

EXPERIMENTAL INVESTIGATION OF THE ACETYLENE- CARBON DIOXIDE CO-CRYSTAL UNDER TITAN CONDITIONS.

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Introduction: Titan's hydrocarbon lakes and active methane cycle, paired with methane photolysis in the atmosphere, offers a unique laboratory to explore prebiotic chemistry [1–3]. Clouds of methane and ethane, ice clouds, and an organic haze layer are all present in the atmosphere [4–6]. The clouds and lakes allow compounds to interact with each other, creating complex organic molecules [3, 7–9].

In recent years, the field of Titan cryomineralogy has greatly expanded, which is timely given the selection of the *Dragonfly* mission, a rotorcraft designed to explore the habitability of Titan's atmosphere and surface [10]. One type of cryomineral, co-crystals, are crystalline structures formed when two molecular compounds bond together in specific stoichiometric ratios [7, 8]. Co-crystals have unique spectral features compared to that of their constituent pure species [e.g., 11]. It is predicted that co-crystals may be present in Titan's lakes, around dry basins, in hydrocarbon clouds, as well as the dunes (Fig. 1) [7].

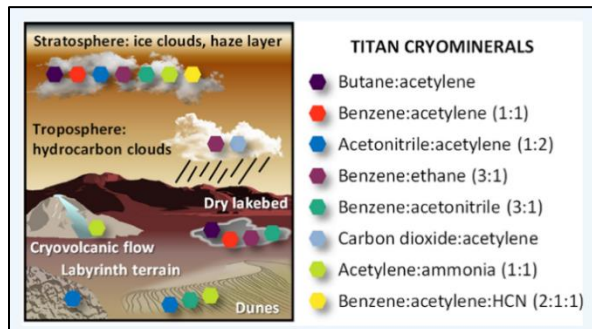


Figure 1: Co-crystals and their possible locations on Titan. Graphic from [7].

Acetylene (C_2H_2) and carbon dioxide (CO_2) have both been detected in Titan's atmosphere [3, 12]. These compounds (and others) may interact in the clouds, condense/deposit on the surface, and interact with surface liquids. Previous studies have shown that a $C_2H_2:CO_2$ (2:1) co-crystal forms under cryogenic conditions (90 K) and is metastable [13, 14], but it has neither been tested under Titan-specific conditions (93 K, 1.5 bar N_2) nor in the presence of hydrocarbon solvents (methane and ethane). Acetylene and carbon dioxide have similar Titan-relevant condensation temperatures (~ 95 K at 1.5 bar) [15], which increases the probability of co-crystal formation. Therefore, the objective of our work is to

investigate the formation and stability of the acetylene-carbon dioxide co-crystal under Titan conditions.

Experimental Methods: The Titan Surface Simulation Chamber (TSSC), located at the University of Arkansas [16], is used to perform these experiments under Titan surface conditions (93 K, 1.5 bar N_2). This setup (Fig. 2) has been used in previous studies, paired with FTIR spectroscopy and optical images, to confirm the formation of a co-crystal at Titan surface conditions [11]. The temperature of the TSSC is cooled and maintained with liquid nitrogen that flows through cryogenic lines that wrap in and around the chamber and temperature control box (TCB). The experiment takes place inside the TCB and is monitored in real-time with an FTIR probe collecting near-IR spectra, eight thermocouples recording temperature, four cameras providing optical imagery of the sample, and a balance recording the change in mass of the sample. The FTIR wavelength range is from 1 to 2.5 μm .

Experimental Protocol: To begin an experiment, the chamber and condenser are both purged with nitrogen gas to expel any contaminants. Once these purges finish,

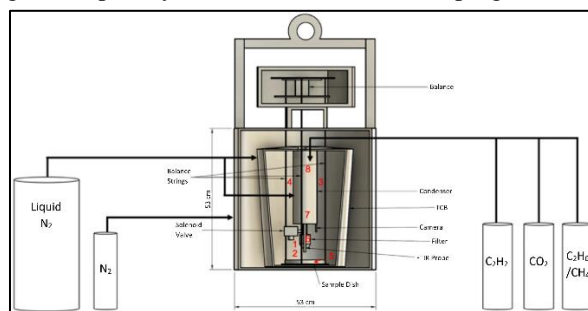


Figure 2: The Titan module, which houses the balance and TCB. The TCB contains the condenser, solenoid valve, thermocouples, FTIR probe, endoscopic cameras, and the sample dish. Gas cylinders of the desired compounds are connected to inlet valves on the chamber exterior. Modified from [17]

the exhaust ports are closed off, while the flow of gaseous N_2 continues in order to establish a 1.5 bar N_2 atmosphere inside the chamber. The flow of liquid nitrogen cools the TCB, but is restricted from the condenser. This allows the compounds to pass through the condenser without risk of clogging the solenoid. Once the TCB reaches 190 K, CO_2 is introduced. It passes through the warmer condenser, through the open solenoid, and

deposits onto the cooler sample dish as a solid. This deposition is confirmed via FTIR spectroscopy, optical imagery, and change in the mass of the sample. Next, the TCB is cooled to 175 K and acetylene is introduced via the same procedure. After both samples have been added, the liquid nitrogen to the condenser is initiated to assist with cooling of the overall system. The TSSC is cooled to Titan temperatures, and a hydrocarbon solvent is introduced (100% methane, 100% ethane, or a mixture of 50% methane and 50% ethane, by mol ratio). The chamber is held at this temperature for 30 minutes, allowing the compounds to mix and interact with each other. Then, the chamber is gradually warmed, and the solvents evaporate, leaving behind only acetylene and carbon dioxide or their reaction product. By comparing the FTIR spectra of the pure species (Fig. 3) to the mixture of compounds (examining the spectra for new bands, band shifts, or changes in band depths), and analyzing optical images (changes in morphology/structure) we can assess the formation and stability of the co-crystal.

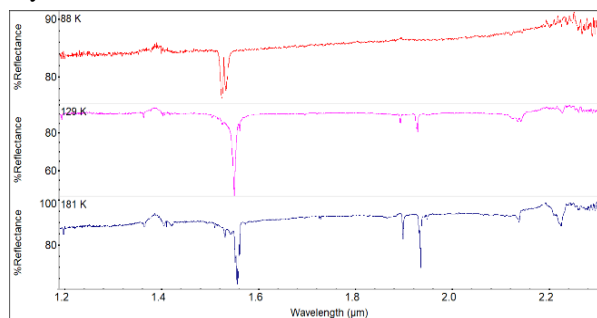


Figure 3: Pure spectra of C_2H_2 at three different temperatures. Top: 88 K. Middle: 129 K. Bottom: 181 K. There are three band transitions that occur at 89 K, 140 K, and 184 K. It is important to account for these transitions so as to not mistake them for indicators of co-crystal formation. These spectra were acquired from a C_2H_2 sample inside of the TSSC, using a Nicolet 6700 FTIR spectrometer. Spectra from [11].

Expected Results:

We hypothesize that the carbon $C_2H_2:CO_2$ co-crystal will form under Titan conditions when using 100% methane as the solvent. However, ethane, which has been confirmed to form a co-crystal with another compound [18, 19], could interfere with the formation of the $C_2H_2:CO_2$ co-crystal. We expect to see new spectral bands, observable in the near-IR, as well as band shifts. This will be assessed with future experiments.

Summary: With the launch of *Dragonfly* quickly approaching and the expansion of the field of Titan criminology, there is a growing need for experiments that investigate Titan's surface chemistry. We aim to

contribute to this field by investigating the $C_2H_2:CO_2$ co-crystal and its stability. While this co-crystal has formed under cryogenic conditions, albeit in a metastable state, it has yet to be investigated further under Titan conditions. It is our goal to fill this gap of knowledge, providing more experimental data for mission and data scientists.

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