LOW-TEMPERATURE RAMAN SPECTROSCOPY OF MATERIALS RELEVANT FOR PLANETARY EXPLORATION. P. Sobron, Alian Wang. Dept. Earth and Planetary Sciences and McDonnell Center for Space Sciences, Washington University, St. Louis, MO, 63130 USA (psobron@levee.wustl.edu).

**Introduction:** Raman spectroscopy is based on the Raman effect, which is the inelastic scattering of photons by molecules. A small fraction of the scattered photons (10^6 to 10^9) from a sample is wavelength-shifted (from the wavelength of excitation source) by Raman effect[1]. The wavelength shift depends on the molecular bondings and the crystalline structure in the sample interrogated by the excitation laser beam. Raman photons exhibit distinct energies (i.e., wavelengths) and scattering efficiencies (fingerprint spectral pattern) for particular molecular species and their structure. Therefore, the chemical composition and the structure of a given solid, liquid or gaseous sample can be discerned from its characteristic Raman spectrum. The Raman spectral features can vary as a function of temperature. The change of Raman peak positions, peak widths and peak intensities results from anharmonic terms in the potential energy of molecular vibrations[2], explained in terms of the thermal expansion of the crystal[3].

Raman spectroscopy will be used for the first time on another planetary surface during the ExoMars mission. A Raman spectrometer placed inside the rover will analyze martian subsurface powdered samples obtained by a deep drill. Although no data on working temperature inside of ExoMars rover has been publicly disclosed by the European Space Agency to our knowledge, we can expect the temperature in the analytical laboratory to be somewhere between -40 and +10 °C during the Raman experiments. As outlined above, the Raman spectral features of the analyzed samples will be influenced by the temperature at which the Raman spectra will be acquired. Our objective is to quantify these changes, to evaluate and to correct the temperature effects towards the phase identification and characterization that will be made by a flight laser Raman spectrometer (RLS) during the ExoMars mission.

For that purpose, we have installed a Raman probe inside our newly built Planetary Environment and Analysis Chamber (PEACH)[4] to monitor the changes in the Raman peak properties as a function of temperature. The Raman spectra collected in this paper have been processed using a set of routines that include noise reduction algorithms based on the Fast Fourier Transform, baseline calculations through linear interpolation, band Fourier self-deconvolution, and peak fitting algorithms based on the Marquardt method.

In this paper we report the characterization of the bands features of H2O and several hydrated sulfates as a function of temperature. We have selected these materials since hydrated minerals are particularly important for the characterization of the saline mineral assemblages identified at the martian surface and the putative aqueous solutions necessary for their formation. This has implications in martian surface processes and Mars’ hydrological history. On the other hand, the investigation of the structural properties of ice in planetary bodies (e.g., Mars ice caps, Europa, asteroids…) may reveal clues about formation processes and constraints (mainly pressure and temperature) and atmosphere-surface materials interactions.

**O–H vibrations in H2O and hydrated sulfates:**

The stretching vibrational modes of H2O are in the 3000-3800 cm^-1 Raman spectral range are often used to study the hydration state of minerals[5,6] and to investigate the structural properties of ices[7]. The design of the PEACH[4] allows for *in situ* and non-invasive monitoring the evolution of the Raman peaks associated to O–H vibrations in any kind of sample as a function of variable temperature. To illustrate the effect of temperature in the spectral features of H2O, Fig. 1 shows the normalized and offset Raman spectra of water and water ice at different temperatures in the 2600-4000 cm^-1 range. The spectrum of liquid water (21 and 11 °C) is a complex envelope contributed by the symmetrical (ν_s) and asymmetrical (ν_a) stretching vibrations of O–H bonds in H2O and the second overtone of symmetric bending of H2O–H bonds, as well as intra- and intermolecular couplings. The spectral profile observed in the subzero spectra corresponds well with those observed in the spectra of ice Ih (a distribution of four molecules in a hexagonal cell) reported by Whalley[7]. From 21 to -76°C, we can readily observe a notable peak intensity decrease of the ν_s mode near 3410 cm^-1 and a peak position downshift of the ν_s mode from 3211 to 3114 cm^-1 as temperature decreases. These observations are consistent with the strong dependence of the O–H stretching vibration of water with the hydrogen bond strength; lowering the temperature increases the strength of hydrogen bonding.

To evaluate the effect of temperature in the H2O/OH stretching spectral region of hydrated minerals, we have recorded Raman spectra of synthetic epsomite (MgSO4·7H2O), starkeyite (MgSO4·4H2O), gypsum (CaSO4·2H2O), and bassanite (CaSO4·0.5H2O) in the range 21 to -95 °C. The normalized and offset spectra of the MgSO4·7H2O temperature-series is plotted in Fig. 2 (H2O/OH modes only). The spectra of MgSO4·7H2O show overlapped O–H stretching vibrations and overtone of H-O-H bending.
vibrations in structural water. Peak widths decrease as temperature is lowered. This allows for a better deconvolution of the overlapped Raman peaks and a more accurate characterization of the peak features. This reduction in peak widths is mainly due to a decrease of the thermal broadening at low temperature. Another interesting effect associated to sample cooling is the arising of new peaks at low temperatures (-95 °C). This phenomenon seems to be due to an increase of structural ordering of the water molecules in epsomite crystal lattice and the formation of a low-temperature form of MgSO$_4$·7H$_2$O that has a specific stability field[8].

Figure 3 shows the normalized and offset spectra of the CaSO$_4$·2H$_2$O at different temperatures. The two distinct bands arise as a consequence of the presence of two water molecules at two crystallographic distinct sites within the unit cell of gypsum. The higher wavenumber peak is assigned to the ν$_3$ mode of H$_2$O whereas the lower wavenumber mode is ascribed to the ν$_1$ mode[9]. The decreasing Raman shift and the narrowing for the ν$_3$ mode has been explained in terms of the strengthening of hydrogen-bonding and weakening of the O-H bond as temperature decreases[10].

**Conclusion:** The Raman spectroscopic measurements inside the PEACh reported here have demonstrated the potential to monitor, and more importantly, to quantify temperature-effects in the Raman spectral features of hydrated salts. We have characterized peak shifts and peak narrowing as a function of temperature for other Mars relevant minerals. The results will be reported in detail at the conference.

**Acknowledgment:** The construction of PEACh and this study were supported the McDonnell Center for Space Sciences at Washington University in St. Louis. We acknowledge partial support from several NASA grants NNG05GM95G (ASTID), NNX07AQ34G (MFRP), NNX10AM89G (MFRP), #853076 (MRO), #39361-6452 (MER), #1295053 (MoO for ExoMars), #09-030 (MIDP).