Chapter I:
Spectrometry and Raman scattering.

Introduction:

Raman spectroscopy is a vibrational molecular spectroscopic analysis technique based on the detection of scattered photons following the interaction of the sample with a monochromatic beam of light.

A phenomenon discovered in 1928 by Raman, winner of the Nobel Prize in Chemistry in 1930.

Chandrashekhara Venkata Raman (November 7, 1888 – November 21, 1970) was a physicist Indian . He discovered and explained Raman scattering . He was awarded the 1930 Nobel Prize in Physics "for his work on the scattering of light and for the discovery of the effect bearing his name . "

A very small fraction of the incident radiation is affected by the scattering phenomenon.

Like infrared (IR) spectroscopy, Raman spectroscopy allows access to the vibrational and rotational levels of molecules. The process involved is linked to a change in the molecule's polarizability during a vibrational transition. Unlike IR spectroscopy, which it complements through its selection rules, Raman spectroscopy remained relatively underutilized for a long time despite its many attractive advantages. First, sample preparation can be minimized since it is possible to work with liquid, gaseous, or solid substances. Finally, this technique opens up applications in the biological and medical fields because the Raman scattering of water is very low, allowing its use as a solvent.

Definition:

Raman spectroscopy is a vibrational molecular spectroscopic analysis technique based on the detection of scattered photons following the interaction of the sample with a monochromatic light beam.

Light/matter interaction:

An electromagnetic wave can interact with the vibrations of atoms. When a photon interacts with a phonon, two main cases can occur:

- **If the incident photon has an energy equal to that of a vibrational level,** it is **absorbed.** This is the principle of **infrared (IR) spectroscopy.**
- **If the incident photon has a much higher energy than the vibrational levels,** it cannot be absorbed in the same way. In this case, a **scattering phenomenon** (Rayleigh or Raman) is observed.
- A **phonon** is a concept in **quantum physics** used to describe vibrations in a solid:
- In a crystal, atoms are not stationary: they vibrate around their equilibrium position.
- These collective vibrations of atoms can be described as **quantized sound waves.**
- In quantum mechanics, each vibration is associated with a fictitious elementary particle called **a phonon,** in the same way that light is described in terms of photons.
- The **photon** = quantum of light (electromagnetic wave).
- The **phonon** = quantum of vibration of the crystal lattice (sound wave/ lattice vibration).

They are involved in spectroscopy (e.g. Raman) because incident photons can **exchange energy** with phonons, which changes the frequency of the scattered photon.

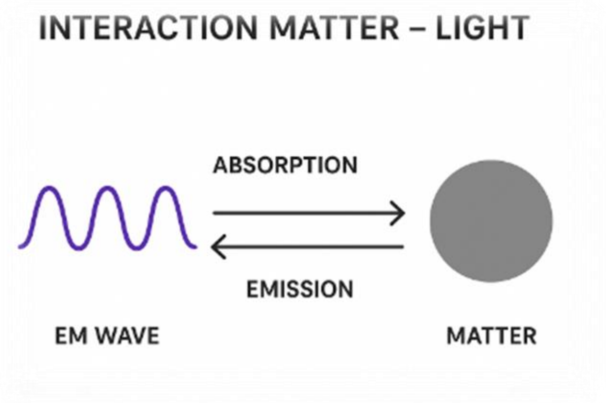


Fig. I.1. Diagram of the interaction between light and matter

Principle:

intense monochromatic radiation of frequency $\underline{\nu_0}$ (from a laser source), the photons constituting this radiation can be transmitted, absorbed or scattered in all directions of space.

Energy **E_0** The incident radiation is defined by the following relationship:

$$E_0 = h\upsilon_0 = \frac{hC}{\lambda}$$

With

- *h:* Planck constant (6.63×10^{-34} J·s).
- υ_0 : frequency of the incident radiation.
- *c* : speed of light in a vacuum (3×10^8 m/s).
- λ_0 : wavelength of the incident radiation.

A fraction of the incident radiation is:

•If it is scattered at the same frequency as the incident radiation ν_0 , this is elastic light scattering called: ***Rayleigh scattering.***

•the light is scattered at a frequency ν different from that of the incident radiation, this is inelastic light scattering, called ***Raman scattering.*** In the case of Raman scattering:

- $\nu \succ \nu_0$ Anti-Stokes process.
- $\nu \prec \nu_0$ Stokes process.

Noticed:

• **$\Delta\nu$:** is of the order of magnitude of the molecular vibration and rotation frequencies.

•1 on 10^8 is affected by Raman scattering, hence the need to use sources of very high intensities.

Complement:

- **Elastic Scattering:** Incident light is scattered without a change in energy, which provides no information about molecular vibrations.
- **Inelastic Scattering:** Part of the light is absorbed by the molecules, which excites them to a higher vibrational state; when these molecules return to their ground state, they emit light with a different energy than the incident light.
- **Stokes lines:** When scattered light has less energy than the incident light, this corresponds to a change towards a lower vibrational state. These transitions are called "Stokes lines".
- **Anti-Stokes lines:** When scattered light has higher energy than the incident light, this corresponds to a change towards a higher vibrational state. These transitions are called "anti-Stokes lines".

- **Raman Spectrum:** The spectrum obtained represents the intensity of scattered light as a function of frequency (or wavelength). The peaks in this spectrum correspond to the different vibrations of the molecular bonds in the sample.

The intensity of the peaks can be correlated with the concentration of the compounds present

Energy diagram:

Diffusion occurs when electrons transition to a virtual energy level that is neither electronic, vibrational, nor rotational. Relaxation can occur in either:

- Towards the initial energy level: ***Rayleigh scattering.***
- Towards an energy level lower than the initial energy level: ***Anti-Stokes Raman scattering.***
- Towards a higher energy level than the initial energy level: ***Raman Stokes scattering.***

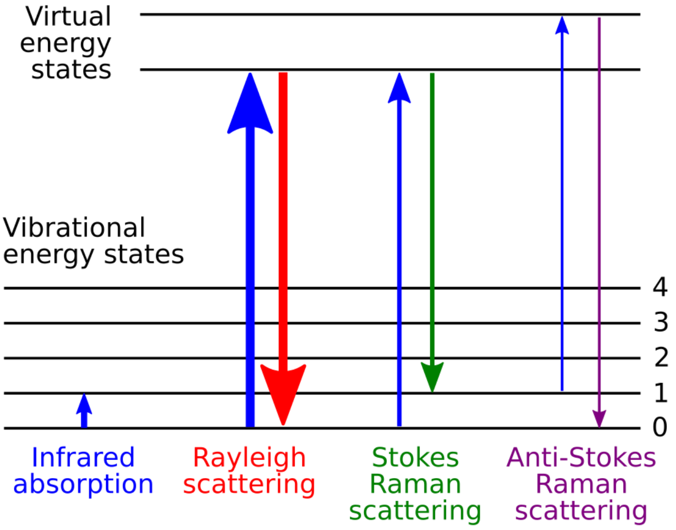


Fig.II.2. Schematic representation of Rayleigh and Raman Stokes and anti-Stokes scattering processes in a semi-classical approach.

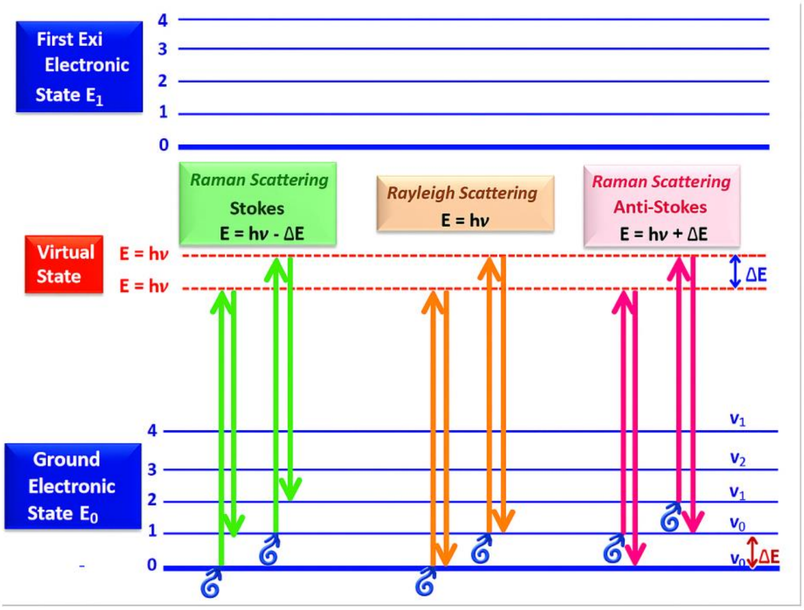


Fig.II.3. Schematic representation of Rayleigh and Raman Stokes and anti-Stokes scattering processes in a semi-classical approach

The RAMAN shift:

The **Raman shift corresponds** to the difference in frequency (or **energy)** between the **incident light** (that sent by the laser) and the **scattered light** (that which is observed after interaction with matter).

In other words, when a photon from the laser beam interacts with a molecule, it can **exchange energy** with it (by exciting or de-exciting a molecular vibration). The energy difference between the incident photon and the scattered photon then corresponds to **the energy of a molecular vibration.**

Expression of the Raman shift

The Raman shift is expressed in **wavenumber (cm^{-1}),** that is to say in spatial frequency:

$$\Delta\bar{\upsilon}=\bar{\upsilon}_0-\bar{\upsilon}_d$$

with:

- $\bar{\upsilon}_0$: wavenumber of the incident radiation (laser),
- $\bar{\upsilon}_d$: wavenumber of the scattered radiation,
- $\Delta\bar{\upsilon}$ Raman shift.

This shift is **independent** of the wavelength of the laser used (an essential property of Raman spectroscopy).

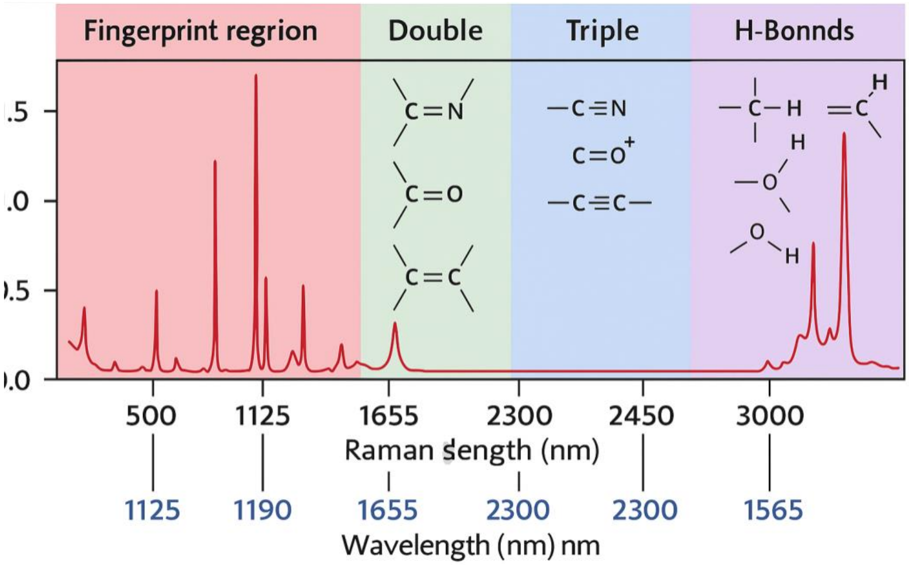
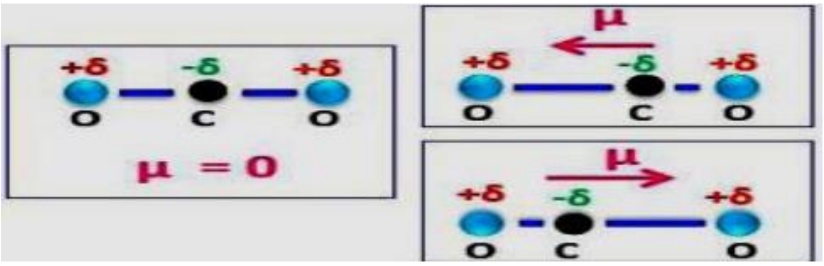


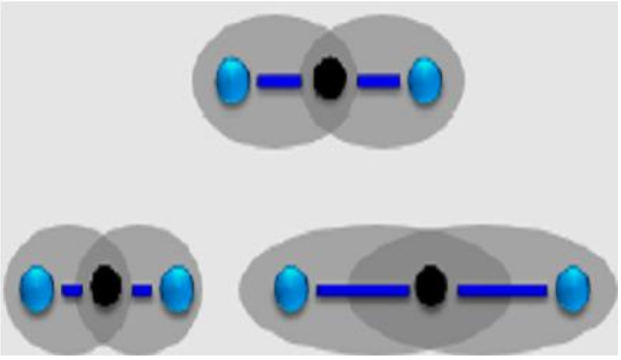
Fig.II.4. RAMAN offset

Vibration selection rule and symmetry

In Infrared Spectroscopy: An active vibration is accompanied by a change in the dipole moment.



In Raman spectrometry: An active vibration is accompanied by a change in **polarizability.** Polarizability is due to a momentary deformation of the electron cloud distributed around a bond.



The value of Raman spectra:

In some cases, there is no IR spectrum; this is the case for symmetrical diatomic molecules such as H_2 , O_2 , and N_2 ; however, they do have a Raman spectrum. The observed frequencies relate to the vibrations and rotations of the molecules, as in the case of infrared. The same information (functions, distances, and angles within the molecules) can be derived from them. The observed lines are finer and more precise than in IR.

Example:

In a molecule such as ethene $(CH_2 = CH_2)$, the stretching vibration of the double bond is symmetrical because the two ends of the molecule are identical. In infrared spectroscopy, no absorption band will be observed for the valence vibration of the double bond, and it will be very weak in ethenes whose carbons are substituted by comparable groups. In contrast, in Raman spectroscopy, this vibration appears strongly and provides evidence of the symmetrical structure of ethylene.

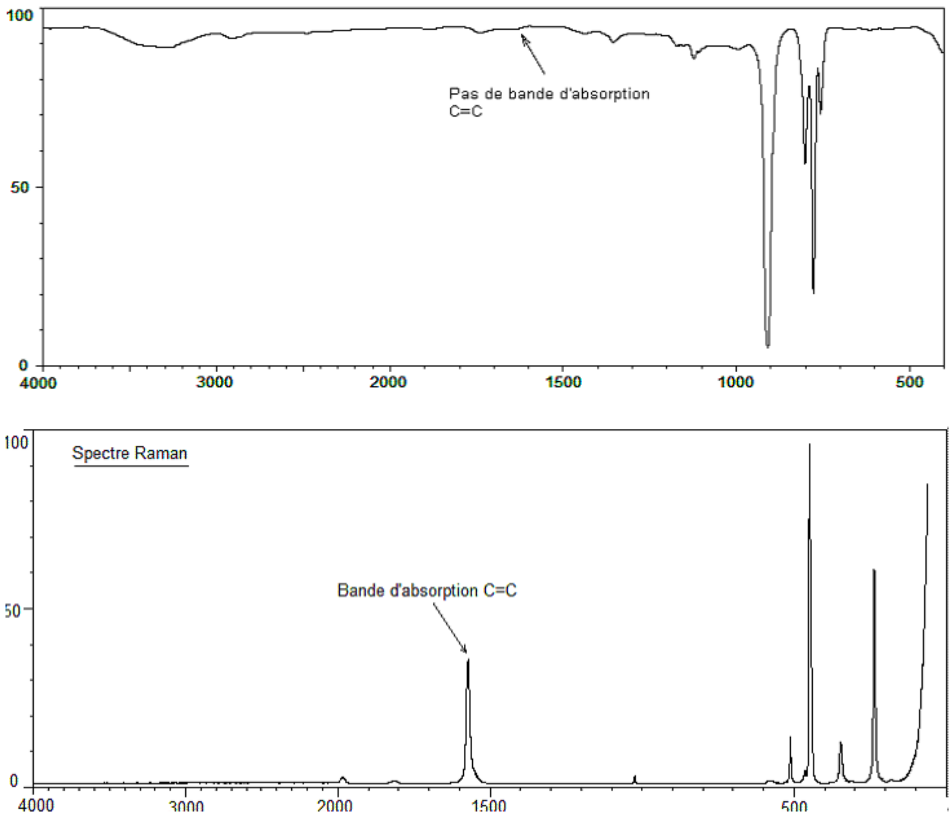


Fig.II.5. Interest of Raman spectra

RAMAN-IR Complementarity

Raman and infrared (IR) spectroscopies share many similarities. Indeed, it follows from the above that the energies detected in IR:

$$E = h.(\upsilon_1 - \upsilon_0)$$

These are the same as those detected by Raman:

$$E = h.\upsilon_i \pm h.(\upsilon_1 - \upsilon_0).$$

The wavelength of the incident radiation is disregarded. $h\,.\,(\upsilon_1 - \upsilon_0\,)$Thus, the Raman shift corresponds to the IR absorption of radiation of the same frequency.

In IR spectroscopy (direct absorption)

We observe the **absorption** of a photon if its energy corresponds exactly to the difference between two vibrational levels of the molecule:

$$E=h\,(\nu_1 - \nu_0)$$

- ν_0 : fundamental level (basic vibrational state).
- ν_1 : excited vibrational level.
- h : Planck constant.

In IR, the absorbed energy corresponds **directly** to the vibrational transition.

In Raman spectroscopy (inelastic scattering)

Here, the incident photon of frequency ν_i interacts with the molecule. It can emerge with a different frequency.

The energy measured in Raman is written as:

$$E = h\nu_i \pm h(\nu_1 - \nu_0)$$

- The first term $h\nu_i$ corresponds to the energy of the incident photon.
- The second term $(\pm h(\nu_1 - \nu_0))$ translates the exchange of energy with vibration:
  - **Stokes** : the photon loses energy → lower frequency.
  - **Anti-Stokes** : the photon gains energy → higher frequency.

Why do we say they are complementary?

In Raman spectroscopy, the same vibrational difference as that detected in IR is **subtracted from** or **added** to the incident energy $h\nu_i$:

$$\Delta E=h\,(\nu_1 - \nu_0)$$

Therefore, the **Raman shift** corresponds exactly to the **same vibrational energy** as that observed in IR absorption.

Simple summary

- **IR:** we directly measure the energy absorbed to go from ν_0 to ν_1 .
- **Raman:** we measure the difference in frequency (Raman shift) between the incident photon and the scattered photon → this difference is the **same vibrational energy** as that measured in IR.

Raman intensity:

A Raman spectrum shows the scattered Raman intensity as a function of the frequency difference between the incident and scattered photons:

$$\Delta\bar{\upsilon}=\left|\bar{\upsilon}_{\text{incident}}-\bar{\upsilon}_{\text{diffuse}}\right|$$

If we consider Stokes lines, this difference is positive, and zero in the case of Rayleigh scattering. In practice, it is common to convert this frequency difference between the incident and scattered photons into a wavenumber. The wavenumberv is defined by the following relationship:

$$\bar{\upsilon}=\frac{1}{\lambda}=\frac{\upsilon}{c}$$

With :

- $\bar{\upsilon}$ Number of waves (cm^{-1}) .
- λ: Wavelength of the radiation (cm).
- υ: Frequency of radiation (Hz).
- c: Speed of light in a vacuum.

Theoretical aspect

Theoretically, we can write the ratio of the intensities of the Stokes and Anti-Stokes diffusions, which are proportional to the initial population level. Let's estimate the ratio between the intensities of the Stokes and Anti-Stokes rays, knowing that:

$$I_{\text{stokes}}\approx N_0$$
$$I_{\text{anti-stokes}}\approx N_\upsilon$$

With:

$$N_\upsilon=N_0\,e^{-\left(\frac{E_\upsilon-E_0}{kT}\right)}$$

$$\frac{I_{\text{stokes}}}{I_{\text{anti-stokes}}}=\frac{N_0}{N_\upsilon}=\frac{N_0}{N_0e^{-\left(\frac{E_\upsilon-E_0}{kT}\right)}}\approx e^{\left(\frac{E_\upsilon-E_0}{kT}\right)}=e^{\frac{\left(h\Delta\bar{\upsilon}\right)}{kT}}$$

We can therefore see that anti-Stokes lines will always be less intense than the corresponding Stokes lines.

- They become unobservable as soon asΔv becomes important and/or the temperature drops.
- Measuring their ratio allows us to determine the temperature of a sample under the impact of laser beams. According to **Placzek 's theory** , the intensity of a Raman line scattered at a right angle to the excitation direction follows the following relationship:

$$I=K\frac{(\upsilon_0+\upsilon_{Raman})^4}{\upsilon_{Raman}}\times\frac{N\times I_0}{1-e^{-\left(h\upsilon/kT\right)}}\times\left[45\alpha'_S+13\alpha'_a\right]^2$$

Or:

- N: Number of scattering molecules. I0: Intensity of the excitation line.
- α'_s and α''_a : Are the derivatives of the symmetric and asymmetric components of polarizability.

This means that the intensity of a Raman line is: All the more intense the shorter the wavelength of the excitation line.

•Proportional to the intensity of this exciting line.

•Proportional to the number of scattering molecules seen by the spectrometer.

•Proportional to the square of the change in polarizability produced during vibration.

Rules for Vibration Selection and Symmetry

Introduction

Molecules possess **normal modes of vibration** (stretching, deformation, twisting).

Not all of these vibrations are observable in IR or Raman spectroscopy.

Their **observability** depends on **selection rules** related to molecular symmetry.

Selection rules in IR spectroscopy

A vibration is **active in IR** if:

- It causes a **change in the dipole moment** of the molecule.
- Examples:
  - **C=O** stretch vibration (strongly polar) is very active in IR.
  - The symmetrical vibration of a perfectly homonuclear molecule (O_2 , N_2) is **not IR active** (no dipole moment).

IR rule:

$$\frac{d\mu}{dq}\neq 0$$

Or:

- μ : dipole moment
- q : vibration coordinate.

Selection rules in Raman spectroscopy

A vibration is **active in Raman** if:

- It causes a **variation in molecular polarizability.**
- **Example:**
  - **Symmetrical** vibrations (C=C in an aromatic ring) are very intense in Raman.
  - Some antisymmetric vibrations (such as the asymmetric stretch CO_2) are weak in Raman.

Raman rule:

$$\frac{d\alpha}{dq} \neq 0$$

- where α is the molecular polarizability.

IR-Raman Complementarity

- IR and Raman spectroscopies are **complementary:**
  - An active vibration in IR may be weak or inactive in Raman.
  - Conversely, a vibration that is inactive in IR may be active in Raman.

Example: CO_2:

- Symmetrical stretching (inactive IR, active Raman).
- Antisymmetric stretching (active IR, low Raman).

Symmetry and group theory

Molecular symmetry analysis (group theory) allows us to **predict the active modes** in IR and Raman spectroscopy:

- Each vibrational mode belongs to an **irreducible representation** of a symmetry group (C_{2v}, D_{3h}, Oh, etc.).
- Character tables indicate whether a representation is IR active (linked to x , y, z) or Raman active (linked to x2, xy , …).

Summary (comparative table)

Spectroscopy	Selection rule	Typical vibration observed
IR	Variation of the dipole moment ($d\mu / dq \neq 0$)	Asymmetrical stretches, polar vibrations
Raman	Variation of polarizability ($d\alpha / dq \neq 0$)	Symmetrical stretches, aromatic cycles

Additional Information

The **polarizability** (α) of a molecule is a physical quantity that measures how **easily the electron cloud of a molecule can be distorted** by an external electric field (such as incident light).

Simple explanation

- When a molecule is subjected to an electric field (E), the electrons move slightly relative to the nuclei → the molecule acquires an **induced dipole** .
- The intensity of this induced dipole (μ) is proportional to the applied electric field:

$\mu_{ind} = \alpha E$

Or :

- μ : induced dipole moment
- E: applied electric field
- α : polarizability

In Raman spectroscopy

- A vibration is **Raman active** if it causes a **change in the polarizability** of the molecule during the oscillation.
- Example :
  - **symmetrical** vibration (such as the symmetrical stretching of CO_2) strongly modifies polarizability → very active in Raman.
  - An **antisymmetric vibration** may not change polarizability → inactive or weak in Raman.

Factors that influence polarizability

- The **size of the electron cloud** (heavy and bulky molecules are more polarizable).
- The **nature of the bonds** (π or conjugated bonds are more polarizable than σ bonds).
- **Molecular geometry** (symmetry, electronic distribution).

: Homonuclear molecules (N_2 , Cl_2 , H_2 …)

- Elongation causes a change in polarizability without a change in the dipole moment:

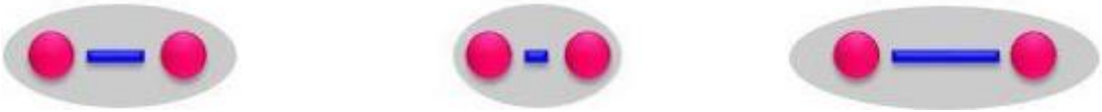


Fig.II.6. Vibration active in RAMAN and inactive in IR

- **Symmetrical stretching vibration:** change in polarizability without change in dipole moment

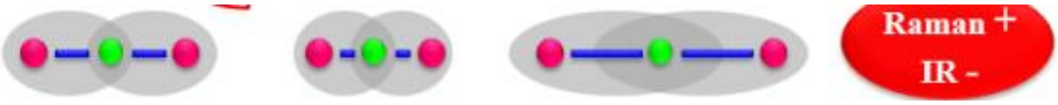


Fig.II.7. Vibration active in RAMAN and inactive in IR

- **Antisymmetric stretching vibration** : no change in polarizability and modification of the dipole moment.

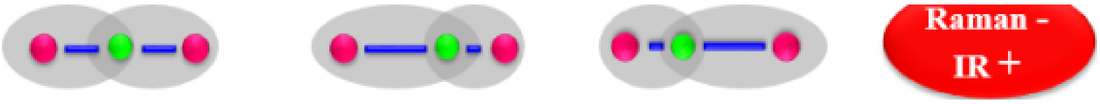


Fig.II.8. Vibration inactive in RAMAN and active in IR

- **vibration deformation:** no change in polarizability and modification of the dipole moment.

Fig.II.9. Vibration inactive in RAMAN and active in IR

Some vibrations are only active in the infrared spectrum, while others are only active in the Raman spectrum (mutual exclusion rule). Others are active in both, or neither. Raman spectroscopy is a complementary technique to infrared spectroscopy. Both techniques provide a complete vibrational signature of the analyte.

DIFFERENT RAMAN EFFECTS:

Classic Raman effect: The virtual state corresponds to an intermediate energy between that of the ground state and the first excited electronic state.

Pre-resonance Raman **effect:** The virtual state corresponds to an energy close to that of the first excited electronic state with $Ev \prec E_1$.

Resonance Raman effect: The virtual state corresponds to an energy close to that of the first excited electronic state with $Ev \succ E_1$.

Rule of Mutual Exclusion Law -

Definition

The rule of mutual exclusion stipulates that:

- For a molecule possessing an inversion center (symmetry **i**):
  - A vibrational mode that is active in IR spectroscopy is inactive in Raman.
  - An active vibrational mode in Raman is inactive in IR.

In other words, **no mode can be active in both IR and Raman at the same time** .

Justification (molecular symmetry)

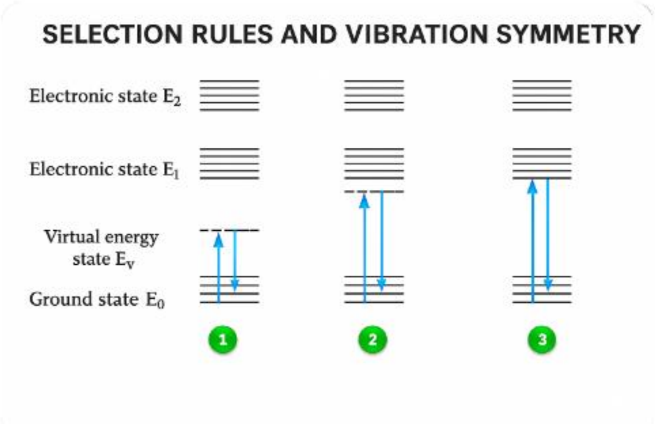
- Molecules with an **inversion center** obey this rule (for example: CO_2, C_2H_2, benzene).
- This stems from the fact that:
  - **Gerade (g)** modes (symmetric with respect to the center of inversion) are active in Raman but not in IR.
  - **Ungerade (u) (antisymmetric)** modes are active in IR but not in Raman.

Consequences

- IR and Raman spectra are **complementary for** centrosymmetric molecules .
- For molecules without an **inversion center** (e.g. H2O , NH3) , the same mode can be active in **IR and Raman** .

Example: CO_2 ($D_{\infty h}$)

- **ν_1 : symmetric stretching (g)** → Active Raman, inactive IR.
- **ν_2 : deformation (u)** → IR active, Raman inactive.
- **ν_3 : antisymmetric stretching (u)** → IR active, Raman inactive.



Equipment:

The basic elements forming a Raman spectrometer are shown **in figure (10).** and explained later.

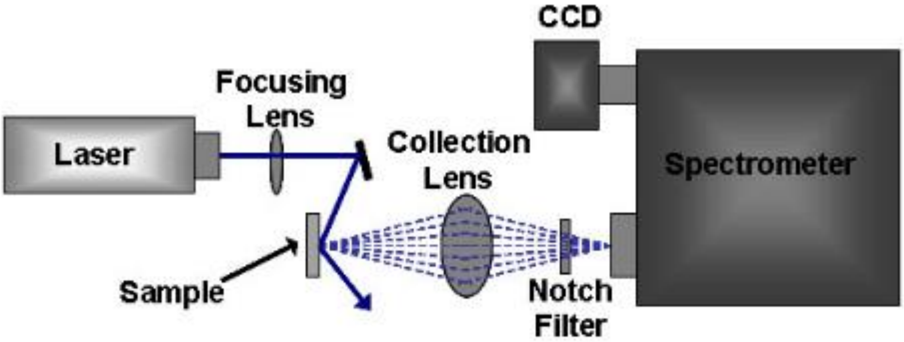


Figure 4.3.5 Schematic of a macro-Raman spectrometer.

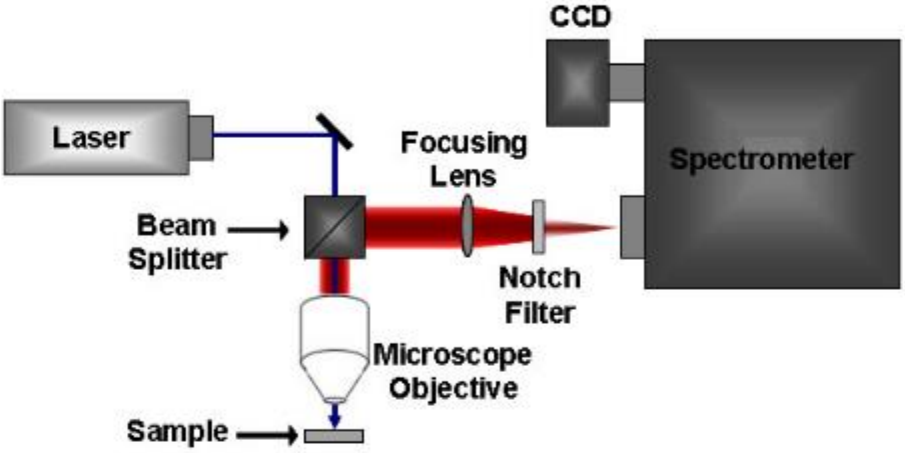


Fig.II.10. Diagram of a typical apparatus used in Raman spectroscopy.

(a) Laser source:

The laser provides monochromatic radiation of a stable and known frequency. Laser sources are available in the ultraviolet (UV), visible, and near-infrared (NIR) ranges, depending on the nature of the sample to be analyzed and the purpose of the analysis. A pre-monochromator or interference filter located immediately after the laser eliminates spurious plasma lines found near the excitation laser line. The beam then passes through a polarizer placed at the microscope's entrance, fixing the incident polarization.

(b) Microscope:

The microscope focuses the incident laser spot onto the sample surface, via the appropriate objective lens, and then directs the scattered photons to the spectrometer. An analyzer fixes the polarization of the scattered wave.

(c) Rejection filter:

Since the Raman process is not very intense, a holographic ″notch ″or ″edge filter ″is used to separate the signal of interest from the much more intense Rayleigh signal.

(d) Monochromator:

The scattered photons enter the monochromator through a slit (or confocal hole) that allows the light to be precisely localized. A prismatic mirror The photons are then directed onto a holographic grating of 600, 1200, 1800, 2600, or 3600 lines/mm, dispersing them according to their wavelength (the number of lines chosen depends on the incident wavelength). Each radiation is then focused onto the detector by a lens. Some instruments have several monochromators to improve spectral resolution and rejection rate (i.e., the ability to *eliminate the Rayleigh line).*

(e) Detector:

There are two types of detectors on the market: CCD or InGaAs depending on the range of wavelengths that one wishes to analyze.

- CCD Detector (Charge Coupled Device): This is a multi-channel detector that simultaneously collects spatial and spectral information about the analyzed sample. Its spectral range is between 400 nm and 1 µµm
- InGaAs detector (single channel): This is a detector specifically designed for IR. It has a better signal-to-noise ratio than a CCD detector, but lower resolution.

Fourier transform Raman spectrometer:

The more recent Fourier transform Raman spectrometer allows for the separation of radiation. Indeed, it is essential to first remove the background noise caused by fluorescence, which masks the signals of interest. Fluorescence originates from the sample or its impurities. For example, for a flux of 10 million photons, only 1 will be scattered by the Raman effect, whereas for impurities, 10 photons will come from fluorescence. Therefore, highly fluorescent impurities or a moderately fluorescent sample can cause significant background noise. Initially, the use of Nd:YAG lasers , emitting at 1.06 mm, i.e., below the fluorescence threshold, was considered, but with this method, the cross-section (or probability of scattering) of light scattered by the Raman effect is considerably reduced compared to the use of other lasers. Furthermore, there is a lack of efficient detectors, such as a photomultiplier tube, in this wavelength range.

Advantages of the Raman spectrum over the infrared spectrum:

The advantages of Raman spectroscopy are summarized below:

Non-destructive and non-intrusive method, which allows it to be applied to real systems.

- Easy to implement. The nature of the samples (solids, liquids, or gases) is irrelevant. Furthermore, it requires only a small quantity of samples (1 μg).
- It can be coupled with other analytical methods and offers the possibility of in situ measurements.
- It can be used on very small samples (down to $1 \mu m^3$)

Disadvantages of the Raman spectrum

- In principle, all molecules are susceptible to the Raman effect. However, the limitations of sensitivity (related to the dispersion of spectrographs used in the visible range) and in the precision of observations related to this effect result in a more limited number of applications.
- Experimentally, significant difficulties are observed in measuring the intensity of spectral lines. Since these lines provide information on species concentration, it is understandable that the Raman effect is not a generalized approach for this purpose.
- Rotation structure difficult to obtain, this being due to the presence of strong Rayleigh scattering and the characteristics of the light sources used, although the introduction of monochromatic laser sources has made it possible to significantly increase the performance of Raman devices.

Application areas of Raman spectroscopy:

Numerous instrumental developments over the past twenty years have led to a resurgence of Raman spectroscopy, which, conceptually complementary to infrared spectroscopy, is also complementary in terms of applications. Examples discussed in the literature demonstrate its potential for a wide range of applications, including:

- Determination of the chemical structure (C=O, C=C, OH, CO, CC, CS, ... etc).
- Configuration (cis, trans .) tacticity for polymers.
- Conformation (planar arrangement, helical arrangement α, α, ... etc. in sheets): domain of biology.
- Determination of crystallinity and lamellar thickness (low frequency modes) for polymers.
- The study of intra- and intermolecular forces (hydrogen bonding).
- The study of the orientation of molecules (polarization).
- Trace analysis.
- Quantitative analyses.