Protic Ionic Liquids

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Hydrogen Bonding in Protic Ionic Liquids: Reminiscent of Water**

Koichi Fumino, Alexander Wulf, and Ralf Ludwig*

Ionic Liquids (ILs) constitute a promising class of technologically useful and fundamentally interesting materials. Potential applications include novel synthesis, electrolyte devices, photochemical cells, separations, and catalysis.[1–3] Protic ionic liquids (PILs) are a subset of ionic liquids formed by combination of equimolar amounts of a Brønsted acid and a Brønsted base.[4,5] The key property that distinguishes PILs from other ILs is the proton transfer from the acid to the base, leading to the presence of proton-donor and proton-acceptor sites, which can be used to build a hydrogen-bonded network. PILs have a number of unique properties compared to other ILs, just as water is different from "normal" molecular liquids. Thus it has been suggested that the hydrogen bonds between ammonium cations and nitrate anions, for example, induce a network structure which in some respects mimics the three-dimensional hydrogen-bonded network of water.[6–9]

In principle, these H-bond networks can be studied by measuring the low-frequency range below 300 cm^{-1} (9 THz) using far-IR or Raman spectroscopy. However, only a few infrared studies of ILs have been performed in the far-infrared regime.[10–12] Experimental difficulties arise from the very low intensities of infrared sources. Herein, we demonstrate that these far-IR spectra can be measured for PILs, which show characteristic intramolecular bending modes above 250 cm^{-1} and intermolecular stretching and bending vibrational bands of hydrogen bonds between 50 and 250 cm^{-1}. Interestingly, the intermolecular vibrational bands of the PILs show the same structure as the recently measured connectivity bands of water. This finding suggests that PILs form a three-dimensional hydrogen-bonded network that very much resembles that of water.

The low-frequency spectra for the neat protic ionic liquids ethylammonium nitrate (EAN), propylammonium nitrate (PAN), and dimethylammonium nitrate (DMAN) in the range between 30 and 600 cm^{-1} are shown in Figure 1. Overall, the spectra show significant differences but also share some common features. Because we kept the anion (NO_3^-) constant, the differences can only stem from weak intramolecular vibrations of the various cations and/or from specific cation–anion interactions.

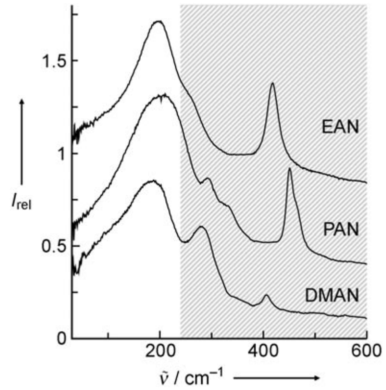

Figure 1. Low-frequency vibrational FTIR spectra of the protic ionic liquids ethylammonium nitrate (EAN), propylammonium nitrate (PAN), and dimethylammonium nitrate (DMAN) measured at 353 K.

Strong support for the interpretation of the low-frequency vibrational bands is provided by DFT calculations of the aggregates ([alkyl ammonium][NO_3])$_x$, where x is the number of ion pairs contributing to the overall cluster. In Figure 2 the measured spectrum of DMAN is shown along with the calculated vibrational frequencies of the clusters with $x = 1, 2, 3, 4, 6$. In addition, in Figure 3, all low-frequency vibrational spectra are deconvoluted into Voigt functions. The main features of the measured spectra of DMAN (Figure 3c) are reproduced by the calculated and deconvoluted vibrational bands. The bands above 250 cm^{-1} can be assigned to the intramolecular bending and torsional modes of the respective

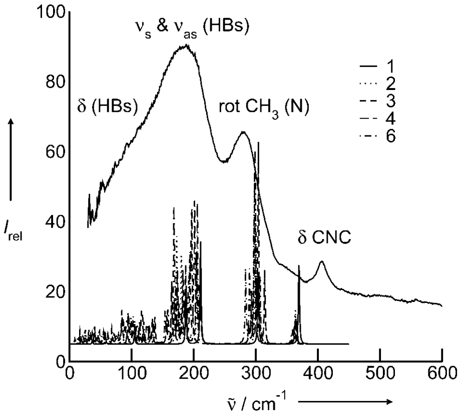

Figure 2. Measured low-frequency vibrational FTIR spectrum of dimethylammonium nitrate (DMAN) at 353 K compared to the vibrational modes of the corresponding PIL clusters $[(DMA)(NO_3)]_x$ with $x = 1$, 2, 3, 4, and 6 calculated by DFT at the B3LYP/6-31+G* level of theory. The major vibrational bands are in agreement with the calculated frequencies, which are corrected for the harmonic approximation.

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[*] Dr. K. Fumino, Dipl.-Chem. A. Wulf, Prof. Dr. R. Ludwig
Institut für Chemie, Abteilung Physikalische Chemie, Universität Rostock, Dr.-Lorenz-Weg 1, 18051 Rostock (Germany)
E-mail: ralf.ludwig@uni-rostock.de
Prof. Dr. R. Ludwig
Leibniz-Institut für Katalyse an der Universität Rostock
Albert-Einstein-Strasse 29a, 18059 Rostock (Germany)

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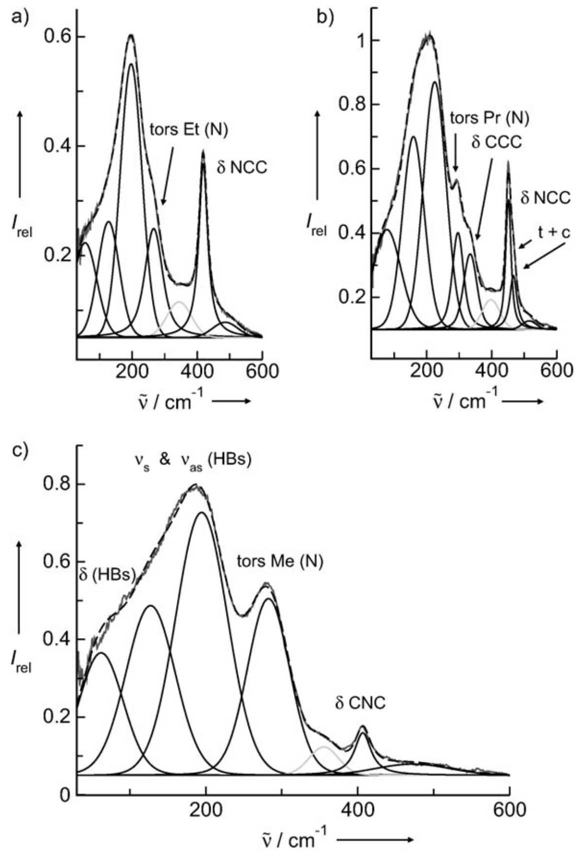

Figure 3. Measured low-frequency vibrational FTIR spectra of a) ethylammonium nitrate (EAN), b) propylammonium nitrate (PAN), and c) dimethylammonium nitrate (DMAN) deconvoluted into distinct vibrational bands, which can all be assigned with the help of the frequencies calculated by DFT. For DMAN in (c), the detailed assignment to intramolecular bending modes and intermolecular stretching and bending modes is shown.

cations. For all ammonium nitrates, a weak band can be assigned to torsional motions of the ammonia groups around 500 cm^{-1}. In EAN, this band is flanked by an intense contribution around 418 cm^{-1}, which can be clearly assigned to the bending mode δ(NCC) of the cation. Consequently, in PAN (Figure 3 b) this band is split into two contributions referring to the δ(NCC) bending modes of the *trans* and *cis* isomers, respectively. Overall, both contributions occur at higher wavenumbers (465.0 and 451.9 cm^{-1}) than the corresponding bending mode in EAN (418.7 cm^{-1}). For DMAN, (Figure 3 c) this band does not occur. Instead, a δ(CNC) bending mode shows up at 406 cm^{-1} with significantly lower wavenumber and intensity. For PAN an additional band is detected around 332.6 cm^{-1}, which can easily be assigned to the δ(CCC) bending mode and which cannot be present in the spectra of EAN and DMAN.

Vibrational bands from torsional motions occur for all three PILs: at 265.2 cm^{-1} for EAN, at 296.3 cm^{-1} for PAN, and at 282.6 cm^{-1} for DMAN. So far, all vibrational modes above 250 cm^{-1} can be clearly assigned to the intramolecular bending mode of the various cations. The most interesting bands occur below 250 cm^{-1}. For all three alkyl ammonium nitrates, three contributions can be deconvoluted from the measured spectra. The calculated frequencies of the PIL clusters suggest that the bands between 199 and 224 cm^{-1} as well as between 134 and 159 cm^{-1} can be attributed to the asymmetric and symmetric stretching modes of the hydrogen bonds NH···O (ν_{as}(HBs) and ν_s(HBs)). The vibrational bands around 60–78 cm^{-1} can be assigned to corresponding bending modes of these hydrogen bonds (δ(HBs)). As for the intramolecular modes, the asymmetric stretches have higher intensities than the symmetric ones. The frequency difference between the asymmetric and the symmetric stretches for all alkyl ammonium nitrates are around 65 cm^{-1}, suggesting comparable interaction strengths for all PILs. The asymmetric and symmetric stretching as well as the bending modes of the hydrogen bonds can be compared to those found for liquid water and ice.

For liquid water, characteristic bands in the low-frequency range up to 250 cm^{-1} are known. Cluster vibrations such as translational vibrations involve combinations of hydrogen-bond OH···O stretching and bending at around 200 cm^{-1}.[13] In ice I_h at 263 K, a major sharp band is found at 215 cm^{-1} and a minor sharp band is detected at 155 cm^{-1}.[14] Bending vibrations of the hydrogen bonds also occur, owing to out-of-alignment translations relative to the hydrogen bonds between 40–60 cm^{-1}.[15] More recently, Brubach et al.[16] fit the structure of the connectivity band of water by a sum of four Gaussians. For all temperatures they obtained constant bands at 88, 130, 195, and 251 cm^{-1}. The intensity of the hydrogen-bond stretch absorbance increases with decreasing temperature. Overall, the ice and liquid water bands found in the far-IR spectra of water can be related to our measured bands at 199–224, 134–159, and 60–78 cm^{-1} in the PILs, thus indicating similar strength of hydrogen bonding and related network structures. Obviously both water and the alkyl ammonium nitrates can form three-dimensional H-bond networks of similar strength.

In water, each molecule has two donor and two acceptor sites to form a tetrahedral H-bond network. In alkyl ammonium nitrates, the ammonium hydrogen atoms can interact through hydrogen bonding with the oxygen atoms of the nitrate, thus also leading to a three-dimensional network structure. For water the typical tetrahedral network is responsible for most of the anomalous properties of this liquid. It is interesting to see whether the alkyl ammonium nitrates also display some of these unique properties. This comparison has been already done for EAN by Evans et al.[7–9,17] They could show that EAN possesses a number of similarities to water. In particular, the phase transfer of rare gases and hydrocarbons from cyclohexane to this PIL is accompanied by negative enthalpy and entropy changes. Obviously EAN shares with water the ability to form a three-dimensional hydrogen-bonded network. However, the values for EAN are only half as large as those for water. EAN can form only three hydrogen bonds per solvent ion, and the tetrahedral structure of the cation and the planar structure of the anion in addition to the Coulomb forces must impose a very different type of solvent ordering than that in water. These differences are reflected in the low heat capacities observed in EAN solutions compared to those of water.[18] Additional support comes from DFT calculations of clusters of EAN and water (Figure 4). The typical tetrahedral structure only occurs in water, whereas it is missing in the three-dimensional network of EAN.

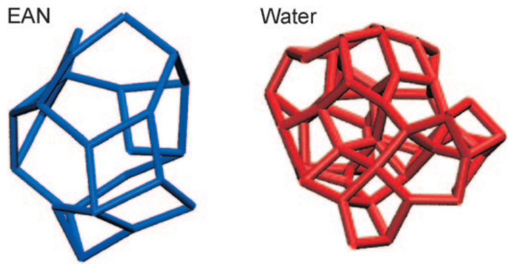

Figure 4. Network structures of ethylammonium nitrate (EAN) and water obtained from DFT calculations on larger aggregates. For EAN the connections between the nitrogen atoms of the cation and anion are shown, whereas for water the oxygen–oxygen distances are displayed. Both liquids have three-dimensional networks, but a tetrahedral network is only present for water.

Herein we present the first far-IR spectra of the protic ionic liquids EAN, PAN, and DMAN. Supported by DFT calculations, the deconvoluted vibrational bands could be assigned to intermolecular bending and stretching modes of the hydrogen bonds $^{+}NH\cdots O^{-}$. The characteristics of the low-frequency spectra closely resemble those of water. Obviously, both liquids form three-dimensional network structures. However, only water exhibits a tetrahedral H-bond network. For EAN such a network is impossible, owing to the different structures and donor–acceptor abilities of the ions.

Experimental Section

The ionic liquids were purchased from Iolitec GmbH (Denzlingen, Germany) with a stated purity of greater than 98%. All substances were dried in vacuum ($p = 8\times10^{-3}$ mbar) for approximately 36 h. The water content was then determined by Karl Fischer titration and was found to be 251 ppm in ethylammonium nitrate (EAN), 288 ppm in propylammonium nitrate (PAN), and 249 ppm in dimethylammonium nitrate (DMAN). 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 windows for the internal optical path. The accessible spectral region for this configuration lies between 30 and 680 cm^{-1}.

DFT calculations were performed at the B3LYP level with the Gaussian 2003 program[19] (6-31+G* basis set). The basis set superposition error (BSSE) corrected binding energies and average binding energies per ion for clusters comprising up to six ion pairs are given in Table 1 in the Supporting Information.[20] The vibrational frequencies for all clusters were corrected by the standard factor 0.96. Larger clusters could not be calculated on this level of theory owing to computational limitations.

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