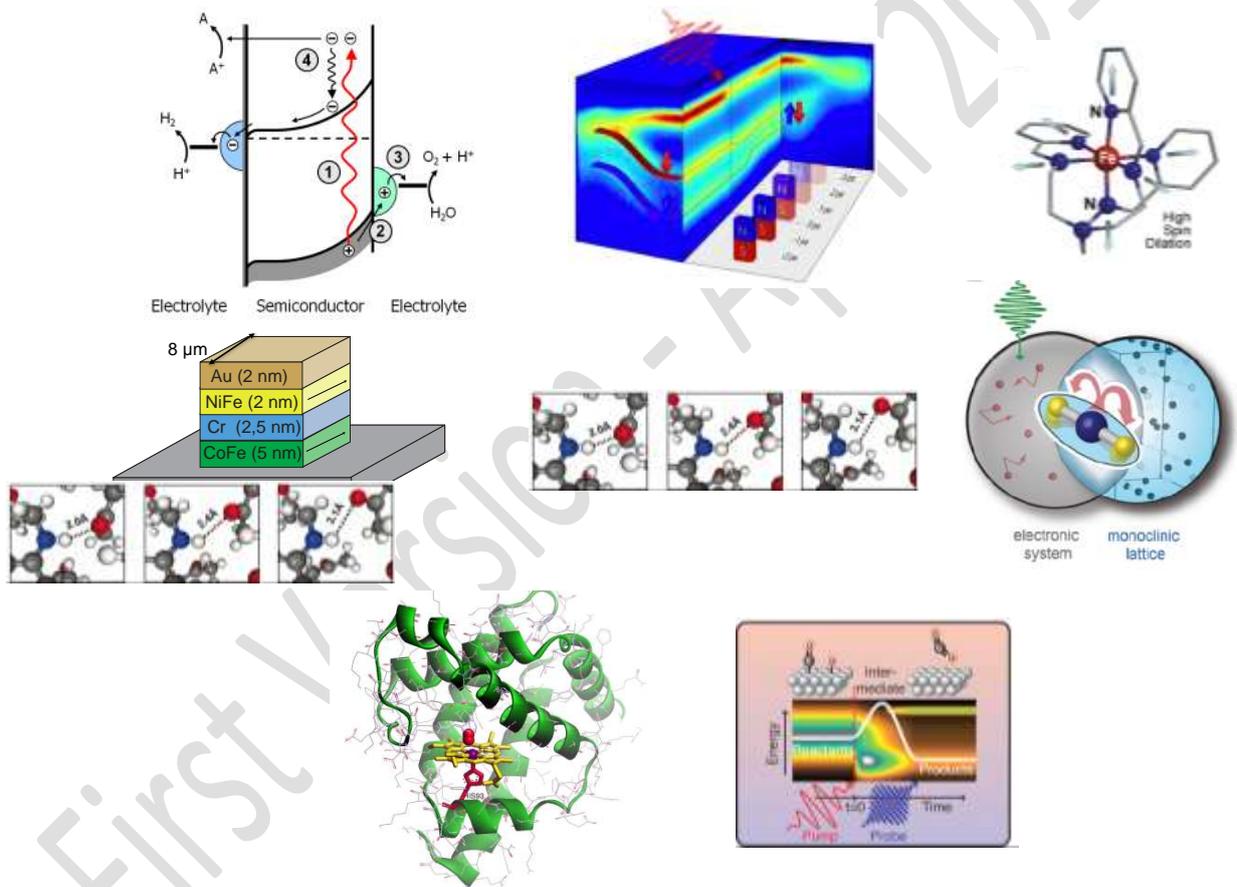


BESSY VSR

The variable pulse-length storage ring

Scientific Case



First Version - April 2013

Helmholtz-Zentrum Berlin für Materialien und Energie GmbH

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1. BESSY-VSR – Unique science opportunities

BESSY-VSR, the „Variable Pulse Length Storage Ring” proposed by HZB, is aimed at the grand challenges of basic science of how to harvest, convert and store energy, how to transmit and archive information efficiently and how to govern rate and selectivity for clean chemistry. The key to these challenges is to move from observing and understanding to *controlling* function. BESSY-VSR will be the science-driven step from the observation and quantum mechanical description towards the control of materials and chemical function. This new light source will push the excellent properties of synchrotron radiation storage rings into the so far underexplored dimension of time and transient states and give users the free choice of observable time and length scales. User will thus be uniquely enabled to correlate chemical function with molecular dynamics on multidimensional potential energy surfaces and to attribute the active principles underlying functional materials to elementary structures and processes of condensed matter. This unprecedented ability to create and detect transient states and the associated dynamic pathways of excitations in matter with BESSY-VSR will form the basis for controlling materials’ function.

In the past, science with third generation synchrotron radiation has brought for materials science and physics as well as chemistry and biology a deep understanding and description of their electronic and structural properties on a fully quantum mechanical basis. Here photon science with soft X-rays has brought tremendous insight through its element specific, chemical and spin selective probes. As a consequence, materials characterization has been developing towards increasing complexity regarding dimensionality, concentration and extreme or ambient environments.

With the new synchrotron-light source BESSY-VSR users will be able to freely switch between the high precision determination of electronic and structural parameters in the ground state in order to prepare and detect low-energy excited states in a controlled way. BESSY-VSR will deliver ultra-stable radiation from the THz to the soft X-ray region with highest spatial and energy resolution in combination with short pulses for dynamic studies. Due to high average brilliance, it will allow for high-throughput measurements as users are accustomed to from storage rings.

BESSY-VSR will open up *Unique science opportunities* for quantum materials for energy and materials for future information technologies, in basic energy science and green chemistry and for unveiling structure and function in biological systems. It will provide a unique photon source as a MHz precision probe that allows switching between highest spectral, spatial resolution and temporal resolution.

Quantum materials for energy and materials for *Future information technologies* are the most intriguing and most promising materials for novel functionality where the coupling between different internal degrees of freedom and the coupling to the environment lead to complex energy landscapes. These intra- and intersystem interactions determine the material’s dynamic response to external fields and thermodynamic heat baths. Ultimately, all functionality is coupled to the dynamic response of the system and therefore determined by the respective energy landscape. Often, complex energy landscapes give rise to complex spatial patterns. Domain formation and phase separation on the nanoscale occur if several local minima in the energy landscape are accessible for the system. Material function can then be determined by segregation and percolation phenomena and spatially resolving probes in real and reciprocal space are required. An understanding of the shape and the dynamic pathways in these multidimensional energy landscapes allows controlling and

ultimately tailoring materials' functionality. This goes well beyond characterizing static properties of the constituents and thus provides a means to address the fundamental science underlying functional materials.

The relevant parameter space extends over many orders of magnitude in space and in time. These quantum materials have in common that their dynamic response cannot be described by a single degree of freedom alone. Energetically, the coupling between different degrees of freedom and to the environment leads to highly non-trivial low-energy excitation spectra, which require the combined use of various spectroscopic as well as structural probes over a wide energy range in order to provide complementary selective access to all relevant degrees of freedom. Time-resolved X-ray probes at BESSY-VSR will allow following directly the pathways through the multidimensional landscapes in real time, thus complementing techniques that identify the ground state and excitations based on an instantaneous response.

The deep correspondence and complementarity of such fundamental phenomena determine molecular properties and the functionality of materials. *Basic energy science* at BESSY-VSR will address these fundamental questions. The transfer, stabilization and localization of charges, e.g., at functional centers in solution, at surfaces and interfaces and in solids are at the heart of technologically and elementary processes in nature. Understanding and the ability to control such elementary reaction steps therefore builds the basis for the development of alternative sustainable technologies. Electron excitation, transfer and solvation not only govern photochemical molecular reactions but also determine bio-molecular function. Understanding and the ability to control the elementary reaction steps with BESSY-VSR therefore holds the key to revealing the structure-function relationship in bio-molecules. Charge-transfer processes steer the primary steps in photovoltaic devices, in vision and they drive conformational changes in single molecules and of the optical or magnetic properties and conductance in functional materials. The effects of symmetry and bonds work similarly in molecular systems and solids. Screening, the effect of the ligand field on the orbital state, the coupling between orbital occupation and magnetic properties and geometric frustration can be found in simple molecules as well as in complex materials. Quite generally, a strong relation between electronic and structural degrees of freedom, between energetics and structure plays a crucial role in their dynamics. As a key to determining materials' dynamical functionality, BESSY-VSR will thus allow addressing spatial complexity, the response time of the system and the relevance of long range interactions and low energy excitations with multidimensional X-ray probes.

Since low energy excitations on spin, orbital and electron degrees of freedom occur in the THz and far IR these controlled states of materials live on picosecond and sub-picosecond timescales. In addition, the typical timescale of phonon excitation of a picosecond per nanometer brings the dynamics of nanoscale objects and large amplitude motions in chemistry and bio-molecules well into the pico- and nanosecond domain. Also, spin-stabilized as well as chemically relevant metastable states can easily be detected with this temporal resolution. BESSY-VSR targets exactly at these time scales and, with the high MHz repetition rate of BESSY-VSR, intrinsic limitations like radiation damage or space charge to electron spectroscopy can be overcome. In addition to the picosecond and sub-picosecond timescale of correlated excitations and large amplitude motions, there is a scientific need to determine electron dynamics between a few hundred femtoseconds down to the attosecond domain. BESSY-VSR will be designed to produce picosecond pulses in its standard mode, with pulse lengths in the sub-picosecond range, possibly as low as 100 femtoseconds in special operating modes. Certainly, BESSY-VSR will also improve the existing time slicing by one order of magnitude

due to the higher bunch compression which will create femtosecond pulses with 10^8 ph/s perfectly synchronized to driving pulses ranging from the THz to the UV region. Sub-femtosecond and femtosecond processes will be best studied at low repetition rate with complementary laboratory-based High Harmonic Laser Sources and large-scale X-ray Free Electron Lasers, once they reach their design parameters regarding pulse length and synchronization to external stimuli.

BESSY-VSR will merge experimental cutting-edge x-ray tools and cover a broad energy spectrum while addressing time scales from quasi-static to sub-picoseconds and length scales from Ångström to micrometers. With these tools, materials' functionality and dynamics will be addressed in the full parameter space and, for the first time, ultimate spatial, momentum, spin *and* energy information can be combined with the relevant time resolution at a MHz repetition rate.

2. BESSY-VSR – Science drivers

2.1. Quantum materials for energy

2.1.1. Superconductivity

Superconducting transition temperatures as high as 130 K in copper oxide materials open the way to lossless transport of electrical energy and to applications in fast and energy-saving information technology. Even after 25 years of research in this field, the understanding of high-temperature superconductivity remains a great challenge. This is due to the fact that the properties of these materials arise from complexity. Insight into the mechanism underlying high temperature superconductivity promises to develop design principles to enhance the critical temperature in superconductors. Understanding the interaction leading to superconductivity is still controversial for high- T_c materials. What is widely accepted is that either spin fluctuations, phonons, or a combined excitation of both are responsible for the microscopic interaction leading to formation of a superconducting ground state. Analysis of these excitations has therefore a high priority in these materials. The strong interaction of the electrons with charge, spin, and orbital degrees of freedom lead to a number of competing ground states and the superconducting state is one of them while others are energetically very close (Figure 1). Ultrafast excitation of the superconductors provides a completely new approach to understand the various competing states around the superconducting state by driving the system out of equilibrium into neighboring states for a short period of time. In this way, even new states that cannot be observed in equilibrium may be created.

Ultrashort synchrotron radiation pulses as delivered by BESSY-VSR will provide a unique probe to study these phenomena. While in the ground state, angle-resolved photoemission spectroscopy and neutron scattering are among the momentum and excitation specific tools, time-domain methods such as time-resolved resonant soft x-ray diffraction have been established as promising complementary methods to analyze such excitations and their dynamics.

In a recent experiment, e.g., it was shown that transient superconductivity can be stimulated by selective optical excitation in a material, where a competing ground state, the so-called charge-ordered state, wins over the superconducting state [1]. The understanding of charge order in the cuprates, on the other hand, has recently been pushed forward by resonant soft x-ray diffraction,

which is a method that exploits the tunability of synchrotron radiation and provides particular sensitivity to this subtle type of ordering [2].

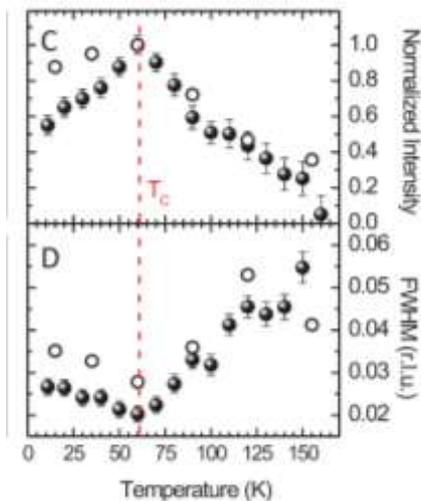


Figure 1. Charge order competing with superconductivity: Cooling below the superconducting ordering temperature T_c results in a decay of charge order, as demonstrated by the decrease of the corresponding diffraction peak intensity. (Courtesy E. Weschke, HZB).

Angle-resolved photoelectron spectroscopy (ARPES) plays a particular role for the investigation of superconductivity as it addresses the superconducting quasiparticles in a straightforward way including control of the quasiparticle momentum. In laboratory-based experiments, the dynamics of pair breaking and the time evolution of the superconducting gap was studied [3]. Another example is the recent time- and angle-resolved photoemission work by the group of U. Bovensiepen (Universität Duisburg-Essen) on the parent compound EuFe_2As_2 Fe-pnictide superconductor, which vividly demonstrates the influence of a bosonic excitation on the spectral function near the Fermi level (Figure 2).

However, only in a limited momentum range due to the rather small photon energy in laboratory-based experiments could be reached. BESSY-VSR will readily allow extending this type of studies to cover the full Fermi surface of the materials. Together with the time structure envisaged with BESSY-VSR the method will open a new field of time-resolved studies of subtle ordering phenomena not only in superconductors, but in complex materials in general. For this particular case, the destruction of charge order in favor of superconductivity can be studied in detail.

Femtosecond time-resolved soft x-ray scattering and spectroscopy, which is currently carried out at the femtoslicing facility FEMTOSPEX at BESSY II, provides element specificity and momentum sensitivity. This method is very valuable to analyze the coupling between a particular boson excitation $\Omega(k)$ and the material's ground state. Limitations of the current experimental facility are two-fold and exemplify the novel opportunities offered by BESSY-VSR: (1) Most experiments at the femtoslicing facility FEMTOSPEX at BESSY II were carried out in transmission geometry which strongly limits the materials that can be investigated. (2) The photon flux hinders systematic studies which provide similarly detailed information as, e.g., time-resolved ARPES does already now. The first point has improved recently by implementation of a reflection geometry. In fact the group of U. Bovensiepen has very recently carried out first proof of principle experiments using time-resolved soft-x-ray spectroscopy in reflection geometry on a 122 Fe-pnictide material. The second point is more fundamental and here BESSY-VSR will enable novel insight. With a photon pulse duration of 1 ps the modifications in the photo-excited state could be probed (see Figure 2). This would increase the opportunities for time-resolved soft-x-ray pulses tremendously due to the improved time-

resolution. In addition, the time resolution of 100 fs at the femtoslicing facility with a will allow studying the coherent nature and phase of bosonic excitation in an element specific manner because frequency and phase can be resolved in time (see Figure 2). Thereby, boson-mediated changes in the material become accessible in a mode-specific and time-resolved mode. It is important to note that the increased flux at the femtoslicing facility at BESSY-VSR uniquely enables systematic experiments beyond the current heroic efforts for selected samples. It is the systematics and level of detail that can be expected by ps to femtosecond experiments at BESSY-VSR that could boost studies of the ultrafast dynamics in complex materials, which are in the focus of current efforts in material science.

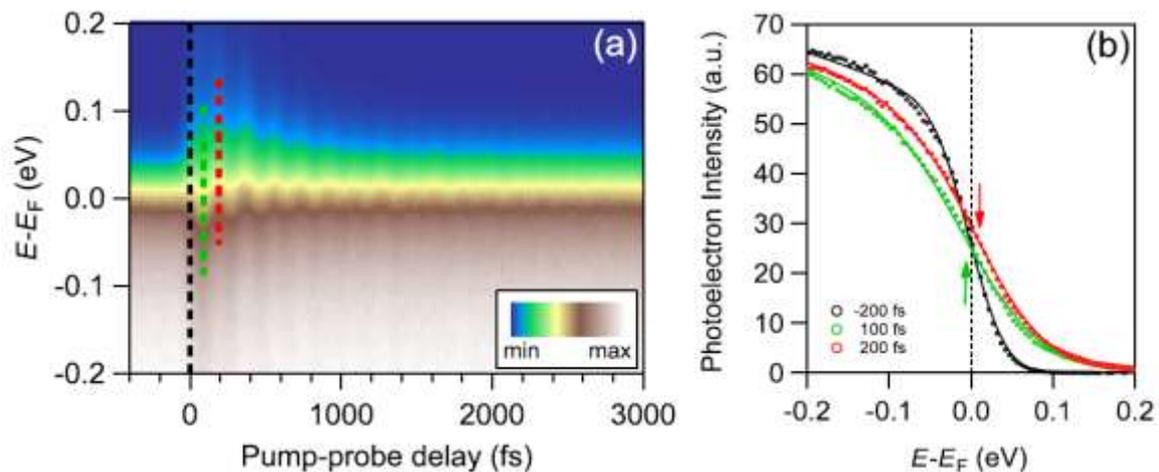


Figure 2. Panel (a) shows the time-dependent photoelectron intensity in femtosecond time-resolved ARPES measured on a parent compound of the 122 Fe-pnictide high- T_c superconductor EuFe_2As_2 . The transient changes in the spectral weight in the vicinity of the Fermi level depicted in panel (b) are strongly modified by coupling to a bosonic excitation. [taken from ref. 4, Avigo et al., *J. Phys.: Condens. Matter* **25**, 094003 (2012)].

The time structure of BESSY-VSR will, in addition, allow for angle-resolved time-of-flight electron spectrometers to be employed. The flexible fill pattern combined with a mechanical chopper or an electronic gating scheme for the spectrometer gives access to a 1.25 MHz source with variable pulse length down to the fs regime, ideally matched to the performance of spectrometers such as the ArTOF. With the advent of femtosecond table top lasers and X-ray FELs it has now become possible to determine the structural dynamics from time resolved diffraction experiments and obtain in separate experiments dynamic information on the electronic or magnetic properties. However, it has remained a conceptual challenge to access simultaneously the dynamics of the valence electrons in combination with the chemical state and the local coordination atom by atom. The extreme high transmission in combination with the angle resolving capabilities of the ArTOF will now open a new route to extract simultaneously the structural dynamics in an element selective way through time resolved photoelectron diffraction (trPED) and determine the temporal evolution of the chemical state through time resolved ESCA (trESCA) or even the femtosecond charge transfer dynamics through excited state core-hole-clock spectroscopy. All these experiments require femtosecond and picosecond pulse length at moderate photon flux per pulse as provided by BESSY-VSR to avoid space charge in combination with high repetition rates. Ideal candidates for phase transition dynamics are mixed valence and correlated materials that exhibit geometric distortions, charge separation and orbital order on the nanometer scale and are prone to spectacular ultrafast switching of materials properties in metal-insulator transitions as well as magnetic switching. In this context, layered transition metal dichalcogenides are known to exhibit structural distortions accompanied by charge

separation manifested through the appearance of characteristic charge-density wave (CDW) phases. A great number of experiments addressed the evolution of the electronic system after optical excitation using high-harmonic generation (HHG) and free-electron laser (FEL) sources in these systems [5-7] or the structural dynamics using femtosecond electron diffraction [8]. However the complete pathways of the photoexcitation could only be resolved by the simultaneous determination of the structural and electronic dynamics in the system via simultaneous trPED and trESCA.

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2.1.2. Photovoltaics

Research for renewable energies at the HZB focusses on the direct conversion of light into electricity, i.e. photovoltaics (PV), and on the direct conversion of abundant resources such as water and CO₂ into hydrogen or hydrocarbons using sunlight, i.e. solar fuels (see section 2.4.2).

Silicon and compound semiconductor based thin-film PV represent the technological base of the Solar Energy Research activities at HZB. A self-consistent scientific approach enables research and development on the full chain from the very fundamentals of the materials ending at scalable prototype devices that demonstrate industrial relevance. The requirement of short-term support of industrial partners is facilitated by the Competence Centre for Thin Film and Nanotechnology for Photovoltaics Berlin (PVcomB). The aim is to provide the scientific and technological base to advance present and develop next generation thin film photovoltaics.

The long-term goal of HZB's PV research is to develop even more cost effective and more efficient devices. Here, new materials and concepts for future photovoltaic devices are explored. Solar cell concepts based on, e.g. nano-particles will provide extended chemical flexibility and include quantum-size and optical coherence effects. The research strategy behind this activity is to generate the scientific knowledge needed to create photovoltaic devices beyond the present cost and efficiency limitations.

The most prominent techniques used at BESSY II for this at the current stage are photoemission spectroscopy, x-ray absorption and emission spectroscopy, photoemission electron microscopy and energy-dispersive x-ray diffraction and fluorescence. While most of the methods make full use of and require a tunable soft x-ray source of high brilliance, BESSY II is also able to provide x-rays at much higher energies as needed for diffraction and fluorescence experiments. A crucial extension of the experimental capabilities using X-rays at BESSY II will be realized by the Energy Materials In-situ Laboratory Berlin, EMIL.

In recent years, thin film solar cell devices have impressed by their very successful development and fast progress. Today's thin film photovoltaic systems are hence on the verge to commercialization. In addition to the continuous need for higher efficiencies, respective solar cell devices have thus to face

new challenges in particular in terms of stability, cost, and scale-up potential. At this point, the next crucial level of performance can only be reached by a knowledge-based optimization, extending current trial-and-error device improvement. Thus, in order to lead the thin film solar cell technology to a breakthrough, a detailed knowledge about potential inherent limitations is necessary in order to identify new routes to overcome these obstacles. Since each layer in the photovoltaic device thin film layer stack has a different chemical (lattice constant, crystal structure, thermal expansion or diffusion coefficient, mechanical adhesion, chemical affinity) and electronic structure (work function, electron mobility, doping level, defect concentration, electronic band position, conductivity), the interfaces between those layers can cause stresses and are often the place of an increased density of defect states which can act as recombination centers when not designed carefully. In addition, interdiffusion processes can take place at those interfaces leading to significant interfacial intermixing, which induce changes in the optoelectronic properties of the whole device. Furthermore, the interfaces not only influence, but in most cases determine the local electric fields necessary for efficient charge carrier separation.

The key to more efficient PV systems is the exact knowledge of the interface properties and the dynamics of charge carrier excitation, generation, transfer, and recombination. BESSY-VSR will be essential in elucidating these. Usually charge carrier lifetimes in today's PV devices are in the ms – ns regime. Thus, recombination mechanisms occurring in these solar cells are already accessible by BESSY II today. However, e.g., the formation of free charge carriers after optical excitation, the processes involved in photon up- and/or down-conversion systems, and/or the charge carrier lifetimes in new PV materials/concepts take places on time scales a few ps. In particular the use of novel concepts (e.g. excitonic) in solar cells depends crucially on understanding generation and recombination. In order to study these key mechanisms in next-generation PV materials and solar cell devices BESSY-VSR with the option to use short X-ray pulses at high repetition rates will be essential. It will be in particular the flexibility of BESSY-VSR with radiation from the Terahertz to the hard x-ray range with flexible time-structure and filling patterns that will enable unprecedented insight into the interface properties and the charge carrier dynamics of PV systems and solar cells.

2.1.3. Topological insulators

Topological Insulators are materials which are bulk insulators but exhibit conducting surface states. These surface states require strong spin-orbit interaction, are highly spin polarized, have their spin locked perpendicular to the electron momentum, enjoy protection of their existence by time-reversal symmetry and have promising implications for electrical transport and spin transport. They exist as two-dimensional topological insulators with protected one-dimensional edge states and three-dimensional topological insulators with protected two-dimensional surface states. In both cases the dispersion near the Fermi energy is that of massless Dirac fermions, and on three-dimensional topological insulators they form a Dirac cone similar to graphene. In graphene, the Dirac cone is characterized by a pseudospin, in topological insulators by the real spin. Topological insulators are characterized mathematically by a topological invariant ν which is an odd integer. Along with the topological invariant ν also other quantities such as the electrical conductivity are robust, and the discrete value $\nu=1$ leads to a discreteness or quantization of the conductivity - the robustness of this quantization renders it extremely accurate. This has been demonstrated for two-dimensional topological insulators from HgTe quantum wells in 2007. The first three-dimensional topological

insulators studied are $\text{Bi}_{1-x}\text{Sb}_x$, Bi_2Te_3 , and Bi_2Se_3 (Figure 3), of which the latter two have emerged as standard systems, due to their simple electronic structure with one surface state and their two-dimensional geometry which allows for simple cleavage.

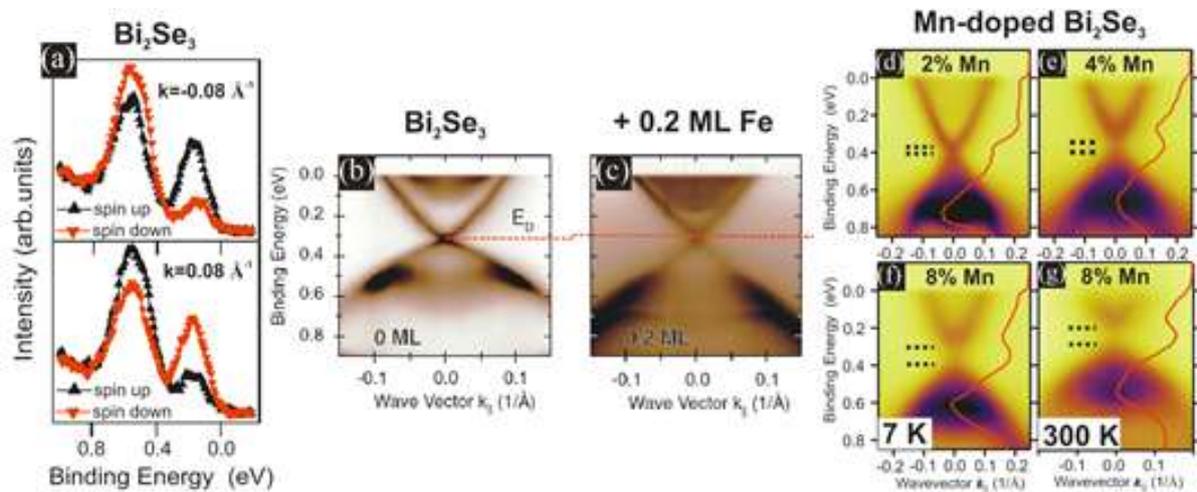


Figure 3. (a) Spin-resolved photoemission from Bi_2Se_3 showing $\sim 50\%$ spin polarization in the surface state at ~ 0.2 eV binding energy while the bulk admixture reduces the polarization at 0.6 eV. (b, c) The Dirac point of Bi_2Se_3 remains intact after deposition of 0.2 monolayer Fe at low temperature (8 K) where the surface doping becomes p-type and modifies the dispersion. (d-g) Mn doping in the bulk opens a large (~ 100 meV) gap in the Dirac cone but it does not change with temperature indicating that it may not be due to ferromagnetic order. (Courtesy O. Rader, HZB).

It has been shown by ARPES that the states are robust against surface impurities in line with the topological protection, that their spin polarization is high, and that they can be modified by surface doping. It has been shown at BESSY II that they are tolerant towards deposited magnetic moments. An external magnetic field or exchange field is expected to open a gap but attempts to demonstrate this with three-dimensional topological insulators have failed so far. With the inclusion of ferromagnetically ordered magnetic moments, new topological phases are predicted such as the quantized anomalous Hall insulator and a three-dimensional Weyl-fermion system.

Other important questions surround the scattering properties because scattering is reduced due to the high spin-polarization and time-reversal symmetry. Deviations from the circular shape of the Dirac cone can lift these constraints. Related to this is the electron-phonon coupling the strength of which is controversial. Topological insulators have promising optical properties in the infrared range and circularly polarized light is considered to allow for photo-induced spin currents.

The time structure of BESSY-VSR will allow for angle-resolved time-of-flight electron spectrometers such as the ArTOF to be employed. Using time resolved measurements, the evolution of the electronic structure can be probed by ARUPS/ARPES measurements, chemical changes can be monitored through time-resolved chemical shift measurements and structural changes can be studied by following the evolution of the Photoelectron Diffraction patterns.

2.1.4. Nanoscale materials

At the nanoscale, materials exhibit novel physical, chemical, electrical, magnetic, and optical properties that can be exploited for a wide variety of applications ranging from catalysis to magnetic

data storage. An understanding of static and dynamic properties of such low-dimensional structures is only accessible to spectro-microscopic tools capable of appropriate lateral and temporal resolution. Synchrotron based imaging techniques, such as coherent x-ray scattering (CXRS) or photoemission electron microscopy (PEEM), offer a unique toolbox for nanoscale science. The combination of multi-specific contrast with temporal and lateral resolution at the relevant time and length scales enables these microprobes to follow chemical reactions in a catalyst or image the magnetic switching in a nanoparticle. Complemented by structural analysis, such as transmission electron microscopy (TEM), they provide unmatched insight into the structure-function relationship at the nanometer level.

It has been demonstrated that the electronic structure and magnetic response of the same single ferromagnetic nanoparticle can be correlated with the morphology and crystal structure using x-ray photoemission microscopy in combination with electron microscopy (Figure 4). Magnetic states and interactions can be analyzed for different particle arrangements. The element-specific electronic structure can be probed and correlated with the changes of magnetic properties. This approach opens new possibilities for a deeper understanding of the collective response of magnetic nanohybrids in multifunctional materials and in nanomagnetic colloidal suspensions used in biomedical and engineering technologies.

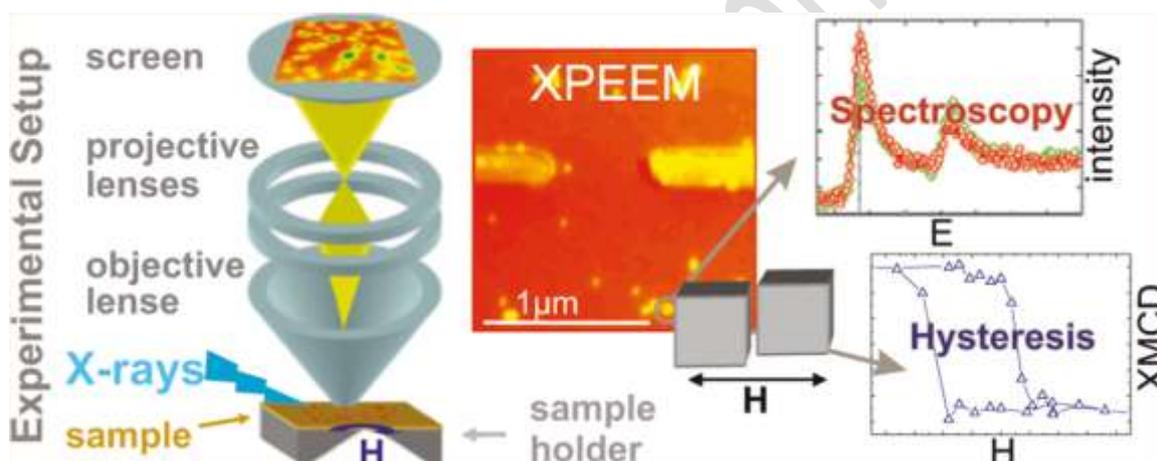


Figure 4. Magnetic imaging and spectromicroscopy of individual Fenanocubes in an applied magnetic field of up to 33 mT. (Courtesy F. Kronast, HZB).

Another important application is on materials that are inhomogeneous on the nanoscale due to spontaneously developing order phenomena or coexistence of different phases. Both kind of effects have clear influence on macroscopic properties and affect hence functionality. Techniques that have both temporal and spatial resolution can unravel on a nanoscale how functionality can best be achieved. In addition to the aforementioned imaging technique, x-ray photon correlation spectroscopy will be an essential tool.

BESSY-VSR offers X-ray pulses at variable pulse length in combination with variable filling patterns with, e.g., alternating patterns of ultra-short and long pulses. The availability of ultra-short X-ray pulses with a pulse duration below one picosecond will provide experimental access to new phenomena such as direct spin-excitations in individual nanoparticles or magnetic fluctuations in particle ensembles.

The variability of BESSY-VSR could also be used to solve a problem of electron-detection-based imaging such as PEEM at current X-ray sources. Above a certain X-ray intensity their resolution is limited by space charging effects. Recent studies at BESSY II and Elettra (Trieste, Italy) demonstrate that even with the present X-ray pulse duration and intensity, the lateral resolution in PEEM can be limited by space charging. With BESSY-VSR we could overcome this space charging with particularly long X-ray pulses. If technically feasible, this would pave the way towards nm resolution X-PEEM, as predicted by electron optical simulations.

Shorter X-ray pulses, in turn, as provided by BESSY-VSR would enable new insights with ultrafast hard X-ray diffraction experiments:

Nonlinear phononics: The dynamics of phonons in an anharmonic crystal potential

The decomposition of atomic motion in phonon modes is a fundamental concept in solid state physics. Phonons describe elementary processes and excitations, such as heat transport, sound propagation, pyro- and pizo-electric processes, phase transitions and others. For structural phase transitions with unit cell doubling the zone boundary phonons are relevant, which have a decay constant in the 1 picosecond range. Coherent phonons can be generated and probed by ultrashort light pulses. The accessible phonon wavevector \mathbf{q} in the probe process is however very limited for optical wavelengths. It is therefore advantageous to reduce the probe wavelength by using radiation in the hard X-ray regime.

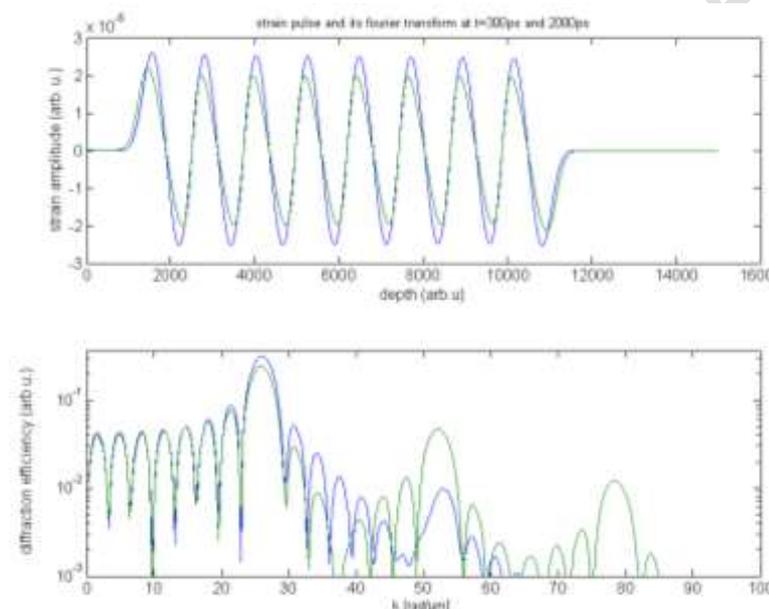


Figure 5. (upper panel) Nonlinear phononics: the initial acoustic strain pattern (blue) is distorted (green) after propagation in an anharmonic crystal. (lower panel) The excitation of new phonon modes can be observed in reciprocal space by ultrafast X-ray diffraction. (Courtesy P. Gaal, R. Shayduk, M. Bargheer, Universität Potsdam).

In particular, for the study of anharmonic effects, e.g. the decay of coherent sound waves due to phonon-phonon interactions, the sensitivity to a large set of phonon wavevectors and a sufficient temporal resolution is required. The decay time constant for acoustic phonons with a frequency of 140 GHz is approximately 100 picoseconds [1]. In general, the phonon decay follows a $1/\omega^2$ -rule, i.e. high-frequency phonons and localized lattice distortions decay on a sub - 100 picosecond timescale [2]. Such high-frequency modes can be probed by Ultrafast X-Ray Diffraction (UXRD) techniques, due to the larger k-vector of X-rays compared to optical light (Figure 5) [3]. However, UXRD experiments on the decay of phonons are rare, since they rely on ultrastable and brilliant X-ray probe pulses that

can be delivered uniquely by accelerator-based sources, which typically deliver a temporal resolution of only 100 picoseconds [4].

The generation of large strain amplitudes leads to nonlinear propagation effects and to the excitation of new phonon modes due to anharmonic phonon interaction [5]. A better understanding of nonlinear phononics could pave the way to new devices, e.g. modulators and switches [6,7].

For such studies, an increase in temporal resolution as provided by BESSY-VSR for accelerator-based UXR experiments is essential.

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2.2. Future information technologies

2.2.1. Magnetism dynamics

Controlling magnetic states of matter is crucial for understanding the underlying fundamental physical phenomena and for engineering the next-generation magnetic devices combining ultrafast data processing with ultrahigh-density data storage. The elementary building blocks governing magnetism are the magnetic moment, the spin-orbit coupling and the exchange interaction - the short-range force that couples the constituent spins. Thus, in order to generate, manipulate and eventually control such magnetic states of matter one needs to understand the dynamical behavior of these key parameters on their characteristic time and length-scales i.e. from femtoseconds to nanoseconds and from local spin moments to extended nanostructures on the nanometer length scale.

Being equally a science- and technologically-driven research area, the field of ultrafast magnetization dynamics has witnessed an intense activity, both experimentally and theoretically, leading to a rapid development over the past decade. Despite of this progress there are several fundamental, yet unanswered questions that form the 'terra incognita' of ultrafast magnetism, as for instance:

- What is the ultimate speed at which magnetic order can be manipulated and eventually controlled?
- What are the microscopic processes responsible for magnetization dynamics on elementary length- and time-scales?
- What are the channels of ultrafast angular momentum transfer to and from the spin system?

Next to purely fundamental interest, the answers to these questions are essential for the development of future technologies for ultrafast and energy-saving recording and processing of magnetically stored information (Figure 6).

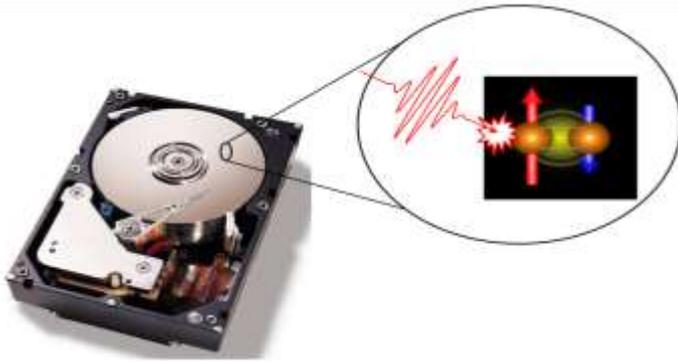


Figure 6. BESSY-VSR will provide novel and fundamental knowledge about the microscopic processes responsible for magnetization dynamics, which will allow for developing and designing novel materials and approaches that could boost the magnetic recording write/read rates of the magnetic bits to unprecedented speeds. (Courtesy I. Radu, HZB).

The outline below summarizes the scientific case for magnetism dynamics going from femtosecond phenomena at the atomic scale to nanosecond phenomena in extended structures at the nanometer length scale.

Ultrafast magnetism on elementary time and length scales

The use of femtosecond soft X-ray pulses with variable polarization, available at the femtosecond slicing facility FEMTOSPEX of BESSY II Berlin has provided unprecedented insights into the physics of ultrafast magnetism as demonstrated, for instance, by the latest investigations of various material systems [1-5]. Although groundbreaking, these measurements suffered due to the relatively low photon flux achieved in the slicing mode (10^6 photons/s) while momentum-resolved investigations were limited to specific samples showing high diffraction efficiency. Moreover, experiments imaging the nanoscale with fs time resolution, a crucial ingredient in understanding ultrafast magnetism, were impossible.

The envisioned capabilities of BESSY-VSR are indispensable in addressing all these fundamental questions, which will ultimately provide us with the required fundamental knowledge about the genuine magnetization and spin dynamics. In particular, using its high photon flux and short X-ray pulses we will obtain quantitative information on ultrafast dynamics of the spin and orbital magnetic moments as well as on the transient dynamics of the spin-orbit coupling and of the exchange interaction – the key ingredients governing the magnetic order. Moreover, BESSY-VSR will allow us to monitor the elementary length scales pertinent to magnetization dynamics in highly non-equilibrium states, i.e. comparable with the exchange length of 10 nm and below, using X-ray scattering techniques. In addition, imaging of the magnetic domains/macroscale dynamics at the nanoscale on picosecond to femtosecond timescales and with element specificity will become feasible with BESSY-VSR.

In addition to the fs-X-ray studies, the ultrashort electron bunches and their flexible time structure will provide us with a powerful spectroscopic tool covering the far-IR and THz spectral range. Such a tool will enable us to identify and disentangle the various quasiparticles (e.g. phonons, magnons) which are driving and/or involved the ultrafast magnetization dynamics on ultrashort timescales as described in the following.

Ultrafast magnetization dynamics upon resonant excitation of phonon and magnon modes

In a pilot experiment at the free-electron laser FLASH (Hamburg) a collaboration including I. Radu, M. Gensch, F. Radu, R. Abrudan, T. Kampfrath, and A. Kimel studied the ultrafast magnetization dynamics of magnetic garnets upon resonant excitation of the relevant phonon and magnon modes using intrinsically synchronized THz and X-ray pulses. The Terahertz radiation served as pump beam and the X-ray radiation was used to probe the system [6].

This is a new type of experiment with the aim to understand the role of spin and lattice excitations during the THz-induced magnetization dynamics; in particular during demagnetization and magnetization reversal processes. So far the experiment was only partially successful because of insufficient intensity of the THz source. Similar experiments would be enabled at BESSY-VSR, as the intensity of THz radiation at BESSY-VSR will be very high and the THz and X-ray pulses will be intrinsically synchronized.

The combination of resonant THz excitation and resonant x-ray magnetic scattering at BESSY-VSR can be expected to open up a new field exploring phase transitions on ultrashort time scales in transient and metastable states. These non-equilibrium states may unleash new and exciting properties, as has recently been demonstrated in the case of ferrimagnetic GeFe alloys, which show a transient ferromagnetic state in an otherwise antiferromagnetically coupled system [4].

BESSY-VSR will thus provide unique tools, both in the frequency and time domain, which will allow observing, understanding and ultimately controlling the fundamental interactions driving magnetic order at the nanoscale with femtosecond time resolution. These could be uniquely complemented with BESSY-VSR by investigations focusing on the ps time scale.

New frontiers in spin-dependent band mapping – Magnetization dynamics in lanthanides and their compounds

The magnetization dynamics of Gadolinium and Terbium have recently been analyzed by the group of M. Weinelt (FU Berlin) by time- and angle-resolved photoemission with VUV radiation from a HHG-source [7] (Figure 7) as well as using X-ray magnetic circular dichroism (XMCD) at the BESSY femtoslicing facility FEMTOSPEX [8]. The results indicate that the magnetic anisotropy plays an important role in ultrafast demagnetization.

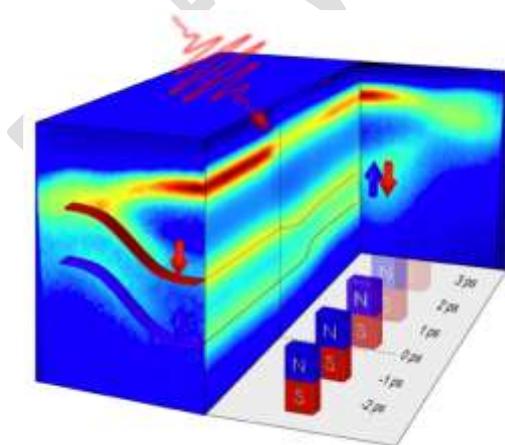


Figure 7. Time- and angle-resolved photoemission result with VUV radiation from a HHG-source on the magnetization dynamics of Gadolinium and Terbium [7]. An asymmetric collapse of the exchange splitting of the valence bands is observed; the upshift of the majority band (blue) is delayed by one picosecond (ps) with respect to the instantaneous response of the minority spin band (red). This indicates that Gd valence and 4f spin-systems are out of equilibrium within the first few picoseconds after laser excitation. (Courtesy M. Weinelt, FU Berlin).

Using the spin-filter momentum microscope that is currently being built for installation at the Russian-German beamline at BESSY II will offer the opportunity to simultaneously analyze the transient, spin-polarized band structure and Fermi surface in 4 dimensions, i.e. for parallel momenta

k_x and k_y , at a given binding energy and delay time. Thereby, it will be possible to discriminate between spin transport and spin-flip phenomena and unravel the controversial details of laser-driven magnetization dynamics. At BESSY-VSR, the repetition rate of short 1.5 ps pulses in the low MHz regime fits perfectly well to the acceptance of the delay-line detector used in the time-of-flight spectrometer. Together with the highly efficient spin detector, the described experiment will make accessible new frontiers in spin-dependent band mapping. The reduced pulse length down to 1.5 ps will allow for time-resolved measurements with dramatically increased flux and availability compared to the current situation at BESSY II.

The analysis of the valence band-structure of ferromagnets will be fostered with time-resolved measurements of linear and circular dichroism in 4f (resonant) photoemission [9] and X-ray scattering at the lanthanide M-edges. Both techniques are element specific and thus generally applicable to compounds and multilayer systems, i.e., material systems of technological relevance. All of the above experiments will greatly profit from the increased flux and ps time-resolution of the proposed BESSY-VSR mode.

Precessional Magnetization Dynamics in Complex Magnetic Layer Structures and Spintronic Materials

Complex magnetic layer stacks are the building blocks of spintronics devices, such as magnetic tunneling junctions, spin transistors, and they play an important role in the magnetic data storage or processing such as in complex circuits and logical gates. The dynamic response of these layer stacks to external stimuli, such as magnetic field pulses, spin polarized currents or light pulses differs considerably from the single layer response. It is determined by a complicated interplay of interactions and magnetic coupling mechanisms in the stack. Such structures in fact take advantage of the combination of the different magnetic properties of the different coupled layers either by direct or indirect exchange coupling, or of magnetoresistive effects. The influence of a certain coupling mechanism such as the interlayer exchange coupling, e.g., may depend strongly on the time scale of the magnetic excitation. The transient change in magnetic properties following the optical excitation of the electronic system can lead to a change in the magnetization state, either by magnetization precession or by all-optical magnetization reversal. An understanding of the dynamic response of the stack therefore requires an understanding of the behavior of the individual magnetic and nonmagnetic entities in the layered structure.

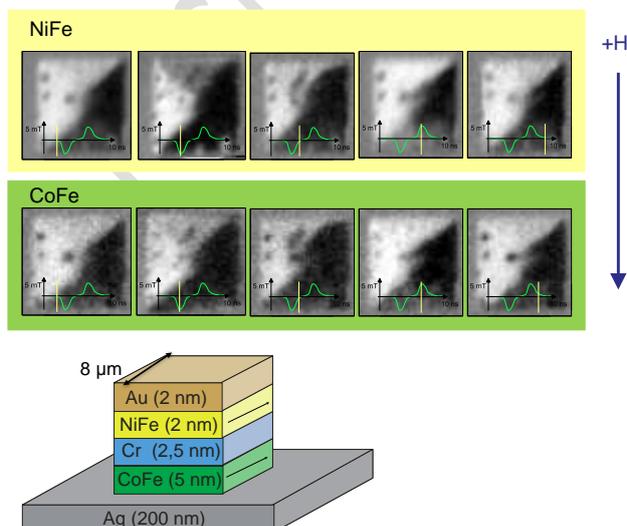


Figure 8. Time-resolved photoemission microscopy (TR-PEEM) used to disentangle the individual magnetic responses of the different layers, NiFe and CoFe, in a stack. (Courtesy C. M. Schneider, Forschungszentrum Jülich).

Typically the fastest magnetization reversal is obtained by precessional motion in the 100 ps regime, but even faster modes may become within reach with ultrafast laser pulse excitation. The transient response of the system can be studied by pump-probe experiments on an element-resolved basis by employing the XMCD effect. Such experiments can either laterally integrate over a wide area of the sample, or microscopically image the sample as in PEEM. The latter has the advantage that also local effects, caused by variations in the local effective field by, for example, domain walls, may be studied.

Time-resolved photoemission microscopy (TR-PEEM) has proven to be a very powerful technique to disentangle the individual magnetic responses of the different layers in a stack. The use of aberration-corrected electron optics enhances the transmission and increases the sensitivity of this approach. The group of C. M. Schneider (Forschungszentrum Jülich) recently implemented a temporal gating and a laser-based excitation in their aberration-corrected PEEM to enable time-resolved studies of magnetization dynamics (Figure 8). In earlier studies they already demonstrated a best time-resolution of 10 ps in the low-alpha mode, which allowed them to directly map precessional modes in simple Permalloy elements.

BESSY-VSR will offer much better conditions for time-resolved magnetodynamic imaging down to the picosecond limit and may even provide a bridge to the sub-ps regime to access the time span shortly after the excitation with TR-PEEM. This would allow identifying the mechanisms starting the reversal mechanisms on an element-resolved, and thus layer-resolved basis. Compared to the femtosecond slicing facility FEMTOSPEX at BESSY II, BESSY-VSR would allow for higher flux at short time scales, thus enabling imaging experiments with, e.g., TR-PEEM.

Another example of precessional dynamics by the group of H. Zabel (Universität Bochum) addresses the free precessional dynamics and damping of spins in spintronic materials (Figure 9).

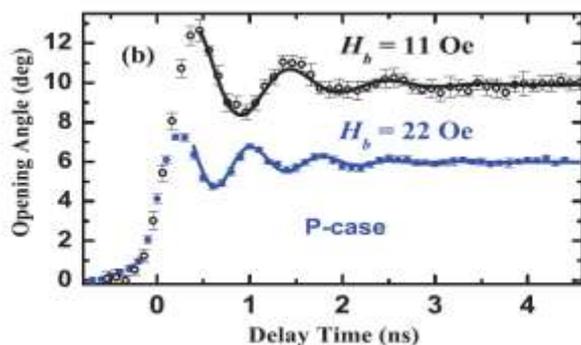


Figure 9. Time resolved precessional dynamics of Fe in a Py/Cu/Fe spin valve determined by pump-probe methods at the Fe L_3 - edge. Taken from ref. 14, R. Salikhov et al., *Phys. Rev. B* **86**, 144422 (2012).

From these experiments, which were performed at BESSY II, the g-factor and the Gilbert damping was determined in an element-selective way and as a function of external magnetic field, opening angle, temperature, doping concentration, etc. [10-14]. The bunch length at BESSY II determined the time resolution. With present pulse length of about 50 ps in single bunch mode at BESSY II it was possible to resolve the precessional frequency but the investigations are limited to magnetic materials with low exchange coupling and therefore low precessional frequencies of below 1-2 GHz. Because of this, Fe and Ni spins in Py can very well be probed, but not, for instance, Fe spins in Fe, which has much higher exchange energy. A pulse length of 15 ps or even down to 300 fs as provided by BESSY-VSR would greatly enhance the frequency range that we can probe. This in turn, would allow investigating the free precession and the damping in a much wider range of materials,

including those with high relevance for magnetic storage devices, such as FePt_x and CoPt_x alloys and the spin precession of magnetic quantum dots. The higher repetition rate and higher current would, in addition, greatly expedite the described experiments.

Time-Resolved Investigations of Resistive Switching Dynamics

Nonvolatile memory concepts involving resistive switching phenomena promise the ultimate scaling behavior. The microscopic mechanisms behind resistive switching and particularly the dynamics are far from being fully understood. Depending on the material system, the resistive switching involves either crystalline phase changes, the formation of metallic filaments, or local valence changes (Figure 10). Disentangling the physical processes, which govern the voltage time-dilemma and determining the limits of the switching speed are pivotal for a future use of RRAM's in microelectronics. For this purpose, time-resolved studies in the nano- and picosecond regime are needed.

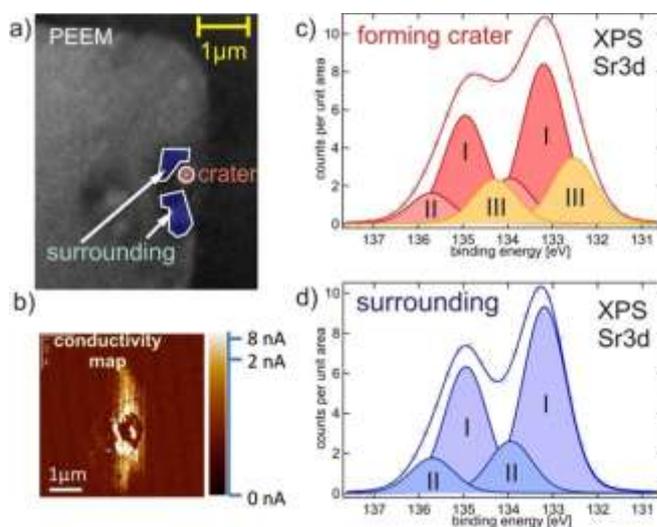


Figure 10. Soft x-ray PEEM investigations of chemical changes in Fe:SrTiO₃ – a prototypical resistive switching material – after removal of the top electrode used for electroforming. In the switched region (“forming crater”) the photoemission spectra of the Sr 3d states exhibit a significant change, as compared to the surrounding area. This spectral signature can be used for time-resolved experiments. (Courtesy C. M. Schneider, Forschungszentrum Jülich).

The experimental challenge in time-resolved studies of the resistive switching dynamics is to obtain precise chemical information from a buried layer underneath a metallic electrode with high lateral resolution. This requires a combination of hard x-ray photoemission with photoemission microscopy, i.e. hard x-ray photoemission (HAXPEEM). Since preliminary investigations suggest the dynamics to take place on the subnanosecond time scale, a time-resolution in the low picosecond regime will be needed to address the time-dependent changes in the electronic/chemical structure. Based on state-of-the-art time-resolved PEEM and HAXPEEM results at BESSY II a dedicated pump-probe experiment at BESSY-VSR would allow for mapping the chemical changes underneath the top electrode taking place during the application of short current/voltage pulses. The changes will be determined by means of hard x-ray photoemission from characteristic core levels in the resistive switching material.

The dynamics of information storage – Going to extended nanostructures

One example for the future use of variable-duration pulses from BESSY-VSR for studying the dynamics of magnetic data storage and manipulation is the investigation of magnetic bubble states. Such a circular magnetic domain in perpendicular anisotropy material is shown in Figure 11.

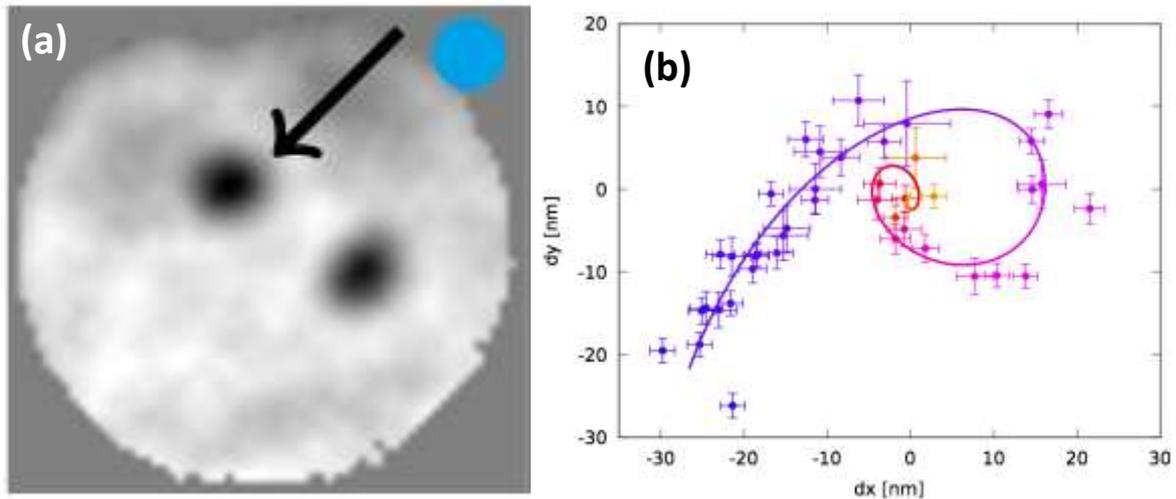


Figure 11. (a) Two-bubble state in a circular thin film medium of 550 nm diameter with perpendicular magnetic anisotropy, imaged via Fourier Transform holography with XMCD contrast at BESSY II in single bunch mode. The trajectory of the bubble indicated by an arrow is traced. (b) Trajectory of the bubble displacement (data points) after excitation via the magnetic field of a microcoil together with a theoretical model (line). The entire trajectory has a duration of 15 ns (color coded purple to yellow). (Courtesy S. Eisebitt, Technische Universität Berlin).

The image was obtained via x-ray holography, using the high brightness of BESSY II to record a hologram of the sample with magnetic contrast. Such magnetic bubbles have topologic properties that make them of interest for both basic science research and future information storage units. To study the dynamic properties of this system, it was crucial to initially bring the system into a well-defined two bubble state, close to nucleation of an additional domain. In this study, this was achieved via the (iterative) adjustment of the external magnetic field and analysis of the resulting state via holography. As such adjustments in a (in general multi-dimensional) parameter space are time consuming, the ability to quickly characterize the resultant state is crucial. Here, multibunch acceptance of all pulses of BESSY-VSR would enable this steering of the system to the desired initial state. Once prepared, BESSY-VSR will allow switching to the specific temporal resolution required to study the dynamic phenomenon in question. In the example here, the magnetic bubble was excited via an external field pulse administered via a microcoil, and the resulting dynamics of the bubble was traced holographically. The results shown here were achieved very tediously in single bunch mode and allow e.g. the determination of the topological mass of the soliton-like bubble [AG Eisebitt et al, in preparation]. BESSY-VSR will enable much more efficient preparation of the desired excited state of a system to be studied, even in more complex phase diagrams (B,T, sample composition), and thus enable new studies of intrinsic and controlled dynamic behavior, e.g. in nanomagnetic systems for information storage and processing.

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2.2.2. Phase transitions

One hope for faster and more energy efficient information technology is in the use of the unique properties of functional materials beyond classical semiconductors. In particular correlated materials exhibit a wealth of phases with drastically different macroscopic properties. Since these phases exist in close proximity, a phase transition can be induced by comparably small external stimuli [1]. Examples are metal-insulator transitions that occur upon temperature change or when the material is exposed to a magnetic field. Such effects can be truly dramatic with changes in the conductivity of 6 orders of magnitude [2]. Moreover, some of these transitions are among the fastest switching processes ever observed in solids [3], which qualifies them even more for future information processing applications.

Besides driving the whole material through a phase transition novel concept for functionality haven been developed, that apply perfectly for such materials with complex phase diagrams [1]. In many correlated materials different phases can coexist under identical conditions. By driving, say, the metallic phase through the percolation transition, the whole material can be rendered macroscopically metallic with a much smaller energy investment than a full phase transition would require. Additionally such states with phase coexistence are typically metastable such that their respective state remains conserved until it is actively changed.

Many of these materials turn out to be multiferroic which mean that ordering effects in one degree of freedom is coupled to another order in a second degree of freedom. The best studied class of multiferroics is those where magnetic order and electric polarization are coupled, promising, e.g., to write magnetic information electronically instead of using bulky coils. This field has been dramatically growing recently because more and more concepts how to obtain multiferroicity are developed [4] including bringing materials with different ferroic properties in close proximity in order to couple them.

This latter approach is just one aspect of a much wider approach to create novel functional materials by creating heterostructures of correlated materials [5]. At interfaces completely new properties can be created (like a two-dimensional electron gas at the interface between two insulators); strain and charge transfer can affect the properties of one of the layers; and – as for the case of the heterogeneous multiferroics - a coupling of the properties of the different layers can be achieved.

On the way from interesting functionality to application the switching behavior is a central point. What is the most efficient way to control properties? How fast can properties be changed, how stable are the states? Time resolved x-ray techniques have made enormous progress in the last decade mainly focusing on magnetic materials. Recently, scientists have extended such studies towards phase transitions in correlated materials [3, 6-9].

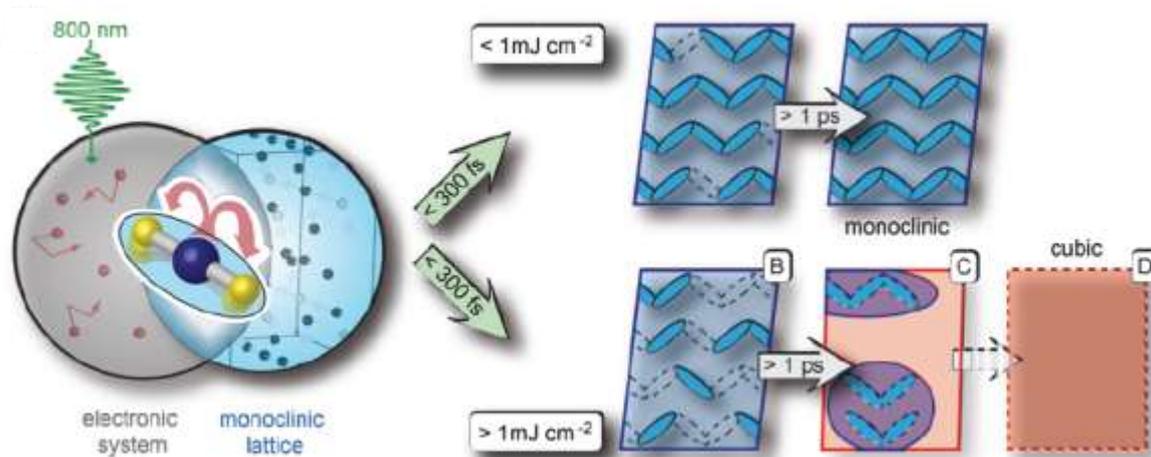


Figure 12. Processes during the Verwey transition of magnetite when induced by an optical laser pulse [11]. (Courtesy C. Schüssler-Langeheine, HZB).

So far such experiments are limited by the few available sources of short x-ray pulses. Despite this, detailed studies of phase-transition behavior could be carried out showing the effects of optical excitations as well as THz pulses that directly couple to phonon modes. A large role play experiments with soft x-ray pulses that combine high spectroscopic sensitivity with magnetic information.

Besides switching material from one phase to another in the most controlled and/or efficient way, another option in time-resolved experiments is to reach phases that do not occur in equilibrium. The observation of critical fluctuations for at least two different phases have been reported, e.g., for magnetite, only one of which develops in equilibrium [10]. One may hope that far from equilibrium the other phase could be reached and studied. For the same material a laser-induced metastable phase separation was recently observed, which again is a state of matter that does not exist in equilibrium (Figure 12) [11].

While some of these processes are very fast, some occur on timescales of a few picoseconds and some are considerably slower. Even experiments that cannot resolve the ultimate switching time scales can still be used to characterize the excited state. As a matter of fact, free electron lasers are not always the ideal source for such kind of experiments since the high peak brightness may affect the sample too much for a controlled experiment. BESSY-VSR with its high repetition rate at moderate peak brightness may be much better suited in many cases. Furthermore only a storage ring allows for recording resonance spectra by variation of the incoming photon energy over a wide range. Understanding of such correlated materials has been mainly advanced with x-ray spectroscopic methods like x-ray absorption spectroscopy. First attempts to transfer these methods to time-resolved experiments have proven successful. BESSY-VSR would certainly be the ideal source for such kind of research.

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2.2.3. Molecular electronics

Transition metal ions (TMIs) form the core units of vital catalytic process in proteins as well as in synthetic compounds. TMIs frequently exhibit high spin (HS) paramagnetic electronic ground states, as crucial catalytic intermediates. Their properties constitute not only fascinating objects of basic (bio) inorganic chemistry but render TMI complexes prime candidates for blue prints of future energy production devices. The interest in this important class of compounds even increased when the potential of HS TMI based single molecule magnets as potential nano scale data processing units was discovered. Both catalytic as well as magnetic properties result from a subtle interplay between the ion's oxidation and spin states, their coordination geometry, interactions with surrounding ligands as well as spin-spin couplings. Although outstanding progress has been made in the synthesis of TMI complexes and their quantum chemical description, further spectroscopic knowledge is mandatory to unravel their structure-dynamic-function relationships. The vision of these efforts is the production of tailor-made systems featuring systematically tuneable properties.

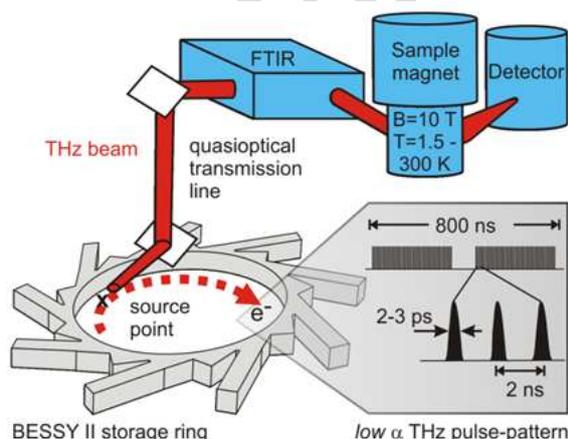


Figure 13. Quasi-optical FD-FT THz-EPR set-up consisting of radiation extraction optics in the storage ring, the quasi-optical THz transmission line, the FTIR spectrometer, the superconducting magnet with variable temperature insert (Oxford Spectromag 4000, $B_0 = \pm 11$ T, $T = 1.5 - 300$ K), and the detector. The THz pulse pattern in low α is depicted in the gray box. The depicted excitation scheme provides sufficient power for continuous wave THz-EPR excitation, but does not allow for spin flips with a single pulse, a requirement for advanced EPR excitation. (Courtesy A. Schnegg, K. Holldack, HZB).

The ideal technique for studying paramagnetic systems is electron paramagnetic resonance (EPR) spectroscopy. However, standard EPR techniques frequently fail to detect HS TMI's in cases where EPR transition energies exceed the quantum energy of the EPR spectrometer (typically < 4 cm⁻¹). Very recently we demonstrated that Frequency Domain Fourier Transform (FD-FT) THz-EPR (Figure 13)

based on coherent synchrotron radiation (CSR) [1] provides a unique tool to lift these restrictions. Our novel approach allows for EPR excitations over a broad energy (7 cm^{-1} to 35 cm^{-1}) and magnetic field (-11 T to 11 T) range in a single spectrometer and with a single source. FD-FT THz-EPR was set-up in the frame of the BMBF funded network project EPR-Solar and is now further developed with funds from the DFG priority program 1601. It is part of the Berlin Joint EPR Lab, a common research infrastructure of Freie Universität Berlin and HZB. FD-FT THz-EPR has been successfully applied to high spin TMIs in single molecule magnets [2-5] catalytic mononuclear integer HS TMIs [5] and proteins [6]. A further drastic increase in the capabilities of CSR based THz-EPR could be achieved by the employment of ultra-short THz pulses of high repetition rate from BESSY-VSR. Following the path of state-of-the-art FT-NMR spectroscopy the availability of ultra-broad band THz-EPR experiments with sub ns time resolution would pave the way for completely new EPR experiments and access paramagnetic states relevant for (photo) catalysis and data processing. Such experiments are currently out of reach due to the fixed pulse duration (see Figure 13) and the limited THz pulse power. High power CSR THz pulses with variable duration would allow for coherent electron spin manipulation and control, laser/x-ray-pump EPR-probe experiments on function determining short lived (photo) catalytic states as well as in operando studies on HS TMIs in systems relevant for energy conversion and storage.

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2.2.4. Spintronics

The aims of spintronics are the manipulation of electronic spin for the storage, transmission, and processing of information. Spintronics is promising to revolutionize data storage and processing in a development which commences with smaller devices that consume less power than present charge-based ones and may culminate in the implementation of quantum computing. Spintronics demonstrated first success already in metallic multilayers, most notably the oscillatory long-range magnetic coupling and its applications, i.e., the giant magnetoresistive reading head and the magnetic random access memory. The central unit of these devices is a quantum cavity for electrons and spin. The boundary layers are ferromagnets which impose their spin dependence on the electronic states inside the cavity.

Second-generation spintronic devices shall directly use spin-polarized currents. To generate these spin currents, spin injection from ferromagnets into semiconductors is being studied intensively, but the direct interfaces between these materials suffer from severe conductance mismatch problems. It is principally possible to create a spin current without ferromagnetic materials or external magnetic fields altogether if the polarization is created by virtue of the spin-orbit interaction instead of the Pauli principle. The spin-orbit interaction induced by an electric field E at a two-dimensional interface, i.e., the Rashba effect, has been studied intensively in semiconductor heterostructures and at metal surfaces. The main concept for a spin-field-effect transistor, however, still requires ferromagnets as polarizer and analyzer, and only the active element requires the Rashba spin-orbit

interaction to perform spin rotation. The stronger the Rashba effect, the shorter is the distance required for spin rotation which is important for miniaturization.

The Rashba spin-orbit interaction has in recent years increased strongly. Giant values of the Rashba parameter a_R on the order of 10^{10} eV Å have been reported for a Bi-Ag surface alloy ($3 \cdot 10^{10}$ eVÅ), for an Ir(111) surface state ($1.3 \cdot 10^{10}$ eVÅ), and for the three-dimensional system BiTeI ($3.8 \cdot 10^{10}$ eVÅ). On graphene intercalated with Au, also a giant spin-orbit splitting is observed 4 orders of magnitude larger than the intrinsic values of graphene (Figure 14).

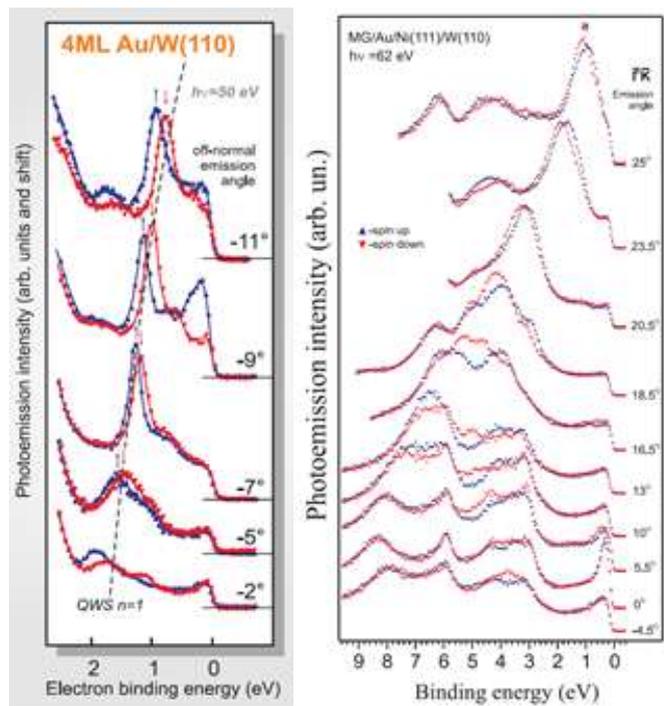


Figure 14. Left: Spin-resolved photoemission from a 4-monolayer film of Au on W(110). With increasing emission angle, the Rashba splitting of a Au quantum-well state increases. Right: Graphene on Ni(111) intercalated with a monolayer Au shows a giant Rashba splitting of ~ 100 meV on the π state near the Fermi energy. Following its dispersion through the hybridization with Au d-states, the origin of the spin polarization can be traced to the d-states. (Courtesy O. Rader, HZB).

The next challenge is to transfer these to a semiconducting or insulating platform. This has been achieved for Pb and Bi on Si. Also topological insulators, which ideally are insulating in their volume, form extra Rashba-split states at their surface.

Similarly as in section 2.1.3, the time structure of BESSY-VSR will allow for angle-resolved time-of-flight electron spectrometers to be employed (ArTOF type). The gain in efficiency will allow for a more widespread usage of spin detectors.

2.3. Basic energy science

2.3.1. Photochemistry

Understanding and controlling photochemical reactions is the key to mastering some of the most important processes to be addressed in energy and environmental science such as artificial photosynthesis and water splitting, and CO₂ recycling. Understanding how the correlated motion of electrons and nuclei is linked to the reaction kinetics and controlling their coupled dynamics clearly motivates the need for information on photoexcited electronic and structural changes in molecular systems and in particular on their temporal evolution. The key is to capture intermediate molecular states that may occur during photochemical reactions and to reveal their sequence through transient

configurations all the way from educt to product states. This is the basis for understanding photochemical reactions as it allows for elucidating the elementary reaction steps of molecular dissociation, charge transfer and isomerisation. Furthermore, it is the basis for learning how to control photochemical reactions, i.e., to learning how to drive reactions along desired pathways and how to drive them to desired products.

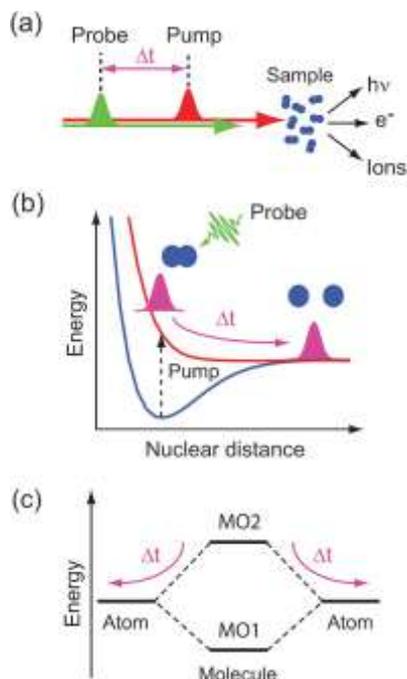


Figure 15. Schematic representation of (a) a pump–probe experiment, (b) the nuclear dynamics of a molecule in a dissociation reaction of a diatomic molecule and (c) a molecular orbital level scheme illustrating the transient electronic structure in a dissociation reaction of a diatomic molecule. (b) The nuclear dynamics of the photo-excited and dissociating molecules are represented with nuclear wavepackets (magenta) in a potential energy diagram. The pump pulse induces a transition from the ground state of the molecule (blue) to a dissociative state (red) and the evolution of the nuclear wavepacket is probed with the probe pulses (green) at time delays Δt after initiation of the dissociation. (c) The electronic structure of the diatomic molecule is represented in an orbital energy level diagram with two arbitrary molecular orbitals MO1 and MO2 in the molecule at bonding distance of the nuclei and atomic orbitals for infinite nuclear distances. Taken from ref. 1, Wernet, PCCP **13**, 16941 (2011).

Understanding photochemical processes requires following the structural dynamics and the valence charge density ground and excited transient states (Figure 15). Especially the latter can be uniquely probed via time-resolved X-ray spectroscopy because it provides a complete picture of chemical bonding from the perspective of selected atomic sites. This applies in particular to third-row transition-metal complexes which play a key role in most areas of chemistry and are vital for essentially all forms of life. The chemistry of the transition-metal complexes is largely determined by the metal-3d valence charge density. Dipole-allowed core-level excitations of the metal-2p electrons provide an excellent probe thereof, revealing symmetry, delocalization, and spin-state of ground and transient states (Figure 16).

These transitions lie in the soft X-ray range covered by BESSY-VSR, where lighter elements that are essential in photochemical processes as well, carbon, nitrogen, and oxygen, can be uniquely probed via 1s core-level excitations. These elements typically act as the coordinating nearest-neighbor atoms of the metal center and probing their core-level transitions delivers the complementary ligand view. Furthermore, probes of non-metallic chemistry can be accessed, allowing for the study of elementary photochemistry in organic molecules.

X-ray spectroscopy at BESSY-VSR will uniquely allow for investigating the evolution of the valence charge distribution and bonding during ultrafast photochemical dynamics. The increased flux at the femtoslicing facility FEMTOSPEX at BESSY-VSR will allow for femtosecond X-ray absorption spectroscopy for mapping the transient changes in the valence-charge distribution during ultrafast molecular transformation of dilute solvated species.

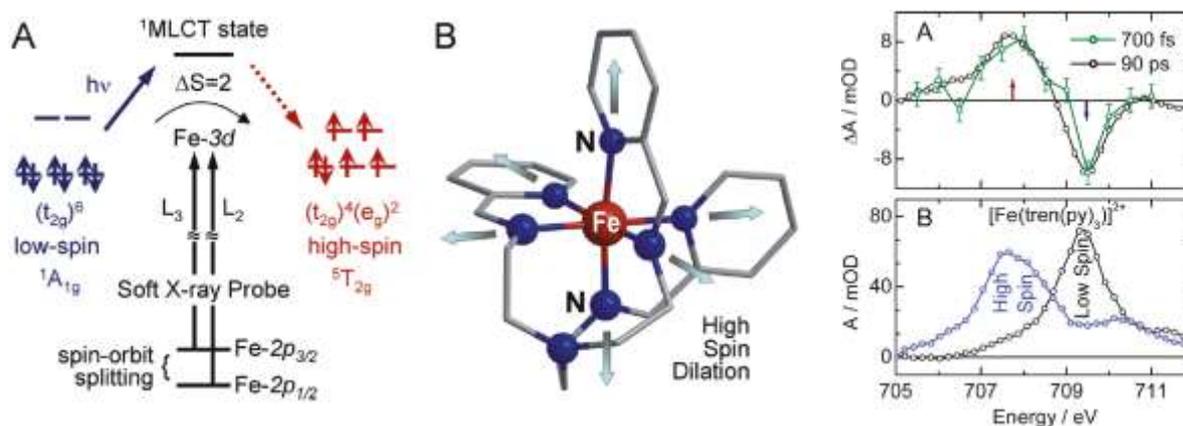


Figure 16. Left: (A) Qualitative orbital diagram for an octahedral Fe(II) complex, illustrating how the photoinitiated spin crossover is probed via metal $2p \rightarrow 3d$ dipole transitions. (B) Schematic drawing of the molecular structure of $[\text{Fe}(\text{tren}(\text{py})_3)]^{2+}$. Photoinduced metal-to-ligand charge transfer results in ultrafast structural changes that have been previously characterized by picosecond time-resolved EXAFS measurements. Right: (A) Time-resolved differential X-ray absorption spectra of $[\text{Fe}(\text{tren}(\text{py})_3)]^{2+}$ in CH_3CN solution at the Fe L_3 -edge. (B) L_3 -edge spectra of $[\text{Fe}(\text{tren}(\text{py})_3)]^{2+}$ in CH_3CN in the low-spin ground state (black) and the transient high-spin excited state (blue) at $\Delta t = 90$ ps. Taken from ref. 2, Huse et al., *J. Phys. Chem. Lett.* **2**, 880 (2011).

X-ray spectroscopy with the few-ps pulses at BESSY-VSR will in addition allow for addressing the subsequent and more subtle changes of chemical bonding resulting from solvation, complexation and subtle but essential changes of molecular symmetry in photochemical reaction intermediates. With this, BESSY-VSR will uniquely complement studies on the femtosecond time scale from free-electron lasers on the one hand and investigations on the ns time scale at current synchrotrons.

Charge-transfer reactions in metalloenzymes

Metalloenzymes are present in all areas of cellular metabolism and display remarkable properties through coupling of transition metal complexes to the amino acids of a protein's peptide chain. Metalloenzymes are thus capable of catalyzing (multi)electron chemical reactions while circumventing highly reactive radical intermediates or oxidizing unwanted radical side products of other metabolic cell activity, thereby reducing the influence of toxic species. The inverse process has also been observed, making use of cell toxicity of certain substances for immune defense or infiltration of host cells. Prominent examples of metalloproteins and -enzymes are myoglobin (Figure 17) the oxygen-binding protein of muscle tissue in vertebrates and the photosystems of plants in the reaction center of which a manganese complex splits water subsequent to absorption of sunlight, leading to the well-known photosynthesis (section 2.4.1). Generally, metalloenzymes use many oxidation states of transition metal complexes (mainly vanadium to zinc) for their catalytic function. The metal reaction centers gain specific activity by lowered potential barriers and undergo redox cycles during substance turnover.

The role of metal centers during chemical reactions or phase transitions can be uniquely studied via X-ray spectroscopy due to their characteristic absorption in the X-ray regime. The corresponding core-level transitions are not only element-specific but deliver information of oxidation and spin states as well as changes in metal-ligand interactions which determine the chemistry of the valence charge density.

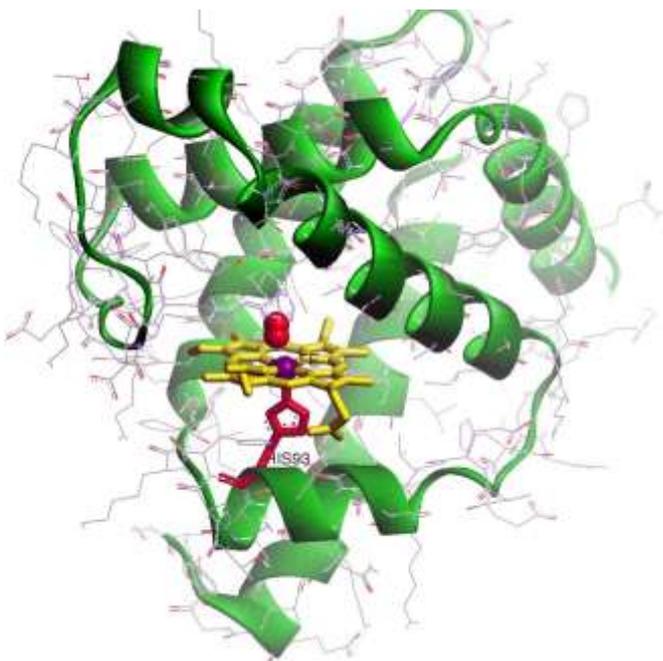


Figure 17. Structural model of Myoglobin emphasizing the heme cofactor. Atoms shown in purple (red) correspond to Fe (O) (adapted from <http://www.fizyka.umk.pl/~wiesiek/>).

The combination of results from time-resolved X-ray spectroscopic studies from BESSY-VSR and state-of-the-art simulations will allow gaining unique insight into reaction mechanisms and their intermediates on fs and ps time scales. Access to information on valence charge density is complementary to structural methods such as diffraction and scattering, delivering essential ingredients for a comprehensive understanding of transient states and chemical transformations of matter. Possible reaction triggers have traditionally been photoinduced charge-transfer reactions but additional chemical triggers such as heat and pH jumps as well as use of caged compounds will allow for the study of any other classes of chemical reactions.

Photo-triggered proton-transfer reactions in solution

Proton transfer is a key process in nature and can be considered as important as electron transfer. Essential functionality of biological systems in terms of cellular energy management is accomplished by proton transfer mechanisms which are provided by proton pump proteins. Proton transfer is a key mechanism behind the hydrogen bond, e.g. in DNA, and might lead to disturbance of the genetic code through formation of tautomers of the base pairs (Figure 18). The proton transport mechanism at the intermolecular level, e.g. in aqueous solutions is currently described by a proton hopping mechanism through water bridges [3, 4]. On the intramolecular level, proton transport occurs by means of proton donor and proton acceptor sites within complex molecules. In order to understand how protons transfer, an element-specific look at the molecular groups involved in the proton transfer process is highly desirable.

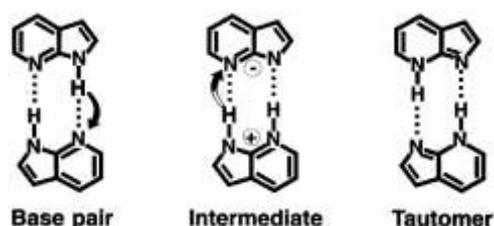


Figure 18. Molecular structures involved in the cooperative double-proton transfer dynamics of the base pair 7-azaindole dimer. Taken from ref. 5, Douhal et al., *Nature* **378**, 260 (1995).

The unique possibility offered at BESSY-VSR with time-resolved X-ray absorption spectroscopy is in the investigation of photoinduced proton transfer. In a femtosecond pump-probe setup the proton transfer will be initiated by an optical pump pulse. The changes in the electronic and nuclear wavefunction of the molecule at the selected atomic center will then be probed by transient X-ray absorption. By this, the ultrafast dynamics of elementary biological processes become accessible on the femto- to picosecond time scale, i.e. in photo-tautomerization [5, 6].

Nonequilibrium processes in hydrogen-bonded systems

Hydrogen bonds (HBs) constitute one of the most important interactions in a large class of (bio)molecular systems. Compared with covalent bonds, hydrogen bonds are relatively weak but their directional nature is important and essential to a manifold of structures, chemical processes and physical properties. For instance, the special properties of water are largely due to the possibility of water molecules to form tetrahedrally arranged hydrogen bonds, forming a rapidly fluctuating network of dissolving and reforming bonds. The resulting solvent properties are essential for all living matter and are also relevant for the global climate. Furthermore, secondary structures of proteins (α -helices and β -sheets) are generated by hydrogen bonds among the building blocks of proteins (amino acids). Tertiary contacts between protein subunits are often formed via hydrogen bonds as well. Furthermore, hydrogen bonds are vital for the incorporation and functionality of protein cofactors – small molecules such as the oxygen-binding heme group in of the relevant proteins in human blood.



Figure 19. Schematics of the hydrogen-bonded adenine-thymine and guanine-cytosine building blocks of DNA. Adapted from Wikipedia.org, author: Iñaki Silanes.

The multitude of hydrogen bonds formed between stacked base pairs (shown schematically in Figure 19) in combination with interactions of π -electron systems allows for very stable structures (e.g. DNA helices) as well as the possibility of breaking double-stranded helical arrangements to allow for genome replication, essential for cell division (replication and translation) and alterations of genetic mutations avoiding tumors (repair). Time-resolved X-ray spectroscopy can track changes in valence charge density of hydrogen-bonded systems (Figures 20, 21) undergoing chemical transformations by exploiting the spectrally well-separated core-level transitions of light elements with atomic resolution intrinsic to such probe transitions.

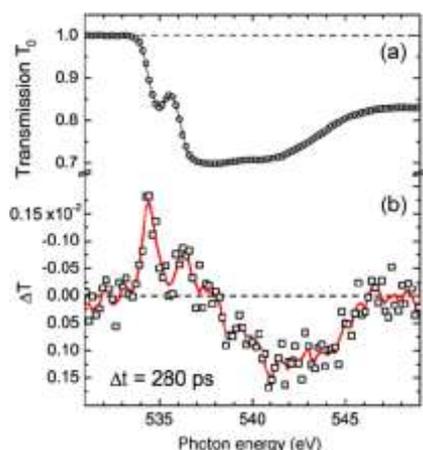


Figure 20. (a) X-ray transmission of liquid water at the O K-edge. (b) Transient changes of the x-ray transmission $\Delta T = (T - T_0)$ with T_0 and T transmission before and after excitation at a pump-probe delay time of 280 ps as a function of photon energy across the O K-edge. Measured raw data are shown as markers (squares), and smoothed data are shown as solid line. Taken from ref. 7, Wernet et al., *Appl Phys A* **92**, 511 (2008).

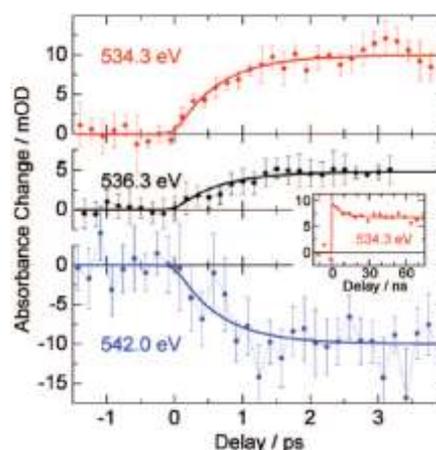


Figure 21. Absorbance change as a function of time delay between the infrared pump pulses and the X-ray probe pulses at three characteristic spectral positions in the O K-edge: 534.3 eV (red), 536.3 eV (black), and 542.0 eV (blue). Solid lines are single exponential fits to the data with a time constant of 0.7 ps. The inset shows a time transient on nanosecond time scales. Taken from ref. 8, Wen et al., *J Chem. Phys.* **131**, 234505 (2009).

BESSY-VSR with the available temporal resolution from fs to ps covers the essential time scales for unprecedented insight into the nonequilibrium processes in hydrogen-bonded systems. Compared to the present situation at BESSY II where hydrogen-bond dynamics were studied water (Figures 20, 21), BESSY-VSR with increased flux for temporal resolutions in the femtosecond to few-ps regime will in particular allow investigating the dynamics of dilute hydrogen-bonded systems such as solvated organic compounds (Figure 22) and nucleic acids with time-resolved X-ray absorption spectroscopy for the first time.

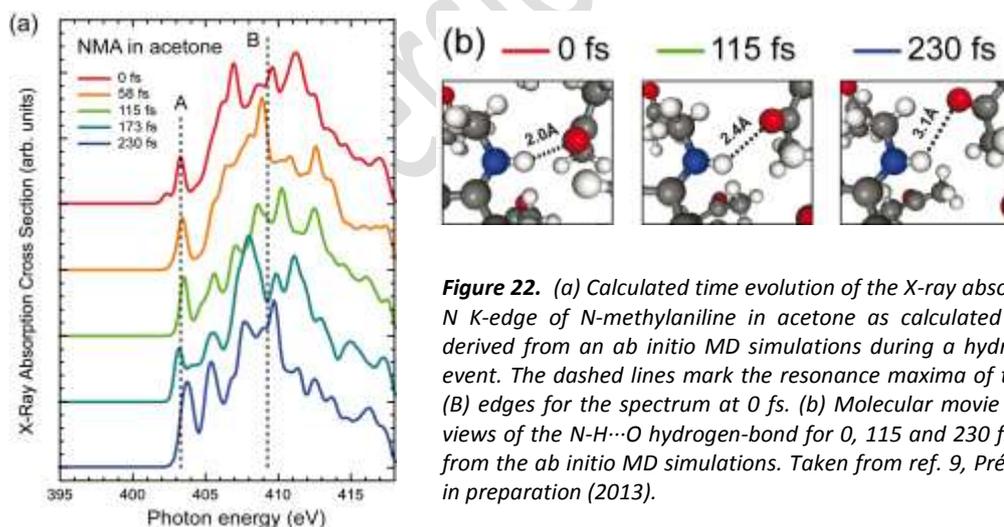


Figure 22. (a) Calculated time evolution of the X-ray absorption spectra at the N K-edge of N-methylaniline in acetone as calculated with configurations derived from an *ab initio* MD simulations during a hydrogen bond breaking event. The dashed lines mark the resonance maxima of the pre (A) and main (B) edges for the spectrum at 0 fs. (b) Molecular movie depicting zoomed-in views of the N-H...O hydrogen-bond for 0, 115 and 230 fs from (a) as derived from the *ab initio* MD simulations. Taken from ref. 9, Prémont-Schwarz et al., *in preparation* (2013).

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2.3.2. Photosynthesis

Oxygen is vital for all aerobic life forms and is abundant in the atmosphere due to continuous regeneration by photosynthetic water oxidation in green plants, algae, and cyanobacteria. This photosynthetic reaction is catalyzed by a Mn_4CaO_5 cluster located inside the photosystem II membrane protein complex. This cluster undergoes four consecutive redox states known as the Si ($i = 1$ to 4) states by the consecutive absorption of four photons by the PS II reaction center (Kok cycle). The accumulated energy is used for water oxidation and the catalyst returns to the S_0 state in the Kok cycle (Figure 23).

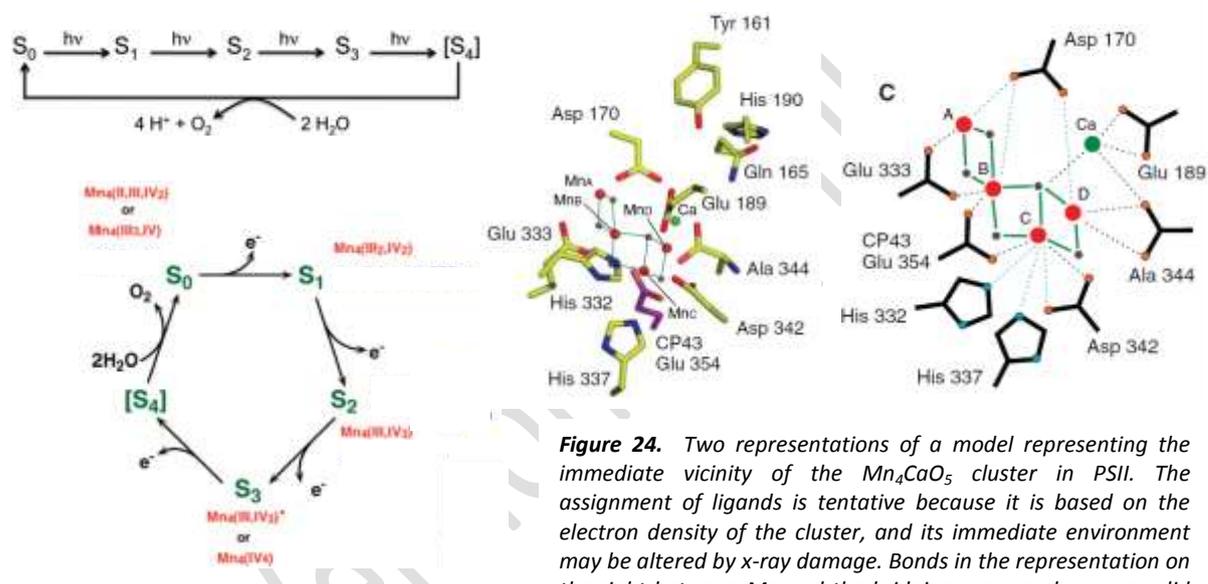


Figure 23. Reaction cycle for water oxidation in PSII with the four states S_0 - S_4 reached by consecutive absorption of four photons [top, taken from J. Kern et al., *Science*, 14 February 2013 DOI: 10.1126/science.1234273 (2013)] and with the corresponding proposed oxidation states of the Mn cluster [bottom, adapted from ref. 1, J. Yano, V. Yachandra, *Inorg. Chem.* **47**, 1711 (2008)].

Figure 24. Two representations of a model representing the immediate vicinity of the Mn_4CaO_5 cluster in PSII. The assignment of ligands is tentative because it is based on the electron density of the cluster, and its immediate environment may be altered by x-ray damage. Bonds in the representation on the right between Mn and the bridging oxo are shown as solid green lines. Bonds to proposed ligand amino acid groups and to Ca atoms are shown as dotted lines (black, less than 3.0 Å; blue, more than 3.0 Å). Taken from ref. 2, J. Yano et al., *Science* **314**, 824 (2006).

Understanding the mechanism of the photosynthetic water oxidation on a molecular level can be considered to be one of science's grand challenges (Figure 24). The structure and catalytic activity of PSII have been studied intensively, but a description of the photochemical processes on a molecular level all the way from photon absorption to water-oxidation is still largely missing. Explaining the reaction kinetics though requires knowledge of the dynamics pathways of the Mn_4CaO_5 cluster.

This is essential to answer several key questions for understanding the mechanism of photosynthetic water oxidation (Figure 24). Is Mn(V) involved during O-O bond formation and, if yes, in which spin state? How does the ligand environment modulate the Mn d orbitals and the electronic structure of the Mn cluster? How does this relate to the change of the redox potential during the catalytic

process? Are water molecules bound to the cluster and do they participate in the oxidation? What is the role of the Ca atom in the cluster? How does it bind to the ligands and to the Mn atoms?

BESSY-VSR with its few-ps pulses at MHz repetition rate could uniquely complement a series of investigations recently started at the Linac Coherent Light Source (LCLS, USA) using diffraction to reveal the geometric structure of the catalytic center and femtosecond spectroscopy to address the electronic structure of the Mn_4CaO_5 cluster. The pulse length at BESSY-VSR of a few picoseconds will be important in two respects: First, it will be essential to overcome X-ray damage to the catalytic center reported from studies at conventional synchrotrons with pulse lengths in the 100 ps domain [3]. At BESSY-VSR we can anticipate to be able to probe the system before the X-ray radiation destroys it. For this, the protein will be studied at ambient conditions and ideally in solution at a millimolar concentration. Second, BESSY-VSR with its high repetition rate compared to LCLS (MHz compared to Hz) and accordingly with its better signal to noise ratio will enable studying more subtle changes of the electronic structure accompanying the catalytic activity on a nanosecond and millisecond time scale.

Time-resolved Mn and Ca L-edge X-ray absorption spectroscopy could be used to map the electronic structure locally around the Mn and Ca atoms in the Mn_4CaO_5 cluster in photosystem II. An optical laser would be used to advance the complex throughout the catalytic cycle. By varying the delay between the visible-pump and X-ray-probe pulses dynamics of the water-oxidation reaction will be revealed on a pico- to millisecond time scale.

References for section 2.3.2.

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2.3.3. Catalysis

One of the main promising routes to solve the energy problem in a sustainable way is to convert sunlight into fuels that have a high energy density and are easy to store and transport. Here, hydrocarbons have proven to be superior and despite decades of efforts to substitute the oil economy, no other approach prevailed. Thus, the question remains how to convert sunlight into energy containing hydrocarbons.

The fundamental idea is to mimic a photosynthetic process, where sunlight is absorbed in a material (solid) and the energy is used to form and break specific bonds at active parts of the material, where it interacts with reactants to form fuels. The fuel formation will thus happen on the surface of the material and the missing part to fulfill this dream is to find the ideal catalyst material, which can trigger the desired reactions on its surface in a heterogeneous catalytic reaction. Well defined solid surfaces offer the possibility to selectively break the chemical bonds of the reagents and to form the new bonds of the products. In order to improve and eventually control the output of such catalytic reactions a deeper understanding of the surface-adsorbate interaction is necessary.

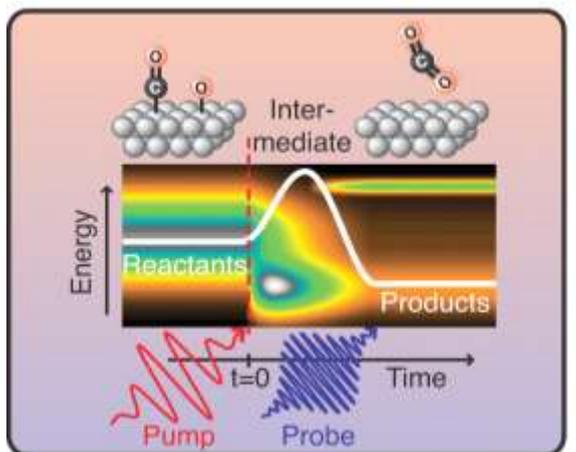


Figure 25. Pump-probe spectroscopy for triggering and following chemical reactions on surfaces in real time. (Courtesy M. Beye, HZB).

But catalysis is not only relevant for solar fuels: 70% of all industrially produced chemicals stem from catalytic reactions. The ideally tailored catalyst is cheap, abundant and catalyzes the desired reaction with high turnover rates, while suppressing undesired reactions (selectivity).

In the past, identifying the best catalyst for a desired reaction was a task for trial-and-error studies, sampling only a small number of possible materials. We are just starting into an age where computerized simulations can model the electronic structure of catalysts with high accuracy and identify the impact on the energy balance in every reaction step in a catalytic reaction cycle. Nevertheless, these simulations are based on a detailed knowledge of each and every single step in the reaction process and get thus inaccurate if the detailed reaction mechanism is unknown.

Here, time-resolved soft X-ray spectroscopy with ps and sub-ps time resolutions (Figure 25) plays a crucial role to identify the exact reaction pathways. The initial and final states of a reaction could often be prepared and soft X-ray spectroscopy was key to derive the local electronic structure of molecules adsorbed on catalytic surfaces as well as their geometry and orientation. Only soft X-rays with their element specificity allow singling out the ultra-low density of adsorbed molecules from the catalyst surface and the inactive surrounding. Nevertheless, in a steady state thermally activated reaction, the concentration of molecules that just take part in a reaction and that are thus in an intermediate configuration is extremely small and undetectable. Ultrafast laser techniques have proven to overcome this issue.

The excitation of a surface that is prepared with adsorbed molecules by an intense ultrashort laser pulse raises the temperature of the substrate on an ultrashort time scale and can thus trigger chemical reactions on the whole surface at once. The excited molecules start the reaction cycle at the same well-defined point in time and will proceed together through the reaction intermediates. Thus the instantaneous concentration of molecules in these hidden states, that are extremely important to deduce the correct reaction mechanism, is high enough to be easily detected with time-resolved soft X-ray spectroscopy.

With the ultrashort soft X-ray pulses from BESSY-VSR, synchronized to the exciting laser system, we expect that breakthrough research in the field of surface science and catalysis can thus be performed. BESSY-VSR will enable studies of the reaction mechanisms in heterogeneous catalysis reactions that have so far been limited to rather indirect probes (i.e. rate modeling with purely chemical methods, analyzing the products of a reaction depending on reaction parameters).

An ideally suited spectroscopic method to follow catalytic reactions in real time is time-resolved Electron Spectroscopy for Chemical Analysis (tr-ESCA). Several state of the art electron analyzers with high acceptance angles and transmission have been successfully tested and commissioned at BESSY II in the past years. These analyzers offer the possibility to perform time-resolved electron spectroscopy at a synchrotron with a MHz repetition rate with a time resolution of a few ten picoseconds during normal operation. The low-alpha operation mode of BESSY II even gives access to the domain of only a few picoseconds.

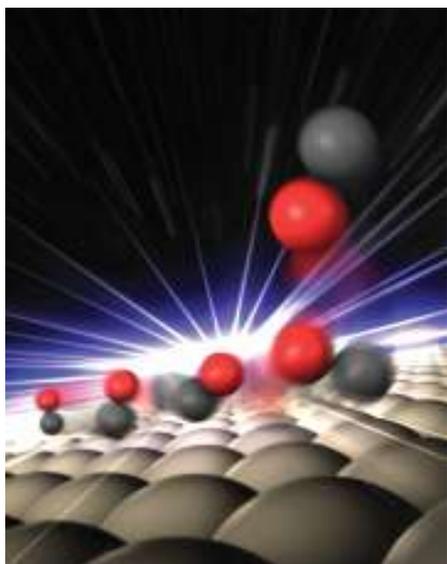


Figure 26. . The role of transient states on catalytic surfaces can be investigated with the selectivity of X-ray methods on a fast picosecond time scale available at BESSY-VSR. The important initial step of CO oxidation in the presence of a suitable catalyst has been observed recently, ref. 1, Dell'Angela et al., *Science* **339**, 1302 (2013). Artwork by Gregory Stewart at SLAC National Accelerator Laboratory.

Having access to picosecond pulses at any time of the year and to sub-picosecond pulses with greatly enhanced flux at the femtosecond slicing source FEMTOSPEX with BESSY-VSR would clearly boost the capabilities for heterogeneous catalysis and allow for further insight into the real-time dynamics of chemical reactions on surfaces.

To address the pathways that govern chemical rate and selectivity in heterogeneous catalysis and surface chemistry (Figure 26), both resonant photoemission and photoelectron diffraction have led to a wealth of information regarding the ultrafast charge transfer processes on surfaces through the core-hole-clock method and have given us highly relevant insights to the chemical state and the molecular orientation of molecules on surfaces respectively [2]. Here it would be highly desirable to drive the catalyst or the adsorbate through external stimuli and thus determine the interplay between femtosecond charge transfer, local coordination and the electronic or vibrational excitations present in the system. This systematic is now becoming feasible with the ArTOF in combination with the femtosecond and picosecond pulses of BESSY-VSR. The adsorbate is driven from equilibrium by electronic excitation or by the selective excitation of IR and THz modes associated to the low energy vibrational and rotational modes. Here simultaneously the structural dynamics in an element selective way through time resolved photoelectron diffraction (trPED) of excited species will be combined with the femtosecond charge transfer dynamics from excited state core-hole-clock spectroscopy collected in time-resolved resonant photoemission. These results could lead to the insight-driven design of future catalysts, with applications to solar fuels, clean combustion and green chemistry.

References for section 2.3.3.

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[2] A. Föhlisch et al., *Nature* **436**, 373 (2005).

2.3.4. Solar fuels

The direct conversion of abundant resources such as water and CO₂ into hydrogen or hydrocarbons using sunlight provides an attractive solution for the intermittent nature of solar energy. These solar fuels have up to 100 times higher energy and power densities than the best batteries, and offer a viable solution for long-term energy storage on the required terrawatt-hour scale. Photoelectrochemistry (Figure 27) is a promising, cost-effective route towards solar fuels that combines photovoltaic and electrocatalytic functionalities within a single material or composite. The light absorbing component is a semiconductor that needs to be stable in water under strongly oxidizing and/or reducing conditions. The semiconductor is electronically coupled to an electrocatalyst, which provides the right environment for the desired chemical reactions to occur at high rates and low overpotentials.

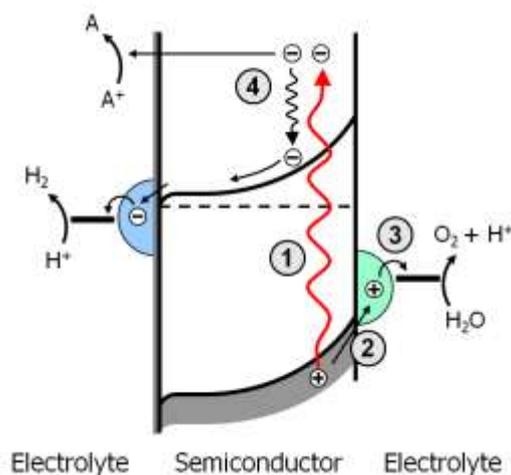


Figure 27. Schematic representation of the photoelectrochemical processes taking place during light-induced water splitting. (Courtesy R. van de Krol, HZB, and M. Bär, HZB).

Transition metal oxides are promising light absorbers that combine reasonable semiconducting properties with excellent chemical stability and low cost. Most efforts so far have focused on simple binary oxides, but efforts are currently shifting towards multinary (complex) oxides. The bulk and surface electronic structures of most of these oxides are highly complex and still poorly understood. To get a better understanding of the performance-limiting loss mechanisms it is essential to explore the charge carrier dynamics of these materials. Processes occurring on ms – ns time scales can already be accessed by standard optical and electrical spectroscopies available in many laboratories, and with the facilities available at BESSY II.

However, processes that occur on the ns – fs time scales are much harder to probe. This is especially true for transition metal oxides, whose low carrier mobilities and broad, non-distinct optical features preclude standard THz and fs transient absorption spectroscopy. BESSY-VSR would allow us to access this exciting regime, and probe the generation, recombination and charge-transfer dynamics of solar fuel materials in unprecedented detail. Some specific challenges that BESSY-VSR would be able to address are the following:

- The carrier lifetimes in many important transition metal oxides are significantly shorter than 10⁻⁹ s. For example, the carrier lifetimes in p-type Cu₂O and n-type α-Fe₂O₃, two of the best-

known photoelectrodes for light-induced water splitting, are 147 ps and < 8 ps, respectively. Despite extensive studies, it is not yet clear whether these extremely short lifetimes are an intrinsic characteristic of the material or whether these are due to the presence of defects. A clear answer to this question is the first step towards a possible solution strategy.

- The time scales and energy losses associated with charge transfer across the semiconductor-catalyst interface are still unexplored territory. A recent perspective in *Nature Chemistry* on the role of a cobalt phosphate-catalyzed $\alpha\text{-Fe}_2\text{O}_3$ surface (“Catalyst or Spectator”, *Nature Chem.* 4 (2012) 965) illustrates how little we know about this interface. Insight into the charge transfer dynamics will help us to understand why certain catalysts work well with some semiconductors, but not with others.
- The water oxidation reaction is often found to be the bottleneck in solar fuel devices. This is a complicated four-electron proton-coupled electron transfer process that, despite many studies, is still poorly understood. Most efforts focus on the slowest step in this process, which occurs on the ms timescale. By looking instead at much faster processes, which presumably involve momentary occupation of a hybrid orbital formed by the catalyst and chemisorbed water, additional pieces of this important four-electron transfer puzzle might be obtained.
- Hot-electron injection is a mechanism that would allow next-generation photovoltaic and solar fuel devices to break traditional theoretical performance limits. For this process to work, charge transfer to the catalyst or to an adsorbed water species should be faster than thermalization of the carriers. For a metal oxide like $\alpha\text{-Fe}_2\text{O}_3$, thermalization of conduction band electrons occurs within 0.3 ps. This is within the temporal range offered by BESSY-VSR.