Ionic Liquids

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Spectroscopic Evidence for an Enhanced Anion–Cation Interaction from Hydrogen Bonding in Pure Imidazolium Ionic Liquids**

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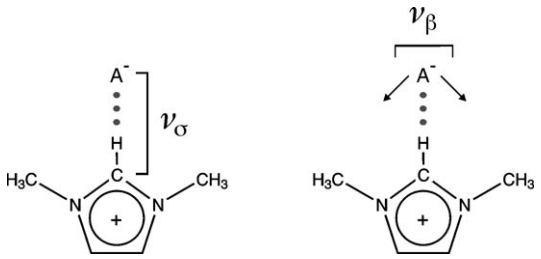
Ionic liquids (ILs) have many valuable applications in chemistry and technology.[1–6] They are understood as liquids consisting entirely of ions and having melting points below 100 °C. The interesting properties of ionic liquids are governed by the type and strength of interaction between its constituents. It is assumed that hydrogen bonding plays an important role for the properties and reaction dynamics of these Coulomb systems. The presence of hydrogen bonding in the structure of 1-alkyl-3-methylimidazolium salt was first reported by Seddon et al. in 1986.[7] Since then, evidence for hydrogen bonding has been obtained from X-ray diffraction and mid-infrared and NMR spectroscopy. Local and directional interactions, such as hydrogen bonds, in imidazolium-based ILs are indicated by shorter C–H···anion distances, red-shifted C–H frequencies, and downfield-shifted C–H proton chemical shifts.[8–18] Indications of hydrogen bonding is also provided by theoretical studies.[19–22] Recently however, some authors have strongly challenged the presence of hydrogen bonds in ionic liquids, and claimed that hydrogen bonding need not be invoked for explaining IL properties.[23–25]

For this reason, we initiated a program of direct spectroscopic observation of hydrogen bonds by successively increasing hydrogen bond abilities in a set of well-chosen imidazolium-based ionic liquids. Studying and understanding these interactions is a real challenge, and in particular for ILs. For imidazolium-based ILs, hydrogen bonding in infrared spectroscopy has been primarily concerned with the shift ($\Delta\nu_s$) of the C–H stretching frequency in the mid-infrared region. However, it is more pertinent to observe the stretching (ν_σ) and bending (ν_β) frequencies of hydrogen bonds themselves in far-infrared (FIR) spectra.[26–28] These modes are shown and assigned in Scheme 1.

The force constants obtained from these frequencies provide information about the hydrogen-bonding potential function as well as being a measure of the bond strength. Unambiguous assignment of the hydrogen-bond frequencies has provided a major difficulty in the FIR investigations. In particular, the low-frequency spectrum is surprisingly rich in information. Even for light molecules, low-energy intramolecular vibrations, such as torsions and certain skeletal motions, fall in the FIR region. Recently, we presented the low-frequency vibrational spectra of imidazolium-based ionic liquids in the range 30–300 cm^{-1} obtained by FIR spectroscopy.[27,28] We could show that the wavenumbers above 150 cm^{-1} can be assigned to intramolecular bending and wagging modes of cations and anions in the ionic liquid. The contributions below 150 cm^{-1} were assigned to the bending and stretching vibrational modes of the intermolecular anion–cation interactions. This assignment was supported by DFT calculations, which gave wavenumbers for the bending and stretching modes of ion pairs and ion-pair aggregates in this frequency range. We also suggested that the frequencies and intensities of the FIR vibrational bands may contribute to the development of forcefields in molecular dynamics simulations.[29]



Scheme 1. The stretching (ν_σ) and bending (ν_β) frequencies of a hydrogen bond shown for the $^+$C2–H···A$^-$ interaction in a 1,3-dimethylimidazolium cation.

However, important issues could not be clarified definitively. To what extend does the intermolecular vibrational band stem from localized short-ranged H-bonds and/or from non-localized long-ranged Coulomb forces? This question is addressed herein by choosing the same anion for all the ILs and successively increasing the H-bond abilities of the depicted cations. The second unclear point concerns the origin of the frequency shifts for the intermolecular vibrational bands. Following the solution of the equation for simple harmonic oscillators, $\omega = (k/\mu)^{1/2}$, those shifts can occur either from the changing force constant and/or the reduced masses. This problem is addressed herein by choosing cations that give comparable or even the same reduced masses in combination with the same anion. If that is the case, the frequency shifts can be attributed to changing force constants and thus the changing strength of cation–anion interaction only.

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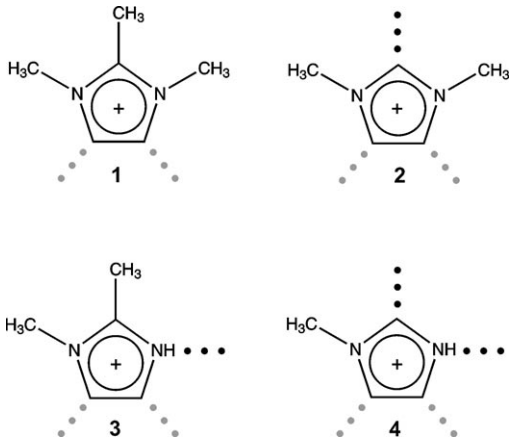
The purpose of this work is to give direct spectroscopic evidence for hydrogen bonding in imidazolium ILs by clarifying these important issues. First, we show that the different reduced masses have negligible effects on the frequency shifts because the interaction is local in nature. Second, we enhance the anion–cation interaction by increasing the number and strength of H-bond abilities, thereby indicating that we clearly observe H-bond stretching frequencies in ILs. These experimental findings are supported by ab initio calculations on larger IL aggregates.

We measured IR spectra of imidazolium ILs containing the same anion, bis(trifluoromethylsulfonyl)imide (NTf_2^-), but various cations: 1,2,3-trimethylimidazolium (1,2,3-trimethyl-im$^+$, **1**), 1,3-dimethylimidazolium (1,3-dimethyl-im$^+$, **2**), 1,2-dimethylimidazolium (1,2-dimethyl-im$^+$, **3**), and 1-methylimidazolium (1-methyl-im$^+$, **4**).[11,29–31] We should find similar contributions arising from the anions and different contributions stemming from the varying cations of these particular ILs. For direct spectroscopic observation of hydrogen bonds in molecular liquids, certain criteria have been established for making more positive assignments. The most convincing identification can be made when a hydrogen atom is substituted by a group that is incapable of hydrogen bonding; the bands associated with hydrogen-bond stretches or bends then disappear completely. In the present examples, the formation of hydrogen bonds is possible by C4–H and C5–H of the cation in all the ILs (Scheme 2). We gradually



Scheme 2. The cations of the imidazolium-based ILs **1**–**4**. The different position and numbers of H-bond abilities are indicated by the dotted lines. Black dotted lines: Additional H-bonds relative to **1**.

substituted the methyl group for the hydrogen at the C2–H and N–H positions. In **1**, both interactions C2–H and N–H are suppressed; in **2** and **3**, additional H-bonds are possible, either with C2–H or N–H, whereas in **4**, both interactions are allowed. The potential H-bond capabilities increase in the order **1**–**4**.

The measured FIR spectra in the frequency range 30–300 cm^{-1} are shown in Figure 1. First, we focus on the maximum intensities of the measured spectra below 150 cm^{-1}, which occur at 62.3 cm^{-1} (**1**), 85.7 cm^{-1} (**2**), 96.7 cm^{-1} (**3**), and

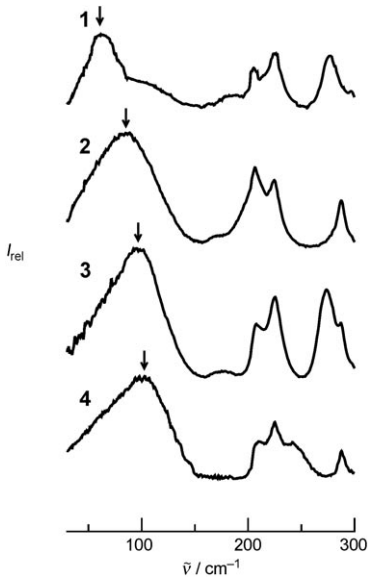


Figure 1. FIR spectra of imidazolium-based ILs **1**–**4** at 323 K for **2**–**4** and 383 K for **1**. The arrow indicates the maximum intensity of the anion–cation interaction.

100.7 cm^{-1} (**4**). These values were obtained from the deconvoluted spectra (see the Supporting Information). These contributions can be assigned to the stretching vibrational bands of hydrogen bonds $^+C–H\cdots A^-$ and/or $^+N–H\cdots A^-$. Obviously, the interaction between the cation and anion is of significantly different strength. The maxima of these bands shift to higher wavenumbers in the order from **1** to **4**; such a trend suggests enhanced interaction energy in this series. Increasing strength of a hydrogen bond results in shorter bond distances and larger force constants. The stronger the hydrogen bond, the higher the wavenumber and the corresponding intensity of the vibrational band. This effect is shown in the FIR spectra. Furthermore, we refer the measured low vibrational frequencies to average binding energies obtained for ab initio calculated clusters of ILs (Table 1). For that purpose, we have taken the average binding energies per ion pair of IL tetramers and plotted them versus the measured frequencies ν_σ (Figure 2, filled symbols). The nearly linear relationship indicates that the measured low vibrational bands truly describe the intermolecular forces and can be related to hydrogen bonding.

Another important issue can also be clarified. In principle, the origin of the frequency shifts for the intermolecular vibrational bands can occur either from the changing force constants or the reduced masses. This problem is addressed herein by choosing cations **1**–**4**, which give comparable or even the same (**2** and **3**) reduced masses in combination with the same anion. We know from ab initio calculations on large IL aggregates that the shifts to higher wavenumbers are mainly given by increasing force constants and only to minor extent by decreasing reduced masses. This finding is in accord with FIR studies on H-bonded molecular liquids, such as alcohols.[32,33] In these studies, it could be shown that the hydrogen-bond vibrations are to a large extent localized within the O–H···O part of the structure. Despite the

Table 1: Ab initio calculated energies E_{RHF}, counterpoise-corrected energies $E_{RHF}{}^{CP}$, and average binding energies per calculated ion pair E_{bin} of tetramers for ILs **0**–**4**.[a]

	IL	E_{RHF} [Hartrees]	$E_{RHF}{}^{CP}$ [Hartrees]	E_{bin} per ion pair [kJ mol^{-1}]
0	[1,2,3,4,5-m-im][NTf_2]	−8918.37359083	−8918.206618	−310.45
1	[1,2,3-m-im][NTf_2]	−8607.77470364	−8607.774703	−329.67
2	[1,3-m-im][NTf_2]	−8452.46713284	−8452.315770	−351.94
3	[1,2-m-im][NTf_2]	−8452.55835401	−8452.395913	−370.15
4	[1-m-im][NTf_2]	−8297.23866900	−8297.077549	−384.41
	1,2,3,4,5-m-im$^+$	−418.078716407		
	1,2,3-m-im$^+$	−340.42320286		
	1,3-m-im$^+$	−301.59058177		
	1,2-m-im$^+$	−301.60368286		
	1-m-im$^+$	−262.76866075		
	NTf_2^-	−1811.35431203		

[a] The calculated energies E_{RHF} are also given for the isolated cations and anions.

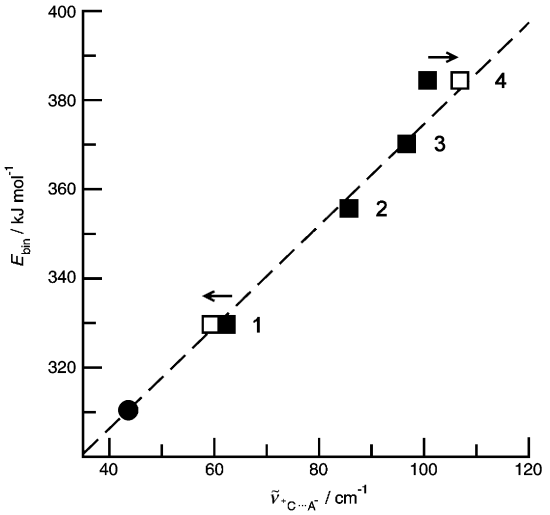


Figure 2. Average interaction energies E_{bin} per ion pair in tetramers of the ILs **1**–**4** plotted versus the measured H-bond frequencies $\nu_{+C\cdots A^-}$. Using the obtained linear relationship, the H-bond frequency for the calculated IL ([1,2,3,4,5-pentamethyl-im][NTf_2]) can be predicted (filled circle). Filled symbols: measured frequencies; open symbols: frequencies corrected for the reduced masses.

theoretical and experimental evidence for localized interactions, we assume that the entire masses of cation and anion involved in hydrogen bonding move during the ν_σ vibrations. The calculated reduced masses of ion pairs are given in Table 2. The measured frequencies for ILs **1** and **4** are then corrected for the reduced masses relative to those for ILs **2** and **3**. Correspondingly, the frequency of IL **1** is shifted to lower wavenumbers owing to its slightly higher mass (CH_3 in place of the H at C2 in **2**) and that of IL **4** to higher wavenumbers owing to its slightly lower mass (H in place of CH_3 at C2 in **3**), as indicated by the open symbols and arrows in Figure 2 (see also the Supporting Information). Overall, it can be seen that the maximum possible corrections for the different reduced masses change the wavenumbers only slightly. If that is the case, the frequency shifts can be attributed to changing force constants and thus only changing cation–anion interaction strength. In Figure 2, the binding energies and the corrected wavenumbers give a linear relationship. Obviously, the interaction energies increase characteristically with the H-bond abilities in the given ILs.

Table 2: Masses of the cations and anions and calculated reduced masses μ of the ionic liquids **1**–**4**.[a]

IL	cation [amu]	Anion [amu]	μ [amu]	ν_σ [cm^{-1}]	correction	corr. ν_σ [cm^{-1}]
1	111.092	279.917	79.529	62.3	−4.80%	59.3
2	97.076	279.917	72.079	85.7	0	85.7
3	97.076	279.917	72.079	96.7	0	96.7
4	83.061	279.917	64.054	100.7	+6.08%	106.8

[a] The reduced-mass corrections for the intermolecular frequencies ν_σ are given in percent and referred to the values of the ILs **2** and **3**.

The advantage of theoretical methods is that we can calculate binding energies of ionic liquids that are currently not accessible. This calculation has been done for [1,2,3,4,5-pentamethyl-im][NTf_2] (called IL **0** herein) which was synthesized by Ngo et al.[31] In this IL, all the ring protons are replaced by methyl groups; therefore, the H-bond abilities at C4–H and C5–H are suppressed, resulting in the lowest binding energies of all ILs. Using the obtained linear relationship, we can predict a maximum frequency for the intermolecular interactions of about 43 cm^{-1}. Because the interaction is purely ionic in nature, it is an open issue as to whether this vibrational contribution is detectable in the FIR region. A clear trend can be seen in the calculated binding energies (Figure 3): Starting from 310 kJ mol^{-1} for IL **0** with no H-bond abilities, we win about 20 kJ mol^{-1} by switching on H-bonds C4–H and C5–H, as present in ILs **1**–**4**. If additional H-bonding is possible with C2–H, we gain another

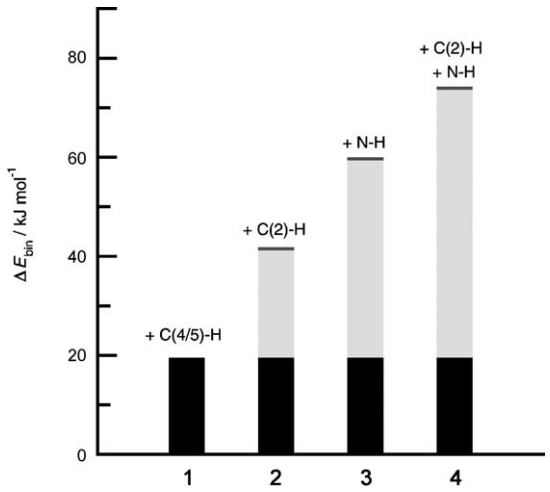


Figure 3. Dissection of the interaction energies for the tetramers of the ionic liquids **1**–**4** into different H-bond contributions depending on the H-bond strength and abilities. The energy for the calculated IL [1,2,3,4,5-pentamethyl-im][NTf_2] with no H-bond abilities is used as a reference and set to zero.

23 kJ mol^{-1} for IL **2**. If we now allow additional H-bonding with N–H instead of C2–H, as in IL **3**, we find stronger H-bonds up to 40 kJ mol^{-1}. And finally, if we switch on the H-bonds at both C2–H and N–H, we obtained the largest additional H-bond contribution of about 53 kJ mol^{-1} in total. Although the H-bond energies are typically overestimated at the present ab initio level, we find a clear trend and reasonable absolute values of enhanced anion–cation interaction owing to increasing hydrogen bonds in imidazolium ILs.

So far, we have discussed the intermolecular frequencies of the IL **1**–**4**. However, the intramolecular modes in the low frequency range also give some evidence for the H-bond strength and H-bond capabilities. The frequencies between 200 and 250 cm^{-1} can be assigned to intramolecular vibrations of the NTf_2^- anion. For example, the double peak slightly above 200 cm^{-1} represents the wagging modes of O=S=O groups. These bands are relatively sharp if only one H-bond is possible via C2–H or N–H, but broader and giving an additional third contribution if both H-bonds are possible (Figure 1). The vibrational band at about 270 cm^{-1} in the spectra for the ILs **1** and **3** represents the out-of-plane bending mode of the CH_3–C2 methyl groups in the imidazolium cation. Consequently this band is missing for the ILs **2** and **4**. The vibrational band at about 290 cm^{-1} stems from the out-of-plane bending mode of the CH_3–N methyl groups in the imidazolium cation and is present in all the ILs.

In summary, we report the direct observation of H-bond stretching frequencies in pure imidazolium ionic liquids from FIR spectroscopy. Reduced mass effects could be excluded, and the frequency shifts were related to the increasing force constants, thus indicating stronger cation–anion interactions. Ab initio calculations suggest a linear relationship between the interaction energies and the intermolecular stretching frequencies. Both properties are related to the increasing H-bond capabilities in the varying imidazolium cations. This finding clearly indicates that the stretching frequencies are a direct measure for hydrogen bonding in the ILs. We are currently extending our FIR studies to include a much wider range of hydrogen-bonded ILs and their mixtures in apolar solvents, from which we hope to obtain an even better description of hydrogen bonding in this new liquid material.

Experimental Section

1–**4** (purity > 98 %) were purchased from Iolitec GmbH (Denzlingen, Germany). For the IL **2**, the water content was found to be 56 ppm, as determined by Karl Fischer titration. The other ILs were solids at room temperature and used as delivered. Further purification was not carried out.

The FTIR measurements were performed with a Bruker Vertex 70 FTIR spectrometer equipped with an extension for measurements in the FIR region that consists of a multilayer mylar beam splitter, a room temperature DLATGS detector with preamplifier, and polyethylene (PE) windows for the internal optical path. The accessible spectral region for this configuration lies between 30 and 680 cm^{-1}. IL **1** was been measured slightly above the melting point (which we determined to be at 105.4 °C); the spectra for the ILs **2**–**4** were recorded at 50 °C throughout.

Ab initio calculations were performed at the Hartree–Fock level with the Gaussian 03 program[34] using the internal 3–21G basis set. The basis-set superposition error (BSSE)-corrected binding energies and average binding energies per ion were given for clusters comprising up to four ion pairs.[35]

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