

# A Theoretical Investigation of the Interactions between Water Molecules and Ionic Liquids

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Quantum chemical calculations have been used to investigate the interaction between water molecules and ionic liquids based on the imidazolium cation with the anions  $[\text{Cl}^-]$ ,  $[\text{Br}^-]$ ,  $[\text{BF}_4^-]$ , and  $[\text{PF}_6^-]$ . The predicted geometries and interaction energies implied that the water molecules interact with the  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{BF}_4^-$  anions to form  $\text{X}^-\cdots\text{W}$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ,  $\text{W} = \text{H}_2\text{O}$ ),  $2\text{X}^-\cdots 2\text{W}$ ,  $\text{BF}_4^-\cdots\text{W}$ , and  $\text{W}\cdots\text{BF}_4^-\cdots\text{W}$  complexes. The hydrophobic  $\text{PF}_6^-$  anion could not form a stable complex with the water molecules at the density functional theory (DFT) level. Further studies indicate that the cation could also form a strong interaction with the water molecules. The 1-ethyl-3-methylimidazolium cation ( $\text{Emim}^+$ ) has been used as a model cation to investigate the interaction between a water molecule and a cation. In addition, the interaction between the ion pairs and the water was studied by using 1-ethyl-3-methylimidazolium chloride ( $\text{Emim}\cdot\text{Cl}$ ) as a model ionic liquid. The strengths of the interactions in these categories follow the trend  $\text{anion}-\text{W} > \text{cation}-\text{W} > \text{ion pair}-\text{W}$ .

## Introduction

The ionic liquids based on imidazolium cations such as 1-ethyl-3-methylimidazolium ( $\text{Emim}^+$ ) and 1-butyl-3-methylimidazolium ( $\text{Bmim}^+$ ) have been extensively investigated over the last several years.<sup>1–5</sup> They are finding increasing use in many areas of technology.<sup>6</sup> The possibility of driving the course of chemical reactions makes these fluids an attractive alternative to traditional organic solvents for both laboratory and industrial purposes.<sup>7,8</sup>

Most of the ionic liquids can absorb water from the atmosphere.<sup>9</sup> Even some can react dramatically with the water, such as the  $\text{Emim}\cdot\text{Cl}/\text{AlCl}_3$  ionic liquids.<sup>10</sup> It has been reported that the commonly called “hydrophobic” ionic liquids are actually hygroscopic and can absorb significant amounts of water from the atmosphere, such as the  $\text{PF}_6^-$  anion based ionic liquids.<sup>11</sup> The presence of water could dramatically affect the activity of the ionic liquids and it is often presented as a contaminant in hydrophilic as well as in hydrophobic ionic liquids, highly affecting their physical properties (such as the polarity, viscosity, conductivity, etc.).<sup>12</sup> For example, it has been reported that the water could destroy the  $\text{PF}_6^-$  anion based ionic liquid and produce  $\text{HF}$ .<sup>13,14</sup> Seddon and co-workers investigated the influence of water on the physical properties of ionic liquids and proposed that efficient drying is necessary if ionic liquids are used as solvents for moisture-sensitive substances.<sup>15</sup> The water content of mixtures may also affect the rates and selectivity of reactions.<sup>16</sup> The solubility of water is also an important factor in industrial use of ionic liquids as green solvents. One potential problem with ionic liquids is the possible pathway into the environment through wastewater. Therefore, obtaining information on the interactions between the water molecule and the ionic liquids is important to improve the properties and performances ionic liquids.

The water content of various ionic liquids may be strongly influenced by the nature of the cation and the anion. Various trials have been made to obtain a fundamental understanding

of the interaction between the water and the ionic liquids. Welton and co-workers investigated the state of water in room temperature ionic liquids based on the 1-alkyl-3-methylimidazolium cation with several anions using IR spectroscopy and suggested that the water molecules preferentially interact with anions.<sup>11</sup> Lendl and co-workers studied the interactions of water and methanol in ionic liquids and concluded that water and methanol molecules tended to be isolated from each other and to interact with the anion of the ionic liquids via H bonding.<sup>17</sup> Baldelli and co-workers investigate the influence of water on the surface of hydrophilic and hydrophobic ionic liquids.<sup>18,19</sup> They found that the water affects the surface of hydrophobic ionic liquids but not hydrophilic ones. Hardacre and co-workers studied the crystalline 1-alkyl-3-methylimidazolium chloride ionic liquid and characterized strong hydrogen bonding interactions between the chloride ions and water molecules forming an  $\text{O}-\text{H}\cdots\text{Cl}$  chain.<sup>20</sup> Hamaguchi and co-workers reported the effect of water on the molecular structure and arrangement of Nitrile-Functionalized ionic liquids, and the water molecule is found to change the conformation of the *n*-butyronitrile chain of the cation.<sup>21</sup> Tran et al. reported differences in the near-infrared (NIR) spectrum of water dissolved in different ionic liquids.<sup>22</sup> Ludwig and co-workers investigated the association of the water molecules in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and 1-ethyl-3-methylimidazolium ethyl sulfate ionic liquids.<sup>23</sup> In recent years, the studies focusing on liquid-state characteristics by molecular dynamics (MD) appeared in the literature.<sup>24–28</sup> For example, Chaumont et al. reported an MD investigation of the aqueous interface of two ionic liquids that form distinct phases with water at the macroscopic level.<sup>24</sup>

The first principle quantum chemistry (QM) calculation is a valuable technique for giving insight at the molecular level into the interactions between the water molecule and the ionic liquids. However, the previous studies with QM calculation focused on the structures of ion pairs and their thermodynamic properties.<sup>29–38</sup> For example, Kirchner et al. have analyzed in an excellent article the cooperative effects in ionic liquids.<sup>37</sup> Hunt and Gould reported the relative energy and halide ion position

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for isomers of 1-butyl-3-methylimidazolium chloride.<sup>38</sup> Using QM to investigate the interaction between the water–cation and water–anion is absent from the literatures. In this paper, we applied the QM calculation to study the interactions between the water molecule and the ionic liquids.

It is the objective of the present paper to carry out a systematic comparison of the various interactions in which the ionic liquid and water molecule might conceivably participate. All four sorts of anions ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ) are considered separately and compared to one another. The 1-ethyl-3-methyl imidazolium ( $\text{Emim}^+$ ) is used as a model cation. Along with the energetic aspects of the interactions, structural and spectroscopic markers are computed.

## Methods of Calculation

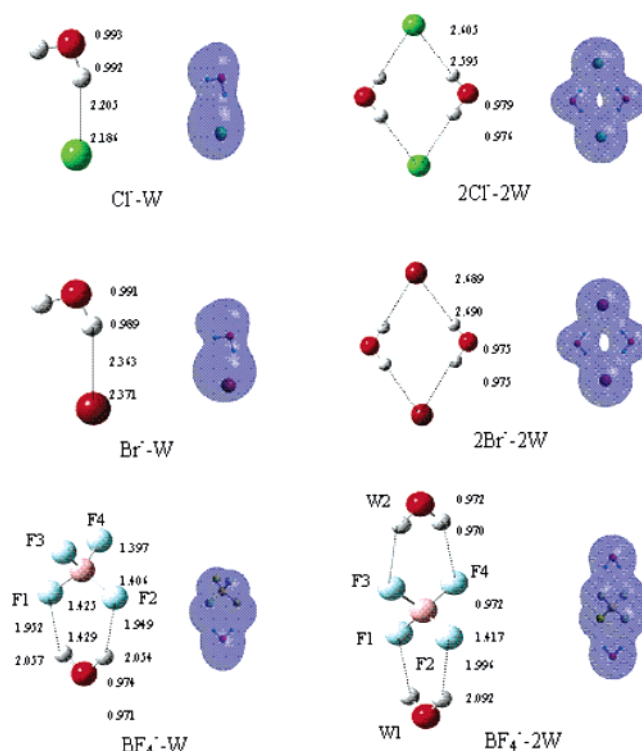
All the calculations were performed with the Gaussian 03 program.<sup>39</sup> The hybrid Becke 3-Lee–Yang–Parr (B3LYP) exchange–correlation functional and the correlated second-order Moller–Plesset (MP2) with the 6-31G\* and 6-31++G\*\* basis sets were employed.<sup>40–42</sup> No restrictions on symmetries were imposed on the initial structures, therefore the geometry optimization for the saddle points occurred with all degrees of freedom. The hydrogen-bonded complexes between the anion and the water molecule were first optimized at the B3LYP/6-31G\* level and also fully characterized as minima by frequency analysis. Subsequent geometry optimizations were performed at the B3LYP/6-31++G\*\* level starting from the B3LYP/6-31G\* geometries. The optimized structures were then subjected to further optimization at the MP2/6-31++G\*\* and B3LYP/aug-cc-pvtz levels, followed by frequency calculations to verify the reasonability of the optimized structures and to determine the thermal energy and entropies. Hydrogen-bonded complexes between the  $\text{Emim}^+$  cation, ion pairs, and the water molecules were optimized at the B3LYP/6-31G\* level and fully characterized as minima by frequency analysis at the B3LYP/6-31++G\*\* level.

## Results and Discussion

### The Interaction of the Anion with the Water Molecule.

Most of the early investigations suggested that the miscibility of an ionic liquid with water is mostly determined by the associated anion.<sup>11,18,23</sup> Anions such as halides and  $\text{BF}_4^-$  are miscible, while  $\text{PF}_6^-$  is immiscible.<sup>11</sup> The crystallographic and spectroscopic data revealed that the anion might be involved in an attractive hydrogen-bonding interaction.<sup>11,20</sup> There are a variety of ways in which the water molecules can interact with the anion species under consideration. Different hydrogen-bonded complexes of water molecules with the  $\text{BF}_4^-$ ,  $\text{Br}^-$ , and  $\text{Cl}^-$  anions were constructed and preoptimized at the B3LYP/6-31G\* level of theory. Those minima structures were fully optimized at the B3LYP/6-31++G\*\* and MP2 (FC)/6-31++G\*\* levels, giving rise to the final geometries. The optimized structures revealed from the B3LYP/6-31G\*, B3LYP/6-31++G\*\*, and MP2 (FC)/6-31++G\*\* levels are very similar to each other as depicted in Figure 1, and their corresponding charge density surfaces are shown on the right. Vibrational frequency analysis on these optimized structures gave no imaginary frequencies, suggesting that they are true minimum energy structures.

In the case of the chloride ion and water system, Bieske and co-workers investigated the solvent shell closure in salt solutions using infrared spectra.<sup>43</sup> Jungwirth and co-workers presented a novel and microscopic view of the interfacial structure of aqueous salt solutions using molecular dynamics simulations.<sup>44,45</sup>



**Figure 1.** Structure of minimum energy found for the anion with the water molecules calculated at the B3LYP/6-31G\* (top), B3LYP/6-31++G\*\* (middle), and MP2/6-31++G\*\* (bottom) levels. The distances are in angstroms. Total charge density surfaces are shown for each complex. Blue means negative. W1 and W2 indicate the water molecules.

Previous investigations about the ionic liquids–water systems had proposed two interaction models. Lynden-Bell and co-workers had demonstrated that the water molecule is strongly hydrogen bonded to two chloride ions effectively forming the negatively charged species  $[\text{O}(\text{HCl})_2]$  at the MD simulation level.<sup>26</sup> The crystalline studies revealed that  $\text{Cl}^-$  and  $\text{H}_2\text{O}$  form an  $\text{O}-\text{H}\cdots\text{Cl}^-$  chain and suggested that  $\text{Cl}^-$  and  $\text{H}_2\text{O}$  associated with the linear headgroups form a  $\{[\text{H}_2\text{O}]\text{Cl}\}_2^{2-}$  (Figure 1,  $2\text{Cl}^- - 2\text{W}$ ) square dimer.<sup>20</sup>

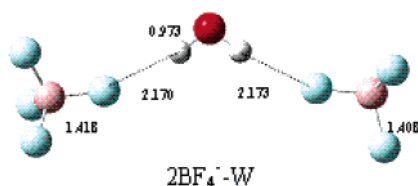
At our QM level, the optimized geometries suggested that there are two types of complexes, one is  $\text{Cl}^- - \text{W}$  and the other is  $2\text{Cl}^- - 2\text{W}$  (Figure 1). In  $\text{Cl}^- - \text{W}$ , the chloride ion interacts with one water molecule. The  $[\text{O}-\text{H}\cdots\text{Cl}^-]$  distance and angles are 2.190 Å and 164.7° at the MP2/6-31++G\*\* level. In  $2\text{Cl}^- - 2\text{W}$ , two chloride ions interact simultaneously with two water molecules. This structure is consistent with the crystalline studies (the  $\{[\text{H}_2\text{O}]\text{Cl}\}_2^{2-}$  square dimer).<sup>20</sup> The  $[\text{O}-\text{H}\cdots\text{Cl}^-]$  distance and angles for  $2\text{Cl}^- - 2\text{W}$  are 2.502 Å and 177.5° at the MP2/6-31++G\*\* level. Compared with the  $\text{Cl}^- - \text{W}$  complex, the hydrogen bond distance of  $2\text{Cl}^- - 2\text{W}$  increased significantly.

The interaction energies and interaction entropies at different levels are listed in Table 1. The MP2/6-31++G\*\* interaction energy is −58.60 kJ/mol in  $\text{Cl}^- - \text{W}$  and 75.98 kJ/mol in  $2\text{Cl}^- - 2\text{W}$ . In other words, the structure of  $\text{Cl}^- - \text{W}$  is favored and  $2\text{Cl}^- - 2\text{W}$  is prohibited in thermodynamics. In complex  $2\text{Cl}^- - 2\text{W}$ , there must be a balance between the attractive and electrostatic repulsion forces. The distance between the two chloride ions is 5.670 Å in the  $2\text{Cl}^- - 2\text{W}$  complex, and the electrostatic repulsion forces are present in the two ions. This may be what leads the interaction energies to positive values.

The optimized structures of the  $\text{Br}^-$ –water complexes are also listed in Figure 1 ( $\text{Br}^- - \text{W}$  and  $2\text{Br}^- - 2\text{W}$ ). These structures are very similar to the  $\text{Cl}^-$ –water complexes. The interaction

**TABLE 1: Thermochemical Parameters Obtained from Different Levels of Calculations for the Anion–Water Complexes (kJ/mol)**

complex	B3LYP/6-31G*		B3LYP/6-31++G**		MP2/6-31++G**		B3LYP/aug-cc-pvtz		
	$\Delta E$	$\Delta H$	$\Delta E$	$\Delta H$	$\Delta E$	$\Delta H$	$\Delta E$	$\Delta E^a$	$\Delta H$
Cl <sup>−</sup> –W	−67.38	−70.73	−57.25	−60.66	−58.60	−62.08	−55.81	−56.50	−58.29
2Cl <sup>−</sup> –2W	68.38	61.63	86.60	79.84	75.98	68.56	96.92	98.88	89.48
Br <sup>−</sup> –W	−71.20	−74.39	−56.03	−59.28	−55.96	−59.08	−47.54		−49.62
2Br <sup>−</sup> –2W	42.90	35.22	67.55	59.80	59.18	51.65			
BF <sub>4</sub> <sup>−</sup> –W	−69.71	−71.65	−46.69	−47.83	−50.17	−51.39	−39.79	−42.15	−42.27
BF <sub>4</sub> <sup>−</sup> –2W	−129.69	−133.04	−87.76	−89.91	−95.57	−97.57	−74.55	−77.45	−79.51
2BF <sub>4</sub> <sup>−</sup> –W	106.54	109.08							

<sup>a</sup> BSSE-corrected interaction energies.**Figure 2.** Structure of minimum energy found for the BF<sub>4</sub><sup>−</sup>...W...BF<sub>4</sub><sup>−</sup> complex calculated at the B3LYP/6-31G\* level. The distances are in angstroms.

energies listed in Table 1 suggest that the structure of Br<sup>−</sup>–W is favored and the structure of 2Br<sup>−</sup>–2W is prohibited.

For the interactions of water molecules with the BF<sub>4</sub><sup>−</sup> and PF<sub>6</sub><sup>−</sup> anions, Welton and co-workers had suggested an anion...W...anion model.<sup>11</sup> In their model, each water molecule interacts with two anions. Therefore, we first optimized this model structure 2BF<sub>4</sub><sup>−</sup>–W (Figure 2) at the B3LYP/6-31G\* level and found a stable structure at this level (no stationary point was found for the 2PF<sub>6</sub><sup>−</sup>–W complex). However, this structure has been proved to not be a stationary point at the B3LYP/6-31++G\*\* and MP2/6-31++G\*\* levels. The large positive interaction energy (109.08 kJ/mol, Table 1) of 2BF<sub>4</sub><sup>−</sup>–W at the B3LYP/6-31G\* level also implies that it is not a stable structure. The distances between the two B atoms and the two closed F atoms are 8.252 and 5.436 Å, respectively. Similar to the complex 2Cl<sup>−</sup>–2W, the electrostatic repulsion forces of the two anions may be responsible for the instability of the structures of 2BF<sub>4</sub><sup>−</sup>–W. This inspires us to investigate other possible interaction models. Welton and co-workers advanced that the water molecules interact via a hydrogen bond with the anions in a symmetric complex according to the ATR-IR spectra (antisymmetric ( $\nu_3$ ) and symmetric ( $\nu_1$ ) stretching modes of water) of the water–ionic liquids mixtures. They suggested that the difference in the positions of the  $\nu_3$  and  $\nu_1$  bands of water ( $\nu_3 - \nu_1$ ) remains almost constant within the range of 70–80 cm<sup>−1</sup>, indicating a similar type of bonding of water. Thus, the symmetric structures BF<sub>4</sub><sup>−</sup>–W and BF<sub>4</sub><sup>−</sup>–2W (Figure 1) were considered and optimized at different levels. Vibrational frequency analysis on the B3LYP/6-31G\*, B3LYP/6-31++G\*\*, and MP2(FC)/6-31++G\*\* levels suggested that they are true minima energy structures. However, for the structure BF<sub>4</sub><sup>−</sup>–2W, no stationary point was found at the B3LYP/aug-cc-pvtz level. In complex BF<sub>4</sub><sup>−</sup>–W, both of the protons of the water molecule interact simultaneously with one anion. The H...F distance is about 2.065 Å. In complex BF<sub>4</sub><sup>−</sup>–2W, two water molecules interact simultaneously with one anion and all of the protons of the water molecules interact simultaneously with the anion. The H...F distance in complex BF<sub>4</sub><sup>−</sup>–2W is about 2.095 Å. The large negative interaction energies of these complexes (Table 1) indicate that they are stable structures. The interaction energies of BF<sub>4</sub><sup>−</sup>–W and BF<sub>4</sub><sup>−</sup>–2W at the MP2/6-31++G\*\* level are −50.17 and −95.57 kJ/mol, respectively. The calcu-

**TABLE 2. Wavenumber (cm<sup>−1</sup>) of the Vibrational Modes of H<sub>2</sub>O in Water–Ionic Liquid Complexes<sup>a</sup>**

		$\nu_1$	$\nu_2$	$\nu_3$	$\nu_3 - \nu_1$
W	DFT	3638	1528	3756	118
	MP2	3618	1516	3756	138
Cl <sup>−</sup> –W	DFT	3219	1589	3696	477
	MP2	3284	1576	3692	408
2Cl <sup>−</sup> –2W	DFT	3458	1565	3558	100
	MP2	3450	1559	3575	125
Br <sup>−</sup> –W	DFT	3284	1584	3692	408
	MP2	3362	1568	3689	327
2Br <sup>−</sup> –2W	DFT	3469	1573	3567	98
	MP2	3472	1560	3596	124
BF <sub>4</sub> <sup>−</sup> –W	DFT	3592	1620	3635	43
	MP2	3577	1596	3646	69
BF <sub>4</sub> <sup>−</sup> –2W	DFT	3602	1613	3652	50
	MP2	3585	1589	3661	76

<sup>a</sup> Symmetric ( $\nu_1$ ) and antisymmetric ( $\nu_3$ ) stretching modes of water.

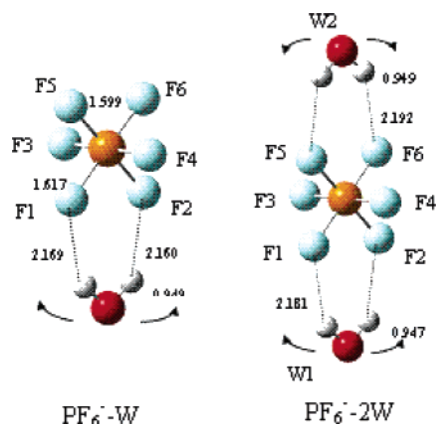
lated wavenumbers (cm<sup>−1</sup>) of the vibrational modes of the water molecule in the BF<sub>4</sub><sup>−</sup>–W and BF<sub>4</sub><sup>−</sup>–2W complexes at the B3LYP/6-31++G\*\* (DFT) and MP2/6-31++G\*\* (MP2) levels are listed in Table 2. From Table 2 we can see that the vibrational modes of the water molecule in the BF<sub>4</sub><sup>−</sup>–W and BF<sub>4</sub><sup>−</sup>–2W complexes are very similar. The values of  $\nu_3 - \nu_1$  of complexes BF<sub>4</sub><sup>−</sup>–W and BF<sub>4</sub><sup>−</sup>–2W at the MP2/6-31++G\*\* level are 69 and 76 cm<sup>−1</sup>, respectively. The experimental difference in the positions of the  $\nu_3$  and  $\nu_1$  bands of water ( $\nu_3 - \nu_1$ ) is 80 cm<sup>−1</sup>, and the calculated frequency for the structure BF<sub>4</sub><sup>−</sup>–2W is consistent with the experimental result.

For the PF<sub>6</sub><sup>−</sup> water system, to our surprise, no stationary point was found at the B3LYP/6-31G\* level. Therefore, we optimized the complexes at the HF/6-31G\* level and found two stationary points PF<sub>6</sub><sup>−</sup>–W and PF<sub>6</sub><sup>−</sup>–2W (Figure 3). However, these structures were proved to be unstable at the B3LYP/6-31G\* and MP2/6-31G\* levels.

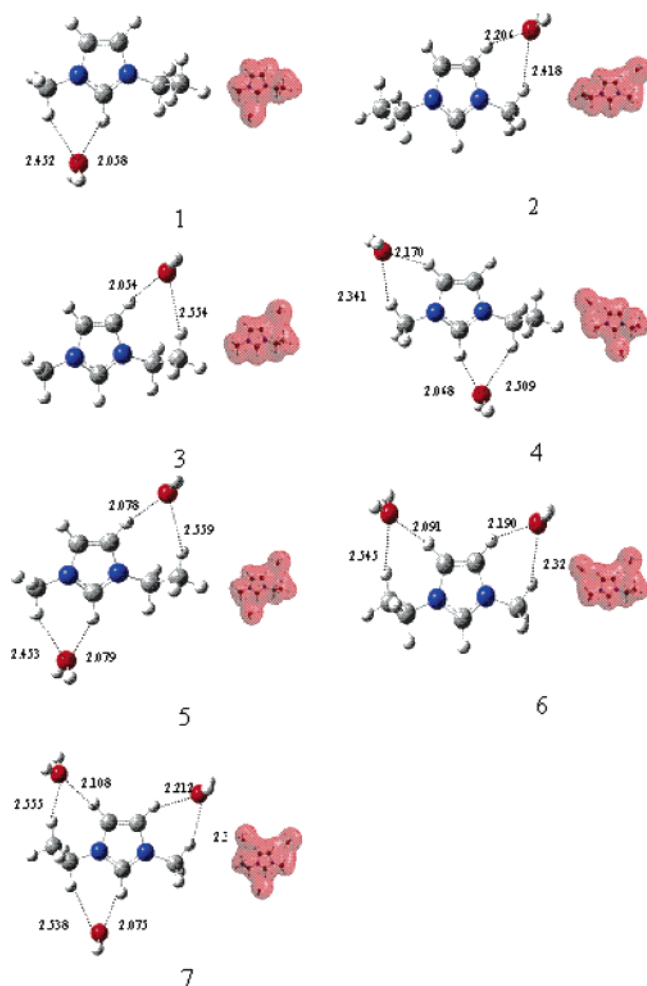
**The Interaction of the Emim<sup>+</sup> Cation with the Water Molecule.** Although previous investigations had suggested that the interaction between the water molecules and the cation is secondary, the experimental result shows that the hydrophobic PF<sub>6</sub><sup>−</sup> based ionic liquids (such as [Bmim][PF<sub>6</sub>]) can also absorb some water from the air.<sup>11</sup> This should be caused by the cations. This inspired us to investigate the interaction between the cation and the water. The Emim<sup>+</sup> cation had been used as a model cation to investigate the contribution of this interaction. The optimized structures are listed in Figure 4. As indicated in Figure 4, there are different interaction patterns between the imidazolium cation and the water molecule.

The NMR spectroscopy indicates that the water molecule could form hydrogen bonds with the cation involving imidazolium ring protons H2, H4, and H5.<sup>46</sup> Therefore, we first investigated the interaction between water oxygen and the C2–H, C4–H, and C5–H of the imidazolium ring. All three C–H





**Figure 3.** Structure of minimum energy found for the PF<sub>6</sub><sup>-</sup> anion with the water molecules calculated at the HF/6-31G\* level. The distances are in angstroms.



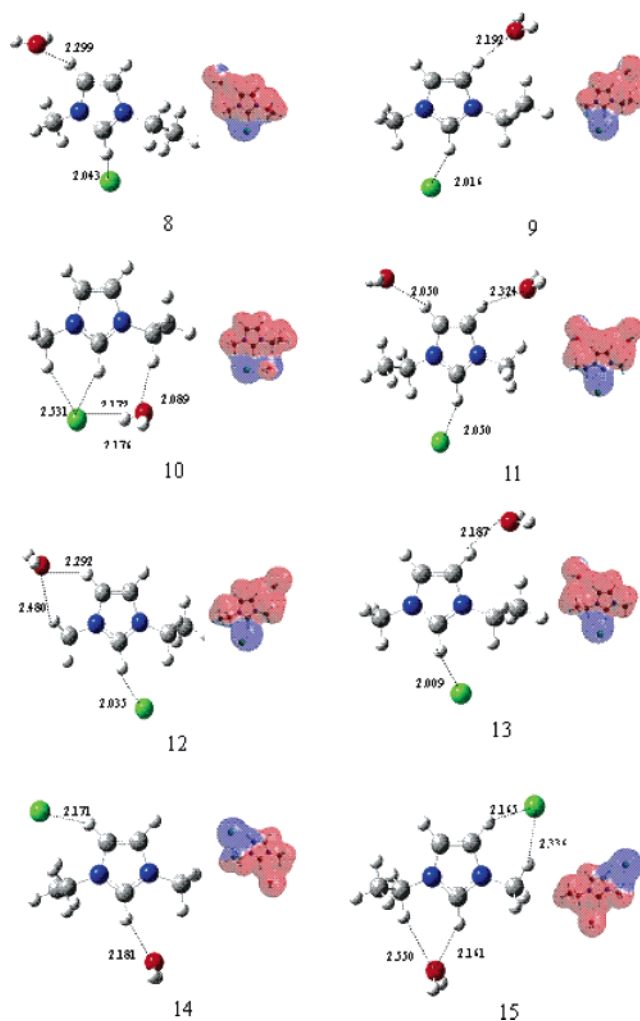
**Figure 4.** Structure of minimum energy found for the Emim<sup>+</sup> cation with the water molecules calculated at the B3LYP/6-31G\* level. Total charge density surfaces are shown for each complex. Red means positive. The distances are in angstroms.

can form stable complexes with the water molecules. The interaction energies at the B3LYP/6-31++G\*\*//B3LYP/6-31G\* level for [C2-H...O] (Figure 4, 1), [C4-H...O] (Figure 4, 2), and [C5-H...O] (Figure 4, 3) are -38.03, -30.72, and -34.09 kJ/mol (Table 3), respectively. These interaction energies are in the energy range of the traditional strong hydrogen bond. The presence of the two N atoms and the positive charge in the imidazolium ring makes an acidic C2-H bond between them;

**TABLE 3: Thermochemical Parameters Obtained from Different Levels of Calculations for the Cation-Water Complexes (kJ/mol)**

complex	B3LYP/6-31G*		B3LYP/6-31++G**//B3LYP/6-31G*		
	$\Delta E$	$\Delta H$	$\Delta E$	$\Delta E^a$	$\Delta H$
1	-49.28	-50.11	-38.03	-38.04	-39.46
2	-41.36	-41.51	-30.72	-30.02	-31.64
3	-43.06	-43.44	-34.09	-34.34	-34.06
4	-88.22	-88.63	-67.11	-68.92	-69.09
5	-87.52	-88.23	-66.36	-66.66	-68.54
6	-80.84	-80.94	-60.24	-62.12	-62.00
7	-123.08	-122.81	-92.92	-94.80	-95.28

<sup>a</sup> BSSE-corrected interaction energies.



**Figure 5.** Structure of minimum energy found for the ionic liquid pairs with the water molecules calculated at the B3LYP/6-31G\* level. Total charge density surfaces are shown for each complex. Red means positive and blue means negative. The distances are in angstroms.

therefore, the [C2-H...O] interaction possesses a more negative interaction energy.

The second sort of interaction involves the approach of the two water oxygen atoms toward the protons in the imidazolium ring. Three minimum structures were found as listed in Figure 4 (4, 5, 6). The interaction energies of the three complexes at the B3LYP/6-31++G\*\*//B3LYP/6-31G\* level are -69.09, -68.54, and -62.00 kJ/mol (Table 3), respectively, suggesting these complexes are stable. The third sort of interaction involves three water molecules interacting with one imidazolium simultaneously (Figure 4, 7). The interaction energy of the three

**TABLE 4: Thermochemical Parameters Obtained from Different Levels of Calculations for the Ion Pair–Water Complexes (kJ/mol)**

complex	B3LYP/6-31G*			B3LYP/6-31++G**//B3LYP/6-31G*			
	$\Delta E$	$\Delta E_{\text{Cl}}^a$	$\Delta E_{\text{W}}^b$	$\Delta E$	$\Delta E^a$	$\Delta E_{\text{Cl}}^b$	$\Delta E_{\text{W}}^c$
<b>8</b>	−429.78	−416.90	−12.88	−391.00	−402.03	−379.83	−11.17
<b>9</b>	−429.34	−416.90	−12.44	−392.52	−398.49	−379.83	−5.31
<b>10</b>	−469.78	−416.90	−12.88	−426.88	−429.80	−379.83	−47.05
<b>11</b>	−447.80	−416.88	−30.92	−401.62	−407.30	−379.09	−22.53
<b>12</b>	−429.33	−416.88	−12.45	−392.78	−399.67	−379.09	−13.69
<b>13</b>	−428.62	−416.88	−11.74	−390.47	−396.30	−379.09	−11.38
<b>14</b>	−405.38	−384.56	−20.82	−367.75	−372.73	−346.54	−21.21
<b>15</b>	−402.16	−382.22	−19.94	−366.00	−371.30	−345.58	−20.42

<sup>a</sup> BSSE-corrected interaction energies. <sup>b</sup> The interaction energies of the ion pairs from ref 28. <sup>c</sup>  $\Delta E_{\text{W}} = \Delta E - \Delta E_{\text{Cl}}$ .

complexes at the B3LYP/6-31++G\*\*//B3LYP/6-31G\* level is −95.28 kJ/mol.

#### The Interaction of the Ion Pairs with the Water Molecule.

In our previous studies, we had found that the imidazolium cation could interact with the chloride ion using C2–H, C4–H, and C5–H<sup>31,34</sup> and a series of stable ion pairs had been optimized. These ion pairs are used to detect the interaction between the ion pairs and the water molecule. Figure 5 reveals the optimized structures of (Emim•Cl) (water) with the participation of the C–H•••O interactions. Using complexes **10** and **11** as references, in complex **10**, the water molecule interacts with both the chloride ion and the side chain. The distance of (C2–H)•••Cl, (O–H)•••Cl, and O•••(H–C) are 2.172, 2.176, and 2.089 Å, respectively. In complex **11**, the ion pair interacts with two water molecules. Table 4 lists the interaction energies of these complexes. Compared with the interaction energies of the anion–water and cation–water complexes, the interaction energies of these ion pair–water complexes are smaller. The interaction energies of the complexes **8**, **9**, **13**, **14**, and **15** are 12.88, 12.44, 11.74, 20.82, and 19.94 kJ/mol (Table 4), respectively.

#### Conclusion

In summary, the interactions between the water and several anions, imidazolium cation, and the ion pairs are investigated in detail. The water molecules can form strong interactions with the Cl<sup>−</sup>, Br<sup>−</sup>, and BF<sub>4</sub><sup>−</sup> anions. The halide ions and the water molecules form X<sup>−</sup>•••W or 2X<sup>−</sup>•••W dimmer and the BF<sub>4</sub><sup>−</sup> anion could interact with the water molecules via BF<sub>4</sub><sup>−</sup>•••W and W•••BF<sub>4</sub><sup>−</sup>•••W models. At the B3LYP and MP2 level, the hydrophobic PF<sub>6</sub><sup>−</sup> anion could not form a stable complex with the water molecule (no stationary points have been found). The energies of hydrogen bonds between water and these anions were estimated at the MP2/6-31++G\*\* level, with enthalpies in the range 50–100 kJ mol<sup>−1</sup>. In the case of the cation–water complex, the calculated results indicate that the cation could also form a stable complex with the water molecules. The interaction energies of these complexes are in the range of 35–100 kJ mol<sup>−1</sup> at the B3LYP/6-31++G\*\*//B3LYP/6-31G\* level, which indicates these interactions are as strong as the traditional strong hydrogen bond. In addition, the ion pairs can also form complexes with the water molecules, although the interaction energies indicate these interactions are very weak.

Although the gas-phase calculation may be different from the liquid and solid states, the results obtained here show us some new insights on the interaction details of the ionic liquids and water systems. These calculations may be valuable to develop force field parameters to study liquid properties of the ionic liquids and water systems.

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**Supporting Information Available:** List of Cartesian coordinates. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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