LABORATORY INVESTIGATIONS OF TITAN EVAPORITE MATERIALS.

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

Some of these molecules will be transported via fluvial or pluvial processes into the methane and ethane lakes of Titan. Those that have dissolved in the lakes may precipitate via evaporation or other mechanisms, forming 'bathtub rings' similar to those observed by the Cassini Visual and Infrared Mapping Spectrometer (VIMS) and Synthetic Aperture Radar (SAR) around some of the northern lakes [2].

We have demonstrated in previous work [3-5] that two common organic molecules on Titan, ethane and benzene, form a unique and stable co-crystalline structure at Titan surface temperatures. This material represents an exciting new class of compounds for Titan's surface, and implies that lake edges and evaporite basins could serve as hydrocarbon reservoirs on Titan.

This finding has motivated our search for other co-crystals that may form under Titan surface conditions. We report here the formation of a co-crystal between acetylene and ammonia, two other potential Titan surface molecules, as well as preliminary evidence for a third co-crystal with benzene and acetylene.

Experimental: *Acetylene-ammonia experiment.* Anhydrous ammonia was condensed from the gas phase onto a liquid nitrogen-cooled cryostage (Linkam Scientific Instruments Ltd.) at 94 K. Acetylene was then condensed onto the solid ammonia. Raman spectra within the cryostage were obtained using a high-resolution confocal dispersive micro-Raman spectrometer (Horiba Jobin Yvon LabRam HR) equipped with a Nd:YAG laser (frequency-doubled 532 nm, 50 mW) as the excitation source. Thermal stability studies were performed by warming to a specific temperature and obtaining Raman spectra following a 10 minute equilibration time.

Benzene-aceteylene experiment. Approximately 1 cubic centimeter of solid acetylene was condensed at 94 K in a custom-built cryostat under N_2 atmosphere at 1 bar. About 5 mL of liquid ethane was condensed and mixed with the acetylene, forming an opaque suspension. A 200 μL aliquot of benzene was frozen on a glass substrate in the liquid nitrogen-cooled cryostage maintained at 90 K. A ~2 mL aliquot of the acetylene-ethane mixture was deposted on top of the solid benzene. The ethane was evaporated by heating to 110 K and purging with N_2.

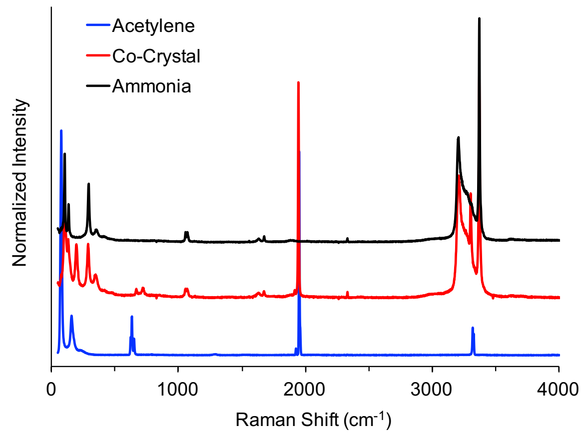

Figure 1. High-resolution Raman spectrum of acetylene-ammonia co-crystal at 94 K (red) shows new features compared to acetylene (blue) and ammonia (black) alone. All spectra are vertically off-set for clarity.

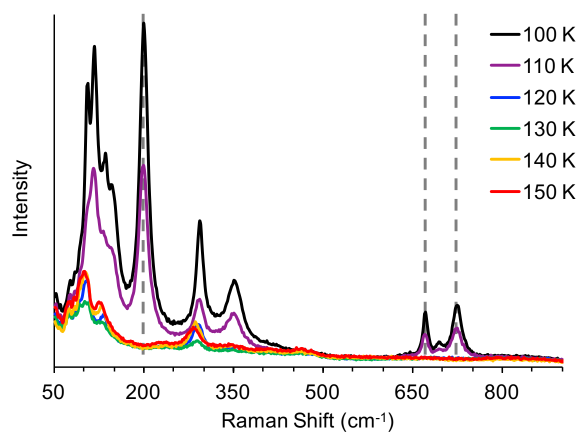

Figure 2. Unique spectral features of the acetylene-ammonia co-crystal (dashed gray lines) are present up to 110 K. The melting points of acetylene and ammonia are 192 K and 195 K, respectively, so loss or change in phase of the precursors cannot explain the disappearance of these features.

Results: *Acetylene-ammonia experiment.* New spectral features were observed in the Raman spectrum at 197, 669 and 722 cm^{-1}, in the low frequency regions of lattice vibrations and C-H bending modes (Fig. 1). These new features, as well as a red shift from 3316 to 3300 cm^{-1} of the C-H stretching mode, suggest the formation of a co-crystal. This structure forms within minutes, and appears to be stabilized by a network of C-H···N interactions. Thermal stability studies indicate that this co-crystal remains intact until 110 K (Fig. 2). Thus, an ammonia-acetylene co-crystal can be expected to occur readily and remain stable under Titan surface conditions.

Benzene-acetylene experiment. A preliminary experiment where acetylene was dissolved in liquid ethane at 94 K and mixed with solid benzene generated interesting features once the ethane evaporated (Fig. 3). These new features are stable up to 143 K, are not consistent with benzene, acetylene or ethane alone, and are distinct to the signature from the known co-crystals of acetylene:benzene [6]. Further work is needed to determine if this is indeed a benzene-acetylene co-crystal, and if so, whether ethane is required for it to form.

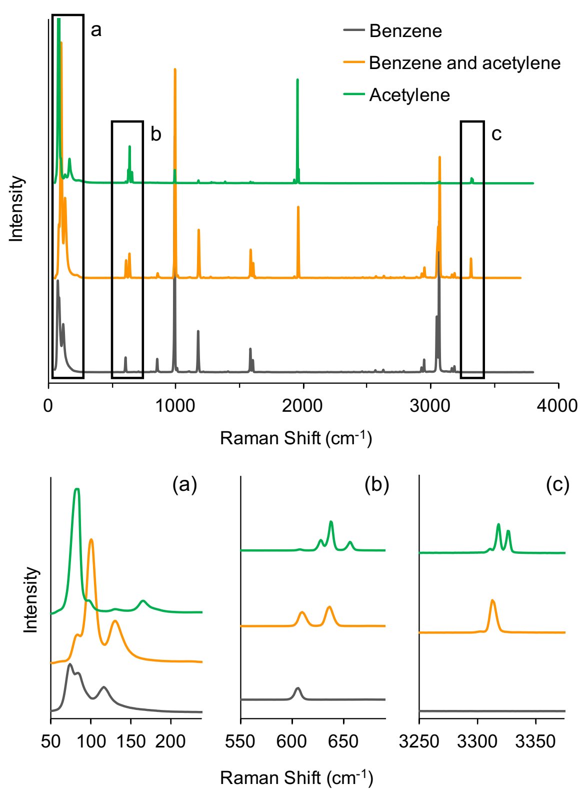

Figure 3. New features in the Raman may indicate a co-crystal between benzene and acetylene. All spectra are vertically off-set for clarity.

Conclusions: Ammonia and acetylene form a co-crystal at Titan surface temperatures. The structure is stable up to 110 K. While the acetylene-ammonia co-crystal has been observed previously in aerosols at 78 K and lower pressures [7-8], this is the first report of acetylene and ammonia forming a co-crystal under Titan surface conditions.

The confirmation of a second organic co-crystal, and preliminary evidence for a third, suggests that organic co-crystals may be abundant on Titan. These structures may influence evaporite characteristics such as particle size and dissolution rate. They may also be responsible for dynamic surface phenomena, such as the selective sequestration and storage of certain species over others (i.e., ethane over methane).

Acetylene was detected in Titan's atmosphere by the Cassini Ion and Neutral Mass Spectrometer (INMS) [9] and on the surface with the Huygens GC-MS [10]. The origin of Titan's nitrogen-rich atmosphere is most likely ammonia ice [11], meaning ammonia may still exist in the atmosphere, on the surface and in Titan's subsurface ocean [12]. Mixing of acetylene and ammonia could occur via cryovolcanism or other surface processes [13]. Subsequent experiments are underway to put acetylene and ammonia in contact under some of these conditions.

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