WHY RAMAN AND LIBS FOR EXPLORING ICY MOONS? P. Sobron[1], C. Lefebvre[1], A. Koujelev[1], A. Wang[2], [1]Canadian Space Agency, Canada (pablo.sobron@asc-csa.gc.ca), [2]Dept Earth and Planetary Sciences and McDonnell Center for Space Sciences, Washington University, St. Louis, USA.

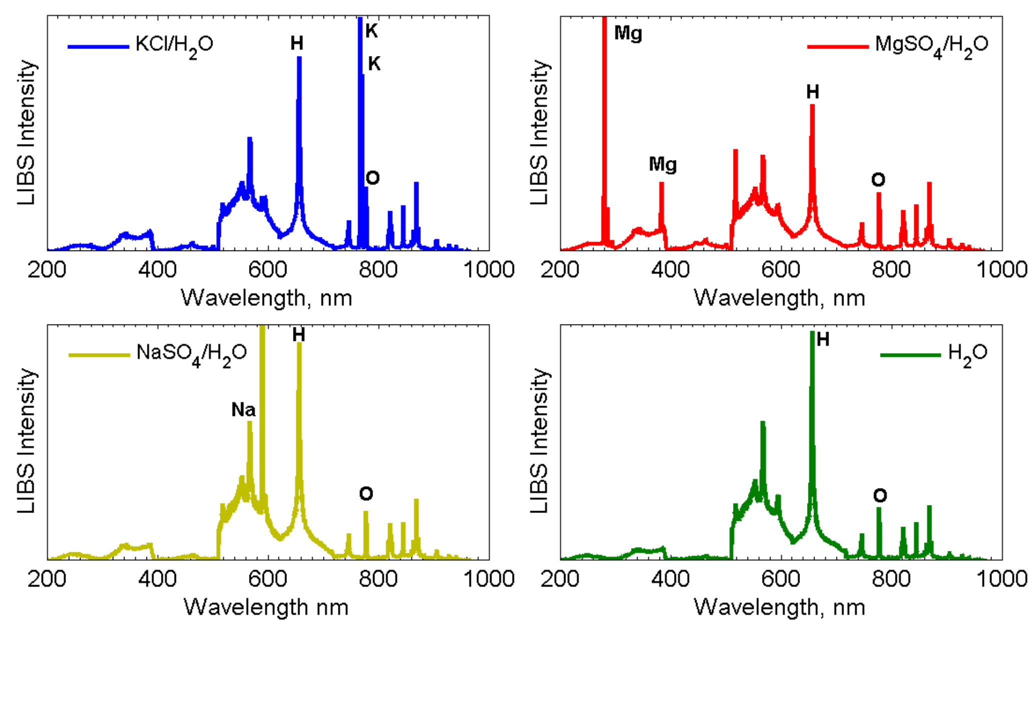
Past and Present Exploration of Icy Moons: Both Europa and Enceladus are thought to harbor liquid water oceans below their icy crusts; therefore, they are the most compelling locations to seek an answer to the question of whether life exists beyond our own planet. Besides characterizing the composition of their oceans, analysis of the composition of the icy crust is critical for determining the availability of nutrients; radiolysis may be a source of oxidants (1,2) for life that may be present in subsurface liquid reservoirs depleted in redox-pairs (3). The primary source of compositional information for the surfaces of Europa and Enceladus is orbital and flyby remote sensing through the Near Infrared Mapping Spectrometer (NIMS) and the Visual and Infrared Mapping Spectrometer (VIMS) instruments aboard the Galileo and the Cassini spacecrafts, respectively.

Based on NIMS data from Europa, McCord et al. (4) and Carlson et al. (5) have proposed the presence of hydrated salt materials, and frozen sulfuric acid hydrate. Laboratory spectral signatures that match NIMS data have also been recorded from brines (6), salt hydrates (7), chlorides and bromides/water mixtures (8), and even biological materials (6). On the other hand, Enceladus' surface and plumes are composed mostly of pure water ice, mainly in crystalline state, mixed with organics, carbon dioxide, and ammonia; amorphous water ice has also been detected using VIMS (9-11).

Future Missions to the Icy Moons: Remote sensing analyses of Europa and Enceladus materials has provided a wealth of information on the surface composition of these icy moons. However: (1) NIMS and VIMS are resolution (both spatial and spectral) limited; (2) we have limited understanding of the possible range of materials that may occur on the surface of both icy moons; (3) we have not yet characterized the chemical and radiolytic processes that might alter the surface materials. To answer these questions and other question related to the possibility of life in these icy planetary bodies, concepts of landed missions are currently under development by NASA and ESA (12,13).

Raman+LIBS, a Case of the Right Tool for the Right Job: During a surface exploration mission, laser Raman and laser-induced breakdown spectroscopy (LIBS) techniques are uniquely suited tools for detailed mineralogy and geochemistry investigations on planetary bodies including Mars, the Moon, and Venus, (14-16), as well as for icy planetary bodies. In addition to working in contact mode (in situ), the major advantage of stand-off Raman and LIBS is the ability conduct rapid analyses of targets at distances, ranging from <1 to tens of meters. This capability allows identify potentially interesting samples to be examined in further detail by additional in-situ payload instruments.

The advantages of combining both techniques for the analysis of a given sample are evident: LIBS can reveal the relative concentration of major (and often trace) elements present in a bulk sample, whereas Raman yields information on the individual mineral species and their chemical and structural nature. Thus combining the data from both tools enables definitive mineral phase identification with precise chemical characterization of most major and minor and some trace mineral species. In the context of planetary surface exploration, a combined can provide a rapid mineralogical/chemical evaluation of the target that will be



very useful for selecting samples to be eventually collected for sample return purposes, or for selecting sample sites to be drilled in the search for other species (e.g., organics).

In this paper we show the Raman and LIBS spectra of mixtures of water ice with salts and organics that may be representative of the materials on icy planetary bodies in our solar system and discuss their spectral features.

LIBS data: Figure 1 shows the LIBS spectra of ionized H_2O and frozen supersaturated solutions of KCl, $MgSO_4$, and $NaSO_4$ in water. The spectra were recorded at -25 °C and 1020 mbar of air with instrumentation described in (17). The emission lines related to H and O were monitored at 656.3 and 777.4 nm, respectively. K, Mg, and Na are monitored at 766.6, 285.6, and 568.8 nm, respectively, although many more lines related to the emission of these elements are also present throughout the spectral range analyzed. In general, our preliminary results show that LIBS can be used to analyze water ice and ice/salt mixtures, and major and minor elemental species can be readily identified by their characteristic emission lines. We are currently analyzing these LIBS spectra to define the limits of detection for key elements, and to develop quantitative analysis methods to accurately determinate elemental abundances in these icy mixtures.

Raman data: Figure 2 shows the Raman spectra of several mixtures, including a mixture of Ca, Mg, Na, and K-sulfates and H_2O ice (sulfates/H_2O). The spectra were obtained at -50 °C. A particular characteristic of the vibrational spectrum of ice and ice mixtures is the strong intermolecular couplings between neighboring molecules as a consequence of the networking of hydrogen bonds; thus, the in-phase and out-phase couplings and other intermolecular water interactions have to be considered for the correct interpretation of the spectra. In the Figure 2, we have labeled some of the molecular vibrational modes readily identified in the analyzed samples, which in turn inform about potential associated ions, thus complementing LIBS.

Conclusion: We have demonstrated that the elemental and molecular features of water ice mixed with salts and organics, relevant to icy planetary bodies, can be qualitatively analyzed using laser Raman and LIBS instrumentation. Current efforts by our group are focused in developing quantitative methods for the determination of species' abundances in complex mixtures. Our preliminary results are encouraging and warrant further investigation of the use of these two techniques for scientific investigations in future landed missions to the icy planetary bodies.

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