Guest-Host Interactions in Gas Clathrate Hydrates Under Pressure

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First-principles calculations were performed to determine equilibrium geometries, static equation of state parameters, the energetics and orientation of the guest molecule inside the 5^{12} and $5^{12}6^2$ cages, and vibrational frequencies of methane clathrate hydrate. According to our results, the progressive inclusion of one CH_4 molecule in each clathrate cavity is always a stabilizing process up to saturation, being the released energy very similar for both types of cages. In agreement with the experimental observation of roto-vibrational spectra in this hydrate, we calculate an energy barrier for methane to freely rotate inside the cages of less than 0.5 kcal/mol. The stabilizing effect of applied pressure leads to a red shift of the O-H stretching frequencies of the water molecules of around 80 cm^{-1} at 1 GPa.

Keywords: methane clathrate hydrate; DFT calculations; eos; vibrational modes.

1.   Introduction

Gas clathrate hydrates have oustanding implications in diverse knowledge areas such as planetology, origin of life or the exploitation of natural resources. Although gas clathrate hydrates have not been detected out of our planet, it is well-known that the appropriate conditions for their presence are achieved in different planetary environments along the Solar system. For example, clathrate hydrates are proposed as constituents of the frozen crusts and water deep reservoirs in the moons of the giant planets of our Solar system [1] and, specifically, methane clathrate hydrates as the source for the methane component of Titan atmosphere. Experimental and theoretical investigations have been focussed on the structural characterization of these systems, the energetics of their formation or the analysis of their Raman and infrared spectra (see Refs. [2–4] and references therein). In all these cases, computational simulations constitute valuable tools to recreate conditions and to interpret experimental data in terms of microscopic interactions.

The modelling of water, both in static DFT calculations and in molecular dynamics, is a challenge of the first magnitude and currently a subject of intense research. In the last few years it has been shown that the exchange-hole dipole moment (XDM) model, proposed by Becke and Johnson [5], provides accurate intermolecular interaction energies, thus making this methodology an adequate choice to study gas clathrate hydrates. In

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this contibution, DFT+XDM computational tools are used to investigate the response of the low pressure sI cubic phase of methane clathrate hydrate, $CH_4@sI$ for short, to hydrostatic pressure (p) up to 1 GPa. Specifically, structural data, energetics involved in the cage saturation, equation of state parameters and vibrational frequencies of the guest and water molecules are discussed.

2.   Computational aspects

The cubic spatial group $Pm\bar{3}n$ (223) reported by Loveday [6] for the sI phase was chosen as the starting structure in our optimizations. The unit cell has 46 molecules of water that form eight cages. Two of these cages are formed by pentagonal faces (5^{12}) that make a stretched dodecahedron. We call them pentagonal or P cages. The other six cages are hexagonal truncated trapezohedrons, or tetrakaidecahedrons ($5^{12}6^2$). We call them hexagonal or H cages. The carbon atom of the guest gas molecule CH_4 is situated at the centers of these cages [6]. It is important to note that, either in the experiments (where hydrogen atoms do not have specific coordinates) or in the simulations (hydrogen atoms are unequivocally localized and the symmetry can be lowered down to the triclinic $P1$ space group), it is mainly the oxygen sub-lattice which supports the clathrate network.

Our simulations follow DFT methodologies under the static approximation using cluster and periodic models. We performed cluster calculations using the aug-cc-pVDZ basis set of Dunning *et al.* [7] implemented in the `Gaussian09` code [8]. These calculations were carried out using the B3LYP [9] and the PW86PBE [10] functionals. Care must be taken to correct for basis set incompletenes (BSSE) in the calculation of binding energies. In order to account for BSSE, we have employed the traditional counterpoise method [11], proposed by Boys and Bernardi. Non-covalent interactions, such as those arising in clathrate hydrates, are not well described by common density functionals. In this work, we employ the exchange-hole dipole moment (XDM) model [5] to add a dispersion energy correction to the electronic energy calculated using B3LYP or PW86PBE functionals.

Regarding periodic calculations, we have used the projector augmented wave all-electron description of the electron-ion-core interaction [12], the exchange-correlation functional was PW86PBE, and the dispersion interactions were accounted for by the XDM model. In a recent study, it has shown that this election works quiet well for non-equilibrium geometries [13]. The XDM parameters were obtained from [5]: $a1=0.136$ and $a2=3.178$ Å. The plane wave energy cutoff was selected to 60 Ry (checking that the total energy is converged at that value) and the reciprocal space was divided into a Monkhorst-Pack [14] grid of $2\times2\times2$ points. The convergence threshold for the SCF procedure was set to 10^{-8} Ry. Geometry optimization was performed using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) [15] algorithm included in the `Quantum Espresso` package [16], relaxing lattice parameters and all crystallographic positions.

3.   Results

3.1.   *Structure and energetics*

We have carried out two different geometrical optimizations of the unit cell in the empty (sI) and $CH_4@sI$ lattices. Notice that all the cavities are occupied with the guest molecule in the last system. In the first one, all the degrees of freedom are relaxed without any restriction for the space group (triclinic, $P1$). These calculations are very expensive in terms of computational time and provide us with the equilibrium geometry of the two clathrate systems at zero pressure. In Table 1, we collect the lattice and angle

Table 1.   Cell parameters for sI and $CH_4@sI$. Å and degrees are used.

Parameter	a	b	c	α	β	γ	Volume
sI	11.665	11.650	11.646	89.90	89.83	89.92	1582.72
$CH_4@sI$	11.646	11.657	11.633	89.87	89.83	89.94	1579.32

parameters of the unit cell obtained from these calculations. The average lattice parameter does not deviate noticeably from the specific a, b and c values for each structure. In all cases the lattice angles are very close to 90 degrees. Notice that the cell parameters in the two systems are very close between them, being slightly larger in the empty clathrate. The carbon atom of the guest molecules lays at the center of each cage.

In the second type of calculations, we carried out optimizations of the atomic positions at different volumes assuming a cubic unit cell. These results will be discussed later regarding pressure effects. Here we show the zero pressure lattice parameter and equilibrium volume (in brackets) for empty sI and $CH_4@sI$, respectively: 11.673 Å (1590.55 Å^3) and 11.663 Å (1586.47 Å^3). We omit the optimized oxygen and hydrogen atomic coordinates that show very similar values to the ones from the fully relaxed-type calculations (see Supplemental material). From these results we conclude that the cubic restriction is a reasonable option to simulate the hydrate systems, which is also in concordance with the experimental indexation using fractional occupancies for hydrogen atoms.

As regards the comparison with available experimental data (only in $CH_4@sI$), our calculated values are in good agreement with the lattice parameters reported at 123 K (11.877 Å [17]) and at 280 K (11.964 Å [6]), considering that the effect of temperature is to increase the lattice parameter. Furthermore, the crystallographic positions of the oxygens do not vary noticeably from the experimental ones, being most of the variations around 0.005 (crystallographic coordinates) or less. It is also to be noted that these internal coordinates remain with similar values in the empty clathrate (see Supplemental material). As a result, our calculated intermolecular O-O distance (~ 2.71Å), which is the most relevant distance in the structure, agrees with the experimental value of around 2.75 Å found in a number of gas hydrates of sI type [17].

A study of the energetics of the system with different orientations of the guest molecule was performed. It was done by means of partial optimizations in which the coordinates of the guest were frozen and the rest of the unit cell was allowed to relax. The difference in energy between the lowest and highest energy configurations is around 0.5 kcal/mol, regardless of the cage. That means that methane can rotate freely inside both cages and has no preference for one orientation or another.

Let us present now the results of the energetics involved in the saturation of all the cavities with CH_4 molecules. Firstly, we performed calculations using cluster models of 65 and 77 atoms for P and H cages, respectively. From the analysis of these results, it can be stated that dispersion is the most important stabilizing term. Secondly, we present results of the energetics of progressive occupations of P and H cages by methane molecules using the periodic approach. In each step we include one more molecule and optimize the system. The release of energy is calculated with respect to the empty clathrate and the free CH_4 molecules. All the results are displayed in Fig. 1, where numbers over arrows stand for the energy released in the corresponding step. We obtain a total energy difference from empty to saturation (the eight cavities are occupied) of 47.04 kcal/mol. It is clear that there is no a significant preference of methane for one cage or another, obtaining a mean energy of occupation of 5.88 kcal/mol for H cages and 5.69 kcal/mol for P cages, in agreement with other theoretical values calculated and quoted by Marion *et al.* [18]. Overall, assuming perfect diffusion and guest molecule excess, the clathrate should undergo to saturation.
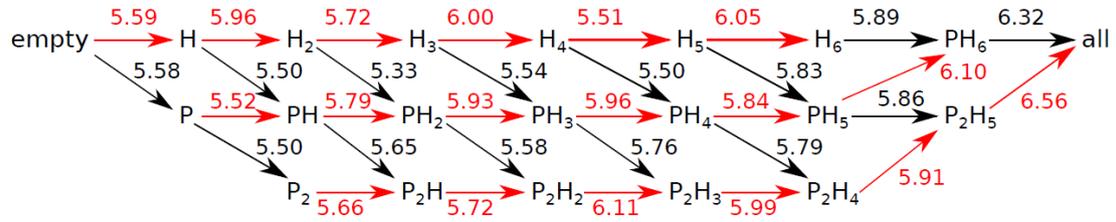
Figure 1. Energetics of the progressive occupation of P and H cages by CH_4 molecules up to saturation
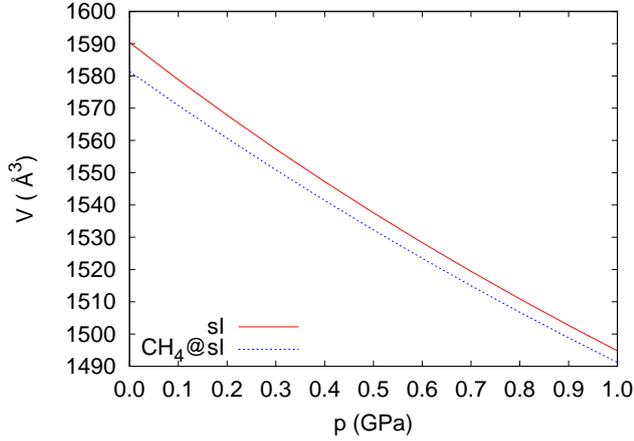
(a) Volume-pressure diagram
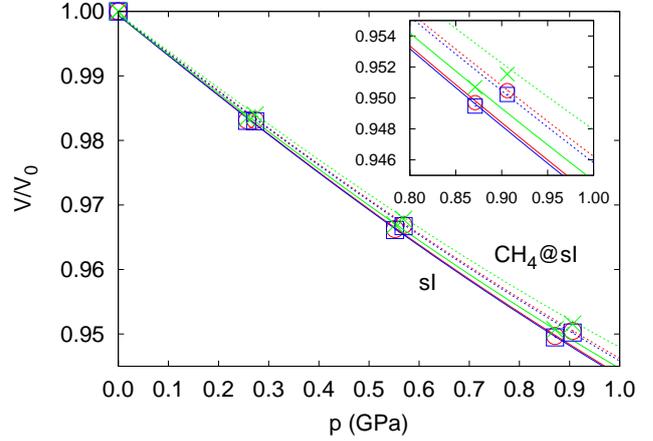
(b) Normalized volume-pressure diagram for bulk (circles), and P (crosses) and H (squares) cages

Figure 2. Pressure effects on $CH_4@sI$ (dotted lines) and empty (solid lines) clathrates

3.2. *Pressure effects*

We have studied the effects of hydrostatic pressure on the structure of empty sI and $CH_4@sI$ clathrates, and on the energy involved in the process of formations of the gas clathrate hydrate. Results are given up to 1 GPa, beyond the pressure stability range of this phase [6].

The static equations of state (EOS) of sI and $CH_4@sI$ are displayed in the volume-pressure (V-p) diagram of Fig. 2 (left). From the energy-volume computed points, we calculate pressure-volume data using numerical fittings to polynomial of different degrees. Using a fixed value for the first pressure derivative of the bulk modulus, $B'_0=4$, and assuming a linear dependence of the bulk modulus with pressure, $B=B_0 + B'_0 \times p$, we found B_0 values of 15.7 GPa and 16.5 GPa for, respectively, sI and $CH_4@sI$. These values are also consistent with the rate the relative volume decreases with pressure, as displayed in Fig. 2 (right). Given the fact that the cages fill up the unit cell, it is possible to carry out a partition of the crystal compressibility (κ) (similar to the one proposed using atoms and polyhedra [19]) in terms of P- and H-cage contributions:

$$\kappa = f_P\kappa_P + f_H\kappa_H, \tag{1}$$

where f_P and f_H are the relative volumes (occupation fractions) in the unit cell, and κ_P and κ_H the compressibilities associated to P and H cages, respectively:

$$\kappa_P = -\frac{1}{V_P}\frac{\partial V_P}{\partial p}, \quad \kappa_H = -\frac{1}{V_H}\frac{\partial V_H}{\partial p}, \quad f_P = \frac{2V_P}{V}, \quad f_H = \frac{6V_H}{V}. \tag{2}$$

Table 2. Relevant vibrational frequencies, in cm^{-1}, of CH$_4$@sI clathrate.

P (GPa)	SS$_P$	SS$_H$	AS$_P$	AS$_H$	B$_{H_2O}$	S$_{H_2O}$
0.009	3069	3050	3194	3140	1680–1809	3059–3504
0.282	3070	3050	3194	3173	1681–1812	3022–3492
0.578	3074	3051	3200	3174	1681–1818	2997–3480
0.915	3077	3052	3204	3177	1683–1819	2970–3467

In these equations V_P and V_H stand for the volumes of P and H cages, respectively.

As not all P (or H) cages have the same volume, an accurate determination of the EOS parameters for these cages is not straightforward. Using average values, we have evaluated the trends that the normalized volumes of these cages exhibit as pressure is applied (see Fig. 2 (right)). H cages are greater than P cages and occupy around 80% of the unit cell. As a consequence, H cages are more compressible than P ones, with higher and lower compressibilities, respectively, than the bulk (see inset of Fig. 2 (right)). These cage-like EOS could be transferred to other phases (sII, sH) of CH$_4$ clathrate hydrates where these cages are also present.

We also examined how the stabilization of the sI lattice induced by the occupation of CH$_4$ molecules changes as pressure is applied. Using average values, our calculations inform that the stabilization of CH$_4$@sI with respect to the empty clathrate is enhanced as pressure increases at least up to 1 GPa by about 1 kcal/mol.

3.3.   *Vibrations*

Here, results come from cluster calculations with a cluster model consisting of one P and one H cage sharing a pentagonal face. The analysis is limited to the most important modes of water and the guest molecule. For water, we discuss the stretching (S$_{H_2O}$) and bending (B$_{H_2O}$) modes, whereas for methane the symmetric and antisymmetric stretching (SS and AS, respectively) frequencies are reported.

We performed *in vacuo* geometry optimizations of methane and water molecules obtaining their frequencies at the same level of theory as the cluster calculations. Calculated values for methane are 3044 cm^{-1} (SS) and 3067 cm^{-1} (AS), and for water 1619 cm^{-1} (B$_{H_2O}$), 3618 cm^{-1} (symmetric S$_{H_2O}$) and 3783 cm^{-1} (antisymmetric S$_{H_2O}$).

In Table 2, we present the frequencies of the relevant normal modes of the CH$_4$@sI hydrate. As the symmetry is lost in the cluster, we average the values of the originally degenerated, by symmetry, components. For water modes there are a lot of contributions, so we give the values of the lower and higher frequencies in the band. As the stretching vibrations of water are very difficult to classify into symmetric and antisymmetric, we decided to collect under the symbol S$_{H_2O}$ the values of the frequencies of this band. Cage dependencies are also studied, and we include a P or H subindex (for P and H cages respectively) into the normal mode nomenclature.

The enclathration effect produces a blue shift in the frequencies of methane, with larger shifts in the P than in the H cage due to the smaller size of the former cavity. The influence of pressure is not very important in the guest molecule stretching modes, as the slight changes in their values reveal, except for AS$_H$. With respect to the water normal modes, we have checked in similar calculations of the the empty sI structure that the frequencies are quite independent on the guest, but experience blue (B$_{H_2O}$) and red (S$_{H_2O}$) shifts upon clathrate formation. Pressure has not any meaningful effect on the bending modes of water. However, the stretching modes are redshifted around 80 cm^{-1} as pressure increases up to 1 GPa. This is a consequence of the enhanced strength of the H-bonds induced by hydrostatic pressure.

4.   Conclusions

Using DFT+XDM methodologies, static simulations of the gas clathrate hydrate CH_4@sI provide a full optimized unit cell very close to the X-ray cubic structure in which H atoms present fractional occupations. The fundamental oxygen framework is supported by H-bonds that strengthen as pressure is applied and display very similar O-O distances in the calculations and in the experiments. Guest-host interactions are dispersive and weak enough to leave methane to freely rotate inside the cages. The total occupation releases around 47 kcal/mol, being pressure a favorable factor for the saturation of clathrate cavities. Shifts with respect to gas phase values are to higher frequencies for stretching modes of the guest and to lower frequencies for the stretching modes of water. Pressure does not affect appreciably methane frequencies, but enhances the red shifts of water stretchng modes. All these results reveals that gas enclathration is more a mechanical process than a chemical one, with size effects dominating the structural, energetic, and vibrational properties of this CH_4@sI clathrate hydrate.

Acknowledgements

Supplemental material

Supplemental material includes two tables with the calculated optimized crystallographic coordinates of oxygen and hydrogen atoms in sI and CH_4@sI clathrates.

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