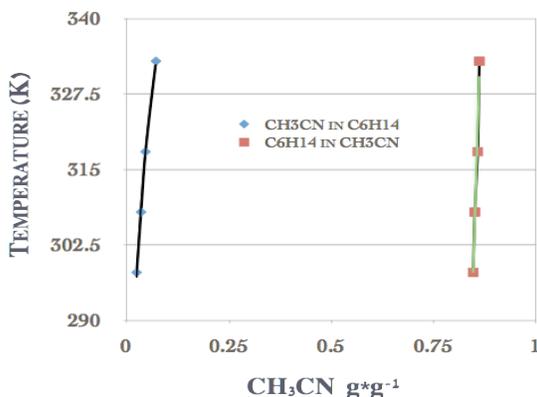


**SOLUBILITY AND DETECTABILITY OF ACETONITRILE IN TITAN LAKES.** M. Leitner<sup>1,2</sup>, S. Singh<sup>1</sup>, V.F. Chevrier<sup>1</sup>, <sup>1</sup>Arkansas Center for Space and Planetary Sciences, University of Arkansas, Fayetteville, Arkansas 72701, <sup>2</sup>Dept. of Physics and Astronomy, Humboldt State University, Arcata, California 9521, mal174@humboldt.edu.

**Introduction:** Titan is the only body aside from Earth on which stable bodies of liquid have been found [1]. Its lakes contribute to a methane-driven hydrological cycle making it a good analog to an early Earth. The exact composition of its lakes however is still a subject of study. They are thought to be composed predominantly of methane (CH<sub>4</sub>) and ethane (C<sub>2</sub>H<sub>6</sub>) as well as a variety of other hydrocarbons and hydrocarbon ices [2, 3]. However current results lack precision and the solubility of these various molecules under Titan conditions is not very well studied. Acetonitrile (CH<sub>3</sub>CN) in particular is of great interest due to its astrobiological implications and its role as a potential precursor in the formation of amino acids [4].

In order to study acetonitrile's solubility in CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> and whether it can be spectrally detected, bench-top experiments were performed in which spectra was taken of acetonitrile-saturated hexane (C<sub>6</sub>H<sub>14</sub>). To study CH<sub>3</sub>CN under Titan conditions, it was mixed with liquid CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> within a chamber which simulates Titan surface temperature, pressure and atmosphere [5].



**Figure 1.** Phase diagram for C<sub>6</sub>H<sub>14</sub> and CH<sub>3</sub>CN. The left curve of the graph represents the saturation of CH<sub>3</sub>CN in C<sub>6</sub>H<sub>14</sub> at various temperatures. Image credit [6].

### Methods:

*Bench-top experiment.* The bench-top experiment was performed by saturating liquid C<sub>6</sub>H<sub>14</sub> with liquid CH<sub>3</sub>CN. C<sub>6</sub>H<sub>14</sub> was chosen because it remains in liquid form at ambient temperatures and because of its spectral similarities to other simple chained hydrocarbons like ethane.

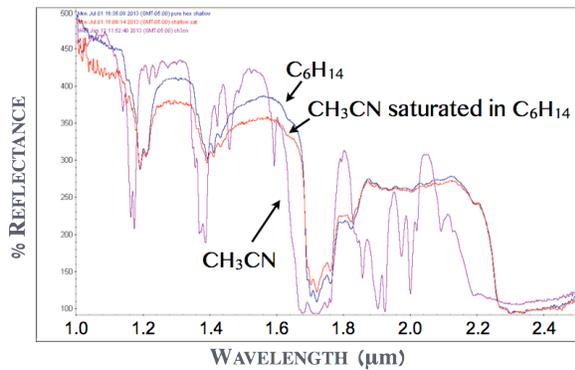
CH<sub>3</sub>CN was saturated in C<sub>6</sub>H<sub>14</sub> by gradually mixing it drop by drop. Mixing between drops was performed using a closed container. The solution was then transferred to an open container covered by spectralon (reflectance background), in which spectra were taken using FTIR so that comparisons could be made with increasing concentration. The saturation concentration was estimated using a phase diagram (Fig. 1).

*Chamber experiments.* Experiments under Titan conditions were performed using a Titan simulation chamber in which Titan temperatures and pressures are reached using liquid or gaseous nitrogen [5].

N<sub>2</sub> gas was first bubbled through liquid CH<sub>3</sub>CN at ambient temperature allowing us to introduce CH<sub>3</sub>CN to the chamber in gas form. The gas mixture flowed into the condenser over a time-span of approximately 20 minutes, during which time the pressure valve was kept open to allow the CH<sub>3</sub>CN-N<sub>2</sub> gas to flow as well as the bottom solenoid valve which allowed the N<sub>2</sub> gas to escape after the CH<sub>3</sub>CN condensed onto the condenser's walls. Next, CH<sub>4</sub> or C<sub>2</sub>H<sub>6</sub> was condensed over CH<sub>3</sub>CN ice within the condenser. The liquid then passes through a fritted glass filter (25-60 μm) and collects onto a petri dish exposed to the Titan-simulated atmosphere at approximately 94 K and 1.5 bar where spectra is then taken.

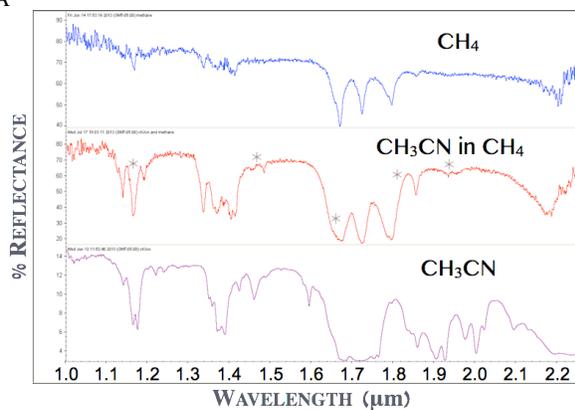
### Results and Discussion:

*Bench-top experiment.* CH<sub>3</sub>CN-saturated C<sub>6</sub>H<sub>14</sub> spectra can be seen in Figure 2 with pure CH<sub>3</sub>CN and C<sub>6</sub>H<sub>14</sub> spectra present for comparison. No definite CH<sub>3</sub>CN features could be identified in the spectrum of saturated hexane, although potential features might be made clearer with further analysis. This suggests that the solubility of CH<sub>3</sub>CN is below the detection limit by FTIR, since the solubility of CH<sub>3</sub>CN is about 2 wt% at ambient temperature (e.g. Fig. 1). It is also possible that slow kinetics prevented full saturation from being reached during sample preparation.

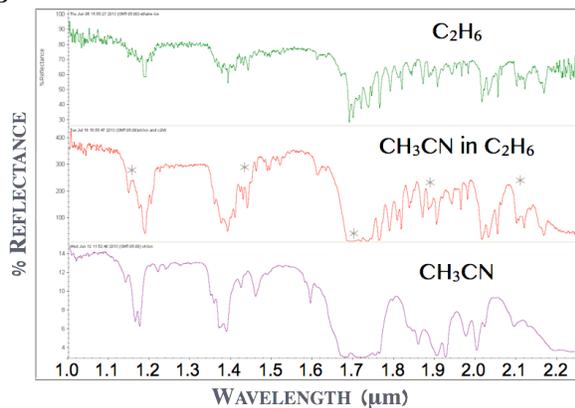


**Figure 2.** NIR spectra from bench-top experiment of  $\text{CH}_3\text{CN}$ -saturated  $\text{C}_6\text{H}_{14}$  with pure  $\text{CH}_3\text{CN}$  and  $\text{C}_6\text{H}_{14}$  spectra for comparison.

A



B



**Figure 3.** NIR spectra from chamber experiments of  $\text{CH}_3\text{CN}$  in  $\text{CH}_4$  (A) and  $\text{C}_2\text{H}_6$  (B). \* indicate  $\text{CH}_3\text{CN}$  spectral features.

*Chamber experiments.*  $\text{CH}_3\text{CN}$  features are clearly identified in both liquid  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  experiments as is seen in Fig. 3A and Fig. 3B, respectively. In  $\text{CH}_4$ , features can be seen at wavelengths: 1.14, 1.46, 1.48 and 1.94  $\mu\text{m}$  with distinct widening between 1.65-1.68  $\mu\text{m}$ . The features at 1.46 and 1.48  $\mu\text{m}$  correspond to  $\text{CH}_3\text{CN}$  CN stretch. In  $\text{C}_2\text{H}_6$ , features can be seen at

wavelengths: 1.14, 1.46 and 2.8  $\mu\text{m}$  with clear evidence of approaching saturation point between 1.68-1.74  $\mu\text{m}$ . Once again, evidence of the CN stretch is present in the 1.46  $\mu\text{m}$  feature. The band depth of the absorption band centered at 1.46  $\mu\text{m}$  is greater in  $\text{C}_2\text{H}_6$  than in  $\text{CH}_4$ , which reflects greater solubility in liquid ethane. The negative slope at 2.0  $\mu\text{m}$  in  $\text{CH}_4$  and  $\text{CH}_3\text{CN}$  mixture is overlaying with the absorption band at 2.2  $\mu\text{m}$  but clear there is shift the band due to  $\text{CH}_3\text{CN}$ . In  $\text{C}_2\text{H}_6$ - $\text{CH}_3\text{CN}$  mixture, the occurrence of negative slope reflects high solubility.

**Conclusion:** We have studied the solubility of  $\text{CH}_3\text{CN}$  in Titan liquid hydrocarbons and found out  $\text{CH}_3\text{CN}$  might be more soluble in  $\text{C}_2\text{H}_6$  than  $\text{CH}_4$ . Solubility experiments of hydrocarbon ices within Titan lakes is not very well studied nor understood under Titan conditions. Knowledge of this can be very useful when studying the compositions of evaporites as lake levels decrease through evaporation. The absorption bands 1.59  $\mu\text{m}$  and a negative slope at 2.0  $\mu\text{m}$  lies in the two of VIMS atmospheric windows and can be used to detect  $\text{CH}_3\text{CN}$  in the Titan lakes. Observations made in lab will be necessary to determine the amount of solutes present in Titan lakes. Spectrally studying  $\text{CH}_3\text{CN}$  in particular under Titan conditions is of value to the astrobiological studies being done as  $\text{CH}_3\text{CN}$  is one of the precursors in the formation of amino acids--one of the hypothesized first steps in the creation of life.

**Future Studies:** Future studies will include attempting to use a spectral-unmixing program along with mass data obtained from chamber experiments to calculate values for the solubility of  $\text{CH}_3\text{CN}$  in  $\text{C}_2\text{H}_6$  and in  $\text{CH}_4$ . Future studies could also extend to other hydrocarbon ices such as benzene ( $\text{C}_6\text{H}_6$ ), acetylene ( $\text{C}_2\text{H}_2$ ) or butane ( $\text{C}_4\text{H}_{10}$ ) and applying the same methods to calculate the solubilities of each compound. It will also be of interest to observe the effects of  $\text{CH}_4$  as it evaporates, leaving  $\text{CH}_3\text{CN}$  evaporites behind.

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**References:** [1] E.R. Stofan, et al. (2007) *Nature*, 445:61. [2] D. Cordier, et al. (2011) *PSS*, 3101. [3] G. Mitri, et al. (2007) *Icarus* 186, 385-394. [4] F. Raulin (2008) *Space Sci. Reviews* 135, 37-48. [5] Wasiak, F. C., Luspay-Kuti, A., Welivitiya, W. D. D. P., Roe, L. A., Chevrier, V. F., Blackburn, D. G. and Cornet, T., 2012. A facility for simulating Titan's environment. *Adv. Space Res.* 51, 1213-1220. [6] V.A. Keskinov, A.K. Pyartman, N.A. Charykov, 2009, *Zhurnal Neorganicheskoi Khimii*, 54, 701-704