

# Pentagonal dodecahedron methane hydrate cage and methanol system — An *ab initio* study

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**Abstract.** Density functional theory based studies have been performed to elucidate the role of methanol as a methane hydrate inhibitor. A methane hydrate pentagonal dodecahedron cage's geometry optimization, natural bond orbital (NBO) analysis, Mullikan charge determination, electrostatic potential evaluation and vibrational frequency calculation with and without the presence of methanol using WB97XD/6-31++G(d,p) have been carried out. Calculated geometrical parameters and interaction energies indicate that methanol destabilizes pentagonal dodecahedron methane hydrate cage ( $1\text{CH}_4@5^{12}$ ) with and without the presence of sodium ion. NBO analysis and red shift of vibrational frequency reveal that hydrogen bond formation between methanol and water molecules of  $1\text{CH}_4@5^{12}$  cage is favourable subsequently after breaking its original hydrogen bonded network.

**Keywords.** Density functional theory; natural bond orbital; red shift of vibrational frequency; electrostatic potential.

## 1. Introduction

Methane hydrate is a non stoichiometric compound pertaining to clathrate group and constructed by hydrogen bonded water molecules (host) lattice trapping methane gas (guest) inside the lattice. Huge accumulations of methane hydrate in sea bed near continental margin and underneath of permafrost region of arctic are considered to be potential future energy source.<sup>1</sup> Thus, methane hydrate has evolved into an important global research topic. Gas hydrate has three types of structures namely structure-I, structure-II and structure-H.<sup>2</sup> Unit cell of structure-I (S-I) has two pentagonal dodecahedron ( $5^{12}$ ) cages and six hexagonal truncated trapezohedron ( $5^{12}6^2$ ) cages. Structure II (S-II) unit cell has sixteen  $5^{12}$  cages and eight  $5^{12}6^4$  cages, where as structure H (S-H) has three  $5^{12}$  cages, two  $4^35^66^3$  cages, and one  $5^{12}6^8$  cage. Density functional study of diffusion and absorption of different guest molecules in various clathrate cages,<sup>3</sup> thermodynamic stability analysis of clathrate,<sup>4,5</sup> guest host interaction study of clathrate structure,<sup>6,7</sup> IR spectroscopy analysis of vibrational form of guest molecule inside clathrate cages<sup>8</sup> and molecular dynamics study of nucleation of methane

hydrate<sup>9–11</sup> have been performed by researchers. Gas hydrate formation in oil pipeline is of great concern for petroleum industry as it plugs the oil flow.<sup>12</sup> Restriction of hydrate plug formation can be achieved through adjusting gas hydrate phase equilibrium boundary by thermodynamic inhibitors<sup>13,14</sup> and lingering of gas hydrate nucleation by kinetic inhibitors<sup>13,15</sup> and anti-agglomerates.<sup>13</sup> Methanol is a thermodynamic inhibitor and its role for altering gas hydrate phase equilibria along with ethylene glycol and NaCl has been reported by Lee *et al.*<sup>16</sup> Relaxed geometry and vibrational spectra have been reported using *ab initio* simulation of one-one species water-methanol system by Bakkas *et al.*<sup>17</sup> Spectroscopic analysis, experimental and theoretical studies<sup>18–21</sup> of methanol water complex are also documented in literature. Detail theoretical analysis of methanol and clathrate cage configuration using *ab initio* method has not been reported so far. Impact of placing methanol on surface of the methane pentagonal dodecahedron hydrate cage with and without the presence sodium ion is investigated in this paper by analysing optimized structures, Mullikan charge distribution, electro static potential, natural bond orbital (NBO)<sup>22,23</sup> interaction and vibrational spectra. This work will help to understand electronic structure–property correlation based insight of methane hydrate inhibition characteristics of methanol.

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## 2. Theoretical background

Interaction energy ( $\Delta E$ ) for cluster formation has been determined using equation (1),

$$\Delta E = E_{CLUSTER} - \sum E_{COMPONENTS}, \quad (1)$$

where,  $E_{CLUSTER}$  and  $E_{COMPONENTS}$  are optimized energy of cluster and individual components, respectively. A structure is more stable if its interaction energy is more negative compared to other configurations. In case of NBO analysis, donor–acceptor interplay strength between filled orbital of the donor ( $\phi_i$ ) and the empty orbital of acceptor ( $\phi_j$ ) has been estimated by calculation of second order perturbation energy ( $\Delta E_{ij}^{(2)}$ ) using equation (2),

$$\Delta E_{ij}^{(2)} = 2 \frac{\langle \phi_i | F | \phi_j \rangle}{\varepsilon_i - \varepsilon_j}, \quad (2)$$

where,  $\varepsilon_i$  and  $\varepsilon_j$  are NBO energies,  $F$  is Fock matrix element between the  $i$  and  $j$  NBO orbitals. NBO analysis helps to understand intra and intermolecular interactions by providing details of interplays in filled as well as virtual orbital. It is a well-known method for analysing hyperconjugative interactions.<sup>24</sup> Hyperconjugation interaction at conventional hydrogen bond formation causes red shift in vibrational spectroscopy of hydrogen bonded structures.<sup>25</sup>

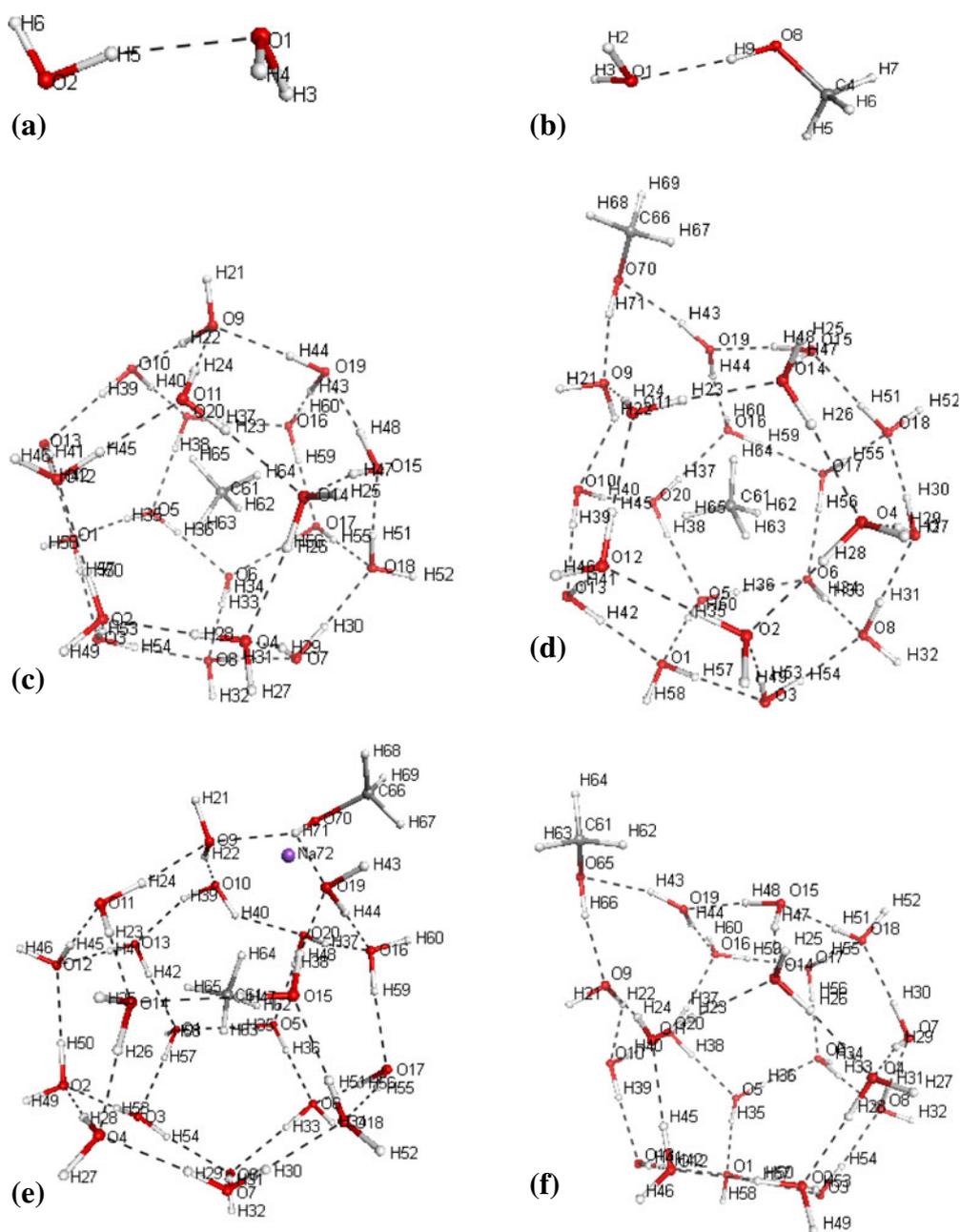
## 3. Simulation details

Geometry optimization of methane encapsulated pentagonal dodecahedron ( $1\text{CH}_4@5^{12}$ ) and methanol system have been performed by density functional theory using WB97XD/6-31G(d) and WB97XD/6-31++G(d,p) methods. Relaxed geometry of  $1\text{CH}_4@5^{12}$  and methanol cluster in the presence of sodium ion ( $\text{Na}^+$ ) has been calculated using WB97XD/6-31++G(d,p) level of theory: Vibrational spectra of  $1\text{CH}_4@5^{12}$  and methanol cluster has been simulated using WB97XD/6-31++G(d,p) method. WB97XD<sup>26</sup> functional incorporates the dispersion energy with Kohn–Sham density-functional theory<sup>27,28</sup> and uses unscaled correction of dispersion term. WB97XD functional is a good choice for density functional theory calculation of the hydrate clathrate system studied here, having van der Waals interactions. NBO analysis has been performed at WB97XD/6-31++G(d,p) level of theory. All the simulations have been carried out by using Gaussian 09 software package.<sup>29</sup> Visualization of molecules have been carried out in Discovery Studio

v3.1 of Accelrys Software Inc. Calculated vibrational frequency is scaled using scaling factor 0.975.<sup>30</sup>

## 4. Result and discussion

Optimized structure of water dimer, water–methanol system,  $1\text{CH}_4@5^{12}$  cage,  $1\text{CH}_4@5^{12}$ -methanol complex,  $1\text{CH}_4@5^{12}$ -methanol–sodium ion and  $5^{12}$ -methanol complex are shown in figure 1. It is observed that hydrogen bond between two water molecules (H21-O9-H22 and H43-O19-H44) of  $1\text{CH}_4@5^{12}$  (figure 1c) cage is broken in the presence of methanol. Methanol forms bifurcated hydrogen bonds (O70-H71...O9 and O70...H43-O19) with water molecules of pentagonal dodecahedron methane hydrate cage ( $1\text{CH}_4@5^{12}$ ) (figure 1d). Methanol in the presence of sodium ion ( $\text{Na}^+$ ) also deforms the cage structure. Hydrogen (H71) of the hydroxyl group of methanol is found to have formed hydrogen bonds (O70-H71...O9 and O70-H71...O19) with oxygen atoms of the nearby water molecules present in hydrate cage in the presence of sodium ion. The average and range of O–H bond length, hydrogen bond distance and hydrogen bonded angle (O–H...O) of  $1\text{CH}_4@5^{12}$  cluster with and without the presence of methanol, methanol and sodium ion are summarized in table 1. The calculated average values of O–H and hydrogen bond distance for  $1\text{CH}_4@5^{12}$  cage correspond well with the reported experimental values.<sup>31,32</sup>  $5^{12}$ -cage-methanol complex shows similar O–H bond lengths of water molecule, hydrogen bond distances and hydrogen bond angles as in  $1\text{CH}_4@5^{12}$ -methanol complex. It is identified after comparing the results of methanol-3 water ( $\text{M}_1\text{W}_3$ ) cluster studied using MP2/6-311++G(d,p) by Mandal *et al.*<sup>19</sup> and the results of methane hydrate ( $1\text{CH}_4@5^{12}$ ) investigated here using WB97XD/6-31++G(d,p) and WB97XD/6-31G(d,p) the calculated ranges of O–H bond lengths are almost same for  $1\text{CH}_4@5^{12}$  methane hydrate and  $\text{M}_1\text{W}_3$  cluster (i.e. 0.976 Å–0.981 Å) but the calculated ranges of hydrogen bond distance and hydrogen bond angle of  $1\text{CH}_4@5^{12}$  are of little larger values in comparison with those ranges of  $\text{M}_1\text{W}_3$  cluster (i.e. hydrogen bond distance range 1.745 Å–1.791 Å and hydrogen bond angle range 165.7°–167°). An increment on average value of O–H bond lengths in the presence of methanol and methanol- $\text{Na}^+$  as per WB97XD/6-31++G(d,p) calculation are observed. Maximum value of hydrogen bond distances are increased in the presence of methanol and methanol-sodium ion. As a consequence, some hydrogen bonds of  $1\text{CH}_4@5^{12}$  near methanol and methanol–sodium become weaker. It is found that the range of hydrogen bonded angle



**Figure 1.** Optimized structure using 6-31++G(d,p)/WB97XD of (a) water dimer, (b) water-methanol complex, (c)  $1\text{CH}_4@5^{12}$  cage, (d)  $1\text{CH}_4@5^{12}$  cage and methanol system and (e)  $1\text{CH}_4@5^{12}$  cage and methanol-sodium ion system, (f)  $5^{12}$  cage- methanol complex (colour-legend: red  $\rightarrow$  oxygen; black  $\rightarrow$  carbon; whitish grey  $\rightarrow$  oxygen; violet  $\rightarrow$  sodium).

(O–H...O) is significantly broadened and standard deviation is very high for  $1\text{CH}_4@5^{12}$  - methanol– $\text{Na}^+$  cluster compared to  $1\text{CH}_4@5^{12}$  structure (table 1). This also suggests that the cage structure is distorted in the presence of methanol– $\text{Na}^+$ .

Interaction energies are mentioned in table 2 for all three  $1\text{CH}_4@5^{12}$  cage,  $1\text{CH}_4@5^{12}$ -methanol cluster and  $1\text{CH}_4@5^{12}$ -methanol– $\text{Na}^+$  cluster systems. Formation of  $1\text{CH}_4@5^{12}$  cage is favourable and stable because interaction energy of relaxed undistorted

structure of  $1\text{CH}_4@5^{12}$  cage is founded to be negative at WB97XD/6-31++G(d,p) calculations. The deformed structure of  $1\text{CH}_4@5^{12}$  cage is found to be stable in the presence of methanol and methanol–sodium ion, as the interaction energies for both the cases are negative for the deformed structures obtained after optimization. It is obvious that methanol alone as well as along with sodium ion distorts  $1\text{CH}_4@5^{12}$  cage and prone to inhibit methane hydrate formation. It is observed from table 2 that the calculated interaction

**Table 1.** Calculated average O–H bond length and H bond distance along with their ranges. (Standard deviation is given in parenthesis.)

Systems	Basis set	O–H bond length (Å)			H–bond distance (Å)			H–bonded angle (°)		
		Range	Avg.	Exp.	Range	Avg.	Exp.	Range	Avg.	
1CH <sub>4</sub> @5 <sup>12</sup>	6-31G(d)	0.963–0.996	0.976 (0.009)	0.861 (ref. 31, 32)	1.881–1.997	1.919 (0.037)	1.911 (ref. 31, 32)	169.9–180.0	175.6 (2.4)	
		0.960–0.991	0.971 (0.008)		1.878–2.008	1.927 (0.031)		165.8–178.0	173.5 (3.2)	
1CH <sub>4</sub> @5 <sup>12</sup> -methanol cluster	6-31G(d)	0.964–0.994	0.976 (0.009)		1.878–1.996	1.920 (0.034)		167.8–179.2	174.6 (3.1)	
		0.960–0.988	0.972 (0.008)		1.892–2.084	1.928 (0.045)		167.3–179.0	174.7 (3.1)	
1CH <sub>4</sub> @5 <sup>12</sup> -methanol cluster and Na+	6-31++G(d)	0.962–0.991	0.973 (0.008)		1.876–2.112	1.930 (0.049)		158.8–178.9	173.9 (4.6)	
		0.961–0.988	0.972 (0.008)		1.813–2.085	1.922 (0.050)		139.3–179.0	172.8 (8.2)	

**Table 2.** Interaction energy for different cluster using WB97XD functional and 6-31++G(d,p) basis set.

Systems	Interaction energy (kcal/mol)
1CH <sub>4</sub> @5 <sup>12</sup>	–7.32
1CH <sub>4</sub> @5 <sup>12</sup> -methanol cluster	–21.17
1CH <sub>4</sub> @5 <sup>12</sup> -methanol-Na+ cluster	–94.96
Empty 5 <sup>12</sup> -methanol cluster	–21.83

energy (–21.17 kcal/mol) for 1CH<sub>4</sub>@5<sup>12</sup>-methanol cluster using WB97XD/6-31++G(d,p) is comparable with the literature reported interaction energies (i.e., –22.00 kcal/mol by HF/6-311++G(d,p) and –24.85 kcal/mol by MP2/6-311++G(d,p) calculation) for M<sub>1</sub>W<sub>3</sub> cluster.<sup>19</sup> The interaction energies of empty 5<sup>12</sup>-methanol cluster and 1CH<sub>4</sub>@5<sup>12</sup>-methanol cluster are found to be almost same as evident in table 2.

Calculated values of Mullikan charges and electrostatic potentials of selective hydrogen bond forming atoms (as shown in figure 1) using WB97XD/6-31++G(d,p) level of theory are listed in table 3. The absolute Mullikan charge difference of O9 and H44 of 1CH<sub>4</sub>@5<sup>12</sup> cage is decreased from 1.26 a.u. to 1.21 a.u. in the presence of methanol and to 1.22 a.u. in the presence of methanol-Na<sup>+</sup>. The absolute electrostatic potential difference of O9 and H44 of 1CH<sub>4</sub>@5<sup>12</sup> cage is decreased from 21.31 a.u. to 21.26 a.u. in the presence of methanol. The decrease of Mullikan charge difference as well as electrostatic potential difference between O9 and H44, in the presence of methanol causes breaking of hydrogen bond between them originally there in 1CH<sub>4</sub>@5<sup>12</sup> cage. It is observed that absolute Mullikan charge difference between O9 of 1CH<sub>4</sub>@5<sup>12</sup> cage and H71 of methanol is 1.25 a.u. and 1.34 a.u. for 1CH<sub>4</sub>@5<sup>12</sup>-methanol and 1CH<sub>4</sub>@5<sup>12</sup>-methanol-Na+ systems, respectively, which are higher than Mullikan charge difference of O9 and H44 atoms of 1CH<sub>4</sub>@5<sup>12</sup> cage in the presence of methanol as well as methanol and sodium ion. As a result it is observed that hydrogen bond between O9 and H44 atoms in 1CH<sub>4</sub>@5<sup>12</sup> (figure 1c) has broken and a hydrogen bond is formed between O9 and H71 atoms in the presence of methanol (figure 1d). It is also identified that absolute Mullikan charge differences between O19 and H71 are 1.32 a.u. in 1CH<sub>4</sub>@5<sup>12</sup> cage-methanol system and 1.36 a.u. in 1CH<sub>4</sub>@5<sup>12</sup> cage-methanol-Na<sup>+</sup> system. Thus, hydrogen bond (O70-H71...O19) formation between O19 and H71 in the presence of sodium ion is more favourable. The calculated second order perturbation energies of some

**Table 3.** Calculated Mullikan charge difference and electrostatic potential difference (a.u.) of some selective hydrogen bond forming atoms using WB97XD/6-31++G(d,p).

Selective atoms	Mullikan charge difference			Electrostatic potential difference	
	1CH <sub>4</sub> @5 <sup>12</sup> cage	1CH <sub>4</sub> @5 <sup>12</sup> cage + methanol	1CH <sub>4</sub> @5 <sup>12</sup> cage + methanol + Na <sup>+</sup>	1CH <sub>4</sub> @5 <sup>12</sup> cage	1CH <sub>4</sub> @5 <sup>12</sup> cage + methanol
O9 and H44	1.26	1.21	1.22	21.31	21.26
O9 and H71		1.25	1.34		21.26
O19 and H71		1.32	1.36		

selective donor and acceptor interaction from NBO analysis using 6-31++G(d)/WB97XD are shown in table 4. The presence of donor–acceptor interplays are obvious from the calculated second order perturbation energy ( $\Delta E_{ij}^{(2)}$ ) values of 1CH<sub>4</sub>@5<sup>12</sup> and 1CH<sub>4</sub>@5<sup>12</sup>-methanol configurations. It is found from NBO analysis that the interactions of lone pair of oxygen atom with the anti bonding orbital of O–H of water molecules are common donor–acceptor types in 1CH<sub>4</sub>@5<sup>12</sup> and 1CH<sub>4</sub>@5<sup>12</sup>-methanol clusters. Calculated second order perturbation energy values of donor–acceptor interactions (table 4) is found to be higher for hydrogen bond forming oxygen (O19) atom and hydroxyl part (O15-H48<sup>-</sup>) of 1CH<sub>4</sub>@5<sup>12</sup> cluster than hydrogen bond forming oxygen atom (O1) and hydroxyl part (O2-H5<sup>-</sup>) of water dimer. This is due to hydrogen bond effect between water molecules in 1CH<sub>4</sub>@5<sup>12</sup> cluster. This hydrogen bond cooperativity strengthens the hydrogen bonded network of 1CH<sub>4</sub>@5<sup>12</sup> cage and consequently stabilizes the clathrate cage. Second order perturbation energy ( $\Delta E_{ij}^{(2)}$ ) for donor–acceptor interaction between one oxygen of 1CH<sub>4</sub>@5<sup>12</sup> cluster and O–H anti bonding orbital of methanol is 19.32 kcal/mol, more than that of the donor–acceptor interaction between one oxygen of single water and O–H anti bonding orbital of methanol.

It is also found that the second order perturbation energy ( $\Delta E_{ij}^{(2)}$ ) for donor–acceptor interaction

between O19 and OH<sup>-</sup> (O15-H48) anti bonding orbital of 1CH<sub>4</sub>@5<sup>12</sup> cluster decreases from 14.43 kcal/mol to 0.08 kcal/mol in the presence of methanol. Methanol actually weakens the nearby hydrogen bond (e.g., H48-O15...O19) between water molecules of 1CH<sub>4</sub>@5<sup>12</sup> cluster. It is also noted from NBO analysis that hydrogen bond formation between methanol and water molecules of 1CH<sub>4</sub>@5<sup>12</sup> cage is favourable after breaking original hydrogen bonded network of 1CH<sub>4</sub>@5<sup>12</sup> structure.

Calculated vibrational frequencies of O–H stretching in water, methanol, water dimer, water methanol cluster, 1CH<sub>4</sub>@5<sup>12</sup> cage and 1CH<sub>4</sub>@5<sup>12</sup>-methanol cluster are summarized along with some experimental values in table 5. It is observed that red shifts of O–H vibrational frequencies for all the clusters are taken place due to the formation of hydrogen bonded network. The calculated red shifts of stretching vibration of O–H bond of water molecule for water dimer, water–methanol cluster, 1CH<sub>4</sub>@5<sup>12</sup> cage and 1CH<sub>4</sub>@5<sup>12</sup>-methanol cluster are 77 cm<sup>-1</sup>, 35 cm<sup>-1</sup>, 252 cm<sup>-1</sup>, 243 cm<sup>-1</sup>, respectively. These red shifts of vibrational frequencies are the consequence of hyperconjugation interaction for conventional hydrogen bond formation. It is found that red shift of O–H stretching of water molecule is highest in 1CH<sub>4</sub>@5<sup>12</sup> cage. Hydrogen bond cooperativity effect increases from dimer water to 1CH<sub>4</sub>@5<sup>12</sup> cage and consequently stabilizes 1CH<sub>4</sub>@5<sup>12</sup> cage. It is also found that the red shift of O–H stretching of water molecule in 1CH<sub>4</sub>@5<sup>12</sup>-methanol cluster is

**Table 4.** Calculated second order perturbation energy ( $\Delta E_{ij}^{(2)}$ , kcal/mol) using WB97XD/6-31++G(d,p).

Donor NBO	Acceptor NBO	$\Delta E_{ij}^{(2)}$ water dimer	$\Delta E_{ij}^{(2)}$ water-methanol	$\Delta E_{ij}^{(2)}$ 1CH <sub>4</sub> @5 <sup>12</sup>	$\Delta E_{ij}^{(2)}$ 1CH <sub>4</sub> @5 <sup>12</sup> -methanol
LP(2)O1	BD*(1)O2-H5	13.62			
LP(2)O1	BD*(1)O8-H9		16.08		
LP(2)O19	BD*(1)O15-H48			14.43	0.08
LP(2)O9	BD*(1)O70-H71				19.32

**Table 5.** Calculated vibrational frequency ( $\text{cm}^{-1}$ ), red shift ( $\text{cm}^{-1}$ ), IR intensity ( $\text{km}\cdot\text{mol}^{-1}$ ) and experimental values (in  $\text{cm}^{-1}$ ) of O–H bond stretching using WB97XD/6-31++G(d,p).

Systems	O–H stretching of water			O–H stretching of methanol		Exp. vibrational frequency
	Scaled freq. ( $\text{cm}^{-1}$ )	Red shift ( $\text{cm}^{-1}$ )	IR intensity ( $\text{km}\cdot\text{mol}^{-1}$ )	Scaled freq. ( $\text{cm}^{-1}$ )	Red shift ( $\text{cm}^{-1}$ )	
Water	3802		8.2			3756 (ref. 33)
Methanol				3840		
Water dimer	3587	215	344.4			3601 (refs 33, 34)
Water–methanol	3767	35		3697	143	
1CH <sub>4</sub> @5 <sup>12</sup>	3550	252	1286.6			3300 (ref. 8)
1CH <sub>4</sub> @5 <sup>12</sup> -methanol	3559	243	807.5	3587	253	
Empty 5 <sup>12</sup> -methanol cluster	3610	192	356.5	3588	252	

less than that of 1CH<sub>4</sub>@5<sup>12</sup> cage. The calculated red shifts of O–H stretching of methanol in water methanol complex (MW) i.e., 143  $\text{cm}^{-1}$  using WB97XD/6-31++G(d,p) in this paper and 87  $\text{cm}^{-1}$  obtained by Mandal *et al.*<sup>19</sup> using MP2/6-311++G(d,p), are less than the red shift of O–H stretching of methanol (253  $\text{cm}^{-1}$ ) obtained here in 1CH<sub>4</sub>@5<sup>12</sup>-methanol cluster using WB97XD/6-31++G(d,p). Methanol makes stronger hydrogen bond with water molecules of 1CH<sub>4</sub>@5<sup>12</sup> cage than single water molecule. The calculated frequency value (i.e., 3587  $\text{cm}^{-1}$ ) for hydrogen bonded O–H bond of water dimer using WB97XD/6-31++G(d,p) is very close to experimental value (i.e., 3601  $\text{cm}^{-1}$ )<sup>33,34</sup> in comparison to the reported calculated values of 3732  $\text{cm}^{-1}$  at MP2/6-311++G(d,p) by Mandal *et al.*<sup>19</sup> and 3584.6  $\text{cm}^{-1}$  at CCSD(T)/AVQZ by Schofield *et al.*<sup>35</sup> The red shift for hydrogen bonded O–H bond of water dimer calculated using WB97XD/6-31++G(d,p) here (i.e., 215  $\text{cm}^{-1}$ ) is more when compared to red shift value of 31  $\text{cm}^{-1}$  obtained by Mandal *et al.*<sup>19</sup> using MP2/6-311++G(d,p). The red shift as well as intensity of O–H stretching for water molecule in empty 5<sup>12</sup>-methanol cluster are less compared to that of O–H stretching for water molecule in 1CH<sub>4</sub>@5<sup>12</sup>-methanol. However, the presence of encapsulated methane molecule hardly affects the red shift of O–H stretching of methanol in 5<sup>12</sup> cage -methanol cluster, as evident in table 5. The calculated scaled vibrational frequency values of O–H stretching of water molecule, water dimer and pentagonal dodecahedron methane hydrate cage are in agreement with the corresponding experimental values.<sup>8,33,34</sup> Calculated IR intensities of O–H stretching are in order of water molecule (8.2  $\text{km}\cdot\text{mol}^{-1}$ ) < water dimer (344.4  $\text{km}\cdot\text{mol}^{-1}$ ) < 1CH<sub>4</sub>@5<sup>12</sup>-methanol cluster (807.5  $\text{km}\cdot\text{mol}^{-1}$ ) < 1CH<sub>4</sub>@5<sup>12</sup> cage (1286.6  $\text{km}\cdot\text{mol}^{-1}$ ) cage are also presented in table 5. The rise in IR intensity

of O–H stretching of water molecule in these hydrogen bonded systems are due to the increased ionic character of O–H normal mode as proposed by Barrow.<sup>36</sup> According to some other researchers,<sup>37,38</sup> this type of rise in IR intensity is due to charge transfer. Hydrogen bonds among water molecules of 1CH<sub>4</sub>@5<sup>12</sup> cage become weaker in the presence of methanol as revealed by the higher IR intensity of O–H stretching (of water molecule) in 1CH<sub>4</sub>@5<sup>12</sup> cage than that of 1CH<sub>4</sub>@5<sup>12</sup>-methanol cluster.

## 5. Conclusions

First principle based calculation has been performed to explain scientifically the role of methanol as inhibitor of methane hydrate. Calculated interaction energies and geometrical parameters reveal that methanol decreases the stability of pentagonal dodecahedron methane hydrate cage (1CH<sub>4</sub>@5<sup>12</sup>) with and without the presence of sodium ion. Studies of Mullikan charges, electrostatic potentials and NBO analysis elucidate that hydrogen bond formation between methanol and water molecules of 1CH<sub>4</sub>@5<sup>12</sup> cage is more favourable. The calculated scaled vibrational frequency values of O–H stretching of water monomer, water dimer and pentagonal dodecahedron methane hydrate cage are in agreement with the corresponding experimental values. Encapsulated methane in 5<sup>12</sup> cage -methanol complex does not affect the geometrical parameters, interaction energy and red shift for O–H bond stretching of water molecule. The presence of methanol decreases the hydrogen bond strength and consequently stability of 1CH<sub>4</sub>@5<sup>12</sup> cage, as revealed by NBO analysis, red shift and IR intensity of vibrational frequency studies. This work could help to conceptualize the role of methanol inhibitor for methane hydrate and the compendium of

this work can be extended to bring insight into electronic structure–property correlation based understanding of different methane hydrate inhibitors.

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