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Topical Perspectives

Exploring the possibility to store the mixed oxygen-hydrogen cluster in clathrate hydrate in molar ratio 1:2 ($O_2 + 2H_2$)

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ABSTRACT

An interesting possibility is explored: storing the mixture of oxygen and hydrogen in clathrate hydrate in molar ratio 1:2. The interaction energies between oxygen, hydrogen, and clathrate hydrate are calculated using high level quantum chemical methods. The useful conclusion points from this study are summarized as follows. (1) The interaction energies of oxygen-hydrogen mixed cluster are larger than the energies of pure hydrogen molecular cluster. (2) The affinity of oxygen molecules with water molecules is larger than that of the hydrogen molecules with water molecules. (3) The dimension of O_2–$2H_2$ interaction structure is smaller than the dimension of CO_2–$2H_2$ interaction structure. (4) The escaping energy of oxygen molecules from the hydrate cell is larger than that of the hydrogen molecules. (5) The high affinity of the oxygen molecules with both the water molecules and the hydrogen molecules may promote the stability of oxygen-hydrogen mixture in the clathrate hydrate. Therefore it is possible to store the mixed ($O_2 + 2H_2$) cluster in clathrate hydrate.

1. Introduction

The gas clathrate hydrates exist in the natural world in large scale [1–3]. The most abundant gas hydrate is the methane-hydrates, which are buried in the continental shelf, constituting the earth's largest energy resource, more than twice the amount of all other fossil energy, including petroleum, natural gas and coal in the continents [1–3]. The hydrate 5^{12} cell is the smallest and basic unit of clathrate hydrate. The structure of 5^{12} hydrate cell is shown in Fig. 1, which is a dodecahedron consisting of 20 hydrogen-bond bound water molecules in 12 pentagon faces [4]. The average experimental side length (distance between two neighboring oxygen atoms) of the methane-hydrate is $R_{O\text{-}O} = 2.82$ Å and the diameter of 5^{12} hydrate cell is 7.92 Å [1].

In recent years the gas hydrates have been considered for potential applications in clear energy, space exploration, environmental and ecological protections [5–11]. The carbon dioxide (CO_2) was suggested to be trapped in the clathrate hydrate and buried in the ocean floor in order to solve the global warming problem [12,13]. The clathrate hydrate was proposed to store hydrogen molecules (H_2) as clean fuel for automobiles, space rockets and shuttles [14–17].

Hydrogen molecules (H_2) stored in clathrate hydrate was first reported in 2002, but requires very high pressures to be stable [14]. In order to store hydrogen molecules in lower pressure, the larger promoter molecules, such as tetrahydrofuran (THF) [15,18] and tetrabutyl ammonium bromide (TBAB) [19], are introduced. In 2004 the experiment by Sloan and colleagues showed that the solid H_2-containing hydrates could be formed at ambient temperature and tens of bar by adding small amounts of promoting substance tetrahydrofuran (THF) [20–23]. On the other hand the partner molecules (such as CO_2 and SF_6) are used to help the storage of hydrogen molecules in clathrate hydrate. The H_2–CO_2 mixed hydrates were reported by Kim [24], Grim [25], and Kumar [26], respectively. Unlike promoter molecules, which occupy the hydrate cells alone, the partner molecules may share the same hydrate cells with hydrogen molecules.

In many fields we need both oxygen as oxidant and hydrogen as deoxidizer. For example, in space travels the rockets and shuttles need the hydrogen molecules as the fuel and the oxygen molecules as the oxidant. Usually the oxygen and hydrogen were stored separately. The mixed storage of oxygen molecules and hydrogen molecules may have enormous advantages over the traditional storages separately, because less containers and equip-

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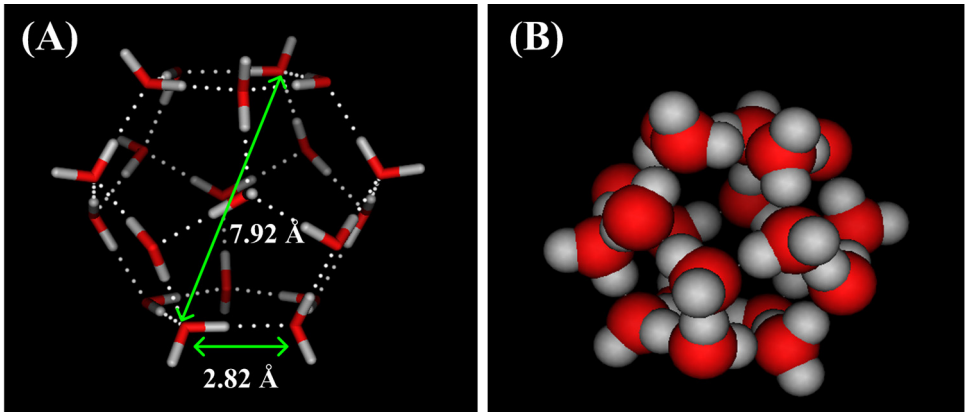

Fig. 1. The structures of the clathrate hydrate 5^{12} cell. (A) The clathrate hydrate 5^{12} cell is a dodecahedron consisting of 20 water molecules in 12 pentagon faces. The hydrogen bond energy $\Delta E_{H\text{-}b}$ of 30 water–water hydrogen bonds is around −1000 kJ/mol. (B) The water van der Waals surface of the clathrate hydrate 5^{12} cell. The experimental side length of the clathrate hydrate 5^{12} cell is $R_{O\text{-}O}$ = 2.82 Å, and the diameter is 7.92 Å.

Table 1
The interaction energies of molecular clusters in gaseous phase and comparison of three methods (MP2/cc-pV5Z, CCSD/cc-pV5Z and CCSD (T)/cc-pV5Z).

Cluster	MP2/cc-pV5Z		CCSD/cc-pVQZ		CCSD (T)/cc-pV5Z	
	ΔE(kJ/mol)	Structure	ΔE (kJ/mol)	Structure	ΔE (kJ/mol)	Structure
$2H_2$	−0.285	'T'[a]	−0.172	'T'[a]	−0.328	'T'[a]
$3H_2$	−0.631	Angle[b]	−0.299	Angle [b]	−0.789	Angle[b]
O_2–H_2	−1.742	'T'[a]	−1.365	'T'[a]	−1.853	'T'[a]
O_2–$2H_2$	−2.486	Angle[b]	−2.158	Angle[b]	−3.002	Angle[b]
CO_2–H_2	−1.675	Free[c]	−1.558	Free[c]	−2.352	Free[c]
CO_2–$2H_2$	−3.312	Free[c]	−2.325	Free[c]	−3.574	Freet[c]

[a] 'T': The H_2 molecule perpendicularly points to the center of the O_2 molecule.
[b] Angle: Two H_2 molecules point the center of O_2 (or H_2) forming an angle.
[c] Free: No special geometrical structure.

ments are used. However, in ordinary condition the mixed storage of hydrogen molecules and oxygen molecules is extremely dangerous because of the violent reaction between oxygen molecules and hydrogen molecules, which may cause serious explosion.

In order to solve the problem of oxygen-hydrogen mixed storage, the clathrate hydrate may be a useful method. If one oxygen molecule and two hydrogen molecules are trapped in a small hydrate cell, the chemical reaction is almost impossible, because such reaction needs very high activation energy, or frequent collision among thousands oxygen and hydrogen molecules. If no platinum catalysis, the explosion reaction of oxygen and hydrogen in the hydrate cells almost wouldn't happen.

Molecular modeling [27,28] is a powerful tool in the study of clathrate hydrates [4,29]. In this study the possibility of oxygen and hydrogen mixed storage in clathrate hydrates is explored using computational chemistry methods. The results and conclusions from this study may open an effective approach for clean energy, transportation, space travel, and submarine navigation in ocean.

2. Results

In the storage of hydrogen in clathrate hydrate the typical partner molecules are CO_2 and SF_6. Usually the partner molecules possess higher affinity with both water molecules and hydrogen molecules, which may enhance the stability of hydrogen molecular cluster in hydrate cells. The oxygen molecules could be a good molecular partner for hydrogen storage in clathrate hydrate. The reasons and evidences for above prediction will be presented in this study.

2.1. Interaction energies of small molecular clusters

The interaction energies inside the molecular clusters in gaseous phase are calculated using three methods MP2 [30–32], CCSD [33], and CCSD(T) [33,35] with basis set cc-pV5Z [35,36]. The calculation results are listed in Table 1, and the optimized interaction structures are shown in Fig. 2. The interaction energies of four hydrogen and oxygen clusters ($2H_2$, $3H_2$, O_2–H_2, and O_2–$2H_2$) are listed in Table 1. For comparison the interaction energies between hydrogen and carbon dioxide (CO_2–H_2 and CO_2–$2H_2$) are also listed in Table 1. The results of MP2 method are better than that of CCSD, little poorer than the results of the state-of-the art method CCSD(T). However, the results of MP2 method are consistent with the CCSD(T) method and uses much less CPU-time than the CCSD(T) method.

The optimized interaction structure of O_2–H_2 is in 'T' form (Fig. 2B), in which the H_2 perpendicularly points to the center of the O_2 molecule. The optimal structure of H_2–H_2 is basically the 'T' form (Fig. 2A). However, the dihedral angle ($D^{2,3,4}_{1,2,3}$) between the four hydrogen atoms is 177.65°, and the angle formed by the two hydrogen molecules and the center of the other H_2 molecule is 173.13°. The optimized interaction structure of O_2-$2H_2$ cluster is the cross form '+' (Fig. 2C), in which the two H_2 molecules perpendicularly point to the center of oxygen molecule (O_2). The dimension of the O_2-$2H_2$ cross interaction structure is 7.354 Å that is very difficult to be put in the 5^{12} hydrate cell, whose diameter is 7.92 Å (see Fig. 1). A scanning calculation is performed for the angle $\angle H_2—O_2—H_2$, and the curve of O_2-$2H_2$ interaction energy ΔE_{clst} as function of angle $\angle H_2—O_2—H_2$ is shown in Fig. 3. In the energy curve there are two local minimums (−3.002 kJ/mol at 63° and 297°). The O_2-$2H_2$ interaction structure at the local minimum is shown in Fig. 2D. The