

***In situ* infrared studies of water and CO₂ frost between 1 and 5 μm : from the grain to the icy surfaces signatures.**

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Introduction

Carbon dioxide has been detected on several icy surfaces of the moons of Jupiter[1], [2] and Saturn[3]. In these environments where the temperature is below 120 K, CO₂ might be either in a solid state mixed with water ices, or trapped in a clathrate hydrate structure. In fact, except for Titan where the pressure is sufficient, clathrate hydrate structures are probably not stable near the surfaces. In this work, the near IR signatures of the carbon dioxide and water ices are investigated using an experimental system which reproduces P-T conditions of the icy moons. Investigation is conducted from the microscopic to the macroscopic scale in order to understand how the diffusion processes through the grains modify the spectral signatures. It will be shown that, at temperatures much below the theoretical temperature of sublimation, IR signature of CO₂ crystals is variable. Possibly, the gas could be trapped within the icy grains and remain stable over a long period of time.

Experimental procedure

Icy samples are prepared and analysed in an Oxford cryostat under a primary vacuum (10⁻⁴ bar) and at low temperatures (80 K-120 K). *In situ* infrared signatures of the samples are investigated at the microscopic scale from the grain level (10 μm) to the level of grains mixtures (100 μm). Studies are conducted with an infrared microscope (*Continuum*) coupled to a Fourier Transform Infrared Spectrometer (*Nicolet 5700*). A white light source, a CaF₂ beamsplitter and an InSb detector are used in the apparatus for all the experiments. The resolution of the spectrometer is 2 cm⁻¹. We focus on the 1 to 5 μm (10000 to 2000 cm⁻¹) wavelength range, which corresponds to the wavelength range covered by the NIMS and VIMS imaging spectrometers in the jovian and saturnian environments. There is a 1 mm thick sapphire window between the sample and the objective of the microscope. For the background, a polished copper disc has been preferred to the smooth gold disc which is commonly used because of its perfect reflectance. The copper disc is relevant because it does not present any absorption bands between 1 and 5 μm. Samples are prepared by deposition of a gaseous species on a copper foil at low pressure. The system being cooled below the sublimation temperature of the considered species, small grains of solid ice condensate on the surface. The *Con-*

tinuum microscope is used to control the crystal growth. At the beginning, very small grains condensate on the foil, and IR signatures at the grain level can be investigated (Figure 1a). By controlling the gaseous flux, several grain sizes can be obtained. If the gaseous flux is maintained over a longer period of time, the sample thickens up to several micrometers and the IR signature of the mixture of grains can be studied.

Infrared analysis of CO₂ and H₂O grains

Preliminary results obtained on pure CO₂ or H₂O samples are presented in this section. Figure 1 shows the photography of a water crystal (a), and IR signatures of water ice at 90 K for different grain sizes (b). The spectrum presents two broad bands around 1.50 μm and 2.00 μm and two narrow bands at 1.55 μm and 1.65 μm which depend on the temperature (bands are deeper when the temperature decreases). These *in situ* experimental spectra are consistent with those obtained from optical constants[4]. Figure 2 shows CO₂ crystals with different sizes (a-c). IR spectra at 90 K are shown in figure 2d and 2e. The spectrum of solid state CO₂ presents three narrow bands around 2 μm, a double band around 2.7 μm a band at 3.34 μm and a very broad band between 4.1 and 4.5 μm. These experimental spectra are consistent with theoretical spectra[4], and other experimental spectra[5]. Figure 1b shows spectra of water ices with different grain sizes. The same background is used for all three measurements. The size of the spotlight is therefore not fully corrected in these spectra. The reflectance decreases when the grain size and the spotlight size decrease. As a contrary, in case of CO₂, figure 2d displays a decrease of the reflectance when the grain size increases for a constant spotlight size. In the case of thick deposits, it seems that the smaller the grains are, the higher the reflectance is (figures 2b, c and e).

From the grain to the thick sample : diffusion effects

Figure 2e displays spectra of thick deposits. Significant differences can be noticed compared to single grains signatures (figure 2d). On the thick deposits, bands around 2 μm are thin and the broad band between 4.1 and 4.5 μm presents two spikes around 4.08 μm and 4.23 μm. Since the process of condensation on the copper foil is slow, we suggest that gaseous CO₂ could be trapped either within the icy grains (inclusions) or between the grains

during the deposition and be responsible for the apparition of these peaks. This signature remains stable even at temperatures much below the condensation temperature which could indicate that bubbles are trapped within the grains. Nonetheless, these inclusions have not been directly observed in the grains. In addition, the signature is much stronger when the acquisition is made on several small grains, *i.e.* when diffusion processes through the grains are included in the signal (Figure 2e). Our interpretation is that the double peak appears in the broad band between 4 and 4.4 μm either due to the presence of gaseous CO_2 or due to diffusion processes within the grains. Further studies are now in progress in order to better understand this phenomena.

Discussion and conclusion

Experimental studies of near-IR signatures of both pure water ice grains and CO_2 ice grains have been conducted. During these experiments, visualization of the samples was achieved before each spectral acquisition. The diffusion effect of gaseous CO_2 trapped between icy grains has been investigated and the analysis is still in progress. Trapping of gaseous CO_2 in an icy matrix at P-T conditions compatible with icy moons surfaces was suggested ten years ago on the jovian moons. McCord *et al.*[1] noticed the presence of the 4.26 μm signature in the spectra of Ganymede and Callisto. It was suggested then that gaseous CO_2 was trapped between fine grains of water ice. In this work, we may have observed experimentally the possible influence of gaseous CO_2 on the IR signature of an icy matrix.

The next step will be to study $\text{H}_2\text{O}-\text{CO}_2$ mixtures in order to constrain more thoroughly the interpretation of near-IR spectra of the icy moons.

References

- [1] T. B. McCord *et al.* *Science*, 278, 1997.
- [2] R. E. Johnson. *Chemical Dynamics in Extreme Environment*, 2001.
- [3] G. Filacchione *et al.* *Icarus*, 186(1), 2007.
- [4] W. M. Grundy and B. Schmitt. *J. Geoph. Res.*, 103, 1998.
- [5] W.D. Smythe. *Icarus*, 24, 1975.

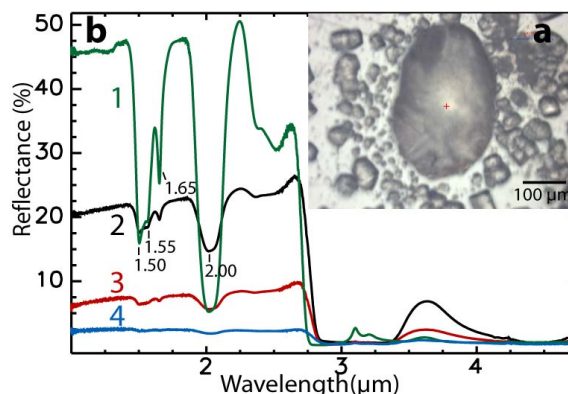


Figure 1: a) Photography of water crystal. b) Experimental spectra of different grain size water crystals (1 : $370 \times 230 \mu\text{m}^2$, 2 : $60 \times 50 \mu\text{m}^2$, 3 : $45 \times 30 \mu\text{m}^2$ and 4 : $20 \times 16 \mu\text{m}^2$)

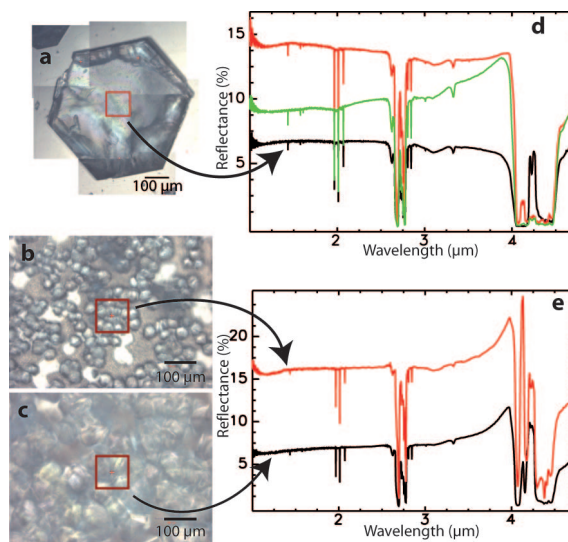


Figure 2: Photography of a) CO_2 crystal, b) several CO_2 grains, c) several bigger CO_2 grains. d) Experimental spectra of CO_2 crystal for different grain sizes (red $75 \times 75 \mu\text{m}^2$, green $130 \times 130 \mu\text{m}^2$ and black $600 \times 550 \mu\text{m}^2$). e) Spectra of b (red) and c (black). The red square is the spotlight.