STAND-OFF DETECTION OF AMINO ACIDS AND ORGANICS USING A COMPACT REMOTE RAMAN INSTRUMENT. T. E. Acosta-Maeda¹, A. K. Misra¹, P. J. Gasda¹ and S. K. Sharma¹. Hawai‘i Institute for Geophysics and Planetology, University of Hawai‘i, Mānoa, 1680 East West Road, Honolulu, Hawai‘i 96822; ¹email: tayro@hawaii.edu.

Introduction: Water, water bearing minerals, organic compounds, and elements such as C, N, O, S, P, H, Fe, Mn, etc., are necessary for biological processes. The detection of these elements and compounds play a significant role in NASA’s search for past and present life in the Solar System.

The detection of biological materials and biomarkers is an important part of the NASA planetary exploration program [1]. Amino acids and nucleobases are of particular interest because they are essential for life as the basic constituents of proteins and nucleic acids. Amino acids and nucleo bases have been reported in Martian meteorites (glycine, β-alanine, and γ-amino-n-butyric acid) [2], carbonaceous chondrites [3], and glycine has been reported in samples returned by NASA’s Stardust spacecraft from comet 81 P/Wild 2 [4]. Among the amino acids found, there are both proteinogenic (protein building blocks such as L-alanine or L-Glutamic acid) and non-proteinogenic amino acids (e.g. β-aminoisobutyric acid).

Raman spectroscopy has been recognized as a powerful technique capable of identifying a large variety of chemicals, including pure elements (e.g., carbon, silicon, sulfur, etc.), simple molecules (e.g., diatomic oxygen and nitrogen, water, carbon dioxide, etc.), inorganic chemicals (e.g., carbonates, oxides, perchlorates, nitrates, sulfates, etc.), organic compounds (e.g., polyaromatic hydrocarbons (PAHs), methane, methane hydrates, etc.), biogenic compounds (e.g. amino acids, proteins, sugars, etc.), and rock forming minerals (calcite, gypsum, olivine, etc.). Raman spectra can be obtained from any state of aggregation (solid, liquid, and gas phase). Raman spectroscopy has successfully been used for the detection and characterization of amino acids and nucleo bases [5, 6], which demonstrates the potential of Raman spectroscopy for planetary exploration. as also described in the recent Mars 2020 rover Science Definition Team Report.

Instrument description: A micro-Raman spectrometer could be mounted in the payload of a lander vehicle as a contact instrument, e.g. the RLS Raman spectrometer onboard the Exomars Rover Instrument Suite for future ESA Mars exploration mission. However, a stand-off system would save precious time and risky traverses. At the University of Hawaii, we have developed a compact, portable remote Raman, Fluorescence, and Laser-Induced Breakdown Spectroscopy (LIBS) system with a 532 nm pulsed laser for planetary exploration under the Mars Instrument Development Program 7, 8. The compact time-resolved remote Raman, Fluorescence and LIBS system (Fig. 1.) consists of (i) a telescopic 500 nm Bower (F/8) camera lens as collection optics, (ii) a miniature spectrograph that occupies 1/14th the volume of a comparable commercial spectrograph from Kaiser Optical Systems Inc., (iii) a custom mini-ICCD detector, and (iv) a small frequency-doubled 532 nm Nd:YAG pulsed laser (30 mJ/pulse, 20 Hz) with a 10x beam expander. In the standoff Raman mode the system is capable of measuring various minerals, water, ices, and atmospheric gases from a 50 meter range with a 10 s integration time. At shorter distances of 10 m or less, good quality Raman spectra can be obtained within 1 s. The time-gated system is capable of detecting both the target mineral as well as the atmospheric gases before the target using their Raman fingerprints. Various materials can easily be identified through glass, plastic, and water media. The time-gating capability makes the system insensitive to window material, which is highly desirable for future missions to Venus (where instruments are expected to be within the lander), and allows for time resolved spectroscopy. Using time resolution, fluorescence can be minimized during Raman measurements and fluorescence life-time measurements can be performed as well. The standoff LIBS range is 10 m and LIBS spectra of various minerals can be obtained with single laser pulse excitation. The standoff LIBS capability provides additional elemental verification of the targeted material 8.
Samples and methodology: We measured all of the proteinogenic amino acids (21 L-amino acids and glycine kit, Fluka), sarcosine, and five nucleobases (Sigma), along with several polyaromatic hydrocarbons, such as anthracene. Samples were placed and measured inside glass vials. Glass has a significantly lower Raman cross-section in comparison to that of organics and amino acids. Remote Raman measurements were recorded from 8 m distance with 200 laser pulses excitation (10 s at 20 Hz) using a 10 mJ/pulse laser power output, and an approximately 8 mm laser spot on the target. The delay of the gated ICCD camera was adjusted at -400 ns to pre-trigger the camera at the arrival of the Raman signal, with a 400 ns camera gate width. Since the ICCD is only exposed for 80μs the Raman signal is easily measured in well lit environments.

Results: Figure 2 shows the Raman spectra of five amino acids in the range 140 to 1800 cm⁻¹ (the Raman fingerprint region). The majority of the Raman bands in this region arise from CH, CH₂, and CH₃ deformational vibrational modes. Figure 3 shows the range between 2600 and 3400 cm⁻¹ for the same amino acids. The bands between 2850 and 3000 cm⁻¹ result from C–H stretching and are about 4 times more intense than the strongest bands in the fingerprint region (Fig 2).

The complexity of the bands in the low frequency region, and the sensitivity of these bands to shift due to fine structural changes, provides a fingerprint for each organic molecule. The CH deformational modes are found at slightly different positions because of the influence of the side-chain characteristic of each amino acid. Some bands result from vibrational modes on the side-chains. For example, L-phenylalanine is an aromatic amino acid and some Raman bands arising from CH rings are expected. The most prominent are found at 1003 cm⁻¹ and at 3069 cm⁻¹, arising from the ring-breathing vibration in mono-substituted aromatic compounds and from aromatic C–H stretch vibrations, respectively [4]. The same bands in L-tryptophan are shifted to 1009 and 3057 cm⁻¹, making the distinction between both amino acids straightforward and unequivocal. Both L-phenylalanine and L-Tryptophan show some fast fluorescence, which may be indicative of biological origin of the measured material.

Conclusions: Daytime detection of amino acids and nucleobase from a distance of 8 m has been demonstrated here using a portable, compact remote Raman-Fluorescence+LIBS instrument. The remote Raman system is well suited for planetary exploration applications, with no requirement for sample preparation or collection, and rapid measurement times.

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