Raman Spectroscopy
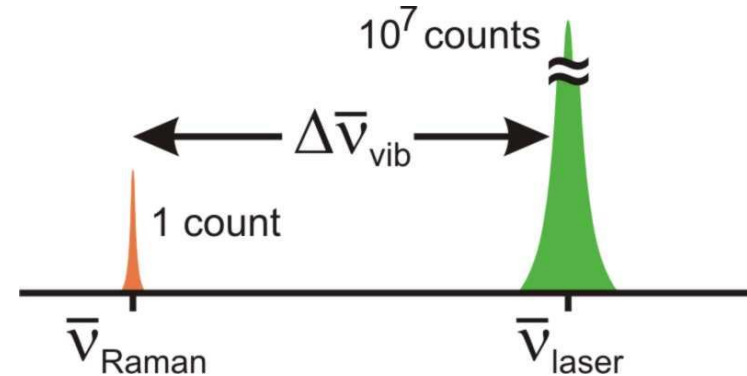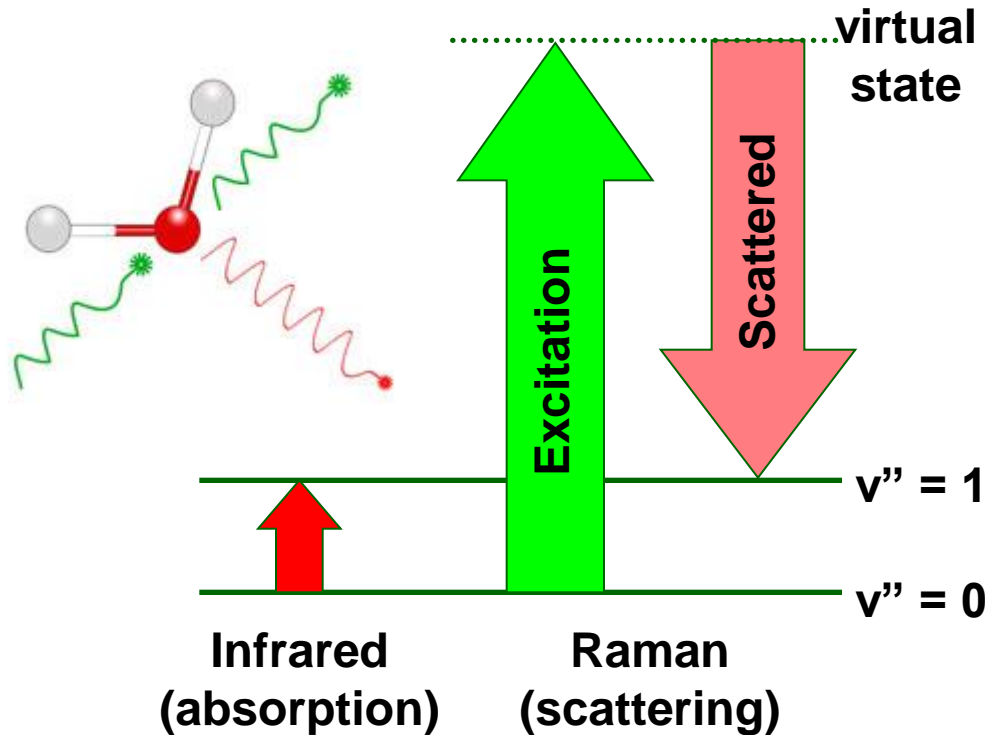
► The Raman effect is based on **inelastic scattering** of a monochromatic incident radiation

- routine energy range: 200 - 4000 cm^{-1}
- comprises a very small fraction, about **$1/10^7$** of the incident photons.

► Great for many samples!
- minimal sample preparation (gas, liquid, solid)
- compatible with wet samples and normal ambient
- *sample fluorescence is problematic!!*

The history of Raman effect

► Discovered in 1928 by Sir Chandrasekhra Venkata Raman, using sunlight as a source, telescope as a collector, his eyes as a detector.
► Subsequent mercury sources replaced by lasers in 1962
► Photographic plates replaced by photomultiplier tubes by 1953
► Double and triple monochromators introduced in 1960s; holographic gratings in 1968
► FT-Raman, array detectors, Raman microscopes more recent

► Sir Chandrasekhara Venkata Raman was the first scientist to describe and explain in the review Nature, in 1928 March 31, the experimental observation of this phenomenon in liquids.

It must be recalled that the theoretical principle of this effect was predicted in 1923 by A. Smekal, an Austrian physicist.

Other research groups was working on similar subjects at the same time (during 1928):
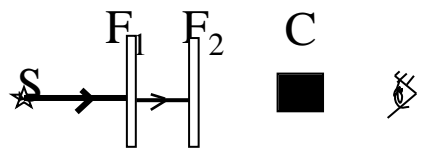
- L. Mandelstam, G. Landsberg in URSS (May 6)
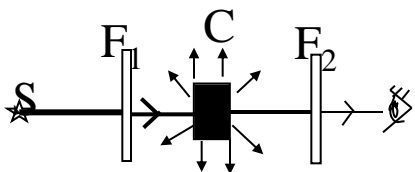- Jean Cabannes in France (ending of 1928).
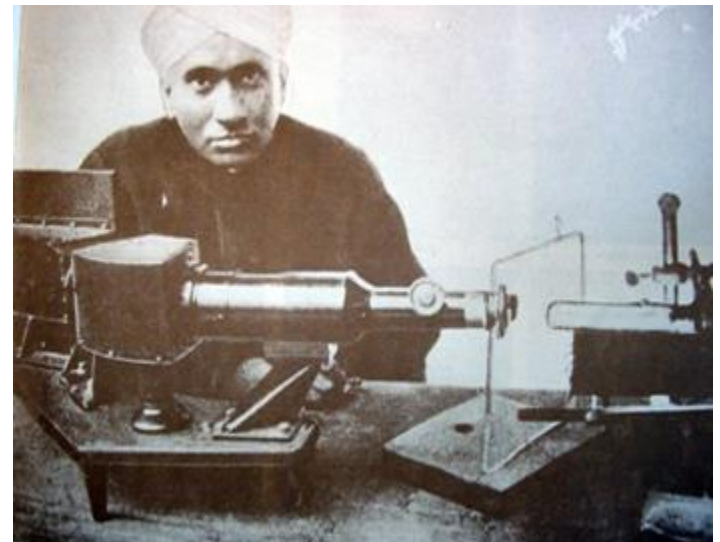
If we assume that the X-ray scattering of the 'unmodified' type observed by Prof. Compton corresponds to the normal or average state of the atoms and molecules, while the 'modified' scattering of altered wave-length corresponds to their fluctuations from that state, it would follow that we should expect also in the case of ordinary light two types of scattering, one determined by the normal optical properties of the atoms or molecules, and another representing the effect of their fluctuations from their normal state. It accordingly becomes necessary to test whether this is actually the case. The experiments we have made have confirmed this anticipation, and shown that in every case in which light is scattered by the molecules in dust-free liquids or gases, the diffuse radiation of the ordinary kind, having the same wave-length as the incident beam, **is accompanied by a modified scattered radiation** of degraded frequency.

The new type of light scattering discovered by us naturally requires very powerful illumination for its observation. In our experiments, a beam of sunlight was converged successively by a telescope objective of 18 cm aperture and 230 cm focal length, and by a second lens was placed the scattering material, which is either a liquid (carefully purified by repeated distillation in vacuum) or its dust-free vapor. To detect the presence of a modified scattered radiation, the method of complementary light-filters was used. A blue-violet filter, when coupled with a yellow-green filter and placed in the incident light, completely extinguished the track of the light through the liquid or vapor. The reappearance of the track when the yellow filter is transferred to a place between it and the observer's eye is proof of the existence of a modified scattered radiation. Spectroscopic confirmation is also available.
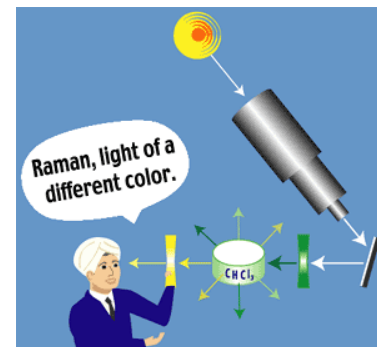
Some sixty different common liquids have been examined in this way, and every one of them showed the effect in greater or less degree. That the effect is a true scattering, and secondly by its polarization, which is in many cases quite strong and comparable with the polarization of the ordinary scattering. The investigation is naturally much more difficult in the case of gases and vapors, owing to the excessive feebleness of the effect. Nevertheless, when the vapor is of sufficient density, for example with ether or amylene, the modified scattering is readily demonstrable.

"dark"

"light"

Raman, light of a different color.

Hg lamp

C_6H_6 Raman spectrum

Nanometers

Ring Breathing Mode
992 cm^{-1}

Aromatic C-H Stretch
3063 cm^{-1}
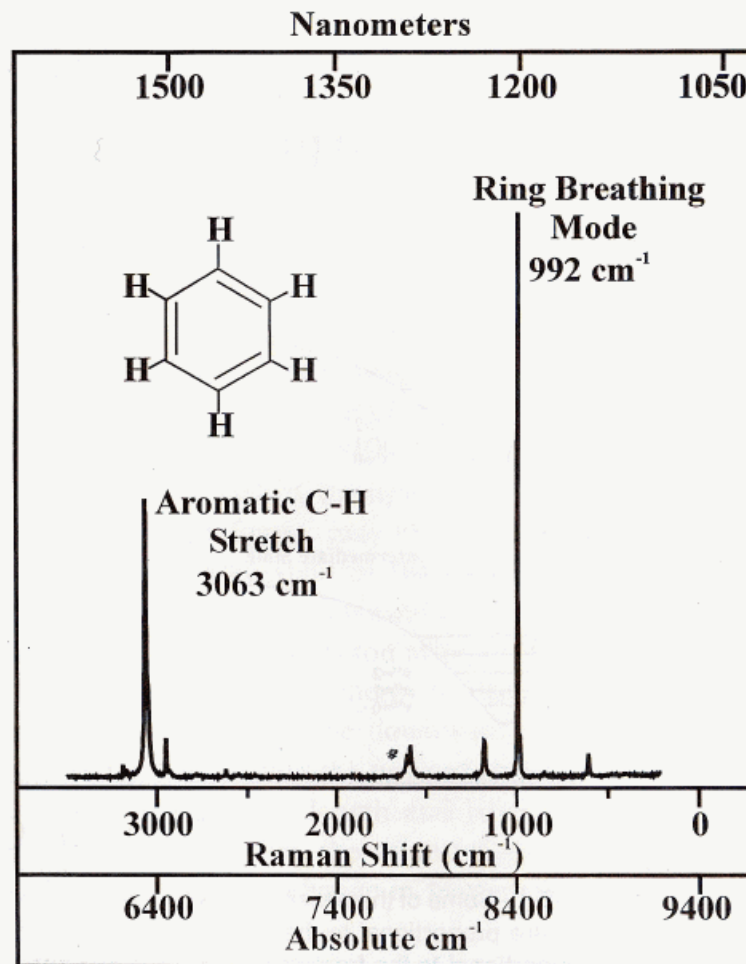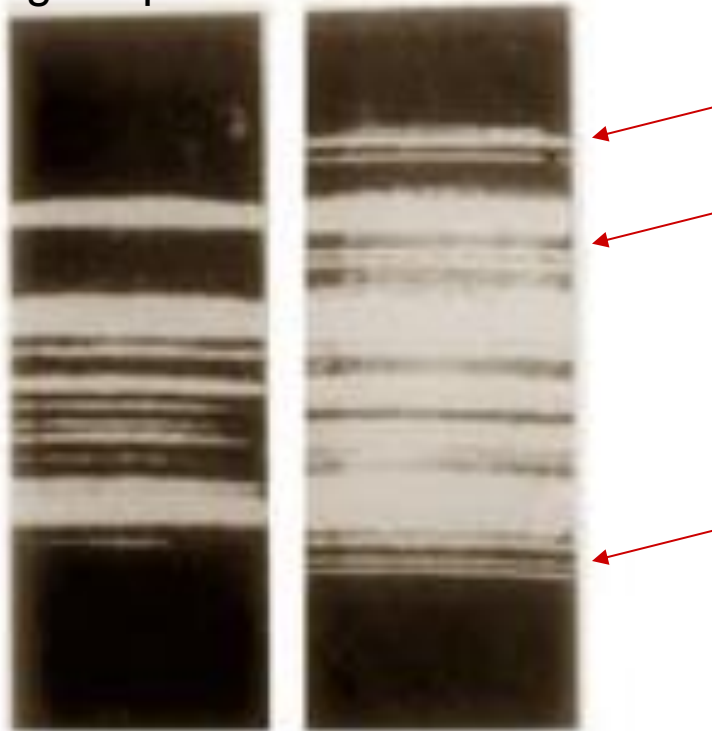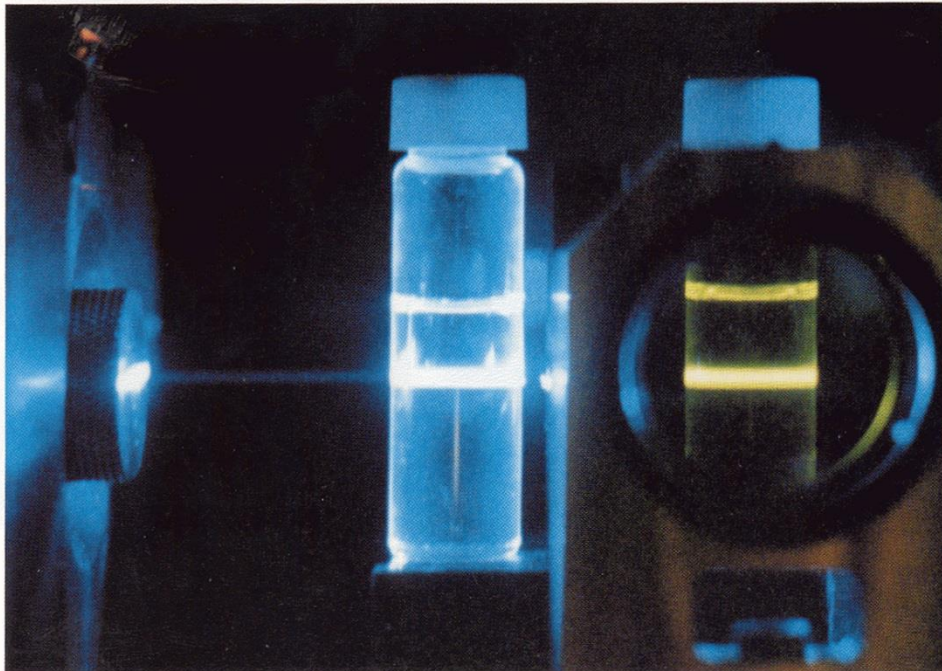
Raman Shift (cm^{-1})

Absolute cm^{-1}

FIGURE 2 FT-Raman spectrum of neat benzene.

Raman's experiment:

sunlight (white) → violet filter → violet → Scattering liquid

Rayleigh-scattered light / Raman-scattered light

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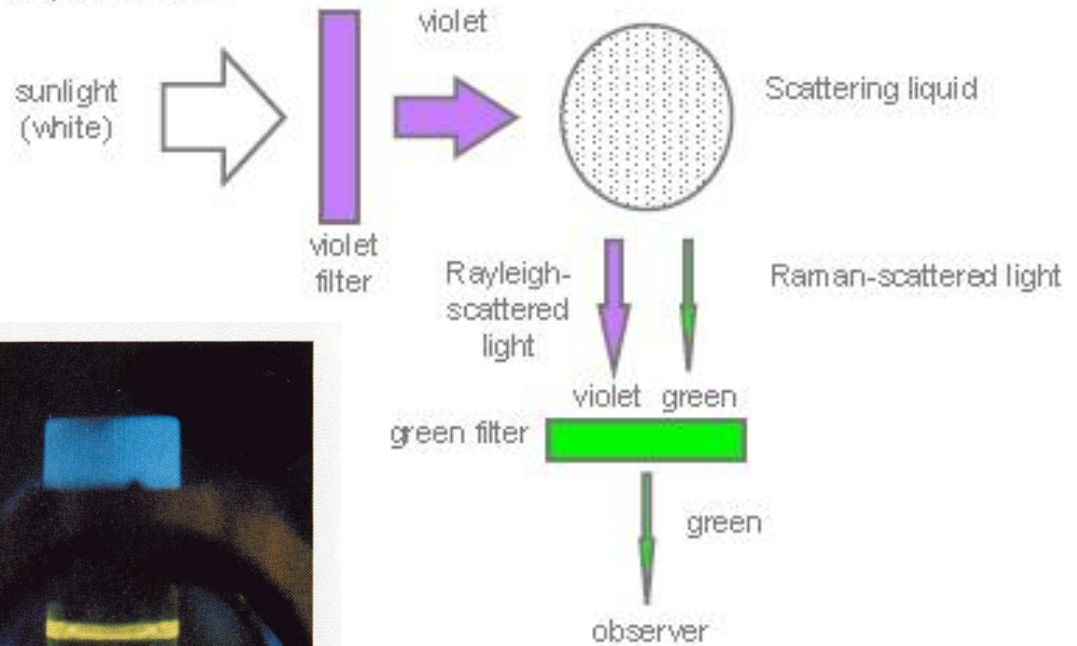
Raman scattering visible to the unaided eye, from a 488 nm laser beam passing through liquid cyclohexane. Left vial exhibits mostly Rayleigh scattering which obscures much weaker Raman scattering. Right vial is viewed through a 488 nm band rejection filter, which permits observation of longer wavelength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

Chandrasekhara Venkata Raman (1888-1970)

1928 ► Discovered the inelastic scattering phenomenon
1930 ► The Nobel Prize for Physics

Raman scattering: polarizability of molecule changes during vibration!

► *Polarizability is related to how easily the molecular orbital of a molecule can be deformed*

►An electric field will distort the molecular orbital (electron cloud)

►This is a weak effect that *grows with the square of the electric field intensity*
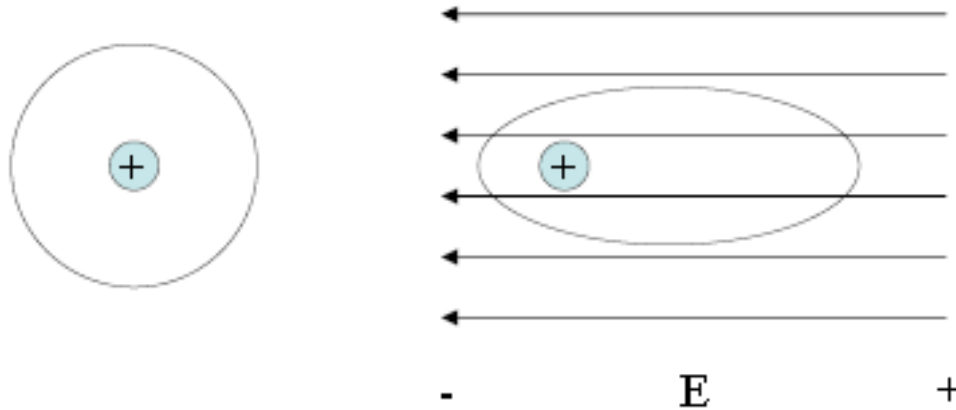
The electric field can distort the electron cloud of a molecule, creating an "induced" electric dipole moment

$$\mu_{ind} = \alpha E$$ Polarizability (α)

The induced electric dipole moment

► The oscillating electric field of the incident electromagnetic radiation will create an oscillating induced electric dipole moment which will **emit** *electromagnetic radiation (scattered radiation)*
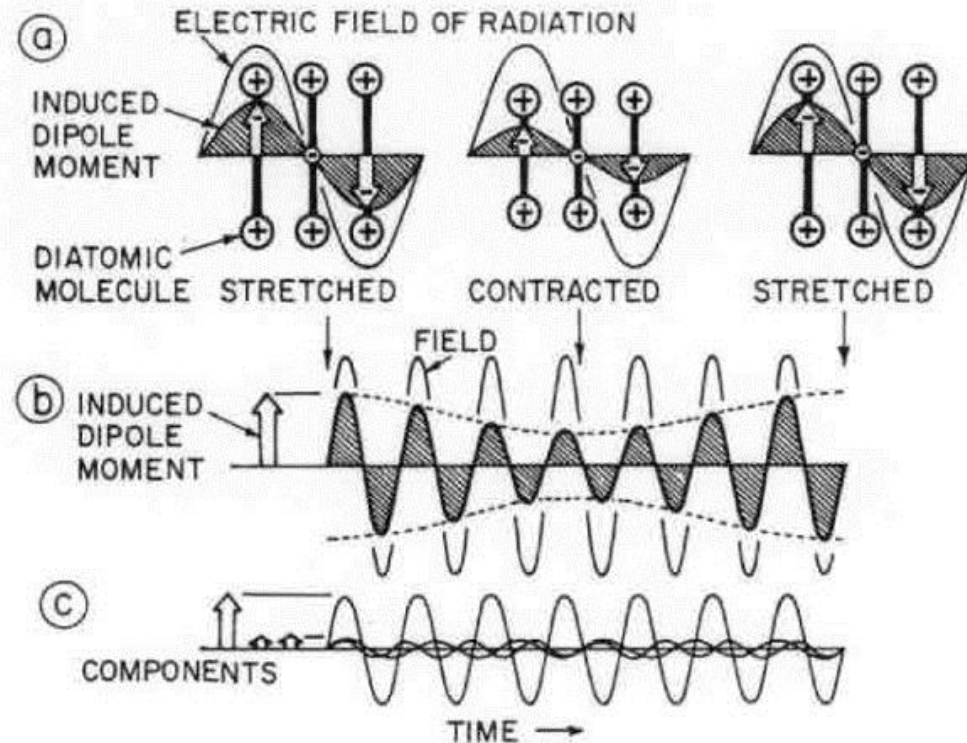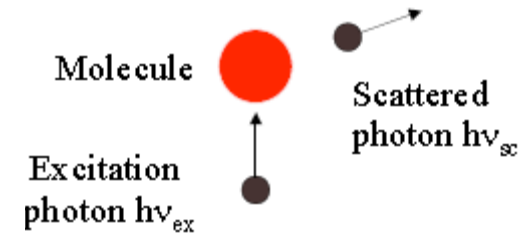

FIG. 1.32. Classical theory for the origin of the Raman effect. In (a) we see a diatomic molecule where "+" represents protons and "−" represents the center of gravity of the electrons. The electrons are displaced by the external field of the photon and an induced dipole moment is generated which changes 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.

►Rayleigh scattering: $\nu_{sc} \approx \nu_{ex}$ elastic interaction;

(no transfer of energy between molecule and photon)

► Raman scattering: $\nu_{sc} \neq \nu_{ex}$ inelastic interaction;

(transfer of energy between molecule and photon)

Stokes
Anti-Stokes

Virtual Energy States

Anti-Stokes Raman Scattering

Rayleigh Scattering

Stokes Raman Scattering

Excitation Energy

Vibrational Energy States

IR Absorbance

Molecule

Excitation photon $h\nu_{ex}$

Scattered photon $h\nu_{sc}$
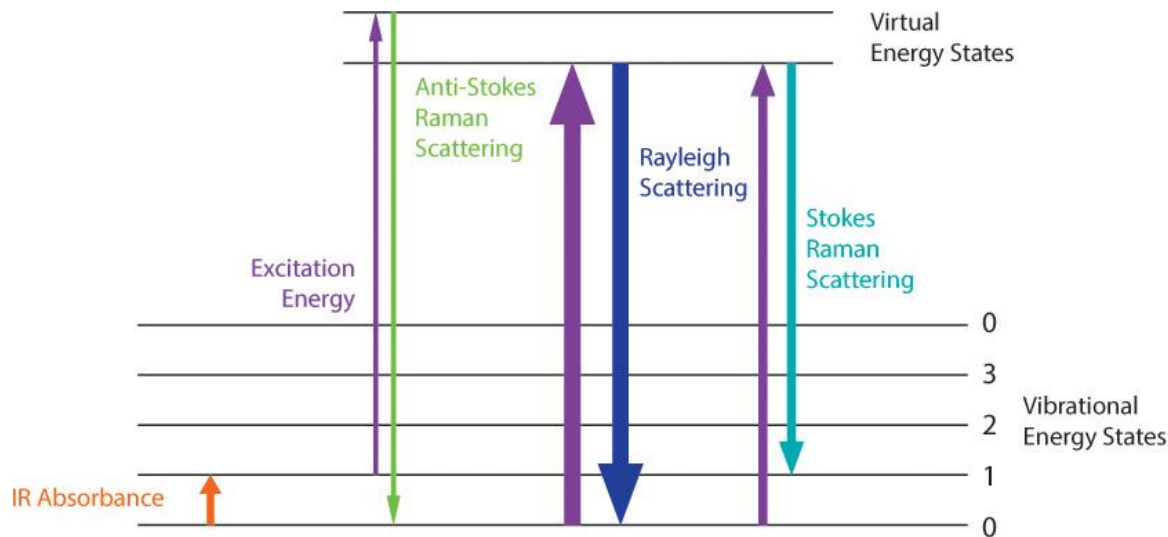
Stokes lines: energy of photon decreases:
$\nu_{sc} < \nu_{ex}$ (vibrational energy of molecule increases)

Anti-stokes lines: energy of photon increases:
$\nu_{sc} > \nu_{ex}$ (vibrational energy of molecule decreases)

$$\nu_{AS} = \nu_{ex} + \nu_{vb} \quad \text{or} \quad \nu_S = \nu_{ex} - \nu_{vb}$$

Vibrational Raman selection rules:

► *Polarizability of molecule must change* during a particular vibration (gross selection rule)

► $\Delta v = \pm 1$ (vibrational quantum number/vibrational energy levels) (specific selection rule)

Classical theory of Raman scattering

$$E = E_0 \cos 2\pi \nu_0 t$$

Fluctuation with time of incident electromagnetic wave (laser beam)

$$\mu \text{ (or } P) = \alpha E = \alpha E_0 \cos 2\pi \nu_0 t$$

Induced electric dipole moment (P or μ) in irradiated molecule; α is the polarizability

$$I = \frac{16\pi^4}{3c^3} \nu_0^{\,4} \mu_0^2$$

Classical expression for average rate of total scattered radiation

$$Q_k = Q_k^0 \cos 2\pi \nu_k t$$

Normal mode of vibration in molecule at frequency ν_k with amplitude Q_k^0

$$\alpha = \alpha_0 + \left(\frac{\partial \alpha}{\partial Q_k}\right)_0 Q_k + \cdots$$

Polarizablity is changed by vibration

$$\alpha E = \mu \text{ (or } P) = \alpha_0 E + \left(\frac{\partial \alpha}{\partial Q_k}\right)_0 Q_k E$$

Induced dipole is linear function of normal mode for small amplitude vibration

(Fourier series)

$$\alpha E = \mu \ (\text{or} \ P) = \alpha_0 E + \left(\frac{\partial \alpha}{\partial Q_k}\right)_0 Q_k E$$

Substitute time dependence of E and Q_k.

$$\mu = \alpha_0 E_0 \cos 2\pi \nu_0 t + E_0 Q_k^0 \left(\frac{\partial \alpha}{\partial Q_k}\right)_0 \cos 2\pi \nu_0 t \cos 2\pi \nu_k t$$

Apply trigonometric identity for product of two cosines

$$\mu = \alpha_0 E_0 \cos 2\pi \nu_0 t + \frac{1}{2} E_0 Q_k^0 \left(\frac{\partial \alpha}{\partial Q_k}\right)_0 \left[\cos 2\pi (\nu_0 + \nu_k) t + \cos 2\pi (\nu_0 - \nu_k) t\right]$$

| Rayleigh scattering | Anti-Stokes Raman scattering | Stokes Raman scattering |

Classical theory correctly predicts that Raman scattering should be weaker than Rayleigh scattering and that there is a simple linear dependence of Raman scattering on incident intensity and on sample concentration.

$$\mu = \underset{\sim}{\alpha}\mathbf{E}$$

• Expression for induced dipole moment can be written in terms of Cartesian components.

$$\mu_x = \alpha_{xx}E_x + \alpha_{xy}E_y + \alpha_{xz}E_z$$
$$\mu_y = \alpha_{yx}E_x + \alpha_{yy}E_y + \alpha_{yz}E_z$$
$$\mu_z = \alpha_{zx}E_x + \alpha_{zy}E_y + \alpha_{zz}E_z$$

• For μ we can use a matrix equation.
(μ and **E** are vectors, α is a tensor)

• Polarizability tensor is usually symmetric

$$\begin{bmatrix} \mu_x \\ \mu_y \\ \mu_z \end{bmatrix} = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix}$$

$$\alpha_{xy} = \alpha_{yx}; \quad \alpha_{yz} = \alpha_{zy}; \quad \alpha_{xz} = \alpha_{zx}$$

•Polarizability is divided into isotropic (s) and anisotropic (a) parts: $\alpha = \alpha^s + \alpha^a$

$$\alpha^s = \tfrac{1}{3}\left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right)$$

$$\alpha^a = \tfrac{1}{2}\left[\left(\alpha_{xx} - \alpha_{yy}\right)^2 + \left(\alpha_{yy} - \alpha_{zz}\right)^2 + \left(\alpha_{zz} - \alpha_{xx}\right)^2 + 6\left(\alpha_{xy}^2 + \alpha_{yz}^2 + \alpha_{xz}^2\right)\right]^{1/2}$$

$$I = \text{constant} \frac{(\nu_0 + \nu_{mn})^4}{\nu_{mn}} \cdot \frac{NI_0}{1 - \exp(-h\nu_{mn}/kt)} \left[45(\alpha'^s)^2 + 13(\alpha'^a)^2 \right]$$

$$\frac{I_{Stokes}}{I_{anti\text{-}Stokes}} = \frac{(\nu_0 - \nu_{mn})^4}{(\nu_0 + \nu_{mn})^4} \exp(h\nu_{mn}/kt) \qquad \text{for } m \to n \text{ transition, far from resonance}$$

α' = ∂α/∂Q (the polarizability derivative)

Boltzmann distribution is a major factor in determining relative Stokes and anti-Stokes intensity.
The excited vibrational state will be only thermally populated, *and Stokes intensity will be much larger than anti-Stokes.*

$$\frac{I_{Stokes}}{I_{antiStokes}} = \left(\frac{\nu_0 - \nu_{vib}}{\nu_0 + \nu_{vib}} \right)^4 e^{\frac{h\nu_{vib}}{kT}} = \left(\frac{\overline{\nu}_0 + \overline{\nu}_k}{\overline{\nu}_0 - \overline{\nu}_k} \right)^4 e^{\frac{hc\overline{\nu}_k}{kT}}$$

$$I(\omega_0, \omega_s) = k'_\omega \omega_s^4 (\mu_\alpha^I)^2 \sin^2 \theta \qquad\qquad k'_\omega = \frac{1}{32\pi^2 \varepsilon_0 c_0^3}$$

Intensity from induced electric dipole moment as function of scattering angle

$$\mu_\alpha^I(t) = \sum_\beta \alpha_{\alpha\beta}(t) E_\beta^{(0)}(t) = \alpha_{\alpha\beta}(t) E_\beta^{(0)}(t)$$

Induced electric dipole moment in explicit Cartesian summation or implied summation over x, y and z of repeated Greek indices

$$E_\beta^{(0)}(t) = E_{\beta,0}^{(0)} \cos\omega_0 t \qquad \alpha_{\alpha\beta}(t) = \alpha_{\alpha\beta,0} + \left(\frac{\partial\alpha_{\alpha\beta}}{\partial Q_a}\right)_{Q_a=0} Q_a \cos\omega_a t$$

$$\mu_\alpha^I(t) = \alpha_{\alpha\beta,0} E_{\beta,0}^{(0)} \cos(\omega_0 t) + \left(\frac{\partial\alpha_{\alpha\beta}}{\partial Q_a}\right)_0 Q_a E_{\beta,0}^{(0)} \cos(\omega_0 t)\cos(\omega_a t)$$

$$\mu_\alpha^I(t) = \alpha_{\alpha\beta,0} E_{\beta,0}^{(0)} \cos(\omega_0 t) + \frac{1}{2}\left(\frac{\partial\alpha_{\alpha\beta}}{\partial Q_a}\right)_0 Q_a E_{\beta,0}^{(0)} \left[\cos(\omega_0 - \omega_a)t + \cos(\omega_0 + \omega_a)t\right]$$

Rayleigh   Stokes   Anti-Stokes

Raman intensity is proportional with **Raman scattering cross-section** (σ [cm^2])

Raman scattering cross-sections = target area presented by a molecule for scattering – depend on excitation frequency

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

Ω - the scattering solid angle

Process	Cross-Section of	σ (cm^2)
absorption	UV	10^{-18}
absorption	IR	10^{-21}
emission	Fluorescence	10^{-19}
scattering	Rayleigh	10^{-26}
scattering	Raman	10^{-29}
scattering	RR	10^{-24}
scattering	SERRS	10^{-15}
scattering	SERS	10^{-16}

λ_{ex} (nm)	σ (x10^{-28} cm^2)
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$_3$:   C-Cl stretch at 666 cm^{-1}
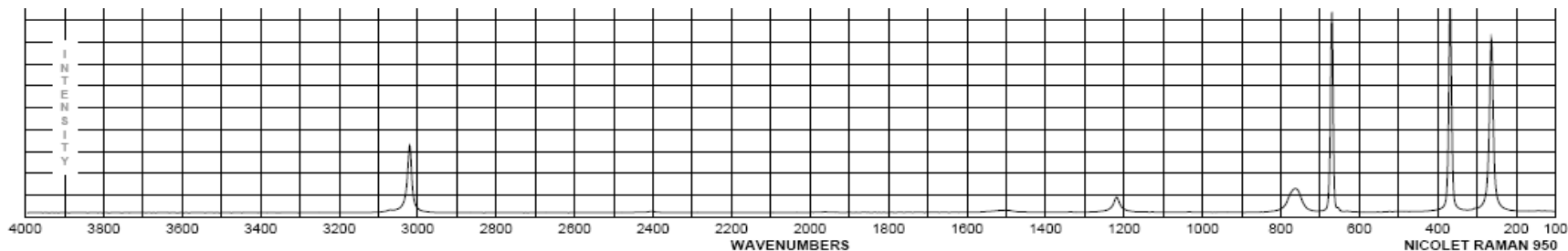
Stokes vs Anti-Stokes

Rayleight $\quad \nu_{Ray} = \nu_{ex} \qquad\qquad \overline{\nu}_{Ray} = \overline{\nu}_{ex}$

Stokes $\qquad \nu_{Stokes} = \nu_{ex} - \nu_{vib} \qquad \overline{\nu}_S = \overline{\nu}_{ex} - \overline{\nu}_{vib} \qquad \overline{\nu}_{ex} = \dfrac{1}{\lambda_{ex}}$

Anti-Stokes $\quad \nu_{AntiStokes} = \nu_{ex} + \nu_{vib} \qquad \overline{\nu}_{AS} = \overline{\nu}_{ex} + \overline{\nu}_{vib}$

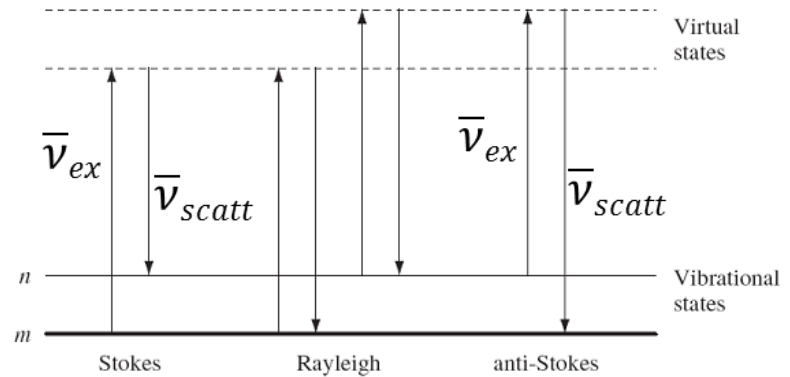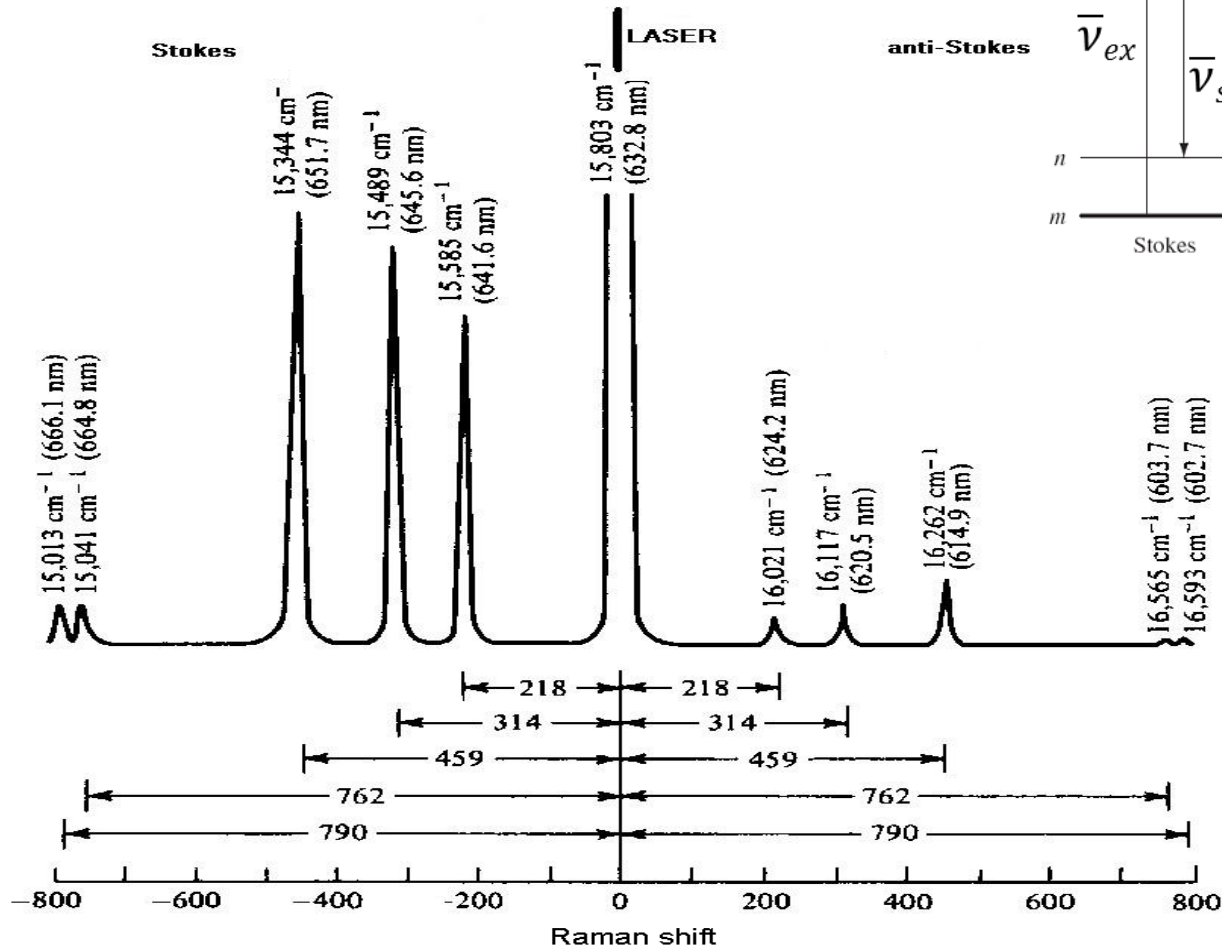Raman Scattering — CCl$_4$
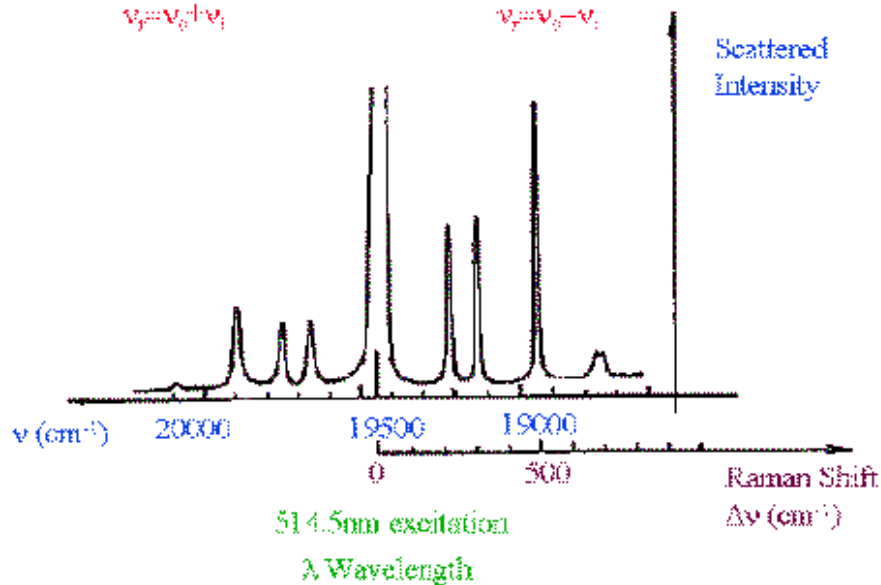
Raman spectrum of Sulfur
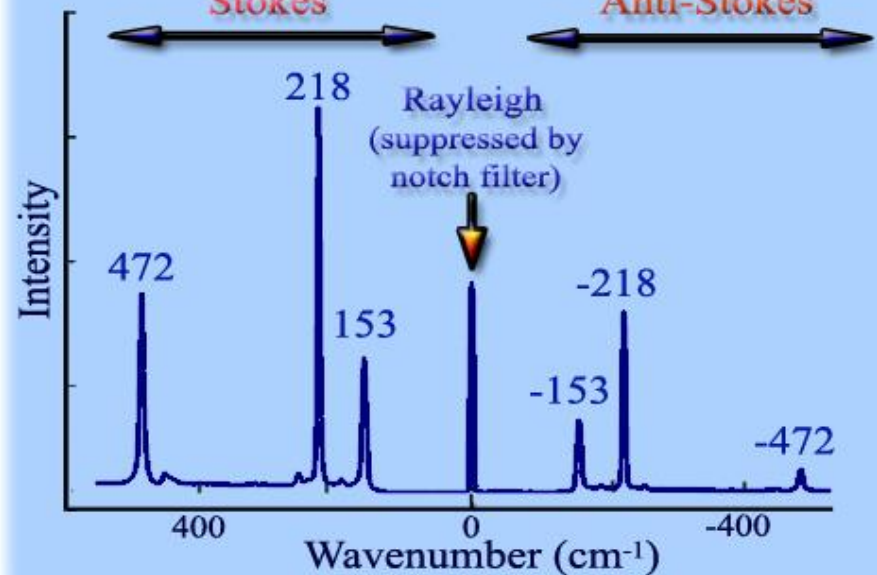
Raman shift ($\Delta\bar{\nu}$) = difference between excitation radiation wavenumber ($\bar{\nu}_{ex}$) and scattered radiation wavenumber ($\bar{\nu}_{scatt}$).

Stokes:

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

Anti-Stokes:

$$\Delta\bar{\nu}_{AS} = \bar{\nu}_{ex} - \bar{\nu}_{AS} = -\bar{\nu}_{vib}$$

The intensity of Stokes bands is not temperature dependent.
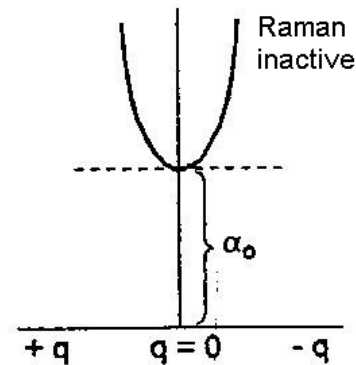The intensity of Anti-Stokes bands is temperature dependent.

A vibration is Raman active if the **polarizability of molecule changes during vibration**:

$$\left(\frac{\partial \alpha}{\partial Q_k}\right)_0 \neq 0$$

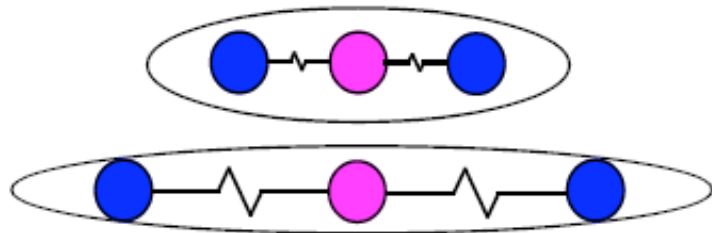The value of first derivative of polarizability at the origin (tangent, slope) influence the intensity of Raman band.

Raman active

α_o

+q   q = 0   - q

$(d\alpha/dq)_0 \neq 0$

Raman inactive

α_o

+q   q = 0   - q
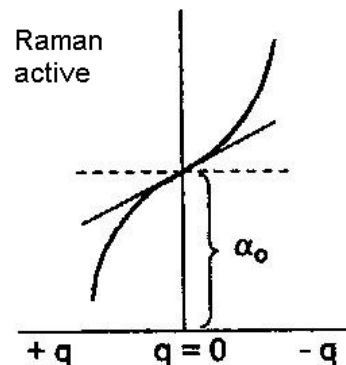
$(d\alpha/dq)_0 = 0$

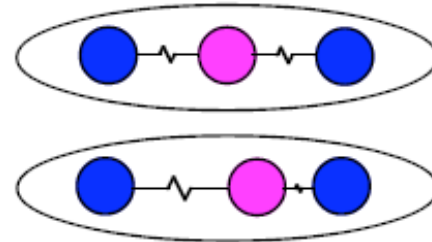For small molecule, polarizability can be figured like an <u>ellipsoid</u>:

Symmetric stretching vibration of CO_2

► Polarizability changes during vibration
  → Raman band at 1340 cm^{-1}
►Dipole moment does *not*
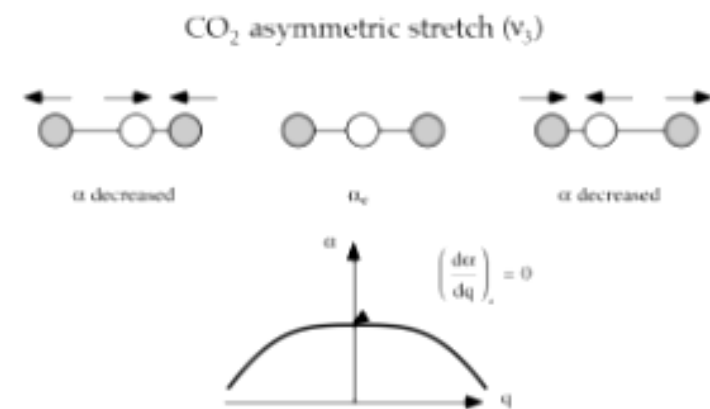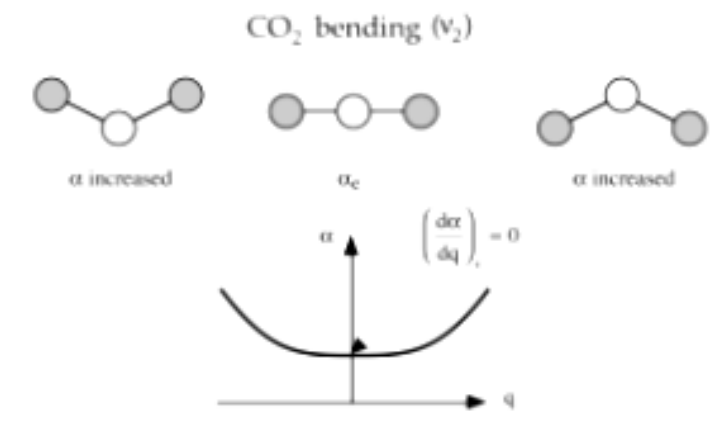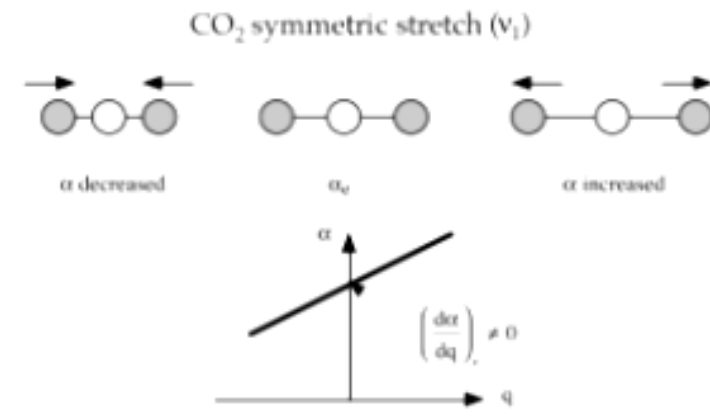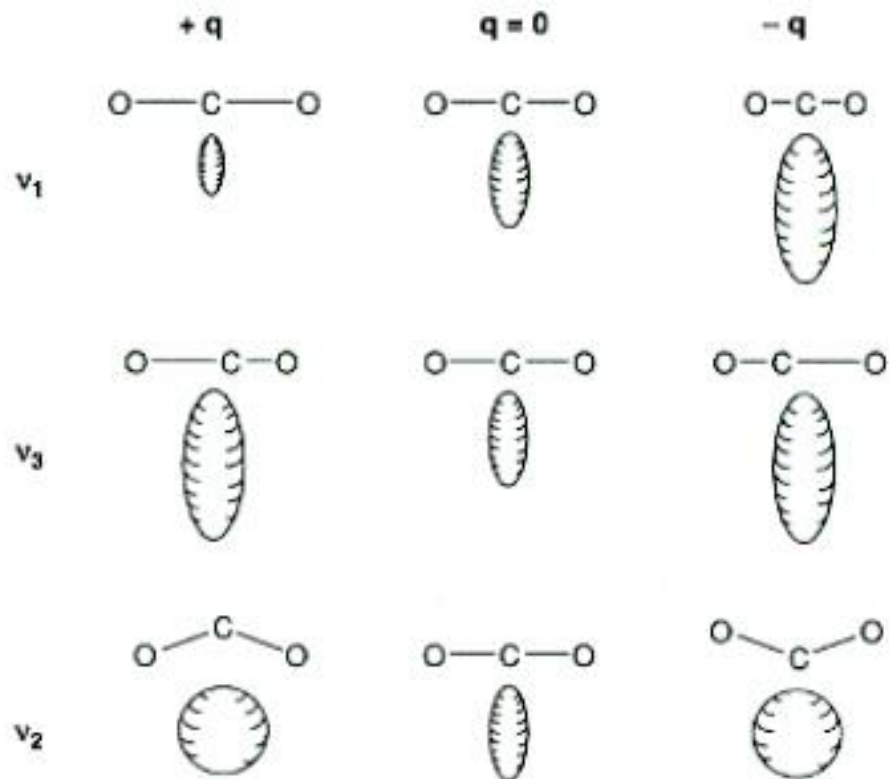→ no IR absorption band at 1340 cm^{-1}

Asymmetric stretching vibration of CO_2

► Polarizability does *not* change during vibration
  → no Raman band near 2350 cm^{-1}
► Dipole moment does change
→ IR absorption band at 2349 cm^{-1}

CO$_2$ symmetric stretch (ν_1)

α decreased α_e α increased

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

CO$_2$ bending (ν_2)

α increased α_e α increased

$\left(\dfrac{d\alpha}{dq}\right)_e = 0$

CO$_2$ asymmetric stretch (ν_3)

α decreased α_e α decreased

$\left(\dfrac{d\alpha}{dq}\right)_e = 0$

ν_1 vibration is **Raman active** (the ellipsoid size is changing).

ν_2 and ν_3 vibrations are *Raman inactive* (the variations of size and shape are only apparent!)

- in extreme positions the ellipsoid has the same shape and size therefore, the function $(d\alpha/dQ)_0$ slope at the origin is zero.

	+ q	q = 0	- q

v_1

v_2

v_3
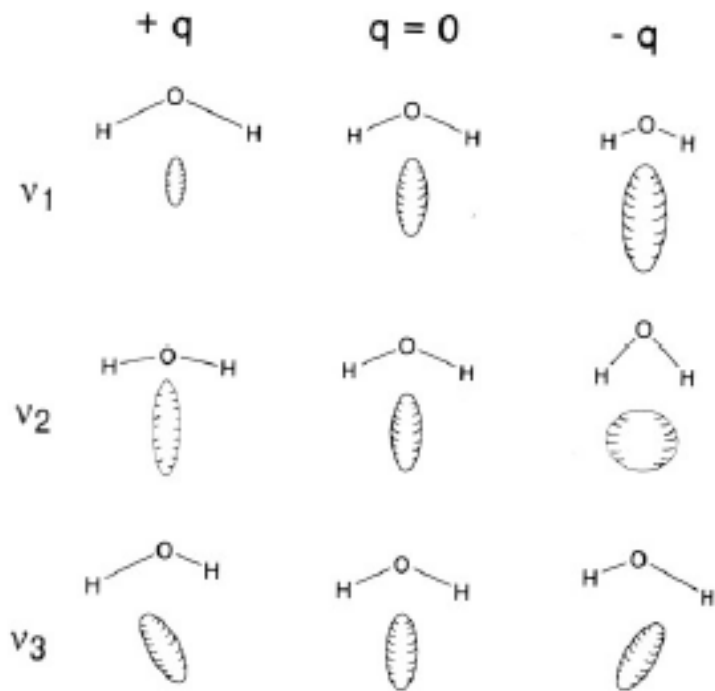
All the modes are both
Raman & IR Active

v_1 vibration - **Raman active** (the ellipsoid size is changing).

v_2 vibration - **Raman active** (the ellipsoid shape is changing).

v_3 vibration - **Raman active** (the ellipsoid orientation is changing).

The symmetric stretch (v_1) determine a very strong Raman band, while asymetric vibration (v_3) are very weak.

In practice is accepted the idea that Raman spectrum of H_2O molecule has a single band at 3652 cm^{-1}!!! (due to symmetric stretching)

Depolarization ratio

The Raman scattered light is emitted by the stimulation of the electric field of the incident light. Therefore, the direction of the vibration of the electric field (polarization direction) of the scattered light might be expected to be the same as that of the incident light.

In reality, however, some fraction of the Raman scattered light has a polarization direction that is perpendicular to that of the incident light. This component is called the **perpendicular component**.

The component of the Raman scattered light whose polarization direction is parallel to that of the incident light is called the **parallel component**, and the Raman scattered light consists of the parallel component and the perpendicular component.
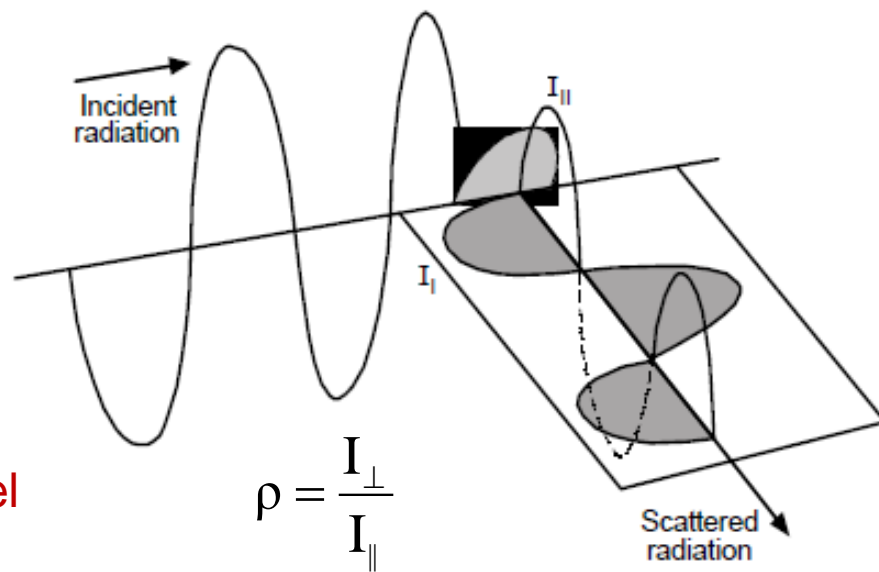
The **depolarization ratio** ρ (in Raman spectroscopy) is the intensity ratio between the perpendicular component and the parallel component of the Raman scattered light

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

Incident radiation

$I_\parallel$

$I_\perp$

Scattered radiation

$$I \approx \mu^2 \cdot \nu^4 \qquad \mu_x = \alpha_{xy}E_y \qquad \mu_y = \alpha_{yy}E_y$$

$$\boxed{\rho = \frac{I_\perp}{I_\parallel} = \frac{I_x}{I_y} = \frac{\alpha_{xy}^2}{\alpha_{yy}^2}}$$

Rayleigh:
$$\bar{\rho} = \frac{3\gamma^2}{45\bar{\alpha}^2 + 4\gamma^2}$$

$$\begin{cases} \bar{\alpha} = \dfrac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \\ \gamma^2 = \dfrac{1}{2}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6(\alpha_{xy}^2 + \alpha_{yz}^2 + \alpha_{xz}^2) \end{cases}$$

α is non-zero only for totally symmetric vibrations.

For totally symmetric vibrations $\quad 0 \le \rho \le 3/4$

For non-totally symmetric vibrations $\quad \rho = 3/4$

Raman:
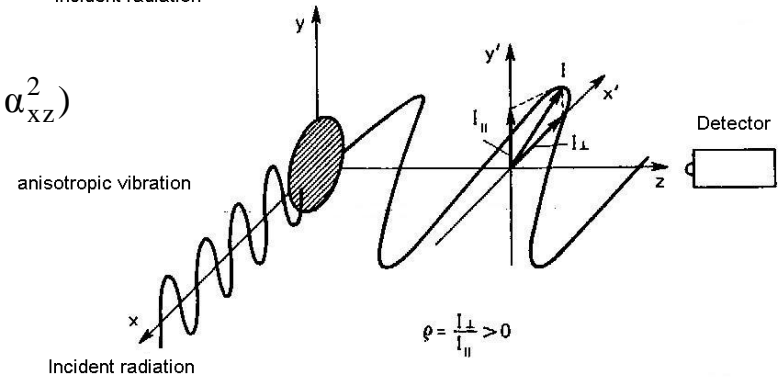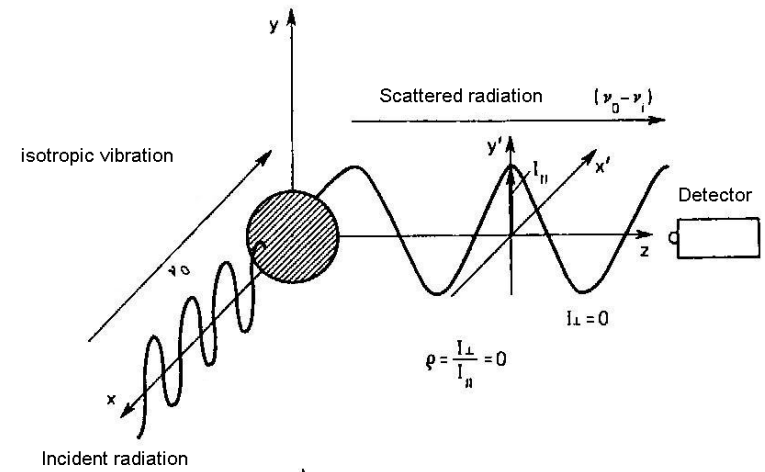$$\boxed{\rho = \frac{3\gamma'^2}{45\bar{\alpha}' + 4\gamma'^2}}$$
(Polarised laser radiation: $\rho_{max} = 3/4$)

$$\bar{\alpha} \Rightarrow \frac{\partial \bar{\alpha}}{\partial Q_k} = \bar{\alpha}' \qquad \gamma \Rightarrow \frac{\partial \gamma}{\partial Q_k} = \gamma'$$

If laser radiation is unpolarised:
$$\rho_{max} = 6/7.$$

$$\boxed{\rho = \frac{6\gamma'^2}{45\bar{\alpha}'^2 + 7\gamma^2}}$$

► $\rho = 0$ *total symmetric vibration*
► $0 < \rho < 3/4$ *partial symmetric vibration*
► $\rho = 3/4 = \rho_{max}$ *total asymmetric vibration*

The value of the depolarization ratio of a Raman band depends on the **symmetry of the molecule** and on the **symmetry of normal vibrational mode**.

$\rho = 0$ total symmetric vibrational mode (cubic point grups)
$0 < \rho < 0.75$ partial symmetric vibrational mode
$\rho = 0.75$ total asymmetric vibrational mode

$\rho < 0.75$ polarized band
$\rho = 0.75$ depolarized band

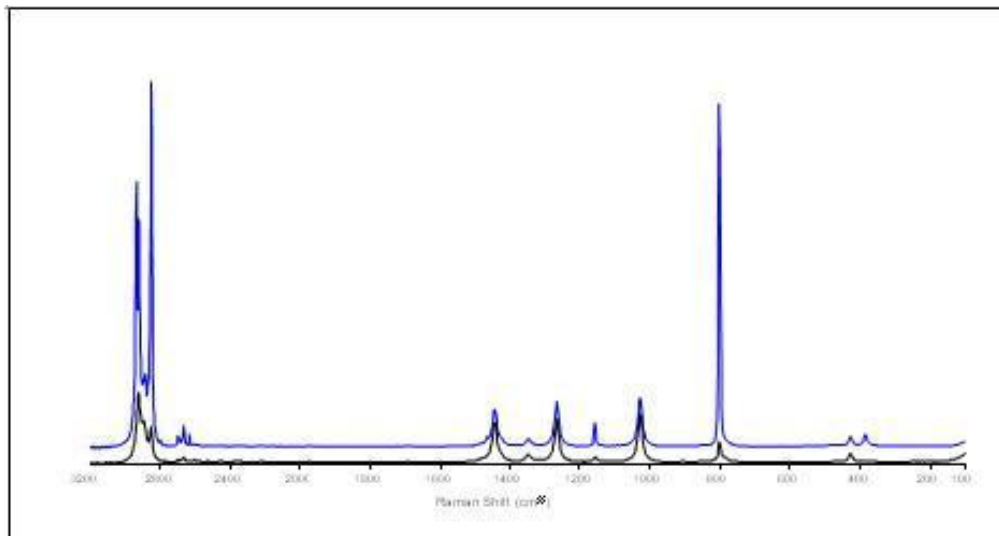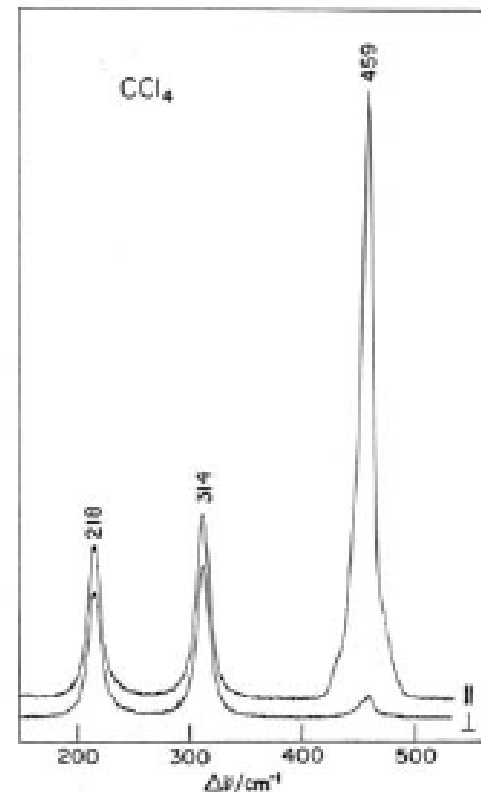$$\rho = \frac{3\gamma'^2}{45\overline{\alpha'} + 4\gamma'^2}$$

Figure 1, Raman spectra of cyclohexane arising from analysis Parallel (Blue) and Perpendicular (Black) to the excitation laser polarisation.

Raman Scattering vs IR Absorption

Raman Scattering

► involves changes in the polarizability (α) of the molecule (induced dipole)
► the electric field of the molecule oscillates at the frequency of the incident wave (the induced dipole emits electromagnetic radiation!)
► if induced dipole is not constant, inelastic scattering is allowed (Raman)
► if induced dipole is constant, scattering is elastic (Rayleigh/Mie)

Raman spectroscopy
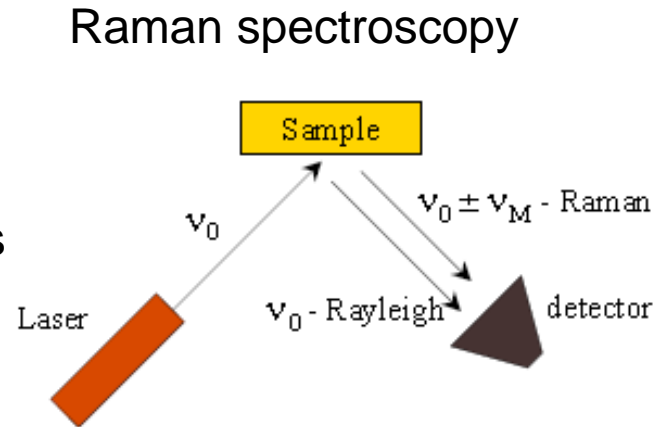
IR absorption

- involves changes in the dipole moment (μ) of the molecule (during vibrations)
- - some vibrational modes are both IR and Raman active!
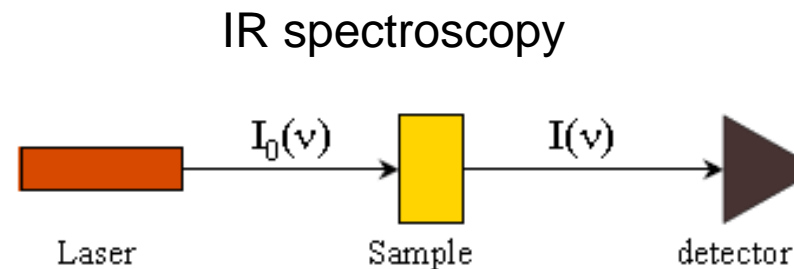
IR spectroscopy

Infrared and Raman spectroscopy are two kinds of spectroscopy
- the spectrum is a graph of light intensity as a function of light frequency
- peaks in the spectrum give information about molecular structure
- from molecular structure, the compound can be identified

The rule of "mutual exclusion"

If a molecule has a *center of symmetry*, then no transition is allowed in both its Raman scattering and IR absorption, but only in one or the other.

CO_2:	Band	Infrared	Raman
	v_1 - symmetric stretching (1330 cm^{-1})	inactive	active
	v_2 - asymmetric stretching (2349 cm^{-1})	active	inactive
	v_3 - bending (667 cm^{-1})	active	inactive

For CO_2, vibrational modes that are IR active are Raman inactive and vice-versa.

The general rule: *symmetric vibrations give intense Raman bands and weak IR bands.*

The fact that H_2O does not obey the rule of mutual exclusion indicates that the H_2O molecule is not centrosymmetric (it is bent).

As expected, the v_1 symmetric stretch is also strongly Raman active.

H_2O:	Band	Infrared	Raman
	v_1 - symmetric stretching (3652cm^{-1})	strong	strong
	v_2 - asymmetric stretching (3755cm^{-1})	very strong	weak
	v_3 - bending (1595cm^{-1})	very strong	weak

Raman and infrared active modes

Diatomics

		IR	Raman
Homonuclear		No	Yes
Heteronuclear		Yes	Yes

- A vibrational mode is active for IR-absorption if the **dipole moment** of the molecule **changes** when the atoms are displaced relative to one another (note that the molecule need not have a permanent dipole moment to be IR active).

- A vibrational mode is **Raman-active** if the **polarizability** of the molecule **changes** when the atoms are displaced relative to one another.

Triatomics

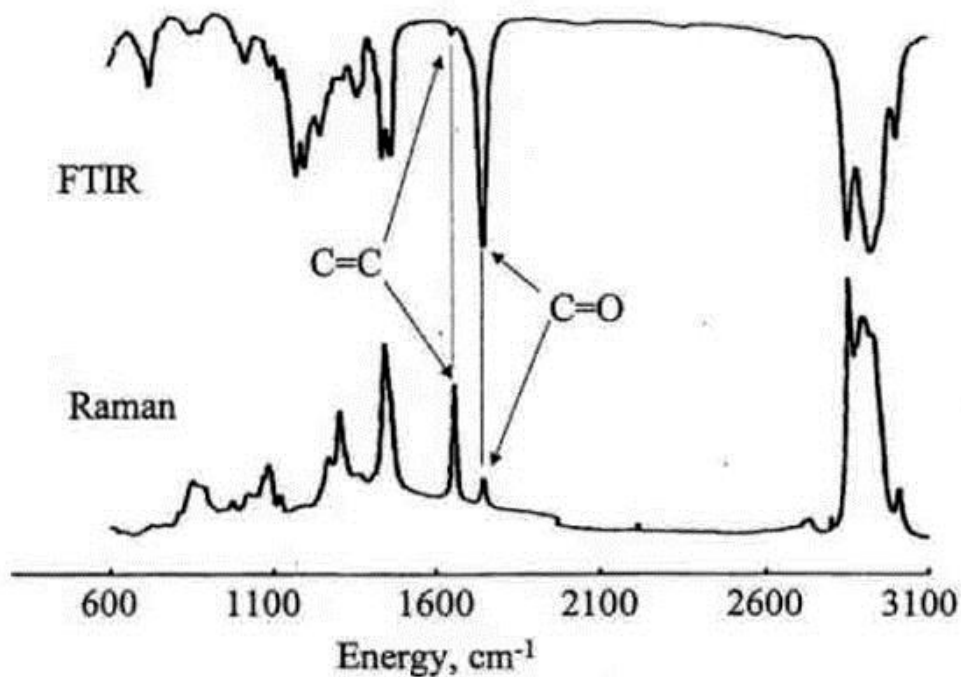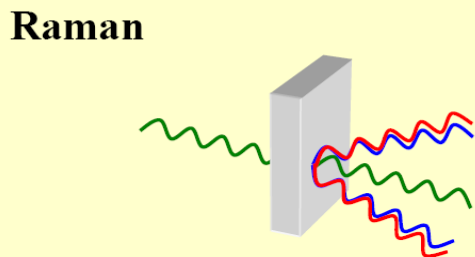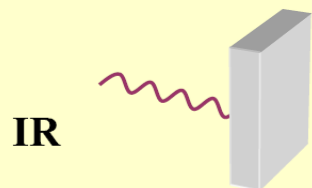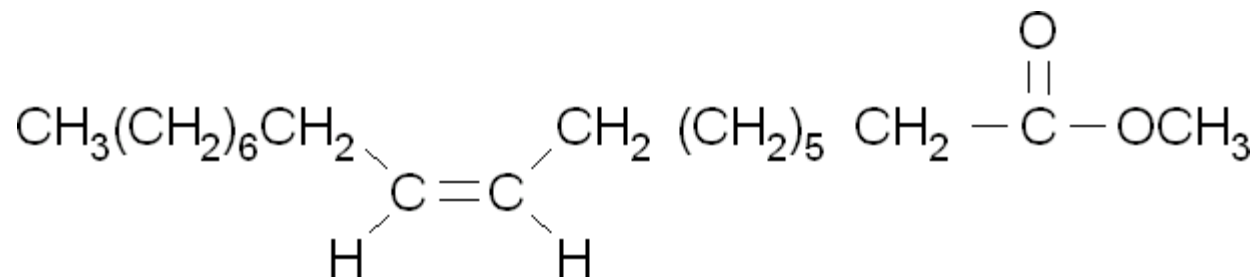|	IR	Raman
Symmetric linear		
Symmetric stretch	No	Yes
Asymmetric stretch	Yes	No
Bending	Yes	No
Symmetric non-linear		
All modes	Yes	Yes
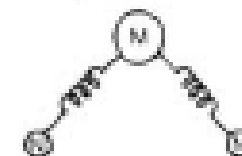
FTIR (upper) transmission and Raman scattering (lower) of oleic acid methyl ester.

Combined Infrared and Raman: structure determination and band assignment

Structure determination and band assignment rely on several factors:

(i) Number of fundamental vibrational modes

There are $(3N - 5)$ vibrational modes for linear molecules and $(3N - 6)$ vibrational modes for bent molecules. Note that if a molecule is linear, perpendicular vibrations are always doubly degenerate, and thus appear in spectra as a single bands.

Hot bands are likely to be present, but are generally weaker because of population considerations. Hot bands which involve transitions between different vibrational modes may also appear.

Anharmonicity leads to overtones, which are also expected to be weak compared to fundamental bands.

(ii) Vibrational frequency

Bending modes occur at the lowest frequencies (wavenumbers), while asymmetric stretches modes are highest.

Modes above 2500 cm^{-1} always involve H atoms!

Use group vibrational frequencies to exploit isotopic frequency shifts.

(iii) Q branches

The presence of Q branches in the IR indicates either a non-linear molecule, or a bending vibration in a linear molecule.

To establish which, look for the stretching modes: if these have no Q branch the molecule is linear.

(iv) Rule of mutual exclusion

This indicates whether the molecule is centrosymmetric (possesses a centre of inversion).

(v) Vibrational dipole moments and polarizability

Whether a particular vibration generates a large dipole change, or a significant change to the polarizability can be related qualitatively to the strengths of the IR or Raman bands.

For example the more symmetric the vibration, the more Raman active the mode (e.g. HCN ν_1).

Raman and infrared spectra of chloroform
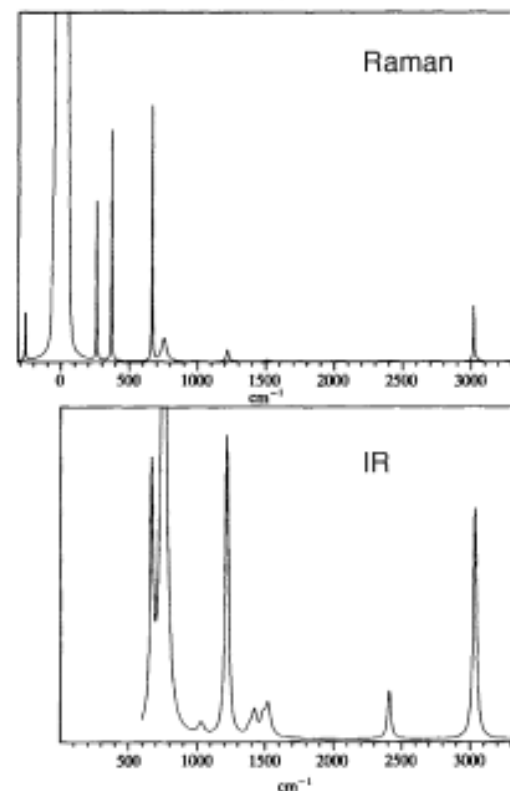
N₂O

$\tilde{v}(cm^{-1})$	Infrared	Raman	band assignment
580	PQR m.(+ T dept.)	m.	$2v_2 \leftarrow v_2$ hot band
589	PQR s.	v.w.	v_2 bend
1167	PR m.	v.w.	$2v_2$ overtone
1285	PR v.s.	v.s.	v_1 symmetric stretch
2223	PR v.s.	s.	v_3 asymmetric stretch

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

Reasoning behind assignments

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

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

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

589 cm⁻¹	low frequency	$\therefore$ bending mode (note PQR also)
2223 cm⁻¹	highest frequency	$\therefore$ asymmetric stretch
1285 cm⁻¹	intermediate frequency	$\therefore$ symmetric stretch

(3) Q branches (fundamentals only):

PQR branches in v_2, but absent in v_1 and v_3 $\therefore$ molecule is linear

(4) Mutual exclusion?

No $\therefore$ molecule is not centrosymmetric $\therefore$ N₂O is N–N–O

(5) Other bands:

These must be overtones or hot bands. The fact that the band at 580 cm⁻¹ is temperature dependent implies it is a hot band. That and its position leads to its assignment. The 1167 cm⁻¹ band is at ca. twice the frequency of the v_2 fundamental, hence its assignment.

C_2H_2

vibrational modes of C_2H_2

Raman active

IR active

612 cm⁻¹ (×2)

1974 cm⁻¹

3374 cm⁻¹

729 cm⁻¹ (×2)
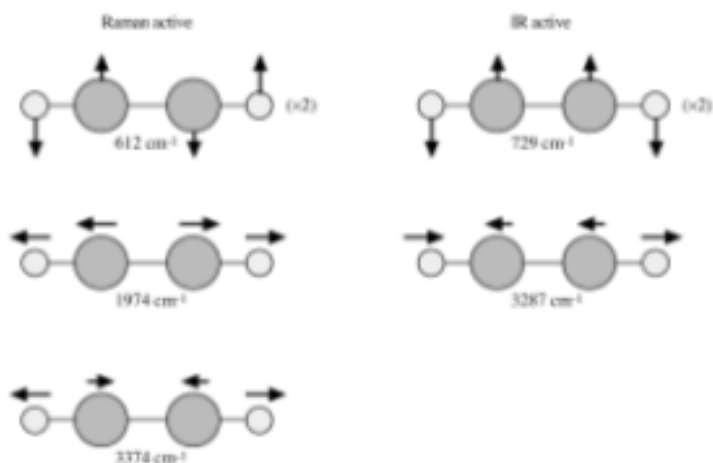
3287 cm⁻¹

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

Reasoning behind assignments

(1) Q branches

There is a missing Q branch at 3287 cm⁻¹   ∴ molecule is linear

⇒ 729 cm⁻¹ band is bending mode

(2) Mutual exclusion?

Yes   ∴ molecule is centrosymmetric

∴ C_2H_2 is H–C≡C–H

(3) Strong bands in IR or Raman

1974 cm⁻¹   very strong Raman   ∴ symmetric stretch

3287 and 3374 cm⁻¹   high frequency   ∴ C–H stretch

3287 cm⁻¹   IR active   ∴ asymmetric stretch

3374 cm⁻¹   Raman active   ∴ symmetric stretch

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

Two doubly degenerate bending modes   ∴ 5 distinguishable vibrational modes

⇒ remaining 612 cm⁻¹ band is bending mode

Comparison of Raman and IR Intensities

Table 1.1. Characteristic Wavenumbers and Raman and Infrared Intensities of Groups in Organic Compounds

Vibration[a]	Region(cm^{-1})	Intensity[b]	
		Raman	Infrared
ν(O—H)	3650–3000	w	s
ν(N—H)	3500–3300	m	m
ν($\equiv$C—H)	3300	w	s
ν(=C—H)	3100–3000	s	m
ν(—C—H)	3000–2800	s	s
ν(—S—H)	2600–2550	s	w
ν(C$\equiv$N)	2255–2220	m–s	s–0
ν(C$\equiv$C)	2250–2100	vs	w–0
ν(C=O)	1820–1680	s–w	vs
ν(C=C)	1900–1500	vs–m	0–w
ν(C=N)	1680–1610	s	m
ν(N=N), aliphatic substituent	1580–1550	m	0

Table 1.1. (*Continued*)

Vibration[a]	Region (cm^{-1})	Intensity[b] Raman	Intensity[b] Infrared
$\nu(N{=}N)$, aromatic substituent	1440–1410	m	0
$\nu_a((C{-})NO_2)$	1590–1530	m	s
$\nu_s((C{-})NO_2)$	1380–1340	vs	m
$\nu_a((C{-})SO_2({-}C))$	1350–1310	w–0	s
$\nu_s((C{-})SO_2({-}C))$	1160–1120	s	s
$\nu((C{-})SO({-}C))$	1070–1020	m	s
$\nu(C{=}S)$	1250–1000	s	w
$\delta(CH_2)$, $\delta_a(CH_3)$	1470–1400	m	m
$\delta_s(CH_3)$	1380	m–w, s, if at $C{=}C$	s–m
$\nu(CC)$, aromatics	1600, 1580	s–m	m–s
	1500, 1450	m–w	m–s
	1000	s (in mono-; m-; 1,3,5- derivatives)	0–w
$\nu(CC)$, alicyclics, and aliphatic chains	1300–600	s–m	m–w

v_a(C—O—C)	1150–1060	w	s
v_s(C—O—C)	970–800	s–m	w–0
v_a(Si—O—Si)	1110–1000	w–0	vs
v_s(Si—O—Si)	550–450	vs	w–0
v(O—O)	900–845	s	0–w
v(S—S)	550–430	s	0–w
v(Se—Se)	330–290	s	0–w
v(C(aromatic)—S)	1100–1080	s	s–m
v(C(aliphatic)—S)	790–630	s	s–m
v(C—Cl)	800–550	s	s
v(C—**Br**)	700–500	s	s
v(C—**I**)	660–480	s	s
δ_s(CC), aliphatic chains	400–250	s–m	w–0
C_n, $n = 3, \ldots, 12$	2495/n		
$n > 12$			
Lattice vibrations in molecular crystals (liberations and translational vibrations)	200–20	vs–0	s–0

[a] v, stretching vibration; δ, bending vibration; v_s, symmetric vibration; v_a, antisymmetric vibration.
[b] vs, very strong; s, strong; m, medium; w, weak; 0, very weak or inactive.

Examples of Raman and IR Frequencies[a]

	Frequency (cm^{-1})	IR[a]	Raman[b]
Alkanes			
CH_3 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_2 asym stretch	1530–1600	vs	m–w
R—NO_2 sym stretch	1310–1397	s	vs
C—S stretch	580–704	—	vs
S—H stretch	2560–2590	w	s
R_2 S_2 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

[a]Taken from Reference 8.
[b]vs = very strong, m = medium, w = weak, dash = absent.

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

Nature of the Raman and IR processes

Raman scattering	IR absorption
2-photon process (ν_{ex} ν_{scatt})	1-photon process ($\nu_{incident}$)
conserves wave function parity	changes wave function parity
Raman cross sections weak (10^{-29} cm^2)	(10^{-21} cm^2)

Selection rules	Raman	IR
rotational transitions	$\Delta J = 0, \pm 2$ (anisotropic polarisability)	$\Delta J = 0,\ \pm 2$ (only roto-vibrational!)
vibrational transitions	$\Delta v = \pm 1$ (polarisability change)	$\Delta v = \pm 1$ (dipol moment change)

IR vs Raman
a) Complementarity for vibrational modes (Rule of mutual exclusion for centrosymmetric molecules)
b) Experimental considerations (Raman):
i) Wavelength of primary radiation can be conveniently chosen
ii) Polarisation features can help with identification of nature of modes
iii) Resonance Raman: stronger signal (and potentially selective)
iv) Raman can be applied with good spatial resolution
v) Raman scattering by water is weak (compared to IR)
vi) Raman has an essentially frequency independent penetration depth
vii) For samples with significant fluorescence background (excited by the primary radiation),
it may be difficult to distinguish the Ramansignal from the background.

Raman instrumentation

Instrumentation for modern Raman spectroscopy consists
of three components:
- a laser source,
- a sample illumination system
- a suitable spectrometer.

Source

The sources used in modern Raman spectrometry are nearly always
lasers because their high intensity is necessary to produce Raman scattering of
sufficient intensity to be measured with a reasonable signal-to-noise ratio.
Because the intensity of Raman scattering varies as the fourth power
of the frequency, argon and krypton ion sources that emit in the blue and green
region of the spectrum have and advantage over the other sources.

Typical lasers:

Ultra-violet: 244, 257, 325, 364 nm
Visible: 457, 473, 488, 514, 532, 633, 660 nm
Near Infra-red: 785, 830, 980, 1064 nm

Laser Type	Wavelength, nm
Argon ion	488.0 or 514.5
Krypton ion	530.9 or 647.1
Helium-neon	632.8
Diode	785 or 830
Nd-YAG	1064

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Sample Illumination System

- simpler than for IR spectroscopy
(glass can be used for windows, lenses,
and other optical components) .

- the laser source is easily focused on a
small sample area and the emitted
radiation efficiently focused on a slit.

- very small samples can be
investigated.
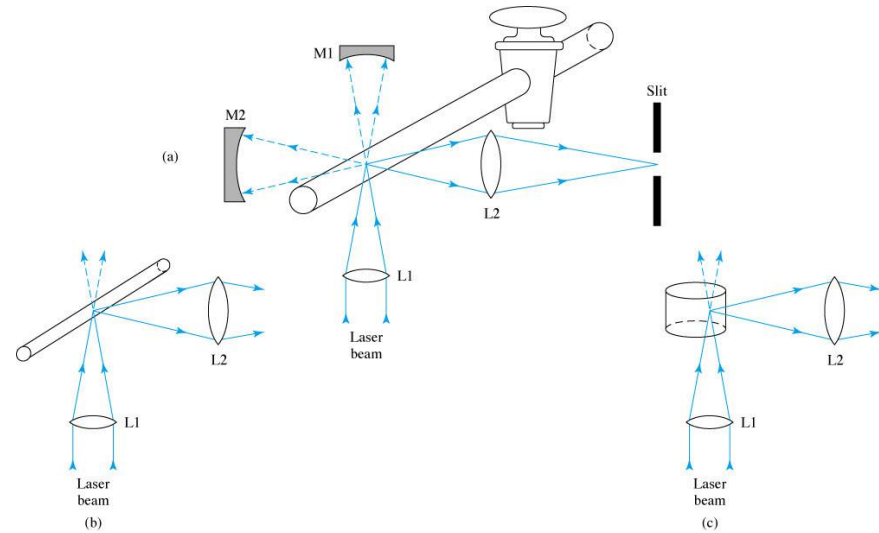

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Liquid Samples: Aqueous solutions can be studied by Raman spectroscopy (water is a weak Raman scatterer) but not by infrared! This advantage is particularly important for biological and inorganic systems and in studies dealing with water pollution problems.

Solid Samples: Raman spectra of solid samples are often acquired by filling a small cavity with the sample after it has been ground to a fine powder. Polymers can usually be examined directly with no sample pretreatment.

In order to block Rayleigh scattering from reaching the detector it is use a **Raman notch** or **Raman edge filter**.
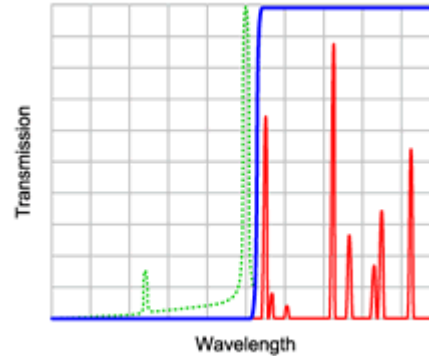
► Notch filters transmit both Stokes and anti-Stokes Raman signals while blocking the laser line.

►Edge filters (also known as barrier filters) transmit either Stokes (longpass) or anti-Stokes (shortpass).
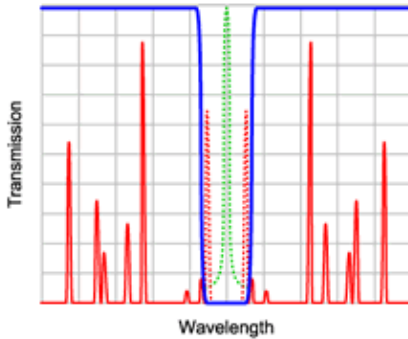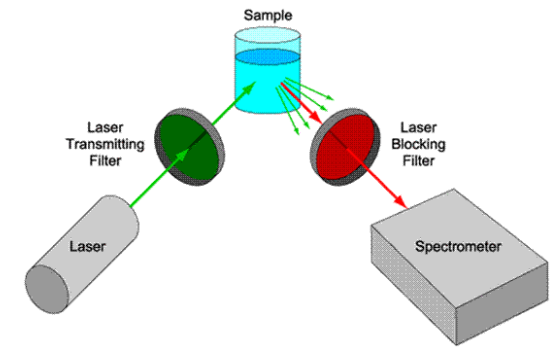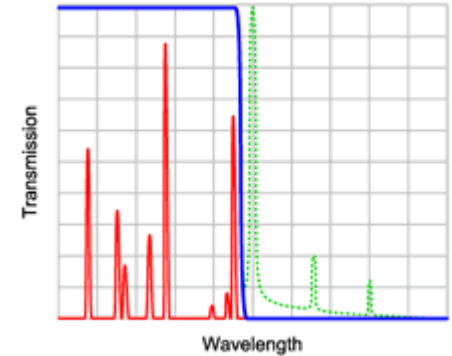
Notch filter

Filters for simultaneous Stokes and Anti-Stokes measurements

LWP edge filter

Filters for only Stokes measurements

SWP edge filter

Filters for only Anti-Stokes measurements

An edge filter can provide a superior alternative, as they offer the narrowest transition to see Raman signals extremely close to the laser line.

Raman Spectrometers

- Classical Raman spectrometers (monochomators with photomultipliers as transducers)

- FT Raman spectrometers (Fourier transform instruments equipped with cooled germanium transducers or multichannel instruments based upon charge-coupled devices).

- Micro-Raman spectrometers
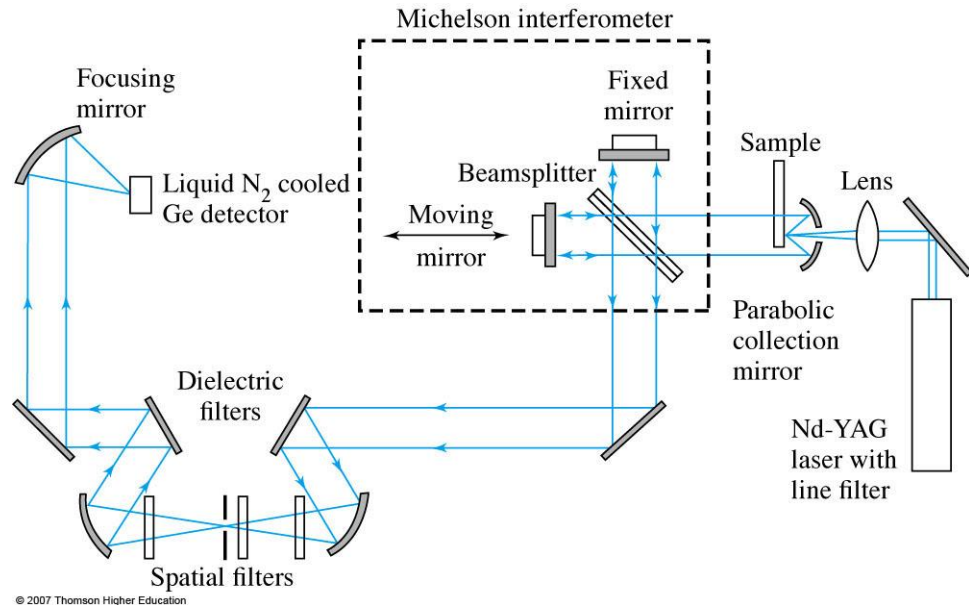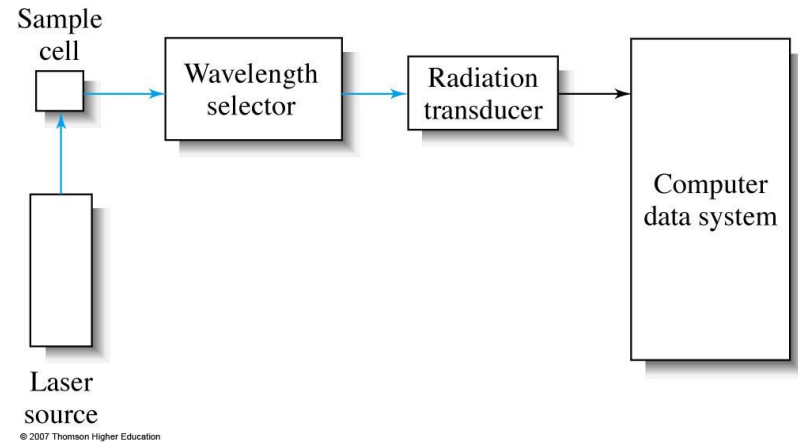
NON-CLASSICAL RAMAN EFFECTS

. 1 Surface-enhanced Raman effect

The influence of small metal (silver, gold, copper) particles such as colloids or roughened surfaces on the elementary process of Raman scattering can enhance the intensity of the Raman effect by several orders of magnitude. This effect is used in *surface-enhanced Raman spectroscopy* (**SERS**).

2 Resonance Raman effect

Resonance Raman spectroscopy (**RRS**) makes use of an excitation source with frequency close to a molecular electronic absorption frequency. Under these conditions a resonance occurs which may enhance the intensities of the Raman lines by several orders of magnitude, especially those connected with totally symmetric vibrations of the chromophore

Resonance and surface-enhanced Raman effects may be combined to produce *surface-enhanced resonance Raman spectroscopy* (**SERRS**).

RRS, SERS, and SERRS can be recorded with the same spectrometers as classical Raman spectra, although different conditions of the excitation and special sample techniques are used.

They are important techniques for trace chemical analyses.

SERS (Surface enhanced Raman spectroscopy or **surface enhanced Raman scattering)** is a surface-sensitive technique that enhancesRaman scattering by molecules adsorbed on rough metal surfaces. The enhancement factor can be as much as 10^{10} to 10^{11}, which means the technique may detect single molecules.

Two mechanisms (still in debate!):
1)the *chemical theory*: the formation of charge-transfer complexes – applies only for molecule which have formed a chemical bond with the surface.
2)the *electromagnetic theory* : the excitation of localized surface plasmons - apply even in those cases where the molecule is only physisorbed to the surface.

Surface plasmon resonance (SPR) is the collective oscillation of valence electrons in a solid stimulated by incident light.

The resonance condition is established when the frequency of light photons matches the natural frequency of surface electrons oscillating against the restoring force of positive nuclei.

Surface plasmon resonance in *nanometer*-sized structures is called **localized surface plasmon resonance (LSPR)**

Different sizes of colloidal gold particles

2   5   6   12   16   18   24   60   90   150 nm
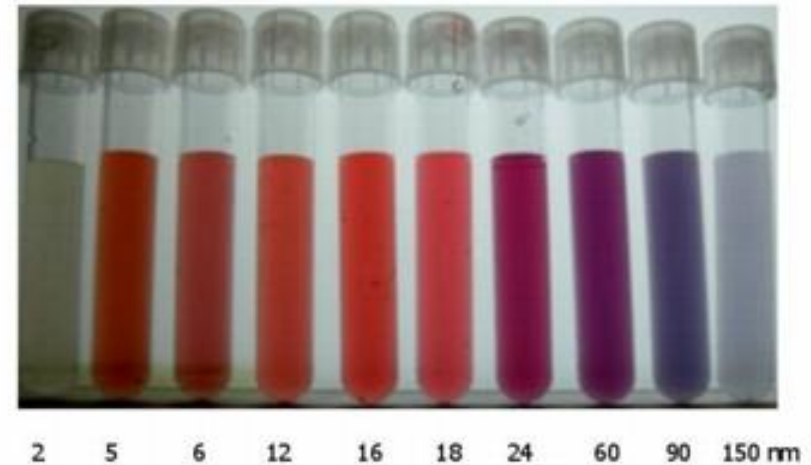
Resonance Raman spectroscopy

Resonance Raman spectroscopy uses incident radiation of frequency nearly coinciding with the frequency of electronic transitions of the sample. The intensity of scattered radiation is considerably increased in comparison with conventional Raman. Because often only a few vibrational modes contribute to the more intense scattering, the spectrum is greatly simplified.

The nine peaks in the spectrum of solid K_2CrO_4 are Stokes lines corresponding to the excitation of the symmetric breathing mode of the tetrahedral chromate anion and the transfer of up to nine vibrational quanta during the photon-ion collision.

The technique is used for the examination of metal ions in biological macromolecules (such as the iron in hemoglobin and cytochromes or the cobalt in vitamin B), which are present in too low abundances for conventional Raman to detect.

resonance Raman spectrum of solid K_2CrO_4

Hemoglobin
excitation = 418 nm

Hemoglobin
excitation = 230 nm
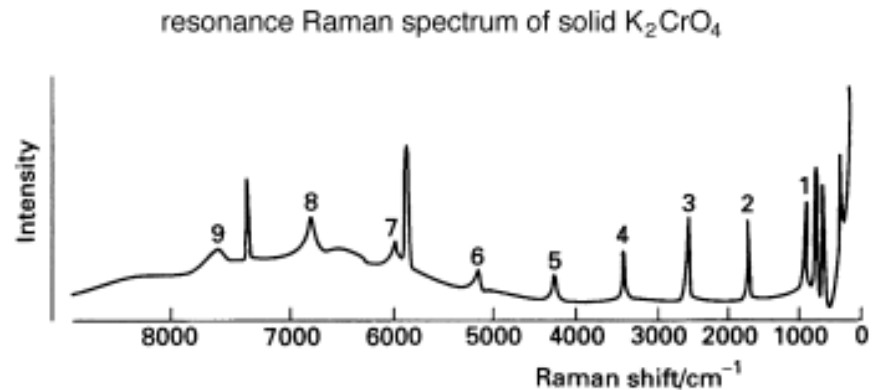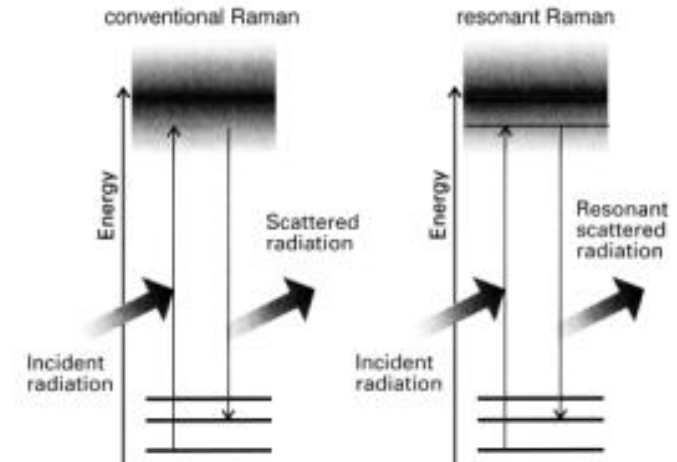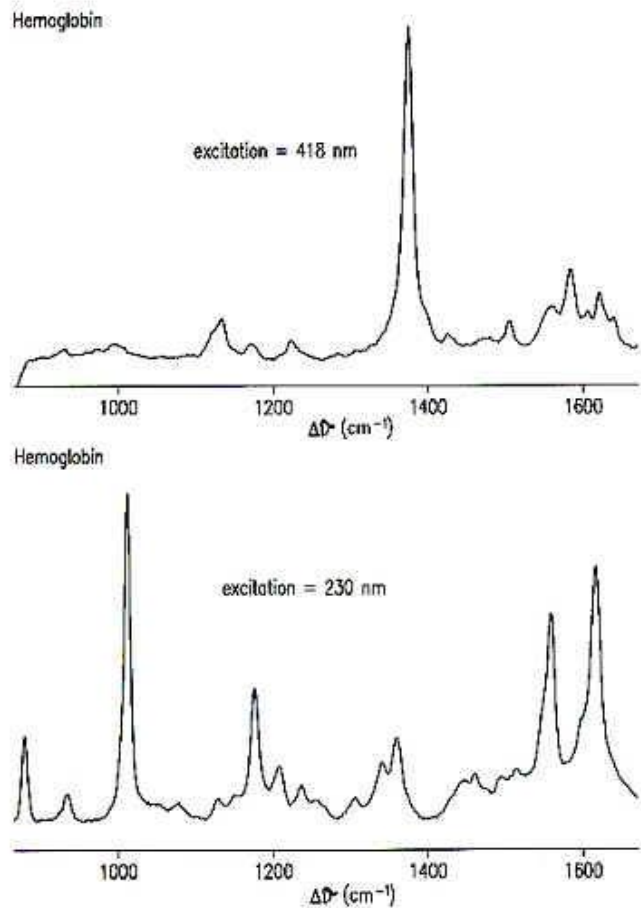
Different excitation wavelengths enhance Raman
signal from different parts of the molecule

418 nm: Excitation into heme absorption band.
RR spectra from the heme
230 nm: Excitation into absorption band of Tyr
and Trp. UVRR spectra arises from those
residues in the protein

The Raman signal can be strongly enhanced (at least 3 orders of magnitude) by exciting directly into an absorption band of the molecule. The advantage lies in the fact that by tuning the excitation wavelength, we can now selectively examine different parts of the molecule.

In figure, we can see how much difference this can make when obtaining **resonance Raman** spectra of hemoglobin. If we use an excitation wavelength of 418 nm, this is right in the center of the absorption band for the heme group and therefore the molecular vibrations that are enhanced all arise predominately from the heme group. If an excitation wavelength of 230 nm is used, this primarily enhances the vibrations from tyrosine (Tyr) and tryptophan (Trp) amino acid residues in the protein.

The Raman spectrum obtained with 230 nm excitation is completely different from the one obtained with 418 nm excitation because of the resonance enhancement. This gives us a great deal of selectivity in our experiments and by choosing the excitation wavelength we can decide which part of the molecule we want to monitor.
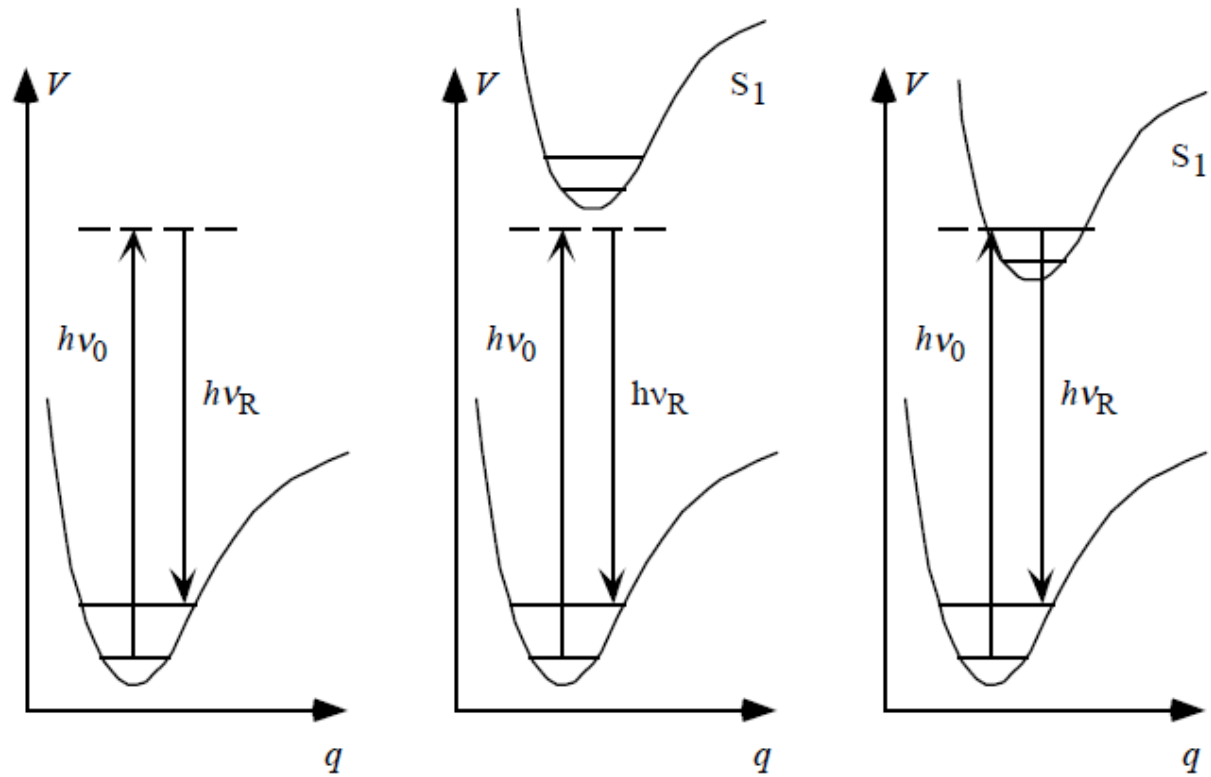
Fig. 3. a.) Raman scattering; b.) near-resonance Raman; c.) resonance Raman

3 Non-linear Raman effects   If the exciting radiation has a very high intensity, then the higher terms of the polarizability expansion have to be considered:

$$p = \alpha \vec{E}_i + \frac{1}{2} \beta \vec{E}_i \vec{E}_j + \frac{1}{6} \gamma \vec{E}_i \vec{E}_j \vec{E}_k + \cdots$$

β is the *1st molecular hyperpolarizability*, and γ is the *2nd molecular hyperpolarizability*, leading to non-linear Raman effects.

Coherent Raman effects (**two or three laser beams** of different frequency):

CSRS - coherent Stokes Raman spectroscopy
CARS - coherent anti-Stokes Raman spectroscopy
SRS - stimulated Raman spectroscopy
IRS - inverse Raman spectroscopy
SRLS - stimulated Raman loss spectroscopy
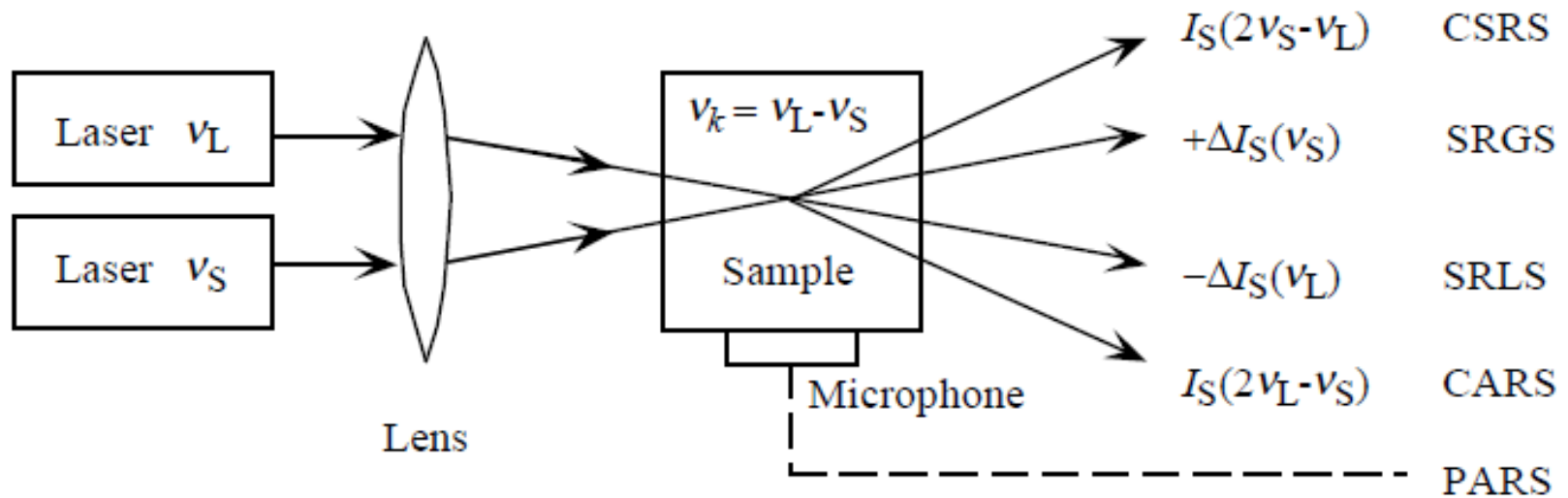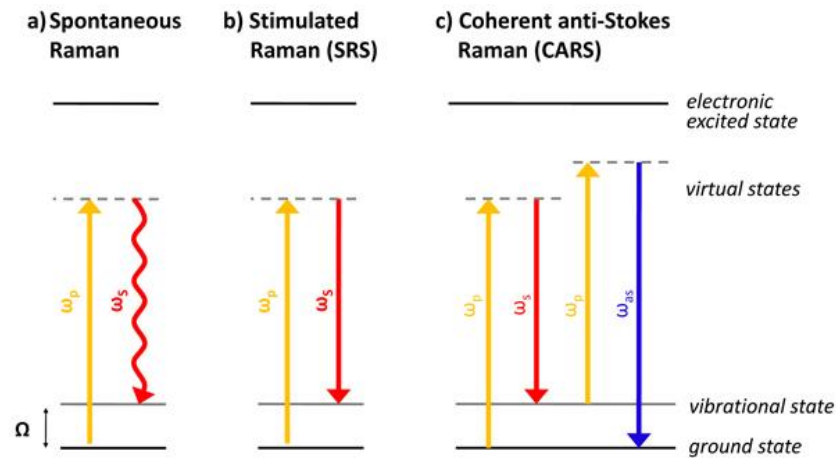PARS - photoacoustic Raman spectroscopy

Fig. 4. The most analytically useful coherent Raman effects (after Kiefer in Ref. 3, p.168)

Coherent Anti-Stokes Raman Scattering (CARS)

For sample irradiated by two high-energy laser beams (ν_P -pump and ν_S - Stokes) ($\nu_P > \nu_S$) in collinear direction, *beams interact coherently* to produce strong scattered light of frequency ($2\nu_P - \nu_S$). When ν_S *is tuned to resonance*: $\nu_S = \nu_P - \nu_M$ (ν_M = Raman active mode of thesample) a strong beam at frequency $\nu_P + \nu_M$ is emitted:

a) Spontaneous Raman b) Stimulated Raman (SRS) c) Coherent anti-Stokes Raman (CARS)

electronic excited state
virtual states
vibrational state
ground state

$$2\nu_P - \nu_S = 2\nu_P - (\nu_P - \nu_M) = \nu_P + \nu_M$$

CARS signal is coherent and emitted in one direction and can be observed without monochromator.   It is on Anti-Stokes side and thus avoids fluorescence.
All modes that are Raman active and some inactive Raman and IR modes are active in CARS.

instrumental arrangement for the CARS experiment
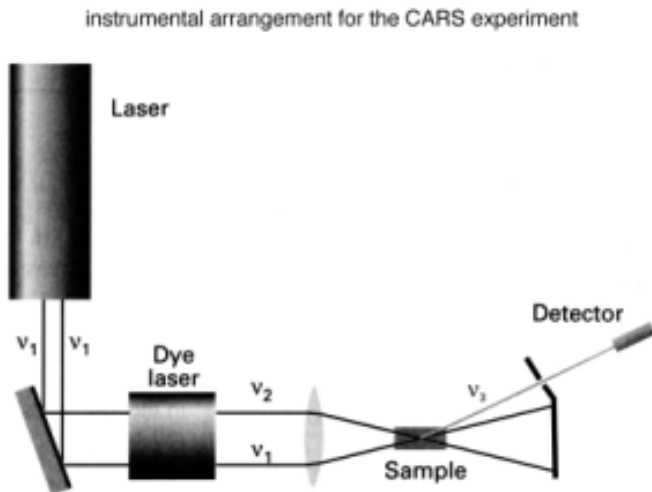
The advantage of CARS is that it can be used to study Raman transitions in the presence of competing incoherent background radiation, and so it can be used to observe the spectra of species in flames.

Spectral intensity is then interpreted in terms of the temperature of different regions of the flame.

Hyper-Raman scattering is produced by very high intensity pulses. Two photons of the exciting radiation produce the Raman spectrum.

A non-linear effect in which *the vibrational modes interact with the second harmonic of the excitation beam.* This requires very high power, but allows the observation of vibrational modes that are normally "silent".
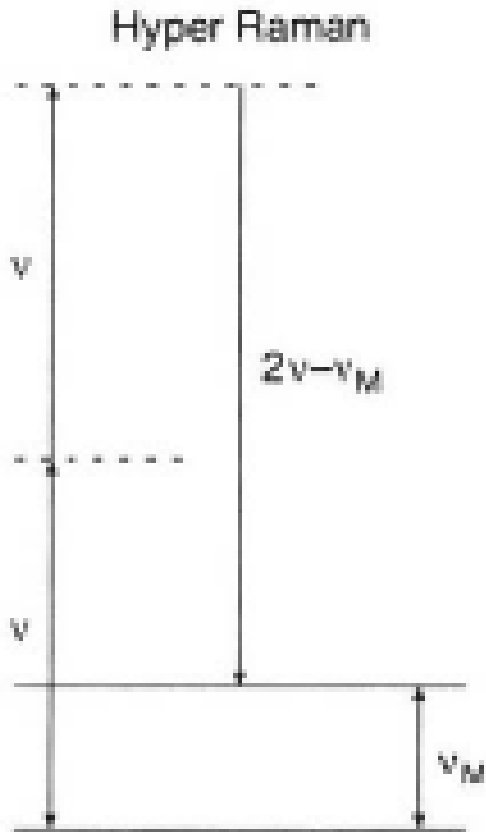
Hyper Raman

With high intensity pulse at frequency ν, scattered radiation contains frequencies 2ν (hyper-Rayleigh scattering) and $(2\nu \pm \nu_M)$ (Stokes and anti-Stokes hyper-Raman scattering), where ν_M is normal vibration of molecule, caused by two incident photons (2ν) of the laser.

Different symmetry selection rules apply, and hyper- Raman effect contains all IR active modes.

Photoacoustic Raman Spectroscopy (PARS)

Two laser beams, ν_P (pump beam) and ν_S (Stokes beam) impinge on gaseous sample, interact when $\nu_P - \nu_S = \nu_M$ for Raman active mode. The Stokes beam is amplified and the pump beam is attenuated.
The vibrationally excited molecules lose excitation to translational energy, changing the pressure in the cell, which can be detected with a microphone.
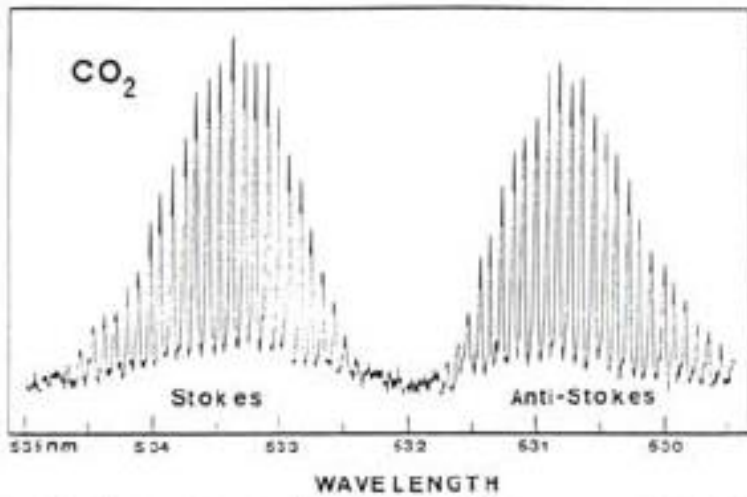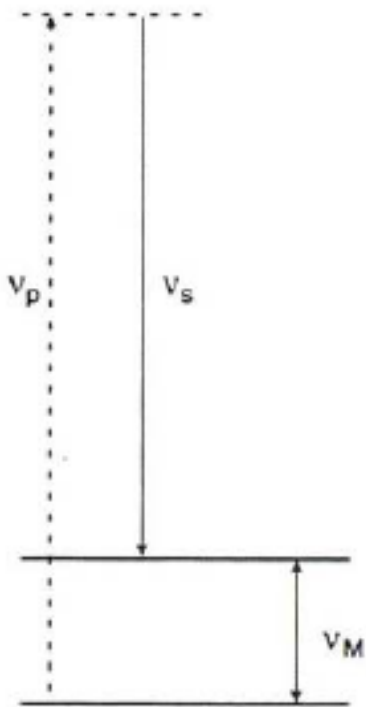In this case there is no Rayleigh line, and low energy rotational lines can be studied.

For each Stokes photon created by the Raman process, one molecule is transferred from the lower state to the upper state of the transition. Collisional relaxation of these excited molecule produces changes that is detected by a microphone.

Figure 3-5 Photoacoustic rotational Raman spectrum of CO_2 at a pressure of 80 kPa (600 torr). The rotational line spacing is about 3.1 cm^{-1}. Laser powers of the pump and Stokes beams were 3.3 MW and 120 kW, respectively. (Reproduced with permission from Ref. 4)
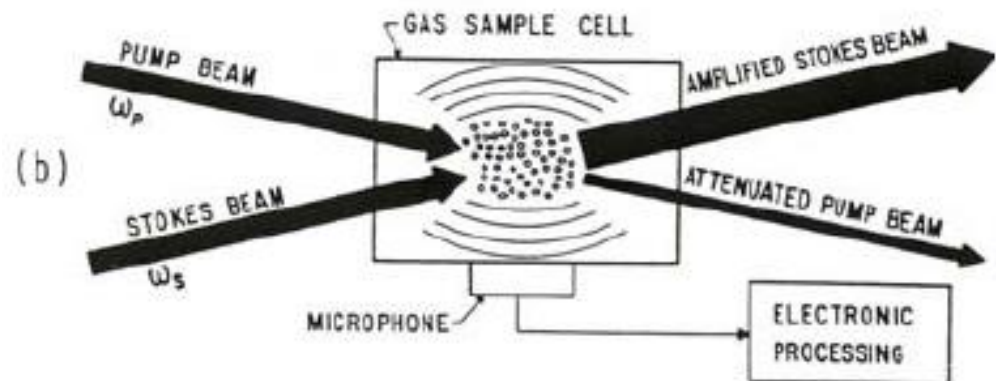
Problems

1. Consider the vibrational mode that corresponds to the uniform expansion of the benzene ring.

      a) Is it Raman active or infrared active?

      b) Why?

2. A linear molecule has the following fundamental vibrational transitions: 370 cm^{-1}, 520 cm^{-1}, 880 cm^{-1} and 1550 cm^{-1} (all Raman active) The wavelength of the excitation radiation is 500 nm.

      a) Calculate the wavenumbers of scattered radiation in Stokes range.

      b) How many atoms has this molecule?

3. Calculate the temperature of the sample (CCl_4) from Raman spectrum, knowing the excitation wavelength and I_S/I_{AS} ratio for 460 cm^{-1} band ($I_S/I_A = 6$; $\lambda_{ex} = 488$ nm)

    $h = 6{,}63 \cdot 10^{-34}$ J·s, $c = 3 \cdot 10^8$ m/s, $k_B = 1{,}38 \cdot 10^{-23}$ J/K