

UNDERSTANDING CHLORINE SALT SPECTRA THROUGH COMPUTATIONAL METHODS WITH IMPLICATIONS FOR MARTIAN GEOCHEMISTRY. R. M. Huchmala¹, J. Hanley², G. E. Lindberg¹, and B. N. Horgan³. ¹Northern Arizona University, Flagstaff, AZ (rmh278@nau.edu); ²Lowell Observatory, Flagstaff, AZ (jhanley@lowell.edu); ³Purdue University, West Lafayette, IN.

Introduction: Detecting chlorine salts on Mars has become critical for determining the habitability of the planet. Higher concentrations of chloride, chlorate, and perchlorate salts suppress the freezing temperature of water resulting in lower activity brines. This affects the possibility of finding liquid water and ultimately life on Mars. These hydrated salts have been identified in Columbus Crater using CRISM images to determine the complex mineralogy, including chlorine and sulfate salts [1-3]. The spectral similarities between chlorine and sulfate salts has led us to analyze the spectra using a different approach in order to find slight differences between the salts.

Key features of the chlorine salt spectra investigated are shifts between hydration states, as well as the presence of the 2.15 μm absorption feature. Studying hydration state features can lead to the identification of a hydrated mineral along with determining the exact hydration state of salts seen on Mars. The 2.15 μm feature is characteristic of hydrated perchlorate salts and is used as an identifying feature in their detection on Mars [1,4]. Although the origin of this feature is currently unknown, this new approach may aid in understanding what fundamental vibrations could be combined to cause it.

Using quantum mechanical calculations, we have predicted fundamental vibrational modes of many chlorine salts common on Mars. This method will lead to data that can be used to identify the specific molecular stretches causing the absorption bands of interest. The fundamentals calculated can be scaled by harmonic approximations in order to reflect the wavelengths measured by CRISM. This will provide a better basis for understanding the shifts, overtones, and potential combination bands seen in the CRISM spectra.

Methods: First, a spectral rubric was prepared to define the absorption features of interest in the CRISM data [3,5]. This rubric was used as a starting point for investigating the vibrational modes causing these bands. Density functional theory as implemented in the Gaussian 09 [6] computational chemistry software package was used to calculate the vibrational modes. This theory uses exchange and correlation terms in order to provide a better solution to the idealized many electron problem. Starting with a single water molecule, the fundamental frequencies were calculated. These initial calculations were used to define calculation parameters such as the basis set,

number of steps, and level of theory. To better support the parameter designation, we used a single water molecule, perchlorate anion, and sodium cation. Sodium perchlorate monohydrate was chosen as the first salt to test because it has a single water molecule and has been detected on Mars [4]. The calculations consisted of two steps: first the atomic configuration was optimized to find a local minima in the potential energy, and second the vibrational frequencies were predicted for the structure. All of these values were calculated using the PBEPBE hybrid functional and using 3-21G and 6-31G split valence basis sets. Differing levels of basis sets were used in order to complete the calculations while keeping the computational cost low. The predicted vibrational modes showed similarities to the stretches observed in experimental studies of perchlorate salts [1,7]. Special attention was paid to the shifts in the water frequencies due to the addition of perchlorate. The differences between the fundamental frequency shifts and the frequency shifts in the near-infrared (NIR) were then compared. This showed promise that calculating the fundamental frequencies could be a viable resource in describing the NIR salt spectra.

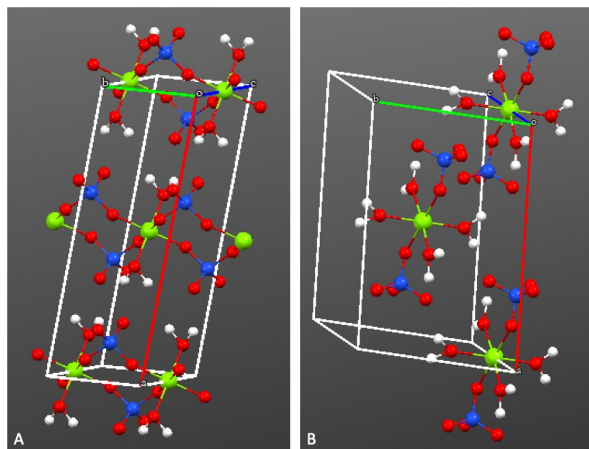


Figure 1: (A) One unit cell of $\text{MgClO}_4 \cdot 2\text{H}_2\text{O}$ (B) One unit cell of $\text{MgClO}_4 \cdot 4\text{H}_2\text{O}$. Both using data from Robertson and Bish [8]. In this structure, green represents magnesium, blue is chlorine, red is oxygen, and the white atoms are hydrogen. We are working toward systematically introducing complexity to predict the effect of the crystal environment on vibrational frequencies.

More complex structures are needed to account for intermolecular interactions. By using more than just the base components of the salt, the frequencies will shift with the influence of the surrounding atoms. Starting with the magnesium perchlorate crystal structures found by XRD by Robertson and Bish [8], we are using the same procedure described above using one unit cell (Fig. 1). By running these calculations on the dihydrate, tetrahydrate, and hexahydrate states of magnesium perchlorate we will be able to introduce greater complexity therefore revealing trends in frequency shifts resulting from changes in the molecular environment. Although it has been determined that the $\text{MgClO}_4 \cdot 6\text{H}_2\text{O}$ hydration state is the most abundant on Mars [8], using all of the characterized states will provide us with enough data to describe these hydration shifts and relate them to the amount of water within the structure. Finally, the overtones and combinations of the fundamental frequencies described in Bishop et al. [7], will be used as a comparison to these methods to better describe the absorption bands found in the CRISM spectra and their relation to perchlorate salts.

Results: First, the calculated vibrational modes of water were compared between the initial calculations. The frequencies calculated from a single water molecule and a water molecule with one sodium cation and a perchlorate anion were converted to microns so they could be compared to the experimental results in Hanley et al. [1]. Each frequency was analyzed and related to a specific stretch or bend. The three IR active modes of water are a symmetric bend, symmetric stretch, and an asymmetric stretch of the hydrogens. These three frequencies can be observed and compared between calculations showing the differences between hydrated and non-hydrated chlorine salt spectra (Table 1). The observed band shifts in the calculations lined up with shifts seen experimentally, and scale appropriately when considering the overtones observed as opposed to the fundamental modes.

Implications and Future Work: We have shown that these calculations have the potential to model the band shifts seen in the salt spectra. If the single unit cell of magnesium perchlorate calculations are successful, we will be able to take the fundamentals defined by the vibrational frequency calculations and determine overtones and shifts observed in the NIR. These findings may be able to better describe the absorption features of the NIR data that was collected from CRISM, ultimately helping to determine the concentrations of perchlorate, chlorate, and chlorine salts in Columbus Crater and elsewhere on Mars.

Table 1: *Fundamental IR active modes of water. Band shifts are calculated by subtracting the frequency from the $\text{NaClO}_4 \cdot 1\text{H}_2\text{O}$ by the frequency of the H_2O molecule alone. These shifts closely resemble the shifts in the bands seen between hydrated and non-hydrated salt spectra from Hanley et al. [1]*

Type of Water Stretch	Band Frequency (water only) (μm)	Band Frequency (water and perchlorate) (μm)	Band Shift due to Perchlorate (μm)
Symmetric Bend	6.27	6.37	0.10
Symmetric Stretch	2.85	2.88	0.03
Asymmetric Stretch	2.73	2.77	0.04

We intend to use the calculated modes as predictors of the shifts seen due to the presence of water leading to the ability to better define hydration states of similar salts based on the overall structure of the spectra. If we are able to compare the frequency ranges between various chlorine salts to their structures, then we can also apply this method to other chlorine salts and eventually sulfate salts known to exist on the Martian surface and within the salt ring in the Columbus Crater. These calculations will provide stricter limits on the range of frequencies for specific features and hydration levels in the NIR making it easier to identify these salts on Mars.

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