MONOLITHIC SPATIAL HETERODYNE RAMAN SPECTROMETER: PRELIMINARY CHARACTERIZATION RESULTS. Abigail Waldron[1], Ashley Allen[1], Arelis Colón[1], J. Chance Carter[2], and S. Michael Angel[1], [1]University of South Carolina, Columbia, SC 29208, USA. (SMANGEL0@mailbox.sc.edu), [2]Lawrence Livermore National Laboratory, Livermore, CA 94550-5507, USA

Overview: Raman spectroscopy is a vibrational technique and is a good candidate for planetary exploration, because it can be used to make remote geochemical measurements and to identify organic and inorganic biomarkers of life [1]. In previous work we described a spatial heterodyne Raman spectrometer (SHRS) that is small with no moving parts, and ideally suited for planetary spacecraft and rovers. The SHRS is based on a fixed grating interferometer and has high spectral resolution and high light throughput. The resolution of the SHRS is not dependent on a slit, so miniature systems can be made without sacrificing resolution. A miniature SHRS we recently described used a cell-phone detector and imaging optics with 2.5 mm sized diffraction gratings, and the performance was compared to a standard laboratory instrument [2]. In this paper we describe an extension of this idea, using monolithic construction techniques to make a solid state SHRS (mSHRS), which is very stable and better suited to space applications. The mSHRS spectrometers are about 35x35x25mm in size, weigh about 80g, with a 3500 cm^{-1} spectral range and 4-5 or 8-9 cm^{-1} resolution, depending on the device.

Experimental: Fig. 1 shows a monolithic SHRS next to a US Quarter for scale. The mSHRS interferometer consists of two 15 mm by 15 mm diffraction gratings, a BK7 50:50 cube beam splitter, and two angled BK7 spacers, cemented together with UV cured epoxy into a solid piece. The device pictured was designed for 532nm and has ~8-9 cm^{-1} resolution with a 3500 cm^{-1} spectral range.

Results and Discussion: The basic design and operation of the SHRS has been discussed previously. In the interferometer, collimated light is passed through a 50/50 beam splitter, diving the beam into two parts which are directed onto tilted diffraction gratings. After being diffracted off the gratings, the beams recombine at the beamsplitter as crossing wave fronts. The gratings are titled at an angle, θ_L, such that a particular wavelength, the Littrow wavelength, λ_L, is retro-reflected and recombined so that no interference pattern is produced. For any wavelength other than Littrow, the crossed wave fronts will generate a fringe pattern, which is imaged onto the CCD to produce a fringe image.

Figure 2 shows Raman spectra of (a) sulfur, (b) cyclohexane, and (c) potassium perchlorate using the mSHRS pictured in Fig. 1, with 150 gr/mm gratings and a Littrow wavelength of 531.6 nm. The inserts in Figure 2 show the Raman interferograms (fringe image cross sections) for each spectrum.

The FWHM of the 219 cm^{-1} sulfur band is 8 cm^{-1}, twice the theoretical resolution of 4 cm^{-1}, likely due to improper optical alignment or input collimation. The 2850 cm^{-1} and 2930 cm^{-1} cyclohexane bands are shown. The spectral range was determined to be >3500 cm^{-1}.

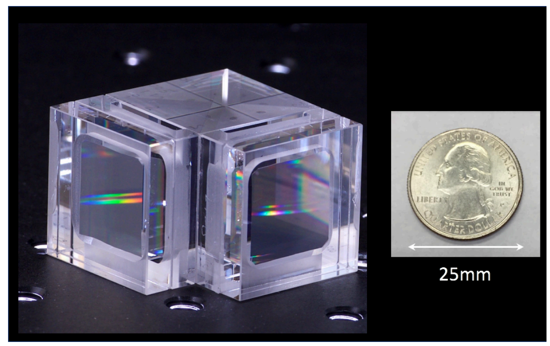

Fig 1. Monolithic spatial heterodyne Raman spectrometer compared to the size of a US Quarter.

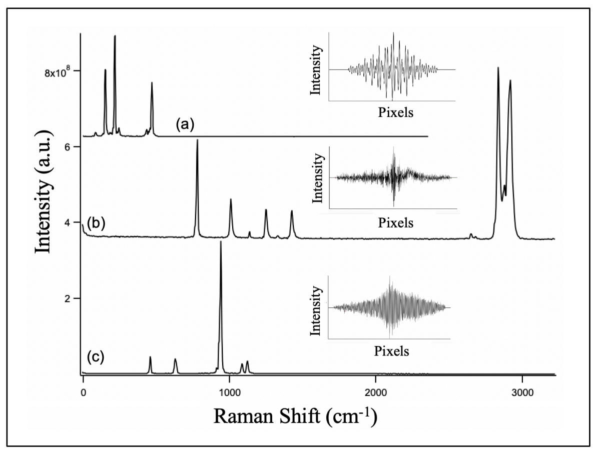

Fig 2. Raman spectra of (a) sulfur, (b) cyclohexane, and (c) potassium perchlorate with the mSHRS. The inserts show the cross section for each spectra.

Figure 3 shows Raman spectra of sulfur collected with (a) a Horiba LabRam micro-Raman with an 1800 gr/mm grating, and (b) a 2D mSHRS with 600 gr/mm gratings and 541.05 nm Littrow wavelength (314 cm^{-1}). The 2D mSHRS shows Raman bands both above and below Littrow, thus doubling the spectral range. The FWHM of the 219 cm^{-1} band for the micro Raman was ~8 cm^{-1}, and ~4.5 cm^{-1} for the mSHRS.

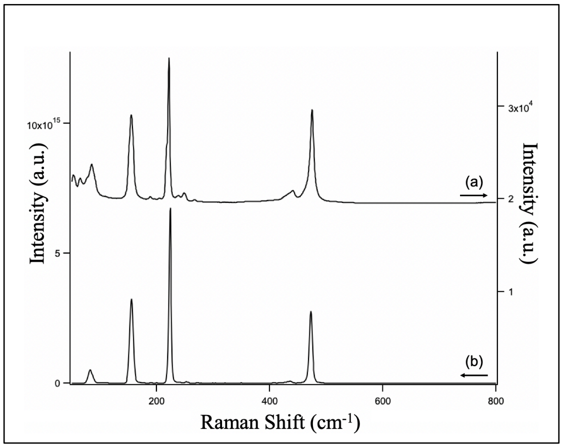

Fig 3. Raman spectra of sulfur using (a) LabRAM micro Raman with 1800 gr/mm grating, and (b) 2D mSHRS with 15mm, 600 gr/mm gratings.

The stability of the mSHRS was compared to that of a free standing SHRS instrument by tracking changes in wavelength calibration over a 10 day period. While both instruments had similar FWHM of 8-9 cm^{-1}, the mSHRS had a higher short term signal to noise ratio (SNR), nearly double the free standing SHRS. In the 10-day study, it was found that the calibration of the free standing SHRS varied a few wavenumbers from day to day, while the mSHRS calibration was stable over the entire 10 day measurement period, within the error of the calibration procedure.

We also tested the mSHRS for remote Raman measurements with samples at a distance of ~5m. In these measurements no collection optics were used. Instead, Raman scattered light was collected using only the mSHRS 15-mm gratings. At this distance, the collection solid angle of the mSHRS is $9x10^{-6}$ sr, so relatively high laser power, 500 mW at 532 nm, was used to compensate, with a 300 sec exposure time. Fig. 4 shows remote Raman spectra of (a) potassium perchlorate, (b) barite, and (c) acetaminophen measured in this way with the 150 gr/mm mSHRS. The SNR is relatively poor, not surprising considering the small collection optic. However, this does suggest the possibility of building extremely small remote Raman spectrometers for use in small spacecraft of the types that might be used for landers on the outer planets or comets.

In regard to designing an instrument that might be used for missions to the Jovian planetary systems, where radiation levels are high, it would be useful to design the system in such a way that the CCD detector can be shielded. With this in mind we added a fiber optic image guide to the output of one of the mSHRS spectrometers, to allow the CCD to be located at a remote distance from the spectrometer. This is shown schematically in Fig. 5 (top). Light from the mSHRS is imaged first onto a flexible fiber optic image guide that is made of many thousands of 10 µm fibers. The fiber transmits the Raman fringe image with good fidelity to the distal end where it is reimaged onto the remotely located CCD. Fig. 5 shows the Raman fringe image from the mSHRS with and without the fiber image guide, and example spectra of ethanol with and without the fiber image guide.

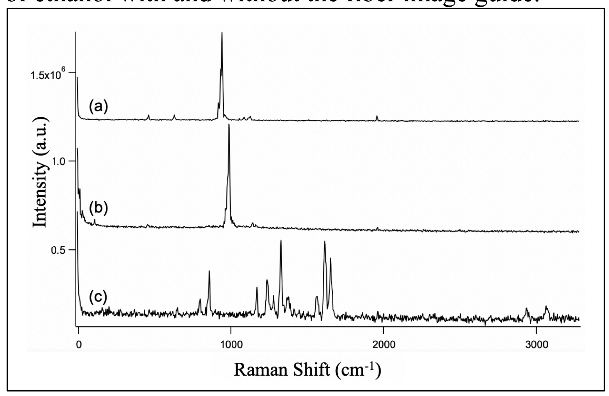

Fig. 4 Remote Raman spectra at ~5 m: (a) $KClO_4$, (b) $BaSO_4$, and (c) acetaminophen using a mSHRS.

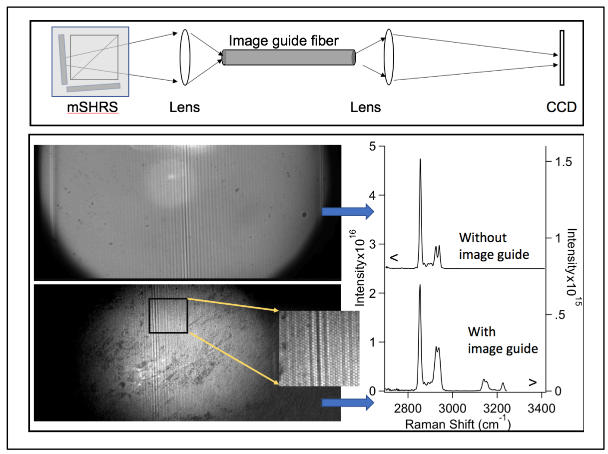

Fig. 5. mSHRS (150 gr/mm, 616.5 nm λ_L) with image guide to take the output to a remotely located CCD.

Conclusion: Monolithic spatial heterodyne Raman spectrometers of about 35x35x25mm in size, weighing ~80g, with >3500 cm^{-1} spectral range and up to 4-5 resolution are described.

Acknowledgments: Funding provided by NASA [grant 80NSSC19K1024] and the National Science Foundation [grant OCE-1829333].

References: [1] Angel S. M. et al., *Appl. Spectrosc., 66,* 137-150 (2012). [2] Barnett P. et al., *Appl Spectrosc.*, *71*, 988-985 (2017).