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# Structural Organization in Aqueous Solutions of 1-Butyl-3-methylimidazolium Halides: A High-Pressure Infrared Spectroscopic Study on Ionic Liquids

Hai-Chou Chang<sup>\*,†</sup>, Jyh-Chiang Jiang<sup>‡</sup>, Chao-Yen Chang<sup>‡</sup>, Jong-Chang Su<sup>‡</sup>, Chao-Hsin Hung<sup>‡</sup>, You-Chang Liou<sup>‡</sup>, and Sheng Hsien Lin<sup>§,⊥</sup>

Department of Chemistry, National Dong Hwa University, Shoufeng, Hualien 974, Taiwan, Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan, Institute of Atomic and Molecular Sciences, Academia Sinica, P.O. Box 23-166, Taipei 106, Taiwan, and Department of Chemistry, National Taiwan University, Taipei 106, Taiwan

Received: September 12, 2007; In Final Form: January 25, 2008

High-pressure infrared spectroscopy was applied to study the hydrogen-bonding structures of 1-butyl-3-methylimidazolium halides/D<sub>2</sub>O mixtures. No drastic changes were observed in the concentration dependence of the alkyl C–H band frequency at high concentration of 1-butyl-3-methylimidazolium chloride. Nevertheless, the alkyl C–H exhibits an increase in frequency upon dilution at low concentration. These observations may indicate a clustering of the alkyl groups at high concentration and the formation of a certain water structure around alkyl C–H groups in the water-rich region. The imidazolium C–H band at ca. 3051 cm<sup>−1</sup> displays a monotonic blue-shift in frequency as the sample was diluted at high concentration of 1-butyl-3-methylimidazolium chloride. That is, water can be added to change the structural organization of 1-butyl-3-methylimidazolium chloride in the ionic liquid-rich composition region by introducing water–imidazolium C–H interactions. Analyzing the pressure dependence of the imidazolium C–H stretches yielded anomalous nonmonotonic pressure-induced frequency shifts. This result may reflect the strengthening of C–H–O interactions between imidazolium C–H groups and the water clusters. Density functional theory calculations also revealed that the characteristic bonded C<sup>2</sup>–H vibration may be shifted via the modification of C<sup>2</sup>–H–Cl<sup>−</sup> associations.

## Introduction

Recently, there has been an increased interest in the determination and understanding of the physical properties of room-temperature ionic liquids due in part to their potential for greener solvents in chemical industries.<sup>1–4</sup> The key property is that the vapor pressure of ionic liquids is negligibly small. By selecting a different combination of ions, a tunable range of physical properties is obtained, which, combined with their low vapor pressure, provide a good substitute for volatile organic compounds. Ionic liquids have a melting temperature around room temperature and are built up by a bulky, asymmetric organic cation, such as 1-alkyl-3-methylimidazolium, to prevent ions from packing easily.<sup>1–8</sup> The liquid structure of ionic liquids results from a competition between screening and packing. This means a balance between long-range electrostatic forces and geometric factors. Ionic liquids are generally miscible with water, being ionic compounds. However, they could be designed to be made hydrophobic by choice of anion species. The water miscibility of ionic liquids is also affected by the hydrophobicity of the alkyl substituents of the imidazolium cation. The presence of water changes the physical and chemical properties of ionic liquid materials considerably.<sup>9–14</sup> However, the majority of these studies have paid attention to the water-poor or the ionic liquid-

rich composition region. The role of water in ionic liquids is complex and depends on the supramolecular structures of ionic liquids. It seems to be safe to state that water modifies the self-organization patterns of ionic liquids. Although ionic liquids have been attracting much attention of scientists owing to their useful characteristics, there still remain some fundamental questions to be answered regarding the nature of the liquid state. Previous studies to the structure of ionic liquids have included the use of X-ray crystallography and vibrational spectroscopy under the condition of ambient pressure.<sup>15–18</sup> Nevertheless, interest in pressure as an experimental variable has been growing in physicochemical studies recently. In this study, we use variable pressure as a window into the structural organization of the hydrogen-bonding network in aqueous ionic liquids.

Theoretical studies found that ionic liquids containing dissolved water may not be regarded as homogeneous solvents but have to be considered as nanostructured with polar and nonpolar regions.<sup>3,19</sup> At high ionic liquid concentrations ionic liquids seem to form clusters, as in the pure state, and water molecules interact with the clusters without interacting among themselves. Nevertheless, direct experimental evidence at the molecular level was not easy to obtain to corroborate these simulation results. Both experiments and simulations have found that the alkyl side-chain length has an influence on the physical properties of ionic liquids.<sup>19–21</sup> Previous investigations have also studied the structure of alkyl side chains under ambient pressure. 1-Butyl-3-methylimidazolium chloride forms two different crystal polymorphs at room temperature, monoclinic and orthorhombic.<sup>15,16,22</sup> In the monoclinic form, the butyl side chain is all anti, and in the orthorhombic form the chain is gauche around

\* To whom correspondence should be addressed. E-mail: hcchang@mail.ndhu.edu.tw. Fax: +886-3-8633570. Phone: +886-3-8633585.

<sup>†</sup> National Dong Hwa University.

<sup>‡</sup> Department of Chemical Engineering, National Taiwan University of Science and Technology.

<sup>§</sup> Academia Sinica.

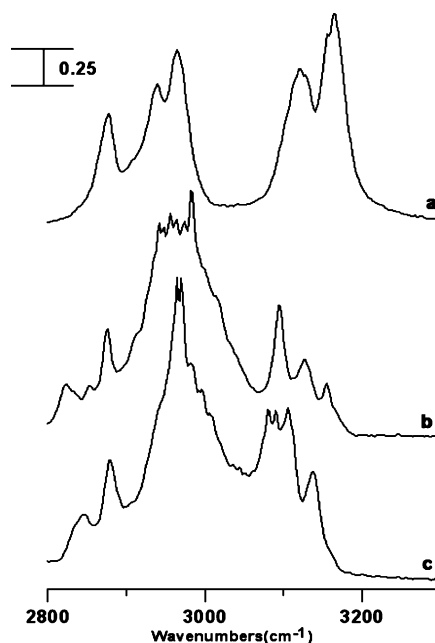
<sup>⊥</sup> Department of Chemistry, National Taiwan University.

C<sup>7</sup>–C<sup>8</sup>. In a convenient notation, these conformers are referred to here as the AA and the GA forms. There is a significant change in conformational preference as the counteranion Cl<sup>–</sup> is replaced by Br<sup>–</sup>. The only stable alkyl structure of 1-butyl-3-methylimidazolium bromide observed under ambient pressure is the GA form.<sup>15,16,22</sup> The Raman spectra of AA and GA conformers differ considerably, when recorded at room temperature and ambient pressure. The presence of two crystalline polymorphs suggests that the potential energy surface for 1-butyl-3-methylimidazolium chloride contains two, or more, local conformational energy minima. Inhibition of crystallization through provision of a large number of similarly stabilized solid-state structures may lead to plasticity and low melting points.

Various studies have been made to elucidate the role of C–H–O and C–H–X in the structure of ionic liquids.<sup>5,6,22–24</sup> Nevertheless, experimental evidence of C–H–O and C–H–X hydrogen bonds are notoriously difficult to obtain, mainly because C–H–O and C–H–X usually coexist with other strong interactions making the contribution from C–H–O and C–H–X hydrogen bonding difficult to be distinguished. One of the intriguing aspects of C–H–O and C–H–X is that the C–H covalent bond tends to shorten as a result of formation of blue-shifting hydrogen bonds.<sup>25–27</sup> Associated with this contraction is a shift of the C–H stretching frequency to the blue. This behavior is opposite to that of the classical hydrogen bond, and its underlying mechanism is not well understood. Two schools of thought have emerged in trying to explain the physical basis for blue-shifted C–H frequencies.<sup>25–27</sup> Hobza and Havlas suggested the strengthened C–H bond originates from a new mechanism called anti-hydrogen-bonding in which a secondary effect or structural reorganization of the proton donor framework occurs upon contraction of the C–H bond directly involved in weak hydrogen bonding.<sup>25</sup> However, Gu et al.<sup>26</sup> and Masunov et al.<sup>27</sup> concluded that there are no fundamental differences between red-shifting and blue-shifting hydrogen bonding and explain the differences solely on the basis of a combination of electrostatic, polarization, charge transfer, dispersion, and steric repulsion forces between the proton donor and acceptor. One of the underlying reasons for this controversy is the weakness of C–H–O and C–H–X interactions. Therefore, the methods that enhance weak hydrogen bonding are crucial if we are to obtain a clear and unified view of this important phenomenon. Several studies have shown the potential significant effect that pressure has on controlling the strength of C–H–O and C–H–X interactions.<sup>22–24,28–30</sup> Strengths of weak hydrogen bonding (typically less than 4 kJ/mol) can also be enhanced in molecular aggregates containing charges.<sup>30</sup> In this study, we present a novel means of looking at this controversy, by using variable pressure as a window into the nature of charge enhanced C–H–O and C–H–X interactions.

## Experimental Section

Samples were prepared using 1-butyl-3-methylimidazolium chloride (>90%, Fluka), 1-butyl-3-methylimidazolium bromide (>97%, Fluka), and D<sub>2</sub>O (99.97%, Merck). A diamond anvil cell (DAC) of Merrill–Bassett design, having a diamond culet size of 0.6 mm, was used for generating pressures up to ca. 2 GPa. Two type-IIa diamonds were used for mid-infrared measurements. The sample was contained in a 0.3 mm diameter hole in a 0.25 mm thick inconel gasket mounted on the DAC. To reduce the absorbance of the samples, CaF<sub>2</sub> crystals (prepared from a CaF<sub>2</sub> optical window) were placed into the holes and compressed firmly prior to inserting the samples. A droplet of a sample filled the empty space of the entire hole of the gasket



**Figure 1.** IR spectra of 1-butyl-3-methylimidazolium tetrafluoroborate (curve a), 1-butyl-3-methylimidazolium chloride (curve b), and 1-butyl-3-methylimidazolium bromide (curve c).

in the DAC, which was subsequently sealed when the opposed anvils were pushed toward one another. Infrared spectra of the samples were measured on a Perkin-Elmer Fourier transform spectrophotometer (model Spectrum RXI) equipped with a LITA (lithium tantalite) mid-infrared detector. The infrared beam was condensed through a 5× beam condenser onto the sample in the DAC. Typically, we chose a resolution of 4 cm<sup>–1</sup> (data point resolution of 2 cm<sup>–1</sup>). For each spectrum, typically 1000 scans were compiled. To remove the absorption of the diamond anvils, the absorption spectra of DAC were measured first and subtracted from those of the samples. Pressure calibration follows Wong’s method.<sup>31,32</sup> The pressure dependence of screw-moving distances was measured.

## Results and Discussion

Figure 1 displays infrared spectra of 1-butyl-3-methylimidazolium tetrafluoroborate (curve a), 1-butyl-3-methylimidazolium chloride (curve b), and 1-butyl-3-methylimidazolium bromide (curve c) obtained under ambient pressure in the region of C–H stretching vibrations. As indicated in Figure 1a, the infrared spectrum of pure 1-butyl-3-methylimidazolium tetrafluoroborate exhibits three discernible peaks, i.e., 2876, 2940, 2964 cm<sup>–1</sup>, respectively, in the 2800–3000 cm<sup>–1</sup> region. On the basis of our DFT calculations (B3LYP/6-31+G\*) performed on the C–H stretching vibration of 1-butyl-3-methylimidazolium cation, these peaks can be assigned to C–H stretching modes of the methyl and butyl groups, cf., Table 1.<sup>33</sup> We also found that the 3122 and 3163 cm<sup>–1</sup> bands in Figure 1a can be attributed to coupled imidazolium C–H stretching vibrations. Significant changes in infrared absorption spectra occur upon switching the counteranion from BF<sub>4</sub><sup>–</sup> (Figure 1a) to Cl<sup>–</sup> (Figure 1b) and Br<sup>–</sup> (Figure 1c). This observation indicates that C–H–Cl<sup>–</sup> and C–H–Br<sup>–</sup> interactions seem to play a non-negligible role in Figure 1, parts b and c. Recently, attention has been paid to the effect of C–H–Cl<sup>–</sup> interactions in dimethylimidazolium chloride with increasing cluster size.<sup>34</sup> The cooperative effect seems to be more important than expected for larger clusters of the dimethylimidazolium cation paired with a chloride anion.<sup>34</sup>

**TABLE 1: DFT-Calculated C–H Stretching Frequencies ( $\text{cm}^{-1}$ ) and Infrared Intensities ( $\text{km/mol}$ ) of 1-Butyl-3-methylimidazolium Cation (AA Conformer)**

calcd frequencies <sup>a</sup>	intensities	assignment <sup>b</sup>
3168	8	sym C <sup>4,5</sup> –H
3157	27	C <sup>2</sup> –H
3152	14	asym C <sup>4,5</sup> –H
3047	0.5	asym C <sup>6</sup> –H (methyl)
3032	0.3	asym C <sup>6</sup> –H (methyl)
3002	9	butyl C–H
2987	21	butyl C–H
2974	41	butyl C–H
2953	12	butyl C–H
2953	6	sym C <sup>6</sup> –H (methyl)
2944	18	butyl C–H
2920	2	butyl C–H
2913	30	butyl C–H
2904	25	butyl C–H
2895	9	butyl C–H

<sup>a</sup> Frequencies scaled by 0.955. <sup>b</sup> Numbering of the skeleton atoms for the 1-butyl-3-methylimidazolium cation.

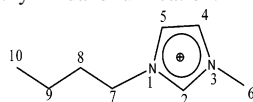
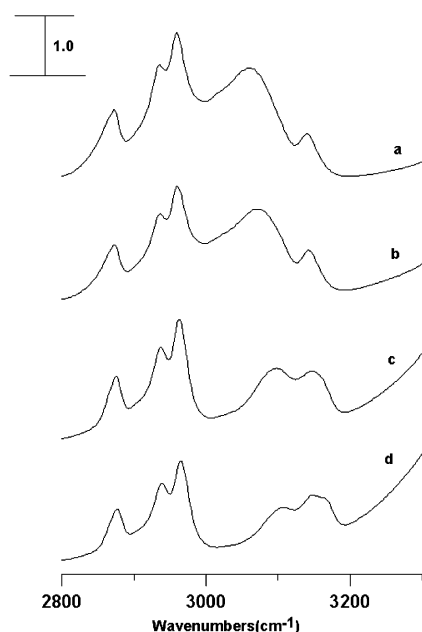
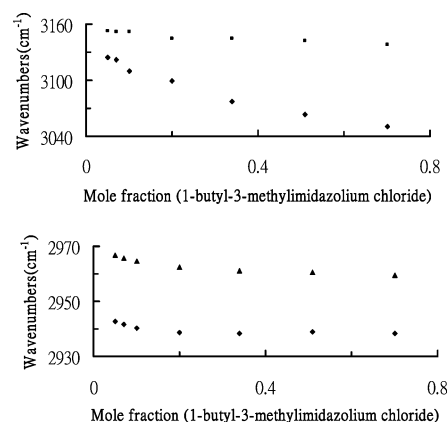


Figure 2 presents IR spectra of 1-butyl-3-methylimidazolium chloride/ $\text{D}_2\text{O}$  mixtures having mole fractions of 1-butyl-3-methylimidazolium chloride equal to (a) 0.7, (b) 0.5, (c) 0.2, and (d) 0.1 within the frequency range of  $2800\text{--}3300\text{ cm}^{-1}$ . The C–H stretching of 1-butyl-3-methylimidazolium chloride overlaps with the O–H stretching bands of  $\text{H}_2\text{O}$ , so we studied C–H stretching vibrations at ambient pressure for 1-butyl-3-methylimidazolium chloride in a solution of  $\text{D}_2\text{O}$ , rather than  $\text{H}_2\text{O}$ , by varying its concentration. As revealed in Figure 2a, the alkyl C–H stretching modes underwent changes as  $\text{D}_2\text{O}$  was added. The spectrum in Figure 2a shows the alkyl C–H stretching modes locating at 2864, 2939, and 2959  $\text{cm}^{-1}$ , respectively. This behavior may be due to a perturbation of solid structures by the presence of  $\text{D}_2\text{O}$ , because the network



**Figure 2.** IR spectra of mixtures of 1-butyl-3-methylimidazolium chloride/ $\text{D}_2\text{O}$  with the mole fraction of 1-butyl-3-methylimidazolium chloride equal to 0.7 (curve a), 0.5 (curve b), 0.2 (curve c), and 0.1 (curve d).

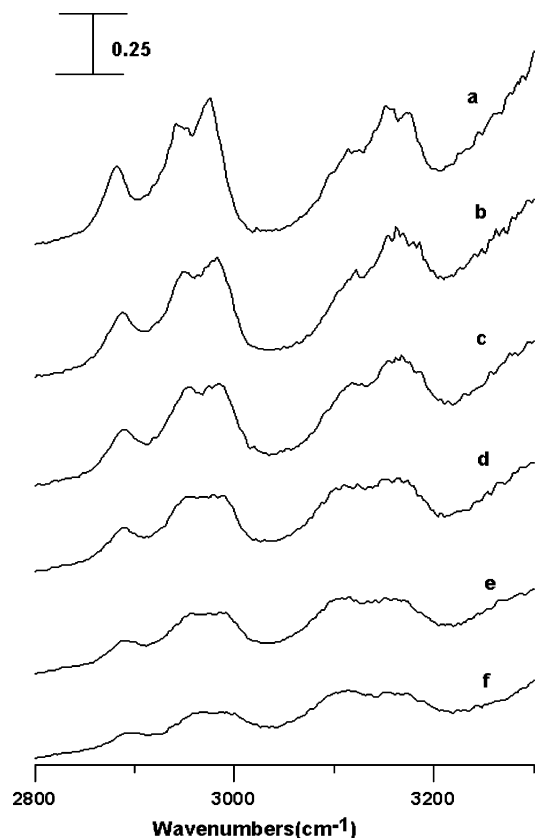


**Figure 3.** Concentration dependence of the C–H stretching frequency of 1-butyl-3-methylimidazolium chloride/ $\text{D}_2\text{O}$  vs the mole fraction of 1-butyl-3-methylimidazolium chloride.

structures are directly related to the stretching vibrations.<sup>23,28,29</sup> We see that further dilution of 1-butyl-3-methylimidazolium chloride leads to a slight shift of the alkyl C–H signal to higher frequency, and the alkyl C–H stretches were blue-shifted to 2877, 2940, and 2965  $\text{cm}^{-1}$  in Figure 2d. Significant spectral changes in the  $3000\text{--}3200\text{ cm}^{-1}$  region were also observed in the presence of  $\text{D}_2\text{O}$ , as the imidazolium C–H stretching bands became separated into two bands at 3051 and 3139  $\text{cm}^{-1}$  in Figure 2a. The spectral features of the imidazolium C–H stretching modes showed further evolution upon dilution through the observation of blue-shifts in frequency and decreases in intensity for the peak at ca. 3051  $\text{cm}^{-1}$ . We note that the 3051  $\text{cm}^{-1}$  band is more concentration-sensitive than the band at ca. 3139  $\text{cm}^{-1}$ . Inspection of the concentration dependence shows that the 3139  $\text{cm}^{-1}$  band broadened in bandwidth (Figure 2c) and became separated into two bands in Figure 2d.

To illustrate the frequency shift, the concentration dependence of the maximum positions of the characteristic C–H bands is plotted in Figure 3. Looking into more detail in Figure 3, we observe no drastic change in the concentration dependence of the alkyl C–H band frequency at high concentration of 1-butyl-3-methylimidazolium chloride, that is  $0.2 < \text{mole fraction} < 0.7$ . This observation may indicate a clustering of the alkyl groups at high concentration. Nevertheless, the alkyl C–H stretching absorption exhibits an increase in frequency upon dilution at low concentration of 1-butyl-3-methylimidazolium chloride (mole fraction  $< 0.2$ ). This discontinuity in frequency shift should be related to the mechanism of C–H hydration. The investigations so far have suggested the formation of a certain water structure around alkyl C–H groups in the water-rich region, but the details remain controversial. It is interesting to note that the imidazolium C–H band at ca. 3051  $\text{cm}^{-1}$  displays a monotonic blue-shift in frequency as the sample was diluted at high concentration of 1-butyl-3-methylimidazolium chloride, that is  $0.2 < \text{mole fraction} < 0.7$ , in Figure 3. This result is remarkably different from that revealed for the alkyl groups in Figure 3. A possible explanation for this effect is the hydrophobic hydration, i.e., C–H–O interactions, between imidazolium C–H groups and  $\text{D}_2\text{O}$ . The imidazolium C–H groups seem to be more favorable sites for hydrogen-bond-like C–H–O than the alkyl C–H groups. In other words, water can be added to change the structural organization of 1-butyl-3-methylimidazolium chloride in the ionic liquid-rich composition region by introducing water–imidazolium C–H interactions. Recent theoretical investigations have suggested that the structure of ionic liquids exhibits spatial heterogeneity that results from their polar/nonpolar phase separation.<sup>3,19</sup> Ionic

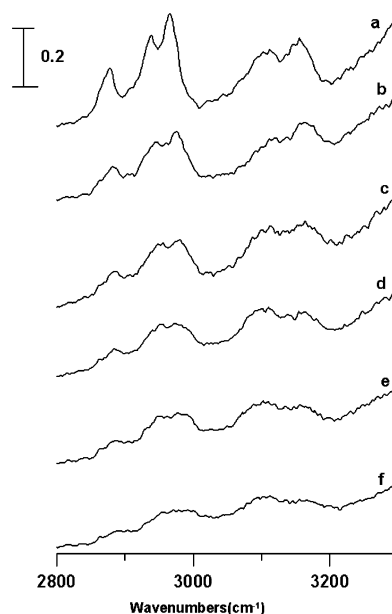




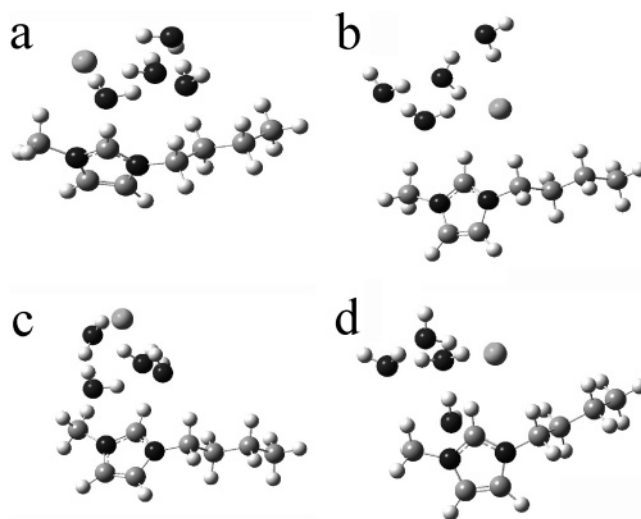
**Figure 4.** Pressure dependence of the C–H modes in a 1-butyl-3-methylimidazolium chloride/D<sub>2</sub>O mixture with a 1-butyl-3-methylimidazolium chloride mole fraction of 0.09 under the following pressures: (a) ambient and (b) 0.3, (c) 0.9, (d) 1.5, (e) 1.9, and (f) 2.3 GPa.

liquids tend to segregate into stable nonpolar regions by aggregation of the alkyl groups for C<sub>4</sub> and longer and polar regions by charge-ordering of the anions and the imidazolium rings.<sup>3,10–12</sup> Our results in Figures 2 and 3 indicate that the presence of water significantly perturbs the ionic liquid–ionic liquid associations in the polar region.

Figure 4 displays IR spectra of a 1-butyl-3-methylimidazolium chloride/D<sub>2</sub>O mixture having its mole fraction of 1-butyl-3-methylimidazolium chloride equal to 0.09 obtained under ambient pressure (curve a) and at 0.3 (curve b), 0.9 (curve c), 1.5 (curve d), 1.9 (curve e), and 2.3 GPa (curve f). Analyzing the pressure dependence of the alkyl C–H stretches yielded bandwidth broadening and slightly blue frequency shifts, which correspond to contraction of C–H bonds. The blue-shifts may originate from the overlap repulsion effect enhanced by hydrostatic pressure. Pressure might also change the anharmonic nature of the potential well for C–H stretching in such a way as to increase the observed frequency. Nevertheless, the imidazolium C–H bands in Figure 4 display anomalous nonmonotonic pressure-induced frequency shifts. As the mixture was compressed to 1.5 GPa (Figure 4d), we observed a red-shift in frequency for the imidazolium band. Appreciable changes in the relative band intensities of the imidazolium bands also occurred upon compression (cf., Figure 4, parts c and d). This discontinuity in frequency shift should be related to the mechanism of C–H–O hydrogen bonding.<sup>25–30</sup> From the point of view of fundamental studies, the nature of C–H–O interactions continues to be an important and controversial subject.<sup>25–27</sup> Masunov et al. have illustrated that electric fields can affect the strength of C–H–O interactions.<sup>27</sup> For example, when a molecule that is capable of forming blue-shifting hydrogen



**Figure 5.** Pressure dependence of a 1-butyl-3-methylimidazolium bromide/D<sub>2</sub>O mixture having its mole fraction of 1-butyl-3-methylimidazolium bromide equal to 0.08 under the following pressures: (a) ambient and (b) 0.3, (c) 0.9, (d) 1.5, (e) 1.9, and (f) 2.3 GPa.



**Figure 6.** Optimized structures of 1-butyl-3-methylimidazolium chloride–(D<sub>2</sub>O)<sub>4</sub> complexes.

bonds binds to a site with a sufficiently strong electrostatic field to dominate over the overlap effect, that molecule is predicted to display a red-shifting hydrogen bond;<sup>27</sup> experimental evidence is still lacking, however. In this article, we present a means of looking at this issue by employing the high-pressure method. The spectral features in Figure 4, that is, their sensitivity to changes in pressure, may also arise from changes in geometrical properties of the hydrogen-bond network. In the case of 1,3-dimethylimidazolium methyl sulfate, the enhancement of C–H–O interactions is attributed to both the cooperative effect and geometric reorganization of hydrogen bonds as the high pressures were applied.

Figure 5 displays IR spectra of a 1-butyl-3-methylimidazolium bromide/D<sub>2</sub>O mixture having its mole fraction of 1-butyl-3-methylimidazolium bromide equal to 0.08 obtained under ambient pressure (curve a) and at 0.3 (curve b), 0.9 (curve c), 1.5 (curve d), 1.9 (curve e), and 2.3 GPa (curve f). The prominent absorption at ca. 3100 cm<sup>−1</sup> also appears in Figure 5d–f, and this result may reflect the strengthening of C–H–O

**TABLE 2: DFT-Calculated Imidazolium C–H Stretching Frequencies (cm<sup>-1</sup>) and Intensity (km/mol) of (a) 1-Butyl-3-methylimidazolium Chloride–(D<sub>2</sub>O)<sub>4</sub> Complexes and (b) 1-Butyl-3-methylimidazolium Chloride–(H<sub>2</sub>O)<sub>4</sub> Complexes<sup>a,b</sup>**

(a) 1-Butyl-3-methylimidazolium Chloride–(D <sub>2</sub> O) <sub>4</sub> Complexes		
species <sup>a</sup>	calcd frequencies (intensities) <sup>b</sup>	assignment
A	2929(438), 3153(4), 3172(2)	C <sup>2</sup> –H, asym C <sup>4,5</sup> –H, sym C <sup>4,5</sup> –H
B	3065(356), 3149(4), 3166(2)	C <sup>2</sup> –H, asym C <sup>4,5</sup> –H, sym C <sup>4,5</sup> –H
C	3082(213), 3153(6), 3170(2)	C <sup>2</sup> –H, asym C <sup>4,5</sup> –H, sym C <sup>4,5</sup> –H
D	3011(363), 3151(4), 3168(1)	C <sup>2</sup> –H, asym C <sup>4,5</sup> –H, sym C <sup>4,5</sup> –H
(b) 1-Butyl-3-methylimidazolium Chloride–(H <sub>2</sub> O) <sub>4</sub> Complexes		
species <sup>a</sup>	calcd frequencies (intensities) <sup>b</sup>	assignment
A	2928(286) and 2924(244), 3153(4), 3172(2)	C <sup>2</sup> –H, asym C <sup>4,5</sup> –H, sym C <sup>4,5</sup> –H
B	3065(356), 3149(4), 3166(2)	C <sup>2</sup> –H, asym C <sup>4,5</sup> –H, sym C <sup>4,5</sup> –H
C	3082(213), 3153(6), 3170(2)	C <sup>2</sup> –H, asym C <sup>4,5</sup> –H, sym C <sup>4,5</sup> –H
D	3011(363), 3151(4), 3168(1)	C <sup>2</sup> –H, asym C <sup>4,5</sup> –H, sym C <sup>4,5</sup> –H

<sup>a</sup> Structure illustrated in Figure 6. <sup>b</sup> Frequencies scaled by 0.955.

interactions between imidazolium C–H groups and the water clusters upon compression, that is, a switch to imidazolium C–H–O hydrogen-bond-like. An ab initio study<sup>35</sup> also predicted that the C<sup>2</sup>–H–O interactions of aqueous imidazolium are very strong, in the neighborhood of 10 kcal/mol, and should exhibit the features of a strong hydrogen bond, that is, a red-shifted C–H frequency. The similarity between Figures 4 and 5 suggested that the hydrogen-bonding patterns in diluted aqueous ionic liquid solution are mainly determined by imidazolium cation–water cluster interactions instead of the relative hydrogen-bonding acceptor strength of Br<sup>-</sup> and Cl<sup>-</sup>.

To develop further insight into the hydration mechanism, we calculated the optimized density functional theory (DFT)-calculated structures of 1-butyl-3-methylimidazolium chloride–(D<sub>2</sub>O)<sub>4</sub> complexes with the butyl side chain in the AA forms, which are shown in Figure 6.<sup>33</sup> All ab initio calculations were performed by using the Gaussian 03 program package.<sup>33</sup> We employed the B3LYP functional together with a standard 6-31+G\* basis set. This combination of method and basis set (B3LYP/6-31+G\*) has been successfully applied to protonated ammonia–water clusters<sup>36</sup> and neutral benzene–water clusters<sup>37</sup> before. We thus expect it to describe comparably well the intermolecular hydrogen bonds in 1-butyl-3-methylimidazolium chloride–water clusters. The geometry optimizations and the vibrational analyses were made by analytical determinations of the first and second derivatives of the total energy. No symmetry constraints were used. Several reports have shown that CP does overestimate the BSSE for single-point a posteriori calculations because the geometry of the CP-corrected species is not optimized on the CP-corrected surface. However, the CP correction on the CP-optimized surface does not overestimate BSSE.<sup>38–40</sup> Therefore, all the geometries and harmonic frequencies were determined on the CP-optimized surface.

Table 2 displays the predicted imidazolium C–H stretching frequencies of 1-butyl-3-methylimidazolium chloride–(D<sub>2</sub>O)<sub>4</sub> (Table 2a) and 1-butyl-3-methylimidazolium chloride–(H<sub>2</sub>O)<sub>4</sub> (Table 2b) complexes in isomeric forms, and energy results are shown in Table 3. The similarity between parts a and b of Table 2 indicates that the isotope effect is minor. The difference observed is the splitting of C<sup>2</sup>–H absorption of species A in Table 2b. Table 3 reveals that total interaction enthalpies (–Δ*H*) are larger than total interaction energies (–Δ*E*). These results suggest Δ*V* < 0, and the negative Δ*V* values correspond to complex formation. The scaling factor for the calculated frequencies is 0.955.<sup>22–24</sup> As illustrated in Figure 6, the energetically favored approach for water molecules to interact with the imidazolium cation is through the formation of C<sup>2</sup>–H–O. This fact could be related to the well-known acidity of

**TABLE 3: Relative Energies (hartree/mol), BSSE (hartree/mol), Total Interaction Energies (kcal/mol), and Enthalpies (kcal/mol)**

species <sup>a</sup>	relative energies <sup>b</sup>	BSSE <sup>b</sup>	–Δ <i>E</i>	–Δ <i>H</i>
A	–1189.038285	0.0090664	118.7	121.4
B	–1189.037345	0.0081845	118.6	121.0
C	–1189.022596	0.0105334	107.9	111.0
D	–1189.040837	0.0088479	120.4	122.7

<sup>a</sup> Structures illustrated in Figure 6. <sup>b</sup> B3LYP/6-31+G\* level.

C<sup>2</sup>–H. Our calculated results indicate that the C<sup>2</sup>–H stretches in all clusters in Table 2 are red-shifted from the isolated cation (Table 1). Therefore, the blue-shifts of C<sup>2</sup>–H stretches observed in Figure 2 may be due to the replacement of a strong interaction between the C–H and an anion with an interaction with water. In other words, the blue-shift appears to be the difference between two red-shifts. No appreciable changes in calculated frequencies of C<sup>4,5</sup>–H stretching modes occurred as revealed in Table 2. Nevertheless, the characteristic bonded C<sup>2</sup>–H vibration is shifted to 2929 (Figure 6a), 3065 (Figure 6b), 3082 (Figure 6c), and 3011 cm<sup>-1</sup> (Figure 6d) due to the modification of C<sup>2</sup>–H–Cl<sup>-</sup> associations. Interestingly, our experimental observations also found that the 3051 cm<sup>-1</sup> band (C<sup>2</sup>–H) is more water-sensitive than the band at ca. 3139 cm<sup>-1</sup> (C<sup>4,5</sup>–H) in Figures 2 and 3. These calculation results, predicting the frequency shift of the imidazolium C–H vibrations, are consistent with our experimental observations in Figures 2–5 and correlate with an ab initio calculation study of pure 1-butyl-3-methylimidazolium hexafluorophosphate that supports a strong interaction between the C<sup>2</sup> hydrogen and the fluorine atoms in PF<sub>6</sub><sup>-</sup>. In light of this finding, we may be able to attribute the frequency shift of the imidazolium C–H modes to the reorganization of the hydrogen-bonded network by the presence of water molecules. The formation of ionic liquid clusters<sup>41</sup> in ionic liquid/water mixtures has been investigated by electrochemical method,<sup>42</sup> NMR studies,<sup>43–45</sup> thermochemical studies,<sup>46</sup> and mass spectrometry.<sup>47</sup> This study provides further understanding of aggregation behaviors in ionic liquid/water mixtures via high-pressure methods. As the clusters increase in size, the structural identification of the isomers is complicated by numerous different isomeric configurations. The questions of which clusters are responsible and how the weak hydrogen bond looks in detail may be settled by molecular dynamics. It is known that cohesion in ionic liquids is strong and mostly electrostatic. Nevertheless, this study elucidates the non-negligible role of weak hydrogen bonds, such as C–H–X and C–H–O, in the structure of ionic liquids.

## Conclusion

IR bands in the C–H stretching region may prove useful as potential spectroscopic probes for studies of molecular interactions in ionic liquids. Increasing water content was found to appreciably change the structure of pure 1-butyl-3-methylimidazolium chloride through the participation of water in imidazolium C–H and alkyl C–H mediated hydrogen bonds. Nevertheless, the imidazolium C–H groups seem to be more favorable sites for hydrogen-bond-like C–H–O than the alkyl C–H groups. The pressure-dependent results indicate that the peak frequencies of imidazolium C–H stretching bands have a nonmonotonic pressure dependence for diluted aqueous mixtures. This result reflects the strengthening of C–H–O interactions.

**Acknowledgment.** The authors thank the National Dong Hwa University and the National Science Council (Contract No. NSC 95-2113-M-259-013-MY3) of Taiwan for financial support.

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