Laboratory infrared reflection spectrum of carbon dioxide clathrate hydrates for astrophysical remote sensing applications

Adriana Oancea*, Olivier Grasset, Erwan Le Menn, Olivier Bollengier, Lucile Bezacier, Stéphane Le Mouélic, Gabriel Tobie

Laboratoire de Planétologie et Géodynamique de Nantes, UMR-CNRS 6112, Université de Nantes, Nantes, France

A R T I C L E   I N F O

Article history:
Received 23 March 2012
Revised 19 September 2012
Accepted 20 September 2012
Available online 3 October 2012

Keywords:
Ices, IR spectroscopy
Experimental techniques
Satellites, Surfaces

A B S T R A C T

We present 1–5 μm IR reflectance spectra of CO₂ clathrate hydrates acquired under temperature and pressure conditions representative of the icy moons’ surfaces. The IR reflectance spectrum of the CO₂ clathrate hydrates is similar to the water ice IR reflectance spectrum except for two main absorption bands corresponding to the CO₂ guest molecule at 2.71 and 4.28 μm (3693 and 2334 cm⁻¹). The specific configuration of the clathrate hydrate structure is identified through the v₁ absorption band splitting which produces a band at 4.26 μm (2347 cm⁻¹) for molecules trapped in small cages and a band at 4.28 μm (2334 cm⁻¹) for molecules trapped in large cages. In general, the reflection spectra are similar to spectra obtained in transmission spectroscopy. But, it appears that the aspect of the v₁ absorption band is strongly influenced by physical (roughness, thickness, mixing properties) and optical (n and k) characteristics of the sample. A qualitative discussion of the effects of these sample properties on near-IR signatures of clathrate hydrates is proposed. Finally, a comparison between the absorption bands of CO₂ clathrate hydrates obtained in this work and CO₂ absorption bands as detected by VIMS on the icy satellites of Saturn is achieved. The experimental near-IR reflection spectra, made in pressure-temperature (P-T) conditions close to those of the icy surfaces, confirm that VIMS data are not consistent with the presence of structure I CO₂ clathrate hydrates on the surface of the icy moons.

© 2012 Elsevier Inc. All rights reserved.

1. Introduction

Carbon dioxide has been identified with the Visible Infrared Mapping Spectrometer (VIMS) onboard the Cassini spacecraft on several Saturn’s icy satellites, Iapetus, Hyperion, Phoebe and Dione spectral maps have a prominent CO₂ band, while on Mimas, Rhea and Tethys the CO₂ signature is weak (Dalton et al., 2010; Cruikshank et al., 2010; Clark et al., 2005; Buratti et al., 2005). CO₂ has also been detected on the three icy Galilean satellites (Europa, Ganymede, Callisto) by the Galileo Near-Infrared Mapping Spectrometer (NIMS) (Hibbitts et al., 2000; Dalton, 2010; Dalton et al., 2010). CO₂ is often correlated with dark terrains. However, it is unclear if CO₂ is trapped in H₂O ice or in some minerals or complex organic compounds (Buratti et al., 2005). Both the origin of CO₂ and the way it is incorporated on surfaces remain controversial.

The source of CO₂ may be internal (Choukroun et al., 2012), or CO₂ may be produced by radiolytic processes at the surface (Hansen and McCord, 2008). On Jupiter’s satellites and on the four Saturn’s satellites which display strong CO₂ signatures (Phoebe, Iapetus, Dione and Hyperion) the antisymmetric CO₂ stretching mode is shifted to shorter wavelength with respect to pure CO₂. This suggests that the molecule is incorporated in the icy crust as a gaseous or as a fluid inclusion. If CO₂ comes from the moon’s interior, it is likely to be stored in the form of clathrate hydrates (Choukroun et al., 2012). It is thought that clathrate hydrates play a significant role in the chemistry of the solar nebula (Mousis et al., 2009, 2010) and in the physical evolution of astrophysical objects (Choukroun et al., 2012). Clathrate hydrates are non-stoichiometric inclusion compounds, with a hydrogen bonded water ice network forming cages in which gas molecules can be trapped (up to 0.15 molar fraction) (Sloan, 1998). These compounds are largely found on Earth in the oceanic seafloor sediments, in the permafrost or in polar ice caps (Kargel and Lunine, 1998). So far, they have not been detected in astrophysical environments, but they are expected to be present in significant amounts in icy moons (e.g. Choukroun et al., 2012), they may also be present in cometary nuclei (Marboeuf et al., 2010) and Trans-Neptunian Objects (TNOS), and finally are also suspected in the martian environment (Chastain and Chevrier, 2007). In a planetary context the most common gases that can form clathrate hydrates are CO₂, CO, SO₂, CH₄, N₂ or C₂H₆ (Osegovic and Max, 2005). Although these structures are a powerful way to store CO₂ in icy bodies, their stability and their storage capacity (cage occupancies) under moderate to high
pressures is still poorly understood. Identification of CO$_2$ clathrate hydrates on icy moons relies on remote sensing observations, but the CO$_2$ clathrate hydrates infrared signature is not yet entirely characterized. Moreover the remote sensing observations of clathrate hydrates are particularly difficult because of the strong vibrations modes of the waterice matrix.

The CO$_2$ IR signatures have been extensively studied in pure phases, in different ice mixtures (Sandford and Allamandola, 1990; Baratta and Palumbo, 1998; Baratta et al., 2000; Oberg et al., 2007; Ehrenfreund et al., 1997), and in the clathrate hydrates. CO$_2$ clathrate hydrate physical properties and structure were investigated using different spectroscopic tools like X-ray and neutron diffraction (Udachin et al., 2001; Circone et al., 2003), nuclear magnetic resonance (NMR) (Ratcliffe and Ripmeester, 1986; Seo and Lee, 2004), Raman spectroscopy (Sum et al., 1997), infrared transmission spectroscopy (Fleyfel and Devlin, 1988, 1991; Dartois and Schmitt, 2009) or attenuated total reflection spectroscopy (Kumar et al., 2009). Under suitable temperature and pressure conditions the CO$_2$ forms preferentially the structure I clathrate hydrate, characterized by a unit cell having 2 small cages and 6 large cages. The formation of a structure II having the unit cell with 16 small cages and 8 large cages was observed only when the CO$_2$ is mixed with a type II hydrate forming molecule (Seo and Lee, 2004; Kumar et al., 2009).

The reflection spectra for CO$_2$ ice or for CO$_2$ clathrate hydrates were investigated by Kieffer (1970), Hapke et al. (1981), and Smythe (1975). Kieffer (1970) studied the reflectance spectra of CO$_2$, H$_2$O and CO$_2$–H$_2$O thin films from 12,500 to 3125 cm$^{-1}$ (0.8–3.2 μm). The major conclusion of his work was that in near and mid IR, water ice strongly absorbs the incident light and it masks the absorption bands of other compounds trapped in the ice matrix. Smythe (1975) encountered the same problem when he studied reflection spectra of CO$_2$ and CH$_4$ gas hydrates obtained by pressurizing gas over the pure water ice. Over the entire wave-number region, 10,000–1600 cm$^{-1}$ (1–6 μm), the reflectance IR spectral signature for these compounds was found to be very similar to pure H$_2$O ice reflectance spectra. For CO$_2$ clathrate hydrate the only difference between the pure water ice and the clathrate hydrate spectra was an absorption band at ~3703 cm$^{-1}$ (2.7 μm). In the case of methane clathrates no apparent CH$_4$ feature was found (Smythe, 1975). The first assignment of the IR ν$_1$ vibration band for the CO$_2$ clathrate hydrate was made by Fleyfel and Devlin (1988, 1991). Using Fourier-Transform Infrared (FT-IR) transmission spectroscopy they analyzed the IR signature of the CO$_2$ clathrate hydrate when prepared with a cryogenic thin-film vapor deposition technique. This work was recently continued with the study of Dartois and Schmitt (2009) that gives the spectroscopic assignments of the combination bands and overtone bands for the CO$_2$ molecules trapped in the clathrate hydrate structure.

This study presents the first experimental IR reflectance spectra of CO$_2$ clathrate hydrates obtained in conditions that allow direct comparison with planetary surfaces. A special attention has been given to the detectability of clathrate hydrates using reflectance spectroscopy, the technique on which planetary observations are based on. Reflectance strongly depends on the physical characteristics of the sample (in term of shape, thickness or surface properties) and on the two optical constants $n$ and $k$, the real and the imaginary parts of the refraction index, respectively. The impact of these factors on the reflection spectrum is negligible when the absorption coefficient of the material is very small ($k$ ≪ 0.1) but cannot be ignored when the icy material is characterized by strong absorption coefficients ($k$ ≳ 0.1) (Hapke, 1993; Baratta and Palumbo, 1998). In the following, the experimental set-up and the clathrate hydrate synthesis procedure is presented. The experimental IR reflectance spectrum of the CO$_2$ clathrate hydrate structure 1 is described in details and compared with the available literature data. The planetological implications of this work are discussed in the last part of this paper.

2. Experimental methodology

2.1. Experimental set-up

All experiments were performed in primary vacuum (~10$^{-5}$ bar) in a low temperature and low pressure experimental set-up (Oxford Instrument) that is shown schematically in Fig. 1a. The pressure is measured using a Pirani pressure gauge (Thyracont-VSP 521, 1 × 10$^{-5}$–0.1 bar; relative accuracy 15%) and the primary vacuum is obtained with a Varian DryScroll SH110 pump. Temperature is controlled using a liquid nitrogen circulation system. It is measured with a Pt100 temperature sensor (accuracy of ±0.1 K). The sample is placed in the cryostat as shown schematically in Fig. 1b.

Reflectance Fourier Transform spectra of the water-rich ices were recorded using a Thermo Fisher Nicolet 5700 Continuum Infrared Microscope equipped with an infrared objective (15X Reflachromat), a tungsten filament source, a CaF$_2$ beam splitter and an InSb detector cooled with liquid N$_2$. The spectrometer optical bench is continually purged with dried air to eliminate water vapor, carbon dioxide, and other airborne contaminants. The spectra are recorded in the 10,000–2000 cm$^{-1}$ (1–5 μm) domain with a resolution of $R = 4$ (data spacing 1.9 cm$^{-1}$), using a total of 200 scans. Background spectra were acquired in a similar manner using a copper plate, prior to sample introduction for each experiment. Spectra displayed in this paper have been corrected for the background contribution. All spectra are acquired at normal incidence using unpolarized light.

2.2. Clathrate hydrates synthesis procedure

Structure 1 CO$_2$ clathrate hydrate samples were prepared as compact polycrystalline films using an high pressure autoclave (Autoclave France 50 ml, 300 bar). First, a film of crystalline ice is formed between two copper surfaces at $T = 255$ K in a cold room from a few drops of water deposited on the copper plate using a micro-pipette (see inset of Fig. 1a). The ice film thickness is constrained with tungsten thin wires having diameters of 25 or 100 μm. The ice film is introduced into the autoclave and is pressurized with gaseous carbon dioxide for three days at $T = 255$ K and $P = 20$ bar. During the CO$_2$ gas introduction the temperature is controlled carefully so that it does not rise above 273 K. A type K thermocouple introduced in the autoclave enables to control the sample temperature during the synthesis. The synthesis of CO$_2$ clathrate hydrate can be accelerated if a liquid water film is used. In this case the CO$_2$ hydrate film is obtained within 24 h. The tungsten wires permit the estimation of maximum film thickness. After clathrate hydrates synthesis, copper plates are set apart (see inset of Fig. 1a) and the clathrate hydrates films are usually broken. The sample introduced into the cryostat is composed of film fragments with a maximum thickness constrained by tungsten wires.

2.3. Samples recovery and loading into the cryostat

Loading of the sample into the cryostat is achieved in the cold room at $T = 255$ K and at atmospheric pressure. In these experimental conditions, the clathrate hydrates are outside their field of stability. Fig. 2 displays the experimental conditions in which the clathrate hydrates samples are manipulated and analyzed. At 1 bar, CO$_2$ clathrate hydrate is stable only below 218 K (Stoan, 1998; Fray et al., 2010). But below the melting point of ice, CO$_2$
Clathrate hydrates undergo “the self-preservation phenomena” that relates to the fact that it protects itself from further decomposition without external intervention (Falenty and Kuhs, 2009). This phenomenon is commonly observed at 1 bar between 240 and 270 K, but it has also been observed under vacuum or at moderate pressure. This anomalous behavior has been reported for other molecules like CH$_4$, O$_2$, or N$_2$ (Takeya and Ripmeester, 2008). As it has been shown in laboratory studies, gas hydrates in this metastable state may retain a substantial volume of gas for a few months (Stern et al., 2001; Circone et al., 2003). Circone et al. (2003) have made investigations on the dissociation of the CO$_2$ clathrate hydrate at 1 bar. Using temperature ramping experiments performed between 240 and 277 K they have shown that only 20% max of the total CO$_2$ gas content was released by 270 K, while the remaining 80% of the gas was abruptly released above 270 K. Similarly, during isothermal pressure-release experiments, they showed that at 240 K (~0.4 h) and 268 K (~1.2 h) respectively, the samples released less than 10% of their total gas content. Falenty and Kuhs (2009) studied the self-preservation of CO$_2$ clathrate hydrates on a much boarder P–T field, with T between 200 and 270 K and pressures far outside the stability domain (6 mbar). In their experiments at 6 mbar (the closest to our experimental conditions) the speed of decomposition gradually decreases, for temperatures from 240 K toward the melting point of ice. At 6 mbar and 250 K a CO$_2$ clathrate hydrate sample will lose 0.3 weight fraction in ~5 min, but at T = 200 K a very slow decomposition was also observed (hydrate weight fraction = 0.6 after 1 h).

In this work, after synthesis, the clathrate hydrates are at T = 255 K and ~18 bar. The loading procedure takes less than 5 min and it is as follows. In the cold room the cryostat temperature is set at 125 K. The clathrate hydrates sample is then slowly depressurized (25 s) at 1 bar and taken out of the autoclave. The slow depressurization prevent drastic drop of the temperature and the CO$_2$ ice formation in the autoclave. The copper plates used for the film synthesis are screwed together on the cryostat and only after that the top plate is removed. The cryostat is then closed and is cooled down to 80 K after air pumping. This procedure places, within 5 min, the clathrate hydrates samples back to their stability domain where all spectral analyses will proceed.

For better constraining the loss of CO$_2$ during the loading procedure, the clathrate hydrate mass loss was measured on three samples issued from three different clathrate hydrate icy blocks. The question to answer is: how much gas is lost in the 5 min after the clathrate hydrate is taken out of the high pressure chamber? A small fraction of clathrate hydrate has been taken from the samples, crushed and then deposited on a Sartorius micro-balance (type 1465, with ±0.001 g precision). The clathrate hydrate mass was then monitored during 5 min, the longest time for the loading procedure where the sample is outside of its field of stability at

**Table 1**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$m_i$ (g)</th>
<th>$m_f$ (g)</th>
<th>$m_{H_2O}$ (g)</th>
<th>$\Delta m/m$ (%)</th>
<th>$n_i$</th>
<th>$n_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>0.368</td>
<td>0.363</td>
<td>0.296</td>
<td>1.36</td>
<td>10.04</td>
<td>10.79</td>
</tr>
<tr>
<td>Sample 2</td>
<td>0.490</td>
<td>0.486</td>
<td>0.391</td>
<td>0.82</td>
<td>9.65</td>
<td>10.06</td>
</tr>
<tr>
<td>Sample 3</td>
<td>0.503</td>
<td>0.500</td>
<td>0.393</td>
<td>0.60</td>
<td>8.73</td>
<td>8.97</td>
</tr>
</tbody>
</table>

...
The mass loss experiments results are reported in Table 1. During these 5 min, the very small weight loss which was observed (0.6–1.36%) is attributed to the clathrate hydrate gas loss by decomposition into ice and CO₂. Using the liquid H₂O weight measured after complete dissociation, hydration numbers between 9 and 11 were found for the samples. The results listed in Table 1 demonstrate that the grains of clathrate hydrates are indeed stable in the 5 min time slot outside the stability field. As for the films that are used in this work the loading procedure is simpler and shorter than for grain preparation (i.e. no crushing, etc.). Thus, the loss of the gas from the hydrate film, after it was taken out of the autoclave, is expected to be even lower than that for the grains. The film synthesis is favorable to the formation of an entirely filled clathrate, but a loss of gas during the samples depressurization is also expected. From the weight loss of grain samples, we can also estimate the minimum gas concentration in the clathrate hydrate films. As the synthesis procedure is similar and the water to gas ratio in the autoclave was lower, the hydration number for the film samples could not be higher than 9. Therefore, the films could only be formed by either a mixture of ice and fully filled clathrate hydrate or by a partially filled clathrate hydrate.

3. Results

3.1. Main characteristics of reflection IR spectra of CO₂ clathrate hydrates

The IR reflection spectrum of CO₂ clathrate hydrates is displayed in Fig. 3 from 1.25 to 5 μm (8000–2000 cm⁻¹) at T = 110 K and P = 2 × 10⁻5 bar. For comparison, the reflectance laboratory spectra of hexagonal ice Ih and of solid CO₂ are also plotted. In general, the position and shape of absorption bands in spectra of clathrate hydrates are very similar to those of pure water ice. Nevertheless, the presence of the CO₂ molecules trapped in the ice matrix is clearly indicated by the absorption bands at ~2.71 μm (3693 cm⁻¹) and those at ~4.28 μm (2334 cm⁻¹).

Fig. 3. The 1.25–5 μm (8000–2000 cm⁻¹) IR reflectance spectrum of a CO₂ clathrate hydrate acquired from a broken film less than 100 μm thick. For comparison an ice Ih spectrum and a CO₂ solid spectrum are shown. All spectra are taken with the same experimental set-up under vacuum at P ~ 2 × 10⁻5 bar. One can see that the water ice matrix dominates the IR signature of the CO₂ clathrate hydrate. CO₂ molecules trapped in the clathrate cages is observed around ~4.28 μm (2334 cm⁻¹) and ~2.71 μm (3693 cm⁻¹).

Fig. 4. Influence of sample thickness on the CO₂ clathrate hydrates reflectance spectra. (a) spectrum acquired on a clathrate hydrate film having a thickness of ~100 μm; (b) spectrum acquired on a broken film of a clathrate hydrate that had an initial maximum thickness of ~25 μm. On the right, the nature of the surface of acquisition is imaged. The beam was centered and 50 μm in diameter.
grains, the same variations of reflectance in the 2.6 (3800) to 5 μm (2000 cm⁻¹) domain are observed from sample to sample. Grains reflectance spectra are, most of the time, similar to the spectrum in Fig. 4a. Very few grains produced a spectrum similar to the one displayed in Fig. 4b. The possible causes for these differences will be discussed in Section 4.2.

In the next sections, the spectrum of CO₂ clathrate hydrates is displayed and discussed for each spectral region using as a reference a spectrum acquired from a broken film sample less than 100 μm thick. Table 2 summarizes the vibration band positions observed in this work for the CO₂ molecules in different physical states, and compares our results with data found in the literature.

### 3.2. Spectral signature of the antisymmetric vibration mode

Fig. 5 compares the infrared spectrum of the clathrate hydrates obtained in this work with solid and gas infrared signatures of pure CO₂ in the 2500–2200 cm⁻¹ (4.4–5.5 μm) spectral range. This spectral region contains the contributions of the fundamental C=O asymmetric stretching vibration modes ν₃ for the CO₂ and ¹³C₂O₂ molecules. At T = 290 K and 1 bar pressure, the gas phase presents a double absorption band at 2360 and 2341 cm⁻¹ (4.23 and 4.27 μm, that corresponds to the envelopes of the R and P branch, respectively, of the rotational transitions that occur for the asymmetric stretching band), while the solid phase is characterized by an absorption band at 2343 cm⁻¹ (4.268 μm). The second band, at ~2379 cm⁻¹ (4.203 μm), on the high-frequency side of the solid CO₂ reflection spectrum, is not listed in literature as an absorption band. This feature was already observed in the IR transmission spectra for the CO₂ ice films and its intensity was found to depend on the geometric configuration of the experiment and of the polarization of the incident light. When transmission spectra are taken with normal unpolarized light, this feature is present as a weak shoulder on the reflection spectrum, is not listed in literature as an absorption band (Osberg and Hornig, 1952; Baratta and Palumbo, 1998). Instead, when the angle of incident light varies between 0° and 60° and a p-polarized light is used (the electric vector is parallel to the plane of incidence), a strong feature centered at ~2377 cm⁻¹ (4.207 μm) is present in the transmission spectra (Baratta and Palumbo, 1998; Baratta et al., 2000). According to Osberg and Hornig (1952) and to Baratta and Palumbo (1998), this feature is not due to absorption (k) but to an increased reflectivity in the domain of the absorption band where n < 1.

### Table 2
Carbon dioxide vibration band positions in different physical states. (w) – weak band.

<table>
<thead>
<tr>
<th>CO₂ gas</th>
<th>CO₂ ice</th>
<th>H₂O:CO₂ = 5:1</th>
<th>CO₂ Clathrate</th>
<th>Mode</th>
<th>Experimental Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>v/cm⁻¹ (μm)</td>
<td>v/cm⁻¹ (μm)</td>
<td>v/cm⁻¹ (μm)</td>
<td>v/cm⁻¹ (μm)</td>
<td>T/K</td>
<td>P/bar</td>
</tr>
<tr>
<td>2360 (4.237); 2341 (4.272)</td>
<td>2343.3 (4.267); 2343 (4.268)</td>
<td>2341.5 (4.272); 2338.8 (4.276); 2337.4 (4.278)</td>
<td>2347 (4.261); 2336 (4.281)</td>
<td>ν₃</td>
<td>80</td>
</tr>
<tr>
<td>2283 (4.38)</td>
<td>2282.4 (4.381); 2281 (4.384)</td>
<td>2277.5 (4.391); 2277.8 (4.390); 2282 (4.382)</td>
<td>2271.3 (4.403); 2280 (4.386)</td>
<td>ν₃</td>
<td>80</td>
</tr>
<tr>
<td>3704 (2.7); 3726 (2.697)</td>
<td>3707.5 (2.697); 3706 (2.698)</td>
<td>3702.1 (2.701); 3707.7 (2.697); 3695 (2.706)</td>
<td>3703.4 (2.7); 3692.7 (2.708)</td>
<td>ν₁</td>
<td>80</td>
</tr>
<tr>
<td>3600 (2.778); 3626 (2.758)</td>
<td>3598 (2.779)</td>
<td>3592 (2.784)</td>
<td>3589.7 (2.786); 3596 (2.781)</td>
<td>ν₂</td>
<td>85</td>
</tr>
<tr>
<td>5087 (1.966); 5110 (1.957)</td>
<td>5087 (1.966)</td>
<td>5083 (1.967) (w)</td>
<td>5066.2 (1.974); 5072.3 (1.971)</td>
<td>ν₃</td>
<td>80</td>
</tr>
<tr>
<td>4963 (2.015); 4990 (2.004)</td>
<td>4969 (2.012)</td>
<td>4962 (2.015) (w)</td>
<td>4950.2 (2.002); 4962.2 (2.015)</td>
<td>ν₁</td>
<td>15</td>
</tr>
<tr>
<td>4838 (2.067); 4865 (2.055)</td>
<td>4830 (2.07)</td>
<td>4982.7 (2.007) (w)</td>
<td>4819.7 (2.075); 4825.6 (2.072)</td>
<td>ν₂</td>
<td>15</td>
</tr>
</tbody>
</table>

a Pure gas CO₂ spectrum measured, in this work, at T = 290 K and P = 1 bar, using a closed cell placed inside the cryostat.
b Band assignments from Sandford and Allamandola (1990) and from Quirico and Schmitt (1997).
c T – Transmission, R – Reflection and ATR – Attenuated Reflection Spectroscopy; EQ – thermodynamic equilibrium. d – Sandford and Allamandola (1990); e – Bernstein et al. (2005); f – Kumar et al. (2009); g – Fleyfel and Devlin (1991); h – Dartois and Schmitt (2009).
When IR reflection spectra of solid and gaseous CO$_2$ are compared to IR reflection spectra of the CO$_2$ clathrate hydrates, one can see that the $v_3$ vibrational frequency for carbon dioxide varies from one phase to another (Fig. 5). Clathrate hydrates present an absorption band at 2334 cm$^{-1}$ (4.28 μm) including a prominent shoulder at 2347 cm$^{-1}$ (4.26 μm) and two smaller absorption bands at 2280 and 2272 cm$^{-1}$ (4.386 and 4.40 μm). These bands correspond to $v_3$ vibration modes of CO$_2$ and $^{13}$CO$_2$ molecules respectively, trapped into the ice matrix. In a clathrate structure, the $v_3$ vibration bands are shifted to lower frequencies compared to the gas phase. In Fig. 5 we can see that the clathrate absorption bands are disposed on both sides of the CO$_2$-$v_3$ band in the pure solid phase. The same conclusion is drawn when the comparison is made with the absorption band for the H$_2$O:CO$_2$ = 5:1 ice mixture (Table 2). Similarly, the $v_3$ – $^{13}$CO$_2$ band positions are shifted to lower frequencies compared to the gas phase (∼2283 cm$^{-1}$ (4.380 μm) (Dartois and Schmitt, 2009)) but also compared to the solid phase (∼2282 cm$^{-1}$ (4.382 μm) – at T = 80 K (Sandford and Allamandola, 1990)).

The split displayed by the $v_3$ absorption band for the CO$_2$ clathrate hydrates, deconvoluted with two bands, at 2347 cm$^{-1}$ (4.26 μm) and at 2334 cm$^{-1}$ (4.28 μm), is attributed to the presence of CO$_2$ molecules in both the small and large cages of the clathrate structure. According to the previous IR experiments on the CO$_2$ clathrate hydrates (Fleyfel and Devlin, 1988, 1991), the band at 2334 cm$^{-1}$ (4.28 μm) can be attributed to the CO$_2$ asymmetric stretching vibration in the large cage. The band at 2347 cm$^{-1}$ (4.26 μm) corresponds to the molecule asymmetric stretching vibration in the small cage. This interpretation is in agreement with the “loose cage-tight cage” model for guests trapped in clathrate hydrates cages (Subramanian and Sloan, 2002), that predicts that the larger the cavity the lower is the frequency of the stretching mode vibration. Similar interpretation can be made for the $v_5$ – $^{13}$CO$_2$ observed at 2280 and 2272 cm$^{-1}$ (4.386 and 4.40 μm). CO$_2$ molecules trapped in the small cages produce the band at 2280 cm$^{-1}$ (4.386 μm) while the molecules trapped in the large cages absorb at 2272 cm$^{-1}$ (4.401 μm). Our results, obtained in reflectance on icy films put into P–T planetary conditions, are in good agreement with the spectra obtained in transmission by Dartois and Schmitt (2009), and Fleyfel and Devlin (1988, 1991).

While the band positions for molecules in small cages do not display a significant change among different samples, CO$_2$ signatures in the large cages present a shift to lower frequencies up to 3 cm$^{-1}$. This variation of the band positions could be related to the cage occupancy, and to a lesser extent to temperature variations. Unfortunately, it was not possible to measure experimentally the cage occupancies, and no quantitative estimate of this dependency can be provided.

### 3.3. Spectral range of the combination modes

Figs. 6 and 7 highlight the spectral range that contains the strongest combination transitions of the CO$_2$ molecule known as Fermi resonances. Again, the spectral signature of CO$_2$ clathrate is compared with CO$_2$ gas and solid IR signatures in 3800–3500 (2.6–2.85) and 8000–4000 cm$^{-1}$ (1.25–2.5 μm) respectively.

The second most important CO$_2$ absorption feature of the clathrate hydrates structure is found in the spectral window 3800–3500 cm$^{-1}$ (2.6–2.85 μm). This band is centered at 3693 cm$^{-1}$ (2.71 μm) and displays a weak shoulder on the high-frequency side, at 3702 cm$^{-1}$ (2.70 μm). This band can be attributed to the $v_1$ + $v_3$ transition, as already noticed in the experimental FT-IR transmission observations of Dartois and Schmitt (2009). Similarly to the $v_3$ absorption band, the high frequency shoulder can be attributed to molecules in small cages and the band at 3693 cm$^{-1}$ (2.71 μm) to molecules trapped in large cages. An other absorption band has been observed at 3591 cm$^{-1}$ (2.78 μm) and can be attributed to the $2v_2 + v_3$ transition (Dartois and Schmitt, 2009). For this latter band, no high frequency shoulder is observed which can suggest a splitting induced by the trapping of molecules in the two different cages of the clathrate structure. This band is on the high frequency wing of the strong and broad water absorption band corresponding to the O–H stretching mode of water matrix, therefore a CO$_2$ and H$_2$O band overlap can explain the missing high frequency shoulder.
The water matrix also displays strong absorption bands in the 8000–4000 cm\(^{-1}\) (1.25–2.5 \(\mu\)m) spectral range. The clathrate hydrate IR reflection spectrum, displayed in Fig. 7, is dominated in this region by the absorption bands at 6650 (1.5), 6401 (1.56), 6064 (1.64) and 4928 cm\(^{-1}\) (2.03 \(\mu\)m), all due to water ice combinations and overtone absorption bands (Eisenberg and Kauzmann, 1969). Also displayed in the figure are the gas and solid spectra of pure carbon dioxide that presents three combination modes in this spectral range. These modes are not observed in the clathrate hydrate reflection spectrum. In the water band at 4928 cm\(^{-1}\) (2.03 \(\mu\)m), only a very small \(v_1 + 2v_2 + v_3\) combination band at \(\sim 4950\) cm\(^{-1}\) (2.02 \(\mu\)m) has been noticed. The absence of these modes from the spectra will be discussed in the Section 4.1, but again, a band overlap between the strong 2 \(\mu\)m water absorption band and the \(\text{CO}_2\) absorption bands must be taken into account when dealing with water rich environments.

### 4. Discussion

#### 4.1. Comparison to previous results

The IR reflection spectra of \(\text{CO}_2\) clathrate hydrates have been studied experimentally under \(P-T\) conditions comparable to the surfaces of icy moons. \(\text{CO}_2\) clathrate hydrates IR signatures, obtained on film samples, have been displayed and compared to pure water and carbon dioxide phases. In the first part of this section, our results are compared to previous studies, especially with those made under transmission. In a second part, a discussion about the implications of this work for planetary observations is proposed.

The IR signature of clathrate hydrates structures is very similar to that of pure water ice. The main differences relate to the special configuration of clathrate cages, because of the interactions between the guest molecules and the clathrate hydrate structure. When compared to the pure \(\text{CO}_2\) phases, the \(\text{CO}_2\) vibration modes are shifted toward lower frequencies. As noted in Table 2 and shown in Fig. 5, the guest molecules trapped in large and small cages have absorption bands at 2334 cm\(^{-1}\) and 2347 cm\(^{-1}\), respectively. This band assignment is in good agreement with previous data obtained by Fleyfel and Devlin (1988, 1991), who investigated the IR-transmission spectral signature of a metastable thin film of \(\text{CO}_2\) clathrate hydrates. Samples were prepared using a cryogenic thin-film vapor deposition technique. This approach has been found to be a viable option in the formation and the study of clathrate hydrates for many gases (Devlin, 2001). When grown epitaxially on an ethylene oxide clathrate hydrate substrate at 120 K, \(\text{CO}_2\) forms a type I clathrate hydrate structure where both small and large cages are occupied, as indicated in transmission spectra by the \(\text{CO}_2\) combination frequencies at 2347 and 2335 cm\(^{-1}\) (4.26 and 4.28 \(\mu\)m), respectively.

The absorption bands at 2280 and 2272 cm\(^{-1}\), observed in Fig. 5 and attributed to the \(^{13}\text{CO}_2\) antisymmetric stretching mode, are in agreement with the work of Dartois and Schmitt (2009). Using a high pressure cell, they obtained a \(\text{CO}_2\) type I clathrate hydrate by pressurizing an ice film with \(\text{CO}_2\) gas. They identified the presence of clathrate hydrates via the \(v_1\) vibration mode of the \(^{13}\text{CO}_2\) molecules at 2280 and 2271 cm\(^{-1}\) (4.38 and 4.40 \(\mu\)m) as the main isotopomer transitions at 2334 and 2347 cm\(^{-1}\) (4.28 and 4.26 \(\mu\)m) were saturated.

In the spectral range 8000–3000 cm\(^{-1}\), Dartois and Schmitt (2009) reported on the combination modes of \(\text{CO}_2\) clathrate hydrates. In our experimental reflection spectra only two combination modes were observed: the \(v_1 + v_3\) and \(2v_1 + v_3\) Fermi resonances combination modes at 3693 cm\(^{-1}\) and 3591 cm\(^{-1}\), respectively. No absorption band around 5000 cm\(^{-1}\) is present in the reflection spectra of this work. Water rich systems are difficult to analyze because of the strong absorption bands of the water matrix in this spectral range. Kieffer (1970) studied the reflection spectra of \(\text{CO}_2-\text{H}_2\text{O}\) films and observed that a water ice surface layer of only a few ng cm\(^{-2}\) can hide entirely the IR signature of a thick layer of \(\text{CO}_2\) ice in this spectral range. Similar observations are also made for the amorphous \(\text{H}_2\text{O}:\text{CO}_2\) = 5:1 solid mixture (Bernstein et al., 2005). Our samples correspond either to a partially filled clathrate or to a mixture of a fully filled clathrate and ice grains (as discussed in Section 2.3). Then, the absence of these combination bands from our reflection spectra may be the combination of two factors: the presence of the strong water absorption bands, and the lack of a significant amount of \(\text{CO}_2\) molecules in the clathrate. Therefore, we argue that, the absence of the “2 \(\mu\)m” \(\text{CO}_2\) combination modes from our reflection spectra is due to the overlapping of water absorption “2 \(\mu\)m” band (much intense) over the carbon dioxide absorption bands.

### 4.2. \(\text{CO}_2\) clathrate hydrates IR reflectance in the 4.28 \(\mu\)m spectral range

From Fig. 4, one can see that significant discrepancies of IR signatures are observed in the spectral range from 3800 (2.6) to 2000 cm\(^{-1}\) (5 \(\mu\)m), while in the spectral range from 8000 (1.25) to 3800 cm\(^{-1}\) (3.3 \(\mu\)m) spectra are similar. The most striking difference is encountered for the absorption band at 4.28 \(\mu\)m, corresponding to the \(\text{CO}_2\) fundamental asymmetric stretching mode. When samples with different thicknesses and surface properties are analyzed, this absorption band is either present or missing from the spectrum. The first explanation to this variability is that the sample is not fully clathrated or that an important amount of gas has been lost during the depressurization of the ice film. Nonetheless, it has been shown, in Section 2.3, that the samples studied in these experiments were synthesized using a protocol which guarantees that a significant amount of \(\text{CO}_2\) is trapped within the cages. This is proven by the fact that the absorption band corresponding to the combination mode \(v_1 + v_3\) is always observed, no matter the sample characteristics. Since the combination bands are always weaker than their corresponding fundamental modes, we think that this high variability of the 4.28 \(\mu\)m band cannot be
explained only by a compositional variation of our samples, but is rather due to optical transfer effects as explained below.

The reflected light from a large grain or film surface is the combination of two main processes (Hapke, 1993). First, there is the surface scattering, that occurs when the light is scattered from the outer surface of a sample. Second, there is the internal or volume scattering, that occurs when the light has been refracted into the interior of the grain and scattered back out. The later process is due to imperfections such as crystal boundaries, micro-inclusions or density striations. The volume scattering depends on the absorption coefficient of the sample and it is proportional to $e^{-td}$, where $\alpha = 4\pi k/\lambda$ is the absorption coefficient and $d$ is the particle size (Hapke, 1981; Clark and Roush, 1984; Verbscer et al., 1998).

Two types of surface reflection occur when light interacts with a surface: specular reflection for a smooth surface or diffuse reflection for an irregular surface geometry. The surface scattering at normal incidence is proportional to the Fresnel reflection coefficient $R = (n - 1)/(n + 1)^2$. Combination of optical and physical sample characteristics determine which of these processes is predominant (Hapke, 1993).

When $k < 0.1$, meaning small absorption coefficient, the main process is the volume backscattering (Hapke, 1993) and the reflectance spectrum is qualitatively similar to a transmission spectrum. In the case of CO$_2$ clathrates, both water ice and carbon dioxide have $k < 0.1$ in the spectral region from 8000 (1.25) to 3800 cm$^{-1}$ (2.6 $\mu$m), where no spectral variations were observed (Fig. 4). Furthermore, there is no influence of the surface characteristics on the total reflectance. In this spectral region, the reflectance is only influenced by the thickness of clathrate hydrates films via deeper absorption bands when the film thickness increases (Jaumann et al., 2008; Taffin et al., 2012).

When $k > 0.1$, the absorption coefficient is very large, the surface scattering becomes important and the total reflectance is sensitive to both surface properties and sample thickness. When thicker films are analyzed ($\geq 100 \mu$m), most of the refracted component is absorbed and the volume backscattering contribution is negligible. This explains the absence of absorption bands around $\sim$2334 cm$^{-1}$ (4.28 $\mu$m) from Fig. 4a spectrum. Furthermore, if the surface presents asperities, the surface reflection is strongly reduced so that the total reflectance is lowered down to a few percent. When $k > 0.1$, a dominated surface reflection region can become a volume backscattering region for small and rough surface samples (Hapke, 1993). This was observed in our study for clathrate films having thickness $\leq$100 $\mu$m for which absorption bands were detected in the spectral region corresponding to the CO$_2$ vibrations, normally a surface scattering dominated region.

The specular reflection becomes important when the surface sample is smooth. In Fig. 8a, a spectrum obtained from a smooth clathrate hydrates film surface is displayed. The reflectance peak at $\sim$3200 cm$^{-1}$ corresponds to the ice reflection Fresnel peak. The second peak around 2335 cm$^{-1}$, is very intense, and corresponds to the CO$_2$ asymmetric vibration mode. In Fig. 8b, one can see from the spectrum associated to the smooth surface, that the peak at $\sim$2335 cm$^{-1}$ (4.28 $\mu$m) is accompanied by a much less intense peak at 2347 cm$^{-1}$ (4.26 $\mu$m). We believe that these reflection peaks are the Fresnel reflections corresponding to the CO$_2$ clathrate hydrates crystalline structure. For comparison, a spectrum corresponding to a rough surface has been plotted in Fig. 8b. Here the volume backscattering contribution is significant. One can see that the two reflection peaks from spectrum (1) correspond to absorption bands in the spectrum (2) that were attributed to the CO$_2$ molecules trapped in the large and small cages of the clathrate hydrates crystalline structure.

While the sample physical properties influence strongly the 4.28 $\mu$m domain, no influence was observed for the absorption band at 2.71 $\mu$m. By comparing the spectrum of the CO$_2$ clathrate of Fig. 3 with the one in Fig. 4b one can see that the intensity of this absorption band certainly depends on the clathration degree and the sample thickness. But the 2.71 $\mu$m band was never absent from the reflection spectra obtained in this work, even when very poorly clathrated – water rich samples were analyzed. Even though the clathrate hydrate presence in the sample should be best identified through the fundamental mode at 4.28 $\mu$m, it seems that the band at 2.71 $\mu$m is a better indicator, in IR reflectance experiments, that CO$_2$ molecules are enclathrated.

### 4.3. Clathrate hydrates vs. H$_2$O:CO$_2$ solid ice mixture

The results obtained in this work with reflectance spectroscopy can be used to show that spectral differences occur between IR clathrate signatures and H$_2$O:CO$_2$ ice mixtures. In Table 2, one can see that positions of the CO$_2$ absorption bands in a clathrate hydrates structure are different from the band positions of CO$_2$ in a H$_2$O–CO$_2$ mixture. When CO$_2$ is trapped into an ice matrix formed by the deposition of a gaseous mixture of H$_2$O:CO$_2$ at low

![Fig. 8](https://example.com/fig8.png)
temperatures (10–80 K) it produces relatively broad bands shifted to lower frequencies than those of pure CO$_2$ under the same conditions. For example, for a H$_2$O:CO$_2$ = 5:1 ice mixture the v$_3$ stretching is temperature dependent. It gives a single band which shifts from 2339.8 cm$^{-1}$ (4.273 μm) at 10 K down to 2338.6 cm$^{-1}$ (4.276 μm) at 100 K (Sandford and Allamandola, 1990). In addition to the difference between band positions, the v$_3$ band splitting is not observed for the ice mixtures. Moreover, the CO$_2$ 2v$_3$ forbidden overtone near 4685 cm$^{-1}$ (2.134 μm) specific to CO$_2$ isolated in an ice matrix (H$_2$O, N$_2$, Ar) (Bernstein et al., 2005; Quirico and Schmitt, 1997) is not active for the clathrate hydrates.

4.4. From laboratory measurements to natural planetary surfaces

The remote sensing planetary observations obtained through space missions provide now valuable information about the composition and planetary surface texture of the Solar System objects. But in order to interpret these observations, laboratory data (spectra and optical constants) about the molecular species suspected to be present at the surface or in the atmosphere of the icy objects are needed. First, thin samples spectra are used to determine optical constants and also to set up models describing planetary surfaces. Second, thick samples spectra are needed to reproduce the near infrared combination modes that can be weaker than their corresponding fundamentals (Dalton et al., 2010). These absorption bands are, most of the time, noticed in planetary observations because the optical paths of light through the planetary regoliths are usually very long (Dalton et al., 2010). In our investigation of CO$_2$ clathrate hydrates IR signatures, temperature, pressure and sample size were comparable to the surface planetary conditions. The laboratory measurements were performed in the temperature range of the surfaces of icy bodies, 80–110 K, and the samples were sufficiently thick (>20 μm) for the near-infrared absorptions to be noticeable. The IR properties of CO$_2$ clathrate hydrates were investigated in the 1–5 μm domain, which corresponds to the spectral range of the Galileo NIMS and Cassini VIMS imaging spectrometers.

A recent paper, published by Cruikshank et al. (2010), reviews the CO$_2$ spectral bands discovered by VIMS on the Saturn satellites Phoebe, Iapetus, Hyperion and Dione. As shown by Cruikshank et al. (2010), the CO$_2$ spectral band detected on Phoebe is indistinguishable from that of solid CO$_2$ or that of CO$_2$ molecules trapped in the small cages of a clathrate hydrates structure II. The band position from the three other satellites corresponds to CO$_2$ trapped in a complex material, but no indication exists whether this later is water or some mineral or complex organic compound.

The Fig. 9a presents the CO$_2$ bands of the four satellites, along with the reflectance spectra obtained in the present study for the CO$_2$ clathrate hydrates structure I. This figure reinforces the conclusion of Cruikshank et al. (2010): the spectral bands detected by VIMS do not correspond to a clathrate hydrates structure I. The band position for Phoebe could suggest the presence of clathrate hydrates structure II on the surface but raises another question: how these clathrate hydrates are produced? Two possibilities exist: first, clathrates hydrates form at the moon's surface by slow co-deposition of gaseous mixtures of H$_2$O–CO$_2$ or second, clathrate hydrates formed into the planet interior have been released to the surface. The CO$_2$ molecule is a clathrate type I forming molecule. The low pressure deposition technique, successfully formed type II structure only when a pre-organized structure was used as a substrate (Flefel and Devlin, 1991). Under high pressure conditions, the formation of a structure II has never been observed. The only case where a transient CO$_2$ structure II was observed, is at moderate pressures during the early stages of clathrate hydrates formation from ice exposed to CO$_2$ gas (Staykova et al., 2003) or in multiple guests systems (N$_2$–CO$_2$) (Chazallon et al., 2011). We believe that comparison of VIMS data to lab data, and especially the new evidences provided in reflectance in this work, together with the apparent difficulty to form structure II with CO$_2$, are arguments against the existence at planetary scales of CO$_2$ clathrate hydrates on the surface of the moons.

As shown in our spectra, the CO$_2$ clathrate hydrates present an important absorption band at 2.71 μm. The 4.26 μm has been extensively used, contrarily to the 2.71 μm domain. In this work we have shown that the reflectance spectra of CO$_2$ clathrate are strongly influenced by the surface properties but also by sample optical properties. These influences are important in the 4.26 μm region, but not in the 2.71 μm domain, since this band was always observed during our experiments, independently of the sample properties. This domain is not easy to investigate due to the presence of the strongly "3 μm" absorbing water ice band. In Fig. 9b the re-sampling at VIMS resolution of the lab spectrum of the CO$_2$ in 2.7 μm spectral range is presented. VIMS have in this spectral range channels at 2.66, 2.68, 2.69, 2.71 and 2.73 μm. The narrow laboratory band became only a small inflection in the re-sampled spectra at VIMS resolution. In fact, this combination band is between two VIMS channels and only the right wing of the band

![Fig. 9.](image-url)
is actually re-sampled, leading to the conclusion that a less intense band will not appear in the VIMS spectra. The discrimination between CO\textsubscript{2} gas, solid and clathrate seems to be possible only if a sufficient amount of molecules are present. However the discrimination between CO\textsubscript{2} clathrate and CO\textsubscript{2} into an icy mixture with water ice is not possible at this resolution. The combination band around 2.78 \textmu{}m that occurs for the CO\textsubscript{2} in gas, ice, icy mixtures and clathrates is dependent on the amount of the carbon dioxide molecules in the samples. This band is even more difficult to detect in ices dominated by water since it occurs on the high frequency side of the strong O–H stretching mode. In this case, a band overlap occurs between water and carbon dioxide.

5. Conclusions

In this study, we have analyzed experimentally the IR reflectance spectra of the CO\textsubscript{2} clathrate hydrates under P–T conditions comparable to the surfaces of the icy moons. Film samples have been obtained experimentally and their spectral characteristics have been determined in the infrared domain from 1 to 5 \textmu{}m. It has been shown that CO\textsubscript{2} clathrate hydrates IR reflection signature has the fingerprint of the water ice structure and it is strongly influenced by the optical radiative transfer. However unique spectral features, related to the absorption bands of CO\textsubscript{2} guest molecules in clathrate hydrates cages, have also been identified. In this work three main absorption bands have been described at 2.71, 4.26, 4.28 \textmu{}m (3693, 2347, 2334 cm\textsuperscript{-1}) as corresponding to CO\textsubscript{2} trapped in the clathrate structure.

The 4.26 and 4.28 \textmu{}m (2347, 2334 cm\textsuperscript{-1}) bands correspond to the same absorption mode (asymmetric stretching vibration) but for molecules trapped in small and large cages, respectively. These absorption bands are influenced by optical and physical characteristics of the sample. The large cage band position seems to be influenced by the amount of CO\textsubscript{2} into clathrate cages but it was out of the scope of this experimental work to quantify this effect.

The band at 2.71 \textmu{}m (3693 cm\textsuperscript{-1}) was found to be the most prominent combination band of carbon dioxide trapped in clathrate cages. By contrast to the asymmetric absorption mode, the strength of this band was not influenced by any optical parameter. This absorption band was always observed during our experiments and did not depend on sample properties.

Comparison between the absorption bands of CO\textsubscript{2} clathrate, pure CO\textsubscript{2} and CO\textsubscript{2}–H\textsubscript{2}O ice mixtures showed that spectral discrimination can be achieved easily, especially in the domain of the fundamental absorption modes. The carbon dioxide in CO\textsubscript{2}–H\textsubscript{2}O ice mixtures is distinguished from pure phases by the presence of the forbidden CO\textsubscript{2} 2\nu\textsubscript{3} overtone (2.134 \textmu{}m) along with the other band positions spectral shift. Besides the band positions, clathrate hydrates are distinguished from pure phases and ice mixtures by the \nu\textsubscript{3} absorption band splitting induced by the special configuration of clathrate cages.

A comparison between the absorption bands of CO\textsubscript{2} clathrate hydrates obtained in the 4.28 \textmu{}m region and the CO\textsubscript{2} absorption bands detected by VIMS on the icy satellites of Saturn has been discussed. This experimental work confirms that VIMS data are not consistent with the presence of structure I CO\textsubscript{2} clathrate hydrates on the surface of the icy moons. Possibility of having metastable structure II still remains unsolved, but the natural condition at the icy satellites surfaces and the difficulty to form this latter structure are arguments against its existence at planetary surfaces. Finally, the clathrate hydrates structure is also characterized by the 2.71 \textmu{}m absorption band. This specific spectral domain, has not been extensively investigated so far for planetary purposes, because most of the time this range is dominated by the strong decrease of the 3 \textmu{}m water absorption. Moreover, the 2.71 \textmu{}m band occurs between two VIMS channels, which complicates the identification of the CO\textsubscript{2} clathrate hydrates on Saturn's icy moons. High spatial resolution data obtained by VIMS may allow a better investigation of subtle features in this spectral range, by possibly investigating purer exposures of CO\textsubscript{2} clathrate hydrate. On the other hand, systems with a higher spectral resolution might be able to detect a potential signature, if any.

CO\textsubscript{2} clathrates might also be present on the polar caps of Mars. However, their detection using orbital remote sensing observations might be complicated by the signatures of the CO\textsubscript{2} which is present in the atmosphere, and by the CO\textsubscript{2} ice on the cap itself. Finally, our experimental results might also prove to be useful to analyze data from other forthcoming missions toward icy bodies such as the Rosetta spacecraft, which will reach the Churyumov–Gerasimenko comet in 2014, New-Horizon which will reach the system of Pluto in 2015, or the JUICE mission planned to reach the system of Jupiter in 2030.

Acknowledgments

The research leading to these results has received funding from the European Research Council under the European Community’s Seventh Framework Programme (FP7/2007–2013 Grant Agreement No. 259285) and from the University of Nantes. We also thank the PRES-UNAM and the Centre National d’Etudes Spatiales (CNES agency) for their support.

References

Fleyfel, F., Devin, J.P., 1988. FT-IR spectra of 90 K films of simple, mixed and double clathrate hydrates of dimethylamine oxide, methyl chloride, carbon dioxide,
tetrahydrofuran and ethylene oxide containing decoupled D$_2$O. J. Phys. Chem. 92, 631–635.


