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A molecular dynamics study of ethanol–water hydrogen bonding in binary structure I clathrate hydrate with CO₂

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Guest–host hydrogen bonding in clathrate hydrates occurs when in addition to the hydrophilic moiety which causes the molecule to form hydrates under high pressure–low temperature conditions, the guests contain a hydrophilic, hydrogen bonding functional group. In the presence of carbon dioxide, ethanol clathrate hydrate has been synthesized with 10% of large structure I (sI) cages occupied by ethanol. In this work, we use molecular dynamics simulations to study hydrogen bonding structure and dynamics in this binary sI clathrate hydrate in the temperature range of 100–250 K. We observe that ethanol forms long-lived (>500 ps) proton-donating and accepting hydrogen bonds with cage water molecules from both hexagonal and pentagonal faces of the large cages while maintaining the general cage integrity of the sI clathrate hydrate. The presence of the nondipolar CO₂ molecules stabilizes the hydrate phase, despite the strong and prevalent alcohol–water hydrogen bonding. The distortions of the large cages from the ideal form, the radial distribution functions of the guest–host interactions, and the ethanol guest dynamics are characterized in this study. In previous work through dielectric and NMR relaxation time studies, single crystal x-ray diffraction, and molecular dynamics simulations we have observed guest–water hydrogen bonding in structure II and structure H clathrate hydrates. The present work extends the observation of hydrogen bonding to structure I hydrates. © 2011 American Institute of Physics. [doi:10.1063/1.3548868]

I. INTRODUCTION

Clathrate hydrates form when suitably sized molecular species are combined with water or ice under high pressure and/or relatively low temperature conditions.¹ To minimize water–guest interactions, which form at the expense of more stable water–water interactions, the water molecules crystallize into cage structures which encapsulate the guests, but at the same time satisfy the hydrogen bonding requirements of the ice rules. For some guest species, the solid icelike clathrate hydrates form at temperatures above the freezing point of water at ambient pressure. Early in the history of clathrate hydrate studies, it was realized that some water soluble species [such as tetrahydrofuran, (THF)] form clathrate hydrates when their aqueous solutions are cooled or pressurized. Even aqueous solutions of strongly polar water soluble molecules such as ethanol and 1-propanol were discovered to form clathrate hydrates when cooled and compressed with hydrophobic help gases.² In these cases, the hydrophilic molecules have a hydrophobic moiety which helps drive the hydrate formation process.

In describing clathrate hydrate stability, the statistical mechanical van der Waals–Platteeuw theory, which was inspired by the Lennard-Jones–Devonshire cage theory of the liquids was developed in 1958 and used to predict the temperature–pressure phase diagram of clathrate hydrates of simple hydrocarbon and nonpolar guest species successfully.³ In principle, this theory can be used to describe the spe-

cific interactions of spherical, nonspherical nonpolar, and polar molecules. The widely used practice, however, has been to assume spherically symmetric average guest–cage interactions described, for example, by a Kihara potential.⁴ As a result, details of the geometric shape and specific guest–host interactions are lost in the application of the theory. The fact that water soluble guests affect hydrate formation as they inhibit hydrate formation was included indirectly in the van der Waals–Platteeuw formalism by allowing for a reduction in activity of the solution in equilibrium with the hydrate compared to water.⁵ The van der Waals–Platteeuw theory has been extended to include nonspherical molecules,⁶ multiple guest molecules⁶ in clathrate hydrate cages, and water lattice vibrations. Strong, specific guest–host interactions can be formally incorporated into the formalism allowing for guest–water hydrogen bonding. However, due to the complexity of the possible bonding patterns in the cages (see below), such a formalism would be difficult to implement.

It has been known that dielectric relaxation and guest reorientation energies of clathrate hydrates of guests with similar geometrical structures such as cyclopentane and THF can vary considerably, with THF having higher activation energies to rotation in the cages.⁷ Similarly, it was observed that the hydrate decomposition temperature of guests with similar structures depends on the functional groups in the guest molecules. For example, of the three guests, CH₃CH₂CH₃, CH₃OCH₃, and CH₃SCH₃, the hydrate decomposition temperature is considerably lower in the ether.⁸ These trends cannot be easily explained by the van der Waals–Platteeuw theory and were attributed to hydrogen bonding of specific guests to

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the cage water molecules. The hydrogen bonding however, was not observed directly in the powder x-ray diffraction patterns of the hydrates or in the single crystal diffraction data recorded previously.

We recently performed molecular dynamics simulations of structure II (sII) (Refs. 8 and 9) and structure H (sH) (Ref. 10) clathrate hydrates with hydrogen bonding guests and observed explicit hydrogen-bond formation between the guests and cage for a number of guest molecules with ether, alcohol, or amine functional groups. Additionally, the guests have large dipole moments, which point in the direction of the hydrogen bonding atoms. Furthermore, we observed that the guests preferentially hydrogen bond with the water molecules in the hexagonal faces of the cages. The 108° angles between the sides in the pentagonal faces of the cages are closer to the stable $\text{H}-\text{O}\cdots\text{H}$ angles of hydrogen bonds, as opposed to the 120° angles between sides of the hexagonal cage faces. The hydrogen bonding in the pentagonal faces are thus expected to be more stable and less prone to hydrogen bonding with the guests.

A proton-donating hydrogen bond of a water molecule with the guest forms by breaking a water–water hydrogen bond of configuration shown in Fig. 1(a) and leads to the formation of Bjerrum L-defects in the clathrate hydrogen bonding network [see the blue dashed line in Fig. 1(b)]. In a pure water hydrogen bond network, Bjerrum defects always form in pairs of L- and D-defects. However, in the case of clathrate hydrate guest–host hydrogen bonds, an L-defect is formed in the water hydrogen bonding network, without the formation of a corresponding D-defect. Furthermore, the guest induced L-defect formation in the water network forms without a large energy penalty associated with the formation of L- and D-defect pairs by the rotation of water molecules. Indeed, the guest–host hydrogen bond formation is accompanied by an energy decrease (see below), since the guest–water hydrogen bonding breaks a water–water hydrogen bond but leads to the formation of a guest–water hydrogen bond of similar strength.

The guest–host hydrogen bonds are dynamic and can break and re-form at different time intervals. Specifically, the α -water molecule in Fig. 1(b) can rotate back into its configuration shown in Fig. 1(a), annihilating the L-defect. The fraction of the time the guests are hydrogen bonded to the cage water molecules gives the probability of guest–host hydrogen bonding in the clathrate. The probability and average lifetimes of hydrogen bonds depends on the nature of the guest and the temperature.

If the guest–host hydrogen bond is long lived, the guest-induced Bjerrum L-defect in the cage water network may migrate from its original site. This happens when a second nearest neighbor water molecule to the guest (for example, water β) rotates from its initial position as shown in Fig. 1(c). This second nearest neighbor water molecule also rotates in the water lattice without the formation of the corresponding Bjerrum D-defect. Thus the guest–host hydrogen bond decreases the energy barrier to the migration of Bjerrum defects in the water lattice, assisting in the partial randomization of the orientations of the water molecules and increases the dielectric relaxation rate of water in the hydrate.

FIG. 1. A schematic representation of Bjerrum L-defect formation between two adjacent water molecules in the hydrate phase as a result of proton-donating hydrogen bonding with the guest. (a) A configuration of the free ethanol guest and adjacent water molecules in the cage. (b) The rotation of a proton-donating water molecule (water α) toward ethanol leads to the formation of a guest–host hydrogen bond (shown by blue dashed line) and a Bjerrum L-defect between the water and its neighbor water β (shown in red color). (c) The rotation of the β water molecule causes the L-defect to migrate to a site removed from the guest (red dashed line) has the effect of locking in the guest–water hydrogen bond and prolonging its lifetime.

When the guest–water hydrogen bonds break, the water molecule bonded to the guest can rotate back and once again be incorporated in the hydrate water hydrogen bond network. If a neighboring water molecule has not rotated into the empty L-defect site [as in the configuration shown in Fig. 1(b)], the rotation of the guest-bound water back into the water lattice will annihilate the Bjerrum L-defect and return the system to the configuration shown in Fig. 1(a). However, for a system in configuration shown in Fig. 1(c), the energy barrier to rotation of the guest-bound water back into the cage water lattice is higher (due to the formation of a D-defect) and this increases the lifetime of the guest–host hydrogen bond.

The presence of guest–host hydrogen bonding contributes to trends in dielectric relaxation, guest and/or host rotational activation energies, and stability ranges in the phase diagrams of guest molecules with related structures. Parallel to MD simulations, we performed NMR relaxation time and single crystal x-ray diffraction experiments^{8,10} on the clathrate hydrates systems where MD simulations showed the presence of hydrogen bonding. The NMR relaxation times strongly supported the interpretation of hydrogen bonding in the case of the *tert*-butylmethylether guests and the absence of such hydrogen bonding in the isoelectronic neo-hexane guest in the sH clathrate hydrate.¹⁰ The single crystal x-ray diffraction showed the direct observation of hydrogen bonding for the pinacolone (sH) and *tert*-butyl amine (sII) guests.⁸ Buch, Devlin, and co-workers¹¹ performed IR experiments and MD

FIG. 2. Snapshot of a large sI hydrate cage with an ethanol guest. The cage is shortened in the polar directions and is bound by hexagonal faces in this direction. Nonspecific van der Waals repulsive interactions favor the alignment of the guests in the equatorial plane. In this snapshot, the guest lies near the equatorial plane of the cage.

simulations of binary sII clathrate hydrates of HCN or SO₂ with ethylene oxide and observed evidence of guest–host hydrogen bonding in these materials. They have discussed the implication of the hydrogen bonding on L-defect and vacancy defect formation in the water lattice of the hydrate phase and its contribution to low temperature secondary guest diffusion in the hydrate phase, hydrate nucleation and hydrate phase transitions. Many aspects of their work is complementary to the discussion of the present work and Refs. 8–10.

In this work, we perform molecular dynamics simulations on recently synthesized ethanol + CO₂ binary structure I (sI) clathrate hydrate.¹² The goal is to study the possibility of hydrogen bond formation between ethanol guest molecules and lattice waters in the large sI cages. These cages have 24 water molecules arranged in two staggered hexagonal faces in the “polar” direction of the cage and twelve pentagonal faces in the “equatorial” direction of the cage (see Fig. 2). For linear molecules, the equatorial direction of the cages is found to be the preferred direction of orientation of the molecules¹³ and so it is of interest to determine (i) whether hydrogen bonding occurs between the ethanol guests and the cage waters in this compact cage, and (ii) whether the hydrogen bonding occurs with the water molecules of the pentagonal faces in the equatorial plane or the water molecules of the hexagonal faces in the polar direction.

II. COMPUTATIONAL METHODS

The initial coordinates of the water oxygen atoms in the sI clathrate hydrate cubic unit cell ($a = 12.09$ Å) are taken from x-ray crystallography¹⁴ and the positions of the water hydrogen atoms in the sI unit cell were determined by a Monte Carlo procedure which determines the proton configuration of the unit cell consistent with the ice rules¹⁵ with the lowest energy and dipole moment. The TIP4P model was used for water and $3 \times 3 \times 3$ replicas of the unit cell with 1242 water molecules were used in the simulations. The experimental composition of the sI binary ethanol + CO₂ clathrate hydrate

shows 10% of the large cages are occupied by ethanol and the rest by CO₂. In the setup, ethanol molecules were placed inside 16 randomly chosen large cages from among the 162 large cages of the simulation cell.

The ethanol molecule is flexible with intramolecular force field parameters taken from the general AMBER force field (GAFF).¹⁶ The linear CO₂ molecule is considered rigid with the C–O bond length of 1.17 Å. The van der Waals interactions between atoms i and j on different molecules are taken as Lennard-Jones (LJ) potentials with σ_{ij} and ϵ_{ij} parameters for atoms of guest ethanol molecules taken from GAFF, CO₂ molecules from the Harris and Yung potential¹⁷ and water from the TIP4P potential.¹⁸ See Table S1 of the supporting information for parameter values.¹⁹ Standard Lorentz–Berthelot combination rules are used for unlike atom-type interactions. Partial electrostatic point charges on the atoms of the guest molecules were determined from charges from electrostatic potential grid calculations²⁰ with the GAUSSIAN 03 suite of programs²¹ at the B3LYP/6–311++G(d,p) level of theory. The point charges q_i on the atoms are given in Table S1. Lennard-Jones and electrostatic interactions between atoms at 1–4 positions in the ethanol molecule are scaled by a factor of 0.5.

Isotropic constant pressure–temperature NpT molecular dynamics simulations were performed using DL_POLY 2.20 (Ref. 22) at temperatures in the range of 100–250 K at ambient pressure. The equations of motion were integrated with the Verlet leapfrog algorithm with 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 evaluated using the Ewald summation method²³ and all intermolecular interactions in the simulation box were calculated within a cutoff distance of $R_{\text{cutoff}} = 13.0$ Å. Temperature and pressure in the simulation were regulated using the modified Nosé–Hoover barostat algorithm²⁴ with thermostat and barostat relaxation times of 0.2 and 0.5 ps, respectively.

The dynamics and hydrogen bonding calculations at each temperature were studied with constant energy, constant volume simulations starting from final configurations of the corresponding NpT simulation. Dynamical simulations were run for a total of 600 ps, with the first 100 ps used for further equilibration.

Quantum chemical calculations were performed to determine the binding energy of an isolated ethanol–water complex and compared with those of other guest–water hydrogen bonding complexes. This can give an indication of importance of the guest–water interaction in forming guest–water hydrogen bonds in the hydrate phase. The structures of the ethanol–water complex were optimized at the B3LYP/6–311++G(d,p) level of theory with the GAUSSIAN 03 suite of programs.²¹ The basis set for these calculations is large and basis set superposition contributions to the binding energy is not expected to be significant.²⁵

III. RESULTS AND ANALYSIS

The MD simulations show that in the temperature range of 100–250 K the lattice constants of the 10% ethanol

FIG. 3. The RDFs of the ethanol hydroxyl O atom with the water H atoms (top panel), the carbon dioxide–O atoms with the water H atoms (middle panel), and the ethanol hydroxyl H atom with the water O atoms at 220 K (bottom panel). Hydrogen bonding of the hydroxyl H and O atoms with the cage water atoms is indicated by the peaks at distances less than 2 Å.

+ CO₂ sI hydrates vary between 11.75 and 11.92 Å. In the pure CO₂ sI hydrate the lattice constant varies between 11.73– and 11.88 Å in the same range, so there is a small expansion of the lattice with the replacement of some of the CO₂ guests with ethanol. The structures of the hydrates remain intact during the simulations in this temperature range.

The average positions of the ethanol and CO₂ guests in the water cages can be characterized by the radial distribution function (RDF) plots shown in Fig. 3 for the simulation at 220 K. In this figure, the short distances (<2.0 Å) of the ethanol O atom (O_H) from the water hydrogen atoms (HW) in the top panel and the ethanol H atom (H_O) from the water oxygen atoms (OW) in the bottom panel are consistent with hydrogen bonding of these ethanol hydroxyl group atoms with water. The RDF plots in the middle panel show that the carbon dioxide–O atoms in the large and small cages are at larger distances from the cage HW atoms and no hydrogen bonds are formed between cage water molecules and CO₂ guests. The difference in the placement of the CO₂ and ethanol guests in the cages is partly due to their different sizes, where the O···O distance in CO₂ is ~2.34 Å and the O···C₂ distance in ethanol is ~2.41 Å with hydrogen atoms contributing further to the size of the ethanol molecule. In addition to size, an important difference between the CO₂ and ethanol guests is the larger partial atomic charges on the hydroxyl group atoms in ethanol ($\delta_{\text{O}} = -0.7096$; $\delta_{\text{H}} = +0.3989e$) compared to oxygen atoms ($\delta_{\text{O}} = -0.3322e$) in CO₂. The large charges increase the strength of the ethanol–water electrostatic interactions and lead to the formation of guest–host hydrogen bonds. Evidence for the hydrogen bonding is also seen in the short O_H–O_W distance (<3 Å) in the RDF plot shown in Fig. S1 of the supporting information.

In previous simulations of host–guest hydrogen bonding in sII and sH clathrate hydrates,^{8–10} hydrogen donating water molecules were located in the hexagonal faces of the large cages. The angles in clathrate hydrate pentagonal faces are ~108° which is closer to the natural 104° H–O–H angle of the water molecules, while in the cage hexagonal faces, the

FIG. 4. The hydrogen bonding between ethanol and the cage water molecules from hexagonal faces in the polar end of the cage. (a) Hydrogen bonding of ethanol with adjacent (1,2) water molecules in the hexagonal large cage face. (b) Hydrogen bonding with next nearest neighbor (1,3) water molecules in the hexagonal large cage face.

angles are 120°. The H–O···H hydrogen bonding angles between water molecules are thus more stable for the pentagonal faces. Snapshots of ethanol molecules in the large sI cages are shown in Figs. 4 and 5. The water–ethanol hydrogen bonding is clearly visible. In Fig. 4(a) the ethanol O_H and H_O atoms are hydrogen bonded to adjacent water molecules of the hexagonal face. In Fig. 4(b), the ethanol O_H and H_O are hydrogen bonded to second nearest neighbour water molecules of the hexagonal face which was not observed previously. The

FIG. 5. Hydrogen bonding between ethanol and the cage water molecules from pentagonal faces. (a) Hydrogen bonding with two adjacent water molecules from pentagonal faces in the equatorial region. (b) Hydrogen bonding with a water molecule from the hexagonal face (proton donating water) and a water molecule from a pentagonal face (proton accepting).

TABLE I. Average binding energy (kJ mol⁻¹) for isolated water complexes determined at the B3LYP/6-311++G(d,p) level of theory.

Complex	E_{bind}
H ₂ O... H ₂ O	-24.4
H ₂ O... ethanol	-25.5
H ₂ O... 1-propanol	-25.4
H ₂ O... 2-propanol	-30.6
H ₂ O... tetrahydrofuran	-28.2
H ₂ O... <i>t</i> -butylamine	-32.4
H ₂ O... <i>t</i> -butylmethylether	-25.9
H ₂ O... pinacolone	-23.5

guest–host hydrogen bonds (particularly the latter type) distort the hexagonal faces of the cages. In Fig. 5(a), a snapshot is shown with an ethanol molecule hydrogen bonded to two water molecules from pentagonal faces of the cage equatorial plane, and in Fig. 5(b) we see the interesting case where the HW-donating water is from a hexagonal face and the H_O accepting water is from the pentagonal faces of the large cage. Trajectory files for the guests and cages in Figs. 4 and 5 are given in the supporting information and can be viewed with standard molecular viewing software.

The small size of the sI large cages as compared to the ethanol guest leads to new patterns of hydrogen bonding in this hydrate. The flattened structure of the cage favors orientations of ethanol in the equatorial plane, exposing the hydroxyl group to the water molecules of the pentagonal faces. However, as discussed above, water–water hydrogen bonds in the hexagonal faces are weaker and therefore ethanol–water hydrogen bonds with the hexagonal plane water molecules are energetically favored. A combination of these two factors allows ethanol to hydrogen bond with water molecules from both parts of the cage.

The strength of the guest–water hydrogen bond and the relative geometric size of the guest and cage both contribute to guest–host hydrogen bonding. To study the effect of hydrogen bond strength, we determined the binding energy of a water dimer, the ethanol–water complex, and other guest molecules in sI, sII, and sH clathrates. These binding energies are given in Table I and the coordinates for the optimized complexes are given in Table S2 of the supporting information. It is interesting to note that the binding energies of all guest molecules studied are stronger than the water–water binding energy. The much greater probability of *tert*-butylamine (TBA) hydrogen bonding to the cage water molecules,⁸ compared to tetrahydrofuran⁹) can be partially attributed to stronger TBA...water hydrogen bonding (−30.6 kJ mol⁻¹) compared to THF...water hydrogen bonding (−28.2 kJ mol⁻¹), but is more likely to be due to the larger volume of the TBA molecule which forces the hydrogen bonding −NH₂ functional group adjacent to the cage walls. Similarly, the driving force for water–ethanol hydrogen bonding in the present system is likely not the strength of ethanol...water hydrogen binding energy (−25.5 kJ mol⁻¹) compared to the water...water hydrogen binding energy (−24.4 kJ mol⁻¹), but rather the close proximity of the ethanol −OH group to the cage walls. In the

clathrate cages, hydrogen bond formation with the guests may relieve some of the steric tension built into the hydrogen bonding network (particularly in the large cage hexagonal faces) and so the binding energy in the hydrate can be different from those of the isolated guest–water complexes. In Table II we give the differences in configurational energy (sum of van der Waals and electrostatic energies) between the pure CO₂ sI hydrate and the binary ethanol (10%) + CO₂ sI hydrate from MD simulations. Incorporating ethanol in the hydrate reduces the energy content in the hydrate phase, perhaps by relieving some of the steric stress of the hydrogen bonding network of the hydrate phase.

As a result of hydrogen bonding, the ethanol molecules have different orientation distributions in the large cages from the nonhydrogen bonding CO₂ molecules. The ¹³C NMR line-shape measurements²⁶ and molecular dynamics simulations¹³ show that CO₂ molecules are oriented preferably in the equatorial plane of the cages as the cages have a large radius in this direction.

To quantify hydrogen bonding, the probability of hydrogen bond formation from the MD simulations is defined as

$$P(\text{O}_X \cdots \text{H}_Y) = \frac{1}{N_t} \sum_t \frac{1}{N_i} \sum_i n_i (\text{O}_X \cdots \text{H}_Y, t),$$

where the index i represents the ethanol guests, Y is the proton donating molecule (water or ethanol) and X is the proton accepting molecule (water or ethanol). The variable n_i at any time t is a step function equal to 0 or 1 depending on whether the O_X...H_Y bond is greater or less than 2.1 Å, respectively. The variable N_t is the total number of timesteps and N_i is the number of ethanol guest configurations at each time. The probabilities of hydrogen bonding of the ethanol hydroxyl O with water HW atoms, the ethanol H atoms with water OW atoms, and the probability of simultaneous hydrogen bonding of ethanol O and H atoms with two water molecules are given in Table III. The probability of hydrogen bonding is >85% which is a high value for hydrogen bond forming guests in clathrate hydrates.^{8–10} Upon viewing the ethanol guest motions in large sI cages, we observe that some ethanol–water hydrogen bonds are retained for the entire 500 ps duration of the simulation trajectory (see below). These guest–host C₂H₅OH...H_W^{*}O_W^{*}H_W hydrogen bonds lead to the formation of a Bjerrum L-defect at the site of the former water O_W...H_W^{*}O_W^{*}H_W hydrogen bond in the lattice, as seen for example in Figs. 4 and 5 and shown

TABLE II. The difference in configurational energy per ethanol guest (kJ mol⁻¹) between the 10% ethanol + CO₂ binary hydrate compared to pure CO₂ sI hydrate at different temperatures.

Temperature (K)	$E_{\text{config}}(\text{CO}_2) - E_{\text{config}}(\text{EtOH} + \text{CO}_2)$
90	55.2
120	56.5
150	49.4
170	57.3
200	57.3
220	39.2

TABLE III. Average hydrogen bonding probabilities of ethanol guest molecule at different temperatures.

Temperature (K)	$P(\text{O}_\text{H}-\text{H}_\text{W})$	$P(\text{H}_\text{O}-\text{O}_\text{W})$	P (Simulation)
90	0.827	0.949	0.756
120	0.979	0.987	0.974
150	0.987	0.971	0.963
170	0.992	0.974	0.967
200	0.955	0.915	0.886
220	0.915	0.859	0.810

schematically in Fig. 1. As discussed in the introduction, migration of the Bjerrum L-defect caused by rotation of a water molecule and H-donating hydrogen bonds from the second nearest neighbor water locks in the guest–host hydrogen bond. This phenomenon, is seen in the ethanol + CO₂ clathrate hydrate. Given the variety of patterns in which the ethanol guests can hydrogen bond with water, we see that the hydrate water lattice can be greatly distorted in the vicinity of the ethanol-containing large cages.

The stability of the ethanol–water hydrogen bonds and the large distortions they cause in the hydrate lattice can indicate why the hydrate forms with a maximum ~10% ethanol content in the large cages with CO₂ required in other sI large cages. Each large cage in the sI hydrate shares faces with ten other large cages. If the occupancy of ethanol in the large cages becomes more than 10%, adjacent large cages will begin to hold ethanol molecules. The large distortions in the hydrate lattice of adjacent cages may destroy the mechanical stability of the framework.

The rotational dynamics of the ethanol molecules in the large cages is characterized by the change in orientation of a unit vector $\mathbf{u}(t)$ defined in the direction of the C–O bond. The function $\cos \theta(t) = \mathbf{u}(t) \cdot \mathbf{u}(0)$ represents the orientational autocorrelation function for this unit vector and is a measure of the rotation of the molecule. The ensemble average of the moments of $\cos \theta(t)$, such as,

$$M_1(t) = \langle P_1 [\cos \theta(t)] \rangle = \langle \cos \theta(t) \rangle,$$

and

$$M_2(t) = \langle P_2 [\cos \theta(t)] \rangle = \langle 3 \cos^2 \theta(t) - 1 \rangle,$$

where P_1 and P_2 are the first and second order Legendre polynomials, respectively, and can be related to Raman adsorption or NMR relaxation times for the guests. An alternative unit vector $\mathbf{u}'(t)$ can be defined in the direction of the ethanol molecular dipole moment. Since the ethanol molecule is flexible in the simulations, the variations of the dipole moment vector reflect both changes in the orientation and the intramolecular structure of ethanol. The force field used in this work does not incorporate atomic polarizabilities, which can make important contributions to the changes in the total molecular dipole moment. The $M_1(t)$ functions for ethanol and CO₂ guest molecule in the large cages are shown in Figs. 6 and S2 of the supporting information, respectively. Similar $M_2(t)$ plots at different temperature for ethanol and CO₂ guests are given in Figs. 7 and S3 of the supporting information. As expected, the $M_1(t)$ functions decay more quickly

FIG. 6. The decay of the $M_1(t)$ autocorrelation function with time at temperatures from 90 to 220 K for the ethanol guest molecules. The hydrogen bonding guests have slower decaying $M_1(t)$ functions than the CO₂ guest molecules in the sI large cages (shown in Fig. S2 of the supporting information).

at higher temperatures. Furthermore, the decay of CO₂ $M_1(t)$ function is much faster than the corresponding ethanol functions since CO₂ does not form hydrogen bonds with the water molecules.

For non- or weakly hydrogen bonding guests in the clathrate hydrate phase, the decay of the $M_1(t)$ and $M_2(t)$ functions are described in terms of double exponential decay functions with decay times τ_1 and τ_2 ,^{13,27}

$$M_2(t) = A \exp\left(-\frac{t}{\tau_1}\right) + B \exp\left(-\frac{t}{\tau_2}\right).$$

From Fig. 7, we see that the strong guest–host hydrogen bonding changes this smooth behavior.

To further clarify the guest dynamics and orientational relaxation in the cages, $n(\text{ethanol-water})$, the number of

FIG. 7. The decay of the $M_2(t)$ autocorrelation function with time at temperatures from 90 to 220 K for the ethanol guest molecules. The hydrogen bonding guests have slower decaying $M_2(t)$ functions than the CO₂ guest molecules in the sI large cages (shown in Fig. S3 of the supporting information).

FIG. 8. The hydrogen bond formation and breaking dynamics at 90, 150, and 200 K.

hydrogen bonds of a sample ethanol molecule with cage water molecules along the trajectory are shown in Fig. 8 at three temperatures. As before, the criterion for hydrogen bonding is that the distance between oxygen and water hydrogen atoms is less than 2.1 Å. At 90 K, the single hydrogen bond of ethanol with a water molecule is stable for the entire duration of the simulation. At 150 K, the ethanol–water hydrogen bond breaks and re-forms, but individual hydrogen bonds are stable for long periods of time. Situations where two HW atoms from different water molecules meet the distance criterion for hydrogen bonding are seen at this temperature. At 200 K, hydrogen bond formation and breaking occur at much more frequent intervals and the lifetime of each hydrogen bond is reduced to the order of tens of picoseconds (from hundreds of picoseconds at lower temperatures). The shorter lifetimes of the hydrogen bonds at 200 K correlate with the rapid decay of the orientational autocorrelation functions seen in Figs. 6 and 7. Similar behavior is seen for the $n(\text{H}_2\text{O}-\text{OW})$ hydrogen bonds and simultaneous proton donating and accepting hydrogen bonding with ethanol guests, $n(\text{simultaneous})$, in Figs. S4 and S5. The $n(\text{O}_\text{H}-\text{HW})$ hydrogen bonds of ethanol guests from other cages during the simulation trajectory are given in the Fig. S6 of the supporting information. It is interesting to note that even at low temperatures, some ethanol guests can have no hydrogen bonding with the cage for extended periods of time.

The total dipole moment of the clathrate hydrate system at any time t in the simulation, $\mathbf{M}(t)$, is the sum of the dipole moments of the individual molecules,

$$\mathbf{M}(t) = \sum_i \mu_i(t).$$

The time-correlation function of the total dipole moment is defined as $C(t) = \langle \mathbf{M}(0) \cdot \mathbf{M}(t) \rangle / \langle M^2 \rangle$. There are three contributions to the decay of $C(t)$. First, there is a contribution from the rotational motion and intramolecular geometry changes of the dipolar ethanol guest molecules during the simulation. These motions are captured by the time scale of the MD simulation. A second contribution arises from the ethanol–water hydrogen bonding. As observed in Fig. 1, the ethanol–water hydrogen bonding results in Bjerrum L-defects

forming in the water lattice. The propagation of these defects in the water lattice can be observed in the time-scale of the simulation. In the cage trajectories provided in the supporting information, the motion of the L-defect can be observed. This defective propagation causes changes in the dipole moment autocorrelation function, $C(t)$. The third contribution is from thermal motions of the water molecules, which at higher temperatures lead to their rotation in the clathrate hydrate lattice. The rotation of water molecules causes the formation of a pair of Bjerrum L- and D-defects in the lattice, which either annihilate or propagate independently in the lattice after subsequent water rotations. These water rotations occur in all clathrate hydrate (and ice) phases and lead to the averaging of the hydrate cage environments at higher temperatures. The spectroscopic evidence for these water rotations is seen in the narrowing of guest NMR lineshapes and the dielectric relaxation of the hydrate phase at higher temperatures. This third motion occurs on time scales of hundreds of nanoseconds to microseconds and is not captured in the present simulations.

IV. CONCLUSIONS

The strong hydrogen bonding between ethanol and water can explain why the ethanol + CO₂ structure I hydrate is only stable with a small percentage of large cages filled with ethanol guests at relatively high temperatures. In the sI hydrate, the large cages are arranged in columnar form along the three perpendicular directions and share hexagonal faces. In the sI hydrate, each large cage is in contact with ten other large cages, two of which share hexagonal faces, and the other eight share pentagonal faces with the reference cage. The ethanol guest disrupts the water hydrogen bonding network. The presence of ethanol molecules in adjacent large cages can disrupt the local hydrogen bonding network so severely as to cause hydrate instability. This could explain the experimentally observed 10% maximum concentration of ethanol in the large cages.

The MD simulations give insight into the mechanism of clathrate inhibition by small polar molecules such as ethanol or methanol. It is interesting that despite the fact that ethanol is a clathrate inhibitor, at low concentrations it acts as a hydrate promoter and lowers the CO₂ gas pressure required for hydrate formations compared to the pressure required for pure CO₂ hydrate formation. The inhibitor effect of ethanol becomes effective at high ethanol concentrations.

The aqueous solution of ethanol forms a binary sII clathrate hydrate²⁸ when compressed with methane gas, whereas the pure methane hydrate is sI. The smaller solubility of methane in water and the larger pressure (2 MPa or greater) required for hydrate formation may play a role in the formation of the ethanol + CH₄ hydrate in sII form. In this binary hydrate, methane is found to occupy some of the large cages of the hydrate. In contrast, the binary sI hydrate of ethanol + CO₂ is formed at a pressure of 0.58 MPa or greater. The solubility of CO₂ in water is considerably larger than methane. Furthermore, CO₂ is known to have greater solubility in aqueous ethanol solutions than in pure water.²⁹ The effect of the water-soluble hydrate promoter on the solubility

of the gas forming the hydrate phase may be exploited in designing clathrate hydrate phases with different structures and formation pressures. The unique property of ethanol as a hydrate promoter is that it is incorporated in the hydrate phase to a lesser degree than other hydrate promoters like tetrahydrofuran. These properties may make it a useful alternative to more commonly used hydrate promoters.

Comparison of the molecular dynamics simulations of the sII binary ethanol + CH₄ binary hydrates² with the present work for the sI binary ethanol + CO₂ hydrate, show that the probability of hydrogen bonding in the latter case is significantly greater. The size of the cage thus plays an important role in determining the extent of guest–water hydrogen bonding in the hydrate. The *tert*-butylamine guest in large sII binary *tert*-butylamine + H₂S(Xe) hydrate also hydrogen bonds with strong probability to the cage water molecules. The balance between the size of the molecule, the size of the hydrophobic moiety, the size of the cage, the hydrogen bonding strength of the functional group all play roles in determining the probability of hydrogen bond formation in the hydrate.

We see the importance of considering specific guest–water and guest–guest interactions in determining clathrate hydrate properties. This specificity implies that we cannot use general thermodynamic models like the van der Waals–Platteeuw theory to determine the stability conditions of these hydrates. More sophisticated molecular dynamics free energy or Monte Carlo methods which considered the molecular details of the interactions are needed in these case.

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