The 3rd Banff Meeting on Structural Dynamics
Ultrafast Dynamics with X-Rays and Electrons

February 17–20, 2013
The Banff Centre, Banff, Alberta, Canada

www.sun.ac.za/banff
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Ultrafast Dynamics with X-Rays and Electrons

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Conference Chair   R. J. Dwayne Miller  (CFEL, Hamburg)
CoChair   Heinrich Schwoerer  (U Stellenbosch)

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Jiro Matsuo (Kyoto)
Bryan Reed (LLNL)
Christoph Rose-Petruck (Brown)
Robert Scholten (Melbourne)
Bradley Siwick (McGill)

Invited Speakers
Daniel Comparat (Paris Sud)
James Evans (PNNL)
Alexander Föhlisch (BESSY Berlin)
Kristoffer Haldrup (U Lyngby)
Jom Luiten (Eindhoven)
Bastian Pfau (TU Berlin)
Claus Ropers (Göttingen)
Kai Rossnagel (Kiel)
Germán Scaini (MPSD, CFEL)
Klaus Sokolowski-Tinten (U Duisburg-Essen)
John Spence (Arizona State)
Nobuo Tanaka (Nagoya)
Peter Weber (Brown U)

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10:30-12:30 Registration  
*Central Foyer, Professional Development Centre*

12:30 – 13:30 Lunch  
*Vistas Dining Room, Sally Borden Building*

**13:50**  
**Start of the Meeting, welcome – opening remarks**  
*Auditorium, Max-Bell Building*

14:00-14:30 Structural Dynamics in Vanadium Dioxide and Graphite Studied with Radio-Frequency Compressed Ultrafast Electron Diffraction  
*Bradley Siwick, McGill University, Montreal, CA*

**methods I**

14:30-15:00 X-ray vs Electrons for Fast Imaging  
*John Spence, Arizona State University, USA*

15:00-15:30 Movie Mode Dynamic Transmission Electron Microscopy (DTEM)  
*Bryan Reed, LLNL Livermore, USA*

15:30-15:45 Coffee Break

15:45-16:15 Space-Charge in Charged Particle Bunches from Cold Atom Photoionization  
*Robert Scholten, University of Melbourne*

16:15-16:30 Sub-Picosecond, Table Top X-Ray Absorption Spectroscopy Using Superconducting Microcalorimeters  
*L Miaja, NIST, Boulder Colorado*

16:30-17:00 Ultracold and Ultrafast Electrons Diffracted from Graphene  
*Wouter Engelen, Eindhoven University of Technology*

17:00-17:30 Phasing by Enhanced Anomalous X-ray Diffraction at High-Intensity  
*Henry Chapman, DESY Hamburg*
Monday, 18th February

8:00-10:00  Registration  
*Foyer, Max-Bell Building*

**magnetic/spin systems**

8:30-9:00  Ultrafast Optical Demagnetization manipulates Nanoscale Spin Structure in Domain Walls  
B. Pfau, *Institut für Optik und Atomare Physik, Berlin, Germany*

9:00-9:15  Combined femtosecond X-ray absorption and optical spectroscopies reveal photo-switching structural pathway in a spin-crossover crystal.  
R. Bertoni, *University Rennes, France.*

9:15-9:45  Spin-polarized transmission electron microscope toward an analysis of sub-picosecond dynamics  
M. Kuwahara, *Nagoya University, Japan*

9:45-10:00  Atomic motion associated with the coherent optical phonon in charge and orbitally ordered manganites  
A. Caviezel, *Swiss Light Source, Switzerland*

10:00-10:15  Ultrafast dynamics of magneto-structural phase transitions  
S. O. Mariager, *Swiss Light Source, Switzerland.*

10:15-10:30  Coffee Break

**organic systems I**

10:30-11:00  X-ray Free Electron Laser investigations of picosecond and sub-ps dynamics in and around photo-excited transition metal complexes  
K. Haldrup, *Danish Technical University, Lyngby, Denmark*

11:00-11:15  Structural Dynamics and Reactivity in Neuroglobin from Experiment and Simulations  
M. Meuwly, *Department of Chemistry, University of Basel, Switzerland*

11:15-11:45  Exploiting Simultaneous Ultrafast X-Ray Spectroscopy and Scattering to Study Intra- and Intermolecular Dynamics  
C. Bressler, *CFEL Hamburg, Germany*

11:45-12:00  Time-Resolved Laue Diffraction of Light-Induced Changes in Highly Luminescent Cu(I) Complexes  
Philip Coppens, *University of Buffalo, NY, USA*

12:00-13:00  Lunch  
*Vistas Dining Room, Sally Borden Building*

**Free Afternoon**
Tuesday, 19th February

metals/correlated system

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<tr>
<th>Time</th>
<th>Title</th>
<th>Speaker, Institution</th>
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<tr>
<td>8:30-9:00</td>
<td>Time-domain identification of an excitonic insulator by time-resolved ARPES</td>
<td>K. Rossnagel, University of Kiel, Germany</td>
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<td>9:00-9:15</td>
<td>Formation Dynamics of a Charge Density Wave in 1T-TaS₂ studied by Femtosecond Electron Diffraction</td>
<td>N. Erasmus, Stellenbosch University, South Africa,</td>
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<td>9:15-9:30</td>
<td>Comparison of the Lattice Response to Femtosecond Laser Excitation of Bismuth by Time Resolved Electron Diffraction in Reflection and Transmission Geometry</td>
<td>A. Kalus, University of Duisburg-Essen, Germany</td>
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<td>9:30-9:45</td>
<td>Nonlinear Direct Coupling of Femtosecond Laser Pulses with the Lattice Observed by Time Resolved Electron Diffraction</td>
<td>P. Zhou, University of Duisburg-Essen, Germany</td>
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<td>9:45-10:15</td>
<td>Quenching of sequential bond breaking and non continuous bond breaking seen through time resolved and sub-natural linewidth RIXS</td>
<td>A. Föhlisch, Institute for Methods and Instrumentation in Synchrotron Radiation Research, Helmholtz-Zentrum, Berlin, Germany</td>
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<td>10:15-10:30</td>
<td>Coffee Break</td>
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<td>10:30-11:00</td>
<td>Femtosecond X-ray diffraction on LiBH₄ and LiH: quasi-instantaneous electronic response to strong laser electric fields</td>
<td>V. Juvé, Max-Born-Institut, Berlin, Germany</td>
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<td>11:00-11:30</td>
<td>Switching dynamics in laser-driven phase change materials probed by time-resolved X-ray diffraction</td>
<td>F. Quirin, University of Duisburg-Essen, Germany</td>
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methods II

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<td>11:30-12:00</td>
<td>Ultrafast low-energy electron diffraction using nanotip emitters</td>
<td>C. Ropers, University of Göttingen, Germany</td>
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<td>12:00-12:15</td>
<td>Electron effective mass: A route to ultra-bright photocathodes</td>
<td>W. Schroeder, University of Illinois at Chicago, USA</td>
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<td>12:15-12:30</td>
<td>Single-Shot Ultrafast Electron Diffraction Using Electrons Accelerated by an Intense Femtosecond Laser Pulse</td>
<td>S. Tokita, Kyoto University, Japan</td>
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12:30-13:30 Lunch  
*Vistas Dining Room, Sally Borden Building*

14:00-14:30 Quantifying In-situ Reactions in the STEM/DTEM  
*N.D. Browning, Fundamental and Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, USA*

14:30-14:45 Development of Femtosecond Time-resolved MeV Electron Microscopy  
*J. Yang, Osaka University, Japan*

14:45-15:00 Nanofluidic cells with controlled path length and liquid flow for rapid, high-resolution in situ electron microscopy  
*C. Müller, University of Toronto, Canada*

15:00-15:30 High flux monochromatic ion and electron beams based on laser-cooled atoms  
*D. Comparat, Université Paris-Sud, France*

15:30-16:00 Coffee Break

16:00-17:30 **postdeadline papers and poster jam session**

18:00 Reception / Poster Session  
*Max-Bell Building*
Tuesday, 19th February, Poster Session

17:00-17:30 poster jam session (max 3 min per poster!)

thereafter Reception / Poster Session
Max-Bell Building

Poster contributions

From time-averaged to time-resolved electron diffraction in Edinburgh
Derek A. Wann, Paul D. Lane, and Matthew S. Robinson, University of Edinburgh, UK

Lattice Response of Nickel to Femtosecond Laser Excitation Studied by Time Resolved Transmission Electron Diffraction

Data Post-Processing and Structure Refinement of (EDO-TTF)$_2$PF$_6$ in UED Experiment
Lai Chung Liu, Meng Gao, Alexander Marx, Germán Sciaini & R.J. Dwayne Miller, University of Toronto CA, CFEL Hamburg, Germany

Review of ‘The Workshop on Ultrafast Electron Sources for Diffraction and Microscopy Applications (UESDM)’
Renkai Li, Pietro Musumeci, and Xijie Wang, UCLA, USA

Pauli Driven Cold Explosion in Alkali Halides
Masaki Hada, Dongfang Zhang, Regis Gengler, Toshio Seki, Jiro Matsuo, German Sciaini and R. J. Dwayne Miller, CFEL Hamburg Germany, Kyoto University, Japan

Local Structural Dynamics of a DNA Hairpin Studied by Ultrafast Fluorescence Down-Conversion Spectroscopy
Patricia Tourón Touceda, Thomas Gelot, Olivier Crégut, Jérémie Léonard and Stefan Haacke, Université de Strasbourg-CNRS, France

Ultrafast Dynamics of Charge Density Waves in 4H$_b$-TaSe$_2$ Probed by Femtosecond Electron Diffraction
N. Erasmus, M. Eichberger, K. Haupt, I. Boshoff, G. Kassier, R. Birmurske, H. Berger, J. Demsar, and H. Schwoerer, Stellenbosch University SA, Konstanz University, Germany

Atomic Level Structural Information from Correlated X-ray Scattering
D. Ratner, SLAC, USA

Transition-edge microcalorimeter sensors for X-ray science
Galen O’Neil, Luis Miaja, Kevin Silverman, Jens Uhlig, Dan Swetz, Doug Bennett, Joel Ullom, NIST Boulder, USA

Observation of Photoinduced ‘Over-Neutralization’ in TTF-CA by Time-Resolved Single Crystal X-ray Structure Analysis
Manabu Hoshino, Shunsuke Nozawa, Tokushi Sato, Ayana Tomita, Shin-ichi Adachi, Shin-ya Koshihara, Tokyo Institute of Technology, Japan
Controlled molecules for time-resolved electron diffraction experiments
Sebastian Trippel, Terence G. Mullins, Nele Müller, Jens Kienitz, Karol Długolecki, and Jochen Küpper, CFEL, Hamburg, Germany

Radiofrequency phase space manipulation of ultrashort electron beams

Simulating the beam profile and time resolution for a new electron diffractometer
Paul D. Lane, Matthew S. Robinson, and Derek A. Wann, University of Edinburgh, UK
Wednesday, 20th February

methods III

8:30-8:45  Streaking of Non-Relativistic Electron Diffraction Patterns with a sub-ps Resolution Streak Camera  
Max Eichberger, University of Konstanz, Germany

8:45-9:00  Improving the Temporal Resolution of the Hybrid DC-RF Gun System  
Meng Gao, University of Toronto

9:00-9:15  Single-shot 35 fs Temporal Resolution Electron Shadowgraphy  
Renkai Li, UCLA, USA

9:15-9:30  Femtosecond x-ray Diffraction of Photochromic Diarylethenes  
Yusaku Hontani, Kyoto University

9:30-9:45  Ultrafast Electron Diffraction Study of the Ring-Closing Reaction in a Thermally Irreversible Photochromic Crystal  
Jean-Ruel Hubert, University of Toronto, Canada

9:45-10:15  Coffee Break

organic systems II

10:15-10:45  Femtosecond X-ray Diffraction from Two-Dimensional Protein Crystals  
James Evans, Pacific Northwest National Laboratory, USA

10:45-11:00  Watching Chemical Dynamics in Real Time: Can Gas-Phase x-ray Diffraction Probe the Dynamics of 1,3-Cyclohexadiene?  
James Budarz, Brown University, Providence, USA

11:00-11:15

11:15-11:30  Protein crystallography at free-electron laser sources  
T. Barends, Max-Planck-Institut für Medizinische Forschung, Heidelberg, Germany

11:30–12:00  Ultrabright femtosecond Electron Diffraction Breaks the Barrier to Atomic Exploration on Organic Materials  
Germán Sciaini, University of Toronto Canada, CFEL Hamburg Germany

12:00-12:05  Closing remarks – end of the scientific meeting

12:05  Lunch  
Vistas Dining Room, Sally Borden Building
Abstracts – Talks
Structural Dynamics in Vanadium Dioxide and Graphite Studied with Radio-Frequency Compressed Ultrafast Electron Diffraction

Bradley J. Siwick¹, Robert P. Chatelain¹, Vance R. Morrison¹, Ali Hendaoui² and Mohamed Chakker²

¹Departments of Physics and Chemistry, Center for the Physics of Materials, McGill University, 801 Sherbrooke St. W, Montreal, QC Canada H3A 2K6
²Institut National de la Recherche Scientifique, Centre Énergie, Matériaux, Télécommunications, 1650 Lionel Boulet boulevard, Varennes, QC, Canada, J3X 1S2

In this talk I will describe how we have recently used ultrafast electron diffraction (UED) with radio-frequency compressed pulses [1] to study photo-induced structural dynamics in vanadium dioxide and graphite at an unprecedented level of detail. Using a pair distribution function analysis of the UED data, we have mapped changes in the structure of the vanadium dioxide unit cell through the optically-induced ultrafast insulator-to-metal transition. This analysis has, for example, allowed us to identify the timescales associated with both the formation of the vanadium-vanadium bonding and the oxygen coordination consistent with the high temperature tetragonal phase. In addition, we have studied the complex structural dynamics in graphite following femtosecond laser excitation over a wide-range of fluences in both HOPG and single crystal graphite. I will describe the coherent and incoherent structural dynamics, including changes to both \( a \) and \( c \) lattice constants and the stacking arrangement of the planes that follow femtosecond laser excitation as suggested by these observations.

X-ray vs Electrons for fast imaging

John C.H. Spence

Physics Dept., Arizona State University, Tempe Az 85282. USA and LBNL, Ca. spence@asu.edu

The relative strengths and weaknesses of X-ray and electron beams for fast, high-resolution imaging will be discussed, toward the goal of making a molecular movie. Both produce femtosecond pulses (8,2), and for both efforts are under way to construct "table-top" apparatus. New electron sources are under development, using, for example, ionized trapped atoms (1). We note: i). The much higher scattering cross section of electrons (including the slower nuclear interaction) giving more signal but resulting in multiple scattering perturbations. ii). The discovery that radiation damage can be avoided by using a sufficiently fast pulses which terminates before damage begins (2). This "diffract-and-destroy" approach allows study of irreversible atomic processes, which has yet to be demonstrated using electrons. iii) The existence of aberration-corrected lenses for electrons, providing sub-Angstrom probes. iv) Field emission sources are brighter than current-generation synchrotrons, fully coherent, and laser-pulsed, but not brighter than an XFEL. (Our measurements of degeneracy for photofieldemission sources will be reviewed). A cold field-emitter generates perhaps a hundred electrons per picosecond, insufficient to form an image, so requiring "stroboscopic" methods. An X-ray free electron laser produces more than 1E12 photons in ten fs (with 1E6 then scattered from a virus (5)), but practically all either do not interact with the sample, or are annihilated in production of photoelectrons. This reduces background greatly compared with electron diffraction, where beam-electrons which lose energy in the sample continue on the detector to make background. v) The use of pump-probe methods if a suitable fast trigger can be found. Since a broad energy spread cannot be generated by an XFEL, a new method of monochromatic pump-probe time-resolved protein nanocrystallography has been developed using a continuous liquid jet to supply samples in the absence of a goniometer (3). vi) The search for suitable triggerable systems in materials science, such as electronic excitations (e.g surface plasmons). vii) Differences in time resolution between the methods. viii) The effects of coulomb interactions on electron beams in producing unwanted energy spread and beam divergence, and the reduction of these effects at high energy due to relativistic effects, suggesting the use of a specially designed high voltage electron microscope. This raises the issue of coherence requirements, which appears to exclude the reconstruction of lensless atomic resolution fast electron images. Energy-loss spectroscopy is conveniently combined with fast electron diffraction at the nanoscale, giving excitation lifetimes and the time-dependent dielectric response function. XFEL diffraction from protein nanotaxls provides atomic resolution and femtosecond time resolution, opening up new possibilities for structural biology (7, 2) including solution of the phase problem (4). The use of scattering from many identical molecules, randomly oriented in solution may also be useful (6), since "snapshot SAXS" patterns are two-dimensional, containing more information than conventional isotropic SAX patterns for particles frozen in space or time.

Movie Mode Dynamic Transmission Electron Microscopy (DTEM)


Physical and Life Sciences Directorate, Lawrence Livermore National Laboratory, 7000 East Ave. L-356, Livermore, CA, 94551, USA
reed12@llnl.gov

Materials do extraordinary things when subjected to extraordinary driving forces. Between femtosecond-scale processes of nonequilibrated electrons and millisecond-scale processes of deformation and transformation lies a gulf of phenomena that are as richly complex as they are difficult to capture. The Dynamic Transmission Electron Microscope (DTEM) at LLNL is designed specifically to access unique material processes on the scale of nanometers and nanoseconds, and especially to use real-space TEM imaging to directly visualize micro- and nano-structural evolution that is completely invisible to any other technique. For some years, the DTEM has been capable of capturing a complete TEM image in a single 15-nanosecond exposure. While valuable, this left many details of complex material evolution out of the picture. Recent upgrades have dramatically increased the flexibility of this instrument. An arbitrary-waveform laser system now allows the time resolution to be continuously varied from a few ns to multiple μs but, better yet, when combined with a new electrostatic deflector system it has enabled a new operation mode that we call "movie-mode DTEM." This system is capable of capturing multiple exposures of fast-evolving material processes within the span of a few μs. We will show how this enables an entirely new class of experiments and conclude with some comments on how the hardware may develop in the future.

This work was performed under the auspices of the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, by Lawrence Livermore National Laboratory under contract DE-AC52-07NA27344.
Charged particle sources based on photoionisation of laser cooled atoms can in principle create bunches shaped in three dimensions and hence achieve the transverse spatial coherence and brightness needed for picosecond diffractive imaging with nanometre resolution. We have used the arbitrary shaping capability of cold-atom electron and ion source (CAEIS) to investigate the interactions within charged particle bunches. We see remarkable ion bunch shape formation and evolution, with direct visualisation made possible by the very cold (milli-Kelvin) ions of a CAEIS. For example, nine small closely spaced ion bunches expand to form a wagonwheel structure (see figure). To simulate the structures, we have developed a detailed model for ionisation from a cold atom cloud, based on four-level optical Bloch equations. The bunches are propagated using standard particle tracking software. The unusual shapes depend on a “halo” formed by absorption of scattered light prior to ionisation.

We have also investigated production of ultrafast electron bunches using a two-step coherent excitation with a femtosecond laser from ground to excited state, and a nanosecond laser from excited state to the continuum. Our measurements show evidence of sub-nanosecond electron bunches, and the transverse coherence of the electron bunches is surprisingly good given the large energy spread of the femtosecond excitation laser. The effect is readily explained in terms of spatially dependent field ionisation which selects electrons with momenta parallel to the external electric field.

These results will contribute to the development of ultrafast electron diffraction imaging systems using cold atom electron sources.
Sub-picosecond, table-top x-ray absorption spectroscopy using superconducting microcalorimeters


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The ability to capture molecular structural dynamics on ultrashort timescales has been a goal of the scientific community for decades. The understanding of molecular dynamics is fundamental for the development of next-generation solar cells, industrial catalysts, and energy storage materials among others. Here we present a table-top x-ray imaging system to capture the motion of electrons, atoms, and molecules on sub-picosecond time scales. Our x-ray imaging system comes from combining a newly acquired 20mJ, 1kHz Ti:Sapphire laser for x-ray generation and a recently assembled, 160-pixel superconducting microcalorimeter array for x-ray detection with high energy resolution and high efficiency. In our experimental setup, a portion of the laser energy is sent through an optical parametric amplifier to produce photons with excitation wavelengths in the visible part of the spectrum. The rest of the laser energy is focused onto a water jet to produce a plasma and sub-picosecond x-ray pulse that is synchronized to the excitation pulse. We use a polycapillary x-ray optic to extract x-rays from the vacuum chamber containing the water jet and to focus them on a sample. Finally, the x-rays transmitted through the sample are sensed by our microcalorimeter array detector.

Utilizing this table-top setup, we are working to observe the insulator-to-metal transition in vanadium dioxide (VO$_2$). This strongly correlated material undergoes a transition between a monoclinic insulator and a rutile metal when heated above 340K. To date, VO$_2$ has been heavily studied with a variety of ultrafast techniques. Ultrafast vanadium K-edge x-ray absorption measurement of this system will be an important complement to previous studies since the large changes in electronic structure are concomitant with atomic-structural rearrangements. Our tabletop setup is capable of achieving an energy resolution near 3 eV for the x-ray absorption spectrum of VO$_2$, both in the metallic and insulating states. Progress is being made in the dynamic study of this insulator-to-metal transition with a time resolution of 1ps.
Ultracold and ultrafast electrons diffracted from graphene

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A recent development in electron microscopy and diffraction is the achievement of ultrafast time resolution using high-repetition rate single electron sources and single-shot many-electron sources. Intrinsic heating mechanisms due to inter-particle Coulombic forces make it difficult to achieve large coherence lengths under these conditions.

We have developed a new class of electron source by using near-threshold, pulsed photoionization of laser-cooled, trapped rubidium atoms which allows us to produce intense electron pulses with large intrinsic coherence length. Several properties of electron pulses extracted from such an ultracold source have already been investigated, showing in particular that temperatures of a few Kelvin and emittances in the nanometer-radian range can be achieved with tens of thousands electrons per pulse for nanosecond pulse lengths. Photoionization also permits charge shaping in order to reduce emittance growth.

We have recently extended this work to produce picosecond electron pulses by using ultrafast lasers for the ionization step. We show that few-Kelvin electron temperatures can still be achieved under these conditions, despite the spread in photon energy. We explain this surprising result using a classical hydrogen model that considers the electron trajectories resulting from photoionization in detail. A more realistic rubidium model using the GPT particle tracking code confirms the results. In addition, we show how polarization effects arise and that these can be used to further control the electron beam properties.

To demonstrate application of the ultracold electron source, we are currently studying diffraction from graphene-like samples at few-kV beam energy. We observe the familiar powder diffraction rings and use these to characterize the transverse coherence properties of the electron beam. This work in progress will be followed by a characterization of the bunch length using a radio-frequency streak cavity.
Phasing by Enhanced Anomalous X-ray Diffraction at High-Intensity

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At the first Banff meeting on Structural Dynamics we introduced the new method of serial femtosecond crystallography, or SFX [1]. This uses X-ray free-electron laser pulses to collect single-pulse diffraction data from a flowing suspension of protein nanocrystals. The method allows protein structures to be solved from sub-micron crystals that would be impossibly small for synchrotron measurements, and the first new biological structure using the method has been recently determined [2]. The femtosecond pulses outrun the effects of radiation damage, so that exposures with up to 40 GGy dose per crystal have been recorded compared with a tolerable limit of 30 MGy for synchrotron measurements on cryogenically frozen samples. The X-ray intensity in this case approaches 10\textsuperscript{20} W/cm\textsuperscript{2}. Although the pulses outrun all motion of atoms they undergo considerable ionization, due to the initial photoabsorption and to subsequent impact ionization from photoelectrons. Nevertheless, under these conditions it was predicted that phasing crystal structures by anomalous diffraction would still work [2]. In fact, the high degree of ionization that occurs at photon energies above the absorption edge lead to dramatic changes to the atomic scattering factors that enhance the dispersive signals (that is, it enhances differences at different wavelengths). The anomalous term (imaginary part of the scattering factor) is also predicted to be largely preserved under these conditions. These studies have led to proposals for various types of phasing schemes. Very recent experiments at LCLS have shown that anomalous signals can indeed be measured. These results will be presented and discussed.

Ultrafast Optical Demagnetization manipulates Nanoscale Spin Structure in Domain Walls

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Demagnetization of a ferromagnet by an optical excitation pulse is known to proceed on an ultrafast timescale, typically in the femtosecond regime. Since the discovery of this ultrafast process by Beaurepaire et al. in 1996, its mechanism has been intensely debated. So far, most work has focused on homogeneous samples to understand the intrinsic demagnetization mechanisms. In particular, the transfer of energy and (spin) angular momentum between the light pulse used for excitation, the electrons, their spin configuration and the crystal lattice has been addressed. Additional extrinsic mechanisms arising due to nanoscale heterogeneity have only recently entered the discussion. It was proposed in a theoretical study, that superdiffusive spin transport could significantly contribute to the ultrafast demagnetization. [1] Experimentally, the influence of spin transport was particularly investigated in thin-film systems with (anti)-ferromagnetically coupled layers. [2]

Here we use femtosecond X-ray pulses from a free-electron laser to study thin-film Co/Pt multilayer samples exhibiting a labyrinth-like network of nanometer-sized magnetic domains. [3]

We observe an infrared-pump-induced change of the spin structure within the domain walls on the sub-picosecond timescale. This domain-topography-dependent contribution connects the intrinsic demagnetization process in each domain with spin-transport processes across the domain walls, demonstrating the importance of spin-dependent electron transport between differently magnetized regions as an ultrafast demagnetization channel. This pathway exists independent from structural inhomogeneities such as chemical interfaces, and gives rise to an ultrafast spatially varying response to optical pump pulses.

Combined femtosecond X-ray absorption and optical spectroscopies reveal photo-switching structural pathway in a spin-crossover crystal

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Controlling matter with light poses a key scientific challenge. In the family of spin-transition compounds studied here, there exist two competing electron states with different spin multiplicity: low spin (LS) and high spin (HS). For changing the magnetic state we can use different external stimuli such as temperature, magnetic fields, pressure and light. The possibility of tuning the system’s spin state with light has been well known for twenty years, but until now, mainly cw light excitation has been used to investigate slow macroscopic dynamics. Ultrafast lasers give the possibility to follow in real time the spin state switching and understand the mechanism involved in such transformation. Most of these studies have been carried out in liquid state with molecules in solution [1]. Studying solid state is essential in material science, where the medium in not passive but active [2,3], hence it may give rise to cooperative response induced by light excitation. The structural reorganization plays a key role in the stabilization of the photoinduced HS state. But the pathway driving the system from the initial LS to the HS state involves different electronic and structural degrees of freedom and is therefore complex to describe. Interaction also observed by time resolved x-ray diffraction at Biocars beam line at the APS.

We address here the ultrafast response of such materials to femtosecond light excitation by using femtosecond x-ray absorption spectroscopy. The experiment, performed at the XPP beam line at LCLS reveals structural reorganization within 140 fs. Optical pump-probe studies also show that a coherent structural dynamics is driven by the laser flash. It involves breathing modes associated with the elongation of the Fe-Ligand distance as well as torsion modes as the ligand rearrange in the HS state. On longer time scale, where cooperative effects between the molecules constituting the material take place, we could detect cooperative switching driven by elas.

Great advances have recently been made in magnetic recording technology and spintronic devices, which are promising for high-density storage devices. Such devices are expected to lead to the development of systems that can analyze magnetic and spin states with a nanometer-order spatial resolution. Already electron holography and Lorentz microscopy have been used for observation of magnetization state of magnetic recording media as well as spin-detection scanning electron microscopy, whose image resolution is, however, restricted to larger than 5 nm. It is important that the inner spin-state can be observed directly in arbitrary direction with an atomic scale.

We have been seeking to combine electron microscopy and accelerator technology to realize a spin-polarized transmission electron microscope (SPTEM), which consists of a polarized electron source (PES) and a conventional TEM. We have commenced developing a PES for a TEM [1-3]. Spin-polarized electrons can be generated using an optical orientation of III–V semiconductors and vacuum extraction that uses a negative electron affinity (NEA) surface. Several beam parameters of the PES are vastly superior to those of conventional thermal electron beams. In addition, it has the ability to generate a sub-picosecond multibunch beam. A high polarization ratio of 92% and a high QE of 0.5% have been realized using a GaAs–GaAsP strained superlattice photocathode with a 100-nm-thick active layer that was excited with 780 nm wavelength light[4, 5]. This high-performance PES will enable dynamic observation of magnetic structures with high spatial and temporal resolutions as pulsed TEM or DTEM.

We have succeeded in development of the SPTEM [1]. The SPTEM consists of a PES, a TEM lens system that includes a spin manipulator, an objective-lens system, a projector-lens system, and an image-detection system including EELS. The beam energy is set to be below 40 keV, that is a kind of lower energy TEM, because the spin interaction with condensed matters is very small comparing with the Coulomb interaction. We have already demonstrated that the SPTEM can provide both TEM images and the diffraction patterns [1]. The TEM images can be obtained in a spatial resolution of 1 nm at 30 kV acceleration voltage. The apparatus can provide a 0.24-eV energy width of electron beam in the TEM without any monochrometers. We would like to talk about these results and future plans.

Atomic motion associated with the coherent optical phonon in charge and orbitally ordered manganites

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La\textsubscript{0.25}Pr\textsubscript{0.375}Ca\textsubscript{0.375}MnO\textsubscript{3} (LPCMO) belongs to the three dimensional mixed valence manganites of the form R\textsubscript{1-x}A\textsubscript{x}MnO\textsubscript{3}. Jahn-Teller interactions distort the Mn\textsuperscript{3+} octahedra at this specific doping inducing charge and orbital ordering (CO/OO) below TCO/OO ≈ 210 K. The structural reorganisation in the low temperature phase leads to a doubled unit cell establishing a structural superlattice. The main atomic motion needed to adapt to the new symmetry are displacements along the crystal x-direction of the Mn\textsuperscript{4+}O\textsubscript{6} sites and of the rare earth ions.

A low frequency coherent Ag phonon present only below TCO/OO serves as signature for the CO/OO state\textsuperscript{1}. Based on an oxygen isotope Raman study\textsuperscript{2} we had attributed this phonon in a previous work on La\textsubscript{0.42}Ca\textsubscript{0.58}MnO\textsubscript{3} (LCMO) to the motion of the La/Ca cations\textsuperscript{3}. We concluded that the distortions at the Mn\textsuperscript{3+} sites must persist at low fluences. Reflectometry data featuring more comprehensive fluence dependencies suggest a more continuous picture since we observe a linear increase of the displacement until the complete phase transition is reached\textsuperscript{4}. Additionally, the higher frequency for this mode measured in LPCMO appears to be inconsistent with the 25\% higher mass of the La/Pr/Ca sublattice relative to the La/Ca sublattice in LCMO. These new observations suggest that the atomic motion corresponding to the observed displacement is primarily the translational mode of the Mn\textsuperscript{4+}O\textsubscript{6} sites.

Here we present time resolved x-ray diffraction measurements on several superlattice peaks with different sensitivities to the atomic motion of the unit cell constituents. The results of these new x-ray diffraction measurements further support the assignment of the phonon to the motion of the Mn\textsuperscript{4+}O\textsubscript{6} octahedra as the most probable scenario.

\textsuperscript{1}K.-J. Jang \textit{et al.}, PRB 81, 214416 (2010)

\textsuperscript{2}V. A. Amelitchev \textit{et al.}, PRB 63, 104430 (2001)

\textsuperscript{3}P. Beaud \textit{et al.}, PRL 103, 155702 (2009)

\textsuperscript{4}A. Caviezel \textit{et al.}, (submitted to PRB)
Ultrafast dynamics of magneto-structural phase transitions

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In modern technology the race is on to decrease the lengths scales and increase the speed at which matter can be manipulated. For instance ferromagnetic systems can be demagnetized or switched on sub-ps timescales while one can also imagine change the magnitude of or inducing a magnetic moment. As an example the magneto-structural transition of FeRh in which a structural expansion couple to an antiferromagnetic to ferromagnetic change in magnetic order allows the latter case to be realized. Here we use optical and x-ray probes to study the dynamics of laser induced magneto-structural phase transitions in search for their origins and fundamental time limits.

In FeRh we have compared the structural and magnetic dynamics of the phase transitions two components. The laser induced transition can be described by a simple nucleation model and has two time scales, one for the nucleation of the ferromagnetic phase and a second for alignment to an external magnetic field. Comparing optical and magnetic data we find the same time-scale for the magnetic and structural changes which thus are intimately coupled [1].

The Heusler alloy Ni₃MnGa is a magnetic shape memory alloy which owes its fascinating properties to the coexistence of the structural martensitic transition and ferromagnetism, but while technical applications already exist the microscopic origin of the phase transition is not understood. With time-resolved x-ray diffraction and laser reflectivity [1] we have studied how the different structural components of the martensite phase evolve in time, as Ni₃MnGa is excited through the martensitic transition with a fs laser pulse. We demonstrate the existence of several coherent optical phonon modes and their relation to the phase transition.

X-ray Free Electron Laser investigations of picosecond and sub-ps dynamics in and around photo-excited transition metal complexes


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This presentation will focus on the results from a series of recent hard X-ray experiments conducted at the XPP end-station at LCLS and at SACLA in Japan. In these experiments, we investigated the ultrafast solvent response as well as structural and electronic dynamics in Fe(bpy)₃ as well as in a structurally related, linked Ru-Co complex. In a second set of experiments, we studied the ultrafast structural dynamics following excited-state bond formation in Ir₂(dimen)₄. In several of the experiments we utilized concurrent detection of complementary data, namely both X-ray Diffuse Scattering and X-ray Spectroscopy. Doing so allows us to simultaneously address both the electronic and structural degrees of freedom, greatly enhancing the information obtained from a single experiment. This also significantly aids in the interpretation, as solid information from one set of measurements can inform the analysis of the complementary data set. While the focus of this presentation will be on the results of our investigations, some discussion of data analysis methods and important lessons learned will also be included.
Structural Dynamics and Reactivity in Neuroglobin from Experiment and Simulations

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Structural dynamics in proteins is one of the important areas in which experimental and computational approaches can be ideally combined for a detailed characterization of complex processes. To understand how a protein functions it is crucial to know not only its 3-dimensional structure, but also how that structure evolves as a function of time. While time-resolved methods (IR, electronic, Laue, WAXS, SAXS) have made tremendous progress, each method has its particular limitations (time scales, packing forces, local information). Since there is no single experimental technique that can be used to investigate all time and spatial scales, combination with computational explorations of the systems provides additional valuable insights.

Chemical reactivity and directly influencing it has been at the heart of understanding transformations of matter. By combining IR spectroscopy and advanced computational techniques we demonstrate that it is possible to direct a chemical reaction with two possible pathways in neuroglobin (Ngb). Unlike Hemoglobin, Ngb binds an endogenous ligand, i.e., the imidazole side chain of the distal histidine, His64. Photodissociation of CO generates a metastable pentacoordinate deoxy species which relaxes back to CO-bound Ngb along different pathways. The CO molecules compete with His64 for the vacant sixth coordination site at the heme iron. First, CO or His64 bind at the heme iron; the second, slower step indicates that the hexacoordinate deoxy species (bound His64) persists until the ligand thermally dissociates and is replaced by a CO molecule. This sequence of events can be modified through suitable mutations around the active site. In this way, the pathway leading to His-bound Ngb is gradually eliminated. By using computation, we were able to provide quantitative data and the necessary atomistic details about the structural changes involved in ligand binding in Ngb. Such knowledge is required for a deep understanding of structure-dynamics-function relationships in proteins.
Exploiting Simultaneous Ultrafast X-Ray Spectroscopy and Scattering to Study Intra- and Intermolecular Dynamics

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Time-domain identification of an excitonic insulator by time-resolved ARPES

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Since the concept of the excitonic insulator was introduced about 50 years ago, the identification of a real excitonic insulator has remained elusive. The reason probably is that the excitonic insulator instability is mathematically and physically almost indistinguishable from the more familiar Peierls instability, which explains charge-density wave (CDW) formation in low-dimensional materials as a consequence of strong electron-lattice interaction. In its canonical form, the excitonic insulator model starts from an indirect semiconductor with a small band gap or from a semimetal with a small band overlap and considers the limit when the band gap or overlap go to zero. At some point either the band gap becomes smaller than the exciton binding energy or the band overlap and number of free carriers become so small that screening turns negligible; in both cases the system will become unstable toward spontaneous exciton formation and a CDW instability. The essential and intriguing difference to the Peierls instability is that the excitonic insulator instability is purely electronically driven, the periodic lattice distortion concomitant with the CDW being only an accidental by-product [1].

Here we report time-resolved ARPES measurements, using a high-harmonic-generation source, on the candidate excitonic insulator 1T-TiSe2. Exploiting the technique’s unique combination of femtosecond time resolution and full momentum selectivity [2] and using the well-known Peierls-Mott insulator 1T-TaS2 [3] at different doping levels as a reference, we establish a hierarchy of melting times for different types of electronic order in momentum space and we specifically demonstrate that the CDW state of 1T-TiSe2 can be quenched on a sub-vibrational, i.e., electronic time scale [2,4]. We argue that these results provide the most conclusive evidence for the existence of the excitonic insulator state in a real material so far.

Formation Dynamics of a Charge Density Wave in 1T-TaS$_2$

studied by Femtosecond Electron Diffraction

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The transition from the nearly commensurate to the incommensurate charge density wave (CDW) phase in the transition-metal dichalcogenide 1T-TaS$_2$ was studied by femtosecond electron diffraction (FED). The dynamics of the structural part of the CDW phases was observed with a temporal resolution of 400 fs. The superstructure of the incommensurate CDW is rotated by an angle of 12° in respect to the one of the nearly commensurate CDW. Therefore the diffraction peaks of both phases are spatially separated in the diffraction pattern and could be analysed independently.

We found that the nearly commensurate phase is partly or completely suppressed on a timescale faster than our temporal resolution, while the formation of the incommensurate phase happens with time constants of about one picosecond, depending on the pump fluence. A temporal delay of up to one picosecond for the onset of the formation of the new phase was also observed. After the fast initial suppression / formation of the phases, a stabilisation into a quasi-equilibrium state was observed on nanosecond timescales.

Our results are in accordance with and complementary to previous FED experiments on transition-metal dichalcogenides [1,2].

Comparison of the Lattice Response to Femtosecond Laser Excitation of Bismuth by Time Resolved Electron Diffraction in Reflection and Transmission Geometry

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Time resolved electron diffraction is an ideal tool for studying the response of the crystal lattice upon femtosecond laser pulse excitation. Studies of the excitation and relaxation of the lattice is of fundamental interest for the understanding not only of the energy transfer between the laser, the electron system and the lattice but also to acquire a more detailed understanding of the complex interplay between surface and bulk phonons. In order to obtain a complete picture on the structural response upon laser excitation we have combined surface sensitive reflection high energy electron diffraction (RHEED) and transmission electron diffraction (TED) to investigate laser excited bismuth films.

A limitation for time resolved RHEED is the velocity mismatch between laser and electrons under grazing incidence. We realized an optical setup to tilt the laser pulse front by 70° in order to achieve temporal and spatial overlap with the 30 keV electron pulse over the entire width of the sample. The tilted pulse was characterized by a cross-correlator based on second harmonic generation. The time resolution of the RHEED setup has been proven to be at least better than 1.8 ps [1]. In the RHEED experiment a 6 nm thin Bi(111)-film epitaxially grown on a Si(111)-substrate was studied. The response time constant of the lattice heating was found to be about 10 ps. The change of the lattice temperature is proportional to the excitation fluence. This behavior indicates that the lattice is heated by the relaxation of hot electrons.

In contrast, time resolved TED experiments, that were carried out on a thin free standing single crystalline Bi(111) film of 22 nm thickness, revealed different time constants for the response of the lattice depending on the diffraction order in the range of 1 to 5 ps. TED is dominantly sensitive to bulk lattice motions within the surface plane, while RHEED is a surface sensitive method and most sensitive to motions normal to the surface. Comparing the experimental results leads to a complementary understanding of the energy dissipation mechanisms in thin Bi(111) films itself.

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Nonlinear Direct Coupling of Femtosecond Laser Pulses with the Lattice Observed by Time Resolved Electron Diffraction

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Time resolved transmission electron diffraction (TED) is an ideal tool to study the lattice response of femtosecond laser excited crystalline material. The lattice vibration can be driven either indirectly by the relaxation of hot electrons or directly by the coupling of the laser pulses with the lattice via nonlinear-optical mechanisms. These different excitation mechanisms produce distinct signatures in the electron diffraction patterns.

Here we report on the observation of a laser-induced directional motion of the lattice atoms in Bismuth using time resolved transmission electron diffraction.

The experiment was performed on free-standing single crystalline thin Bismuth films with (111) surface orientation. The electron probe pulses had an energy of 30 keV, and the pulse duration was less than 700 fs. The intensity of all observed diffraction orders decreased by a few percent within a few picoseconds after excitation. The comparison of the various diffraction orders revealed an anisotropic pattern of the intensity decay which depends in a characteristic manner on the azimuthal angle of the diffraction spots.

In addition, a rotation of the laser polarization caused a rotation of the orientation of the anisotropy decay pattern. This behavior is attributed to a direct excitation of transverse acoustic modes via photoelastic interaction [1].

For the TED scattering geometry the diffraction pattern is only sensitive to atomic displacements in the surface plane. In addition, we performed experiments with an off-axis incidence of the electron pulse with respect to the surface normal. These experiments allow for studies of dynamics along the (111)-crystalline direction. Using this geometry, we observed a modulation of the diffraction intensity which will be discussed in this contribution.

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Quenching of sequential bond breaking and non continuous bond breaking seen through time resolved and sub-natural linewidth RIXS

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Changes in chemical bonding, in particular bond breaking and bond creation seem conceptually simple, but as a result of coherent wave packet motion, the intricacies of symmetry and spin of create difficult to catch dynamic pathways in a multidimensional potential energy landscape. In this contribution the quenching of sequential dissociation through ultrafast solvent capture is explored in the prototypical metal carbonyl Iron pentacarbonyl (Fe(CO)$_5$) based on results from time resolved X-ray spectroscopy. Iron pentacarbonyl photodissociates in the gas phase via sequential detachment along a singlet pathway with a first CO splitting time constant below 100 fs and a second of 3.3 ps. The quenching of the second detachment in ethanol solution has been approached by competing models of concentrated ligand substitution or by diffusive complexation. From the valence electronic structure dynamics of optically triggered Iron pentacarbonyl and its transients in solution observed with time resolved resonant inelastic x-ray scattering (RIXS) at a free-electron laser it is found that the detachment of the second CO ligand is quenched by subpicosecond solvent capture. In this process the bond breaking modes of vibrationally hot Fe(CO)$_4$ deexcite through the additional modes of the captured solvent moiety.

A complementary experiment to the time domain constitutes the application of sub-natural line-width resonant inelastic X-ray scattering to track the wave packet dynamics of excited states. Here the non-continuous nature of bond breaking in diatomic systems is explored. As an outlook, the potential of combining time resolved and sub-natural line width probes towards RIXS at the Heisenberg limit is illustrated.
Femtosecond X-ray diffraction on LiBH$_4$ and LiH: quasi-instantaneous electronic response to strong laser electric fields

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The recent development of pulsed X-ray sources with femtosecond duration allows for direct measurements of the atomic displacements and the electronic motion in crystalline structures. A plasma-based source has been developed in our group and is capable of delivering X-ray pulses of a 100 fs duration and a photon flux on the sample of about $10^6$ photons/s [1]. We combine this X-ray source to a standard pump-probe scheme in a Debye-Scherrer configuration in order to study condensed matter at a femtosecond timescale with a sub-angstrom spatial resolution.

Many Debye-Scherrer diffraction rings are recorded simultaneously for different time delays between the laser pump pulse and the X-ray probe pulse. From these diffraction patterns, changes of intensity on different rings are monitored. The interference of X-rays diffracted from the many unexcited cells, with known structure factors coming from steady-state measurement, and X-rays diffracted from the few excited cells allows the detection of the transients structure factors in intensity and phase. Then, electron density maps are reconstructed by the mean of 3D-Fourier transform. Nevertheless, this method could give rise to artifacts due to the fact that the X-ray reflections are collected only up to a maximum angle $2\theta_{\text{max}}$. In order to overcome this issue, the maximum entropy method can be used, which is maximally non-committal with regard to missing information [2]. The time-dependent electron density maps are computed with a sub-angstrom spatial and a 100 fs time resolutions. This technique is applied to two lithium based insulators, LiBH$_4$ and LiH. We use a nonresonant excitation with a pump pulse energy of 1.5 eV, much smaller than the energy gap of the materials (around 7 eV and 5 eV respectively). In both materials, a fully reversible charge transfer is observed within the time resolution of the experiment (around 100 fs). This electron transfer takes place from the anion to the cation in the LiBH$_4$ crystal [3] and from the cation to the anion in the LiH crystal. Since the core electrons of a Li$^+$ ion are too tightly bonded in order to be transferred, the latter behavior is a consequence of the not completely ionic character of the material and the existence of a significant covalent contribution to the bond between the Li and H atoms.

Switching dynamics in laser-driven phase change materials probed by time-resolved X-ray diffraction

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Phase change materials (PCMs) exhibit rapid and reversible phase transitions between an amorphous and a crystalline state, which can be triggered by short light or electrical pulses. Since the structural changes are associated with large differences in the electronic and optical properties of the two phases, PCMs are widely used in rewritable optical data storage technology (e.g. RW-DVDs) and also considered for future non-volatile electronic memory applications.

We have used time-resolved X-ray scattering using at the XPP end station of the Linear Coherent Light Source (LCLS) to directly probe the structural dynamics in PCMs after laser irradiation over an extended time range from fs to µs. Thin films of the PCMs Ge₂Sb₂Te₅, AgIn₃Sb₆Te₂₆, and Ge₁₅Sb₈₅ deposited on free-standing Si₃N₄-membranes were irradiated by fs optical laser pulses. The structural changes during the laser-induced transitions were monitored by scattering of a time-delayed 50 fs X-ray probe pulse at 9.5 keV from the LCLS in normal-incidence transmission geometry. Taking full advantage of the high flux and the short pulse duration of the LCLS the measurements allowed to measure transient scattering pattern with high signal-to-noise and thus to obtain information on the structural properties of PCMs during switching. The behavior of the PCMs has been compared to the response of “simple” materials like Ge and Bi.

From a very preliminary analysis of the data (beamtime finished Oct. 30) we have to conclude that all transitions (amorphous-to-crystalline and crystalline-to-amorphous) seem to involve melting of the material. Depending on the excitation strength melting can occur very fast on a sub-ps time-scale as a non-thermal process driven by the strong laser-induced electronic excitation. However, it takes ns up to tens of µs for the material to resolidify and to reach the final amorphous or crystalline state. While these time-scales imply purely thermal mechanisms, most probably determined by the nucleation and growth kinetics for the given material and sample geometry, we observe in some cases distinct fluence-dependent differences in the structure of the final state. Additionally, we will compare the structural response of PCMs as obtained from the X-ray scattering experiments with time-resolved measurements of the optical properties to be performed soon.
Ultrafast low-energy electron diffraction using nanotip emitters

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Ultrafast structural dynamics in solids and nanostructures can be investigated by an increasing number of sophisticated electron and x-ray diffraction techniques. Despite successful implementations of ultrafast reflection high-energy electron diffraction, the time-resolved diffractive probing of structural processes at surfaces remains an experimental challenge.

We have recently implemented ultrafast low-energy electron diffraction (ULEED) to study structural changes with high temporal resolution and ultimate surface sensitivity, at electron energies from 100 eV to 500 eV. We utilize nanoscopic needle emitters in an electrostatic lens geometry as high-brightness sources of pulsed electrons. The spatial confinement of the source is realized by the local enhancement of nonlinear photoemission at the tip apex.

In this talk, the benefits of nanoscopic cathodes for ultrafast diffraction studies will be discussed, and first time-resolved data will be presented. Specifically, the ultrafast melting dynamics of ordered adsorbate structures on freestanding graphene is investigated in transmission with a temporal resolution below 5 ps.
Electron effective mass: A route to ultra-bright photocathodes

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Robust and low divergence laser-driven pulsed electron sources are the ideal high brightness sources for ultrafast electron diffraction and microscopy, and indeed for pulsed x-ray FEL radiation sources. It is now evident that the electron effective mass, \( m^* \), of the state from which the electron is emitted plays a key role in determining the transverse emittance, and hence brightness, of such pulsed electron sources. In particular, the maximum emission angle (with respect to the photocathode surface normal) for an electron is given by \( \sin^{-1}\sqrt{m^*/m_0} \) (for \( m^* < m_0 \)), where \( m_0 \) is the free electron mass [Z. Liu et al., J. Vac. Sci. Technol. B 23 (2005) 2758]. A detailed theoretical formalism shows that the narrowing of the emission cone for low \( m^* \) photocathodes is associated with a transverse emittance proportional to \( \sqrt{m^*} \), and therefore a \((m^*)^{-1}\) brightness dependence. The presented theoretical formalism will be shown to be in very good agreement with our experimental data on direct single-photon photoemission from silver (for Ag, \( m^* \approx m_0 \)) and excited state thermionic emission from the III-V semiconductor GaSb (\( m^* \approx 0.3m_0 \)), and measurements by others on negative electron affinity (NEA) GaAs photocathodes (\( m^* \approx 0.067m_0 \)). The resultant understanding of the influence that \( m^* \) has on electron emission provides a clear new route towards laser-driven, ultra-low divergence, planar photocathodes.

The analysis also strongly indicates that, in general, only low \( m^* \) cubic or uni-axial single crystal photocathode materials of the appropriate orientation should be employed if cylindrical symmetry in the low divergence electron emission is to be maintained.

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Single-Shot Ultrafast Electron Diffraction Using Electrons Accelerated by an Intense Femtosecond Laser Pulse

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To observe atomic-scale ultrafast structural changes in matters during phenomena time-resolved electron diffraction and microscopy using short electron pulses is useful. The key issue to realize single-shot ultrafast electron diffraction (UED) is to develop intense short electron-pulse sources. With conventional UED instruments, an electron pulse is generated at a photocathode irradiated by a femtosecond laser pulse and accelerated in an additional external static electric field. The amount of electrons in the pulse is limited because the electron pulse expands during its flight by space-charge forces in the pulse. There are two ways considerable to avoid the space-charge effect, those are reduction of electrons in the pulse and acceleration to relativistic energy by RF accelerators. However, for the former, large amount of pulses are necessary to obtain an UED image, which is not available to observe irreversible phenomena, and for the latter, the energy is too high for conventional transmission electron microscopy (TEM). Furthermore, for the mid-energy range of around 100keV to 1MeV, corresponding to the energies of conventional TEM, there is no satisfactory method for generating femtosecond electron pulses.

We have demonstrated single-shot UED using electron pulses accelerated by intense femtosecond laser pulses and compressed by a static phase rotator [1, 2]. The electron pulses of several hundreds keV are generated by irradiating tightly focused terawatt femtosecond laser pulses on a polyethylene foil target at an intensity of $10^{18}$ W/cm$^2$, and the pulses are compressed to be 300 fs by using an achromatic bending magnet system. These femtosecond electron pulses could have an intensity to take a single-shot diffraction pattern. A single-shot diffraction pattern has been imaged from a gold single crystal as a test sample.

To develop higher quality electron sources which are more appropriate for the UED, we are investigating the properties of electrons emitted by laser-foil interactions [3-5], and have proposed and demonstrated guiding and collimating electrons using a metal wire target [6].

(Publications related to the present work)
Quantifying In-situ Reactions in the STEM/DTEM

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The goal of the Dynamic Transmission Electron Microscope (DTEM) is to be able to directly observe transient phenomena in materials/biological systems with both high spatial (~1nm or better) and high temporal (~1\mu s or faster) resolution. The main issue in the design of experiments in the DTEM is that for many of the key scientific challenges involving structure-property relationships in materials science and structure-function relationships in biology, the transient processes involve significant re-arrangement of the atoms/molecules in the structure at specific locations – making dynamic observations essentially irreversible in nature. This requirement for “single shot” imaging effectively limits the temporal resolution that can be obtained, and defines the types of reactions that can be studied in the microscope.

A key first step in the use of DTEM to study transient processes is to control the environment around the sample. An in-situ gas stage has been developed in collaboration with Fischione Instruments that allows atmospheric pressure in a range of reactive gases to be maintained around the sample while atomic resolution images can be obtained in a high resolution microscope. By utilizing a novel laser heating source, temperatures up to 2000\degree C can also be obtained in small areas of the sample. Such capabilities allow for direct imaging of oxidation and reduction processes in metals, ceramics and catalytic systems. In addition, an in-situ liquid stage has also been developed in collaboration with Hummingbird that allows atomic scale images and electron energy loss spectra to be obtained from samples suspended in solution. This has a wide range of applications from corrosion in materials science to live biological systems.

The use of these in-situ stages to quantify in-situ reactions will be discussed using results obtained from aberration corrected scanning transmission electron microscopes (STEM) with particular emphasis on the control of the electron dose in determining the reaction rate and the compatibility of the results with ex-situ chemical reactions. In addition, the progress in incorporating the high spatial resolution of an aberration corrected microscope into the DTEM configuration will also be discussed along with design optimizations that are underway that may extend the DTEM into the ultrafast regime.

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Development of Femtosecond Time-resolved MeV Electron Microscopy

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The visualization of fundamental dynamic processes in matter occurring on femtosecond time scales over sub-nanometer (even atomic) spatial dimensions has attracted much attention in chemistry, material science and biology. Ultrafast electron microscopy (UEM) provides a direct observation (“real-time” and “real-space” probe) of structural dynamics in matter by recording the change in the characteristics of electron images in the pump state and the unpump state. Unfortunately, however, the space-time resolution of UEM is still limited to 1-10nm·ns (>1000 nm·ps), because the space-charge forces expand the electron bunch length and the energy spread or limit the number of electrons in a pulse in low-voltage electron microscopy. To suppress the space-charge expansion, a possible way out is to accelerate the electrons to relativistic speeds using a radio-frequency (RF) acceleration technology, such as a photocathode RF gun.

We have developed a prototype of relativistic-energy UEM by combining the high-voltage electron microscopy (HVEM) with the advanced accelerator technology. In UEM, a photocathode S-band (2856 MHz) RF gun, which is driven by a femtosecond laser, is used to generate a femtosecond-bunch electron beam and to accelerate it up to 1~3 MeV with a high accelerating field of ~100 MV/m. The space charge force in the ultrashort electron bunch is thus suppressed. A relativistic beam with a larger electron number of 10^7-8 can be achieved in a single 100 fs long bunch.

In this paper, we will report the results of the femtosecond electron bunch generation in the RF gun and the first experiments of electron imaging using the relativistic-energy femtosecond electron bunches. We succeeded to obtain a relativistic low-emittance, low-energy-spread femtosecond electron bunches which is sufficiently suitable on the electron imaging. We have used these bunches to produce high-quality single-shot diffraction patterns of single crystal gold and the MeV electron imaging of condense materials. Further improvements and developments of UEM will be discussed in the paper.
Nanofluidic cells with controlled path length and liquid flow for rapid, high-resolution in situ electron microscopy

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Electron microscopy has presented itself as an elegant and powerful tool for high resolution imaging and diffraction on the molecular and atomic level. However, most studies nowadays are limited to static or video rate imaging, not allowing for real time resolution. Dynamic transmission electron microscopy (DTEM) offers a solution to this limitation introducing laser excitation and a pulsed electron probe beam, while allowing for nanosecond time resolution. Utilizing this technique various solid state samples have been studied, e.g. with respect to their phase transitional behaviour. Yet, experiments are limited to solid state samples as experimental limitations are hardly overcome within current sample preparation. Nanometre thin vacuum compatible (in) liquid samples, which are additionally reliable and allow for high sample throughput, are pending. Here, we present a nanofluidic sample cell with exquisite control over the liquid layer thickness down to currently 50 nanometre in order to preserve the highest possible spatial resolution for in situ solution phase electron microscopy. We provide liquid flow through the nanocell by applying differential pressure control mechanism with feedback operated external to the microscope column and thereby allowing for on-the-fly sample exchange within the imaging area. We illustrate the efficacy of our approach by imaging a variety of nanoparticles in several independent experiments. The first studies demonstrate the ability to tune the liquid layer thickness, therewith adopting optimal resolution conditions for different applications. Furthermore, we demonstrate unidirectional flow in the design concept using gold nanorods pumped directionally through the imaging area upon an external flow being applied; while these same particles show random Brownian motion once the external pressure is released. Having shown the capabilities of our nanofluidic design with these initial experiments, we further show preliminary results in imaging non-stained biological samples as well as first studies of the assembly process of gold nanorods in water/DMF solution. These latter experiments illustrate dynamics at the 1 nm scale resolution limit, using commercially available detectors. With further advances in detector sensitivity and probing schemes, it will be possible to capture molecular scale details for both equilibrium and non-equilibrium processes and illustrate the utility of this new nanofluidic flow cell concept for DTEM, as well as in time resolved ultrafast electron diffraction experiments.

References
High flux monochromatic ion and electron beams based on laser-cooled atoms

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We propose a new source for high brightness ion and electron beams based on the ionization of an effusive atomic beam which is transversely cooled and compressed. As a new source for Focused Ion Beams and Electron Beams, we propose here to ionize the high flux of an effusive atomic beam which is transversely cooled and compressed by lasers to increase its brightness. The very low transverse temperature (mK range) and the relative low density of the starting atomic sample ensure excellent initial conditions for obtaining bright and monochromatic charge sources.

In contrast to the standard photoionization techniques used by similar sources, we utilise field ionization of Rydberg atoms which ameliorates several existing problems, including the required laser power, the effects of chromaticism created during the ionization process and the stochastic space charge effect. Theoretical modeling and perspective ideas of this emerging technology are given.
Streaking of Non-Relativistic Electron Diffraction Patterns with a sub-ps Resolution Streak Camera

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In the field of femtosecond electron diffraction, higher flux, increased signal-to-noise ratio and better temporal resolution are some of the main goals sought after. Here we present the streaking of an electron diffraction pattern with a low-jitter, photo-triggered streak camera as an alternative approach to scanning femtosecond electron diffraction. For the streaking experiment we combine a table-top, 30 kV, femtosecond electron diffraction setup with a compact streak camera [1].

To demonstrate the power of the technique we have studied the optically induced commensurate to incommensurate Charge Density Wave phase transition in $4H_b$-TaSe$_2$ using both, the conventional scanning [2] and the streaking approach. Delivering a temporal resolution of ~600 fs, the streak-data clearly demonstrate an increase in the signal-to-noise ratio in comparison to the conventional scanning method [3]. We show that with further optimization steps sub 250 fs temporal resolution can be achieved with the established experimental configuration.

Improving the temporal resolution of the hybrid DC-RF gun system

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UED with RF compressed electron pulses has been recently demonstrated with high bunch density (10\textsuperscript{6} electrons per pulse and good temporal resolution 200-400 fs primarily limited by timing jitter) \textsuperscript{1}. However, to further push the boundaries of UED and examine the fastest possible dynamical processes, we want to ideally achieve sub-100 fs resolution. We discuss jitter measurements, various RF schemes, and solutions to the synchronization problem as well as novel ways of attempting to break the 100 fs barrier.

\textsuperscript{1}Gao, Meng et al., Full characterization of RF compressed femtosecond electron pulses using ponderomotive scattering. \textit{Opt.Express} \textbf{20} (11), 12048 (2012).
Single-shot 35 fs temporal resolution electron shadowgraphy

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The rapidly evolving electromagnetic field, associated with a ultrashort laser-induced charge cloud, can scatter a well timed probe electron pulse. This effect is used to find the 'time-zero' in pump-probe UED experiments [1] and also the study of ultrafast plasma dynamics and short pulse laser ablations [2]. As an extension of the previously demonstrated 'movie-mode' radio-frequency (rf) deflector assisted UED technique [3], we obtained single-shot continuously time-resolved shadowgraph images of the electromagnetic fields resulting from the interaction of a high intensity ultrashort laser pulse with a metal surface. Using a high brightness relativistic electron beam and a high streaking speed rf deflector we report 35 femtosecond temporal resolution enabling a direct visualization of the retarded-time dominated field evolution which follows the laser-induced charge emission. A model including the finite signal propagation speed (at the speed of light) well reproduces the data and yields measurements of fundamental parameters in short pulse laser-matter interaction such as the amount of total emitted charge and the time scale of emission. We envision this unprecedented temporal resolution be useful in resolving many very fast processes.

Femtosecond X-ray Diffraction of Photochromic Diarylenes

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Diarylethene derivatives are among the organic photochromic compounds [1] that undergo a reversible color and structural change upon exposure to UV and visible light. With an ultrafast photoreaction of several picoseconds, high repetition of more than 10,000 times and thermal irreversibility, diarylenes can be used in various applications such as optical memory and optical switches. Elucidation of the photoreaction mechanisms is valuable for the application.

Photoreactions that occur in several picoseconds were reported for diarylethene single crystal in a number of papers [2, 3]. However, although these works provide important information on ultrafast reactions, only the transient outer shells electronic states were observed in these measurements, which are insufficient for understanding the mechanism of the photochromic reactions. To elucidate the mechanism of these reactions real-time observation of atomic movements during the photoreactions is required. Our group aims to study the ultrafast photochromatic reactions of diarylenes in real time on the atomic scale with the time-resolved X-ray diffraction (XRD) method, which provides both femtosecond temporal resolution and atomic scale spatial resolution.

For the time-resolved XRD measurements, we prepared high quality photochromic single crystals of 1,2-Bis(3,5-dimethyl-2-thienyl)perfluorocyclopentene, which is a diarylethene derivative that turns yellow upon exposure to UV light, with the evaporation crystallization method. We conducted static XRD measurements on the two stable states of the diarylethene, colored and colorless, with femtosecond pulsed X-rays produced by the laser-plasma technique [4]. A 30% difference in XRD peak intensity between the two stable states was observed, which could be attributed to the difference between the molecular structures. As a preliminary experiment for time-resolved XRD measurements, we confirmed the enhancement of the XRD spectrum with a single-shot pump light (wavelength: 400 nm, pulse width: 300 fs, laser intensity: 2 mJ/cm²). The spectrum was enhanced 15% with the single shot laser pulse. Furthermore, stable repeatable enhancement of the diffractograms was observed, suggesting that time-resolved XRD can be applied for the diarylethene single crystals.

Ultrafast Electron Diffraction Study of the Ring Closing Reaction in a Thermally Irreversible Photochromic Crystal

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Diarylethene derivatives are a family of molecules which are said to be photochromic because they have the ability to undergo photoinduced reversible isomerization between the open- and closed-ring forms, including in its crystalline phase [1]. Here we present the complete ultrafast electron diffraction (UED) study of the ring closing reaction in one such compound, 2-bis(2,4- dimethyl-5-phenyl-3-thienyl) perfluorocyclopentene. The reversibility and repeatability of the structural changes associated to the subsequent cyclization and cycloreversion reactions in crystalline diarylethene were first confirmed with static electron diffraction measurements. The time-resolved measurements were then performed with a 100 kV DC electron gun combined to a RF compression system capable of delivering sub-500 fs electron bunches with $10^6$ electrons per pulse [2]. The UED system has near single-shot diffraction pattern acquisition capability, which was essential to perform this study because of the requirements imposed by the experiment with respect to the pumping repetition rate (lower than 0.1 Hz) and the number of repeatable cycles for each sample (less than 300). The UED measurements were performed for multiple orientations, using a large number of different crystals. Changes in diffraction intensities with a time constant of 6 ps were observed, which is in agreement with the results of a complementary femtosecond transient absorption study performed recently which demonstrated that the actual ring-closing proceeds with such a time constant [3]. Sub-ps structural changes were also observed, again in agreement with the findings of the all-optical study; they are attributed to the initial evolution of the open-ring molecules on the excited state potential energy surface prior to the ring-closing. \textit{Ab initio} calculations including a novel hybrid method with CASSCF and DFT levels of theory were also performed in order to assist the assignment of the time-resolved diffraction data. The complete analysis of the UED measurements will be presented.

Femtosecond X-ray Diffraction from Two-Dimensional Protein Crystals

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Although conventional x-ray crystallography using synchrotron sources has proven extremely successful for structural analysis of biological macromolecules arranged as three-dimensional (3-D) crystals, to date, it has not been possible to acquire forward x-ray diffraction from individual two-dimensional (2-D) protein crystals due to radiation damage. However, the intense and ultrafast pulses generated by X-ray Free Electrons Lasers like the Linac Coherent Light Source (LCLS) permits a new method of collecting diffraction data before the sample is destroyed. Utilizing a diffract-before-destroy methodology with 50 femtosecond duration x-ray pulses at LCLS, we observed Bragg diffraction to better than 8.5 Å resolution for two different 2-D protein crystal samples that were maintained at room temperature. These proof-of-principle results show promise for structural analysis of both soluble and membrane proteins arranged as 2-D crystals without requiring cryogenic conditions or the formation of three-dimensional crystals. In this presentation, I will discuss the results from our first beam time run dedicated to interrogating 2-D crystals at LCLS in May 2012 and will detail future plans for facilitating \textit{in situ} pump-probe experiments on fixed targets to better understand membrane protein conformational dynamics.

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Watching Chemical Dynamics in Real Time: Can Gas-Phase x-Ray Diffraction Probe the Dynamics of 1,3-Cyclohexadiene?

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The study of the chemical reaction dynamics of molecular systems in the gas phase provides a detailed understanding of fundamental chemical processes: the flow of energy across potential energy surfaces, the redistribution of energy amongst vibrational degrees of freedom, and the structural rearrangements that accompany the chemical transformations. The time scales of such processes are often in the sub-picosecond regime, necessitating the development of novel experimental tools.

To study chemical reaction dynamics of isolated molecules, i.e. of molecules in dilute gases, spectroscopic methods such as multi-photon ionization mass spectrometry or photoelectron spectroscopy have traditionally been used. Those methods are favored because of their high time resolution and their inherently high sensitivity. Even so, time-resolved spectroscopic techniques rarely yield structural parameters and therefore give only indirect views of the structural transformations accompanying chemical reactions. Diffraction measurements have the advantage that patterns can be Fourier transformed to obtain structures. In choosing between electron and x-ray diffraction, one has to balance difficult trade-offs: electron diffraction is favored for gas-phase systems because scattering cross sections are governed by Coulomb interactions and consequently are large. For samples with low molecular densities, such as dilute gases, this gives electrons a compelling advantage. However, for all but the highest electron energies, space-charge interactions between the electrons, as well as the extended samples size of most gaseous targets, introduce experimental complexities that are difficult to surmount.

X-ray diffraction of gas phase samples is challenging because of the small cross sections for interaction between the photons and the molecules. However, the recent development of high intensity, ultrashort pulsed x-ray sources offers an opportunity to investigate chemical dynamics using x-ray diffraction from dilute gases with excellent time resolution: even though the molecular density is low, observable signals can be obtained from x-ray pulses with sufficient photon numbers.

In October 2012, we performed exploratory x-ray diffraction measurements of gaseous samples at the XPP beamline of SLAC’s LCLS source. As a molecular dynamics system we chose 1,3-cyclohexadiene, which upon excitation crosses multiple electronic surfaces while opening the ring to form 1,3,5-hexatriene. The reaction was induced with a 9 μJ laser pulse at 275 nm, and probed with x-rays stemming from the third harmonic at 20 keV. The talk will discuss experimental considerations and showcase a first look at the time-resolved x-ray diffraction data.
Time-resolved Laue Diffraction of Light-induced Changes in Highly Luminescent Cu(I) complexes

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A variety of organometallic Cu(I) complexes undergo metal-to-ligand electron transfer on photoexcitation, leading to highly luminescent states, the details of which can be manipulated by chemical substitution. They have attracted considerable attention because of their potential use in a series of devices, including chromophores in photovoltaic cells and the active component of light-emitting diodes. The chemical changes that are induced can be measured by pump-probe experiments at light sources, backed up by spectroscopic measurements and theoretical calculations. We will discuss two series of compounds of which prototype molecules are as follows:

Measurements are made with the modified Laue technique using software specifically developed to optimize the accuracy of the results.\(^1\),\(^2\) For complexes of the type A, a flattening of the pseudo-tetrahedral arrangement is observed, which is considerably smaller than calculated for the isolated molecules, indicating the constraining effect of the crystal lattice. This is confirmed by analysis of a structure with two independent molecules in the asymmetric unit which behave differently in agreement with the bi-exponential decay of the luminescence.\(^3\) Complexes of type B have very long lifetimes\(^4\) and according to preliminary results appear to show different distortions at short and long delay times, an effect that is further being analyzed.

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Protein crystallography at free-electron laser sources

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Protein crystallography using synchrotron radiation sources has had tremendous impact on biology, having yielded the structures of thousands of proteins and given detailed insight into their working mechanisms. However, the technique is limited by the requirement for macroscopic crystals, which can be difficult to obtain, as well as by the often severe radiation damage caused in diffraction experiments, in particular when using tiny crystals.

With the advent of free-electron lasers (FELs), capable of delivering extremely intense femtosecond pulses, this situation appears remedied. Theoretical considerations predict that with sufficiently short pulses, useful diffraction data can be collected before the onset of significant radiation damage. Initial proof-of-principle experiments performed in the CAMP instrument at the LCLS demonstrated that tiny protein crystals yield useable diffraction patterns despite an absorbed dose of 3 GGy (Chapman \textit{et al.}, 2011). In follow-up experiments the dependence of the diffracted signal on pulse length and fluence was analyzed, observing both dose and dose rate dependent damage (Lomb \textit{et al.}, 2011). The observed decrease of high-resolution diffraction was attributed to a gating by the FEL pulse (Barty \textit{et al.}, 2012), localized damage hotspots were predicted but could not be verified due to the limited resolution of the experiments. High resolution data collection became feasible with the commissioning of the CXI end-station, establishing serial femtosecond crystallography (SFX) as a useful tool for the analysis of tiny crystals, and thus the large group of proteins that resist yielding macroscopic crystals. In addition to briefly summarizing some of these highlights, we will describe recent results obtained at SACLA and the LCLS that have implications for radiation damage and phasing and thus for the general prospects of SFX.

Ultrafast diffraction has overcome the barrier to atomic exploration by combining the atomic spatial resolution of diffraction techniques with the temporal resolution of ultrafast spectroscopy. X-ray free electron lasers, slicing techniques, and femtosecond (fs) laser-driven X-ray, and electron sources have been successfully applied for the study of ultrafast structural dynamics in a variety of samples. Yet, its application to labile organic crystals which can provide a molecular basis for the understanding of various attractive properties such as organic conductivity and optical switching remains unexplored. Composed by weak scattering centres, organic compounds often present low melting points and poor heat conduction. These facts impart tremendous constraints on source brightness and repetition rate (~ 10 Hz) to attain high-quality diffraction data before accumulative heating effects from the laser excitation degrade the sample or mask the structural dynamics. We implemented ultra-bright femtosecond electron diffraction, to obtain an atomically-resolved map of the relevant molecular motions driving the photo-induced insulator-to-metal phase transition in the organic charge-transfer salt (EDO-TTF)₂PF₆. On the first few picoseconds (0 - 5 ps) the structural evolution in the excited electronic state, well-described by three main reaction coordinates, reaches a transient intermediate state (TIS). Our model refinement calculations indicate that fast “sliding” of flat EDO-TTF molecules with correlated motion of PF₆ counter-ions drive the formation of the TIS. The complete flattening of initially bent EDO-TTF moieties seems to be assisted by thermal relaxation which brings the system into a high temperature-type state in the 100-ps timescale. The aforementioned structural dynamics and associated charge-order melting may open new vistas in molecular design aimed at fine tuning electronic and optical properties virtue of electron-lattice cooperative phenomena.
Abstracts – Poster Section
Nickel is an important ferromagnetic material and used as a model system to investigate the basics of ultrafast magnetization dynamics. From this point of view there is a great interest in obtaining information about the response of the lattice to femtosecond laser excitation. Here we present a study of the lattice response to laser excitation of thin Nickel films using time resolved transmission electron diffraction.

Nickel samples were prepared as free standing single crystalline films with a thickness of 20 nm with (001) surface orientation. The electron probe pulses had the energy of 30 keV, and the pulse duration was less than 700 fs. The samples were laser-excited using pulses of 50 fs at 800 nm.

The diffraction patterns were recorded as function of delay time between optical pump and electron probe. The integrated intensity of all the diffraction spots decreased after the laser excitation. Our analysis indicated that the observed decrease does not scale with the scattering vector which is inconsistent with the Debye-Waller effect resulting from lattice heating. Furthermore, the drop of the diffraction intensity followed the intensity of the laser pulse rather than the laser fluence. The latter behavior also argues against the excitation of the lattice by hot electrons. Possible alternative excitation mechanisms will be considered.

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From time-averaged to time-resolved electron diffraction in Edinburgh

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After many years of performing time-averaged electron diffraction experiments in Edinburgh, we are now building a 100 keV DC pulsed electron diffractometer to carry out time-resolved structure determinations. We will present the design of the new apparatus, which is based on a compact gun to ensure short electron pulses, as well as some initial observations.

We will also show details of both SIMION ¹ and GPT ² simulations that have been used to predict the initial time resolution of the new apparatus of around 500 fs. Similar simulations have also been used to plan improvements in the temporal resolution by accounting for the velocity mismatch ³ in the experiment, as well as using a magnetic lens before the sample.

In Edinburgh our focus has long been on gas-phase structures, and it is our intention to put this expertise to use by studying photoinduced structural changes. One of the first experiments we have planned involves looking at bond breaking upon excitation with UV light, perhaps for a disulfide bond. We will present quantum chemical simulations of this structural change.

Atomic Level Structural Information from Correlated X-ray Scattering

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Correlated X-ray Scattering (CXS) was first proposed by Kam for determining atomic level structural information from non-crystalline samples. Due to the need for multiple photons scattering from a single molecule, the advent of bright X-ray Free Electron Lasers has led to renewed interest in CXS. A number of recent papers have looked at CXS both from a theoretical standpoint (e.g. Kirian et al. and Kurta et al.) as well as in experiments at longer length scales (Wochner et al.). Kirian showed that at atomic length scales, the signal to noise level of the CXS analysis is independent of the number of molecules in the beam, implying that CXS may be more feasible than single molecule imaging, where the signal is swamped by other scattering sources. In this paper we present an alternative derivation of the same result by considering the incoherent superposition of randomly oriented, identical particles. This method requires no additional assumptions, and confirms Kirian's result. We also show that by looking at the difference between inter- and intra-shot correlations, it is possible to remove the background CXS signal from the experimental setup, an otherwise significant impediment to CXS.
Transition-edge microcalorimeter sensors for X-ray science

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Traditionally, wavelength-dispersive X-ray sensors have provided excellent spectral resolution and energy-dispersive devices have provided large collecting areas, but no detector technology combined these two desirable properties. However, recently developed Transition-Edge Sensor (TES) microcalorimeter arrays now combine high resolving powers with technologically useful collecting areas. TES devices consist of superconducting thin films electrically biased in the superconducting-to-normal transition where resistance is a strong function of temperature. The energy deposited by a single photon changes the temperature and resistance of a device, and the resulting reduction in bias current is sensed by a nearby Superconducting Quantum Interference Device (SQUID) ammeter. The amplitude of the current pulse is proportional to the deposited energy, thus allowing single photon spectroscopy. The high spectral resolution of these devices is derived from the low thermal noise at typical operating temperature near 0.1 K.

Using TES sensors, we have demonstrated single-pixel energy resolutions as good as 2.3 eV full-width-at-half-maximum (FWHM) for 6 keV x-rays and 22 eV FWHM for 97 keV gamma-rays. Reliable scaling arguments predict that resolution values near 1 eV FWHM will be possible in devices optimized for the detection of 1 keV photons. To overcome the size and count rate limits of single TES pixels, we are developing sensor arrays of up to 256 pixels. These arrays follow in the footsteps of much larger TES bolometer arrays whose size can now exceed 10,000 pixels.

One such array is deployed at NIST Boulder as with a pulsed-laser X-ray source to create an ultrafast EXAFS measurement system. The array consists of 160 pixels optimized for 6 eV, read out by SQUID amplifiers, and operated at ~80 mK in a liquid cryogen free cryostat. We also describe plans to upgrade this system to 1000 pixels.
We showed recently that the use of type II difference frequency mixing (DFG) in a fluorescence down-conversion scheme provides high signal-to-noise for biologically relevant near-UV emitting fluorophores [1,2]. In particular when broadband recording of time-resolved spectra with a CCD is aimed for, the high acceptance bandwidth afforded by the type II process is advantageous. As matter of fact, when using an intense near-IR gate pulses, most of the DFG signal is in the visible, i.e. in the wavelength range of highest CCD sensitivity [1].

The flexibility of DNA is known to play an important role for many processes, such as protein binding, transcription or packaging. Characterization of the structural dynamics and the resulting heterogeneity can be performed at specific sites of the biomolecule when environment-sensitive, fluorescent analogues like 2-Aminopurine (2-AP) are incorporated into the DNA sequence. Then, 2-AP fluorescence undergoes significant quenching, most probably due to oxidation of neighbouring guanines (G) or other bases.

We investigate the structural heterogeneity and dynamics of (-)PBS, a fragment of the HIV Primary Binding Site DNA hairpin, labelled with 2-AP in positions 6, 8 or 10, that is close to the primary and secondary binding sites of the chaperone protein NCp7. Since femtosecond spectroscopy takes snap-shots of the heterogeneous ensemble of molecular conformations, these are expected to show up in the form of differing fluorescence lifetimes dominated by quenching.

For the bare oligonucleotide, we identify four decay times for the 2-AP fluorescence: 1-3ps, 10- 40ps, 100-150 ps and > 2ns, but with site-specific amplitudes [2,3]. The fluorescence anisotropy decay shows that 2-AP labels are constrained in their orientational dynamics, with the fastest time scale being in the 130 ps range. We can thus coarsely assign the decay processes into fast, sub-100 ps static quenching and slower motion-enabled collisional quenching. The ultrafast static quenching has the largest amplitude in position 10, when 2-AP can perform stacking interactions with G-11 of the rigid stem. Molecular dynamics simulations aiming at rationalizing the four different time scales in terms of molecular motion are in progress.

Experiments on the (-)PBS/NCp7 complexes were also performed using a fluorescence streak camera. Here the fluorescence quenching will be assessed alternatively via the 2-AP labels and via the single Trp residue of the chaperone protein. The latter is expected to compete with 2-AP for the stacking interactions with the G's, leading to new yet unresolved classes of structures [3].

Using ultrafast electron diffraction (UED), we studied the atomic motions in the weakly scattering organic salt (EDO-TTF)$_2$PF$_6$ during photo-induced insulator-to-metal phase transition. Data analysis of measurements allowed us to observe the formation of a transient intermediate state and subsequent structural evolution to the final state. We discuss data post-processing techniques and structure refinement models used respectively to improve S/N ratio and decompose the dynamics of the molecular system into three key reaction coordinates: motion of PF$_6$ counter-ions, sliding of flat EDO-TTF moieties, and flattening of bent EDO-TTF moieties.
The Workshop on Ultrafast Electron Sources for Diffraction and Microscopy Applications (UESDM) [1] was held on the UCLA campus from December 12th to December 14th, 2012. The topics of this workshop included: i) beam sources for ultrafast electron diffraction: rf guns, laser-plasma based injectors, and dc photo-guns; ii) compression methods: magnetic, rf structures; iii) timing, synchronization, and jitter control; iv) samples: liquid, gas and solid phases, and electron damage; v) detectors and diagnostics; vi) strong electron lenses, imaging mode and electron microscopy; and vii) scientific opportunities.

In this talk we will give a brief review of the presentations and discussions at the UESDM workshop.

[1] UESDM workshop webpage:
http://pbpl.physics.ucla.edu/UESDM_2012/
Pauli Driven Cold Explosion in Alkali Halides

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Electron localization and charge (electron) transfer governs chemical reactions and determines the physical properties of materials. Alkali halides are usually stabilized through the provision of one electron from the alkali metal atom to the halogen atom; nevertheless, this electron, now localized at the halogen atom, can be transferred back to the alkali site when absorbing an ultraviolet photon.\textsuperscript{[1–4]} Here, we characterized this charge transfer process in the alkali halide crystals of NaCl and CsI using single-shot time-resolved reflection measurements and time-of-flight mass spectrometry. We observed an intense repulsive force on sub-picosecond timescales, i.e., Pauli repulsion. The size of the neutralized alkali metal atom is bigger than the alkali metal ion; the size of the halogen atom is almost the same in its neutralized as the ionized form. If a charge transfer occurs between them, the atom centered electronic orbitals in the neutralized alkali metal and halogen atoms would have to overlap, which is forbidden by the Pauli exclusion principle. This effect, therefore, introduces strong repulsive forces. The observed phenomena and its ultrafast dynamics are unprecedented with respect to the released forces and opens a new area of research of strongly driven atomic motions that could broaden our understanding of atomic and molecular physics. We will also present the dynamics of this strong repulsive effect in alkali halides with the single-shot electron diffraction method.\textsuperscript{[5]}

\textsuperscript{[2]} E. Rabinwitch, Rev. Mod. Phys., 14, 112 (1942).
Observation of Photoinduced ‘Over-Neutralization’ in TTF-CA by Time-Resolved Single Crystal X-ray Structure Analysis

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TTF-CA is a charge-transferred complex and shows photoinduced phase transition from quasi-neutral (the degree of charge transfer $\rho \sim 0.3$) to quasi-ionic ($\rho \sim 0.7$) phase around 90 K [1]. Recent ultrafast spectroscopy reported that a more neutralized (over-neutralized) phase than the initial one was reached and remained at least 200 ps after photoinduced phase transition [2]. In this study, the over-neutralized phase of TTF-CA was characterized utilizing time-resolved X-ray diffraction technique and precise single crystal structural analysis about photoexcited molecule[3].

Time-resolved single crystal X-ray diffraction experiment (100 ps time-resolution) was performed at PF-AR NW14A in KEK. Femtosecond laser was used as the excitation light source. Diffraction data were collected at the selected delay times ($\Delta t = 150$ ps, 500 ps, 800 ps, and 1 ns) after laser irradiation (light-on). At those times, photoinduced quasi-ionic phase is completely decayed ($\tau \sim 20$ ps). The data without laser irradiation (light-off) were also collected at all times.

Photoinduced positional change of Cl and O in CA were observed in the photo-difference Fourier maps, which using observed structural factor change by laser irradiation as the coefficient ($F_{\text{light-on}} - F_{\text{light-off}}$). Those temporal changes represent photoinduced relaxation of intermolecular interactions in increasing order of potential energy densities. Moreover, shortening of C=O in CA was shown at $\Delta t = 800$ ps. LUMO of CA is the antibonding orbital around C=O. Therefore, that shortening indicates back charge transfer to TTF and decreasing of $\rho$ (i.e., reaching the over-neutralized phase). The 10 K heating causes larger lattice expansion than by laser irradiation, but no significant C=O shortening was observed in that case. Therefore, over-neutralization is triggered by light excitation and not a simple thermal-induced phenomenon.

In sum, the over-neutralized phase of TTF-CA, which generated at $\Delta t = 800$ ps after laser irradiation, is classified a unique one in a photoinduced process.

Controlled molecules for time-resolved electron diffraction experiments
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Controlled-molecule imaging increases the amount of information gained when investigating molecular dynamics by electron diffraction, photoelectron measurements, or FEL light sources. In our group, we control and study gas phase molecules, which are prepared in cold, supersonic beams. These samples can be size, isomer, and quantum-state selected by means of electric deflection [1,2]. The force, which is exerted on a neutral polar molecule by an inhomogeneous electric field, is exploited to spatially separate quantum states due to their distinct effective dipole moments.

The prepared ensembles of quantum-state-selected molecules can be laser aligned and mixed-field oriented by the combined action of strong picosecond laser fields and weak dc electric fields. Thus, the molecules are studied directly in the molecular frame. Here, this is demonstrated for the prototypical iodobenzene (C₆H₅I) molecule at high repetition rates. The angular distribution of the molecules is probed by strong-field ionization using a femtosecond laser pulse and velocity-map imaging of the produced ions. The degrees of alignment and orientation, up to $<\cos(\theta)>_{2D} = 0.95$ and $N_{\text{up}}/N_{\text{down}} = 0.65$, respectively, are characterized as a function of repetition rate, deflection, and laser parameters. The experiment is conducted with repetition rates up to 1 kHz, which will provide the necessary statistics to investigate complex molecular dynamics in detail, for instance, along which pathways on a highly corrugated potential energy surface a molecule converts from one isomeric structure to another one.

Structural information can be gained by molecular-frame photoelectron angular distributions [3], as well as by electron-diffraction imaging. An electron-gun setup for a temporal resolution of tens of picoseconds is currently under construction and will be combined with the existing molecular beam setup. State-selection will provide a well-defined starting point for studying molecular dynamics, and spatial orientation, combined with tomographic approaches, permits the retrieval of three-dimensional structural information from the electron diffraction patterns.

Ultrafast Dynamics of Charge Density Waves in $4H_b$-TaSe$_2$ Probed by Femtosecond Electron Diffraction

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Reduced dimensionality seems to be a decisive property governing phenomena like high-temperature superconductivity and charge density wave (CDW) formation. It is proposed that in CDW compounds a lower dimensionality favours Fermi-surface nesting, making the formation of a band gap more efficient. This explains why CDW formation is prevalent in quasi one- or two-dimensional metals like transition-metal dichalcogenides. Recently, this classical picture has been challenged since the nesting condition derived from the topology of the Fermi surface and the observed CDW modulation vectors are not generally equal.

Here we investigate the dynamics of the photoinduced commensurate-to-incommensurate CDW phase transition in $4H_b$-TaSe$_2$ by means of femtosecond electron diffraction at room temperature [1]. While $4H_b$-TaSe$_2$ is a quasi two-dimensional crystal it consist of alternating layers of CDW carrying and non-CDW carrying layers at room temperature. The non-CDW carrying layers decouple the CDW carrying layer from each other making $4H_b$-TaSe$_2$ more two-dimensional (i.e. lower dimensional) than for instance $1T$-TaS$_2$ which has a CDW present in all layers.

In our results we show that in the perturbative excitation regime the CDW recovery time in $4H_b$-TaSe$_2$ (~150 ps) is found to be two orders of magnitude larger than previously observed structural recovery times in $1T$-TaS$_2$ (~4 ps) [2] indicating a less stable CDW in $4H_b$-TaSe$_2$. This observation contradicts the classical picture of reduced dimensionality favouring CDW formation and therefore could highlight the importance of three-dimensionality for the existence of CDWs in layered compounds.

Radiofrequency phase space manipulation of ultrashort electron beams


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The realization of high quality ultrashort electron beams is mainly due to the development of sources that are based on femtosecond photoemission from metal cathodes and, more recently, on femtosecond photoionization of laser-cooled gases. To fully exploit the potential of these high-brightness beams, development of ultrafast time-dependent electron optics is required as well. We are investigating various ways to manipulate the 6D phase space distribution of pulsed electron beams with resonant radiofrequency (RF) cavities.

We have demonstrated compression, i.e. longitudinal focusing, of space-charge-dominated electron bunches down to 100 fs bunch durations using a 3GHz cavity in TM_{010} mode. Alternatively, a TM_{010} cavity operated at a different RF phase may be employed to lower the longitudinal energy spread of an electron bunch, and thus reduce chromatic aberration effects. TM_{010} cavities can be used as transversely (de)focusing elements as well. Since Scherzer’s theorem does not apply for time-dependent optics, this makes it possible to correct spherical aberrations.

Deflecting cavities in TM_{110} mode are usually applied for high resolution bunch length diagnostics. We have shown that they may also serve as fast beam choppers which produce 100-fs pulses, while conserving the extremely low beam emittance of high-performance TEMs. This will enable significant improvements of ultrafast electron microscopy in stroboscopic mode, both in terms of peak brightness and repetition rate. By combining TM_{110} and TM_{010} cavities, time-of-flight femtosecond EELS may be realized without the need for a photoemission laser or an expensive magnetic spectrometer.
Simulating the beam profile and time resolution for a new electron Diffractometer

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The Wann group in Edinburgh is currently constructing a new pulsed-source electron diffractometer for use with gaseous and solid-state samples. As part of the preparations and design of the apparatus we have undertaken simulations to predict both the beam characteristics and the potential time resolution of the experiment.

The electron gun itself uses a gold photocathode illuminated in transmission mode using the 3rd harmonic of an 800 nm femtosecond laser. The bunches of order $10^4$ electrons are accelerated across a 100 keV potential. Our plan is to introduce the sample relatively close to the source of the electrons – a so-called “compact” electron gun – so as to minimize the space-charge repulsion effects.

We have used the simulation packages SIMION $^1$ and GPT $^2$ to predict the pulse duration at key points between its birth and reaching the detector. We predict that an initial pulse 50 fs long containing $10^4$ electrons will stretch to $\sim 140$ fs when it reaches the molecular beam 40 mm away. By the time it reaches the detector, placed 500 mm from the anode, the same pulse will have stretched to $\sim 600$ fs. In order to maximize the performance of our apparatus, we would like to maximize the number of electrons in a pulse whilst keeping the pulse length as short as possible. In this work we consider the effects on the temporal resolution of our experiment of changing the initial pulse length, using methods to overcome velocity mismatch $^3$, and employing a magnetic lens in the diffraction chamber.

2. S. B. van der Geer and M. J. de Loos, “General Particle Tracer”, *Elements*, 2009, **1**.