Exploring the possibility to store the mixed oxygen-hydrogen cluster in clathrate hydrate in molar ratio 1:2 (O₂+2H₂)

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Key words: Clathrate hydrate; Hydrogen storage; O₂-2H₂ mixed storage; Gas-hydrate stability; Escaping energy

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.

Key words: Clathrate hydrate; Hydrogen storage; O_2-2H_2 mixed storage; Gas-hydrate stability; Escaping energy

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 $R_{O-O}=2.82 \text{ \AA}$ and the diameter of 5^{12} hydrate cell is $7.92 \text{ \AA}$ [1].

(Figure 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 equipments 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 , $\text{O}_2\text{-H}_2$, and $\text{O}_2\text{-}2\text{H}_2$) are listed in **Table 1**. For comparison the interaction energies between hydrogen and carbon dioxide ($\text{CO}_2\text{-H}_2$ and $\text{CO}_2\text{-}2\text{H}_2$) 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.

(Table 1 and Figure 2)

The optimized interaction structure of $\text{O}_2\text{-H}_2$ is in ‘T’ form (**Fig 2 B**), in which the H_2 perpendicularly points to the center of the O_2 molecule. The optimal structure of $\text{H}_2\text{-H}_2$ is basically the ‘T’ form (**Fig 2 A**). However, the dihedral angle ($\text{D}_{1,2,3}^{2,3,4}$) 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 $\text{O}_2\text{-}2\text{H}_2$ cluster is the cross form ‘+’ (**Fig 2 C**), in which the two H_2 molecules perpendicularly point to the center of oxygen molecule (O_2). The dimension of the $\text{O}_2\text{-}2\text{H}_2$ cross interaction structure is $7.354 \text{ \AA}$ that is very difficult to be put in the 5^{12} hydrate cell, whose diameter is $7.92 \text{ \AA}$ (see **Fig 1**). A scanning calculation is performed for the angle $\angle\text{H}_2\text{-O}_2\text{-H}_2$, and the curve of $\text{O}_2\text{-}2\text{H}_2$ interaction energy ΔE_{clst} as function of angle $\angle\text{H}_2\text{-O}_2\text{-H}_2$ is shown in **Fig 3**. In the energy curve there are two local minimums (-3.002 kJ/mol at 63° and 297°). The $\text{O}_2\text{-}2\text{H}_2$ interaction structure at the local minimum is shown in **Fig 2 D**. The dimension $3.709\text{\AA} \times 3.842\text{\AA}$ of the $\text{O}_2\text{-}2\text{H}_2$ interaction structure at local minimum is suitable to be put in the 5^{12} hydrate cell.

(Figure 3)

In **Table 1** the interaction energies of pure hydrogen molecular clusters (2H_2 and 3H_2) are very weak, less than 1 kJ/mol . The interaction energies of oxygen-hydrogen

clusters $\text{O}_2\text{--H}_2$ and $\text{O}_2\text{--}2\text{H}_2$ are much larger than that of pure H_2 clusters, very close to that of the $\text{CO}_2\text{--H}_2$ and $\text{CO}_2\text{--}2\text{H}_2$ clusters. However, the dimension (9.543 Å) of $\text{CO}_2\text{--}2\text{H}_2$ interaction structure is much larger than the diameter (7.92 Å) of 5^{12} hydrate cell (see **Fig 1 A** and **Fig 2 E**).

2.2 Interaction energies of H_2 , O_2 and CO_2 with water molecules

The interaction energies and structural parameters of three types of molecules (H_2 , O_2 , and CO_2) with water molecule (H_2O) are calculated at the CCSD(T)/cc-pV5Z level. The calculation results are listed in **Table 2**, and the optimized interaction structures are shown in **Fig 4**. The interaction energy (-8.662 kJ/mol) of $\text{H}_2\text{O--O}_2$ cluster is much larger than that (-0.5101 kJ/mol) of $\text{H}_2\text{O--H}_2$ cluster, and reached the 2/3 of the interaction energy (-12.719 kJ/mol) of $\text{H}_2\text{O--CO}_2$ cluster. The solubility of H_2 , O_2 , and CO_2 are listed in **Table 2**. In aqueous solution the solubility of oxygen molecules is 26 times higher than the solubility of hydrogen molecules, very close to the concentration of CO_2 in water. Therefore, oxygen molecules possess larger affinity with the water molecules than that of hydrogen molecules. The higher affinity of oxygen molecules with both the hydrogen molecules and the water molecules may enhance the stability of hydrogen molecules in the clathrate hydrate.

(Table 2 and Figure 4)

2.3 Stable energies of guest molecular clusters in hydrate cell

The interaction energies $\Delta E_{\text{cell-clst}}$ between the hydrate cell and the guest molecular cluster and the stable energies ΔE_{stable} of the gas-hydrate cell are calculated using **Eq 3** and **Eq 5** (see Method section), respectively, and the results are listed in **Table 3**.

From the data in **Table 3** two phenomena are observed. (1) The cell-cluster interaction energies $\Delta E_{\text{cell-clst}}$ are larger than the gas-hydrate stable energies ΔE_{stable} .

As evaluated by the **Eq 5**, the gas-hydrate stable energy ΔE_{stable} is the sum of the cell-cluster interaction energies $\Delta E_{\text{cell-clst}}$ and the cluster interaction energy ΔE_{clst} :

$\Delta E_{\text{stable}} = \Delta E_{\text{cell-clst}} + \Delta E_{\text{clst}}$. In many cases the guest cluster interaction energies ΔE_{clst} are repulsive (positive values) because of the small room and the high electrostatic

potential in hydrate cells. (2) The gas-hydrate stable energies ΔE_{stable} and the cell-cluster interaction energies $\Delta E_{\text{cell-clst}}$ of the mixed oxygen-hydrogen clusters ($\text{O}_2\text{-H}_2$ and $\text{O}_2\text{-2H}_2$) are remarkably larger than that of the pure hydrogen molecular clusters (2H_2 and 3H_2). A reasonable explanation is that the higher affinity of oxygen molecules with both hydrogen molecules and water molecules promotes the stability of the clathrate hydrate of oxygen-hydrogen mixture.

(Table 3)

2.4 Thermodynamic and frequency calculations

Thermodynamic calculations are performed for studying the contributions of inner energies, thermal enthalpies and entropies, including the zero-point correction and other corrections. For comparison the frequency calculations are carried out at 273K (0°C) using B3LYP/6-311+G(d,p) method for guest molecular cluster (O_2+2H_2) and (CO_2+2H_2) in 5^{12} hydrate cell, respectively. The results of frequency calculations are summarized in Table 4.

(Table 4)

In 5^{12} hydrate cell although the guest-host interaction energy ΔU° and enthalpy ΔH° of (CO_2+2H_2) cluster are larger than that of (O_2+2H_2) cluster, the guest-host interaction free energy $\Delta G^\circ(\text{O}_2+2\text{H}_2) = -782.40 \text{ kJ/mol}$ of (O_2+2H_2) cluster is much larger than $\Delta G^\circ(\text{CO}_2+2\text{H}_2) = -320.64 \text{ kJ/mol}$ of (CO_2+2H_2) cluster. The reason is that in 5^{12} hydrate cell the guest cluster (CO_2+2H_2) encounters larger repulsive interaction than (O_2+2H_2) cluster does.

2.5 Escaping energies of O_2 and H_2 molecules from hydrate cell

Could the hydrogen and oxygen molecules escape from the clathrate hydrate cells? The escaping energies $\Delta E_{\text{escape}}(r)$ of the hydrogen and oxygen molecules from the 5^{12} hydrate cell are calculated using **Eq 6** (see Method section). The escaping energies $\Delta E_{\text{escape}}(r)$ of hydrogen molecule and oxygen molecule are the functions of the distance r between the center of 5^{12} hydrate cell and the position of guest molecule (H_2 or O_2), as shown in **Fig 5**.

(Figure 5)

Based on the MP2/6-311+G (d, p) [32] calculations, the escaping energy barrier of hydrogen molecule from the 5^{12} hydrate cell is 74 kJ/mol at the distance $R=3.8 \text{ \AA}$. The escaping energy barrier of oxygen molecule is 152.5 kJ/mol at $R=3.2 \text{ \AA}$, much higher than that of the hydrogen molecule. Therefore the mixture of oxygen and hydrogen molecules may stabilize the storage of hydrogen molecules in clathrate hydrates.

3. Discussion

The large promoter molecules, such as tetrahydrofuran (THF) [15,18] and tetrabutyl ammonium bromide (TBAB) [19], can help the storage of H_2 molecules in hydrate cells at moderate pressure and temperature. However, it is very difficult to achieve high capacity by using the promoter molecules, because the promoter molecules being larger in size preferably occupies the large cavities, thus only small cells are available for hydrogen molecules, which significantly reduces the storage capacity. Unlike the promoter molecules THF and TBAB, in the mixed storage the O_2-2H_2 cluster may occupy the same cells in the clathrate hydrate, including the small cells and large cells, without the losing of the storage capacity.

On the other hand, the O_2-2H_2 mixed storage is different from the co-guest storage, such as SF_6+H_2 , CO_2+H_2 , and other co-guest molecules [9,39-42]. In the O_2+2H_2 mixed storage the partner molecules O_2 are an important component in the high density energy materials, as important as the hydrogen molecules. In contrast, the partner molecules CO_2 and SF_6 are waste for energy purpose, and toxin to environmental protection.

4. Conclusion

Some useful conclusions are summarized as follows. (1) The interaction energies of the oxygen-hydrogen mixed clusters are larger than the interaction energies in pure hydrogen molecular clusters. (2) The affinity of oxygen molecules with water molecules is larger than the affinity of the hydrogen molecules with the 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 barrier 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. The (O_2+2H_2) mixed storage in clathrate hydrate may find potential applications in several fields, such as transportation, submarine, and space travel [43].

5. Theory and Method

The practical experiments to store the oxygen and hydrogen mixture (O_2+2H_2) in the clathrate hydrate may be very difficult. However, exploring the possibility of mixed hydrogen-oxygen storage using computational chemistry is relatively easy. Quantum chemistry modeling the gas hydrates has been carried out by several authors [4,44,45]. In this study the state-of-the art method CCSD(T) [34,35] is used in the calculations of guest molecular clusters (nH_2 , O_2/H_2 and CO_2/H_2), MP2 [30-32] method is applied in the calculations of guest molecules (nH_2 , O_2/H_2 and CO_2/H_2) in 5^{12} hydrate cell. In the enthalpy and free energy calculations CBS-4M [36-38] method is used in 1 atm and 300K.

The definition of the stable energies of guest molecular cluster in host hydrate cells is given as follows. The dissociation energy ΔE_{diss} of a guest molecular cluster in hydrate cell is the energy difference between the total energy of the gas-hydrate cell and the energy summation of individual water molecules and guest molecules,

$$\Delta E_{\text{diss}} = E_{\text{cell}}(\text{cluster}) - \sum_i^n E_{w,i} - \sum_j^m E_{\text{guest},j} = \Delta E_{\text{H-b}} + \Delta E_{\text{cell-clst}} + \Delta E_{\text{clst}} \quad (1)$$

where $E_{\text{cell}}(\text{cluster})$ is the total energy of the hydrate cell with the guest molecular cluster inside, $E_{w,i}$ is the energy of individual water molecule, and $E_{\text{guest},j}$ is the energy of individual guest molecule. The dissociation energy ΔE_{diss} of gas-hydrate cell can be divided into three energy contributions. The first contribution is the hydrogen bond energy $\Delta E_{\text{H-b}}$ between water molecules in the hydrate cell,

$$\Delta E_{\text{H-b}} = E_{\text{cell}}(\text{empty}) - \sum_i^n E_{\text{w},i} \quad (2)$$

where the term $E_{\text{cell}}(\text{empty})$ is the total energy of an empty hydrate cell. The second contribution is the interaction energy $\Delta E_{\text{cell-clst}}$ between the hydrate cell and the guest molecular cluster,

$$\Delta E_{\text{cell-clst}} = E_{\text{cell}}(\text{cluster}) - E_{\text{cell}}(\text{empty}) - E_{\text{clst}} \quad (3)$$

where the term E_{clst} is the total energy of the guest molecular cluster keeping the structure inside the hydrate cell. The third contribution is the interaction energy ΔE_{clst} in the guest molecular cluster,

$$\Delta E_{\text{clst}} = E_{\text{clst}} - \sum_j^m E_{\text{guest},j} \quad (4)$$

The dissociation energy ΔE_{diss} of the gas-hydrate cell cannot be directly used to describe the stability of the gas-hydrate cell, because the total water hydrogen bond energies in a hydrate cell ($\Delta E_{\text{H-b}}$) are in the range -800 to -1000 kJ/mol, the interaction energies $\Delta E_{\text{cell-clst}}$ between the guest molecular cluster and the hydrate cell are in the range -10 ~ -50 kJ/mol, and the interaction energies ΔE_{clst} inside the guest molecular cluster are often less ± 10 kJ/mol. Small fluctuation of the hydrogen bond energy $\Delta E_{\text{H-b}}$ may completely conceal the contributions of the other two energy terms.

The hydrogen bond energy $\Delta E_{\text{H-b}}$ is the function of side length ($R_{\text{O-O}}$) of hydrate cell. If the side length ($R_{\text{O-O}}$) keeps constant, the hydrogen bond energy $\Delta E_{\text{H-b}}$ is a constant. The stable energy ΔE_{stable} of gas-hydrate cells is defined as follows.

$$\Delta E_{\text{stable}} = E_{\text{cell}}(\text{cluster}) - E_{\text{cell}}(\text{empty}) - \sum_j^m E_{\text{guest},j} = \Delta E_{\text{cell-clst}} + \Delta E_{\text{clst}} \quad (5)$$

In hydrate cell the interaction energy ΔE_{clst} of guest molecular cluster is not always attractive (negative values). In many cases it may be repulsive (positive values) because of the small room in the hydrate cell and high electrostatic potential from the water molecules, which could change seriously with the side length ($R_{\text{O-O}}$) of hydrate cells.

The escaping energies $\Delta E_{\text{escape}}(r)$ of a hydrogen molecule (or oxygen molecule)

from the 5¹² hydrate cell are defined by the following equation,

$$\Delta E_{\text{escape}}(r) = E_{\text{total}}(\text{H}_2, r) - E_{\text{total}}(\text{H}_2, \text{center}) \quad (6)$$

where $E_{\text{total}}(\text{H}_2, \text{center})$ is the total energy of a hydrogen molecule in the center of the hydrate cell, and $E_{\text{total}}(\text{H}_2, r)$ is the total energy of a hydrogen molecule at the position r from the center of the hydrate cell.

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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	
	$\Delta E(\text{kJ/mol})$	Structure	$\Delta E(\text{kJ/mol})$	Structure	$\Delta E(\text{kJ/mol})$	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	Free ^c

^a ‘T’: The H₂ molecule perpendicularly points to the center of the O₂ molecule.

^b Angle: Two H₂ molecules point the center of O₂ (or H₂) forming an angle.

^c Free: No special geometrical structure.

Table 2. Interaction energies of H₂, O₂, and CO₂ with water molecule H₂O calculated at CCSD(T)/cc-pV5Z level.

Molecular clusters	Interaction energy kJ/mol	Parameter (Å)	Aqueous solubility ^a g/kg
H ₂ O–H ₂	-0.5101	R _{h-o} =2.554	0.0016 (H ₂)
H ₂ O–O ₂	-8.662	R _{h-o} =2.528	0.0430 (O ₂)
H ₂ O–CO ₂	-12.719	R _{c-o} =2.791	0.0519 (CO ₂) ^b

^a http://www.engineeringtoolbox.com/gases-solubility-water-d_1148.html

^b The solubility of CO₂ at 30°C in water is 1.250 g/kg, includes all species (CO₂, HCO₃⁻, CO₃²⁻, and H₂CO₃). The concentration of CO₂ in water is 0.0519 g/kg.

Table 3. The interaction energies ^a and stable energies of guest molecular clusters in the hydrate 5¹² cell ^b (side length of the dodecahedron R_{OO}= 2.82 Å).

Guest cluster	MP2/ cc-pV5Z		
	$\Delta E_{\text{cell-clst}}$	ΔE_{clst}	ΔE_{stable}
2H ₂	-12.87	7.53	-5.34
3H ₂	-15.72	12.48	-3.24
O ₂ -H ₂	-28.68	4.82	-23.86
O ₂ -2H ₂	-33.32	13.86	-19.46
CO ₂ -2H ₂	-43.25	27.83	-15.42

^a Energy in kJ/mol.

^b The positions of the guest molecules in the 5¹² cell are optimized, and the side length (R_{OO}= 2.82 Å) of the dodecahedron cell keeps constant.

Table 4. The inner energies, enthalpy, and free energies of (O₂+2H₂) in 5¹² hydrate cell and (CO₂+2H₂) in 5¹² hydrate cell (B3LYP/6-311+G(d,p), 0 °C).

Molecular Group	Energy (a.u.) ^a	Enthalpy(a.u.)	Free Energy (a.u.)
(O ₂ +2H ₂) @ 5 ¹² Cell	-1680.755245	-1680.753272	-1681.147332
Σ(20W)	-1527.85376	-1527.83646	-1528.22276
Σ(O ₂ +2H ₂)	-152.582591	-152.579996	-152.626714
Guest-Host	ΔU°(kJ/mol)	ΔH°(kJ/mol)	ΔG°(kJ/mol)
Interaction	-837.66	-884.73	-782.4
Molecular Group	Energy (a.u.) ^a	Enthalpy(a.u.)	Free Energy (a.u.)
(CO ₂ +2H ₂) @ 5 ¹² Cell	-1719.164666	-1719.163801	-1719.264507
Σ(20W)	-1527.85376	-1527.83646	-1528.22276
Σ(CO ₂ +2H ₂)	-190.873089	-190.870495	-190.919681
Guest-Host	ΔU°(kJ/mol)	ΔH°(kJ/mol)	ΔG°(kJ/mol)
Interaction	-1150.04	-1200.02	-320.64

^a 1 a.u. = 627.509469 kCal/mol = 2626.754637 kJ/mol

[Figure captions]

Figure 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 ΔE_{H-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 $R_{O-O}=2.82$ Å, and the diameter is 7.92 Å.

Figure 2. The interaction structures of O_2 and H_2 clusters. **(A)** The interaction structures of H_2-H_2 cluster is in 'T' form, in which the H_2 perpendicularly points to the center of the other H_2 molecule. **(B)** The interaction structures of O_2-H_2 cluster is in 'T' form, in which the H_2 molecule perpendicularly points to the center of oxygen molecule. **(C)** The optimized structure of O_2-2H_2 cluster is in cross form, in which the two H_2 molecules perpendicularly point to the center of oxygen molecule. **(D)** The O_2-2H_2 interaction structure of local minimum is in angle form, $\angle H_2-O_2-H_2=60^\circ$ or 300° . The dimension $3.709\text{Å}\times 3.842\text{Å}$ at local minimum is suitable to be put in the 5^{12} hydrate cell. **(E)** The interaction structures of CO_2-2H_2 clusters.

Figure 3. The cure of interaction energy of O_2-2H_2 cluster as function of $\angle H_2-O_2-H_2$ angle. The global minimum (-3.217 kJ/mol) is at the position 180° . There two local minimums (-3.002 kJ/mol) at positions 60° and 300° , respectively. The dimension $3.649\text{Å}\times 3.889\text{Å}$ of the local minimum structure is suitable to be put in the 5^{12} hydrate cell.

Figure 4. The optimized interaction structures of H_2 , O_2 , and CO_2 with water molecule H_2O . **(A)** The optimized structures of H_2O-H_2 interaction cluster. The distance between H_2O and H_2 is 2.554 Å. **(B)** The optimized structure of H_2O-O_2 interaction cluster. The distance between H_2O and O_2 is 2.527 Å. **(C)** The optimized structure of HO_2-CO_2 interaction cluster. The distance between H_2O and CO_2 is 2.798 Å.

Figure 5. The escaping energy ΔE_{escape} of molecule H_2 and O_2 from the 5^{12} hydrate cell. **(A)** The escaping energy ΔE_{escape} of molecule H_2 as the function of distance R from the center of the 5^{12} hydrate cell. **(B)** The escaping energy ΔE_{escape} of molecule O_2 as the function of distance R from the center of the 5^{12} hydrate cell. The escaping energy barrier (~ 160 kJ/mol) of oxygen molecule is much larger than the escaping energy barrier (~ 70 kJ/mol) of hydrogen molecule.

Figure-1

Figure-2

Figure-3

Figure-4

Figure-5