CO clathrate hydrate stability with pressure : a DFT approach

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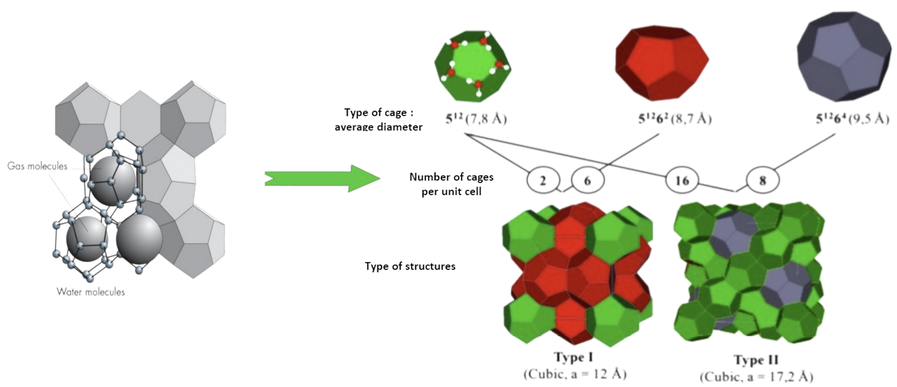
Abstract

After hundreds of years of studying the solid state of the water, we find yet another structure in specific pressure and temperature conditions. One of the more interesting forms is called **clathrate hydrate**, which can trap a molecule of gas of a different nature. These clathrates hydrates can have many different structures, different properties and many applications in the industry. The CO-clathrate is an ice structure around carbon monoxide, in this lab work i have to study the stability with pressure of 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

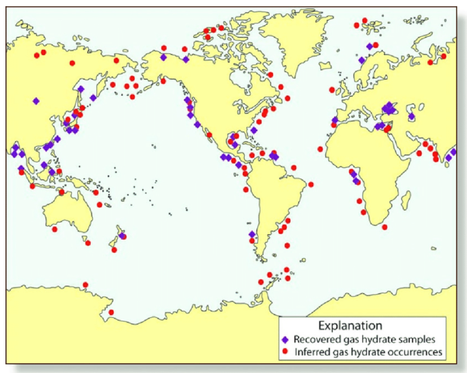
Clathrates hydrates can be stable with different structures made with 2-dimensional planar elements, more precisely with a many tetrahedral network of water molecules and a guest molecule trap inside. They are different type of cage, the most important are: $5^{12}, 5^{12}6^2, 5^{12}6^4, 5^{12}6^8, 4^3 5^{16} 6^3$
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 formed with **sI and sII structures**:



Clathrates structures from Mr. Martin-Gondre lectures

Application

On earth clathrate can be found in the ocean and in permafrost because these environments have the necessary conditions of temperature and pressure.
The discovery of clathrates hydrates was in **1810** by Humphry Davy, since this the industry was very interested by their application in many domains for example: - in the energy field because the most important clathrate on earth is methane hydrate (CH_4) and this is a **huge quantity of potential energy**. - in transport field pipelines can have conditions favoring the formation of clathrate forming sealing in a pipeline with a risk of explosion its interesting to study them to disfavoured their 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 performing with the **Density Functional Theory**, this theory can resolve the Schrödinger's equation to electronic structure of an atom or molecules. Unfortunately, this equation has no analytical solution, the approximation of born Oppenheimer approximates 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 resolves this equation by taking into account the functional electronic density and reducing it to a minimum:

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

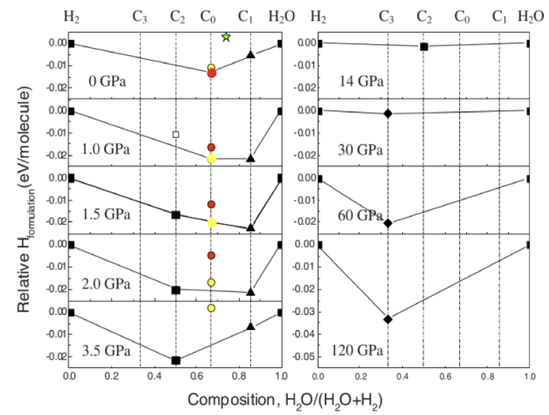
There are numerous algorithms which implement DFT, in our work we will use **VASP**.

2. VASP

VASP stands for **Vienna Ab initio Simulation Package** which performs numerous computations on complex systems. This name means without experimental results, but this designation is controversial because the DFT contains an unknown formula and this formula is approached or achieved with experimental results. I am going to use this software to perform structure relaxation computation in order to minimize the functional electronic density.

3. Future work

The study of this CO-hydrate will be performed for two structure sI and SII or for two different **exchange–correlation functional**. The structural relaxation calculation takes a lot of computation time, so we need to study the phenomenon to provide a coherent calculation and get data to analyze. 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

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$Convex hull for N2, clathrate hydrates, from first - principles calculations$