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**Interactions and stabilisation of acetone, sulfur dioxide and water with 1-octyl-3-methylimidazolium tetrafluoroborate [OMIM][BF<sub>4</sub>] at low temperatures.**

Matthew Buckley, Karen L. Syres<sup>†</sup>, Robert G. Jones\*

Department of Physical Chemistry, School of Chemistry, University of Nottingham,  
Nottingham NG7 2RD

<sup>†</sup>Current address: Jeremiah Horrocks Institute, University of Central Lancashire,  
Fylde Road, Preston, PR1 2HE

\* robert.g.jones@nottingham.ac.uk

**Electronic Supplementary Information****Desorption of [OMIM][BF<sub>4</sub>]**

Figure SI 1A shows the mass spectrum of the ionic liquid, obtained from the vapour of a bulk sample, while Fig.SI 1B shows the TPD scans monitored using the cracking fragments.  $m/z = 195$  is the [OMIM]<sup>+</sup> ion and is representative of desorption of the ion pair in the gas phase. The  $m/z = 214$  ion is due to a fluorinated form of the imidazolium cation which is formed on ionisation of the IL ion pair in the mass spectrometer<sup>1</sup>; it was not present in the vapour or on the surfaces being studied. The TPD curves for all fragments have the correct relative intensities except for  $m/z = 83$  and 96 which are smaller relative to the 195 ion for the bulk vapour. It is thought that the bulk measurement had a contaminant giving rise to these peaks, which was reduced in the experiments here. That some of this contaminant (< 10%) was still present in the surface work was shown by a small desorption peak (<10%) at  $\approx 300$  K for  $m/z = 83$ .

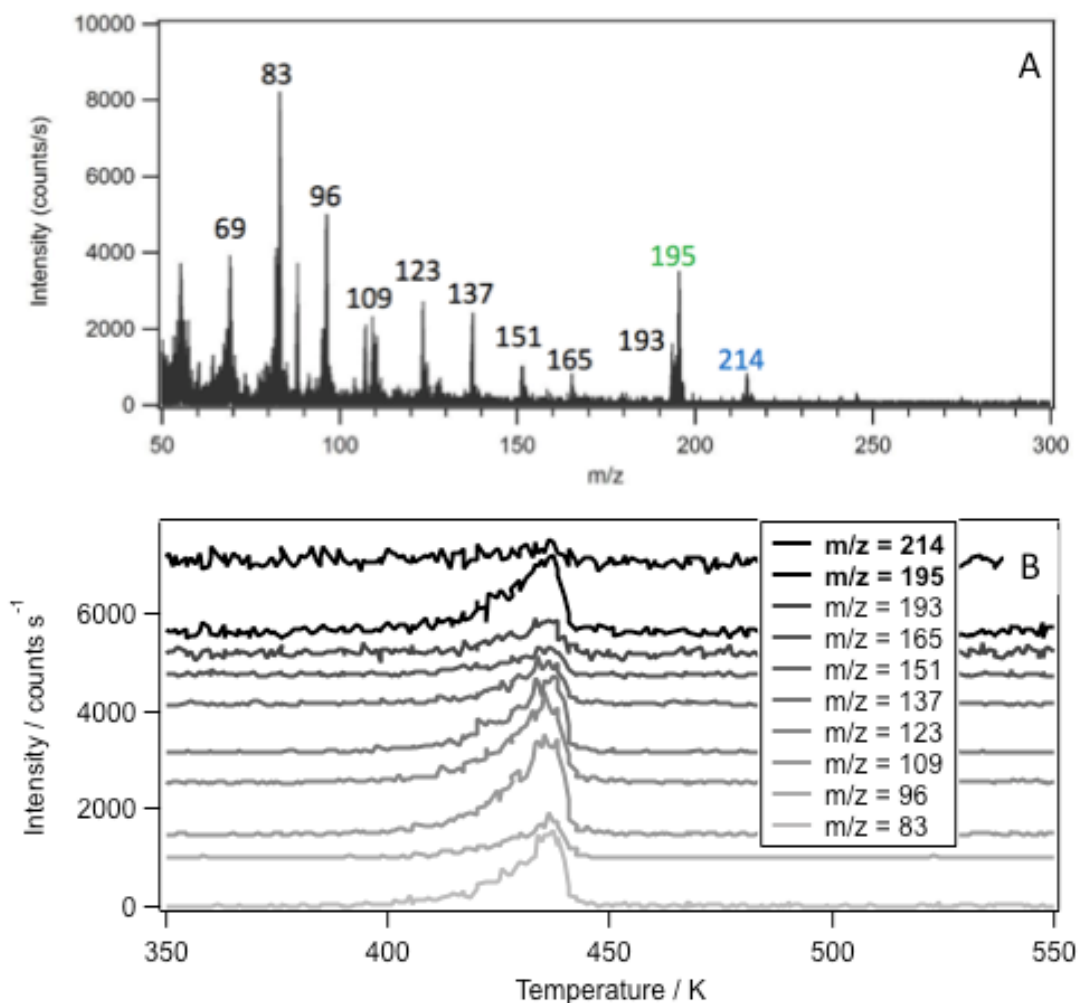


Figure SI 1 A, line of sight mass spectrum of vapour emitted from a bulk sample of [OMIM][BF<sub>4</sub>]. B, temperature programmed desorption of about 11 layers of [OMIM][BF<sub>4</sub>] from the CCAu surface monitored using the *m/z* fragments shown. The scans are offset for clarity.

### Acetone on CCAu

$E_a = 38(2) \text{ kJ mol}^{-1}$  and a pre-exponential of  $A = 4 \times 10^{15(1)} \text{ s}^{-1}$  have been used to fit the TPD curves by simulation, Fig. SI 2. The monolayer fit is not very good at higher temperatures, consistent with an activation energy that increases somewhat with decreasing coverage indicating that some of the acetone in the first layer is slightly more strongly bonded to the carbonaceous layer on the CCAu sample.

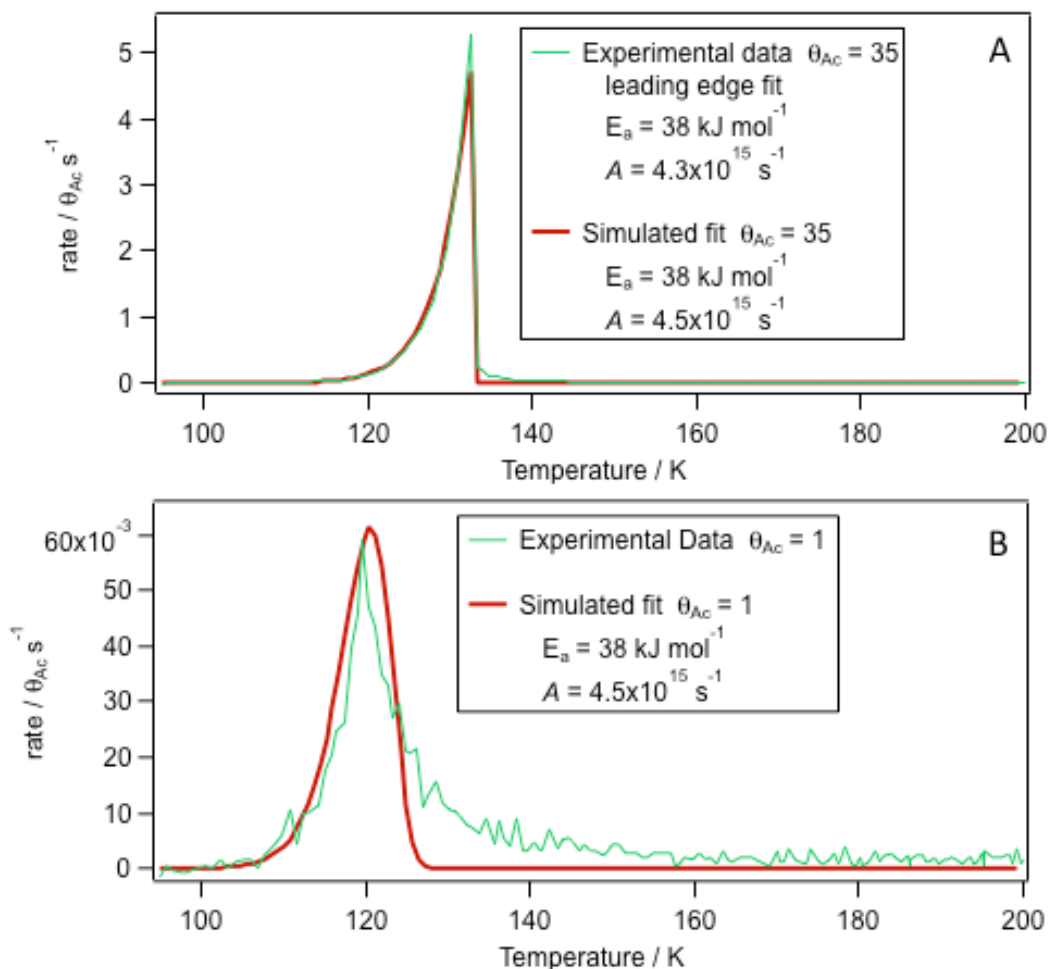


Figure SI 2 TPD scans of acetone on CCAu using  $m/z = 58$  and simulated fits. A,  $\theta_{Ac} = 35$ . B,  $\theta_{Ac} = 1$ . Both simulations used  $E_a = 38 \text{ kJ mol}^{-1}$  and  $A = 4 \times 10^{14(1)} \text{ s}^{-1}$ .

### Acetone adsorption beneath IL snow

The stabilised region from 140 - 200 K for three IL coverages ( $\theta_{IL} = 34, 20$  and 5) was fitted using the sum of 7 first order simulation curves with activation energies from 45 - 57  $\text{kJ mol}^{-1}$  in increments of 2  $\text{kJ mol}^{-1}$ , region A, and an eighth with an activation energy of 61  $\text{kJ mol}^{-1}$ , region B. A pre-exponential of  $4.3 \times 10^{15} \text{ s}^{-1}$  was used and the coverages were adjusted to obtain a good fit to the overall shape of the experiment. Fig.SI 3 shows the fit for  $\theta_{IL} = 20$  and 5, while the fit to  $\theta_{IL} = 34$  is shown in the main paper.

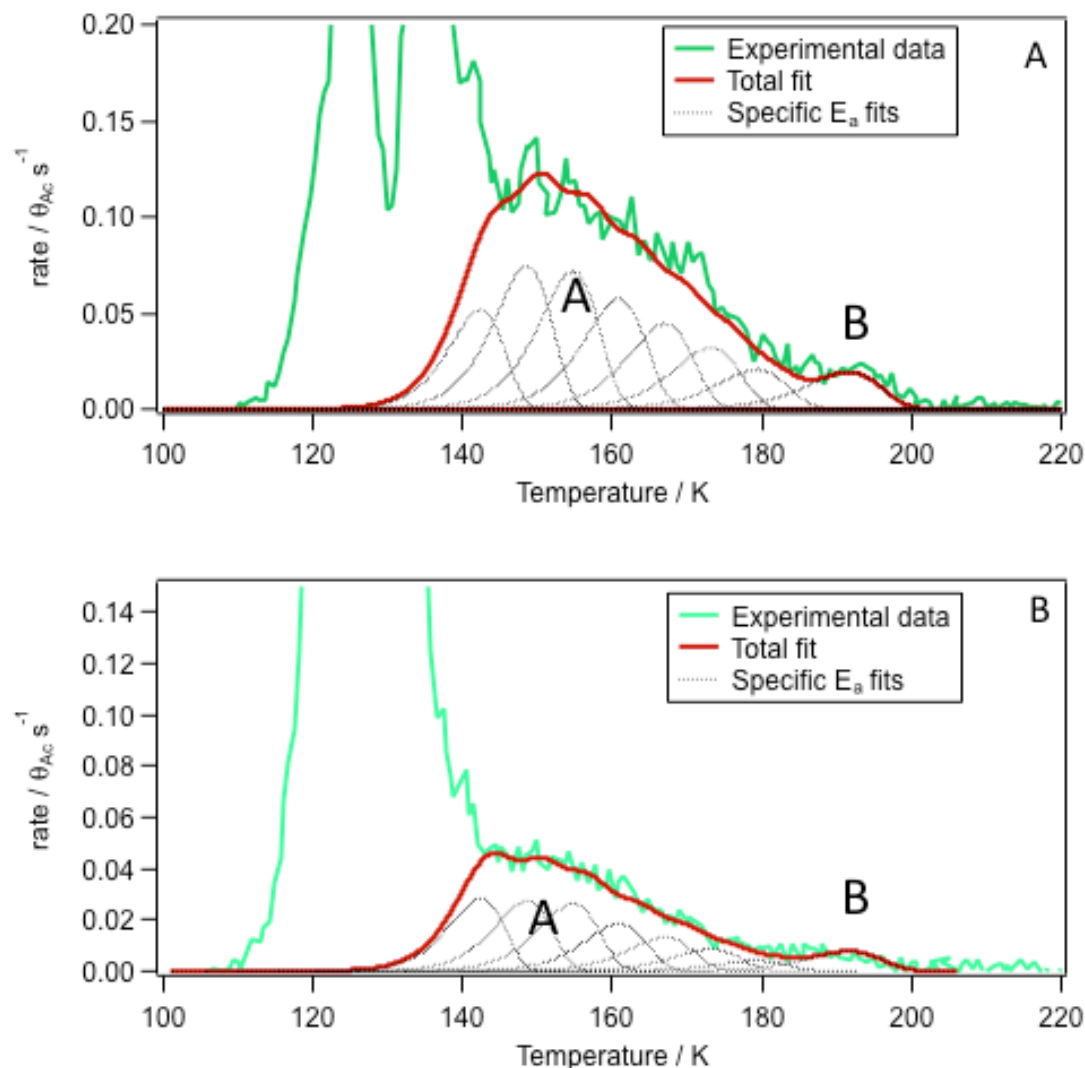


Figure SI 3 TPD scan of acetone ( $\theta_{Ac} = 35$ ) beneath IL snow using  $m/z = 58$ , each fitted with the sum (solid line) of eight first order TPD curves (dotted lines). A,  $\theta_{IL} = 20$ . B,  $\theta_{IL} = 5$

### Desorption of water

$\theta_{H_2O} = 1$  was defined as the highest coverage that exhibited a first order desorption profile and is shown in Fig. SI 4A. The monolayer could be simulated with  $E_a = 47(1)$  kJ mol<sup>-1</sup> and a pre-exponential of  $2 \times 10^{15(0.5)}$ . For  $\theta_{H_2O} = 31$  the low temperature side due to amorphous ice, Fig. SI 4B, was fitted using a leading edge plot and simulated giving  $E_a = 49(5)$  kJ mol<sup>-1</sup> and a pre-exponential of  $3 \times 10^{17(2)}$  s<sup>-1</sup>. The highest multilayer for  $\theta_{H_2O} = 821$  could be fitted using a leading edge for the higher temperature side and simulated using  $E_a = 43(1)$  kJ mol<sup>-1</sup> and a pre-exponential of  $2 \times 10^{15(0.5)}$  s<sup>-1</sup>.

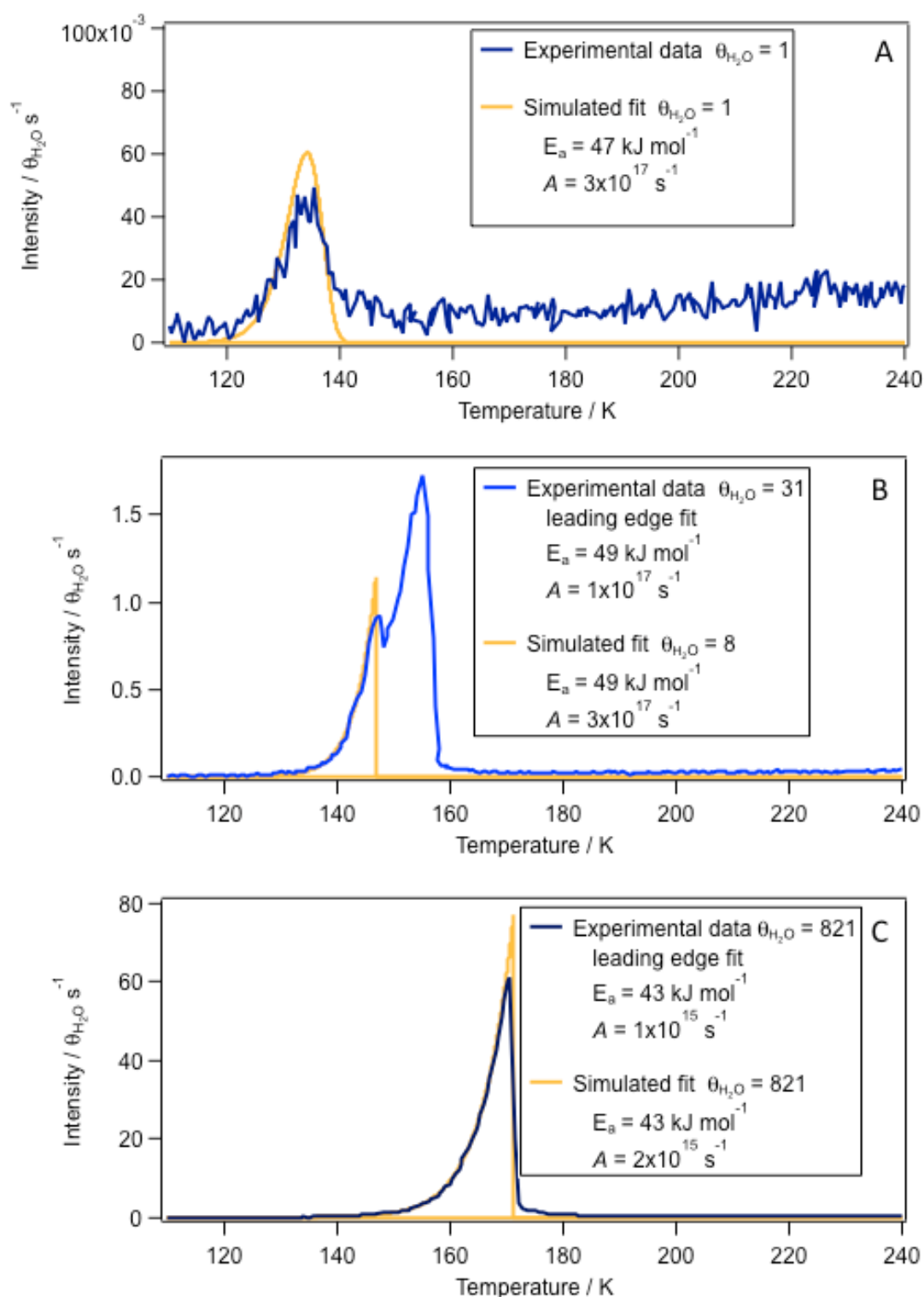


Figure SI4 TPD of pure H<sub>2</sub>O from CCAu using  $m/z = 18$  A,  $\theta_{H_2O} = 1$  and simulated fit. B,  $\theta_{H_2O} = 31$  and simulated fit to low temperature side of phase transition. C,  $\theta_{H_2O} = 821$  and simulated fit to high temperature side of phase transition.

#### References

1. A. Deyko, K. R. J. Lovelock, P. Licence and R. G. Jones, *Physical Chemistry Chemical Physics*, 2011, **13**, 16841-16850.