LIQUID ETHANE SUBSTITUTION OF METHANE IN CLATHRATE HYDRATES UNDER TITAN-LIKE CONDITIONS. E. Gloesener[1], T. H. Vu[1], M. Choukroun[1], A. G. Davies[1], A. Desmedt[2] and C. Sotin[3], [1]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, United States (elodie.d.gloesener@jpl.nasa.gov), [2]Institut des Sciences Moléculaires, CNRS UMR 5255, Talence, France, [3]Nantes Université, Laboratoire de Planétologie et Géosciences, Nantes, France.

Introduction: Laboratory experiments [1] have shown that methane clathrates can be formed on Saturn's largest moon, Titan, whose substantial nitrogen-methane atmosphere (1.5 bar) and cold temperatures (92-94K) allow CH_4 clathrates to be thermodynamically stable from its surface down to the bottom of its hydrosphere. Clathrate hydrates are believed to play a significant role in the hydrocarbon cycle on Titan [2] and could contribute to the replenishment of atmospheric methane. In addition to clathrate destabilization processes including interactions with ammonia [1,3-5] or impacts, methane could be released from clathrate hydrate reservoirs via substitution by ethane. In the hydrocarbon cycle proposed by Choukroun and Sotin [2], ethane precipitates in the polar regions of Titan and percolates into the CH_4 clathrate crust where it could substitute methane in the large cages of structure I (sI) clathrate. The resulting increase in clathrate density could explain the flattening of Titan observed by Cassini [6].

In order to better assess the contribution of clathrates to methane outgassing and exchange processes on Titan, it is essential to understand the mechanism of ice-to-clathrate formation and substitution kinetics, which are currently poorly constrained. In this study, we carry out Raman spectroscopic investigations of the CH_4-C_2H_6 replacement kinetics in clathrate hydrates at pressure and temperatures conditions relevant to Titan. This is the first attempt to study methane substitution in clathrates by ethane in the liquid phase.

Methods: Methane clathrate formation is performed by mixing liquid methane and spherical water ice grains of 36-micron mean diameter prepared by ultrasonic atomization in a stainless steel cell under conditions of 1 bar and 77 K. Once loaded, the cell is sealed by a nickel gasket compressed under 35 N m torque and placed in a -80C freezer during a few days. In the Raman experiments, methane clathrates are transferred onto a microscope slide precooled at 140 K inside a Linkam LTS350 cryostage. Spectra of the sample are first taken to ensure successful formation of methane clathrates. Liquid ethane, produced from direct condensation of gaseous ethane, is then deposited on top of the sample. Clathrate formation/substitution is monitored at specific temperatures by acquiring sequential Raman spectra using a high-resolution confocal dispersive micro-Raman spectrometer (Horiba Jobin Yvon LabRam HR). The sample is excited at 532 nm by an external Nd:YAG laser with a nominal output power of 50 mW, and spectra are obtained using an 1,800 grooves/mm grating.

Preliminary results: Figure 1 shows Raman spectra of our sample acquired over time after exposure to liquid ethane at 163 K. Note the growth of the features at 1,000, 2,886, and 2,942 cm^{-1}, which are characteristic of ethane trapped in the large $5^{12}6^2$ cages (LC) of sI clathrate [7], and the decrease in intensity of the liquid ethane peaks at 992, 2883 and 2940 cm^{-1} [8]. Methane clathrate peaks can also be seen at 2902 cm^{-1} for the large cage (LC) and 2914 cm^{-1} for the small cage (SC).

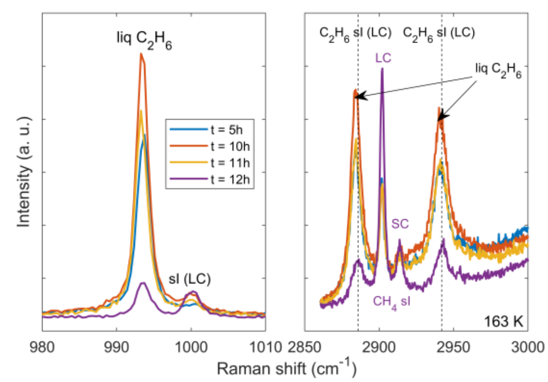

Figure 1: *Raman spectra of ethane and methane clathrates formed from a liquid ethane-methane clathrate mixture at 163 K.*

The experimental results obtained show that ethane clathrate hydrates can form from the reaction of liquid ethane with methane clathrates and ice. It is an experimental proof that liquid ethane can be trapped in Titan's subsurface. Furthermore it supports the model that methane could be released as ethane replaces it.

Acknowledgments: This work has been conducted at JPL/Caltech, under contract with NASA. Government sponsorship acknowledged.

References: [1] Choukroun M. et al. (2010) *Icarus, 205*, 581-593. [2] Choukroun M. and Sotin C. (2012) *Geophys. Res. Lett., 39*, L04201. [3] Vu T. H. et al. (2014) *J. Phys. Chem. B, 118*, 13371-13377. [4] Muñoz-Iglesias V. et al. (2018) *ACS Earth Space Chem., 2*, 135-146. [5] Petuya C. et al. (2020) *Chem. Commun., 56*, 12391-12394. [6] Zebker H. A. et al. (2009) *Science, 324*, 921-923. [7] Vu T. H. et al. (2020) *Geophys. Res. Lett., 47*, e2019GL086265. [8] Vu T. H. et al. (2014) *J. Phys. Chem. A, 118*, 4087-4094.