

gas phase systems with femtosecond temporal resolution to watch even the fastest atomic motions. Some of the important scientific problems to be addressed with ultrabright electron sources will be discussed to give an impression of the potential impact of this emerging field.

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Measuring femtosecond structural dynamics at a hard X-ray laser: challenges and successes

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The World's first hard X-ray laser, the Linac Coherent Light Source (LCLS), is now operational at the SLAC National Accelerator Laboratory [1]. The LCLS routinely produces femtosecond pulses of 9 keV photons with 2 mJ of pulse energy at a 120 Hz repetition rate. The unprecedented combination of photon flux, spatial and time resolution of the LCLS promises to revolutionize the observation of structural dynamics by measuring the time evolution of the electron density during a photo-induced transformation.

Although many of the attributes of X-ray laser are ideal for studying structural dynamics, there are significant experimental challenges involved that must be overcome before successful experiments are realized. Unlike storage ring based sources, X-ray pulses from the LCLS exhibit inherent fluctuations due to the self-amplified spontaneous emission (SASE) process through which the radiation is generated. As such the spatial, spectral, temporal and intensity properties vary on a pulse-by-pulse basis. These fluctuations are particularly problematic for experiments studying stimulated dynamics.

The first hard X-ray experimental station, the X-ray Pump-Probe (XPP) instrument, began user operations in the Fall of 2010. The XPP instrument is designed specifically for time-resolved studies and includes a synchronized optical laser. The first experiments included time resolved studies of optically initiated ferroelectricity, photoactive proteins (myoglobin) and iron spin crossover complexes. Many challenges associated with a SASE based X-ray source were encountered. However, most challenges were overcome and a time resolution of 150 fs was achieved.

[1] P. Emma et al., *Nature Photon.* **2010**, *4*, 641647.

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Structural dynamics of proteins conformers and conformer selection in chemical reactions

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Characteristic for all chemical reactions are bond breaking and bond making processes. Our vision is to optimize chemical reactions towards specific product states by a clever combination of chemical site-specificity, self-assembly and state-selectivity which can be "tuned" from orbital control through the structure of the local environment and selective excitation schemes (heat / optical pulses) to bulk structural changes – or to say it in other words – from the simple to the complex. We would like to understand - what are the driving forces of environment tuning chemistry? Most motors are defined through gradients in the chemical potential. Are chemical redox potential changes or the changes of chemical potential the most efficient chemical ways for storing energy?

To do so we need to gain a deeper understanding of the mechanism of chemical reactions from a structural point of view – besides its understanding of energetic. In order to elucidate information about reactions and their pathways multidimensional reaction landscapes are required for their description – not only in the energy coordinate but also in the reaction coordinate. In order to elucidate information about the reaction coordinate of complex systems we apply time-resolved x-ray techniques allowing us to obtain a real-time picture of the structural dynamics of chemical and biochemical systems in the crystalline and in the liquid phase.

Common for all time-resolved x-ray experiments is the applied pump / probe scheme, where an optical pump-laser initiates a reaction whose structural time evolution is then investigated by x-ray probe pulses at various time delays. The x-ray photon-in / photon-out techniques are based on diffraction or spectroscopic techniques like near edge spectroscopy or x-ray emission spectroscopy. Meanwhile x-ray spectroscopic techniques probe the local environment around specific atoms in a molecule such as orbitals, crystallographic experiments (monochromatic or Laue) reveal the structure of the bulk of periodic systems. Time-resolved diffuse x-ray scattering experiments give information about the structure of liquids.

In the current contribution we will present our latest efforts in that respect. We will reflect capabilities and limitations of state-of-the-art x-ray techniques for the investigation of two different kind of chemical reactions in complex environment: addition reactions in the solid state and dissociation reactions in the liquid state. We will discuss our current status in reaching this goal (proof-of-principle experiments with free electron laser radiation [1], [2]) and how the investigation of chemical reactions benefits from pulsed synchrotron radiation and Free Electron Laser science as they have been performed at the FLASH facility and at LCLS.

[1] I. Rajkovic et al., *Phys. Rev. Lett.* **2010**, *104*, 125503-6. [2] J. Hallmann, et al., *J. Phys.* **2010**, *B 43*, 194009-194016.

Keywords: FEL research, ultrafast chemistry, structural dynamics

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Single-pulse laue TR diffraction: Methods, results and use of QM/MM theory

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Time-resolved X-ray diffraction experiments including those performed at XFEL sources require modification of data analysis procedures as sample destruction in the X-ray and/or laser beam typically requires multi-crystal data collection. Modifications introduced include a scaling technique for relative scaling within multi-crystal data sets, use of the RATIO technique in which measured I_{ON}/I_{OFF} ratios are used in combination with conventional data [1], and the use of refinement methods [2] and R-factors [3] specific for dynamic-structure crystallography. The procedures have been applied to several sets of Laue data collected at beamline 14-ID at the Advanced Photon Source [4]. The extended bandwidth of the pink Laue technique allows use of one or a few X-ray pulses per data frame, thus minimizing crystal damage by laser exposure and optimizing the attainable time-resolution.

Results for the α -modification of $Rh_2(\mu\text{-PNP})_2(\text{PNP})_2(\text{BPh}_4)_2$ (PNP = $\text{CH}_3\text{N}(\text{P}(\text{OCH}_3)_2)_2$, Ph = phenyl) (**1**) show a shortening of the Rh-Rh distance of 0.136(8) Å and significant displacements of the ligands on excitation. This may be compared with those on an earlier monochromatic study of the $[\text{Rh}_2(1,8\text{-diisocyno-p-menthane})_4]^{2+}$ ion in which a Rh-Rh shortening of 0.85(5) Å was observed [5]. The polychromatic results on (**1**) are clearly the more accurate ones. They are not well reproduced by isolated molecule calculations, but can be accounted for quantitatively by taking into account the confining effect of the crystal environment with the QM/MM (Quantum Mechanics/Molecular Mechanics) method [6], thus underlining the differences between isolated molecules and molecules in crystals. Additional data have been collected on a number of phosphorescent Cu(I)-phenanthroline chromophores which are candidates for use in photovoltaic cells.

The modified Laue method is capable of producing excited state structures at atomic resolution of a quality compatible with or better than those of monochromatic synchrotron experiments. The modifications described are relevant for monochromatic data sets collected at X-ray Free Electron Laser sources.

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Dynamic Investigation of photoinduced phase transition in prussian blue analogs by picosecond time-resolved XAFS

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Prussian blue analogs have recently attracted great interest due to their various characteristics in the photoinduced phase transition (PIPT) as a photo-induced magnetization as well as photo-induced structural change.[1], [2] The investigation of the dynamics of PIPT allows us to obtain information how the photo-excitation in the single site expands into a macroscopic phase transition. Picosecond time-resolved XAFS experiments were performed on the NW14A at the Photon Factory Advanced Ring (PF-AR).[3], [4] The time-resolved XAFS spectra were collected by the pump-probe technique with a femtosecond laser system. In EXAFS and XANES regions, transient features attributed to the PIPT were obtained at 100 ps resolution. The detailed results will be presented.

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X-ray diffraction methods as a complementary tool for analyses of historical objects

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This presentation summarizes the research done by our team using different X-ray diffraction (XRD) methods to characterize historical objects such as paintings, ceramics, metals and stones. Also pigments and salts are typified since XRD is essential for analyzing materials with similar elemental composition but differing mineralogy. Our goals are to apply XRD methods as non-destructive, routine laboratory analyses combined with complementary techniques to fully characterize historical items, and thus, to draw artistic/archaeological conclusions and supply information to enable conservation/restoration interventions.

X-ray thermodiffraction (XRTD) is a powerful tool to track time-resolved, *in situ* mineralogical and phase transitions of varied materials such as pigments and hydrated salts. Using XRTD we studied the azurite decarbonation process [1] and sulfate-rich salt dehydration. New routines for 2D mapping allow us to better interpret reaction trends and kinetic rates [2].

Micro-XRD is a non-destructive technique that enables direct analysis of small (<1mm) artwork samples. Via micro-XRD we characterized pigments used in Islamic palaces from Granada (e.g. the Alhambra), bricks, potteries, enamels, bronze artifacts, patinas and stones, as well as newly formed minerals (salts and high T silicates) [3]. We used a single-crystal diffractometer and the software XRD2Dscan [4] to transform Debye-Scherrer rings into conventional powder diffractograms. The microtextural data of crystalline phases obtained from the Debye-Scherrer rings were used to determine crystal sizes of mineral grains and quantify grain sizes of phases present in the same layer. This novel micro-XRD application used on painting samples sheds light on the nature, manufacture and weathering of pigments [5].

Grazing incidence XRD (GIXRD) is a potent method for surface characterization of thin films and monolayers such as metal and alloys, providing information on corrosion processes. Few papers are published on the application of GIXRD to artworks, and most focus