Monolithic Spatial Heterodyne Raman Spectrometer : Preliminary Characterization

Abigail Waldron[1], Ashley Allen[1], Arelis Colón[1], J. Chance Carter[2], and S. Michael Angel[1]

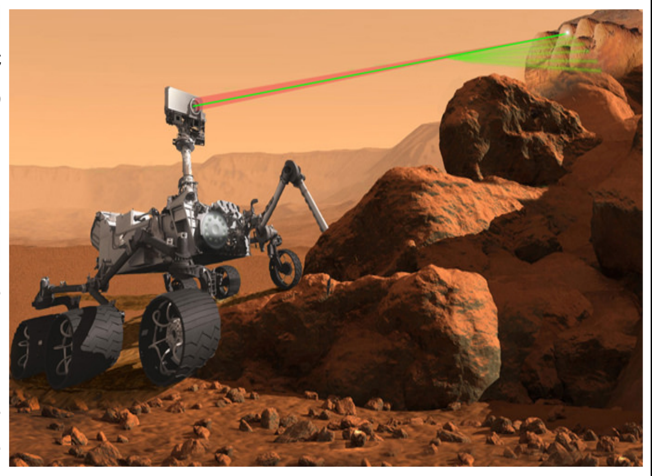
[1]*Department of Chemistry and Biochemistry, The University of South Carolina, Columbia, SC 29208,* [2]*Lawrence Livermore National Laboratory, Livermore, CA 94550-5507, USA*

Abstract

A monolithic spatial heterodyne Raman spectrometer (mSHRS) is described, where the optical components of the spectrometer are bonded to make a solid, one-piece structure, which is small, compact and stable. The SHRS is based on the spatial heterodyne spectrometer (SHS) which is a fixed grating interferometer that offers high spectral resolution and high light throughput in a small footprint. The resolution of the SHS is not dependent on a slit, and high resolution can be realized without a long optical path since it is not a dispersive device. Thus, the SHS can be used to make a very small Raman spectrometer with high spectral resolution and a large spectral range. This can be extended to the smallest possible footprint, for a given size diffraction grating, by building the SHRS using monolithic construction techniques. Here, we present two different mSHRS spectrometers, each about 3.5 x 3.5 x 2.5 cm in size and weighing about 80g, providing ~3500 cm^{-1} spectral range with 4-5 cm^{-1} and 8-9 cm^{-1} resolution, for 600 grooves/mm and 150 grooves/mm grating based devices, respectively. We present the stability, spectral resolution, spectral range, and signal to noise ratio of the mSHRS spectrometers as compared to our bench top SHRS that uses free standing optics, and signal to noise comparisons are also made to a Kaiser Holospec based Raman spectrometer.

Raman Spectroscopy is Ideal for Planetary Exploration

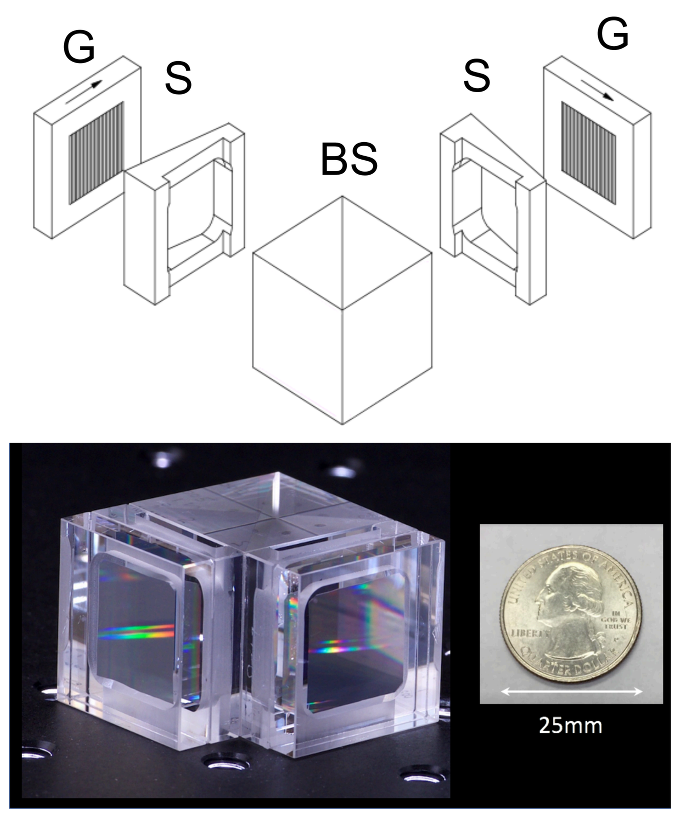
- Raman spectra provide detailed molecular and structural information for organic and inorganic molecules and minerals, and is uniquely suited to the search for chemical indicators of life.
- Raman spectra are information-rich, containing information about crystal structures, mineral polymorphism, hydration states, solvation, and the state of water (liquid or ice).
- Raman spectra of minerals on planetary surfaces can be acquired without sample contact or sample preparation (i.e., for in-situ and remote analysis).
- Remote, standoff Raman spectroscopy greatly extends the area that can be measured around a planetary rover.



NASA has selected a Raman spectrometer as part of SuperCam, one of the major instruments on a planned Mars lander mission, Mars 2020.

Monolithic Spatial Heterodyne Raman Spectrometer

- The SHRS is small and compact with no moving parts. It has a high optical throughput.[1,2]
- The SHRS has a high spectral resolution and a large spectral range.[1,2]
- The SHRS has a very high light throughput because of a wide field of view and large entrance aperture.[1,2]
- The SHRS is compatible with pulsed lasers and gated detector, necessary for daylight measurements. It is also compatible with deep UV excitation.[3,4]
- The SHRS has been shown to have imaging abilities in both 1D and 2D spectral imaging.[5]
- The resolution is dependent on the number of grooves illuminated allowing for miniaturization while maintaining high spectral resolution.[6]



Above: (Top) A monolithic spatial heterodyne Raman spectrometer (mSHRS). BS = beam splitter, S = spacers, G = diffraction gratings. (Bottom) A mSHRS compared to a US quarter

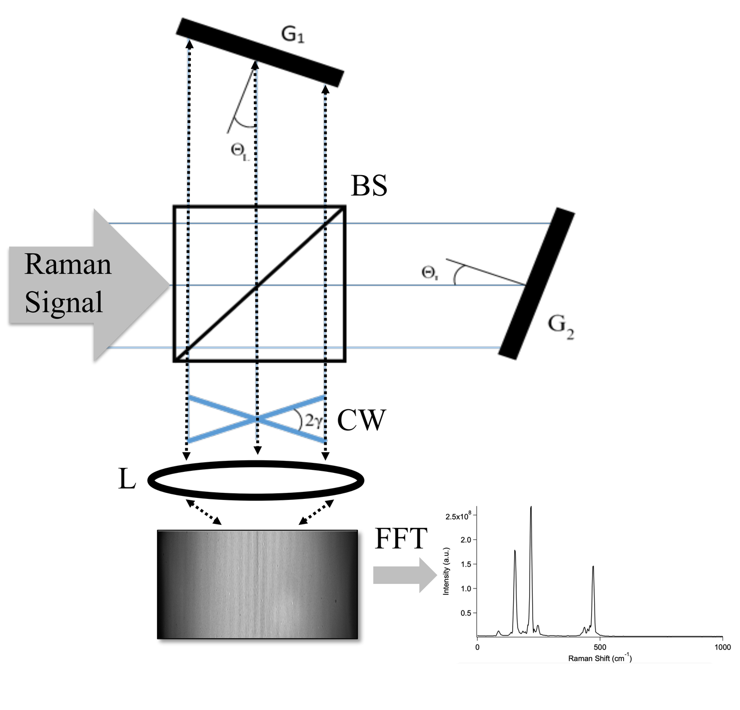
Spatial Heterodyne Raman Spectrometer: Design and Set Up

- The SHRS is an FT-Raman spectrometer that uses stationary diffraction gratings to produce an interferogram directly on a detection camera.
- Light that enters the SHRS is heterodyned at the Littrow wavelength, determined by the grating angle, θ_L. Light at the Littrow wavelength retro-reflects with 0° crossing angle.[2]
- For Raman scattered light at wavenumber σ_R, diffraction leads to crossed wavefronts that produce interference fringes when imaged onto the detector (shown at right). The frequency of the fringe pattern is given by:

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

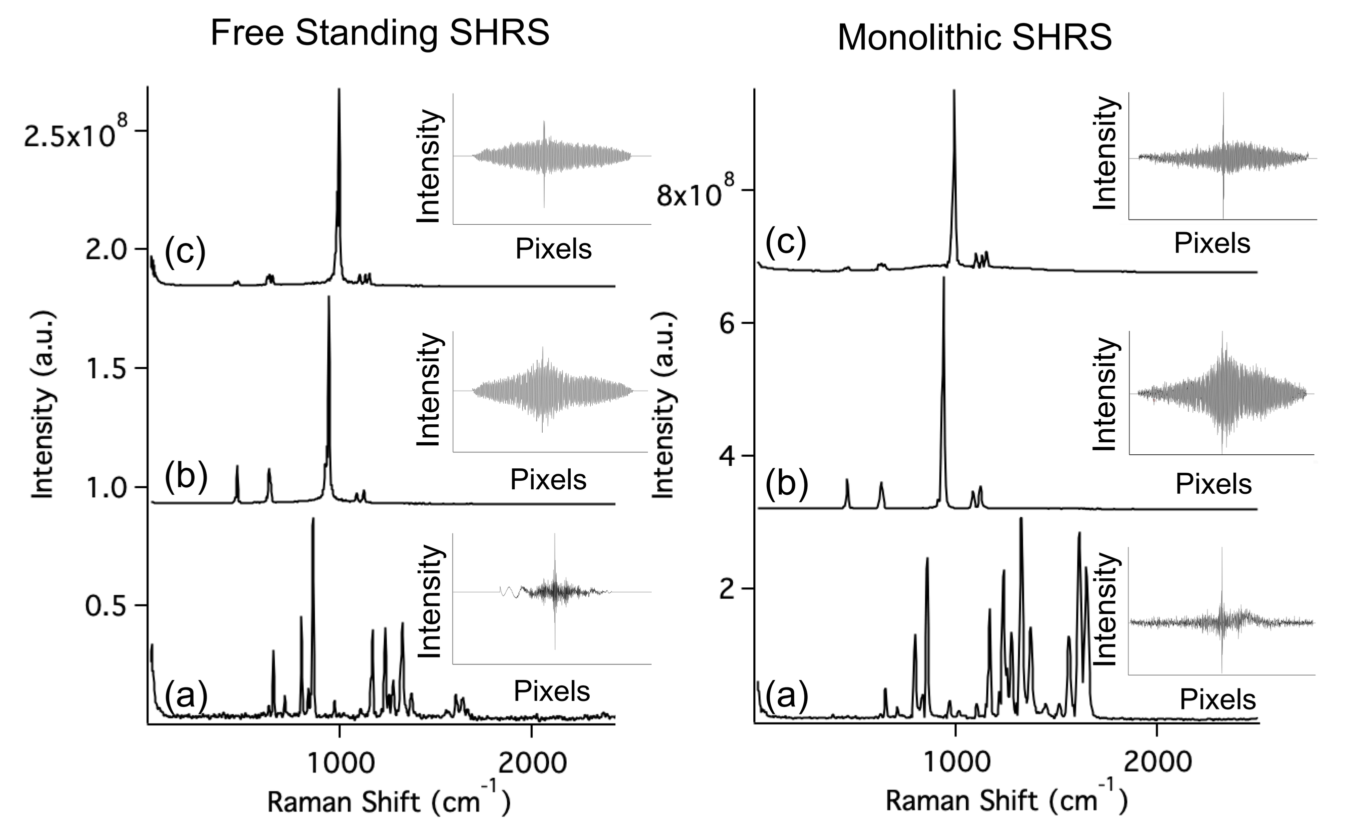
where f is in fringes/cm.[2]

- The Raman spectrum is the Fourier transform of the interference pattern (shown at right).



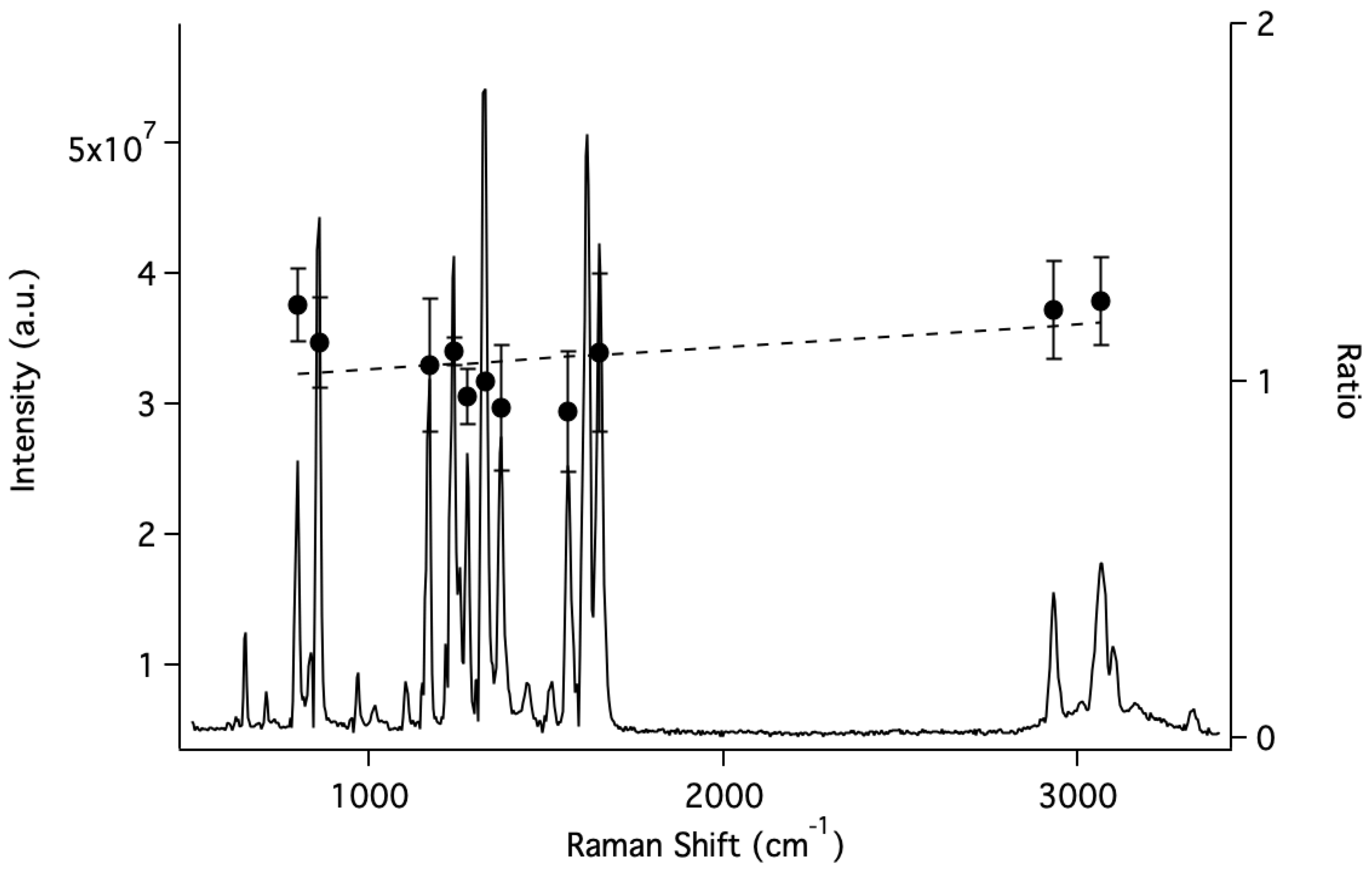
Above: The design of the mSHRS. G = grating, CW = crossing wavefront, BS = beamsplitter, Θ_L = Littrow angle, L = lens, FFT = fast Fourier transform.

The mSHRS Shows Improvements as Compared to a Free Standing SHRS



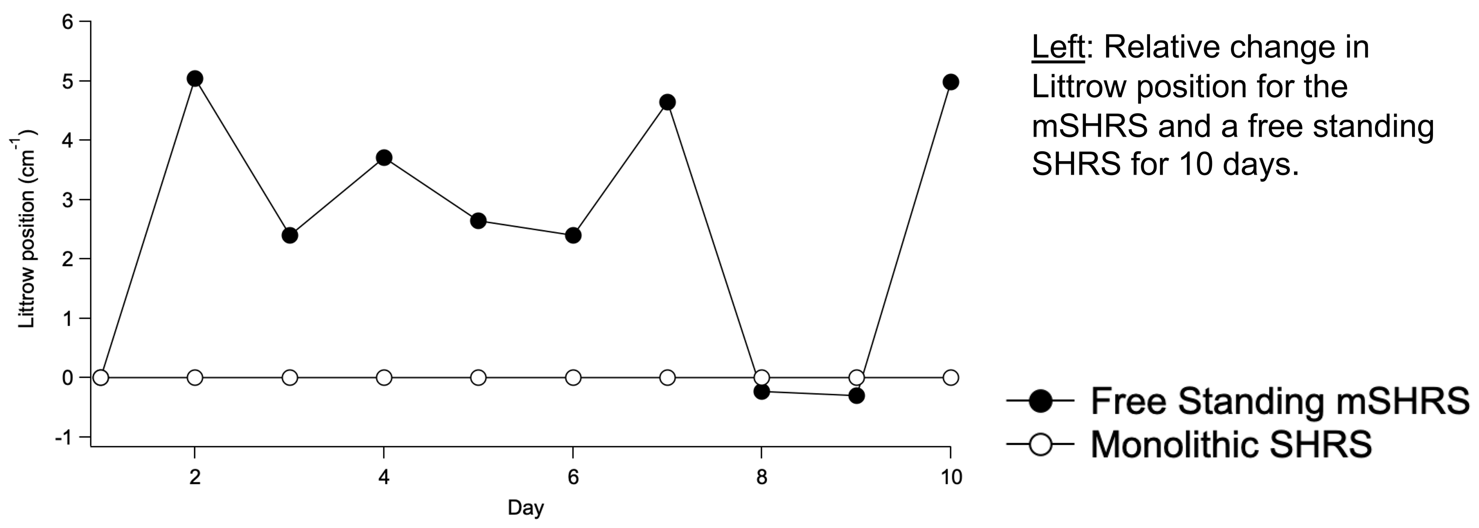
Above: Remote Raman spectra of (a) acetaminophen, (b) potassium perchlorate, (c) sodium sulfate measured with a free standing bench top SHRS (left) and a mSHRS (531.6 nm Littrow, 150 gr/mm) (right).

Instrument Response Function of the mSHRS



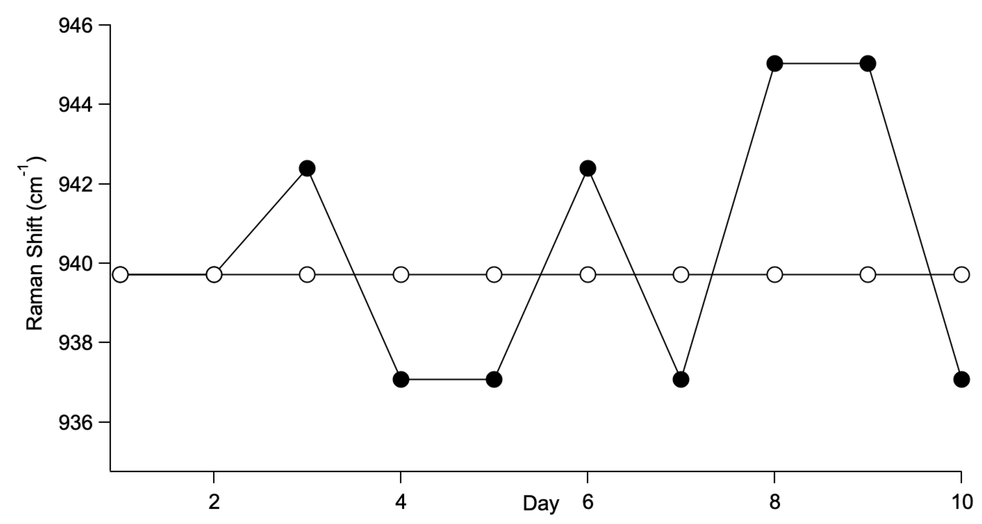
Above: Raman spectrum of acetaminophen measured with a mSHRS (531.6 nm, 150 gr/mm) overlaid with the ratio of standard relative intensity of the Raman shift to the measured relative intensity. The dashed line is the estimated instrument response for the mSHRS based on the calculated ratios.

Stability of a mSHRS vs. a Free Standing SHRS



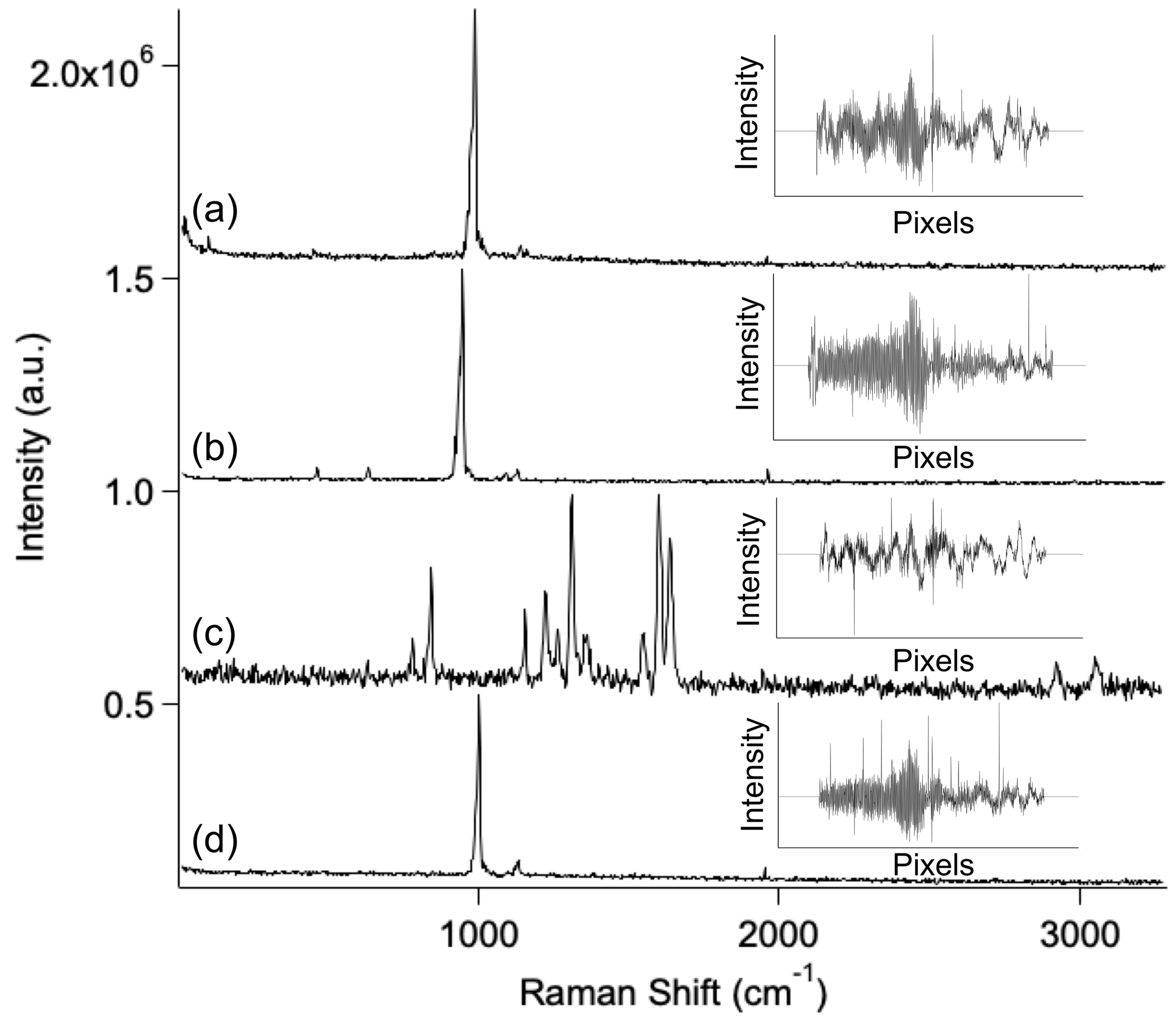
Left: Relative change in Littrow position for the mSHRS and a free standing SHRS for 10 days.

Right: Change in the peak position of potassium perchlorate based on



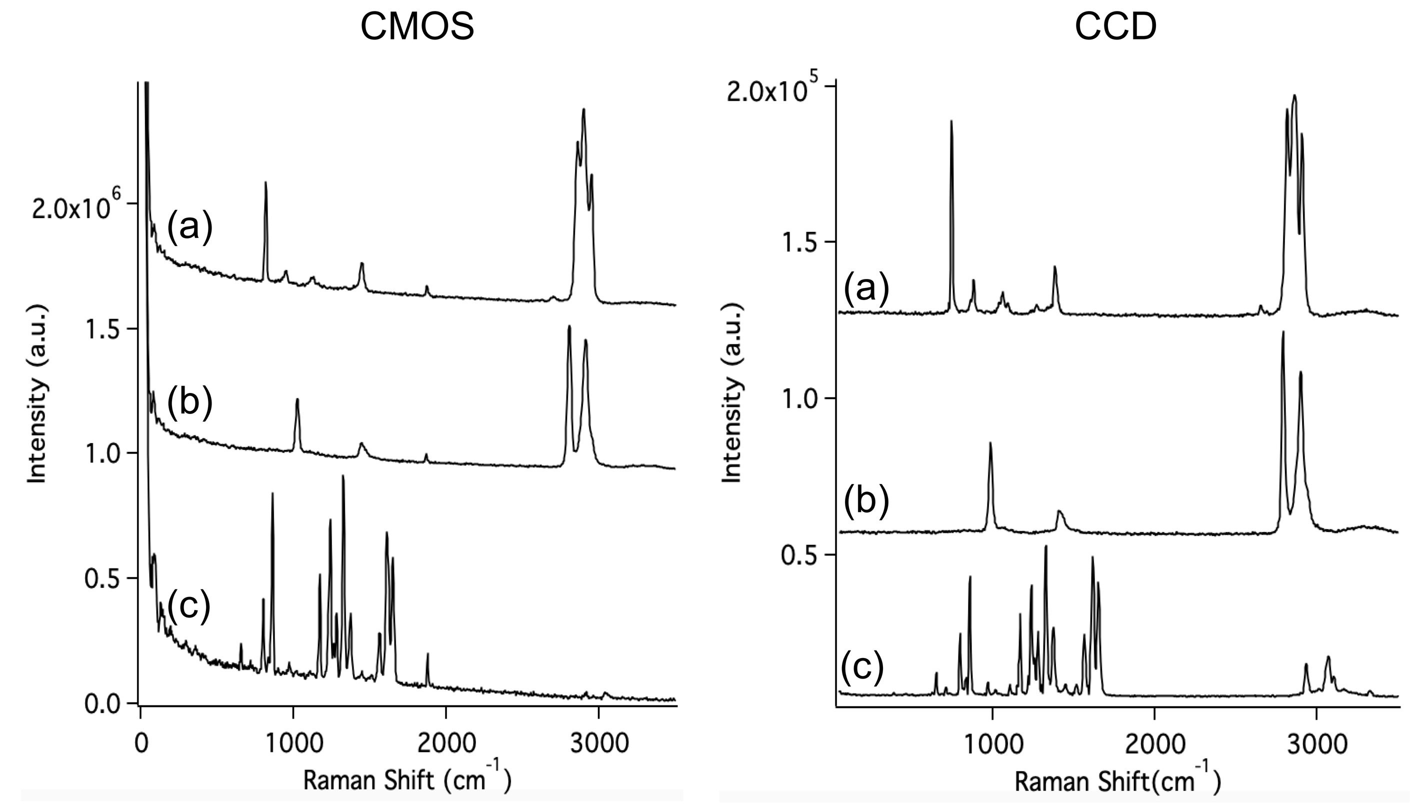
The stability of the monolithic SHRS was compared to that of a free standing bench top SHRS. A spectrum of potassium perchlorate was measured every day for 10 days. The change in Littrow and the peak position of the 941 cm^{-1} shift was graphed over 10 days for both instruments. The free standing SHRS shows a slight change in calibration, while the mSHRS does not, showing an improved stability over the free standing SHRS.

Remote Raman Spectra with mSHRS



Above: Remote Raman spectra of (a) barite, (b) potassium perchlorate, (c) acetaminophen, and (d) gypsum measured at 5.13 m with a mSHRS (531.6 nm Littrow, 150 gr/mm). All spectra were measured with a 30 s exposure time, 530 mW of laser power., and no collection optics other than the 15 mm grating face. The cross sections for each spectra are shown as inserts.

Comparing detectors: CMOS vs CCD



Above: Raman spectra of (a) isopropanol, (b) methanol, (c) acetaminophen, measured with a complementary metal-oxide-semiconductor (CMOS) (left) and a charged coupled device (CCD) (right).

Conclusions

- We have developed a monolithic spatial heterodyne Raman spectrometer with a large spectral range and high resolution
- We have shown improvements over a free standing bench top spatial heterodyne Raman spectrometer in terms of signal to noise, instrument response function, and stability
- We have demonstrated improved signal to noise over a conventional dispersive Raman spectrometer.
- We showed remote Raman data at 5.13 m with the mSHRS

Acknowledgments

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References

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