

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.

[1] Kong Q.Y., Lee J.H., Kim K.H., Kim J., Wulff M., Ihee H., Koch M.H.J. *J. Amer. Chem. Soc.* 2010, 132, 2600. [2] Kong Q.Y., Lee J.H., Plech A., Wulff M., Ihee H., Koch M.H.J. *Angew. Chem. Int. Ed.* 2008, 47, 5550.

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.*
E-mail: meedom@fys.ku.dk

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].

[1] Morten Christensen, Kristoffer Haldrup, Klaus Bechgaard, Robert Feidenhans'l, Qingyu Kong, Marco Cammarata, Manuela Lo Russo, Michael Wulff, Niels Harrit, and Martin Meedom Nielsen, *J. Am. Chem. Soc.*, 131, 502-508, (2009). [2] Kristoffer Haldrup, Morten

Christensen, Marco Cammarata, Qingyu Kong, Michael Wulff, Simon O. Mariager, Klaus Bechgaard, Robert Feidenhans'l, Niels Harrit, Martin M. Nielsen, *Angew. Chem. Int. Edit.*, 48, 4180-4184 (2009). [3] Morten Christensen, Kristoffer Haldrup, Kasper S. Kjær, Marco Cammarata, Michael Wulff, Klaus Bechgaard, Høgni Weihe, Niels H. Harrit, and Martin M. Nielsen, *Phys Chem Chem Phys*, accepted.

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

FA5-MS42-T05

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.
E-mail: wouter@esrf.fr

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.

[1] D. Baurecht, and U.P. Fringeli, *Rev. Sci. Instrum.* (2001) 72, 3282. [2] A. Urakawa, T. Bürgi and A. Baiker, *Chem. Eng. Sci.* 63 (2008), p. 4902.

Keywords: in-situ time-resolved powder diffraction, structure solution, indexing