

**STUDY OF THE SPECTROSCOPIC DETECTABILITY OF CH<sub>4</sub>-N<sub>2</sub> CLATHRATE HYDRATES FOR IN-SITU AND REMOTE OBSERVATION OF TITAN AND OTHER ICY MOONS.** D. Nna-Mvondo, E. Le Menn, G. Tobie, O. Grasset, Laboratoire de Planétologie et Géodynamique, LPG Nantes, CNRS UMR 6112, Université de Nantes, France (delphine.nnamvondo@univ-nantes.fr).

**Introduction:** The presence of clathrate hydrates in icy moons may have interesting relevance to Astrobiology. Clathrate probably play a key role in the storage and transport of gas compounds in water-rich environments. As a consequence, clathrate hydrates could possibly act as a transporting agent of potential nutrients and products of biological activity, from the deep interior to the icy shell [1], and maybe used by extra-terrestrial life to sustain their metabolism? [2]. In Titan, one of the possible reservoirs to allow the replenishment of atmospheric methane throughout its history could be CH<sub>4</sub> clathrate hydrates [3], and gas hydrates could be a possible sink for other chemical species on Titan's surface [4]. At pressure and temperature conditions encountered in Titan, clathrate hydrates may be present at its surface [2]. The large reservoir of several guest compounds in Titan's atmosphere is expected to result also in the formation of multicomponent clathrate hydrates on the surface, stable relative to water ice [2, 4]. The detection of clathrate hydrates on Titan's surface, and more extensively on icy planetary surfaces, could be of crucial importance in understanding their role and constraining their relevance in the chemical processes occurring in the outer Solar System. We note that laboratory spectroscopic studies on methane clathrates, at low and high pressures, applied to Earth and planetary icy bodies, have been carried out to a large extent. However, experimental measurements for multicomponent clathrates are very scarce or non-existent, and therefore have to be addressed. In this context, we have studied the formation and spectral signatures of CH<sub>4</sub>-N<sub>2</sub> clathrate hydrates at low temperature and low pressure conditions, looking for discriminating criteria for their possible detection.

**Experimental method:** Clathrate hydrates samples were synthesized in an autoclave combined with a cooling system and a multi-gas mixer. Few ml of de-ionized water was introduced in the autoclave and pressurized with the N<sub>2</sub> and CH<sub>4</sub> gases for a couple of days, at controlled low temperature and low pressure, within the field of formation and stability of the clathrate. The clathration rate was previously monitored and quantified by gas chromatography. The spectral characterization, at low temperature (94K) and under vacuum (10<sup>-5</sup> bar), was performed by FTIR reflectance spectroscopy in the mid-near IR (2000 - 10000 cm<sup>-1</sup>) and Raman spectroscopy from 50 to 4000 cm<sup>-1</sup>, by using a nitrogen-cooled cryostat. We have tried to give

constraints on the composition, structure and cage occupancy of the formed clathrates using these techniques.

**Results:** IR and Raman spectra were obtained for different CH<sub>4</sub> molar fractions in the CH<sub>4</sub>-N<sub>2</sub> clathrates, varying from 0.32 to 1. For each clathrate composition, a dozen of single crystals have been analyzed (Fig. 1).

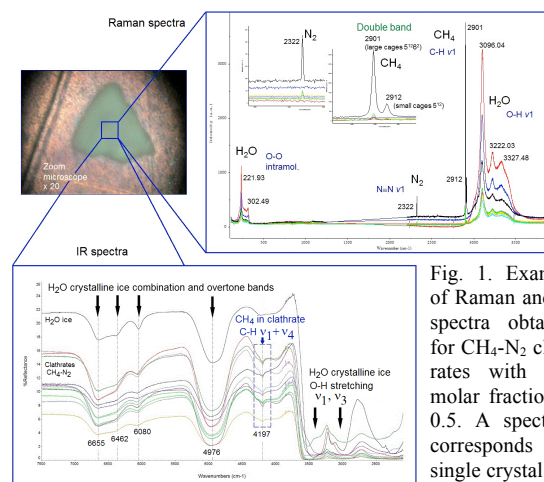


Fig. 1. Example of Raman and IR spectra obtained for CH<sub>4</sub>-N<sub>2</sub> clathrates with CH<sub>4</sub> molar fraction of 0.5. A spectrum corresponds to a single crystal.

The CH<sub>4</sub> double peak in Raman at 2901 cm<sup>-1</sup> (higher intensity) and 2913 cm<sup>-1</sup> (smaller intensity) is a characteristic signature of the small (2913 cm<sup>-1</sup>) and large (2901 cm<sup>-1</sup>) cages of the clathrate structure and appears to be a sI structure. It is also observed the N<sub>2</sub> vibration band at 2322 cm<sup>-1</sup> of sI small/large cage type and the vibration of H<sub>2</sub>O within the hydrate structure at 221 cm<sup>-1</sup>, and 302 cm<sup>-1</sup> and 3096 cm<sup>-1</sup>. We will present the quantification results we have obtained for the Raman study. For IR spectra, the position and shape of the main absorption bands of the clathrates are very similar to those of pure water ice. The ice matrix dominates the IR signature of the CH<sub>4</sub>-N<sub>2</sub> clathrate. However, the vibration of C-H in the first combination mode v1 + v4 appears at 4197 cm<sup>-1</sup> which shows the presence of CH<sub>4</sub> trapped in the clathrate cages. Efforts are currently made to examine if the ratio of the areas of CH<sub>4</sub> and H<sub>2</sub>O IR bands can be related to the composition of the gas guests sequestered in the clathrate.

**References:** [1] Tobie G. et al. (2003) *J. Geophys. Res.: Planets*, 108 (E11), 5124. [2] Choukroun M. et al. (2013) *The Science of Solar System Ices*, Springer New York, pp 409–454. [3] Tobie G. et al. (2006) *Nature*, 440, 61–64. [4] Osegovic J.P. et al. (2005) *J. Geophys. Res.: Planets*, 110 (E8), E08004.