Investigations with Infrared Spectroscopy on Films of the Ionic Liquid [EMIM]Tf$_2$N

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The reflection–absorption infrared (RAIRS) spectra of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM]Tf$_2$N) are presented as a function of temperature between 114 and 292 K. A comparison is made with the corresponding infrared spectra (obtained with transmission spectroscopy) from bulk [EMIM]Tf$_2$N. The liquid and amorphous films show rather similar spectra, indicating that the film structure is similar in both cases. On the other hand, these spectra differ considerably from those of crystalline films. Characteristic differences seen between the film and bulk spectra are attributed to the different structures of the respective networks. There are, however, indications that under all studied conditions the cation–anion interaction is between the C–H groups of the [EMIM] ring and the SO$_2$ groups of the anion.

1. Introduction

Room temperature ionic liquids (RT-ILs) have attracted much attention for their excellent properties, the most obvious ones being their wide temperature range of liquid phase, very low vapor pressure at RT, chemical stability, their potential as "green" solvents,[1,2] and their high heat capacities. These properties make them good candidates for the use in many fields,[2,3] such as thermal storage,[4] electrochemical applications,[5] homogeneous catalysis,[2,6,7] and dye-sensitized solar cells.[8] Moreover, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM]Tf$_2$N) is member of a class of ILs that can apparently be distilled at reduced pressure with moderate temperatures.[9,10] Important applications of ionic liquids require the knowledge of their surface properties. This includes, for instance, new electrolytes for electrodeposition,[11] electrochemical devices such as Li ion batteries,[12] and fuel cells.[13] The potential application of ionic liquid films for submicrometer-resolution lithographic imaging[14]

and for the construction of a Lunar Liquid Mirror[15] should also be mentioned here.

In order to be able to refine the performance of RT-ILs, detailed knowledge of the geometric, electronic, and vibrational structure of RT-ILs, in particular also in the near-surface region (up to a depth of about 1 nm below the surface), appears indispensable in the temperature regime between 100 and 700 K.

Our previous results obtained with electron spectroscopic techniques delivered considerable insight into the structure of the surface-near region at room temperature (RT);[16–18] the change of the structure of the films during the liquid-to-amorphous solid phase transition, taking place during fast cooling, remained, however, poorly understood. In order to obtain additional information on the eventual differences in the bonding properties in the liquid and solid (amorphous and crystalline) states, we have applied reflection–absorption infrared spectroscopy (RAIRS) to liquid and solid films of [EMIM]Tf$_2$N. IR measurements on bulk liquid [EMIM]Tf$_2$N for the same temperature range are presented for comparison. Support for the interpretation of the results can be expected from the recent density-functional theory (DFT) and molecular dynamic (MD) calculations, carried out on [EMIM]Tf$_2$N clusters[19] and the bulk liquid.[20,21]

The present results extend those presented in ref 22 and allow to test the conclusions drawn from this earlier work.

2. Experimental Section

The ultrahigh vacuum (UHV) system (base pressure 5×10^{-10} mbar) employed for the present studies was equipped with MIES,

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(1) Yoshimura, D.; Yokoyama, T.; Nishi, T.; Ishii, H.; Ozawa, R.; Hamaguchi, H.; Seki, K. *J. Electron Spectrosc. Relat. Phenom.* **2005,** *144–147,* 319.
(2) Wasserscheid, P.; Keim, W. *Angew. Chem.* **2000,** *112,* 3926.
(3) Binnemanns, K. *Chem. Rev.* **2005,** *105,* 4148.
(4) Crosthwaite, J. M.; Muldoon, M. J.; Dixon, J. K.; Anderson, J. L.; Brennecke, J. F. *J. Chem. Thermodyn.* **2005,** *37,* 559.
(5) Endres, F.; Abedin, S. Z. E. *Phys. Chem. Chem. Phys.* **2006,** *8,* 2101.
(6) Kölle, P.; Dronskowski, R. *Inorg. Chem.* **2004,** *43,* 2803.
(7) Welton, T. *Chem. Rev.* **1999,** *99,* 2071.
(8) Pinalla, C.; Popolo, M. G. D.; Lynden-Bell, R. M.; Kohanoff, J. *J. Phys. Chem. B* **2005,** *109,* 17922.
(9) Rebelo, L. P. N.; Canongia Lopes, J. N.; Esperanca, J. M. S. S.; Filipe, E. *J. Phys. Chem B* **2005,** *109,* 6040.
(10) Earle, M. J.; Esperanca, J.; Gilea, M. A.; Canongia Lopes, J. N.; Rebelo, L. P. N.; Magee, J. W.; Seddon, K. R.; Widegren, J. A. *Nature* **2006,** *439,* 831.
(11) Freyland, W.; Zell, C. A.; Abedin, S. Z. E.; Endres, F. *Electron. Acta* **2003,** *48,* 3053.
(12) Garcia, B.; Lavalle.; Perron, G.; Michot, C.; Armand, M. *Electrochim. Acta* **2004,** *49,* 4583.
(13) Noda, A.; Susan, A.; Kudo, K.; Mitsushima, S.; Hayamizu, K.; Watanabe, M. *J. Phys. Chem. B* **2003,** *107,* 4024.
(14) Rutten, F. J. M.; Tadesse, H.; Licence, P. *Angew. Chem., Int. Ed.* **2007,** *46,* 1.

(15) Borra, E. F.; Seddiki, O.; Angel, R.; Eisenstein, D.; Hickson, P.; Seddon, K. R.; Worden, S. P. *Nature* **2007,** *447,* 979.
(16) Höfft, O.; Bahr, S.; Himmerlich, M.; Krischok, S.; Schaefer, J. A.; Kempter, V. *Langmuir* **2006,** *22,* 7120.
(17) Krischok, S.; Öttking, R.; Beenken, W. J. D.; Himmerlich, M.; Lorenz, P.; Höfft, O.; Bahr, S.; Kempter, V.; Schaefer, J. A. *Z. Phys. Chem.* **2006,** *220,* 1407.
(18) Krischok, S.; Eremtchenko, M.; Himmerlich, M.; Lorenz, P.; Uhlig, J.; Neumann, A.; Öttking, R.; Beenken, W. J. D.; Höfft, O.; Bahr, S.; Kempter, V.; Schaefer, J. A. *J. Phys. Chem. B* **2007,** *111,* 4801.
(19) Köddermann, T.; Wertz, C.; Heintz, A.; Ludwig, R. *ChemPhysChem* **2006,** *7,* 1944–1949.
(20) Qiao, B.; Krekeler, C.; Berger, R.; Delle Site, L.; Holm, C. *J. Phys. Chem. B* **2008,** *112,* 1743.
(21) Fujii, K.; Soejima, Y.; Kyoshoin, Y.; Fukuda, S.; Kanzaki, R.; Umebayashi, Y.; Yamaguchi, T.; Takamuku, T.; Ishiguro, S. *J. Phys. Chem. B* **2008,** *112,* 4329.

UPS(He I and II), XPS, allowing for a cross referencing with earlier data on [EMIM]Tf$_2$N, and RAIRS. A polycrystalline Ag sample served as support for the IL film. [EMIM]Tf$_2$N (Merck/EMD) was purchased in high purity quality. For purification, the ionic liquid was dried under vacuum and stirring conditions for 12 h at a temperature of 80 °C to a water content below 3 ppm (by Karl Fischer titration).

The samples were prepared by spin-coating the Ag substrate with one droplet of the RT-IL and were, after outgassing carefully, introduced into the UHV chamber. Naked eye control gave several micrometers as a rough estimate for the film thickness; at any rate, XPS provided a lower limit of 10 nm for the film thickness. The [EMIM]Tf$_2$N samples prepared in this way have very low vapor pressure, and no change of the UHV chambers base pressure could be detected during measurements performed at RT. The Ag sample could be cooled to 114 K using liquid nitrogen cooling facilities, and the sample temperature could be measured with a thermocouple in direct contact with the front of the Ag target. It was verified by MIES and UPS that, as far as the electronic structure of the films prepared on Ag is concerned, their properties are identical with those prepared by similar procedures on Au.[16−18]

The RAIRS setup contained a Bruker IFS 66v/S vacuum Fourier transform infrared spectrometer, connected directly to the UHV chamber. The mid-IR beam was coupled to the UHV system through KBr optics and focused under an angle of 83.5° to the surface normal onto the silver substrate. The MCT (mercury−cadmium telluride) detector's cutoff was at 700 cm^{-1}; thus, the region from 4000 cm^{-1} down to 700 cm^{-1} could be used for interpretation of the vibrational spectrum of the adsorbed [EMIM]Tf$_2$N film. The spectra were recorded with a resolution of 4 cm^{-1}, and 270 scans were added prior to the Fourier transformation and the calculation of the absorbance (as the negative logarithm of the ratio of a sample spectrum to a spectrum of the clean surface).

The IR measurements on bulk liquid [EMIM]Tf$_2$N were also carried out with a Bruker IFS 66v Fourier transform infrared spectrometer. The bulk sample was prepared by pressing a liquid droplet between two KBr pellets. The entire IR cell was attached to a liquid nitrogen cooled reservoir, allowing to perform measurements down to about 100 K. The IR spectra were recorded in transmission; the same spectral region and resolution were chosen as when recording the RAIRS spectra.

3. Results

3.1. Assignment of Spectral Structures. Figures 1 and 2 present a comparison of the IR spectra from film (RAIRS results) and bulk (IR in transmission) samples for selected conditions (liquid and crystalline samples; see below). Shown are the CH stretching spectra (Figure 1) and the spectral region dominated by the bands originating from the anion (Figure 2). The identification of the spectral features (as indicated in the figures; see also the following text) seen for the bulk sample follows from available Fourier transform infrared spectroscopy (FTIR) and Raman results on liquid [EMIM]Tf$_2$N.[19,23−28] In the identification of the spectral features, seen for the films in the range between 2850 and 3200 cm^{-1} (see Figure 1) and between 800 and 1600 cm^{-1} (see Figure 2), we are guided by the corresponding spectra for the liquid and solid bulk samples.

Accordingly, the aliphatic C−H modes of the CH$_2$ group, the CH$_3$ terminal group of the ethyl chain, and the CH$_3$ group bonded
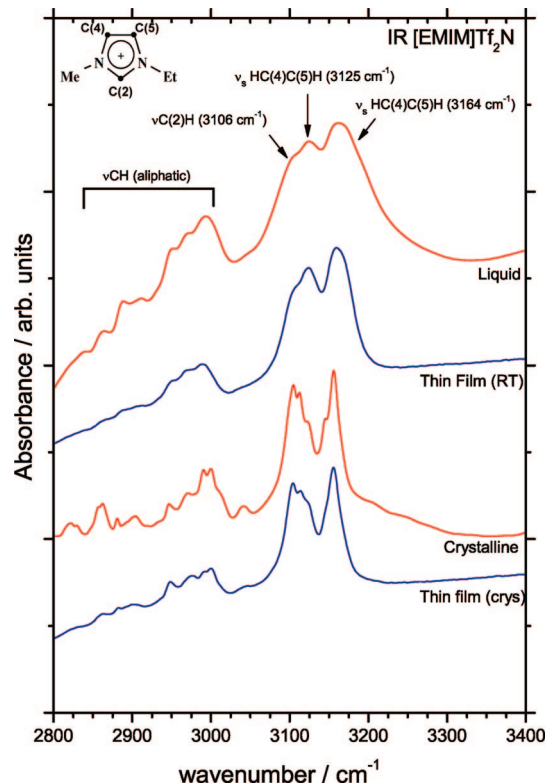

Figure 1. Infrared spectra collected between 2850 and 3200 cm^{-1}: comparison of the spectra (RAIRS) from liquid and crystalline [EMIM]Tf$_2$N films on Ag with the corresponding bulk spectra (IR in transmission).
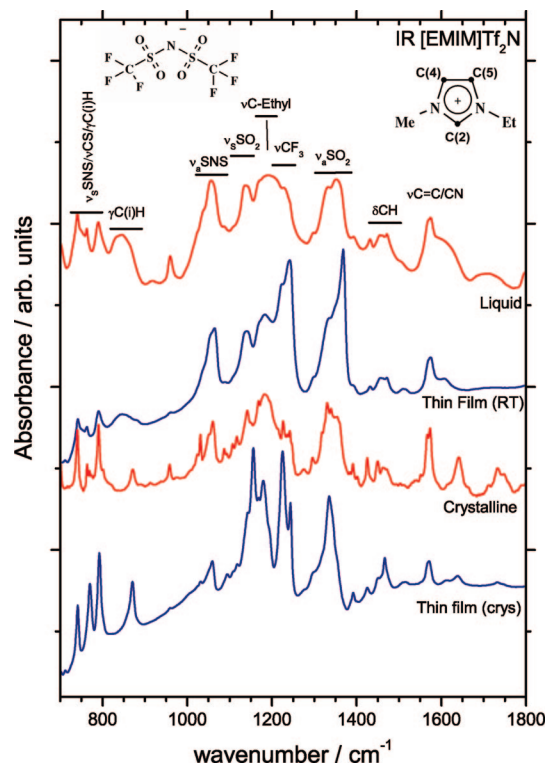

Figure 2. Infrared spectra collected between 800 and 1800 cm^{-1}: comparison of the spectra (RAIRS) from liquid and crystalline [EMIM]Tf$_2$N films on Ag with the corresponding bulk spectra (IR in transmission).

(22) Höfft, O.; Bahr, S.; Kempter, V. *Anal. Sci.*, in press, **2008**.

(23) Carter, D.; Pemberton, J. *J. Raman Spectrosc.* **1997**, *28*, 939.

(24) Talaty, E. R.; Raja, S.; Storhaug, V. J.; Dölle, A.; Carper, W. R. *J. Phys. Chem. B* **2004**, *108*, 13177.

(25) Fitchett, B. D.; Conboy, J. C. *J. Phys. Chem. B* **2004**, *108*, 20255.

(26) Yokozeki, A.; Kasprzak, D. J.; Shiflett, M. B. *Phys. Chem. Chem. Phys.* **2007**, *9*, 5018.

(27) Jeon, Y.; Sung, J.; Seo, C.; Lim, H.; Cheong, H.; Kang, M.; Moon, B.; Ouchi, Y.; Kim, D. *J. Phys. Chem B* **2008**, *112*, 4735.

(28) Jeon, Y.; Sung, J.; Kim, D.; Seo, C.; Cheong, H.; Ouchi, Y.; Ozawa, R.; Hamaguchi, H. *J. Phys. Chem. B* **2008**, *112*, 923.

to the [EMIM] ring are seen between 2850 and about 3000 cm^{-1}. A recent detailed discussion of the structure of the only partially resolved bands can be found elsewhere.[28]

The structure seen between about 3100 and 3200 cm^{-1} is attributed to the C–H stretching modes involving the C atoms of the [EMIM] ring. We assign the peaks at 3125 (3164) cm^{-1} to the antisymmetric and symmetric stretching modes of HC(4)–C(5)H (in the following denoted as ν_aHC(4)C(5)H and ν_sHC(4)C(5)H, respectively) and the shoulder seen around 3106 cm^{-1} to the C(2)–H stretching mode, further on denoted as νC(2)H.[23,25,27]

The assignment of the various groups of spectral features seen between 800 and 1600 cm^{-1}, i.e., the coarse structure in that spectral regime (see bars in Figure 2), was made on the basis of the available literature, in particular refs 29 and 30 for Tf$_2$N, and refs 24 and 31 to 33 for EMIM. In particular, strong activity is due to the modes ν_sSNS/ν_sCS (720 to 800 cm^{-1}), ν_aSNS (1010 to 1080 cm^{-1}), νC-ethyl (methyl) (1160 to 1200 cm^{-1}), ν_aCF$_3$ (1200 to 1240 cm^{-1}), ν_aSO$_2$ (1300 to 1400 cm^{-1}), and νC=C/ νCN (1420 to 1490 cm^{-1}) (ν indicates stretching modes). All spectral features are seen both in the spectra from the liquid (amorphous) and crystalline states for both film and bulk, although with different relative intensities. In particular, the sharp features terminating the high energy side of the ν_aCF$_3$ and ν_aSO$_2$ bands are practically absent for the bulk.

On the other hand, the full understanding of the fine structure of the various bands, seen for the films, requires further research.

3.2. Comparison with Literature Spectra. In general, the bulk spectra in Figure 1 appear less well resolved than the film spectra, and, as far as the CH stretching bands are concerned, show high-energy tails (between about 3200 and 3300 cm^{-1}). We consider this as indication that the components of the ionic liquid molecules are better ordered in the films. While the general structure appears to be the same in all spectra displayed in Figure 2, there are significant differences in the shape of the ν_aCF$_3$ and ν_aSO$_2$ stretching bands. Even though most of the fine structure, seen for the bulk liquid, is also visible in the spectra of the films prepared on Ag, the relative contribution of the various fine structure components is different for the films, in particular for the CF$_3$ and SO$_2$ stretching bands. On the other hand, the EMIM-related absorption bands, in particular those originating from the ring stretching (around 1570 cm^{-1}), and the CH$_3$ bending modes (around 1450 cm^{-1}) appear to be more similar for the films on Ag and for the bulk liquid. We have the impression that most of the EMIM-related spectral features are more pronounced for the bulk than for the film; this is particularly obvious for the band attributed to νC-ethyl (methyl) (around 1170 cm^{-1}).

We suggest that the differences observed in the anion-induced bands for bulk and films are caused by substrate effects. They can originate as follows: under the studied conditions the first liquid layer, when adsorbed on Ag, could be composed preferentially of either cations or anions. One possible reason for the latter type of preferential adsorption could be the soft base character of the N atom. As a consequence, the preferential adsorption in the first layer could affect the growth of additional layers, leading to local structures that are different from those found in the bulk liquid. Such local structures manifest themselves
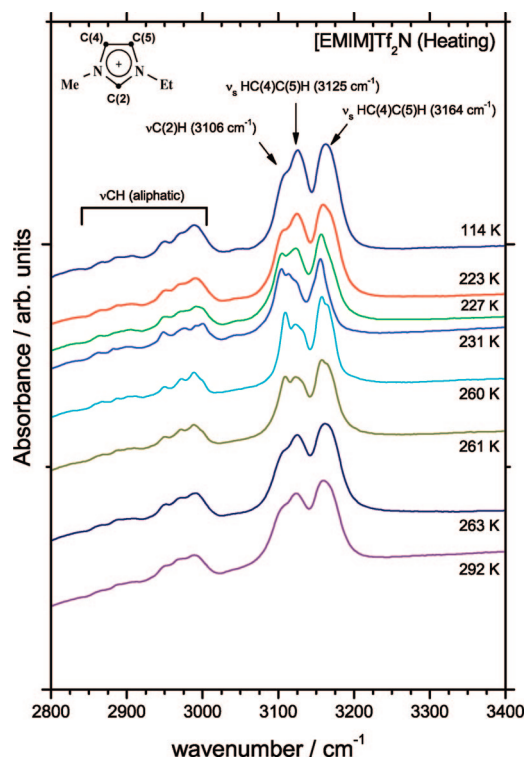

Figure 3. Temperature dependence of the RAIRS spectra collected between 2850 and 3200 cm^{-1} during heating (114 to 292 K) of an amorphous [EMIM]Tf$_2$N film on Ag.

most clearly in the bands that originate from groups that are directly involved in the cation–anion interaction, not so much in bands that involve the ring skeleton. Although RAIRS spectra for the crystalline state, to our knowledge, were not reported so far, it is likely that a preferential adsorption would affect the crystalline growth as well.

3.3. Temperature Dependence of the Film Spectra. Figures 3 and 4 display the temperature dependence of the RAIRS spectra originating from films; shown are spectra obtained when gradually heating (amorphous; see below) films produced by fast cooling of a liquid film from 292 to 114 K. The CH stretching spectra are shown in Figure 3 and the spectral region, dominated by the bands originating from the anion, in Figure 4.

As far as the cation-related activity in the considered spectral range is concerned, we will concentrate on the C–H stretching modes of the [EMIM] ring (3100 to 3200 cm^{-1}). For the anion-related intensity we will concentrate on that of the strong bands between about 1200 and 1400 cm^{-1}, assigned to the antisymmetric stretching modes ν_aCF$_3$ and ν_aSO$_2$ of the CF$_3$ and SO$_2$ groups, respectively; these bands show the most pronounced dependence on the phase of the film, and, moreover, the CF$_3$ and SO$_2$ groups are directly involved in the cation–anion interaction, at least in the crystalline state.[34] Thus, they can be expected to supply detailed information on eventual changes of the cation–anion bonding properties during the liquid-to-solid phase transition.

Differential scanning calorimetry (DSC)[34] and TOF-SIMS[35] have shown that, at cooling rates faster than 0.2 K·s^{-1}, a transition from the liquid state into an amorphous (glassy) state takes place whereby small changes only are observed in the SIMS spectra.[35]

(29) Kiefer, J.; Fries, J.; Leipertz, A. *Appl. Spectrosc.* **2007**, *61*, 1306.
(30) Rey, I.; Johansson, P.; Lindgren, J.; Lassegues, J. C.; Grondin, J.; Servant, L. *J. Phys. Chem. A* **1998**, *102*, 3249.
(31) Katsyuba, S. A.; Dyson, P. J.; Vandyukova, E. E.; Chernova, A. V.; Vidis, A. *Helv. Chim. Acta* **2004**, *87*, 2556.
(32) Katsyuba, S. A.; Zvereva, E. E.; Vidis, A.; Dyson, P. J. *J. Phys. Chem. A* **2007**, *111*, 352.
(33) Heimer, N. E.; Del Sesto, R. E.; Meng, Z.; Wilkes, J. S.; Carper, W. R. *J. Mol. Phys.* **2006**, *124*, 84.

(34) Choudhury, A. R.; Winterton, N.; Steiner, A.; Cooper, A. I.; Johnson, K. A. *CrystEngComm* **2006**, *8*, 742–745.
(35) Günster, J.; Souda, R.; Höfft, O.; Krischok, S. Manuscript in preparation, 2008.
(36) Lassègues, J. C.; Grondin, J.; Holomb, R.; Johansson, P. *J. Raman Spectrosc.* **2007**, *38*, 551–558.
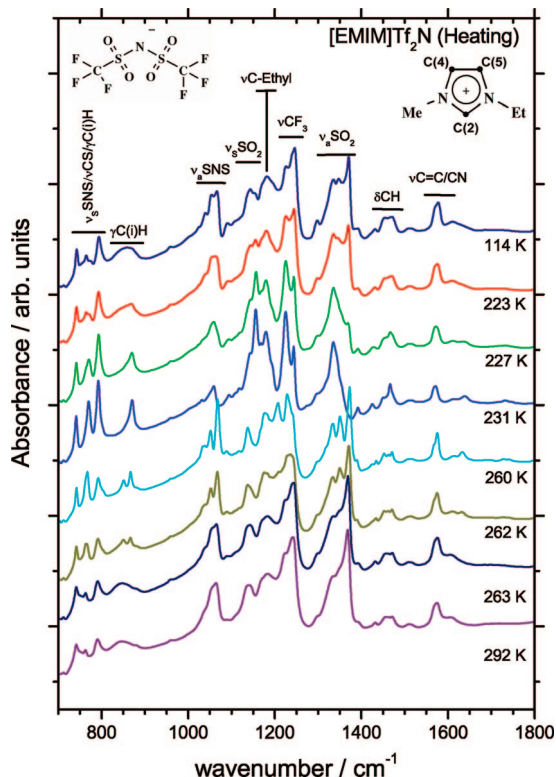
Figure 4. Temperature dependence of the RAIRS spectra collected between 800 and 1600 cm^{-1} during heating (114 to 290 K) of an amorphous [EMIM]Tf$_2$N film on Ag.

Thus, the amorphous state of [EMIM]Tf$_2$N can be obtained directly from the liquid state when employing a moderate cooling speed. On the other hand, it has been demonstrated that at sufficiently slow cooling rates a liquid-to-crystalline transition takes place upon cooling.[35] It has been established by DSC[34] and SIMS[35] (and confirmed in this work) that crystallization of an amorphous film sets in when the temperature (heating rate 0.5 K·s^{-1}) approaches the glass transition temperature of 227 K. It is also known from DSC[34] and SIMS[35] (and from this work) that, when increasing the temperature further, the crystalline film starts to melt around 260 K.

Only small changes are seen in the RAIRS spectra during the liquid-to-amorphous transition (occurring around 220 K during the cooling) (compare the top and bottom spectra). According to ref 36, the structures present in the liquid film are preserved upon cooling; i.e., the ionic species present in the liquid film have not enough time to reorganize in form of a crystalline film at the used cooling rate. This implies that also the bonding properties, found in the liquid film, remain essentially the same upon cooling to an amorphous phase, explaining the comparatively small changes observed in the corresponding RAIRS spectra. On the basis of what is known from DSC and TOF-SIMS, we attribute the drastic changes seen in the RAIRS spectra when heating to more than 227 K to an amorphous-to-crystalline transition and those around 260 K to the crystalline-to-liquid transition. During this melting process, the spectral structures characteristic for the amorphous state are largely recovered, both as far as the C−H stretching modes, involving the C atoms of the [EMIM] ring, and the anion-induced structures, ν_aCF$_3$ and ν_aSO$_2$, in particular, are concerned.

For a more quantitative analysis of the bands resulting from C−H stretching modes of the [EMIM] ring (3100 to 3200 cm^{-1}, see Figure 3), we have, as demonstrated successfully in ref 27, decomposed them into three Gaussian-shaped peaks, representing

the three stretching modes introduced above. This analysis shows that, as a result of the crystallization, the intensity of both ν_aHC(4)C(5)H and ν_sHC(4)C(5)H decreases by a factor of 2 while the intensity of νC(2)H remains practically constant.

For both the ν_aCF$_3$ and ν_aSO$_2$ bands (see Figure 4) the sharp peaks, forming the high-wavelength cutoffs of the respective bands, disappear as a consequence of the crystallization; the center of both bands shifts toward lower wavenumbers.

4. Discussion

For the following considerations, we rely on the recent theory results of refs 20 and 21 in these works, static distributions (radial and spatial distributions) of the anions and cations around a chosen cation were obtained with the help of classical MD calculations. Of particular importance for the present work are the following findings. (1) The cation−anion interaction in the liquid phase is mainly between the C(i)−H groups ($i = 2$, 4, and 5) of [EMIM] ring and the O atom of the SO$_2$ groups of the Tf$_2$N anion. In contrast, we had assumed in ref 22 that the interaction with the C(4;5)H groups is comparatively weak and can be neglected. (2) Linear complexes of the type C−H···O do not dominate the interaction;[20,21] instead, the O atoms are located preferentially above and underneath the [EMIM] ring, although in the neighborhood of the C(2)−H groups. On the basis of our results, i.e., the similarity of the RAIRS spectra in the liquid and amorphous solid states, we anticipate that in the amorphous phase the interaction mechanism is the same as in the liquid phase, i.e., in both situations the interaction is characterized by (1) and (2).

In the crystalline state, the Tf$_2$N anions do also interact with the C(i)−H groups of [EMIM] ring, again via the O atoms of the SO$_2$ groups. However, other than in the liquid, linear complexes of the type C−H···O are formed that can be described as moderately strong "standard" H-bonds.[34] The resulting layers of the H-bonded network are linked to each other via the CF$_3$ groups.

On the basis of these findings, we explain our results as follows: in the liquid films, other than in the bulk liquid, not all of the CF$_3$ and SO$_2$ groups of the anion interact with cations. These noninteracting groups give rise to the sharp peaks in the bands of the CF$_3$ and SO$_2$ stretching modes around 1240 and 1340 cm^{-1}, respectively, seen in the film, but not in the bulk spectra. These peaks are located close to the positions where the corresponding bands would be expected for isolated CF$_3$ and SO$_2$ groups. In the crystalline state, all SO$_2$ and CF$_3$ groups contribute to the formation of the H-bonded network and its (interlayer) stabilization, respectively. As a consequence, the sharp peaks at the high-wavenumber cutoff of the ν_aSO$_2$ and νCF$_3$ bands (attributed to the presence of SO$_2$ and CF$_3$ groups not involved into the interaction with cations) disappear, and the center of the corresponding bands moves to lower wavenumbers.

The changes, seen in the CH stretching bands (3100 to 3200 cm^{-1}) during the amorphous-to-crystalline transition, are qualitatively similar in the film and bulk spectra. This holds true, in particular, for the change in the relative intensity and shape of the ν_aHC(4)C(5)H and νC(2)H bands. Thus, these changes are not caused by a different structure of films and bulk. Moreover, these changes can also not be attributed to changes in the coordination of the C(i)−H groups because all these groups can be expected to be contacted by O species of the anions.[20,21] Thus, the spectral changes observed when going from the amorphous to the crystalline state are more likely to reflect the above-mentioned changes in the preferred location of the O species with respect to the C(i)−H groups, namely from

preferentially above/below the ring (in the liquid state)[20,21] to their integration into a "normal" C–H···O H-bond (in the crystalline state).[34] In addition, the changes in the CH stretching bands may reflect the fact that the C(2)–H groups are contacted with two anions through the O species of their SO_2 groups.

During melting, i.e., when heating the film beyond about 260 K, the H-bonded crystalline network is destroyed, and, according to the similarity of the RAIRS spectra for the amorphous and the liquid states, the structures present in the amorphous state are recovered to a large extent.

5. Summary

The reflection–absorption infrared (RAIRS) spectra of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM]-Tf_2N) films were measured as a function of temperature between 114 and 292 K. A comparison is made with the corresponding IR spectra (obtained with transmission spectroscopy) from bulk [EMIM]Tf_2N. Amorphous films were produced when quenching a liquid film (deposited on Ag at 292 K) to 114 K under ultrahigh vacuum conditions. Crystalline films are obtained from the amorphous ones by heating; the glass transition temperature at which the amorphous-to-crystalline transition takes place is about 227 K. Melting of the crystalline structure occurs around 260 K. The bands from the CH stretching modes of the [EMIM] ring and those from the CF_3 and SO_2 stretching modes of the anion

were analyzed in detail. Liquid and amorphous films show rather similar spectra suggesting that their film structure is similar. Marked differences are noticed in the spectra for the liquid and the crystalline state: the shape of the C–H bands of the [EMIM] ring and of the CF_3 and SO_2 stretching bands of the anion is characteristically different. This supports theoretical predictions that the cation–anion interaction involves the C–H groups of the [EMIM] ring and oxygen species of the SO_2 groups of the anions mainly. The observed changes in the CF_3 stretching band suggest that the CF_3 play an important role in the network formation.

Differences seen in the film and bulk spectra for the liquid and solid state are attributed to differences in the structure of the [EMIM]Tf_2N film and bulk networks.