

**EXPLORING OCEAN WORLDS USING A COMPACT STANDOFF RAMAN AND FLUORESCENCE SPECTROMETER.** M. W. Sandford<sup>1\*</sup>, A. K. Misra<sup>1</sup>, T. E. Acosta-Maeda<sup>1</sup>, S. K. Sharma<sup>1</sup>, M. N. Abedin<sup>2</sup>, P. G. Lucey<sup>1</sup>, C. M. Ferrari-Wong<sup>1</sup>, E. Costello<sup>1</sup>, <sup>1</sup>Hawaii Institute of Geophysics and Planetology, Univ. of Hawaii at Mānoa, Honolulu, HI 96822, USA, <sup>2</sup>NASA Langley Research Center, Hampton, VA 23681, USA. \*msandfor@hawaii.edu

**Introduction:** Analyses from the past few decades of outer Solar System satellites reveal the potential habitability of Jupiter and Saturn’s icy moons. The term “ocean world” describes those icy moons that likely have a liquid water ocean underneath their outer ice shell (i.e. Europa, Ganymede, Calisto, Enceladus, Titan [1]). The Galileo spacecraft collected many initial measurements of the Jupiter satellites that include images of surface characteristics and the detection of induced magnetic fields that give rise to the theory that these icy moons foster a liquid ocean underneath the outer icy shell [2]. However, this data set is not sufficient to determine habitability. NASA’s 2011 decadal survey, Vision and Voyages for Planetary Science in the Decade 2013–2022, promotes a flagship mission to explore the potential of ocean worlds in the outer Solar System to host life [3]. Further exploration would require an explorer on the surface.

Raman and fluorescence spectroscopy provide unique capabilities for detection and characterization of materials of high astrobiological potential, including organic compounds and minerals that may host biosignatures. This technique provides high confidence in the detection of specific molecules based on their Raman-active vibrational modes [4]. At the University of Hawai‘i at Manoa (UH), we develop Raman and fluorescence instruments (Figure 1) that provide measurements remotely, including high quality Raman spectra at hundreds of meters range for a wide variety of compounds. Since an Ocean World

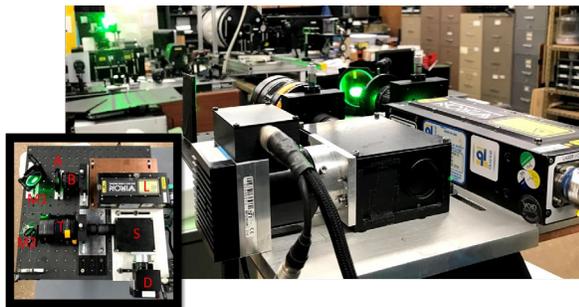


Figure 1: Compact remote Raman+LIBS system developed at the University of Hawaii. The system consists of the following; L: Nd:YAG pulsed laser 532 nm, B: 8x beam expander, A: aperture, M1: folding mirror, M2: folding mirror, T: 3” diameter telescope, S: compact Raman/ LIBS spectrograph, D: mini-ICCD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

lander or other in situ explorer will have limited mass and power, we explore using a compact Raman and fluores-

cence system that operates at low power for more modest ranges of 5-10 meters, sufficient to extend the range of static explorers beyond the reach of many robot arms. With this system we are able to routinely measure pure liquid quantities in the nanoliter range, and minerals in the cubic millimeter range. 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 [6-10].

The surface composition of Europa and the energy from radiation trapped in Jupiter’s intense magnetic field yield a unique environment on Europa’s surface where complex molecules can be created and sustained [11]. Creating and measuring samples with these characteristics is relevant to a potential lander or other explorer mission to Europa’s surface. We present the detection of Ocean World simulant samples such as frozen and liquid brines, hydrous minerals, and amino acid solutions with our Raman system. The specificity and simplicity of Raman and fluorescence spectroscopy make them ideal techniques for Ocean World exploration.

**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) [10]. 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:** Samples in this work include liquids, particulate ices, and solid blocks of ice. Amino Acids glycine and beta-alanine as well as sulfuric acid are from Sigma Aldrich. Drug store Epsom salt ( $MgSO_4 \cdot 7H_2O$ ) was purchased from a grocery store labeled as containing 100% magnesium sulfate USP (heptahydrate). Hydrated Epsom salt ( $MgSO_4 \cdot 7H_2O$ ) and anhydrous Epsom salt ( $MgSO_4$ ) are from Ward Scientific. The table salt ( $NaCl$ ) used in the solutions is iodized. Hydrogen peroxide is from the drug store at 3% concentration in  $H_2O$ . Organics naphthalene, nitrobenzene (ACS grade), and methanol are from Fisher Scientific. Distilled  $H_2O$  from the UH

chemistry stock room was used as the solvent in the solutions. Liquid samples were made by simply dissolv-

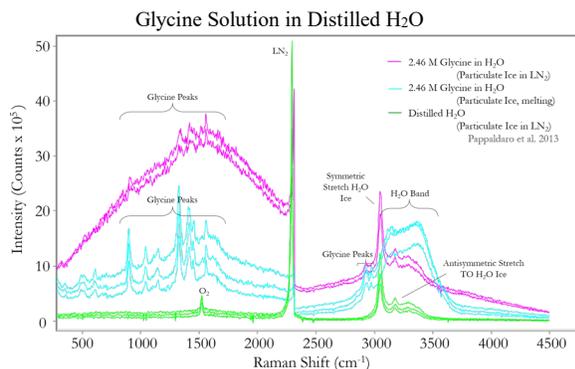


Figure 2: Raman spectra of glycine dissolved in distilled H<sub>2</sub>O as particulate ice in LN<sub>2</sub> and particulate ice as it melts. A spectrum of pure distilled H<sub>2</sub>O as particulate ice is shown as well. Spectra were taken at a distance of 5 meters with 12.5 mJ/pulse and an integration time of 30 s.

ing the solutes in the solvent. Particulate ice was created using a Paasche VL#3 airbrush with a 0.75 mm head to spray droplets of the solutions into liquid nitrogen. Solid ice was created by pouring liquid solutions into liquid nitrogen. The liquid nitrogen (LN<sub>2</sub>) used in this process is from the UH chemistry stock room.

**Results:** Our compact standoff Raman system covers the entire Raman spectral range ( $\sim 100$  cm<sup>-1</sup> to 4500 cm<sup>-1</sup>) with a 12 cm<sup>-1</sup> spectral resolution. Molecules containing hydrogen show Raman peaks in the high frequency region (2400–4500 cm<sup>-1</sup>). For example, H<sub>2</sub>O in various phases gives very strong Raman signal in the 3100–3600 cm<sup>-1</sup> spectral region (Figure 1 and Figure 2). The high

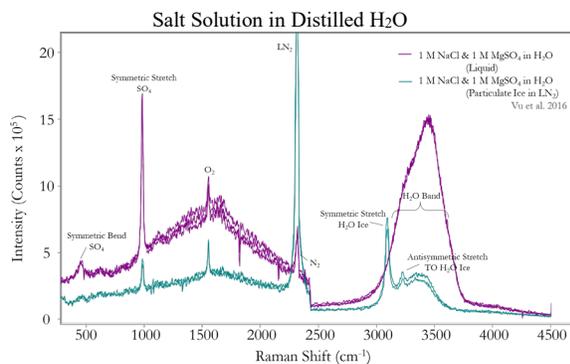


Figure 3: Raman spectra of NaCl and MgSO<sub>4</sub> dissolved in distilled H<sub>2</sub>O as a liquid and as particulate ice in LN<sub>2</sub>. Spectra were taken at a distance of 5 meters with 12.5 mJ/pulse and an integration time of 30 s.

frequency region contains features from lighter molecular bonds because 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 [4]. In liquid water, the broad Raman bands at approximately 3278 and 3450 cm<sup>-1</sup> are the symmetric ( $\nu_1$ ) and antisymmetric stretching ( $\nu_3$ ) vibrational modes of the molecule, respectively [2]. These features in water ice also exist but are sharper and represent the crystal structure that defines the solid. In general, the stretching modes of vibrations produce the most intense Raman signal [4].

In this experiment, distilled H<sub>2</sub>O is used to make various solutions relevant to the surface, sub-surface, and ocean of Ocean Worlds, i.e. particulate ice, solid ice, and liquids [1]. These samples include 1 M equimolar solution of NaCl and MgSO<sub>4</sub> in distilled H<sub>2</sub>O [13], 3.07 M NaCl and 1.44 M MgSO<sub>4</sub> solution in distilled H<sub>2</sub>O [13] (Figure 3), 2.46 M glycine in distilled H<sub>2</sub>O (Figure 2), 2.46 M beta-alanine in distilled H<sub>2</sub>O, 3% hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) in distilled H<sub>2</sub>O, and 1 M sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). We have pending collaborations for further samples that may be presented at the conference.

**Discussion:** Showing that our compact standoff Raman spectrometer can detect various samples relevant to Ocean World exploration is the first step in qualifying Raman spectroscopy as an ideal technique for a mission to an Ocean World. The next step is to determine the minimum concentration of relevant solutes that Raman spectroscopy can detect. This includes presenting our spectral features in terms of radiance rather than counts in order for our findings to be relevant to any Raman spectrometer intended to successfully detect minerals and organics on Ocean Worlds. Using an integrating sphere, we will present the detection of various concentrations of our relevant samples in terms of absolute radiance.

**Summary:** Based on the findings of this research, we present standoff Raman spectroscopy to be an ideal instrument for an Ocean World mission.

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**References:** [1] K. P. Hand and C. R. German (2018) *Nature Geoscience*, **11**, 2-5. [2] J. Kimura and N. Kitadai (2015) *Astrobiology*, **15**. [3] Space Studies Board (2011) *Vision and Voyages for Planetary Science in the Decade 2013–2022*. [4] J. R. Ferraro et al. (2003) *Introductory Raman Spectroscopy*, 2nd ed. [5] L. Beegle et al. (2015) *IEEE*, 1-11. [6] T. Acosta-Maeda et al. (2016) *Applied Optics*, **55**, 10283-10289. [7] M. N. Abedin et al. (2018) *Applied Optics* **57**, 62-68. [8] P. J. Gasda et al. (2015) *Appl. Spectrosc.* **69**, 173-192. [9] A. K. Misra et al. (2015) *46<sup>th</sup> LPSC*, Abstract #1553. [10] T. Hoehler (2004) *Geobiology*, 2:205–215. [11] L. Wackett et al. (2004) *Appl Environ Microbiol*, 70:647–655. [12] R.T. Pappalardo et al. (2013) *Astrobiology*, **13**. [13] T. H. Vu et al. (2016) *The Astrophysical Journal*, **816**.