

**STRUCTURE ANALYSIS OF PHOTO-INDUCED REACTIVE INTERMEDIATE IN A CRYSTAL**

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Our research interests include the direct observation of unstable intermediates in a crystal by X-ray crystallography. Our target compounds are open-shell species having more than one spin. Open-shell species such as radical, carbene, and nitrene have been extensively studied spectroscopically in inert matrices or in a gas phase, for the understanding of their role as intermediates in various chemical reactions and also for the investigation of their potential use for magnetic materials.

To design and develop functional materials, it is essential to obtain structural knowledge. However, few diffraction studies of open-shell species have been reported except stable radicals and relatively stable singlet species, because of the difficulty of their isolation and their high lability. Our basic technique used is a well-known cryo-trapping method to freeze reactive species. A key to retaining crystallinity during photoreaction is to design suitable reaction cavity. This talk will review the *in situ* study of photo-induced unstable reactive intermediates, radical, carbene, and nitrene, by X-ray analysis and also introduce some applications of an X-ray vacuum camera developed by Toriumi (Himeji Inst. Tech.) in combination with synchrotron radiation at BL02B1 in SPring-8.

**Keywords:** IN SITU CRYO TRAPPING UNSTABLE INTERMEDIATE

**STROBOSCOPIC TIME-RESOLVED DIFFRACTION AT ATOMIC RESOLUTION**

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Results of time-resolved experiments, combining X-ray diffraction and spectroscopic methods in the study of photo-induced changes in solids, will be described. In a first study, the shortening of the Pt-Pt distance upon excitation of the  $\text{Pt}_2(\text{pop})_4$  ion (pop = pyrophosphate,  $(\text{H}_2\text{P}_2\text{O}_5)^{2-}$ ) has been measured. The experimental design, including timing and optics, is fine-tuned to the spectroscopic properties of the system being investigated. Parallel quantum-chemical calculations have been performed for calibration of both theory and experiment. In the first studies conversion percentages have been small. Methods to increase the fraction of excited molecules will be discussed. They include the use of supramolecular solids in which photoactive molecules are embedded in a host framework, which in addition offers the possibility of studying at the atomic level the effect of the environment, and its distortion, on photochemical properties.

**Keywords:** TIME RESOLVED STROBOSCOPIC LIGHT INDUCED

**CRYSTAL STRUCTURE OF AN IRON(II) COMPLEX IN A METASTABLE LIGHT INDUCED MAGNETIC STATE**

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The iron(II) molecular complex  $[\text{Fe}(\text{Phen})_2(\text{NCS})_2]$  undergoes a magnetic transition from a diamagnetic low spin state to a paramagnetic high spin state at low temperature upon irradiation by light. We first determined the crystal structure of this complex at 30 K in the low spin state (LS). Then, the relatively long life time of the photoinduced metastable high spin state at 30 K allowed us to determine the crystal structure of  $[\text{Fe}(\text{Phen})_2(\text{NCS})_2]$  in the low temperature high spin state (HS-2). The LS to HS-2 transition corresponds to an increase of the unit cell volume of 1.1 % ( $24 \text{ \AA}^3$ ). The geometry of the  $\text{FeN}_6$  octahedron is also strongly modified at the transition which corresponds to a distortion together with an expansion of the bond lengths. Indeed, the iron-nitrogen bond lengths increase by  $0.2 \text{ \AA}$  and the N-Fe-N bond lengths angles are deviated from  $90^\circ$ , which results in an increase of the  $\text{FeN}_6$  octahedron volume from  $10 \text{ \AA}^3$  to  $13 \text{ \AA}^3$ . Moreover, the crystal structure of HS-2 shows significant differences with the room temperature high spin state crystal structure, HS-1. For instance, the crystal packing appears much more compact in HS-2 than in HS-1. Such a result is important because the intermolecular contacts are responsible for the cooperativity of the spin crossover phenomenon. Consequently, using the structural parameters in the stable high spin state to interpret the photomagnetic properties may be not adequate.

**References**

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**BEYOND CLASSICAL RIETVELD ANALYSIS USING LE BAIL FITTING**

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The Idea about iterating the Rietveld decomposition formula for  $[F]$ s came during a long night experiment at ILL in 1987. In Le Mans, the method was tested successfully in the ARIT Rietveld. A first structure was determined in 1988 [1], followed by a dozen during the next three years. The algorithm was presented during the IUCr Toulouse satellite meeting.[2] At that time, FULLPROF already included it and after the conference, D.E. Cox wrote and discussed a lot about the algorithm so that it was soon introduced into GSAS. Described in a 1991 review paper by Cheetham and Wilkinson [3], it was called probably for the first time the 'Le Bail method' in the Coppens book[4] or in a structure solution published in Nature (1992)[5]. Structures determined have increased by more than 400% since 1992. Le Bail fitting is considered as standard functionality in any modern Rietveld software and applications include its use in determining the volume of Oxygen in the Earth's outer core.[6]

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**Keywords:** RIETVELD REFINEMENT LE BAIL METHOD CRYSTALLOGRAPHIC COMPUTING