Interaction Energy

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Dissecting Anion–Cation Interaction Energies in Protic Ionic Liquids**

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Knowledge of intermolecular forces is a requisite for understanding material properties. These forces determine whether matter sticks together, gases condense to liquids, and liquids freeze to solids. The study of these forces in ionic liquids is particularly interesting.[1–4] Although the structure and properties of these fluid materials are determined to a large extent by the Coulomb forces, hydrogen bonding and dispersion forces can play a crucial role. The strong anion–cation interaction in these Coulomb fluids is reflected in their extremely low vapor pressures and high enthalpies of vaporization.[5–12] These properties, among others, make ionic liquids (ILs) attractive for science and technology.

However, measuring intermolecular interactions in ionic liquids is still a challenge. In principle these interactions can be studied by experimental techniques that cover the frequency range of these interaction energies. Meanwhile there are numerous spectroscopic techniques available covering the frequency range of interest between 1 and 300 cm^{-1}, corresponding to 0.03 and 9 THz. The palette of spectroscopic methods includes optical heterodyne-detected Raman-induced Kerr effect (RIKE), far-infrared (FIR), Raman, and THz spectroscopy as well as low-energy neutron scattering.[13–23]

Although it has been shown that this spectral region may be extremely useful for studying intermolecular forces, we concede that the measured spectra are quite complicated and difficult to dissect. In particular the unequivocal assignment of the vibrational bands to intermolecular interactions is a challenge. Low-frequency absorption can arise from internal molecular vibrations, librational modes, and torsional modes such as alkyl group rotation. Usually, DFT and MD methods are required for the interpretation of the measured spectra.[24–31] In principle, these methods are suitable to indicate low-frequency intramolecular vibrational modes. However, a serious problem still remains. It is not clear to what extent DFT methods or force fields typically used in classical molecular dynamics (MD) simulations are able to describe intermolecular interactions accurately.[32] In principle ab initio molecular dynamics (AIMD) simulation is the method of choice for analyzing this frequency range, as shown by Heyden et al. for the case of liquid water.[33] However, for the relatively viscous ionic liquids the small system sizes and short simulation runs provide insufficient statistics and result in noisy and unspecific spectra in the far-infrared region.[34] But even if this frequency range is analyzed properly and the vibrational modes giving the intermolecular interaction between anion and cation can be assigned correctly, another problem persists. It is unclear to what extent frequency positions and frequency shifts of intermolecular vibrational bands can be fully referred to changing force constants indicating stronger or weaker interaction between the anion and the cation. Following the equation for the simple harmonic oscillator $\tilde{\nu} = (1/2\pi c)(k/\mu)^{1/2}$, frequency shifts to lower or higher wavenumbers can be referred to both parameters, either the force constant or the reduced mass. For example, the intermolecular interaction in ionic liquids can be reduced by increasing the molecular volume of the ions. That automatically means that the reduced mass increases as well and the intermolecular frequency shifts to lower wavenumbers result from both parameters. Thus further work is needed to establish the pure contribution of the intermolecular interaction from low-frequency vibrational bands.

In this study we have combined the synthesis of a select set of ionic liquids with systematic FIR measurements and suitable DFT calculation of frequencies, reduced masses, and force constants of the ionic liquid aggregates to enable the full analysis of the FIR spectral region. More importantly, frequency shifts describing the intermolecular interactions between the anions and cations in the ionic liquids can be dissected into reduced mass and pure interaction effects. The dissection of the intermolecular forces is crucial for understanding the special and tuneable properties of ionic liquids.

First, we selected a set of suitable protic and aprotic ionic liquids. All cations and anions in these ionic liquids have specific features and functions to overcome the typical difficulties in evaluating the far-infrared spectra and assigning the interaction contributions. We synthesized a total of six protic ionic liquids (PILs); the aprotic ionic liquid was purchased and already measured in earlier studies.[35,36] The full set of ILs comprises $[(C_2H_5)_3NH][CH_3SO_3]$ (**Ia**), $[(C_2H_5)_3NH][CF_3SO_3]$ (**IIa**), $[(C_2H_5)_3NH][NTf_2]$ (**IIIa**), and $[C_2mim][NTf_2]$ (**IV**; C_2mim = 1-ethyl-3-methyl-imidazolium). Additionally the PILs **Ib**–**IIIb** were synthesized which have

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including deuterated ethyl groups in the triethylammonium cations: $[(C_2D_5)_3NH][CH_3SO_3]$ (**Ib**), $[(C_2D_5)_3NH][CF_3SO_3]$ (**IIb**), and $[(C_2D_5)_3NH][NTf_2]$ (**IIIb**) (see SI 1–2 in the Supporting Information).

For the PILs the same triethylammonium cation is used throughout. Thus changes in the interaction strength cannot result from varying cations. Thanks to the three flexible ethyl groups in the ammonium cations the PILs are liquid at room temperature. Highly mobile ethyl groups lead to a larger variety of states and are consequently entropically favored. Another important feature of the cations is that they possess a single proton-donor function, N–H. The only possible directional interaction $^+N–H\cdots A^-$ provides isolated vibrational bands in the far-infrared spectra which can be clearly attributed to the H-bond-enhanced anion–cation interaction.[37] The anions of choice show decreasing interaction strength in the order $[CH_3SO_3] > [CF_3SO_3] > [NTf_2]$ due to fluorination of the methyl groups. The difficulty here is that the decreasing interaction strength is accompanied by the increasing reduced mass of the anions. Thus both properties result in shifts to lower vibrational frequencies and it is not possible to differentiate between the effects of the reduced masses and the force constants. To overcome this problem we deuterated the three ethyl groups in the ammonium cations for the PILs **I**–**III**. Without changing the anion–cation interaction strength we can now measure the frequency shifts resulting from the reduced mass only.

The measured FIR spectra covering the frequency range from 20 to 220 cm^{-1} of all ILs are shown in Figure 1. All spectra are deconvoluted into Voigt functions and given in the Supporting Information (SI3). The frequencies above 180 cm^{-1} can be clearly attributed to intramolecular vibrational modes mainly of the anion as described earlier.[34,35] For the ILs **II** and **III**, which include $CF_3SO_3^-$ and NTf_2^- anions, the vibrational modes above 200 cm^{-1} stem from wagging modes of the O=S=O groups within the anions.

Below this frequency only contributions from intermolecular interaction can be observed. The intramolecular bending and rotational contributions of the cation ethyl groups in this frequency range are relatively weak compared to the distinct local interactions $^+N–H\cdots A^-$. There are two main features characterizing the low-frequency spectra of the ILs. There is a broad and unspecific vibrational mode at about 80 cm^{-1} which can be assigned to librational modes overlapped by H-bond bending modes. This interpretation is supported by calculated frequencies of IL aggregates of different sizes including up to four ion pairs (see the Supporting Information). The most interesting and distinct vibrational mode shows up at 149.4 cm^{-1} for **Ia** and shifts down to 105.2 cm^{-1} for the PIL **IIIa** and finally to 83.2 cm^{-1} for the only IL **IV**; here this contribution cannot be distinguished from the librational modes. Recently, this behavior raised the controversy whether the contribution at about 83 cm^{-1} in aprotic ILs such as $[C_2mim][NTf_2]$ can be assigned to the anion–cation interaction and H-bonding at all.[38,39] With the present study we can clearly address and answer this question. When the anion–cation interaction due to enhanced H-bonding is increased, this vibrational mode continuously moves to higher frequencies as indicated by the straight line in Figure 1. However, the full frequency shift from 149.4 cm^{-1} down to 83.2 cm^{-1} for **I** to **IV** cannot be attributed to the decreasing interaction strength between anions and cations. Following the simple equation of the harmonic oscillator $\tilde{\nu} = (1/2\pi c)(k/\mu)^{1/2}$ frequency shifts can stem from both different reduced masses and different force constants indicating the interaction strength between anion and cation. In Table 1 we have listed the reduced masses of ILs **I**–**IV** and calculated the expected frequency shifts due to increasing μ relative to the highest wavenumber of 149.4 cm^{-1} for **Ia**.

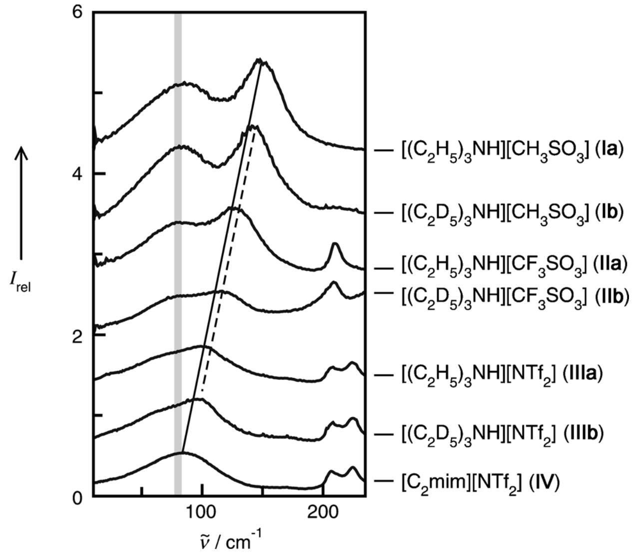

Figure 1. FIR spectra of PILs **Ia/b**–**IIIa/b** and of IL **IV**. The vibrational band at 149 cm^{-1} for **Ia** can be assigned to the $^+N–H\cdots CH_3SO_3^-$ intermolecular interaction. This interaction strength decreases along the series of PILs **Ia**–**IV** as indicated by the solid line. For the deuterated PILs the reduced mass effect is shown by the dotted line. The vertical gray line denotes diverse librational and intermolecular bending modes.

Table 1: Masses of cations and anions in ILs **I**–**IV**, reduced masses of ion pairs relative to those of **Ia**, measured FIR vibrational frequencies $\tilde{\nu}_{exp}$, expected frequencies due to reduced masses only $\tilde{\nu}_{\mu}$, and calculated interaction energies E per ion in IL aggregates.

IL	Mass cation	Mass anion	$[\mu_{I\alpha}/\mu]^{1/2}$	$\tilde{\nu}_{exp}$ [cm^{-1}]	$\tilde{\nu}_{\mu}$ [cm^{-1}]	E [kJ mol^{-1}]
Ia	102.13	94.98	1	149.4	149.4	−224.9
Ib	117.13	94.98	0.969	143.2	144.8	−224.9
IIa	102.13	148.95	0.901	128.9	134.6	−202.0
IIb	117.13	148.95	0.865	116.9	129.2	−202.0
IIIa	102.13	279.92	0.811	105.2	121.2	−182.2
IIIb	117.13	279.92	0.772	99.9	115.3	−182.2
IV	111.09	279.92	0.787	83.2	117.6	−164.2

If the frequencies would be dominated by increasing reduced masses only, a frequency shift from 149.4 cm^{-1} for **Ia** to 117.6 cm^{-1} for **IV** with $\Delta\tilde{\nu} = 31.8$ cm^{-1} is expected. Instead a larger frequency shift of about $\Delta\tilde{\nu} = 66.2$ cm^{-1} is observed. Thus the additional frequency shift of about $\Delta\tilde{\nu} = 34.4$ cm^{-1} can be clearly assigned to decreasing force constants indicating decreasing interaction strength. Here the deuterated PILs **Ib**–**IIIb** come into play. The measured frequencies for the deuterated compounds are about 6–12 cm^{-1} lower than those of the protonated species which is in agreement with the calculated frequency shifts (see SI4 in the Supporting Information). The trend of the frequency shifts for the deuterated PILs is indicated by the dotted line which is nearly parallel to that for the protonated species. The slope of the dashed line is somewhat smaller than that of the solid line, because the additional mass (15 a.u.) becomes less significant for the heavier PILs. The frequency shifts given by the straight line include both increasing reduced masses and decreasing force constants (ILs **Ia**, **IIa**, **IIIa**, and **IV**). The shift of the dotted line for the deuterated PIls (ILs **Ib**, **IIb**, and **IIIb**) versus the straight line for the protonated species reflects the effect of the reduced masses only. Overall, the measurements suggest that frequency shifts can be attributed to same extent to changing force constants and reduced masses.

In Figure 2 all the DFT-calculated reduced masses and force constants are plotted versus the resulting vibrational frequencies for the PIL aggregates with $n = 1$–4 (n = number of ion pairs). As expected from the equation of the simple harmonic oscillator, the frequencies decrease with increasing reduced mass and increase with increasing force constant. For the PIL **III** the spreading of the data increases with weaker and less directional interactions between the anion and the cation. However, for the frequency range between 80 and 180 cm^{-1} the square roots of reduced masses decrease by a factor 0.67, whereas the force constants increase by a factor of 1.47, respectively (see SI4 and SI5 in the Supporting Information). Thus the reduced masses shift the frequencies to same extent as the force constants. Hence, the theoretical result is in perfect agreement with our prediction that the measured frequency shift of about $\Delta\tilde{\nu} = 66.2\ \text{cm}^{-1}$ for ILs **I**–**IV** can be dissected into $\Delta\tilde{\nu} = 31.8\ \text{cm}^{-1}$ stemming from increasing reduced masses and $\Delta\tilde{\nu} = 34.4\ \text{cm}^{-1}$ resulting from decreasing force constants.

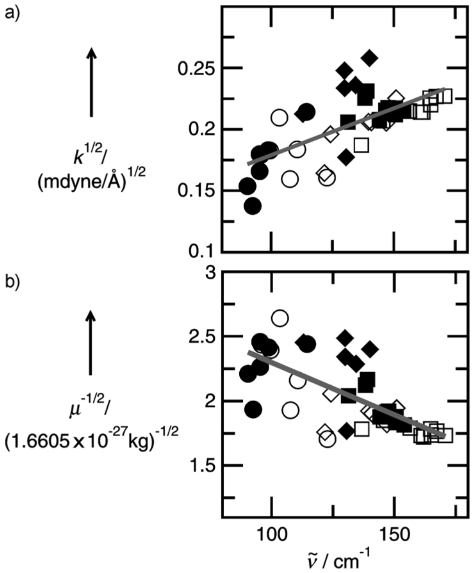

Figure 2. a) Square roots of force constants and b) inverse square roots of reduced masses of the vibrational modes describing the anion–cation interactions in PILs **I** (squares), **II** (diamonds), and **III** (circles) from DFT calculations on aggregates with $n = 1$–4. The open symbols indicate the properties of the protonated and the filled symbols those of the deuterated PIL aggregates.

Plotting the measured frequencies versus the calculated binding energies per ion in the IL tetramers we obtain perfect linear behavior as shown in Figure 3 (see SI6 in the Supporting Information). This procedure was applied already in earlier studies.[20,23,35] both the resulting linear dependency still includes reduced mass and force constant effects (filled symbols), the expected frequency shifts due to increasing reduced masses only are given by the second slope (open symbols). The area between the two lines indicates the frequency shifts resulting from the change in interaction strength only. The linear regression of the two data sets suggests a total frequency shift of $\Delta\tilde{\nu} = 67.8\ \text{cm}^{-1}$ between PILs **I** and **IV** where $\Delta\tilde{\nu} = 33.1\ \text{cm}^{-1}$ and $\Delta\tilde{\nu} = 34.7\ \text{cm}^{-1}$ can be related to decreasing force constants and increasing reduced masses, respectively (see SI7). Obviously, the two parameters contribute to same extent to the observed frequency shift.

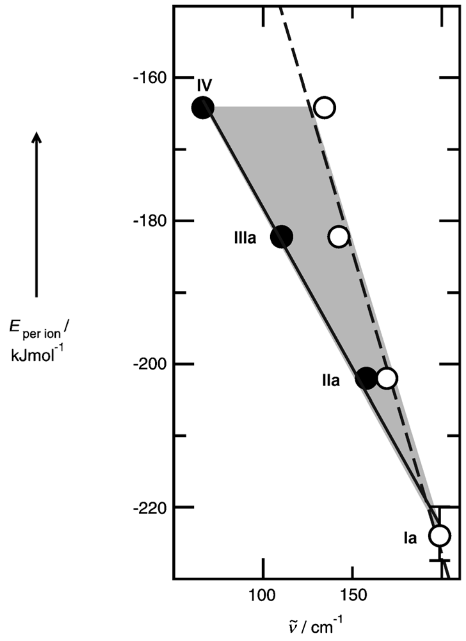

Figure 3. DFT-calculated energies per ion of tetramers for the ILs **I**–**IV** plotted versus the corresponding vibrational modes of the intermolecular interaction $^{+}$N–H⋯anion (○). The open symbol (○) indicates the frequencies that are expected if only the reduced mass contributes to the frequency shift. PIL **Ia** (149.4 cm^{-1}) was chosen as a reference system. See the text for details.

Finally we are in the comfortable situation that we can relate the frequency shifts in the far-infrared region to changing interaction strength between the anion and the cation in the ILs. The variation of the binding energies per ion due to different conformers has been checked for PIL **I** (see SI9 in the Supporting Information). Four different conformers have been calculated for the aggregates with $n = 1$–4. The binding energies per ion vary at most by 8 kJ mol^{-1}, which is 3.5 % of the overall binding energies. This uncertainty is indicated by the error bar in Figure 3. The variation in the binding energies at different levels of theory is on the same order of magnitude (see SI9 and SI10). Thus a redshift of about 1 cm^{-1} for the vibrational band corresponds to a weakening in the interaction energy between the cation and the anion on the order of (1.69 ± 0.06) kJ mol^{-1}. Although this relation was derived mainly from a set of PILs, it should also hold for aprotic ionic liquids. However, this relation was obtained by assuming that the full masses of anions and cations are involved in the vibrational motion. If that is not the case, deviations from the given relation can be expected.

We have presented a reliable estimate for the changing interaction strength between anions and cations in protic and aprotic ionic liquids. Frequency shifts in the far-infrared spectra can be referred to stronger or weaker interactions in these Coulomb fluids. This relation opens a new path for studying the variation of interaction strengths due to changing temperature or physical environment. Overall we also have access to thermophysical properties of ILs such as heat capacities and enthalpies of vaporization. The linear relationship between the FIR frequencies and enthalpies of vaporization as introduced recently still holds, but it is not corrected for reduced mass effects.[40] This relation between FIR frequency shifts and changing interaction strengths provides further options. Frequency shifts observed for the solid–liquid phase transition could give some estimate for enthalpies of melting. Another possibility is to analyze changing interaction energies for ILs in solution by using solvents of different polarity. It would be possible to study whether ion-pair or aggregate formation in diluted ILs leads anion–cation interactions that are stronger than those in the neat liquid. Some of these investigations are currently underway in our laboratories.

Experimental Section

The FTIR measurements were performed with a Bruker Vertex 70 FTIR spectrometer equipped with an extension for measurements in the FIR region that consists a multilayer Mylar beam splitter, a room-temperature DLATGS detector with a preamplifier, and polyethylene (PE) windows for the internal optical path. The accessible spectral region for this configuration lies between 30 and 680 cm^{-1} (0.9 and 20.3 THz). Further improvement could be achieved by using a high-pressure mercury lamp and a silica beam splitter. This configuration allowed measurements down to 10 cm^{-1} and significantly better signal-to-noise ratios.

The geometries and frequencies of all PILs **I**–**III** and IL **IV** aggregates were calculated at the DFT level B3LYP, using the internal stored 6-31+G* basis set of the Gaussian 09 program.[41] The binding energies were corrected for the basis set superposition error (BSSE).[42] For PIL **I** aggregates with $n = 1$–4, three more conformers (**Ia**–**c**) were calculated at the same level of theory. The resulting geometries, energies, and intermolecular frequencies are given in SI9 in the Supporting Information. Additionally we calculated the PIL **I** aggregates with $n = 1$–4 at the RHF level and aggregates with $n = 1$–2 at the MP2 level of theory. The binding energies per ion are presented in SI10 in the Supporting Information.

The synthesis of six ethylammonium-containing PILs described in the Supporting information. IL **IV** was purchased from Sigma–Aldrich, Steinheim. Further details of the theoretical and experimental approaches are given in the Supporting.

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