

RAMAN SPECTROSCOPY AS A TOOL TO IDENTIFY BRINE FORMATION. E. Fischer¹, G. M. Martínez^{1,2} and N. O. Rennó¹, ¹Department of Climate and Space Sciences and Engineering, University of Michigan, Ann Arbor, MI, USA, ²Lunar and Planetary Institute/USRA, Houston, TX, USA.

Introduction: Pure liquid water is not stable at present-day Mars conditions. It would rapidly evaporate in the extremely dry Martian atmosphere and freeze at most times of the Martian day due to the low temperature. Brines, highly saline solutions of salts in water, on the other hand, can have a much reduced freezing point and evaporation rate and are therefore the most likely form of temporarily stable bulk liquid water on the surface or in the shallow subsurface of Mars. Perchlorate salts are among the most promising candidates for Martian brine formation. These salts have been detected in the Martian regolith in polar latitudes by the Phoenix lander [1], in mid-latitudes by the Mars Reconnaissance Orbiter [2], as well as in equatorial latitudes by the Curiosity rover [3].

Two methods of brine formation on Mars have been suggested. The first is brine formation by deliquescence, where the hygroscopic salt absorbs atmospheric water vapor when the humidity passes a threshold, the deliquescence relative humidity [4-7]. The second method is brine formation by lowering the melting point of water ice through contact with salts in the regolith [6,8]. Since perchlorate salts are suggested to be distributed globally [9], this would happen wherever water ice such as frost or subsurface ice is in contact with the regolith and the temperature is above the eutectic temperature of the brine.

Here, we show experimentally obtained Raman spectra of the above mentioned materials involved in brine formation on Mars and analyze their characteristics that can aide in their identification in more complex in-situ measurement campaigns on Mars. As an example of a perchlorate salt we use $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ due to its low eutectic temperature of 199 K [11] and its ubiquity on Mars [1-3].

Methodology: All our Raman spectra, except the reference spectrum of pure liquid water, were obtained under Martian pressure, temperature and relative humidity conditions in the Michigan Mars Environmental Chamber (MMEC). The MMEC can simulate the full range of Martian surface conditions. The chamber and full experimental setup are described in detail in [6,8,10]. The Raman spectrometer used in this study is a Kaiser Optical Systems Inc. RamanRXN1 with a 532 nm laser. Our study focuses on two Raman band regions with the strongest signal of the materials studied: the perchlorate symmetric stretching band between ~ 900 and 1000 cm^{-1} and the O-H stretching band between ~ 3000 and 3800 cm^{-1} [10]. We further

used Gaussian decomposition with baseline subtraction to determine individual peak positions, full widths at half maximum and relative amplitudes to quantitatively analyze the obtained spectra.

Results: We obtained Raman spectra of pure liquid water at ambient conditions, water ice and calcium perchlorate tetrahydrate at 190 K and 800 Pa (to prevent deliquescence or hydration state changes), calcium perchlorate brine at 255 K and 800 Pa, and calcium perchlorate salt recrystallized out of a brine at 190 K and 800 Pa [10].

Table 1 lists the observed peaks of the decomposed spectra obtained from the samples. These values, obtained under idealized laboratory conditions, can be used to identify perchlorate brines in in situ measurements on Mars.

	ClO_4 band	O-H band
H_2O (l)		3230(217), 3420(218), 3540(206), 3620(109)
H_2O (s)		3046(99), 3115(57), 3227(206), 3336(56), 3399(140)
$\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$	939(16)*, 952(9)	3115(81)*, 3249(113)*, 3437(147)*, 3437(27), 3467(23), 3487(15), 3509(25), 3536 (23), 3560(155)*, 3602(13), 3630(18)
$\text{Ca}(\text{ClO}_4)_2$ saturated in H_2O	936(17)	3256(219)*, 3495(249), 3555(106)
$\text{Ca}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$ recrystallized	934 (13)	3311(271), 3389(66), 3456(38), 3496(31), 3520(19), 3543(17), 3546(132)

Table 1: Decomposed peak positions and widths (in parentheses) of the Raman spectra shown in this study. Asterisks indicate weak peaks with low intensities. [10]

Pure Liquid Water and Ice. Fig. 1 shows the Raman spectra of pure water at ambient conditions (top) and water ice at 190 K and 800 Pa (bottom). The four observed wide Gaussian peaks for liquid water are similar to those reported in [12]. The first two are ice-like components whereas the other two are unique for liquid water. In our experiments the 3230 cm^{-1} peak increased in wavenumber with decreasing temperature, while the 3420 cm^{-1} peak decreased in wavenumber with decreasing temperature. Both show a rate of change of $\sim 0.2\text{--}0.5 \text{ cm}^{-1}/\text{K}$. We also observed an

increase of the 3230 cm^{-1} peak's relative intensity compared to the 3420 cm^{-1} peak with decreasing temperature [10,13]. Of the five Gaussian peaks for water ice, the two with the highest wavenumber coincide with the ice-like peaks in the liquid water spectrum. The prominent 3115 cm^{-1} peak has the strongest intensity and can be used as an indicator of the presence of water ice in a sample. Similar to liquid water, the ice wavenumbers decrease by $\sim 0.3\text{--}0.5\text{ cm}^{-1}/\text{K}$ with decreasing temperature.

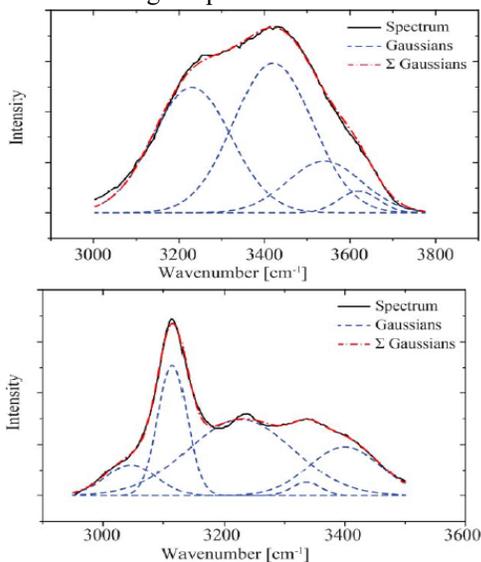


Fig. 1: Decomposition of the Raman spectrum of liquid water (top) and water ice (bottom) in the O-H stretching band. [10]

Crystalline Calcium Perchlorate Tetrahydrate. Fig. 2 shows the Raman spectrum of this salt in the O-H stretching band. It shows a number of very narrow peaks, typical for crystalline hydrated perchlorates [6]. The prominent peak at 952 cm^{-1} in Table 1 is representative of the tetrahydrate. Impurities of higher hydration states result in the weak 939 cm^{-1} peak.

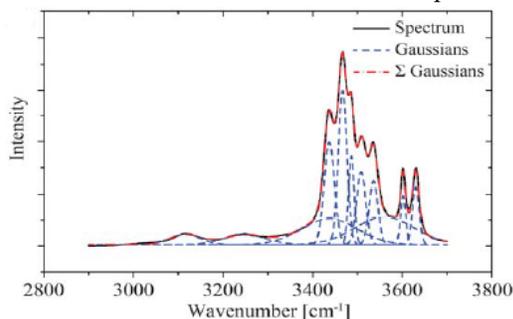


Fig. 2: Decomposition of the Raman spectrum of hydrated perchlorate salt in the O-H stretching band. [10]

Calcium Perchlorate Brine. Fig. 3 shows the Raman spectrum of the saturated brine in the O-H stretching band. The perchlorate band shows that the tetrahydrate peak of the crystalline salt has completely shifted to 934 cm^{-1} , typical for perchlorate solutions.

The O-H band shows three wide peaks at similar positions to those of the pure liquid water sample, but shifted to higher wavenumbers. Additionally the highest wavenumber peak is much more intense in the solution compared to pure water and its relative intensity increases with the saturation level.

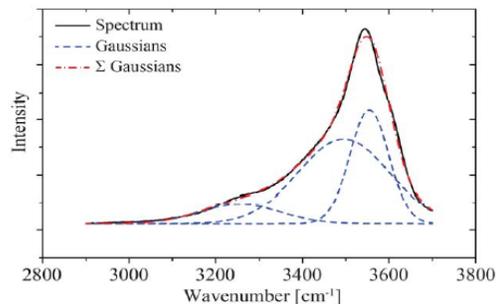


Fig. 3: Decomposition of the Raman spectrum of saturated perchlorate solution in the O-H stretching band. [10]

Recrystallized Calcium Perchlorate. Table 1 shows that the perchlorate band of the recrystallized salt shows a single peak at 934 cm^{-1} , indicating that it is not the tetrahydrate but a higher hydration state. In the O-H band we see a return to the narrow peaks indicative of the crystalline hydrated perchlorate salt.

Discussion and Conclusions: Our spectra provide a reference for the detection of perchlorate salt hydrates and liquid brine of perchlorate salts in the Martian soil. While the perchlorate band can be used to distinguish different hydration states of salts, the O-H band can help identify and distinguish liquid brine and crystalline hydrated salts. A change in the O-H spectrum from the numerous narrow peaks to the wider water-like peaks are a clear indication of brine formation. Furthermore, our reference spectra of water ice at Martian conditions can aid in the identification of thin ice layers such as surface frost by Raman spectrometer onboard landers and rovers. These results show that Raman spectroscopy is a useful tool for liquid water detection on Mars.

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