Communications

The Cation–Anion Interaction in Ionic Liquids Probed by Far-Infrared Spectroscopy**

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Understanding cohesion energies and studying intermolecular forces are real challenges. Cohesion energies determine whether matter sticks together, gases condense to liquids, or liquids freeze to solids. Knowledge of intermolecular forces is in particular interesting for the class of ionic liquids. Although ionic liquids consist purely of ions they show a broad liquid range, and some of them have melting points well below 0°C.[1–3] On the other hand, ionic liquids show extremely low vapor pressures and high enthalpies of vaporization, which make them attractive as "green" solvents that could replace traditional industrial solvents.[4,5] Thus in some cases ionic liquids show typical liquid behavior, whereas in other cases they display more molten salt like behavior. However, the understanding of intermolecular forces is crucial for the development of special and tuneable properties of ionic liquids.

In principle, the interaction energies between cations and anions of an ionic liquid can be calculated by ab initio and DFT calculations. This has been done for a large number of ionic liquids comprising various cations and anions. Typical interaction energies lie between 300 and 400 kJ mol^{-1}.[6–12] However, these are calculated interaction energies for selected ion-pairs, and do not give the average interaction energies in the bulk ionic liquids. So far there is no direct evidence for the cation–anion interaction in ionic liquids. In principle, these interactions can be studied by experimental methods, such as optical heterodyne-detected Raman-induced Kerr-effect spectroscopy,[13–17] THz spectroscopy,[18–20] and low-energy neutron scattering, [21] which cover the frequency range of these interaction energies. FTIR and Raman studies on ionic liquids have focused on the mid infrared range and on investigations of the intramolecular stretching and bending modes.[22–35] The very little Raman work known does not discuss the low frequency range (0–300 cm^{-1}) in terms of intermolecular forces.[36]

To the best of our knowledge we present here the first FTIR measurements of imidazolium-based ionic liquids [C$_2$mim][SCN], [C$_2$mim][N(CN)$_2$], [C$_2$mim][EtSO$_4$], and [C$_2$mim][NTf$_2$] in the far infrared spectral region. The interpretation of the measured spectra is supported by ab initio calculated frequencies of ionic liquid clusters. The low-frequency vibrational bands between 50 and 120 cm^{-1} can be clearly assigned to the bending and stretching modes of the cation–anion interaction represented by the $^+$C—H$\cdots$A$^-$ hydrogen bonds in these ionic liquids. By varying the anion in these imidazolium-based ionic liquids, these bands shift in frequency and change intensity in a characteristic way corresponding to the strength of the calculated interaction energies. Thus we present a direct probe for studying the strength of interaction energies between cations and anions in ionic liquids.

The low-frequency FTIR spectra for the neat ionic liquids [C$_2$mim][SCN], [C$_2$mim][N(CN)$_2$], [C$_2$mim][EtSO$_4$], and [C$_2$mim][NTf$_2$] in the range between 30 and 300 cm^{-1} are shown in Figure 1. Overall it can be seen that the spectra show
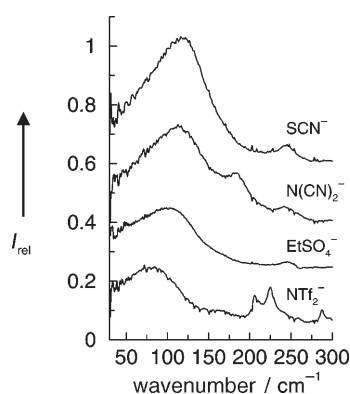

Figure 1. Low-frequency vibrational FTIR spectra of the ionic liquids [C$_2$mim][SCN], [C$_2$mim][N(CN)$_2$], [C$_2$mim][EtSO$_4$], and [C$_2$mim][NTf$_2$] measured at 273 K.

significant differences. Because we kept the imidazolium cation (C$_2$mim$^+$) constant, the differences can only arise from weak intramolecular vibrations of various anions and/or specific cation–anion interactions. Beside wavenumbers also the vibrational intensities vary significantly with the anions used.

Strong support for the interpretation of the low-frequency vibrational bands is provided by ab initio calculations of ionic liquid aggregates ([C$_2$mim][A])$_x$, where x is the number of ion-pairs contributing to the overall cluster, and A$^-$ represents the chosen anion. It is assumed that the largest clusters

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give the most liquid-like frequency spectra. In large clusters C(2)−H as well as C(4/5)−H are involved in hydrogen bonds of differing strength, which leads to slightly different intermolecular frequencies und intensities. A detailed interpretation of such a spectrum is given, for example, for the ionic liquid [C$_2$mim][N(CN)$_2$]. In Figure 2 the measured spectrum
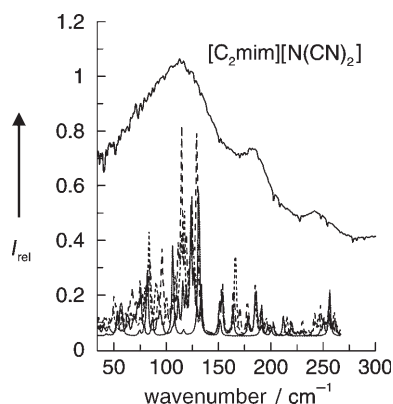

Figure 2. Measured low-frequency vibrational FTIR spectrum of [C$_2$mim][N(CN)$_2$] at 273 K compared to the ab initio calculated vibrational modes of the corresponding ionic liquid clusters [C$_2$mim][N(CN)$_2$]$_x$ with $x = 2$, 4, 6, and 8. The major vibrational bands are in agreement with the calculated frequencies, which are corrected for the harmonic approximation.

is shown along with the ab initio calculated vibrational frequencies of the ionic liquid clusters with $x = 2$, 4, 6, 8. In addition, in Figure 3, the low-frequency vibrational spectrum is deconvoluted into Voigt functions. It is clearly seen that the main features of the measured spectrum are reproduced by the calculated and deconvoluted vibrational bands. The band
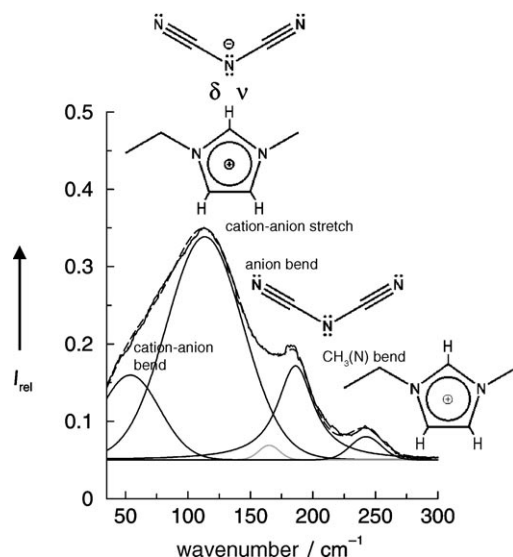

Figure 3. Measured low-frequency vibrational FTIR spectrum of [C$_2$mim][N(CN)$_2$] deconvoluted into four main vibrational bands, which can be assigned to the bending mode of the cation–anion bend ($\delta_{CH\cdots A}$), the cation–anion stretch ($\nu_{CH\cdots A}$), the anion bend ($\delta_{NC\text{-}N\text{-}CN}$), and the cation bend ($\delta_{CH_3\text{-}(N)}$), respectively.

around 240–250 cm^{-1} can be assigned to the out-of-plane bending mode of the CH$_3$−(N) methyl group in the imidazolium cation (C$_2$mim$^+$). This contribution therefore occurs in the measured spectra of all ionic liquids. The vibrational band at 170 cm^{-1} is attributed to the intramolecular bending mode of the N(CN)$_2^-$ ion of this ionic liquid. This assignment is supported by the calculated frequencies in this spectral range (see Figure 4 and the Supporting Information). Consequently,
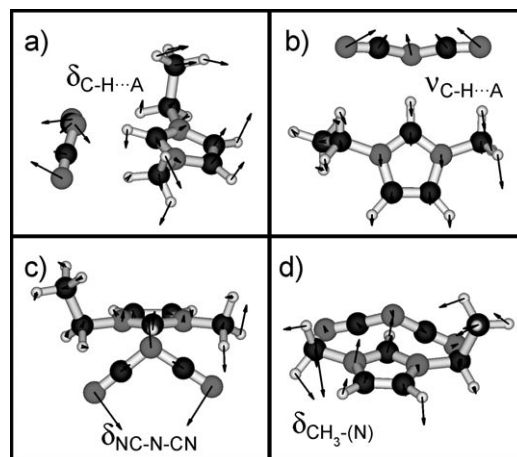

Figure 4. Calculated low-frequency vibrational modes of a [C$_2$mim][N(CN)$_2$] ion-pair bonded via C(2)−H. The vibrational modes contributing to the measured low-frenquency FTIR spectrum are shown: a) cation–anion bend ($\delta_{CH\cdots A}$), b) cation–anion stretch ($\nu_{CH\cdots A}$), c) anion bend ($\delta_{NC\text{-}N\text{-}CN}$), and d) cation bend ($\delta_{CH_3\text{-}(N)}$).

this vibrational contribution is missing in the spectra of all the other ionic liquids. The most interesting bands occur below 150 cm^{-1}. The calculated frequencies of differently sized ionic liquid clusters suggest that the highest intensity band at about 120 cm^{-1} can be clearly attributed to the stretching modes of the hydrogen bonds $^+$C−H$\cdots$A$^-$, where C−H can be either C(2)−H or C(4/5)−H (see Figure 2 and 3). The vibrational bands of lower intensity at about 50–60 cm^{-1} are attributed to the corresponding bending modes of these hydrogen bonds. The frequency range for the stretching mode of the hydrogen bond is a sensitive probe for the cation–anion interaction in a particular ionic liquid.

Regarding the low-frequency vibrational spectra of the other ionic liquids we can conclude the following: The vibrational bands at about 250 cm^{-1} can be assigned to the out-of-plane bending mode of the CH$_3$−(N) methyl group in the imidazolium cation (C$_2$mim$^+$) of each ionic liquid throughout. Whereas for [C$_2$mim][N(CN)$_2$] the vibrational band at 170 cm^{-1} can be assigned to the bending mode of the anion, this band is consequently missing for the ionic liquid [C$_2$mim][SCN]. For the ionic liquid [C$_2$mim][NTf$_2$], additional bands occur between 150 and 250 cm^{-1}, which can be assigned to intramolecular vibrations of the complex anion. For example, the double peak slightly above 200 cm^{-1} belongs to the wagging modes of O=S=O groups in the NTf$_2^-$ ion. Moreover, the shapes of the measured spectra show significant differences below 150 cm^{-1}. We assigned these contributions to the stretching and bending vibrational bands of the

hydrogen bonds $^+$C−H⋯A$^-$. Clearly, the strengths of the interactions between the cation and anion differ significantly. The maxima of these bands shift to lower wavenumbers in the order SCN$^-$, N(CN)$_2^-$, EtSO$_4^-$, and NTf$_2^-$. Such a trend suggests a decrease in interaction energy between cations and anions following this series. An increase in the strength of the hydrogen bond $^+$C−H⋯A$^-$ is accompanied by a lengthening of the covalent bonds C−H and a shortening of the hydrogen bonds $^+$C−H⋯A$^-$. The weaker force constants for the C−H bonds lead to lower wavenumbers and thus redshifted vibrational bands. This was shown for the region in which the C−H stretch vibrations of imidazolium-based ionic liquids appear. It could be demonstrated that the intramolecular C−H frequencies are redshifted inverse to the above given order of anions.[33,34] The opposite behavior is expected for the stretching modes of hydrogen bonds. Stronger hydrogen bonds means shorter intermolecular bonds and larger force constants. Thus the stronger the hydrogen bond, the larger the wavenumber and the corresponding intensity of the vibrational band. This behavior is reflected in our low-frequency vibrational spectra. In the order SCN$^-$, N(CN)$_2^-$, EtSO$_4^-$, and NTf$_2^-$, the wavenumbers and the intensities decrease. The maxima are found at 117.6, 113.5, 106.4, and 83.5 cm^{-1}, respectively. Here we should emphasize that the resulting wavenumbers for the vibrational modes are determined not only by the force constants but also by the reduced masses via $\tilde{\nu} = (1/2\pi c)\sqrt{k/\mu}$, where c is the speed of light, k the force constant, and μ the reduced mass. However the ab initio calculations clearly show that the shifts to lower wavenumbers in the order SCN$^-$, N(CN)$_2^-$, EtSO$_4^-$, and NTf$_2^-$ are attributed primarily to decreasing force constants and only to a minor extent to increasing reduced masses. Although the masses of the anions in the ionic liquids [C$_2$mim][SCN] and [C$_2$mim][NTf$_2$] differ significantly, the reduced masses contributing to the low vibrational modes are very similar. Whereas SCN$^-$ moves completely, NTf$_2^-$ is only partly involved in the vibrational motion, which results in reduced masses of comparable size. Also the relationships between binding energies and vibrational modes as well as those between intra- and intermolecular vibrational modes, as discussed in the next section, could not have been explained otherwise.

Already in the 1940s Badger and Bauer proposed a relationship between O−H infrared stretching frequencies and hydrogen bond energies.[37,38] We propose a similar procedure for the intermolecular vibrational frequencies and the corresponding interaction energies in ionic liquids. There are numerous calculated binding energies of isolated ion-pairs available.[6–12] However, isolated ion-pairs do not represent the structure and binding energy that is valid in the liquid phase. For example, some of the ab initio calculated energy-minimized ion-pairs give anions sitting on top of the imidazolium ring. Such configurations may be possible in the gas phase but do not occur in the solid and liquid phases.[39] Thus we assigned the measured low vibrational frequencies to average binding energies obtained for the larger ionic liquid clusters (Table 1). The average binding energies per ion of the hexamers ([C$_2$mim][N(CN)$_2$])$_6$, ([C$_2$mim][SCN])$_6$, ([C$_2$mim]-[EtSO$_4$])$_6$, and ([C$_2$mim][NTf$_2$])$_6$, respectively, were plotted

Table 1: Ab initio calculated energies E_{RHF}, counterpoise-corrected energies E_{RHF}^{CP}, and average binding energies per ion E_{bin} of the ionic liquid hexamers studied, as well as E_{RHF} for the cation and anions.

	E_{RHF} [Hartree]	E_{RHF}^{CP} [Hartree]	E_{bin} [kJ mol^{-1}]
([C$_2$mim][SCN])$_6$	−4967.925731550	−4967.922445339	−217.34
([C$_2$mim][N(CN)$_2$])$_6$	−3469.921367370	−3469.826269711	−205.40
([C$_2$mim][EtSO$_4$])$_6$	−6671.972255055	−6671.630734454	−194.05
([C$_2$mim][NTf$_2$])$_6$	−12911.662250800	−12911.379824060	−168.29
C$_2$mim$^+$	−340.414132021		
SCN$^-$	−487.407464350		
N(CN)$_2^-$	−237.733852763		
EtSO$_4^-$	−771.376576845		
NTf$_2^-$	−1811.35431203		

against the measured intermolecular frequencies (Figure 5). The obtained relationship indicates that the measured low-frequency vibrational bands really describe the intermolecular forces. Recently, we used the association of water
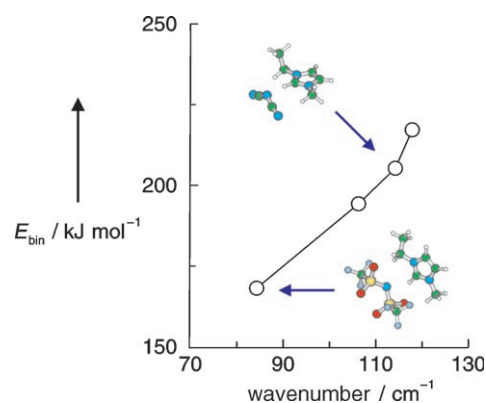

Figure 5. Calculated average binding energies per ion (E_{bin}) of ionic liquid hexamers ([C$_2$mim][SCN])$_6$, ([C$_2$mim][N(CN)$_2$])$_6$, ([C$_2$mim]-[EtSO$_4$])$_6$, and ([C$_2$mim][NTf$_2$])$_6$ versus deconvoluted stretching vibrational modes from the low-frequency FTIR spectra of the same ionic liquids.

molecules in similar ionic liquids as sensitive probes for hydrogen bonding by measuring the intramolecular symmetric and asymmetric stretching vibrations of H$_2$O and D$_2$O.[40] In Figure 6 the average frequencies of ν_1 and ν_3 of the water molecules (H$_2$O) are plotted versus our measured intermolecular frequencies of the neat ionic liquids. We find a nearly linear relationship, which suggests that the intramolecular vibrational frequencies of water and the intermolecular cation–anion vibrational modes both reflect the ionic strength of the anion in the ionic liquid. This supports our earlier statement that the shift of the intermolecular vibrational bands results from decreasing force constants and not from different reduced masses due to the anions. The intramolecular O−H stretching frequencies show the same anion dependency as the intermolecular vibrational modes, although the intramolecular vibrational frequencies of water are completely independent of the anion masses. That less interacting anions such as NTf$_2^-$ show lower interaction
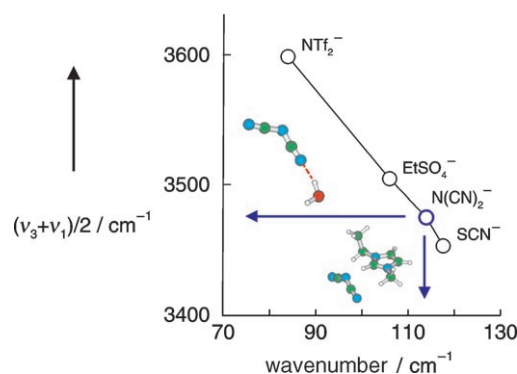
Figure 6. Relationship between the average of the symmetric (v_1) and asymmetric stretching (v_3) frequencies of water molecules dissolved in [C$_2$mim][SCN], [C$_2$mim][N(CN)$_2$], [C$_2$mim][EtSO$_4$], and [C$_2$mim][NTf$_2$] (taken from reference [40]), and the intermolecular stretching vibrations between cations and ions of the corresponding neat ionic liquids.

energies is in agreement with recent findings on the viscosity of ionic liquids.[41]

With a combination of FTIR measurements in the far-infrared region and ab initio calculations, we have studied the cohesion energies between cations and anions in imidazolium-based ionic liquids. We showed that the bands with the lowest frequencies can be assigned to the bending and stretching vibrational modes of the cation–anion interaction represented by the hydrogen bond $^+$C—H···A$^-$. The intermolecular stretching modes are shifted to higher wavenumbers with increasing ionic strength of the used anion and can be correlated to the calculated average binding energies of the ionic liquid. They clearly reflect the cohesive energy between cations and anions in ionic liquids.

Experimental Section

The ionic liquids were purchased from Iolitec GmbH (Denzlingen, Germany) with a stated purity of > 98 %. All ionic liquids were dried in vacuum ($p = 8 \times 10^{-3}$ mbar) for about 36 h. The water content was then determined by Karl-Fischer titration and was found to be 336 ppm ([C$_2$MIM][EtSO$_4$]), 228 ppm ([C$_2$MIM][N(CN)$_2$]), 220 ppm ([C$_2$MIM][SCN]), and 113 ppm ([C$_2$MIM][NTf$_2$]). Further purification was not carried out.

The FTIR measurements were performed with a Bruker Vertex 70 FTIR spectrometer. The instrument was equipped with an extension for measurements in the far infrared region. This equipment consisted 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}. The spectra were deconvoluted into a number of Voigt functions as described elsewhere.[40]

Ab initio calculations were performed at the Hartree–Fock level with the Gaussian 98 program.[42] using the internal stored 3-21G basis set. The basis set superposition error (BSSE) corrected binding energies and average binding energies per ion of [C$_2$mim][N(CN)$_2$], [C$_2$mim][SCN], [C$_2$mim][EtSO$_4$], and [C$_2$mim][NTf$_2$] for clusters comprising six ion-pairs are given in Table 1.[43] We are aware that numerous calculations of isolated ion-pairs of ionic liquids are available. However, we needed consistent binding energies for the ionic liquids considered in this work. The vibrational frequencies for the clusters ([C$_2$mim][C(CN)$_2$])$_x$ with x = 2, 4, 6, and 8 were corrected

by the standard factor 0.89 (see Supporting Information). The cluster frequencies could not be calculated at higher ab initio levels than RHF/3-21G due to computational limitations.

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