

Since the discovery of x-ray generation by Wilhelm Conrad Roentgen about hundred years ago a wide range of x-ray based probes were developed which allows to characterize not only the structure but also the electronic configuration of matter [1-8]. Besides fully ordered crystalline materials partially ordered or better, materials without any long-range order like glasses are investigated. Most commonly a combination of extended x-ray absorption fine structure (EXAFS), and wide/small angle x-ray scattering (WAXS/SAXS) is applied to reveal the structure from atomic resolution to the overall shape of the particle itself [9-16]. The atomic selectivity of near edge x-ray spectroscopy (NEXAFS) permits to study the influence of local symmetry breaks on localized electronic states and moreover provides a tool to characterize the electron density at the absorber atom [17-21].

Even if most of these techniques were first applied in the first half of the 20th century, and many theoretical and experimental solutions were worked out, these experiments were restricted to expert-groups only. In the early 90th dedicated user facilities at storage rings were developed providing the necessary infrastructure, know-how, and the necessary flux to allow for high through-put experiments making the highly demanding experiments to standard characterization tools in materials, chemical, and earth sciences.

The increased through-put was early on utilized to follow the temporal evolution of materials during chemical reactions and mechanical and heat treatments. Special setups like Quick-EXAFS or dispersive XAFS were used to study reversible and irreversible processes [22-28]. Temporal structural studies using WAXS techniques were enabled by the development of area detectors with high-count rate capabilities [29-33]. Typical time resolutions were in the range of seconds to milliseconds [25, 31, 32]. With the development of the third-generation synchrotrons, storage rings optimized to produce highly brilliant x-ray beams with focus on so-called insertion device beamlines (dedicated structures to produce x-rays independent from the beam guidance magnet structure) new experimental techniques were feasible to increase the time resolution. Due to the radiation losses the particle beam has to be accelerated in accelerator cavities which are integral part of the storage ring. The radio frequency in combination with the geometry of the ring results in a timing structure of the electron beam and therefore of the produced x-ray beams. The individual bunches show typically 100ps pulse-length and are typically separated from each other by 2-150ns. This timing structure was used to apply a laser pump x-ray probe experiment which is a well known concept in laser spectroscopy. A laser pulse creates an excited state which will be probed by the x-ray pulse [34-37]. The time resolution is given by the convolution of laser excitation and the x-ray probe pulse length. State of the art time resolution is about 50ps-100ps. To achieve the necessary statistics the signal of thousands of excitation/probe pulses has to be averaged [38-41]. Over the past decade various pioneering experiments on solutions and solid-state samples were successfully performed, first general user facilities established, and the power of the technique demonstrated [42-61].

The nature of most relaxation processes is far more complex than described in a two level system. After an excitation pulse hits an ensemble of matter a fraction will be excited and will relax over various pathways to intermediates with relative long lifetimes. This temporal development results in a de-phasing of the originally coherent state [62]. Depending on the potential surface and on the reaction coordinates multiple pathways are in general possible. At a given time after the excitation a set of different excited states

inclusive the ground state will be observed. By changing the time delay the ratio of the various states can be changed. At present only the simplest two or three level systems are investigated [63-65].

The sample damage threshold and the effects of de-phasing and various reaction pathways will determine the maximal possible excitation rate of the investigated state. An additional complication is caused by the largely different absorption cross section for pump and probe wavelength resulting in an even more reduced excitation rate. As a consequence the LITR XAFS/WAXS experiment will generally suffer under a low signal/noise ratio which finally limits what can be measured. This problem is even enhanced by a technical detail; typically the excitation rep-rate is significantly smaller than the probe rep-rate. This results in an effective intensity loss of a factor 1000-10000 in respect to a conventional x-ray experiment [47, 65].

Even if these restriction are limiting the general use of time dependent investigations at synchrotrons, many improvements can be achieved in dedicated beamlines to allow good data quality with reasonable through put. To compensate for the intensity loss the beamline should be a high flux line with multiple optimized insertion devices and an optimized band pass monochromator. To fully benefit from this high flux the detection systems have to be optimized. To explain the magnitude of this task we want to show numbers for a 1mmol solution of an Fe-containing sample, a typical dilute sample. In the case of 11-ID-D at Advanced Photon Source, a dedicated high flux beamline, about 3000-4000 fluorescence photons/per bunch will hit a detection system which covers 10% of the solid angle. To avoid deadtime a conventional detection system will be in the order about 10000-elements. Even if such systems are presently not available there are various routes feasible. It will be important that the cost per element will significantly drop in comparison to nowadays available systems. To use detection systems which count multiple photons per bunch equipped with an energy filter, either by a combination of Z-1filter and soller slit, or by integration of crystal optics, is a cost effective alternative. The detection system at 11-ID-D can detect up to 100 photons per bunch the full dynamic range is about 5-6 orders of magnitude.

Many experimental techniques exist to improve the signal to noise ratio; however they are typically very specific to the individual sample system. Utilizing grating incident techniques for x-rays and using normal incidence for the excitation is one way to overcome the various absorption cross sections. Another way is to optimize the excitation wavelength and the optical density of the material. Moreover, the excitation wavelength, polarization, and pulse length can be tuned to specifically excite specific excited states. The excitation range spans a wide range of the spectrum from RF, THz, optical to the UV-spectrum. First proposals are suggesting to guide the excited state with multiple excitations through the reaction path way overcoming the de-phasing problem [66-71].

Concluding one can say that the largest limitation of time dependent X-ray measurements are the low signal to noise ratios achievable at synchrotrons. By utilizing state of the art beamline design, detector technology, and optimized sample setup most of these disadvantages can be compensated so that good data quality can be achieved with reasonable throughput. However, the beamline has to be highly specialized providing cutting edge technology. At present, there is no beamline worldwide focused on time dependent measurements on glasses.

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