

DETECTION OF “SEARCH FOR LIFE” ELEMENTS USING COMPACT REMOTE RAMAN SYSTEM FROM 122 METERS. M. Sandford¹, A. K. Misra¹, T. E. Acosta-Maeda¹, J. Porter¹, M. Egan¹, S. K. Sharma¹, S. M. Clegg², R. C. Wiens², and M. N. Abedin³, ¹Hawaii Institute of Geophysics and Planetology, Univ. of Hawaii at Mānoa, Honolulu, HI 96822, USA; ²Los Alamos National Laboratory, Los Alamos, NM 87545, USA; ³NASA Langley Research Center, Hampton, VA 23681, USA. msandfor@hawaii.edu

Introduction: The priority to gain knowledge surrounding the origin and evolution of the planets and other objects in our Solar System has been outlined in the NASA Decadal Survey (2013-2022) and is essential to carry out the search for life outside Earth. Elements included in the “search for life” criteria are Carbon (C), Nitrogen (N), Oxygen (O), Sulfur (S), Phosphorous (P), Hydrogen (H), etc., which are all part of biological processes as they are understood today. Raman spectroscopy provides a very high level of confidence in identifying molecules because the Raman spectrum of a molecule is unique to the molecule and is normally used as a fingerprint method for chemical identification [1]. Presence of life or elements needed for supporting life can be detected through Raman spectroscopy by its ability to identify whole molecules such as water, amino acids, organics, sulfur, sulfates, nitrogen (N₂), nitrates, oxygen (O₂), oxides, hydrous minerals, etc. [2-4]. Using a compact portable remote Raman system, detection of water, ice, dry ice, H₂O/OH bearing minerals, organics, amino acids etc. were successfully tested at a range of 122 m in daylight conditions. The detection of materials with high astrobiological significance using Raman spectroscopy at remote distances demonstrates the applicability of Raman spectrometers for Mars missions as well as those in the future, traveling past the asteroid belt and towards moons such as Europa.

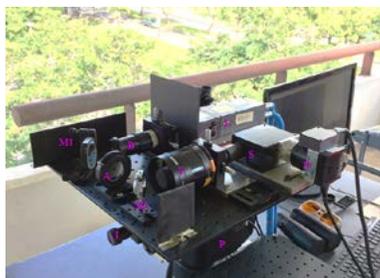


Figure 1: Compact remote Raman+LIBS system developed at the University of Hawaii using 3” diameter telescope. L: Nd:YAG pulsed laser 532 nm, B: 8x beam expander, M1: laser mirror, A: aperture, M2: Mirror, T: 3” diameter telescope, S: compact Raman LIBS spectrograph, D: mini-ICCD detector, P: Pan and Tilt scanner, I: imaging camera. [5]

System Set-up: The compact portable remote Raman system used in this experiment, shown in Figure 1, consists of a frequency-doubled mini Nd:YAG pulsed (532 nm, 10 ns pulse width, 20 mJ/pulse, 20Hz) laser source, 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. The system details have been previously discussed in Misra et al. (2015) [5]. The spectra in this experiment were collected in daylight conditions from 122 m using the intensified CCD in gated mode with 70 ns gate width. A short gate width helps in minimizing the background signal from daylight and mineral phosphorescence.

Samples: Rock and mineral samples were obtained from Ward’s Natural Science Establishment, Inc., Rochester, New York. These samples were not cut or polished after being received. The amino acids were obtained from Sigma Aldrich and procured in 20 ml glass vials for measurement. Liquid chemicals (ACS grade) were obtained from Fisher Scientific and portioned into glass containers for measurement. Potassium nitrate, ammonium nitrate, potassium chlorate, sulfur and urea were obtained from Fisher Scientific. Tap water from the city of Honolulu, Hawai’i was used for both liquid and solid water (H₂O) samples. Dry ice (CO₂ ice) was obtained from the University of Hawaii chemistry stock room in the form of pellets.

Results: Figure 2 shows remote Raman spectra of water, water ice, and CO₂ ice with an integration time of 30 seconds from a distance of 122 m. The compact remote Raman system covers the entire Raman spectral range (~ 100 cm⁻¹ to 4500 cm⁻¹) with 12 cm⁻¹ spectral

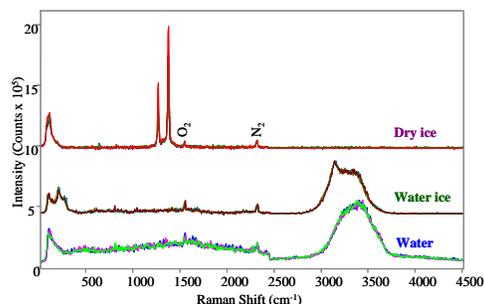


Figure 2: Remote Raman detection of water, ice and dry ice from 122 m with 30s integration time. Three measurements of the same sample are overlaid to show the reproducibility of the system.

resolution. Because frequency of a vibrational mode is inversely proportional to square root of the reduced mass of the atoms involved in the molecular vibration, molecules containing hydrogen show Raman peaks in the high frequency region (2400-4500 cm⁻¹). This

makes it easy to identify water, organics and biological materials through their Raman spectra. Water gives very strong Raman signal in the 3100 – 3600 cm^{-1} spectral region, and it is easy to detect water in various phases using Raman spectroscopy. In liquid water, the strong, broad Raman bands at 3278 and 3450 cm^{-1} are the symmetric (ν_1) and antisymmetric stretching (ν_3) vibrational modes of the water molecule, respectively. The stretching modes of vibrations usually produce the strongest Raman signals. Ice can be distinguished from liquid water by the presence of a sharper band at 3150 cm^{-1} . In contrast, the CO_2 ice contains no hydrogen and shows no high frequency Raman feature. The Raman spectra of carbon dioxide ice have a characteristic doublet at 1284 cm^{-1} and 1392 cm^{-1} which are easily identifiable. Remote Raman spectra also show the presence of atmospheric gases, oxygen at 1556 cm^{-1} and nitrogen at 2331 cm^{-1} from the interaction of the laser and the atmosphere as the laser travels towards the targets. [2,6]

Remote Raman spectra of hydrous minerals, Gypsum ($\text{CaSO}_4 \cdot 7\text{H}_2\text{O}$) and Epsom ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), from 122 m target distance with 30 seconds integration time are shown in Figure 3.

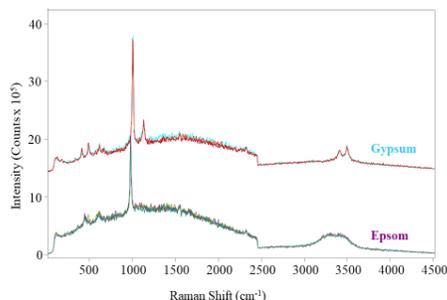


Figure 3: Remote Raman detection of Gypsum and Epsom from 122 m with 30s integration time. Three measurements of the same sample are overlaid to show the reproducibility of the system.

Various functional groups such as nitrates, sulfates, phosphates, carbonates etc. can be easily identified in the Raman spectra by identifying their vibrational modes. The sulfate anion gives a strong Raman band near 1000 cm^{-1} . The symmetric stretching vibrations (ν_1) in the sulfate ions, SO_4 , is observed at 1008 cm^{-1} in Gypsum and at 984 cm^{-1} in Epsom. The position of the sulfate band can also determine the hydration state of the chemical [7]. The chemically bonded water molecules in Gypsum are observed at 3405 cm^{-1} and 3493 cm^{-1} .

Figure 4 shows the remote Raman spectrum of the amino acid Beta-Alanine (98% purity) [8] from a distance of 122 m with 30 seconds integration time. The biological nature of the amino acid is confirmed by the presence of biofluorescence background and presence

of Raman bands in the CH stretching region (2800–3100 cm^{-1}). We have previously reported remote Raman spectra of various amino acids and DNA bases using this system from 10 m distance [9].

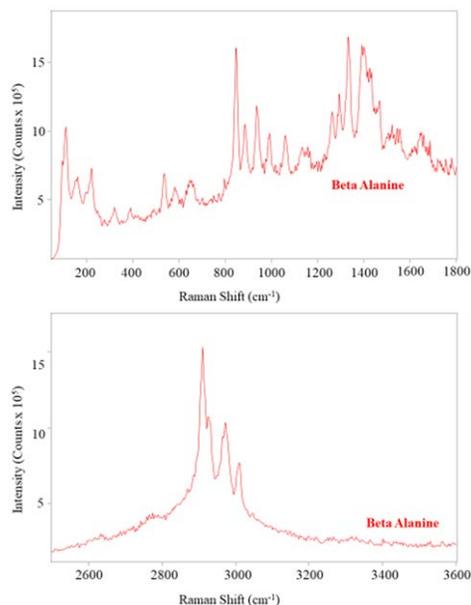


Figure 4: Remote Raman detection of Beta Alanine from 122 m with 30s integration time

Summary: Using a compact portable remote Raman system, we were able to successfully demonstrate the detection of “search for life” elements and minerals with Raman spectra from a distance of 122m during daylight hours. This work is relevant in the planetary science field as longer range Raman detection can heighten the capabilities of a rover to analyze targets in a planetary setting. Targets which are difficult to reach by wheels such as cliffs, deep trenches, lakes etc. are more readily available for analysis of the presence of water and organics using a system capable of long distance Raman detection.

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References: [1] J. R. Ferraro, et al., (2003) *Introductory Raman Spectroscopy*, 2nd ed. (Academic Press, San Diego). [2] T. Acosta-Maeda, et al. (2016) *Applied Optics*, 55, 10283-10289. [3] M. N. Abedin, et al., (2018) *Applied Optics* 57, 62-68. [4] P. J. Gasda, et al., (2015), *Appl. Spectrosc.* 69, 173-192. [5] A. K. Misra et al., (2015) *46th LPSC*, Abstract #1553. [6] A. K. Misra et al., (2012) *Appl. Spectrosc.* 66, 1279-1285. [7] A. Wang et al., (2006) *Geochim. Cosmochim. Acta* 70, 6118–6135. [8] A. Culka, et al. (2010) *Spectrochimica Acta Part A* 77, 978-983. [9] T. Acosta-Maeda, et al. (2014), *45th LPSC*, Abstract #2331.