Commission on XAFS

THE IUCR COMMISSION ON XAFS: ROADMAP AND 2018 ACTIVITIES

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Keywords: X-ray Absorption Spectroscopy, electronic structure, local order, long range order, instrumentation.

Abstract

There are many successes in XAS by groups in experiment and theory across the world and there are many new insights to come. We discuss some of these successes, promising directions and new avenues including those in which the Commission is participating.

Introduction

XAFS is an acronym standing for X-ray Absorption Fine Structure, and refers to the oscillatory behaviour of the absorption cross section above an absorption edge in condensed matter. XAFS spectroscopy uses X-rays and provides atomic selective local order and electronic information on a large variety of materials encompassing crystalline and amorphous solids, liquids or gases.

The Commission on XAFS (CXAFS) was founded more than 20 years ago in 1996 at the XVII IUCr Congress in Seattle. The main aim of the CXAFS is to create a bridge between XAFS and Crystallographic communities. In fact, while XAFS provides details about the electronic state, local coordination chemistry and atomic structure around the absorber in the few Å scale, diffraction techniques describe the crystallographic structure of long range coherent phases. Therefore, these techniques can be very successfully combined to achieve full and reliable understanding of the physico-chemical properties of complex systems.

While the Commission title is XAFS, the broader reach of XAS (X-ray Absorption Spectroscopy) in all its forms, including transmission and fluorescence experiments, X-ray Emission Spectroscopy and Electron Yield, RIXS (Resonant Inelastic X-ray spectroscopy) and HERFD (High Energy Resolution Fluorescence Detection) provides a very rich and indeed complex dialogue. There is a strong overlap between X-ray crystallography and XAS in the Multiple Wavelength Anomalous Dispersion (MAD) techniques, and DAFS (Diffraction Anomalous Fine Structure) is the Kramers-Kronig transform of XAS.

The terms of reference of CXAFS are stated at the webpage
https://www.iucr.org/resources/commissions/xafs.
Particularly, the CXAFS wishes to promote international cooperation between researchers using principally XAS techniques and other IUCr commissions who have the common goal of understanding the structure of matter and its structure-property relationship. This implies an interaction and coordination among researchers who are involved in XAS or XRD techniques by sharing common microsymposia at IUCr Congresses in relevant scientific fields such as catalysis, energy storage, cultural heritage, life science to cite only a few. Its roadmap is also to promote the use of XAS by teaching advanced methods of measurement and analysis and to develop among the communities standards and criteria in order to improve the overall quality of the research being performed in the field. This later encompasses cooperation with other IUCr commissions in establishing adequate guidelines and standards for articles to be published in IUCr journals reporting structural investigations of materials by XAS. The coordination of a database on XAS is also one of the key aims of the Commission together with the promotion of inter-facility comparison of the results gained at different beamlines in order to evaluate the influence of data quality on the extracted structural parameters [1] . A round robin activity is now preparing to be launched across many major facilities with great support from many synchrotrons and XAFS beamlines. CXAFS is finally also involved in advising the IUCr on organizing or sponsoring sessions on XAFS at congresses and in interacting with organizing committees of the International XAFS society to contribute to the organization of the triannual International XAFS meetings.

The organization of recurrent two-day format meetings on improving data quality in XAFS spectroscopy as satellite workshops to the main IUCr Congresses is one of the activities of the Commission in the field of standardization of methods and analysis. Three international workshops were already organized in the past: in Tsukuba (Japan) in 2011 [2], in Hamburg (Germany) in 2015 and the last one, at Diamond Light Source (UK) in 2017 [3]. CXAFS is working in the preparation of the fourth meeting in the series. The purpose of those meetings is to share expertise of active XAFS researchers for discussing several factors on new theory, new technology, advanced data collection and analysis which could be optimized to achieve good quality data and reliable structural parameters from XAS analysis. A special issue in J Synchrotron Rad. has been recently published with the outcome of the discussions held at the Q2XAFS2017 meeting [3].

XAS: a key role in so-many studies of materials and recent achievements.

XAS has particularly benefitted from the unique properties of synchrotron radiation (SR) such as a broad photon energy range and the high brilliance. The availability of X-ray absorption spectrometers at synchrotron light sources around the world has contributed greatly to the popularity

and success of XAS, that over the last four decades has progressed from being a technique only suitable for specialists to becoming a tool applicable to many scientific disciplines.

In situ studies: The high brilliance of SR sources together with the development of proper samples environment have made in situ studies possible. In these the spectra are recorded as a function of external stimuli such as temperature and/or pressure, or electric and magnetic fields. This implies sometimes bulky environments such as in high pressure research where the samples in most of the cases are placed between two diamond anvils. In this particular field XAS has emerged as a crucial probe to understand the local and electronic structure in compressed matter [4, 5].

Operando XAFS: The high brilliance of third generation SR sources has allowed data collection with a time frame down to milliseconds [6, 7] and also to the sub-μs range [8]. The significant *shortening of data collection* in the past decade allows time-resolved studies of dynamic processes, looking at the materials in working conditions. For instance XAS can be used to monitor the active phases in catalytic reactions [9], and in batteries the phase transformation and the redox chemistry [10, 11] providing unique insights for the development of powerful materials used in our daily life.

Biomedical and Life Sciences: The chemical selectivity of XAS, permitting selection of a specific element and orbital to study in a complex sample, together with the *high level of detection* provided today with efficient high counting rates fluorescence detectors, is one of the great strengths of the technique for many fields. In life sciences, for instance, XAS has been shown to be very powerful for shedding light on the bindings of metals such as copper or zinc with amyloid-β peptides and the monitoring of change of coordination of metallic centres during the aggregation process of amyloid-β peptide leading to the formation of senile plaques responsible for the Alzheimer's disease [12-14].

Data analysis: The increasing use of XAS is also linked to the continuous effort in the development of data analysis. In the pioneering work of D. E. Sayers, E. A Stern and F. W. Lytle [15] , the structural parameters determined from XAFS measurements were gained from the EXAFS analysis based on Fourier Transformed peak isolation and further simulation within the one-electron single scattering approximation. Later on, *ab-initio* theoretical approaches based on multiple scattering calculation have been introduced [16-20]. In the early days, the analysis of the XANES part of the spectra was essentially done on the basis of fingerprint identification. The improvement of computational capabilities and the development of more sophisticated codes for the calculation of the final state wave function of the photoelectron entering in the calculation of the absorption cross section has progressively made XANES a powerful spectroscopy passing from qualitative to quantitative in nature [21-23].

XANES and XAFS theory: On the basis of XANES calculations, the experimentalist can today quantitatively confirm or discard a structure, gaining structural parameters with high reliability and accuracy, and sometimes unique when dealing with extra-dilute metal centres in a protein or a catalyst for instance. This improvement in XANES analysis is crucial when the dilution of the photoabsorber prevents recording a high S/N ratio EXAFS data over an extended photoelectron wavevector *k*-range necessary for accurate EXAFS analysis. The new FDMX [21, 22] and other approaches are now working towards new theory able to model both the EXAFS and XANES regions to gain new information and more accurate physical parameters. In addition, the progress in *ab-initio* calculations of XANES spectra offers today matter to the development of machine-learning methods based on the computational modelling of several hundred thousand model structures and the teaching by the computers of a neural network allowing to establish a relationship between spectral XANES features and structural characteristics [24].

Databases: Operando studies mentioned above, such as the investigation of a catalytic reaction or of a charge-discharge of a battery leads to the recording in a couple of minutes of a huge amount of data for which the classical fitting analysis procedure reaches limits. In these cases statistical methods must be employed. The use of multivariate data analysis, and in particular the so-called Multivariate Curve Regression with Alternating Least Square (MCR-ALS) fitting method allows to isolate from the experimental spectra the spectra of pure species involved in the reaction and their concentration profiles according a bilinear decomposition which is formally the expression of the Beer-Lambert law at which XAFS spectroscopy obeys [25-26]. Even in this case machine learning approaches were also used recently to create a database of computed reference spectra which will help the experimentalist for the identification of unknown compounds, which could be for instance very helpful for the interpretation of MCR-ALS extracted species [27]. As observed today with the huge increase in the number of spectra to analyse, as the consequence of *operando* or fast experiments, and more so tomorrow with the diffraction-limited storage ring, the community will face major increases in number of both spectra and images to analyze. Multivariate data analysis and machine learning approaches will be invaluable and powerful skills for helping the researcher to extract the useful information from the data.

Information Content: Related exciting methodology developments lead to greater information content and new structural and dynamic insights onto materials. In particular, an improved understanding of uncertainties and their propagation allows the evaluation of subtle features and discrimination between models with e.g. the same coordination number, when high quality data are provided [28]. Novel techniques such as XERT and Hybrid [28-30] have pushed the sensitivity of transmission XAFS to 10 mM and 1.5 mM; and similarly shown new structure in fluorescence XAFS.

Spatial Resolution: Considering the progress of the techniques in lowering detection limits and improving the ability to retrieve information from the data, XAS is ready to face the planned upgrades at several major facilities [31]. Due to the expected decrease of source sizes towards dif-

fraction limit values, imaging techniques based on X-ray absorption process (STXM, TXM at the nanometer scale and μ-microspectroscopy) will be boosted dramatically with better spatial resolution and better time resolution for spectral acquisition [32].

One other exciting area of new inquiry is the pursuit of identifying that different modalities of XAS measurement (transmission, fluorescence, grazing incidence; and the selection of the edge for investigation) in fact have different information content permitting the technique to be more tailored to the question or physical parameter of direct interest in an inquiry. This will be an exciting topic for future understanding.

Recent Activity of CXAFS

Activity of the CXAFS in 2018 particularly included active participation of the XAFS international conference and preparation for the 25th IUCr Congress in Prague (Czech Republic).

1. At the XAFS 2018 Conference held at Krakow (Poland) from the 22th to the 27th of July 2018, two events were co-organized. A one-day workshop on Advances in XAFS Experimental Techniques with a special emphasis on the advent of 4th generation light sources was co-organized by Hiroyuki Oyanagi (IXAS) and Steve Heald (CXAFS). A CXAFS/IXAS joint session (2h30), chaired by Chris Chantler, in the regular program of the XAFS2018 conference was also organized with 4 lectures given by Farideh Jalilehvand, Peter Krüger, Hidekazu Ikeno, Ryan Trevorah covering reactivity of antitumoral Rh complexes, new developments within the ligand field multiplet theory for L edge absorption and RIXS and RIXS-XMCD spectra calculations and robust self-absorption correction methods for fluorescence data.

2. During the XAFS 2018 Conference, a meeting of the CXAFS commission was held with the participation of 9 members out of the 10 members, 3 consultants out of 5 and two invited visitors (Matt Newville (future chair of the Q2XAFS workshop) and Wojtek Kwiatek (chair of XAFS 2018)). The main topic discussed during this meeting was the preparations for the next IUCr Congress which will be held at Prague from the 22th to the 30th of August 2020. The detailed programme of the Microsymposia and Keynote nominations proposed by the CXAFS commission will be submitted to the International Programme Committee (IPC) by the 15th of March 2019 and presented by our IPC member Giuliana Aquilanti during the IPC meeting connected with the workshop "Current Trends and Future of Crystallography" that will be held in May 2019 in Prague. We also discussed the Workshop and next Q2XAFS meetings. C Chantler also encouraged the IXAS to remember fallen colleagues including Ed Stern, Mark Ridgeway and others in celebration of their science, areas of research and achievements. C Chantler attended the IXAS exec meeting as the IUCr Observer, a relation which we have been encouraging for mutual assistance.

3. IUCr International Tables for Crystallography Volume I: XAFS Federico Boscherini, Bruce Ravel and Chris Chantler have been working very hard and energetically on the International Tables. Most of the chapters have been received and reviewed. An update of references could be asked to the authors who have submitted chapters at the very beginning of the process. We are still receiving good and authoritative chapters and everyone is being fully refereed, and usually revised.

4. Conference Support and Proposals: CXAFS makes priorities about the meetings, workshops etc. for which the commission wish to receive funding support from IUCr. Current priorities are 25th IUCR Congress related activities, ie. the Workshop which will be held at the coming IUCr Congress; and the Workshop and Q2XAFS satellite. The next International XAS Conference which will be held in 2021 in Australia.

5. IXAS Newsletter: IXAS encourages and welcomes CXAFS to contribute to the IXAFS newsletter with anything about meeting, joint activity, commission activity, Q2XAFS or other important and interesting topics.

6. IUCr Journals: IUCr has sent a new directive in which each commission should publish in IUCr journals, [at least] once every three years. CXAFS has published in the Journal of Synchrotron Radiation a special issue with 10 publications related to the Diamond Q2XAFS meeting (J. Synchrotron Rad. (2018). 25,), following the satellite of the 24th IUCr Congress at Hyderabad (India). Additionally, Sofia and Richard have prepared a summary of the Q2XAFS meeting and outcomes.

References

1. C. T. Chantler, B. A. Bunker, H. Abe, M. Kimura, M. Newville, and E. Welter, "A call for a round robin study of XAFS stability and platform dependence at synchrotron beamlines on well defined samples," *J. Synchrotron Radiat*., vol. **25**, no. 4, pp. 935–943, 2018.
2. I. Ascone, K. Asakura, G. N. George, and S. Wakatsuki, "International workshop on improving data quality and quantity for XAFS experiments (Q2XAFS 2011)," *J. Synchrotron Radiat.*, vol. **19**, no. 6, pp. 849–850, 2012.
3. S. Diaz-Moreno and R. W. Strange, "Third International Workshop on Improving Data Quality in XAFS Spectroscopy, Q2XAFS2017," *J. Synchrotron Radiat*., vol. **25**, no. 4, pp. 918–919, 2018.
4. G. Aquilanti, O. Mathon, and S. Pascarelli, "Achievements in high-pressure science at the high-brilliance energy-dispersive X-ray absorption spectrometer of ESRF, ID24," *J. Synchrotron Radiat.*, vol. **16**, no. 6, pp. 699-706, 2009.
5. G. Aquilanti et al., "Melting of iron determined by X-ray absorption spectroscopy to 100 GPa," *Proc. Natl. Acad. Sci*., vol. **112**, no. 39, pp. 12042–12045, 2015.
6. O. Müller, M. Nachtegaal, J. Just, D. Lützenkirchen-Hecht, and R. Frahm, "Quick-EXAFS setup at the SuperXAS beamline for in situ X-ray absorption spectroscopy with 10ms time resolution," *J. Synchrotron Radiat*., vol. **23**, pp. 260–266, 2016.
7. V. Briois et al., "ROCK: The new Quick-EXAFS beamline at SOLEIL," *J. Phys. Conf. Ser.*, vol. **712**, no. 1, 2016.
8 S. Pascarelli et al., "The Time-resolved and Extreme-conditions XAS (Texas) facility at the European Synchrotron Radiation Facility: The energy-dispersive X-ray absorption spectroscopy beamline ID24," *J. Synchrotron Radiat.*, vol. **23**, pp. 353–368, 2016.

9. A. R. Passos, C. La Fontaine, L. Martins, S. H. Pulcinelli, C. V. Santilli, and V. Briois, "Operando XAS/Raman/MS monitoring of ethanol steam reforming reaction-regeneration cycles," *Catal. Sci. Technol.*, vol. **8**, no. 24, pp. 6297–6301, 2018.
10. R. Dominko et al., "Polysulfides Formation in Different Electrolytes from the Perspective of X-ray Absorption Spectroscopy," *J. Electrochem. Soc.*, vol. **165**, no. 1, pp. A5014–A5019, 2017.
11. G. Aquilanti et al., "Operando characterization of batteries using x-ray absorption spectroscopy: Advances at the beamline XAFS at synchrotron Elettra," *J. Phys. D. Appl. Phys*., vol. **50**, no. 7, 2017.
12. R. W. Strange and M. C. Feiters, "Biological X-ray absorption spectroscopy (BioXAS): a valuable tool for the study of trace elements in the life sciences," *Curr. Opin. Struct. Biol.*, vol. **18**, no. 5, pp. 609–616, 2008.
13. C. Hureau, V. Balland, Y. Coppel, P. L. Solari, E. Fonda, and P. Faller, "Importance of dynamical processes in the coordination chemistry and redox conversion of copper amyloid-ß complexes," *J. Biol. Inorg. Chem.*, vol. **14**, no. 7, pp. 995–1000, 2009.
14. V. A. Streltsov, R. S. K. Ekanayake, S. C. Drew, C. T. Chantler, and S. P. Best, "Structural Insight into Redox Dynamics of Copper Bound N-Truncated Amyloid-ß Peptides from in Situ X-ray Absorption Spectroscopy," *Inorg. Chem*., vol. **57**, no. 18, pp. 11422–11435, 2018.
15. D. E. Sayers, E. A. Stern, and F. Lytle, "New Technique for Investigating Noncrystalline Structures: Fourier Analysis of the Extended X-Ray—Absorption Fine Structure" vol. 27, no. 18, pp. 1204-1207, 1971.
16. A. Filipponi, A. Di Cicco, and C. R. Natoli, "X-ray-absorption spectroscopy and n -body distribution functions in condensed matter. I. Theory," *Phys. Rev. B*, vol. **52**, no. 21, pp. 15122–15134, Dec. 1995.
17. A. Filipponi and A. Di Cicco, "X-ray-absorption spectroscopy and n -body distribution functions in condensed matter. II. Data analysis and applications," *Phys. Rev. B*, vol. **52**, no. 21, pp. 15135–15149, Dec. 1995.
18. J. J. Rehr and R. C. Albers, "Theoretical approaches to x-ray absorption fine structure," *Rev. Mod. Phys*., vol. **72**, no. 3, pp. 621–654, 2000.
19. N. Binsted, "EXCURV98: CCLRC Daresbury Laboratory computer program." 1998.
20. Y. Joly, "X-ray absorption near-edge structure calculations beyond the muffin-tin approximation," *Phys. Rev. B - Condens. Matter Mater. Phys*., vol. **63**, no. 12, pp. 1–10, 2001.
21. J. D. Bourke, M. T. Islam, S. P. Best, C. Q. Tran, F. Wang, and C. T. Chantler, "Conformation Analysis of Ferrocene and Decamethylferrocene via Full-Potential Modeling of XANES and XAFS Spectra," *J. Phys. Chem. Lett*., vol. **7**, no. 14, pp. 2792–2796, 2016.
22. J. D. Bourke, C. T. Chantler, and Y. Joly, "FDMX?: extended X-ray absorption fine structure calculations using the finite difference method ," *J. Synchrotron Radiat.*, vol. **23**, no. 2, pp. 551–559, 2016.
23. A. A. Guda et al., "Quantitative structural determination of active sites from in situ and operando XANES spectra: From standard ab initio simulations to chemometric and machine learning approaches," *Catal. Today,* no. July, pp. 1–19, 2018.
24. J. Timoshenko, D. Lu, Y. Lin, and A. I. Frenkel, "Supervised Machine-Learning-Based Determination of Three-Dimensional Structure of Metallic Nanoparticles," *J. Phys. Chem. Lett*., vol. 8, no. 20, pp. 5091–5098, 2017.
25. W. H. Cassinelli et al., "Multivariate curve resolution analysis applied to time-resolved synchrotron X-ray Absorption Spectroscopy monitoring of the activation of copper alumina catalyst," *Catal. Today*, vol. 229, pp. 114–122, 2014.
26. A. Martini et al., "Composition-driven Cu-speciation and reducibility in Cu-CHA zeolite catalysts: A multivariate XAS/FTIR approach to complexity," *Chem. Sci.*, vol. **8**, no. 10, pp. 6836–6851, 2017.
27. K. Mathew et al., "Data descriptor: High-throughput computational X-ray absorption spectroscopy," *Sci. Data*, vol. 5, pp. 1–8, 2018.
28. M. J. Schalken and C. T. Chantler, "Propagation of uncertainty in experiment: structures of Ni (II) coordination complexes," *J. Synchrotron Radiat*., vol. **25**, no. 4, pp. 920–934, 2018.
29. C. T. Chantler, Z. Barnea, C. Q. Tran, N. A. Rae, and M. D. De Jonge, "A step toward standardization: Development of accurate measurements of X-ray absorption and fluorescence," *J. Synchrotron Radiat*., vol. **19**, no. 6, pp. 851–862, 2012.
30. M. T. Islam et al., "Accurate X-ray absorption spectra of dilute systems: Absolute measurements and structural analysis of ferrocene and decamethylferrocene," *J. Phys. Chem. C*, vol. **120**, no. 17, pp. 9399–9418, 2016.
31. E. Weckert, "The potential of future light sources to explore the structure and function of matter," *Acta Crystallogr*. Sect. A Found. Adv., vol. **70**, no. a1, pp. C31–C31, 2015.
32. L. Mino, E. Borfecchia, J. Segura-Ruiz, C. Giannini, G. Martinez-Criado, and C. Lamberti, "Materials characterization by synchrotron x-ray microprobes and nanoprobes," *Rev. Mod. Phys*,. vol. **90**, no. 2, p. 25007, 2018.

We thank the wider community of IXAS and all XAS practitioners and users for working towards new insight and for collegiate support in all of our activities.