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Hydrogen Bonding of Hydrates of Double Acetic Acid Molecules

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In the chemical industry, the separation of the acetic acid from the HAc/H_2O system is always influenced by the hydrogen bonding. In the present work, an investigation on the hydrogen bonding of various hydrates of double acetic acid (HAc) molecules is carried out with two first-principle methods including ab initio molecular dynamics (AIMD) simulation and quantum chemical calculations (QCC). From the AIMD simulation, the distribution of the head-on rings of acetic acid is revealed and shows that the favorable structures tend to be the acetic acid hydrates rather than the HAc cyclic dimer. The 6- and 10-membered head-on rings involving single and double HAc molecules, respectively, appear to be the dominant structures. According to the QCC, the most stable structure is found to be the conformer with the biggest head-on ring in each group. The energetics of the rings indicates that the stability of the ring increases with increased ring size (with the exception of the 9-membered ring), and the 10-membered ring is the most stable. The relative stability of the ring structures implied by the static QCC result is in good agreement with the statistical ring distribution of the AIMD simulation.

1. Introduction

Distillation is a common method to separate acetic acid from the HAc/H_2O mixture and to obtain a high-purity product of acetic acid in a modern chemical process. However, the distillation efficiency is dramatically low when the solution becomes very dilute (e.g., the concentration of HAc is lower than 2 wt %). This long existing problem has often caused many frustrations and failures of industrial distillation tower design and revamping in the separation of the system, at least in China, in the past decade. One of the crucial reasons is that one still never completely knows the interaction in the microworld of the dilute HAc aqueous solution. The hydrogen bonding (H-bonding) between acetic acid and water molecules represents the strongest force governing the physical and chemical properties of the mixtures, and therefore it affects the vapor−liquid equilibrium of the HAc/H_2O system.

The functional group in HAc plays a very important role in the formation of the aggregates. As a hydrophobic site, the methyl group weakly interacts with water under general condition, which can be enhanced at extremely high pressure.[1] However, the carbonyl and hydroxyl are both active groups and hydrogen bonded (H-bonded) to each other. Therefore, the HAc molecules have been found to form a cyclic dimer with two strong hydrogen bonds (H-bond) in gas.[2−4] In some nonpolar solutions, the aggregate of HAc tended to be a similar cyclic dimer as in gas.[5,6] This cyclic dimer structure is also found in pure HAc liquid, though it is less favorable than the chain structures.[7] As for the aqueous solution, the case is more complicated.

Some simple aggregates in the HAc aqueous solution have been studied with various experimental and theoretical methods. In earlier works,[8−13] HAc monomer and cyclic dimer were considered to coexist with an equilibrium dimerization constant K_D. By applying factor analysis and band contour resolution techniques to the Raman spectra, Ng and Shurvell[11,12] found that K_D approached a value of 0.06 $L \cdot mol^{-1}$ when the concentration decreased. Also by analyzing the Raman spectra of the aqueous solution of some carboxylic acids, Tanaka et al.[13] indicated that the increase of the K_D value was caused mainly by the enhancement of the hydrophobic interaction.

In other works, the favorable structure in HAc aqueous solution is suggested to be the hydrates of the single HAc molecule rather than the HAc cyclic dimer.[14,15] Studies of solvent effects of the acetic acid dimer indicated that the formation of dimer in strong polar solvent (water) was not favorable because of a large disturbing effect.[14,15] Chocholoušová et al.[16] suggested that water molecules are incorporated into the HAc dimer, leading to water-separated structures, and acetic acid does not form any dimer structures in the aqueous solution, according to their ab initio and molecular dynamics simulations. Using mass spectrometric analysis, Nishi et al.[17,18] observed the acetic acid monomer, dimers, and their hydrates, for which the hydrates of the single HAc molecule are more favorable than those of the HAc dimer. In dilute solution, interaction between molecules of acetic acid and water increases competitively.[11,12] In particular, the ATR-IR and Raman spectra of CH_3COOD and CD_3COOD in D_2O solution measured by Génin et al.[19] inferred that the hydrates of the single HAc molecule are the only species in 0.1−1 M solutions.

Both the experimental and theoretical studies tend to support that the interactions between acetic acid and water molecules are more competitive than those between HAc molecules in dilute aqueous solution. However, the specific local structure and the nature of H-bonding are still far from precisely understood.[20] Gao et al.[21] reported the equilibrium structures and the H-bonding of the mono- and dihydrates of the single

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acetic acid molecule with a density functional theory method. We extended the work to more complicated hydrates.[22] Because of the special characteristic of the HAc cyclic dimer, the present work particularly focuses on its behavior in aqueous solution. Some investigation has been performed by molecular dynamics simulation; however, the approach employed was empirical force field.[16] In this work, we use two first-principle methods including ab initio Molecular Dynamics simulation (AIMD)[23] and the static quantum chemical calculations (QCC) to carry out a more systematic investigation on the H-bonding of the hydrates of double HAc molecules.

2. Computational Method and Details

2.1. AIMD. The AIMD simulation is carried out in the isothermal−isobaric (NPT) ensemble with use of the CPMD package.[24] Under the condition of a constant pressure of 1 bar, a constant temperature of 300 K, and a density of 1.0 $g \cdot cm^{-3}$, 2 acetic acid and 20 water molecules are involved with a periodic image reproduction. The initial structure is constructed upon the HAc cyclic dimer with 2 water molecules H-bonded to every O atom of the carboxyl. Then 12 water molecules are randomly added in a simple flexible cubic cell with a length of 9.1732 Å.

The Kohn−Sham orbitals are expanded in a plane wave basis set up to an energy cutoff of 70 Ry. A fictious mass of 1100 au is used in the thermostating equation of motion. With a time step of 7 au (0.169 fs), the trajectory is collected every 10 steps during the 16.9 ps production run after a 1.69 ps equilibrium. The gradient-corrected Becke, Lee, Yang, and Parr (BLYP)[25,26] exchange correlation functional is employed in this simulation because it has been shown to give a good description of aqueous systems.[27−29]

The system is composed of 2 HAc and 20 water molecules, labeled as 2A20W, where the uppercase letter A stands for acetic acid and W denotes water, and 2 and 20 indicate the number of water and HAc molecules, respectively.

2.2. QCC. We have chosen a method as follows: The hydrates are optimized with the second-order Møller−Plesset theory with the basis set 6-31+G(d,p) (MP2/6-31+G(d,p)); the energy is recalculated at a level of the fourth-order Møller−Plesset theory with the same basis set (MP4/6-31+G(d,p)). For this basis set, various hydrates that are categorized into four groups including mono-, di-, tr-, and tetrahydrate contain 221, 250, 279, and 308 basis functions, respectively. The total binding energy of a hydrate is denoted as ΔE_T derived by eq 1, where $E_{hydrate}$ stands for the total energy of the hydrate that has 2 HAc and n water molecules, E_{HAc} denotes the energy of the HAc molecule and E_{water} stands for that of water, and 2 and n indicate the number of HAc and water molecules in the hydrate, respectively. On calculating ΔE_T, the basis set superposition error (BSSE) is considered by using the counterpoise correction of Boys and Bernardi's method,[30] where the energy of a single molecule in a hydrate is calculated by considering the atoms of its own but using the basis functions of the entire hydrate. Totally 8 monohydrates, 9 dihydrates, 14 trihydrates, and 15 tetrahydrates are considered in the current work. In the Results section, the top 6 or 8 will be presented and others can be found in the Supporting Information. All the calculations are performed by using Gaussian 98 or 03 programs[31,32] on SGI 3800 and SGI 4700 high performance computers.

$$\Delta E_T = E_{hydrate} - (2E_{HAc} + nE_{water}) \qquad (1)$$

The group is labeled as nAmW and correspondingly the hydrate as nAmW-k. The uppercase letter A stands for acetic acid and W for water and the lowercase letters n and m for the number of HAc and water molecules, respectively, while k stands for a number just distinguishing the conformers without a practical meaning. As an example shown in Figure 1, the monohydrate with two HAc molecules is named as 2A1W-1. Accordingly, the acetic acid cyclic dimer is labeled as 2A and the water dimer as 2W.

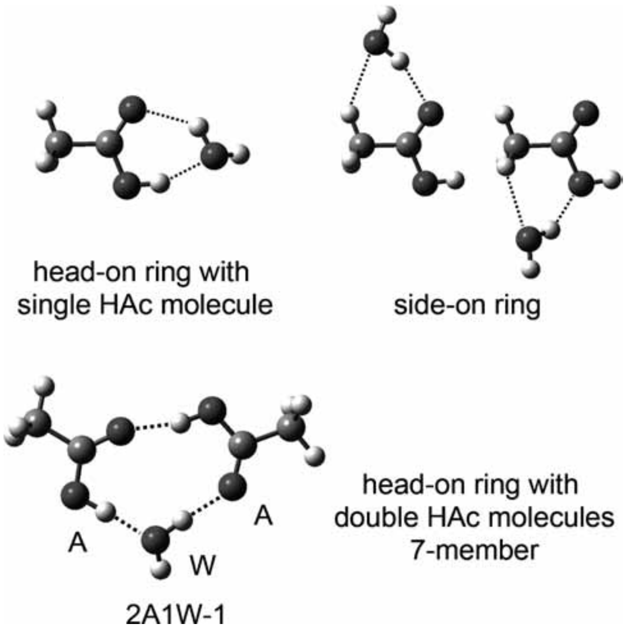

Figure 1. The structure of the head-on ring and the side-on ring.

The relative position of the water molecule with respect to the acetic acid is defined as the head-on site and side-on site, and the H-bonded ring at the corresponding position is called the head-on ring or the side-on ring. Examples are given in Figure 1, including two kinds of head-on rings with one or two HAc molecules.

The size of an H-bonded ring is derived by counting its number of heavy atoms. For example, in Figure 1, the two head-on rings involving one and two HAc molecules are the 4- and 7-membered rings, respectively, and the two side-on rings are 4-membered. The H-bond is denoted as $X_{FG} \cdots H_{FG}$, in which the uppercase letters X and H stand for the H-bond acceptor and donor atoms, respectively, and the subscript FG indicates the functional group of water and HAc molecules (including W, OH, CO, and CH_3) to which the atom belongs (W means water; and OH, CO, and CH_3 stand for the hydroxyl, carbonyl, and methyl of acetic acid, respectively).

3. Results and Discussion

3.1. AIMD. Our study has shown that the favorable structures of the hydrates of the single HAc molecule tend to be the head-on rings, especially the 6-membered head-on ring, demonstrated by both the results of the QCC and the AIMD simulation.[22] That system was composed of 1 HAc and 20 water molecules, labeled as 1A20W. The ring distribution from the AIMD simulation for 1A20W is provided in the Supporting Information. We now obtain two kinds of head-on ring distributions with one or two HAc molecules using the same ring perception and statistical method.[33] Figure 2a,b presents the distributions only with one HAc molecule, and Figure 2c presents the one with two HAc molecules. Note that the average in Figure 2 is derived over all the configurations at the production time.

Because of two HAc molecules in the structure, two head-on ring distributions with one HAc molecule are derived for

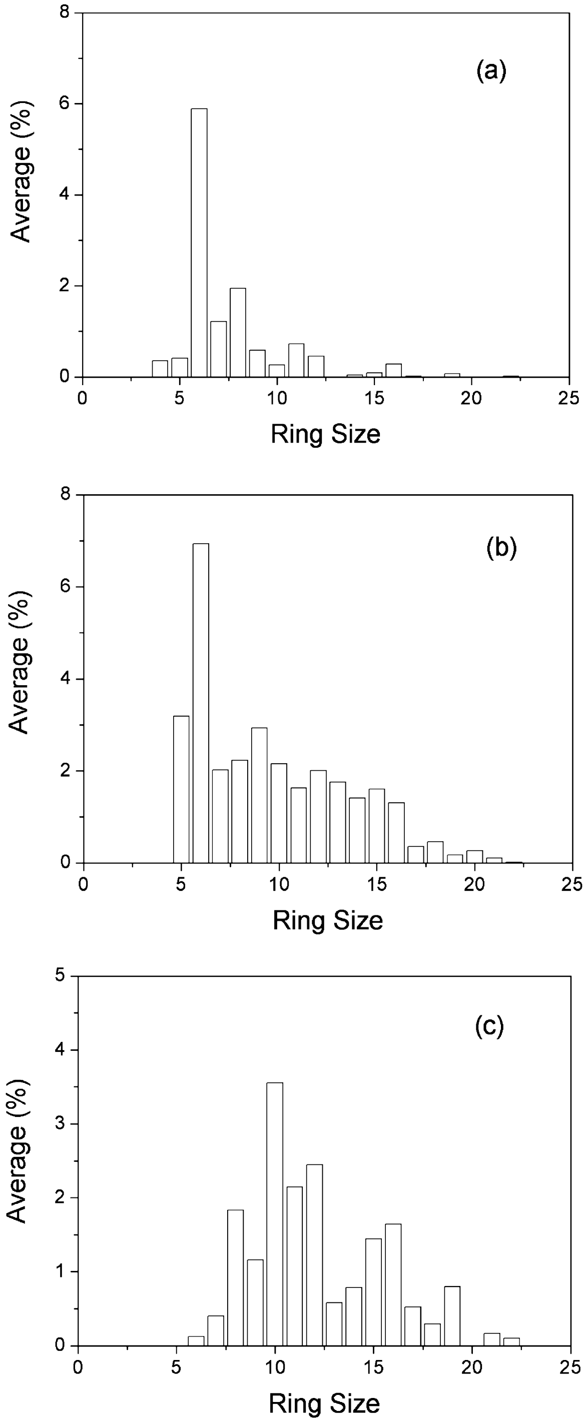

Figure 2. Distributions of the hydrogen bonded head-on rings involving only (a) HAc α or (b) HAc β and (c) double HAc molecules obtained from the AIMD simulation.

each of them and are shown in Figure 2a,b. And the HAc molecule in Figure 2a,b is labeled as HAc α and β, respectively. Note that HAc α and β just denote two individual HAc molecules without practical meaning. The statistical result shows that the total configurations having a head-on ring with HAc α or β reach 12.3% or 30.6% of all the configurations. The average of the two numbers is similar to the case of 1A20W (see the Supporting Information), where about 22.0% configurations had head-on rings.

The most evident and striking feature in Figure 2a,b is that the average population of the 6-membered head-on ring is the largest in both distributions, consistent with the case of 1A20W. And the 6-membered head-on rings with HAc α or β appear to be approximately 6.0% and 7.0%, respectively, larger than that of 1A20W (~4.0%). On the basis of the results of 1A20W and 2A20W, the 6-membered head-on ring is suggested to be the most dominant structure in the dilute HAc aqueous solution.

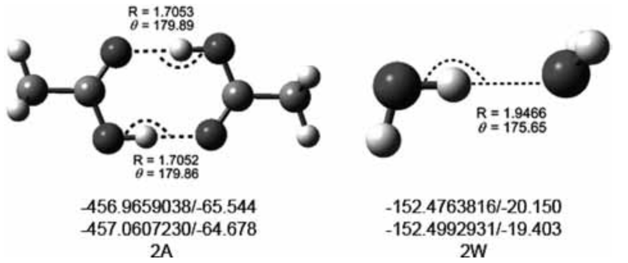

Figure 3. Acetic acid cyclic dimer, 2A, and water dimer, 2W, optimized at the MP2/6-31+G(d,p) level. The hydrogen bond and angle are displayed as the dashed line, the corresponding value of the length R (in Å) and angle θ (in deg) are given. The total energy E (in hartrees)/binding energy ΔE_T (in kJ·mol^{-1}), at both the MP2 (top) and the MP4 (middle) level with the 6-31+G(d,p) basis set, and the conformer's name (bottom) are listed below each structure.

The configurations having head-on ring with only HAc α are less than those with only HAc β. For HAc α (Figure 2a), the second dominant ring is the 8-membered (~2.0%) and the third is the 7-membered (~1.2%). Besides 6-, 7- and 8-membered rings, other structures are all less than 1%. The planar rings, 4- and 5-membered, appear to be 0.3−0.4%, less than the case of 1A20W. For HAc β (Figure 2b), the range of the size is wider compared with the case of HAc α. And most rings are larger than 1%. In particular, the 5- and 9-membered rings reach 3%. Different from the case of HAc α, the second dominant ring is the planar 5-membered ring with an approximate 3.2%, about half of that of 6-membered ring. The third dominant ring is the 9-membered ring with approximate 2.8%. Besides the top three, rings smaller than 17 members are found to be about 2% and others are rare.

Figure 2c shows the distribution of the H-bonded head-on rings with two HAc molecules. It is of note that the total configurations of this type are found to be 18% of all the configurations, less than that with one HAc molecule. The smallest ring is the acetic acid cyclic dimer, a 6-membered ring. As shown in Figure 2c, the percentage of the 6-membered ring is very small (~0.1%). This result indicates that the HAc cyclic dimer is unfavorable in the aqueous solution, similar to Chocholoušová's study.[16]

Clearly shown in Figure 2c, the 10-membered H-bonded head-on ring is the most favorable structure (~3.6%). The 10-membered ring is composed of four water molecules besides the two acetic acid molecules. This percentage is less than that of the dominant 6-membered head-on ring with single HAc. The second dominant is the 12-membered ring (~2.5%), with six water molecules. The 11-membered ring, with five water molecules, is the third favorable structure (~2.2%). The percentage of the 11- or 12-membered ring appears to be two-thirds of that of the 10-membered ring. The configurations of the 8-, 9-, 15-, and 16-membered rings are larger than 1% but less than 2% and those of the rest are less than 1%.

It is interesting that the even-membered ring is more favorable than the adjacent odd-membered ring with the structure in the range of 7- to 13-members. For instance, the percentage of the 8-membered ring (1.8%) with two water molecules is larger than that of the 7-membered ring (0.4%) with a single water molecule, or the 9-membered ring (1.2%) with three water molecules. This case is easy to understand in that the even-

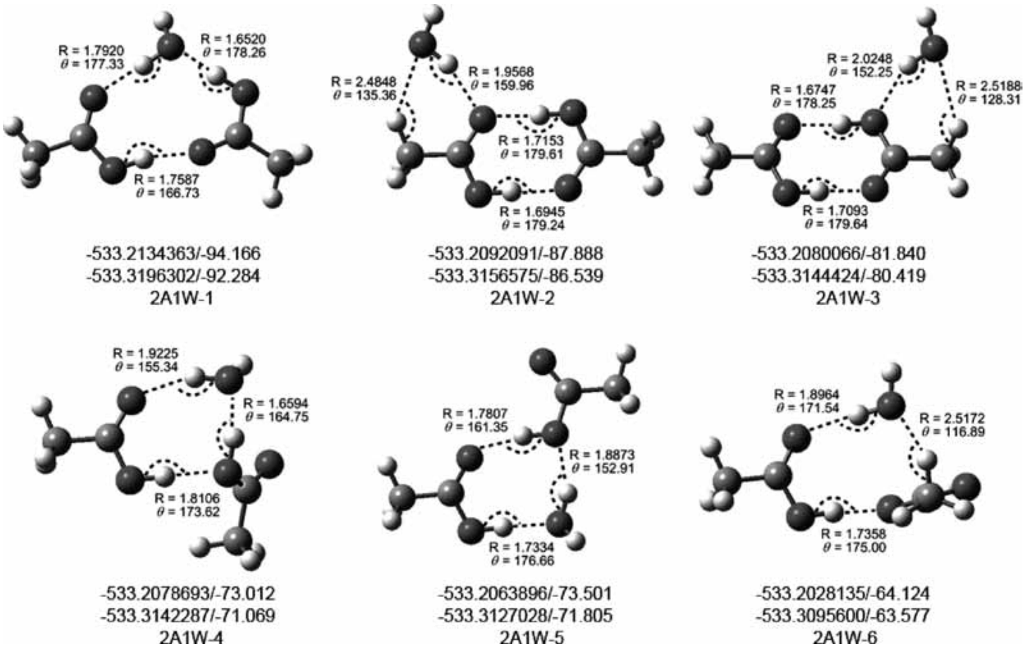

Figure 4. Equilibrium structures of the top six conformers in the monohydrate group of double HAc molecules, 2A1W, optimized at the MP2/6-31+G(d,p) level. The hydrogen bond and angle are displayed as the dashed line, the corresponding value of the length R (in Å) and angle θ (in deg) are provided. The total energy E (in hartrees)/binding energy ΔE_T (in kJ·mol^{-1}), at both the MP2 (top) and the MP4 (middle) level with the 6-31+G(d,p) basis set, and the conformer's name (bottom) are listed below each structure.

membered ring involves even-numbered water molecules and therefore a more geometrically symmetrical and compatible structure is provided.

3.2. QCC. The above discussion indicates that acetic acid in the aqueous environment tends to form ring hydrates with one or two HAc molecules rather than the HAc cyclic dimer. Therefore, the specific equilibrium structures of four groups of hydrates with two HAc and 1 to 4 water molecules are determined by static ab initio calculations.

Before introducing the structure of hydrates, we present the equilibrium structures of the acetic acid cyclic dimer, 2A, and water dimer, 2W. The structure, along with the parameters of H-bonds (the length, in Å, and the angle, in deg), the total energy E (in hartrees) and the total binding energy ΔE_T (in kJ·mol^{-1}) obtained at both the MP2 and the MP4 level with the 6-31+G(d,p) basis set, of each conformer are provided in Figure 3. The total energies calculated by the MP4 method are found to be more negative than those with the MP2 method and the binding energies seem to be less negative by the MP4 than by the MP2 method.

A. Monohydrate 2A1W. The equilibrium structures of the top six monohydrates, 2A1W, are presented in Figure 4, along with the parameters of H-bonds (the length, in Å, and the angle, in deg), the total energy E (in hartrees), and the total binding energy ΔE_T (in kJ·mol^{-1}), obtained at both the MP2 and the MP4 level with the 6-31+G(d,p) basis set. The total energy of conformer 2A1W-1 is the most negative in the six, at least 10 kJ·mol^{-1} lower than the others. Conformer 2A1W-1 involves a 7-membered head-on ring. This ring can be regarded as that a water molecule cuts into one of the strong H-bonds $O_{CO}\cdots H_{OH}$ of the HAc cyclic dimer and two H-bonds, $O_W\cdots H_{OH}$ and $O_{CO}\cdots H_W$, are formed. It is found that the H-bond $O_W\cdots H_{OH}$ in 2A1W-1 appears to be shorter than $O_{CO}\cdots H_{OH}$ in the HAc cyclic dimer, whereas the similar H-bond $O_{CO}\cdots H_{OH}$ in 2A1W-1 tends to be longer and less collinear. For the two H-bonds between water and HAc, $O_{CO}\cdots H_W$ is 0.1400 Å longer and 0.93° less collinear than $O_W\cdots H_{OH}$, suggesting that the H-bond involving hydroxyl H is stronger than that with carbonyl O.

Conformers 2A1W-2 and 2A1W-3 can be regarded as the combination of the HAc cyclic dimer and a 4-membered side-on ring. Conformers 2A1W-4, 2A1W-5, and 2A1W-6 appear to be more complicated than the former three. The accompanying strain of the structure brings a higher energy.

B. Dihydrates 2A2W. For the dihydrates 2A2W, the equilibrium structures of the top six conformers are presented in Figure 5, provided along with the length and angle of each H-bond, the total energy E, and the total binding energy ΔE_T. The global minimum is conformer 2A2W-1, with an 8-membered head-on ring. Conformer 2A2W-2 also has a similar 8-membered head-on ring structure. The two conformers can be regarded as the HAc dimer mediated by water molecules. In 2A2W-1, the two water molecules are connected by one H-bond $O_W\cdots H_W$, which cuts the 8-membered head-on ring into two 5-membered head-on rings with a single HAc molecule. In conformer 2A2W-2, the two water molecules are not connected by an H-bond. Such difference results in stronger binding interaction of conformer 2A2W-1 than 2A2W-2. For conformer 2A2W-1, one of the H-bond $O_W\cdots H_{OH}$ appears to be shorter and slightly less collinear than those in conformer 2A2W-2 or 2A1W-1, while the H-bond $O_{CO}\cdots H_W$ on the same side in the 8-membered ring is found to be longer and less collinear. The other H-bond $O_W\cdots H_{OH}$ in 2A2W-1 tends to be much longer and less collinear than in conformer 2A2W-2 or 2A1W-1, whereas the other H-bond $O_{CO}\cdots H_W$ seems to be shorter.

The other four conformers can be regarded as a combination of the most stable monohydrate 2A1W-1 and a 4-membered side-on ring. These side-on rings appear to be more favorable at the carbonyl side than at the hydroxyl side.

C. Trihydrates 2A3W. For the trihydrates 2A3W, the equilibrium structures of the top eight are presented in Figure 6, along with the length and angle of each H-bond, the total energy E, and the total binding energy ΔE_T, at the MP2 and the MP4 level with the 6-31+G(d,p) basis set. The lowest structure is

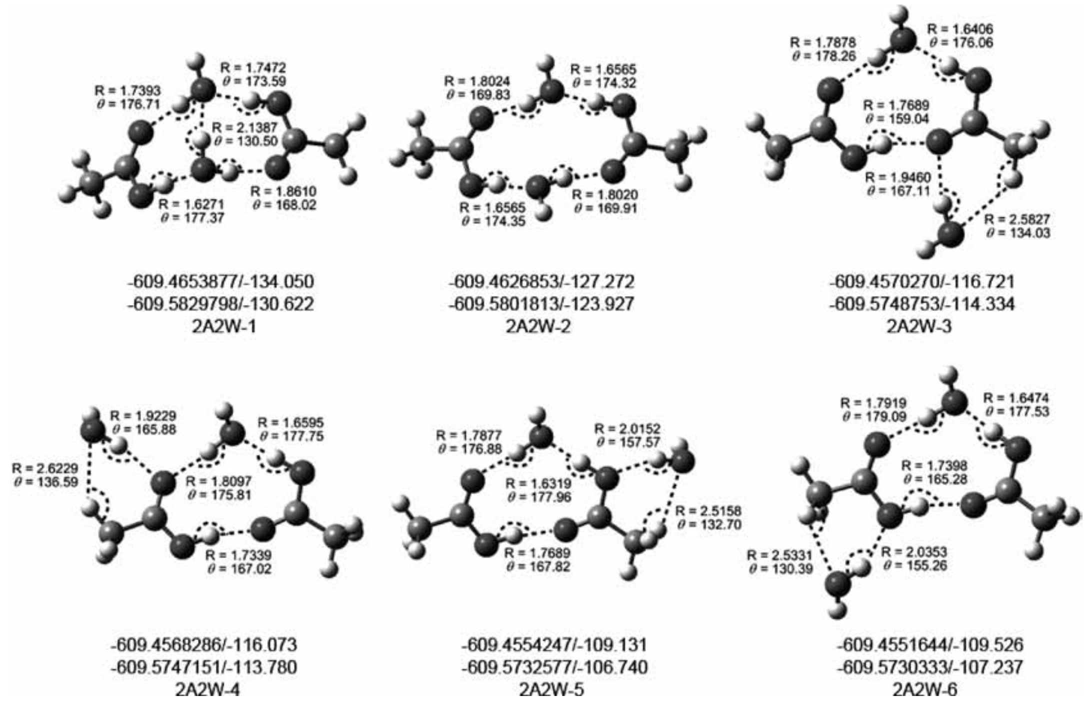

Figure 5. Equilibrium structures of the top six conformers in the dihydrate group of double HAc molecules, 2A2W, optimized at the MP2/6-31+G(d,p) level. The hydrogen bond and angle are displayed as the dashed line, the corresponding value of the length R (in Å) and angle θ (in deg) are provided. The total energy E (in hartrees)/binding energy ΔE_T (in kJ·mol^{-1}), at both the MP2 (top) and the MP4 (middle) level with the 6-31+G(d,p) basis set, and the conformer's name (bottom) are listed below each structure.

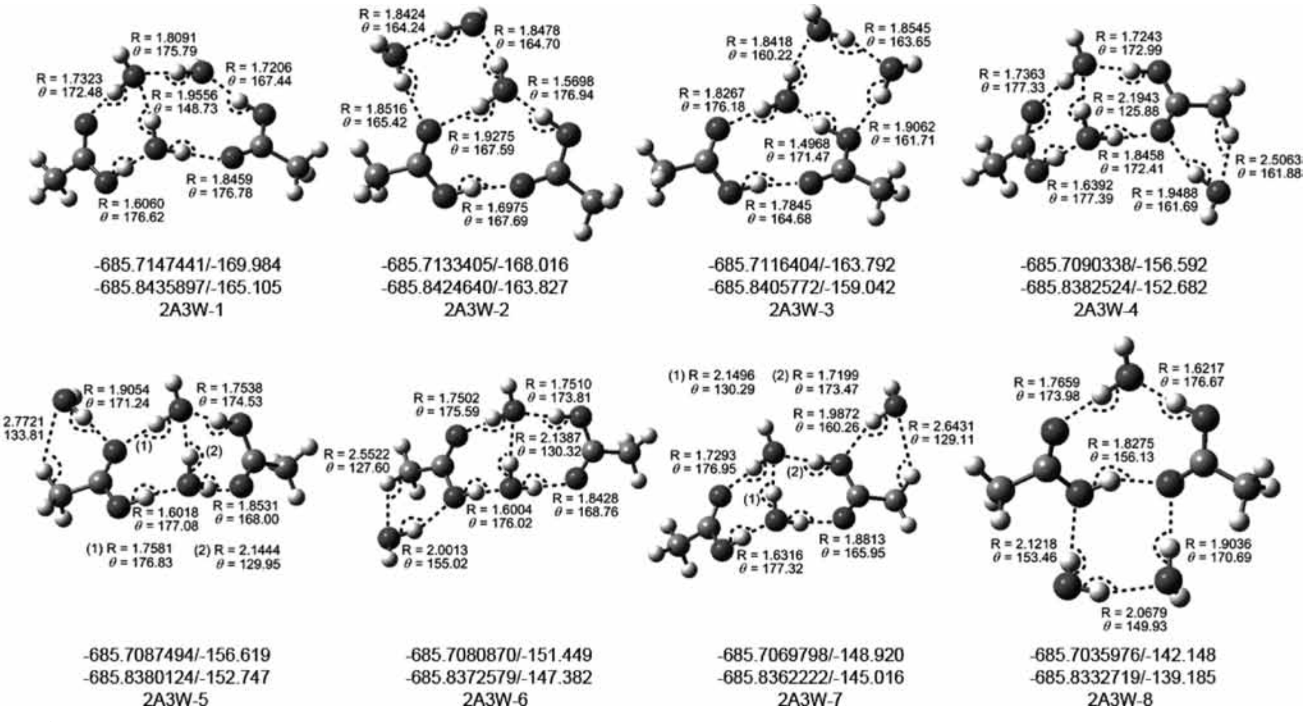

Figure 6. Equilibrium structures of the top eight conformers in the trihydrate group of double HAc molecules, 2A3W, optimized at the MP2/6-31+G(d,p) level. The hydrogen bond and angle are displayed as the dashed line, the corresponding value of the length R (in Å) and angle θ (in deg) are provided. The total energy E (in hartrees)/binding energy ΔE_T (in kJ·mol^{-1}), at both the MP2 (top) and the MP4 (middle) level with the 6-31+G(d,p) basis set, and the conformer's name (bottom) are listed below each structure.

conformer 2A3W-1, with a 9-membered head-on ring. This hydrate can be regarded as the HAc dimer mediated by a single water or a water dimer. Similar to 2A2W-1, the dangling H of the single water is H-bonded to one of the water dimer molecules, dividing the 9-membered head-on ring into two smaller head-on rings. Conformer 2A3W-1 has two H-bonds for each of $O_{CO}\cdots H_W$, $O_W\cdots H_{OH}$, and $O_W\cdots H_W$. All the H-bonds $O_W\cdots H_{OH}$ and $O_{CO}\cdots H_W$ are shorter and less collinear in 2A3W-1 than in 2A2W-1. The H-bond $O_W\cdots H_W$ connecting the single water and water dimer appear to be shorter and more collinear than that in 2A2W-1.

Conformer 2A3W-2 or 2A3W-3 can be regarded as the combination of 2A1W-1 and a 4-membered side-on ring without the weak interaction of methyl. Conformer 2A3W-8 can also

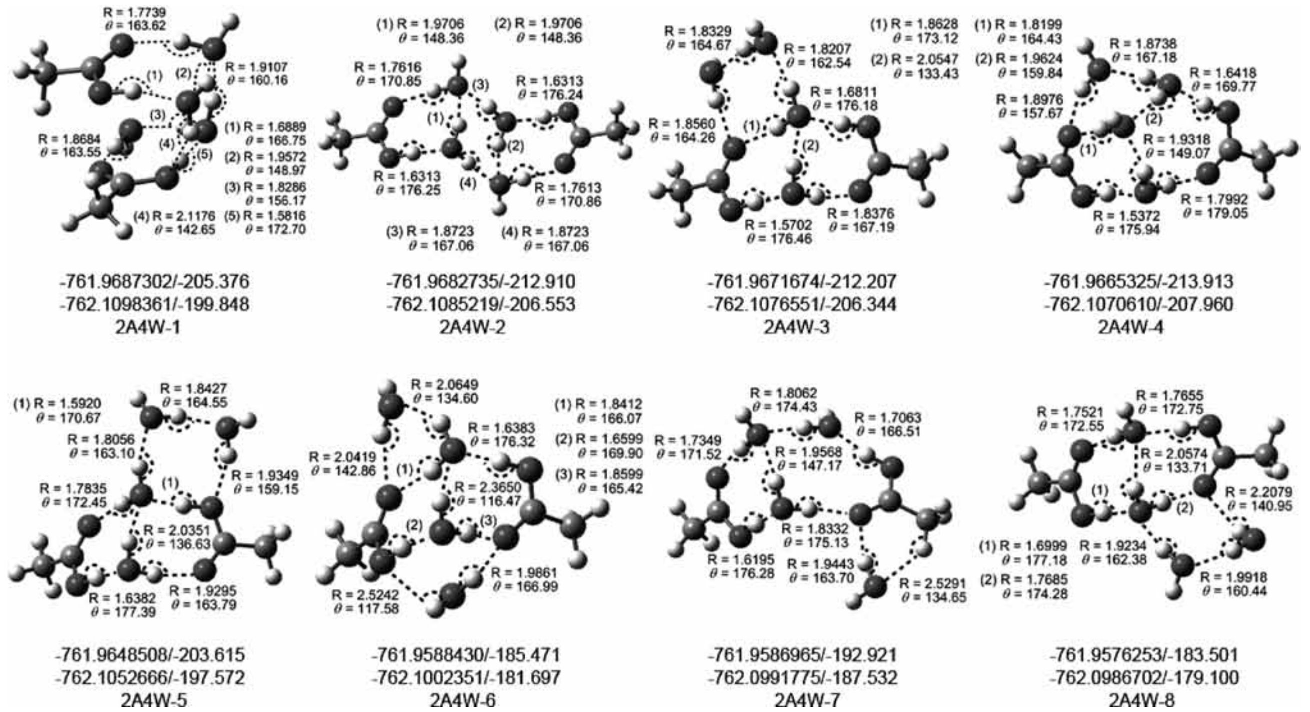

Figure 7. Equilibrium structures of the top eight conformers in the tetrahydrate group of double HAc molecules, 2A4W, optimized at the MP2/6-31+G(d,p) level. The hydrogen bond and angle are displayed as the dashed line, the corresponding value of the length R (in Å) and angle θ (in deg) are provided. The total energy E (in hartrees)/binding energy ΔE_T (in kJ·mol^{-1}), at both the MP2 (top) and the MP4 (middle) level with the 6-31+G(d,p) basis set, and the conformer's name (bottom) are listed below each structure.

be regarded as 2A1W-1 combined with a water dimer, forming a 4-membered side-on ring. However, the carbonyl and the hydroxyl both act as the H-bond acceptors and the two dangling H atoms in the water dimer act as the donors. This feature enhances the strain of the side-on ring, resulting in ~20 kJ·mol^{-1} less negative of the ΔE_T value of conformer 2A3W-8 than that of 2A3W-2 or 2A3W-3. Other conformers can be regarded as the combination of 2A2W-1 with the 4-memebered side-on ring involving the methyl group.

D. Tetrahydrates 2A4W. The equilibrium structures of the top eight tetrahydrates 2A4W are presented in Figure 7, along with the length and angle of each H-bond, the total energy E, and the total binding energy ΔE_T. The global minimum of the tetrahydrates is conformer 2A4W-1, a cubic structure. Conformer 2A4W-2 is the second lowest tetrahydrate, with a 10-membered ring that is similar to that of the smaller lowest hydrates (2A1W-1, 2A2W-1, and 2A3W-1). However, the total energy of this conformer is only 3.450 kJ·mol^{-1} less negative than that of 2A4W-1, whereas the binding energy is 6.705 kJ·mol^{-1} more negative. This difference indicates that conformer 2A4W-2 also can be considered as the most dominant structure in the tetrahydrates. For 2A4W-1, the structure of the top or the bottom face is similar to the planar 5-membered head-on ring; that of the right face is a 4-membered ring having two H-bonds $O_{OH}\cdots H_W$ and $O_W\cdots H_W$ besides the two coshared H-bonds $O_W\cdots H_{OH}$ and $O_W\cdots H_W$. For 2A4W-2, the structure is similar to the combination of two 5-membered rings connected by two H-bonds $O_W\cdots H_W$.

Conformers 2A4W-3, 2A4W-5, 2A4W-,7 and 2A4W-8 can be regarded as the combination of the smaller stable hydrate and a 4-membered side-on ring with or without the weak interaction of methyl. For some other conformers, the initial structures are constructed upon the smaller stable hydrate, attached by one water molecule with a 4-membered side-on ring involving the methyl group. However, after optimization, one water molecule on the head-on ring draws away the attached water molecule from the methyl and is H-bonded to it, forming a 3- or 4-membered side-on ring. The examples are such as conformers 2A4W-4 and 2A4W-6 and some less favorable provided in the Supporting Information.

E. Energetics. Various hydrates involving the head-on ring of double HAc molecules can be categorized by the size of the head-on ring, shown in Table 1. In contrast to the above hydrate group, this categorization is labeled as the ring group. Note that a hydrate has the total binding energy ΔE_T, and its head-on ring also has the ring binding energy, labeled as ΔE_R. For the derivation of ΔE_R, the head-on ring is considered as a single hydrate and ΔE_R is calculated by eq 2, where E_{ring} is the total energy of the head-on ring that has 2 HAc and n water molecules, E_{HAc} stands for the energy of the HAc molecule, E_{water} denotes that of the water molecule, and 2 and n indicate the number of HAc and water molecules, respectively. The BSSE correction using the Boys and Bernardi's method[30] is also considered for the calculation of ΔE_R. Table 1 presents the ΔE_R values for various hydrates obtained at the MP2/6-31+G(d,p) level (The energies obtained at the MP2 level are enough for the present discussion.).

$$\Delta E_R = E_{\text{ring}} - (2E_{\text{HAc}} + nE_{\text{water}}) \qquad (2)$$

From Table 1, it can be found that the ΔE_R values are very close in the same ring group. For the most stable structure of a hydrate group, the ΔE_R of its head-on ring is not always the lowest in its ring group. However, those in some hydrates with a side-on ring have lower ΔE_R. These hydrates are always found to be involving the H-bonding of carbonyl group at the side-on site, suggesting that the side-on interaction at the carbonyl site would result in the strengthening of the H-bonding of the head-on ring.

TABLE 1: Various Head-On Rings with Double HAc Molecules, the Corresponding Hydrates, and the Ring Binding Energy ΔE_R (in kJ·mol^{-1}) Derived at the MP2/6-31+G(d,p) Level

size of head-on ring	hydrate	ΔE_R
6	2A1W-2	−63.259
6	2A1W-3	−64.240
6	2A	−65.544
7	2A2W-6	−91.247
7	2A2W-4	−92.874
7	2A3W-2	−93.710
7	2A1W-1	−93.997
7	2A3W-3	−94.166
7	2A2W-5	−94.228
7	2A3W-8	−95.409
7	2A2W-3	−96.082
8	2A3W-4	−128.678
8	2A3W-7	−128.687
8	2A3W-5	−129.902
8	2A2W-2	−130.899
8	2A4W-3	−131.324
8	2A3W-6	−131.840
8	2A4W-8	−132.278
8	2A2W-1	−132.907
8	2A4W-5	−134.050
8	2A4W-6	−135.270
9	2A4W-7	−167.622
9	2A4W-4	−168.367
9	2A3W-1	−170.158
10	2A4W-2	−212.910

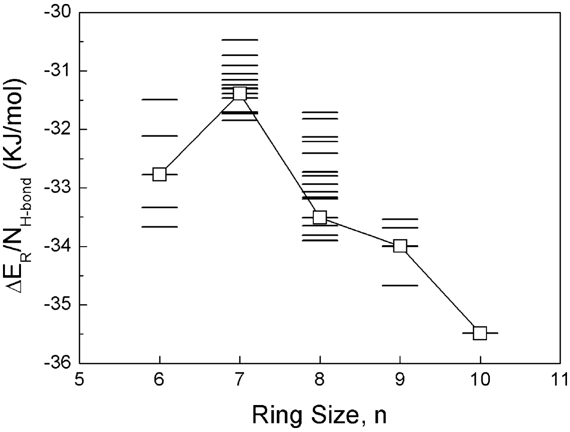

Figure 8. The average binding energy of the head-on ring divided by the number of strong H-bonds ($\Delta E_R/N_{\text{H-bonds}}$) versus the ring size. The line is drawn through the most stable hydrates.

The overall strength of the H-bonding can be demonstrated by the average binding energy. The head-on rings always involve strong H-bonds besides the weak H-bond that cuts the head-on ring into smaller ones; therefore the average ΔE_R over the number of strong H-bonds ($\Delta E_R/N_{\text{H-bonds}}$) is derived and presented in Figure 8, versus the size of the head-on ring. In Figure 8, the line is drawn through the most stable conformer of each hydrate group with the exception of 2A4W-2 for the 10-membered ring (these hydrates are not only the conformers with the lowest energy, but also those with only a head-on ring.). For the rings involving water molecules (larger than 6-membered), the average ΔE_R value appears to be lower than that of the HAc cyclic dimer (6-membered) except for the 7-membered ring. This feature indicates that the incorporation of the water molecules into the HAc cyclic dimer is favorable and would result in the HAc cyclic dimer hardly existing in an aqueous environment, which corresponds to the ring distribution of the AIMD simulation in Figure 2c.

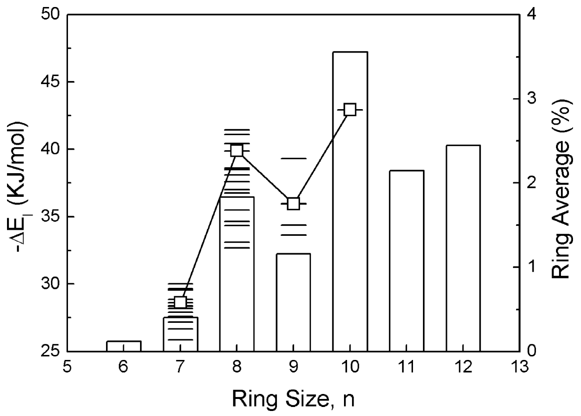

Figure 9. Incremental binding energies ($-\Delta E_I$, the short line, the unfilled square, and line) and the ring distribution (the column) from AIMD simulation versus the ring size. The line is drawn through the most stable hydrates.

One quantity that can clearly and directly reveal the relative stabilities of different rings is the incremental binding energy labeled as ΔE_I, which indicates the energy change of the process

$$HAc_2(H_2O)_{n-1} + H_2O \rightarrow HAc_2(H_2O)_n \qquad (3)$$

And ΔE_I is derived by

$$\Delta E_{I,n} = \Delta E_{R,n} - \Delta E_{R,n-1} \qquad (4)$$

On calculating the ΔE_I values from eq 4, the smaller ring ($HAc_2(H_2O)_{n-1}$) is always chosen the most stable conformer in the hydrate group, including 2A, 2A1W-1, 2A2W-1, and 2A3W-1. The incremental binding energy derived at the MP2/6-31G+(d,p) level is presented in Figure 9, versus the size of the head-on ring. The line is drawn through the hydrates the same as in Figure 8. As can be seen, the $-\Delta E_I$ value increases while the ring grows except for the 9-membered ring and the 10-membered ring has the biggest ΔE_I.

The relative stability implied from the $-\Delta E_I$ values (Figure 9) is consistent with the trend of the average ΔE_R (Figure 8). In Figure 8, the line between the 7- and 8-membered or the 9- and 10-membered rings decreases more rapidly than that between the 8- and 9-membered rings. In Figure 9, the $-\Delta E_I$ value for the 8-membered ring is larger than that for the 7- or the 9-membered ring and the $-\Delta E_I$ for the 10-membered ring is the largest. In Figures 4−7, it can be found that from the 7- to the 8-membered ring, it is a structure change from asymmetrical to symmetrical and from complicated to simple. So does that from the 9- to the 10-membered ring. However, the growth from the 8- to the 9-membered ring is contrary: the incorporation of the third water molecule produces additional instability, resulting in the incremental binding energy being less exothermic.

Part of the ring distribution from the AIMD simulation (in Figure 2c) is also shown in Figure 9 (the column). With comparison of the ΔE_I to the ring distribution, it can be found that the trend of the former (especially for the 7-, 8-, and 9-membered rings) is very similar to that of the latter. The case of the $-\Delta E_I$ value for the 10-membered ring being larger than the others is consistent with the 10-membered ring dominating the ring distribution. Finally, a conclusion can be drawn that the relative stability of the rings implied by the static QCC result corresponds well to the statistical result of the AIMD ring distribution.

4. Conclusion

The H-bonding interactions in the hydrates of double HAc molecules have been investigated by AIMD and static ab initio calculations. According to the distribution of the head-on rings from the AIMD simulation, the favorable structures are the hydrates of single or double HAc molecules rather than the HAc cyclic dimer. For the hydrates of a single HAc molecule, the 6-membered head-on ring appears to be the most favorable. For the hydrates of double HAc molecules, the most dominant structure tends to be the 10-membered head-on ring.

The equilibrium structures and energies of four groups of hydrates involving double HAc molecules are obtained from QCC. The global minima are found to be the structures with the 7-, 8-, and 9-membered head-on ring involving both the HAc molecules for the mono-, di-, and trihydrates, respectively. For tetrahydrate, the lowest energy conformer is the hydrate with a cubic structure. The one with the 10-membered head-on ring has the second lowest energy, but its binding energy is more negative than that of the former.

Various hydrates involving the head-on ring of double HAc molecules also can be categorized according to the ring size. The energetics of the rings shows that the corresponding stability increases when the ring size grows except for the 9-membered ring, and the 10-membered ring is the most favorable. The relative stability of the ring structures agrees well with the ring distribution of the AIMD simulation.

On all accounts, for the dilute aqueous solution of acetic acid, the H-bonding between the HAc and water molecules is found to play a decisive role in the composition of the solution and leads to the domination of the hydrates of single or double HAc molecules. For this reason, the isolation of acetic acid from the mixture of HAc−H_2O would need more effort than that for the usual organics−water system like methanol−water. This is much different from the more concentrated case, in which more aggregates of HAc appear according to the work by Génin et al.,[19] so as to separate acetic acid from water more easily.

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Supporting Information Available: The H-bonded head-on ring distribution of 1A20W reported in the previous work[22] and the equilibrium structures of the remaining less favorable configurations of the four hydrate groups with double acetic acid molecules. This material is available free of charge via the Internet at http://pubs.acs.org.

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