

EXPLORING EUROPA WITH RAMAN AND LIBS. P. Sobron, Carl Sagan Center, SETI Institute, Mountain View, CA & MalaUva Labs, St. Louis, MO (psobron@seti.org).

Past and Present Exploration of Europa: Remote sensing has provided a wealth of sometimes-contradictory information on Europa's surface composition. McCord et al. (1) reported the ubiquitous presence of hydrated salts, mostly magnesium sulfate hydrate within a water ice matrix. Carlson et al. (2) proposed a simpler explanation that the material is frozen sulfuric acid hydrate, which could be abundant (3). Shirley et al. (4) suggested that combining cryogenic spectra of sulfuric acid hydrates, brines, and salt hydrates provides the best spectral matches to the NIMS spectra. Recently, Brown and Hand (5) reported the first detection of magnesium sulfate salts, thought to be a radiation product of ocean material transported to the surface. Water vapor ice plumes have been observed on Europa (6), thus potentially confirming this hypothesis. More recently, Hand and Carlson have suggested that long, dark fractures on Europa's surface may actually be made of irradiated NaCl, which could have emerged to Europa's surface from its liquid ocean below (7).

Remote sensing provides valuable information on the composition of Europa. However, obstacles remain: (i) the low spatial and spectral resolution of existing instrumentation, (ii) the insensitivity of reflectance spectroscopy to chlorides, (iii) our limited understanding of the range of materials that may occur on the surface, and (v) our limited understanding of the weathering processes that alter them. These obstacles compromise attempts to characterize Europa's surface accurately, and attempts to characterize the moon's interior.

Future Missions to Europa: To address these challenges, and to answer question related to the possibility of life on Europa, Congress has directed NASA to expand the 2022 Europa mission by adding a small lander. The main goal of the lander would be to sample material from the (surface-exposed) interior ocean to see if the chemicals needed to support life are present and whether complex organic molecules suggesting biotic or pre-biotic activity exist.

Raman+LIBS, a Case of the Right Tools for the Right Job: The laser Raman technique enables more definite phase identifications than reflectance methods because: (a) water is a poor scatterer – OH and H₂O vibrations can be resolved in LRS; (b) Raman spectroscopy is extremely sensitive to slight changes in molecular structures and so provides fingerprint spectral profiles; (c) unlike reflectance spectroscopy, Raman lends itself to the study of chlorides because Raman bands associated with cation-Cl and OH-Cl can

be readily identified and analyzed. For example, **Figure 1** shows the Raman spectra of icy mixtures. The sample labeled *Sulfates / H₂O* is a mixture of Ca, Mg, Na, and K-sulfates and H₂O. The spectra were obtained at -50 °C, using 5-10 second acquisition times. Raman spectra of other ice-sulfate and ice-organic mixtures have also been reported (8). These results highlight three advantages of Raman that are critical for Europa exploration: (a) there are strong, Raman-active intermolecular couplings between neighboring molecules as a consequence of hydrogen bond networks; (b) the Raman spectral bands of in- and out-phase couplings and other intermolecular water interactions facilitate the accurate identification of icy materials; (c) we can perform real-time (< 10 s) Raman analysis of such materials.

An additional advantage of LRS is that measures of crystallinity can be derived by ratioing the intensities of the OH stretching vibrations at 3138 cm⁻¹ and 3360 cm⁻¹, as we've shown previously (9).

In LIBS the atomic spectral lines from plasma emission are used to determine elemental composition. **Figure 2** shows LIBS spectra of H₂O and frozen supersaturated solutions of KCl, MgSO₄, and NaSO₄ in water. The spectra were recorded at -25 °C and 1020 mbar of air, using a one-second integration time. The emission lines of H and O were monitored at 656.3 and 777.4 nm, respectively. K, Mg, and Na were examined at 766.6, 285.6, and 568.8 nm.

These results show that LIBS is a powerful tool for analyzing water ice and ice/salt mixtures in real time (< 1s), and that major and minor elemental species are readily identifiable with their characteristic emission lines. The strong LIBS signals allow quantitative analysis methods to be used for accurately determining elemental abundances in icy mixtures.

The advantages of combining both techniques for *in-situ* analysis on Europa are clear: 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 and organic species and their chemical and structural nature. Thus combining the data from both tools enables definitive phase identification with precise chemical characterization of most major and minor and some trace species. In the context of Europa exploration, a combined instrument can provide rapid mineralogical/organic/chemical evaluations. In addition to working in contact mode, the major advantage of stand-off Raman and LIBS is the ability conduct rapid analyses at distances ranging from <1 to 10s of meters.

Figure 1

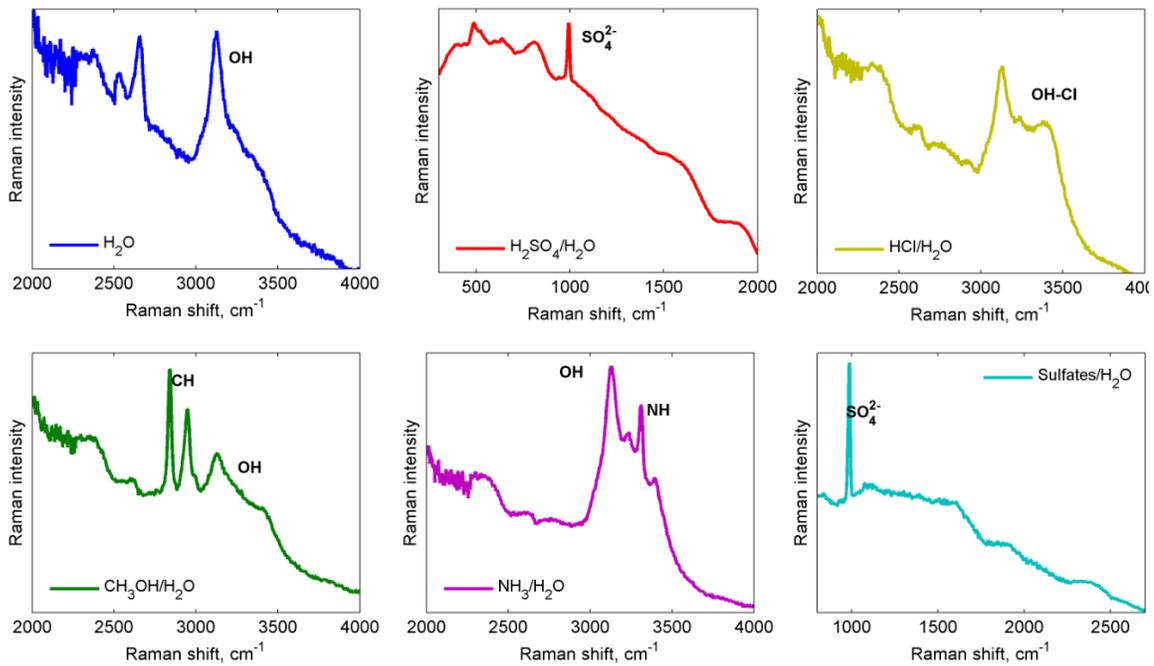
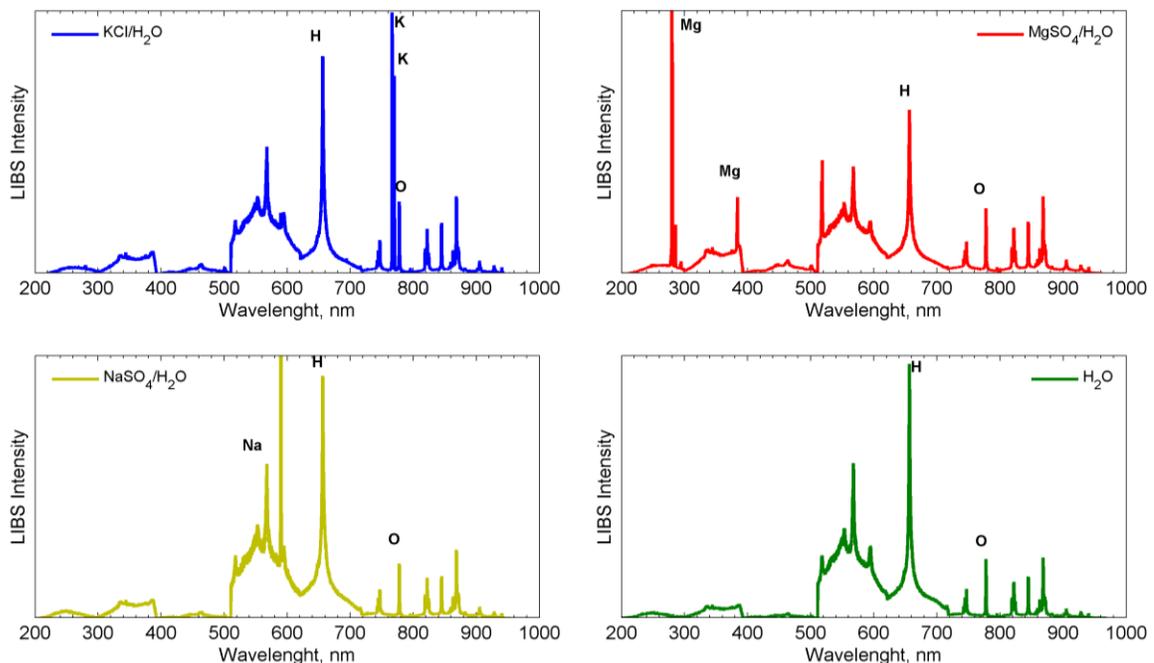


Figure 2



Conclusion: The elemental and molecular features of water ice mixed with salts and organics relevant to Europa can be qualitatively and quantitatively analyzed using laser Raman – a superior tool for the analysis of icy materials – and LIBS – a definitive technique for the characterization of elemental species – instrumentation. Our groups at the Carl Sagan Center and MalaUva Labs are currently developing and maturing new instrument concepts for the *in-situ* exploration of Europa, including instrument requirements, concepts of operation, and science-driven measurement strategies for the exploration of Europa.

References: (1) T. B. McCord et al., JGR 104, 11827 (1999). (2) R. W. Carlson et al., Icarus 177, 461 (2005). (3) H. E. Maynard-Casely et al., JGR Planets 118, 1895 (2013). (4) J. H. Shirley et al., Icarus 210, 358 (2010). (5) M. E. Brown, and K. P. Hand, The Astronomical Journal 145, 110 (2013). (6) L. Roth et al., Science 343, 171 (2014). (7) K. P. Hand and R. W. Carlson, GRL 42, 3174 (2015). (8) S. K. Sharma et al., LPSC 2014. (9) F. Rull et al., Spectrochimica Acta Part A 80, 148 (2011).