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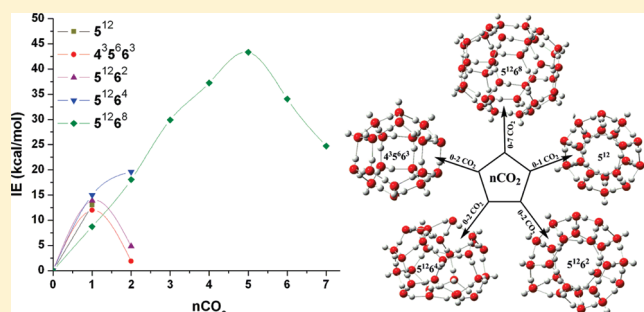
Viability of Clathrate Hydrates as CO₂ Capturing Agents: A Theoretical Study

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Supporting Information

ABSTRACT: Capture and sequestration of green house gas CO₂ is a major challenge for scientists and identifying right materials for this purpose is a task of outstanding importance. Through reliable computational studies, we have demonstrated that the clathrate cages (5^{12} , $4^3 5^6 6^3$, $5^{12} 6^2$, $5^{12} 6^4$, and $5^{12} 6^8$) have a great potential to store CO₂. All the considered clathrates and their CO₂ inclusion complexes are optimized at B3LYP/6-31G(d) level of theory. The impact of DFT-D, M05-2X, and MP2 functionals on interaction energy were tested using various basis sets. Although different functionals and basis sets show variation in absolute IE values, the trend is consistent and does not depend on the level of the calculations. Dispersion was found important for these complexes and DFT-D shows comparable IE values with MP2 functional. The optimum and maximum cage occupancy for all the considered cages were tested on the basis of quantum chemical calculations. The maximum cage occupancy for all five considered cages (5^{12} , $4^3 5^6 6^3$, $5^{12} 6^2$, $5^{12} 6^4$, and $5^{12} 6^8$) is one, two, two, two, and seven CO₂ molecules, respectively, and the optimum cage occupancy is one, one, one, two, and five CO₂ molecules, respectively. Thus, $5^{12} 6^8$ cages can host up to 7 CO₂ molecules, resulting in about 32 wt %, which makes them highly promising materials.



INTRODUCTION

Enhanced greenhouse gas effect, mostly due to carbon dioxide emissions, is unquestionably responsible for climate warming and thus reducing the quantities of CO₂ released into the environment is a major challenge of the current world. Identification of smart materials to capture CO₂ by absorption, adsorption, membrane separation, and so on, is a problem of immense contemporary interest.^{1–3} A number of materials have been proposed for CO₂ adsorption, such as activated carbon,^{4,5} zeolites,^{6,7} silica adsorbents,^{8,9} carbon nanotubes,¹⁰ nanoporous silica-based molecular basket,^{11,12} and so on. Two major bottlenecks for industrial applications of these materials are (a) the lower weight percentage and (b) regeneration of the captured gas. The hydrate formation from water and gaseous CO₂ was reported by North et al., where these authors observed the growing hydrate crystals optically and by means of calorimetric methods.¹³ X-ray diffraction studies showed the time-resolved macroscopic hydrate formation in the stirred water–CO₂ bulk mixture.¹⁴ A combined experimental and molecular dynamics study has provided the first unambiguous evidence for the formation of CO₂ gas hydrates at molecular length scales.¹⁵ Clathrates are an excellent source for the formation of inclusion complexes and, thus, can be of great potential for gas storage.^{16–18} The inclusion complexes of clathrates are supramolecular structures with host–guest arrangement, where the host molecules are hydrogen-bonded water cages and the guests are small gaseous molecules.¹⁹ A number of guest molecules have been proposed

earlier, such as noble gases, halogens, low molecular weight hydrocarbons, and light gases.^{16–21} Among them, hydrogen storage in clathrates has generated tremendous interest in recent years.²⁰

Hydrogen-bonded cages of clathrates can be of different shapes and sizes like pentagonal dodecahedron (12 pentagonal faces; 5^{12}), tetrakaidecahedron (12 pentagonal and 2 hexagonal faces; $5^{12} 6^2$), hexakaidecahedron (12 pentagonal and 4 hexagonal faces; $5^{12} 6^4$), irregular dodecahedron (3 square, 6 pentagonal and 3 hexagonal faces; $4^3 5^6 6^3$), and icosahedron (12 pentagonal and 8 hexagonal faces; $5^{12} 6^8$).²¹ The hydrogen-bonded water network that forms the clathrate frame accounts for the stability of these clathrates. The three known structure types of unit cell of clathrates are *sI* (cubic structure that contains 46 water molecules and form two 5^{12} and six $5^{12} 6^2$ cages in one unit cell), *sII* (cubic structure that contains 136 water molecules and form sixteen 5^{12} and eight $5^{12} 6^4$ cages in one unit cell) and *sH* (hexagonal structure that contains 36 water molecules and form three 5^{12} , two $4^3 5^6 6^3$, and one $5^{12} 6^8$ cages in one unit cell). It has been observed that guest molecules can be accommodated 0 to 100% in the small cages and nearly 100% in the large cages in a unit cell of clathrates.¹⁹ The guest molecules strongly interact with the host molecules and are necessary for the stability of clathrate complexes.^{21,22} Empty clathrate cages were shown to be mechanically

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stable and can be subjected to computational studies. Recently, in two different studies using different models and simulation methodologies, Jacobson et al.²³ and Conde et al.²⁴ suggested that the guest-free *sII* clathrate structure is a stable phase of water under extension. The stability and capacity of *sH* clathrates to store CO₂ was studied by Alavi et al. by using molecular dynamics calculations.²⁵ They observed the large cage ($5^{12}6^8$) occupancy of five at low temperature and three at high temperature, however, the small cages (5^{12} , and $4^35^66^3$) occupancy was only one CO₂ molecule. They report that CO₂ inclusion complexes are more stable compared to experimentally observed methane inclusion complexes of clathrates.²⁵ The stability and phase changes of CO₂ clathrates below 280 K and between 0.2 and 3.0 GPa was studied by Hirai et al. using high pressure and low temperature experiments.²⁶ The structural and energetic properties of 5^{12} and $4^35^66^3$ clathrate cages with various guest molecules (CH₄, C₂H₆, CO₂, and N₂) was studied by Krallafa et al., and they did not consider the $5^{12}6^8$ cage or multiple occupation of gas molecules.²⁷ Stability, adsorption, and diffusion of CH₄, CO₂, and H₂ in clathrate hydrates was studied by Roman-Perez et al. by using SIESTA method^{28,29} of DFT calculations.³⁰ Adsorption energies for methane and carbon dioxide are similar being higher than that of hydrogen inclusion complexes, based on the calculations considering single guest molecules. Chialvo et al. analyzed the thermophysical and structural properties of methane and carbon dioxide *sI* clathrate hydrates by molecular dynamics simulation under isobaric–isothermal conditions.³¹ Wen et al. studied the structures and stability of type *sI* CH₄ and CO₂ hydrates using molecular dynamics simulations.³² Jordan et al. studied the equilibrium and nonequilibrium MD simulations to calculate the structural, dynamical, and thermal properties of methane, xenon and CO₂ *sI* hydrate and observed that the CO₂ molecules are the most delocalized in the water cages.³³ Sandler et al. established a method for calculating the interaction energies between guests and the hydrate lattice at varying guest positions and orientations using ab initio quantum chemical calculations and presented the prediction formula of guest occupancies in the hydrate cavities; however, absolute cage occupancies were dependent on the method.³⁴ In this paper, we computationally explore the viability of clathrate cages as CO₂

storage agents, which seem to have a high wt % and easily regenerate the captured gas. In this systematic computational analysis, the optimum and maximum cage occupancies of five different clathrate cages (5^{12} , $4^35^66^3$, $5^{12}6^2$, $5^{12}6^4$, and $5^{12}6^8$) have been examined. The rigidity of all considered cages and their CO₂ inclusion complexes are studied.

METHODOLOGY

In this study, our focus is to computationally examine the stability of clathrate cages and their CO₂ inclusion complexes. All considered cages of clathrate hydrates have been fully optimized at the B3LYP/6-31G(d) level of theory using the Gaussian 03 program package.³⁵ Frequency calculations characterize the obtained stationary points as minima on the potential energy surface. We sequentially added CO₂ molecules in 5^{12} , $4^35^66^3$, $5^{12}6^2$, $5^{12}6^4$, and $5^{12}6^8$ clathrates and probed their cage occupancy. In general, the optimizations of clathrates were found to be quite tricky and challenging with the Gaussian and GAMESS programs. Normally most optimizations of clathrate cages take a few hundred optimization steps and are notoriously difficult to reach the convergence.³⁶ The B3LYP/6-31G(d) level was found to be reasonable for optimizations of clathrates and various other water clusters.^{20d,37} Among the DFT functionals, getting convergence at the M05-2X level was found to be very tough in the current study for the considered clathrates. Thus, all geometry optimizations of CO₂ inclusion complexes of clathrate hydrates have been carried out using the B3LYP/6-31G(d) method. A recent study on clathrate hydrates shows that the constrained optimization technique in clathrate hydrates enables accountability for the making and breaking of both water–water and water–guest hydrogen bonds and helps in conserving the clathrate structure of the cage during optimization.³⁸ Considering the above computational issues, we resorted to benchmark the result obtained by enforcing cages with unconstrained cages (see SI, Table S2). After confirming that the geometry of inclusion complexes with and without constraints is virtually unchanged for the model system, we performed constrained optimizations at the B3LYP/6-31G(d) level on all the considered CO₂ inclusion complexes by freezing the optimized coordinates of clathrates. Comparison of optimized geometric parameters with and without the dispersion correction show negligible structural differences.³⁸ However, it is important to get proper functions with dispersion correction for obtaining reliable IE values. Considering this, we performed single point energy calculations with the DFT+D³⁹ functional that is available in Gaussian 09 and includes a dispersion correction. Interaction energies [IE = ($E_{\text{clathrate}} + E_{\text{CO}_2}$) – E_{complex}] were calculated at various levels of theory (see SI, Table S1). The IE obtained by DFT+D calculations is close to the IE at the MP2 functional and shows the good performance and importance of dispersion correction.

Table 1. Cage Rigidity of Various Clathrates Gauged by Various Energetic Measures^a

| clathrates | <i>n</i> | <i>A</i> | <i>B</i> | CR |
|-------------|----------|----------|----------|--------|
| 5^{12} | 20 | −347.57 | 17.38 | −45.51 |
| $4^35^66^3$ | 20 | −283.28 | 14.16 | −56.90 |
| $5^{12}6^2$ | 24 | −410.58 | 17.11 | −36.11 |
| $5^{12}6^4$ | 28 | −481.19 | 17.19 | −40.73 |
| $5^{12}6^8$ | 36 | −618.26 | 17.17 | −35.63 |

^a *n* = number of H₂O molecules; *A* = ($E_{\text{clathrate}} - E_n$); *B* = (*A*/*n*); CR = [$E_{\text{clathrate}} - (E_{\text{clathrate}} - 1\text{H}_2\text{O}) - E_{1\text{H}_2\text{O}}$]; all the reported numbers are in kcal/mol at the B3LYP/6-31G(d) level of theory.

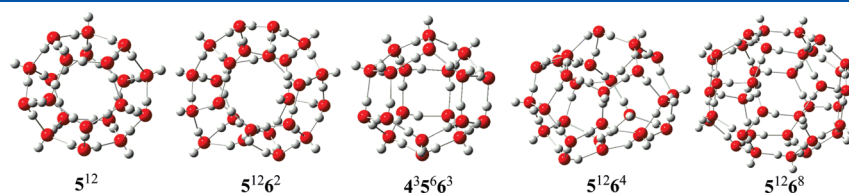


Figure 1. B3LYP/6-31G(d) optimized structures of various clathrates considered in the study.

RESULTS AND DISCUSSION

Five clathrate cages (5^{12} , $4^35^66^3$, $5^{12}6^2$, $5^{12}6^4$, and $5^{12}6^8$) have been considered in the present study, and the measure of their stability is gauged irrespective of the complexation energy of cage formation. Table 1 indicates that, when normalized for a single unit of water molecule, all cages have comparable stabilities (i.e., around 17 kcal/mol complexation energy/unit water molecule, except for $4^35^66^3$). B3LYP/6-31G(d) optimized structures of all the considered cages are depicted in Figure 1. After assessing the stability of clathrates, the rigidity of the cluster is gauged by removing a single water molecule from the cage. According to this, the removal of the first water molecule from the cage is more difficult as compared to the subsequent water molecules. Among the considered clathrates, the $4^35^66^3$ cage exhibits the highest resistance for triggering the cage breakage. It is interesting to note that the cage with the least complexation energy, as can be gauged

Table 2. Interaction Energy (kcal/mol) of $n\text{CO}_2$ Encapsulation into Different Clathrate Cages along with Dispersion Correction (DC), Electron Correlation (EC), and Cage Rigidity (CR) of Inclusion Complexes

| complexes | IE ^a | IE ^b | IE ^c | IE ^d | EC ^e | DC ^f | CR ^g |
|--|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 1CO ₂ @5 ¹² | 5.02 | 14.79 | 14.28 | 10.99 | −0.02 | 14.71 | −42.65 |
| 2CO ₂ @5 ¹² | −25.55 | −3.11 | −6.21 | −11.11 | 5.90 | 38.08 | −42.23 |
| 3CO ₂ @5 ¹² | −115.54 | −86.41 | −86.28 | −89.34 | 39.46 | 88.25 | −44.54 |
| 1CO ₂ @4 ³ 5 ⁶ 6 ³ | 2.95 | 11.93 | 12.37 | 8.46 | −0.14 | 14.05 | −57.63 |
| 2CO ₂ @4 ³ 5 ⁶ 6 ³ | −17.69 | 4.23 | 1.85 | −1.89 | −4.95 | 35.79 | −51.34 |
| 1CO ₂ @5 ¹² 6 ² | 5.02 | 13.86 | 13.89 | 9.37 | 0.62 | 13.75 | −35.06 |
| 2CO ₂ @5 ¹² 6 ² | −11.25 | 11.91 | 8.83 | 1.60 | 4.83 | 37.34 | −36.85 |
| 3CO ₂ @5 ¹² 6 ² | −65.37 | −32.98 | −34.09 | −42.42 | 14.41 | 62.01 | −34.91 |
| 1CO ₂ @5 ¹² 6 ⁴ | 3.08 | 13.13 | 14.98 | 8.74 | 0.90 | 15.77 | −39.15 |
| 2CO ₂ @5 ¹² 6 ⁴ | −4.76 | 18.89 | 20.52 | 10.31 | 3.45 | 37.46 | −38.66 |
| 3CO ₂ @5 ¹² 6 ⁴ | −63.47 | −30.18 | −26.84 | −37.39 | 13.20 | 65.10 | −25.67 |
| 1CO ₂ @5 ¹² 6 ⁸ | 2.49 | 5.98 | 8.73 | 2.68 | −0.53 | 5.75 | −35.85 |
| 2CO ₂ @5 ¹² 6 ⁸ | 3.79 | 16.92 | 17.14 | 8.61 | 0.61 | 20.07 | −36.24 |
| 3CO ₂ @5 ¹² 6 ⁸ | 4.93 | 25.74 | 27.45 | 14.46 | 1.10 | 33.20 | −36.06 |
| 4CO ₂ @5 ¹² 6 ⁸ | 0.86 | 31.41 | 32.91 | 16.17 | 2.07 | 48.50 | −35.90 |
| 5CO ₂ @5 ¹² 6 ⁸ | −1.74 | 37.81 | 40.44 | 18.57 | 3.89 | 64.54 | −36.74 |
| 6CO ₂ @5 ¹² 6 ⁸ | −22.28 | 28.65 | 30.53 | 8.83 | 8.36 | 85.23 | −35.01 |
| 7CO ₂ @5 ¹² 6 ⁸ | −39.82 | 22.30 | 25.18 | 1.12 | 12.33 | 106.60 | −36.71 |

^a Interaction energy [IE = ($E_{\text{clathrate}} + E_{\text{CO}_2}$) − E_{complex}] at B3LYP/6-31G(d) level. ^b Dispersion corrected IE using DFT+D functional at B3LYP/6-31G(d) level. ^c IE at MP2/6-31+G(d)//B3LYP/6-31G(d) level. ^d IE at M05-2X/6-31+G(d)//B3LYP/6-31G(d) level. ^e Electron correlation [MP2/6-31+G(d)−HF/6-31+G(d)]. ^f Dispersion correction [B3LYP/6-31+G(d)−HF/6-31+G(d)]. ^g CR is [$\{E_{\text{clathrate}} - (E_{\text{clathrate}} - 1\text{H}_2\text{O})\} - E_{1\text{H}_2\text{O}}$] at B3LYP/6-31+G(d) level, and thus, the number corresponds to loss of stability of cage complexation energy upon removal of a single water molecule.

with the complexation energy per unit water, is the most rigid one. In comparison, the largest clathrate has around 20 kcal/mol lower resistance to knock off the first water from the cage. So, from this analysis it is clear that the smaller cages 5^{12} and $4^35^66^3$ may breakdown quickly upon removal of the first water molecule. The rigidity of various clathrate cages is in the following order $4^35^66^3 > 5^{12} > 5^{12}6^4 > 5^{12}6^8 > 5^{12}6^2$.

After identifying that these clathrates are stable and rigid, we undertake the study of CO₂ inclusion complexes by sequentially increasing the number of CO₂ molecules inside the clathrate cages. Table 2 provides the IE for all the inclusion complexes at various levels of theories and shows that all cages form stable complexes upon inclusion of a single CO₂ molecule. However, the addition of a second CO₂ molecule was not possible for the 5^{12} cage. The $4^35^66^3$, $5^{12}6^2$, and $5^{12}6^4$ cages appear to accommodate a maximum of two CO₂ molecules. In the case of the $5^{12}6^8$ cage, the IE is lowest for the first CO₂ inclusion. Encouragingly, the IE continues to increase upon addition of CO₂s sequentially up to five, and the bound complexes were formed with up to seven molecules in the cage. Efforts to optimize eight CO₂ molecules in the cage were futile, and therefore, this cage can have a maximum of seven CO₂ molecules. However, we should not that the optimum number of inclusion of CO₂ molecules for 5^{12} , $4^35^66^3$, $5^{12}6^2$, $5^{12}6^4$, and $5^{12}6^8$ clathrate cages is one, one, one, two, and five CO₂ molecules, respectively. As the nature of interaction between CO₂ and clathrates are mostly dispersive in nature, B3LYP functional is not expected to give meaningful energetics for complexation. Therefore, the energy evaluations were done employing MP2 and M05-2X methods, which are capable of modeling dispersion bound complexes (Table 2). In addition, DFT+D calculations were carried out to compare the IE with and without dispersion correction and presented in Table 2. As has been expected, the dispersion has a strong effect on the energy, and therefore, the IE of CO₂ inclusion complexes of clathrates is reliable only when it properly treats the dispersion effect. Although different functionals and basis sets show a variation in absolute IE values, the trends in interactions energies are essentially identical. Interestingly, MP2, M05-2X, and DFT+D methods provide similar interaction energy values and trends. The effect of dispersion correction (DC) and electron correlation (EC) has been examined for each of the clathrate complexes studied and is given in Table 2. We have also measured the cage rigidity (CR) for each of the inclusion complexes and presented this in Table 2. In most of the cases, the rigidity of inclusion complexes is very comparable with the stability of their pristine cages. Figure 2 provides B3LYP/6-31G(d) optimized structures with maximum possible CO₂ inclusion complexes in all five clathrates. It has also been observed that the dispersion correction and electron correlation are lower for favorable and higher for unfavorable inclusion complexes, Table 2. Figure 3 shows the orientation of 1–8 CO₂

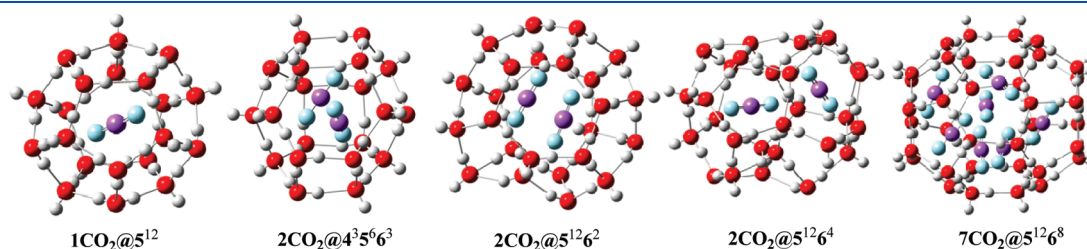


Figure 2. B3LYP/6-31G(d) optimized structures of maximum possible CO₂ inclusion complexes in all four clathrates considered in the study.

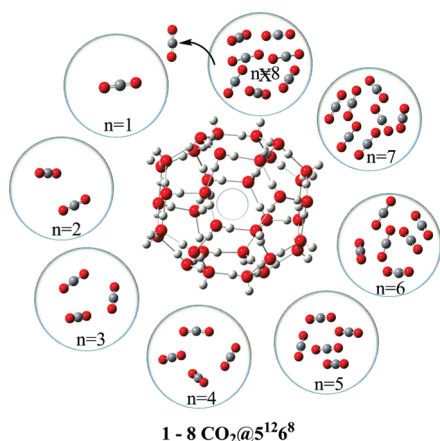


Figure 3. Orientation of CO_2 molecules ($n = 1-8$) in the cage of $5^{12}6^8$ clathrate based on B3LYP/6-31G(d) optimizations.

molecules in the $5^{12}6^8$ clathrate cage and indicate that the inclusion of eight CO_2 molecules is not possible in the cage.

CONCLUSIONS

The current computational study clearly reveals a high potential of clathrate cages as CO_2 capturing agents. The weight percentages for the five considered clathrate cages 5^{12} , $4^35^66^3$, $5^{12}6^2$, $5^{12}6^4$, and $5^{12}6^8$ are about 10, 14, 14, 16, and 32, respectively. Thus, the maximum weight percentage of structural types *sI*, *sII* and *sH* are 30, 36, and 42, respectively. The study establishes that the rigidity remains intact upon CO_2 storage in all considered water clathrates. Dispersion has a strong role on the host–guest interaction energy of CO_2 inclusion complexes of clathrates. The current computational results corroborate very well with the observation that the CO_2 molecule is less suitable for the small cage (5^{12}) because of its larger size compared with the CH_4 .³² The inclusion of CO_2 is much more feasible as the cage size increases. The past few years have witnessed potential application in energy materials as hydrogen storage substances. We hope that the current study triggers new experimental efforts in this direction and may lead to a breakthrough technology for the effective capture of CO_2 .

ASSOCIATED CONTENT

Supporting Information. The IE values at various levels of theory; B3LYP/6-31G(d) optimized structures of CO_2 inclusion complexes of various clathrates; complete ref 35. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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