

Characterization of the Temperature Dependence of O-H Vibrational Modes in Hydrated and Hydroxylated Minerals, with Application to Planetary Exploration.

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Introduction: The presence of hydrated and hydroxylated minerals chronicles surface chemical evolution, and their detection on bodies such as Mars and Europa has motivated new missions to discover novel environments [1]. Minerals containing structurally bound water and -OH functional groups suggest past (or present) aqueous and oxidizing environments, and contain well-defined absorption features in the infrared (IR) region; however, key features within the resultant IR spectra can be misinterpreted due to shifts of OH vibrational modes at non-ambient temperatures. Additionally, this experimentally determined phenomenon is worth studying as a fundamental mineral physics issue.

Here we present experimental data on the shifts of OH vibrational modes with temperature for a suite of hydrated and hydroxylated minerals of varying hydrogen bond strengths. Fourier transform infrared (FTIR) (4000-400 cm^{-1}) spectra collected from 77 K to 873 K show noticeable shifts in the positions of OH vibrational mode. Neutron diffraction data collected at variable temperatures between 77 and 300 K show the changing position of hydrogen within the crystal structure. X-ray diffraction was used to determine the room temperature oxygen positions within the structure, and the O...O hydrogen bond lengths. The observed shifts in peak position with temperature correlate with the measured H...O and O...O bond lengths, suggesting a fundamental relationship between peak position, crystal structure, and temperature[2-4].

Methods:

Sample preparation: Mineral samples were obtained from commercial sources; clays were provided by T.D. Glotch and were sourced from the Clay Minerals Society. All samples were crushed to < 2 μm size fractions, measured out to 1-2 mg, and mixed with 300 mg KBr powder to form KBr pellets; remaining powder was saved for neutron and X-ray diffraction measurements.

FTIR measurements: Low temperature measurements of the prepared KBr pellets were taken in duplicate at Cornell using a Linkam FDCS196 cryostage with a temperature range from -196 $^{\circ}\text{C}$ to 125 $^{\circ}\text{C}$. Transmission measurements were taken from 4000 to 400 cm^{-1} using a Bruker Hyperion 1000 FT-IR microscope with a 15X objective lens, KBr beam splitter,

and MCT detector. High temperature measurements were taken at Caltech using a Linkam THMS600 cryostage from 30 $^{\circ}\text{C}$ to 500 $^{\circ}\text{C}$; transmission measurements were taken on a Thermoscientific Nicolet iS50 FTIR spectrometer with a 15X objective lens, KBr beam splitter, and MCT detector. All measurements were taken at a resolution of 1 cm^{-1} .

Neutron and X-ray diffraction measurements: Epsomite, deuterated gypsum, and deuterated natron were used for temperature-dependent (77-300 K) neutron diffraction measurements using NCNR's BT-1 high resolution powder diffractometer. Scans were collected from a 2θ of 3 $^{\circ}$ -168 $^{\circ}$ and a step size of 0.05 $^{\circ}$ for a 4-5 hour total scan time per temperature. Room temperature powder measurements were taken using the Scintag Theta-Theta powder diffractometer at the Cornell Center for Materials Research (CCMR). Scans were taken at a 0.02 $^{\circ}$ step size with a 1.5s per step count time for a 1-1.5 hour total scan time.

Preliminary Results: O-H stretching and bending fundamentals, and overtones and combination modes were identified based on previously published results. Identified absorption bands were then subset from the remainder of the spectra, baseline corrected, and fit with Voigt amplitude profiles using the SigmaPlot PeakFIT software. Band parameters, such as band center, amplitude, and peak area, were calculated for each OH vibrational mode at each temperature. Total shifts in band center with temperature were on the order of tens of wavenumbers ($\sim 10\text{s}-100\text{s nm}$), and band amplitudes decreased significantly during heating. Herein we report preliminary results for three minerals, each representing different hydrogen bonding environments and bond strength:

Weak hydrogen bond: Brucite. Weaker hydrogen bonds correspond to OH vibrational modes positioned at higher wavenumbers. Brucite contains a single, sharp O-H stretching fundamental band at 3698 cm^{-1} , with a weak shoulder at 3688 cm^{-1} at room temperature (25 $^{\circ}\text{C}$) [5]; a broad O-H bending fundamental band is present at 1622 cm^{-1} . Over the temperature range from -196 $^{\circ}\text{C}$ to 500 $^{\circ}\text{C}$, the O-H stretching band position shifts from 3704 cm^{-1} to 3684 cm^{-1} (15 nm overall shift). The O-H bending band shifts from 1622 cm^{-1} to 1652 cm^{-1} (112 nm overall shift), and becomes broader and nearly indistinguishable as temperature

increases. In this case, the weak OH bending mode experiences a dramatic increase in band position, which is unexpected, as stronger bonds should undergo greater shifts. This phenomenon might be due to the broadness of the OH bending band, and error in determining its true center, which needs to be revisited.

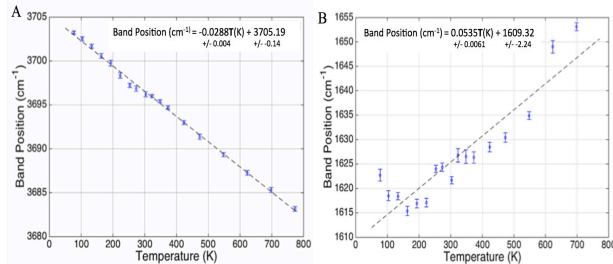


Figure 1. A. Plot showing linear relationship between brucite OH stretching fundamental and temperature; B. Similar plot for brucite OH bending fundamental.

Medium hydrogen bond: Kaolinite. Kaolinite contains a more complex hydrogen bonding environment and contains 4 distinct absorption bands, each corresponding to O-H stretching fundamentals for the 3 inner surface hydroxyl groups and 1 inner surface hydroxyl. These 4 bands are located at 3694, 3669, 3653, and 3620 cm^{-1} at room temperature [6]. Over the complete temperature range from -196°C to 500°C , the band at 3704 cm^{-1} shifts by 69 cm^{-1} (22 nm); the band at 3677 cm^{-1} shifts by 16 cm^{-1} (12 nm); the band at 3654 cm^{-1} shifts by 3 cm^{-1} (2 nm); and the band at 3617 cm^{-1} shifts by 11.5 cm^{-1} (9 nm). The inner surface hydroxyl bands have an O-H bending fundamental at 938 cm^{-1} , while the inner surface O-H bending fundamental is located at 915 cm^{-1} at room temperature. These bands were only measured from -196°C to 125°C ; the band at 938 cm^{-1} shifts 1.5 cm^{-1} overall (5 nm) while the band at 915 cm^{-1} shifts 2.25 cm^{-1} (27 nm).

Strong hydrogen bond: Natrochalcite. Natrochalcite has a very strong hydrogen bond corresponding to an H_3O_2^- group within the structure; the O-H stretching fundamental is a broad band centered near 1300 cm^{-1} , but this band is so broad, it is lost within the overall baseline of the spectra. A weaker hydrogen bond has an O-H stretching fundamental centered at 3154 cm^{-1} with weak shoulders at 3210 and 3080 cm^{-1} at room temperature [7]. Data was analyzed only from -196°C to 150°C , as the bands were indistinguishable beyond this temperature; the overall shift for this temperature range was 47 cm^{-1} (47 nm). The O-H bending fundamental at 981 cm^{-1} (at -196°C) shifted 9 cm^{-1} (94 nm) from -196°C to 125°C . Again, in this case, the bending fundamental has a larger magnitude of change than the stretching fundamental.

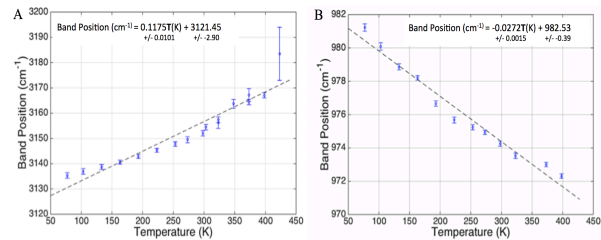


Figure 2. A. Plot showing linear relationship between natrochalcite OH stretching fundamental and temperature; B. Similar plot for natrochalcite OH bending fundamental.

Discussion: Early results from FTIR data suggest a linear relationship between band center and temperature for OH vibrational modes. Studies of diaspore (not shown here) reveal that overtone/combination modes have larger, non-linear shifts in band position, suggesting multiple phonon processes. Fits still need to be re-evaluated in order to determine whether identified band centers are true band centers, especially for broader bands. Future work will involve improving the Rietveld refinements for the neutron and X-ray diffraction data in order to determine the O...O and H...O bond distances, and verify the results, based on previous experimental data. Using the calculated bond lengths and final slopes of the change in band position versus temperature, we will determine the relationship between OH vibrational modes and mineral structure with changing temperature, furthering existing calibration curves which relate OH stretching fundamental positions to bond length. Using this data, we hope to predict, based on existing knowledge of hydrogen bond length, which minerals will experience the greatest shift in bond position with temperature. This will be particularly useful for any future remote sensing observations or ground based high-resolution spectrometer measurements of planetary surfaces at non-ambient temperatures.

Acknowledgements: The authors would like to acknowledge support of the National Institute of Standards and Technology, U.S. Department of Commerce, in providing the neutron research facilities. This work also made use of the Cornell Center for Materials Research Shared Facilities which are supported through the NSF MRSEC program (DMR-1120296).

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