NSLS 2001 Annual Users' Meeting Workshops

Advanced Methods and Tricks of EXAFS Data Modeling

With the development of the *ab initio* theories and data analysis techniques, the EXAFS method is evolving into a routine materials characterization method, on a par with other well established structural techniques. The goal of this workshop was to demonstrate how to make the most use of the experimental EXAFS signal via smart modeling and yet not to overinterpret the data. In addition, many typical mistakes in the data analysis and some common examples of unphysical interpretations of the data, which are often overlooked, were discussed. The workshop attracted 77 participants, the largest audience of EXAFS workshops at the NSLS to date, reflecting the growing interest among physicists, materials scientists, chemists, biologists, environmental scientists and engineers to be up to date with modern techniques of EXAFS data modeling, beyond the trivial first-shell analysis. All presentations may be downloaded from the workshop web page: http://pubweb.bnl.gov/people/frenkel/workshop.html.

In the first talk, "Avoiding Some Pitfalls in XAFS Analysis," Professor Edward A. Stern (University of Washington) emphasized the importance of being able to eliminate the false models and to assess correctly the errors in the model. He discussed physical conditions the correct model should satisfy, such as limitations on spatial resolution, positive sigma squared and minimum bond distances. The importance of including systematic uncertainties in estimating the errors in the final model was also emphasized.

Professor Alain Michalowicz (University of Paris XII) gave a talk entitled: "2π-Shift and Ligand-Swapping EXAFS Modeling Tricks in Applications to Catalysis and Biology." In his talk, he showed how EXAFS modeling can lead to systematic artifacts and erroneous nearest neighbor distances. Some of the examples discussed the possibility of obtaining incorrect ΔE_0 values and associating with them false distances. He also demonstrated the power of the ligand-swapping method allowing the elegant structure refinement of the metallic site of metalloenzymes that frequently contain inequivalent axial and equatorial ligands.

The next speaker, Dr. Stephen R. Wasserman (MediChem Life Sciences), in his talk "Principal Component Analysis: Getting an Edge on EXAFS," supplemented the traditional EXAFS analyses approaches to phase speciation problems through a global view of speciation within the entire series of spectra.

For many inorganic crystal structures, the bond valence model gives a simple and accurate prediction of bond distances given cation and anion type, valence and coordination number. Dr. Matthew Newville (University of Chicago), in his talk on "The Use of Bond Valence Sums in XAFS Analysis," demonstrated that the bond valence model can be used as a reality check on the results of fitting XAFS data for a wide class of systems.

Professor James E. Penner-Hahn (University of Michigan, Ann-Arbor) gave a talk entitled "X-ray Absorption Spectroscopy of Zinc Sites in Proteins—When is a Tetrathiolate not a Tetrathiolate?" Jim demonstrated how, by carefully controlling the number of variable parameters, to obtain an accurate determination of Zn ligation in proteins, namely to distinguish between the cysteine ligands and the low-Z ligands (histidine, carboxylate, water). This problem has been previously regarded as being extremely difficult to solve unambiguously, i.e., to distinguish between the sulfur/nitrogen ligations.

Dr. Bruce Ravel (Naval Research Laboratory), in his talk on "Robust Structural Modeling Using Multi-Edge Refinements," discussed one of the most important tools from the EXAFS bag of tricks, the multi-edge refinement. Many materials have two or more edges accessible to an EXAFS measurement. Bruce demonstrated how data, collected from all accessible edges and refined simultaneously, yielded more and better results than those available from the analysis of individual edges.

Professor Ralph G. Nuzzo (University of Illinois, Urbana-Champaign) highlighted modeling methods useful for the EXAFS characterization of nanoscale materials in his talk "Emergence of Materials Properties at the Nanoscale." Through the combination of the multiple-scattering analysis and constrained fits of monometallic and bimetallic, supported nanoparticles, their size, shape, crystal structure, surface orientation and non-statistical distribution of atoms within the particles were reliably established.

Dr. Daniel Haskel (Argonne National Laboratory) discussed several analysis methods making use of the polarized nature of synchrotron radiation in his talk "XAFS in Anisotropic Structures: Exploiting Angular Dependence for Better Modeling." He reviewed the origin of such angular dependence and discussed sample requirements needed to observe it. His talk combined practical examples with the elegant excurses to the basics of EXAFS theory. ■

Acknowledgement

Research carried out (in part) at the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Division of Materials Sciences and Division of Chemical Sciences.

ANATOLY I. FRENKEL
Frederick Seitz Materials Research Laboratory, University of Illinois at Urbana Champaign
Present Address: Physics Department, Yeshiva University