FTIR AND RAMAN SPECTRAL ANALYSIS OF CLATHRATES IN CRYOGENIC CONDITIONS J. R. Sandtorf-McDonald[1] and V. F. Chevrier[2], [1]Arkansas Center for Space and Planetary Science, University of Arkansas, Fayetteville, AR 72701, jrm071@uark.edu, [2]Arkansas Center for Space and Planetary Science, University of Arkansas, Fayetteville, AR, 72701, vchevrie@uark.edu.

Introduction: Clathrate hydrates are crystalline structures of water ice with trapped guest gas molecules hidden inside. Because clathrates aren't easily identified via remote sensing, it is difficult to know how much ice in the outer solar system is clathrate. It is important to know how and when these materials formed so that we can estimate how prevalent they are in gas giants, ice giants, and icy bodies.

We know that the materials required to form clathrates were present in the protosolar nebula.[1] Current information about clathration kinetics during solar system formation is largely extrapolated from measurements taken at higher temperatures and pressures. This lack of relevant condition laboratory data leads to large uncertainties when estimating the volatile budget of icy parts of the solar system. We attempt to show that clathrate hydrates can form at lower temperature and pressure conditions analogous to those during solar system formation.

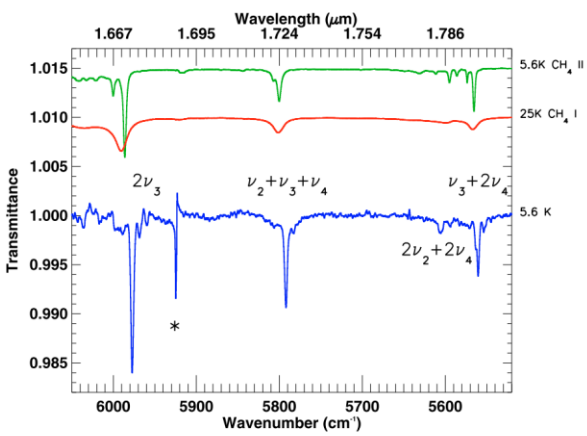

Figure 1: Dartois & Deboffle, methane clathrate made at 40 bar pressure and 255 K, then observed at 5.6K and 25K. [2]

Experimental Approach: The Keck Laboratory at the University of Arkansas houses the Outer Solar System Simulation Chamber (OSSC), which is capable of recreating conditions relevant to the protosolar nebula. A custom-built clathrate observation cell allows for precise control of pressure and temperature inside the OSSC. [4] A sapphire window allows spectroscopic observations.

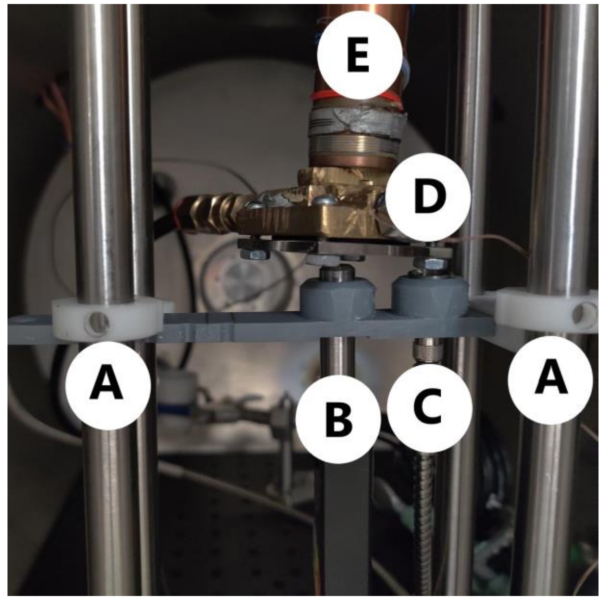

Figure 2: Actuator arm assembly. A. Leveling supports B. Raman probe C. FTIR probe D. Clathrate observation cell, facing downward E. Cold finger.

Clathrates are notoriously difficult to characterize remotely as most spectral properties of clathrates closely mimic hexagonal ice in the near infrared. But high resolution IR spectroscopy shows fine structures that can help distinguish clathrates from pure ices (Fig. 1). In addition to FTIR, a new Stellarnet 532 nm Raman spectrometer will facilitate clathrate identification by showing vibrational modes of trapped gases [REF]. This work addresses the problem of obtaining both Raman and Fourier Transform Infrared spectra inside a sealed vacuum chamber.

Fourier Transform Infrared (FTIR) observations by Dartois and Deboffle in 2010 [2] show characteristic clathrate spectral features observed at 5.6 K. These ice samples were made at higher temperatures and pressures of 40 bars and 255 K, then the temperature was reduced to the observation temperatures shown in Figure 1. [3] Our previous work shows similar spectral features in ice made at 12K, suggesting that clathrate formation may be possible outside the currently-accepted stability zones.

The position of the data collection probes is crucial. Each probe must be held precisely perpendicular to the target surface for maximum signal strength. In addition, the working distance for FTIR is 1cm, while Raman requires 7.5 mm between the probe and the sample. Due to the small surface area within the clathrate observation cell [4], each probe must be moved into place for data collection.

A sturdy 3-D print resin was chosen to build the carriage assembly. This carriage consists of support brackets (A in Figure 2) held in place by lab stand rods and a probe holder which slides between the supports and connects to the vacuum-tight actuator outside the chamber.

The FTIR and Raman probes are mounted in the carriage assembly which allows the user to position the probe for the desired analysis method. Probe positions were calibrated before closing the chamber to ensure correct positioning for each data collection required. These settings include (1) FTIR background position, (2) FTIR data collection position, and (3) Raman data collection position.

Experimental Protocol: The actuator and probe carriage assembly was tested by performing clathrate condensation protocol as described in our previous work[4]. In this experiment, a two-step condensation process freezes pure water ice onto the target surface, then the guest gas (methane) is allowed to flow over the water ice. A vacuum pump evacuated atmosphere from the OSSC and the temperature was decreased to 60K. A background FTIR spectrum was collected at this point, shown in Figure 3 in red.

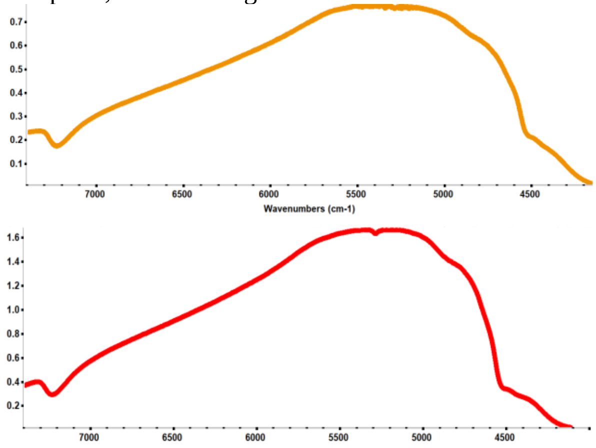

Figure 3: Top: Background spectrum (orange) before installing carriage assembly. Bottom: Background spectrum (red) after carriage assembly installation.

To eliminate contamination, helium gas was bubbled into pure water and then carried into the clathrate cell. This mixture was allowed to flow into the clathrate cell for 60 seconds, with the pressure kept below 100 mTorr, while keeping the temperature steady at 60K. Then a guest gas, in this case methane, was inserted into the cell via a stainless-steel tube and allowed to flow for 60 seconds, maintaining a pressure below 100 mTorr and temperature at 60K.

One FTIR spectrum was taken at 60K, then the temperature was raised to 70K and another spectrum was collected. These spectra are shown in Figure 4, with 60K in blue and 70K in green. OMNIC was used to collect and process the spectra.

Preliminary Results: FTIR spectroscopy requires a background image of Spectralon, a standard material used to normalize the detector at all observed wavelengths. Figure 3 compares the background images obtained before and after installing the probe actuator assembly. These spectra are very similar, though there is a slight intensity valley at 5,300 cm^{-1}. Figure 4 shows a strong water identifying peaks at 7,200 cm^{-1} and 4,500 cm^{-1}.

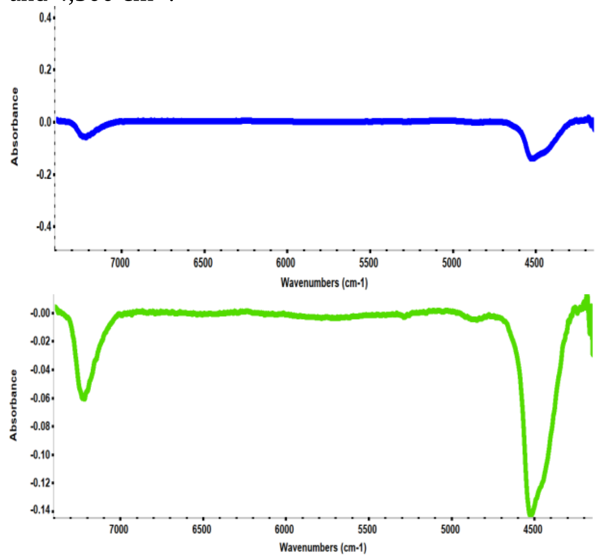

Figure 4: FTIR Test Spectra with Actuator Assembly. Water ice and methane frozen using HCP protocol. Top (blue) is 60K, bottom (green) is 70K.

Conclusions: The actuator assembly performs well for collecting FTIR data. Background and FTIR spectra are comparable to those taken previously under similar conditions.

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References: [1] Mousis, et al., (2015) Astrobiology, 15(4), 308-326. [2] Dartois, E., Deboffle, D., & Bouzit, M. (2010). *Astronomy and Astrophysics*, *514*(5). [3] Dartois, E., & Deboffle, D. (2008). *Astronomy and Astrophysics*, *490*(3). [4] Sandtorf-McDonald, J., Ahrens, C. J., & Chevrier, V. F. (2020). *LPSC LI , Abstract # 2605*. [5] Sandtorf-McDonald, J., Ahrens, C. J., & Chevrier, V. F. (2021) *LPSC LII, Abstract # 2623*.