

Surface-Enhanced Raman Spectroscopy

Recent Advancement of Raman Spectroscopy

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In Raman spectroscopy, inelastic scattering of photons from an atom or molecule in chemical entities is utilized to analyze the composition of solids, liquids and gases. However, the low cross-section limits its applications. The introduction of surface-enhanced Raman spectroscopy in 1974 has attracted a lot of attention from researchers due to the large enhancement of weak Raman signal, which facilitates identification in chemical and biological systems. Recently, single-molecule Raman scattering has enhanced the detection sensitivity limit of Raman Spectroscopy.

What is Raman Effect?

Raman scattering or Raman effect is the inelastic scattering of photons from an atom or a molecule. This effect was discovered by the famous Indian physicist C V Raman in the year 1928. In general, most photons are elastically scattered from an atom or a molecule, with the scattered photons having the same energy and wavelength as the incident photons. This phenomenon is known as 'Rayleigh scattering' and it accounts for the blue colour of the sky. However, a small fraction (1×10^{-7}) of the scattered photons have a frequency different from the incident photons. Raman who was working on the molecular diffraction of light, which ultimately led to his discovery of Raman effect observed this effect in liquid. The Russian scientists Grigory Landsberg and Leonid Mandelstam first observed this effect in crystals. Raman received the Nobel Prize in 1930 for his work on inelastic scattering of photons.

Figure 1 shows a schematic diagram to explain the principle of Raman scattering. The shift in wavelength of the inelastically scattered radiation provides the chemical and structural information of the molecule. Raman shifted photons can be of either

Keywords

Raman scattering, surface enhanced Raman scattering, Raman cross section, surface plasmon resonance, tip-enhanced Raman scattering.



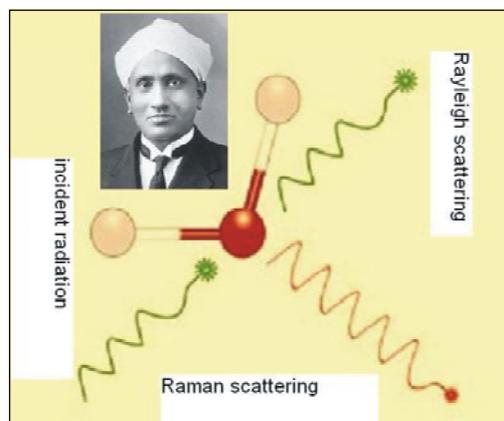


Figure 1. Schematic diagram to explain the principle of Raman scattering along with the picture of Professor C V Raman.

higher or lower energy, depending upon the vibrational state of the molecule under study. Stokes radiation occurs at lower energy (longer wavelength) compared to Rayleigh scattering, whereas anti-Stokes radiation occurs at higher energy (shorter wavelength). Thus, the observed Raman shift of the Stokes and anti-Stokes are a direct measure of the vibrational energy of the molecule. In a gas, Raman scattering can occur with a change in vibrational, rotational or electronic energy of a molecule. The Raman effect has been applied as a vibrational spectroscopic tool for analyzing the composition of solids, liquids and gases. The versatility of this technique can be utilized in diverse applications such as analysis of minerals and ores as well as detection of explosives.

Introduction to Raman Spectroscopy

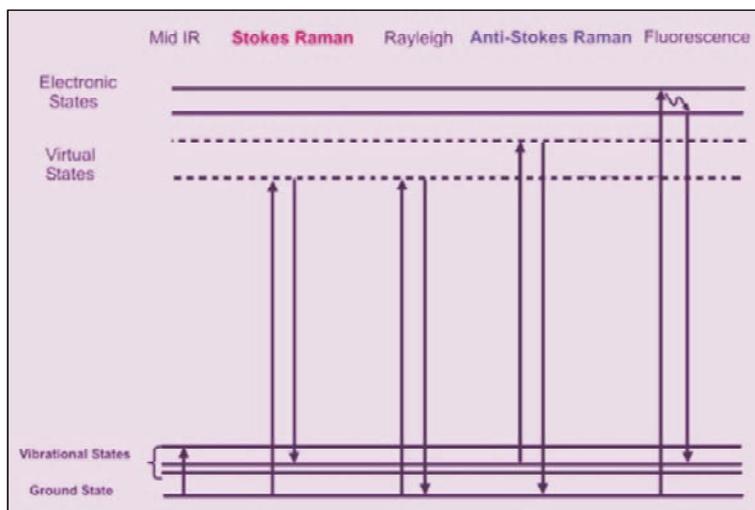
Raman spectroscopy is a spectroscopic technique used in condensed matter physics and chemistry to study vibrational, rotational, and other low-frequency modes in a system. It depends on the inelastic scattering, or Raman scattering of monochromatic light, usually from a laser in the visible, near-infrared or near-ultraviolet range of electromagnetic spectra.

The shift in energy in Raman effect gives information about the phonon modes in the system, which are the quantized modes of vibration occurring in a rigid crystal lattice. Fluorescence involves the relaxation of the vibration, while Raman scattering is

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Figure 2. Jablonski energy diagram showing Raman scattering, Rayleigh scattering and fluorescence.



sensitive to different vibrational modes. Therefore, Raman scattering is more sensitive than fluorescence and is called the fingerprint of a molecule. Raman spectroscopy is commonly used in chemistry, since vibrational information is very specific for the chemical bonds in molecules.

Figure 2 shows the quantum description of Raman scattering, fluorescence and infra-red (IR) in a Jablonski energy diagram. This diagram explains Raman effect quantum mechanically. When the energy of the incident radiation is not large enough to excite the molecule from the ground state to the lowest electronic state, the molecule will be excited to a virtual state between the ground state and lowest electronic state. In case of Rayleigh scattering, the wavelength of the scattered photon is the same as the incident photon. In case of Stokes scattering, the photon is scattered at a lower energy (shifted wavelength towards the red end of the spectrum). At room temperature, the molecule is principally in its ground vibrational state. This is the larger Raman scattering effect. A small number of molecules will be in a higher vibrational level and as a result, the photon is scattered at higher energy (shifted wavelength towards the blue). Thus, anti-Stokes scattering is much weaker compared to Stokes scattering.

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Raman scattering can also be explained classically. According to



the classical model, light is treated as electromagnetic waves and the molecules are treated as small spheres connected by a spring. The energy of the molecule can be expressed in terms of the energy of a harmonic oscillator. Not all vibrations will be observed in Raman spectroscopy. It is determined by the symmetry of the molecule. The rule of thumb predicts that symmetric = Raman active, asymmetric = IR active. Thus, IR spectroscopy is a complementary technique to Raman spectroscopy. The dipole moment μ of the molecule changes as the molecule vibrates in case of IR, whereas in case of Raman active molecule, the polarizability α of the molecule must change during vibration. In a molecule with a center of symmetry, a change in dipole is accomplished by loss of the center of symmetry, while a change in polarizability is compatible with preservation of the center of symmetry. Thus, in a centrosymmetric molecule, asymmetrical stretching and bending will be IR active and Raman inactive, while symmetrical stretching and bending will be Raman active and IR inactive. Hence, in a centrosymmetric molecule, IR and Raman spectroscopy are mutually exclusive. For molecules without a center of symmetry, each vibrational mode may be IR active, Raman active, both, or neither. However, symmetrical stretching and bending tend to be Raman active.

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Raman line intensity I_r is proportional to $\nu^4 * \sigma * I * \exp(-E_i / kT) * c$, where ν and I are the frequency and intensity of incident radiation, σ is the Raman cross-section, $\exp(-E_i / kT)$ is the Boltzmann factor for state i , and c is the concentration of the molecule which scattered the radiation to produce the Raman line. The low cross-section ($10^{-31} \sim 10^{-26}$ cm² per molecule) of Raman scattering limits its sensitivity.

Instrumentation for Raman Spectroscopy and its Limitations

In Raman spectroscopy, the sample is illuminated with a laser beam. Wavelengths close to the laser line (due to the Rayleigh scattering) are filtered out and the rest of the unfiltered light is dispersed onto a detector. Spontaneous Raman scattering is very



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weak compared to the Rayleigh scattering and separation of these two signals is necessary. Historically, Raman spectrometers used holographic diffraction gratings to achieve a high degree of laser rejection. However, modern instrumentation universally employs notch filters for laser rejection. Introduction of fast-Fourier transform (FFT) based spectrometers, confocal microscopes and charge coupled device (CCD) detectors has brought a new dimension in Raman instruments, providing very high sensitivity. Raman spectroscopy can be further applied for microscopic analysis of materials, such as polymers, ceramics and cells. This technique is known as Raman microspectroscopy.

The weak Raman signal is the biggest disadvantage of Raman spectroscopy; thus it was not widely used for a long time.

There are a number of advanced types of Raman spectroscopy such as resonance Raman, surface-enhanced Raman, polarized Raman, stimulated Raman, and transmission Raman.

A Raman microscope consists of a standard optical microscope, an excitation laser, a monochromator and a sensitive detector (such as CCD). The correct selection of the laser wavelength is an important consideration for Raman spectroscopy. With modern Raman instruments, often several laser wavelengths may be employed to obtain the best detection limit of the Raman signal with sensitivity. For example, many samples, especially organic or biological, will be quite fluorescent in nature. Exciting these samples with a laser in the green (532 nm) light may promote this fluorescence, and this fluorescence background may suppress any underlying Raman spectrum to such an extent that it is no longer detectable. In this case, the use of a laser in the red (633 nm) or near infrared (NIR) (785 nm) region may provide a solution. With the lower photon energy, a red or NIR laser may not promote the electronic transition (and hence the fluorescence) and so the Raman scatter may be far easier to detect. The cross-section for fluorescence is $\sim 10^{-16}$ cm² per molecule, but for Raman scattering, the value is between $10^{-31} \sim 10^{-26}$ cm² per molecule. *Figure 3* shows the schematic diagram of a modern Raman instrument along with a typical Raman spectrum. As seen from the figure, a typical Raman spectrum is a plot of Raman scattering intensity versus Raman shift, expressed in wavenumbers. The weak Raman signal is the biggest disadvantage of Raman spectroscopy; thus it was not widely used for a long time. There are a number of advanced types of Raman spectroscopy such as



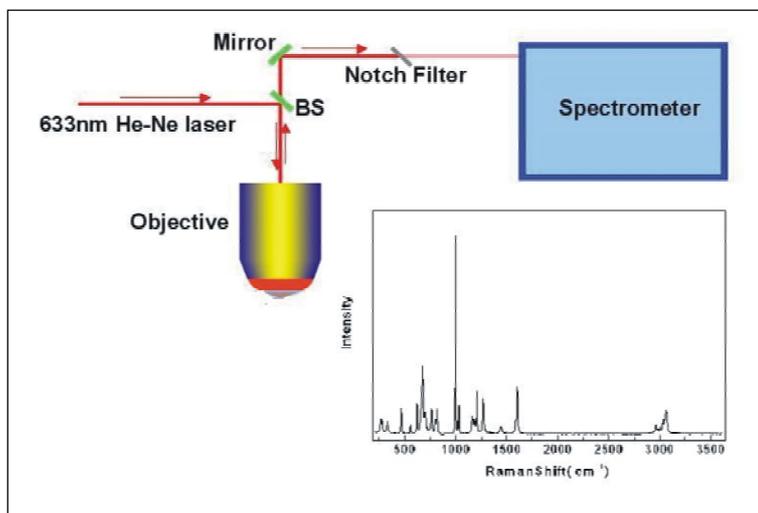


Figure 3. Schematic diagram of a modern Raman instrument along with a typical Raman spectrum.

resonance Raman, surface-enhanced Raman, polarized Raman, stimulated Raman, and transmission Raman.

Introduction to Surface-Enhanced Raman Spectroscopy

The name ‘surface-enhanced Raman spectroscopy’ implies that it provides the same information that normal Raman spectroscopy does, but with a greatly enhanced signal. The weak Raman signal can be greatly enhanced by the introduction of surface-enhanced Raman scattering (SERS) spectroscopy. It was accidentally discovered in 1974 by Fleischmann, Hendra and McQuillan of the University of Southampton, UK when they tried to do Raman with an adsorbate of very high Raman cross-section, such as pyridine (Py) on the roughened silver (Ag) electrode. The initial idea was to generate high surface area on the roughened metal surface. The Raman spectrum obtained was of unexpectedly high quality. They initially thought that the intense surface Raman signal of Py was due to increased surface area. Later in 1977, Jeanmaire and Van Duyne from Northwestern University, USA, realized that surface area is not the main point in the above phenomenon. Albrecht and Creighton of the University of Kent, UK, reported a similar result in the same year. These two groups provided strong evidence to demonstrate that the strong surface Raman signal must be generated by a real enhancement of the

The strong surface Raman signal must be generated by a real enhancement of the Raman scattering efficiency (10^5 to 10^6 enhancement).

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Raman scattering efficiency (10^5 to 10^6 enhancement). The effect was later named as surface-enhanced Raman scattering and now, it is a universally accepted surface sensitive technique. Although the first SERS spectra were obtained from an electrochemical system (Py+roughened Ag electrode), all important reactions on surfaces including electrochemical processes can be studied by SERS.

A schematic diagram to explain the principle of SERS is shown in *Figure 4*. The technique is so sensitive that even a single molecule can be detected. The exact mechanism of the enhancement effect of SERS is still a matter of controversy in the literature. There are two main mechanisms for the large enhancement of weak Raman signal from Py adsorbed on electrochemically roughened Ag. Jeanmaire and Van Duyne proposed an electromagnetic effect for the enhancement. The electromagnetic theory is based on the excitation of localized surface plasmons. Albrecht and Creighton proposed a theory based on the charge transfer effect of the adsorbed molecule on the enhancement efficiency. This chemical enhancement theory relies on the charge transfer complex formation of the adsorbed molecule. However, it is very difficult to separate these two effects experimentally. The choice of surface metal is also dictated by the plasmon resonance frequency. Visible and near-infrared radiation (NIR) is used to excite the Raman modes. Silver (Ag), gold (Au) and

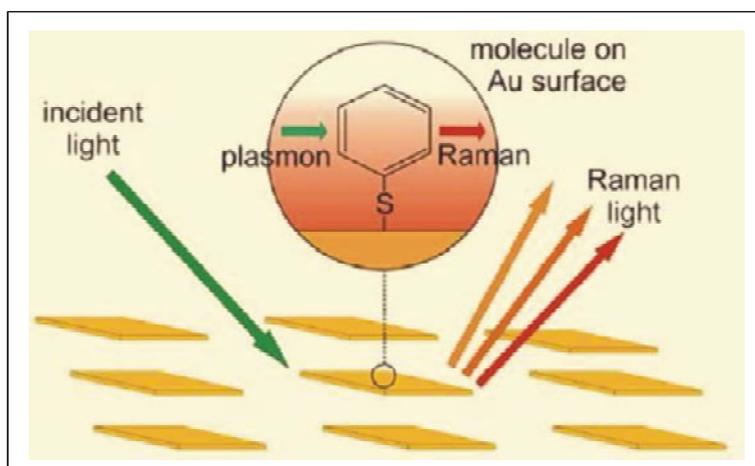


Figure 4. Schematic diagram to explain the principle of SERS.

copper (Cu) are typical metals for SERS experiments because their plasmon resonance frequencies fall within these wavelength ranges, providing maximal enhancement for visible and NIR light. Recently, SERS effect has been demonstrated in metals like platinum (Pt), ruthenium (Ru), palladium (Pd), iron (Fe), cobalt (Co) and nickel (Ni). They exhibit surface enhancements from one to three orders of magnitude. The enhancement value is very low compared to the enhancement factors obtained for Au and Ag. This is due to the difficulty of exciting the surface plasmon resonances in the visible light region. However, large enhancement ($\sim 10^4$) can be obtained from these transition metals using excitation wavelength in the near ultraviolet (UV) region. The main features of SERS technique are summarized briefly as follows:

- 1) It is a highly surface-sensitive, non-destructive and *in situ* vibrational spectroscopic technique.
- 2) SERS occurs when target molecules are brought within a few nanometers of the surface of SERS active substrates of different morphologies.
- 3) The excitation profile (scattering intensity versus excitation frequency) deviates from the fourth power dependence of normal Raman scattering.
- 4) It has extremely high spatial resolution. The enhancement range is several nanometers, effective for one or several molecular layers close to the SERS active substrate.
- 5) SERS activity strongly depends on the nature of metal and surface roughness. Therefore, SERS active substrate fabrication is a very important field in SERS research. The two most common SERS active substrates are metal colloids of coinage metals of Au, Ag and Cu obtained from chemical reduction, and the metal electrode surfaces roughened by one or more electrochemical oxidation–reduction cycles. The recent advancement of nanotechnology has been utilized to fabricate various nanostructures from nanoparticles to nanowires, which can be used as SERS active substrates.

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Applications of SERS

It is highly desirable to apply *in situ* SERS to obtain molecular-level information about the breaking and formation of bonds in the reaction, observe the reaction intermediate on the surface and finally, to distinguish the reaction products. The microscopic structure and dynamics of interfacial water molecules is important in understanding the electrode/electrolyte interface and is still an ongoing issue in electrochemistry as well as surface science. However, the interactions between water molecules and electrolyte ions as well as between water and electrode surface are very complex. Recently, Tian *et al* of Xiamen University, China, have characterized the surface water on Au core Pt group metal shell nanoparticles coated electrodes. Scientists are optimistic that SERS will become an indispensable tool in the study of interfacial structures and various surface processes involving interfacial water molecules without any interference from bulk water.

Nie and Emory carried out one of the earliest experiments on single-molecule SERS by combining SERS with transmission electron microscopy (TEM) and scanning tunneling microscopy (STM) techniques. This study enabled them to study the relationship between the morphology of the SERS active nanoparticles and SERS effect. They observed Raman enhancement as high as 10^{14} to 10^{15} for single rhodamine 6G (R6G) molecule adsorbed on selected Ag nanoparticles. In case of single-molecule SERS, they observed a single event rather than an ensemble averaged value generally obtained for conventional SERS measurements. Introduction of single molecule SERS technique has brought a new dimension in biomedical research as a versatile probing tool to study various biological molecules like virus, bacteria, protein, DNA and RNA.

SERS is among the most sensitive techniques available to study surface science. This technique can be coupled with a wide range of other surface techniques to study corrosion, catalysis, advanced materials, biology and sensors. In a recent development, a



new approach has been introduced to enhance the Raman scattering intensity by combining Raman spectroscopy with scanning probe microscopy such as atomic force microscopy (AFM) or STM. Its central element consists of an illuminated AFM or STM tip placed in the close vicinity of a substrate. The tip is operated in contact or tunneling mode. Upon illumination with a laser beam, localized surface plasmons are excited in the tip–substrate gap, producing a large, local enhancement of electromagnetic field compared to the incident radiation. In this way, Raman spectroscopy and scanning probe technique can be combined; this new technique is known as tip-enhanced Raman spectroscopy (TERS). The technique was invented by Pettinger *et al* in 2004 to probe malachite green isothiocyanate adsorbed on Au(111) surface. *Figure 5* illustrates the schematic diagram to explain the principle of TERS. TERS has been used to study surface reactions on single crystal and smooth surfaces, as surface roughness of the substrate does not play any role in this enhancement. The *in-situ* and non-destructive nature of SERS has been utilized to study various physiological and biochemical processes *in vivo* in a living cell. Although the theory to quantify the exact mechanism of SERS effect is yet to be developed, 30 years of this versatile technique has reached a new height due to the increased

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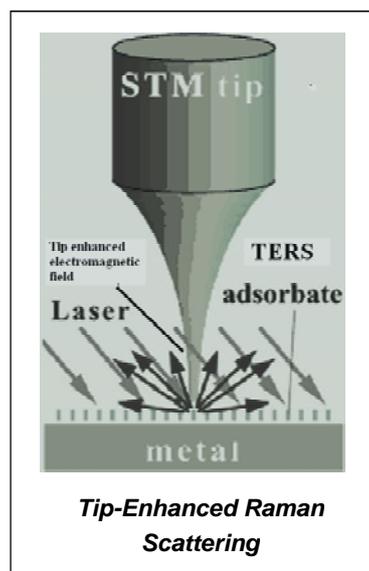


Figure 5. Schematic diagram to explain the principle of TERS.

efficiency of modern Raman instrumentation and recent advancement in nanotechnology.

Suggested Reading

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