# Understanding Chlorine Salt Spectra Through Computational Methods with Implications for Martian Geochemistry

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# Motivation: Columbus Crater

- Continued exploration of Mars has led to a need to characterize the toxicity and habitability of the planet.
- We have focused on Columbus Crater which contains a “Bathtub Ring” of hydrated minerals.
- By mapping the distribution of these minerals, we can determine potentially toxic areas.

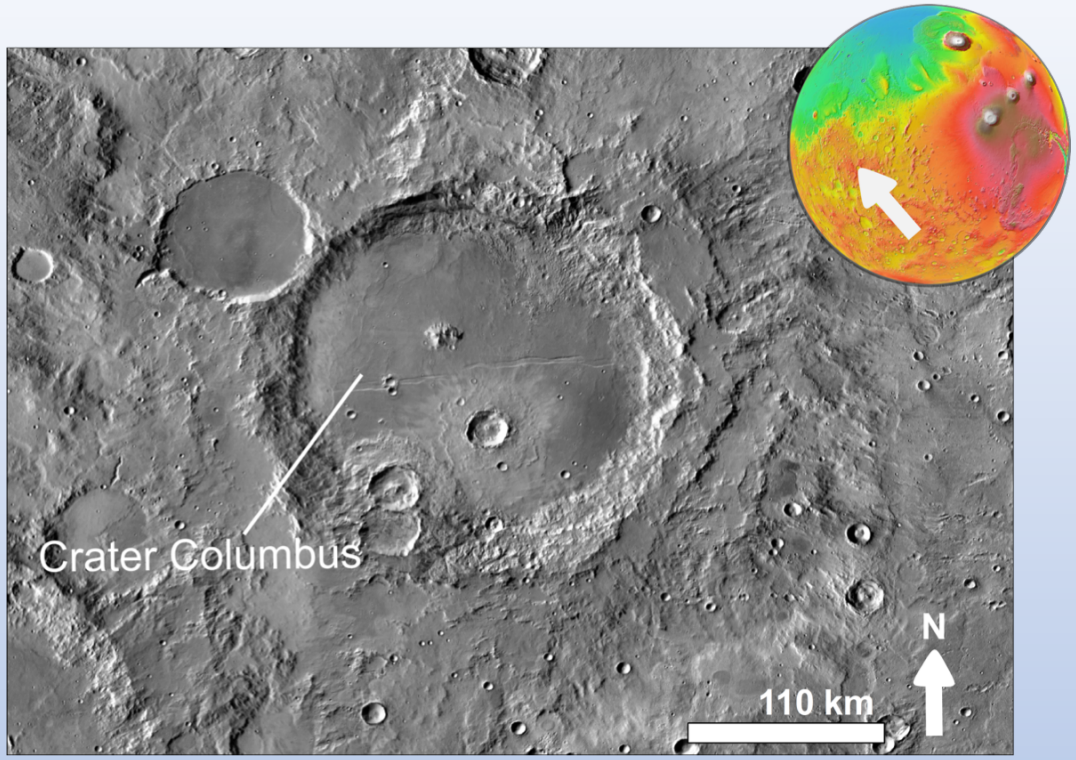



Image complied from: NASA THEMIS and MOLA data

“Bathtub Ring”

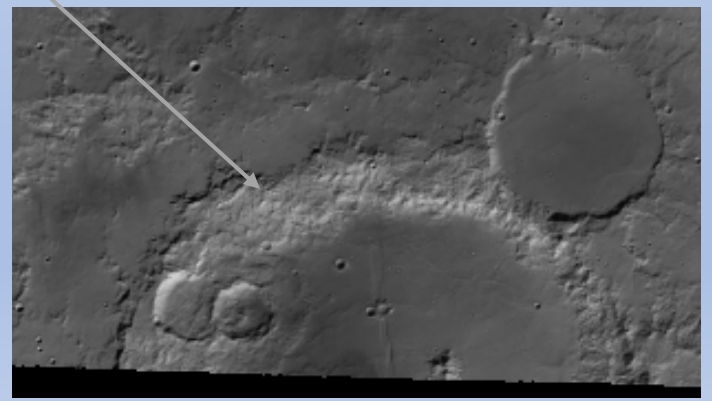


Image from: MEx HRSC (H0538_0000_DA4) Credit: ESA/DLR/FU Berlin

# Data: Compact Reconnaissance Imaging Spectrometer

- The Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) collects visible and infrared spectra.
- For each pixel of a CRISM image, there is a corresponding spectra in the wavelength range from 0.362-3.92 microns.
- Using the near-infrared spectra, we can start to distinguish minerals in the salt ring of Columbus Crater.

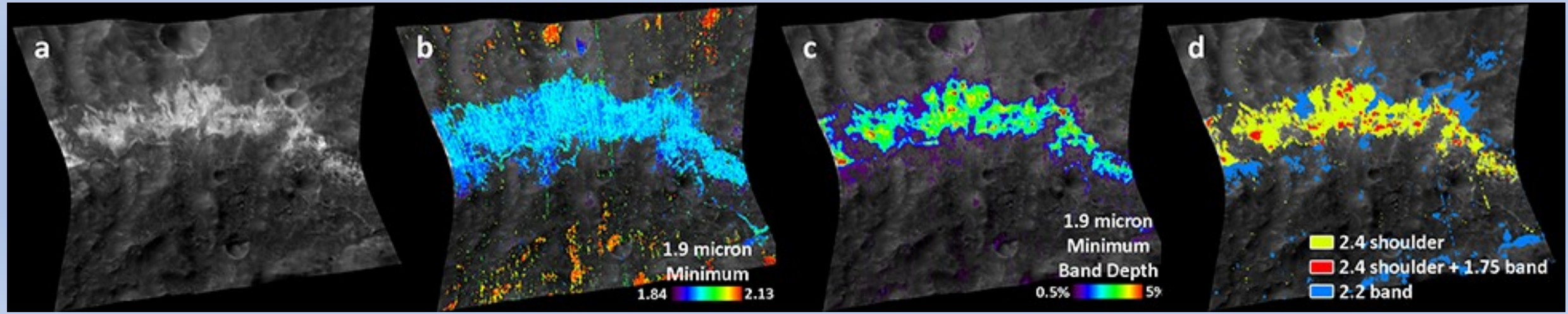



*Image From: Hanley et al, LPSC (2017)*

# Making the Distinction

- Laboratory spectra from Hanley *et al.* [2015] show bands for magnesium perchlorate hexahydrate at 2.12 µm and 2.20 µm that are unique, but a result of some unknown cause.
- Could finding possible causes of these absorptions be the key to making the distinction?

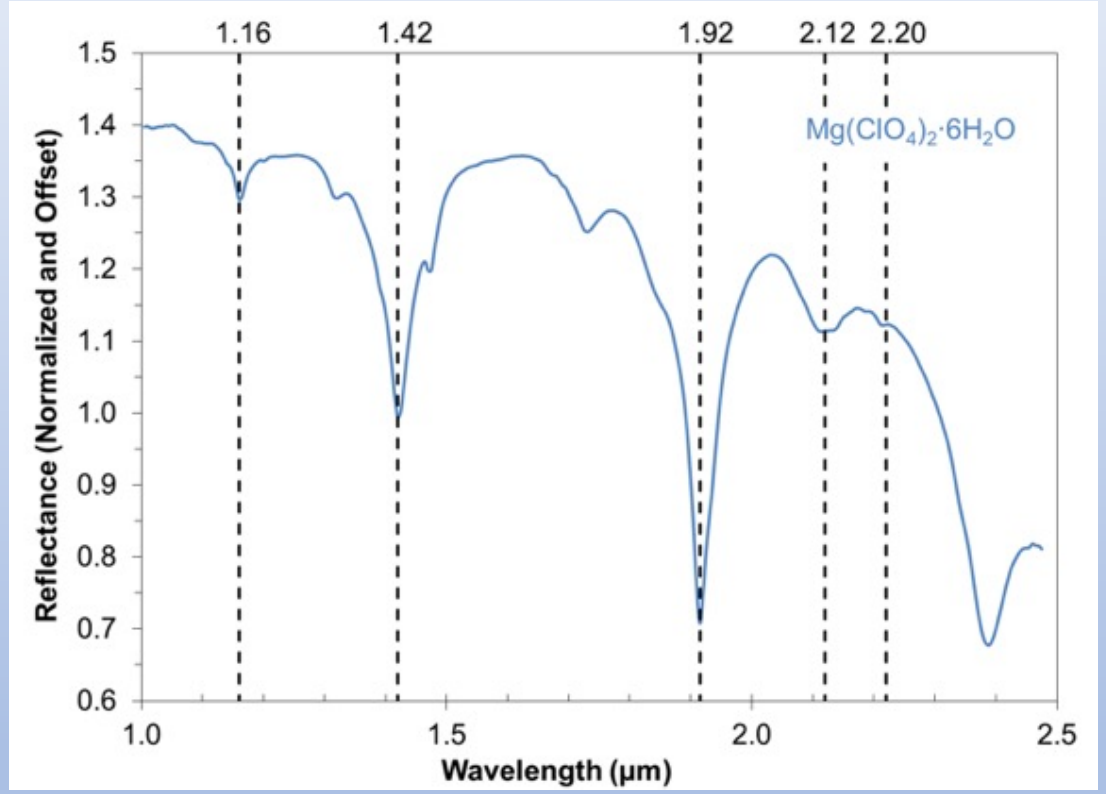
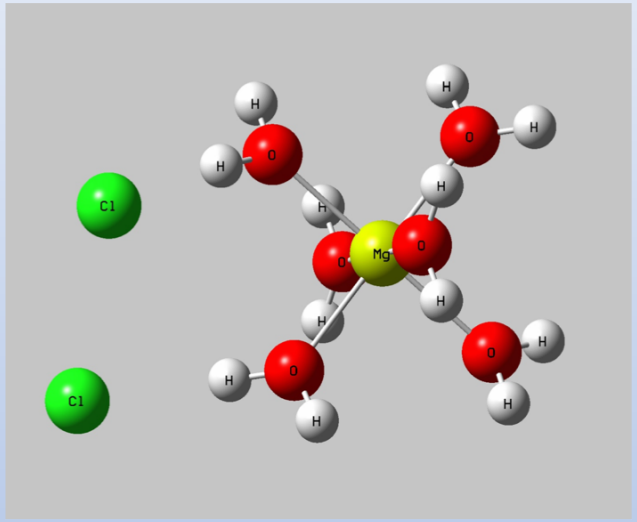
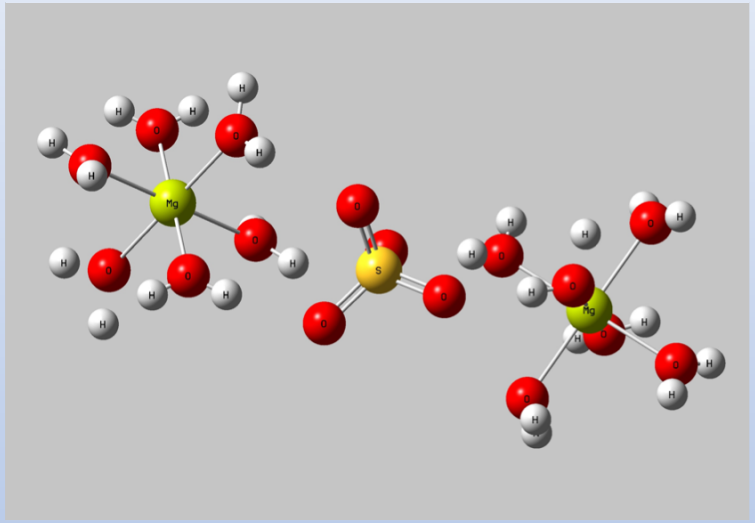



Image from: Hanley et al., JGR (2015)

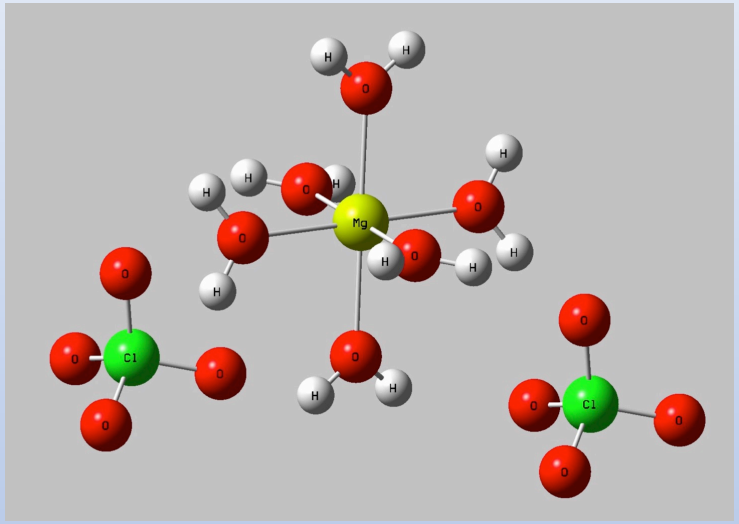
# Spectral Properties



Bischofite ($MgCl_2 \cdot 6H_2O$)



Hexahydrite ($MgSO_4 \cdot 6H_2O$)



Magnesium perchlorate hexahydrate ($Mg(ClO_4)_2 \cdot 6H_2O$)

- Due to the structural similarities, the infrared spectra are very similar.
- Making this determination is crucial, as perchlorates can be toxic, especially to humans, and cause a much lower freezing point depression of water.

# Methods: Density Functional Theory

- The electronic wave function is constructed with the 6-31G basis set, which represents core atomic orbitals by one set of Gaussian functions and valence atomic orbitals by two sets of Gaussian functions.
- We use cam-B3LYP, a hybrid functional of Hartree-Fock exchange and DFT correlation exchange with a split-valence basis set, 6-31G.

$$E_T + E_V + E_J + E_C = E^{DFT}$$

Kinetic

Electron-nuclear Potential

Coulomb

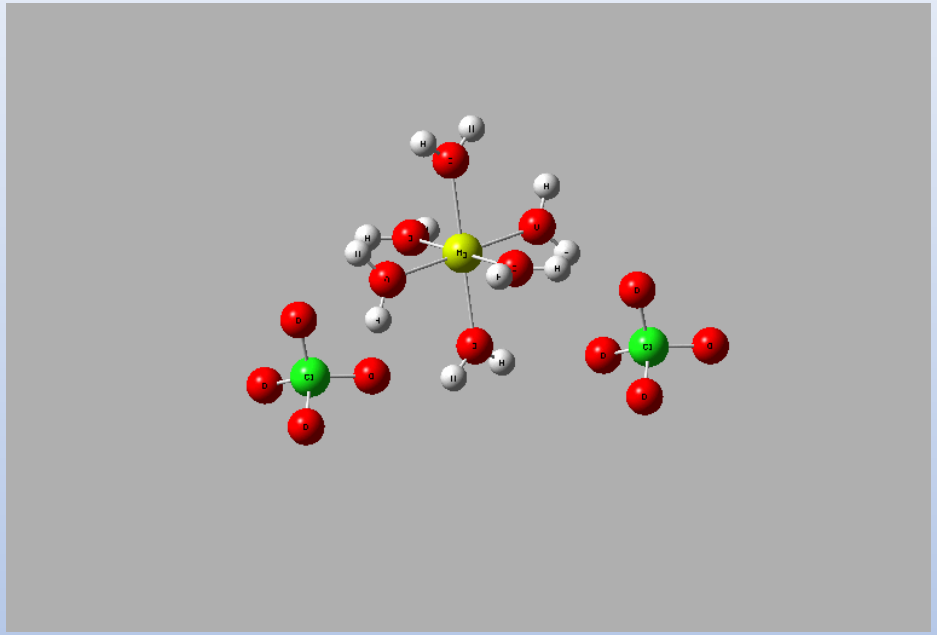
Exchange/ Correlation

$\longrightarrow$ Take the second derivative to calculate *k* $\longrightarrow$

$$\frac{1}{2\pi}\sqrt{\frac{k}{\mu}} = \nu$$

Predicted Vibrational Frequencies!

# Analysis



Magnesium perchlorate hexahydrate ($MgClO_4 \cdot 6H_2O$)

| Fundamental Vibrational Mode | Stretch Type | Computational Frequency (µm) |
|---|---|---|
| $\nu_{asy(H2O)}$ | Asymmetric Water Stretch | 2.51 |
| $\nu_{sys(H2O)}$ | Symmetric Water Stretch | 2.58 |
| $\nu_{syb(H2O)}$ | Symmetric Water Bend | 5.94 |
| $\nu_{asy(ClO4)}$ | Asymmetric Perchlorate Stretch | 7.42 |
| $\nu_{sys(ClO4)}$ | Symmetric Perchlorate Stretch | 8.99 |
| $\nu_{asb(H2O)}$ | Asymmetric Water Bend | 17.50 |

# Computing Overtones and/or Combinations

- Overtone: Multiples of a fundamental vibrational mode
- Combination: Sum of fundamental vibrational modes and/or overtone bands
- Using the fundamental modes that were calculated, possibilities for the 2.12 µm and 2.20 µm bands are as follows:
  - $\boldsymbol{\nu}_{sys(H2O)} + \boldsymbol{\nu}_{sys(ClO4)} = 2.00\ \mu m$
  - $\boldsymbol{\nu}_{asy(ClO4)} + 2(\boldsymbol{\nu}_{sys\ (ClO4)}) + \boldsymbol{\nu}_{asb(H2O)} = 2.11\ \mu m$
  - $2(\boldsymbol{\nu}_{asy(ClO4)}) + \boldsymbol{\nu}_{sys(ClO4)} + \boldsymbol{\nu}_{asb(H2O)} = 2.27\ \mu m$

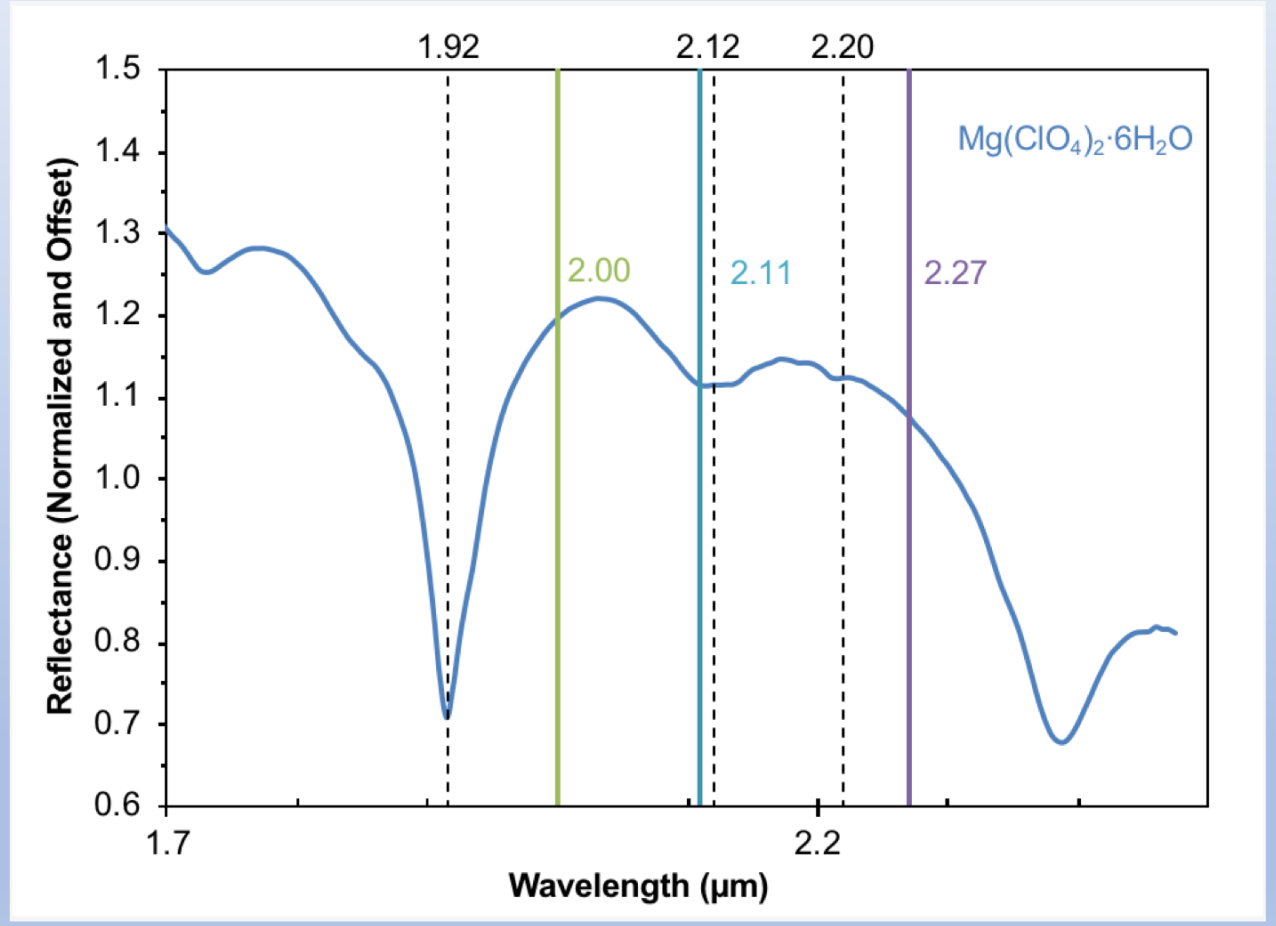



Image from: Hanley et al., JGR (2015)

# Conclusions

- Our method is working!
- Identifying the fundamental modes of magnesium perchlorate hexahydrate, has provided us with a basis for calculating overtones.
- Results from these computations have enabled us to assign fundamental vibrations of commonly found stable salts on Mars.

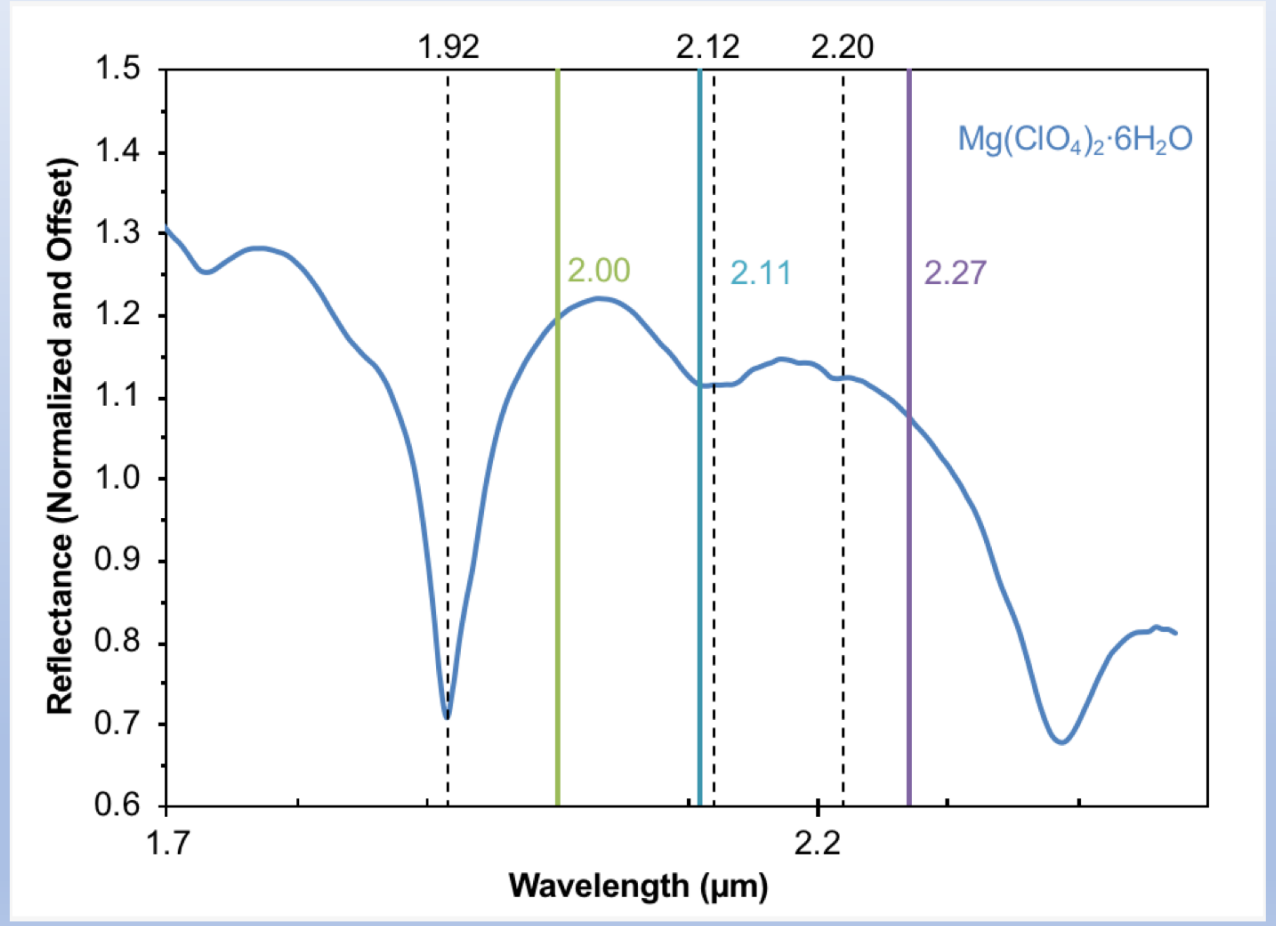



Image from: Hanley et al., JGR (2015)

# Acknowledgments


I'd like to thank…

- The NASA/NAU Space Grant
- Dr. Jennifer Hanley, my project mentor
- Dr. Gerrick Lindberg, my computational research mentor
- My officemates for dealing with me yelling at my computer.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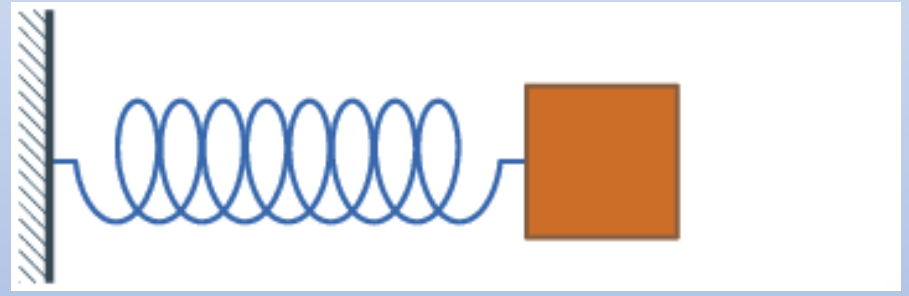
# Back-up Slides

# Vibrational Spectra

- From the simple harmonic oscillator, we know:
  - Hooke's Law: $F = -k \cdot X$
  - The frequency of a vibration is defined by the equation:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$



- The frequencies are then seen in an infrared spectra.
- The force constant ($k$) is obtained by taking the second derivative of the potential energy.

# Water Fundamentals

Magnesium Perchlorate Hexahydrate ($Mg(ClO_4)_2 \cdot 6H_2O$)

| Assignment | Computational | Experimental | | |
|---|---|---|---|---|
| | | Hanley *et al.*, 2015 [4] | Bishop *et al.*, 2014 [6] | Hunt 1977 (Ice/Liquid) [7] |
| Asymmetric Stretch | 2.51 | 2.76 | 2.77 | ($\nu_3$) 2.94/2.66 |
| Symmetric Stretch | 2.58 | 2.76 | 2.77 | ($\nu_1$) 3.10/2.74 |
| Symmetric Bend | 5.94 | 6.04 | 6.06 | ($\nu_2$) 6.06/6.27 |

Hexahydrite ($MgSO_4 \cdot 6H_2O$)

| Assignment | Computational | Experimental | |
|---|---|---|---|
| | | Cloutis *et al.*, 2006 [8] | Hunt 1977 (Ice/Liquid) [7] |
| Asymmetric Stretch | 1.32 | 1.75 | ($\nu_3$) 2.94/2.66 |
| Symmetric Stretch | 2.59 | 2.54 (2.45) | ($\nu_1$) 3.10/2.74 |
| Symmetric Bend | 6.25 | | ($\nu_2$) 6.06/6.27 |

Bischofite ($MgCl_2 \cdot 6H_2O$)

| Assignment | Computational | Experimental | |
|---|---|---|---|
| | | Hanley *et* al., 2014 [5] | Hunt 1977 (Ice/Liquid) [7] |
| Asymmetric Stretch | 2.37 | 2.42 | ($\nu_3$) 2.94/2.66 |
| Symmetric Stretch | 2.55 | 2.82 | ($\nu_1$) 3.10/2.74 |
| Symmetric Bend | 6.22 | 6.11 | ($\nu_2$) 6.06/6.27 |