ELECTRONIC STRUCTURE OF IONS IN SOLUTION USING THE CORE-HOLE CLOCK: IONS IN MOLECULAR SOLVENTS VS IONS IN IONS

DR. KEVIN LOVELOCK
k.r.j.lovelock@reading.ac.uk

CONEXS CONFERENCE 2020
EMERGING TRENDS IN X-RAY SPECTROSCOPY

19th FEBRUARY 2020

University of Reading

Introduction

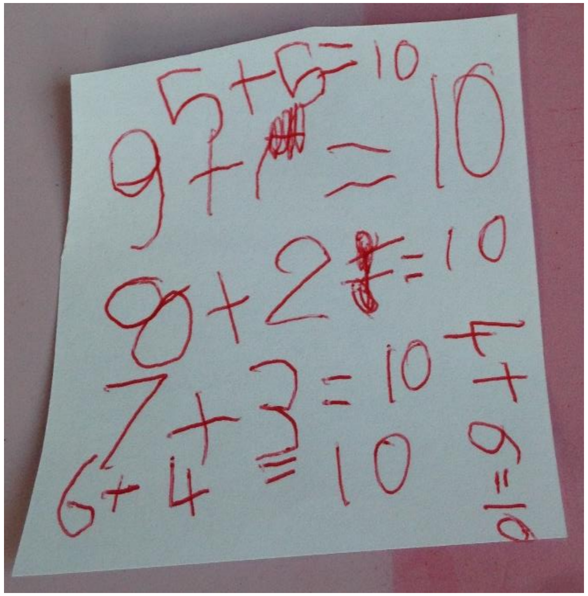
- Motivation: why ions in solution are important
- Technique: core-hole clock
- Apparatus for X-ray spec of liquids

Results

- S 1s NEXAFS
    - Unoccupied MO identification
- Core-hole clock
    - Unoccupied MO identification
    - MO screening by the solvent
    - Electron transfer times

Motivation

Curiosity



Ions (at High Concentration) in Solution

Electrochemistry

- Water-in-salt battery electrolytes
  Suo *et al.*, *Science*, 2015, **350**, 938.
- Thermoelectrics
  Lazar *et al.*, *Phys. Chem. Chem. Phys.*, 2016, **18**, 1404.
- Ions under confinement, *e.g*. supercapacitors
  Smith *et al.*, *J. Phys. Chem. Lett.*, 2016, **7**, 2157.

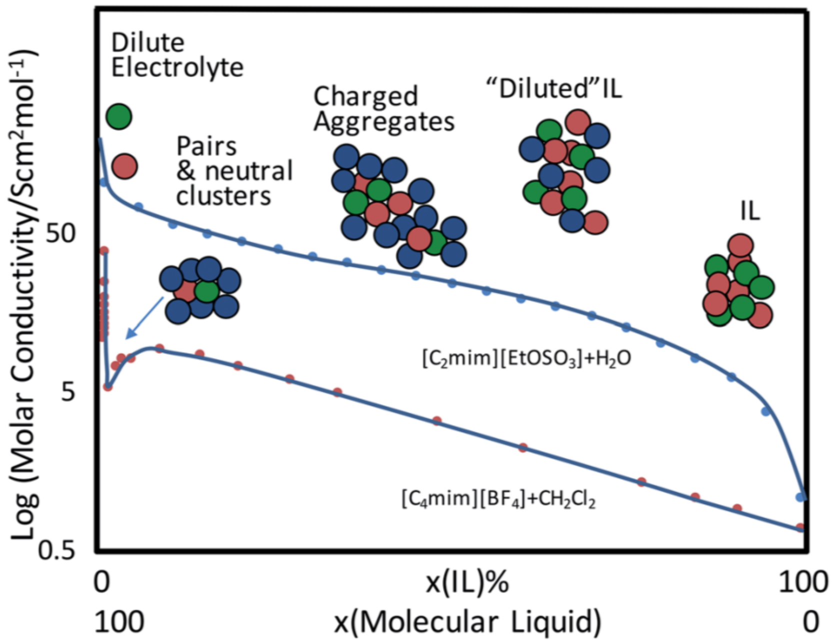
"Bio"

- Dead Sea (~4.7 M)
- Hofmeister series for biology
  Lo Nostro *et al.*, *Chem. Rev.*, 2012, **112**, 2286.
- Hydrated ionic liquids for biocatalysis *etc*.
  Schröder, *Top. Curr. Chem.*, 2017, **375**, 25.
- Solutions for biomass deconstruction
  Brandt *et al.*, *Green Chem.*, 2015, **17**, 5019.

Ionic liquid properties

- Impurities in ionic liquids
  Seddon *et al.*, *Pure Appl. Chem.*, 2000, **72**, 2275.

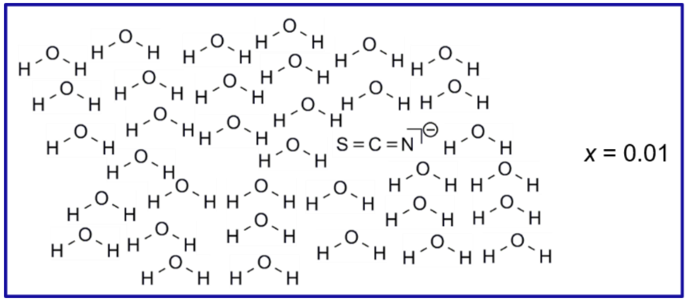
Question to Answer:
How Does Ion Solvation Affect Ion Reactivity?



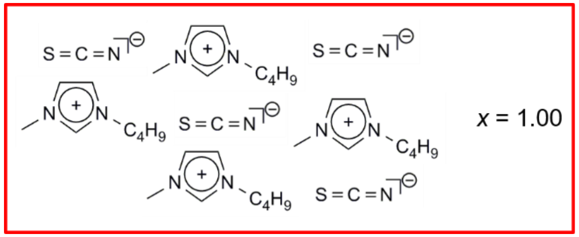
MacFarlane *et al.*, *Faraday Discuss.*, 2018, **206**, 9.

Fig. 1 Molar conductivity trends in water–$[C_2mim][EtOSO_3]$[14] and dichloromethane–$[C_4mim][BF_4]$[15,16] mixtures.

Ions in molecular liquids



Ions in ions



Solutes in Liquids:
Relating Electronic Structure and Reactivity

Nobel Prize for Chemistry 1981

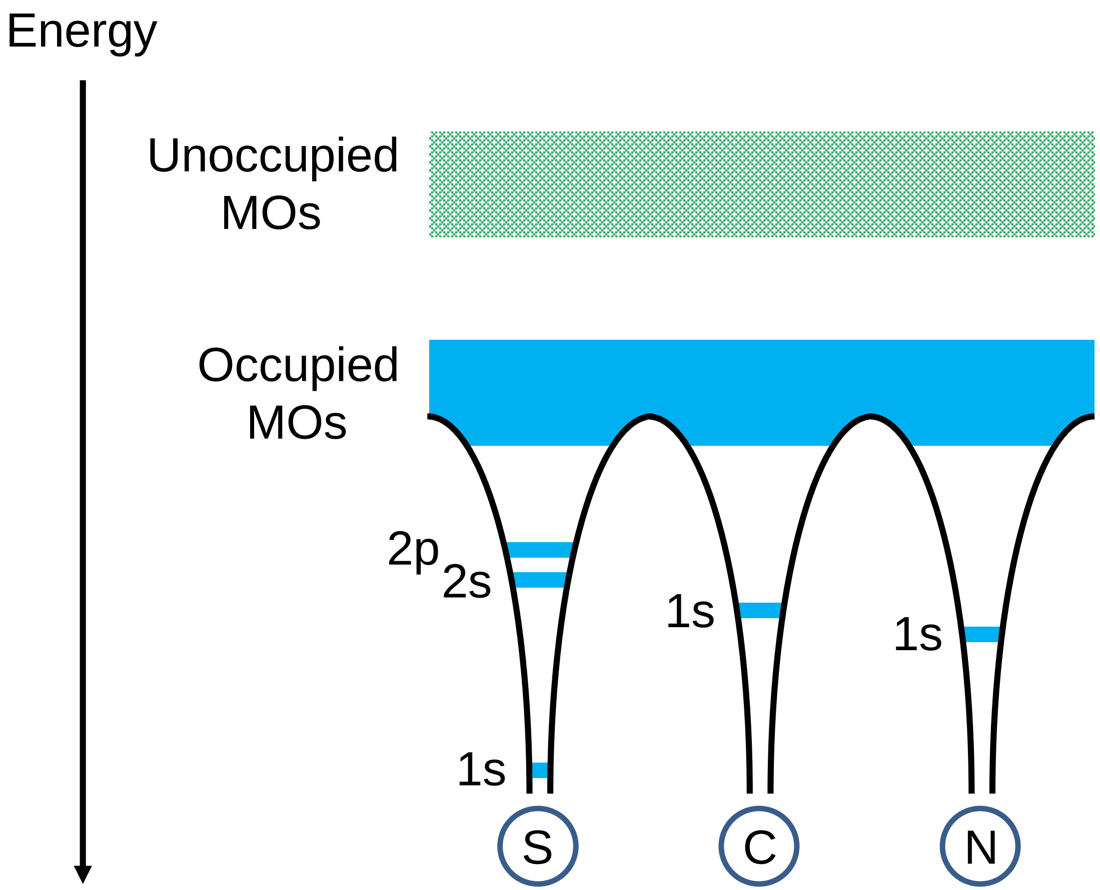
"In the electronic theory, the static and dynamic behavior of molecules are explained by the electronic effects which are based solely on the distribution of electrons in a molecule."

"reactivity of molecules is explained by electron location"

https://www.nobelprize.org/prizes/chemistry/1981/fukui/lecture/
https://www.nobelprize.org/prizes/chemistry/1981/fukui/auto-biography/

Techniques

Probing Electronic Structure: X-ray Spectroscopy



XAS
Core-hole clock (CHC)
Lab XPS
Variable $h\nu$ XPS
Resonant XPS
AES
VtC XES
RIXS

Probing Unoccupied MOs: Traditionally… NEXAFS

2 steps:

1. X-ray absorption leaves core-hole

2. Electron dynamics fills core hole
   - Electron detection
   - Photon detection
   - (Transmission)

Core-Hole Clock: Interfaces and Polymers

Experimental evidence for sub-3-fs charge transfer from an aromatic adsorbate to a semiconductor

Joachim Schnadt*, Paul A. Brühwiler*, Luc Patthey†, James N. O'Shea*, Sven Södergren*, Michael Odelius‡, Rajeev Ahuja*, Olof Karis*, Margit Bässler§, Petter Persson*, Hans Siegbahn*, S. Lunell* & Nils Mårtensson§*

Schnadt *et al.*, *Nature*, 2002, **418**, 620.

- Soft X-rays
- Monolayer on single crystal
- Monitor participator Auger

Anisotropic attosecond charge carrier dynamics and layer decoupling in quasi-2D layered SnS_2

Calley N. Eads[1], Dmytro Bandak[1], Mahesh R. Neupane[2], Dennis Nordlund[3] & Oliver L.A. Monti[1,4]

Eads *et al.*, *Nat. Commun.*, 2017, **8**, 7.

- Soft X-rays
- Single crystal
- Monitor spectator Auger

Femtosecond Electron Delocalization in Poly(thiophene) Probed by Resonant Auger Spectroscopy

C. Arantes,[†,§] B. G. A. L. Borges,[†] B. Beck,[†] G. Araújo,[†] L. S. Roman,[‡] and M. L. M. Rocco*[,†]

Arantes *et al.*, *J. Phys. Chem. C*, 2013, **117**, 8208.

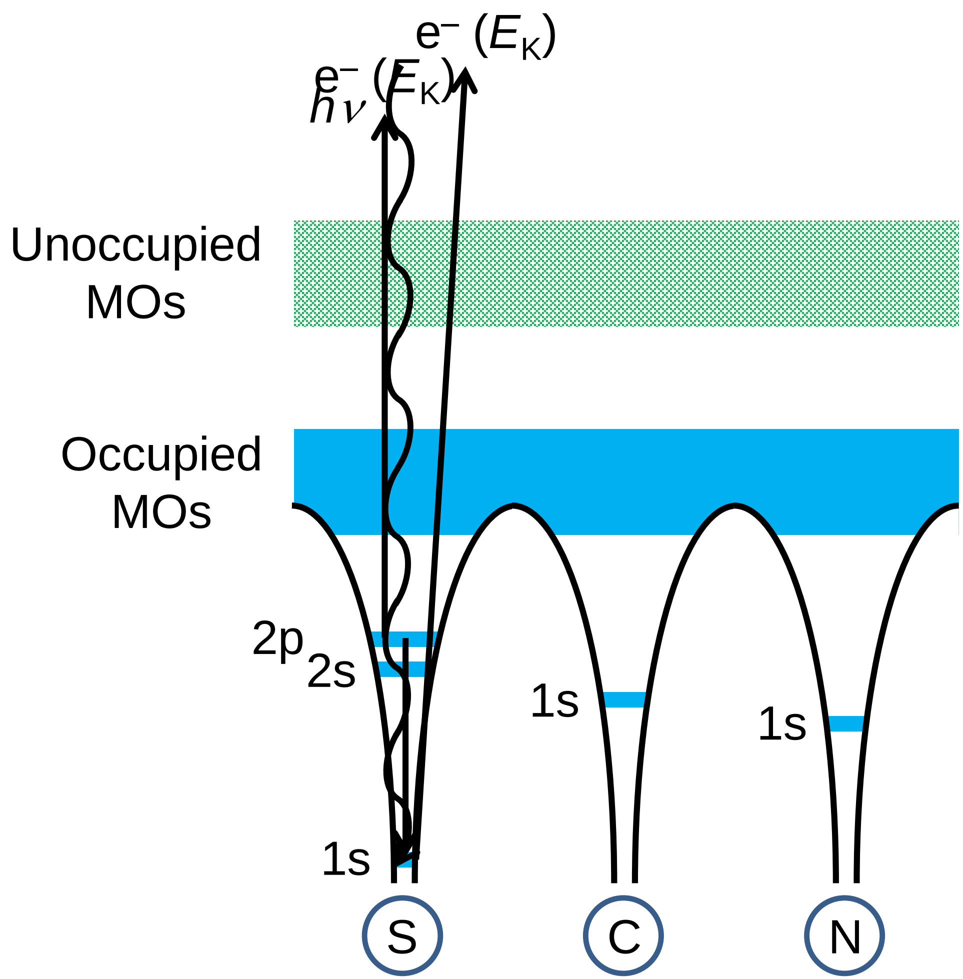
- Tender X-rays
- Polymer
- Monitor spectator Auger

Core-Hole Clock: 2 Competing Processes

2 competing electron processes to fill core-hole important here:

- Resonant normal Auger
- (Resonant) spectator Auger

(Non-resonant) Normal Auger

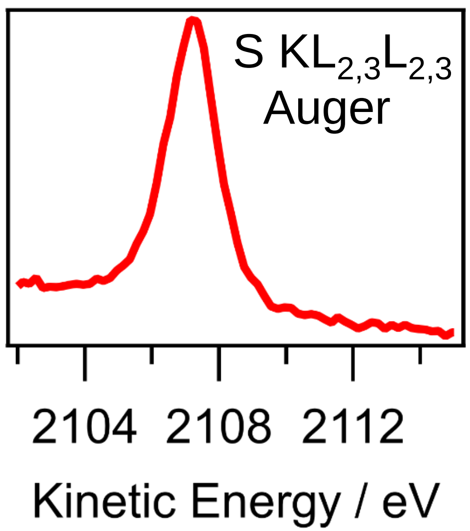


Step 1

- Non-resonant X-ray photoemission
- Produces S 1s core-hole
- S ground state → S $1s^{-1}$

Step 2

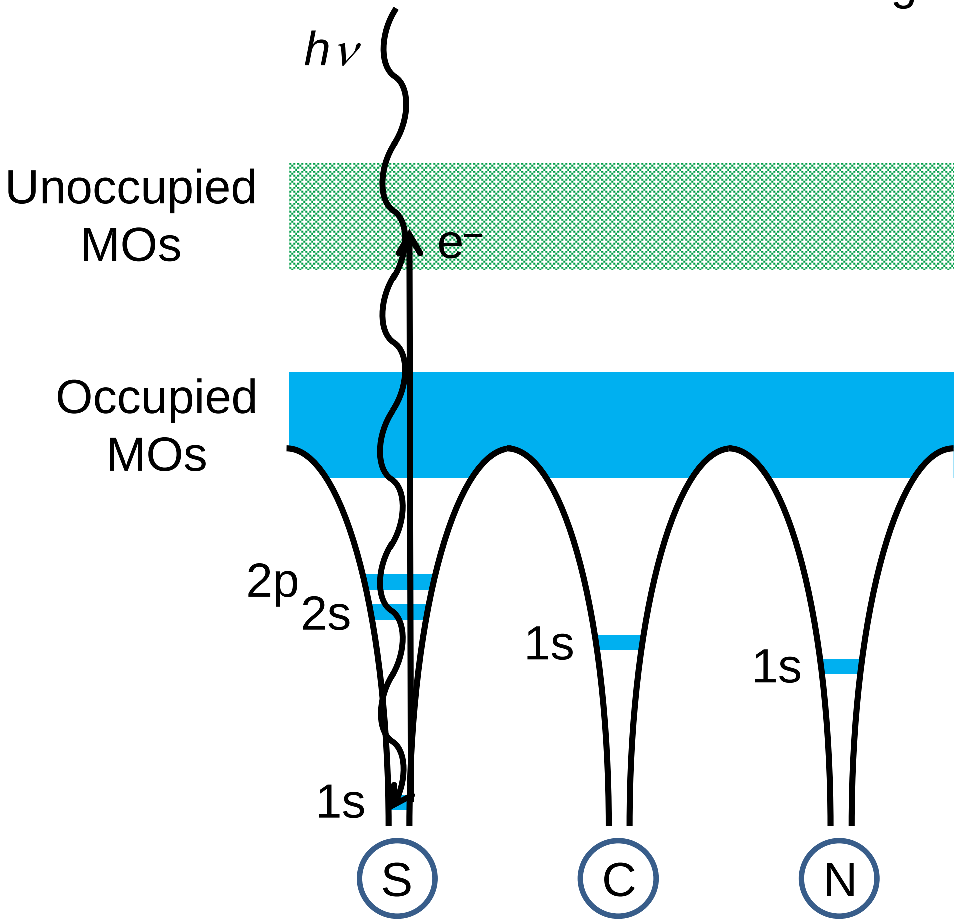
- Monitor S $KL_{2,3}L_{2,3}$ (S 1s2p2p) Auger
- S $1s^{-1}$ → S $2p^{-2}$
- S atom final state: +2
- E_K = constant; independent of $h\nu$



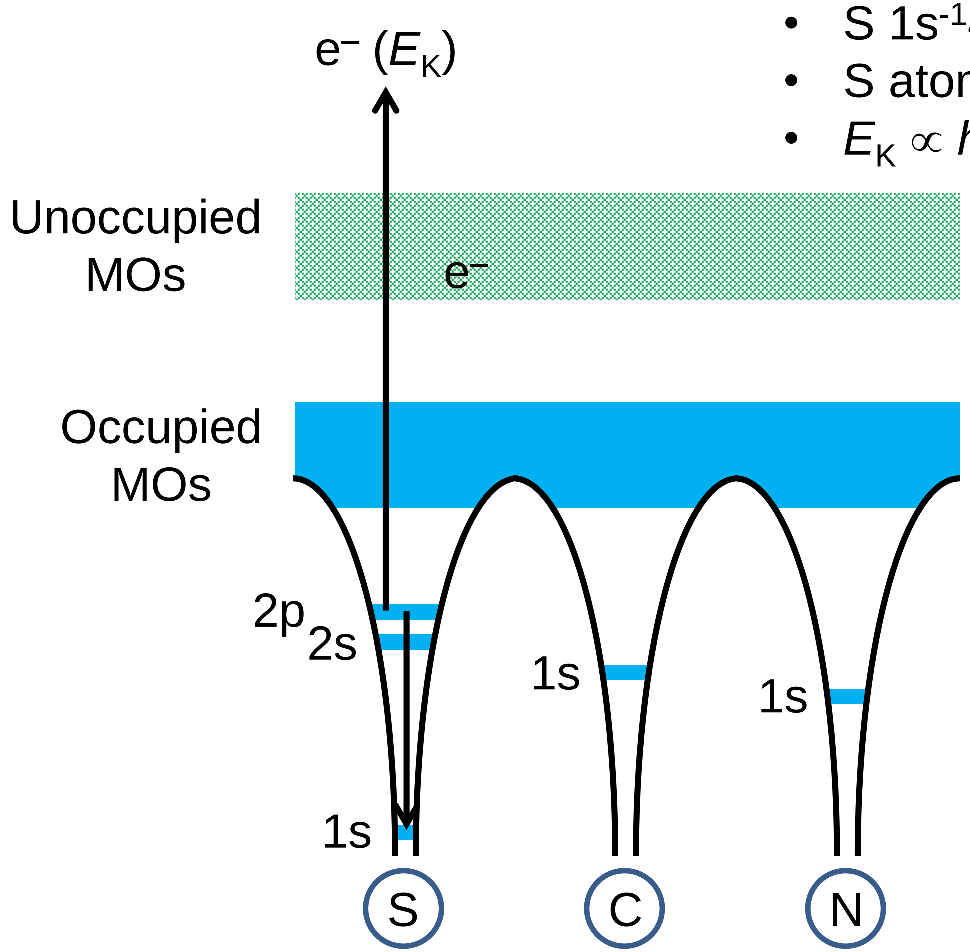
Core-Hole Clock: Step 1

<u>Step 1</u>

- Resonant X-ray absorption (no e^- emission)
- Produces S 1s core-hole
- S ground state → S $1s^{-1}4p$



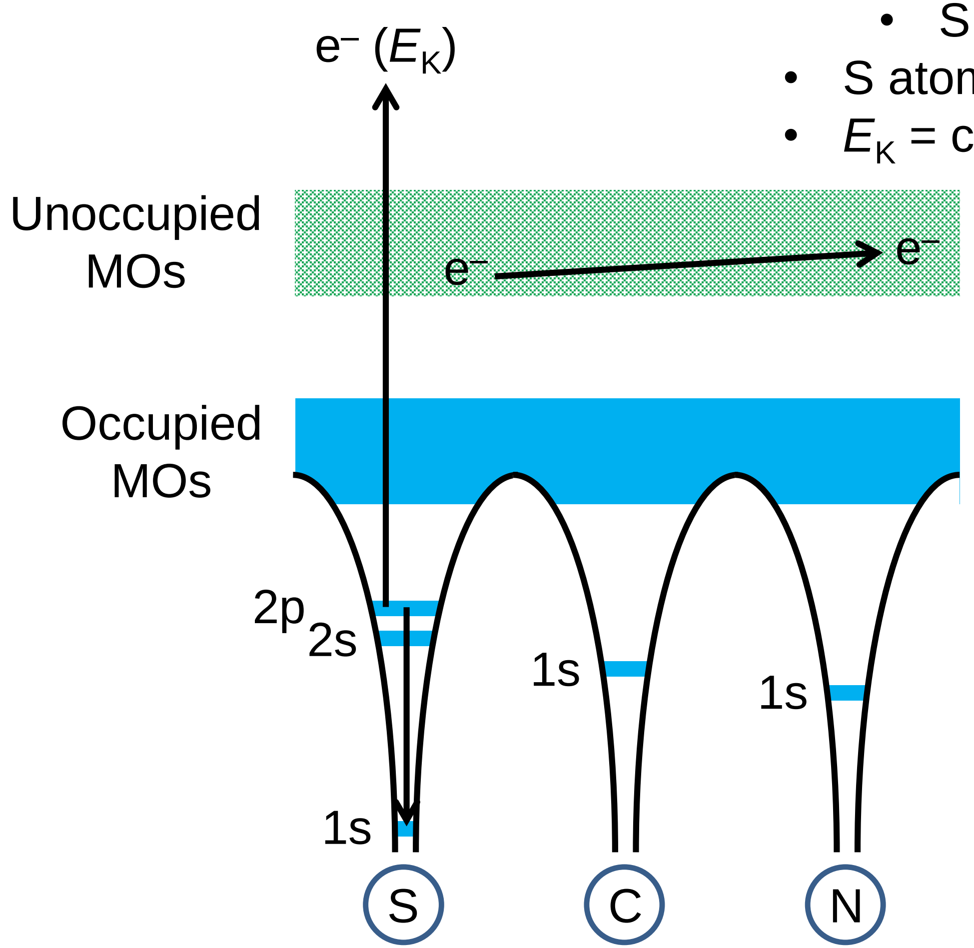
Core-Hole Clock: Step 2 Option A



<u>Step 2, Option A</u>

- **Spectator** Auger transition
- Same process as normal Auger apart from…
- Electron in previously unoccupied MO remains located very close to S 1s core-hole
- S $1s^{-1}4p \rightarrow$ S $2p^{-2}4p$
- S atom final state: +1
- $E_K \propto h\nu$

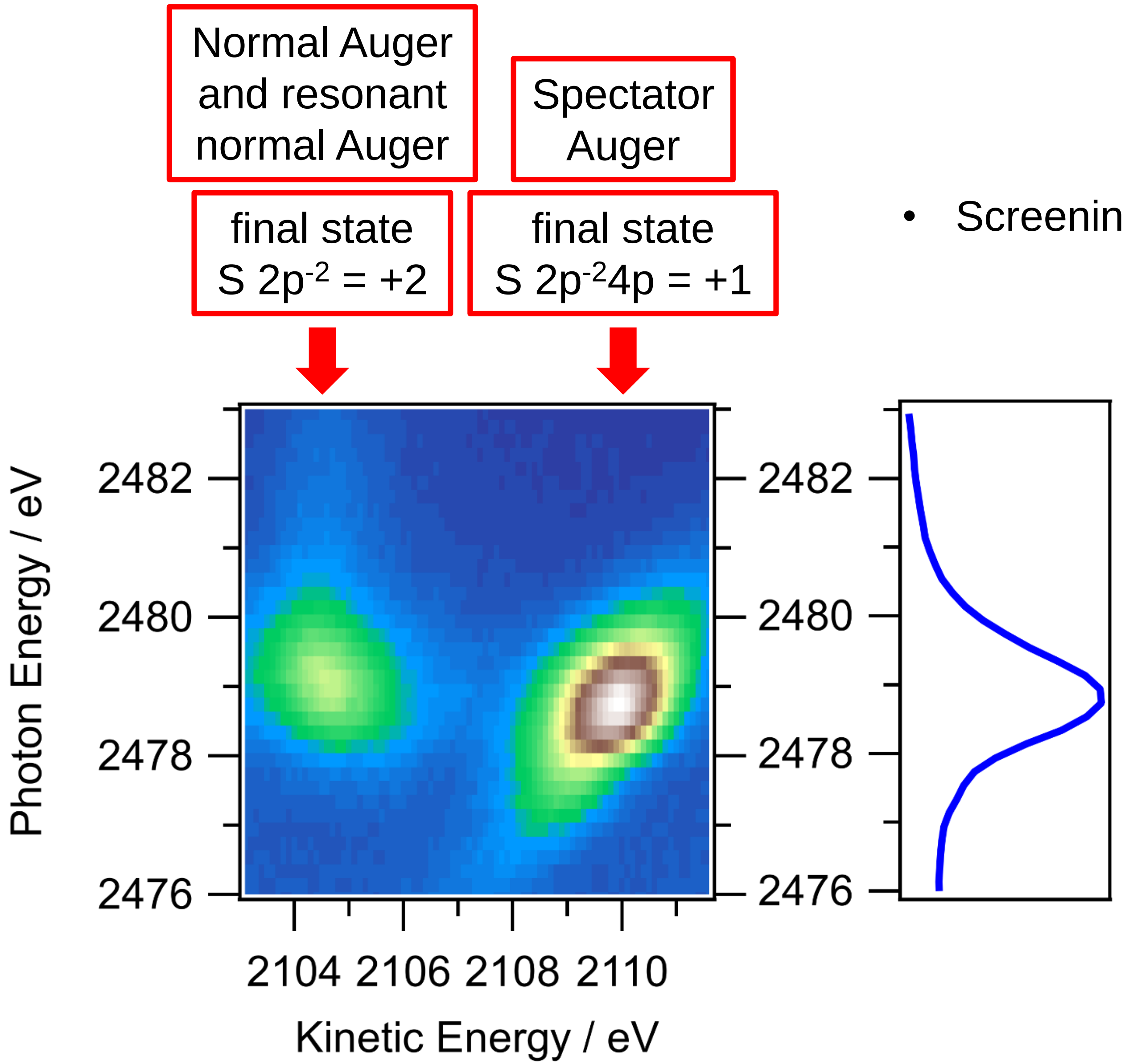
Core-Hole Clock: Step 2 Option B



Step 2, Option B

- **Resonant normal** Auger transition
- Part (i) Electron transfer; electron no longer screens S 1s core-hole
- Part (ii) = same process as normal Auger
  - S $1s^{-1}4p \rightarrow$ S $1s^{-1} \rightarrow$ S $2p^{-2}$
- S atom final state: +2
- E_K = constant

Normal and Spectator Augers at Different E_K?

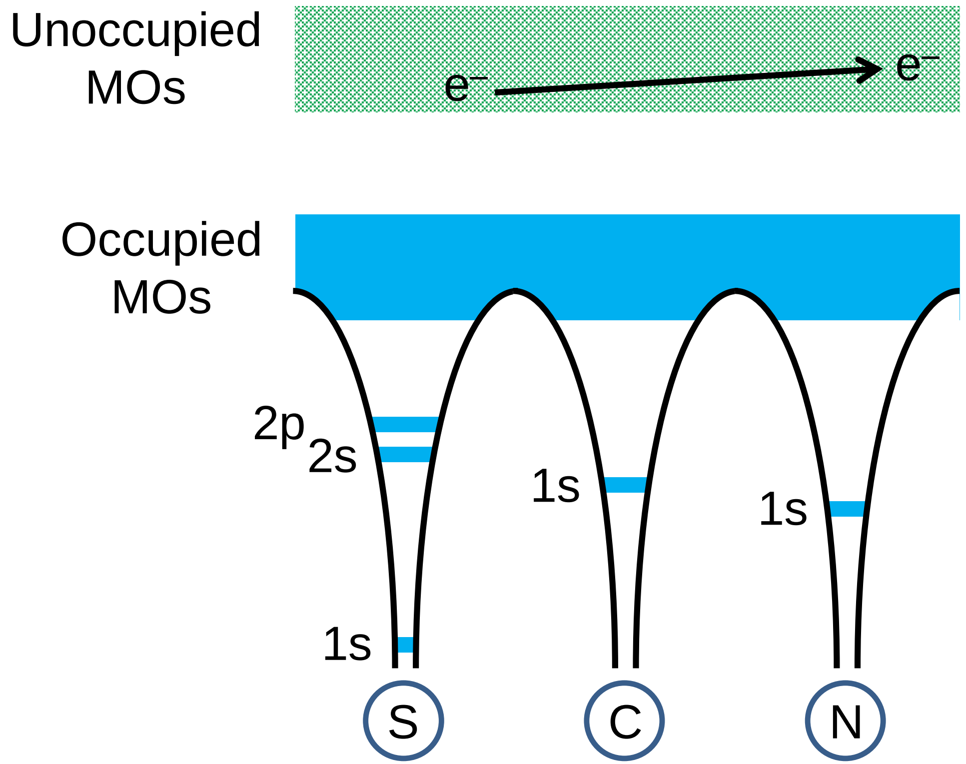


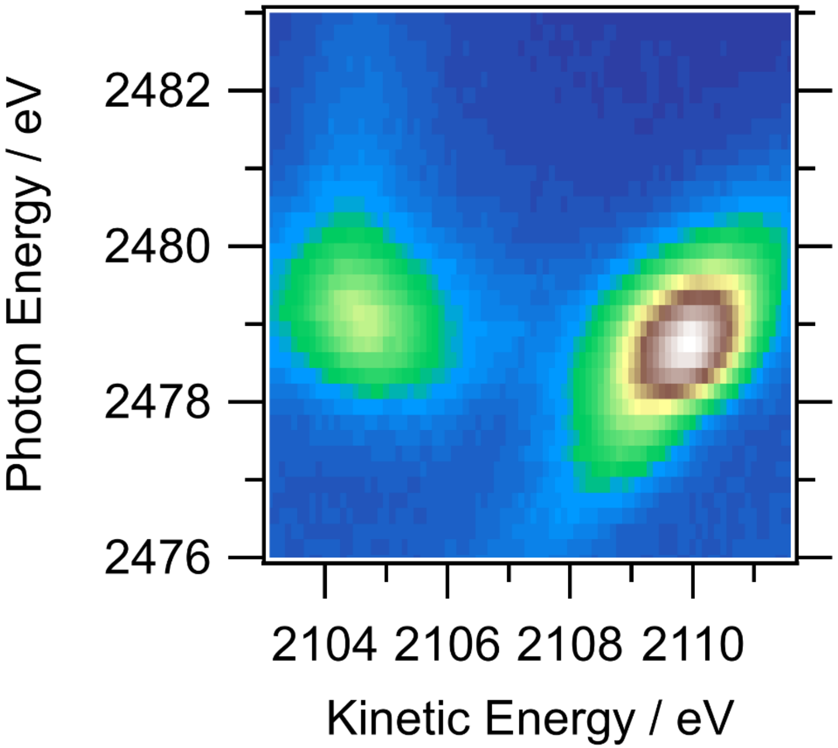
- Screening of core-hole

Results: Electron Transfer Times

Competition between two processes:

- resonant normal Auger transition
- spectator Auger transition





Menzel, *Chem. Soc. Rev.*, 2008, **37**, 2212.
Föhlisch *et al.*, *Chem. Phys. Lett.*, 2007, **434**, 214.

Results: Electron Transfer Times

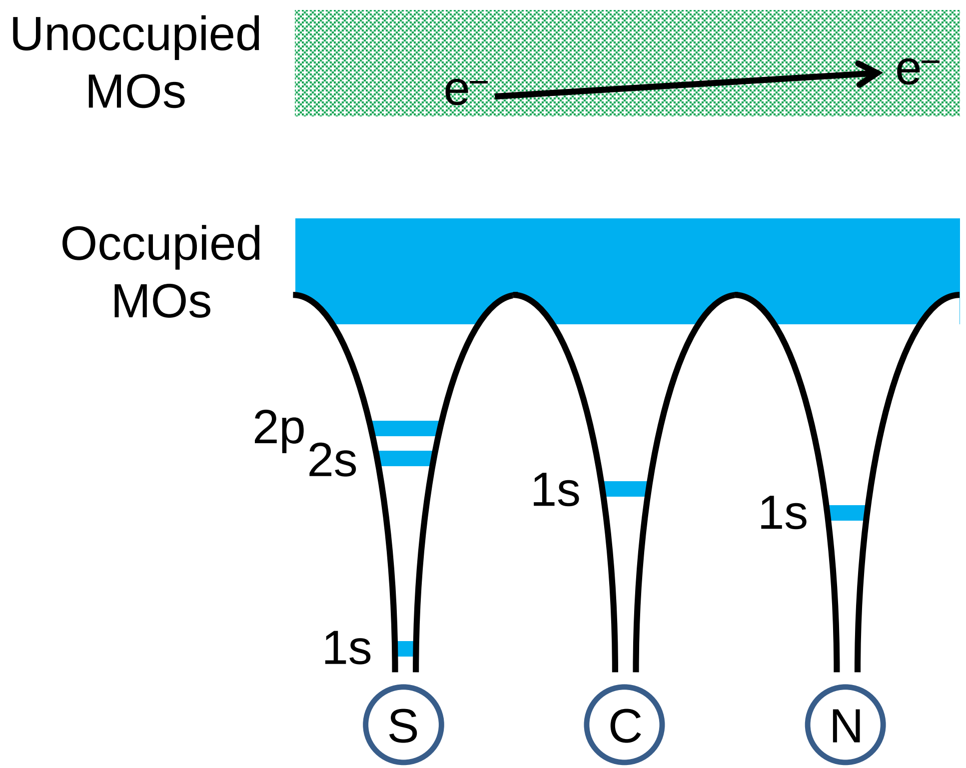
electron transfer time

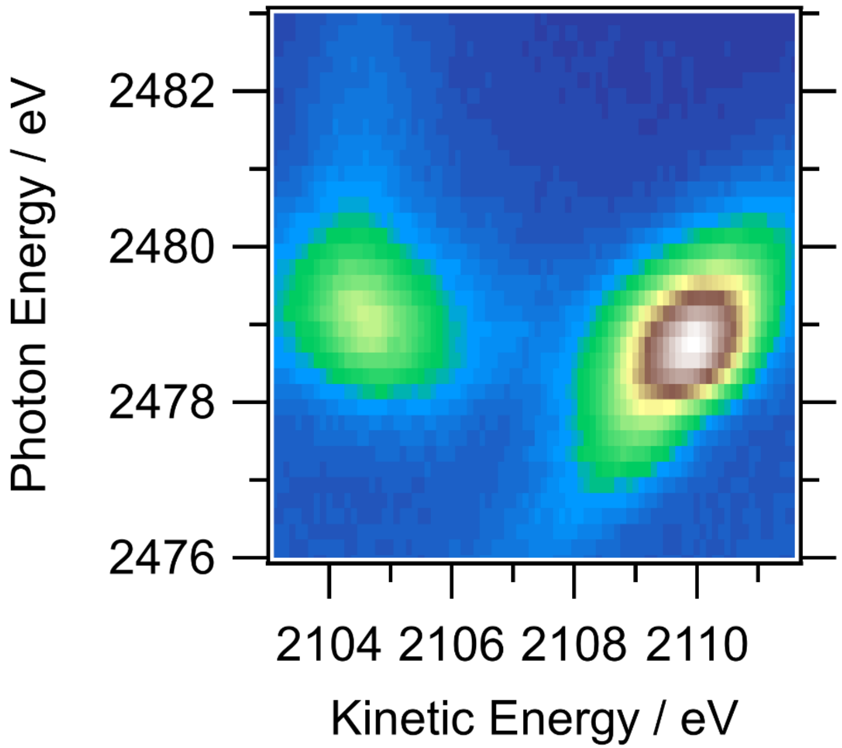
area of spectator Auger peaks

S 1s core-hole lifetime = 1 fs

$$\tau_{CT} = \left(\frac{I_{\text{spectator}}}{I_{\text{resonant normal}}}\right)\tau_{CH}$$

area of resonant normal Auger peaks

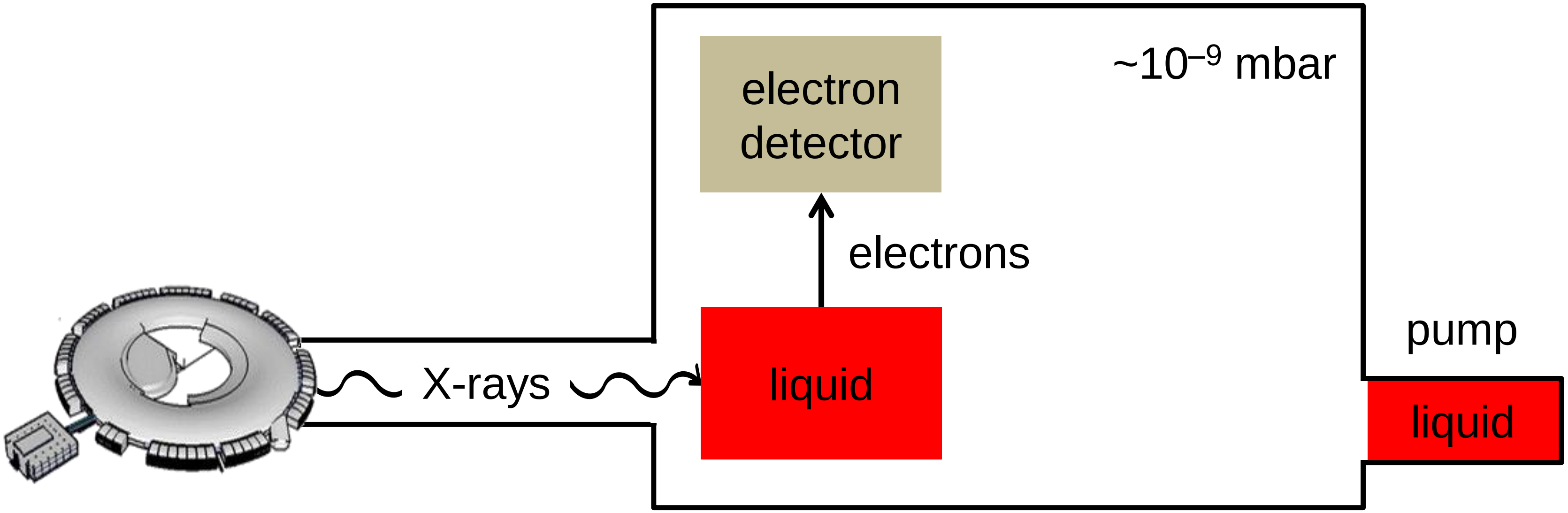




Menzel, *Chem. Soc. Rev.*, 2008, **37**, 2212.
Föhlisch *et al.*, *Chem. Phys. Lett.*, 2007, **434**, 214.

Electron Spectroscopy of Liquids: Apparatus

CHALLENGE



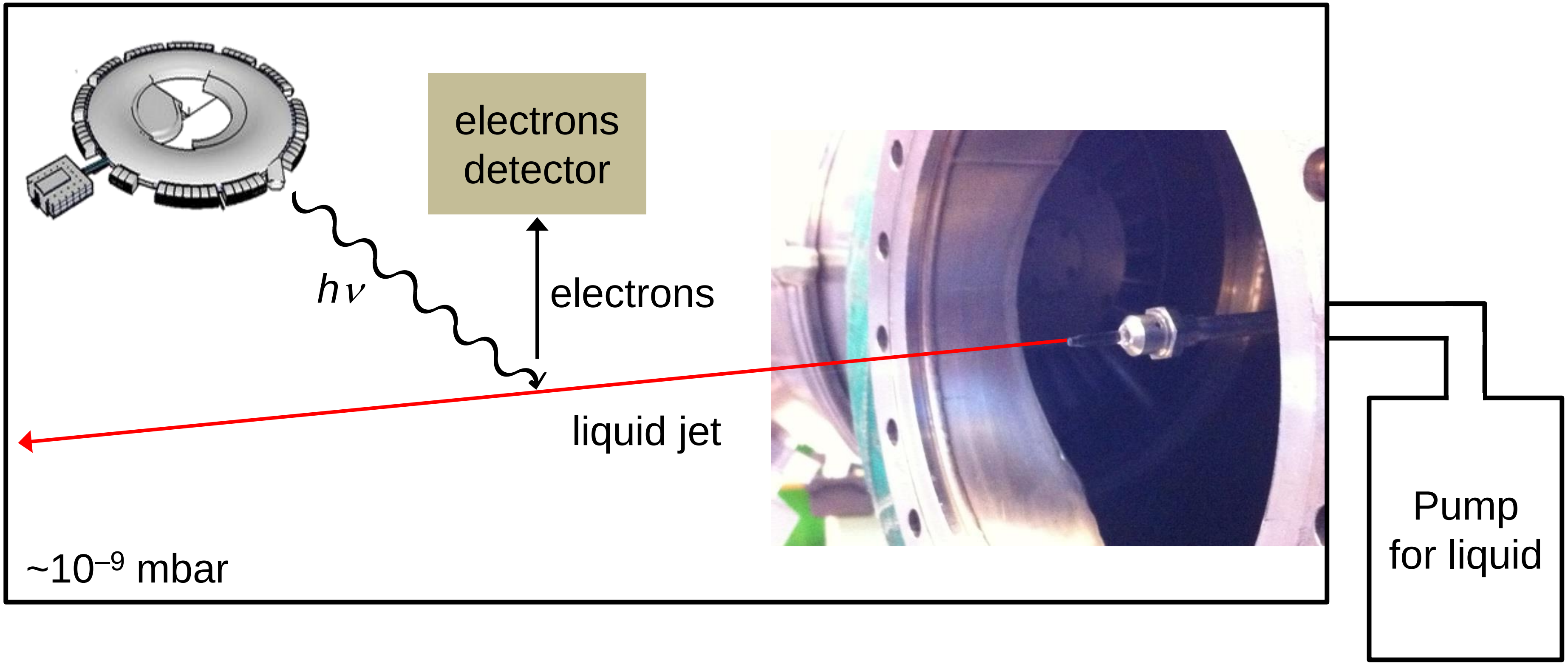
electron
detector
~10–9 mbar
electrons
X-rays
liquid
pump
liquid

X-ray Spectroscopy of Liquids: How?

Method	**Apparatus**	**Samples**
1	Very rare	Ions in (some) molecular liquids
2	Common	Ions in ions

Method 1: Ions in (some) Molecular Liquids

Liquid Microjet Apparatus



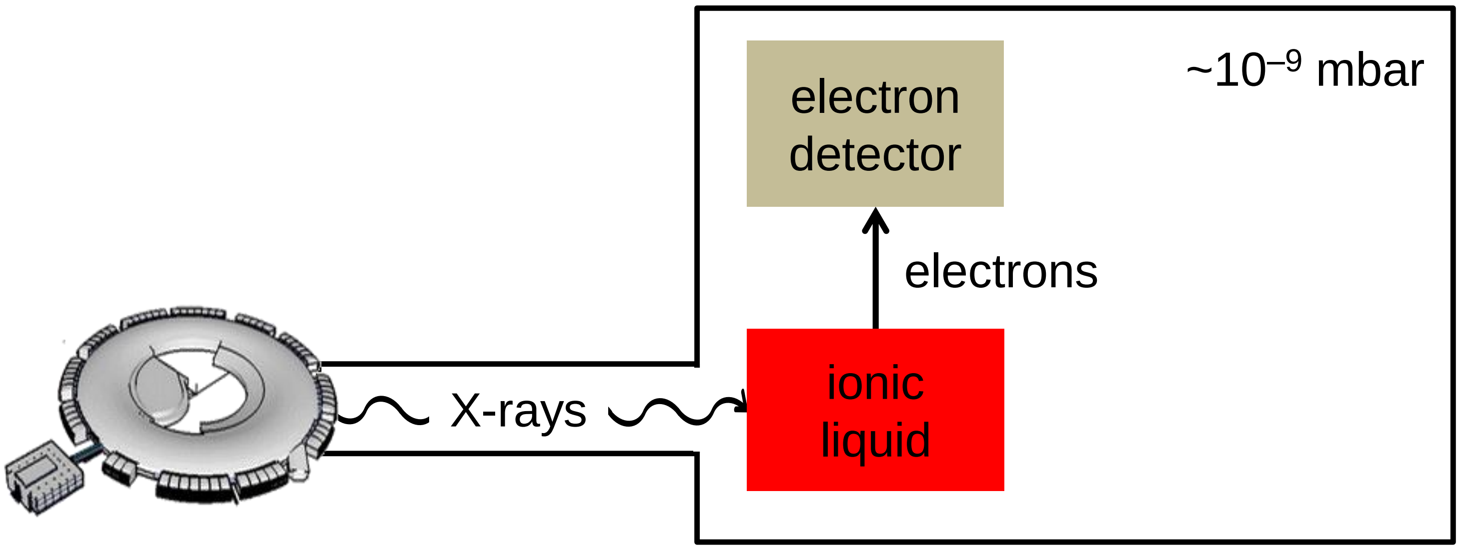
MAX IV LABORATORY — Soft X-rays

BESSY — Soft X-rays

SOLEIL SYNCHROTRON — Tender X-rays

Method 2: Ions in Ions

Static Liquid Drop in UHV



MAX IV LABORATORY

Soft X-rays

diamond

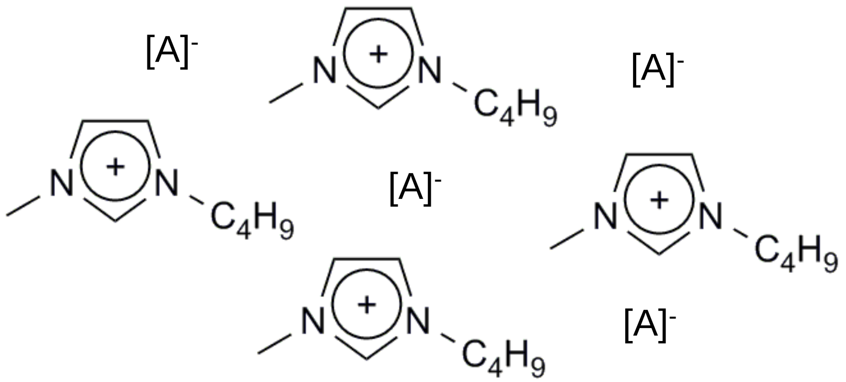
Soft, tender and hard X-rays

Fogarty *et al.*, *Phys. Chem. Chem. Phys.*, 2017, **19**, 31156.
Fogarty *et al.*, *J. Chem. Phys.*, 2018, **148**, 193817.
Fogarty *et al.*, *Faraday Discuss.*, 2018, **206**, 183.
Fogarty *et al.*, *Phys. Chem. Chem. Phys.*, 2019, **21**, 18893.

Results

Samples Studied: 8 Different Solutions

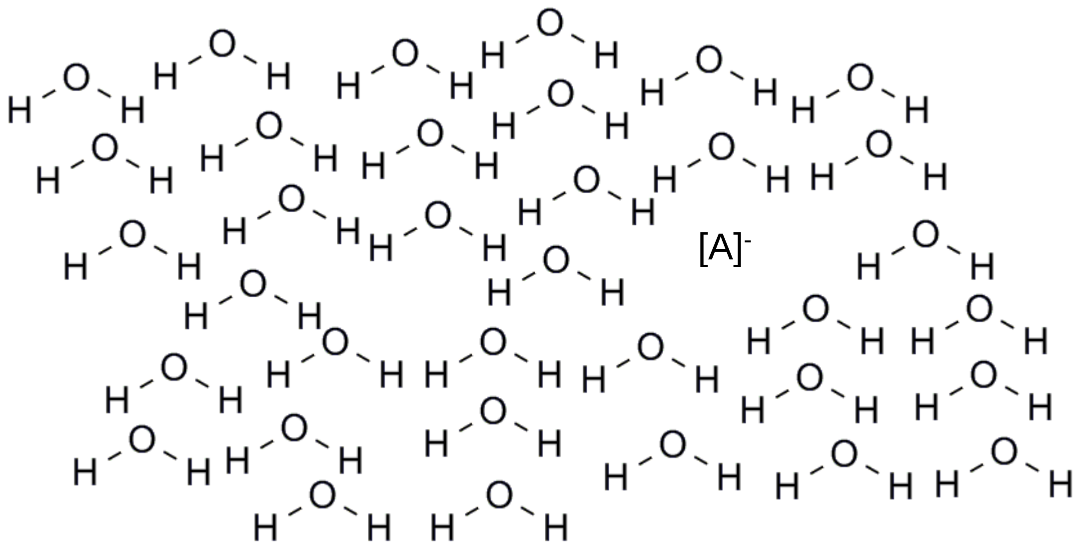
$([C_4C_1Im][A])_x(H_2O)_{1-x}$



$x = 1.00$
$x = 100\%$

<u>$[A]^-$ studied</u>

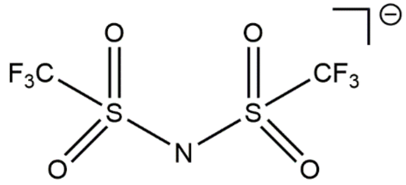
$[SCN]^-$
$[CF_3SO_3]^-$
$[(CF_3SO_2)_2N]^-$
$[HSO_4]^-$

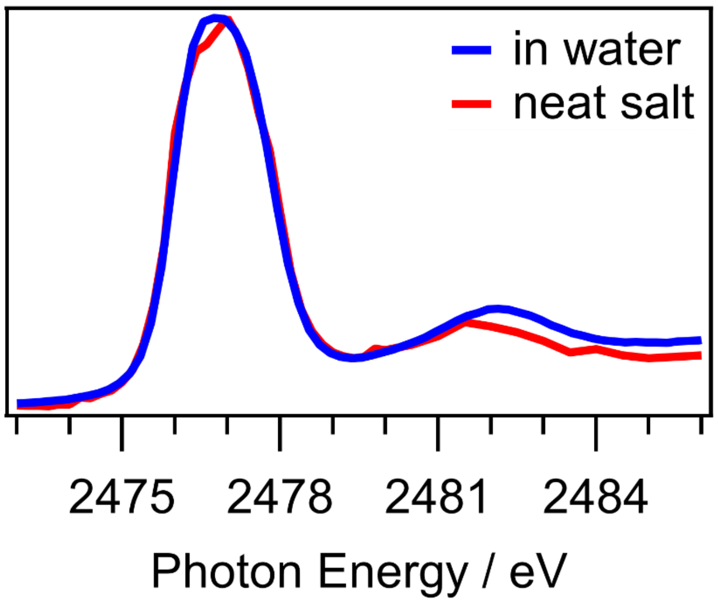


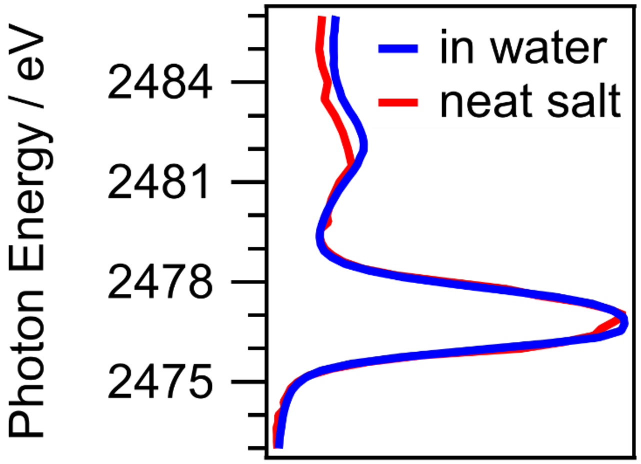
$x = 0.0025$
$x = 0.25\%$

399 H_2O molecules for every $[A]^-$ anion

Results: Partial Electron Yield NEXAFS

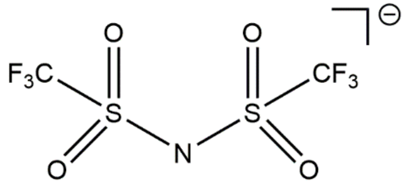






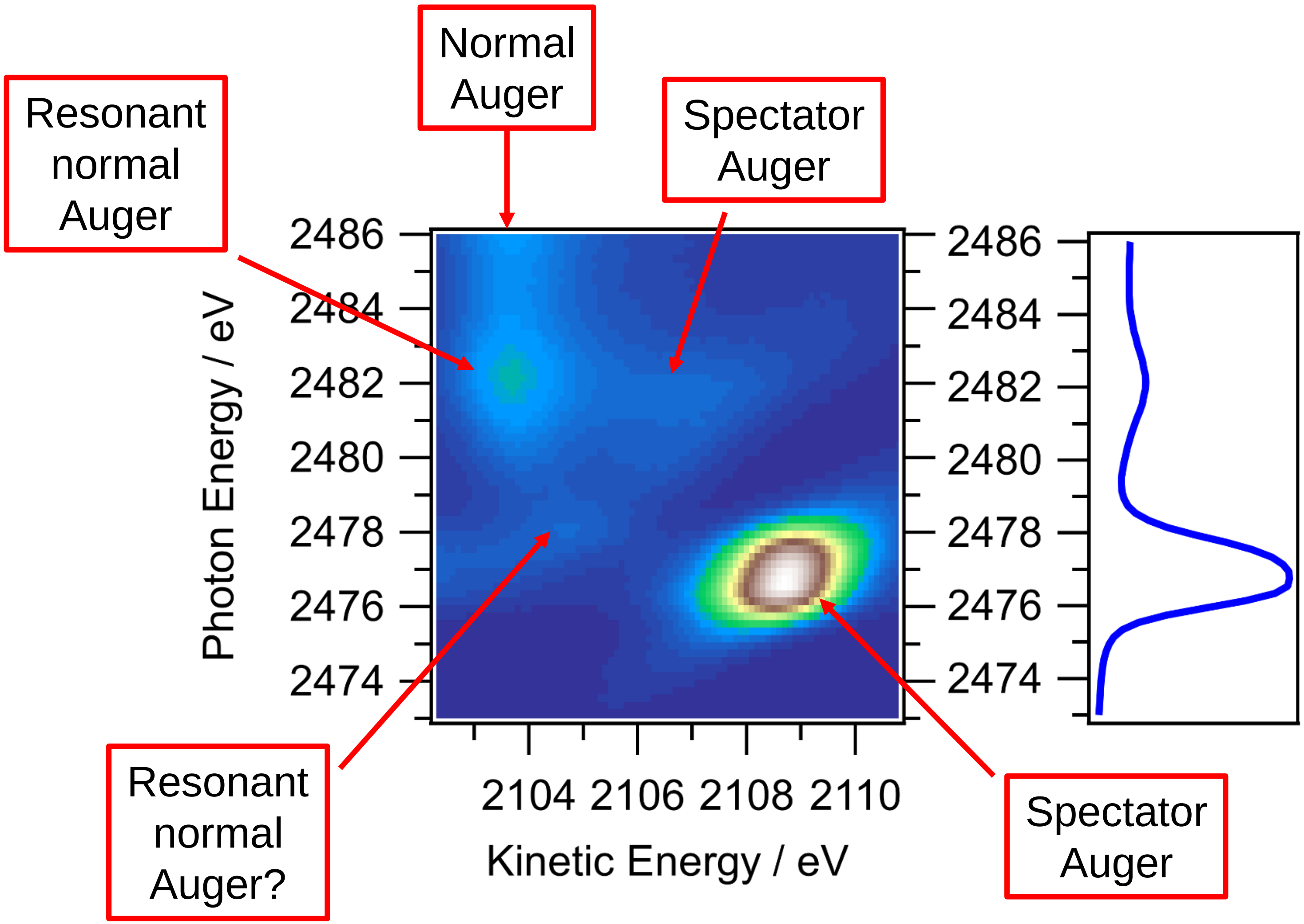
- Very little difference between solvation in ions and solvation in water

Results: CHC Peak Identification

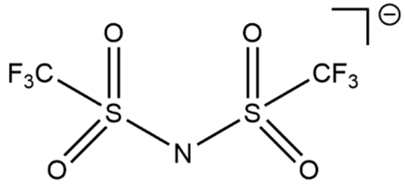


$[(CF_3SO_2)_2N]^-$ in H_2O

$x = 0.0025$



Results: CHC Peak Identification



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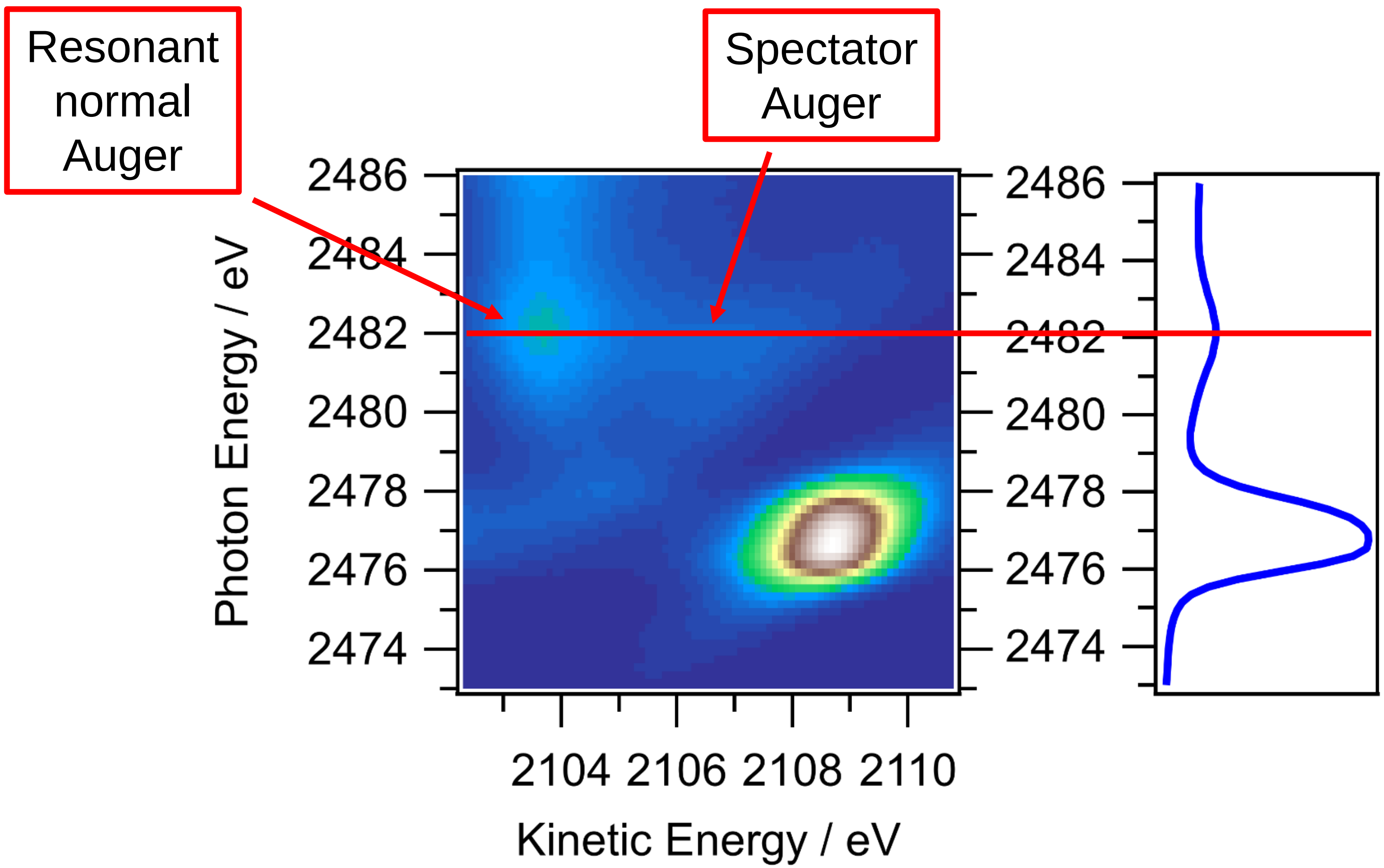
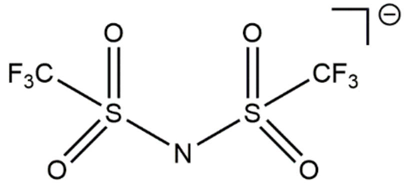
x = 0.0025

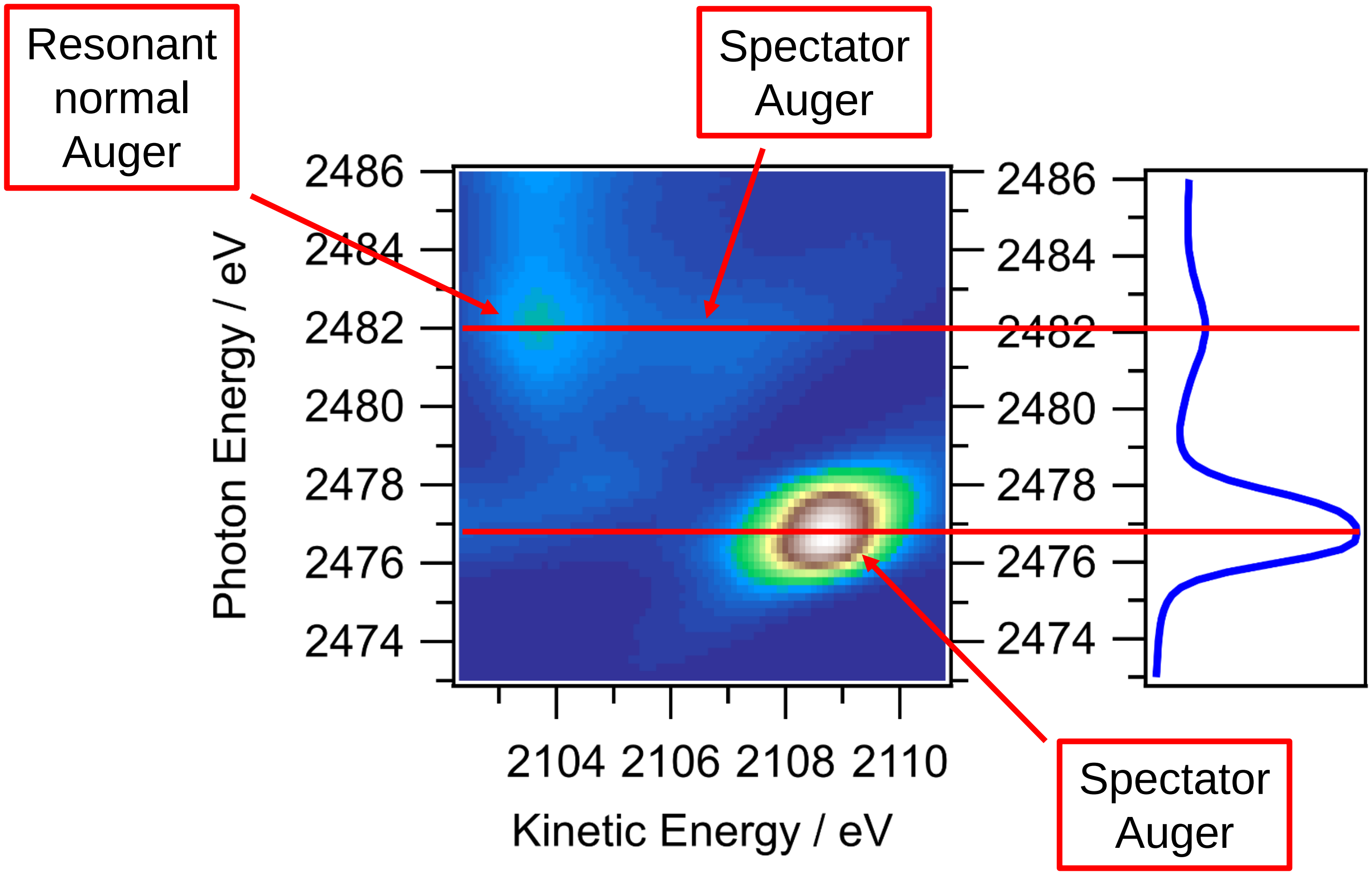


Results: CHC Peak Identification

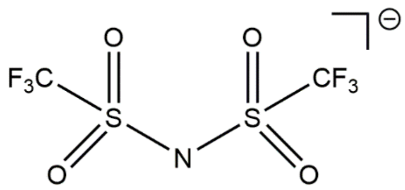


$[(CF_3SO_2)_2N]^-$ in H_2O

$x = 0.0025$

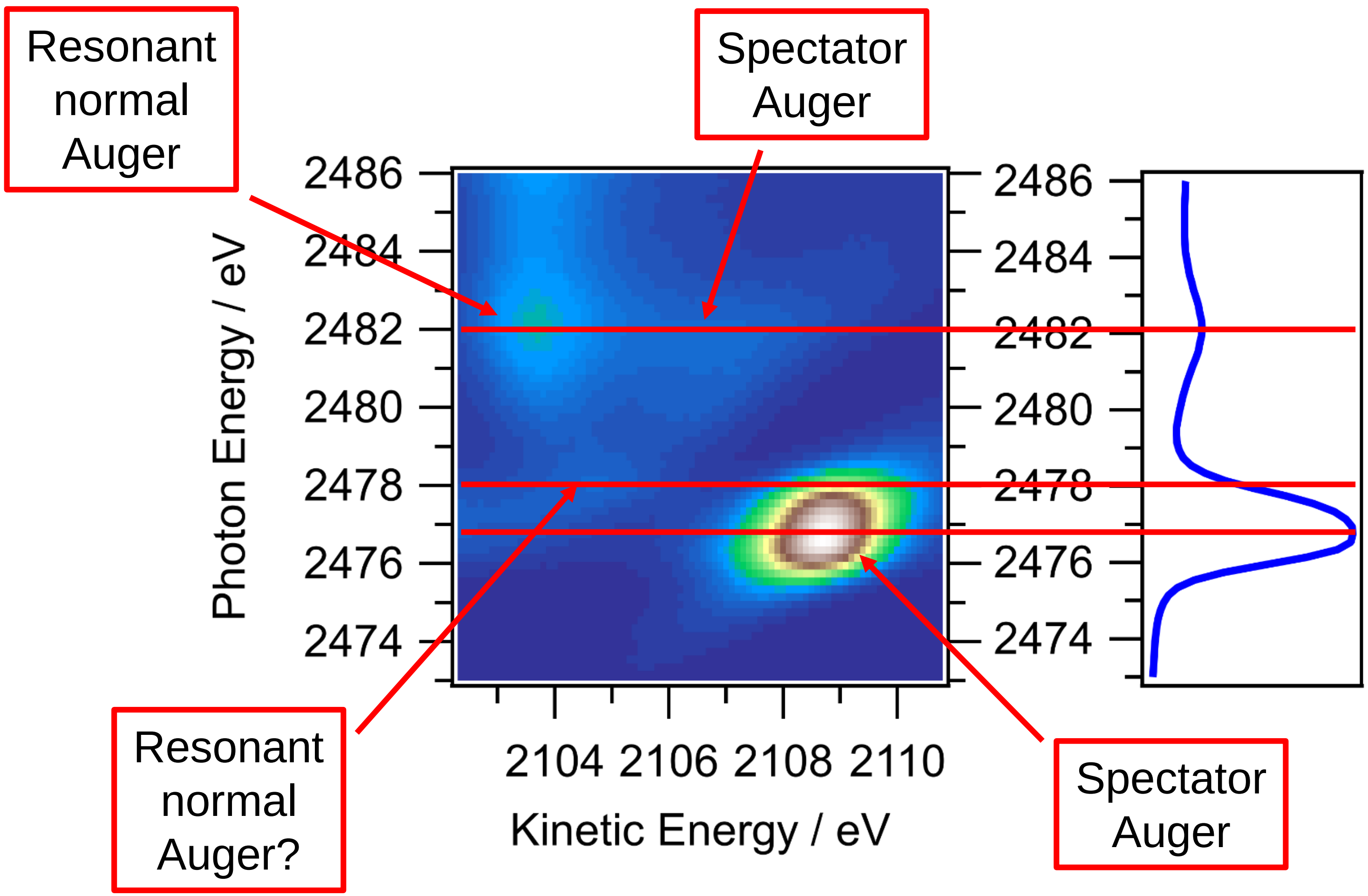


Results: CHC Peak Identification

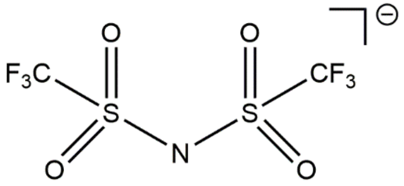


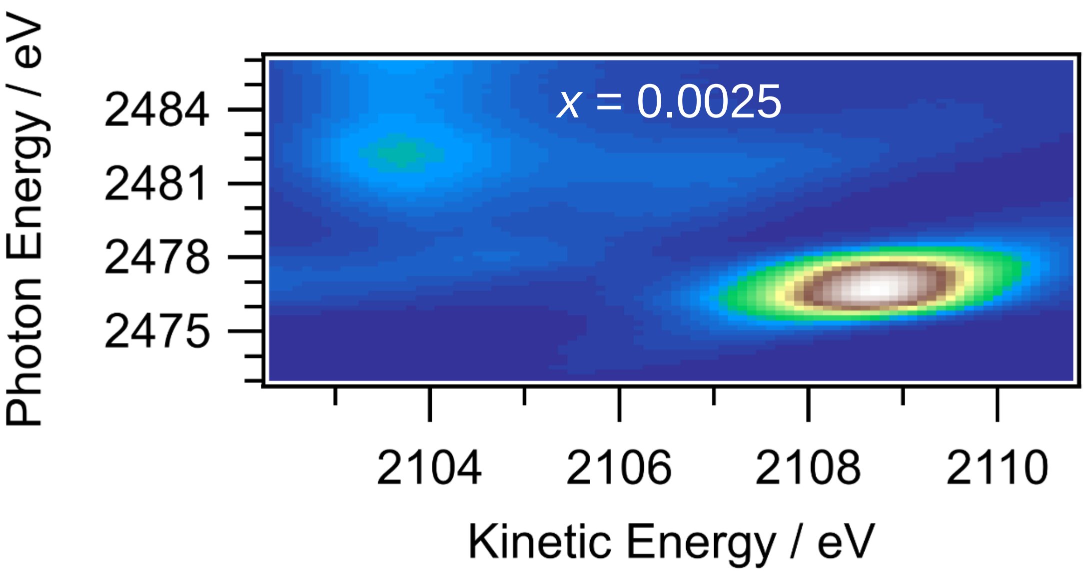
$[(CF_3SO_2)_2N]^-$ in H_2O

$x = 0.0025$

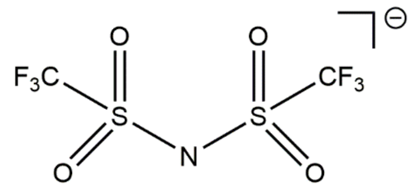


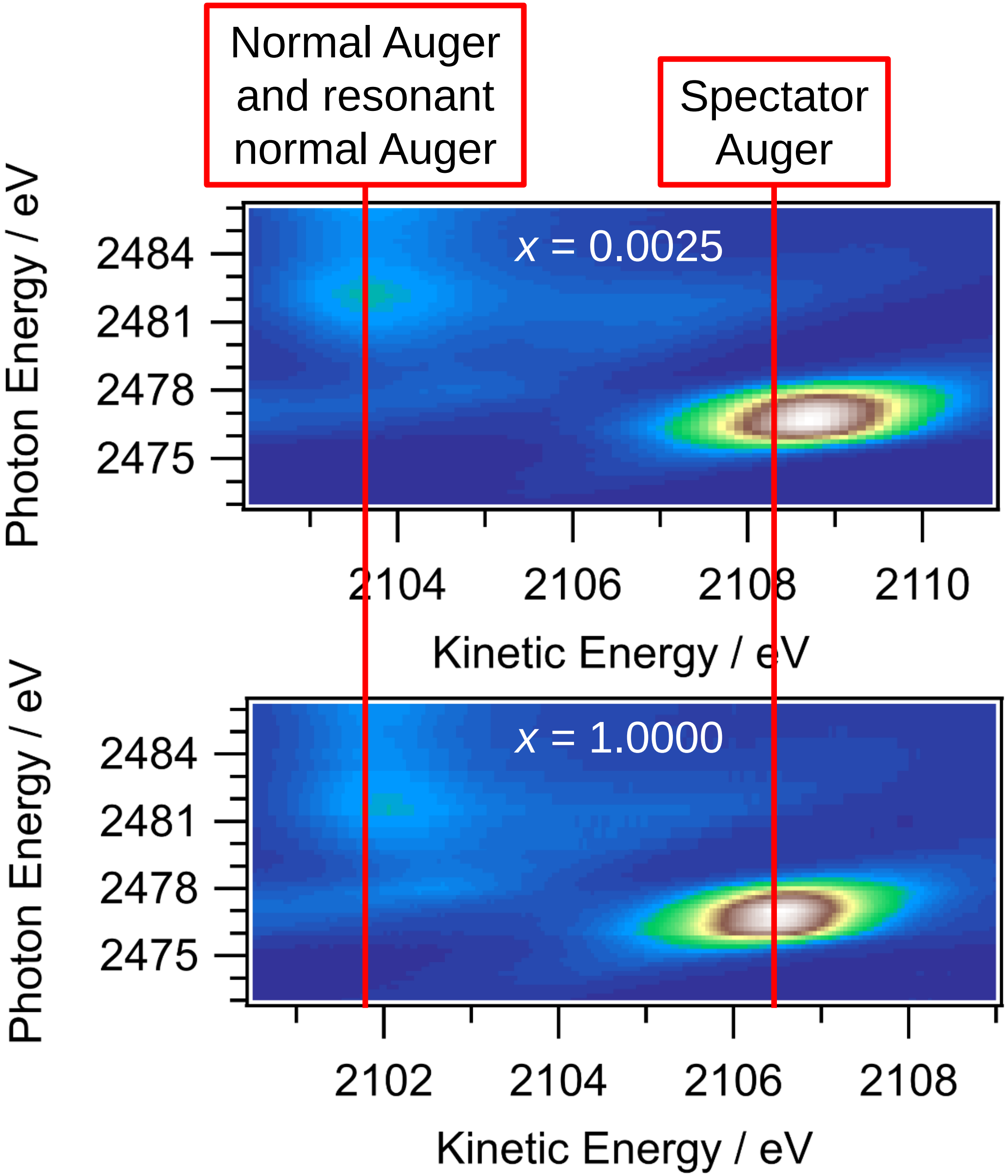
Results: CHC Peak E_K





Results: CHC Peak E_K



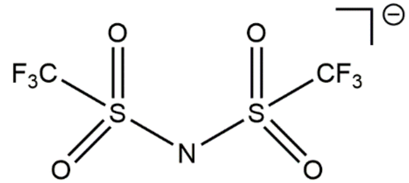


- Shift of large spectator peak
- Relative to normal Auger peak
- Shift ~0.3 eV
- Similar shift occurred for other solutions (larger shift for $[SCN]^-$)

- E_K separation always **larger** for solvation in **water** than solvation in ions

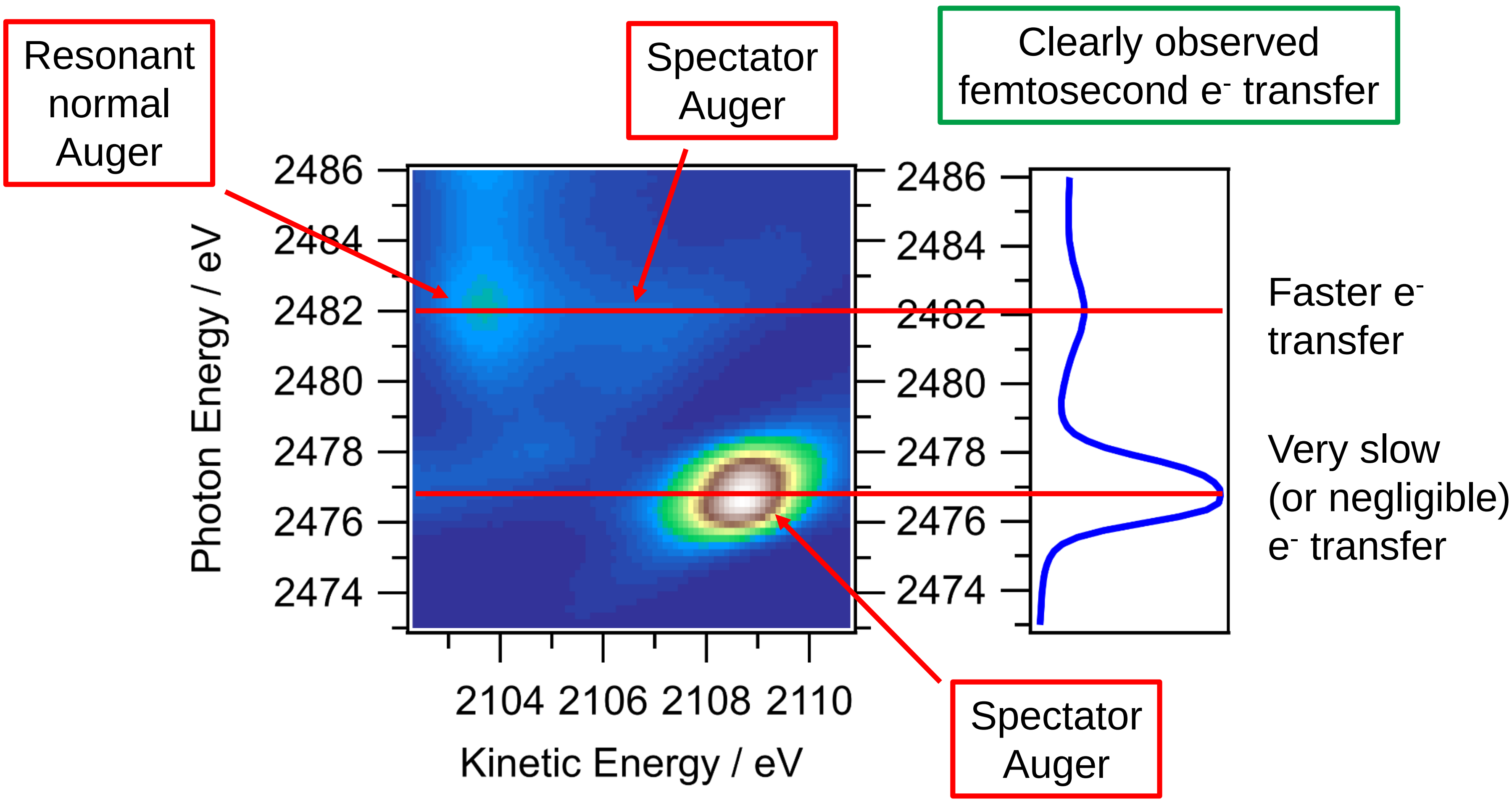
- What does this shift mean?

Results: Femtosecond Electron Transfer



$[(CF_3SO_2)_2N]^-$ in H_2O

$x = 0.0025$



Summary and Conclusions

- X-ray spectroscopy of ions in solution
  - Succesfuly investigated electronic structure of ions in solution across whole concentration range
  - NEXAFS not greatly affected by solvation environment
  - Solvation environment affects E_K of normal vs spectator Auger
  - Observed femtosecond e^- transfer

- Future challenges
  - Fit all of our current CHC data
    - Quantify e^- transfer timescales
  - Apply methods to (more) solutes in (more) molecular liquids
    (*e.g*. ethanol, propylene carbonate, acetonitrile)
  - Identify all peaks/features in CHC spectra - calculations
    - Are there any methods than can cope with these sizes of ions?
    - How many solvent molecules/ions needed?
      (Fogarty *et al.*, *Phys. Chem. Chem. Phys.*, 2017, **19**, 31156.)

Acknowledgements

Experiments

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UCL
diamond
SOLEIL SYNCHROTRON

XAS calculations

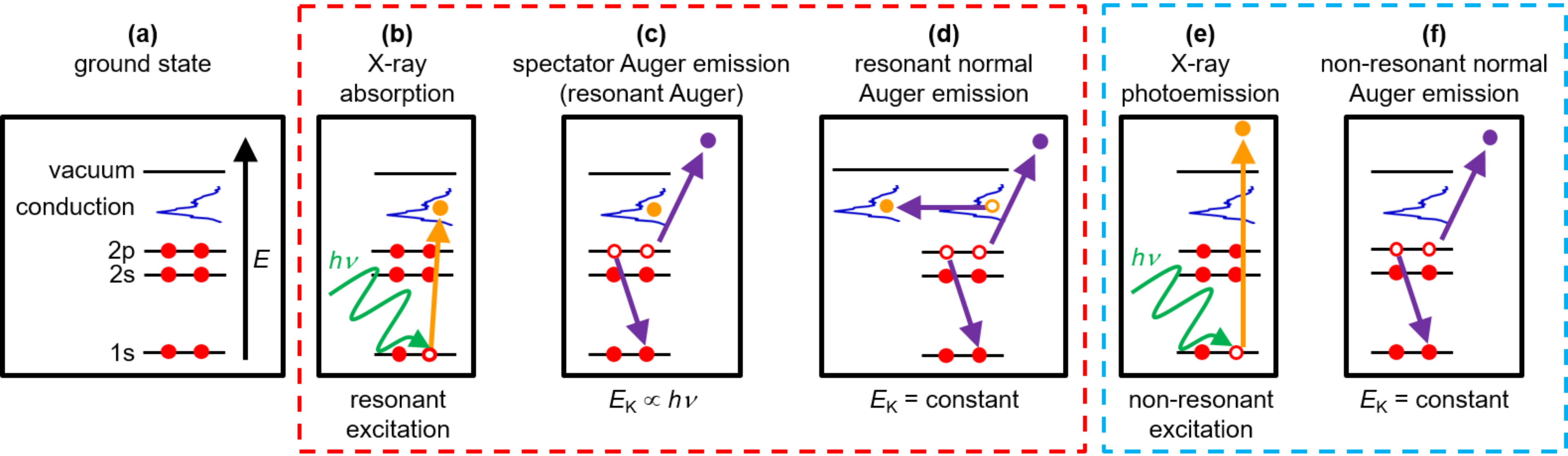
Tricia Hunt
Richard Fogarty
Richard Matthews
Claire Ashworth
Rebecca Rowe
Nick Besley

Imperial College London
The University of Nottingham

I09 — diamond
Galaxies — SOLEIL SYNCHROTRON

Imperial College London
JRF
Tom Welton

THE ROYAL SOCIETY
URF + Ph.D.



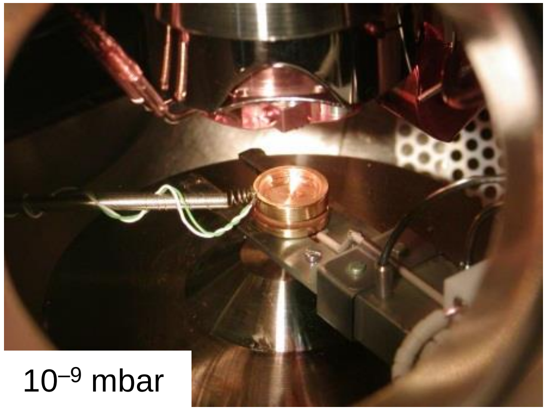
(a)
ground state
vacuum
conduction
2p
2s
1s
E
(b)
X-ray
absorption
hν
resonant
excitation
(c)
spectator Auger emission
(resonant Auger)
E_K ∝ hν
(d)
resonant normal
Auger emission
E_K = constant
(e)
X-ray
photoemission
hν
non-resonant
excitation
(f)
non-resonant normal
Auger emission
E_K = constant

Ionic Liquids: Vapour Pressure

	$\Delta_{vap}H$ / kJ mol^{-1}
Cu, Ag, Au	250 → 340
Ionic liquids	130 → 200
Alkali metals	70 → 150
Molecular liquids	25 → 100
Halogens	3 → 27
Nobel gases	0.08 → 16

K. R. J. Lovelock, *Ph.D. Thesis*, **2008**.

XPS ☺

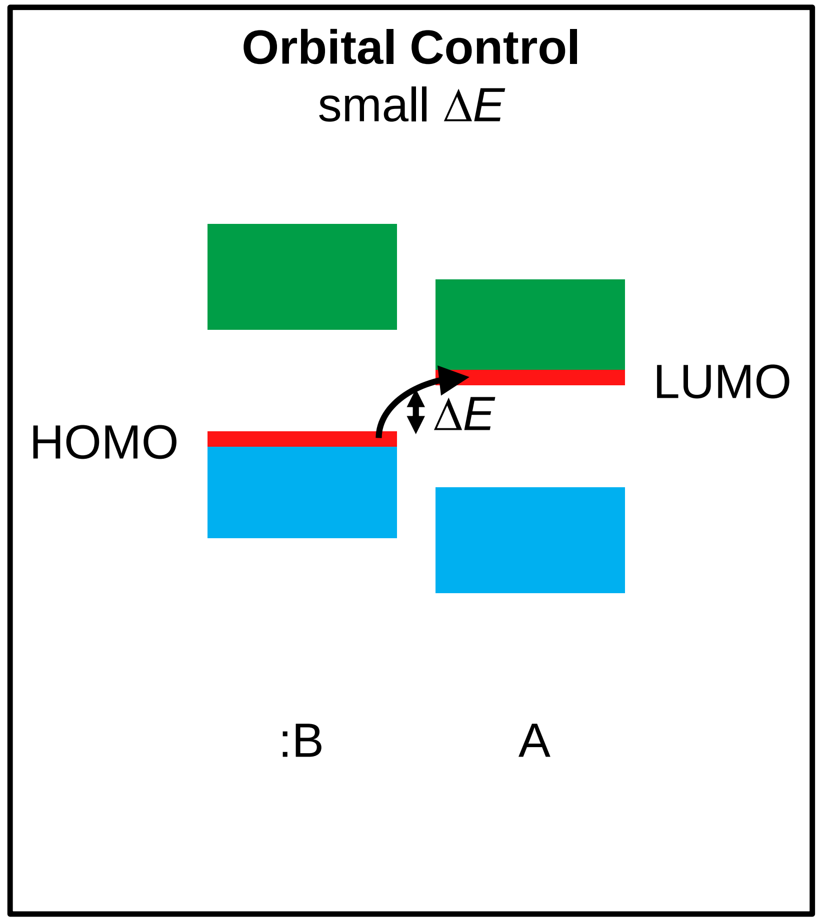


10^{-9} mbar

“Organic” Reactivity

A + :B $\rightleftharpoons$ A:B

Where the electrons start

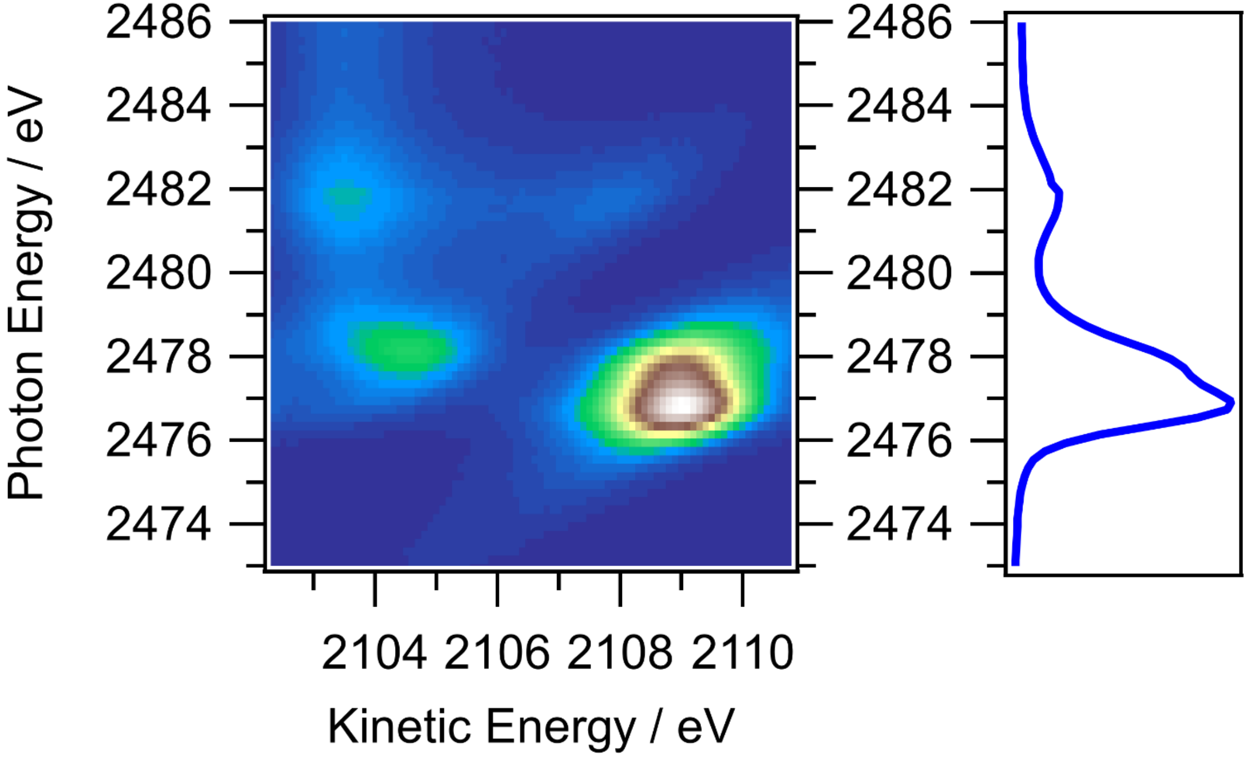


Where the electrons can go

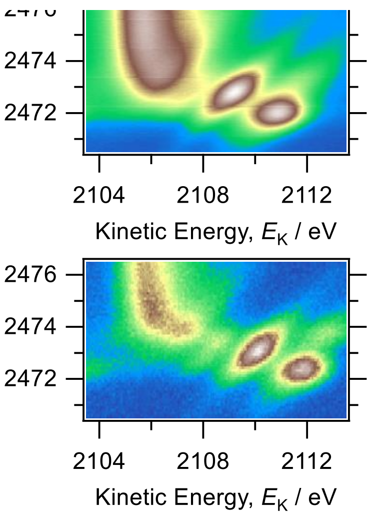
Fleming, *Molecular Orbitals and Organic Chemical Reactions*, Wiley, 2010.
Fukui, *Angew. Chem.-Int. Edit. Engl.*, 1982, **21**, 801.
Hoffmann, *Angew. Chem.-Int. Edit. Engl.*, 1982, **21**, 711.

Results: Peak Identification

$([C_4C_1Im][CF_3SO_3])_{0.0025}(H_2O)_{0.9975}$
i.e. $x = 0.0025$



Results: Solvent Screening of Core-Hole



$[C_4C_1Im][SCN]$
i.e. $x = 1.00$

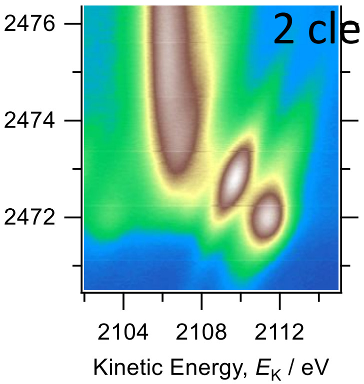
- Shifts of 2 large spectator peaks
- Relative to normal Auger peak
- Both ~1.0 eV

$([C_4C_1Im][SCN])_{0.0025}(H_2O)_{0.9975}$
i.e. $x = 0.0025$

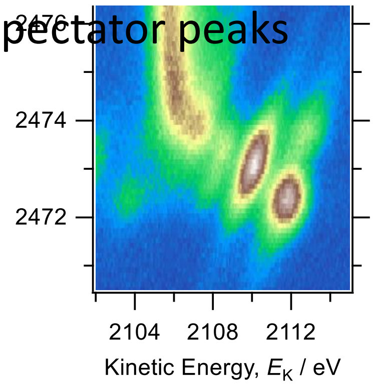
Results: Peak Identification

[C_4C_1Im][SCN]
i.e. $x = 1.00$

([C_4C_1Im][SCN])$_{0.0025}$(H_2O)$_{0.9975}$
i.e. $x = 0.0025$

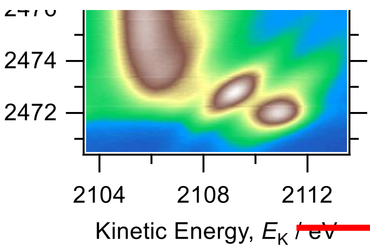


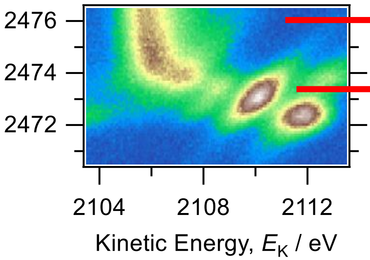
2 clear spectator peaks



3 clear spectator peaks

Results: Electron Transfer Times

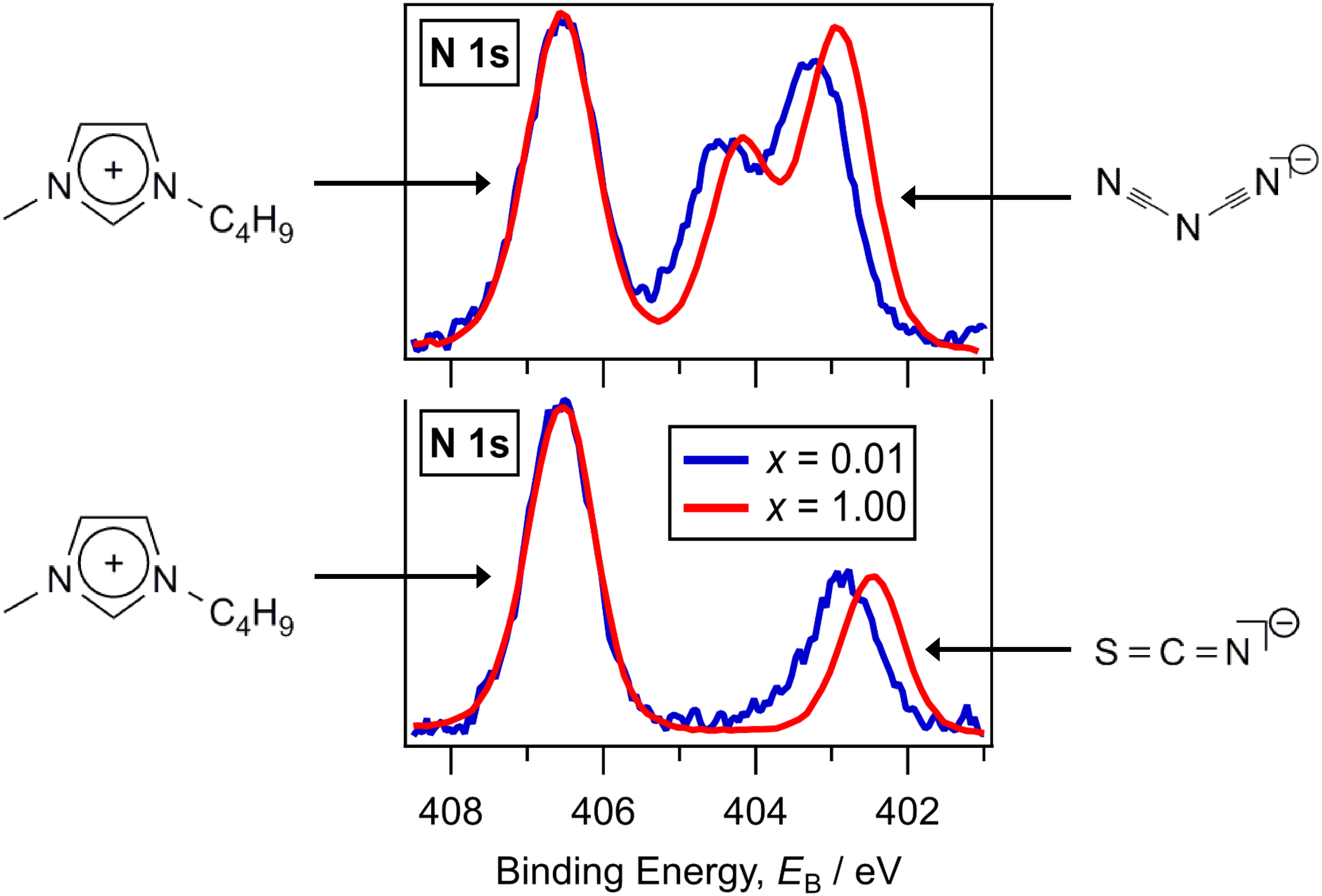




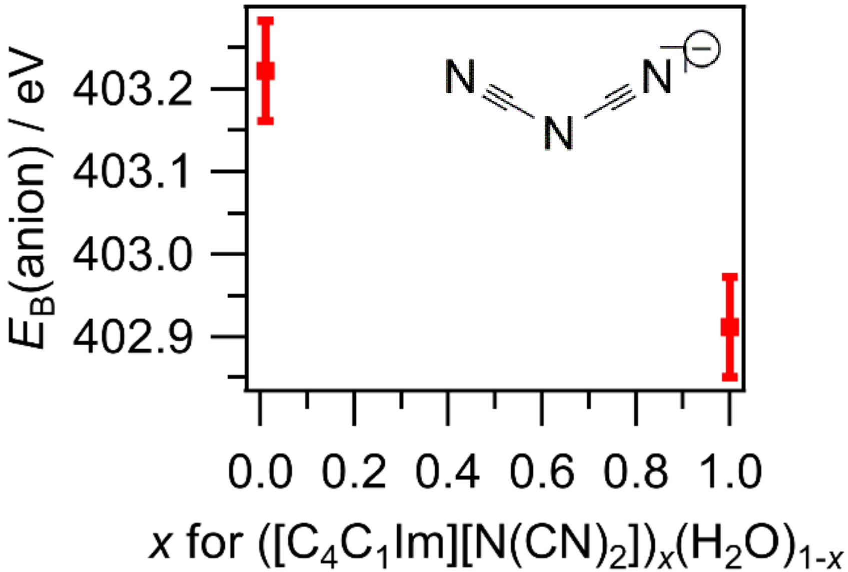
$[C_4C_1Im][SCN]$
i.e. $x = 1.00$

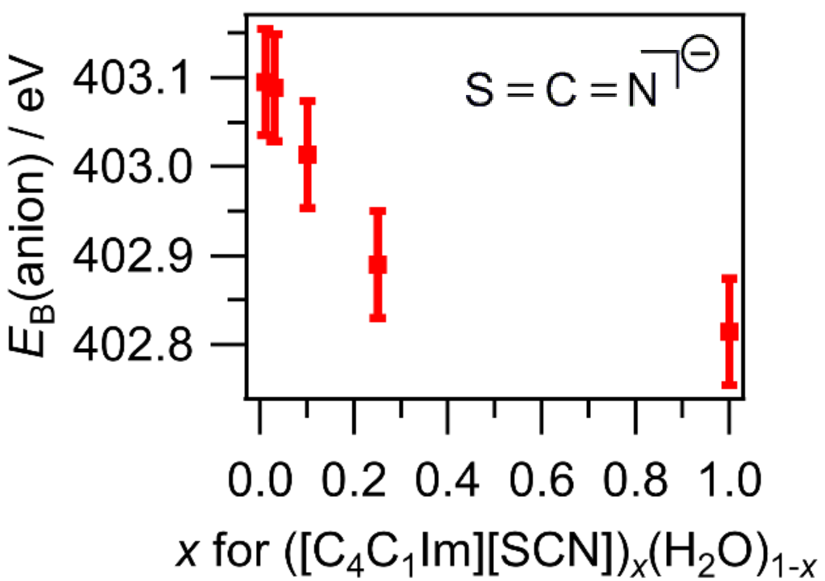
$([C_4C_1Im][SCN])_{0.0025}(H_2O)_{0.9975}$
i.e. $x = 0.0025$

Core Orbital XPS



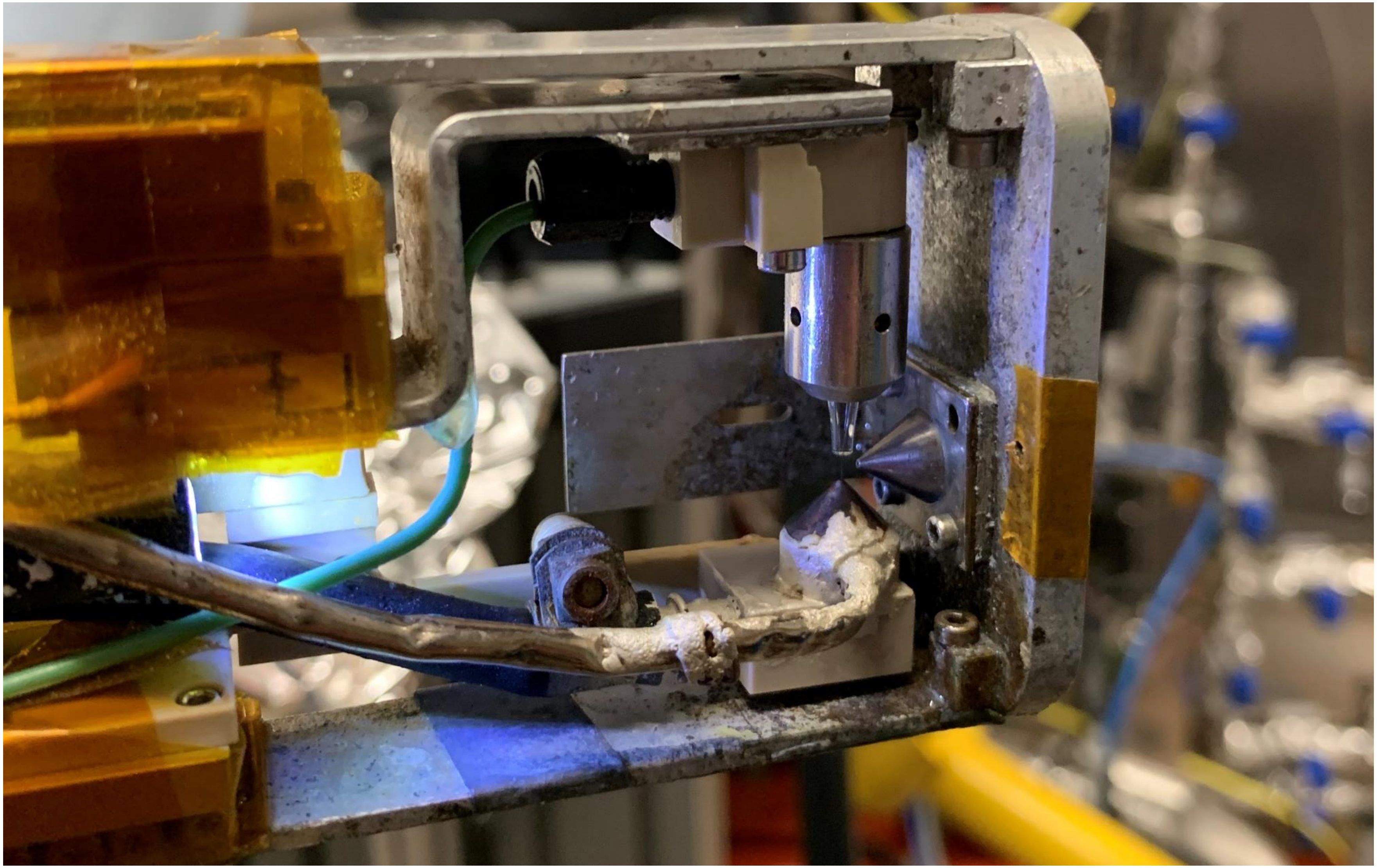
Core Orbital XPS



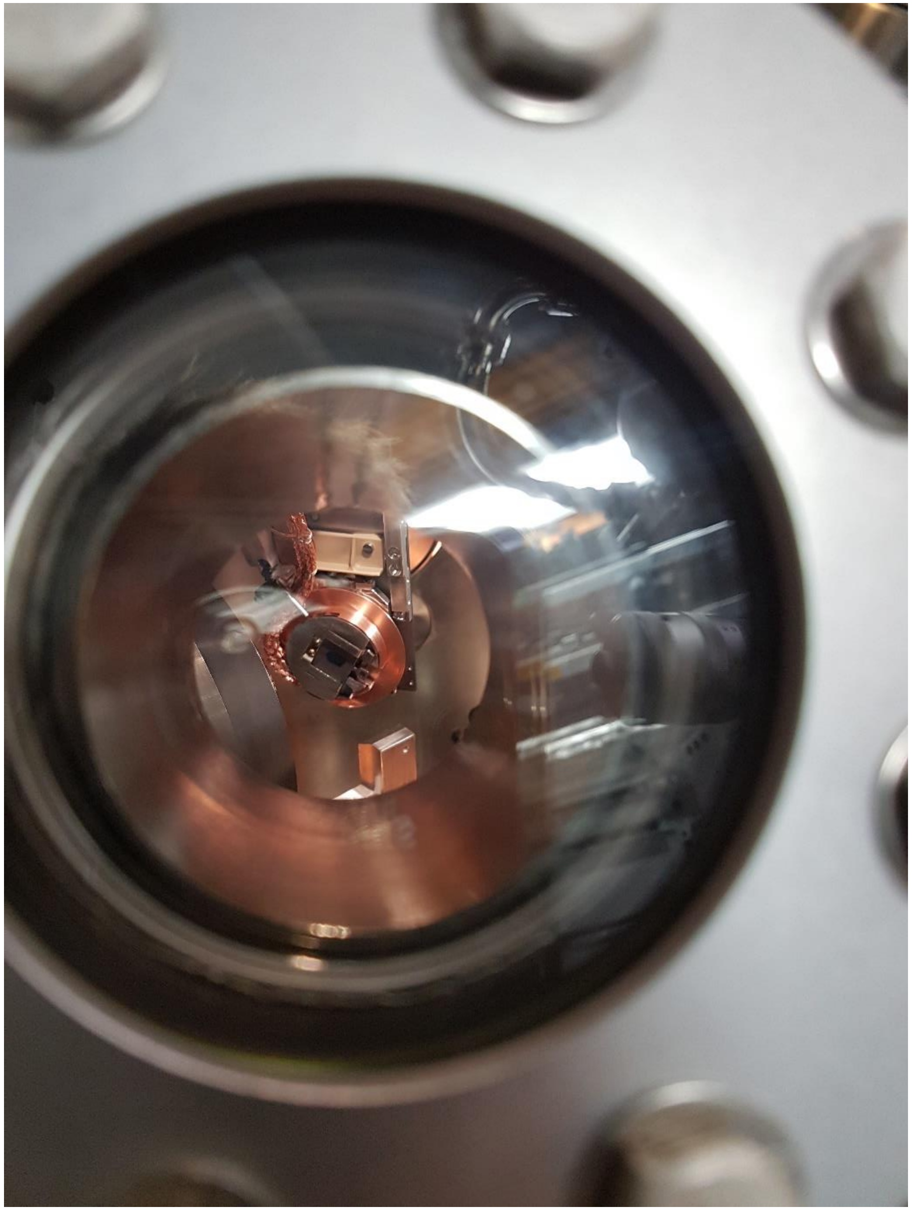


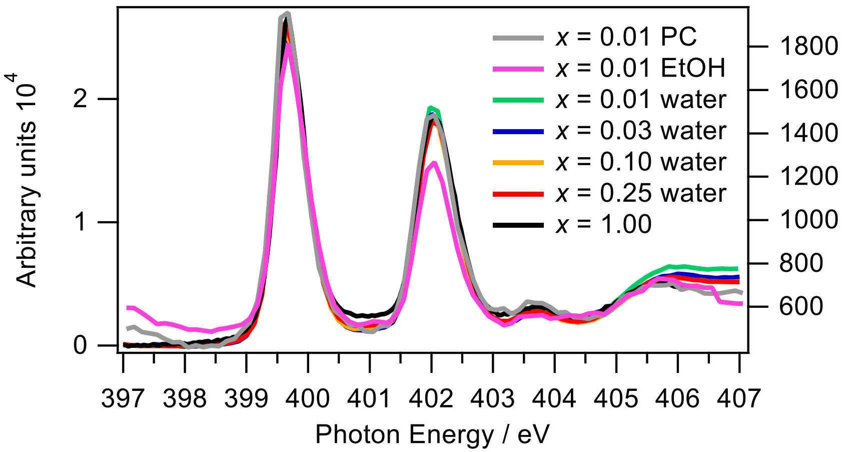
- Larger x (more IL) $\Rightarrow$ smaller E_B(anion)
- Larger x (more IL) $\Rightarrow$ N_{anion} more -ve
  (more valence electrons near N_{anion} for larger x)
- Same trend observed for $[C_4C_1Im][A]$ ILs: $[A]^-$ = Cl^-, I^-, $[TfO]^-$, $[HSO_4]^-$, $[BF_4]^-$

Galaxies Liquid Jet



I09 Static Liquid Sample





Arbitrary units 10^4
2
1
0
397 398 399 400 401 402 403 404 405 406 407
Photon Energy / eV
1800
1600
1400
1200
1000
800
600
x = 0.01 PC
x = 0.01 EtOH
x = 0.01 water
x = 0.03 water
x = 0.10 water
x = 0.25 water
x = 1.00