Accuracy and insight possible with advanced methods in absorption and fluorescence XAS

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Introduction:

Developments over the last two decades have achieved accuracies in attenuation coefficient and X-ray absorption fine structure of below 0.2%. This generally requires careful sample characterisation, monochromator and detector characterisation and additional experimental components to measure and correct for a range of systematics. More recently similar levels of accuracy have been obtained in fluorescence measurement.

Method:

Over the past two years parts of this system have been implemented at the Australian Synchrotron with excellent precision and control of a range of systematics using XERT and Hybrid techniques in both transmission and fluorescence geometries.

Results and Discussion:

Insight includes high accuracy of derived dynamical bond length, thermal parameters, consistency and inconsistency of energy offsets revealed from the data, and structural determination of nearby shells approaching an ab initio manner with XAS. It has allowed exploration of atomic form factors [1], XAFS dynamical bonding [2], electron inelastic mean free paths [3] and nanoroughness [4] appropriate for circuit quality control for microcomputers, with technological offshoots into detector and synchrotron diagnostics. As a consequence, the accurate characterization of fluorescence spectroscopy is developing [5], together with the accurate investigation of organometallic complexes. Further it has allowed investigation of several types of dynamic behaviour including the investigation of the reaction coordinate [6], thermal isotropy, and potentially Debye behaviour. Perhaps intriguingly, it has permitted the first X-ray measurements of electron inelastic mean free path [7]. This paper will explore the requirements for and applicability of higher accuracy in XAFS, the advantage of theory simultaneously fitting XANES and XAFS [8], and the opportunities for advanced dynamics and Debye studies, in addition to the potential for resolving challenges in catalytic and active centres.

Conclusion:

The quality of XAFS data and the intrinsic information content can be outstanding, and its ability to determine bonding and dynamical modes can be unsurpassed. The talk will also look towards future opportunities not yet realised in advanced analysis and disorder measurement.

References

1. de Jonge, MD et al., Measurement of the x-ray mass attenuation coefficient and determination of the imaginary component of the atomic form-factor of tin over the energy range of 29 keV – 60 keV, *Phys. Rev.* **A75** 032702 (2007)

2. Glover, JL et al. Measurement of the X-ray mass-attenuation coefficients of gold, derived quantities between 14 keV and 21 keV and determination of the bond lengths of gold, *J. Phys. B* **43** 085001 (2010)

3. Chantler, CT, Bourke, JD, X-ray Spectroscopic Measurement of the Photoelectron Inelastic Mean Free Paths in Molybdenum, *Journal of Physical Chemistry Letters* **1** 2422 (2010); Bourke, JD, Chantler, CT, *Phys. Rev. Lett.* **104**, 206601 (2010)

4. Glover, JL et al., Nano-roughness in gold revealed from X-ray signature, *Phys. Lett.* **A373** 1177 (2009)

5. Chantler, CT, et al., Stereochemical analysis of Ferrocene and the uncertainty of fluorescence XAFS data, *J Synch. Rad.***19** 145 (2012)

6. Best, SP et al., Reinterpretation of Dynamic Vibrational Spectroscopy to Determine the Molecular Structure and Dynamics of Ferrocene, *Chemistry - A European Journal*, **22** 18019-18026 (2016)

7. Chantler, CT, Bourke, JD, Electron Inelastic Mean Free Path Theory and Density Functional Theory resolving low-Energy discrepancies for low-energy electrons in copper, *Journal of Physical Chemistry* **A118** 909-914 (2014)

8. Bourke, JD et al., FDMX: Extended X-ray Absorption Fine Structure Calculations Using the Finite Difference Method, *J Synchrotron Radiation* **23** 551-559 (2016)