Carbon Dioxide Clathrate Hydrate Study under Ganymede Conditions

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Introdution: Gas clathrate hydrates are proposed as constituents of the icy moons of the giant planets in the Solar System [1].
Carbon dioxide has been detected on the surface of the moons of Jupiter, supposedly originated by internal degasification [2-5]. In Ganymede, an aqueous ocean is proposed to exist under a thick ice crust in coexistence with several forms of ice, with pressure reaching up to 1.3 GPa [6].
Due to the limited available data on these systems under these conditions, we propose a combination of computational and experimental studies to describe microscopically and macroscopically its mechanical, chemical and energetic properties. This will allow us to understand how their presence affect the geophysical structure and activity and its impact on the habitability of the icy moon.

Structures: Clathrates hydrates are composed by a lattice of water molecules (guest), bonded by hydrogen bonds, that forms cages, and a host molecule that occupies those cages. Depending on the host molecule and the conditions the hydrates can take several structures [7]. We will focus on the two structures related with the carbon dioxide, the cubic sI and the FIS (Filled Ice Structure), a picture of both structures can be found below.

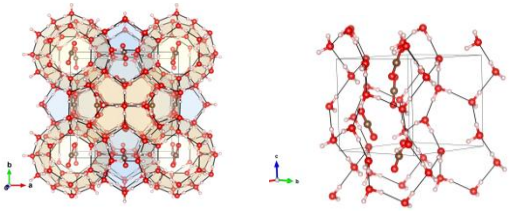

Fig. 1. *FIS (*

The sI unit cell is formed by 46 water molecules that can host up to 8 CO_2 molecules in 2 different type of cages ($6^2 5^{12}$ and 5^{12}) [7]. The FIS structure has not yet been clearly determined, although there have been some propositions as the type MH-III by Tulk [8]. We will use the alternatively proposed (but not yet published) C0 structure of the hydrogen hydrates. This structure has 6 water molecules and 3 CO_2 molecules in a unit cell.

Methodology: Density functional theory (DFT) in periodic boundary conditions calculations are performed to describe the behavior of the system under hydrostatic pressures. We obtain the equation of state (EOS), energetic stability, intermolecular interactions and vibrational frequencies. The codes Quantum Espresso, Gibbs2 and Critic2 are being used.
High pressure experiments are being done in a newly designed chamber, called VHPPC (very high pressure planetological chamber), able to reach 1 GPa. It is equipped with a sapphire window to allow the measurements of Raman spectra. In Figure 2 we can find a diagram of the experimental setup.

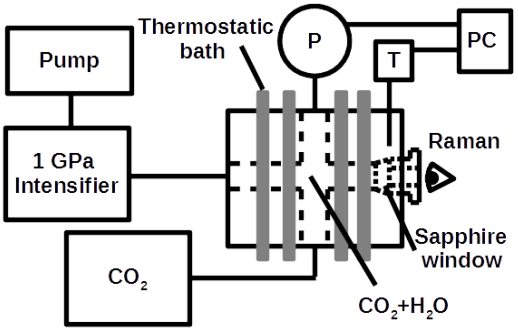

Fig. 2. *VHPPC setup.*

References:
[1] Buffet B. A., *Ann. Rev. Earth Plan. Sci. 28*, 477, 2010. [2] Dalton, J.B. *Space Sci. Rev. 153*, 219, 2010. [3] Waite Jr., J.H. et al. *Nature 460*, 487, 2009. [4] Niemann, H.B. et al. *J. Geophys. Res. 115*, E12006, 2010 [5] Mousis, O. et al. *Astron. Astrophys. 448*, 771, 2006. [6] Bland, M.T. et al. *Icarus 200*, 207, 2009. [7] Sloan E. D., Koh C. A., *Clathrate hydrates of natural gases*, *CRC Press*, 2008. [8] Tulk, C.A. et al. *J. Chem. Phys. 141*, 174503, 2014

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