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# Water proton configurations in structures I, II, and H clathrate hydrate unit cells

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Position and orientation of water protons need to be specified when the molecular simulation studies are performed for clathrate hydrates. Positions of oxygen atoms in water are experimentally determined by X-ray diffraction analysis of clathrate hydrate structures, but positions of water hydrogen atoms in the lattice are disordered. This study reports a determination of the water proton coordinates in unit cell of structure I (sI), II (sII), and H (sH) clathrate hydrates that satisfy the ice rules, have the lowest potential energy configuration for the protons, and give a net zero dipole moment. Possible proton coordinates in the unit cell were chosen by analyzing the symmetry of protons on the hexagonal or pentagonal faces in the hydrate cages and generating all possible proton distributions which satisfy the ice rules. We found that in the sI and sII unit cells, proton distributions with small net dipole moments have fairly narrow potential energy spreads of about 1 kJ/mol. The total Coulomb potential on a test unit charge placed in the cage center for the minimum energy/minimum dipole unit cell configurations was calculated. In the sI small cages, the Coulomb potential energy spread in each class of cage is less than 0.1 kJ/mol, while the potential energy spread increases to values up to 6 kJ/mol in sH and 15 kJ/mol in the sII cages. The guest environments inside the cages can therefore be substantially different in the sII case. Cartesian coordinates for oxygen and hydrogen atoms in the sI, sII, and sH unit cells are reported for reference. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4795499>]

## I. INTRODUCTION

Clathrate hydrates are crystalline inclusion compounds consisting of water molecules in a hydrogen-bonded network forming cages that can encapsulate small guest molecules. Depending on the size and shape of the guest molecules, water molecules form different combinations of space filling cages that form the hydrates structures, with the three most common being structures I (sI), II (sII), and H (sH).<sup>1</sup> In recent years, molecular studies have been successfully applied for studying the formation and growth of clathrate hydrates,<sup>2-4</sup> their thermodynamic stability,<sup>5-10</sup> and guest-host interactions.<sup>11-14</sup> One of the most significant problems in performing molecular studies, especially simulations, of clathrate hydrates is the proton disorder of the water molecules. Every oxygen atom of the water molecules in the clathrate hydrate lattice is covalently bonded to two hydrogen atoms (which act as proton donation sites to other water molecules) and must be hydrogen bonded to two other hydrogen atoms from other water molecules. These two conditions constitute the ice rules. There are many different ways of distributing the protons among the oxygen atoms of the water molecules such that the ice rules are satisfied.<sup>15,16</sup> The proton positions in the different cages in the hydrate structures can be different and this leads to differences in the molecular environment of the guest

molecules inside the hydrate cages. The differences in the position and orientation of the protons manifest in a number of ways, for example, in the widening of the nuclear magnetic resonance (NMR) line shapes at low temperatures.<sup>17-22</sup> At low temperatures, the proton distributions in the hydrate structure are locked in, but as the temperature rises, the water molecules begin to rotate in their lattice position and the configurations of the protons in the hydrate structure reorient. As a result of this rapid flipping, the proton environment of all cages becomes uniform and the NMR line shapes become narrower. The effect of the proton disorder of water lattice on the dynamical properties of guest molecules is also reported. The distributions of the local potential surface in the cages depend on the proton configuration and affect the molecular motions and vibrations of guest molecules.<sup>23,24</sup> These water molecule rotations occur on time scales of microseconds or more and cannot be presently captured in the time scales of molecular simulations.<sup>21</sup> Therefore, it is important to start the simulations in such a way that the proton positions are the most “reasonable” ones, as this configuration is maintained in the simulations.

Okano and Yasuoka<sup>5</sup> determined the coordinates of the hydrogen atoms in water molecules of the hexagonal structure H clathrate hydrate by calculating the net dipole moment

and potential energy of the unit cell for the various orientations of water molecules that follow the ice rules. The proton configuration with lowest energy and dipole moment was chosen from among all configurations which satisfy the ice rules. This method is called an “energy-based” method. There are purely “topology-based” methods which only use the minimum dipole moment criterion.<sup>25–27</sup> These latter methods determine the proton configurations between water molecules by a Monte Carlo algorithm and weigh configurations based on their adherence to the ice rule. From among all possible configurations that obey the ice rule, those with zero dipole moment are chosen. Since bulk clathrate hydrates have zero net dipole moment, the unit cell chosen to construct a simulation must also have zero dipole moment.

While the position of the oxygen atoms in water molecules have been experimentally determined by X-ray diffraction analysis,<sup>28,29</sup> the position and orientation of protons in water molecules for sI and sII hydrates have not been determined in a systematic way. Recently, Kirov<sup>30</sup> investigated the proton configurations of sI hydrate using symmetry arguments. However, the molecular coordinates were not explicitly reported. In this study, we determine the orientation of water molecules in sI and sII hydrates following the procedure used by Okano and Yasuoka<sup>5</sup> for studying the proton distributions in the sI clathrate hydrate. We also calculate the Coulombic energy on a unit test charge placed in the center of the cages in the lowest energy/lowest dipole moment unit cell structures to study the different environment inside the cages. The details of the method in the calculations, calculated results, and the determined coordinates of the hydrogen atoms in water molecules are reported in this study.

## II. DETERMINING THE PROTON DISTRIBUTIONS AMONG WATER OXYGEN ATOMS

In this study, we employed the method by Okano and Yasuoka<sup>5</sup> for determining the water molecule orientations. A description of the method follows. We adopt the unit cell of sI or sII hydrate without any guest molecules as the system of interest. The proton configurations of the water molecules in the hydrate structure should satisfy the following conditions: (i) all water molecules in unit cell obey the ice rules;<sup>31</sup> (ii) the net dipole moment in unit cell should be zero (or as small as possible), and (iii) the chosen proton orientation for the water molecules has the lowest potential energy. Since macroscopic clathrate hydrate phases have zero net dipole moment, the second constraint is always preferred over the third. A more detailed description of the procedure to generate the proton configurations of sI and sII hydrates satisfying the ice rule is discussed in Sec. II A.

### A. Structure I hydrates

The cubic sI unit cell has 46 water molecules and  $Pm\bar{3}n$  space group symmetry. The position of oxygen atoms of water in a unit cell of sI hydrates and the hydrogen-bonding between water molecules are shown in Figure 1. The oxygen atom positions in the unit cell belong to the Wyckoff positions  $c$ ,  $i$ , and  $k$ , with multiplicities of 6, 16, and 24, respectively. The

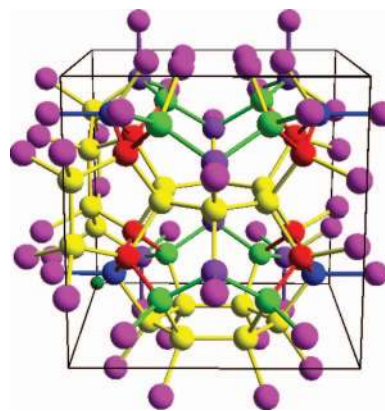


FIG. 1. Positions of oxygen atoms of water molecules and hydrogen-bonding in sI hydrate unit cell. The dark green sphere at the lower back, left-hand corner of the unit cell is the origin of the coordinate system. The other spheres and solid lines are water molecules and hydrogen-bonding inside the unit cell. The color of spheres and lines show group of the assignment of protons in each water molecule (see Figure 2).

positions of the protons of water molecules cannot be specified unambiguously by X-ray structure determination due to proton disorder.

In the unit cell, oxygen atoms from the  $c$  and  $k$  symmetry groups are in water molecules which form six-member hexagonal rings. The water molecules with oxygen atoms in the  $i$  and  $k$  symmetry groups participate in the formation of pentagonal rings. There are three independent hydrogen-bonded six-member rings of water molecules in a sI unit cell which do not share water molecules with the other hexagonal rings. The water oxygen atoms in these rings are shown by yellow spheres in Figure 2(a). The hexagonal faces connect large sI cages ( $5^{12}6^2$ ) that are aligned in the same direction. For an efficient generation of the proton configuration satisfying the ice rule, we focused on these hexagonal rings.

There are four distinct hydrogen bonding configurations for each water in a hexagonal face: (i) the water may have both hydrogen atoms in the hexagonal face, (ii) the water may have one hydrogen atom in the hexagonal face pointing towards its neighbor to the right hand side, (iii) the water may have one hydrogen atom in the hexagonal face pointing towards its neighbor to the left hand side, or (iv) the water may have no hydrogen atoms in the hexagonal face. There are  $4^6 = 4096$  possible proton configurations in the hexagonal face, but of these only 730 ( $3^6 + 1$ ) configurations satisfy the ice rules. The number of possible proton configurations for  $N$ -member rings of water molecules which obey the ice rules is  $3^N + 1$ . First, we assign the 730 configurations of water molecule arrangement to each of the three six-member rings in a sI unit cell as shown in Figure 2(a). Second, we assign proton positions to the eight red colored water molecules and bonds shown in Figure 2(b) that have two hydrogen bonds with yellow water molecules and the other two hydrogen bonds with other water molecules in the unit cell. There are three combinations of hydrogen bonds between the red water molecule and the two yellow water molecules: (a) the red water molecule accepts two hydrogen atoms from the two yellow water molecules; (b) the red water molecule donates two hydrogen atoms to the two yellow water molecules; (c) the red water molecule

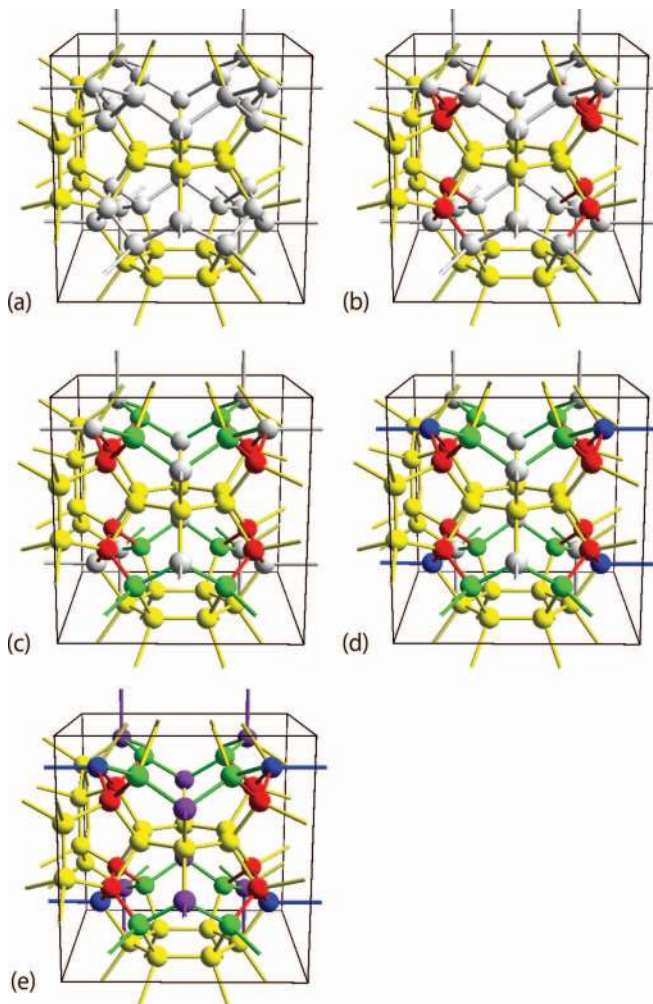


FIG. 2. Details of the assignment of proton positions of water molecules in a sI hydrate unit cell. (a) The yellow spheres and full lines show water molecules and hydrogen-bonding initially assigned as three independent hydrogen-bonded hexagonal rings; (b) the red spheres are secondary assigned water molecules that have two hydrogen bonds with the yellow water molecules, and two hydrogen bonds to other water types; (c) the blue spheres are the third group of water molecules that have one hydrogen bond with the yellow water molecule, two hydrogen bonds with the red water molecules, and one hydrogen bond to another blue molecule; (d) the green spheres are the fourth group of water molecules to be assigned proton positions. These waters have a hydrogen bond with a yellow water molecule, a hydrogen bond with the red water molecule, and two hydrogen bonds to other water molecules; (e) the purple spheres are last group of water molecules assigned proton positions. These water molecules have hydrogen bonds with a yellow, two green, and other purple colored water molecules. Every assignment of proton positions is performed based on the ice rules.

donates a hydrogen atom to the one yellow water molecule and accepts a hydrogen atom from the other yellow water molecule. In the case (c), we need to consider two combinations of hydrogen bonds for the two yellow water molecules. The selection of these three cases depends on the assignment of the red water molecules. Third, the proton positions of the eight green colored water molecules are assigned, as shown in the Figure 2(c). These water molecules have one hydrogen bond with a yellow water molecule, one hydrogen bond with a red water molecule, and two other bonds with other water molecules (see below). The red and green molecules only participate in pentagonal faces and together their oxygen atoms

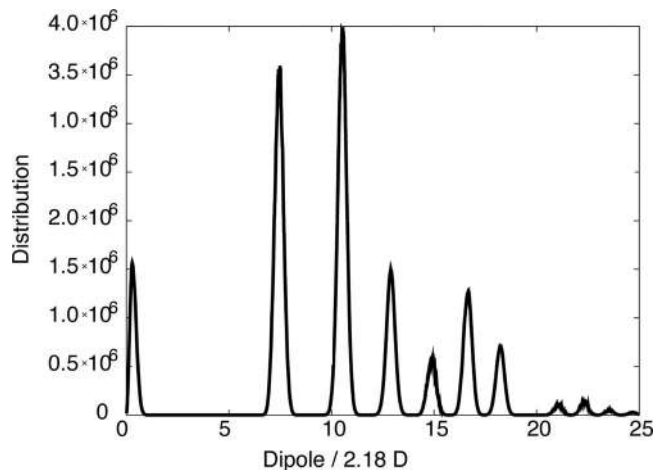


FIG. 3. Histogram of the net dipole moment of sI unit cell. The abscissa is in units of the TIP4P water molecule dipole moment 2.18 D.

constitute the 16  $i$  symmetry points of the space group. Fourth, proton positions for four blue colored water molecules are assigned. These water molecules form one bond with a yellow water molecule and two bonds with red water molecules and one other bond with a green molecule, as shown in Figure 2(d). We can consider the possible configurations of these blue and green hydrogen bonds to be similar to the red water molecules. Finally, we considered proton positions of the eight purple colored water molecules, as shown in Figure 2(e) that have hydrogen bonds with the one yellow, two green, and one other purple colored water molecules. If all purple colored water molecules follow the ice rules, it is determined that all water molecule configurations in the unit cell follow the ice rules.

Based on the procedure described above, we find 685 686 200 configurations of water-molecule orientations in the sI unit cell to satisfy the ice rules. Chiral or symmetric unit cell configurations are not rejected from these configurations. Figure 3 shows the distribution of the net unit cell dipole moments calculated for all configurations of the water molecules. When calculating the net unit cell dipole moment,

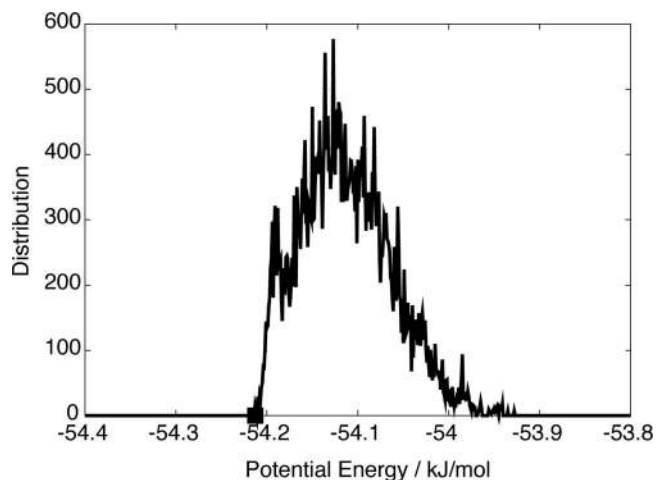


FIG. 4. Histogram of the potential energy distribution of protons in the sI unit cell with a net zero dipole moment. The square point represents the configuration with lowest energy.

the dipole moment of water molecules is fitted in the direction of bisector of the corresponding oxygen-oxygen-oxygen angle. We found that 53 200 proton position configurations have nearly zero ( $<1.0 \times 10^{-10}$  D) net dipole moment in the unit cell. These are the lower portion of the distribution making up the first peak on the left in Figure 3.

We then calculated the potential energy for these configurations using the TIP4P potential<sup>32</sup> as the water model. The zero dipole moment configurations with the lowest potential energy, as shown by the square in Figure 4, should be thermo-

dynamically the most stable. It is recognized that the energy differences between the proton configurations with zero net dipole moment span a range of only  $\sim 0.3$  kJ mol<sup>-1</sup> and so other proton configurations will be energetically accessible. However, the activation barrier for transformations between these low energy configurations could be high as the structures would have to pass through states with pairs of *D* and *L* Bjerrum defects<sup>33</sup> to be transformed to one another.

The coordinates of the water molecules of the lowest energy configuration of the sI unit cell are given in Table I. The

TABLE I. Cartesian coordinates of the 46 water molecules in sI hydrate unit cell for the lowest energy configuration with zero dipole moment.

No.	Color	Oxygen			Hydrogen 1			Hydrogen 2		
		<i>x</i> (Å)	<i>y</i> (Å)	<i>z</i> (Å)	<i>x</i> (Å)	<i>y</i> (Å)	<i>z</i> (Å)	<i>x</i> (Å)	<i>y</i> (Å)	<i>z</i> (Å)
1	Yellow	0.00000	0.00000	3.00607	-0.79896	0.02937	3.53241	-0.02935	0.79945	2.48047
2	Yellow	0.00000	0.00000	9.02393	0.79896	-0.02937	8.49759	0.02935	-0.79945	9.54953
3	Purple	0.00000	2.32078	1.42200	-0.78565	2.80392	1.67806	-0.01418	2.32950	0.46494
4	Purple	0.00000	2.32078	10.60800	-0.00161	1.53077	10.06753	-0.78215	2.80013	10.33468
5	Purple	0.00000	9.70922	1.42200	0.00161	10.49923	1.96247	0.78215	9.22987	1.69532
6	Purple	0.00000	9.70922	10.60800	0.78565	9.22608	10.35194	0.01418	9.70050	11.56506
7	Yellow	6.01500	3.00607	0.00000	5.21604	3.53241	-0.02937	5.98565	2.48047	-0.79945
8	Yellow	6.01500	9.02393	0.00000	6.81396	8.49759	0.02937	6.04435	9.54953	0.79945
9	Blue	6.01500	1.42200	2.32078	6.01339	1.96247	1.53077	5.23285	1.69532	2.80013
10	Blue	6.01500	10.60800	2.32078	5.22935	10.35194	2.80392	6.00082	11.56506	2.32950
11	Blue	6.01500	1.42200	9.70922	6.80065	1.67806	9.22608	6.02918	0.46494	9.70050
12	Blue	6.01500	10.60800	9.70922	6.01661	10.06753	10.49923	6.79715	10.33468	9.22987
13	Yellow	3.69468	4.59285	0.00000	3.67667	5.54948	0.02780	3.19573	4.32094	0.77029
14	Yellow	3.69468	7.43715	0.00000	4.48544	7.97652	0.00167	3.19969	7.73931	-0.76152
15	Yellow	2.32032	0.00000	4.59285	1.52956	0.00167	4.05348	2.81531	-0.76152	4.29069
16	Yellow	2.32032	0.00000	7.43715	2.33833	0.02780	6.48052	2.81927	0.77029	7.70906
17	Green	2.26337	3.71265	2.20970	2.78150	3.12469	2.75931	1.49688	3.19584	1.96146
18	Green	2.26337	3.71265	9.82030	2.72098	3.99406	10.61253	1.49535	3.24035	10.14173
19	Green	2.26337	8.31735	2.20970	2.75258	7.98645	1.45643	1.99545	7.53142	2.68590
20	Green	2.26337	8.31735	9.82030	2.80737	8.84439	9.23504	2.00356	7.56276	9.29178
21	Red	3.75163	2.20970	3.71265	3.26243	1.45644	4.04358	4.01946	2.68599	4.49855
22	Red	3.75163	9.82030	3.71265	4.01141	9.29172	4.46720	3.20762	9.23510	3.18556
23	Red	3.75163	2.20970	8.31735	4.51812	1.96146	8.83416	3.23350	2.75931	8.90531
24	Red	3.75163	9.82030	8.31735	3.29402	10.61253	8.03594	4.51965	10.14173	8.78965
25	Yellow	8.33532	4.59285	0.00000	7.54456	4.05348	-0.00167	8.83031	4.29069	0.76152
26	Yellow	8.33532	7.43715	0.00000	8.35333	6.48052	-0.02780	8.83427	7.70906	-0.77029
27	Yellow	9.70968	0.00000	4.59285	9.69167	-0.02780	5.54948	9.21073	-0.77029	4.32094
28	Yellow	9.70968	0.00000	7.43715	10.50044	-0.00167	7.97652	9.21469	0.76152	7.73931
29	Green	9.76663	3.71265	2.20970	9.22263	3.18561	2.79496	10.02644	4.46724	2.73822
30	Green	9.76663	3.71265	9.82030	9.27742	4.04355	10.57357	10.03455	4.49858	9.34410
31	Green	9.76663	8.31735	2.20970	9.30902	8.03594	1.41747	10.53465	8.78965	1.88827
32	Green	9.76663	8.31735	9.82030	9.24850	8.90531	9.27069	10.53312	8.83416	10.06854
33	Red	8.27837	2.20970	3.71265	8.73598	1.41747	3.99406	7.51035	1.88827	3.24035
34	Red	8.27837	9.82030	3.71265	7.51188	10.06854	3.19584	8.79650	9.27069	3.12469
35	Red	8.27837	2.20970	8.31735	8.01859	2.73828	7.56280	8.82238	2.79490	8.84444
36	Red	8.27837	9.82030	8.31735	8.76757	10.57356	7.98642	8.01054	9.34401	7.53145
37	Yellow	3.00607	6.01500	6.01500	3.53241	6.81396	5.98563	2.48047	6.04435	5.21555
38	Yellow	9.02393	6.01500	6.01500	8.49759	5.21604	6.04437	9.54953	5.98565	6.81445
39	Purple	1.42200	6.01500	8.33578	1.70685	5.24474	8.82751	1.96425	6.01021	7.54700
40	Purple	10.60800	6.01500	8.33578	10.34743	6.78909	8.83490	11.56496	6.03292	8.34734
41	Purple	1.42200	6.01500	3.69422	1.68257	5.24091	3.19510	0.46504	5.99708	3.68266
42	Purple	10.60800	6.01500	3.69422	10.32315	6.78526	3.20249	10.06575	6.01979	4.48300
43	Yellow	4.59285	3.69468	6.01500	4.04997	4.48303	6.01965	4.30818	3.20271	6.78517
44	Yellow	7.43715	3.69468	6.01500	6.48019	3.68314	5.99711	7.69769	3.19545	5.24097
45	Yellow	4.59285	8.33532	6.01500	5.54981	8.34686	6.03289	4.33231	8.83455	6.78903
46	Yellow	7.43715	8.33532	6.01500	7.98003	7.54697	6.01035	7.72182	8.82729	5.24483

TABLE II. Cartesian coordinates of the centers of the small and large cages in the sI hydrate unit cell.

Cage	$x$ (Å)	$y$ (Å)	$z$ (Å)
Small 1	0.000	6.015	0.000
Small 2	6.015	0.000	6.015
Large 1	3.008	0.000	0.000
Large 2	9.023	0.000	0.000
Large 3	0.000	2.992	6.015
Large 4	0.000	9.038	6.015
Large 5	6.015	6.015	2.992
Large 6	6.015	6.015	9.038

“color” of the oxygen atoms in each water molecule for sI as shown in Figure 2 is also specified. These coordinates are recommended as the initial coordinates in molecular simulations on sI hydrates. In the determination of the coordinates, the lattice constant  $a$  for the cubic unit cell is set at 12.03 Å.<sup>19</sup> The origin of the coordinate system in Figure 2 is chosen to be the dark green sphere at the lower back, left-hand corner of the unit cell. The coordinates of the water molecules and the center of the cages in sI are available in  $xyz$  coordinate file format (see the supplementary material<sup>34</sup>).

The positions of the center of the small and large cages in sI unit cell are given in Table II. With the coordinates of the water molecules of the lowest energy configuration, it is obvious that the guest molecules occupying the cages will experience slightly different proton environments in the different cages of the same type. Table III lists the Coulomb potential energy from the water molecules to a test point charge of 1.0e at the center of the different cages in the sI unit cell. In the TIP4P model of water, Lennard-Jones parameters are only assigned to oxygen atoms in water and as a result, the centers of all similar cages have identical van der Waals potential energies. The Coulomb potential energies were calculated by the cutoff method.<sup>35</sup> The cutoff length was 500 Å and the oxygen atoms were used for screening of the cutoff. The energies of the guests in the different cages vary by 0.021 kJ mol<sup>-1</sup> and 0.465 kJ mol<sup>-1</sup> for the small and large cages, respectively.

The different water proton environments experienced by guests in the cages are used to explain the width of low temperature NMR guest line shapes.<sup>17-22</sup> As the temperature rises, the water molecules rotate about their positions and the proton configurations change in all cages, the guest en-

TABLE III. Coulomb potential energies for a point charge placed at center of the each cage for sI hydrates.

Cage	Coulomb potential (kJ mol <sup>-1</sup> )
Small 1	-15.7312
Small 2	-15.7104
Large 1	-50.6478
Large 2	-50.6478
Large 3	-51.1132
Large 4	-51.1132
Large 5	-51.1022
Large 6	-51.1022

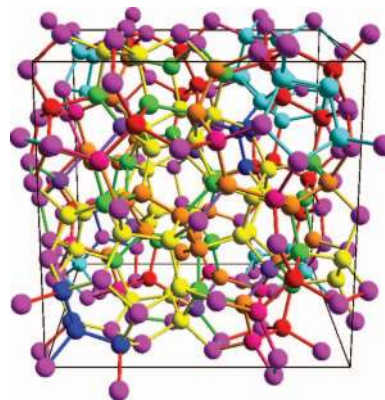


FIG. 5. Position of oxygen atoms of water molecules and hydrogen-bonding in the sII hydrate unit cell. The spheres and solid lines are water molecules and hydrogen-bonding inside the unit cell. The color of the spheres and lines show the groups of the assignment of protons in each water molecule (see Figure 6). The origin of the coordinate system is same as the sI (shown in Figure 1), the lower back, left-hand corner of the unit cell. In this figure, the origin coincides with one of the aqua colored water molecules.

vironments become uniform, and NMR line shapes become narrower.

## B. Structure II hydrates

The cubic sII hydrate unit cell has 136 water molecules and  $Fd3m$  space group symmetry. The position of the oxygen atoms of water molecules and the hydrogen-bonding between water molecules in a unit cell of sII hydrate are shown in Figure 5.<sup>28</sup> The oxygen atom positions in the unit cell belong to the Wyckoff positions  $b$ ,  $e$ , and  $g$ , with multiplicities of 8, 32, and 96, respectively. In a manner similar to that used for sI hydrate described in Sec. II A, we can find sets of the hydrogen-bonded water molecules that form five- and six-member rings. The oxygen atoms of  $b$ ,  $e$ , and  $g$  symmetry points are from water molecules that form pentagonal faces and the oxygen atoms of the  $g$  symmetry point also contribute to hexagonal faces in the unit cell structure. There are six independent hydrogen-bonded five-member rings and three independent hydrogen-bonded six-member rings of water molecules in a sII unit cell (Figure 5). As described in Sec. II A, there are 730 possible combinations of the orientations of the six water molecules forming a hexagonal ring and 244 ( $3^5+1$ ) possible proton configurations for the five water molecules forming a pentagonal ring that satisfy the ice rules (from a total of  $4^5 = 1024$  water configurations). We tried to assign the 730 configurations of water-molecule arrangement to each of the three six-member rings and 244 configurations of water-molecule arrangement to each of the six five-member rings in a sII unit cell, respectively. If we attempt to determine all water-molecule configurations in the unit cell which obey the ice rules by using the same procedure described for sI hydrate (Figure 6), we will find that the number of possible positions of protons in water molecules for sII is greater than for sI by approximately 24 orders of magnitude. It is impossible to perform calculations of net dipole moment and potential energy on all of these combinations.

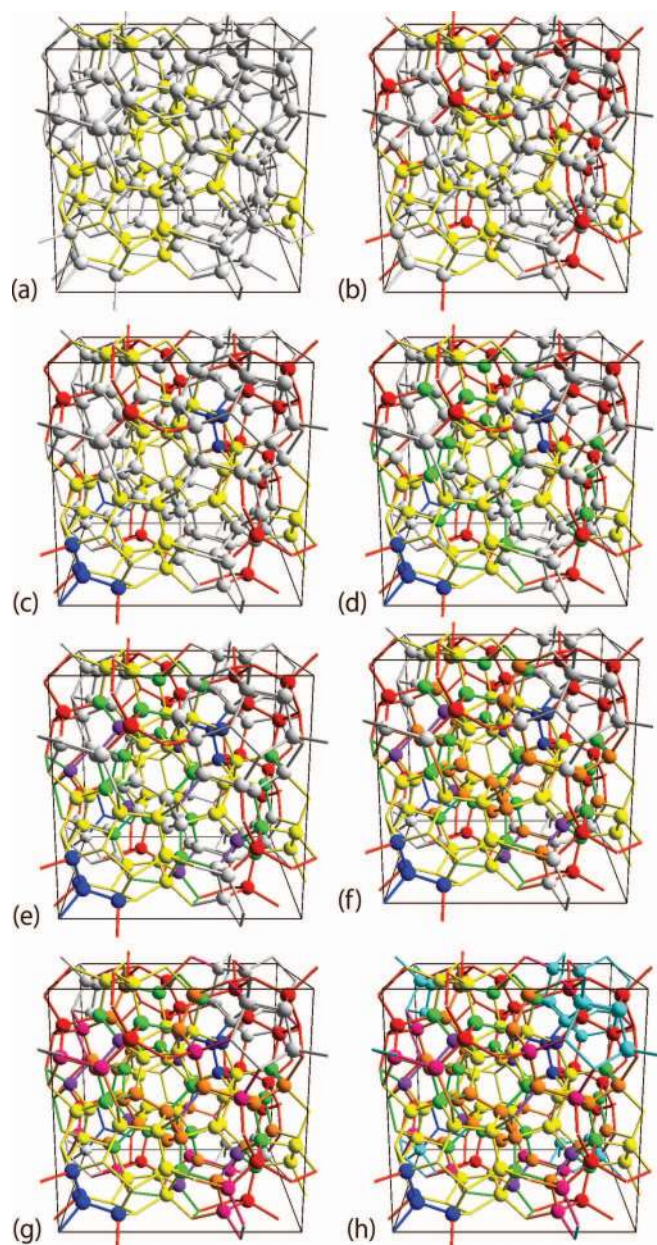


FIG. 6. Details of the assignment of proton positions of water molecules in a sII hydrate unit cell. (a) The yellow spheres show water molecules that are initially assigned as six independent hydrogen-bonded hexagonal rings with almost zero dipole moment. (b) The red spheres are secondary assigned water molecules as three independent hydrogen-bonded hexagonal rings that have almost zero dipole moment. (c) The blue spheres are thirdly assigned water molecules that have hydrogen bonds with the yellow waters in hexagonal faces and the red waters in pentagonal faces. (d) The green spheres are fourthly assigned water molecules that have hydrogen bonds with the yellow and the red water molecules. Similarly, (e) purple, (f) orange, (g) magenta, and (h) aqua spheres are assigned to other water molecules that have hydrogen bonds with already assigned water molecules. All assignments of proton positions are performed based on the ice rules.

To more efficiently sample the proton positions for the sII unit cell, we use an observation made in determining zero net dipole moment configurations in the sI hydrates unit cell for the six-member rings. When the arrangement of the water molecules of sI hydrates were determined, only 28 specific arrangements in 730 combinations of the six-member ring were actually accepted, while the other 702 arrangements were re-

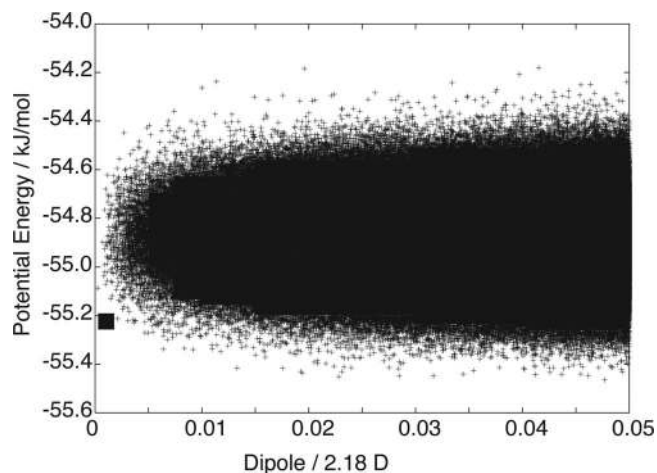


FIG. 7. The relationship between the net dipole moment and the unit cell potential energy of the sII hydrate. We adopted the proton configuration indicated by the square in this figure.

jected due to having large values of the dipole moment. In these 28 arrangements, the value of the net dipole moment for the six water molecules is nearly zero. In other words, in getting distributions of the water molecules for which net dipole moment is nearly zero in a unit cell, it is assumed that the value of the net dipole moment in water molecules forming the hexagonal rings is also a low value. Therefore, in determining the arrangements of water molecules in sII unit cell, we assigned a limited number of 28 proton arrangements for six-member rings and 12 arrangements for the five-member rings. We adopted these arrangements to satisfy the ice rules and to have nearly zero dipole moment in the unit cell.

We find about  $3.4 \times 10^9$  configurations of water molecules in the sII unit cell satisfy the ice rules with the above procedure. In these combinations, we find 6 150 251 configurations which have a dipole moment of 0.05 D or less for the unit cell. The chiral or symmetric structures in these 6 150 251 are not rejected. Figure 7 shows the values of the dipole moment and the potential energies corresponding to the configurations of these water molecules. The configuration shown by the square in Figure 7 satisfies the conditions that the net dipole moment is nearly zero and the potential energy is sufficiently low. The coordinates of the water molecules of this configuration are given in Table IV. The center of mass of the unit cell is chosen to correspond to oxygen number 129 in the sII unit cell.<sup>19</sup> This configuration is recommended as the initial orientation of the water molecules in molecular simulation on sII hydrates. Table V shows the positions of the center of the cages in the sII unit cell. The lattice constant  $a$  for the cubic unit cell is 17.31 Å. The coordinates of the water molecules and the center of the cages in sII are available in  $xyz$  coordinate file format (see the supplementary material<sup>34</sup>). The energy differences for the net zero dipole moment configurations in Figure 7 differ by about  $1 \text{ kJ mol}^{-1}$ . Different proton configurations should thus be accessible to the system at normal temperatures, although the activation barrier for transformation of these systems could be high as it passes through states with a pair of  $D$  and  $L$  Bjerrum defects.



TABLE IV. Cartesian coordinates of the 136 water molecules in the sII hydrate unit cell.

No.	Color	Oxygen			Hydrogen 1			Hydrogen 2		
		<i>x</i> (Å)	<i>y</i> (Å)	<i>z</i> (Å)	<i>x</i> (Å)	<i>y</i> (Å)	<i>z</i> (Å)	<i>x</i> (Å)	<i>y</i> (Å)	<i>z</i> (Å)
1	Yellow	5.92487	5.92487	5.92487	5.75998	6.83792	5.68955	6.84272	5.77984	5.69518
2	Yellow	5.32179	5.32179	8.56620	5.53914	5.52632	7.65672	6.12716	4.95217	8.92812
3	Green	7.66071	4.23870	9.64929	8.03033	4.60062	10.45466	7.45618	3.32922	9.86664
4	Orange	9.64929	4.23870	7.66071	8.95131	4.25234	8.31559	9.24946	4.61362	6.87598
5	Orange	8.56620	5.32179	5.32179	8.58169	4.66966	4.62128	8.94432	6.10740	4.92673
6	Yellow	4.23870	7.66071	9.64929	4.60062	6.85534	9.27967	3.32922	7.44336	9.85382
7	Yellow	4.20371	9.63809	7.64989	4.22695	8.98285	8.34728	4.58643	10.42187	8.04415
8	Yellow	5.26439	8.54844	5.30462	4.86620	8.92706	6.08841	4.56904	8.57135	4.64720
9	Green	7.59104	9.68721	4.25266	6.78722	9.29891	4.59812	7.39129	9.87671	3.33592
10	Orange	9.65672	7.66856	4.26340	9.00013	8.36495	4.27642	10.44563	8.07583	4.62115
11	Yellow	11.38513	11.38513	5.92487	11.60951	11.60961	6.82792	11.94514	11.94889	5.39121
12	Yellow	11.98821	11.98821	8.56620	11.19030	12.26079	9.01927	12.26079	11.19030	9.01927
13	Yellow	9.64929	13.07130	9.64929	8.97274	13.09949	8.97274	9.83821	13.99046	9.83821
14	Yellow	7.66071	13.07130	7.66071	8.03033	12.70938	6.85534	7.45618	13.98078	7.44336
15	Yellow	8.74380	11.98821	5.32179	9.65123	11.75854	5.52191	8.36822	11.18681	4.95720
16	Green	13.07130	9.64929	9.64929	12.71605	9.23914	10.43784	13.06858	8.95167	8.99389
17	Orange	13.10629	7.67190	7.64989	14.01431	7.44697	7.44707	12.73716	6.86979	8.01947
18	Orange	12.04561	8.76156	5.30462	11.82119	9.66486	5.52804	12.40739	8.39732	6.11250
19	Blue	5.92487	11.38513	11.38513	5.68711	10.48536	11.60901	5.36855	11.92674	11.94495
20	Blue	5.32179	11.98821	8.74380	6.12716	12.35783	8.38188	5.53914	11.78368	9.65328
21	Blue	8.56620	11.98821	11.98821	8.92812	12.35783	11.18284	7.65672	11.78368	11.77086
22	Blue	5.26439	8.76156	12.00537	4.56555	8.73596	12.65898	4.87305	8.37812	11.22048
23	Yellow	7.59104	7.62279	13.05734	7.87445	6.83584	12.59191	6.79843	7.90076	12.59828
24	Yellow	9.65672	9.64144	13.04660	8.95375	8.99183	13.03861	9.25796	10.43107	12.68094
25	Yellow	11.38513	5.92487	11.38513	11.62289	6.82464	11.60901	11.94145	5.38326	11.94495
26	Orange	11.98821	5.32179	8.74380	11.77086	5.52632	9.65328	11.18284	4.95217	8.38188
27	Yellow	8.74380	5.32179	11.98821	9.66128	5.51484	11.79534	8.77794	4.64916	12.66838
28	Yellow	12.04561	8.54844	12.00537	11.25391	8.92365	12.39094	12.69038	8.57004	12.71250
29	Aqua	15.71263	15.71263	15.71263	14.79521	15.93879	15.86570	15.86570	15.93879	14.79521
30	Aqua	16.31571	16.31571	13.07130	16.71554	15.53098	12.69638	17.01369	16.97059	13.05766
31	Red	13.07130	16.31571	16.31571	12.71622	16.72167	15.52492	13.05840	17.01388	16.97040
32	Aqua	16.37311	13.08906	16.33288	17.03457	13.12668	17.02374	16.16997	14.00539	16.14497
33	Green	10.25237	10.25237	15.71263	10.10154	10.02603	14.79489	11.16961	10.02692	15.86779
34	Orange	13.97679	8.56620	13.97679	13.70421	9.01927	14.77470	14.77470	9.01927	13.70421
35	Orange	12.89370	9.64929	16.31571	13.26862	10.43402	16.71554	12.90734	8.99441	17.01369
36	Red	8.53121	13.96560	13.98761	8.89891	13.56350	14.77460	8.55663	13.27135	13.32912
37	Red	9.59189	12.87594	16.33288	10.39794	13.24711	16.69170	9.81892	11.97105	16.11872
38	Orange	15.71263	10.25237	10.25237	14.79478	10.10734	10.02268	15.87752	11.16543	10.01705
39	Magenta	16.31571	9.64929	12.89370	16.11118	9.86664	11.98422	16.68533	10.45466	13.25562
40	Magenta	16.37311	12.87594	9.63213	15.57951	13.33442	9.35602	16.64109	13.32245	10.43528
41	Orange	14.04646	14.01471	8.58016	13.35308	13.35482	8.58260	13.63522	14.79630	8.94925
42	Green	10.25237	15.71263	10.25237	11.15567	15.93656	10.02844	9.71933	16.27481	9.69019
43	Red	9.64929	16.31571	12.89370	9.27152	15.51360	13.25446	9.85323	16.09707	11.98439
44	Orange	12.89370	16.31571	9.64929	12.90660	17.01388	8.99459	13.24878	16.72167	10.44008
45	Green	7.05763	7.05763	15.71263	7.26711	7.27823	14.80506	7.62476	7.62521	16.23460
46	Red	3.33321	8.74380	13.97679	3.60579	8.29073	14.77470	2.53530	8.29073	13.70421
47	Red	4.41630	7.66071	16.31571	4.05438	6.85534	16.68533	5.32578	7.44336	16.11118
48	Orange	8.77879	3.34441	13.98761	8.33196	3.61954	14.78816	8.31747	2.55096	13.71586
49	Orange	7.71811	4.43406	16.33288	6.91206	4.06289	16.69170	7.49108	5.33895	16.11872
50	Aqua	1.59737	1.59737	15.71263	1.43248	2.51042	15.94795	2.51522	1.45234	15.94232
51	Aqua	0.99429	0.99429	13.07130	0.62467	1.79966	12.70938	1.19882	1.21164	13.98078
52	Aqua	4.23870	0.99429	16.31571	4.59378	0.58833	15.52492	4.25160	0.29612	16.97040
53	Red	0.93689	4.22094	16.33288	1.74161	4.66336	16.60293	0.67474	4.66932	15.52885
54	Orange	7.05763	1.59737	10.25237	7.59067	1.03519	9.69019	6.15433	1.37344	10.02844
55	Magenta	7.66071	0.99429	12.89370	8.33726	0.31774	12.86551	7.47179	1.18321	11.97454
56	Magenta	4.41630	0.99429	9.64929	3.95982	1.79483	9.39044	3.98001	0.71929	10.45568
57	Orange	3.32578	3.34106	8.59090	4.00494	4.01486	8.55977	3.13755	3.14743	7.67258
58	Green	1.59737	7.05763	10.25237	1.36010	6.15760	10.02904	1.03889	7.59862	9.69410
59	Red	0.99429	7.66071	12.89370	1.18321	7.47179	11.97454	0.31774	8.33726	12.86551

TABLE IV. (*Continued.*)

No.	Color	Oxygen			Hydrogen 1			Hydrogen 2		
		$x$ (Å)	$y$ (Å)	$z$ (Å)	$x$ (Å)	$y$ (Å)	$z$ (Å)	$x$ (Å)	$y$ (Å)	$z$ (Å)
60	Orange	0.93689	4.43406	9.63213	1.73034	4.05962	9.24942	0.29735	4.42012	8.92008
61	Green	7.05763	15.71263	7.05763	6.14021	15.93879	7.21070	7.21070	15.93879	6.14021
62	Orange	7.66071	16.31571	4.41630	8.35869	16.97059	4.40266	8.06054	15.53098	4.04138
63	Red	4.41630	16.31571	7.66071	4.03818	15.53010	8.05577	4.40081	16.96784	8.36122
64	Orange	8.74380	13.97679	3.33321	8.73090	13.27862	3.98791	8.38872	13.57083	2.54242
65	Red	3.32578	13.96894	8.71910	2.53558	13.56369	8.36192	3.97867	13.26900	8.71198
66	Green	1.59737	10.25237	7.05763	2.51469	10.10393	7.28723	1.43557	11.16569	7.29405
67	Orange	0.99429	9.64929	4.41630	1.19882	9.86664	5.32578	0.62467	10.45466	4.05438
68	Orange	3.33321	8.56620	3.33321	3.11586	7.65672	3.12868	2.52784	8.92812	3.70283
69	Red	0.93689	12.87594	7.67788	0.54043	13.26009	6.89591	0.24131	12.89787	8.33508
70	Orange	7.05763	10.25237	1.59737	7.59067	9.69019	1.03519	6.15433	10.02844	1.37344
71	Magenta	4.41630	9.64929	0.99429	4.40266	8.95131	0.33941	4.04138	9.24946	1.77902
72	Magenta	7.71811	12.87594	0.97713	8.37957	12.83832	0.28627	7.51497	11.95961	1.16503
73	Aqua	1.59737	15.71263	1.59737	1.37344	15.93656	2.50067	1.03519	16.27481	1.06433
74	Red	0.99429	16.31571	4.23870	1.78375	16.71722	4.60170	0.34106	17.01522	4.25281
75	Aqua	4.23870	16.31571	0.99429	3.32922	16.09836	1.19882	4.60062	15.51034	0.62467
76	Aqua	0.93689	13.08906	0.97713	1.16392	13.99395	1.19129	1.74294	12.71789	0.61831
77	Yellow	15.71263	7.05763	7.05763	15.93656	7.28156	6.15433	16.27481	7.61981	7.59067
78	Yellow	16.31571	7.66071	4.41630	16.71554	6.87598	4.04138	17.01369	8.31559	4.40266
79	Green	13.97679	8.74380	3.33321	14.76322	8.36955	3.73032	13.32694	8.73773	4.03598
80	Yellow	16.37311	4.43406	7.67788	16.13596	5.33719	7.46730	15.57173	4.05295	8.03674
81	Green	14.04646	3.29529	8.72984	13.36439	3.96665	8.74704	14.22237	3.10822	9.65195
82	Yellow	10.25237	1.59737	7.05763	11.16979	1.44430	7.28379	10.09930	2.51479	7.28379
83	Yellow	9.64929	0.99429	4.41630	9.85382	1.21164	5.32578	9.27967	1.79966	4.05438
84	Yellow	12.89370	0.99429	7.66071	13.32906	0.71297	6.85600	13.36996	1.78001	7.92915
85	Green	8.56620	3.33321	3.33321	8.91702	3.71009	2.52629	7.65537	3.12538	3.12483
86	Blue	15.71263	1.59737	1.59737	15.94990	2.49740	1.37404	16.27111	1.05638	1.03910
87	Blue	16.31571	0.99429	4.23870	15.50775	0.62425	4.59437	16.10454	1.20109	3.32828
88	Blue	13.07130	0.99429	0.99429	12.72048	0.61741	1.80121	13.98213	1.20212	1.20267
89	Blue	16.37311	4.22094	0.97713	15.58103	4.59514	0.59135	17.01490	4.23351	0.26707
90	Yellow	10.25237	7.05763	1.59737	10.00587	6.14631	1.43937	10.02890	7.21098	2.51540
91	Yellow	12.89370	7.66071	0.99429	11.98422	7.45618	1.21164	13.25562	8.03033	1.79966
92	Yellow	9.59189	4.43406	0.97713	10.38397	4.05986	0.59135	8.95010	4.42149	0.26707
93	Green	11.38513	2.73013	14.57987	11.53976	2.95616	15.49706	10.46925	2.96231	14.42660
94	Yellow	11.98821	3.33321	17.22120	12.68619	3.98809	17.23484	12.38804	2.54848	17.59612
95	Red	12.04561	0.10656	13.95962	11.23956	-0.26461	13.60080	11.81858	1.01145	14.17378
96	Aqua	2.73013	11.38513	14.57987	2.95629	10.46771	14.42680	2.95629	11.53820	15.49729
97	Aqua	3.33321	11.98821	17.22120	3.73304	11.20348	17.59612	4.03119	12.64309	17.23484
98	Aqua	0.08880	11.98821	13.97679	-0.26202	12.36509	14.78371	0.99963	11.78038	14.18517
99	Green	14.57987	5.92487	14.57987	14.35436	6.82740	14.35447	14.01672	5.38993	14.02047
100	Yellow	13.97679	5.32179	17.22120	13.60717	6.12716	17.58312	14.18132	5.53914	16.31172
101	Red	17.22120	5.32179	13.97679	17.58312	6.12716	13.60717	16.31172	5.53914	14.18132
102	Aqua	5.92487	14.57987	14.57987	6.84219	14.43143	14.35027	5.76307	15.49319	14.34345
103	Aqua	5.32179	13.97679	17.22120	5.53296	14.18359	16.31078	6.12975	13.60675	17.57687
104	Aqua	5.26439	17.20344	13.95962	6.05647	17.57764	13.57385	4.62260	17.21601	13.24956
105	Green	2.73013	2.73013	5.92487	1.81228	2.87516	5.69518	2.89502	1.81708	5.68955
106	Yellow	0.08880	3.33321	5.32179	-0.35044	3.60538	6.12754	-0.36827	2.53489	5.05719
107	Red	3.39061	0.10656	5.30462	3.78707	-0.27759	6.08659	4.08619	0.08463	4.64742
108	Aqua	2.73013	14.57987	11.38513	2.95217	14.35267	10.48219	3.29371	14.01991	11.91903
109	Aqua	0.08880	13.97679	11.98821	1.00796	14.16571	11.79929	0.11699	13.30024	12.66476
110	Aqua	3.39061	17.20344	12.00537	3.16358	16.29855	11.79121	2.58456	17.57461	12.36419
111	Orange	14.57987	2.73013	11.38513	15.49772	2.87516	11.61482	14.41498	1.81707	11.62045
112	Magenta	17.22120	3.33321	11.98821	17.57628	3.73917	11.19742	17.23410	4.03138	12.64291
113	Magenta	13.91939	0.10656	12.00537	13.27760	0.09399	12.71543	14.71147	-0.26764	12.39115
114	Green	14.57987	14.57987	5.92487	15.49674	14.35765	5.76300	14.44142	14.36965	6.84838
115	Red	17.22120	13.97679	5.32179	17.59612	14.76152	4.92196	17.23484	13.32191	4.62381
116	Yellow	13.91939	17.20344	5.30462	13.25793	17.16582	4.61376	14.12253	16.28711	5.49253
117	Orange	5.92487	2.73013	2.73013	5.36421	3.27049	3.28682	5.68810	1.82983	2.95291
118	Magenta	5.32179	3.33321	0.08880	5.52632	3.11586	0.99828	4.95217	2.52784	-0.27312

TABLE IV. (Continued.)

No.	Color	Oxygen			Hydrogen 1			Hydrogen 2		
		$x$ (Å)	$y$ (Å)	$z$ (Å)	$x$ (Å)	$y$ (Å)	$z$ (Å)	$x$ (Å)	$y$ (Å)	$z$ (Å)
119	Magenta	5.26439	0.10656	3.35037	6.06911	-0.33586	3.62042	5.00224	-0.34182	2.54634
120	Green	2.73013	5.92487	2.73013	1.82683	5.70085	2.95395	3.26316	5.35892	3.28854
121	Red	3.33321	5.32179	0.08880	4.00976	4.64524	0.11699	3.14429	5.51071	1.00796
122	Yellow	0.08880	5.32179	3.33321	0.07590	4.62362	3.98791	-0.26628	4.91583	2.54242
123	Orange	14.57987	11.38513	2.73013	14.35371	10.46771	2.88320	14.35371	11.53820	1.81271
124	Magenta	13.97679	11.98821	0.08880	13.32356	12.68772	0.07469	14.76625	12.38972	-0.27420
125	Magenta	17.22120	11.98821	3.33321	16.31037	11.78038	3.12483	17.57202	12.36509	2.52629
126	Green	11.38513	14.57987	2.73013	10.48234	14.35492	2.95508	11.91945	14.01830	3.29172
127	Red	11.98821	13.97679	0.08880	12.35783	14.78216	-0.27312	11.78368	14.19414	0.99828
128	Yellow	12.04561	17.20344	3.35037	11.23956	17.57461	3.70919	11.81858	16.29855	3.13621
129	Aqua	0.00000	0.00000	0.00000	-0.53524	-0.53524	-0.58588	0.53524	0.53524	-0.58588
130	Purple	4.32748	4.31665	4.31671	4.86142	4.85453	4.90137	3.79093	3.78405	4.90380
131	Purple	8.65500	8.65500	0.00000	9.24088	9.19024	-0.53524	9.24088	8.11976	0.53524
132	Purple	0.00000	8.65500	8.65500	0.53524	9.24088	8.11976	-0.53524	9.24088	9.19024
133	Purple	8.65500	0.00000	8.65500	8.11976	-0.53524	8.06912	9.19024	0.53524	8.06912
134	Purple	12.98252	12.99335	4.31671	13.56838	13.52462	4.85592	13.56837	12.45413	3.78543
135	Aqua	4.32748	12.99335	12.99329	4.86407	13.52592	13.58037	3.79358	12.45544	13.57796
136	Purple	12.98252	4.31665	12.99330	12.44593	3.72957	13.52588	13.51643	3.73198	12.45540

With the water coordinates given in Table IV, it is obvious that the guest molecules occupying the different cages of the same type experience slightly different proton environments. Table VI lists the Coulomb potential energies from the water molecules to a test point charge of  $1.0e$  at the center of the different cages calculated for the sII unit cell. The energies of the guests in the different cages vary by large

amounts ranging from  $14.80 \text{ kJ mol}^{-1}$  for small cages and  $13.70 \text{ kJ mol}^{-1}$  for large cages. These energy differences are much greater than those between the cages in the sI unit cell. These energy differences are significant and will affect the local environments of the guests in the different small and large cages of the hydrate phase. The energy differences in the cages are considerable, but the cage shapes in the sII unit

TABLE V. Cartesian coordinates of centers of the cages for initial placement of guest molecules in sII hydrate unit cell.

Cage	$x$ (Å)	$y$ (Å)	$z$ (Å)
Small 1	6.491	2.165	6.492
Small 2	2.159	6.491	6.491
Small 3	6.485	6.494	2.164
Small 4	10.824	2.164	10.819
Small 5	2.159	10.817	10.818
Small 6	10.819	10.821	2.164
Small 7	10.822	15.147	6.491
Small 8	15.154	10.821	6.490
Small 9	6.489	15.144	10.819
Small 10	15.154	6.490	10.819
Small 11	6.484	10.816	15.146
Small 12	10.820	6.490	15.146
Small 13	15.097	2.213	15.359
Small 14	2.164	15.147	15.147
Small 15	15.146	15.147	2.163
Small 16	2.164	2.163	2.163
Large 1	8.651	8.655	8.654
Large 2	4.322	4.327	12.984
Large 3	12.991	4.327	4.326
Large 4	4.319	12.983	4.326
Large 5	12.988	12.983	12.984
Large 6	0.004	0.000	8.655
Large 7	8.655	0.000	0.001
Large 8	0.000	8.655	0.000

TABLE VI. Coulomb potential energies for a point charge placed at the center of the each cage for sII hydrates.

Cage	Coulomb potential ( $\text{kJ mol}^{-1}$ )
Small 1	-30.6274
Small 2	-27.6689
Small 3	-20.8737
Small 4	-30.2331
Small 5	-25.2360
Small 6	-21.0696
Small 7	-32.3738
Small 8	-25.3936
Small 9	-25.7720
Small 10	-28.1847
Small 11	-27.4084
Small 12	-28.3898
Small 13	-17.5738
Small 14	-24.2486
Small 15	-22.2669
Small 16	-25.8379
Large 1	-60.0211
Large 2	-48.2347
Large 3	-57.4767
Large 4	-61.9297
Large 5	-53.4989
Large 6	-48.8333
Large 7	-56.8615
Large 8	-54.9082

TABLE VII. Cartesian coordinates of 68 water molecules in two sH hydrates unit cells which are combined to form an orthorhombic cell as described in the text.

No.	Oxygen			Hydrogen 1			Hydrogen 2		
	<i>x</i> (Å)	<i>y</i> (Å)	<i>z</i> (Å)	<i>x</i> (Å)	<i>y</i> (Å)	<i>z</i> (Å)	<i>x</i> (Å)	<i>y</i> (Å)	<i>z</i> (Å)
1	1.37495	10.62758	6.49512	1.70056	9.80649	6.86393	1.42470	10.50147	5.54757
2	2.29444	8.36449	7.82426	1.51454	7.91647	8.15177	2.76335	8.63743	8.61284
3	0.05118	7.02259	8.72763	-0.74263	7.48290	8.45522	0.02199	7.03931	9.68423
4	2.26050	12.84742	7.86981	1.97837	12.05671	7.41003	2.74099	12.52349	8.63166
5	0.00524	14.15432	8.80244	-0.75272	13.66940	8.47597	0.76119	13.66626	8.47597
6	0.05709	16.76509	7.89731	0.04256	15.85562	8.19547	-0.75983	16.87089	7.40978
7	1.43427	10.61936	3.70701	1.70608	9.84684	3.21146	0.47764	10.59157	3.68918
8	0.05233	7.07640	1.33858	-0.74660	7.49036	1.66505	0.00763	6.17771	1.66505
9	0.04815	4.46984	2.27121	0.00787	3.89176	1.50934	-0.77770	4.31880	2.73100
10	3.63601	9.14557	-0.00099	4.52186	8.78298	-0.00099	3.76492	10.09404	-0.00099
11	2.29444	8.36449	2.31676	1.51454	7.91647	1.98925	2.76335	8.63743	1.52818
12	3.67312	11.92706	-0.04568	3.20188	12.22028	0.73417	4.49592	12.41578	-0.02681
13	2.25813	12.79275	2.19061	2.00021	12.06831	2.76060	2.75684	13.37957	2.75908
14	4.68099	21.10397	6.43401	4.40918	21.87649	6.92956	5.63762	21.13176	6.45184
15	3.85713	18.93058	7.95041	4.11505	19.65502	7.38042	3.35842	18.34376	7.38194
16	8.39944	18.93866	7.82426	7.61954	18.49064	8.15177	8.86835	19.21160	8.61284
17	6.05817	14.95824	7.89731	6.07270	15.86771	8.19547	6.87509	14.85244	7.40978
18	6.15618	17.59676	8.72763	5.36237	18.05707	8.45522	6.12699	17.61348	9.68423
19	2.44214	19.79627	0.04370	2.91338	19.50305	-0.73615	1.61934	19.30755	0.02483
20	4.74031	21.09575	3.64590	4.41470	21.91684	3.27709	4.69056	21.22186	4.59345
21	3.85476	18.87591	2.27121	3.37427	19.19984	1.50936	4.13689	19.66662	2.73099
22	6.15733	17.65057	1.33858	5.35840	18.06453	1.66505	6.11263	16.75188	1.66505
23	6.15315	15.04401	2.27121	6.11287	14.46593	1.50934	5.32730	14.89297	2.73100
24	6.06240	13.36047	0.04370	6.08071	13.91519	-0.73616	6.89706	12.89226	0.02482
25	9.74101	19.71974	-0.00099	10.62686	19.35715	-0.00099	9.86992	20.66821	-0.00099
26	8.39944	18.93866	2.31676	7.61954	18.49064	1.98925	8.86835	19.21160	1.52818
27	2.38127	17.12085	6.43394	1.57729	16.97003	6.93105	2.83589	16.27868	6.45157
28	2.32637	17.02057	3.64590	2.87426	17.71340	3.27709	2.41032	17.12701	4.59344
29	3.77572	14.61616	3.63192	3.30095	15.43847	3.51095	3.83621	14.51141	4.58145
30	3.73536	14.68614	6.40694	4.54416	14.79843	6.90640	3.23352	14.04074	6.90477
31	3.89778	2.19873	7.86981	3.37700	1.94459	8.63167	3.35407	2.83842	7.41001
32	7.47995	0.05341	6.49512	7.80556	-0.76768	6.86393	7.52970	-0.07270	5.54757
33	8.36550	2.27325	7.86981	8.08337	1.48254	7.41003	8.84599	1.94932	8.63166
34	6.11024	3.58015	8.80244	5.35228	3.09523	8.47597	6.86619	3.09209	8.47597
35	6.16209	6.19092	7.89731	6.14756	5.28145	8.19547	5.34517	6.29672	7.40978
36	2.39442	1.43555	-0.04568	2.88397	1.69705	0.73419	2.40626	0.47861	-0.02681
37	3.82237	2.15759	2.24359	4.60396	2.62344	1.94640	3.32397	2.81250	2.73237
38	7.53927	0.04519	3.70701	7.81108	-0.72733	3.21146	6.58264	0.01740	3.68918
39	6.10969	7.84941	-0.00099	6.11358	7.26355	-0.75793	6.11358	7.26355	0.75595
40	6.06918	6.19103	2.24359	6.08183	5.28122	1.94639	6.88555	6.29519	2.73239
41	6.06408	3.55240	1.41339	6.09327	3.53568	0.45679	6.85789	3.09209	1.68580
42	9.77812	1.35289	-0.04568	9.30688	1.64611	0.73417	10.60092	1.84161	-0.02681
43	8.36313	2.21858	2.19061	8.10521	1.49414	2.76060	8.86184	2.80540	2.75908
44	3.78796	6.44814	6.49507	3.23970	7.14023	6.86475	3.70325	6.55518	5.54765
45	3.73529	6.46306	3.73408	3.23365	7.10737	3.23462	4.54516	6.35115	3.23625
46	2.38134	4.02830	3.70700	1.57642	4.17916	3.21147	2.83558	4.87065	3.68918
47	2.33854	4.04372	6.50910	2.81331	4.86603	6.63007	2.27805	3.93897	5.55957
48	10.00278	12.77290	7.86981	9.48200	12.51876	8.63167	9.45907	13.41259	7.41001
49	10.78599	10.52980	6.43401	10.51418	11.30232	6.92956	11.74262	10.55759	6.45184
50	9.96213	8.35641	7.95041	10.22005	9.08085	7.38042	9.46342	7.76959	7.38194
51	12.16317	4.38407	7.89731	12.17770	5.29354	8.19547	12.98009	4.27827	7.40978
52	8.54714	9.22210	0.04370	9.01838	8.92888	-0.73615	7.72434	8.73338	0.02483
53	8.49942	12.00972	-0.04568	8.98897	12.27122	0.73419	8.51126	11.05278	-0.02681
54	9.92737	12.73176	2.24359	10.70896	13.19761	1.94640	9.42897	13.38667	2.73237
55	10.84531	10.52158	3.64590	10.51970	11.34267	3.27709	10.79556	10.64769	4.59345
56	9.95976	8.30174	2.27121	9.47927	8.62567	1.50936	10.24189	9.09245	2.73099
57	12.16740	2.78630	0.04370	12.18571	3.34102	-0.73616	13.00206	2.31809	0.02482
58	12.21469	18.42358	-0.00099	12.21858	17.83772	-0.75793	12.21858	17.83772	0.75595

TABLE VII. (Continued.)

No.	Oxygen			Hydrogen 1			Hydrogen 2		
	$x$ (Å)	$y$ (Å)	$z$ (Å)	$x$ (Å)	$y$ (Å)	$z$ (Å)	$x$ (Å)	$y$ (Å)	$z$ (Å)
59	12.17418	16.76520	2.24359	12.18683	15.85539	1.94639	12.99055	16.86936	2.73239
60	12.16908	14.12657	1.41339	12.19827	14.10985	0.45679	12.96289	13.66626	1.68580
61	8.48627	6.54668	6.43394	7.68229	6.39586	6.93105	8.94089	5.70451	6.45157
62	8.43137	6.44640	3.64590	8.97926	7.13923	3.27709	8.51532	6.55284	4.59344
63	9.88072	4.04199	3.63192	9.40595	4.86430	3.51095	9.94121	3.93724	4.58145
64	9.84036	4.11197	6.40694	10.64916	4.22426	6.90640	9.33852	3.46657	6.90477
65	9.89296	17.02231	6.49507	9.34470	17.71440	6.86475	9.80825	17.12935	5.54765
66	9.84029	17.03723	3.73408	9.33865	17.68154	3.23462	10.65016	16.92532	3.23625
67	8.48634	14.60247	3.70700	7.68142	14.75333	3.21147	8.94058	15.44482	3.68918
68	8.44354	14.61789	6.50910	8.91831	15.44020	6.63007	8.38305	14.51314	5.55957

TABLE VIII. Cartesian coordinates of guest molecules in two sH hydrate unit cells.

Cage	$x$ (Å)	$y$ (Å)	$z$ (Å)
Small 1	3.058	5.288	10.148
Small 2	9.163	15.862	10.148
Small 3	3.057	15.873	10.136
Small 4	9.162	5.299	10.136
Small 5	0.007	10.576	10.137
Small 6	6.112	0.002	10.137
Medium 1	6.109	3.525	5.069
Medium 2	12.214	14.099	5.069
Medium 3	6.118	17.613	5.072
Medium 4	12.223	7.038	5.072
Large 1	0.000	0.000	5.070
Large 2	6.105	10.574	5.070

TABLE IX. Coulomb potential energies for a point charge placed at center of the each cage for sH hydrates. Two hexagonal unit cells are combined to construct an orthorhombic cell. The even number cages are same cages as the odd number cages due to the periodicity.

Cage	Coulomb potential (kJ mol <sup>-1</sup> )
Small 1	-24.5292
Small 2	-24.5292
Small 3	-22.3840
Small 4	-22.3840
Small 5	-28.3748
Small 6	-28.3748
Medium 1	-35.9031
Medium 2	-35.9031
Medium 3	-17.5265
Medium 4	-17.5265
Large 1	-67.2454
Large 2	-67.2454

cell are quasi-spherical and so the NMR line shape anisotropy is unavailable as a method for gauging the different environments of different cages in the sII hydrate.

### C. Structure H hydrates

The hexagonal unit cell of the sH hydrate has 34 water molecules and these coordinates were reported by Okano and Yasuoka.<sup>5</sup> However, in molecular dynamics simulations, implementation of periodic boundary conditions for the non-orthogonal hexagonal coordinate system is computationally more time consuming than orthorhombic systems. We have combined two hexagonal unit cells to construct an orthorhombic cell with coordinates of the water molecules given in Table VII and the position of the center of the cages in Table VIII. The dimension of each side of the super cell are set at  $a = 12.21$  Å,  $b = 21.15$  Å,  $c = 10.14$  Å. The origin of the coordinate system for this simulation cell is at the center of the pentagonal face at the bottom of the 5<sup>12</sup>6<sup>8</sup> cage. The Coulomb potential of the guests in the different cages vary 5.99 kJ mol<sup>-1</sup> and 18.38 kJ mol<sup>-1</sup> for the small and medium cages, respectively. Although the number of the water molecules in the small cages and medium cages are the same (20), the energy differences in the medium cages are much greater than those in the small cages. This trend may be caused by the non-spherical shape of the medium cages. The energy differences in the small cages in sH are larger than that in sI but smaller than that in sII hydrate. The guest environment inside the small cages can be different among these three types of structures (Table IX). The coordinates of the water molecules and the center of the cages in sH are available in xyz coordinate file format (see the supplementary material<sup>34</sup>).

### III. CONCLUSIONS

We determined the coordinates of water molecules in the unit cell of structures I and II hydrates that have nearly zero net dipole moment and the lowest potential energy by testing the various orientations of water molecules that satisfy the ice rules. The resulting net dipole moments are  $0.000 \times 2.18$  D and  $0.001 \times 2.18$  D for sI and sII hydrates, respectively.

The coordinates for these configurations are reported and can be used as the initial water molecule coordinates in molecular simulations of sI and sII hydrates. We also determined water coordinates for an orthorhombic simulation cell of the sH hydrate. In all cases, the centers of the clathrate hydrate cages are specified for the addition of guest molecules in the hydrate structure. These coordinates can be adapted for use in different molecular simulation programs and different water potentials. A theme observed in the determination of the proton arrangements is that water configurations with proton arrangements in the hexagonal faces with smaller net dipole moments are favored.

The different cages of each class in the sI, sII, and sH hydrates have different water proton arrangements and the guest molecules will experience different electrostatic forces in these cages. The maximum differences in electrostatic energies in the different small and large cages of sII clathrate hydrate are large ( $\sim 15$  and  $14$  kJ/mol, respectively) and the environments the guests experience in these cages can be significantly different. Energy differences between other low dipole moment configurations for the unit cell and the configuration chosen in this work are small and as expected many different proton configurations which give zero net dipole moment to the unit cell can be accessible to the actual hydrate system. However, transformation between these different proton configurations would require the formation of multiple Bjerrum defects and have high energy barriers. It should be noted that in actual hydrate samples, the net dipole moment of the entire sample must be zero and dipole moments of individual unit cells are not constrained to be zero (as is imposed in molecular dynamics simulations). Having access to different proton configurations could be useful in modeling the water rotation process as the hydrate sample is heated. The fact that water molecules in the hexagonal faces tend to arrange in low dipole moment configurations may also suggest that water molecules in the pentagonal faces of the hydrate phase may have a lower energy barrier to rotation. Study of such issues will remain for future work.

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<sup>1</sup>E. D. Sloan, Jr., *Nature (London)* **426**, 353 (2003).

<sup>2</sup>M. R. Walsh, K. A. Koh, E. D. Sloan, A. K. Sum, and D. T. Wu, *Science* **326**, 1095 (2009).

<sup>3</sup>S. Liang and P. G. Kusalik, *Chem. Phys. Lett.* **494**, 123 (2010).

<sup>4</sup>S. Liang and P. G. Kusalik, *J. Phys. Chem. B* **114**, 9563 (2010).

<sup>5</sup>Y. Okano and K. Yasuoka, *J. Chem. Phys.* **124**, 024510 (2006).

<sup>6</sup>S. Alavi, J. A. Ripmeester, and D. D. Klug, *J. Chem. Phys.* **125**, 104501 (2006).

<sup>7</sup>T. Miyoshi, R. Ohmura, and K. Yasuoka, *J. Phys. Chem. C* **111**, 3799 (2007).

<sup>8</sup>S. Alavi, J. A. Ripmeester, and D. D. Klug, *J. Chem. Phys.* **126**, 124708 (2007).

<sup>9</sup>T. Miyoshi, M. Imai, R. Ohmura, and K. Yasuoka, *J. Chem. Phys.* **126**, 234506 (2007).

<sup>10</sup>M. M. Conde and C. Vega, *J. Chem. Phys.* **133**, 064507 (2010).

<sup>11</sup>S. Alavi, R. Susilo, and J. A. Ripmeester, *J. Chem. Phys.* **130**, 174501 (2009).

<sup>12</sup>S. Alavi, S. Takeya, R. Ohmura, T. K. Woo, and J. A. Ripmeester, *J. Chem. Phys.* **133**, 074505 (2010).

<sup>13</sup>W. Kluig, P. Kubisiak, and L. Cwiklik, *J. Phys. Chem. A* **115**, 6149 (2011).

<sup>14</sup>S. Alavi, R. Ohmura, and J. A. Ripmeester, *J. Chem. Phys.* **134**, 054702 (2011).

<sup>15</sup>F. Hollander and G. A. Jeffrey, *J. Chem. Phys.* **66**, 4699 (1977).

<sup>16</sup>R. K. McMullan and Å. Kvik, *Acta Crystallogr. B* **46**, 390 (1990).

<sup>17</sup>M. A. Desando, Y. P. Handa, R. E. Hawkins, C. I. Ratcliffe, and J. A. Ripmeester, *J. Inclusion Phenom.* **8**, 3–16 (1990).

<sup>18</sup>D. W. Davidson, C. I. Ratcliffe, and J. A. Ripmeester, *J. Inclusion Phenom.* **2**, 239–247 (1984).

<sup>19</sup>C. I. Ratcliffe and J. A. Ripmeester, *J. Phys. Chem.* **90**, 1259–1263 (1986).

<sup>20</sup>M. J. Collins, D. W. Davidson, C. I. Ratcliffe, and J. A. Ripmeester, in *Dynamics of Molecular Crystals*, edited by J. Lascombe (Elsevier, Amsterdam, 1987), p. 497.

<sup>21</sup>S. K. Garg, D. W. Davidson, and J. A. Ripmeester, *J. Magn. Reson.* **15**, 295–309 (1974); T. M. Kirschgen, M. D. Zeidler, B. Geil, and F. Fujara, *Phys. Chem. Chem. Phys.* **5**, 5247 (2003); Y. Ba, J. A. Ripmeester, and C. I. Ratcliffe, *Can. J. Chem.* **89**, 1055 (2011).

<sup>22</sup>H. Mohammadi-Manesh, S. Alavi, T. K. Woo, and B. Najafi, *Phys. Chem. Chem. Phys.* **13**, 2367 (2011).

<sup>23</sup>J. S. Tse, W. R. McKinnon, and M. Marchi, *J. Phys. Chem.* **91**, 4188 (1987).

<sup>24</sup>C. Gutt, J. Baumert, W. Press, J. S. Tse, and S. Janssen, *J. Chem. Phys.* **116**, 3795 (2002).

<sup>25</sup>V. Buch, P. Sandler, and J. Sadlej, *J. Phys. Chem. B* **102**, 8641 (1998).

<sup>26</sup>E. P. van Klaveren, J. P. Michels, J. A. Schouten, D. D. Klug, and J. S. Tse, *J. Chem. Phys.* **117**, 6637 (2002).

<sup>27</sup>L. G. MacDowell and C. Vega, *J. Phys. Chem. B* **114**, 6089 (2010).

<sup>28</sup>R. K. McMullan and G. A. Jeffrey, *J. Chem. Phys.* **42**, 2725 (1965).

<sup>29</sup>K. A. Udachin, C. I. Ratcliffe, G. D. Enright, and J. A. Ripmeester, *Supramol. Chem.* **8**, 173 (1997).

<sup>30</sup>M. V. Kirov, *Crystallogr. Rep.* **55**, 353 (2010).

<sup>31</sup>J. D. Bernal and R. H. Fowler, *J. Chem. Phys.* **1**, 515 (1933).

<sup>32</sup>W. L. Jorgensen and J. D. Madura, *Mol. Phys.* **56**, 1381 (1985).

<sup>33</sup>N. Bjerrum, *Science* **115**, 385 (1952).

<sup>34</sup>See supplementary material at <http://dx.doi.org/10.1063/1.4795499> for the coordinates of hydrates in xyz coordinate file format. The sI.xyz.txt file contains the coordinates of the water molecules and the location of the center of the cages in a unit cell of the sI hydrate. The sII.xyz.txt file contains the coordinates of the water molecules and the location of the center of the cages in a unit cell of the sII hydrate. The sH.xyz.txt file contains the coordinates of the water molecules and the location of the center of the cages in the combined two hexagonal unit cells of sH hydrate to construct an orthorhombic cell.

<sup>35</sup>M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford University Press, 1989).