

Spectral detectability of CH₄-N₂ clathrates for in-situ and remote observation of Titan and other icy moons

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Abstract

Multicomponent clathrates may be present at the surface of several icy moons, although they have not been detected yet, possibly due to the absence of reliable spectral data. In this work, we present infrared (IR) and Raman spectral studies of CH₄-N₂ clathrates at low temperature and pressure, in order to identify discriminating criteria for their possible detection. These clathrates are particularly interesting for Titan and Pluto. Our experimental results indicate that identification of mixed clathrate from remote sensing is very challenging, and that only in-situ Raman spectroscopy may provide a clear identification of clathrate and constraints on their composition.

1. Introduction

Clathrate hydrates are expected to be present at the surface and in the subsurface of many icy moons [1]. Several gas compounds such as CO₂, CH₄ or N₂ are known to easily combine with water molecules to form clathrate hydrates at the temperature and pressure conditions of many icy moons and can be trapped simultaneously, leading to the formation of multicomponent clathrates. For example, on Titan, many atmospheric compounds, such as N₂, CH₄, C₂H₆ and other light hydrocarbons, are likely to be incorporated in subsurface reservoirs of multicomponent clathrates as they are stable relative to water ice at surface conditions [1]. The presence of clathrate hydrates in icy moons may be especially relevant in Planetary Sciences and Astrobiology. They probably play a key role in the storage and transport of gas compounds in water-rich environments [2]. Consequently, they could possibly act as a transporting agent of potential nutrients and products of biological activity, from the deep interior to the icy shell [3]. The detection of clathrates 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. Studies on methane clathrates, applied to Earth and planetary icy bodies, have been carried out to a large extent. However, experimental measurements for multicomponent clathrates are still scarce or non-existent, and therefore have to be addressed. In the present study, we focus on CH₄-N₂ mixed clathrates, which are the dominant species at Titan's surface. Similar analysis will be extended to other gas compounds in the future.

2. Laboratory experiments

CH₄-N₂ Clathrate samples were synthesized in an autoclave combined with a cooling system and a multi-gas mixer. Few ml of deionized water was introduced in the autoclave and pressurized with the N₂ and CH₄ 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 and molar composition of clathrates were previously monitored and quantified by gas chromatography (GC). The spectral characterization, at low temperature (94K) and under vacuum (10⁻⁵ bar), was performed by FTIR reflectance spectroscopy in the mid-near IR (2000 - 10000 cm⁻¹) and Raman spectroscopy from 50 to 4000 cm⁻¹, using an Liq N₂-cooled cryostat (Fig. 1).

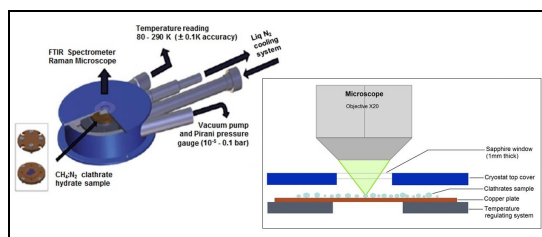


Figure 1: Cooled cryostat used for the spectroscopy.

3. Results

IR and Raman spectra were obtained for different CH_4 molar fractions in the CH_4 - N_2 clathrates, varying from 0.30 to 1. For each clathrate composition, a dozen of single crystals were analyzed (Fig. 2).

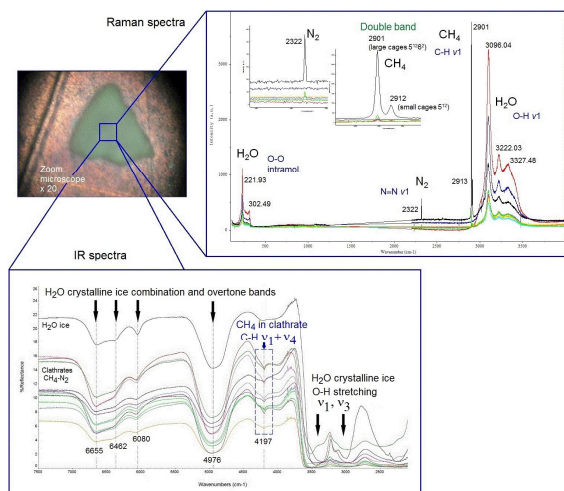


Figure 2: Example of Raman and IR spectra obtained for 0.62/0.38 CH_4 - N_2 clathrates.

The CH_4 double peak in Raman at 2901 cm^{-1} (higher intensity) and 2913 cm^{-1} (smaller intensity) is a characteristic signature of the large and small cages of the sI clathrate structure. It is also observed the N_2 vibration band at 2322 cm^{-1} of sI small/large cage type and the vibration of H_2O within the hydrate structure at 221 cm^{-1} , 302 cm^{-1} and 3096 cm^{-1} . For IR spectra, the position and shape of the main absorption bands of the clathrates are very similar to those of pure crystalline water ice. The ice matrix dominates the IR signature. However, the vibration of C-H in the first combination mode $1 + 4$ appears at 4197 cm^{-1} showing the presence of CH_4 trapped in the clathrate cages. We conducted various quantitative studies consisting in examining if the ratios of the areas and heights of the CH_4 , N_2 and H_2O bands detected in IR and Raman spectroscopy (ratios of CH_4/N_2 , $\text{CH}_4/\text{H}_2\text{O}$, $\text{N}_2/\text{H}_2\text{O}$ and $\text{CH}_{4\text{large cages}}/\text{CH}_{4\text{small cages}}$) could be related to the composition of the gas guests sequestered in the clathrates. We have found that only the CH_4/N_2 band ratio in Raman spectroscopy can be a reliable measure to determine the molar composition of such binary clathrates, as both variables are clearly related together by an exponential proportionality (Fig. 3).

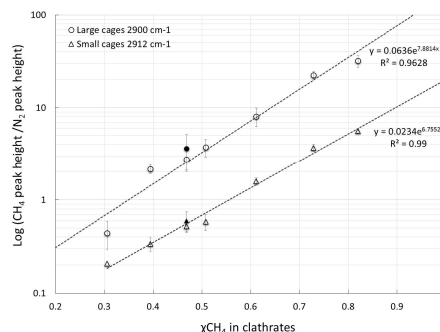


Figure 3: Variation of the ratio of peak heights of CH_4 over the peak heights of N_2 for large (○) and small cages (△) as a function of the molar composition of clathrates. Plain symbols (●▲) are spectra taken under room atmosphere for comparison.

4. Conclusions

Due to the weak appearance of the absorption band of trapped CH_4 with respect to the strong H_2O -ice matrix absorption, it may be problematic to detect CH_4 - N_2 clathrates on icy surface from IR remote sensing, using instruments such as Cassini-VIMS. In any case, IR signatures would not allow the characterization of the clathrate composition. In contrast, our Raman analyses indicate that in-situ Raman investigation is a very promising technique for detecting easily and efficiently multicomponent clathrates and for quantifying the sequestered gases in planetary ices.

Acknowledgements

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