

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 20<sup>th</sup> century, and many theoretical and experimental solutions were worked out, these experiments were restricted to expert-groups only. In the early 90<sup>th</sup> 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 grazing 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.

1. Greaves, G.N. and S. Sen, *Inorganic glasses, glass-forming liquids and amorphizing solids*. Advances in Physics, 2007. **56**(1): p. 1-166.
2. Rehr, J.J., *Theory and calculations of X-ray spectra: XAS, XES, XRS, and NRIXS*. Radiation Physics and Chemistry, 2006. **75**(11): p. 1547-1558.
3. Brown, G.E., Jr., et al., *Environmental interfaces, heavy metals, microbes, and plants: applications of XAFS spectroscopy and related synchrotron radiation methods to environmental science*. Physica Scripta, 2005: p. 8 pp.
4. Kempson, I.M., et al., *Applications of synchrotron radiation in forensic trace evidence analysis*. Talanta, 2005. **67**(2): p. 286-303.
5. Strange, R.W., M. Ellis, and S.S. Hasnain, *Atomic resolution crystallography and XAFS*. Coordination Chemistry Reviews, 2005. **249**(1-2): p. 197-208.
6. Harada, M., et al., *Solvation structure of ions at solution surfaces as studied by total-reflection total-conversion-electron yield X-ray absorption fine structure*. Bunseki Kagaku, 2003. **52**(6): p. 405-418.
7. Crozier, E.D., *A review of the current status of XAFS spectroscopy*. Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms, 1997. **133**(1-4): p. 134-144.
8. Oyanagi, H., *Third generation XAFS using insertion devices: new opportunities of high brilliance photon sources*. Bulletin of the Electrotechnical Laboratory|Bulletin of the Electrotechnical Laboratory, 1997. **61**(8): p. 1-10.
9. Hamoudi, A., et al., *Microstructural evolution of amorphous silica following alkali-silica reaction*. Journal of Non-Crystalline Solids, 2008. **354**(45-46): p. 5074-5078.
10. Fan, W., et al., *In situ small-angle and wide-angle X-ray scattering investigation on nucleation and crystal growth of nanosized zeolite A*. Chemistry of Materials, 2007. **19**(8): p. 1906-1917.
11. Riello, P., et al., *Reduction of concentration-induced luminescence quenching in Eu<sup>3+</sup>-doped nanoparticles embedded in silica*. Optical Materials, 2006. **28**(11): p. 1261-1265.
12. Keil, P., D. Lutzenkirchen-Hecht, and R. Frahm, *Grazing incidence XAFS under non-specular conditions*. Physica B-Condensed Matter, 2005. **357**(1-2): p. 1-5.
13. Kondo, Y., et al., *Filler-induced structural order and mechanical properties of polystyrene-silica nanocomposites*. Nihon Reoroji Gakkaishi, 2005. **33**(5): p. 273-278.
14. Prado, M.O., et al., *Liquid-liquid phase separation in alkali-boro silicate glass. An impedance spectroscopy study*. Journal of Non-Crystalline Solids, 2003. **332**(1-3): p. 166-172.
15. Precht, U. and H.J. Pentinghaus, *Metric characterization of medium range order in silicate glasses and their melts by WAXS*. Applied Mineralogy, Vols 1 and 2, 2000: p. 209-212.
16. Nofz, M., et al., *Structure of Calcium-Aluminosilicate Glasses - Wide-Angle X-Ray-Scattering and Principal Component Analysis*. Journal of Non-Crystalline Solids, 1992. **143**(2-3): p. 191-200.

17. de Groot, F., G. Vanko, and P. Glatzel, *The Ls x-ray absorption pre-edge structures in transition metal oxides*. Journal of Physics-Condensed Matter, 2009. **21**(10).
18. Metrich, N., et al., *The oxidation state of sulfur in synthetic and natural glasses determined by X-ray absorption spectroscopy*. Geochimica Et Cosmochimica Acta, 2009. **73**(8): p. 2382-2399.
19. Giuli, G., et al., *Yellow impact glass from the K/T boundary at Beloc (Haiti): XANES determination of the Fe oxidation state and implications for formation conditions*. Meteoritics & Planetary Science, 2008. **43**(5): p. 981-986.
20. Qiu, D., et al., *An X-ray absorption spectroscopy study of the local environment of iron in degradable iron-phosphate glasses*. Journal of Non-Crystalline Solids, 2008. **354**(52-54): p. 5542-5546.
21. Farges, F., *Ab initio and experimental pre-edge investigations of the Mn K-edge XANES in oxide-type materials*. Physical Review B, 2005. **71**(15).
22. Grunwaldt, J.D., et al., *In situ investigations of structural changes in Cu/ZnO catalysts*. Journal of Catalysis, 2000. **194**(2): p. 452-460.
23. Clausen, B.S., H. Topsoe, and R. Frahm, *Application of combined X-ray diffraction and absorption techniques for in situ catalyst characterization*. Advances in Catalysis, Vol 42, 1998. **42**: p. 315-344.
24. Alsnelsen, J., G. Grubel, and B.S. Clausen, *Qexafs in Seconds at an Undulator Source*. Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms, 1995. **97**(1-4): p. 522-525.
25. Clausen, B.S., et al., *A Combined Qexafs Xrd Method for Online, in-Situ Studies of Catalysts - Examples of Dynamic Measurements of Cu-Based Methanol Catalysts*. Catalysis Letters, 1993. **20**(1-2): p. 23-36.
26. Hagelstein, M., et al., *The Energy Dispersive-X-Ray Absorption Spectrometer Dexafs at Hasylab*. Physica B, 1989. **158**(1-3): p. 324-325.
27. Frahm, R., *Qexafs - X-Ray Absorption Studies in Seconds*. Physica B, 1989. **158**(1-3): p. 342-343.
28. Frahm, R., *Quick Scanning Exafs - 1st Experiments*. Nuclear Instruments & Methods in Physics Research Section a-Accelerators Spectrometers Detectors and Associated Equipment, 1988. **270**(2-3): p. 578-581.
29. Bras, W., et al., *Simultaneous Time Resolved Saxs and Waxs Experiments Using Synchrotron Radiation*. Nuclear Instruments & Methods in Physics Research Section a-Accelerators Spectrometers Detectors and Associated Equipment, 1993. **326**(3): p. 587-591.
30. Ryan, A.J., et al., *Structure Development in Semicrystalline Diblock Copolymers Crystallizing from the Ordered Melt*. Macromolecules, 1995. **28**(11): p. 3860-3868.
31. Rangarajan, P., et al., *Dynamics of Structure Formation in Crystallizable Block-Copolymers*. Macromolecules, 1995. **28**(5): p. 1422-1428.
32. Butler, M.F., A.M. Donald, and A.J. Ryan, *Time resolved simultaneous small- and wide-angle X-ray scattering during polyethylene deformation .1. Cold drawing of ethylene-alpha-olefin copolymers*. Polymer, 1997. **38**(22): p. 5521-5538.

33. Bras, W., *An SAXS/WAXS beamline at the ESRF and future experiments*. Journal of Macromolecular Science-Physics, 1998. **B37**(4): p. 557-565.
34. Kishek, R.A., et al., *Scaled models: Space-charge dominated electron storage rings*. International Journal of Modern Physics A, 2007. **22**(22): p. 3838-3851.
35. Lumpkin, A.H., F. Sakamoto, and B.X. Yang, *Dual-sweep streak camera measurements of the APS user beams*. 2005 Ieee Particle Accelerator Conference (Pac), Vols 1-4, 2005: p. 1946-1948.
36. Schade, U. and W.B. Peatman, *The synchrotron infrared activities at BESSY*. Journal of Biological Physics, 2003. **29**: p. 309-312.
37. Walton, D.T., *Direct measurement of the time structure of ultrashort X-ray pulses from a storage ring*. AIP Conference Proceedings|AIP Conference Proceedings, 2000(521): p. 479-82.
38. Heigl, F., et al., *Dynamic view on nanostructures: A technique for time resolved optical luminescence using synchrotron light pulses at SRC, APS, and CLS*. Synchrotron Radiation Instrumentation, Pts 1 and 2, 2007. **879**: p. 1202-1205.
39. Adachi, S., et al., *Subnanosecond-resolved X-ray diffraction at the SPring-8 high flux beamline BL40XU*. AIP Conference Proceedings, 2004(708): p. 1383-6.
40. Zholents, A., et al., *Development of a source of femtosecond X-ray pulses based on the electron storage ring*. Proceedings of the 1999 Particle Accelerator Conference (Cat. No.99CH36366)|Proceedings of the 1999 Particle Accelerator Conference (Cat. No.99CH36366), 1999: p. 10.1109/PAC.1999.792694.
41. *Time Structure of X-Ray Sources and Its Applications*. Proceedings of the SPIE - The International Society for Optical Engineering|Proceedings of the SPIE - The International Society for Optical Engineering, 1998. **3451**.
42. Chen, L.X., et al., *Molecular structural dynamics of photoactive transition metal complexes in solar energy conversion studied by ultrafast optical spectroscopy and LITR-XAS*. X-Ray Absorption Fine Structure-XAFS13, 2007. **882**: p. 844-848.
43. Fons, P., et al., *Sub-nanosecond time-resolved structural measurements of the phase-change alloy Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>*. Japanese Journal of Applied Physics Part 1- Regular Papers Brief Communications & Review Papers, 2007. **46**(6B): p. 3711-3714.
44. Stern, E.A. and D. Brews, *Ultrafast XAFS measurements on laser excited Ge films*. X-Ray Absorption Fine Structure-XAFS13, 2007. **882**: p. 24-28.
45. Lee, T., et al., *Ultrafast XAFS of transition metal complexes*. Ultrafast Phenomena XV, 2007. **88**: p. 719-721.
46. Fons, P., et al., *Understanding structural changes in phase change memory alloys*. Chalcogenide Alloys for Reconfigurable Electronics. Symposium (Materials Research Society Symposium Proceedings Vol.918), 2006: p. 147-56|x+191.
47. Chen, L.X., *Excited state molecular structure determination in disordered media using laser pump/X-ray probe time-domain X-ray absorption spectroscopy*. Faraday Discussions, 2003. **122**: p. 315-329.
48. Chen, L.X., et al., *Capturing a photoexcited molecular structure through time-domain X-ray absorption fine structure*. Science, 2001. **292**(5515): p. 262-264.

49. Norman, D., *Prospects for X-ray absorption with the super-bright light sources of the future*. Journal of Synchrotron Radiation, 2001. **8**: p. 72-75.
50. Cammarata, M., et al., *Chopper system for time resolved experiments with synchrotron radiation*. Review of Scientific Instruments, 2009. **80**(1).
51. Christensen, M., et al., *Time-Resolved X-ray Scattering of an Electronically Excited State in Solution. Structure of the (3)A(2u) State of Tetrakis-mu-pyrophosphitodiplatinate(II)*. Journal of the American Chemical Society, 2009. **131**(2): p. 502-508.
52. Lee, J.H., et al., *Capturing transient structures in the elimination reaction of haloalkane in solution by transient X-ray diffraction*. Journal of the American Chemical Society, 2008. **130**(18): p. 5834-+.
53. Kong, Q.Y., et al., *Ultrafast X-ray solution scattering reveals an unknown reaction intermediate in the photolysis of [Ru-3(CO)(12)]*. Angewandte Chemie-International Edition, 2008. **47**(30): p. 5550-5553.
54. Cammarata, M., et al., *Tracking the structural dynamics of proteins in solution using time-resolved wide-angle X-ray scattering*. Nature Methods, 2008. **5**(10): p. 881-886.
55. Plech, A., et al., *Small-angle pump-probe studies of photoexcited nanoparticles*. Journal of Synchrotron Radiation, 2007. **14**: p. 288-294.
56. di Stasio, S., et al., *Synchrotron SAXS (in situ) identification of three different size modes for soot nanoparticles in a diffusion flame*. Carbon, 2006. **44**(7): p. 1267-1279.
57. Sondhauss, P., et al., *Picosecond x-ray studies of coherent folded acoustic phonons in a periodic semiconductor heterostructure - art. no. 61180V*. Ultrafast Phenomena in Semiconductors and Nanostructure Materials X, 2006. **6118**: p. V1180-V1180.
58. Anfinrud, P., F. Schotte, and M. Wulff, *Watching proteins function with picosecond time-resolved X-ray crystallography*. Ultrafast Phenomena Xiv, 2005. **79**: p. 581-585.
59. Ihee, H., et al., *Ultrafast x-ray diffraction of transient molecular structures in solution*. Science, 2005. **309**(5738): p. 1223-1227.
60. Qingyu, K., et al., *Photodissociation reaction of 1,2-diiodoethane in solution: a theoretical and X-ray diffraction study*. Journal of Physical Chemistry A, 2005. **109**(45): p. 10451-8.
61. Sondhauss, P., et al., *Picosecond x-ray studies of coherent folded acoustic phonons in a multiple quantum well*. Physical Review Letters, 2005. **94**(12).
62. Chen, L.X., *Probing transient molecular structures in photochemical processes using laser-initiated time-resolved X-ray absorption spectroscopy*. Annual Review of Physical Chemistry, 2005. **56**: p. 221-254.
63. Bourgeois, D., et al., *Time-resolved methods in biophysics. 6. Time-resolved Laue crystallography as a tool to investigate photo-activated protein dynamics*. Photochemical & Photobiological Sciences, 2007. **6**: p. 1047-1056.
64. *Time-Resolved Chemistry: From Structure to Function*. Faraday Discussions, 2003(122).
65. Srajer, V., et al., *Time-resolved studies of carbonmonoxy myoglobin photolysis: protein relaxation and ligand trajectory*. Technical Digest. Summaries of Papers

- Presented at the International Quantum Electronics Conference. Conference Edition. 1998 Technical Digest Series, Vol.7 (IEEE Cat. No.98CH36236)|Technical Digest. Summaries of Papers Presented at the International Quantum Electronics Conference. Conference Edition. 1998 Technical Digest Series, Vol.7 (IEEE Cat. No.98CH36236), 1998: p. 10.1109/IQEC.1998.680206.
66. Nakamura, Y., Y.A. Pashkin, and J.S. Tsai, *Coherent control of macroscopic quantum states in a single-Cooper-pair box*. Nature, 1999. **398**(6730): p. 786-788.
  67. Makhlin, Y., G. Schon, and A. Shnirman, *Quantum-state engineering with Josephson-junction devices*. Reviews of Modern Physics, 2001. **73**(2): p. 357-400.
  68. Tannor, D.J. and S.A. Rice, *Control of Selectivity of Chemical-Reaction Via Control of Wave Packet Evolution*. Journal of Chemical Physics, 1985. **83**(10): p. 5013-5018.
  69. Bonadeo, N.H., et al., *Coherent optical control of the quantum state of a single quantum dot*. Science, 1998. **282**(5393): p. 1473-1476.
  70. Cohen-Tannoudji, C.N., *Manipulating atoms with photons*. Reviews of Modern Physics, 1998. **70**(3): p. 707-719.
  71. Vlasov, Y.A., et al., *Active control of slow light on a chip with photonic crystal waveguides*. Nature, 2005. **438**(7064): p. 65-69.