WORKSHOPS

The Impact of New Detector Technology on Synchrotron Macromolecular Crystallography

Malcolm Capel
(Brookhaven National Laboratory, Biology)

The goals of the workshop, held on May 19, 1997, was to summarize recent developments in imaging x-ray detector technology (predominantly CCD's) and to discuss issues related to their capabilities and performance in regard to macromolecular crystallography as practiced at x-ray synchrotrons. Leaders in the fields of CCD detector, crystallography software and x-ray beamline development gave presentations to an audience of approximately 45 registered attendees.

Ed Westbrook, director of the Structural Biology Center (SBC) at Argonne National Laboratory discussed the status of the Advanced Photon Source Sector 19 SBC beamline and its 3x3 CCD array detector, developed jointly by the SBC and Steve Naday of ANL's Electronics and Communications Technology division. This detector (known as the APS-1) is constructed from 9 CCD-optical fiber taper cells, and has an active area 20x20 cm in size, with 3000 x 3000 pixels, reads out in 3.3 seconds and is capable of resolving approximately 280 diffraction orders from protein crystals. The SBC beamline presently is capable of producing a beam with a flux of 3×10^{15} monochromatic photons/second/mm^2 (0.01 % bandpass). Complete, fine phi-sliced rotation data sets can be acquired from lysozyme in about 20 minutes with merging statistics around the 2-3% level.

Bob Sweet (NSLS X12C, BNL Biology) provided a synopsis of the design and working principals of the mosaic CCD crystallography detector design and a historical summary of various CCD detectors trialed at the NSLS X12C crystallography beamline. Marty Stanton (Brandeis University) described his group's CCD detector development with special emphasis on a programmable CCD controller/sequencer designed by his group for dynamical diffraction studies with muscle. Eric Eikenberry (Princeton University) discussed design and testing of a prototype solid-state pixel-array detector, the likely successor technology to CCD's in crystallography and synchrotron-based diffraction studies.

The afternoon session of the workshop was dedicated to discussion of software topics. The high speed, resolution and sensitivity of CCD detectors have forced the redesign and optimization of crystallography data collection and reduction software packages, originally written to handle crystallographic data from storage phosphor image plate systems. Jim Pflugrath of Molecular Structures Corporation demonstrated his new display, indexing and integration suite called d*trek, developed under DOE contract with the SBC. Sbeyzek Otwinowski (South Western Medical Center) reviewed the progress of the DENZO data reduction and control package with emphasis on data quality and experimental design. Malcolm Capel (NSLS X12B, BNL Biology) described the Linux/Beowulf clustering system used to produce high-performance (Gflops) low-cost (< $100k) multiprocessor systems for acquisition, reduction and storage of CCD crystallographic diffraction data. ■

WORKSHOPS

Biological and Chemical Applications of EXAFS Spectroscopy

Dr. Mark R. Chance
(Albert Einstein College of Medicine)

A workshop entitled "Biological and Chemical Applications of EXAFS Spectroscopy" was held at the National Synchrotron Light Source on May 21, 1997. EXAFS is one of the most widely used techniques at the NSLS and the presentations highlighted recent research from four of the major groups performing EXAFS at the facility. The first presentation however, was from Dr. Frank de Groot of the University of Gronigen entitled "Multiplet Effects in Core Level Spectroscopies". The interesting initial question answered by Dr. de Groot concerned the necessity of multiplet analysis. It is well known that single scattering can work well in describing spectral data. In the case of L-edge spectroscopy, the 2p-3d interactions are very strong and the single particle approximation breaks down. Dr. de Groot provided a description and an analysis of results using atomic multiplet theory, where electron-electron interactions determine the multiplets and spin-orbit couplings determine the fine structure. Introduction of crystal field splittings provided satisfactory molecular simulations providing values of ligand field strength, high or low spin and valency. Further information on the programs is available at http://vsf1.phys.rug.nl/~degroot.

Professor Dale Sayers from North Carolina State University, gave a talk entitled "XAS Determination of Chemical Speciation of Heavy Metals". Dr. Sayers' presentation highlighted the magnitude of the environmental problem presented by heavy metals and the keen ability of XAS to probe the structure of these metals in soil samples. The first example determined the efficacy of hydroxyapatite treatment in the remediation of lead in soil samples, which can successfully sequester the lead as an insoluble form. A second analysis of lead waste from batteries determined the degree of conversion of lead oxide to lead sulfide forms (the latter being relatively insoluble). XAS was very powerful in determining the metal environment. Dr. Sayers also briefly spoke about the International XAS Society, more information can be found at http://ixs.iit.edu

Professor James Penner-Hahn of the University of Michigan gave a talk entitled "Structural Characterization of Organometallic Reagents", providing interesting results refuting the presumed existence of higher order cuprates and providing a better understanding of phenyl copper complexes with very precise titration data.

Professor Mark Chance from the Albert Einstein College of Medicine illustrated a number of applications of FEFF to analyzing structure in biological systems. A program called AUTOFIT 1.0 was outlined that can automatically iterate crystal structure data, simulate the resultant FEFF spectra, and compare the simulations to experimental data in order to map different possible solutions in an evenhanded fashion. Further information on the programs can be found at http://beam.aecom.yu.edu/phys&bio/csb1.htm

Ms. Lijun Shu from the University of Minnesota finished the talks with a discussion of "Diamond Core" structures (Fe_2O_2) in enzymes like methane monoxygenase and ribonucleotide reductase. The Fe-Fe distances for some of the high valent intermediates were as short as 2.4 Å.

Lastly, Dr. Lars Furenlid of the NSLS provided a demonstration of the 100 element solid state detector that was set up at beamline X9B on the NSLS floor. As the workshop attendees clustered about the beamline we were immensely impressed with the miniaturization of the detector elements (30-40 times smaller than conventional solid state detector elements). ■

WORKSHOPS

X-ray Computed Microtomography : Applications & Techniques

Betsy Dowd
(Brookhaven National Laboratory, NSLS)

The availability of synchrotron X-ray sources to the scientific community sparked the first explosion in the development of the field of X-ray Computed Microtomography (XCMT). More recently, technological advances in two-dimensional detector arrays, combined with the recent boom in available parallel architecture computing technology, have lifted the XCMT field to another level. Talks at this workshop highlighted the impact of these technological advances on a variety of applications of XCMT, from the medical to the metallurgical fields.

A detailed synopsis of the rapid progression of Exxon's X-ray CMT facility at the NSLS over the past 15 years, in parallel with improved detector, processor, and 3-D visualization technology, was given by John Dunsmuir (Exxon Corp.). John and his team now routinely use XCMT to characterize reservoir sandstone pore geometries.

Per Spanne (ESRF) discussed XCMT applications and advances at the ESRF. By parallelizing 16 computers, the group at ESRF has significantly reduced the reconstruction time for tomographic volumes. Per and his colleagues at the ESRF have also used the high coherence of the ESRF X-ray source to make phase contrast CMT measurements.

Chris Jacobsen (SUNY, Stony Brook) presented schemes for soft X-ray submicron resolution tomography. Zhong Zhong (NSLS) and Avraham Dilmanian (BNL, Medical Dept.) proposed a plan for Diffraction Enhanced Computed Tomography for biological tissue characterization.

The present status and recent applications of the XCMT facility developed by the NSLS were reported by Betsy Dowd (NSLS). The versatility of this developing user facility was emphasized by the variety of tomographic volumes generated. Among these are reservoir sandstones (Mobil Corp.), basalts (Sahagian, Univ. of N.H., Song, National Taiwan Univ.), porous metals (Schulte, Northrop-Grumman Corp.), and plasma-spray coatings (Herman, SUNY, Stony Brook). Barbara Illman (USDA/ FS Forest Products Lab., U. of Wisconsin) has obtained CMT volumes of beetles and wood at this facility and spoke about her application of CMT to the study of fungal deterioration of wood. Sheng-Rong Song (Geology Dept., National Taiwan U.) spoke about his investigations into volcanic rock, using CMT data he collected at the NSLS facility.

Brent Lindquist (SUNY, Stony Brook) gave an entertaining and informative tutorial on his 3-D Medial Axis (3DMA) program he developed to characterize the pore geometries from tomographic data of rocks. For the final talk by Ballard Andrews (BNL-Computing & Communications Division) , our group moved to the 3D visualization theater at BNL, where each participant donned a pair of polarized glasses, and relaxed to enjoy a stereo demonstration of some tomographic data collected at the NSLS. In addition to demonstrating this impressive facility, Ballard enlightened us with his knowledge of 3-D visualization and rendering techniques, and applications of IBM Data Explorer to viewing and analyzing tomographic data. ■

WORKSHOPS

Inelastic and Resonant Inelastic X-Ray Scattering

Chi-Chang Kao
(Brookhaven National Laboratory, NSLS)

Inelastic x-ray scattering has long been recognized as a potentially important experimental probe of electron and lattice dynamics in condensed matter systems. Recently, several dedicated high resolution (total energy resolution from 0.1 eV to 1.0 eV) and ultra-high resolution (total energy resolution from 1 meV to 10 meV) inelastic scattering beamlines have become operational around the world. The latest experimental results from these beamlines as well as various theoretical aspects of inelastic x-ray scattering were reported at the workshop.

Denis McWhan (BNL) opened the workshop by giving a brief review of the major steps in the development of inelastic x-ray scattering. The relationship between inelastic x-ray scattering and inelastic scattering of visible light was discussed by Miles Klein (University of Illinois-Urbana/Champaign). Although he found little analogy between the two techniques, he did suggest several areas in which inelastic x-ray scattering might provide new information. He also reported recent visible light scattering studies on high temperature superconductors and related compounds.

Inelastic x-ray scattering studies of many-body correlation effects in simple metals were reported by Ben Larson (Oak Ridge National Lab.) and John Hill (BNL-Physics). Ben Larson found that the measured local-field factors of Al are significantly larger those that obtained from a first principle theoretical calculation. To resolve a long standing controversy over the origin of the double-peak feature in the inelastic scattering spectra of many materials, John Hill reported an inelastic x-ray scattering study of solid and liquid Li and Na, in which spectral features from band structure effects are separated from those due tomany-body effects.

There were also several talks on resonant Raman scattering, or resonant inelastic scattering, studies on highly correlated systems. John Hill along with Eric Isaacs (Bell Laboratories) reported recent Cu K-edge resonant inelastic study of Nd_2CuO_4 and $Sr_2CuO_2Cl_2$, respectively. Trever Tyson (New Jersey Institute of Technology) presented high resolution Mn K-beta emission spectra of a series of doped $LaMnO_3$ compounds. On the theory side, Frank de Groot (University of Groningen, The Netherlands) presented an atomic-multiplet based model calculation for resonant Raman scattering. Very good agreement between theory and experimental results, ranging from soft-x-ray to hard-x-ray, were shown.

In addition to the works done at the NSLS, Francesco Sette of the European Synchrotron Radiation Facility (ESRF) reported an ultra-high resolution inelastic x-ray scattering study of the high frequency collective dynamics of disordered systems, a region in the energy-momentum phase space that cannot be accessed by inelastic neutron scattering. The status of the inelastic scattering beamline at the Advanced Photon Source (APS), and first results were reported by Albert Macrander.■

WORKSHOPS

Materials Characterization with Hard and Soft X-ray Reflectivity

Michael Toney
(IBM Almaden Research Center)
Yves Idzerda (Naval Research Lab)

Specular and diffuse X-ray reflectivity are popular methods for characterizing a variety of materials, including organic thin films, magnetic films and surfaces, and semiconducting materials. This motivated a one day workshop held May 19, 1997 in conjunction with the NSLS Users' meeting. The purposes were to gather together novices and experts to discuss these methods and their applications, to educate newcomers on the power of these methods, and for the NSLS reflectivity community to discuss building an endstation dedicated to reflectivity.

Professor Carol Thompson (ANL and Northern Illinois University) kicked off the workshop with an introduction to X-ray reflectivity, including a description of questions that could (and could not) be addressed and of important experimental requirements, such as spectrometer and sample alignment. She also emphasized that hard x-rays can be used under ambient conditions (e.g., in an electrolyte). Examples were given of layering of smectic liquid crystals on glass and of *in situ* swelling of PMDA-ODA in NaOH.

Paul Mansky (U. of Massachusetts) compared and contrasted x-ray reflectivity with neutron reflectivity as applied to organic thin films. The advantages of isotopic substitution (D for H) were demonstrated, and the complementarity of using both x-ray and neutron reflectivity was illustrated. Data for polymer brushes (polymers bound to a surface at one end) showed how the polymers swelled with increasing temperature, consistent with theory. Paul also described studies of islands in di-block copolymer systems.

This was followed by Eric Chason's (Sandia National Lab.) talk on *in situ* reflectivity studies of the evolution of thin film and surface morphology. Eric described an energy dispersive technique for time resolved measurements (ca. 250sec data collection time). He illustrated several examples, including compound formation during Al deposition on Cr/quartz, the formation of pits in porous silicon, the CVD growth of Fe on Si(100), and the surface roughening (smoothing) of quartz during ion bombardment with Xe (He). There was discussion of the possible advantages of synchrotron radiation for such studies and of the need for detectors with higher throughput.

After a break for an enjoyable lunch and a change in energy range, Jack Rife (Naval Research Lab.) talked about UV and soft x-ray reflectance characterization of semiconductor materials. He explained the technique and described the X24C reflectance setup. He then reviewed the application of this method to GaN and compared the experiments to theory with favorable agreement. This was followed by studies of radiation damage in SiO_2 through bombardment with 5eV neutral oxygen atoms (motivated by etching of surfaces of the space shuttle in low earth orbit).

Gavin Watson returned to the hard x-ray regime with a discussion of x-ray resonant magnetic reflectivity. After describing the technique and emphasizing that it is a resonant method, Gavin described the near-surface, antiferromagnetic ordering in UO_2(001) and how this differs from bulk ordering. Gavin also showed how this method could be used to understand the magnetism on Pt in Co_3Pt, and in a brief excursion to lower energies, showed how the magnetic roughness in Co/Cu multilayers was less than the atomic roughness.

The emphasis on third row transition metals was continued by John Freeland (NSLS, U4B) whose talk was entitled “Materials Characterization with Resonant Soft X-ray Scattering”. John explained how this method was related to x-ray circular dichorism and resonant x-ray scattering and how it could be used to obtain magnetic and atomic thickness and roughness. He showed the huge enhancements in cross sections that could be obtained for third row transition elements and described studies of switching in NiFe/Co sandwiches. This was followed by determinations of magnetic and chemical roughness in single Co films and CoFe multilayers.

Near the end of the workshop, there was discussion of a possible endstation dedicated to reflectivity. In this arrangement, the NSLS would provide x-rays up to the hutch and the interested users would fund construction of the endstation. Jerry Hastings (NSLS) explained what had been done by the polymer SAXS community on X27C, and several speakers (Thompson, Watson, Evans-Lutterodt) described what they would like for such a reflectivity endstation. This would cost the interested users approximately $200,000 or more, and with enough support, could be constructed. After much discussion, it seems there is insufficient funding in the user community present at the workshop (either academic or industrial) for the construction of such a beamline/endstation, although some NSLS staff members are actively interested in collaborating on reflectivity experiments and instrumentation. ■