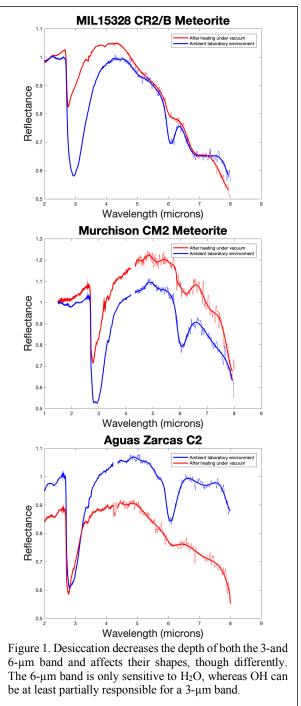
UNDERSTANDING WATER IN THE SURFACES OF AIRLESS BODIES THROUGH LABORATORY MEASUREMENTS OF THE 3- AND 6-MICRON ABSORPTION FEATURES. C. A. Hibbitts¹, K. Stockstill-Cahill¹, D. Takir², C. Honnibal³, P. Lucey³, S. Li³,¹Johns Hopkins University Applied Physics Laboratory, Laurel, MD, ²JETS/ARES, NASA Johnson Space Center, ³University of Hawaii, Honolulu, HI.(Contact: <u>Karl.hibbitts@jhuapl.edu</u>)

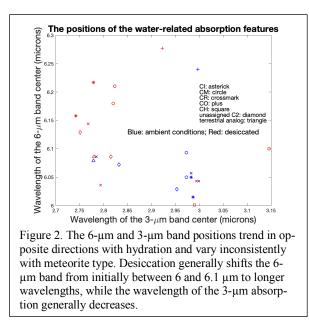
Motivation: Water, as H₂O or OH, is ubiquitous in the surfaces of airless solid bodies through-out the inner solar system. The 3-µm absorption feature has long been known to provide great insight into the hydration states of minerals [e.g. 1,2], meteorite samples [e.g. 3,4,5], and has been used to infer water on asteroids [e.g. 6,7]. More recently the 6-µm absorption feature has been recognized as providing valuable information on the state of water on airless surfaces. Due to the symmetric stretch of the H₂O water molecule, the presense of a a 6-µm band is indicative of molecular water, and, unlike the 3-µm band is insensitive to the dissociated water molecule, or hydroxyl [e.g. 8,9]. Spectroscopy in the 6-µm region has provided the first unequivocal detection of molecular water on the surface of the Moon [10,11]. With the expectation that this new remote sensing technique for characterizing water on airless bodies will quickly be applied to asteroids, we have analyzed the 6-µm region of previously-taken laboratory reflectance spectra of carbonaceous meteorites and compare the nature of the 6-µm feature to the 3-µm feature.

The Laboratory Measurements. Reflectance spectra from the near-infrared to $\sim 8 \,\mu m$ were obtained at the Laboratory for Spectroscopy under Planetary Environmental Conditions (LabSPEC) at the Johns Hopkins University Applied Physics Laboratory (JHU APL) using a Bruker Vertex 70 FTIR spectrometer coupled to an ultra-high vacuum system and an external liquid-nitrogen cooled MCT detector (Figure 1). Measurements were obtained at room temperature under the following conditions: N₂-purged, and after exposure to $\sim 1e^{-7}$ to $1e^{-6}$ torr at ~ 80C for approximately 12 hours in order to desiccate the sample. Samples, powered, are vertically mounted behind a 1-mm thick CaF2 window held into a 1-mm deep sample cup in a copper sample holder. A diffuse gold plate, also behind a 1-mm CaF₂ window, mounted immediately below the sample holder was used as the IR reflectance standard, and a thermocouple attached to the top of the metal retaining flange provided temperature measurement.

Spectra of 13 carbonaceous chondrites and one terrestrial analog were obtained. Postprocessing involved using a box car filter at wavlengths shorter than 4.2 μ m. At longer wavelengths, where the instrument signal was lower and thus noise proportionally greater, a piecewise polynomial model was fit to the data. Figure 1 shows examples of both the as-acquired data (thin line) and post-processed data (thick lines) and provides a qualitative understanding of precision and error. The position



of the $3-\mu m$ band is accurate to several nm, whereas the error in the position of the $6-\mu m$ position can vary from a few nm to several 10s nm. Formal error for the derived spectral parameters will be calculated in future work.



Results and Discussion: The depths and areas the 3and 6-µm absorption features trend similarly, growing with hydration as observed by previous researchers [4,5]. The position of the absorption centers for both the 3 and 6-µm bands trend with hydration for CI meteorites but not obviously so for the other meteorite classes (Figure 2). The spectra of CI meteorites are dominated by a sharp 3-µm OH-strech when desiccated, which only sometimes dominates in other meteorite classes. Under ambient conditions, both the 3 and 6-µm bands of the CI meteorites are similar to that of pure water. The 3um band positions consistently shift to longer wavelength with increasing abundance of adsorbed molecular water, whereas the 6-µm band shifts to shorter wavelengths. The shift in the 3-µm asymmetric stretch to shorter wavelenths when less water is present has been interpreted as indicative of stronger bonding between the residual water molecules and adsorbate than is the bond between water molecules themselves (reference); a stronger bond \rightarrow shorter bond length \rightarrow higher frequency and shorter wavelength for the vibration. The mechanism for the opposite shift in the 6-µm symmetric vibration is not yet clear.

The opposing spectral shifts with hydration in the positions of the 3- and 6- μ m bands seen in Figure 2 result in a roughly linear trend with inverse correlation (Figure 3). In the metric used for Figure 3 (center wavelength under ambient conditions minus center wavelength of desiccated sample), large positive values of the shift of the 3- μ m band correlate with large negative values in the shift of the 6- μ m band, etc. A possible trend with meteorite class present in Figure 2 becomes more pronounced as well.

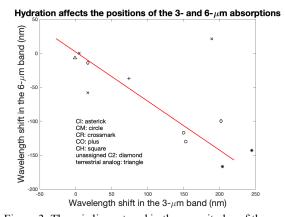


Figure 3. There is linear trend in the magnitudes of the shifts for the 3 and 6- μ m bands as a result of changes in hydration. Both bands can shift up a couple of 100 nm, though they move in opposite directions. CI meteorites exhibit the greatest magnitude of shift. The 'outlier' CR meteorite is MIL15328, and the value may be an effect of limited precision in mapping the position of a shallow absoprion in the desiccated spectrum.

CI meteorites cluster in the lower right, and moving up and to the left come CM, then a single CO, and finally CR and CV. The analog sample also falls on the upper left of trend, implying that as far as spectral interactions with water, it has similarity to CR meteorites. However, the analog does possess a very strong 6-µm feature, suggesting significant adsorbed water under ambient conditions, that also remain deep even after baking. This is different than the two CR meteorites (MIL15328 and DOM10085), which have shallower water absorption bands than average among these meteorites. The spectral shifts for the two unassignd C2 meteorites (Essebi and the recent Costa Rica fall Aguas Zarcas) do not cluster, and if the trend is valid, this would suggest they belong to different categories. However, new work [12] suggests Aquas Zarcas is a CM, and as it plots on the upper left of the trend, its spectral shifts are inconsistent with that assignment. References: [1] Bishop et al., 1994, Clays and Clay Minerals, 42, 6, 702-716. [2] Milliken and Mustard, 2005, J. Geophys. Res., 110, doi:10.1029/2005JE002534. [3] Sato et al., 1997, Met. & Planet. Sci., 32:503-507. [4] Takir et al., 2013, Met. & Planet. Sci., 48, 9, 1618-1637. [5] Takir et al., 2019, Icarus, 333, 243-251. [6] Rivkin et al., 2006, Met. & Planet. Sci., 38, 9, 1383-1398. [7] Takir et al., 2012, Icarus, 219, 641-654. [8] Bartholemew et al., 1980, J. Amer. Ceramic Soc, 63, 481-485. [9] Newman et al., 1986, Amer. Min., 71, 1527-1541. [10] Honniball, C., et al., 2019, GSA 51, 5. [11] Honniball et al., 2020, Nature (submitted). [12] Takir et al., 2020, 51st LPSC. Abstract#2533..

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