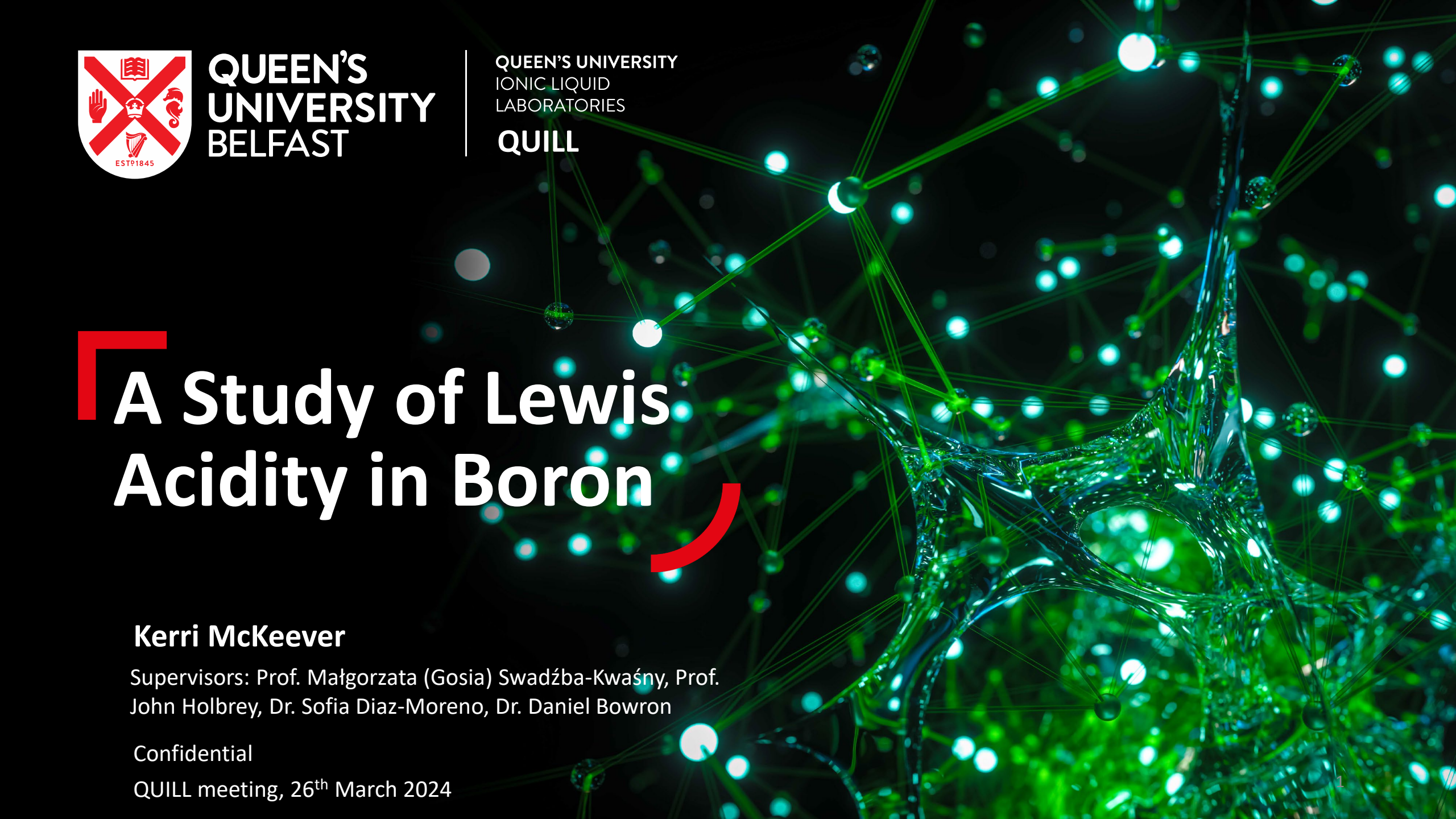
QUEEN'S UNIVERSITY BELFAST

QUEEN'S UNIVERSITY IONIC LIQUID LABORATORIES

QUILL



A Study of Lewis Acidity in Boron

Kerri McKeever

Supervisors: Prof. Małgorzata (Gosia) Swadźba-Kwaśny, Prof. John Holbrey, Dr. Sofia Diaz-Moreno, Dr. Daniel Bowron

Confidential

QUILL meeting, 26th March 2024

Abbreviations

QUEEN'S UNIVERSITY BELFAST
QUEEN'S UNIVERSITY IONIC LIQUID LABORATORIES QUILL

XRS – X-ray Raman Spectroscopy

XAS – X-ray Absorption Spectroscopy

NEXAFS – Near Edge X-ray Absorption Fine Structure

FLP – Frustrated Lewis Pair

FIA – Fluoride ion affinity

HIA – Hydride ion affinity

LUMO – Lowest Unoccupied Molecular Orbital

Presentation Overview

QUEEN'S UNIVERSITY BELFAST
QUEEN'S UNIVERSITY IONIC LIQUID LABORATORIES QUILL

Background

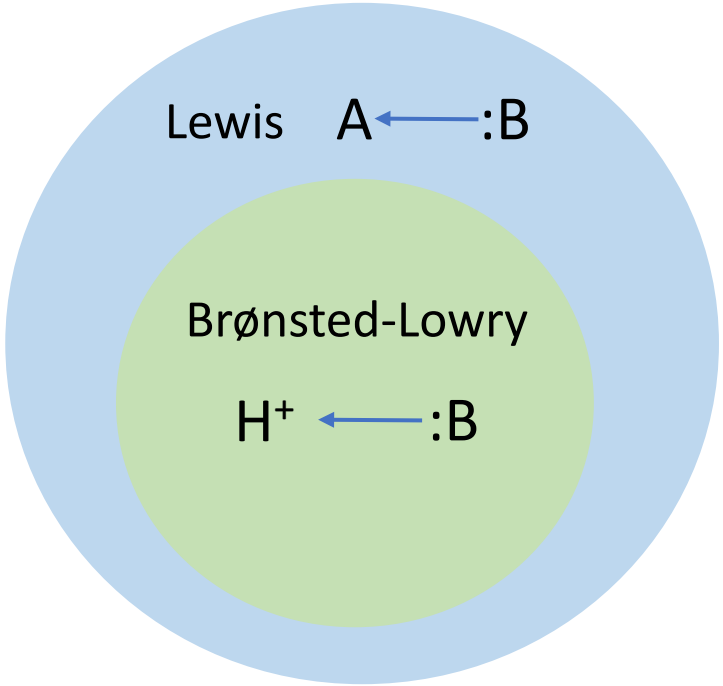
Introduction to XRS

XRS & XAS data

Conclusion and Future Work

Background

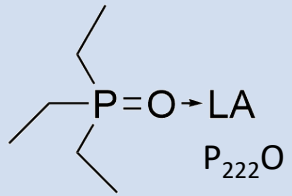
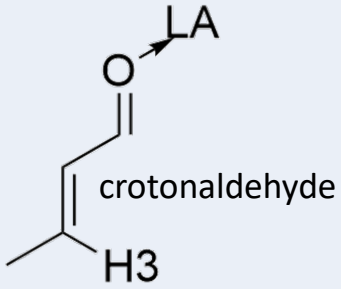
- Quantifying Lewis acidity



Brønsted Acidity:

$$HA + B \rightleftharpoons [HB]^+ + A^-$$

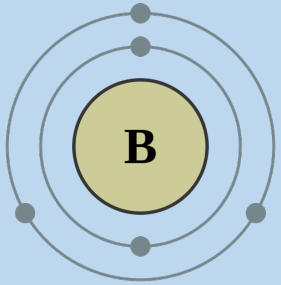
Lewis Acidity:

	NMR	Computational
Hard	 Gutmann-acceptor number method	Fluoride ion affinity (F^-)
Soft	 Childs method	Hydride ion affinity (H^-)

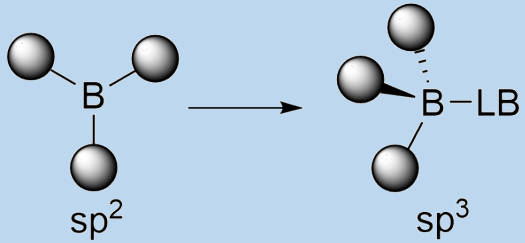
Background

- Factors that affect Lewis acidity:

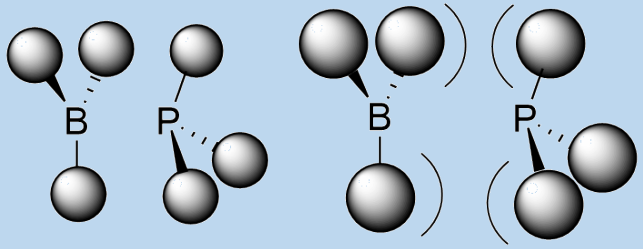
Electrotonic structure of boron centre

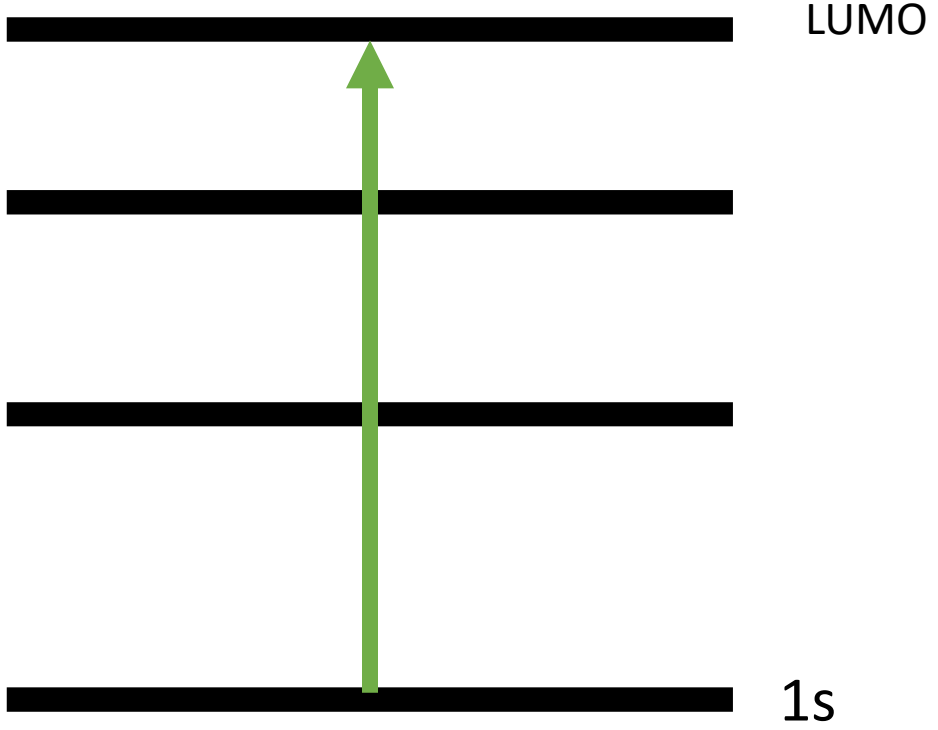


Energy required to change geometry



Steric hindrance





Background

- Challenges with this project:

QUEEN'S UNIVERSITY BELFAST

QUEEN'S UNIVERSITY IONIC LIQUID LABORATORIES QUILL

X-ray absorption

requires ultra-high vacuum

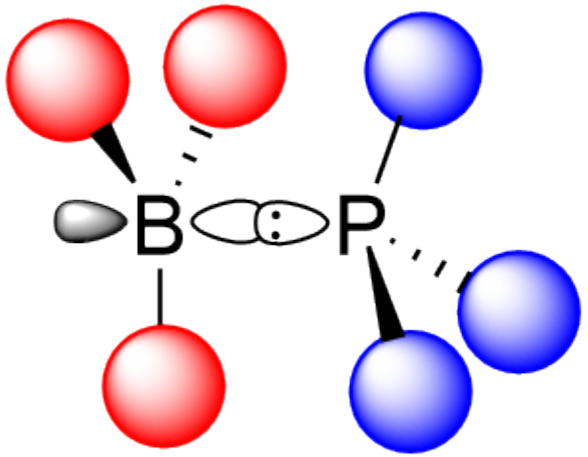
X-ray Raman

niche technique

Background

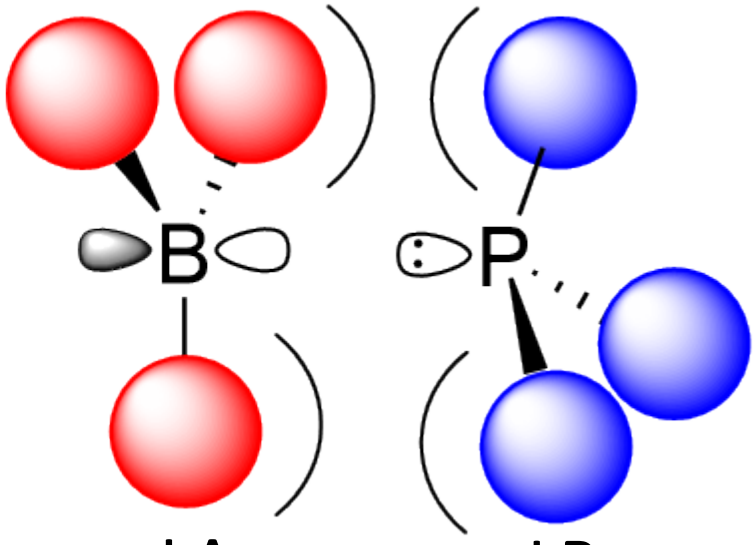
- Frustrated Lewis Pairs

Classical adduct



LA LB

Frustrated Lewis Pair



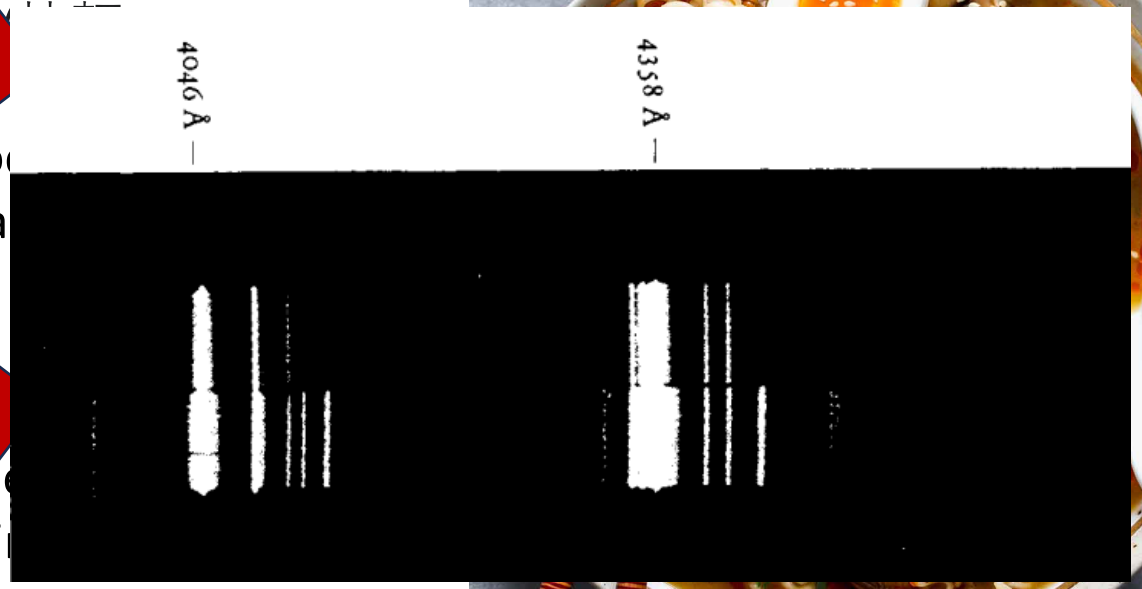
LA LB

1

2

Raman

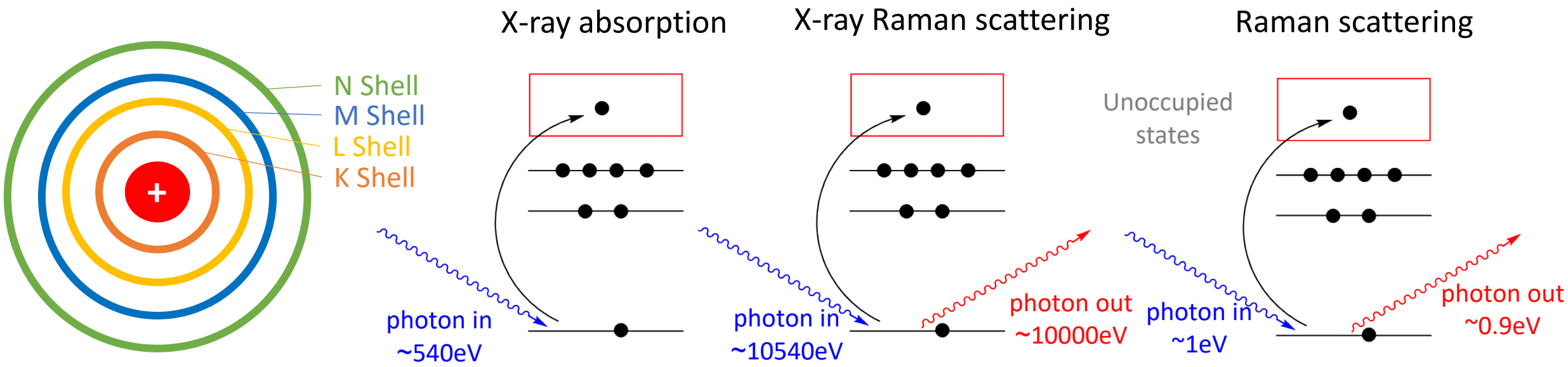
- Ramen is a p…nated in China but w…h century.
- Ramen com… meaning "p…
- The first rep…n o… in 1859, wh…apa… Gongliang, p…ese Emperor.
- Ramen quic…b… early 20th c… even more p…filli… for soldiers



Raman, C. V. (1930). *The molecular scattering of light*

X-ray Raman Spectroscopy (XRS)

QUEEN'S UNIVERSITY BELFAST
QUEEN'S UNIVERSITY IONIC LIQUID LABORATORIES QUILL



High Press Res, 2016, **36**, 275–292.

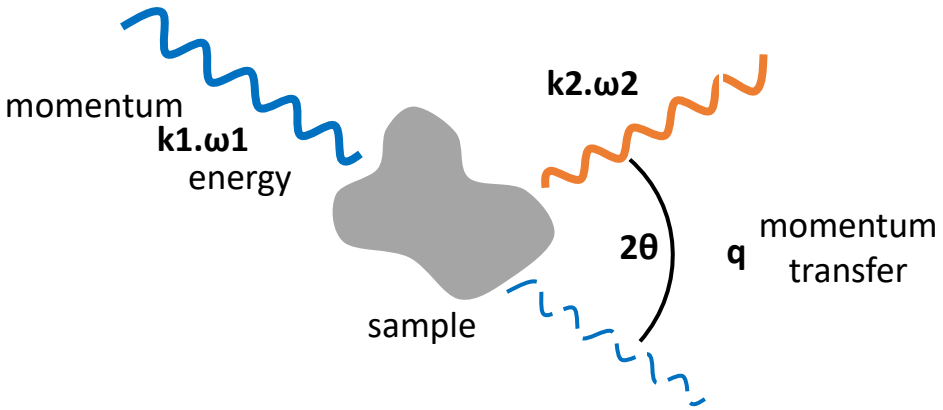
X-ray Raman Spectroscopy (XRS)

QUEEN'S UNIVERSITY BELFAST
QUEEN'S UNIVERSITY IONIC LIQUID LABORATORIES QUILL

A few points to consider…

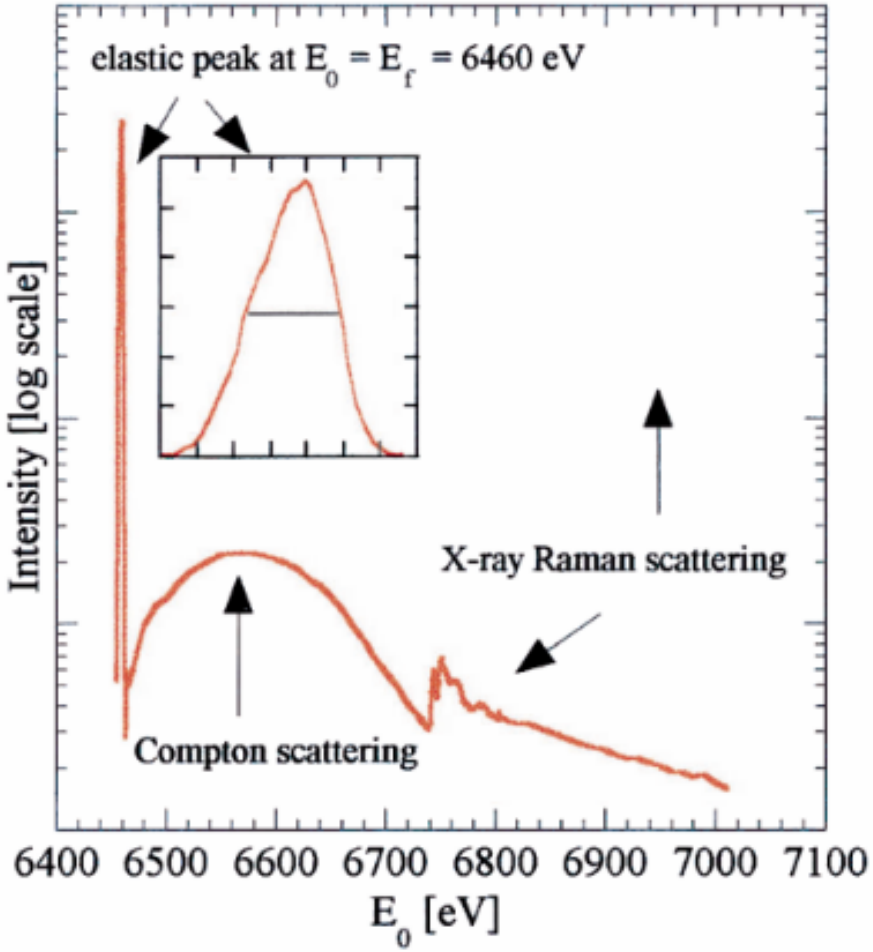
Is it equivalent to XAS?

- Only at low momentum transfer (q) where dipole transitions dominate



Why not use soft XAS?

- Sample environment – vacuum
- Bulk-sensitive vs surface-sensitive

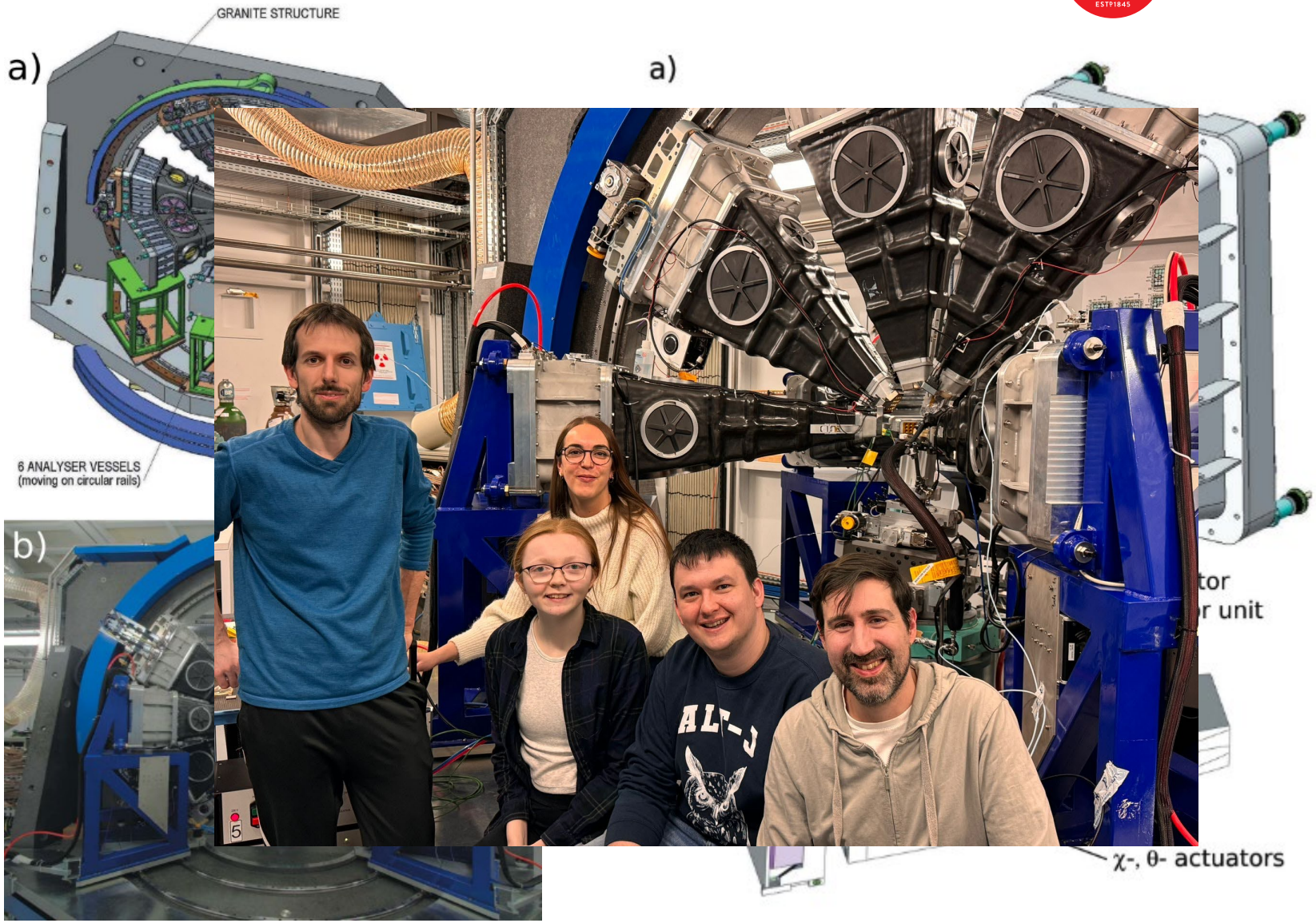


Journal of Synchrotron Radiation, 2015, **22(2)**, 400–409.
Bulk-sensitive XAS characterization of light elements: from X-ray Raman scattering to X-ray Raman spectroscopy, 2002, vol. 71.

X-ray Raman Spectroscopy (XRS)

QUEEN'S UNIVERSITY BELFAST

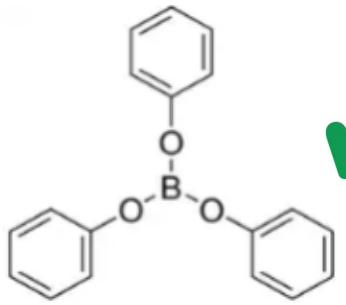
QUEEN'S UNIVERSITY IONIC LIQUID LABORATORIES QUILL



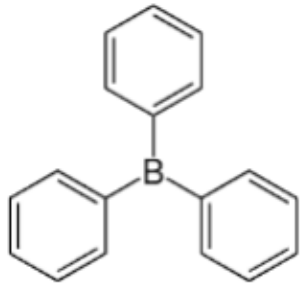
J Synchrotron Radiat, 2017, **24**, 521–530.

XRS – compounds to analyse

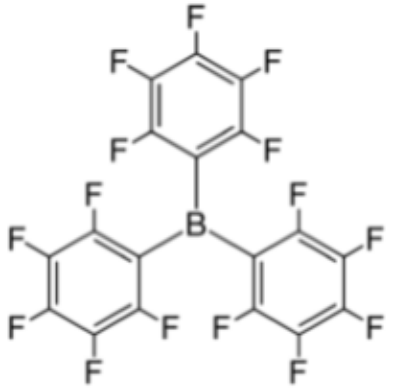
QUEEN'S UNIVERSITY BELFAST
QUEEN'S UNIVERSITY IONIC LIQUID LABORATORIES QUILL



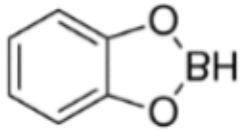
$B(OPh)_3$ – solid ✔



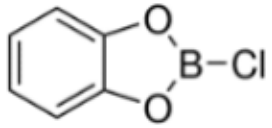
$B(Ph)_3$ - liquid ✔



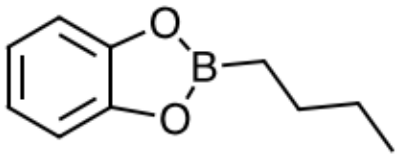
BCF – solid ✔



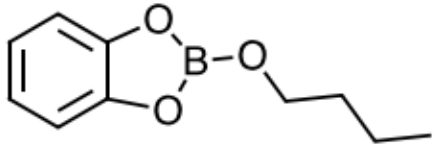
B(cat)H - solid



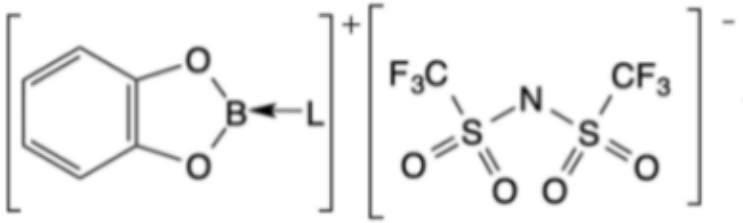
B(cat)Cl - solid



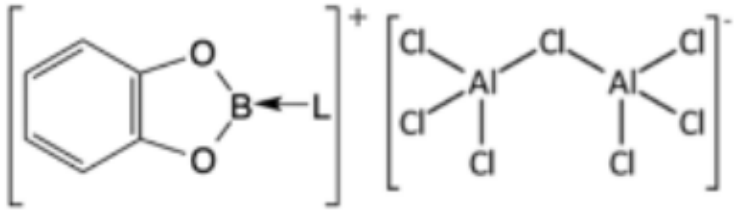
B(cat)Bu - liquid



B(cat)OBu - liquid



$[B(cat)L][NTf_2]$ - liquid

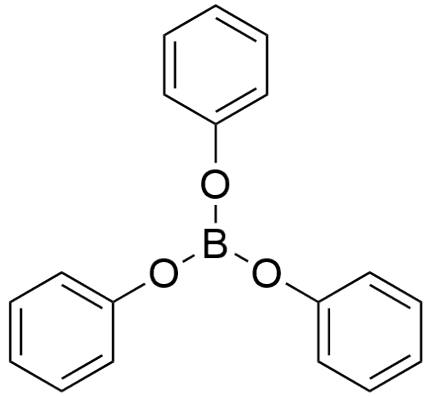


$[B(cat)L][Al_2Cl_7]$ - liquid

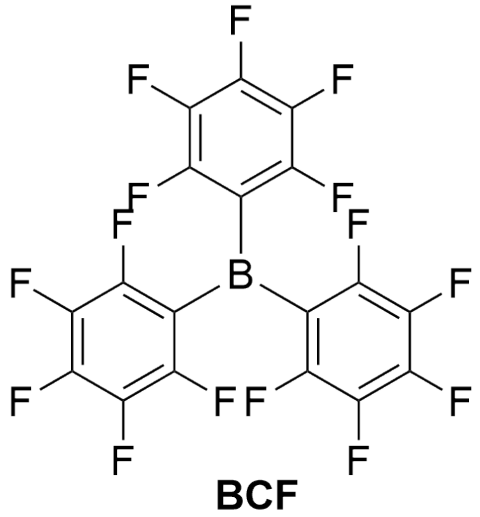
L= 4-picoline

XAS – compounds to analyse

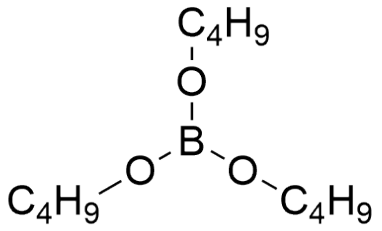
QUEEN'S UNIVERSITY BELFAST
QUEEN'S UNIVERSITY IONIC LIQUID LABORATORIES QUILL



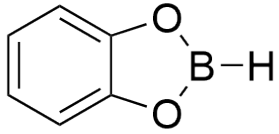
$B(OPh)_3$



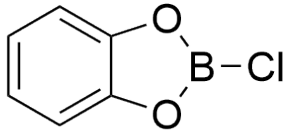
BCF



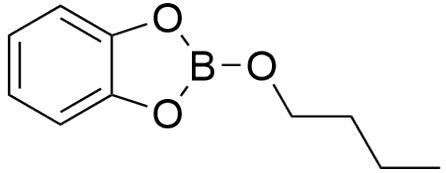
$B(OBu)_3$



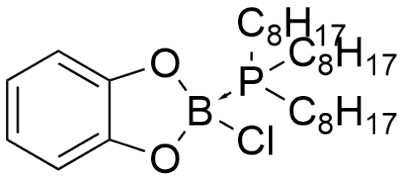
BcatH



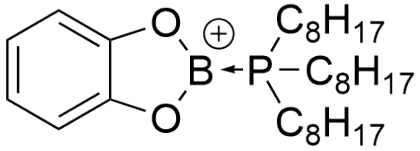
BcatCl

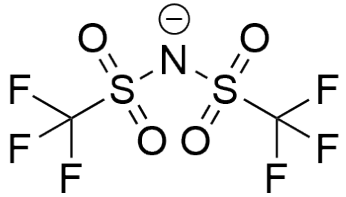


BcatOBu

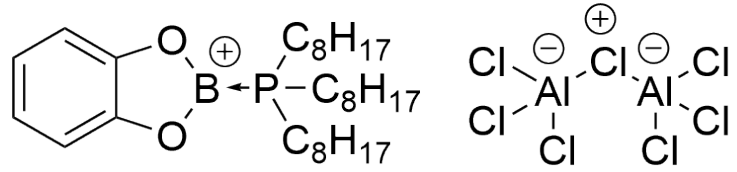


$BcatCl(P_{888})$

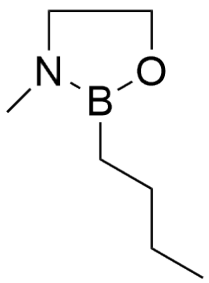


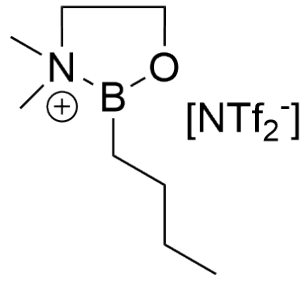


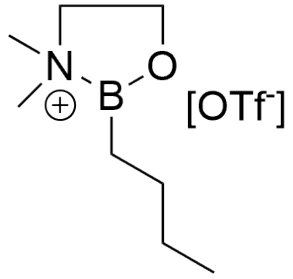
$[Bcat(P_{888})][NTf_2]$

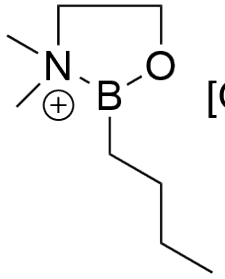


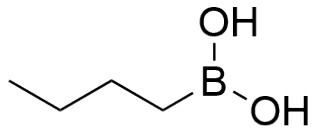
$[Bcat(P_{888})][Al_2Cl_7]$



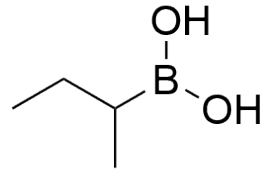






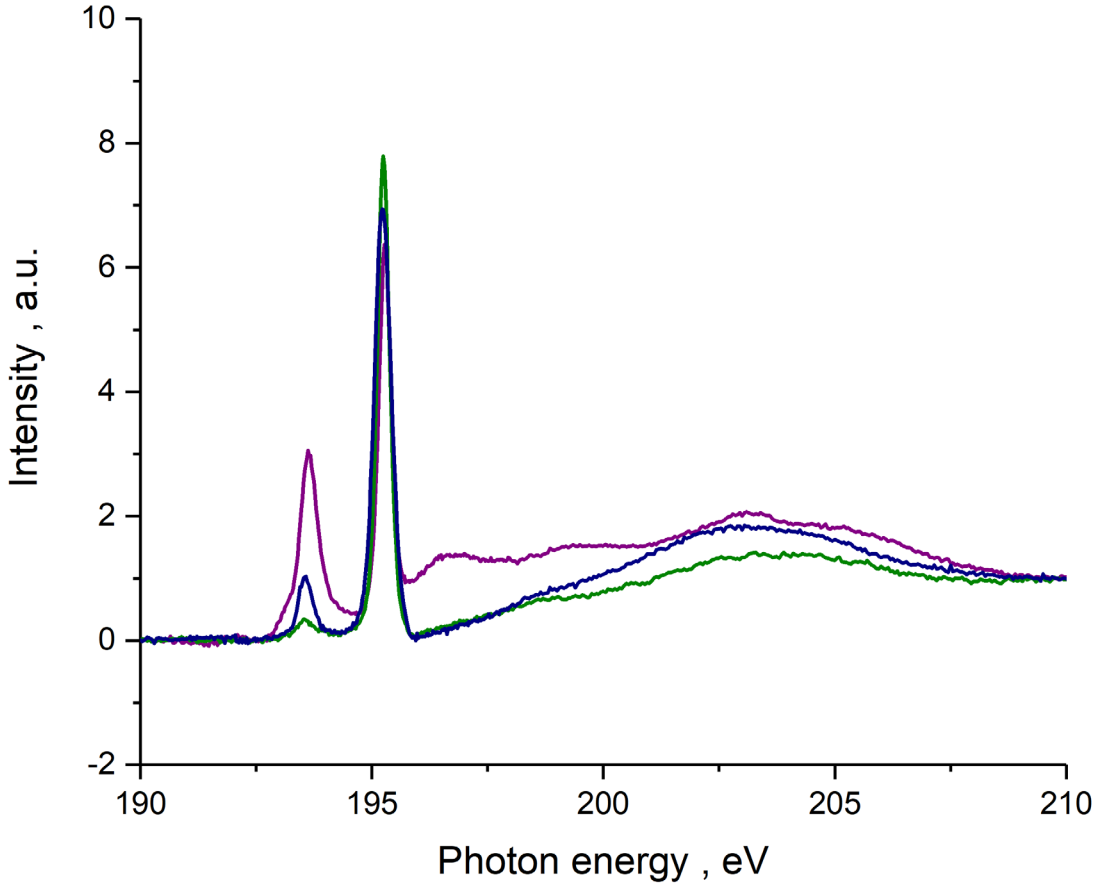


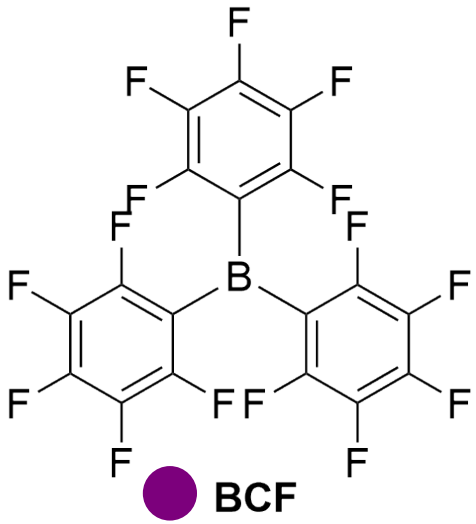
n-butylboronic acid



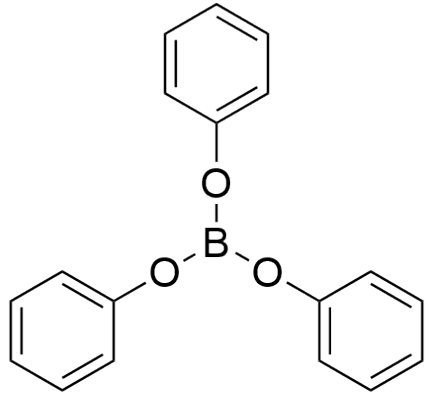
2-butylboronic acid

XAS results – B K-edge

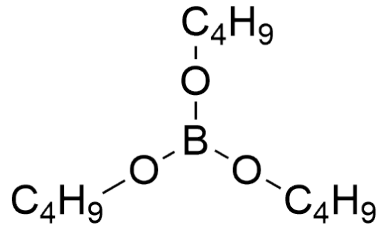




BCF

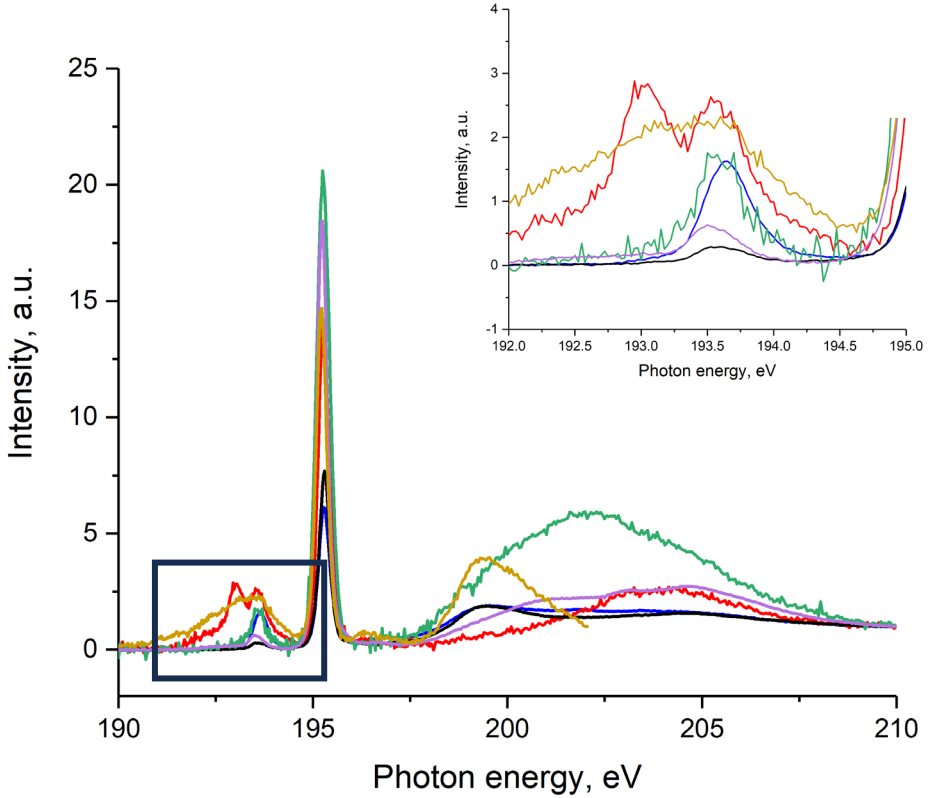


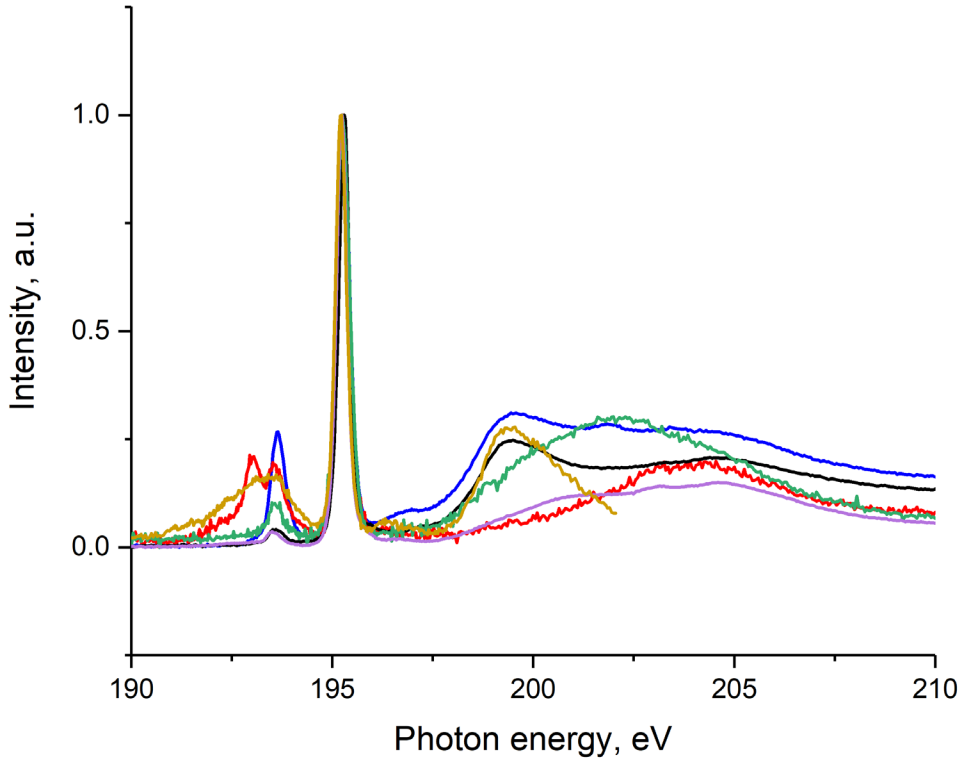
$B(OPh)_3$

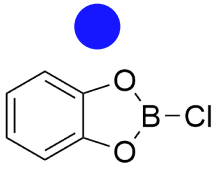


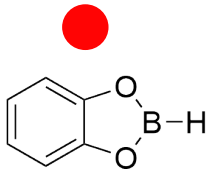
$B(OBu)_3$

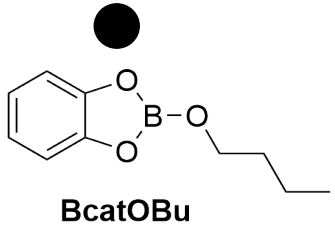
XAS results – B K-edge

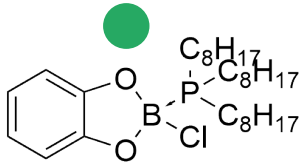


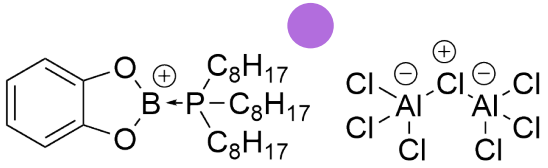


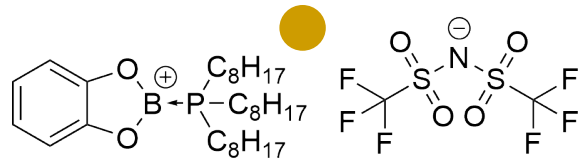

BcatCl


BcatH

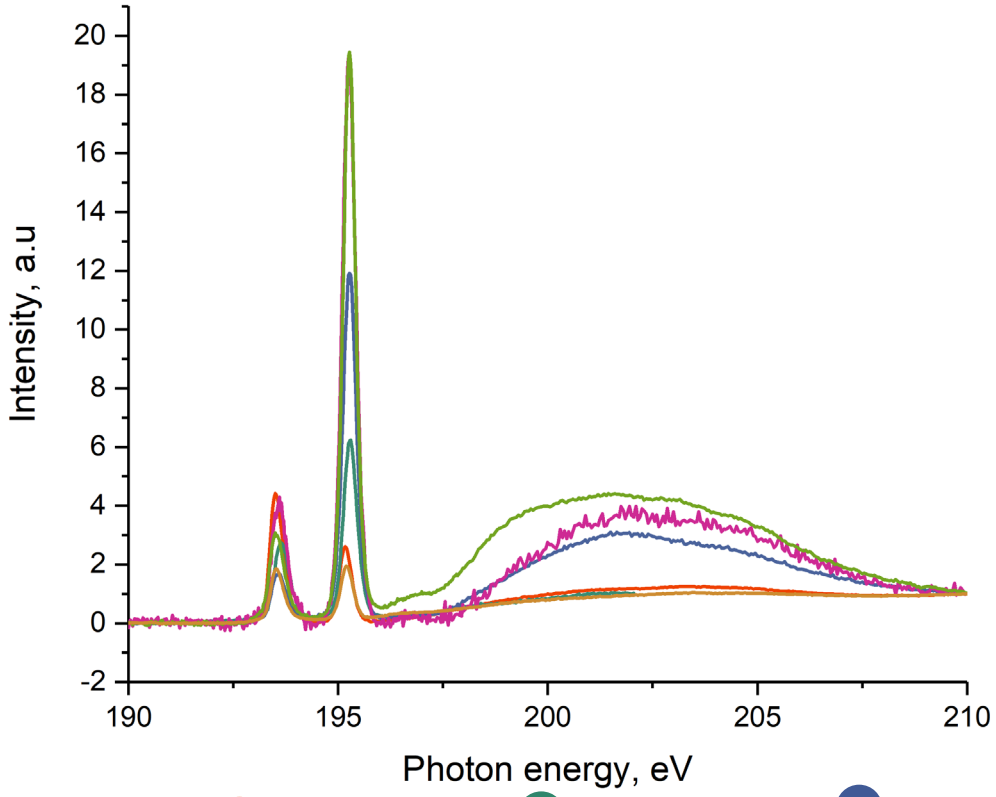

BcatOBu

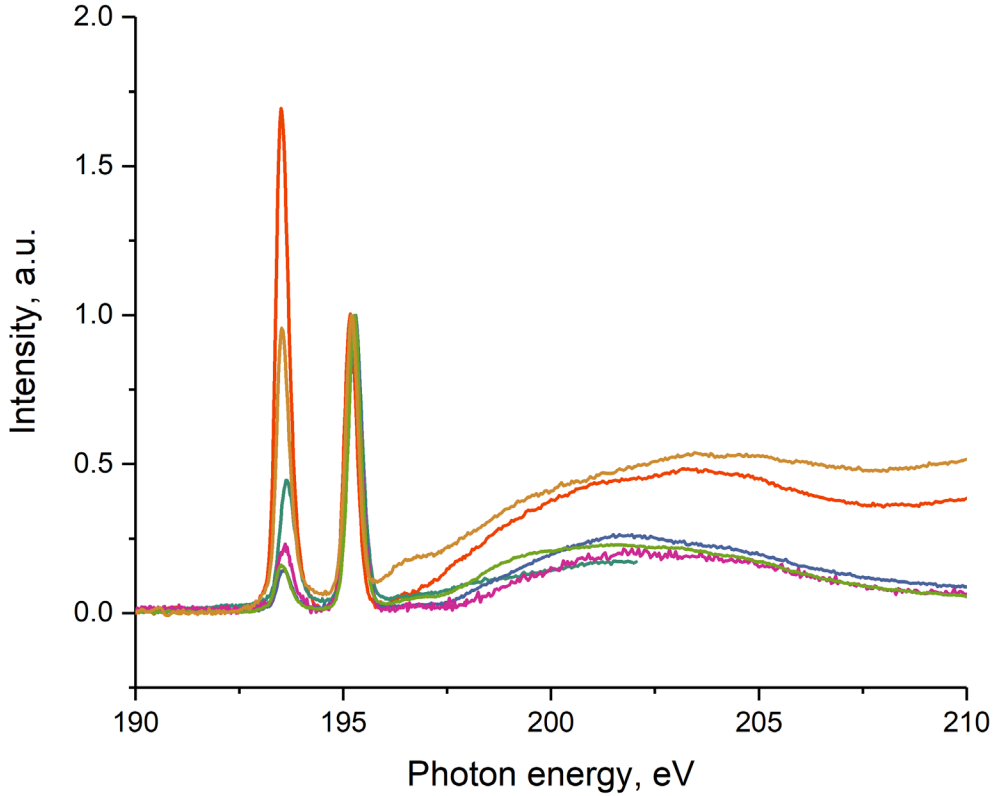

BcatCl(P_{888})

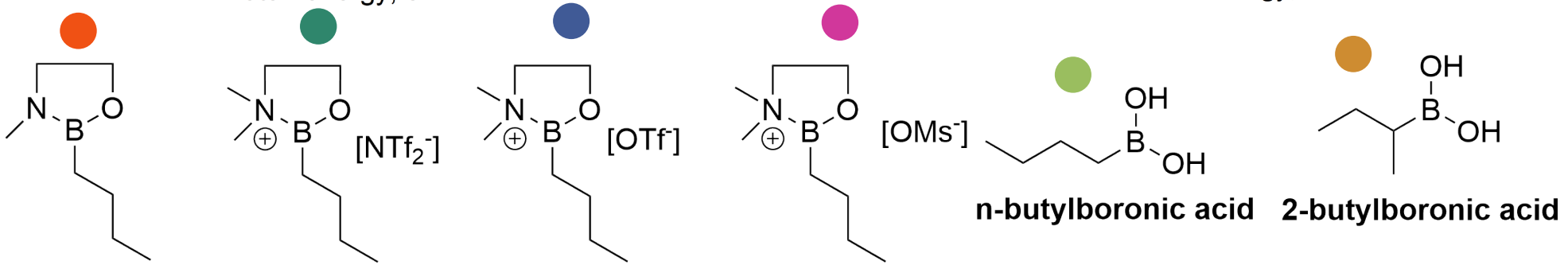

[Bcat(P_{888})][Al_2Cl_7]


[Bcat(P_{888})][NTf_2]

XAS results – B K-edge

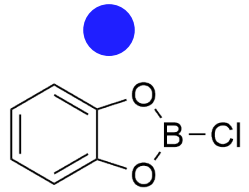






XAS & XRS – B K-edge

QUEEN'S UNIVERSITY BELFAST
QUEEN'S UNIVERSITY IONIC LIQUID LABORATORIES
QUILL

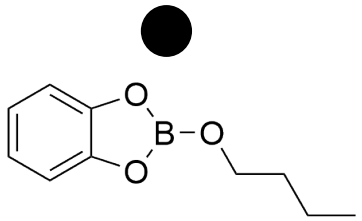


BcatCl

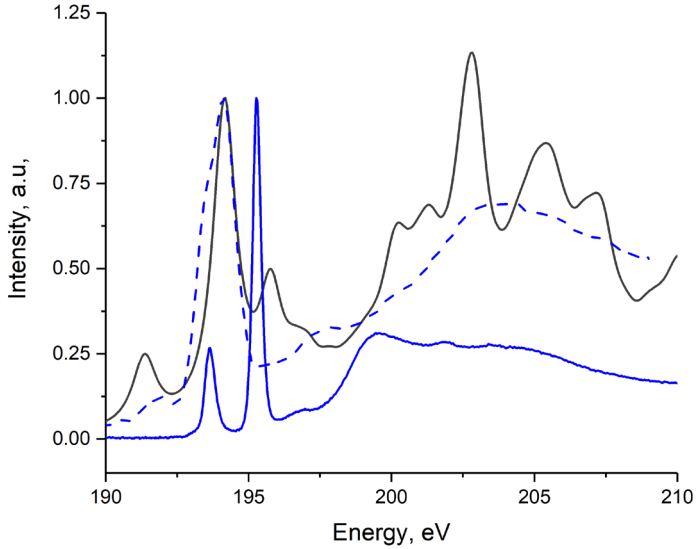
XAS

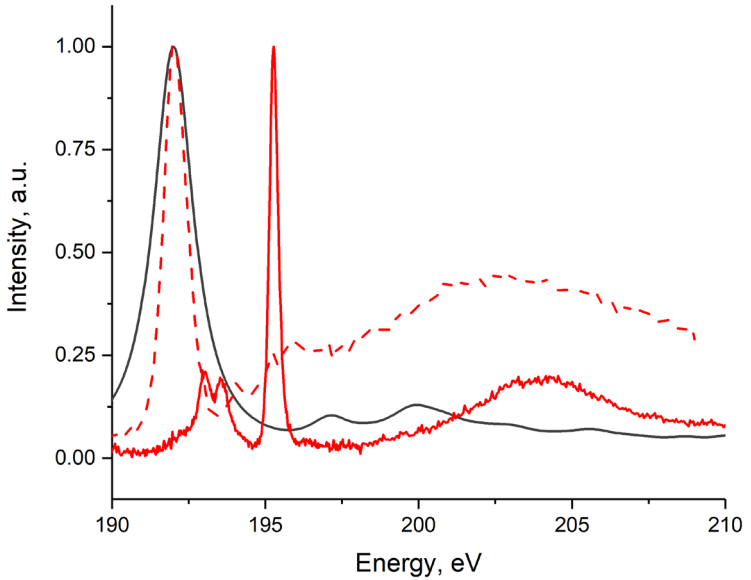
XRS

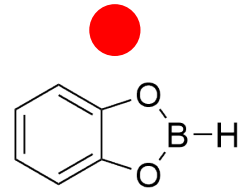
simulation



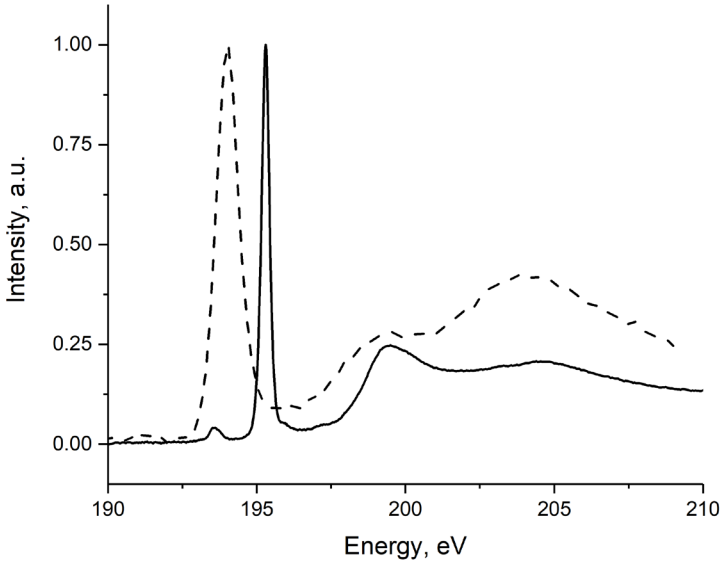
BcatOBu

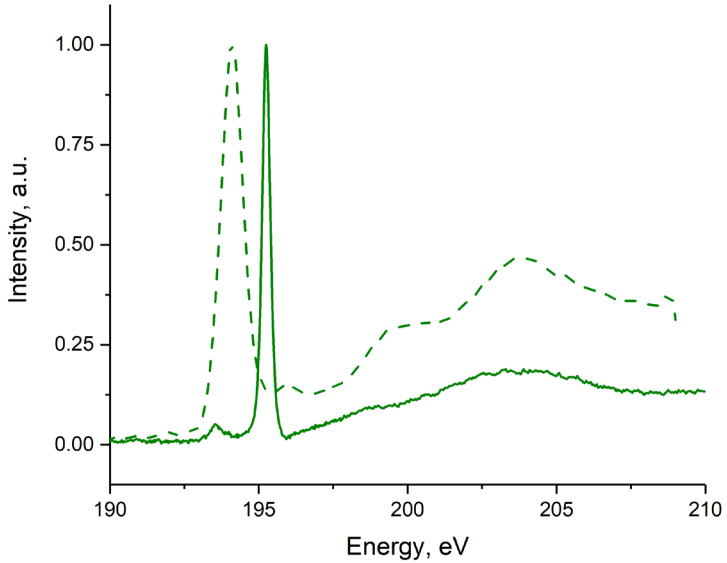


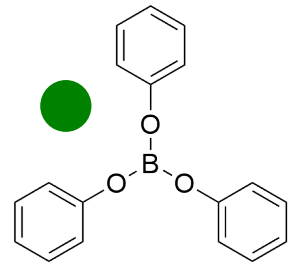




BcatH







B(OPh)$_3$

Summary and Future Work

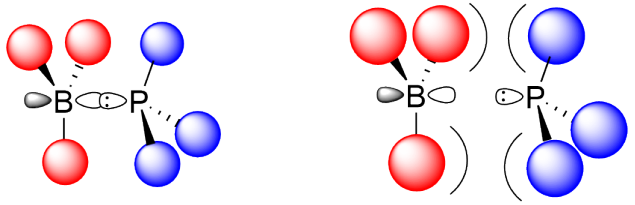
QUEEN'S UNIVERSITY BELFAST
QUEEN'S UNIVERSITY IONIC LIQUID LABORATORIES QUILL

Summary:

- Measured the B K edge of a range of boron Lewis acids using XAS and XRS to measure the 1s→LUMO transition to isolate a component of Lewis acidity

Future work:

- Continue with XRS and XAS analysis
- Applied for beamtime at ESRF to study the B K edge of FLPs
- Conduct operando studies of hydrogenation reactions with FLP-SILP systems.



Acknowledgements

- Prof. Małgorzata (Gosia) Swadźba-Kwaśny
- Prof. John Holbrey
- Dr. Sofia Diaz-Moreno (Diamond)
- Dr. Daniel Bowron (ISIS)
- Dr. Luke Higgins (Diamond)
- Dr. Pilar Ferrer (Diamond)
- Dr Josh Elliott (Diamond)
- Dr. Yoan Delavoux
- Miss Lauren O'Neill
- Miss Emma McCrea
- Miss Beth Murray