

REMOTE UV RAMAN SPECTROSCOPY FOR PLANETARY EXPLORATION USING A MINIATURE SPATIAL HETERODYNE RAMAN SPECTROMETER. Nirmal Lamsal¹, Patrick Barnett¹, S. Michael. Angel¹, S.K. Sharma², T. E. Acosta², ¹University of South Carolina, Columbia, SC 29208, USA (SMANGEL0@mailbox.sc.edu), ²Hawaii Institute of Geophysics and Planetology, University of Hawaii, Honolulu, Hawaii 96822, USA

Overview: Raman spectroscopy is ideally suited for planetary exploration, because Raman spectra provide detailed molecular and structural information, very useful for geochemical measurements as well as to measure organic and inorganic biomarkers in the search for past or present life on other planets [1]. Raman scattering, a very weak process, can be relatively strong at deep UV wavelengths because of the $1/\lambda^4$ dependence of Raman scattering and the possibility of large resonance enhancement for molecules that absorb strongly at UV wavelengths. However, traditional grating based dispersive UV spectrometers are relatively large and require very narrow entrance slits to provide the high resolution needed for deep UV wavelengths, thus limiting light throughput.

We are developing a new type of miniature Fourier transform (FT) Raman spectrometer; the spatial heterodyne Raman spectrometer (SHRS), which provides high spectral resolution in a very small system with high light throughput. The resolution of the SHRS is not dependent on a slit, so miniature systems, $<1\text{ cm}^2$ footprint, can be made with high spectral resolution. The SHRS addresses many of the issues related to the use of UV Raman for planetary exploration and stand-off measurements.

The SHRS is based on a stationary grating interferometer with no moving parts and uses a CCD to record the interferogram (see Fig. 1, left). The wide acceptance angle (field of view, FOV) allows Raman measurements to be made with a large laser spot on the sample, giving low laser irradiance to allow measurements of highly absorbing photosensitive samples that might otherwise be damaged by the laser. The large FOV of the SHRS makes it easy to couple with a telescope (Fig. 1 right), minimizing laser pointing stability issues. Since there are no moving parts and all wavelengths are measured simultaneously, the SHRS is compatible with a pulsed laser and gated detectors allowing measurements to be made in bright light conditions, important for daylight measurements [2]. The SHRS also has a relatively large Raman spectral band pass in the deep UV. All of these characteristics together make the SHRS a potentially powerful system for planetary exploration. Here, we present UV stand-off Raman measurements using a SHRS and show an improved UV SHRS that uses a plate beam splitter and compensator plate.

Experimental: A schematic of the plate beam splitter UV SHRS shown coupled to a stand-off instrument is shown in Fig. 1. The SHRS interferometer consists of a 20 mm fused silica plate beamsplitter and two 300 gr/mm, 25 mm gratings. Interference fringes formed at the grating plane are imaged onto an intensified CCD (ICCD) detector with 1024×256 pixels using a 105 mm focal length, $f/4.5$ lens. For stand-off Raman a 1064 nm Q-switched Nd:YAG laser was used to generate 532 nm and 266 nm laser pulses. The path of the laser was collinear with the field of view of the telescope. Two laser-blocking filters, 266 nm or 532 nm (RazorEdge, Semrock) were used to block laser light.

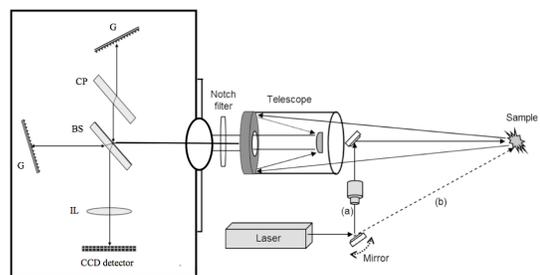


Fig. 1. Schematic of the SHRS with plate beamsplitter and compensator plate (left), shown coupled to a telescope (right) for stand-off UV SHRS Raman measurements. BS= Beamsplitter; G= Grating; IL= Imaging lens.

The design of the UV SHRS is similar to one described earlier [3,4]. Briefly, collected Raman light is collimated and passed through the entrance aperture and divided into two beams by the 50/50 fused silica beam splitter. The two beams are diffracted by the diffraction gratings at an angle that depends on the wavelength. Heterodyning in the interferometer occurs by setting the grating angles, known as the Littrow angle (θ_L), so that light at the heterodyned wavelength, or wavenumber (σ_L), is exactly retro reflected back along the same beam path. Light at the Littrow wavelength recombines at the beamsplitter without producing an interference pattern. However, for any wavenumber other than Littrow, the diffracted beams leave the gratings at an angle, resulting in crossed wavefronts in the beamsplitter, generating an interference fringe pattern, which is imaged onto the detector.

Results and Discussion: Figure 2 shows the Raman

spectrum of diamond using the improved plate beam splitter UV SHRS, along with the interference image and interferogram (inset). The fringe visibility is close to theoretical. Figure 3 shows Raman spectra of several rocks and minerals. In Figure 3 (A), the strongest Raman line at 1005 cm^{-1} is the Raman fingerprint of $\nu_1(\text{SO}_4)$ of gypsum. In Figure 3 (B and C) the strongest lines at 457 , and 1085 cm^{-1} are fingerprints of α -quartz and calcite, respectively [5]. In the spectrum of the sea shell (Figure 3D) the presence of a strong Raman line at 1085 cm^{-1} indicates that the snail sea shell contains biogenic calcite mineral. Biogenic calcite usually produces strong fluorescence in the Raman spectrum when excited with visible laser wavelengths. Excitation with 244 nm allows one to measure the Raman spectrum free from fluorescence.

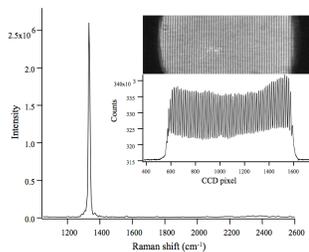


Fig. 2. SHRS UV Raman spectrum of diamond, measured using 10 mW , 244 nm laser with plate beam splitter SHRS design. Inset: interferogram image and cross section.

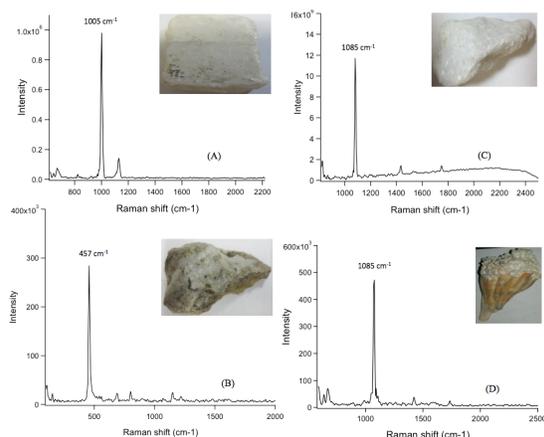


Fig. 3. UV SHRS Raman spectra of rocks and minerals with major constituents of (A) gypsum, (B) α -quartz, (C) calcite, and (D) snail sea shell, using a 10 mW , 244 nm laser.

Pulsed remote Raman using a dispersive spectrometer has been shown for mineralogical analysis at 66 m [5]. To assess the performance of the UV SHRS for remote UV Raman measurements, several compounds were measured at $\sim 18\text{ m}$ using a 266 nm pulsed laser, focused to a 20-mm spot on the sample. The FOV of the

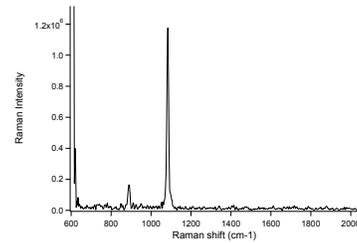


Fig. 4. UV standoff Raman spectra of calcite at 18 m , measured using the cube beam splitter SHRS with 10.3 mJ/pulse , 266 nm laser excitation.

SHRS was $\sim 30\text{ cm}$ at this distance and no degradation of the samples was observed using a 20-mm laser spot. However, sample degradation was often observed when the laser was more tightly focused. Figure 4 shows a standoff SHRS UV Raman spectra of calcite.

Figure 5 (inset) shows a closeup view of our most recent miniature SHRS, using a 2.5 mm beamsplitter and gratings masked down to 2 mm . The Raman spectrum of sulfur is shown with good resolution, measured with this 2 mm size SHRS using 532 nm excitation. Although the lenses and CCD are much larger, this system demonstrates feasibility for making mm-sized high resolution Raman spectrometers. Raman spectrometers of such small size will have many remote and in-situ applications for characterizing mineralogy on planetary surfaces and for downhole measurements.

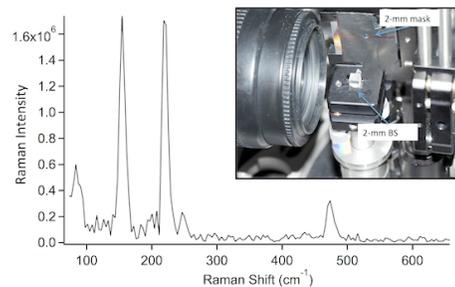


Fig. 5. Raman spectrum of sulfur using 2-mm SHRS (inset).

Conclusion: An improved SHRS UV Raman system is described. Standoff SHRS UV Raman is demonstrated at 18 m . A miniature 2-mm SHRS is demonstrated.

References: [1] Angel S.M. et al. (2012) *Appl. Spectrosc.*, 66, 137–150. [2] Carter J. et al. (2005) *Appl. Spectrosc.*, 59, 769–775. [3] Gomer N.R. et al. (2011) *Appl. Spectrosc.*, 65, 849–857. [4] Lamsal, et al. (2015) *Appl. Spectrosc.*, 69, 525–534. [5] Sharma, S.K. et al. (2002) *Appl. Spectrosc.*, 56, 699–705.

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