



Workshop on Short Pulse Science at the EBS Source

**ESRF Auditorium – Grenoble, France
28 - 29 October 2019**

- **Programme**
- **Abstracts**
- **List of participants**

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ESRF Auditorium

PROGRAMME

Monday 28 October 2019

08:30 - 09:00	Registration in the ESRF Central Building entrance hall	
09:00 - 09:30	Welcome, Introduction	J. Susini, ESRF Director of Research
Session 1	BEAMLIN TALKS – Chair: M. WULFF	
09:30 - 09:50	Time-resolved structural dynamics at the ESRF	M. Levantino (ESRF Grenoble)
09:50 - 10:10	Single pulse XAS measurements at ID24 and the HPLF project	R. Torchio (ESRF Grenoble)
10:10 - 10:30	Serial crystallography at the ESRF Extremely Brilliant Source: the ID29 upgrade project	D. De Sanctis (ESRF Grenoble)
10:30 - 10:45	Coffee break	
Session 2	STRUCTURAL BIOLOGY – Chair: M. LEVANTINO	
10:45 - 11:10	Time resolved X-ray scattering studies at ID09 of structural changes in integral membrane proteins	R. Neutze (University of Gothenburg)
11:10 - 11:35	Use of short X-ray pulses to probe the structural dynamics of the orange carotenoid protein (OCP)	J.-P. Colletier (IBS Grenoble)
11:35 - 12:00	Tracking Ca ²⁺ ATPase intermediates in real-time by X-ray solution scattering	M. Andersson (Umeå University)
12:00 - 12:25	Kinetic pathways in self-assembled soft matter systems: applications of synchrotron TR-SAXS	R. Lund (Oslo University)
12:30 - 14:00	Lunch at the EPN campus restaurant	
Session 3	CHEMISTRY / XES – Chair: P. GLATZEL	
14:00 - 14:25	Towards improving light-activated functional molecules	G. Vanko (Hungarian Academy of Sciences)
14:25 - 14:50	Real-time mapping of photo-induced bond formation and accompanying relaxation dynamics	K. Møller (DTU Copenhagen)
14:50 - 15:15	Spin sensitivity in the X-ray emission of iron compounds	M. Retegan (ESRF Grenoble)
15:15 - 15:40	Ultrafast electron dynamics in real world light activated complexes studied by x-ray spectroscopy	J. Uhlig (Lund University)
15:40 - 16:00	Coffee break	
Session 4	MATERIAL SCIENCE / X-RAY DIFFRACTION AND ABSORPTION – Chair: R. TORCHIO	
16:00 - 16:25	Photoactive materials studied by X-ray techniques	M. Cammarata (CNRS Rennes)
16:25 - 16:50	Studies of structural dynamics in solids using time resolved X-ray diffraction	X. Wang (Lund University)
16:50 - 17:15	Characterization of the shock-induced phase transitions in Bi and Sn using time resolved synchrotron X-ray diffraction	A. Sollier (CEA Paris)
17:15 - 17:40	Investigation of structural transformations in high pressure shocked silicates from in-situ x-ray diffraction	A. Ravasio (Ecole Polytechnique Palaiseau)
19:00 - 22:00	Workshop dinner at the EPN campus restaurant	

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Tuesday 29 October 2019

Session 5	SHORT PULSE IMAGING – Chair: M. WULFF	
09:00 - 09:20	Beamline ID19: a versatile station for time-resolved hard X-ray microimaging	A. Rack (ESRF Grenoble)
09:20 - 09:45	Brittle crack propagation in silicon wafer by diffraction tomography	F. Rieutord (CEA Grenoble)
09:45 - 10:10	Analysing the arc formation and burn-back phenomena in fast industrial fuses at high di/dt	J.M. Chaix (SIMAP Grenoble)
10:10 - 10:35	Multi frame synchrotron radiography of pulsed power driven high energy density physics experiments	S. Bland (Imperial College)
10:35 - 10:50	Coffee break	
Session 6	SOFT MATTER / SAXS – Chair: A. RACK	
10:50 – 11:10	New opportunities for time-resolved SAXS with the EBS	T. Narayanan (ESRF Grenoble)
11:10 - 11:35	Beans, viruses... and synchrotron radiation. Probing the self-assembly dynamics of icosahedral virus by time-resolved small-angle X-ray scattering	G. Tresset (Université Paris-Sud)
11:40 - 14:00	Lunch at the EPN campus restaurant	
Session 7	X-RAY DIFFRACTION AND SCATTERING – Chair: M. CAMMARATA	
14:00 - 14:20	Temperature-jump induced changes in protein crystals studied with pink beam serial crystallography	A. Meents (DESY Hamburg)
14:20 - 14:45	Comprehensive analysis of hierarchical dynamics in ablation by scattering, imaging and spectroscopy	A. Plech (Karlsruhe Institute of Technology)
14:45 - 15:10	Combining femtosecond hard X-ray scattering and spectroscopy to study photochemical dynamics in solution: instrumentation and recent results	D. Khakhulin (European XFEL)
15:10 - 15:35	Strain-induced dynamics monitored by time-resolved x-ray diffraction	P. Gaal (Hamburg University)
15:35 - 16:10	Round table discussion on short pulse experiments at ESRF-EBS	
16:10	End of the workshop	



Abstracts

Tracking Ca²⁺ ATPase intermediates in real-time by X-ray solution scattering

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The Ca²⁺-transporting sarcoplasmic reticulum ATPase (SERCA) is a membrane protein transporter involved in calcium signaling by active Ca²⁺ reuptake to internal stores. Several of the structural transitions associated with transport have been characterized by X-ray crystallography, but critical intermediates of the inward-outward switching are missing. We combined time-resolved X-ray solution scattering (TR-XSS) experiments at beamline ID09, ESRF, and molecular dynamics (MD) simulations to characterize SERCA activation, phosphorylation and calcium release in real-time in the native membrane. Two transient intermediates were identified, one with a 1.5 ms rise-time that showed closing of the cytosolic domains typical of Ca²⁺- and ATP-bound SERCA states. The subsequent 13 ms intermediate, however, showed a completely novel arrangement of the catalytic domains that exposed the ADP-binding site, which remains buried in crystal structures. This conformational arrangement is consistent with the elusive ADP-sensitive, Ca²⁺-bound state in mid-transition between known inward-facing and outward-facing states. Hence, this time-resolved scattering approach enables identification and structural characterization of transient intermediates in irreversible membrane protein reactions, and therefore significantly increases the number of possible targets beyond the light-sensitive proteins.

Multi frame synchrotron radiography of pulsed power driven high energy density physics experiments

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Pulsed power driven underwater wire explosions are accompanied by the efficient generation of strong shockwaves. In the case of cylindrical or quasi-spherical wire arrays, convergence of these shockwaves results in high energy density conditions with multi Mbar pressures being obtained on axis, even in compact ‘table-top’ experiments. However much of the physics underlying wire explosion and shockwave interactions remains undiagnosed.

On ID19 at ESRF we have performed the world’s first high current pulsed power experiments coupled to a synchrotron. The resultant multi-frame, phase contrast radiography images provide absolute density measurements for critical comparison to theory and simulation. Wires in various configurations were exploded in water baths using a simple ~30kA, 500ns rise time current source. In experiments examining single wires, as the wires expanded and ionised, unexpected striation instability growth was observed inside the dense wire material. This could significantly alter our previous understandings of the conductivity of warm dense matter. In two wire experiments, interacting the shockwaves launched into the water with the expanding wire material produced a new test bed for analysing Richtmyer-Meshkov instability growth. With a cylindrical array of wires an increase in density of the water at convergence of the shockwaves agreed well with previous theories demonstrating the techniques use as a driver for extreme pressure research. Finally in arrangements with 2 crossed wires (‘X-pinches’) mass clear out was observed at the cross over point due to the high magnetic fields produced.

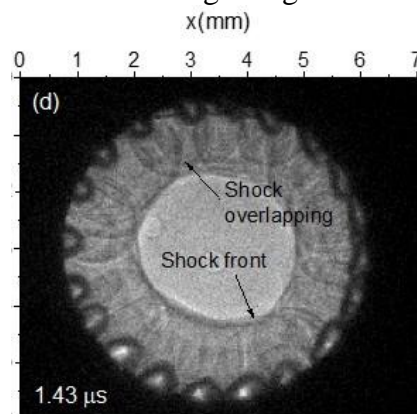


Figure 1: Radiograph through axis of cylindrical wire array showing merger of shockwaves from exploding wires and shock front travelling at high speed towards the axis

This work was sponsored by the ESRF User Program, the Institute of Shock Physics, First Light Fusion, Sandia National Laboratories, EPSRC, the US DOE and the Israeli Science Foundation.

Photoactive materials studied by X-ray techniques

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The capability of transforming matter has accompanied human kind since very early in history. The advent, few decades ago, of intense short pulse lasers have motivated scientists to undertake the difficult task of trying to transform matter with light.

Contrary to molecules, materials are intrinsically multi-scale systems that need to be studied with different techniques and looked at different time scales.

In this presentation I will summarize some recent effort of our group to complement optical spectroscopy studies with a variety of X-ray techniques extending from picosecond to millisecond time delays allowing to explore from the atomic motions to heat diffusion.

Analysing the arc formation and burn-back phenomena in fast industrial fuses at high di/dt

J.-M. Chaix^{1*}, X. Just¹, M. Olbinado², P. Lhuissier¹, J.-L. Gelet³, A. Rack², O. Bonnefoy⁴, G. Thomas⁴, L. Millière³, R. Dendievel¹

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Fuses are old but key devices in electrical technology [1]. They are constituted by conducting blades (Ag, Cu) with locally restricted cross sections (notches), surrounded by compacted silica sand in a protective ceramic cartridge. In case of short circuit, the metal melts and opens the circuit. In practice, the current does not instantaneously fall down to zero: an electric arc appears and transiently maintains the current. During this arcing period, the arc length increases (metal “burn back”) and induces various phenomena (pressure waves, sand melting...). The increasing use of DC current and semi-conductor-based power converters requires fast fuses able to face short circuit situations and stop the current in times of some tenths of microseconds (high di/dt). Understanding the onset, development and end of the arc in such cases is of key importance for designing efficient fuses.

Radiography is a suitable way for *in situ* studying the fuse blade behaviour during breaking, by viewing the highly absorbing metal through the sand and cartridge. High speed radiography (up to $5 \cdot 10^6$ images/s) results were obtained during high di/dt fuse breaking tests at ESRF [2.3]. They enabled getting information at different time scales on various aspects such as the end of pre-arcing period (Fig.1-a) or the effect of sand (Fig.1-b). This paper will discuss scientific and technical issues for fuses understanding and design.

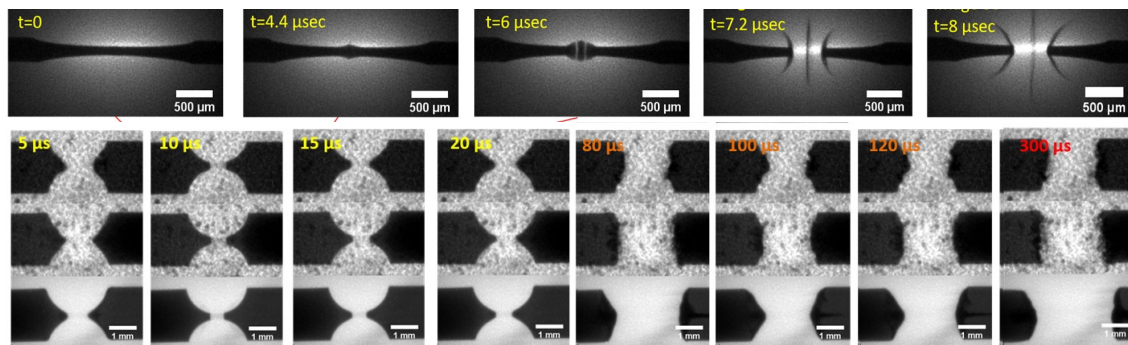


Figure 1: Arc onset without sand (top); burn-back with packed sand, loose sand, without sand (bottom)

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Use of short X-ray pulses to probe the structural dynamics of the orange carotenoid protein (OCP)

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To protect themselves from detrimental light energy excess, cyanobacteria synthesize a small dimeric photoactive Orange Carotenoid Protein (OCP) capable of quenching and dissipating into heat the excess of energy arriving to the cyanobacteria light-harvesting centers. Upon photon absorption, this pigment-encasing two-domain protein, undergoes a transition from a compact orange “non-active” state (OCP^o) to an extended red “photoactive” state (OCP^r) associated with a migration of the carotenoid pigment from the interface between the two domains into the effector N-terminal domain (NTD) of the protein. However, it remains elusive how the energy absorbed by the carotenoid is funneled into the protein scaffold and how the protein structure varies during photoactivation. Using time-resolved (TR) X-ray scattering, we studied the μ s-ms photo-triggered structural dynamics of dimeric OCP in solution. We also used Serial Synchrotron Crystallography (SSX) to shed light on the first intermediate leading to the OCP^r photoactive state. Altogether, our results illustrate how initially localized changes on the ps timescale may trigger global protein structural dynamics of the μ s-s timescale and how the structure of this protein has evolved to enable photoactivation only in case of very strong irradiance, despite the use of one of nature’s most potent chromophore.

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Strain-induced dynamics monitored by time-resolved x-ray diffraction

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The interplay of lattice dynamics with the electronic, magnetic or optical response of solids and nanostructures is a potential route to drive functional processes in novel materials. Photoacoustic generation of strain pulses allows for generation and control of coherent strain pulses on fast time and short length scales.[1] The deformation dynamics due to thermal and coherent strain fields can be monitored by time-resolved x-ray diffraction and reflectivity measurements.[2] The combination of photoacoustic strain generation and time-resolved x-ray diffraction has even found applications as active x-ray optics for synchrotron-based experiments.[3]

This talk will discuss examples of strain-induced dynamics in magnetic thin films and piezoelectric materials and illustrate new possibilities for time-resolved x-ray experiments due to the improved beam properties of the EBS upgrade.

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Combining femtosecond hard X-ray scattering and spectroscopy to study photochemical dynamics in solution: instrumentation and recent results

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Recent development of optical pump/X-ray probe techniques at large scale facilities such as synchrotrons and X-ray free-electron laser (XFEL) sources enabled direct visualization of various fundamental ultrafast phenomena in solution photochemistry. Due to intrinsically much shorter pulses, the temporal resolution of such experiments at XFELs is over three orders of magnitude higher compared to that at conventional synchrotron sources, reaching the sub-100 fs domain – the fundamental timescale of elementary steps in photochemical dynamics.

In particular, understanding photochemistry of transition metal complexes is currently of high interest since they often are the major players in many fundamental photochemical processes that define e.g. biochemical reactivity and photovoltaic/photocatalytic functionality. In these reactions photoexcitation typically triggers ultrafast charge and spin changes of the metal center which intrinsically drives dramatic rearrangements in the structure of the molecule and its solvation shell.

Taking advantage of combining structurally and electronically sensitive probes, namely time-resolved X-ray scattering/diffraction [1], X-ray emission [2] and absorption [3] spectroscopies in one experiment [4,5], it has become possible to accurately monitor intrinsically coupled ultrafast electronic and structural transformations during e.g. ultrafast spin transitions and ligand exchange reactions in solvated iron complexes. A few examples of such studies performed at synchrotrons and XFEL sources are presented in this contribution.

The methodology of combining simultaneous structural and electronic observables is applied for experiments at the Femtosecond X-ray Experiments (FXE) instrument of the European XFEL, which came online only about 1.5 years ago. The new European XFEL source is capable of MHz pulse repetition rate thus providing a 100-fold increase in average flux over other XFELs and can deliver high X-ray photon energies up to 20-25 keV. We report on the progress of the FXE instrument commissioning over the past year, describe current capabilities of the setup as well as the first experimental results.



Figure 1. Schematic representation of the combined time-resolved X-ray methodologies at the FXE instrument.

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Time-resolved structural dynamics at the ESRF

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One of the five scientific drivers at the ESRF is “Pump-and-probe experiments and time-resolved science” [1]. The ID09 beamline is fully dedicated to this scientific mission and leads time-resolved research at the ESRF. Experiments performed at ID09 span through different scientific domains including chemistry, solid-state physics, soft condensed matter and structural biology [2-6]. Two key characteristics of ID09 are the polychromatic (pink) beam option and the possibility of selecting single (100 ps) X-ray pulses or “macro” pulses of variable duration (300 ns, 1-30 μ s, ≥ 1.5 ms). This allows to investigate phenomena over a wide range of time scales: from ultrafast relaxations in chemical compounds [2] or solid-state samples [4] to slow (up to hundreds of milliseconds) conformational changes of biological macromolecules [5]. In my talk I will briefly present: (a) the current status of the beamline and its expected performances in light of the EBS upgrade, (b) our plans for possible future upgrades, and (c) an overview of the research typically performed at ID09.

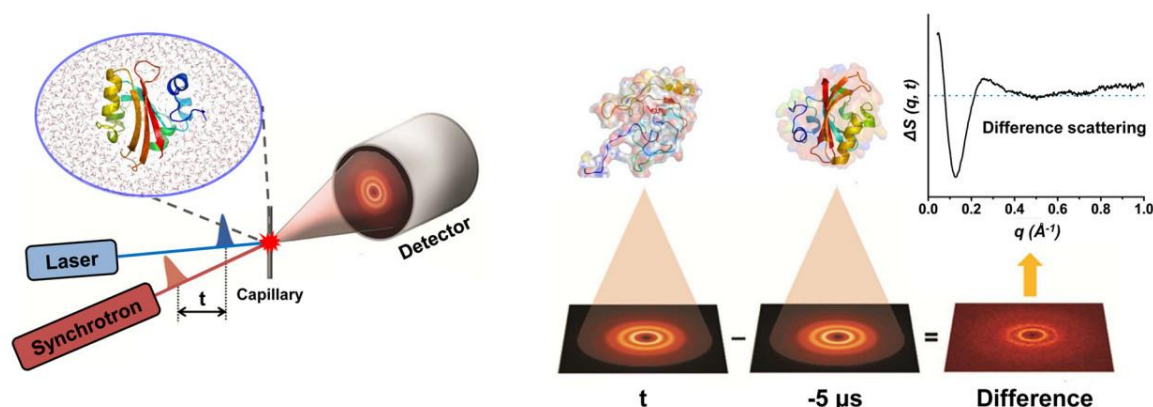


Figure 1: Example of research routinely performed at ID09 - A structural change in a protein solution is triggered by a short (ps) laser pulse and then followed as a function of time (100 ps – 100 ms) with time-resolved X-ray solution scattering (figure adapted from: Kim et al., *Acc. Chem. Res.* 2015).

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Kinetic Pathways in Self-assembled Soft Matter Systems: applications of synchrotron TR-SAXS

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The kinetic pathways regulating the self-assembly of molecules into well-ordered nanostructures such as micelles, membranes and larger complexes are still not understood. Many processes occur far from thermodynamic equilibrium and occurs on microseconds-milliseconds time scales that until now have been too fast for most experimental techniques. For computer simulations, however, we face the opposite problem; the dynamics of self-assembled systems is generally too slow for studies with accurate molecular precision due to the large number of atoms involved. Time-resolved small-angle X-ray/neutron scattering (TR-SAXS/SANS) is powerful technique¹ that allows kinetics processes such as nucleation processes^{2,3} and morphological transitions^{4,5,6} to be followed with structural resolution over time scales starting from microseconds -milliseconds. Although the capabilities of the TR-SAXS technique at synchrotrons, such as at ID02 at ESRF, have undergone a dramatic improvement over the last decade or so, studies of self-assembly are often challenging due to difficulties in triggering the process and probing the process short time scales. Often stopped-flow apparatus is used but it is limited to milliseconds kinetics. Alternatively, light⁷, in particular lasers, offer a convenient way to study faster processes but is again limited in the variety of suitable systems. Another challenge is the interpretation of scattering data obtained from a kinetic process which often contains highly non-equilibrium structures with a variety of morphologies and large polydispersities, In. this context, computer simulation is very useful but requires suitable methods to be able to quantitatively compare with data obtained from scattering techniques.

In this presentation, we shall show some examples of insight into surfactant assembly and membrane solubilization studies obtained using TR-SAXS and aided by computer simulations. We will discuss triggering methods (stopped-flow and light-induced) and show how combination with computer simulations give insight into mechanism of self-assembly.

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Temperature-jump induced changes in protein crystals studied with pink beam serial crystallography

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X-ray crystallography experiments typically yield a static average structure of the molecules under investigation. As proteins function as dynamic entities, it is often desirable to obtain additional information about protein dynamics. Uncovering flexible, connected regions helps in understanding protein functions.

A temperature jump (T-jump) allows to thermally activate a molecules by raising its temperature in very short time. In case of protein crystals such a temperature jump can be relatively easy realized with IR laser pulses, which are absorbed by water molecules present in the crystal structure and then lead to a sudden increase of the temperature [1].

We have studied temperature jump induced structural changes in Ribonuclease A crystals with the method of pink beam fixed target serial crystallography [2, 3]. Here the sample is probed with a polychromatic probe pulse arriving at a defined delay after excitation with the IR pump pulse. Due to the high intensity of the polychromatic X-ray pulses it is possible, to perform T-jumps experiments with high temporal resolution down to the nanosecond time scale.

Whereas our data analysis reveals only very small structural changes induced by the temperature jump, we observe systematic and significant time dependent changes of the thermal displacement parameters (B-factors) of the protein molecule.

References

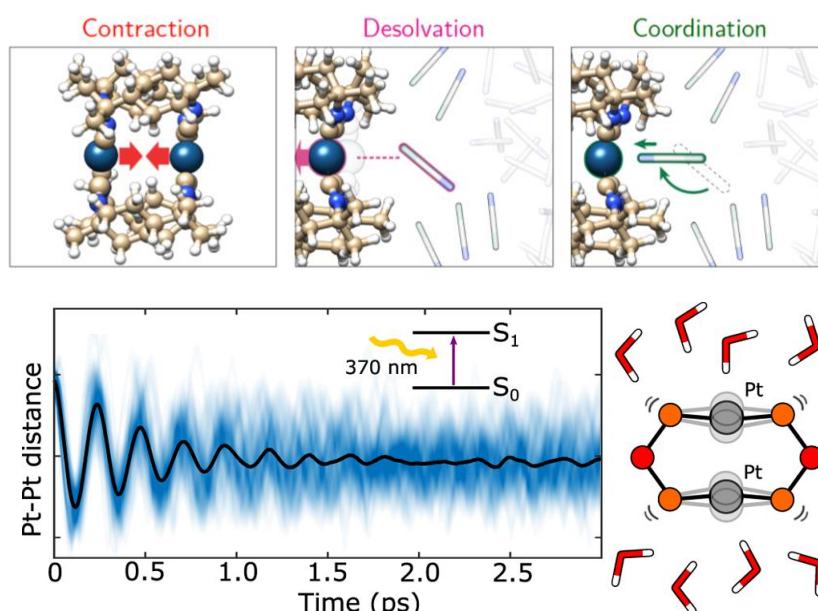
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Real-time mapping of photo-induced bond formation and accompanying relaxation dynamics

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Time-resolved X-ray scattering is used for investigations of structural dynamics in real time. However, analysis and interpretation of the experimental outcomes require support from theory and detailed atomistic simulations. In this contribution, we build on our developments of the theory behind time-resolved x-ray scattering [1,2] and illustrate how we have used computer simulations to assist pico- and femtosecond scattering experiments for mapping of ground- and excited-state bond formation and accompanying solute and solvent relaxations in solvated I_2 [3], $[Ir_2(Dimen)_4]^{2+}$ [4,5], and $[Pt_2(P_2O_5H_2)_4]^{4-}$ [6,7].



Our QM/MM BOMD code was used to model ground-state properties as well as the ultrafast photo-induced bond formation between the metals and the subsequent intra- and inter-molecular relaxation dynamics in solvated $[Ir_2(Dimen)_4]^{2+}$ (top) and $[Pt_2(P_2O_5H_2)_4]^{4-}$ (bottom).

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New opportunities for time-resolved SAXS with the EBS

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In this presentation, I will give a short overview of new possibilities offered by the combination of EBS with advanced pixel array detectors for the investigation of structural dynamics in soft matter and related biological systems. Small-angle X-ray scattering (SAXS) and X-ray photon correlation spectroscopy (XPCS) methods are expected to greatly benefit from these developments. Until now real-time SAXS experiments were primarily limited by the count rate as well as the frame rate of photon counting detectors. On the other hand, fast multispeckle XPCS experiments have been hampered not only by the frame rate of photon counting detectors but also due to the available coherent photon flux. With the EBS, the coherent photon flux is expected to increase by a factor 30 or so. High frame rate photon counting pixel detectors such as Eiger-500k (from PSI) and Ultra high speed sensor (UHSS-500 from Rigaku) offer great promise for microsecond range measurements. As a result, it will become feasible to probe microsecond range kinetic processes and equilibrium dynamics over a broad size scale from nanometer to micron range by real-time scattering methods.

Time resolved X-ray scattering studies at ID09 of structural changes in integral membrane proteins

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Time-resolved X-ray solution scattering (TR-XSS) has become a powerful method for elucidating the nature and number of conformational states of proteins. The key advantage of time-resolved solution scattering is that there is no need for protein crystals and therefore protein crystal contacts do not constrain the motions of the protein studied. Conversely, since data is only one dimensional, TR-XSS does not yield three-dimensional protein structures and conformational changes must be modelled using additional structural and chemical knowledge. Proof-of-principle TR-XSS studies of structural changes in haemoglobin were reported more than a decade ago [1] and our first TR-XSS studies of bacteriorhodopsin [2] followed a year later. We have also observed ultrafast motions in photosynthetic reaction centres under conditions of extreme multiphoton excitation [3].

In this presentation I wish to give an update of the status of our more recent TR-XSS studies at ID09 of the ESRF on three other integral membrane proteins: sensory rhodopsin II (an archaeal photoreceptor) in isolation and in complex with its transducer protein; channel rhodopsin (a light-gated channel); and cytochrome *c* oxidase (the enzyme which reduces oxygen to water in mitochondria). We have excellent quality TR-XSS data for all three integral membrane proteins but have delayed publication due to issues of modelling structural changes within integral membrane proteins embedded within a detergent micelle. I will therefore also update our progress in modelling conformational changes and my reason for believing that this bottleneck will soon be solved. Finally, I will report on time resolved serial millisecond crystallography (TR-SMX) studies of light-driven structural changes in sensory rhodopsin II performed at the protein crystallography station of the Swiss Light Source. All methods appear very promising in future time-resolved studies at the ESRF.

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Comprehensive analysis of hierarchical dynamics in ablation by scattering, imaging and spectroscopy

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Particle synthesis during pulsed-laser ablation in liquid is a multiscale process [1] involving the occurrence of atoms, cluster and nanoparticles, their subsequent interaction and agglomeration, and finally their dynamic confinement within the fluid [2] and vapour formation all of which happening on a hierarchy of time and length scales [3]. The connection between the nanoscale particle formation processes and the macroscopic fluid dynamics is resolved by employing spatially and temporally resolving small-angle X-ray scattering, bright and dark-field X-ray imaging [3,4] methods as well as spectroscopic tools [5].

The presentation will discuss the approaches and limitations of time-resolved techniques to harness scattering, imaging and spectroscopy signals for the understanding of complex dynamics including speciation and spatiotemporal distributions of nanostructures. The ESRF upgrade may help to overcome current flux and size limitations in breaking the microsecond barrier [4,6].

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Beamline ID19: a versatile station for time-resolved hard X-ray microimaging

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The ESRF is the worldwide leader in parallel-beam synchrotron radiation (SR) X-ray imaging. Especially beamline ID19 has become a reference instrument for SR-based X-ray phase contrast microtomography and -radiography. A substantial evolution of the present ID19 beamline is aiming to optimize it for multiscale applications of parallel and coherent imaging techniques as well as the use of polychromatic radiation for (ultra-)short exposure times, i.e. time-resolved imaging.

The potential of hard X-ray imaging to tackle scientific questions especially related to materials sciences can be substantially increased when the dimension time is accessible. Nowadays, unprecedented temporal resolution with hard X-ray imaging can be reached at synchrotron light sources thanks to high-speed CMOS cameras: the latest generation allows in combination with fast scintillators to separate individual bunches from the storage ring.

This presentation will summarise the advantages and possibilities of beamline ID19 and its experimental infrastructure to benefit from imaging using short pulses along recent example studies such as gas gun for impact or a split hopkinson pressure bar.

Investigation of structural transformations in high pressure shocked silicates from in-situ x-ray diffraction

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Accurate models of the Earth, of Earth-Type exoplanets and of putative differentiated cores of giants planets require an improved description of the physical properties of silicates. Of overall importance are olivine (Mg,Fe)₂SiO₄ and orthopyroxene (Mg,Fe)SiO₃ minerals, with enstatite (MgSiO₃) and forsterite (Mg₂SiO₄) as the archetypal members. The knowledge of their phase diagram at high pressures and temperatures both in solid and liquid phases is crucial for planetology. Precise measurements in Diamond Anvil Cells allowed to associate the solid-solid phase transitions that olivine undergoes at high pressure to the major seismic discontinuity detected in the Earth's mantle. Establishing the stability of these phases with pressure and temperature is necessary for super Earth studies and meteorites impacts as well as for high pressure physics. Similarly, the knowledge of properties of liquid silicates under high pressure and high temperature are requested for modelling the dynamics and solidification mechanisms of the Magma Ocean in the early Earth, constraining the presence of partial melting at the present day core-mantle boundary. Reaching these extreme temperatures and pressure in DAC is as today a real challenge. Often, MgSiO₃ and Mg₂SiO₄ glasses under high pressures are studied as liquid analogs, but this approximation has never been validated. In this context, dynamic compression schemes can help in widening the characterised phase diagram region. This research has so far been impeded by the absence of a structural probe able to directly determine phase transformations along shocked states, but new exciting perspectives are today opened by the advent of extremely brilliant and temporally short XFEL x-ray sources allowing in-situ x-ray diffraction (XRD) measurements. In this talk we will present recent results we obtained on in-situ XRD from shock compressed SiO₂, MgSiO₃ crystalline and glass samples. The experiment was carried on at the MEC end-station of LCLS, in Stanford. Main shocked induced structural changes will be reported, comprising first observation of shock-induced metastable amorphous phases as well as unexpected high pressure polymorphs. Direct XRD data of liquid states could also be achieved and will also be discussed. A particular attention will be placed in the comparison between melts and high pressure glass we obtained in both static and dynamic compressions.

Spin Sensitivity in the X-ray Emission of Iron Compounds

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Core-to-core $K\alpha$ and $K\beta$ X-ray emission lines have long been recognized as markers of the local spin states in transition metal complexes [1]. As such, changes in the spectral envelope have been successfully used to track the spin dynamics of short-lived excited states or to quantify local spin moments [2]. However, the spin-related spectral changes, which are intrinsically related differences in the exchange interaction between the core and valence electrons, can be obscured by the changes due to different chemical environments around the metallic center. Also, as the magnitude of the exchange interaction is different in $K\alpha$ and $K\beta$, their spin sensitivity will be different.

To address these points, we have carried out a systematic experimental and theoretical investigation of the $K\beta$ and $K\alpha$ XES spectra on a wide range of iron compounds with different oxidation states (+2, +3, +4, and mixed-valence), spin states (high spin, low spin, and mixed-spin), coordinating ligands (fluorides, oxides, sulfides, etc.), and local symmetry (octahedral and tetrahedral). We have retrieved the spin evolution between complexes by determining various parameters commonly used in X-ray emission studies ($K\beta_{1,3}$ -first moment, $K\alpha_1$ -full width half maximum, and integrated absolute difference (IAD) [3]). Our analysis reveals a significant spread of these parameters even at fixed nominal spin values. Using semi-empirical multiplet calculations we were able to show that this results from changes in the intra-atomic exchange interaction arising from metal-ligand covalency.

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Brittle crack propagation in silicon wafer by diffraction tomography

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Crack propagation in brittle materials is difficult to study due to its propagation within bulk materials and its high speed (km/s range). High penetration of hard X-rays, intense fluxes on undulator beamline ID19 and fast detectors allow one to face these challenges. We will report on the study of the crack propagation in bonded silicon wafer assemblies, a key step of the so-called Smart Cut™ technology [1] used for Silicon-on-Insulator substrates manufacturing. Crack propagates in this case along a weakened implanted layer [2].

Experiments were conducted in diffraction mode using scattering on (220) lattice planes, perpendicular to both crack propagation direction and surface normal [001]. Experiments in both 4- and multi-bunch modes have allowed a clear view of the crack front line and oscillatory behaviour of the two separated parts of the crystals in the wake of the crack propagation. Quantitative data on the post-split movements could be obtained and compared to IR data [3,4].

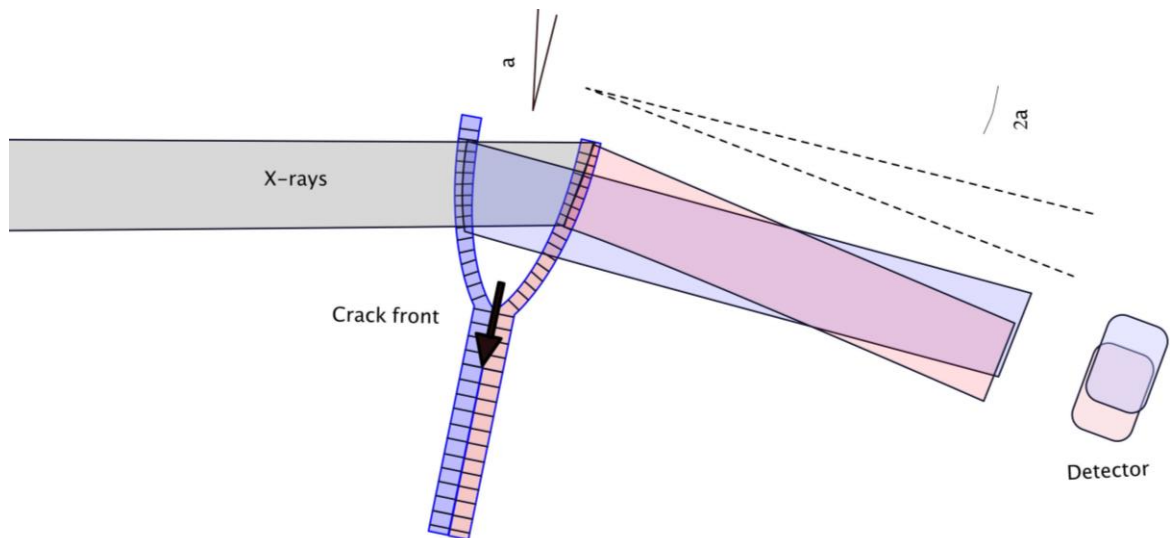


Figure. Geometry of the ID19 experiment.

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Serial crystallography at the ESRF Extremely Brilliant Source: The ID29 upgrade project

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The next generation of storage rings, such as the ESRF Extremely Brilliant Source will be able to produce an electron beam with a greatly reduced horizontal emittance. This will result in a small source size and a low divergent X-ray beam that will increase the brilliance by an order of magnitude and will permit to focalise the full beam on a submicron spot on the sample. The delivered photon flux density will open new opportunities for serial crystallography experiments at room temperature and will permit to define new paradigms for data collection methods. Room temperature data collections and very short exposure time will be used to exploit time-dependant conformational changes that are relevant for biological mechanisms. The EBSL8 project consists in the upgrade of the MAD beamline ID29, to become a new facility entirely dedicated to Serial Synchrotron Crystallography. The end-station will be equipped with a dedicated sample preparation laboratory and a data processing area. The beamline is designed to deliver an X-ray beam of unequalled characteristics on different sample delivery systems and to collect still diffraction images from microcrystals. We will present the design of the new beamline and the current status of the EBSL8 project and discuss future plans and new scientific opportunities.

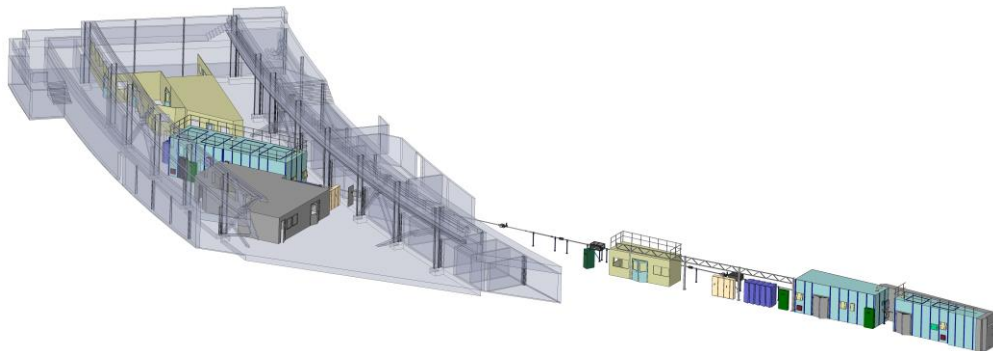


Figure 1: The current layout of the new ID29.

Characterization of the shock-induced phase transitions in Bi and Sn using time resolved synchrotron X-ray diffraction

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Whilst the determination of crystallographic phases at static high pressure is a well established field of research, the structural observation of each phase and their corresponding phase transition boundaries under rapid dynamic compression, (e.g. using ramp- or shock- compression techniques) has been a significant challenge. The first X-ray diffraction (XRD) evidence for a phase transition during shock-wave compression was observed in 1972 [1]. Yet, time-resolved X-ray diffraction of dynamically compressed matter could only be obtained recently by using various large x-ray source facilities, such as KJ laser [2-5], X-ray free electron laser [6-8], and synchrotron [9-12]. Up to now, the differences between dynamic and static data sets have been discussed mostly in terms of the phase transitions kinetics. Observing the structural response of a shocked material now enables rigorous comparisons with the structural phase transitions disclosed by static compression.

In this talk, we will present the results from our first time resolved X-ray diffraction experiments performed at ESRF on ID09 beamline [10, 11]. We will also talk about our future plans and the new prospects offered by the ESRF upgrade.

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Single pulse XAS measurements at ID24 and the HPLF project

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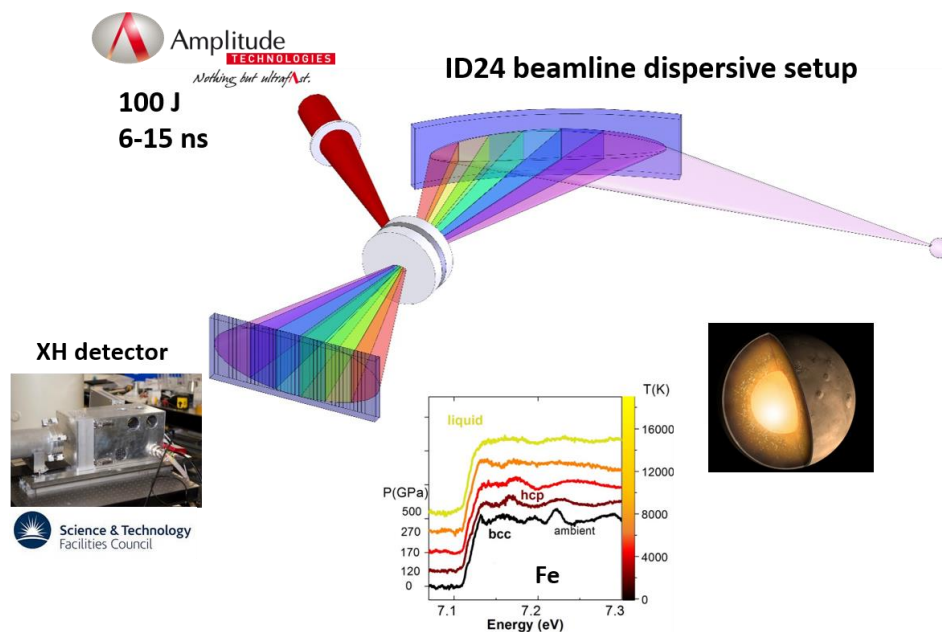
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The energy dispersive beamline ID24 is optimized for time resolved XAS down to the single bunch (100 ps) scale. This is made possible by the energy dispersive geometry, based on an elliptically curved crystal, that allows for the simultaneous measurement of the whole absorption spectrum, and by the development of the fast XH detector (carried out in collaboration with STFC Daresbury laboratory, UK).

This ultimate resolution is required to perform dynamic compression experiments induced by powerful ns lasers, whose interest is driven by planetary, fundamental and material science.

First proofs of principle carried in the 2014-2018 years had an important echo in the community and finally triggered the launching of the High Power Laser Facility (HPLF) project at the ESRF. This two phases project foresees the installation of a 100J laser on beamline ID24 in 2020 to perform dynamic compression experiments. This experimental station, named HPLF-I will be open to users in January 2021. In the second phase (HPLF-II, from 2023) the laser might be shared with an adjacent beamline to extend the applications to time resolved XRD, XRI and XES.

In this talk, details about the beamline will be presented as well as its evolution within the EBS upgrade with particular focus on the HPLF project.



Beans, viruses... and synchrotron radiation. Probing the self-assembly dynamics of icosahedral virus by time-resolved small-angle X-ray scattering

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Viruses are entities that fascinate physicists and biologists. They oppose a relative simplicity in their structure to a surprising sophistication in their function. Although inert, their hundreds or even thousands of molecular components spontaneously assemble and disassemble in a heterogeneous and crowded cellular medium, with near-atomic precision and low error rate. Some single-stranded RNA viruses can even be self-assembled into infectious particles in test tubes from their purified components. This ability to self-assemble always defies theoretical understanding and the kinetic pathways remain largely unknown.

We work on viruses whose spherical capsids adopt icosahedral symmetry with quasi-equivalence and are able to self-assemble around their RNA genome. We focus here on the cowpea chlorotic mottle virus (CCMV), which infects a variety of beans. Its capsid, which displays an icosahedral symmetry $T = 3$, is made of 180 chemically identical and structurally quasi-equivalent copies of a single protein. The assembly implies that 90 dimers of this protein (subunits) find the viral RNA (genome) and fit perfectly around it. We show how our time-resolved X-ray scattering (TR-SAXS) experiments carried out on the ID02 and SWING beamlines at ESRF and SOLEIL synchrotron sources respectively, complemented by *ad hoc* numerical algorithms, have led to significant advances in the understanding of the self-assembly of icosahedral viruses.

In the technically simpler case of empty capsids, we reconstruct the form of metastable intermediate species during assembly (~half a capsid [1]) and disassembly (~half a capsid then two pentameric units [2]). Then, we reveal the very rich dynamic phenomena that occur during the packaging of the genome and of a synthetic polyelectrolyte [3]. These latest data have allowed us to revisit the assembly model of icosahedral viruses, which seemed firmly established on the basis of indirect data.

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Ultrafast electron dynamics in real world light activated complexes studied by x-ray spectroscopy.

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With the recent advances in the development, performance and availability of ultra-short x-rays pulses it has become possible to use element selective spectroscopy as a regular tool in sample characterization. In the field of light sensitization and light activated catalysts these tools are increasingly used to study model complexes and learn the principles behind the observed dynamics. Understanding these principles in turn has led to the development of extraordinary new complexes capable of harvesting and using solar energy. During the recent years the experimental conditions have been improved and now allow the study of samples that are active as catalysts and/or drive light harvesting in dye sensitized solar cells. We will show two examples in which we used x-ray spectroscopy to understand the light induced dynamics in complex molecular systems. The first system an iron carbene sensitizers which now allow the construction of dye sensitized solar cells based on earth abundant materials. [1, 4, 6] We will discuss how we studied the electronic and vibrational dynamics in these complexes with x-ray emission spectroscopy and why the hot electron dynamics we discovered of is of such an import in the design of future light sensitizing complexes of all kinds. The second story is focused on the dynamics at the catalytic reaction center of a well-functioning light activated hydrogen evolving Ru-Pt catalyst. We studied the dynamics of the electron transfer between light sensitizing moiety and the reaction center. We found beside the expected electron transfer clear evidence for a chemical reactions triggered by light that consumed two electrons after the activation with a single absorbed photon and thus a potential pathway to avoid the usual requirement of multi photon processes for hydrogenase in molecular systems.[3]

Lastely we will discuss why we see sources with 100ps temporal resolution as such important tools for the development of novel light harvesting complexes, how we plan to use the novel capabilities at the ESRF and what we see as some of the most important parameter that will lead to its success.[2, 5]

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Towards Improving Light-activated Functional Molecules

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Photo-induced transformations of molecular systems have high potential for realizing high-density molecular devices applicable in data storage, switches, and light-harvesting, to name a few. In order to design efficient light-activated functional molecules, understanding the fine details of the elementary physical steps in related transformations is essential. Combining the traditional toolset of pump-probe experiments, the novel ultrafast hard X-ray probes, and quantum chemical calculations, one can obtain the necessary information to understand the light-induced ultrafast dynamics, and reveal the mechanistic details of the relaxation processes.[1] The experimental data available from XFELs on molecular systems correlates well with theoretical modelling, which encourages us to exploit theoretical methods to design modifications of the functionality *via* introducing changes to the potential energy landscape by substitution or by solvent effects. With this goal in mind, we have studied suitably modified variants of the $[\text{Fe}(\text{terpy})_2]^{2+}$ complex.

A selected approach involved varying the stability of the excited quintet state by way of modifying the ligands of the homoleptic complexes through chemical substitution. DFT calculations suggested that the energy barrier between the quintet and singlet states can be altered significantly upon substitution, inducing the quintet lifetime to vary by an order of magnitude. The corresponding ligands and complexes were synthesized accordingly, the substituent effect on the lifetime was determined experimentally, and good agreement was found with the trend expected from the DFT-calculated energy barriers. X-ray scattering further supports the energetics obtained from DFT. The agreement between theory and experiment demonstrates that once we have obtained a reliable description of the relevant potential energy surfaces of a given molecular system, we can use quantum chemical computations to rationally tailor these properties by introducing suitable modifications. This should pave the way to advancing ligand engineering of functional molecules to a wide range of applications. The potentials for the ESRF ID09 beamline to take part in this adventure will also be discussed.

References

[1] G. Vankó *et al.*, J. Phys. Chem. C **119**, 5888 (2015); M. Pápai *et al.*, J. Phys. Chem. Lett. **7**, 2009 (2016).

Studies of structural dynamics in solids using time resolved X-ray diffraction

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Studies of the structural dynamics of solids can improve our understanding of atomic motion in materials, and may thus help in the manufacture of new devices or the development of materials with novel structures and properties. Ultrashort laser pulses can deliver high energies, and trigger lattice motion in solids such as vibrations and disordering, which can be monitored using time-resolved X-ray diffraction. In my talk, I will present the results from our experiment campaigns at beamline ID09 at ESRF and the recent results from the experiments that were carried out at the FemtoMAX beamline at the MAX IV Laboratory.

MONDAY 28 AND TUESDAY 29 OCTOBER 2019

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