UNIVERSITY OF Southampton
School of Chemistry

Energy Dispersive EXAFS

Steps towards understanding catalytic reactions

John Evans (je@soton.ac.uk)
2 February 2009

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Starting points

IDECAT
Integrated Design of Catalytic Nanomaterials for a Sustainable Production

diamond

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XAFS3

EXAFS and Near Edge Structure III

Proceedings of an International Conference, Stanford, CA, July 16–20, 1984

Editors: K.O.Hodgson, B.Hedman, and J.E.Penner-Hahn

Fundamental Aspects in X-Ray Absorption in Dispersive Mode

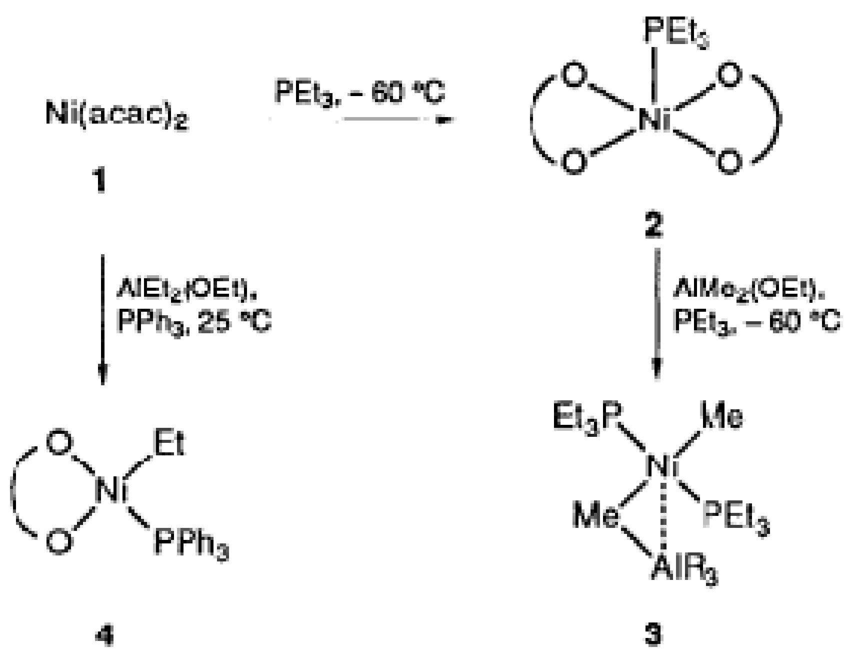
E. Dartyge[1], A. Fontaine[1], A. Jucha, and D. Sayers[2]
LURE, Bât. 209 C, Université de Paris-Sud, F-91405 Orsay Cédex, France and
[1]Laboratoire de Physique des Solides, Bât. 510, F-91405 Orsay Cédex, France and
[2]Physics Department, North Carolina State University, Raleigh, NC 27650, USA

An Energy Dispersive X-Ray Absorption Spectrometer and Its Application to Stopped-Flow Experiment

T. Matsushita
Photon Factory, National Laboratory for High Energy Physics, Oho-machi
Tsukuba-gun, Ibaraki 305, Japan
H. Oyanagi
Electrotechnical Laboratory, Umezono, Sakura-mura, Niihari-gun
Ibaraki 305, Japan
S. Saigo and H. Kihara
Department of Physics, Jichi Medical School, Minamikawachi-machi
Kawachi-gun, Tochigi 329-04, Japan
U. Kaminaga
Rigaku Corporation, Matsubara-cho, Akishima, Tokyo 196, Japan

Background chemistry

- Alkene oligomerisation homogeneous catalysts



Scheme 1 Hacac = pentane-2,4-dione

Scanning XAFS (SRS, Station 7.1)
Only observe steady state after catalyst activation

Catalysts used to convert C_2H_4 into linear α-olefins

(Shell Higher Olefin Process)

J. M. Corker, J Evans
Chem Comm 1991, 1104

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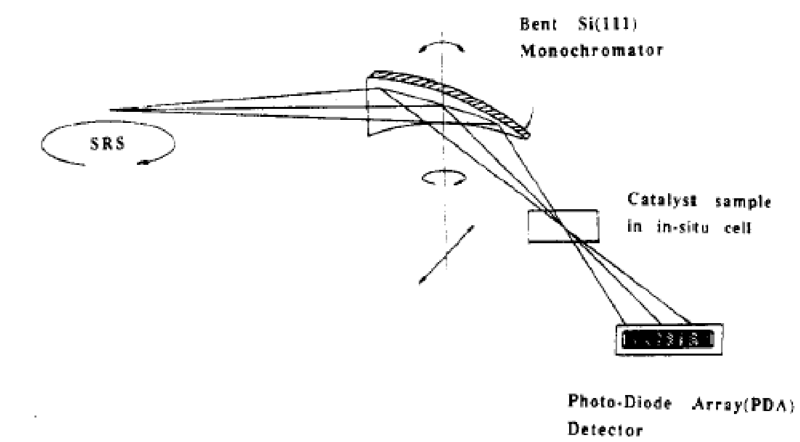
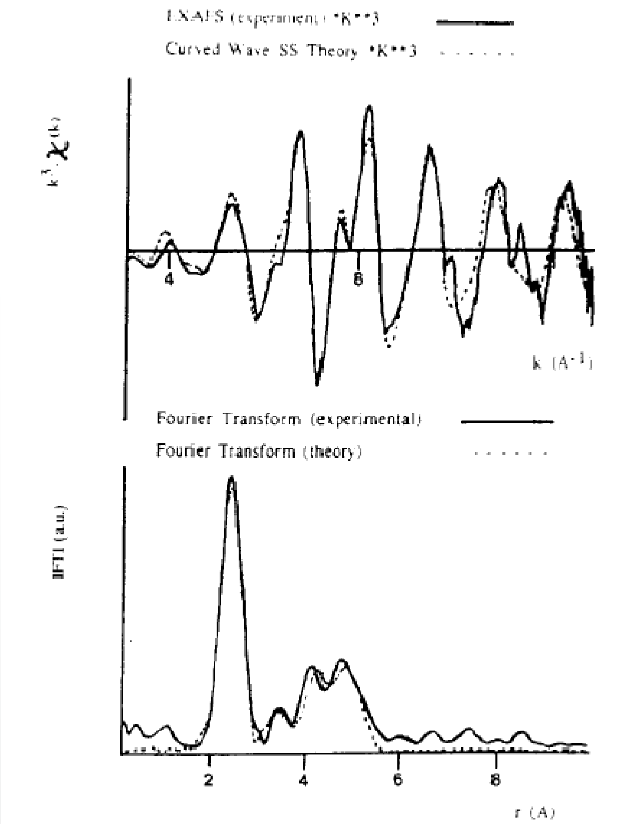
SRS: Prototype Station 7.4

- Photodiode array
  - Minimum time response 6 ms
  - Ni foil in 500 ms
- 3 Point bender



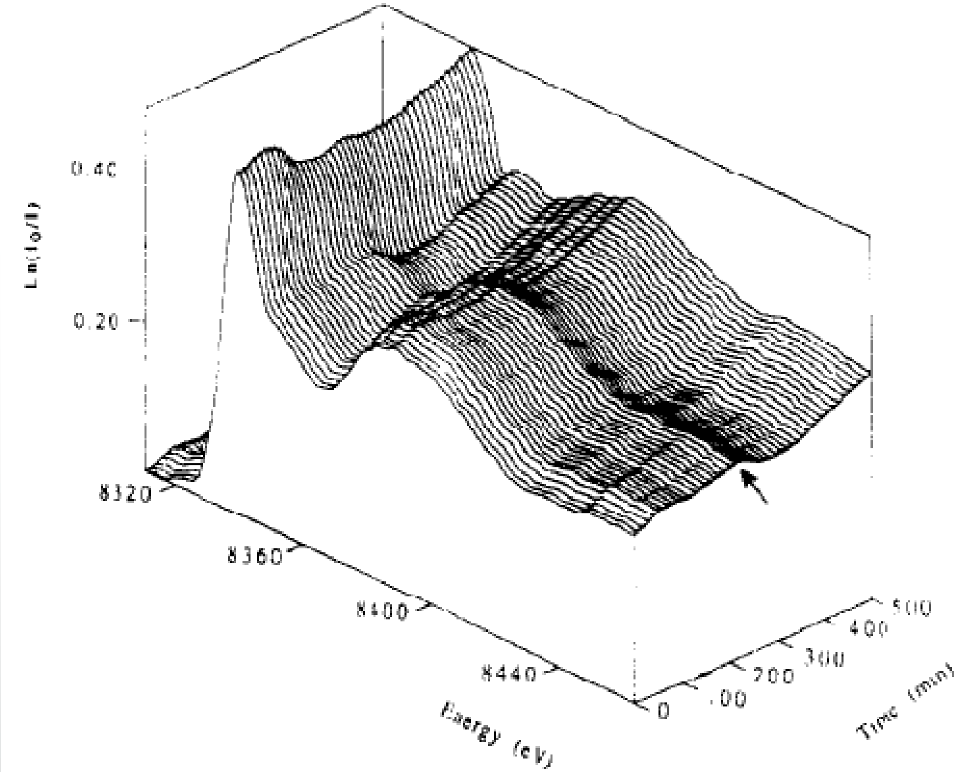
N M Allinson, G Baker, G. N. Greaves, J K Nichol, *Nucl. Inst. Meth. Phys. A* 1988, **266**, 592



J W Couves, J M Thomas, C R A Catlow, G. N. Greaves, G Baker, A J Dent, *J. Phys, Chem.* 1990, **94**, 6517

SRS: Station 7.4: Heterogeneous catalysis

- Dehydration of Ni-Y zeolite
  - Acquisition time 1 min
  - Repetition rate 10 min



J W Couves, J M Thomas, C R A Catlow, G. N. Greaves, G Baker, A J Dent, *J. Phys, Chem.* 1990, **94**, 6517

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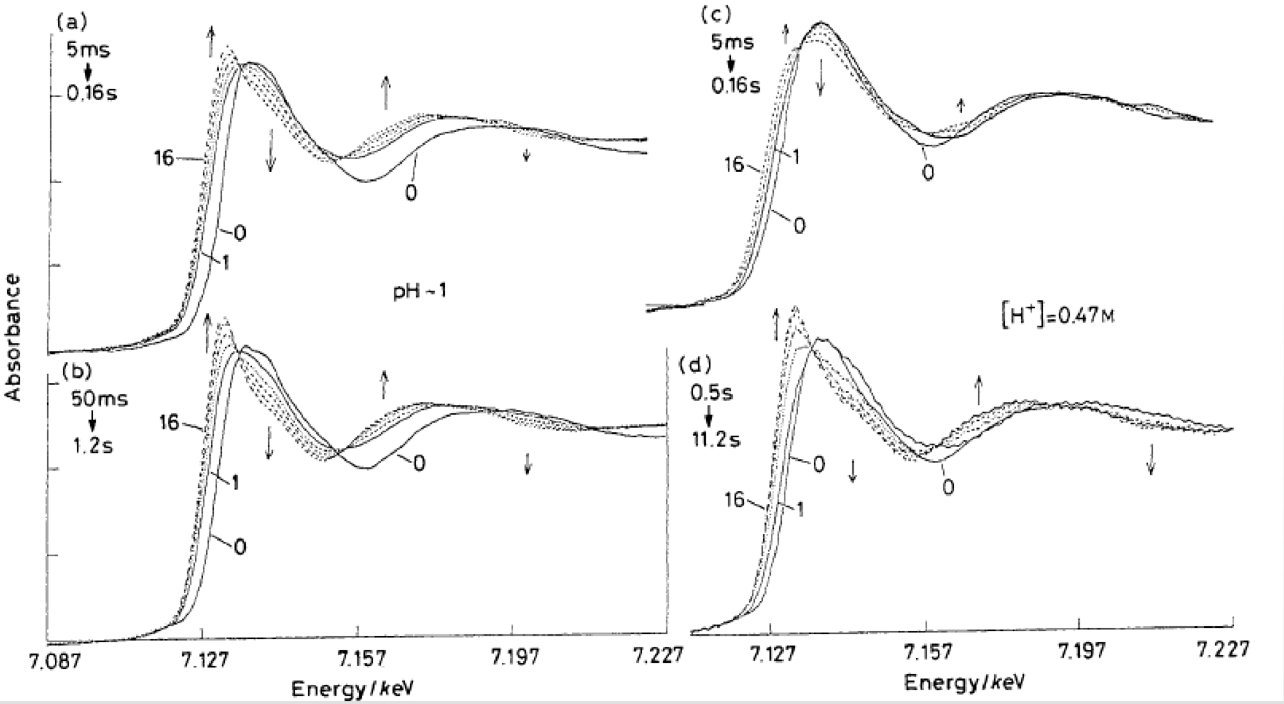
SRS: Station 7.4: Homogeneous catalysis

- Sunday, February 11 1990

Stopped-flow XAFS

- Reduction of Fe^{3+} by hydroquinone (300 mM in H_2O)
  - PDA, 5 ms (400 x), 5 ms intervals (2000ms/ spectrum)



N. Yoshida, T. Matsushita, S. Saigo, H.Oyanagi, H. Hashimoto, M. Fujimoto, *Chem. Comm.* 1990, 354

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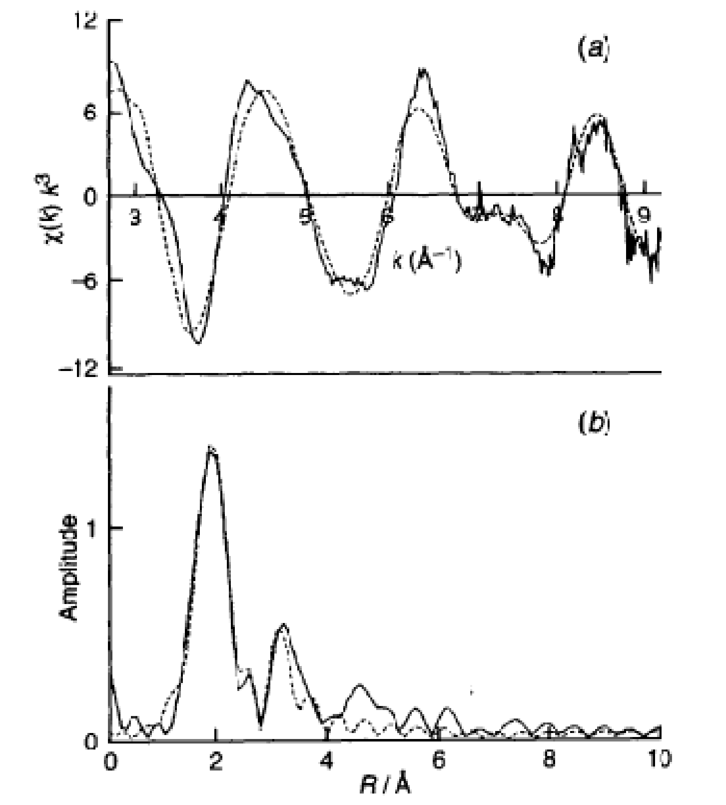
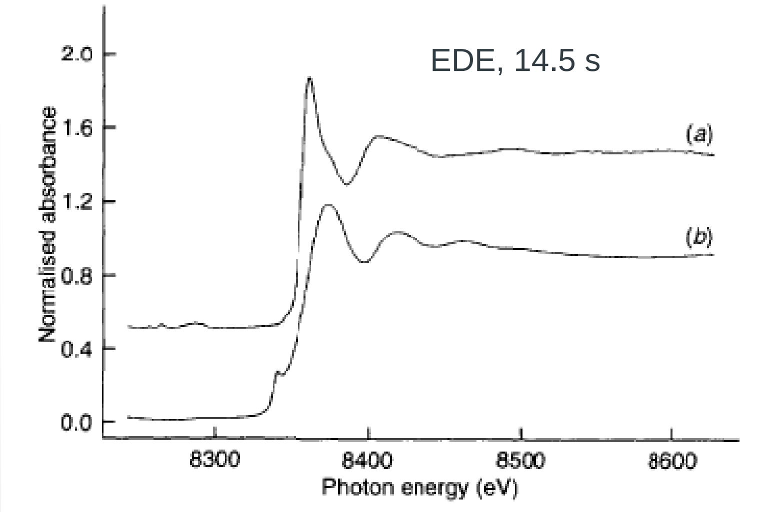
Largely Station 9.3

Station 9.3 ED-XAFS

- Activation of $[Ni(acac)_2]_3$ by $AlEt_2(OEt)$ (70 mM)
  - Reticon 512 element PDA, 2 ms readout

100 x 20 ms

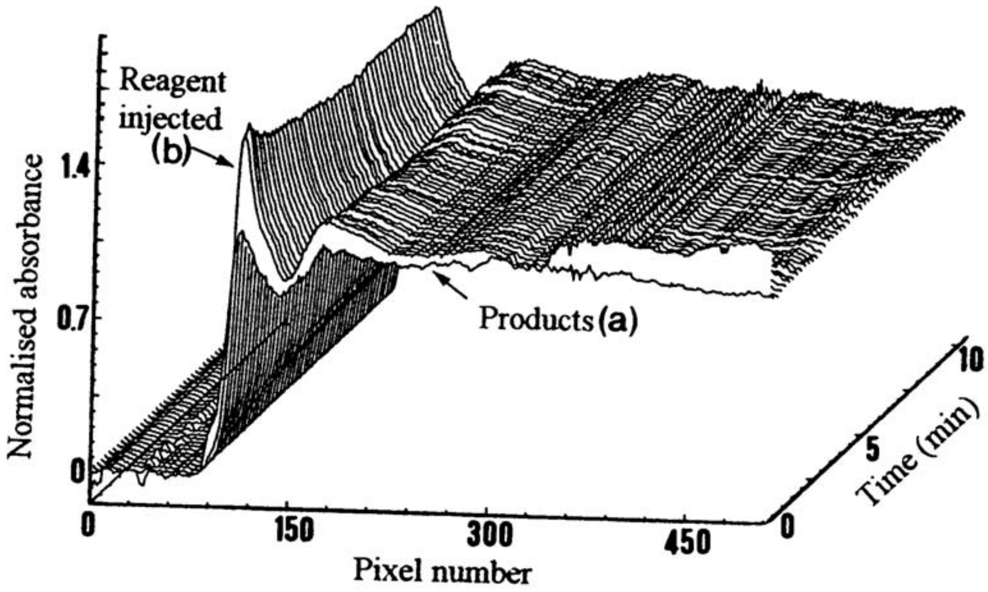




D Bogg, M Conyngham, J M. Corker,A J Dent, J Evans, R C Farrow, V L. Kambhampati, A F Masters, D Niles McLeod, C A Ramsdale, G Salvini *Chem. Comm.* 1996, 647

ID24 ED-XAFS

- Activation of $[Ni(acac)_2]_3$ by $AlEt_2(OEt)$ (35 mM)/hex-1-ene
  - 512x512 CCD PDA emulator, 10 ms readout



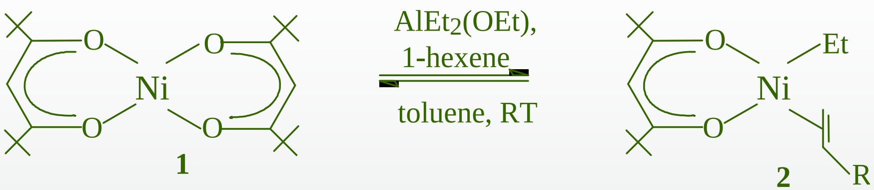
But Rh K-edge ED-XAFS of Rh/Al_2O_3 gave much better data.

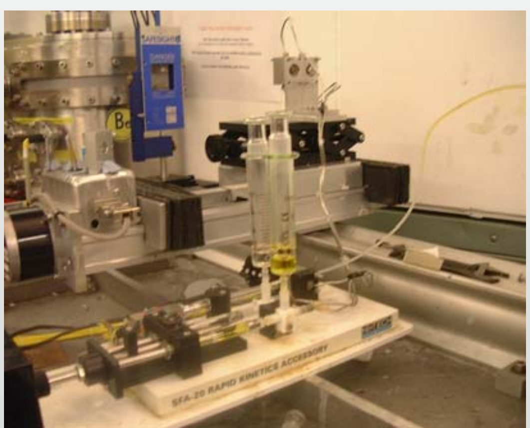
More homogeneous focus than 9.3?

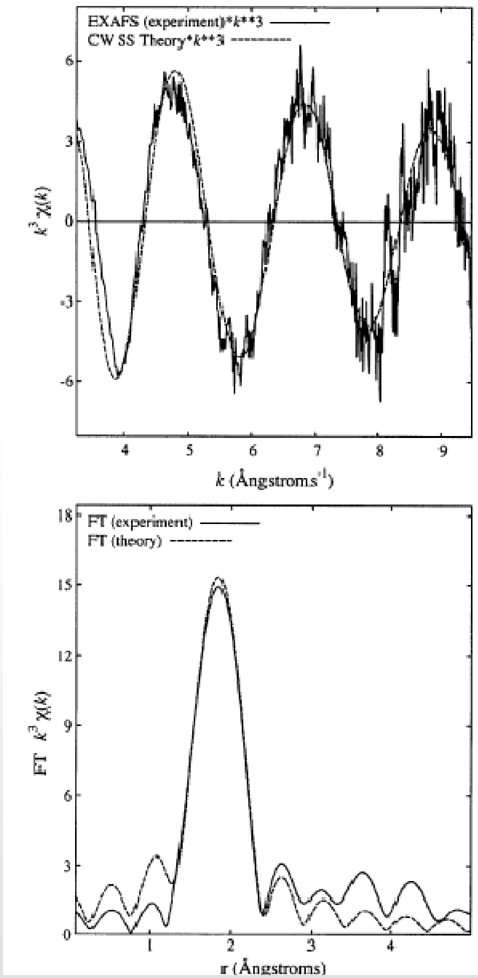
J M. Corker,A J Dent, J Evans, M. Hagelstein V L. Kambhampati, *J. Physique.* 1997, C7, 879

Station 9.3 Stopped flow

- Activation of $Ni(dpm)_2$ by $AlEt_2(OEt)$ (70 mM)
  - Hamamatsu element PDA, 2 ms readout
  - 4 point bender





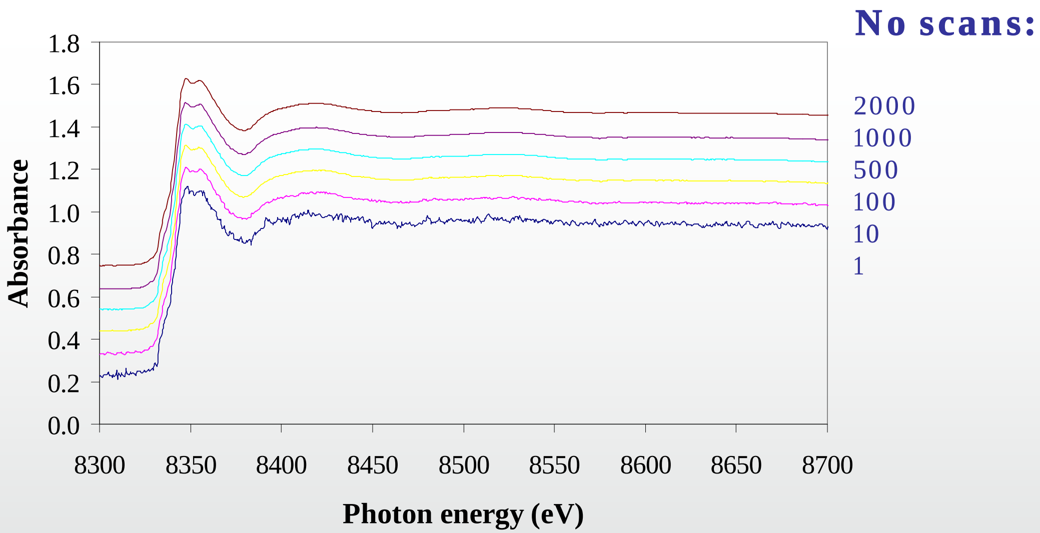


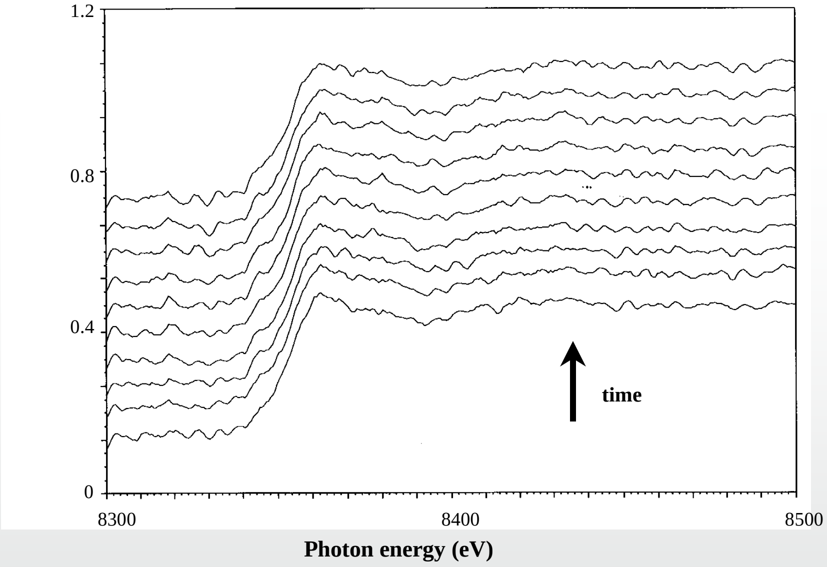
100 x 20 ms

A. J. Dent, J. Evans, M. Newton, J. Corker, A Russell, M.B. Abdul Rahman, S. Fiddy, R. Mathew, R. Farrow, G. Salvini, P. Atkinson *J. Synchrotron Rad.* 1999, **6**, 381.

Station 9.3 Stopped flow

- Activation of $Ni(dpm)_2$
  - Hamamatsu 1024 element PDA, 2 ms readout



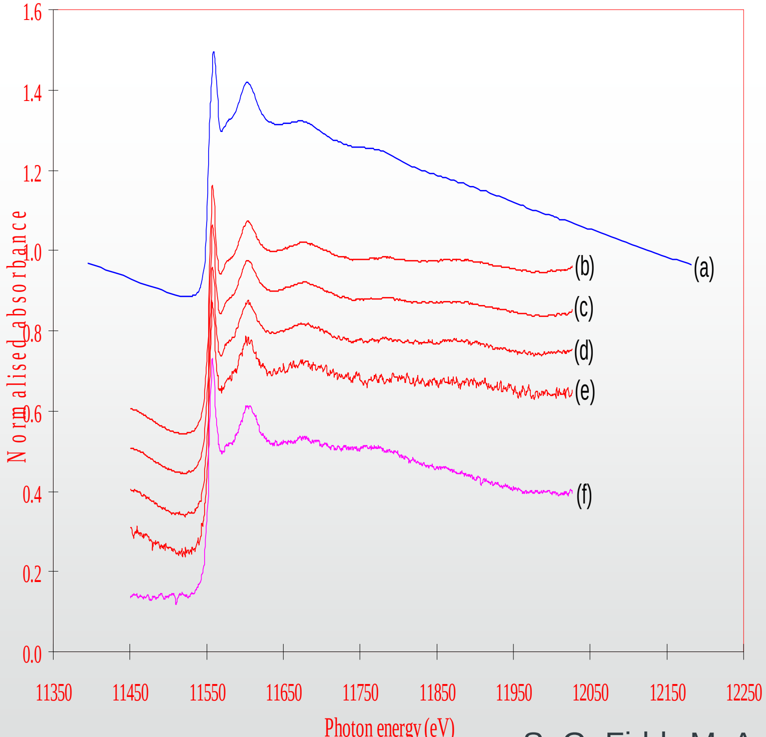


Activation by $AlEt_3$/hex-1-ene
1 x 16 ms

M.B. Abdul Rahman, P. R. Bolton, J. Evans, A. J. Dent, I. Harvey, S. Diaz-Moreno *Faraday Discuss.* 2002, **122**, 211.

Station 9.3 Heterogeneous samples

- Pt L(III): 5 wt% on H1-SiO_2
  - Hamamatsu 1024 element PDA, 2 ms readout



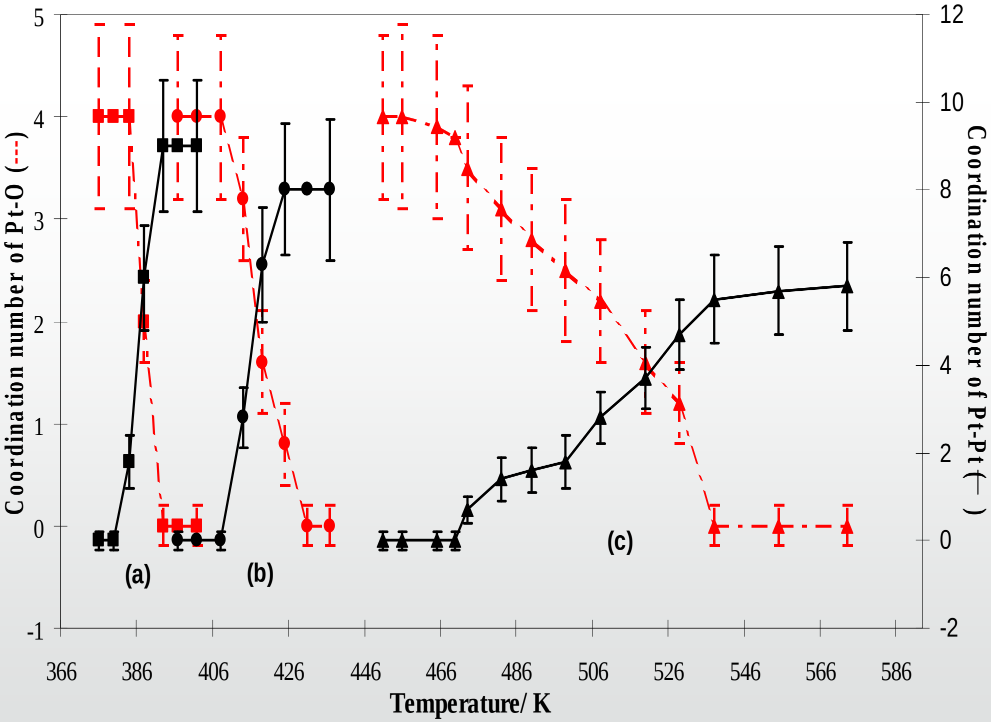
n x 50 ms

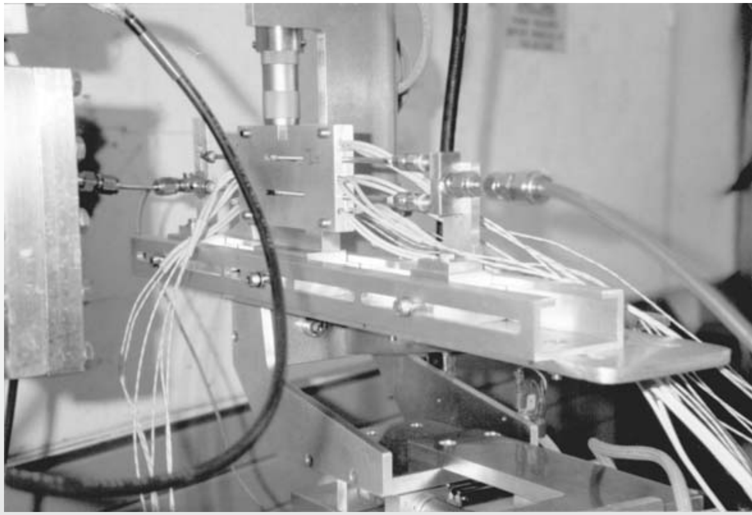
S. G. Fiddy, M. A. Newton, A.J Dent, G. Salvini, J. M. Corker, S. Turin, T. Campbell, J. Evans, *Chem. Comm.* 1999, 851.

Station 9.3 microreactor

- $Pt(acac)_2/H_1\text{-}SiO_2$ under N_2 and H_2

H_2 N_2

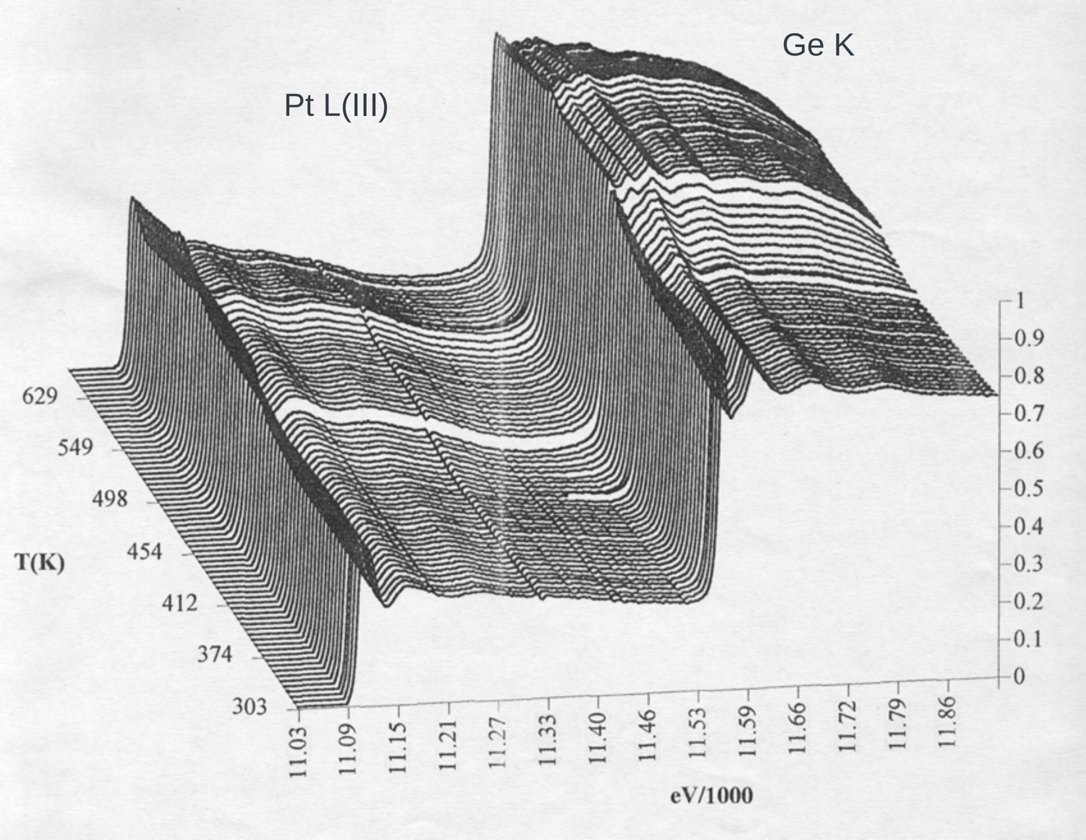


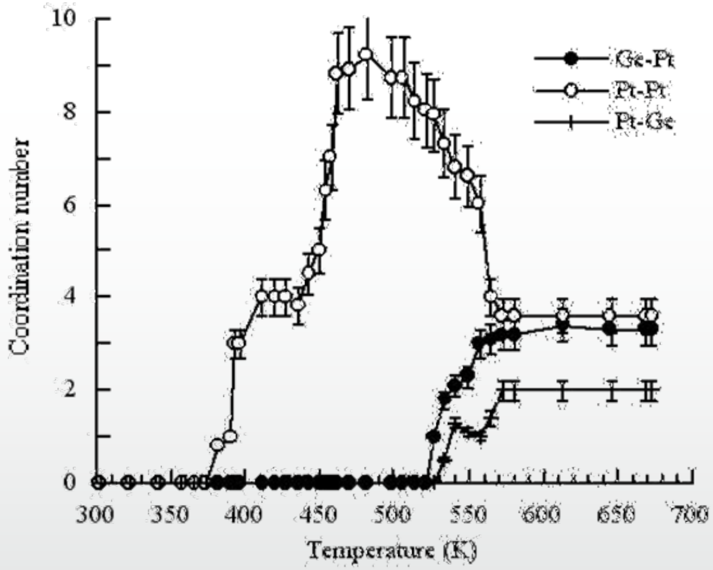


S. G. Fiddy, M. A. Newton, A.J Dent, G. Salvini, J. M. Corker, S. Turin, T. Campbell, J. Evans, *Chem. Comm.* 1999, 851.

Station 9.3 Double-edge measurement

- $Pt(acac)_2$-$GeBu_4/H_1$-SiO_2 under H_2

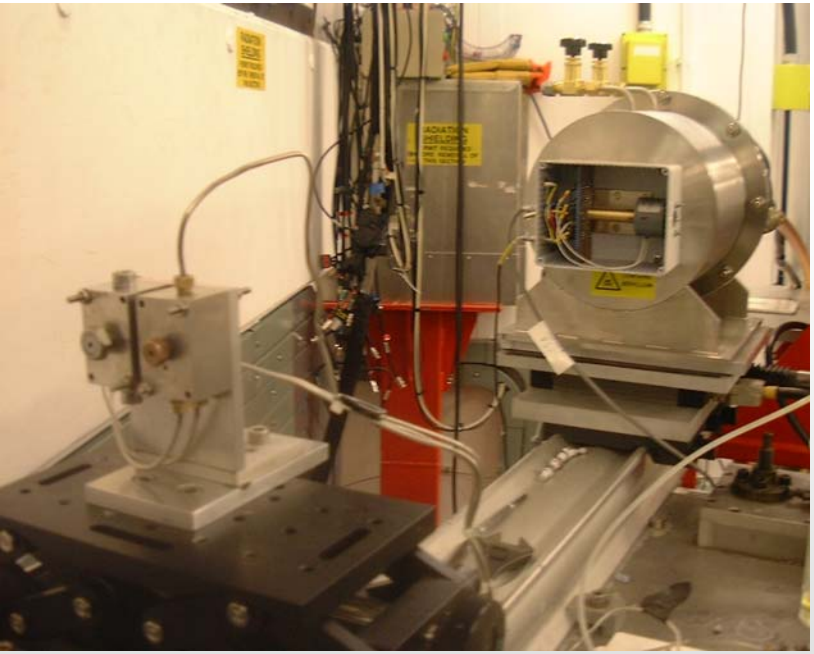




S. G. Fiddy,M. A. Newton, T. Campbell, A.J Dent, J. M. Corker, I. Harvey, G. Salvini, S. Turin, J. Evans, *Chem. Comm.* 2001, 445.

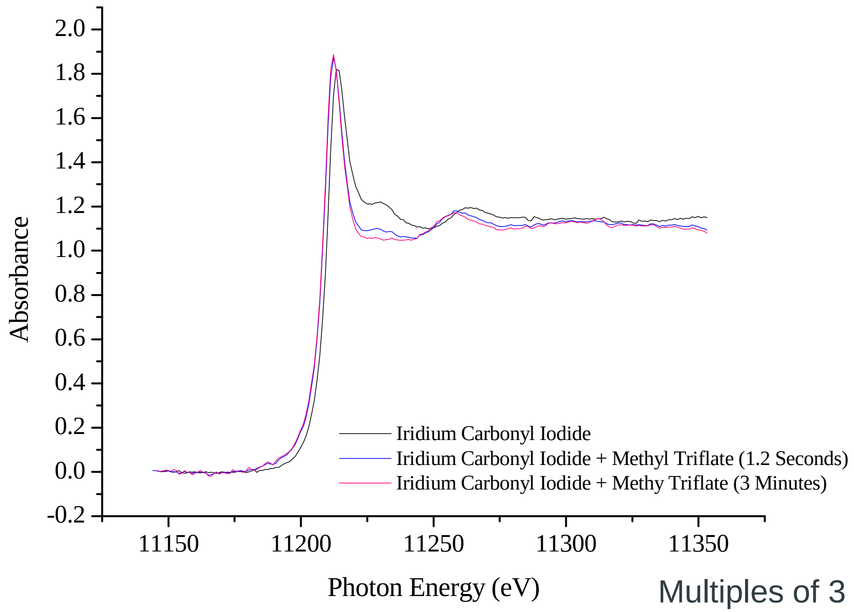
Station 9.3 Stopped flow

- Beyond ms time resolution
  - XSTRIP 1024 element Si microstrip (12μs readout)



J. Headspith, G. Salvini, S.L. Thomas, G. Derbyshire, A. J. Dent, T. Rayment, J. Evans, R. Farrow, C. Anderson, J. Cliché, B. R. Dobson *Nucl. Instrum. Meth. Phys A,* 2003, **512**, 239.

- Reaction of Me-OSO_2CF_3 with $[IrI_2(CO)_2]^-$ (80 mM)



Multiples of 3 x 400 μs

M.B. Abdul Rahman, P. R. Bolton, J. Evans, A. J. Dent, I. Harvey, S. Diaz-Moreno *Faraday Discuss.* 2002, **122**, 211.

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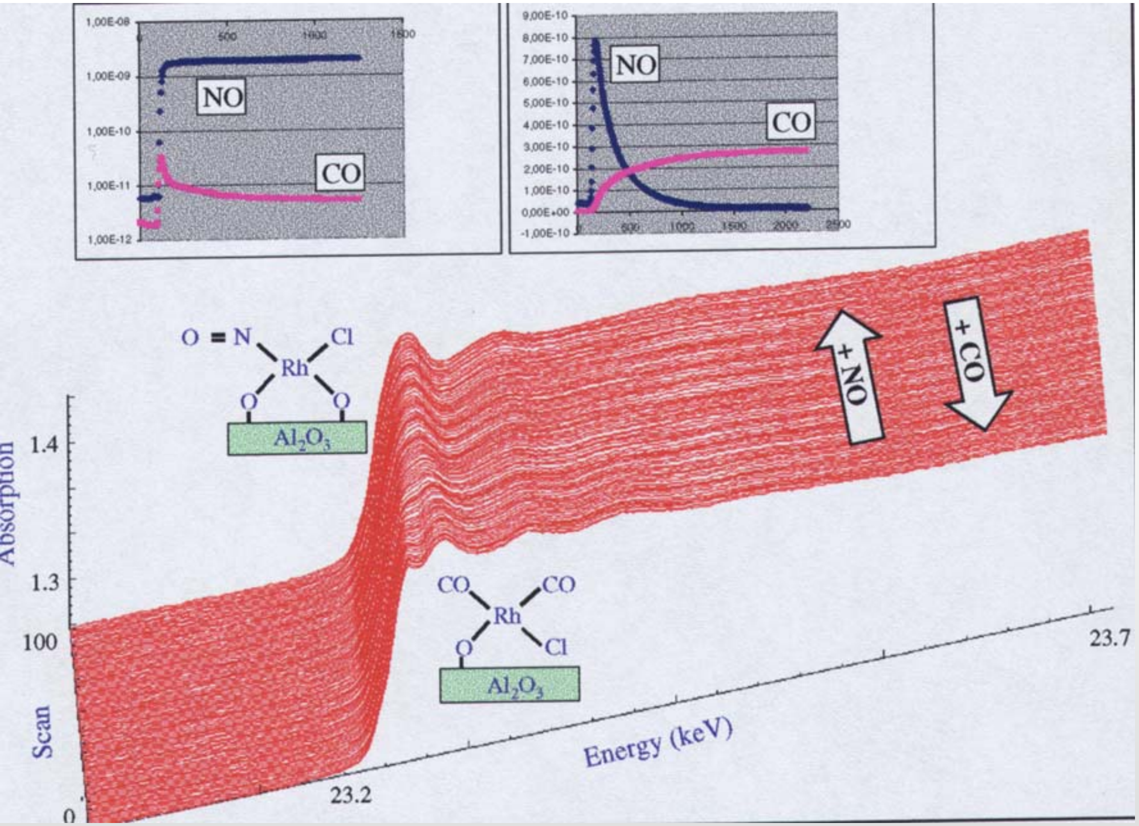
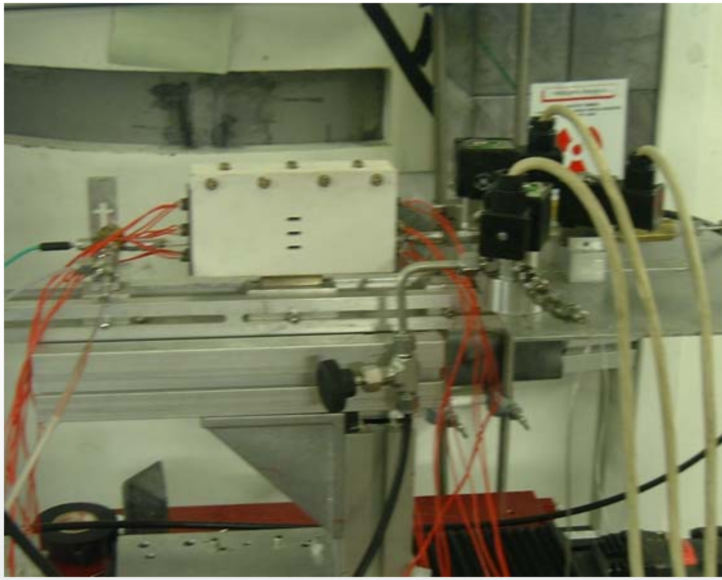
ID24

ID24 microreactor

- $[RhCl(CO)_2]_2/Al_2O_3$





M. A. Newton, D. G Burnaby, A.J Dent, S. Diaz-Moreno, J. Evans, S. G. Fiddy, T. Neisius, S. Pascarelli, S. Turin, *J. Phys. Chem. A* 2001**,105,** 5965.

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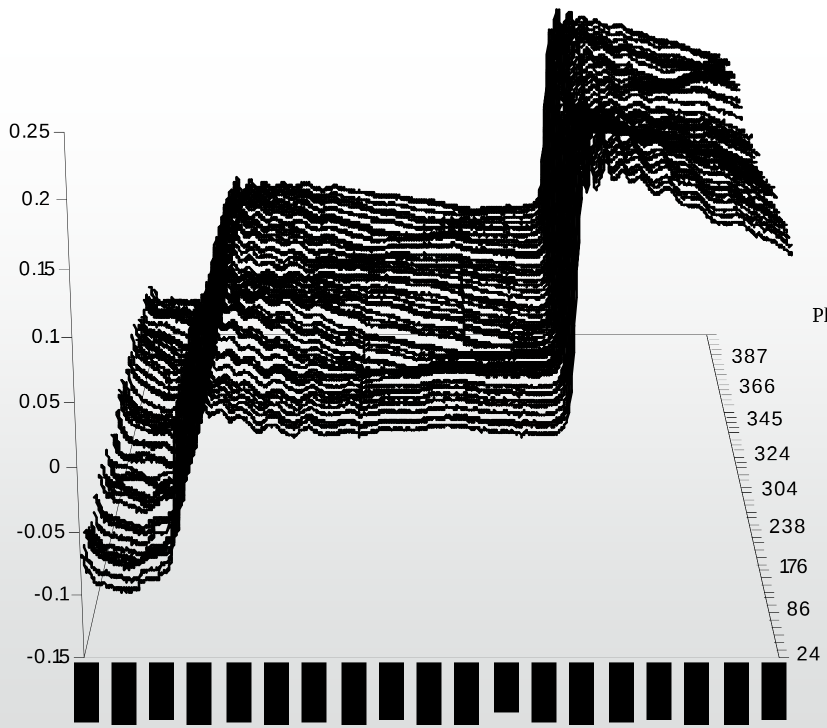
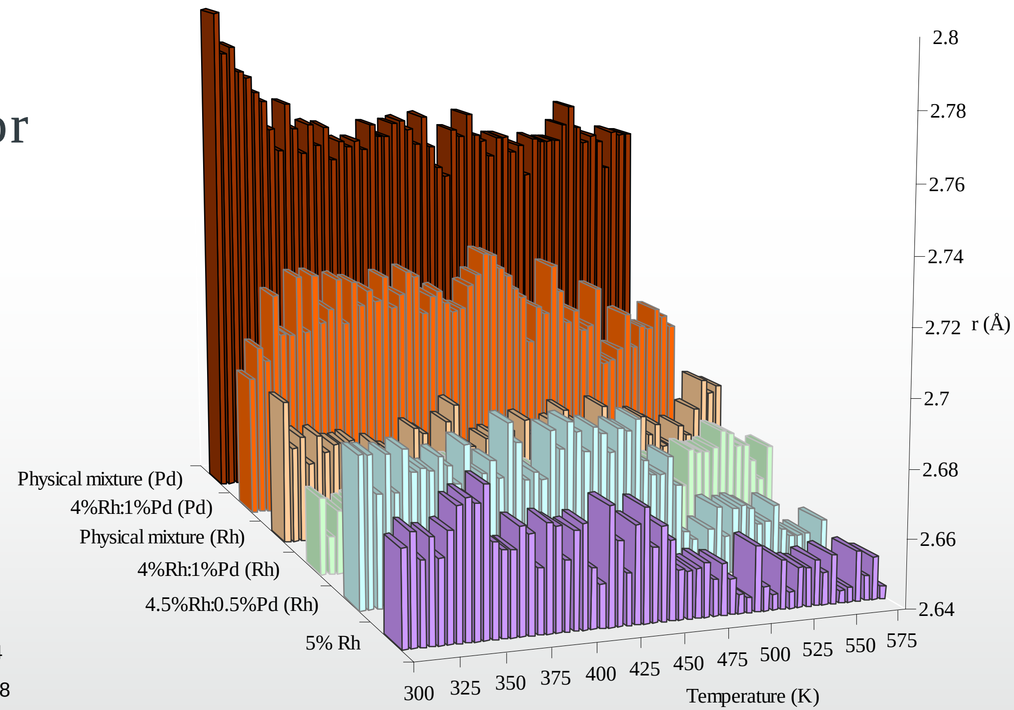
ID24 double edge experiment

- Rh-Pd/Al_2O_3 (under NO-H_2/He)
  - Princeton 1kx1k CCD
  - Si(111) Laue monochromator





M. A. Newton, B Jyoti, A.J Dent, S. Diaz-Moreno, S. G. Fiddy, J. Evans. *ChemPhysChem.*, 2004,**5,** 1056.

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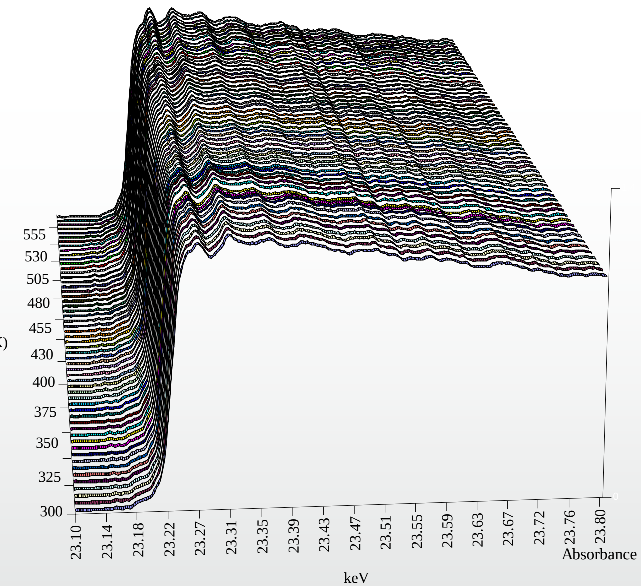
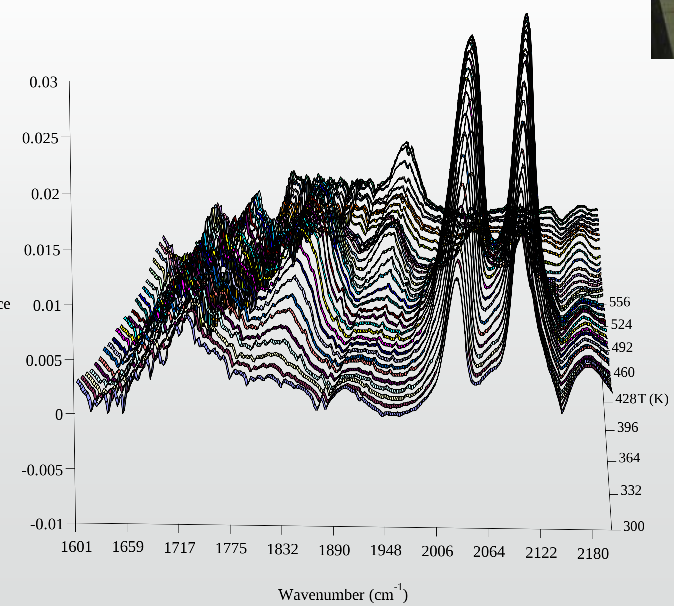
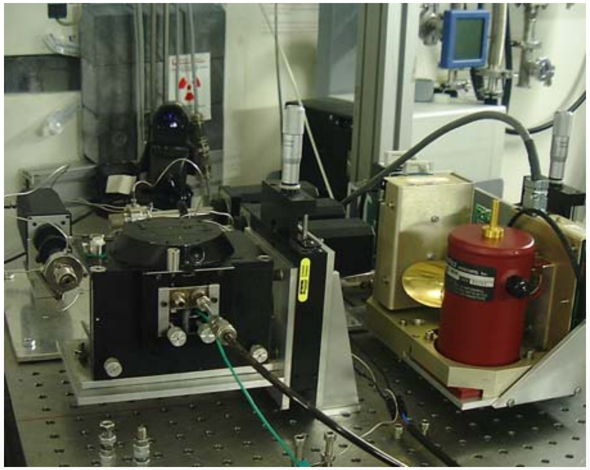
ID24 DRIFTS-XAFS-MS

- 5% Rh/Al_2O_3
  - Princeton 1kx1k CCD



1.2 – 1.5s /spectrum

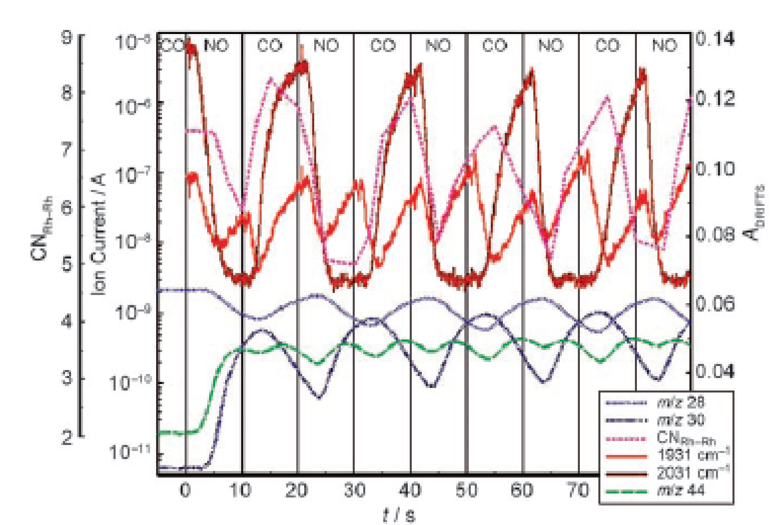


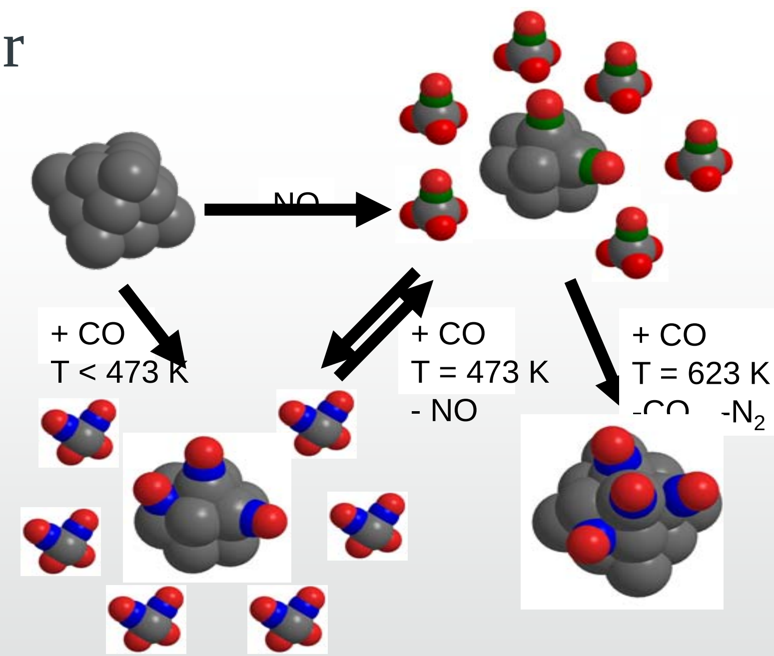


M. A. Newton, B. Jyoti, A.J Dent, S. G. Fiddy, J. Evans, *Chem. Comm.* 2004, 2382.

ID24 Rapid mixing: Gas-solid reactions (ms)

- 5% Rh/Al_2O_3 (5%CO-NO/He switching)
  - FreLoN 2k CCD (1 ms Readout)
  - Si(311) Bragg monochromator





50 ms /spectrum

2 - $8x10^{15}$ atoms
to
~ 10^{14} atoms – fast pulses

A.J Dent, J. Evans, S. G. Fiddy, B. Jyoti, M. A. Newton, M. Tromp, *Angew. Chem. Int. Ed Comm.* 2007, **46**, 5336.

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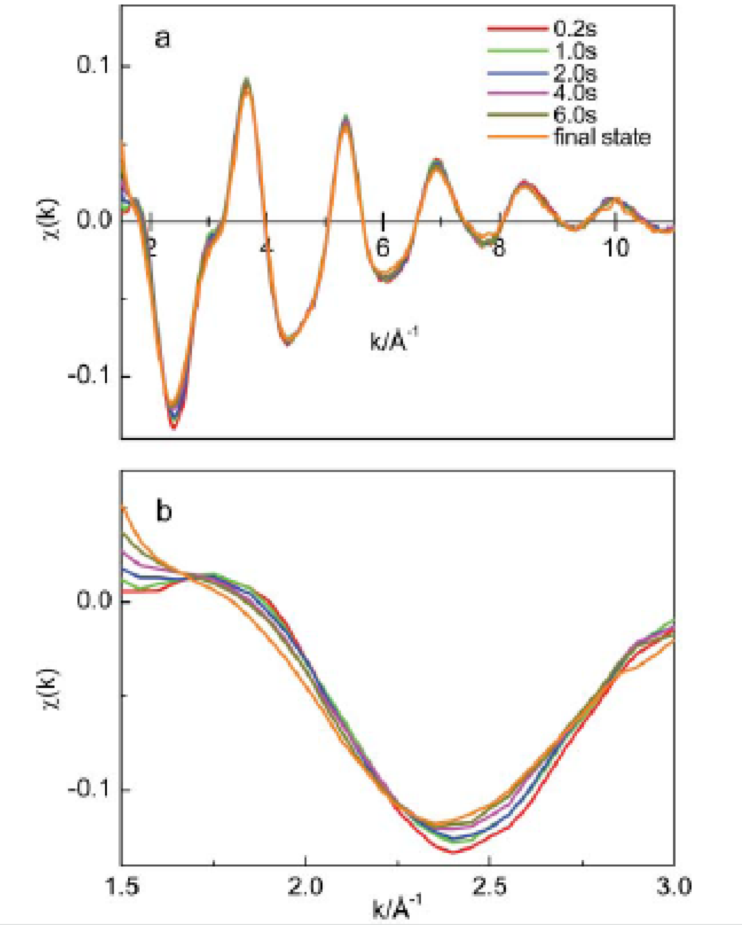
ID24 Stopped flow reprise

- $[IrCl_6]^{2-}/[Co(CN)_5]^{3-}$, inner sphere electron transfer
  - Princeton CCD
  - Combined with uv-visible
  - Ir L(III), 80 mM in water]
  - *Via* $[Cl_5Ir^{III}ClCo^{III}(CN)_5]^{5-}$

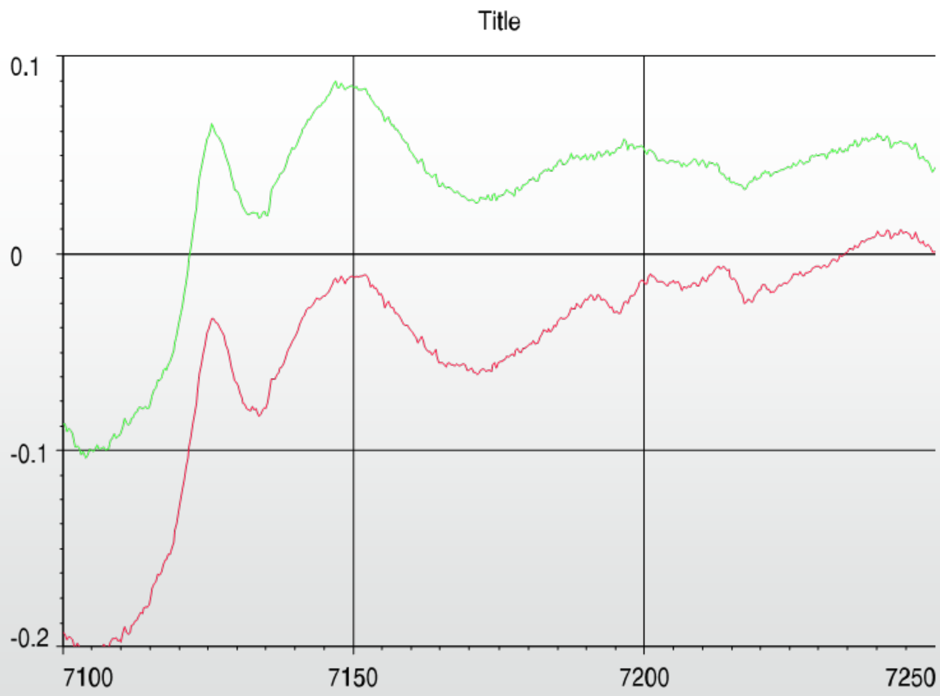
  - Adding freeze quench
  - And diode array uv-vis



S. Diaz-Moreno, D. T. Bowron, J Evans, *Dalton Trans.2005*, 3814

ID24: Beyond the millisecond

- XSTRIP 1024 element Si microstrip (12μs readout)
  - Fe K-edge: $Fe(CO)_5$ (20 mM in MeCN)



1000 x

100x

Multiples of 3
x 90 μs

But XSTRIP damaged with 23 keV photons

G. Salvini, J. Headspith, S.L. Thomas, G. Derbyshire, A. J. Dent, T. Rayment, J. Evans, R. Farrow, S. Diaz-Moreno, C. Ponchut, *Nucl. Instrum. Meth. Phys A,* 2005, **551**, 27.

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Futures

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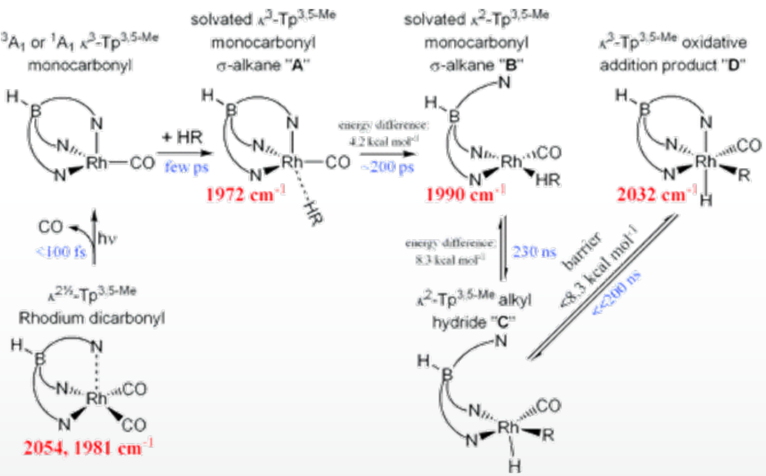
Up to milliseconds

- Homogeneous catalysis (Moniek Tromp, Gill Reid)
  - Stopped flow-quench
    - Selective trimerisation of ethene to hex-1-ene
    - With parallel acquisition of uv-visible spectra
- Heterogeneous catalysis (Moniek Tromp, Chris Hardacre, Alex Goguet)
  - Microreactor with Rapid gas pulses (10^{-2}s)
    - Automotive exhausts
    - With parallel acquisition of mass spectra

Activation: Reaction Transients

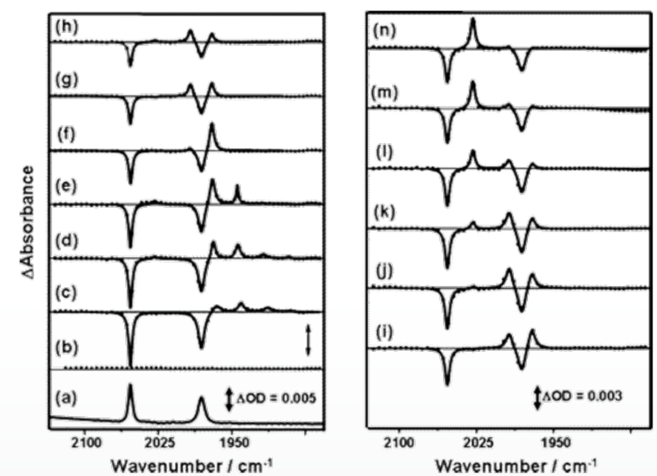
C-H activation

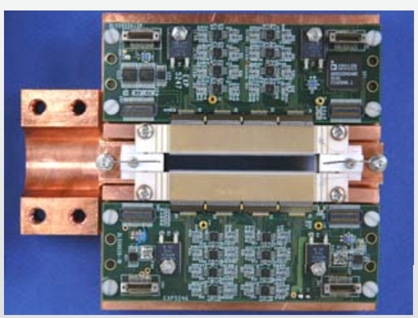
1- 10 x10^{13} atoms



2- 2000 ps

1 – 600 ns

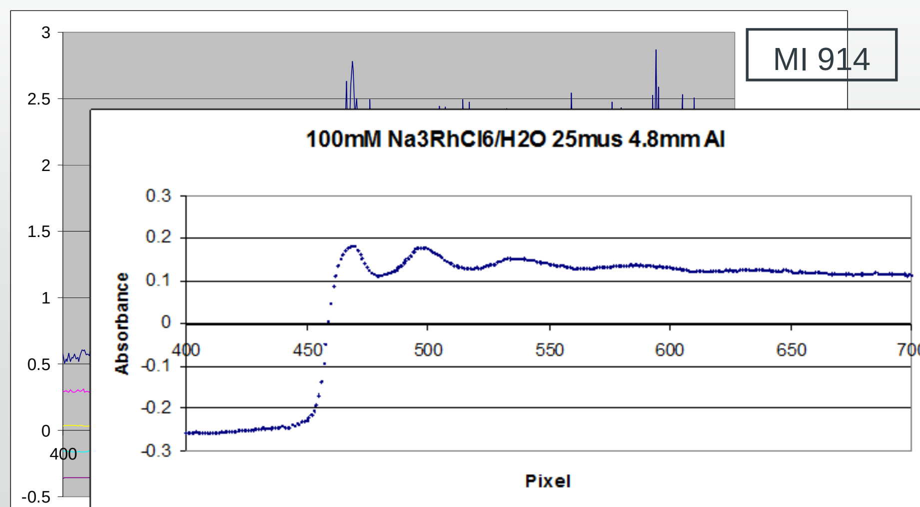




XH: Ge microstrip:

ID24 in 4 bunch mode:
Fe foil

MI 914



J. Headspith, J. Groves, P. N. Luke, M. Kogimtzis, G. Salvini, S.L. Thomas, R. Farrow, J. Evans, T. Rayment, J. S. Lee, W. D. Goward, M. Amman, O. Maton, S. Diaz-Moreno, *IEEE Nucl. Sci., Symp. Conf.*

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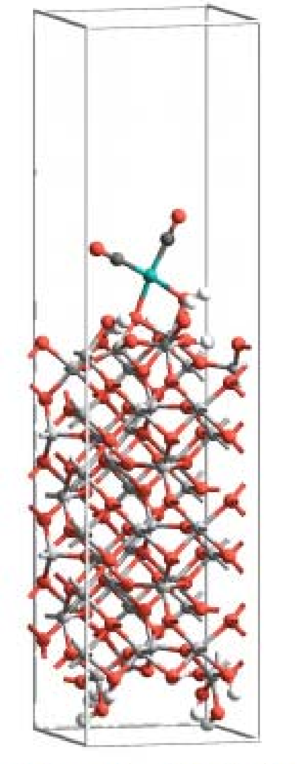
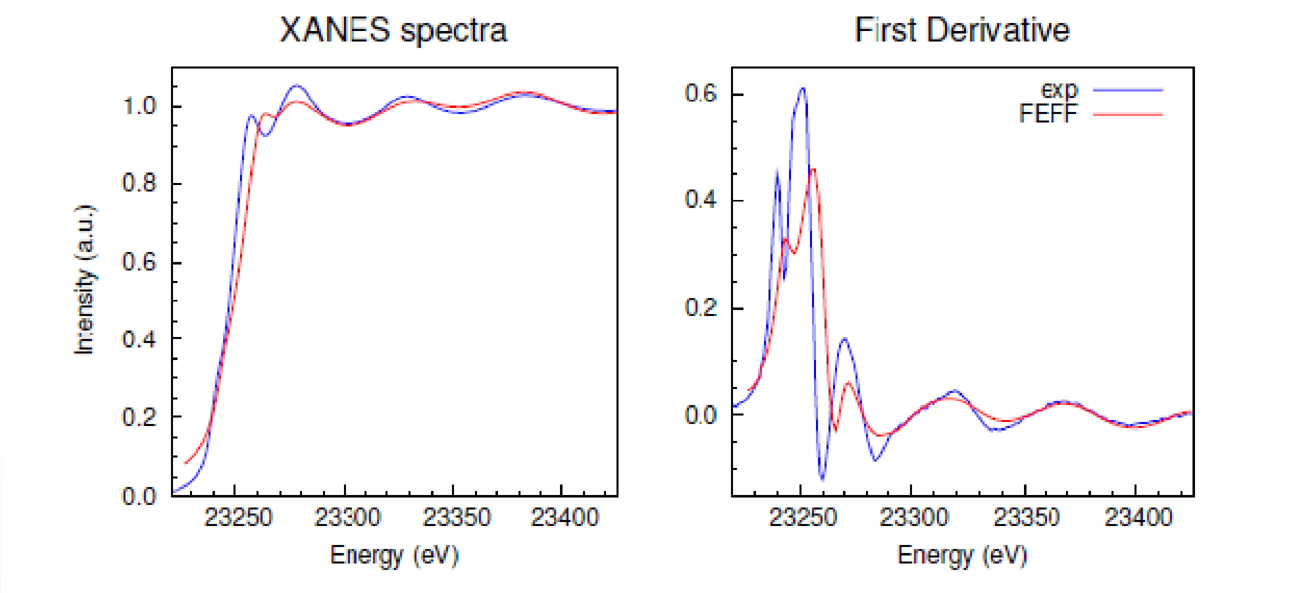
Understanding of the data (1)



Complex (100)-c1



XANES $Rh(CO)_2Cl/Al_2O_3$ (BM29) v. FEFF calculation from CASTEP structure

Ab initio model of 2.5% wt % Rh/Al_2O_3
By CASTEP:
Three structures close in energy – $Rh(CO)_2$ causes surface reconstruction to 1/3 unit cell

Otello Roscioni, John Dyke, Moniek Tromp

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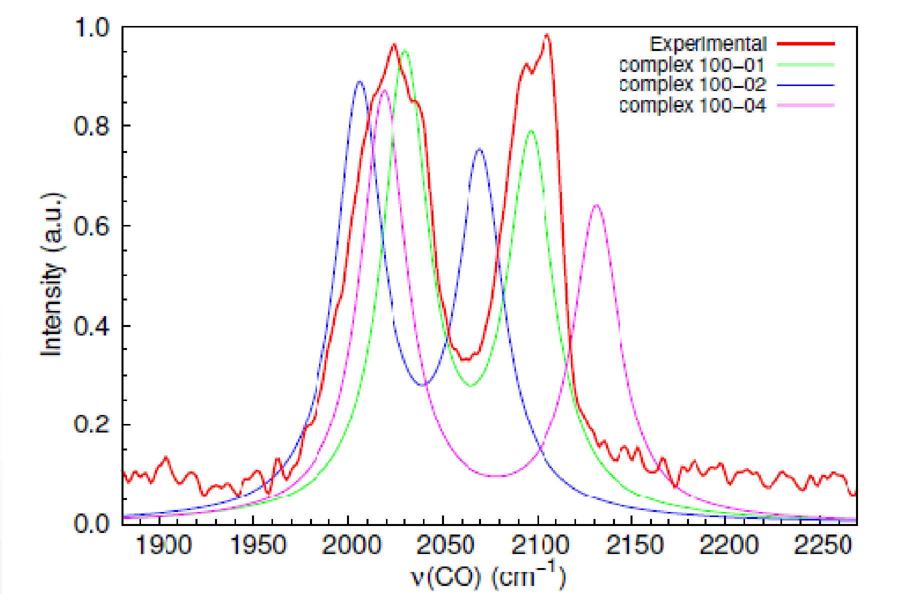
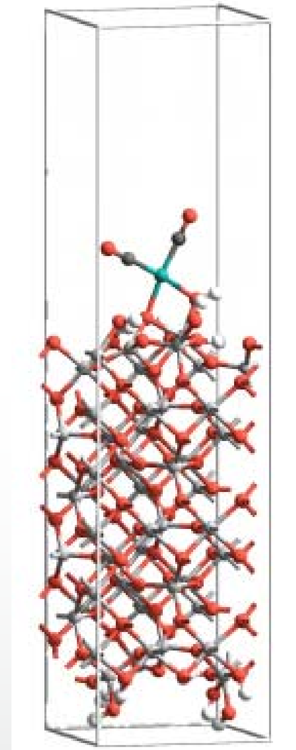
Understanding of the data (2)





Complex (100)-c1

IR calculations v $Rh(CO)_2/Al_2O_3$:
Hybrid calculations v experiment
Hybrid: QM core with MM shell and point charge host (GUESS)

plane (001)		plane (100)	
Complex	Energy (kcal/mol)	Complex	Energy (kcal/mol)
1	-18.205	1	-27.611
2	-12.779	2	-21.527
3	*not computed*	3	-27.300
4	*not computed*	4	-10.850
		5	-14.693

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Acknowledgements

- Collaborations:
  - Judith Corker, **S**
  - Andy Dent, **C, D**
  - Gareth Derbyshire, **C**
  - Richard Farrow, **C**
  - Jon Headspith, **C**
  - Mark Newton, **S, E**
  - Steven Fiddy **S, E, C**
  - Ian Harvey **C**
  - Michael Hagelstein **E**
  - Thomas Neisius **E**
  - Sakura Pascarelli **E**
  - Sofia Diaz-Moreno **E, D**
  - Moniek Tromp **S**
  - Anna Kroner **S/E, D**

  - **Tevor Rayment**
  - **Mike George**

- Funding
  - EPSRC
    - XSTRIP
    - Microreactor
    - IR-XAFS-MS
    - Stopped flow/quench
      - diode array uv-vis – XAFS
  - CCLRC
    - XH
  - ESRF
    - Anna Kroner
- Beamtime and support
  - STFC
    - SRS
    - Detector group
  - ESRF

S Southampton
E ESRF
C CCLRC/STFC
D Diamond