EVIDENCE FOR A NEW TITAN MOLECULAR MINERAL: A CO-CRYSTAL BETWEEN ACETYLENE AND ACETONITRILE. Morgan L. Cable[1], Tuan H. Vu[1], Helen E. Maynard-Casely[2], Michael Malaska[1], Mathieu Choukroun[1] and Robert Hodyss[1], [1]NASA Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA (Morgan.L.Cable@jpl.nasa.gov), [2]Australian Nuclear Science and Technology Organisation, NSW, Australia.

Introduction: Titan, Saturn's largest satellite, contains an impressive inventory of organic molecules and is considered a prebiotic chemical laboratory on a planetary scale. Photochemistry in the atmosphere induced by solar radiation and particles from Saturn's magnetosphere causes a chemical cascade, dissociating N_2 and CH_4 and generating a plethora of small and large organic molecules. These molecules continue to react as they are transported through Titan's thick atmosphere, forming aerosol haze layers and ultimately depositing on the surface [1, 2].

Acetylene (C_2H_2) is the primary solid photochemical product generated in Titan's atmosphere [3-7]. It was first identified in the upper atmosphere of Titan by Voyager 1 and ground-based observations [8]. This was later confirmed by the Composite Infrared Spectrometer (CIRS) [9] and Ion and Neutral Mass Spectrometer (INMS) [10] instruments on Cassini. Acetylene was also detected on the surface by the gas chromatograph mass spectrometer (GC-MS) of the Huygens probe [11].

Acetonitrile (CH_3CN) is also a relatively abundant photochemical product on Titan. It has been detected in Titan's stratosphere using millimeter-wave ground-based spectroscopy [12, 13]. Titan observations performed by the Infrared Space Observatory (ISO) in the range 7–30 µm estimate an upper limit of 5×10^{-10} for the abundance (mixing ratio) of acetonitrile [14].

Given that both acetylene and acetonitrile are relatively abundant on Titan (Table 1) and solid at Titan surface temperatures (90-95 K), these two organic solids could come into contact for extended periods either via co-condensation in the atmosphere (both condense at ~65-70 km altitude) or fluvial/pluvial transport (acetylene is soluble in liquid methane and ethane and could be washed by rain or rivers into areas rich in acetonitrile). Previous work indicates these two molecules can form a co-crystal [15], but this has not been demonstrated at Titan surface temperatures.

Table 1. Net photochemical production rates of acetylene and acetonitrile in Titan's atmosphere from ref [5].

Species	Formula	Production rate ($cm^{-2} \cdot s^{-1}$)
Acetylene	C_2H_2	3.2×10^8
Acetonitrile	CH_3CN	1.7×10^7

We have shown in previous work [16-18] that some organic molecules readily form co-crystals in Titan-relevant conditions, including acetylene [19, 20]. These molecular minerals represent an exciting new class of compounds for Titan's surface [21], which are in the initial stages of being characterized. We report here preliminary evidence for a co-crystal between acetylene and acetonitrile at Titan surface temperatures that could be present at relatively abundant quantities.

Experimental: A 50 µL aliquot of acetonitrile (99.8% purity) was deposited on a microscope slide within a liquid nitrogen-cooled cryostage (Linkam Scientific Instruments Ltd.) and cooled to 90 K. Acetylene (purified to remove acetone stabilizer) was condensed onto the frozen acetonitrile. 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.

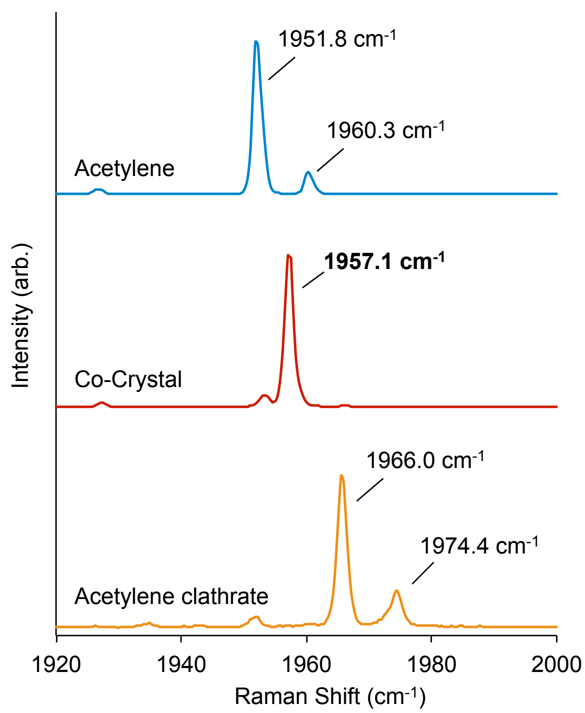

Figure 1. Raman spectra of pure acetylene (blue), the acetonitrile-acetylene co-crystal (red) and acetylene clathrate hydrate (orange). Spectra were collected at 110 K and are vertically offset for clarify. The clearest indication of co-crystal formation is the 5.3 cm^{-1} blue shift in the C≡C stretching mode of acetylene to 1957.1 cm^{-1}, which is very distinct from acetylene trapped in a clathrate hydrate.

Results: Blue shifts (3–37 cm^{-1}) of the C≡C, C≡N and C-H stretching modes suggest the formation of a co-crystal (Figs. 1-2). Similar shifts have been observed for co-crystals of benzene and ethane (2–12 cm^{-1}) [16-18], acetylene and ammonia (7–16 cm^{-1}) [19], and acetylene and butane (7-22 cm^{-1}) [20]. 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 110 K, and is stable when cooled to Titan surface temperatures (90 K). A preliminary thermal stability study indicates that this co-crystal remains intact up to 130 K, although it may be metastable above this temperature.

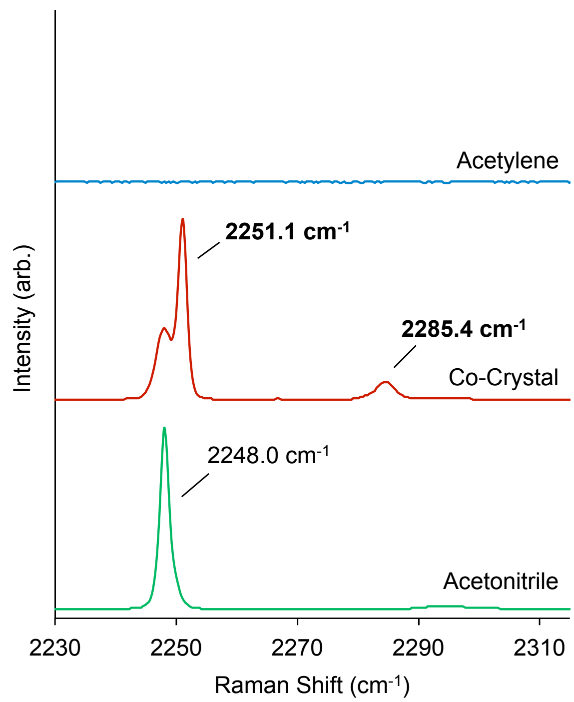

Figure 2. Raman spectra of pure acetylene (blue), the acetonitrile-acetylene co-crystal (red) and pure acetonitrile (green). Spectra were collected at 110 K and are vertically offset for clarify. The C≡N stretching mode of acetonitrile shifts by 3.1 cm^{-1} to 2251.1 cm^{-1}, and a new peak appears at 2285.4 cm^{-1}, a significant blue shift. Note that some pure acetonitrile is still present in the co-crystal spectrum. Acetylene contains no C≡N bond, so its spectrum is featureless in this region.

Conclusions: The acetonitrile-acetylene co-crystal has been confirmed to form rapidly at 110 K and is stable at Titan surface temperatures (90 K). Given that acetonitrile is nearly as abundant as acetylene, this co-crystal may be plentiful on the surface of Titan (almost as abundant as the acetylene-butane co-crystal [21]).

Differences in physical or mechanical properties within these co-crystalline materials may lead to chemical gradients on Titan, which life could potentially exploit [21]. The catalytic hydrogenation of acetylene has been proposed as a possible energy-yielding reaction for metabolism [22-24]. It is possible that acetylene-based co-crystals might be a mode for storing acetylene, in a manner similar to how carbon dioxide is stored in carbonate deposits on Earth, where it might be more easily accessible to a putative microbial community. Further, acetonitrile has been invoked as a potential membrane-forming molecule in nonpolar solvents such as liquid methane and ethane [25]. This co-crystal may therefore host both a molecule suitable for constructing cell membranes as well as energy for such putative life in the same mineral structure.

Future work will involve further characterizing the acetonitrile-acetylene co-crystal, as well as searching for new molecular minerals.

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