

**TWO HIGH PERFORMANCE *In Situ* RAMAN SPECTROMETERS FOR LANDED PLANETARY MISSIONS.** Alian Wang<sup>1</sup>, James Lambert<sup>2</sup>, Ian Hutchinson<sup>3</sup>, Steve Monacos<sup>2</sup>, Melissa McHugh<sup>3</sup>, J. Wei<sup>1</sup>, Y.C. Yan<sup>1</sup>. <sup>1</sup>Dept. Earth and Planetary Sciences and McDonnell Center for Space Sciences, Washington University in St. Louis, <sup>2</sup>Jet Propulsion Laboratory, <sup>3</sup>University of Leicester, UK ([alianw@levee.wustl.edu](mailto:alianw@levee.wustl.edu)).



Fig.1 MMRS on Zoe rover in Atacama (TRL5)

Supported by PIDDP, MIDP, ASTEP, and recently by MatISSE program, we have accomplished the design, building, and testing two high performance *in situ* Raman spectrometers: the Mars Microbeam Raman Spectrometer (MMRS) and the Compact Integrated Raman Spectrometer (CIRS).

MMRS (Fig. 1) has a separate Raman probe connected through optical fiber to Raman spectrometer [1-3]. MMRS was tested during three field seasons (2012-2015) in Atacama Desert, twice on Zoe rover (> 50 km traverse each time) and once stand-alone. These field studies demonstrated a solid science performance and robust engineering of MMRS (TRL 5). A new paper was published in 2015[4].

CIRS (Fig. 2) was developed on the basis of mature MMRS technology but having an all-optics-in-one architecture (i.e., without optical fiber). The development of CIRS was supported by MatISSE program, with a goal to reach TRL 6 [5, 6]. Currently, a prototype of CIRS was built and tested. We will report here the results from a set of performance tests accomplished in August 2016.

**MISSIONS:** Both MMRS & CIRS are suitable for *definitive molecular identification* during landed planetary missions. The detailed requirements of a specific mission will determine the selection among the two.

A few common features of MMRS & CIRS are:

- (1) both have wide spectral range and necessary spectral resolution to achieve the goal of comprehensive molecular ID;
- (2) both are highly sensitive, capable of obtaining a spectrum from a solid sample within <1s to 1min;
- (3). both allow the laser excitation and Raman photon collection through an optically transparent window

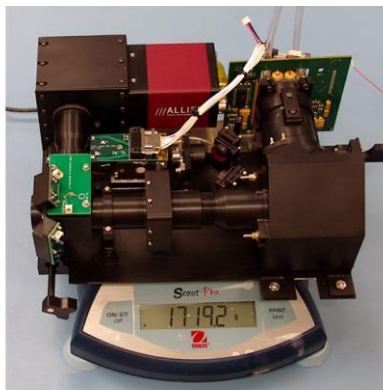


Fig. 2. CIRS prototype (to TRL6)

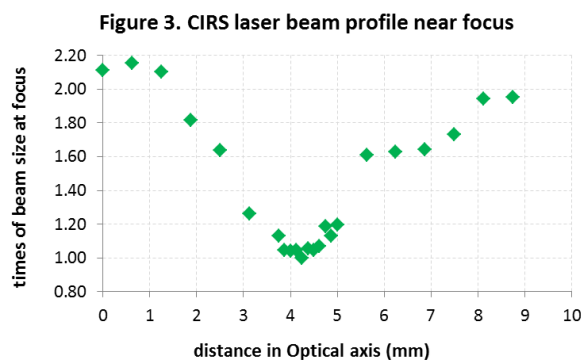
(fused silica or sapphire), thus supporting simple deployments on a Venus lander or on an ISRU platform of a lunar mission, in addition to the direct arm-deployment by a rover on Mars.

### CIRS performance

The Raman spectral range of CIRS is 4432 - 183  $\text{cm}^{-1}$ , with a spectral resolution  $\sim 9 \text{ cm}^{-1}$ .

CIRS has a context imager, illuminated by a set of UV LED (275 nm) and blue LED (467 nm). It has a Field of View (FOV)  $\sim 37 \times 26 \text{ mm}$  and a chip format of 1600x1200 pixels. The laser spot and the context image of the sample are seen in the same image.

A recent test revealed that CIRS laser beam diameter at focus is 35.7  $\mu\text{m}$ . It has a slow-growing beam profile, that only double its diameter at  $\pm 4.5 \text{ mm}$  from the focus, Fig. 3. With this beam profile, the measured *Raman sampling depth* (i.e., the off-focus Raman measurement with recognizable peaks) is > 9.375 mm from a quartz at 8s integration, and  $\sim 3.125 \text{ mm}$  from a dark pyroxene at 64s integration (Fig. 4).



The small diameter of laser beam is designed to detect minor and trace species in a geological sample (rock or soil). The slow-growing beam profile is designed to tolerant the surface roughness of an unprepared geological sample during a robotic exploration.

The optical throughput of CIRS is about 90% in excitation path and about 20% in collection path. It enables the mineral spectrum with good S/N to be obtained in less than 1s for strong Raman scatterers, or

maximum near 1 min for weak Raman scatterers, **Figure 5**. Reduced carbon in chert with  $\text{TOC}@8 \times 10^{-4}$  was detected by CIRS from a 4s integration.

Through a study of nearly 30 extraterrestrial samples (lunar, martian, and other meteorites) using fluorescence microscopy and Raman spectroscopy [7, 8] we have demonstrated that fluorescence emission from these materials are low-to-non-existence. Thus, fluorescence is not a threat to planetary Raman spectroscopy using CW 532 nm excitation. For its occasional occurrence, our solution is to conduct SERDS (Shifted Excitation Raman Differentiate Spectroscopy) without changing any hardware in CIRS [8].

The realization of SERDS in CIRS is by adjusting the excitation wavelength of its CW laser source. We have found a  $15 \text{ cm}^{-1}$  shift can be produced by  $12^\circ\text{C}$  temperature adjustment of the frequency-doubling crystal of the CIRS laser unit, as shown in **Fig 6**. This shift is enough to distinguish Raman peak from fluorescence signals, **Fig. 7**.

#### Comparison with other Raman architectures:

Comparing with *a remote-Raman architecture*, an *in situ* Raman has:

- (1) A capability of detect minor and trace species, due to the small sampling spot ( $20\text{-}30 \mu\text{m}$  vs.  $500\text{-}1000 \mu\text{m}$ );
- (2) A much higher ( $10^2$  to  $10^4$  times) Raman signal collectivity, using a  $f/2$  optics vs.  $f/20$  to  $f/100$  optics;
- (3) A lower risk of sample damage (cw laser vs. pulse laser).

Comparing with *a pulse UV- Raman architecture*, the CW green Raman has:

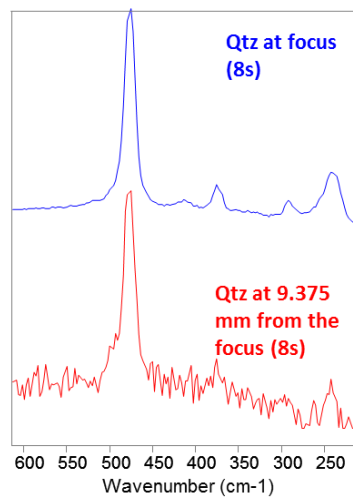
- (1) > two orders of magnitude stronger Raman signal on minerals [5], and on reduced carbon and biomarkers [9, 10];
- (2). A lower risk for sample damage.

In the aspect of engineering, MMRS & CIRS use ordinary CCD, optics and filters for visible light, and a mature compact CW 532nm laser. They have higher TRL (in both component levels and in system level) than other Raman architectures.

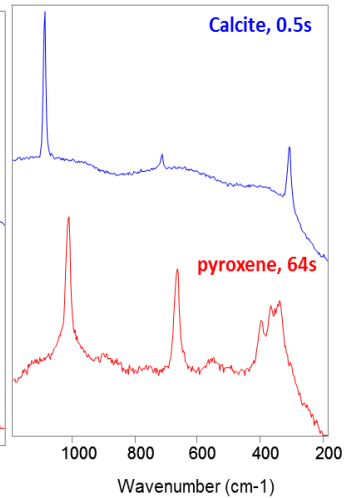
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**References:** [1] Wang et al., 1995, JGR, 100, 21189-21199; [2] Wang et al., 1998, Appl. Spec, 52, 477-487; [3] Wang et al., 2003, JGR, doi:10.1029/2002JE001902; [4] Wei et al., 2015, J.

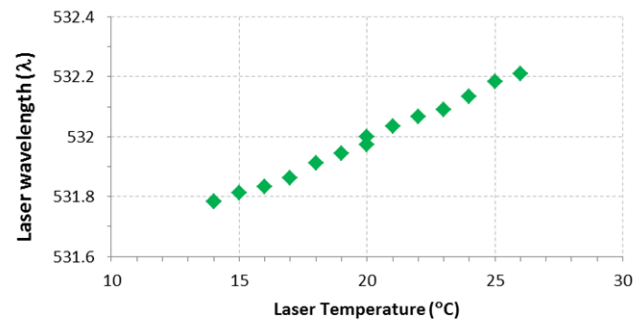
**Figure 4. Test of Raman Sampling depth (raw spectra)**



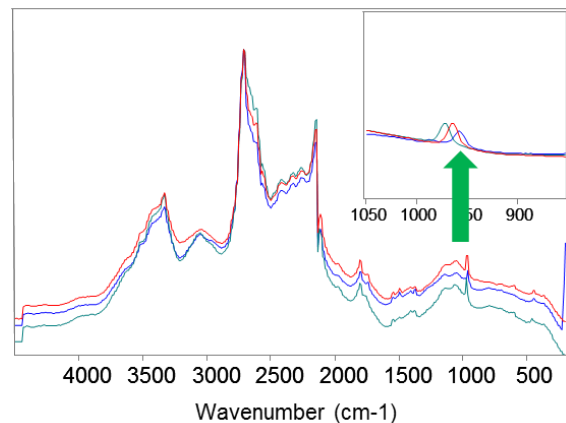
**Figure 5. Raw CIRS spectra of strong and weak Raman scatterers**



**Figure 6. Laser wavelength shift as  $f(T)$**



**Figure 7. To distinguish Raman peak of apatite from REE fluorescence using SERDS**



Raman Spec., v10., DOI: 10.1002/jrs.4656; [5] Wang et al., 2014, abs. 1090, 2<sup>nd</sup> IPM; [6] Lambert et al., 2014, abs 1136, 2<sup>nd</sup> IPM; [7] Wei et al., 2014, abs 1112, 2<sup>nd</sup> IPM; [8] Yan et al., 2016, abs2210, 47<sup>th</sup> LPSC; [9] Wei et al., 2014 LPSC, abs # 2847. [10] Beegle et al., 2014, LPSC, abs# 2835.