

Raman Spectral Analysis of Mars-Analogue Brines at Low Temperatures. D. P. Mason¹ and M. E. Elwood Madden^{1,2}, ¹University of Oklahoma School of Geosciences, 100 Boyd St., Norman, OK 73069; ¹daniel.p.mason-1@ou.edu, ²melwood@ou.edu

Introduction: Raman spectrometry is an ideal tool to analyze the geochemical make up of various compounds, be they solid, liquid, or a combination of the two. Previous work [1] demonstrated that Raman can accurately measure solute composition and concentration in high salinity brines. This research seeks to determine how changes in temperature impact the spectral signatures of various Mars-analogue brines saturated with sulfate, perchlorate, and chloride salts. This will allow a reference dataset to be created, which will facilitate analysis of unknown samples of high salinity brines *in-situ* on other planetary bodies. This will help expand our understanding of the composition of various Solar System bodies thought to contain ice or water-- including Mars, Ceres, Europa, Enceladus, Titan, and other icy moons, and provide an additional tool to use in the search for extraterrestrial life.

Methods: We used both a 532 nm green and a 785 nm red laser with a Renishaw InVia High Resolution Raman Microscope, as well as a Linkam THMS 600/720 temperature-controlled stage to collect spectra from brines over a range of temperatures (200-295K). Twelve solutions of various sodium, magnesium, or calcium chloride, sulfate, and/or perchlorate salts were created in the lab. Seven of these solutions (ultrapure water, Na₂SO₄, NaCl, NaClO₄, Na₂SO₄, MgSO₄, MgCl₂, and CaCl₂) were saturated endmember solutions, while five of them (MgSO₄-NaCl, MgSO₄-NaClO₄, Na₂SO₄-NaCl, Na₂SO₄-NaClO₄, and NaCl-NaClO₄) were created as 50/50 mixtures (by volume) of the saturated endmember brines. All solutions were cooled from room temperature to 200 K, then warmed slowly as spectra were collected over a 95 K temperature range using the Linkam THMS system.

Results: The spectra changed as a function of both temperature and brine composition. While the spectral signature of a liquid chloride brine is similar to that of liquid ultrapure water, the liquid sulfate brines have distinct, identifiable peaks at 982 cm⁻¹. Similarly, liquid perchlorate brines have distinct peaks at 935 cm⁻¹. While both the sulfate and perchlorate peaks are prominent in their spectra, when these brines are mixed, the perchlorate peak appears much more intense than the sulfate peak.

The spectra also change as the brines freeze to form ice. This is best observed in the 3100 to 3600 wavenumber region when using the green laser (Figure 1). When liquid, this portion of the spectra appears as a single broad peak caused by the OH bonds of the water

stretching [2]. When solid, this portion of the spectra has a number of sharper peaks. The exact location of these peaks is dependent upon the composition of the brine.

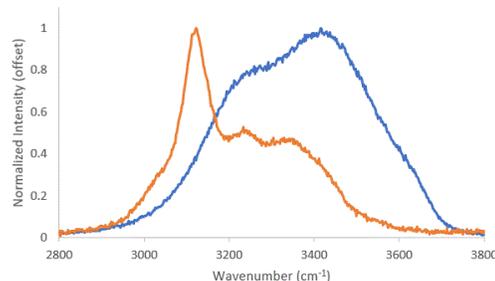


Figure 1: Raman spectra (532 nm green laser) of ultrapure water at 295K (blue) and 200K (orange). While liquid water produces a broad peak, ice produces one sharp peak and two smaller peaks at 200K.

OH-stretching band in mixed brines. Shifts in the peak position depend upon the composition of the brine and are most apparent when examining the mixed brines (e.g. a brine of 50% by volume MgSO₄ and 50% by volume NaCl). For example, in a pure NaCl brine at 295 K, the OH-stretching peak is observed at 3453 cm⁻¹, while in pure MgSO₄ the peak is at 3438 cm⁻¹ and the peak becomes significantly broader. When these brines are mixed, the peak appears at 3443 cm⁻¹ (Figure 2). The mixed brine, therefore, is an average of the OH-stretch peak position between the two end member brines.

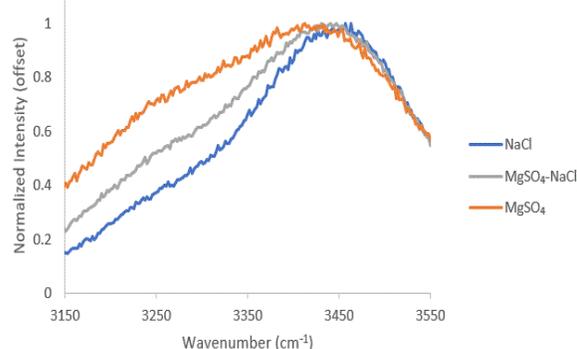


Figure 2: The shift in the OH-stretching band between MgSO₄, NaCl, and MgSO₄-NaCl solutions at 295 K.

This change is even more noticeable at lower temperatures when the brines freeze. At 200 K, a noticeable peak is observed at 3406 cm⁻¹ in the mixed

brine spectra, while in the endmember NaCl brine spectra, this is observed at 3424 cm^{-1} . No sharp peaks are observed in the pure MgSO_4 ; instead, the broad hump maximizes at 3370 cm^{-1} (Figure 3).

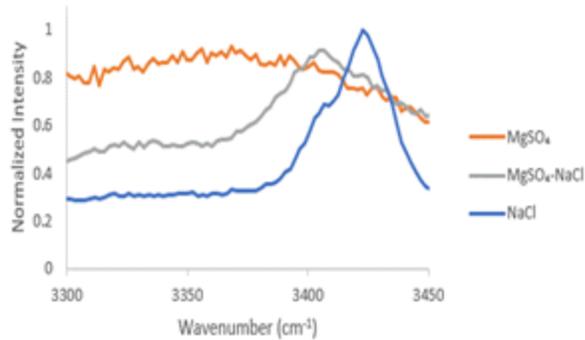


Figure 3: The shift in the 3400 cm^{-1} peak position between the MgSO_4 endmember, the NaCl endmember and the MgSO_4 -NaCl mix brines at 200K.

Effects of freezing rate. We tested the effects of cooling rate on sulfate peak position by cooling the solution at different rates (100, 20, 10, or 5 K/min) and observing how the main sulfate peak position responded. This was tested using a magnesium sulfate brine with the 532 nm green laser and resulted in a bimodal distribution in peak position. At room temperature, the sulfate peak was observed at 982 cm^{-1} in all the endmember and mixed brines containing sulfate salts. When the brine was cooled from 295 K to 200 K at either 100 or 20 K/min, the peak shifted to 987 cm^{-1} . When the solution was cooled over the same interval at a slower rate, 10 or 5 K/min, the peak shifted to 990 wavenumbers (Figure 4). These different peak positions are likely due to the different hydration states of the solid magnesium and sodium sulfate ices [3, 4, 5], forming minerals like meridianiite ($984\text{--}990\text{ cm}^{-1}$), epsomite (984 cm^{-1}), or mirabilite ($988\text{--}990\text{ cm}^{-1}$), as the differently hydrated minerals would lead to slightly different sulfate peak positions.

The Raman data collected for sulfate, chloride, and perchlorate brines at varying temperatures will be instrumental in helping to identify characteristics of unknown samples, including the solid-liquid phase transition, the rapidity of cooling, and the overall chemical composition of *in-situ* brines. This in turn will allow for a more thorough understanding of the role of brines in the Solar System. It is likely that these data and observations will grow in importance in the coming years, as more missions seek to utilize Raman spectroscopy.

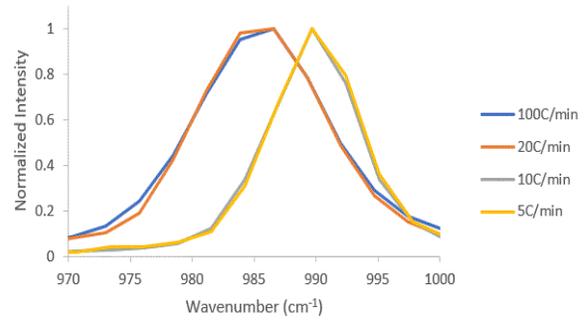


Figure 4: Bimodal distribution of the main MgSO_4 sulfate peak at 200K after the solution is cooled at different rates—slower cooling resulted in a peak at 990 cm^{-1} , while more rapid cooling resulted in a peak around 987 cm^{-1} .

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References: [1] McGraw, L. E. and McCollom, N. D. (2018) *ACS Earth and Space Chemistry*, 2, 1068-1074. [2] Duričković, I. and Clavier R. (2011) *J. Raman Spectrosc.*, 42, 1408–1412 [3] Wang, A. and Freeman, J. (2006) *Geochimica et Cosmochimica Acta*, 70, 6118–6135 [4] Genceli, F. and Horikawa S. (2009) *Journal of Glaciology*, 55, 117–122. [5] Ben Mabrouk, K. and Kauffmann K. H. (2013) *Journal of Raman Spectroscopy*, 44, 1603–1608.