*Icy bodies of the solar system*
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# Low temperature $CH_4$ and $CO_2$ clathrate hydrate near to mid-IR spectra

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**Abstract.** The physical behaviour of methane and carbon dioxide clathrate hydrates, specific crystallographic ice crystals are of major importance for the earth and may control the stability of gases in many astrophysical bodies such as the planets, comets and possibly interstellar grains. Such models claim they provide an alternative trapping mechanism modifying the absolute and relative composition of icy bodies and can be at the source of late time injection of gaseous species in planetary atmospheres. However, there is a clear need to detect them directly. We provide in this study the laboratory recorded signatures of clathrate hydrates in the near to mid-infrared for astrophysical remote detection. These laboratory experiments will in a near future allow to follow the kinetic formation by diffusion in dedicated experiments, another important step to implement, to understand and model their possible presence in space.

**Keywords.** Solar system ices, clathrate hydrates, lines and bands identification, infrared spectra.

## 1. Introduction

Clathrate hydrates (CLH) are crystalline solid with properties close to ice, trapping inside small host molecules, and thus retaining gases into water ice crystal cages. These inclusion compounds may be important for the stability of gases in many astrophysical bodies (planets, comets, interstellar grains) as they provide a trapping mechanism playing a role in the preservation in the solid state of these molecules at temperatures higher than expected, avoiding their early escape. Their occurence would thus modify the absolute and relative composition of astrophysical (icy) bodies as well as increase preservation timescales, or e.g. provide late time (re-)injection of gaseous species in planetary atmospheres.

## 2. Clathrates from the laboratory to astrophysics

Many laboratory studies examined clathrate hydrates thermodynamic or kinetic behaviour (e.g. Lunine & Stevenson 1985; Fray *et al.* 2009 and references therein), but probably the best way to confirm their presence in astrophysical bodies will come from remote infrared spectroscopy observations by telescopes or space probes. Methane and carbon dioxide clathrate crystals were thus produced in our laboratory, and the specific fingerprints betraying these clathrate hydrate presence recorded by infrared spectroscopy (although infrared spectra were recorded for some species, many previous experiments focused on e.g. Raman spectroscopy or neutron diffraction studies, e.g. Klug & Whalley 1973; Davidson *et al.* 1977; Bertie & Jacobs 1982; Richardson *et al.* 1985; Fleyfel &

Devlin 1991; Sum *et al.* 1997; Gutt *et al.* 2002; Kleinberg *et al.* 2003; Nakayama *et al.* 2003; Prager & Press 2006 and upward citations).

To produce and record CLH infrared spectra a specific high pressure evacuable enclosed cell was built and placed in an high vacuum evacuated cryostat ($P < 10^{-7}$mbar). A stainless steel injection tube for gases entrance or evacuation is sealed at the bottom of the cell. The formation of the CLH follow a procedure that satisfies to both its nucleation and prevents the sample from becoming optically thick to the infrared beam. Water vapour is first injected into the evacuated cell and condense on the pre-cooled infrared transmitting windows, immediately followed by the guest (here $CH_4$ or $CO_2$) injection at moderately high pressures. The cell is maintained in this state, typically during two days. The remaining non enclathrated gas is then evacuated while lowering the cell to cryogenic temperatures taking care to follow a path in the P-T phase diagram close to, but just below, the vaporisation and sublimation curves for the pure guest, to stay above the expected clathrate hydrate dissociation curve. The FTIR spectra are recorded in the 5K to 150K range (depending on the CLH) with a Bruker IFS 66v at an adapted resolution of 0.15 to 0.5 $cm^{-1}$, with a globar IR source, KBr beamsplitter, and an HgCdTe detector cooled at $LN_2$.

## 3. Methane and carbon dioxide spectra

### $CH_4$

The temperature dependent methane clathrate hydrate infrared spectra in the CH stretching mode region is displayed in Fig. 1. The striking feature is the observation of sub-structures as compared to typical methane ice bands, ressembling gaseous methane rovibrationnal lines, but shifted to the red. The methane is quasi free to rotate at low temperature, as already observed from neutron diffraction data (Prager & Press 2006). As the temperature increases this ability is partially quenched by collisions with the water ice cage potential surface, and then remains two broad bands assigned to methane trapped in the small and large water cages of the type I clathrate type. Details on the assignments can be found in Dartois & Deboffle (2008) and near infrared combination modes analyses will soon be available.

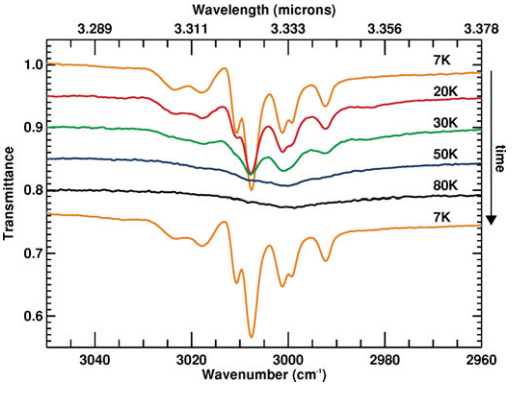


**Figure 1.** Low temperature methane clathrate hydrate infrared spectra in the CH stretching mode region.

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### $CO_2$

Carbon dioxide clathrate hydrate is different from methane in many respect as shown in Fig. 2 (right panel). First, the guest size is larger, the molecule linear, and the rotational ability is hindered. One sees in the antisymmetric mode only two broad bands corresponding to the two unequal cages in which $CO_2$ is trapped. The principal isotope main vibrational band had been recorded previously by Fleyfel & Devlin (1991) and we saturated the known bands to access the isotopes transitions as well as the combinations modes, in Fermi resonance (Fig. 2. left panel). More details are given in Dartois & Schmitt (2009).

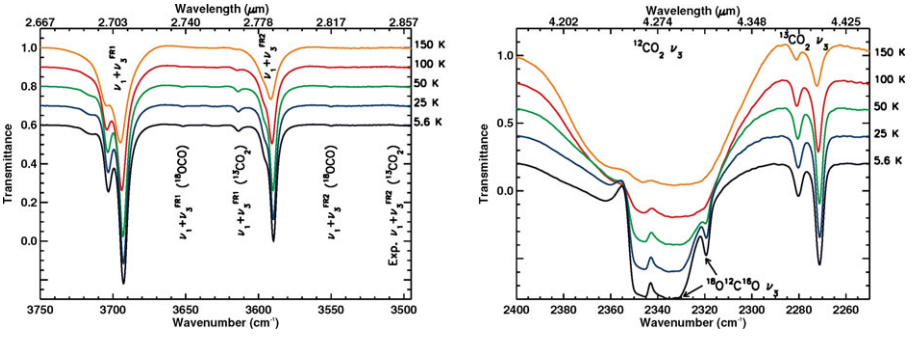


**Figure 2.** Temperature dependent carbon dioxide clathrate hydrate infrared spectra. Right panel : Antisymmetric stretching mode region. Left panel : Fermi resonance region ($\nu_1 + \nu_3$ ).

## 4. Discussion

Methane and carbon dioxide are both abundant molecules found in the solar system. In the martian context, first $CO_2$ and more recently $CH_4$ clathrate hydrates have been invoked, based on thermodynamical models to participate significantly to its cycle through surface and atmosphere interactions, and thus providing for $CO_2$ and $CH_4$ a sink during winter or a reservoir, respectively, to replenish the atmosphere (e.g. Genov & Kuhs 2003; Longhi 2006; Chastain & Chevrier 2007; Chassefiere 2009). In the outer solar system planets, satellites and comets, it could play a role in the icy bodies retention of species and modification of the relative abundances especially for light guest molecules (e.g. Delsemme & Swings 1952; Iro *et al.* 2003; Hersant *et al.* 2004; Mousis & Schmitt 2008 and references therein).

To allow a comparison of experimental work with astrophysical observations, some fundamental (and difficult) questions have to be adressed. In particular the formation kinetic under realistic astrophysical conditions is essential and will be conditioned by the labile water ice network interaction/reconstruction. As many physical interactions are possible with ice, and not necessarily involving the formation of a crystallographic system such as clathrate hydrates, it is of importance to be able to constrain their abundances in astrophysical media, to understand if they represent once observed an epiphenomenon for a widespread dominant crystal in astrophysics or a local state in a few objects.

Clathrate hydrate direct detection is of importance. We have shown through the infrared spectroscopic studies presented here that remote spectroscopy is one important possibility to identify CLH via their specific signatures. In particular the trapped methane molecules in the clathrate hydrate display a gaseous-like behaviour at low temperature in the water cages. Even at higher temperatures (50-150K), the vibrational spectra recorded

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are unique to methane and carbon dioxide clathrate hydrates, they represent a crucial identification pattern for low-temperature astrophysical icy bodies, such as planets, comets and/or interstellar grains. Methane and carbon dioxide were chosen as starting molecule to study, both because of their relevance for cometary or interstellar grains possible detection, but also because of their expected spectroscopic characteristics.

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