National Aeronautics and Space Administration

Experimental Characterization of the Pyridine:Acetylene Co-Crystal and Implications for Titan Surface Chemistry

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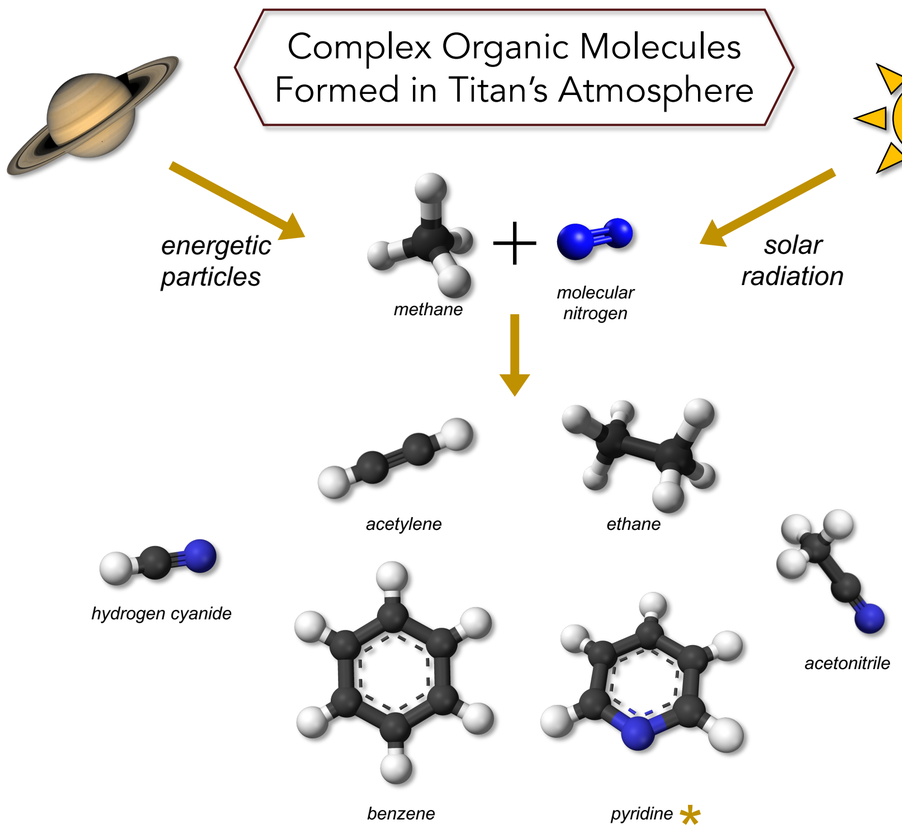
Complex Organic Molecules Formed in Titan's Atmosphere



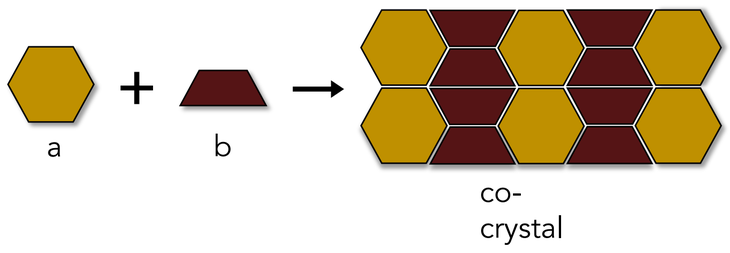
A chemical cascade of organic molecules are created in Titan's atmosphere, including acetylene and potentially pyridine. These molecules are known to interact with each other to create a **co-crystal**, a type of molecular mineral. Co-crystals may have important astrobiological and geological implications as to Titan's surface evolution.

Acetylene and Pyridine: Titan-Relevant Molecules and Known Co-Crystal Formers

	Acetylene (C_2H_2)	Pyridine (C_5H_5N)
Atmospheric Detection	*Voyager 1*, Ground-based telescopes, *Cassini*	Nondetection - 2**σ** upper limit ~1.15 ppb (uniform abundance above 300 km)
Inferred Mole Fraction in Titan's Atmosphere	3.1×10^{-4} (1077 km; Cassini INMS; Cui et al., 2009)	3.0×10^{-7} (1100 km; atmospheric model; Vuitton et al., 2019)
Probable formation Reaction(s)	$C_2H_4 + h\nu \rightarrow C_2H_2 + 2H/H_2$ (Cable et al., 2020)	$CH + C_4H_5N \rightarrow C_5H_5N + H$ (Soorkia et al., 2010)
Melting Point	189 K	231 K

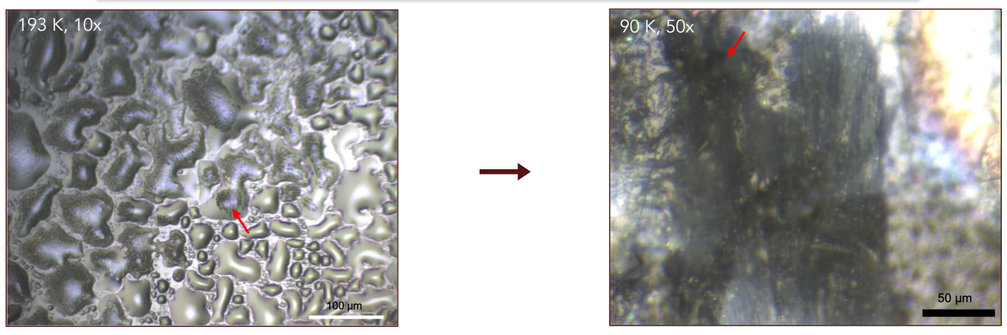
Acetylene is a significant photochemical product in Titan's atmosphere that forms through methane and ethylene photolysis, and is also a **common co-crystal former**.

* While pyridine has not definitively been detected in Titan's atmosphere, it may be present in small amounts; pyridine is **astrobiologically significant** in that it resembles nucleobases and is a stable N-heterocycle.



- Co-crystals are compounds with a crystalline structure in a set ratio.
- Stable structures held together by weak interactions
- "**cryominerals**"
- Can discern the surface-scale composition and **geologic processes**

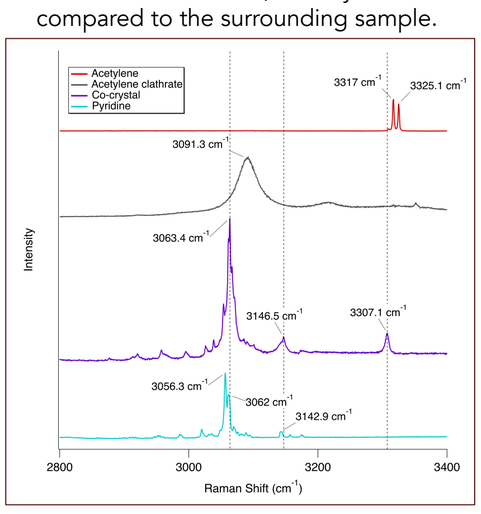
Micro-Raman Spectroscopy Experiments for Discerning Morphology and Molecular Interactions



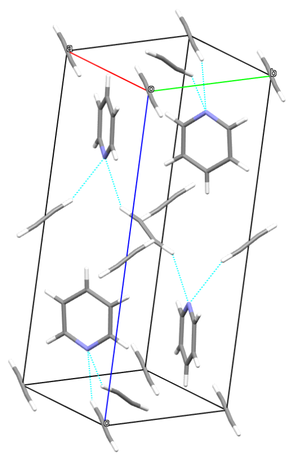
At 273 K, 50 µL of pyridine was deposited in the cryostage. Acetylene gas was deposited until the sample froze at 185 K. Notice the acetylene crystallization within the pyridine droplets (arrow).

Resulting mixture was cooled to ~90 K (Titan surface temp.) as the co-crystal formed. Notice the low albedo, "brainy" texture compared to the surrounding sample.

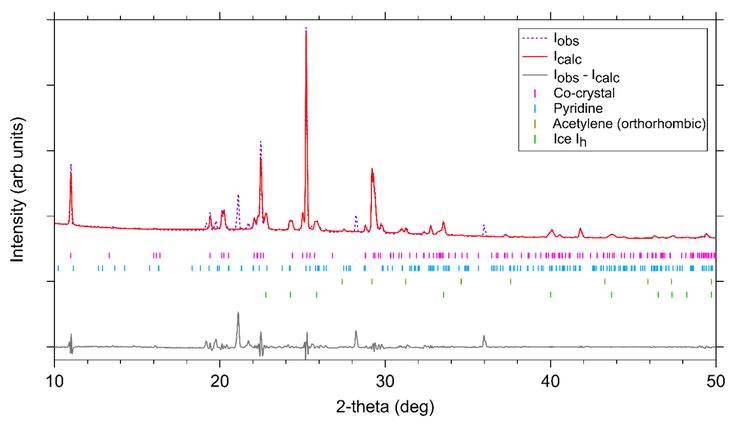
- 90 K Raman spectra of the co-crystal compared to pure compounds
- C–H stretching region
- Lack of splitting in the co-crystal band at 3307.1 cm^{-1} compared to the associated acetylene bands (3317 and 3325.1 cm^{-1}) indicates co-crystal formation
- Co-crystal is also evidenced by changes in shape and intensity of bands near 3063.4 cm^{-1}.
- Co-crystal is stable from 90 K to 190 K
- Co-crystal detectable after ethane "wetting"



X-Ray Diffraction (XRD) Experiments for Determining Crystal Structure



Orthorhombic unit cell represents co-crystal intermolecular reactions. Two half molecules of acetylene are bonded to one pyridine N atom (blue), giving a **1:1 stoichiometry** (cyan). The co-crystal expands along the *b* and *c* axes, which indicates **weaker bonds** along those axes.



110 K XRD pattern of the pyridine:acetylene co-crystal (purple), calculated refinement (red), and residual pattern (gray, offset for clarity). Tick marks below the patterns represent the Bragg peak positions of the co-crystal (magenta) and pure components.

Distinctive diffraction peaks due to co-crystal formation (e.g., at 11°, 19.4°, 20.1°, 20.25°) were immediately apparent after the pyridine-acetylene mixture was cooled to 173 K.

Main Takeaways

The pyridine:acetylene co-crystal requires a liquid phase to form, which suggests **warmer environments** or liquid interactions may be necessary for this co-crystal to form on Titan.

Co-crystals allow for **concentration and increased stabilization of acetylene**, even when exposed to liquid ethane.

Thus, if acetylene-rich deposits exist on Titan's surface and interact with N-heterocycles like pyridine, these interactions could concentrate some of the **ingredients needed to support putative life**.

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Publications:

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Czaplinski, E. C., Yu. X., Dzurilla, K., Chevrier, V. F. (2020) Experimental Investigation of the Acetylene-Benzene Co-Crystal on Titan, *The Planetary Science Journal*, 1, 76.

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