Ab initio energetics and kinetics study of H₂ and CH₄ in the SI clathrate hydrate

Qi Li,1 Brian Kolb,1 Guillermo Román-Pérez,2 José M. Soler,2 Felix Yndurain,2 Lingzhu Kong,3 D. C. Langreth,1 and T. Thonhauser1,*

1Department of Physics, Wake Forest University, Winston-Salem, North Carolina 27109, USA
2Departamento de Física de la Materia Condensada, Universidad Autónoma de Madrid, Cantoblanco, E-28049 Madrid, Spain
3Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854, USA

(Received 30 May 2011; revised manuscript received 22 September 2011; published 17 October 2011)

We present ab initio results at the density functional theory level for the energetics and kinetics of H₂ and CH₄ in the SI clathrate hydrate. Our results complement a recent article by some of the authors [G. Román-Pérez et al., Phys. Rev. Lett. 105, 145901 (2010)] in that we show additional results of the energy landscape of H₂ and CH₄ in the various cages of the host material, as well as further results for energy barriers for all possible diffusion paths of H₂ and CH₄ through the water framework. We also report structural data of the low-pressure phase SI and the higher-pressure phases SII and SH.

DOI: 10.1103/PhysRevB.84.153103 PACS number(s): 71.15.Mb, 66.30.je, 84.60.Ve, 91.50.Hc

Clathrate hydrates are crystalline, ice-like structures formed out of water molecules.¹ The water framework creates cavities in which gas molecules—typically O₂, H₂, CO₂, CH₄, Ar, Kr, Xe—can be trapped, which stabilize the framework. The existence of clathrates was first documented in 1810 by Sir Humphry Davy, and clathrates became the subject of intensive studies in the 1930s, when oil companies became aware that clathrates can block pipelines.² Nowadays, clathrate hydrates are of particular interest for two reasons: (i) they are filled with hydrogen (up to four H₂ per cage), but the lattice transforms into a new cubic phase SII, consisting of sixteen 5₁₂ and eight 5₁₂₄ cages, containing 136 water molecules in its unitcell.² When the pressure is increased to 600 MPa, the structure undergoes another phase transition to the hexagonal phase SH.² This phase has a smaller unitcell of three 5₁₂, two 4₃5₆₄, and one 5₁₂₆₄ cages, with only 34 water molecules. Very nice graphical representations of the different cages and structures can be found in Refs. 2, 4, 6, and 8. While other clathrate-hydrate structures exist, structure SI, SII, and SH are the most common ones.²

Guest molecules such as H₂ and CH₄ in the cavities of the clathrate hydrates interact with the water framework through van der Waals forces. But even the water framework itself, i.e., the interaction of water molecules through hydrogen bonds, has a van der Waals component.³ To capture these effects, we perform here density functional theory (DFT) calculations utilizing the truly nonlocal vdW-DF functional, which includes van der Waals interactions seamlessly into DFT.¹⁰⁻¹² We implemented vdW-DF using a very efficient FFT formulation¹³ into the latest release of PWSF, which is a part of the QUANTUM-ESPRESSO package.¹⁴ For our calculations we used ultrasoft pseudopotentials with a kinetic energy cutoff for wave functions and charge densities of 35 and 280 Ry, respectively. A self-consistency convergence criterion of at least 1×10⁻⁶ Ry was used. All structures were fully optimized with respect to volume and atom positions, and the force convergence threshold was at least 10⁻⁴ Ry/a.u. for SI and SH. We have also performed structural calculations on SII, but—due to the large unit cell with 136 water molecules, i.e., 408 atoms—we used a slightly less tight force convergence criterium of 5×10⁻⁴ Ry/a.u. For SI and SH we used a 2×2×2 Monkhorst-Pack k-mesh,¹⁵ while for SII we performed Γ-point calculations only.

The empty cages are experimentally not stable, but they have been shown to be a good starting point for calculations like ours.⁶ We have calculated the optimized lattice parameters for the SI, SII, and SH structures and the results are collected in Table I. We have also calculated the structures when filled with methane (one methane molecule per cage) and filled with hydrogen (up to four H₂ per cage), but the lattice parameters expand less than 0.1% upon filling, such that we have used the parameters for the empty cages henceforth. Overall, our optimized lattice constants agree well with previous calculations⁶ and experiment.⁸ In Table I we further analyze the structure of the host materials by calculating the
TABLE I. Calculated and experimental lattice constants $a$ and $c$ for the SI, SII, and SH clathrate hydrates. In addition, calculated and experimental average nearest-neighbor and next-nearest-neighbor distances are given, as well as bond angles. Standard deviations are provided in square brackets. Experimental values for the lattice constants are taken from Ref. 8 for methane-filled cages. Experimental values for the averaged quantities are calculated from the structures given in the supplemental materials of Ref. 8. The experimental distances $d_{O-H}^{nn}$ ($d_{O-O}^{nn}$) seem to be underestimated (overestimated), most likely due to the difficulty of accurately determining H positions in x-ray experiments. For SI, neutron scattering experiments suggest $d_{O-H}^{nn} = 0.973 \text{ Å}$ and $d_{O-O}^{nn} = 2.755 \text{ Å}$.\textsuperscript{16} Also note that there is some variation in the experimental results for the lattice constants in Refs. 1, 4, and 8.

<table>
<thead>
<tr>
<th></th>
<th>$a$ [Å]</th>
<th>$c$ [Å]</th>
<th>$d_{O-H}^{nn}$ [Å]</th>
<th>$d_{O-H}^{nn}$ [Å]</th>
<th>$d_{O-O}^{nn}$ [Å]</th>
<th>$\omega_{H-O-H}$ [°]</th>
<th>$\omega_{O-O-O}$ [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SI</td>
<td>Calc.</td>
<td>11.97</td>
<td>–</td>
<td>0.994 [0.001]</td>
<td>1.790 [0.014]</td>
<td>2.781 [0.013]</td>
<td>107.1° [1.0]</td>
</tr>
<tr>
<td></td>
<td>Exp.</td>
<td>11.88</td>
<td>–</td>
<td>0.861 [0.031]</td>
<td>1.911 [0.022]</td>
<td>2.761 [0.017]</td>
<td>109.3° [3.0]</td>
</tr>
<tr>
<td>SII</td>
<td>Calc.</td>
<td>17.35</td>
<td>–</td>
<td>0.994 [0.001]</td>
<td>1.792 [0.016]</td>
<td>2.784 [0.016]</td>
<td>107.1° [0.6]</td>
</tr>
<tr>
<td></td>
<td>Exp.</td>
<td>17.19</td>
<td>–</td>
<td>0.812 [0.016]</td>
<td>1.959 [0.025]</td>
<td>2.768 [0.013]</td>
<td>109.5° [2.0]</td>
</tr>
<tr>
<td>SH</td>
<td>Calc.</td>
<td>12.32</td>
<td>10.01</td>
<td>0.994 [0.001]</td>
<td>1.793 [0.015]</td>
<td>2.782 [0.011]</td>
<td>107.2° [0.9]</td>
</tr>
<tr>
<td></td>
<td>Exp.</td>
<td>12.33</td>
<td>9.92</td>
<td>0.781 [0.040]</td>
<td>1.955 [0.022]</td>
<td>2.775 [0.005]</td>
<td>108.9° [5.1]</td>
</tr>
</tbody>
</table>

average nearest-neighbor and next-nearest-neighbor distances and important bond angles. In general, the calculated average distances and angles vary only insignificantly among SI, SII, and SH, whereas they show a slightly larger spread for some experimental values. As a side-note, for a single water molecule we calculate $d_{O-H}^{nn} = 0.973 \text{ Å}$ and $\omega_{H-O-H} = 104.9°$, in good agreement with the experimental numbers of 0.958 Å and 104.5°.\textsuperscript{17} Note that vdW-DF is known to give slightly too large binding distances.\textsuperscript{18,19} Small deviations are visible in the distances $d_{O-H}^{nn}$ and $d_{O-O}^{nn}$, which in sum mostly cancel to give very good agreement with the experimental O–O distances. Reference 8 also gives the O–O distances for all structures explicitly as between 2.725 and 2.791 Å, in remarkable agreement with our calculations. Also, our calculated angles $\omega_{O-O-O}$ agree very well with experiment. However, the good agreement between oxygen distances and angles—which describe the structure as a whole—is closely related to the agreement for the lattice constants.

We next focus on the binding energies of guest molecules in the SI structure. In particular, we study the binding energies of CH$_4$ and H$_2$ in the $D$ and $T$ cages as a function of the number of molecules; results are depicted in Fig. 1 for calculations where molecules are added to only one cage in the unitcell, while all other cages are kept empty. Here, we define the binding energy as the energy difference between the “water-framework + guest-molecules” system minus the energy of the single constituents. In case of $n$-fold occupied cages, we subtract $n$ times the energy of the single molecule. Methane is a large molecule compared to the cage sizes and it can be seen that in both $D$ and $T$ only one methane molecule can be stored. Upon adding another methane molecule, the binding energy increases drastically. The situation is different for the much smaller H$_2$ molecules. In the smaller $D$ cage we can store up to two H$_2$ molecules, but increasing the number to three or four results in a positive binding energy; i.e., work is required to place more than two molecules into this cage. Note that the binding energy that we find for double H$_2$ occupancy is rather small, i.e., $\sim 8$ meV/per molecule. It is, thus, likely that at nonzero temperatures cages are only singly occupied. Experimentally, while the majority of recent work seems to favor single occupancy of the $D$ cages (see, e.g., Ref. 20), there are also reports that propose double occupancy or that find inconclusive evidence.\textsuperscript{21–25} On the other hand, the larger $T$ cage can store four H$_2$ molecules. If a fifth molecule is added, it escapes through one of the hexagonal faces into the neighboring, empty $T$ cage. Our calculated H$_2$ storage capacity of four molecules in the $T$ cages is in agreement with experiment.\textsuperscript{3} The binding energy for one H$_2$ molecule compares well with quantum-chemistry calculations on isolated cavities, which give $-0.123$ eV.\textsuperscript{21} Overall, our binding energies are slightly smaller than the ones in Ref. 6. Note that quantum motions have been neglected in our approach, which may play an important role in the binding process and when determining the cage occupancy. A more precise treatment requires the computation of the corresponding thermodynamic partition function, as, for example, shown in Ref. 26. Nevertheless, we consider our calculations for the binding energy an important first step that already reveals important information.

It is also interesting to study where and how the H$_2$ and CH$_4$ molecules bind in the cages. If only one molecule is present in the cages, it binds in the center of the cage. Rotations and small displacements of H$_2$ in that situation are on an energy scale of approximately 1 meV and approach the accuracy of our calculations. At room temperature, such
perturbations are thus easily thermally activated. Since the methane molecule is larger, it cannot move/rotate as easily. We have studied the rotation of a single methane molecule centered in the $D$ and $T$ cages as a function of rotation about two mutually perpendicular axes. The energy landscape for this rotation is depicted in Fig. 2 for the $D$ cage. The $D$ cage with its 12 pentagons and the methane molecule have a related symmetry, which allows us to choose the (0,0) point of the plot such that all methane hydrogens point exactly to an oxygen of the host lattice. At this point, hydrogen bonds are created and the total energy is the lowest. Upon rotation of the methane, the hydrogen bonds break and the energy increases. The difference between the lowest and highest point of this energy landscape is 22 meV, suggesting thermal activation of rotations at room temperature and quantifying an experimental assumption.\(^8\) We have also studied the rotation of a methane molecule in a $T$ cage and the results are very similar to the results presented in Fig. 2, with the difference that the maximal energy barrier is slightly smaller, i.e., 18 meV, which is not surprising, as the $T$ cage is slightly larger and the methane molecule can rotate more easily. Calculations for both rotation-energy landscapes have independently also been performed using SIESTA\(^{27,28}\) and give essentially identical results.

Finally, we present results for barriers to diffusion through the water framework in the SI structure. In the case of $H_2$ and hydrogen storage this is of much interest, as practical storage solutions require fast kinetics, i.e., low barriers. In the case of $CH_4$, the barriers can help us understand the natural formation of the filled clathrates. We have calculated the barriers to diffusion with nudged elastic band (NEB) calculations, using 12 images along the path from the center of one cage to the center of the next cage; the results for all possible paths are plotted in Fig. 3. Note that the relaxation of the host lattice is crucial to obtain accurate barrier energies,\(^6\) and NEB calculations allow for such relaxations perpendicular to the path automatically. The plots are labeled as $A \rightarrow B$, where $A$ is the type of the starting cage, $B$ is the type of the ending cage, and $x$ refers to either pentagon (p) or hexagon (h), indicating the opening being used for traversing. The symbols are the results from 12-image NEB calculations and the lines are fitted cubic splines, serving as a guide to the eye.

For hydrogen-storage applications, the low barrier of $\sim$0.3 eV between $T$ cages (going through a hexagon) is important. Through these $T$-cage channels, which thread through the material in all three dimensions, the hydrogen can quickly be absorbed or released. However, to achieve the material’s full storage potential, some hydrogen molecules will also have to get into the $D$ cages, with a much higher barrier of $\sim$1.4 eV for methane diffusion suggests that the methane molecules get trapped while the clathrate is formed, rather than diffusing into an already existing empty clathrate.

To conclude, we have performed an \textit{ab initio} study of structural, energetic, and kinetic properties of the guest molecules $H_2$ and $CH_4$ in hydrate clathrates. We have also shown first results for the difficult-to-model, high-pressure phase SII with a large unit cell, finding good agreement with experiment. While we have used vdW-DF for our study, it is conceivable that its successor, vdW-DF2,\(^{19}\) may further

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{energy_landscape.png}
\caption{(Color online) Energy landscape in meV for a rotating methane molecule in a $D$ cage. The $x$ and $y$ axes correspond to rotations about two mutually perpendicular axes. At the (0,0) point of the plot, the hydrogen atoms of the methane point exactly toward four oxygens of the $D$ cage. The difference between the minimum and maximum energy is 22 meV.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{barriers.png}
\caption{Barriers to diffusion of $H_2$ and $CH_4$ through the water framework along different paths, as a function of the relative progress along the path. The plots are labeled as $A \rightarrow B$, where $A$ is the type of the starting cage, $B$ is the type of the ending cage, and $x$ refers to either pentagon (p) or hexagon (h), indicating the opening being used for traversing. The symbols are the results from 12-image NEB calculations and the lines are fitted cubic splines, serving as a guide to the eye.}
\end{figure}
improve upon our results. We encourage additional studies of the hydrate clathrates using vdW-DF2, also including other types of cages, and more detailed studies of the SII phase, which is one of the more promising phases among the hydrate clathrates for hydrogen-storage applications.

We would like to dedicate this report to the memory of Professor David Langreth, who passed away just days before it was submitted—he is the “father” of vdW-DF and his research inspired many. All calculations were performed on the WFU DEAC cluster.

\[ \text{thonhauser@wfu.edu} \]

7Here, we define the diameter as twice the average distance between oxygen atoms and the cage center.