



A time-of-flight secondary ion mass spectroscopy study of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide RT-ionic liquid

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ABSTRACT

Time-of-flight secondary ion mass spectroscopy (TOF-SIMS) has been used to investigate the surface structural transformation of room temperature ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][Tf₂N]), in the temperature range between 300 and 160 K. The intensity of the [EMIM]⁺ cation from the crystal surface becomes about twice as large as that from the glassy and liquid surfaces, whereas the fragment ions from the [Tf₂N]⁻ moiety are almost unchanged upon crystallization. This phenomenon can be ascribed to the steric effect of the cation relative to the counter anion at the topmost surface layer rather than their surface compositions: a specific layered structure of the crystal surface, in which the imidazolium ring of [EMIM]⁺ is aligned parallel to the surface plane, is thought to be responsible for the enhancement of the [EMIM]⁺ ion emission. The smaller [EMIM]⁺ intensity from the glassy and liquid films evidences that the imidazolium ring is not parallel to the surface.

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1. Introduction

There is a rapidly growing interest in room temperature ionic liquids (RTILs) due to their unique physicochemical properties. They are molten organic salts with a high solvent power for both polar and non-polar compounds. Furthermore, ionic liquids are non-flammable, thermally and chemically stable, electrically conductive and non-volatile [1,2]. A recent issue of Accounts of Chemical Research gives a very good overview about the present activities in this field [3]. Among these properties, their negligible vapor pressure at room temperature makes them accessible to surface science techniques. As a consequence, ionic liquids have been subject to comprehensive studies, by employing classical surface sensitive methods such as X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS) [4–6], metastable impact electron spectroscopy (MIES) [4,5], secondary ion mass spectroscopy (SIMS) [6], direct recoil spectrometry (DRS) [7–9], high resolution electron energy loss spectroscopy (HREELS) [5], and sum frequency generation spectroscopy (SFG) [10–12]. An introduction in the surface chemistry of ionic liquids (non-UHV and UHV techniques) was given by Aliaga et al. [13]. The phase transition of ionic liquids is of great importance for possible applications, such as multiphasic homogeneous catalytic reactions and selective solvation of gaseous

species [4,13]. The species solvated in the ionic liquid could segregate to the crystals surface. For the liquid state, surface enrichment and depletion effects are reported by Maier et al. [14].

To date, composition and orientation of the molecules at the gas-liquid interface of the RTIL have attracted considerable attention because the interfacial structure is of crucial importance for understanding of the chemical processes at the molecular level. A consensus appears to be reached that cations and anions share the surface without segregation for pure RTILs [4–12], but the orientation of the ions at the topmost layer of the gas-liquid interface is still controversial. The DRS analyses of 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF₆] and tetrafluoroborate [BMIM][BF₄] suggested that imidazolium ring is perpendicular rather than parallel to the surface and that the butyl tails are surface parallel (pointing into the bulk) for [BMIM][PF₆] ([BMIM][BF₄]) [7–9]. On the other hand, the SFG study suggested that the imidazolium ring of [BMIM]⁺ lies nearly parallel to the surface with its butyl tail protruding out of the surface [10]. Based on the primary-energy dependence in HREELS, Krischok et al. [5] reported that the ion pair of [EMIM][Tf₂N] might be reoriented in the outermost surface region at low temperatures because the surface vibrational structure is largely different from the bulk structure, although no such difference was observed between the bulk and surface structures at room temperature. In this respect, surface layering of the imidazolium-based ionic liquids has been reported to occur by an X-ray reflectivity study [15] and molecular dynamics simulation [16]. In contrast to the well-known surface layering of

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liquid metals, only a surface layer about one molecular thickness is shown to have a higher density than that in the bulk; the cations in this layer might be strongly aligned.

Although crystal structures of RTILs have been revealed by X-ray crystallography [17,18], the precise structural determination of the liquid surface is very difficult because of disordering. Therefore, it might be a promising approach to investigate the structural transformation of RTIL during crystallization. In fact, previous studies on [BMIM][PF₆] [19] and 1,3-dimethylimidazolium chloride and hexafluorophosphate [20,21] suggested that the local structures of these ionic liquids in their fluid states are very much like those of crystals. Very recently, Smith et al. [6] have utilized time-of-flight (TOF) SIMS for the surface composition analyses of [EMIM][Tf₂N] and [EMIM][C₂H₅OSO₃] in combination with XPS. During a temperature-ramped experiment, they observed that the [EMIM][C₂H₅OSO₃] sample exhibits a sharp transition into a non-conductive state at temperatures below ca. -90 °C; however, the TOF-SIMS spectra below this temperature are almost indistinguishable from those collected at higher temperatures, suggesting the formation of glassy state. Höfft et al. [4] observed surface charging of [EMIM][Tf₂N] when the sample was cooled below ~230 K. In these studies, nothing has been revealed about the phase transition of RTIL at low temperatures. In the present paper, we study the surface structural transformation of [EMIM][Tf₂N] during crystallization and melting using temperature-programmed TOF-SIMS. We demonstrate that the phase transition of RTIL can be monitored at the molecular level using TOF-SIMS.

2. Experimental

[EMIM][Tf₂N] (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 substrate was a gold covered silicon wafer, which was formed by sputter deposition of the polycrystalline gold film (thickness 200 nm) onto the supporting Si(100) substrate precovered by a 10 nm thick Ti adhesion layer. Samples were prepared by spreading a droplet of the ionic liquid onto the substrate by spin coating. The film thickness was ~0.1 μm. For TOF-SIMS measurements, He⁺ ions produced in an electron-impact-type ion source were accelerated to 2 keV, chopped into 60 ns (fwhm) pulses by means of an electrostatic deflector, and finally scattered at the sample surface [22]. Negatively and positively charged sputter fragments released from the sample surface were measured by floating the sample with a bias voltage of ±500 V, respectively. A stainless steel mesh placed 4 mm in front of the sample surface facilitates the extraction of the charged sputter fragments into the field-free drift region of a TOF tube. In order to minimize surface damage, the incident He⁺ flux was kept below 0.1 nA/cm² after chopping. The sample holder was mounted on the cold-finger of a closed-cycle He refrigerator which allows for sample cooling down to 10 K. The sample temperature was controlled by a commercial PID controller.

3. Results and discussion

Fig. 1 presents SIMS spectra of the positively and negatively charged sputter fragments (top (a) and bottom (b) panels, respectively). The spectra were obtained from the as-prepared [EMIM][Tf₂N] film at room temperature. The most prominent species in the positive ion spectrum (a) is the [EMIM]⁺ cation at 111 atomic mass units (amu). It is the parent species for the majority of smaller molecular fragments in the positive ion spectrum. Only F⁺ (19 amu), CF⁺ (31 amu), and CF₃⁺ (69 amu) peaks unambiguously originate from fragments of the bistriflimide [Tf₂N]⁻ anion. The

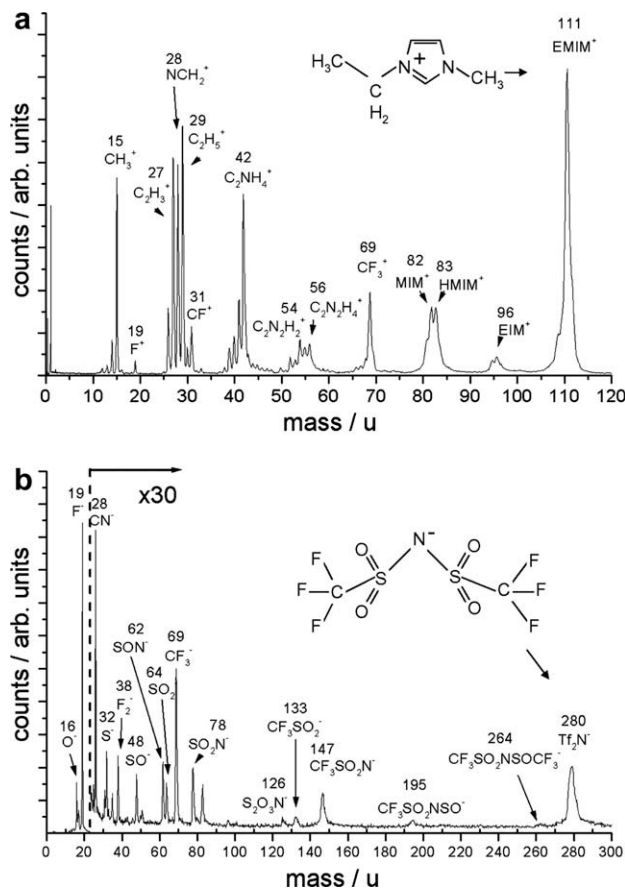


Fig. 1. Positive (a) and negative (b) TOF-SIMS spectra taken from a [EMIM][Tf₂N] ionic liquid film supported on a gold covered Si-substrate at room temperature. The spectra are obtained by employing He⁺ ions as a primary projectile at a kinetic energy of 2 keV.

negative ion spectrum (b) is clearly dominated by smaller fragments of the [Tf₂N]⁻ anion, such as O⁻ (16 amu) and F⁻ (19 amu); a signal from the intact [Tf₂N]⁻ anion at 280 amu is also detected. The identification of the higher mass peaks in the spectra is based on the assumption that single bond cleavage of the intact [EMIM]⁺ cation and [Tf₂N]⁻ anion dominates their fragmentation.

TOF-SIMS spectra from [EMIM][Tf₂N] have been reported previously by Smith et al. [6] using 25 keV Ga⁺ ions as projectiles. The spectra of Fig. 1 resemble those obtained in [6] closely for masses smaller or equal to the intact [EMIM]⁺ cation and [Tf₂N]⁻ anion. Moreover, no significant differences are observed in the relative abundance of the secondary positive ions between He⁺ and Ga⁺ projectiles. The cluster ions in the form [EMIM]_n[Tf₂N]_{n-1}⁺ and [EMIM]_{n-1}[Tf₂N]_n⁻, which are observed by the Ga⁺ excitation, are almost completely absent by the He⁺ excitation. This might be caused by poor ion mass resolution or ion detection efficiency at higher masses (see Fig. 1). We employed a linear (no-reflectron type) TOF-SIMS setup in the present study.

In order to investigate how the phase transition of the ionic liquid influences the secondary ion yields, TOF-SIMS spectra were recorded continuously every 30 s by cooling the sample from RT to 180 K at a rate of 0.06 K s⁻¹. Fig. 2a presents the intensities of the CH₃⁺, C₂H₃⁺, CF₃⁺ and [EMIM]⁺ ions as a function of temperature. At around 224 K, the [EMIM]⁺ intensity nearly doubles, while the CH₃⁺ and C₂H₃⁺ signals reveal a 15% loss in intensity. We assign this phenomenon to crystallization of [EMIM][Tf₂N]. In fact, the existence of a crystalline phase can be easily confirmed visually: crystallization results in the formation of a polycrystalline film

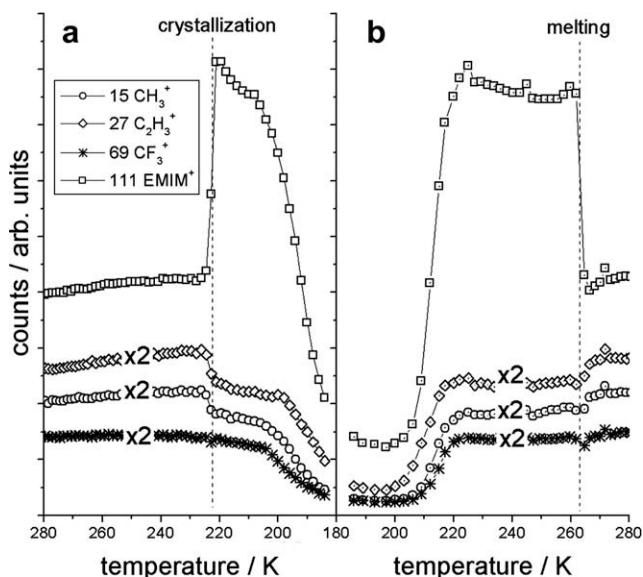


Fig. 2. TOF-SIMS intensities of the CH_3^+ , C_2H_3^+ , CF_3^+ , and $[\text{EMIM}]^+$ sputter fragments obtained from a $[\text{EMIM}][\text{Tf}_2\text{N}]$ ionic liquid film as a function of the film's temperature: (a) cooling at a rate of 0.06 K s^{-1} and (b) annealing at a rate of 0.075 K s^{-1} .

revealing a macroscopic domain pattern. Shortly after crystallization the sample surface charges up. Sample charging is deduced from a peak shift and broadening observed in the individual TOF-SIMS spectra, see also Fig. 3. Since the TOF-SIMS data analysis software integrates the peak area over fixed channels, the shift in the peak position results in the decreases of ion signal intensities from 200–185 K in Fig. 2a. The reverse temperature programmed experiment is presented in Fig. 2b; the temperature was increased from 180 K to 280 K at a rate of 0.075 K s^{-1} . The secondary ion intensities increase at around 220 K, where the conductivity of the film is thought to recover. The intensity of all three signals plateaus between about 220 K and 260 K. At a temperature of 262 K, the CH_3^+ and C_2H_3^+ signals reveal a subtle increase in intensity while the $[\text{EMIM}]^+$ signal drops sharply. All signals reached their respective room temperature intensities at 265 K. We attribute this abrupt change in the secondary ion intensities to melting of the crystalline $[\text{EMIM}][\text{Tf}_2\text{N}]$ film. In contrast to the pronounced temperature dependence of these ions from the $[\text{EMIM}]^+$ ion, the CF_3^+ ion sputtered from the $[\text{Tf}_2\text{N}]^-$ anion do not show any characteristic changes in intensity upon crystallization of the film. The negative ions such as F^- and O^- also exhibited no changes in intensity during crystallization and melting (not shown).

For a more detailed overview of the collected SIMS data, Fig. 3a and b presents two sequences of TOF-SIMS spectra corresponding to Fig. 2a and b, respectively. In the cooling process shown in Fig. 3a, the abruptly increasing $[\text{EMIM}]^+$ cation intensity upon crystallization at around 223 K is clearly noticeable. Furthermore, it can be seen that a subsequent charge-up of the sample at lower temperatures results in a broadening of the individual peaks accompanied by a shift towards lower masses (or shorter TOF). The peak shift is caused by the additional acceleration of the secondary ions by the positive charges accumulated at the sample surface. During annealing the ionic liquid film (Fig. 3b), charge neutrality of the surface is achieved at around 220 K. At this temperature, the $[\text{EMIM}]^+$ intensity exhibits its maximum value. The $[\text{EMIM}]^+$ signal drops sharply at 262 K as the crystalline film melts.

In the present experiment, since the temperature of the cold finger close to the sample is monitored, there might exist a temperature differential between the sample and cold finger. Therefore, we

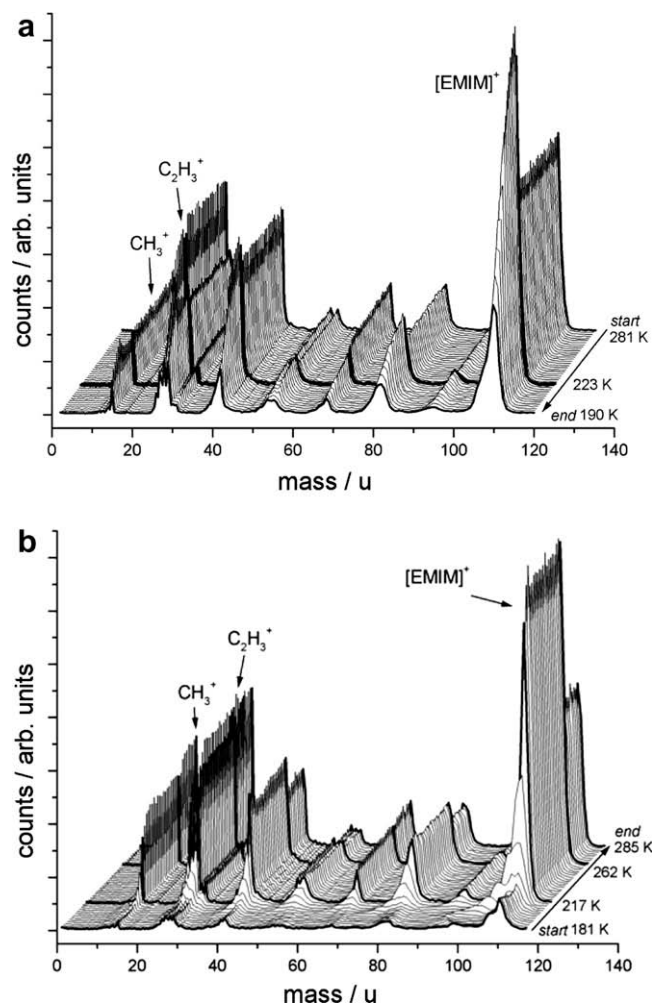


Fig. 3. Sequence of TOF-SIMS spectra corresponding to the cooling (a) and annealing (b) of a $[\text{EMIM}][\text{Tf}_2\text{N}]$ ionic liquid film.

have carefully checked the melting temperature at lower heating rates. We have found that the crystalline $[\text{EMIM}][\text{Tf}_2\text{N}]$ melts at 257 K at the lowest heating rate. By varying the heating rate systematically, we found that melting of the crystalline $[\text{EMIM}][\text{Tf}_2\text{N}]$ is observed in a temperature range between 257 K and 265 K. This temperature agrees well with the melting temperature determined from a differential scanning calorimetry (DSC) [18]. On the other hand, the crystallization temperature can be altered from 220 K and 240 K by changing the cooling rates from 0.06 K s^{-1} to 0.01 K s^{-1} , respectively. At cooling rates higher than 0.2 K s^{-1} , a transition from the liquid state into a glassy state takes place whereby no noticeable changes in the SIMS signals can be recognized. Thus, the supercooled liquid and glass of $[\text{EMIM}][\text{Tf}_2\text{N}]$ can be obtained at a moderate cooling speed, which is consistent with the absence of the crystallization behavior in the DSC measurement during the cooling scan [18].

We prepared a glassy $[\text{EMIM}][\text{Tf}_2\text{N}]$ film by quenching the liquid film to 150 K; then, the sample was heated at a rate of 0.075 K s^{-1} . The TOF-SIMS experimental results are shown in Fig. 4. The glassy film undergoes severe charging at low temperatures, but the conductivity recovers at temperatures higher than 185 K as confirmed from disappearance of the shift and broadening of the spectral peaks. The $[\text{EMIM}]^+$ intensity (CH_3^+ and C_2H_3^+ intensities) increases (decrease) drastically at around 220 K due to crystallization. The ion intensities change again at 263 K because the crystalline $[\text{EMIM}][\text{Tf}_2\text{N}]$ film melts. There is no noticeable change

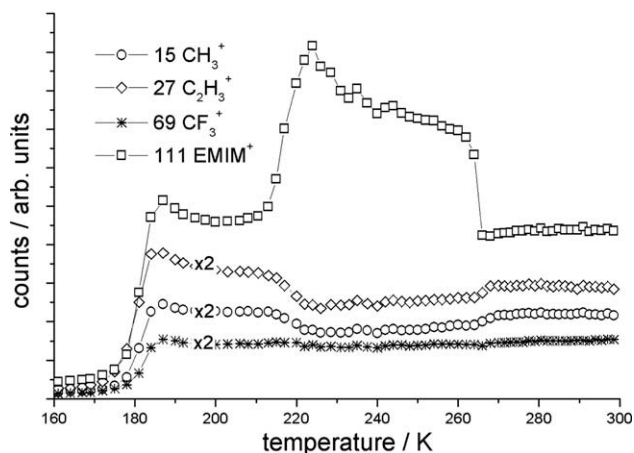


Fig. 4. Temperature-programmed TOF-SIMS intensities of the CH_3^+ , C_2H_3^+ , CF_3^+ and $[\text{EMIM}]^+$ ions sputtered from a $[\text{EMIM}][\text{Tf}_2\text{N}]$ ionic liquid film. A glassy film was formed by quenching the liquid film to 150 K; then the temperature was increased at a rate of 0.075 K s^{-1} .

in the CF_3^+ signal during crystallization and melting of the ionic liquid film. The observed crystallization and melting temperatures are in excellent agreement with those determined by the DSC study [18]. The temperature at which charge neutrality of the glassy sample is reestablished (185 K) is considerably lower than that for the crystalline film (215–220 K). The recovery of the conductivity for the initially glassy film at 185 K might be explained by the evolution of supercooled liquid since the glass–liquid transition is likely to occur at 175 K [23]. On the other hand, the charging of crystalline film shown in Fig. 2 cannot be attributed to any important materials properties. A further discussion of the sample charging is beyond the scope of the present paper. The HREELS study by Krischok et al. [5] revealed the occurrence of surface ordering of $[\text{EMIM}][\text{Tf}_2\text{N}]$ at 100 K. They observed that the low-temperature HREELS data differ markedly from the RT data especially with low primary energy because of high surface sensitivity. It was suggested that ion pairs are reoriented with the $[\text{EMIM}]^+$ ring lying parallel to the surface. This phenomenon might be related to crystallization although the surface structural transformation during the phase transition has not been observed.

Here, we demonstrated that TOF-SIMS reveals undoubtedly the crystallization and melting of the $[\text{EMIM}][\text{Tf}_2\text{N}]$ film based on the drastic change in the secondary ion intensities. The increase of the $[\text{EMIM}]^+$ intensity during crystallization might be ascribed to the surface segregation of $[\text{EMIM}]^+$. However, this simple idea should be discarded because the CF_3^+ intensity is almost unchanged during crystallization. This phenomenon is most likely explainable by the steric properties of the ion pair in the outermost surface layer. Crystallographic data of $[\text{EMIM}][\text{Tf}_2\text{N}]$ [18] are informative as a guide in constructing the surface structure model. $[\text{EMIM}][\text{Tf}_2\text{N}]$ crystallizes in non-centrosymmetric space group $\text{Pca}2_1$. The ions are packed in the crystal lattice via several C–H...O hydrogen bonds between the imidazolium ring and the $>\text{SO}_2$ moieties of the $[\text{Tf}_2\text{N}]^-$ ion, thereby forming a characteristic layered structure with an ABAB... type arrangement (refer to Fig. 3 of Ref. [18] for the crystal packing). The imidazolium rings are parallel to the plane; each layer is shared by the same number of cations and anions. We consider that this specific layered structure of the crystal surface is responsible for the enhanced $[\text{EMIM}]^+$ intensity. In fact, the enhancement of the cation yield during crystallization has not been observed for other RTILs that crystallize into different structures, such as $[\text{BMIM}][\text{PF}_6]$ and $[\text{BMIM}][\text{BF}_4]$, but a quite similar phenomenon has been observed for $[\text{BMIM}][\text{CF}_3\text{SO}_3]^-$ that crystallizes in the layered structure [24]. The ion emission

from the partly ionic system has been explained by the bond breaking model [25], in which breaking of the ionic bonds during collisions between anions and cations leads to the ionic emission. The $[\text{EMIM}]^+$ ion in the topmost surface layer is thought to be kicked out by collision with the second-layer $[\text{Tf}_2\text{N}]^-$ ion. On the other hand, it is suggested that the ion intensity is reduced considerably due to the presence of hydrogen bonding [26,27] because the ionic hole can be delocalized through the hydrogen bond with some covalency. Note that the anion–cation interaction of the crystalline $[\text{EMIM}][\text{Tf}_2\text{N}]$ surface is highly anisotropic: the inter-layer interaction is basically ionic while some covalency should exist in the intra-layer interaction because of the C–H...O hydrogen bonds. As schematically shown in Fig. 5, when the imidazolium rings are parallel to the surface, the $[\text{EMIM}]^+$ ions can be emitted perpendicularly to the surface mainly via the ionic interaction. On the other hand, the hydrogen bonds are reinforced inevitably during collisions if the imidazolium ring is not parallel to the surface, thereby reducing the $[\text{EMIM}]^+$ intensity. We therefore tend to assign the reduction of the $[\text{EMIM}]^+$ intensity for glassy and liquid films to distortion of the imidazolium ring from the surface-parallel arrangement. We should address the contrary behaviors of the CH_3^+ and C_2H_3^+ intensities during crystallization. These ions are emitted either from the 1-position ethyl group or the 3-position methyl group. They are reduced in intensity when the layered structure is formed during crystallization because the $>\text{N}-\text{CH}_3$ and $>\text{N}-\text{C}_2\text{H}_5$ bond directions become parallel to the surface. The phase transition of $[\text{EMIM}][\text{Tf}_2\text{N}]$ has recently been studied using reflection absorption infrared spectroscopy (RAIRS) [28]: the shape

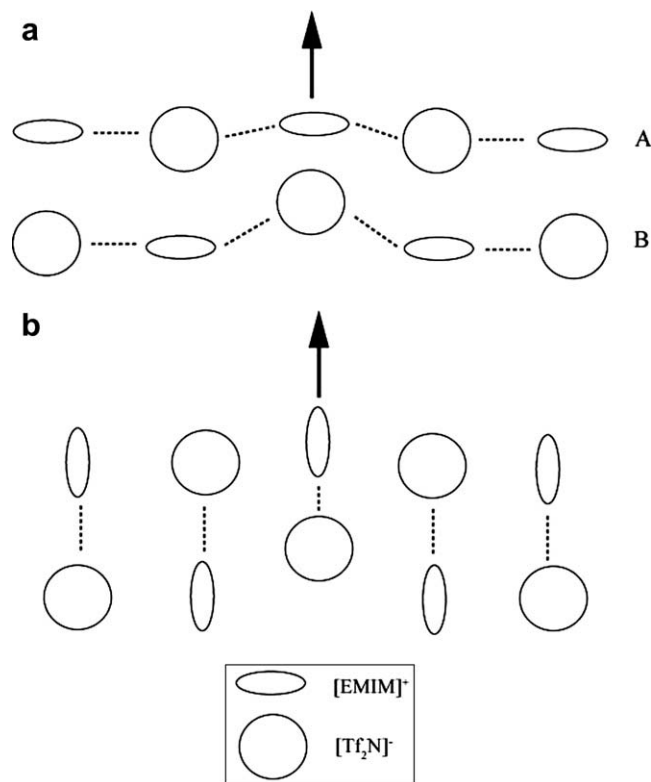


Fig. 5. A schematic view of the ion emission mechanism of the $[\text{EMIM}]^+$ ion. (a) The crystalline film consists of a ABAB... type layered structure with the imidazolium ring parallel to the surface, so that $[\text{EMIM}]^+$ is emitted via a highly ionic collision with the second-layer $[\text{Tf}_2\text{N}]^-$ anion. (b) When the imidazolium ring is perpendicular to the surface, the hydrogen bond between the anion and cation (shown by a broken line) is reinforced during collisions, thereby reducing the sputtered $[\text{EMIM}]^+$ yield.

of the IR absorption band changes due to crystallization and melting at around the same temperature observed in the present study.

4. Summary

We have measured positive and negative TOF-SIMS spectra of the [EMIM][Tf₂N] ionic liquid film using the primary He⁺ ions at temperatures of 160–300 K. Although the He⁺ ion has a large internal electronic energy, the secondary ions are emitted mainly via the kinetic sputtering process since the observed ion spectra are basically identical to those obtained by the Ga⁺ excitation. In the temperature-programmed TOF-SIMS measurements, the [EMIM]⁺ intensity increases drastically during crystallization at 220 K, whereas the CH₃⁺ and C₂H₃⁺ ions decrease in intensity. The CF₃⁺ ion from the [Tf₂N]⁻ moiety is almost unchanged during crystallization. These behaviors are explicable by the steric effect of the anion and cation in the crystals, forming the characteristic layered structure. The cation, which is arranged with its imidazolium ring parallel to the surface, is not influenced by the C–H...O hydrogen bonds significantly during collisions with the counter anion in the second layer, thereby facilitating the [EMIM]⁺ emission perpendicular to the surface. The imidazolium rings at the liquid and glassy film surfaces are not parallel to the surface; as a result, the ethyl and methyl groups of the [EMIM]⁺ ion tend to be exposed to the vacuum. The surface ion composition is fundamentally unchanged during the phase transition. Thus, we have monitored not only the bulk phase transition of RTIL but also its surface structural transformation by using temperature-programmed TOF-SIMS.

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