

# A Review on Raman Rays with Respect to Raman Spectroscopy

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## Review Article

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## Abstract

Raman Spectroscopy, one of the most leading technology uses a laser light source to irradiate a sample, and generates an infinitesimal amount of Raman scattered light, which is detected as a Raman spectrum using a CCD camera. To know about the working of Raman Spectroscopy, first the knowledge of Raman Effect is important. Light interacts with matter in different ways like refraction, absorption and reflection. Refracted light changes direction while absorbed photons disappear, giving off their energy to the absorbing material. During reflection light bounces off the surfaces of materials. If you think of light in terms of photons, reflection from surfaces is a type of scattering. The easiest way to explain Raman effect is that photons sometimes have a tendency to emit at a lower or higher energy than their incident state. When a photon is scattered from a molecule it is scattered elastically. A very few percent of the photons scatter inelastically. The elastic scattering of photons is known as Rayleigh scattering and the inelastic scattering of photons is known as Raman scattering. And this paper we are going to discuss in detail how Raman Effect has application in Raman Spectroscopy.

**Keywords:** Lasers; Molecular Vibrations; Polarizability; Raman Effect; Raman Spectroscopy

## Introduction

Quick and immediate identification of a substance is the prime key to a latest identification technology. Organisations like Homeland security, CIA, Interpol all select and use technologies that give them quick results with minimal contact. Instruments that can be used in the field to accurately identify explosives are essential tools for bomb technicians involved in public safety throughout the world. The first thing discussed soon after an explosion is the source of the explosion and its origin. There are many techniques used to analyse samples collected from the explosion site. But identifying an explosive after the damage has been done is pointless when looked from the humanity side. Moreover, there is always some damage following the explosion. To prevent such damages and loss of life it is more important and

efficient to use technologies that can identify the explosives before the occurrence of the explosion. This helps in reducing the aftermath damages and also in preventing the loss of life. Because of this in recent times more focus is given to invention or upgradation of existing technology for proactive use. A lot of technologies can be used for detection and identification of explosives. But Raman Spectroscopy is one device that can be used for both detection and identification. Till date Raman Spectroscopy is widely used for the identification of explosive substances. But with a little modification it can be used for the detection also. While in detection only the nature of the substance is checked, in identification the content and composition of that substance is checked. So in this paper we will be discussing about the technique which is used for this purpose, which is the Raman Spectroscopy and how it entirely relies on Raman Rays.

## Raman Effect

Raman Effect is observed when molecules deflect light with the change in wavelength. Also known as Raman scattering this is a process in which light emits molecules with a different frequency than that of the incident one. Light interacts with the matter in different ways like refraction, absorption and reflection. Refracted light changes direction and travels in a different path length while absorbed photons disappear, giving off energy to the absorbing material. During reflection light bounces off the surface of materials. In terms of photons, reflection from surfaces is a type of scattering. The easiest way to explain Raman Effect is that the photons sometimes have a tendency to emit themselves at a lower or higher energy than their incident state. When a photon is scattered from a molecule, it is scattered elastically, i.e., they have the same frequency and wavelength as the incident photon. A very few percent of the photons scatter in an inelastic way, i.e., they have different wavelength and frequency than the incident photon. The elastic scattering of photons is also known Rayleigh scattering and the inelastic scattering of photons is Raman Effect.

## Molecular Vibration in Raman Spectroscopy

When a molecule absorbs radiation it is excited to a higher energy level this can occur in three processes, first usually occurs when excited by microwave or infrared radiation and result in rotational energy level transition. The next one occurs when infrared or visible light is used which results in vibrational energy level transition and lastly when a molecule is radiated by a uv light an electronic energy level transition occurs [1].

Vibrational spectroscopy is generally used to describe some of the analytical techniques like Raman spectroscopy, since this technique measures vibrational energy levels associated with particular chemical bonds in a sample [2]. This theory use chemical bonds as springs from Hooke's law rather than the traditional ball-and-stick model and shows how an input of energy into molecule will cause it to vibrate. Molecules have vibrational modes that are dependent on the orientation of atoms and bonds the atomic mass of the atoms bond order and hydrogen bonding, the number of possible vibrational modes in a molecule depends on the following formulas, Nonlinear molecules can have  $3n-6$  possible vibrational modes while linear molecules can have  $3n-5$  possible variations where 'n' represents the number of atoms. These patterns of vibration relate to the molecular symmetry of the molecule and allow us to deduce the

molecular shape and determine information about the strength of each bond [3].

In Raman spectroscopy the sample is radiated with visible light which the molecules absorb and re-emit however some of the energy is absorbed by the molecular vibrations causing a small portion to re-emit at a different frequency than the incident light. Light can be scattered in two ways, elastically commonly known as Rayleigh scattering in which there is no non kinetic transfer of energy between the molecules and photons or inelastically known as Raman scattering, it involves the transfer of energy between molecule and photon. Modern Raman spectroscopy instruments are designed to filter out the Rayleigh light because only one in every million photons will be Raman scattered. Raman spectroscopy occurs because of a molecular vibration that causes a "change in the polarizability" of the molecule. On the other hand, for a molecule to be an active infrared, the vibration must cause a permanent change in the dipole moment. An active Raman molecule would be a species like CS<sub>2</sub>. The symmetrical stretching will then be detected by Raman spectroscopy. Since the molecule does not have a permanent dipole, this range would be invisible in the infrared spectrum. If the molecule has a center of symmetry, active Raman vibrations would not be visible in the infrared. For example, the symmetrical slice of CS<sub>2</sub> is active Raman. Asymmetrical sections, which induce a dipole, are active infrared. Because of this difference, it is said that the Raman and infrared spectra are reciprocal, which means that between the two, the analyst should be able to obtain a complete picture of the vibration modes of a molecule.

## Stokes and Anti-Stokes

At the point when a monochromatic light is scattered by particles, a large portion of reflected light has a similar recurrence of the incident light; this process is called Rayleigh scattering.

A part of scattered light has fewer frequencies (higher wavelengths) than incident light, offered beginning to the Stokes lines in a Raman range. This happens when a photon exchanges some portion of its energy to the particle and, since it loses energy, its frequency is moved towards lesser frequencies. The particle ingests energy to experience change to higher vibrational states. It is conceivable to the particle exchanging energy to the incident photon and shifting frequencies of scattered light to higher values (lesser wavelengths). At the point when this happens, the atom that is in energized vibrational

state experiences change to the lower state or even to the ground state. An arrangement of lines shows up in a Raman range (anti Stokes lines) [4]. A normal Raman range is focused at the frequency of incident light (normally a laser in the visible part of spectrum), with high power intensity from Rayleigh scattering. Stokes lines can be seen towards lower frequencies and anti-Stokes towards higher frequencies, similar to them are reflected at the spectrum. All things considered, Stokes lines are more intense than their anti-Stokes counterparts, in light of the fact that vibrational ground state is more populated than energized states. The Stokes and Anti-Stokes lines are each a set of lines found in the Raman Scattered Spectra. These lines arise due to inelastic scattering of photons due to molecular scatterers in addition to the Rayleigh lines in the spectra which corresponds to elastic scattering and has the same wavelength as the incident photon. Stokes' lines are those lines whose wavelengths are longer than that of the incident light whereas, Anti-Stokes' lines are those with wavelengths shorter than the incident line!

### Polarizability

Electric polarizability is the relative tendency of a charge distribution, like the electron cloud of an atom or molecule, and of any material body, to have its charges displaced by any external electric field [5].

Polarizability is a proportion of how effortlessly an electron cloud is distorted by an electric field. Typically, the electron cloud will belong to an atom or molecule or ion. The electric field could be caused, for example, by an electrode or a nearby cation or anion. If an electron cloud is easy to distort, we say that the species it belongs to is polarizable. Polarizability, which is spoken to by the Greek letter alpha, is tentatively estimated as the proportion of initiated dipole moment  $p$  to the electric field  $E$  that induces it.

In general, polarizability correlates with the interaction between electrons and the nucleus. The number of electrons in a molecule affects how tight the nuclear charge can control the overall charge distribution. Atoms with fewer electrons will have smaller, denser electron clouds, as there is a strong interaction between the few electrons in the atoms' orbitals and the positively charged nucleus. There is also less shielding in atoms with less electrons contributing to the stronger interaction of the outer electrons and the nucleus. With the electrons held tightly in place in these smaller atoms, these atoms are typically not easily polarized by external electric fields.

In contrast, large atoms with many electrons, such as negative ions with excess electrons, are easily polarized. These atoms typically have very diffuse electron clouds and large atomic radii that limit the interaction of their external electrons and the nucleus.

### Factors that Effect Polarizability

- The greater the number of electrons, the less control the nuclear charge has on charge distribution, and thus the increased polarizability of the atom.
- The greater the distance of electrons from nuclear charge, the less control the nuclear charge has on the charge distribution, and thus the increased polarizability of the atom.
- Molecular orientation with respect to an electric field can affect polarizability (labelled Orientation-dependent), except for molecules that are: tetrahedral, octahedral or icosahedral (labelled Orientation-independent).

Raman Effect can be explained using classical electromagnetic theory with quantum mechanical treatment:

$$P = \alpha E \quad (1)$$

Since the magnitude of E- vector of electromagnetic field varies with the time 't' in a sinusoidal manner:

$$E = E_0 \cos 2\pi vt \quad (2)$$

Polarization becomes:

$$P = \alpha E_0 \cos 2\pi vt \quad (3)$$

$\alpha$  Consists of two parts,  $\alpha_0$  ability to polarizability when atoms are in equilibrium position. And,

$\alpha_1$  Is the sum of polarizability of the molecule due to various rotational and vibrational motions:

$$\alpha = \alpha_0 + \left( \sum \frac{\delta \alpha_n}{\delta r} \right) r_n \cos 2\pi \nu_n t \quad (4)$$

$\alpha_n$  Is the polarizability associated with nth rotational or vibrational mode.

$r_n$  Is the maximum displacement of involved atoms:

$$P = \alpha_0 E_0 \cos 2\pi vt + E_0 \left( \sum \frac{\delta \alpha_n}{\delta r} \right) r_n \cos 2\pi \nu_n t \cdot \cos 2\pi vt \quad (5)$$

$$P = \alpha_0 E_0 \cos 2\pi vt + \frac{1}{2} E_0 \left( \sum \frac{\delta \alpha_n}{\delta r} \right) r_n \{ \cos 2\pi (\nu - \nu_n) t + \cos 2\pi (\nu + \nu_n) t \} \quad (6)$$

First term has frequency of incident radiation and hence Rayleigh scattering. Second term represent stokes ( $\nu - \nu_n$ ) and anti-stokes ( $\nu + \nu_n$ )

Raman bonds  $\left[ \frac{\delta \alpha_n}{\delta r} \neq 0 \right]$

### Heisenberg's energy time principle

Due to this principle, photon can be absorbed without conservation of energy as long as it is emitted after a short time. This is called virtual absorption and the virtual excited state is called intermediate state: [6]

$$\Delta T \Delta E \geq \frac{1}{2} h \quad (7)$$

The intensities of Raman lines are 0.001% of the intensity of source. The intensity or radiant power of a normal of a normal Raman bond depends in a complex way on the polarizability of the molecule, the intensity of the source and the concentration of the active group. In addition to intensity and frequency, Raman measurements also provide the depolarization ratio:

$$P = \frac{I_{\perp}}{I_{\parallel}} \quad (8)$$

When light is scattered by a molecule, the incident radiation has usually a frequency less than the characteristic ultraviolet frequencies of the molecules; hence the energy of the incident quantum of radiation is insufficient to cause the electrons in the molecule to pass definitely into a higher energy level. Nevertheless, it is the tendency of the incident radiations to disturb these electrons that is responsible for the classical scattering of light. As the characteristic infrared molecular vibrations or rotations contribute to a negligible extent to the refractivity for visible light, it follows that they do not play any important part in the process of light-scattering as conceived in the classical theory. The quantum of radiation exchanges energy with the molecule on which it is incident. Part of the energy of the quantum is taken over by the molecule which thus passes into an excited condition. Vice versa, an excited molecule may give up its energy to the quantum which then goes off with increased energy. The first process naturally occurs more frequently, as there are more unexcited molecules than excited ones. The process pictured is one which can actually occur, for the incident quantum of energy is greater than the quantum of energy absorbed by the molecule; that the interpretation is a valid one is shown by the fact that the difference between the frequencies of the incident and scattered radiations is characteristic for the molecule, and in not a few cases agrees with known infrared absorption frequencies.

When a beam of light interacts with matter 99% of the scattered radiation has the same frequency as the incident beam: Mie and Rayleigh. The remaining one percent has a frequency that is different from the incident one: non-selective scattering. This non-selective scattering contains Raman Rays which are used in Raman Spectroscopy.

### Raman Spectroscopy

It is a technique which relies on inelastic scattering of Raman Rays for the identification of a sample based on its rotational and vibrational frequency. It typically consists of:

- Excitation Source
- Sampling Apparatus
- Detector

A laser light is excited on a surface. Radiations get scattered and the emitted Raman Rays are collected. Raman Rays that get scattered from every sample are unique for that material. It is like the fingerprint of compounds. From analysing the collected Rays one can find out about the existing compounds in that sample. The spectra are diagnostic of the molecular structure of the sample. No sample preparation is needed.

In Raman spectroscopy where visible laser radiation is used, the photons excited are of much higher energies than those of common chemical bonds. The basic process of a Raman spectroscopy is that a laser is mounted on a sample. The light from the sample is concentrated on a monochromator which filters out the Rayleigh scatterings leaving behind only Raman rays. These rays are then passed to the detector which converts the optic rays to electrical ones.

#### Excitation Source

Light intensity refers to the strength or amount of light produced by a specific lamp source. It is the measure of the wavelength-weighted power emitted by a light source.

The Intensity is directly proportional to energy which is hence directly proportional to frequency which is indirectly proportional to wavelength.

So we can say that the source of smallest wavelength will have the highest intensity and higher the intensity the more distance it will cover according to newton's inverse square law.

$$I_1/I_2 = D_2^2/D_1^2 \quad (9)$$

Lasers for Raman spectroscopy need to meet certain performance criteria. Preferred, but not a pre-requisite, is that the laser operates single longitudinal mode, has a very stable mode and has an accurate and stable wavelength. The advantage of using a laser operating single longitudinal mode is that the extremely weak Raman signals very close to the excitation wavelength can be resolved. A stable wavelength thus means there is

lower chance the excitation wavelength will float around risking swallowing the weak Raman signal.

The Raman signal is very weak and must be carefully discriminated from the excitation beam, Rayleigh scattering and the back-ground fluorescence. However, the introduction of new types of Raman spectroscopy such as surface-enhanced Raman, resonant Raman, tip-enhanced Raman has helped to increase the strength of the Raman signal significantly and enabled rapid penetration of Raman into new applications areas [7,8].

Laser wavelengths ranging from ultra-violet through visible to near infra-red can be used for Raman spectroscopy. Typical examples include (but are not limited to):

Ultra-violet: 244 nm, 257 nm, 325 nm, 364 nm

Visible: 457 nm, 473 nm, 488 nm, 514 nm, 532 nm, 633 nm, 660 nm

Near infra-red: 785 nm, 830 nm, 980 nm, 1064 nm

The choice of laser wavelength has an important impact on experimental capabilities:

Sensitivity- laser decreases scattering intensity.

Scattering intensity is the amount of radiation scattered at any particular angle

$$I(q) = |F(Q)|^2 |S(Q)| \quad (10)$$

$$= |P(q)| \left[ \frac{|F(q)|^2}{|P(q)|} \right] \cdot |S(q)| \quad (11)$$

$$I(q) = P(q) \cdot S(q) \quad (12)$$

$q$  = momentum transfer

Momentum transfer is a vector in the 3D reciprocal space that denotes the change in momentum between incoming and scattered radiation. It describes the interaction between radiation and sample.  $q = 2\pi s$

$P$  - Is the form factor. This is the scattering which results from the shape of a particle.

$S$  - Is the structure factor. It is encoding the structural information about a sample.

Raman scattering intensity is proportional to  $\lambda^4$  where  $\lambda$  is the laser wavelength. Thus, an infra-red laser results in a decrease in scattering intensity by a factor of 15 or more, when compared with blue/green visible lasers.

Spatial resolution- The diffraction limited laser spot diameter can be calculated using the formula  $1.22\lambda/NA$  NA - numerical aperture of the microscopic objective used. The spatial resolution is dependent on the laser used.

## Spectral Resolution

By increasing the density of the grating in the spectrometer, the spectral resolution will be improved.

The focal length of the spectrometer must also be considered because doubling the focal length will increase the spectral dispersion of a spectrometer.

Larger optics maintains throughput and sensitivity of the longer focal length system and will enable ultimately greater spectral resolution to be achieved as there are no restrictions.

In practice if you need to push the spectral resolution of a Raman measurement, a combination of longer focal length and good grating selection will provide the answer.

## Detectors

One the most important component of a Raman spectrometer is in fact is a detector, as when Raman rays are scattered, they must be collected and analysed. Classically the very first one used in Raman spectroscopy was a photographic plate, in which the Raman rays are spread out and fallen over the surface and later is developed. But it had a limited timeline. But the next detector that helped Raman spectroscopy in its practical field was a photomultiplier tube. It's basically an electron amplifying tool that helped in analysis. Though in modern Raman spectrometer the solid-state detector that is usually used in it is charge coupled device. It's a multi-channel detector, highly sensitive, similar like a photographic plate where the Raman signal falls over it and is later analysed. And if by chance there are low light levels in order to increase the focus in high speed imaging processes we can usually use an EMCCD. These are the 4 types of detectors usually used in this instrument, while the first two are quite historical, whereas the main one is a CCD [9].

## Sampling Apparatus

Although the other components of the Raman spectrometer are always said as the most technically important, many important tools have been applied to optimizing and amplifying the signal by improving how the sample interfaces between the source and the spectrometer. The relative weakness of the Raman Effect has always required that the Raman spectrophotometer be as efficient as possible at generating, collecting, and detecting the scattered Raman photons. Because the entrance to the spectrometer was a slit, and the slit

needed to be as narrow as possible to maintain spectral resolution, the focus of the laser on the sample also had to be as small as possible, since the focus of the laser was imaged onto the spectrometer slit.

Because the Raman signal ideally scatters uniformly in every direction, the signal photon flux drops off rapidly with distance from the sample, and the collection optics needed a low f-number set as close to the sample as possible for efficient signal collection. This made the apparatus of the sample to the Raman system extremely uncompromising, if the sample could not be adapted to the limitations of the spectrometer, the experiment could not be performed.

Because both the laser and the signal photons were open beam, they needed to be directed by multiple lenses and mirrors to keep the system properly aligned.

Hence, Band pass filters are used to isolate a single laser beam. A combination of notch filter and high-quality grating monochromator is most frequently used in dispersive instruments. Double or even triple grating monochromators, super notch filters, rejection filters, holographic notch or edge filters and holographic filters are used to separate relatively weak Raman lines from intense Rayleigh scattered radiations. A filter collects the specific Raman scattered light (Stokes) and filters out the Raleigh and Anti Stokes light.

## Conclusion

Raman Spectroscopy is a technique that has application in almost every field. Its accuracy and readiness makes it an undeniable choice. It has major applications in geology, pharmaceuticals, cosmetics, life sciences and even forensics. No sample preparation is needed for it and it has a precision higher than Ion mobility spectrometer or laser induced breakdown spectrometry. But, this process completely relies on the

inelastic scattering of light. The fact that the light scattered from a sample has very negligible percentage of non-selective rays are diagnostic of the molecular structure of the sample is the main principle of this technique. The excitation source and detectors and sampling apparatus are being modified on a regular basis, but the quality of this technique lies in the instruments power to collect and detect Raman from a particular sample. So, the entire working of Raman Spectroscopy is dependent on the phenomenon of Raman Effect which takes place due to Raman rays.

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