

Eric Shen, 2020

Physics; Chemistry and Chemical Biology

Surface-Enhanced Raman Scattering (SERS)
Composite Nanoparticles for Tracer Detection

Statement of Purpose

Raman spectroscopy is an analytical technique used to provide information on molecular vibrations and crystalline structure. This technique is a method of quantification and can be used on a wide range of systems with minimal restrictions on state or metallic character. Raman spectroscopy can detect minute changes in vibronic excitations within molecules, which allows for fingerprinting of molecules and identification in dilute concentrations. This process has been applied to the detection of trace levels of additives in food, oilfield markers, bacterial spores, and structural identification of chemicals. Surface-Enhanced Raman Spectroscopy (SERS) is an extension of traditional Raman spectroscopy and can detect the presence of single molecules through molecular excitations and subsequent relaxation.

Raman spectroscopy functions by shining a high intensity beam of light from a laser to produce an oscillating polarization of the molecule in addition to exciting the vibronic (vibrational and electronic) energy states and produce an inelastic scattering of light. The scattered light can either be equal (Rayleigh), less (Stokes), or greater (Anti-Stokes) in energy than the incident radiation (Fig. 1). Because visible or near-infrared region light is used for Raman analysis, the resulting emission is significantly lower energy and subsequently much weaker and harder to detect. Generally, only approximately 0.000001% of the scattered light will be Raman active, meaning either Stokes or Anti-Stokes scattering. And at room temperature, molecules are much more likely to start at the ground (lowest energy) vibrational state, thus favoring Stokes over Anti-Stokes scattering. As a result, Raman spectrometers are built to detect only lower energy radiation, which increases the sensitivity and applicability of these detectors.

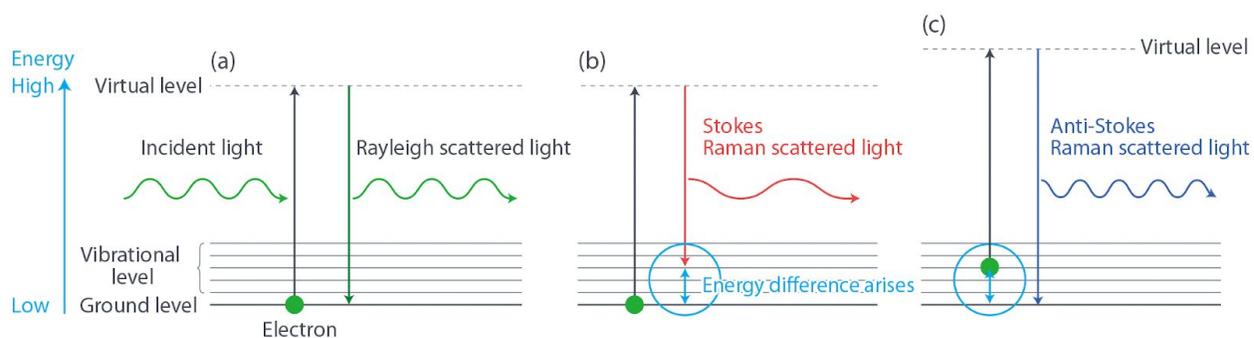


Fig. 1 - Energy transitions of Raman scattering

SERS was discovered half a century later and further developed to increase the intensity of Raman scattering by up to a factor of 10^{11} , greatly improving the resolution and number of molecules detected. By adsorbing molecules of interest on metal substrates or various nanostructures, the effect of individual Raman scattering events compound into stronger and better defined signals. There are two possible mechanisms for this drastic amplification.

The first theory is an electromagnetic effect where the incident light is in resonance with the plasmon frequency and excites localized surface plasmons perpendicular to the Raman substrate. Resonance normal to the plane is in the same orientation as the Raman scattering that The electromagnetic mechanism is more widely supported because it does not have any limitations on separation between the molecule and nanostructure. In addition, it supports the double field enhancement (once by the molecule and once by the substrate) generally observed.

The second, less prominent, model is a chemical theory that involves molecules covalently bonding to metal substrates, which act as charge-transfer intermediates and facilitate visible light to cause energetic transitions that would normally require UV radiation. However, the chemical mechanism is necessary to explain the larger energy enhancements observed in some cases. Because of the electronically fluid nature of transition metals, when organic and non-metallic ligands bind, they are able to delocalize the Raman excitation of the metal-ligand bond. This process increases the stability of complexes and allows for a ripple effect in the metal such that a low energy photon can affect the collective electron cloud and amplify the strength of the Raman resonance.

SERS based sensors have been widely studied for developing biological and chemical monitoring applications. In my work last summer, we demonstrated SERS based sensor for in-situ optical sensing of chemical tracers, which have been deployed in oil fields to study reservoir surveillance. In our study, SERS composite nanoparticles were designed to detect one of the fields tested optical tracers, dipicolinic acid (DPA), which also are known as an excellent marker compound for bacterial spores. Functionalization of outer shell of SERS composite nanoparticles for the selective coating allows to improve sensitivity of the detection. By investigating various molecular selective coatings, we were able to develop an efficient detection

platform using SERS composite nanoparticles for in-situ monitoring trace levels of DPA molecules. In addition, integration SERS with microfluidic systems and magnetic competent is progressively developed for detection of low volume analysis of the samples and constant monitoring of produced water.

In my past work, I synthesized gold and silver nanoparticles to use as SERS substrates for DPA. The choice of gold and silver comes from the literature, which details of their efficacy in facilitating Raman scattering in the visible light region. By adding toluene-thiol to the silver nanoparticle solution, it strongly chelates to form a transition metal complex capable of attracting and improving the strength of Raman scattering. This method allowed us to establish a new limit of detection ten times lower than observed at the time. In addition, the toluene-thiol silver nanoparticles were able to detect a newly synthesized, complex tracer: BCPDCA.

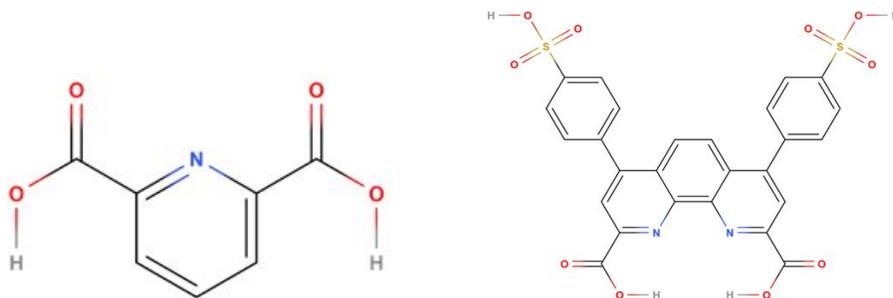


Fig. 2 - DPA (left) and BCPDCA (right)

This coming summer, my areas of focus will be increasing the applicability of SERS for molecular detection and work on establishing a theory to predict the SERS enhancement for a given molecule and which additive will augment the signal. There are several ideas to explore to broaden the use of SERS. The most prominent would be to functionalize DPA and generate chemical barcodes that are bioorthogonal, distinct from each other, and not found in nature.

Because DPA is a well studied system, it is a molecule of choice to derivatize and manipulate. Being well studied also makes it clearer what intermolecular forces are responsible to helping or hindering SERS processes once experiments are performed. The end goal of this would be to create a library of DPA derivatives and under what conditions they are optimized. It is the first step to allow DPA and silver nanoparticles to be used in practice, and a

comprehensive set of data would be available to study the forces at work altering the SERS enhancement.

The second facet of SERS to develop is possible substrates that will bind nanoparticles and foster SERS effects. For our last round of experiments, all measurements were performed on droplets sitting on sterilized silicon wafers. One factor to control is the surface on which the measurement is carried out or if the nanoparticles/molecule of interest is in solution. Substrates such as glass fiber, quartz, and alumina membranes foster coagulation of nanoparticles to create nano-structures that greatly improve SERS response. Likely approaches will be soaking and spin-coating in addition to direct synthesis, followed by scanning electron microscopy (SEM) to visually assess the coverage and quality of nanoparticles.

This project involves chemistry, physics, and materials science with applications that extend to various fields pharmaceutical or biological. A large repertoire of skills from organic synthesis to nanofabrication/assembly to spectroscopy and imaging will be required for this investigation. As a person of diverse interests, this research offers a clear goal with countless possibilities to attempt, allowing me to contribute to scientific literature while helping myself better understand what I wish to pursue in my future studies and research.

References

1. <https://www.nanophoton.net/raman/raman-spectroscopy.html>