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Steric and Electronic Effects in the Host–Guest Hydrogen Bonding in Clathrate Hydrates

Waldemar Kulig,[†] Piotr Kubisiak,[†] and Lukasz Cwiklik*,[‡,§]

[†]K. Gumiński Department of Theoretical Chemistry, Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30060 Krakow, Poland

[‡]J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic v.v.i., Dolejskova 3, 18223 Prague 8, Czech Republic

[§]Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic v.v.i., and Center for Complex Molecular Systems and Biomolecules, Flemingovo nám. 2, 16610 Prague 6, Czech Republic

ABSTRACT: Clathrate hydrates with polar guest molecules (dimethyl ether, ethylene oxide, trimethylene oxide, tetrahydrofuran, and tetrahydropyran) were studied by means of the density functional theory. A model of a large cage of structure-I clathrate was employed. Optimal configurations of encaged guests were investigated with a focus on the host–guest hydrogen bond formation. Weak hydrogen bonds were found to be formed by each guest, while for THP a strong hydrogen bond and formation of L-defect was also observed. This is in accord with previous computational and experimental stud-

ies. Steric factors were shown to play a key role for the strength of the hydrogen bond formed. Interestingly, the host–guest binding is influenced not only by the size of a guest molecule but also by its shape. This work demonstrates that both electronic and steric properties of a polar guest should be considered for a full description of clathrate systems.
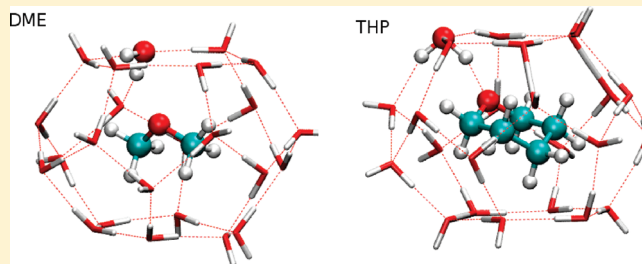
1. INTRODUCTION

Clathrate hydrates are formed typically by water accompanied with hydrophobic nonpolar guest molecules under low-temperature and high-pressure conditions.[1] In such clathrates host water molecules form a hydrogen-bond network with cages in which the hydrophobic guests reside. The guest molecules interact weakly and nonspecifically with water molecules located at cage walls. Nevertheless, some hydrophilic polar molecules, usually accompanied by a hydrophobic partner, are also capable of forming clathrate hydrates. These "nonclassical" clathrates exhibit unusual properties, for example, low dielectric reorientation activation energy and high activation energy of guest reorientation with regard to the "classical" clathrates.[2] Surprisingly, clathrates with polar guests can be formed at relatively low temperature (<100 K) and at low pressure (<1 Torr).[3] These unusual properties were explained as a result of the injection of orientational Bjerrum defects into the structure of clathrates and creation of hydrogen bonds between guest molecules and host water.[4]

Clathrate hydrates with polar guests were recently a subject of intensive studies, both experimental and computational, some of which are reported in a review by Buch et al.[5] Different classes of guest molecules were investigated including alcohols, ketones, and amines.[6,7] However, the main attention was directed toward clathrates with ether and oxide guest molecules.[5] A series of such clathrates was studied computationally by employing empirical potentials by Alavi and co-workers where creation of hydrogen bonds between ether molecules and host water was found for

both tetrahydrofuran (THF) and tetrahydropyran (THP) guests.[8] Guest–host hydrogen bonds in the case of THF were experimentally studied by Conrad et al.[9] It is worthwhile to note that, in addition to typical guest–water hydrogen-bonded structures, new types of configurations were found in the presence of ethers. Namely, structures formed by two guest molecules that reside in neighboring cages and that interact via hydrogen bonds with water molecules in the intercage wall were reported by us on the basis of both experimental and computational results for the mixed clathrate of dimethyl ether (DME) with HCN.[10] Along with the structural properties also the remarkably fast creation kinetics of clathrates with hydrogen-bonding guests as well as their ability to exchange guest molecules were investigated.[5,11]

These recent studies confirm Davidson's hypothesis that polar guest molecules are capable of forming guest–host hydrogen bonds.[4] In most cases (e.g., ethers or oxides) the guest molecules act as hydrogen bond acceptors whereas host water molecules are hydrogen bond donors, although the opposite situation is possible (e.g., for clathrates with alcohol guests). However, in spite of many similarities, the clathrates with hydrogen bonding guests differ in both their macro- and microscopic properties. An example of the remarkable differences at the macroscopic scale

are diverse formation rates that strongly depend on the type of an ether guest.[11] At the microscale these dissimilarities include both structural and dynamic properties. First, the strength of the formed hydrogen bonds varies among the polar guests. It is manifested in the different local structure of these bonds (i.e., hydrogen—oxygen distance, localization of the bonding site in the cage, number of water molecules participating in the bonding), their different lifetimes, and the temperature dependence. For example, at 150 K in the structure-II cages THP forms relatively strong hydrogen bonds with the donor—acceptor distance of about 1.6 Å whereas much weaker host—guest interactions are observed for THF under the same conditions.[8] Regarding the influence of the temperature, for instance, in the structure-H mixed *tert*-butyl methyl ether + methane clathrate the number of host—guest bonds decreases between 100 and 250 K whereas the opposite tendency is observed for pinacolone + H_2S guests.[12,7]

The two most important factors employed to rationalize the above differences are the diversity of the guest molecules dipole moments and differences in their molecular size. Whereas the influence of the dipole moment on the extent of host—guest bonds creation seems obvious, the role of the molecular size is elusive. Generally, the larger size of guest molecules should promote hydrogen bonding with water, as the distance between acceptor and donor atoms is shortened (this is the case for THP when compared with the relatively smaller THF). However, as will be shown here, the relation between the size of a guest molecule and the tendency for hydrogen bond formation is not straightforward.

Here, we study host—guest interactions for a series of ethers and oxide guest molecules enclosed in a large cage of structure I clathrate. We employ density functional theory (DFT) calculations to look for preferred guest configurations and for the details of host—guest bonding. In particular, we analyze the role and interplay between the steric and electronic effects. Previous theoretical studies of guest orientation and host—guest interactions in the presence of hydrogen bonding guest in clathrates were conducted mainly by employing empirical potentials, one of few DFT studies is the recent work of Conrad and co-workers regarding clathrates with THF.[9] The DFT approach, in comparison with empirical potential simulations, is limited to a relatively small size of the system under study (a single clathrate cage, in our case). However, in contrast to the empirical methodology, it allows us to directly describe the host—guest bonds formation due to inclusion of the electronic effects.

2. COMPUTATIONAL METHODS

The structure of a representative $5^{12}6^2$ clathrate cage was taken from our previous study in which the structure-I mixed clathrate of ethylene oxide and carbon monoxide employing polarizable empirical potential was investigated.[13] The cage corresponds to a large cage of structure-I clathrate hydrate and it consists of 24 water molecules. To account for the finite-temperature structure of host water, the structure of the cage was taken from a molecular dynamics trajectory performed at 108 K. Thus the hydrogen-bond structure was distorted, reflecting the thermal motion of water; however, no Bjerrum-type defects were present. We studied five guest molecules (see Figure 1): dimethyl ether (DME), ethylene oxide (EO), trimethylene oxide (TMO), tetrahydrofuran (THF), and tetrahydropyran (THP). According to previous experimental studies, three of the guests: DME, TMO, and THP form both structure-I and structure-II clathrates.[5,14] EO forms only structure-I, and THF forms only structure-II clathrate.[11,15] In experiments, the type of the clathrate structure formed is both temperature and


Figure 1. Polar guest molecules considered in this study: dimethyl ether (DME), ethylene oxide (EO), trimethylene oxide (TMO), tetrahydro-furan (THF), and tetrahydropyran (THP).

pressure dependent, it is also influenced by the presence of other guest molecules. Here, to study all guests in the same type of structure, the cage of structure-I was chosen.

The geometry of guest molecules was optimized in the gas phase. Subsequently, each molecule was placed in the clathrate cage of 24-water and the geometry of the whole system was optimized. For each guest molecule few randomly chosen initial orientations in the cage were generated and optimized. Among these structures, the configurations containing L-defects were also present. Upon optimization, the three lowest-energy structures were chosen for further analysis. Note that all initial L-defects were annihilated in the course of optimization. During optimization the positions of oxygen atoms of water molecules were restrained. It allowed us for conserving the clathrate structure of the cage during optimization and, at the same time, enabled us to account for both water—water and water—guest hydrogen bonds making/breaking. A similar method, i.e., re-straining positions of water oxygen atoms in the crystal structure, was employed in our previous study of ionic defects in hexagonal ice.[16] Geometry optimizations were performed with the RI-DFT+D method employing the BLYP functional[17,18] with the dispersion correction of Grimme[19] and the SVP split-valence basis set.[20] We want to note here that we found negligible structural differences comparing optimization both with and without the dispersion correction. Resolution-of-identity (RI) approximation was used to shorten computational time.[21] Upon optimization with the BLYP functional all structures were further optimized by employing the B3LYP hybrid functional. To compare guest—water hydrogen bonding in the clathrate cage with that in the gas phase, additional geometry optimizations of dimers of each guest molecule with a single water molecule were performed. Calculations were completed using the TURBO-MOLE 6.1 software package.[22] The choice of the computational method, i.e., the DFT with the BLYP functional and the double-ζ type of the basis set was rationalized by its good performance in our previous studies of clathrate systems.[5] Here, we additionally employed the hybrid-type B3LYP functional and the empirical correction for the dispersion interactions for a better description of guest—host interactions in the clathrate cage. It is worthwhile to note that the basis set superposition error (BSSE) was not playing an important role in the present study because the relative energies between the structures containing the same number of atoms were compared, and the changes in the system geometry involved only reorientation of guests in the cage. However, our test calculations (results not shown here) demonstrate that BSSE is significant if calculations of the guest—cage interaction energy are of interest, and augmented basis sets should be employed for such calculations.

3. RESULTS AND DISCUSSION

Optimized structures with guest molecules in a large cage of a structure-I clathrate are depicted in Figure 2. The $5^{12}6^2$ cage is

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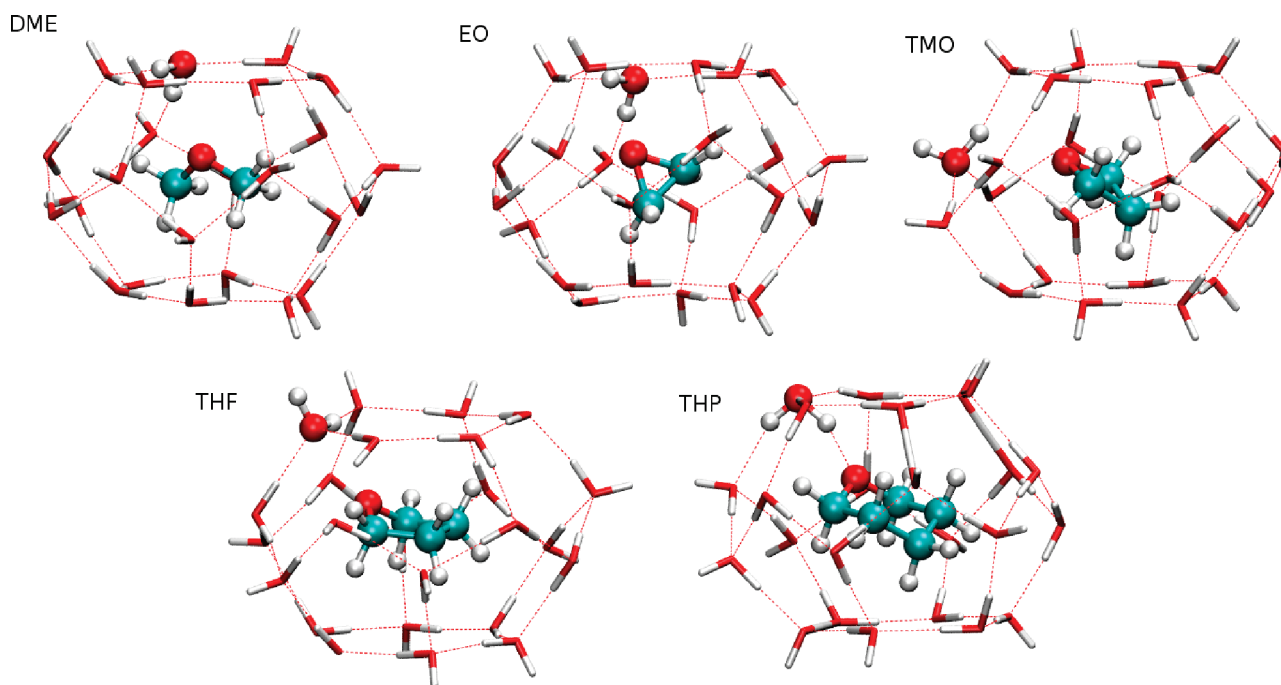
Figure 2. Optimized systems with guest molecules in a large cage of structure-I clathrate. For each guest the lowest-energy minimum is shown with the exception of THF where the system with an L-defect and the strong hydrogen bond is presented. Color coding: red, oxygen; white, hydrogen; blue, carbon. The guest molecules and the water molecules with which the host–guest bond is formed are highlighted.

anisotropic and consists of two six-membered rings and twelve five-membered rings. A comparison of optimized systems shows that orientational preference varies among the guests. For dimethyl ether in two cases the guest molecule prefers an orientation with its oxygen atom pointing toward a six-membered ring, and in one case it points toward an O–H bond formed by an O-atom shared between two five-membered rings. For both ethylene oxide and trimethylene oxide another orientation is preferred, namely, with the guest's oxygen atom pointing toward an O–H bond formed by O-atom shared between a six-membered and a five-membered ring. For tetrahydrofuran the oxygen atom of a guest molecule points preferentially toward one of five-membered rings. In the case of tetrahydropyran, either the five-membered ring or one of the O–H bonds between the five-membered rings is preferred.

In the majority of optimized structures we observed the creation of one weak hydrogen bond formed between the oxygen atom of a guest and a hydrogen atom of one of water molecules from the cage. The water molecules that form these hydrogen bonds are reoriented to shorten the H–O distance to the guest; however, in every case the hydrogen atom that points toward the guest is also donated toward the neighboring water molecule. In other words, one original host–host hydrogen bond is slightly weakened and a new weak host–guest hydrogen bond is formed. Notably, in one optimization for THP we observed spontaneous creation of an L-defect in the structure of water accompanied by creation of a strong host–guest hydrogen bond (with an acceptor–donor distance equal to 1.65 Å). In Table 1 the closest host–guest H–O distances calculated for each optimized structure are presented along with the relative energies of the structures and the average values of the closest H–O distance. To compare host–guest hydrogen bonds formed in the clathrate cage with hydrogen bonds formed in the gas phase, we optimized dimer structures, each consisting of one guest molecule and a

single molecule of water. The values of H–O distances and energies in these clusters are presented in Table 1. There are no large energy differences between the optimized structures. Most of them vary by ≤4 kcal/mol with the exception of two structures for THF and THP where the energy varies by 7 and 8 kcal/mol, correspondingly. It proves that the orientational minima for considered guests are relatively shallow and thus many minima would probably be populated at finite temperature. The larger energy spread for THF and THP results, most likely, from relatively big sizes of these two molecules. Interestingly, the structure with the L-defect created in the presence of THP is not the lowest-energy one, it is about 2 kcal/mol above the minimum found for THP.

In Figure 3 average values of H–O distance in the clathrate cage are presented, the corresponding distances calculated in dimers are shown for comparison. There is a clear trend in the average length of host–guest hydrogen bond—it lengthens in a row: THP < THF < TMO < EO < DME. Assuming that the strength of the hydrogen bond increases with the decrease of the bond length, the studied guests can be ordered with the increasing strength of host–guest hydrogen bonding as follows: THP > THF > TMO > EO > DME. Noteworthy, significant differences in the hydrogen bond length occur between encaged systems and dimers. Namely, for each guest the H–O length in the dimer (1.86–1.92 Å) is always shorter than that in the cage; moreover, the length of hydrogen bond in dimers does not significantly vary for considered guests (up to 0.06 Å). The only exception is the system with an L-defect, the hydrogen bond length is in that case in a range of the corresponding bond length in the dimer.

On the basis of the comparison between dimers and the cage, we can conclude that relatively large differences in H–O distances in the host–guest hydrogen bond originate mainly from steric effects. For three of the guests, TMO, THF, and THP, which have molecules comparable in size with the diameter of the

Table 1. Values of Distances between the Oxygen Atom of Guest Molecules and the Hydrogen Atom of the Water Molecule with Which the Host–Guest Hydrogen Bond Is Formed (r_{OH}) for Three Optimized Structures (S1, S2, S3) for Each Encaged Guest[a]

guest	dipole moment (D)	r_{OH} dimer	r_{HO} in cage (Å); relative energy in parentheses (kcal/mol)		
			S1	S2	S3
DME	1.1	1.90	2.90 (0.0)	2.90 (2.7)	2.72 (0.9)
EO	1.8	1.92	2.51 (0.0)	2.69 (0.9)	2.71 (1.4)
TMO	1.8	1.86	2.41 (0.0)	2.47 (3.0)	2.41 (2.6)
THF	1.7	1.86	2.39 (0.0)	2.45 (0.1)	2.30 (7.1)
THP	1.3	1.85	2.45 (0.0)	1.65 (2.1)	2.46 (8.4)

[a] The calculated relative energy of the structures is also presented. Corresponding H–O distances in dimers are given. The values of the molecular dipole moment of guest molecules are also shown.
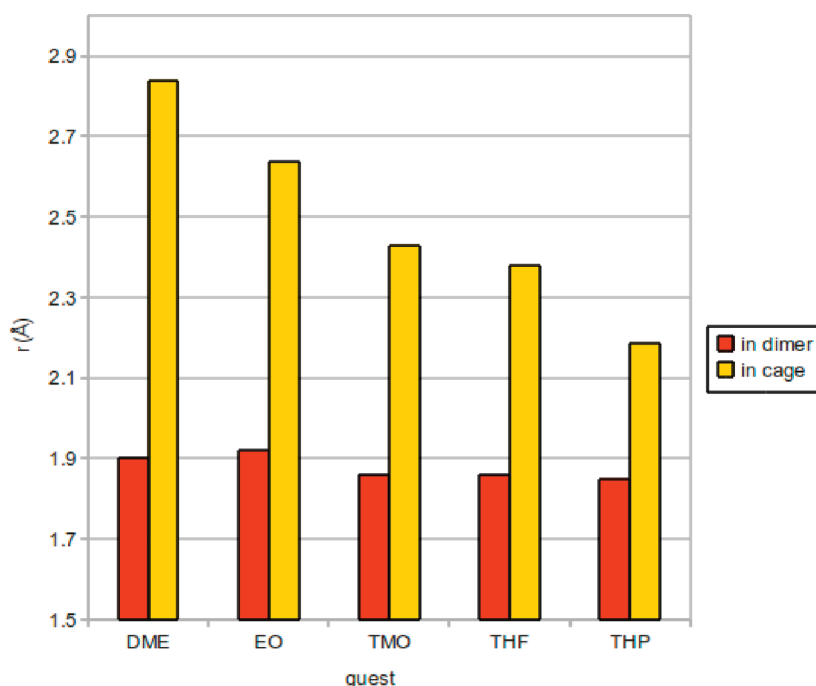
Figure 3. Hydrogen–oxygen distances in hydrogen bonds formed between the hydrogen atom of water and the oxygen atom of each guest molecule. For clathrate cages an average value from three optimized structures is shown.

cage, a relatively strong repulsion between methylene groups of the carbon ring and the cage occurs. This repulsion promotes the shortening of the distance between the oxygen atom of the guest and the hydrogen atom of host water; thus this distance is shorter for these bulky guests than for the remaining molecules under study. In the case of THP the steric repulsion leads to such a significant strength of the oxygen–hydrogen interaction that a strong hydrogen bond is formed with an L-defect in the host water structure. A comparison between the case of encaged DME and EO demonstrates another type of a steric effect influence. As depicted in Figure 4, these molecules differ significantly in the value of C–O–C angle and thus their shapes differ. The DME molecule is effectively more "bulky" than the molecule of EO. As a result, the relatively big methyl groups are limiting the DME molecule in its approach to the clathrate cage walls. This also seems to be a reason for a preferential orientation of DME oxygen atom toward a six-membered ring—such a configuration minimizes the distances between methyl groups and water. EO molecule is relatively more compact and thus is able to easier approach the cage walls. As a consequence, the O–H distance is on average shorter for EO than for DME. The comparison
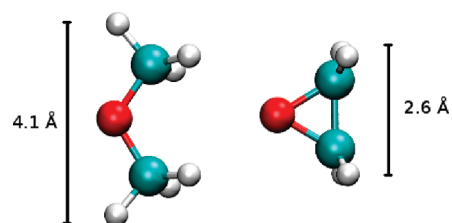
Figure 4. Comparison of the molecular size of DME (left) and EO (right). The relatively high value of the C–O–C angle in DME results in a larger size of the molecule and stronger steric effects in the clathrate cages due to the repulsion between methyl groups and host water.

between small and large guests shows that the steric repulsion for large guests promotes the shortening of the host–guest hydrogen bond while it promotes elongation of this bond for smaller guests.

As mentioned earlier, in most of the optimized structures L-defects were not present. Water molecules that participated in host–guest bonding were reoriented; nevertheless, the original water–water hydrogen bonds were preserved, with exception of

one system for THP. For each guest we additionally tried to facilitate creation of stable L-defects by performing additional optimizations that were started from structures with a prear-ranged L-defect and a strong host—guest hydrogen bond. How-ever, for none of those prearranged structures was the L-defect stable; it was annihilated, and the water—water hydrogen bond was re-formed during optimization. The absence of L-defects is the reason for the absence of strong host—guest hydrogen bonds. It is also reflected in a relatively long H—O distances for encaged guests in comparison with those in dimer structures. The optimized structures discussed here correspond to the absolute zero temperature. We can conclude that creation of L-defects and subsequent creation of strong host—guest hydrogen bonds would require, for all guests considered here except THP, finite temperature conditions and thermal motions of the host water (even the optimized structure for THP with an L-defect found here corresponds to a relatively high energy). This is in accord with previous studies employing empirical potential molecular dynamics simulations.[5,7] Please note that the tendency to create strong host—guest hydrogen bonds is probably a function of the difference between water—water and water—guest interaction energy and thus for some guests it can be possible to observe L-defects already in absolute zero.

A comparison of the present results with the data obtained in the studies based on empirical potential calculations is not straightforward because the different conditions are considered in both these cases. The main sources of differences are the influence of the finite temperature, the presence of coguests, and differences in the type of clathrate structure studied. Of particular importance is the fact that at finite temperature many different orientational configurations of guest are populated, and an ensemble of states is observed. Moreover, the lifetimes of host—guest hydrogen bonds vary significantly with tempera-ture.[8,12] For instance, the H—O distance of about 2.8 Å was found for DME in our previous work where mixed DME + SO_2 in the structure-II clathrate was investigated at temperatures below 100 K.[13] This value is in accord with the absolute-zero H—O distance calculated for DME here. For THF in the structure-II clathrate a wide spread of H—O distances was observed (2.2—3.8 Å) at 250 K; under the same conditions, strong hydrogen bonds accompanied by L-defects were present between THP and water.[8] This tendency to form L-defects and stronger hydrogen bonds by THP with regard to THF is in accord with results shown here. In an ab initio molecular dynamics study of EO in a large cage of structure-I clathrate, weak hydrogen bonds were formed with H—O distances in a range of 2.2—2.5 Å.[5] Regarding comparison with experimental studies, the low-temperature strength of the host—guest hydrogen bonds discussed here corresponds well with the tendency for ultrafast formation of clathrates (DME < EO < TMO < THF) investigated recently.[11]

Alavi and co-workers formulated three conditions for forma-tion of host—guest hydrogen bonds in clathrates: (1) the presence of electronegative atom in the guest molecule, (2) large dipole moment of the guest that is oriented toward the electro-negative atom, and (3) large size of the guest in comparison with the cage.[8] While the first two conditions hold, the present study demonstrated that the condition 3 should be modified. The presence of an electronegative atom (condition 1) is demanded for formation of a hydrogen bond. Regarding the dipole moment of the guest molecule (condition 2), the guest's dipole moment is a necessary condition for host—guest hydrogen bonding. Please note that steric factor can overwhelm the electrostatic

interactions. For instance, the dipole moments of THP and EO are equal to 1.3 and 1.8 D, respectively; but due to the steric factor, THP is forming shorter hydrogen bonds with host water than those formed by EO. THP was even able to induce formation of an L-defect and a strong hydrogen bond with water. Regarding the size of a guest molecule (condition 3), for bulky guest molecules (TMO, THF, THP) a larger guest size shortens the hydrogen bond, as predicted by Alavi et al. However, for small guests, not the size but rather the shape of a guest molecule influences the host—guest bonding (see the case of DME vs EO). This shape should allow for a close approach of the guest to water molecules of the cage.

One should be aware of the influence of the limited size of the single-cage model employed in the present study. Regarding the structure of water, in actual clathrates each water molecule participates in four hydrogen bonds and thus its reorientation would be most probably limited in comparison with the present model. On the other hand, in our model we constrained positions of oxygen atoms of water molecules and thus we limited water reorientation. Therefore, we can expect these two effects to cancel out to a certain extent. Another important feature of the present model is the absence of cage—cage interactions. In our previous study these interactions were shown to promote crea-tion of both guest—host hydrogen bonds and nonclassical defects.[13] From this point of view we expect that the present model may underestimate both the guest—host bonding and the tendency for creation of L-defects.

4. CONCLUSIONS

We employed DFT+D calculations to find optimal structures for a series of polar guest molecules enclosed in a large cage of a structure-I clathrate hydrate. We found that most of the con-sidered guests form weak hydrogen bonds with host water molecules, the length of these bonds is in a range 2.3—2.8 Å. Formation of host—guest bonds in most cases does not induce creation of stable L-defects. It proves that even in the presence of a polar guest in the cage, the thermal motion of water is necessary for creation of L-defects. One notable exception is THP, which was shown to be able to form both L-defects and strong hydrogen bonds with host water even in the absence of thermal motions. In dimers with water (i.e., in the absence of steric obstacles), each of the considered guests forms hydrogen bonds of similar lengths. However, when guest molecules are located in the clathrate cage, the steric factors play a significant role. Their influence is twofold. For bulky guests (TMO, THF, and THP) the increase of the guest's size shortens the host—guest hydrogen bond and makes it stronger. This is a consequence of repulsive interactions between nonpolar parts of the guest molecules and the cage. For small guests (EO, DME) the opposite effect occurs. Namely, repulsive guest—cage interactions elongate the host—guest hydrogen bond. In this case, the strength of the hydrogen bond strongly depends on a shape of a guest molecule. For instance, the shape of EO allows for a close approach of the guest's oxygen atom to the cage wall and, in the case of EO, the resulting hydrogen bond is stronger than that for DME. These findings are in accord with previous computational studies in which empirical potentials were employed. There are also correlations between the calcu-lated length of guest—host hydrogen bonds and the experimen-tally observed tendency for ultrafast formation of clathrates. To conclude, in the group of guests considered here not only the electronic properties but also the steric factors, namely the shape

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and size of a guest molecule, strongly affect host—guest hydrogen bonding. Therefore, both electronic and steric properties of a guest should be considered for a full description of these clathrate systems.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: lukasz.cwiklik@uochb.cas.cz.

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