

Probing Electron Density of H-Bonding between Cation–Anion of Imidazolium-Based Ionic Liquids with Different Anions by Vibrational Spectroscopy

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Attenuated total reflection infrared spectroscopy and density functional theory calculation have been employed to study the spectral properties of imidazolium-based ionic liquids (ILs) with different anions. ILs based on 1-butyl-3-methylimidazolium cation with different anions, OH^- , CF_3CO_2^- , HSO_4^- , H_2PO_4^- , Cl^- , PF_6^- , and BF_4^- , are investigated in the present work. It has been shown that the $\text{C}_2\text{--H}$ stretching vibration of the imidazolium ring is closely related to the electron density of H-bonding between the two closest cations and anions for pure ILs. The electron density of H-bonding between cation and anion with different anions decreases in the order $[\text{OH}]^- > [\text{H}_2\text{PO}_4]^- > [\text{HSO}_4]^- > [\text{CF}_3\text{CO}_2]^- > [\text{Cl}]^- > [\text{BF}_4]^- > [\text{PF}_6]^-$. For aqueous ILs, with increasing water content, the aromatic C--H stretching vibration of the imidazolium cation showed systematic blue-shifts. Especially for BmimOH, the $\nu_{\text{C}_2\text{--H}}$ undergoes a drastic blue-shift by 58 cm^{-1} , suggesting that the formation of the strong hydrogen bonds $\text{O--H}\cdots\text{O}$ may greatly weaken the electron density of H-bonding between the cation and anion of ILs.

1. Introduction

Ionic liquids (ILs) are salts composed of cation and anion at room temperatures, or below $100\text{ }^\circ\text{C}$.^{1,2} As a “green” solvent, it has been used in many industrial processes, such as synthesis, catalysis, polymerization, industrial cleaning, solvent extraction, and separations.^{3–5} Therefore, obtaining information on the molecular details of ILs is important to improve their properties. Since ILs are entirely composed of ions, the interaction of ion pairs is expected to be one essential feature. However, the presence of water in ILs could dramatically affect the chemical and physical properties such as viscosity, electrical conductivities, polarity, and reactivity.^{6–12} Consequently, the study on the interactions between ILs and water also appears distinctly significant for improving their properties and performance.

A wealth of studies have been carried out to examine the structure of ILs by using diversified approaches,^{13–41} such as IR and Raman spectroscopy,^{13–24} nuclear magnetic resonance (NMR),^{25–30} sum frequency generation (SFG) spectroscopy,^{31–33} X-ray crystallography,¹⁷ thermodynamic study,^{34–37} and theoretical works.^{38–41} As we know, vibrational spectroscopy is a very powerful tool to explore the structural and dynamic properties of the mixtures between ILs and water. Especially, the hydrogen bonding can be most straightforwardly exhibited in vibrational spectra.^{13,17,42–49} For example, Kazarian et al. have systematically used attenuated total reflection infrared (ATR-IR) spectroscopy to study the molecular states of water absorbed from air in ILs and concluded that most of the water molecules at these concentrations (up to 1.5%, w/w) interact mainly with the anions and exist in symmetric 1:2 type H-bonded complexes: $\text{anion}\cdots\text{HOH}\cdots\text{anion}$.¹³ Hamaguchi and co-workers have found that the presence of water molecules can change the conformation of the *n*-butyronitrile side chain of the cation in 1-butyronitrile-3-methylimidazolium halide ILs by Raman spectroscopy.¹⁷ Mele et al. have presented direct experimental evidence of the interaction between ILs and water, which indicates the

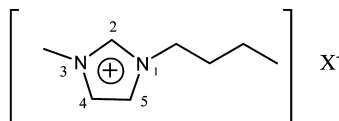
existence of tight ion pairs in the pure liquid, even with the presence of small amounts of water.²⁵ Katsyuba have investigated possible variations of molecular structure of the ion pairs of several imidazolium-based ILs by vibrational spectroscopy and the DFT method, and found that vibrations of the ion pairs influence mainly the stretching and out-of-plane vibrations of the imidazolium C--H groups.⁴⁹ Recently, Ludwig et al. have further studied the cohesion energies between cations and anions in imidazolium-based ionic liquid with a combination of FTIR measurements in the far-infrared region as well as ab initio calculations and indicated that intermolecular stretching modes are shifted to higher wavenumbers with increasing ionic strength of the used anion.⁴⁴

Great efforts have been devoted to the investigation of the interaction of imidazolium-based ionic liquids. Despite numerous computational and experimental studies on ILs until now, less attention has been paid to the effect of the electron density of H-bonding between anion and cation on the changes in frequencies. To investigate the relationships between the electron density of H-bonding and frequencies, several ILs based on 1-butyl-3-methylimidazolium cation with the different anions OH^- , CF_3CO_2^- , HSO_4^- , H_2PO_4^- , Cl^- , PF_6^- , and BF_4^- have been used for ATR-IR and theoretical calculations. The present work will focus on the following aspects: (i) investigate the infrared spectrum changes in pure ILs; (ii) interpret the underlying reason of the spectral changes by density functional theory (DFT) calculations; (iii) study the infrared spectrum changes as a function of the concentration of water $x_{\text{H}_2\text{O}}$.

2. Materials and Methods

Chemicals and Preparation of Solutions. 1-Butyl-3-methylimidazolium tetrafluoroborate (Bmim BF_4) IL was prepared according to the literature,⁵⁰ and the other ILs were prepared by related procedures. They were all dried under 30 Pa for 24 h and protected from moisture. All of the materials were analytical reagents and purchased from J&K Chemical. Aqueous solutions of ILs were gravimetrically prepared with the mole fraction of H_2O ranging from 0.10 to 0.90. The uncertainty in the mole

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$X^- = \text{OH}^-, \text{H}_2\text{PO}_4^-, \text{HSO}_4^-, \text{CF}_3\text{CO}_2^-, \text{Cl}^-, \text{BF}_4^-, \text{PF}_6^-$

Figure 1. Sketch map of ionic liquids.

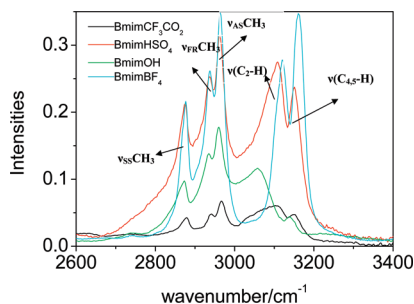


Figure 2. ATR absorption spectra in the range 2600–3400 cm^{-1} for four pure ILs: BmimOH, BmimBF₄, BmimCF₃CO₂, and BmimHSO₄.

TABLE 1: Frequencies and Assignments for ILs in the C–H Stretching Region Shown in Figure 2 according to Our DFT Calculations

	BmimCF ₃ CO ₂	BmimHSO ₄	BmimBF ₄	BmimOH
$\nu_{\text{ss}}\text{CH}_3$	2889	2888	2888	2897
$\nu_{\text{FR}}\text{CH}_3$	2960	2959	2960	2958
$\nu_{\text{AS}}\text{CH}_3$	2974	2975	2974	2973
$\nu(\text{C}_2\text{--H})$	3105	3107	3122	3057
$\nu(\text{C}_{4,5}\text{--H})$	3150	3151	3162	3138

fraction of the mixture is estimated to be less than 0.001 over the whole concentration range.

ATR-IR Experiment. IR spectra were obtained at a resolution of 2 cm^{-1} with an ATR accessory of Nicolet Fourier-transform infrared (FTIR)/Nexus470 spectrometer at room temperature. A small droplet of ILs was placed on the top of the Ge crystal, and each ATR-IR spectrum contains 16 signal-averaged scans.

DFT Calculations. The density-functional theory (DFT) has been successfully applied to predict the geometrical and electronic properties of some ILs,^{44,51–57} and the geometries of the complexes of ILs were optimized at the B3LYP/6-31++G** level of theory and without any imaginary frequencies. The effect of basis set superposition error (BSSE) has been analyzed by means of the counterpoise correction method at B3LYP/6-31++G**.⁵⁸ All of the calculations were performed with the Gaussian 03 program.⁵⁹ In addition, the properties of the electron density at the bond critical point (BCP) have been analyzed by AIM code.⁶⁰

3. Results and Discussion

3.1. One-Dimensional ATR-IR Spectral and Peak Assignment. The chemical structure and atom numbering for ILs are shown in Figure 1. The IR spectra of the four ILs BmimBF₄, BmimCF₃CO₂, BmimHSO₄, and BmimOH in the region 2600–3400 cm^{-1} are displayed in Figure 2, and correspondingly, assignments for these four ILs in the C–H stretching region are shown in Table 1. The previous study reported the BmimBF₄ spectrum in this range has been studied, and the peaks were assigned in a previous report.⁴³ In the IR spectral region from 3000 to 3200 cm^{-1} , the bands observed are mainly attributed to the coupled aromatic C–H stretching vibrations

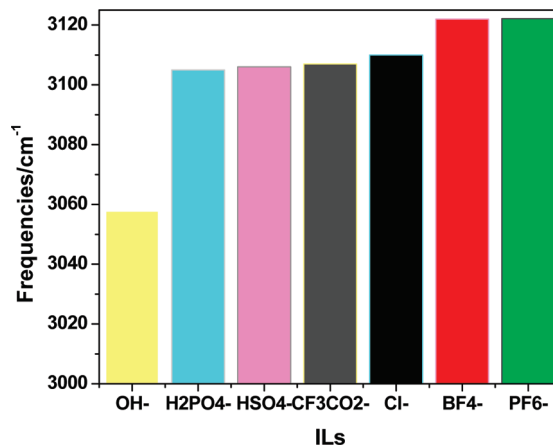


Figure 3. C₂–H stretching frequencies of seven pure ILs.

of the three hydrogen atoms bound to the imidazolium ring.^{49,61} As revealed in Figure 2, the peak positions and intensities are absolutely different at C₂–H and C_{4,5}–H bands. With respect to BmimOH, the intensity and width of the C₂–H band are much larger than those of C_{4,5}–H; that is to say, the anion interacts mainly with C₂–H. With respect to BmimCF₃CO₂ and BmimHSO₄ shown in Figure 2, the intensities and widths of ratios of C₂–H and C_{4,5}–H bands are smaller than those for BmimOH. With respect to BmimBF₄, the width of both C₂–H and C_{4,5}–H bands are narrower than the other three ILs, and the ratios of these two bands are opposite. The frequencies decrease in the order BmimBF₄ > BmimCF₃CO₂ ~ BmimHSO₄ > BmimOH.

3.2. Vibration Frequencies and Cation–Anion Interaction in Pure ILs. The frequencies for seven pure ILs with different anions are shown in Figure 3. It is interesting to note that the frequencies of C₂–H for BmimOH are significantly lower than those for the other ILs. The ILs such as BmimCF₃CO₂, BmimH₂PO₄, and BmimHSO₄ are slightly lower than other three ILs with neutral anions. Compared to that of the BmimPF₆, the frequencies of the other six ILs are all red-shifted. The frequencies of pure ILs with different anions decreased in the order [OH][−] < [H₂PO₄][−] < [HSO₄][−] < [CF₃CO₂][−] < [Cl][−] < [BF₄][−] < [PF₆][−]. The frequencies are related to the cohesive energy between cation and anion.⁴⁴ Thus, we predict that the cation–anion interaction in BmimOH is the strongest, and the sequence is [OH][−] > [H₂PO₄][−] > [HSO₄][−] > [CF₃CO₂][−] > [Cl][−] > [BF₄][−] > [PF₆][−]. However, the cohesive energies calculated by DFT illustrate that the ΔE values for BmimCl are larger than those for BmimH₂PO₄, BmimHSO₄, and BmimCF₃CO₂, which is not coherent with the frequency orders. A probable reason for this abnormal energy is that the ion size of the Cl[−] group is much smaller than the others, and we presume that Cl[−] are closer to the C₂–H of the imidazolium and the interaction of the ILs of C₂–H...Cl are stronger than other ILs.

3.2.1. Correlations between Frequencies and Cohesive Energy. In an effort to unveil the reason for this assumption, we performed DFT theory calculations using the Gaussian 03 program.⁵⁹ Although the DFT function has some limitation on the interparticle energies, it has been successfully applied to predict the geometrical properties and estimate the cohesive energy of the cation–anion of some ILs.^{40,44,54} Herein, all of the geometries of the ILs were optimized at the B3LYP/6-31++G** level of theory (Figure 4). The cohesive energies for cation–anion of these ILs are listed in Table 2. The cohesive energy of cation–anion ΔE_{BmimOH} is −532.42 kJ/mol, which is more negative than others. In other words, the corresponding interaction between cation and anion in BmimOH is the largest.

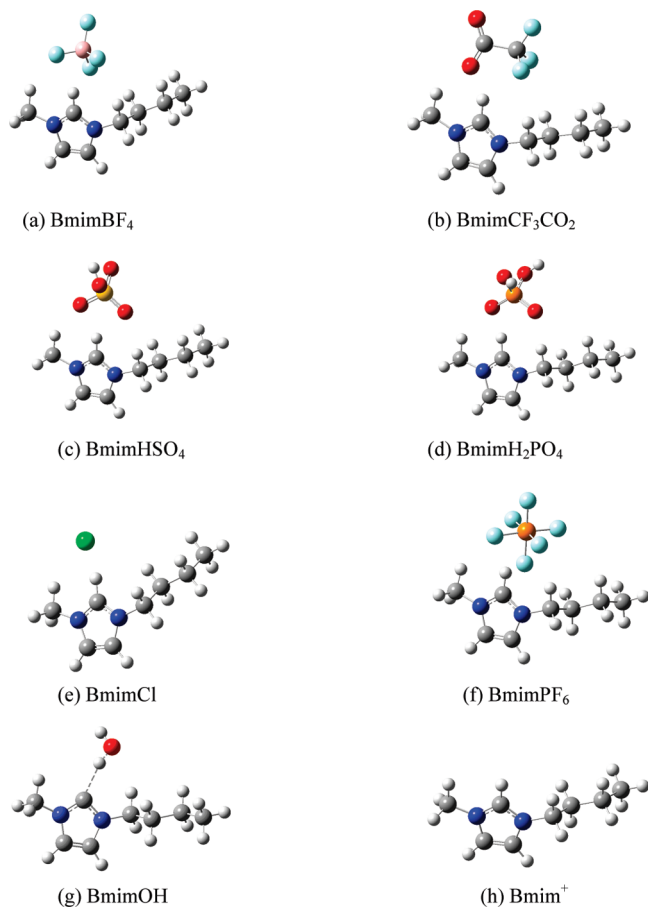


Figure 4. Optimized geometries of seven ILs and cation: (a) BmimBF₄ ion pairs; (b) BmimCF₃CO₂ ion pairs; (c) BmimHSO₄ ion pairs; (d) BmimH₂PO₄ ion pairs; (e) BmimCl ion pairs; (f) BmimPF₆ ion pairs; (g) BmimOH ion pairs; (h) Bmim⁺ cation.

That is why the IR frequency of BmimOH is the lowest. For BmimCl, the cohesive energy of cation–anion ΔE_{BmimCl} is -352.62 kJ/mol, which is still much larger than the others expected for BmimOH. Comparing with Table 2, the cohesive energy in BmimH₂PO₄ and BmimHSO₄ are similar. The ΔE values of BmimH₂PO₄ and BmimHSO₄ are -319.20 and -317.14 kJ/mol, respectively, which is smaller than BmimCl by 33.42 and 35.48 kJ/mol, respectively. With respect to BmimCF₃CO₂, the cohesive energy is -297.18 kJ/mol which is also smaller than BmimCl by 55.44 kJ/mol. The cohesive energy between cations and anions increases in the order $[\text{PF}_6]^- < [\text{BF}_4]^- < [\text{CF}_3\text{CO}_2]^- < [\text{HSO}_4]^- < [\text{H}_2\text{PO}_4]^- < [\text{Cl}]^- < [\text{OH}]^-$. Because H-bond strength is only a fraction of the interaction between cation and anion, the cohesive energies and frequencies do not strictly correlate. As we know, the position and the ion size of the anion can also affect the interaction of the cation and anion.^{21,24} The ion size of the OH[−] and Cl[−] group is much smaller than the others. As shown in Table 2, the $r_{[\text{Y} \cdots \text{H}-\text{C}(2)]}$ values of BmimCl and BmimOH are 1.977 and 1.598 Å, respectively, reflecting that OH[−] and Cl[−] are closer to the C₂–H of the imidazolium and the interactions of C₂–H \cdots O–H and C₂–H \cdots Cl are stronger than those of other ILs. Thus, the electron density of hydrogen bonds is used in this paper to support another probable reason for the correlation between interactions and frequencies.

3.2.2. Correlations between Frequencies and Electron Density of Hydrogen Bonds. AIM allows us to study the bonding properties of the systems, to observe the switches in bonding, and to see whether the bonds are covalent or ionic,

among other properties. It has also been applied to ILs to obtain the hydrogen-bond properties of the ion pairs.⁵⁴ The AIM parameters at the bond critical points (BCPs) are summarized in Table 3, and the electron density (ρ_{BCP}) correlates with the strength of a H-bonding interaction.⁶² The values of ρ obtained for (C₂–H) \cdots Y[−] interaction of all of the complexes are in the range of the neutral hydrogen bonds ($\rho_{\text{Hbond}} \approx 0.002\text{--}0.04$ e Å^{−3}), suggesting that the strength of the (C₂–H) \cdots Y[−] interactions compete with that of the traditional hydrogen bonds. It is worth noting that the values of BmimOH, BmimHSO₄, and BmimH₂PO₄ are larger than 0.04 e Å^{−3}, suggesting that these interactions are very strong. Frequencies as a function of electrodensity at BCPs are shown in Figure 5, and the value of BmimOH is about 0.26 e Å^{−3}, which is significantly larger than others. It can be concluded that the strength of interaction for BmimOH is much larger than that for other ILs. The frequencies for other six ILs as a function of electrodensity at BCPs show monotonous changes in Figure 5. With increasing electron density of H-bonding between cation and anion, the frequencies decrease. Thus, the electron density of H-bonding between cations and anions increases in the order $[\text{PF}_6]^- < [\text{BF}_4]^- < [\text{Cl}]^- < [\text{CF}_3\text{CO}_2]^- < [\text{HSO}_4]^- < [\text{H}_2\text{PO}_4]^- < [\text{OH}]^-$.

3.2.3. Explanations for Why the Cohesive Energy of Cation–Anion ΔE_{BmimCl} is Abnormal. The Laplacian $\nabla^2\rho$ represents the curvature of the electron density in three-dimensional space at the BCP of the (C₂–H) \cdots Y[−] interaction.⁶³ The values listed in Table 3 are all negative except for OH[−] and Cl[−], suggesting that the (C₂–H) \cdots Y[−] interaction has a covalent character. The electrostatic character of (C₂–H) \cdots Cl[−] and (C₂–H) \cdots OH[−] interactions suggests that the binding energies for OH and Cl are larger than others, which can explain the abnormal cohesive energy for BmimCl. Furthermore, it can be concluded that, when the ion size of the anion is very small, the (C₂–H) \cdots Y[−] interaction has an electrostatic character. It has been reported that the total energy density (H_{BCP} [kinetic $G(r)$ plus potential $V(r)$ energy density], instead of the Laplacian, is a more appropriate index to approach a better understanding of the weak nonbonded interaction.⁶⁴ According to the values of H listed in Table 3, it seems that the H values of (C₂–H) \cdots Cl[−] and (C₂–H) \cdots OH[−] are all negative, which suggests that the (C₂–H) \cdots Y[−] have some covalent character. The H values of the (C₂–H) \cdots Cl[−] are far larger than those of the (C₂–H) \cdots OH[−], indicating that the covalent character of the (C₂–H) \cdots OH[−] is larger than that of the (C₂–H) \cdots Cl[−]. Thus, the interaction of (C₂–H) \cdots OH[−] is larger than that of (C₂–H) \cdots Cl[−]. However, the (C₂–H) \cdots H₂PO₄[−] and (C₂–H) \cdots HSO₄[−] have a covalent character, and the electrostatic character of (C₂–H) \cdots Cl[−] interactions suggests that the binding energies for Cl are larger than others. On the basis of this reason, the similarities in energies between Cl[−], H₂PO₄[−], and HSO₄[−] (cohesive energy and H values at BCP) can distinguish. The interaction for some ILs such as BmimCl, Bmim BF₄, and BmimPF₆ has also been investigated in previous reports,^{32b,40} which was in agreement with our experiment. As a consequence, the electron density of H-bonding between cations and anions can be another probable reason for the correlation between interactions and frequencies.

3.3. ILs and Water Mixture. The absorption bands of BmimBF₄, BmimCF₃CO₂, BmimHSO₄, and BmimOH with four typical anions as a function of the water content are illustrated in Figure 6. With increasing water concentration, both the C₂–H and C_{4,5}–H absorption peaks yield a monotonic blue-shift for all ILs. The C₂–H and C_{4,5}–H absorption peaks of BmimBF₄ almost keep constant. When water is added, the environment

TABLE 2: The Binding Energy Parameters for Cation–Anion of ILs and the Distance between C2–H and the Mass Center of Y[−]

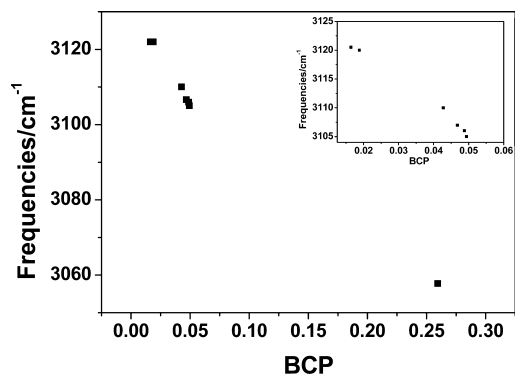
species	ΔE^a (kJ/mol)	$r_{[Y \cdots H-C(2)]}$	species	ΔE (kJ/mol)	$r_{[Y \cdots H-C(2)]}$
BmimOH	−532.42	1.598	BmimCl	−352.62	1.997
BmimH ₂ PO ₄	−319.20	2.528	BmimBF ₄	−295.47	2.432
BmimHSO ₄	−317.14	2.518	BmimPF ₆	−274.60	2.853
BmimCF ₃ CO ₂	−297.18	2.687			

^a BSSE-corrected interaction energies.**TABLE 3: AIM Parameters for Seven ILs**

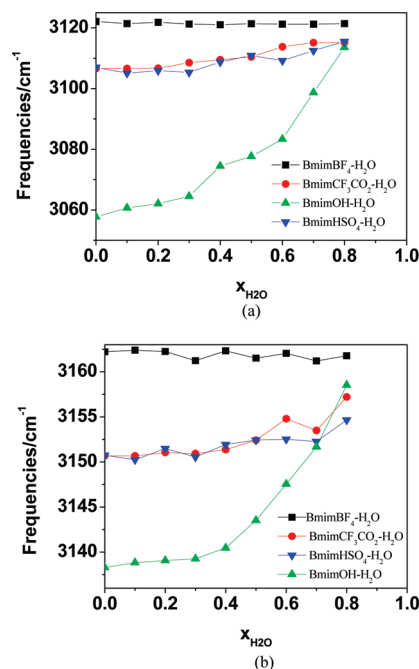
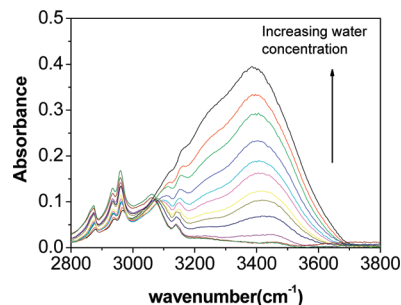
complexes, (C2–H)⋯Y [−]	ρ	$\nabla^2\rho$	G	V	H
(C2–H)⋯OH [−]	0.2595	0.2610	0.1068	−0.4746	−0.3678
(C2–H)⋯H ₂ PO ₄ [−]	0.0494	−0.0331	0.0345	−0.0359	−0.0013
(C2–H)⋯HSO ₄ [−]	0.0488	−0.0338	0.0359	−0.0381	−0.0021
(C2–H)⋯CF ₃ CO ₂ [−]	0.0468	−0.0346	0.0352	−0.0358	−0.0006
(C2–H)⋯Cl [−]	0.0428	0.0075	0.0246	−0.0300	−0.0053
(C2–H)⋯BF ₄ [−]	0.0188	−0.0166	0.0164	−0.0162	0.0002
(C2–H)⋯PF ₆ [−]	0.0164	−0.0151	0.0146	−0.0141	0.0004

provided by the anion is similar to the water molecule, which is interestingly in agreement with the literature.²⁰

Meanwhile, the C₂–H and C_{4,5}–H absorption peaks shift from 3106 to 3115 cm^{−1} for BmimCF₃CO₂ and from 3107 to 3115 cm^{−1} for BmimHSO₄. With respect to the BmimOH + H₂O mixture, the dramatic changes are shown in Figures 6 and 7. Of which, the band of the C₂–H stretching vibrations (centered around 3058 cm^{−1}) is blue-shifted in a much larger scale than the C_{4,5}–H stretching vibrations, which moves from 3058 to 3117 cm^{−1}. The intensities and bandwidth of this band are decreasing all the time, and the C_{4,5}–H stretching vibrations (centered around 3138 cm^{−1}) are blue-shifted from 3138 to 3158 cm^{−1}. When the concentration of water is very low (0.1 < x_{H₂O} < 0.3), ν_{C₂–H} and ν_{C_{4,5}–H} slightly shift. The most significant changes occurred in the concentration range 0.30 < x_{H₂O} < 0.90: the ν_{C_{4,5}–H} has been blue-shifted by 20 cm^{−1} with the increase of the water concentration, and the ν_{C₂–H} undergoes a drastic blue-shift, which was 58 cm^{−1}. Apparently, the blue-shift of the C_{4,5}–H stretching vibrations is not as significant as that of the C₂–H but still largely blue-shifted. The different extent of the blue-shift can distinguish the different extent of the influence of water on different sites of the cation. Subsequently, it is interesting to note that the frequencies of the other two ILs are similar to BmimBF₄ at about 3122 cm^{−1} in the water-rich region. Various experimental measurements and *ab initio* calculation methods have been used to investigate the blue-shifted hydrogen bond,^{65–67} which can be compared with our results. When a water

**Figure 5.** Frequencies as a function of electrodensity at BCPs. The inset shows the enlarged frequencies as a function of electrodensity at BCPs from 0.00 to 0.06.

molecule is added into the ILs, the formation of strong hydrogen bonds occurs: the O–H⋯O bond may significantly weaken the H-bonding of the cation–anion of ILs, thereby leading to a C–H bond contraction and an increase of the respective stretch frequency (blue-shift). For BmimCF₃CO₂, the electron density of H-bonding of the cation–anion is comparatively weaker than BmimOH shown by our DFT calculations. When water molecules interact with anion, simultaneously, the C–H bonds of BmimCF₃CO₂ and BmimHSO₄ are shortened, but the degree for weakening the H-bonding of cation and anion is smaller than that for BmimOH. As a result, the blue-shift of C–H bands is not as dramatic as that of BmimOH. In summary, the C₂–H

**Figure 6.** (a) C₂–H stretching frequencies of four ILs as a function of x_{H₂O}. (b) The C_{4,5}–H stretching frequencies of four ILs as a function of x_{H₂O}.**Figure 7.** ATR absorption spectra of BmimOH + H₂O mixtures in the 2800–3800 cm^{−1} range. The bottom-most green line represents the absorption spectrum of pure BmimOH. All lines are the absorption spectra for IL–water mixtures with changing of x_{H₂O}: 0.1, 0.15, 0.2, 0.25, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0.

and C_{4,5}–H absorption peaks of BmimCF₃CO₂, BmimHSO₄, and BmimOH show a systematic blue-shift with different degrees. Meanwhile, in the water-rich region, the frequencies of C₂–H and C_{4,5}–H for all ILs shift to the same level. With increasing water concentration, the C–H stretching vibration showed a blue-shift, reflecting the weakening of the H-bonding between cation and anion of the ILs. Many literatures have suggested that the interaction of anion–water plays the dominant role in determining IL solubility in water.^{13,68,69} With increasing water concentration, the pure ILs are destroyed gradually. Finally, when $x_{\text{H}_2\text{O}} > 0.8$, water may absolutely dissolve the ILs and surround the ion pairs; then, the environments of the three ILs are similar to each other. The frequencies of C₂–H and C_{4,5}–H for BmimCF₃CO₂ and BmimOH tend to the BmimBF₄, and the peaks shift to the same positions at about 3122 cm^{−1}. Therefore, the C₂–H vibrational frequencies with different anions follow the trend OH[−] > HSO₄[−] > CF₃CO₂[−] > BF₄[−].

In summary, the ion size of the anion may also affect the frequencies. Instead, the electron density of H-bonding between anion and cation dominates C–H bond stretching, supporting these frequency changes.

4. Conclusions

We investigated the interactions of seven ILs using ATR-IR and DFT methods, and the frequency sequence is [OH][−] > [H₂PO₄][−] > [HSO₄][−] > [CF₃CO₂][−] > [Cl][−] > [BF₄][−] > [PF₆][−]. On the basis of calculation results, the electron density (ρ_{BCP}) combined with the cohesive energy (ΔE) can reflect the frequency changes. With increasing electron density of H-bonding between cation and anion, the frequencies decrease, and show monotonous changes. The electron density between cation and anion with different anions decreases in the order [OH][−] > [H₂PO₄][−] > [HSO₄][−] > [CF₃CO₂][−] > [Cl][−] > [BF₄][−] > [PF₆][−]. Nevertheless, the nature of the (C₂–H)⋯Cl[−] and (C₂–H)⋯OH[−] interactions is mainly electrostatic; thus, it can be inferred that ILs with small ion size have an electrostatic character. Furthermore, the addition of water dissolved in ILs can weaken the electron density C–H⋯Y between anion and cation. Therefore, the extent of blue-shift decreases in the order [OH][−] > [HSO₄][−] > [CF₃CO₂][−] > [BF₄][−]. When $x_{\text{H}_2\text{O}} > 0.8$, the H-bonding between cations and anions may be mostly weakened, and the environments of the three ILs are similar to each other.

As a preliminary investigation on relationships between the electron density of H-bonding and stretching frequencies by IR and DFT, this work will make a contribution to the study of the microstructure for ILs in pure and aqueous states.

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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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