Ab Initio Study of Hydrogen Storage in Hydrogen Hydrate Clathrates

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Recently, for the first time a hydrate clathrate was discovered with hydrogen. Aside from the great technological promise that is inherent in storing hydrogen at high density at modest pressures, there is great scientific interest as this would constitute the first hydrate clathrate with multiple species per cage. The multiple cage occupancy is controversial, and reproducibility of the experiments has been questioned. Therefore, in this study we try to elucidate the stability of the hydrogen hydrate clathrate, and determine the thermodynamically most favored cage occupancy using highly accurate *ab initio* computer simulations.

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1. Introduction

Hydrate clathrates were discovered about two centuries ago when chlorine gas was found to increase the melting point of ice.¹) At first hydrate clathrates were a curiosity but with the advent of piped natural gas hydrate clathrates of methane and other hydrocarbons became of great technological importance. Hydrocarbon hydrate clathrates can obstruct pipelines when gas contains water. Naturally, early research focussed on inhibiting the formation of hydrate clathrates by adding so-called inhibitors such as methanol. Later on it was realized that hydrocarbon hydrate clathrates might be a good source of natural gas and extensive deposits were discovered. It is suspected that the total amount of methane trapped in clathrates in the deep sea and in permafrost regions is greater than the known reserves of fossil fuels.¹) The fact that methane hydrates occur most often at the limit of their thermodynamic stability has raised concerns that slight temperature changes could release vast quantities of methane in the atmosphere. This would provide a powerful positive feedback for global warming because methane is more than an order of magnitude more potent as a greenhouse gas than CO₂. Efforts to counter global warming rely also mostly on clathrates, as the most promising technologies aim to sequester CO₂ in the form of hydrate clathrates. Recently, the fact that hydrate clathrates can contain several hundred times their own volume in gas has drawn attention. Almost a year ago,²) for the first time, a hydrate clathrate of hydrogen gas was created. Such a clathrate hypothetically contains 500 times its volume in H₂ gas (under standard conditions 0.1 MPa (1 atm) and 273 K) while stable at 145 K at a pressure of 0.01 MPa (0.1 atm). At this temperature hydrogen hydrate clathrate contains as much H₂ as pure H₂ gas at a pressure of 25 MPa (250 atm). This suggests that clathrates may be candidates for hydrogen storage. Aside from the important technological aspects, hydrogen hydrate clathrate is hypothesized to be the first known hydrate clathrate in which a cage in the structure is stabilized by clusters of molecules rather than by a single individual molecule. Almost all known hydrate clathrates fall structurally in the classification, cubic structure 1, cubic structure 2, and hexagonal. In all these structures the cages are much too large for an individual H₂ molecule and therefore the existence of hydrogen hydrate clathrates was not suspected. Although about a decade ago a report of a hydrogen hydrate clathrate³) appeared, the structure discovered at that time was an ice (Ice II) with dissolved hydrogen, see Fig. 1, which is not a cage-like structure and which requires much higher pressures for stability. The hydrogen hydrate clathrate discovered recently is of cubic structure 2 type. This structure has two types of cages. Both cages are much too large to be stabilized by the small individual H₂ molecules, rather, there are indications that the large (small) cage is stabilized by a cluster of 4 (2) H₂ molecules as is shown in Fig. 2. Incidentally, the multiple H₂ cage occupancy is also the reason for the large H₂ content in the clathrate. It has been surmised that the interatomic bonding between the hydrogen atoms in the H₂ molecules might be affected by enclathration and that the hydrogen atoms in a given cage form a cluster.²)
The present study seeks to answer several cardinal questions relating to the new hydrogen hydrate clathrates:

1) do clusters of H\textsubscript{2} stabilize the open cage clathrate structure?

2) what is the most favored occupancy of the large and small cages?

3) is the chemical bond within the hydrogen molecule affected by enclathration?

4) do the hydrogen molecules in a given cage form a cluster?

5) is density functional theory capable of describing the thermodynamics for the H\textsubscript{2}hydrate clathrate system?

Below, we try to answer these questions using highly accurate state of the art electronic density functional methods and vibrational theory.

2. Computational Details and Method

Non-spin polarized electronic structure calculations were performed with the all-electron full-potential mixed-basis approach in which the electronic wavefunctions are expanded as a linear combination of localized atom-centered orbitals and plane waves. The localized orbitals are derived from wavefunctions of non spin-polarized atoms by truncation within non-overlapping atomic spheres and subsequent ortho-normalization. The cutoff energy for the plane wave expansion of the wavefunctions was 200 eV. Studies on H\textsubscript{2}O have shown that this rather low cutoff kinetic energy gives an accurate description already. This illustrates that the mixed-basis approach is well-suited for hydrogen hydrate calculations as it does not rely on pseudopotentials. The local density approximation was used\textsuperscript{4} and integrations over the Brillouin zone were carried out with the \Gamma point only. Geometries of the H\textsubscript{2}O framework with guest H\textsubscript{2} molecules were optimized, see Fig. 2. The occupancy of the cages in cubic clathrate structure 1 and cubic clathrate structure 2 are varied from 0 to 5 for the large cage and from 0 to 2 for the small cage. Next the lattice parameter is varied in order to obtain the equation of state for the clathrate framework. This procedure is repeated for clathrate structures 1 and 2 and from a comparison of the enthalpy as a function of cage filling the optimal occupancy is deduced.

In future work we will consider also the effect of the vibrational and librational degrees of freedom on the equation of state and the relative stability as a function of cage filling and temperature. Such an analysis might reveal also the observed preference of cubic structure 2 over cubic structure 1.

3. Results

Starting with approximate coordinates for cubic hydrate clathrates of type 1 and 2 as determined from experiment, the atomic coordinates of these structures were optimized for various cage fillings. It should be mentioned that while the cage structures could be unique optimized, for the enclathrated H\textsubscript{2} molecules rotations around the centers of mass produced negligible changes in the energy confirming the quantum nature of the hydrogen rotation. The local density approximation also gave large energy separation of about 5.3 eV between occupied and unoccupied electronic states for all geometries so that the electronic and ionic degrees of freedom can be treated separately as the Born-Oppenheimer approximation implies. The relative energies are shown in Figs. 3 and 4. It is readily apparent that 4 H\textsubscript{2} molecules in the large cage and 2 H\textsubscript{2} molecules in the small cage produce the most stable cage occupancies for both cubic type 1 and type 2 structures. Figure 3 shows that for cubic structure type 1 the optimal filling is important both for the small and the large cages because cage occupancies 32 and 41 both are much less favorable than cage occupancy 42. For cubic structure type 2 the occupancy of the large cage is the most important factor because energies for cage occupancies 32 and 41 both are much less favorable than cage occupancy 42. For cubic structure type 2 the occupancy of the large cage is the most important factor because energies for cage occupancies 41 and 42 are rather...
close in energy, while one more or one less H₂ molecule, as in cage occupancy 52 and 32, greatly destabilizes the structure, as is evident from Fig. 4. The importance of the large cage in structure 2 is known from experiment also, where an optimal filling of the large cages is essential for the formation of this structure. In some cases the small cages can even remain empty.1)

While the optimized geometries, e.g. Fig. 2, cannot resolve the individual atomic positions of the hydrogen atoms that comprise an H₂ molecule, it is nevertheless possible to calculate the distance between centers of mass. This distance is about 0.28 nm for the most stable geometries. The H₂ distance to the nearest oxygen atom in the cage wall is about 0.23 to 0.26 nm. At these distances the interactions of H₂ molecules with other H₂ molecules and the cage wall is weak. The weak interaction is due to the large gap between occupied and unoccupied states in both the H₂ molecule and in the empty cage structure which prevents the formation of a chemical bond, therefore the molecular orbitals are little affected by placing the H₂ molecules inside the cages. Hence the only bonding mechanism is, within a local density picture, due to the overlap of the tails of the molecular wavefunctions. The exchange-correlation functional is non-linear in the charge density so that overlap creates a more negative (deeper) potential than without overlap. This is a simple local density picture for physisorption in van der Waals-like systems. Naturally, when molecules are gradually removed farther from the cage wall, the charge densities, and consequently the non-linearity of the exchange-correlation potential is much greater also. Calculations on isolated cages with H₂ molecules give an approximate H₂-cage wall interaction energy of 20 to 25 meV/H₂ molecule. This compares rather nicely with the physisorption energy of 86 meV(5) for H₂ onto graphene at the center hexagon position because at the center position the overlap occurs with 6 carbon atoms. It is important to note here that the local density approximation(6) has been used and not the generalized gradient approximation which generally fails to give any bonding for this class of systems.(6) The fact that the H₂ interaction with the cage wall is much stronger than that with other H₂ molecules dispels the notion that the 4 (2) H₂ molecules in a large (small) cage form a cluster in which intramolecular bonding is sacrificed for stronger intermolecular bonding.2) Our study suggests that the H₂ molecules in a cage all bind individually to the cage wall, and that H₂-H₂ interaction plays a role in the case of crowding only. Our calculation indicates that the interatomic distance in H₂ hardly changes when the molecule is enclathrated. Thus, as one would expect from a physisorption description of hydrogen hydrate clathrate formation, the H₂ intramolecular bonding is not affected.

4. Conclusions

An electronic local density functional study of cubic hydrogen hydrate clathrates was performed. It was argued that the enclathration of hydrogen molecules is based on physisorption. Therefore, (local) density functional theory can be applied to describe the interactions in the hydrogen-hydrate clathrate system. The physisorption energy was calculated to be of the order of 20 to 25 meV/H₂ molecule. The small energy involved means that the energetic barrier between absorption and desorption is small, so that little energy is lost in the storage-retrieval process of H₂ in hydrate clathrate. The optimal cage occupancy is 4 H₂ molecules in the large cage and with somewhat less preferentiality, 2 H₂ molecules in the small cage of cubic clathrate structure 2, in agreement with the educated guess made by Mao et al.2) This makes for high H₂ storage capacities in H₂O of about 5% by weight. The hydrogen molecules are individually bonded to the cage walls. The H₂ intramolecular interaction is but weakly affected by enclathration. These results confirm the structural analysis as determined by experiment, but the results also give a completely different physical picture of the bonding than what was surmised in that work.

REFERENCES