Virtual Research Presentation Conference

Exploring Titan's Organic Mineralogy

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Program: Topics

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Jet Propulsion Laboratory
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Introduction

Abstract

Understanding the material properties of Titan's cryogenic organics is critical for future surface missions to Titan – our effort will deliver a new, comprehensive understanding of the physicochemical properties of the most common Titan surface organics. The Cassini-Huygens mission has revealed a wide variety of Earth-like landforms on Titan's surface: plains, mountains, dunes, lakes, seas and rivers. Titan's surface appears to be constructed from organic molecules, rather than rocks and minerals that make up Earth's surface. At a surface temperature of ~92 K, the non-covalent interactions are sufficiently strong to enable stable interactions among these organic molecules, which form an entirely new class of cryogenic organic "minerals," or naturally occurring compounds with a specific composition. The physical properties of these organic minerals have rarely, and in most cases never, been tested or explored. While simple organic molecules like acetylene, HCN, acetonitrile, etc. in their solid form are expected to be important constituents of the surface, much of their crystal structures and properties in solid state, at Titan relevant temperature, are completely unknown. The crystal structure of a solid material is one of its most fundamental properties, and is necessary for understanding of intermolecular interactions and for prediction of mechanical and chemical properties – such as the ability to support deep valleys, high canyon walls, and resist erosion.

Problem Description

Context

Titan's surface appears to be constructed of an entirely new class of cryogenic organic minerals whose **physical properties are mostly unknown.** This hinders efforts to understand Titan's geology and rationally design surface sampling systems.

The overall objective of this work is to measure the physical and mechanical properties, morphology, heat capacity, and microstructure of the most probable major organic mineral constituents within Titan's surface (i.e. benzene, naphthalene, acrylonitrile), and to use this information to (1) provide the basic scientific foundation for constraining the extent of surface geological processes and (2) determine technological requirements for in-situ surface sampling instruments..

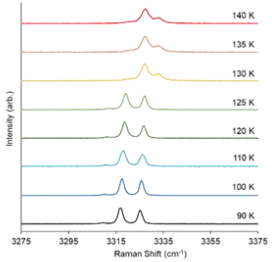
SOA

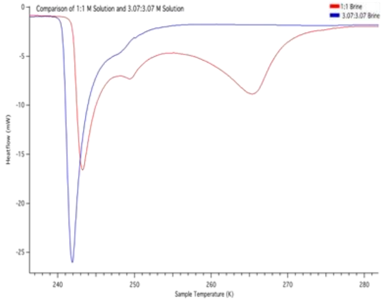
Over the past decade, our labs at JPL have developed extensive, state-of-the-art capabilities for the study of organic materials at cryogenic temperatures. We are currently the world leaders in the study of Titan organic minerals; no other laboratory has access to this combination of instrumentation and expertise.

Relevance to NASA and JPL

This work will help retain and advance JPL's leadership in Titan surface chemistry, leverages the existing Titan NAI node, and would help capture PS positions on Dragonfly

Methodology

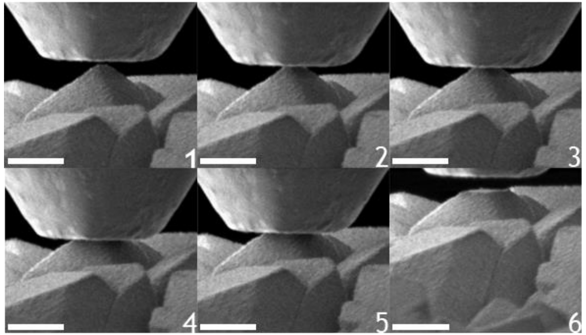




Raman Spectroscopy
Phase transitions
Binary interactions

X-ray diffraction
Phase transitions
Crystal Structure
Density
Thermal expansion coeff.

Cryogenic Calorimetry
Phase transitions
Enthalpy of phase transitions
Heat capacity



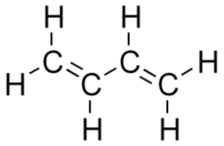
Nanomechanical deformation
strength, Young's, shear, and bulk moduli

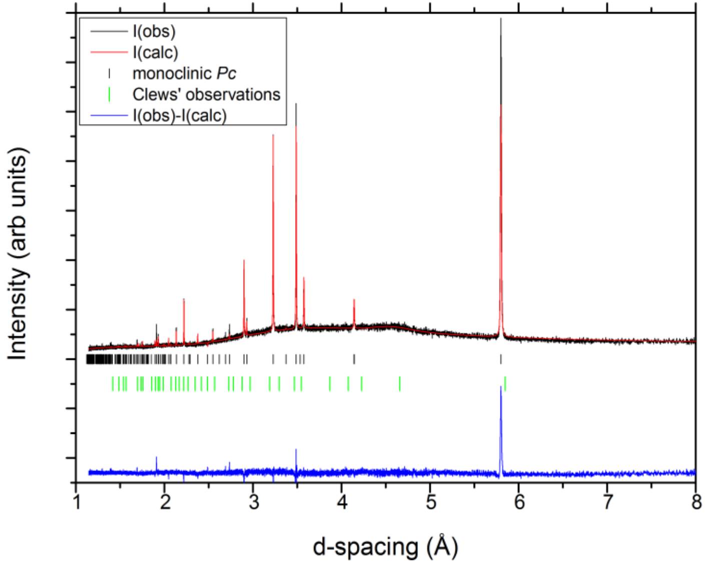
Results

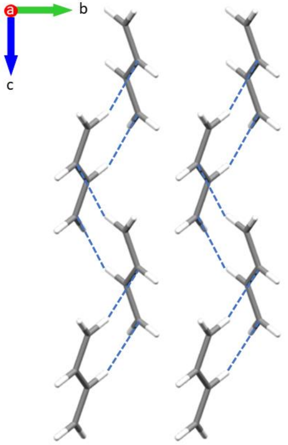
Due to the lab closure due to COVID-19, progress on the experimental objectives was halted from March to August 2020. However, we were able to collect sufficient data before the lab closure to make substantial progress in data analysis and manuscript preparation while the lab was closed. Limited access to our labs was resumed in August, and we have already resumed experiments on propyne. The table summarizes our results relative to our original milestones.

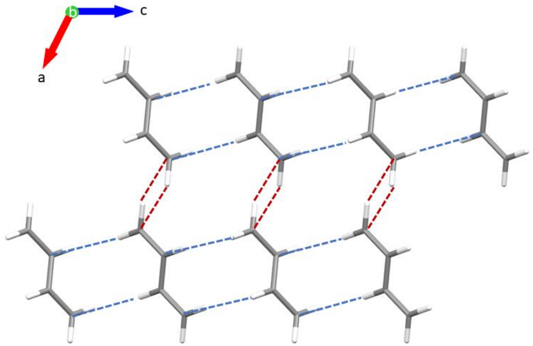
Milestone	**Status/Progress**
Refine list of molecular species based on latest photochemical models (Nov 2019)	List of species to be studied is finalized.
Temperature dependent Raman spectroscopy experiments complete (Mar 2020)	Acrylonitrile, HCN, butadiene Raman experiments complete. Propyne delayed due to shutdown.
Temperature dependent cryogenic X-ray diffraction experiments complete (June 2020)	Acrylonitrile, butadiene XRD complete. HCN in progress, further work delayed due to shutdown.
Calorimetry experiments complete (Sep 2020)	Acrylonitrile experiments in progress; further work delayed due to shutdown.
Determine best four candidates for binary interaction (Apr 2020)	Acetylene-acetonitrile; acetylene-formaldehyde; propyne-NH_3; propyne-acetonitrile
Development of organic sample introduction procedure to SEMentor complete (Jan 2020)	Determined that the sample introduction procedures used previously for benzene will work for acetonitrile experiments
Update pressure/temperature models for Titan's subsurface (Nov 2019)	PT model is finalized.
Additional Accomplishments	**Status/Progress**
Synchrotron XRD patterns of butadiene and acrylonitrile were obtained through the Advanced Photon Source mail-in service at no cost.	Synchrotron data are consistent with lab data. Analysis of high resolution butadiene data to determine crystal structure is underway.
Performed experiments on the interaction of acrylonitrile with liquid ethane and methane, searching for formation of azotosomes (putative membranes, analogous to lipid bilayers, hypothesized to be stable in Titan's seas)	Data are currently being analyzed. No significant changes for ethane, but methane appears to affect Raman signature of acrylonitrile.
Initiated collaboration with Hannah Shelton (postdoc at LLNL) to perform high	Proposal drafted.

Results

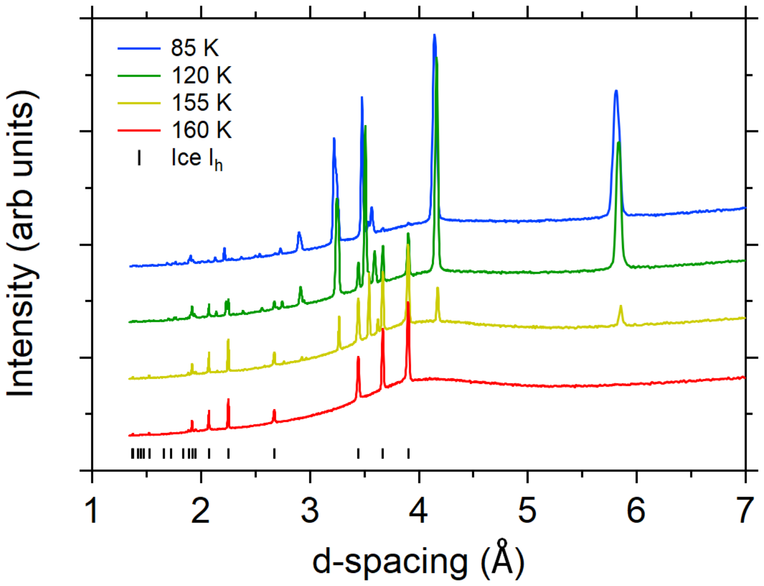


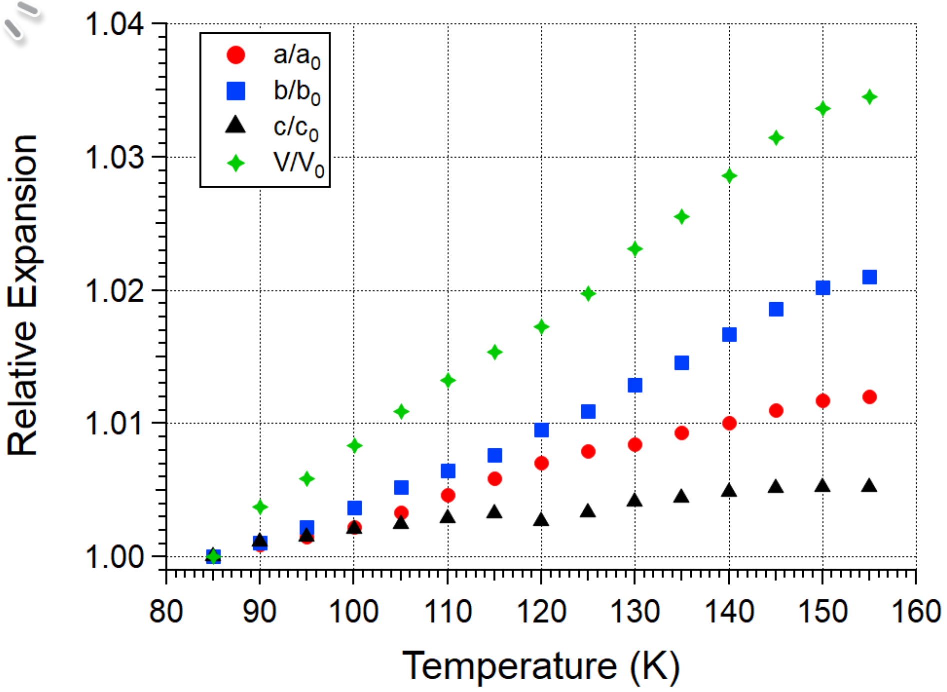

I(obs)
I(calc)
monoclinic *Pc*
Clews' observations
I(obs)-I(calc)
Intensity (arb units)
1 2 3 4 5 6 7 8
d-spacing (Å)


a
b
c


b
c
a

Results


85 K
120 K
155 K
160 K
Ice I_h
Intensity (arb units)
1
2
3
4
5
6
7
d-spacing (Å)


a/a_0
b/b_0
c/c_0
V/V_0
Relative Expansion
1.04
1.03
1.02
1.01
1.00
80
90
100
110
120
130
140
150
160
Temperature (K)

Results

a) Significance

This work will have significant impact on all areas of planetary chemistry and geology, and will serve as the foundation for establishing the framework for a new understanding of possible geological processes on cold hydrocarbon worlds, using Titan as a model. Comprehensive knowledge of the physicochemical properties of these materials together will allow us to form specific hypotheses about the chemistry and geology of Titan's surface. Thermal expansion coefficients and phase change data will enable us to predict the transformations that heat and pressure will have on these substances in Titan's subsurface during deep burial. Irreversible phase changes could be used to identify surface material that once been buried, a form of organic mineral metamorphism. Differences in phase between materials deposited from the atmosphere and materials precipitated from the liquid hydrocarbon lakes may also be possible. Some crystals may be able to template the formation of other crystals, or distinct crystalline forms. Future in-situ Titan missions, such as the proposed New Frontiers Dragonfly mission, require drilling and sample handling of Titan materials and would benefit from this work. In particular, **the mechanical properties obtained in collaboration with Prof. Julia R. Greer (Caltech) will enable us – for the first time - to inform the design and to place requirements on future surface sampling systems.**

b) Next steps

Future work will explore the ability of propyne, a molecule detected in Titan's atmosphere, to form co-crystalline compounds. We will finalize our experiments on acrylonitrile and butadiene, and then apply our results to Titan geology. We will also use our mechanical properties and thermal measurements to constrain the requirements on a Titan in situ sampling system.

Publications and References

Ennis, C.; Cable, M. L.; Hodyss, R.; Maynard-Casely, H. E., Mixed Hydrocarbon and Cyanide Ice Compositions for Titan's Atmospheric Aerosols: A Ternary-Phase Co-crystal Predicted by Density Functional Theory. *Acs Earth Space Chem* **2020,** *4* (7), 1195-1200.

Cable, M. L.; Vu, T. H.; Malaska, M. J.; Maynard-Casely, H. E.; Choukroun, M.; Hodyss, R., Properties and Behavior of the Acetonitrile-Acetylene Co-Crystal under Titan Surface Conditions. *Acs Earth Space Chem* **2020,** *4* (8), 1375-1385.

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