HALF-INCH MONOLITHIC SPATIAL HETERODYNE RAMAN SPECTROMETER – A POLARIZATION STUDY AND POTENTIAL TOOL FOR PLANETARY EXPLORATION

E. M. Kelly[1], M. J. Egan[1], A. Colon[2], S. M. Angel[2], and S. K. Sharma[2], [1] Hawaii Institute of Geophysics and Planetology, University of Hawai'i at Manoā, Honolulu, Hawai'i, [2] Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina. Correspondence email: evamk@hawaiil.edu

Introduction: Raman spectroscopy allows for the unambiguous identification of compounds and, with the recent improvement in such Raman technology, has been implemented on the Perseverance Rover in a remote capacity.[1] A dispersive spectrometer was utilized due to the device's lack of moving parts. However, these devices fall victim to highly sensitive alignments, limited spectral ranges, limited resolutions in smaller devices, and limited light throughput due to their entrance slits. A spatial heterodyne Raman spectrometer (SHRS), which is a fixed grating interferometer, helps overcome some of these problems by combining an interferometer with a dispersive spectrometer. Recently, we described a monolithic 2-gratings SHRS [2], 1 grating SHRS (1g-SHRS) [3], and a 1-grating monolithic SHRS [4] with the 1g-SHRS consisting of one mirror and one grating. In this paper we test a smaller 2-grating monolithic SHRS (½ inch 2g-mSHRS) to determine its instrumental properties as well as perform the first polarization study of organic liquids using a monolithic SHRS.

Experimental: To test the ½ inch 2g-mSHRS device, spectra were collected using a 532 nm pulsed Nd:YAG laser to illuminate a liquid sample. A 2.54 cm collimating lens was used to collimate the light after striking the sample before being collected by a reversed beam expander to shrink the light down to a size that would fit the size of the small SHRS, where it would recombine. This was done due to too much light being lost around the ½ inch monolith reducing the signal to an untenable level. The recombined light was then sent through a collecting lens to an intensity charged-coupled device (ICCD) camera which is displayed in Figure 1. The data collected with ½ inch 2g-mSHRS on organic liquids C_6H_{12}, C_6H_6, CH_3CN, CCl_4, and CH_3OH were then processed using a Fast Fourier transform. To deal with noise, an advanced data processing technique, which was first described by M. J. Egan, was used. [5] A 532 nm long pass (LP) filter was used to block all light below 532 nm while a depolarizer filter was used to eliminate the effect of the grating. A cross-polarizer was used to allow either perpendicular or parallel light into the monolith. It should be noted that the laser used emitted light that was horizontally polarized (in relation to the ground).

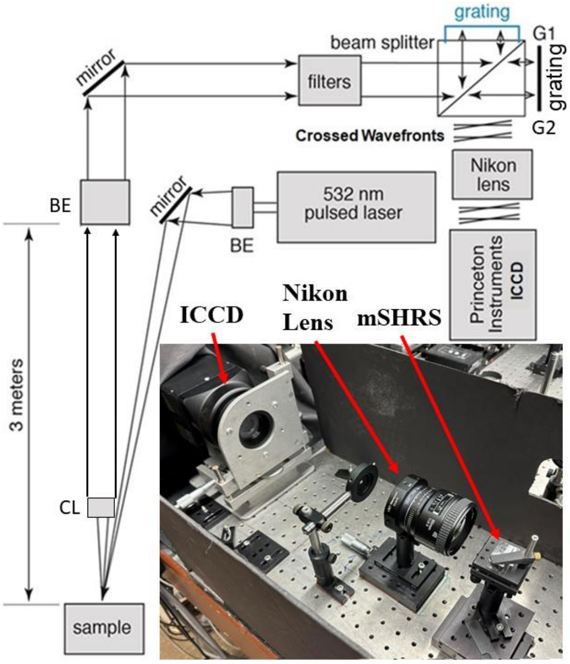

Figure 1: Schematic diagram and image for the half-inch 2g-mSHRS. BE stands for beam expander while CL stands for collimating lens

Results & Discussion: Figure 2 illustrates the time-resolved Raman spectra for cyclohexane (C_6H_{12}) with both the parallel polarized and perpendicularly polarized light displayed for comparison. While the intensities look vastly different, this is a mere scaling effect, with the perpendicular spectrum zoomed in on 1028, 1266, and 1444 cm^{-1} Raman shifts. When the intensities of the 1266 cm^{-1} Raman shifts are compared, they give intensity values of 3642996 and 3814535 for perpendicular and parallel, respectively (or parallel having ~ 5 % higher intensity). When the depolarization ratio of the 801 cm^{-1} band was calculated to have a value of 0.054 which falls in between previously calculated values of 0.06 and 0.04 [6,7]. Similarly, the depolarization ratios of benzene's (C_6H_6) 992 cm^{-1} Raman shifts gave a depolarization ratio of 0.019 which matches with the previously measured depolarization ratio of 0.02. [8]

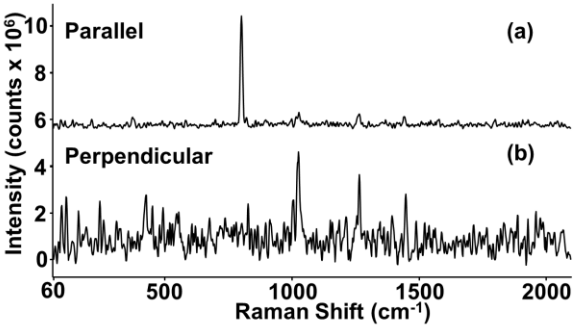

Figure 2: Raman spectra of the cyclohexane measured with the mSHRS at 3 m distance with the crossed polarized and parallel polarized spectra. The spectra were acquired in 1 accumulation with an accumulation time of 120s for each.

In terms of comparison to other mSHRS mentioned in the introduction, the resolving power of the ½-inch 2g-mSHRS was the smallest due to the small grating size but achieved the highest experimental resolution (MRF), when compared to the normal 1-inch 2g-mSHRS and the 1g-mSHRS. The higher resolution was mainly due to the groove density being twice as high as either of the other instruments. In terms of the spectral range the ½-inch 2g-mSHRS the experimental spectral range technically would be double (6505 cm^{-1}) what it is reported in Table 1, which would give it the 2nd largest spectral range out of the series. However, the spectral range is centered on the Littrow wavelength which was 534 nm for the monolith tested. This in combination with the 523 nm LP filter meant that about half of the spectral range (below 532 nm) was cut off and not utilized. The 1g-mSHRS on the other hand had a Littrow wavelength at a higher wavelength pointing to this being able to access much more spectral range below its Littrow wavelength of 595 nm.

Table 1: Contains the experimental values for the two-gratings monolithic SHRS (2g-mSHS), one-grating monolithic SHRS (1g-mSHRS), and half-inch monolith-SHRS (2g-mSHS (1/2 inch)) instrument for comparison. MRF stands for the minimum resolvable feature.

instrument	Resolving Power	Theoretical Resolution (cm^{-1})	MRF (cm^{-1})	Spectral Range (cm^{-1})	Grating Size (mm)	Groove Density (l/mm)
2g-mSHRS (½ inch)	2349	3.48	8	3252	9	300
1g-mSHRS	2376	7.9	9.1	7327	15	150
2g-mSHRS	4752	3.9	9	3500	15	150

With the adjustment of the Littrow wavelength to a higher wavelength, the ½-inch 2g-mSHRS would be an extremely valuable instrument that could be used to unambiguously identify compounds on planetary exploration missions without costing too much money to produce, with the monolith itself being 2.2 x 2.2 x 1.3 cm and weighing less than 60 g. This lightweight and robust nature due to the monolithic construction, along with the improved spectral range and tunable resolution could allow for multiple mSHS systems to be implemented on a single rover with each optimized for different forms of spectrometry (e. g. UV, VIS, IRS, & LIBS). Additionally, the nature of this device allows for implementation on aerial vehicles which are sent to other planets. The success of the Ingenuity helicopter on the Mars 2020 Mission further expands on the utility of the mSHS and shows potential for utilization on projects like NASA's 2027 Dragonfly mission to Titan.[9]

Conclusions: This setup implements a much smaller mSHRS compared to the previously tested monoliths which had sizes of 35 x 35 x 25 mm and a weight of 80 g. This reduces the footprint of the device (22 x 22 x 13 mm with a weight of < 60 g) without compromising the instrument's performance. This instrument provides a high spectral resolution (~8 cm-1) and large spectral range (3252 cm-1) while having a low sensitivity to alignment with a field of view of 4.98 mm at 3m. In conclusion, the ½-inch 2g-mSHRS combines the benefits of both dispersive and FT Raman spectroscopy and miniaturized previous mSHRS to create a robust, lightweight system with a small footprint, high resolution, high light throughput, high SNR, large spectral range, and with no moving parts making it a good candidate for planetary exploration.

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References: [1] *Wiens, R. C. et al. (2020) Space Science Reviews, 217 (1), 4.* [2] Waldron, A. (2020) *Applied Spectroscopy*, 75 (1), 57-69. [3] Egan, M. J. (2020) *Journal of Raman Spectroscopy*, 51 (9), 1794-1801 [4] *Kelly E.M. et al. (2022) Applied Spectroscopy, 0 (0)* [5] *Egan, M. J. (2018) Applied Spectroscopy, 72 (6), 933-942* [6] *Kielich, S. (1967) Physics Letters A, 25 (2), 153-154* [7] *Snyder, R. G. (1970) Journal of Molecular Spectroscopy, 36 (2), 204-221* [8] *Douglas, A. E. & Rank, D. H. (1948) Journal of the Optical Society America, 38 (3), 281-287* [9] Lorenz, R. D. et al. (2021) *The Planetary Science Journal*, 2 (1), 24.