MOLECULAR MINERALS ON TITAN: A NEW CO-CRYSTAL BETWEEN ACETYLENE AND BUTANE.

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Introduction: Titan, the largest moon of Saturn, contains a multitude of organic molecules and is considered a prebiotic chemical laboratory on a planetary scale. Photochemistry in the atmosphere induced by solar radiation and energy from Saturn's magnetosphere causes a chemical cascade, as N_2 and CH_4 dissociate and generate organic molecules ranging from simple (ethane, acetylene, HCN) to complex (>10,000 Da). These molecules continue to react as they move through Titan's atmosphere, forming aerosol haze layers and ultimately depositing on the surface [1].

Some of these organic compounds will be transported via fluvial (rivers, streams) or pluvial (rain) processes into the hydrocarbon lakes of Titan. Molecules that dissolve in these nonpolar liquids may precipitate via evaporation or other mechanisms, and could be responsible for the 5-µm bright evaporite features observed by the Cassini Visual and Infrared Mapping Spectrometer (VIMS) and Synthetic Aperture Radar (SAR) around some of the lakes in the north polar region of Titan [2].

Modeling suggests that precipitation from a Titan lake would result in an evaporite layer enriched in butane (C_4H_{10}) and acetylene (C_2H_2), regardless of whether the solvent was methane- or ethane-rich [3]. We have demonstrated in previous work [4-6] that some organic molecules readily form co-crystals in Titan-relevant conditions, including acetylene [7,8]. These molecular minerals represent an exciting new class of compounds for Titan's surface [9], which are in the initial stages of being catalogued. We report here preliminary evidence for a new co-crystal between acetylene and butane that may be the most ubiquitious on Titan of any molecular mineral discovered thus far.

Experimental: Acetylene (purified to remove acetone stabilizer) and butane (99% purity) were condensed sequentially into a liquid nitrogen-cooled cryostage (Linkam Scientific Instruments Ltd.) at 90 K. Raman spectra within the cryostage were obtained using a high-resolution confocal dispersive micro-Raman spectrometer (Horiba Jobin Yvon LabRam HR) equipped with a 50 mW Nd:YAG laser (frequency-doubled 532 nm) as the excitation source. Thermal stability studies were performed by warming in 5 or 10 K increments and obtaining Raman spectra following a 5-minute equilibration time.

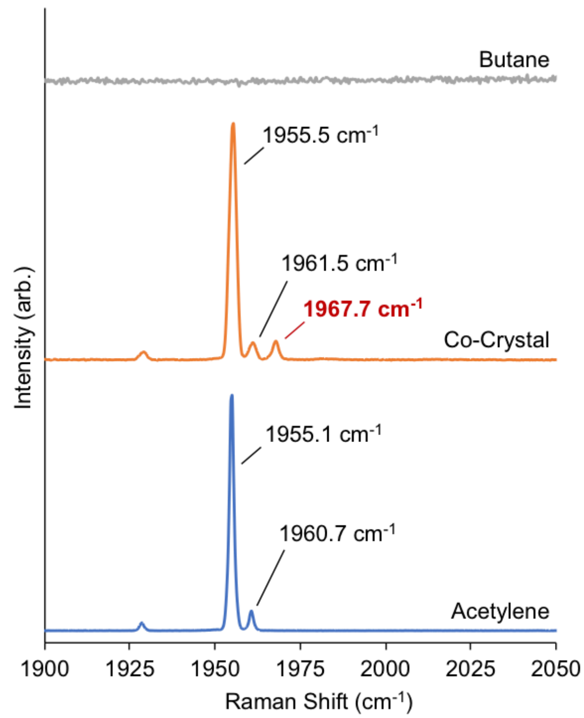

Figure 1. Raman spectra of liquid butane (gray), solid acetylene (blue) and the acetylene-butane co-crystal (orange). Spectra were collected at 130 K and are vertically offset for clarify. The clearest indication of co-crystal formation is the 12 cm^{-1} blue shift in the C≡C stretching mode of acetylene (red).

Results: Blue shifts (12–29 cm^{-1}) of the C≡C and C-H stretching modes suggest the formation of a co-crystal (Fig. 1). Similar shifts have been observed for co-crystals of benzene and ethane (2–12 cm^{-1} red shifts) [4-6] and of acetylene and ammonia (7–16 cm^{-1} red shifts; 42–66 cm^{-1} blue shifts) [7]. These shifts indicate a change in the chemical environment of the molecular species, typically modification of a host crystal lattice to accommodate a guest molecule.

The co-crystal forms within minutes at 130 K, and is stable when cooled to Titan surface temperatures (90 K). A detailed thermal stability study indicates that this co-crystal remains intact up to 180 K (Fig. 2), approximately 20 degrees higher than the point at which acetylene sublimates in our experimental setup. This enhanced thermal stability is consistent with the benzene-ethane co-crystal which persisted up to 160 K, 15 degrees higher than pure ethane alone [5].

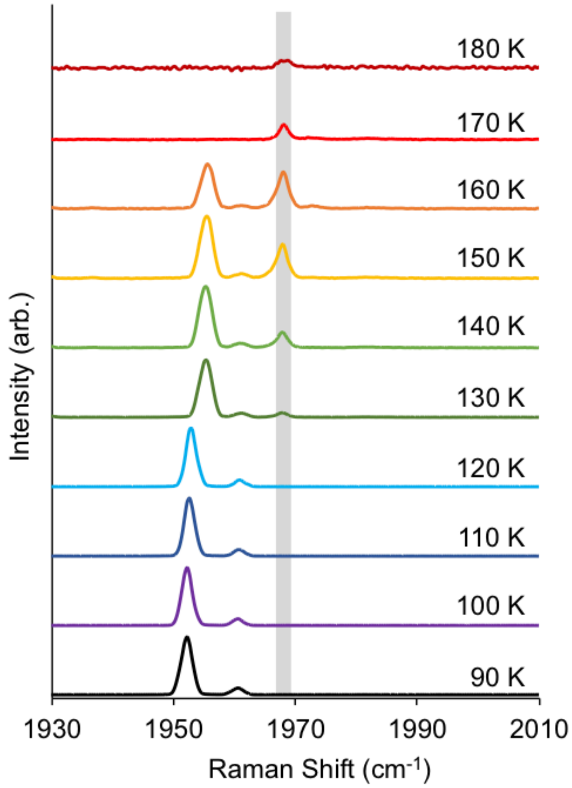

Figure 2. Thermal stability study of the acetylene-butane co-crystal. The C≡C stretch at 1968 cm^{-1} (shaded bar) indicative of the co-crystal forms rapidly at 130 K and is present up to 180 K. Spectra are vertically offset for clarity.

Interestingly, the formation temperature of the acetylene-butane co-crystal (130 K) is the same temperature at which butane melts, and is also the temperature where acetylene exhibits a phase transition from orthorhombic to cubic [10]. Subsequent experiments are underway to better characterize this possible co-crystal, and determine the relationship between co-crystal formation and these phase transitions.

Conclusions: The acetylene-butane co-crystal has been confirmed to form rapidly at 130 K and is stable at Titan surface temperatures (90 K). Given that butane and acetylene are predicted to be the most abundant evaporite materials around Titan lakes, the acetylene-butane co-crystal may be ubiquitous in these regions of Titan's surface.

Co-crystals may influence Titan surface material characteristics such as particle size, dissolution rate, structural hardness, and resistance to erosion. Given that this is the second co-crystal discovered with an alkane, it seems likely that lake edges and evaporite basins could serve as selective hydrocarbon reservoirs, possibly enriching these materials in ethane and butane over non-co-crystal-formers such as methane and propane.

Differences in physical or mechanical properties may also lead to chemical gradients on Titan, which life could potentially exploit [9]. The catalytic hydrogenation of acetylene has been proposed as a possible energy-yielding reaction for metabolism [11-13]. It is possible that acetylene-based co-crystals might be a mechanism for storing acetylene, in a manner similar to how carbon dioxide is stored in carbonate deposits on Earth, where it might be more readily accessible to a putative microbial community.

Future work will involve further characterizing the acetylene-butane co-crystal, as well as searching for new organic co-crystal structures.

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