EUROPA INTEGRATING CAVITY ENHANCED RAMAN SPECTROSCOMETER FOR EXPLORATION OF ICY WORLDS (ERSO) CONCEPT. C. M. Phillips-Lander[1], T. Z. Moore[1], U. Raut[1], P. M. Molyneux[1], M. A. Miller[1], K. Nowicki[3], R. C. Blase[1], M. W. Davis[1], T. J. Veach[1], G. J. Dirks[1], K. B. Persson[1], Y. D. Tyler[1], R. A. Klar[1], P. L. Karnes[1], M. A. Freeman[1], C. J. A. Howett[3], A. Soto[3], K. Mandt[4], L. Roth[5], B. Schmidt[6], E. Spiers, A. Templeton[7], J. D. Mason[8], E. S. Fry[8], K. Retherford[1], [1]Southwest Research Institute, San Antonio, TX (clander@swri.edu), [2]University of Texas at San Antonio, San Antonio, TX, [3]Southwest Research Institute, Boulder, CO, [4]Johns Hopkins University, Applied Physics Laboratory, Laurel, MD, [5]Department of Space and Plasma Physics, KTH, Stockholm, Sweden,[6]Earth and Atmospheric Sciences, Georgia Tech, Atlanta, GA, [7]Geological Sciences, University of Colorado, Boulder, CO, [8]Texas A&M University, College Station, TX.

Introduction: Raman spectroscopy has been identified as a useful technique for determining the identity and concentration of gases [1] and liquids and fluid inclusions [eg 2-9], the salt deliquescence and hydration states [10-14], the type and concentration of organics [15-17] and the mineralogy of meteorites [eg 18-19] under a variety of operating conditions from cryogenic to ~1000ºC [1]. This potential flexibility for applications has aided in the selection of deep ultraviolet (DUV) and 532 nm visible laser Raman instruments for both the Mars2020 and ExoMars rovers.

The Europa Lander Scientific Definition Team (hereafter Europa SDT) Report suggested the potential inclusion of a Raman instrument to detect and quantify both mineralogical and organic signatures of life on the moons surface and shallow subsurface [20]. This included the detection of amino acids, carboxylic acids, lipids, and other molecules of potential biological origin at picomole/gram concentrations (Goal 1A1) and determining the types [and] relative abundances of any amino acids in the sampled material (Goal 1A2) [20]. While Raman spectroscopy is an incredibly powerful technique, it is inherently inefficient with only 1 in 10^{11} photons scattered with useful vibrational information [1]. In order to achieve the objectives outlined in the Europa SDT report, advanced Raman techniques and technologies are required.

Integrating Cavity Enhanced Raman Spectroscopy (iCERS) technique: To address this challenge, we are developing an iCERS instrument. The Europa Raman Spectrometer for Ocean worlds (ERSO) iCERS instrument is similar to the CERS technique, which uses specular reflective dielectric mirrors. However, the iCERS technique employs a highly reflective Lambertian material, which forms the walls of an enclosed cavity. ERSO's cavity is composed of high purity fumed silica, which has a reflectivity of 99.92% based on ringdown measurements [1]. Commercial Lambertian materials typically have reflectivities below 99.3% [21], where a reflectivity greater than 99.5% is required to achieve any significant Raman enhancement [1]. Light is then spatially integrated throughout the cavity volume, which provides enhancement of the Raman signal.

This enhancement is in part due to the used of the high reflecting integrating cavity material, which allows for multiple interaction of the elastically scattered light with the sample. Several hundred to thousands of reflections from the cavity walls provide multiple opportunities for additional interactions between the laser light and the sample, resulting in more Raman scattered photons. This light is spatially integrated throughout the cavity volume simultaneously interacting with the sample volume and/or across the sample surface. For a continuous-wave (CW) laser source, light builds up within the cavity. This means that a 100 mW of laser light entering the cavity can build up and result in as much as 10 W of light circulating within the cavity at any one time [1]. Raman scattered light is collected from all directions before being coupled out via a fused silica optical fiber or light guide. This results in an enhancement of 10^2-10^6, depending on the measured reflectivity of the cavity, the sample phase, and the measurement. Our current data indicate a 10^2-10^4 enhancement for bulk compounds.

Previous research has demonstrated iCERS enhancements on the order of 10^5 [22] Cavity enhanced fluorescence has been demonstrated to make sensitive trace measurements of contaminants like urobilin in liquid water at femtomole levels [22]. iCERS Raman measurements of bulk pyrene have been made at concentrations as low as 37 nM [23].

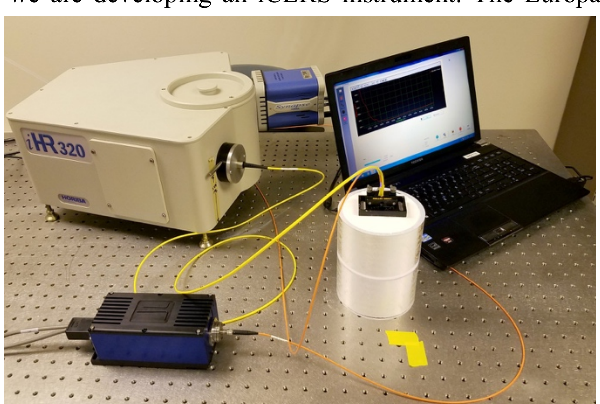

Figure 1: TRL-4 breadboard iCERS cavity operating at SwRI.

Methods: This study examines the detection of both inorganic and organic compounds of interest for icy planetary bodies, including Enceladus and Europa. Results from this study will aid in the testing and development of Raman spectrometers for landed planetary missions. We examined several compounds relevant to the study of Europa and Enceladus using an iCERS Raman with a CW 405 nm,150 mW diode laser fiber coupled to the cavity. The fiber couple transmitted 17 mW of light into the cavity. Data was collected on an Horiba iHR320 spectrometer with a 1200 grooves per centimeter grating. We examined 17.6 mM acetic acid$_{(l)}$ (HAc), 4.0 mM glycine$_{(s)}$ and 31.2 mM methanol at 293K using 100 accumulations of a 3 s laser pulse for a total acquisition time of 300s. We also examined 1 wt% glycine mixed in 5wt% NaCl solution that was frozen at 200K using 20 accumulations of a 5 s laser pulse for a total of 100s exposure time.

Results and Discussion: Analysis of individual organics indicated good agreement with published Raman spectra from the Ruff database [24]. We were also able to detect 1 wt% glycine mixed in 5wt% NaCl (Figure 2), however, either lower wavenumber peaks were partially suppressed, likely due to ion interactions [2], or higher wavenumber peaks reflect stimulated Raman emission. We are currently in the process of determining which of these processes influences the observed spectra. If stimulated Raman emission does occur, it is possible that this will provide a benefit to detecting low concentration organics on icy worlds.

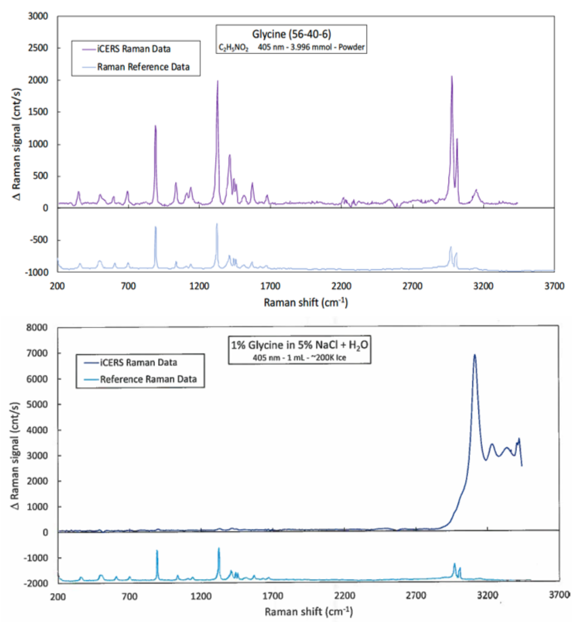

Figure 2: Raman spectra of (A) glycine powder and (B)1 wt% glycine in 5 wt% NaCl collected on the ERSO. ERSO data collected are purple (top line); reference Raman data are in blue (bottom line).

We are currently conducting experiments to determine the limit of detection for iCERS for a suite of amino acids in various brines and ices using a 266 nm deep UV laser, which will resolve the signal suppression observed in Figure 2. Results from this work will aid in addressing the technical readiness of the iCERS system relative to the stated Europa SDT objective 1 [20].

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