PROGRAMMABLE RAMAN SENSING FOR *IN-SITU* PLANETARY EXPLORATION. P. Sobron,[1,2] L. Barge,[3] A. Davila,[4] M. Fahey,[5] M. Krainak,[5] F. Rehnmark,[6] A. Yu,[5] K. Zacny.[6] [1]Impossible Sensing, St. Louis, MO. [2]SETI Institute, Mountain View, CA (psobron@seti.org). [3]NASA Jet Propulsion Laboratory, Pasadena, CA. [4]NASA Ames Research Center, Mountain View, CA. [5]NASA Goddard Space Flight Center, Greenbelt, MD. [6]Honeybee Robotics, Pasadena, CA.

Planetary Raman Spectroscopy: The science value of *in-situ* Raman spectroscopy is widely recognized within the planetary science community: a) two Raman instruments (SHERLOC and SuperCam) will fly on NASA's Mars 2020 mission; b) ESA's 2020 ExoMars rover features one Raman instrument (RLS). Like most research and commercial Raman spectrometers, these Mars flight Raman instruments feature lasers, dispersing optics, and CCD array detectors. Such a combination is ideal for the astrobiological exploration of Mars: SHERLOC will enable detection and characterization of organics and minerals at ~1 ppm [1]; RLS will identify organic compounds and mineral products as indicators of biological activity at <800 ppm [2]; SuperCam's Raman instrument can provide stand-off mineral and organic detection [3], although organic detection is not its priority objective.

The sensitivity (limits of detection) of existing Mars Raman spectrometers is limited by the relatively high signal-to-noise ratio (SNR) that comes with dispersing light across a CCD and recording a spectrum. This SNR "cost" is particularly important in Raman spectroscopy: Raman scattering, though powerful in its ability to inform about a sample, is a relatively weak phenomenon, and signal strength is the limiting factor in data acquisition. To address the science objectives of future life-seeking missions, new detection approaches and system architectures are needed, that will increase the sensitivity of planetary Raman spectroscopy instrument by additional three orders of magnitude.

***i*SEE Innovation**: *i*SEE (*in-situ* Spectroscopic Europa Explorer) is a next-generation ultra-compact Raman system with superior performance that meets the top-level scientific requirements of multiple planetary missions to the inner and outer Solar System (Figure 1).

*i*SEE integrates, for the first time, a digital micromirror device/photomultiplier assembly (DMD/PMT) and a microchip diode laser into a miniature Raman spectrometer that enables unprecedented measurements: in-situ chemical identification and quantitation of complex organic compounds, including pre-biotic compounds (e.g. amino acids); biomolecules (organic biomarkers including proteins, lipids, and nucleic acid polymers); minerals/salts; and volatiles. *i*SEE also provides sample context, including ice composition, crystallinity, and ice phase distribution.

Our architecture provides a 3-order of magnitude SNR enhancement relative to CCD arrays [4], performs chemometric analysis, and calculates the composition of samples on the spectrometer itself. After the Raman scattered light is dispersed by a diffraction grating, it passes through the DMD, whose transmission function can be programmed to represent the multivariate vector of interest (e.g. a particular molecule and its abundance), and measuring the total transmitted intensity on the PMT. Thus, the spectral throughput (data output) of *i*SEE can be programmed by changing the displayed pattern on the DMD. This feature gives *i*SEE a remarkable operational advantage, as it can function as a generalized spectrometer, capable of either full spectral acquisition or compressive detection using programmable optical filter functions.

An additional advantage of DMD/APD spectrometers, one that is particularly relevant for short duration missions with limited ground-in-the-loop feedback, is that it enables onboard analyte quantitation via multivariate optical computing (MOC) [5]. Using MOC, we pre-define spectral masks for a class of compound (e.g., organics) or a specific molecule (e.g., sulfate). This is achieved by turning ON only subsets of
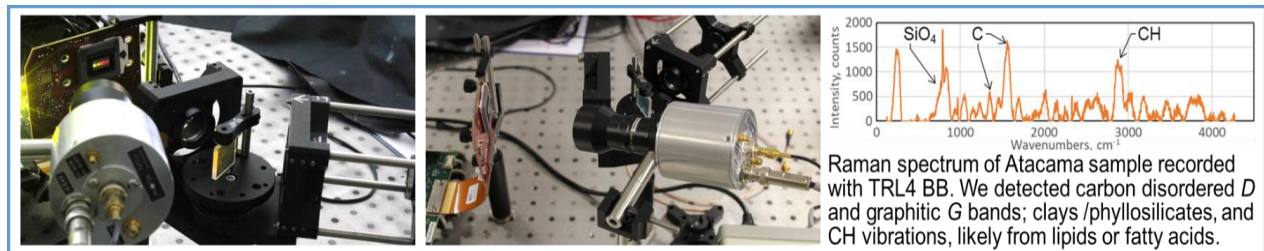

Raman spectrum of Atacama sample recorded with TRL4 BB. We detected carbon disordered *D* and graphitic *G* bands; clays /phyllosilicates, and CH vibrations, likely from lipids or fatty acids.

Figure 1: TRL4 *i*SEE demonstrates the feasibility of our new DMD/PMT-based spectrometer. Key capabilities:

- Organic content ≤ 1 ppb in solid matrices
- Mineralogy and volatile content ≤ 0.1 wt. %
- Spatial resolution ~25 µm
- 250 ms acquisition times for full spectrum
- On-spectrometer chemometrics
- Small footprint: 2.5 Kg, 4,000 cc
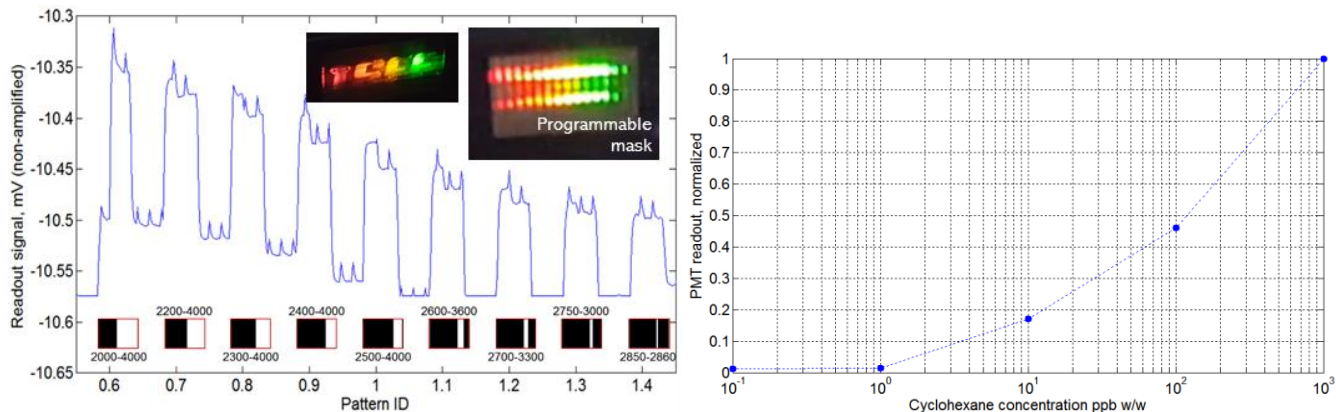- Dual external (arm) and internal laboratory analysis with fiber-Raman heads

Figure 2: (left) *i*SEE's DMD is a programmable filter whose shape is optimized to identify and quantify compounds. Plot shows PMT readings from a 1 ppb w/w cyclohexane solution using variable DMD patterns centered on the 2855 cm^{-1} CH$_2$ vibration. The last reading corresponds to just two columns (10 cm^{-1} range), and represents CH$_2$ Raman photons only, with no contribution from water signals, stray light, or background noise.
(right) PMT readings (integrated over the 2850-2860 cm^{-1} range and normalized) vs cyclohexane concentration. The detection limit of *i*SEE is near 1 ppb for CH$_2$ bondings in aqueous solution. This a conservative estimate, since the value for the 0.1 ppb solution is at or near the same level as the readout noise of the PMT.

micromirrors in spectral regions specific to the compound class or molecule of interest. The DMD transmission function for that specific subset of micromirrors reflects the analyte's concentration. This feature gives *i*SEE a remarkable operational advantage compared to CCD-based Raman systems: quantitative analysis can be implemented, in real-time, directly into the measurement process. CCD systems, on the other hand, require resource-intensive readout and subsequent spectral processing (peak area analysis).

iSEE Performance: In 2017, as part of our NASA STTR-funded R&D, we demonstrated the feasibility of the iSEE concept through test with breadboard subsystems (Figure 2). Specifically, we proved: 1) The flexibility of the DMD programmable slit masks are key to the unique features of *i*SEE, which include specificity to desired molecular species, rejection of background light and fast response in a miniature, rugged, low mass and power instrument. 2) A limit of detection < 1 ppb with the *i*SEE breadboard. While this value is already impressive and beyond the capabilities of CCD-based spectrometers, we are confident that we can lower the limit of detection even more with our ongoing development, which optimizes light emission, collection, and analysis by using more advanced, high-heritage optoelectronics, including a better laser and a

sensitivity-enhanced PMT. 3) The existing *i*SEE breadboard can detect carbon/lipids in low abundance (~ ppb range) and is a suitable diagnostic tool for the presence of carbon compounds in natural samples.

Concepts of Operation (Figure 3): *i*SEE works in two operation modes: *Surface Exploration Mode* for analysis of surface samples and *Analytical Laboratory Mode* for analysis of samples delivered to the spacecraft body. In *Surface Exploration Mode i*SEE could be used after a microimager has taken an image. *i*SEE would take point spectra within the imager field of view. *i*SEE would first use the autofocus mechanism to establish the correct working distance and then record spectra. In *Analytical Laboratory Mode*, owing to its ultra-short integration times, *i*SEE can perform on-line real time point scans when the sample handling system transports the sample and presents it to the internal head via, for example, a refillable container.

References: [1]Beegle L. et al., *LPI Contributions*, 2014. 1783: p. 5101. [2] Hutchinson I. et al., *PSS*, 2014. 103: p. 184-190. [3] Maurice S. et al., *EPSC* 2015, 2015. 10. [4] Smith Z. et al., *Opt Express*, 2011. 19(18): p. 16950-62. [5] Wilcox D. et al., *Analytica Chimica Acta*, 2012. 755: p. 17-27.

Figure 3: *i*SEE ConOps. *i*SEE illuminates a sample with a laser source to induce Raman scattering, and to collect and relay this light to a spectrometer where its intensity and distribution is measured, recorded, and analyzed in real time. (left) rover/lander delivers sample into *i*SEE viewport, where it is analyzed. (right) Spring-driven harpoon with a sensing head (viewport at its tip connected to a fiber optic). Sensing head pushed and held in place for surface analysis.