
UNIT 4 RAMAN SPECTROSCOPY

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4.1 INTRODUCTION

In the previous unit you learnt about IR spectrometry in terms of its principle, instrumentation and applications. You would recall that the IR spectrum is a consequence of transitions amongst the quantised vibrational energy levels of the molecules on absorbing IR radiation. In this unit you would learn about Raman spectroscopy which also involves same energy levels but it differs on many other counts. The nature of radiation used, the mechanism of interaction between the radiation and matter, the necessary condition for the interaction, the selection rules, the sensitivity, required instrumentation and the resulting spectra are different in case of Raman spectroscopy. Further, even the information available from it is different; in fact it is complimentary to the one available from IR spectroscopy.

As in the previous unit, we shall begin by understanding the theory behind Raman spectroscopy in terms of the origin of the spectrum and its characteristic features. It will be followed by an account of the essential components of Raman spectrometers. Thereafter we shall take up the applications of Raman spectrometry in diverse areas. In the next block you will learn about spectrometric methods based on molecular fluorescence and molecular phosphorescence which are important spectroscopic method of analysis.

Objectives

After studying this unit, you should be able to:

- define Raman effect,
- explain the origin of Rayleigh scattering,
- describe Raman effect in terms of classical wave theory and quantum theory of radiation,
- define Stokes and anti-Stokes lines and explain their origin,
- compare and contrast Raman spectra with IR spectra,
- state the rule of mutual exclusion and explain its significance,

- enlist the essential components of the instrument required for Raman spectroscopy,
- describe advantages of Raman spectroscopy, and
- enumerate and discuss various applications of Raman spectroscopy.

4.2 THEORY OF RAMAN SPECTROSCOPY

An electromagnetic radiation when passed through a transparent medium interacts with the particles (e.g., molecules, atoms, or ions) constituting it. If the dimensions of the particles are equal to or smaller than that of its wavelength then it undergoes scattering. It has been observed that most of the scattered radiation has exactly the same wavelength as that of the incident radiation. Such a scattering is referred to as **Rayleigh scattering**. However, a very small fraction (to the tune of about 1 in 10^7) of the scattered radiation is found to have a wavelength different from that of the incident radiation. This is called **Raman scattering** and the existence of Raman scattering is called **Raman effect**. Fig 4.1 gives the spectra of the scattered radiation obtained when a sample of CCl_4 was interacted with a laser beam having a wavelength of 488.0 nm.



C.V. Raman – the discoverer of Raman Effect in 1928. He was awarded the 1930 Nobel prize in Physics. The significance of his discovery can be gauged from the fact that it holds the record for the shortest time from a discovery to awarding of the Noble prize.

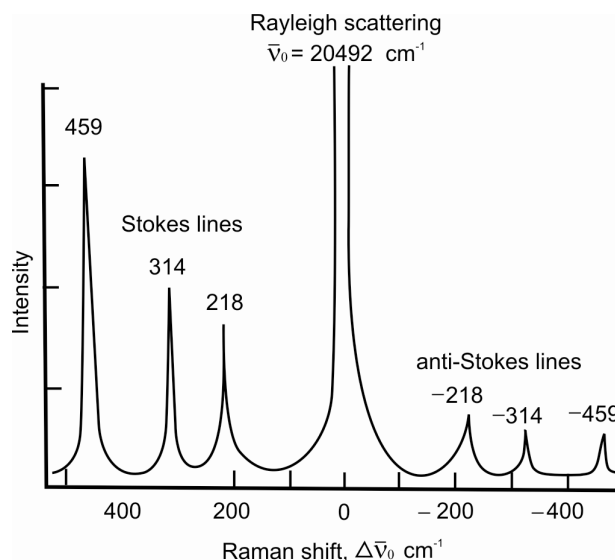


Fig. 4.1: Raman spectra for CCl_4 using 488 nm laser source

You may note that the intense peak in the centre of the spectrum has the same wavelength (or wavenumber) as that of the incident radiation. This is the **Rayleigh peak** and the other signals on either side of the Rayleigh peak are the **Raman lines**. The lines to the left of Rayleigh peak and having lower value of wavenumber are called **Stokes lines** while the ones to the right and having higher value of wavenumber are called **anti-Stokes lines**. Stokes lines are at lower energy while the anti-Stokes lines are at energy greater than the Rayleigh peak.

The positions of Raman lines are expressed in terms of **Raman shift**, $\Delta\bar{\nu}$ which is defined as per the following equation.

$$\Delta\bar{\nu} = (\bar{\nu}_s - \bar{\nu}_0) \text{ cm}^{-1} \quad \dots (4.1)$$

Where, $\bar{\nu}_s$ and $\bar{\nu}_0$ are the wavenumbers of the source (or incident) radiation and the observed scattered lines respectively. It is obvious that the Raman shifts of the Stokes lines would be positive while for **anti-Stokes lines**, these would be **negative**.

Like IR spectrum, the Raman spectra are also given in wavenumber units. This is convenient because the position of other scattered radiations (Raman scattering) can be conveniently expressed in terms of Raman shifts.

There are two more features in the spectrum given above. Locate and write them in the space provided below.

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We are sure that you could notice that, firstly, the Stokes and anti-Stokes lines are equidistant from the Rayleigh line and secondly, the Stokes lines are much more intense as compared to the anti-Stokes lines. Let us understand the mechanism of origin of the Raman lines, the reasons for the Stokes and anti-Stokes lines being equidistant from Rayleigh line and their relative intensities.

There are two theories of Raman effect. These are as follows:

- Quantum or particle theory
- Classical or wave theory

Let us discuss these one by one.

4.2.1 Quantum or Particle Theory

You know that according to the quantum theory of radiation, an electromagnetic radiation is considered to be consisting of a stream of particles called photons. The photons constituting a radiation of frequency ν would have energy equal to $h\nu$ where h is the Planck's constant. The interaction of the radiation with the interacting species can be visualised in terms of collisions between them and the photons. If the collisions are **elastic** (i.e., they do not involve any exchange of energy) the photons would be scattered (deflected) with their incident frequency remaining unchanged. This explains the observance of Rayleigh line in the spectrum. Since most of the collisions are elastic in nature, most of the scattered photons would have same frequency as the incident frequency. Therefore the Rayleigh line is observed to be quite intense.

Elastic collisions: The collisions that do not involve any exchange of energy.

A small fraction of the collisions between the photons and particles of matter is found to be **inelastic** in nature i.e., these involve exchange of energy. When the photons constituting the radiation undergo inelastic collisions with the absorbing species, they either gain or lose energy. These energy exchanges bring about transitions in the quantised energy levels of the molecules. In such an event of inelastic collisions, the molecules are either vibrationally (and/or rotationally) excited or they may undergo vibrational (and/or rotational) relaxation. In both the cases the photons get scattered with a frequency different from their initial frequency. In former case i.e., when the molecules undergo excitation, they are of lower frequency. In the later case, where the molecules undergo relaxation, the scattered photons are of a higher frequency. These scattered photons give rise, respectively to the **Stokes** and **anti-Stokes Raman lines** in the spectrum.

Inelastic collisions: The collisions that involve exchange of energy.

Let us understand the mechanism of Raman and Rayleigh scattering with the help of an energy level diagram. Fig. 4.2 gives a schematic energy level diagram of a molecule. The set of lines at the bottom end represent the electronic ground state and the corresponding vibrational energy levels. Similarly the set of lines at the top end represent the first electronic excited state and the corresponding vibrational energy levels. The region of continuum in the middle represents virtual states whose energies are not quantised.

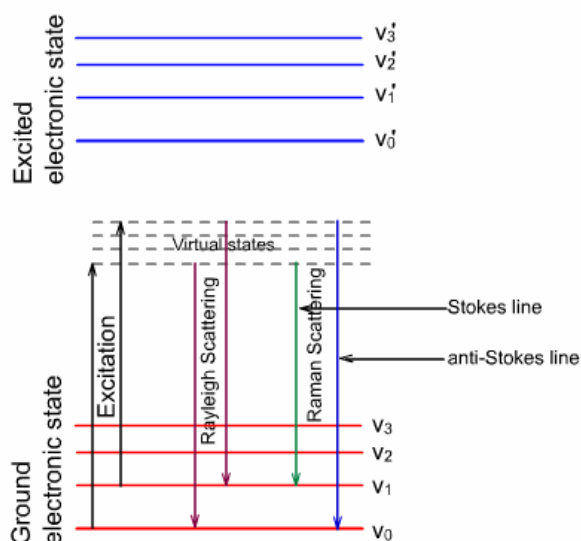


Fig. 4.2: Schematic representation of the energy changes associated with the excitation, Rayleigh scattering and Raman scattering

When a radiation, having a wavelength that is different from any of the absorption maxima of the molecule, interacts with the molecule; the energy of the molecule increases by an amount equal to $h\nu$. The energy change can be represented by the upward arrow (black) to the far left in the figure. This suggests that the molecule in the lowest vibrational state of the electronic ground state gets excited to a virtual state. The second arrow from the left represents a situation in which the incident photon (of same energy) encounters the molecule in its first vibrationally excited state and accordingly the virtual state has higher energy. As the virtual state is extremely short lived (of the order of 10^{-14} seconds), the molecule soon drops back down to its ground state, releasing a photon. The next two down arrows (purple) indicate these processes in which there is no transfer of energy and the scattered photon has the same frequency as that of the incident photon. This explains the Rayleigh scattering.

The next two down arrows (green and blue) represent the situations which arise in case of inelastic collisions. The first (green) of these corresponds to the relaxation from the virtual state that was acquired by the molecule in the electronically as well as vibrationally ground state by absorbing the incident photon. In this case, the molecule does not relax back to the vibrational ground state; instead it comes down to a vibrationally excited state. In other words the inelastic collision has brought in a vibrational excitation in the molecule. The scattered photon would be of lower frequency i.e., it will give a Stokes line.

The arrow on the extreme right (blue) represents the situation wherein the molecule in the virtual state obtained by absorption of incident photon by the molecule in the vibrational excited state of the ground electronic state releases a photon. On releasing the photon the molecule comes down to the vibrational ground state of the ground electronic state. The overall process of excitation and relaxation is equivalent to the vibrational relaxation of a molecule as a consequence of the inelastic collision. The energy of the scattered photon is greater than that of the incident photon; this gives rise to anti-Stokes line.

The most likely event in these interactions is the energy absorption and re-emission by the molecules in the ground state. Therefore, the Rayleigh lines are the most intense. Further, since the virtual state from which the Stokes line originates is more populated than the one for anti-Stokes lines, the Stokes lines are more intense than the anti-Stokes lines (Fig. 4.1).

Before proceeding to the classical theory, try to answer the following SAQs.

SAQ 1

Calculate the wavenumber (in cm^{-1}) of the radiation having a wavelength of 488 nm.

.....

SAQ 2

What is Raman shift? The Raman shift positions of Stokes and anti-Stokes lines are equal but opposite. Comment.

.....

4.2.2 Classical or Wave Theory

The concept of the polarisability of a molecule is fundamental to the understanding of the classical theory of Raman effect. Let us first understand it before we move to the explanation of the Raman effect.

Polarisability of molecules

When a molecule is placed in a static electric field, the positive and negatively charged particles constituting the molecule get attracted to the opposite poles of the applied field. This leads to a charge separation and consequently to the development of an induced dipole moment. In simple words, we say that the molecule has become polarised. This tendency of the molecule to get polarised is called **polarisability** i.e., the ability to get polarised. The magnitude of the induced dipole moment is proportional to the strength of the applied field and is given by the following equation.

$$\mu = \alpha E \quad \dots (4.2)$$

The proportionality constant α is called *polarisability*. It is a measure of the ease with which the molecule (or a bond in it) can get polarised. A weaker bond with loosely held electrons is more polarisable; a single bond is more polarisable than a double bond between the same set of atoms. Further, the polarisability can be anisotropic, that is the electrons of a bond may be polarised to different extents when the field is applied in different directions. For example, the hydrogen molecule gets polarised to different extents when the field is applied in the direction of the bond or in the direction perpendicular to it, as shown in Fig. 4.3.

The polarisability (α) of the molecule depends on the bond length; shorter bonds being difficult to polarise than longer bonds.

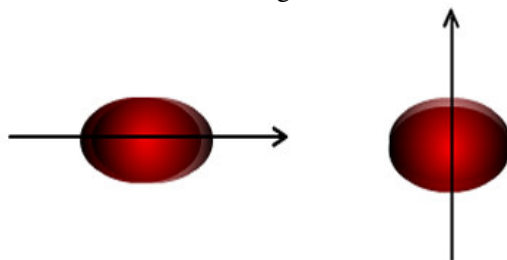


Fig.4.3: Schematic representation of the anisotropic polarisability of a molecule

What would happen if we place a molecule in an oscillating electric field like that of an electromagnetic radiation? Let us see.

The electric field associated with a radiation having a frequency ν_{ex} varies as per the following equation.

$$E = E_0 \cos(2\pi\nu_{ex}t) \quad \dots (4.3)$$

where E is the electrical field strength at any time t and E_0 is the amplitude of the wave. When such a radiation is made to interact with a molecule it would induce a dipole moment in it. Further, as the electrical field of the radiation is oscillating the resulting induced dipole moment would also oscillate at the same frequency as that of the radiation. That is,

$$\mu = \alpha E = \alpha E_0 \cos(2\pi\nu_{ex}t) \quad \dots (4.4)$$

This oscillating dipole would immediately generate a radiation of the frequency, ν_{ex} and we have a ready explanation for Rayleigh scattering.

As you are aware, the molecules are never stationary and always undergo vibration (and may be rotation) motions. These motions may cause a change in the polarisability of the molecule. For example, in the process of a vibration the bond length of a bond in the molecule keeps varying and as the polarisability depends on the strength of the bond, it may change the polarisability of the molecule. It can be shown (see the box given below) that when such a system vibrating with a frequency of ν_{vib} interacts with the oscillatory electric field of the electromagnetic radiation then the scattered radiation may have three different components. One of these has frequency equal to the incident frequency (ν_{ex}) while the frequencies of the other two are equal to $(\nu_{ex} + \nu_{vib})$ and $(\nu_{ex} - \nu_{vib})$ respectively. The first component with a frequency of ν_{ex} is the reason for the Rayleigh scattering. The other two components are the sources of the anti-Stokes and Stokes lines respectively.

Interaction of oscillatory electric field with vibrating molecule

Suppose a bond with an equilibrium bond length of r_0 and equilibrium bond polarisability of α_0 is vibrating with a vibrational frequency equal to ν_{vib} . If the rate of change in the polarisability with the change in bond length r , during vibration is $(\partial\alpha/\partial r)$, then the polarisability of the bond as a function of the change in bond length is given as

$$\mu = \alpha_0 + (\partial\alpha/\partial r)r_0 \cos(2\pi\nu_{vib}t) \quad \dots (4A)$$

Substituting Eq. (4A) in Eq. (4.3) we get

$$\mu = [\alpha_0 + (\partial\alpha/\partial r)r_0 \cos(2\pi\nu_{vib}t)]E_0 \cos 2\pi\nu_{ex}t \quad \dots (4B)$$

Eq. (4B) on expansion gives,

$$\mu = \alpha_0 E_0 \cos 2\pi\nu_{ex}t + (\partial\alpha/\partial r)r_0 E_0 \cos(2\pi\nu_{vib}t) \cos(2\pi\nu_{ex}t) \quad \dots (4C)$$

In order to simplify Eq.(4C), we can make use of an identity from trigonometry, i.e.,

$$\cos A \cos B = \frac{1}{2} [\cos(A + B) + \cos(A - B)] \quad \dots (4D)$$

Substituting this identity in Eq. (4C) we get,

$$\mu = \alpha_0 E_0 \cos 2\pi \nu_{ex} t + (\partial\alpha/\partial r) r_0 \frac{E_0}{2} \cos[2\pi(\nu_{ex} + \nu_{vib})t] + (\partial\alpha/\partial r) r_0 \frac{E_0}{2} \cos[2\pi(\nu_{ex} - \nu_{vib})t] \quad \dots (4E)$$

The three terms in the equation suggest for the presence of three different components of the oscillating electrical dipole moment. Accordingly, there are three components in the scattered radiation. These oscillate with the frequency equal to ν_{ex} , $(\nu_{ex} + \nu_{vib})$ and $(\nu_{ex} - \nu_{vib})$ respectively. In other words we may say that the incident frequency of the radiation has been modulated by the vibration frequency as $\pm \nu_{vib}$.

If $(\partial\alpha/\partial r)$ is equal to zero then Eq. (4E) reduces to $\mu = \alpha_0 E_0 \cos 2\pi \nu_{ex} t$ which means that only Rayleigh scattering is observed.

The three components in the scattered radiation are observed only when the vibration causes a change in the polarisability. **If the polarisability does not change in the course of vibration only Rayleigh scattering is observed. Therefore, we can conclude that in order to observe Stokes and anti-Stokes lines the polarisability of the bond must change in the course of vibration.**

The necessary condition to observe vibration Raman spectrum is that the polarisability of the bond must change in the course of vibration

Let us raise a question. Since both the IR and Raman spectra involve transitions amongst the same vibrational levels, would the two spectra be the same?

However, before proceeding further why don't you assess your understanding of the meaning and the explanation of the Raman effect by answering the following SAQ.

SAQ 3

Fill up the blanks in the following.

- When the collisions between the photons and molecules are, the photons would be.....with the same frequency.
- If in the event of an inelastic collision with photons the molecules get vibrationally excited, the frequency of the scattered photon will bethan the incident photon.
- In order to observe Raman scattering the of the bond must change in the course of vibration.

4.2.3 Raman Activity of Vibrations

As a first response, the answer to the question about the similarity of IR and Raman spectra raised above, could be in a firm affirmative or one may respond, 'may be'.

However in actual practice the two spectra are generally not identical and in case of a number of molecules, the spectra in fact do not have anything in common (Sec. 4.2.4). This is so because the very mechanisms by which the two spectra arise are different. This feature actually is an important indicator about the symmetry of the molecule.

The Raman and IR spectra for a simple molecule CCl_4 is given in Fig. 4.4. You may note that only some of the signals are common in the two spectra and also the common signals are of different relative intensities.

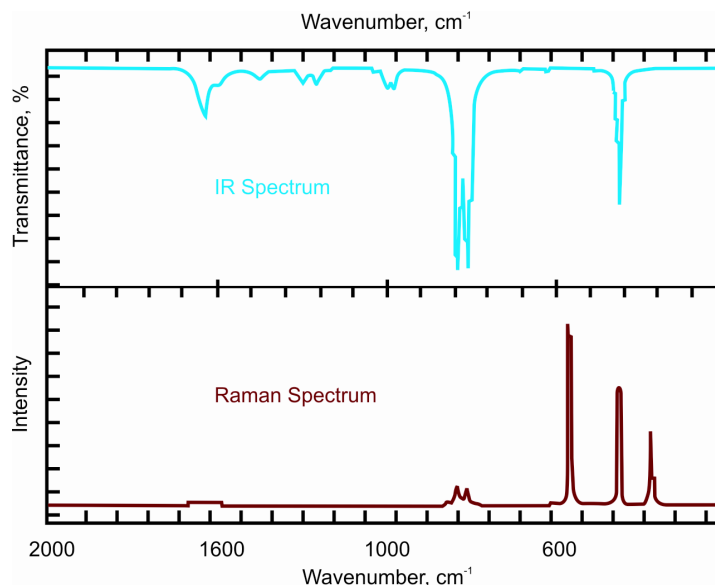


Fig. 4.4: IR and Raman spectra of CCl_4 ; note the similarities and the differences

You would recall from the previous unit on IR spectrometry that all the possible vibrational modes of a molecule may not be IR active. Only those modes which have an associated change in dipole moment are IR active and show up in the spectrum while the other modes are absent. As mentioned above, in Raman spectrum only those vibrational modes are active which are associated with a change in polarisability. Due to this difference in the requirements for showing the two types of spectra, the IR and Raman activities of the vibration modes may differ from each other.

The Raman activity of different vibrational modes can be predicted on the basis of whether or not the polarisability changes during the vibration. However, it is not very simple and in many cases requires a detailed analysis. We would not get into these details. It would be suffice to mention here that in addition to the CCl_4 example where only some modes have IR as well as Raman activities, we may have situations where all the vibration modes are active in IR as well as in Raman and in some cases there is no mode which is active in both. Water is an example of the former while carbon dioxide belongs to the later category. The IR and Raman activities of the vibration modes of H_2O and CO_2 are compiled in Table 4.1.

Table 4.1: The IR and Raman activities of the vibration modes of water and carbon dioxide molecules

Molecule	Vibration mode			Infra red	Raman
H_2O	ν_1	Symmetric stretching	3651.7 cm^{-1}	Active	Active
	ν_2	Bending	1595 cm^{-1}	Active	Active
	ν_3	Asymmetric stretching	3755.8 cm^{-1}	Active	Active
CO_2	ν_1	Symmetric stretching	1330 cm^{-1}	Inactive	Active
	ν_2	Bending	667.3 cm^{-1}	Active	Inactive
	ν_3	Asymmetric stretching	2349.3 cm^{-1}	Active	Inactive

4.2.4 Rule of Mutual Exclusion

The IR and Raman activities of different modes of vibration of a molecule depend on its symmetry properties. An analysis of the IR and Raman spectra of a large number of molecules has led to an extremely important general rule known as the **rule of mutual exclusion**. It states that, **“for a molecule having a centre of symmetry the Raman active vibrations are IR inactive and vice versa”**. However, if the molecule does not have a centre of symmetry then some vibration may be Raman as well as IR active.

The application of this rule can provide very useful structural information. For example, the fact that the Raman and IR spectra for N_2O have signals at same wavenumber suggests that the molecule does not have a centre of symmetry. This information can be used to conclude that the structure of the molecule is $\text{N}=\text{N}=\text{O}$ and not $\text{N}=\text{O}=\text{N}$. Have a look at the Table 4.1 again and check which of the two molecules given there has a centre of symmetry.

4.2.5 Depolarisation Ratio

You know that the Raman scattered light is a result of the interaction of the **electric field** of the incident light with the scattering species. Further, the laser used for the excitation are polarised, i.e., the electric field of the radiation vibrates in a specific direction. It is expected that the scattered light would also be similarly polarised. However, in actual practice some of the scattered light is found to be depolarised to varied extents. This depends on the symmetry of the molecular vibration causing the scattering and is a result of the nature of the polarisability changes during the vibration. Let us try to understand it.

You must not mix up the terms polarisability and polarisation. The polarisability refers to the ability of a bond to get polarised while polarisation of radiation concerns the plane in which the electrical field of the radiation vibrates.

The polarisability of the scattered light is measured by passing it through a **Nicol prism** or a **polaroid film** called **analyser**. The intensity of the light passing through the analyser is measured as the analyser is rotated. The intensity would be maximum when the analyser is parallel to the plane of maximum polarisation and would decrease as the analyser is rotated. It will be minimum when the analyser is perpendicular to the plane of maximum polarisation. For the convenience of expression, the nature of the scattered light is expressed in terms of **degree of depolarisation** rather the degree of polarisation. The degree of depolarisation, ρ , is defined as

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

where I_{\perp} and I_{\parallel} are the minimum and the maximum intensity measured by the analyser.

The degree of depolarisation helps in the assignment of the signals in the Raman spectrum. In general, a symmetric vibration gives a polarised or partially polarised Raman line whereas the nonsymmetric vibrations give depolarised signals. According to scattering theory estimates the minimum degree of depolarisation for a nonsymmetric vibration is $6/7$ and it is termed as depolarised. On the other hand the degree of depolarisation for the symmetric vibrations is always less than $6/7$ and the vibration is called polarised.

SAQ 4

Fill up the blanks in the following.

- The polarisability of the scattered light is measured by passing it through aor a
- All the vibration modes of water are active in IR as well as in Raman. This means that water a centre of symmetry.

- c) The refers to the ability of a bond to get polarized while..... concerns the plane in which the electrical field of the radiation vibrates.

4.3 INSTRUMENTATION FOR RAMAN SPECTROSCOPY

There are two main issues in Raman spectroscopy that need to be addressed by suitable instrumentation. First is the inherent weakness of the Raman scattering signal as compared to the intense Rayleigh scattering and the second is about the spectral resolution i.e., the ability to resolve features within the spectrum. Like the IR instruments, there are five basic components of a Raman spectrometer. These are given below:

- An intense laser source
- Sample handling unit
- Monochromator or interferometer
- Detector
- Signal processing and output device

The schematic representations of the general set up of the monochromator based dispersion Raman spectrometer is given in Fig.4.5 and that of the interferometer based FT-Raman spectrometer is given in Fig. 4.6.

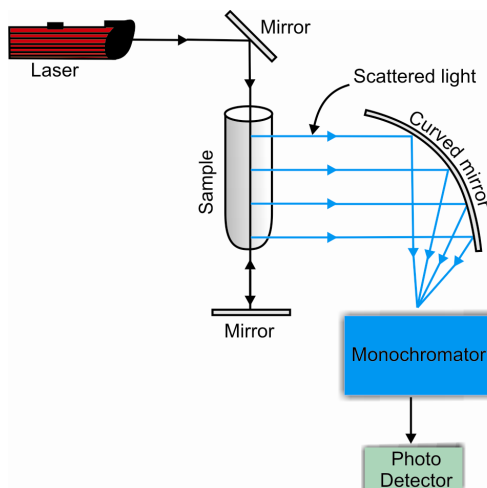


Fig. 4.5: Schematic representation of the experimental set up of a dispersion Raman spectrometer

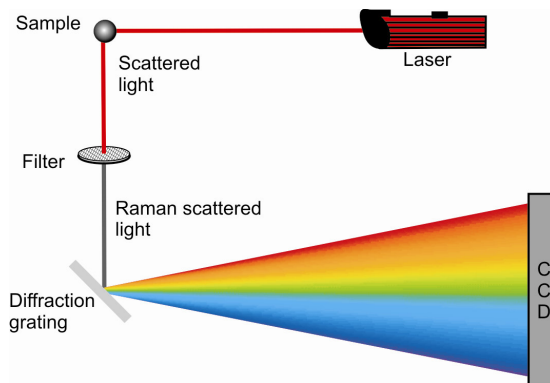


Fig. 4.6: Schematic representation of the experimental set up of a FT-Raman spectrometer

You may find the arrangements to be similar to that of the corresponding IR instruments with the only difference being that the scattered radiation is collected at right angles to the radiation and it is passed through a filter before sending to a transducer for detection. The Raman spectrometers differ from the IR instruments in terms of the sources, the sample handling devices and the transducers used for detecting the scattered radiation. Let us learn about these

4.3.1 Radiation Sources for Raman Spectroscopy

The first ever Raman instrument was constructed in 1928 which used the Sun light focused by a telescope to achieve a high enough intensity in the scattered signals. The spectrometers that followed used mercury arc lamps as a light source. With the advent of lasers with highly desirable properties of high intensity, single wavelength and coherence, the modern spectrometers almost exclusively use laser sources. The commonly used lasers and their characteristics are compiled in Table 4.2.

Lasers used for Raman spectroscopy must exhibit good wavelength stability and low background emission.

Table 4.2: Commonly used lasers sources in Raman spectroscopy and their characteristics

Laser source	Wavelength (nm)	Frequency $\times 10^7, s^{-1}$	Wavenumber (cm^{-1})
Argon ion	488.0 or 514.5	6147 or 5831	2049.2 or 1943.6
Krypton ion	530.9 or 647.1	5651 or 4636	1883.6 or 1545.4
Helium/Neon	632.8	4740	1580.3
Diode laser	782 or 830	3836 or 3614	1278.8 or 1248.2
Nd/YAG	1064	2819	939.9

The intensity of Raman scattering is dependent on the fourth power of the frequency of the exciting radiation, besides concentration and other factors. Therefore, the argon and krypton ion laser sources are more intense than the other lasers being used at the same power and accordingly give better spectra. On the other hand the low frequency lasers i.e., diode laser and Nd/YAG laser can be used at higher power and also have an added advantage that these do not generate the interfering fluorescence spectral lines.

As Raman experiments always involve the measurement of small energy shifts of the order of 100 to 3000 cm^{-1} from the excitation energy, a monochromatic source is highly desirable and lasers meet this requirement the most.

There is a need for many more new sources which will give still better spectra and the way technology is developing we can hope to get them soon.

4.3.2 Sample Handling Devices

Raman spectrometer has a distinct advantage over IR spectrometry because it permits the use of glass for holding aqueous solutions. The possibility of using aqueous samples is particularly important as it allows ascertaining water pollutants besides biological and inorganic samples. More so, since the laser source provides a focused coherent radiation, the sample container can be very small which in turn requires exceedingly smaller sample volume. This is a highly desirable attribute. A number of sampling devices are in use we would take some examples of the devices for handling solid, liquid and gaseous samples.

A solid sample is ground to a fine powder and packed into a small cavity to be kept in the path of incident radiation. The liquid samples on the other hand are taken in a fine

Unlike most chemical analysis techniques, Raman spectrometry does not require any special preparation of the sample. Since Raman spectrometry involves only illuminating a sample with a laser and collecting the scattered photons, no contact with the sample is needed at all. This makes Raman spectroscopy a **non-destructive technique**.

capillary which is about 5 cm long and has an outer diameter of about 1 mm. For analysing **gaseous samples**, the cuvette consists of a cylindrical glass tube with mirrors on both the ends; one of the mirrors has a small window to let the incident radiation to pass through. When the cuvette containing the sample is placed in the radiation path the incident laser beam enters the sample through the window and undergoes multiple reflections in the sample. The scattered light at the right angles to the sample is then suitably collected and measured.

Fibre-optic probes are a recent advancement in sample handling. These probes exploit the fact that the visible or near IR radiation can be transmitted to distances as large as 500 m using optical fibre as the vehicle. This allows handling samples much farther from the instrument and without any physical manipulation of the sample. In a typical fibre-optic probe the laser beam from the source is focused onto a fine bundle of optical fibres called **input fibres** that transport it to the sample. These input fibres are enclosed by a set of optical fibres called **collection fibres**. These are meant to collect the scattered radiation from the sample and send it back to the instrument where it is directed to a suitable monochromator.

4.3.3 Transducers or Detectors

The original Raman instrument that lead to the discovery of the Raman effect used **eyes as the detector**. In initial versions of the spectrometers, photographic plates were used to detect the scattered radiation. This was followed by more sensitive **photomultiplier tubes (PMTs)** that allowed electronic data collection and manipulation. However they had the disadvantage for they could count only one wavelength at a time. Today most of the Raman spectrometers are FT instruments which use cooled **germanium photoconductors as** transducers. The multi channel dispersive instruments however employ **charge-coupled devices** (CCDs) as transducers.

As the scattered radiation has a major component of the Rayleigh scattering, this is eliminated by using a suitable filtering device like **holographic grating** or **interference filters** before the detector. Therefore, the radiation reaching the transducer is primarily the Stokes component. You would have realised that this feature is specific to Raman spectrometers and is not required in IR spectrometers.

We hope you would have understood the basic features of a Raman spectrometer and the choice and function of various components. Why don't you check it yourself?

SAQ 5

State whether the following statements are true or false.

- a) The intensities of the Raman lines depend on the frequency of the exciting radiation.

.....

- b) Argon ion lasers would give better Raman spectra in terms of intensities as compared to helium/ neon laser.

.....

- c) Photomultiplier tubes are ideal detectors for FT-Raman spectrometers.

.....

- d) The Raman spectra are generally taken for aqueous solutions only.

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4.4 ENHANCEMENT OF RAMAN SPECTRAL INTENSITIES

Raman Spectroscopy

Raman lines are intrinsically very weak. You would recall that only 1 in 10^7 of the scattered photons causes the Stokes and anti-Stokes signals. It is because of this weak spectra and unavailability of powerful source, that Raman spectroscopy was not much used for the structural studies till about 1960 when intense laser sources became available. The intrinsic weakness of the spectra required high concentrations ($\sim 0.1\text{M}$) of the analyte that further limited its applications. Once the problem of intense source was solved, there have been efforts to further improve the spectral intensities, so as to be able to analyse the analytes at lower concentrations. This could be achieved when tunable dye lasers became available. Let us learn about some techniques for enhancing the spectral intensities and the principles behind them.

We should be able to appreciate that Raman observed this effect using sunlight (focused by telescopes) and mild radiation sources.

4.4.1 Resonance Raman Spectroscopy

In a normal Raman spectral measurement the spectrum is obtained by irradiating the sample in a region where it does not have an absorption band. Generally green, red or near-infrared lasers are used for the purpose and the wavelengths are below the first electronic transitions of most molecules. The situation however changes when the wavelength of the exciting laser lies close to the electronic absorption of a molecule. Under these conditions a resonance occurs which may enhance the intensities of a few (often only one) Raman lines to the tune of 10^2 to 10^6 . This phenomenon is exploited in Resonance Raman Spectroscopy (RRS) in the incident photon causes an electronic transition of the molecule and the excited state immediately relaxes down to one of the vibrational levels of the electronic ground state as shown in Fig.4.7 and an intense signal results. The signal enhancement is found to depend on the closeness of the excitation beam to the λ_{max} of the absorption band.

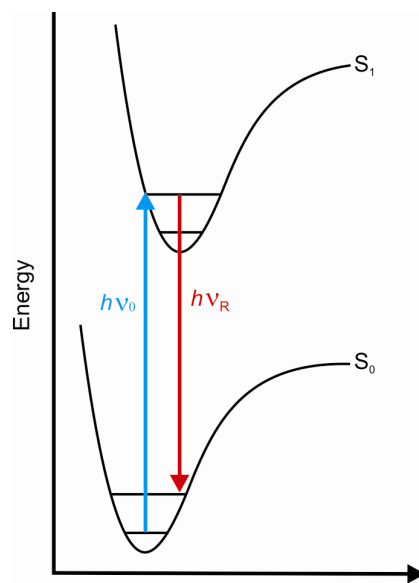


Fig. 4.7: A schematic diagram showing energy changes during Resonance Raman Spectroscopy

Further, since this resonance enhancement is observed only for the Raman bands associated with the chromophore, the spectrum is quite simple and easy to analyse. With this technique there has been a tremendous improvement in the sensitivity of the technique and today we may go down to a concentration of the order of 10^{-8}M . Resonance Raman spectroscopy is used extensively in the chemistry of fullerenes, polydiacetylenes and other such molecules which strongly absorb in the visible region.

4.4.2 Coherent Anti-Stokes Raman Spectroscopy

Coherent anti-Stokes Raman Spectroscopy (CARS) is a technique that uses two lasers. One has a **fixed frequency ν_1** and the other can be **tuned to a lower frequency ν_2** . When combined, these two lasers result in coherent radiation at a frequency equal to $(\nu = 2\nu_1 - \nu_2)$, besides a number of other frequencies. The energy changes during the CARS experiment are given in Fig.4.8.

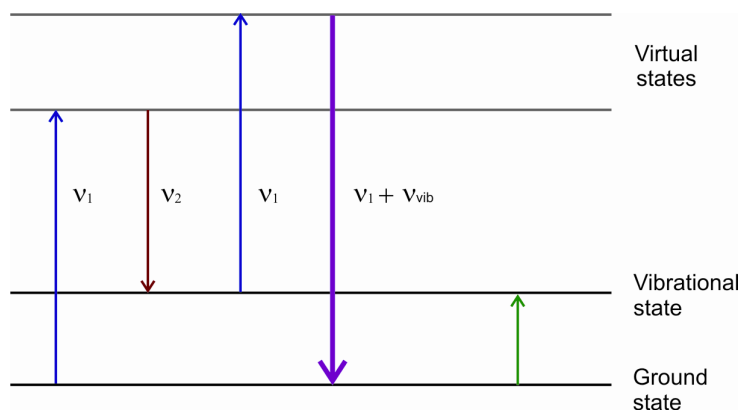


Fig. 4.8: Schematic representation of the energy changes during the CARS experiment

In CARS measurements two laser beams are passed through the sample and the second laser is tuned until it matches one of the Raman frequencies (say $\nu_1 - \nu_{vib}$). Under such conditions the coherent emission would be at a frequency given by the following equation

$$\nu = 2\nu_1 - (\nu_1 - \nu_{vib}) = \nu_1 + \nu_{vib}$$

This, in fact, is the frequency of the corresponding anti-Stokes line; hence the name. The schematic diagram of the experimental set up for the CARS experiment is given in Fig.4.9. The advantage of CARS spectrum is that the Raman transitions in the presence of incoherent background radiations can also be studied.

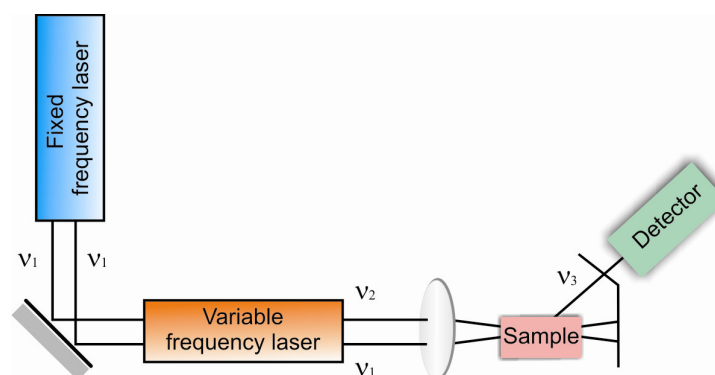


Fig. 4.9: Schematic diagram of the experimental set up for the CARS experiment

4.4.3 Surface Enhanced Raman Scattering

Surface Enhanced Raman Scattering (SERS) was discovered in 1974 when it was found that pyridine molecules adsorbed on an electrochemically roughened surface gave intense Raman Signals; much larger than the normally expected. This technique further developed in 1970s and involves taking spectra of the samples adsorbed on the surfaces of colloidal metal particles like gold or silver. The Raman scattering from a compound (or ion) adsorbed on such a metal surface can be 10^3 - 10^6 times greater than in solution.

The surface-enhanced Raman scattering is found to be strongest on silver, but is observable on gold and copper as well. Though the exact mechanism of the effect is not known but it is believed that SERS is a combination of chemical enhancement of polarisability by the bonds formed between the sample and the surface, and the electromagnetic resonance of small gold or silver particles. SERS combined with RRS can give a large increase in the sensitivity and the detection limits may go down to nano or even picomolar range.

SERS finds applications in diverse areas. For example, in forensic sciences it can be used to examine the microstructure of forged handwriting by analysing whether the type (or types) of the ink used are different. SERS is also important in life sciences as it can be used for biological materials in their physiological media.

There are many more ways of improving the quality of the Raman spectra but these are beyond the scope of present context. Now you can check whether you have understood the three techniques discussed here.

SAQ 6

Can the RES technique be used in enhancing the intensities of Raman lines in the spectrum of a saturated hydrocarbon? Give reason for your answer.

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SAQ 7

What should be the frequency of the tuneable laser in CARS experiment and why?

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4.5 APPLICATIONS OF RAMAN SPECTROSCOPY

Since its discovery in 1928, Raman spectroscopy has been recognised as a very powerful analytical tool capable of providing information not available from other analytical techniques. The recent advances in instrumentation have made Raman spectroscopy the tool of choice for an increasing number of chemical and biological applications and the study of coordination complexes.

Raman spectroscopy can be used for quantitative and qualitative analysis of inorganic, organic and biological samples. The quantitative analysis is based on the intensity of the Raman scattered light being proportional to concentration while the qualitative determinations depend on the wavelength shifts being different for a wide range of different molecular vibrations. Since a Raman spectrum typically contains a number of well-resolved spectral bands, the information available as the band positions, intensities, and shapes etc. constitute a unique fingerprint of the molecule that can be exploited for qualitative analysis.

The Raman spectrum of water is relatively weak in the fingerprint region as compared to the high absorption in the mid-IR or near-IR.

The organic compounds contain functional groups with highly deformable electron clouds and are good scatterers of the radiation. Some important functional groups include alkenes, alkynes, cyano etc. The stretching vibrations of these functional groups give rise to weak and undetectable IR signals whereas in Raman spectra these are quite strong and can provide useful information about the environment of the group in the molecule. In addition, Raman spectroscopy is very useful for measuring symmetric vibrations from the C-C bonds in the backbone of polymers and diatomic molecules like N₂, O₂, etc.

Further, since in Raman spectrum we measure the shifts in the frequencies rather than the frequencies themselves it makes regions below 600 cm⁻¹ accessible which otherwise can not be explored in IR spectroscopy. This feature is quite significant for analysing inorganic samples especially the coordination compounds because the metal – ligand bonds generally absorb in this region. As water does not scatter much, Raman spectroscopy can be used to measure species dissolved or suspended in aqueous solutions. This opens up the field for inorganic species.

Due to the remote non-invasive sampling, minimal sample preparation requirements and tolerance of water, Raman spectroscopy is beginning to play a significant role in environmental analysis. The current environmental applications apply mainly to the heavily contaminated situations it is expected that with newer sampling technologies Raman spectroscopy may soon be more applicable to the analysis of potable water, in remote sensing and in analysis of gaseous pollutants.

Having read and understood the whole unit, please express yourself in the next SAQ

SAQ 8

Enlist a few applications of Raman spectroscopy?

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4.6 SUMMARY

In Raman spectroscopy, an intense radiation, preferably a laser, in the visible region interacts with the molecules and gets scattered. The scattered radiation is measured perpendicular to the sample. Most of the scattered light is of the same frequency as that of the incident radiation and is called **Rayleigh scattering**. A small fraction (1 in 10⁷) of the scattered radiation has frequencies different from that of the incident radiation. This is called **Raman scattering**. These scatterings can be explained in terms of elastic and inelastic collisions of the photons constituting the radiation with the molecules. The wave theory on the other hand explains it in terms of the induced polarisation of the molecule on interaction with the radiation.

Like IR spectra, the origin of Raman spectra also involves transitions amongst the vibrational levels of the molecules. However due to the differences in the way these signals originate the two spectra may differ significantly. For a vibrational mode to be Raman active it must have an associated change in polarisability. The IR and Raman activities of different modes of vibration of molecules can provide useful structural information. The rule of mutual exclusion states that, “for a molecule having a centre of symmetry the Raman active vibrations are IR inactive and vice versa”.

Some of the scattered light in Raman spectra is found to be polarised. This depends on the symmetry of the molecular vibration causing the scattering and is a result of the nature of the polarisability changes during the vibration. The nature of the scattered light is expressed in terms of degree of depolarisation. A symmetric vibration gives a polarised or partially polarised Raman line whereas the non-symmetric vibrations give depolarised signals.

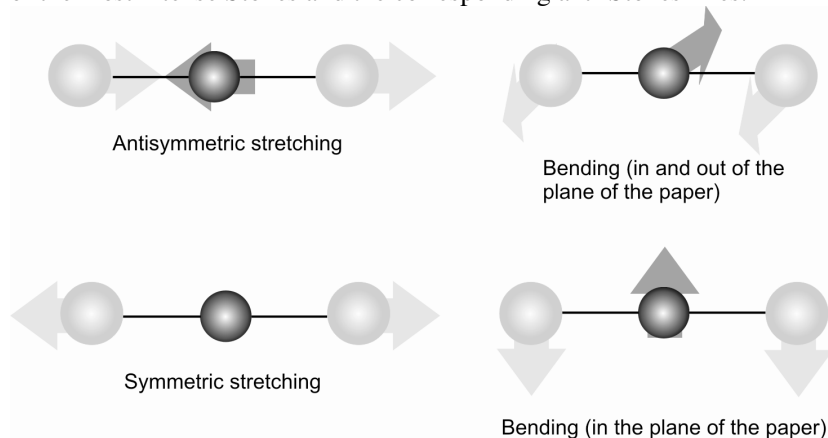
Like the IR instruments, there are five basic components of a Raman spectrometer. The general set up of the Raman spectrometer is similar to that of the corresponding IR instruments. The difference being that the scattered radiation is collected at right angles to the radiation and it is passed through a filter before sending it to a transducer for detection. In terms of the components, the Raman spectrometers differ from the IR instruments in terms of the sources, the sample handling devices and the transducers.

Raman lines are intrinsically very weak. The spectral intensities in Raman spectroscopy can be enhanced by using some special techniques like Resonance Raman spectroscopy, Coherent Anti-Stokes Raman Spectroscopy (CARS) and Surface Enhanced Raman Scattering (SERS) etc.

Raman spectroscopy can be used for quantitative and qualitative analysis of inorganic, organic and biological samples. The quantitative analysis is based on the intensity of the Raman scattered light being proportional to concentration while the qualitative determinations depend on the wavelength shifts being different for a wide range of different molecular vibrations.

4.7 TERMINAL QUESTIONS

1. The Raman spectrum of an amino acid cystine is given below. If the spectrum was obtained by using a 488 nm laser, compute (using spectrum) the positions of the most intense Stokes and the corresponding anti-Stokes lines.



2. State mutual exclusion principle for deciding IR and Raman activities.
3. What do you understand by depolarisation ratio? What is the significance of the ratio being less than 6/7?
4. Compare the sample handling procedures in Raman spectrometry with that in IR spectrometry.
5. Describe the working of a fibre-optic Raman probe.
6. Why do we need to have means of enhancing the intensities of Raman lines? Give the names of three techniques employed for the purpose.
7. What is the importance of CARS experiment in Raman spectroscopy?
8. What does SERS stand for? Give some applications of SERS experiment.

4.8 ANSWERS

Self Assessment Questions

1. You know that for a photon,

$$E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu} \quad \text{or} \quad \bar{\nu}(\text{cm}^{-1}) = \frac{1}{\lambda(\text{cm})}$$

Given wavelength = 488 nm =

$$488 \times 10^{-9} \text{ m} \quad \text{or} \quad 488 \times 10^{-9} \times 10^2 \text{ cm} = 488 \times 10^{-7} \text{ cm}$$

Substituting it in the above formula we get, wave number,

$$\bar{\nu}(\text{cm}^{-1}) = 1 \times 10^7 / 488 = 20491 \text{ cm}^{-1}$$

2. Raman shift refers to shift in the observed scattered frequency from the frequency of the excitation radiation. Raman shift, $\Delta\bar{\nu}$ is defined as $\Delta\bar{\nu} = (\bar{\nu}_s - \bar{\nu}_0) \text{ cm}^{-1}$.

Both the Stokes lines and anti-Stokes lines arise from inelastic collisions with the incident radiation. A Stokes line arises when the radiation excites a given vibration mode whereas the corresponding anti-Stokes line arises due to relaxation of the same vibration. The Raman shifts of the two are equal because they involve same vibration and are opposite because one involves excitation while the other concerns relaxation.

3. a) elastic, scattered b) lesser c) polarisability
4. a) Nicol prism, polaroid film
b) does not have
c) polarisability
d) polarisation
5. a) True b) True c) False d) False
6. No, because the saturated hydrocarbons do not have an electronic absorption band
7. The frequency of the tuneable laser should be equal to that of one of the Raman bands i.e., $\nu_1 - \nu_{\text{vib}}$
8. The Raman spectroscopy has many features; some of its important features are as follows
- It involves scattering of radiation.
 - The spectra are inherently weak.
 - The scattered radiation is collected at the right angles to the sample.
 - It is a non-destructive technique.
 - It can be used to analyse a sample at a distance

Terminal Questions

- 1 From the answer to SAQ 1 you may note that the wavenumber of a 488 nm laser is 20491 cm^{-1} . The spectrum shows that the Raman shift of the most intense Stokes line is at about 105 cm^{-1} . So its wavenumber would be about, $20491 - 105 = 20386 \text{ cm}^{-1}$; the corresponding anti-Stokes line would be at about $20491 + 105 = 20596 \text{ cm}^{-1}$.
- 2 The mutual exclusion principle states that, “for a molecule having a centre of symmetry the Raman active vibrations are IR inactive and vice versa”.

- 3 The depolarisation ratio refers to the ratio of the minimum and the maximum intensity measured by the analyser when the scattered light is passed through it. Mathematically, the degree of depolarisation, ρ , is defined as

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

where I_{\perp} and I_{\parallel} are the minimum and the maximum intensity measured by the analyser.

- 4 The sample handling procedures are much simpler than that in IR spectrometry. For example a solid sample is simply grinded to a fine powder and packed into a small cavity in case of Raman spectroscopy whereas in IR these have to be mulled with a mull or pelleted with KBr. Similarly the liquid samples can be taken in an ordinary glass capillary while in case of IR we need to use highly specialised windows. More so, in Raman spectrometry we can use aqueous solutions and also we can analyse a sample at a distant location using a fibre-optic probe.
- 5 In a fibre-optic probe the laser beam from the source is focused onto input fibres that transport it to the sample. The collection fibres that surround the input fibres in the probe collect the scattered radiation from the sample and send it back to the instrument. It is then directed to a suitable monochromator.
- 6 We need to have means of enhancing the intensities of Raman lines because firstly these lines are intrinsically weak and secondly these get masked by much more intense Rayleigh line. The three techniques employed for the purpose
- i) Resonance Raman Spectroscopy (RRS)
 - ii) Coherent Anti-Stokes Raman Spectroscopy (CARS)
 - iii) Surface Enhanced Raman spectroscopy (SERS)
- 7 The CARS experiment permits the study of the Raman transitions in the presence of incoherent background radiations.
- 8 SERS stands for Surface Enhanced Raman Scattering. Some of the applications of the SERS experiment are:
- Analysis of the type (or types) of the ink to decipher the forged handwriting — a forensic application
 - Determination of the degree of cross-linking in a polymer sample
 - Analysis of biological materials in their physiological medium

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