

Planetary surface characterization using a 633nm Laser to reduce the background radiation in Raman signal

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Introduction: Raman spectroscopy has proven to be a versatile planetary exploration tool able to provide insight into the chemical composition of organic and inorganic samples with little to no preparation being required [1][2]. Compact remote Raman instruments allow for reliable characterizations to be made during on-surface missions.

Typical incident laser light for Raman spectrometers at LaRC utilize a Nd:YAG laser frequency-doubled to 532nm, due to laser light's exceptional excitation efficiency at higher frequencies, being directly proportional to λ_i^{-4} [3]. Usage of an incident laser wavelength (λ_i) in the visible light spectrum also places most Raman scattered light in the high quantum efficiency. However, the many benefits of shorter λ_i do come with some drawbacks.

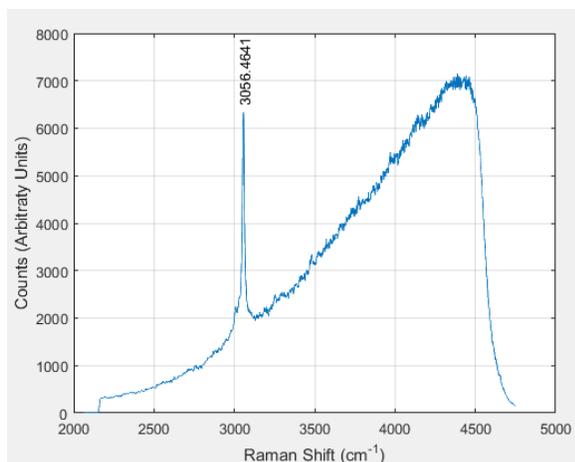


Figure 1. Interference in High Frequency Region Naphthalene Raman Spectra, NASA LaRC 2017

High intensity, short wavelength, incident lasers are prone to causing sample fluorescence relative to near infrared wavelengths due to the higher photon energy absorption efficiency of visible light that many materials exhibit. This issue is highlighted in figure 1, which shows the high frequency region Raman spectra of naphthalene, collected with one of our compact Raman spectrometer systems, along with a large fluorescence signal which is intense enough to potentially mask any Raman spectra in that area on similarly effected samples. We have also found that sample fluorescence is not a unique issue to a specific type of sample or spectrometer form factor.

Prevalence of Noise: It has been found that sample noise is not a unique issue to any one specific sample or spectrometer form factor.

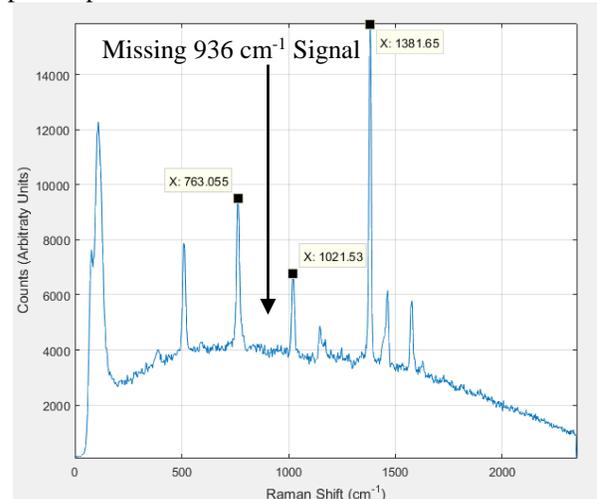


Figure 2. Naphthalene Background Radiation Overpowering 936(cm^{-1}) signal, NASA LaRC 2006

Figures 2 and 4 show analyzed low frequency region naphthalene Raman spectra and a raw CCD image of calcite Raman spectra collected in 2006 with a pre-built Kaiser VPH "Holospec" Raman spectrometer, respectfully. While the more intense Raman spectra of both samples are able to be easily found, both show the presence of background fluorescence noise which can overpower and mask out weaker Raman spectra. Past research conducted at LaRC has also shown that while time resolved operation of a Raman spectrometer is able to lower background radiation, the laser induced fluorescence, potentially caused by contaminants, is not always removed due to its generation from the sample itself [5]. While there are several potential solutions which can be performed in a lab setting, such as the modification of optics, procurement of purer samples, or a change in λ_i all together, such strategies cannot be practically be used on a spectrometer once it leaves earth, making the λ_i a critical design choice when preparing a Raman spectroscopy instrument for planetary characterization missions.

The majority of information currently available on this topic is mostly theoretical and existing studies exploring the pros and cons of varying excitation wavelengths are generally investigating biological and medical applications with limited studies being available on

geological characterization and planetary science applications [4].

Experiment: NASA LaRC's Raman Spectroscopy Lab are investigating the sample-caused interference masking reduction of longer λ_i in Raman spectrographs designed for planetary surface characterization missions. This is being accomplished by collecting spectra of various mineral and biogenic samples using a pulsed 532nm Nd:YAG laser and a continuous NIR 633nm HeNe laser and comparing both the presence and relative intensity of any fluorescence which is detected.

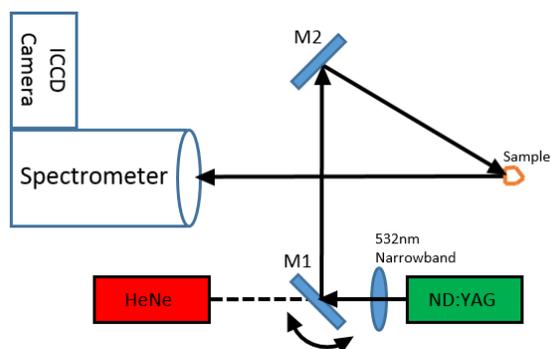


Figure 3. Experimental Setup, configured for collection of 532nm data.

To ensure that only the effect of excitation wavelength is being tested, the experimental setup is designed to stay as consistent as possible with the only difference between the 532nm and 633nm configurations being the addition of a RazorEdge notch filter for their respective laser systems. Other parameters such as beam path length, sample distance from the spectrometer, and sample strike point location will remain constant between configurations. Spectra are collected using the same PIMAX I camera and Kaiser split grating spectrometer.

Data Analysis: LaRC's Raman Spectroscopy Lab has developed a program suite which is capable of completing all steps of Raman data analysis, from spectral line profile extraction to calculation of Raman shift from any incident wavelength. Development of the program using Matlab allows for cross compatibility and backwards compatibility with any ".txt" delimited data, such as the line profile from 2006 used in

Figure 2. Testing has shown the software to have accuracy comparable to GramsAI, a spectroscopy analysis standard.

Experiment Significance: This experiment offers insight into the sample noise reduction potential of a near infrared λ_i within the context of planetary characterization missions. Past research conducted at NASA LaRC has shown that sample fluorescence emitted during imaging may be related to presence of certain organic molecules in a sample and that while there is an optimal gating delay which can reduce background noise and sample fluorescence, the overall intensity of the Raman signal may be reduced as well potentially resulting in the loss of signal entirely [5].

Some instruments, such as Mars 2020's SHERLOC, utilize a deep UV λ_i to eliminate fluorescent interference from samples, however, usage of these shorter λ_i results in a loss of silicate structural signatures and limits the instrument to analysis of organic compounds [6]. Results of our experiment will show if a NIR λ_i is able to reduce sample noise while retaining the ability to analyze silicate materials.

References: [1] Mars.nasa.gov. (2017). *SHERLOC For Scientists - Mars 2020 Rover*. [online] Available at: <https://mars.nasa.gov/mars2020/mission/instruments/sherloc/for-scientists/> [Accessed 11 Jul. 2017]. [2] Grasselli, Jet al., (1980), Amsterdam: North Holland Publishing Company. [3] Zhou, P., Newark, DE: B&W Tek, Inc., 2015. [4] Synytsya, A., (2014), *Journal of Raman Spectroscopy*, 45(10), pp.903-911. [5] Garcia, C.S. et al (2009) *Proc. SPIE 7312*, 731210/1-8. [6] L. Beegle et al. (2015) SHERLOC, IEEE, doi:10.1109/AERO.2015.7119105

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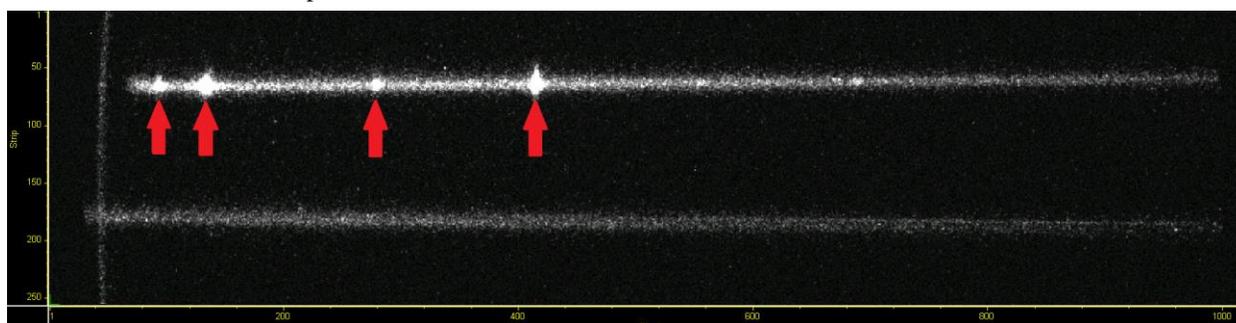


Figure 4. CCD Image of Calcite Spectra. $\lambda_i = 532\text{nm}$, NASA LaRC 2006. 155.42, 281.7, 711, and 1085 (cm^{-1}) Spectral Peaks Marked With Red Arrows (Left to Right)