What far-infrared spectra can contribute to the development of force fields used in molecular dynamics simulations

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INTRODUCTION

Ionic liquids (ILs) are organic salts with melting points below 100°C. They represent a new class of non-molecular liquid materials with unique properties. The field of ionic liquids offers phenomenal opportunities for new advances in science and technology. The increased interest in these new materials can be attributed to the diversity of possible applications, either as solvents for reactions and material processing or as extraction media and working fluids in mechanical applications. Any use of an ionic liquid entails the knowledge of its physical properties and solvent behavior. Some of their unique properties include their extremely low volatility, low melting point, high ionic conductivity as well as thermal and electrochemical stability. The unique variability of the ions often allows the properties of interest to be imparted, so that ILs are denoted as designer solvents.

For a rational design of ionic liquids it is important to understand their nature and interactions. In principle Molecular dynamics (MD) simulation is a powerful tool to obtain structural, dynamical and thermodynamic properties of such kind of liquids. The crucial point is the derivation of a reliable force field that can describe the interactions between ions in an appropriate way. For H-bonded liquids such as water, alcohols or amides this is usually done by fitting charges and Lennard-Jones parameters to experimentally well known properties. Force fields are parameterized to be in agreement with pair correlation functions from neutron or X-ray structure factors, self-diffusion coefficients from NMR and heats of vaporization from vapor pressure measurements. Until recently, most of these properties were not available for ionic liquids. Moreover, they are not easy to determine with sufficient accuracy, and they are effectively known only for a few members of some ionic liquid families. One of the first and most prominent force fields used for ILs was developed by two of us (J. N. Canongia Lopes, A. A. H. Pádua, (CLA)) using as starting point Lennard-Jones parameters taken from the OPLS force field describing similar organic (and neutral) molecules. The missing parameters (mainly atomic point charges and dihedral angles) were parameterized using data obtained using ab-initio and MD calculations. Due to the scarcity of data mentioned in the previous paragraph, the force field could only be validated by comparison of the MD simulation results with the corresponding crystalline structures and liquid densities of selected ionic liquids. A series of four articles represent the CLaP force field at this stage and establish a general protocol for the molecular simulation of common ionic liquids within the framework of statistical mechanics. It must be stressed out that the force field has been developed in the spirit of the OPLS model and is thus primarily oriented towards the calculation of structural and equilibrium thermodynamic properties of liquid phases. Moreover, the force field was built in a stepwise manner that allows the construction of models for entire families of ionic liquids and allows the mutual interchange of their anions or cations without further re-parameterization. However, the wide coverage of such a protocol comes at the expense of its accuracy for specific cases.

For the ionic liquids of the 1-alkyl-3-methylimidazolium bistriﬂamide family, \([\text{C}_n\text{mim}]\text{NTf}_2\), the measured density and the MD density differed by about 3% using the CLaP force field. It is more difficult to assess the ability of the this force field to predict transport properties. Calculation of diffusion coefficients through equilibrium molecular dynamics methods appears to lead to values that are one order of magnitude lower than experimental ones. It has been shown that inclusion of polarizable charges leads to faster dynamics when using equilibrium methods [12] resulting in a drop of about 1/3 in viscosity and a 3-fold increase in the ion diffusion coefficients. But other studies [13–15] have shown that use of nonequilibrium methods can lead to viscosities and diffusion coefficients that agree very well with experiment even for fixed-charge models, and in some of these calculations ions were parameterized through the CLaP model. Regarding transport properties, the roles of the model or of the simulation method in attaining quantitative predictions are not yet completely resolved. Finally, the estimated enthalpies of vaporization were too large (by 20 and
50%) when compared to the available experimental data.[16–20] In this case one can assume that some of the interactions in the \([\text{C}_n\text{mim}][\text{NTf}_2]\) ionic liquids are overestimated by the CLaP force field, leading to large enthalpy of vaporization values and also likely to slower dynamics. Bearing this assumption in mind, Köddermann et al. [21] parameterized a refined version of the CLaP force field against the liquid density, accurately measured self-diffusion coefficients of the cation and anion in \([\text{C}_2\text{mim}][\text{NTf}_2]\) at 303 K.[22, 23] as well as NMR rotational correlation times for the imidazolium cation and for water in \([\text{C}_2\text{mim}][\text{NTf}_2]\) at the same temperature.[24] The refined force field was then validated for the temperature behavior and the chain length dependence of these and other dynamics and thermodynamic properties. In a subsequent paper it has been shown that a number of thermodynamical properties such as densities, enthalpies of vaporization, as well as dynamical and transport properties of the pure IL could be reproduced almost quantitatively.[25] We could also show that this new refined force field was capable of semiquantitatively describing the solvation behavior of small apolar particles.[26] More importantly, it was clearly demonstrated that the solvation is characterized by an enthalpy-entropy compensation effect. The hydrophobic hydration behavior of small apolar particles is qualitatively similar to that in liquid water.[27–30] In addition, Köddermann et al. could prove for the first time the existence of a "solvophobic interaction" of apolar particles in ILs. Similar to the hydrophobic interaction of small solutes in water, the "solvophobic interaction" is stabilized by entropic and counterbalanced by enthalpic contributions. However, this force field refinement was only developed for a specific imidazolium-based ionic liquid \([\text{C}_2\text{mim}][\text{NTf}_2]\) and was only extended to \([\text{C}_n\text{mim}][\text{NTf}_2]\) ionic liquids with varying alkyl chain lengths \((n=2,4,6,8,\ldots).\) A more general protocol that is able to describe different ionic liquid families but that takes into account specific interaction features between selected anions and cations is highly desirable at this point.

With a combination of FTIR measurements in the far-infrared region and ab initio calculations, Fumino et al. [31] have studied the interaction energies between cations and anions in imidazolium-based ionic liquids. They 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 \(+\text{CH} \cdots \text{A}^{-}.\) The intermolecular stretching modes were shifted to higher wavenumbers with increasing ionic strength of the used anion and could be correlated to the calculated average binding energies of the ionic liquid. They clearly reflected the interaction energy between cations and anions in ionic liquids.

In a following work the same authors could show that the properties of imidazolium-based ILs can be tuned by adjusting the ratio between H-bond energies and Coulomb interactions.[32] These interactions are evident in the far-FTIR spectra, which show very pronounced, localized H-bond bands at 83.5 \(\text{cm}^{-1}\) for \([\text{C}_2\text{mim}][\text{NTf}_2]\) and increasing, well-distributed Coulomb interactions from 100 to 200 \(\text{cm}^{-1}\) for \([\text{C}_2\text{C}_1\text{mim}][\text{NTf}_2]\). Thus the far-infrared spectra are sensitive probes for the strength and type of interaction occurring between cations and anions in ionic liquids. It is exactly the information which will be needed to validate force fields.

In this paper we want to demonstrate that the intermolecular vibrational spectra of ionic liquids obtained from far IR measurements allow the testing of the quality of force fields used in molecular dynamics simulation. In particular the characteristic shape of the spectra suggests how to modify the force fields for a better description of this new class of compounds.

**EXPERIMENTAL SECTION**

**Far infrared spectroscopy**

The ionic liquids were purchased from Iolitec GmbH (Denzlinge, Germany) with a stated purity of \(>98\%\). All substances were dried in vacuum \((p=8 \times 10^{-3}\text{mbar})\) for approximately 36 h. The water content was then determined by Karl Fischer titration and was found to be 113 ppm in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide \(([\text{C}_2\text{mim}][\text{NTf}_2]=1)\) and 57 ppm in 1-ethyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide \(([\text{C}_2\text{C}_1\text{mim}][\text{NTf}_2]=2).\) 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 \(\text{cm}^{-1}\).
Molecular dynamics simulations

We performed constant pressure (NPT) MD simulations at 303 K and at a pressure of 1 bar using different force fields available for the imidazolium-based ionic liquids [8, 21]. In addition to the CLaP force field [8], we used our improved (nonpolarizable) fully-flexible all-atom force field which has been parameterized for imidazolium-based ILs of the type [C₈ mim][NTf₂]. The model is composed of atom-centered point-charges and Lennard-Jones interactions for non-bonded interactions [21]. The proper stereochemistry and conformational representations of the molecules are guaranteed by appropriately parameterized bond-angle and dihedral interactions taken from the CLaP force field [8]. This force field for [C₂ mim][NTf₂] has been refined in such a way that the simulated properties mostly agree with experimental densities, accurately measured self-diffusion coefficients for cations and anions in neat [C₂ mim][NTf₂] and NMR rotational correlation times for the cations in [C₂ mim][NTf₂] and water molecules in a 1 w% solution of water in [C₂ mim][NTf₂] at 303 K. [24] For this purpose the TIP4P-Ew water model was employed. [33] This kind of parameterization seems to be unusual but has significant benefits. The diffusion coefficients can be fitted separately to cations and anions no matter whether the ions exist as single particles, ion pairs or in larger aggregates. The same is true for the NMR rotational correlation times. Unfortunately these reorientation dynamics are available only for the CH(2) vector of the imidazolium cations. Thus we used NMR reorientational correlation times of water in [C₂ mim][NTf₂] to fit the anion parameters. This unusual procedure is based on recent experimental findings showing that the structure and dynamics of single water molecules are sensitive probes for anion properties. [34] We show that the single water behavior is mainly determined by anions in the ionic liquid; thus the water dynamics may serve as a good indicator for anion properties and can be used for deriving force-field parameters.

RESULTS AND DISCUSSION

In this paper we give more evidence by measuring a mixture of both ionic liquids and subtracting the background of the neat ILs [C₂ mim][NTf₂] and [C₂ C₁ mim][NTf₂], respectively. We then explain, in which way the shape of the spectral bands in the far IR region can be used for developing new or refined force fields in MD simulations. This will be done by comparing the measured spectra for [C₂ mim][NTf₂] and [C₂ C₁ mim][NTf₂] with those for [C₂ mim][NTf₂] obtained by using the Fourier Transform of the velocity autocorrelation functions by using different force fields. We find better agreement for the calculated spectra using force fields which in particular focus on strong H-bond interactions between C(2)-H and the anion. Instead we find characteristic deviation for force fields which treat all C-H bonds in equal way not leading to strong asymmetry and reduced dynamics in the ion liquid. In principle, the various C(2)-H-anion interactions could be described by an additional parameter taking the diverse acidities into account. This work is in progress in our laboratories. The importance of H-bonds is planned to be taken into account in extending the mostly used CLaP force field [8].

To confirm the assignment of the low vibrational frequencies we measured the mid FTIR as well as the far FTIR spectra of [C₂ mim][NTf₂] and [C₂ C₁ mim][NTf₂], [32] The 2-methyl-substituted analogue [C₂ C₁ mim][NTf₂] was chosen in order to determine whether the spectra are significantly affected by suppressing the C(2)-H⋯A-H-bonding in [C₂ mim][NTf₂]. In Figure 1 we show the mid FTIR spectra for both ionic liquids in the frequency range between 3000 and 3300 cm⁻¹. The spectral bands between 3070 cm⁻¹ and 3200 cm⁻¹ can be assigned to C-H stretching modes of the imidazolium ring. In a recent study we could show for [C₂ mim][NTf₂] that the vibrational bands at higher wavenumbers in this region can be referred to C(4/5)-H stretching modes whereas those at lower wavenumbers can be assigned to C(2)-H stretching modes. [35] By replacing the C(2)-H proton by a methyl group C(2)-CH₃, we switch off the cation-anion interaction via C(2)-H. Consequently the stretching modes between 3080 cm⁻¹ and 3150 cm⁻¹ are now completely missing in the mid IR spectra (Figure 1). The remaining C(4/5)-H contributions are slightly shifted to the red compared to those in [C₂ mim][NTf₂] because intermolecular interaction can only take place via C(4/5)-H. This finding further underlines that the C(2)-H⋯A-H-bonds are significantly stronger than those formed by C(4/5)-H which has been

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<th>TABLE I: Charges and Lennard-Jones parameters used in the force fields by Köddermann [21] and CLaP [8]. Please not that the atomic point charges are left unchanged in both force fields and that the major differences in the Lennard-Jones parametrization are concentrated in the CR and HA sites (atoms)</th>
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<td>Köddermann et al. [21]</td>
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considered in the development of recent force fields used in molecular dynamics simulations.\cite{21, 25}

Recently, we measured the low frequency vibrational spectra of imidazolium-based ionic liquids [C$_2$ mim][NTf$_2$], [C$_2$ mim][EtSO$_4$], [C$_2$ mim][N(CN)$_2$] and [C$_2$ mim][SCN] in the range between 30 and 300 cm$^{-1}$ by far infrared spectroscopy.\cite{31} 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 intermolecular interactions between cations and anions describing the bending and stretching vibrational modes of hydrogen bonds. This assignment was supported by DFT calculations giving wavenumbers for the bending and stretching modes of the imidazolium cation but different anions.

In this paper we measured the low-frequency spectra of [C$_2$ mim][NTf$_2$] and [C$_2$C$_1$ mim][NTf$_2$] as given in Figure 2. Although we have used the same path length for the IR cell, all intensities of [C$_2$C$_1$ mim][NTf$_2$] are substantially lower except those for the cations above 250 cm$^{-1}$. The intramolecular bending and wagging modes of anions NTf$_2^-$ are affected by suppressing the important H-bonds via C(2)-H. But most importantly, the intensities of the vibrational bands which we assigned to the bending and stretching modes of the C(2)-H and C(4/5)-H interactions are now significantly reduced. Additionally, the remaining low intensity band is shifted to the red from 83.5 cm$^{-1}$ to 79.0 cm$^{-1}$ wavenumbers. Although the shift is small relative to the rather broad bands, this behavior is seen for the spectra of all temperatures.

Switching off the C(2)-H interaction leads to H-bonds via C(4/5)-H. Those interactions are weaker leading to a slight redshift of this measured intermolecular band. The overall H-bond contributions are significantly suppressed in favor of increasing Coulomb interactions in [C$_2$C$_1$ mim][NTf$_2$]. This can be seen in the far FTIR spectra by the increasing contribution above 100 cm$^{-1}$ represented by a long tail up to 200 cm$^{-1}$. The Coulomb interactions are stronger than the H-bonds and occur at higher wavenumbers. What we see here is the following: substituting the C(2)-H proton in [C$_2$ mim][NTf$_2$] by the C(2)-CH$_3$ methyl group in [C$_2$C$_1$ mim][NTf$_2$] we replace a strong, localized and highly directional H-bond in favor of a non-localized and smeared-out Coulomb interaction.

The following experiments have also been performed for further support of this interpretation. Additionally to the spectra of the pure ionic liquids we measured the far IR spectra for the 50 mol\% mixture of both ionic liquids versus the background of the pure ionic liquids [C$_2$ mim][NTf$_2$] and [C$_2$C$_1$ mim][NTf$_2$], respectively (see Figure 3). In general, it is clear that the two spectra of the equimolar mixtures when taken in relation to one or the other pure compound have almost symmetrical intensities (peaks in one correspond to valleys in the other and vice-versa). If the background spectrum of [C$_2$C$_1$ mim][NTf$_2$] is subtracted from that of the 50 mol\% mixture, we still find positive intensities around 84 cm$^{-1}$, indicating that these contributions in [C$_2$C$_1$ mim][NTf$_2$] are significantly weaker than those in [C$_2$ mim][NTf$_2$].

**FIG. 1:** Mid-FTIR spectra of ionic liquids [C$_2$ mim][NTf$_2$] (top) and [C$_2$C$_1$ mim][NTf$_2$] (bottom) as a function of temperature. Enlarged spectra are given to the right for the C-H stretches of the imidazolium ring between 3100 and 3200 cm$^{-1}$.

**FIG. 2:** Far-FTIR spectra of ionic liquids [C$_2$ mim][NTf$_2$] (top) and [C$_2$C$_1$ mim][NTf$_2$] (bottom) as a function of temperature. Enlarged spectra are given to the right for intermolecular vibrational modes between 30 and 150 cm$^{-1}$. 
The negative intensity at about 270 cm\(^{-1}\) stems from the strong intramolecular out of plane bending mode of the methyl group at the C(2) position in \([\text{C}_2\text{C}_1\text{mim}][\text{NTf}_2]\).

In contrast, if we measure the 50 mol\% mixture versus the background spectrum of \([\text{C}_2\text{mim}][\text{NTf}_2]\), we obtain negative intensities at about 90 cm\(^{-1}\), indicating that these contributions which we referred to the C(2)-H interaction are now missing. Instead, the contributions at lower wavenumbers (at about 80 cm\(^{-1}\)) remain and the C(1)-CH\(_3\) out of plane bending mode is now present. With these additional experiments we underline that we did not detect an overall decrease in intensities for all inter and intra molecular vibrational modes between 30 and 300 cm\(^{-1}\) on going from \([\text{C}_2\text{mim}][\text{NTf}_2]\) to \([\text{C}_2\text{C}_1\text{mim}][\text{NTf}_2]\), but measured characteristic interactions which can be referred to strong C(2)-H-anion interactions in \([\text{C}_2\text{mim}][\text{NTf}_2]\).

Here, we would like to show that these characteristic features in the far FTIR spectra can be used to evaluate force fields of ionic liquids which have been developed for Molecular dynamics and Monte Carlo simulations. For the simulation of the far FTIR spectra we used two different force fields.[8, 21] In the CLaP force field [8] the same charges and Lennard-Jones parameters for all the ring protons H\(_1\)/C2-H, H\(_2\)/C4/5-H are used throughout (see Table 1). Instead, in the refined force field by Köddermann et al. [21], the Lennard-Jones parameters \(\sigma\) and \(\epsilon\) were changed in such a way, that the C(2) interaction became significantly favored over the C4/C5 interactions with the anion. This was achieved by decreasing the \(\sigma\) and increasing the \(\epsilon\) values for these protons (given in Table 1). The parameters were varied to reproduce NMR rotational correlation times for cations and water molecules in \([\text{C}_2\text{mim}][\text{NTf}_2]\).

The far FTIR spectra of the simulated ionic liquids can be calculated from the Fourier transform of the velocity autocorrelation function, using the equation

\[
g(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \langle \vec{v}(0)\vec{v}(t) \rangle \exp(-i\omega t) dt \tag{1}
\]

where \(g\) and \(\omega\) correspond to the intensity and the frequency of the vibrational state in the equilibrium condition, respectively.

The experimental and simulated spectra of the pure ionic liquids are shown in Figure 4. It is not expected that all inter and intramolecular spectral feature are given quantitatively in wavenumbers and intensities. Despite shortcomings, the power spectrum should be broadly representative of motions occurring in the ionic liquid. The simulations reproduce the positions of the absorption maxima fairly well, although in the simulations the absorption peaks occur at lower frequencies than in the experimental results.

Here we want to focus on the shapes of the low vibrational bands below 150 cm\(^{-1}\) which can be referred to the cation-anion interactions. Whereas the shape of the spectral band obtained from the simulation using the Köddermann’s force field resembles the measured shape of \([\text{C}_2\text{mim}][\text{NTf}_2]\), the spectral feature obtained from the simulations based on the CLaP force field looks different. The latter more resembles the characteristics of the spectral band obtained experimentally for the ionic liquid \([\text{C}_2\text{C}_1\text{mim}][\text{NTf}_2]\). Both spectra, the simulated spectrum for \([\text{C}_2\text{mim}][\text{NTf}_2]\) as well as the measured spectrum for \([\text{C}_2\text{C}_1\text{mim}][\text{NTf}_2]\) show long tails towards higher wavenumbers.

FIG. 3: Far-FTIR spectra: ionic liquid \([\text{C}_2\text{mim}][\text{NTf}_2]=1\), a 50 mol\% mixture of 1 and 2 versus the background spectrum of ionic liquid 1, a 50 mol\% mixture of 1 and 2 versus the background spectrum of ionic liquids 2 and ionic liquid \([\text{C}_2\text{C}_1\text{mim}][\text{NTf}_2]=2\). From the top to the bottom.

FIG. 4: Measured far-FTIR spectra of \([\text{C}_2\text{mim}][\text{NTf}_2]\) (green line) and \([\text{C}_2\text{C}_1\text{mim}][\text{NTf}_2]\) (blue line) as well as simulated far-FTIR spectra of the \([\text{C}_2\text{mim}][\text{NTf}_2]\) using the force field by Köddermann et al. [21] (dotted green line) and the CLaP force field [8] (dotted purple line), respectively. From the top to the bottom.
wavenumbers, whereas the low vibrational bands are less pronounced. In our opinion this feature is no surprise. The CLaP force field suggests no specific preference for the C(2)-H interaction and treats all ring protons in a similar way indicated by similar Lennard-Jones parameters. Thus it is similar to the measured spectra of $\text{C}_2\text{C}_1\text{min}[\text{NTf}_2]$ where this specific interaction is suppressed by methylation of the C(2) position.

Obviously, the preference of the C(2) interaction is not only required to reproduce the NMR reorientational correlation times of the cation but also to mimic the low vibrational spectra obtained by far FTIR measurements. Thus it is highly desirable to consider this specific interaction in force fields representing a more general protocol. In principle, the various C(2)-H-anion interactions could be described depending on the ionic strength of the chosen anion into account. This work is currently in progress in our group.

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