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Experimental techniques to study clathrate hydrates in the context of giant icy moons.

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1. Introduction

Gas clathrate hydrates probably play a key role in the storage and transport of gas compounds in water-rich environments, especially for icy moons [1]. In order to understand how they may affect the exchange processes in these objects, a series of experiments has been set up to realise controlled synthesis of mixted gas hydrates, to perform infrared and Raman diagnostics, and to constrain their phase diagram. Experiments cover a wide pressure range, from 10^{-2} mbar up to 30 GPa and are focused on three gas compounds of high interest for the icy satellites of the outer solar system: methane, carbon dioxide and nitrogen.

2. Experimental techniques

Sample preparations:

Recent developments realised at LPGNantes have consisted in clathrate hydrate preparation and their *in situ* analyses during synthesis. We have developed an analytical facility composed of a three entrances high pressure gas mixer and an autoclave coupled to a gas chromatograph. This apparatus permits us to obtain clathrate hydrate samples with a known composition. This information is necessary in forward thermodynamical and spectroscopic diagnostics under moderate to high pressure experiments using IR and Raman techniques.

Clathrate samples are synthesised from a gas mixture using three mass flow controllers (CH_4, CO_2, N_2) in association with a 100 mL autoclave. A control panel permits to define the composition of the gas mixture with a high accuracy, up to 200 bar. During the synthesis, small volumes of gas are taken by a high pressure sampler (Rolsi™) and are analyzed by a gas chromatograph to control the kinetic of clathrate formation. This system is also equipped with a pressure sensor recording the pressure drop during the clathrate synthesis. After the synthesis, samples are manipulated in a cold chamber (253 K). This temperature is favorable for crushing and sieving operations of icy samples as described by Taffin et al. [2]. Prepared samples are then loaded into a cryostat or into a high-pressure cell for further investigations.

Infrared signatures of clathrate hydrates in icy surface conditions:

In order to reproduce the surface conditions of the icy moons, the sample is maintained at low pressure and temperature conditions using a liquid nitrogen cryostat (Microstat, Oxford instruments). *In situ* near-IR and Raman spectra of the samples are acquired using a Thermo Nicolet FTIR and a Raman spectrometer (LabRam 300, Horiba group), respectively. The Infrared spectrometer is set up to work in reflection mode on the spectral range 1-5µm. This permit a good comparison with the Cassini/VIMS spectra.

In the case of the CO_2 clathrate hydrate, two main absorption bands at 2.71 µm and 4.28 µm have been identified, which are characteristics of the clathrate structure [3](Fig1). The presence of the clathrate structure was confirmed by Raman analyses realised on the sample. This work represents the first determination of IR reflectance spectra of CO_2 clathrate hydrates. Spectra of other gas clathrate hydrates will be acquired in the future. Such reference spectra are important to assess the possible existence of clathrates on planetary surfaces.

Stability of clathrate hydrates within icy mantles:

Determining the stability of gas clathrate hydrates over a wide range of pressure is of primary importance to constrain the chemical exchange processes in water-rich interiors. For that purpose, an experimental approach using high-pressure cells coupled to Raman spectroscopy has been developed.

These equipments are composed of Diamond and Sapphire Anvil Cells (DAC, SAC) and a hydrostatic cell. Pressures up to 30 GPa can thus be obtained (Fig2). The pressure is measured *in situ* by ruby fluorescence [4] in the case of the DAC and by diamond sensors [5] for the SAC. A classical quartz pressure sensor is used for the hydrostatic cell.

Studies have been focused so far on H_2O-CO_2 and H_2O-CH_4 systems. For the H_2O-CO_2 system, new stability data have been obtained with the SAC and DAC up to 1.7 GPa. This offers new constraints on water-rich environments, with Ganymede as an example [6]. Another study with the SAC in cryogenic conditions has been performed on the CH_4-H_2O system up to 1.2 GPa. New results on the methane hydrate dissociation curve have also been acquired, with important implications for cryovolcanic processes on Titan [7]. Finally, recent studies using the DAC coupled to the Raman spectrometer have been conducted up to 5 GPa. Preliminary results and their implications will be presented in this meeting [8].

Conclusions and perspectives

Recent developments have been realised in order to study clathrate hydrates in planetary conditions. First results on the CO_2 clathrate infrared spectra are available for remote sensing applications and new methane hydrate phase diagram data are also available. Next steps will imply the study of mixed clathrate hydrates, particularly CH_4-N_2 compositions for applications to Titan's atmosphere-surface interactions, and CH_4-CO_2 mixtures to better understand the carbon stability in the interior of large icy moons.

Acknowledgements

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References

[1] Choukroun, M. et al. (in press): Gudipati, M., and Castillo-Rogez, J.C. (eds), The Science of Solar System Ices, 3rd edn. Springer.
[2] Taffin, C. et al. Planet. Space Sci. 61, 124-134, 2012.
[3] Oancea, A. et al. submitted (Icarus)
[4] Grasset, O. High Pressure Research, Vol 21, pp.139-157, 2001.
[5] Grasset, O. et al. High Pressure Research, Vol 25, pp.255-265, 2005.
[6] Bollengier, O. et al. 43rd Lunar and Planetary Science Conference, 2012.
[7]Choukroun, M. et al. Icarus 205, pp581-593, 2010.
[8] Bezacier, L. et al. This meeting.

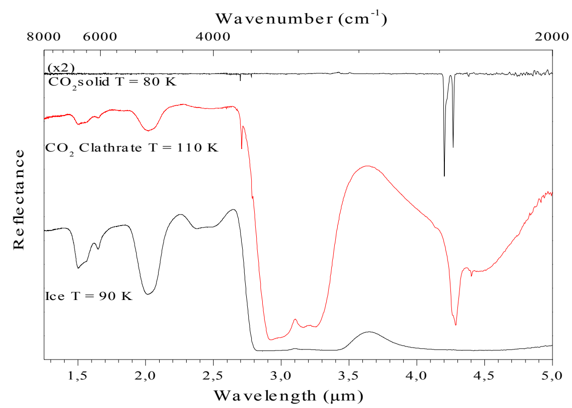

Fig1:CO_2 clathrate infrared spectrum (red) compared to CO_2 ice I and H_2O ice I spectra

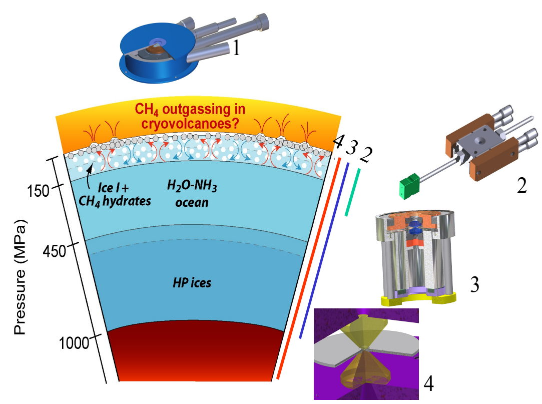

Fig2: Facilities in application to Titan: 1) Liquid nitrogen cryostat for surface spectroscopy 10^{3}-10^{-2} mbar, 2) Hydrostatic cell (0-350 MPa), 3) Sapphire anvil cell (0-1 GPa), 4) Diamond anvil cell (0.1-30 GPa)