

We developed a combined imaging and dynamic light scattering (DLS) system for routine measurements in droplets of multi-well plates as well as in gel tubes used for protein crystallization. The system is of high value for rapid identification of good crystallization conditions. Today automated methods to crystallize macromolecules are widely used and can easily generate thousands of crystallization droplets. Nevertheless the evaluation of crystallization experiments to find optimal growth conditions remains a bottleneck. Therefore we have investigated methods to improve the process of evaluating results and finding crystal growth conditions. One method is DLS, the second is the use of combined white/UV illumination for determination of whether crystal-like objects are biomolecular and identification of crystals in crystallisation set-ups. Up to now, it has been impossible to determine the particle size directly in protein solution droplets because of size and configuration constraints. We have developed a CCD camera-based imaging instrument and combined a laser source and a detector to perform DLS measurements in situ. The plate-screening system allows to monitor and evaluate the entire crystallization process in an automated way. For example the stages of nucleation and the progress of crystal growth without disrupting the course of equilibration can be analyzed. The data provide information to understand in greater detail the process of crystal initiation and growth and will allow further optimisation, thereby leading to better crystals. Finally we will also describe a method to support the identification of protein crystals, exploiting the fact that most proteins and other biomolecules fluoresce when illuminated with UV light.

Keywords: crystallization process, dynamic light scattering, instrumentation and software

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Watching photo-induced dynamics with picosecond time-resolved X-ray diffraction

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Picosecond time-resolved X-ray experiments using synchrotron radiation sources are becoming general and powerful tools to explore structural dynamics of condensed matters in material and biological sciences. The beam line NW14A is a newly constructed undulator beam line for 100-ps time-resolved X-ray experiments at the Photon Factory Advanced Ring, KEK [1]. This beam line was designed to conduct a wide variety of time-resolved X-ray measurements, such as time-resolved X-ray diffraction, scattering and absorption. The beam line has been operational for two years, and current status of the beam line and scientific activities utilizing shock-induced lattice deformation [2] will be presented.

Reference:

- [1] Nozawa et al. (2007) *J. Synchrotron Rad.* 14, 313.
[2] Ichiyanagi et al. (2007) *Appl. Phys. Lett.* 91, 231918.

Keywords: time-resolved diffraction, synchrotron X-ray instrumentation, structural dynamics

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Photo-crystallographic studies of dimerisation processes: From picoseconds to hours transformation

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Though photo-induced solid state reactions are known since over hundred years, the structural mechanism underlying photo-induced solid state reactions have not been explored yet to a sufficient stage. In the following contribution we will present photo-crystallographic studies on [2+2] photodimerisation reactions of cinnamic acid derivatives. Common for all the investigated systems is the homogeneous character of the reaction (single crystal to single crystal transformation). We will report on high resolution photo-crystallographic studies / electron density studies monitoring the structural mechanism of the seconds to hours photodimerisation processes - and how to speed up these processes which can then only be investigated by ultrafast time-resolved crystallography (picosecond time resolution).

- [1] G. Busse, Th. Tschentscher, A. Plech, M. Wulff, B. Frederichs & S. Techert, *Faraday Discuss.* 122 105117 (2002)
[2] J. Davaasambuu, S. Techert, *J. Physics D: Appl. Physics* 38, A204 – A207 (2005)
[3] J. Davaasambuu, G. Busse, S. Techert, *J. Phys. Chem. A* 110 (Juergen Troe Festschrift), 3261-3265 (2006).

Keywords: photodimerization, time-resolved crystallography, organic crystals

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Picosecond and femtosecond X-ray absorption studies of the photoinduced spin change in Fe-complexes

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Because of close-lying low spin (LS) singlet and high spin (HS) quintet states, molecular FeII-complexes are particularly interesting in relation to the spin cross-over (SCO) phenomenon, where conversion from the LS ground state to the HS excited state (or the reverse) can be induced either by temperature, pressure or light. Several steady-state and ultrafast studies of the light-induced SCO have been carried out by optical spectroscopies, concluding that population is funneled to the HS state in < 1 ps, through intermediate singlet and triplet metal-centred (MC) states upon excitation into the singlet metal-to-ligand-charge-transfer state. However, the pathways of this cascade remain unclear, in part because the intermediate and final states are optically silent. In addition, depending on the ligand, the lifetime of the HS state spans several decades, and the origin of this large variation is unclear. In [FeII(bpy)₃]²⁺ at room temperature, the HS lifetime is 660 ps. Using X-ray absorption spectroscopy (XAS) studies with 50-100 ps resolution, we found that the Fe-N bond elongates by 0.2 Å in the HS state. This elongation is similar in Fe-complexes having much longer HS lifetimes, leading us to conclude that the structure of the HS spin does not determine its lifetime, but rather it is its energetics that does. Our results show important spectral changes between the LS and HS states in the X-ray Absorption Near-Edge Structure (XANES) of the Fe K-edge.

Exploiting this result, we carried out a fs XANES study of the ultrafast light-induced SCO in $[\text{FeII}(\text{bpy})_3]^{2+}$, which allowed us to unravel the detailed mechanism of the ultrafast spin conversion in FeII-complexes. This is the first femtosecond X-ray study of a molecule in solution ever to be carried out.

Keywords: molecular dynamics, femtosecond phenomena, X-ray absorption spectroscopy

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Photocrystallographic studies on metastable linkage isomers of transition metal complexes

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Photocrystallography is a technique that allows the structure of materials to be determined when the species are in an energetically activated state [1,2]. A proportion of the molecules within a crystal are activated by illumination with a light source and then the structure of the material, which contains percentages of both ground state and metastable structures, is determined using single crystal X-ray diffraction techniques. The technique has met with considerable success and the structures of a range of metastable linkage isomers have been determined [3, 4]. However, the technique remains challenging because of the relatively low levels of excitation that can be obtained. This is because the light penetrates only a few microns into the crystal which means that only surface molecules are excited. This introduces strain into the crystal causing fragmentation. Similarly, if the structural change caused by the change of the coordination mode of the ligands is large then strain is introduced into the crystal and fragmentation occurs. We now describe a systematic series of photocrystallographic studies using synchrotron X-ray radiation, small crystals, and a variety of light sources, on transition metal nitrosyl, nitrite and carbonyl complexes, with a range of ancillary ligands and counter ions that show how optimum activation may be achieved. The incorporation of the complexes to be activated into Metal Organic Frameworks prior to irradiation also shows high levels of excitation.

[1] P. Coppens, et. al., *Acta Crystallogr.*, Sect. A, 2005, 61, 162; [2] J. M. Cole, *Chem. Soc. Rev.*, 2004, 33, 501; [3] A. Yu. Kovalevsky, et. al., *Chem. Eur. J.*, 2005, 11, 7254; [4] K. F. Bowes, et. al., *Chem. Commun.*, 2006, 2448.

Keywords: photochemistry coordination compounds, metastable structure determination, isomers

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Metastable photoisomerism in materials targeted for optical data storage

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Recent developments in single-crystal X-ray diffraction have enabled light-induced electronic perturbations in chemical structures to be directly probed. Such structural information is key to understanding many photoactivated processes. Photoisomerism in the crystalline state is particularly noteworthy due to its potential applications in media for holographic data storage. Although holograms were first successfully used for this purpose over a decade ago, their widespread adoption has been heavily hampered by two factors: the high optical precision required for writing and reading data, and a dearth of suitable light-sensitive materials. We aim to overcome this materials supply bottleneck using photocrystallographic techniques. Our group's recent studies on the series $[(\text{SO}_2)\text{Ru}(\text{NH}_3)_4 \text{X}]\text{Y}$ are of particular interest in this regard as the SO_2 ligand undergoes photoinduced linkage isomerisation, providing a means by which one might encode binary information into these materials. The photorefractive properties observed in these compounds arise from the electric dipolar changes directly associated with photoisomerism, in contrast to the mechanistic origin of conventional photorefractive materials. Photocrystallographic results of these compounds and related materials will be presented, in tandem with complementary results from density-functional theory and optical measurements of their holographic characteristics. The paper will include a description of the key experimental parameters that are required for a successful photocrystallographic experiment, and will highlight the important interplay of the complementary theoretical and optical studies. We will conclude with an outlook on new X-ray facilities whose incipient operation will facilitate further work in this area.

Keywords: photochemistry, holography, optical materials

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Web assisted crystallography teaching and learning

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The part dedicated to crystallography teaching in the science curriculum is getting shorter and this tendency seems to continue. Under these conditions, crystallography teachers are thus under heavy pressure to improve their teaching in order to maintain the highest standards in the subject. Fortunately, the web can be of great help for this endeavour and many interesting tools are currently available. Presenting the three-dimensional characteristics of structures, the concept of symmetry and diffraction can take full advantage of applets, i.e. self-contained applications directly available on the web. Currently, many authors have created applets, which are useful for teaching every aspect of crystallography covering the representation of structures, point and space group symmetry, the diffraction phenomena and all its variants, the resolution of structures, databases and many others. The possibility to benefit from a web access in the classroom has greatly contributed to improve teaching. It should also be mentioned that the use of applets is not only limited to teachers. The advantage is that the students can also use them for reviewing lectures or preparing exams. In this presentation, we propose to explore and demonstrate the various possibilities available on open websites in order to facilitate the understanding of the many faces of crystallography.

Keywords: teaching aids in crystallography, web resources, simulation software