Rewritable Imaging on the Surface of Frozen Ionic Liquids

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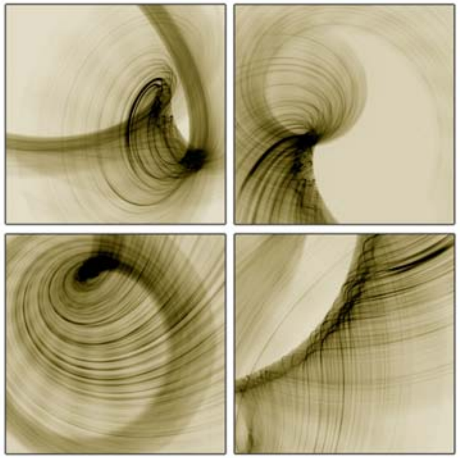


- An ionic liquid is a salt in which the ions are poorly coordinated, which results in these solvents being liquid below 100 °C, or even at room temperature.

- 99.99% of the liquid is made up of ionic species

- Ionic liquids are electrically conductive and have extremely low vapor pressure

1-butyl-3-methylimidazolium nitrate (BMIM nitrate)
1-butyl-3-methylimidazolium tetrafluoroborate (BMIM BF4)

INTRODUCTION

Chemical reactions, such as Diels-Alder reactions and Friedel-Crafts reactions, can be performed using ionic liquids as solvents

Due to their non-volatility, ionic liquids have been considered as having a low impact on the environment and human health, and thus recognized as solvents for green chemistry

A magnetic ionic liquid was identified based on the imidazole 1-butyl-3-methylimidazolium chloride and ferric chloride.

MALDI, Electrospray, Fuel cells, Food science,…

XPS can be used to investigate liquid samples based on room temperature ionic liquids (RTILs)

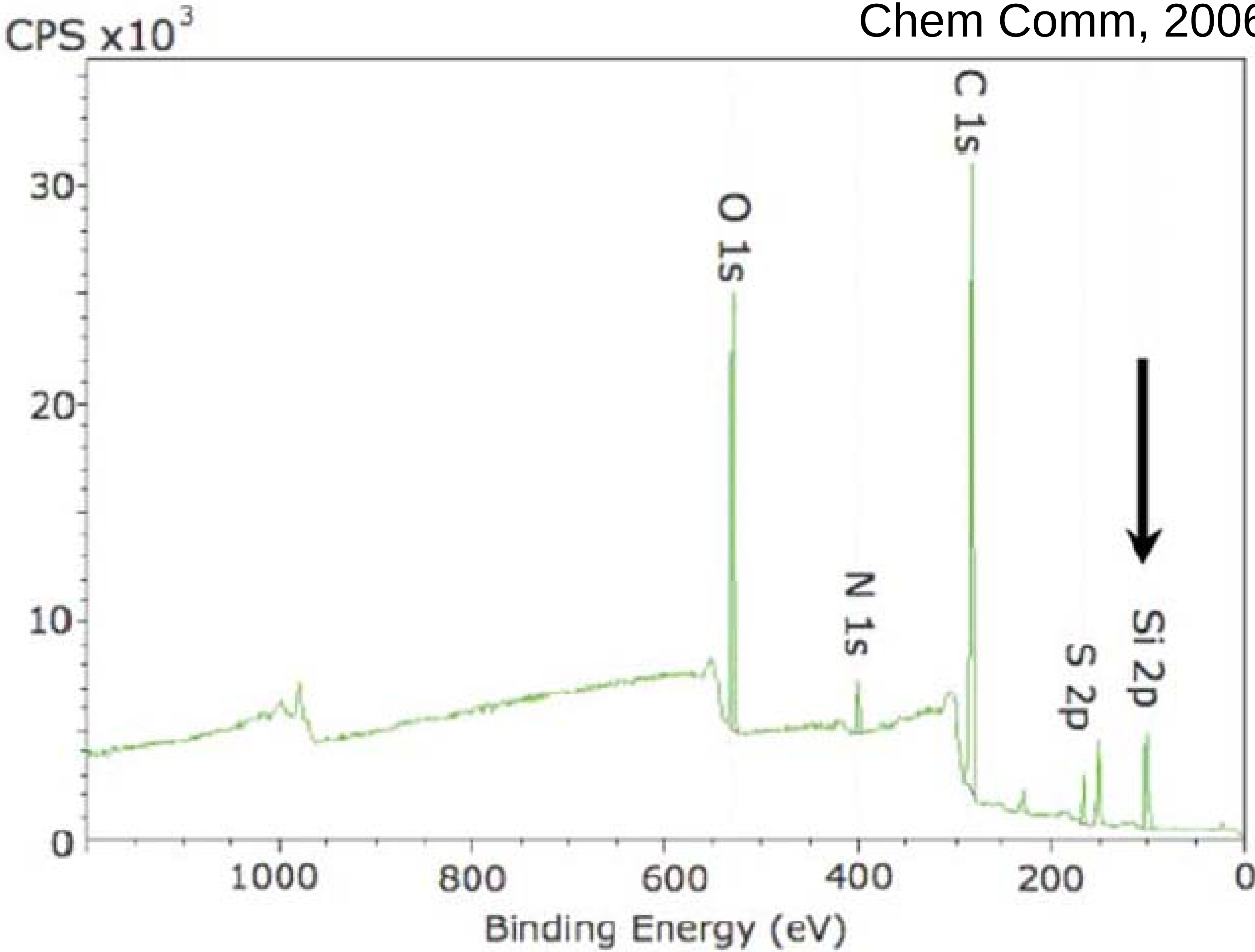
Liquid RTILs emit good photoelectron flux; hence, excellent XPS data can be obtained

Since the RTIL is electrically conducting, none of the problems associated with differential charging are encountered, and charge neutralisation is not required.

RTILs appear to be very stable during exposure to the X-ray source (no out-gassing, or beam damage to the sample).

XPS survey spectrum

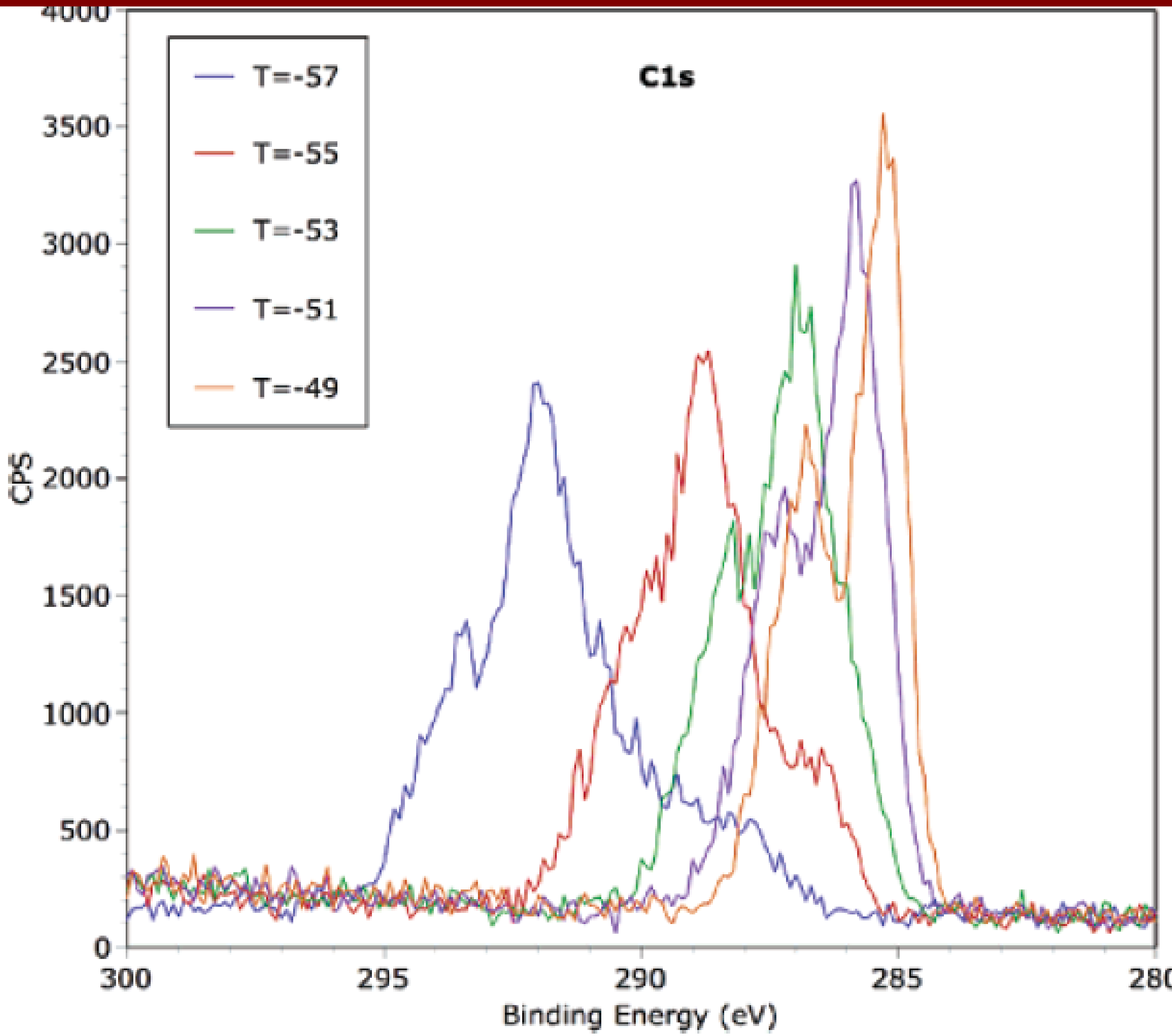
Chem Comm, 2006



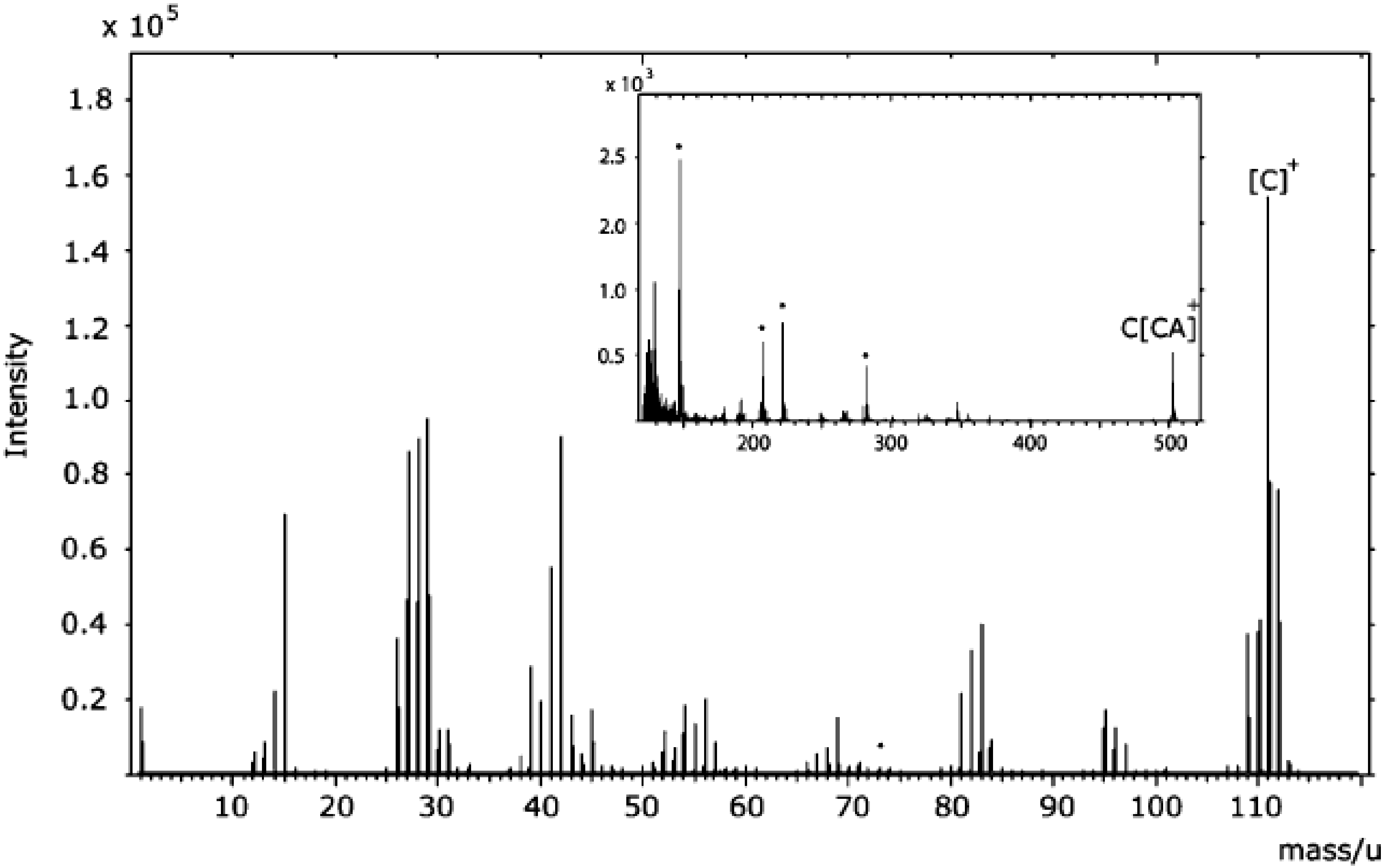
1-butyl-3-methylimidazolium ethyl sulphate

High resolution XPS

Langmuir, 2006



ToF SIMS



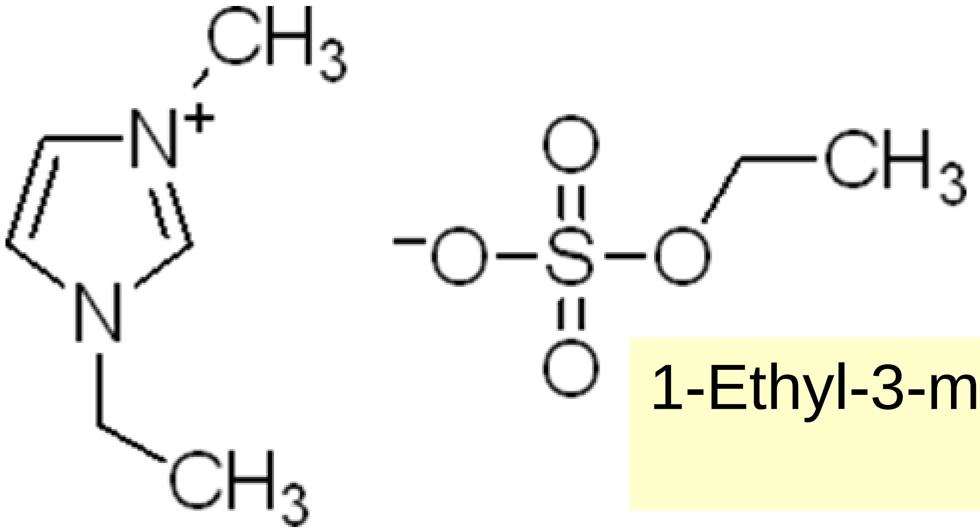
ToF-SIMS spectra recorded for [EMIM][NTf2]

Successive rounds of photolithography, or sequential milling, are used to build up complex patterns of conducting, insulating, semiconducting regions, or arrays of channels and grooves upon the substrate.

These techniques produce a permanent, write-once image or pattern, which is difficult or impossible to alter once they have been formed.

Here, a method for producing localized charge patterns that allow the recording of a rewritable image or data set on the surface of a frozen ionic liquid

Re-writable imaging



1-Ethyl-3-methylimidazolium ethyl sulfate
[EMIM][EtSO4]

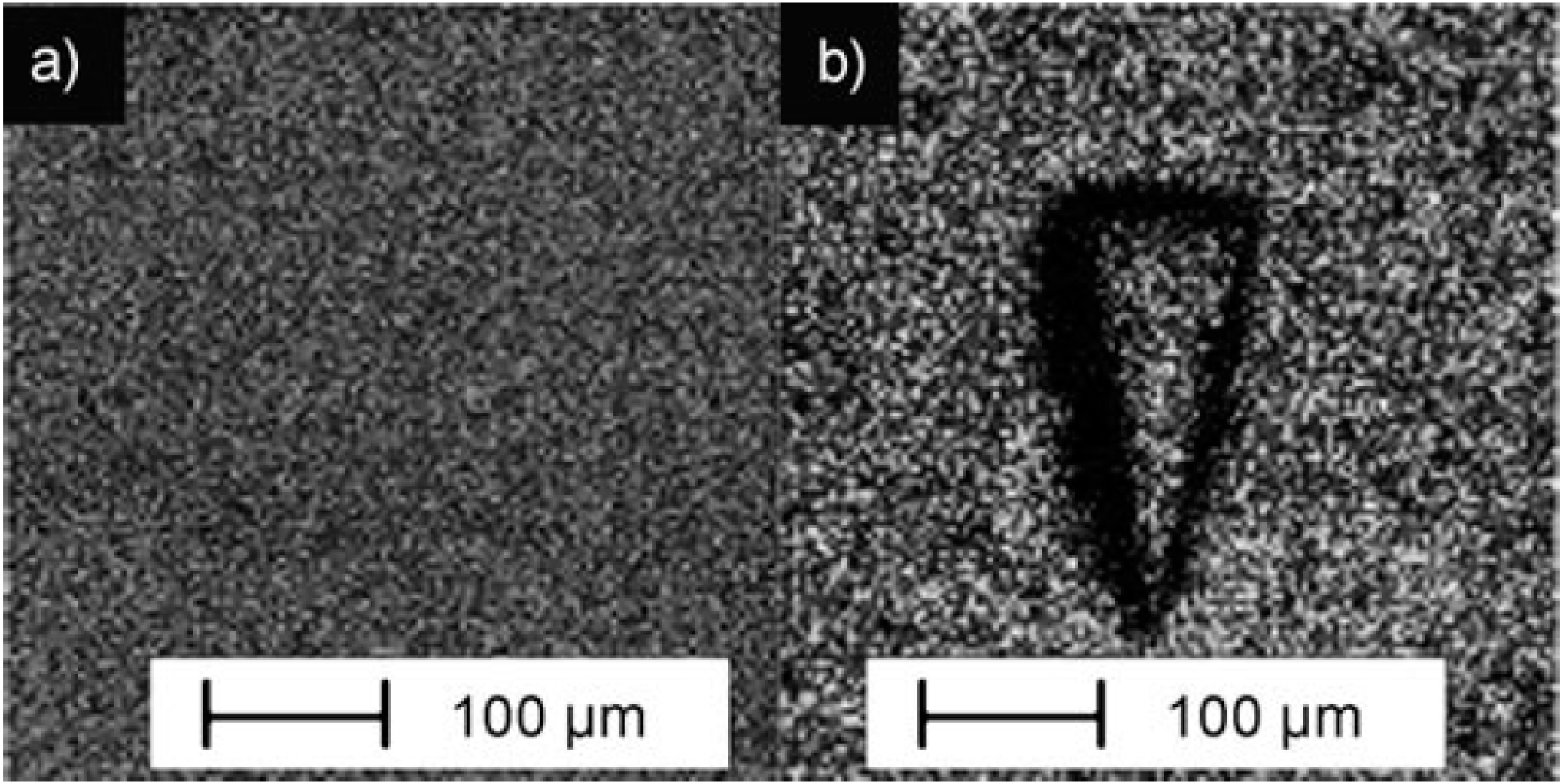
- All UHV experiments: (<5x10^{-9} mbar)
- TOF-SIMS instrument: (IONTOF GmbH, Munster, Germany) equipped with a liquid-nitrogen cooled sample stage,
- Ion gun: Ga metal
- Primary-ion energy of 25 keV
- Ion-beam diameter of approximately 5 μm
- Samples were presented on clean aluminum foil

Experimental

The sample [EMIM][EtSO4] solidify and turn opaque at stage temperatures less than 188 K

Flooding the charged surface with low-energy electrons (<20 eV),

Here we exploit this change in conductivity by using static TOF-SIMS to both create and image patterns with the focused Ga+ ion beam, which is used as a primary-ion source during TOF-SIMS.

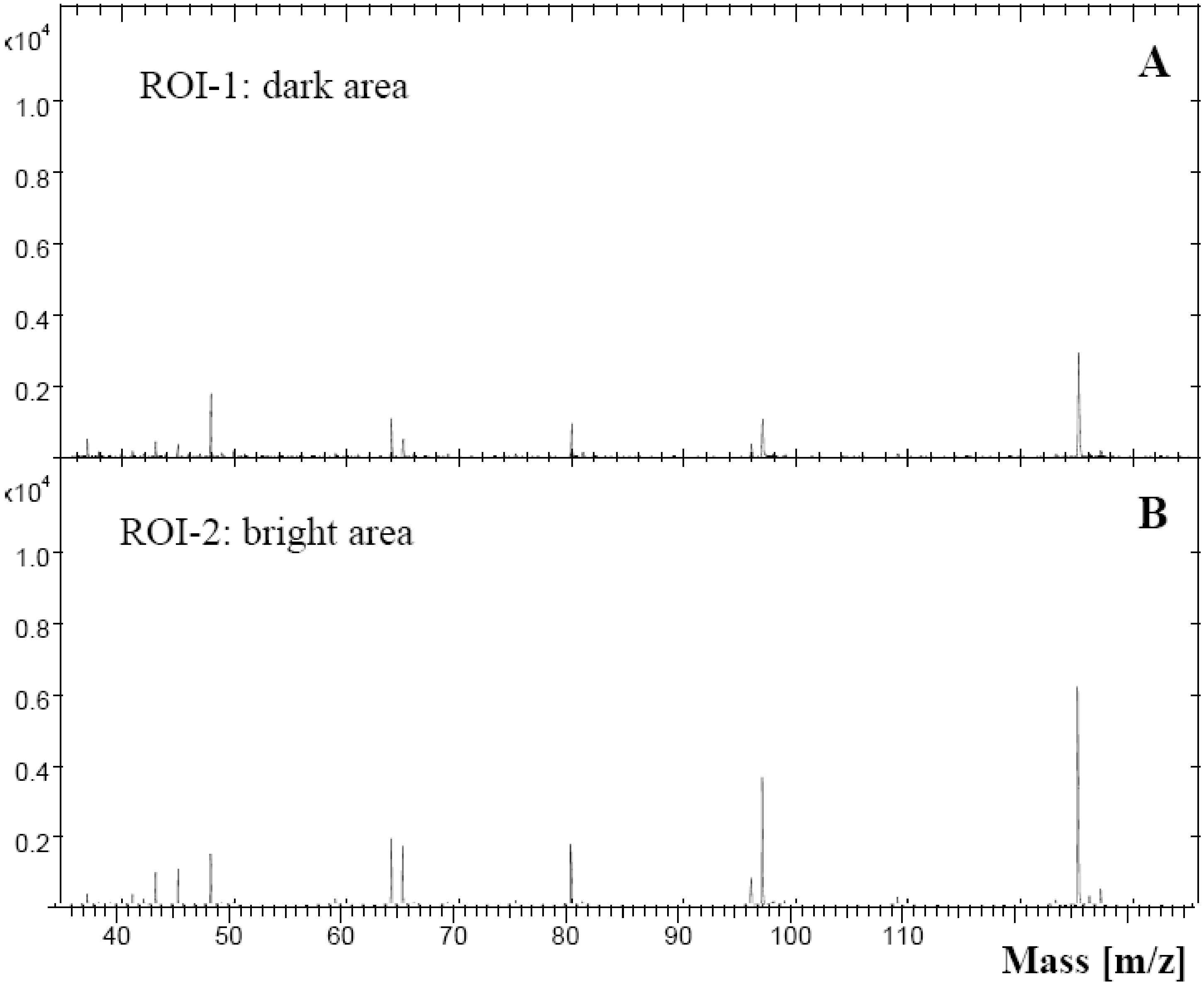


a) Total negative ion SIMS map of [EMIM][EtSO$_4$] at T>188 K

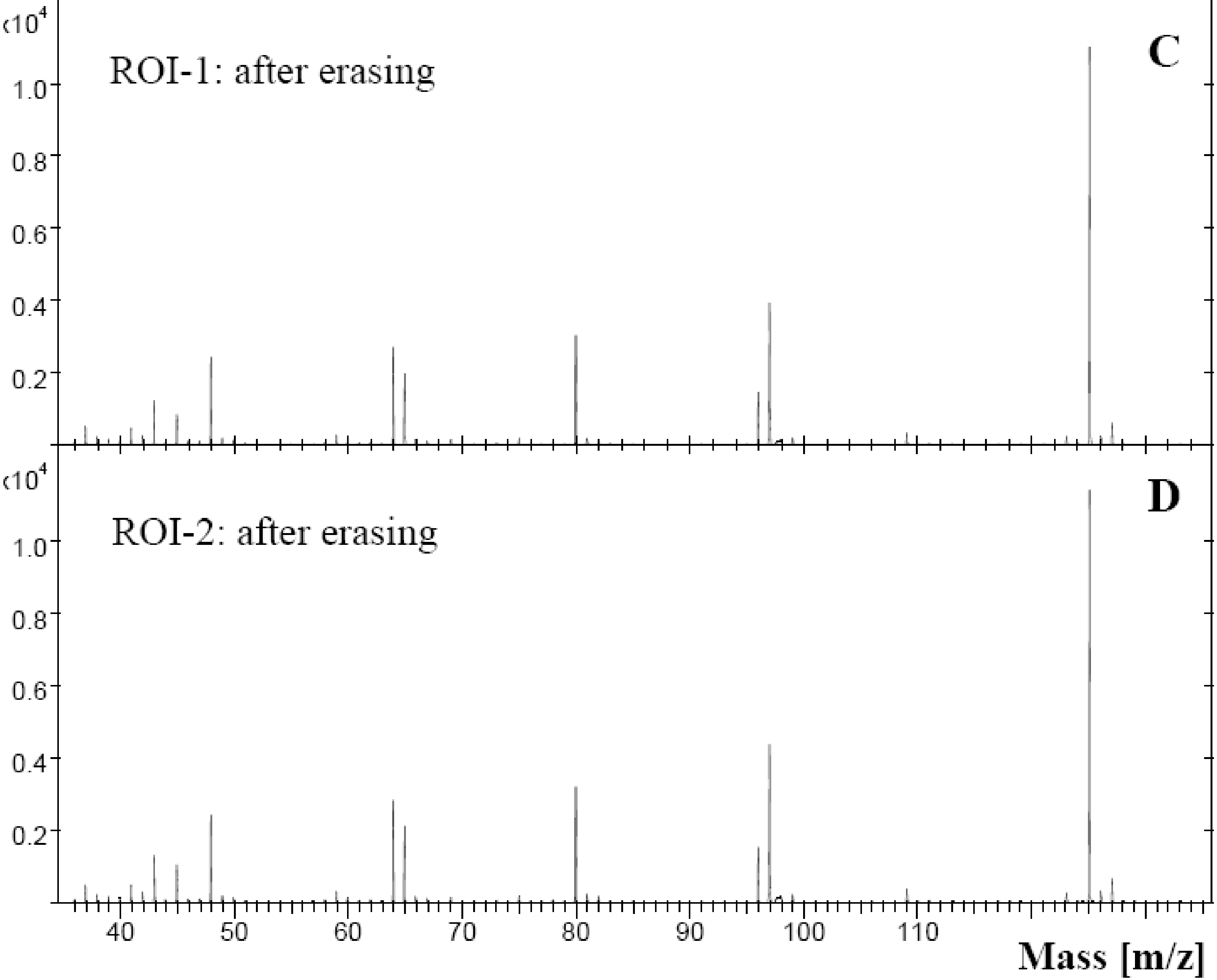
b) Total negative ion SIMS map of [EMIM][EtSO$_4$] at T<188 K

1) The primary-ion beam damages the surface layers of the sample leading to localized chemical changes at the surface

2) Exposure to the Ga^{+} ion source leaves positively charged areas that are frozen into specific sites on the sample surface.



Comparison of negative SIMS



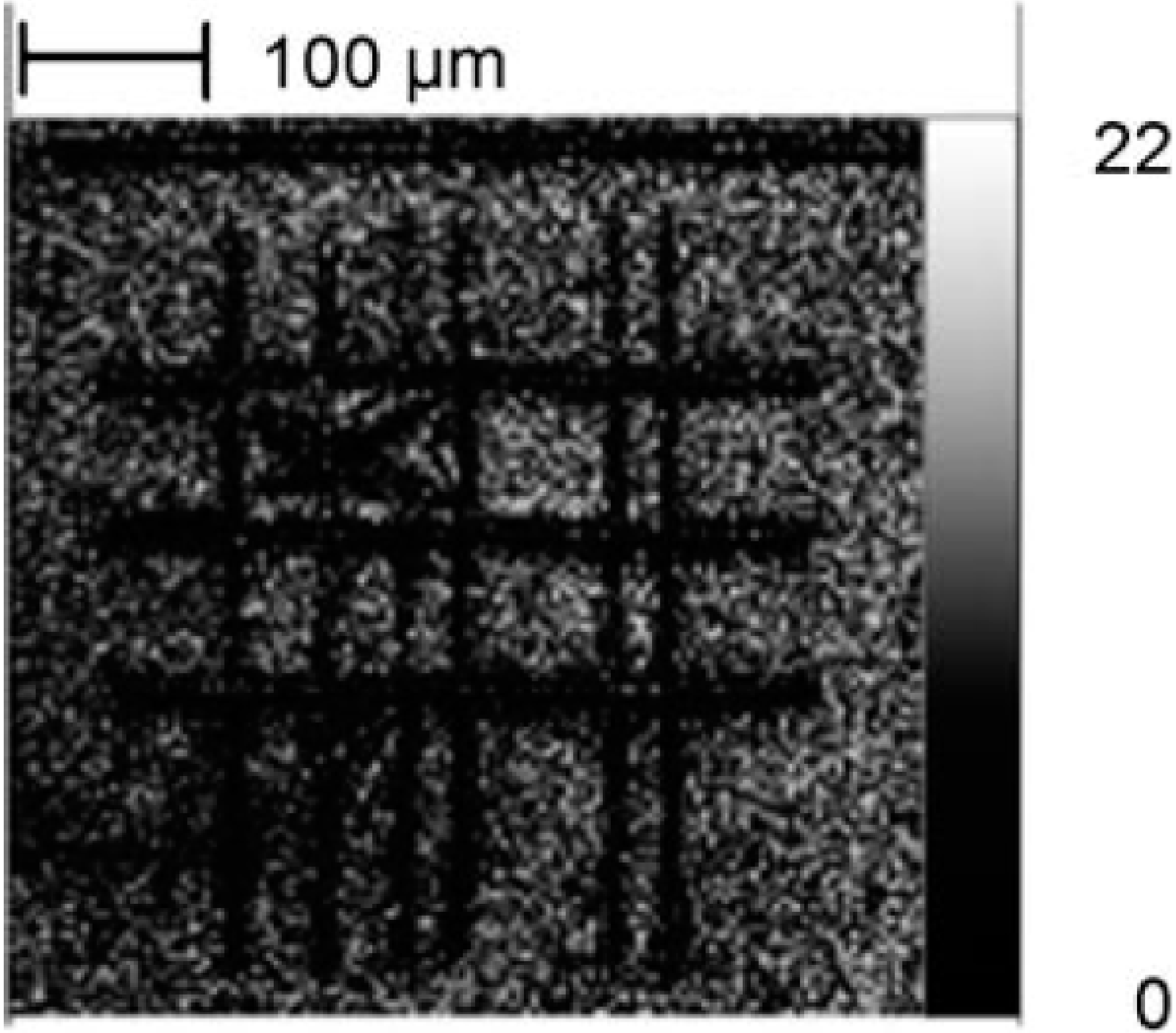
Comparison of negative SIMS

The disappearance of the image is consistent with dissipation of the frozen charges into the bulk of the melted, liquid sample.

Rewriting of a new image was made possible by cooling the sample below the noted transition point, consequently refreezing the RTIL surface.

The second expmnt which confirms the charge based explanation, was simply the neutralization of the frozen positively charged areas by using a standard low-energy electron gun.

Controlled experiments



Total negative ion image of a pattern written on the surface of a frozen [EMIM][EtSO4] at 178 K

After an image was written on a surface of frozen [EMIM][$EtSO_4$], the sample stage was transferred to a preparative chamber adjacent to the analytical chamber of the TOF-SIMS instrument.

The preparative chamber was subsequently vented to 1 atm of dry N_2 gas,

The preparative chamber was then re-evacuated and the sample returned to the main chamber for visualization. The image was still present !!!

This methodology has allowed the investigation of changes in the thermal and physical properties of RTILs at and in the region of their melting points.

The minimum beam width can be generated by instruments is less than 10 nm. If image formation can be achieved with such instruments, then the density of data storage will be extremely high.

Conclusion

Chemical modification by low energy ions

Imaging of prepared patterns

Ionic liquids as substrate (conductor- insulator transition)

A good class of liquids for XPS

Relevance