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In situ IR reflectance spectroscopy of clathrate hydrates at low and moderate pressures: application to icy moons

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Abstract

Using infrared spectroscopy the carbon dioxide clathrate hydrates have been analyzed under different pressure and temperature conditions. The IR reflectance spectra of this compound are obtained at low pressure and low temperature conditions relevant to icy moons' surfaces. The clathrate hydrates stability and their storage capacity (cages occupancies) under moderate to high pressures relevant to icy moons shells are also investigated.

1. Scientific context

Clathrate hydrates are non-stoichiometric inclusion compounds, with a hydrogen bonded water ice network forming cages in which gas molecules can be trapped. The gas presence stabilizes the icy structure that can contain up to 15 mole % gas [1]. These compounds are largely found on Earth. So far, they have not been detected in astrophysical environments, but it has been proposed that clathrate hydrates could also play a significant role in the chemistry of the solar nebula and in the physical evolution of astrophysical objects [2]. The most common gases that form clathrate in a planetary context are CO_2, CH_4, N_2, C_2H_6. The focus of the present study, is CO_2, which has been observed on many astrophysical objects, including Mars, comets and icy moons (in particular on Enceladus, Phoebe, Iapetus, Titan, Europa, Callisto [3]). On icy moons, the origin of CO_2 as well as the way it is incorporated in icy surface remains controversial. Trapped CO_2 has been identified on several moons [4, 5, 6, 7]. CO_2 is often correlated with dark terrains, however, it is unclear if CO_2 is trapped in H_2O ice or in some mineral or complex organic compound [7]. The source of CO_2 may be internal, or possibly CO_2 is produced by some radiolytic processes at the surface [6]. If CO_2 comes from the interior, it is likely to be stored in the form of clathrate hydrates [8]. Although these structures are a powerful way to store CO_2 in icy bodies, their stability and their storage capacity (cage occupancies) under moderate to high pressures is still poorly understood.

In this context, our research group conducts laboratory studies to provide new experimental data on the stability and storage capacities of CO_2 clathrate hydrates under temperature and pressure conditions relevant to icy moons. The experimental data on the dissociation curve and the cage occupancies will be used to constrain a thermodynamic model that is under current development in our research group [9]. A second objective is to produce reflectance spectra of the carbon dioxide clathrate hydrates which may be used for the characterization of these compounds on icy surfaces. To our knowledge, thin cryogenic CO_2 clathrate films prepared at low temperature and low (or high) pressure have been studied only with the IR transmission spectroscopy [10, 11] and by attenuated total reflection spectroscopy [12]. In this work we investigate experimentally the spectral reflectance signature of carbon dioxide clathrate hydrate.

2. Experimental study

2.1 In situ IR spectra of clathrate hydrates at low pressure

We have developed an experimental spectroscopic method to analyze clathrate hydrates which also permits to characterize the structure and the guest composition of these compounds under different conditions of temperature and pressure. The CO_2 clathrate hydrates are obtained using a high pressure autoclave, where a thin film of ice (~100 µm), formed on a copper surface, is pressurized with gaseous carbon dioxide for approximately three days at T = 256 K and P = 20 bars. The sample is transferred into a low temperature and low pressure experimental set-up and analyzed using a Fourier Transform-Infrared spectrometer at 100 K in primary vacuum (~10^{-5} bar). The formation of the CO_2 clathrate hydrate is identified in the reflectance spectra by the band at ~2.7 µm and the double bands at ~ 4.26 µm. The presence of two distinct bands in the antisymmetric stretching region indicates that CO_2 is trapped in both large and small cages. The integration of the band areas can be used in order to obtain the hydrate guest composition. The working pressure being so low, with this experimental set-up we obtain a clathrate hydrate structure, which possesses a low proportion of gas trapped within the cages. Infrared characteristics of these low pressure clathrate hydrates will be presented.

2.2 In situ IR spectra of clathrates hydrates at moderate pressure

For the study of thin CO_2 clathrate hydrate films under high pressures, a large volume cell has been preferred. Samples are pressurized hydraulically with a capstan pump. This experimental set-up permits the study of a clathrate hydrate film in a pressure range of 1-300 MPa and at temperatures between 240 and 310 K. The temperature is controlled using Peltier elements coupled with a Lauda chiller maintained at 278 K. The top and bottom faces of the high-pressure cell are equipped with sapphire windows, which provide optical access to the sample. Clathrates are synthesized in a high pressure autoclave, and transferred into this set-up. IR in situ measurements are acquired with the FT-IR spectrometer. Preliminary results obtained with this experimental set-up on the stability and filling properties of CO_2 clathrate hydrates under high pressure conditions will be presented during the meeting.

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