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## Near threshold photodissociation study of EMIMBF<sub>4</sub> vapor

 I. Kuusik,<sup>a</sup> M. Tarkanovskaja,<sup>a</sup> J. Kruusma,<sup>b</sup> V. Reedo,<sup>a</sup> R. Välbe,<sup>a</sup> A. Lõhmus,<sup>a</sup> V. Kisand,<sup>a</sup> E. Lust,<sup>b</sup> E. Kukk<sup>c</sup> and E. Nõmmiste<sup>a</sup>

Photodissociation of the [EMIM][BF<sub>4</sub>] ionic liquid vapors following excitation with light in the vacuum ultraviolet region was studied at different liquid temperatures. For this purpose time-of-flight mass spectra and partial ion yield spectra were recorded. From the partial ion yield measurements the appearance energies of the main positive fragments were determined. The appearance energies of the two dominating fragments were determined to be 8.2 eV (MIM<sup>+</sup>) and 7.4 eV (dehydrogenated EMIM<sup>+</sup>). The second threshold energy of the dehydrogenated EMIM cation was found to be 9.4 eV. The supporting *ab initio* calculations explain and agree with these experimentally determined energy values. EMIMF and EMIMBF<sub>2</sub> cations were also identified as possible photodissociation fragments. The possible presence of hydrogenated and dehydrogenated EMIM cations was shown. The [EMIM][BF<sub>4</sub>] ion-pair was shown to dissociate after photoexcitation (even below the ionization threshold). No significant thermal decomposition of the [EMIM][BF<sub>4</sub>] molecules was observed.

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### 1. Introduction

Ionic liquids (IL) have possible applications in diverse fields, such as synthesis, catalysis, biocatalysis, separation technology, electrochemistry, analytical chemistry, and nanotechnology, *etc.*<sup>1</sup> With the selection of many available anions and cations it is possible to synthesize a vast number of different ionic liquids with different properties.

Although ionic liquids have very low vapor pressures, vaporization is still occurring and gas phase experiments are possible. Some of the ionic liquids can even be distilled in vacuum with minor thermal degradation.<sup>2,3</sup>

The fragmentation behavior of IL under electron, ion and photon excitation is also useful to help differentiate between decomposition and vaporization processes.<sup>4</sup> Also the ionization energy of the IL and appearance energies of the fragments can give insights into radiation chemistry in the bulk phase.<sup>4</sup> Strasser *et al.* pointed out that near threshold investigations are informative.<sup>5</sup> Indeed, the energy and the symmetry constraints of the photoabsorption process may help to infer additional information from the spectra. Furthermore, experimental ion spectra can help to validate the *ab initio* studies and the theoretical models used.

We have thus chosen a simple ionic liquid ([EMIM][BF<sub>4</sub>]) and studied its mass spectra under VUV excitation.

Using similar methods we have previously investigated fragmentation of simpler molecules like CsCl<sup>6</sup> and rubidium halides<sup>7,8</sup> and also very complicated molecules like tributyltin chloride<sup>9</sup> and thymidine.<sup>10</sup>

[EMIM][BF<sub>4</sub>] (1-ethyl-3-methylimidazolium tetrafluoroborate) consists of the EMIM cation and the BF<sub>4</sub> anion. Different designations have been used for this compound: [emim][BF<sub>4</sub>], EMIM-BF<sub>4</sub>, [C<sub>2</sub>mim][BF<sub>4</sub>], [C<sub>2</sub>C<sub>1</sub>IM][BF<sub>4</sub>], [EMI][BF<sub>4</sub>], EMI-BF<sub>4</sub> *etc.*

To the best of our knowledge this is the first presentation of a full fragmentation mass spectra of [EMIM][BF<sub>4</sub>]. Deyko *et al.* published a low resolution mass spectrum of [EMIM][BF<sub>4</sub>] with a limited mass range.<sup>11</sup> The similar [BMIM][BF<sub>4</sub>] (1-butyl-3-methylimidazolium tetrafluoroborate) fragmentation mass spectrum has also been investigated by Deyko *et al.*<sup>4</sup>

### 2. Experimental

The experiment was performed at an undulator beamline I3 of the MAX-III synchrotron radiation facility (Lund, Sweden).<sup>12</sup> The beamline is equipped with a normal incidence monochromator. A MgF<sub>2</sub>/Al coated grating was used in the monochromator and the higher harmonics of the undulator radiation were blocked using a LiF crystal. This limits the highest energy dependent TOFMS spectra to about 10.5 eV.

The [EMIM][BF<sub>4</sub>] sample with a stated purity of >99% was purchased from Sigma-Aldrich and was used without further treatment. It was evaporated to the sample region of the analysis vacuum chamber from a quartz crucible of an effusion cell (MBE Komponenten NTEZ-40).

<sup>a</sup>Institute of Physics, University of Tartu, Ravila 14c, 50411 Tartu, Estonia

<sup>b</sup>Institute of Chemistry, University of Tartu, Ravila 14a, 50411 Tartu, Estonia

<sup>c</sup>Dept. of Physics and Astronomy, University of Turku, FIN-20014 Turku, Finland

The time of flight mass spectra (TOFMS) and partial ion yield (PIY, *i.e.* yield of ions as a function of photon energy) spectra were recorded using a Wiley–McLaren type ion time-of-flight (TOF) spectrometer with a 320 mm drift tube and a 77 mm diameter Hamamatsu microchannel plate detector.

Due to the relatively low vapor density of the ionic liquid, a number of background gases ( $N_2$ ,  $O_2$ ,  $H_2O$ ,  $CO_2$  *etc.*) also present inside the vacuum chamber, were observed as well, similarly to other works.<sup>13</sup> Small peaks due to spectrometer memory (due to contaminants retained inside the TOF chamber from previous experiments) were also observed ( $m/z = 43$ – $46$ ,  $57$ ,  $71$ ,  $85$ ,  $127$ ,  $149$ ,  $154$ ,  $167$ ) like in some other studies.<sup>4,13,14,15</sup> Fortunately, there are very few overlaps between the peaks from the contaminants and the ionic liquid fragments (see Fig. 1).

The incident energy was scanned in the photon energy range of 7.0–10.5 eV and the energy dependent TOFMS spectra of the ionic liquid vapor were measured. The resulting spectra were afterwards scaled by the silicon photodiode (AXUV-100, International Radiation Detectors, Inc.) current to account for the differences in the flux at the experimental chamber. The PIY spectra of some relevant fragments were then extracted from these spectra (see Fig. 2).

The threshold energies were determined by fitting a linear function to the PIY spectra.<sup>10</sup> The appearance energies were determined by simply analyzing the TOFMS spectra (see Fig. 3 as an example).

*Ab initio* DFT calculations were performed using Spartan 14 (ref. 16) software using the hybrid B3LYP functional. The gaussian basis sets 6-31G\*\* (typical d,p-polarized basis sets) have been used in the calculations. The *ab initio* activation energies of the fragments were determined by the energy difference between the parent [EMIM][BF<sub>4</sub>] molecule and the resulting fragments. All calculated structures were geometry optimized except for the  $m/z = 40$ – $56$  fragments which were calculated as in their equilibrium structure in the cation. This calculation therefore estimates the minimum energy required for the fragmentation process. The actual energy required may be higher due to transition state energy barriers.

To make comparisons to other *ab initio* calculations, the ethyl-imidazolium (EIM,  $m = 96$ ) ionization energy (8.5 eV) and the methyl loss activation energy (11.2 eV) were calculated in the M06 level of DFT theory. The agreement with the calculation of Chambreau *et al.*<sup>17</sup> is within 0.2 eV. The ionization energy of [EMIM][Br] in the MP2 level of theory was also calculated to be 6.8 eV.

Chambreau *et al.* stated that the B3LYP functional did not provide sufficient accuracy in case of [EMIM][Br] and that the M06 functional was better in that regard. However with the BF<sub>4</sub> anion, generally the two functionals agree rather well, with B3LYP underestimating all energies. The B3LYP functional was chosen because of its extensive use in a wide range of systems and its well-known properties. Also, the excited state analysis is possible with this functional. Together with (full) geometry optimization this calculation mode therefore tends to underestimate energies.

### 3. Results and discussion

It has been already established that the ionic liquid vapor is composed of neutral species,<sup>14,17</sup> as there are no ions detected in the absence of excitation light or in case of excitation below the threshold (*i.e.* low energy photons or electrons).<sup>4,13</sup> It is also known that under ionization, the ionic liquids are relatively unstable to fragmentation.<sup>4</sup> All of these points are also confirmed in this work.

The TOFMS spectrum of [EMIM][BF<sub>4</sub>] measured using excitation with high energy photons (20.0 eV) is shown in Fig. 1. The most prominent peaks at  $m/z = 82$ , 110 that originate from the ionic liquid, are assigned to methyl-imidazolium (MIM<sup>+</sup>)<sup>4,5,13,14,17,18</sup> and to the dehydrogenated ethyl-methyl-imidazolium cations respectively. The parent (intact) cation – EMIM ( $m/z = 111$ ) – is also clearly visible in the TOFMS spectra (Fig. 1). The reader is referred to Table 1 for the peak assignment, abbreviations, calculated activation energies and experimental appearance energies.

At lower excitation energies (roughly below 10 eV) and mostly at lower ionic liquid temperatures multiple strong peaks around  $m/z = 185$ – $193$  appear in the TOFMS spectra. These peaks are not visible in the higher excitation energy spectra shown in Fig. 1. The nature of these peaks is not fully understood and their (and other fragments) temperature dependencies will be discussed in a forthcoming paper.

Fig. 2 shows the photon energy dependent partial ion yield spectra of several fragments. The two slope shape of the yield curve is clearly evident in case of the EMIM cation. A linear fit to the slopes was made to find the threshold energies of the fragments from the PIY spectra. The first threshold energy of the dehydrogenated EMIM ( $m/z = 110$ ) is about 7.9 eV (Fig. 2) and the appearance energy at temperature 250 °C is about 7.4 eV. The appearance and threshold energies show very little dependence on temperature. This is of course expected, since they are mostly determined by the electronic properties. However, the intensities of some fragments show strong dependence on temperature (see Fig. 4). Most PIY spectra display saturation or decrease in intensity starting from about 10 eV. The origin of this effect can be both physical (*i.e.* due to the properties of the compounds under study) and/or

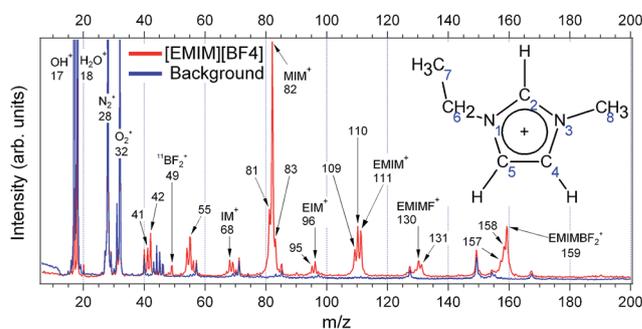


Fig. 1 Non-background corrected time of flight mass spectrum of [EMIM][BF<sub>4</sub>] vapor excited at photon energy 20.0 eV. The liquid cell was at temperature 190 °C. The inset illustrates the EMIM cation.

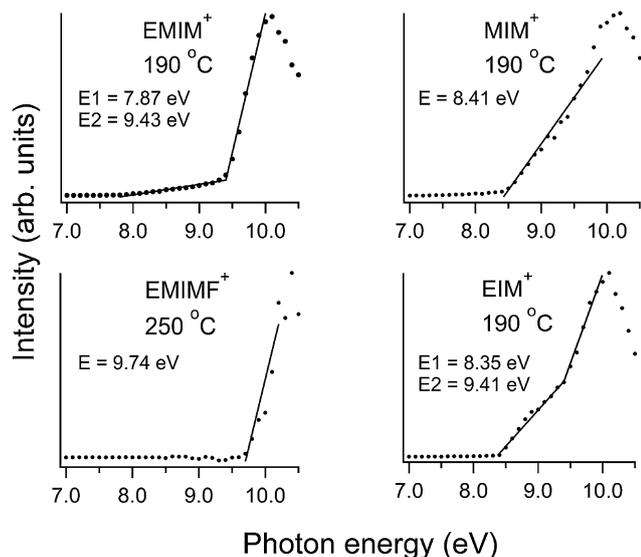


Fig. 2 Partial ion yield spectra of several cations showing the linear fits used to determine the threshold energies. In all cases the whole area of the corresponding peak complex (including the dehydrogenated peaks for example) has been used to determine the intensity (yield).

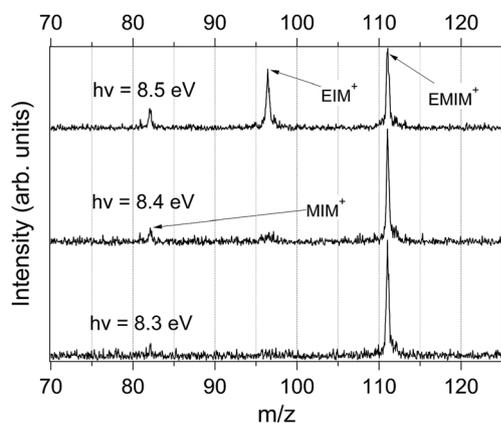


Fig. 3 TOFMS spectra of [EMIM][BF<sub>4</sub>] vapor showing the appearance of MIM and EIM fragments. The liquid cell temperature was at 190 °C.

experimental (strong LiF window absorbance at energies higher than 10 eV).

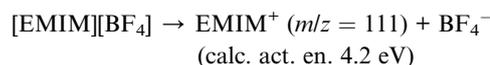
The appearance energies are generally somewhat smaller than the threshold energies, which were determined from the fits. Indeed, due to the used methodology and experimental conditions, it is expected that the experimental appearance energy slightly underestimates and the threshold energy overestimates the (actual or real) appearance energy. The EMIM cation appearance energy corresponds roughly to the B3LYP calculated LUMO–HOMO difference of [EMIM][BF<sub>4</sub>] (6.9 eV). The LUMO–HOMO difference of 7.5 eV calculated by the M06 functional, coincides with the appearance energy even better.

However, detailed B3LYP TDDFT excited state analysis predicts first significant dipole-allowed excited state at about 6.7 eV and the next significant ones at 8.2–8.7 eV. Since, the *ab*

*initio* TDDFT calculation probably underestimates the excited state energies, a Hartree–Fock type (CIS) calculation of the excited states was also performed. The strong UV absorption lines are predicted at 7.6 eV and at 9.5–10.1 eV. Thus it seems that the calculated 6.7 eV TDDFT value is smaller and the calculated 7.6 eV CIS value is closer to the experimental first threshold energy of EMIM at 7.9 eV. The EIM and EMIM fragments second threshold energy at 9.4 eV falls in-between the DFT and HF excited state calculation with DFT underestimating the second threshold energy (8.2 vs. 9.4 eV) and HF somewhat overestimating it (9.5 vs. 9.4). Overall, the first and second thresholds are explained by two strong dipole transitions to excited states of [EMIM][BF<sub>4</sub>], that are separated in energy. It is also evident, that the ion yield is much larger at the second threshold energy. Indeed, the calculated absorption cross section at the second threshold energy is many times larger (approx. by a factor of 6–10) than in the case of the first threshold energy. However, the fragmentation rates and pathways may also differ significantly.

The excited states are mostly localized on the cation as the calculated excitation profile is very similar in case of a bare EMIM<sup>+</sup> cation. Furthermore, the calculated excited states and the threshold energies in case of [BMIM][BF<sub>4</sub>] are also similar, therefore the excitation is mostly in the (methyl-)imidazolium part of the cation.

The fragmentation pathway to form the EMIM cation is simple:



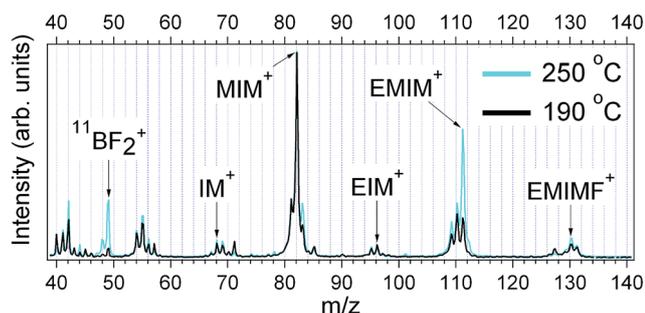
Although the calculated activation energy (equivalent to the ion pair binding energy) of the EMIM cation is smaller than the first excited state energy, this process is not possible before photoabsorption takes place. Therefore the fragmentation should be at least energetically possible as soon as the excitation to the LUMO level occurs. This is in agreement with the determined first threshold energy of EMIM and the *ab initio* excitation threshold energy value, as mentioned above. Fragmentation following photoexcitation is therefore the dominant process in the gas phase.

The somewhat small energy of the electrostatic bond between the cation and anion also explains why fragmentation occurs in most of the excited molecules and also why no EMIMBF<sub>4</sub><sup>+</sup> ions are seen in the TOFMS spectra (they should lie at *m/z* = 198). They are unstable.<sup>14</sup> Strasser *et al.* also did not observe the parent mass peaks in the TOFMS spectra in case of [EMIM][Tf<sub>2</sub>N] ionic liquid and claimed that ionization leads to dissociation.<sup>5</sup> Parent molecule ions were also not observed by Chambreau *et al.*<sup>17</sup> or Armstrong *et al.*<sup>14</sup> For comparison, the energy of the electrostatic bond between the cation and anion in [EMIM][Br] was calculated to be 3.8 eV by Chambreau *et al.*<sup>17</sup> The smaller energy is in agreement with the smaller electron affinity of bromide.

The B3LYP *ab initio* calculation shows that the (vertical) ionization energy of [EMIM][BF<sub>4</sub>] is about 9.8 eV. Chambreau

**Table 1** Identification of the important peaks in the TOFMS spectra. The numbers in parenthesis are explained in the text

<i>m/z</i>	Assignment	Calc. act. energy (eV)	Exp. appearance energy (eV)
40	(C <sub>2</sub> NH <sub>2</sub> )		
41	(C <sub>2</sub> NH <sub>3</sub> )	>13	>10.5
42	(C <sub>2</sub> NH <sub>4</sub> )		
48	B <sup>10</sup> F <sub>2</sub> <sup>+</sup>		>10.5
49	B <sup>11</sup> F <sub>2</sub> <sup>+</sup>		>10.5
54	(C <sub>3</sub> NH <sub>4</sub> )		
55	(C <sub>3</sub> NH <sub>5</sub> )	>14	>10.5
56	(C <sub>3</sub> NH <sub>6</sub> )		
68	Dehydrogenated imidazolium – IM (C <sub>3</sub> N <sub>2</sub> H <sub>4</sub> )	10.1	>10.5
69	Imidazolium – IM (C <sub>3</sub> N <sub>2</sub> H <sub>5</sub> )	10.6	>10.5
81	Dehydrogenated methyl-imidazolium – MIM (C <sub>4</sub> N <sub>2</sub> H <sub>5</sub> )	7.2	7.9
82	Methyl-imidazolium – MIM (C <sub>4</sub> N <sub>2</sub> H <sub>6</sub> )	8.1 (5.5)	8.2 (7.7)
83	Hydrogenated methyl-imidazolium – MIM (C <sub>4</sub> N <sub>2</sub> H <sub>7</sub> )	5.5	7.8
95	Dehydrogenated ethyl-imidazolium – EIM (C <sub>5</sub> N <sub>2</sub> H <sub>7</sub> )	7.0	7.5
96	Ethyl-imidazolium – EIM (C <sub>5</sub> N <sub>2</sub> H <sub>8</sub> )	8.6	8.3–8.4
95	Dehydrogenated 1-methyl-3-methyl-imidazolium – MMIM (C <sub>5</sub> N <sub>2</sub> H <sub>7</sub> )	10.5	
96	1-Methyl-3-methyl-imidazolium – MMIM (C <sub>5</sub> N <sub>2</sub> H <sub>8</sub> )	9.3	
109	Doubly dehydrogenated methyl-ethyl-imidazolium – EMIM (C <sub>6</sub> N <sub>2</sub> H <sub>9</sub> )		
110	Dehydrogenated methyl-ethyl-imidazolium – EMIM (C <sub>6</sub> N <sub>2</sub> H <sub>10</sub> )	(4.2)	7.4
111	Methyl-ethyl-imidazolium – EMIM (C <sub>6</sub> N <sub>2</sub> H <sub>11</sub> )	(4.2)	7.6
112	Hydrogenated methyl-ethyl-imidazolium – EMIM (C <sub>6</sub> N <sub>2</sub> H <sub>12</sub> )	(4.1)	7.0
129	3-Methyl-1-ethyl-2-fluoride-imidazolium EMIMF (C <sub>6</sub> N <sub>2</sub> H <sub>10</sub> F)	7.0	
130	Hydrogenated 3-methyl-1-ethyl-2-fluoride-imidazolium EMIMF (C <sub>6</sub> N <sub>2</sub> H <sub>11</sub> F)		9.8
157–158	Dehydrogenated EMIMBF <sub>2</sub> (C <sub>6</sub> N <sub>2</sub> H <sub>9</sub> B <sup>10,11</sup> F <sub>2</sub> )	10.8	>10.5
158–159	EMIMBF <sub>2</sub> (C <sub>6</sub> N <sub>2</sub> H <sub>10</sub> B <sup>10,11</sup> F <sub>2</sub> )		>10.5



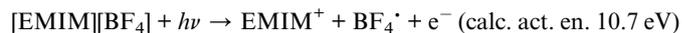
**Fig. 4** Non-background corrected TOFMS spectra of [EMIM][BF<sub>4</sub>] vapor excited at energy 20.0 eV. The two spectra correspond to the liquid cell temperatures of 190 or 250 °C. The spectra have been normalized to the MIM peak intensity.

*et al.* calculated the ionization energy of [EMIM][Br] as 6.8 eV (ref. 17) using MP2 level of theory. The calculated ionization energy of [EMIM][BF<sub>4</sub>] in the MP2 level of theory is 10.4 eV. Again, it is reasonable to conclude that due to the higher electron affinity of BF<sub>4</sub>, the ionization energy should be higher for [EMIM][BF<sub>4</sub>] compared to [EMIM][Br].

Deyko *et al.* stated that the ionization energies of [OMIM][BF<sub>4</sub>] (1-octyl-3-methylimidazolium tetrafluoroborate) and [BMIM][BF<sub>4</sub>] are very similar (around 13 eV) because the electron is not removed from the side chains. Therefore the ionization energies of [EMIM][BF<sub>4</sub>] and [BMIM][BF<sub>4</sub>] should also be similar. Indeed the calculated (vertical) ionization energy of [BMIM][BF<sub>4</sub>] is about 9.6 eV. Chambreau *et al.*

measured an experimental appearance energy value of 9.4 eV for the pyr14 cation (*N*-butyl-*N*-methylpyrrolidinium – a somewhat similar cation to BMIM) in [pyr14][Tf<sub>2</sub>N] and a similar appearance energy value in case of BMIM cation in [BMIM][dca] (1-butyl-3-methylimidazolium dicyanamide).<sup>19</sup> However, Strasser *et al.* found the ionization energy of [EMIM][Tf<sub>2</sub>N] to be 8.9 ± 0.2 eV (ref. 5) which is somewhat smaller than for [BMIM][dca], [pyr14][Tf<sub>2</sub>N] and the theoretical estimates.

The ionization and fragmentation (dissociative ionization) of the [EMIM][BF<sub>4</sub>] ion-pairs to the EMIM cation and to the BF<sub>4</sub> radical has higher calculated activation energy:



However, Chambreau *et al.* considered this pathway involving ionization (electron emission) as the main dissociation channel.<sup>17,19</sup>

It was experimentally shown by Koh *et al.* that it is possible to transfer kinetic energy to the cation–anion species, *i.e.*, both decay channels are possible: dissociative ionization in which the energy is carried by the photoelectron plus ion-pair and also dissociation in which the photon energy is transferred to the fragments.<sup>20</sup> Our experimental data and the calculation results show that the ion-pair dissociation is at least operating below the dissociative ionization threshold energy. However, due to experimental limitations we were not able to investigate the branching ratio between dissociative ionization and dissociation without electron emission (ion-pair dissociation) under

VUV light excitation. Thus only qualitative conclusions about these two decay channels can be drawn.

Therefore dissociative ionization should only weakly influence the PIY spectra shown in Fig. 2, where the ion-pair dissociation process dominates. However, dissociative ionization is definitely contributing to the TOFMS spectra shown in Fig. 1, because of the higher excitation energy (20.0 eV) used.

The MIM<sup>+</sup> fragment (at  $m/z = 82$ ), which is the most intense peak in the spectra, appears when the ethyl group dissociates from the EMIM cation. The loss of one or more methyl groups is a well known fragmentation pathway.

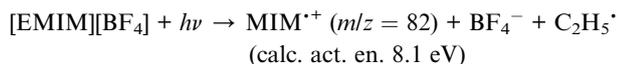
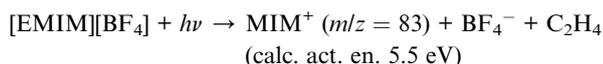


Fig. 3 shows an example of the appearance energy determination from the TOFMS spectra. There is excellent agreement between the experimental appearance energy (8.2 eV) and the calculated activation energy for this  $m/z = 82$  fragment (8.1 eV). The threshold energy of the MIM fragment is somewhat larger at 8.4 eV. The appearance energy of the MIM cation at  $m/z = 82$  in case of  $[\text{EMIM}][\text{Br}]$  was also similar at 8.6 eV.<sup>17</sup> However, the proposed fragmentation pathway involved ionization of the bromide anion.

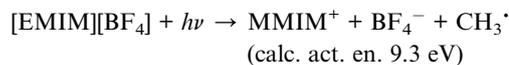
In case of  $[\text{OMIM}][\text{Cl/I}]$ , which were recently studied by Lovelock *et al.*,<sup>13</sup> the most intensive peak in the ion spectra was also MIM<sup>+</sup>. They found the appearance energy of the MIM ( $m/z = 82$ ) fragment to be 11.2 eV, which is larger than our measurements and higher than the *ab initio* calculations seem to indicate. This difference is probably due to the reason that electron excitation instead of photon excitation was used in that study. It is interesting to note that in case of chloride anion the strongest fraction of the MIM ions was observed at  $m/z = 82$ , while in case of iodide anion it was at  $m/z = 83$ , which was called the 'protonated' MIM (HMIM) by Bundaleski *et al.*<sup>21</sup> The calculated activation energy of the hydrogenated MIM cation (at  $m/z = 83$ ) has lower value than either of the  $m/z = 81$  or  $m/z = 82$  peaks, but the peak is weaker in our measured spectra:



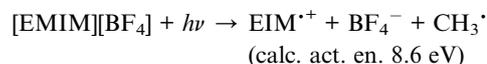
The  $m/z = 81$  peak, that corresponds to the dehydrogenated MIM fragment, is rather weak, similar to other studies.<sup>4,13,17</sup> Although the calculated activation energies for the other MIM fragments at  $m/z = 81, 83$  are lower than the main fragment at  $m/z = 82$ , it is difficult to estimate their experimental appearance energies, since the corresponding peaks are quite weak in the spectra. In other words, the  $m/z = 82$  peak is the dominating MIM peak observed at low excitation energies. At higher (20.0 eV) excitation energy however, both  $m/z = 81, 83$  peaks are clearly visible (see Fig. 4).

It has been demonstrated that any number of methylene ( $\text{CH}_2$ ) groups can be lost from the cation in case of  $[\text{OMIM}][\text{Tf}_2\text{N}]$ <sup>21</sup> or  $[\text{OMIM}][\text{BF}_4]$ .<sup>4</sup> Therefore the loss of one

methyl group from the ethyl group (C7 in Fig. 1) should also be possible, similar to the case considered by Chambreau *et al.*, where the EIM molecule lost a methyl group upon ionization to create a MIM cation.<sup>17</sup> However, the resulting methyl-methylimidazolium (MMIM) ions have higher energies and the calculated activation energy is also somewhat higher (than in the case of EIM fragments):



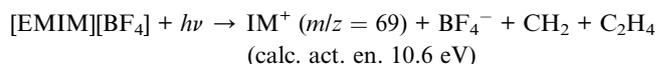
It is also possible to lose the single methyl group (C8 in Fig. 1) from the cation and this pathway has lower calculated activation energy:



This activation energy also agrees well with the measured EIM ( $m/z = 96$ ) appearance energy of  $[\text{EMIM}][\text{Br}] - 8.5$  eV (ref. 17) and the corresponding calculated activation energy of 8.6 eV.<sup>17</sup> Based on this discussion about the activation energies, it is reasonable to conclude that the  $m/z = 95$  and  $m/z = 96$  correspond to the EIM rather than MMIM cation fragments. The  $m/z = 96$  fragment was also assigned to EIM by Armstrong *et al.*,<sup>14</sup> Chambreau *et al.*<sup>17</sup> and Günster *et al.*<sup>18</sup> It is also evident, that in the case of this EIM fragment, the agreement between both theory and experiment in this study and in the study of Chambreau *et al.*, is excellent. However, Chambreau *et al.* did not observe the dehydrogenated EIM ( $m/z = 95$ ) fragment, while Günster *et al.* did.

The *ab initio* calculation predicts the activation energies of the MIM ( $m/z = 82$ ) and EIM ( $m/z = 96$ ) fragments to be similar, but the MIM fragment has a somewhat lower calculated activation energy. Indeed, this is confirmed by the TOFMS spectra, where the MIM peak appears at somewhat lower energies than the EIM peak (see Fig. 3 and Table 1).

Günster *et al.* identified the peak at  $m/z = 69$  as  $\text{CF}_3^{(-,+)}$  in  $[\text{EMIM}][\text{Tf}_2\text{N}]$ .<sup>18</sup> In case of SIMS measurements and the high energies involved, this peak may indeed originate from the  $\text{Tf}_2\text{N}$  anion, however the peak is also visible in our spectra. In case of  $[\text{EMIM}][\text{BF}_4]$  the  $m/z = 69$  peak is probably not due to  $\text{CF}_3$ . Tolstogousov *et al.* claimed that this  $m/z = 69$  peak may originate from either the cation or anion.<sup>22,23</sup> Therefore the peaks at  $m/z = 68$  and  $m/z = 69$  are probably from the bare imidazolium ring. Bundaleski *et al.* already identified the  $m/z = 69$  peak as the protonated imidazolium ring cations -  $[\text{HIM}]$ .<sup>21</sup> Thus the  $m/z = 68, 69$  peaks result from the loss of both methyl and ethyl groups from the EMIM cation - sharing similarities with both MIM and EIM fragments.



At this point it is again worthwhile to point out, that the activation energy for the fragmentation of the neutral EIM

molecule to the IM cation has been calculated by us and Chambreau *et al.* to be around 11 eV (ref. 17) – similar to the fragmentation pathway discussed above.

It is also interesting to note that both EIM and IM peaks have roughly equal intensity, but are much weaker than MIM peak(s). It was shown that the (bare) EIM molecules have IM ions in their fragmentation products, but the MIM molecules do not lose the methyl group to form IM cations (ref. 62 in ref. 17). Bundaleski *et al.* also stated that the loss of the ethyl group is more favorable than the loss of the methyl group.<sup>21</sup> This is indeed the case – the MIM peak is much stronger than the EIM peak in the recorded TOFMS spectra (see Fig. 1 and 4).

The peaks at  $m/z = 48$  and  $m/z = 49$  were assigned to  $^{10}\text{BF}_2$  and  $^{11}\text{BF}_2$  cations by Deyko *et al.*<sup>4</sup> The peak intensity ratio matches the boron isotope ratio and thus supports this assignment. The intensity of these peaks is highly temperature dependent (Fig. 4) probably because some thermal decomposition (TD) process. For example, Deyko *et al.* proposed that thermal cracking was responsible.<sup>4</sup>

Deyko *et al.* claimed that peaks at  $m/z < 80$  were not due to ionization and subsequent fragmentation of the ionic liquid vapor,<sup>4</sup> while Chambreau *et al.* claimed that ion masses between  $m/z = 40$ – $81$  are dissociation fragments formed mainly from neutral EIM and only with a small contribution from neutral MIM.<sup>17</sup>

However Bundaleski *et al.* argued that the peaks at  $m/z = 28$  and  $m/z = 42$  are due to two-bond scission of the imidazolium ring. They observed a rather strong peak at  $m/z = 42$  in the TOFMS spectra of  $[\text{EMIM}][\text{Tf}_2\text{N}]$ , which was identified as  $\text{C}_2\text{NH}_4$ , but curiously did not observe significant intensity at  $m/z = 54$ – $56$ .<sup>21</sup>

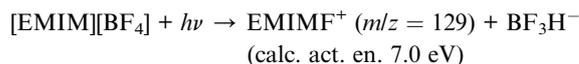
The origin of the peaks at  $m/z = 54$ – $56$  is not fully understood. They probably originate from the EMIM cation and were also seen by Armstrong *et al.*,<sup>14</sup> Smith *et al.*,<sup>15</sup> Günster *et al.*,<sup>18</sup> Chambreau *et al.*,<sup>17</sup> Tolstogousov *et al.*<sup>23</sup> and Deyko *et al.*<sup>4</sup>

As expected, there are many similarities between our results and those of Chambreau *et al.*,<sup>17</sup> because of the presence of the same EMIM cations in the ionic liquids. However, Chambreau *et al.* did not observe the main ( $m/z = 111$ ) EMIM cation itself and the thermal decomposition of  $[\text{EMIM}][\text{Br}]$  was strong and so was the signal of EIM in their TOFMS spectra.<sup>17</sup> They also observed the EIM with higher intensity than the MIM fragment. Due to the strong (thermally decomposed) EIM signal, they claimed that the dehydrogenated MIM peak at  $m/z = 81$  is a decay product of EIM. Also, the intense signal of the IM fragment originated from the strong EIM presence. For that reason they also explained the  $m/z = 42$  and  $m/z = 54$  fragments as arising from the fragmentation of EIM. However, in this study the MIM and dehydrogenated EMIM peaks are dominating the TOFMS spectra and the  $m/z = 42$  and  $m/z = 54$  peaks are stronger than either EIM or IM peaks.

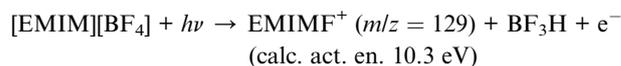
Chambreau *et al.* identified the peaks at  $m/z = 42$ ,  $54$  as  $\text{C}_2\text{NH}_4$ ,  $\text{C}_3\text{NH}_4$  respectively and also explained their origin.<sup>17</sup> In case of  $[\text{EMIM}][\text{Tf}_2\text{N}]$  Tolstogousov *et al.* had the  $m/z = 54$  peak marked as  $\text{C}_3\text{H}_4\text{N}$  and the  $m/z = 56$  peak marked as  $\text{C}_2\text{H}_4\text{N}_2$ .<sup>22</sup> Bundaleski *et al.* identified the  $m/z = 56$  peak as  $\text{C}_3\text{NH}_6$  in  $[\text{EMIM}][\text{Tf}_2\text{N}]$  and the  $m/z = 55$  peak as  $\text{C}_4\text{H}_7$  in  $[\text{OMIM}][\text{Tf}_2\text{N}]$ .<sup>23</sup>

We also believe that the  $m/z = 42$ ,  $43$  and  $m/z = 54$ ,  $55$ ,  $56$  peaks are due to double bond breaking in the EMIM cation. They were also seen in the mass spectrum of  $[\text{EMIM}][\text{acetate}]$ .<sup>24</sup> The calculated activation energy for these kinds of fragmentation processes is larger than 13 eV (probably around 16 eV).

Deyko *et al.* detected fluorinated cation peaks in the mass spectra of  $[\text{BMIM}][\text{BF}_4]$  and  $[\text{OMIM}][\text{BF}_4]$ , *i.e.* peaks at 19  $m/z$  units higher than the main cation peak.<sup>4</sup> The peak at  $m/z = 130$  is therefore identified as the fluorinated EMIM cation – EMIMF, where the fluorine atom has been added to the C2 carbon. A possible fragmentation pathway for this process is:



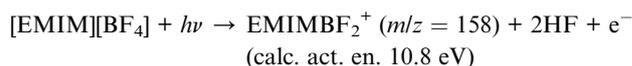
Again, the comparable dissociative ionization pathway has higher calculated activation energy:



The experimental appearance energy is about 9.8 eV and the threshold energy is about 9.7 eV. As explained before, the underestimation of the appearance energy is probably due to the full degree of fragment structure optimization used in the *ab initio* calculation and also the fact that the B3LYP functional somewhat underestimates these energies. For example, if after the excitation the fluorine atom does not move at all (is very weakly bound to the C2 carbon) the activation energy is 14.2 eV and if it reaches half-way point between the stable EMIMF<sup>+</sup> structure and the  $[\text{EMIM}][\text{BF}_4]$  structure, the activation energy is 11.5 eV and at 75% relaxation, the activation energy is about 9.3 eV. The general agreement also justifies the claim that in case of the EMIMF structure, the fluoride atom is covalently bound to the C2 (Fig. 1) carbon.<sup>25</sup> Deyko *et al.* also claimed that the  $\text{C}_n$ -MIMF radical is formed after the excitation rather than due to some liquid phase decomposition process.<sup>4</sup>

Unfortunately, this pathway is able to explain the peak at  $m/z = 129$ , but not the strongest experimental peak at  $m/z = 130$ , which could arise from the hydrogenated EMIM cation.

Deyko *et al.*<sup>4</sup> and Taylor *et al.*<sup>26</sup> identified the peak at  $m/z = 187$  as  $\text{BMIM}^{11}\text{BF}_2$  in case of  $[\text{BMIM}][\text{BF}_4]$  ionic liquid. Thus in our case of  $[\text{EMIM}][\text{BF}_4]$ , the peak at  $m/z = 159$  is identified as  $\text{EMIMBF}_2^+$ . A possible fragmentation pathway for this process is:



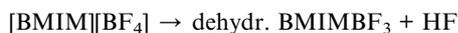
However, this pathway is able to explain the peak at  $m/z = 158$  (and the corresponding  $\text{B}^{10}$  isotope peak at  $m/z = 157$ ), but not the strongest experimental peak at  $m/z = 159$ , which could arise from the hydrogenated EMIM cation.

Smith *et al.* and Günster *et al.* observed strong peaks around  $m/z = 28$  and  $m/z = 42$  in the ToF-SIMS spectra of  $[\text{EMIM}][\text{Tf}_2\text{N}]$

ionic liquid.<sup>15,18</sup> They also observed a weaker peak around  $m/z = 69$ . However, they did not observe intense peaks around  $m/z = 49$  or  $m/z = 159$ . The fact, that the cation of the ionic liquid under study by Smith *et al.* was the same and anion was different, helps to validate our assignments.

## 4. Thermal decomposition and other modifications

So far in our discussion, the assumption, that only [EMIM][BF<sub>4</sub>] ion pairs are evaporated from the sample, has been made. However, the thermal stability of many ILs is not high. For example, in case of [BMIM][BF<sub>4</sub>] it was shown that under sufficiently high temperatures this reaction can occur:<sup>26</sup>

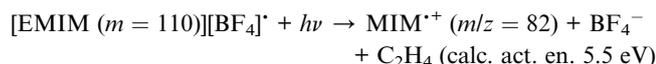


These borane-substituted fragments<sup>26</sup> were not seen in this work. In case of dehydrogenated EMIMBF<sub>3</sub> they should lie at  $m/z = 177$ – $178$ .

In case of [OMIM][Cl/I] ionic liquid a strong argument has been in favor of TD of the ionic liquid at higher temperatures with nucleophilic substitution at the imidazolium ring.<sup>13</sup> In case of [EMIM][BF<sub>4</sub>] ionic liquid the similar TD products should be CH<sub>3</sub>BF<sub>4</sub> and C<sub>2</sub>H<sub>5</sub>BF<sub>4</sub>. However there are no corresponding peaks in our measured spectra up to the highest temperature studied – 250 °C. Either the vaporization enthalpy of the TD products is larger or similar TD does not occur significantly in this case (at least at temperatures below 250 °C).

Lovelock *et al.* claimed that the MIM fragment at  $m/z = 82$  is due to TD – nucleophilic substitution. It is also interesting to note that at lower excitation energies and lower temperatures the  $m/z = 110$  dehydrogenated EMIM peak dominates, while at higher energies and temperatures the  $m/z = 111$  EMIM peak is relatively more intensive. Chambreau *et al.* did not observe the  $m/z = 111$  EMIM<sup>+</sup> cation itself.<sup>17</sup> For this reason Lovelock *et al.* claimed that Chambreau *et al.* did not see EMIM cation from the vaporization of neutral [EMIM][Br], only products of TD! Lovelock *et al.* also claimed that the  $m/z = 83$  MIM and  $m/z = 111$  EMIM peaks confirm that (some) non-TD ionic liquid was present. In this work the peaks at  $m/z = 82$  (MIM) and  $m/z = 110$  (dehydrogenated EMIM) peaks are dominating the spectra, rather than the expected  $m/z = 83$  MIM and  $m/z = 111$  EMIM peaks.

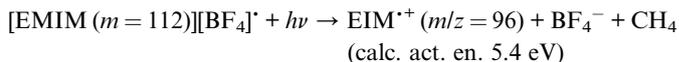
The activation energy of the  $m/z = 82$  MIM fragment in case of dehydrogenated EMIM cation is small:



At high temperatures the  $m/z = 82$  MIM peak indeed shows a lower appearance energy of 7.7 eV (not shown).

Also, if the hydrogenated EMIM ( $m = 112$ ) is present, then the presence of the hydrogenated EMIMF, EMIMBF<sub>2</sub> (see above)

and the rather low activation energy of  $m/z = 96$  EIM would be explained:



A low activation energy EIM component is visible in the PIY spectra recorded at 250 °C (see Fig. 5). This  $m/z = 95$  fragment has a threshold energy of about 7.5 eV – again this energy is close to the photoabsorption threshold energy (7.4 eV). Fig. 5 also shows the result when the  $m/z = 96$  EIM PIY spectrum is subtracted from the dehydrogenated EIM ( $m/z = 95$ ) PIY spectrum, highlighting the low energy behavior.

The hydrogenated EMIM ( $m/z = 112$ ) fragment itself also appears as a shoulder to the EMIM cation ( $m/z = 111$ ) peak in the higher temperature TOFMS spectra (Fig. 4). This weak peak is still too intense to be explained by the C<sup>13</sup> or N<sup>15</sup> isotopes (intensity of 11% relative to the  $m/z = 111$  peak vs. the expected 7.4%). Not surprisingly, the hydrogenated EMIM cation has the calculated lowest activation energy and also the lowest experimental appearance energy (see Table 1). The *ab initio* calculated lowest excitation energy of the hydrogenated [EMIM][BF<sub>4</sub>] molecule is also much lower (at about 4.7 eV).

The hydrogenated (and dehydrogenated) EMIM (and corresponding other) fragments could form due to some bimolecular process.

The dehydrogenated EIM ( $m/z = 95$ ) fragment only appears at higher temperatures or excitation energies and has a lower calculated activation energy than the  $m/z = 96$  EIM fragment. It can also arise from the dehydrogenated EMIM cation, but the calculated *ab initio* activation energy is then still similar (7.4 eV vs. 7.0 eV).

The ionization energy of the neutral EIM is also predicted to be around 8.4 eV. A strong (thermally decomposed) EIM presence was seen in the work of Chambreau *et al.*<sup>17</sup> If for some reason the same would be the case in this work, then the EIM signal would not be due to [EMIM][BF<sub>4</sub>] fragmentation but could also be due to EIM ionization.

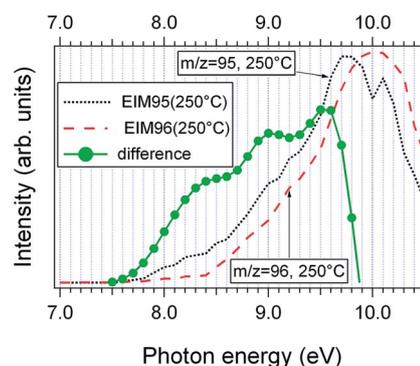


Fig. 5 Partial ion yield spectra of  $m/z = 95, 96$  EIM fragments at temperature 250 °C. The circles are the resulting points when subtracting the two spectra. All spectra have been arbitrarily scaled (normalized).

The threshold energy for the EIM cation coincides exactly with the calculated (neutral EIM) ionization energy. The fact that our *ab initio* calculation somewhat overestimates rather than underestimates the EIM dissociation activation energy also seems to hint to the presence of some neutral EIM in the ionic liquid. But the hydrogenated EMIM component may mask (lower) the threshold energy of the  $m/z = 96$  EIM fragment and it may appear smaller than it would be without the hydrogenated EMIM component. Therefore the presence of some neutral EIM can neither be confirmed nor denied.

However, the issue of hydrogenated vs. dehydrogenated EMIM and MIM fragments, their intensity, temperature dependency and thermal decomposition (TD) will not be discussed any further, but will be investigated in a forthcoming paper.

## 5. Conclusion

Excitation energy dependent TOFMS spectra of [EMIM][BF<sub>4</sub>] ionic liquid vapor have been measured. The VUV excitation reveals that dissociation without electron emission (ion-pair dissociation channel) is operating below the ionization threshold. The experimental data and the *ab initio* calculations indicate, that not only is the ion-pair unstable to ionization, fragmentation also occurs after photoexcitation. In other words: the threshold energy for the dissociation of the [EMIM][BF<sub>4</sub>] ion-pair is well below the ionization energy of the ion-pair. VUV excitation reveals additional information to electron excitation.

Most of the TOFMS peaks have been identified. The new peaks at  $m/z = 129$  and  $m/z = 158$  are due to EMIMF<sup>+</sup> and EMIMBF<sub>2</sub><sup>+</sup>, respectively. Most assignments are supported by *ab initio* activation energy calculations.

The important experimental thresholds have been explained by *ab initio* calculations: first and second threshold energies and the MIM fragment appearance energy.

The temperature dependence of the TOFMS spectra and thermal decomposition effects will be discussed in a forthcoming paper.

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