

Searching for brine on Mars using Raman spectroscopy

Erik FISCHER¹

¹Department of Climate and Space Sciences and Engineering, University of Michigan, Ann Arbor, MI, USA, erikfis@umich.edu.

Recibido: 25/04/2016

Aceptado: 18/09/2016

Abstract

In the last few years, water ice and perchlorate salts capable of melting this ice and producing liquid solutions have been discovered at the surface and shallow subsurface of Mars. In addition to via melting of ice, perchlorate salts may also form liquid solutions by absorbing water vapor when the relative humidity is above a certain threshold in a process known as deliquescence. Formed either by melting or deliquescence, liquid solutions (brine) are the most likely way of liquid water activity on the Martian surface and in the shallow subsurface and are therefore important to understand the habitability of Mars. Using Raman spectroscopy, we provide reference spectra of various mixing states of liquid water, water ice and calcium perchlorate, all of which can occur during brine formation. We focus on the perchlorate symmetric stretching band and the O-H stretching vibrational band to distinguish brine from crystalline salt and water ice. We show that perchlorate brines can be identified by analyzing the peaks and their widths in the decomposed Raman spectra of the investigated samples. This serves as an important reference for future in-situ Raman spectrometers on Mars, such as those on the ExoMars and Mars 2020 rovers and can aid in the detection of brine formation on Mars.

Key words: Mars; water; brine; Raman spectroscopy; perchlorate.

Detección de salmueras en Marte mediante espectroscopia Raman

Resumen

En los últimos años se han descubierto hielo de agua y sales de perclorato en la superficie y subsuelo de Marte capaces de fundir este hielo. Además de vía fusión del hielo, las sales de perclorato pueden formar soluciones líquidas al absorber vapor de agua cuando la humedad relativa supera un determinado límite en un proceso denominado deliquesencia. Formadas bien por fusión o por deliquesencia, las soluciones líquidas (salmuera) son la forma más probable de actividad de agua líquida en la superficie y subsuelo poco profundo de Marte y, por lo tanto, son importantes para comprender la habitabilidad de este planeta. Mediante el uso de la espectroscopia Raman, obtenemos espectros de referencia de varios estados mixtos de agua líquida, hielo de agua y perclorato de calcio, todos los cuales pueden tener lugar durante la formación de la salmuera. En este artículo nos centramos en la banda de *stretching* simétrica de perclorato y en la banda de *stretching* vibracional O-H para diferenciar la salmuera de la sal cristalina y del hielo de agua. Demostramos que la salmuera de perclorato puede ser identificada mediante el análisis de los picos y anchura en el espectro Raman de-compuesto de las muestras estudiadas. Nuestro análisis es importante para la posible detección de salmuera en Marte mediante la comparación con medidas de espectrómetros Raman que operarán a bordo de los vehículos exploradores Exomars y Mars 2020.

Palabras clave: Marte; agua; salmuera; espectroscopia Raman, perclorato.

Summary: Introduction 1. Methods and Setup 2. Results 3. Discussion 4. Conclusion. Acknowledgements. References.

Normalized Reference

Fischer, E. (2016). Searching for brine on Mars using Raman spectroscopy, *Física de la Tierra*, Vol., 28, 181-195.

Introduction

Liquid water is one of the ingredients needed for potential past or present habitability of Mars. One of the likely forms in which liquid water can temporarily form and persist on the Martian surface or in the shallow subsurface is in a salty solution as brine. The salt stabilizes the liquid state against the low pressure and temperature environment. Other possible forms of liquid water are undercooled liquid interfacial water, subsurface melt water and ground water (Martínez and Renno, 2013). Here, we focus on brine because it is the most likely form of temporarily stable bulk liquid water on the surface or in the shallow (~10 cm) subsurface of Mars.

Perchlorate salts have been shown to be a promising candidate for brine formation on Mars. Perchlorate salts of calcium, magnesium and sodium were detected in-situ at the Phoenix landing site in Mars' northern polar region using data from the Wet Chemistry Laboratory instrument (Hecht et al., 2009; Kounaves et al., 2014), as well as at Gale crater using data from the Sample Analysis at Mars instrument (Glavin et al., 2013; Leshin et al., 2013). Furthermore, perchlorate salts have been detected at mid-latitudes using satellite measurements by the High Resolution Imaging Science Experiment and some studies indicate that they might temporarily produce brines, explaining the evolution of Recurring Slope Lineae (Ojha et al., 2015). Furthermore, evidence suggesting temporarily liquid brine has been observed by the Phoenix lander (Rennó et al., 2009). Two different types of brine formation from perchlorate salts have been suggested. One is brine formation by deliquescence, the absorption of atmospheric water vapor by hygroscopic salts (e.g. perchlorates) (Chevrier et al., 2009; Gough et al., 2011; Nuding et al., 2015). The other is brine formation by melting of water ice in contact with the salt (Fischer et al., 2014). Water ice has been detected in the shallow subsurface from mid-latitude to polar regions of Mars, both remotely using satellite measurements and in-situ (Boynton et al., 2002; Feldman et al., 2002; Mitrofanov et al., 2002; Byrne et al., 2009; Smith et al., 2009).

Raman spectroscopy is a useful tool to detect brine. In the upcoming years two ground-based missions are planned to use Raman spectroscopy to analyze surface material on Mars. The ExoMars Rover, to be launched in 2020, will carry a Raman spectrometer as part of the Pasteur instrument suite, primarily to search for biosignatures on Mars (Rull et al., 2013). Mars 2020 will carry the Scanning Habitable Environments with Raman and Luminescence for Organics and Chemicals (SHERLOC) instrument, a Raman spectrometer used to detect organic compounds

(Beegle et al., 2014). Here, we show Raman spectra of material samples involved in the formation of brine on Mars. We show spectra for water ice, liquid water, hydrated calcium perchlorate, calcium perchlorate brine, saturated calcium perchlorate brine and hydrated (solid) calcium perchlorate that has been dried out from a solution. We focus on brines formed from calcium perchlorate because of its very low eutectic temperature (~ 199 K) (Marion et al., 2010). This low eutectic point allows a possible brine to stay liquid for long parts of the diurnal cycle. Furthermore, calcium perchlorate is the most common perchlorate salt at the Phoenix landing site and Gale crater (Kounaves et al., 2014; Glavin et al., 2013). Our spectra have been obtained in the Michigan Mars Environmental Chamber (MMEC), a custom chamber able to accurately simulate Martian conditions in pressure, temperature and relative humidity. The goal of this study is to give an overview of the type of Raman spectra to expect when studying brine formation.

1. Methods and Setup

We obtained Raman spectra under Martian conditions using a combination of the MMEC and a Raman spectrometer. The MMEC is a cylindrical chamber with internal measurements of 64 cm in diameter and 160 cm in length, used for Martian environmental simulations and instrument testing (Figure 1). Pressure control is achieved by a dry scroll vacuum pump in combination with an MKS 653B butterfly valve and an MKS 1651C pressure controller. The chamber pressure can be adjusted between 10 and 10^5 Pa and bone-dry CO_2 is used as the Martian air simulant. The sample temperature can be set between 145 and 500 K using LN_2 in combination with Watlow cartridge heaters and is controlled by a Watlow EZ-ZONE[®] temperature controller and thermocouples. The MMEC uses a temperature controlled water bath to add water vapor to the chamber atmosphere for relative humidity control. A Buck CR1-A chilled mirror hygrometer is used to monitor the relative humidity at the sample. The entire range in relative humidity from ~ 0 to 100% can be simulated.

The Raman spectrometer used in this study to acquire the sample spectra is a Kaiser Optical Systems Inc. RamanRXN1 unit operating at a wavelength of 532 nm, with a spectral range of $100 - 4375$ cm^{-1} , a power at the sample of 74 mW and a 17 inch standoff distance. This allows for the sensor head to operate from outside the vacuum chamber through a viewport. The spectrometer was calibrated using a neon light source, white light and cyclohexane. The spectral resolution is 1 cm^{-1} . All spectra were obtained by accumulating seven laser exposures of the sample with an integration time of 7 s each. We focus on the Raman spectroscopic regions of the perchlorate symmetric stretching band at $\sim 900 - 1000$ cm^{-1} and the O-H stretching vibrational band at $\sim 3000 - 3800$ cm^{-1} to detect characteristic peaks of the tested materials.

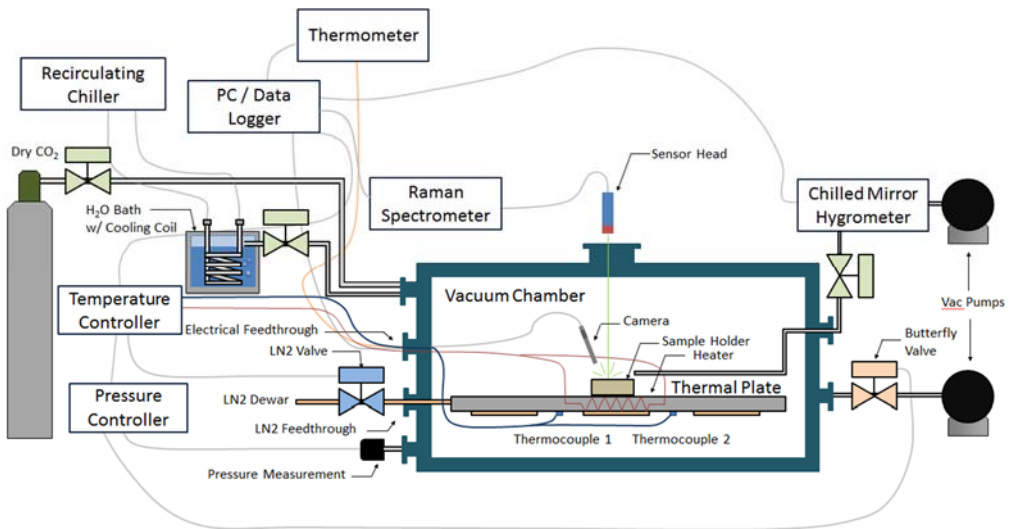


Figure 1. Setup of the Michigan Mars Environmental Chamber (MMEC).

We chose calcium perchlorate tetrahydrate for simulating Martian brine as it is a likely brine candidate due to its ubiquity on Mars, its hygroscopic properties and its low eutectic temperature (Hecht et al., 2009; Kounaves et al., 2014; Glavin et al., 2013; Leshin et al., 2013; Ojha et al., 2015; Marion et al., 2010). Other perchlorate hydrates like those of sodium or magnesium show similar spectra as calcium perchlorate (Fischer et al., 2014), but especially magnesium perchlorate tends to show fluorescence when excited by a 532 nm laser. Lower wavelengths have shown to be successful in preventing this (Nikolakakos and Whiteway, 2015).

We use a 0.3 cm^3 cylindrical sample holder cup for all experiments. For the liquid water spectrum it was filled with 0.15 cm^3 of distilled water. The spectrum was taken at ambient pressure and temperature to prevent evaporation. All remaining spectra were obtained at a Martian pressure of 800 Pa. To obtain the water ice spectrum we froze distilled water at 190 K. We obtained Raman spectra of a thin layer ($< 2 \text{ mm}$) of calcium perchlorate tetrahydrate with average particle diameter $< 300 \text{ }\mu\text{m}$ at 190 K to prevent hydration state changes or deliquescence. We chose this particle size because particles of this size can be transported by saltation on Mars and may accumulate locally (Kok and Renno, 2009). Next, we obtained a Raman spectrum of an unsaturated calcium perchlorate solution (brine) with a concentration of about 600 g/L and a saturated brine, both at $\sim 255 \text{ K}$. We obtained the saturated brine spectrum by letting excess water evaporate from the solution at $\sim 255 \text{ K}$ until the salt recrystallized while regularly taking Raman spectra. The final spectrum is of calcium perchlorate, recrystallized from a brine by evaporation of the water. The sample was inspected visually and no liquid component was found after the water was evaporated

for 10 hours. The spectrum was then taken after the sample was cooled to 190 K to compare the recrystallized calcium perchlorate with the original salt at the same temperature and to ensure that any remaining solution has frozen.

We use Gaussian decomposition to analyze the obtained spectra quantitatively. A baseline is subtracted and each spectrum is decomposed into a number of Gaussian curves. The Gaussians' positions, full width half at half maximum (FWHM) and their relative amplitude are obtained. We imposed the condition that each local maximum (outside of the noise) has to be resolved and that the final fit shows an $\bar{R}^2 \geq 98\%$. It should be noted that the accuracy in peak position in the decomposition is greater with more narrow peaks, and wider peaks present a larger uncertainty in the exact position of the Gaussian.

2. Results

Here we show Raman spectra and their Gaussian decompositions of six materials and mixtures that are related to the formation of brine on Mars. In-situ spectra will likely be more complex mixtures of these materials or mixtures with other materials, the most likely being the regolith. The spectra shown here are obtained under simplified mixture conditions to develop a database for comparison with more complex spectra that might be observed in-situ on Mars. All Gaussian decomposition peaks described here are summarized in Table 1.

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

	ClO₄ band	O-H band
H₂O (l)		3230 (217), 3420 (218), 3540 (206), 3620 (109)
H₂O (s)		3046 (99), 3115 (57), 3227 (206), 3336 (56), 3399 (140)
Ca(ClO₄)₂·4H₂O	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)
Ca(ClO₄)₂ solution	934 (13)	3282 (268), 3454 (178), 3582 (125)
Ca(ClO₄)₂ solution (saturated)	936 (17)	3256 (219)*, 3495 (249), 3555 (106)
Ca(ClO₄)₂·xH₂O (recrystallized)	934 (13)	3311 (271), 3389 (66), 3456 (38), 3496 (31), 3520 (19), 3543 (17), 3546 (132)

In the first experiment we obtained the Raman spectrum of pure liquid water at ambient conditions (Figure 2). The band of interest for liquid water is the O-H stretching vibrational band from $\sim 3000 - 3800 \text{ cm}^{-1}$. Since this is a pure liquid water,

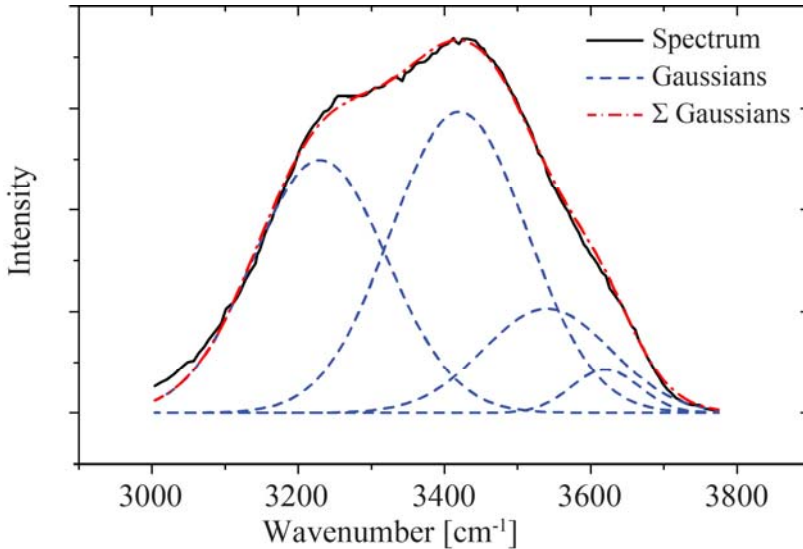


Figure 2. Decomposition of the Raman spectrum of liquid water in the O-H stretching vibrational band.

no peaks are observed in the perchlorate symmetric stretching band. The Gaussian decomposition shows 4 main components in the O-H band, similar to those reported by Zhang and Chan, (2003), at 3230, 3420, 3540 and 3620 cm^{-1} . The first two are ice-like components, while the other two are unique for liquid water. All four peaks show FWHM values greater than 100 cm^{-1} . Furthermore, there is a small temperature dependence of the peak positions and relative intensities observable between the 3230 and 3420 cm^{-1} peaks (Dolenko et al., 2000). We observed a shift of the 3230 cm^{-1} peak towards higher wavenumbers with decreasing temperature, while the 3420 cm^{-1} peak shifted towards lower wavenumbers with decreasing temperature. Both shifts show a rate of $\sim 0.2 - 0.5 \text{ cm}^{-1}/\text{K}$. We also observed an increase of the 3230 cm^{-1} peak's relative intensity compared to the 3420 cm^{-1} peak with decreasing temperature.

In the second experiment we obtained the Raman spectrum of water ice at various temperatures. Figure 3 shows the spectrum at 190 K. Similar to liquid water, the band of interest for water ice is the O-H stretching vibrational band. The Gaussian decomposition shows 5 peaks at 3046, 3115, 3227, 3336 and 3399 cm^{-1} . The latter two peaks coincide with the ice-like peaks in the liquid water spectrum. The 3115 cm^{-1} peak shows the strongest intensity and can be used as an indicator of the presence of water ice in a mixture. Similar to the 3420 cm^{-1} peak in the liquid water spectrum, the

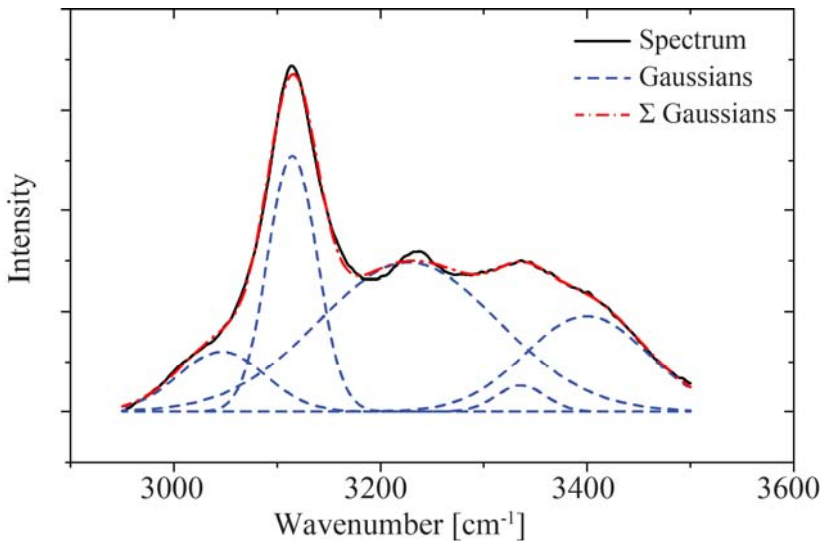


Figure 3. Decomposition of the Raman spectrum of water ice in the O-H stretching vibrational band.

peaks in the water ice spectrum shift towards lower wavenumbers with decreasing temperature at the same rate of $\sim 0.3 - 0.5 \text{ cm}^{-1}/\text{K}$. A non-negligible change in peak position with pressure was not observed, even for the large atmospheric pressure difference between ambient and Mars pressures.

In the third experiment we obtained the Raman spectrum of $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ at 190 K. There are two spectral bands of interest for perchlorate salts: the perchlorate symmetric stretching band ($\sim 900 - 1000 \text{ cm}^{-1}$) (Figure 4a) and the O-H stretching vibrational band (Figure 4b). The perchlorate band shows a prominent peak at 952 cm^{-1} , representative of the tetrahydrate. In the case of an anhydrous perchlorate salt, the perchlorate band shows a peak at 990 cm^{-1} and the O-H band does not show any peaks (Nuding et al., 2014). The minor Gaussian at 939 cm^{-1} in the perchlorate band might be due to a small amount of a higher hydration state in the sample. The O-H band shows a number of very narrow peaks at $3437, 3467, 3487, 3509, 3536, 3602$ and 3630 cm^{-1} , with FWHM values of less than 50 cm^{-1} , typical for crystalline hydrated perchlorates (Fischer et al., 2014). The first three low-intensity peaks at $3115, 3248$ and 3437 cm^{-1} are close in position and width to water ice peaks (see Table 1).

In the fourth experiment we obtained the Raman spectrum of a calcium perchlorate solution (brine) at 255 K, 56 K above the eutectic temperature and typical for midday temperature values at the Phoenix landing site (Savijärvi and Määttänen, 2010). The perchlorate stretching band (Figure 5a) shows a single Gaussian peak centered at 934 cm^{-1} , indicating that no $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ phase remains. The O-H band (Figure 5b) shows three wide Gaussian peaks centered at $3282, 3454$ and 3582

cm^{-1} , with FWHM values greater than 100 cm^{-1} . These peaks show strong similarities in position and width to the liquid water peaks described above, with only the highest wavenumber and lowest intensity water peak missing. The addition of the perchlorate to the water results in a shift of the liquid water peaks to higher wavenumbers. The exact shift cannot be quantified here, due to the above-mentioned uncertainty in exact position of the wide peaks. Another change from the pure water spectrum is the stronger relative intensity of the 3882 cm^{-1} peak due to the addition of the perchlorate salt. The intensity of this peak in the brine is similar to the two lower wavenumber peaks, while for pure liquid water its relative intensity was less than half.

In the fifth experiment we obtained the Raman spectrum of a saturated calcium perchlorate brine at 255 K. The perchlorate stretching band of the saturated solution (Figure 6a) shows no significant difference from the non-saturated case.

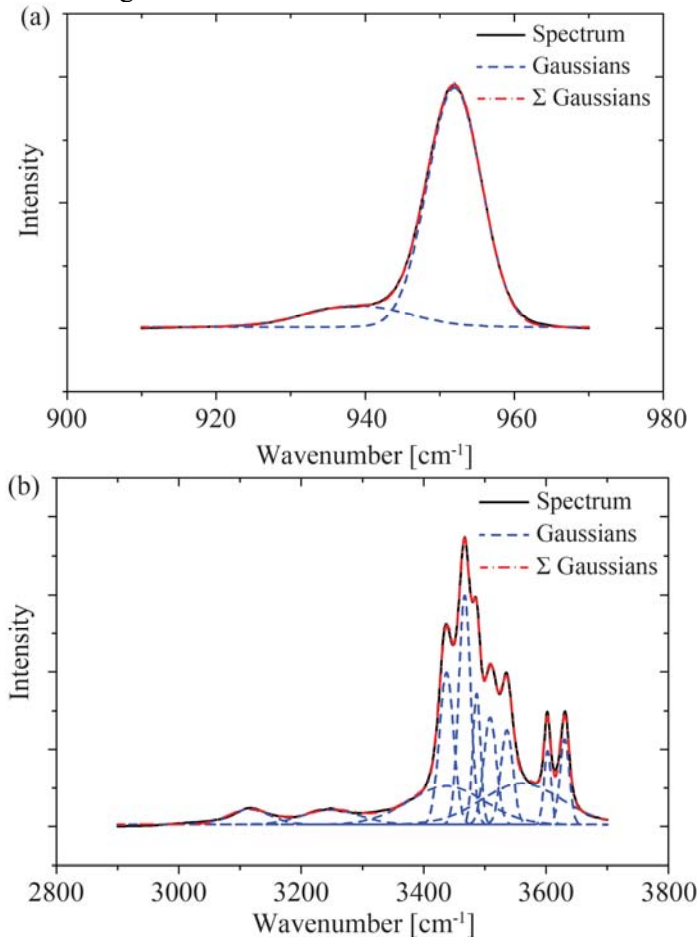


Figure 4. Decomposition of the Raman spectrum of hydrated perchlorate salt. (a) Perchlorate symmetric stretching band. (b) O-H stretching vibrational band.

The peak is centered at 936 cm^{-1} and no peak at higher wavenumbers appears in this band. The O-H spectrum shows 3 Gaussian peaks at 3256 , 3495 and 3555 cm^{-1} with FWHM values greater than 100 cm^{-1} . These positions and widths are comparable to those of the non-saturated case. The major difference lies in the relative intensities of the peaks. With an increasing perchlorate salt concentration in the solution, the

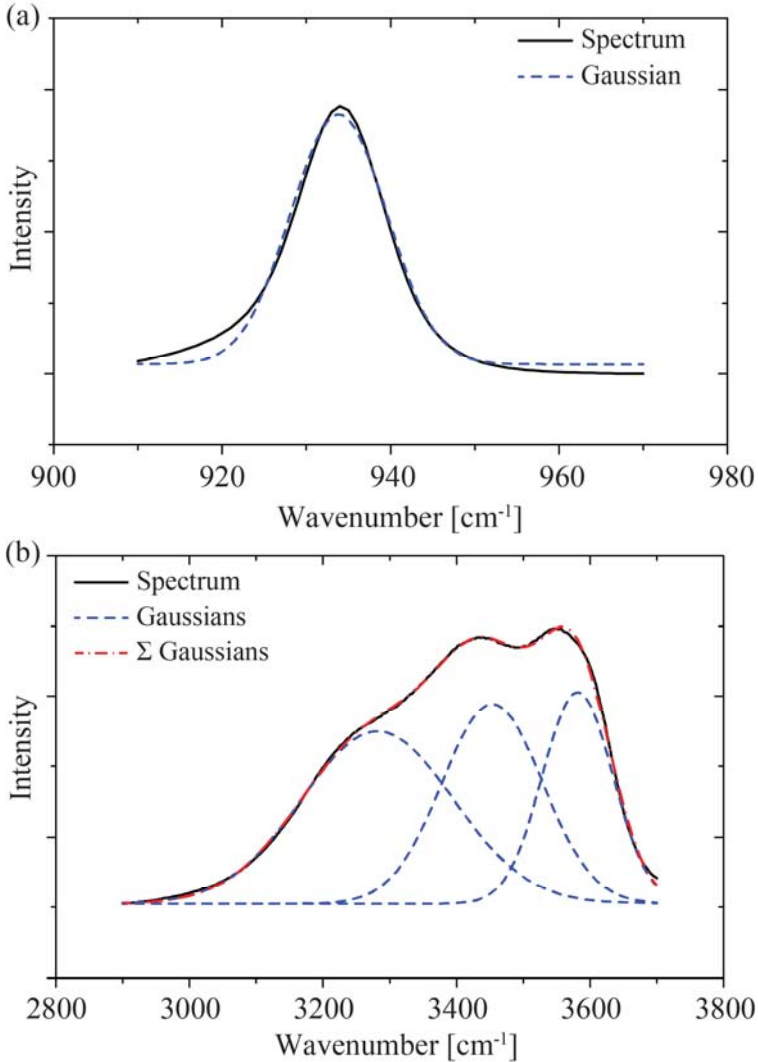


Figure 5. Decomposition of the Raman spectrum of a perchlorate salt solution. (a) Perchlorate symmetric stretching band. (b) O-H stretching vibrational band.

3555 cm^{-1} peak's relative intensity increases compared to those of the other two Gaussians in the O-H spectrum. We did not observe a continued trend of a peak position shift towards higher wavenumbers.

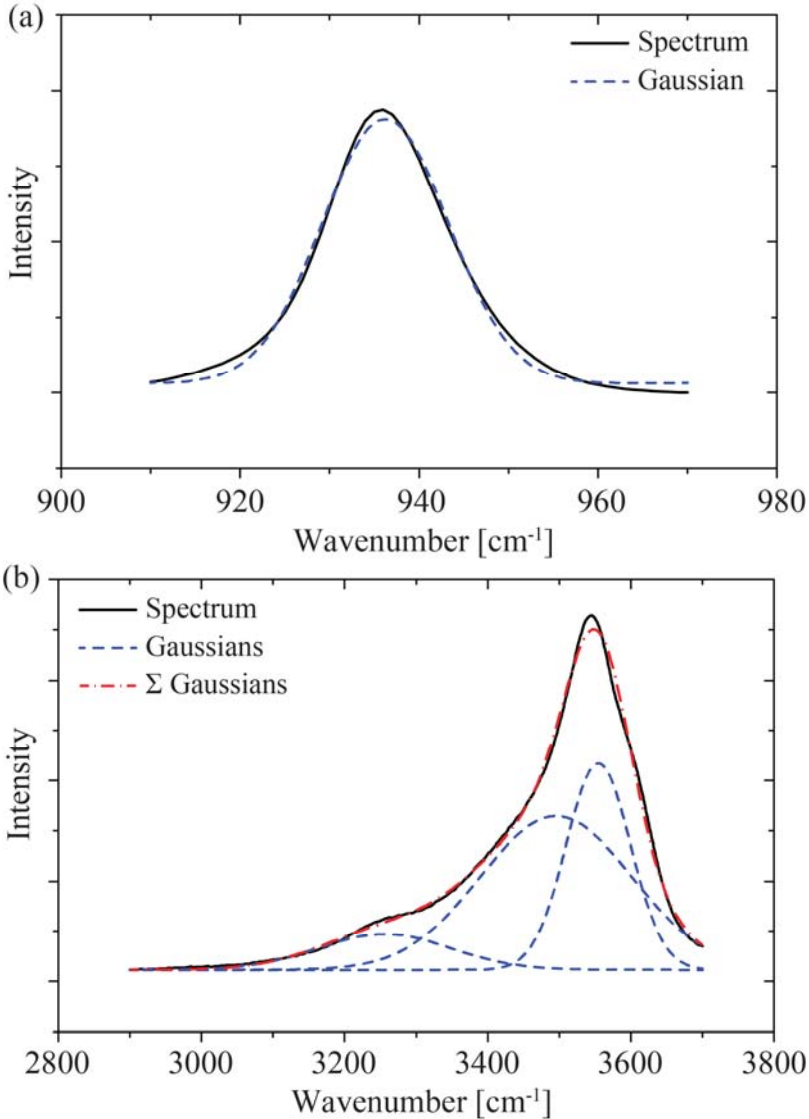


Figure 6. Decomposition of the Raman spectrum of a saturated perchlorate salt solution. (a) Perchlorate symmetric stretching band. (b) O-H stretching vibrational band.

In the sixth and final experiment we obtained the Raman spectrum of calcium perchlorate recrystallized from a solution to simulate a dried out brine under Martian

conditions. We ensured that the entire sample was dried out by stirring the sample and visual inspection. The spectrum was obtained at 190 K to compare with the original tetrahydrate. While the sample is crystallized and dried out, the perchlorate band (Figure 7a) shows a single Gaussian peak at 934 cm^{-1} , at the same position as for the liquid solution and lower than the 952 cm^{-1} peak of the calcium perchlorate tetrahydrate shown in Figure 4a.

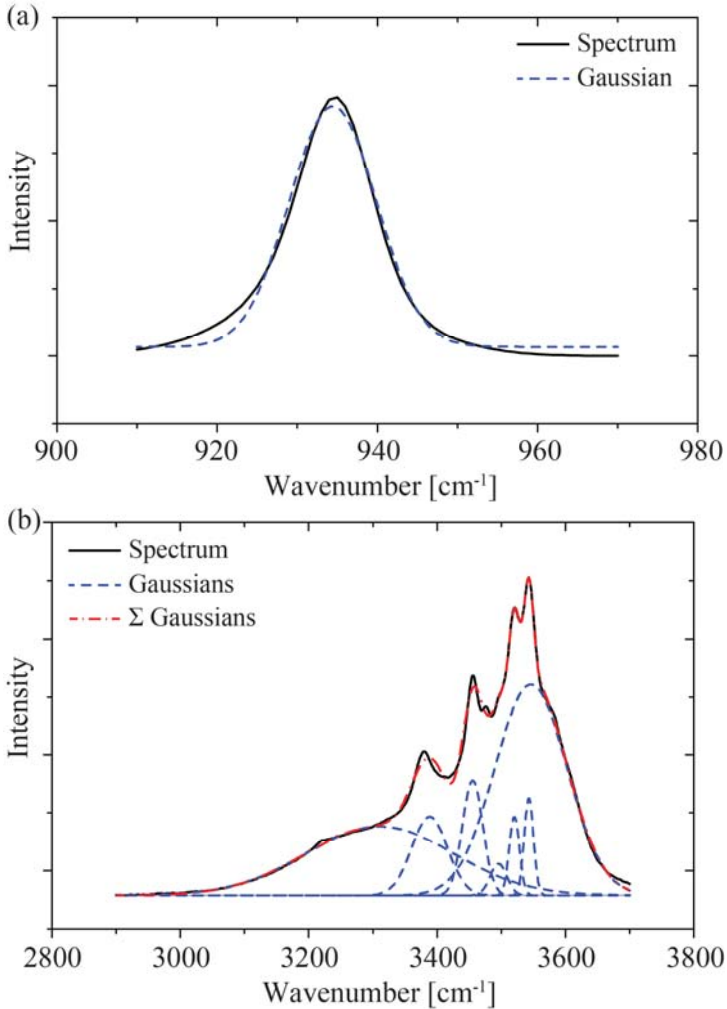


Figure 7. Decomposition of the Raman spectrum of a dried out perchlorate salt solution. (a) Perchlorate symmetric stretching band. (b) O-H stretching vibrational band.

The O-H band is more complex, showing two wide peaks (FWHM $> 100\text{ cm}^{-1}$) at 3311 and 3546 cm^{-1} , and five narrow peaks (FWHM $< 100\text{ cm}^{-1}$) with similar

positions and widths to those of the calcium perchlorate tetrahydrate shown in Figure 4b, showing that the salt is indeed crystalline again.

3. Discussion

The Raman spectrum obtained in the first experiment (Figure 2) serves as a reference for the detection of a liquid water state. Although pure liquid water is unlikely to exist at Martian atmospheric conditions, the existence of the wide Gaussian peaks (FWHM $> 100 \text{ cm}^{-1}$) around 3230 , 3420 and 3540 cm^{-1} in any obtained sample is strong evidence for the existence of a form of liquid water. This can help identifying any liquid water state in a mixed sample obtained in-situ on Mars. Care has to be taken with the 3230 and 3420 cm^{-1} water peak since they are both ice-like peaks and also existent in water ice.

The identification of water ice peaks in the second experiment (Figure 3) helps detecting subsurface ice on Mars as in the polar or mid-latitude regions for example (Smith et al., 2009; Rennó et al., 2009). Furthermore, frost events have been suggested at Gale crater (Martínez et al., 2015). Raman spectroscopy at equatorial latitudes can help identifying frost events such as those suggested.

The Raman spectrum of calcium perchlorate hydrate obtained in the third experiment (Figure 4a/b) provides a reference for the verification of the existence of perchlorate salt hydrates in the Martian soil using Raman spectroscopy. The positions and narrow widths of the decomposed peaks clearly differentiate the hydrated (but crystalline) perchlorate salts from their briny solutions. The appearance of the O-H peaks for the perchlorate salts indicate hydration from an anhydrous state. Further hydration state changes between hydrated states show shifts in the perchlorate vibration band. The wider peaks in Figure 4b at 3115 , 3248 and 3437 cm^{-1} typical for water ice (see Table 1) indicate that a small amount of water existed on the surface of the salt grains and froze when the temperature was lowered below the eutectic point. While the anhydrous perchlorate salts show a peak at $\sim 990 \text{ cm}^{-1}$, hydrated states shift this peak to lower wavenumbers, such as $\sim 952 \text{ cm}^{-1}$ for the calcium perchlorate tetrahydrate or 934 cm^{-1} for higher hydration states (Zhang and Chan, 2003).

Figure 5a/b shows the Raman spectrum of a calcium perchlorate brine. The differences in the O-H spectrum between the wide, water-like peaks here and the narrower, more numerous peaks described above for the crystalline salt, are a clear method to identify the onset of brine formation from a crystalline perchlorate salt. This may aide in the detection of brine pockets in the Martian soil. The perchlorate vibrational band also shows a clear shift from the 952 cm^{-1} peak of the crystalline salt to the 934 cm^{-1} peak here, implying that this is another indicator (although not definitive) of brine formation.

Figure 6 shows the impact of an increased salt concentration on the Raman spectrum when compared to Figure 5. While the perchlorate peak shows no significant difference with concentration, the relative intensity of the O-H peaks

changes dramatically. Increasing the perchlorate salt concentration in the solution increases the relative intensity of the third O-H peak at 3555 cm^{-1} , compared to the other two peaks. We assume that this is the most likely Raman spectrum to be encountered on Mars when looking at a perchlorate brine.

We investigate the recrystallized perchlorate salt spectrum in Figure 7 a/b to test the hypothesis that both the existence of the wide water-like peaks in the O-H band and the perchlorate band peak shift to 934 cm^{-1} are clear indicators of brine formation. The perchlorate vibrational band shows the single Gaussian peak at 934 cm^{-1} , in the same position as that of the liquid states, even though the sample was fully recrystallized. This suggests that the shift from 952 to 934 cm^{-1} observed for the liquid solution is not a sufficient indicator of the existence of a brine. We assume that this shift is an indicator of a change to a higher hydration state, such as calcium perchlorate octahydrate for example. Further research has to be performed to clarify this. The O-H vibrational band shows a return to the narrow ($\text{FWHM} < 50\text{ cm}^{-1}$) peaks in similar positions to those of the original calcium perchlorate tetrahydrate in Figure 4. This change in the O-H spectrum can be used to detect efflorescence of brine. Results of this experiment show that the O-H stretching vibrational band is better suited to distinguish between a solid perchlorate salt and a perchlorate brine.

4. Conclusion

The materials necessary to form brine at Martian conditions have been shown to exist from polar to equatorial latitudes on Mars. Perchlorate salts such as calcium perchlorate with their ability to form liquid solutions at very low temperatures are suggested to exist globally in the top layer of the Martian regolith. They can potentially form these brines by absorbing the limited amounts of water vapor from the atmosphere or by melting bulk water ice that exists at the surface of polar latitudes and in the shallow subsurface of mid to polar latitudes. Here we show decomposed Raman spectra of various materials or mixtures involved in this brine formation process. We focus on calcium perchlorate as our example perchlorate salt because of its very low eutectic temperature ($T_e \approx 199\text{ K}$). Other perchlorate salts known to exist in the Martian regolith, such as magnesium or sodium perchlorate, show similar spectra in the O-H and perchlorate bands. The spectra shown here serve as a reference for future studies and in-situ measurements by Raman spectrometers on future landers or rovers. We show that the O-H spectrum is preferential in the detection of brine due to its clear changes in peak positions and widths with the change from crystalline salt to a solution. The perchlorate spectrum also shows a clear shift in the peak positions with changes in hydration state and state of matter, but our experiments show that this shift by itself is not a sufficient indicator of a brine. Our results show that Raman spectroscopy is an excellent tool for the in-situ detection of brine on Mars. A large database of experimentally obtained spectra can aid in the identification of constituents in mixed samples on Mars.

Acknowledgments

Experimental data used to plot the figures can be requested from the first author at the corresponding email address. Funding for this project was provided by the NASA Astrobiology Program: Exobiology and Evolutionary Biology Award #09-EXOB09-0050.

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