CO clathrate hydrate stability with pressure : a DFT approach

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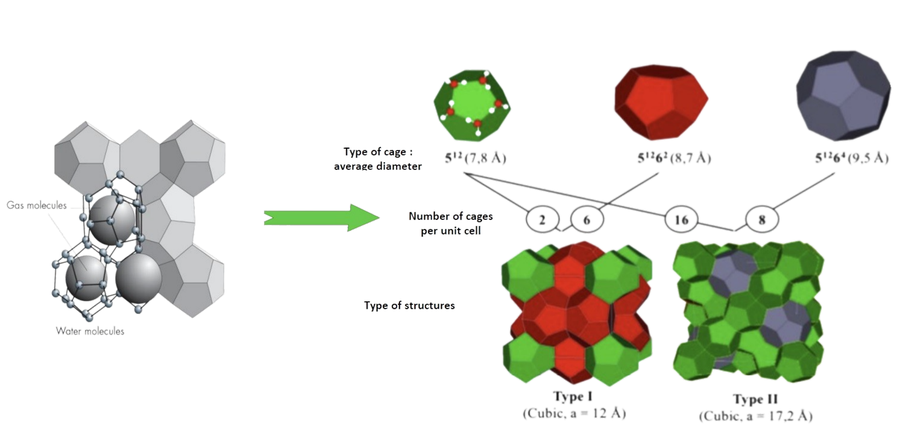
Abstract

After one hundred years to study the solid state of water, we still find another structure under specific conditions of pressure and temperature. One of the most interesting form is called clathrate hydrate, this state of ice can trap some or just one molecule of gas of different nature. Theses clathrathes hydrates can have many different structures and have different properties and have many applications in industry. The CO-clathrate is an ice structure around carbon monoxide, in this lab work i have to study the stability with pressure for carbon monoxide for two different structures. 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.

Clathrhate hydrates

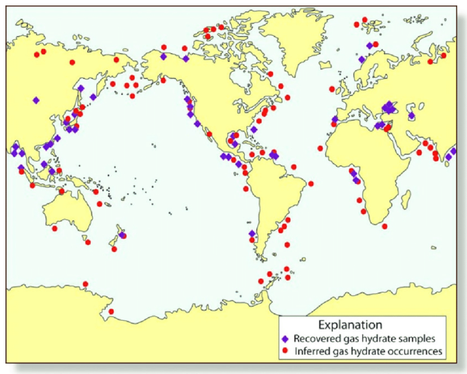
Clathrates hydrates can be stable with different structures their are for with 2-dimension planar elements, more precisely with tetrahedral network of water molecules and a guest molecules trap inside. They are different type of cage, the most important are : $5^{12}, 5^{12}6^2, 5^{12}6^4, 5^{12}6^8, 4^3 5^{16} 6^3$
They cage form unit cell and a type of structure with different average diameter respectively on their composition of type of cages.
The CO-clathrate is form with sI and sII structures :



Clathrates structures from Ludovic's Martin-Gondre lectures

Application

On earth clathrate can be found in ocean and in permafrost because these environment have the necessary condition of temperature and pressure.
The discovery of clathrates hydrates was in 1810 by Humphry Davy ,since this the industry was very interest by they application in many domain for example : in energy field because the most important clathrate on earth is methane hydrate (CH_4) and this is a huge quantity of potential energy, in pipeline for different reasons we have high pressure and high temperature and theses conditions favoring the formation of clathrate forming sealing in pipeline with a risk of explosion.



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

Theory and future work

1. Theory

The stability and the dynamics of clathrates is perform with the Density Functional Theory, this theory can resolve the Schrödinger's equation to electronic structure for a atom or molecules. Unfortunately this equation has no analytical solution, the approximation of born Oppenheimer approximate the previous equation to :

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

The DFT solve this equation by considering electronic density functional and minimize it :

$$E[n(\vec{r})]\,(E[n(r)] = \langle \psi \,|T_e + V_{ee} + V_{ext}|\, \psi \rangle\rangle$$

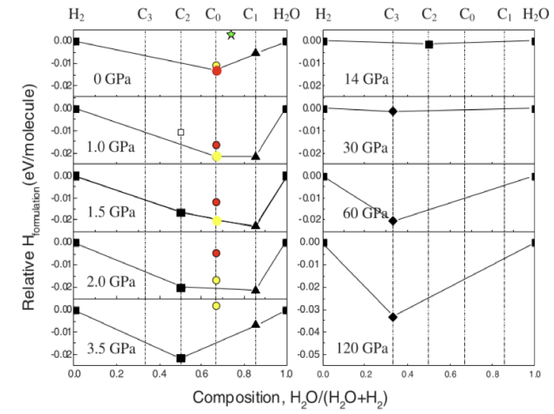
There exist many algorithm that implement the DFT, for our work we will use VASP

2. VASP

VASP the acronym for Vienna Ab initio Simulation Package that perform many calculation on complex system. This name means without experimental result but this appellation controversial because the DFT contains some formula that are unknown and this formula are approximate or obtained with experimental result. I will use this software to do Structure relaxation to minimize the electronic density functional.

3. Future work

The study of this CO-hydrate will be perform for two structure sI and SII or for two different exchange–correlation functionals. The structure relaxation calculus take long time to finish, so we have to study the phenomenon to provides consistent computation and get data to analyse. The stability of the clathrate will be characterized by the minimisation of energy functional. I can present this with Convex Hull graph that represent the Gibbs free energy $G = H - TS + uN$(in our case the study will be at $T = 0K$ to get the stability on pressure without influence this by the temperature) on Y-axis and the clathrate's composition on X-axis in percent(we will study a whole system of CO-hydrates not just one for each simulation and this hydrate can take two molecules of CO in a cage)



convex hull for H2 /H2O system (Dong et al. Sci. Rep. 4 (2014) 1-5)

references