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Hydrogen-bonding alcohol-water interactions in binary ethanol, 1-propanol, and 2-propanol+ methane structure II clathrate hydrates

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The small alcohols ethanol, 1-propanol, and 2-propanol are miscible in water, form strong hydrogen bonds with water molecules, and are usually known as inhibitors for clathrate hydrate formation. However, in the presence of methane or other help gases, clathrate hydrates of these substances have been synthesized. In this work, molecular dynamics simulations are used to characterize guest-host hydrogen bonding, microscopic structures, and guest dynamics of binary structure II clathrate hydrates of methane (small cages) with ethanol, 1-propanol, and 2-propanol in the temperature range of 100–250 K to gain insight into the stability of these materials. We observe that these alcohols form structures with dynamic long-lived (~ 10 ps) guest-host hydrogen bonds in the hydrate phases while maintaining the general cage structure of the sII clathrate hydrate form. The hydroxyl groups of ethanol, 1-propanol, and 2-propanol act as both proton acceptors and proton donors and there is a considerable probability of simultaneous hydrogen bonding between O and H hydroxyl atoms with different cage water molecules. The presence of the nonpolar methane molecule and the hydrophobic moieties of the alcohols stabilize the hydrate phase, despite the strong and prevalent alcohol-water hydrogen bonding. The effect of the alcohol molecules on the structural properties of the hydrate and the effect of guest-host hydrogen bonding on the guest dynamics are studied. © 2010 American Institute of Physics. [doi:10.1063/1.3469776]

I. INTRODUCTION

Clathrate hydrates form when mixtures of water and sufficiently hydrophobic molecular species are subject to high pressures and/or low temperatures.^{1–3} To minimize the water-hydrophobic interaction, water molecules form space filling frameworks with cages which encapsulate the guest molecules, while at the same time forming a complete ice-like water-water hydrogen-bonding network. Both water-soluble and water-insoluble species (liquid or gas) can form clathrate hydrates. It is clear that suitable guest molecules may have a hydrophilic functionality, but that this must be balanced by the hydrophobic moieties in the molecule.⁴ Thus, we may expect a range of behavior as the relative sizes of the hydrophobic and hydrophilic parts of guest molecules vary. The special nature of hydrates with water-miscible guests has been recently clarified and effects of guest-host hydrogen bonding on structure, stability, and guest-host dynamics were clearly illustrated.⁵

Small hydrophilic molecules such as methanol generally disrupt the hydrogen-bonding network of water and inhibit clathrate hydrate formation (*vide infra* for further discussion).⁶ Ethanol, 1-propanol, and 2-propanol are soluble

in water, and do not form pure clathrate hydrates at higher temperatures. At low temperatures, ethanol forms hydrate phases with water or binary hydrate phases with air as the help gas.⁷ It has recently been observed that in the presence of small help gas molecules such as methane^{8–10} and carbon dioxide,¹¹ water-soluble ethanol, 1-propanol, and 2-propanol form stable sII clathrate hydrates, presumably because the hydrophobic portion of the guest molecules is larger than methanol. On their own, these alcohols are miscible in water and disrupt the water-water hydrogen-bonding network in such a way as to prevent formation of stable pure alcohol clathrate hydrates. However, the presence of the sufficiently hydrophobic help gas molecules and the sufficiently large hydrophobic moieties on the alcohols provide enough thermodynamic driving force for the water molecules to rearrange into clathrate hydrates to isolate these small gas molecules in clathrate cages.

The structure of the hydrate formed in the presence of the alcohols and hydrophobic help gases depends on the size of the alcohol molecule and the nature of the helper gas. Structure I (sI), structure II (sII), and structure H (sH) binary hydrates with alcohols have been observed. The *tert*-butanol molecule forms two stoichiometric hydrates¹² but under a pressure of a help gas such as methane it also forms a sII hydrate,¹³ thus behaving in much the same way as other large

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FIG. 1. The three phase aqueous liquid+hydrate+methane-rich vapor equilibrium phase lines for the ethanol, 1-propanol, and 2-propanol+methane binary sII hydrates in the pressure-temperature plane from experimental data. The methane+propane equilibrium curves were calculated at two different large cage propane occupancies. The methane+butane equilibrium curves are calculated for the four phase aqueous liquid+organic liquid+hydrate+methane-rich vapor equilibrium lines. The propane and butane hydrate calculations were performed with CSMGEM (Ref. 3).

sII guests that require a help gas. The even larger isoamyl alcohol (3-methyl-1-butanol), which has only limited solubility in water, behaves much like other larger hydrophobic molecules in that it forms a sH hydrate in the presence of a help gas.¹⁴

Viewed from a different perspective, formation of pure methane or carbon dioxide hydrates requires relatively high pressures. Addition of a large molecule guest species to the water-gas system promotes clathrate hydrate formation at lower pressures than those required for the pure CH₄ or CO₂ hydrates. Ethanol, 1-propanol, and 2-propanol act as methane hydrate promoters that lead to the formation of a binary sII clathrate hydrate with the alcohol in the large cage (either in full or partial occupancy) and methane in the small cages of the hydrate. The three phase (aqueous liquid+hydrate+methane-rich vapor) boundary lines of these hydrates^{8–10} are shown in Fig. 1. The three phase boundary line for the sII methane+propane clathrate hydrate at two compositions and the four phase boundary line for the (aqueous liquid+organic liquid+hydrate+methane-rich vapor) *n*-butane and isobutane calculated with CSMGEM (Ref. 3) are given for comparison. The alcohols reduce the pressure required for hydrate formation compared to the pressure required to form pure methane sI hydrate. However, at each temperature, the three phase equilibrium line of the binary sII methane+alcohol hydrates occurs at higher pressures than the corresponding curves for the sII methane+alkane hydrate. The alcohols thus destabilize the hydrate compared to the methane+alkane binary hydrate, much as expected for water-miscible guests.⁵

The effect of the alcohol solute in reducing the pressure of the (liquid+hydrate+gas) equilibrium phase boundary can be partially explained in terms of the change in the macroscopic thermodynamic activity of the aqueous hydrate-forming water-alcohol solution compared to pure water.³ In contrast, this work focuses on the molecular scale understanding of the water molecule-guest interaction in hydrate cages to shed light on the relative stability of different binary

alcohol+methane clathrate hydrates. To this end, we perform molecular dynamics simulations of the structure II binary methane+ethanol, 1-propanol, and 2-propanol clathrate hydrates at ambient pressure and temperature in the range of 100–250 K. We recently studied hydrogen-bond formation between ketone, ether, and amine guest molecules and water cages in the sII and sH clathrate hydrates with molecular dynamics simulation, NMR guest relaxation time, dielectric relaxation, and single crystal x-ray crystallography.¹⁵ Guest-host hydrogen bonding was found to affect both guest and host static and dynamic properties and the hydrogen-bonding nature of the alcohol guests raises the possibility of these phenomena occurring in the alcohol hydrates as well. There have also been recent IR, Raman, and molecular dynamics (MD) studies of hydrates and evidence of hydrogen-bond formation with the guests has been observed.¹⁶

Unlike ketone and ether guests studied previously, alcohols act as both hydrogen-donors and hydrogen-acceptors in hydrogen bonding with water and both types of bonds are considered and analyzed. The dynamics of the guest motions are studied and correlated with the effects of guest-water hydrogen bonding. The results of the MD simulations are correlated with experimental measurements of properties of these systems. Details of the molecular dynamics methodology are presented in Sec. II.

II. COMPUTATIONAL METHODS

The initial coordinates of the water oxygen atoms in the sII clathrate cubic unit cell ($a=17.31$ Å) are taken from clathrate x-ray crystallography¹⁷ and the positions of the water hydrogen atoms in the sII unit cell were determined by a Monte Carlo procedure¹⁸ which determines the proton configuration of the unit cell consistent with the Bernal-Fowler ice rules¹⁹ with the lowest energy and dipole moment. The TIP4P model²⁰ was used for water and $2 \times 2 \times 2$ replicas of the unit cell with 1088 water molecules were used in the simulations. Guest molecules were initially placed in cage centers and allowed to equilibrate during the simulation. In these simulations, all large sII cages are filled with alcohol, propane, or butane molecules and all small sII cages are filled methane molecules. In the experimental binary methane+alcohol phases, some large cages are occupied by methane.^{8,9}

The intermolecular van der Waals potentials between atoms i and j on different molecules are taken as a sum of Lennard-Jones and electrostatic point charge interactions. The Lennard-Jones σ_{ij} and ϵ_{ij} parameters for atoms of guest alcohol molecules are taken from the general AMBER force field²¹ and CH₄ molecules are modeled with the Murad-Gubbins potential.²² The values for the parameters σ_{ii} and ϵ_{ii} for selected atom types are given in Table S1 of the supporting information.²³ Potentials between unlike atoms are calculated using the standard combination rules $\epsilon_{ij}=(\epsilon_{ii}\epsilon_{jj})^{1/2}$ and $\sigma_{ij}=(\sigma_{ii}+\sigma_{jj})/2$. Partial electrostatic point charges on the atoms of the guest molecules were determined from charges from electrostatic potential grid calculations²⁴ with the GAUSSIAN 03 suite of programs²⁵ at the B3LYP/6-311++G(d,p) level of theory. The point charges q_i on the water

FIG. 2. The experimental temperature dependence of the lattice constants of binary sII hydrates of *i*-butane (12.4%)+methane (87.6%) [Ref. 17], 1-propanol+methane, 2-propanol+methane [Ref. 8(a)], propane (40%)+methane (60%) [Ref. 17], and ethanol+methane [Ref. 9(b)] at ambient pressure. The alcohol hydrates have some methane in the large cages. Calculated MD lattice constants for the binary sII hydrates with methane are shown (with similar filled symbols) for comparison. In MD simulations, all large cages are filled with alcohol guests and small cages are filled with methane.

and ring oxygen atoms, along with the calculated dipole moment for the optimized guest molecules, are given in Table S2 of the supporting information. It is noteworthy that electrostatic point charges on H and O atoms of the three alcohol hydroxyl groups are similar. Consistent with the OPLS force field, Lennard-Jones and electrostatic interactions between atoms at 1–4 positions in the same molecule are scaled by a factor of 0.5.

Isotropic constant pressure-temperature NpT molecular dynamics simulations on periodic simulation cells were performed using the DL_POLY 2.20 program.²⁶ Temperatures in the range of 100–250 K at ambient pressure were studied for each clathrate. The equations of motion were integrated with the Verlet leapfrog algorithm using a time step of 1 fs. All simulations were performed for a total time of 500 ps, with the first 100 ps used for temperature scaled equilibration. Long-range electrostatic interactions were calculated using the Ewald summation method²⁷ with a precision of 1×10^{-6} and all intermolecular interactions in the simulation box were calculated within a cut-off distance of $R_{\text{cutoff}} = 13.0$ Å. Temperature and pressure in the simulation were regulated using the modified Nosé–Hoover barostat algorithm²⁸ with thermostat and barostat relaxation times of 0.2 and 0.5 ps, respectively. The dynamics and hydrogen-bonding calculations at each temperature and pressure were studied with constant energy, constant volume (NVE) simulations starting from final configurations of previous NpT simulations. Dynamics studies were performed for a total of 250 ps with an equilibration time of 50 ps.

III. RESULTS AND DISCUSSION

Calculated lattice constants for binary sII hydrates of ethanol, 1-propanol, 2-propanol, propane, and butane at temperatures between 100 and 250 K are shown in Fig. 2, with experimental data^{8–10,29,30} for related hydrates given for comparison. Simulations have all large cages occupied by alcohols, while experiments show evidence of partial methane

occupancy of large sII clathrate hydrate cages. These comparisons are nonetheless useful for discerning trends in both sets of data. As expected, the calculated lattice constants for the guests with four heavy atoms (butane, 1-propanol, and 2-propanol) are larger than those of the guests with three heavy atoms (propane and ethanol).

At low temperatures, the slopes of the temperature dependence of the lattice constants from the MD simulations are larger than the slope from experimental measurements and the MD simulations overestimate the thermal expansion of the hydrate phase at low temperatures (from 100 to 150 K). At higher temperatures, the calculated and predicted slopes are closer in magnitude. The TIP4P-AMBER-(Murad–Gubbins) force field simulations underestimate the experimental lattice constants by $\sim 1\%$, but the agreement of the lattice constants between experiment and MD predictions becomes better at higher temperatures near 250 K. This can be due to the fact that the TIP4P potential was parametrized for water and ice phases near 273 K. Empirical potentials are often parametrized with limited experimental data at a particular temperature. The predictions of the potential model will not necessarily reproduce the properties of the system with the same degree of accuracy at other temperatures. We believe this could be a reason for the different accuracy of the TIP4P potential for predicting the lattice constants at different temperatures. In the experimental measurements, the sII binary methane hydrates with the alkane guests have larger lattice constants than those with the alcohol guests, while in the simulated results the lattice constants for the hydrates with alcohol were generally the same as the hydrates with a corresponding alkane molecule. This shortcoming of the simulations could be due to the use of nonpolarizable force fields to model the alcohol+water interactions in the hydrates.³¹

We performed similar MD simulations of sI binary clathrates of methanol (large cages) and methane (small cages) at 100 and 250 K. At 100 K, for times up to 1 ns the binary methanol/methane hydrate structure was found to be mechanically stable, but at 250 K the hydrate lattice in the simulation decomposes. There is some experimental evidence for the formation of metastable binary methanol clathrate hydrates with ethylene oxide (sI) and tetrahydrofuran (sII).^{32–34} We leave detailed simulation studies of methanol systems for a later publication.

The radial distribution functions (RDFs) for the guest alcohol (ROH) hydroxyl oxygen (O_H) and hydrogen (H_O) atoms and the cage water atoms (H_W and O_W) are shown in Fig. 3(a). The RDF plots show that first peaks for the O_H-H_W [i.e., $R(H)O \cdots HOH$] and H_O-O_W ($ROH \cdots OH_2$) interactions are at distances of ~ 1.8 Å, which are within the range of normal hydrogen bonding. The O_H-O_W RDFs in Fig. 3(a) show a peak at ~ 2.8 Å, which is also consistent with hydrogen bonding. For reference, the C_3-O_W RDFs for the alcohols along with propane and butane reference guests are shown in Fig. 3(b), where C_3 is the terminal carbon atom. For the C_3-O_W pairs, the peak in the RDF is at ~ 4 Å. This shows that the proximity of the O_H atoms to the cage O_W atoms is due to hydrogen bonding and not the encapsulation of the guests in the large cages.

FIG. 3. (a) The $\text{O}_\text{H}-\text{H}_\text{W}$, $\text{H}_\text{O}-\text{O}_\text{W}$, and $\text{O}_\text{H}-\text{O}_\text{W}$ RDFs for atom pairs on the alcohol hydroxyl groups with lattice water atoms. The first peaks at <2 Å show the occurrence of hydrogen bonding. (b) RDF peaks for C_3 atoms at the end of the guest molecules with cage water oxygen atoms. The location of the end group is positioned further out from the cage wall than the analogous O_H atom of the hydroxyl end of the molecule.

Typical snapshots of the 1-propanol, 2-propanol, and ethanol guests in the large sII cages are shown in Fig. 4. The guest-host hydrogen bonds observed are results of rotation of water molecules in the lattice and hydrogen bonding of these water molecules to the hydroxyl oxygen of the 1- and 2-propanol guests. Additionally, the guests are positioned in the large cages such that the hydroxyl hydrogen atoms can form hydrogen bonds with the O_W atoms of the cage waters. Such interactions are not seen for propane or butane in the large sII cages, snapshots of which are shown in Fig. S1 of the supporting information. The guest-water hydrogen bonding leads to the formation of Bjerrum defects in the clathrate hydrogen-bonding network of the large cage. The cage faces are greatly distorted by the formation of the guest-host hydrogen bonds.

To quantify the hydrogen bonding, the guest positions in large sII cages were inspected at 0.25 ps intervals during the 200 ps NVE simulation trajectory (a total of $N_\text{tot}=800$ sampling points). At each discrete sampling time, hydrogen-bond counters for each guest i , $b_i(\text{O}_\text{H}-\text{H}_\text{W}, t)$ and $b_i(\text{H}_\text{O}-\text{O}_\text{W}, t)$, were assigned values of either 1 or 0 depending on whether the $\text{O}_\text{H}-\text{H}_\text{W}$ or $\text{H}_\text{O}-\text{O}_\text{W}$ distances were less than 2.1 Å. The total probability of H-bond formation was determined by

FIG. 4. Snapshots of a large sII clathrate cage with 1-propanol, 2-propanol, and ethanol guest molecules. The hydrogen bonding of the hydroxyl O and H atoms is seen in the snapshots for 1-propanol and 2-propanol. Ethanol is only hydrogen bonded from the H atoms of the hydroxyl group in this snapshot.

$$P(\text{O}_\text{H}-\text{H}_\text{W}) = \frac{1}{N_\text{tot}} \sum_{i,t} b_i(\text{O}_\text{H}-\text{H}_\text{W}, t) \quad (1)$$

with a similar relation for $P(\text{H}_\text{O}-\text{O}_\text{W})$. N_tot is the total number of sampling points. The sampling time t corresponds to $t=0.25j$ (in picosecond), where j is the particular discrete sample time step (i.e., $j_\text{max}=N_\text{tot}=800$). The probabilities of hydrogen-bond formation of each guest (the average fraction of time in a trajectory when the alcohol is hydrogen bonded) to large sII cage water molecules at different temperatures are shown in Fig. 5. The details of the hydrogen-bonding events for 1-propanol at four temperatures are shown in Fig. S2 of the supporting information. The alcohol guests show strong hydrogen-bonding probability ($>50\%$) for both the O_H and H_O atoms. The formation of the $\text{O}_\text{H}-\text{H}_\text{W}$ hydrogen bond is generally more probable than the $\text{H}_\text{O}-\text{O}_\text{W}$ bond. The reason for this could be stronger electrostatic charges on the hydroxyl O_H atom compared to H_O (see Table S1 of the supporting information) and the relaxation of neighboring water molecules at the site of lattice defects, which lock in the guest-host $\text{O}_\text{H}-\text{H}_\text{W}$ hydrogen bonds, see below. From Fig. 5 we observe that the guest-host hydrogen-bonding probability decreases somewhat at higher temperatures. This indicates the presence of strong guest-host hydrogen bonding

FIG. 5. The probability of (a) O_H-H_W hydrogen-bond formation, (b) H_O-O_W hydrogen-bond formation, and (c) simultaneous O_H-H_W and H_O-O_W hydrogen-bond formation for 1-propanol, 2-propanol, and ethanol at temperatures between 100 and 250 K.

which is disrupted by the thermal motions of the guest and cage water molecules at higher temperatures.¹⁵ Similar behavior, where the guest HCN molecules show increased hydrogen bonding at lower temperatures in the binary HCN/ether sII clathrate hydrate, has been observed experimentally.^{16(b)}

To study the formation of structures where both O and H atoms of the hydroxyl guests are simultaneously hydrogen bonded to different water molecules, we determined the probabilities of simultaneous hydrogen bonding of both O_H and H_O atoms. The probability of observing simultaneous $O_H \cdots H_W$ and $H_O \cdots O_W$ hydrogen bonding is also shown in Fig. 5. Even at high temperature, the fraction of guests that form O_H and H_O hydrogen bonds is between 30% and 40%. This indicates that the alcohol hydrates have strong hydrogen-bonding probability while maintaining the local sII form. The stability of the local sII form can be due to a number of reasons. As mentioned, experimentally methane helper gas is required for the sII clathrate hydrates of these alcohols to form and despite the disruption of the water hydrogen bonds by the alcohols, the nonpolar methane molecules keep the framework intact. The alcohol guests of this study have small hydrophobic segments which can still be incorporated into the large sII cages of the binary hydrate. The small size of the hydrophobic organic segments of the alcohols makes them water-soluble and inhibits the formation of the pure hydrate. The larger size of the hydrophobic fragments of *tert*-butylammonium guests makes their incorporation into the canonical clathrate hydrate forms impossible. In these cases, salt-hydrates with completely different structures are formed.

In addition to the total probability of hydrogen-bond formation given in Eq. (1) we also determine the average lifetime of the hydrogen-bonding events. The lifetime of hydrogen bonds, $\tau(O_H-H_W)$ and $\tau(H_O-O_W)$, is determined by counting the number of consecutive sampling points for which hydrogen bond remains intact. The average lifetime of hydrogen bonds at each temperature is defined as

FIG. 6. The lifetimes (picosecond) of (a) O_H-H_W hydrogen-bond formation, (b) H_O-O_W hydrogen-bond formation, and (c) simultaneous O_H-H_W and H_O-O_W hydrogen-bond formation for 1-propanol, 2-propanol, and ethanol at temperature between 100 and 250 K.

$$\langle \tau \rangle (O_H-H_W) = \frac{1}{N_{HBOND}} \sum_i \tau_i(O_H-H_W), \quad (2)$$

where N_{HBOND} is the number of H-bonding events during the trajectory. The lifetimes of individual hydrogen bonds as defined in Eq. (2) are shown in Fig. 6. The lifetimes of the $R-O_H \cdots HOH$ hydrogen bonds are generally longer than the $H_O \cdots OH_2$ hydrogen-bonding events. The lifetimes of simultaneous O_H-H_W and H_O-O_W hydrogen bonding are generally determined by the $H_O \cdots OH_2$ lifetimes. The longer lifetime of the $O_H \cdots HOH$ hydrogen bonds can be due to the effect of relaxation of neighboring water molecules of the cage in the vicinity of the hydrogen-bonding water, see below.

Dynamics of rattling motions and rotations of the guests in the clathrate cages were extracted from NVE simulations. Hydrogen bonding tethers alcohol guests to cage water molecules and greatly affects their translational and rotational mobility in the cages. To determine the effect of tethering on the guest rotations in the cages, we calculate the cosine of the rotation angle $\cos(\theta) = \mu(t) \cdot \mu(t)$ of the guests at different times t , where $\mu(t)$ is a unit vector which defines a fixed direction inside each guest molecule, see Fig. S3 of the supporting information. The correlation function $M_2(t)$ related to second-order Legendre polynomial $P_2(\cos \theta) = 3 \cos^2 \theta(t) - 1$ characterizes the guest rotation and has also been shown to correlate with NMR relaxation times,³⁵

$$M_2(t) = \langle 3 \cos^2 \theta(t) - 1 \rangle, \quad (3)$$

where the brackets represent an ensemble average over all guests and time origins. The motion of the vector $\mu(t)$ is affected by the tethering of guests to the cage water molecules such that tethered guests retain their orientations for longer times than guest molecules not hydrogen bonded to the cage waters.

The $M_2(t)$ autocorrelation functions for the guest molecules are plotted in Fig. 7. By virtue of their larger size, the 1-propanol, 2-propanol, and butane molecules have slower $M_2(t)$ decay rates. The effect of hydrogen bonding on slow-

FIG. 7. The decay of the $M_2(t)$ autocorrelation function with time at four temperatures for the five guest molecules studied in this work. The hydrogen-bonding guests have slower decaying $M_2(t)$ functions than the corresponding alkane reference molecules in the sII large cages.

ing the decay of $M_2(t)$ is particularly noticeable at higher temperatures. This is observed by comparing the decay of $M_2(t)$ for butane with hydrogen-bonding 1-propanol and 2-propanol, and also propane with ethanol. The orientational autocorrelation function $M_2(t)$ can be fit to a biexponential form,

$$M_2(t) = A \exp(-t/\tau_1) + B \exp(-t/\tau_2), \quad (4)$$

with decay times τ_1 and τ_2 . The values of the fit parameters for the alcohols are given in Table I and the values for propane and *n*-butane guests as references are given in Table S3 of the supporting information. The longer relaxation times τ_1 are related to the contribution of guest rotation in the cages to the decay of $M_2(t)$, while the short relaxation times τ_2 can be related to the effect of high-frequency guest rattling motions about a cage face. The shorter τ_1 decay times of $M_2(t)$ for ethanol compared to that of the other alcohols are related to the smaller length of this guest. At higher temperatures, the probability and lifetime of guest-host hydrogen bonds decrease and the τ_1 decay times become smaller. At all temperatures, the decay of $M_2(t)$ for the alcohols is slower than the corresponding alkane molecules. Also, as the lifetime of the hydrogen bonding decreases at higher temperatures, the contribution of short decay time to the decay of $M_2(t)$ in-

TABLE I. Biexponential decay parameters from Eq. (4) for the $M_2(t)$ autocorrelation functions for guests in the sII large cages.

Guest (Temp.)	A	τ_1 (ps)	B	τ_2 (ps)
C ₂ H ₅ OH (100 K)	1.286 (0.002)	619 (11)	0.67 (0.2)	0.42 (0.02)
C ₂ H ₅ OH (150 K)	0.978 (0.003)	499 (18)	0.84 (0.03)	0.76 (0.05)
C ₂ H ₅ OH (200 K)	0.706 (0.003)	111 (1)	1.21 (0.02)	0.45 (0.02)
C ₂ H ₅ OH (250 K)	0.626 (0.004)	96 (1)	1.27 (0.03)	0.42 (0.02)
1-C ₃ H ₇ OH (100 K)	1.609 (0.002)	1373 (31)	0.228 (0.005)	4.2 (0.2)
1-C ₃ H ₇ OH (150 K)	1.417 (0.002)	218 (1)	0.44 (0.01)	1.56 (0.06)
1-C ₃ H ₇ OH (200 K)	0.759 (0.008)	322 (17)	0.72 (0.01)	7.4 (0.3)
1-C ₃ H ₇ OH (250 K)	0.472 (0.009)	63 (2)	1.10 (0.02)	2.40 (0.10)
2-C ₃ H ₇ OH (100 K)	1.694 (0.002)	842 (12)	0.167 (0.006)	3.6 (0.2)
2-C ₃ H ₇ OH (150 K)	1.420 (0.002)	745 (14)	0.388 (0.009)	2.8 (0.1)
2-C ₃ H ₇ OH (200 K)	1.016 (0.004)	221 (3)	0.68 (0.01)	2.5 (0.09)
2-C ₃ H ₇ OH (250 K)	0.742 (0.008)	90 (2)	0.81 (0.02)	3.0 (0.1)

creases and A/B in Eq. (4) decreases. These changes in the rattling frequencies with temperature for the different clathrate hydrates should be observable through measurement of NMR relaxation times. For references, the behavior of $M_1(t) = \langle \cos \theta(t) \rangle$ for the guests is shown in Fig. S4 and the biexponential fit parameters are given in Tables S4 and S5.

Propagation of Bjerrum L-defects in the cage water lattice is observed in the simulations. A sequence of snapshots (spaced 0.25 ps apart) of a large sII cage with an ethanol guest is shown in Fig. 8, where hydrogen bonding is shown by the thin blue lines connecting molecules. Water molecules

FIG. 8. Snapshots of a large sII cage with a hydrogen bonded ethanol guest. The formation of Bjerrum L-defects and the distortion of the cage faces are seen at different times in the trajectory. See text for further explanation.

forming a hexagonal face of this cage are highlighted and are shown in blue color. These six water molecules are discussed below. The highlighted water molecules (shown in blue color) form a hexagonal face of the large cage. Emphasis of the analysis is on the configuration of the α water molecule shown by the yellow dashed ellipse in all panels of Fig. 8. In snapshot 1, water α forms two proton-donating hydrogen bonds with its neighbors in the hexagonal face. The neighboring water β (shown by a red circle in Fig. 8) is hydrogen bonded to the ethanol hydroxyl oxygen atom and has a Bjerrum L-defect with a coordinating water molecule of lattice (not shown in the figure). In snapshot 2 of Fig. 8, the guest alcohol-water β hydrogen bond is broken and this water begins to rotate back into the water lattice of hexagonal face. The rotation of water β is coupled to the rotation of water α and continues in snapshot 3 of Fig. 8. At the end of snapshot 3, one of the two H-donating hydrogen bonds of water α is pushed out of the hexagonal face. In snapshot 4, water α forms a proton-donating hydrogen bond with the ethanol oxygen and a Bjerrum L-defect forms between it and water γ (shown with the green circle in snapshot 4) of the hexagonal face. In snapshot 5, water α rotates to form a hydrogen bond with neighboring γ water molecule while maintaining its hydrogen bond to the guest ethanol molecule. The Bjerrum L-defect of snapshot 4 has thus migrated out of the highlighted hexagonal plane. From snapshot 5 onward, we see that water α has lost the freedom to rotate back into the hexagonal face of the large cage without forming a Bjerrum D-defect between it and waters β and γ . Other L-defects also form in this hexagonal face (see, for example, the bottom left hand side of snapshot 3). These could be the result of guest-host hydrogen bonding in the neighboring large sII cages. The L-defects greatly distort the faces of the cages, leading to larger pore radii between cages and the possibility of enhanced diffusion of small helper guest molecules through the clathrate hydrate phase. The formation of guest-host hydrogen bonds and lattice defects increases the range of water vibrational motions and cage deformations in the hydrate cages. All these contribute to a decrease in the activation barrier to dielectric relaxation in the clathrate phase. Long-lived L-type lattice defects in adjacent sII cages (both large and small) and can lead to structural correlations among guest positions in adjacent cages. These issues will be studied in later work.

As seen in Table S1 of the supporting information, the partial electrostatic charges of the hydroxyl O and H atoms in the three alcohols studied in this work are similar. The difference in hydrogen bonding in the three guests is therefore related to their geometrical structures. Accommodating the larger 1-propanol and 2-propanol molecules in the sII large cages leads to configurations where the OH group is adjacent to the cage water molecules and this enhances the guest-host interactions.

IV. CONCLUSIONS

We studied the sII binary clathrate hydrates of ethanol, 1-propanol, and 2-propanol with methane with MD simulations and observed hydrogen bonding between the guest hy-

droxyl group and the cage water molecules. The alcohol-water hydrogen bonding is the result of large partial charges on the O and H hydroxyl atoms and their geometric positioning at the end of the alcohol molecules. Both $\text{O}_\text{H} \cdots \text{HOH}$ and $\text{H}_\text{O} \cdots \text{OH}_2$ hydrogen bonds are observed with the former occurring with greater probability at high temperatures. Simultaneous hydrogen bonding of both O and H atoms of the hydroxyl group, where the alcohol molecule injects itself into the hydrogen-bonding network of the cage waters to form a “semiclathrate-like” configuration, is significant. The hydrogen bonds, however, are not permanent and are accommodated while maintaining the cage structure of the sII hydrate. The alcohol can detach from the water molecules, rotate in the cage, and form new hydrogen bonds with other cage water molecules. The formation and breaking of the alcohol-cage water hydrogen bonds are consistent with the view of the alcohol hydrates being an equilibrium mixture of classical and nonclassical local structures, as described by Devlin and co-workers.^{16(a),16(b)}

Experimentally, it is observed that the presence of methane and carbon dioxide helper gas is required for the formation of the water-miscible alcohol clathrate hydrates. Presumably, the hydrophobicity of these help gases stabilizes the clathrate hydrate phase. Interestingly, at temperatures below 140 K, hydrophilic methanol has been observed to be incorporated into the small cages to form a metastable binary sII clathrate hydrate with tetrahydrofuran.^{32–34} The exact role of the help gases in the formation of clathrate hydrate phases in different cases is complex and merits further study. Cases where the guests in the clathrate hydrate large cages are relatively hydrophobic (tetrahydrofuran and trimethylene oxide) and the help gas occupying the small cages (HCN) forms hydrogen bonds have been recently studied.^{16(b)} The large guest molecules in these clathrate hydrates form stable hydrates on their own, without the presence of a help gas, and these clathrate hydrates can incorporate the hydrogen-bonding small cage guests and remain thermodynamically stable. Determining more general guidelines for the presence of hydrophilic guests in stable clathrate hydrate phase will be the topic of future studies.

The behaviors of the binary sII alcohol+methane hydrates are interesting to compare with the quaternary ammonium salt-hydrates.² The tetra-alkylammonium cations in these hydrates are too large to be incorporated into the canonical sII hydrate structures and new hydrate structures form where the anion is incorporated into the hydrogen-bonding network of the waters. The water molecules form cage structures that are large enough to encapsulate the large cation alkyl groups. In the case of the sII binary alcohol hydrates of this work, the alkyl hydrophobic moieties of the alcohols are small enough that they can be incorporated in the sII cages, and with the methane helper gas molecules the alkyl chains make the environment hydrophobic enough that the sII clathrate hydrate remains stable.

Large hydrogen-bonding guest molecules which form structure H (sH) clathrate hydrates such as pinacolone and *tert*-butylmethylether have weak probabilities of hydrogen-bond formation with the water molecules of the large cages.¹⁵ Furthermore, the large sH forming alcohols such as

3-methyl-2-butanol and 2-methyl-2-butanol are observed to have O–H stretch frequencies near 3600 cm^{-1} , which indicates nonhydrogen bonded hydroxyl groups.^{16(c)} From these observations it can be concluded that the relatively tight confines of the large sII cages lead to the close proximity of the guest hydroxyl to the cage water molecules and enhance the guest-host hydrogen bonding.

The hydrogen bonding tethers guest molecules to the cage wall and affects the rotational dynamics of the guests in the large cages. Furthermore, the hydrogen bonding leads to the formation of Bjerrum L-defects that allow greater rotational freedom for neighboring water molecules. The rotation of water molecules into the L-defects adjacent to the alcohol guest prolongs the lifetime of the guest-host hydrogen bond by blocking the simple rotation of the guest-bonded water molecule into its original water lattice site.

The probabilities of guest-host hydrogen-bond formation for the alcohols are high at all temperatures, which show that the guest-water hydrogen bonds are strong in these hydrates. The lifetime of these hydrogen bonds is determined to be between 1 and 10 ps. As seen in Fig. 1, these hydrogen bonds decrease the stability clathrate hydrate framework and cause the stability zone of the binary sII methane+alcohol clathrates to be pushed into higher pressure regions of the phase diagram.

The lattice defects and water relaxation around them caused by guest-water hydrogen bonding severely distort the faces of the clathrate hydrate cages and may lead to enhanced diffusion of guests between the hydrate cages. A detailed study of the migration of the defects and the effect of the defects on guest migration will remain for future work.

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