

VIVEKANAND COLLEGE, KOLHAPUR  
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## Raman Spectroscopy

BY

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Date :

25/08/2023

# Raman Spectroscopy

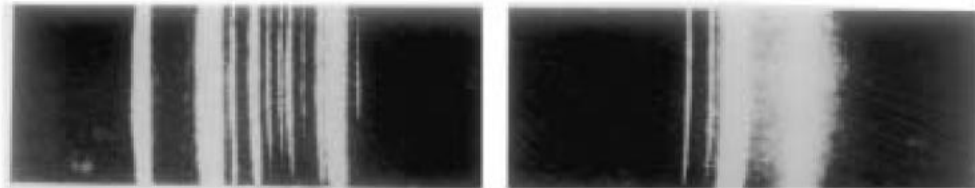
1923 – Inelastic light scattering is predicted by A. Smekel

1928 – Landsberg and Mandelstam see unexpected frequency shifts in scattering from quartz

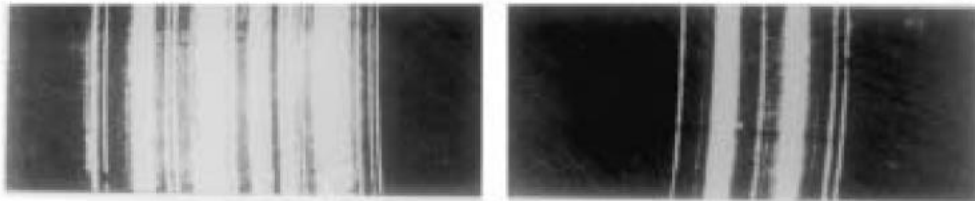
1928 – C.V. Raman and K.S. Krishnan see “feeble fluorescence” from neat solvents

## First Raman Spectra:

Filtered Hg arc  
lamp spectrum:



$C_6H_6$   
Scattering



# *Raman Spectroscopy*

1923 – Inelastic light scattering is predicted by A. Smekel

1928 – Landsberg and Mandelstam see unexpected frequency shifts in scattering from quartz

1928 – C.V. Raman and K.S. Krishnan see “feeble fluorescence” from neat solvents

1930 – C.V. Raman wins Nobel Prize in Physics

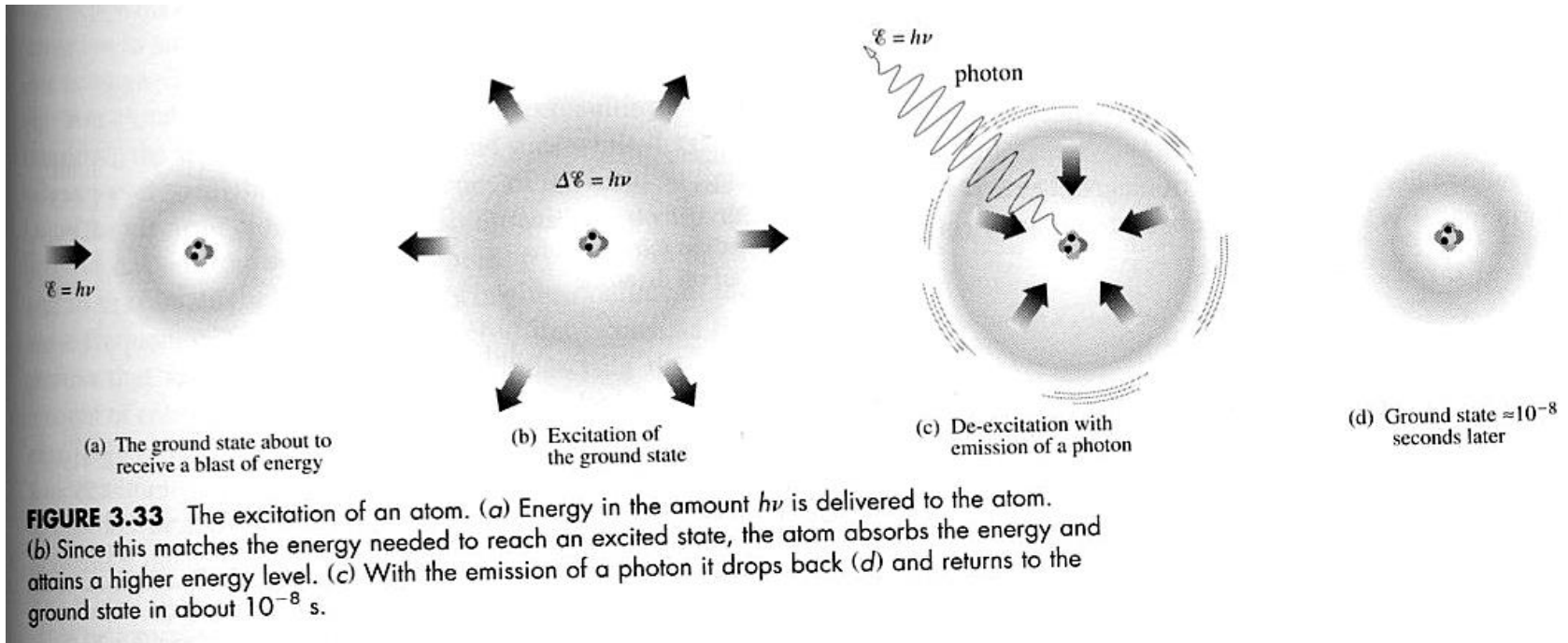
1961 – Invention of laser makes Raman experiments reasonable

1977 – Surface-enhanced Raman scattering (SERS) is discovered

1997 – Single molecule SERS is possible



# Rayleigh Scattering

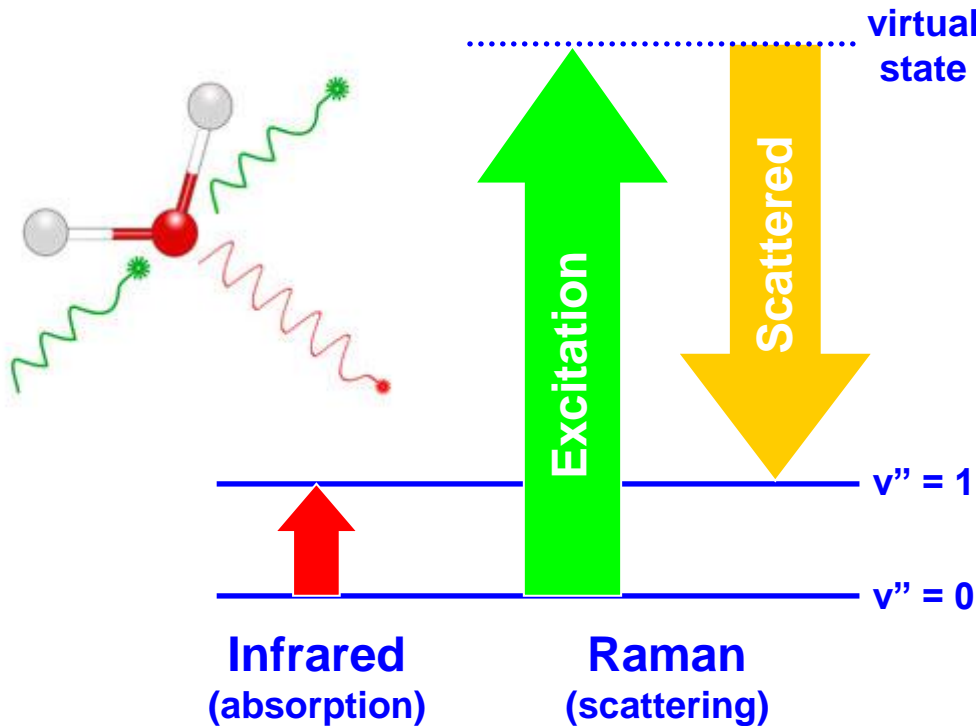


- Elastic ( $\lambda$  does not change)
- Random direction of emission
- Little energy loss

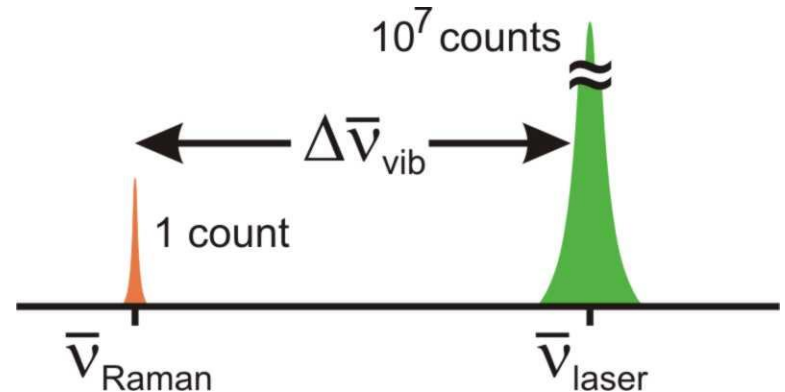
$$(E_{sc})_{\theta} = \frac{8\pi^4 (\alpha')^2 (1 + \cos^2 \theta) E_0}{\lambda^4 d^2}$$

# Raman Spectroscopy

1 in  $10^7$  photons is scattered inelastically



Rotational Raman  
Vibrational Raman  
Electronic Raman



# Classical Theory of Raman Effect

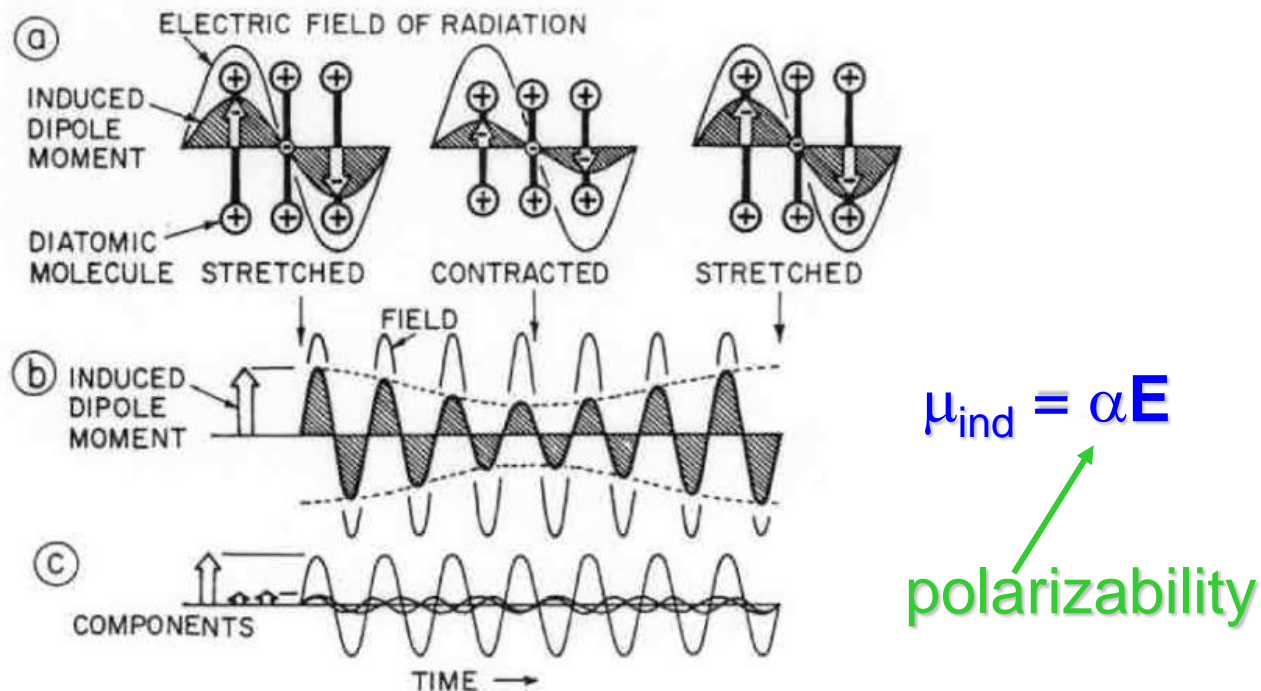
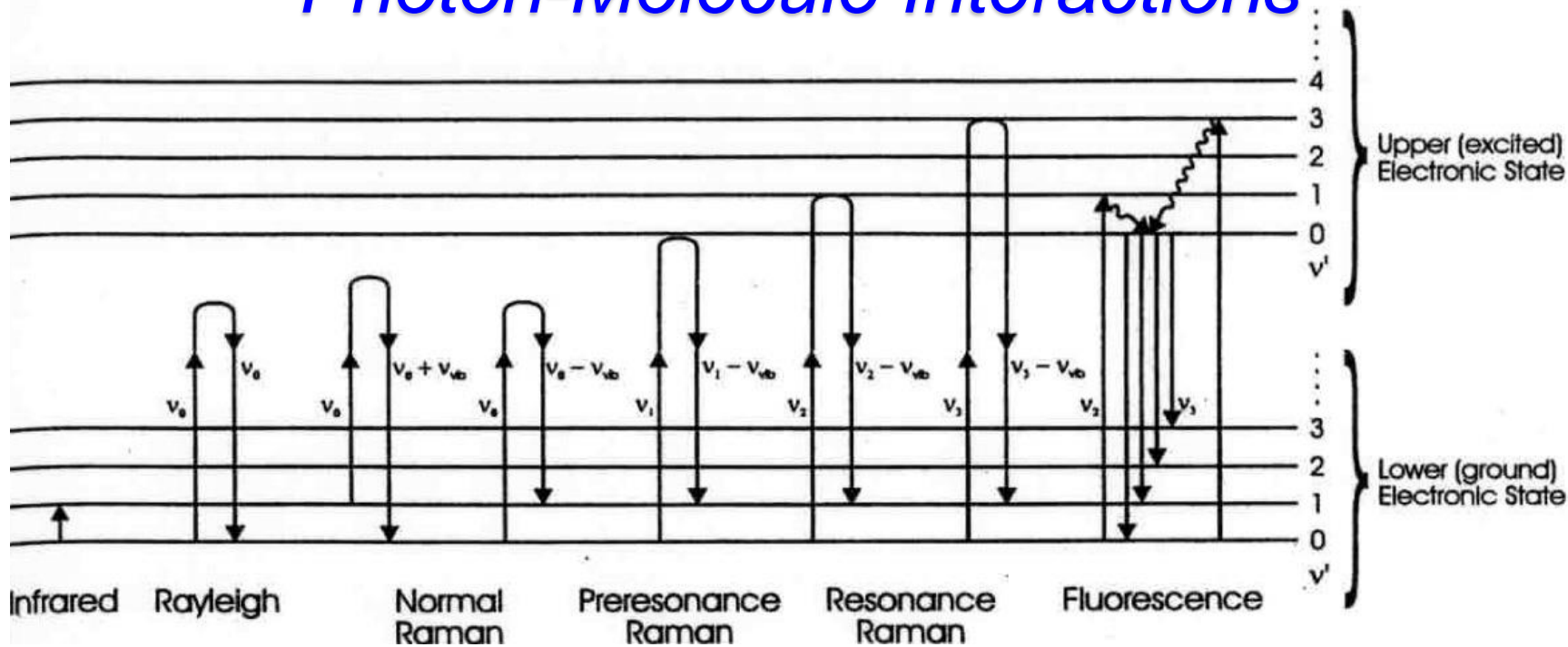


FIG. 1.32. Classical theory for the origin of the Raman effect. In (a) we see a diatomic molecule where “+” represents protons and “-” represents the center of gravity of the electrons. The electrons are displaced by the external field of the photon and an induced dipole moment is generated which changes when the bond length changes during the molecular vibration. The induced dipole moment is plotted in (b) as an amplitude modulated wave with steady amplitude components shown in (c) from which scattered radiation is generated.

# Photon-Molecule Interactions



When light interacts with a vibrating diatomic molecule, the induced dipole moment has 3 components:

$$\mu_z(t) = \alpha_{zz}^{equil} \vec{E}_{max} \cos 2\pi\nu_0 t +$$

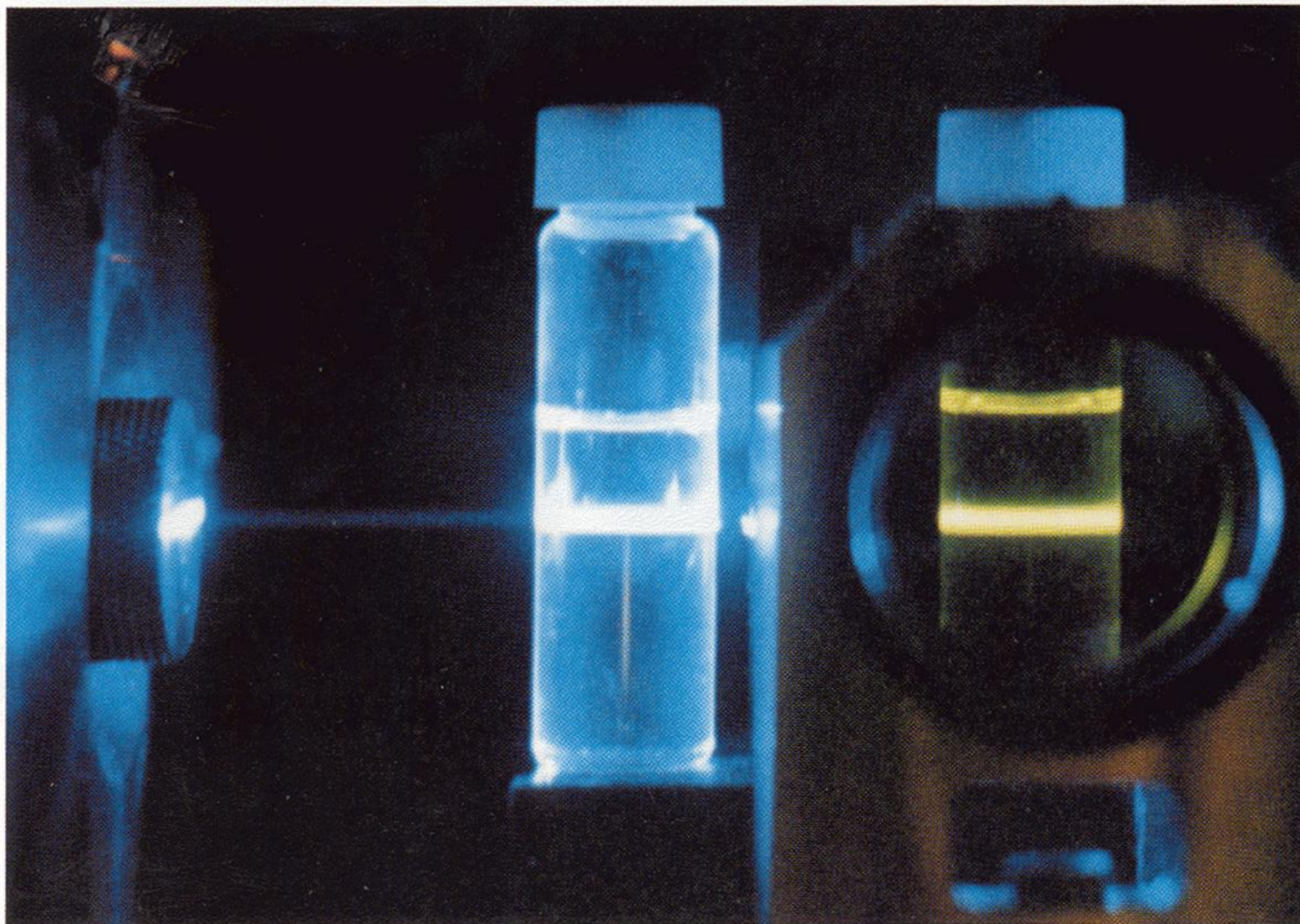
Rayleigh scatter

$$\frac{1}{2} \frac{d\alpha_{zz}}{dr} \Delta r_{max} \vec{E}_{max} \cos 2\pi(\nu_0 + \nu_{vib}) t +$$

Anti-Stokes Raman scatter

$$\frac{1}{2} \frac{d\alpha_{zz}}{dr} \Delta r_{max} \vec{E}_{max} \cos 2\pi(\nu_0 - \nu_{vib}) t$$

Stokes Raman scatter



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.

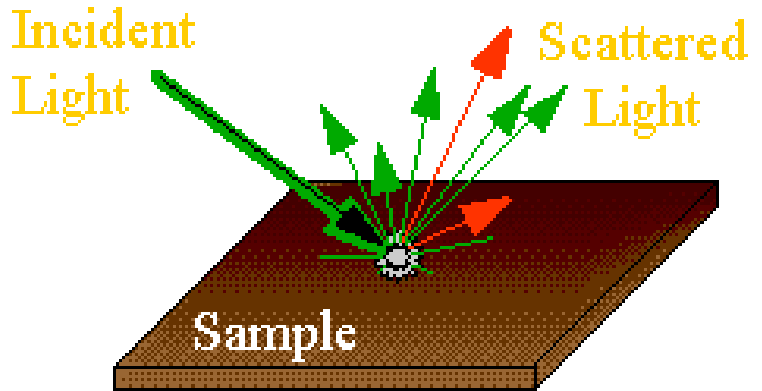


# Raman Scattering

Selection rule:  $\Delta v = \pm 1$

Overtones:  $\Delta v = \pm 2, \pm 3, \dots$

$$\mu_z(t) = \alpha_{zz}^{equil} \vec{E}_{max} \cos 2\pi\nu_0 t + \frac{1}{2} \frac{d\alpha_{zz}}{dr} \Delta r_{max} \vec{E}_{max} \cos 2\pi(\nu_0 + \nu_{vib})t + \frac{1}{2} \frac{d\alpha_{zz}}{dr} \Delta r_{max} \vec{E}_{max} \cos 2\pi(\nu_0 - \nu_{vib})t$$



Must also have a change in polarizability

Classical Description does not suggest any difference between Stokes and Anti-Stokes intensities

$$\frac{N_1}{N_0} = e^{-\frac{h\nu_{vib}}{kT}}$$

## *Are you getting the concept?*

Calculate the ratio of Anti-Stokes to Stokes scattering intensity when  $T = 300 \text{ K}$  and the vibrational frequency is  $1440 \text{ cm}^{-1}$ .

$$h = 6.63 \times 10^{-34} \text{ Js}$$

$$k = 1.38 \times 10^{-23} \text{ J/K}$$

# Presentation of Raman Spectra

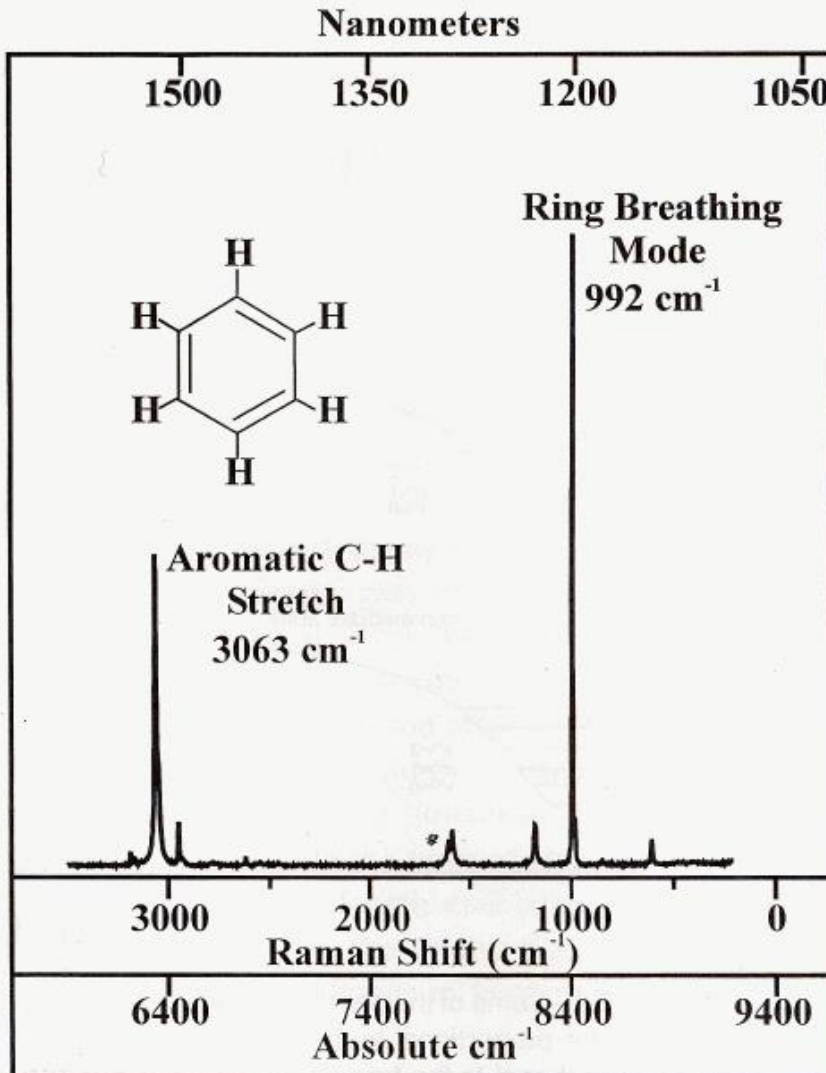


FIGURE 2 FT-Raman spectrum of neat benzene.

$$\lambda_{\text{ex}} = 1064 \text{ nm} = 9399 \text{ cm}^{-1}$$

Breathing mode:

$$9399 - 992 = 8407 \text{ cm}^{-1}$$

Stretching mode:

$$9399 - 3063 = 6336 \text{ cm}^{-1}$$

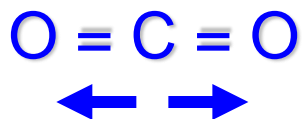
# *Mutual Exclusion Principle*

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

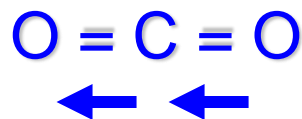
⇒ *Symmetric molecules*

IR-active vibrations are not Raman-active.

Raman-active vibrations are not IR-active.



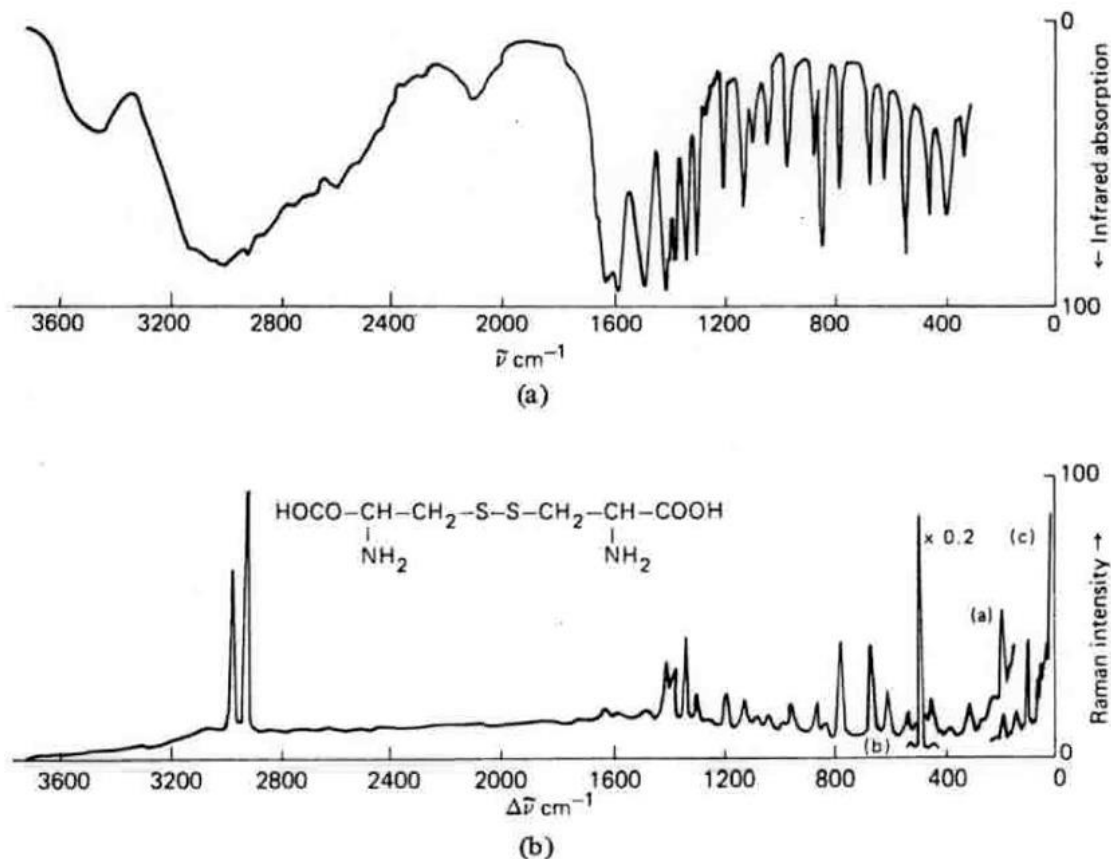
Raman active  
IR inactive



Raman inactive  
IR active

# Raman vs IR Spectra

**FIGURE 16-13** Infrared (a) and Raman (b) spectra of crystalline cystine. Note that the  $\text{NH}_3^+$  stretching vibration dominates the  $3000\text{-cm}^{-1}$  region in the IR spectrum, whereas the Raman spectrum shows sharp bands due to CH and  $\text{CH}_2$  stretching modes. The  $\text{NH}_3^+$  deformation and the carboxylate antisymmetric vibrations near  $1600\text{ cm}^{-1}$  are much stronger in the IR spectrum. The strong Raman band at  $410\text{ cm}^{-1}$  is due to the  $\text{—S—S—}$  stretch; this band is somewhat obscured and weak in the IR spectrum. [With permission of VCH Verlagsgesellschaft from B. Schrader, *Angew. Chem. Int. Ed. Engl.*, 12, 884 (1973).]



# Raman vs Infrared Spectra

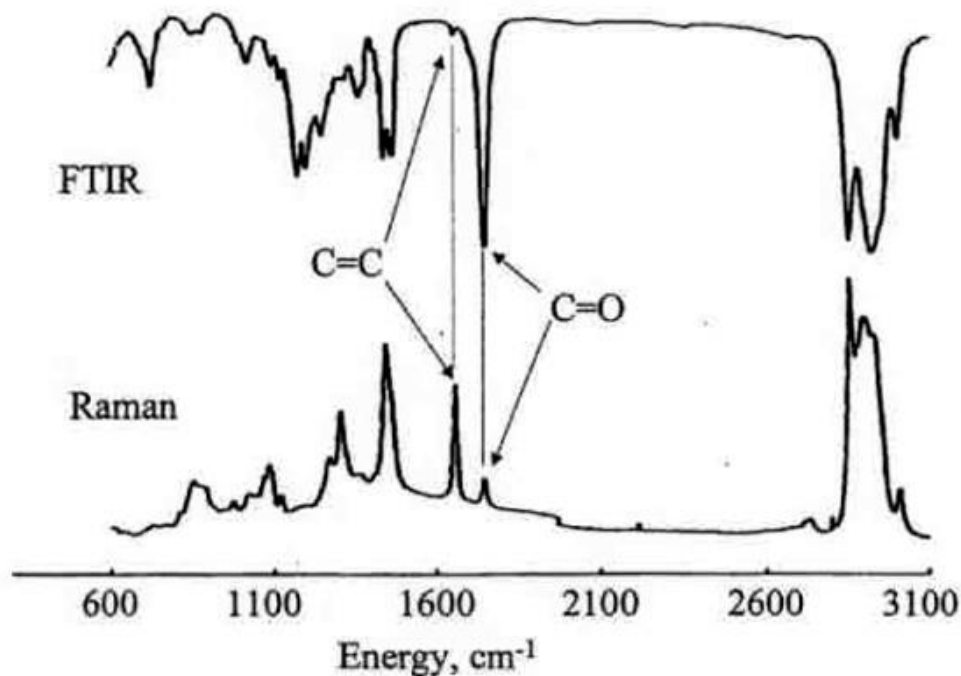
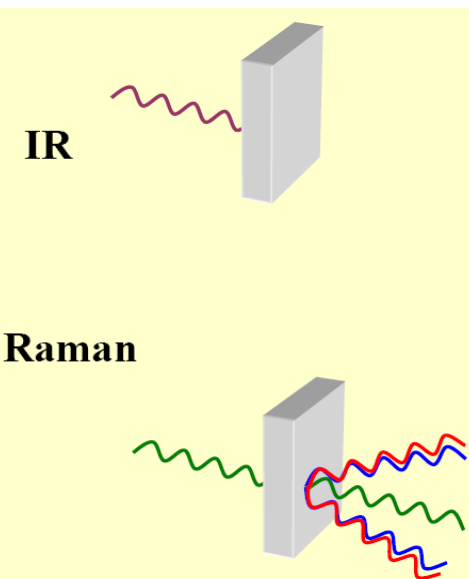
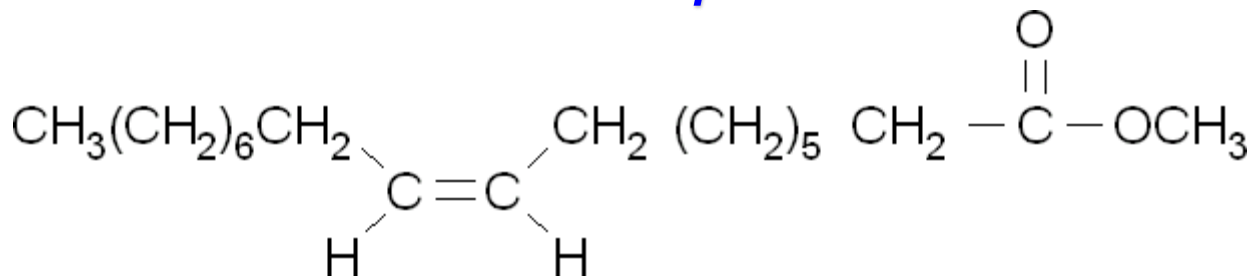


Figure 2.2. FTIR (upper) transmission and Raman scattering (lower) of oleic acid methyl ester.

# Raman vs Infrared Spectra

Table 2.1. Examples of Raman and IR Frequencies<sup>a</sup>

	Frequency (cm <sup>-1</sup> )	IR <sup>a</sup>	Raman <sup>b</sup>
<b>Alkanes</b>			
CH <sub>3</sub> sym stretch	2862–2882	vs	vs
C—C stretch	1040–1100	—	s
Cyclopentane ring breathing	889	—	s
Alcohol O—H stretch	3635–3644	m	w
Acetylene C—H bend	825–640	s	w
Acetylene C≡C	2230–2237	—	s
C≡N stretch in R—CN	2230–2250	s	vs
Cyanate C≡N	2245–2256	s	vs
C—H in R—CHO	2800–2850	m	—
C=O in R—CHO	1730–1740	vs	w
R—NO <sub>2</sub> asym stretch	1530–1600	vs	m–w
R—NO <sub>2</sub> sym stretch	1310–1397	s	vs
C—S stretch	580–704	—	vs
S—H stretch	2560–2590	w	s
R <sub>2</sub> S <sub>2</sub> S—S stretch	507–512	m–w	s
Benzene ring breathing	992	—	vs
Primary R—Cl	650–660	s	s
Primary R—Br	565–560	s	vs
Primary R—I	500–510	s	vs

<sup>a</sup>Taken from Reference 8.

<sup>b</sup>vs = very strong, m = medium, w = weak, dash = absent.

# Raman Intensities

Radiant power of Raman scattering:

$$\Phi_R \propto \sigma(\nu_{ex}) \nu_{ex}^4 E_0 n_i e^{\frac{-E_i}{kT}}$$

$\sigma(\nu_{ex})$  – Raman scattering cross-section (cm<sup>2</sup>)

$\nu_{ex}$  – excitation frequency

$E_0$  – incident beam irradiance

$n_i$  – number density in state i

exponential – Boltzmann factor for state i

$\sigma(\nu_{ex})$  - target area presented by a molecule for scattering



# Raman Scattering Cross-Section

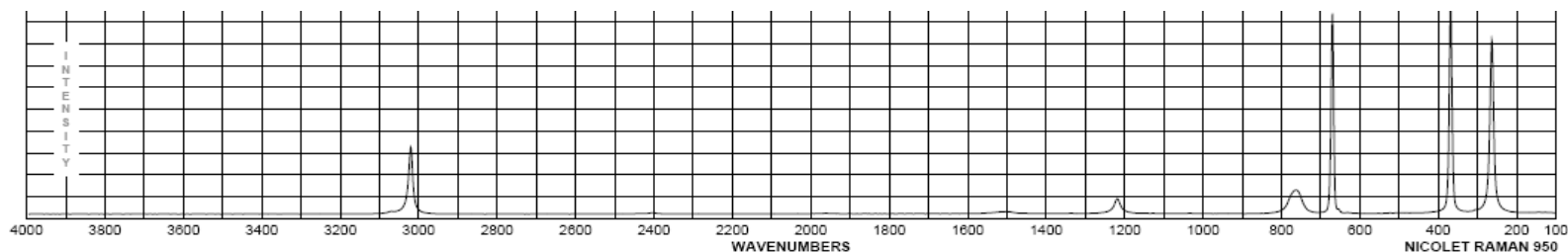
$$\frac{d\sigma}{d\Omega} = \frac{\text{scattered flux/unit solid angle}}{\text{incident flux/unit solid angle}}$$

$$\sigma = \int d\Omega \frac{d\sigma}{d\Omega}$$

Process	Cross-Section of	$\sigma$ (cm <sup>2</sup> )
absorption	UV	10 <sup>-18</sup>
absorption	IR	10 <sup>-21</sup>
emission	Fluorescence	10 <sup>-19</sup>
scattering	Rayleigh	10 <sup>-26</sup>
scattering	Raman	10 <sup>-29</sup>
scattering	RR	10 <sup>-24</sup>
scattering	SERRS	10 <sup>-15</sup>
scattering	SERS	10 <sup>-16</sup>

$\sigma(\nu_{\text{ex}})$  - target area presented by a molecule for scattering

# Raman Scattering Cross-Section



$\lambda_{\text{ex}}$ (nm)	$\sigma$ ( x $10^{-28}$ cm <sup>2</sup> )
532.0	0.66
435.7	1.66
368.9	3.76
355.0	4.36
319.9	7.56
282.4	13.06

CHCl<sub>3</sub>:  
C-Cl stretch at 666 cm<sup>-1</sup>

Table adapted from Aroca, *Surface Enhanced Vibrational Spectroscopy*, 2006

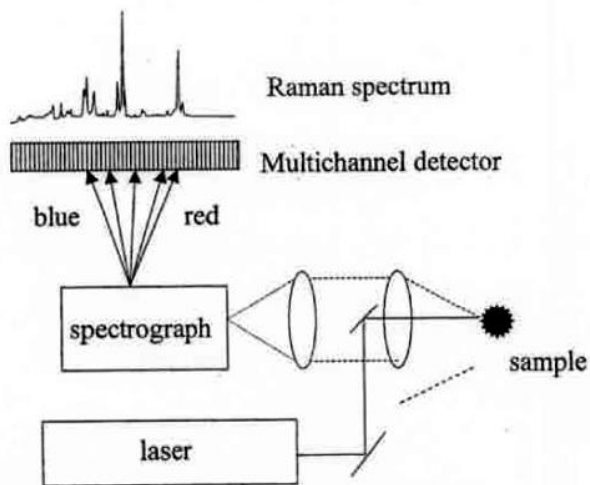
# *Advantages of Raman over IR*

- 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  $\propto$  to concentration and laser power.

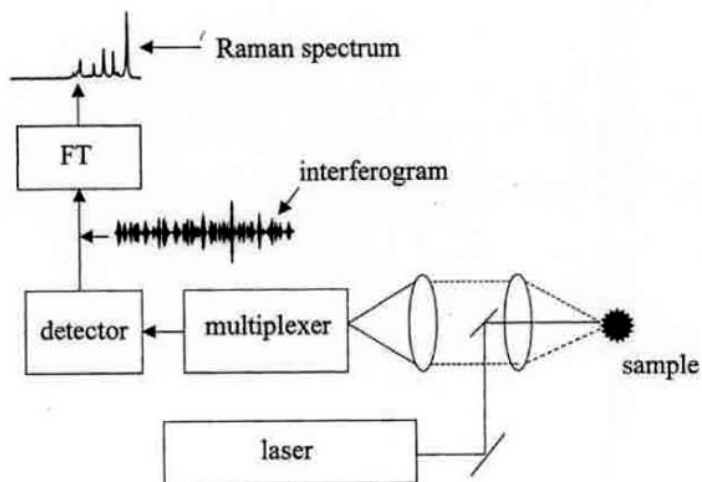
## *Advantages of IR over Raman*

- 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).

# Dispersive and FT-Raman Spectrometry



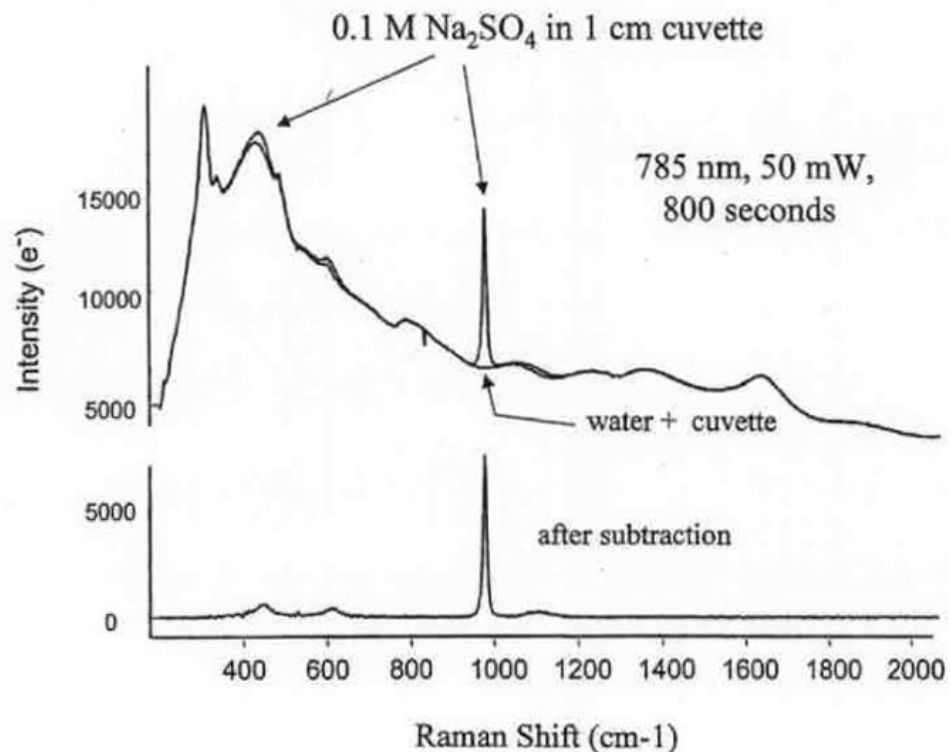
**Figure 5.1.** Schematic of the operation of a dispersive multichannel Raman spectrometer. Each detector element detects photons of a different Raman shift, and the spectrum is read out directly in terms of intensity (number of photons) vs. detector position (Raman shift).



**Figure 5.2.** Schematic of a nondispersive, FT-Raman spectrometer. A single detector monitors photons with all Raman shifts, after each has been modulated by a multiplexer such as an interferometer. Raman spectrum is obtained by Fourier transformation of the detector output (interferogram).

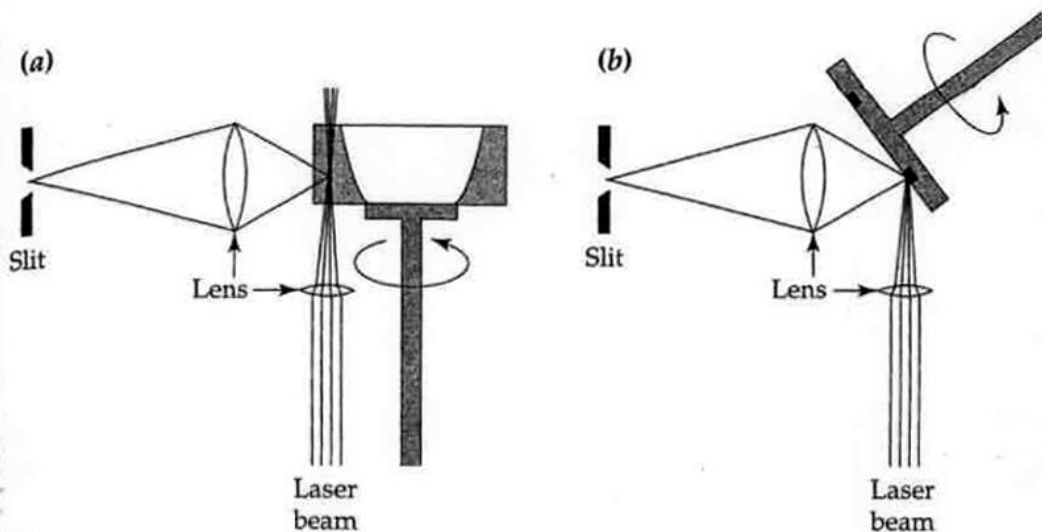
McCreery, R. L., *Raman Spectroscopy for Chemical Analysis*, 3rd ed., Wiley, New York: 2000

# Spectra from Background Subtraction



**Figure 5.9.** Spectra of 0.1 M Na<sub>2</sub>SO<sub>4</sub> in a 1 cm quartz cuvette in water obtained with a Chromex Raman 2000 spectrometer and EEV 15-11 deep depletion CCD (−90°C), 50 mm slit, 600 line/mm grating, 50 mW of 785 nm light at sample, 20 integrations of 40 sec each were averaged. Lower spectrum is difference between the two upper spectra.

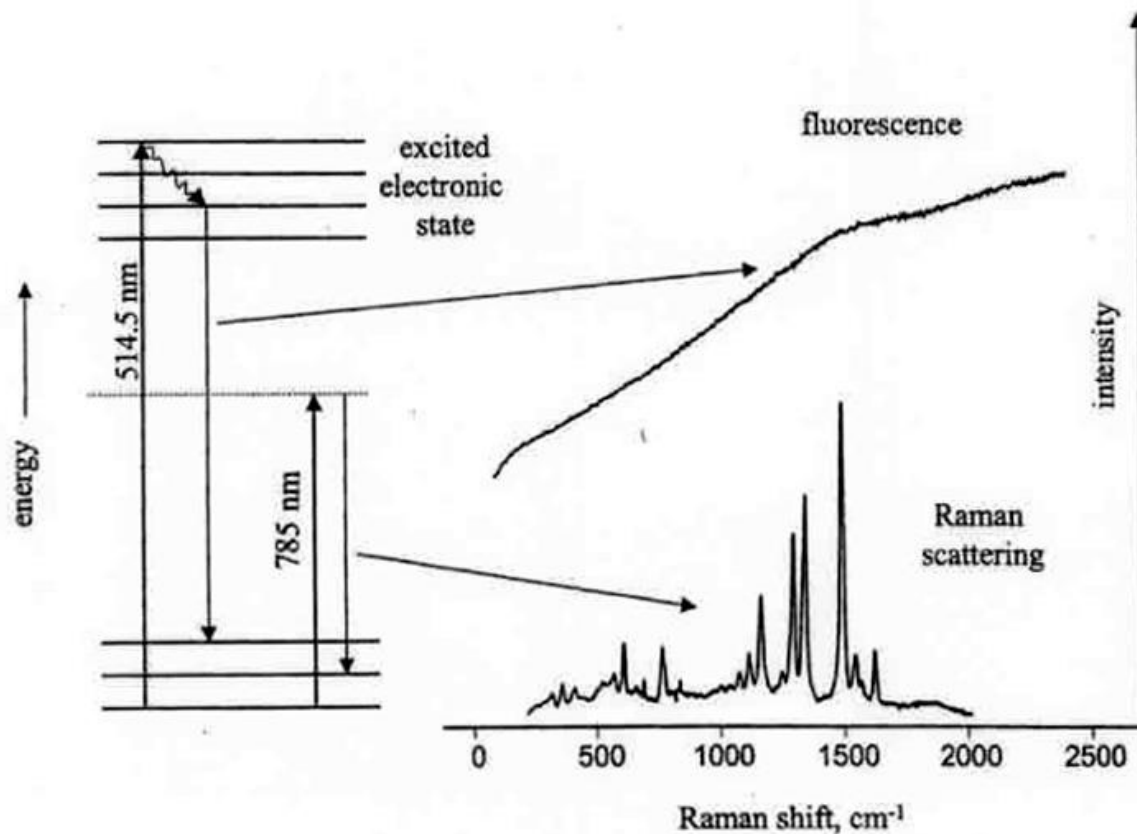
# Rotating Raman Cells



◀ FIGURE 10.17  
Handling of highly colored Raman samples.

To prevent overheating of colored samples by the laser radiation, the sample is constantly exchanged by rotating the sample. This spreads the heat over a larger area. (a) A liquid sample (shaded) is held in a cell, which is rotated. The laser beam irradiates the sample from below, and the reemitted light is collected by the lens and focused to the monochromator. (b) Solid samples can be packed into an incised ring on a rotating wheel (which can be cooled as well).

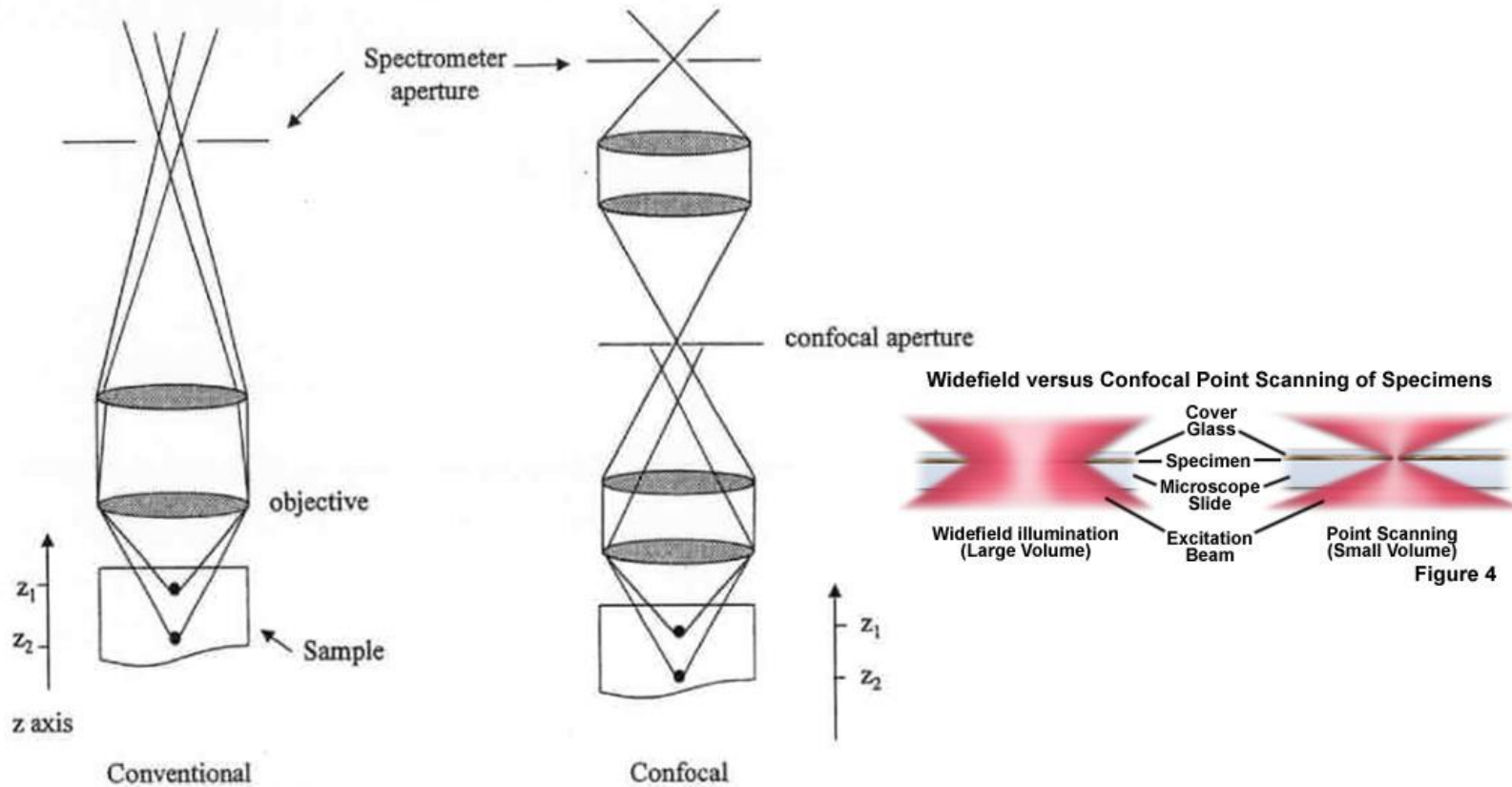
# Fluorescence Background in Raman Scattering



**Figure 1.3.** Energy levels associated with 514.5 and 785 nm light incident on a fluorescent sample. Energy and intensity scales are not to scale, and fluorescence intensity is several orders of magnitude greater than Raman scattering. Raman shift axis is relative to the incident laser frequency.



# Confocal Microscopy Optics



**Figure 11.9.** Schematic of confocal microscope optics, showing addition of a “confocal aperture” that restricts sampling depth;  $z_1$  and  $z_2$  represent two depths in a transparent sample.

# Confocal Aperture and Field Depth

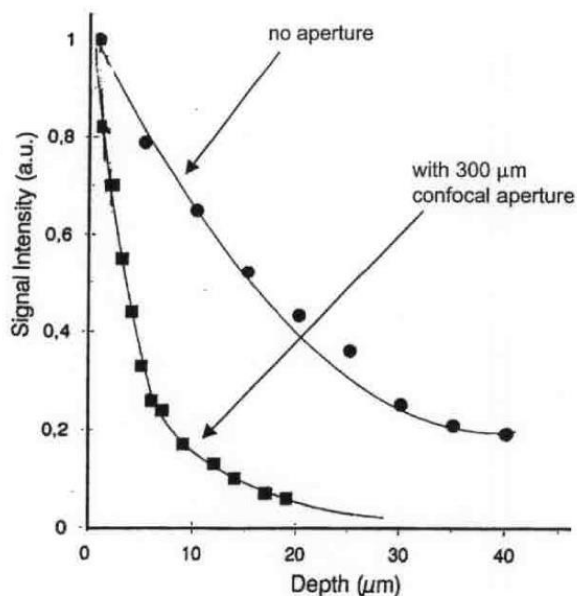


Figure 11.10. Effect of a confocal aperture on the signal for a 10  $\mu\text{m}$ -thick polyethylene film as a function of focus. An infinitesimal depth of field would yield a step function at zero depth. (Adapted from Reference 7.)

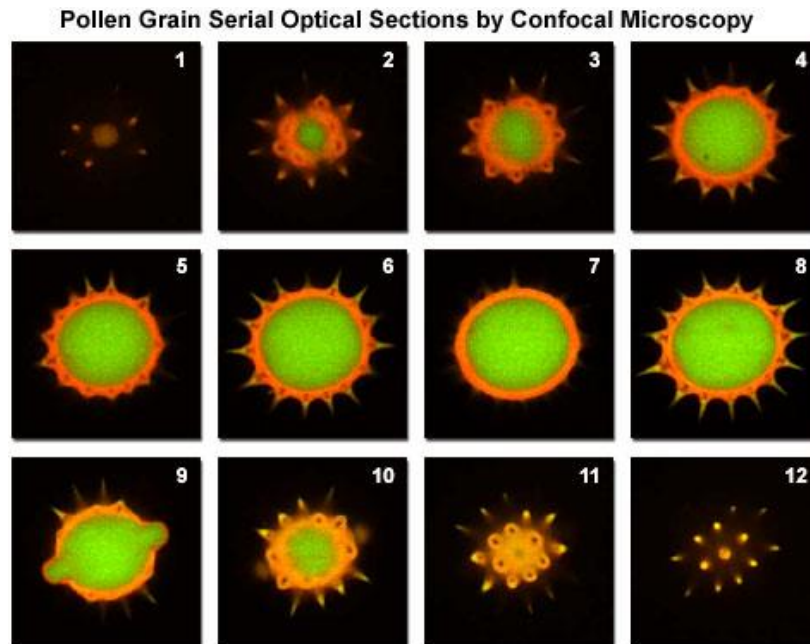
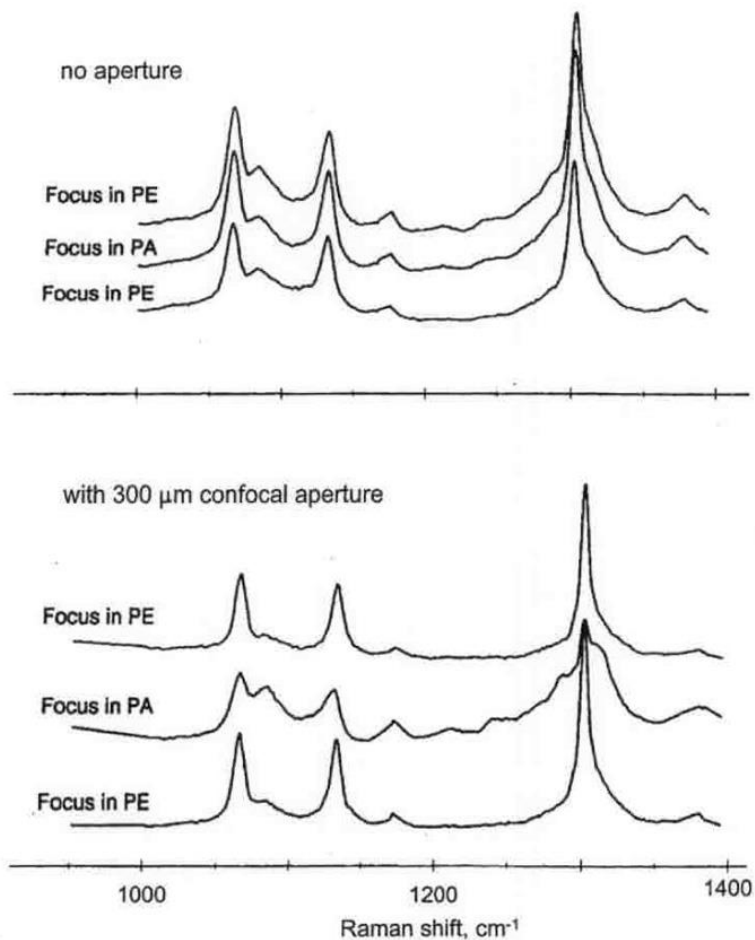


Figure 6

# Confocal Aperture and Field Depth



**Figure 11.11.** Raman spectra of a polyethylene (26 μm thick)/ polyamide (30 μm)/polyethylene (26 μm) laminate with and without a confocal aperture. The improved depth resolution with the aperture permits discrimination of polyethylene and polyamide spectral features. (Adapted from Reference 7.)

**Table 11.4. Depth Resolution (μm)**

Objective	Confocal Diameter (μm)			Reference
	500	300	100	
50 × LWD	>16			7
50 ×	>8	<6		7
100 ×	≈2	<2		7
100 ×			1.8	10

*THANK YOU*