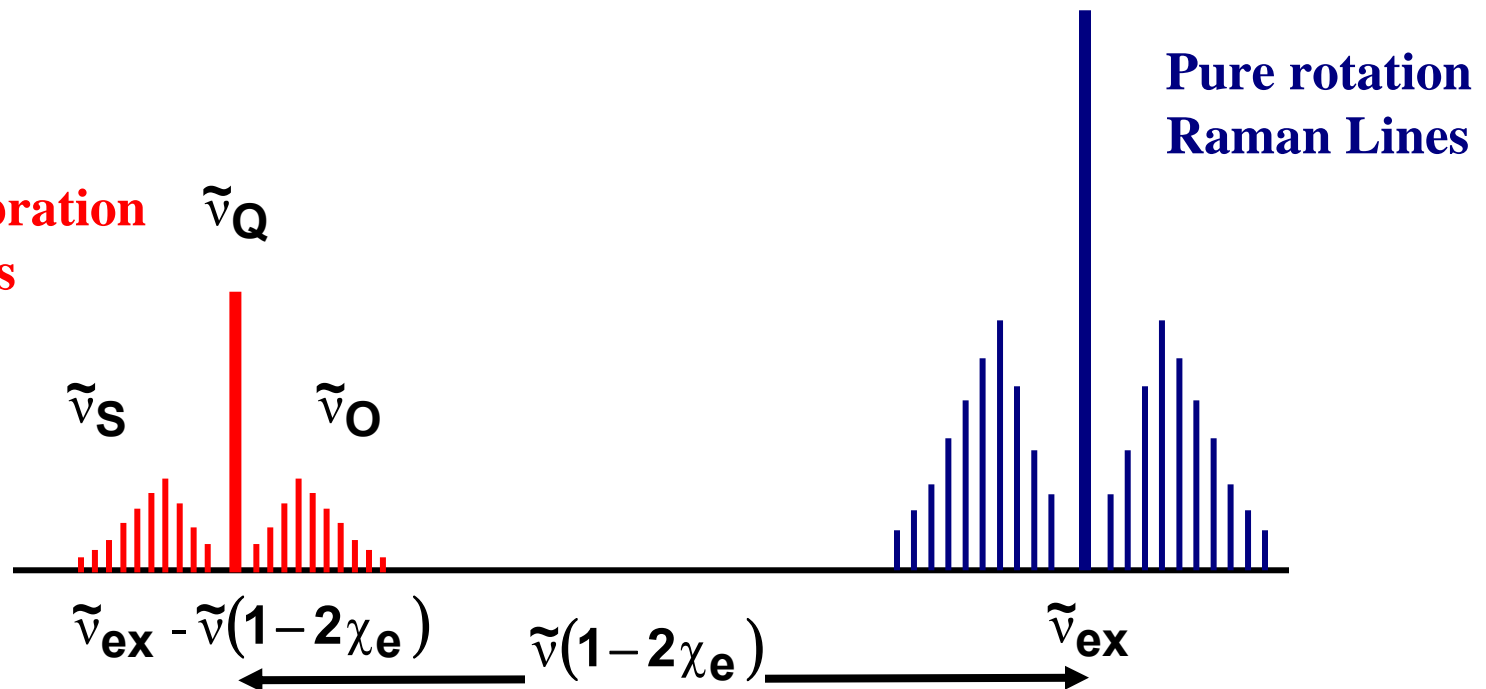
$$\tilde{\nu}_Q = \tilde{\nu}_{ex} - \Delta\varepsilon_Q = \tilde{\nu}_{ex} - \tilde{\nu}(1 - 2\chi_e) \text{ cm}^{-1} \quad J = 0, 1, 2, 3, \dots$$

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

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

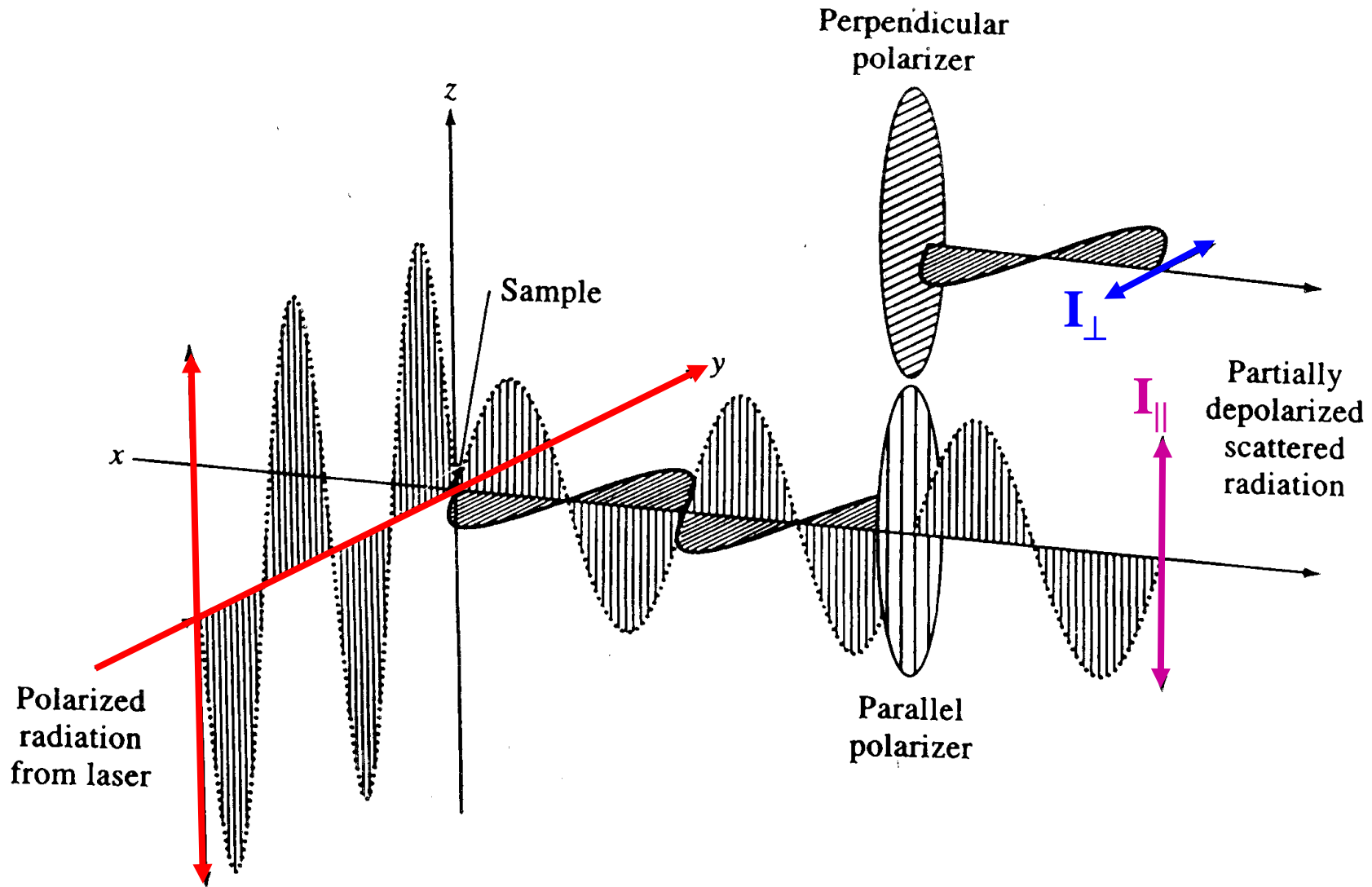
$\nu_{ex}$  is the frequency of the incident (exciting) radiation, e.g. laser frequency

**Rotation Vibration  
Raman Lines**



# 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 lines 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 and 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  $\Rightarrow$

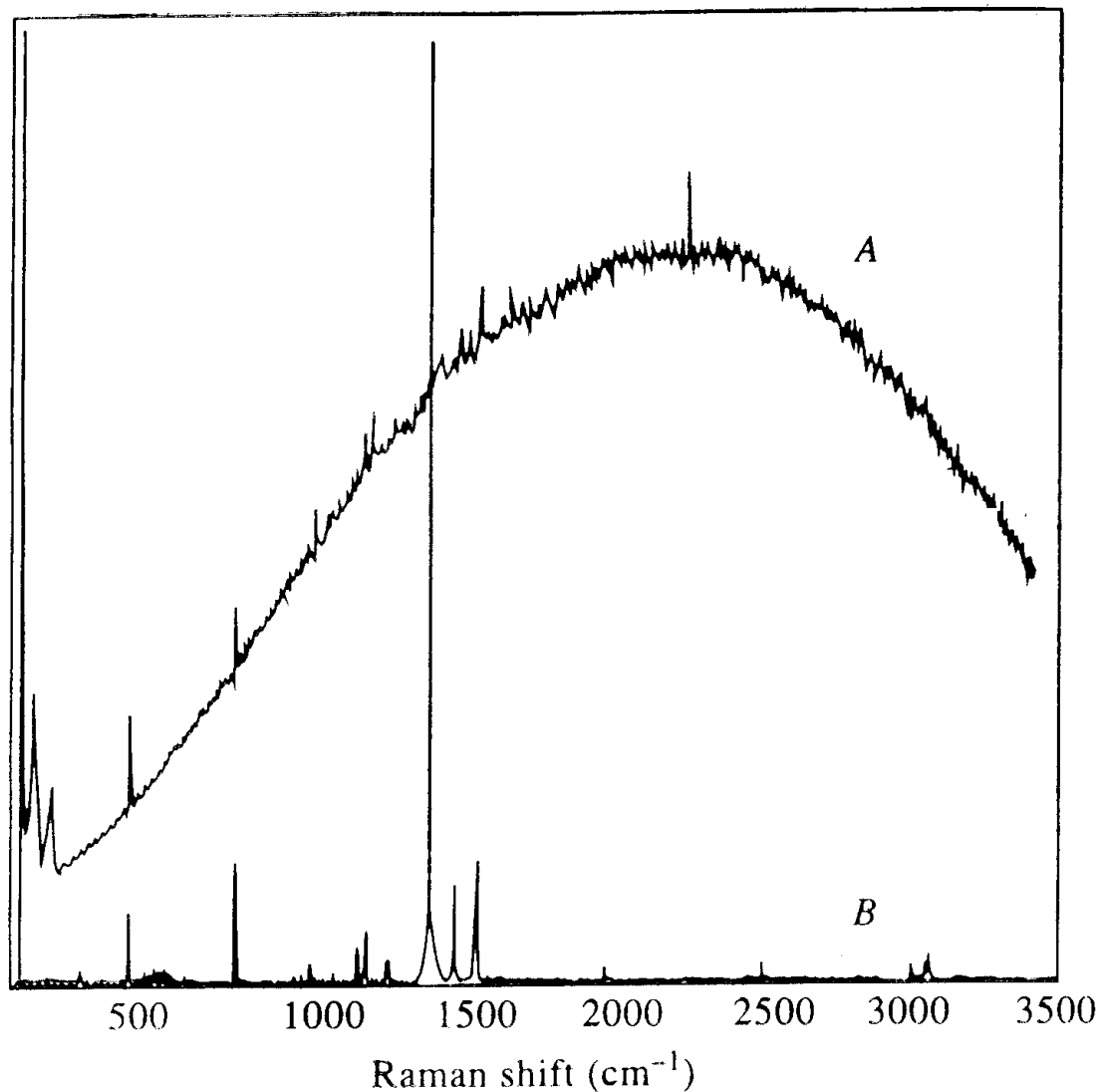
- 1) They can be operated at much higher power without causing **photodissociation** of the sample (up to 50 W).
- 2) These photons are not energetic enough to excite electronic states in the molecule so there is little or no fluorescence radiation to swamp the Raman signal. (see figure on next overhead)

**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.

See **Banwell and McCash Section 4.7 AND Skoog, Nieman and Holler Section 18 B** For details on Instrumentation

# Ar Ion versus Nd YAG source



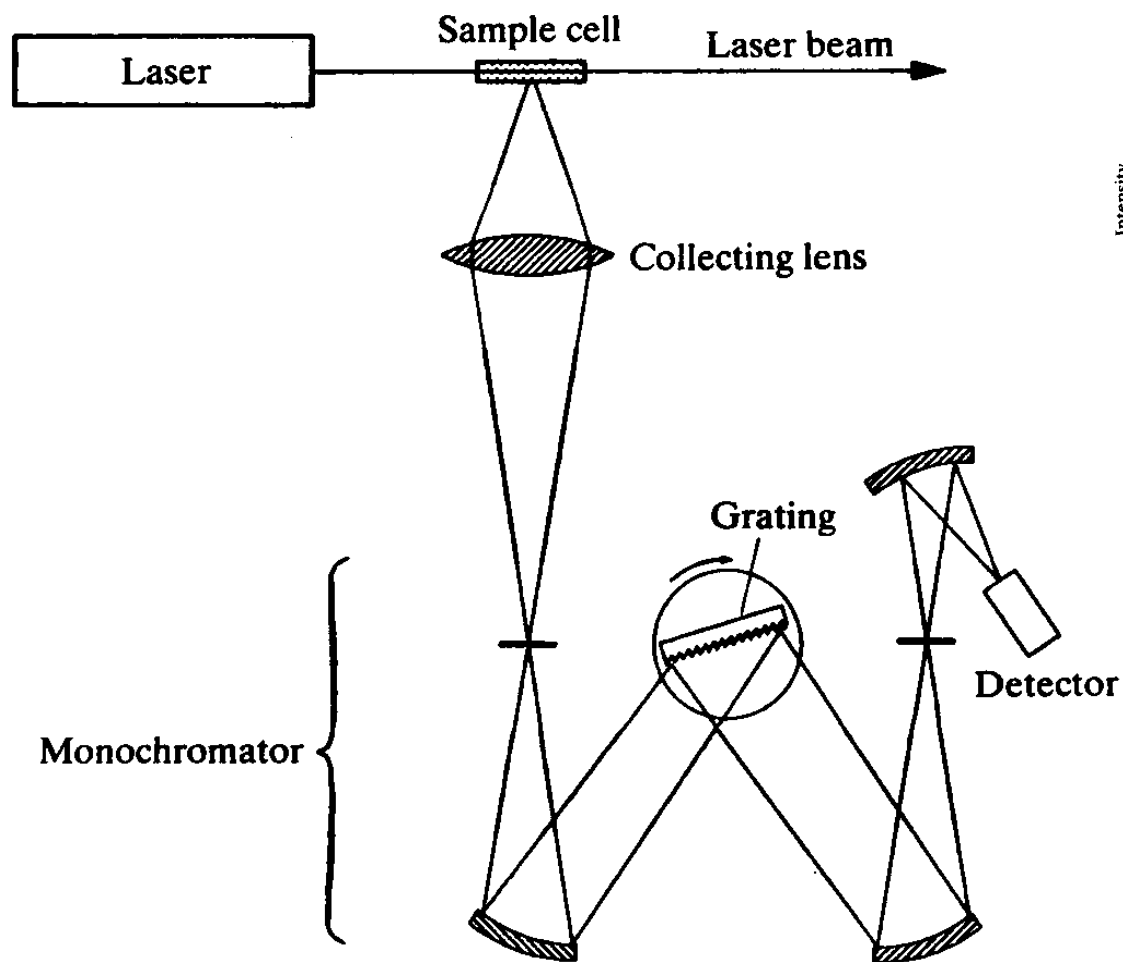
Raman spectrum of anthracene.

**A:** conventional Raman instrument using a Ar Ion laser.

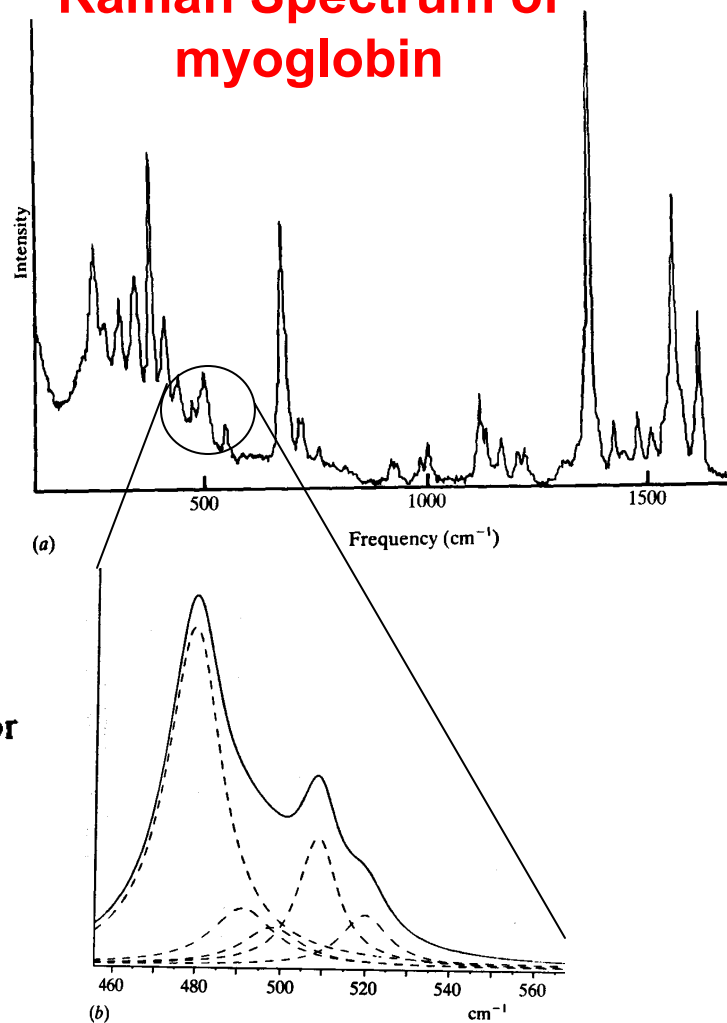
**B:** Fourier Transform instrument using Nd/YAG laser.

Note huge fluorescence contribution to the spectrum taken with Ar Ion laser.

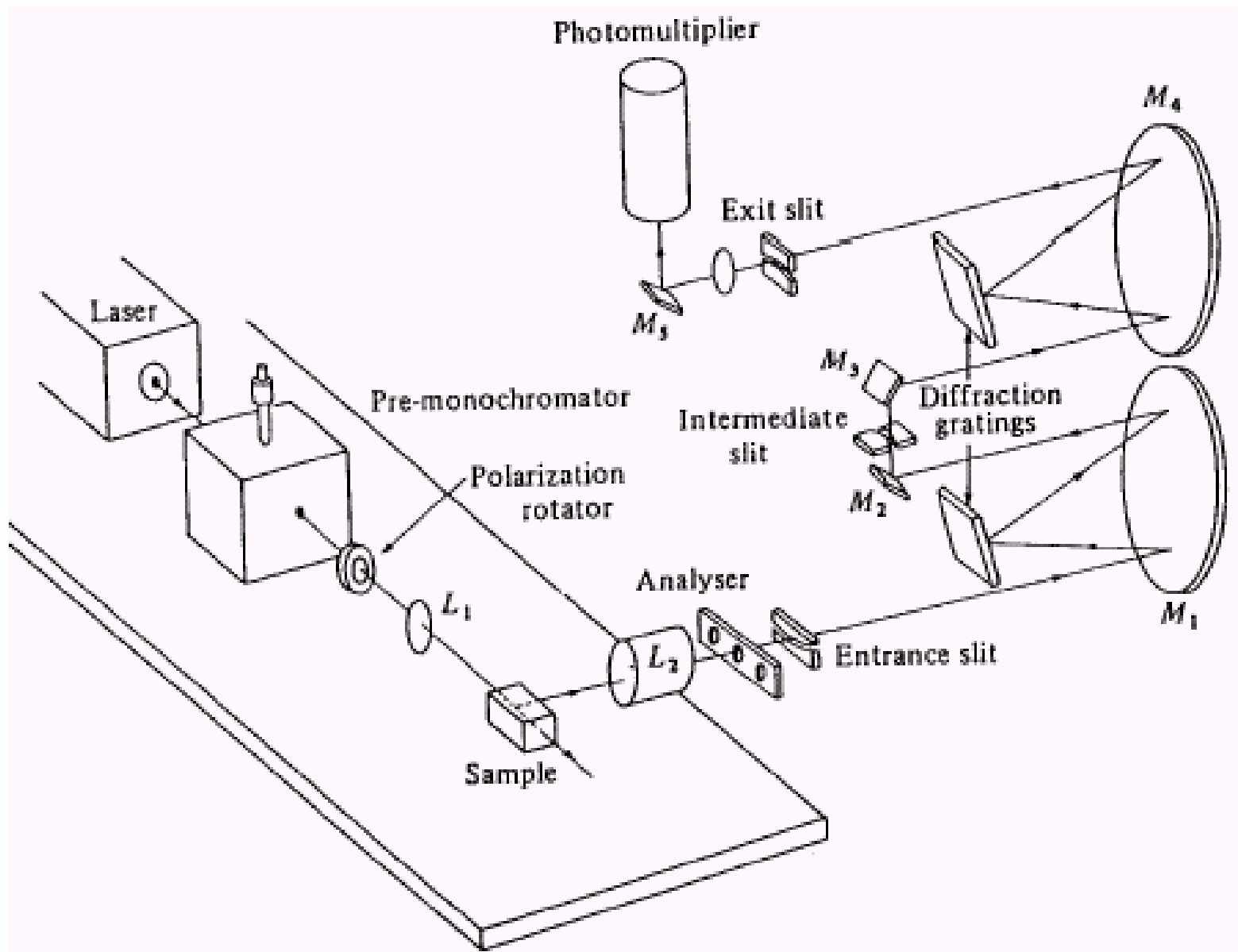
# Conventional Raman Spectrometer



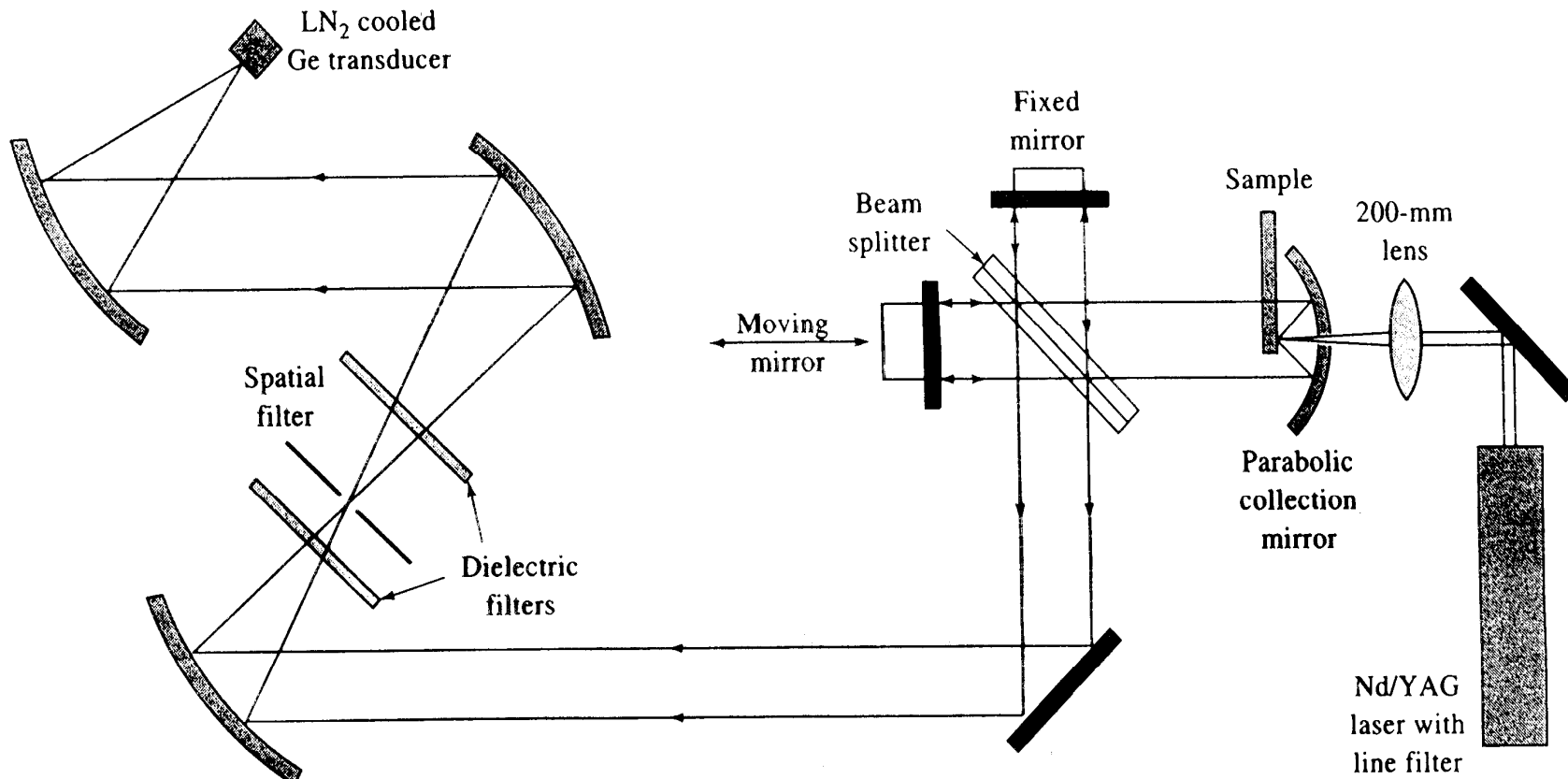
## Raman Spectrum of myoglobin



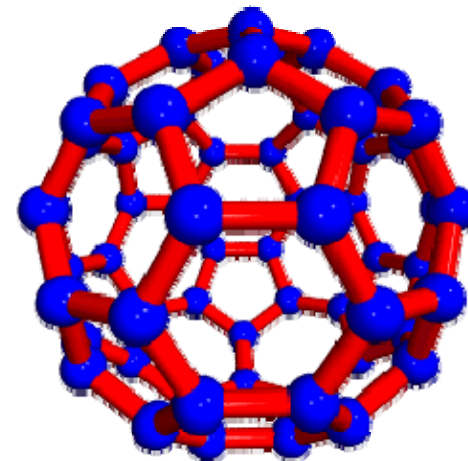
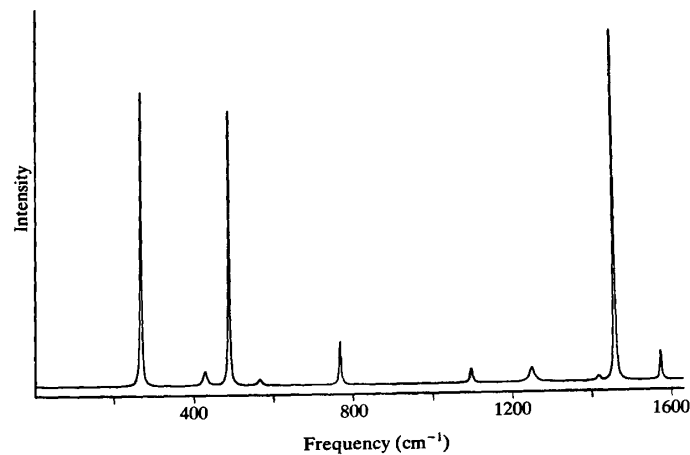
# Conventional Raman Spectrometer



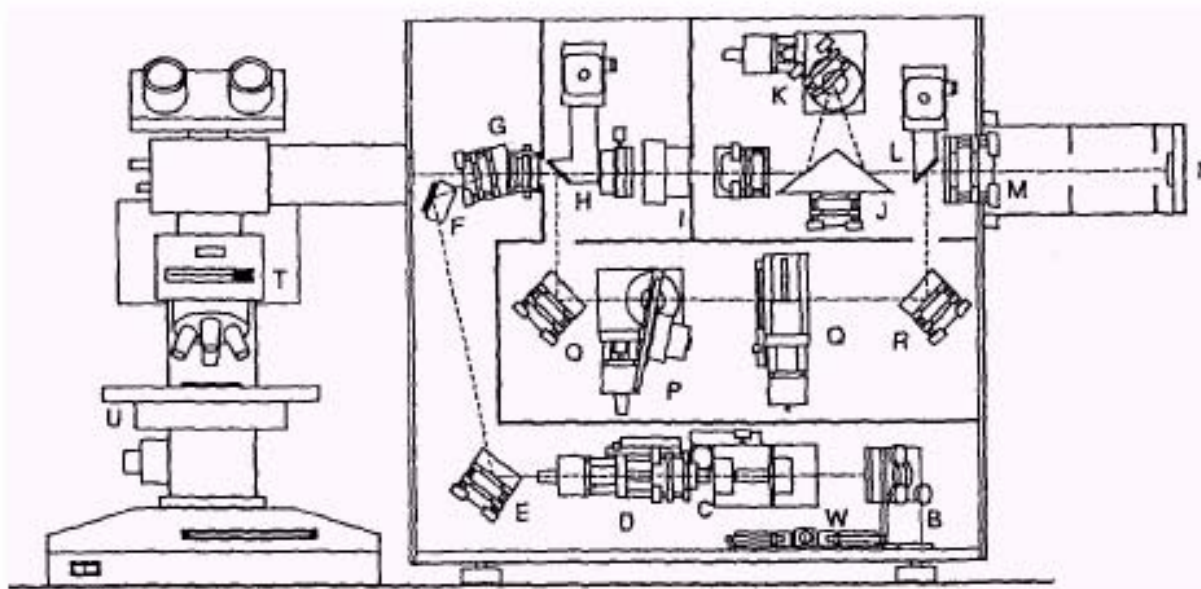
# Fourier Transform Raman Spectroscopy



**FT Raman spectrum of powdered C<sub>60</sub>**



# Raman Microscope



# Coherent AntiStokes Raman Spectroscopy

See Atkins Physical Chemistry (6th edition) Section 16.16 (d)

The intensity of Raman transitions may be enhanced by **Coherent anti-Stokes Raman Spectroscopy (CARS)**. The technique relies on the fact that, if two laser beams of frequencies  $\nu_1$  and  $\nu_2$  pass through a sample, then they may mix together (non-linear optical mixing) and give rise to coherent radiation of several different frequencies, e.g.

$\nu_1 + \nu_2$ ,  $\nu_1 - \nu_2$ ,  $2\nu_1 + \nu_2$ ,  $2\nu_1 - \nu_2$ , ... If we consider the mixed beam at frequency

$$\nu_3 = 2\nu_1 - \nu_2$$

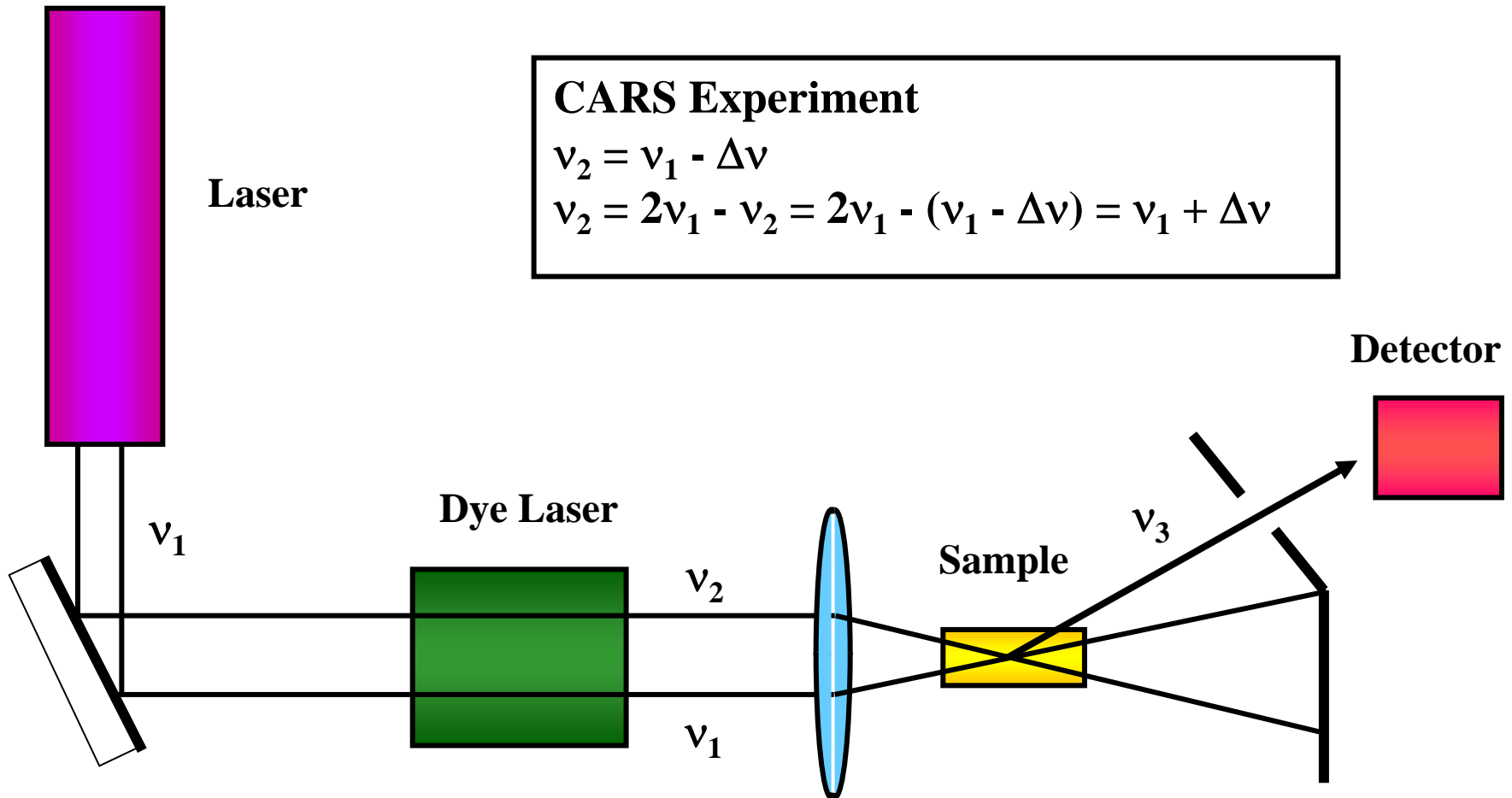
Then suppose that  $\nu_2$  (dye laser) is varied until it matches any of the Stokes lines from the sample, such as one with frequency  $\nu_1 - \Delta\nu$ , then the coherent radiation will have frequency

$$\nu_3 = 2\nu_1 - (\nu_1 - \Delta\nu) = \nu_1 + \Delta\nu$$

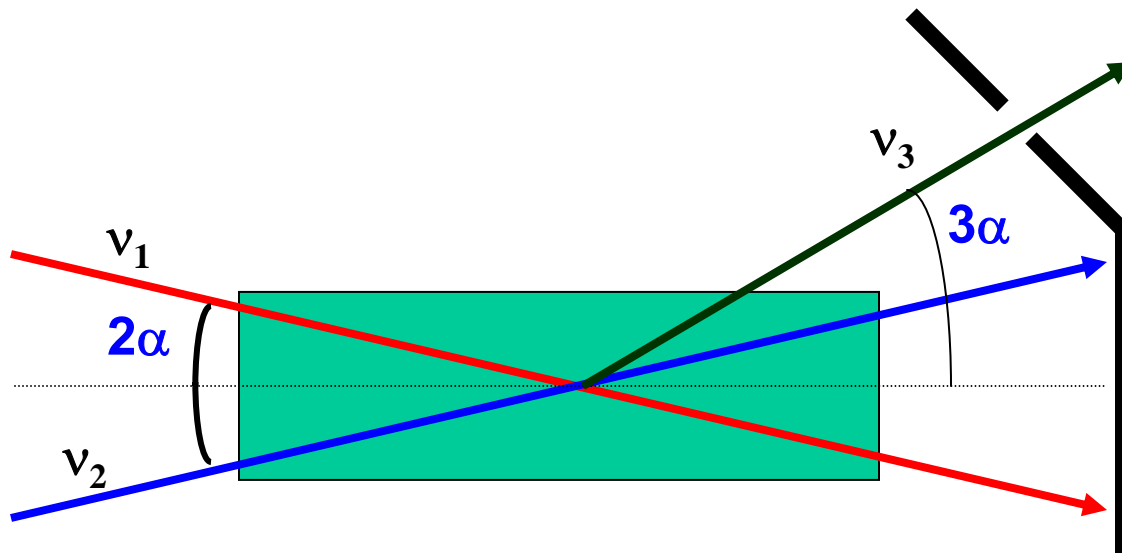
which is the frequency of the corresponding **anti-Stokes line**. This coherent radiation forms a narrow beam of high intensity, and since it is in the anti Stokes region of the spectrum there will be no fluorescent or background radiation to interfere with it.



# Coherent AntiStokes Raman Spectroscopy



# Coherent AntiStokes Raman Spectroscopy



If the two incoming beams are focused at a small angle  $2\alpha$  at the sample then the collimated CARS radiation emerges at an angle  $3\alpha$  to the optic axis and can be easily filtered from  $\nu_1$  and  $\nu_2$  using a pinhole.

**Advantage of CARS:** It can be used to look at Raman transitions in the presence of competing incoherent background radiation, for example it can look at the Raman Spectra of species in flames. The intensities of transitions can be interpreted in terms of the temperature in different regions of the flame.

We could also tune the dye laser  $\nu_2$ , until it matched an anti-Stokes transition at  $\nu_1 + \Delta\nu$  then

$$\nu_3 = 2\nu_1 - (\nu_1 + \Delta\nu) = \nu_1 - \Delta\nu$$

= a frequency corresponding to a Stokes line  $\Rightarrow$  **Coherent Stokes Raman Scattering (CSRS)** not used much

# Raman vs. IR Spectroscopy

## Advantages:

- 1) The incident and scattered radiation is in the visible or UV  $\Rightarrow$  **conventional optics**, monochromators and sample cells can be used
- 2) Can focus the laser beam to very small spot size (difficult to focus IR) $\Rightarrow$  can use **small samples**
- 3) Water absorbs strongly in the IR (see vib notes, double beam spectrometer) but water is a very weak Raman scatterer  $\Rightarrow$  can use **aqueous solutions** for Raman Spectroscopy (not possible for IR where other solvents are required for liquid samples.  $\Rightarrow$  can examine **biological samples**).
- 4) Using Pulsed laser sources we can look at time dependence of Raman Intensities  $\Rightarrow$  can observe transient species in reactions.

## Disadvantages:

- 1) **Sample heating** when lasers are used
- 2) **fluorescence** in sample can swamp Raman signal