**Characteristic Spectroscopic Features because of Cation–Anion Interactions Observed in the 700–950 cm⁻¹ Range of Infrared Spectroscopy for Various Imidazolium-Based Ionic Liquids**

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**ABSTRACT:** The 700–950 cm⁻¹ range in infrared spectroscopy was investigated for various imidazolium-based ionic liquids (ILs). Two main vibrational modes of the methylimidazolium cation exist in this region. At 700–800 cm⁻¹, there is an out-of-plane C(2)−H and C(4,5)−H bending mode with a large motion of C(4,5)−H in the imidazolium ring, whereas at 800–950 cm⁻¹, there is an out-of-plane C(2)−H and C(4,5)−H bending mode with a larger motion of C(2)−H in the imidazolium ring. The molar-concentration-normalized absorbance spectrum of the former band at 700–800 cm⁻¹, which is related to the bending mode with a large C(4,5)−H motion in the imidazolium ring, is not particularly sensitive to the interactions with anions. The molar-concentration-normalized absorbance spectrum of the latter band at 800–950 cm⁻¹ was nearly identical for ILs that have methylimidazolium cations with carbon chains of different lengths and the same anions. The band shape of the latter band, which is related to the bending mode with a large out-of-plane C(2)−H bending motion, was highly sensitive to the interactions with anions and, interestingly, both blue- and red-shifted tendencies in the spectrum for each system were observed.

**INTRODUCTION**

Room-temperature ionic liquids (ILs), comprising entirely of ions in a liquid state below 100 °C, have striking characteristics, such as low melting points, extremely low volatility, enhanced chemical and thermal stability, high ionic conductivity, lubrication ability, and enhanced solubility for various materials. The unique and fascinating features of ILs have resulted in a wide array of scientific and industrial applications. For these applications, it is important to understand the physicochemical properties of ILs as Coulomb systems. Accordingly, the elucidation of the nature of noncovalent interactions in ILs that include Coulomb forces, hydrogen bonds, and dispersion forces as well as the liquid structure of ILs are crucial. Experimentally, infrared (IR), Raman, and NMR spectroscopies have been utilized as fundamental and powerful tools for characterizing ILs, which provided us with significant insights into the assignment of vibrational modes, hydrogen bond-type interactions, and molecular conformations. Computational studies have also been extensively performed to address the noncovalent interactions and the liquid structure of ILs. The low-frequency intermolecular vibrational modes have been studied by using far IR (FIR) spectroscopy and terahertz time-domain spectroscopy (THz-TDS). In determining the center frequencies of the broad absorption band below 150 cm⁻¹ for some imidazolium-based ILs, the major contribution of the force constant in the angular frequency of the harmonic oscillator, ω = (k/μ)¹⁄², and the significance of the local and directional hydrogen bond were pointed out. On the other hand, we previously reported that THz-TDS and FIR spectroscopy can directly explore the intermolecular vibrations because of the cation–anion interactions in methylimidazolium ILs that originated in Coulomb interactions and hydrogen-bond-type interactions and argued that the central frequencies of intermolecular vibrations are on the essential contribution of the reduced mass μ calculated from the respective masses of the methylimidazolium ring cation [mim⁺] and the anion [A⁻] as well as the force constant k, which was established for a wide variety of methylimidazolium ILs. In IR spectroscopic studies for imidazolium-based ILs, C(2)−H stretching vibration, and C(4,5)−H asymmetric and symmetric stretching vibrations in the 3000–3200 cm⁻¹ range were intensively investigated because most characteristic features of local hydrogen-bond-type interactions appear in the frequency range; that is, the red-shifted C−H stretching vibrations in “C−H···A” interactions are the...
ILs were all highly pure (>98%), and some IL samples with carbon chains of di- or longer were purchased from Kanto Chemical Co., Tokyo, Japan, or Merck Ltd., Tokyo, Japan. The standard abbreviations of \([\text{C}_n\text{mim}^+]\) for alkyl-methylimidazolium cations and some anions are used in this paper.

Experimental evidence for hydrogen-bond-type interactions. We systematically discussed the correlation between the +C\(\text{H}\) stretching vibrational frequencies, the chemical shift (\(\delta\) ppm) of the corresponding proton obtained from the NMR spectra, and the center frequencies of intermolecular vibrational modes because of ion pairs obtained from THz-TDS and FIR. In other IR frequency ranges, extensive studies on the assignment of vibrational modes and molecular conformers have been performed for various ILs, and Paschoal et al. recently systematically reviewed the vibrational spectroscopy of ILs.

In this paper, we systematically investigated the 700–950 cm\(^{-1}\) range in IR spectroscopy for various methylimidazolium ILs. Two main bands of the methylimidazolium cation exist in this region. At 700–800 cm\(^{-1}\), there is an out-of-plane +C\(\text{H}\) and +C\(\text{H}\) bending mode with a larger motion of +C\(\text{H}\) which is coupled with small motions of the alkyl-chain part. At 800–950 cm\(^{-1}\), there is an out-of-plane +C\(\text{H}\) and +C\(\text{H}\) bending mode with a larger motion of +C\(\text{H}\)–H. The investigation of these bands that are related to the motions of +C\(\text{H}\)–H and +C\(\text{H}\)–H is very important, whereas these bands have been rarely explored. We found that the molar-concentration-normalized absorbance of the former band at 700–800 cm\(^{-1}\) is partly affected by anti/gauche conformations of the alkyl-chain part, and the molar-concentration-normalized absorbance of the latter band at 800–950 cm\(^{-1}\) is nearly identical in terms of the intensities and bandshapes for ILs that have methylimidazolium cations with carbon chains of different lengths and the same anions, whose validity was established for a wide range of methylimidazolium ILs. Moreover, the band shape of the latter band is highly sensitive to the interactions with anions and, interestingly, both blue- and red-shifted tendencies in the spectrum for each system were observed.

**RESULTS AND DISCUSSION**

First, we show the calculated vibrational spectra in the 700–950 cm\(^{-1}\) range of \([\text{C}_2\text{mim}^+], [\text{C}_3\text{mim}^+], [\text{C}_4\text{mim}^+], [\text{C}_5\text{mim}^+], [\text{C}_6\text{mim}^+], [\text{C}_7\text{mim}^+], [\text{C}_8\text{mim}^+], [\text{C}_9\text{mim}^+]\), as shown in Figure 2a,b. In Figure 2a, the vibrational spectra of \([\text{C}_n\text{mim}^+]\) with all trans-conformations of the alkyl-chain part were calculated, whereas in Figure 2b, those of \([\text{C}_n\text{mim}^+]\) with all gauche-conformations of the alkyl-chain part were calculated for simplicity, where all gauche-conformers of \([\text{C}_n\text{mim}^+]\), in which \(C_n\) is greater or equal to 4, are meaningful.

In Figure 2a, we can find two main bands for all \([\text{C}_n\text{mim}^+]\). The first is an out-of-plane +C\(\text{H}\)–H and +C\(\text{H}\)–H bending mode with a larger motion of +C\(\text{H}\)–H in the imidazolium ring with the peak at 830–835 cm\(^{-1}\) and nearly the same intensity. The second is an out-of-plane +C\(\text{H}\)–H and +C\(\text{H}\)–H bending mode with a larger motion of +C\(\text{H}\)–H in the imidazolium ring with the peak at 750–755 cm\(^{-1}\) and nearly the same intensity. Thus, these two main vibrational modes are the vibrational modes within the imidazolium ring, essentially. There are vibrational modes at 730–740 cm\(^{-1}\) with a moderately strong intensity, which mainly originate from the rocking motions of the alkyl-chain part. Accordingly, the peak frequencies and intensities differ depending on the alkyl-chain length of \([\text{C}_n\text{mim}^+]\) and no peak for \([\text{C}_3\text{mim}^+]\). In actual ILs, the peak at 750–755 cm\(^{-1}\) and the peaks at 730–740 cm\(^{-1}\) tend to overlap. There are very small peaks at around 800 and 900 cm\(^{-1}\), depending on the alkyl-chain length. In Figure 2b, we can find two main bands for all \([\text{C}_n\text{mim}^+]\). The origin of the two main bands is the same as explained in Figure 2a. There are vibrational modes at 720–740 cm\(^{-1}\), which mainly originate from motions of the alkyl chain part with all gauche...
conformations. The vibrational modes exist in a wider frequency region compared with those in Figure 2a, and the peak frequencies and intensities differ. There are small peaks at around 800 and 900 cm\(^{-1}\), depending on the alkyl-chain length. As an example, the vibrational modes at 834, 754, and 736 cm\(^{-1}\), which are two main vibrational modes and the rocking mode of the alkyl-chain part with a moderately strong intensity, are illustrated for [C\(_6\)mim\(^+\)] with all trans conformations of the alkyl-chain part in Figure 3a–c, respectively.

**Figure 2.** (a) Calculated vibrational spectra of [C\(_n\)mim\(^+\)] with \(n = 2, 3, 4, 6, 8, \) and 10, having all trans-conformations of the alkyl-chain part and (b) calculated vibrational spectra of [C\(_n\)mim\(^+\)] with \(n = 4, 6, 8, \) and 10, having all gauche conformations of the alkyl-chain part. The absorption bandwidth was set at 5 cm\(^{-1}\) for the absorption bands to make them easily visible.

**Figure 3.** Calculated vibrational modes at (a) 834, (b) 754, and (c) 736 cm\(^{-1}\) for [C\(_6\)mim\(^+\)] with all trans conformations of the alkyl-chain part. The out-of-plane +C(2)−H and +C(4,5)−H bending mode with a larger motion of +C(2)−H at 834 cm\(^{-1}\) and the out-of-plane +C(2)−H and +C(4,5)−H bending mode with a larger motion of +C(4,5)−H at 754 cm\(^{-1}\) were schematically illustrated, where the sizes of the circles near “H”s represent the magnitude of the motions.

**Figure 4a−j** shows the molar concentration normalized absorbance spectra in the 700−950 cm\(^{-1}\) range obtained by ATR−FTIR and density measurements for various kinds of alkyl-methylimidazolium ILs, as shown in Figure 1. The original ATR−IR spectra in the 700−950 cm\(^{-1}\) range are shown (see Figure S1a−j, Supporting Information).

Kim et al. reported that the penetration depth change arising in relation to differences in refractive indices under the ATR geometry is of little consequence, and IR measurements in transmission geometry bring in very similar results for some imidazolium-based ILs.\(^{38}\) We also previously showed the usefulness of molar concentration normalized absorbance spectra in the 2800−3300 cm\(^{-1}\) range for various imidazolium-based ILs.\(^{28}\) Because the molar concentration normalization is equivalent to the normalization by the number of ion pairs, the molar-concentration-normalized absorption spectra enable us to distinguish the vibrational modes, whose absorption intensities and frequencies are decided by the number of ion pairs from the vibrational modes whose absorption intensities and frequencies are not decided by the number of ion pairs; for instance, vibrational modes depending on alkyl-chain length and its conformation of imidazolium cations. In Figure 4, we found that the molar-concentration-normalized absorbance spectra in the 800−950 cm\(^{-1}\) range for IL samples that have methylimidazolium cations with carbon chains of different lengths and the same anions are nearly identical as for absorption intensities and absorption frequencies, whereas those in the 700−800 cm\(^{-1}\) range are moderately identical.

First, we discuss molar-concentration-normalized absorbance spectra in the 700−800 cm\(^{-1}\) range. According to the calculations shown in Figure 2, there are out-of-plane +C(2)−H and +C(4,5)−H bending mode with a larger motion of +C(4,5)−H at the peak at 750−755 cm\(^{-1}\) and the strong intensity, vibrational modes at 730−740 cm\(^{-1}\) with moderately strong intensities that are related to motions of alkyl-chain part for trans-conformers, vibrational modes at 720−740 cm\(^{-1}\) with moderately strong intensities that are related to motions of alkyl-chain part for gauche conformers. Hereinafter, we call the...
out-of-plane 'C(2)—H and 'C(4,5)—H bending mode with a larger motion of 'C(4,5)—H as the out-of-plane 'C(4,5)—H bending mode. Because of the broadening of absorption bands in actual ILs, the peak at 750–755 cm⁻¹ and the peaks at 730–740 cm⁻¹ tend to overlap. Additionally, in the 700–800 cm⁻¹ range, there are IR-active vibrational modes of anions of [SCN]⁻, [TfO]⁻, [Tf₂N]⁻, and [PF₃(C₂F₅)₃]⁻. Particularly for [Cₙmim]⁺[Tf₂N]⁻ and [Cₙmim]⁺[PF₃(C₂F₅)₃]⁻, very strong absorption bands because of [PF₃(C₂F₅)₃]⁻ and [Tf₂N]⁻ exist as shown in Figure 4, which makes it difficult to analyze the vibrational modes of imidazolium cations in this range. Therefore, we do not analyze the data in the 700–800 cm⁻¹ range for [Cₙmim]⁺[Tf₂N]⁻ ILs and [Cₙmim]⁺[PF₃(C₂F₅)₃]⁻ IL.

In Figure 4, we found a very broad absorption band for [Cₙmim]⁺[Cl⁻] ILs and [Cₙmim]⁺[Br⁻] ILs, and [Cₙmim]⁺[I⁻] ILs, we found a very broad absorption band for [Cₙmim]⁺[Cl⁻] and [Cₙmim]⁺[Br⁻] and a broad absorption band for [Cₙmim]⁺[I⁻] with the peak at around 745–765 cm⁻¹. The main contribution of this band is due to vibrational modes that are related to the motions of the alkyl-chain part. Weak peak or shoulderlike structures in the 720–740 cm⁻¹ range for [Cₙmim]⁺[Br⁻] with a long alkyl chain of n = 6, 8, or 10 suggest the contribution of gauche conformations in the alkyl-chain part. In return, we can recognize the existence of gauche conformations in the alkyl-chain part for these IL systems.

In Figure 4a–c for [Cₙmim]⁺[Cl⁻] ILs, [Cₙmim]⁺[Br⁻] ILs, and [Cₙmim]⁺[I⁻] ILs, we found a very broad absorption band for [Cₙmim]⁺[Cl⁻] and [Cₙmim]⁺[Br⁻] and a broad absorption band for [Cₙmim]⁺[I⁻] with the peak at around 745–765 cm⁻¹. The main contribution of this band is due to vibrational modes that are related to the motions of the alkyl-chain part. Weak peak or shoulderlike structures in the 720–740 cm⁻¹ range for [Cₙmim]⁺[Br⁻] with a long alkyl chain of n = 6, 8, or 10 suggest the contribution of gauche conformations in the alkyl-chain part. In return, we can recognize the existence of gauche conformations in the alkyl-chain part for these IL systems.
shoulderlike structures at 750−760 cm⁻¹ and a weak peak or shoulderlike structure at 730−740 cm⁻¹. The main contribution of this band is the out-of-plane 'C(4,5)−H bending mode, and a part of the contribution of this band is due to vibrational modes that are related to the motions of the alkyl-chain part and a vibrational mode of the anion. According to the calculation in Figure 2a, the vibrational modes that are related to the motions of the alkyl-chain part exist at 730−740 cm⁻¹. Moreover, [SCN⁻] has a vibrational mode at 730 cm⁻¹ (see Figure S2, Supporting Information). These two contributions lead to the elevation of the absorption intensity at 730−740 cm⁻¹. The out-of-plane 'C(4,5)−H bending mode may exist at around 750−760 cm⁻¹. In Figure 4e for [C₆mim⁺][N(CN)₂⁻] ILs, we found a broad absorption band with a peak at around 750−760 cm⁻¹. The main contribution of this band is the out-of-plane 'C(4,5)−H bending mode, and a part of the contribution of this band is due to vibrational modes that are related to the motions of the alkyl-chain part. There are no IR-active vibrational modes for [N(CN)₂⁻] in the 700−800 cm⁻¹ range. In Figure 4f for [C₆mim⁺][TO⁺] ILs, we found a broad band with a peak at around 750−760 cm⁻¹. The main contribution of this band is the out-of-plane 'C(4,5)−H bending mode, and part of the contribution of this band is due to vibrational modes that are related to the motions of the alkyl-chain part and the vibrational modes of the anion. According to the calculation, [TO⁺] has a vibrational mode at 735 cm⁻¹ (see Figure S3, Supporting Information). In the actual IL systems, the vibrational mode of [TO⁺] may exist at around 750−760 cm⁻¹ and the contribution is superimposed as a sharp peak structure. The shoulderlike structures in the 720−730 cm⁻¹ region for [C₆mim⁺][TO⁺] with a long alkyl-chain of n = 6 and 8 indicate the existence of gauche conformations in the alkyl-chain part. In Figure 4h, for [C₆mim⁺][BF₄⁻] ILs, a broad absorption band with a peak at around 750−760 cm⁻¹ was observed. The main contribution of this band is the out-of-plane 'C(4,5)−H bending mode, and part of the contribution of this band is due to vibrational modes that are related to the motions of the alkyl-chain part. There are no IR-active vibrational modes for [BF₄⁻] in the 700−800 cm⁻¹ range. The shoulderlike structures at 720−730 cm⁻¹ for [C₆mim⁺][BF₄⁻] with a long alkyl-chain of n = 6, 8, and 10 indicate the existence of gauche conformations in the alkyl-chain part. In Figure 4i for [C₆mim⁺][PF₆⁻] ILs, we found a broad band with a peak at around 750−760 cm⁻¹ and a bump structure around at 740 cm⁻¹. Although there are no IR-active vibrational modes for [PF₆⁻] in the 700−800 cm⁻¹ range (see Figure S4, Supporting Information), the totally symmetric stretching mode of [PF₆⁻] that is not IR active for an isolated anion may become IR active because of the condensed phase effect of the IL₄⁺[PF₆⁻] which may appear as the bump structure. The main contribution of this band is the out-of-plane 'C(4,5)−H bending mode, and part of the contribution of this band is due to vibrational modes that are related to the motions of the alkyl-chain part. [PF₆⁻] has an extremely strong absorption band with a peak at 810−820 cm⁻¹, as shown in Figure 4i (824 cm⁻¹ in the calculation) (see Figure S4, Supporting Information). The broad band with a peak at around 750−760 cm⁻¹ is partly affected by the low-frequency side of the extremely strong absorption band. Note that the scale of the vertical axis in Figure 4i is significantly different from the others. As an overall view, molar-concentration-normalized absorbance spectra at the 700−800 cm⁻¹ region in Figure 4 are moderately identical for IL samples that have methylimidazolium cations with carbon chains of different lengths and the same anions, and the main contribution of the broad band in the 700−800 cm⁻¹ range is the out-of-plane 'C(4,5)−H bending mode, for which peaks exist at 745−765 cm⁻¹, regardless of anion species. [Cl⁻] and [Br⁻] are very strong proton acceptors; [I⁻], [SCN⁻], and [N(CN)₂⁻] are strong proton acceptors; [TO⁺] is a relatively strong proton acceptor; and [TF,N⁺], [BF₄⁻], [PF₆⁻], and [PF₆(C₆F₅)₃⁻] are assigned to weakly coordinated anions.32−34 Accordingly, the out-of-plane 'C(4,5)−H bending is not particularly sensitive to the local interactions with anions, such as hydrogen-bond-type interactions, although the absorption band in the 700−800 cm⁻¹ range for [C₆mim⁺][Cl⁻] and [C₆mim⁺][Br⁻] is broader in both the red and blue sides, compared with the other IL samples.

Next, we discuss molar-concentration-normalized absorbance spectra in the 800−950 cm⁻¹ range. Molar-concentration-normalized absorbance spectra in the 800−950 cm⁻¹ range are nearly identical in terms of the absorption intensities, absorption frequencies, and shapes of absorption bands for IL samples that have methylimidazolium cations with carbon chains of different lengths and the same anions. The tendency was surprisingly observed for a wide range of methylimidazolium ILs. According to the calculations, the main band in the 800−950 cm⁻¹ region for all C₆mim⁺ is the out-of-plane 'C(2)−H and 'C(4,5)−H bending mode with a larger motion of 'C(2)−H, and the peaks at around 800 and 900 cm⁻¹ depending on the alkyl-chain length are small. The data in the 800−950 cm⁻¹ range in Figure 4 indicate that the out-of-plane 'C(2)−H and 'C(4,5)−H bending mode with a larger motion of 'C(2)−H is essentially the intramolecular vibrations within the imidazolium ring cation, and the absorption intensities, absorption frequencies, and band shapes are determined by the number of ion pairs and interactions with the counter anions. Hereinafter, we refer to the out-of-plane 'C(2)−H and 'C(4,5)−H bending mode with a larger motion of 'C(2)−H as the out-of-plane 'C(2)−H bending mode. However, in the 800−950 cm⁻¹ range, there are IR-active vibrational modes of anions of [N(CN)₂⁻], [PF₆⁻], and [PF₆(C₆F₅)₃⁻]. Among these, [PF₆⁻] and [PF₆(C₆F₅)₃⁻] have very strong absorption bands in the 800−950 cm⁻¹ range, as shown in Figure 4, which make it difficult to analyze the out-of-plane 'C(2)−H bending mode in this range. Accordingly, we do not analyze the data in the 800−950 cm⁻¹ range for [C₆mim⁺][PF₆⁻] ILs and [C₆mim⁺][PF₆(C₆F₅)₃⁻] IL. In Figure 4a,b, we found a very broad absorption band for [C₆mim⁺][Cl⁻] ILs and [C₆mim⁺][Br⁻] ILs, which covers from the red to the blue region at 800−950 cm⁻¹. The very broad absorption band cannot be analyzed as a single Gaussian peak. Accordingly, the out-of-plane 'C(2)−H bending mode for [C₆mim⁺][Cl⁻] and [C₆mim⁺][Br⁻] strongly shows both blue- and red-shifted tendencies. In Figure 4c for [C₆mim⁺][I⁻] ILs, we found a broad absorption band that has a red-shifted peak with the long tail and a weak shoulder structure in the blue region. In Figure 4d for [C₆mim⁺][SCN⁻] ILs, we found a broad absorption band that has a red-shifted peak with the long tail in the blue region. In Figure 4e for [C₆mim⁺][N(CN)₂⁻] ILs, we found a broad absorption band that has a red-shifted peak with the long tail in the blue region and an additional peak at around 900−910 cm⁻¹ because of the vibrational mode of the anion (913 cm⁻¹ in the calculation) (see Figure S5, Supporting Information). In Figure 4f for [C₆mim⁺][TO⁺] ILs, we found
a moderately broad absorption band, whereas in Figure 4g,h for \([\text{C}_n\text{mim}^+][\text{Tf}_2\text{N}^-]\) ILs and \([\text{C}_n\text{mim}^+][\text{BF}_4^-]\) ILs, we found a simple absorption band. To proceed with further analysis, we performed a multipeak fitting using the data at 800–920 cm\(^{-1}\) in Figure 4, as shown in Figure 5. Because the normalized absorbance spectra are nearly identical concerning the absorption intensities, absorption frequencies, and shapes of the absorption bands for IL samples that have methylimidazolium cations with carbon chains of different lengths and the same anions, the data of IL samples with \([\text{C}_6\text{mim}^+]\) or \([\text{C}_4\text{mim}^+]\) were representatively chosen.

Interestingly in Figure 5, we found both blue- and red-shifted tendencies in the out-of-plane \(+C(2)−H\) bending mode for each IL sample, although the red-shifted portion is relatively larger than the blue-shifted portion. The order of the red-shifted tendencies for anions is \([\text{Cl}^-]\), \([\text{Br}^-]\), \([\text{I}^-]\), \([\text{SCN}^-]\), \([\text{N(CN)}_2^-]\), \([\text{TfO}^-]\), and \([\text{Tf}_2\text{N}^-]\) ≈ \([\text{BF}_4^-]\). The order of the blue-shifted tendencies for anions is \([\text{Cl}^-]\), \([\text{Br}^-]\), \([\text{I}^-]\) ≈ \([\text{SCN}^-]\) ≈ \([\text{N(CN)}_2^-]\), \([\text{TfO}^-]\), and \([\text{Tf}_2\text{N}^-]\) ≈ \([\text{BF}_4^-]\). In fact, \([\text{C}_6\text{mim}^+][\text{Tf}_2\text{N}^-]\) and \([\text{C}_6\text{mim}^+][\text{BF}_4^-]\) do not show both red-shifted and blue-shifted tendencies because these two were observed as a simple Gaussian peak. In the present paper, we take the peak wavenumber (848 cm\(^{-1}\)) of the \(+C(2)−H\) bending mode for \([\text{C}_6\text{mim}^+][\text{BF}_4^-]\) as the reference wavenumber to classify the bands as being shifted to lower value or higher value. As an overall view, both red-shifted and blue-shifted orders are well-correlated with the order of the hydrogen bond basicity.\(^{42}\) Highly characteristic behaviors are the fact that the shifted tendencies of the out-of-plane \(+C(2)−H\) bending mode are emphasized in both the red and blue sides by the strength of the hydrogen-bond-type interactions. As far as stretching modes are concerned, the hydrogen-bond-type interaction in \(+C(2)−H\)···\(A\)−interactions for imidazolium-based ILs\(^{28,30−35,42,43}\) or the hydrogen bond in \(X−H···Y\) interactions for the other general liquid systems have been thoroughly investigated.\(^{44−47}\) General spectroscopic features of the hydrogen bond formation in stretching modes include the red shift of the peak position, the enhancement of the intensity, and the broadening of the absorption band.\(^{39,44−46}\) The red shift of the peak because of the hydrogen-bond-type interaction in \(+C(2)−H···A\) interactions in imidazolium-based ILs has been explained as a lengthened covalent bond \((+C−H)\) by increasing the strength of the hydrogen bond, which phenomenologically means a weaker force constant of

![Figure 5. Molar-concentration-normalized absorbance spectra in the 800–920 cm\(^{-1}\) range for (a) \([\text{C}_6\text{mim}^+][\text{Cl}^-]\), (b) \([\text{C}_6\text{mim}^+][\text{Br}^-]\), (c) \([\text{C}_6\text{mim}^+][\text{I}^-]\), (d) \([\text{C}_4\text{mim}^+][\text{SCN}^-]\), (e) \([\text{C}_6\text{mim}^+][\text{N(CN)}_2^-]\), (f) \([\text{C}_6\text{mim}^+][\text{TfO}^-]\), (g) \([\text{C}_6\text{mim}^+][\text{Tf}_2\text{N}^-]\), and (h) \([\text{C}_6\text{mim}^+][\text{BF}_4^-]\). Multipeak fitting was performed for each figure. The data in the 800–920 cm\(^{-1}\) range were fitted by one or two Gaussian peaks shown as dotted lines. In (e), an additional Gaussian peak at around 900–910 cm\(^{-1}\) because of the vibrational mode of the anion was shown as a dot-dash line. In (h), the data between 800 and 810 cm\(^{-1}\) were not used for fitting because the data between 800 and 810 cm\(^{-1}\) includes the influence of the tail of the absorption band because of the vibrational mode of the anion whose peak exists at the lower frequency (see Figure 4h).]
the intramolecular \(^{1}\text{C}−\text{H}\) stretching mode.\(^{22−24,33}\) On the other hand, the blue-shifting phenomena in stretching modes by the hydrogen bond formation have been observed in some specific liquid systems. To interpret the origin of the blue-shifting phenomena, numerous efforts have been made both experimentally and computationally.\(^{48−52}\) It has been pointed out that whether it is the red shift or blue shift is determined by the balance between the attractive and repulsive interactions between (X, Y) and (Y, H).\(^{51}\) In the interactions of \([\text{C}(2)−\text{H}]−\text{······A}−\) in imidazolium-based ILs and \([\text{H}_2\text{O}]−\text{······A}−\) in imidazolium-based ILs in the presence of a slight amount of water, the blue-shifting phenomena in stretching modes have not been observed.\(^{28,33}\) As far as bending modes are concerned, the hydrogen-bond-type interaction in \([\text{C}(2)−\text{H}]_{\text{bending}}−\text{······A}−\) interactions in imidazolium-based ILs has rarely been studied.\(^{26}\) In some conventional liquids such as water, the hydrogen bonds for the in-plane bending modes have been studied. In water systems, the comparison between gas phase and liquid systems is possible, and the bending modes exist at 1595 cm\(^{−1}\) in water vapor (isolated water molecules) and 1645 cm\(^{−1}\) in liquid water. Thus, the blue shift of 50 cm\(^{−1}\) was observed. The shift of the water bending mode toward higher frequency is a measure of stronger hydrogen bond networks, and the water bending mode has been utilized as a suitable vibrational mode for studying the hydration structure and dynamics of water.\(^{33−36}\) In IL systems, we should bear in mind the fact that the comparison between gas-phase and liquid systems is generally difficult because of their nonvolatility. In return, we can investigate the hydrogen-bond-type interaction in \([\text{C}(2)−\text{H}]_{\text{bending}}−\text{······A}−\) interactions for various imidazolium-based ILs with different anion species. Interestingly, in the present studies, we found that the shifted tendencies because of the hydrogen bonding in \([\text{C}(2)−\text{H}]_{\text{bending}}−\text{······A}−\) interactions are emphasized in both the red and blue sides by the strength of the hydrogen bonding, which means that both weaker and stronger force constants of intramolecular \(^{1}\text{C}(2)−\text{H}\) bending mode because of the hydrogen-bond-type interactions exist phenomenologically. In general, hydrogen bonds are the local and directional interactions. Intramolecular \(^{1}\text{C}(2)−\text{H}\) bending mode under the hydrogen-bond-type interactions may be sensitive to the relative positions and orientations between \(^{1}\text{C}(2)−\text{H}\) and \(\text{A}−\) and their distributions, which make both weaker and stronger force constants of intramolecular \(^{1}\text{C}(2)−\text{H}\) bending mode phenomenologically. Our data provide insights on the strength, relative positions and orientations, and their distributions involved in hydrogen-bond-type interactions, which also related to the hydrogen-bond network in IL systems.\(^{57,58}\) The study of the dynamics of intramolecular \(^{1}\text{C}(2)−\text{H}\) bending mode would be interesting.

Finally, we discuss the correlation between the concentration-normalized absorbance of imidazolium-based ILs because of the \(^{1}\text{C}(2)−\text{H}\) stretching vibration and the \(^{1}\text{C}(4/5)−\text{H}\) stretching vibration in the 3000 and 3200 cm\(^{−1}\) region, the center frequency of the broad absorption band below 150 cm\(^{−1}\) because of intermolecular vibrations in our previous study,\(^{26−28}\) and the concentration normalized absorbance because of the \(^{1}\text{C}(2)−\text{H}\) bending vibration and the \(^{1}\text{C}(4/5)−\text{H}\) bending vibration in the 700 and 950 cm\(^{−1}\) region in the present study for the \(^{1}\text{C}(2)−\text{H}\) and \(^{1}\text{C}(4/5)−\text{H}\) stretching vibrations in the 3000 and 3200 cm\(^{−1}\) region, the molar-concentration-normalized absorbance for ILs that have methylimidazolium cations with carbon chains of different lengths and same anions were nearly identical regarding the absorption intensities and frequencies and absorption band shapes, which were determined by the number of ion pairs.\(^{28}\) This essentially holds for the \(^{1}\text{C}(2)−\text{H}\) bending vibration and the \(^{1}\text{C}(4/5)−\text{H}\) bending vibration in the 700–950 cm\(^{−1}\) region, although the absorption bands in the 700–800 cm\(^{−1}\) region are moderately identical because of the influence of the vibrations of the alkyl-chain part and anions. For the \(^{1}\text{C}(4/5)−\text{H}\) symmetric stretching vibration observed as a higher frequency absorption band in the 3000 and 3200 cm\(^{−1}\) region, the absorption frequency was slightly red-shifted or almost unchanged with the strengthening of hydrogen-bond-type interactions with the anion.\(^{28}\) For the \(^{1}\text{C}(4/5)−\text{H}\) bending vibration, the peaks of the absorption bands exist at 745–765 cm\(^{−1}\) regardless of the anion species, and it is not particularly sensitive to the strength of the hydrogen-bond-type interactions. For very strong proton acceptors [Cl\(^{−}\)] and [Br\(^{−}\)], the absorption bands are a little broader to both the red and blue sides. Accordingly, close correlations between the \(^{1}\text{C}(4/5)−\text{H}\) symmetric stretching vibration and the \(^{1}\text{C}(4/5)−\text{H}\) bending vibration were observed, which was shown to be valid for a wide range of methylimidazolium ILs. For the \(^{1}\text{C}(2)−\text{H}\) stretching vibration that exists at lower frequency in the 3000 and 3200 cm\(^{−1}\) region, the absorption band becomes broader and the peaks of the absorption band are red-shifted with the strengthening of the hydrogen-bond-type interactions or proton acceptor of anions.\(^{28}\) For the \(^{1}\text{C}(2)−\text{H}\) bending vibration, the absorption band becomes broader and has both red- and blue-shifted tendencies with the strengthening of the hydrogen-bond-type interactions or proton acceptor of anions. Moreover, regardless of the differences in the frequency regions or the differences in the types of the mode, we note that the absorption band shapes of \([\text{C}_n\text{mim}^+]\, [\text{I}^{−}],\, [\text{C}_4\text{mim}^+]\, [\text{SCN}^{−}],\) and \([\text{C}_n\text{mim}^+]\, [\text{N(CN)}_2^{−}]\) with strong acceptors, and the absorption band shapes of \([\text{C}_n\text{mim}^+]\, [\text{BF}_4^{−}]\) with weakly coordinated anions are similar in each frequency region or mode. Accordingly, close correlations between the \(^{1}\text{C}(2)−\text{H}\) stretching vibration and the \(^{1}\text{C}(2)−\text{H}\) bending vibration were observed, which was shown to be valid for a wide range of methylimidazolium ILs.

In the previous and present studies, we investigated the influence of hydrogen-bond-type interaction in \([\text{C}−\text{H}]_{\text{bending}}−\text{······A}−\) and \(\text{C}−\text{H}−\text{······A}−\) interactions. It should be noted that the red-shifted \(^{1}\text{C}(2)−\text{H}\) stretching vibrations in the 3000–3200 cm\(^{−1}\) region and both red- and blue-shifted \(^{1}\text{C}(2)−\text{H}\) bending vibrations in the 700–950 cm\(^{−1}\) region were observed by the frequency change of intramolecular vibrational modes interacting with anions with IR spectroscopy. Accordingly, these vibrations are thought to be more sensitive to the local interactions such as hydrogen-bond-type interactions. On the other hand, THz-TDS and FIR spectroscopy can directly explore intermolecular vibrations because of the cation–anion interactions that include Coulomb interactions as well as local and directional hydrogen-bond-type interactions. We previously found that the central frequencies of intermolecular vibrational modes phenomenologically are on the essential contribution of the reduced mass \(\mu\) calculated from the respective masses of the methylimidazolium ring cation \([\text{mim}^{−}]\) and the anion \([\text{A}^{−}]\), as well as the force constant \(k\), which is established for a wide variety of methylimidazolium ILs.\(^{26−28}\) The correlation between the intramolecular \(^{1}\text{C}(2)−\text{H}\) stretching vibrations (or \(^{1}\text{C}(2)−\text{H}\) bending vibration) and the intermolecular vibration is not necessarily observed for a wide range of methylimidazolium ILs.
CONCLUSIONS

We systematically investigated the 700–950 cm\(^{-1}\) range of IR spectroscopy for imidazolium-based ILs in conjunction with the data with DFT calculations. In this range, there are two main and important vibrational modes (out-of-plane \(^{\text{C}(2)}\)–H bending mode and out-of-plane \(^{\text{C}(4,5)}\)–H bending mode) for studying the nature of interactions between cation and anions, especially on the hydrogen-bond-type interaction in ILs. We found that the normalized absorbance spectra in the 700–800 cm\(^{-1}\) range for IL samples that have methylimidazolium cations with carbon chains of different lengths and the same anions are moderately identical as for absorption intensities and absorption frequencies, and that those in the 800–950 cm\(^{-1}\) range are nearly identical, which means that the absorption intensities and frequencies and the absorption band shapes are decided by the number of ion pairs and the interactions between ion pairs. With respect to the out-of-plane \(^{\text{C}(4,5)}\)–H bending mode, we found that the out-of-plane \(^{\text{C}(4,5)}\)–H bending mode is not particularly sensitive to local interactions with anions, such as hydrogen-bond-type interactions. With respect to the out-of-plane \(^{\text{C}(2)}\)–H bending mode, we found that the absorption band becomes broader and has both red- and blue-shifted tendencies in the strengthening of the hydrogen-bond-type interactions or the proton acceptor of anions, although the red-shifted portion is relatively larger than the blue-shifted portion. Accordingly, the out-of-plane \(^{\text{C}(2)}\)–H bending mode is highly sensitive to local and directional hydrogen-bond-type interactions, and the shifted tendencies of the out-of-plane \(^{\text{C}(2)}\)–H bending mode are very characteristic and interesting. Intramolecular \(^{\text{C}(2)}\)–H bending mode under the hydrogen-bond-type interactions may be sensitive to the relative positions and orientations between \(^{\text{C}(2)}\)–H and \(^{\text{A}}\) and their distributions. We also discussed the correlation between the concentration-normalized absorbance of imidazolium-based ILs because of \(^{\text{C}(2)}\)–H and \(^{\text{C}(4,5)}\)–H stretching vibrations, \(^{\text{C}(2)}\)–H and \(^{\text{C}(4,5)}\)–H bending vibrations, and low-frequency intermolecular vibrations. We found a close correlation between \(^{\text{C}(2)}\)–H and \(^{\text{C}(4,5)}\)–H stretching vibrations and \(^{\text{C}(2)}\)–H and \(^{\text{C}(4,5)}\)–H bending vibrations for a wide range of imidazolium-based IL systems, whereas the correlation between these intramolecular vibrations and the low-frequency intermolecular vibrations is not necessarily observed for a wide range of imidazolium-based IL systems. Our systematic data and analysis on the \(^{\text{C}(2)}\)–H and \(^{\text{C}(4,5)}\)–H bending vibrations obtained in the present paper and comparisons with other theoretical and experimental studies are useful for elucidating the nature of noncovalent interaction in imidazolium-based ILs such as long-range Coulomb interactions, dispersion interactions, hydrogen-bond-type interactions, and their networks.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00938.

Original ATR-IR spectra in the 700–950 cm\(^{-1}\) range without molar concentration normalization and calculated vibrational spectra for molecular anions ([SCN\(^{-}\]), [TFO\(^{-}\]), [PF\(_6^{-}\]), and [N(CN)\(_2\)]\(^{-}\)] in the 700–950 cm\(^{-1}\) range (PDF)

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Notes

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