



Clathrate hydrate of carbon dioxide above 0.2 GPa: new experimental results and theoretical developments

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Abstract

New diamond anvil cell experiments were carried out to explore the stability of the CO₂ sI clathrate hydrate. Our results support the existence of a “high-pressure” structure above 0.6~0.8 GPa and provide the first Raman analysis for this new phase. Ongoing experiments in the H₂O-CO₂ system are performed to constrain the carbon dioxide solubility in water above 0.2 GPa. These results will help to improve the thermodynamic model of aqueous solutions developed in Nantes.

1. Introduction

Clathrate hydrates are compounds of major interest in the study of the icy satellites of the outer solar system. Existing experimental data indicate that compounds of many gas, including carbon dioxide, are stable in icy moon interiors [e.g. 2]. Although we have no direct evidence as to which clathrate hydrates forming volatiles may be present inside these bodies, the relative abundance of carbon dioxide in comets suggest this species is a major volatile in icy moons. So far, carbon dioxide has been identified on the surface of icy satellites of the four giant planets [4 and references therein], though its state on these surfaces remains unclear, not to speak of the mechanisms that led to its presence.

In spite of its planetological interest, the H₂O-CO₂ binary is still poorly known, especially at pressures above 0.2 GPa relevant to the largest icy moons. Regarding experimental data, the existence of a new phase above 0.6 GPa and below 270 K was not reported until very recently [6]. As for the theoretical approach, no existing model is intended to describe the behavior of CO₂ clathrate hydrate beyond 0.2 GPa, the main reason being that no data are available beyond this pressure to constrain the solubility nor the fugacity of carbon dioxide in water.

This work aims to: (1) present new data on the stability of the known CO₂ sI clathrate hydrate and the new “high-pressure” phase, (2) give new constraints on the solubility of carbon dioxide in water at high pressures, and (3) use these experimental data to improve thermodynamic modeling of aqueous solutions under elevated pressure.

2. New stability data

New data on the stability of the CO₂ sI clathrate hydrate have been acquired. Experiments were carried out in a diamond anvil cell with temperatures ranging from 252 to 282 K and pressures up to 2 GPa. Visual observations and Raman spectroscopy allowed for continuous follow-up and precise determination of the present phases. While exploring the known sI structure phase domain to determine its upper pressure limit, experiments led to the synthesis of another “high-pressure” phase, as reported recently [6]. Our current results agree well with this previous work, except for the reported stability of this new phase below 260 K, which has not been reproduced in our experiments so far (fig. 1).

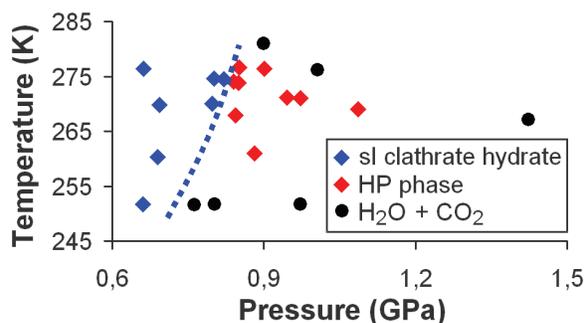


Figure 1: sI clathrate hydrate and “high-pressure” phase stability. The blue dotted line is a proposed high-pressure stability limit for the sI structure.

Experiments were performed along isothermal profiles between 252 and 276 K. Results regarding the stability of the known sI structure clathrate hydrate agree with previous study, with a pressure stability limit decreasing from 0.8 GPa at 276 K to 0.7~0.75 GPa at 252 K. Above these pressures, the sI structure changes into a new “high-pressure” phase with significantly different Raman signatures (fig. 2).

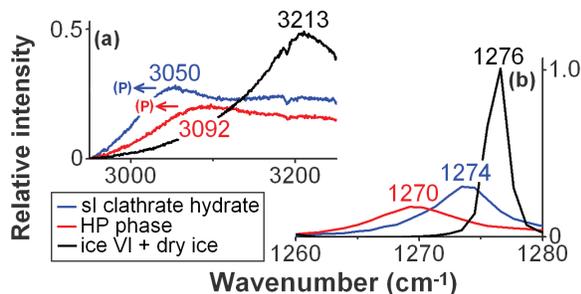


Figure 2: Raman signatures near 0.8 GPa for the H₂O lattice (a) and the CO₂ (b). Dry ice signature at 1276 cm⁻¹ is halved. Intensity is set relatively to this signal. Arrows show the shift trend with increasing pressure.

The distinctive clathrate lattice signatures near 200 cm⁻¹ and 3100 cm⁻¹ exhibit strong evidences for a phase transition. With increasing pressure, the ~3100 cm⁻¹ O-H intramolecular vibrations signature shifts towards lower wavenumbers (fig. 2.a) while the ~200 cm⁻¹ O-O intermolecular vibrations signature displays an opposite trend. At phase transition, both signatures jump back to their “lower pressure position”, thus opposing the pressure tendency. The CO₂ signature near 1270 cm⁻¹ seems to be sensitive to the phase in presence as well, with distinct bands positions at similar pressure (fig. 2.b). Dissociation of the new “high-pressure” phase is observed in P,T ranges similar to previous studies [6]. It is dissociated into liquid water and dry ice above 280 K near 0.8 GPa, and to dry ice and ice VI beyond 1GPa at lower temperatures. However, our current results do not support the stability of the new phase below 260 K [6]. Both isothermal profile at 252 K and cooling of the new phase from higher temperature synthesis led to the formation of dry ice and ice VI. Experiments are ongoing to support these first results and try to understand this discrepancy with previous works.

3. Modeling above 0.2 GPa

All current models describing the CO₂ clathrate hydrate stability are limited to the known sI structure,

below 0.2 GPa [e.g. 1]. As clathrate hydrates are non-stoichiometric compounds, these models first calculate an empty water lattice potential before adding an activity coefficient from the cages occupancies. This late term is directly related to the fugacity of the guest gas filling the lattice. To this day, no data were acquired in the H₂O-CO₂ system beyond 0.35 GPa in the low-temperature region relevant to the two phases of interest in this study, and to the icy moons interiors in general [5].

Experiments are being conducted in the H₂O-CO₂ system to bring new constraints in the higher pressure region. As the solubility of carbon dioxide in water at lower pressures may reach a few percents [5], we aim to use the H₂O solidus temperature depletion in presence of carbon dioxide to estimate the solubility of this gas. In the mean time, clathrate hydrate modeling is being implemented in the thermodynamic model previously developed to describe phase equilibrium in the H₂O-NH₃ [3]. The aim is to provide equilibrium calculation in aqueous solutions in pressure and temperature ranges relevant to the mantles of icy satellites. Preliminary results will be presented.

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