

**EXPERIMENTAL STUDIES OF ETHYLENE AND BENZENE EVAPORITES ON TITAN.**

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**Introduction:** Titan's dynamic lakes of liquid methane/ethane have intrigued scientists for over a decade. Using the Visual Infrared Mapping Spectrometer (VIMS) onboard Cassini, regions described as 5- $\mu\text{m}$ -bright were first observed in the Xanadu (110°W, 15°S) and Tsegihi (15°W, 40°S) Regios [1]. In-depth studies of these 5- $\mu\text{m}$ -bright regions have concluded that they are non-water ice materials, similar to the 5- $\mu\text{m}$ -bright signatures found in the Tui and Hotei Regios (near 25°S) [2]. A 5- $\mu\text{m}$ -bright ring was also found around Ontario Lacus [3,4]. Described as "bathtub rings" of low water ice condensates, they may have been deposited in the past when lake levels were higher. Further, VIMS observations identified additional 5- $\mu\text{m}$ -bright annuli surrounding many empty north polar lakes [5,6]. Combined, these observations provide the foundation on which evaporites can be studied on Titan.

Current evaporite studies focus on models and theoretical work [7,8], but some experimental work is also being undertaken to constrain potential solvents and solutes that may be active in evaporite production [9,10]. This study expands the compounds studied by analyzing both ethylene and benzene evaporites.

**Methods:**

*Simulation Chamber:* The University of Arkansas owns a specialized Titan simulation chamber that reproduces the same conditions that are present on Titan's surface [11]. This chamber is unique in that it provides real-time experimental data on the composition of Titan's lakes. The chamber is made of stainless steel with a height of 2.08 m and internal diameter of 0.61 m. A 1.5 bar atmosphere is maintained with N<sub>2</sub>. Temperatures of 90 K – 94 K are reached with the use of a liquid nitrogen refrigeration system. Liquid nitrogen flows through copper cooling coils and cryogenic lines that surround the chamber and temperature control box (TCB). The TCB is cooled using this method, while the rest of the chamber serves to maintain the atmospheric pressure of 1.5 bar.

Compounds in gaseous phase at room temperature (CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>) are contained in gas cylinders, and introduced to the condenser via gas lines. C<sub>6</sub>H<sub>6</sub>, however, is a liquid at room temperature, so an Erlenmeyer flask was modified and connected to the condenser. N<sub>2</sub> is bubbled through the Erlenmeyer flask for ~10 min until the N<sub>2</sub> is saturated with respect to C<sub>6</sub>H<sub>6</sub>. Then, the line to the condenser is opened, which allows N<sub>2</sub> to carry

gaseous C<sub>6</sub>H<sub>6</sub> into the condenser where C<sub>6</sub>H<sub>6</sub> condenses in the solid phase. After the compounds are added to the condenser and given time to condense and dissolve into a mixture, a solenoid valve is turned on, which allows the sample to be transferred from the condenser to the petri dish at the bottom of the chamber. The petri dish is covered with a layer of Spectralon® reflectance material, which serves as a background for two way transmission infrared spectral measurements. Here, the sample is analyzed via Fourier transform infrared (FTIR) spectroscopy probes connected to a Nicolet 6700 FTIR (wavelength 1–2.5  $\mu\text{m}$ ).

*Spectral Unmixing Model:* Various spectra of the pure compounds (CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>6</sub>) were recorded before use in experiments. Any compound mixture should have a spectrum that is some combination of the spectra of its parts. A Python code was written to decompose a given spectrum into a best fit of pure spectra added together. This provides the weighted composition of the mixture through the evaporation process. For compound spectra ( $C$ ) with  $i$  components, the Python code would break  $C$  down into pure spectra ( $P$ ) as follows:

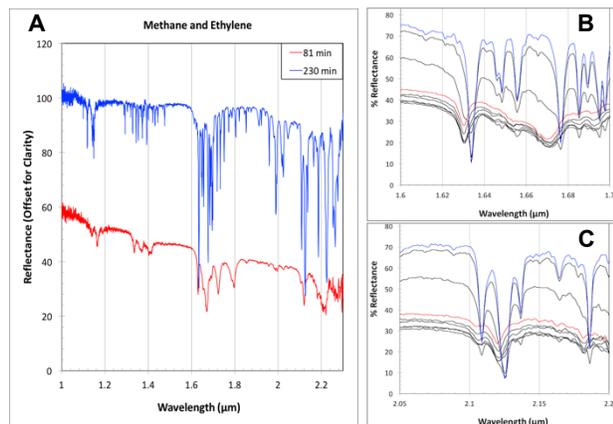
$$C = A + \sum_i w_i P_i$$

The  $A$  term allows for a constant offset to be applied, as the spectra tends to increase in reflectance over the time of the evaporation process. The weight of a pure spectrum ( $w$ ) is normalized so the sum adds to 100%. This unmixing process is similar to previous studies [9], but is an original process for these experiments.

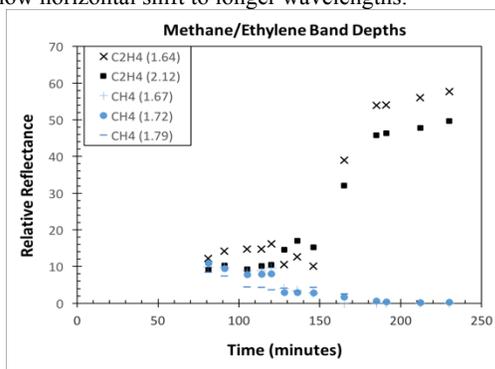
**Results and Discussion:**

*Ethylene:* Three different experiments were analyzed for C<sub>2</sub>H<sub>4</sub> evaporites: CH<sub>4</sub>/C<sub>2</sub>H<sub>4</sub> (Fig. 1,2), C<sub>2</sub>H<sub>6</sub>/C<sub>2</sub>H<sub>4</sub>, and CH<sub>4</sub>/C<sub>2</sub>H<sub>6</sub>/C<sub>2</sub>H<sub>4</sub>. Through band depth measurements, mass data, and spectral data, we determined that a solid C<sub>2</sub>H<sub>4</sub> evaporite deposit only formed in the CH<sub>4</sub>/C<sub>2</sub>H<sub>4</sub> experiment (Fig. 1A). This is due to the fact that CH<sub>4</sub> evaporates at Titan surface conditions, thus CH<sub>4</sub> evaporated in the conditions of our chamber. Band depth measurements confirm this evaporation, as the CH<sub>4</sub> band depths decreased to zero throughout the experiment, while C<sub>2</sub>H<sub>4</sub> band depths increased because of an increase in reflectance (Fig. 2). We also observe horizontal band shifts in the characteristic C<sub>2</sub>H<sub>4</sub> absorptions (1.64 and 2.12  $\mu\text{m}$ ) (Fig. 1B, 1C). This band shift

represents a phase change of the mixture from liquid phase to solid phase.



**Figure 1:** Spectra from the  $\text{CH}_4/\text{C}_2\text{H}_4$  experiment. (A): Initial spectrum is shown in red, final spectrum is shown in blue. (B), (C): Zoom of the 1.64  $\mu\text{m}$  and 2.12  $\mu\text{m}$   $\text{C}_2\text{H}_4$  band to show horizontal shift to longer wavelengths.



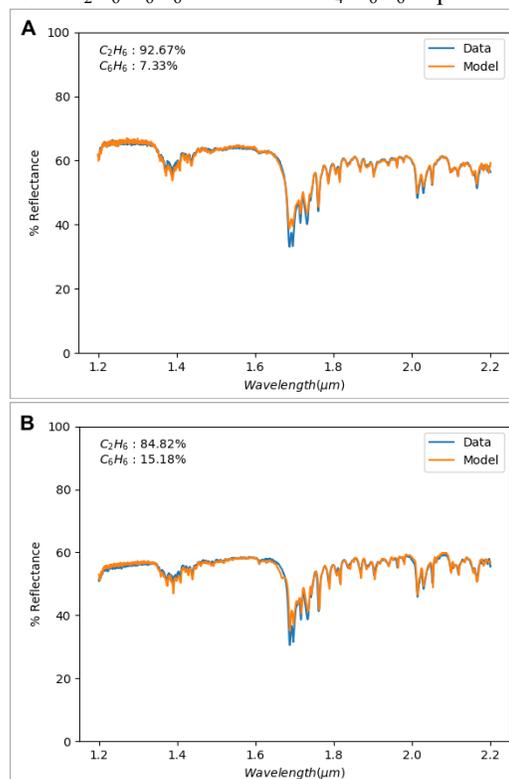
**Figure 2:** Band depth results for the  $\text{CH}_4/\text{C}_2\text{H}_4$  experiment.  $\text{CH}_4$  band depths (blue) decrease to 0, while  $\text{C}_2\text{H}_4$  band depths (black) increase.

**Benzene:** The  $\text{C}_6\text{H}_6$  data presented here represents one experiment of both  $\text{C}_2\text{H}_6/\text{C}_6\text{H}_6$ . Using spectral data acquired from this experiment, we were able to produce a model (described in methods section) of a best fit spectrum to compare the experimental spectrum to (Fig. 3). Similar to the  $\text{C}_2\text{H}_4$  experiment, the initial and final spectra were compared with each other to determine if the mixture evaporated. Figure 3 shows that from (A) to (B), the percentage of  $\text{C}_2\text{H}_6$  in the spectra decreased from 92.67% to 84.82%. This can be interpreted in one of two ways: 1) the  $\text{C}_2\text{H}_6$  evaporated or 2) the  $\text{C}_2\text{H}_6$  and  $\text{C}_6\text{H}_6$  formed a co-crystalline structure [10]. We are still in the process of analyzing this data to more accurately constrain these answers.

**Conclusions:** Under Titan conditions, we have experimentally formed  $\text{C}_2\text{H}_4$  evaporites in a solution of  $\text{CH}_4$ . The formation of the  $\text{C}_2\text{H}_4$  evaporite is confirmed

by observations of spectral data and band depth measurements. We also observe a horizontal band shift to longer wavelengths in the characteristic  $\text{C}_2\text{H}_4$  bands.

Although still preliminary, we have detected  $\text{C}_6\text{H}_6$  in the  $\text{C}_2\text{H}_6/\text{C}_6\text{H}_6$  experiments and have observed a decrease in the abundance of  $\text{C}_2\text{H}_6$ . This data is being analyzed to determine if the decrease in  $\text{C}_2\text{H}_6$  is due to evaporation, or the formation of a co-crystal of  $\text{C}_2\text{H}_6/\text{C}_6\text{H}_6$ . Future work includes additional experiments of  $\text{C}_2\text{H}_6/\text{C}_6\text{H}_6$  as well as  $\text{CH}_4/\text{C}_6\text{H}_6$  experiments.



**Figure 3:** Spectra from one experiment of  $\text{C}_2\text{H}_6/\text{C}_6\text{H}_6$ . Experimental data (blue) is compared to our model data (orange) to determine specific percentages of each compound. Initial spectrum is shown by (A) and final spectrum is shown by (B).

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**References:** [1] Barnes, J.W. et al. (2005) *Science*, 310, 92-95. [2] MacKenzie, S.M. and Barnes, J.W. (2016) *ApJ*, 821, 1-13. [3] Barnes, J.W. et al. (2009a) *Icarus*, 201, 217-225. [4] Cornet, T. et al. (2012) *Icarus*, 218, 788-806. [5] Hayes, A. et al. (2008) *GRL*, 35, L09204. [6] Barnes, J.W. et al. (2011) *Icarus*, 216, 136-140. [7] Cordier, D. et al. (2013) *Icarus*, 226, 1431-1437. [8] Cordier, D. et al. (2016) *Icarus*, 270, 41-56. [9] Singh, S. et al. (2017) *GCA*, 208, 86-101. [10] Cable, M. L. et al. (2014) *GRL*, 41, 5396-5401. [11] Wasiak, F.C. et al. (2012) *Adv. Space Res.*