VISIBLE AND UV STANDOFF RAMAN MEASUREMENTS IN AMBIENT LIGHT CONDITIONS USING A GATED SPATIAL HETERODYNE RAMAN SPECTROMETER.

Nirmal Lamsal[1], S. Michael. Angel[1], S.K. Sharma[2], T. E. Acosta[2], [1]University of South Carolina, Columbia, SC 29208, USA (SMANGEL0@mailbox.sc.edu), [2]Hawaii 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, the traditional grating based dispersive monochromators are relatively large and require very narrow entrance slits to provide the high resolution needed for deep UV wavelengths, thus limiting light throughput. Recently, we developed a new type of Fourier transform (FT) Raman spectrometer; the spatial heterodyne Raman spectrometer (SHRS), which provides high spectral resolution in a very small system without limiting light throughput. The SHRS addresses many of the issues related to the use of UV Raman for planetary exploration and standoff measurements.

The SHRS is based on a stationary diffraction grating interferometer that uses an imaging detector to record an interferogram (see Fig. 1). The interferometer has no moving parts, and provides high spectral resolution in a very small package. Also, the SHRS has a large entrance aperture with a wide acceptance angle or field of view (FOV), which allows Raman measurements to be made using a large laser spot on the sample with low laser irradiance. This allows the SHRS to be used to measure highly absorbing photosensitive samples that might otherwise be damaged by the laser.

Since there are no moving parts and all wavelengths are measured simultaneously, the SHRS is compatible with a pulsed laser and gated detectors allowing the measurements to be made in ambient light conditions, important for daylight measurements [2]. The use of gated detection also minimizes the need for special vibration isolation. Moreover, the SHRS is relatively easy to couple with a telescope with fewer laser pointing stability issues. 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 the first UV standoff Raman measurements using a SHRS. High spectral resolution Raman spectra are measured using a pulsed laser and gated detector in ambient light conditions with both visible and UV laser excitation, and without the use of a vibration isolation table.

Experimental: A schematic of the standoff SHRS instrument is shown in Fig. 1. The SHRS interferometer consists of a 20 mm fused silica beamsplitter and a pair of 300 grooves/mm, 25 mm square diffraction gratings. The gratings were mounted in piezo motor driven optical mounts for precisely setting the grating angle. 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. A Q-switched Nd:YAG laser with fundamental frequency at 1064 nm was used to generate 532 nm and 266 nm laser pulses. The path of laser was collinear with the field of view of telescope. Light collected by the telescope was collimated and passed into the 20-mm aperture of the interferometer. Two laser-blocking filters, 266 nm or 532 nm (RazorEdge, Semrock) were used to block laser light. Spectra were produced from cross sections of the fringe images using a Fast Fourier transform (FFT) function.

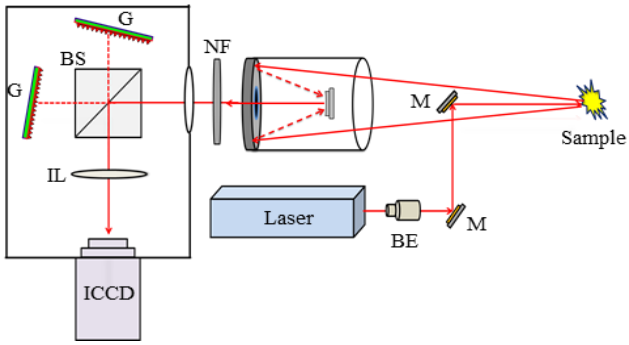

Fig. 1. Schematic of the standoff UV SHRS Raman system. BE= Beam expander; M= Mirror; BS= Beamsplitter; G= Grating; NF= Notch filter; IL= Imaging lens

The design of the UV SHRS is similar to one described earlier [3]. 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 this wavelength, the Littrow wavelength

or wavenumber (σ_L), 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. The number of fringes produced on the detector is given by Eqn. 1, where *f* is fringes/cm. The intensity of fringes obtained as a function of detector position, *x*, is given by Eqn. 2, where *B(σ)* is the input spectral intensity at wave number σ [4, 5]. The Fourier transform of *I(x)* yields the Raman spectrum.

$$f = 4\,(\sigma-\sigma_L)\tan\theta_L \quad (1)$$

$$I(x) = B(\sigma)\,[1+\cos\{\delta\pi\,(\sigma-\sigma_L)\tan\theta_L\}]d\sigma \quad (2)$$

Results and Discussion: Figure 2 illustrates a standoff SHRS Raman measurement of sulfur at a distance of 10 m measured using a 5.3 mJ/pulse, 20 Hz repetition rate, 532 nm laser with a 60 second exposure time. The scattered light was collected using a 10 cm diameter Cassegrain telescope that was directly coupled to the SHRS. The Figure shows the interferogram fringe image (top), the fringe image cross section (middle), and Raman spectrum of sulfur that was produced by applying a FFT to the fringe image cross section. The SHRS spectrum of sulfur has several well-known Raman features, and although no attempt was made to correct for the instrument response, the spectral features and the relative intensities match the values reported in the literature. The spectral resolution of the bands at 154 cm^{-1} and 220 cm^{-1} were ~8 cm^{-1} and ~6 cm^{-1}, respectively, close to the theoretically calculated resolution of 5 cm^{-1}.

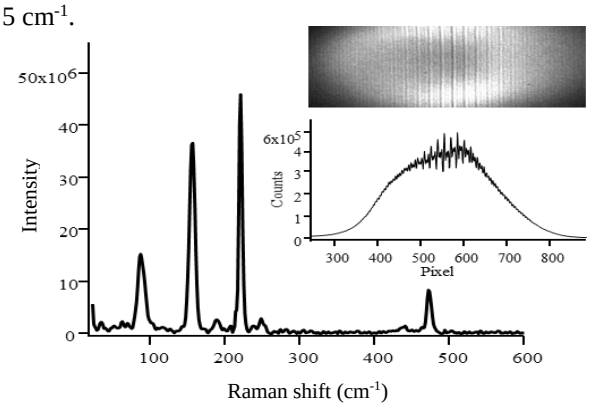

Fig. 2. Sulfur SHRS Raman spectrum showing interferogram fringe image (top inset) and intensity cross-section (middle inset), measured using a 532 nm pulsed laser and 10-cm telescope, at a sample distance of 10 m.

To assess the performance of the SHRS for standoff UV Raman measurements, several compounds were measured at ~18 m using a 266 nm pulsed laser focused to a 20-mm spot on the sample. The FOV of the SHRS was ~30 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 3 shows standoff SHRS UV Raman spectra of $KClO_3$, urea, KNO_3 and calcite, obtained using ~ 100 mW (10 mJ/pulse) on the sample, 60 second exposure time and using a 31 cm diameter Cassegrain telescope. As can be seen, all the samples exhibit characteristics Raman features with good signal to noise ratio and high spectral resolution, demonstrating the effectiveness of standoff SHRS measurement.

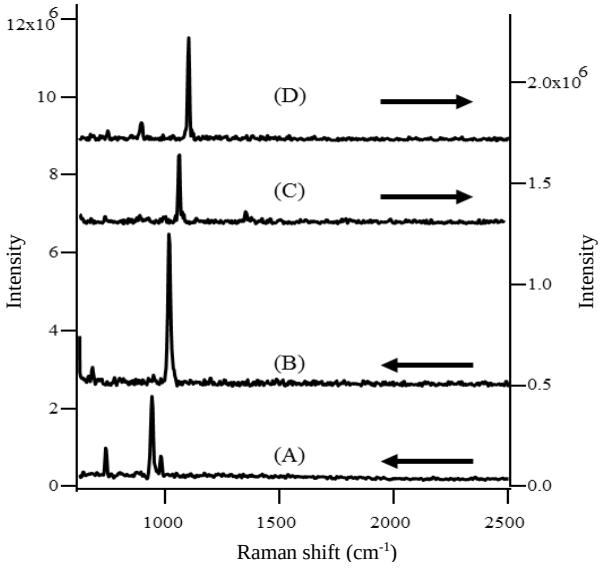

Fig. 3. UV standoff SHRS Raman spectra of (A) $KClO_3$, (B) urea, (C) KNO_3, and (D) calcite measured at ~18 m using the SHRS spectrometer with a 266 nm pulsed laser and 31-cm telescope. The arrows above each spectrum refer to the appropriate intensity axis for that spectrum. Spectra are offset vertically for clarity

Conclusion: Standoff visible and UV Raman measurements are demonstrated for the first time using a spatial heterodyne Raman spectrometer. Standoff SHRS measurements are made for a wide variety of samples using both visible and UV pulsed lasers with a gated detector, in bright ambient light conditions. UV standoff measurements are demonstrated using a large laser spot to minimize laser-induced sample degradation.

References:

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