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CSX 2012

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at ETH Zurich
4 - 6 July
Switzerland

3rd Workshop on the
Simultaneous Combination of Spectroscopies with X-ray
Absorption, Scattering and Diffraction Techniques

in Catalysis, Materials, Nanomaterials & Life Sciences

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**3rd Workshop
on the Simultaneous Combination
of Spectroscopies with X-ray Absorption,
Scattering and Diffraction Techniques**

July 4th – 6th, 2012

Zürich, Switzerland

The workshop

is organized by the Paul Scherrer Institute



hosted by ETHZ



Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

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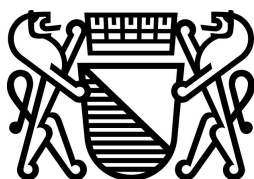
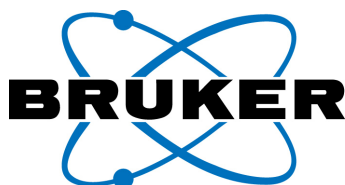


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Workshop Program

Sessions:

Biological	Catalysis	Materials & Time resolution
Materials Science	Posters	Formal & Excursion

	Wednesday July 4 th , 2012	Thursday July 5 th , 2012	Friday July 6 th , 2012
09:00	from 08:30 Registration & Coffee	Frenkel A.	Bus transfer to PSI
09:30		Khodakov A.	
10:00	Van der Veen, F.: Welcome Fuchs, M.: Introduction	Sippel D.	Coffee
10:30	Bourgeois D.	Nachtegaal M.	
11:00	Pearson A.	Posters & coffee break	Tour of SLS Ring and Beamlines
11:30	Okumura H.		
12:00	Von Stetten D.		
12:30	Dworkowski F.		
13:00	Lunch	Lunch	Lunch
13:30	Beale A.	Orville A.	
14:00	Newton M.	Hough M.	
14:30	Makosch M.	Knipp M.	
15:00	Rochet A.	Martinoli C.	Bus transfer to Zürich main station
15:30	Abdala P. M.	Hersleth H.-P.	
16:00	Coffee break	Coffee break	
16:30	Round Table	Round Table	
17:00	Van Beek W.	Cole J.	
17:30	Milanesio M.	Yot P. G.	
18:00	Ferri D.	Gnutzmann T.	
18:30	Silatani M. & Lima F. A.	Ghigna P.	
19:00	Rittmann-Frank M. H.	Marcelli A.	
19:30	Dinner Reception until 21:00		

Daily Program

The workshop is taking place in the main building (HG) of the ETHZ:

The talk sessions are in conference room E3. The poster session is in the entrance hall and the coffee breaks are in room E30.

The secretariat is opened between 8:30 and 17:00 in room HG E33.1.

Wednesday, July 4th, 2012

8:30 - 10:00		Registration & Coffee
Session: Welcome & Introduction		
10:00 - 10:10		Welcome VAN DER VEEN, Friso <i>Paul Scherrer Institut, Switzerland</i>
10:10 - 10:20		Introduction FUCHS, Martin R <i>Paul Scherrer Institut, Switzerland</i>
Session : Biological 1 (Chair: Allen Orville)		
10:20 - 10:50	Wed_Bio1_1 <i>Invited</i>	Combining spectroscopy and crystallography: a tool to investigate fluorescent proteins BOURGEOIS, Dominique <i>IBS, France</i>
10:50 - 11:20	Wed_Bio1_2 <i>Invited</i>	Dynamic Structural Science: developing tools for time-resolved structural studies PEARSON, Arwen <i>Astbury Centre for Structural Molecular Biology, University of Leeds, UK</i>
11:20 - 11:40	Wed_Bio1_3	Present status of micro-spectroscopic instruments in SPring-8 macromolecular crystallography beamlines OKUMURA, Hideo <i>JASRI/SPring-8, Japan</i>
11:40 - 12:00	Wed_Bio1_4	Status of the Cryobench in crystallo spectroscopy laboratory of the ESRF VON STETTEN, David <i>European Synchrotron Radiation Facility, France</i>
12:00 - 12:20	Wed_Bio1_5	Third generation of on-axis in situ optical spectroscopy - Extending the scope of macromolecular crystallography DWORKOWSKI, Florian <i>Paul Scherrer Institut, Switzerland</i>
12:20 - 13:20		Lunch

Session: Catalysis 1 (Chair: Anatoly Frenkel)

13:20 - 13:50	Wed_Cat1_1	An eye on the inside: imaging of catalytic particles under reaction conditions BEALE, Andrew <i>Inorganic Chemistry and Catalysis, Utrecht University, Netherlands</i>
13:50 - 14:20	Wed_Cat1_2	Chasing changing catalysts with XAFS and high energy X-ray techniques combined with infrared spectroscopy NEWTON, Mark <i>ESRF, Grenoble, France</i>
14:20 - 14:40	Wed_Cat1_3	Combination of HERFD XAS and ATR IR for in situ investigation of the liquid phase hydrogenation of nitrobenzene MAKOSCH, Martin <i>ETH Zürich, Switzerland</i>
14:40 - 15:00	Wed_Cat1_4	Operando characterisation of heterogeneous catalysts by combination of Quick-XAS with Raman Spectroscopy ROCHET, Amelie <i>SOLEIL, France</i>
15:00 - 15:20	Wed_Cat1_5	XAS, XRD and Raman study on nanostructured CeO₂-Gd₂O₃ solid solutions ABDALA, Paula M. <i>SNBL at ESRF, France</i>
15:20 - 15:50		Coffee Break

Session: Materials & Time resolution 1 (Chair: Augusto Marcelli)

15:50 - 16:20	Wed_TR_1	Modulation Excitation Spectroscopy applied to Crystallography VAN BEEK, Wouter <i>SNBL at ESRF, France</i>
16:20 - 16:50	Wed_TR_2	Combined modulation enhanced X-ray powder diffraction and Raman spectroscopic study of structural transitions in the spin crossover material [Fe(Htrz)(trz)](BF₄) MILANESIO, Marco <i>Università Piemonte Orientale, Italy</i>
16:50 - 17:10	Wed_TR_3	Modulation excitation spectroscopy coupled with synchrotron X-ray methods to unravel dynamic processes on supported Pd catalysts FERRI, Davide <i>Empa, Switzerland</i>
17:10 - 17:30	Wed_TR_4	Probing the structure of proteins in physiological conditions by X-ray absorption and UV/Visible spectroscopies SILATANI, Mahsa; LIMA, Frederico Alves <i>Ecole Polytechnique Fédérale de Lausanne, Switzerland</i>
17:30 - 17:50	Wed_TR_5	Time-resolved X-ray absorption studies on charge carrier dynamics in aqueous TiO₂ nanoparticles RITTMANN-FRANK, Mercedes Hannelore <i>Ecole Polytechnique Fédérale de Lausanne, Switzerland</i>
18:00 - 21:00		Dinner Reception in the GP Pavillon

Thursday, July 5th, 2012

Session: Catalysis 2 (Chair: Andrew Beale)

9:00 - 9:30	Thu_Cat2_1 <i>Invited</i>	In situ X-ray studies of model and real catalysts: Bridging the complexity gap FRENKEL, Anatoly <i>Yeshiva University, USA</i>
9:30 - 9:50	Thu_Cat2_2	In-situ QXAS investigation of the genesis of cobalt active phases in supported Fischer-Tropsch catalysts KHODAKOV, Andrei <i>UCCS, CNRS, Université Lille 1, ENSCL, Ecole Centrale de Lille, France</i>
9:50 - 10:10	Thu_Cat2_3	Evidence for central carbon in nitrogenase FeMo cofactor SIPPEL, Daniel <i>Institut für organische Chemie und Biochemie, Albert-Ludwigs-Universität Freiburg, Germany</i>
10:10 - 10:30	Thu_Cat2_4	Identifying dynamic structural changes in catalysts with time and energy-resolved XAS and XES NACHTEGAAL, Maarten <i>Paul Scherrer Institut, Switzerland</i>

Session: Posters

10:30 - 12:00		Posters & Coffee Break
12:00 - 13:00		Lunch

Session: Biological 2 (Chair: Arwen Pearson)

13:00 - 13:30	Thu_Bio2_1 <i>Invited</i>	Systems biology in Prokaryote - Eukaryote symbiosis: single-crystal spectroscopy correlated with X-ray crystallography and other complementary methods ORVILLE, Allen <i>Brookhaven National Laboratory, USA</i>
13:30 - 13:50	Thu_Bio2_2	Fingerprinting redox/ligand states and driving catalysis in protein single crystals HOUGH, Michael <i>University of Essex, UK</i>
13:50 - 14:10	Thu_Bio2_3	Iron-porphyrin coordinates an arginine guanidine side-chain in a protein pocket – Insights from microspectrophotometry and crystallography KNIPP, Markus <i>Max-Planck-Institut für Bioanorganische Chemie, Germany</i>
14:10 - 14:30	Thu_Bio2_4	Structural and spectroscopic observation of an enzyme at work MARTINOLI, Christian <i>University of Pavia, Italy</i>
14:30 - 14:50	Thu_Bio2_5	Using in situ single-crystal UV-vis and Raman spectroscopy to study the effect of X-ray radiation damage on the crystal structures of haem proteins HERSLETH, Hans-Petter <i>Department of Molecular Biosciences, University of Oslo, Norway</i>
14:50 - 15:20		Coffee Break
15:20 - 15:40		Round Table

Session: Materials Science (Chair: Marco Milanesio)

15:40 - 16:10	Thu_MS_1	En-Light-ening photo-crystallography with X-ray absorption COLE, Jacqueline <i>University of Cambridge, UK & University of New Brunswick, Canada</i>
16:10 - 16:30	Thu_MS_2	Exploration of the mechanical properties of flexible MOFs by coupling experimental and modeling approaches YOT, Pascal G. <i>Université Montpellier 2, France</i>
16:30 - 16:50	Thu_MS_3	Investigation of crystallization processes using Synchrotron X-ray diffraction and Raman spectroscopy GNUTZMANN, Tanja <i>BAM Federal Institute for Materials Research and Testing, Germany</i>
16:50 - 17:10	Thu_MS_4	Pushing microbeam probes to nanoscale resolution for the study of buried interfaces GHIGNA, Paolo <i>Dipartimento di Chimica, Università di Pavia, Italy</i>
17:10 - 17:40	Thu_MS_5 <i>Invited</i>	In-situ time-resolved x-ray and IR combinatorial approach for materials science investigation using 3rd generation synchrotron radiation sources MARCELLI, Augusto <i>INFN – LNF, Italy</i>

Friday, July 6th, 2012

Visit to Paul Scherrer Institut

9:00 - 10:00		Bus transfer to Paul Scherrer Institut
10:00 - 10:30		Coffee Break
10:30 - 13:00		Tour of SLS Ring and Beamlines
13:00 - 14:00		Lunch
14:00 - 15:00		Bus transfer to Zurich train station

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Oral Contributions



Wed_Bio1_1

Combining spectroscopy and crystallography: a tool to investigate fluorescent proteins

BOURGEOIS, Dominique¹¹IBS**Abstract:**

Structural biology relies increasingly on complementary methods that are applied to the same sample. In crystallo optical spectroscopy is a method of choice to assess the relevance of crystallographic structures, characterize colored ligands, monitor chemical changes induced by the X-ray beam, or identify intermediate states trapped in the crystal. Specifically, combining optical (absorbance, fluorescence or Raman) spectroscopy with kinetic crystallography allows the precise monitoring of structural changes and dynamical properties of proteins “in action”□. The principles of kinetic crystallography and *in crystallo* spectroscopy will be presented. Examples concerning the fascinating world of photo-transformable fluorescent proteins from the GFP-family will be detailed.

Wed_Bio1_2

Dynamic Structural Science: developing tools for time-resolved structural studies

PEARSON, Arwen¹; YORKE, Briony²; OWEN, Robin³; WEBB, Mike²¹*Astbury Centre for Structural Molecular Biology, University of Leeds*²*University of Leeds*³*Diamond Light Source***Abstract:**

The fundamental aim of structural biology is to understand the molecular basis of life. To achieve this, a high resolution description of how the system changes with time is required. Single time-averaged structures, for example those of cryotrapped intermediates, provide snap-shots of a reaction that yield considerable information. However, cryotrapping approaches are limited to the study of longer lived, metastable, states. To observe short-lived species a time-resolved approach is required.

We are developing a new approach to time-resolved crystallography that combines the new developments in microfocus beams and beamline automation with information from single crystal spectroscopy to study non-reversible enzyme reactions. Here we will present initial results using our test system, aspartate decarboxylase.

Wed_Bio1_3

Present status of micro-spectroscopic instruments in SPring-8 macromolecular crystallography beamlines

OKUMURA, Hideo¹; SHIMIZU, Nobutaka²; HIKIMA, Takaaki³; KAWANO, Yoshiaki³;
BABA, Seiki¹; UENO, Go³; KUMASAKA, Takashi¹; YAMAMOTO, Masaki³

¹JASRI/SPring-8

²JASRI/SPring-8, KEK (present affiliation)

³RIKEN SPring-8 Center

Abstract:

Spectroscopic measurement combined with X-ray diffraction study is an important technique to elucidate the structure-function relationships of proteins. At SPring-8, two types of on-line micro-spectrophotometer (MS) for absorption spectroscopy have been dedicated to macromolecular crystallography (MX). The one is designed to measure Vis absorption spectra simply and at high-speed with CCD array detector installed at BL26B2. Another type has features of high-sensitivity and wide dynamic range by photomultiplier and monochromatic light source which covers UV-Vis region in BL38B1. Both have been used for validation of radiation damage or protein cofactor state (e.g. photoreceptor, oxidation-reduction, etc.).

As our study using MS, radiation damage against protein structure was evaluated by absorption spectroscopy at BL38B1. As the results, decrease of the absorption maximum at UV region was observed, and it indicates the state change of aromatic residue, in spite of only modest change of electron density map.

We are now planning to build a new on-line MS at the MX beamlines in SPring-8. This is expected to target the UV-Vis absorption and Raman spectroscopy for precise evaluation of radiation damage, detailed validation of cofactor state, and detection of entrapped reaction intermediates on protein crystals. It hopefully performs simultaneous measurement with diffraction data collection.

Wed_Bio1_4

Status of the Cryobench in crystallo spectroscopy laboratory of the ESRF

VON STETTEN, David¹; GIRAUD, Thierry¹; ROYANT, Antoine¹;
NOIRCLERC-SAVOYE, Marjolaine²; BATOT, Gaelle¹; DOBIAS, Fabien¹;
TERRIEN, Maxime¹; SEVER, Franc¹; WEIK, Martin²;
CARPENTIER, Philippe¹; DE SANCTIS, Daniele¹

¹*European Synchrotron Radiation Facility*

²*Institut de Biologie Structurale*

Abstract:

The Cryobench laboratory of the ESRF has been founded in 1999 in order to record UV-visible absorption and fluorescence emission spectra of protein crystals [1]. The possibilities of recording Raman spectra and fluorescence lifetime histograms were later added, while the laboratory was rebuilt and expanded [2,3]. In the context of the ESRF upgrade programme, the Cryobench was rebuilt in 2009 in the vicinity of the structural biology beamlines ID29 and ID30A, opening up the possibility of routine on-line spectroscopy experiments.

The so-called “in crystallo” spectroscopy techniques allow to verify the state of a crystalline protein in comparison to solution (redox state, photoactive state, nature and state of ligand) and, in combination with crystallographic data, to correlate structure and function. It can also serve to monitor the extent of radiation damage or the progress of a reaction. Over the years, Cyan Fluorescent Proteins (CFPs) have become a favourite topic at the Cryobench laboratory. In this talk, I will review several projects that took advantage of complementary techniques to understand the underlying mechanism of efficient fluorescence by CFPs [4], which in fine led to the development of a fluorescent protein with an almost-perfect quantum yield [5].

References:

- [1] J. Appl. Cryst. 35, 319 (2002).
- [2] J. Appl. Cryst. 40, 1105 (2007).
- [3] J. Appl. Cryst. 40, 1113 (2007).
- [4] Biochemistry 48, 10038 (2009).
- [5] Nature Comm. 3, 751 (2012).

Wed_Bio1_5

Third Generation of On-axis in situ Optical Spectroscopy – Extending the Scope of Macromolecular Crystallography

DWORKOWSKI, Florian¹; POMPIDOR, Guillaume¹; THOMINET, Vincent¹;
SCHULZE-BRIESE, Clemens²; FUCHS, Martin¹

¹*Paul Scherrer Institut*
²*Dectris Ltd*

Abstract:

Macromolecular Crystallography of proteins is one of the fundamental tools of a structural biologist. However, this method does not yield information on, for example, the chemical state of co-factors, the redox state of metal centers or disulphides, or the identity of bound ligands. Many of these observations can be directly or indirectly linked to radiation damage, one of the central limitations of synchrotron X-ray diffraction data collection [1]. To be able to better quantify the extent of this effect and obtain additional complementary data on the sample, the on-axis geometry for in-situ combination of optical spectroscopic methods with the diffraction experiment has proven highly effective [2]

At beamline X10SA at the Swiss Light Source we now are commissioning the third generation of an on-axis multi-mode micro-spectrophotometer (SLS-MS3). It is fully integrated into the completely rebuilt beamline endstation and designed to remain always online, thereby dramatically reducing setup times for the support UV/Vis, Fluorescence, Raman and Resonance Raman spectroscopic modes.

We also present quantitative mappings of the on-axis sampling geometry to demonstrate its advantages for aligning the sampling volumes. We show applications of UV/Vis spectroscopy and resonant and non-resonant Raman spectroscopy toward monitoring the photo reduction of metal centers, ligand abstraction and bond breakage.

References:

- [1] Garman, E. F. and M. Weik. Journal of Synchrotron Radiation (2011), **18**(3): 313-317
- [2] R. L. Owen, A. R. Pearson, et al., Journal of Synchrotron Radiation (2009), **16**, 173-182

Wed_Cat1_1

**An eye on the inside:
imaging of catalytic particles under reaction conditions**

BEALE, Andrew¹; JACQUES, Simon²; OBRIEN, Matthew¹;
DI MICHIEL, Marco³; WECKHUYSEN, Bert¹

¹*Inorganic Chemistry and Catalysis, Utrecht University*

²*University of Manchester*

³*ESRF*

Abstract:

Industrial catalysis utilizes mainly μm to mm -sized catalyst particles in catalytic reactors instead of powders since this minimizes problems associated with for example back pressure and clogging. In recent times, efforts have been made to study and characterize these “real life” single particles so as to determine the nature of chemical species present in 2D and 3D during various stages of the catalyst lifetime such as preparation, reaction and deactivation. Traditionally this sort of analysis is performed on ex situ samples using invasive approaches which often interfere with the chemical process under study and the subsequent conclusions that can be drawn. As a result there has been a recent move towards studying these processes non-invasively and where possible, dynamically in order to understand in detail how the chemistry evolves within catalyst particles and how this and the spatial distribution of the various chemical components influence catalytic behaviour. For this purpose we have developed the technique of synchrotron-based X-ray Diffraction Computed Tomography (XRD-CT), sometimes in combination with absorption-CT, for imaging catalytic solids in real time in order to examine how the active phases form, how they behave under reaction conditions and why they eventually deactivate.

Wed_Cat1_2

Chasing changing catalysts with XAFS and high energy X-ray techniques combined with infrared spectroscopy

NEWTON, Mark¹¹ESRF, Grenoble, France**Abstract:**

Starting from a synchronous combination of XAFS with Diffuse reflectance infrared spectroscopy (DRIFTS), a novel combination of very hard (86 keV) X-ray diffraction with DRIFTS will be outlined. The potential for combining these techniques for the in situ study of the dynamic structural-reactive behaviour of working catalysts with high ($\ll 1$ second) time resolution will be demonstrated using the examples of nanoparticulate Pd/Al₂O₃ and Pd/CeZrO₄/Al₂O₃ catalysts during CO/NO cycling. Further, recent results, obtained from 1 wt% Pt/Al₂O₃ catalysts during stoichiometric - lean CO/O₂ cycling, using a time resolved Pair distribution function (PDF) approach to analysis of hard (60 keV) X-ray scattering data will be presented and contrasted with time resolved XAFS measurements of the same system. Lastly, the combination of total X-ray scattering/PDF techniques with DRIFTS, and the possibility of directly combining XAFS with total scattering approaches in one beamline, will also be discussed.

Wed_Cat1_3

Combination of HERFD XAS and ATR IR for in situ investigation of the liquid phase hydrogenation of nitrobenzene

MAKOSCH, Martin¹¹ETH Zürich**Abstract:**

Hydrogenation of nitroarenes is the industrial method to produce functionalized amines. Supported gold showed interesting features for selectivity towards the nitro-group in the presence of other reducible groups. Despite the fact that the reaction mechanism and the origin of the selectivity are well understood, the nature of the active site especially the structure and oxidation state of the Au nanoparticles during the reaction are still debated. We show that Au⁰ is the predominant oxidation state during the hydrogenation reaction by combination of HERFD XAS and ATR IR employing an in situ spectroscopy reaction cell for pressurized liquid phase batch reactions. The combination of these methods allows to follow electronic and geometric structures of the catalyst and to link it to the conversion of the substrate. By employing Au/CeO₂ precursors with a high Au³⁺ fraction we found that the conversion of nitrobenzene is not dependent on the oxidation state.

Wed_Cat1_4

Operando characterisation of heterogeneous catalysts by combination of Quick-XAS with Raman Spectroscopy

ROCHET, Amelie¹; MOIZAN, Virginie²; PICHON, Christophe²; BRIOIS, Valérie¹¹SOLEIL²IFPEN**Abstract:**

Combining Raman with XAS offers a simultaneous access to a multitude of information. Not only complementary information on the local order of the catalyst are obtained when both techniques probe the catalyst at the same spatial point but information on the catalytic activity can be also obtained by Raman spectroscopy when the Raman probe head analyses the reaction products at the cell gas outlet. In this presentation we will describe two studies carried out on the SAMBA beamline [1, 2].

First, a detailed description of the calcination and activation processes of two metal species of a bimetallic hydrosulfurisation catalyst will be presented. The combination of Raman and high time resolution of Q-XAS enabled to identify upon calcination the presence of an intermediate phase such as tetrahedral molybdate (MoO₄²⁻). Additionally the Raman analysis of the outlet gas composition upon activation under H₂S/H₂ of catalysts provides us unique information on the sulfiding mechanism as a function of the temperature comparable to the information obtained by means of temperature-programmed sulfiding (TPS).

Finally we will present a study of a cobalt based Fischer-Tropsch (FT) catalyst combining structural characterisation (by Quick-XAS combined with XRD) and Raman time-resolved monitoring of hydrocarbons produced by FT synthesis [3].

References:

- [1] V. Briois et al. UVX 2010, EDP Sciences 2011.
- [2] E. Fonda, et al. J. Synchrotron Rad., 19 (2012) 417.
- [3] A. Rochet et al. Catal. Today, submitted.

Wed_Cat1_5

XAS, XRD and Raman study on nanostructured CeO₂-Gd₂O₃ solid solutions

ABDALA, Paula M.¹; SAFONOVA, Olga V.²; LAMAS, Diego G.³

¹*SNBL at ESRF*

²*Paul Scherrer Institut, 5232 Villigen, Switzerland*

³*Universidad Nacional del Comahue, Buenos and CONICET, Argentina*

Abstract:

Ceria (CeO₂) and ceria-based materials have received a lot of attention for many technological applications since they exhibit a number of interesting properties, including high ionic conductivity and excellent catalytic performance for oxidation reactions. The incorporation of metal oxide in the CeO₂ structure significantly improves the oxygen storage capacity, ionic conductivity and surface area of these materials. Doped ceria (CeO₂-Gd₂O₃, -Y₂O₃, -Sm₂O₃) is considered as a promising candidate for electrolytes in intermediate temperature solid oxide fuel cells (IT-SOFCs). Moreover, composite of doped ceria and a metal phase (Ni, Cu, Pt or Pd) have shown excellent performance as anode for IT-SOFCs. Recent researches have shown that reducing the crystallite size in the nanometric or even submicrometric range significantly improves the ionic transport properties and catalytic performance of these materials. This work aims at revealing size dependent structural feature in CeO₂-Gd₂O₃ (GDC) solid solutions by XRD, XAS and Raman spectroscopy. We have studied GDC powders with a composition of Ce_{0.8}Gd_{0.2}O_{1.9} treated at different temperature in order to yield crystallite sizes ranging from 5 to above 100 nm. The use of complementary techniques provided information on the long range and local order of these materials as a function of crystallite size. The influence of the crystallite size on the defect structure can be a key in understanding the properties of the nanostructured GDC.

Wed_TR_1

Modulation Excitation Spectroscopy applied to Crystallography

VAN BEEK, Wouter¹¹SNBL at ESRF**Abstract:**

This presentation will focus on our recent methodological developments. Periodic external stimulations such as concentration light flux, pressure and temperature were introduced. Periodic perturbations are already used frequently in spectroscopic investigations because they enhance the sensitivity and introduce selectivity into experiments. This technique has been called Modulation Excitation Spectroscopy (MES). We transferred this methodology to diffraction and named it Modulation-Enhanced Diffraction (MED). First we present the theory that is developed to explain the kinematic diffraction response of a crystal when it is subjected to a periodically varying external perturbation. We show that if a part the local electron density varies linearly with an external stimulus, the diffracted signal is not only a function of the stimulation frequency Ω , but also of its double 2Ω . These frequency components can provide selective access to partial diffraction contributions that are normally summed up in the interference pattern. MED simulations and experiments will be presented where a phasing process applied to partial diffraction terms allow to recover directly the substructure actively responding to the stimulus. MED can be applied when crystals are changing physically (i.e. electron density/site occupies) but also when varying the x-ray energy and thus the resonant contributions. When comparing MED with existing phasing tools it indicates that there is future potential.

Wed_TR_2

Combined, Modulation Enhanced X-ray Powder Diffraction and Raman Spectroscopic Study of Structural Transitions in the Spin Crossover Material [Fe(Htrz)(trz)](BF)

MILANESIO, Marco¹; PALIN, Luca¹; VAN BEEK Wouter²; URAKAWA, Atsushi³

¹*Università Piemonte Orientale*

²*SNBL*

³*ICIQ*

Abstract:

The structure of [Fe(Htrz)₂(trz)]BF₄ (1, Htrz)1,2,4-4-H-triazole, trz) 1,2,4-triazolate) at the low-spin (LS) and high-spin (HS) states and structural transitions between the two states were investigated by in situ high-resolution synchrotron X-ray powder diffraction (XRPD) combined with Raman spectroscopy using a modulation-enhanced technique. The differences in the behavior of the spin transition observed by XRPD and Raman spectroscopy were explained by the local sensitivity of the two different techniques and also by the spatial propagation of spin crossover phase transition within the crystallite and the body of the grain. Moreover, we demonstrated that the two-dimensional correlation analyses facilitate (i) understanding the data obtained by combined techniques, (ii) clarifying correlation between the signals gained by the different probes, and (iii) extracting information on temporal evolution of transformation processes. The stimulus have been applied periodically to exploit modulation enhanced [ME]techniques in both spectroscopy, i.e. MES [1], and diffraction, i.e. MED [2]. The power and potential of MED as well as the combined two powerful modulation-enhanced techniques, MES-MED, will be shown taking spin-crossover materials as example [3].

References:

- [1] Urakawa, A. et al. Chem. Eng. Sci. 2008, 63 (20), 4902
- [2] D. Chernyshov et al. Acta Crystallographica Section A 2011, A67, 327
- [3] A. Urakawa et al., 2011, J. Phys. Chem. C, 115 (4), 1323

Wed_TR_3

Modulation excitation spectroscopy coupled with synchrotron X-ray methods to unravel dynamic processes on supported Pd catalysts

FERRI, Davide¹; CHIARELLO, Gian Luca¹; NEWTON, Mark²; MATAM, Santhosh Kumar¹; LU, Ye¹; WEIDENKAFF, Anke¹

¹*Empa*
²*ESRF*

Abstract:

Automotive catalysts operate under fast transients and periodic reaction conditions that are challenging to reproduce for mechanistic studies. Improved data evaluation is required to separate the contribution of dynamic species from that of typically overwhelming static signals. This is achieved by a demodulation technique that has been applied to synchrotron techniques in an effort to capture the structural changes under fast transient conditions. Examples are discussed for time-resolved ED-EXAFS of Pd/Al₂O₃ during CO-NO pulsing and time-resolved hard-XRD of Pd/CeZrO₄ during CO-O₂ pulsing. The demodulation algorithm generates a set of phase-resolved data where static envelopes and all other features responding at a different frequency than that of the external stimulation are removed. This processing also considerably reduces the noise. Hence, small features in the both the EXAFS spectra and XRD data can be then clearly resolved.

The whole approach provides a sort of surface sensitivity to both EXAFS and XRD. The phase-resolved EXAFS data permit to observe the formation of PdCx in a CO pulse. In the XRD experiment, obvious reflections of reduced Pd appear only in the phase-resolved data set, apparently exceeding the detection threshold of conventional XRD for particles in the nano-scale. The data allow recognizing that the observed subtle changes occur at different rates thus uncovering the detailed structural-dynamic behaviour of the system with unprecedented sensitivity.

Wed_TR_4

Probing the structure of proteins in physiological conditions by X-ray absorption and UV/Visible spectroscopies

LIMA, Frederico Alves¹; SILATANI, Mahsa¹; ABELA, Rafael²; VAN MOURIK, Frank¹;
CHERGUI, Majed¹; MILNE, Chris¹; AMARASINGHE, D.C.V.³;
VAN DER VEEN, Renske M⁴; REINHARD, Marco¹; RITTMAN-FRANK, Mercedes Hannelore¹;
RITTMANN, Jochen¹; GROLMUND, Daniel⁴; BORCA, Camelia⁴

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³*Lund University*

⁴*SLS, Paul Scherrer Institut, Villigen, Switzerland*

Abstract:

Myoglobin (Mb) is one of the best-characterized metalloproteins found in mammalian muscle cells, which facilitates oxygen diffusion in muscle cells. It has the ability to bind small ligand molecules to the Fe atom at the center of its heme plane. Despite extensive studies, a microscopic description of ligand detachment and rebinding in Mb remains unclear. X-ray absorption spectroscopy (XAS) is an ideal probe to retrieve the local geometric and electronic structure in disordered systems. In order to draw meaningful conclusions about the XAS it is important to know the form of the protein during the course of the measurements. UV-Visible spectroscopy is particularly sensitive to the form of the protein, including the oxidation state of the Fe and the bound ligand, so by combining it simultaneously with XAS we can ensure measurements on undamaged and uncontaminated protein. Using these two techniques we have measured six different forms of Mb under physiological conditions (in solution, pH 7). EXAFS features were investigated using MXAN code, and the TDDFT analysis scrutinizes details of pre-edge features show their remarkable sensitivity to the local protein geometry and the chemical nature of the ligand. We will report on the structures obtained for Mb and on some recent time-resolved XAS measurements where we investigate the binding of CO and NO to Mb. Our results are in good agreement with the structures determined by x-ray crystallography.

Wed_TR_5

Time-resolved X-ray absorption studies on charge carrier dynamics in aqueous TiO₂ nanoparticles

RITTMANN-FRANK, Mercedes Hannelore¹; MILNE, Chris¹; RITTMANN, Jochen¹;
REINHARD, Marco¹; SILATANI, Mahsa¹; CHERGUI, Majed¹

¹*Ecole Polytechnique Fédérale de Lausanne*

Abstract:

Significant effort has been put into understanding electron/hole dynamics in electronically excited TiO₂ nanoparticles (NPs) and how the kinetics of the charge carriers are affected by changes in the electronic and structural properties of such systems. This is necessary in order to understand the underlying mechanisms occurring in photocatalysis and in dye-sensitized solar cells, for which TiO₂ is the main material. Here we present a new approach investigating the charge carrier dynamics in nanoparticles using our recently developed high repetition-rate pump-probe XAS setup at the Swiss Light Source, pumping at 355 nm and probing the spectral changes at the Ti K-edge (4.9 keV), which show how the electron dynamics affect not only the electronic but also the structural properties of colloidal TiO₂ NPs. The transient Ti K-edge spectrum shows significant changes in the pre-edge region below 4.981 keV, which contain information on the conduction band states of the semiconductor NP. There is a contribution due to the shift of the edge to lower energies, pointing to a change from Ti⁴⁺ to Ti³⁺, and indicating the presence of a trapped electron at the Ti site. The EXAFS region also indicate a change of structure around the Ti atom, which points to a transition from anatase towards a more disordered local geometry. These results underscore the correlation between electronic relaxation and the electronic and geometrical structural changes in the NPs.

Thu_Cat2_1

In situ X-ray studies of model and real catalysts: Bridging the complexity gap

FRENKEL, Anatoly¹¹*Yeshiva University***Abstract:**

In the last decade, there has been a surge in advancing synchrotron-based characterization methods to study catalytic materials. Most notable innovations include combining the X-ray absorption and scattering methods, and coupling of one or both of them to vibrational spectroscopies. I will report on recent developments at the Synchrotron Catalysis Consortium (SCC) at Brookhaven National Laboratory (BNL) on combining XAS, XRD, IR and Raman measurements in the same experiment for investigations of Water-Gas Shift reaction catalysts.

While well-defined, model catalysts can be characterized by ensemble-average methods, new methodologies are sought to study real catalysts that possess broad compositional and structural distributions. XAS and XRD are not sensitive to local fluctuations in size, shape, structure and composition of nanomaterials, and the local information, such as one provided by electron microscopy, is needed. I will describe our advances at the SCC in coupling the in situ XAFS to the in situ environmental TEM measurements. The use of these methods will be demonstrated on the example of supported Pt clusters that exhibited unique thermodynamic properties. I will demonstrate the feasibility of conducting in situ and in operando catalytic experiments on the same system by XAS and TEM techniques using a specially designed environmental cell that is compatible both with x-ray absorption and electron microscopy probes.

Thu_Cat2_2

In-situ QXAS investigation of the genesis of cobalt active phases in supported Fischer-Tropsch catalysts

KHODAKOV, Andrei¹; HONG, Jingping²; MARCEAU, Eric³; GRIBOVAL-CONSTANT, Anne²;
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Abstract:

Cobalt Fischer-Tropsch catalysts are typically prepared by impregnation, followed by calcination in oxidizing atmosphere and activation in hydrogen. Decomposition of cobalt nitrate is a crucial step in the genesis of active phase and could involve several short-living intermediate species. In the present work, in-situ quick X-ray absorption spectroscopy (QXAS) in combination with other techniques has been used to investigate the genesis of active phases in silica-supported cobalt catalysts prepared using either activation under 5%NO/He or sub-stoichiometric addition of sorbitol.

Cobalt nitrate decomposition in air or helium proceeds via dehydrated species at 140 °C. These species convert into Co₃O₄ crystallites below 200 °C. In diluted NO, in contrast to activation in air or He, an intermediate cobalt (II) hydroxynitrate phase is detected by both XANES and EXAFS above 110 °C, before the formation of Co₃O₄. The quantitative QXAS results are consistent with FEFF, in-situ Raman and ex-situ XAS and XRD. In the catalysts prepared with sorbitol addition, the in-situ XANES/EXAFS is indicative of higher temperature of cobalt nitrate decomposition in the presence of sorbitol. Organic acids produced during sorbitol oxidation stabilize cobalt precursor. The in-situ QXAS at Ru K-edge suggests incorporation of Ru ions into mixed CoRu oxides in the calcined catalysts, better catalyst reducibility and formation of CuRu bimetallic particles in the reduced catalysts.

Thu_Cat2_3

Evidence for central carbon in nitrogenase FeMo cofactor

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ANDRADE, Susana L. A.¹; SCHLEICHER, Erik²; WEBER, Stefan²;
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Division of Chemistry and Chemical Engineering*

Abstract:

The dissociation of the stable triple bond of atmospheric dinitrogen (N₂) and the reduction to bioavailable ammonia (NH₄⁺) is called nitrogen fixation. Biological nitrogen fixation is carried out by the nitrogenase¹, an enzyme complex consisting under turnover condition of two metallo proteins, the MoFe- and the Fe-protein². Nitrogen reduction takes place at the MoFe-protein, whereas the Fe-protein is the physiological and unique electron donor. The *Azotobacter vinelandii* MoFe-protein is a 230 kDa $\alpha_2\beta_2$ -heterotetramer and contains two metal clusters, the P-cluster [8Fe:7S] and the FeMo-cofactor [Mo:7Fe:9S:X:homocitrate] (FeMoco), per $\alpha\beta$ -heterodimer. FeMoco is the active site for nitrogen binding and fixation. It is a highly symmetrical cluster and the most complex cluster known in nature. High resolution X-ray diffraction data revealed the presence of an interstitial light atom X (X = C, N or O) in FeMoco³. Due to its complexity, the actual site for nitrogen binding and the mechanism for nitrogen reduction are not understood in detail so far. A combination of X-ray crystallography and electron paramagnetic resonance spectroscopy evidences the central atom in the FeMoco to be a carbon^{4,5}. This provides new insights towards understanding biological nitrogen fixation by nitrogenase.

Thu_Cat2_4

Identifying dynamic structural changes in catalysts with time and energy-resolved XAS and XES

NACHTEGAAL, Maarten¹¹*Paul Scherrer Institut***Abstract:**

The directed development of new catalysts necessitates an understanding of the structure - performance relation. Two continuous developments at the SuperXAS beam line of the Swiss Light Source, sub second XAS and XES, allow determining the dynamic electronic and geometric structures of catalysts under in situ conditions. When combined with a quadrupole mass spectrometer or gas chromatograph, direct structure-performance relationships can be determined. Identifying the relevant catalytic structure, e.g. that of the reactive intermediate and / or active site, poses a real challenge. In this talk, I will show how sub-second XAS and XES enable to identify the relevant structure of a catalyst.

Thu_Bio2_1

Systems Biology in Prokaryote - Eukaryote Symbiosis: Single-Crystal Spectroscopy Correlated with X-ray Crystallography and Other Complementary Methods

ORVILLE, Allen¹; LI, Feifei¹; ALLAIRE, Marc¹; ROESSLER, Christian¹; SOARES, Alexei¹

¹*Brookhaven National Laboratory*

Abstract:

We are creating a multidisciplinary, high throughput pipeline for the structural and biophysical analysis of macromolecules involved in bacterial N₂-fixation in plants. *Sinorhizobium meliloti* 1021 and WSM419 are free-living or N₂-fixing microbes. But, they only fix N₂ under symbiotic, microaerobic conditions within root nodules of legumes such as alfalfa and its diploid model, *Medicago truncatula*. The genome sequences of *S. meliloti* and *M. truncatula* are known. Scientists from BNL, WA State Univ. (M. Kahn et al), Pacific Northwest National Lab (M. Lipton et al), Stanford Univ. (S. Long et al), the City Univ. of New York (H. Chen et al) and the NY Structural Genomics Research Consortium (S. Almo et al) collaborate to better understand this symbiotic relationship. The initial *S. meliloti* targets include annotated genes to proteins that bind either iron (~144 ORFs), heme (63 ORFs), copper (28 ORFs), or is an oxidoreductase (535 ORFs). They are being characterized by small/wide angle X-ray scattering and by X-ray crystallography that is often correlated with single-crystal spectroscopy. In complementary studies, whole root nodules have been analyzed by mass-tag metabolomic and microproteomic analysis, as well as by microprobe X-ray fluorescence. Together these results provide the identity and relative abundance of bacterial and plant proteins, as well as the total distribution of first row transition metals in N₂-fixing root nodules.

Supported by NIH/BTRC and USA DOE/BER

Thu_Bio2_2

Fingerprinting redox/ligand states and driving catalysis in protein single crystals

HOUGH, Michael¹; FUCHS, Martin²; POMPIDOR, Guillaume²;
ANTONYUK, Svetlana³; STRANGE, Richard³; HASNAIN, Samar³

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Abstract:

Single crystal spectroscopic analysis may be used to gain a complete and accurate identification of the redox and ligation states of metal (redox) centres in protein crystals [1,2]. Combining this approach with controlled X-ray radiolysis can allow the generation and characterisation of functional species and intermediates [3].

Cytochrome c' (CYTc') is a haem protein with the remarkable ability to discriminate between NO and CO by binding them to opposite faces of the haem while excluding O₂ [4]. The binding of NO to CYTc' provides a model for the activation of soluble guanylate cyclase. We will describe the use of UV-visible absorption and resonance Raman spectroscopies to monitor radiolysis and "fingerprint" key redox and ligand states in crystals of native and mutant CYTc', from which high resolution crystal structures have been determined. We will also describe the radiolysis-driven conversion of substrate-to-product in crystals of copper nitrite reductase.

References:

- [1] Ellis, M. J. et al. (2008) J. Synchrotron Rad. 15, 433-439.
- [2] Antonyuk, S. V. & Hough, M. A. (2011) BBA Proteins and Proteomics 1814, 778-784.
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Thu_Bio2_3

Iron-porphyrin coordinates an arginine guanidine side-chain in a protein pocket - Insights from microspectrophotometry and crystallography

KNIPP, Markus¹; HE, Chunmao¹; FUCHS, Martin²; OGATA, Hideaki¹¹*Max-Planck-Institut für Bioanorganische Chemie*²*Paul-Scherrer-Institut***Abstract:**

Nitrophorin 4 (NP4) is a ferriheme protein that is found in the saliva of the blood-sucking insect *Rhodnius prolixus*. The purpose of the protein is to transport NO from the saliva of the insect into the tissue of a victim, for which purpose the heme iron is maintained in the Fe(III) state. A novel protein mutant NP4(L130R) was generated to explore the recently reported nitrite disproportionation reaction of nitrophorins. It is expected to have the positively charged guanidine group close to or in the distal site of the heme pocket. The protein was crystallized and the X-ray structure was solved. Unexpectedly, the Arg130:N atom appeared to coordinate the heme iron. However, studies of the protein by UV/Vis absorption and resonance Raman (RR) spectroscopy in solution did not suggest Arg coordination. Microspectrophotometry performed at crystals under synchrotron radiation revealed that under the rapid photon induced reduction via X-ray, Arg130 coordination is enabled upon reduction to Fe(II). This can be rationalized by the stronger Lewis acidity of Fe(III) compared to Fe(II). Overall, this appears to be the first description of a metalloporphyrin-guanidine coordination complex and the third example of a metal-guanidine coordination in a biomolecule. This is the more remarkable because deprotonation of the guanidinium group is difficult to accomplish in aqueous media, but becomes apparently possible in the protein pocket of NP4.

Thu_Bio2_4

Structural and spectroscopic observation of an enzyme at work

ORRU, Roberto¹; MATTEVI, Andrea¹; WEIK, Martin²; FRAAIJE, Marco W.³; MARTINOLI, Christian¹; ROYANT, Antoine²

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²*European Synchrotron Radiation Facility*

³*University of Groningen*

Abstract:

Baeyer-Villiger monooxygenases (BVMOs) are promising targets for biocatalytic applications in synthetic and pharmaceutical chemistry. These flavoenzymes mainly convert ketones into their corresponding esters using NAD(P)H as electron donor by catalyzing the insertion of a single oxygen atom nearby the carbonyl group. Fundamental property of BVMOs is their ability to stabilize the flavin-peroxide intermediate. Understanding its formation is crucial to understand the catalytic mechanism in flavin dependent monooxygenases, gaining insight into the reactivity of flavoproteins with oxygen. Along this way, phenylacetone monooxygenase (PAMO) from *Thermobifida fusca* has been adopted as a model: its flavin cofactor has well-defined spectroscopic properties which makes it ideal for absorption spectroscopy investigations. Each flavin redox state, including the flavin-peroxide intermediate, could be characterized by UV/Vis absorbance. X-ray crystallography and single crystal microspectrophotometry experiments were performed on PAMO crystals. Microspectrophotometric studies were most useful to correlate diffraction X-ray data with UV/Vis solution studies. They also showed the formation of hydrated electrons and chlorine radicals during data collection. In parallel, we are currently investigating the reactivity of the flavin-peroxide intermediate performing chemical engineering experiments on the catalytic core, by replacing the original flavin cofactor with other FAD analogues.

Thu_Bio2_5

Using in situ single-crystal UV-vis and Raman spectroscopy to study the effect of X-ray radiation damage on the crystal structures of haem proteins

HERSLETH, Hans-Petter¹; LOFSTAD, Marie¹; VAN BEEK, Wouter²;
POMPIDOR, Guillaume³; RØHR, Åsmund K.¹; ANDERSSON, K. Kristoffer¹

¹*Department of Molecular Biosciences, University of Oslo, Norway*

²*Swiss-Norwegian Beamlines at ESRF, France*

³*Swiss Light Source, Paul Scherrer Institut, Switzerland*

Abstract:

To be able to correctly interpret the crystal structure of redox- and metalloproteins caution must be employed. The influence of X-ray radiation damage to protein crystals is well known to occur even at cryogenic temperatures, and redox active sites like metal sites seem especially vulnerable for radiation-induced reduction [1,2,3]. We have used in situ (online) UV-vis and Raman spectroscopy to study how different haem and flavoproteins are influenced by X-rays during crystallographic data collection [1,2]. The spectroscopic changes have been monitored as a function of X-ray exposure (dose absorbed). Our studies show that these redox states are very fast reduced by X-rays resulting in very short lifedoses. Structurally we have observed for haem proteins a lengthening of the Fe-O bond, and for flavoproteins a bending of the flavin ring during X-ray induced radiation damage, in agreement with DFT [1,2,3]. We have recently started to investigate if varying the doserates and wavelengths can increase the lifedoses. In general our studies show the need of combining protein crystallography with in situ single-crystal spectroscopy when redox and metalloproteins are studied.

References:

- [1] H.-P. Hersleth, K.K. Andersson, *Biochim. Biophys. Acta* 2011: 1814, 785
- [2] Å. K. RØHR, et al., *Angew. Chem. Int. Ed.* 2010, 49, 2324
- [3] H.-P. Hersleth et al. *Chem. Biodiv.* 2008, 5, 2067

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Thu_MS_1

En-Light-ening Photo-crystallography with X-ray Absorption

COLE, Jacqueline¹¹*University of Cambridge, UK ; University of New Brunswick, Canada***Abstract:**

Photo-excited state crystal structures are now possible via photo-crystallography - a technique that pumps optical light upon a crystal which is, in turn, probed by X-ray diffraction. While this technique is still very much in a developmental phase, results have already demonstrated important findings in the area of optoelectronics.

Such photo-crystallography experiments are now being technically extended to incorporate X-ray absorption spectroscopy and anomalous X-ray scattering. Two case studies are shown. In the first case, XANES has been used to identify solid-state photoisomerism in these materials where suitable crystals could not be grown for photo-crystallography. The XANES data analysis also clarified the redox property changes owing to light-excitation. In the second case, anomalous X-ray scattering has been embraced within photo-crystallography experiments in order to gain superior scattering contrast in the areas of the molecule that pose special interest with respect to light-induced effects. The associated X-ray absorption cross-sections are determined using EXAFS spectra that are obtained in tandem with the X-ray diffraction experiment.

The paper concludes by forecasting the likely combinations of techniques that will create a result whose sum is far greater than its parts.

Thu_MS_2

Exploration of the mechanical properties of flexible MOFs by coupling experimental and modeling approaches

YOT, Pascal G.¹; MA, Qintian²; HAINES, Julien¹; PUENTE ORENCH, Inès³;
DMETRIEV, Vladimir⁴; GHOUFI, Aziz⁵; DEVIC, Thomas⁶; SERRE, Christian⁶;
YANG, Qingyuan²; ZHONG, Chongly¹²; FÉREY, Gérard⁶; MAURIN, Guillaume¹

¹Université Montpellier 2

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⁵Institut de Physique de Rennes

⁶Université de Versailles St-Quentin

Abstract:

Metal Organic Framework materials have been the focus of intense research activities over the past 10 years. Owing to their potential applications in storage/separation of strategic gases and to constraints related to their shaping [1], investigations of the behaviour of porous MOFs under operating conditions has become an increasingly important area of characterization. In the same time there is a growing interest in characterizing the behavior of these solids, upon mechanical stimuli [2]. In this work we aim at comparing the mechanical behavior of three isostructural MOFs materials: rigid MIL-47(V) and flexible MIL-53(Cr, Al) solids (MIL: Materials of Institute Lavoisier) under high mechanical pressure. Experimental techniques including X-ray and Neutron powder diffractions, Raman spectroscopy and Hg-porosimetry, coupled with Molecular Dynamics simulations have evidenced two different behaviours that differ with those previously observed upon chemical stimuli [3]: (i) a reversible structural transition between a large and a narrow pore forms with a large hysteresis for MIL-47(V) (125 MPa) [4] and MIL-53(Cr), (55 MPa), corresponding to a unit cell variation of ~40%, (ii) an irreversible structural transition for MIL-53(Al) which drastically differs with the behaviour of the MIL-53(Cr) [5]. These findings further demonstrate that these solids are promising alternative candidates to hydrophilic silica [6] for mechanical energy storage applications: dampers or shock absorbers.

Thu_MS_3

Investigation of crystallization processes using Synchrotron X-ray diffraction and Raman spectroscopy

GNUTZMANN, Tanja¹; KLIMAKOW, Maria¹;
RADEMANN, Klaus²; EMMERLING, Franziska¹

¹BAM Federal Institute for Materials Research and Testing

²Humboldt-Universität zu Berlin, Department of Chemistry

Abstract:

The crystallization of polymorphic compounds is investigated in different fields of materials science to understand the stability of materials and their various conversions. The need to control and manipulate the crystallization processes and particularly the final crystal product requires thorough understanding of the underlying crystallization mechanisms and kinetics. This is especially true for drug compounds as the different polymorphs might vary in their physical and chemical properties.

Only in situ characterization methods like X-ray diffraction using synchrotron radiation, enable such detailed investigation of crystallization processes with high time-resolution. By employing an ultrasonic levitator as sample holder the influence of the surface of container walls on the crystallization process can be eliminated. Such setup was used to investigate the crystallization of various organic model compounds. Among those, the compound ROY (5-methyl-2-[(2-nitrophenyl)amino]-3-thiophenecarbonitrile) for which our investigations showed that the resulting crystallization product can be controlled by the choice of the solvent. The combination of synchrotron X-ray diffraction with Raman spectroscopy was used for the characterization of the crystallization process of the organic polymorphic compound nifedipine. Our investigation revealed a strong influence of the solvent on the crystallization mechanism.

Thu_MS_4

Pushing microbeam probes to nanoscale resolution for the study of buried interfaces

GHIGNA, Paolo¹; PIN, Sonia²; SPINOLO, Giorgio¹¹*Dipartimento di Chimica, Università di Pavia*²*Paul Scherrer Institut, General Energy Research (ENE), Laboratory for Bioenergy and Catalysis***Abstract:**

In this work, a specific preparation procedure is described, to make possible to obtain in one shot structural and compositional characterization of a buried interface at the nanometre scale using a micrometre scale probe. Specific examples based on dispersive micro X-ray absorption spectroscopy, shows that nearly-atomic scale changes in local structure, composition, as well as local disorder are faithfully detected: the reactivity of thin films of NiO and ZnO onto differently oriented Al₂O₃ single crystals can be studied with an unprecedented level of detail. The result obtained allowed us to speculate about the mechanisms and the rate determining step of the interfacial reactions. The approach could in principle be applied to any probe with a micrometric resolution, for example by using micro diffraction. It can be speculated that the simultaneous application of X-ray absorption and diffraction with microbeams to samples prepared as here described would be of great relevance in the study of the structure of buried interfaces.

Thu_MS_5

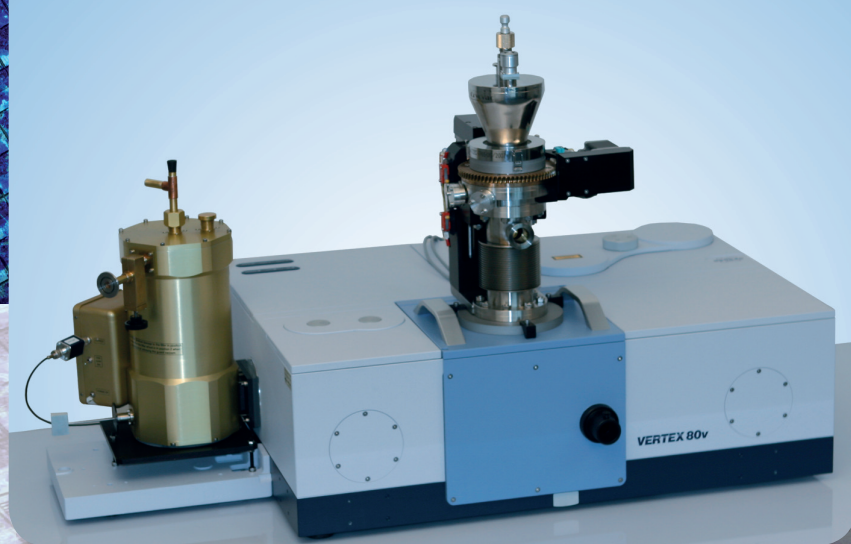
In-situ time-resolved x-ray and IR combinatorial approach for materials science investigation using 3rd generation synchrotron radiation sources

MARCELLI, Augusto¹¹INFN - LNF**Abstract:**

Third generation synchrotron radiation (SR) facilities are designed to host powerful brilliant radiation sources like undulators and wigglers. The next frontier of SR experiments is represented by the combination in a concurrent set up of different wavelengths, to characterize complex systems where different processes due to the interplay between localized and delocalized electrons, charge transfers, collective excitations and molecular vibrations may occur.

After the first attempt, a simultaneous IR and x-ray analysis made at Daresbury in 1995, many SR radiation experiments have been performed probing systems at different wavelengths using X-ray techniques and optical methods in UV/Vis and IR domains, providing scientists with unique complementary information. As an example the concurrent approach has been used at Elettra to the study of non-equilibrium processes in mesostructured systems. A proposal for a IR and X-ray simultaneous spectroscopy beamline has been submitted in 2007 at Diamond and, later, similar projects have been proposed elsewhere. The optical design for a conceptually new beamline allowing time-resolved concurrent X-ray and IR experiments, has been published and advantages, challenges, and opportunities to combine SR-based X-ray techniques with vibrational spectroscopies have been discussed. Here, we will present the science case and the status of the project for a time-resolved beamline combining IR and X-ray radiation.

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Poster Session



Poster Bio_1

High-Pressure Freezing of Protein Crystals

BURKHARDT, Anja¹; WARMER, Martin²; PANNEERSELVAM, Saravanan¹; WAGNER, Armin³; ZOUNI, Athina⁴; GLOECKNER, Carina⁴; REIMER, Rudolph⁵; HOHENBERG, Heinrich⁵; MEENTS, Alke¹

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Abstract:

Protein crystals can contain up to 90% of solvent (mainly water). Cryocooling of such crystals requires cryoprotectants like glycerol or ethylene glycol to suppress hexagonal ice formation and convert the water to amorphous ice (vitrification). Finding ideal cryoconditions can be very time and crystal consuming. Moreover, the crystal quality is often degraded upon cryocooling even if adequate cryoprotectants have been found.

A promising approach which allows sample vitrification without cryoprotectants is high-pressure freezing (HPF). This technique is well established in the field of electron microscopy for cryofixation of cells or tissue [1] and was recently optimized for protein crystals by our group [2].

The crystals are directly frozen in their mother liquor at 210 MPa and 77 K using a Baltec HPM 010 high-pressure freezer. First HPF trials were carried out on hen egg-white lysozyme and porcine insulin giving crystals of very good diffraction quality. In addition, a non-cryoprotected crystal of the membrane protein photosystem II (PSII) was successfully frozen for the first time. The HPF PSII crystal diffracted down to 4.5 Å and showed mosaic spreads of 0.22°. Thus, our HPF protocol is ideally suited for large unit cell systems with weak crystal contacts which are usually sensitive to osmotic shock and therefore difficult to cryoprotect.

References

- [1] H. Hohenberg et al., J. Microsc. 175, 24 (1994).
- [2]. A. Burkhardt et al., Acta Cryst. F68, 495 (2012).

Poster Bio_2

Integration of complementary spectroscopy on ID29 ESRF MAD beamline

DE SANCTIS, Daniele¹; VON STETTEN, David²; GIRAUD, Thierry³;
DOBIAS, Fabien⁴; ROYANT, Antoine²

¹ESRF
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Abstract:

ID29 is an ESRF undulator beamline with a routinely accessible energy range of between 20.0 keV and 6.0 keV dedicated to the use of anomalous dispersion techniques in macromolecular crystallography.

Since 2009 it became the home to the ESRF Cryobench facility, ID29S. In order to take advantage of their close location a novel on-line setup has been developed and commissioned. It will permit to perform Raman and fluorescence spectroscopy analysis while the crystal is mounted on the diffractometer. UV-RIP will also be possible. An outline of the beamline and insights into the recently available on-line facilities is shown.

Poster Bio_3

MS3 - the always-online on-axis in-situ Raman, Absorption, and Fluorescence Microspectrophotometer of the Swiss Light Source MX beamlines

FUCHS, Martin R.¹; DWORKOWSKI, Florian S. N.¹; FROMMHERZ, Ulrich¹;
PANEPUCCI, Ezequiel¹; SCHULZE-BRIESE, Clemens²; POMPIDOR, Guillaume¹;
THOMINET, Vincent¹; PRADERVAND, Claude¹; WELTE, Joerg¹; TOMIZAKI, Takashi¹;
SCHNEIDER, Roman¹; SCHNEIDER, Joerg¹; GABADINHO, Jose¹

¹*Paul Scherrer Institut*

²*Dectris GmbH*

Abstract:

The new unified diffractometer for the three macromolecular crystallography beamlines of the Swiss Light Source (SLS) – the D3 – has recently been installed at beamline X10SA.

A core component of this new endstation is the on-axis micro-spectrophotometer MS3 for microscopic sample imaging with one micron image resolution. For combined spectroscopy and diffraction measurements, its multi-mode optical spectroscopy module is always online and supports in-situ UV/Vis absorption, fluorescence and Raman spectroscopy.

Adjacent to the beamline is the off-line SLS SpectroLab Facility, with an additional complete microspectrophotometer-goniometer system to complement the online system for preparatory measurements not requiring X-irradiation.

Crystallography, Spectroscopy and other Capabilities of the CMCF beamlines at the Canadian Light Source

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LABIUK, Shaun¹; JANZEN, Kathryn¹; COTELESAGE, Julien²

¹Canadian Light Source

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Abstract:

The Canadian Macromolecular Crystallography Facility (CMCF) is composed of two beamlines, 08ID-1 and 08B1-1. The 08ID-1 beamline is a highly-specialized protein crystallography beamline suitable for collecting diffraction data from small crystals of macromolecules and crystals with large unit cell dimensions. It is equipped with a Roentec fluorescence detector which allows X-ray absorption near-edge structure (XANES) experiments to identify the electronic states of atoms, as well as facilitate MAD experiments. The 08B1-1 beamline is fully automated and equipped with an MD2 goniometer and mini-KAPPA, allowing routine data collection on crystals of small molecules. Recently, a Vortex ME4 four-element fluorescence detector was installed on this beamline. It allows researchers to perform both XANES- and X-ray absorption fine structure (EXAFS)-based X-ray spectroscopy experiments on metal-containing crystal samples. Structural information from X-ray absorption spectroscopy can be of great benefit to protein crystallographers in cases where it is not possible to obtain easily interpretable data from crystallography alone for regions around metal atoms (<6 Å). Moreover, the metal-ligand distances obtained from EXAFS spectra are determined with about 10 times better accuracy than those obtained from MX structures determined at moderate resolutions (~ 2 Å). Software controlling the X-ray absorption spectroscopy portion of experiments is fully integrated.

Poster Bio_5

A possible mechanism for X-ray induced photoreduction

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Abstract:

Oxidation state changes of metal organic complexes play an important role in many chemical and biological processes. X-ray absorption near edge spectroscopy (XANES) is a powerful tool to follow these changes since it can directly probe the oxidation state of a metal center[1]. However, X-rays themselves are known to cause photoreduction in photosensitive samples[2, 3,]. In order to reduce X-ray induced photoreduction, it is important to gain a deeper understanding of this process. XANES was used to investigate the influence of temperature, solvent content and chemical composition on three model systems.

Based on our results, we could propose a model for X-ray induced photoreduction of metal organic complexes: A low energy electron[4] generated upon X-ray irradiation attaches to the metal center, yielding a short-lived excited state. Photoreduction of the metal center becomes permanent by an oxidation in the ligand, accompanied by the release of a leaving group and an electron. A possible temperature dependence can be explained by the temperature dependence of the oxidation reaction.

References

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- [3] I. Schlichting, K. Chu, Curr. Op. Struct. Biol. 10, 744-750, 2000.
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Poster Bio_6

Identification, structural and biochemical characterization of a RsmD-like Methyltransferase from *Mycobacterium tuberculosis*.

KUMAR, Atul¹¹IGIB**Abstract:**

As many as 29 post- translational modifications in 16S and 23S ribosomal RNA of *Escherichia coli* are known; 10 of which are located in the 16S RNA and 19 are present in 23S RNA. These modifications are brought about by specific methyltransferases. Nine of ten methylated nucleotides of *Escherichia coli* 16 S rRNA are conserved in *Mycobacterium tuberculosis*. All the 10 different methyltransferases are known in *E. coli*, whereas only TlyA and GidB have been identified in mycobacteria. We have identified Rv2966c of *M. tuberculosis* as an ortholog of RsmD protein of *E. coli* based on its structure and activity. Rv2966c can complement rsmD-deleted *E. coli* cells confirming this role for the enzyme. Recombinant Rv2966c can use 30 S ribosomes purified from rsmD-deleted *E. coli* as substrate and methylate G966 of 16 S rRNA in vitro. Three-dimensional structure of the protein shows the protein to consist of two independent domains; a short hairpin domain at the Nterminus and a C-terminal domain with the S-adenosylmethionine-MTfold. We show that the N-terminal hairpin is a minimalist functional domain that helps Rv2966c in target recognition. Deletion of the N-terminal domain prevents binding to nucleic acid substrates, and the truncated protein fails to carry out the m2G966 methylation on 16 S rRNA. We have shown that 30 S ribosome is required for the activity of Rv2966c but the role of ribosome on methyltransferase activity remains an area of interest for future research.

Structural changes during the enzymic action of isopropylmalate dehydrogenase

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Abstract:

IPMDH is essential for leucine biosynthesis in bacteria and plants catalysing the oxidation of 3-isopropylmalate (IPM) to 2-oxo-isocaproate by NAD in the presence of Mn²⁺. Single crystal microspectrometry has shown that in crystals of IPMDH*Mn*IPM and of IPMDH*Mn*NAD the diffusion of the other substrate (respectively NAD or IPM) causes the appearance of the NADH band. The reaction might be limited by diffusion of the substrate or by lattice forces. An active site mutant (K185A) has been produced that exhibits 0.06 % catalytic activity of the native enzyme. The possibility of obtaining a crystal of the mutant enzyme containing both bound substrates before occurring the reaction has been exploited, but resulted in a crystal with the bound reaction products. This structure (2.2 Å, R_{free}=23%) shows an enzyme conformation similar to the IPMDH*Mn*IPM*NADH complex, and possibly to the active IPMDH*Mn*IPM*NAD⁺ complex. We thus plan to grow crystals of the above reported complexes of the mutant enzyme in order to be able to follow the enzymic reaction upon diffusion of the omitted NAD⁺ or Mn*IPM into them. Simultaneous combination of X-ray diffraction and in situ spectroscopy is expected to reveal the structural changes during catalysis by IPMDH.

Selective X-ray induced NO-photodissociation in hemoglobin crystals: evidences from a crystallography-assisted Raman microscopy study

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Abstract:

Despite the high physiological relevance, hemoglobin crystal structures with NO bound to heme are less than 1% of the total ligated hemoglobins (Hbs) deposited in the Protein Data Bank. One of the major difficulties in obtaining nitrosyl-ligated Hbs is probably related to oxidative denitrosylation, with nitrosylated species being very reactive toward O₂. Raman-assisted crystallography can be a valuable tool to follow derivative crystal preparation [1,2], metal coordination states [3,4], and X-ray photodamage [5,6]. Here, using X-ray crystallography-assisted Raman microscopy, we show that upon X-ray exposure (SLS, X10SA beamline), crystals of nitrosylated hemoglobin from *Trematomus bernacchii* [7] undergo a selective photodissociation of the Fe-NO bond at the β chains generating penta-coordinate species. These data provide a physical explanation of the small amount of nitrosylated Hbs structures available in the literature, suggesting that X-ray induced photodissociation is a frequent and underestimated phenomenon [8,9].

References

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Monitoring flavin X-ray radiation damage using single crystal spectroscopy

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Abstract:

Considering that more than one thousand structures in the Protein Data Bank contain flavin cofactors [1], it is of interest to verify the flavin geometry and electronic state when using these structures for deducing reaction mechanisms and when analyzing the conformational interplay between the cofactor and its protein scaffold. Inspecting flavin structure with QM/MM methods and monitoring of flavin vibrational modes with single-crystal spectroscopic methods during X-ray data collection provide important information regarding the actual flavin state. Here we present data collected from crystals of the flavoprotein NrdI, comparing high resolution crystal structures, geometry optimized models, and single crystal Raman spectra, showing that flavin geometry and state indeed are changed when exposed to X-ray radiation [2].

References:

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Combined X-ray crystallographic, in-situ UV-Vis and QM/MM studies highlight alternate retinal binding modes in CRALBP

STOCKER, Achim¹; PEARSON, Arwen R²; PALCZEWSKI, Krzysztof³; HELBLING, Rachel¹; CASCELLA, Michele¹; OWEN, Robin⁴; BOLZE, Christin S¹; AESCHIMANN, Walter¹; HE, Xiaoqin⁵; POMPIDOR, Guillaume⁶; DWORKOWSKI, Florian⁶; FUCHS, Martin R.⁶; GOLCZAK, Marcin³

¹University of Bern

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⁶Swiss Light Source

Abstract:

11-cis-retinal is the photon accepting cofactor of rhodopsin in the primary light reaction within rod- and cone receptor cells. Persistent vision affords the enzymatic re-isomerization of accumulating all-trans-retinal to 11-cis-retinal in the retinal pigment epithelium (RPE). Cellular retinaldehyde binding protein (CRALBP) is essential for vision by routing 11-cis-retinoids for the conversion of photobleached opsin molecules into photosensitive rhodopsin pigments.

Here, we report the high-resolution (1.8 Å) crystal structure of the R234W mutant of CRALBP (R234W) in complex with its less abundant isomer 9-cis-retinal, a naturally occurring alternate isomer that is used in retinal replacement therapies. A structural overlay with the known 11-cis:R234W complex reveals alternate binding for the 9-cis-aldehyde tail and a strong deformation of the ligand around position C11/C12. We have complemented our structural study with single crystal UV/Visible spectroscopy of the 9-cis:R234W complex, as well as spectrally characterizing crystals of the 11-cis:WT and the 11-cis:R234W complexes. The single crystal spectral data has provided detailed information as to the nature of the bound ligand within the crystal through the observation of a dose dependent X-ray induced radical peak at 545nm. The chemical nature of the 9-cis-retinal has been further probed by QM/MM simulation and has allowed us to propose a mechanism for the stabilization of a ground-state radical of retinal within R234W.

Poster Bio_11

X-ray absorption spectroscopy studies of ubiquinol oxidase membrane protein

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KATONA, Gergely¹; NASEDKIN, Alexander²; NEUTZE, Richard¹

¹*Gothenburg University*

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Abstract:

We report the X-ray absorption spectroscopy studies of the Cu and Fe edges of the cytochrome bo3 quinol oxidase from *Escherichia coli* at the room temperature. Hemecopper oxidases are integral membrane proteins in which proton pumping takes place. Most proposed proton-pumping mechanisms involve CuB and its histidine ligands. The existence and identity of such reorganization of the CuB geometry caused by protonation/deprotonation and/or breakage of one of the Cu-N(His) bonds is a difficult matter to either prove or disprove since CuB is spectrally silent.

The experimental setup which combined the optical microspectrometer and X-ray absorption measurements in fluorescence mode has been tested. The optical microspectrometer has been used to control the photoreduction of the protein sample. Our experimental results shown that at the iron K-edge the photoreduction of the sample happened very fast (dozens seconds) otherwise at the copper K-edge the photoreduction occurred after several minutes that allowed us to measure the XANES part without using a cryojet.

Final results indicate that CuB varied its associated ligands for oxidised Cu(II) and reduced Cu(I) states of the protein. However room temperature copper K-edge X-ray absorption spectra remains unchanged in the pH range 6.5-9.5 for both oxidised and reduced forms of copper correspondently, indicating that no structural changes takes place at CuB depending on pH.

Poster Cat_1

**Low temperature synthesis of amorphous nickel silicide colloids
and their use as precursors for the preparation
of highly dispersed sup-ported nickel nanoparticles.**

BAUDOUIN, David¹

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Abstract:

The preparation of Ni nanoparticles smaller than 2-3 nm still remains a challenge today. Yet, using a colloidal approach for the synthesis of Nickel-Silane based nanoparticles, $[\text{Ni}_x\text{Si-C}_8\text{H}_{17}]$, we successively prepared silica supported nickel NPs having a size of $1.3\text{Å}\pm 0.2\text{ nm}$, corresponding to a dispersion of $71\text{Å}\pm 5\%$. XAS and in situ liquid NMR indicated that the initial colloidal nanoparticles were $\text{Ni}_x(\text{Si-C}_8\text{H}_{17})_y$ aggregates, the nickel environment being close to amorphous nickel silicide (Ni_3Si_2).

Poster Cat_2

A novel setup for combined in situ XAS, DRIFTS and MES

CHIARELLO, Gian Luca¹; FERRI, Davide¹; ALTORFER, Heinz¹;
NACHTEGAAL, Maarten²; QUARONI, Luca²; WEIDENKAFF, Anke¹

¹*Empa*²*Paul Scherrer Institut***Abstract:**

In situ DRIFTS and XAS are two complementary techniques in catalysis, allowing a deeper insight into reaction mechanisms and the dynamic of redox processes. However, XAS provides only bulk information due to the penetration depth of X-rays. The combination with modulated excitation spectroscopy (MES) through periodic switch of gas composition, and phase sensitive detection (PSD), has demonstrated to be a powerful tool to bring surface sensitivity to XAS. MES exploits the PSD algorithm used to demodulate the time-resolved data to filter the signals of spectator species and the noise present in the time domain. This approach is here used to enhance the response of time-resolved XAS (and DRIFTS) to the subtle variation of the surface of metal oxides.

Existing examples of combined IR-XAS setups are adaptations of commercial DRIFT cells to X-rays, whose use is limited to transmission and to selected materials because of the long optical path length. Our new cell, consisting of a plug-flow design, offers a wide surface for IR collection and a variable thin sample thickness for transmission measurements of difficult highly absorbing materials. Moreover, MES is facilitated by the absence of dead volume around the sample contrary to commercial DRIFT cells. The IR beam will be shined over the samples by means of a proper set of mirrors and positioning motors, placed along the X-ray beam. Preliminary results will be presented for oxidation of volatile organic compounds on metal oxides.

Poster Cat_3

**In situ X-ray absorption investigation of the effect
of Sm₂O₃ and CeO₂ promoters on the structure of Rh/Al₂O₃ catalysts
in methane steam reforming**

DUARTE, Renata Bessa¹; VAN BOKHOVEN, Jeroen Anton¹; BUENO, José Maria Correa²

¹ETH Zurich

²UFSCar

Abstract:

The role of Sm₂O₃ and CeO₂ promoters on the structural properties and catalytic behavior of 0.5 wt% Rh/xSm₂O₃-yCeO₂-Al₂O₃ catalysts during methane steam reforming (MSR) was investigated by in situ X-ray absorption spectroscopy and other characterization methods. Catalytic tests were performed at 773 and 1033 K. The combination of XAS measurements with mass spectrometer provided a way to analyze conversion and structure simultaneously. The effect of the addition of Sm₂O₃ and CeO₂ on the catalytic behavior of Rh/Al₂O₃ catalysts was revealed by changes on the structure properties of Rh particles. The high activity observed for the studied Rh catalysts during reaction was mainly attributed to the high dispersion of the active phase. The improvement in the activity and stability of promoted catalysts is due to the greater Rh-support interaction, which inhibited Rh oxidation and the sintering of the Rh particles, thus maintaining the high dispersion during the drastic reaction conditions. The EXAFS experiments clearly illustrate the alteration of the topology and therefore the lack of stability of rhodium particles when supported in unpromoted alumina.

Poster Cat_4

Fischer-Tropsch synthesis from biosyngas: Operando investigation of bimetallic cobalt-iron catalysts

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Abstract:

Biosyngas obtained from biomass gasification can be used to produce clean hydrocarbon fuels by Fischer-Tropsch reaction (FT). H₂/CO ratio in biosyngas could be adjusted if water gas shift reaction may occur simultaneously with FT synthesis. Cobalt and iron bimetallic catalysts are active in these two reactions. The present work focuses on in-situ and operando studies of iron and cobalt phases in alumina or silica supported catalysts during catalyst activation and during FT synthesis using biosyngas. Bimetallic catalysts have better reducibility and higher dispersion compared with the monometallic ones. The presence of cobalt-iron alloys in the reduced activated catalysts was also confirmed using in-situ XRD and magnetism. Operando magnetization measurements during FT reaction are consistent with the formation of iron and possibly cobalt carbides during the catalytic tests. The operando XAS/XRD experiments with simultaneous measurements of catalytic activity under realistic conditions of FT reaction (H₂/CO= 1, P=20 bar) suggest an enhanced stability of bimetallic catalysts to sintering compared to cobalt monometallic counterparts.

Poster Cat_5

Towards an understanding of carbon materials in energy storage applications by X-ray Raman Scattering and optical Raman Spectroscopy

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¹Karlsruher Institute of Technology

Abstract:

Due to the growing awareness of environmental concerns and the threat of depleting conventional fossil energy resources, low emission renewable energy processes are required. The key technologies for the energy economy of the 21st century are electrochemical energy conversion and storage technologies, like fuel cells, lithium ion and redox flow battery systems. Although the mentioned systems are very different in their requirements, they all use carbon materials in the electrodes. In lithium ion and redox flow batteries, carbon is the active material offering functional centers for intercalation and reaction, respectively.

However, in fuel cells the carbon works as catalyst support material anchoring the noble metal nanoparticles. All the processes taking place at the carbon surface are poorly understood leading to limitations in life time and/or charge/discharge rate in these systems. A better understanding of these processes requires in-situ studies which will further support the development of new materials. For this we are currently developing a fingerprint method to investigate carbon materials by X-ray Raman Scattering. In this contribution, we will show first ex-situ results of different carbon materials using XRS. In a second step a combination with optical Raman Spectroscopy would be an asset in order to correlate the electronic structure with the disorder of carbon materials.

Poster Cat_6

Catalytic decomposition of guanidinium formate as novel ammonia precursor for selective catalytic reduction of NO_x

PEITZ, Daniel¹; ELSENER, Martin¹; KROECHER, Oliver¹¹Paul Scherrer Institut**Abstract:**

Selective catalytic reduction (SCR) of nitrogen oxides (NO_x) with ammonia (NH₃) is a common method in emission control. Mobile SCR systems inject aqueous urea solution (AdBlue®) into the hot exhaust gas to catalytically decompose it to NH₃. However, AdBlue® shows poor temperature stability in cold or hot climates. In contrast, Guanidinium formate (GuFo) solutions can be stored between -30 and 60 °C, and contain 1.5x the amount of NH₃.

GuFo needs a hydrolysis catalyst to yield NH₃, commercial TiO₂-anatase coated on cordierite support enabled complete conversion from 300 °C. However, formic acid is a side product, it can further react to methanamide and HCN. The decomposition was elucidated by the combination of experiments with FTIR spectroscopy of reaction products and DFT calculations.

A catalyst screening determined Au-doped TiO₂-anatase (Au/TiO₂) to be an excellent catalyst for the simultaneous decomposition of formic acid and the release of NH₃ stored in GuFo. Thus, complete decomposition of GuFo to NH₃ and CO₂ could be achieved from 250 °C, without the formation of side products.

The Au/TiO₂ catalyst was also investigated regarding its stability upon hydrothermal aging at temperatures around 750 °C or sulfur-poisoning using SO₂, both procedures barely affected the catalyst's performance. These promising results were already transferred to an industrial company for commercialization, but the catalytic activity is still to be understood by advanced spectroscopic techniques

**Mechanism of oxygen storage capacity of nano-ceria:
Correlation of in situ XAS, RIXS, XRD and Raman spectroscopy**

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NACHTEGAAL, Maarten¹; VAN BOEKHOVEN, Jeroen Anton²

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Abstract:

Oxygen storage capacity (OSC) is a unique property of ceria (CeO_2) allowing this oxide to store oxygen in its structure and provide it for catalytic processes under reducing conditions [1]. This property is extensively used in exhaust catalysis. The surface oxygen in ceria is much more active compared to the bulk one and its activity can be further enhanced by addition of noble metals (Pt, Pd, Rh). However, the structural reasons for higher activity is still not clear as well as the structure of Ce^{3+} defects forming in reducing atmospheres. In the present work we studied the structure of well-defined ceria nanoparticles of different size and shape promoted by Pt under different redox conditions. OSC was determined in pulse experiments and correlated to the structural changes observed in situ by Ce K-edge XANES, RIXS across Ce L3-edge, XRD and Raman spectroscopy under identical reaction conditions. The changes in the Ce K-edge XANES indicate reversible change in the oxidation state of cerium (from 4+ to 3+) while RIXS shows unexpectedly large variations in its charge state that can be related to unusual local geometry of Ce^{3+} defects. XRD and Raman spectra also show reversible changes suggesting that bulk structure of ceria nanoparticles is affected by formation of Ce^{3+} defects on the surface.

Reference:

[1] A. Trovarelli, Catalysis by Ceria and Related Materials, Imperial College Press, London, 2002.

Poster Cat_8

SNBL – a dedicated beamline for combined XRD-XAFS-RAMANVAN BEEK, Wouter¹; ABDALA, Paula¹; WIKER, Geir¹; EMERICH, Hermann¹¹SNBL at ESRF**Abstract:**

The Swiss Norwegian Beamlines at the ESRF have been equipped with a permanent online Raman Spectrometer in June 2007. The Raman spectrometer serves two experimental stations operating in parallel. High Resolution Powder Diffraction, EXAFS combined with on-line Raman spectrometry has become routine. Many experiments are profiting from the possibilities for rapid changeovers from powder diffraction to EXAFS, facilitated by new X-ray optics which has been installed. The rapid in-situ developments did not compromise on the historical strengths of the beamline (HRPD and XAFS). To the contrary extreme high quality acquisitions before and after the in-situ experiments often underline the findings. Combining techniques only makes sense when samples are exposed to some external parameter (temperature, pressure etc.) The wide and growing interest within our user community in catalysis has led to the development of in-situ techniques at SNBL. A fully automated gas mixing system permits a wide variety of gas mixtures to be prepared and passed through the sample under different conditions of temperature and gas pressure while carrying out the synchrotron experiment. An on-line mass spectrometer is available for analyzing the products of the (catalytic) reaction. The beamline is almost continuously being further developed to enhance time and space resolution, sensitivity and selectivity.

Nitrous oxide reductase with a unique [4Cu:2S] centre from the denitrifying *Pseudomonas stutzeri*

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¹*Albert-Ludwigs-Universität Freiburg, Institut für Organische Chemie und Biochemie, workgroup Oliver Einsle*

²*Universität Konstanz, Dept. of Biology*

Abstract:

Denitrification is the microbiological reduction of nitrate via nitrite, nitric oxide and nitrous oxide, followed by the subsequent two-electron reduction of nitrous oxide to dinitrogen.

Nitrous oxide reductase, NosZ, is a dimeric multi-copper protein with 638 residues per subunit and the reported Cu content depends on the purification strategy. Because of the sensitivity of the enzyme toward dioxygen, the clusters of the soluble periplasmic enzyme degrade and it therefore loses its activity under oxic conditions. Several different forms were described, that can be distinguished by their typical absorption and EPR spectra. The active purple form of the enzyme carries the well-characterized mixed-valent binuclear CuA centre and the tetranuclear CuZ site, that was first described as a unique [4Cu:2S] centre for *Pseudomonas stutzeri*, instead of a [4Cu:S] cluster⁵ found previously. This cluster was observed after the isolation and crystallization under the exclusion of dioxygen. In nitrous oxide reductase the substrate N₂O is bound between the two copper centres, it is activated by side-on binding to CuZ, so that then electrons can be transferred directly from CuA to the N₂O. To determine the unknown mechanistic details, several spectroscopic methods can be used to take a closer look at different redox states of the copper ions. Several accessory proteins were identified for the biogenesis of the active N₂O reductase, with predicted functions as Cu chaperone or ABC transporters.

Poster_Cat_10

In situ EXAFS and XRD studies on formation of molybdenum carbides for higher alcohol synthesis

WU, Q.¹; CHIARELLO, G. L.²; CARVALHO, H.²; CHRISTENSEN, J. M.¹; TEMEL, B.³;
BOUBNOV, A.²; JENSEN, A. D.¹; GRUNWALDT, J.-D.^{1,2}

¹*Department of Chemical and Biochemical Engineering, Technical University of Denmark*

²*Institute of Chemical Technology and Polymer Chemistry, Karlsruhe*

³*Haldor Topsøe A/S, Nymøllevej 55, 2800 Kgs. Lyngby, Denmark*

Abstract:

Poster MS_1

Thermal motion induced forbidden reflections

BEUTIER, Guillaume¹; COLLINS, Steve²; NISBET, Gareth²;
OVCHINNIKOVA, Elena³; DMITRIENKO, Vladimir⁴

¹CNRS²Diamond Light Source³Moscow State University⁴Shubnikov Institute of Crystallography**Abstract:**

Reflections forbidden by crystallographic rules can be observed when the energy of the incident x-rays is tuned to an absorption edge of the material. When the site symmetry of the resonant atoms is such that dipole-dipole resonant scattering is also forbidden, one can still measure intensity at the position of the forbidden reflection: it is related to the transient atomic displacements of the resonant atoms from their high-symmetry sites, due to thermal motion [1]. These so-called Thermal Motion Induced (TMI) resonant reflections have been measured in Germanium and Wurtzites crystals ZnO, GaN and CdSe [2,4]. The intensity can be reproduced with a single low energy optical phonon mode.

This experimental method can be used to measure atomic displacements correlations [3] and has potential applications to study systems with interesting electron-lattice coupling effects. It would benefit from the possibility to excite selectively a single optical phonon mode.

References:

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Poster MS_2

In situ XRD study of sulfidation of pure and Cu-doped ZnO nanoparticles by H₂S

BEZVERKHYY, Igor¹; SKRZYPSKI, Jonathan¹;
SAFONOVA, Olga²; BELLAT, Jean-Pierre¹

¹ICB CNRS University of Burgundy

²Paul Scherrer Institut

Abstract:

Hydrogen sulfide is a strong catalytic poison and its complete removal from gaseous streams is of key importance for successful industrial implementation of emerging technologies like low-temperature fuel cells (PEMFC) or Fischer-Tropsch synthesis. Currently the most successful approach to deep desulfurization (< 0.1 ppm S) relies on a gas-solid reaction between H₂S and ZnO- based sorbents. However, the existing materials exhibit low sulfur capacity under the mild conditions (200-300 °C) needed for these applications. In order to improve the efficiency of the sorbents a detailed understanding of the mechanism of ZnO sulfidation would be highly desirable. To obtain the relevant information we applied in situ synchrotron radiation XRD to follow the transformation of ZnO and Cu-doped ZnO nanoparticles during their reaction with H₂S. The sulfided samples were also characterized by transmission electron microscopy. Based on the obtained experimental data we will propose in our presentation an atomic scale description of the mechanism of ZnO-ZnS transformation.

Poster MS_3

**Structural investigations of $\text{Li}_2\text{MnO}_3\cdot\text{Li}(\text{Ni}_{0.5}\text{Co}_{0.5}\text{Mn})\text{O}_2$ □
Neutron diffraction, in situ X-ray diffraction, and in situ Raman spectroscopy**

BLEITH, Peter¹; VILLEVIEILLE, Claire¹; LANZ, Patrick¹; NOVAK, Petr¹

¹Paul-Scherrer-Institute

Abstract:

LiCoO_2 is today's standard cathode material for Li-ion batteries. $\text{Li}_2\text{MnO}_3\cdot\text{Li}(\text{Ni}_{0.5}\text{Co}_{0.5}\text{Mn})\text{O}_2$ (NCM) is a very promising candidate to replace LiCoO_2 since it shows an approx. 2 times higher specific charge and is less expensive. We investigated the structural changes of NCM upon charge and discharge with ex situ neutron diffraction, in situ X-ray diffraction, and in situ Raman spectroscopy.

The in situ XRD measurements were performed at SLS (X04) in a "coffee bag" □ – cell using an automatic sample changer. The neutron diffraction was performed at SINQ (HRPT). The in situ Raman spectroscopic measurements were performed on a LabRAM HR (HoribaJovinYvon SA), using a He-Ne laser as excitation source (632.8 nm, 18 mW) in a cell which allows for recording of Raman spectra from the backside of the electrode.

Data from the diffraction techniques showed the phase transitions during galvanostatic cycling. NCM showed an expansion of the c axis during charging and proved a release of oxygen at 4.5 V which was also detected with Differential Electrochemical Mass Spectrometry (DEMS). NCM also showed changes in Raman spectroscopy according to the processes visible in the galvanostatic curve. The new set of peaks cannot yet be ascribed to a phase and two hypotheses are under investigation: An NCM layer without lithium or MnO_2 created by Li_2MnO_3 activation, which means release of oxygen.

In short, the combination of these techniques gave the opportunity to understand the reaction mechanism of NCM.

Poster MS_4

Time-resolved Powder Diffraction at the SLS Materials Science beamline

CERVELLINO, Antonio¹¹*Paul Scherrer Institut***Abstract:**

The Materials Science beamline - Powder station of the Swiss Light Source synchrotron is equipped with a state-of-the-art Mythen II detector, designed for simultaneous acquisition of up to 2X30720 channels covering 120 deg with 0.0037 deg resolution with double-layer sensors for higher efficiency at high energies; a second detector placed at up to 5 m from the sample allows the simultaneous acquisition of SAXS patterns. The U14 undulator source, together with advanced optics, guarantees a thin, brilliant, monochromatic X-ray beam, continuously tunable in the range 5 to 40 keV. This setup is able to record patterns in real time with sub-millisecond acquisition time and < 0.1 ms lag time and with good signal strength. Therefore it offers an ideal setup for in-situ powder diffraction studies of irreversible transitions and phenomena happening on the few-millisecond scale. The detectors accept gating, so strobing methods can be employed for reversible phenomena.

Redox pathways of CuO-based, Al₂O₃ stabilized oxygen carriers for chemical looping combustion

IMTIAZ, Qasim¹; BRODA, Marcin¹; KIERZKOWSKA, Agnieszka¹; KOENIG, Christian²; SAFONOVA, Olga²; NACHTEGAAL, Maarten²; SCHILDHAUER, Tilman²; MUELLER, Christoph²

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Abstract:

Chemical looping combustion (CLC) is one of the most promising CO₂ capture processes. Copper oxide is an attractive candidate as oxygen carrier for CLC owing to its (i) exothermic reduction reactions, (ii) fast kinetics in both the reduction and oxidation reactions and (iii) low tendency for carbon deposition. To evaluate the potential of Cu-based oxygen carriers for CLC, the redox pathways of CuO with CO, H₂ and CH₄ must first be determined at operating conditions relevant for CLC. The aim of this work was to understand the reaction pathways of Cu-based, Al₂O₃-supported, oxygen carriers with H₂. A co-precipitation technique was used to synthesize a Cu-rich (82 wt. % CuO) oxygen carrier. In-situ X-ray absorption spectroscopy (XAS) probing the redox reactions was performed at 500 °C using H₂ and air as the reducing and oxidizing gases, respectively. Preliminary in-situ XAS measurements show that under the operating conditions studied here the reduction and the oxidation of Al₂O₃-stabilized CuO proceeded via the CuO – Cu₂O – Cu transition. Additionally, it was observed that at 500 °C the Cu₂O intermediate did not fully reduce to Cu (within a reaction time of 15 min). Furthermore, the induction period for the reduction reaction of co-precipitated CuO was found to be negligible at 500 °C. These findings have important consequences with regards to the numerical modeling of the chemical looping process.

Poster MS_6

XAS/XRD Study on Amphoteric Behavior of Lanthanide Dopants in BaTiO₃

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BUSCAGLIA, Maria Teresa²; BUSCAGLIA, Vincenzo²; LUDWIG, Christian¹

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Abstract:

Barium titanate (BaTiO₃, BT) is the most extensively used perovskite dielectric ceramic material in the electronic industry. Its application includes multilayer ceramic capacitors (MLCs) traditionally made by covering BT with a layer of precious metal and firing. In order to reduce production costs, precious metal electrodes are replaced by base metal electrodes (BME) producing low-cost BME-MLCs and doped with trivalent rare-earth elements such as erbium (Er), holmium (Ho) and dysprosium (Dy) to improve the dielectric properties and lifetime of BME-MLCs. However, fundamental understanding of the role of the dopants is still lacking.

Using a combination of XAS spectroscopy and XRD (conventional/high-resolution), we studied site substitution of 1 at.% of Er³⁺, Ho³⁺ and Dy³⁺ in BT ceramics as functions of Ba/Ti stoichiometry and firing conditions (oxidising and reducing), as well as the effect of doping on the structure and microstructure of BT. Our first results suggest that the Ho³⁺ incorporated into the BaTiO₃ lattice at the Ti⁴⁺ sites (Ho³⁺) are compensated by ionized vacancies in the oxygen sublattice (V[•]); whereas Dy³⁺ can enter the BaTiO₃ lattice at the Ba²⁺ as well as the Ti⁴⁺ sites. XRD results showed the doped BT exhibit complete solid solubility over all compositions with a tetragonal structure. The findings of this study can help better understand different amphoteric behaviours of the three dopants, which is of great importance for capacitor fabrication.

Poster MS_7

**New high temperature-high pressure XAS cell
to study salt precipitation at- and near- supercritical conditions of water.**

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Abstract:

Above or near the critical point (374 °C, 22.1 MPa) the behavior of water as a solvent is entirely reversed. Organic compounds become completely miscible with supercritical water, whereas inorganic salts precipitate. This is of particular interest for several disciplines and technological applications, i.e. geochemistry, hazardous waste treatments and Synthetic Natural Gas (SNG) production. For the latter, removal and recovery of the inorganic components is crucial. We have designed a new spectroscopic cell suitable for low energy X-ray transmission measurements at pressures up to 40 MPa and temperatures up to 600 °C. The titanium made cell hosts a small compartment in its center, where the liquid is pumped between two thin (~7µm) diamond windows (diameter ~100 µm). The distance between the windows is of a few tens of microns, thin enough to allow transmission of low energy X-rays for the experiments. The constant flow setup will prevent measurement artifacts due to radiation damage to the sample. Measurements will be taken at isothermal conditions at different temperatures. XAS in transmission mode, at the M-K edge (where M = P, S, K and Ca), will be applied to structurally characterize ion-pairs in solution. The aim of this contribution is to show how this new cell allows XAS measurements at low energies to provide insight about: i) formation, evolution and structure of ion-pairs in hydrothermal salt solutions; ii) identifying the specific p/T conditions at which these ion-pairs occur.

Poster MS_8

Vacuum FT-IR Spectrometer: Research Tool at IR Beamlines of Electron Synchrotrons

WIRZ, Ronny¹¹*Bruker Optics***Abstract:**

In the 1970's of the last century attempts to use the advantage of the bright and highly collimated e-synchrotron radiation (SR) not only in the short wavelength (UV, X-Ray) but also in the long wavelength ranges (typically 4000 to 10 cm^{-1}) of the electromagnetic spectrum were unsuccessful. The theoretically expected advantage of the synchrotron radiation as bright but expensive IR source could not be demonstrated.

Today the system parameters for the e-synchrotron beam generating radiation as well as for the optics design for guiding the synchrotron radiation to an IR beamline are known. Successful experiments providing new insights have lead to the adoption of synchrotron radiation as a brilliant radiation source for spectrometers and consequently an increase in the number of IR beamlines with spectrometers attached.

Poster MS_9

Highly uniform metallic and metal alloy nanocrystals, and their superlattices

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²*EMPA/ETHZ*

Abstract:

We present cost-effective and fast solution-processed synthesis of metallic and metal alloy nanocrystals with accurate size and composition control. In particular, we prepare Bi, In, In(1-x)Snx, Sn, and Ga nanocrystals. The average size of nanocrystals can be tuned in wide range for each material by means of reaction parameters: growth temperature, time, and precursor concentrations. Furthermore, we achieve unprecedented size distributions (e. g. 2.2% for In and In(1-x)Snx nanocrystals), allowing us to create long-range ordered 2D and 3D nanocrystal superlattices. Obtained materials might find their applications in catalysis, electrochemical energy storage as well as in shape-memory devices. Nanocrystal superlattices can be considered as porous material for effective gas adsorption process.

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Zürich Information



Transportation in Zürich

From Zürich Airport to Zürich (main station)

(Information about the airport: www.zurich-airport.com)

After reclaiming baggage, follow the signs "Bahn/Railway" to ticket counters and machines. There are English instructions on the machine; follow them or simply press the left (red) key at the bottom where it says "Zürich City". The machine accepts coins as well as banknotes and gives change. The machines with interactive screens also accept major credit cards.

The ticket is valid during the next 2 hours for any train to Zürich as well as for the trams and buses in the city (streetcar, Strassenbahn). Take an escalator down to the platforms 3 or 4.

Trains to city centre leave approximately every 10 minutes and take about 10 minutes to reach the main station (main station : Zürich HB).

From the main station to ETH

(Information about the railway station: www.sbb.ch/home.html)

At the main station walk to the head of the train and follow any signs to "Bahnhofstrasse". Once outside the station walk about 50 meters up the street (Bahnhofstrasse) to the tram stop on the left-hand side.

If you have not yet got a tram ticket (the ticket from the airport is still valid!), you must now buy one from the blue ticket machine. Press the yellow button to get a ticket (2,40 CHF) which is valid for one hour and in the centre (zone 10).

In six minutes with tram no. 6 (direction Zoo) from the main station (Bahnhofstrasse) or with tram no. 10 (direction Seebach) from the main station (Bahnhofplatz) to the stop ETH / Universitätsspital (the 3rd stop).

You are now standing exactly opposite the main building of ETH Zürich; as you enter the building you will see an information desk in the main hall on your right. (see www.ethz.ch)

In three minutes with tram n° 3 from the main station (Bahnhofplatz) you reach the stop Central (1 stop); take the Polybahn (leaves every three minutes) up to the Polyterrasse.

In Zürich and Switzerland

Maps, timetables and prices for trams, buses and boats are available on www.zvv.ch. The centre of the town is in zone 10. If you want to go to the other zones around Zürich you have to buy a complementary ticket.

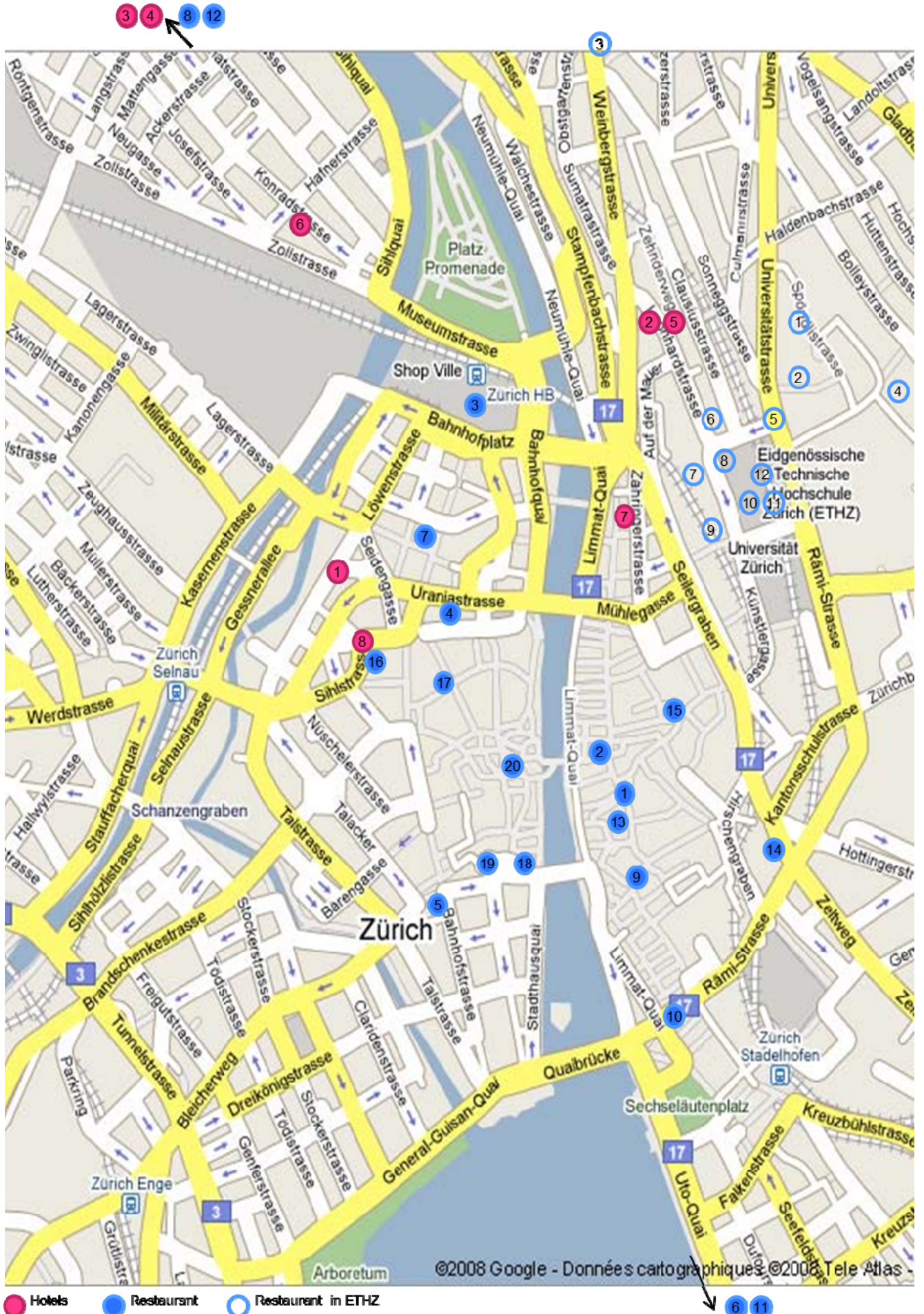
"Zürich rollt" (<http://zuerirollt.ch>) rent a bike for free in the city. You will find it on the Velogate Hauptbahnhof (main train station), in front of the store Globus and at the Opera house.

The most convenient way to travel in Switzerland is to use public transportation. Trains, buses, trams, boats bring you to every town and village and also in the countryside and mountains. They are frequent, on time and comfortable.

The web-site www.sbb.ch (in English, German, French and Italian) is very efficient to find the right way to go everywhere and the timetables.

Emergencies in Zürich

- Police: 117
- Medical emergency: 144
- Pharmacy/drugstore :
 - open 24 hours : Bellevue Apotheke – Bellevueplatz – Theaterstrasse 14
 - open 7:00 – 24:00 : Bahnhof Apotheke – Bahnhofplatz 15



Hotels and restaurants in Zürich

Hotels

- | | |
|--|--|
| 1. City-Hotel,
Löwenstrasse 34 | 5. Hotel Leoneck
Leonhardstrasse 1 |
| 2. Hotel Comfort Inn Royal
Leonhardstrasse 6 | 6. Hotel Montana, Best Western Hotel
Konradstrasse 39 |
| 3. Hotel Etap, Zürich City-West
Technoparkstrasse 2 | 7. Rütli, Sorell Hotel
Zähringerstrasse 43 |
| 4. Hotel Ibis, City-West
Schiffbaustrasse 11 | 8. Seidenhof, Sorell Hotel
Sihlstrasse 9 |

Restaurants

Here is a suggestion list of some restaurants. Many good restaurants are in the City of Zürich and you will find more addresses on the site www.zuerich.com.

- | | |
|---|--|
| 1. Bodega Espanola
Münstergasse 15 | 11. Lake Side
Bellerivestrasse 170 |
| 2. Barrique Wine and Bar
Marktgasse 17 | 12. LaSalle
Schiffbaustrasse 4 |
| 3. Brasserie Federal
Bahnhofplatz 15 | 13. Mère Catherine
Nägelihof 3 |
| 4. Brasserie Lipp
Uraniastrasse 9 | 14. Restaurant Kunsthaus
Heimplatz 1 |
| 5. Confiserie Sprüngli
Bahnhofstrasse 21 | 15. Restaurant Neumarkt
Neumarkt 5 |
| 6. Fischstube
Bellerivestrasse 160 | 16. Take away Mishio
Sihlstrasse 9 |
| 7. Globus Cafeteria
Schweizergasse 11 | 17. Widder
Rennweg 7 |
| 8. Gnüsserei
Giessereistrasse 18 | 18. Zunfthaus zur Meisen
Münsterhof 20, |
| 9. Karl der Grosse
Kirchgasse 14 | 19. Zunfthaus zur Waag
Münsterhof 8 |
| 10. Kronenhalle
Rämistrasse 4 | 20. Weggen
Weggengasse 4 |

Restaurants and bars in ETHZ

http://www.gastro.ethz.ch/locations/eth_zentrum/index_EN

- | | |
|----------------------|--------------------------|
| 1 CHN bistrot | 7 Mensa Polyterrasse |
| 2 restaurant foodLab | 8 Cafeteria Polyterrasse |
| 3 Informatikbar | 9 bQm |
| 4 Gloriabar | 10 Dozentenfoye |
| 5 Tannenbar | 11 Polysnack |
| 6 Clausiusbar | 12 Cafebar |

About Switzerland

If you want to know everything about Switzerland like geography, history, politics, economy, culture, science etc consult the official web-site www.ch.

Currency

The Swiss currency is the Franc (CHF)

1 CHF is around 0,8 euros (€) or 1,1 dollar US (USD) (May 12)

Power supply



Electric power is supplied at 220 volts, 50 Hz.

The Swiss 3-pin plug is a unique domestic standard (Type J, standard SEV 1011 10A/250V).

Swiss sockets can take 2-pin europlugs (Type C, CEE 7/16).

More information on Wikipedia.(<http://en.wikipedia.org>)

Adaptations are sold in airport and main station shops in Zürich.

Post-Conference Travel Ideas

The following represent only the highlights of travel in Switzerland. For more details consult travel guides, web-sites and travel bureaus.

There is an excellent Travel Bureau in the Zürich Hauptbahnhof (Zürich's main train station).

The web-site www.myswitzerland.com has a great deal of information about Switzerland, including events.

Most of the web-sites have a choice of language, including English.

For the transportation by train, bus or boat, consult www.sbb.ch

Recommended Travel Guides:

- Eyewitness Travel Guides – Switzerland
- Michelin Green Guide – Switzerland

A Few Cities

- **Basel** – Excellent museums including the Beyeler and Tinguely museums, interesting old town. www.basel.com, www.beyeler.com, www.tinguely.ch
- **Bern** – Switzerland's capital, lovely old town. www.bern.com
- **Geneva** – Magnificent setting on the Lake of Geneva, headquarters of several international organizations, Jet d'Eau, Flower Clock. www.geneve-tourisme.ch
- **Interlaken** – Lovely city between two lakes, starting point for Jungfrauoch and Schynige Platte. www.interlaken.ch
- **Lausanne** – Olympic Museum, wonderful view of the French Alps, Chateau de Chillon nearby. www.lausanne-tourisme.ch
- **Lucerne** – Wonderful wooden bridge, mountains all around. Near Mt. Pilatus, Rigi, and the Glasi Factory. - www.luzern.org, www.gletschergarten.ch
- **Zürich** – A beautiful city on the Lake of Zürich. with many cultural events and cinemas. Different open air swimming facilities along the Limmat or the Lake. - www.zuerich.com, www.kulturinfo.ch, www.cineman.ch

Some Mountains

- **Jungfrauoch** – Top of Switzerland, train ride up through the Eiger, impressive mountain scenery, grand view of the Aletsch Glacier. - www.jungfraubahn.ch
- **Schynige Platte** – Alpine Flower garden, magnificent view of Eiger, Monch and Jungfrau. www.alpengarten.ch
- **Zermatt** – Justifiably famous views of the Matterhorn. - www.zermatt.ch
- **Glacier Express** - Train trip through the Alps. - www.glacierexpress.ch
- **Four Passes Tour** – Trip by car through high mountain scenery. Grimsel, Furka, St. Gotthard, and Nufenen Passes.

Several Museums

- **Ballenberg** – Open air museum with 100 historic rural Swiss buildings. Workshops with Swiss crafts. - www.ballenberg.ch
- **Château de Chillon** - www.chillon.ch
- **Paul Klee Museum** in Bern - www.paulkleezentrum.ch
- **Technorama** – Hands-on science museum in Winterthur - www.technorama.ch

Items of interest just over the border in Germany

- **Insel Mainau** – Flower garden island near Konstanz - www.mainau.de
- **Zeppelin Museum** – Friedrichshafen - <http://www.zeppelin-museum.de>
- **Black Forest** – www.blackforestinfo.com

ETH-Zürich: Main Building, Ground Floor

