EPSC Abstracts
Vol. 10, EPSC2015-849, 2015
European Planetary Science Congress 2015

Study of high pressure carbon dioxide clathrates hydrates on Ganymede

F. Izquierdo-Ruiz (1, 2), A. S. J. Méndez (2), O. Prieto-Ballesteros (2) and J. M. Recio (1)
(1) Dept. de Química Física y Analítica, Univ. Oviedo, Spain, (2) Centro de Astrobiología, INTA-CSIC, Spain
(fizquierdo@cab.inta-csic.es)

Abstract

We present a combined experimental and theoretical investigation of carbon dioxide clathrate hydrates at high pressure. Experimental studies are carried out using several high pressure chambers reaching pressures up to 1 GPa. Using finite cluster and periodic models, we perform computer simulations under the density functional theory approximation that complement and provide a microscopic interpretation of these experiments, thus improving our knowledge of icy satellites such as Ganymede.

1. Introduction

Gas clathrate hydrates are thought to be relevant in the geological evolution and activity of several Solar System bodies where the appropriate conditions of high pressure and low temperature are achieved. Relevant examples of these bodies are the icy moons of the giant planets, in which gas hydrates have been proposed as significant constituents of their icy crusts and water rich reservoirs [1].

Carbon dioxide ice has been detected in the surface of the icy moons of Jupiter, and is supposedly originated by internal degasification. [2-5] Inside of these moons pressure can rise up to 1.3 GPa, as in the case of Ganymede. [6] Prompted by the limited available data and the current interest on the behavior of CO_2 hydrates at high pressure, a combination of new experiments and simulations of this system at different thermodynamic conditions is proposed.

2. Gas clathrate structures

There are several gas clathrate crystallographic structures. All of them have in common that they are composed by a network of water molecules connected via hydrogen bonds following the ice rules, and usually enclosing nonpolar gas molecules showing guest-host van der Waals interactions.

Among all the possible structures, we will focus on the ones commonly related with the carbon dioxide clathrate hydrates. These are of two types: (i) with cages or polyhedral as in the cubic sI and sII, and in the hexagonal sH structures, and (ii) with channels instead of cages, as in the orthorhombic Filled Ice Structure (FIS). The polyhedra forming these clathrates are labeled as following: 5^{12}, which are present in the sI, sII and sH structures; $6^2 5^{12}$, which are in the sI structure; $6^4 5^{12}$, in the sII structure; and $6^8 5^{12}$ and $4^3 5^6 6^3$, both in the sH structure. In this notation, A^b means that b faces of A vertices can be found in the surface of the cage.

A common reference on the behavior of gas clathrate hydrates at high pressure is the review of Loveday and Nelmes. [7] Unfortunately, information on carbon dioxide clathrates is not included in that work. The reason might be the lack of interesting results on this system at the time when the review was written. More recently, several studies have appeared, helping to understand a little more the behavior of carbon dioxide-water mixtures at high pressure using XRD and Raman spectroscopy. [8-11] These studies inform of a phase transition from the sI clathrate phase to the FIS structure at 0.7 GPa followed by decomposition of this new phase above 1.0 GPa.

3. Methodology

3.1 Experimental

High pressure experiments are carried out in a new design chamber, called VHPPC (very high pressure planetological chamber). It is able to reach 1 GPa, and temperatures down to 180 K. This chamber has a sapphire window that allows monitoring the system via Raman spectroscopy. A specific Raman head probe is built for spectroscopy analysis inside

VHPPC. The chamber is attached to a high pressure pump that uses a pressure intensifier to reach the required high pressures of Ganymede's interior. To control the temperature we employ a thermostatic bath introducing silicon oil as thermostating liquid. Pressure is measured directly *in situ* inside the chamber using a high pressure manometer, while temperature is measured indirectly as close as possible to the sample (See Figure 1). In addition to these experiments, Sapphire Anvil Cell (SAC) experiments are being also designed.

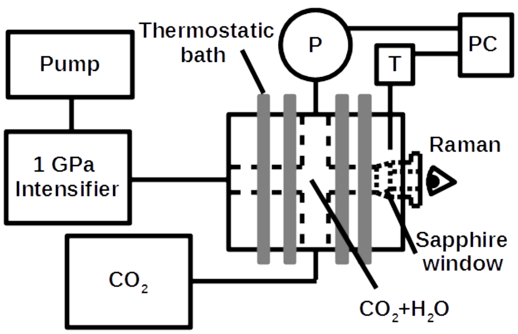

Figure 1: Scheme of experimental setup.

We start forming sI CO_2 clathrates from liquid water saturated with CO_2 gas. Once they form, the system is pressurized up to 1 GPa.

3.2 Theoretical

Density functional theory (DFT) first-principles calculations are also performed to describe the structures and behavior of the carbon dioxide-water system under hydrostatic pressure conditions. Obtaining the equation of state (EOS), energetic stability and infrared and Raman spectrum are the main objectives of these calculations. These properties help to analyze the experimental results. A detailed study of guest-host interactions is also underway. Quantum Espresso, [12] Gibbs2 [13] and Gaussian09 [14] are the main codes used to obtain these properties.

4. Summary

High pressure behavior of carbon dioxide-water mixtures, at 180-280 K and 0-1 GPa conditions, is studied combining both experimental and theoretical approaches using a new VHPPC that can reach the GPa regime for experiments and first-principles DFT finite and periodic simulations.

Acknowledgements

Thanks are due to financial support from Spanish MINECO under projects CTQ2012-38599-C02-01, Quimapress (S2009/PPQ-1551) and Spanish Consolider-Ingenio 2010 program under project CSD2007-00045. FIR thanks Principado de Asturias FICYT and FPU program from MECD for a PhD grant.

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