Clathrates hydrates FTIR and Raman spectroscopy to understand cometary ices. N. Esteves Lopez[1], A. Guilbert-Lepoutre[1], A. Desmedt[2], F. Adamietz[2], C. Aupetit[2], S. Coussan[3], G. Tobie[4] and E. Le Menn[4]. [1]LGL-TPE, UMR 5276, Université Claude Bernard Lyon1, Villeurbanne, France (natalia.esteves@univ-lyon1.fr, aurelie.guilbert-lepoutre@univ-lyon1.fr), [2]GSM - ISM, UMR 5255, Université de Bordeaux, Talence, France (arnaud.desmedt@u-bordeaux.fr), [3]PIIM, UMR 7345, Université d'Aix-Marseille, Marseille, France (stephane.coussan@univ-amu.fr), [4]LGP, UMR 6112, Université de Nantes, Nantes, France (gabriel.tobie@univ-nantes.fr)

Introduction: When stored in the transneptunian region, comet nuclei can be subjected to temperatures from 30 to 50 K over the age of the solar system. The timescale for sublimated volatiles to escape the objects at these temperatures is long though [1], so that a gas phase remains in contact to an icy matrix in the porous internal structure. Once these nuclei enter the inner solar system and become active, subsurface sublimation puts once again a gas phase in contact of the porous and tortuous ice structure of cometary material. In this work, we examine whether these gases can be trapped as gas hydrates in subsurface layers of comet nuclei. This would allow some of the most volatile species to survive in cometary material at temperatures higher than the sublimation temperature of the corresponding pure solid [2,3].

State of the art: Gas hydrates constitute a class of ice-like structures in which the guest molecules occupy cages made of H-bonded water molecules. They are found in a variety of natural environments where they are formed under pressure from gas-ice or gas-water mixtures. In the context comet nuclei, theoretical phase diagrams of clathrate hydrates suggest that it would be possible to form these structures under extreme conditions [4], but no experimental data currently support this claim. Indeed, most experiments on gas hydrates [5] start by forming gas hydrates under high pressure and high temperature (typically 100 bar and 0 °C), then cool the structures down to 80 K, to examined their stability at low temperature and pressure.

Methods: We developed a dedicated experimental setup, specifically designed to perform water-gas deposition experiments in a cryogenic cell device, able to reproduce (T,P) conditions met in the Kuiper belt and the active phase of comets (4<T<200 K, 10^{-10}<P<1 bar). With a design adapted to control the formation conditions (gas/water flow rate, T/P, substrate, etc), this device makes it possible to obtain a set of complementary data on the same deposit (FTIR, Raman, Xray). We can thus fully characterise the water-gas deposits in conditions relevant to cometary nuclei, and ultimately address the issue of secondary trapping mechanisms of volatile species.

Results: We present results (Fig 1 and 2) for several water-gas mixtures (CO_2, CH_4, N_2, CO) at selected temperatures and vacuum conditions relevant to cometary nuclei (10<T<200 K and P~10^{-7} mbar). Both

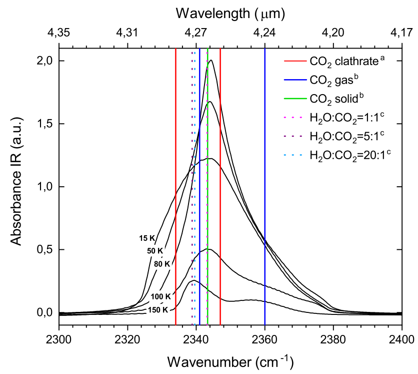

Figure 1. **Example of the υ_3 $^{12}CO_2$ region FTIR spectra from a H_2O-CO_2 deposit at 15 K and 10^{-7} mbar.**

[a]**Dartois et al. (2009)**
[b]**Oancea et al. (2012)**
[c]**Standford et al. (1990)**

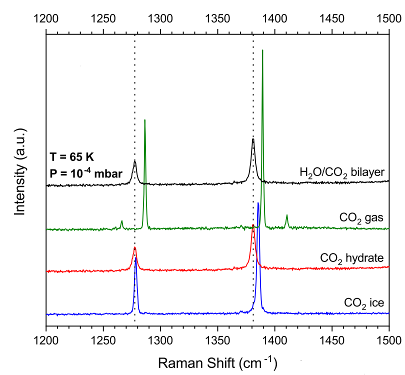

Figure 2. **Raman spectra of the Fermi diad of CO_2 from CO_2 solid, gas, hydrate, and from a H_2O-CO_2 sequential deposit (black spectrum) at 65 K and 10^{-4} mbar.**

infrared absorption and Raman scattering spectroscopy (complementary vibrational signatures) have been performed [6], to characterise and understand the nature of the structures formed under these conditions.

Acknowledgments: This project received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (Grant Agreement No 802699).

References: [1] Prialnik et al. (2004) in Comets II. [2] Mandt et al. (2017) in Comets as Tracers of Solar System Formation and Evolution. [3] Gkotsinas et al. (2022) ApJ, 928,43. [4] Choukroun et al. (2003) in The Science of Solar System Ices. [5] Dartois et al. (2008) A&A, 490, 19. [6] Esteves-Lopez et al. (in prep.)