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Light induced structural changes in photosynthetic reaction centres. Gergely Katona^a, Annemarie Wöhri^b, Linda C. Johansson^a, Emelie Fritz^b, Erik Malmerberg^a, Magnus Andersson^b, Jonathan Vincent^c, Mattias Eklund^c, Marco Cammarata^d, Michael Wulff^d, Jan Davidsson^e, Gerrit Groenhof^e, Richard Neutze^a.

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Photosynthetic reaction centres are responsible for the conversion of light energy to chemical energy in purple bacteria. These membrane proteins contain a special bacteriochlorophyll dimer, two accessory bacteriochlorophylls, two bacteriopheophytins and a statically bound quinone molecule. On the cytoplasmic side, a binding site for a mobile ubiquinone can be located, which is reduced stepwise following light induced charge separation events.

Using continuous illumination we were able to trap a light induced conformational substate at low temperature that develops in response to prolonged intense illumination.[1] This conformational change mainly affects the H-subunit and proposed to play a role to prevent futile charge recombination. More recently we studied a light induced structural change by Laue diffraction techniques in a related photosynthetic reaction center from *B. viridis*. [2] The time-resolved pump-probe experiments were performed at the ID09 beamline of the ESRF using narrow band polychromatic ("pink") X-ray pulses. Laue diffraction images were recorded before and following light activation (3 ms delay) with multiple crystal orientations, until highly complete data was obtained.

In these experiments we observed that residue Tyr-L162 moves closer to the special pair upon illumination which we interpreted as the electrostatic attraction between the positively charged special pair and the deprotonated tyrosine residue. This subtle conformational change highlights the diverse roles tyrosine residues play in various photosystems.

[1] Katona G., Andréasson U., Gourdon P., Snijder A., Hansson Ö., Andréasson L.-E. & Neutze R. *Nat. Struct. and Mol. Biol.* 2005, 12(7), 630. [2] Wöhri A.B., Katona G., Johansson L.C., Fritz E., Malmerberg E., Andersson M., Vincent J., Eklund M., Cammarata M., Wulff M., Davidsson J., Groenhof G. & Neutze R. *Science* 2010, 328, 630.

Keywords: time-resolved crystallography, membrane protein, Laue diffraction, photosynthesis

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Probing catalysis in real time with time resolved x-ray spectroscopy. Matthias Bauer, Jan-Dierk Grunwaldt. *Inst. Für techn. Chemie und Polymerchemie, Karlsruhe Institut für Technologie KIT – Campus Süd, Engesserstraße 18, 76128 Karlsruhe, Germany.*

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X-ray spectroscopy offers many powerful techniques to study catalysts at work. Depending on the catalytic reaction and the scientific question, time and/or spatial resolution is necessary. With the present contribution, the possibilities of X-ray absorption spectroscopy to approach the different time-scales from hours to milliseconds, needed to study heterogeneous and homogeneous catalytic reactions of various experimental requirements are discussed with selected examples, in which also the combination with other spectroscopic methods is highlighted. As such examples will serve: the heterogeneous catalytic partial oxidation of methane and the reduction and re-oxidation of Cu/Al₂O₃, and the homogeneous cerium catalyzed hydroxylation of diketons as well as the copper-catalyzed Kharash-Sosnovsky reaction.

In both the heterogeneous and homogeneous case, mostly the quick scanning EXAFS technique (QEXAFS) has been successfully applied at the synchrotrons ANKA, APS and SLS, whereas the dispersive EXAFS technique (DEXAFS) was used at the ESRF. In addition we show the importance of complementary techniques like XRD and Raman/UV-Vis spectroscopy as available for example at the Swiss-Norwegian Beamline at the ESRF, in order to understand the total oxidation of methane over Pd/ZrO₂ catalysts and the iron-catalyzed Michael addition.

Keywords: X-ray absorption, Catalysis, Time-resolution

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Chemical reactions of small molecules in solution studied by ultrafast (ps) X-ray scattering. Qingyu Kong^a, Michael Wulff^b, Hyotcherl Ihee^c, Michel H. J. Koch^d. ^aSociété civile Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin - BP 48, 91192 GIF-sur-YVETTE CEDEX. ^bEuropean Synchrotron Radiation Facility, 6 Rue Jules Horowitz, BP220, F-38043 Grenoble Cedex, France. ^cCenter for Time-Resolved Diffraction, Department of Chemistry, Graduate School of Nanoscience & Technology (WCU), KAIST, Daejeon, 305-701, Republic of Korea. ^dEuropean Molecular Biology Laboratory, Hamburg Outstation, EMBL c/o DESY, Notkestrasse 85, D-22603 Hamburg, Germany. E-mail: kong@synchrotron-soleil.fr

Reaction dynamics are traditionally studied by time-resolved spectroscopy employing picosecond or femtosecond optical pulses, in which a reaction is initiated by an optical pulse (pump) and its dynamics is monitored by another optical pulse (probe) at different time delays between the pump and probe pulses. The limitation of optical pump-probe spectroscopy is that the optical pulse only interacts with the outer shell electrons (valence electrons) and the spectroscopic signals are sensitive to only specific energy states, achieving a nanometer resolution. Hard X-rays from synchrotron radiation with a

wavelength around 1 Å, which is of the same order as chemical bond lengths, can yield direct structural information such as atomic coordinates, bond lengths and angles, about reaction intermediates. Each interatomic distance in the volume probed by the X-rays gives a characteristic scattering signal, which makes it in principle possible to identify all intermediates at least in the case of simple systems. The application of this method to the photodissociation of Ru₃(CO)₁₂ dissolved in cyclohexane at 260 [1] and 390 [2] nm revealed an unknown intermediate which had escaped detection in spectroscopic studies, thereby demonstrating the advantage of X-ray scattering in the detection of optically-silent transient molecules. In the talk, the optical pump and X-ray probe setup and ultrafast solution scattering on small molecules studied in ID09B ESRF will be introduced briefly, then the photofragmentation reaction of Ru₃(CO)₁₂ dissolved in cyclohexane will be used as an example to show the complementary nature of ultrafast X-ray scattering and ultrafast spectroscopy in the determination of transient molecular structures and chemical reaction mechanisms. Aided with high resolution X-ray (88 keV) scattering pattern of pure liquid C₆H₁₂, the solvent dynamics at early and later time delays will be briefly presented.

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Keywords: ultrafast, X-ray scattering, photochemistry

FA5-MS42-T04

Tracking Chemical Reactions in Solution by Time-Resolved X-Ray Scattering. Martin Meedom Nielsen. *Centre for Molecular Movies, Niels Bohr Institute, University of Copenhagen, Denmark.*
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Every photochemical reaction starts with an electronically excited state and ends with a ground state molecule. The pathway taken of the atomic nuclei, while molecules are partaking in such reactions, and hence their intermediary molecular structures, is a fundamental question in chemistry, and a host of systems have been studied by laser spectroscopy down to the femtosecond time scale. However, while spectroscopic methods provide information on energy levels, direct structural information is in general not available. In the last few years, this gap of information has been bridged by X-ray scattering experiments on time scales down to picoseconds. Initially this has been made for crystalline systems with their inherent amplification of the scattered intensity and recently also for liquid systems, the natural environment for most chemical reactions.

We present results, based on which we have successfully determined key structural parameters directly for the highly reactive excited state of the square-planar platinum compound PtPOP (Pt₂(P₂O₄H₂)₄(4-)) in aqueous solution [1]. Furthermore we were able to obtain the first direct structural fingerprint of a bimolecular reaction between the excited state PtPOP and TI⁺ and Ag⁺ ions in solution [2, 3].

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Keywords: Chemical reactions, Time-resolved x-ray scattering

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Modulation-Enhanced Diffraction: a new tool to study transient structural phases and solve structures. Wouter van Beek^{a,c}, Dmitry Chernyshov^a, Atsushi Urakawa^b, Luca Palin^c, Davide Viterbo^c, Marco Milanesio^c. ^aSwiss Norwegian BeamLines at ESRF Grenoble, France. ^bInstitute of Chemical Research of Catalonia (ICIQ) Tarragona, Spain. ^cDISTA - Università del Piemonte Orientale "A. Avogadro" Alessandria Italy.
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When a system is perturbed by a periodic external stimulation, e.g. concentration, pH, light flux, pressure and temperature, for many crystalline materials the structural response is also periodic. A component of the diffraction pattern, sensitive to periodic external stimuli, can be selectively detected and the signal-to-noise ratio can be significantly improved by post experimental data treatment (demodulation). A similar approach utilizing periodic perturbations in spectroscopy (e.g. IR and Raman spectroscopy) has already shown its great strength, giving insights into mechanisms and pathways of chemical reactions and phase transformations; this technique has been called Modulation Excitation Spectroscopy (MES) [1,2]. Here we present, for the first time, a combination of this modulation approach with powder X-ray diffraction, which we called Modulation-Enhanced Diffraction (MED). Similarly to MES, it allows to follow the temporal evolution of crystal structures and to observe short-living transient phases with a life shorter than the data acquisition rate. Our first experimental results using MED data collected with the help of synchrotron radiation will be presented.

Diffraction intensity, being correlated with the external stimulation, also contains crystallographic phase information from the differently responding structural entities. This so called cross-term mixing contribution can be exploited in direct structure solution methods. For multiphase samples, MED can also help to assign peaks to an unknown phase and consequently help with indexing by choosing an appropriate stimulus, since demodulation allows extracting selectively the information of phases responding to the stimulus.

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