determination, photochemistry coordination compounds

P01.13.86

Acta Cryst. (2008). A**64**, C197

Picosecond crystallography of homogeneous [2+2] photodimerisation reactions

Joerg Hallmann, Jav Davaasambuu, Gerhard Busse, Simone Techert
Max Planck Institute for biophysical Chemistry, Am Fassberg 11, Goettingen, Niedersachsen, 37070, Germany, E-mail：jhallma1@gwdg.de

In the following we will present ultrafast crystallographic studies on the photo-induced single-crystal-to-single-crystal dimerisation of α -styrylpyrylium(TFMS) ($C_{23}H_{29}O_5F_3S$). α-styrylpyrylium(TFMS) is well known as an optical switcher with the ability to be used as a storage device. The mechanism underlying the storage process is a ultrafast [2+2] photodimerisation reaction, which is reversible (higher temperature) or irreversible (lower temperature) implying temporal stability. In this contribution we show the possibility to switch the material between the ground state (monomer phase) and the photoactivated state (dimer phase) in an ultrafast manner with time-scales below 50 ps. The static x-ray diffraction studies have been performed down to electron density resolutions. For the time-resolved studies of the structural dynamics in the solid, picosecond time-resolved crystallography has been employed. Additionally, we discuss the influence of the exciting photon energy on the structural photoswitching of α-styrylpyrylium(TFMS) and its influence on the dimersiation mechanism.

[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. Davasaambuu, G. Busse, S. Techert, , J. Phys. Chem. A 110 (Juergen Troe Festschrift), 3261-3265 (2006).
[4] submitted

Keywords: photodimerization, time-resolved crystallography, organic crystals

P01.14.87

Acta Cryst. (2008). A**64**, C197

Modeling of single molecule imaging by X-ray free electron laser

Gyula Faigel, Gabor Bortel, Zoltan Jurek, Gabor Oszlanyi, Miklos Tegze
Research Institute for Solid State Physics and Optics, X-ray diffraction, POB 49, Budapest, Hungary, H-1525, Hungary, E-mail：gf@szfki.hu

We study the possibility of imaging a small cluster of atoms by short x-ray free electron laser pulses. Since this type of sources are under construction no experimental data is available, which could reliably tell the conditions of successful imaging. Therefore modeling of the experiment and evaluation process is crucial. On the experimental part one of the most important questions is how fast the sample deteriorates in the beam. We have developed a special molecular dynamics model for the description of the Coulomb explosion of the clusters. Using this model we can follow the time evolution of all particles (including atoms, ions, electrons) of the sample. Beside the modeling of samples with different compositions, we also studied the effect of a thin sacrificial temper layer about the sample. We found that with a proper choice of the temper layer the deterioration of the sample can be significantly slowed down. This may help the realization of the planed experiment. Based on the results of molecular dynamics modeling we can calculate the 2D continuous elastic scattering pattern of the sample for a given shot. However, the most often used density modification type algorithms needs 3D data in the reciprocal space. Therefore the full dataset have to be built from scattering patterns of several independent exploding clusters taken at various unknown sample orientations. The first and most critical step in the evaluation process is the classification of the many million 2D patterns into a few thousands of bins. In every bin the sample orientation is the same, so that one can add the intensities of these patterns to improve the statistics to a level where reconstruction is possible. We show the results of our numerical study of the classification process.

Keywords: free electron laser, single molecule imaging, X-ray diffraction

P01.11.88

Acta Cryst. (2008). A**64**, C197

Geometry and resolution of area detectors for X-ray powder diffraction

Bob B He
Bruker AXS, 5465 East Cheryl Parkway, Madison, WI, 53711, USA, E-mail：bob.he@bruker-axs.com

Application of area detectors for powder x-ray diffraction has dramatically increased in recent years due to many advantages, including high speed and better sampling statistics with small samples or textured samples. In high-throughput x-ay diffraction screening, such as pharmaceutical research and discovery, two-dimensional x-ray diffraction is the preferred choice for many users. The Bragg-Brentano (BB) geometry has long been the classic configuration for collecting phase identification data from bulk powder or polycrystalline samples. With the increased usage of area detector, many users have noticed some discrepancies between the diffraction patterns collected with a BB system and an area detector system. In the BB geometry, the 2θ resolution is controlled by the divergence slit, receiving slit and scanning steps of the point detector. With an area detector, the 2θ resolution is mainly determined by the spatial resolution of the detector and the sample-to-detector distance. In order to have the optimum combination of 2θ range and resolution with an area detector, several frames covering different 2θ ranges may have to be collected and merged. The 2θ resolution may vary with 2θ range, sample shape and detector geometry. The relative peak intensity from a textured sample may be different from the results measured with BB geometry. It is imperative to study the nature of these discrepancies so that the diffraction patterns collected with area detectors can be used for phase ID with proper understanding and correction. This presentation compares the conventional Bragg-Brentano diffractometer with diffractometers using area detectors in terms of geometry convention, detector resolution, data collection and processing strategies.

Keywords: area detectors, X-ray powder diffraction, instrumentation

P01.15.89

Acta Cryst. (2008). A**64**, C197−198

Effect of pressure and temperature on the crystallization behavior of As Te glasses with selenium

T K Mondal

Indian Institute of Science, Bangalore, INDIA, INSTRUMENTATION, Dr T K Mondal, Dept of Instrumentation, IISC Bangalore, INDIA, Pin 560012, BANGALORE, KARNATAKA, 560012, India, E-mail：tushar@isu.iisc.ernet.in

$As_x Te_{100-x}$ glasses with $x \leq 40$ show single stage crystallization and those with $x \geq 40$ exhibit a double stage crystallization and at $x = 40$, this is associated with "rigidity percolation" and "chemical stoichiometric ordering". In the present study the effect of pressure on the thermal crystallization of $As_x Te_{100-x}$, $As_x Te_{100-x-y} Se_y$ glasses has been investigated by differential thermal analyzer at high pressure (HP-DTA). For As = 40 and 50 system, in $As_x Te_{100-x}$ and $As_x Te_{100-x-y} Se_y$, the first exothermic peaks are converted to endothermic under pressure and this is considered as rigidity percolation. The second exothermic peak do not converted to endothermic or no structural transformation takes place. This is considered as electron localization to delocalization. In As = 30, 40 and 50 system, as the Se content increases, the volume decreases from the initial value and the shifting of the temperature of the peaks reduces than the basic system because of less structural transformation. Thus it is concluded that the second peak is generated because of the electron localization.

Keywords: glasses, crystallization, coordination

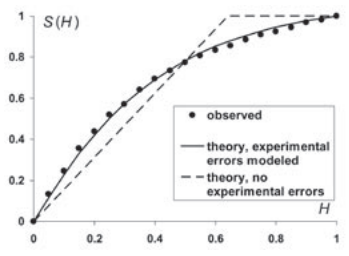
P01.11.90

Acta Cryst. (2008). A**64**, C198

The modelling of experimental errors improves statistical description of merohedrally twinned data

Vladimir Y. Lunin[1], Natalia L. Lunina[1], Manfred W. Baumstark[2]
[1]Institute of Mathematical Problems of Biology, Laboratory of Macromolecular Crystallography, 4, Institutskaya str., Pushchino, Moscow Region, 142290, Russia, [2]Medizinische Universitätsklinik Freiburg, Hugstetter Str. 55, 79106 Freiburg, Germany, E-mail：lunin@impb.psn.ru

An advanced statistical model is suggested, designed to estimate the twinning fraction in merohedrally twinned macromolecular crystals. The model takes into account experimental errors of the measured intensities and is adapted to the accuracy of a particular X-ray experiment through the standard deviations of the reflection intensities. The theoretical probability distributions for the improved model are calculated using a Monte Carlo-type simulation procedure. The use of different statistical criteria (the method of moments, likelihood, chi-square, Kolmogorov-Smirnov criterion) to choose the optimal statistical model is discussed. The improved model enables obtaining better qualitative agreement of theoretical and observed cumulative distribution functions and produces twinning fraction estimates closer to the refined ones in comparison to the conventional model, which disregards experimental errors. Cumulative distributions for Yeates's statistic H are shown below for Low Density Lipoprotein data. The work was supported by RFBR and DFG grants.



Yeates, T. O. (1988). Acta Cryst. A44, 142-144.
Lunin V.Y., Lunina N.L., Baumstark M.W. (2007). Acta Cryst.. D63, 1129-1138.

Keywords: merohedral twinning, statistical modelling, likelihood

P01.11.91

Acta Cryst. (2008). A**64**, C198

Statistical properties of measured X-ray intensities affected by counting loss of detection system

Takashi Ida, Akihisa Oya, Hisashi Hibino
Nagoya Institute of Technology, Ceramics Research Laboratory, Asahigaoka 10-6-29, Tajimi, Gifu, 465-0097, Japan, E-mail：ida.takashi@nitech.ac.jp

Counting methods are widely used to measure the intensity of X-rays. Statistical errors of measured intensities are usually assumed to be equal to the square root of the observed number of counts, because independently generated signal pulses obey the Poisson distribution, where the statistical variance is exactly identical to the average number of pulses. However, the intensity measured with a realistic counting system does not strictly obey the Poisson distribution because of finite response time of the detection system. Statistical properties of two conventional theoretical models for counting loss, non-extended and extended deadtime models, examined by Monte Carlo simulations, have shown that statistical variances as well as means deviated from those predicted by the Poissson model are well approximated by simple mathematical formulae [1]. In this study, experimental evaluation of statistical variance of counted pulses based on a repeated Chipman's method [2] has been conducted for a laboratory powder x-ray diffractometer (Rigaku RAD-2C) and a synchrotron powder diffractometer (KEK-PF BL-4B2 MDS system). The dependence of the observed average count on the expected count rate has been rather well fitted by an intermediately extended deadtime model [3] than the conventional models. It has been suggested that the statistical errors of the observed counts can also be predicted by applying the intermediate model, assuming hypothetical series of detection components with non-extended and extended deadtime characters.

[1] T. Ida, J. Appl. Cryst. 40, 964 (2007).
[2] D. R. Chipman, Acta Cryst. A25, 209 (1969).
[3] T. Ida & Y. Iwata, J. Appl. Cryst. 38, 426 (2005).

Keywords: counting loss, statistical error, counting method

P01.15.92

Acta Cryst. (2008). A**64**, C198–199

The XtalFinder imaging system

Erik Brostromer, Jie Nan, Xiao-Dong Su
Peking University, College of Life Sciences, College of Life Sciences R417, Peking University, Beijing, Beijing, 100 871, China, E-mail：brostromer@gmail.com

The XtalFinder is an automated imaging system for collecting crystallization results from SBS format (48-, 96-, 192-, 384-wells) microplates. The system has previously been described [1]. Our recent updates include: A mono microscope for straight viewing angle of the sample; An LED cold light source with center and radial intensity control, to improve the contrast and sample illumination for multiple sample types; A new software version with a more user-friendly graphical interface and simpler, straight forward, functions; Use of a third party software for Z-batching of multiple images (slices) of the same drop, with different focus levels, to generate one focused image per collected drop. For future developments, algorithms and software to automatically recognize crystals or potential crystalline states are underway.

References:
1. Brostromer E, Nan J, Su XD. "An automated image-collection system for crystallization experiments using SBS standard