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EPSRC

The future of XAS studies on heterogeneous and homogeneous catalysts: time-resolved high-throughput, in situ, and operando spectroscopy of dynamic and complex systems

Sven L. M. Schroeder, The University of Manchester

[a] N. Tsapatsaris, [a] A. M. Beesley, [a] N. Weiher, [a] M. Tromp, [b] J. Evans, [b] S. Russu, [b] A. J. Dent, [c] I. Harvey, [d] S. Hayama, [d] H. Tatton

a. School of Chemical Engineering and Analytical Science, **The University of Manchester**
b. School of Chemistry, **The University of Southampton**
c. **Diamond Light Source Ltd.**
d. Synchrotron Radiation Source (SRS), **Daresbury Laboratory**
e. School of Chemistry, **The University of Manchester**

University of Southampton

diamond

CCLRC

- Societal need to understand catalytic processes better, in the context of
  - energy
  - organic transformations
  - sustainable sources
  - clean environment
  - handling of hazardous intermediates
  - security
- Heterogeneous Catalysis
- Homogeneous Catalysis

In situ vs *operando*

- **In situ** Spectroscopy

  Term used for a long time to indicate that the conditions of pressure, atmosphere and temperature are controlled during data acquisition, **<u>or</u>** that the sample is not exposed to ambient conditions after specific treatments.

- **Operando** Spectroscopy

  Indicates that spectroscopic measurements of catalysts under working conditions (temperatures, pressures and all required reactants at right amounts — gas as well as liquid) **<u>with simultaneous on-line product analysis</u>**.
  Used in the literature from 2002 [B.M. Weckhuysen, Chem. Commun. (2002) 97; M.A. Bañares *et al*., Chem. Commun. (2002) 1292].

  For many it was already a subset of **in situ** spectroscopy in the past…

Current UK Situation in XAS: switchover from the SRS (2nd generation) to DIAMOND (3rd generation)

- SRS, Daresbury

Station 3.4	Soft XAS (900 eV – 3 keV)	shut down 2005
Station 7.1	High-flux XAS (5 keV – 15 keV)	shut down 2005
Station 9.2	Microfocus XAS (5 keV – 30 keV)	shut down 2006
Station 9.3	XAS workhorse (5 keV – 30 keV)	to 2008
Station 16.5	High flux XAS (5 keV – 30 keV)	to 2008

+ several very soft XAS stations (< 1 keV)

- DIAMOND

I18	Microfocus XAS (5 keV – 30 keV)	since 2007
	Standard XAS	from 2009
	???	2011 (???)

- Fewer beamlines
- Additional **competition:** new science enabled by high photon flux and brilliance
- **Must use available time more efficiently**

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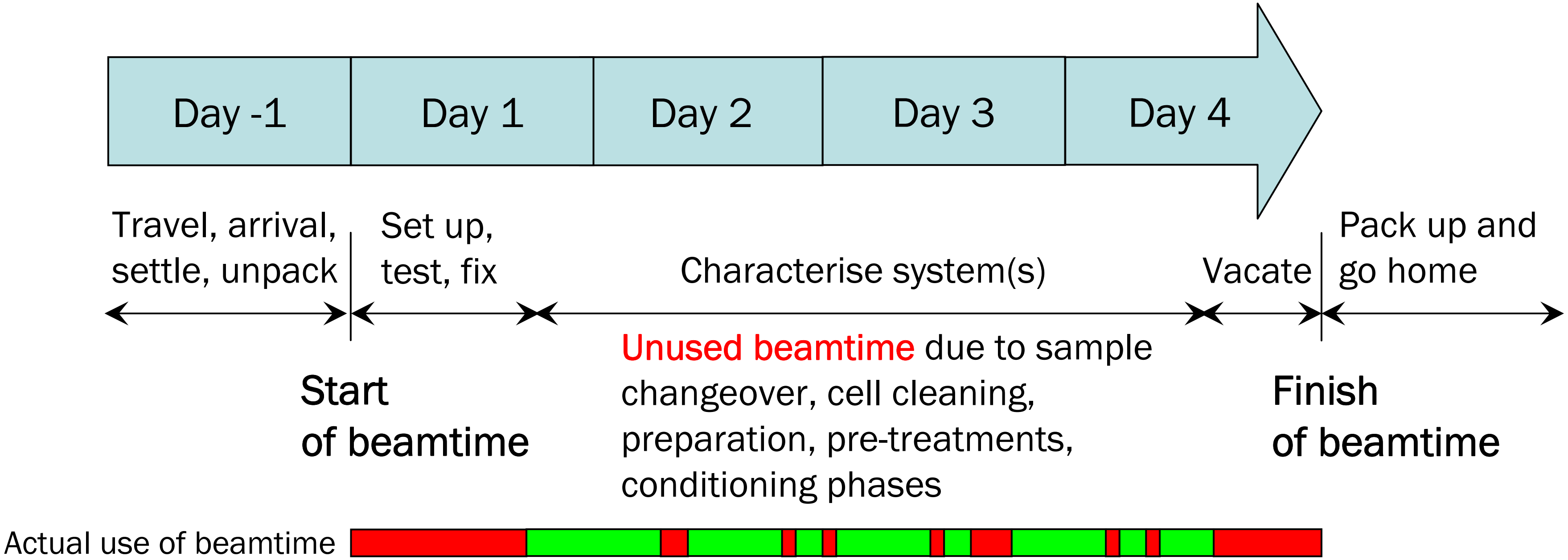
A typical *In situ* or *Operando* XAS run at a synchrotron radiation beamline

Assumptions

- Awarded 4 days beamtime
- Users bring along *in situ* or *operando* setup
- Smoothly running equipment and well-behaved materials



Inefficient use of beamtime due to…

- Long equipment set-up times
- Sample change-over
- Cell cleaning
- *In situ* preparation / pre-treatment / conditioning
- Establishing steady-state conditions (sample must be stable over duration of a scan)
- **Activation, conditioning or de-activation of catalysts often requires continuous operation of reactor for hours, sometimes days**

Actual use of beamtime 

You can shorten the green bars with more flux, but the red blocks remain the same

Solution: Multiplexing the Experiment

- Basic idea: do the sample treatments while other sample is in the beam
- Switching between two identical *in situ* reactors used in some groups (e.g., Koningsberger since 1980s)
- However, independent *operando* reactors can become expensive…
- Much competing high-profile science is done *without* any requirement for *in situ* or *operando* instrumentation

Ideally, there should always be a sample in the SR beam

- Find more elegant multiplexing solutions – learn from industrial high-throughput experimentation and laboratory automation
- But one needs high photon flux to put more samples through

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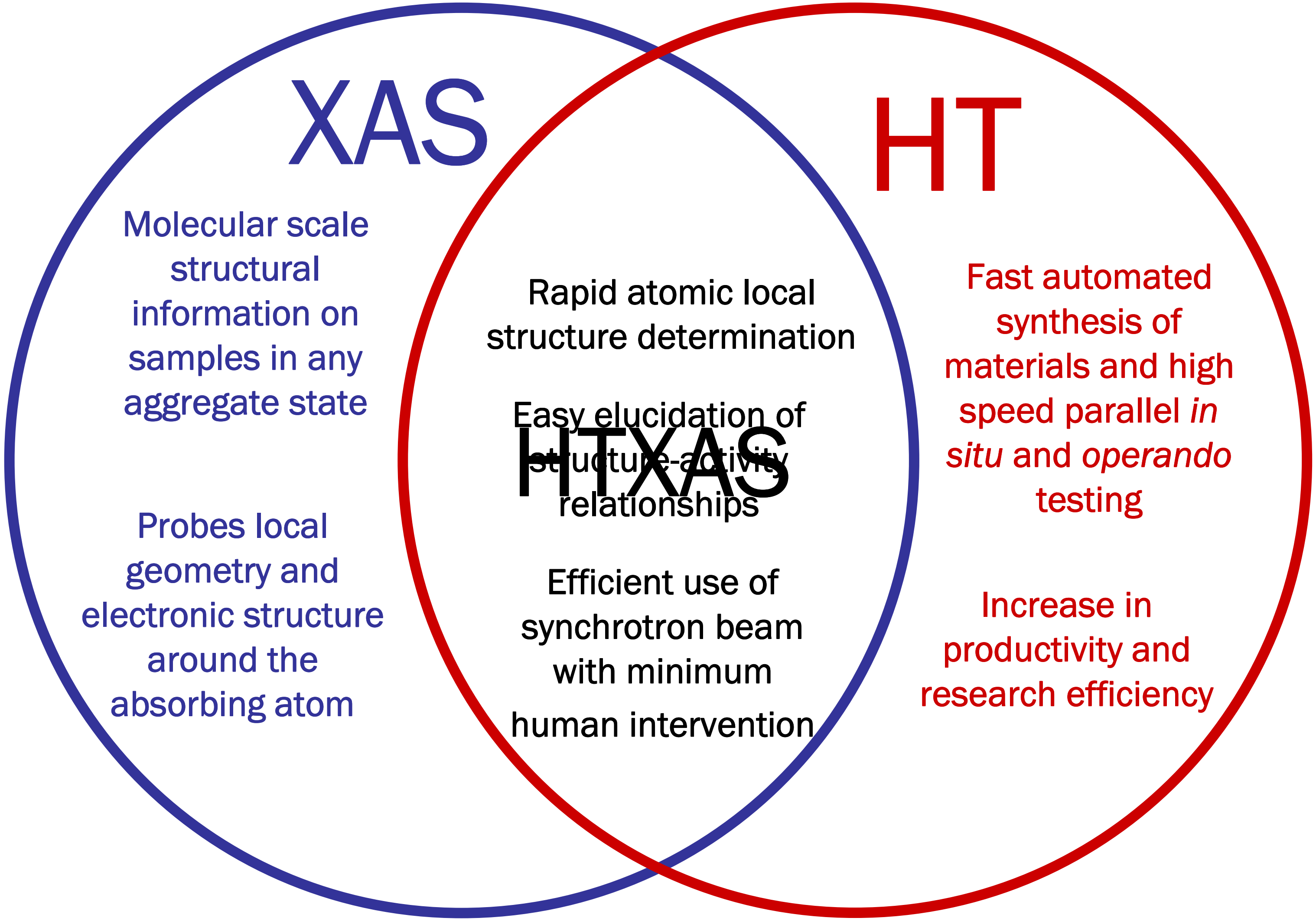
HT XAS

High-throughput X-ray absorption spectroscopy



Heterogeneous Catalysis

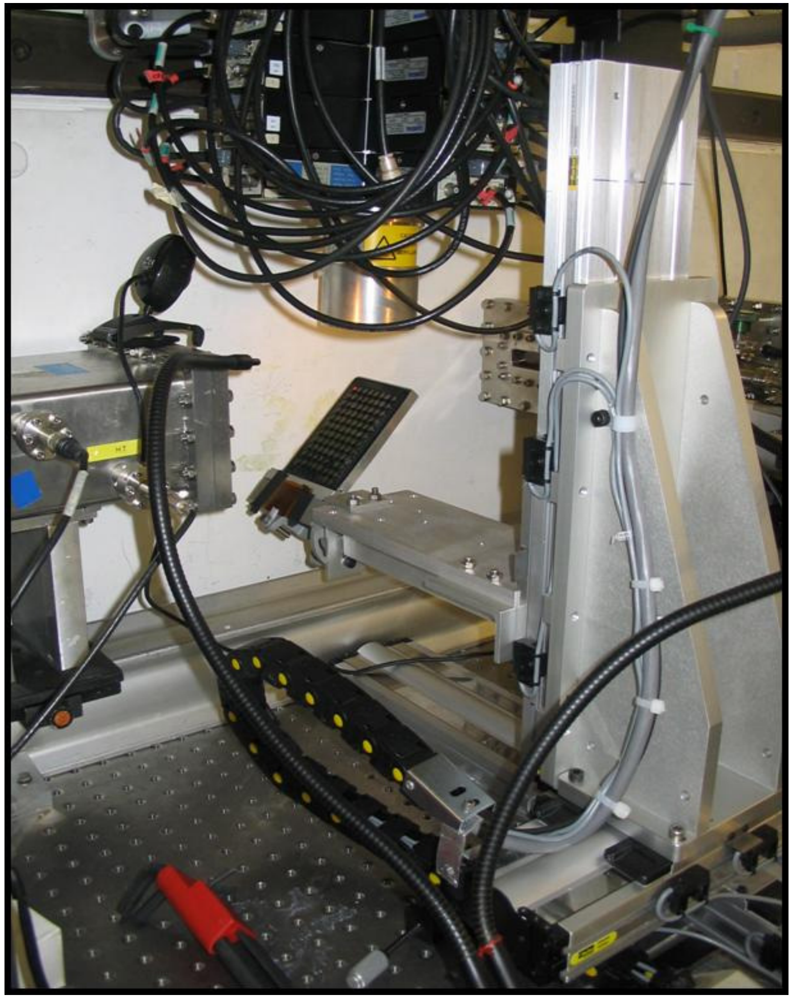
Simplest Microreactor Array

SBS 96 well plate standard

- Inexpensive, widely used, compact
- Reactions can be performed at the 100 μl level in open wells
- Existing commercial technologies for automated (robotic) loading and synthesis, and UV, IR, Raman, XRF and XRD high-throughput infrastructures

New to XAS

High-throughput X-ray absorption spectroscopy (HTXAS)



Experiments carried out in station 9.3 at Daresbury Synchrotron Radiation Source

96-well plate containing catalysts precursors

- Data acquisition
- XYZ stage automatic movement
- Synchronization with the station main computer (TCP/IP protocol)

LabVIEW 8

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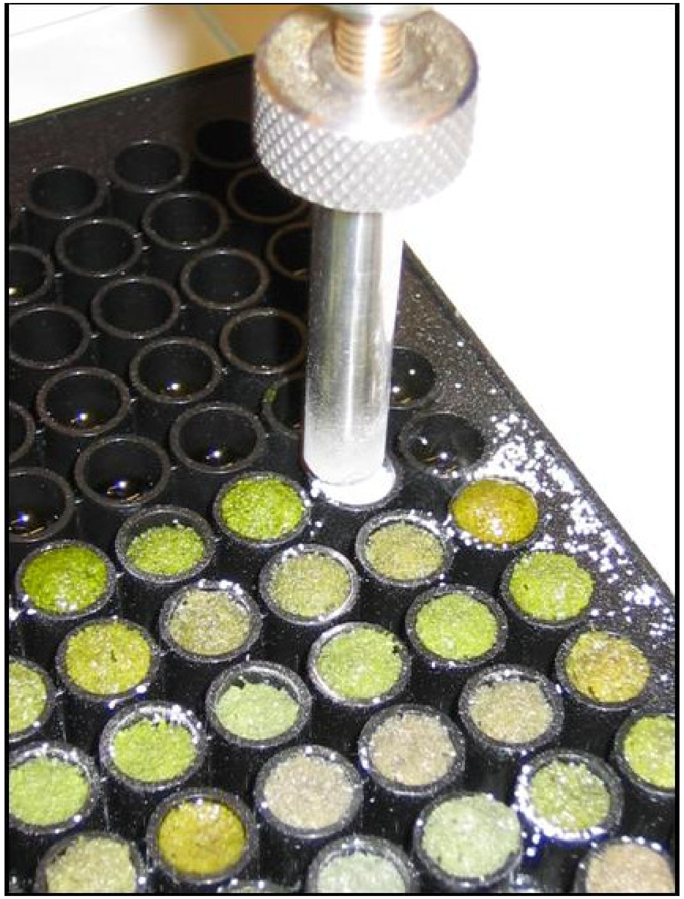
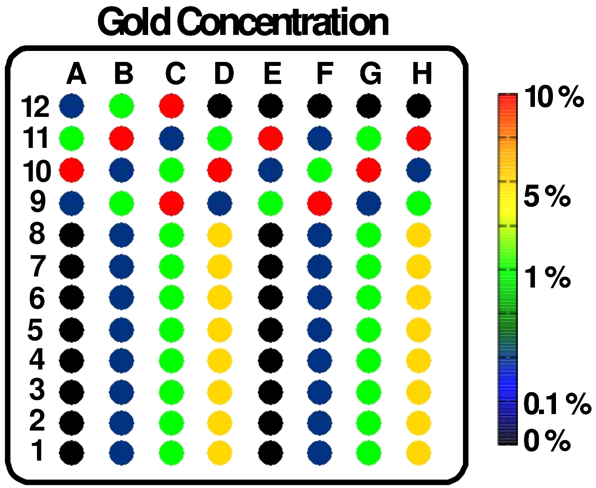
Example for Complex System Analysis: Library of ternary catalyst precursors

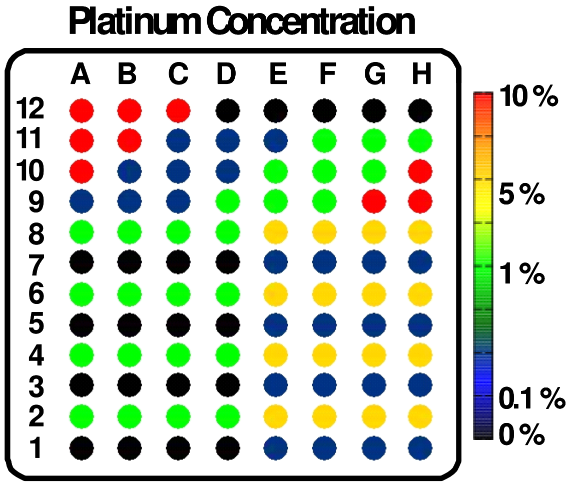


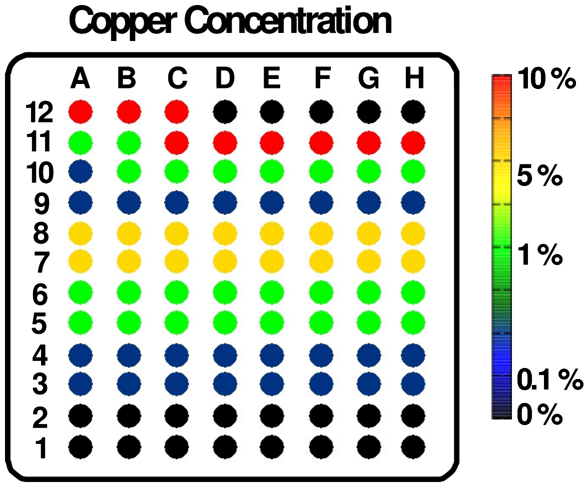
Impregnation of $CuCl_2$, $PtCl_2$ and $HAuCl_4$ on γ-Al_2O_3.

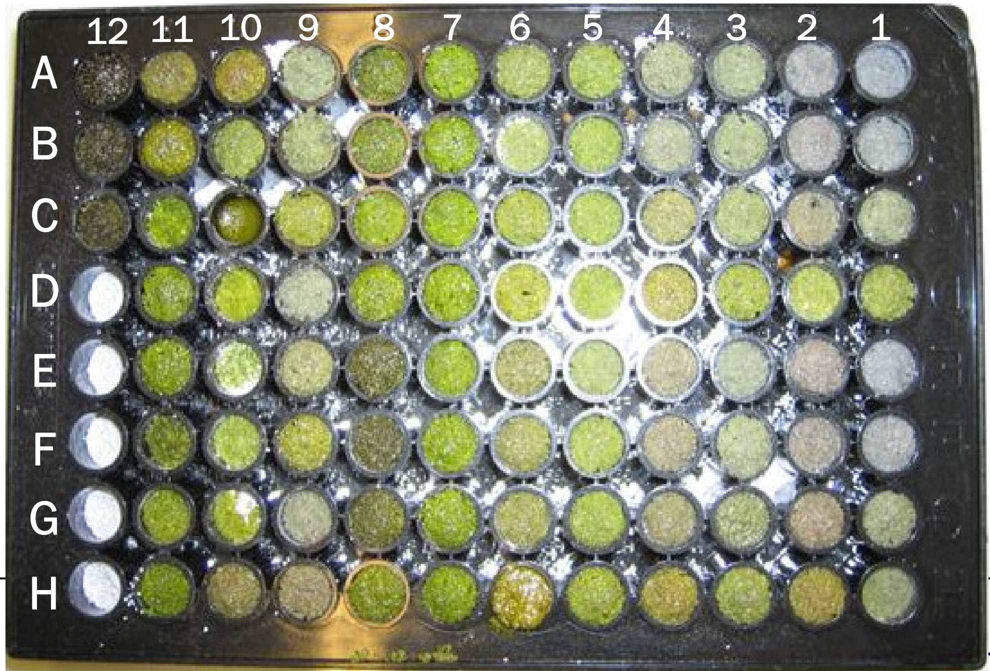
- Use of SBS 96-well plate
- Combinations of 3 metal species in 4 concentrations: 0.1, 1, 5 and 10 wt%.
- The volume of each solution in the wells corresponds to the pore volume of the alumina.

Preparation: Concentration Maps





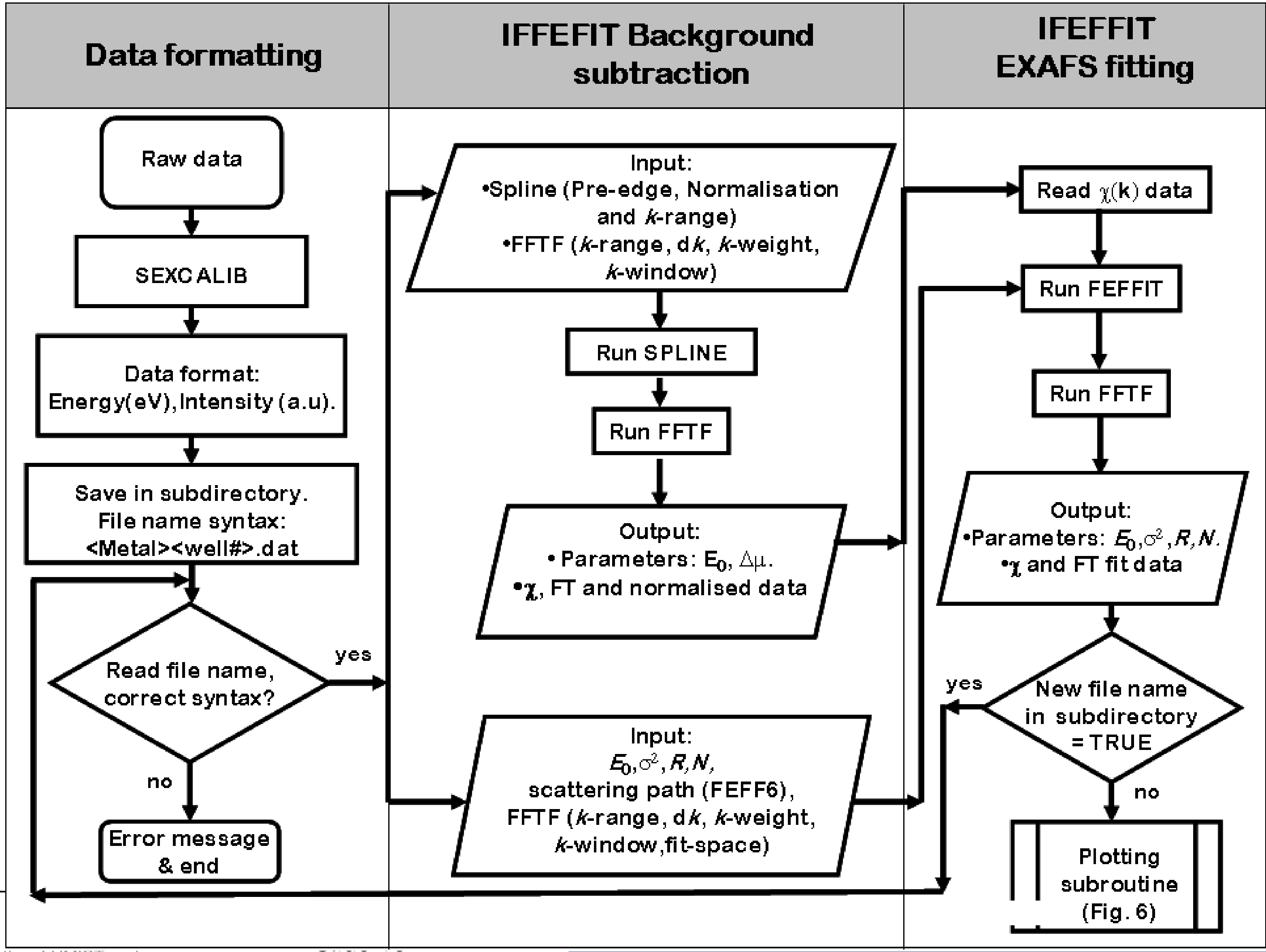


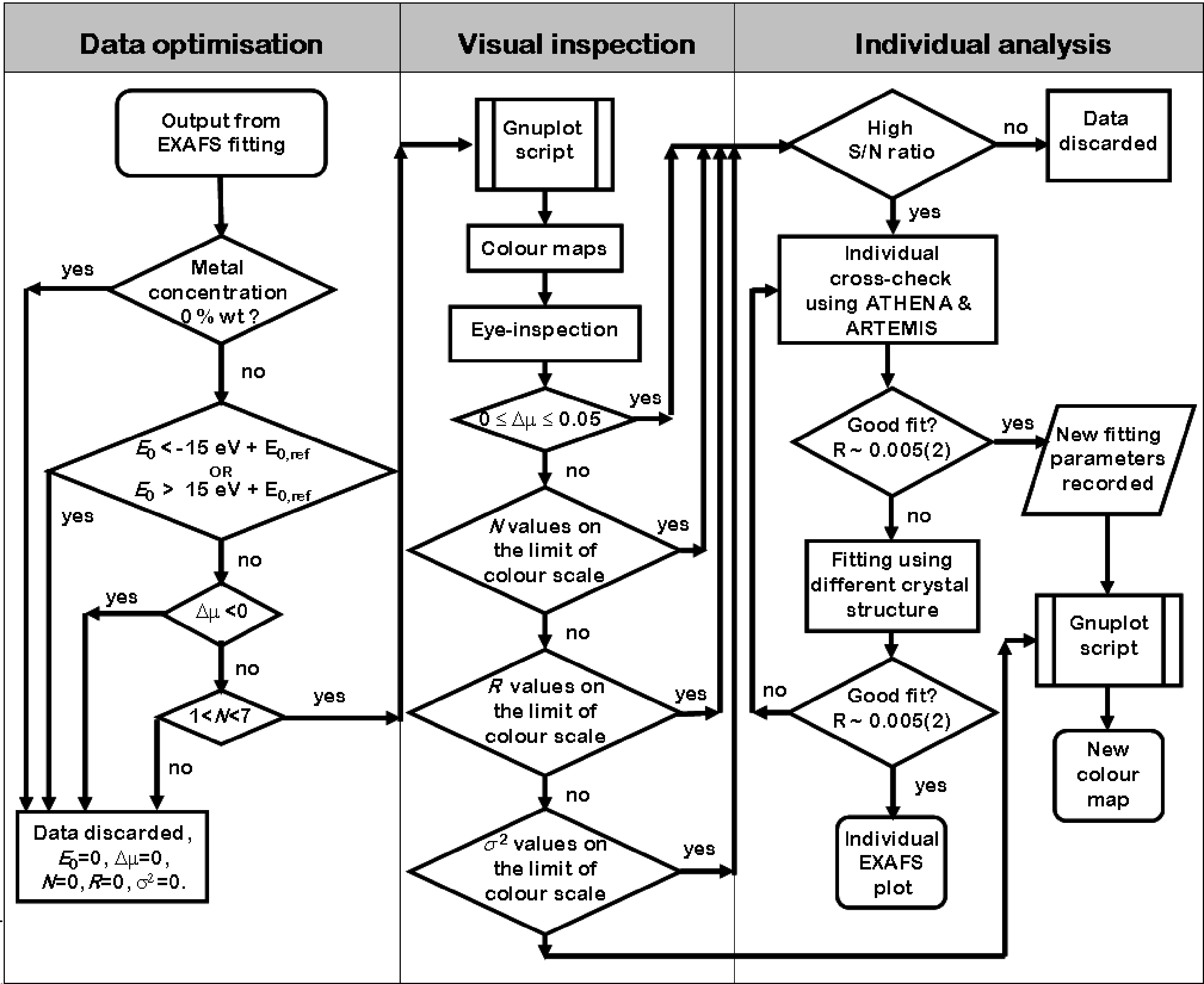


- Use of Well-Plate Standard Facilitates Compatibility with Design of Experiments (DoE) Software
- Combinatorial and statistical experimentation

- Lots of data – need to consider e-science…
- Data processing will rapidly become bottleneck
- Data mining
- Data documentation (metadata)

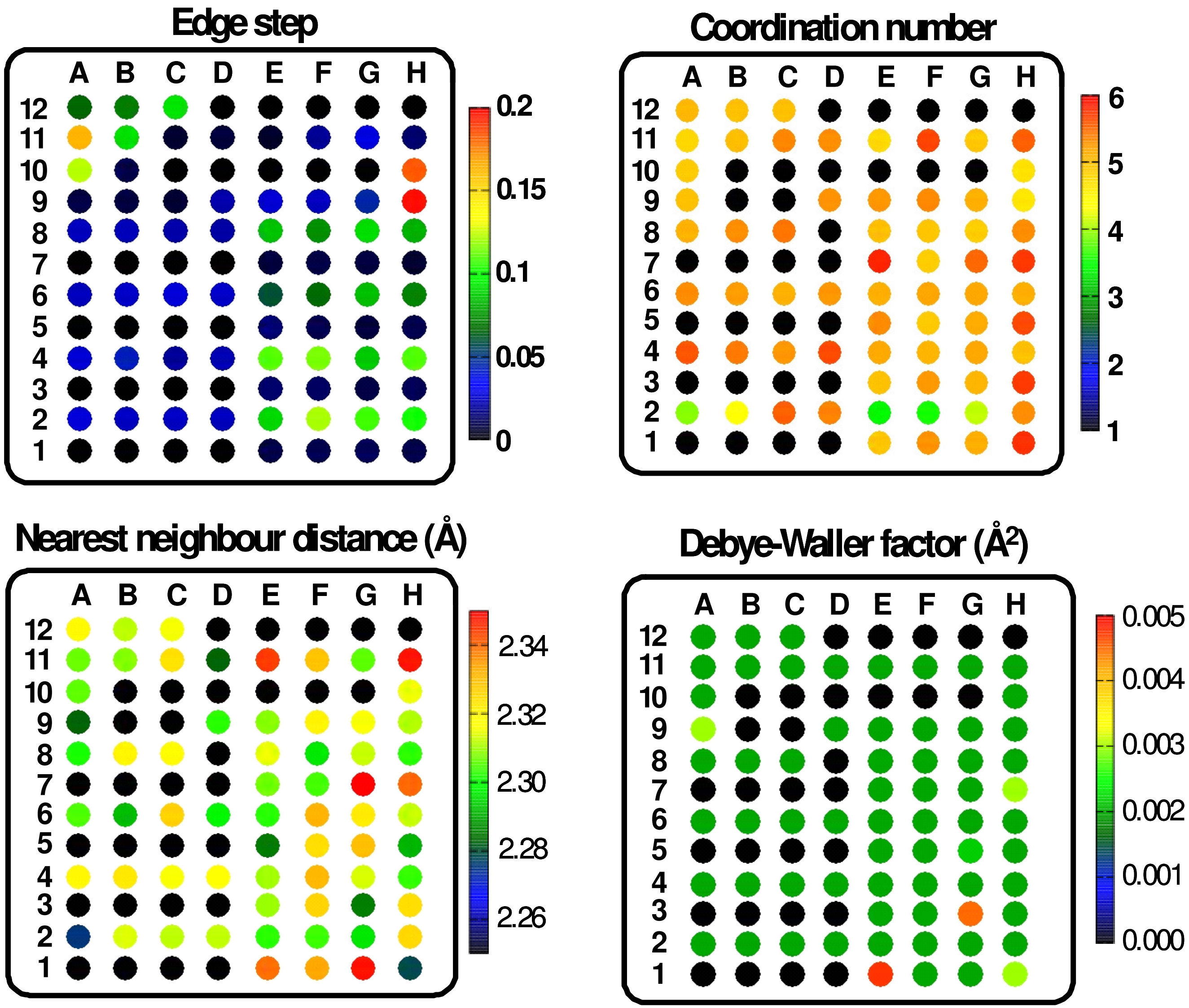
HT XAS data analysis




Data optimisation
Visual inspection
Individual analysis
Output from EXAFS fitting
Metal concentration 0 % wt ?
yes
no
E0 < -15 eV + E0,ref OR E0 > 15 eV + E0,ref
yes
no
Δμ <0
yes
no
1<N<7
yes
no
Data discarded, E0=0, Δμ=0, N=0, R=0, σ2=0.
Gnuplot script
Colour maps
Eye-inspection
0 ≤ Δμ ≤ 0.05
yes
no
N values on the limit of colour scale
yes
no
R values on the limit of colour scale
yes
no
σ2 values on the limit of colour scale
yes
High S/N ratio
no
Data discarded
yes
Individual cross-check using ATHENA & ARTEMIS
Good fit? R ~ 0.005(2)
yes
New fitting parameters recorded
no
Fitting using different crystal structure
Good fit? R ~ 0.005(2)
no
yes
Individual EXAFS plot
Gnuplot script
New colour map

Example of the HT EXAFS results obtained

Platinum



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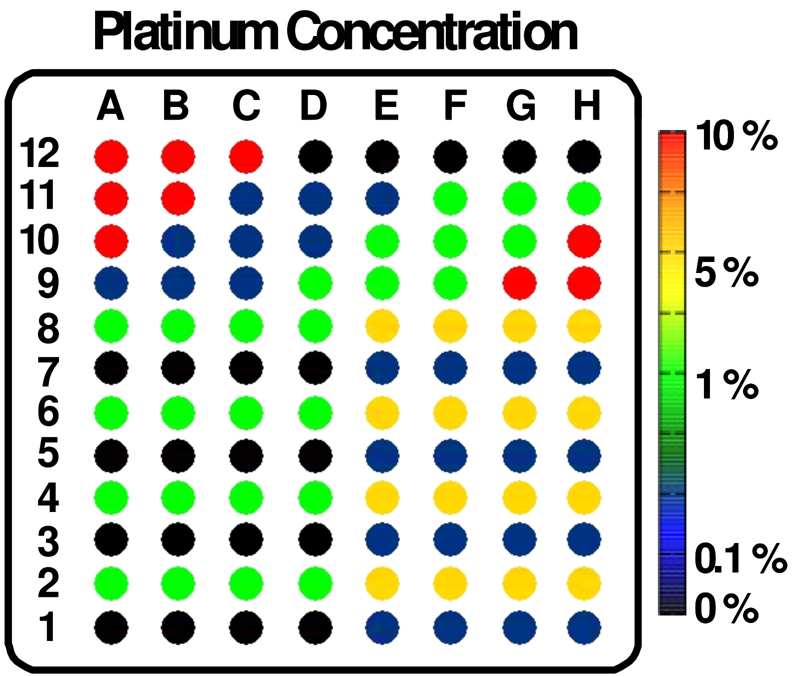
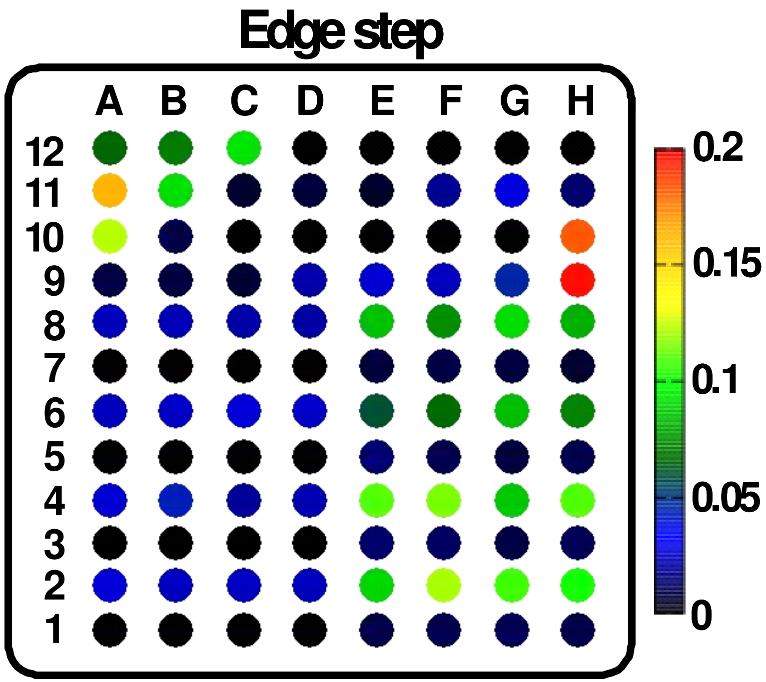
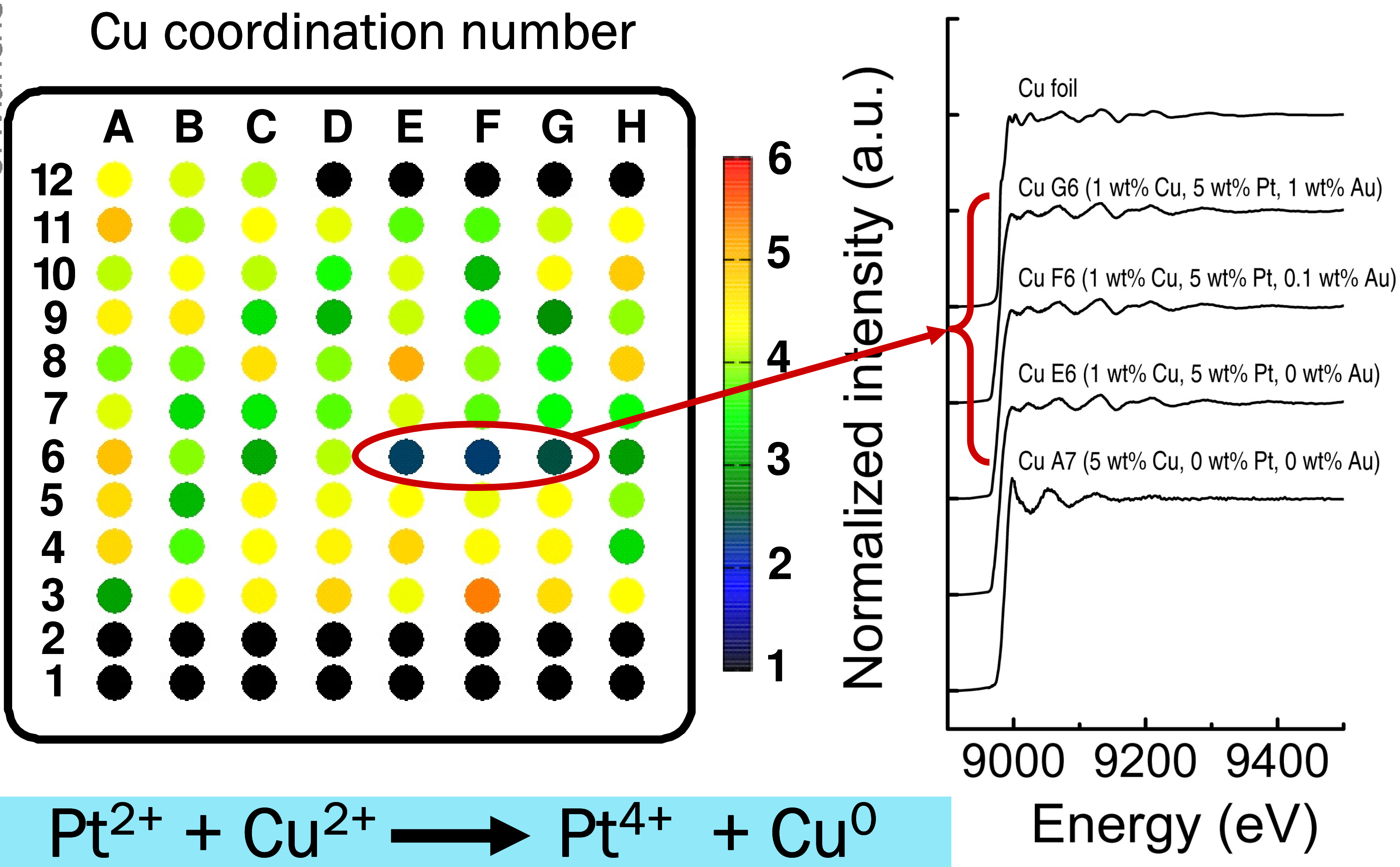
Validation: Correlation between concentration and edge-step





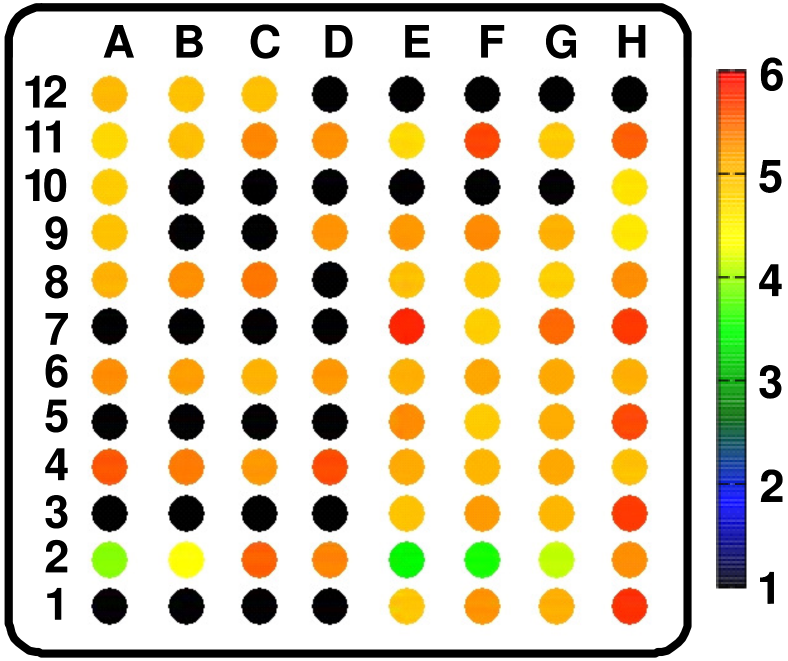
Rapid phase identification

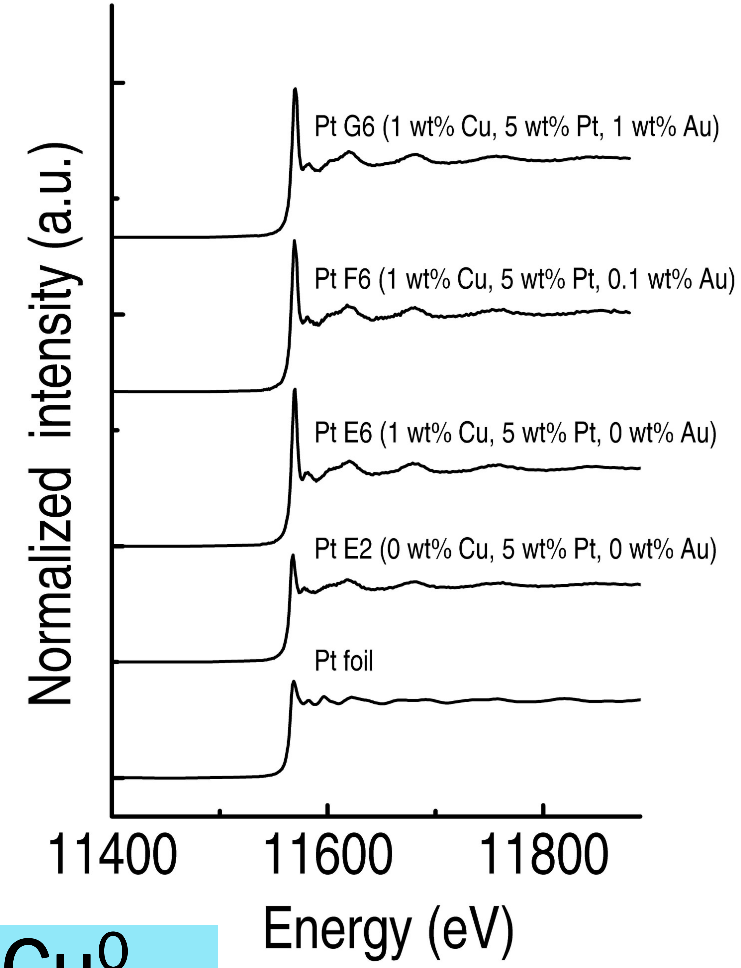


$$Pt^{2+} + Cu^{2+} \longrightarrow Pt^{4+} + Cu^{0}$$

Cu reduction due to Pt oxidation

Pt coordination number

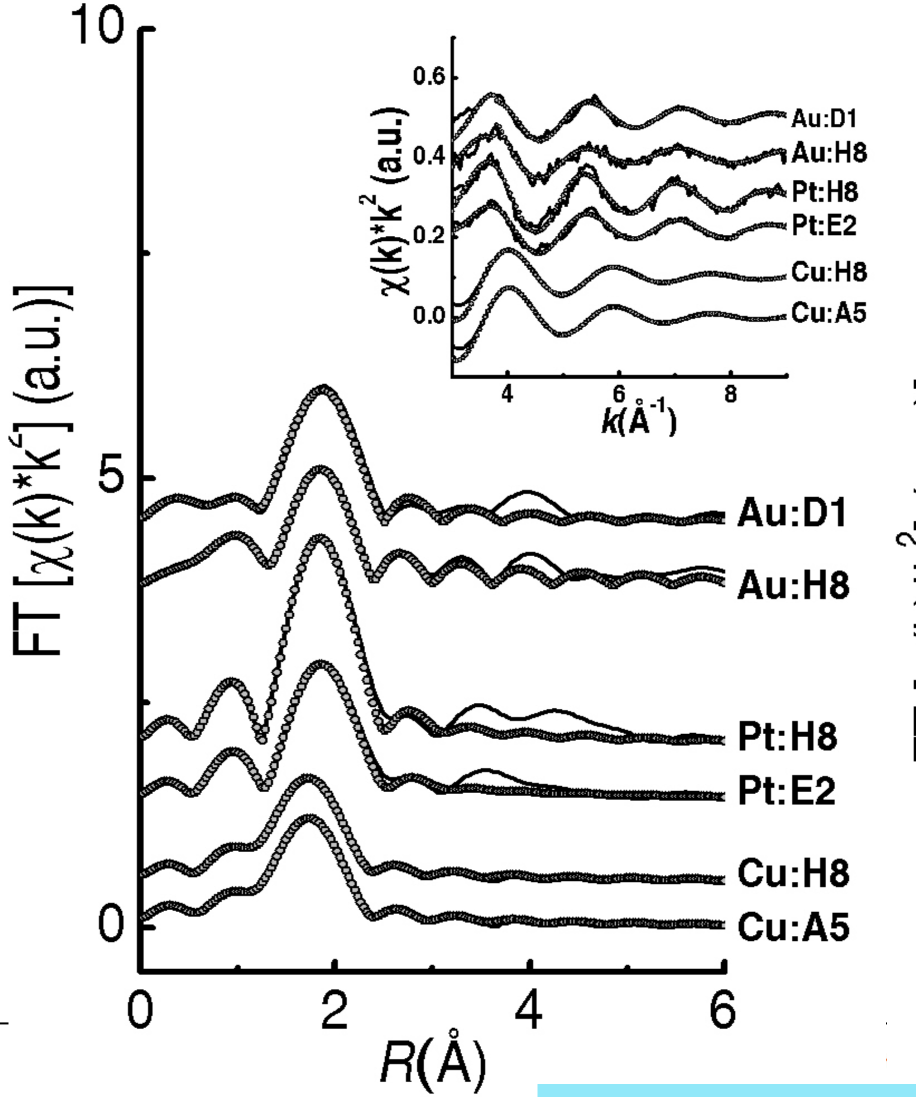




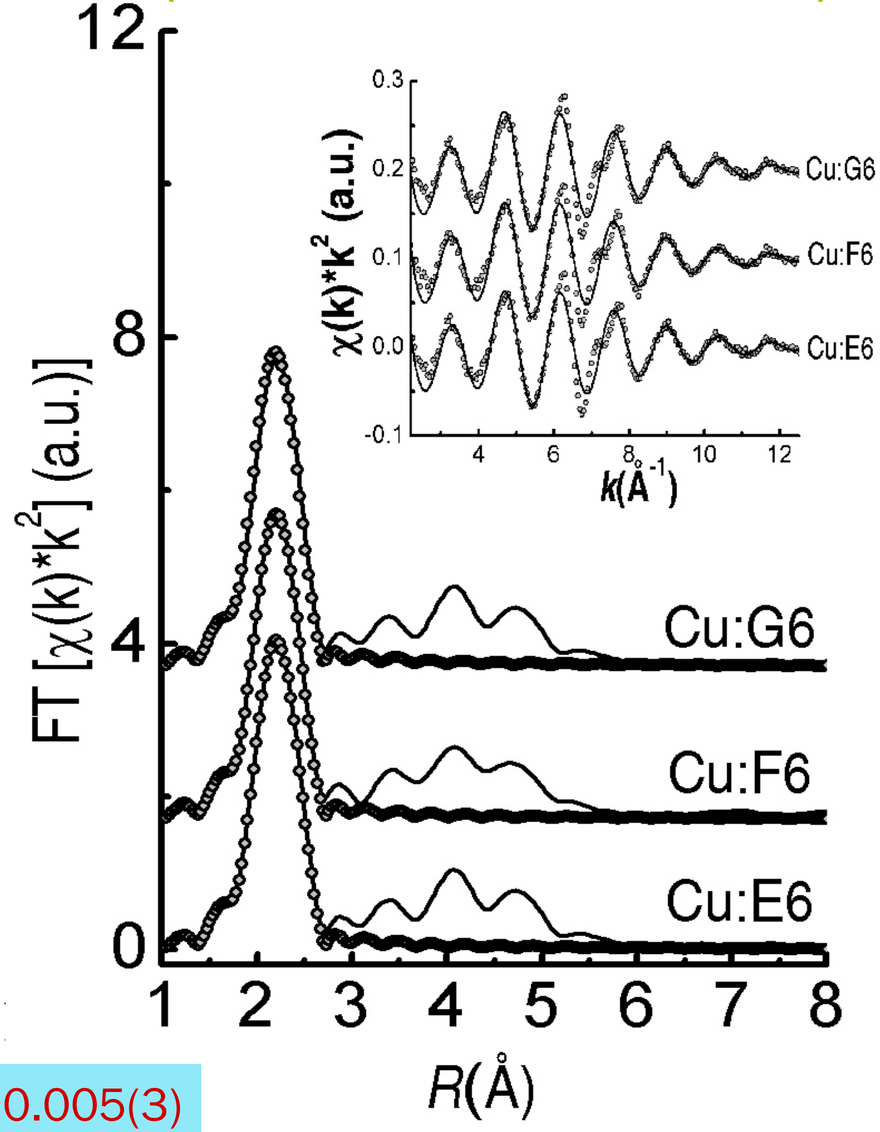
$$Pt^{2+} + Cu^{2+} \longrightarrow Pt^{4+} + Cu^{0}$$

HT EXAFS fitting of selected samples

Individual samples
(results are in line with metal chlorides)



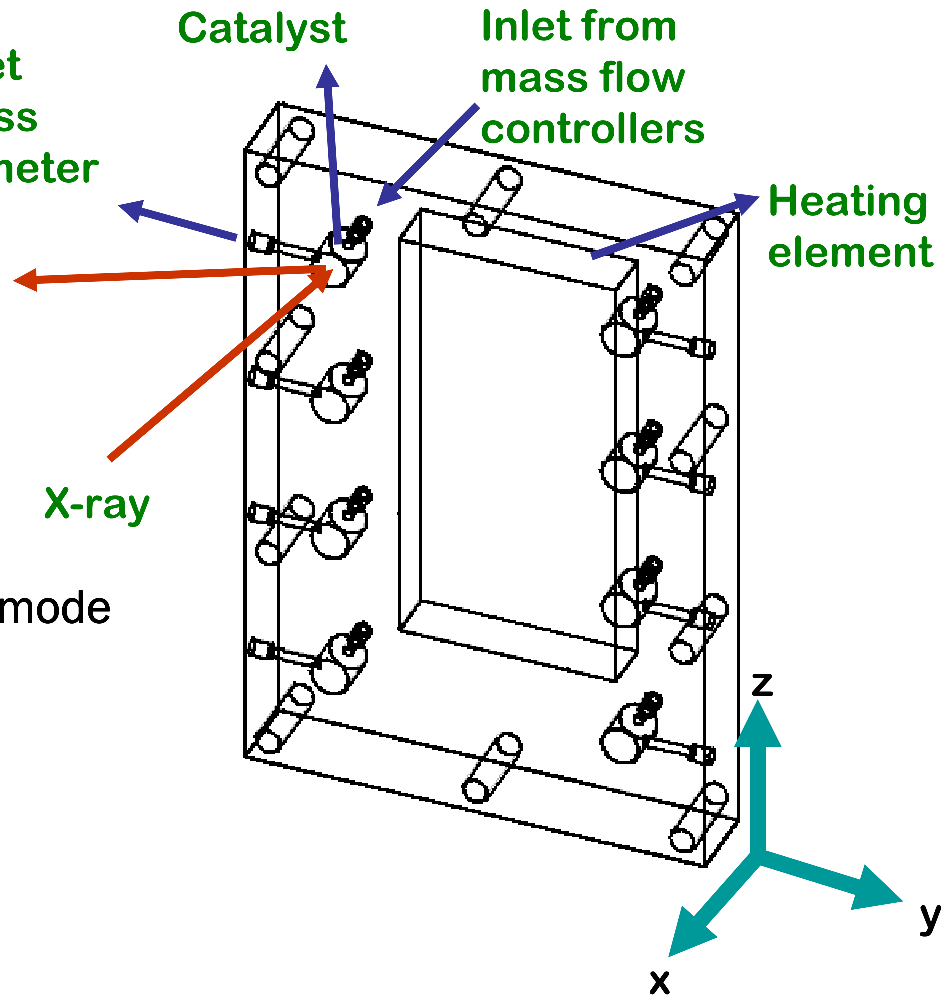
Notable samples from the coordination number plot
(results are in line with Cu metal)



Fit goodness R~0.005(3)

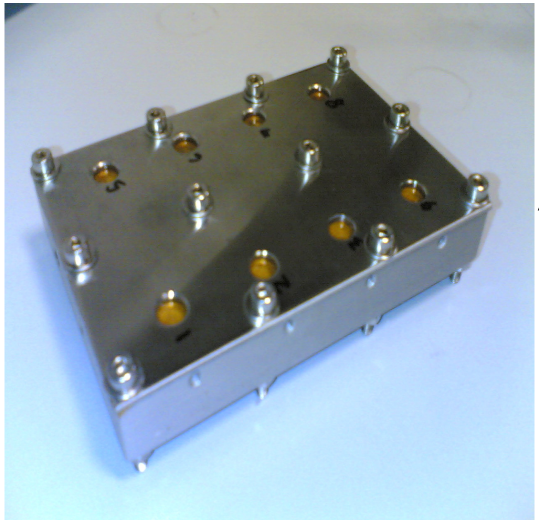
Operando Microreactor Arrays

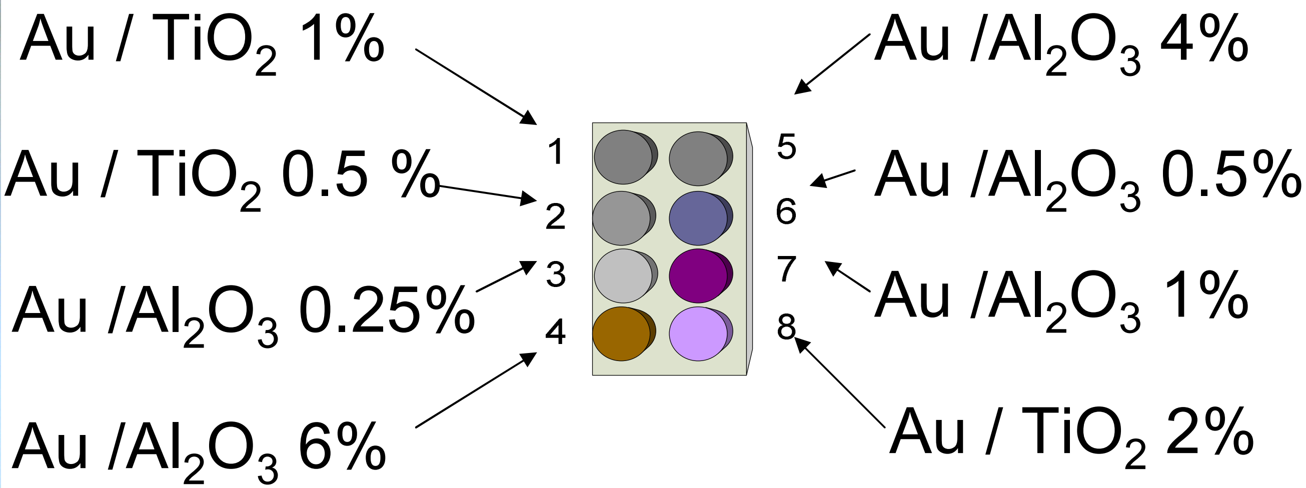
8x flow-microreactor array



- Based on the SBS -8 well plate standard
- *Operando* XAS: fluorescence-yield mode
- One gas flow
- One temperature

Application Example: Catalysis by Au





- Nominal Concentrations
- Powder Catalysts

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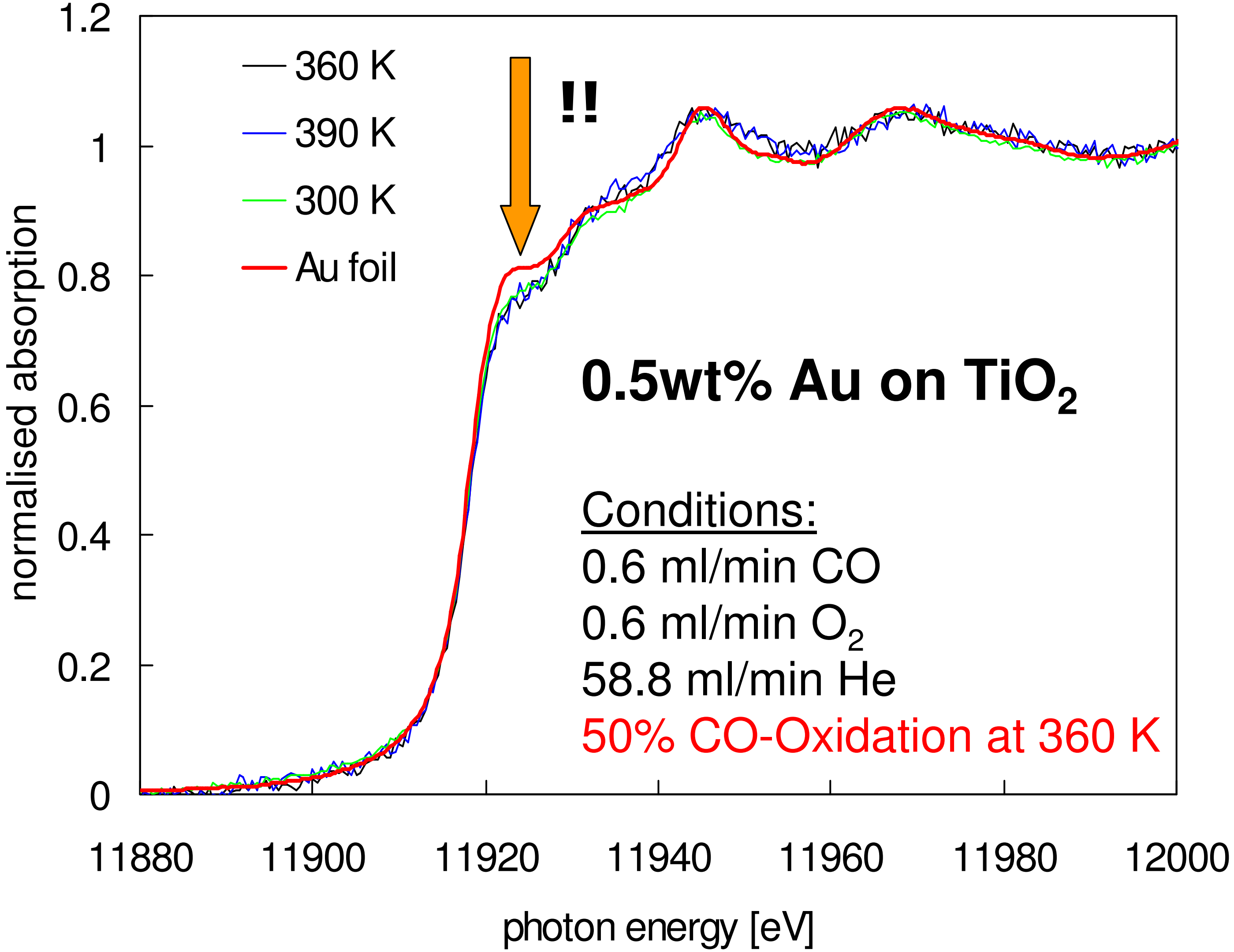
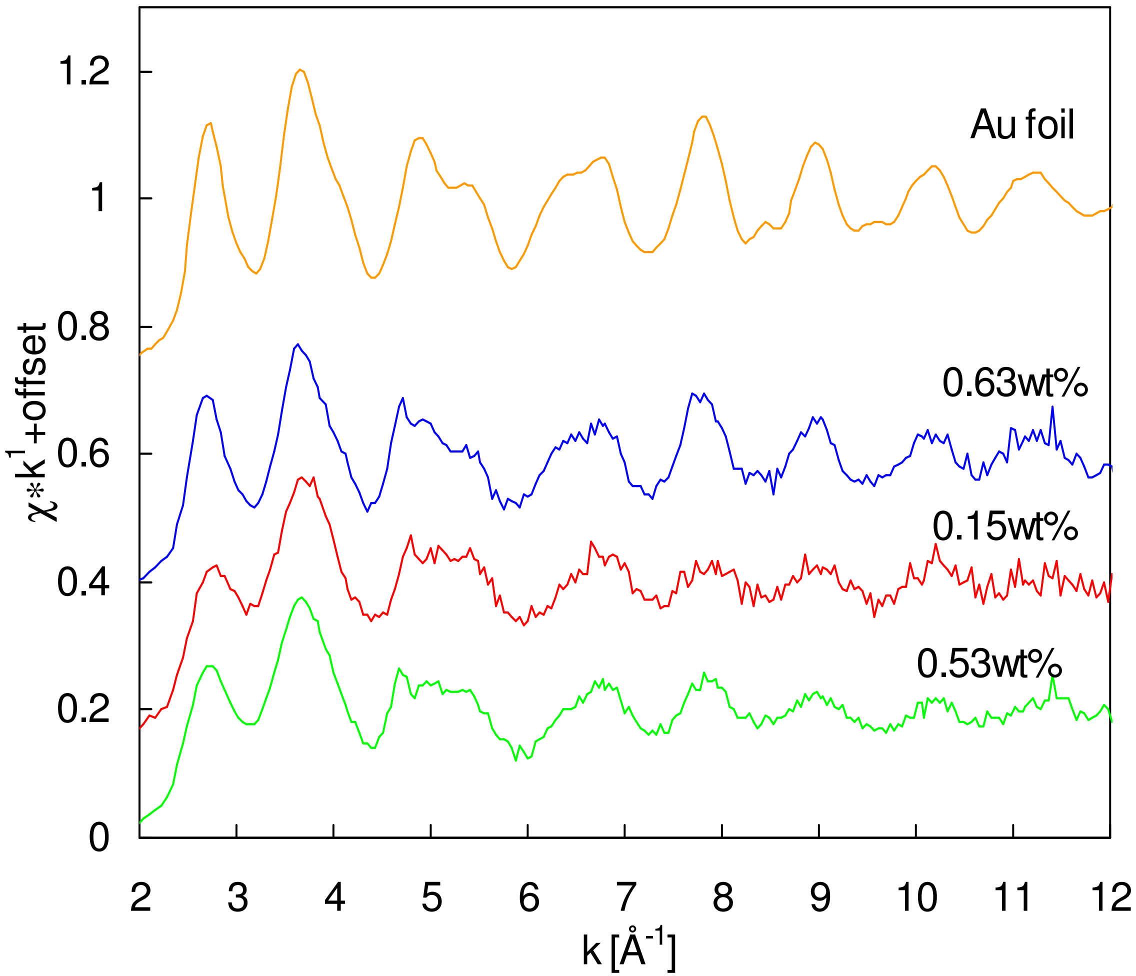
In Situ Au L_3-edge XANES



Room Temperature EXAFS (SRS)

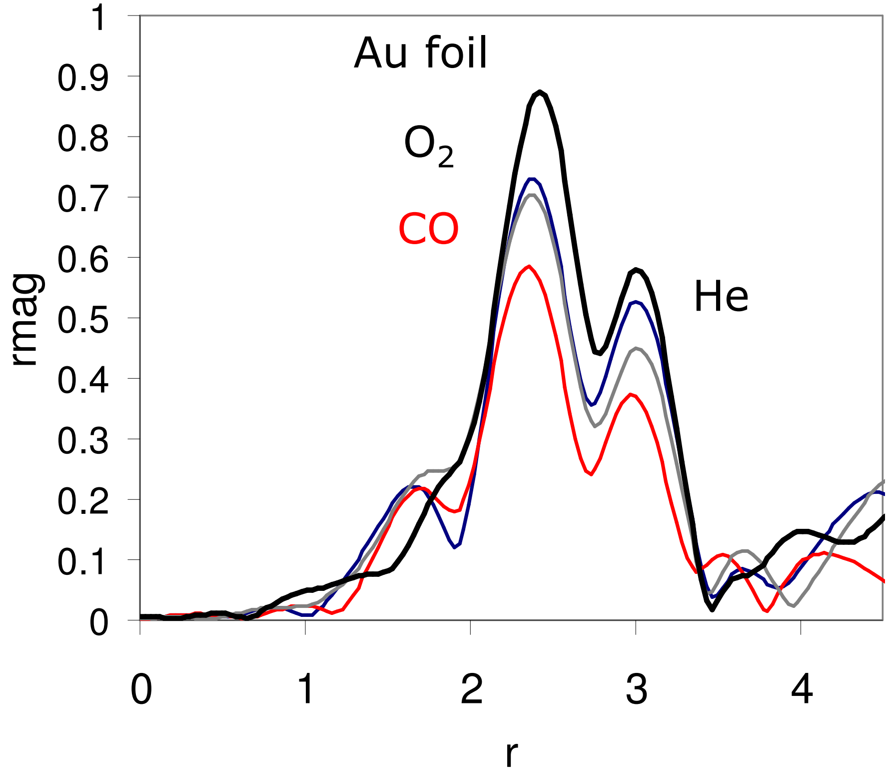


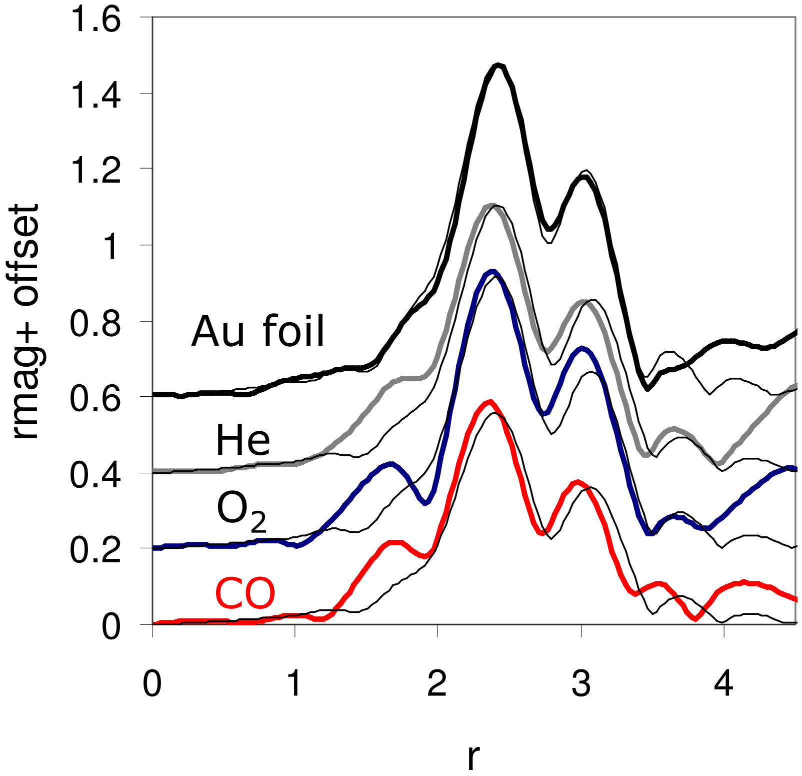
Considerable Amplitude Reductions

Very small particles

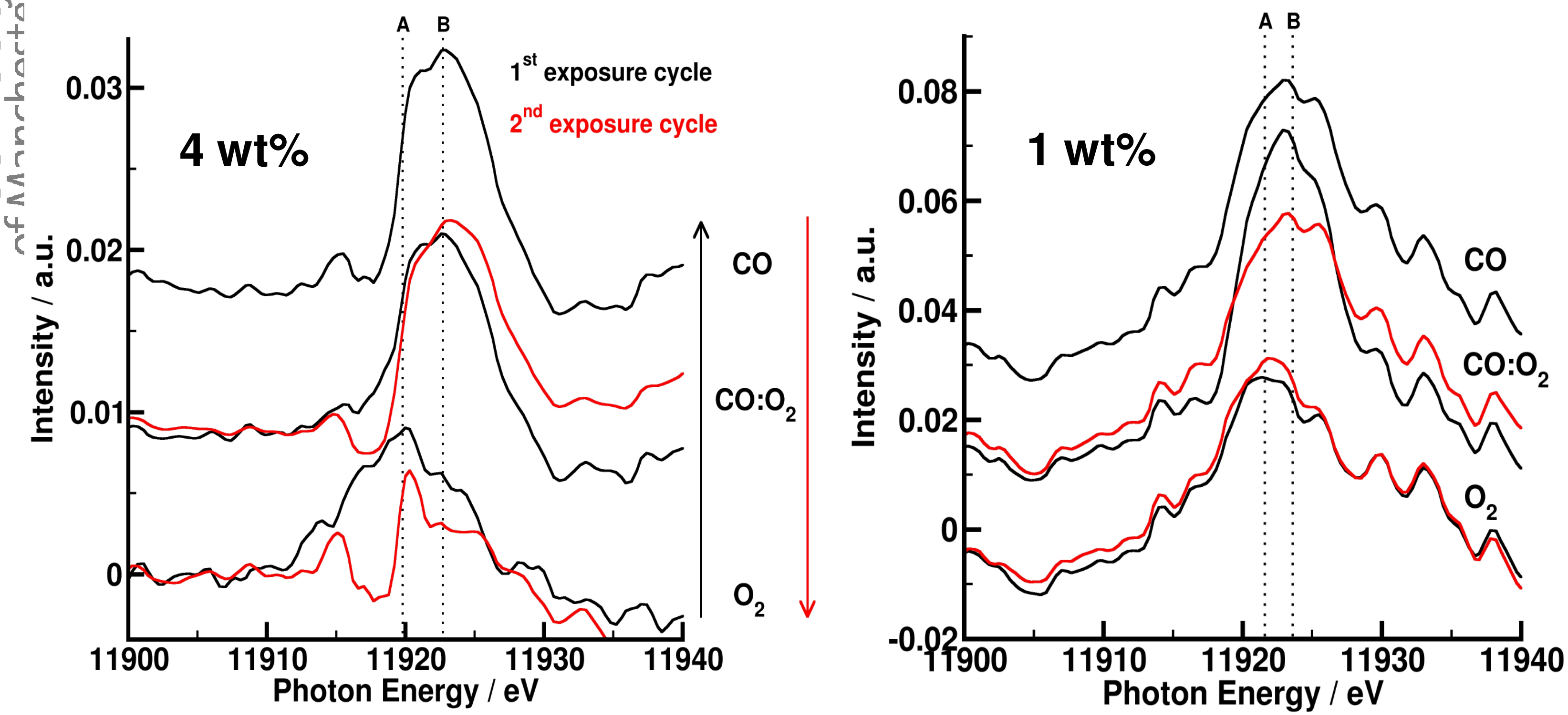
Note the noise.
Need more flux!

Average Au-Au Coordination Number as a Function of Gas Environment





O_2 activation over Au/TiO_2: Difference XANES



- **Near-edge resonance visible in CO and O_2.** Weiher *et al. JACS*, 2007
- **Weaker resonance at lower energy in O_2 compared to CO.**
- **Resonance more intense for 1 wt% catalyst than for 4 wt% catalyst**
- **NEED A LOT OF FLUX TO DO THIS HIGH-THROUGHPUT**

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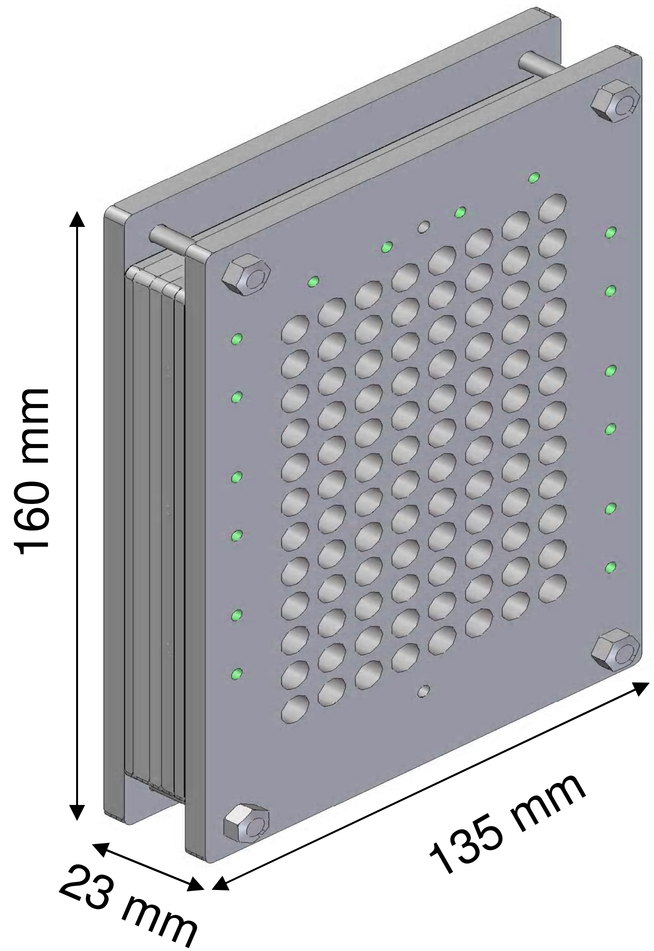
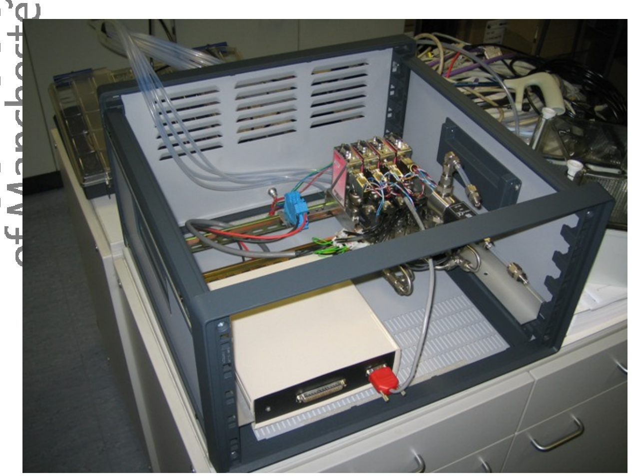
Microreactor arrays

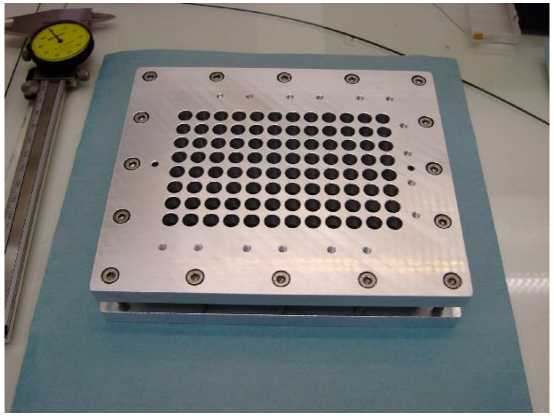
96x flow-microreactor array



- *Operando* XAS: transmission, fluorescence
- Compatible with industry standard
- Control of gas flows and composition
- Mixtures of up to 4 different gases
- Fluid dynamics of the reactors have been modelled
- Temperature control
- Mass spectrometric analysis of individual reactor effluents

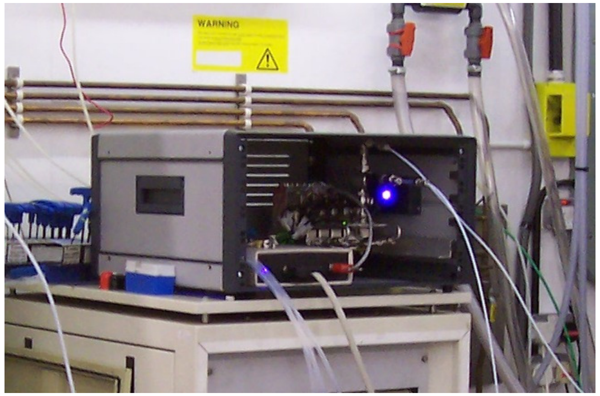
Hardware



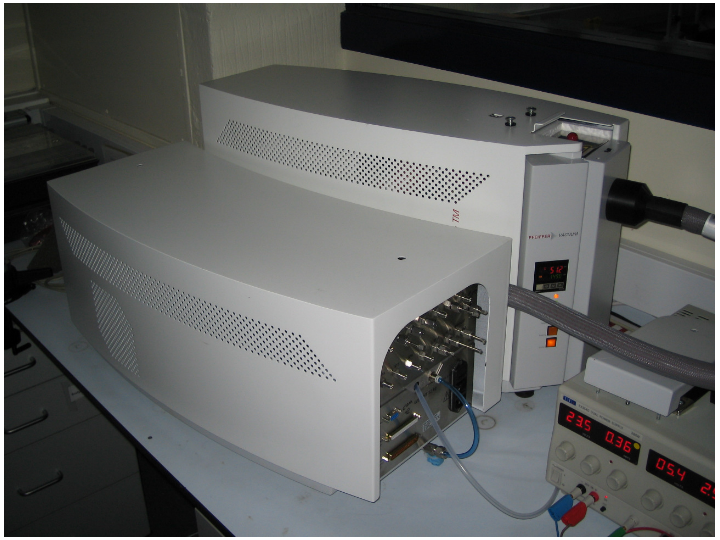


Reactor

Array



4x Mass
Flow Control

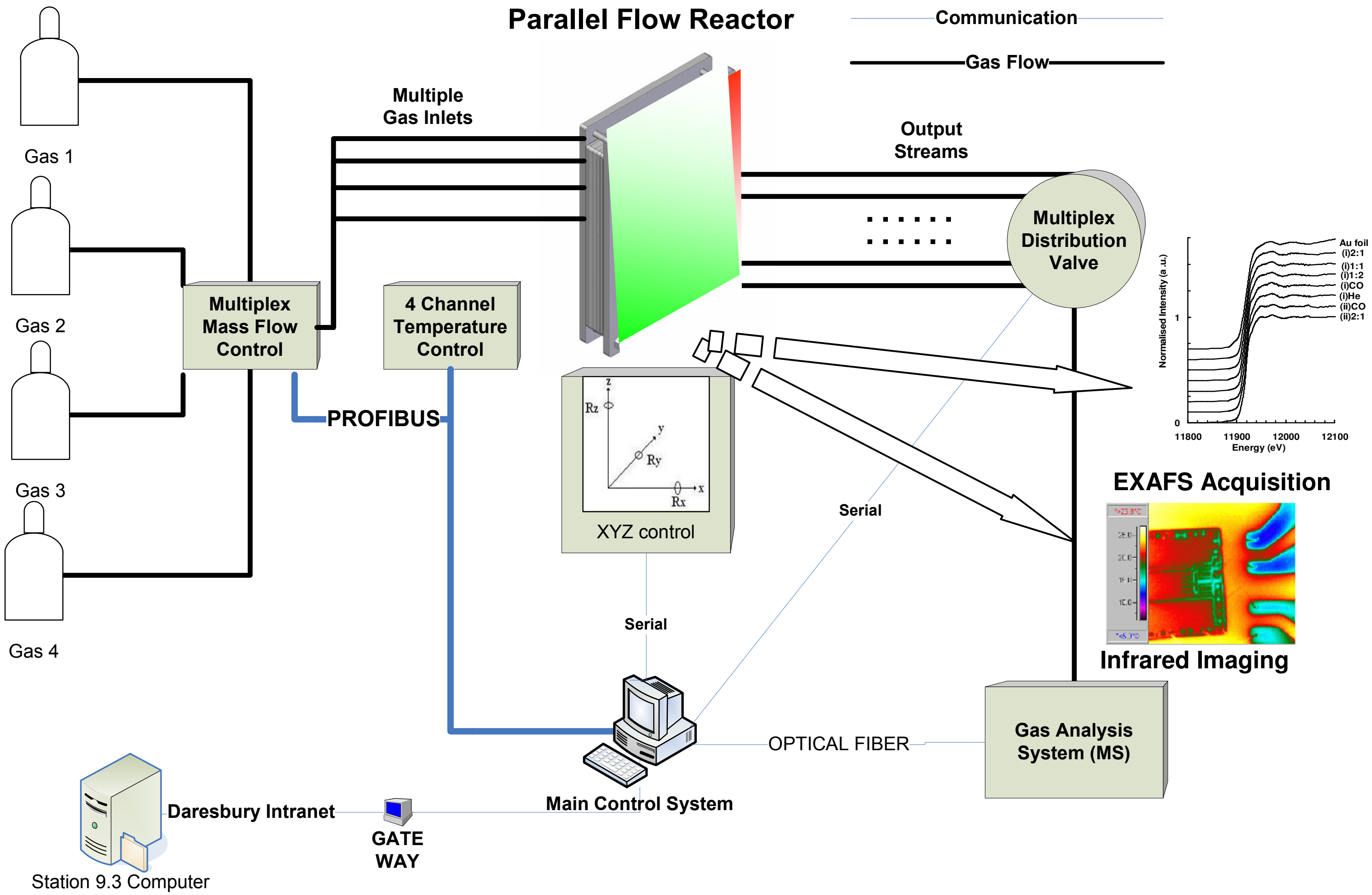


12x Gas Distribution

and Gas Analysis

Positioning
XYZ

XAS beamline becomes part of an automated laboratory



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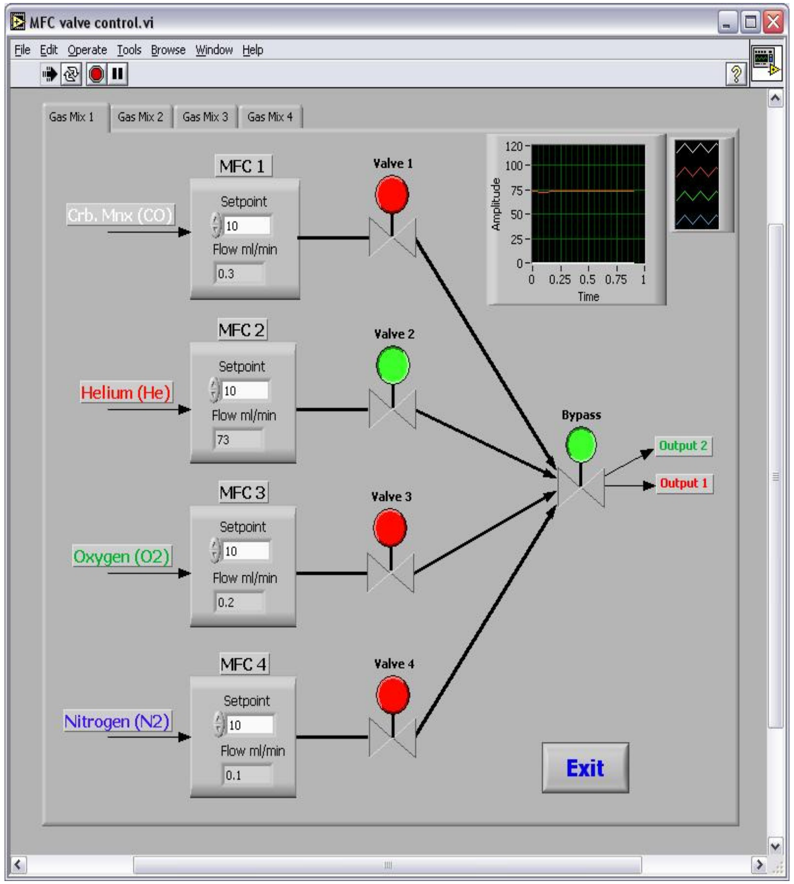
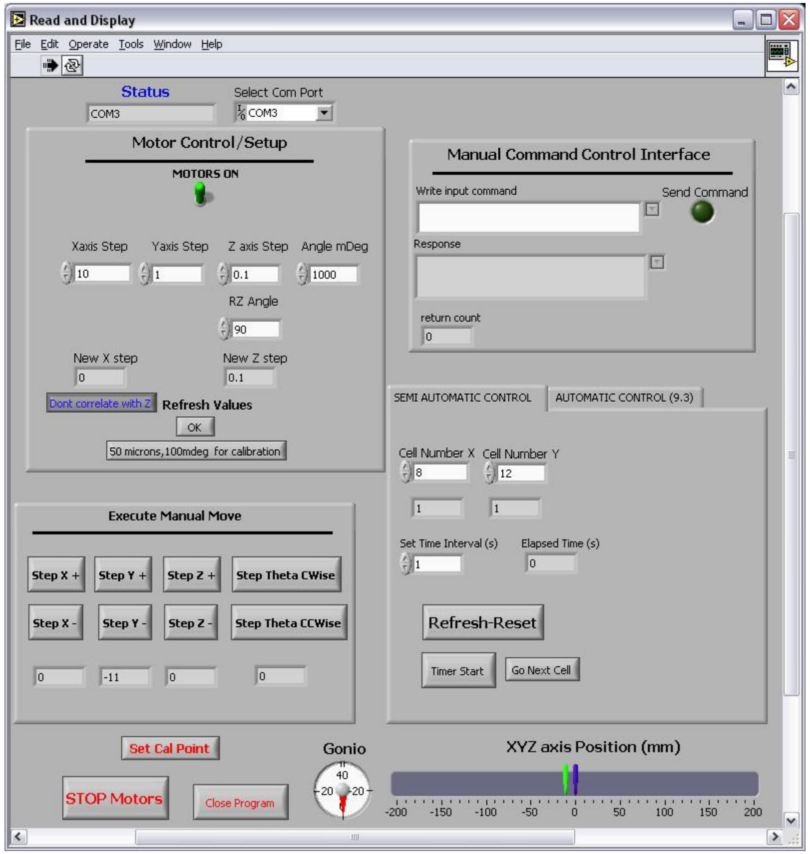
User Interface



Multiplex Gas Control



Automated positioning

Efficient *operando* XAS experimentation but *not* primarily a catalyst discovery tool…

- Screening of catalysts is based on activity measurements – MS, GC, GC-MS, HPLC, etc - no need for *operando* XAS in screening
- Role of *operando* XAS is generation of *deep understanding* of structure-activity relationships – enabling the formation of new hypotheses for further catalyst synthesis

- *Operando* HT XAS allows studies of more complex systems
- Optimisation of the use of photons
- Small samples – need small beams
- Compatibility with 96-well standard facilitates efficient ‘send-in’ service measurements

Lots of experiments - do not under-appreciate serendipity…

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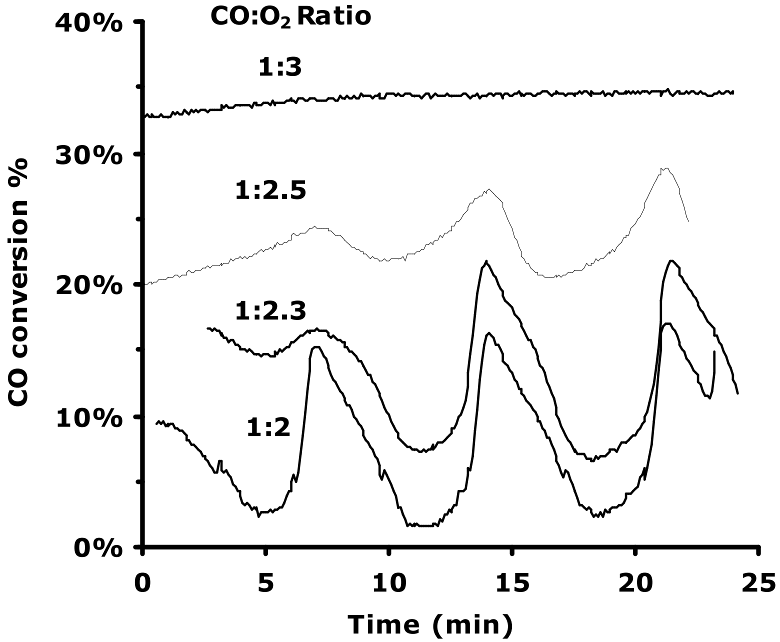
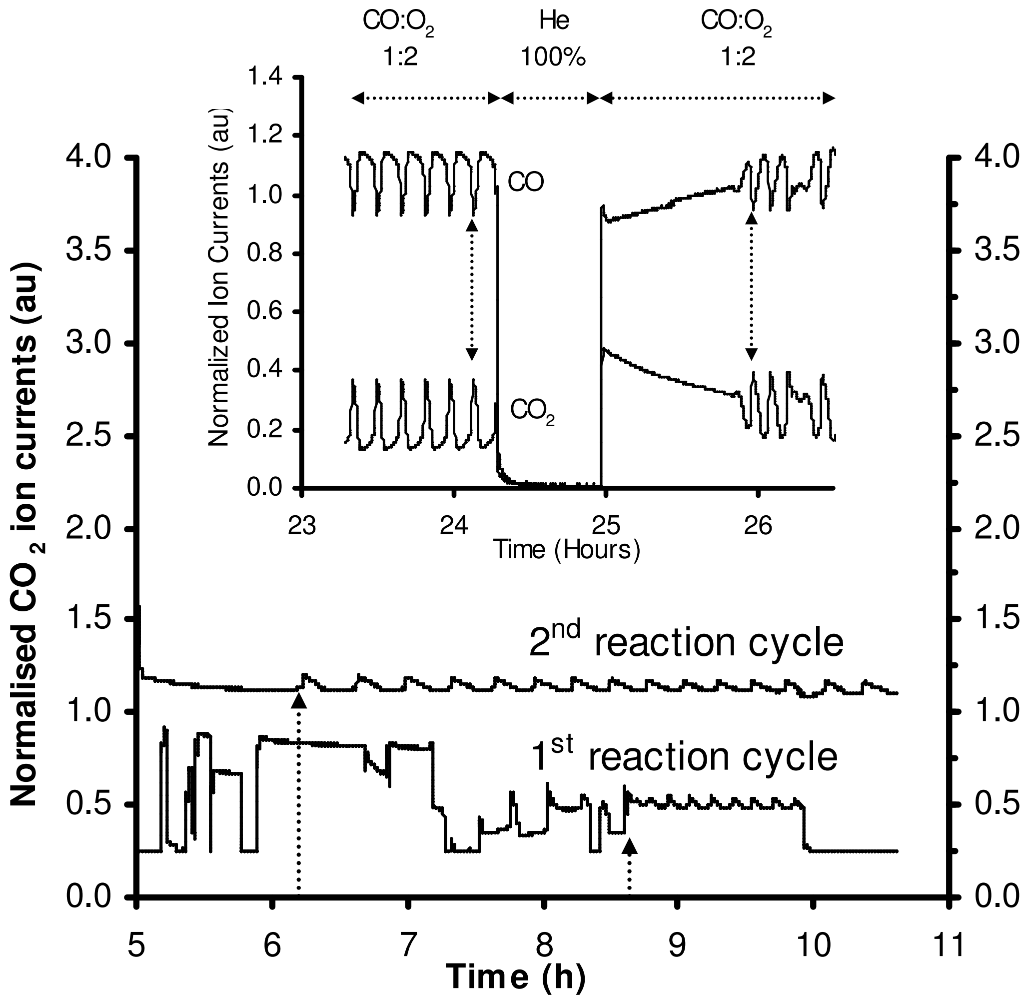
Discovery of an oscillatory catalytic reaction during XAS experiments...

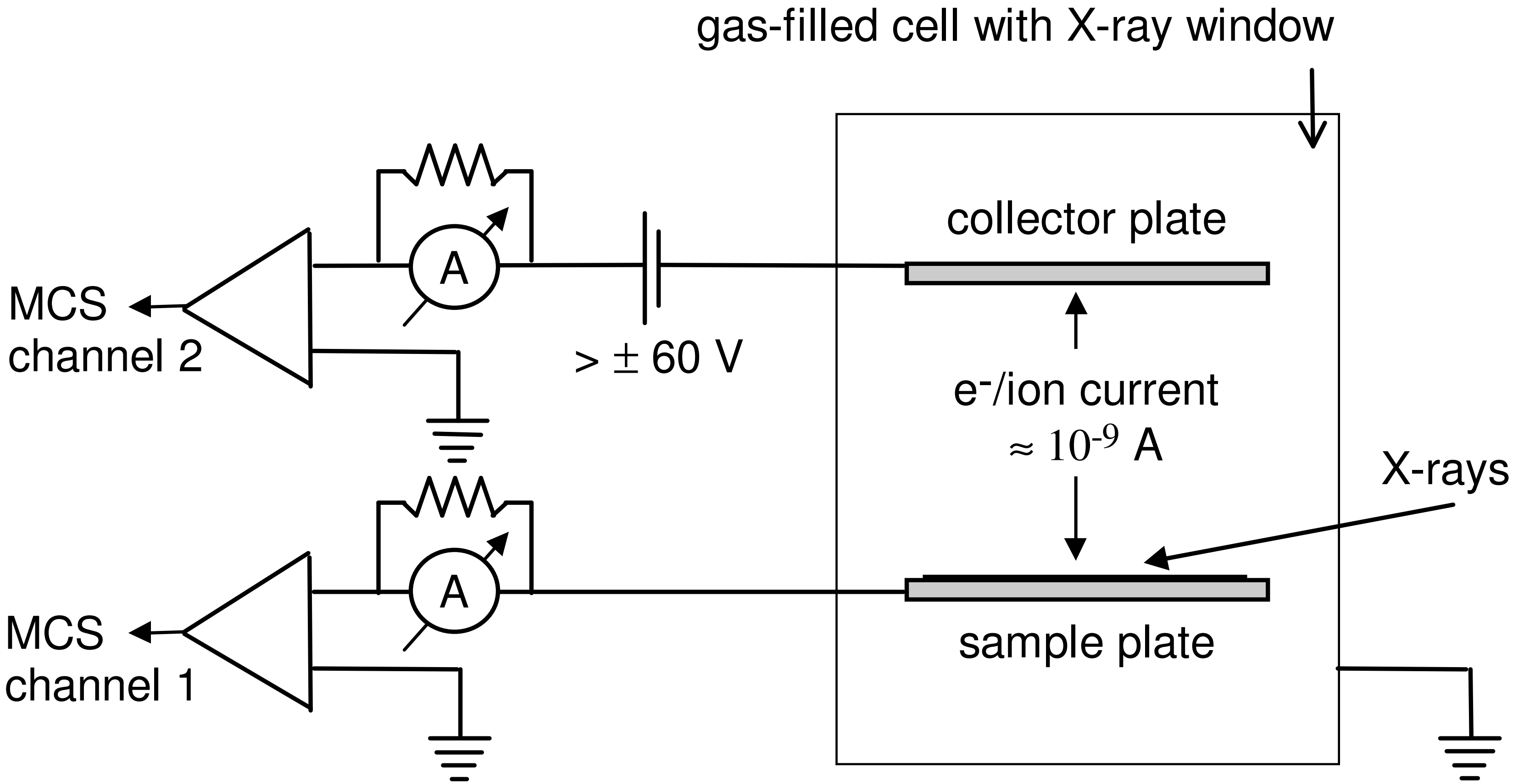




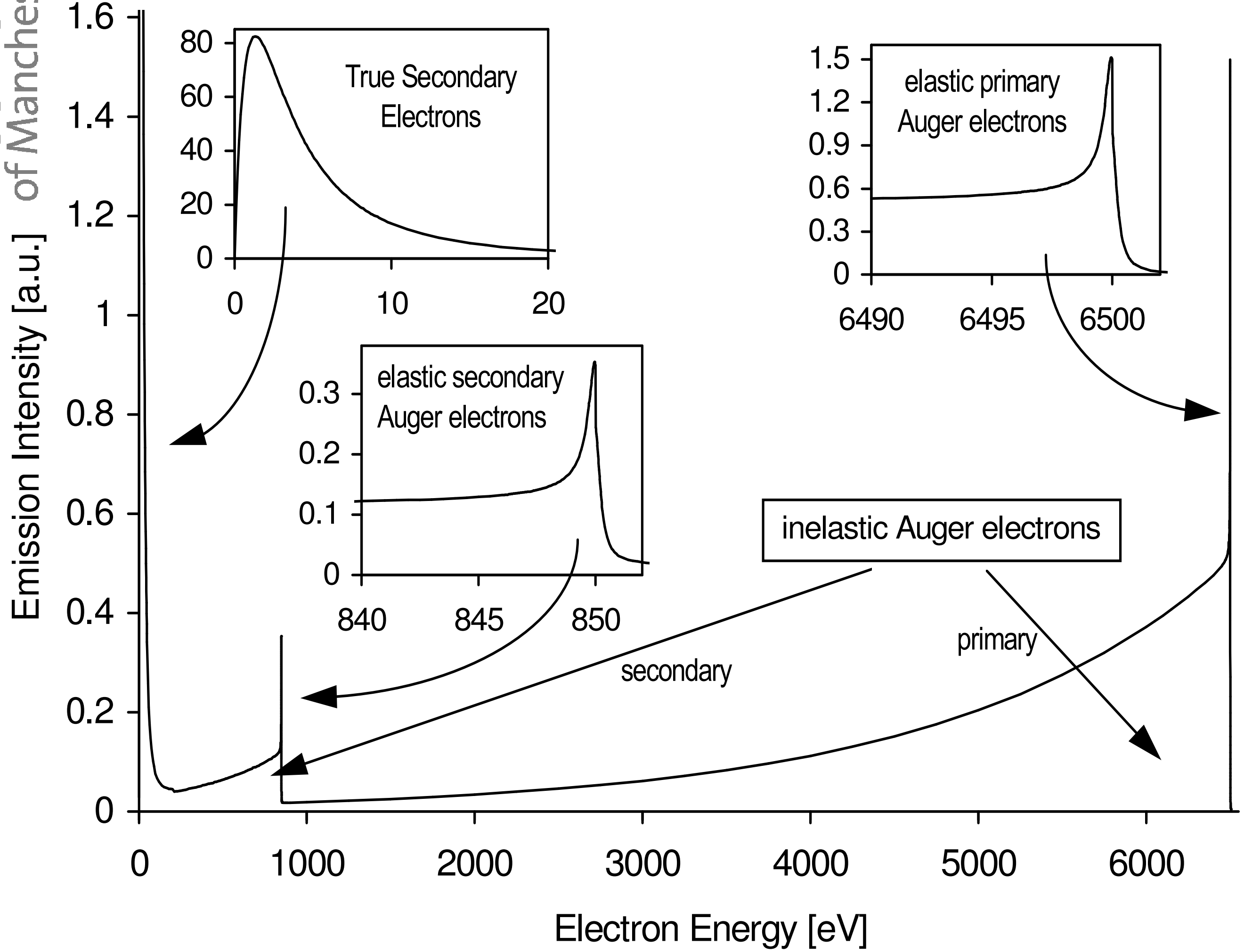
Time-resolved XAFS would be nice...

Non-Destructive Microanalysis

Total electron-yield XAS in gaseous environment



Secondary vs. Auger vs. Total Electron-Yield



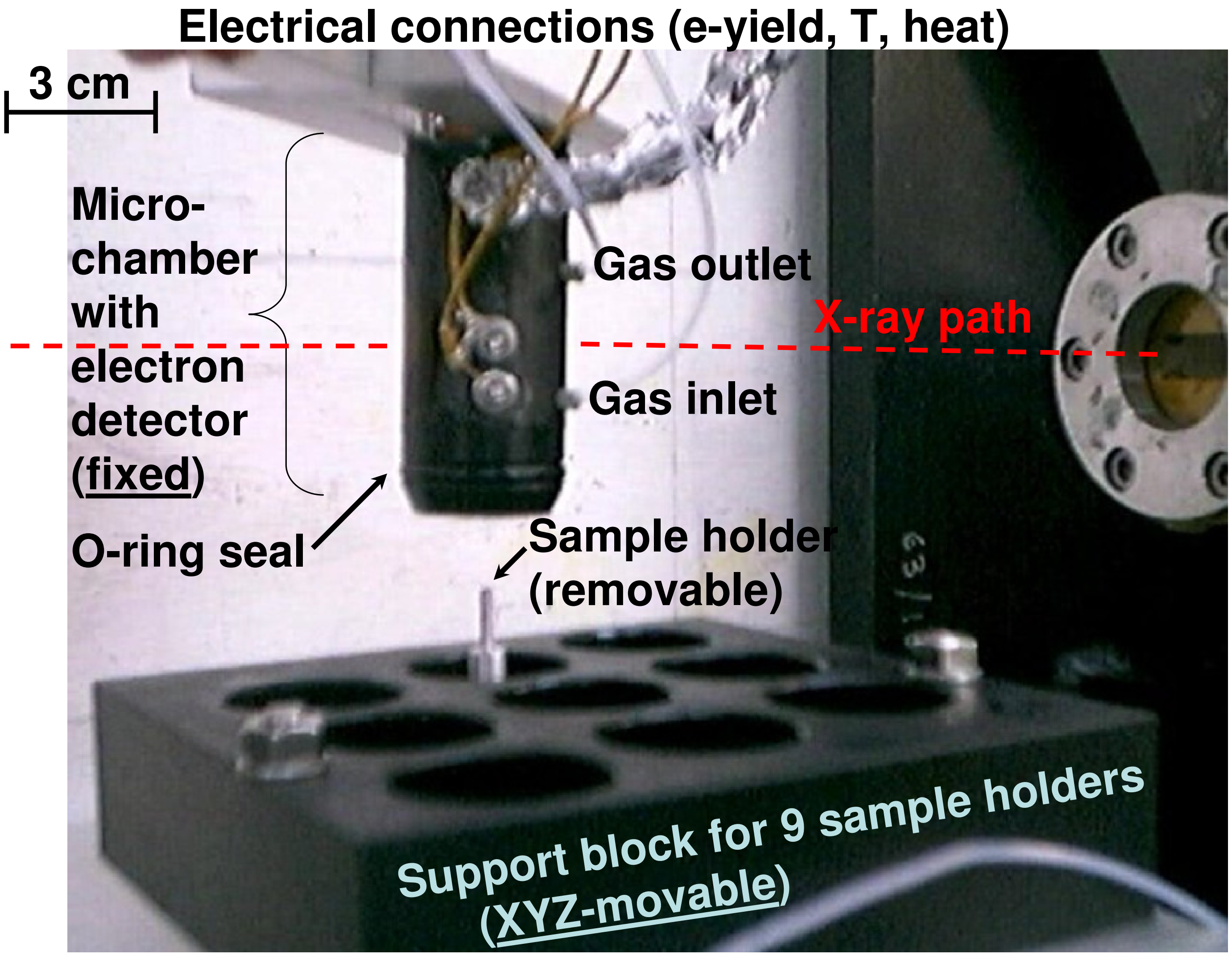
- Auger-yield: most surface sensitive, but very low intensity
- Total yield = inelastic Auger electron yield + secondary yield
- Inelastic Auger and Secondary yield: less surface sensitive

9-sample array for *operando* TEY XAS spectroscopy

Small samples (< 1 mm)

Thin films

In principle polarisation dependent measurements possible



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Homogeneous Catalysis

High/Medium-Throughput Liquid Phase Platform

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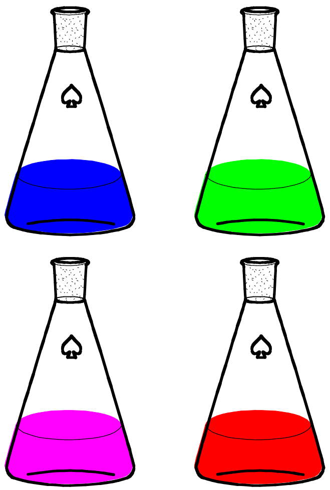
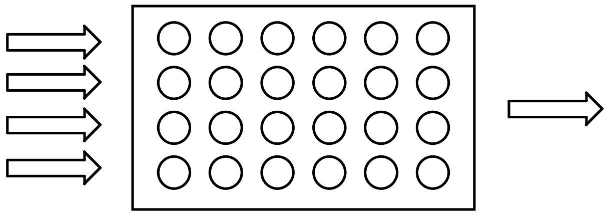


<u>Closed</u> Liquid Flow Reactor Arrays (5 x 4 cm)



- **<u>Removable</u>**
- **<u>Storable</u>**
- **<u>Disposable</u>**

Analytical Methods (current)

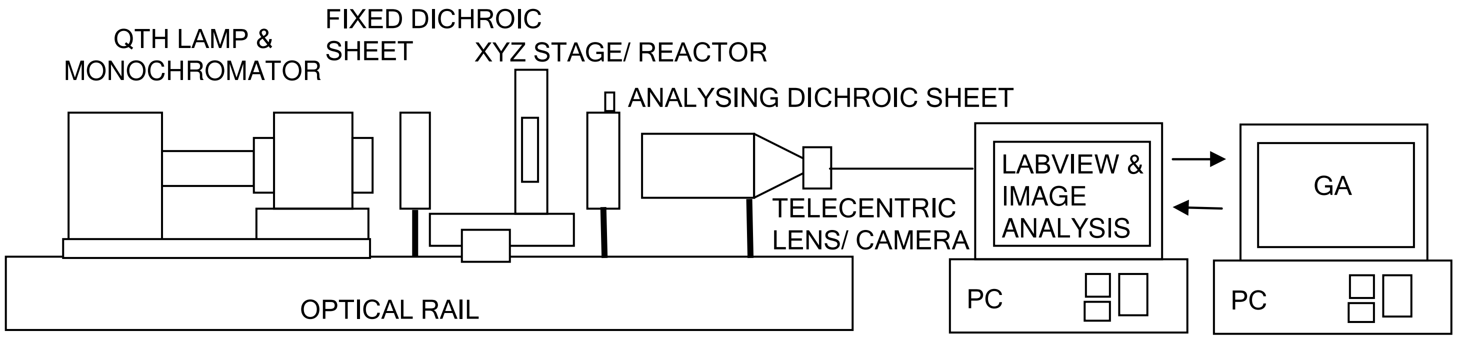
CMOS Camera
Image analysis
Polarimetry (birefringence)
XAS (synchrotron)
UV-Vis
Powder XRD
Temperature (IR camera)

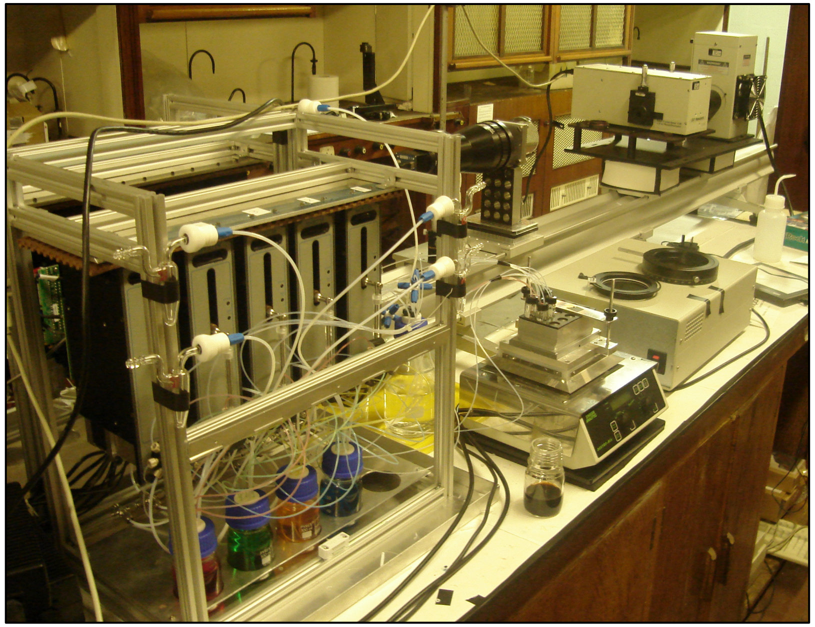
- Currently 20 reactors (300 μl), up-scaleable in increments of further 20 (£1-2k per reactor)
- Individually addressable
- Batch operation
- On-line *and* off-line analysis techniques
- Self-optimising target search (24h operation, GA/neural net parameter search)
- Cleaning cycles integrated (solvents/N_2 gas)

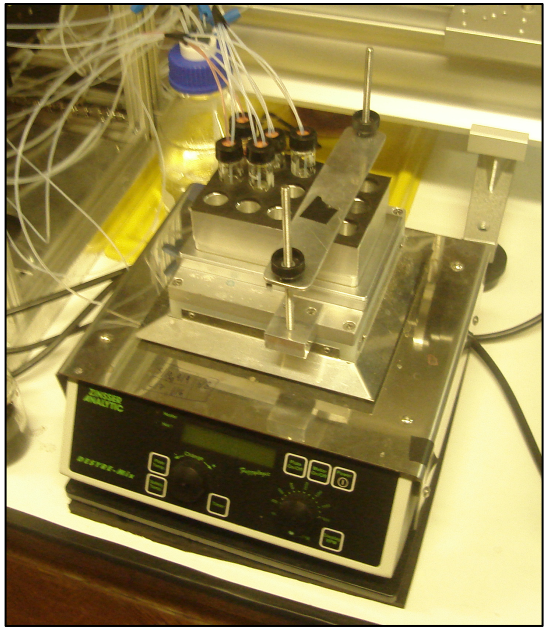
Analytical Methods (planned)

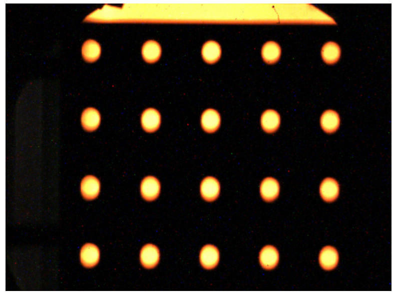
Fluorescence
Light scattering
Electrochemical Methods

Automated Batch Reactor Synthesis with Spectroscopic Readouts









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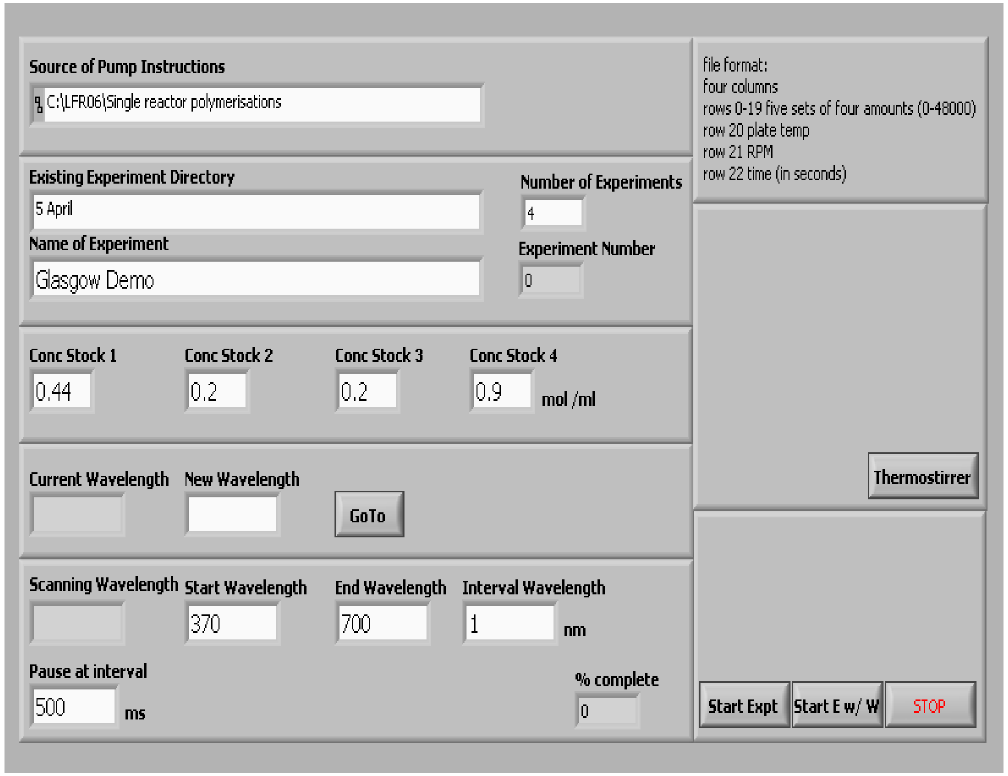
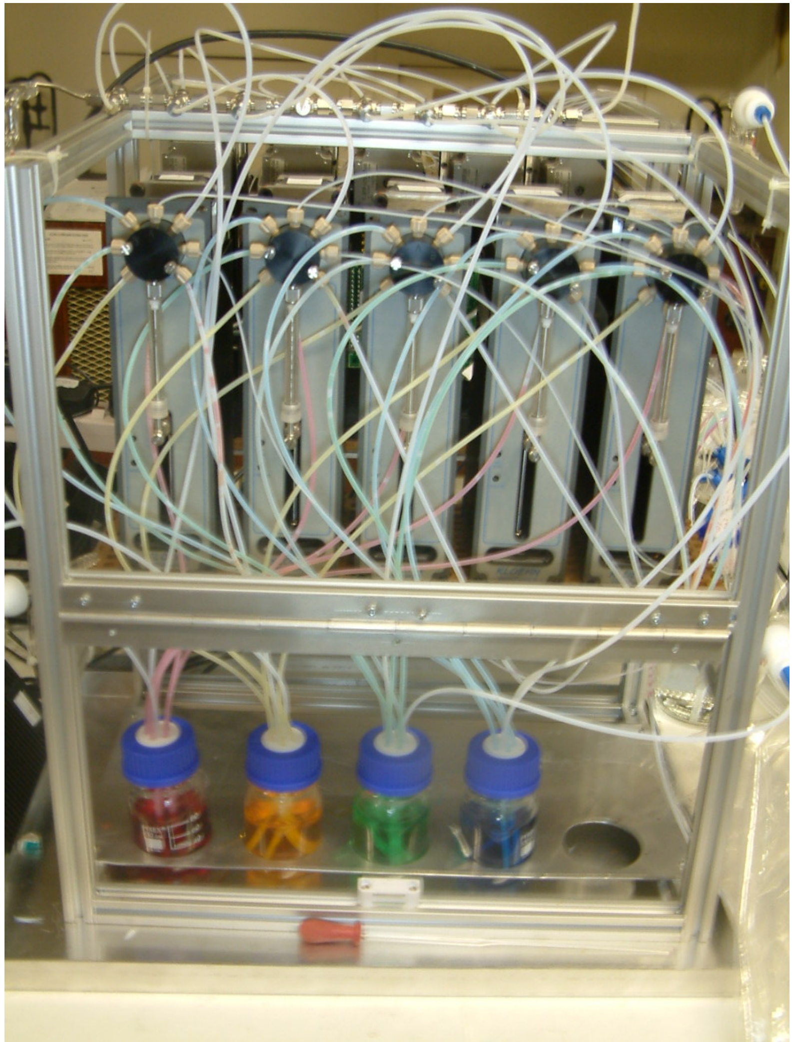
Reactants

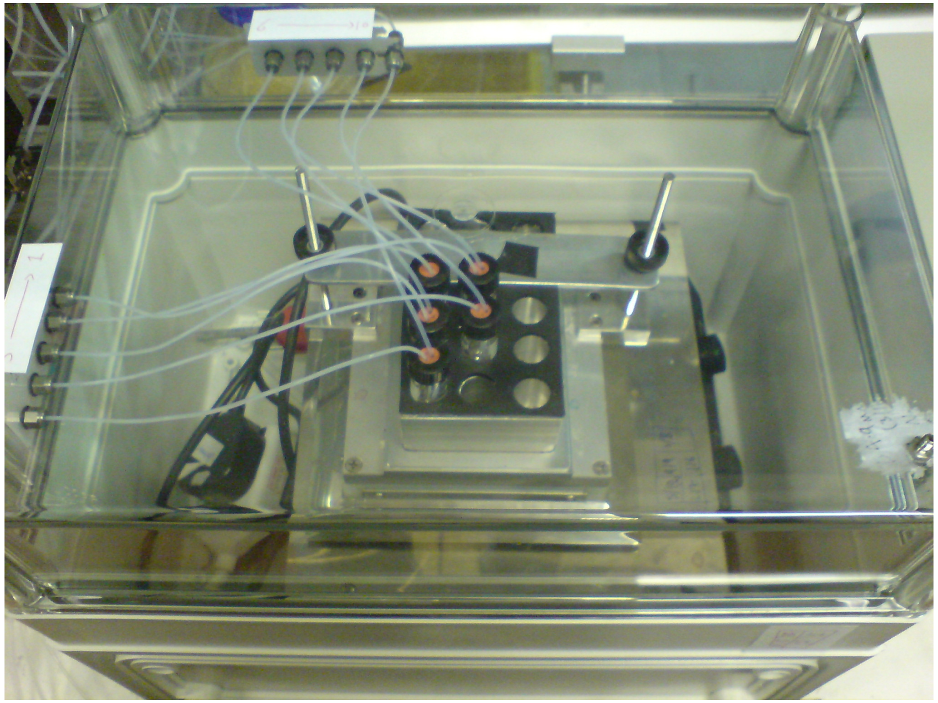
Syringe pump rack

Labview control interface



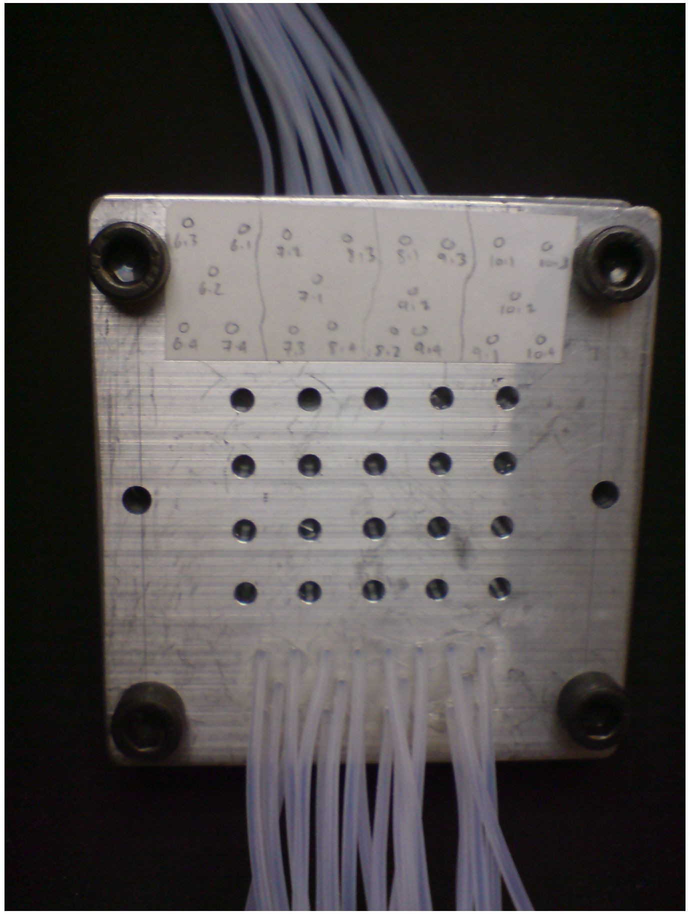


Batch reactors



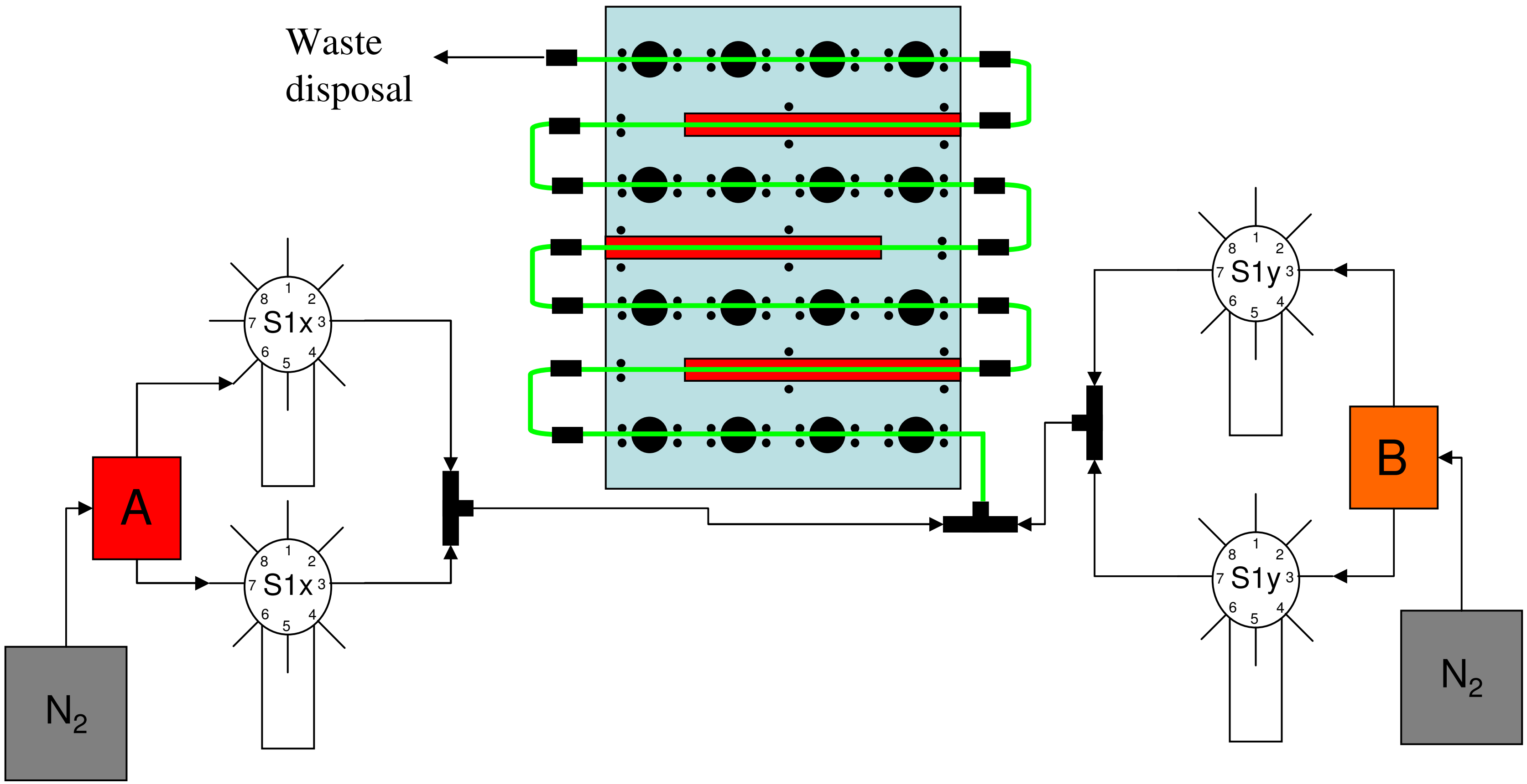
Inert atmosphere enclosure computer-controlled heater/vortexer

Plastic Chips for Assaying by Spectroscopy



Low cost, disposable, storable, easily re-designed for purpose

Continuous Flow Reactor for In Situ Assaying of Reactions, and for Dynamic Libraries

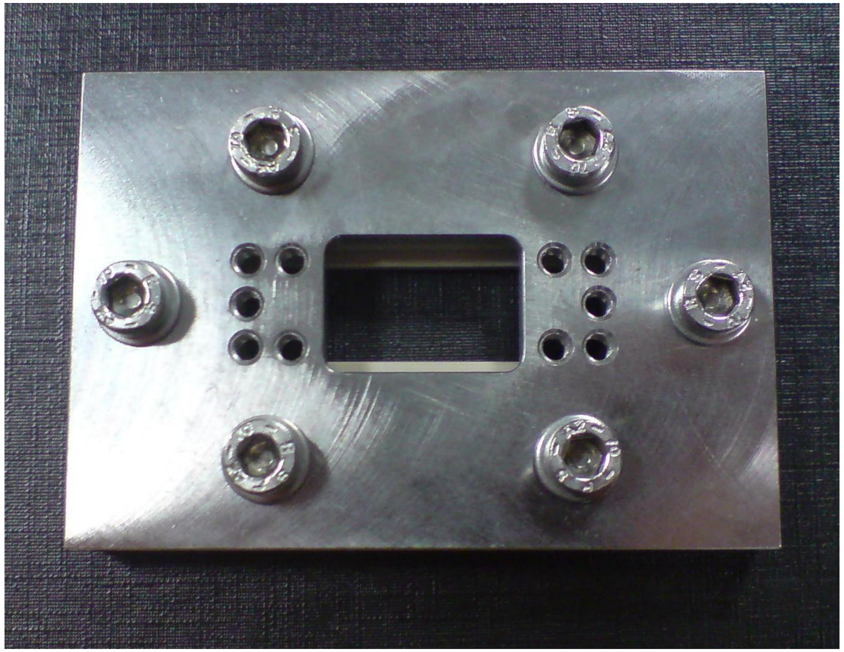


Microfluidic Continuous Flow Reactor

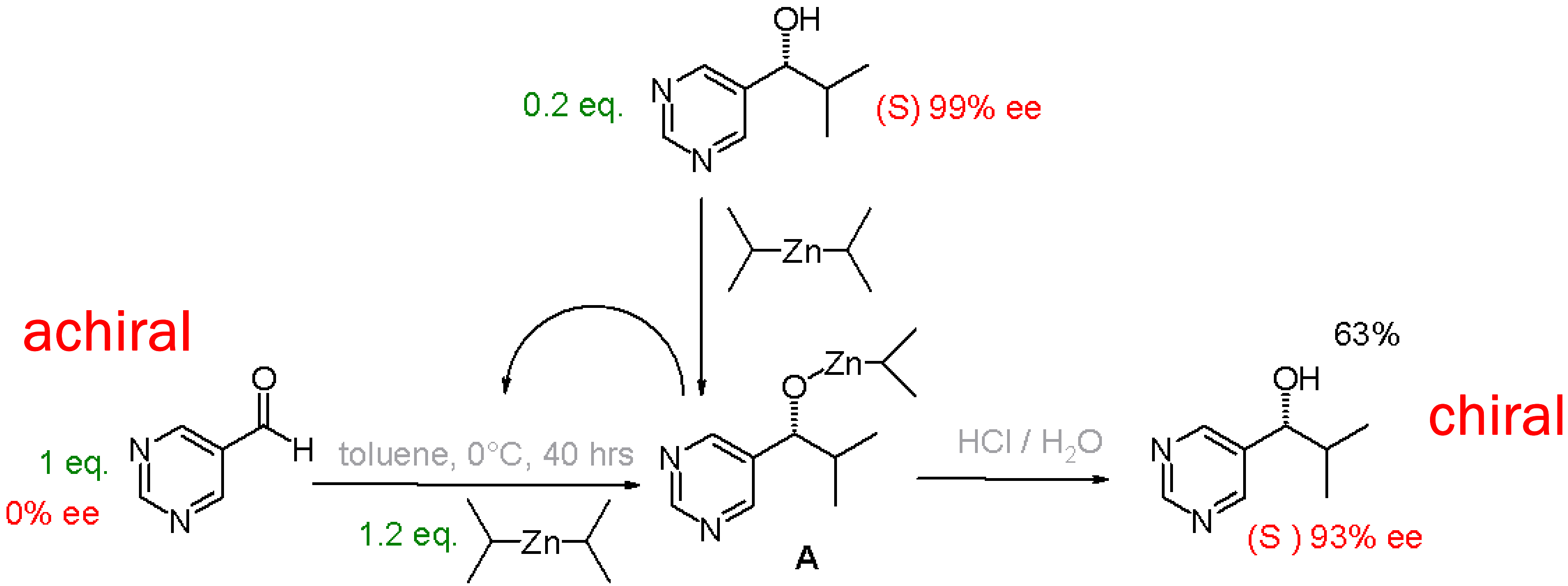
Microfluidic glass chip

Heatable

Size determined to suit **Soai chiral amplification**

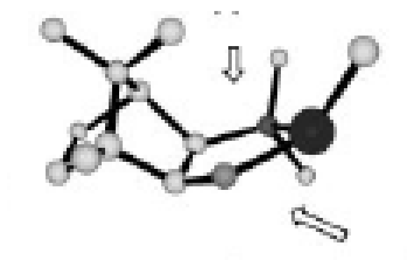


Soai autocatalytic reaction

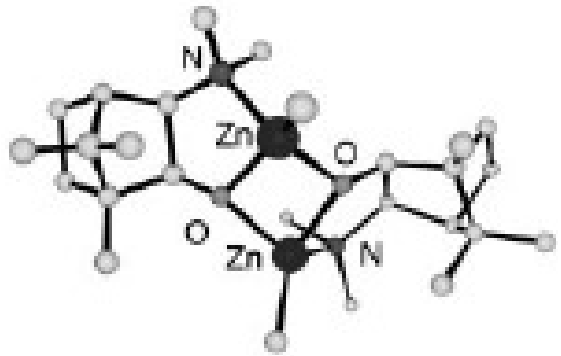


Small imbalances in enantiomeric excess and/or very small concentrations of chiral auxiliaries can generate almost enantiopure product

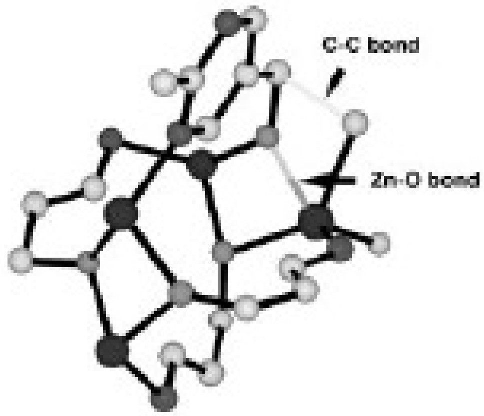
Mechanistic aspects of the Soai reaction



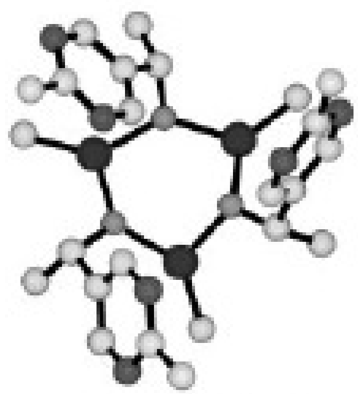
Monomer



Dimer



Tetramer



Trimer

Transition state structures proposed from NMR, calorimetric and computational studies

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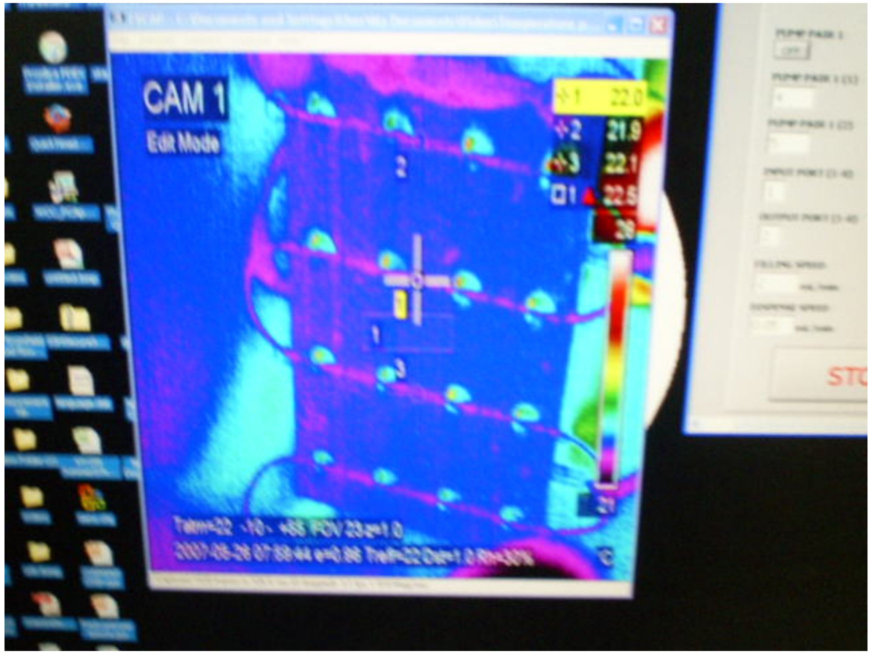

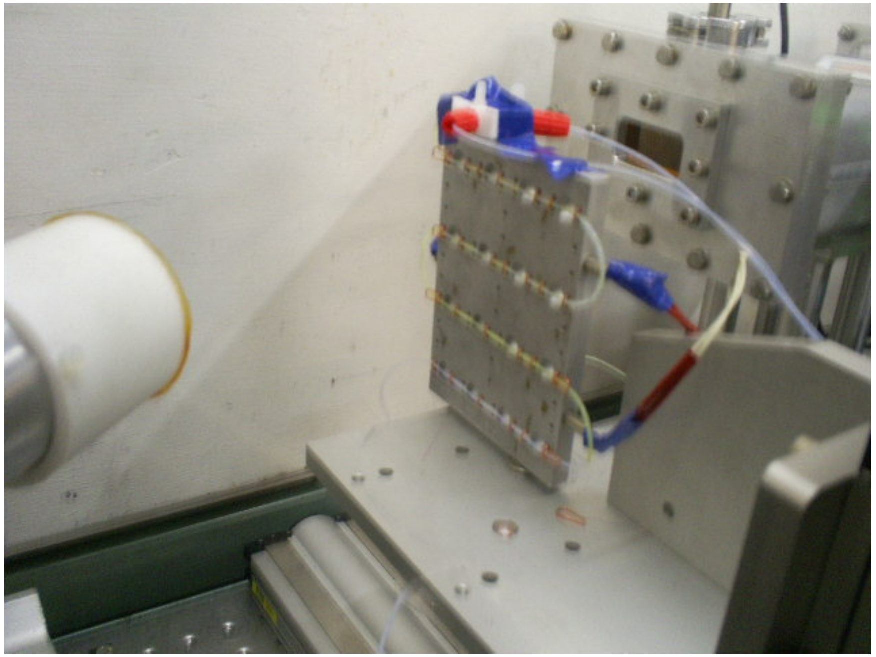

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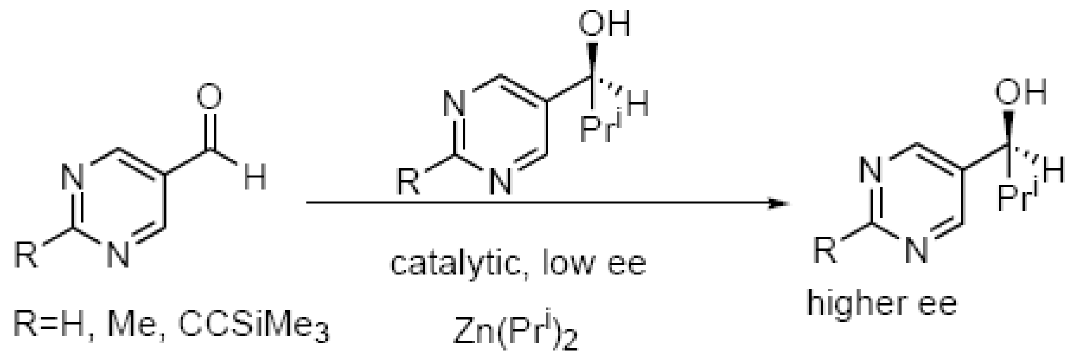
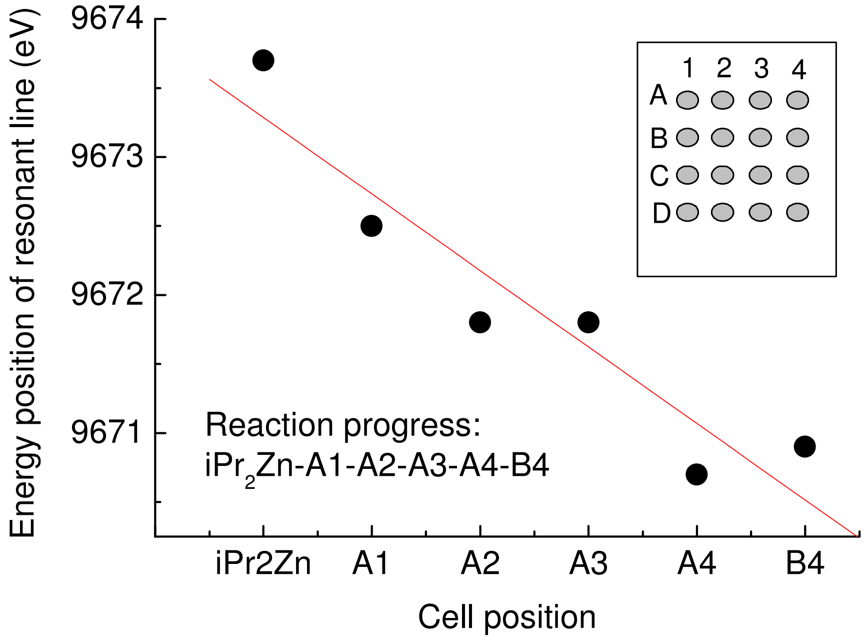
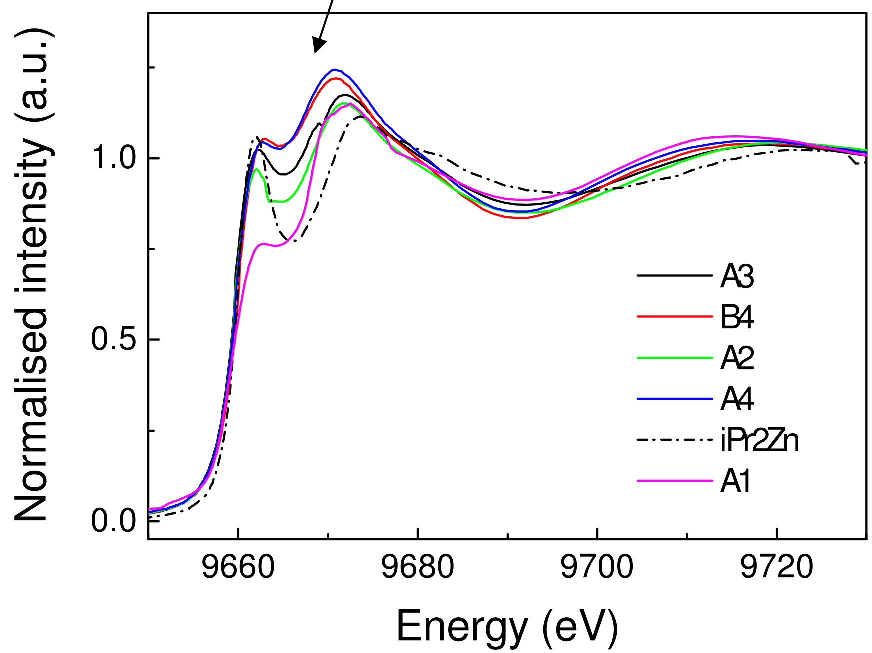
In situ XAS HT dynamic experimentation

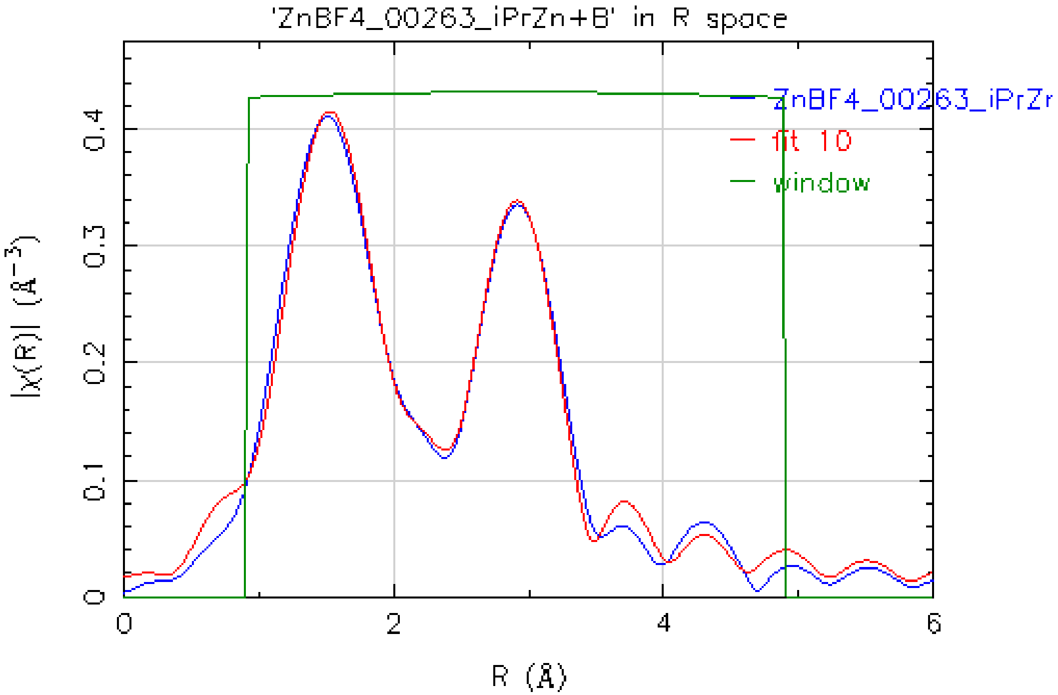


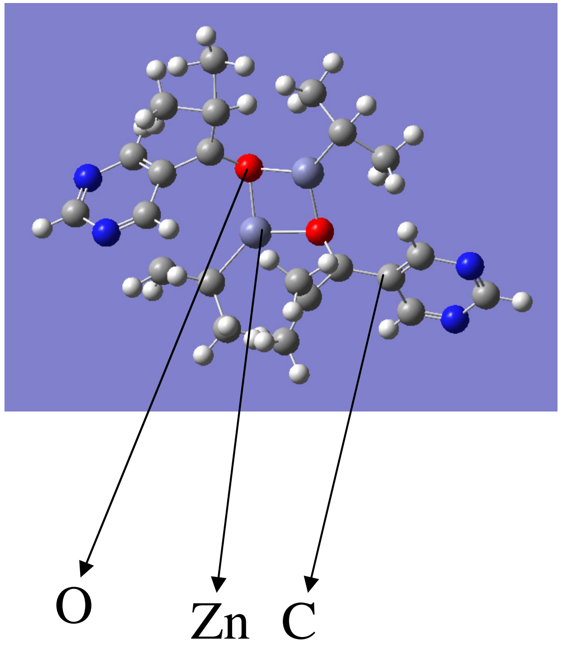
Enormous variations in valence orbitals !!





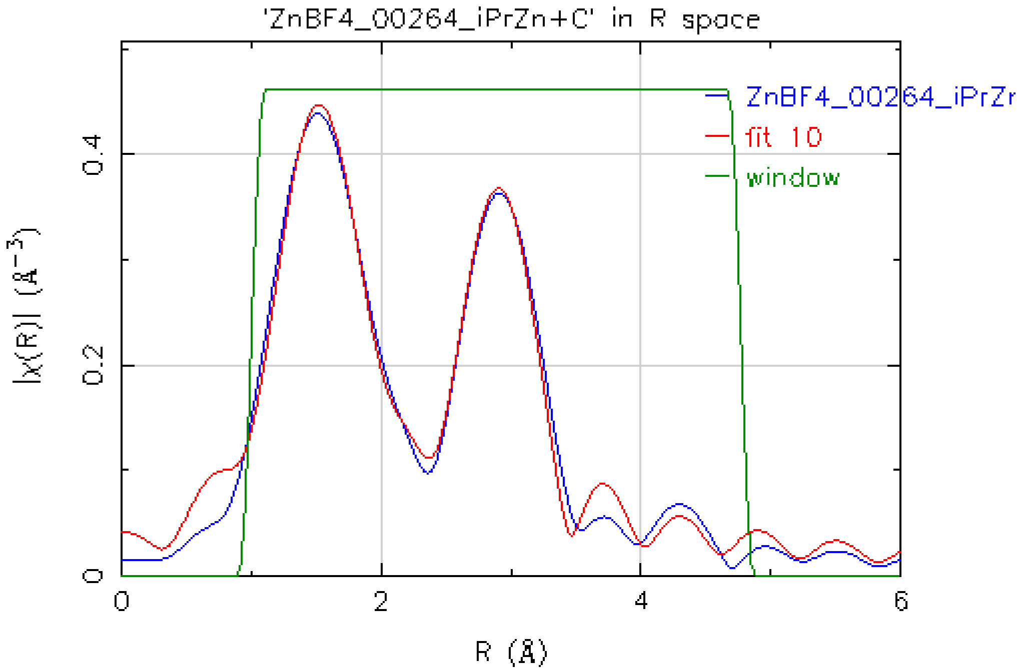
iPr2Zn + Aldehyde B

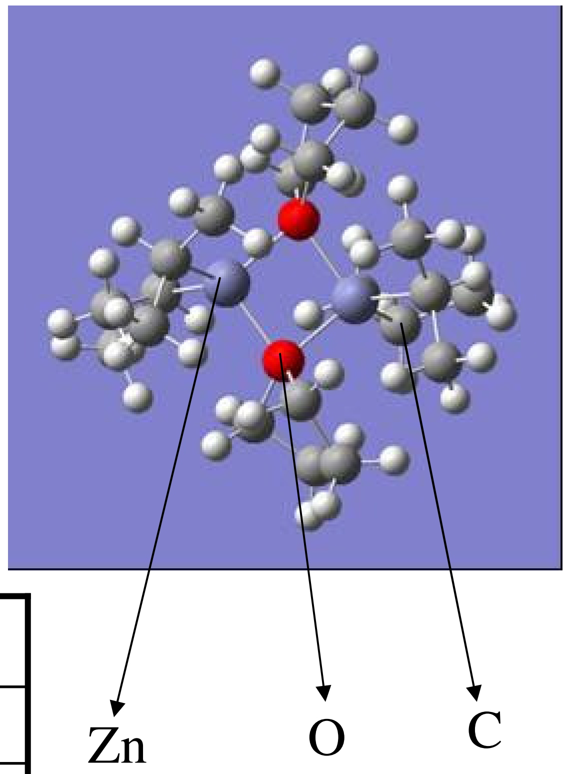




	d(Å)	N	σ^2 (10^{-3}Å^2)	E_o(eV)	R(%)
Zn-O/C	1.953	2.046	11	5.652	0.5
Zn-Zn	3.2093	0.77	27		
Zn-O/C	3.8371	5.859	13		

iPr2Zn + Aldehyde C





	d(Å)	N	σ^2 (10^{-3}Å^2)	E_o(eV)	R(%)
Zn-O/C	1.953	2.23	10	5.095	0.7
Zn-Zn	3.2093	0.94	39		
Zn-O/C	3.8371	5.37	11		

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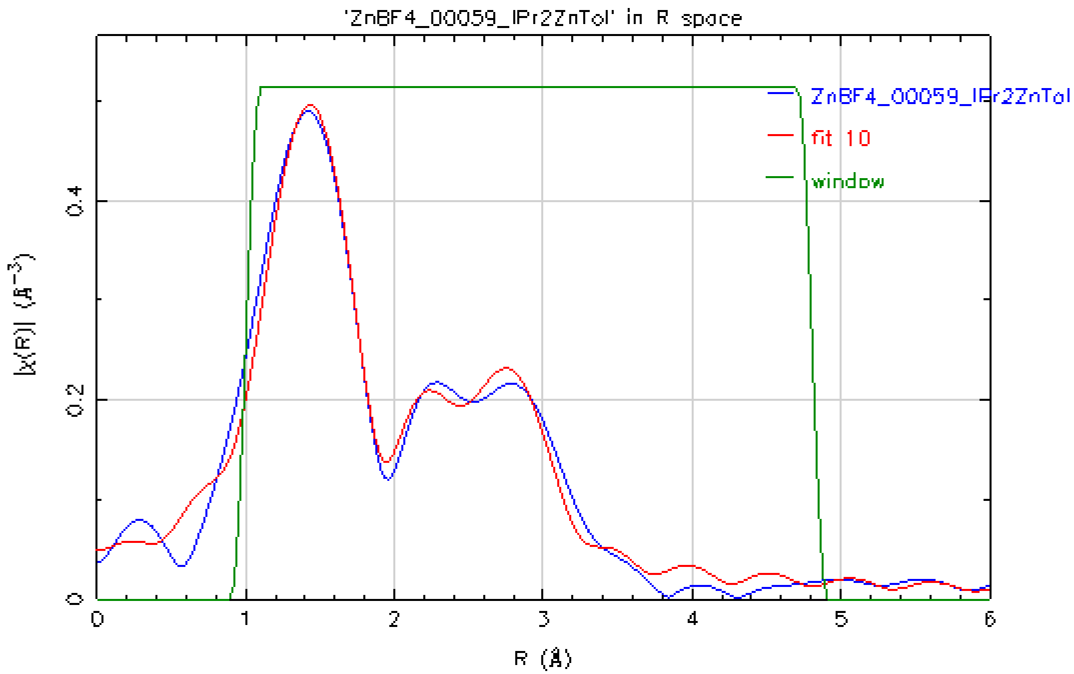
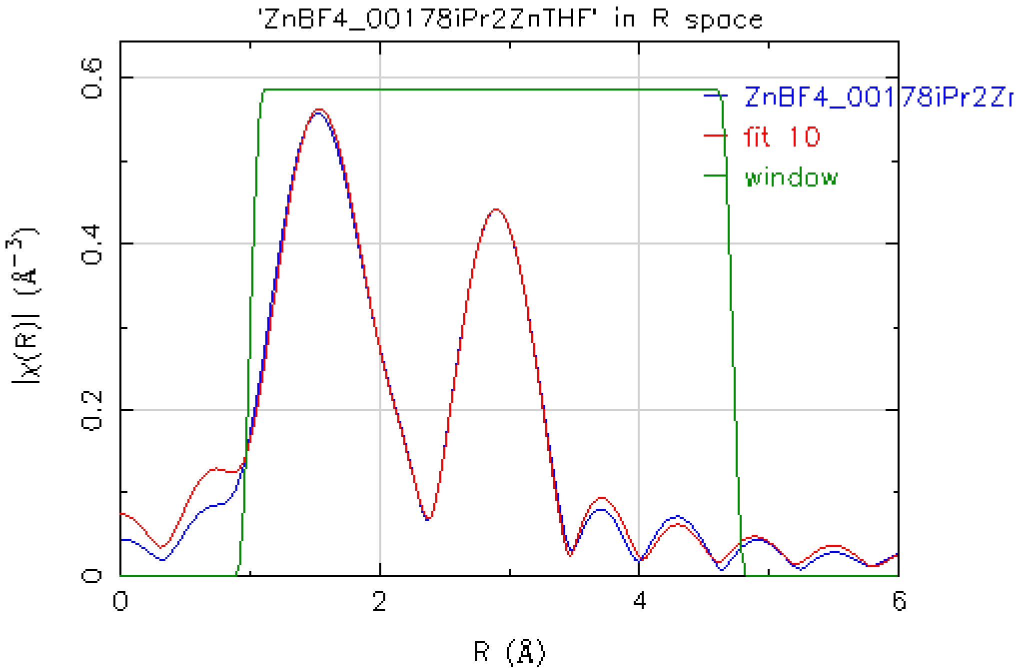
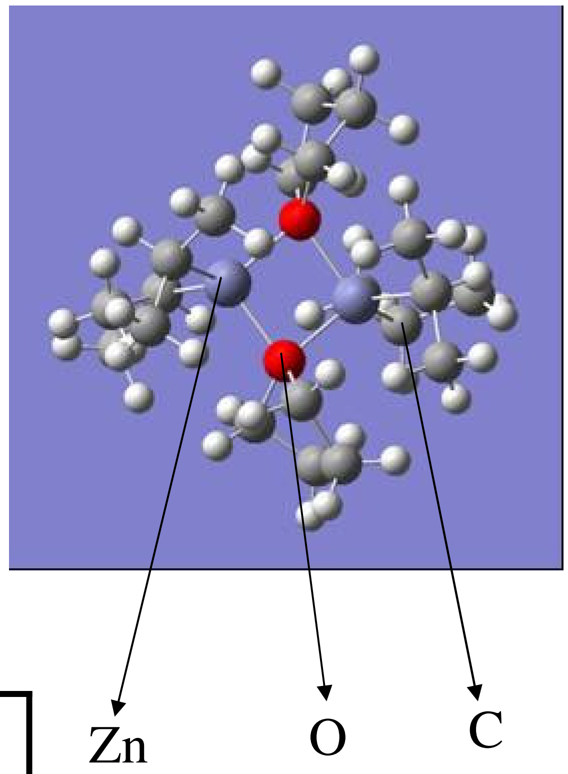
Solvent Effects: iPr_2Zn in Toluene



	d(Å)	N	σ^2 (10^{-3}Å^2)	E_o(eV)	R(%)
Zn-C	1.953	1.52	4.67	1.49	10.5
	-	-	-		
Zn-C	3.8371	5.41	22		

Solvent Effects: iPr_2Zn in THF





	d(Å)	N	σ^2 (10^{-3}Å^2)	E_o(eV)	R(%)
Zn-O/C	1.953	2.59	6.3	4.69	0.14
Zn-Zn	3.2093	1.24	14		
Zn-O/C	3.8371	6.06	3.9		

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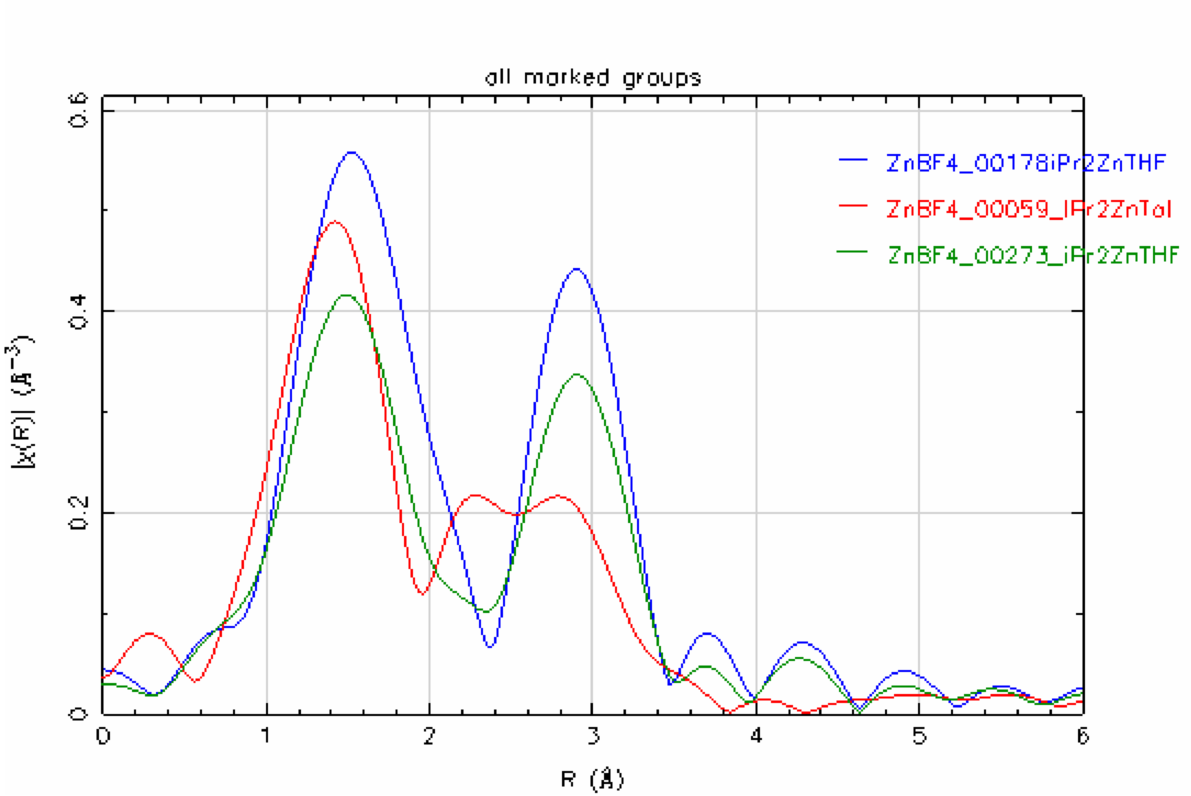
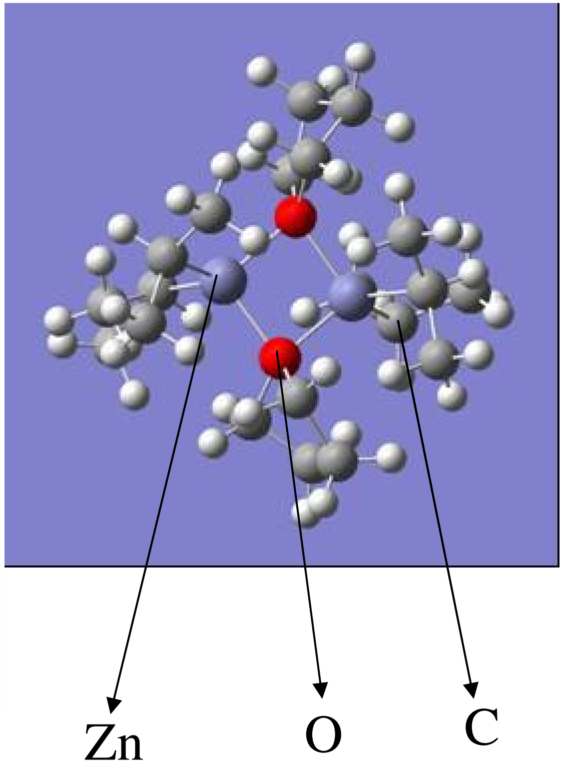
Solvent Effects: Mixture of THF/toluene

THF (tetrahydrofuran)





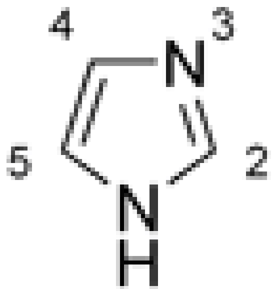
THF forms a stable dimer with *i*Pr_2Zn

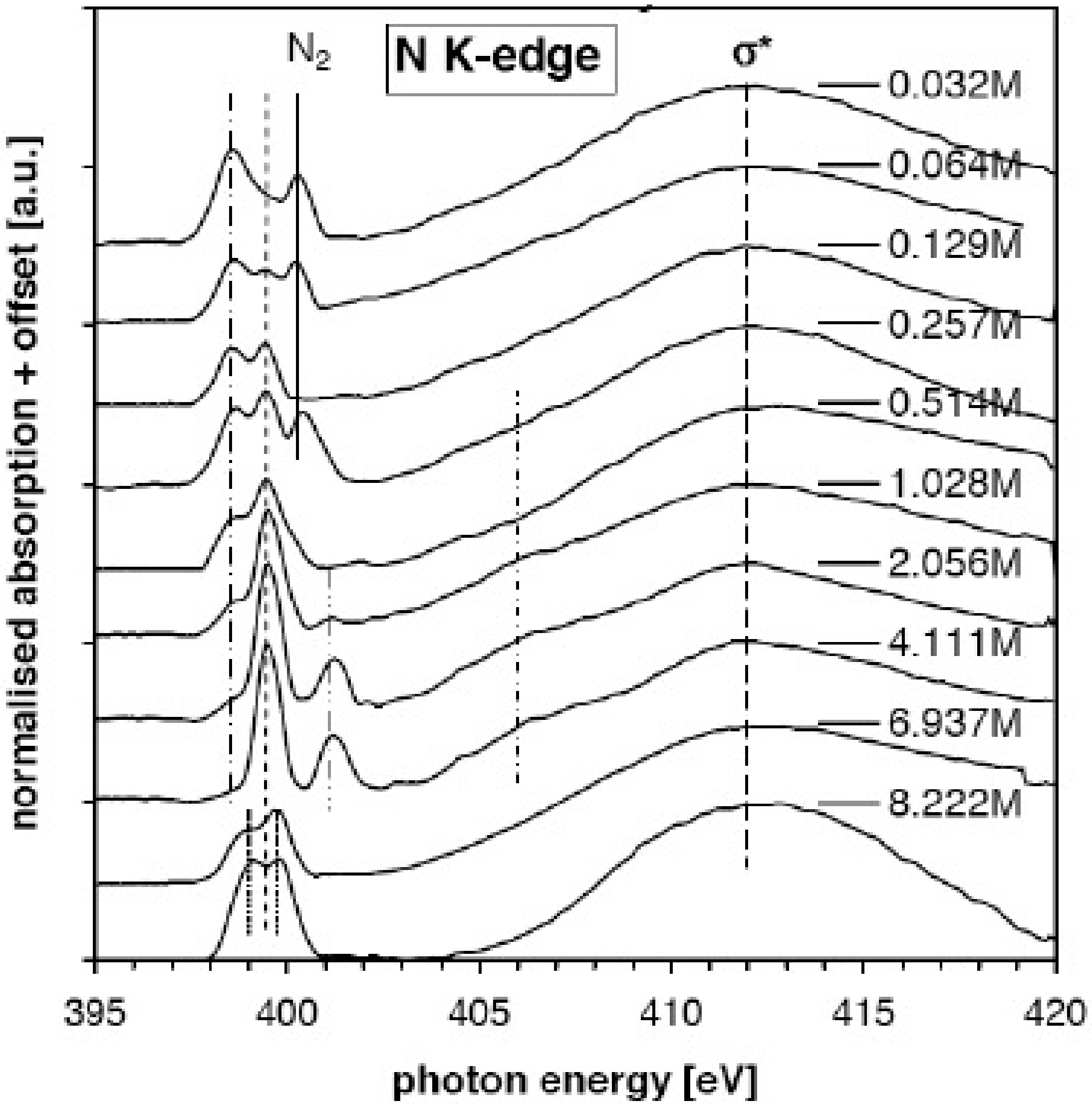
Outlook

Structure formation in solution / crystallisation: soft XAS

Example

Aqueous solutions of imidazole

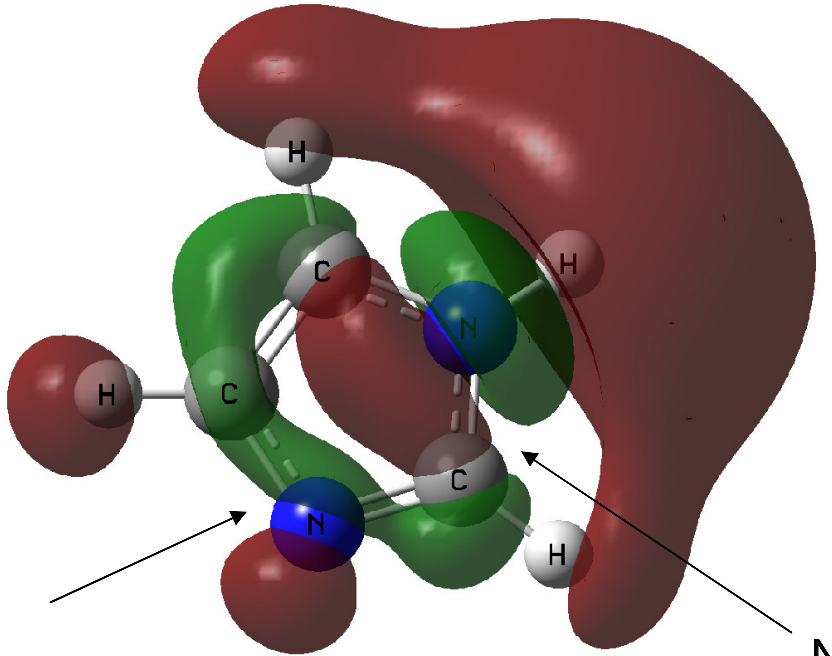




Virtual MOs in Isolated Molecule

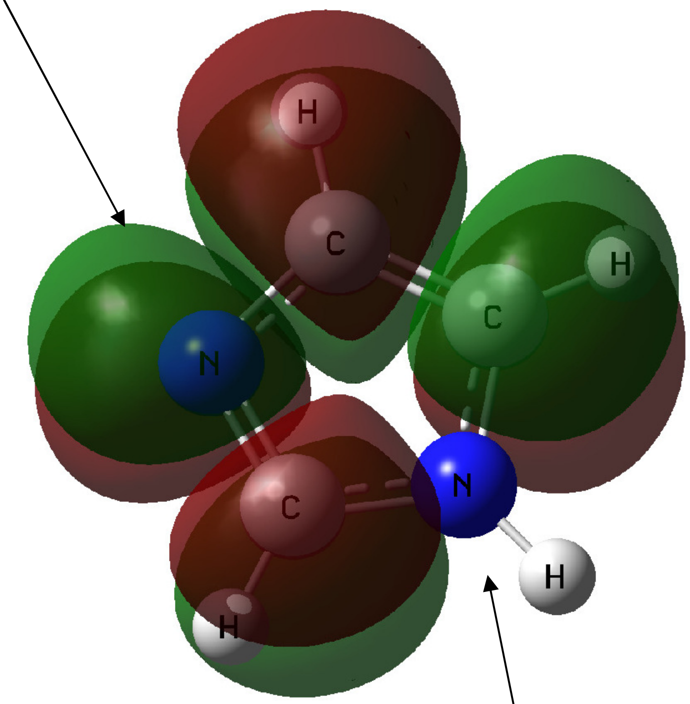
LUMO

N=



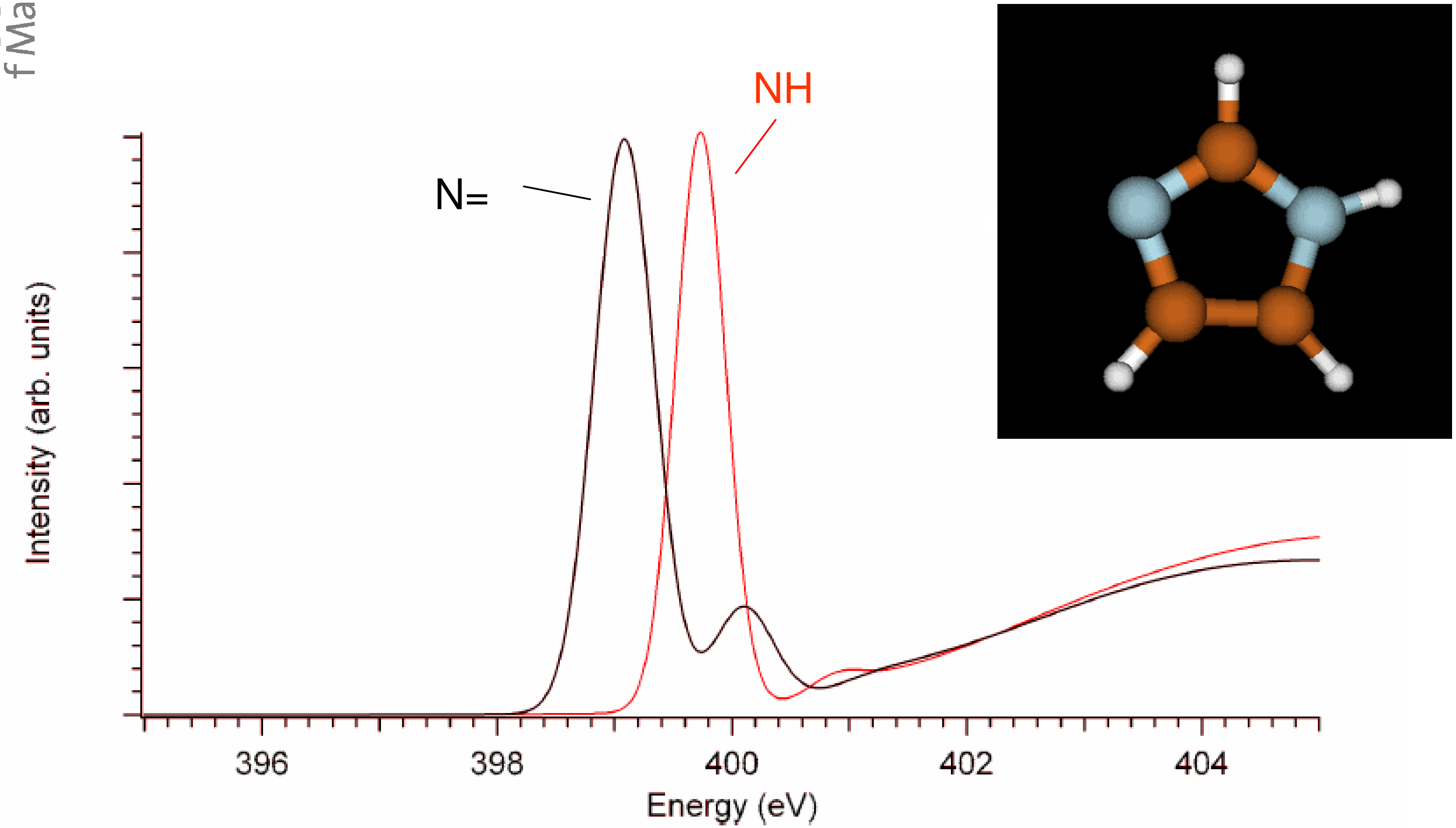
N=

NH

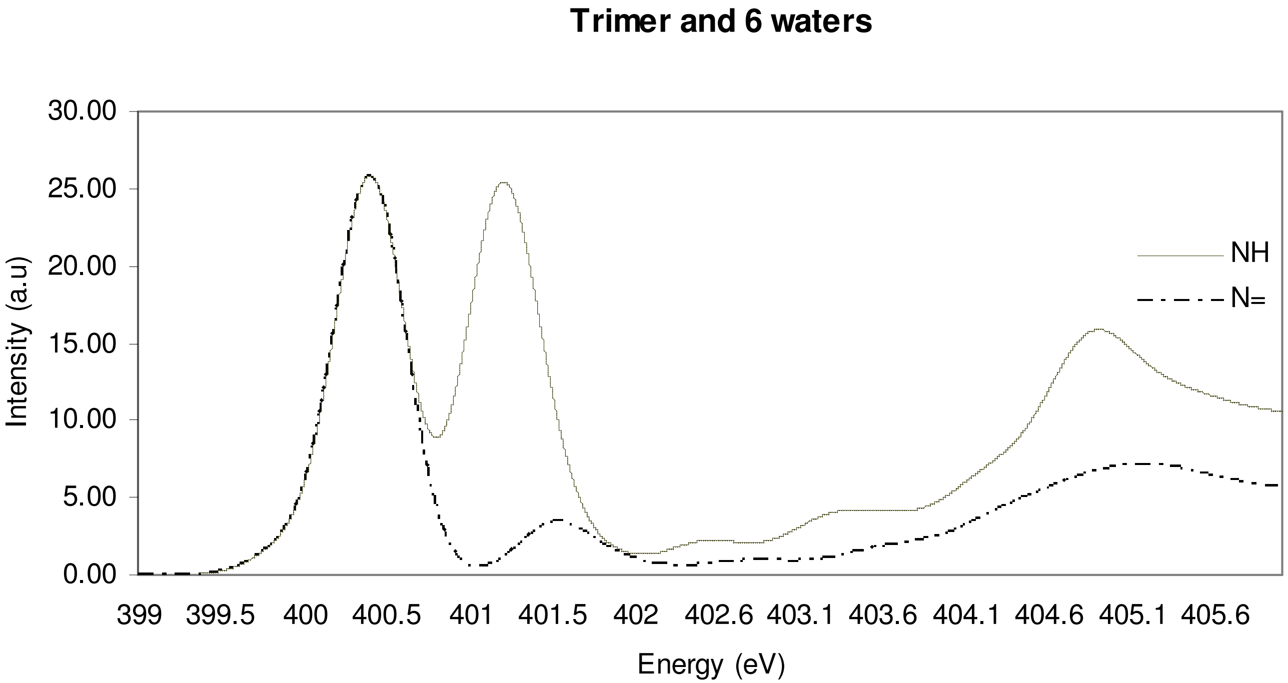


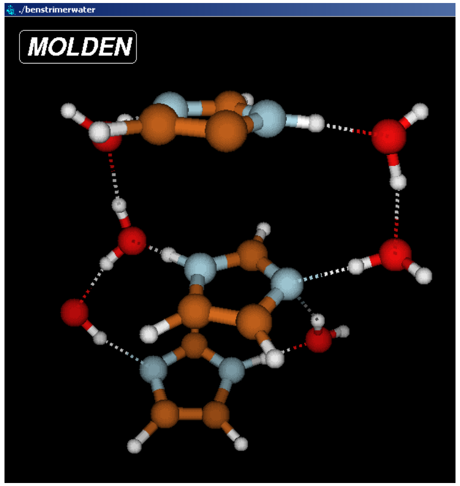
NH ‘excluded’

X-ray Absorption Calculated with StoBe Code



Stobe simulation of Gaussian optimised π-stacked trimer with waters





- Gaussian level of theory bhandh/6-311G **

Structure formation in solution / crystallisation: soft XAS

- Growth area for the future
- Opening up X-ray beamlines to new applications
- Currently cumbersome experiment at soft X-ray beamlines
- Would be great to do with LERIX-type experiment

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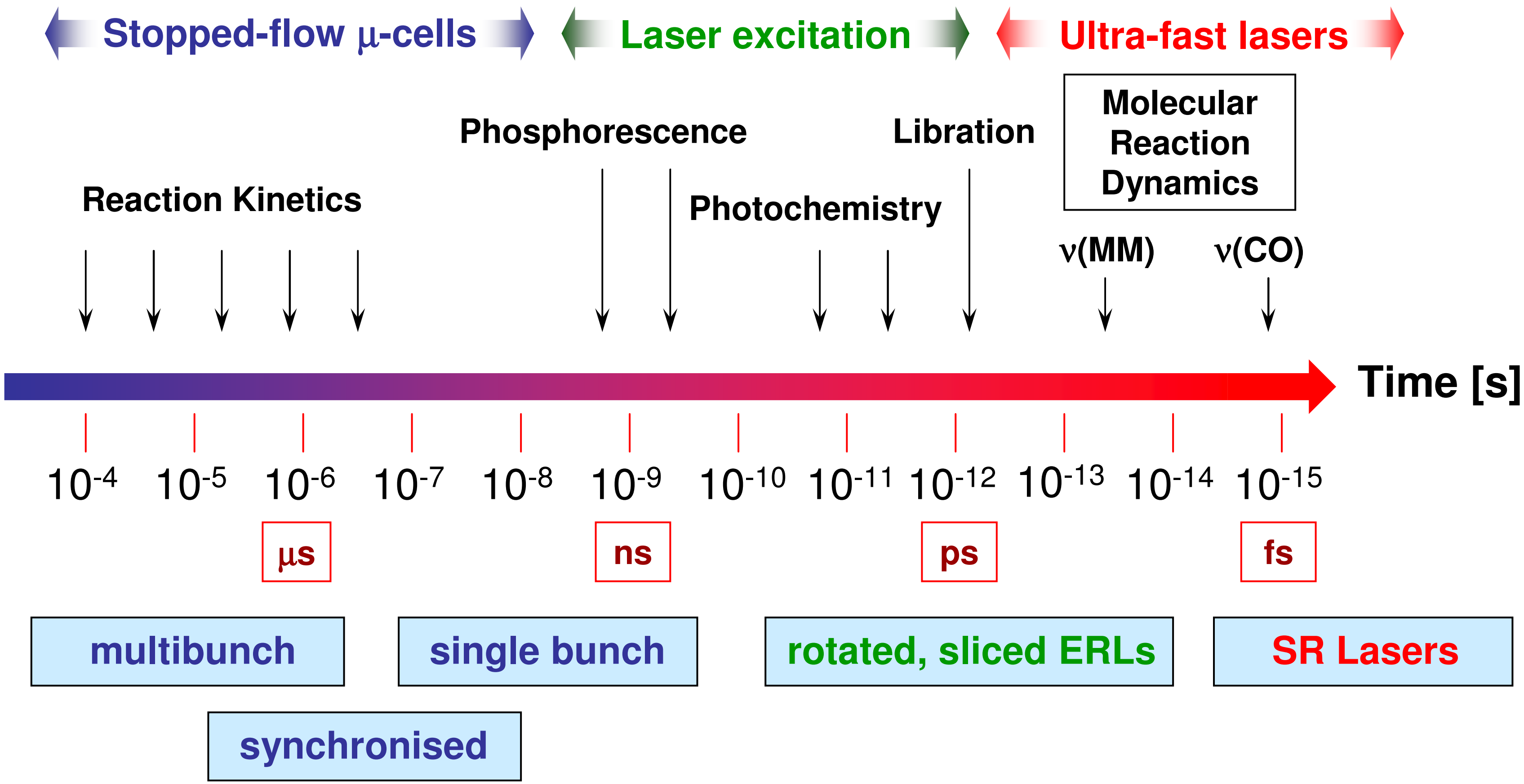
Time resolution: pump-probe spectroscopy



Challenges for Pump and Probe Experiments in Catalysis

- Most relevant chemical reactions are driven by temperature (kT) not optical excitations
- Selective detection of molecules on surfaces, differentiate between species
- Synchronization between pump and probe
- Control of reaction coordinate system

Laser and THz pump → XAS, XPS, XES probe

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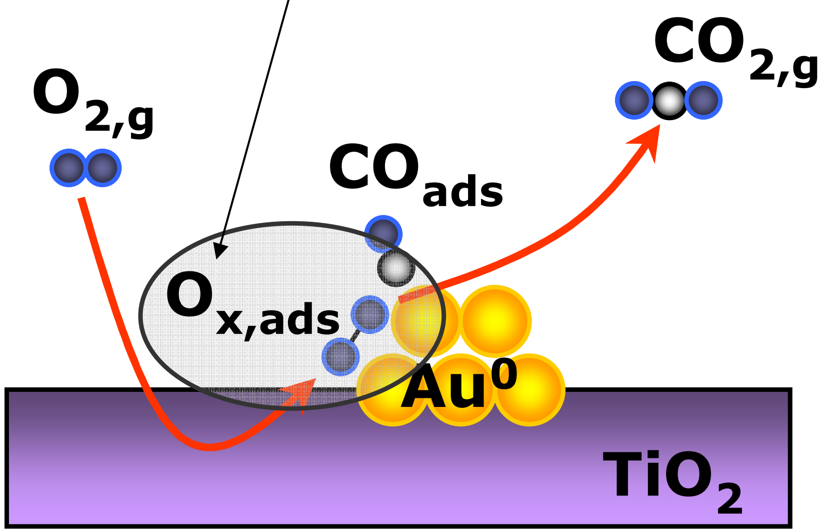
Current Hot Topic: Oxygen Species during Catalysis by Gold

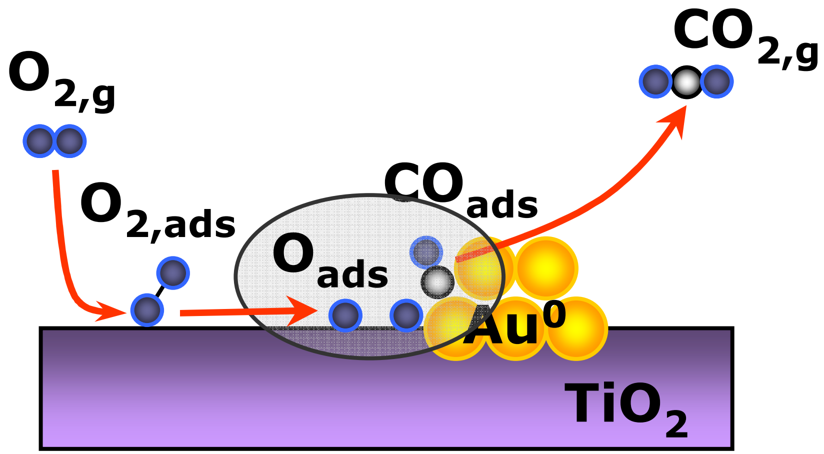
$CO + O_2 \rightarrow CO_2$ **A 'simple' reaction?**

What is it? Molecular, atomic, ionic…?
Where is it? Oxide? Gold? Interface?
Dynamic electronic state of gold?

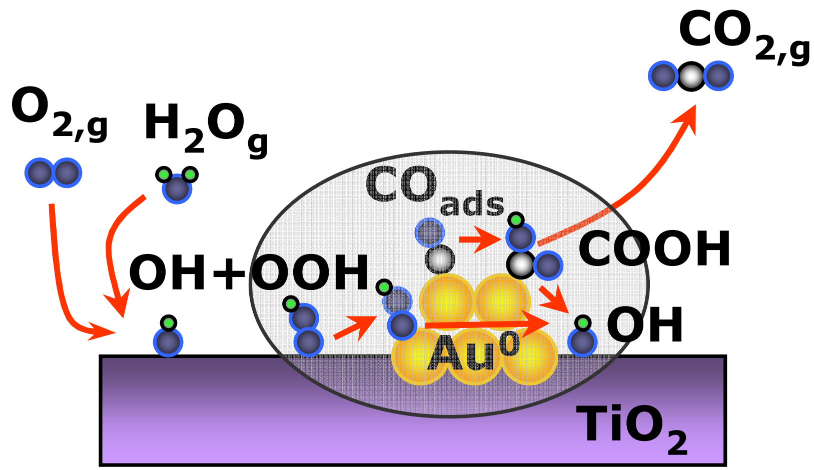


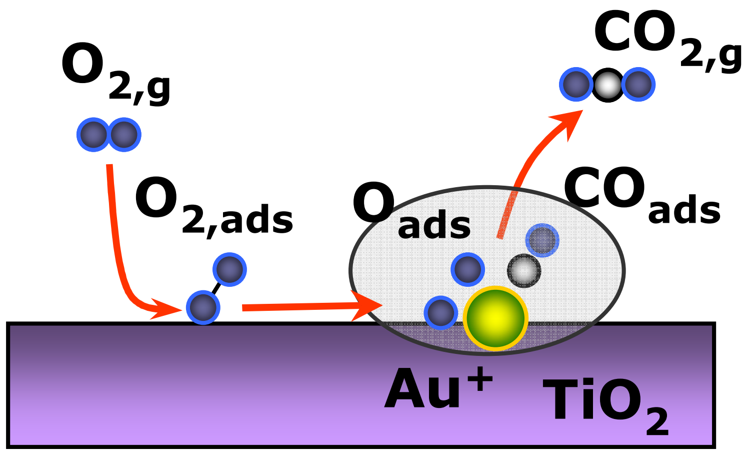
Weiher et al
JACS 2007
Willneff et al
JACS 2006

Oxidation Catalysis by Gold



Plausible possible mechanisms - cannot currently be resolved





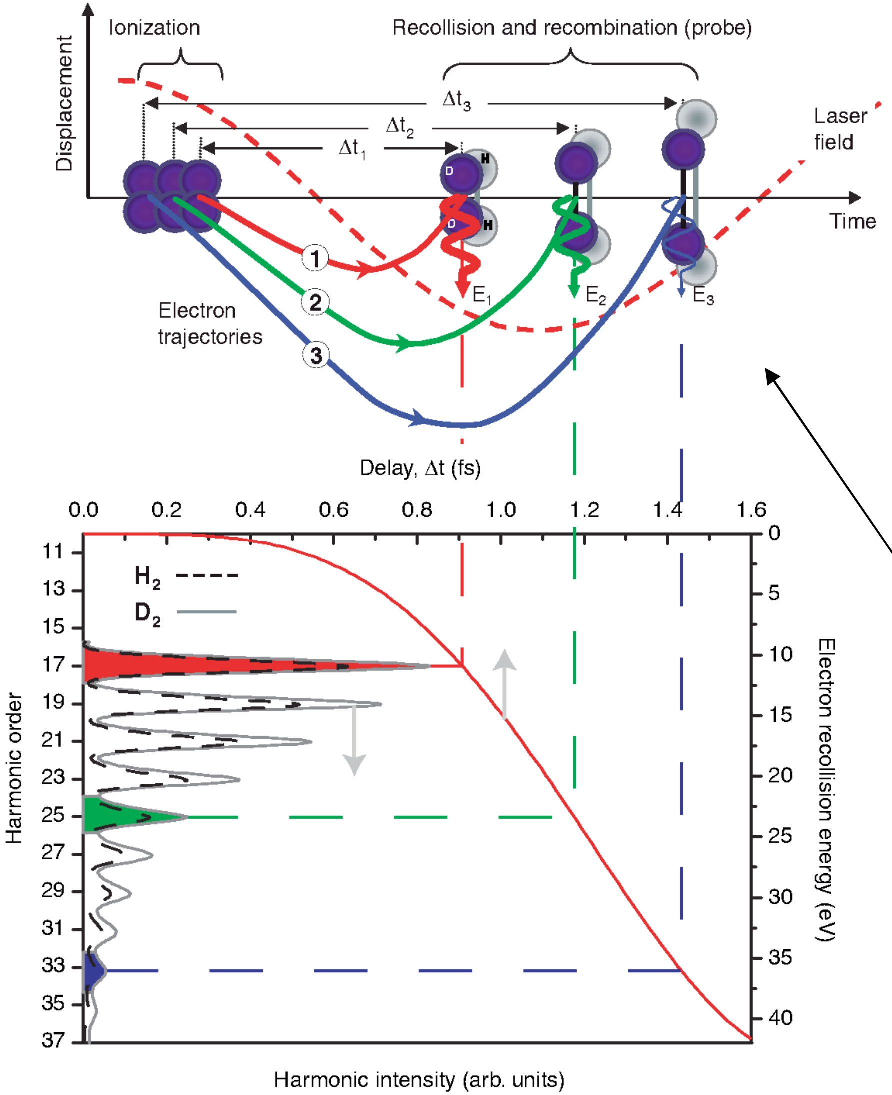
Need more incisive probes !!

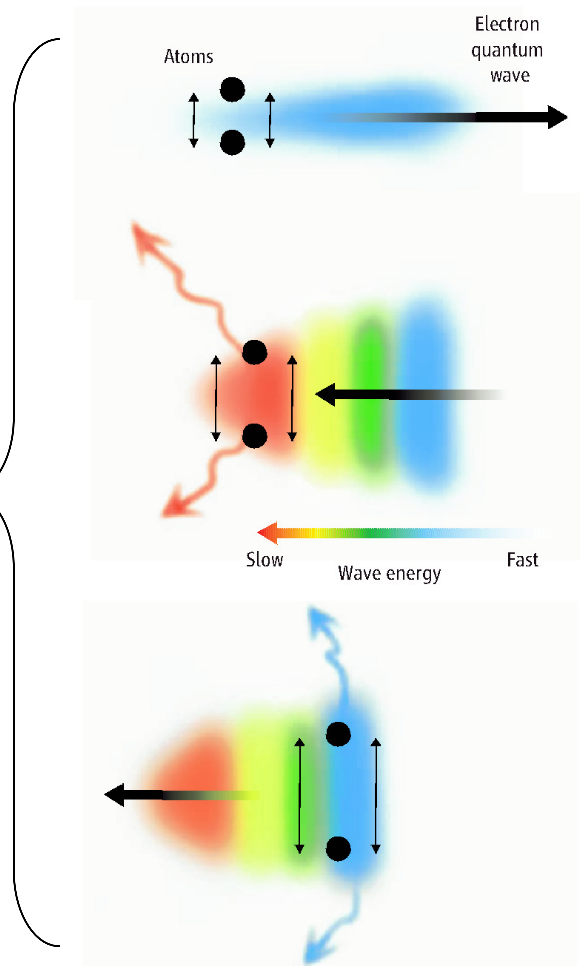
IR/Vis Laser-Induced Soft X-ray Emission

Probing Proton Dynamics in Molecules on an Attosecond Time Scale

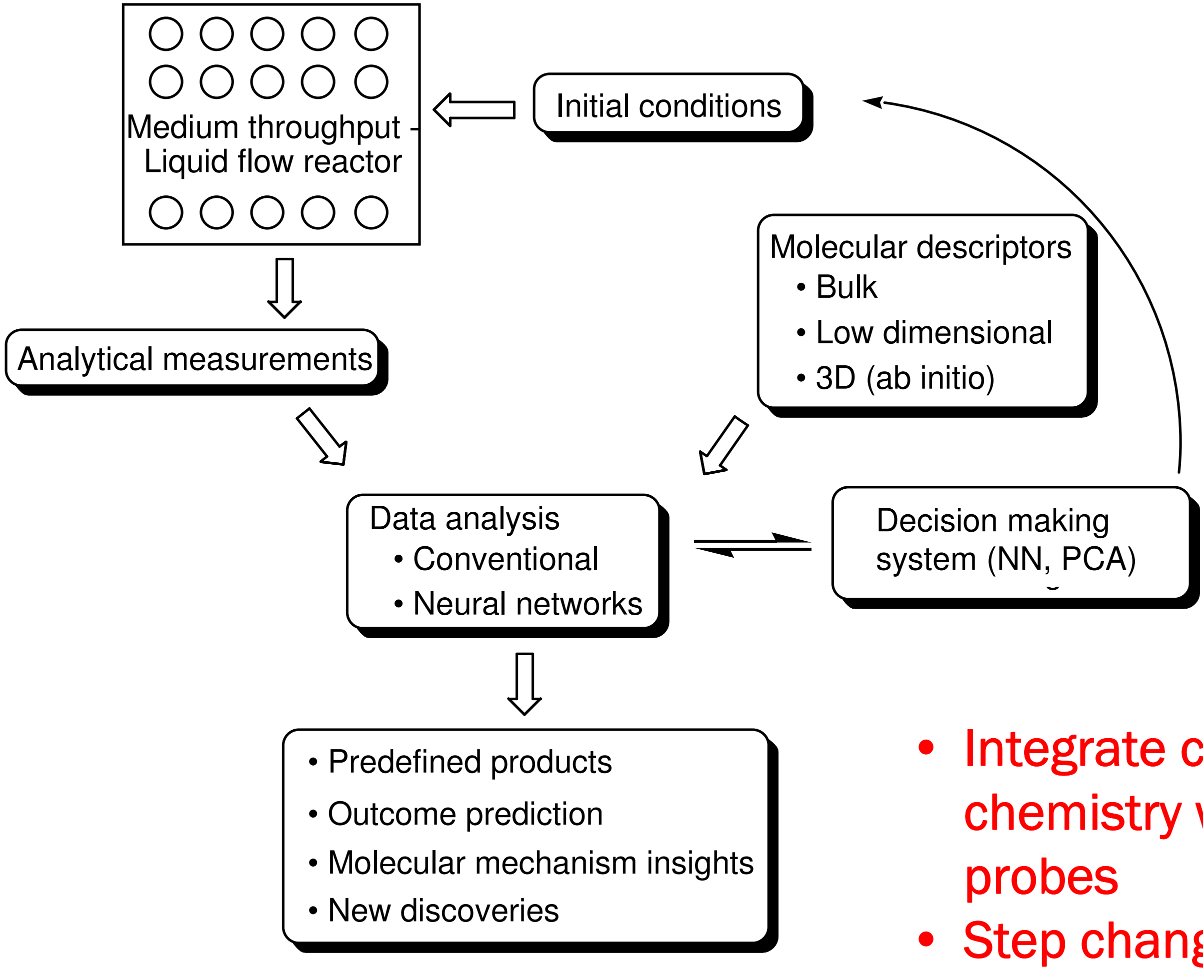
S. Baker,[1] J. S. Robinson,[1] C. A. Haworth,[1] H. Teng,[1] R. A. Smith,[1] C. C. Chirilă,[2] M. Lein,[2] J. W. G. Tisch,[1] J. P. Marangos[1*]

Science 312 (2006) 424





Closing the Loop: Dynamic Combinatorial Chemistry, Formulation, Crystallisation



- Integrate computational chemistry with moelcular level probes
- Step changes in chemistry possible

Summary / recommendations

- Lots of photons – but less beamtime – heterogeneous catalysis need **parallel *operando* reactors**, and ideally **compliance with industry standards** for **lab automation** and **high-throughput experimentation**
- **Faster scans**
- **Smaller samples** – need **smaller beam footprint**, and **stable beams**
- More experiments in a given time permit analysis of **more complex systems** – step changes in science possible in the future
- **E-science** aspect will be crucial to facilitate the required efficiency
- Lots of exciting science can still be done by 'conventional' XAFS measurements, but we can minimise time by putting lots of samples through
- Microanalysis
- Do not forget 'new' techniques – high-resolution fluorescence spectroscopy, inelastic X-ray scattering, combination with lasers, pump-probe, etc