Density functional theoretic studies of host–guest interaction in gas hydrates

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ABSTRACT

Recently we reported the host–guest interaction between a dodecahedral water cage and a variety of guest species that include diatomic (CO, H_2, N_2, O_2), triatomic (CO_2, O_3) and polyatomic (CH_4, NH_3) molecules at the MP2/CBS limit (Kumar and Sathyamurthy, 2011). Since high computational costs involved in the application of MP2 and CCSD (T) methods limit the size of the clathrate that can be studied, the performance of the density functional theoretic method using functionals like B3LYP, M06-HF, M06-L, M06-2X and BLYP-D3 is evaluated for its ability to predict the interaction energy as well as the geometry. The computed results are compared with the estimated CCSD/CBS values, which were obtained with the help of the MP2/CBS values reported earlier. The DFT/BLYP-D3 method seems to be the best; the functionals M06-2X and M06-HF performed reasonably well, while B3LYP failed to predict any attraction between the guest and the host.

1. Introduction

Natural gas hydrates, also known as clathrate hydrates, are crystalline solids in which small atoms/molecules are trapped inside a polyhedral water cage of different sizes [1]. Structurally, gas hydrates are host–guest complexes in which the water cages have the capacity to host a variety of gas molecules [2]. A hollow dodecahedral cage is energetically less stable than its cuboid counterpart [3], yet a guest molecule like methane can stabilize it [4]. Among the water cages of various possible sizes the dodecahedral cage can be considered the simplest, consisting of 12 pentagonal rings made up of 20 water molecules. Depending upon the orientation of the dangling O–H bonds, one can obtain a variety of dodecahedral cages [5,6]. In the present study, we have selected one such dodecahedral cage (5^{12}) in which there are three sets (one set separated from the other two) of two dangling O–H bonds in adjacent locations and another four arranged in locations without any adjacent dangling O–H bond (Fig. 1). It is well known that this cage is relatively more stable than the other dodecahedral cages [5,7]. Because of its high stability and symmetry, it can act as a building block for larger hydrates.

Recently, there have been several reports on methane hydrates, owing to their abundance and potential application as hydrocarbon fuels for imminent energy crises [5,8–19]. The methane molecule was found to form stable complexes with the water cages of 5^{12} and $5^{12}6^2$ geometry. Another molecule of interest has been carbon dioxide, given its role in the greenhouse effect [20,21]. Srivastava and Sastry [22] have reported the encapsulation of several CO_2 molecules in various water cages such as 5^{12}, $4^3 5^6 6^3$, $5^{12}6^2$, $5^{12}6^4$, and $5^{12}6^8$. Another important application of clathrates is due to their role in gas storage, which is a topic of interest globally [23–25]. Chattaraj and co-workers [26] studied hydrogen storage in clathrates and they found that the water cages 5^{12} and $5^{12}6^2$ can trap up to two H_2 molecules, while the water cage $5^{12}6^8$ can trap up to six.

Recently, we have estimated the interaction energy of various host–guest complexes at MP2/CBS level of theory [27]. Since the interaction involved in such host–guest complexes is weak in nature, it is essential to account for the dispersion interaction as accurately as possible. The B3LYP method has been used frequently to study the gas–hydrate interaction. However, it is now established that this functional does not predict the interaction energy accurately for dispersion-bound complexes [28,29]. The computational cost for the MP2 method using a large basis set limits the size of the water cage that can be investigated. Some of the recently developed DFT functionals seem promising in terms of accuracy and computational resources required. In particular, the M06 suite of functionals developed by Truhlar and co-workers and dispersion-corrected density functionals developed by Grimme and co-workers are seen to perform adequately for weakly bound systems.

In the present study we have used the B3LYP [30], M06-HF [31], M06-L [32], M06-2X [33] and BLYP-D3 [34] functionals to

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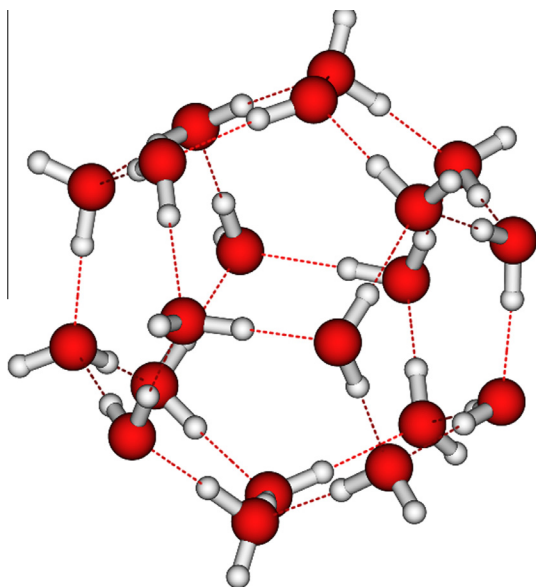*E-mail address:* nsath@iitk.ac.in (N. Sathyamurthy).

Fig. 1. Schematic representation of the geometry of dodecahedral water cage $(H_2O)_{20}$.

investigate the host–guest interaction between the dodecahedral water cage and several guest species. For the guest species, we have considered a variety of molecules present in the atmosphere. These include diatomic (CO, H_2, N_2, O_2), triatomic (CO_2, O_3) and polyatomic (CH_4, NH_3) molecules. The results obtained using the DFT method and different functionals are compared with those from the CCSD/CBS method. The deformation of the cage due to the presence of guest molecules and the change in the structural parameters is also examined.

2. Computational method

Geometry optimization for the guests, host and the adduct molecules was carried out using the DFT method and the functionals B3LYP, M06-L, M06-HF, M06-2X and BLYP-D3 in conjunction with the aug-cc-pVDZ basis set. Subsequently, single-point energy calculations were performed with the aug-cc-pVTZ basis set, based on which the interaction energy of the host–guest complex was determined. In general, geometry optimization for the clathrates was challenging. Most of the optimization calculations took a few hundred optimization steps and showed a convergence problem. Among the functionals used, achieving convergence using M06-HF was found to be more difficult than with others. All

Table 1
The calculated values of interaction energy (E_{int}) and the zero-point energy correction using the B3LYP, M06-L, M06-2X, M06-HF, BLYP-D3 functionals and the aug-cc-pVTZ basis set for the geometries optimized using the aug-cc-pVDZ basis set and the corresponding functionals. MP2* is taken from Ref. [39], while experimental (exp*) value (D_0) is taken from Ref. [40].

	E_{int} for $(H_2O)_2$ (kcal/mol)	ZPE-correction for E_{int} of $(H_2O)_2$ (kcal/mol)	E_{int} for the dodecahedral cage (kcal/mol)	ZPE-correction for E_{int} of $(H_2O)_{20}$ (kcal/mol)
B3LYP	−4.57	2.08	−185.58	51.88
M06-L	−4.74	2.09	−192.50	50.79
M06-HF	−5.23	2.86	−225.98	46.95
M06-2X	−5.19	2.55	−203.62	49.20
BLYP-D3	−5.02	2.04	−210.46	50.13
MP2*	−5.18	2.12	−200.1	52.0
exp*	−3.59			

Table 2
The calculated values of geometrical parameters for the dodecahedral water cage using the B3LYP, M06-L, M06-2X, M06-HF, BLYP-D3 density functionals and the aug-cc-pVDZ basis set. Values in parentheses correspond to the standard deviation.

	Diameter of the cage (Å)	$O_w \cdots O_w$ (Å)	$O_w \cdots H_w \cdots O_w$ (o)	$H_w \cdots O_w$ (Å)
B3LYP	7.759 (0.07)	2.77 (0.01)	175.99 (1.80)	1.79 (0.11)
M06-L	7.804 (0.06)	2.79 (0.09)	176.01 (1.94)	1.81 (0.10)
M06-HF	7.310 (0.13)	2.62 (0.11)	175.63 (2.15)	1.62 (0.14)
M06-2X	7.715 (0.08)	2.76 (0.10)	175.81 (2.02)	1.76 (0.12)
BLYP-D3	7.721 (0.06)	2.75 (0.09)	176.29 (1.82)	1.75 (0.11)
MP2	7.703 (0.06)	2.75 (0.10)	177.01 (1.59)	1.78 (0.16)

Table 3
The calculated values of E_{int} and mean absolute deviation (MAD) obtained using the B3LYP, M06-L, M06-2X, M06-HF, BLYP-D3 density functionals and the aug-cc-pVTZ basis set for the optimized geometry with the same functional using the aug-cc-pVDZ basis set. MP2* values are taken from Ref. [27]. MAD (mean absolute deviation) is a standard term in statistics. For present table data set X1, X2, ..., Xn, the MAD is defined as the median of the absolute deviations from the CCSD/CBS values.

	B3LYP (kcal/mol)	M06-L (kcal/mol)	M06-2X (kcal/mol)	M06-HF (kcal/mol)	BLYP-D3 (kcal/mol)	MP2*/CBS (kcal/mol)	CCSD/CBS (kcal/mol)
$H_2@(H_2O)_{20}$	0.82	−4.72	−2.18	−3.31	−1.59	−1.65	−1.28
$O_2@(H_2O)_{20}$	10.47	−10.61	−5.37	−5.84	−4.37	−6.88	−4.13
$N_2@(H_2O)_{20}$	2.45	−10.63	−5.71	−6.59	−5.65	−6.70	−4.74
$CO@(H_2O)_{20}$	2.44	−11.13	−6.17	−6.95	−6.41	−5.77	−4.36
$CO_2@(H_2O)_{20}$	3.47	−13.38	−9.49	−9.61	−8.32	−9.18	−7.16
$O_3@(H_2O)_{20}$	3.14	−14.05	−8.11	−8.20	−7.80	−9.33	−5.80
$CH_4@(H_2O)_{20}$	3.44	−11.79	−6.76	−6.98	−7.08	−6.14	−4.30
$NH_3@(H_2O)_{20}$	0.04	−12.43	−15.97	−9.81	−8.45	−8.11	−6.63
MAD	**8.08**	**6.29**	**2.67**	**2.36**	**1.41**		