KINETICS OF CLATHRATE HYDRATE FORMATION FROM LIQUID ETHANE UNDER TITAN-LIKE CONDITIONS T. H. Vu, V. Muñoz-Iglesias, A. Mahjoub and M. Choukroun, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr, Pasadena, CA 91109 (mathieu.choukroun@jpl.nasa.gov)

Introduction: Clathrate hydrates are inclusion compounds where small guest molecules are trapped inside highly symmetric water cages. These ice-like crystalline solids are an abundant source of hydrocarbons on Earth that primarily exist in permafrost and marine sediments. Icy celestial bodies whose pressure/temperature conditions are favorable to the formation of gas hydrates are also expected to contain substantial amounts of these materials. One such example is Saturn's moon Titan where clathrates are conjectured to be a major crustal component [1]. In fact, clathrate dissociation has been suggested to play a significant role in the replenishment of atmospheric methane on this satellite [e.g. 2 and therein].

In addition to having a substantial atmosphere dominated by nitrogen, Titan is the only body in the Solar System aside from Earth that has standing bodies of liquid on its surface. Liquid ethane has been identified as a principal component in the hundreds of lakes observed by the Cassini spacecraft on Titan's surface [3]. As the temperature and pressure conditions on Titan fall within the clathrate stability zone [4], layers of clathrate phases could progressively form as the lake fluids percolate through a preexisting icy crust. This research focuses on the kinetics of ethane clathrate formation upon ice-liquid contact via micro-Raman spectroscopy. As ethane clathrate formation is a critical step in the methane outgassing pathway (Figure 1), these experiments help bring forth information on the timescales required for methane substitution by ethane in subsurface clathrates to occur at Titan's conditions, providing some constraints for geophysical modeling.

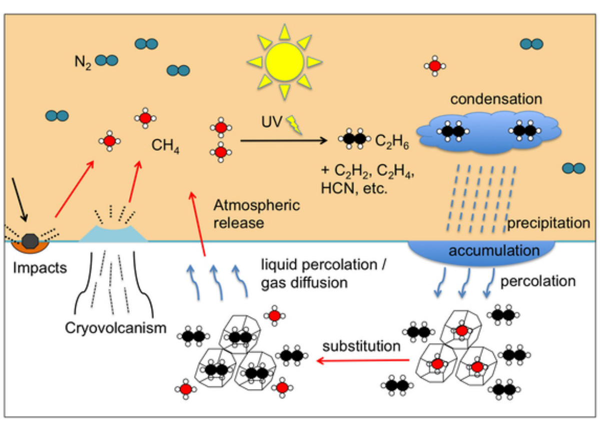

Figure 1. Proposed hydrocarbon cycle on Titan, including methane substitution by liquid ethane in subsurface clathrates [5].

Methods: A series of experiments were performed in which water ice and liquid ethane were co-deposited into a cryogenic optical stage (Linkam LTS 350) at ambient pressure close to that on Titan. The ethane-ice mixtures were allowed to interact at different temperatures between 150-173 K while the enclathration process was monitored over time using a high-resolution confocal dispersive micro-Raman spectrometer (Horiba Jobin Yvon LabRam HR). Raman spectroscopy is employed due to its ability to uniquely identify guest environments in various clathrate cages. All samples are excited by a frequency-doubled Nd:YAG laser (532 nm, 50 mW) and spectra are obtained in duplicates at 0.4 cm^{-1} resolution using a 1800 grooves/mm grating.

Results and Discussion: Mixtures of liquid ethane and water ice deposits at 150-173 K result in clathrate formation within minutes. Conversion of ice into clathrates is confirmed by the emergence of the characteristic peak at 999 cm^{-1} [6] which represents the C-C stretch of enclathrated ethane (Figure 2). This feature is clearly distinctive from the liquid ethane signature at 992 cm^{-1}. Further evidence can be seen in the C-H stretching mode of ethane, where the clathrate also exhibits two new peaks at 2886 and 2942 cm^{-1}. The growth of this resonance has been monitored as a function of time until it reaches a plateau after ~2-3 hrs. Standard Arrhenius analysis yields a fairly modest activation energy of 7-13 kJ/mol.

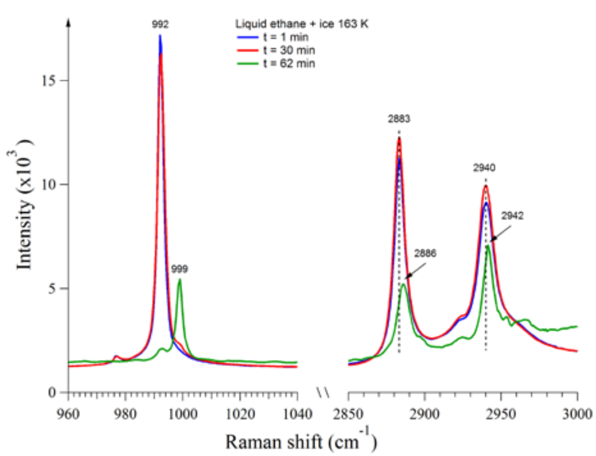

Figure 2. High-resolution Raman spectra of ethane clathrate formation from a liquid ethane-ice mixture at 163 K. The features at 999, 2886, and 2942 cm^{-1} are characteristic of ethane clathrate.

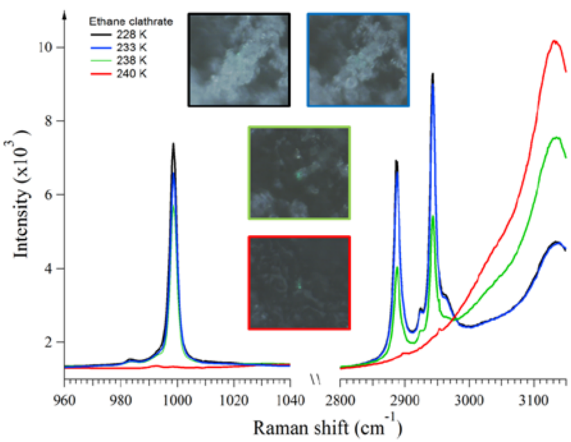

Figure 3. High-resolution Raman spectra of ethane clathrate with increasing temperatures. Note that ethane clathrate is stable up to 240 K under an ethane vapor pressure of 1 bar.

Following conversion of ice into clathrates, the stability of the formed products is assessed by incrementlly increasing the temperature of sample. Figure 3 shows the Raman spectra and representative microscopic images of the liquid ethane/ice system above 228 K. At these temperatures, all excess liquid ethane that has not been enclathrated evaporates completely, leaving only the clathrate feature at 999 cm^{-1}. As the sample's temperature is raised, the intensity of this peak decreases gradually but continues to persist until all the clathrates disintegrate at 240 K (red). This observed "melting" temperature is consistent with a prior study of ethane clathrate formation at sub-atmospheric pressures using ice/gas mixtures [7]. Dissociation of clathrates can also be seen visually in the microscopic images, confirming that ethane clathrates was indeed formed by reaction at the liquid ethane-ice interface. The fast timescale and ease of ethane clathrate formation under Titan-relevant conditions could hold important implications for ethane-methane exchange kinetics and outgassing processes on this icy satellite.

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