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

Introduction: Clathrate hydrates are believed to play a significant role in the hydrocarbon cycle on Titan [1] and could contribute to the replenishment of atmospheric methane [2-3]. In the hydrocarbon cycle proposed by Choukroun and Sotin [1], ethane precipitates in the polar regions of Titan and percolates into the CH\textsubscript{4} clathrate crust where it could substitute methane in structure I (sI) clathrate. Note that methane fits into the small and large cavities of the clathrate structure while ethane can only enter into the large cages.

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 the substitution kinetics, which are currently poorly constrained. In this study, we carried out Raman spectroscopic investigations of the CH\textsubscript{4}-C\textsubscript{2}H\textsubscript{6} replacement kinetics in clathrate hydrates at pressure and temperature conditions relevant to Titan.

Methods: Methane clathrate formation was 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 was sealed by a nickel gasket compressed under 35 N m\textsuperscript{-1} torque and placed in a -80°C freezer for 2-3 days. For the Raman experiments, methane clathrates were transferred into a Linkam LTS350 cryostage. Raman spectra of the sample were first taken to ensure that formation of methane clathrates had been successful (see Figure 1).

![Figure 1: Methane clathrate synthesized from the atomized water ice – liquid methane mixture at 173 K and 1 bar.](image)

Liquid ethane, produced from direct condensation of gaseous ethane, was then deposited on top of the sample. Clathrate formation/substitution was monitored at specific temperatures (150, 155, 163, 168 and 173 K) by acquiring sequential Raman spectra using a high-resolution confocal dispersive micro-Raman spectrometer (Horiba Jobin Yvon LabRam HR). The sample was excited at 532 nm by an external Nd:YAG laser with a nominal output power of 50 mW, and spectra were obtained using an 1,800 grooves/mm grating.

We calculated the integrated intensity ratio of CH\textsubscript{4} in the large cage (5\textsuperscript{12}6\textsuperscript{2}) to small cage (5\textsuperscript{12}) to obtain the cage occupancy ratio of methane clathrates as a function of time. As the ethane molecule can only enter the large cages of the clathrate structure, the occupancy of methane in the large cages should be lower at the end of the substitution experiment.

A typical experiment usually runs over night and lasts for ~20 h. At the end of the run we heated the sample and determined at which temperature the mixed clathrates dissociated.

Results: Figure 2 shows Raman spectra of the sample acquired over time after exposure to liquid ethane at 173 K. Note the growth of the features at 1,000, 2,886, and 2,942 cm\textsuperscript{-1}, which are characteristic of ethane trapped in the large 5\textsuperscript{12}6\textsuperscript{2} cages (LC) of sI clathrate [4], and the decrease in intensity of the liquid ethane peaks at 992, 2883 and 2940 cm\textsuperscript{-1} [5]. Methane clathrate peaks can also be seen at 2902 cm\textsuperscript{-1} for the large cage (LC) and 2914 cm\textsuperscript{-1} for the small cage (SC).

![Figure 2: Raman spectra of our samples acquired over time after exposure to liquid ethane at 173 K. The magnitude of the yellow and purple spectra, recorded after 3h30 and 4h30 of exposure, was multiplied by 2.5 for a better visualization of the peaks.](image)
We determined the evolution of the large-to-small cage occupancy ratio by comparing the integrated Raman intensity of CH₄ clathrate peaks for the large and small cages during our experiments. This ratio declined over time indicating that methane occupancy in large cages decreased relative to its occupancy in small cages and that the substitution of methane by ethane was indeed taking place.

Note that, at 1 bar, pure methane clathrate destabilizes at 193.2 K and ethane clathrate dissociates at 240.8 K. For mixed CH₄-C₂H₆ clathrates, we would expect their dissociation temperature to fall between these two values. In each run, the experimental dissociation temperature was well within this range, confirming that mixed CH₄-C₂H₆ clathrates were formed.

**Conclusions:** Our results show the successful formation of ethane clathrate hydrates from the reaction of liquid ethane with methane clathrates and ice. This supports the hypotheses that liquid ethane can be trapped in Titan’s subsurface and that methane could be released as ethane replaces it in clathrate hydrates.

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