

**TITAN ORGANIC CO-CRYSTALS: MORE COMMON THAN WE THINK?** M. L. Cable<sup>1</sup>, T. H. Vu<sup>1</sup>, H. E. Maynard-Casely<sup>2</sup> and R. Hodyss<sup>1</sup>, <sup>1</sup>NASA Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA (Morgan.L.Cable@jpl.nasa.gov), <sup>2</sup>Australian Nuclear Science and Technology Organisation, NSW, Australia.

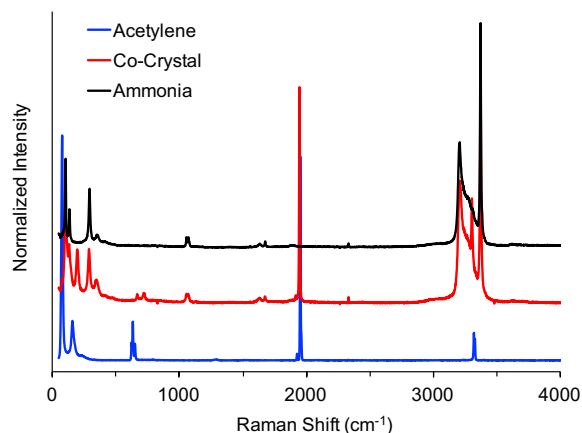
**Introduction:** Titan contains a vast inventory of organic molecules and is considered a prebiotic chemical laboratory on a planetary scale. Solar radiation and energy from Saturn's magnetosphere cause N<sub>2</sub> and CH<sub>4</sub> to dissociate and recombine, generating organics ranging from simple (ethane, acetylene, HCN) to complex (>10,000 Da) molecules that ultimately deposit onto 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 dissolve 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 suggests that lake edges and evaporite basins could serve as hydrocarbon reservoirs on Titan.

We have recently identified an organic co-crystal between acetylene and ammonia, two other potential Titan surface molecules, and have preliminary evidence for a third co-crystal with benzene and acetylene.

**Experimental:** Anhydrous ammonia was condensed 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.

**Results:** New spectral features were observed in the Raman spectrum in the low frequency regions of lattice vibrations and C-H bending modes (Fig. 1). 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. Thus, an ammonia-acetylene co-crystal can be expected to occur readily and remain stable under Titan surface conditions.



**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). All spectra are vertically off-set for clarity.

**Conclusions:** Ammonia and acetylene form an organic co-crystal that is stable up to 110 K. While this co-crystal has been observed previously in aerosols at 78 K and lower pressures [6-7], 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). Noncovalent interactions such as this also inform us about possibilities for the chemistry of cold non-aqueous life.

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**References:** [1] Cable, M.L. et al. (2012) *Chem. Rev.*, 112, 1882-1909. [2] Barnes, J.W. et al. (2009) *Icarus*, 201, 217-225. [3] Vu, T.H. et al. (2014) *J. Phys. Chem.*, 118, 4087-4094. [4] Cable, M.L. et al. (2014) *GRL*, 41, 5396-5401. [5] Maynard-Casely, H.E. et al. (2016) *IUCrJ*, 3, 192-199. [6] Boese R. et al. (2009) *JACS*, 131, 2104-2106. [7] Preston, T.C. and Signorell, R. (2012) *Mol. Phys.*, 110, 2807-2815.