CO clathrate hydrate stability with pressure : a DFT approach

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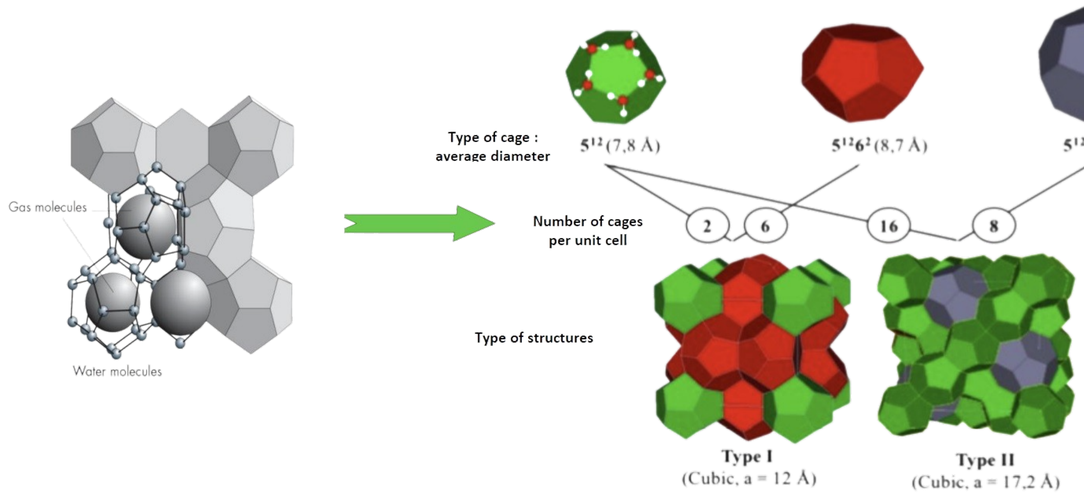
Abstract

The solid state of water, exists in several structures according to pressure and temperature conditions. One of the most interesting forms is called **clathrate hydrate**, which can trap various gas molecules [1,2]. These clathrate hydrates can have different structures, different properties and many applications in the industry. In this lab work I will study the stability with pressure of CO gas hydrate for two different structures[3]. In order to do that, I will use **VASP** a powerful software that perform quantum dynamics calculations based on the Density Functional theory called more commonly **DFT** [4].

Clathrate hydrates

Clathrate hydrates can be crystallized with different structures made of various cages composed of water molecules and stabilized by the guest molecules trapped inside.
CO clathrates are formed with **sI and sII structures**:

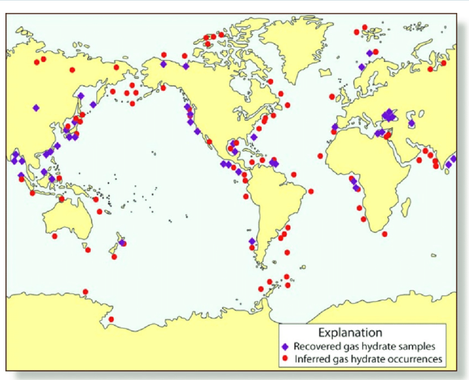


from hydrate.eu/hydrate.html

Application

Clathrate hydrates were discovered in **1810 by Humphry davy** and nowadays they have many applications :

- they can be a **huge quantity of potential energy** because we have $10^{17}m^3$ of CH_4 on earth.
- they can form **sealing in pipelines** we can reduce that by studying they conditions of formation.



Location of sampled and inferred gas hydrate occurrences worldwide. (Map courtesy of Timothy S. Collett, USGS)

Theory and future work

1. Theory

Clathrate stability and dynamics are governed by **Density Functional Theory**. This theory can resolve the Schrödinger's equation to obtain electronic structure of atom and molecules. The Schrödinger's equation for electrons is:

$$H\Psi = \left[-\sum_i^N \frac{\hbar^2}{2m}\nabla_i^2 - \sum_{i,I} \frac{Z_I e^2}{|\vec{r}_i - \vec{R}_I|} + \sum_{i<j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \right] \Psi = E\Psi$$

With N electrons indexed i and j, and nuclei indexed I.
The DFT resolves this equation by taking into account the functional electronic density and reducing it to a minimum:

$$E[n] = T_e[n] + V_{en}[n] + V_{ee}[n]$$

There are numerous softwares which implement DFT, in our work we will use **VASP**.

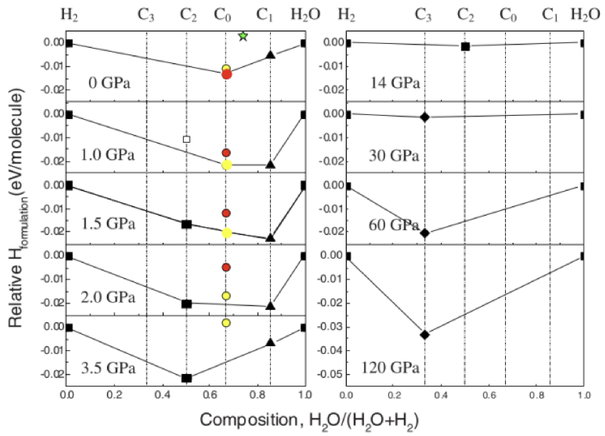
2. VASP

VASP stands for **Vienna Ab initio Simulation Package** I will use it because :

- DFT is implemented
- well adapted to periodic systems
- allows to perform structural relaxation

3. Future work

The main objective of my project is to study the stability of both structures sI and sII of CO clathrate. To deal with this issue, I will build a convex hull diagram that represent the enthalpy in function of clathrate compositions :



convex hull for H_2 /H_2O system (Dong et al. Sci. Rep. 4 (2014) 1-5)

References

[1] Sloan, E. D. and Koh, C. A., Clathrate Hydrates of Natural Gases, 3rd ed. (Taylor Francis-CRC Press, Boca Raton, FL, 2008).
[2] Broseta, D., Ruffine, L., and Desmedt, A. (Eds.), Gas Hydrates 1: Fundamentals, Characterization and Modeling (Wiley-ISTE, London, UK, 2017).
[3] Petuya, C., Damay, F., Talaga, D., and Desmedt, A., "Guest partitioning in carbon monoxide by Raman spectroscopy," J. Phys. Chem. C 121, 13798–13802(2017).
[4] Kresse, G. and Furthmuller, J., "Efficient of ab initio total energy calculations for metals and semi-conductors using plane-wave basis set," Comput. Mater. Sci.6, 15–50 (1996a).