Raman Scattering and Surface Enhanced Raman Spectroscopy

Spectroscopic techniques are often classified by the type of interaction between light and matter in from which information is obtained. Raman spectroscopy uses the inelastic scattering process discovered by C. V. Raman and K. S. Krishnan, now known as the Raman effect, which had been predicted by Adolf Smekal in 1923. Due to the unique nature of the scattering process, Raman spectroscopy is used to probe lower frequency modes of an atom or molecule. This is typically done by first illuminating a sample with a laser followed by collection of the scattered light. Scattered wavelengths close to that of the laser are filtered out while the rest of the collected light is put through a spectrometer. The spectrometer separates the scattered light by wavelength and the results are usually viewed as a graph of the Intensity vs Wave-number (Raman Shift) as seen in the figure below:

![Raman Spectroscopy Graph](image)

*Figure 1: A typical representation of measurements taken using Raman Spectroscopy*

The intensity 'peaks' that stand out from the background are unique to a specific bond in a molecule, and can be used
essentially as a fingerprint to identify them. In addition the intensity of the scattered light is directly proportional to the concentration of the sample, hence it is possibly to make quantitative as well as qualitative measurements. The drawback to Raman spectroscopy however is that the scattered light is usually very weak, especially in comparison to other light-matter interactions such as Rayleigh scattering, Fluorescence, and Phosphorescence. To get around this problem various methods of amplifying, or enhancing, the intensity of the Raman scattered light are used which can achieve values up to $10^{11}$ orders of magnitude greater, allowing for detecting the presence of a single molecule.

The scattering of light by matter can be divided into two categories: Elastic and Inelastic. For the most part matter scatters light elastically in the form of Rayleigh or Mie scattering, however a few photons are scattered through in-elastic mechanisms that induce a change in the energy of the photon. This change, or shift, in energy is observed by the difference in frequency (or wavelength) between the initial (illumination/excitation) and the final (collected/detected) photon. Elastic scattering is used in spectroscopic techniques such as crystallography, while in-elastic scattering process are used in techniques such as Raman and Infra-red absorption spectroscopy. The important thing to note is that processes such as Raman scattering are different from absorption processes such as Fluorescence, in that a photon perturbs molecule into a higher vibration (or virtual) state while the latter induces electronic transitions. This means that Raman scattering is almost instantaneous while processes such as Fluorescence have nano-second lifetimes. This virtual state can be vibrational, rotational or some other form of low-frequency modes and it is not restricted to specific wavelengths of incident light. This is the fundamental mechanism of Raman spectroscopy, the intensity peaks that constitute the Raman spectrum of a molecule are separated from the excitation wavelength by specific values, and are dependent only on the available vibrational states of the molecule. To clarify, Raman scattering is not dependent on resonance (though it is possible) with existing electronic states which means the incident light is not restricted to exact values corresponding to the difference in energy between the states. For the most part Raman spectroscopy deals with Spontaneous Raman scattering, however there are techniques that utilize other forms of Raman scattering such as Stimulated and Resonant Raman scattering.

Background

When an incident photon is Raman scattered by a molecule, the emitted photon differs in energy. The shift in energy of an emitted photon from a Raman scattering process is typically negative, meaning the emitted photon has a lower energy than the incident photon, and is called a Stokes shift. Alternatively the emitted photon could have gained energy from the molecule leading to an emitted photon with higher energy than the incident photon. This case is called an Anti-Stokes shift. Typically the Stokes shift have stronger signals (higher intensity) than Anti-Stokes transitions, however they both correspond to an emitted photon with the same energy difference to the incident photon. The following simplified Jablonski diagrams illustrates this concept:
In the figure above the electronic states are denoted by $S_i$ containing various vibrational states, $v_i$. Note that the excited state does not necessarily have to be 'real', in the sense that it does not have to align with the natural excited state $S_1$ nor its associated vibrational states of the molecule, since it is the difference in initial and final vibrational states (regardless of electronic state) that determines the energy of the emitted photon. When the excited state does align with $S_1$, the effect is called Resonant Raman Scattering.

Conceptually Raman scattering can be thought of as a process by which the energy of an incident photon is absorbed and converted into vibrational energy of a bond in a molecule. A photon is then emitted upon relaxation to a lower vibrational state. This emitted photon is the Raman scattered light.

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**Mathematical Description**

Mathematically the Raman scattering process can be explained by analogously relating it to oscillating dipoles.

Take an oscillating dipole with angular frequency $\omega$ consisting of two charges $+q$ and $-q$ moving back and forth with amplitude $x = a\cos(\omega t)$ along the $\vec{e}_p$ direction. The dipole is then given by:

$$\vec{p}(t) = qx(t)\vec{e}_p$$

Utilizing Maxwell equations, the far field power per solid angle $\frac{dP_{Rad}}{d\Omega}$ and the total power $P_{Rad}$ radiated by a dipole $\vec{p} = p\vec{e}_z$ is given by:

$$\frac{dP_{Rad}}{d\Omega} = \frac{\omega^4}{32\pi\epsilon_0c^3}\left|\vec{p}\right|^2\sin^2\theta$$

Integrating over the solid angle $4\pi$ gives:

$$P_{Rad} = \frac{\omega^4\left|\vec{p}\right|^2}{12\pi\epsilon_0c^3}$$

This radiated light (i.e. the power) can essentially be seen as the light emitted from the scattering process. However it should be noted that the above example is still lacking critical parts to correlate the entire process to the radiation from a dipole. Specifically the above example assumes a driven harmonic oscillator, thus it is necessary to explain how the incident light drives the oscillating dipole, and how the molecule itself can be seen as an oscillating dipole.
To start, consider a molecule at equilibrium, meaning that the structure of the molecule consists of the atoms and electrons distributed according to molecular orbital theory. If the molecule is then placed inside a static electric field \( \vec{E} \), the charges are redistributed and results in an overall change of the dipole moment of the molecule. The change in state from equilibrium is defined as the induced dipole moment \( \vec{p} \) and given by:

\[
\vec{p} = \hat{\alpha} \cdot \vec{E}
\]

Where \( \hat{\alpha} \) is the polarizability tensor. Note that this is only valid for the static case, under the linear approximation (perturbations from equilibrium are small), and is not related to any inherent dipole moment associated with the equilibrium state of the molecule, such as the permanent dipole moment of water. Applying linear response function theory the dipole moment induced by the presence of an oscillating electric field is given by:

\[
\vec{p}_L = \int_0^\infty \hat{\alpha}(\tau) \cdot \vec{E}(t-\tau) \, \mathrm{d}\tau
\]

Here \( \vec{p}_L \) is the induced dipole moment created by the oscillating electric field of the incident light \( \vec{E}_L \). Also \( \hat{\alpha}(\tau) \) is the linear response function and has no relation to the \( \hat{\alpha} \) for the static case. Fourier transforming this equation and simplifying for monochromatic light (laser light) gives:

\[
\vec{p}_L(\omega) = \hat{\alpha}_L(\omega) \cdot \vec{E}(\omega)
\]

Where \( \vec{p}_L(\omega) \) is the induced dipole moment. The term \( \hat{\alpha}_L(\omega) \) is the linear polarizability tensor.

Since the emitted radiation from Raman scattering is different in energy from the incident light, the above equation needs to be developed a little further. Incorporating the possible vibrational transitions into the tensor leads to a final solution of:

\[
\vec{p}_R(\omega_R) = \hat{\alpha}_R(\omega_L, \omega_v) \cdot \vec{E}(\omega_L)
\]

Where \( \hat{\alpha}_R \) is the Raman Polarizability tensor. Thus Raman scattering can be modeled using induced oscillating dipole moments i.e. the incident laser light induces oscillating dipole moments in the molecule which in turn radiate light corresponding the the Raman wavelength attributed to the particular vibrational transition.

Surface Plasmons (SPs) are generally described as the stimulated collective oscillation of electron densities along interface of two materials in response to an incident light source. Essentially SPs are electromagnetic (EM) waves bound to the interface surface that are a response to illumination. Because SPs can only be generated in the presence of free electrons, one of the materials is typically a metal to provide the free conduction of electrons.

### Mathematical Description

The electric field \( \vec{E} \) an EM plane wave propagating in a medium with refractive index \( n \) is mathematically described as:

\[
E = E_0 e^{i \omega t - ik \cdot r} = E_0 e^{i \omega t - ik_x x - ik_y y - ik_z z}
\]
Where \( E_0 \) is the amplitude of the electric field, \( \omega \) is the angular frequency, and \( \vec{k} \) is the wavevector. The wavevector with direction parallel to the direction of propagation is defined as:

\[
|k| = \sqrt{k_x^2 + k_y^2 + k_z^2} = n\frac{2\pi}{\lambda} = n\frac{\omega}{c}
\]

For light passing through the interface of two materials with refractive indices \( n_1 \) and \( n_2 \) for orientation such that \( k_z = 0 \) as seen in the figure below, Snell's law dictates that \( k_{x_1} = k_{x_2} \equiv k_x \).

![Figure 3: Refraction of light between two media.](image)

The component of the wavevector perpendicular to the interface is thus:

\[
k_{y_2}^2 = n_1^2\left(\frac{2\pi}{\lambda}\right)^2\left(\frac{n_2^2}{n_1^2} - \sin^2\alpha\right)
\]

Assuming \( n_1 > n_2 \) it can be determined that \( \sin\alpha > \frac{n_2}{n_1} \), hence \( k_y \) is purely imaginary. This leads to the conclusion that in medium two only a traveling wave parallel to the interface exits:

\[
E_2 = E_0e^{-\kappa_{y_2}y}e^{i\omega t - ik_xx}
\]

This is called an evanescent field. With this knowledge in had the construction of the plasmon frequency can be established. For p-polarized light incident on an interface between a conductor and dielectric the complex reflection coefficient, \( \tilde{r}_p \) is described by Fresnel's equations:

\[
|\tilde{r}_p| = \frac{E_i}{E_r} = |r_p|e^{i\phi} = \left|\frac{\tan(\alpha-\beta)}{\tan(\alpha+\beta)}\right|e^{i\phi}
\]

Where \( |E_i| \) and \( |E_r| \) are the incident and reflected electric fields. Using Snell's law again, the reflectance (ratio of intensities) can be found:

\[
R_p = |r_p|^2
\]

Now consider the following two cases. First if \( \alpha + \beta = \frac{\pi}{2} \) then \( r_p \rightarrow 0 \). This describes the case where there is no reflection for p-polarized incident light. The second case, \( \alpha - \beta = \frac{\pi}{2} \) then \( R_p \).
\( \rightarrow \infty \) which is when resonance occurs. From here the dispersion relation can be found for \((\alpha - \beta = \frac{\pi}{2})\):

\[
\begin{align*}
\cos \alpha &= -\sin(\beta) \\
\tan \alpha &= \frac{k_{1_x}}{k_{1_y}} &= \frac{-n_2}{n_1} \\
k_x^2 &= k_1^2 - k_{y_1}^2 &= k_1^2 - k_x^2\frac{\epsilon_1}{\epsilon_2} \\
k_{yi} &= \frac{\omega}{c}\sqrt{\frac{\epsilon_i^2}{\epsilon_1+\epsilon_2}} \\
\end{align*}
\]

Where \(\epsilon_i\) is the dielectric constant of the material for \(i=1\) or \(i=2\). Taking material 2 to be a conductor and the plasma frequency \(\omega_p\) to be \((\omega < \omega_p)\), \(\epsilon_2\) is then negative:

\[
\epsilon_2(\omega) = 1 - \frac{\omega_p^2}{\omega^2}
\]

For a free electron density \(n_e\):

\[
\omega_p = \sqrt{\frac{4\pi n_e e^2}{m_e}}
\]

Where \(m_e\) and \(e\) are the mass and charge of an electron. This means that in most cases when \(\omega < \omega_p\) there is no EM field in the metal. For cases when \(\epsilon_2 > -\epsilon_1\) it means that \(k_{yi}\) is imaginary while \(k_x\) is real, which is an EM wave traveling along the interface surface with evanescent waves on each side of the interface.

### 2.2 Localized Surface Plasmon Resonance

It is important to understand that the previous discussion and mathematical description of SPs is actually only valid for a smooth interface between the metal and dielectric. It is actually a second type of SPs, known as Localized Surface Plasmons (LSP) that are used in SERS to gain enhancement of the Raman signal. If the surface of the interface is 'roughened' with structures on the scale of the wavelength of incident light, the SPs can become confined to specific locations, much like light in a cavity or waveguide. In cases where the geometry and dimensions are matched to the incident wavelength such that standing waves are formed out of the SPs, Localized Surface Plasmon Resonance (LSPR) occurs. The relationship between the geometry and LSPs is mathematically complex and unique to each case. This means there is not an overall mathematical theory that describes LSPR, however most cases can now be solved numerically and LSPs can be simulated with EM software. In addition the plasmon frequency (or wavelength) can be determined experimentally by measuring the reflectance absorption spectrum of the interface. For example white light is used to illuminate a particular interface. The transmitted light can then be collected and passed to a spectrometer. Next the intensity of the collected light is graphed vs wavelength, and the observed 'gap' in transmission for a specific wavelength of light (i.e the light that is absorbed by the interface) is the plasmon wavelength.

In SERS, LSPs are coupled into the Raman scattered light which can yield significant increases in the intensity of the scattered light. The increase to the intensity of Raman scattered light can be understood to come from extra energy being put into the transition via coupling the LSP to the change in vibrational states. When the plasmon frequency is close (or in resonance) with the frequency of the scattered Raman light, the largest increase in intensity is obtained.
3.1 Semi-Classical Explanation

In general there are three components to enhancing the Raman Signal: the local field enhancement, the radiation enhancement, and the chemical enhancement. Often the third component is ignored and can be seen as a secondary effect to the first two. However it should be noted that it only the chemical enhancement actually affects values of the Raman Polarization Tensor derived previously. Specifically the local and radiative field enhancements are independent of the tensor completely. In addition a new quantity is introduced, the enhancement factor \((M)\), which relates the relative Raman intensities to the enhancements from the Raman signal produced by the incident light.

First, the local field enhancement is essentially the coupling of the incident light to a specific surface plasmon mode. For simplicity, let the localized electric field be given by \(\langle \vec{E}_{Loc} \rangle\) and the electric field due to the incident light by \(\langle \vec{E}_{L} \rangle\). This local field is the macroscopic electric field. When the wavelength of the incident light \((\lambda_L)\) is close to the plasmon resonance \((\lambda_M)\) of the SERS substrate, the local electric field can vary greatly from the electric field due to the the incident light. Specifically when the incident light gives rise to the localized surface plasmons described in the previous section, it is possible for magnitude of the local electric field to be much greater than the magnitude of the electric field due to the incident light, i.e. \(\langle |\vec{E}_{Loc}| \rangle \gg \langle |\vec{E}_{L}| \rangle\). From here it can be seen that the local field gives rise to an induced Raman dipole:

\[
\vec{p}_R(\omega_R) = \alpha_R \vec{E}_{Loc}(\omega_L)
\]

Note the tensor notation has been dropped, and can be interpreted as the solution given by an isotropic tensor. It should also be noted that the induced dipole and radiative emission is not a two step process as it is often perceived, rather it is an instantaneous process which means the two components cannot be decoupled. Assuming that this dipole then radiates into free space and all light is collected, the power is proportional to \(\langle |\vec{p}_R| \rangle^2 \) which gives rise to a term defined as the Local Field Intensity Enhancement Factor:

\[
M_{Loc}(\omega_L) = \frac{|\vec{E}_{Loc}(\omega_L)|^2}{|\vec{E}_{L}(\omega_R)|^2}
\]

Ideal conditions can give rise to local field enhancement factors on the order of \((10^5)\) or greater.

The second component, the radiation enhancement, can be similarly seen as the coupling of the dipole emission to a Plasmon mode. The plasmon mode affects the emission of the dipole in two ways: i) modifying the radiation pattern and ii) enhancing or quenching the emission in comparison to the emission in free space. The first affect is illustrated by the example of a dipole radiating in close proximity to a perfectly reflecting surface. Specifically it modifies \(\langle \psi | \vec{p}_{\omega_R} \mathcal{R} | \psi \rangle \) since the surface acts as a mirror, completely reflecting the emitted field thus no power is radiated through the space behind the mirror. The second enhancement is not as easily explained, but can conceptually understood. For example it is well established that the power radiated from a dipole oscillating near a metal surface can be significantly greater than the same dipole radiating in free space. It is the comparison of these two circumstances that defines the radiation enhancement factor \((M^d_{Rad}(\omega_R))\). Again under ideal conditions this enhancement factor can be on the order of \((10^5)\) or greater.

Combining these two components gives rise to the Single Molecule Enhancement Factor (SMEF):

\[
\text{SMEF}(\omega_L,\omega_R) \approx M_{Loc}(\omega_L)M^d_{Rad}(\omega_R)
\]
Using the approximation $M^d_{Rad}(\omega) \approx M_{Loc}(\omega)$ the SMEF can be reduced to:

\[
\begin{align*}
\mathrm{SMEF}(\omega_L, \omega_R) & \approx M_{Loc}(\omega_L)M_{Loc}(\omega_R) & \approx \frac{|\vec{E}_{Loc}(\omega_L)|^2}{|\vec{E}_L|^2} \frac{|\vec{E}_{Loc}(\omega_R)|^2}{|\vec{E}_L|^2}
\end{align*}
\]

This simplification can be justified conceptually. First the coupling mechanisms for both the Local Enhancement and Radiation Enhancement are qualitatively similar, even if they are not identical. Second invoking optical reciprocity requires both the forward and backward transitions to be allowed. This means if an excitation light source at the Raman wavelength was used the emitted Raman photon should be the wavelength of the original laser (similar to an Anti-Stokes transition). In fact the full quantum mechanical construction requires use of the optical reciprocity theorem, however it is also outside the scope of the paper.

Finally in most cases the Raman shift is relatively small leading to the approximation $\omega_R \approx \omega_L$ giving the Single Molecule Enhancement Factor seen in most publications:

\[
\mathrm{SMEF}(\omega_L) \approx \frac{|\vec{E}_{Loc}(\omega_L)|^4}{|\vec{E}_L|^4}
\]

It is important to realize that this is an approximation. Though verified both numerically and experimentally to be 'ballpark' accurate, it should be noted that in certain circumstances the simplification of the Radiation Enhancement should not be followed explicitly. In addition there are several cases where the Raman Shift is not small enough to justify the latter assumption. However the overall classical description presented here is in general good enough to explain how a typical SERS substrate leads to an enhanced Raman Signal.

Historically the first use of SERS has been attributed to Dr. Martin Fleischmann of the University of Southampton. In 1973 his group saw an enhanced Raman signal from pyridine that had been adsorbed to roughened silver electrodes. However it was not until 1977 that mechanisms in the previous sections were proposed to describe how the enhanced signal was generated. Since this time various substrates have been developed to maximize the resonance of LSPs to increase the enhancement factor up to $(10^{11})$.

In general, the main difference from one SERS method to the next is attributed to the different type of plasmonic substrates employed. These plasmonic substrates range from simple metallic nano-particles to complex nano-scale structures created via lithographic processes. Metallic nano-particles can now be engineered with specific sizes and shapes, in addition to being coated with special materials to tune their plasmonic properties. This has given rise to the Shell-isolated nano-particle enhanced Raman spectroscopy (SHINERS) method. Another type of substrate is created by depositing thin films of metal on top of plastic nano-spheres. The plasmonic properties of these substrates are controlled by the distribution and size of the nano-spheres as well as the thickness of the coated metal, and are called film over nano-sphere (FONs) substrates. Advancements in nano-scale lithographic fabrication over the last 20 years have lead to the ability to actually design nano-scale structures with specific geometries and dimensions. These photo-resist derived structures are then coated with a thin metal film. The plasmonic properties of these substrates are highly tunable due to the ability directly control the geometry and dimensions of the surface structures.

Typically a metal such as gold, or silver is employed due to their ability to support LSPs with wavelengths in the visible and
near infrared, which is where most Raman signals are generated, and their stability in air. In recent years materials such as graphene, semiconductors and quantum dots have been shown to give rise to SERS enhancement, however these materials are believed to be associated with the chemical enhancement and are not true SERS substrates by definition.

Recently a novel SERS substrate has been developed at UC Davis that is both tunable and flexible in addition to being fairly inexpensive to fabricate. The fabrication process is similar to that of FONs, however the ending structure is actually the inverse in this case. These nano-void (or nano-well) substrates have been shown to give enhancement factors as large as \(10^8\). This unique SERS substrate is shown in the figure below:

![Microscope Image of a substrate fabricated at UC Davis from 1 μm latex spheres](image)

Figure 4: Microscope Image of a substrate fabricated at UC Davis from 1 μm latex spheres

Over the last 40 years SERS has grown to broad field with a vast array of applications. Its true power lies in its ability to determine chemical existence at very small concentrations as well as structural information via non-destructive means. The list below is a small example of some of the fields SERS is used in today:

- Single Molecule Detection
- Imaging
- Biosensing
- Ultrahigh Vacuum Science
- Ultrafast Laser Science
- Materials Science
- Electrochemistry

Two real-world applications of SERS technology are the development of an in vivo glucose sensor and the use of SERS to detect and identify explosive/toxic chemicals. These examples highlight the main benefit of SERS: identification of a specific molecule even at significantly low concentrations.
In the first example, a functionalized SERS substrate has been developed that is capable of accurately detecting glucose concentrations in blood. This substrate has been surgically implanted in rats and combined with the spatially offset Raman spectroscopy (SORS) technique, giving rise to surface enhanced SORS (SESORS). This technology allows for measuring the blood glucose concentration through the skin, eliminating the need to draw blood from the subject.

In the second example SERS has been used in the detection of explosives and toxic materials used in chemical warfare. This is done by combining a microfluidic SERS sensor with water soluble agents that convert the harmful chemicals from the gas phase to the liquid phase. In addition, the need to detect these compounds in the field has driven the development of small, portable Raman spectrometers such as those made by Thermo Scientific and Intavec Inc. Due to its ability to uniquely identify a molecule at low concentrations, SERS has been of significant interest to chemical species investigated by homeland security.