# Portable Shifted Excitation Raman Difference Spectrometer For In-Situ Field Measurements

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## ABSTRACT

Building upon the principle of Raman spectroscopy, Shifted Excitation Raman Difference Spectroscopy (SERDS) is a method that has promising advantages over its predecessor. Already proven to minimize the effect of background noise, and reduce measurement time, the advent of smaller light sources, detectors, and controllers is allowing these spectroscopic techniques to be moved from the lab to the field. Researchers from Berlin, at the Ferdinand-Braun-Institut, Leibniz-Institut für Höchstfrequenztechnik have presented a handheld, highly precise SERDS probe that is portable. This portability allows *in-situ* measurements of apple leaves as a proof of concept. This method could potentially be used in the medical and security fields in the future.

## INTRODUCTION TO RAMAN SCATTERING

First discovered by Sir C. V. Raman in 1928, Raman scattering is an inelastic process. It is comprised of photons interacting with the different energy states of a molecule. The energy states that the photons interact with can either be electronic levels, or their neighboring vibronic levels.

Prior to the discussion of Raman scattering, some of the formalism of scattering will be developed using Rayleigh scattering as an example.

Rayleigh scattering is an elastic process, meaning that the energy of the photon is conserved. It has no dependence on vibrational states of the molecule, and can be described by the energy-level diagram in **Figure 1**.

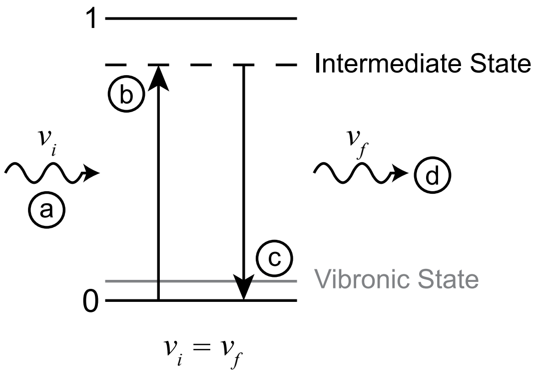

**Figure 1. Energy-level diagram for Rayleigh scattering. (a) An incoming photon interacts with the medium. (b) The medium gets excited to an intermediate state. (c) The medium de-excites back to the ground state. (d) The scattered photon exits with the same frequency.**

The mathematics that describes the energy-level diagram are based on the relationship between photon frequency ($v$) and energy ($E$),

$$E = hv\,, \tag{1}$$

where $h$ is Planck's constant. Thus, the overall energy change of the photon is

$$\begin{aligned} \Delta E &= E_f - E_i\,, \\ \Delta E &= hv_f - hv_i\,, \\ \Delta E &= 0\,, \end{aligned} \tag{2}$$

since, for Rayleigh scattering, the incoming and outgoing photons have the same frequency.

Raman scattering, however, has a dependence on the vibronic states, and the photon has a net energy change. Depending on whether this net energy change is negative or positive, the scattering is called "Stokes-Raman scattering" or "Anti-Stokes-Raman scattering." The two energy-level diagrams are shown in **Figure 2**.

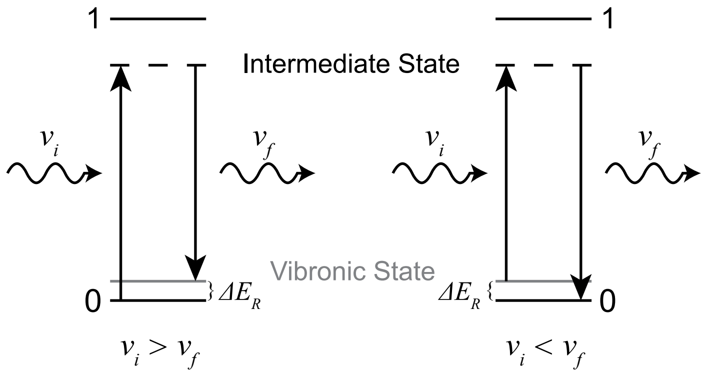

**Figure 2. Energy-level diagram for Raman scattering. On the left is Stokes-Raman and on the right is anti-Stokes-Raman scattering.**

In the two Raman cases, the net energy change of the photon is non-zero (making it an inelastic collision), since the medium does not return to its original state post-scattering.

Let the energy difference between the ground state (0) and the vibronic state be defined as

$$\Delta E_R = h\nu_R \,. \qquad \textbf{(3)}$$

In the Stokes case, the net energy of the medium is higher than it was originally, meaning that the scattered photon must have less energy (lower frequency) than it did initially. The opposite is true for the anti-Stokes case. The original energy of the medium is higher than the final, meaning that the scattered photon must have more energy (higher frequency) than the incoming photon.

Letting Stokes-Raman and anti-Stokes-Raman scattering be denoted by the subscript "S" and "AS" respectively, the net energy change of the photon due to the scattering in the two cases is

$$\Delta E_{\gamma,S} = -h\nu_R \,, \qquad \textbf{(4)}$$

for Stokes scattering, and

$$\Delta E_{\gamma,AS} = +h\nu_R \,, \qquad \textbf{(5)}$$

for Anti-Stokes scattering.

In equilibrium, the majority of the population of the medium is in its lowest energy state (0). A small fraction can be in various excited states. Due to this, the Stokes-Raman scattering is much more likely than anti-Stokes-Raman. With respect to spectroscopy, this also means that the signal due to Stokes-Raman scattering is much higher.

As a spectroscopic example, for a laser illuminating a homogenous medium with frequency $\nu_L$, the resulting spectrum can be illustrated as shown below in **Figure 3**.

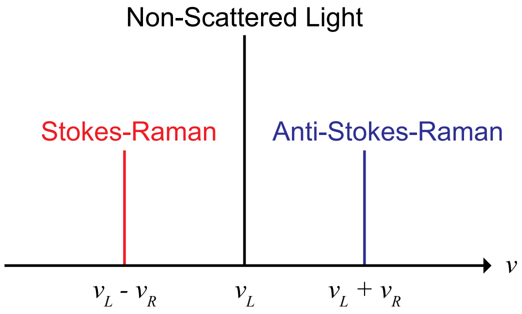

**Figure 3. After the sample has been illuminated, the scattered light returning to the detector is either Stokes-shifted, non-scattered, or anti-Stokes-shifted.**

An important note to make about both Rayleigh and Raman scattering is that there is no "absorption" of the photon by the medium. The photon interacts with the medium via an elastic (Rayleigh) or an inelastic (Raman) collision. In Raman scattering, there is an energy transfer between the medium and the photon due to this collision. This energy transfer causes the energy of the photon to not be conserved.

Raman spectroscopy involves illumination of a sample with a laser, and subsequent detection of the scattered light with a spectrometer. Since Raman scattering involves energy transitions between the ground state and the neighboring vibronic states, which are very close in energy, the Raman signals can be very hard to distinguish. Care must be taken to filter out the original illumination beam, laser-induced fluorescence, as well as extraneous light. All of these signals impact the resolution of the Raman spectrum, as they can be orders of magnitude stronger than the collected Raman signals.

Additionally, it is worth noting that the presentation of Raman spectra typically take a different form than other spectra. Where other spectra might have the horizontal axis in terms of wavelength, frequency, or wavenumber, Raman spectra present the horizontal axis as a shift in wavenumber from the incident light. This choice is made because of the small energy differences being measured.

## SHIFTED EXCITATION RAMAN DIFFERENCE SPECTROSCOPY

Raman spectroscopy has found applications ranging from geology to medicine. With the advancement of near-infrared (NIR) light sources, the ability to make accurate measurements has made Raman spectroscopy a highly useful tool in many fields.

Raman spectroscopy has many different variations. These variations all are fundamentally based on Raman scattering, and have been modified to fit specific applications. The researchers from Berlin chose to utilize a method called Shifted Excitation Raman Difference Spectroscopy (SERDS). It is a method of accurately detecting chemical composition.

As described in their paper, SERDS offers advantages over classic Raman spectroscopy, by "[being] a powerful spectroscopic tool to separate Raman signals from background interferences," and "[having] the potential to reduce the overall measurement time."

The ability to remove the background signal is one of the key elements to making *in-situ* measurements, as the ambient daylight conditions can saturate the measurement system.

A shorter time of measurement is ideal for practical applications of SERDS, including mid-surgery diagnoses.

In SERDS, illumination occurs by two laser beams that are slightly shifted in wavelength (less than a nanometer). Both of these beams excite the sample, and two separate Raman spectra are acquired. These two Raman spectra are then subtracted in order to discard extraneous signals, such as those described above. Once the subtracted spectra are obtained, an algorithm then creates a reconstructed SERDS Raman spectrum.

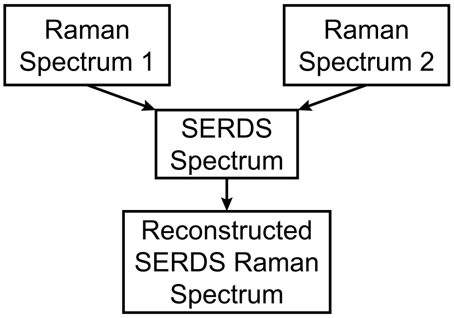

**Figure 4. Method for obtaining accurate SERDS Raman spectra.**

## A PORTABLE SERDS SYSTEM

In order for the researchers to take full advantage of their SERDS system, it needed to be able to make *in-situ* measurements. This meant that the whole system needed to be portable.

They built upon previous design iterations, and designed a handheld[1] SERDS probe, that included the light source, sensing optics, and was fiber coupled to the spectrometer.

### LIGHT SOURCE

The laser line at 785nm was chosen to minimize laser-induced fluorescence of the sample. Another advantage of this wavelength choice is that typical silicon (Si) CCD detectors are still sensitive at this wavelength.

Since SERDS requires two excitation wavelengths, slightly shifted, the laser system has the ability to emit at two wavelengths around 785nm, separated by approximately $10\text{cm}^{-1}$. Utilizing ridge waveguides, the system is able to combine the two beams into a single output beam.

### SENSING OPTICS

The probe is designed such that the output beam and the collected signal beam are colinear. As such, the filtering required must be able to discard the ambient light, fluorescence, and 785nm light to maximize the Raman signal to the spectrometer. The researchers also chose to design the system such that the anti-Stokes shifted light was also discarded.

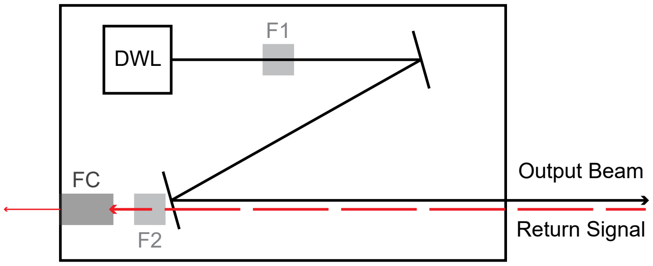

**Figure 5. Schematic of handheld SERDS probe. DWL is the dual wavelength laser, F1 filters out wavelengths other than 785nm, F2 filters out non-Stokes-shifted signal, FC is the fiber coupler. The return signal (dashed line) is offset for clarity.**

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[1] 120 mm x 28 mm x 12 mm (4.72" x 1.10" x 0.47")

## WAVELENGTH'S ROLE

The researchers chose to use Wavelength Electronics laser drivers and temperature controllers for this application. The four laser drivers provided accurate current, while the temperature controller provided a stable operating temperature. Both are necessary for precise wavelength control of the laser.

### LASER DIODE DRIVERS - LDD400

In order to have control over both excitation wavelengths, a Y-branch coupler was utilized. This coupler had four independent current control points, allowing complete control and adaptability for wavelength and power output of the probe. Each point was controlled by a Wavelength LDD400.

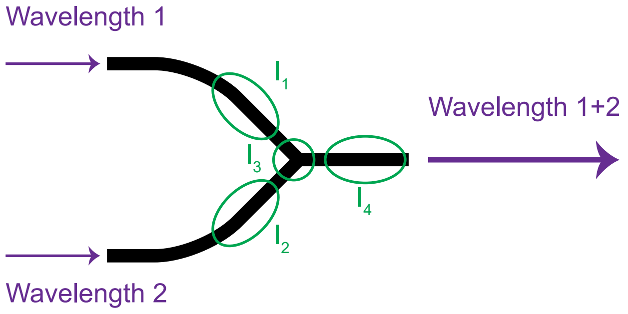

**Figure 6. Illustration of the Y-branch used to control the two independent wavelengths and output power. Current control sites are labeled $I_1$-$I_4$. Wavelength 1 and 2 come into the Y-branch separately, and are combined to a single output.**

By having precision current control, the researchers were able to ensure that the SERDS system would be stable throughout the whole measurement range, in addition to keeping the 10cm$^{-1}$ difference between the two. By varying the currents used, they were able to tune the output power anywhere from 0mW to 120mW, while keeping the center wavelength within approximately 1.5cm$^{-1}$ of the desired output. Additionally, the stability of the bandwidth (FWHM) was kept under 0.8cm$^{-1}$ throughout the whole power range.

The LDD400 offers low noise operation up to 400 mA, which offered crucial laser control for each of the current control locations on the Y-branch.

### TEMPERATURE CONTROLLER - HTC1500

Another key element to the stability of the laser system is the temperature control. The output wavelength of diode lasers is dependent on their operating temperature. Since the Raman shift is inherently dependent on the incident wavelength (or frequency), it is crucial that the temperature of the laser be stable.

The researchers chose to use the Wavelength Electronics HTC1500 to control the thermoelectric used for temperature control. This allowed them to keep the laser operating temperature at 25°C.

Operation of the probe was studied while using a hot plate on the probe casing to determine if handheld use would impact the stability of the laser. With the probe casing at 36°C, the HTC1500 kept the laser temperature stable at 25°C. The researchers found that there was no noticeable change in stability due to simulated handheld use of the probe in an hour long test.

With its 0.009°C stability, and low-profile design, the HTC1500 met the standards required for performance and size to enable portability of the SERDS system.

## RESULTS

With the stable, portable SERDS system, the researchers moved their measurements from the lab to the field. They took their system to an apple orchard in Switzerland, where they studied leaves on the apple trees.

Utilizing two laser wavelengths around 785, separated again by approximately 10cm$^{-1}$, the researchers performed their SERDS experiment on the apple leaves.

In the initial Raman spectra, the background noise is enormous due to the ambient daylight conditions, and atmospheric absorption. Only a single Raman line is discernable in the original spectra.

After subtracting the two initial spectra, and reconstructing the SERDS Raman spectra, the researchers found an 11-fold improvement on the signal-to-noise ratio of the Raman line that was visible previously.

In addition to clarifying that Raman line, the reconstructed SERDS spectrum has minimal background noise, and is able to resolve Raman lines of cholorophyll and carotenoids, which match known values.

For plots of the results, see the full paper here.

## SUMMARY

Researchers from Berlin designed and built a portable measurement system to make field measurements. The system utilized Shifted Excitation Raman Difference Spectroscopy (SERDS), which is a variation of Raman spectroscopy.

In addition to the portability, the stability of the laser system, driven by four LDD400s and temperature controlled by an HTC1500, was found to be better than the resolution of the spectrometer being used to analyze the signal. Thorough stability tests were performed, varying the temperature of the case, the injection currents, and the power output.

Raman spectroscopy, dealing with very small energy changes, can have difficulties if the background signal is high. SERDS, by collecting two spectra, and taking the difference between them, allowed the unwanted background to be effectively discarded.

With the background greatly reduced, and the Raman signal resolved, the researchers studied apple leaves with great resolution in the field. Chlorophyll and cartenoid lines could be resolved with the leaves still on the tree.

## REFERENCES

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4. G. S. He, *Nonlinear Optics and Photonics* (Oxford University Press, 2015), Chap. 7.
5. MIT Spectroscopy - Research in Biomedical Optics, "Non-Invasive Measurement of Blood Analytes using Raman Spectroscopy," http://web.mit.edu/spectroscopy/research/biomedresearch/Methods.html

## USEFUL LINKS

- LDD400 Product Page
- HTC1500 Product Page

| PRODUCTS USED |
|---|
| LDD400, HTC1500 |

| KEYWORDS |
|---|
| Raman, scattering, spectroscopy, Shifted Excitation Raman Difference Spectroscopy, SERDS, laser driver, temperature controller, in-situ, near infrared, NIR |

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