The Acetylene-Butane Co-Crystal: A Potentially Abundant Molecular Mineral on Titan

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Introduction: Titan is the largest moon of Saturn, and hosts a complex organic chemistry in its atmosphere and on its surface. Of particular interest is how organic molecules – generated in the atmosphere and deposited on the surface – interact with the hydrocarbon lakes in Titan's polar regions. Some small, nonpolar species may dissolve in the liquid methane and ethane, and precipitate when the liquid evaporates. Such molecules 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 (Barnes et al. 2009).

Modeling suggests that an evaporite layer produced by such a mechanism would be enriched in butane (C_4H_{10}) and acetylene (C_2H_2), regardless of whether the solvent was methane- or ethane-rich (Cordier et al. 2013). We have demonstrated previously (Vu et al. 2014; Cable et al. 2014; Maynard-Casely et al. 2016) that some organic molecules readily form co-crystals in Titan-relevant conditions, including acetylene (Cable et al. 2018). We report here preliminary evidence for a third co-crystal between acetylene and butane, which could be the most common molecular mineral discovered so far.

Experimental: Acetylene (purified to remove acetone stabilizer) and butane (99% purity) were condensed into a liquid nitrogen-cooled cryostage (Linkam Scientific Instruments Ltd.) at 90 K or 130 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.

Results: Blue shifts (12–29 cm^{-1}) of the C≡C and C-H stretching modes indicate the formation of a co-crystalline compound. We observed similar shifts for co-crystals comprised of benzene and ethane (2–12 cm^{-1} red shifts; Vu et al. 2014) and of acetylene and ammonia (7–16 cm^{-1} red shifts; 42–66 cm^{-1} blue shifts; Cable et al. 2018). 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 thermal stability study indicates that this co-crystal remains intact up to 180 K, 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 to temperatures 15 degrees higher than pure ethane alone (Cable et al. 2014).

Conclusions: The acetylene-butane co-crystal 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.

Differences in physical or mechanical properties may lead to chemical gradients on Titan, which life could potentially exploit (Maynard-Casely et al. 2018). The catalytic hydrogenation of acetylene has been proposed as a possible energy-yielding reaction for metabolism (Schulze-Makuch et al. 2005; McKay et al. 2005; Tokano et al. 2009). 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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