Raman Spectroscopy
(Raman Scattering Effect)

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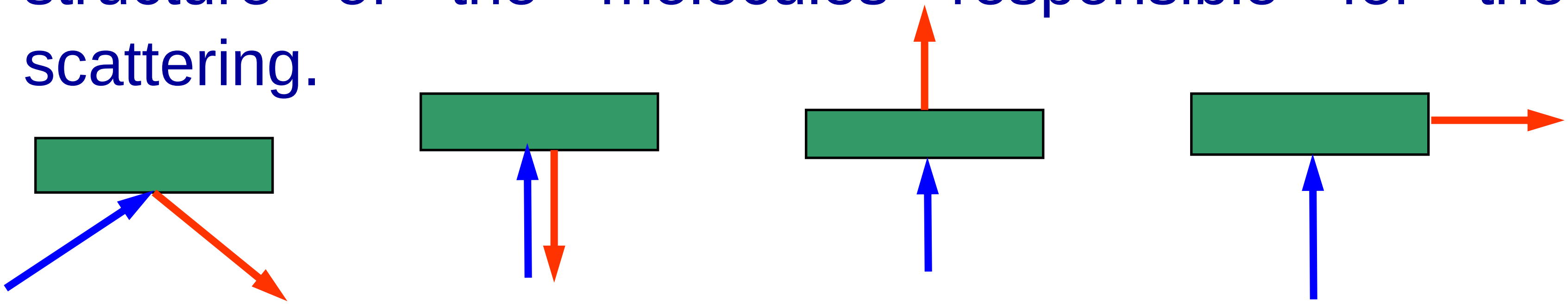
The Raman effect

- It is predicted by Adolf Smekal in 1923, and named according to the Indian scientist Sir Chandrasekhara Venkata Raman, after one of its discoverers in 1928.
- It is used to study vibrational, rotational, and other low-frequency modes in molecules. It relies on inelastic scattering of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range.

Sir C. V. Raman

Raman scattering is an inelastic scattering of a photons, which leads to change in photon energy. By nature it is a weak effect since approximately 1 in 10^7 photons is scattered.

- When radiation passes through a transparent medium, the molecules of the present sample scatter a fraction of the beam in all directions.
- It was found that the wavelength of a small fraction of the radiation scattered by certain molecules differs from that of the incident beam, and furthermore that the shifts in wavelength depend upon the chemical structure of the molecules responsible for the scattering.



“Brewster” Setup

Back Scattering

Forward Scattering

Right-angle Scattering

non-transparent sample

transparent sample

- The theory of Raman scattering shows that this phenomenon results from the same type of quantized vibrational (or rotational) transitional changes that are associated with infrared absorption (or microwave) radiations. Thus, the difference in wavelength between the incident and scattered visible radiation in Raman spectroscopy corresponds to wavelengths in the mid-infrared region.
- Therefore, the Raman scattering spectrum and infrared absorption spectrum for a given molecules often resemble one another quite closely.

Photons are incident into the material at one energy, but emerge at slightly different energies (or wavelengths), due to the inelastic scattering. In reality, the photons change their energy by exchanging some energy with molecular vibrational states of the material. The scattered photon can either release a quantum of vibrational energy, and emerge at a lower energy (longer wavelength), or it can absorb a quantum of vibrational energy, and emerge at a higher energy (shorter wavelength).

EMR can be considered as a stream of particles, so;

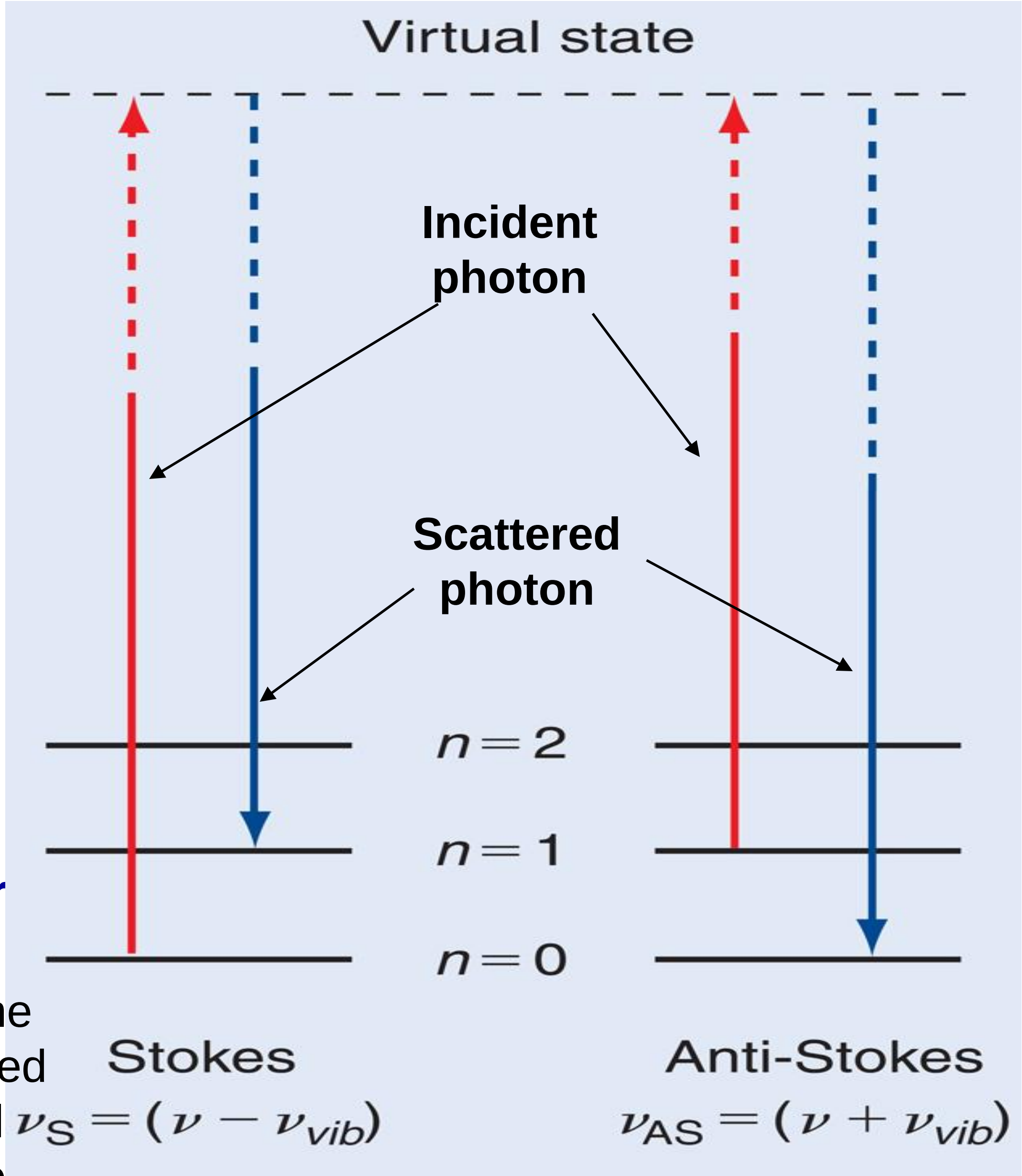
Elastic scattering : no change in energy of photons (or frequency)

Inelastic scattering : change in energy of photons (or frequency) which is corresponding to the suitable change in the rotational and/or vibrational state of the molecule.

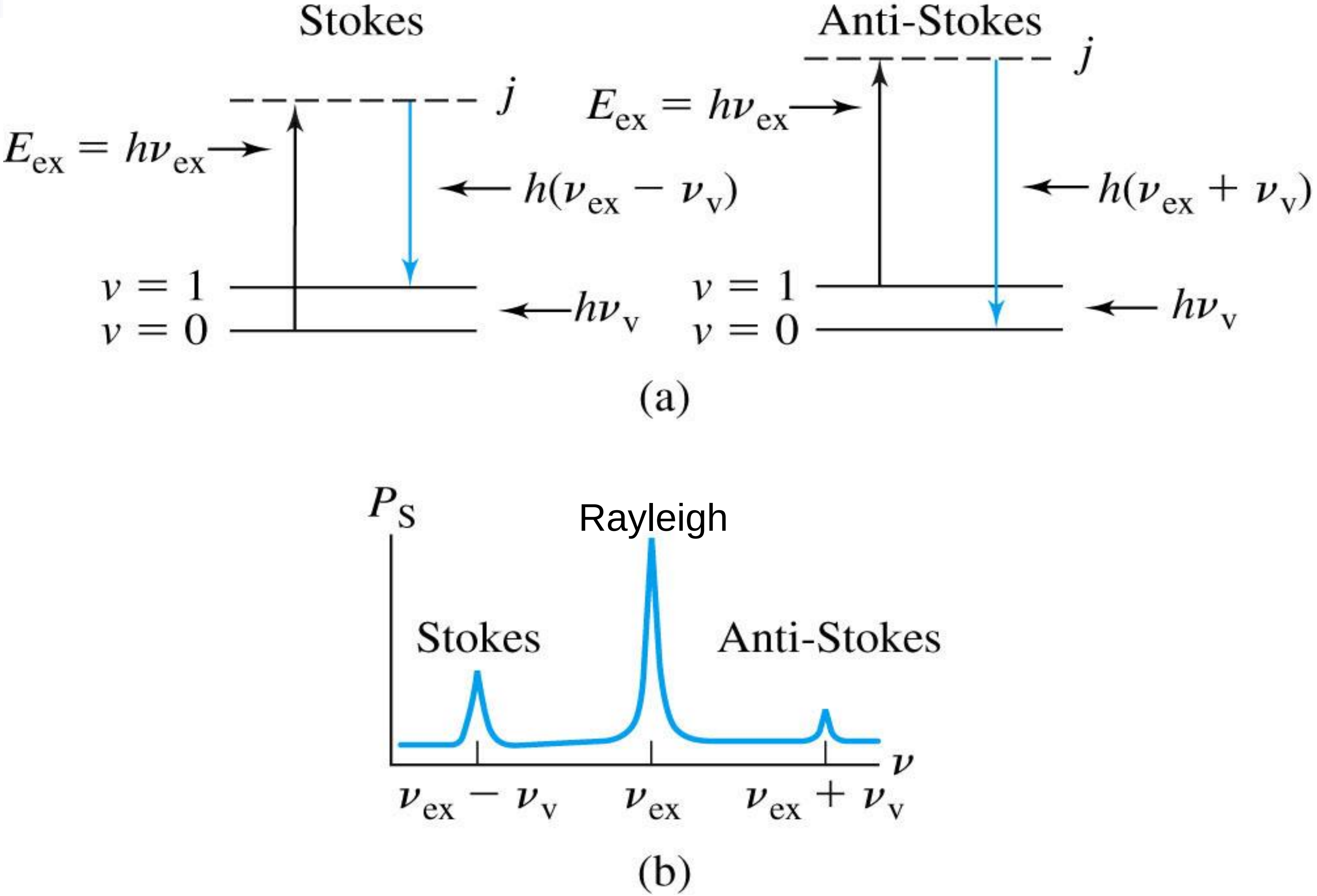
For the spontaneous Raman effect, a photon excites the molecule from the ground state to a virtual energy state. When the molecule relaxes it emits a photon and it returns to a different vibrational state. The difference in energy between the original state and this new state leads to a shift in the emitted photon's frequency away from the excitation wavelength. If the final vibrational state of the molecule is more energetic than the initial state, then the emitted photon will be shifted to a lower frequency. This shift in frequency is called as a Stokes lines. If the final vibrational state is less energetic than the initial state, then the emitted photon will be shifted to a higher frequency, and this is called as an Anti-Stokes lines.

That is to say; the inelastic-scattered radiation can occur at lower frequencies (Stokes lines) or at higher Frequencies (anti-Stokes lines) relative to that of the incident light (or elastically scattered), corresponding to the vibrational transition frequencies of the sample or of the medium or Rayleigh.

Energy is still conserved overall with the photon energy loss or gain compensated by the suitable change in the rotational and/or vibrational state of the molecule



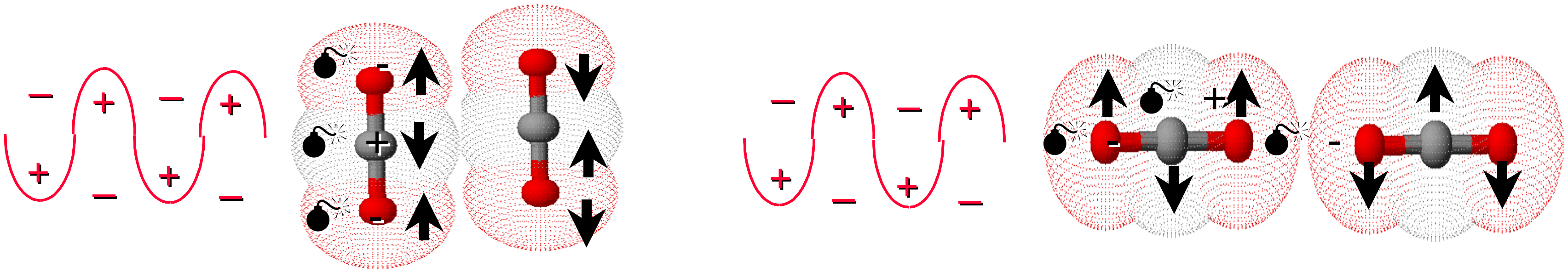
Transitions involved in Raman Effect



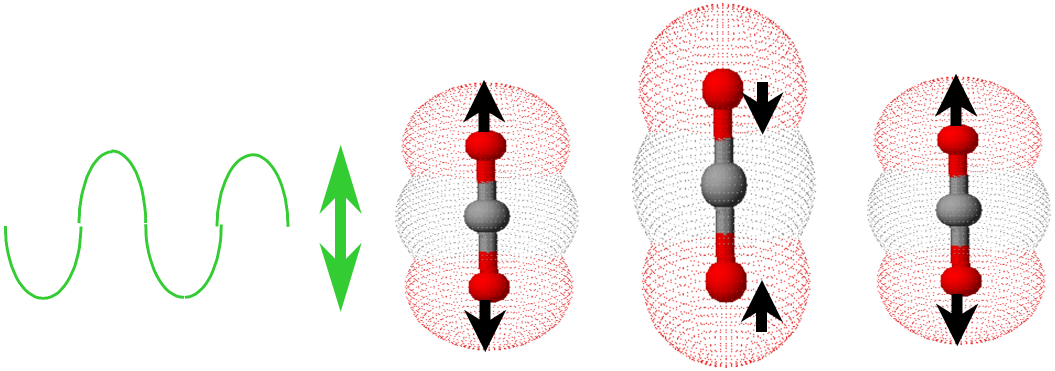
The Raman transition is a two-photon process.

Why Raman is Different from IR?

IR requires change in dipole moment



Raman requires change in polarizability



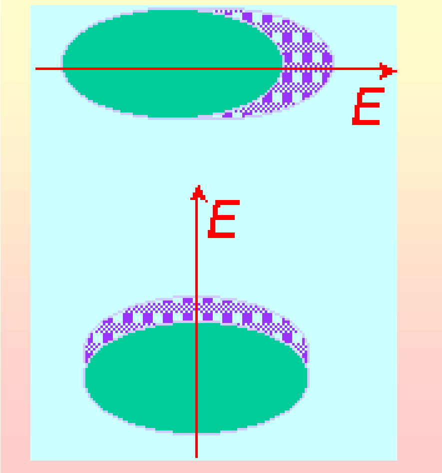
- Selection rules are therefore different and can be exclusive for centrosymmetric molecules which are IR inactive.

Selection rules for Raman spectroscopy

- Vibration is active if it has a change in polarizability, α. Polarizability is the ease of distortion of a bond (i. e electron cloud).

- For Raman-active vibrations, the incident radiation does not cause a change in the dipole moment of the molecule, but instead a change in polarizability.

In starting the vibration going, the electric field of the radiation (E) at time t, induces a separation of charge (between the nuclear protons and the bonding electrons). This is called the induced dipole moment, μ_{ind}. (Don't confuse it with the molecule's dipole moment, or change in dipole moment, because this is often zero).



$$\vec{\mu}_{ind} = \alpha\vec{E}$$

Selection rules:

1- Must also have a change in polarizability

2- $\Delta v = \pm 1$

3- Overtones: $\Delta v = \pm 2, \pm 3, \ldots$

Mutual Exclusion Principle

For molecules with a center of symmetry, IR inactive transitions are Raman active and vice versa.

Symmetric molecules

- IR-active vibrations are not Raman-active.
- Raman-active vibrations are not IR-active.

O = C = O	O = C = O
symmetric vibration	asymmetric vibration
Raman active	Raman inactive
IR inactive	IR active

More about polarizability;

- Polarizability (α) of a molecule, is related to mobility of electrons (under applied radiation field in our present case).
- For atoms, the same distortion is obtained for field in any direction. Polarizability is Isotropic
- For many molecules, polarizability depends on the direction of the applied field, e.g. H—H easier to distort along bond than $\perp$ bond. Polarizability is anisotropic
- Variation of α with direction is described by polarizability tensor.

Vibrational Raman Spectra

Selection rules: 1) polarizability should change as the molecule vibrates (HCl – yes; H_2 – yes)

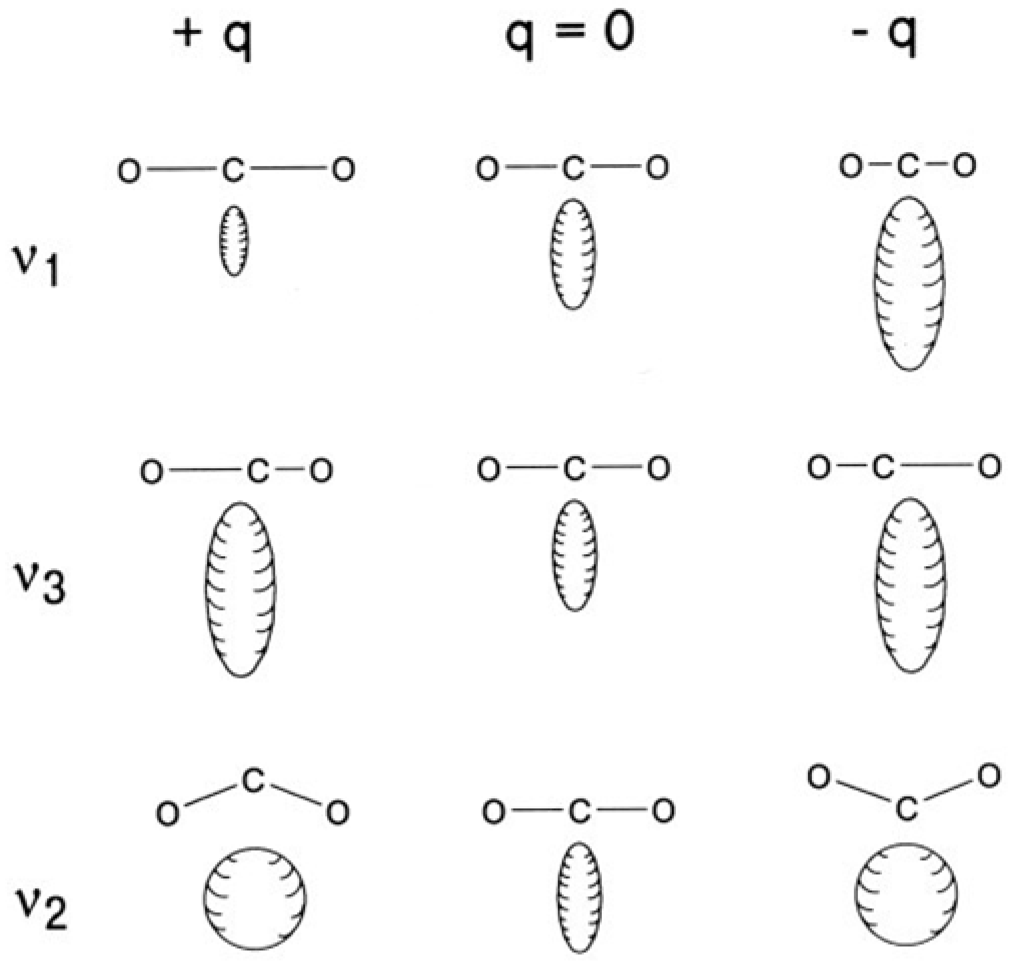
2) $\Delta \upsilon = 0, \pm 1, \pm 2, \ldots$

Note: anti-Stokes lines are very weak

Rule of mutual exclusion: if a molecule has a centre of symmetry then Raman active vibrations are infrared inactive and *vice versa*. If there is no centre of symmetry, some vibrations may be both Raman and infrared active.

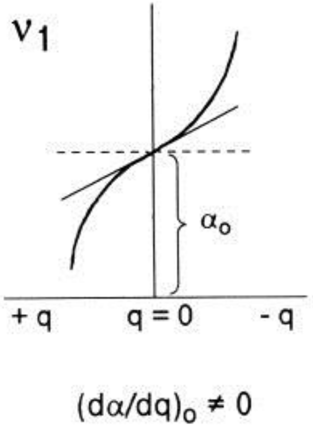
O=C=O	IR	Raman
ν_1 , symmetric stretching	inactive	active
ν_2 , bending	active	inactive
ν_3 , asymmetric stretching	active	inactive

Example 1: the vibration modes of CO_2

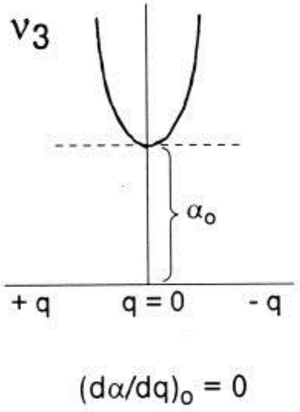


Changes in polarizability ellipsoids during vibration of CO_2 molecul

Symmetric
IR inactive
Raman active

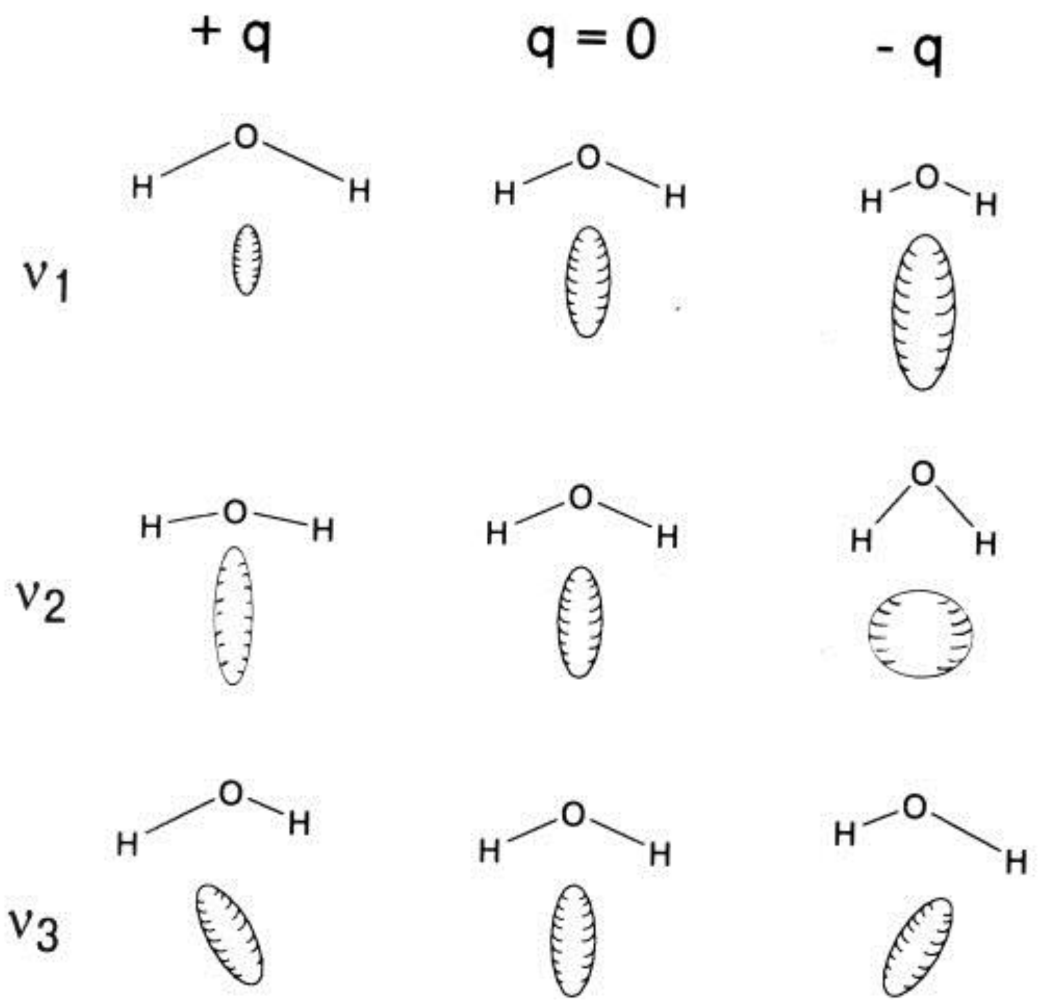


Asymmetric
IR active
Raman inactive



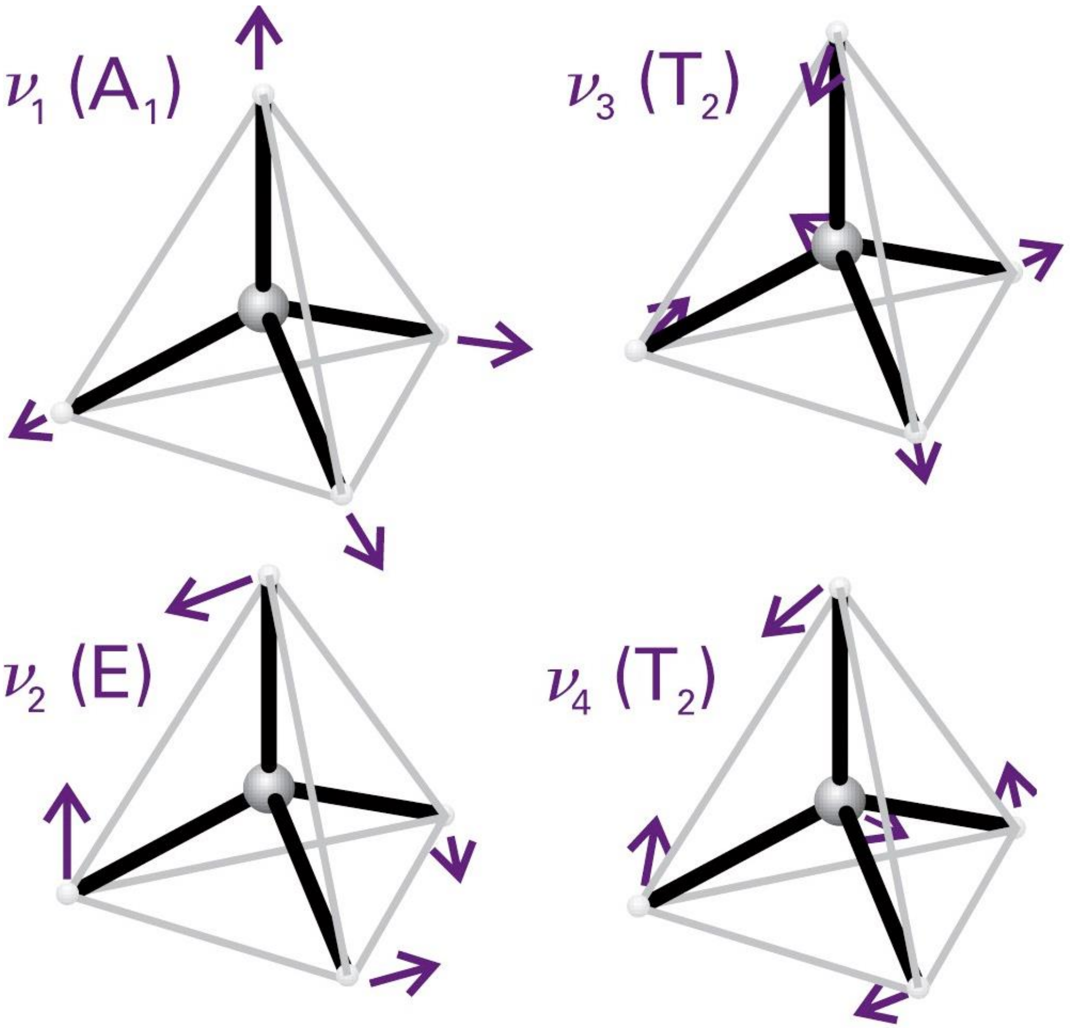
Bending
IR active
Raman inactive

Example 2: the vibration modes of H_2O



All the modes are both Raman and IR Active

Tetrahedral molecules like methane or carbon tetrachloride (no center of inversion) have 3N-6 = 3x5-6 = 9 modes, which are all Raman active



1 of these
IR inactive

3 of these
IR active

2 of these
IR inactive

3 of these
IR active

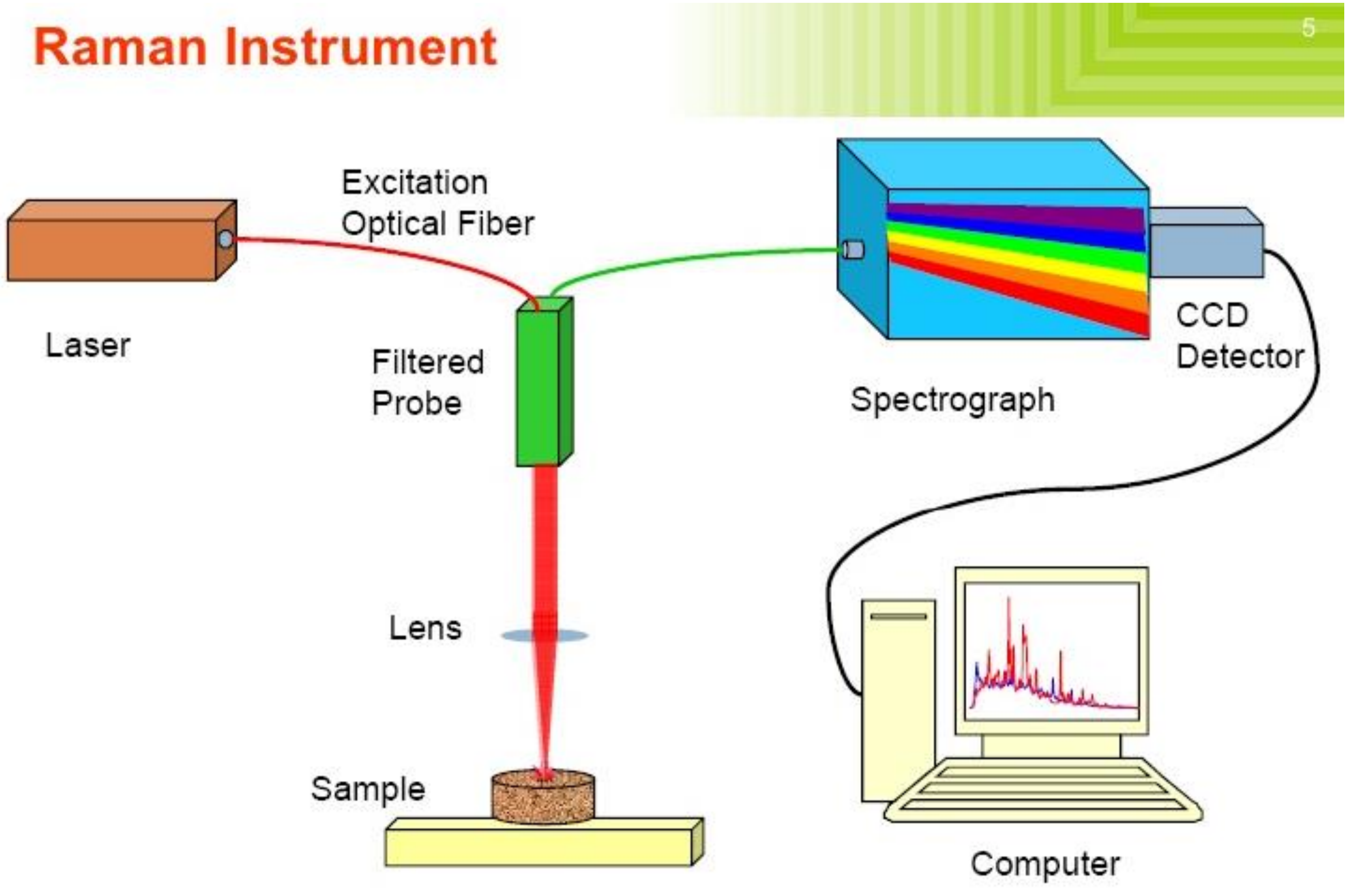
Comparison of Infrared vs. Raman

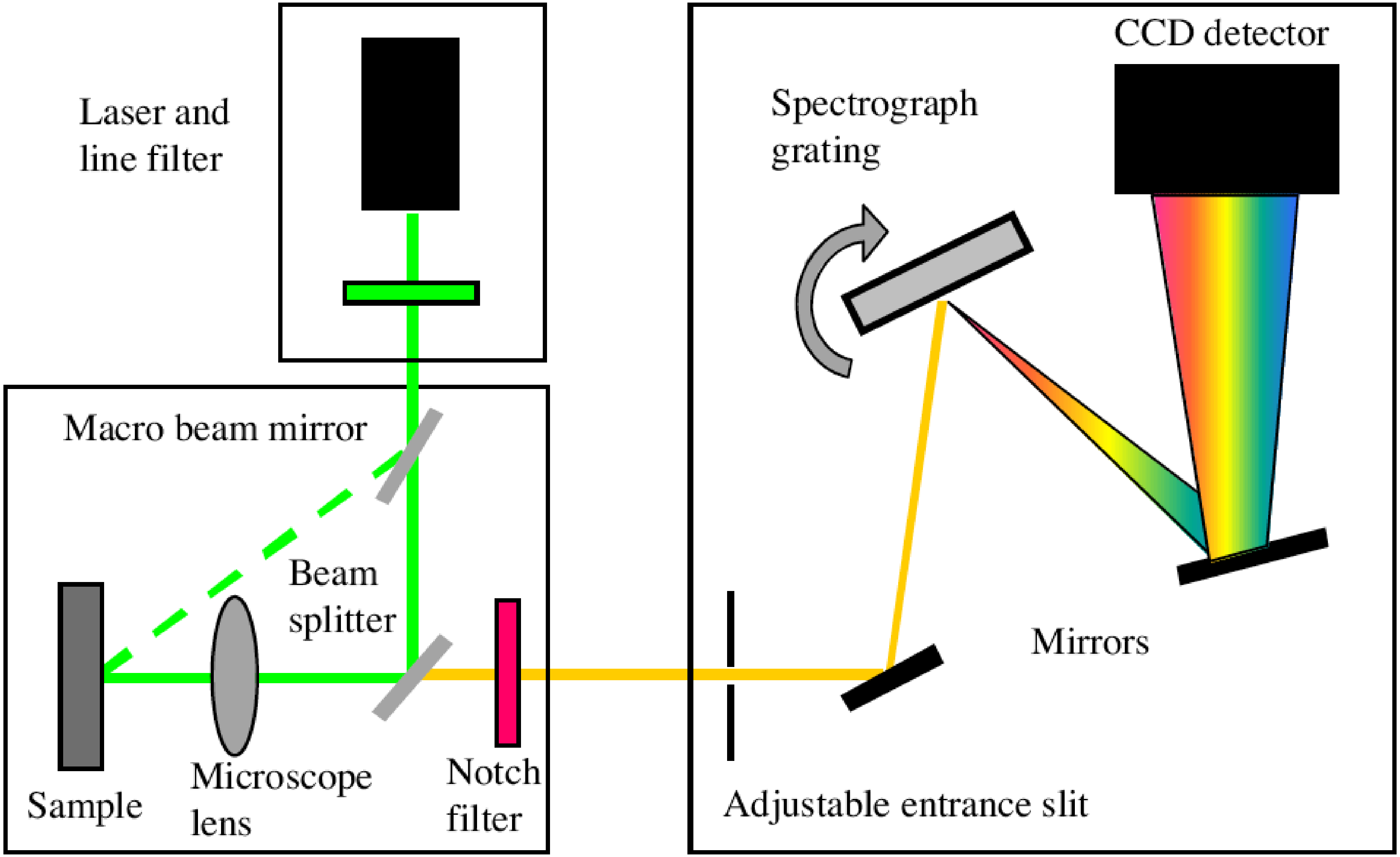
- Both spectroscopic techniques measure the same thing, vibrational energy changes, in different ways.
- IR is an absorption measurement, while Raman measures scattered light from a laser source, which is superimposed with the vibrational structure of the molecule.
- The selection rules are different: IR bands are active if the dipole moment of the vibrating molecule changes. While Raman band are active if the polarizability of the molecule changes.
- Molecules of high symmetry frequently will not show IR activity.

Raman Spectrometer

Raman spectra are acquired by irradiating a sample with a powerful laser source of visible or near-infrared monochromatic radiation. During irradiation, the spectrum of the scattered radiation is measured at some angle (often 90 deg) with a suitable spectrometer. At the very most, the intensities of Raman lines are 0.001 % of the intensity of the source; as a consequence, their detection and measurement are somewhat more difficult than are infrared spectra.

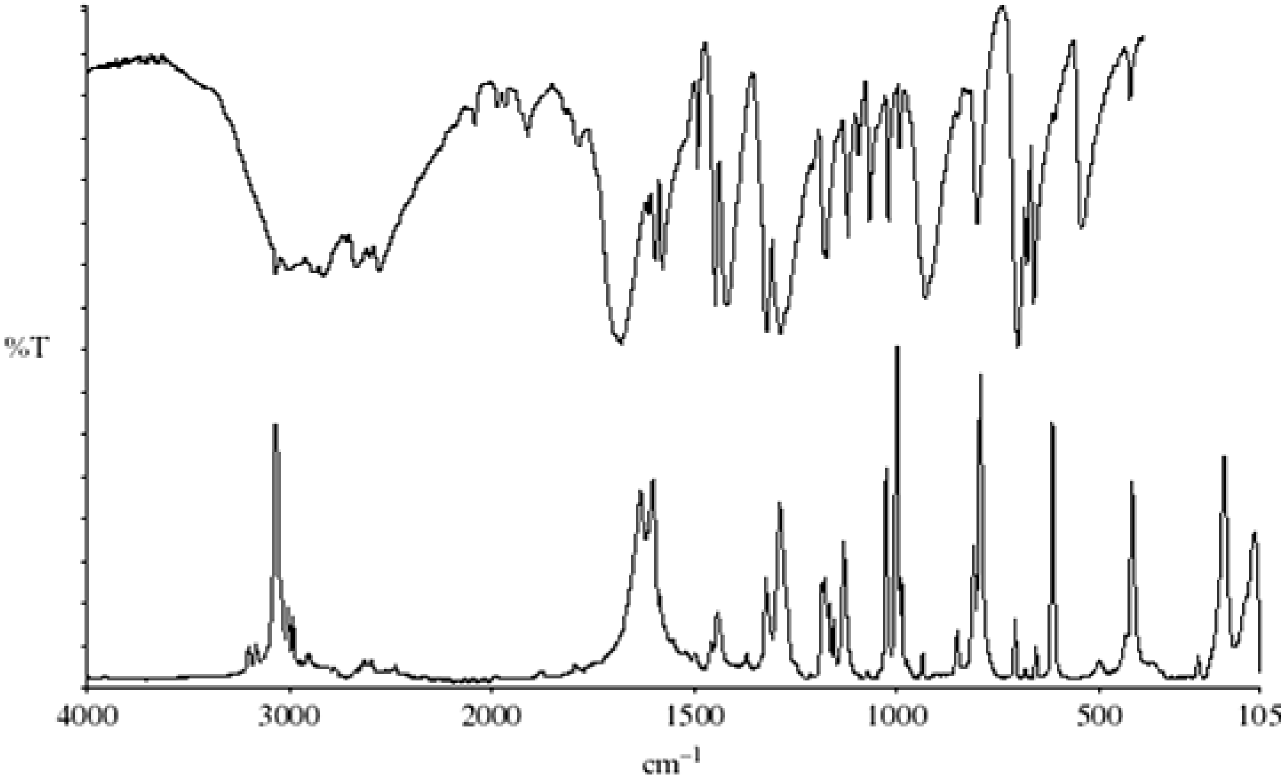
A Raman spectrum can be obtained by irradiating the sample with an intense beam of an argon ion laser having a wavelength of 488.0 nm (20492 cm^{-1}).


Raman Instrument


Laser and
line filter
Macro beam mirror
Beam
splitter
Sample
Microscope
lens
Notch
filter
Spectrograph
grating
CCD detector
Mirrors
Adjustable entrance slit

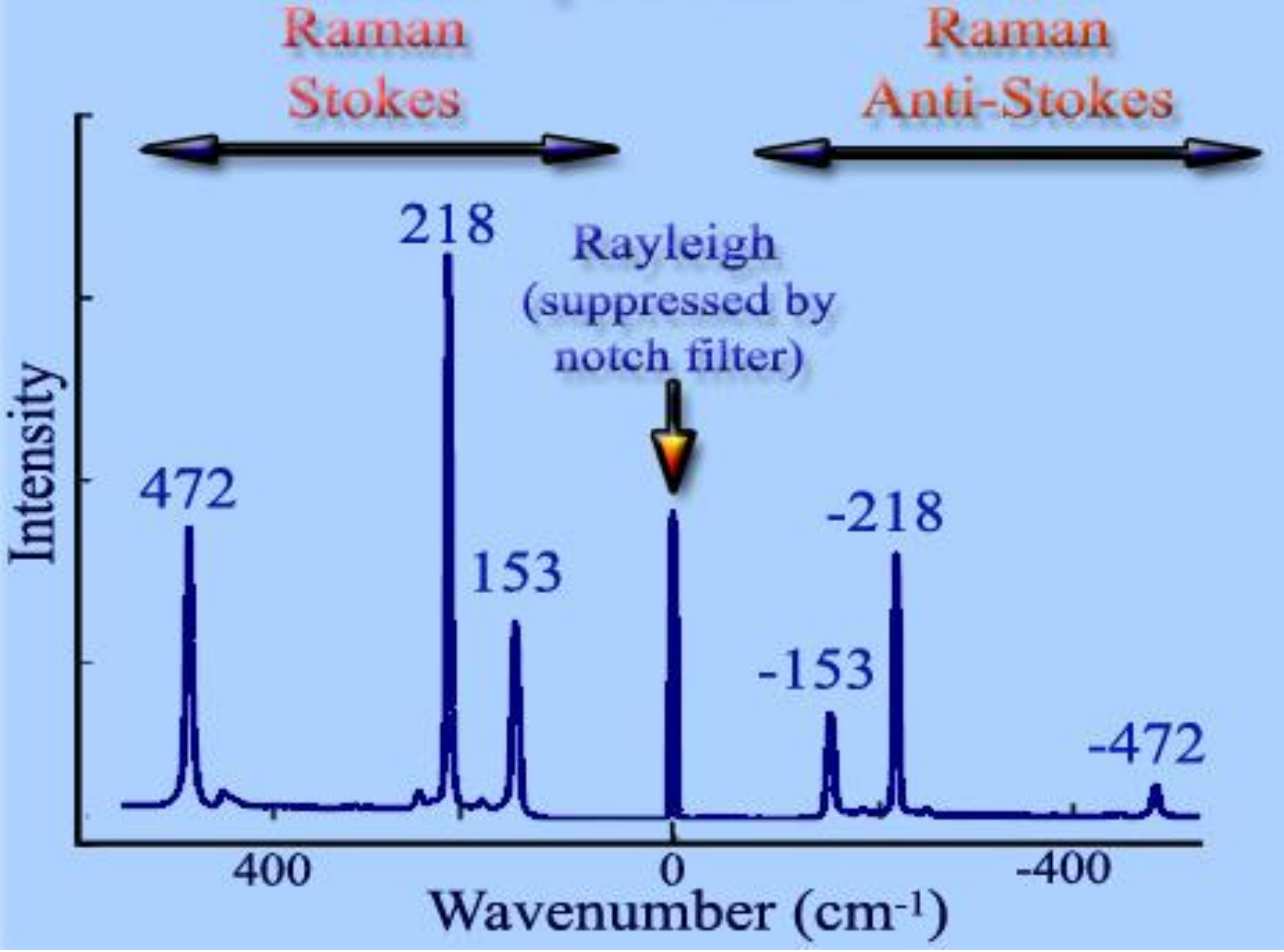
Raman Spectrum

A Raman spectrum is a plot of the intensity of Raman scattered radiation as a function of its frequency difference from the incident radiation (usually in units of cm^{-1}). This difference is called the *Raman shift*.



IR and Raman Spectrum of benzoic acid

Raman spectrum of Sulfur



Applications of Raman spectroscopy

Qualitative tool for identifying molecules from their vibrations, especially in conjunction with infrared spectrometry.

Quantitative Raman measurements

a) not sensitive since Raman scattering is weak. But resonance Raman spectra offer higher sensitivity, e.g. fabric dyes studied at 30-50 ppb.

b) beset by difficulties in measuring relative intensities of bands from different samples, due to sample alignment, collection efficiency, laser power.

Overcome by using internal standard.

Advantages of Raman Spectroscopy

1- Ease of Use for structural identification

- Raman bands can provide structural information (presence of functional groups).
- Raman spectroscopy can be used to measure bands of symmetric linkages which are weak in an infrared spectrum (e.g. -S-S-, -C-S-, -C=C-).
- The standard spectral range reaches well below 400 cm^{-1}, making the technique ideal for both organic and inorganic species.

2- Ease of Use for Process Measurements

- Fiber optics (up to 100's of meters in length) can be used for remote analyses.
- Purging of sample chamber is unnecessary since Water and CO_2 vapors are very weak scatterers.
- Little or no sample preparation is required.
- Water is a weak scatterer, no special accessories are needed for measuring aqueous solutions.
- Inexpensive glass sample holders, non-invasive probes and immersion probes are ideal in most cases.

Disadvantages of Raman Spectroscopy

1. Inherently not sensitive (~ 1 million incident photons are needed to generate 1 Raman scattered photon).
2. Fluorescence is a common background issue.
3. Typical detection limits in the parts per thousand range.
4. Fluorescence Probability versus Probability of Raman Scatter (1 in 10^3-10^5 vs 1 in 10^7-10^{10}).
5. Requires expensive lasers, detectors and filters.
6. Small sample volume can make it difficult to obtain a representative sample.