

IDENTIFYING THE SOLID PHASES OF ETHANE USING RAMAN SPECTROSCOPY AT CONDITIONS RELEVANT TO TITAN'S SURFACE. A. Engle¹, J. Hanley^{1,2}, W.M. Grundy^{1,2}, S. Dustrud¹, G.E. Lindberg¹, S.C. Tegler¹. ¹Northern Arizona University, Flagstaff, AZ (anna.engle@nau.edu), ²Lowell Observatory, Flagstaff, AZ.

Introduction: Exploration of Saturn's largest satellite Titan by the Cassini Spacecraft has shown it to be unique in the Solar System: rich in nitrogen, methane, and ethane, it is the only moon that hosts a dense atmosphere, liquid lakes, and processes akin to Earth's hydrological cycle [1-4]. Ethane has been shown to be a particularly integral component, taking part in a benzene-ethane co-crystal likely present on Titan's surface [1-2], as well as an ingredient of its lakes [3], and possibly partially responsible for the 'magic islands' [4].

Due to its significance to surface processes on Titan, we at the Astrophysical Materials Lab at Northern Arizona University (NAU) have chosen to study the three solid phases of ethane specified by Klimenko *et al.* [5]. Interestingly, these phases are reported to all occur within the range of 89 – 90 K at low pressures. Phase I is characterized by an initially plastic structure that transforms into a cubic configuration [5,6]; phase II is orthorhombic [5] and likely a metastable state [7]; and phase III is a stable monoclinic configuration [5-7].

Unlike previous experiments, this study implements a 2 cm thick sample cell, as opposed to thin film, which may shed light on the behavior of ethane in a bulk volume. The results will be beneficial in the construction of a nitrogen-methane-ethane ternary phase diagram, as well as provide insight into how the various solid phases may present themselves on the surface of Titan.

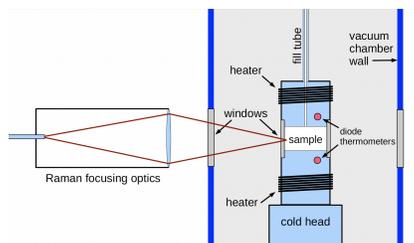


Figure 1. Schematic of cell. Fill tube leads to mixing chamber and hook ups for gas cylinders (not shown).

Hardware: The system (Figure 1) is located in the Astrophysical Materials Laboratory at NAU in Flagstaff, AZ. It consists of multiple vacuum chambers connected to gas cylinders via a series of pipelines. One of the chambers provides volume for mixing substances in the gas phase, which is then deposited into the sampling cell via the fill tube. Our immediate purposes necessitate the use of only one species, which is measured at 600 Torr before being released into the sampling cell. This cell is cooled by helium refrigerators [8] and allows for the system to reach tempera-

tures as low as 30 K.

The sampling cell can be arranged into two configurations: one using FTIR transmission spectroscopy and the other with Raman spectroscopy. Currently, the Raman spectrometer setup is being implemented, and uses a 785 nm laser to gather spectra in a range of 150 – 3425 cm^{-1} .

Ethane Raman Bands: Raman active bands originate from Raman scattering, wherein the photons scattered from a material are inelastic and have differing energies coming out of the system than they did going in. The resulting spectra come from a polarizability in the molecules and demonstrate rotational and vibrational effects (Figure 2) occurring within the material [9]. Raman active modes are often distinct from infrared active ones, meaning Raman spectroscopy provides different information about the system.

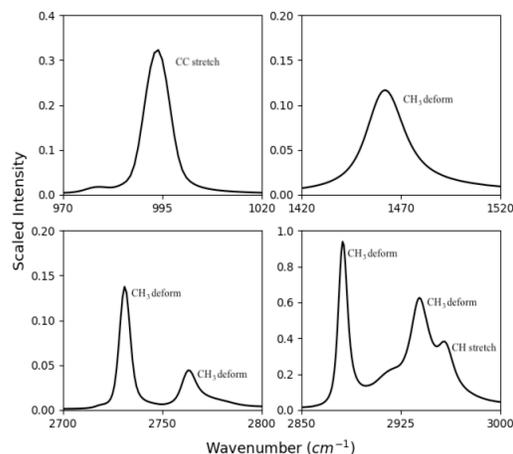


Figure 2. Prominent Raman active ethane bands at 95 K. Bands occur due to rovibrational excitation as photons interact with the ethane.

Previous thin film studies have indicated three solid transitions in a narrow temperature range at 0 bar [5-7]. Phase I occurs between 90.35 K and 89.83 K, phase II between 89.83 K and 89.73 K, and phase III from 89.73 K downward to colder temperatures [5]. To date, we have not seen definitive evidence of phase II, but have witnessed a transition from plastic phase I to cubic phase I. Figure 3 depicts how the various solid phases appear in the cell. Plastic phase I is transparent with cracks scattering light near the meniscus. With a slight decrease in temperature, the opacity resolves into a completely transparent cubic phase I solid. Phase III is most visually apparent as the solid becomes totally opaque.

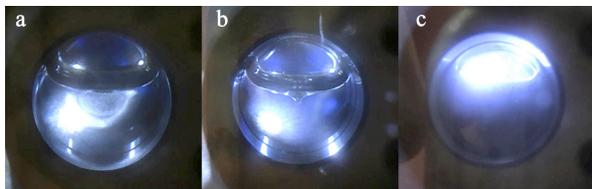


Figure 3. a) plastic phase I, b) cubic phase I, c) phase III.

Results: As mentioned, we have identified the two structures of phase I and the single structure of phase III. However, we have thus far been unable to capture phase II. Klimenko *et al.* suggests it to be a metastable state as it was only witnessed when warming in temperature. So far, our study only encapsulates the effects of cooling, and will soon include warming effects.

Although the plastic and cubic structures of phase I are similar in their Raman shifts, multiple experiments have shown a marked rise in intensity from plastic to cubic in the 1462 cm^{-1} , 2730 cm^{-1} , 2880 cm^{-1} , 2939 cm^{-1} , and 2958 cm^{-1} regions. The transition from cubic I to III has the most noticeable effects in the spectra, as the intensity drops significantly and a double peak forms in the 1462 cm^{-1} region due to a Fermi resonance (Figure 4). Figure 4, is an example of the typical spectra seen in the liquid and solid phases, and Figure 5 demonstrates how intensity and Raman shift are affected by temperature using the band centered around 1460 cm^{-1} .

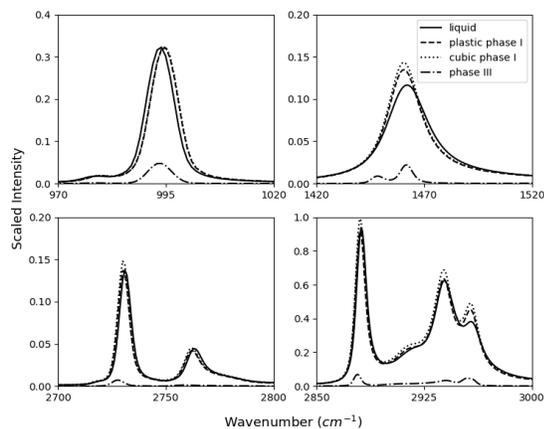


Figure 4. Spectra of liquid and three solid structures.

Due to the use of a 2 cm thick sample cell, as opposed to thin film, we are still running experiments to firmly determine the temperature at which cubic transitions to monoclinic. This transition has a visibly kinematic component and takes >2 hours to fully anneal. This is contrary to thin film studies, wherein the transition occurred with a change in temperature at a rate of $\sim 0.5\text{--}0.7\text{ K/min}$ [5].

Implications: Although the temperature on Titan's surface is $\sim 92\text{ K}$, and therefore higher than the freezing

point of ethane, it is possible for temperature differences to exist immediately below the surface and at depth in the lakes. Since there is such a narrow temperature window in which the liquid and three solid phases occur at low pressures, it is important to study the pure species, so as to better understand how its presence may affect the surrounding environment. On land, this may result in the presence of ethane-based co-crystals that have various configurations depending on the phase of the ethane. In the lakes, the result might be a richer solid ethane deposit on the floor where temperatures are lower.

Ongoing Work: Once we have established a consistent temperature for the transition between cubic I and III, and more thoroughly explored the occurrence of phase II, we will begin instituting various mixing ratios of ethane and methane. This will demonstrate how methane affects the temperatures at which the three ethane phases occur, and whether we can anticipate seeing these phases on Titan's surface. The continuation into the binary system will also contribute to the construction of a ternary phase diagram consisting of nitrogen, methane, and ethane.

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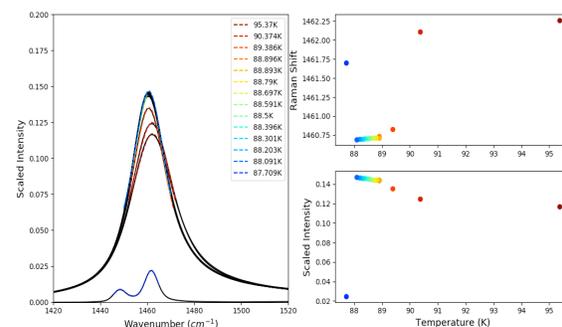


Figure 5. Raman shift and intensity as functions of temperature. A Gaussian fit is used for the single peaks (liquid, plastic I, cubic I) while a double Gaussian is implemented for the double peaks (phase III).