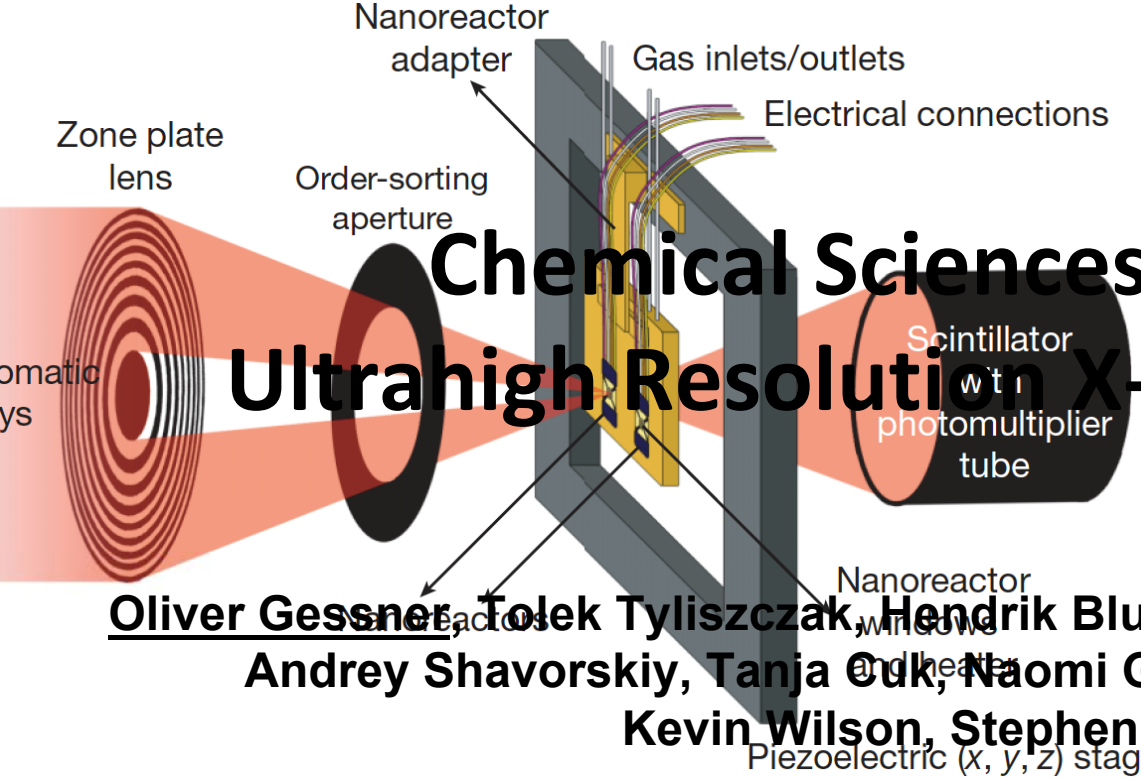
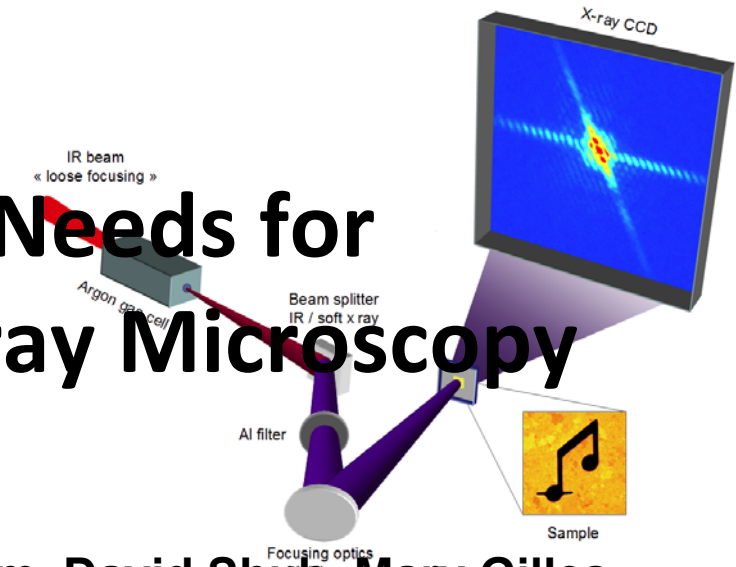
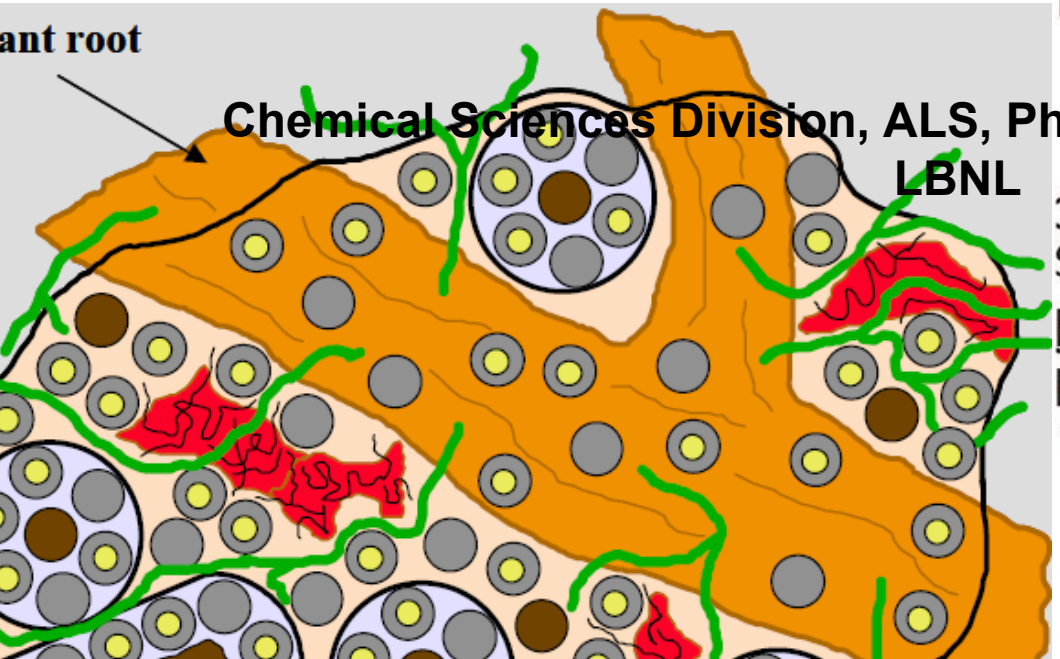
Chemical Sciences Needs for Ultrahigh Resolution X-ray Microscopy

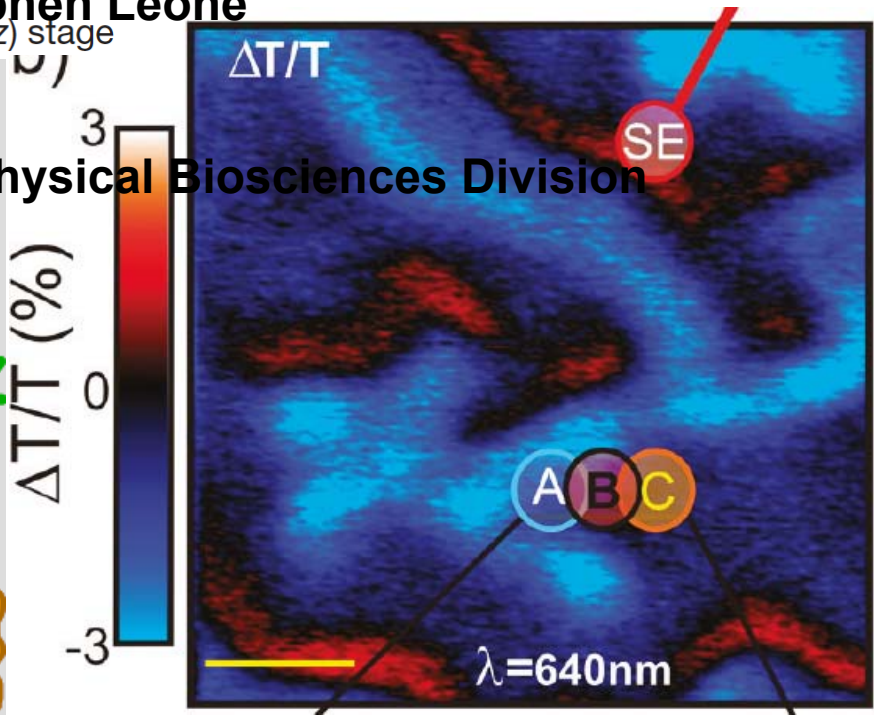
Oliver Gessner, Tolek Tyliszczak, Hendrik Bluhm, David Shuh, Mary Gilles, Andrey Shavorskiy, Tanja Cuk, Naomi Ginsberg, Musa Ahmed, Kevin Wilson, Stephen Leone

Chemical Sciences Division, ALS, Physical Biosciences Division
LBNL

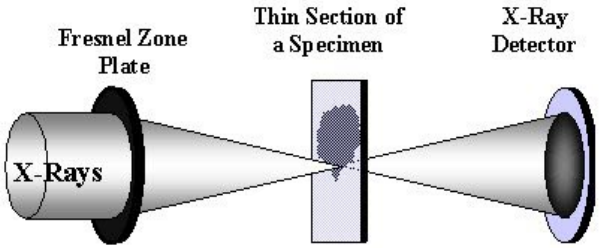




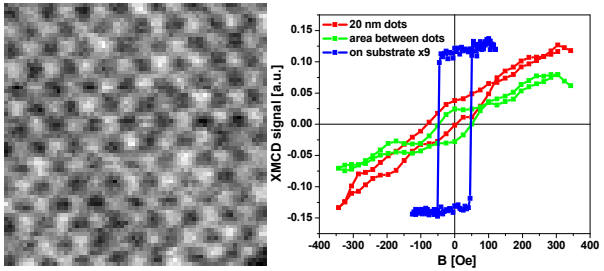




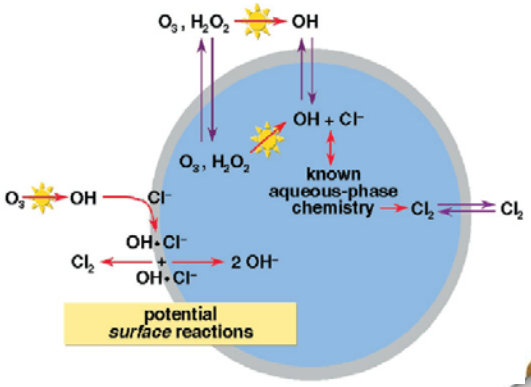
Chemical Sciences Needs for Ultrahigh Resolution X-ray Microscopy



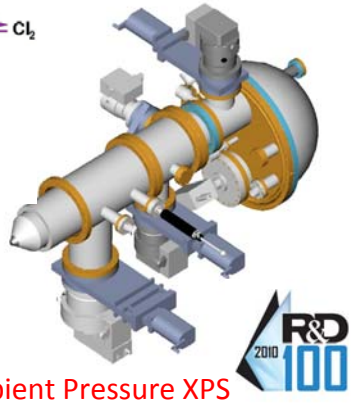
Scanning Transmission X-ray Microscopy (STXM)



Magnetism in Novel Nanostructures



Chemistry of Solution Surfaces



Ambient Pressure XPS

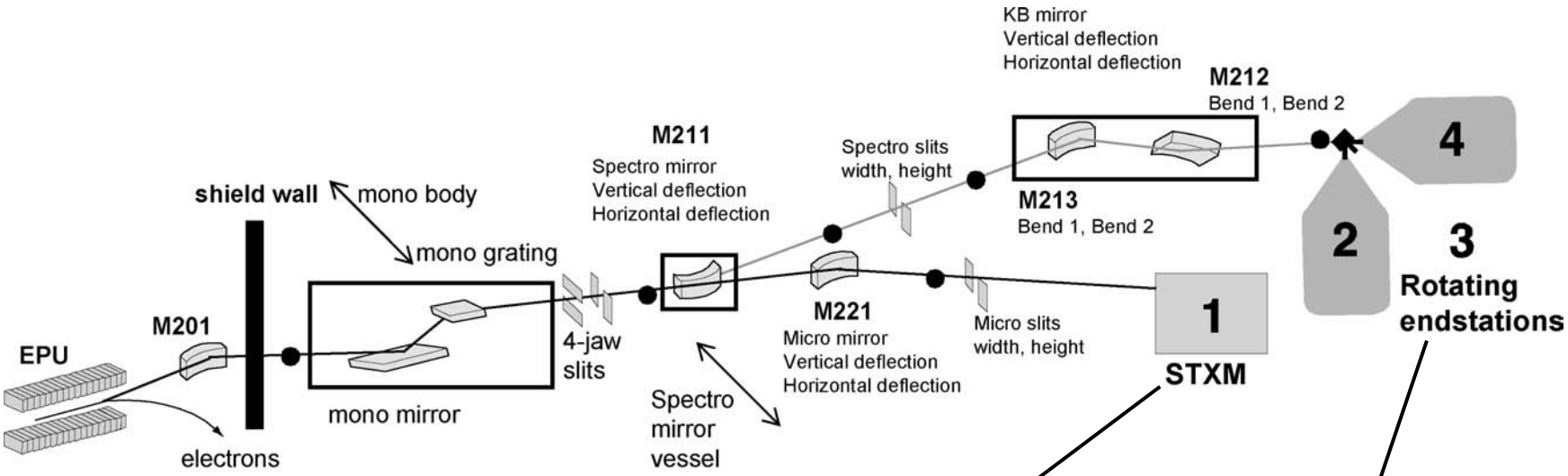
proposed or in progress ....

Soft VUV Ionization Mass Spectrometry

proposed or in progress ....

Imaging Energy- and Charge-Transport in Complex Systems

STXM and High Pressure XPS Beamline 11.0.2

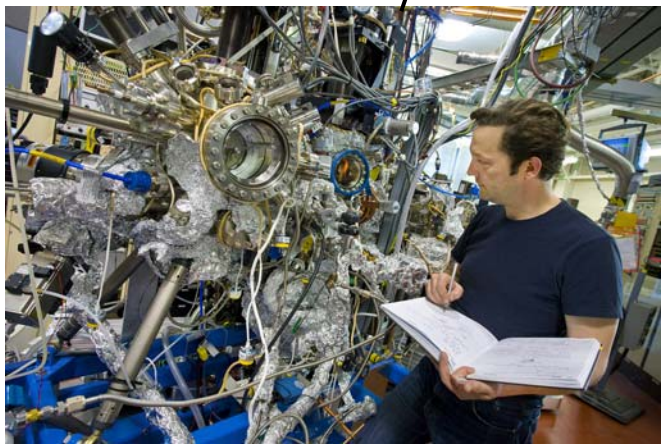


EPU gap
EPU Z
Polarization

Bluhm et al., J. Electron Spectrosc. Relat. Phenom. 150, 86 (2006)

David Kilcoyne

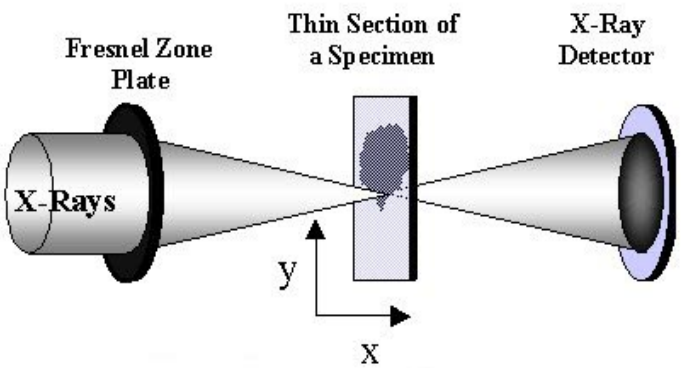
Tolek Tyliszczak

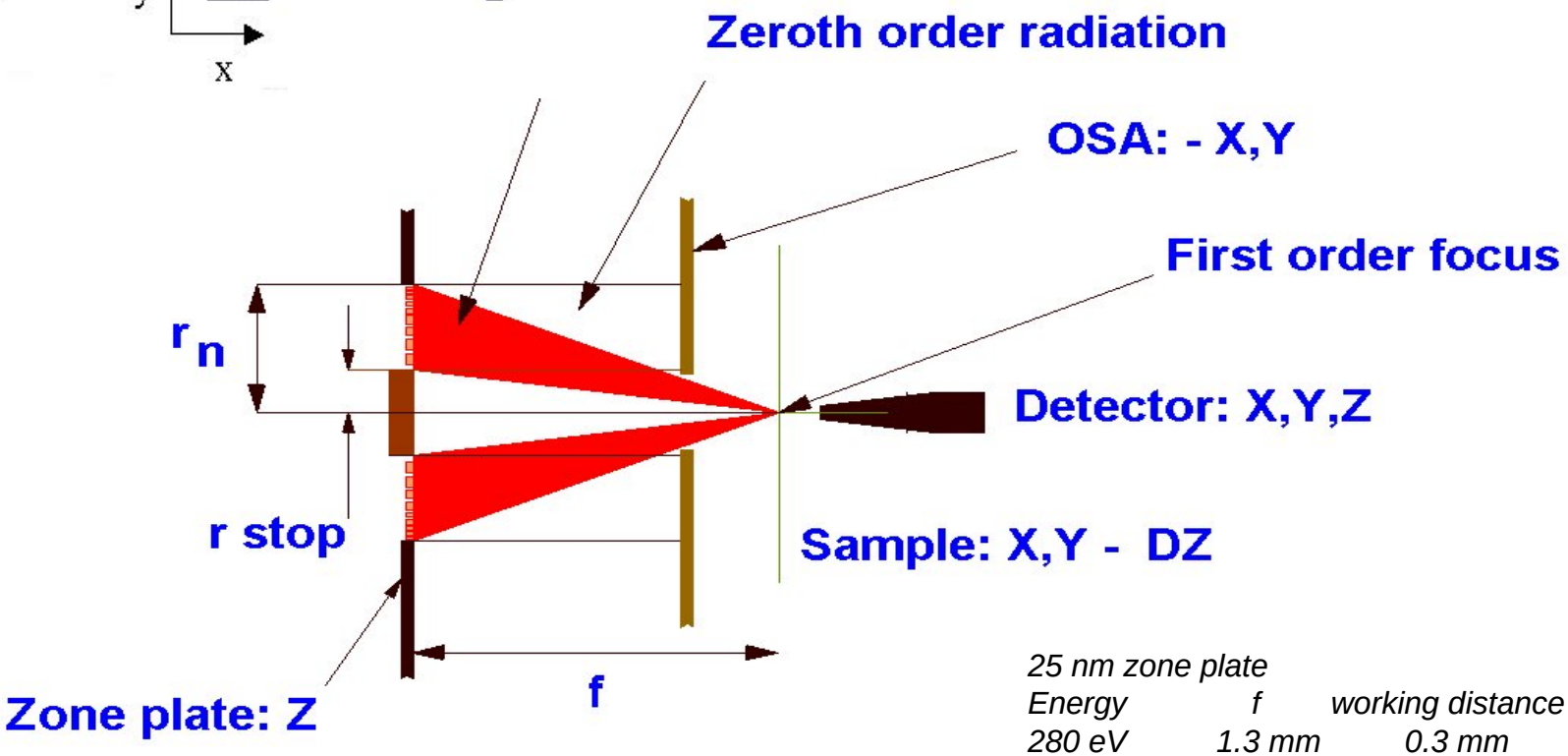


Hendrik Bluhm

BL 11.0.2 Team: Hendrik Bluhm, Tolek Tyliszczak, David Shuh, Mary Gilles, Andrey Shavorskiy, May Ling Ng, John Newberg

Scanning Transmission X-ray Microscopy (STXM)



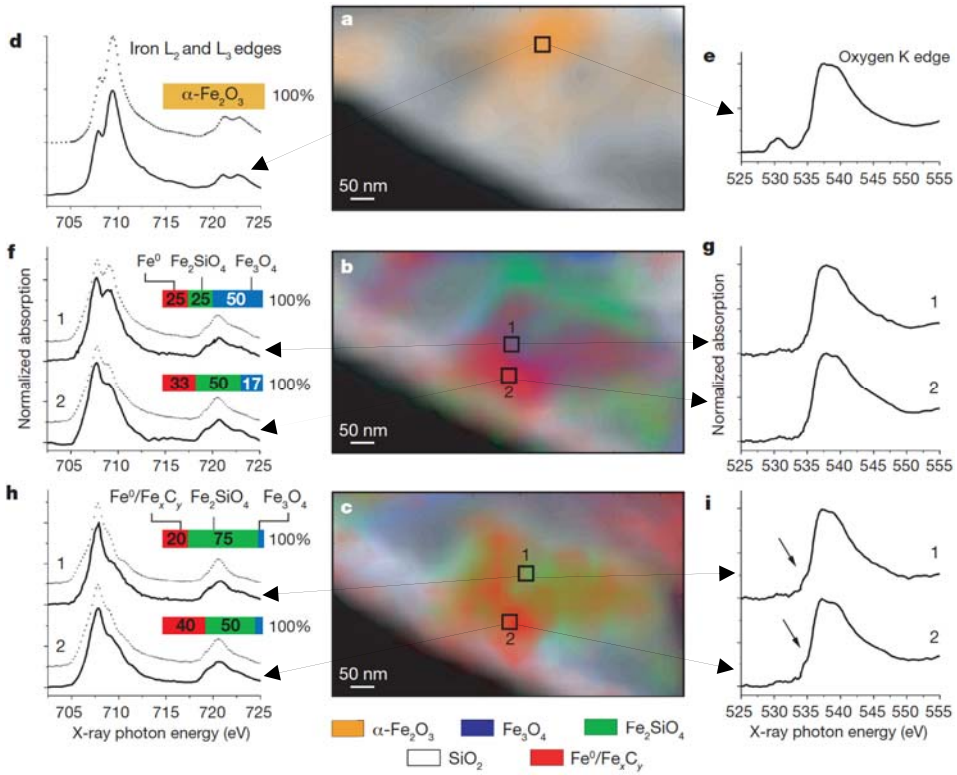


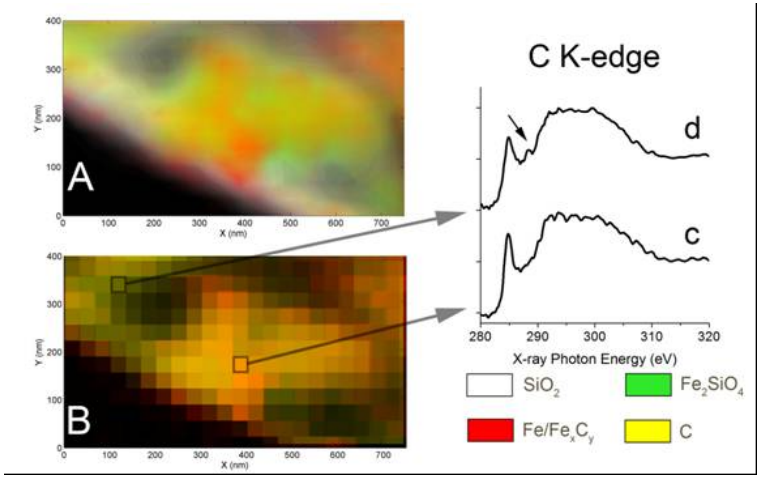
25 nm zone plate

Energy	*f*	*working distance*
280 eV	*1.3 mm*	*0.3 mm*
707 eV	*3.3 mm*	*0.7 mm*
1570 eV	*7.4 mm*	*1.6 mm*
1840 eV	*8.6 mm*	*1.8 mm*

In situ catalytic reactions

complex iron oxide based Fischer-Tropsch catalyst





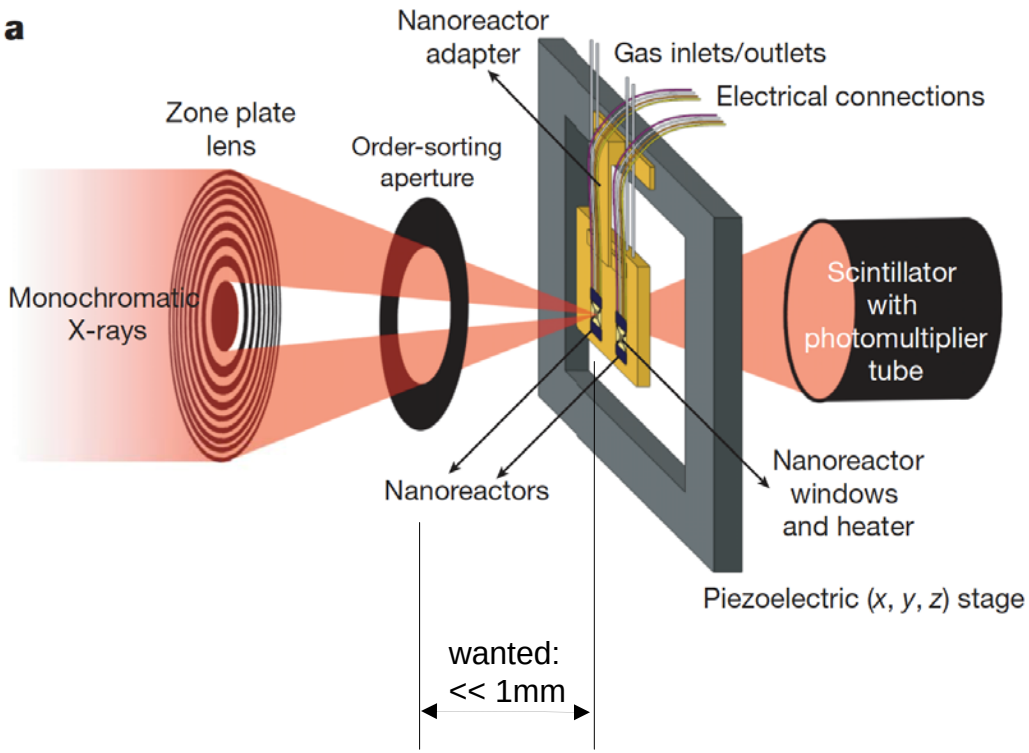
Chemical contour maps of a region of a catalyst particle during the different stages of reaction. A: Before treatment at RT in 1 bar He. B: After 2h in H2 at 350ºC. C: After 4h in CO/H2 at 250ºC. The corresponding regions of the O K-edge (e, g, i) and Fe L2,3-edge spectra (d, f, h) are indicated in the figures. Dotted lines indicate the linear combination fits, with the bars representing the contribution of the different phases to the spectra.

In situ studies, like this one of catalytic reactions, are using gas flow cells which are relatively bulky and the current high resolution zone plates can not be used because they have too short working distance. Diffraction enhanced imaging-spectroscopy using longer focal length zone plates may be the solution.

E. de Smit, I. Swart, J. Creemer, G. H. Hoveling, M. K. Gilles, T. Tyliszczak, P. J. Kooyman, H. W. Zandbergen, C. Morin, B. M. Weckhuysen and F. M. F. de Groot, Nature **456**, 222 (2008).

In situ catalytic reactions

Space limitations in STXM / flow cell measurement



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1840 eV	*8.6 mm*	*1.8 mm*

used here: 35 nm zone plate,
40 nm spatial resolution

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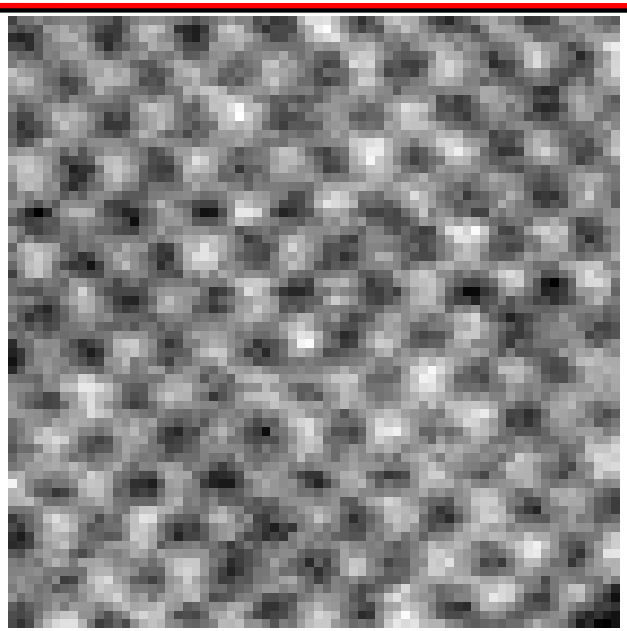
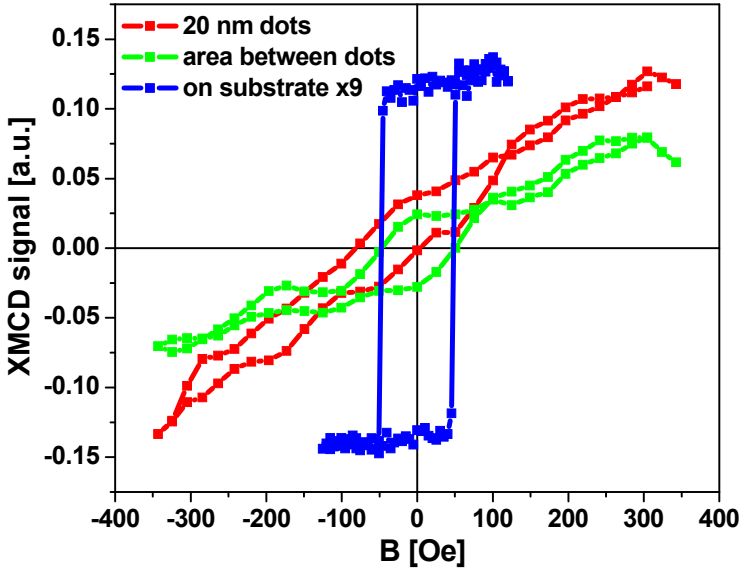
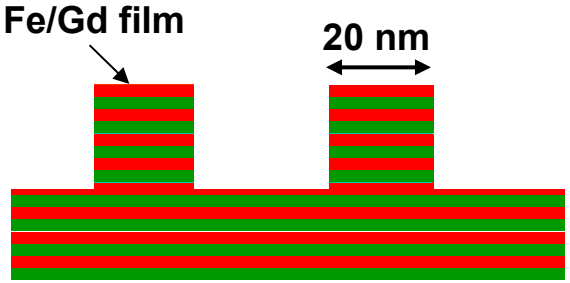
Magnetic characterization of 20 nm dots



STXM XMCD image of EUV structured Fe/Gd dots with a diameter of 20 nm and a periodicity of 70 nm recorded at the Fe L_3 edge



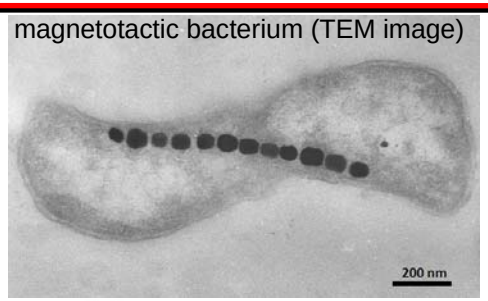
Hysteresis loop of a single 20 nm dot and of the film between the dots measured by XMCD

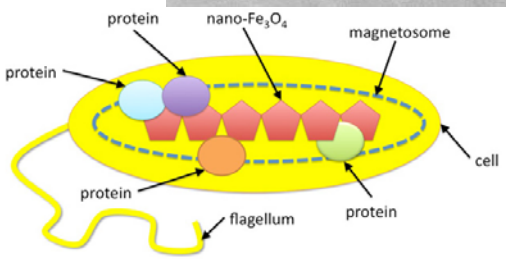


Studies of the magnetic behaviour of small elements relevant to current interest reached the spatial resolution limit. Future progress requires better spatial resolution with magnetic sensitivity – ptychography is a potential solution.

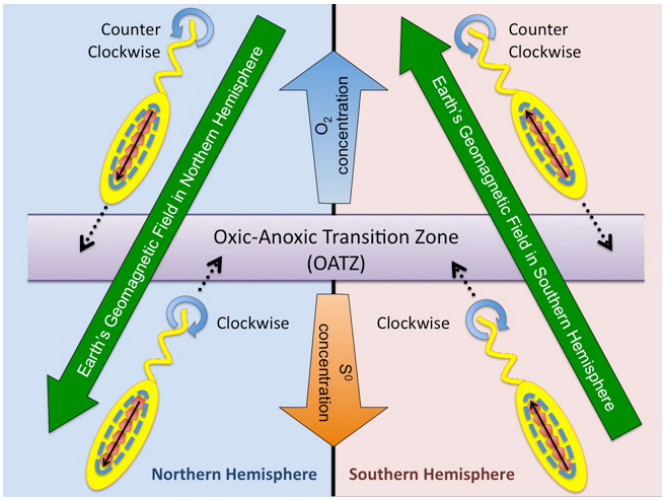
T. Eimüller, E. Amaladass, F. Luo, T. Tyliszczak

Magnetotactic Bacteria

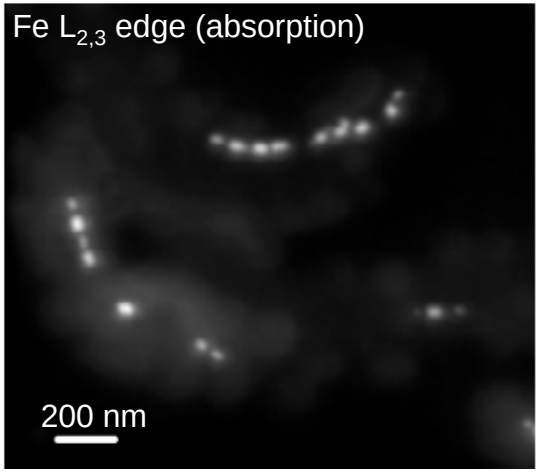


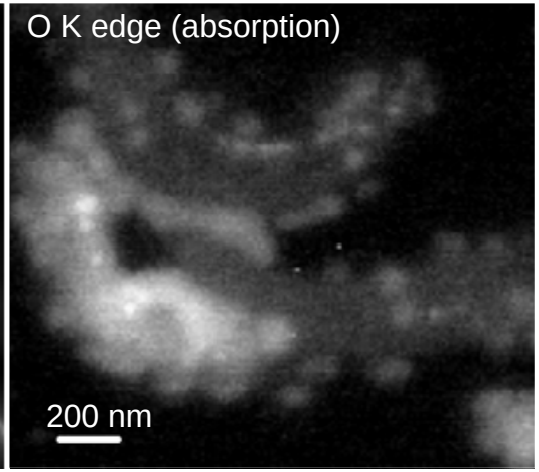


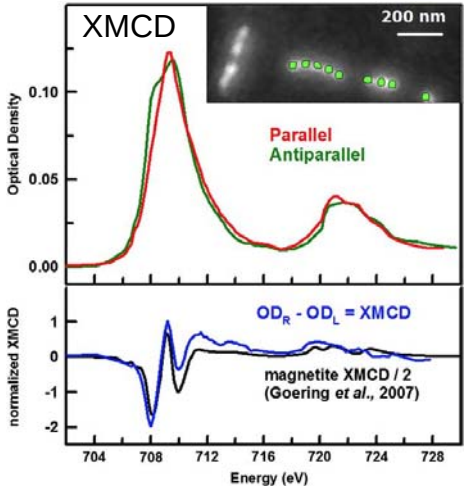
Single-domain Fe_3O_4 nanocrystals line up inside a bacterium's magnetosome, creating a permanent magnetic dipole – a compass needle that guides the bacterium's search for environments with optimum oxygen concentration.



STXM images and XMCD measurements of single magnetosome nanocrystals (marine vibrio strain MV-1), confirming common orientation of magnetic moments within linear nanocrystal chains and virtually saturated magnetization.



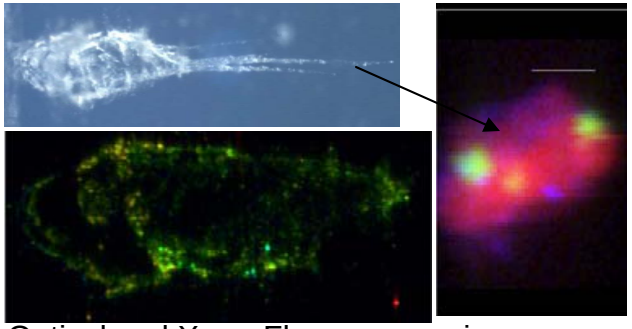




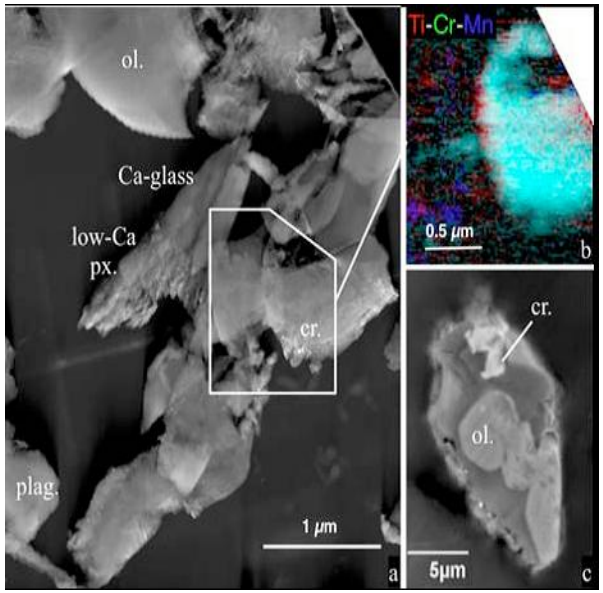
Lam, K.P., A.P. Hitchcock, M. Obst, J.R. Lawrence, G.DW. Swerhoneb, G.G. Leppard, T. Tyliszczak, C. Karunakara, J. Wang, K. Kaznatcheev, D.A. Bazylinskif, and U. Lins, "Characterizing magnetism of individual magnetosomes by X-ray magnetic circular dichroism in a scanning transmission X-ray microscope", Chemical Geology **270**(1-4), 110-116 (2010).

Cometary Particles

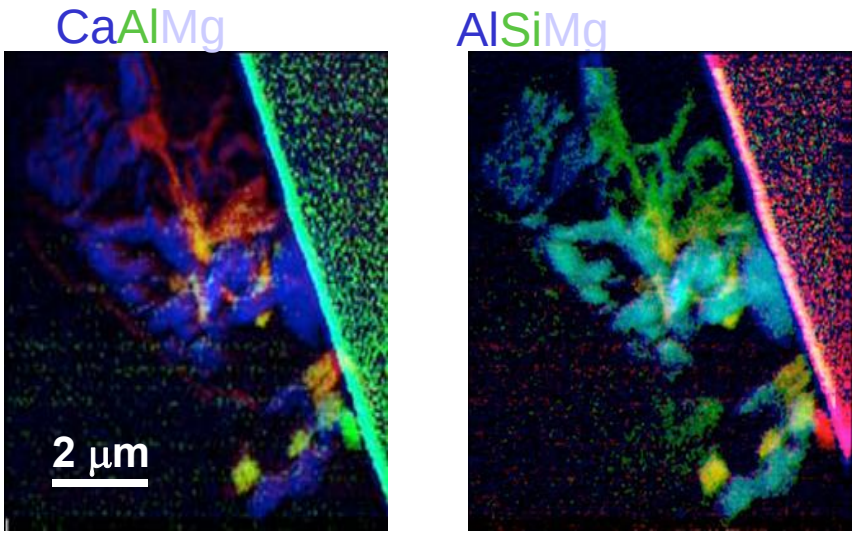
TYPE IIA CHONDRULE FRAGMENT FROM COMET 81P/WILD2 IN STARDUST TRACK C2052,2,74



Optical and X-ray Fluorescence images



TEM images



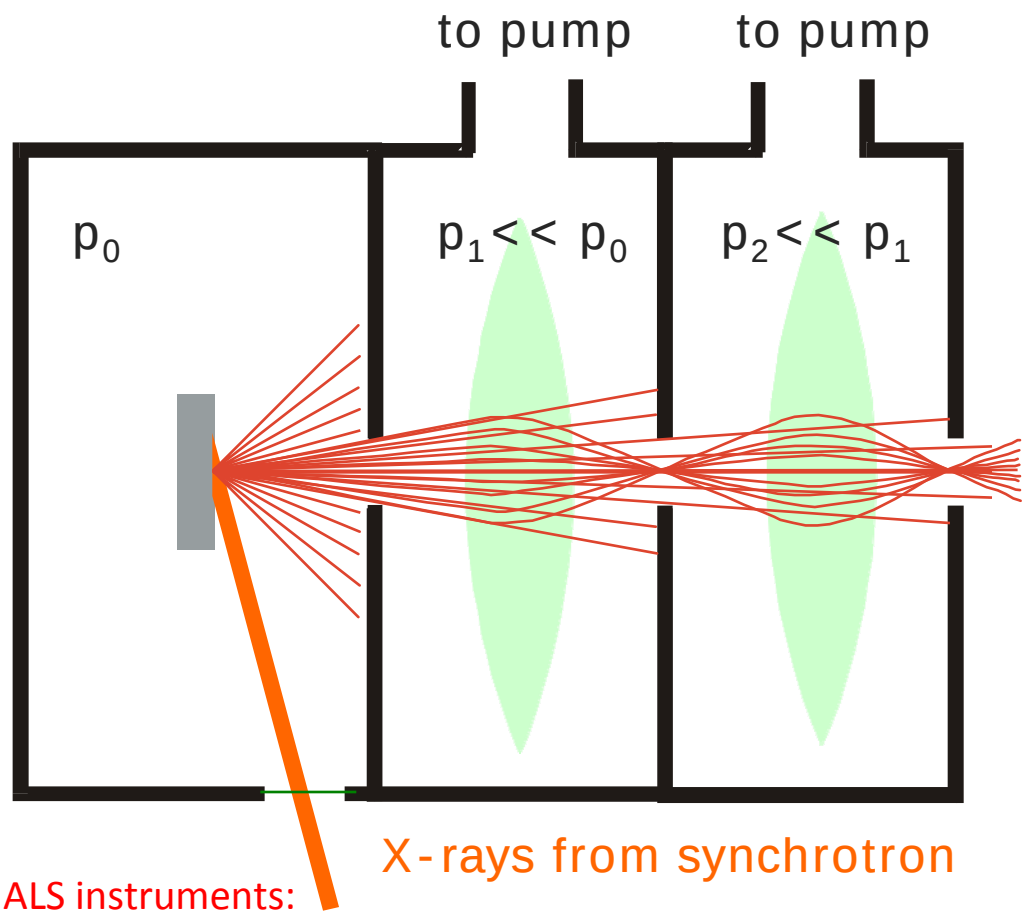
STXM element maps of Iris,9. Absorption difference maps, pixel size 100 nm. a) Ca-Al-Mg-. Yellow regions are Ca-Al rich, Purple regions are Ca-bearing Mg-Fe silicates. b) Al-Si-Mg map, the minerals are labeled as for Fig. 3.

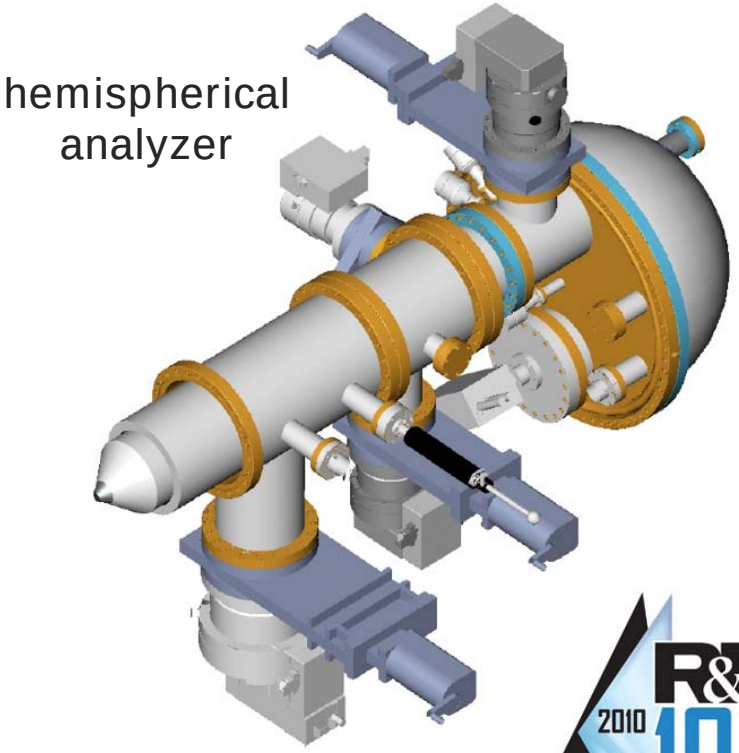
STXM provided detailed understanding of chemical composition before the TEM work to identify crystalline structure, but because of much lower spatial resolution it misses some important features,

A. L. Butterworth Z. Gainsforth, A. Bauville, L. Bonal, D. E. Brownlee, S. C. Fakra, G. R. Huss, D. Joswiak, M. Kunz, M. A. Marcus, K. Nagashima, R. C. Ogliore, N. Tamura, M. Telus, T. Tyliszczak, A. J. Westphal

LBNL/FHI Ambient Pressures XPS Design

D.F. Ogletree, H. Bluhm, G. Lebedev, C.S. Fadley, Z. Hussain, M. Salmeron, Rev. Sci. Instrum. 73 (2002) 3872.





LBNL/FHI Berlin/Specs

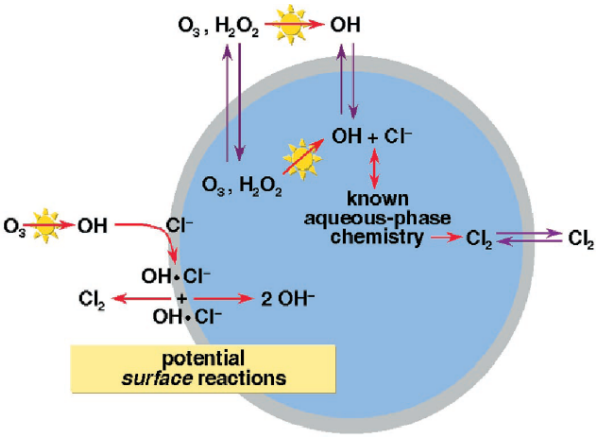
ALS instruments:

1st generation: BL 9.3.2 (funded by LBNL LDRD)
2nd generation: BL 11.0.2 (co-designed with FHI Berlin)
3rd generation: BL 9.3.2 and 11.0.2 (in-house and commercial)

Instruments at other facilities:

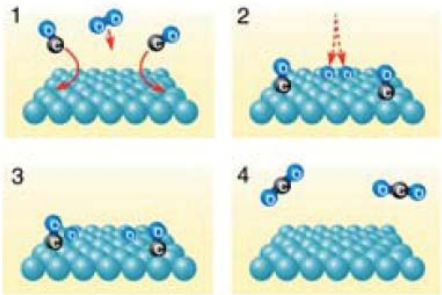
BESSY, NSLS, MAXLab, SSRL, Campinas, DELTA, Photon Factory
(funded: SOLEIL, SLS, ALBA; in planning: SPring-8, Diamond)

Examples for Ambient Pressure XPS experiments at ALS BL 11.0.2

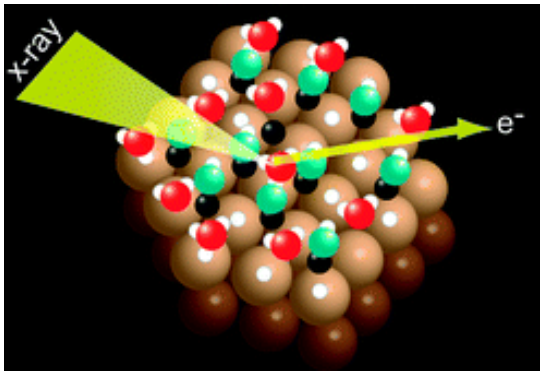


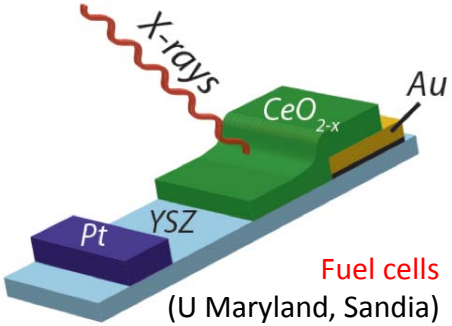
Chemistry of solution surfaces
(Hemminger, Ghosal, Krisch)

Heterogeneous catalysis (Somorjai, Salmeron, Besenbacher, de Groot, Lundgren, Nilsson, Starr)

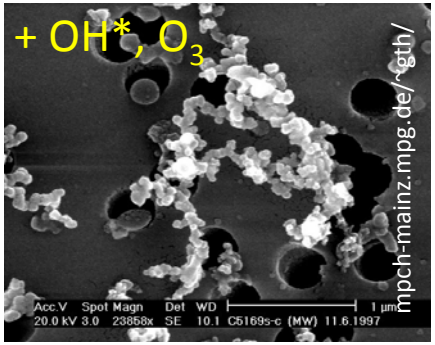


Reaction of water with oxides and metals
(Brown, Salmeron, Nilsson, Held, St. Gobain)

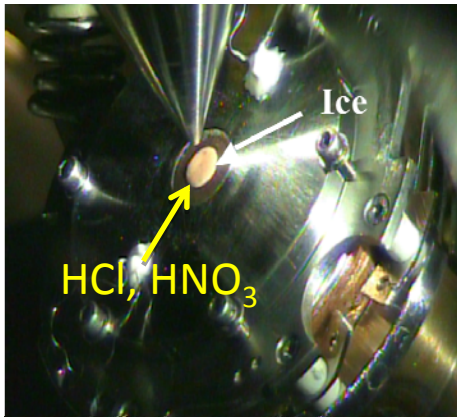




Fuel cells
(U Maryland, Sandia)



Heterogeneous chemistry of soot particles (Wilson)



Chemistry of ice surfaces (PSI, Newberg)

Zone-Plate Based Imaging Ambient Pressure XPS

proposed or in progress ....

Visualizing chemical change at surfaces and interfaces: Cells, bacteria, soil, aerosols and nanoparticles…….

Musa Ahmed Kevin Wilson

proposed or in progress ....

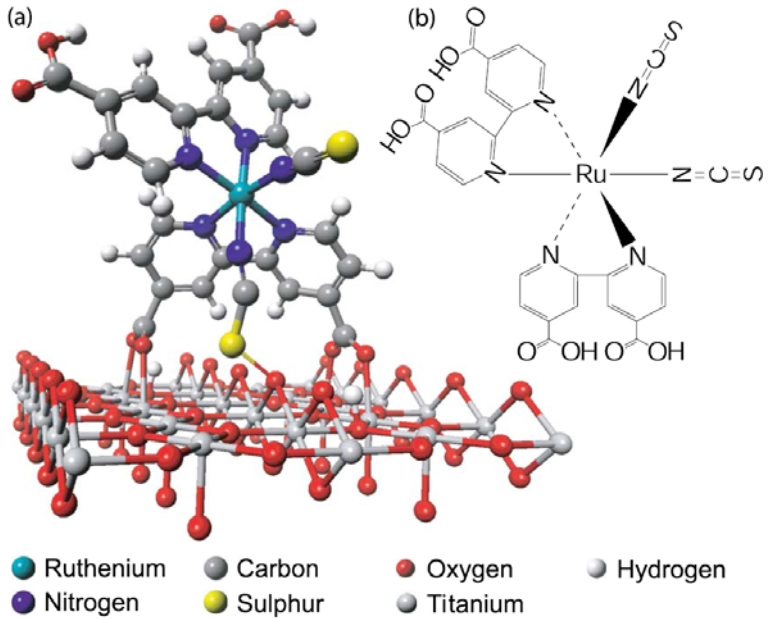
Time-Resolved Near-Edge Coherent Diffractive Imaging

Gessner, Belkacem, Leone et al.

proposed or in progress ....

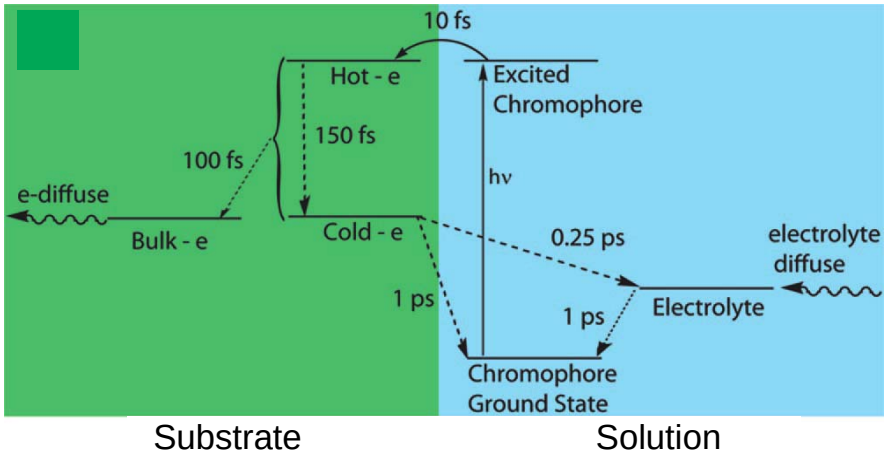
Interfacial Charge Transfer Dynamics Studied @ LCLS & ALS

Ru 535 dye on TiO_2 substrate

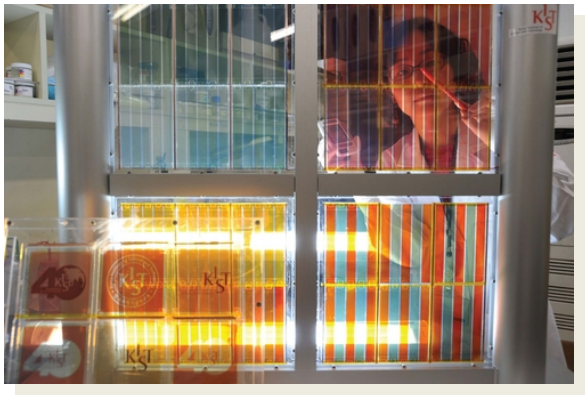


Mayor et al., JCP 129, 114701 (2008)

Interfacial Processes and Rates



Prezhdo et al., Acc. Chem. Res. 41, 339 (2008)



Dye Sensitized
Solar Cell Windows

Probing Interfacial Dynamics by Time-Resolved Photo- and Auger-Electron Spectroscopy

proposed or in progress ....

Imaging Energy- and Charge-Transport in Complex Systems

proposed or in progress ....

Chemical Sciences Needs – A Wish List

Core Drivers

- Chemical sensitivity within few nm to few μm spatial resolution
- Electronic structure sensitivity
- Magnetization sensitivity
- Imaging intermediates / Time domain capability
- Depth sensitivity
- "Real world" (e.g. soil, wet surfaces) and "Laboratory" (e.g. He droplets) samples

Technical Requirements

- Spatial resolution ≤5 nm
- Energy resolving power better than 10,000
- Photon energies covering at least K-edges from C to S (280 eV – 2500 eV)
- External magnetic fields up to 50 mT for magnetization studies
- Sample scanning in arbitrary planes, e.g. to probe magnetization in plane
- 3D imaging capability
- Relaxed zone plate focusing conditions
- Complex sample compatibility (e.g. flow cells, organic matter, clusters, …)
- Time-resolution at the limit of the ALS (e.g. w/ ps pulse, MHz fiber laser)