Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

The vapour of imidazolium-based ionic liquids: a mass spectrometry study

A. Deyko, K. R. J. Lovelock*, P. Licence, R. G. Jones

School of Chemistry

The University of Nottingham

University Park

Nottingham

NG7 2RD, UK

* denotes Corresponding Author

email: k.lovelock@ucl.ac.uk

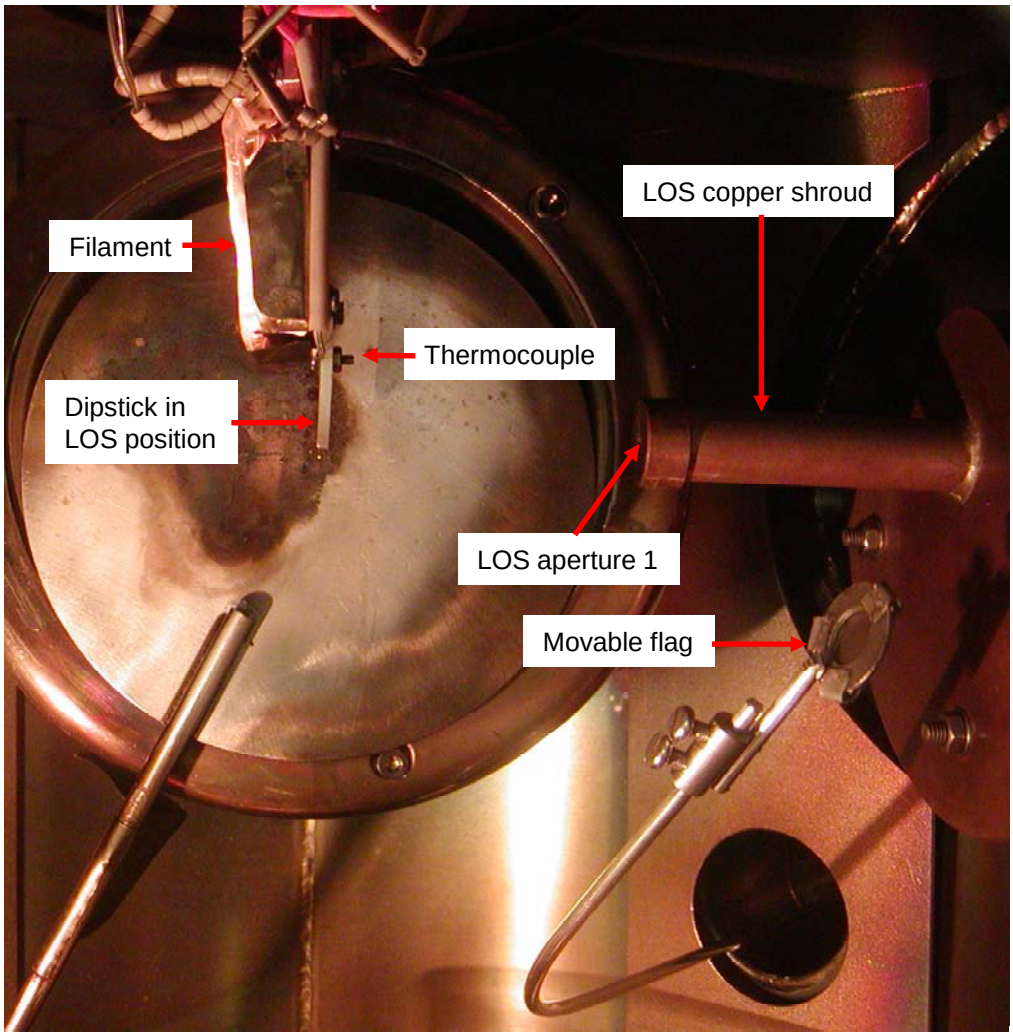


Figure S1. Annotated photograph of the LOSMS set-up. The sample heating filament was on when this photograph was taken.

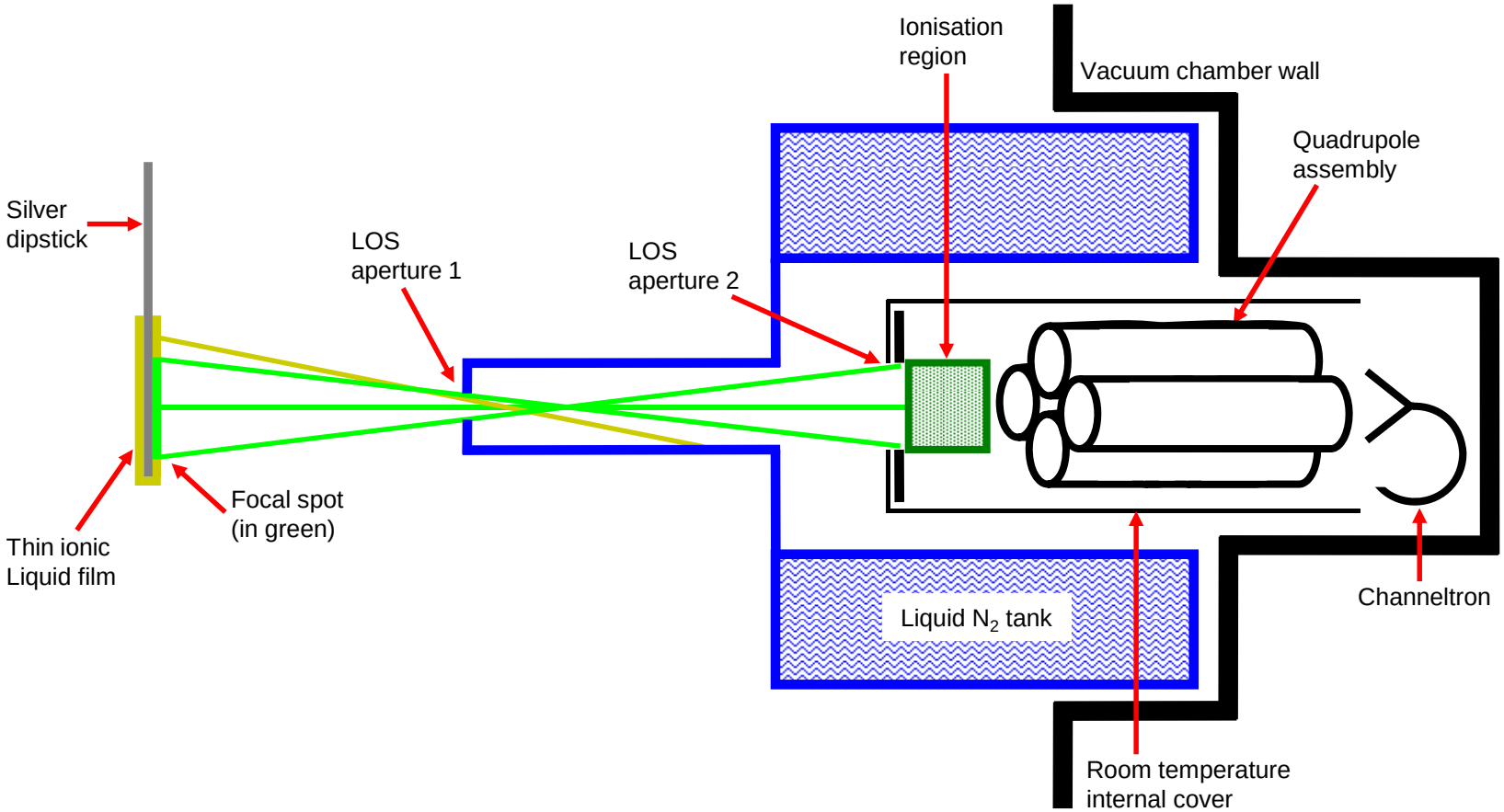


Figure S2. Schematic of LOS mass spectrometer (not to scale). Two LOS apertures define a focal spot on the surface of the sample, diameter ≈7 mm, in LOS with the ionisation region. The green species are in the field of view of the ionisation region; the yellow species are not.

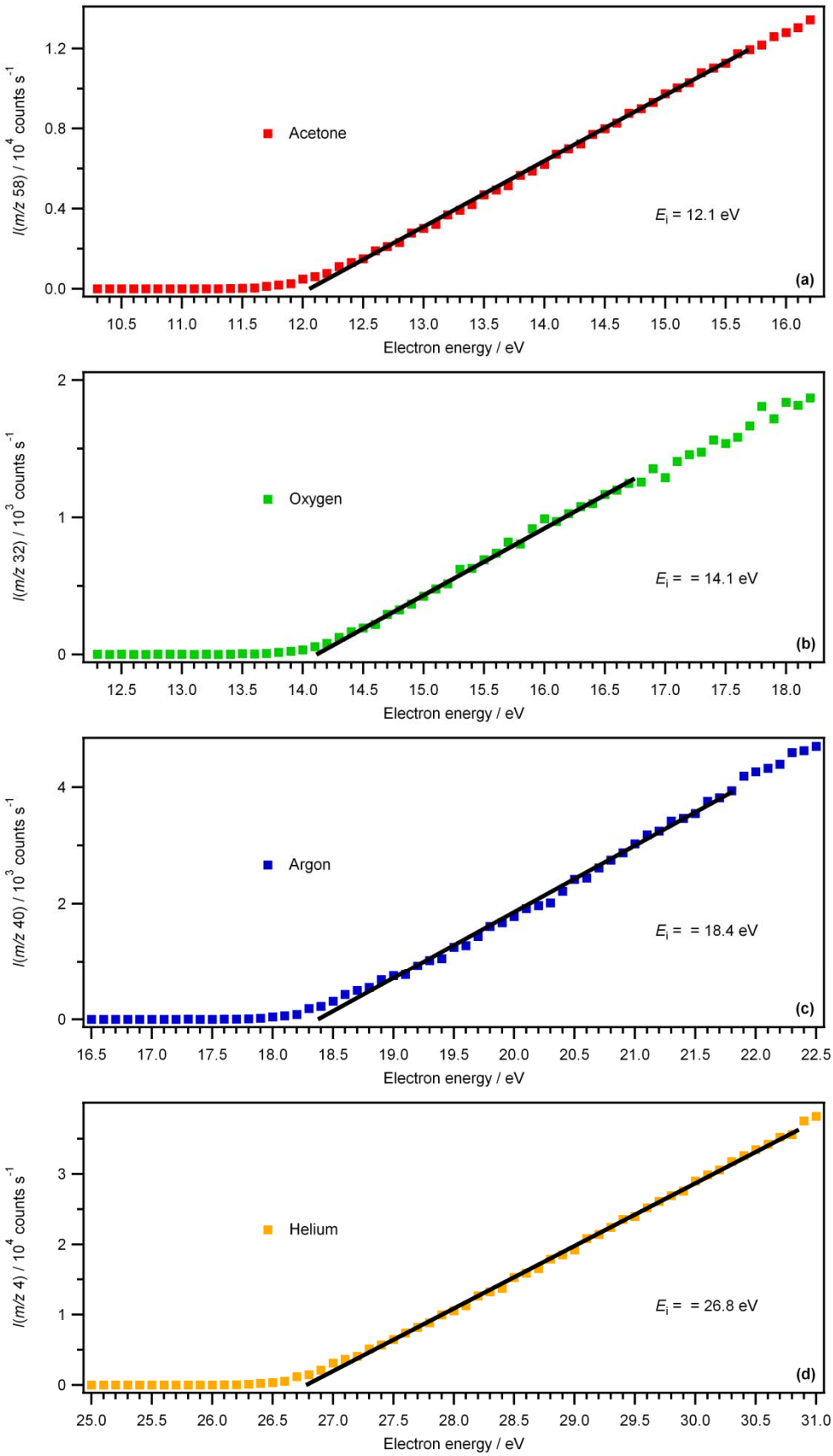


Figure S3. Calibrating electron energy using ionisation energies for (a) acetone, *m/z* 58 (b) oxygen, *m/z* 32 (c) argon, *m/z* 40 (d) helium, *m/z* 4.

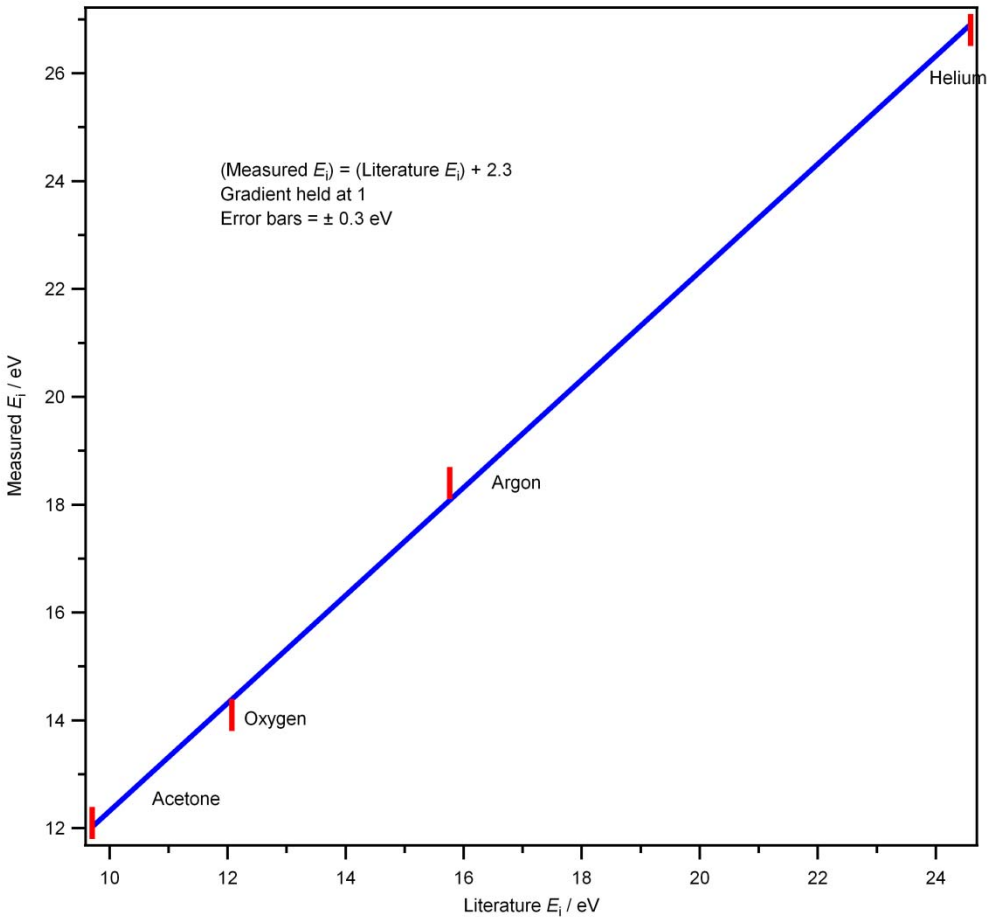


Figure S4. Calibrating electron ionisation energy scale using molecules with well-known ionisation energies.

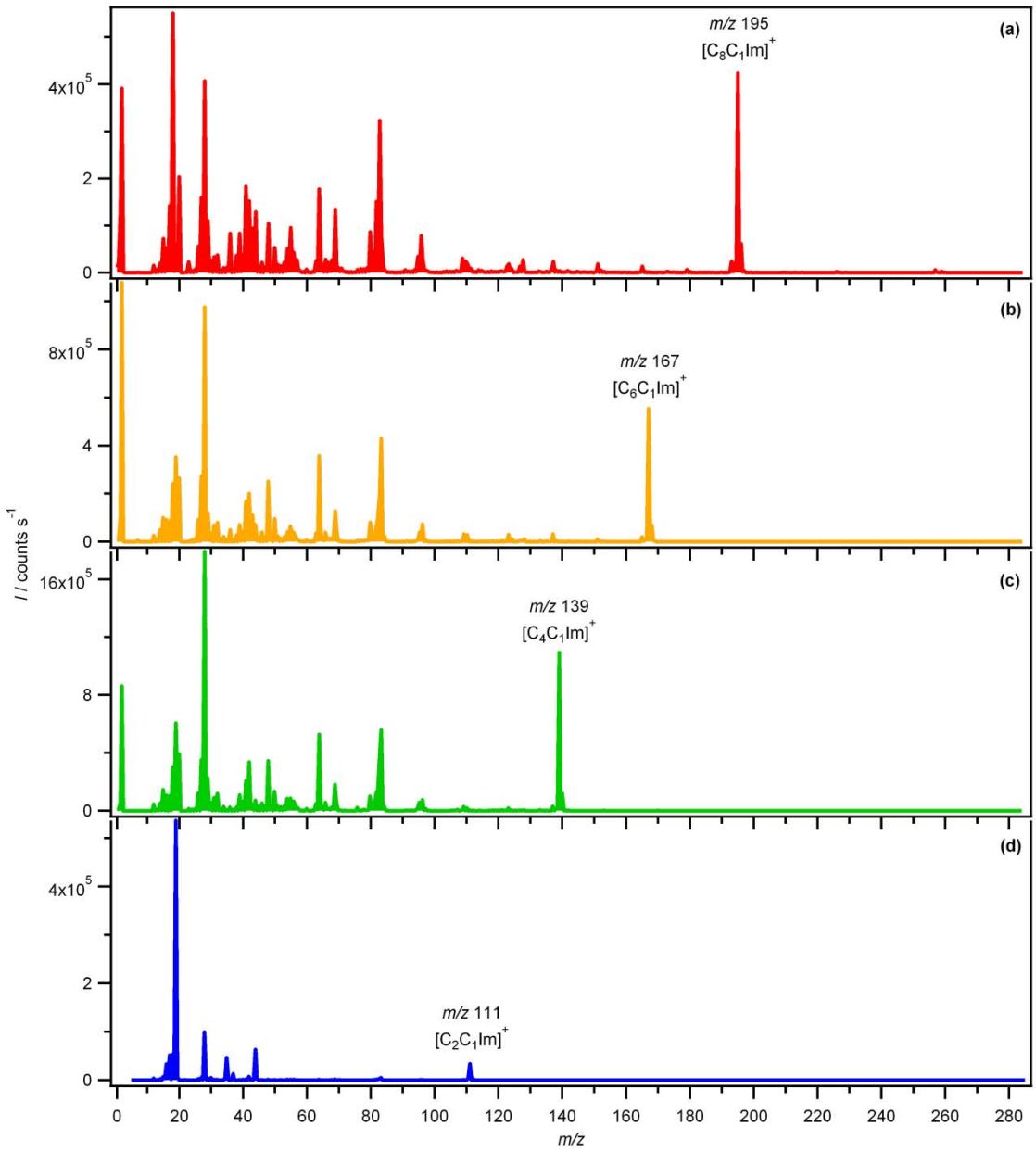


Figure S5. Non-background-subtracted mass spectra of $[C_nC_1Im][Tf_2N]$ vapour where: (a) n = 2, T = 446 K, (b) n = 4, T = 483 K, (b) n = 6, T = 488 K, (d) n = 8, T = 497 K.

Flag experiments for the vapour of $[C_8C_1Im][BF_4]$

The sharp cut-off observed for *m/z* 195, $[C_8C_1Im]^+$, when the flag was placed in the line of sight (LOS) position, as shown in Figure S6a, demonstrates that the parent cation was a product of ionisation of $[C_8C_1Im][BF_4]$ neutral ion pairs (NIPs) only. A $[C_8C_1ImF]^{+\bullet}$ ion was observed at *m/z* 214 for $[C_8C_1Im][BF_4]$. For $[C_8C_1Im][BF_4]$ no cations were observed above *m/z* 214 apart from cations due to contamination. Figure S6b, an *m/z* 214 spectrum, shows a sharp cut-off almost to zero when the flag was introduced into the LOS position. Therefore, the $[C_8C_1ImF]^{+\bullet}$ ion was mainly a product of ionisation of $[C_8C_1Im][BF_4]$ NIPs.

The most intense peak due to the anion was *m/z* 49, $[^{11}BF_2]^+$. The relative abundances of 11B and 10B are 80.2 % and 19.8 % respectively. The molecular ion for BF_3, $[^{11}BF_3]^{+\bullet}$, is at *m/z* 68. This cation is isobaric with a fragment ion of the cation, $[HIm]^{+\bullet}$. For this reason, *m/z* 49 rather than *m/z* 68 was used to monitor the behaviour of cations produced from the anion. The *m/z* 49 mass spectrum, Figure S6c, shows no sharp cut-off when the flag was introduced into the LOS position. The decrease in signal was a smooth transition that shows that little or no $[BF_2]^+$, and consequently $[BF_3]^{+\bullet}$, was produced by dissociative ionisation of $[C_8C_1Im][BF_4]$ NIPs. This result shows that little or no BF_3 was present in the ionic liquid vapour phase before ionisation. There was only one source of the $[BF_2]^+$ cation: thermal cracking of $[C_8C_1Im][BF_4]$ NIPs inside the mass spectrometer, followed by evaporation.

Relationship with respect to temperature for the vapour of $[C_8C_1Im][BF_4]$

An example of variation in the intensity of the $[C_8C_1Im]^+$ and $[C_8C_1ImF]^{+\bullet}$ cations with respect to temperature for $[C_8C_1Im][BF_4]$ is given in Figure S7. The traces have a very good visual overlap (both show an exponential increase and a sharp high temperature cut-off) and the activation energies of desorption determined for both cations are the same (within error limits). These results strongly suggest that both $[C_8C_1Im]^+$ and $[C_8C_1ImF]^{+\bullet}$ cations are produced from the same source. We are confident that $[C_8C_1Im]^+$ is produced by ionisation of NIPs. Therefore, these observations confirm that the $[C_8C_1ImF]^{+\bullet}$ ion was mainly a product of ionisation of $[C_8C_1Im][BF_4]$ NIPs, and not a liquid phase decomposition reaction.

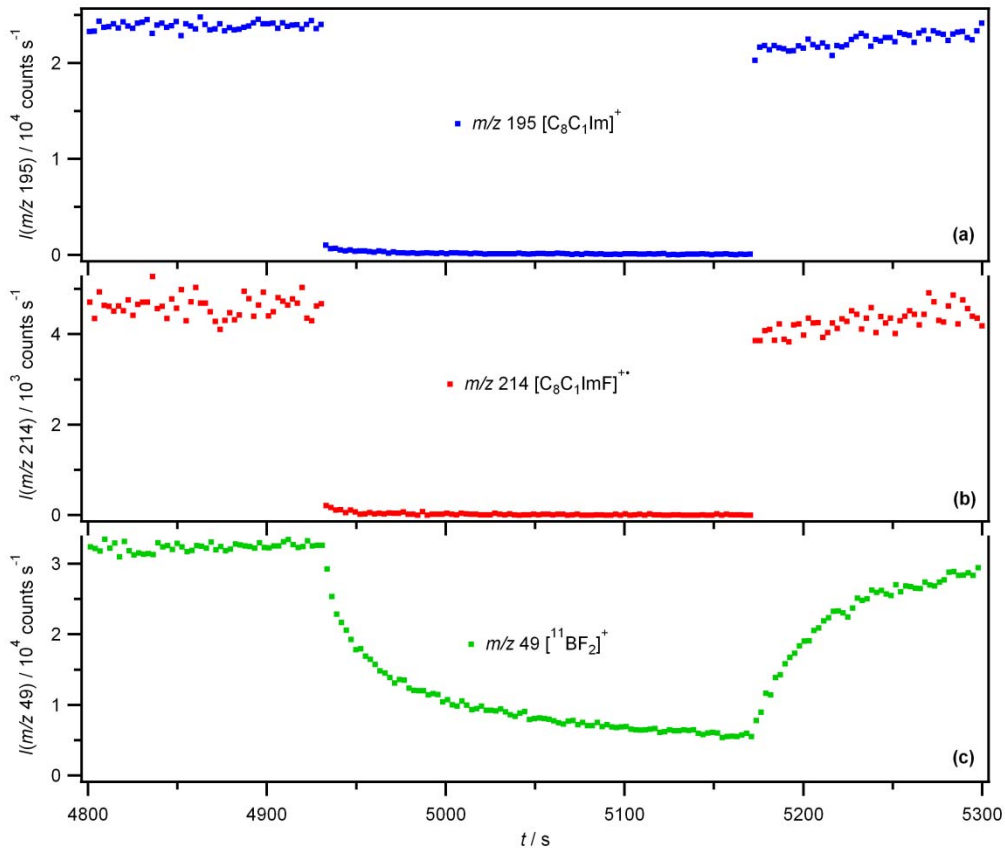


Figure S6. Line of sight (LOS) mass spectrum intensity versus time for $[C_8C_1Im][BF_4]$ at 508 K. The flag was placed in the LOS position at t = 4928 - 5171 s. (a) *m/z* 195, $[C_8C_1Im]^+$, (b) *m/z* 214, $[C_8C_1ImF]^{+\bullet}$, (c) *m/z* 49, $[^{11}BF_2]^+$.

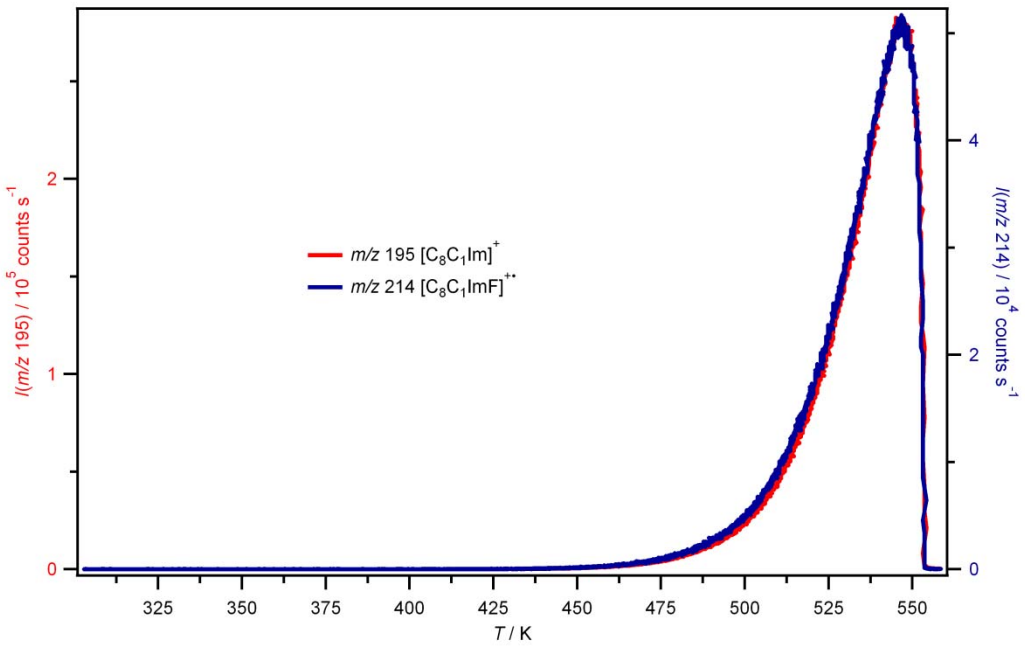
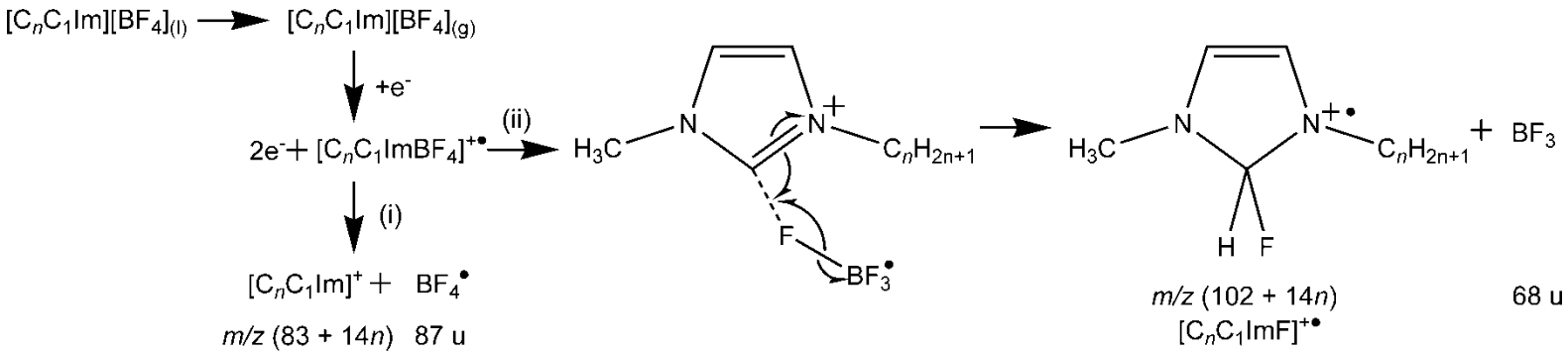


Figure S7. LOS mass spectrum intensity versus temperature for $[C_8C_1Im][BF_4]$ for *m/z* 195 and 214.



Scheme S1. Postulated structure and formation mechanism of the $[C_nC_1ImF]^{+\bullet}$ radical cation for $[C_nC_1Im][BF_4]$. Vaporisation as a neutral ion pair (NIP), followed by dissociative ionisation to form: (i) parent cation, $[C_nC_1Im]^+$, and neutral radical, $BF_4^\bullet$, (ii) radical cation $[C_nC_1ImF]^{+\bullet}$ and neutral molecule, BF_3.