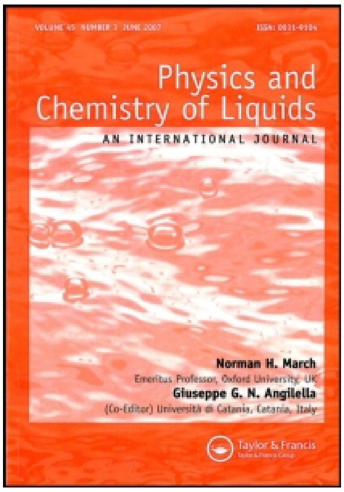

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Maximum capacity of the hydrogen storage in water clusters

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Maximum capacity of the hydrogen storage in water clusters

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Hydrogen molecules inserted into water clusters have been investigated by means of both density functional theory and *ab initio* calculations in order to determine a limit to the hydrogen storage capacity of water clusters. Three water clusters, $(H_2O)_m$ ($m = 20, 24$ and 28), were examined as the water cages, while the guest hydrogen molecules up to nine were tested in the calculations. The maximum capacities of hydrogen storage for $m = 20$, 24 and 28 were determined to be $n = 3$, 6 and 8, respectively, at the MP2/6-311G(d, p)//B3LYP/6-311G(d, p) level of theory. In order to elucidate thermal behaviour of the hydrogen hydrate, direct molecular orbital–molecular dynamics calculations were carried out for $(H_2)_n(H_2O)_m$ ($n = 6$ and 8, $m = 28$). It was found that the hydrogen molecule escapes from the hexagonal site without large deformation to the water lattice. The electronic states of the hydrogen molecules in the water clusters were discussed on the basis of theoretical results.

Keywords: hydrogen storage; water cluster; DFT; *ab initio* calculation; cavity radius; electronic states

1. Introduction

Gas hydrate is a crystalline solid where a gas molecule is trapped in the lattice of water ice [1]. Also, it has potential utility as a new energy source because the gas hydrate is easily flamed and has a large amount of combustion heat. In addition, the gas hydrate may easily carry itself and keep itself as a solid-state material. In particular, methane gas hydrate (generally called methane hydrate) is the most important species as a new energy source. This is due to the fact that the amount of CO_2 gas formed by the combustion of methane hydrates is significantly less than that of liquid methane gas because CO_2 is dissolved easily into the water.

As well as methane hydrate, hydrogen gas hydrate, the hydrogen molecule trapped in water ice, is one of the most important and simplest gas hydrates. Also, the hydrogen gas hydrate is a promising medium for hydrogen storage [2]. The storage density of hydrogen gas hydrates is $50\,g\,L^{-1}$ (5.3 wt%) around 200 MPa and 250 K [3]. It was experimentally [3] and theoretically [4] confirmed that two hydrogen molecules and four hydrogen molecules are stably encaged in the small and large cavities (5^{12} and $5^{12}6^4$), respectively, of type II gas hydrates.

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The structures of gas hydrates have been investigated mainly by density functional theory (DFT) calculations. Patchkovskii and Tse carried out DFT and MP2 calculations on the guest hydrogen molecules in water cages, $(H_2)_n(H_2O)_m$ ($n = 1$–5 and $m = 20$ and 28) to elucidate the stability of the hydrogen molecules in the water cage [4]. In their calculations, the geometries of the water cage $(H_2O)_m$ were fixed to those obtained by X-ray diffraction method, while the position of H_2 and the H–H bond lengths of hydrogen molecules were partially optimised using a 3-21G(d) basis set. They concluded that two and four hydrogen molecules can be occupied in small and large cages ($m = 20$ and 28), respectively.

In the present study, the structures and electronic states of hydrogen molecules trapped in water clusters, $(H_2)_n(H_2O)_m$ ($n = 0$–9, $m = 20, 24$ and 28), have been investigated by means of *ab initio* and DFT methods with a 6-311G(d, p) basis set to determine a limit of capacity of water cluster as a hydrogen storage material. This cluster is one of the models for a hydrogen gas hydrate. Also, a direct molecular orbital–molecular dynamics (MO–MD) calculation was applied to the hydrogen hydrate system in order to elucidate temperature effect on the dynamical feature.

2. Computational methods

We used the GAUSSIAN 03 program package for all *ab initio* and DFT calculations [5]. Three water clusters, $(H_2O)_m$ ($m = 20, 24$ and 28), were examined as the water cages. The cages for $m = 20$, 24 and 28 are defined as small, medium and large cages, respectively. The geometry optimisations of the isolated hydrogen molecule H_2, the lattice water cluster, and complex systems were carried out at the B3LYP/6-311G(d, p) level of theory. Initial configurations between hydrogen molecules in the water cages were constructed on the basis of structure of pure hydrogen clusters *in vacuo* calculated at the MP2/6-311++G(d, p) level. Several configurations were examined as initial geometries. The optimisation of $(H_2)_n(H_2O)_m$ ($n = 5$ and 7, $m = 28$) gave two meta-stable structures. The structures at the lowest energy were employed in the present study.

The dynamic feature of hydrogen hydrate was investigated by means of a direct MO–MD method [6–10]. The total energy and energy gradient on the multi-dimensional potential energy surface of the $(H_2)_n(H_2O)_m$ system were calculated at each time step at the AM1 level of theory, and then the classical equation of motion is fully dimensionally solved. Therefore, charges and electronic states of all atoms are exactly treated within the level of theory. This point is very different from usual classical molecular dynamics (MD) calculation, where the charges of all atoms are constant during the diffusion.

3. Results

3.1. *Maximum capacity of the hydrogen storage in water clusters*

The structures of $(H_2)_n(H_2O)_m$ ($n = 0$–9, $m = 20, 24$ and 28) are fully optimised at the B3LYP/6-311G(d, p) level of theory. As sample structures, the optimised structures of $(H_2)_n(H_2O)_m$ ($n = 5$, $m = 20, 24$ and 28) are illustrated in Figure 1. The cavity radii of water cages for $n = 20$, 24 and 28 are calculated to be $\langle R(\mathrm{cmO})\rangle = 3.8441$, 4.2472 and 4.5808 Å, respectively, where the cavity radius of water cage is defined as an average distance of oxygen atoms from the centre of mass of the water cluster. The cavity radius of the water cage increases gradually with increasing m.

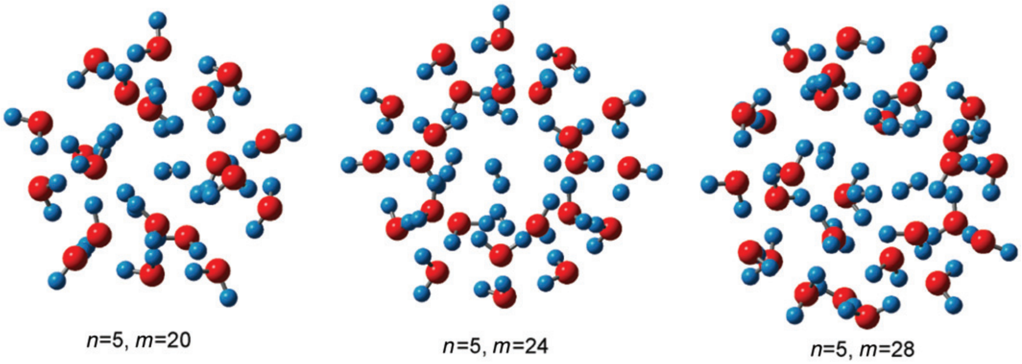

Figure 1. Optimised structures of $(H_2)_n(H_2O)_m$ ($n = 5$, $m = 20, 24$ and 28) calculated at the B3LYP/6-311G(d, p) level.

In the case of the small-sized water cage ($m = 20$), the cavity radius of $(H_2O)_{20}$ is calculated to be 3.8441 Å without hydrogen molecules ($n = 0$). When one hydrogen molecule is inserted in the cage of $(H_2O)_{20}$, the radius is slightly shortened from 3.8441 to 3.8350 Å. On the other hand, if the water cage with $m = 20$ includes two water molecules, the radius is elongated to 3.8564 Å. In multiple occupations ($n > 2$), the radius increases gradually with increasing n. For example, the cavity radii for $n = 0$, 3 and 5 are calculated to be 3.8441, 3.8777 and 3.9614 Å, respectively. If the water cluster ($m = 20$) includes six hydrogen molecules, one hydrogen molecule has escaped from the cage.

In the middle sized-water cage ($m = 24$), the cavity radius without hydrogen molecules is calculated to be 4.2472 Å, which is 0.4031 Å larger than that of $m = 20$. When the water cage includes a hydrogen molecule, the radius is slightly shortened from 4.2472 to 4.2442 Å, which is similar to that of $m = 20$. The position of the hydrogen atom of H_2 is calculated to be $\langle R(cmH) \rangle = 0.487$ Å, which is not zero. This result indicates that the hydrogen molecule is not located at the centre of mass of the water cage, but it is positioned in a point deviated from the centre of mass. Similar features are obtained in $m = 20$ ($\langle R(cmH) \rangle = 0.3750$ Å) and in $m = 28$ ($\langle R(cmH) \rangle = 1.5666$ Å). The cavity radius increases with increasing n. For example, the radii for $n = 2$, 4 and 6 are 4.2501, 4.2772 and 4.3236 Å, respectively. The insertion of H_2 into the water cluster ($m = 28$) causes a slight decrease of cavity radius ($\langle R(cmO) \rangle = 4.5808$ Å for $n = 0$ and $\langle R(cmO) \rangle = 4.5779$ Å for $n = 1$) as well as $n = 20$ and 24. After further insertion of H_2, the cavity radius increases gradually with increasing n: for example, $n = 2$ (4.5814 Å), $n = 4$ (4.5884 Å), $n = 6$ (4.6170 Å), $n = 8$ (4.6397 Å). In the case of the insertion of $n = 9$, a hydrogen molecule has escaped from the cage.

The stabilisation energies of $(H_2)_n$ to the inside of water clusters $(H_2O)_m$ are plotted in Figure 2 as a function of the number of hydrogen molecules (n). It seems that the B3LYP method underestimates the stabilisation energy of H_2 because the dispersion interaction between hydrogen molecules is not efficiently included in the B3LYP method as shown in Figure 2(a) and (b). Therefore, we discuss the stabilisation energy using the MP2 results.

In the case of the small-sized cage ($m = 20$), the stabilisation energy of one hydrogen molecule is calculated to be 3.47 kcal mol^{-1}. The stabilisation energy reaches the maximum value at $n = 2$ (4.58 kcal mol^{-1}), and it decreases gradually as a function of n. In $n = 4$, the stabilisation energy shows a negative value (-0.61 kcal mol^{-1}), but it is close to zero.

Further insertion of H_2 to $(H_2)_4(H_2O)_{20}$ (i.e. $n = 5$) gives larger negative stabilisation energy ($-7.20\,\mathrm{kcal\,mol^{-1}}$).

In the case of the middle-sized water cage ($n = 24$), the stabilisation energy of H_2 ($n = 1$) is calculated to be $2.13\,\mathrm{kcal\,mol^{-1}}$ which is smaller than that of the small-sized water cage. The stabilisation energy has a maximum at $n = 3$ with $8.73\,\mathrm{kcal\,mol^{-1}}$, while it decreases gradually as a function of n. For example, the stabilisation energies for $n = 4$, 5 and 6 are 7.29, 6.74 and $5.17\,\mathrm{kcal\,mol^{-1}}$, respectively. After further insertion of H_2, the hydrogen molecule escapes from the water cage.

In the case of the large-sized water cage ($n = 28$), the stabilisation energy increases linearly up to $n = 5$ and then it decreases as a function of n. The maximum of stabilisation energy is located at $n = 5$ with the stabilisation energy of $10.85\,\mathrm{kcal\,mol^{-1}}$. The maximum capacity as a hydrogen storage is calculated to be $n = 8$. From the curve of Figure 2(b), it seems to be expected that the $(H_2O)_{28}$ cluster has storage above $n > 9$ hydrogen molecules in its cage as an upper limit.

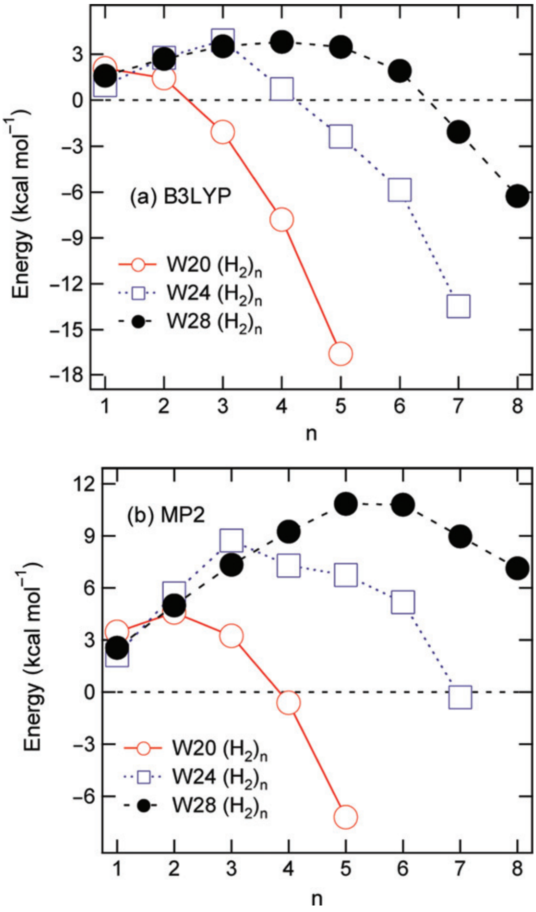

Figure 2. Stabilisation energies of hydrogen molecules in the water clusters, $(H_2)_n(H_2O)_m (n = 1\text{–}8, m = 20, 24$ and 28). (a) Stabilisation energies calculated at the B3LYP/6-311G(d, p) level, and (b) stabilisation energies calculated at the MP2/6-311G(d, p)//B3LYP/6-311G(d, p) level.

The charges of H_2 in the water cages are calculated using natural population analysis (NPA) at the MP2/6-311G(d, p) level. Almost all hydrogen molecules have neutral charges (0.0), but it was found that each hydrogen molecule is internally polarised by the electronic field from the water clusters as $H^{\delta+}$–$H^{\delta-}$. This is induced by the electrostatic potential from the water clusters.

3.2. *Dynamical behaviour of hydrogen hydrate*

To elucidate the dynamical behaviour of the hydrogen hydrate, direct MO–MD calculation is carried out for $(H_2)_n(H_2O)_m (n = 8 \text{ and } m = 28)$. The result at 50 K is given in Figure 3, where snapshots are illustrated as a function of time. At time zero,

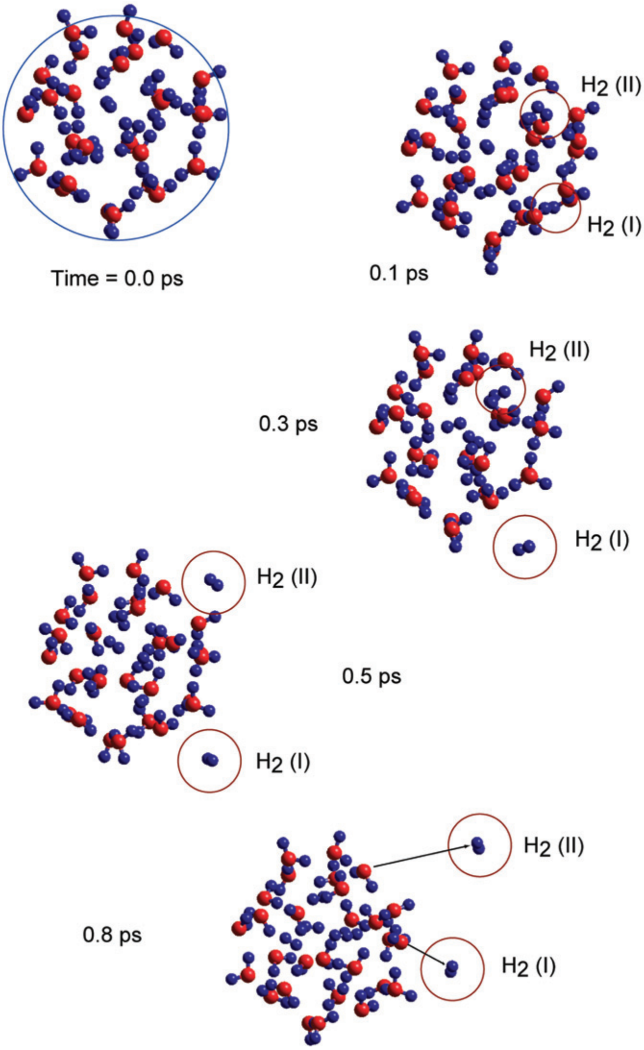

Figure 3. Snapshots of hydrogen hydrate at 50 K calculated by means of direct MO–MD method.

the structure corresponds to that of the optimised structure. By thermal activation (50 K), the hydrogen molecules vibrate strikingly in the cavity of the water cluster. First, one of the hydrogen molecules (denoted by H_2(I)) escaped from the cage at 0.3 ps. The hydrogen molecule H_2(I) is located at 3.652 Å from the nearest water molecule. The escape of the second hydrogen molecule H_2(II) occurs at 0.5 ps. At 0.8 ps, H_2(II) has completely escaped from the water cluster (the distance of H_2(II) is 7.210 Å from the cluster surface). The rotation of H_2(II) is excited after the escape. On the other hand, the first hydrogen molecule H_2(I) is still bound on the surface of the water cluster. Thus, two types of hydrogen molecule are formed by the escape of H_2 from the hydrogen hydrate. It should be noted that the lattice structure of the water cluster is hardly deformed during the escape of the hydrogen molecule. Also, it is found that the hydrogen molecule escaped from the hexagonal site made of six water molecules. This result suggests that the escape of H_2 proceeds without a large deformation of the lattice structure.

4. Summary of the present study

The results of the present study can be summarised as follows. Hydrogen molecules inserted into water clusters have been investigated by means of both DFT and *ab initio* calculations in order to determine a limit of hydrogen storage capacity in water clusters. Three water clusters, $(H_2O)_m$ ($m = 20, 24$ and 28) were examined as the water cages, while guest hydrogen molecules up to nine were tested in the calculations.

The maximum capacities of hydrogen storage for $m = 20$, 24 and 28 were determined to be $n = 3$, 6 and 9, respectively, at the MP2/6-311G(d, p)//B3LYP/6-311G(d, p) level of theory. The electronic states of hydrogen molecules in the water clusters were discussed on the basis of theoretical results. The direct MO–MD calculations showed that the hydrogen molecule escapes from the hexagonal site composed of six water molecules without causing large deformation to the water lattice.

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