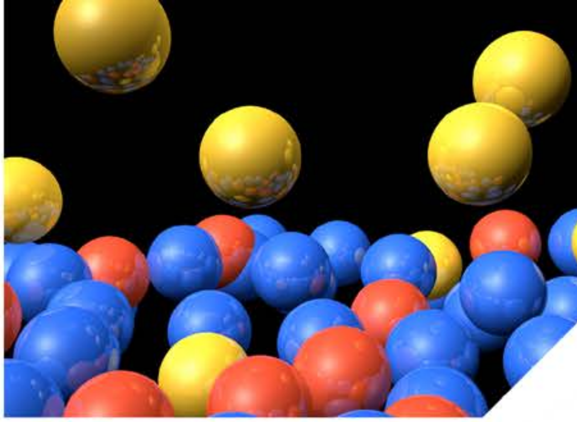
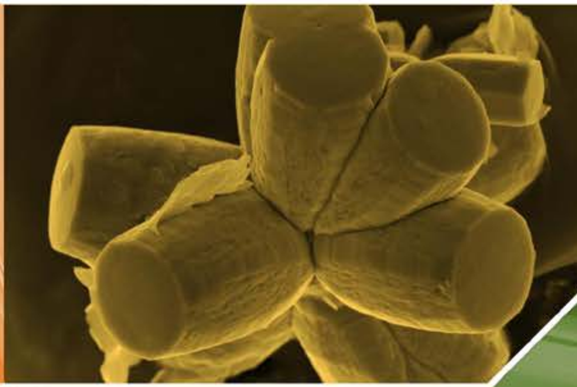
Workshop Report



Compact X-ray Light Source



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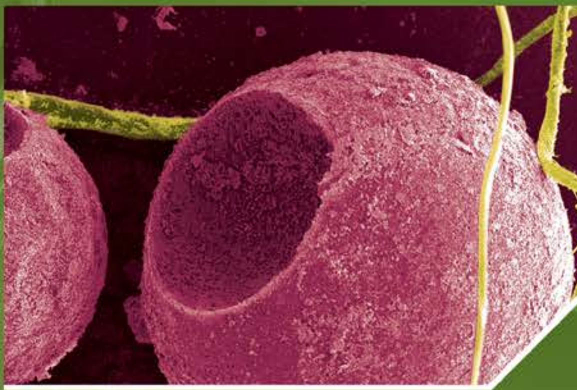

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operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

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PNNL-22145

Compact X-ray Light Source Workshop Report

Workshop Committee

December 2012

Prepared for
the U.S. Department of Energy
under Contract DE-AC05-76RL01830

Pacific Northwest National Laboratory
Richland, Washington 99352

Executive Summary

This report is the result of a workshop held in September 2011 that examined the utility of a compact x-ray light source (CXLS) in addressing many scientific challenges critical to advancing energy science and technology. The U.S. Department of Energy (DOE) and National Academy of Sciences (NAS) have repeatedly described the need for advanced instruments that "predict, control, and design the components of energetic processes and environmental balance," most notably in biological, chemical, environmental, and materials science. In numerous DOE and NAS reports, direct molecular-scale imaging and time-dependent studies are seen as a powerful means to develop an atomistic-level understanding of scientific issues associated with current and future energy and environmental needs, including energy production and storage from both fossil-based and fossil-free sources and cleanup of government and industrial sites worldwide.

One of the major enabling capabilities for meeting these needs is a high-brightness x-ray light source. The DOE report, *Next-Generation Photon Sources for Grand Challenges in Science and Energy*, identifies "spectroscopic and structural imaging of nano-objects (or nanoscale regions of inhomogeneous materials) with nanometer spatial resolution and ultimate spectral resolution" as one of the two aspects of energy science in which current and next-generation x-ray light sources will have the deepest and broadest impact. The report further stresses the power of direct observation in understanding transformational chemical processes. The report also discusses the importance of molecular "movies" of complex reactions that show bond breaking and reforming in natural time scales, along with the intermediate states to understand the mechanisms that govern chemical transformations. Existing accelerator-based x-ray sources have greatly extended capabilities in the time and space domain for scientific investigations in many disciplines. Despite these successes, a number of scientific challenges would benefit greatly from having an x-ray resource that has much of the attractive capability of these large machines but lends itself to operating in conjunction with other characterization tools in a correlative fashion. Such an integrated multiscale and multimodal approach could fully address the fundamental needs expressed by DOE's Office of Biological and Environmental Research (BER) in regards to understanding how genomic information is translated with confidence to redesign microbes, plants, or ecosystems (http://science.energy.gov/).

Fortunately, recent advances in laser and super-cooled linear particle accelerator, or linac, technology have enabled development of a long-promised CXLS that uses inverse Compton scattering for generating x-rays. The new CXLS holds the promise of simultaneous energy tuning—from the soft to hard x-ray regime—as well as a pulsed structure closely coupled to the laser pulse duration of pico- to femto-seconds. With a projected brilliance equal to third-generation light sources, a cost of around $35 million, and footprint of less than 10,000 square feet, these compact sources are exceedingly attractive for inclusion in existing facilities (that lack advanced x-ray capabilities) to influence a much broader segment of the scientific population. Some of the attractive methods that such a light source would enable or enhance include phase contrast imaging for organic or low-Z material systems, high spatially resolved x-ray microscopies and tomographies, time-resolved pump-probe dynamic observations, and other single-crystal diffraction methods. The flexibility of these sources will enable a multimodal approach to solving energy science and technology challenges by coupling advanced x-ray methods with in-house laboratory capabilities in existing user facilities, such as the Environmental Molecular Sciences Laboratory (EMSL). Combining the matter-penetrating feature of x-ray methods with exquisite high-resolution, in-house tools, such as *in situ* electron microscopy, can accelerate the discoveries needed to address energy and environmental challenges.

The CXLS workshop, held at Pacific Northwest National Laboratory (PNNL) and EMSL on September 21-22, 2011, attracted more than 75 scientists from across the country. These scientists identified numerous ways that a CXLS would close current capability gaps in biology, chemistry, environmental science, and materials sciences as outlined herein.

Biology: Experimental gaps in biological research currently prevent a complete chemical, functional, and structural understanding of biological mechanisms across length scales, which hinder rational biodesign. CXLS operating modes, including x-ray absorption spectroscopy, macromolecular crystallography, and whole cell imaging/tomography, can overcome current limitations by extending the sensitivities and dynamic range of investigations of biological processes to permit time-resolved measurements of energy relevant to proteins, macromolecular complexes, and intact cells.

Environmental Science: The fate and transport of contaminants in the environment is controlled by molecular-level processes, including aqueous complexation, surface complexation to mineral phases, and electron transfer between respiring microorganisms and biogeochemical reductants that occur in the presence of molecular diffusion in moving water. These molecular processes often are linked in complex ways that challenge their isolation, quantification, and mechanistic understanding. Studying the structure, chemistry, and nanoscale geometric properties of mineral/water and microbe/mineral interfaces with an array of imaging methods enabled by a CXLS could provide needed insights.

Catalysis: With an economic influence estimated at more than $10 trillion per year worldwide, resolving problems in catalysis can have a significant impact. Catalysis is an essential technology for chemical and materials manufacturing, global food production, and engineered plastics inherent in virtually all manufactured products. To understand, model, and ultimately control catalytic processes, we need to conduct *in situ* experiments that isolate elementary steps on catalytic surfaces or molecular docking locations in picosecond time increments. This approach, which would use multimodal measurements on CXLS, offers the potential for site-specific understanding of catalytic function, leading to rational, rather than experimental, design.

Materials Science: Materials exhibiting complex multi-property behavior and responses and sophisticated dynamic functionalities, as well as nanomaterials with entirely new properties compared to their bulk counterparts, have opened new frontiers of investigation. In particular, the dynamic properties of these new materials are being exploited for applications in the energy science and technology research areas. The ability to study materials properties and transformations with spatial and temporal resolution over a range of space and time scales is critical to designing materials and optimizing their structure and function. These experimental needs match the characterization capabilities of a CXLS in a multimodal laboratory setting.

Acknowledgments

Funding and logistics for this workshop were provided by the Chemical Imaging Initiative and EMSL at Pacific Northwest National Laboratory. The authors gratefully acknowledge the contributions from the workshop presenters and participants and thank all contributors to the final workshop report.

Acronyms and Abbreviations

3-D	three-dimensional
ALS	Advanced Light Source
APPES	ambient pressure photoemission spectroscopy
APS	Advanced Photon Source
ATP	adenosine triphosphate
BER	Office of Biological and Environmental Research
BES	Office of Basic Energy Sciences
CCN	cloud condensation nuclei
CII	Chemical Imaging Initiative
CT	computed tomography
CXLS	compact x-ray light source
CW	continuous wave
DFT	density functional theory
DOE	U.S. Department of Energy
DPA	displacements per atom
EFRC	Energy Frontier Research Center(s)
EMSL	Environmental Molecular Sciences Laboratory
EPS	extracellular polymeric substance(s)
EXAFS	extended X-ray absorption fine structure
FE^0	zero-valent iron
FEL	free electron laser(s)
FTIR	Fourier transform infrared spectroscopy
HOMO	highest occupied molecular orbital
ICS	inverse Compton scattering
JLab	Thomas Jefferson National Accelerator Facility
KB	Kirkpatrick-Baez
LBNL	Lawrence Berkeley National Laboratory
LCLS	Linac Coherent Light Source
linac	linear particle accelerator(s)
LUMO	lowest unoccupied molecular orbital
MGD	molybdopterin guanidine dinucleotide(s)
MIT	Massachusetts Institute of Technology
MM	molecular mechanics
NAS	National Academy of Sciences
NFS	nanostructured ferritic steels
NMR	nuclear magnetic resonance

NPS	Naval Postgraduate School
NSLS	National Synchrotron Light Source
NSR	NO_x storage reduction
OA	organic aerosols
OLED	organic light-emitting diode(s)
P3HT	poly(3-hexylthiophene)
PNNL	Pacific Northwest National Laboratory
PTM	post-translational modification(s)
QM	quantum mechanics
RF	radio frequency
RMS	root mean square
SC	Office of Science
SeCys	selenocysteine
SRF	superconducting radio frequency
UHV	ultra-high vacuum
VUV	vacuum ultraviolet
XAFS	X-ray absorption fine structure
XANES	X-ray absorption near-edge structure
XAS	X-ray absorption spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence
YLF	yttrium lithium fluoride

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1.0 Introduction

1.1 Advancing Energy Science and Technology: Background

One of the most pressing societal challenges is meeting future global energy needs in a secure, economically viable, and sustainable manner. In response, the nation has turned with great urgency to the scientific community for innovation and discovery that will significantly impact this universal need (DOE-BESAC 2008) and the U.S. Department of Energy (DOE) has embraced this challenge in meaningful ways through new vehicles, such as Energy Frontier Research Centers (EFRCs), Hubs, and enhancements to the Energy Technology Offices. In particular, DOE's Office of Science (SC) has articulated several grand challenges strongly aligned with accelerating the path of taking discoveries to useful and impactful energy technologies. Central to DOE-SC's strategy to address these challenges are the tools needed by the scientific community to accelerate discovery and translation to new energy technology and paradigms—with a special emphasis on the large tools needed for discovery.

A number of SC Basic Research Needs documents and other reports list chemical imaging and analysis as critical needs for advancing energy research. The National Academy of Sciences (NAS) 2006 report, *Visualizing Chemistry: The Progress and Promise of Advanced Chemical Imaging*, noted that "the ability to visualize molecular structures and chemical composition in time and space as actual events unfold" could revolutionize many areas of scientific exploration. Meanwhile, DOE's report, *Next-Generation Photon Sources for Grand Challenges in Science and Energy* (2009), identifies "spectroscopic and structural imaging of nano-objects (or nanoscale regions of inhomogeneous materials) with nanometer spatial resolution and ultimate spectral resolution" as one of the two aspects of energy science in which next-generation vacuum ultraviolet (VUV) and x-ray light sources will have the deepest and broadest impact. Both reports stress that the major goal of chemical imaging should be focused on gaining fundamental understanding of complex structural dynamics to enable the creation of structures on demand or enhance control over chemical processes. The challenges inherent in achieving this goal can be met by imaging a material or process using multiple techniques across all lengths and scales.

Since their discovery more than 115 years ago, x-rays have proven to be the most effective and prolific method for structural analysis of both organic and inorganic materials as evidenced by the investment in and commissioning of more than 60 large-scale synchrotron light source user facilities worldwide. Interestingly, 15 of the 19 Nobel Prizes awarded for x-ray-based discoveries used in-house, rotating-anode-based x-ray sources. While fourth-generation light sources, such as the Linac Coherent Light Source (LCLS), are further expanding the types of samples and temporal resolutions amenable to x-ray analysis, the large size of these dedicated x-ray facilities inhibit direct multimodal and multiscale analysis of a sample due to the lack of other proximal instrumentation. Recent developments in laser technology, along with advancements in radio frequency (RF) cavities for the super-cooled linear particle accelerators, or linacs, are pushing compact x-ray light source (CXLS) technology to the forefront, and these versatile capabilities promise to open up new scientific frontiers, particularly in ultrafast dynamics and spectroscopy. Although these capabilities will not match the standard expected for fourth-generation light sources, CXLSs, such as coherent inverse Compton scattering (ICS) sources, are expected to provide x-ray parameters equivalent to or better than the current third-generation light sources for a fraction of the cost (Figure 1.1). In addition to the economic benefits, the flexibility of these sources can provide multimodal capabilities coupled with in-house laboratory capabilities in a user facility such as the Environmental Molecular Sciences Laboratory (EMSL), which currently houses state-of-the-art instrumentation, including both conventional and *in situ*-based electron and scanning probe microscopies, nuclear magnetic resonance (NMR), and mass spectrometry. Therefore, it is incumbent upon us to continue exploring the utility of x-rays for the next generation of scientific challenges that can be transformed by in-house x-rays.

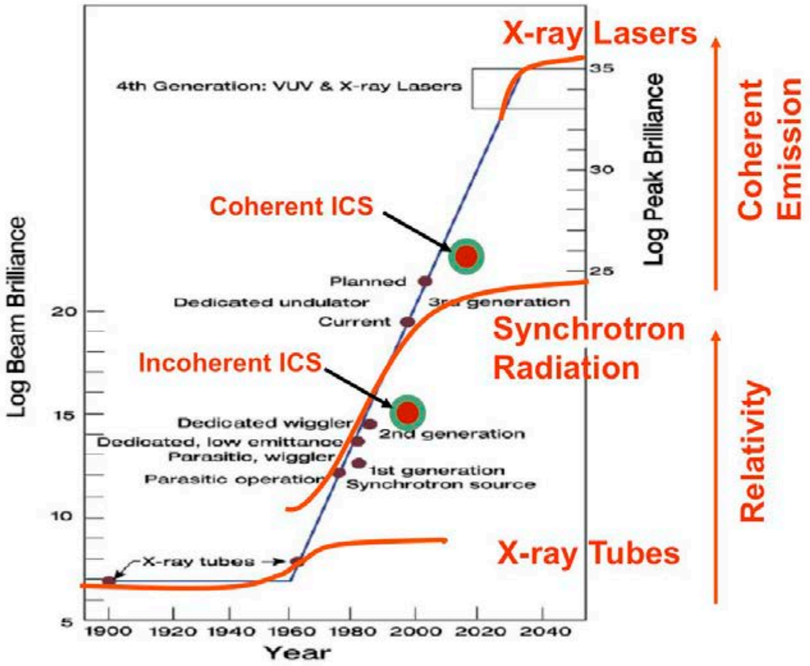


Figure 1.1. History of x-ray source technology plotted according to brightness. Higher brilliance permits more versatility in sample geometry, resolution, and chemical sensitivity.

1.2 Workshop to Examine How Energy Science and Technology can be Addressed with X-rays

Light-source imaging capabilities, including x-ray tomography and scanning transmission x-ray microscopy at existing light sources, have defined the direction for high-impact science. However, other high-resolution laboratory-based imaging capabilities, including aberration-corrected transmission electron microscopy and scanning probe microscopy, have significantly improved over recent years, and research can be performed with unprecedented lateral resolution using these techniques. In particular, the ability to perform *in situ* experiments at ambient or elevated temperatures have advanced high-impact science toward understanding reaction kinetics of individual nanoparticles and the analysis of biological materials in their native environment without freezing, chemical fixation, or physical sectioning.

The deployment of fourth-generation x-ray light sources (free electron lasers, or FELs) has opened new frontiers in ultrafast dynamics, structure, and spectroscopy. The LCLS at the SLAC National Accelerator Laboratory was built on the principles of x-ray FELs, and it services a small number of experiments at one time due to their linear geometry and their operation at a defined wavelength. As a result of the limited number of experiments in facilities such as LCLS, these resources are generally oversubscribed. Conversely, new developments in ultrafast laser technology, along with coherent high harmonic (HHG) soft x-ray beams, have established CXLSs as viable options in the ultrafast dynamics and spectroscopy arena. While these sources are no substitute to x-ray FEL-based sources, they are complementary to x-ray FELs with a much lower cost per instrument enabling broader access.

Due to their size, CXLSs can be effectively implemented in small-scale scientific user facilities, such as EMSL, where multiple experimental capabilities can be used in parallel to advance scientific discovery. Coupling light-source and laboratory-based capabilities is something new. In comparison to what any single capability can offer, this multimodal approach of collecting, integrating, and analyzing data from several sources will provide missing information needed for temporal and spatial resolution of chemical, materials, and biological reactions *in situ* and across scales (Figure 1.2). This is a difficult task, and the planned initiative at Pacific Northwest National Laboratory (PNNL) will help generate solutions to this grand challenge.

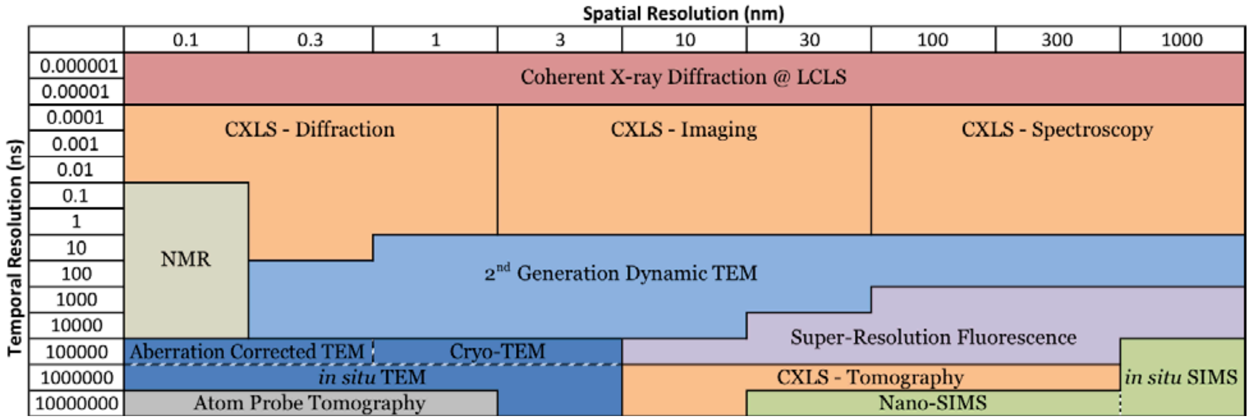


Figure 1.2. Correlating structure, function, and chemistry of biological systems via multiscale and multimodal analysis.

The PNNL/EMSL Chemical Imaging Initiative (CII) leadership team evaluated the science needs that can be clearly addressed by either pushing the science to the forefront using the development of new capabilities and methods or emphasizing technology so high-impact science can be done. These questions capture the importance of focusing the initiative in the right direction. The research to address the first question clearly identifies x-ray tomography, scanning transmission x-ray microscopy, inelastic scattering imaging, and coherent diffractive imaging as the main light-source-imaging capabilities that can be effectively connected to the scientific problems in which PNNL scientists have established world-class leadership.

1.3 Science Themes Explored in This Workshop

The science needs in biology, biogeochemistry, environmental science, catalysis, and materials science that are addressable with a CXLS in combination with other in-house capabilities at EMSL was the basis of a workshop held at PNNL on September 21-22, 2011. Brief summaries of the needs in each main focus area include (as follows):

Biology: Experimental gaps in biological research currently prevent an understanding of biological mechanisms across length scales. For example, the availability of large amounts of high-resolution structural data for a range of biomolecules, including proteins, is not generally applicable in the analysis of cellular behavior. The lack of structural tools that resolve atomic-level structural information about the component parts of cells limits the ability to interrogate cellular systems at the molecular level. Newly available light sources, such as those at the LCLS, can overcome current limitations by extending the sensitivities and dynamic range of investigations of biological processes to permit time-resolved measurements of structural changes for biomolecules within intact cellular structures. Understanding the context of these dynamic structural changes requires an integration of these advanced imaging capabilities with current state-of-the-science instrumentation available at EMSL. X-ray microscopy with a CXLS provides unique capabilities for ultrasensitive structural measurements of the component parts of both whole cells and cellular communities. In combination with light-source-based infrared spectromicroscopy, these capabilities permit simultaneous measurements of macromolecular structural changes and their relationship to functional changes involving metabolism.

While these x-ray and infrared imaging capabilities currently are available at several large synchrotron light source facilities across the United States, bringing a CXLS to PNNL will provide an integrated capability made possible by the suite of unique complementary tools available within EMSL. For example, in combination with electron microscopy and super-resolution fluorescence microscopy, the proposed compact light source is anticipated to allow high-resolution structural mapping of intact cells with nanometer resolution and tens of micrometers field-of-view. Currently, EMSL only has laboratory-based rotating anode x-ray sources with, at best, 10-micrometer spatial resolution for imaging and requires100-micrometer three-dimensional (3-D) protein crystals or larger for efficient diffraction collection. Figure 1.3 illustrates the benefits of a CXLS in comparison to a rotating anode source and relative to third- and fourth-generation light sources. Both incoherent and coherent ICS provide significant improvement in temporal resolution for pump-probe macromolecular crystallography experiments.

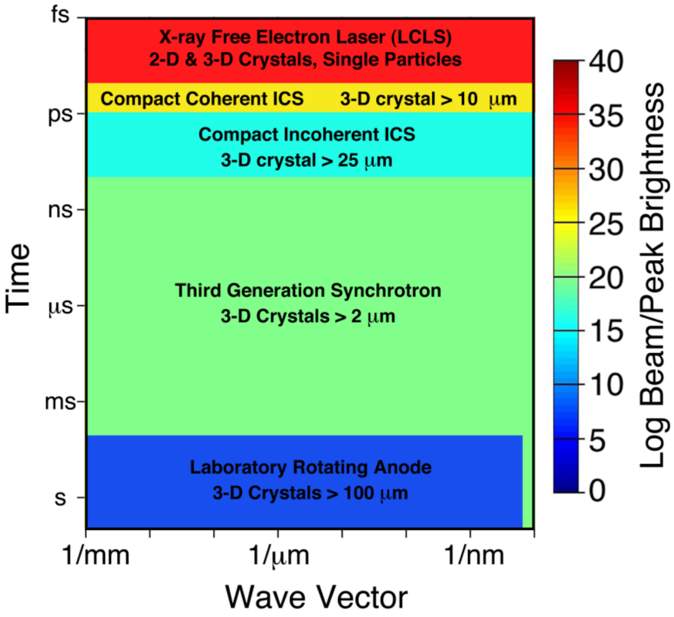


Figure 1.3. Resolution plot of various light source capabilities distinguished according to brightness and amenable protein crystal dimensions.

In addition, the development of a coherent ICS CXLS would enable protein structure determination from 3-D crystals 1000 times smaller than currently possible at PNNL. Although Figure 3 only highlights the benefits to x-ray diffraction experiments, similar improvements in resolution and chemical sensitivity exist for X-ray microscopy, tomography, and spectroscopy. Therefore, a CXLS located at EMSL could drastically improve the range of characterization experiments and spatial resolution for chemical imaging at PNNL and available through DOE's Office of Biological and Environmental Research (BER) user facilities. Given the large number of bioscientists using EMSL (40% of total users), it is expected that providing advanced biological x-ray and infrared imaging capabilities at PNNL will have an immediate and significant impact on biological sciences, enabling a team approach toward elucidating a comprehensive picture of the fundamental processes of life in a way not available in any single laboratory today.

Environmental Science: Gas-particle heterogeneous reactions play a critical role in a variety of environmental processes, including atmospheric aerosols and engineering chemical processes such as catalysis. These processes are pertinent to energy production and emissions control, particle nanotoxicology, and health effects. Fundamental understanding of these reaction processes requires advanced analytical approaches for chemical imaging of particles down to 1 nm in reactive environments. In particular, x-ray-based microscopy and analysis capabilities, including x-ray absorption spectroscopies and scanning transmission x-ray microscopy, will play an important role in obtaining molecular-level understanding of the chemical composition of organic aerosols (OA) and their reaction chemistry pertaining to atmospheric environment. Such measurements will offer an analytical platform to study multi-phase particle reaction and *in situ* chemistry with broad applications to understand the aerosol formation and the dynamic changes in the aerosols over time. The realization of a CXLS, potential to combine CXLS with other state-of-the-art capabilities, and time-resolved measurement structures at EMSL will allow PNNL to take a revolutionary step forward for dynamic chemical studies of reactant aerosol particles and will extend studies of particles well beyond the current capabilities. In addition, it will enhance and guide complementary molecular-level spectromicroscopy investigations.

The fate and transport of contaminants in the environment is controlled by molecular-level processes including aqueous complexation, surface complexation to mineral phases, and electron transfer between respiring microorganisms and biogeochemical reductants that occur in the presence of molecular diffusion in moving water. These molecular processes occur in chemically and physically heterogeneous subsurface environments and often are linked in complex ways that challenge their isolation, quantification, and mechanistic understanding. The structure, chemistry, and nanoscale geometric properties of mineral/water and microbe/mineral interfaces and the surrounding physical environment markedly influence these processes. Determining the biochemical and biophysical structures of biofilms and their interactions with inorganic substrates, including metal ions and mineral surfaces, will provide critical new knowledge for development of improved biogeochemical reaction and fate models. Understanding process interactions and environmental variables that control the reaction rates and products is a critical scientific need that must be resolved to predict subsurface reactivity.

A CXLS that can generate x-rays in the sub-micron size with variable energies and short-pulse time structures, coupled with the existing state-of-the-art capabilities at EMSL, will enable unique investigations of mineral-microbe-contaminant systems under realistic environmental conditions. Structure-property relationships can be investigated along with physical and chemical heterogeneities that exist within the micron- to nanometer-scale zones of mineral/microbe interaction. X-ray-based measurements, including crystallography, scanning transmission microscopy, and absorption spectroscopies, would enormously complement EMSL capabilities, providing new scientific breakthroughs in environmental science and biogeochemistry.

Catalysis: Catalysis is the key to both life and the lifestyle to which we are accustomed. It is an essential technology for chemical and materials manufacturing, producing fertilizers on which the global food production systems relies, producing gasoline and diesel fuel for transportation, and for engineering plastics inherent in virtually all manufactured products, to name a few. Some of the specific challenges under the umbrella of this national challenge include: 1) to establish firm relationships between catalyst structure, rates, and selectivity of elementary reaction steps using the latest characterization methods; 2) to build close interactions between theoretical/computational and experimental researchers to develop advanced modeling and simulation tools; 3) to develop understanding of the thermodynamics and kinetics of the nucleation and growth of model single-crystal oxide thin films, nanostructures, and supported metal catalysts; 4) to create bases of theoretical and experimental data and methodologies to perform data mining with the goal of optimizing the design of new catalytic systems; and 5) to prepare highly reactive, coordinately unsaturated catalytic sites stably isolated on support surfaces, including single-crystal surfaces.

The potential impact of the techniques available using synchrotron light sources on understanding catalysts was recognized in the earliest days of the modern era of synchrotron science. One of the overarching reasons for this was that x-rays from these sources are able to penetrate the reaction medium and walls (or via suitable windows) of the catalytic reactor so that the structure of the catalyst can be probed in working conditions. Over the last 30 years, the range of synchrotron x-ray techniques and methodologies that have been applied to catalysis research essentially has only been limited by researcher ingenuity, time available, and, of course, the funding for the research. The primary techniques have been diffraction, scattering, and absorption spectroscopy, in both static and time-resolved modes. One of the more recent advancements has been the development of these techniques to image the catalyst using either full-field or microbeam techniques at spatial resolution down to the tens of nanometer range. In addition, the capability of probing the structure of catalysts under *in situ* or *operando* conditions, such as elevated temperatures and pressures, provided additional understanding as it has been shown that the structure of the catalyst responds to its environment. It is envisioned that the CXLS would have similar dramatic impact on catalysis research at EMSL and PNNL. A dedicated facility combined with a group of world-leading scientists and staff, as well as a world-class suite of characterization and testing tools at EMSL, will produce world-leading research and could be a game-changer in the application of x-ray-based techniques to catalyst characterization. The CXLS will allow PNNL and its collaborators to advance the level of catalysis science and enhance understanding of catalytic materials and phenomena through the use of state-of-the-art synchrotron techniques under *operando* reaction conditions.

Material Science: Advances in materials dramatically enhance the human experience through their diverse functionalities. Early functionalities included enhancement of existing properties, particularly static features such as strength, durability, and thermal insulation. More recently, materials exhibiting complex multi-property behavior and responses, sophisticated dynamic functionalities, and nanomaterials with entirely new properties compared to their bulk counterparts have become important. Complex materials include engineered systems, such as the layered complex oxides that display emergent electronic and magnetic properties depending on the collective behavior of their individual layers, and nano-foams and core-shell nanoparticles finding application in areas from targeted drug delivery to reduction of biomass into fuel to electrical energy storage. In parallel, the dynamical properties of new materials are being exploited for high-speed digital computation, efficient conversion of sunlight to electricity and fuel, and catalytic capture of toxic combustion products in automobiles. The ability to study materials properties and transformations with spatial and temporal resolution over a range of spatial and time scales starting from nanometers and picoseconds is critical to materials design and optimization. For example, photovoltaics convert one photon to one electron in a sequential process. To design and control this process, we must be able to observe each step: the excitation of an electron by a photon from the conduction to the valence band in a semiconductor, the separation of the electron from the hole it left behind in a p-n junction, and the transport of the electrons and holes in opposite directions without loss due to recombination. These processes require simultaneous high spatial and temporal resolution to explore, understand, and control.

The proposed CXLS, in combination with existing state-of-the-art materials preparation and analysis capabilities at PNNL and the ultrafast electron microscopy capabilities currently being installed at EMSL, would provide a world-class center for advanced materials science. The combination of these capabilities along with other capabilities within EMSL is well suited to studies of materials control at an electronic level. The spectroscopic capabilities envisioned interrogate both the occupied and unoccupied electron levels of materials, and the unique temporal resolution will allow a more detailed investigation of electronic processes. Without this time resolution, alternative techniques provide information averaged over multiple energetic states, restricting opportunities to fully understand and control their properties. In this regard, the CXLS will impact many materials development programs, especially those focused on electrode processes, energy storage, and photon/electron interactions in which greater control over electronic structure is expected to drive breakthroughs.

Technology: Figure 1.4 shows a conceptual design of a single accelerator driving multiple independently tunable beamlines—each dedicated to a different energy range. The accelerator structure is the same as the single beamline devices, but it has additional equipment controlling the cathode and the electron beam path after acceleration. Instead of a single cathode laser, there are as many cathode lasers as there are beamlines (three in the illustrated case). Each cathode laser is individually controlled by the beamline to set the repetition rate, charge per pulse, and photon energy of its own beamline. They may switch the beam off by turning off the cathode laser. In addition to separate cathode lasers, the multi-beamline source has a fast electron beam switch at the linac exit, consisting of a deflecting RF cavity and septum magnets. The deflector sends individual pulses to each beamline separately. The maximum repetition rate for any one beamline is set by the deflection frequency that will be 1/N, where N is the number of beamlines. Practical designs allow switching at frequency up to ~100 MHz.

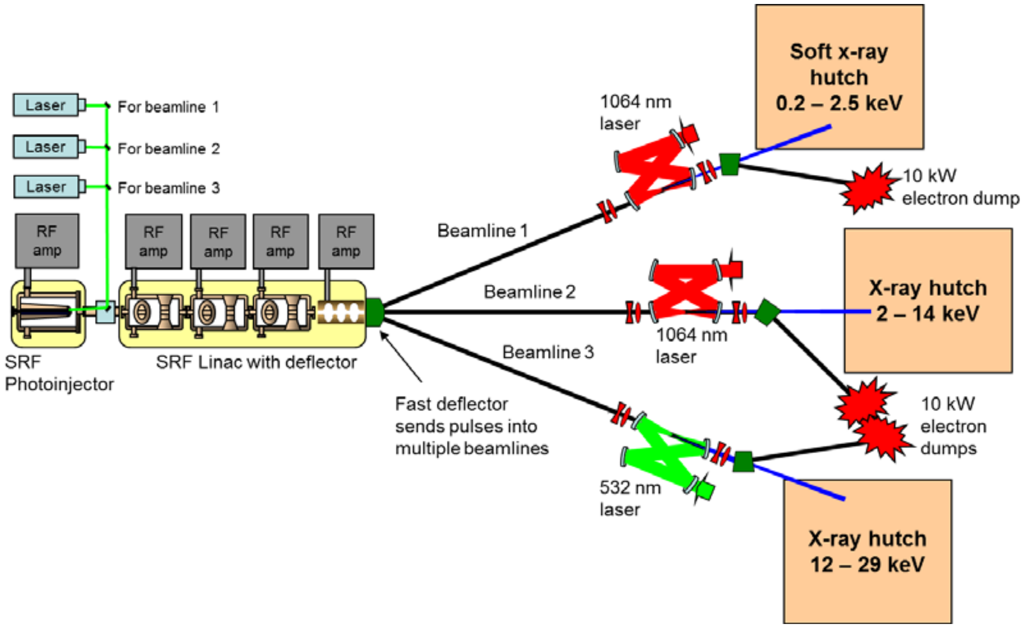


Figure 1.4. Concept for multiple independently tunable beamlines driven by a single accelerator. Each beamline controls its own cathode drive laser, setting photon energy and repetition rate independently. A fast RF deflector at the linac exit sends individual pulses to each beamline.

The photon characteristics at different energies are suitable for many soft and hard x-ray experiments. For example, the full beam at 12 keV is anticipated to be at 10^{14} photons/sec with a low heat load along the beam path. After monochromatization, the flux level is expected to be ~10^{12}/sec. The output radiation from the CXLS has cylindrical symmetry divergence, typically a few mrads. The CXLS produces a small source size beam (~2 microns), which is ideally suited for imaging applications, and it also supports the performance of the optics for pre-monochromator conditioning of the beam. The CXLS itself can be quickly tuned over a wide photon energy range by varying the electron energy, either by reducing the RF amplitude or shifting the electron bunch timing with respect to the RF. There are no higher harmonics to consider because the laser radiation intensity is equivalent to a weak undulator field. In principal, the repetition rate can be as high as the 100 MHz linac repetition rate, but it is determined by the rate of the photocathode laser and, therefore, is adjustable to very low rates. Typical pulse lengths are ~0.5 ps, which is 100 times shorter than a typical third-generation synchrotron radiation. Thus, the CXLS is ideal for time-resolved x-ray scattering with sophisticated timing systems that can provide accurate signals for synchronizing x-ray beams to pump laser pulses used to excite sample dynamics.

1.4 How Coupling the CXLS with EMSL Can Transform Our Scientific Discoveries

EMSL, a national scientific user facility sponsored by DOE-BER, provides integrated experimental and computational resources for discovery and technological innovation in the environmental molecular sciences to support the needs of DOE and the nation. It consists of various state-of-the-art crosscutting capabilities and expertise under one roof that enable users to access multiple experimental and computational capabilities to address complex energy and environmental issues. These capabilities can be used by scientists and scientific teams to accelerate new discoveries through a no-cost collaboration with

EMSL. Incorporation of a CXLS in EMSL would advance EMSL users' research in the following three aspects:

1. Multimodality characterization through the coupling of various experimental capabilities at EMSL with the CXLS
2. Controlling radiation damage in light-sensitive materials, particularly biological and biogeochemistry materials
3. Fill the capability gaps for EMSL users by providing soft and hard x-rays with high temporal resolution through short pulses in, at least, the picosecond time scale—far beyond the current rotating anode capabilities available on site.

Coupling in-house capabilities at EMSL with CXLS-enabled capabilities can significantly contribute to advancing discovery science. For example, 3-D information of a biological cell can be imaged using x-ray tomography with spatial resolution better than 40 nm to achieve contextual information of the intact cell and its local environment with simultaneous unambiguous identification of organelles. The fine details within the cell's components also can be imaged using super-resolution optical microscopy and near-atomic resolution electron microscopy. The results from such multimodal-correlated microscopy could enable a complete atoms-to-microns picture of the biological cell.

Currently EMSL is working on planning activities to establish an ultrafast transmission electron microscopy capability to further advance high temporal resolution measurements of biological systems. The complementary CXLS capability with multiple beamlines of variable energy will be valuable for EMSL users. In particular, the combination of ultrafast transmission electron microscopy and CXLS capabilities could reveal ultrafast dynamics involved with chemical, biological, and materials transformations.

1.5 Organization and Conclusions of the Workshop and Report

The workshop was a two-day event organized by PNNL and EMSL. The event brought together experts from across the country to discuss key scientific challenges and the application of CXLS to those challenges. Panel sessions brought together scientists from different fields to discuss current and future scientific needs from an interdisciplinary view. With input from these scientists, thrust leads and PNNL's CII management team developed this report. For a list of the workshop's attendees, see Appendix A.

This report describes outstanding scientific challenges in biology, environmental science, catalysis, and materials science. The sections then discuss the application of CXLS to these challenges with a focus on the relevant spatial and temporal resolution requirements. The workshop organizing committee selected these areas because of their relevance to the DOE mission in ensuring the nation's energy and environmental security. Each area has a significant impact on questions vital to the nation by addressing its energy and environmental challenges through transformative science and technology solutions.

The presence of a CXLS at PNNL would enhance onsite capabilities and establish multimodal imaging as a gateway to the science of scalability. The CXLS also would:

- Enable exciting new science via the unique opportunity for multimodal imaging
- Complement state-of-the-art tools at EMSL and state-of-the-art methods at other light sources

- Fill a potentially important niche in x-ray capabilities that can enable scientific discovery
- Drive new energy technology development.

2.0 Biology: Scientific Challenges

2.1 Overview

Biological organisms have evolved mechanisms that provide for a sensitive response to changes in their environment through the capture and utilization of both photochemical energy and organic molecules. The processes of life are rich and complex, involving not only the interactions of thousands of macromolecules organized into the structure of a cell, but the interactions of cells with each other. Cellular communities can take a variety of forms, as represented by tissues of higher organisms or microbial communities present in, for example, soils and the intestines of mammals. A central goal of biology is to obtain a mechanistic understanding of cellular processes. Development of a predictive understanding of underlying processes across length and time scales so community systems can be understood in terms of their individual cellular components and associated intracellular processes is critical to this goal.

New methods are enabling interrogation of changes in protein function caused by post-translational modification (PTM) or genetic mutation. These measurements, coupled with a structural understanding of macromolecular protein complexes, provide a basis for synthetic biology applications, such that binding interactions (between protein complexes, ligands, and cofactors) can be adjusted to enhance energy fluxes within individual cells and communities. To obtain this predictive understanding, complementary measurements, such as those made possible using a CXLS, are required to extend currently available omics-based information to understand and predict how cells respond to stressors. Such a strategy requires a model-dependent approach to data analysis that incorporates the current understanding of the system, and which allows data integration from different sources. This understanding is a fundamental need expressed by DOE-BER: to understand how genomic information is translated with confidence to redesign microbes, plants, or ecosystems (http://science.energy.gov/). Building a team of scientists with complementary skills that, together, will provide a basis to understand complex biological, climatic, and environmental systems across vast spatial and temporal scales requires building intense x-ray light sources proximal to state-of-the-science experimentalists and computational scientists to allow an integrated understanding of the system.

Three main CXLS operating modes—spectroscopy, macromolecular crystallography, and whole cell imaging—promise significant benefits to research at PNNL and DOE-BER. X-ray absorption spectroscopy is a powerful tool for identifying and characterizing redox products generated both *in vivo* and *in vitro* by using the spectral region near an absorption edge to infer information about distances from one atom to electron orbitals in its neighbors or to identify the symmetry at a metal site or the metal valence. For example, with higher oxidation states, the absorption edge shifts to higher energy by a few electron volts. For many transition elements with unfilled *d* orbitals, the shape of the x-ray absorption near edge structure profile reflects the geometry of the first coordination sphere. Such detailed redox information afforded by liberal access to CXLS would not only benefit bioremediation studies from the cellular to molecular level but would also be valuable for the study of metalloproteins, including in the growing field of peptide-enhanced metal catalysis. When coupled with macromolecular crystallography, CXLS-derived molecular structure information could be used to help design the next-generation, novel uranyl reductase, whether as a metalloprotein or a bioinspired electrocatalyst. Moreover, using fast pump-probe imaging on 3-D microcrystals would allow dynamic observations of conformational changes of proteins to better correlate structure with function.

Achieving this goal is now possible, as recent technology developments offer unprecedented opportunities to measure how biomolecular structures (and their time-dependent changes) modify interactions between biomolecules to affect cellular pathways within individual cells (Figure 2.1) and how these interactions affect cellular interactions within community structures. An ability to effectively integrate multimodal measurements across scales will provide an understanding of the molecular mechanisms underlying biological processes. However, to rationally design a more efficient biosystem for any synthetic application, it would be useful to have whole cell contextual information correlated with the chemical, functional, and structural information described. The ability to perform soft x-ray tomography on hydrated or frozen-hydrated specimens would permit a detailed understanding of cellular architecture within microbial biofilms, while hard x-ray tomography can be used to understand the ultrastructural health effects of cellular exposure to nanomaterial or the distribution of inorganic minerals within native soil samples. Thus, coupling CXLS with existing EMSL capabilities and expertise can provide unique solutions for a range of energy- and environmental-related biosystems, including bioremediation, contaminant transport, and molecular details of metal-reducing cells and enzymes.

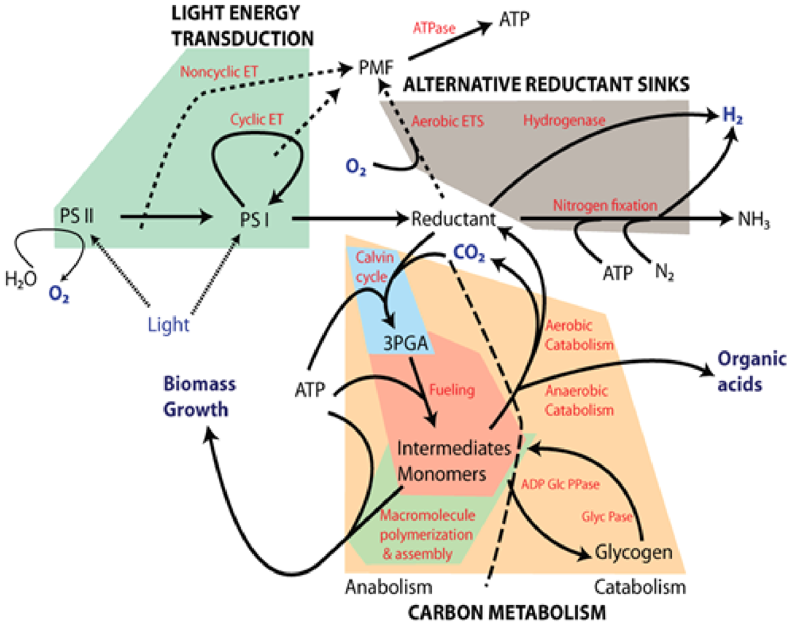


Figure 2.1. Schematic overview of coordinated metabolic pathways linked to light energy transduction (photosynthesis and reductant generation), carbon metabolism (carbon fixation and biosynthesis), and alternative reductant sinks linked to formation of energy-rich compounds important for bioenergy applications.

2.2 Fundamental Insights Require Knowledge of Dynamic Structures Across Scales

A central goal of the biological sciences is to understand fundamental regulatory mechanisms involving cellular responses to environmental change, with a focus on both microbial communities and multicellular eukaryotic organisms. In all cases, cellular responses are understood to involve a range of mechanisms that typically correlate with the time scale of the response. For example, cellular metabolism efficiently modulates energy partitioning between different metabolic pathways using feedback mechanisms involving allosteric control mechanisms, where the product of a pathway binds to oligomeric regulatory proteins to adjust enzymatic function. Rapid responses to environmental change typically involve PTMs to proteins that result in shifts to metabolism involving the modulation of protein associations. PTMs involve both enzyme-mediated processes (e.g., phosphorylation; acetylation), as well as the chemical modification of sites by metabolites (e.g., oxygen) that typically are grouped as involving oxidative stress. These latter rapid responses involving PTMs at protein sites are in contrast to long-term adjustments to metabolic pathways, which commonly involve transcriptional control mechanisms that adjust the concentrations of protein catalysts to allow efficient control of energy use. Significant advances in the genomic sciences require coupling high-throughput measurements of individual proteins and associated structural changes to their cellular context to identify the important control mechanisms underlying cellular and community behavior.

Current approaches that build upon successes in genomic biology commonly focus on an analysis of transcriptional control mechanisms and their relationship to changes in protein abundance, such that a correspondence between these measurements (i.e., correlated abundance changes of transcript and protein) suggests a simple, long-term regulatory strategy involving linear responses to environmental change (i.e., signal → transcriptional control → altered rates of protein synthesis). In comparison, it has proven problematic to understand nonlinear metabolic control mechanisms that mediate rapid responses to an ever-changing environment. An understanding of these latter control mechanisms have been aided by the considerable strengths that permit cataloging of proteins and their PTMs using top-down and bottom-up proteomic capabilities, which represent major tools that are revolutionizing biological sciences. As configured, these omic methods typically are coupled with a data-driven computational analysis pipeline that acts to reliably analyze a range of different samples, providing an opportunity to obtain unprecedented identification of possible changes involving metabolic networks within cells. Coupled with emerging metabolic capabilities, it is becoming possible to interrogate changes in protein function in response to identified post-translational changes to provide predictive understanding essential to the redesign of biological systems that are critical to the implementation of synthetic biology approaches. Using this information, targeted imaging measurements can validate the mechanistic underpinning of observed correlations to provide a means for real-time measurements of cellular reprogramming in response to environmental change. These latter measurements, coupled with a structural understanding of the protein complexes, provide a basis for synthetic biology applications wherein binding interactions between protein complexes can be adjusted to modify energy fluxes within individual cells and communities. To obtain such a predictive understanding, complementary measurements, including those possible using a CXLS, are required to extend currently available omics-based information to determine how cells respond to stressors. This strategy requires a model-dependent approach to data analysis that incorporates the current understanding of the system and allows data integration from different sources. This latter goal requires a team of scientists with complementary skills, which, when combined, will provide a basis to understand complex biological, climatic, and environmental systems across vast spatial and temporal scales.

Combining omics approaches with advanced imaging, spectroscopy, and structural biology is necessary to probe the organizational principles of biology involving environmental sensing, energy transduction, and chemical storage systems to develop fundamental design principles that control molecular interactions regulating living systems. Understanding how cells balance dynamic needs for synthesis, assembly, and turnover of cellular machinery in response to changing environmental signals will be possible through integrated approaches that include proteomics, structural biology, and high-resolution imaging. Parallel measurements of these integrated processes are necessary to obtain the predictive ability necessary for synthetic redesign that enhances the ability to introduce multi-component biological functional modules and manipulate genetic control systems. High-throughput measurements, such as those generated using compact light sources, are critical toward achieving these goals. These measurements validate biological function and facilitate the interoperability of biological modules and processes in both laboratory- and environmental-based systems.

2.3 Advantages of X-ray Sources

Experimental gaps in biological research currently prevent an understanding of biological mechanisms across length scales. For example, the availability of large amounts of high-resolution structural data for a range of biomolecules, including proteins, is not generally applicable in cellular behavior analysis. The lack of structural tools that resolve atomic-level structural information about the component parts of cells limits the ability to interrogate cellular systems at the molecular level. Newly available light sources, such as those at LCLS, can overcome current limitations by extending the sensitivities and dynamic range of investigations of biological processes to permit time-resolved measurements of biological assemblies such as microcrystals, nanocrystals, and large viruses (Chapman et al. 2011; Seibert et al. 2011). Understanding the context of these dynamic structural changes requires an integration of advanced imaging capabilities with current state-of-the-science instrumentation available at EMSL.

X-ray and infrared spectroscopy and microscopy provide unique information that complement the capabilities of other established imaging techniques at EMSL, such as electron and light microscopy. Life exists in the presence of water, which requires hydrated specimens to preserve native structure. Electron microscopes provide remarkable detail from such specimens but only for sample thicknesses less than about a micrometer—limited by the fundamental interaction length of electrons with matter (Sayre et al. 1977a, 1977b; Grimm et al. 1998; Jacobsen et al. 1998). However, compact sub-keV (i.e., soft) x-ray microscopes can accommodate greater specimen thicknesses up to about 5 micrometers (resolution up to 2.5 nm) (Hertz et al. 2012), and even thicker specimens can be viewed with multi-keV (i.e., hard) x-ray microscopes at resolutions up to 1 angstrom. This ability to view thicker specimens is important for imaging biomolecular interactions within soils, microbes, and extracellular exudates or biofilms or for examining how nanoparticles move from aeration surfaces to become incorporated into lung tissues. Moreover, x-rays are much less likely to undergo multiple scattering events in materials compared to electrons, which leads to more straightforward interpretations of signals and dramatically increases sensitivity (Winick and Doniach 1980; Sparks Jr. 1980) as observed in studies of the location of trace elements and their chemical environment. While advanced light microscopy methods have been demonstrated to deliver exquisitely high-resolution images from pre-selected fluorescent molecules, x-ray and infrared spectroscopy and microscopy provide important complementary information on the entirety of the specimen and its overall biochemical organization—independent of the need to fluorescently tag specific selected molecules. This advantage is particularly important in studies of difficult-to-label samples, such as bacteria within biofilms. Infrared imaging also provides a way to measure the distribution of specific biomolecules through characteristic vibrational modes associated with the signatures of distinct organic bonds in metabolites without complications of damage from ionizing radiation. Furthermore, recent advances in infrared imaging have improved spatial resolution to the sub-micrometer regime, which is critical to the analysis of intracellular structures in biology.

2.4 Metals and Biology

A primary advantage of x-ray-based methods is identifying metals and their oxidation states, both in solution and following their incorporation into proteins, within relevant samples (i.e., thicknesses in excess of 10 microns, depending on photon energy). Given the importance of metalloproteins in biology, which represent more than one-third of all proteins (Thomson et al. 1998; Waldron and Robinson 2009), understanding relationships between metal oxidation states and cell function is of particular interest. Metalloproteins play central roles in mediating energy metabolism and a range of challenging chemical reactions (e.g., decomposition of complex organic contaminants) important toward understanding community ecosystems. In addition, extracellular metals commonly represent electron acceptors/donors important in understanding a range of microbial community interactions, with considerable importance in subsurface biogeochemistry (Fredrickson and Zachara 2008). The fate and transport of environmental contaminants is of considerable importance to human health. Additional importance associated with understanding metals and their oxidation states relates to their widespread use in the formulation of a range of nanoparticles used to control, for example, bacterial growth and environmental exposures (e.g., sunscreens). These nanoparticles present possible dangers to biological communities due to their ability to rapidly enter cells, albeit current effects on biological system remain largely unknown (NIOSH 2009). Using a compact light source to identify relationships between biological function and the oxidation states of metals extends current capabilities to allow direct measurements of the mechanistic underpinning of changes in cellular metabolism under environmental conditions within natural communities. Here, the use of spectroscopy and imaging modalities would provide both structural and chemical information of individual cells as a function of time.

2.5 Natural Community Systems

Microorganisms and plants function as members of natural communities to play fundamental roles in controlling carbon and nutrient cycles in terrestrial ecosystems and represent a source of genetic diversity that encodes a range of functions capable of contributing to pressing societal needs, including CO_2 sequestration, bioenergy production, and contaminant bioremediation. Currently, harnessing the capacities of organisms and communities is limited by fundamental gaps in knowledge regarding the diversity of biochemical pathways and functions that exist in natural systems. For example, many new biochemical functionalities almost certainly remain to be discovered. A specific and major limitation in the understanding of biological systems is the fact that we do not know the function of at least one-third of all proteins (Hanson et al. 2010).

In addition to general biochemical roles, natural microbial populations host an even wider diversity of proteins that are fine-tuned through sequence variation. At a fundamental level, effective experimental strategies are needed that address how site-specific amino acid variations impact the dynamic structure, associations, and function of proteins. For example, site-specific variations in a sequence may modify protein domain interactions through the formation of salt-bridges or alter post-translational control mechanisms by varying binding affinities of regulatory proteins (e.g., kinases). Likewise, sequence variations affect the sensitivities of proteins to direct chemical modification, thereby acting to modulate sensitivities to environmental conditions involving, for example, light intensity and the formation of singlet oxygen. Such sequence-specific sensitivities can be envisaged to allow organisms to optimally inhabit a defined niche within a community structure, resulting in enhanced community stability. Integrating these measurements with an understanding of the control mechanisms that regulate cellular targeting and maintenance of proteins and other biomolecules to maintain cell function ultimately is needed to obtain a predictive understanding from genomic information. In the future, such knowledge may be harnessed for functional enhancements via genetic engineering. Similarly, the function of many proteins requires either transient or stable interactions with other proteins to form supramolecular complexes. The function of these larger complexes is further modified by changes in cellular localization, whose control is affected by associations with other cellular components (e.g., lipid membranes).

Understanding the cellular regulation that controls protein complex formation requires extending current high-throughput cellular measurements to catalog proteins and their PTMs. These measurements must include data-driven computational models enabled by improved structural measurements to use available high-resolution structural data of individual proteins (and other biomolecules) to interrogate their cellular functions within natural community structures. Methods are needed that address how the cellular context of individuals within a community structure affects specific proteins' functions using structural data of individual proteins (or complexes) in different functional states. These *in situ* measurements of cellular processes will enable scientists to monitor emerging behaviors that vary from an understanding of which protein complexes form in response to environmental change to an appreciation of the underlying mechanisms responsible for more complex phenotypes that include functional relationships between microbes in natural communities and their responses to, for example, diel cycles. These measurements will provide the necessary data to enable modeling of the metabolic capabilities of microbial communities, allowing a predictive understanding and development of synthetic biology capabilities that afford manipulation of complex biological systems.

2.6 Observations of Living Tissue

Measurements of cellular responses to environmental exposures (e.g., low-dose radiation) typically require destructive methods that fix tissues at time-points following exposures to arrest activity, preventing longitudinal measurements of cellular responses. Such limitations hinder using existing high-resolution imaging methods to measure metabolite fate and transport, which involves using analogs of common metabolites with incorporated radioisotopic tracers, providing a sensitive means to interrogate organ function through real-time measurements of uptake and turnover kinetics. Extending these measurements to understand intracellular mechanisms and their relationship to intercellular interactions (akin to community function) requires simultaneously imaging changes in overall cellular properties with specific changes in subcellular structures, including changes in protein complex formation.

2.7 Importance of X-ray Sources to Imaging Biological Interactions

As already indicated, high-energy x-ray sources have the potential to provide critical insights into the fundamental design principles that control molecular interactions to regulate living systems. Of particular importance, x-ray diffraction methods remain the most effective approach to resolve protein structural changes at atomic resolution (about 1 Å). Furthermore, advances in synchrotron-based light source intensities have permitted the development of diffract-and-destroy approaches prior to the onset of radiation damage. Such approaches have been shown to permit imaging of large intact viruses (including supramolecular protein assemblies) and nanocrystals.

High-throughput approaches that screen large numbers of constructs to assess function and possible relationships to overall structural composition are expected to permit synthetic biology applications involving, for example, reconstitution of large multi-enzyme collections (such as metal reductase complexes and cellulosomes) that may aide in biofuel applications. Following cryo-freezing, more detailed structural measurements that are applicable *in situ* for cells are possible. Extension of these methods to consider entire organisms is proposed using cryo-methods to image samples tens of microns in size and thickness, which may help measure polymeric structures in living cells, such as lignocelluloses, to aid in identifying mechanisms that overcome its recalcitrance to degradation for biofuel applications. At the community structure level, the proposed x-ray approaches provide the unique ability to quantify the 3-D structures of biofilms (with overall dimensions of tens of microns) with nanometer-scale spatial resolution, whereas conventional x-ray micro-computed tomography (CT) has a resolution of 5–10 microns and, therefore, is insufficient to image structures within individual cells.

2.8 Examples of Structural Measurements Made Possible by a Compact X-ray Light Source

Experimental approaches aimed at understanding life science research involve a diverse range of methodologies. These approaches reflect the inherent complexities of living systems and the associated challenges of making measurements across length and time scales, ranging from molecular interactions involving electron transfer and coupled reactions involving bond making and breaking to complex ecosystems involving diverse organisms that functionally interact to enhance environmental stability. A fundamental challenge is developing approaches that operate across these length scales to connect molecular structural information to obtain a predictive understanding of complex ecosystems, allowing development of interventions to restore ecological balance. Examples of experimental systems of increasing complexity are described later herein. The examples focus on new insights made possible with increases in the availability of CXLSs. In particular, the experiments focus on three capabilities that have recently been demonstrated with a compact light source, including solving structures from large 3-D crystals using x-ray diffraction (Abendroth et al. 2010), determining the chemical composition of samples with x-ray absorption spectroscopy (Iwasaki et al. 1998), and directly imaging whole cells in 3-D without sectioning or chemical fixation (Hertz et al. 2012).

2.9 Biocatalysis and Time-resolved Measurements of Enzyme Reaction Mechanisms

Synthetic biology approaches aimed at mediating climate change are of considerable interest and require an understanding of individual components (e.g., proteins) within natural microbial systems capable of catalyzing carbon fixation, such as the formate hydrogen lyase complex. This complex is a supramolecular complex containing [Ni-Fe]-hydrogenase and formate dehydrogenase (FDH_H) enzyme components that normally consume formate to generate hydrogen (Figure 2.2).

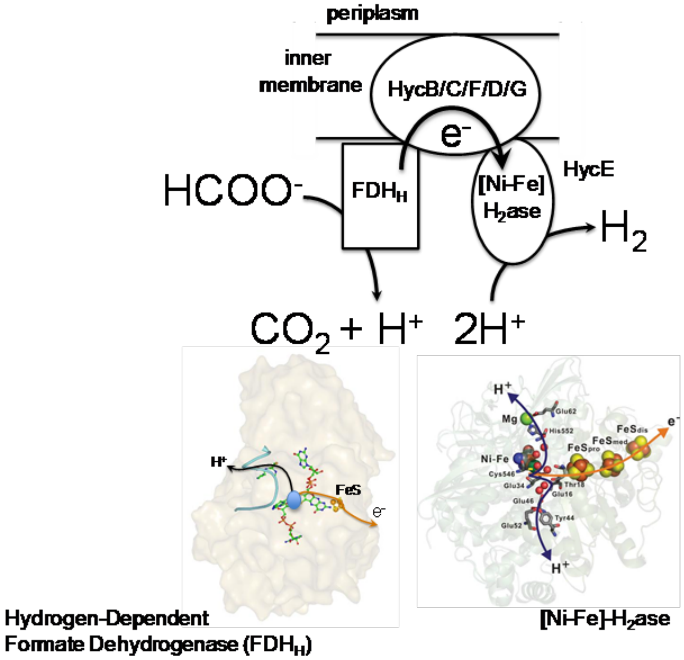


Figure 2.2. Depiction of formate hydrogen lyase complex, highlighting structural coupling between formate dehydrogenase (FDH_H) and [Ni-Fe]-hydrogenase enzymes through integral membrane protein complex HycB/C/F/D/G.

While structures are available for each of the enzymes following their isolation and, in isolation, the catalyzed reactions are readily reversible, it remains unclear how they are structurally coupled to permit efficient catalysis. This information is critical to their redesign to promote synthetic biology applications associated with enhanced carbon capture and formation of biofuels. Likewise, a molecular understanding of these natural mechanisms will guide the synthesis of effective molecular catalysts, which currently are unable to catalyze CO_2 reduction (carbon fixation) that is catalyzed readily by FDH_H (Reda et al. 2008; Galan et al. 2011). Under biological conditions, FDH_H exists as part of a formate hydrogen lyase complex that decomposes formate to hydrogen and CO_2under anaerobic conditions in the absence of exogenous electron acceptors. This reaction is readily reversible. Therefore, FDH_H promotes CO_2 reduction, a difficult reaction, and permits electrochemical reduction of CO_2 in a manner that avoids excessive overpotentials (which are energetically wasteful) with chemical specificity not possible using non-protein catalysts, resulting in a mixture of products (Reda et al. 2008). As a result, understanding the reaction mechanism of FDH_H is important for the design of effective catalysts for CO_2 fixation. In this respect, FDH_H from *E. coli* represents the best-understood formate dehydrogenase, whose mechanism is consistent with the goal of understanding the design of biomimetics for CO_2 fixation. The structure of FDH_H was first solved in 1997 and subsequently corrected in 2006 (Boyington et al. 1997; Raaijmakers and Romao 2006). The presence of a selenocysteine (SeCys) ligand to the Mo metal, where the Se-Mo binding is thought to be critical to efficient catalysis, is central to the reaction mechanism. The substitution of SeCys with a Cys at this position results in a 99% reduction in catalytic rate, which may be related to the complete ionization of SeCys ($pK_a = 5.3$) and increased nucleophilicity of selenium compared with sulfur that promotes nucleophilic attack following formate binding (Jacob et al. 2003; Jacob et al. 2006; Arner 2010). The active site of FDH_H comprises a SeCys, Mo, two molybdopterin guanidine dinucleotides (MGD), and a single [4Fe-4S] cluster, which catalyzes the two-electron oxidation of formate to CO_2 (Boyington et al. 1997). An inorganic sulfur (S_i) ligand is bound to Mo (at least in some states) and may participate in modifying the reactivity of the active site. The reduction mechanism involves $SeCys^{140}$ and His^{141} in the rate-limiting step of proton abstraction and the Mo, molybdopterin, Lys^{44}, and the [4Fe-4S] cluster in promoting electron transfer, where the [4Fe-4S] cluster is thought to permit a sequential ping-pong one-electron transfer mechanism (Boyington et al. 1997). However, while the function of the Mo-molybdopterin cofactor is clear, the precise role of the active site Se remains uncertain (Boyington et al. 1997; Raaijmakers and Romao 2006; Mota et al. 2011). The high-resolution structures of FDH_H in the reduced (Mo^{IV}) and oxidized (Mo^{VI}) states illustrate that Mo coordinates four cis-dithiolene sulfurs of the MGD cofactors and the Se of $SeCys^{140}$ in a square planar geometry (reduced state), which upon oxidation assumes a trigonal prismatic coordination geometry (Boyington et al. 1997). The loop ^{138}RV-SeCys-HGPSVA^{146} is weakly diffracting using conventional x-ray sources for FDH_H following formate oxidation and reduction of the Mo-active center and has been reported to have been misassigned in the original structure (1aa6.pdb). Reinterpretation of the diffraction data has led to an alternative, and controversial, mechanism involving a large-scale movement of this loop, resulting in a 12 Å separation between Se in $SeCys^{140}$ and the Mo(IV) metal center (2iv2.pdb) in reduced FDH_H relative to the oxidized Mo(VI) form (Raaijmakers and Romao 2006). What remains uncertain is:

- The possible role of the loop mobility and SeCys bond formation with Mo in promoting formate oxidation, proton abstraction, and electron transfer from the metal center to the [Fe-S] cluster
- The precise role of $SeCys^{140}$ (or alternatively, the proximal His^{141}) in mediating proton transfer from bound formate
- The role of Arg^{333} in either stabilizing the free seleno following formate binding to FDH_H (Option 1), acting as a proton acceptor (Option 2), or in the alignment of the formate to facilitate catalysis at the metal center (Option 3) (Heider and Bock1993; Boyington et al. 1997; Raaijmakers and Romao 2006).

Understanding these steps in the reaction mechanism of FDH_H will be facilitated by time-dependent structural measurements of individual reaction steps that are possible using the intense x-ray sources made possible via compact light sources. For example, upon laser stimulation, formate could be released (uncaged) on the microsecond time scale, allowing collection of diffraction patterns at various times following photoactivation. Analyses of diffraction patterns from both types of experiments will provide information about protein structure and how it changes during the reaction cycle, permitting both experimental validation of the proposed structure and an understanding of how the loop structure (and SeCys) modulates catalysis (Figure 2.3).

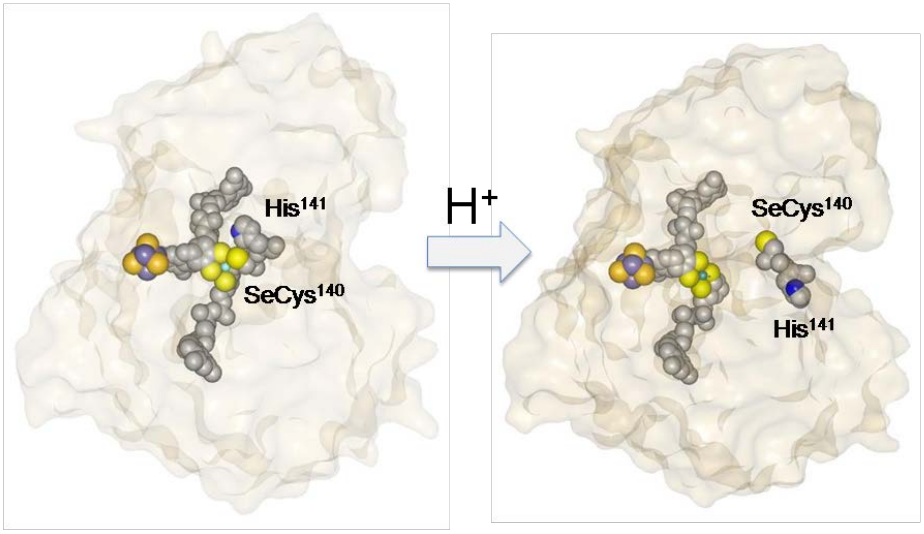


Figure 2.3. Proposed structural change in the proximity between SeCys^{140} and active site Mo in FDH$_H$ upon proton transfer, acting to prevent substrate recombination to enhance reaction efficiency.

2.9.1 Protein Control of Reactivity and Catalytic Bias

Biological enzymes reversibly catalyze a range of reactions important to energy metabolism, whose efficiencies serve as the basis for small molecule biomimetic catalysts that have commercial potentials to both fix carbon and efficiently generate energy (e.g., hydrogen). Model catalysts developed at PNNL have demonstrated that catalytic rates of biomimetic catalysts can be enhanced by minimizing the distortions from the square planar coordination of the metal center (bite angle) and proper placement of pendant bases to facilitate proton transfer and stabilization of the transition state (Raebiger et al. 2004; Henry et al. 2006; Wilson et al. 2006; Redin et al. 2007; Wilson et al. 2008). This empirical correlation between changes in metal coordination and reactivity are consistent with an analysis of different [Ni-Fe]-hydrogenase active site structures, which demonstrate threefold changes in hydrogen production rates correlated with differences in coordination geometry (bite angles) (Figure 2.4). However, unlike enzymes, biomimetic catalysts require substantial overpotentials for efficient catalysis. To understand the design principles required to synthesize catalytically efficient biomimetic catalysts, structural measurements that identify how active site structures control the reaction bias are needed to identify how changes in the geometry around the metallic active centers control the overall reaction mechanism involving the control of proton and hydride transfer reactions. A compact light source will provide a means to measure structural linkages within hydrogenase protein matrices that control the reactivity of their metal centers.

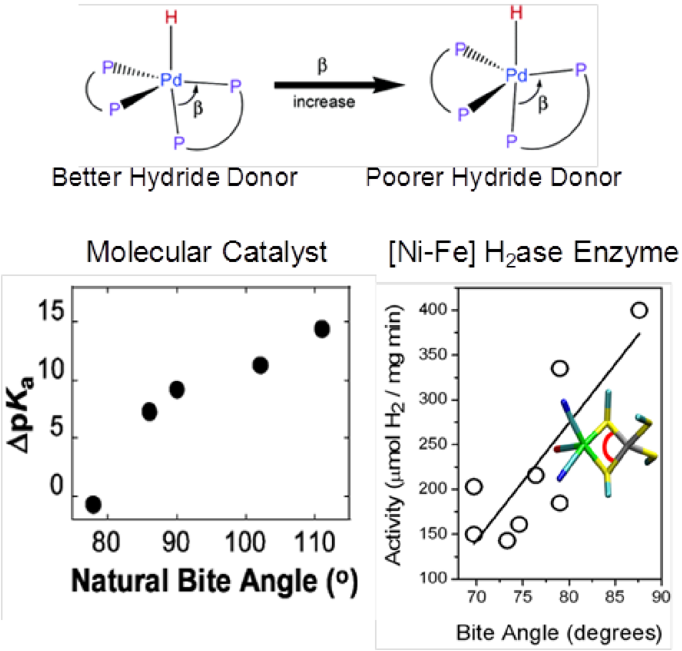


Figure 2.4. Coordination geometry around active site metal control reactivity for molecular catalysts developed at PNNL (left) (Raebiger et al. 2004) or from a consideration of available structures of [Ni-Fe]-hydrogenase enzymes (right).

2.10 Structural Regulation Through Redox Control Mechanisms and Covalent Post-translational Protein Modifications

Understanding molecular mechanisms that underlie community interactions and their stability in response to environmental change (e.g., light intensity, oxygen concentrations, and nitrogen availability) requires an appreciation of regulatory controls that act to coordinate intracellular metabolic shifts to maintain requisite species diversity. Such shifts include relatively straightforward mechanisms with well-understood transitions between aerobic and fermentative metabolisms involving transcriptional regulation through oxygen or nitric oxide binding to heme or 4Fe-4S clusters in protein sensors (Erbil et al. 2009; Smith et al. 2010). These sensors act over relatively long time scales and include histidine kinases or electron transport regulator A, which acts to coordinately regulate gene expression that reprograms cellular metabolism (Price et al. 2007). Such changes in transcriptional activation involve formation of supramolecular protein complexes that include the reprogramming of RNA polymerase binding affinities to favor transcription of different operons (Ptashne and Gann 1997; Ptashne 2003; Verma et al. 2007). Identification of the signatures of key regulatory control elements available from the proposed complementary systems-level measurements will enable the construction of predictive models of microbial metabolism. What remains largely unclear is the mechanism of the rapid response regulators to environmental change that allow proximal organisms in microbial communities to maintain optimal growth rates and function under highly variable and changing environmental conditions involving, for example, high light levels (1700 microeinsteins/m^2 sec) and oxygen concentrations (600% air saturation). In this respect, there is a well-understood adaptive value in maintaining long-lived proteins, such as the outer membrane metal reductase MtrC in *Shewanella oneidensis*, that retain fundamental metabolic capabilities under changing environmental conditions (Plotkin 2011; Xiong et al. 2011). For this reason, metabolic shifts in response to environmental change are hypothesized to involve reversible PTMs and a limited subset of sensor proteins that include both traditional kinase/phosphatase signal transduction cascades, as well as redox-dependent mechanisms involving reversible oxidative modifications. Redox-dependent mechanisms include disulfide bond formation, methionine oxidation, and nitrotyrosine formation, which are all known to be reversible through enzymatic control mechanisms (Smallwood et al. 2007; Poole and Nelson 2008; Bae et al. 2011; Bigelow and Squier 2011). To permit an appreciation of key cellular sensors, extension of conserved mechanisms documented in model systems under controlled cultivation to natural communities is anticipated. The sensors coordinate observed differences in metabolic sensitivities between different organisms to environmental conditions. These different metabolic sensitivities allow proximal organisms in mat communities to exhibit varied optimal metabolic efficiencies during the diel cycle (Liu et al. 2011a; Garcia Costas et al. 2012; Liu et al. 2012).

As indicated, reversible changes in the oxidation state of redox sensors result in structural changes and alterations in protein function, representing key regulatory points in cell metabolism to enhance energy efficiencies and cell survival under rapidly changing environmental conditions (e.g., O_2 content, light intensity, and nitrate levels result in metabolic shifts in phototrophs). Likewise, post-translational protein modifications involving, for example, phosphorylation commonly induce changes in protein associations that reflect changes in cellular metabolism.

A compact light source will permit high-throughput measurements that monitor structural changes involving protein conformation and macromolecular associations following affinity isolation of trapped complexes from lysates. This approach will provide a rapid means to assess changes in metabolic capability and relationships to metabolic function. Of note, current mass spectroscopy measurements that identify protein modifications are unable to provide functional correlations to direct imaging because samples are typically analyzed following proteolytic digestion and result in the loss of structural information. In contrast, coupling a high-throughput structural tool in concert with standard sample identification strategies offers a means to use orthogonal structural information to identify the important regulatory elements that can be used to construct better predictive models. These measurements have considerable importance to ongoing efforts aimed at understanding molecular mechanisms used by natural communities to control metabolic flux through dominant pathways that function to mediate energetic efficiencies and stability. This includes an understanding of metabolic exchange mechanisms involving the following:

- Secretion of glycolate upon increased rates of photorespiration by RuBisCO under conditions of high light intensity
- Secretion of acetate and formate derived from fermentative metabolic breakdown of glycogen at night when the mat becomes anoxic.

These latter measurements are directly relevant to mechanistic measurements of the formate dehydrogenase. Based on preliminary data, it is hypothesized that there are critical switch points that act to redirect redox equivalents between different pathways associated with, for example, carbon fixation and reductive biosynthesis or the formation of proton motive force and adenosine triphosphate (ATP) synthesis. New approaches are needed to understand mechanistic relationships between changes in the specific activities of individual proteins within central metabolic pathways that link photosynthetic electron capture, reductant partitioning, and respiratory proteins associated with formation of the proton motive force and ATP synthesis to the release (secretion) of extracellular metabolites that collectively contribute to the formation of efficient and stable community organizations. For these experiments, pump-probe diffraction on microcrystals (initiated by the photo release of caged-ATP) will be performed in the hydrated state using the compact light source. The resulting 3-D structures determined before, during, and after reaction initiation for both wild type and mutated proteins will identify critical amino acid positions related to normal cellular function.

2.11 High-throughput Structural Measurements of Heterogeneous Supramolecular Complexes

Compact light sources will open a path forward for dynamic protein structural analysis, providing a high-throughput approach to obtain structural insights and clues to function for the plethora of identified proteins, which commonly exist in multiple functional states not currently experimentally accessible. Many macromolecular associations happen as a series of transient intermediates with short lifetimes. For example, a large number of sigma-factor regulators have been identified that direct RNA polymerase to form stable complexes with different promoter sequences, controlling transcription to reprogram cellular metabolism. Such a regulator has been identified in *Rhodobacter*, involving a key regulator of RNA polymerase (i.e., sigma^E) that selectively detects singlet oxygen to modulate transcription (Anthony et al. 2005; Campbell et al. 2007). Likewise, there are large changes in the supramolecular composition of the RNA polymerase complex in response to environmental conditions that act to modify optimal growth efficiencies (Uljana Mayer et al. 2005; Verma et al. 2007). We expect that important insights can be obtained regarding cellular adaptive strategies through parallel bottom-up efforts involving the isolation of key response regulators (such as RNA polymerase complexes) with top-down global measurements of transcripts and associated pulse-chase measurements of protein turnover. By comparing the presence and associations of large protein complexes and organelles within individual microbes in isolation and following mutualistic community associations, key principles regarding how diverse metabolisms are coupled to enhance the stability of the system can be identified.

In addition to conserved biochemical mechanisms for specific enzymes linked to the catalysis of specific chemical transformations, genomic information from natural populations indicates a diversity of protein structures whose function and cellular regulation are fine-tuned through sequence variation. Understanding cellular regulation and community stability requires an understanding of how observed amino acid variations and specific PTMs within protein families (typically measured using mass spectrometry) impact the structure, binding interactions, and catalytically important motions linked with key steps involving enzyme function (e.g., catalysis, sensing, or transport). In the future, such knowledge may be harnessed for enhancement of function via genetic engineering. Similarly, the function of many proteins requires interactions with other proteins, complexes, or cellular components (e.g., lipid membranes). High-throughput x-ray diffraction approaches available in conjunction with existing EMSL capabilities will identify how protein complexes form, the slow steps in their association, and the components required for specific functions.

Extending measurements to high-throughput structural determination and correlations between protein sequence, structural dynamics, and binding affinities involving subunits of supramolecular complexes is uniquely possible using high-resolution x-ray diffraction methods. These approaches will complement existing spectroscopic and/or activity-based chemical probes, ion mobility mass spectrometry, and computational infrastructure, allowing meaningful data integration from high-throughput data collection and predictive simulations of protein structure using both classical and quantum mechanical methods to quantitatively include contributions from metal active sites (>45% of all proteins contain bound metals or complex centers). These latter measurements build on current structural genomics measurements involving high-resolution structure determinations using both NMR methods and x-ray diffraction. We envision rapidly acquiring information from a variety of difficult-to-characterize proteins. For example, hundreds of multiheme *c*-type cytochromes are encoded in the genomes of metal-reducing bacteria and play critical roles in subsurface geochemistry. However, the structure and kinetics of this diverse protein family are largely unknown. X-ray diffraction technologies provide a straightforward means to image arrays of proteins under defined redox conditions. Time-resolved changes in native protein structure in response to reaction initiation will provide a direct readout of structural changes linked to protein complex formation and cellular functions. These structural biology insights are critical to understanding the assembly and functional maintenance of molecular complexes prior to their export as modules in toolkits for synthetic biology applications that seek to extend initial efforts that primarily focus on low-efficiency, proof-of-principle methods that introduce new pathway components into model organisms, such as the creation of electrically conductive *E. coli* using introduced metal reductases originally identified in *Shewanella* (Shi et al. 2007; Jensen et al. 2010; Ross et al. 2011).

2.12 Assembly and Functional Dynamics of Molecular Machines

High-impact applications of x-ray diffraction will provide important insights regarding the efficient energy transduction mechanisms relating to different classes of energy transformation, including the assembly and molecular actions of supramolecular protein machines, as well as interfacial electron transfer mechanisms to mineral surfaces. These activities are broadly relevant to a predictive understanding of microbial communities and synthetic biology applications. Time-resolved x-ray measurements that resolve catalytically important protein motions linked to function are essential to achieve molecular understanding. Such measurements provide the necessary linkage between atomic-level protein movements and steps in the catalytic mechanism. Likewise, experiments that target an understanding of the mechanisms responsible for assembling and maintaining extracellular supramolecular complexes, such as MtrABC metal reductase systems that mediate electron transfer to extracellular minerals, are important for a range of processes that include bioremediation and synthetic biology applications, as the molecular machinery is likely to be highly conserved and applicable to exporting various molecular cassettes (modules) for creating desired functionalities that both test community interactions and are relevant for bioenergy applications.

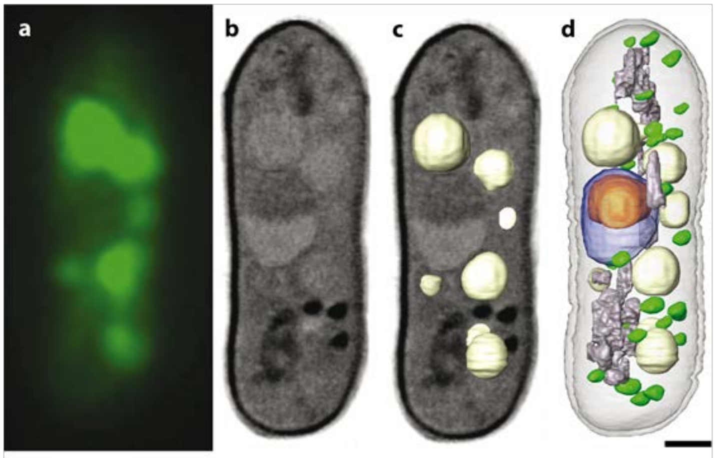
The metal reductase system originally identified in *Shewanella*, now found to be more widespread, has the potential to reveal fundamental regulatory processes important to both biogeochemical processes and microbial community interactions, which commonly require trafficking specific proteins to the outer membrane. These proteins mediate a host of activities associated with metabolism (e.g., terminal electron acceptors), defense, and possible mutualistic associations underlying environmental stability. In addition, metal reductase and other enzyme systems, such as the hydrogenase system, mediate bioremediation through the biogeochemical reduction of actinides. For example, Cr(VI), U(VI) and Tc(VII) are reduced into less soluble oxide forms Cr(III), U(IV)O_2, and Tc(IV)O_2, respectively. Newly released structures are available for the terminal subunit of the metal reductase, MtrF, and time-resolved spectroscopic measurements indicate an important role for subunit dynamics in promoting electron transfer following association with the metal oxide surface (Xiong et al. 2006). Building on these insights, time-resolved x-ray diffraction measurements will interrogate the molecular steps involved in interconversion of aqueous U species to initial precipitates by *c*-type cytochromes and how these steps vary among different cytochrome variants. Typically, first-formed biogenic mineral products are nanoparticles ~1.5–2.5 nm in diameter (Banfield et al. 2000; Baker et al. 2010). Using compact light sources, we anticipate resolving aspects of the mechanism and products of reduction reactions through pump-probe x-ray diffraction studies of 3-D microcrystals. The experiments take advantage of the diversity of cytochrome variants recovered both from single organisms and strain variants. Specifically, we foresee measurements for proteins in the presence of aqueous actinide ions in a fluid cell after photolysis of caged reagents allows reduction to proceed.

Coupled with quantum mechanics/molecular mechanics (QM/MM) calculations, we anticipate identifying the molecular switches that control electron transfer rates as electron transfer efficiencies are dramatically enhanced upon small changes in cytochrome orientation. An understanding of the hydrogenase enzyme system, which functions to catalytically mediate proton-coupled electron transfer mechanisms to form hydrogen and has been shown to reduce Tc(VII) (Shi et al. 2011), also is relevant to bioremediation. The availability of high-resolution crystal structures of hydrogenase enzymes stabilized in specific intermediate states will enable analysis of how function is characterized by conformational changes. For example, time-resolved measurements of dynamic structural intermediates with high spatial resolution (1 Å) can track reactions initiated by rapid changes in electrochemical potentials or photoactivation, following engineering of enzymes to contain site specifically bound photosensitizers. These measurements offer a means to interrogate how changes in the geometry around active site metals are coupled to the protein matrix, permitting direct measurements of catalytic mechanisms that control the activity of the metal center, e.g., the hydricity of the active site in hydrogenase enzymes, which are predicted to arise through first and second coordination sphere influences of the protein that alter bite angles. Likewise, changes in protonation states of sites proximal to hemes or Fe-S clusters are expected to influence their relative geometries and electron transfer efficiencies, providing a means to understand how electron flux is regulated. Such measurements will reveal mechanistic insights critical for efficient hydrogen production at low potentials with minimal side reactions commonly associated with catalytic inactivation and will be critical to the eventual synthesis of inorganic catalysts.

2.13 Imaging Cellular Systems

The highly organized and finely structured interior of a cell is an important factor in determining how the cell functions. For example, aberrations in the structure of the nucleus can cause the cell to function abnormally, potentially leading to diseases such as cancer (Zink et al. 2004). Understanding cellular function, therefore, requires detailed knowledge of the subcellular architecture. This is best achieved by imaging the cell using a high-resolution, 3-D imaging technique capable of quantitative, high-throughput analyses. In addition, the technique used should preserve delicate internal structures in their *in vivo* state. In this regard, soft x-ray tomography has been a recent success story because this new modality meets all of these requirements (Leis et al. 2009; Larabell and Nugent 2010). Moreover, this technique also allows “thick” specimens, such as eukaryotic cells, to be imaged intact, which is not the case in more established techniques, such as microscopy, where eukaryotic cells have to be sectioned into slices that are 500 nm thin or less (Leis et al. 2009).

The structures inside a cell create a range of microenvironments that support specific chemical reactions and processes. Therefore, understanding how cells function requires detailed knowledge of both the subcellular architecture and location of molecules within this framework. In an ideal world, molecular localization also could be obtained directly by using soft x-ray tomographic imaging. In some instances, this is perfectly feasible by labeling the molecules of interest with heavy metal tags, which are easily identifiable in the x-ray image. However, a better method is to use a correlated imaging approach and employ fluorescence imaging to determine the location of molecules inside the cell that have been tagged with, for example, green fluorescent protein. This became possible with the development of high numerical aperture cryogenic light microscopy (Le Gros et al. 2009). This type of microscope can be readily integrated into a soft x-ray microscope. Consequently, it is now possible to localize tagged molecules directly into a high-resolution, 3-D reconstruction of a cell (Figure 2.5) (Le Gros et al. 2009; McDermott et al. 2009).



McDermott G, et al. 2012.
Annu. Rev. Phys. Chem. 63:225–39

Figure 2.5. Correlated soft x-ray tomography and cryo-light imaging (wide-field fluorescence). a) The vacuoles fluorescently labeled and imaged by cryo-light microscopy. b,c) Slices through the volumetric reconstruction calculated from soft x-ray tomography data, with the vacuoles shown as segmented volumes in panel c. The segmented vacuoles correlate closely with the locations determined from cryo-light microscopy. d) The same cell after the major organelles have been segmented. The nucleus is shown in blue, the nucleoli in orange, mitochondria in gray, vacuoles in light gray, and lipid droplets in green. Scale bar = 1 μm. Taken from review by Larabell and coworkers (McDermott et al. 2012b).

Identifying the precise location of individual proteins and organelles within the cellular context has been a long held ambition of both structural and molecular biologists. In recent years, cryogenic soft x-ray CT of whole cells using synchrotron radiation light sources has proven capable of visualizing subcellular structures at up to 36 nm spatial resolution (Larabell et al. 2004; Le Gros et al. 2005; Parkinson et al. 2008; Le Gros et al. 2009; McDermott et al. 2009; Uchida et al. 2009; Larabell and Nugent 2010; Hanssen et al. 2011; Uchida et al. 2011; Hanssen et al. 2012; McDermott et al. 2012a; McDermott et al. 2012b; Parkinson et al. 2012; Schneider et al. 2012).

The lack of availability of high-intensity light sources limits these approaches, but could be remedied using a compact light source. Existing bench-top ambient temperature x-ray microscopes have increased global accessibility to whole cell tomography of chemically fixed, resin-embedded, and freeze-dried samples (Maser et al. 2000; Bech et al. 2009; Bertilson et al. 2009, 2011). However, the required sample preparation can result in substantial structural artifacts, including cell shrinkage and deformation of proteins and organelles. Fortunately, rapid plunge freezing into a liquid ethane slurry bypasses many of these deleterious artifacts. The cryogenic samples are preserved in a hydrated state surrounded by amorphous non-crystalline ice (Adrian et al. 1984).Thus, there is a need for a laboratory-based compact soft x-ray microscope that can be operated under cryogenic conditions to image unstained cellular material in a hydrated state while avoiding physical sectioning or chemical fixation of samples. It is conceivable that cryo-fluorescence and x-ray imaging could be integrated into a single instrument, allowing simultaneous acquisition of directly correlated fluorescence and x-ray data.

Clearly, a compact cryogenic soft x-ray microscope has the potential to bridge the resolution gap between light and electron microscopy and reveal new ultrastructural information in a completely laboratory-based setting. James Evans (now at PNNL) and coworkers recently demonstrated the ability to use a completely laboratory-based instrument to resolve structures as small as 90 nm in the reconstructed tomogram of an intact yeast cell following a low cumulative radiation dose of 7.2 MGy that did not cause significant structural damage. Coupled with the capability to image whole cells up to 5 µm thick without staining or sectioning, the ability to get whole cell contextual information under non-destructive conditions and at spatial resolutions between 50 and 70 nm makes this novel laboratory-based cryogenic soft x-ray microscope ideal for multimodal imaging. These measurements demonstrate the value of a compact light source in allowing immediate access to multimodal approaches that allow high-resolution correlative measurements on biological samples. For example, molecular details of processes ranging from mitochondrial division/fusion to flagellar genesis could be investigated using either organisms (i.e., bacteria, yeast, *Giardia*) or large isolated/purified organelles (i.e., mitochondria, centrosomes). Cultured neurons and cell monolayers, such as serum-starved PtK1 cells, could be used to study axonal secretion, viral infection pathways, and oncogenesis. Additionally, *Shewanella* biofilms could be imaged with depth profiling to study the formation of microbial communities. Finally, thin cryo-sections of tissues could visualize cellular ultrastructure and help localize and identify the tissue-specific health effects associated with inhaled or instilled nanomaterials. Combined with super-resolution fluorescence microscopy, it should be possible to identify interactions between individual fluorescently labeled proteins with surrounding structures. In future experiments, fluorescent polystyrene beads could act as 3-D fiducial markers for improved alignment and tomogram matching between cryo-fluorescence, cryo-soft x-ray, and cryo-electron microscopy.

In summary, the availability of a compact light source to complement existing methods is of substantial importance, as nanoimaging of cells is critical across the entire spectrum of cell biology—from fundamental biological studies to biomedical research to practical applications, such as the optimization of biofuel production. Soft x-rays are an illumination source for cellular imaging because their characteristics allow specimens to be imaged in a near-native state. This criterion is enormously important to the biological community—even relatively minor damage to the structure of a cell can lead to erroneous interpretation of images. Conducting correlated imaging studies on the same cell followed by some type of genetic or proteomic analysis is likely to be the future standard in the quest to understand form, function, and mechanisms at work in biological systems. At present, studies of this type are carried out using chemical fixation and plastic embedding in an anaerobic environment prior to transport to a remote synchrotron light source. However, this approach introduces significant artifacts in structure and, possibly, chemistry, and it effectively precludes the use of soft x-ray carbon near-edge spectroscopy to look at the association of different organic functional groups with metals and radionuclides. By having a CXLS at PNNL, researchers instead could use PNNL's existing expertise in preparing frozen hydrated specimens for electron microscopy and apply it to x-ray microscopy, so these subsurface processes could be studied without changing hydration state or introducing changes otherwise caused by chemical fixation and plastic embedding and with considerably lowered sensitivity to radiation damage. Additional chemical resolution of cellular components will involve taking advantage of infrared capabilities, which provide a straightforward means to obtain detailed chemical imaging analysis with a submicron spatial resolution using x-ray imaging and tomography methods (Holman et al. 2010).

2.14 Cultivating Microorganisms

Using soft x-ray capabilities to image cellular structures highlights the importance of a compact light source in characterizing natural communities. This follows from the observation that many microorganisms have defied attempts at cultivation. Community metagenomic studies have opened pathways to the organismal diversity, and metabolic potential of natural systems can be defined. However, topological information, including details of the ultrastructure of uncultivated cells and their interactions with other community members, is lacking. When natural microbial communities have been surveyed by transmission electron microscopy, distinct structures and organelles often are recognized (Sharp et al. 2009). Information about membership, cellular features, and community organization information is vital because nutrient, biochemical, and other transformations almost certainly depend on consortium-level phenomena that are not well captured through studies of isolated cells.

Single-particle cryo-transmission electron microscopy and cryo-electron tomography have increasingly provided 3-D structural information, bridging the information gap between knowledge of the existence of a genomically encoded protein and structure-function relationships. Using a compact light source, whole cell imaging without physical sectioning or chemical fixation will permit better characterization of enigmatic organelles, such as tubular structures, localized macromolecular complexes, viral infection stages and features, polysaccharide, and other cell-associated polymers. The approach can be applied to as yet unidentified cells and be used to characterize organism-organism interaction structures (Molina et al. 2011).

2.15 Microbial Communities

Direct examination of natural and engineered environments has revealed the majority of microorganisms in these systems live in structured communities termed “biofilms,” which have been extensively reviewed (Costerton et al. 1987, 1995; Decho 1990, 2000; Stoodley et al. 2002; Flemming and Wingender 2010). Biofilms are composed of microbial cells and a poorly characterized organic matrix commonly referred to as “extracellular polymeric substances” (EPS), which can consist of high-molecular-weight organic macromolecules, including polysaccharides, proteins, nucleic acids, and phospholipids (Wingender et al. 1999; Starkey et al. 2004). Biofilm EPS is highly hydrated, often containing >95% water (Decho 1990; Wingender et al. 1999; Starkey et al. 2004). Therefore, accurate characterization of EPS in its native state has been elusive because it is easily distorted or damaged. Along with controlling mass-transfer reactions, biofilm-associated EPS is hypothesized to play a role in facilitating microbial interactions such as cell-to-cell recognition and signaling, mediating biogeochemical reactions (including extracellular electron transfer), and biomineralization.

Structural components of the biofilm EPS matrix contain ionizable functional groups that can bind an array of ions and, in some cases, also may contain catalytic proteins that alter the redox state and/or solubility of multivalent ions. As a result, biofilm EPS can facilitate biogeochemical redox reactions that influence the fate and transport of heavy metals and radionuclides, i.e., extracellular electron transfer reactions (Marshall et al. 2006), and precipitation reactions that influence the sequestration of carbon, i.e., the formation of $CaCO_3$ precipitates (Braissant et al. 2007). However, biofilm EPS structure and function are inadequately characterized to the point that mechanisms of metal (ion) binding/biotransformation are poorly understood. Limited by the availability of imaging techniques that facilitate visualization of biofilm EPS without dehydration or chemical modifications, attempts to understand the chemical signatures within biofilm EPS remain unsuccessful.

Researchers at PNNL employ state-of-the-art technologies for imaging the native-state structure/architecture of biofilms and hydrated EPS using high-resolution cryogenic electron microscopy and analysis techniques developed at EMSL (Figure 2.6).

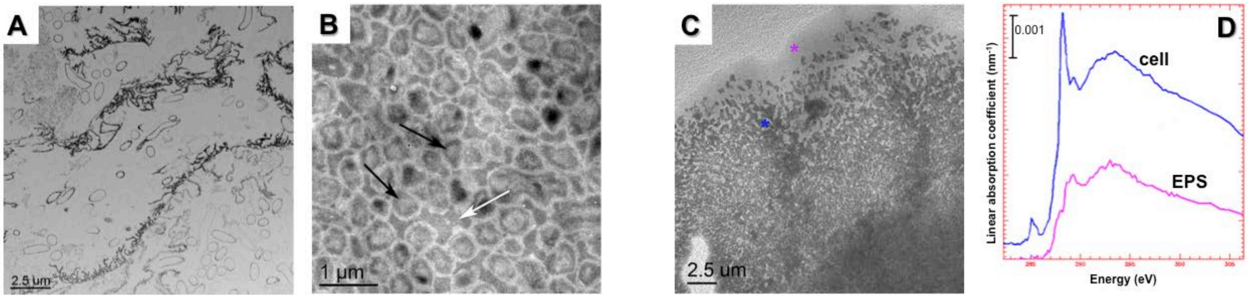


Figure 2.6. High-resolution morphologies of extracellular polymeric substance (EPS) in *Shewanella* biofilms (originally 200 µm thickness). A) Conventional electron micrograph of biofilm ultrathin section after chemical fixation (glutaraldehyde and osmium tetroxide), alcohol dehydration, and resin embedding. B;C) Electron micrographs prepared by cryo-sectioning and imaged at room temperature. Note the dense packaging of cells (black arrows) in EPS (white arrow), whose presence is visualized in a depth profile near the outside surface of the biofilm (C). D) EPS (pink line) is clearly distinguishable from cells (blue line), which become less tightly packed near the outside face of the biofilm.

Although electron microscopy provides excellent high-resolution structural analysis, its capabilities for elemental detection and oxidation state determination, as well as its measurements of microcrystallinity, are at their best with submicrometer-thick materials. Investigations of thicker samples, as in soils, are possible via the correlated use of synchrotron-based analysis methods such as x-ray fluorescence micro-imaging (µXRF), which can investigate the local chemical composition of elements and produce high-sensitivity, element-specific distributions for correlation with electron microscopy data (Marshall et al. 2006; Daly et al. 2007). Soft x-ray microscopy techniques now are being applied with a synchrotron light source to fully hydrated biological samples for imaging in their close-to-native state (McDermott et al. 2009; Ogura 2010). In addition, soft x-ray scanning transmission x-ray microscopy combines the chemical speciation sensitivity of x-ray absorption near-edge structure (XANES) spectroscopy with high spatial resolution (<25 nm) and maps the biochemical composition of bacteria and biofilms at a subcellular scale (Obst et al. 2009). Clearly, the integration of cryo-electron microscopy with x-ray analysis will facilitate the acquisition of high-sensitivity chemical information at spatial resolutions required to enhance the overall understanding of biofilms as a complex, biological system that catalyzes important biogeochemical reactions. By 1) determining the chemical composition and spatial coordination of biofilm-associated EPS with inorganic substrates, including metal ions, and 2) investigating the reactivity of catalytic proteins that alter the redox state and/or solubility of multivalent ions in biofilms, we can significantly advance the understanding of how molecular-scale biogeochemical reactions can influence subsurface contaminant fate and transport on larger scales.

To generate highly reproducible biofilms for imaging studies and chemical analysis, *Shewanella* cultures were grown using anaerobic minimal medium containing lactate and fumarate in a constant-depth (bio)film fermenter to a thickness of ~200 µm on 5-mm-diameter plastic (GelBond™) substrates. This substrate is amiable to thin sectioning and facilitates high-resolution, depth-resolved biofilm morphology studies using electron microscopy. Unfortunately, the amount of chemical information that can be collected during electron microscopy analysis is relatively limited and is complicated by the addition of chemicals for electron microscopy fixation, dehydration, staining, and embedding.

Correlative soft x-ray-based imaging techniques present an excellent opportunity to gain chemical and/or elemental information from ultrathin biofilm sections at relevant spatial resolution(s). The addition of traditional sample processing chemicals, such as aldehydes, that can interfere with carbon edge spectra during scanning transmission x-ray microscopy or produce interfering infrared signatures does limit obtaining high-quality data. However, Matt Marshall and colleagues at PNNL recently developed a new cryo-sample preparation technique that omits the adverse traditional sample processing chemicals and electron microscopy analysis has confirmed that this protocol preserves excellent depth-resolved biofilm morphology and cellular ultrastructure. These samples were then imaged by scanning transmission x-ray microscopy to obtain nanometer-scale resolution of the differences in the chemical composition of structures resolved in high-resolution electron microscopy images. Such measurements revealed compositional differences with EPS matrix structures encompassing biofilm cells in response to environmental conditions.

2.16 Functional and Non-functional Metals in Organisms

Metals are used for the most industrially relevant, difficult, and (arguably) interesting chemistry in biology. Detailed knowledge of the active sites of these enzymes is key to a physical and chemical understanding of their function. X-ray absorption spectroscopy can be used as part of a holistic approach to studying metalloprotein structure. Crystallography can provide an overall structural map at atomic resolution, extended X-ray absorption fine structure (EXAFS) can describe the environment around metal sites in detail, and density functional theory (DFT) and XANES can provide vital geometrical details that neither EXAFS nor crystallography can provide alone. EXAFS was previously demonstrated over 10 years ago on a CXLS (Iwasaki et al. 1998). However, new increases in the available brightness of current x-ray sources will provide improved chemical sensitivity.

If given in sufficient quantity, almost all elements are toxic but only a handful pose problems in substantial human populations. These include arsenic, selenium, lead, and mercury. In some cases, the level of human exposure is significant. Worldwide, close to 100 million individuals consume drinking water from aquifers geologically contaminated with inorganic arsenic (Lan et al. 2011). In Bangladesh, between 35 and 77 million people are at risk of drinking water contaminated with arsenic (Smith et al. 2000). In excess of 2 billion people, mostly in the developing world, rely on marine fish as a sole protein source, and the safety levels for consuming methylmercury in marine fish have yet to be fully defined. In many cases, the biochemical mechanisms underlying the toxicity of these metals are unknown. In addition, many diseases involve dysregulation of otherwise functional metals. For example, copper is essential for health, but when not properly regulated, it causes severe problems, including metabolic disorders such as Wilson's and Menkes diseases. Metals have long been known to accumulate in brains of sufferers from neurodegenerative diseases, such as Alzheimer's and Parkinson's diseases, and multiple sclerosis, although the exact nature of the accumulation and whether this is a cause or an effect of the pathology is still unknown.

New metal-based drugs are showing increasing promise for treating a number of diseases. For example, ruthenium compounds show promise for treating tumors resistant to conventional chemotherapy, and arsenic compounds are effective in treating some leukemias and show particular promise for childhood leukemias. At the same time, unexpected adverse effects recently have been reported for metal-based magnetic resonance imaging (MRI) contrast agents. In almost all cases, the biotransformation and chemical mechanism underlying the biological activity of these compounds is unknown, and knowledge of chemical mechanism is key for optimizing biological activity. X-ray methods provide an essential *in situ* probe that can provide essential information relating to mechanism.

2.17 Toxicity of Nanoparticles

Ultrafine particles sized from 1 to 100 nm, i.e., nanoparticles, with their enhanced surface-to-volume ratios, exhibit unexpected properties relative to the same bulk materials, including increased photostability, lower melting temperatures, quantum confinement in semiconductor particles, surface plasmon resonance, superparamagnetism, and emulsion stabilization. As such, new applications of nanoparticles are available for a host of new commercial and research products. Their high surface-to-volume ratios also result in enhanced reactivity and concomitant increases in human toxicology. These new health hazards are yet uncharacterized, as both the small size and proportionally large surface area leads to different behavior in fluids and gas flow, as well as possibly different rates of ingestion or inhalation in humans. In addition, their reactivity and ability to penetrate far into the lungs can lead to changes in the oxidation state of the nanoparticle material with subsequent oxidative stress on tissues. To elucidate the interaction of nanoparticles with human tissues, Galya Orr and colleagues at PNNL are currently focused on using scanning electron microscopy for initial examination, followed by helium ion microscopy with an extended depth of focus to allow particles to be viewed *in situ* on the “rough” surfaces of lung alveoli. A central focus of this research is to understand how differences in the size and chemical composition of different nanoparticles affect their distribution and uptake in the lungs.

The potential toxicity or biocompatibility of engineered nanoparticles is governed by their physical and chemical properties, which dictate the cellular interactions and fate of the particles that, in turn, determine the cellular response. The relationships between particle properties and these cellular processes are only poorly understood mostly because nanoparticles are highly reactive entities that are easily modified by their environment. For example, inhaled nanoparticle properties are modified as the particles enter the respiratory tract; settle in different regions, such as the bronchial or alveolar regions; and penetrate distinct cells and organelles.

Multiple biological processes can impact the properties of the particles along the way and eventually dictate the cellular interactions and fate of the particle. For example, the biological environment determines the degree of agglomeration that, in turn, determines the target region and mechanisms by which the particles penetrate the cellular environment or distinct organelles (Conner and Schmid 2003). Coronas, created by proteins and other molecules specific to the tissue, cell and organelle, determine the destination, interactions, and fate of the particles (Dutta et al. 2007; Horie et al. 2009). The enzymes or pH within distinct tissue regions or organelles can determine oxidation state (reactivity) or degree of dissolution or degradation of certain particles (Yang and Xie 2006; Song et al. 2010). These properties will determine the fate of the particle and whether it is toxic or biocompatible.

To better understand and eventually predict the relationships between nanoparticle properties and cellular response, particle properties should be characterized along the exposure pathway, using hydrated specimens that preserve the native character of the tissue and particle.

X-ray imaging and tomography could provide precise chemical characterization of the nanoparticles within their microenvironment in the intact hydrated cell and organelles with nanometer resolution. These measurements are complementary to existing tools in EMSL, where nanomaterials currently are investigated within the intact (or sectioned) cell with nanometer resolution using transmission electron microscopy and tomography, scanning electron microscopy, and helium ion microscopy. The cellular interactions and fate of the nanoparticles and their dynamic behavior within the intact cell and organelles currently are investigated using super-resolution fluorescence, time-lapse single molecule fluorescence, and other fluorescence imaging techniques for intact or live cell imaging with nanometer resolution. X-ray tomographic imaging with a compact light source, in combination with EXAFS, would enhance the capabilities for determining the chemical state of nanomaterial uptake and their relationship to cellular toxicity.

2.18 Subsurface Environments

The Hanford Site near PNNL has a rich historical legacy as the first place internationally where plutonium was produced in large quantities. Unfortunately, it also has a significant detrimental environmental legacy as a result of the substantial waste left from plutonium processing, both in metals and radionuclides present in soils and in onsite storage tanks with soluble uranium, technetium (^{99}Tc), and other toxic redox-sensitive metals and radionuclides (Wall and Krumholz 2006). DOE manages these sites and, due to the long-term environmental risks these contaminants pose, is committed to cleaning them up. To understand the transport of these contaminants, one must understand their binding with groundwater minerals, such as ferrihydrite. To preserve the native redox chemistry, experiments aimed at elucidating contaminant transport must be conducted in the same anaerobic conditions that exist in subsurface soils. By using x-ray microprobes, the distribution of both iron and radionuclides can be quantitatively determined, spectroscopic studies can reveal their oxidation state, and microdiffraction can be used to identify mineral phases. In this way, one can understand the generation of Fe^{2+} in ferrihydrite under anaerobic conditions, as well as its surface reactivity and binding with contaminants, such as TcO_2. For example, while TcO_2 might sometimes be present at a concentration of one part per billion, which is below the standard for drinking water, incorporation into soil bacteria can result in a hundredfold increase in its concentration, which is well above the limit for clean drinking water.

Bioremediation of these contaminants through the precipitation of reduced metal oxides is being explored at PNNL as a possible low-cost solution, using microbes to change the solubility of a contaminant through a change in redox status, e.g., conversion of the soluble species, U(VI) to the relatively insoluble U(IV). Bacterial candidates for such bioremediation strategies include dissimilar metal-reducing bacteria that reduce iron, sulfate, chromate, or uranyl ions as a form of anaerobic respiration (Lovley and Phillips 1992; Fredrickson et al. 2008). Some of the enzymes responsible for the metal redox chemistry have been identified. For example, researchers at PNNL recently solved the crystal structure for a NAD(P)H-dependent flavin mononucleotide (FMN) reductase (PDB ID 3S2Y), which has high reductase activity against both chromate (CrO_4^-) and urinate ($UO_2(CO_3)_3^{4-}$) anions. While the crystal structure of the protein is providing insights into the mechanism for metal reduction, detailed information regarding the redox products is necessary to fully describe the biochemistry and enzyme kinetics that will permit strategies to be developed for optimizing bioremediation.

EXAFS spectroscopy is a powerful tool for identifying and characterizing the redox products generated both *in vivo* and *in vitro*, which uses the region several hundred electron volts above an absorption edge to infer information about distances from one atom to electron orbitals in its neighbors. At energies within about 10 eV of an absorption edge, XANES provides information to identify the metal, metal valence, and symmetry at the metal site, as well as serving as a fingerprint for the local structure around the absorber (Buchko et al. 2000). For example, with higher oxidation states, the absorption edge shifts to higher energy by a few electron volts. For many transition elements with unfilled *d* orbitals, the shape of the XANES profile reflects the geometry of the first coordination sphere. Such detailed redox information afforded by liberal access to CXLS would not only benefit bioremediation studies from the cellular to molecular level but would also be valuable for the study of metalloproteins, including in the growing field of peptide-enhanced metal catalysis (Jain et al. 2011). When coupled with macromolecular crystallography, CXLS-derived molecular structure information could be used to design the next-generation, new uranyl reductase, whether as a metalloprotein or a bioinspired electrocatalyst. Thus, as described herein, the combined use of CXLS and existing EMSL capabilities can provide solutions for bioremediation from information obtained regarding contaminant transport and reduction in the complex environment of soil, as well as molecular details of metal-reducing cells and enzymes.

2.19 Terrestrial Environments

Terrestrial ecosystems have a major importance in global nutrient cycling and represent a major source of genetic diversity, which is thought to be central to their community stability. Of practical interest, an understanding of the structure and function of cellulosic structures in wood, and their degradation by cellulases, will benefit greatly from the imaging and spectroscopy capabilities of a compact light source. X-ray tomography and EXAFS of varying wood samples will provide molecular information relating how compositional differences affect rates of degradation. Combined with genomic sciences, these measurements will have substantial impact with respect to developing conversion systems of lignocellulosic biomass to biofuels and bioplastics, improving technologies for biobased (wood) products and wood durability through rationale re-engineering of forestry products.

3.0 Environmental Science: Scientific Challenges

3.1 Overview

The fate and transport of contaminants in the environment is controlled by molecular-level processes, including aqueous complexation, surface complexation to mineral phases, and electron transfer between respiring microorganisms and biogeochemical reductants diffusing within moving water. These molecular processes occur in chemically and physically heterogeneous subsurface environments and often are linked in complex ways that challenge their isolation, quantification, and mechanistic understanding. The structure, chemistry, and nanoscale geometric properties of mineral-water and microbe-mineral interfaces—and the surrounding physical environment—markedly influence these processes. Variation of microbial community structures in space and time and how these variations influence geochemical conditions and microbiologically mediated reactions with dissolved constituents, contaminants, and different kinds of earth materials remain to be understood. Therefore, a multimodal and multiscale understanding of the functionality of microbiologic biofilms in the subsurface, where extracellular electron transfer reactions influence contaminant valence mobility within microscale environments, is essential to develop science-based remediation technologies.

A CXLS that can generate hard and soft x-rays of variable energies could enable unique investigations of mineral-microbe-contaminant systems under realistic environmental conditions. Determining the biochemical and biophysical structures of biofilms and their interactions with inorganic substrates, including metal ions and mineral surfaces, will provide critical knowledge need to improve biogeochemical reaction and fate models. Structure-property relationships could be investigated along with physical and chemical heterogeneities that exist within the micron- to nanometer-scale zones of interaction between mineral and microbe. X-ray-based measurements, including crystallography, scanning transmission microscopy, and absorption spectroscopies, would enormously complement EMSL's capabilities and provide new scientific breakthroughs in environmental science and biogeochemistry. The CXLS would provide a unique capability and capacity for accelerating research progress as experiments could be conducted in a more regular and convenient manner while simultaneously complementing existing and new capabilities at the DOE general user light sources that possess higher sensitivity.

3.2 Introduction to Environmental Science Needs

Understanding process interactions and environmental variables that control reaction rates and products is a critical scientific need that must be resolved to predict environmental reactivity. Fundamental understanding of processes pertinent to a range of atmospheric and occupational environments, energy production and emissions control, particle nano-toxicology, and catalysis each require advanced analytical approaches for chemical imaging of particles down to 1 nm in reactive environments. Furthermore, we must appreciate how microbial community structures vary in space and time and how these variations influence geochemical conditions and microbiologically mediated reactions with dissolved constituents (including contaminants) and different kinds of earth materials. Understanding the functionality of microbiologic biofilms in the subsurface—where extracellular electron transfer reactions influence contaminant valence mobility within microscale environments—is essential to develop science-based remediation technologies. Determining the biochemical and biophysical structures of biofilms and their interactions with inorganic substrates, including metal ions and mineral surfaces, will provide critical knowledge need to improve biogeochemical reaction and fate models.

A CXLS that can generate x-rays in the submicron size range with variable energies, along with existing state-of-the-art capabilities at EMSL, will enable unique investigations of mineral-microbe-contaminant systems under realistic environmental conditions. Structure-property relationships can be investigated along with physical and chemical heterogeneities that exist within the micron- to nanometer-scale zones of mineral-microbe interactions. X-ray-based measurements, including crystallography, scanning transmission microscopy, and absorption spectroscopies, would enormously complement EMSL's capabilities, providing new scientific breakthroughs in environmental science and biogeochemistry.

3.3 Aerosols: Background, Challenges, and Case

Thrust areas for DOE's atmospheric research are on regional and continental chemistry and fate of tropospheric air pollutants, extracontinental and global chemistry and fate of tropospheric air pollutants, and aerosol genesis. Laboratory and field-based studies are conducted to understand reaction chemistry on surfaces, advective influences on the chemical composition of aerosols, and air-surface exchange processes. Gas-particle heterogeneous chemistry plays a critical role in a variety of environmental and engineering chemical processes. These processes are pertinent to atmospheric and occupational environment, catalysis, technologies related to energy production and emissions control, particle nanotoxicology, and health effects. Fundamental understanding of gas-particle heterogeneous chemistry requires advanced analytical approaches for chemical imaging of particles, down to nanometer scale, in reactive environments. The unique, complementary analytical and imaging approaches provided by EMSL's capabilities permit insights into the evolution of particle internal structures and interfaces. The use of the proposed CXLS-based spectromicroscopy instruments will offer an analytical platform to study multi-phase particle reaction and *in situ* chemistry with broad applications in environmental and chemical engineering research.

Chemical analysis of reacting particles is an especially challenging task because no single analytical method can provide information, which ranges from high-resolution microscopy to molecular characterization of complex constituents of particulate matter. The ultimate goal is to add both CXLS-based analytical tools for chemical imaging analysis of reacting particles and time resolution that can interrogate interfacial chemical transformations. Adding both capabilities will allow researchers to bring particle analysis to an unprecedented level of sophistication and develop unique capabilities for research in the areas of complex particle interfacial chemistry and *in situ* reactivity.

The proposed CXLS capability will be used to develop complementary experimental setups that afford chemical imaging of changes in particle physical and chemical properties, including morphology and composition in reactive environments. Specific plans for these efforts are outlined in the following sections. The plans include development of these experimental capabilities:

1. X-ray microspectroscopy experiments for chemical speciation of particle internal heterogeneity, including *in situ* studies of gas-particle reactions and using complementary methods of electron microscopy, electron probe microanalysis, and vibrational spectroscopy available at EMSL

2. *In situ* spectroscopy studies of airborne particles, using complementary capabilities of CXLS-based atmospheric pressure x-ray photoelectron spectroscopy (XPS) and single-particle mass spectrometry and characterization approaches
3. Photoemission x-ray microscope for examining surface reaction dynamics at environmental interfaces.

3.3.1 Spectroscopy and Microscopy Studies of Immobilized Particles

To study chemistry of individual environmental particles—especially focused on probing real-time changes at the gas-particle interface with nanoscale resolution in reactive environments—we propose development of the scanning transmission x-ray microscopy/XANES end station, employing microreactor cells, where particles deposited on the x-ray transparent substrates will be imaged and analyzed in real time under controlled conditions of gas-phase reactant concentrations, temperature, and relative humidity.

The challenging aspect of studying environmental samples in scanning transmission x-ray microscopy/XANES is defining the scientific problem narrowly enough for efficient use of limited experimental time at light-source-based instruments. Focusing on a specific scientific problem often is based on data and insights obtained from other methods. As illustrated in Figure 3.1, the application of complementary analytical methods provides comprehensive information, ranging from microscopy-level details of individual particles to advanced molecular characterization of complex molecules comprising particulate matter. For example, micro-Fourier transform infrared spectroscopy (FTIR) (Ghorai and Tivanski 2010) and Raman spectroscopy (Moffet et al. 2012), surface probe mass spectrometry (Hopkins et al. 2008), and electron microscopy techniques (Moffet et al. 2010a,b,c) can guide specific scanning transmission x-ray microscopy measurements focused on the internal composition of individual particles. Then, those results can be linked to broad complementary data obtained from other techniques (Laskin 2010; Moffet et al. 2010a and references therein). A unique advantage of collocation of the proposed CXLS-based scanning transmission x-ray microscopy/XANES capability, with an array of other microscopy, surface probe spectroscopy, and mass spectrometry techniques available in EMSL, is it will afford more investigations to combine these complementary techniques for research.

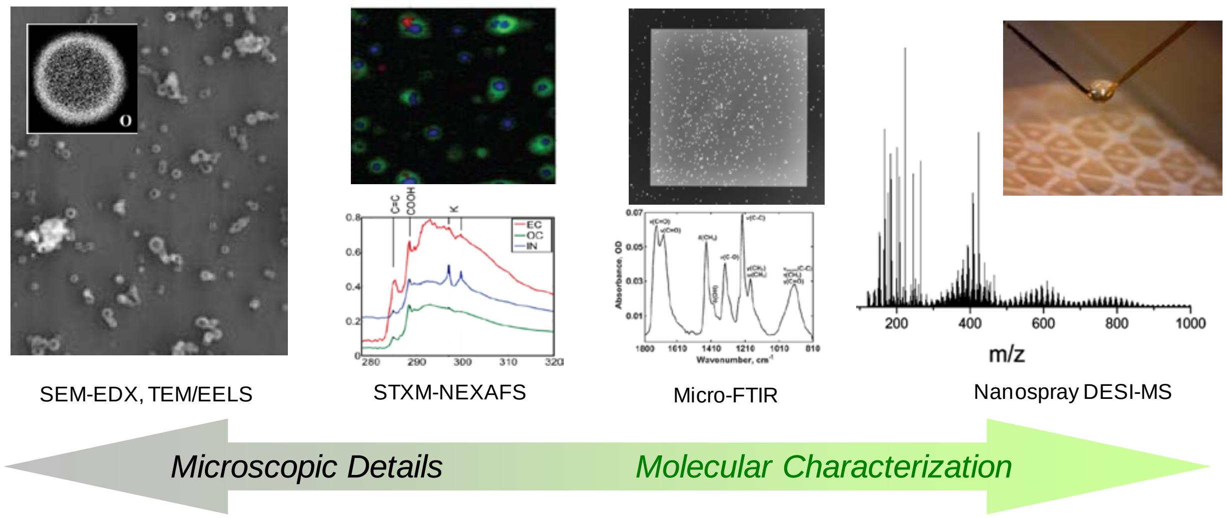


Figure 3.1. Illustrative presentation of complementary analytical methods applied for comprehensive analysis of particle samples. Credit: Alex Laskin and Mary Gilles.

Microreactor cell designs will be based on a sandwich-type nanoreactor that was demonstrated as an insertion device for synchrotron-based scanning transmission x-ray microscopy instruments (de Smit et al. 2008). This device allows studies of materials with lateral resolution at the nanoscale during exposure to gases at ambient pressures and elevated temperatures. The basic design of these microreactor cells is compatible with most of the offline particle analysis techniques, such as scanning electron and transmission electron microscopy microscopes, micro-FTIR, and micro-Raman spectrometers. Therefore, scientists can use similar microreactor cells to replicate gas-particle processes that can be monitored using complementary microscopy and microspectroscopy capabilities hosted at EMSL. Detailed design and implementation of microreactor cell technology will need to be modified for each specific instrument. In ongoing collaborative efforts between EMSL/PNNL and Advanced Light Source (ALS)/Lawrence Berkeley National Laboratory (LBNL) scientists, the first generation of these cells now is being developed. First, microreactor cells will be designed and constructed for ambient temperature studies. Second, the generation of microreactors will employ cells with resistive heating elements. Finally, later developments will be advanced toward modifications exploring reactions at liquid-particle interfaces relevant to environmental remediation and sensing applications of engineered nanoparticles.

Development of these capabilities will provide the ability to probe changes in chemical bonding and oxidation states of pure organic and mixed organic-inorganic environmental particles in controlled, *in situ* studies relevant to particle atmospheric chemistry and physics, such as particle hygroscopicity (Ghorai and Tivanski 2010; Ghorai et al. 2011) and heterogeneous gas-particle reactions (Liu et al. 2011b).

3.3.2 *In Situ* Studies of Airborne Particles: XPS of Nucleated Droplets, SPLAT Characterization, and Experimental Selection of Specific Nuclei

In the fields of atmospheric/environmental science and heterogeneous catalysis, the investigation of surfaces under realistic conditions of temperature, gas composition, and pressure is essential for a fundamental understanding of the molecular processes at liquid-vapor and solid-vapor interfaces that govern interfacial chemistry. Ambient pressure photoemission spectroscopy (APPES), originally developed at the ALS, has made important contributions toward understanding the surface chemistry of many systems, spanning fuels cells, free radical surface reactions, interfacial solvation, etc. (Bluhm 2010). Herein, we suggest building an APPES end station for the proposed CXLS to examine interfacial reactions of environmental and atmospheric surfaces at the nanoscale.

In atmospheric chemistry, an ongoing challenge is understanding the fundamental relationship between OA composition and the ability of a particle to act as cloud condensation nuclei (CCN). Of the many types of organic molecules found in atmospheric particles, surface active (surfactant) molecules present a particularly interesting and important class. A monolayer of surfactant molecules on the surface of an aerosol particle has the potential to determine the interactions between the particle and the gas-phase surroundings. The presence of a surfactant layer alters the rate that molecules can enter or leave a coated droplet by orders of magnitude. The important question is whether or not the rate change is significant enough on atmospherically relevant time scales to affect the CCN activity of these particles. It also is important to keep in mind the susceptibility of the organic layer to oxidation by ozone and hydroxide.

We propose to use a CXLS-APPES capability as a critical part of an integrated experimental system that would allow characterization of physicochemical properties of cloud nuclei particles followed by probing the surface composition of cloud droplets nucleated from these particles. A single-particle mass spectrometer will be used to characterize (in real-time) size-dependent composition and reactivity, morphology, density, and the shape of individual particles (Zelenyuk and Imre 2009). To quantify their hygroscopic growth factor and CCN activity, these particles will be subjected to increases in relative humidity under well-controlled conditions characteristic of an atmospheric environment. The activated micron-sized droplets then will be introduced as a stream into an APPES spectrometer for real-time XPS surface characterization.

The droplet surface and the subsurface itself will be directly probed using tunable x-ray radiation from the proposed CXLS. This will be done by collecting the resulting photoelectrons through a specially designed, differentially-pumped hemispherical electron energy analyzer. This approach will provide quantitative atomic and functional group information about the surface and subsurface region of the CCN droplet. Previously, this approach was shown to yield entirely new information about the radial distribution of organic molecules at an aqueous interface (Starr et al. 2008).

A combined single-particle laser ablation time of flight mass spectrometer, or SPLAT, with XPS characterization of aerosol particles at a CXLS will allow entirely new measurements of how aerosol composition and morphology impact droplet formation in clouds. This combination of complementary instruments, hosted by EMSL, will enhance studies of the atmospheric cycle of organic particles and relate their chemistry as nuclei in cloud droplet formation.

3.3.3 A Photoemission X-ray Microscope for Surface Reaction Dynamics at Environmental Interfaces

Although state-of-the-art APPES instruments can now examine surfaces under near-thermodynamic equilibrium conditions with a spatial resolution on the order of photon beam dimensions (~100 μm in diameter or larger), there are many important solid-vapor interfaces in catalysis and aerosol chemistry that are spatially and chemically inhomogeneous on the nanometer scale. We propose to build an APPES imaging end station for the proffered CXLS to examine nanoscale interfacial reactions in chemically inhomogeneous samples with a spatial resolution of 100 nm.

While conceptually similar to the existing scanning transmission x-ray microscopy approach, this new end station also would provide a novel way for XPS to obtain both depth-resolved (angstrom resolution) and laterally resolved (100 nm) chemical maps of complex interfaces, ranging from OA to catalytic nanoparticles during a chemical reaction. Scanning transmission x-ray microscopy is a well-established technique for the measurement of the chemical composition of an array of samples with high spatial resolution. Bluhm, Tyliszczak, and Hussain at LBNL are working to combine the principal approaches of zone-plate-based scanning transmission x-ray microscopy and APPES to develop an instrument that measures surface chemistry under realistic conditions of temperature and pressure with a spatial resolution better than 100 nm. The APPES instrument is a differentially pumped electrostatic lens system that separates the electron energy analyzer (kept in vacuum) from the high-pressure region in the sample cell. By positioning the sample close to the differentially pumped entrance aperture of the lens system, the path length of the electrons through the high-pressure region is kept as short as possible, allowing operation at pressures up to several Torr. Therefore, it is well suited for the investigation of surfaces in gaseous environments, particularly in the presence of water vapor. The combination of zone-plate-based focusing with APPES also will allow increasing the pressure limit in APPES experiments by reducing the necessary aperture size.

Using a two-dimensional delay line detector, we will be able to collect data with high temporal resolution (up to 81 ps), which would afford the study of laser-initiated transient surface processes, such as charge transfer, conformational dynamics, and chemical reactions. For example, a laser could be used to excite a surface molecule or nanoparticle to initiate a chemical transformation, which then would be monitored using photoelectron spectroscopy to examine the formation of new surface chemical bonds, molecular conformations, or reaction intermediates—all with 100 nm spatial resolution. Furthermore, a laser could be used to form gas-phase radicals, such as OH, which would react at the surface of a model OA. Light from the CXLS would be used to monitor the heterogeneous reaction at the subsurface and surface of the OA particle. Because the APPES instrument is well suited to higher-pressure investigations, heterogeneous reactions in the presence of water can be conducted. This would allow entirely new investigations of heterogeneous reactions on simulated cloud and fog water droplets.

In addition to photoemission imaging, we also will be able to collect x-ray absorption images because the CXLS will be able to access the K-edges of the most abundant elements on the Earth’s surface (C, N, O, Na, Mg, Al, and Si) and the L-edges of all the important transition metals (Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn). By combining highly surface-sensitive electron yield and bulk-sensitive fluorescence yield, XPS will allow different surface phenomena to be investigated, including interfacial segregation in inhomogeneous mixed organic/inorganic aerosols particles; bi-metallic nanoparticles and fuel cell electrodes under reaction conditions; surface chemical reactions, such as metal oxidation; and soot growth and oxidation. Variable polarization, available via the CXLS, will allow studies to probe local surface geometry (upright/flat orientation; domains with different chirality), providing new insight into the surface of complex atmospheric particulate matter.

3.4 Soils and Sustainability: Background, Challenges, and Case

Synchrotron-based spectroscopies are the workhorse of modern soil chemistry research. Studies of inorganic contaminant reactions on mineral colloids, organic matter, and soil aggregates are important examples, and they share many characteristics with biogeochemical research.

Synchrotron research in soils includes the biogeochemical cycling of fertilizer macronutrients: C, N, and P. For more than 100 years, it has been known that soil type, landscape position, biological communities, climate, and land management have a tremendous influence on the chemical properties of soils. This explicitly means that landscape/ecosystem-level processes are linked to molecular-scale chemistry. However, integrating field-scale soil science sampling and research programs with molecular-scale research into soil structure, biochemistry, and reactivity remains challenging due to the interdisciplinary requirements of understanding a system as dynamic and spatially heterogeneous as soils. The contemporary research approach in this field is to combine different analytical techniques at a variety of spatial and temporal scales to answer research questions. In fact, instrumentation already available at EMSL—electron microscopy, NMR, force microscopies, vibrational spectroscopy, secondary ion mass spectroscopy, and the proposed CXLS—could provide unique opportunities for the soil science community to probe soil biogeochemical processes from multiple analytical perspectives using collocated, advanced instrumentation. Significant scientific advances would occur toward understanding the varied soil chemical processes that underpin natural systems sustainability. These are important global research areas with enormous implication for human health and environmental quality.

3.4.1 Soil Carbon Storage and Sustainability

It is well established that the cycling of terrestrial carbon is key to sustaining global food sources, land quality and land use decisions, global carbon storage, and contaminant transport. Soil organic matter is one of the major energy sources for microorganisms in natural systems and, therefore, is tightly coupled to biogeochemical cycling and reactivity. Because many metal contaminants strongly sorb to organic matter, understanding soil carbon chemistry is important for predicting contaminant fate and transport. However, the structure and dynamics of soil organic matter still is poorly understood.

To study the structure and reactivity of soil carbon, researchers currently use a combination NMR, FTIR, C- and N-XANES, scanning transmission x-ray microscopy, UV-induced excitation-emission matrices, pyrolysis techniques, and mass spectrometry. Not one of these techniques alone is conclusive, and debate persists in the literature about whether or not the C and N forms in soil samples are real or a result from artifacts (Ihori et al. 1995). For many of these techniques, sample preparation requires extractions, and they may change soil C before analysis. In the environment, soil carbon is strongly associated with both mineral and microbial surfaces, and the resulting matrix may have significantly different properties from any single component. An integrated capacity that allows studies of how soil carbon forms, reacts, and transforms in realistic conditions using existing PNNL instrumentation—with CXLS—could make significant advances in this area. The interface between computational and theoretical research on this subject also would be of interest, for example, how organic matter folds into unique and complex 3-D structures with mineral material. These results could, in the long term, be scaled up to improve estimates of greenhouse gas fluxes and carbon transformations based on land use and ecozones, leading to improvements in global carbon budgets.

3.4.1.1 Sustainable Agriculture

The sustainable development of improved agronomic practices with low/inexpensive fertilizer inputs is a key component in the path to food security in developing countries (Pretty 2008). In addition, agronomic crop production remains important to the economies of developed countries, and research improving the fertilizer efficiency and reducing the environmental footprint of agriculture will continue to be important. Global populations will place increasing pressure on soils to sustain human life, and some fertilizer sources are either finite, with natural resources obtained via mining or produced via costly chemical synthesis. Improved understanding of the chemical speciation and fate of fertilizer elements, such as P in soil systems, would greatly improve efficiently using these nutrients, benefitting all populations. Applying the same multiscale approach to studying macronutrients that already has been successfully employed in trace contaminant biogeochemistry would be one area where the CXLS capabilities could make an immediate and important contribution to soil science.

The agricultural chemistry of P is a major challenge for molecular soil science research (Figure 3.2). Agronomists typically obtain average P levels in agricultural fields by taking a composite soil sample to represent an entire field. Low concentrations of P in these composite samples challenge the application of advanced analytical techniques because of sensitivity limitations. However, if one preserves the spatial variability originally present in the field (fertilizer often is injected as a concentrated band into the soil), it is possible to characterize the system chemistry in far more detail. By coupling wet chemistry, biological studies, molecular-scale spectroscopy, and imaging, one can obtain a complete picture of P speciation and transformation in a soil. This information then can be used to improve soil testing and fertilizer recommendations to increase profitability of agronomy or decrease environmental risk to surface waters. This same approach also may be useful in studying nutrient chemistry in low input or organic farming systems.

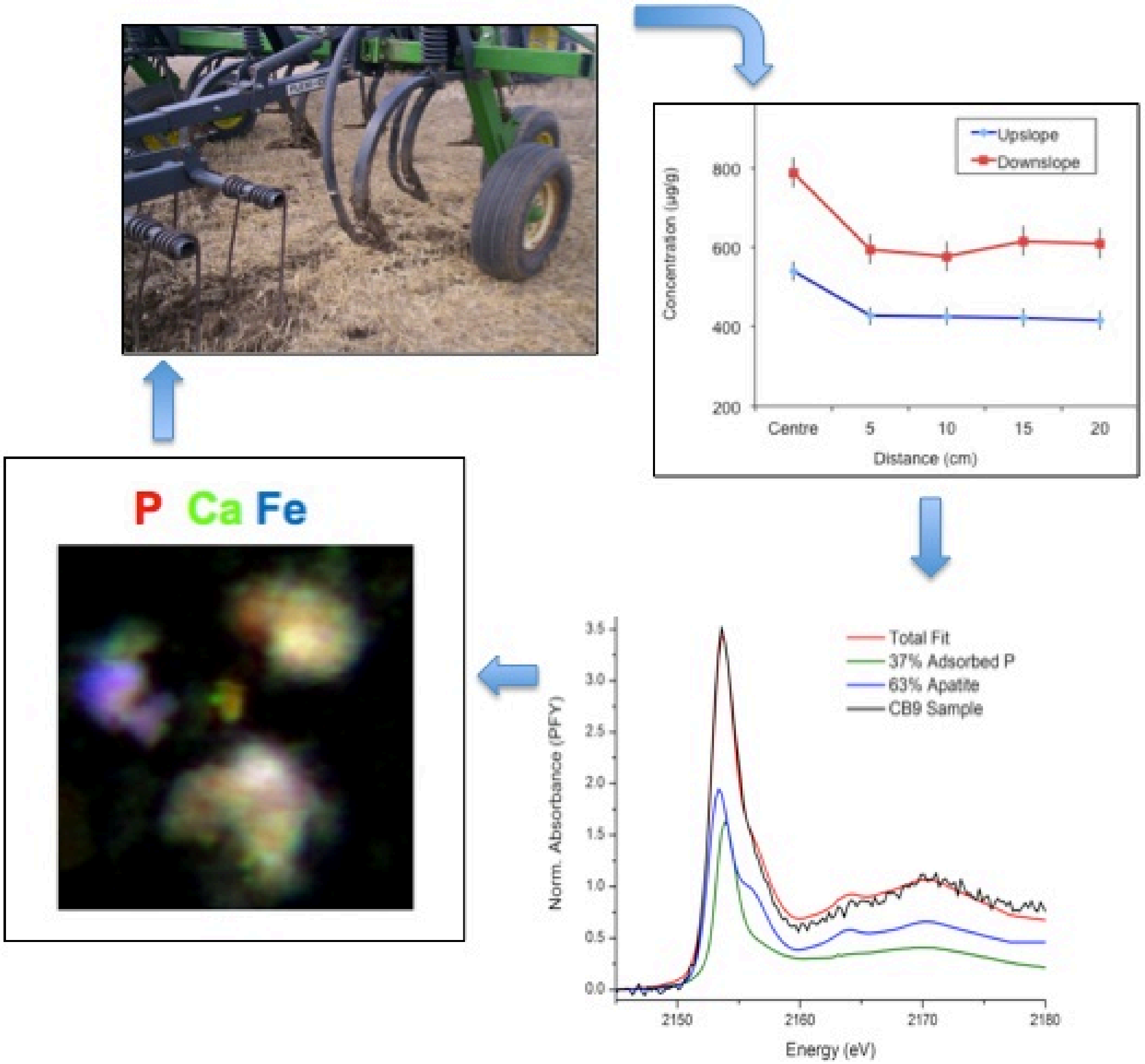


Figure 3.2. The importance of spatial scale to Pp speciation in a typical agronomic system. Band injection of an ammonium phosphate fertilizer occurs on a meter scale (top left). Wet chemical analysis of soil P at the centimeter scale reveals variability as a function of distance from the band (top right). Bulk (~500 µm scale) P K-edge XANES provides quantitative speciation of P as calcium phosphate and phosphate adsorbed on iron oxides (bottom right). Scanning transmission x-ray microscopy imaging at the nanometer scale verifies that the major components from XANES are tightly correlated in the soil (bottom left). Note, the results of speciation can improve agronomic practices at the field scale and complete the circle. Credit: Derek Peak.

3.4.1.2 Reclamation of Contaminated/Degraded Soils

As both bulk and micro-focused x-ray absorption spectroscopy techniques commonly have been employed by soil chemists to study the fate of metal contaminants in soil environments, this likely is the most familiar aspect of soil science research to the rest of the synchrotron community. This area of research will continue, but the scope is anticipated to expand and focus more upon: 1) *in situ* remediation of hydrocarbon-contaminated soils (a result of petroleum production and exploration), 2) reclamation of salt-affected soils, and 3) soil ecotoxicology and the study of how chemical speciation affects the mobility and toxicity of contaminants through an ecosystem's trophic levels.

In many ways, the fundamental obstacle in solving all of these research challenges is the heterogeneous and dynamic nature of soils. Soils exhibit obvious variability as a function of climate, landscape, parent material, and land use. This variability extends to the micron scale. Many important soil components, such as organic matter and poorly ordered metal oxides, remain vague. Thus, structural refinements would promote huge advances to the field. Perhaps, the largest challenge remains that any soil sample collected, regardless of how carefully handled or thoroughly interrogated at the molecular scale, offers only a snapshot of the time and position at which it was collected.

3.5 Challenges in Biogeochemistry

3.5.1 Metals, Microbes, and Interfaces: Background, Challenges, and Case

Past defense-related activities at government facilities—in particular, activities associated with the mining, extraction, and processing of uranium for nuclear fuel and weapons—have introduced a range of chemical contaminants into the environment, including organic compounds, heavy metals, and radionuclides. As a group, radionuclides and heavy metals represent the largest fraction of contaminants in the soil and groundwater at DOE sites (DOE 1997), and nearly 70% of DOE facilities report groundwater contamination by radionuclides (Riley et al. 1992). The transport properties of metal and radionuclide contaminants through these subsurface environments are highly dependent on chemical interactions of the contaminant with subsurface biological and/or geochemical materials and on transformations of the contaminant.

The biogeochemistry of manganese and iron in aquatic, terrestrial, and subsurface environments is a critical determinant of the fate and transport of a wide spectrum of inorganic and organic contaminants. Driven by metal-reducing and oxidizing microorganisms, these processes control the distribution of Mn(III/IV) and Fe(II/III) oxides, which are key solid-phase reactants, redox buffering phases, and electron acceptors for anoxic microbial respiration. These microbial processes are of profound concern and the focus of current research because:

4. Their solid-phase products are highly reactive with polyvalent metal contaminants, including U and Tc.
5. Their enzymatic systems also engage and react with soluble redox-sensitive contaminants.

Developing a predictive understanding of these processes involving Mn and Fe is a grand challenge in biogeochemistry with significant potential impacts to environmental remediation. The microenvironment at and adjacent to actively metabolizing cell surfaces (~0.1–10 μm) can be significantly different from ensemble averages for environments across larger spatial scales. Metabolic products can set up steep chemical gradients over very short distances. Furthermore, characteristics of the chemical gradients created at the mineral-microbe interface might differ in response to metabolic rate, nutrient flux, water advection, and various other system attributes and properties. Predicting the behavior of contaminant radionuclides and metals in microenvironments is a major challenge because the localized chemical composition and fluxes are difficult or impossible to define. However, transformations of contaminants in such microenvironments are critical and affect transport and persistence at larger environmental scales important to humanity. Therefore, knowledge about biogeochemical interactions at the microbe-mineral interface is of paramount importance.

3.5.1.1 The Technical Challenge in Understanding the Interface of Metals and Microbes

Information about chemical speciation of heavy metals and contaminants associated with the mineral-microbe microenvironment can be obtained with submicron-sized hard x-ray beams (Kemner et al. 2004, 2005; Kemner 2008). However, complementary higher spatial resolution imaging of these environments with electron microscopy usually requires transporting the sample to another far-flung facility. Similarly, complementary spectroscopic imaging of the same sample with a soft x-ray beam or another technique to gain insights into organic chemical interactions may require transport of the sample from a hard x-ray to a soft x-ray beamline or another facility while simultaneously preserving its spatial registry.

Access to submicron-sized x-ray beams with energies from ~200 eV to ~20 keV, similar to proposed CXLS characteristics, will enable unique investigations of the chemical heterogeneities that exist within and near mineral-microbe microenvironments while providing knowledge on reaction pathways, products, and more complex process interactions. Specifically, ~200 eV submicron x-ray beams will enable probing of carbon chemistries in the solid phase, shedding light on the types of organic molecules in the vicinity of the mineral-microbe microenvironment. Similarly, ~7 keV and ~17 keV submicron x-ray beams will enable probing iron and uranium chemistries, respectively, in that same region. In addition, colocation of EMSL electron microscopes and other characterization techniques with submicron x-ray probes featuring a broad range of energies will enhance the sophistication and scientific impact of investigations of mineral-microbe microenvironments relevant to metal and radionuclide contaminants at the Hanford Site in southeastern Washington state and other former plutonium production sites. The aforementioned combination of capabilities also will support investigations into the molecular transformations of carbon in these highly reactive microscopic zones, contributing to both global climate change and fate of organic contaminants research areas.

As described, the instrumentation also will support the development of improved environmental remediation technologies in applied research. These technologies often involve contaminant valence changes or the targeted precipitation (abiotic or biotic) of trace metal, radionuclide, or selective host or sorbent phases to reduce the solubility and sequester contaminants from the fluid phase. X-ray absorption spectroscopy and spectromicroscopy provided via CXLS, combined with scanning and transmission electron microscopies and microdiffraction, are a powerful analytical suite to characterize remediation reaction products (e.g., phase identity and composition) as part of a broader research campaign to optimize reagent delivery and mixing systems, evaluate technology effectiveness vis-à-vis end states, and maximize sustainability for long-term treatment.

3.5.1.2 Sequestration of Technetium by Stimulating Sulfidogenesis with Zero-valent Iron

Technetium is a highly mobile subsurface contaminant at certain nuclear waste sites, and its mobility makes it one of the highest radiative risks for exposure. The predominant and mobile form of Tc in the subsurface is the Tc^{VII} oxyanion pertechnetate (TcO_4^-). Under anoxic conditions, TcO_4^- is readily reduced to Tc^{IV}, which forms highly insoluble oxides, such as $TcO_2 \cdot nH_2O$. Many studies have investigated reduction of TcO_4^- by abiotic and biotic means—on the premise this could be used for long-term immobilization of the contaminant as part of remediation activities. However, this strategy is difficult because (re)oxidation of Tc^{IV} oxides is relatively rapid. Therefore, the possibility of remobilization is significant (Zhong et al. 2005).

One way to minimize the prospect of remobilization is to effect reduction under sulfidogenic conditions, so that most Tc^{IV} is immobilized as Tc2S7, which should remain relatively insoluble even under oxic conditions (Wharton et al. 2000; Lukens et al. 2004). For this purpose, a feasible and practical way to create well-poised sulfidogenic conditions is the addition of injectable micron- to nano-scale zero-valent iron (Fe^0). Under these circumstances, Fe^0 oxidation will scavenge dissolved oxygen and nitrate and generate significant concentrations of dissolved H_2, thereby favoring microbial sulfate reduction and contributing directly to the reduction of Tc^{VII} to Tc^{IV} (Icenhower et al. 1999).

Sequestration of Tc as sulfides could provide the basis for a more sustainable approach to remediation of Tc-contaminated groundwater. Micron- and nano-sized Fe^0 have further advantages: they can be emplaced by air/foam injection in the vadose zone or aqueous slurry injection in the saturated zone and could be useful for *in situ* chemical reduction at the Hanford Site or other like areas with Tc vadose zone and groundwater contamination.

However, the outcome of such treatment scenarios will depend on a complex series of multiscale, interactive processes, where the spatial distribution of the injected material will have heterogeneous effects on *in situ* biogeochemistry that, in turn, will determine what mixture of fundamental processes will control the overall (im)mobilization of Tc. The potentially complex relationships between the solid phases that might arise from these sequestration processes are illustrated in Figure 3.3, which is a conceptual model superimposed on an electron micrograph of the nano Fe^0.

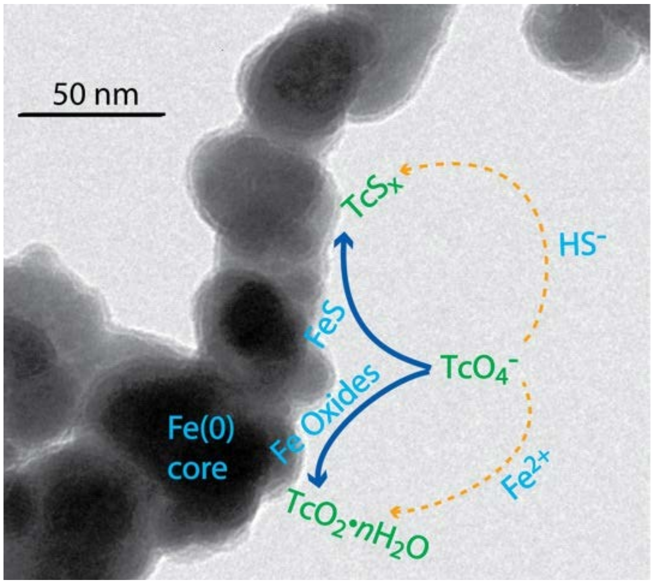


Figure 3.3. Conceptual model for technetium sequestration under sulfidogenic conditions stimulated by nano zero-valent iron. Provided by D. Fan and P. Tratnyek.

A DOE-supported research project is underway to investigate this conceptual model with a goal of providing the scientific basis for a reliable remediation technology. Still, the project is challenging because multiple kinetic pathways exist that may lead to Tc(IV)-containing products of different chemical character and oxidation potential, including Tc-sulfides, oxides, and co-precipitates with Fe. The small size and dilute concentration of the product Tc(IV) phases require a range of characterization methods, including many accessed through a user agreement with EMSL (scanning electron microscopy, transmission electron microscopy, x-ray diffraction , XPS, and Mössbauer spectroscopy), as well as x-ray absorption spectroscopy at synchrotron radiation user facilities. All methods need be applied over a short time period because samples are heterogeneous, oxygen-sensitive, reactive with water, and (likely) sensitive to drying.

In biogeochemical research, this situation is both challenging and common. Scientific productivity and impact would be significantly improved by the proposed CXLS' capabilities because it would enable robust, proximate, multimodal analyses of time-sensitive samples that have resulted from costly experimentation.

3.5.2 Actinide Biogeochemistry/Environmental Science: Background, Challenges, and Case

Over the past two decades, experiments with radioactive materials conducted at DOE general user facility light sources have provided valuable knowledge on radioactive materials, primarily the actinides from thorium through curium, that has been used to understand their fundamental chemistry and assist in the environmental remediation of waste legacies from the Cold War (Gorden et al. 2003). Although frequently focused on the aforementioned actinides, Tc, cesium, iodine, and other radionuclides are of equal importance. Furthermore, there is an entire diverse class of materials and chemistry issues associated with nuclear activities resulting in important environmental science considerations (Gephart 2010).

Synchrotron radiation techniques have been vitally important to the field of actinides and actinide biogeochemistry/environmental science as full speciation information, especially with spatial resolution among the actinide/radionuclide component, is extremely difficult to obtain from laboratory-based methods at realistic environmental concentrations. Over the past decade, knowledge derived from DOE light sources has been the impetus for the construction of new beamlines in the United States and Europe that have been either partly or fully dedicated to investigations of radioactive materials (Reich et al. 2000; Bluhm et al. 2006; Rothe et al. 2006; Solari et al. 2009). Most actinide biogeochemistry/environmental science investigations focus on using x-ray methods for chemical speciation and distribution information on length scales ranging from bulk to micron to nanometer. Recently, there has been an increasing trend toward using methods in the soft x-ray region to obtain direct information about low-Z elements. The spectromicroscopy (chemical imaging) characteristics and capabilities to work with x-ray probes and detection in realistic environments necessary to understand actinide biogeochemistry is a tremendous and prerequisite need for gaining a better knowledge in this critical, emerging field.

Speciation measurements of actinides at DOE light sources are complicated by the overarching need to maintain a safe facility and environment for users, which entails a substantial technical safety effort. Despite the obstacles for conducting research with radioactive materials at general user synchrotron radiation light sources, the results from a range of actinide studies has provided a modern understanding of actinide chemistry and a solid scientific basis for environmental remediation that has resulted in tremendous cost and risk savings at DOE legacy sites (Clark et al. 2006). Development of synchrotron radiation techniques for use with radioactive materials has enabled an effective radiological safety infrastructure to support and facilitate experimentation at several DOE general user light source facilities. Los Alamos National Laboratory maintains the sole, dedicated laboratory-based facility for actinide science, which employs a tunable x-ray source and conducts photoelectron spectroscopy downstream of an x-ray plasma source that has been upgraded since its initial configuration (Arko et al. 1999).

The collocation of a laboratory-based CXLS with leadership scientific programs in actinide biogeochemistry/environmental science, along with the existing state-of-the-art tools at PNNL, would provide a new, unique opportunity to accelerate progress in the field. It would have a tremendous scientific impact not only in actinide biogeochemistry/environmental science, but in other related fields. Such a facility would require careful design to accommodate both biological and radiological concerns. Regular access to specialized actinide spectromicroscopy capabilities, provided by a CXLS in tandem with other major tools, and a comprehensive infrastructure to prepare actinide biogeochemical/environmental samples (leveraging existing resident scientific programs) would be a singular and significant development. Moreover, a CXLS would complement and improve the use of existing and future beamline capabilities at DOE general user light sources.

3.5.2.1 Fundamental Actinide Biogeochemistry/Environmental Science

Improving fundamental knowledge of actinide biogeochemistry/environmental science benefits environmental cleanup activities at DOE legacy sites. This complex topic requires understanding of the interactions of radioactive, multivalent actinide species with a host of geomaterials, along with the simultaneous effects of biologically driven processes. Over the past few years, there has been continual and marked progress in understanding the biogeochemistry of U, Tc, and Pu, which have been found to be remarkably rich from a scientific perspective (Cologgi et al. 2011; Malvankar et al. 2011; Shang et al. 2011). Tremendous opportunities for scientific advancements exist for this topic and have been relatively unexplored because of its complexity. Advanced multimodal analyses are crucial toward unraveling this complexity. There are compelling fundamental and use-inspired reasons to expand biogeochemical research on transuranic and actinide elements to meet current and future challenges (Neu et al. 2010). The new knowledge that could be obtained on a consistent basis with a CXLS would be similar to that recently obtained for the oxidation state analysis of Pu incorporated into rat cells with spatial resolution—with the added capability of acquiring knowledge with greater depth and breadth than seen in the Pu case (Gorman-Lewis et al. 2011). Another example of the studies that could be performed with an appropriate CXLS beamline for U biogeochemistry is illustrated in Figure 3.4, where soft x-ray spectromicroscopy was used to discriminate the impacts of metal-reducing bacteria on U and V solubility from carnotite. PNNL is a world leader in mineral-microbe research, and a CXLS facility that included support for actinide biogeochemistry/environmental science would further encourage high-impact, leadership-quality research while providing new opportunities for future research in carbon sequestration and multidisciplinary fields.

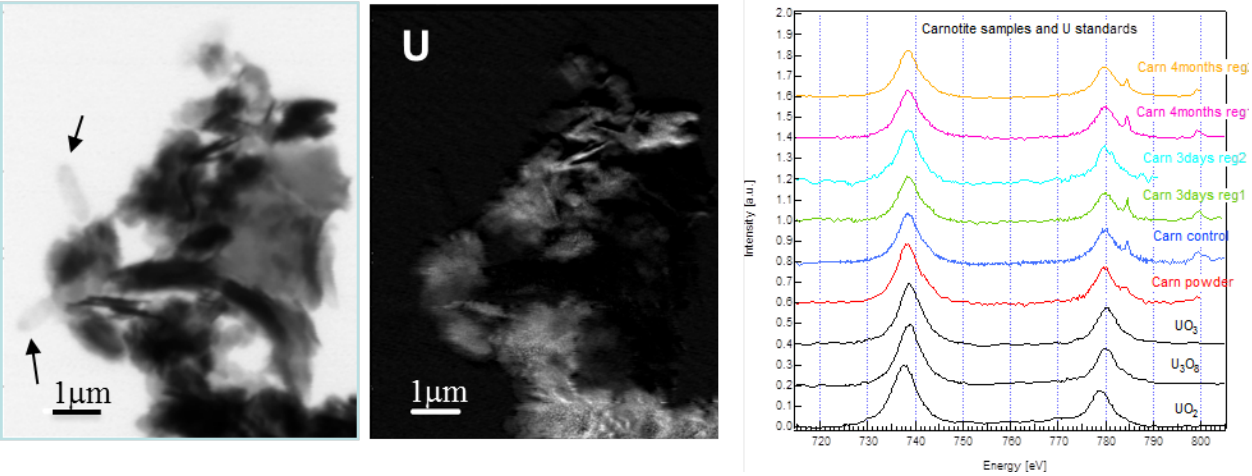


Figure 3.4. Scanning transmission x-ray microscope image (738.5 eV) and corresponding U map of anoxic cultures of *Shewanella putrefaciens* CN32 (pointed with arrows) incubated with a natural U(VI)V(V) carnotite-group mineral for 4 months (left and center, respectively). U N4,5 XANES spectroscopy shows no reduction of U(VI) carnotite by CN32 over time. CN32 cells after 3 days, 4 months, and 8 months of incubation were observed to accumulate V and Fe but no uranium (right). Credit: S. Glasauer, S. Fakra, P. Weidler, T. Tyliszczak, and D. Shuh.

A CXLS at PNNL also would support the development of a unique infrastructure to investigate fundamental actinide chemistry and materials science with tunable x-rays in a safe, controlled laboratory setting. This would overcome some of the difficulties and sensitivities encountered at general user light sources in establishing experimental facilities dedicated to actinide research. The safety considerations are particularly important for soft x-ray investigations, but most of these obstacles have been overcome. The implementation of a CXLS using recent technological advances would present unmatched scientific opportunities for selected sub-fields of actinide science. Important examples include bonding of *f*-electron materials, interfacial science, and materials chemistry. Many of the scientific opportunities and challenges for fundamental and use-inspired actinide science that can be addressed by tunable x-ray methods have been summarized in the *Basic Research Needs for Advanced Nuclear Energy Systems* (DOE 2006a).

3.5.2.2 Energy Range

Overall, the field of biogeochemistry/environmental science, overlapped with actinide science, uses the entire spectrum of synchrotron radiation from ~100 eV to ~25 keV. An increasing, recent emphasis in the soft x-ray region results from the ability to directly probe low-Z elements, C, N, and O, among others. Thus, there are roughly three approximate regions that could be exploited effectively for biogeochemistry with radioactive materials: 1) x-rays from 225 eV–2000 eV, 2) x-rays from 2 keV–6 keV, and 3) x-rays from 6 keV–25 keV. A major priority for biogeochemistry has been the need for enhanced spatial resolution and elemental sensitivity. Spatial resolution is most frequently needed on the length scale from tens of microns to tens of nanometers. It is imperative to have adequate spatial resolution for each of the three energy regions (as noted). For actinide studies centered in life sciences, the first energy region seems to be the most important. The second energy region is enticing as it spans the P and S K-edges and includes strong actinide absorption edges that will increasingly be employed in future studies. The third region is the more traditional range that includes the most useful elemental edges and most used actinide edges.

3.5.2.3 Special Considerations

Because the infrastructure and sample support systems associated with biogeochemistry and actinide science need to be replicated in a general fashion at a sole light source location for optimum preparation of experimental materials, combined research in these fields would benefit from implementation of a CXLS at PNNL. There are natural synergies with several other scientific fields that also would benefit from establishment of dedicated, or partially dedicated, CXLS facilities at PNNL. Notably, EMSL’s highly regarded Instrument Development Laboratory, or IDL, also could fabricate specialized sample cells for dynamic experiments, multimodal interrogation, and instrument transfers.

3.6 National Security: Background, Challenges, and Case

Researchers focused on national security at PNNL deliver high-impact, science-based, practical solutions for clients to prevent and counteract terrorism and the proliferation of weapons of mass destruction. PNNL provides the tools and technologies to support the detection of weapons of mass destruction, helping the United States manage its nonproliferation treaties and securing the nation’s borders. Many of these investigations involve the environmental monitoring of elements and isotopes that can be used as indicators of illicit activities.

3.6.1 Forensics of Environmental Samples

One of PNNL’s missions is the detection, characterization, and mitigation of chemical, biological, radiological, nuclear, or explosive threats. Research efforts often focus on the development of forensic analysis tools to characterize samples collected in the field (e.g., environmental sampling). The specific chemical signatures vary between domains, but most standard analytical techniques are applicable. Incremental development of existing methods offers limited gains. As such, there is a need to develop enhanced chemical imaging and analysis methods that are complementary to current capabilities, adding a new dimension and context to currently available information.

A CXLS at PNNL would provide a unique capability for national security with immediate potential applications within:

- **Imaging to Guide Sampling**: There is a need for survey capabilities that can provide a primary screening for threats and cue additional analyses.
- **Sample Characterization**: This often applies to particulate samples, though other forms are possible. Knowledge of the distribution of species within a sample can provide insight into the sample's history, formation processes, and environmental interactions.
- **Simultaneous, Multidimensional Data**: Samples often undergo individual measurements that are "merged" during post-processing. Many national security domains could benefit from complementary methods and can improve confidence or bound measurements already being made.
- **Automation and Algorithms for Rapid, High-throughput Analysis**: National security problems typically focus on the "needle-in-a-haystack" scenario. Often, we are looking for rare events. Thus, both imaging and analysis tools aimed at rapid analysis, as well as prioritization for additional analysis techniques that may require more labor-intensive sample preparation, are needed.
- **Signature Discovery/Science**: Light source methods can elucidate environmental biogeochemical pathways that are crucial toward understanding fate and transport of threat species and indicators. These types of discoveries could lead to transformational methods for next-generation sensing.

The offsite locations and current business models of large synchrotron light sources generally have been incompatible with national security needs. As a result, relatively little effort has gone into exploiting capabilities of second- and third-generation synchrotron light sources. The advent of laboratory-sized, tunable, intense, and spatially resolving x-ray sources with the potential to be dedicated instruments changes this paradigm and affords new opportunities to apply this technology to national security problems. Light-source-enabled techniques are largely unexplored and untapped for national security. The potential impact of these techniques must be clarified.

One of the early benefits of a CXLS source at PNNL would be the collocation and potential cross-fertilization between light source experts/users and subject matter experts in national security problems. Efforts were made in the past, but the model built from a handful of national security researchers spending a few days every quarter with expert beamline users is insufficient. While experts in their respective problem domains, the national security researchers often do not know what they lack and may not ask the right questions. At the same time, the light source experts understand the capabilities and available techniques and their limitations, but they cannot offer well-matched solutions without understanding the exact problem and its precise requirements. A CXLS at PNNL would play a pivotal role in developing this relationship between domain experts, synchrotron radiation beamline experts, and research experts.

An additional benefit of a CXLS at PNNL is the potential for greater access—at least, relative to the large light sources. Especially in the early stages, national security research will not focus on new scientific advancements as much as applying understood scientific techniques to new problems. To convince clients to invest in light source technology, national security researchers will need to make the case that the capability has the potential to revolutionize a particular domain. This means not only making individual measurements but also determining a process or methodology for applying the technology to a particular problem and interpreting the results with a high degree of confidence. Such a development cycle is generally incompatible with the business models in place at current light source facilities.

While it is understood that a CXLS at PNNL would primarily be a scientific instrument focused on furthering scientific understanding, certain design decisions could provide greater opportunities for national security researchers and clear a future pathway to a fully dedicated, high-performance beamline facility tailored to meet the needs of national security (when proof-of-principle is demonstrated). Initially, state-of-the-art research capabilities on specialized beamlines may not be the optimum place to begin applying light source technology to national security problems. Instead, a more general-purpose beamline that potentially uses off-axis or other “low-value” photons from a beamline located downstream would provide an opportunity to experiment and address national security applications without impacting advanced scientific studies. A critical aspect for the development of the national security applications is sufficient and regular access to experimental time.

3.6.1.1 Energy Range

In general, national security problems are well matched to the CXLS’ potential design parameters. Forensic analysis of environmental samples typically does not require the time-dependent characteristics that the CXLS provides. Photon flux and bandwidth will determine the time required to gather sufficient statistics, but this is not expected to be a limiting factor. The required energy ranges depend on the national security domain. Studies aimed at biological or explosive threats would use lower energies (0.2 keV–4 keV), whereas studies aimed at nuclear or radiological threats would use higher energies (15 keV–20 keV and 3.5 keV–10 keV). The spatially resolving characteristics of beams available from the CXLS are particularly important and, in some cases, constitute a “new” essential capability for national security applications as these spectromicroscopy properties are not readily available via other methods.

3.6.1.2 Special Considerations

To have high impact on the mission of detecting, characterizing, and mitigating chemical, biological, radiological, nuclear, and explosives threats, the end station facilities must be capable of handling threat materials. Special operations may be required to handle samples and/or analytical standards. Possible operations for consideration include: radiological contamination area fume hoods, nuclear material balance-controlled areas, elevated biosafety level (2, possibly 3) capability, and explosives handling up to 10 grams. Several of these special considerations dovetail with the requirements of other scientific communities that would use the PNNL-based CXLS, for example, actinide and life science users.

3.7 Conclusions

Scientific communities in the biogeochemistry, metals, microbes, interfaces, sustainability, actinide biogeochemistry/environmental, aerosol, and forensic sciences all identified vital and compelling reasons supporting the collocation of a CXLS at PNNL. All of the scientific disciplines recognized the potential and extreme value to conduct specialized research in a laboratory-based CXLS environment with essential complementary tools from EMSL and PNNL. There was significant resonance that the special scientific laboratories present at PNNL would be able to translate their unique laboratory-based research and take advantage of the CXLS in a distinct and efficient manner not available at offsite light sources. A concurrent theme in most disciplines was that research could be conducted on a more regular and convenient basis with improved access to experimental time, greatly accelerating research progress. There was additional recognition that the CXLS would provide a great deal of unique capability and capacity, and it would complement existing and new capabilities at other DOE general user light sources that would continue to be used by PNNL research programs. To assist the scientific programs, a nucleus of leadership CXLS scientists also must be established.

Overall, energy region preferences for the biogeochemistry, metals, microbes, interfaces, sustainability, actinide biogeochemistry/environmental, aerosol, and forensic sciences indicate that access to most of the synchrotron radiation spectrum obtainable from current light sources is desired. However, there clearly is a significant emphasis in the soft x-ray region by several disciplines (sustainability, actinide biogeochemistry/environmental sciences, and aerosol communities), whereas harder x-rays were the first choices of the metals, microbes, interfaces, and forensics science communities. All of the scientific areas indicated it would be ideal to have the soft x-ray capability and, at least, one of the harder x-ray capabilities. Three of the disciplines also recognized the new opportunities that might arise from exploiting the photon energy range from approximately 1 keV to 5 keV. There was little mention of the possible use of the CXLS' temporal properties outside of the aerosol group. However, representatives from each of the scientific themes recognized that time-resolved studies could be a major emphasis. Still, the implementation of time-resolved science in these fields must be developed significantly.

Similarly, the Environmental Science participants recognized that a critical aspect for the successful implementation of scientific programs using a CXLS at PNNL would rely on accelerated, early integration of new and existing staff with active synchrotron radiation programs at several light sources before the design and construction of any CXLS beamlines at PNNL.

4.0 Catalysis: Scientific Challenges

4.1 Overview

The potential impact of the techniques available using synchrotron light sources on understanding catalysts was recognized in the earliest days of modern era of x-ray science. One of the overarching reasons for this was that x-rays from these sources are able to penetrate the reaction medium and walls or windows of catalytic reactors so the structure of the catalyst can be probed under working conditions. Over the last 30 years, the increase in productivity due to light source technology has been dramatic. In addition, many new catalysis researchers have been introduced to synchrotron science, and novel methods have been developed, including combined FTIR/EXAFS and phase contrast imaging capabilities.

As a research field, catalysis encompasses a diverse array of scientific research disciplines, from organometallic chemistry to materials science and surface chemistry to chemical engineering. Due to this diversity, interdisciplinary teams generally are required to drive revolutionary technological advancements for catalytic research. At PNNL, this multidisciplinary nature has been recognized, and world-class experts in each topic area are present throughout the laboratory. The installation of a CXLS at PNNL would complete the missing piece of the catalyst characterization toolbox at PNNL and would have a profound effect on how x-ray techniques could be applied to problems of national and international interest. Currently, there is no other laboratory in the United States where the suite of tools present at EMSL, combined with characterization tools being developed and proposed (e.g., dynamic and ultrafast transmission electron microscopy), computational support, materials preparation, and catalytic testing facilities, are combined under one roof with management structure. User facility scientific staffs at existing synchrotron sources frequently are unfamiliar with catalytic processes and cannot respond adequately to user needs. Similarly, those who master the instruments and facilities often are not those who know best how to synthesize catalysts, characterize their performance, or even handle them properly. A dedicated CXLS facility would allow PNNL and its collaborators to advance the level of catalysis science and enhance our understandings of catalytic materials and phenomena through the use of the state-of-the-art techniques under *in situ* reaction conditions localized near a central hub of catalysis expertise.

4.2 Importance of Catalysis

As noted, catalysis is crucial to both modern life and lifestyles. It has been estimated that 90% of all commercially produced chemical products involve catalysts at some stage of their manufacture, leading to products valued in the trillions of dollars annually in the United States alone (R&D Magazine 2005). Recently, the potential for catalysis to play a leading role in energy, energy independence, and energy sustainability, as well as in addressing global climate change issues, has been recognized. The world demand for energy is expected to double by 2050. The growing need to protect the environment by increasing energy efficiency and developing clean, safe, renewable energy sources compounds this challenge. Finding solutions to these challenges is vital for future energy security, to address global climate change, and for continued economic prosperity. A DOE Office of Basic Energy Sciences (BES) report, *Basic Research Needs to Assure a Secure Energy Future*, recognized that solutions will require scientific breakthroughs and revolutionary developments (DOE-BESAC 2003). Moreover, from the DOE-BES reports, *Basic Research Needs: Catalysis for Energy* (DOE 2007), *Basic Research Needs for Solar*

Energy Utilization (DOE 2005), *Basic Research Needs for Clean and Efficient Combustion of 21st Century Transportation Fuels* (DOE 2006b), and *Basic Research Needs for the Hydrogen Economy* (DOE 2004), it is clear that catalysis will play a major role in advancing the research and technology needs for the nation, especially in the areas of energy security and global climate change.

The tools and experimental methods available so the catalysis researcher can probe the structure of working catalysts continue to develop (Bare and Ressler 2009). Among the plethora of techniques available, methods using capabilities at synchrotron light sources are mentioned prominently among the characterization tools essential for rapid advancement of this crucial field. Solid-catalyzed reactions take place on active sites that typically are made up of several atoms each. These may be nanostructures dispersed on high-area porous supports (e.g., dispersed oxide phases). They also may be parts of the surfaces of solids, such as corners, edges, and facets, and these may be parts of nanoparticles dispersed on supports. Essential goals in catalysis science are identification and understanding of the geometric and electronic structures of catalytically active sites and elucidation of the elementary steps that constitute the reactions taking place on catalytic sites. The basis for the research illustrated herein is to understand the structure-function relationship in catalysis. Understanding the structure-function relationship should open the doors to learning how to control the structure that will lead to selectively favoring a particular chemistry or chemical pathway leading to the desired product. Along this line, we can pose three scientific challenges:

1. What determines the atomistic structural details of complex catalytic structures and how do these change under differing reaction conditions?
2. How do structure, morphology, size, support, promoters, etc., affect catalytic performance?
3. What is the atomic-level spatiotemporal structure of a working catalyst in a catalytic reactor?

The CXLS will address these types of questions by providing the necessary understanding to allow significant progress to be made. The CXLS will be able to achieve this lofty goal through synergistic access to catalytic experts and catalyst characterization tools. At PNNL, the catalytic sciences span fundamental, use-inspired, and applied research. The Laboratory has a critical mass of catalytic scientists, including teams in the Institute for Integrated Catalysis and the Center for Molecular Electrocatalysis, an Energy Frontier Research Center. In addition, synergistic tools could be accessed through EMSL.

4.3 Light Sources and Catalysis

Even in the earliest days of modern synchrotron science, the potential impact of the techniques available using synchrotron light sources toward understanding catalysts was recognized (Lytle et al. 1974). One of the overarching reasons was the x-rays from such sources are able to penetrate the reaction medium and walls (or suitable windows) of the catalytic reactor so that the structure of the catalyst can be probed in working conditions (Bare and Ressler 2009). Since those early days, synchrotron x-ray techniques and methodologies have continually advanced. The diverse array of available techniques, combined with the large range of photon energies available at a light source, provides a suite of capabilities with an unprecedented level of structural detail—even on materials lacking long-range order typical of those in catalysis. Primary techniques have been diffraction, scattering, and absorption spectroscopy, in both static and time-resolved modes. One of the more recent advancements has been the development of these techniques to image the catalyst using either full-field or microbeam techniques and to probe the structure of catalysts under *in situ* or *operando* conditions, such as elevated temperatures and pressures, provided by additional understanding that shows the catalyst's structure responds to its environment (Campbell 1990; Rodriguez and Goodman 1992; Tao et al. 2008). The result is a sizable research community in the catalysis field whose research depends upon having access to synchrotron light sources. Indeed, both at the National Synchrotron Light Source (NSLS) (Synchrotron Catalysis Consortium, or SCC) and Advanced Photon Source (APS), there are catalysis research communities assembling to share ideas, equipment, and methodologies to push the frontiers of the field. The importance of collaborative and dedicated efforts in this demanding research field cannot be overstated. As one specific metric, the following shows the number of publications from the beamlines at NSLS associated with the SCC (both before and after the SCC was formed):

Year	Publications
2003 (before the SCC)	9
2004	20
2005	19
2008 (after the SCC)	33
2009	50
2010	68

The increase in productivity is dramatic. In addition, many new catalysis researchers have been introduced to synchrotron science. New techniques have been developed, e.g., combined FTIR and EXAFS. *In situ* cells have been implemented, and new and improved methodologies have been developed (see http://home.yu.edu/scc/). The CXLS would have a similar dramatic impact on catalysis research at Institute of Integrated Catalysis and PNNL. A dedicated facility, combined with a group of world-leading scientists and staff paired with the world-class suite of characterization and testing tools at EMSL, will produce world-leading research and could be a game-changer in the application of x-ray-based techniques to advance catalyst characterization, answering fundamental scientific questions and aiding industrial partners. In summary, the CXLS will allow PNNL and its collaborators to advance the level of catalysis science and enhance the understanding of catalytic materials and phenomena using state-of-the-art synchrotron techniques under *operando* reaction conditions.

4.4 Specific Examples of Catalysis Research and the CXLS

In this section, specific research areas where research resulting from the expected capabilities of the CXLS would have a significant impact on both fundamental and applied research challenges are described.

4.4.1 Toward 100% Selectivity in Heterogeneous Catalysis

Environmental and economic concerns demand development of catalyst systems able to perform chemical transformations at selectivity approaching 100% to eliminate waste or byproducts. While the understanding of factors primarily responsible for determining the activity of heterogeneous catalysts has improved dramatically, the ability to develop catalysts that could achieve 100% selectivity toward the desired products in specific catalytic systems is rather limited. This variation in selectivity is caused, in part, because there is wide variation of the nature and structure of the catalytically active centers in industrial catalysts. In contrast, very high selectivity to desired products over both biological (enzymes) and molecular (homogeneous) catalysts can be achieved because of the well-defined, molecular nature of the active centers. In these systems, selectivity can be controlled with relative ease by modifying the ligands in the coordination spheres of the catalytic centers in such a way that the structure of the activated complex of a chemical reaction can allow for the formation of a certain product only. In these systems, all of the catalytic sites are uniform with respect to their activity and selectivity.

With industrial catalysts, it is challenging to unambiguously determine the critical factors that regulate the selectivity of a specific active center. In many cases, this stems from the lack of understanding of the nature of the actual active sites and their environments. The characterization of active sites requires using a multitude of spectroscopy and microscopy tools that can be applied under practical operating conditions. The combination of these techniques is not readily available at currently existing synchrotron beamlines. At PNNL, we already have developed capabilities for catalyst synthesis, reactivity testing, high-level theoretical methods, and a broad suite of characterization techniques. PNNL’s specific strengths in, for example, high magnetic field NMR and atomic-resolution electron microscopy techniques, greatly contribute toward understanding the workings of practical catalysts. The most important missing characterization techniques are those that require high-intensity x-ray beams (e.g., x-ray absorption spectroscopy) so the measurement can be made in a practical time period using a realistic concentration of elements. These tools are critical in developing catalysts that approach 100% selectivity.

4.4.1.1 Atomically Dispersed Transition Metal Catalysts

Pt/alumina: One of the most interesting examples of the importance of multiple modalities of spectroscopy/microscopy characterization tools is PNNL’s work on alumina-supported Pt catalysts. Pt/alumina catalysts are widely used in a number of industrial processes. The key questions addressed in the PNNL work relate to anchoring catalytically active centers to the support oxide and thermal stability of the metal particles. The availability of very high magnetic field solid ^{27}Al NMR spectroscopy allowed scientists to unambiguously determine the anchoring sites on the γ-Al_2O_3 surface. As Figure 4.1 illustrates, Pt atoms selectively bind to coordinatively unsaturated, five-coordinate Al^{3+} sites on the γ-Al_2O_3 surface. The specific interaction between the catalytically active phase (here, Pt) and the oxide support (here, alumina) was shown to afford control of the dispersion as revealed by high angle annular dark-field transmission electron microscopy images.

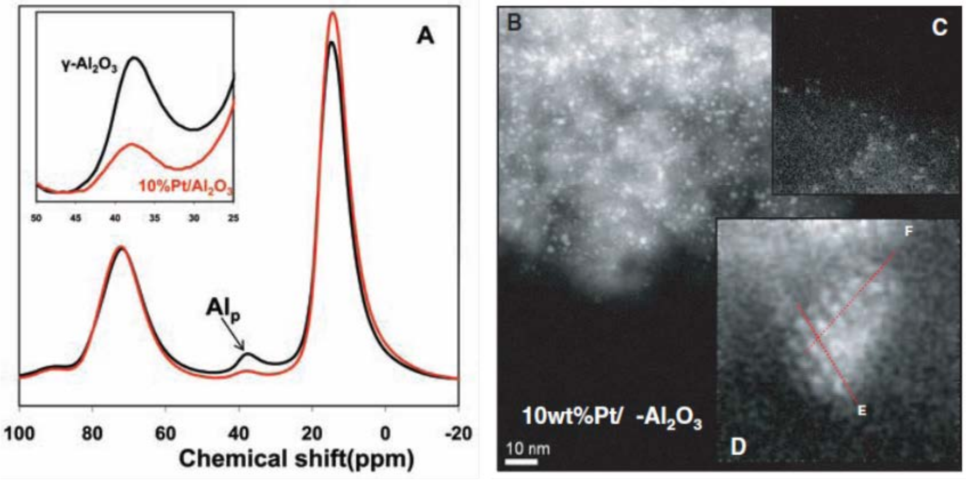


Figure 4.1. Ultra-high magnetic field ^{27}Al solid-state magic angle spinning-NMR spectra of Al_2O_3 and Pt/Al_2O_3 and high angle annular dark-field transmission electron microscopy images of 10 wt.% Pt/Al_2O_3 (Kwak et al. 2009a; Mei et al. 2010).

This knowledge will help in developing the ability to deposit active metals on oxide supports with atomic dispersion. A related question is the thermal stability of these highly dispersed catalytic phases, which required using both atomic-resolution microscopy and x-ray absorption spectroscopy tools. These studies revealed the bimodal Pt distribution on the γ-Al_2O_3 surface, i.e., significant numbers of single Pt atoms were observed even after annealing at 900 K, while the majority of the Pt aggregated into 3-D metal clusters. These results answered the long-debated question as to why the first shell Pt coordination of these large particles did not approach the expected number of 12 for an fcc metal. When the highly dispersed Pt is included, an average coordination of 10.5 is determined, which was observed experimentally in earlier x-ray absorption studies, underlying the importance in using multiple microscopy and spectroscopy tools in catalysts characterization (Kwak et al. 2009a; Mei et al. 2010).

Ba/alumina: The work on BaO-based NO_x storage reduction (NSR) catalysts represents another example of how basic research using an array of spectroscopy and microscopy techniques can contribute to a practical (industrial) application. Ultra-high magnetic field ^{27}Al solid-state magic angle spinning-NMR spectroscopy revealed the active NO_x storage phase of the catalyst (i.e., BaO) binds to the pentacoordinate Al^{3+} sites of the γ-Al_2O_3 support. This provided critical information about the catalyst preparation method needed to obtain a functioning catalyst. Furthermore, FTIR measurements suggested the formation of two distinctly different nitrate phases on the NO_2-exposed BaO/γ-Al_2O_3 storage material (Figure 4.2), suggesting two different catalytic pathways. The importance of these two phases was underlined in studies analyzing the desulfation of sulfur-poisoned NSR catalysts. Time-resolved *operando* synchrotron-based studies (time-resolved x-ray diffraction) and EXAFS and XANES studies (Figure 4.3) clearly showed the mechanism of desulfation and thermal degradation of the fully formulated catalyst. The information obtained from these combined microscopy/spectroscopy/diffraction studies were essential to the successful introduction of this technology by Cummins Inc., in 2007—a remarkable example of detailed, fundamental, *operando* catalyst characterization leading to the development of a commercial technology (Kim et al. 2006; Kwak et al. 2009b).

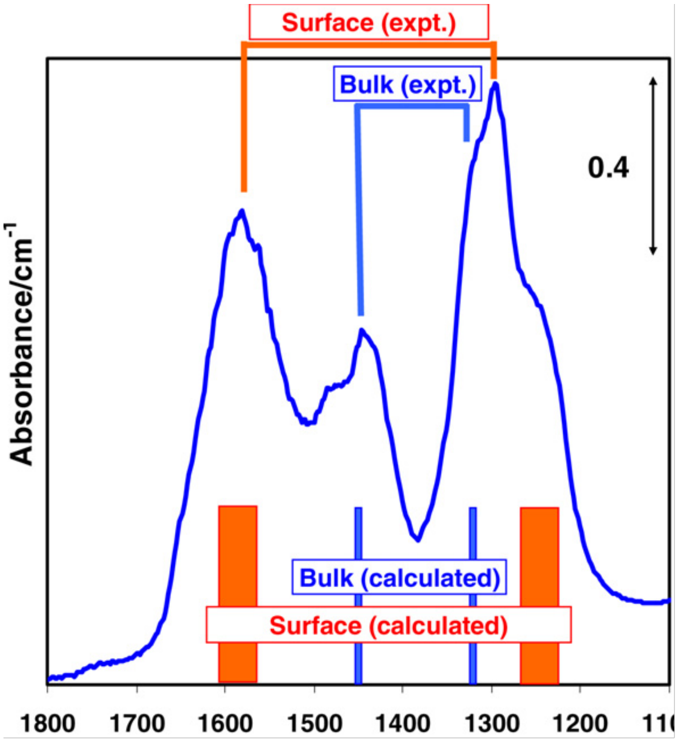


Figure 4.2. FTIR spectra of NO_2-exposed 8 wt.% BaO/Al_2O_3 (Kwak et al. 2009b).

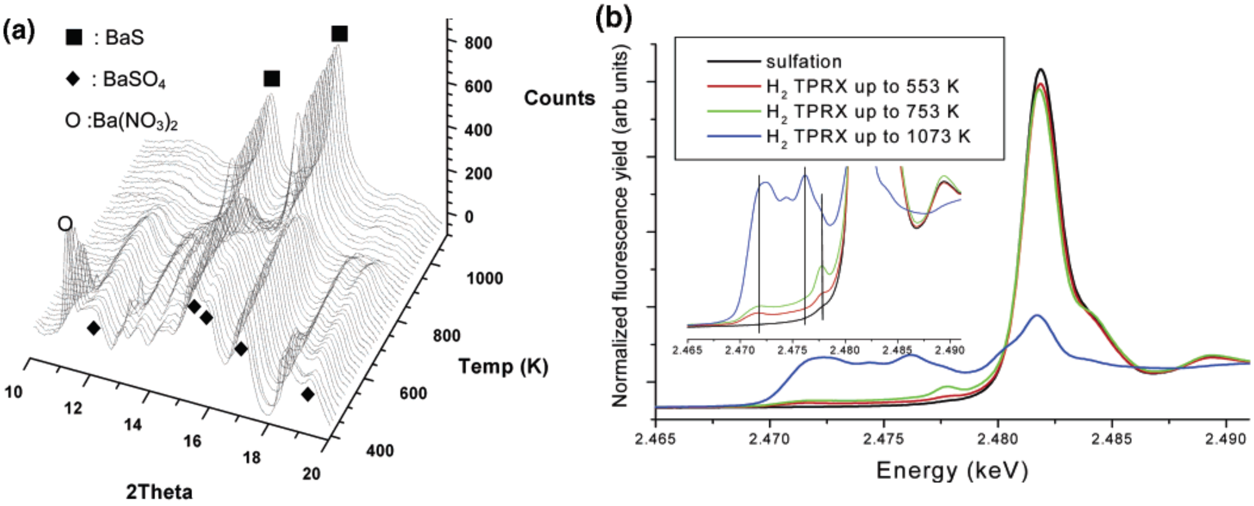


Figure 4.3. Time-resolved x-ray diffraction (a) and S K-edge XANES spectra obtained during desulfation of a sulfated $Pt/BaO/Al_2O_3$ model NSR catalyst under *operando* conditions (Kim et al. 2006).

Pd on La-stabilized alumina: Recent work on Pd automotive catalysts revealed the unique role of La_2O_3. It has long been known that La_2O_3 improves the hydrothermal stability of alumina, preventing the transformation into alpha alumina and surface area loss. The current work shows that La also improves the stability of dispersed Pd species. Researchers found that the dispersed Pd species give rise to low-temperature CO oxidation activity. Further studies will require the combination of infrared spectroscopy coupled with EXAFS and aberration-corrected scanning transmission electron microscopy to investigate how these Pd species could lead to catalysts that provide low-temperature light in automotive catalysts.

Copper on γ-Al_2O_3: The importance of catalytic phase dispersion on overall catalytic activity and selectivity also is highlighted in ongoing work with Cu/γ-Al_2O_3. When Cu is present on the γ-Al_2O_3 surface in atomic dispersion, it catalyzes the reduction of NO primarily to N_2 in an NH_3/NO/O_2 gas mixture. Conversely, over a catalyst containing 3-D copper clusters, the dominating reaction is the oxidation of NH_3 to NO_x—instead of the reduction of NO (Kim et al. 2006) (Figure 4.4). X-ray absorption spectroscopy measurements for the characterization of the electronic state of active catalytic sites under *operando* conditions are crucial toward understand these catalyst systems because it is not known if the copper clusters are metallic or oxidic (Kwak et al. 2012).

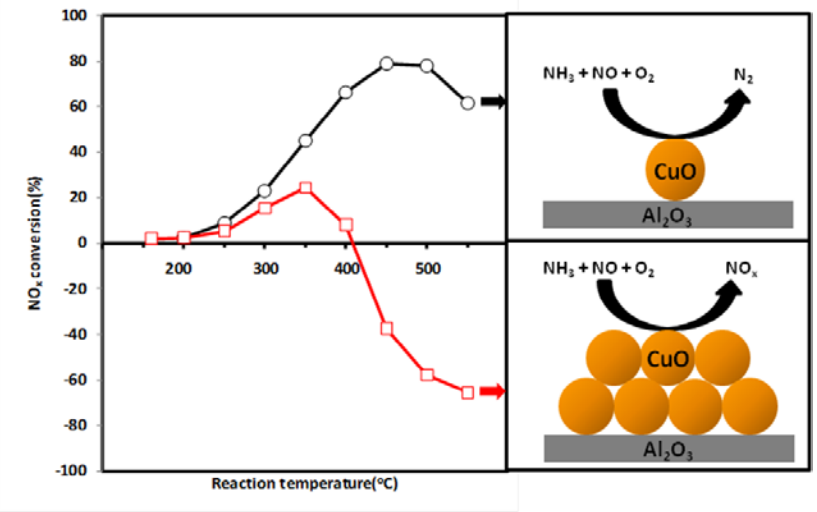


Figure 4.4. NO conversion profiles during NH_3-SCR reaction over 10%- (red) and 0.5%-CuO/alumina (black) (Kwak et al. 2012).

4.4.2 Photocatalysis

Currently, the field of heterogeneous photocatalysis is experiencing remarkable growth due to the world's need for new sources of energy and the potential utility of a variety of heterogeneous catalytic materials converting solar energy into chemical energy (Fujishima et al. 2008). For example, since 1995, there has been a near-exponential increase in the number of publications per year involving TiO_2-based photocatalysts and photocatalytic applications. In 2010 alone, the number of publications exceeded 2,500 (Web of Science). Despite intense research activity, there are no current technologies available for photocatalytic conversion of low-energy molecules, such as water or carbon dioxide, into high-value energy carriers, such as methanol. Low efficiencies and poor matching to the solar spectrum are some of the obvious limitations of heterogeneous photocatalysis. Currently, the majority of research in the literature has approached these problems from an engineering standpoint, where the performance of complex, poorly characterized materials, such as powders and colloids, are optimized through iterative changes to the catalyst and/or reaction conditions (Henderson 2011). These approaches typically sacrifice molecular-level details critical for evaluating overall catalyst performance. To advance the field beyond a phenomenological understanding, fundamental insights are needed into issues such as: charge carrier generation, transport, trapping, and transfer; site specificities; detailed reaction mechanisms; material and structural sensitivities; and interplay between thermal and non-thermal processes.

As noted, one of the significant scientific challenges in heterogeneous photocatalysis is the efficient conversion of absorbed light into useful chemical events. The majority of absorption events in typical photocatalysts, such as TiO_2, that should produce charge carriers instead end up being quenched. Being able to "follow the energy" in time and space from phonon absorption to fate (e.g., charge transfer or charge recombination) will greatly increase understanding into how to optimize photocatalytic efficiencies. Events such as charge separation, energy thermalization, charge trapping, and charge transfer occur in heterogeneous photocatalysis on the picosecond and, in many cases, the sub-picosecond time scales (Henderson 2011). Transient spectroscopy using UV/visible pump pulses and visible/infrared probe pulses have been widely used to track these events. However, these techniques are neither "atom specific" nor spatially resolved. That is, a transient signature in the UV or visible spectra provides no information about the sites in photocatalysts associated with any of these critical phenomena. For example, transient optical spectroscopy has identified the time scales of electron trapping in TiO_2 photocatalysis, but it reveals no information about what or where these electron trap states are. The CXLS offers both probe time scales consistent with the lifetimes and fates of charge carriers in heterogeneous materials, as well as the variability of probe energies to explore the valence band and core-level states of the atoms important in photocatalysis, i.e., those associated with the photocatalyst; added promoters or dopants; unsuspected poisons and quenchers; the solvent; or the reactants, intermediates, and products. Exploring these issues will provide previously unattainable insights needed to further understanding and improve performance in heterogeneous photocatalysis. These issues also can be probed in homogeneous photocatalysis using the CXLS.

4.4.3 Catalysis Using Molecularly Precise Supported Catalysts

Many heterogeneous catalysts consist of an active phase (e.g., a metal or metal oxide) that is highly dispersed on a support phase (e.g., silica or alumina). The individual components generally are inactive or show very low activity. The usual preparation methods for these catalysts, such as deposition-precipitation and wetness impregnation, lead to a variety of active and inactive sites. This is an unavoidable consequence of oligomerization equilibria in the active phase, as well as heterogeneity in the anchoring sites present on the surface of the support phase. It complicates the determination of structures and attribution of catalytic activity to a particular type of site. For example, in the preparation of the Phillips catalyst, Cr/SiO_2, aqueous preparation methods lead to a mixture of isolated monochromate sites and dichromate sites: CrO_3, and Cr_2O_3 (Weckhuysen et al. 1996). While volatile CrO_3 is removed during subsequent high-temperature calcination, the remaining anchored sites can be further altered by interactions with the water vapor generated by dehydration and dehydroxylation of the support (McDaniel 2010).

An alternate, "synthetic" approach to this type of catalyst involves non-aqueous grafting of one or more molecular precursors. The precursors are chosen or designed to lead directly and uniquely to the desired site(s) upon reaction with surface functional groups present in an appropriate support material. For example, the reaction of volatile CrO_2Cl_2 with the hydroxyl groups of a silica surface produces highly uniform, grafted monochromate sites (Demmelmaier et al. 2008). Their structural characterization by x-ray methods (e.g., x-ray absorption spectroscopy) is highly informative due to the presence of short- and medium-range (but not long-range) order, and the resulting structures determined from the x-ray spectroscopic measurements can be directly linked to the reactivity of the catalyst as in Figure 4.5 (Demmelmaier et al. 2009).

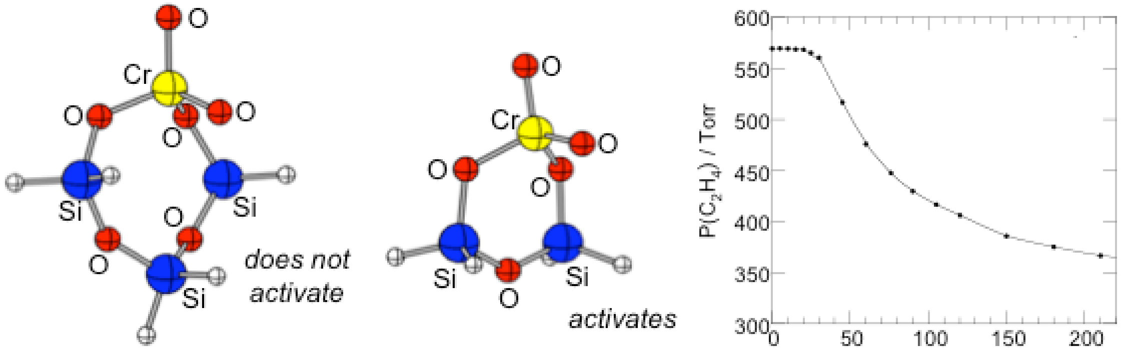


Figure 4.5. Two models for silica-supported chromasiloxanes, showing the effect of ring size on the ability to initiate ethylene polymerization.

The tremendous potential of these molecularly precise catalysts to contribute toward further understanding of active sites and reaction mechanisms is underdeveloped due to the inability to establish their structures under catalytic operating conditions. Often, grafted molecular complexes are thermally sensitive and hydrolytically unstable, and their handling requires a suite of equipment and level of controlled atmosphere purity not available at large, remote facilities such as the synchrotrons. Conversely, the catalysis research facilities at PNNL are ideally suited to making, characterizing, and transferring these materials, and PNNL personnel are highly experienced in this type of chemistry. Some specific equipment needs include: gloveboxes (with sub-ppm levels of moisture and oxygen), Schlenk glassware and vacuum lines, extremely dry solvents, and sensitive reagents. With the proposed CXLS, it is entirely feasible to visualize *operando* x-ray experiments with this type of catalyst using reactors with appropriate, environmentally precise controls.

4.4.4 Challenges in Catalytic Processing of Biomass

Increasing energy demand and diminishing fossil fuels requires using renewable resources for the production of transportation fuels (Huber et al. 2006; Kunkes et al. 2008; Huber and Dale 2009). Replacement of fossil sources for the generation of fuels and commodity chemicals using biologically derived feedstocks has several challenges that must be addressed, including incompatibility with current engines and high reactivity while in storage (Bridgwater 1996; Huber et al. 2006). These challenges stem from the presence of large amounts of organically bound oxygen tied up in sugar molecules. Biomass is both high in oxygen and low in hydrogen. To be compatible with current and future fuels, a biomass conversion process will have to both lower the oxygen content while elevating the hydrogen content. Thus, in most cases, it is desirable to remove some or all of the oxygen from the organic compounds, producing a more stable compound with higher energy content (less oxidized) that also would be closer in structure to current fossil-derived fuels.

Conversion of biomass to transportation fuels and commodity chemicals requires several catalytic processing steps (Elliott et al. 1991; Huber et al. 2006). This processing must be done with high activity and selectivity and often is conducted in liquid water at high temperature and pressure. This environment is extremely harsh for supported catalysts. Fundamental understanding of the nature of these materials has been aided by using specialized *in situ* cells at synchrotron beamlines. Cells, such as the one illustrated in Figure 4.6, can provide information on the oxidation state and bonding of the metals and/or alloys during *in situ*/*operando* conditions and follow the changes that occur to the catalyst structure in catalytic processing.

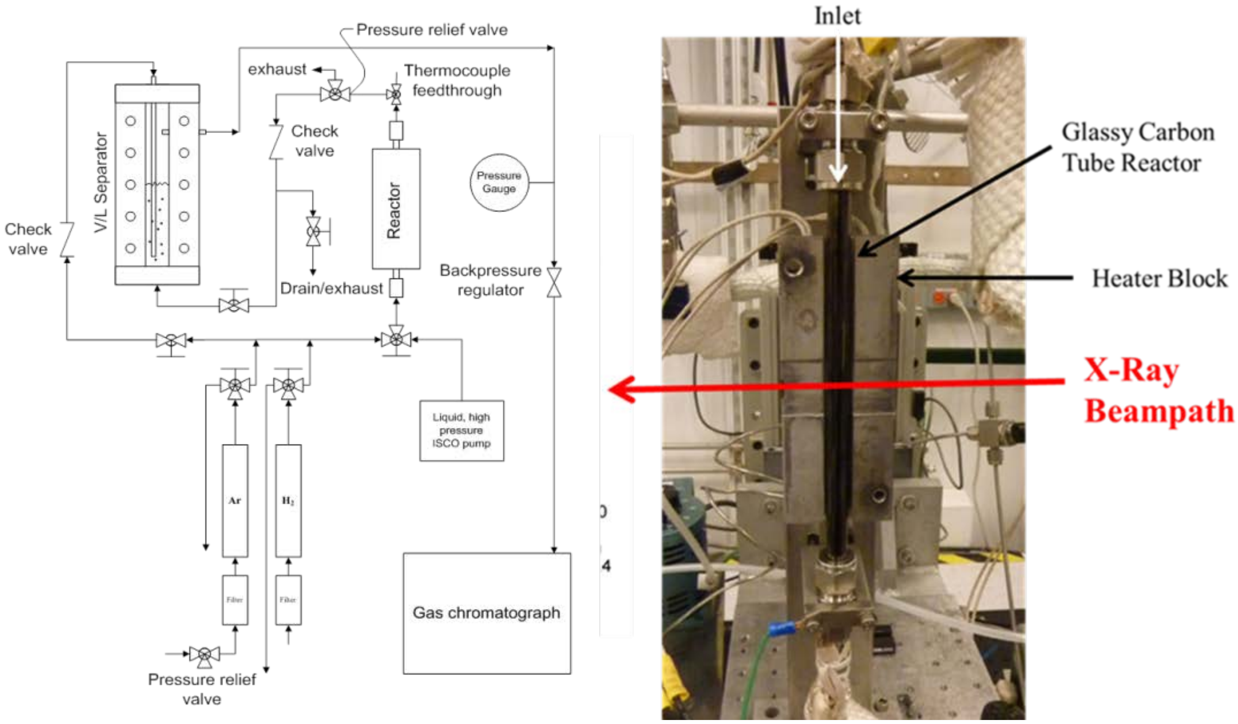


Figure 4.6. High-pressure liquid flow catalytic reactor for biomass conversion.

There is a need for examining the nature of the metal particles (size, composition, support interactions) before, during, and following a catalytic reaction. It is well established that during hydrothermal processing, there often is sintering of the metal ion that results in a major loss in metal surface area. The loss in metal atom surface area can result both in a loss in specific catalytic activity and selectivity. EXAFS is capable of monitoring the change of the average size of metal clusters following processing (Figure 4.7) and providing a correlated average particle size. However, the size derived from EXAFS is only an average as the signal originates from the entire particular element in the sample—typically, there is no spatial information. Determining particle size distribution requires a tie in with other analytical techniques available at facilities such as EMSL, particularly the advanced electron microscopy instrument suite.

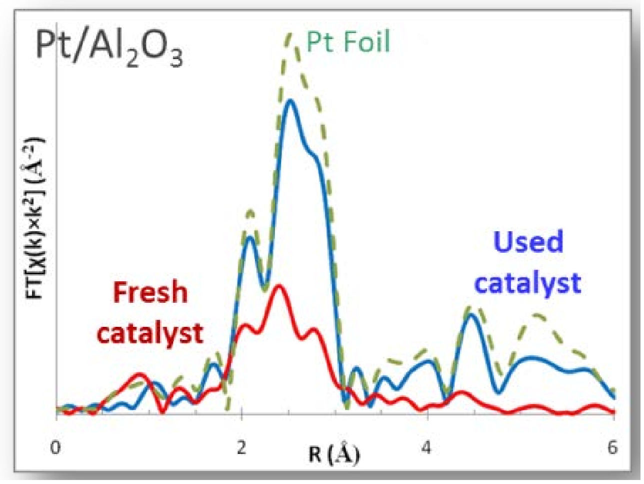


Figure 4.7. Increase in metal particle size following biomass processing.

In addition to the increase in particle size under reaction conditions, *in situ* EXAFS analysis of PtRe/C catalysts showed that Re gets partially oxidized, according to work being conducted at PNNL (Figure 4.8). *In situ* XPS also detected Re oxidation after exposure to hydrothermal conditions. The oxidation of Re under reaction conditions has a significant effect on catalyst activity and selectivity. Re oxidation introduces surface acidity, and the catalyst selectivity shifts from C–C cleavage on Pt/C to C–O cleavage on PtRe/C. Understanding how to control the catalyst selectivity for the cleavage of C–C or C–O bonds is crucial in developing catalysts for the conversion of biomass to liquid transportation fuels.

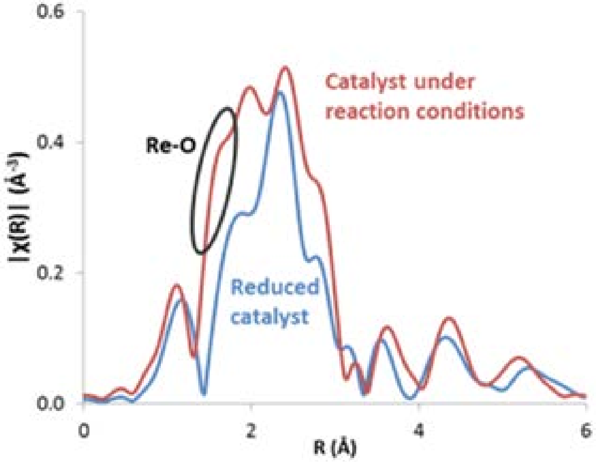


Figure 4.8. Magnitude of Fourier transform of the Re L3-Edge EXAFS, showing oxidation of Re during aqueous phase reforming of glycerol on a PtRe/C catalyst.

With the proposed CXLS at PNNL, appropriately designed *in situ* cells could be easily combined with imaging techniques, such as scanning transmission electron microscopy, and surface sensitive spectroscopy techniques, such as XPS. New transmission electron microscopy cells, currently under development at EMSL, will be able to work in liquid water and provide the necessary particle size distribution typically missing from EXAFS analysis. Additional use could be made of surface-specific sites, which complement the bulk technique of XANES and EXAFS. The complementary information from multiple techniques, such as EXAFS/XANES, scanning transmission electron microscopy, and XPS, would show which particles give rise to activity/selectivity, how they change upon processing, and how their environments influence these factors. Working with EMSL's catalyst team would further improve the research experience because they would be able to suggest other sets of experimental techniques to improve understanding. Ultimately, this should lead to catalysts with improved characteristics for biomass processing.

4.4.5 Link between Model Catalysts and Practical Catalysts

There is a trend of combining complementary *operando* techniques to the measurement of supported heterogeneous catalytic systems (Tinnemans et al. 2006). Because each technique has its particular requirements, not all combinations have proven successful. A recent study of Pd supported on alumina demonstrated the usefulness of combined infrared spectroscopy and high-energy powder diffraction (DRIFT/XRD) (Newton et al. 2010a), as well as with x-ray absorption spectroscopy (DRIFT/XAS). New possibilities could be explored by using CXLS to combine NMR or transmission electron microscopy with x-ray diffraction or x-ray absorption spectroscopy.

To rationalize structure-reactivity relationships for mixed-metal oxide catalysts, well-defined systems are required. Studies involving the deposition of nanoparticles and clusters of VO_x, CeO_x, and WO_x on $TiO_2(110)$ and other well-defined oxide surfaces have shown novel structures with special chemical properties (Figure 4.9) (Rodriguez and Stacchiola 2010) . Model catalyst systems are particularly suited to investigate single- to poly-atom species. These simple models can provide a conceptual framework for modifying or controlling the chemical properties of mixed-metal oxides and engineering industrial catalysts.

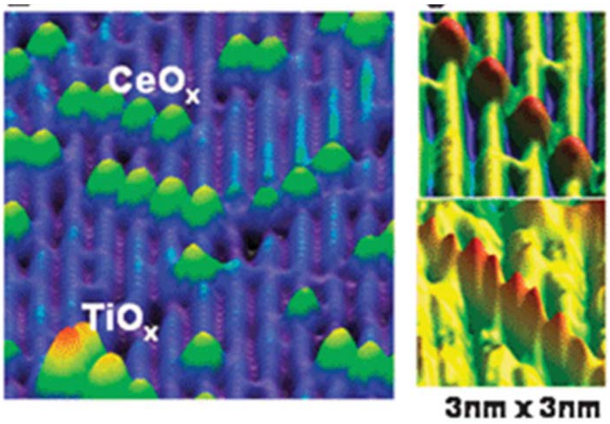


Figure 4.9. Scanning tunneling microscopy images of CeO_x dimers on $TiO_2(110)$ (Rodriguez and Stacchiola 2010).

Surface composition determines the outcome of chemical reactions that provide fuels for energy. XPS is a versatile surface analytical technique that provides quantitative chemical information. However, a significant limitation of traditional photoemission spectroscopy has been its restriction to ultra-high vacuum conditions. To be certain that technologically or environmentally relevant chemical phases are being interrogated, photoemission spectroscopy experiments ideally should be conducted at the conditions where these systems are active. Recently, APPES (Salmeron and Schlogl 2008; Ogletree et al. 2009) has made photoemission spectroscopy measurements at elevated gas pressures possible. This new capability is radically improving the knowledge of surface composition at more representative technological or environmental conditions.

Combining polarization-modulation infrared absorption spectroscopy (PM-IRAS) (Stacchiola et al. 2002) or sum frequency generation (Feng et al. 2011) and APPES for simultaneous vibrational and photoelectron spectroscopy measurements could provide the same capabilities for surface science model catalysts as the combination of DRIFT/XAS for powder catalysts. It would offer a powerful approach to investigating catalytic reactions on model catalysts because they can operate at elevated pressures, ranging from ultra-high vacuum (UHV) to ~10 Torr, and together provide complementary electronic and vibrational spectroscopic information. It also would allow a direct comparison between results obtained by experiments on model systems and industrial powder catalysts using the DRIFT/XRD or DRIFT/XAS combinations. Because infrared (and alternatively Raman) are ubiquitous in most catalytic laboratories, the addition of these techniques to the beamlines would offer two additional operational advantages: 1) it would allow users to optimize their catalytic systems in house then have a point of reference (the vibrational spectrum) to check that they are operating under the same conditions in the light source, significantly optimizing the use of their beam time, and 2) it would allow for using probe molecules to check for beam damage on sensitive samples and adjust exposures to prevent it. Using sum frequency generation as the vibrational spectroscopy, where the beam light for the visible component is extracted from one of the lasers in the CXLS, would allow combined x-ray/vibrational time-resolved experiments.

4.5 Multimodality

In implementing a CXLS, a perceived strength it would bring to PNNL is the development of multimodality in catalyst characterization. As noted, there are many instances in synchrotron-radiation-based catalyst characterization, where more than one technique is used (pseudo-)simultaneously with the x-ray-based method. While adding complexity to the experiment, this methodology makes it possible for both measurements to be made under identical conditions. Thus, the complementarity of the information can be fully used, from an experimental efficiency viewpoint, it also means the experiment only has to be conducted once. In this section, some novel, multimodality-driven research areas are highlighted. These methodologies are meant to be illustrative only and focus on PNNL's current strengths.

4.5.1 Combination of Scanning Tunneling Microscopy and Light-source-based XPS Under Ambient Pressure Conditions to Observe Catalysts at Work

Because the rate of surface catalytic reactions can vary over orders of magnitude with pressure, some reactions do not occur at low pressure ("pressure gap"). High-reactant pressure often is needed to access both the most chemically and less chemically active sites on a surface. Scanning tunneling microscopy has the potential of overcoming the pressure gap in heterogeneous catalysis (Vang et al. 2008). As the tunneling effect is not restricted to a vacuum environment, scanning tunneling microscopy, in principle, can give atomic-scale insight into processes on catalytically active surfaces under the high pressures applied in industrial catalysis. Thus, high-pressure scanning tunneling microscopy opens the possibility to resolve the reacting species in the catalytic process and identify active sites on the working catalyst (Somorjai and Aliaga 2010). The adsorption/desorption experiments up to atmospheric pressures and structural changes of surfaces during reactions can be evaluated with an atomic resolution on model single-crystal or thin-film substrates. The advantage of such a system is that it permits surface studies with the adsorbed species in equilibrium with the gas (Rossler et al. 2005). As such, the adsorption isotherms—with molecular-scale details of surface structures of adsorbed molecules as the coverage changes due to a function of pressure—can be obtained (Somorjai and Aliaga 2010).

However, as scanning tunneling microscopy does not provide information about the chemical identity of surface species, it is essential that additional surface analysis techniques are available. XPS is a well established, chemically specific, and quantitative technique for surface characterization in UHV. Its application in a gaseous environment is hindered by strong scattering of the released photoelectrons in the gas phase (Salmeron and Schlogl 2008). However, the ambient-pressure XPS methodology minimizes signal loss by locating the sample in the vicinity of a differentially pumped aperture system, which also serves as an electrostatic lens system that significantly increases the efficiency of electron collection (Ogletree et al. 2002; Bluhm et al. 2007; Salmeron and Schlogl 2008; Ogletree et al. 2009; Bluhm 2010). Ambient-pressure XPS makes it possible to determine the correlation of catalytic activity with the chemical composition of the working catalyst surface and detection of weakly adsorbed species existing only in equilibrium within the gas phase at high pressure. The high brilliance of the inverse Compton CXLS provides tightly focused, intense x-rays, making it possible to use small front aperture diameters (i.e., improved differential pumping) in ambient-pressure XPS with reduced signal loss at a given pressure and increase the pressure limit in these experiments in general. The application of ambient-pressure XPS with a tunable light source also provides the possibility to measure depth profiles by changing the photon energy, and the kinetic energy of the photoelectrons, without the complications introduced by morphology effects in traditional depth-profiling experiments that rely on changing the detection angle. This kind of measurement affords identification of subsurface species present below the active surface of a working catalyst. Subsurface species might influence the electronic structure of the active surface and influence the catalytic properties of the catalyst. The high-pressure scanning tunneling microscopy system can be attached to a UHV chamber so that sample surfaces can be kept clean using standard surface science techniques.

4.5.2 NMR and X-ray Absorption Fine Structure

Both NMR and X-ray absorption fine structure (XAFS) have a long and successful history in the study of catalysis, yielding complementary information. Because few catalytically active metal nuclei have useful NMR signals, NMR is typically used to gain indirect structural information about the catalyst by using signals from the ligands and/or substrates. In addition, rates of catalysis can be directly determined by measuring either the substrate disappearance or product appearance (if they have appropriate NMR signals). In contrast, XAFS techniques yield direct structural information surrounding the element being interrogated, such as coordination number, oxidation state, types of ligands, and ligand geometries. Combining concurrent NMR with XAFS studies will increase the total amount of information about the catalyst obtained under identical conditions (not two different runs on two different days). In addition, during NMR experiments, the ligand can become detached from the metal center, or other things can happen to nullify all or some of the NMR signal. Meanwhile, the XAFS techniques will continue to yield information. The NMR/XAFS combination could be realized with the CXLS and a horizontal-bore NMR magnet. Proof of principle already has been achieved as normal borosilicate glass and high-pressure (to 5,000 psig) PEEK 5 mm (o.d.) solution NMR tubes have been successfully used in XAFS experiments at APS and in NMR cells. Modifications of the solid NMR experiment also could yield XAFS spectroscopy cells.

4.6 Paradigm Shift in “Beamline Research”

As a research field, catalysis science encompasses a diverse array of scientific research disciplines. Progress usually is only achieved when interdisciplinary teams are assembled to focus on all aspects of the catalyst and catalytic chemistry. A CXLS at PNNL would further this research with broad-reaching consequences. In this section, some specific psychological aspects of conducting catalysis research at a synchrotron light source located on the PNNL campus are highlighted, specifically how the CXLS has the potential to create a new landscape in light-source-based research.

- To facilitate experiments involving sensitive catalyst samples or where some catalyst activation must be done before experimental data collection, sample preparation, testing, and world-class characterization facilities at EMSL will be in close proximity to the experimental end stations at the CXLS.
- Typically, the individual researcher must provide his or her experimental station from the home institution and significant time and cost are involved in shipping and assembly—this would be avoided.
- As previously noted, people working at existing synchrotron source facilities usually are unfamiliar with catalytic processes and cannot respond adequately to user needs, and those who oversee the instruments and facilities often lack the ability to conduct fully involved catalysis science—this would be avoided. Therefore, realizing the CXLS’ potential requires a new style of operation that minimizes barriers to the researchers, not just to access but to skilled assistance with data collection and evaluation. This may best be achieved through direct collaboration with staff scientists at synchrotron radiation facilities, which would be implicit in the CXLS.

5.0 Material Science: Scientific Challenges

5.1 Overview

Recently, materials exhibiting complex multi-property behavior and responses, sophisticated dynamic functionalities, and nanomaterials with entirely new properties compared to their bulk counterparts have become important. Complex materials include engineered systems, such as layered complex oxides that display emergent electronic and magnetic properties depending on the collective behavior of their individual layers, and nano-foams and core-shell nanoparticles with applications in areas from targeted drug delivery to reduction of biomass into fuel to electrical energy storage. The ability to study materials properties and transformations with spatial and temporal resolution over a range of spatial and time scales, starting from nanometers and picoseconds, is critical to materials design and optimization.

A CXLS promises extremely interesting beam properties in terms of pulse duration, photon flux per pulse, and repetition rate that fill the gap between traditional storage-ring-based sources (high repetition rate but very low flux/pulse) and the large-scale, fourth-generation x-ray free electron lasers (very low repetition rate but extremely high flux per pulse). The intermediate beam properties (significant flux per pulse of 106–108 photons), coupled with high and user-modifiable repetition rates (up to 100 MHz), mean that a CXLS has unique potential to study dynamics processes in the linear regime over a diverse range of time scales, from microseconds to approximately 300 femtoseconds. The latter time scale is significantly shorter than what is currently used with third-generation synchrotrons (>30 ps). The flexibility of changing the photon energy from soft x-rays to hard x-rays provides additional benefits to materials science related to improved spectroscopic sensitivity and energy resolution, while the pump-probe experimental regime permits time-resolved interrogation of dynamic phenomena. In addition, x-ray absorption spectroscopy and x-ray tomography capabilities will play a crucial role in the characterization of designer interfaces, which will form the backbone of the materials by design.

The relatively low cost of CXLS sources, along with the short pulses and high repetition rates, makes a CXLS attractive for collocating with existing infrastructure—either complementary characterization, such as PNNL’s materials analysis instrumentation suite, or complex materials synthesis, such as those capabilities located at nanomaterials centers. This integration could include proximity to complex materials fabrication, complementary analysis, or expertise and would have its greatest impact in areas where it is difficult or impossible to displace the infrastructure to a remote synchrotron radiation facility, such as biohazard level 3, highly radioactive materials, or toxic/highly air sensitive materials. At PNNL, there is an emphasis on developing multimodal approaches for materials science, with staff and general PNNL facilities users encouraged to apply multiple techniques where relevant to the scientific problem. The ultimate example of “integration” would be where a sample could be analyzed simultaneously with two or more advanced techniques in conjunction with a CXLS. For example, an appropriately conditioned x-ray beam from a CXLS could be delivered to a sample in the atom probe, aberration-corrected transmission electron microscope, or dynamic transmission electron microscope and measurements performed simultaneously. This could be important for unique samples, where one of the techniques of interest is intrinsically destructive or where dynamic information was the goal. Integration of the CXLS with these instruments also would add a capability not presently possible: chemical, spin, and elemental speciation by tuning the polarized x-ray beam to resonances in the sample. Thus, the collocation of a CXLS proximal to a laboratory with state-of-the-art synthesis and characterization capabilities such as

PNNL would provide the greatest potential for materials sciences applications related to charge transfer dynamics, including exciton generation and charge separation at interfaces, e.g., solar cells, bond breaking, and interfacial chemistry on surfaces, as well as induced phase transition in nanoparticles and thin foils.

5.2 Alignment with the BES Grand Challenges

5.2.1 How Do We Control Materials Processes at the Electron Level?

As mentioned, the CXLS is suitable for materials control studies at an electronic level because it will interrogate both the occupied and unoccupied electron levels of materials with added detail of electronic processes. The CXLS will especially impact materials development focused on electrode processes, energy storage, and photon-electron interactions.

5.2.2 How Do We Design and Perfect Atom- and Energy-efficient Synthesis of New Forms of Matter with Tailored Properties?

Since their discovery 115 years ago, x-rays have been the premier tool to determine structure down to the atomic level. High-flux and high-brightness x-rays in the soft x-ray region are outstanding tools for studying electronic and magnetic structure. With the CXLS' short-pulse time structure, it will be possible to contribute distinctly to time- and space-resolved studies of materials synthesis, as well as characterization of products—all essential components of addressing this grand challenge.

5.2.3 How Do Remarkable Properties of Matter Emerge from the Complex Correlations of Atomic and Electronic Constituents, and How Do We Control These Properties?

Converting light into electrical energy requires a number of steps across varying time scales. The key step in this process is charge separation and charge recombination at donor/acceptor interfaces. To quantitatively understand and control this process, dynamics at the donor/acceptor interface must be followed at the sub-picosecond time scale. Conventional approaches rely on time-resolved absorption and fluorescence spectroscopies in bulk systems. However, interface-specific dynamics often are obscured by a dominating bulk response. The predicted temporal resolution of 100 femtoseconds at the CXLS paired with element specificity would create opportunities for groundbreaking discoveries of the chemical processes that underlie energy conversion across a full range of materials. It also would provide a strategy to accelerate solar-fuel catalyst development by enabling information on structure-dependent, excited-state energy conversion processes to be included in synthetic design.

5.2.4 How Can We Master Energy and Information on the Nanoscale to Create New Technologies with Capabilities Rivaling Those of Living Things?

A significant effort in modern materials science is devoted to understanding and optimizing nanoscale materials for use in energy and information technologies. Research to support biomimetic materials synthesis strategies, as well as direct studies of biological and biochemical processes, would be an important feature of the CXLS because these themes already are well-evolved at PNNL.

5.2.5 How Do We Characterize and Control Matter Away, Especially Far Away, from Equilibrium?

Materials transformations under extreme conditions are critical in future energy technologies, such as next-generation nuclear reactors. A CXLS, equipped with beamlines and suitable sample environments able to contain extreme conditions modifiable *in situ*, will enable studies of these transformations with spatial and temporal resolution.

5.3 Challenges in Materials for Energy Technologies

The performance of current energy conversion devices typically is not dictated by fundamental limitations rather by underperforming materials. The ability to analyze materials using x-ray in/out techniques at high spatial resolution, especially when combined with *in situ* control of the sample environment, and the ability to modify it during measurements, such as real-time changes in temperature, gas composition, electric potential, fuel type, and oxidant, is a powerful approach to solve materials problems in this area. Numerous x-ray techniques—ambient pressure XPS, scanning transmission x-ray microscopy, and small-angle x-ray scattering tomography—are ideally suited to address challenges in energy materials. These techniques would be performed competitively using a CXLS equipped with appropriate beamlines and end stations. Presently, both government-funded initiatives (Li batteries) and private companies (all major car companies have programs in hydrogen fuel cells) are invested in rapidly developing improved technologies for transportation. Various researchers are pushing the performance, reliability, and economic viability of many different alternatives to the internal combustion engine, from batteries to fuel cells to super capacitors (Figure 5.1) (Srinivasan 2008). Better materials for improving energy efficiency in consumer products (electronic devices, lighting, etc.) are another important aspect of this field. CXLS research in this area would have tremendous benefits for energy self-sufficiency, reduced pollution, and decreased carbon emissions.

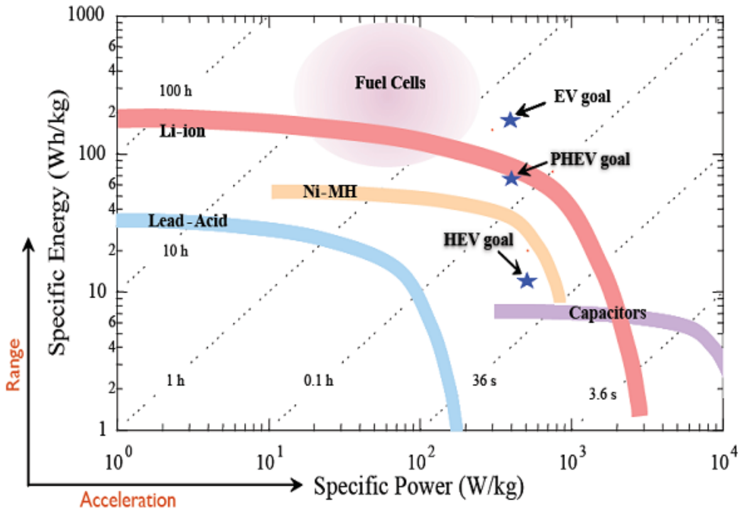


Figure 5.1. Comparison of energy capacity and discharge rate, factors directly related to range and performance of automotive engines, for competing alternatives to the internal combustion engine (Srinivasan 2008).

5.3.1 Solid Oxide Fuel Cells—Dynamics of Phase Transformations

CXLS technology is ideally suited to investigate phase transformations at complex oxide interfaces relevant to energy technology. These interfaces are found in, for example, solid oxide fuel cells, where the oxygen reduction reaction at the cathode is the major performance inhibitor. The stability of these interfaces determines the nature of ionic conduction within the cell and has significant impact on the consistency of fuel cell operation. At a more fundamental level, gaining control over interface formation and stability is important in fulfilling the BES grand challenge to “design and perfect atom- and energy-efficient synthesis of new forms of matter with tailored properties” (Figure 5.2). Because of the exceedingly wide range of functional properties they exhibit in every category—electronic, magnetic, optical, dielectric, and chemical—complex oxides have considerable potential. The richness in properties is derived, at least, in part from the inherent chemical and physical complexities of these materials.

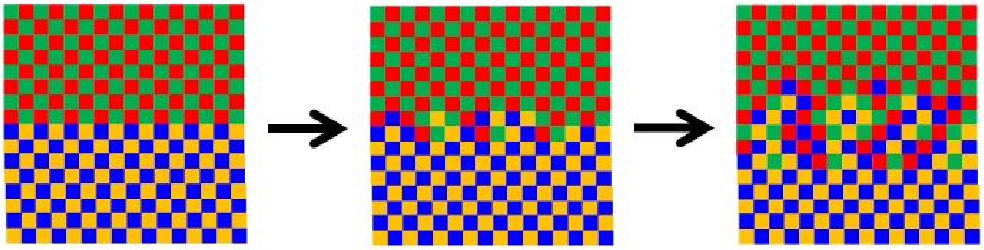


Figure 5.2. Schematic of the time evolution of interfacial intermixing, a process that can be effectively probed using pulsed x-rays from the CXLS. The dynamics of intermixing at the interface can be determined using laser pulses to surmount the energy barrier to intermixing, while time-resolved x-ray scattering monitors the lattice intermixing (courtesy of S.A. Chambers).

The rational design and synthesis of complex oxide interfaces introduces new degrees of freedom to the already wide range of properties found in the bulk. When considering single layers and superlattices prepared by epitaxial thin-film growth techniques, the range of functional properties that can be achieved in bulk complex oxides by mixing and matching cations generates tantalizing possibilities. By combining a high degree of stoichiometric control with reduced dimensionality in the growth direction achievable by ultrathin-film and small-period superlattice growth, it is, in principle, possible to create artificially structured materials with novel properties not realized in the bulk. However, the same forces of nature that afford the ability to generate a range of compositions in complex oxides also can promote solid solution formation at interfaces intended to be abrupt. These forces include mutual solubility and structural similarity, both of which can readily homogenize an otherwise abrupt interface at the junction of materials with different compositions. The problem is exacerbated by the thermal energy available to the system from substrate heating, which, in turn, is required to achieve epitaxial growth, as well as the sometimes high ion energies of species within the laser plume generated during pulsed laser deposition—an exceedingly popular method for complex oxide film growth. Thus, it is of considerable interest to engineer the deposition conditions so intermixing is kinetically constrained at the interface, giving rise to metastable structures that retain a high degree of abruptness.

As envisioned, the CXLS at PNNL has the potential to allow investigators to explore the process parameters that both drive and inhibit intermixing. Using ultrafast XPS and ultrafast x-ray diffraction, the dynamics of interfacial intermixing can be explored by synchronizing heat pulses from a laser with x-ray pulses from the CXLS. The time evolution of interface reaction products and diffusion profiles can be monitored with XPS chemical shifts and intensity profiles, which are determined by atom distributions normal to the interface. Moreover, interfaces prepared by growing amorphous films can be investigated by recrystallizing the amorphous film and following the process using the evolution of Bragg peaks originating in the recrystallized film. Insights from these dynamical studies will guide the formation of rational strategies for making tailored, abrupt interfaces.

5.3.2 Aerogel Supercapacitors

Supercapacitors based on diamond-like carbon aerogels (Pauzauskie et al. 2011) offer the potential for energy storage for transportation applications that rival advanced battery systems. To optimize these systems, it is essential to study the systems *in operando*, or under actual operating conditions of charging, discharging, temperature, humidity, etc. Developing such *in operando* instrumentation is a major challenge that requires good workshops and talented technical and scientific staff. This situation is difficult to establish at a remote facility under extreme time pressures. Thus, many researchers are avoiding such challenges. A CXLS at PNNL, with appropriate end stations for time-dependent x-ray spectroscopy and microscopy, would greatly facilitate this area of research.

5.3.3 Organic Solid-state Lighting

To become a valuable resource, solid-state lighting must demonstrate that it can replace existing technologies. Extensive research is being conducted to develop low-cost devices with high efficacy, reliability, and lifetimes. Progress has been steadily improving, and significant work remains to further improve performance and reduce costs by developing better materials. Organic solid-state lighting relies on stable organic materials with the appropriate electrical and optical properties. To make high-efficiency organic light-emitting diodes (OLEDs) that reduce energy usage and are viable in the marketplace, a number of properties must be simultaneously optimized. Efficiency should be increased by improving the external quantum efficiency and reducing operating voltage, stability increased to provide adequate shelf life and operating lifetime, and cost should be reduced to an appropriate price for consumer adoption (Figure 5.3) (Reineke et al. 2009).

The particular molecular properties that must be optimized relate to the chemical, physical, electrical, and optical properties of the system and its components. A current barrier to progress is the inability to measure electronic structure and transfer under realistic operating conditions. The high photon count per pulse of a CXLS will enable extended and near-edge x-ray absorption spectra to be obtained in dynamic pump-probe experiments, which can be used to follow the electronic states of OLEDs during operation. Simultaneously, the low, time-averaged dose will help prevent radiation damage to the sensitive organic material.

On a basic level, organic building blocks used in OLEDs include donors, acceptors, and emitters with key properties, including the following:

- Electronic structure (highest occupied molecular orbital [HOMO]/lowest unoccupied molecular orbital [LUMO], energy transfer, etc.)
- Stability (photochemical behavior under high photon flux, current, and electric field conditions)
- Optical properties (absorption/emission wavelength, exciton lifetime, quantum efficiency, etc.)
- Packing, 3-D structure and interfaces.

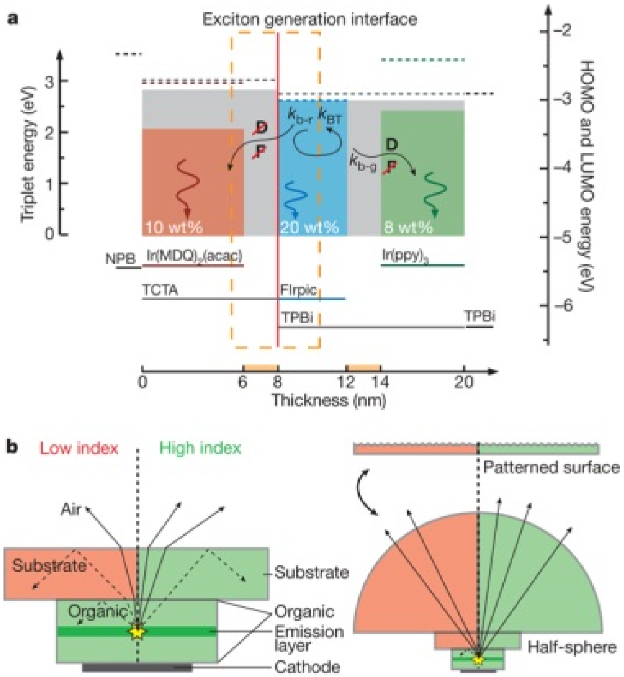


Figure 5.3. Energy-level diagrams and light modes in an OLED: a) Lines correspond to HOMO (solid) and LUMO (dashed) energies. Filled boxes refer to the triplet energies. The orange color marks intrinsic regions of the emission layer. F and D represent Förster- and Dexter-type energy exchange channels, respectively. The orange dashed box depicts the main region of exciton generation. b) The left panel shows a cross section of an OLED to illustrate the light propagation. Solid lines indicate modes escaping the device to the forward hemisphere. Dashed lines represent trapped modes. The right panel shows how a large half-sphere and a patterned surface can be applied to increase light-outcoupling (Reineke et al. 2009).

The measurement of these properties is complicated by the presence of impurities (both innate and from degradation and/or migration of components), the current inability to measure structure and composition under *operando* conditions (in many cases, even *in situ*), the lack of long-range order of the amorphous films used in OLEDs, and the general challenge of the sensitivity of the materials to most probes and environments. The ability to measure compositional, molecular, and device structural changes would offer a new window into the chemical, physical, and photophysical processes that govern the reaction and stability of materials and systems used in OLEDs. Current methods provide some information, but they are inadequate to answer key questions under relevant conditions (Park et al. 2011).

5.4 Advanced Manufacturing and Engineered Materials

With the advent of new nano- and meso-scale materials that may be game-changing for manufacturing, such as nano-reinforced materials for increased stiffness strength or nanostuctured or nanoporous materials for advanced, higher-efficiency battery electrodes, comes new requirements for characterization and understanding the science of advanced manufacturing processes at multiple scales and with time resolution. Self-assembly processes are examples of these advanced manufacturing and scalable synthesis techniques. Light sources are excellent tools for studying these processes because they can provide high-throughput, *in situ* measurements in opaque materials with sub-nanometer resolution. Furthermore, the CXLS would be advantageous for this due to the potential for dedicated *in situ* experiments with high time resolution. This would include specific techniques, such as multiscale and time-resolved diffraction techniques.

5.4.1 Solution Self-assembly for Scalable Synthesis

Biological systems with nanocomposite structures that demonstrate well-controlled architectures based on self-assembly of multiscale and multifunctional building blocks abound. In contrast, traditional approaches for synthesizing these materials rely mostly on mechanical or chemical mixing, which usually produces random distribution of the constitutive phases. Work in this topical area explores a new strategy to integrate controlled nucleation and growth and 3-D self-assembly processes to achieve precise structural control in complex multicomponent materials (Figure 5.4).

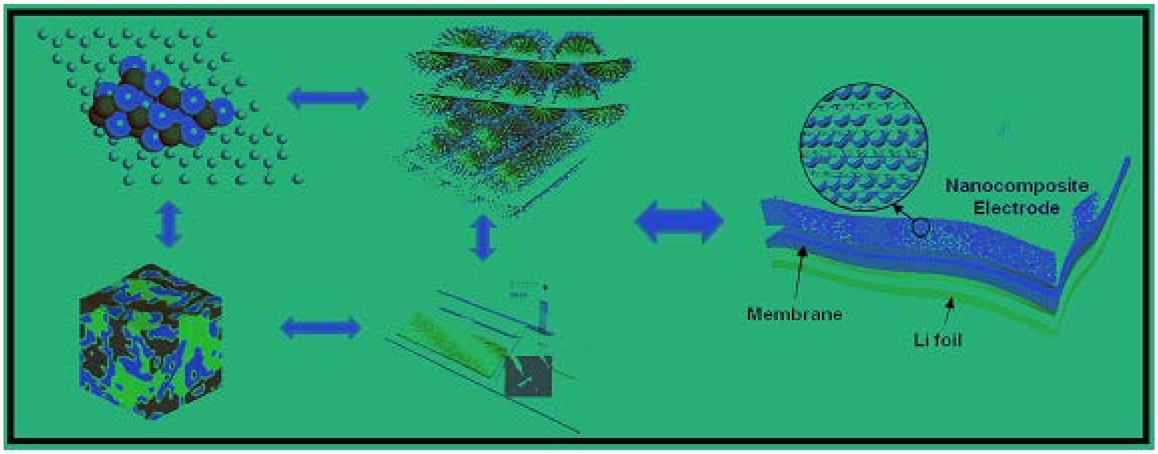


Figure 5.4. Synthesis approach integrates solution self-assembly, computational modeling, and *in situ* characterization to achieve materials with unheralded improvement in properties (courtesy of G.J. Exharos).

This approach points to a new direction for self-assembly using multiple phases and multi-length building blocks. However, due to a lack of knowledge of solution nucleation and self-assembly mechanisms leading to formation of a particular architecture on different length scales, discovering optimum self-assembly routes has proven difficult. Work relies mostly on Edisonian approaches, where chemical precursors are mixed; a material evolves; the material is extracted from solution, cleaned, and dried; then analyzed with respect to structure, chemistry, and function. *In situ* structural and chemical probes are needed to discover, in real time, the formation reactions leading to hierarchical structures. Because these reactions can proceed on time scales ranging from hundreds of picoseconds to days, methods with sufficient time and spatial resolution to probe the intrinsic self-assembly processes are required. A combination of *in situ*, time-resolved x-ray absorption, diffraction, and molecular spectroscopy (Raman) tools represents an effective approach to probe these self-assembly reactions simultaneously to efficiently discover the processing approaches and conditions that lead to a targeted architecture with marked property enhancements. Combining a fast x-ray source with time-resolved Raman methods offers a unique probe of these formation approaches. PNNL researchers have used these probes separately to investigate solution reactions, as exemplified by Raman measurements in a heated, pressurized cell that followed carbon nanoparticle growth kinetics from carbohydrate precursor solutions (Yao et al. 2007). Combining multiple probes to provide time- and spatially-resolved information is crucial to improving the success at achieving these functional architectures. These studies will involve an interdisciplinary team of chemical synthesis experts, materials scientists, computer modelers, and optical spectroscopy experts. Associations with device fabrication specialists and testing facilities established through DOE's applied programs at PNNL also will play a critical role in identifying innovative materials architectures with enhanced properties for device applications.

The development of well-controlled nanocomposite materials and materials architectures that span different length scales has important implications for the next-generation, multifunctional energy storage and conversion technologies that DOE is most interested in pursuing. Work in this area also aligns with the Materials Genome Initiative, launched by President Barack Obama in June 2011, to address the long time frames for incorporating advanced materials into practice. This initiative offers a unique opportunity for the United States to discover, develop, manufacture, and deploy advanced materials at least twice as fast than what is possible today—and at a fraction of the cost.

5.4.2 Dynamics of Solid-state Phase Transformations

A key feature of *in situ* dynamics experiments is their ability to probe the time evolution of condensed matter systems "on-the-fly" as they occur. Consequently, fundamental atomic- and electronic-scale mechanisms can be examined for a range of condensed matter phenomena, including structural changes and electronic transitions occurring during solid-solid phase transformations, melting and re-solidification, phase separation, and nucleation and growth. Solid-solid phase transformations are a fundamental and pervasive phenomenon of materials science whose mechanisms, kinetics, and microstructural development are accessible with time-resolved x-ray analysis. The study of phase transformations often yields high societal impact. The industrial revolution of the late 18th and 19th centuries was enabled by manipulation of steel microstructures through heat treatments that triggered massive and martensitic transformations, an early success of metallurgy. Phase transformations are equally important today, not only in steels, but also in electronic materials, such as phase-change materials for non-volatile memory (Hamann et al. 2006); shape memory materials for medical applications, such as prosthetic implants (Miyazaki 1998); and titanium alloys and nickel-based superalloys for aerospace applications (Boyer and Briggs 2005).

Considerable research activity is focused on understanding mechanisms of phase separation in a range of materials, from metals to compound semiconductor materials. Phase separation is a consequence of positive enthalpy of mixing of two or more elements in a solid solution, which introduces a region of miscibility gap in the phase diagram at lower temperatures. Phase separation can occur through two distinguishable pathways: 1) spinodal decomposition or 2) nucleation and growth. The specific pathway of phase separation operative in materials is determined by the relative position of the material composition within the miscibility gap region of phase diagram, which, in turn, determines their resulting microstructure evolution and properties (Porter et al. 2009). Spinodal decomposition in alloys can be studied by following the evolution of satellite reflections or peak splittings using time-resolved small-angle x-ray scattering at a light source or electron diffraction with high-resolution transmission electron microscopy. *In situ* thermal ageing studies using time-resolved hard x-ray diffraction at a CXLS will provide vital information on the mechanism of phase separation in terms of the kinetics and crystallographic changes. This approach will contribute substantially toward evaluating phase separation tendencies and consequent changes in mechanical and physical properties in a diverse spectrum of materials, from commercial structural alloys to compound semiconductors in microelectronics.

Nucleation of new phases and their growth within the parent phase control the resultant microstructures in materials, which, in turn, govern properties. The interaction of these two processes can either suppress or stimulate phase transformations. Suppression of nucleation occurs when growth of the new phase consumes potential nucleation sites embedded in the parent phase. Stimulation occurs when the stress at the moving phase boundary creates new defects in the parent phase that become nucleation sites, usually associated with martensitic phase transformations. This stimulation of nucleation often is referred to as the “autocatalytic effect” and is responsible for creation of distinct grain morphologies and grain refinement that provide strength in these materials. Nucleation dynamics are commonly viewed in the framework of classical nucleation theory as a competition among three contributions to the total energy: 1) volume, 2) interfacial, and 3) strain energies (Porter et al. 2009). While this framework is generally applicable, the number of quantitative investigations of nucleation is limited because nuclei sizes are small and the event is rapid—conditions perfectly suited to study using time-resolved x-ray diffraction. Recrystallization and martensitic transformations are two areas where research could lead to improved materials. In these processes, materials failure is thought to arise from pre-existing defects, such as dislocations, twin boundaries, and grain boundaries, that promote nucleation. However, nucleation sites for martensite have never been observed directly. Rather, they are inferred from microstructure morphology and interface structure observed in static, post-transition measurements (Zhang et al. 2005). In most descriptions of martensitic transformation, nucleation is considered to be barrierless and governed by interface mobility. Thus, the defect structures at the interface and their interactions with local microstructure dominate the macroscopic transformation behavior, where rates are controlled by the potency of initial sites and those generated by autocatalytic nucleation. Time-resolved x-ray analysis of the interface dynamics and nucleation of new martensite ahead of the propagating phase opens new horizons to observe, understand, and control the detailed mechanisms of phase transformations and better predict transformation behavior and final microstructures.

Another failure of classical nucleation theory is the description of intermediate metastable phases that connect the structure of the parent and new phases. This is a rich, controversial, and potentially widespread phenomenon that remains largely unexplored experimentally. Nucleation of intermediate metastable phases often is suspected when an unexpectedly low energy for nucleation is observed experimentally. The classic example is the formation of Guinier-Preston zones in alloy systems (LeGoues and Aaronson 1984). Other examples of unexpectedly low activation energy for nucleation are steels undergoing the austenite-to-ferrite transformation (Offerman et al. 2002) and strongly driven systems with large undercoolings (van Dijk et al. 2007). These recent findings have generated interest and controversy concerning the prevalence and nature of intermediate metastable nucleation phases (Aaronson et al. 2004). There are no actual observations of nuclei with metastable structures outside the specialized case of Guinier-Preston zones, and observations of nucleation events of any kind have been rare (Xiao and Haasen1991). Observation of new mix mode phase transformations with a composition-dependent displacive component have sparked new interest in experimentally investigating the dynamics of these phase transformations (Pond et al. 2000). CXLS time-resolved x-ray analysis will aid in exploring the phenomenon of intermediate metastable nucleation sites that promote the phase transition, thereby helping to understand the transformation dynamics of the parent phase initial crystal structure to the final product phases. These fleeting phenomena are invisible to static probes applied before and after the phase transition. Detailed observations of the dynamics of interfacial structures using time-resolved x-ray analysis combined with electronic structure calculations using DFT may be used to predict interfacial energies and afford better prediction of transformation behavior.

The structure and kinetics of a moving martensitic interface hold many unexplored opportunities for time-resolved x-ray analysis combined with advanced theory and modeling. Static snapshots of the structures of these interfaces have been characterized (Pond et al. 2000) and modeled traditionally with the phenomenological theory of martensite formation, as well as by the topological theory of martensite formation (Hirth and Pond 1996), which models the interface as a network of defects that more directly relates the interface crystallography to the transformation kinetics. These models have been successful in modeling the static interface. However, the structure of the moving interface and its role on subsequent nucleation events are still a mystery due to the difficulty in observing such a rapidly moving structure.

In summary, time-resolved x-ray analysis provides unprecedented opportunities to elucidate changes in the atomic and electronic configurations occurring during phase transformations in materials. *In situ*, time-resolved measurements at microscopic length scales have the potential to achieve a truly fundamental understanding of phase transformations in condensed matter. Moreover, an important overarching goal of time-resolved x-ray analysis using CXLS is to perform experiments on the time and length scales of numerical simulations. Increasing computational power enables simulations of longer real times and larger physical systems. While the ever-increasing reach of high-performance computational power continues to extend the boundaries of length scales available for numerical simulations, extending the time scale of these simulations is problematic and remains an active area of research. Experimental time-resolved x-ray analysis investigations at the atomic length scale play a singularly important role in filling this knowledge gap.

5.4.3 Phase Transformations in Auxetic Materials

Auxetic materials are those with a negative Poisson's ratio, indicating they expand laterally when stretched. This unusual behavior can be attributed to a hinged microstructure that forms a reentrant network (Figure 5.5) (Valant et al. 2010). However, other mechanisms for this non-intuitive behavior and materials with corresponding microstructures on molecular and macroscopic length scales do exist, including networks of dilating elastic elements, expanding chiral honeycomb lattices, and rotating rigid units.

Auxetic behavior rarely occurs naturally. These materials have long been investigated for their enhanced mechanical properties, for example, shear modulus, break resistance, and superior toughness. Under tensile stress, auxetic materials alter their structure reversibly up to a critical strain when the behavior becomes non-auxetic. Structural changes that occur near this critical point are poorly understood and would benefit from time-resolved measurements as a function of applied load. Studies of crystalline metal oxide systems, where the unit cell shows a hinged structure and associated auxetic properties, are of particular interest. One example is a thin film of the cobalt ferrite spinel structure ($CoFe_2O_4$) that exhibits a high degree of magnetostriction (Valant et al. 2010). Time-resolved x-ray scattering using CXLS would probe this transition near the critical point to understand the mechanical instability in terms of the material's atomic structure.

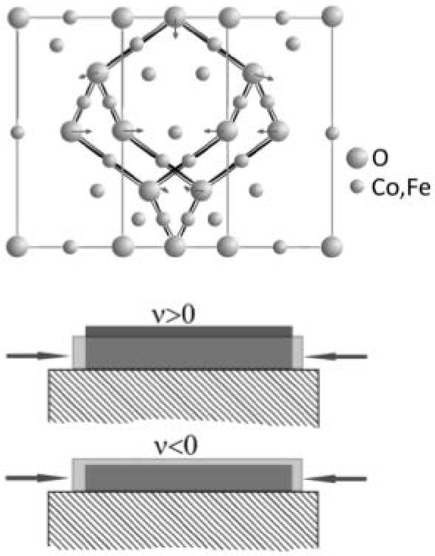


Figure 5.5. The unit cell of $CoFe_2O_4$ (upper); auxetic film distortion under compressive strain (lower) (Valant et al. 2010).

5.4.4 Time-resolved Dynamics of Nanomaterials

The increasing use of highly dynamic and reactive nanoparticles in research and development prompts a need to understand their physical and chemical properties when synthesized, aged in a particular medium, and/or during and following a chemical process for specific applications in energy, environment, and medical sciences. When particle size decreases to the nanometer scale, a number of reasons, including the quantum confinement effect, not only result in different properties from those associated with their bulk form but exhibit novel and unusual behavior that makes characterizing them more difficult. New developments in capabilities, particularly time-resolved measurements such as small and wide-angle scattering along with x-ray absorption measurements using CXLS in native nanoparticle environments, will enable determination of particle size, size distribution, morphology, and crystallinity. The combination of these x-ray capabilities and nonlinear optical methods, such as sum frequency generation vibrational spectroscopy, can be effectively used to understand interactions of organic ligands and nanoparticles.

Bremholm and co-workers used time-resolved x-ray scattering measurements via a synchrotron to demonstrate the use of time-resolved measurements to control synthesis of magnetic nanoparticles with specific properties (Bremholm et al. 2009). Rodriquez and co-workers investigated the structural and electronic properties of $Ce_{1-x}Zr_xO_2$ nanoparticles using time-resolved x-ray diffraction and XANES (Rodriguez et al. 2003). They demonstrated the feasibility of conducting time-resolved x-ray measurements for studying structural transformations in $Ce_{1-x}Zr_xO_2$ nanoparticles as a function of temperature or reaction conditions. In addition to these studies, several others have demonstrated the successful use of time-resolved x-ray analysis to understand the evolution of nanoparticles along with their chemical and electronic properties (Canton et al. 2001; Marmiroli et al. 2010).

5.4.4.1 Time-resolved Interaction of Nanoparticles with Local Environment

Environmental and health impacts from the extensive use of engineered nanomaterials in areas ranging from biomedicine to energy and sensors to cosmetics have attracted concern among researchers and regulating authorities (Oberdorster et al. 1994; Oberdorster et al. 2005; Maynard et al. 2006; Nel et al. 2006). There also is a growing consensus toward understanding and characterizing engineered nanomaterials properties from their as-synthesized conditions to their final state of application and possible release in the environment. Often, it has been noted that nanomaterials do not remain the same from their native state of synthesis to their final state of application and are poorly characterized with respect to their immediate environment (Peralta-Videa et al. 2011). Engineered nanoparticles are known to show perplexing characteristics in biological environments and require detailed characterization to develop a fundamental understanding of the interface interactions. For example, ceria nanoparticles have been shown to possess unique antioxidant properties for scavenging free radicals in both *in vivo* and *in vitro* models, while some researchers found ceria nanoparticles to be toxic via generation of free radicals (Kuchibhatla et al. 2007). While most studies are focused on understanding the impact of engineered nanoparticles to biological systems, few studies have investigated the effect of biological media on the chemical and physical state of the engineered nanoparticles. Because of the dominant role and omnipresence of phosphates in biologically relevant molecules and compounds, phosphates serve as attractive candidates to understand the effect of biological systems on engineered nanoparticles.

It is important to understand the time-dependent nature of the interaction between engineered ceria nanoparticles and phosphate-containing, physiologically relevant media, such as phosphate-buffered saline and various phosphate-based biomolecules (ATP, DNA, RNA, etc.). Combining current characterization techniques available at EMSL with the unique time-resolved capabilities of the CXLS would clarify this interaction. Specifically, monitoring the changes in the P, K-, and Ce L-edges as a function of reaction time and concentration of phosphates, as well as ceria nanoparticles, would shed light on the nature of interactions between them. Cerium oxide nanoparticles prior to and after treatment with varying concentrations of phosphate-buffered saline will be analyzed to characterize the nature of interactions by looking at the P K-edge, $L_{2,3}$-edge, and Ce L-edge. Recently, it was shown that the $L_{2,3}$-edge from phosphorus may overcome some of the limitations of resolving the spectral data and contain more detailed information than the phosphorus K-edge (Kruse et al. 2009). The fine structure will be resolved by analyzing the pre-edge features, edge position, peak shapes, and post-edge features and comparing them with pure phosphate-buffered saline to understand the changes occurring at the surface of cerium oxide nanoparticles as a function of incubation time. In addition, cerium oxide nanoparticles functionalized with various biologically relevant phosphates, such as ATP, phosphoinositols, or other long-chain phosphonates, will be compared with pure compounds to understand the electronic and chemical bonding between the phosphate groups with the surface of cerium oxide nanoparticles.

5.5 Materials Under Extreme Conditions

New materials tolerant to extreme environments, with temperatures up to thousands of degrees and radiation doses up to hundreds of displacements per atom (dpa), are an important necessity for a variety of new engineering applications affecting current and future energy technologies. DOE-BES identified research oriented toward understanding the fundamentals of damage mechanism of materials under extreme environments as an important priority research direction for basic research related to advanced energy technology (DOE 2008). Some examples of such extreme environments include high dpa radiation subjected to structural materials in nuclear fission and fusion reactors and turbine materials in high-temperature and pressure regions of high-efficiency jet engines. The design of next-generation nuclear reactors warrants development of a new class of nanostructured materials, including oxide-dispersion-strengthened steels, nanolayered metallic multilayers, other alloys, and ceramics and oxides that can withstand long-term irradiation under high temperature and pressure. The design of greener and higher-efficiency jet engines with low environmental emissions relies on materials with stable microstructures and very slow microstructure degradation kinetics at high operating temperatures. To obtain unique insights of materials behavior under such extreme environments, state-of-the-art characterization tools, including aberration-corrected transmission electron microscopes and atom probe tomography currently available at EMSL, can be coupled with *in situ* time-resolved x-ray analysis made possible by the CXLS. These experimental investigations, in conjunction with advanced computational modeling, would help develop predictive models of materials behavior under harsh environmental conditions, which would have an enormous impact on overcoming some of the long-term grand challenges related to energy technologies.

5.5.1 Materials for Next-generation Nuclear Reactors

Renewed emphasis on nuclear power has triggered interest in a new class of nanostructured ferritic steels (NFS) now being developed for next-generation nuclear power plant applications (Odette et al. 2008). NFS have the potential for a stable microstructure compatible with operation at high temperatures (>700°C) and under high doses of irradiation (up to 100 dpa) (Ukai and Fujiwara 2002; Akasaka et al. 2004; Klimiankou et al. 2004; Schaublin et al. 2006; Alamo et al. 2007; Kishimoto et al. 2009). In NFS, the key microstructural features are complex Ti-Y-O clusters, which are effective in limiting grain growth and the mobility of dislocations at high temperatures (Ukai and Fujiwara 2002; Akasaka et al. 2004; Klimiankou et al. 2004; Schaublin et al. 2006; Alamo et al. 2007; Kishimoto et al. 2009), affording excellent high-temperature mechanical properties (Alamo et al. 2007). In addition, high surface areas of these clusters are potentially powerful trapping sites for transmutation-produced He atoms, a highly desirable property in nuclear fusion applications. Detailed understanding of the composition and structure of the Ti-Y-O clusters, their resistance to radiation damage, and ability to trap radiation-induced point defects are critical for future atomic-scale design and optimization of NFS materials. While conventional transmission electron microscopy has been extensively used as a tool to study the nature of nanoclusters, it does not have the spectroscopic capabilities or time resolution required to capture the mechanisms associated with the actual primary knock-on atomic displacements, radiation-induced amorphization, dissolution, or reprecipitation. The time resolution afforded by CXLS could shed light on the dynamics of these radiation damage processes. For example, the time scale for the radiation-induced dissolution of nanoclusters is expected to be on the order of a few picoseconds, which also applies to high-energy neutrons generating primary recoiling atoms (at energies up to several hundred keV) and subsequent branching cascades with additional recoiling atoms displaced from lattice sites (Was 2007). Dynamic small-angle x-ray scattering studies of the dissolution of various-sized nanoclusters and structures would reveal relationships between structure, size, and stability and provide fundamental insights into the mechanisms that govern this relationship. Previously, it was shown that a range of composition and interfacial structures for Ti-Y-O clusters (Ukai and Fujiwara 2002) exists, and a core-shell structure with Ti segregation at the interface is expected to produce excellent strength and radiation stability. This hypothesis could be directly tested with a suitable combination of x-ray scattering and ultrafast electron microscopy. The mechanism of point-defect trapping at the interfaces of nanoclusters and other precipitates is another important topic in radiation damage in NFS. This process occurs at a slower rate than the few picoseconds of displacement cascade—well within the realm of imaging via ultrafast electron microscopy. Imaging the trapping events and associated atomic configurations at the coherent and incoherent interfaces of the relevant clusters and nanoscale Y_2O_3, Y_2TiO_5, and $Y_2Ti_2O_7$ precipitates would represent a substantial advancement that would provide insights into the balance between the rate of primary defect generation, such as knock-on displacements, and derivative defect formation, including void and other cluster formations that destabilize the microstructure.

5.5.2 Radiation Damage Tolerance of Nanolayered Composites

By acting as sinks for radiation-induced point defects, the high density of interfaces in nanolayered metallic composites are postulated to reduce radiation damage (Heinisch et al. 2004; Misra et al. 2007; Henager et al. 2009; Hu and Henager 2009; Hu et al. 2009; Nozawa et al. 2009). A detailed understanding of the influence of layer spacing and type of interface on damage tolerance would enable tailoring the interfaces for effective trapping and annihilation of radiation-induced defects. These investigations require experimental and computational capabilities that can analyze dynamic changes in structure and composition of materials at interfaces from a few femtoseconds to several minutes after irradiation. During the initial femtoseconds after a high-energy particle impact, the projectile's energy is transferred to the lattice atoms of the material, generating a collision cascade and producing an avalanche of several point defects. Within a few microseconds, several of the point defects diffuse and annihilate at the nearest interfaces, and remaining point defects cluster together to form larger aggregates. These remaining point defect aggregates eventually interact and generate macroscopic flaws in materials, leading to a catastrophic materials failure. One recent investigation regarding the effect of layer spacing on radiation resistance of Cu-Nb-nanolayered composites demonstrated higher damage resistance of 2.5-nm-layer spaced composites in comparison to bulk Cu or Nb during 150 KeV He ion implantation (Misra et al. 2007). In Figure 5.6, damage-free interfaces without any He bubbles can be observed in the under-focused, cross-sectional transmission electron microscopy image of the Cu-Nb multilayer with 2.5-nm-layer spacing after irradiation with 150 keV He. A high-resolution image of the crystalline, damage-free interface also is shown.

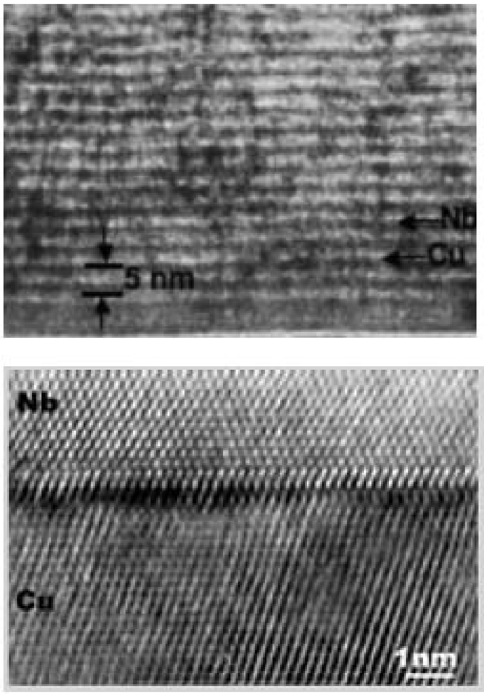


Figure 5.6. Under-focused transmission electron microscopy image of 25-nm layer thickness Cu-Nb multilayer irradiated at room temperature (150 keV helium, 1017/cm^2) (upper); high-resolution transmission electron microscopy image of a Cu-Nb interface from the irradiated region (lower) (Misra et al. 2007).

At present, time-resolved studies of collision cascade and defect annihilation at the interfaces in these nanolayered composites are only performed using computational simulation. Experimental characterization using ion-beam analysis, transmission electron microscope imaging, and diffraction is performed before and after ion irradiations. The combination of computational simulation with *in situ*, experimental time-resolved x-ray analysis using CXLS of different nanolayered metallic multilayers cross-coupled with microstructural characterization using ion-beam analysis, aberration-corrected electron microscopy, and atom probe tomography can offer a conclusive picture of the dynamics of radiation damage evolution in these material systems at unprecedented scales. *In situ* irradiation can be performed using laser- and ion-beam instruments available at PNNL. This would enable probes of the atomic-scale damage mechanism in real time as it occurs in these nanolayered composites at ultrafast time scales and ultra-high spatial resolution. Such a step has enormous implications in advancing the design of radiation-resistant interfaces, which would open doors for designing newer materials with greatly enhanced performance under extreme irradiation conditions for next-generation nuclear reactors.

5.5.3 Damage Initiation and Collision Cascade Analysis in Complex Materials

Radiation damage processes in metals, alloys, ceramics, and biological materials are of paramount importance for nuclear plant safety and future energy needs. Radiation damage in complex multicomponent materials can cause hardening and embrittlement; swelling and volumetric shape changes; impurity segregation, leading to grain boundary chemistry changes; nonequilibrium phase formation; amorphization in complex crystal structures; and a host of physical and chemical changes in material properties. Damage-initiation processes have been widely studied using molecular dynamics simulations with semi-empirical interatomic potentials. However, so far, ultrafast time scales of these processes have eluded real-time experimental study. A collision cascade in a pure metal is a complex event depending on the initial kinetic energy of the primary knock-on atom, or PKA, that can displace several thousand atoms in a few picoseconds of ionization energy loss. Figure 5.7 shows a simulation of the extent of a 200-keV collision cascade in Fe at the peak of damage at 0.67 ps and at the end of the damage event at approximately 14.5 ps (Was 2007) . Time-resolved x-ray analysis using a CXLS would be especially useful to understand the extent and nature of this primary damage event. Although the damage initiation is clearly delineated, the end of the cascade is a bit nebulous and typically consists of several freely migrating defects moving by diffusion in the almost perfect lattice that has been largely restored by recombination events (Was 2007). These initial damage events differ for alloys and ceramics with respect to differences in atomic displacements for each element. In particular for ceramics, amorphous regions might be produced where the crystalline structure is lost completely. The formation of amorphous regions is more typical of covalent or ionic-bonded materials in non-close-packed structures and reduced atomic mobility relative to metals and alloys.

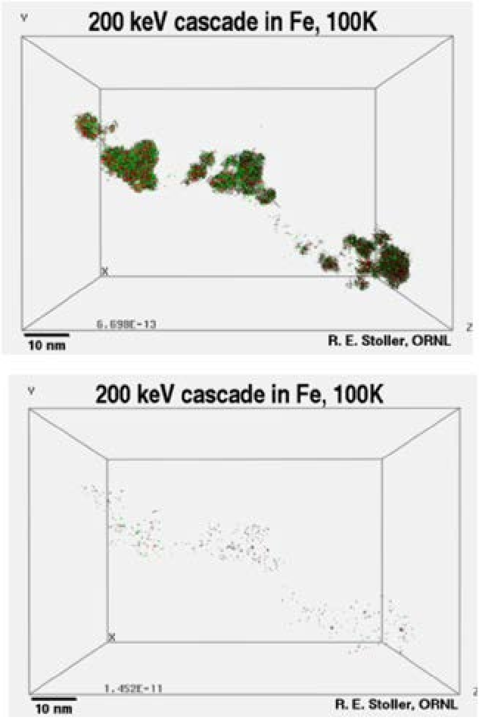


Figure 5.7. Molecular dynamics visualization of a 200-keV collision cascade in pure Fe showing the peak of the damage (top) at 0.67 ps after the initiation of the damage and at about the end of the cascade (bottom) at 14.5 ps. The defects seen in (bottom) are representative of the freely migrating defects produced by the cascade that determine the extent of the radiation damage (Was 2007).

In each case, scientific interest resides in capturing the details of the initial damage event compared to its spatial extent and the atomistic details of the damage formation. The time scales appear to be appropriate for time-resolved x-ray analysis by CXLS. The event trigger would be the incoming ion or charged particle that causes the damage collision cascade. This, of course, considers the case where an ion-beam station or small accelerator is linked to the CXLS beamline end station to allow the damage event to occur during *in situ* time-resolved analysis. Another current research area of damage evolution during cascade overlap, where two or more cascades occur in overlapping or adjacent volumes, also can be studied in this manner. Inert gas injection, such as He, also is of keen scientific interest in this field, especially considering gas bubble formation in irradiated solids. Careful studies of damage annealing in materials by external laser or temperature input would be another important complementary study to damage initiation.

5.5.4 Laser-modified Materials

A picosecond x-ray source would provide unique analytical capabilities for studying laser- or shockwave-compressed materials to analyze emergent behavior under extreme conditions. One major issue relates to fundamental properties of materials under pressures above 3 GPa. Another relates to studies of how rapidly this system equilibrates to resemble a system under static pressure. At such high pressures, hydrogen is expected to become metallic, while sulfur becomes superconducting. Many energy-related materials, such as methane clathrates, have phase diagrams that are unknown but exist in ocean environments. Another possible application of the CXLS at PNNL would take advantage of its location near a working nuclear power reactor to study reactor vessels and other materials under high radiation loads in real time. The performance of such materials in these environments critically determines their performance and applications.

5.6 Engineered Materials

5.6.1 Solid–Liquid Interfaces of Complex Materials

Surface science has an accumulated intellectual capital poised to address problems relevant to present and anticipated societal needs. Our current knowledge of the behavior and reactivity of surfaces has been hard-won and painstakingly carved out on carefully controlled systems prepared in ultra-high vacuum environments. This stringently controlled environment has allowed preparation and characterization of a host of increasingly complex surface systems. However, the majority of natural, industrial, and commercial problems occur at higher ambient pressures. The lack of understanding of such interfacial processes is known as “the pressure gap.” Of all the tools that can probe surfaces, x-rays provide one of the most direct paths to exploring surface interactions in non-vacuum environments.

However, unraveling a complex interface requires a suite of tools beyond the interrogating x-ray beam. Opportunities for solving challenging interfaces will expand by coupling a light source with other probes, such as atomic force microscopy. The CXLS affords the opportunity to collocate the exquisite sensitivity afforded by surface- and interface-scattering capabilities with complementary probes. Examples of near-ambient, but surface-dominated phenomena come from a range of disciplines, and surface/interface x-ray diffraction has made contributions across this range. In geochemistry, the fluid-solid interface has been probed to understand structure and relaxation of the mineral itself (Chiarello et al. 1993), reaction of the mineral with water (Brown 2001), adsorption of dilute species (Qian et al. 1994), and speciation of water near the crystal surface (Fenter et al. 2003). From the point of view of fundamental studies of condensed matter, the (partial) ordering of liquids near the interface with a gas (Magnussen et al. 1995) or solid walls (Yu et al. 2000; Cheng et al. 2001; Reedijk et al. 2003; Fenter and Sturchio 2004) has been revealed in x-ray studies. Still, many open questions remain.

The stable arrangement of the surfaces of polar oxides is another fundamental problem in condensed matter addressed by x-ray scattering. Due to a non-vanishing bulk dipole moment normal to the surface, these materials have an inherently high surface energy (Wolf 1992), but they may lower this energy by forming an air-stable reconstruction (Plass et al. 1998; Barbier et al. 2000a,2000b; Erdman et al. 2000; Finocchi et al. 2004) or by adsorbing materials from the ambient environment (Lazarov et al. 2005). In some cases, reconstruction is stable even under a bulk water layer. Deposition of macroscopic amounts of material from solution (i.e., crystal growth) also has been studied using surface x-ray diffraction (de Vries et al. 1999). Although dating back hundreds of years, the electrochemistry field has been revolutionized by x-rays' ability to penetrate the active medium and directly observe structures (Ocko et al. 1997) and reactions (Renner et al. 2006) at the interface. In particular, the structure of the electrical double-layer has been probed using x-ray scattering not only in an electrochemical cell (Ocko et al. 1990) but with applications in the fields of geochemistry (Predota et al. 2004) and biology (Bitto et al. 2000).

Investigations of catalysis using x-ray diffraction under real-world conditions have given atomic-scale insight to important catalytic reaction mechanisms (Gustafson et al. 2010). Due to weak scattering signals, it has been difficult, but possible, to study surface and interface magnetism (Ferrer et al. 1997) using synchrotron x-ray sources. These studies have an increasing number of applications (Tonnerre et al. 2010). The polarized and tunable CXLS envisioned for PNNL will greatly facilitate studies of interfacial and surface magnetism. In addition to these established fields, a host of potential applications arise in studying, for example, organic-inorganic interfaces important for solid-state lighting (Paoprasert et al. 2008), "top-down" nanopatterning using dip-pen lithography (Braunschweig et al. 2009), or interface reactions found in batteries and supercapacitors (Choi et al. 2006). Thus, a facility capable of coupling incisive x-ray-based interfacial studies with complementary probes would greatly enhance progress in these areas.

5.6.2 Novel Materials—Ferecrystals

Ferecrystals—interwoven structures $[A]_n[TX_2]_m$ (Figure 5.8)—exhibit long-range order along the c axis and in the a-b plane, but they have rotational disorder between the individual dichalcogenide trilayers and the constituents that reduces the structural coherence to ~1 nm in any other crystallographic direction (Rouvimov et al. 2011).

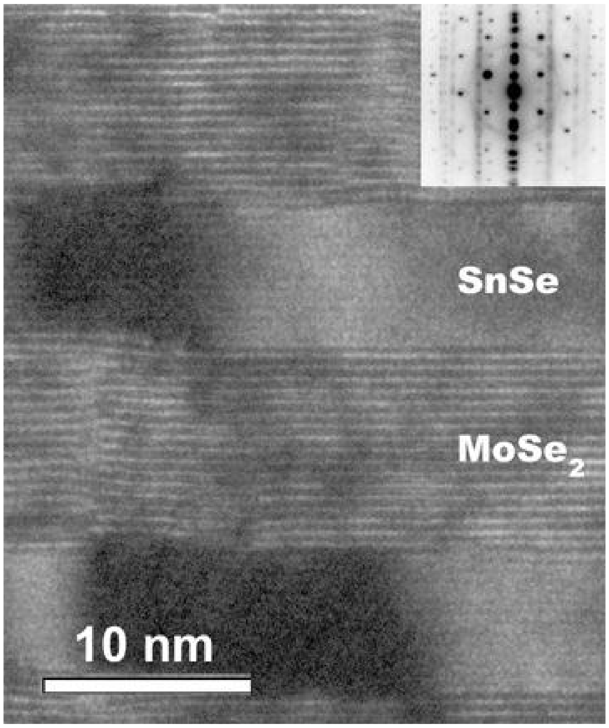


Figure 5.8. Bright-field cross-sectional transmission electron microscopy image of $[(SnSe)_{1+\delta}]16$ $[MoSe_2]_{16}$ ferecrystal grown on Si(001) substrate. Inset shows selected area diffraction (SAD) pattern (Rouvimov et al. 2011)

Materials with extremely low thermal conductivities (down to 0.03–0.05 W/mK) (Heideman et al. 2008; Lin et al. 2008) have been prepared from ultrathin layered elemental precursors, which introduced a novel approach to designing and preparing low thermal conductivity materials. The thermal conductivity of materials is several times lower than theoretically predicted minimum values of the constituent elements. To understand why, the relationship between nanostructure and physical properties must be investigated. Given the absence of long-range order, x-ray diffraction and non-x-ray probes available at PNNL (electron microscopy, atom probe tomography, etc.) are needed to unravel atomic-scale structure and determine bond distances. Synchrotron diffraction data (APS) has been essential in these studies (Zschack et al. 2009). Accurate structural characterization is elemental toward understanding the formation of ferecrystals and their physical properties as new variants of these unique materials are prepared. As extremely coherent interfaces can be fabricated in these films, they, in principle, offer ideal systems where new techniques to study interfaces can be developed.

5.6.3 Novel Materials—Multiferroics

Multiferroics—materials that show simultaneous ferroelectric and ferromagnetic order—are gaining increasing attention as they show promise for the design of new multifunctional devices (ferroelectric memories; new, non-volatile magnetic random access memories; magnetic biosensors). A recent theoretical study predicted that the family of $MTiO_3$ (M = Fe, Mn, Ni) are promising candidate structures where polar lattice distortion can induce weak ferromagnetism (Fennie 2008). Thus far, successful preparation of bulk single crystals or epitaxial films with the desired structure (space group *R3c)* of these materials has proven elusive. Recent efforts at EMSL and PNNL, involving a combination of molecular science computing and thin film deposition, have resulted in the stabilization of $NiTiO_3$ in the predicted multiferroic structure (Varga et al. 2012), and work is underway to pin down the theory-predicted ferromagnetic and ferroelectric properties. Given the subtle structural differences between the thermodynamically stable non-multiferroic ilmenite structure of $MTiO_3$ and the metastable multiferroic *R3c* phase, x-ray probes, including high-resolution x-ray diffraction and XPS, and non-x-ray probes available at PNNL are needed to discern the structures, unravel atomic-scale structure, and determine bond distances. Synchrotron diffraction data (APS) has been essential in these studies (Varga et al. 2012). Accurate structural characterization is elemental toward understanding the formation of these complex oxide thin films and their physical properties as new variants of these unique materials are prepared. The CXLS would offer unique opportunities to study both the structure and ferroic order parameters in these films—systems considered rare in their mechanism to achieve electric-field switching of the magnetization—and contribute to the development of new materials design platforms for complex materials with application in future technologies.

5.6.4 Hybrid Photovoltaics

Recently, semiconductor quantum dots with organic thin-film coating have emerged as promising materials for the production of solution-processed photovoltaic devices. These nanocomposite photovoltaics, also known as “hybrid solar cells,” are promising because they combine the unique size-dependent electronic properties of semiconductor quantum dots with the film-forming ability of π-conjugated conducting polymers (Beek et al. 2006; Guenes and Sariciftci 2008; Kamat 2008; Saunders and Turner 2008; Kippelen and Bredas 2009). They also represent a technology that can be mass-produced at low cost, which is especially important for wider utilization of renewable solar energy.

The conversion of light into electrical energy relies on generation of excitons in quantum dots, conducting polymer from absorption of visible light, and subsequent diffusion of the excitons to the interface where charge separation occurs. The efficiency of the charge separation at the quantum dots-polymer interface depends on the molecular interactions between the polymer and quantum dots, as well as the 3-D distribution of the quantum dots. Agglomeration of quantum dots in polymer can severely limit the charge separation at the interface. The nature of the interface between the quantum dots and the polymer dictates how the charge separation and transfer takes place. In turn, it also influences the overall power efficiency of hybrid solar cells.

One of the leading candidates in hybrid solar cells is CdSe incorporated in a poly(3-hexylthiophene) (P3HT) matrix. The interest in this system arises because the CdSe optical band gap can be tuned by controlling the size and shape of the dots, while P3HT provides better hole-transport compared to most other polymers. Previous studies on CdSe-P3HT were able to indirectly show limited aspects of the charge transfer by monitoring spectroscopic changes in the photoluminescence from these materials. Figure 5.9 (Karakoti et al. 2011) shows how the individual photoluminescence from CdSe quantum dots and P3HT varies and how the photoluminescence is quenched upon incorporation of quantum dots to the P3HT matrix. The quenching of individual photoluminescence peaks is direct evidence of charge transfer. The electrons from the P3HT matrix are transferred to the quantum dots, while the holes from quantum dots diffuse to the polymer.

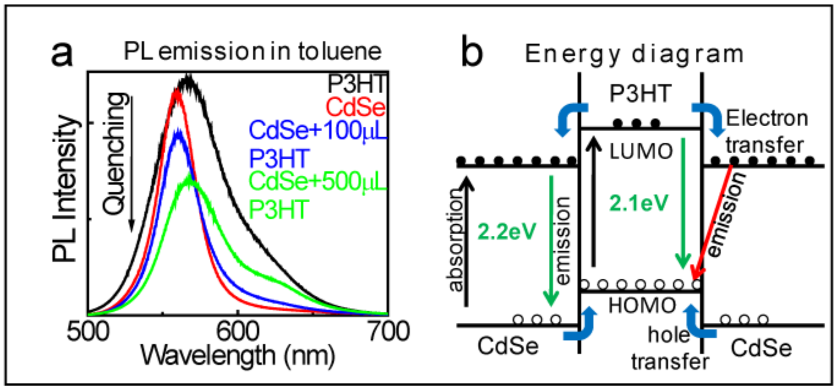


Figure 5.9. a) Photoluminescence L of CdSe (0.25 mg/mL) and poly(3-hexylthiophene) (P3HT) (0.5 μg/mL) before and after mixing shows the quenching of photoluminescence (PL) from both P3HT and CdSe with appearance of a low-energy emission from recombination of electrons in CdSe with holes in P3HT and b) energy-level diagram depicting the origin of new low-energy band (Karakoti et al. 2011).

For the development- and theory-informed design of hybrid photovoltaics, it is necessary to gain a detailed understanding of the hybrid photovolatic structure and corresponding charge transfer characteristics. In this respect, CXLS' sub-picosecond time resolution provides unique capabilities to study charge transfer processes in CdSe P3HT hybrid photovoltaics. For example, the time associated with charge transfer is on the order of tens to hundreds of picoseconds—well within CXLS capability. Thus, ultrafast XANES designed in the pump-probe experiments is expected to provide detailed insights on the photo-induced electronic structure variations and band alignments, which can be directly related to the charge transfer.

Also, CXLS offers a unique platform for integration of x-ray spectroscopy, microscopy, and time-resolved capabilities with additional modes of structural analysis, such as transmission electron microscopy and atom probe tomography. Local access to the CXLS at PNNL would greatly streamline the integration. While the integration of CXLS and transmission electron microscopy would require substantial developments and resources, it is fundamentally feasible due to recent advances in electron optics. In particular, the development of aberration correction now makes it possible to incorporate space-requiring devices in the pole piece gap while maintaining atomic resolution. Electron microscopy characterization will provide an atomic-level view of CdSe quantum dots prior to and following incorporation into the P3HT matrix and enable insights into the nature of the interfaces, which, in direct correlation with time-resolved x-ray spectroscopy, would provide a basis for groundbreaking discoveries in hybrid photovoltaic materials.

5.6.5 Advanced Sensing and Energy-efficient Materials

In the coming decade, materials design will be driven by the challenge of achieving new properties that can provide solutions to emerging issues of energy supply and utilization, information access, and national security. As a prime example, condensed matter physics has had a profound impact on information technology over the past 25 years, and this trend shows little sign of slowing. Conversely, projections for computer processors fabricated with current technology indicate that hard material limits for the power dissipation of transistor junctions soon will be reached. Although parallelization helps, a new approach to power consumption is needed to make more than incremental gains in computing capacity. Simply lowering the energy consumption of semiconductor devices by a few percent will have a transformative impact on the billions of consumer devices now in use (Ellis 2009).

Complex oxides compose a broad class of materials that includes ferromagnetic, ferroelectric, multiferroic, and other systems with intimately connected electronic and magnetic properties (Scott 2007; Vaz et al. 2010). In correlated electron materials, complex coupling between the spin, charge, orbital, and lattice degrees of freedom leads to extraordinarily rich physics that cannot be understood within the conventional theory of metals (Tokura 2003; Dagotto 2005). Tuning the structure to control the ground-state properties of these materials is attractive because tiny stimuli can induce very large transitions in their electronic response that span several orders of magnitude. For example, the electrical conductivity of perovskite manganites can be made exquisitely sensitive to external stimuli, such as temperature, pressure, and optical and magnetic fields (colossal magnetoresistance), by doping and applied strain (Ahn et al. 2004; Kim et al. 2010). This behavior, thought to be due to the coexistence of multiple phases and competition between the various degrees of freedom in these materials, is poorly understood at relevant length and time scales (Israel et al. 2007; Shenoy and Rao 2008; Weber et al. 2009). Despite a large body of experimental work on the average properties of these materials, a general understanding of the individual phases and mechanisms behind their coexistence remains largely unexplored. Clarifying how the domain structure and lattice strain drive the collective behavior of electrons in materials at the mesoscale will enable development of faster and more energy-efficient devices that take advantage of electron spin, as well as charge.

Efforts are accelerating toward realizing the vision of non-volatile, spin-based memory devices; transistors; and “instant-on” computers that require almost no power based on devices that fully exploit electron spin (Zutic et al. 2004). Similarly, research on multiferroic devices that offer control of magnetism with applied electric field and vice-versa (Chu et al. 2008; Choi et al. 2010; Kim et al. 2010; Wu et al. 2010) are of major interest to the data storage and semiconductor industries. The possibility of propagating a spin-polarized supercurrent over long distances also is intriguing for voltage-controlled spintronic and spin-based quantum devices (Eschrig 2011).

The behavior of each of these systems strongly depends on their internal strain, domain structure, and dynamics. The ability to visualize these properties on the mesoscale and determine the order parameters governing them is indispensable for closing the structure-property-function loop for their eventual incorporation into devices. This requires new tools with sensitivity to spin and strain, as well as structure in crystalline samples up to microns in thickness, under *in operando* conditions. Picosecond time resolution is needed to probe the time scales relevant to electron transport and phonon interactions. Scanning x-ray diffraction methods coupled with nanofocusing offer 30-nm spatial resolution and 0.01% strain sensitivity (Klug et al. 2011; Ding et al. 2012). Tuning an intense polarized x-ray beam to the K- and L-edge resonances in the transition metals and rare earth elements in these materials will enable imaging of spin, orbital, and charge-ordered phases. Alternatively, under some conditions, the partially coherent and broadband character of the CXLS beam also may be amenable to non-resonant structure and strain measurement by coherent x-ray diffractive imaging (Whitehead et al. 2009; Abbey et al. 2011), both static (Pfeifer et al. 2006; Robinson and Harder 2009; Newton et al. 2010b) and time-resolved (Dufresne et al. 2011). Although recording weak diffraction signals on these short time scales will require averaging many reproducible events, the CXLS’ sub-picosecond capability opens up new territory currently inaccessible at synchrotron storage rings. Coupling these methods with the CXLS’ brightness and short-pulse widths could result in a substantial impact on our understanding of complex oxides, leading to development of the next generation of smaller, faster, and lower-power devices and sensors.

5.7 Theoretical Support for Materials Science at the CXLS

Next-generation photon sources have made studies of materials of unprecedented precision and sophistication possible. However, their power cannot be fully realized without a quantitative interpretation. This is especially important for spectroscopies, such as resonant inelastic x-ray scattering (RIXS) or x-ray absorption (XAS). Thus, theoretical investigations provide a complementary tool that can significantly improve the CXLS' performance. Moreover, they facilitate the synergy between theory and experiment that would enhance the scientific benefits. This synergy has been exploited, for example, by the European Theoretical Spectroscopy Facility, which developed virtual "theoretical beamlines" that simulate the spectra obtained at modern x-ray sources.

To make this possible in the context of CXLS, it is proposed to simultaneously develop links to a set of theoretical tools developed by John Rehr and others that are highly optimized for materials and chemical investigations with x-rays. These tools also are user friendly and include next-generation theoretical tools, including DFT, molecular dynamics, and next-generation x-ray spectroscopy codes. These would be available either on local PNNL machines or via access to remote sites explicitly set up for this purpose, such as the European Theoretical Synchrotron Facility or the recently launched cloud-based initiative (Rehr et al. 2010).

5.8 Impact of CXLS on Materials Science at PNNL

The preceding examples of scientific challenges in materials science for which CXLS provides unique or enabling capabilities are based on a few of CXLS' intrinsic properties that are worth emphasizing because they are overarching and affect many areas of potential research.

5.8.1 Dynamics

In terms of pulse duration, photon flux per pulse, and repetition rate, CXLS promises extremely interesting beam properties. It can fill the gap between traditional storage-ring-based sources (high repetition rate but very low flux/pulse) and the large-scale, fourth-generation x-ray free-electron lasers (very low repetition rate but extremely high flux per pulse). The intermediate properties (significant flux per pulse (10^6–-10^8 photons)) and high and user-modifiable repetition rates (up to 100 MHz) mean that CXLS has the distinct potential to study dynamics processes in the linear regime over time scales from sub-femtosecond to microsecond. In fact, the greatest potential for materials sciences applications at CXLS is the short-pulse duration enabling time-resolved investigations of dynamic phenomena. For that purpose, pump-probe schemes with optical lasers should be designed into the facility from the beginning (see Section 6.0). In particular, a perfect timing link between the x-rays and optical pump lasers should be stressed.

This type of new probe could address materials science questions such as:

- Charge transfer dynamics, such as exciton generation and charge separation at interfaces in solar cells (time-resolved spectroscopy; femtosecond time level)
- Bond-breaking and interfacial chemistry on surfaces (time-resolved spectroscopy; femtosecond time level)

- Induced phase transition in nanoparticles (time-resolved spectroscopy; scattering, femtosecond to picosecond time level).

5.8.2 Enabling Multimodal Studies: CXLS at PNNL Could Revolutionize Materials Science

CXLS is compact and relatively low cost. Yet, it has powerful x-ray properties that generally are competitive with third-generation light sources. In two areas—flexibility of repetition rate and short-pulse widths—they are superior. These properties proffer several advantages.

5.8.2.1 Local

CXLS facilities are low cost relative to third- and fourth-generation x-ray light sources. Yet, they may provide comparable performance in flux and brightness, as well as some potential advantages in areas of pump-probe time-resolved studies. Their relatively low cost makes them attractive for collocating with existing infrastructure—either complementary characterization, such as PNNL's outstanding suite of materials analysis instrumentation, or complex materials synthesis, such as those at nanomaterials centers. At present, there are significant barriers to using advanced x-ray methods for materials analysis by researchers at DOE, universities, and industrial labs not located at or close by one of the national synchrotron research facilities. For example, at the CXLS workshop, PNNL applications scientist Dan Gaspar described the need to study electronic and structural properties of interfaces of buried organic layers in OLEDs under transient operational conditions. The complexity of setting up the required test situation under the extreme time pressures dictated by the current practice of allocating, at most, a few days at current synchrotron research centers and the long time interval between beam times means it is not practical to use synchrotron x-rays in this research, although there are several x-ray techniques that would be ideal. A CXLS at PNNL would enhance time-critical applications programs in materials science. It also would provide the extended period of access needed to stage complex experiments.

5.8.2.2 Integrated

CXLS facilities can be tightly integrated within the existing infrastructure. This could include proximity to complex materials fabrication, complementary analysis, or expertise. Such integration would have its greatest impact in areas where it is difficult or impossible to displace the infrastructure to a remote synchrotron research facility, including research related to national security, biohazard levels 3 and 4, highly radioactive materials, or toxic/highly air-sensitive materials. PNNL has already assembled a suite of leading capabilities for atomic resolution imaging including atom probe tomography, environmental, dynamic and aberration corrected TEM. The onsite capabilities can be immediately utilized for multimodal and multiscale analysis in concert with the CXLS. For example, an x-ray beam from CXLS could be delivered to a sample inside the dynamic transmission electron microscope to initiate an x-ray induced process or to provide simultaneous measurements of the same sample with both electrons and x-rays. Integration of the CXLS with other instruments at PNNL would further enhance chemical, spin and elemental speciation, by tuning the polarized x-ray beam to resonances in the sample.

5.8.2.3 Novel

The CXLS’ pulse width and power per pulse are tunable. The natural pulse widths (0.5–-10 ps) are significantly shorter than those in third-generation synchrotrons (>30 ps). In addition, the compact size means it is simple to achieve temporally precise coordination of the pump laser timing with the short-pulse lasers used to generate the electron bunch at the photocathode, a synchronization especially challenging at both third- and fourth-generation light sources due to their large size and complex electronic environments. Thus, it would be possible to perform dynamics studies in the few picosecond regime, which currently is not possible or involves special challenges at other light sources. At the workshop, Gwyn Williams suggested another interesting possibility: pass the electron beam after generating the inverse Compton x-rays through a short undulator to generate pulsed THz radiation, which could be routed to act as the pump for studies of electron-phonon coupling in correlated electron materials (high Tc, etc.). Another potential application for understanding THz control of a metal/insulator transition in a correlated electron material, such as $Pr_{0.7}Ca_{0.3}MnO_3$, involves modulation of the electron-phonon coupling.

6.0 Technology

6.1 Overview

In incorporating a CXLS at PNNL, we will exploit recent advances in accelerator and laser technologies that enable a high-brilliance compact source of light from the extreme UV to x-rays that has performance, cost, and size similar to a single beamline at a large synchrotron facility. X-ray beam performance will approach the large synchrotron facilities in general and will exceed them in the important parameters of pulse length and source size.

The proposed CXLS is based on ICS, where a high-brightness electron beam collides with an intense laser pulse and upconverts the laser photons into x-rays. ICS x-ray emission physics (Brown et al. 2004) is quite similar to undulator emission and many of the same relationships hold, particularly the resonance equation that relates the x-ray wavelength to the electron beam energy and laser (or undulator) period. ICS’ key advantage over undulator radiation is that the laser wavelength is orders of magnitude shorter than the undulator period, allowing a much lower energy electron beam to produce the x-rays. The resonance equation that determines radiation wavelength for undulators is $\lambda_x = \frac{\lambda_w}{2\gamma^2}\left(1+a_w^2\right)$, where $\lambda_x \approx 1$ angstrom is the x-ray wavelength, $\lambda_w \approx 3$ cm is the undulator period, $\gamma \approx 10^4$ is the relativistic factor, and $a_w \approx 1$ is the undulator strength parameter. It is the relatively long undulator period of ~3 cm that drives the electron beam up to multi-GeV energy to satisfy this equation for x-ray production. The corresponding resonance equation for ICS, $\lambda_x = \frac{\lambda_L}{4\gamma^2}\left(1+a_o^2\right)$, differs in form only by a factor of 2 due to the change from a static undulator field to propagating laser field. However, because the laser period $\lambda_L \approx 1$ micron is more than four orders of magnitude shorter than an undulator period, the required electron energy is reduced by two orders of magnitude. This change dramatically shrinks the accelerator’s size and cost.

However, a bright ICS x-ray source does put significant demands on the properties of the electron beam and laser, requiring a high-brightness electron beam and a stable short pulse laser with very high average power. A bright electron beam is defined by high density in six-dimensional phase space, i.e., many electrons in a short bunch with low emittance and low energy spread. An electron beam with these properties is necessarily produced only in a linac, where the key beam properties may be separately controlled and manipulated. Synchrotron rings, whether small or large, cannot produce this type of beam because synchrotron emission and ring dynamics lead to equilibrium electron beams of much lower six-dimensional density than a single-pass accelerator. The ring bunch length (tens of picoseconds) and transverse emittance (few mm-mrad) are orders of magnitude larger than a modern high-brightness linac. Both of these properties limit the ring electron focus size at the ICS interaction point to tens of microns. Thus, the x-ray flux is relatively low, is of low coherence, and is not in the femtosecond regime.

Superconducting radio frequency (SRF) technology operating in continuous wave (CW) mode combines the superior electron beam quality possible with a single-pass linac with the stability and high repetition rate of a ring. To limit wall plug power, the very high repetition rates envisioned (~100 MHz) require a superconducting linac. Room temperature copper linacs are limited in repetition rate by the power losses in the cavity walls to, at most, kHz rates. Over the course of the last few years, the

Massachusetts Institute of Technology (MIT) team has pushed the development of SRF accelerators optimized for compact sources, which differs from their traditional role in high-energy physics. This has led to research and development programs, funded by DOE-BES and the Office of Naval Research, to develop SRF photoinjectors at the University of Wisconsin-Madison and the Naval Postgraduate School (NPS) and to a significant DOE-BES effort at the Thomas Jefferson National Accelerator Facility, or JLab, and MIT to develop optimized SRF cavities and a compact, high-efficiency cryomodule for an SRF linac. To reduce the size and cost of the liquid helium equipment, which typically are larger than the linac itself for small facilities, all of the SRF structures under development will operate at 4 K rather than the traditional 2 K. To accomplish this, the structures must operate at lower frequency (<500 MHz) and with lower gradients than those of high-energy physics. Furthermore, they will operate in CW mode rather than pulsed. The surface resistivity of SRF materials scales as the square of the RF and exponentially with temperature below the critical point. Therefore, operating in CW mode at 4 K requires lowering the RF and also reducing the gradients to achieve low heat loads and operating cost.

Figure 6.1 depicts the major components of a CXLS source. They consist of the SRF photoinjector to produce a high-brightness, high-average current electron beam and an SRF linac that accelerates the beam to tens of MeV. A high-average-power cryo-cooled infrared laser, operating at ~1kW average power, is coupled into a coherent enhancement cavity that builds up to ~1 MW of stored optical power. The electrons and laser pulses collide at the interaction point within the coherent enhancement cavity to produce x-rays that are captured and prepared for experiments by a set of beamline optics designed to handle the particular characteristics of the CXLS x-ray beam.

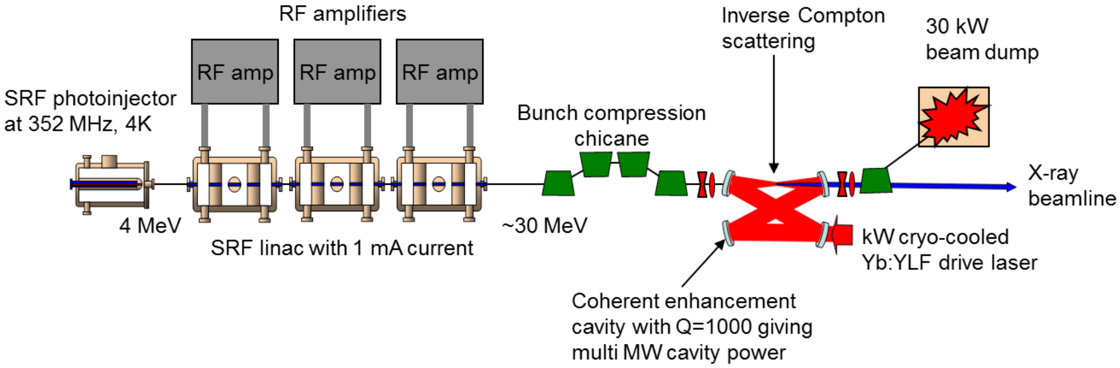


Figure 6.1. CXLS layout showing major components, including SRF photoinjector, SRF linac, electron beam transport magnets, high-power laser, coherent enhancement cavity where ICS takes place, and electron beam dump.

The CXLS flux is optimized for a very small source size (~1 micron) with relatively large divergence (~10 mrad). This format is ideal for coherent imaging and other experiments requiring a large field of view. The product of source size and divergence is equivalent to a synchrotron beamline so that microfocus optics run in their reverse configuration also can produce collimated x-rays, as required.

The major components may be joined in different combinations for different applications. For example, soft x-rays only require a low-energy electron beam that may be produced by the photoinjector alone, making the source even more compact and less expensive. The majority of x-ray science is done in the frequency domain requiring high average flux. The CXLS can meet the needs of multiple users by accelerating the electron beam to full energy then distributing it among multiple beamlines with fast kickers. This would enable operation of several hard x-ray beamlines, each operating at MHz rate with high average flux. Pump-probe and other time-domain experiments require ultrashort pulses below 100 fs with a relaxation time of ~1 ms between shots. By controlling the timing of the cathode drive laser that produces the electron bunches, the CXLS can achieve this pulse format while simultaneously serving high average flux beamlines. We envision each beamline operator independently controlling the timing, repetition rate, and other properties of their own beamline by controlling one or more photoinjector drive lasers that interleave pulses, limited only by the linac's maximum repetition rate of ~100 MHz. This is possible because each electron bunch goes to only a single user that may be independently controlled by the user.

6.2 Accelerator Components

6.2.1 Photoinjector

The SRF photoinjector is a key component needed to reach the CXLS' performance goals because it produces the very-high-quality electron beam at high repetition rate. Photoinjectors have demonstrated extraordinary brightness at lower repetition rates around 100 Hz, especially at low charge (Ding et al. 2009), significantly exceeding the single-bunch parameters required by the CXLS. SRF photoinjectors capable of producing similar electron beam properties at rates of 100 MHz and higher currently are under development at the University of Wisconsin-Madison (Bosch et al. 2009) and NPS (Harris et al. 2011) in collaboration with Niowave Inc. Figure 6.2 shows the Mark I version of the NPS photoinjector that operates at 500-MHz RF and is cooled to 4 K by liquid helium.

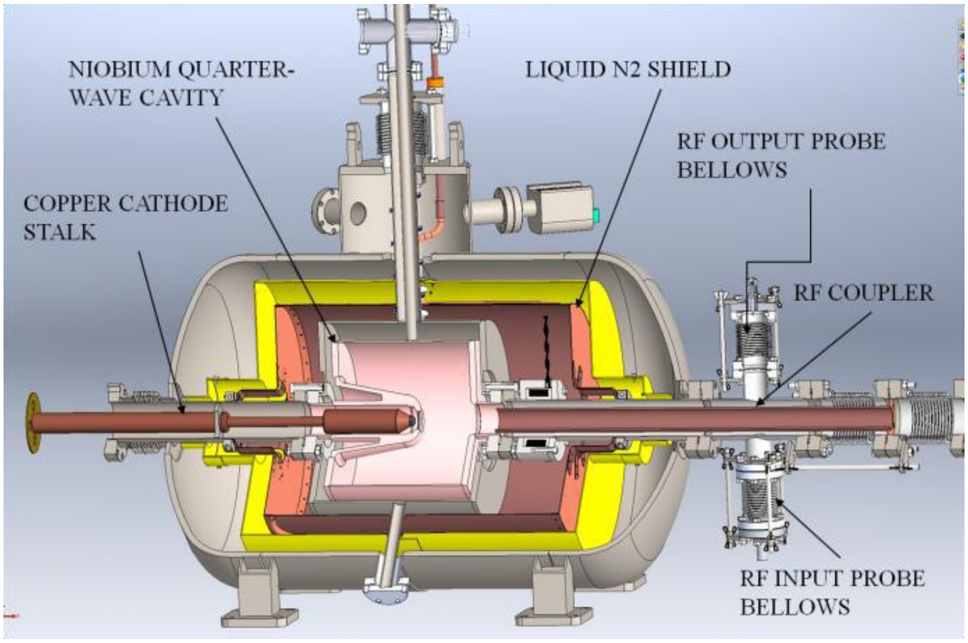


Figure 6.2. Superconducting RF photoinjector developed by the NPS and Niowave Inc. The 500-MHz quarter-wave accelerating cavity with copper cathode stalk is visible at the center of the nested containers. Cryostat length is ~1 m. This cavity geometry will be adapted to the CXLS photoinjector's RF.

The CXLS project will adapt a similar structure to 352 MHz RF with performance goals of producing 40 MV/m accelerating gradient on the cathode and an exit energy of 4 MeV. Electrons are emitted from a Cs:Te cathode excited by a frequency-quadrupled Yb:YLF (yttrium lithium fluoride) laser. The beam consists of a series of bunches with 88-MHz repetition rate and 11-pC charge per bunch. The fields of this photoinjector have been modeled with SUPERFISH (Billen and Young 1993), and electron beam emission and transport has been modeled with the space-charge code PARMELA (Young 2005). The simulations show that bunches can be produced with normalized emittance of 0.3 mm-mrad, 1.1 ps root mean square (RMS) length, and relative energy spread of 3e-4 at 4 MeV. This bunch length is further reduced in the bunch compressor downstream.

6.2.2 Linac

The SRF linac is designed to optimize x-ray production while decreasing the hardware's size and cost. For small facilities, the size and cost are dominated by the cryogenic equipment rather than the linac itself. Currently, this technology is being developed in a research and development effort at JLab jointly with MIT. The research and development effort aims to reduce the complexity and costs of the cryogenic infrastructure; produce excellent stability in energy, timing, and pointing; and enable CW operation with programmable bunch patterns and charge for different user applications. Two types of accelerating cavity geometry are being explored: 1) traditional elliptical cells and 2) innovative "spoke" cavities (Figure 6.3) that are well suited to lower-frequency (< 500 MHz) CW operation.

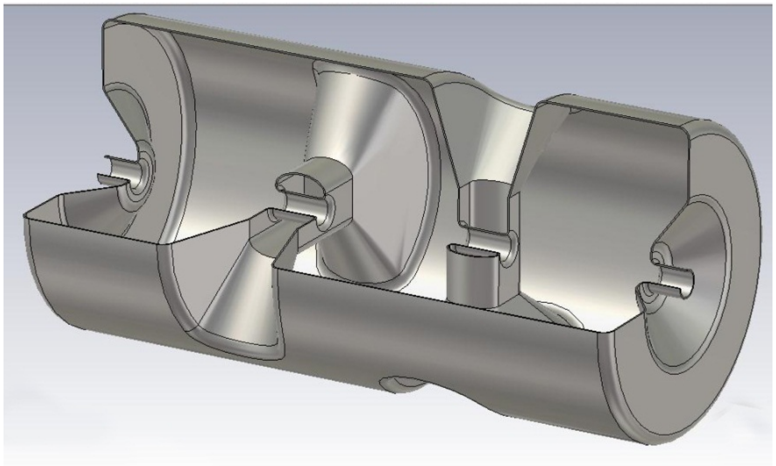


Figure 6.3. Cutaway view of the current JLab dual-spoke RF cavity operating at 352 MHz. The low RF enables operation at 4 K, reducing the size and cost of the cryogenic system. The spoke structure is more rigid and of smaller diameter compared to a standard elliptical cavity.

The spoke cavities are smaller diameter than the elliptical cells, but they require more research and development to demonstrate feasibility. Initial prototypes now are under construction in JLab's research and development program. The RF 352 MHz was chosen due to the availability of standard RF components at that frequency. Considering the cost and performance tradeoffs of operating fewer cavities at a higher gradient versus more cavities operating at lower gradients, an optimum is found near an accelerating gradient of 7–8 MV/m. At an accelerating gradient of 7.2 MV/m, at which Q_0 is above 1.5E9, electromagnetic cavity models show dynamic losses at 4 K are only 87 W/cavity. The cavities' high shunt impedance reduces the cryogenic load and allows for their operation at a higher temperature of 4 K (Ostroumov et al. 2005), reducing the cryogenic plant size, capital cost, and operating costs. The lower gradient also opens the possibility to look at alternative SRF materials. Reactor grade niobium is of lower purity and cost than the residual resistance ratio Nb used for high-gradient structures. Initial studies show promising results for its use in the application. The JLab research and development program also is investigating using Nb3Sn, which has a Q an order of magnitude higher than pure Nb, to reduce the cryogenic heat load by the same factor, further lowering cryogenic size and cost.

Figure 6.4 illustrates the current cryostat designs under consideration for housing the RF cavities. These cryostats have been designed to reduce costs and enhance serviceability. Design features include reducing the number of penetrations through the vacuum shell to simplify construction and reduce heat loads; assembly of the cold mass on a strong back easily loaded into the cryostat; and using standard, readily available industrial materials wherever possible. To demonstrate their properties, the JLab research and development program will construct a complete cryomodule with powered cavities.

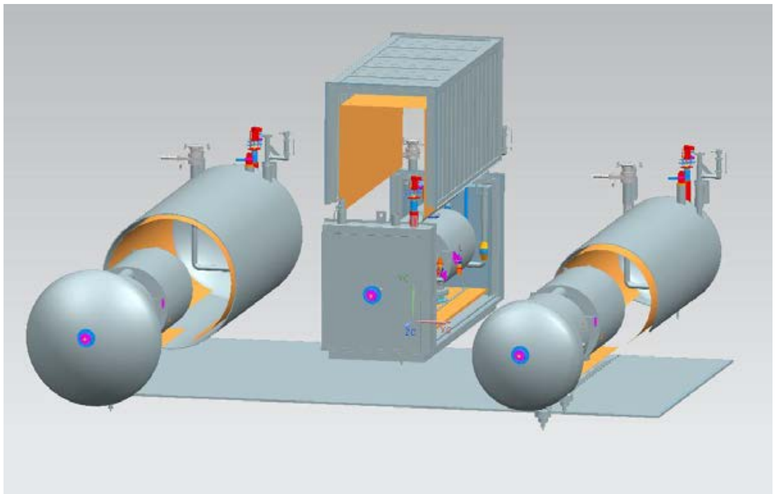


Figure 6.4. Cryostat options under consideration for the SRF linac. From left to right are a traditional end-loaded design; a bottom-loaded box design; and a compact, top-loaded design.

6.3 Electron Beam Studies

6.3.1 Beam Dynamics

Preliminary beam dynamics simulations have been created using the particle tracking codes ASTRA (Floettmann 2011) and PARMELA. Both codes are designed to track macroparticles through user-defined external fields, including the effects of space charge forces. Often, these codes are used for simulating this kind of facility and, in the past, have been benchmarked against one another and real-world measurements. The two tools are being used in this case to provide a cross-check and because they each can simulate non-symmetric components. Each RF component has an associated field map, which can be scaled, and, if appropriate, oscillates with frequency. The electromagnetic field maps for the spoke cavity were generated using CST Microwave Studio software, which can predict the field components from non-symmetric cavities. The SUPERFISH solver was used for the simple, axially symmetric elliptical cavities. For short bunches with moderate charge excellent beam properties are produced by beam blow-out mode (Luiten et al. 2004; Musumeci et al. 2008), where a short, ~100 fs, full-width-at-half-maximum laser pulse is used on the photocathode to generate an electron bunch that expands rapidly under space charge forces to form an ellipsoidal bunch that is then propagated through the beamline. Ellipsoidal bunches are highly desirable because the space charge forces are linear, which preserves the low initial cathode emittance.

A genetic optimization code is used to efficiently search for the set of accelerator parameters that generates the best electron beam performance—defined as producing a beam with the lowest emittance and shortest bunch length. Evolutionary or genetic algorithms are so called because of their close parallels with biological evolution, using techniques inspired by crossover, mutation, selection, and inheritance. Those members of a population that are better in some way are more likely to be selected and preserved into the next generation. Ultimately an optimum set is reached after a number of generations, where all members of the population are equally good (Pareto optimum set). Pareto solutions are those for which improvement in one objective only can occur to the detriment of, at least, one other objective.

A set of 18 variables is chosen, including laser properties, field amplitudes, and phases and positions of components. The objective of the optimization is to minimize the bunch length and transverse emittance at the linac's exit. In addition, there are a number of constraints that define the goals for energy, energy spread, and other electron beam properties. Figure 6.5 shows a comparison of the Pareto front from the spoke and elliptical cavities. For each optimization, the objectives and constraints were identical. The variable range used was large enough for both cases, so the Pareto solutions were not at some limit. The difference between the X and Y emittance values for the elliptical case is small and caused by the statistics of simulating a small number of macroparticles. The larger difference in the case of the spoke cavities arises from the different transverse electric fields. It should be possible to correct this difference with quadrupoles after the linac, but the optimal front will not improve as a consequence. The direct comparison in this optimization shows that elliptical cavities slightly out-perform the spoke cavities.

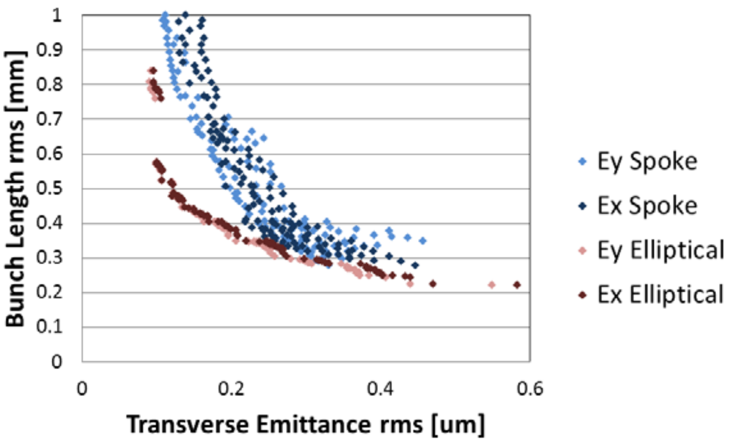


Figure 6.5. Dots show the optimized solutions of electron beam performance, allowing tradeoff between emittance and bunch length. Blue dots are for spoke cavities in X and Y, and red dots are for elliptical cavities.

6.3.2 Jitter Studies

The program, LITRACK (Bane and Emma 2005), was used to estimate effects of RF phase and amplitude jitter and set tolerances on these parameters. LITRACK is a set of MATLAB functions that performs longitudinal tracking, ignoring transverse effects, and finds linac tolerances given user-entered limits on tolerable jitter in energy spread, timing, and peak current. From studies of ICS x-ray production, the limits were chosen to be 0.1% RMS energy spread, 50 fs RMS timing jitter, and 10% variation of peak current. To retain a very low emittance value, the current is deliberately kept low at ~10 Å before compression and 34 Å after compression. For these studies, the compression matrix element R56 = 10.0 cm.

Figure 6.6 plots the sensitivity of the three longitudinal beam parameters to cathode laser arrival time and laser power stability. The tightest specification is set by arrival time jitter, where 175 fs of laser jitter is reduced to 50 fs of electron beam jitter (due to a compression ratio of 3:1). The result of this study is that the laser amplitude must be stable within 10% and its timing jitter must be less than 175 fs. These specifications can be met by commercial systems.

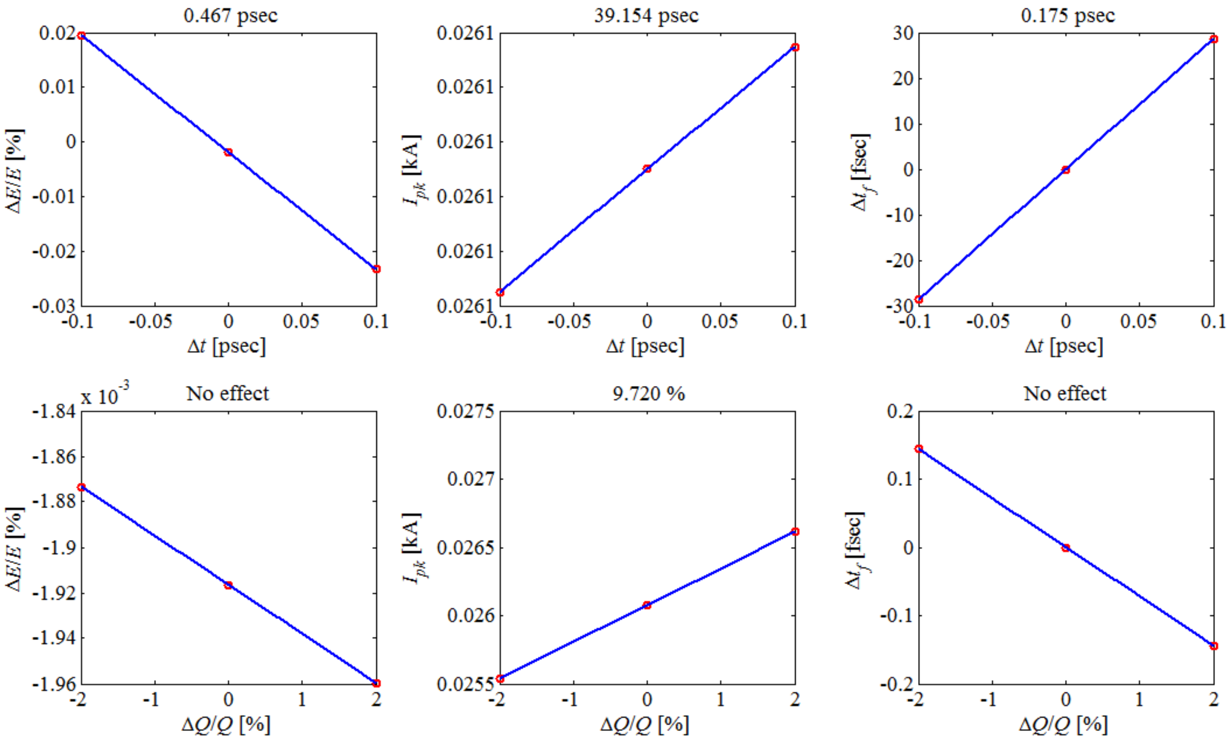


Figure 6.6. From left to right, the graphs show sensitivity of energy spread, peak current, and arrival time to cathode laser timing (top row) and laser amplitude (bottom row) jitter. Laser amplitude jitter results in charge jitter.

Figure 6.7 shows sensitivity of the beam parameters to linac RF phase and amplitude stability. Again, the tightest specification is arrival time, which sets tolerances of 1.3 RF degrees on phase and 0.015% on amplitude. As expected, the phase sensitivity is relatively benign due to the low RF. The amplitude stability tolerance is more challenging but is expected to be met for the CW system chosen, in part, for its excellent stability and lack of transient perturbations due to pulsed operation.

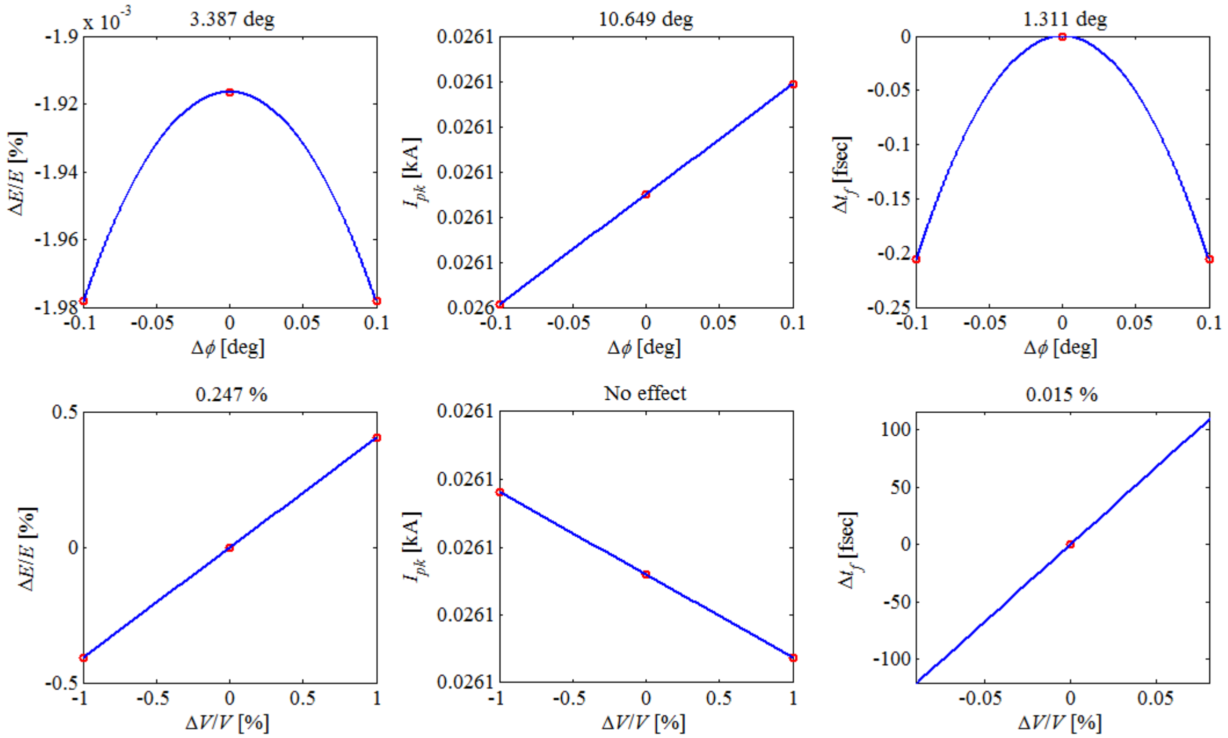


Figure 6.7. From left to right, the graphs show sensitivity of energy spread, peak current, and arrival time, respectively, to linac RF phase (top row) and amplitude (bottom row) jitter.

6.4 Lasers

Since the scattering of optical photons into x-ray photons per collision with the electron beam removes only a minute part of the pulse energy from the optical beam, the optical beam can be recycled many times in an optical enhancement cavity and used for multiple collisions. The CXLS combines a high-power laser amplifier with a coherent enhancement cavity that recycles the laser beam to produce a very-high-average power laser in stable collision with the electron beam. Experiments at MIT's Lincoln Laboratory (Ripin et al. 2004) and campus (Hong et al. 2008) show that cryogenic cooling of the laser gain media is an effective technique for scaling to high-average power by managing thermo-optic effects and improving laser efficiency. All of the key thermo-optic properties, thermal conductivity, refractive-index dependence on temperature, and coefficient of thermal expansion, scale favorably by large amounts as the temperature decreases from 300 K to 77 K. In addition, the efficiency is improved at cryogenic temperatures because these are four-level lasers at 77 K as opposed to a three-level laser at 300 K.

Figure 6.8 shows the layout of a cryogenically cooled Yb:YLF laser driving the coherent enhancement cavity. A fiber seed laser system generates 10 W of femtosecond seed pulses that are injected into the cryogenically cooled Yb:YLF amplifier and amplified to 1 kW. To date, this technique has demonstrated highest power with picosecond Yb:YAG (yttrium aluminum garnet) systems. The Fan group at MIT Lincoln Laboratory also demonstrated extension of the cryogenic cooling concept to sub-ps pulses using Yb:YLF with >100 W average power (Miller et al. 2012).

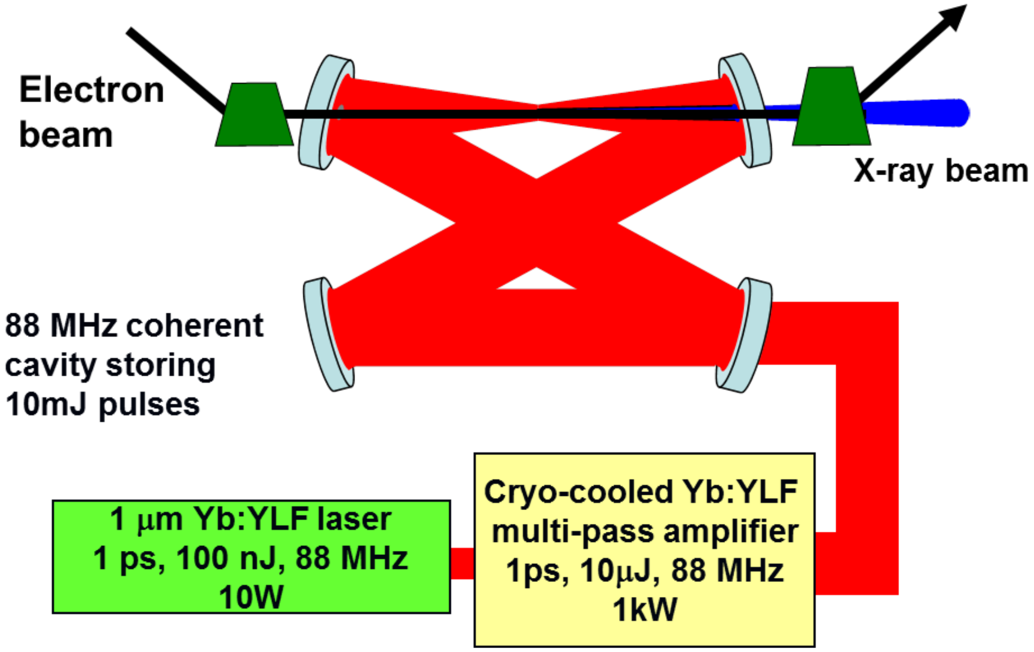


Figure 6.8. High -power lasers including cryo-cooled kilowatt multi-pass amplifier and 88-MHz coherent enhancement cavity that stacks pulses up to the 10 mJ level.

The high-power laser coherently adds pulses in a high-finesse enhancement cavity (Figure 6.9) that enables 1) power enhancement by a factor of 1000 and 2) a well-defined and tightly focused interaction between the high-power electron beam with the high-power laser beam (>1 MW inside cavity). The intracavity power in those cavities is limited by damage due to the peak intensity of the femtosecond pulses, not the average power.

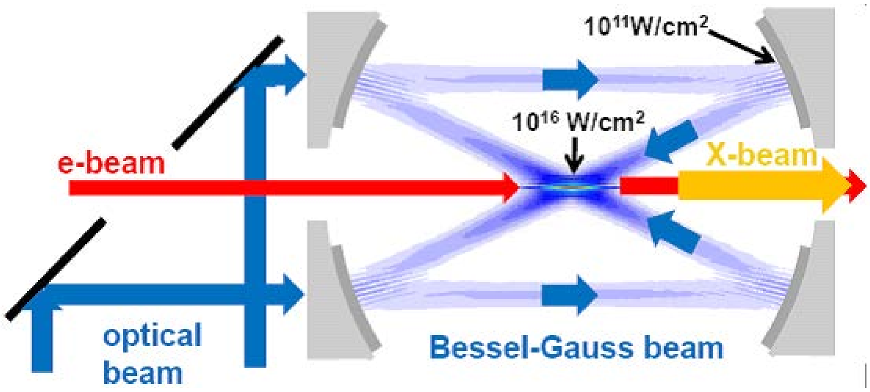


Figure 6.9. Schematic cross-section of the Bessel-Gauss beam enhancement cavity. The cavity and its mode is axially symmetric and fed by a ring-shaped input beam. The Bessel-Gauss beam enables low loss input coupling of the electron beam and output coupling of the electron and generated x-ray beam through central holes in the mirror. The arrows indicate the infrared propagation direction. Propagation consists of a "forward" focusing beam and a "backward" annular beam.

The design of our proposed cavity has two major objectives: first, avoidance of deformation and damage to cavity optics due to ultra-high intracavity average power and intensity, respectively, and second, output coupling of the x-ray beam and input and output coupling of the electron beam without a physical element that would reduce cavity finesse or impede x-ray or electron passage. Because typical quarter-wave Bragg mirrors are expected to handle 1-10 MW/cm^2 of average power for pulses about a picosecond in duration (thresholds exceeding 100 MW/cm^2 for CW lasers have been measured (Meng et al. 2005)), a ~1 MW beam of picosecond pulses at 88 MHz pulse repetition frequency requires an effective beam area of about 0.1-1 cm^2 on the cavity mirrors. Figure 6.9 shows a schematic of a cavity that supports Bessel-Gauss beams (Gori et al. 1987) as cavity modes. These modes enable entrance and exit of the electron and generated x-ray beams, while the cavity mode has a greatly enlarged mode size on the cavity mirrors. The Bessel-Gauss-like beams have an annulus-like beam profile on the mirrors and are Bessel-like at the focus.

To pass the angular extent of x-rays, the hole size in the mirrors must define a full opening angle of 20 mrad, which leads to about a 0.75-cm hole radius for a 88-MHz cavity. Thus, 1–2-inch mirrors are enough to support a cavity mode with a 1–2-cm mode radius (i.e., the annulus center) on the mirrors and a 0.1–1-mm radial annular width. To avoid dielectric breakdown due to high peak intensity, the peak intensity on the mirrors must be below 10^{11} W/cm^2, while the necessary peak intensity in the focus of the cavity will be around 10^{16} W/cm^2. The choice of a Bessel-Gauss beam cavity greatly increases the spot size on the mirror by virtue of the annulus shape of the cavity mode, which increases the mode size in one dimension from about 10 µm to 6 cm, an increase by a factor of 6,000. This ratio of mode size on cavity mirrors versus cavity focus is impossible to achieve stably with a regular Gaussian beam cavity.

There is need for tight synchronization of the photo injector laser and the high-power CXLS drive laser, as well as the RF source powering the superconducting gun and accelerator modules. Over the years, the MIT optics group has made tremendous progress in this area using optical techniques (Kim et al. 2008 and Schibli et al. 2003), which now are implemented in many of the newly constructed x-ray free electron lasers around the world, such as in FERMI@Elettra at Trieste, Italy and Deutsches Elektronen-Synchrotron (DESY) in Hamburg, Germany. For example, long-term stable synchronization of multiple laser sources with 400 attosecond stability over 12 hours has been demonstrated (Schibli et al. 2003). Small versions of these systems will be used to stabilize the timing of the CXLS x-rays to the level of 10 femtosecond or better.

6.5 Source Performance Estimates

Initial photon performance estimates are provided over ranges of photon energies. The photon energy scales inversely as the square of the electron kinetic energy, and because each electron bunch is destined for a single beamline, that beamline’s photon energy may be tuned widely in a matter of seconds by varying the bunch energy. While the electron and x-ray energies may be rapidly tuned, there are practical limits to both the tuning range of beamline optics and the electron energy range for a particular accelerator configuration, i.e., a high-energy accelerator is not well suited to producing softer photon energies. Each of the following subsections briefly describes a possible source configuration and a practical photon energy range it can produce. In a detailed facility design, some of these configurations/energy ranges would be combined into a single accelerator with multiple, independently tunable beamlines, an example concept of which is presented.

The performance estimates are produced with static analytical formulae that are good approximations to fully 3-D, time-dependent numerical simulations (Brown and Hartemann 2004). The approximations account for the effects of electron beam energy spread and emittance. The electron beam parameters are chosen so the time-dependent effects (focus size, pulse length) are minimal. Full time-dependent numerical simulations have been carried out for the case of 12-keV photons and are presented herein. The performance estimates for all other photon ranges are static and will be verified by complete start-to-end numerical modeling as the beamline concepts mature.

The performance numbers depend on the electron beam and laser parameters. For all cases, the design electron beam parameters are bunch charge of 10 pC, RMS energy spread of 1 keV, transverse emittance of 0.2 mm-mrad, and RMS bunch length of 200 fs. The repetition rate is 88 MHz. The electron beam focusing is varied from a larger 5 micron RMS beam size at the softest photon energy to 2 micron RMS size at the higher energies. The laser design parameters are 170-fs RMS pulse length, 10 mJ/pulse, and 88-MHz cavity frequency. Yb:YLF lasers at 1064-nm wavelength are used (except as noted), where the fundamental is frequency doubled to 532 nm to keep electron energy low.

6.5.1 180 eV–700 eV Energy Range

From the resonance equation in Section 6.1, the electron energy needed for this lowest photon energy range in the UV is a maximum of just 4 MeV if the high-power laser is frequency doubled to 532 nm. The photoinjector operating alone, without a linac, is capable of producing this energy, so the source can be quite compact. Figure 6.10 shows the layout, consisting of the photoinjector, transport magnets and chicane bunch compressor, high-power laser at 532 nm wavelength driving the optical coherent enhancement cavity, and electron beam dump. The entire accelerator and transport line is approximately 5-m long.

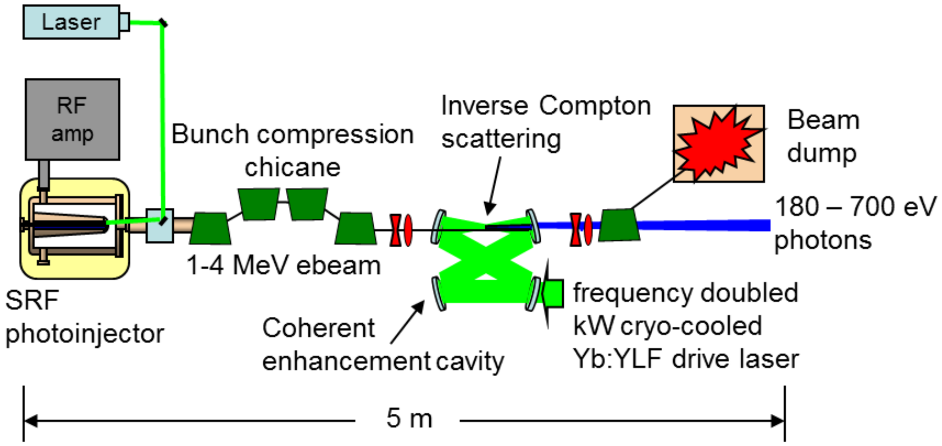


Figure 6.10. Layout of accelerator with an energy range of 180 eV to 700 eV.

Table 6.1 presents the source performance for this beamline. Average flux is 2 × 10^{14} photons/sec, and average brilliance is ~1 × 10^{12} photons/(sec mm^2 $mrad^2$ 0.1% bandwidth) across the spectral range at the maximum repetition rate of 88 MHz. The source size is 4 microns, and the source opening angle ranges from approximately 10–25 mrad, depending on the photon energy. The harder photons are emitted into smaller angles.

Table 6.1. Energy Range 180 eV to 700 eV

Photon Parameters	180 eV	700 eV	Units
Wavelength	69	18	Angstrom
Photons/shot in full bandwidth	1.6e6	2.1e6	
Energy/shot in full bandwidth	22	240	pJ
Average flux in full bandwidth	2.0e14	2.1e14	per sec
Peak brilliance	3.6e16	1.4e17	x-rays/(mm^2 mrad^2 0.1%BW s)
Average brilliance	7.3e11	2.9e12	x-rays/(mm^2 mrad^2 0.1%BW s)
On-axis bandwidth	0.8	0.8	%
RMS source size	4.0	3.7	micron
RMS source divergence	24	12	mrad
M^2	90	180	
RMS pulse length	200	200	fs

6.5.2 X-ray Tomography: Case Example for 180 eV–700 eV Energy Range

As mentioned in Section 2.13, Imaging Cellular Systems, identifying the precise location of individual proteins and organelles within the cellular context has been a long-held ambition of both structural and molecular biologists. To achieve this goal, it is anticipated that 3-D resolution better than 40 nm will be routinely required as this resolution represents the threshold for visualizing many internal details that allow explicit identification of most organelles and large complexes. Although x-ray tomographic reconstructions of whole cells can be segmented and classified based upon respective linear absorption coefficients (Parkinson et al. 2008), this approach does not guarantee unambiguous organelle identification for every visualized subcellular structure, especially those smaller than 100 nm in diameter.

A recent study using synchrotron radiation with partially coherent object illumination rather than quasi-incoherent illumination surpassed this resolution barrier for the first time and achieved 36-nm spatial resolution, which allowed the authors to visualize the double nuclear membrane, nuclear pores, nuclear membrane channels, mitochondrial cristae vacuoles, ribosomes, and lysosomal inclusions. These results were acquired with a total dose of 109 MGy distributed among 121 tilt images of a 5-µm-thick sample with a total exposure of 24 seconds (Schneider et al. 2010). The corresponding photon density was 5×10^8 photons/sec/µm^2. In comparison, a laboratory-based instrument with similar sample stage geometry was only able to achieve 70-nm spatial resolution from a sample of equivalent thickness (Evans et al. 2012). The limited resolution for the laboratory system was attributed to the lower beam coherence and brightness of the source (maximum photon density of 2 × 103 photons/sec/µm^2). In addition to the lower resolution, the laboratory system required 21,600 seconds to record the entire tilt series. The difference in exposure time is directly related to the available photon density. Thus, it accounts for three of the five magnitudes of difference in photon density between the laboratory and synchrotron light sources. Therefore, the remaining two orders of magnitude difference in photon density and improved beam coherence can be credited to the twofold increase in resolution achieved during the synchrotron-based experiment.

As such, a trend exists that supports an increase of tomographic resolution due to increases in brightness and/or spatial coherence of the x-ray beam, which is consistent with previous calculations (Jacobsen et al. 1992). The CXLS presented herein is ideally suited for x-ray microscopy and tomography within the water window because the resulting photon density of 1 × 10^{11} photons/sec/µm^2 is 200-fold time higher than previously used with a third-generation synchrotron source to achieve 36-nm resolution while imaging through 5 µm of frozen hydrated cellular material. The CXLS' high photon density is possible if the expected average flux generated with incoherent ICS (2 × 10^{14} photons/sec) is focused to a spot of 30-µm diameter at the sample. Furthermore, the coherent ICS mode of the CXLS is expected to improve the coherence of the beam while also containing an order of magnitude greater flux compared to incoherent ICS mode. The significant enhancement in photon density made possible by either mode of the CXLS will empower unprecedented spatial resolution for whole cell tomography of energy-relevant biological systems.

6.5.3 200 eV–2.5 keV Energy Range

To reach soft x-rays of 2.5 keV, the minimum accelerator needed consists of the photoinjector and a short linac with a single RF cavity capable of a maximum electron energy of 12 MeV. Figure 6.11 illustrates this type of layout. The electron energy range is from 4 MeV, which the photoinjector alone can reach, up to the max energy of 12 MeV, requiring the linac RF cavity to generate an additional 8 MeV acceleration. The downstream equipment consists of transport focusing magnets; the bunch compressor chicane; a high-power, 1064-nm laser, driving an optical coherent enhancement cavity; and the electron beam dump. The total length of the equipment is ~ 7 m.

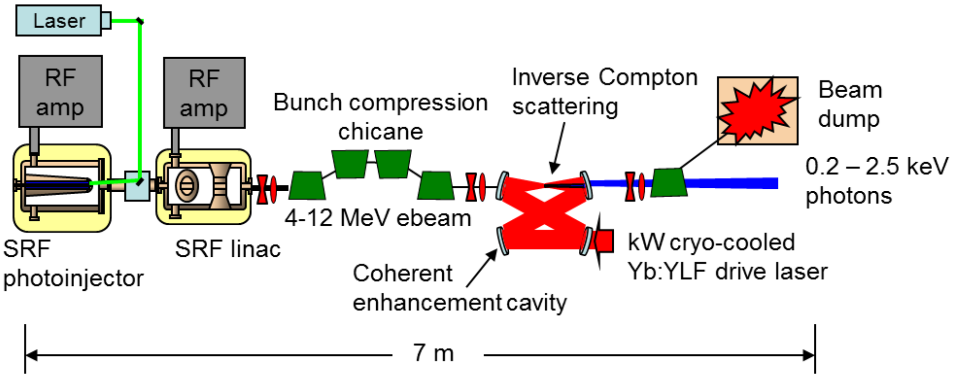


Figure 6.11. Layout of accelerator with an energy range of 200 eV to 2.5 keV.

Table 6.2 presents the source performance for this energy range. The average flux is ~2 × 10^{14} photons/sec across the spectral range, but the average brilliance increases from 5 × 10^{12} to 50 × 10^{12} photons/(sec mm^2 $mrad^2$ 0.1% bandwidth) as the photon energy increases from 200 eV to 2.5 keV. This beamline covers a broad spectral range. The brilliance increases for the harder photons due both to the improving electron beam geometric emittance at higher energy and the reduced opening angle of the radiation that scales as the inverse of the electron energy. The opening angle reduces from 16 mrad at 200 eV to 5 mrad at 2.5 keV, and the source size reduces from 3.5 microns to 2.5 microns over that same range.

Table 6.2. Energy Range 200 eV to 2.5 keV

Photon Parameters	200 eV	2.5 keV	Units
Wavelength	62	5.0	Angstrom
Photons/shot in full bandwidth	1.6e6	2.3e6	
Energy/shot in full bandwidth	53	900	pJ
Average flux in full bandwidth	1.9e14	2.6e14	per sec
Peak brilliance	1.9e17	2.5e18	x-rays/(mm^2 mrad^2 0.1%BW s)
Average brilliance	4.5e12	6.0e13	x-rays/(mm^2 mrad^2 0.1%BW s)
On-axis bandwidth	0.8	0.9	%
RMS source size	3.5	2.5	micron
RMS source divergence	16	5.0	mrad
M^2	45	115	
RMS pulse length	200	200	fs

6.5.4 2 keV–14 keV Energy Range

This energy range from soft to hard x-rays is likely to have the highest demand for the widest range of applications and makes use of the full linac energy. As shown in Figure 6.12, the accelerator components consist of the photoinjector and a linac with three RF cavities. The required electron beam energy range is from 10–28 MeV. The same electron transport components—consisting of focusing magnets; a bunch compression chicane; a high-power, cryo-cooled 1064-nm laser, driving an optical coherent enhancement cavity at 88 MHz; and electron dump— are downstream of the linac. The total system length is ~9 m.

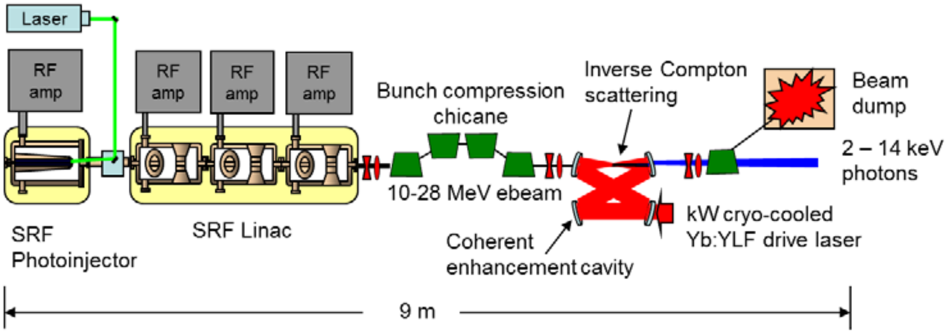


Figure 6.12. Layout of accelerator with an energy range of 2 keV to 14 keV.

The x-ray performance (Table 6.3) includes average flux of 2 × 10^{14} – 4 × 10^{14} photons/sec and average brilliance of 4 × 10^{13} to 3 × 10^{14} photons/(sec mm^2 mrad^2 0.1% bandwidth) as the photon energy increases from 2 to 14 keV, respectively. The source size is ~2 microns across the spectral range, and, as the photon energy increases, the x-ray opening angle decreases from 5.6 to 2.4 mrad.

Table 6.3. Energy Range 2 keV to 14 keV

Photon Parameters	2 keV	14 keV	Units
Wavelength	6.2	0.9	Angstrom
Photons/shot in full bandwidth	2.3e6	3.3e6	
Energy/shot in full bandwidth	720	1100	pJ
Average flux in full bandwidth	2.6e14	3.8e14	per sec
Peak brilliance	2.0e18	1.2e19	x-rays/(mm^2 mrad^2 0.1%BW s)
Average brilliance	4.8e13	2.9e14	x-rays/(mm^2 mrad^2 0.1%BW s)
On-axis bandwidth	0.9	1.2	%
RMS source size	2.5	2.0	micron
RMS source divergence	5.6	2.4	mrad
M^2	103	218	
RMS pulse length	200	200	fs

An extensive optimization of output at 12 keV was conducted using electron transport code PARMELA and an experimentally benchmarked, 3-D, time-dependent ICS code (Brown et al. 2004). Figure 6.13 shows simulation results for the x-ray angular intensity, indicating the several milliradian opening angle and symmetric round beam shape. For this plot, the radiation was filtered with a 0.1% bandwidth at 12 keV. The flux within that bandwidth is 10^{12} photons/sec from the total flux of 4×10^{14} across the entire emission bandwidth of ~10%.

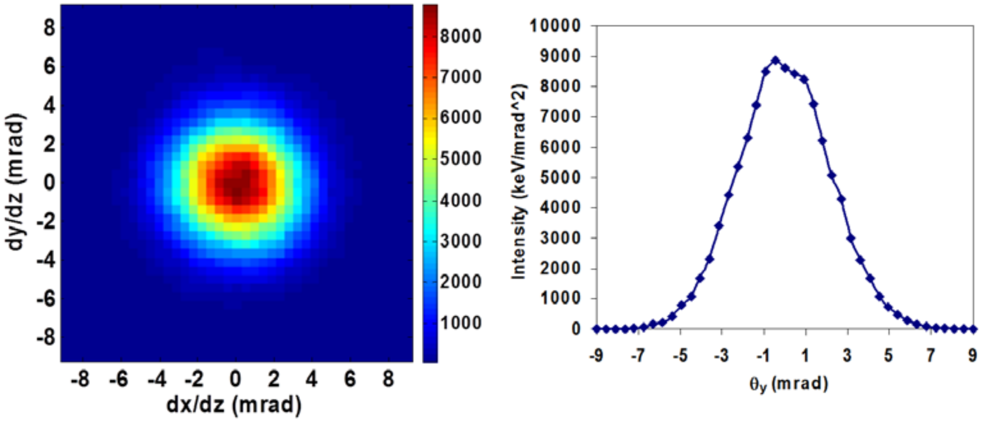


Figure 6.13. Plots of the x-ray source angular intensity at 12 keV from detailed numerical studies, accounting for time dependence of laser and electron beam, as well as electron emittance and energy spread.

6.5.5 12 keV–29 keV Energy Range

This highest energy range uses the same source layout as the 2–14 keV range already described, except the Yb:YLF laser is frequency doubled to 532 nm to provide harder photon output. Drive laser power in infrared must be increased by factor of 2 to have the same cavity power after frequency doubling. The use of a green light instead of infrared allows this beamline to reach 29 keV x-ray output using the same 28-MeV linac as the previous lower-energy beamline. However, because the a_0 parameter (equivalent to undulator K parameter) scales linearly with laser wavelength and the x-ray flux is proportional a_0^2, the peak and average brilliance are reduced by a factor of ~5 compared to the similar parameters using longer wavelength infrared light. The performance still is at or above that of softer photon beamlines. Table 6.4 shows the x-ray performance, including average flux of 3×10^{14} photons/sec and average brilliance of $2–6 \times 10^{13}$ photons/(sec mm^2 mrad^2 0.1% bandwidth) as the photon energy. The source size is ~2 microns across the spectral range, and the x ray opening angle decreases from 3 to 2 mrad as the photon energy increases.

Table 6.4. Energy Range 12 keV to 29 keV

Photon Parameters	12 keV	29 keV	Units
Wavelength	1.0	0.43	Angstrom
Photons/shot in full bandwidth	2.5e6	2.5e6	
Energy/shot in full bandwidth	4.8	12	nJ
Average flux in full bandwidth	2.9e14	2.9e14	per sec
Peak brilliance	1.1e18	2.6e18	x-rays/(mm^2 mrad^2 0.1%BW s)
Average brilliance	2.5e13	6.1e13	x-rays/(mm^2 mrad^2 0.1%BW s)
On-axis bandwidth	1.0	1.0	%
RMS source size	2.0	2.0	micron
RMS source divergence	3.2	2.1	mrad
M^2	200	288	
RMS pulse length	200	200	fs

6.6 Multi-beamline Configuration

Figure 6.14 shows a conceptual design of a single accelerator driving multiple, independently tunable beamlines, each dedicated to a different energy range. The accelerator structure is the same as the single beamline devices, but it has additional equipment controlling the cathode and the electron beam path after acceleration. Instead of a single-cathode laser, there are as many cathode lasers as there are beamlines, three in the case illustrated. Each cathode laser is individually controlled by the beamline control system to set the repetition rate, charge per pulse, and photon energy for that particular beamline. The beam may be deactivated by turning off the cathode laser. In addition to separate cathode lasers, the multi-beamline source has a fast electron beam switch at the linac exit, consisting of a deflecting RF cavity and septum magnets. The deflector sends an electron beam to each beamline separately. The maximum repetition rate for any one beamline is set by the deflection frequency, which will be 1/N, where N is the number of beamlines. Practical designs allow switching at frequencies up to ~100 MHz.

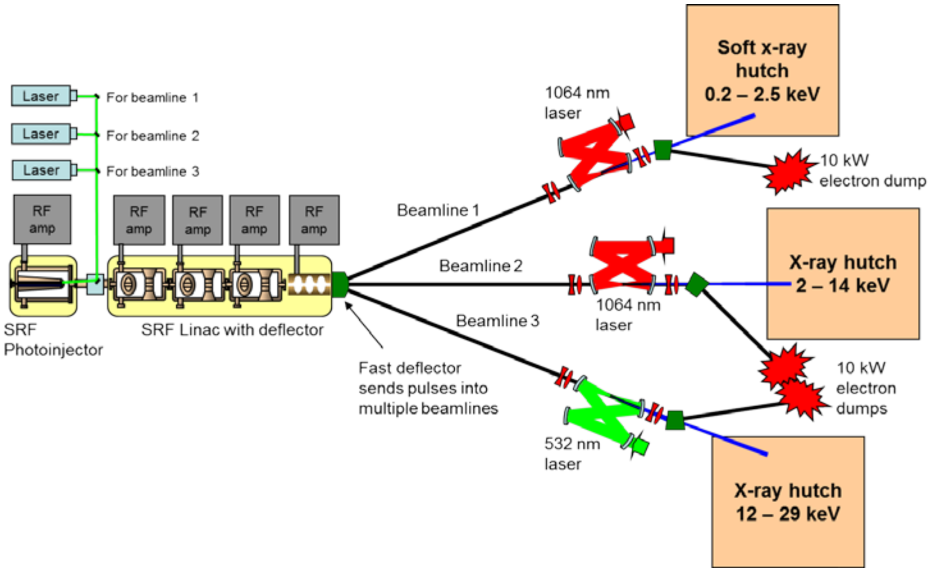


Figure 6.14. Concept for multiple, independently tunable beamlines driven by a single accelerator. Each beamline controls its own cathode-drive laser, setting photon energy and repetition rate independently. A fast RF deflector at the linac exit sends individual pulses to each beamline.

The advantage of this source layout is the reduced cost to run multiple beamlines from a single accelerator. Separate, high-power ICS lasers still are required for each beamline and may be of different wavelengths (as shown) to best match different energy ranges. Using such a facility will put more constraints on the capabilities of each beamline, reducing their maximum average brilliance and flux and reducing the energy tuning range for each. Detailed design of the deflector and tuning ranges remain to be confirmed.

6.7 Beamline Design Considerations

As described in the preceding sections, a linac-driven ICS light source has, from a purely technical standpoint, exciting capabilities that complement, and in some cases exceed, those of second- and third-generation light sources. Such comparisons are useful, but they provide an incomplete picture of the benefits of the CXLS project. The scientific value of a facility depends on the range of applications, the innovative end-station facilities that will be available, and the fit between these methods and the targeted user base. In the present case, the collocation between the ICS light source at PNNL within the EMSL instrument suite leads to robust synergies from the availability of x-ray methods that complement other instruments critical to PNNL science missions, as well as the role that existing PNNL technical expertise can play in the development of uniquely powerful and productive experimental endstations.

These issues are explored herein through a discussion of the general characteristics of the CXLS beam and by examining the concept for one example beamline: a multi-purpose, hard-x-ray beamline that will support a number of key x-ray methodologies.

6.7.1 Photon Beam Characteristics

The CXLS opens the possibility to many possible x-ray applications, and it is beyond the scope of this workshop to develop the full array of beamline designs. However, as an example, we will consider the approach to developing a multi-purpose, hard-x-ray beamline in the range of 2–14 keV (Section 6.5.3). Initially, we will review a few key technical parameters of the photon beam for hard x-rays then examine the consequences for beamline design.

1. **Flux and heat load.** As described in Section 6.5.3, the full beam at 12 keV is expected to be at the level of 10^{14} photons/sec, i.e., ~100 mW. Consequently, the x-ray optics at all locations along the beam path will have low heat-loads and may be water-cooled or, in many cases, radiatively or air-cooled.
2. **Bandwidth.** The output radiation will have a bandwidth of approximately 25%. While large bandwidths will be useful for some applications, such as Laue diffraction, fluorescence analysis, or imaging, x-ray scattering methods, e.g., protein crystallography, generally require monochromatization to levels of about 1–10 eV. This can be accomplished with standard double crystal monochromators provided the beam is suitably collimated beforehand. Typically, following such a monochromator, the flux level would be around 10^{12} /sec.
3. **Divergence.** The CXLS' output radiation has a cylindrically symmetric divergence, typically of a few mrads, which will require highly specialized, multi-layer-coated Kirkpatrick-Baez (KB) optics for collection and either focusing on a sample or collimating to the 10–20 micro-radian levels required for monochromatization.
4. **Source size.** The CXLS produces a beam from a very small source size (~2 microns), which is excellent for use as a microprobe. It also strongly supports the performance of the optics for pre-monochromator conditioning of the beam. Optics placed 200 mm from a 2-micron size source can collimate a beam by a theoretical factor of 10^3, which is more than adequate.
5. **Tunability.** The CXLS itself can be quickly tuned over a wide photon energy range by varying the electron energy, by reducing the RF amplitude and shifting the electron bunch timing with respect to the RF. However, for the application to a general hard x-ray scattering beamline with highly monochromatic radiation, the collimating optics necessary will limit tunability to a few percent. This is adequate for the multi-wavelength anomalous dispersion methods of macromolecular crystallography at the selenium edge, for example, but energies differing by more than a few percent will each require dedicated optics.
6. **Polarization.** We will not consider this further but note that the x-ray beam polarization is determined by the laser polarization, so there is freedom to design it as needed and possibly change it if necessary.
7. **Higher harmonics.** There are no higher harmonics to consider because the intensity of the laser radiation is equivalent to a weak undulator field.
8. **Repetition rate.** In principle, the rate can be as high as the 100-MHz linac repetition rate, but it is determined by repetition rate of the cathode laser and, therefore, is adjustable to very low rates.
9. **Pulse length.** Typical pulse lengths are around 0.5 ps, which is 100 times shorter than typical synchrotron radiation. Thus, the beamline described here could be especially interesting for time-resolved x-ray scattering. The CXLS will have sophisticated timing systems that can provide accurate signals for synchronizing x-ray beams to laser pump pulses used to excite sample dynamics.

6.7.2 Concepts for a Multi-purpose Hard X-ray Beamline

The rapid tuning of the light source, combined with the comparatively low shielding and cooling requirements enable unique flexibility to make substantial changes in beamline configurations quickly. This flexibility will allow a wider range of methods to be efficiently performed than typical on a single beamline at the second- and third-generation sources. With this characteristic in mind, we first divide potential x-ray methods to be supported by this beamline into two broad categories: 1) “upstream” for methods that use minimal modification of the x-ray source or 2) “downstream” for methods that instead require more complex degrees of collimation, focusing, and/or monochromatization of the x-ray beam.

Figures 6.15 and 6.16 depict notional beamline layouts for the multi-purpose hard x-ray beamline. These figures are based on the model accelerator from Section 6.5.3, covering the energy range 2–14 keV. Figure 6.15 shows representative “upstream” options: highly automated, high-throughput microtomography, and both bulk and micro x-ray fluorescence (XRF) analysis. The bulk XRF would be done without optics, whereas the microtomography and micro-XRF options would use a focusing KB mirror. Each of these ambient-condition methods is an outstanding fit with the light source characteristics in the hard x-ray range. They also are natural choices for automated facilities that can run with minimal supervision or on-site support through off-work hours or whenever the downstream user is performing maintenance or extended sample preparation. Trace-level element detection at a CXLS would be significantly more powerful (in terms of detection threshold) than commercial laboratory-based instruments are today, while also providing a few orders of magnitude faster measurement time due to the increased flux. Given that many studies in the fields of public health and environmental science can require thousands to tens of thousands of XRF measurements, an automated XRF endstation at a CXLS could have high impact in those fields. On a more general note, the automated upstream endstations are well-suited to mail-in, remote, or service access, such as those already implemented at several synchrotrons for microtomography, powder x-ray diffraction, and crystallography, and is the current standard for laboratory services providing XRF capabilities. This model will greatly extend the user base for CXLS by providing high-demand capabilities while also eliminating travel expenses and associated inconveniences.

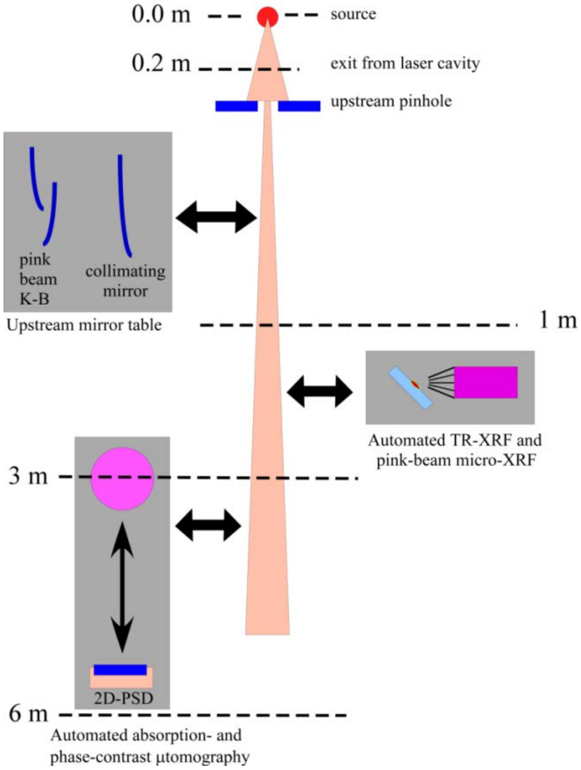


Figure 6.15. Conceptual beamline schematic: "Upstream"

Figure 6.16 shows possible "downstream" instrument options. An upstream collimating KB mirror is inserted after the first aperture, producing a collimated beam similar to that of a synchrotron light source. Ideally, this mirror would be an "L" mirror, such as those being developed for use at NSLS II (Honnicke et al. 2011). The collimation achieved by this optic then permits standard synchrotron double crystal monochromator methods to be employed. A second KB mirror (not shown) could be used to refocus the beam on the sample. Of note, these mirrors would be coated with a graded d-spacing multilayer, offering a few percent bandwidth. While this optic does permit a narrow range of tunability suitable for certain methods, e.g., multiple wavelength anomalous scattering for macromolecular structure determination, a set of interchangeable mirrors will be needed to cover larger energy ranges.

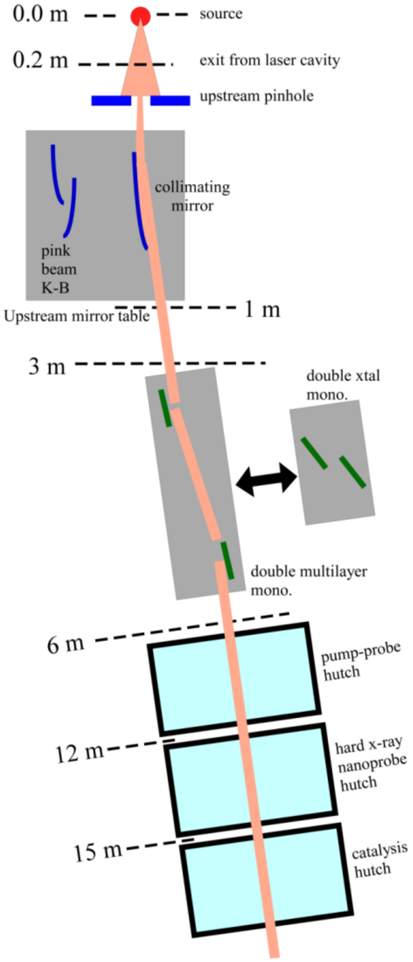


Figure 6.16. Conceptual beamline schematic: "Downstream"

Following the optics, the beam passes into a series of hutches, each dedicated to specific applications, such as microprobe analysis or crystallography. Due to the short pulse length, there will be opportunities to extend these methods to perform pump-probe time-resolved studies. Obviously, much more work must be done to develop actual beamline designs. However, from this discussion, it is clear that options exist to make powerful, multi-purpose beamlines that can serve the variety of needs highlighted in this workshop report.

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Appendix A

Workshop Invitees

Appendix A – Workshop Invitees

Chris Aardahl – Pacific Northwest National Laboratory
Kyle Alvine – Pacific Northwest National Laboratory
Steve Ashby – Pacific Northwest National Laboratory
Dave Asner – Pacific Northwest National Laboratory
Don Baer – Pacific Northwest National Laboratory
Simon Bare – UOP LLC
Suresh Baskaran – Pacific Northwest National Laboratory
Hendrik Bluhm – Lawrence Berkeley National Laboratory
Harvey Bolton – Pacific Northwest National Laboratory
Christoph Bostedt –SLAC, LCLS
Mark Bowden – Pacific Northwest National Laboratory
Rick Brouns – Pacific Northwest National Laboratory
Gary Buchko – Pacific Northwest National Laboratory
Allison Campbell – Pacific Northwest National Laboratory
Scott Chambers – Pacific Northwest National Laboratory
Valerie Copie – Montana State University
Abhaya Datye – University of New Mexico
Barbara Diehl – Pacific Northwest National Laboratory
Alice Dohnalkova – Pacific Northwest National Laboratory
Greg Exarhos – Pacific Northwest National Laboratory
Jim Fast – Pacific Northwest National Laboratory
Andy Felmy – Pacific Northwest National Laboratory
Michael Feser – Xradia Inc.
Jim Fredrickson – Pacific Northwest National Laboratory
John Fulton – Pacific Northwest National Laboratory
Jean Futrell – Pacific Northwest National Laboratory
Bruce Garrett - Pacific Northwest National Laboratory
Charlette Geffen – Pacific Northwest National Laboratory
Graham George – University of Saskatchewan
William Graves – Massachusetts Institute of Technology
Mike Henderson – Pacific Northwest National Laboratory
Greg Herman – Oregon State University
Wayne Hess – Pacific Northwest National Laboratory
Carol Hirschmugl – University of Wisconsin - Milwaukee
Adam Hitchcock – McMaster University
Hoi-Ying Holman – Lawrence Berkeley National Laboratory

Christian Holzner – Xradia Inc.
Edmond Hui – Pacific Northwest National Laboratory
Barbara Illman – University of Wisconsin and SRC
Chris Jacobsen – Northwestern University
Dave Johnson – University of Oregon
Ayman Karim – Pacific Northwest National Laboratory
Kenneth Kemner – Argonne National Laboratory
Moe Khaleel – Pacific Northwest National Laboratory
David King – Pacific Northwest National Laboratory
Mike Kluse – Pacific Northwest National Laboratory
Dave Koppenaal – Pacific Northwest National Laboratory
Libor Kovarik – Pacific Northwest National Laboratory
Rick Kurtz – Pacific Northwest National Laboratory
Ja Hun Kwak – Pacific Northwest National Laboratory
John P. LaFemina – Pacific Northwest National Laboratory
Alex Laskin – Pacific Northwest National Laboratory
Scott Lea – Pacific Northwest National Laboratory
John Linehan – Pacific Northwest National Laboratory
Jun Liu – Pacific Northwest National Laboratory
Paul Lyman – University of Wisconsin - Milwaukee
Igor Lyubinetsky – Pacific Northwest National Laboratory
John Mammosser - Jefferson Lab (JLab)
Kristin Manke – Pacific Northwest National Laboratory
Chris Marshall – Argonne National Laboratory
Matt Marshall – Pacific Northwest National Laboratory
Gerry McDermott – University of California San Francisco
Jim McKinley – Pacific Northwest National Laboratory
David McIlory – University of Idaho
Ian McNulty – Argonne National Laboratory
Blaine Metting – Pacific Northwest National Laboratory
Jerry Seidler – University of Washington
Erin Miller – Pacific Northwest National Laboratory
David Moncton – Massachusetts Institute of Technology
Karl Mueller – Pacific Northwest National Laboratory
Ponnusamy Nachimuthu – Pacific Northwest National Laboratory
Galya Orr – Pacific Northwest National Laboratory
John Peak – University of Saskatchewan
Tony Peurrung – Pacific Northwest National Laboratory

Doug Ray – Pacific Northwest National Laboratory
John Rehr –University of Washington
Karin Rodland – Pacific Northwest National Laboratory
Kevin Rosso – Pacific Northwest National Laboratory
Susanna Scott – University of California – Santa Barbra
Bill Shelton – Pacific Northwest National Laboratory
Gopal Shenoy – Argonne National Laboratory
David Shuh – Lawrence Berkeley National Laboratory
Len Spicer – Duke University
Tom Squier – Pacific Northwest National Laboratory
Dario Stacchiola – Brookhaven National Laboratory
Jana Strasburg – Pacific Northwest National Laboratory
Janos Szanyi – Pacific Northwest National Laboratory
Craig Szymanski – Pacific Northwest National Laboratory
Ray Teller – Pacific Northwest National Laboratory
Louis Terminello – Pacific Northwest National Laboratory
Theva Thevuthasan, Pacific Northwest National Laboratory
Alexei Tivanski – University of Iowa
Paul Tratnyek – Oregon Health Science University
Tamas Varga – Pacific Northwest National Laboratory
Tony van Buuren – Lawrence Livermore National Laboratory
Jud Virden – Pacific Northwest National Laboratory
Chongmin Wang – Pacific Northwest National Laboratory
Yong Wang – Pacific Northwest National Laboratory
Steve Wiley – Pacific Northwest National Laboratory
Gwyn Williams – Jefferson Lab (JLab)
Kevin Wilson – Lawrence Berkeley National Laboratory
Bob Wright – Pacific Northwest National Laboratory
Linda Young – Argonne National Laboratory
John Zachara – Pacific Northwest National Laboratory
Alla Zelenyuk – Pacific Northwest National Laboratory

Appendix B

Workshop Agenda

Fundamental & Computational Sciences Directorate

EMSL

CXLS Workshop
EMSL Auditorium, PNNL

September 21-22, 2011

Organizers:

Ray Teller, Pacific Northwest National Laboratory
Louis Terminello, Pacific Northwest National Laboratory
Theva Thevuthasan, Pacific Northwest National Laboratory
David Moncton, Massachusetts Institute of Technology

Session Chairs:

William Graves, Massachusetts Institute of Technology/Technology
David Shuh, Lawrence Berkeley National Laboratory/Biogeochemistry/ Environmental Science
Chris Jacobsen, Argonne National Laboratory/Biology
Simon Bare, UOP/Chemical Sciences/Catalysis
Adam Hitchcock, McMaster University/Materials Science

Workshop Administrator

Marla Seguin – (509) 372-4029, marla.seguin@pnnl.gov

AGENDA

TIME	TOPIC	LOCATION
Wednesday, September 21, 2011		
8:00 – 8:45am	Welcome and Badging	EMSL Lobby & ETB

TIME	TOPIC	LOCATION
8:45 – 9:00am	Introduction – Doug Ray, Associate Laboratory Director, FCSD	EMSL Auditorium
9:00 – 9:15am	Overview – Louis Terminello	EMSL Auditorium
	Keynote Talks: Session Chair – Louis Terminello	
9:15 – 9:45am	Keynote address – Technology – David Moncton	EMSL Auditorium
9:45 – 10:15am	Keynote address – Technology – William Graves	EMSL Auditorium
10:15 – 10:45am	Keynote address – Biology – Chris Jacobsen	EMSL auditorium
10:45 – 11:15am	Keynote address – Biogeochemistry – David Shuh	EMSL Auditorium
11:15 – 11:45am	Keynote address – Catalysis – Simon Bare	EMSL Auditorium
11:45 – 12:15pm	Key note address – Materials Science – Adam Hitchcock	EMSL Auditorium
Breakout Session I:	**12:15 – 5:00pm** **(Pick up lunch on way to breakout sessions)**	
	Materials Science Session Lead: Adam Hitchcock Co-Chair: Libor Kovarik and Mark Bowden	EMSL Auditorium
	Chemical Sciences/Catalysis Session Lead: Simon Bare Co-Chair: Ayman Karim and Janos Szanyi	EMSL 1044
	CXLS – Technology – Components Session Lead: William Graves Co-Chair: Jerry Seidler	EMSL 2385
	Biogeochemistry/Environmental Science Session Lead: David Shuh Co-Chair: Alex Laskin	EMSL Board Room
	Biology Session Lead: Chris Jacobsen Co-Chair: Matt Marshall	EMSL 1385

TIME	TOPIC	LOCATION
No host dinner by invitation		
Thursday, September 22, 2011		
Presentations from each breakout session: **Session Chair – Ray Teller**		
8:00 – 8:30am	Chemical Sciences/Catalysis Session Lead: Simon Bare	EMSL Auditorium
8:30 – 9:00am	Biogeochemistry/Environmental Science Session Lead: David Shuh	EMSL Auditorium
9:00 – 9:30am	Materials Science Session Lead: Adam Hitchcock	EMSL Auditorium
9:30 – 10:00am	Biology Session Lead: Chris Jacobsen	EMSL Auditorium
10:00 – 10:30am	CXLS Technology – Components: William Graves	EMSL Auditorium
Breakout Session II:	**10:30 – 2:00pm** **(11:45am – Pick up lunch-breakout sessions continued)**	
	Refine ideas – define topic areas – Discussion on the scientific challenges presented.	
	Materials Science Session Lead: Adam Hitchcock	EMSL Auditorium
	Chemical Sciences/Catalysis Session Lead: Simon Bare	EMSL 1044
	Biogeochemistry/Environmental Science Session Lead: David Shuh	EMSL Board Room
	Biology Session Lead: Chris Jacobsen	EMSL 1385
Breakout Session III:	**2:00 – 5:30pm - Writing the Report**	EMSL 1044

Appendix C

Charge to Workshop Session Chairs

Appendix C – Charge to Compact X-ray Light Source (CXLS) Workshop Breakout Session Chairs

Breakout Session I:

The goal of this first breakout session is to create a list of important scientific needs that can be addressed by the compact x-ray light source (CXLS). This brainstorming session will focus on identifying both Scientific Grand Challenges and cases where specific applications of light source techniques from CXLS can provide insight into current materials issues of importance to U.S. Department of Energy (DOE) missions.

During this session, participants are encouraged to provide brief presentations (5 minutes with two slides) to showcase any major areas that should be included. Participants also are encouraged to bring additional information or notes that may be applied to develop the written report.

Wednesday Evening:

Prepare a few slides summarizing the discussions from each breakout session. These will be presented to the workshop audience on Thursday morning.

Thursday Morning:

Present overview of each breakout session and solicit feedback and input from the other workshop participants.

Breakout Session II:

Any ideas developed during the initial (Session I) breakouts will be further refined and expanded into well-defined topic areas to be included in a comprehensive workshop report. As part of this session, writing responsibilities for the report will be assigned (to either groups or individuals).

Breakout Session III:

The writer(s) (groups or individuals) will write at least 1 page on each of the Grand Challenges identified during the workshop. The goal is to have as much written as possible while all of the experts are present at the workshop. At minimum, a description of scientific thrust with clear statements regarding the scientific problems to be addressed should be developed. If possible, the impact on DOE Grand Challenges and potential applications should be detailed. Applicable and usable literature citations and figures also should be included. As such, any cited references must be from publicly available works.

Note: Any copyright or reprinted material will require written permission of the copyright holder.

Workshop Report:

The initial draft of the CXLS Workshop report should be completed within 3 weeks after the workshop and will be provided to participants for review and commentary. In addition to being delivered to the DOE, this report will provide the foundation for a future proposal.

Appendix D

Related Materials

Appendix D – Related Materials

Report of the Basic Energy Sciences Workshop on Compact Light Sources, May 11-12, 2010.
http://science.energy.gov/~/media/bes/pdf/reports/files/CLS.pdf.

Next-Generation Photon Sources for Grand Challenges in Science and Energy, October 27-28, 2008.
http://science.energy.gov/~/media/bes/pdf/reports/files/ngps_rpt.pdf.

National Science Foundation, Light Source Panel Report, September 15, 2008.
http://www.nsf.gov/mps/dmr/LSPanel_FinalRPT_wCorrections9_15_08.pdf.

Science and Technology of Future Light Sources; A White Paper, December 2008. Argonne National Laboratory, Brookhaven National Laboratory, Lawrence Berkeley National Laboratory, and Stanford Linear Accelerator Center. Editors: Arthur L. Robinson (LBNL) and Brad Plummer (SLAC). ANL-08/39, BNL-81895-2008, LBNL-1090E-2009, SLAC-R-917.
http://www-ssrl.slac.stanford.edu/aboutssrl/documents/future-x-rays-09.pdf.

FLASH, the Free-Electron Laser in Hamburg , DESY, Hamburg 2007.
http://www.lightsources.org/images/brochures/FLASHbrochure.pdf.

The Linac Coherent Light Source (LCLS) at SLAC.
http://www-ssrl.slac.stanford.edu/lcls/science.html.

Science Case for a New Light Source (NLS), Jon Marangos et al., October 2008.
http://www.newlightsource.org/documents/NLS%20Science%20Case%203Oct08.pdf.

Collaborative Research: Conceptual Design Study and R&D for a VUV/Soft X-ray Free Electron Laser User Facility, University of Wisconsin-Madison and MIT, November 2007.
http://www.wifel.wisc.edu/WiFEL_R&D_Proposal.pdf.

Additional next-generation light source information:

Free Electron Lasers and Other Advanced Sources of Light: Scientific Research Opportunities.
http://www.nap.edu/openbook.php?isbn=NI000099.

European XFEL. http://xfelinfo.desy.de/en/thema.forschung/2/index.html

XFELinfo: Understandable need-to-knows about the European X-ray laser project XFEL
http://xfelinfo.desy.de/en/druckversion/xfelinfo-2.pdf.

4GLS Science Landscapes. http://www.4gls.ac.uk/Documents/4GLS_Landscapes.pdf.

Pacific Northwest
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