

**HYDROCARBON TRAPPING IN TITAN SURFACE MATERIALS.** M. L. Cable<sup>1</sup>, T. Vu<sup>1</sup>, M. Choukroun<sup>1</sup>, R. Hodyss<sup>1</sup> and P. Beauchamp<sup>1</sup>, <sup>1</sup>Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109 (Patricia.M.Beauchamp@jpl.nasa.gov)

**Introduction:** Titan is the only body in the Solar System other than Earth with standing liquids on its surface. On this cold and distant moon, the liquid phase is comprised of hydrocarbons such as methane and ethane. Modeling of hydrocarbon lake composition suggests that some organic species may be present at or near their saturation levels [1]. Loss of solvent in the lakes via evaporation or other processes could induce precipitation of these dissolved organics. The ‘bathtub rings’ observed by Cassini around some of the Northern lakes on Titan (Figure 1) may be evidence of formation of such evaporites [2], which may play an important role in the surface chemistry of Titan.

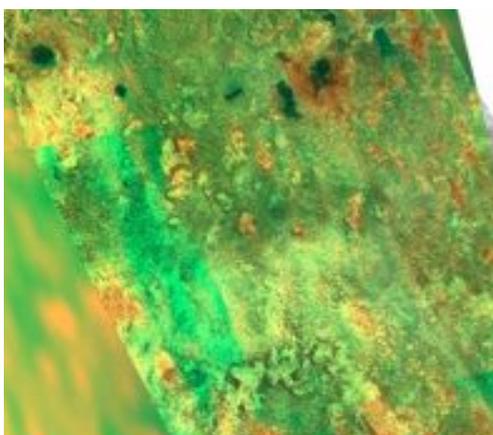
The motivation for this work is to understand the composition and morphology of likely evaporites and other deposits on the shorelines of hydrocarbon lakes on Titan. We focus on benzene, a relatively simple organic molecule that has been detected in Titan’s atmosphere by Cassini [3-4], and was found to be the most abundant heavy molecule in Titan’s thermosphere [4]. Further, benzene was tentatively identified on the surface of Titan by the GC-MS of Huygens [5], a result that is supported by Cassini VIMS measurements [6]. Recent work in our laboratory [7] indicates that benzene has very low solubility in liquid ethane (18 mg/L); thus, it would be one of the first and most abundant evaporites to form as Titan lake levels drop.

We recently investigated the effect of co-depositing benzene and a hydrocarbon (methane or ethane) under vacuum at 12 K, and subsequently warming to Titan surface temperature (94.5 K). Even under dynamic

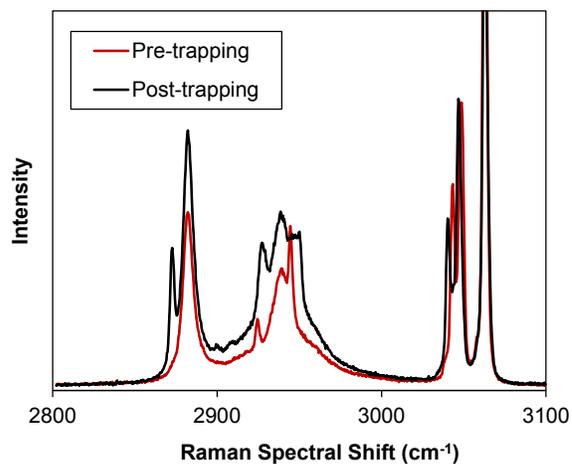
vacuum ( $10^{-10}$  Torr), benzene ice maintained a level of approximately 4% trapped methane or ethane for a significant amount of time (>20 hrs). In the higher pressure conditions (1.5 bar) on the Titan surface, this trapping effect should not only be possible, but may be much more pronounced.

**Methods:** Ethane was condensed at Titan surface temperature (90 K) under N<sub>2</sub> atmosphere in a custom-built cryostat. Benzene was either added to saturation or frozen separately to produce a greater quantity of crystalline material. An aliquot of the sample was transferred to a Linkam LTS 350 liquid nitrogen-cooled cryostage. The sample was then analyzed within the cryostage using a Horiba Jobin Yvon LabRam HR confocal Raman microscope with a Nd:YAG laser (frequency-doubled 532 nm, 50 mW) as the excitation source and a 1800 gr/mm grating, providing a resolution of  $0.4\text{ cm}^{-1}$ .

**Results:** Precipitation of benzene from liquid ethane produces various crystal morphologies, including hexagonal, needle-like and globular crystals. Trapping of ethane in crystalline benzene was induced by warming a mixture of solid benzene and liquid ethane to 110 K for 15 minutes, followed by cooling to 90 K. Figure 2 shows the Raman spectra of this mixture before and after trapping of ethane. Before trapping, the  $\nu_1$  mode of ethane displays a single peak at  $2883\text{ cm}^{-1}$ , indicative of liquid ethane. After trapping, a second peak appears at  $2873\text{ cm}^{-1}$ . The  $\nu_7$  modes of benzene, at  $3047$  and  $3040.5\text{ cm}^{-1}$ , also red-shift on trapping, while the  $\nu_2$  mode at  $3065\text{ cm}^{-1}$  does not. The Raman spectral



**Figure 1.** Overlaid Cassini VIMS and radar data of Titan’s northern lakes, showing bedrock (green) and possible evaporites (yellow/brown). Reproduced from [2].



**Figure 2.** High resolution Raman spectra of crystalline benzene and liquid ethane, pre- and post-trapping.

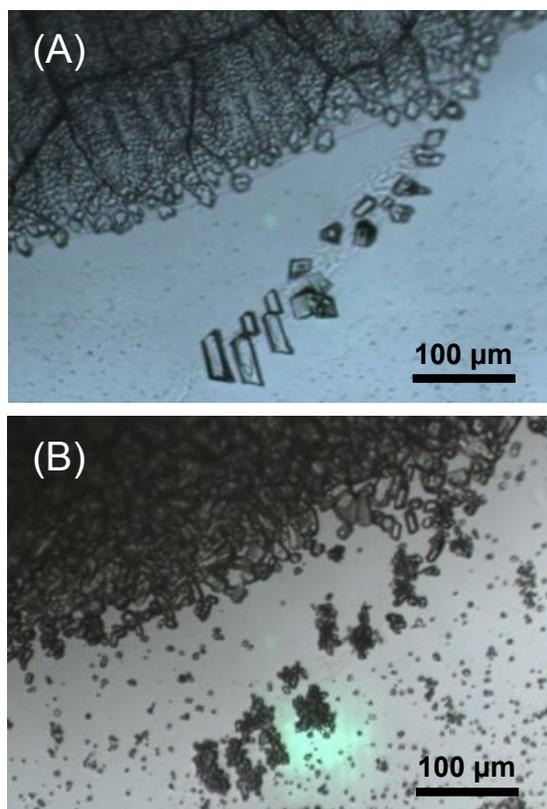
shifts of the ethane and benzene peaks imply that ethane is incorporated into the benzene matrix, and that the interaction occurs between the ethane hydrogens and the  $\pi$  electrons of the benzene.

Microscope images of the crystal before and after trapping (Figure 3) indicate that benzene and ethane form a new crystal structure upon trapping. Together with the Raman spectra, this suggests a change in the crystal structure of the solid to include ethane, most likely as a co-crystal.

Kinetics experiments to explore the temperature dependence of the trapping process yield an activation energy of 10.2 kJ/mol. Extrapolation of the trapping process to Titan surface temperatures indicates saturation will be reached in  $\sim 18$  hrs at 90 K. This suggests that trapping of ethane in a benzene evaporite would occur readily in Titan ambient conditions, implying that evaporite basins may act as important hydrocarbon reservoirs on Titan. Future work will involve investigation of methane trapping in greater detail.

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**References:** [1] Cordier D. et al. (2009) *Ap J*, 707, L128. [2] Barnes J. W. et al (2011) *Icarus*, 216, 136-140. [3] Coustenis A. et al. (2007) *Icarus*, 189, 35-62. [4] Waite J. H. et al. (2005) *Science*, 308, 982-986. [5] Niemann H. B. et al. (2005) *Nature*, 438, 779-784. [6] Clark R. N. et al. (2010) *JGR*, 115, E10. [7] Malaska M. and Hodyss R. (2013) Personal communication.



**Figure 3.** Microscope images (10X) of benzene crystals, pre-trapping (A) and post-trapping (B), showing evidence for re-crystallization.

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