

CLATHRATE HYDRATES: FTIR SPECTROSCOPY FOR ASTROPHYSICAL REMOTE DETECTION

E. Dartois¹, M. Bouzit² and B. Schmitt²

Abstract. Inclusion compounds made of a water ice network, clathrate hydrates, are investigated by infrared spectroscopy. Because they can trap important “guest” volatiles species, they may influence the equilibrium, exchange and flux of volatiles in many bodies of the solar system. Their spectroscopic behaviour at low temperature (10–200 K) are shown and the search for their signatures by comparison to solar system objects remote spectra are discussed.

1 Introduction

Clathrate hydrates are made of a water-molecule connected network paving the three dimensional space, linked via hydrogen bonds. Guest molecules are encapsulated in the network cavities. Small molecules such as methane, carbon monoxide and dioxide, can be trapped in two crystallographic clathrate hydrate structures names type I and type II. The type I structure (see *e.g.* Sloan & Koh 2008) contains two dodecahedral water cages and six larger cages with two hexagonal faces per unit cell. In the type II structure the larger cage is bigger with twelve pentagonal and four hexagonal faces and there are sixteen small cages for eight large cages per unit cell. These ratios are important to decipher which structure is formed using spectroscopic measurements.

These clathrate hydrates 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 occurrence would thus modify the absolute and relative composition of astrophysical (icy) bodies as well as increase preservation timescales, or *e.g.* provide late time injection of gaseous species in planetary atmospheres.

¹ Institut d’Astrophysique Spatiale, UMR-8617, Université Paris-Sud, Bât. 121, 91405 Orsay, France

² Laboratoire de Planétologie de Grenoble, Bât. D de Physique, Domaine Universitaire, BP. 53, 38041 Grenoble Cedex 9, France

Many laboratory studies examined their thermodynamic or kinetic behaviour, but one way to confirm their presence in astrophysical bodies will come from remote infrared spectroscopy observations by telescopes or space probes. Methane CH_4 , carbon dioxide CO_2 and carbon monoxide CO clathrate crystals were produced in our laboratory, and the specific fingerprints betraying these clathrate hydrates presence recorded by infrared spectroscopy at relevant astrophysical temperatures (many previous spectroscopic experiments focused on *e.g.* Raman spectroscopy and/or neutron diffraction studies). In particular, we show that the trapped CH_4 molecules display a gaseous-like behaviour at low temperature in the water cages. Because the vibrational spectra recorded are unique to CH_4 , CO and CO_2 clathrate hydrates, they represent an identification pattern for low temperature astrophysical icy bodies, such as planets, comets and/or interstellar grains.

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 epiphenomenum for a widespread dominant crystal in astrophysics or a local state in a few objects.

2 Clathrate hydrate infrared spectroscopy

2.1 Experiments

Clathrate hydrates are prepared by injecting vapor phase water in a closed cell precooled at 240 K comprising two facing ZnSe windows. The guest gases are then injected, with a predefined molar abundance ratio, in large pressure excess, typically two or three times over the expected stability curve for the considered clathrate hydrate. After a long exposure of the water ice to high pressure of the guests, typically several days, the clathrate is formed and the cell temperature is lowered while the excess gas pressure is evacuated. The cell is maintained at a pressure and temperature above the estimated clathrate stability curve until about 140 K, where the gas is fully evacuated (final $P \leq 10^{-7}$ mbar) while pursuing the temperature descent to its minimum. This 140 K temperature is chosen because the kinetics at these temperature is slow enough that the clathrate hydrate is stable during the depressurization and high enough to evacuate the possible condensates of the guest gases at high pressure or ice layers formed by remaining impurities. Infrared spectra are therefore recorded in the $7000\text{--}650\text{ cm}^{-1}$ range, raising the temperature step by step from its minimum, until the declathration is observed.

2.2 Spectroscopic behaviour of clathrate hydrates

The clathrate hydrate family do present specific spectroscopic behaviours. The existence of two water cage environments implies that the encapsulated molecule will interact differently with the water molecules and, provided the guest fills both cages, different frequency shifts are expected (*e.g.* Schober *et al.* 2003). In addition, in some cages, the guest may be trapped in a local interaction minimum or

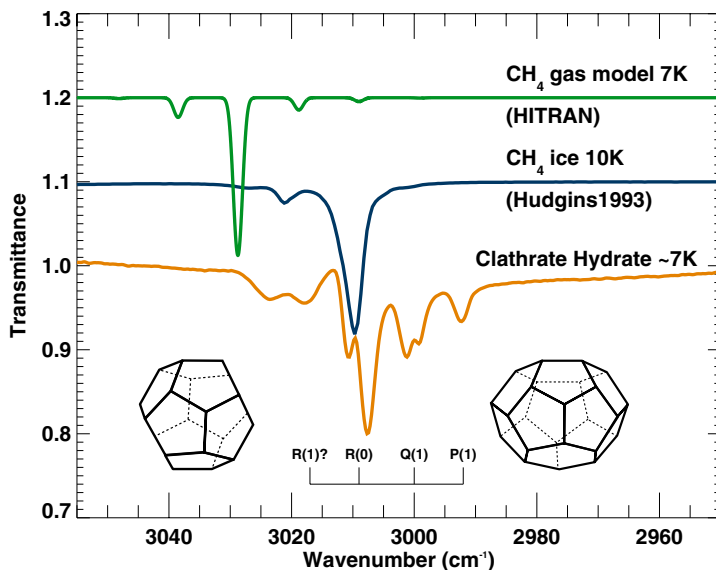


Fig. 1. Low temperature infrared spectrum of the methane CH stretching mode in its type I clathrate hydrate structure (bottom curve), compared to the pure methane ice phase (Hudgins *et al.* 1993) and CH₄ gas model. The band structure shows a rovibrational pattern shifted to lower frequency as compared to the isolated gas phase one, and two distinct cage environments, whose structure is shown close to the corresponding related absorption pattern. See Dartois *et al.* (2008) for details.

even bond to one face of the cage. As shown in Figure 1, at low temperature, CH₄ can rotate almost freely inside the large cage, giving rise to a rovibrational pattern (lower curve), shifted to lower frequency as compared to the one expected for gas phase pattern (upper curve). This pattern is unique and different from methane simple hydrate or pure ice absorption (middle curve) at the same temperature. At temperatures above 30 K, due to the rattling motions and CH₄ mobility, the pattern merges into a broad band, conserving the main interaction shift with the water cage. The occupancy of the cages can be followed experimentally using the relative filling of cages using tailored gas mixtures. In the case of CH₄, a non astrophysically relevant mixture such as CF₄/CH₄ can be used, the CF₄ molecule therefore competing for the filling of the large cages in the structure (*e.g.* Dartois *et al.* 2010).

If the clathrate hydrate family shares generic spectroscopic behaviour related to cages occupancy, each guest molecule must be treated independently, in particular following its chemical nature. Molecules such as CO₂ do occupy both cages in the structure I, but the elongated structure of this molecule hinders the rotation ability observed for methane. Therefore, a broad band associated to each cage environment is observed in the infrared spectrum. The CO molecule forms a type I clathrate structure whereas simple guest size estimates would favour a

type II clathrate hydrate, revealing interactions of this slightly polar molecule with its water network during clathrate formation. The observed cage vibrational shift with respect to pure CO ice is within 5 cm^{-1} . The temperature dependent wavenumber separation between the two encapsulated CO molecules vibrational transitions, in the two distinct type I clathrate cages is less than a wavenumber below 140 K. In addition, the dynamics of the CO molecules in its cage change considerably from 5 K to 140 K. At temperatures above 30 K, the molecule is extremely mobile in the cages, as revealed by the infrared profile, significantly different from CO entrapped in water ice.

3 Comparison with outer solar system spectra

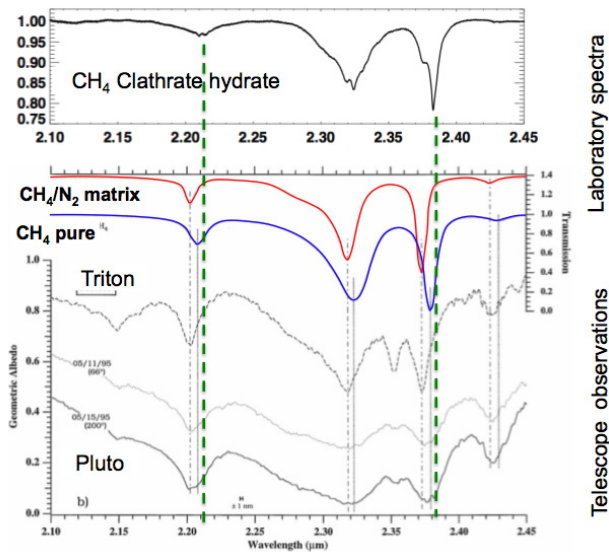


Fig. 2. Comparison of the near infrared spectrum a methane clathrate hydrate of structure I with spectra from the surface of Pluto and Triton as shown in Doute *et al.* (1999).

The specific fingerprints of guest molecules trapped in the clathrate hydrates provide a mean to search for them in remote spectra of solar system ice covered objects. At the surface temperature of Pluto, the methane clathrate hydrate maybe stable. However Pluto's methane transitions observed vibrational shifts are better explained by an effect of a N₂ ice matrix trapping the CH₄ molecules (Doute *et al.* 1999; Grundy *et al.* 2001), leading to a blue shift with respect to the ice position, whereas the clathrate hydrate gives rise to a red shift (see Fig. 2). The Neptune's moon Triton, probably a captured TNO, displays a similar behaviour involving a nitrogen matrix-shift (Cruikshank *et al.* 1993; Quirico *et al.* 1999; Grundy *et al.* 2004).

Outer solar system objects, falling in the thermodynamic stability zone for clathrate hydrates and displaying observed H₂O ice transitions, such as Charon,

Haumea, Orcus, do not display additional transitions related to a guest molecule with a significant strength to allow for a proper constraint on the presence of clathrate hydrate.

Closer to us, CO₂ and H₂O ices are seen in the south pole of Mars (*e.g.* OMEGA/Mars express, Bibring *et al.* 2004) at temperature and pressure close to the clathrate hydrate stability limit. However, the complex neighbouring or crossing of the carbon dioxide sublimation curve, adsorption on water ice, and clathrate hydrate stability curve in the p-T phase diagram makes the prediction purely on the basis of thermodynamics arguments improbable (*e.g.* Dartois & Schmitt 2009). In such a case, the spectroscopic expected band doubling or frequency shift of the bands are mandatory for an identification. In addition, Falenty *et al.* (2011), based on experimentally measured kinetics arguments predict that the formation of CO₂ clathrate hydrates on the Martian (sub) surface at the prevailing low winter temperatures is not possible, as the formation time exceeds by far this seasonal variation.

4 Summary, ongoing and future progress

The possibility to track the presence of clathrate hydrates using remote spectroscopy (teledetection) motivated our recording of near to mid-infrared CH₄, CO₂ and CO clathrate spectra in the 10–200 K range, adapted to the cold environments found in the solar system and beyond. Clathrate hydrate signatures of distinct cage host occupancies still await astrophysical detection whereas clathrate hydrates are predicted in models. The thermodynamics arguments (giving rise to stability curves) are often overused in solar system studies, as they represent necessary conditions but not the unique ones. In particular, the kinetics for their formation is overlooked, especially for outer objects (comets, TNOs) whose temperatures may prevent efficient formation timescale. This difficult aspect of the clathrate hydrate field for astrophysics should take an increasing importance in order to exploit laboratory experiments and drive models. Experiments to follow the low temperature kinetic formation of clathrate hydrates are on the way in our laboratory, based on the knowledge acquired during the spectroscopic measurements. Many other guests as well as mixtures are under spectroscopic investigation (either because they are astrophysically relevant or provide insight into the interactions taking place into the matrix) as well as work in progress with theoreticians. Our measurements clearly point out the specific band profiles and shift associated with guest molecules encapsulation into clathrate hydrate cages, showing that astrophysicists should endeavour to observe them remotely with spectroscopy. With respect to space exploration in the inner solar system, the stability of these compounds implies that they are expected to lie under the surface, and missions to explore the subsurface are in this case necessary.

References

- Bibring, J.-P., *et al.*, 2004, *Nature*, 428, 627
Cruikshank, D.P., Roush, T.L., Owen, T.C., *et al.*, 1993, *Science*, 261, 742

- Dartois, E., Deboffle, D., Bouzit, M., 2010, *A&A*, 514, A49
- Dartois, E., & Schmitt, B., 2009, *A&A*, 504, 869
- Dartois, E., & Deboffle, D., 2008, *A&A*, 490, L19
- Douté, S., Schmitt, B., Quirico, E., *et al.*, 1999, *Icarus*, 142, 421
- Falenty, A., Genov, G., Hansen, T.C., *et al.*, 2011, *J. Phys. Chem. C*, 115, 4022
- Grundy, W.M., & Young, L.A., 2004, *Icarus*, 172, 455
- Grundy, W.M., & Buie, M.W., 2001, *Icarus*, 153, 248
- Hudgins, D.M., Sandford, S.A., Allamandola, L.J., & Tielens, A.G.G.M., 1993, *ApJS*, 86, 713
- Quirico, E., Dout, S., Schmitt, B., *et al.*, 1999, *Icarus*, 139, 159
- Schober, H., Itoh, H., Klapproth, A., Chihaiia, V., & Kuhs, W.F., 2003, *Eur. Phys. J. E*, 12, 41
- Sloan, E.D., & Koh, C.A., 2008, *Clathrate Hydrates of Natural Gases*, 3rd ed. (CRC Press, Taylor & Francis Group, Boca Raton)