

DETECTION LIMITS FOR VARIOUS MOLECULES OF ASTROBIOLOGICAL SIGNIFICANCE USING A COMPACT STANDOFF RAMAN SPECTROMETER. Macey W. Sandford¹, A. K. Misra¹, T. E. Acosta-Maeda¹, S. K. Sharma¹, J. Porter¹, M. Egan¹, and M. N. Abedin², ¹Hawaii Institute of Geophysics and Planetology, Univ. of Hawaii at Mānoa, Honolulu, HI 96822, USA; ²NASA Langley Research Center, Hampton, VA 23681, USA. msandfor@hawaii.edu

Introduction: Raman spectroscopy is a unique technique used in planetary science to determine the presence of specific molecules, and in particular, those that indicate life. This technique provides high confidence in the detection of specific molecules based on their Raman-active vibrational modes [1]. NASA's Mars 2020 mission will conduct the first Raman investigations on another planet, with the arm mounted SHERLOC UV Raman instrument [2] and the Supercam remote Raman system [3]. Substances such as water, amino acids, organics, sulfates, nitrates, oxides, hydrous minerals and several other molecules indicative of life are Raman active and are easily identified with our compact remote Raman system [4-7]. Understanding the detection limits of the system is essential for making a confident identification of minute amounts of such molecules on a planetary surface. It is also useful in determining the applicability of this sys-

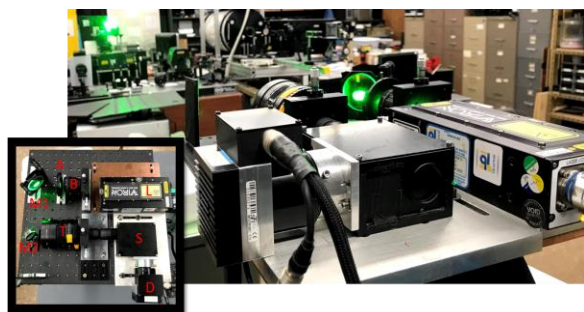


Figure 1: Compact remote Raman+LIBS system developed at the University of Hawaii. The system consists of the following; L: Nd:YAG pulsed laser 532 nm, B: 8x beam expander, A: aperture, M1: folding mirror, M2: folding mirror, T: 3" diameter telescope, S: compact Raman/ LIBS spectrograph, D: mini-ICCD detector, with a Pan and Tilt scanner. [5]

tem and technique to the search for life in our solar system. We will present the detection limits at a 5 meter target distance for various pure and mixed samples which have astrobiological significance.

System Set-up: The optical system used in this experiment consists of a frequency-doubled mini Nd:YAG pulsed laser source (532 nm, 10 ns pulse width, maximum 12.5 mJ/pulse, 20 Hz), a 3 inch diameter telescope, a compact spectrograph with dimensions 10 cm (length) x 8.2 cm (width) x 5.2 cm (height) and a mini-ICCD detector (Figure 1). Further details have been previously discussed in Misra et al. (2015)

[7]. The spectra in this experiment were collected in laboratory conditions with indoor lights turned on. Samples were measured at a distance of 5 meters using the intensified CCD in gated mode at a 40 ns gate width. A short gate width helps in minimizing the background signal.

Samples: The liquid chemicals (ACS grade) used are from Fisher Scientific. They were portioned into sealed glass slides for measurements of samples at small volumes and a tube with an optical window for measurements at larger volumes. In specific, KClO_3 was used for its relation to perchlorates, which oxidize organic molecules. Tap water from the city of Honolulu, Hawai'i was used for liquid water (H_2O) samples and were prepared in the same manner as the liquid chemicals. Solid samples were formed in discs of varying thickness using a 12 mm diameter steel pellet die and a lab press. Mixture series are of sodium stearate from Sigma Aldrich with either quartz grain sand of 210-270 micron or JSC Mars-1 Mars spectral simulant [8]. Sodium stearate exhibits Raman features common to many organics, and mixed with JSC Mars-1 can help us understand the detection limits for organics in Martian soil.

Results: The sampling area of this compact remote Raman system at a 5 meter distance during this experiment was 5.6 mm^2 , with a 50 micron slit. This compact remote Raman system covers the entire Ra-

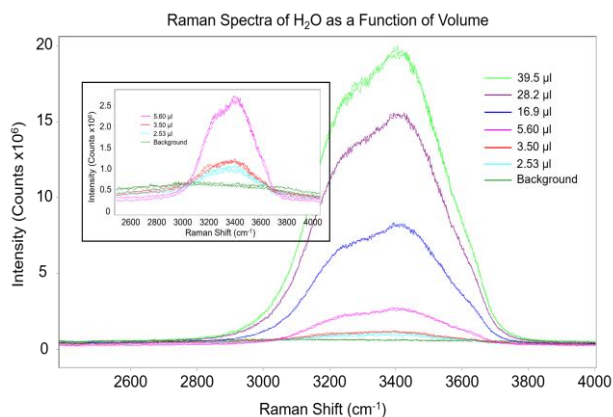


Figure 2: Raman spectra of H_2O at a distance of 5 meters with 12.5 mJ/pulse and an integration time of 30 s. Spectra of various volumes ranging $2.53 \mu\text{l}$ to $39.5 \mu\text{l}$ of H_2O are overlaid to show the difference in intensity, including the background of the glass holder.

man spectral range ($\sim 100 \text{ cm}^{-1}$ to 4500 cm^{-1}) with 12 cm^{-1} spectral resolution [9]. Molecules containing hydrogen show Raman peaks in the high frequency region

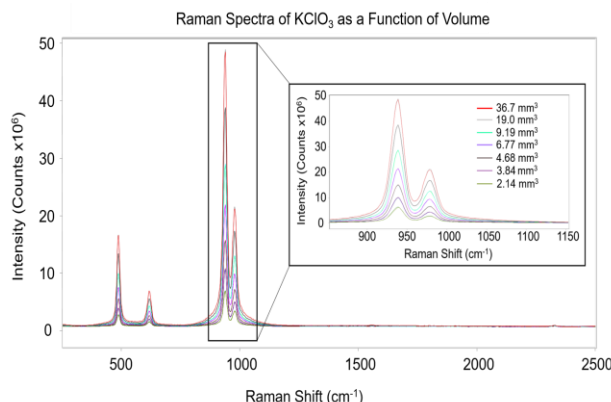


Figure 3: Raman spectra of KClO_3 at a distance of 5 meters with 3.7 mJ/pulse and an integration time of 30 s. Spectra of various volumes ranging 2.14 mm^3 to 36.7 mm^3 ($1 \text{ mm}^3 = 1 \mu\text{l}$) of KClO_3 are overlaid to show the differing intensity at each volume measured.

($2400\text{--}4500 \text{ cm}^{-1}$). This is due to the fact that the frequency associated with vibrational modes are inversely proportional to the square root of the reduced mass of the atoms involved in the molecular vibration [1]. This makes it simple to identify water, organics and biological materials through their Raman spectra. Water in various phases gives very strong Raman signal in the $3100\text{--}3600 \text{ cm}^{-1}$ spectral region. Concerning liquid water, the broad Raman bands at approximately 3278 and 3450 cm^{-1} are the symmetric (ν_1) and antisymmetric stretching (ν_3) vibrational modes of the molecule, respectively [13]. In general, the stretching modes of

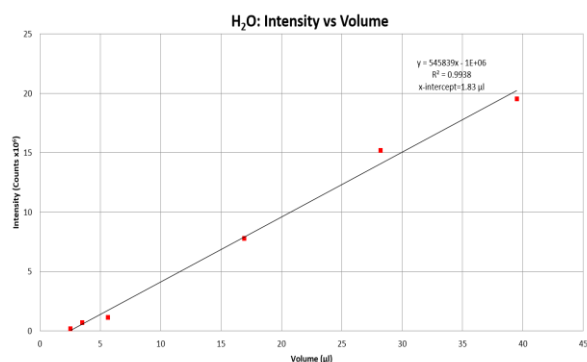


Figure 4: A plot of Raman intensity in millions of counts versus sample volume in microliters (μl) for the H_2O data collected from a 5 meter distance. The linear trend line equation is shown, with a R^2 correlation coefficient of 0.9938. The extrapolated x-intercept is shown to be $1.8 \mu\text{l}$ which can be used as verification for a calculated LOD (Limit of Detection).

vibrations produce the most intense Raman signal [1].

We present Raman spectra for a solid sample as well, potassium chlorate (KClO_3) as a function of volume (Figure 3). KClO_3 has a characteristic peak at 930 cm^{-1} due to the symmetric stretching (ν_1) vibrational mode of the chlorate ions [4].

Discussion: For estimating limit of detection (LOD) for standoff Raman measurements, in our case at a 5 meter distance, one can use either the peak intensity of a Raman line or the integrated area under the peak. The intensity of the Raman peak of water (3450 cm^{-1}) as a function of volume suggest a limit of detection of $1.8 \mu\text{l}$ (Figure 4). We were able to successfully measure $2.53 \mu\text{l}$ of water. The exact LOD for various samples including H_2O and KClO_3 will be presented at the conference.

Summary: Understanding the detection limits of an instrument used to indicate the presence of various molecules is necessary to characterize the data that it collects on a mission. The compact portable remote Raman system discussed has various applications in planetary science, including in relation to the upcoming Mars 2020 mission, which has a remote Raman system (SuperCam). We collected spectra of various pure and mixed samples at a distance of 5 meters in order to characterize the LOD for this system, with specific implications for detecting molecules that are signatures of life on planetary bodies. The University of Hawai'i compact Raman system successfully detected $2.5 \mu\text{l}$ of H_2O and 2.14 mm^3 of KClO_3 at a distance of 5 meters.

Acknowledgments: This work has been supported by NASA PICASSO and the Mars 2020 mission grants.

References: [1] J. R. Ferraro et al. (2003) *Introductory Raman Spectroscopy*, 2nd ed. [2] L. Beegle et al. (2015) *IEEE*, 1-11. [3] R.C. Weins et al. (2016) *47th Lunar and Planetary Science Conference*, #1322. [4] T. Acosta-Maeda et al. (2016) *Applied Optics*, **55**, 10283-10289. [5] M. N. Abedin et al. (2018) *Applied Optics*, **57**, 62-68. [6] P. J. Gasda et al. (2015) *Appl. Spectrosc.* **69**, 173-192. [7] A. K. Misra et al. (2015) *46th LPSC*, Abstract #1553. [8] C.C. Allen et al. (1998) *InSpace*, **98**, 469-476. [9] M. Sandford et al. (2018) *49th LPSC*, Abstract #1695. [10] A. K. Misra et al. (2012) *Appl. Spectrosc.* **66**, 1279-1285. [11] A. Wang et al. (2006) *Geochim. Cosmochim. Acta* **70**, 6118-6135. [12] A. Culka, et al. (2010) *Spectrochimica Acta Part A* **77**, 978-983. [13] T. Acosta-Maeda et al. (2014) *45th LPSC*, Abstract #2331.